



Sulfuric acid-amine nucleation in urban Beijing

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Abstract. New particle formation (NPF) is one of the major sources of atmospheric ultrafine particles. Due to the high
20 aerosol and trace gas concentrations, the mechanism and governing factors for NPF in the polluted atmospheric boundary
layer may be quite different from those in clean environments, which is however less understood. Herein, based on long-
term atmospheric measurements from January 2018 to March 2019 in Beijing, the nucleation mechanism and the influences
of H₂SO₄ concentration, amine concentrations, and aerosol concentration on NPF are quantified. The collision of H₂SO₄-
amine clusters is found to be the dominating mechanism to initialize NPF in urban Beijing. The coagulation scavenging due
25 to the high aerosol concentration is a governing factor as it limits the concentration of H₂SO₄ amine clusters and new particle
formation rates. Besides, the effective amine concentration is another limiting factor in Beijing because amine is sometimes
insufficient for nucleation at the kinetic limit. Based on the synergistic effects of these factors on H₂SO₄-amine nucleation,
governing factors for H₂SO₄-amine nucleation for different conditions are summarized.



30 1 Introduction

New particle formation (NPF) is a major source of ambient particles in terms of particle number concentration. During a typical NPF process, gaseous precursors form stable clusters via nucleation. Some of these clusters survive and grow into cloud condensation nuclei and hence have the potential to influence the global climate (Kuang et al., 2009; Gordon et al., 2017). There has been a considerable number of NPF studies in various atmospheric environments (Kulmala et al., 2004; 35 Kerminen et al., 2018; Lee et al., 2019), but current knowledge on NPF in the polluted atmospheric boundary layer (e.g., the urban environment in megacities) is still limited. In the presence of a high aerosol concentration in the polluted environment, a considerable fraction of the newly formed clusters and particles are scavenged by coagulation within minutes and hence, NPF may be significantly suppressed (McMurry et al., 2005; Kuang et al., 2010). However, frequent NPF events with high formation rates have been reported in polluted environments (Wu et al., 2007; Iida et al., 2008; Wang et al., 2015; Cai and 40 Jiang, 2017; Yao et al., 2018; Deng et al., 2020b). Such unique characteristics of NPF with a high aerosol concentration, moderate gaseous precursor (e.g., H_2SO_4) concentrations, and a high particle formation rate indicate a fast nucleation mechanism in these environments. Various nucleation mechanisms for the real atmosphere have been reported, such as H_2SO_4 -amine nucleation (Chen et al., 2012; Yao et al., 2018), H_2SO_4 - NH_3 nucleation (Chen et al., 2012; Jokinen et al., 2018), oxidized organics nucleation (Bianchi et al., 2016), and HIO_3 nucleation (Sipila et al., 2016). The second and third 45 mechanisms are not efficient enough to explain the observed high particle formation rates in the polluted environment and the last mechanism may dominate NPF only in the coastal regions.

The clustering of H_2SO_4 and amines produces new particles at a high formation rate. Laboratory studies showed that some amines enhance H_2SO_4 nucleation more efficiently than NH_3 (Kirkby et al., 2011; Erupe et al., 2011; Yu et al., 2012; Jen et al., 2014; Dunne et al., 2016; Yu et al., 2018). Atmospheric measurements in Boulder (Zhao et al., 2011) and urban 50 Atlanta (Chen et al., 2012) indicate the H_2SO_4 -amine nucleation mechanism. The CLOUD (cosmics leaving outdoor droplets) chamber experiments and theoretical calculations based on quantum chemistry reported that in the presence of ~ 5 ppt dimethylamine (DMA, $(\text{CH}_3)_2\text{NH}$) as the stabilizing base, H_2SO_4 under a typical atmospheric concentration ($\sim 10^6 - 10^7$ molecules $\cdot \text{cm}^{-3}$) nucleates at a rate approaching the kinetic collision limit where cluster evaporation is negligible (Almeida et al., 2013; Kürten et al., 2014; Kürten et al., 2018). Atmospheric measurements in urban Shanghai (Yao et al., 2018) provide 55 supports for the view that in polluted megacities in China, H_2SO_4 initiates NPF and DMA is perhaps the dominating base to stabilize H_2SO_4 clusters. Elucidating the governing factors for atmospheric nucleation and their quantitative impacts on particle formation rate is a key to understanding the nucleation mechanism in the real atmosphere.

Previous laboratory experiments and atmospheric measurements provide quantitative understandings of H_2SO_4 -DMA nucleation (Chen et al., 2012; Almeida et al., 2013; Jen et al., 2014; Kürten et al., 2014; Kürten et al., 2018). Due to the high 60 aerosol concentration in the polluted atmospheric boundary layer, the loss rates of new particles during NPF in urban Beijing and Shanghai are usually ~ 10 times higher than the total loss rate in chambers. Under such a high aerosol concentration, coagulation scavenging has been found to govern the concentrations of new particles (Cai et al., 2017b; Deng et al., 2020a).



