

1 **Supporting Information for**
2 **Sulfuric acid-amine nucleation in urban Beijing**

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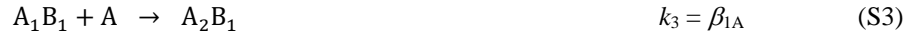
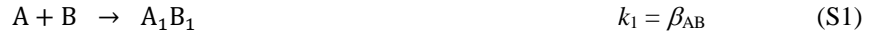
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19

20 Simplified kinetic model

21 The schematic diagram of the simplified kinetic model is shown in Fig. S1. The reactions included in this model are as
 22 follows:



23 where A is H₂SO₄, B is dimethylamine (DMA) or trimethylamine (TMA), (g) represents the gas phase, (p) the represents
 24 particle phase, k_x is the reaction rate and x is the equation number, β is the collision coefficient, γ is the evaporation rate, and
 25 CS is the condensation sink. The subscripts of β , γ , and CS indicate their corresponding equations. The enhancement of
 26 coagulation due to van der Waals forces is considered for β and CS. The Hamaker constant is assumed to be 6.4×10^{-20} J. The
 27 enhancement factor for the coagulation between molecules or clusters was estimated to be 2.3, and it was estimated to be 1.3
 28 for CS (Chan and Mozurkewich, 2001; Kürten et al., 2018; Stolzenburg et al., 2019). The correction factor of 2.3 agrees with
 29 the results obtained by atomistic simulation (Halonen et al., 2019).

30 The concentrations of A_{1,tot}, B, CS, and the ambient temperature are used as the input of this model. A_{1,tot} refers to all the
 31 sulfuric acid monomers regardless of their base number. CS was calculated using the measured aerosol size distributions and
 32 the sticking probability for every collision between a particle and a cluster is assumed to be 100 %. The value of CS varies
 33 with clusters because of their varying diameters (Lehtinen et al., 2007). The value of γ was calculated according to the
 34 theoretical standard molar Gibbs free energy of reaction obtained by quantum chemistry calculation (Ortega et al., 2012).
 35 The influence of temperature on γ is accounted for using the following formula:

$$\frac{\Delta_f G_m^\theta(T_1)}{T_1} = \frac{\Delta_f G_m^\theta(T_0)}{T_0} - \int_{T_0}^{T_1} \frac{\Delta_f H_m^\theta}{T^2} dT \quad (S15)$$

36 where $\Delta_f G_m^\theta$ is the standard molar Gibbs free energy of formation (of A₁B₁), T₁ is the targeted temperature, T₀ = 298.15 K,
 37 $\Delta_f H_m^\theta$ is the standard molar enthalpy of formation.

38 The $\Delta_f G_{m,A_1B_1}^\theta$ is assumed to be -14.0 kcal/mol, which is higher than the value of -13.5 kcal/mol reported in Myllys et al.

39 (2019) but lower than the values of -14.4 and -15.4 kcal/mol reported in Ortega et al. (2012). This value was chosen to fit the
 40 measured H₂SO₄ dimer concentration and particle formation rate of 1.4 nm particles. Due to the measurement uncertainties,
 41 it is difficult to conclude that -14.0 kcal/mol is more accurate than -13.5 or -14.4 kcal/mol for $\Delta_r G_{m,A_1B_1}^0$, yet we use -14.0
 42 kcal/mol for its better accordance with the measurements.

43 Considering the fast conversion between A and A₁B₁, Eqs. S1 and S2 are assumed to be at a quasi-steady state. Hence, the
 44 concentrations of A and A₁B₁ were calculated using Eq. 1. For A₂B₁, A₂B₂, A₃B₃, and A₄B₄, their concentration change rates
 45 derived from Eq. S3-S14 are shown in Eq. S16-S20 and their concentrations are solved numerically in the simplified kinetic
 46 model.