In addition, high DMA concentrations were used in the previous chamber experiments, e.g., up to 200 ppt in Jen et al. (2014) and up to 140 ppt in the CLOUD experiments (Almeida et al., 2013; Kürten et al., 2014; Kürten et al., 2018), whereas the
65 DMA concentration in urban Beijing was observed to be usually lower than 5 ppt in this study. As also pointed out in
previous studies (Kürten et al., 2014; Yao et al., 2018), the characteristics and limiting factors of nucleation in the polluted
atmosphere may be different from those in laboratory experiments, due to differences in the particle loss rate and precursor
gas concentrations. As a result, the molecular scale understanding of H₂SO₄-DMA nucleation under laboratory conditions
(Jen et al., 2014; Kürten et al., 2014; Kürten et al., 2018) may not be directly applicable for the real atmosphere with low
70 DMA concentrations (< 5 ppt) and high aerosol concentrations.

For a better understanding of the nucleation mechanism in the polluted atmosphere, long-term atmospheric
measurements were conducted in urban Beijing from January 2018 to March 2019. Gaseous H₂SO₄ and cluster
concentrations, amine concentrations, and particle size distributions ranging from 1 nm to 10 μm were measured. The
formation mechanism and the factors governing the initial steps of NPF in the polluted environment are explored. A model
75 based on kinetic nucleation theory is shown to well predict the concentrations of H₂SO₄ dimer, trimer, and tetramer and
formation rate of 1.4 nm particles in urban Beijing. The roles of coagulation scavenging and amine concentrations in H₂SO₄-
amine nucleation are revealed and quantified.

2 Measurements

The atmospheric measurement was conducted in urban Beijing. The dataset for this study is from January 2018 to March
80 2019. The observation site is located at the campus of Beijing University of Chemical Technology (39°56' N, 116°17' E).
The west 3rd ring road is ~500 m away from this observation site. State-of-the-art instruments were deployed to capture the
whole NPF process from the very initial step of nucleation to particle growth. The aerosol size distributions ranging from 1
nm to 10 μm were measured using a diethylene glycol scanning mobility particle spectrometer (1-4.5 nm, Jiang et al., 2011;
Cai et al., 2017a; Fu et al., 2019) and a particle size distribution system (3 nm - 10 μm, Liu et al., 2016). The neutral gaseous
85 H₂SO₄ molecule and cluster concentrations were measured using chemical ionization time-of-flight mass spectrometers
(ToF-CIMS, Aerodyne Research, Inc., Jokinen et al., 2012). H₂SO₄ molecules and neutral clusters are charged using a nitrate
chemical ionization source. A long ToF-CIMS and a high-resolution ToF-CIMS were used before and after September 2018,
respectively. These two instruments were calibrated separately and compared during a short-term parallel measurement. The
H₂SO₄ monomer concentrations reported by these two instruments agree with each other within a systematic relative
90 difference of 1.4±0.3 (Fig. S1). The amine molecule in a stable neutral H₂SO₄-amine cluster may detach during the detection
ToF-CIMS. Hence, the concentrations of H₂SO₄ clusters containing the same number of H₂SO₄ molecules were summed up.
NH₃ was not found in the detected neutral H₂SO₄ clusters. In additions to H₂SO₄, organics with low volatilities were
measured using ToF-CIMS. Neutral amine and NH₃ concentrations were measured using a modified ToF-CIMS (Aerodyne
Research, Inc., Zheng et al., 2015) since October 2018. The reagent ions to charge amines and NH₃ are H₃O⁺ or its hydrated



95 clusters. The sampling line for this ToF-CIMS was ~1.5 m long and it was heated to ~60 °C. The temperature of the sampled
air was < 40 °C. A sample flow rate of 6.1 L·min⁻¹ was used to reduce aerosol deposition onto the tube wall. Because the
ToF-CIMS cannot separate isomers, the measured C₂-amine concentration is taken as DMA concentration. Ethylamine is
thought to be less efficient as a stabilizing base for (H₂SO₄)₁(amine)₁ than DMA (Xie et al., 2017), thus, the measured
effective DMA concentration for stabilizing H₂SO₄ clusters might be overestimated. Similarly, the measured C₃-amine
100 concentration is taken as trimethylamine (TMA) concentration. The naturally charged negative clusters were measured using
an atmospheric pressure interface time-of-flight mass spectrometer (APi-ToF-MS, Aerodyne Research, Inc., Junninen et al.,
2010). Ambient temperature, pressure, and relative humidity were measured using a weather station (AWS310, Vaisala Inc.).

When using the measured H₂SO₄ monomer or n-mer (n = 2, 3, 4) concentrations, the concentrations of clusters
containing the same H₂SO₄ molecules are summed up and written as [(H₂SO₄)_{n,tot}] because amines may detach from H₂SO₄-
105 amine clusters during the ionization process imposed by the instrument. For instance, an H₂SO₄ dimer refers to a cluster
containing two H₂SO₄ molecules regardless of its base number.

The loss rates of gaseous precursors and clusters onto particles, i.e., condensation sinks (CS) and coagulation sinks,
respectively, were calculated using the measured aerosol size distributions (Kulmala et al., 2001). The reported CS was
calculated for H₂SO₄. The coagulation sinks of clusters and particles are usually characterized by CS or the Fuchs surface
110 area (McMurry et al., 2005). From the perspective of molecular kinetics, we do not distinguish coagulation and condensation
in this study. Hence, CS is used to characterize the condensation and coagulation scavenging effects of aerosols on gaseous
precursors, clusters, and new particles. The formation rate of 1.4 nm (in electrical mobility diameter) particles, *J*_{1.4}, is
calculated using a population balance formula (Cai and Jiang, 2017). This formula improves the estimation of particle
coagulation scavenging compared to previous formulae.