$$\frac{d[A_1B_1]}{dt} = k_1[A][B] - k_2[A_1B_1] - k_3[A_1B_1][A] - 2k_4[A_1B_1]^2 - k_6[A_2B_2][A_1B_1] - k_7[A_3B_3][A_1B_1] - k_8[A_4B_4][A_1B_1] - k_{10}[A_1B_1] \quad (S16)$$

$$\frac{d[A_2B_1]}{dt} = k_3[A_1B_1][A] - k_5[A_2B_1][B] - k_{11}[A_2B_1] \quad (S17)$$

$$\frac{d[A_2B_2]}{dt} = k_4[A_1B_1]^2 + k_5[A_2B_1][B] - k_6[A_2B_2][A_1B_1] - 2k_9[A_2B_2]^2 - k_{12}[A_2B_2] \quad (S18)$$

$$\frac{d[A_3B_3]}{dt} = k_6[A_2B_2][A_1B_1] - k_7[A_3B_3][A_1B_1] - k_{13}[A_3B_3] \quad (S19)$$

$$\frac{d[A_4B_4]}{dt} = k_7[A_3B_3][A_1B_1] + k_9[A_2B_2]^2 - k_8[A_4B_4][A_1B_1] - k_{14}[A_4B_4] \quad (S20)$$

47 The formation rate of A₄B₄ is taken as the simulated particle formation rate, $J_{A_4B_4}$, and it was calculated using Eq. S21. Note
 48 that according to this simulation, during the campaign in urban Beijing, the clustering of A₂B₂ contributes only a minor
 49 proportion to $J_{A_4B_4}$.

$$J_{A_4B_4} = k_7[A_3B_3][A_1B_1] + k_9[A_2B_2]^2 \quad (S21)$$

50

51 Derivation of equations 1 and 2 in the main text

52 Although $J_{A_4B_4}$ is numerically solved in the simplified model, an illustrative analytical solution based on a series of
 53 approximations for $J_{A_4B_4}$ is given below for a better understanding of Eqs. 1 and 2 in the main text. Putting the time derivative
 54 terms on the left-hand sides of Eqs. S16-S20 to zero yields the following steady-state concentrations of these H₂SO₄-amine
 55 clusters:

$$[A_1B_1] = \frac{k_1[A][B]}{k_2 + k_3[A] + 2k_4[A_1B_1] + k_6[A_2B_2] + k_7[A_3B_3] + k_8[A_4B_4] + k_{10}} \approx \frac{k_1[A][B]}{k_2 + k_{10}} \quad (S22)$$

$$[A_2B_1] = \frac{k_3[A_1B_1][A]}{k_5[B] + k_{11}} \quad (S23)$$

$$[A_2B_2] = \frac{k_4[A_1B_1]^2 + k_5[A_2B_1][B]}{k_6[A_1B_1] + 2k_9[A_2B_2] + k_{12}} \approx \frac{k_4[A_1B_1]^2 + k_5[A_2B_1][B]}{k_{12}} \quad (S24)$$

$$[A_3B_3] = \frac{k_6[A_2B_2][A_1B_1]}{k_7[A_1B_1] + k_{13}} \approx \frac{k_6[A_2B_2][A_1B_1]}{k_{13}} \quad (S25)$$

$$[A_4B_4] = \frac{k_7[A_3B_3][A_1B_1] + k_9[A_2B_2]^2}{k_8[A_1B_1] + k_{14}} \approx \frac{k_7[A_3B_3][A_1B_1] + k_9[A_2B_2]^2}{k_{14}} \quad (S26)$$

56 Due to the comparatively high CS in urban Beijing, the cluster growth rates are usually much smaller than their loss rates.
 57 As a result, the solution for the steady-state concentrations of H₂SO₄-amine clusters can be simplified as above. Such
 58 simplifications are reasonable for the ambient conditions during this campaign (indicated by the horizontal coordinate in Fig.
 59 4).