115 The uncertainty of the measured aerosol size distributions was estimated to be ±10% (Wiedensohler et al., 2012) and
+100%/–50% (Kangasluoma et al., 2020) for particles larger and smaller than 10 nm, respectively. The CS in urban Beijing
is mainly contributed by accumulation mode particles (Cai et al., 2017b), hence the uncertainty of CS was estimated to be
±10%. The formation rate is mainly determined by the product of new particle concentration and CS in urban Beijing (Cai
and Jiang, 2017), hence the uncertainty of the measured *J*_{1.4} was estimated to be +100%/–50%. The uncertainty of the
120 measured H₂SO₄ concentration is +100%/–50% according to Fig. S1 and previous studies (Kürten et al., 2012; Jokinen et al.,
2012). The uncertainty of the measured amine concentrations is estimated to be similar to that of H₂SO₄ concentration.

The occurrence of NPF was determined according to the evolution of the measured aerosol size distributions. A day
was classified as an NPF day if a clear new particle formation and growth pattern was observed. If no NPF event occurs on a
day, it was classified as a non-event day. The rest of the days, mainly with weak NPF events that are difficult to distinguish,
125 were classified as undefined-days. From January 2018 to March 2019, the frequencies of NPF days and undefined days are
35% and 5%, respectively.



3 Model

A kinetic model was used to illustrate the nucleation process of H₂SO₄-amine clusters. Similar models have been reported in previous studies (Chen et al., 2012; McGrath et al., 2012; Jen et al., 2014). The cluster evaporation rate used in the model was based on quantum chemistry calculations but modified to fit the experimental data. The standard molar Gibbs free energy of formation of (H₂SO₄)₁(DMA)₁, $\Delta_f G_{m,A1B1}^{\ominus}(298.15\text{ K})$ was assumed to be -14.0 kcal·mol⁻¹ in this study, which is in the range of values reported in previous studies (Ortega et al., 2012; Mylly et al., 2019). The quantum chemistry results for $\Delta_f G_{m,A1B1}^{\ominus}(298.15\text{ K})$ using the ω B97X-D/6-31++G^{**}, CBS-QB3, and RICC2B3 level of theory were reported to be -13.5 (Mylly et al., 2019), 14.4, and -15.4 kcal/mol (Ortega et al., 2012), respectively. The evaporation rate of (H₂SO₄)₁(TMA)₁ is assumed to be 5 times that of (H₂SO₄)₁(DMA)₁ according to previous experimental results (Jen et al., 2014). Since the measured TMA concentration was usually lower than or comparable to the measured DMA concentration in this study, the uncertainty of the evaporation rate of (H₂SO₄)₁(TMA)₁ does not significantly affect the simulated particle formation rate or cluster concentrations. The value of free energy at different temperatures is calculated using Eq. S15. The evaporation rate of a cluster was derived from its corresponding standard molar Gibbs free energy of formation (Ortega et al., 2012).

In the proposed kinetic model, the evaporation rates of other (H₂SO₄)_n(amine)_n clusters (n = 2, 3, 4) are negligible compared to their coagulation sinks and hence not included. The very unstable clusters, e.g., (H₂SO₄)₁(amine)₃, are omitted. Some studies indicate that other H₂SO₄-amine clusters, e.g., (H₂SO₄)₃(amine)₂, (H₂SO₄)₃(amine)₄ and (H₂SO₄)₄(amine)₃, and their corresponding reaction pathways may contribute to NPF (McGrath et al., 2012; Olenius et al., 2017), but these studies are not consistent with each other due to the uncertainties in quantum chemistry calculation. Within the ranges of these predicted Gibbs free energies of formation, it is similarly arbitrary to assume negligible or high evaporation rates of these clusters. The kinetic model used in this study does not include the reaction pathways via these clusters (see the SI), i.e., it assumes infinitely high evaporation rates of these clusters. Ion-induced nucleation is neglected in this model because it has a minor contribution to H₂SO₄-amine nucleation for typical ambient conditions in the polluted environment (Yao et al., 2018).

The cluster concentrations and particle formation rates were simulated using the kinetic model. Similarly to previous studies (Jen et al., 2014), we assume the A₄B₄ formation rate as the simulated particle formation rate, $J_{1,4}$. Currently, the knowledge of the exact size of H₂SO₄-amine clusters is still limited. Previous studies reported that the electrical mobility of [HSO₄(H₂SO₄)₃(DMA)₃]⁻ (Jen et al., 2015) and [HSO₄(H₂SO₄)₆(DMA)₄]⁻ (Thomas et al., 2016) is 1.0×10⁻⁴ and 9.4×10⁻⁵ m²·V⁻¹·s⁻¹, respectively. According to these values, the electrical mobility diameter of an (H₂SO₄)₄(DMA)₄ cluster was estimated to be ~1.4 nm, which locates within the measurement range of the aerosol size spectrometer. Its geometric diameter is estimated to be ~1.1 nm according to the relationship between geometric diameter and electrical mobility diameter (Ku and de la Mora, 2009; Larriba et al., 2011).

The uncertainty of the model mainly comes from the uncertainty in the evaporation rate of (H₂SO₄)₁(amine)₁. We estimated this uncertainty range using one high and one low evaporation rate from the values reported in the literature



(Ortega et al., 2012; Myllys et al., 2019). According to this estimation, the uncertainty of the model is of the same order of
160 magnitude as the measurement uncertainties (Fig. S2).

4 Results and Discussion

4.1 Kinetic nucleation in the presence of a high aerosol concentration

During this measurement, H₂SO₄-amine nucleation was found to be the dominating nucleation mechanism in the polluted
atmosphere in urban Beijing. As shown in Fig. 1, the H₂SO₄ dimer concentration was simulated at the median values of CS
165 (0.017 s⁻¹), C₂-amine concentration (1.8 ppt), and temperature (281 K). Good consistency ($R^2=0.75$) was observed between
the measured and simulated H₂SO₄ dimer concentrations. The dimer concentration is presented here because it can be
reliably measured and its concentration contributes to understanding the reaction pathways (Chen et al., 2012; Jen et al.,
2014; Kürten et al., 2015).

The measured H₂SO₄ trimer and tetramer concentrations provide further evidence for the kinetic nucleation mechanism
170 of H₂SO₄-amine clusters in urban Beijing. Figure 2 shows that the measured H₂SO₄ dimer, trimer, and tetramer
concentrations are in accordance with their corresponding simulated concentrations when considering the uncertainties in
determining the detection efficiencies of H₂SO₄ trimer and tetramer concentrations. The systematic difference that the
measured H₂SO₄ trimer and tetramer concentrations are lower than the simulated concentrations is presumably caused by
measurement uncertainties, e.g., cluster fragmentation and a declining detection efficiency with the increasing cluster size. In
175 a CLOUD chamber study on kinetic H₂SO₄-DMA nucleation (Kürten et al., 2014) with a high DMA concentration (5-32 ppt),
such differences between simulated and measured H₂SO₄ n-mer concentrations were also observed. If the H₂SO₄ n-mer
concentrations were overestimated in the kinetic model, the measured particle formation rate should also be lower than the
simulated rate, which is inconsistent with the results shown in Fig. 3.

Besides the concentrations of H₂SO₄ clusters, there is also a consistency between the measured and simulated formation
180 rate of 1.4 nm (electrical mobility diameter) particles (Figs. 3 and S3). This consistency indicates that the clustering of
H₂SO₄ and amine is the governing mechanism for nucleation and the initial growth of new particles up to 1.4 nm in urban
Beijing. To compare the formation rates measured at different CS, the measured $J_{1.4}$ in Fig. 3a were scaled to the median CS
(0.017 s⁻¹) during the observed NPF events in this study. The scaling formula is $J_{1.4, \text{scaled}} = J_{1.4} \times (\text{CS} / 0.017 \text{ s}^{-1})^2$, which is
based on the fact that under the high CS, $J_{1.4}$ is theoretically inversely proportional to CS². Similarly, the measured $J_{1.4}$ in Fig.
185 3b were scaled by $J_{1.4, \text{scaled}} = J_{1.4} \times ((3.5 \times 10^6 \text{ cm}^{-3}) / [(\text{H}_2\text{SO}_4)_{1, \text{tot}}])^4$ to compare the formation rates measured at different
H₂SO₄ monomer concentrations. The derivations for these scaling formulae are detailed in the SI. The dependency of
measured $J_{1.4}$ on H₂SO₄ monomer concentrations in Fig. 3a provides supports for the scaling in Fig. 3b and vice versa.

The measured particle formation rate is then compared to previous studies. The CLOUD study reported that particle
formation rate for H₂SO₄-DMA nucleation (red curve in Fig. 3) was obtained at a high DMA concentration (5-32 ppt), a low
190 cluster loss rate (Kürten et al., 2014; Kürten et al., 2018). The wall loss and dilution rates in that study sum up to be ~0.002 s⁻¹



¹. The particle formation rate under the same H₂SO₄ monomer concentration measured in these CLOUD experiments deviates from the measured formation rate in urban Beijing, and the reason for this deviation will be discussed in section 4.2 below. The curves from other previous studies are simulated using their reported equations (Chen et al., 2012; Jen et al., 2014; Hanson et al., 2017) and the parameters measured in this study. Some of these studies reported higher evaporation rates of H₂SO₄-amine clusters according to their experimental data (Chen et al., 2012; Jen et al., 2014). However, the simulated particle formation rates using these models and evaporation rates are orders of magnitude lower than the measured particle formation rates in urban Beijing.

In addition to H₂SO₄ nucleation with amines, the nucleation of oxidized organics with low vitalities was also reported in the atmosphere (e.g., Bianchi et al., 2016). Various organic vapors were observed in urban Beijing (Fig. S4). However, there was a considerable discrepancy between the absolute value and diurnal trend of particle formation rate contributed by organics and those obtained by measurements (Figs. S5 and S6), indicating that oxidized organics nucleation is not a governing mechanism to initialize NPF in urban Beijing during this campaign.

The consistency between the measured particle formation rate and the kinetic model also provides hints on the sticking probability between H₂SO₄-amine clusters and particles. In a previous study (Kulmala et al., 2017), it was discussed that other condensable vapors in addition to H₂SO₄ and amine may contribute to the initial growth of new particles and that the coagulation scavenging effect in the polluted environment may be overestimated because of the overestimated sticking probability between particles or clusters. However, in this study, we found that up to ~1.4 nm particles (in electrical mobility diameter), the particle formation rate estimated using H₂SO₄-amine clustering and a sticking probability of 1.0 is consistent with the measured formation rate. The measured H₂SO₄ trimer and tetramer concentrations are even lower than the simulated concentrations (Fig. 2) due to potential measurement uncertainties, whereas a significant contribution of other condensable vapors or an overestimated coagulation sink will theoretically result in higher measured concentrations compared to the simulated concentrations. However, the further growth of particles beyond ~1.4 nm in polluted environments still needs further explorations.