60 Since the concentrations of A and A₁B₁ are assumed to be at the steady-state and the sum of their concentrations is equal to
 61 the concentration of A_{1,tot}, the relationship between the concentrations of A_{1,tot} and A₁B₁ can be readily obtained according to
 62 Eq. S22:

$$\frac{[A_1B_1]}{[A_{tot}]} \approx \frac{k_1[B]}{k_2 + k_{10} + k_1[B]} = \frac{\beta_{AB}[B]}{\gamma_1 + CS_1 + \beta_{AB}[B]} := \eta \quad (S27)$$

63 Combining Eq. S22-S25, the simplified analytical solution for $J_{A_4B_4}$ is:

$$J_{A_4B_4} = \frac{k_4 k_6 k_7}{k_{12} k_{13}} [A_{1,tot}]^4 \eta^4 \left[1 + \frac{k_3(1-\eta)}{k_4} \frac{k_5[B]}{\eta(k_5[B] + k_{11})} \right] + \frac{k_4^2 k_9}{k_{12}^2} [A_{1,tot}]^4 \eta^4 \left[1 + \frac{k_3(1-\eta)}{k_4} \frac{k_5[B]}{\eta(k_5[B] + k_{11})} \right]^2 \quad (S28)$$

64

65 Considerations on the simplifications of the model

66 This kinetic model is proposed based on both the measured data and the quantum chemistry calculation. The growth of
 67 clusters and particles in an H₂SO₄-amine system is driven by the clustering of H₂SO₄ and amine molecules. The detailed
 68 growth pathway is determined by the evaporation rate of each A_nB_m cluster and their concentrations. The evaporation and
 69 fission rates of each cluster can be estimated according to quantum chemistry calculation and the reaction pathway under a
 70 given condition can thus be derived (McGrath et al., 2012). However, due to the uncertainties in the quantum chemistry
 71 calculation, the evaporation rates estimated using different levels of theory deviates from each other in order of magnitudes.
 72 For instance, at 298.15 K, the evaporation rate of (H₂SO₄)₁(amine)₁ in Ortega et al. (2012) and Myllys et al. (2019) was
 73 estimated to be 0.14 s⁻¹ and 3.1 s⁻¹ (after correcting the influence of van der Waals force), respectively. Note that the
 74 uncertainties in the evaporation rates of larger clusters are perhaps higher because they contain more atoms than A₁B₁ does.
 75 Meanwhile, it is difficult to determine the base number of a neutral H₂SO₄-amine cluster using the mass spectrometer (ToF-
 76 CIMS) because amine may detach from the H₂SO₄-amine cluster due to ionization, evaporation, and fragmentation during
 77 the detection.

78 As a result, we include only A_nB_n (n = 1, 2, 3, 4) and A₂B₁ clusters in the simplified model. Considering measurement
 79 uncertainties, the simulated results using this simplified model were found to agree with the measured data (Figs. 1, 2, and
 80 3). The stability of A₂B₁ is supported by both the quantum chemistry results (Ortega et al., 2012; Myllys et al., 2019). The
 81 estimated relative stability of A_{n-1}B_n (n = 3, 4) under the ambient conditions is still not clear due to the uncertainties of
 82 quantum chemistry calculation. For instance, the total evaporation (including monomer evaporation and fission) rates of A₃B₂
 83 were estimated to be 8.3 s⁻¹ and 0.6 s⁻¹ at 298.15 K in Ortega et al. (2012) and Myllys et al. (2019), respectively. These values
 84 indicate that A₃B₂ is perhaps unstable or semi-stable in the ambient conditions. Due to the measurement uncertainties, it is
 85 difficult to estimate the contribution of A₃B₂ contribution to total H₂SO₄ trimer concentration by comparing the measured

86 data and simulation results. Hence, $A_{n-1}B_n$ ($n = 3, 4$) are not included in the simplified model. Other A_nB_m clusters in addition
 87 to A_nB_n and $A_{n-1}B_n$ are much more unstable compared to A_nB_n , e.g., the evaporation rate of A_3B_1 was estimated to be 8.5 s^{-1}
 88 and 103 s^{-1} at 298.15 K in Ortega et al. (2012) and Myllys et al. (2019), respectively.