4.2 The influence of coagulation scavenging

The scavenging of H₂SO₄-amine clusters due to coagulation with larger particles is a major limiting factor for NPF in urban Beijing. After normalizing the influence of H₂SO₄ monomer concentration, the particle formation rate decreases with an increasing CS (Fig. 3b). Negative dependencies of H₂SO₄ cluster concentration and sub-3 nm particle concentration on CS were also reported in our previous studies in urban Beijing (Cai et al., 2017b; Deng et al., 2020a). However, there was usually a good positive correlation between CS and amine concentrations in urban Beijing, presumably due to the correlation between their sources. As a result, the apparent dependency between the measured $J_{1,4}$ and CS in Fig. 3b was also influenced by amine concentrations.

Although coagulation scavenging does not affect the detailed equilibrium of reactions, it can have significant impacts on the steady-state cluster concentrations. For instance, the particle formation rate of the CLOUD chamber experiments



225 deviates from the measured and simulated formation rates in urban Beijing. This indicates that although the H_2SO_4
concentration in these chamber studies was in the typical ambient range, these results from chamber experiments are not
directly applicable to represent the real atmospheric conditions in urban Beijing due to the difference in coagulation
scavenging rates characterized by CS. The median CS in urban Beijing during the NPF events in this field measurement was
 $\sim 0.017 \text{ s}^{-1}$, which is nearly an order of magnitude higher than the total loss rates in the chamber studies (Kürten et al., 2014;
Kürten et al., 2018; Hanson et al., 2017). Hence, the curve for the CLOUD chamber experiments in Fig. 3 deviates from the
230 measured data in urban Beijing.

The power of particle formation rate to H_2SO_4 monomer concentration, $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]^p$ is consistent with the argument
that coagulation scavenging is a limiting factor for NPF in the polluted environment. It can be proven that under the CS-
controlled regime, the power of the formation rate of $(\text{H}_2\text{SO}_4)_4(\text{amine})_4$ to H_2SO_4 concentration, p , is ~ 4.0 rather than 2.0
(Fig. S7), which is consistent with the measured p in urban Beijing (Fig. 3a). In the perspective of conventional kinetic
235 nucleation theory, the critical step of nucleation is the formation of H_2SO_4 dimer clusters. Accordingly, the p -value is
expected to be 2.0 (Kuang et al., 2008). This power dependency was also used to prove that there was no significant
evaporation of $(\text{H}_2\text{SO}_4)_n(\text{amine})_n$ for $n > 2$ in a previous CLOUD chamber study (Kürten et al., 2014). However, this theorem
is valid only when the external cluster losses are negligible (Ehrhart and Curtius, 2013; Kupiainen-Määttä et al., 2014; Elm
et al., 2020), whereas in the presence of a high aerosol concentration, the loss rates of H_2SO_4 -amine clusters are usually an
240 order of magnitude higher than their growth rates into large clusters. As a result, the cluster concentrations maintain a
pseudo-steady state and their growth fluxes into the next larger clusters are proportional to, rather than independent of,
 H_2SO_4 concentration (as detailed in the SI).

4.3 The influence of amine concentrations

In addition to coagulation scavenging, the low effective amine concentration is another limiting factor for NPF in urban
245 Beijing. During the measurement period in urban Beijing, the median C_2 -amine concentrations for the daytime NPF period
and all the observation periods were 1.8 and 2.7 ppt, respectively. Meanwhile, measured H_2SO_4 dimer concentration and
particle formation rate in urban Beijing were lower than the amine-saturation limit (Figs. 1 and 3). Amine-saturation means
that further increasing the amine concentrations does not significantly enhance the nucleation rate. In contrast, under
unsaturated amine concentrations, with respect to the formation of H_2SO_4 -amine clusters, they are not stable against
250 evaporation. The measured H_2SO_4 dimer concentration and particle formation rate indicate a moderate evaporation rate of
 H_2SO_4 -amine clusters because they were close to but lower than their corresponding amine-saturation limits. This
unsaturated particle formation rate with a low effective amine concentration is consistent with the saturation concentration of
amines reported in previous chamber experiments (Almeida et al., 2013; Jen et al., 2014).

In addition, the dependency of the measured particle formation rate on amine concentrations in Fig. 3a provides support
255 for the view that unsaturated H_2SO_4 -amine nucleation occurs in urban Beijing. Note that the apparent correlation between the
effective amine concentration and CS was minimized in Fig. 3a by scaling the measured $J_{1,4}$ with respect to CS. In contrast,



the apparent negative correlation between the measured $J_{1.4}$ and the effective amine concentration in Fig. 3b is governed by the positive correlation between the effective amine concentration and CS in urban Beijing. For the same reason, a negative correlation between NPF and amine concentrations was also reported in central Germany (Kürten et al., 2016).

260 In the above analysis, DMA is thought to be a major base that stabilizes H_2SO_4 -amine clusters and TMA may also contribute. Other bases, e.g., monomethylamine and NH_3 , were measured but are not included in our analysis due to their relatively weak bond to H_2SO_4 molecules. Although NH_3 concentrations are high (with a median value of 789 ppt during the observed NPF in this study), theoretically NH_3 cannot be the major base to stabilize H_2SO_4 in urban Beijing due to the high evaporation rate of the NH_4HSO_4 molecule (Ortega et al., 2012; Jen et al., 2014; Olenius et al., 2017). However, these
265 relatively weak bases may contribute to the particle growth and their synergistic effects and base substitutions have been reported in previous studies (Kupiainen et al., 2012; Glasoe et al., 2015; Myllys et al., 2019). C_1 - and C_4 -amines stabilized neutral H_2SO_4 trimers are detected during NPF events in this study, as shown in Fig. S4a. Despite these potential contributions, the formation of large clusters until $(\text{H}_2\text{SO}_4)_4(\text{amine})_4$ and ~ 1.4 nm particles (in electrical mobility diameter) in urban Beijing can be quantitatively explained by the kinetic model (Figs. 1, 2, 3, and S5). Some other compounds in addition
270 to amines, such as diamines (Jen et al., 2016) and guanidine (Myllys et al., 2019), are also reported to be possible bases to stabilize H_2SO_4 clusters; however, they were not observed during this measurement.

4.4 The synergistic influences of H_2SO_4 , coagulation scavenging, and amine concentrations

Summarizing the synergistic effect of H_2SO_4 monomer concentration, CS, and the effective amine concentration, the governing factors for H_2SO_4 -amine nucleation at different regimes are illustrated in Fig. 4. The horizontal coordinate is equal
275 to $0.5\beta_{11}\cdot[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]/\text{CS}$, where β_{11} is the collision coefficient of two $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$ clusters. It characterizes the ratio of the condensational growth rate of a molecule or cluster to its loss rate. The vertical coordinate is equal to $\beta_{\text{AB}}[\text{amine}]/(\text{CS}+\gamma)$, where β_{AB} is the collision coefficient of an H_2SO_4 molecule and an amine molecule and γ is the evaporation rate of $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$. As indicated by this formula, this vertical coordinate is linearly proportional to the effective amine concentration. $J_{1.4}$ was estimated using the proposed model and it is normalized by dividing it by its collision limit (J_c) at the
280 same H_2SO_4 monomer concentration. The collision limit refers to the collision rate of two H_2SO_4 monomers, which is theoretically the maximum steady-state particle formation rate. The effective amine concentration is assumed to be independent of $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]$, i.e., it is assumed that the formation of $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$ does not cause a change in amine concentrations. It should be clarified that due to evaporation and the minor reaction pathways, the normalized particle formation rate is governed but not only determined by the normalized sulfuric and amine concentrations. Hence, the
285 background color map shown in this figure is illustrative rather than quantitative.

According to the region of measured data in Fig. 4, particle formation rate is sensitive to both CS and amine concentrations in the real atmosphere of urban Beijing and Nanjing, whereas it is insensitive to amine concentrations in most of the experimental conditions in the CLOUD studies (Almeida et al., 2013; Kürten et al., 2014). A high C_2 -amine concentration was reported for Shanghai (40 ± 14 ppt, Yao et al., 2016) and therefore the effective amine concentration in



290 Fig. 4 locates in a similar range to that in the CLOUD experiments. In the upper right corner of Fig. 4, both the sulfuric and
amine concentrations are sufficiently high so that the steady-state cluster and particle formation rates are governed by the
collision rate of two H₂SO₄ monomers. At the upper left corner, nucleation is controlled by CS because the concentrations of
clusters and particles are governed by both their formation and loss rates (see Eqs. S22 – S28 in the SI). In this CS-controlled
regime, increasing the effective amine concentration in a narrow range does not significantly increase the formation rate
295 because the effective amine concentration is sufficient with respect to the evaporation of H₂SO₄-amine clusters and the
formation rate is close to its amine-saturation limit. At the lower right corner, the formation and growth of H₂SO₄-amine
clusters are not limited by their coagulation losses. However, due to the low effective amine concentration, considerable
evaporation of H₂SO₄-amine clusters limits the formation rate of new particles.

5 Conclusions

300 The predominating mechanism initiating NPF in urban Beijing is illustrated. Compared to previous studies that investigated
H₂SO₄-amine nucleation under high amine concentrations in laboratories (Almeida et al., 2013; Jen et al., 2014; Kürten et al.,
2014) and reported it to be a governing mechanism in the atmosphere (Yao et al., 2018), we further show the governing roles
of H₂SO₄, amines, and the coagulation scavenging effect at the molecular level based on the long-term ambient atmospheric
measurements in urban Beijing. Comparing the measured particle formation rate and cluster concentrations with those
305 simulated using a kinetic model, we demonstrated these new findings. The formation and growth of H₂SO₄-amine clusters
under the strong coagulation scavenging effect seems to be a major pathway for cluster growth up to ~1.4 nm particles (in
electrical mobility diameter). Both theoretical analysis and measured data support that differently from previous chamber
studies (Kürten et al., 2014; Almeida et al., 2013) and atmospheric measurements (Yao et al., 2018), the typical amine
concentrations measured in this study are sometimes insufficient to bound with nearly all the H₂SO₄ monomers into H₂SO₄-
310 amine clusters. The sensitivity of NPF to amine concentrations also indicates that the contributions of NPF to the aerosol
number and surface concentrations will decrease if atmospheric amine concentrations are reduced. Due to the correlated
variables and measurement uncertainties in atmospheric measurements, the quantitative influences of various amines, water
vapor, and coagulation sink on NPF need further verifications from experiments in chambers or other controlled systems.
For future chamber studies, we recommend that the gaseous precursors and condensation sink should be at their typical
315 ambient values, as their values not only affect particle formation rate, but also the detailed nucleation kinetics.