89 As mentioned in the above section and the main text, the depletion of an H_2SO_4 -amine cluster due to its growth is neglected
 90 in Eqs. 1 and S22 – S26. We use the example of A_1B_1 to show that this approximation is reasonable in the polluted
 91 atmospheric boundary layer. Note that this approximation is used when deriving Eq. 1 but not in the model. Under the typical
 92 condition in this field campaign, e.g., $[A_{1,\text{tot}}] = 5 \times 10^6 \text{ cm}^{-3}$, $\text{CS} = 1.7 \times 10^{-2} \text{ s}^{-1}$, $\text{DMA} = 1.8 \text{ ppt}$, $T = 281 \text{ K}$, and the values of
 93 $k_3[A]$ and $2k_4[A_1B_1]$ in Eq. S22 are approximately $4.2 \times 10^{-3} \text{ s}^{-1}$ and $2.0 \times 10^{-3} \text{ s}^{-1}$, respectively. These values are an order of
 94 magnitude smaller than k_2 ($\gamma_1 = 0.11 \text{ s}^{-1}$) and k_{10} ($\text{CS} = 1.7 \times 10^{-2} \text{ s}^{-1}$). The concentrations of H_2SO_4 trimer and tetramer are
 95 orders of magnitudes lower than H_2SO_4 dimer concentrations in urban Beijing, hence, the values of $k_6[A_2B_2]$ and $k_7[A_3B_3]$
 96 are even smaller compared to k_2 and k_{10} . This estimation is supported by the horizontal position of the measured data in Fig.
 97 4. Similarly, the evaporation of some stable clusters, e.g., A_2B_2 , is neglected because its value is orders of magnitudes smaller
 98 than the CS in urban Beijing.

99

100 **Scaling of formation rate in Figure 3**

101 In Eqs. S28, k_4 , k_6 , k_7 , and k_9 are (half of) the collision coefficients between clusters and they are proportional to β_{11} . k_{12} and
 102 k_{13} are coagulation sinks and they are proportional to CS. The term $1 + k_3(1 - \eta)k_5[B]/[k_4\eta(k_5[B] + k_{11})]$ is dependent
 103 on amine concentration and it approaches 1 when $[B]$ increases. Hence, it can be approximated that the formation rate of
 104 A_4B_4 clusters is proportional to $[A_{1,\text{tot}}]^4$ and CS^{-2} . Figures 3a and S7 below indicate that the power of $[A_{1,\text{tot}}]$ should 3.6 instead
 105 of 4 for urban Beijing, yet this minor difference does not significantly affect the conclusions. The size of an A_4B_4 cluster (B
 106 = DMA) was estimated to be $\sim 1.4 \text{ nm}$ (Thomas et al., 2016). Since $[A_{1,\text{tot}}]$ and CS are important factors determining the
 107 formation rate, the measured $J_{1.4}$ has to be scaled with respect to them before comparison. For example, a scaling method for
 108 CS is given below:

$$J_{1.4,\text{scaled}} = J_{1.4,\text{measured}} \frac{\text{CS}^2}{\text{CS}_{\text{ref}}^2} \quad (\text{S29})$$

109 where $J_{1.4,\text{measured}}$ and $J_{1.4,\text{scaled}}$ are the measured and scaled formation rates of 1.4 nm particles, respectively; CS is the measured
 110 condensation sink; CS_{ref} is the reference condensation sink and it is chosen as 0.017 s^{-1} in Fig. 1, which is a typical value (the
 111 median value during NPF events) in urban Beijing during this campaign. The values of the scaled formation rates are mainly
 112 affected by H_2SO_4 concentration and amine concentrations.