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Code availability. The Julia code for the kinetic model is available upon request.

Data availability: The data that support the findings of this study are available from the corresponding author upon request.

Competing interests. The authors declare that they have no conflict of interest.

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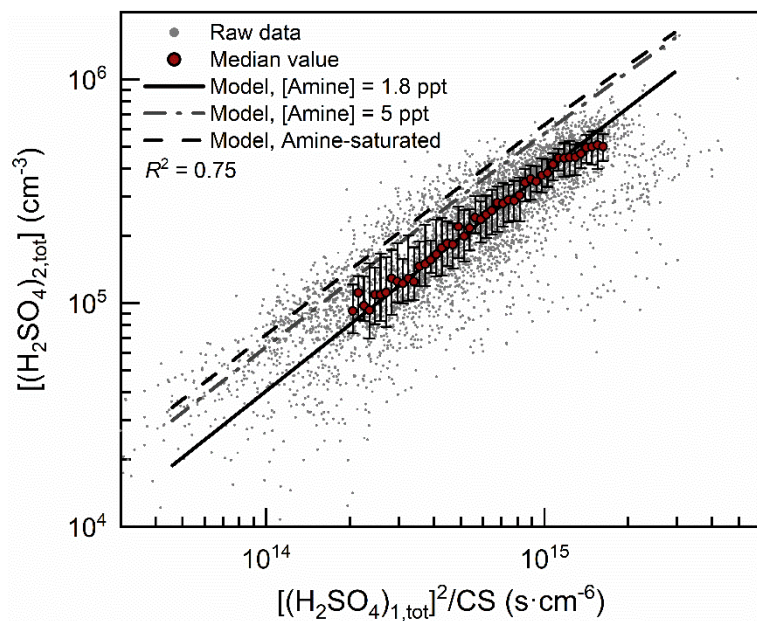
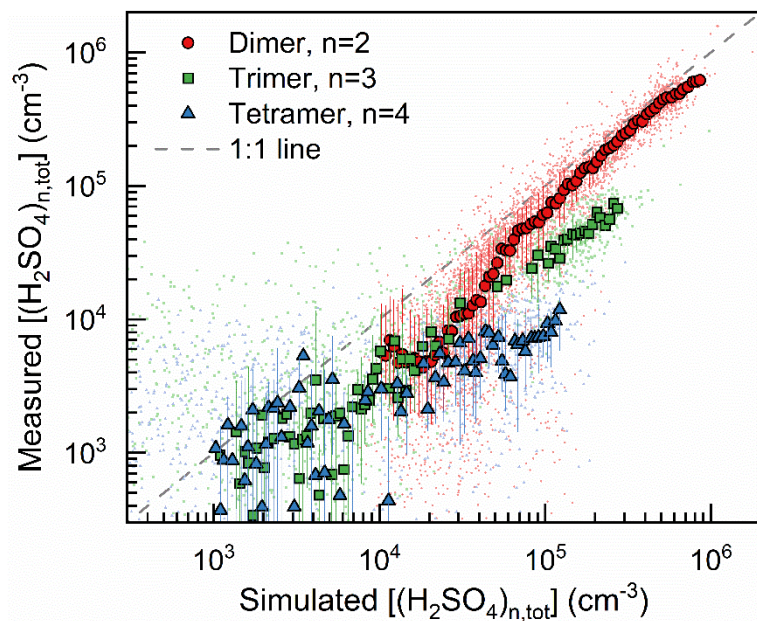


Figure 1: **H₂SO₄ dimer concentration for urban Beijing.** [(H₂SO₄)_{1,tot}] and [(H₂SO₄)_{2,tot}] are the measured H₂SO₄ monomer and dimer concentrations, respectively. The measured raw data with a temporal resolution of 5 min are shown with small dots. The median values of these dots grouped by the horizontal coordinate are shown with big red markers, and the error bars indicate the lower and upper quartiles. The condensation sink (CS) and temperature for the simulated formation rate are their median values during the observed NPF events, i.e., 0.017 s⁻¹ and 281 K, respectively. The amine-saturated limit (dashed black line) is simulated at an ultra-high DMA concentration (10⁶ ppt) so that the evaporation rate of H₂SO₄-DMA clusters are negligible compared to their formation rates. The *R*² value was calculated using logarithmic values.

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545 Figure 2: **The measured and simulated H_2SO_4 dimer, trimer, and tetramer concentrations.** The concentrations of clusters containing the same H_2SO_4 molecule number are summed together. The small dots are the raw data with a temporal resolution of 10 min and their median values are shown with big markers. The error bars indicate the lower and upper quartiles. The uncertainty of instrument detection efficiency contributes to the difference between the measured and simulated values, as explained in the main text.

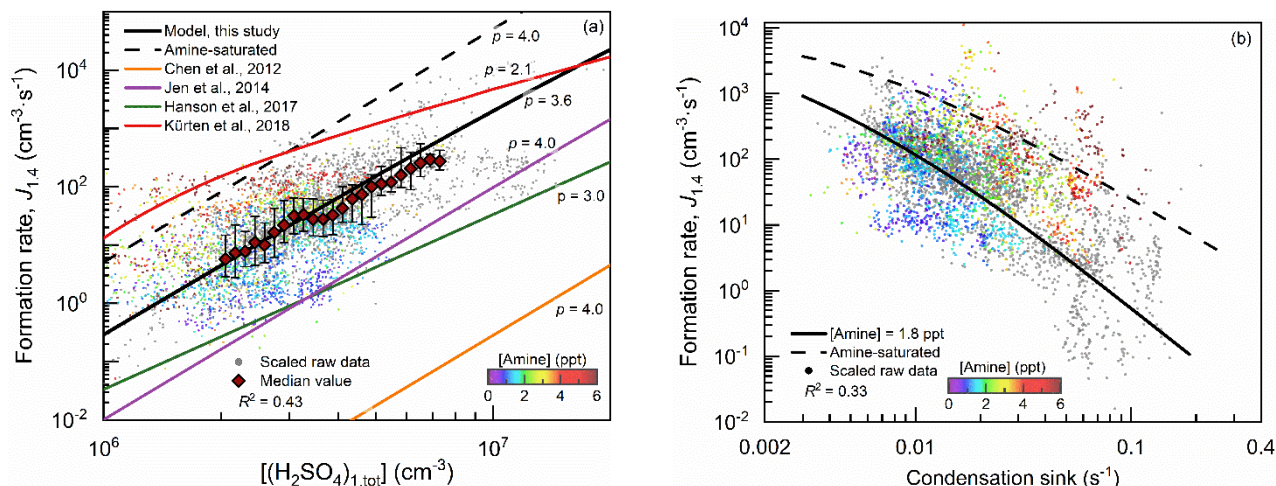


Figure 3: The measured and simulated particle formation rates ($J_{1.4}$) as a function of (a) H_2SO_4 monomer concentration ($[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]$) and (b) condensation sink (CS). The measured raw data with a temporal resolution of 5 min are shown with small dots and colored by the measured effective amine concentration. When amine concentrations are not available, the corresponding dots are shown in grey. The median values of these dots grouped by the horizontal coordinate in (a) are shown with big red markers, and the error bars indicate the lower and upper quartiles. The measured formation rates shown in (a) and (b) are scaled to the median CS and $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]$ for the measured NPF events, respectively. The scaling formulae are given in the main text and illustrated in the SI. Note that the simulated formation rates are not scaled. p is the simulated power of $J_{1.4}$ with respect to $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]$. The R^2 values were calculated using logarithmic values.

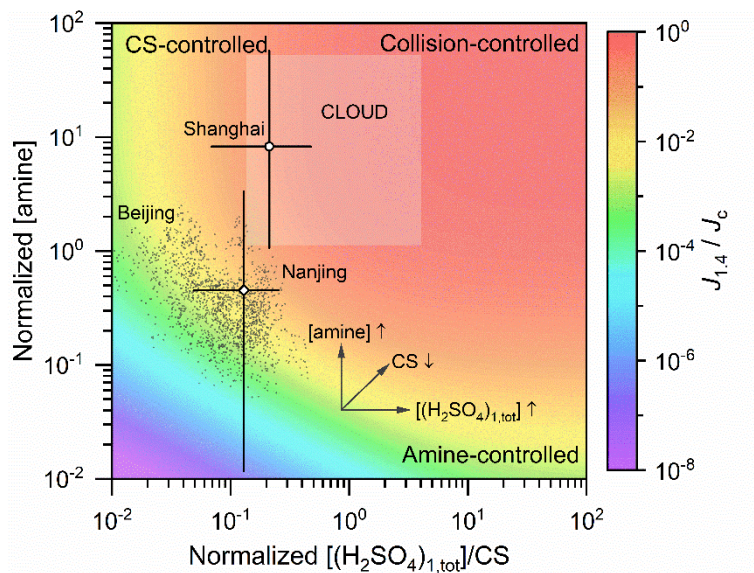


Fig. 4. An illustrative figure for the governing factors of H₂SO₄-amine nucleation in various conditions. The horizontal and vertical coordinates are the normalized H₂SO₄ and effective amine concentrations, respectively, and the normalizing formulae are given in the main text. The color indicates the normalized steady-state formation rate of 1.4 nm particles, $J_{1.4}$. J_c is the formation rate at the collision limit. The dark grey markers are the measured data in Beijing with a temporal resolution of 5 min. The semi-transparent square above the colored contour is the estimated range for experimental conditions of the CLOUD studies (Almeida et al., 2013; Kürten et al., 2014): $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]$ between 5×10^5 and $1.5 \times 10^7 \text{ cm}^{-3}$, $[\text{amine}]$ between 3 and 140 ppt, $T = 278 \text{ K}$, and the sum of wall loss and dilution rates (instead of CS) was estimated to be 0.002 s^{-1} . The open markers and error bars indicate the median values and approximate ranges, respectively, of the normalized H₂SO₄ and effective amine concentrations in Shanghai and Nanjing. The Shanghai data was reported by Yao et al. (2016) and Yao et al. (2018). The Nanjing data was reported by Zheng et al. (2015) and Deng et al. (2020a). Note that for Shanghai and Nanjing, the amine concentrations were measured in different campaigns from those for H₂SO₄ and CS and the amine concentrations are the average of all days rather than new particle formation period only. As a result, there are potential uncertainties in the results for Shanghai and Nanjing.