113

114 **Analytical solution for the model in clean environments**

115 The above discussion is based on the assumption of a high CS, and the approximate solution of $J_{A_4B_4}$ is given in Eq. S28.
 116 However, in clean environments with low CS, the sink for H_2SO_4 -amine clusters is usually determined by their condensation
 117 growth rather than the coagulation scavenging. Considering that the monomer concentration is much higher than the
 118 concentrations of dimer and trimer, Eq. 22-25 is simplified to obtain an approximate analytical solution that applies for clean
 119 environments:

$$[A_1B_1] \approx \frac{k_1[A][B]}{k_2 + k_3[A] + 2k_4[A_1B_1] + k_{10}} \quad (S30)$$

$$[A_2B_1] = \frac{k_3[A_1B_1][A]}{k_5[B] + k_{11}} \quad (S31)$$

$$[A_2B_2] = \frac{k_4[A_1B_1]^2 + k_5[A_2B_1][B]}{k_6[A_1B_1] + 2k_9[A_2B_2] + k_{12}} \quad (S32)$$

$$[A_3B_3] = \frac{k_6[A_2B_2][A_1B_1]}{k_7[A_1B_1] + k_{13}} \quad (S33)$$

120 The solutions for Eq. S32 and S34 are:

$$[A_1B_1] = \frac{\sqrt{(k_1[B] + k_2 + k_3[A_{1,tot}] + k_{10})^2 + 4k_1(2k_4 - k_3)[A_{1,tot}][B]} - \frac{k_1[B] + k_2 + k_3[A_{1,tot}] + k_{10}}{4k_4 - 2k_3}}{4k_4 - 2k_3} \quad (S34A)$$

$$\text{or } [A_1B_1] \approx \frac{k_1[B]}{k_1[B] + k_2 + k_3[A_{1,tot}] + k_{10}} [A_{1,tot}] \quad (\text{assuming } k_3 = 2k_4) \quad (S34B)$$

$$[A] = [A_{1,tot}] - [A_1B_1] \quad (S35)$$

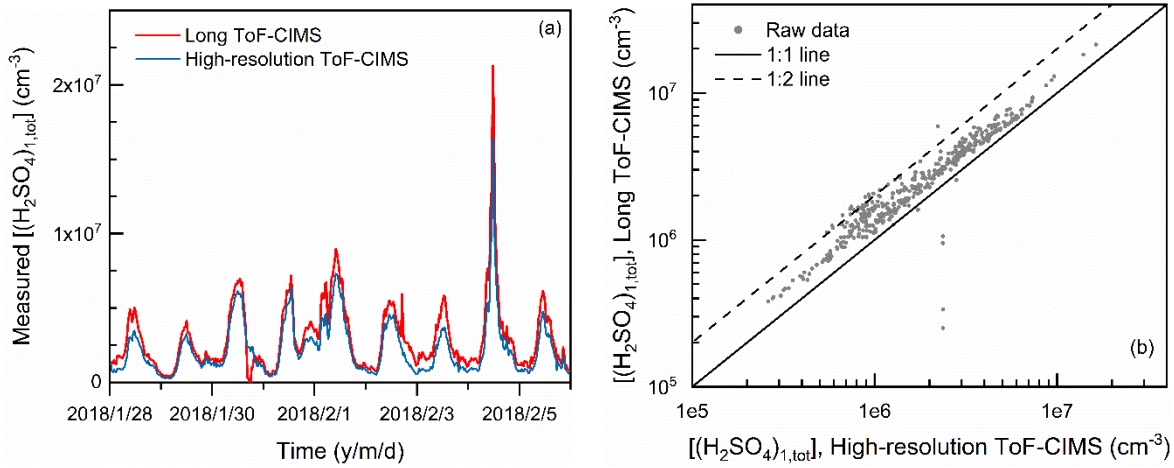
$$[A_2B_2] = \frac{\sqrt{(k_6[A_1B_1] + k_{12})^2 + 8k_9(k_4[A_1B_1]^2 + k_5[A_2B_1][B])} - \frac{k_6[A_1B_1] + k_{12}}{4k_9}}{4k_9} \quad (S36)$$

121 The expression for $J_{A_4B_4}$ is:

$$J_{A_4B_4} = k_7[A_3B_3][A_1B_1] + k_9[A_2B_2]^2 \quad (S37)$$

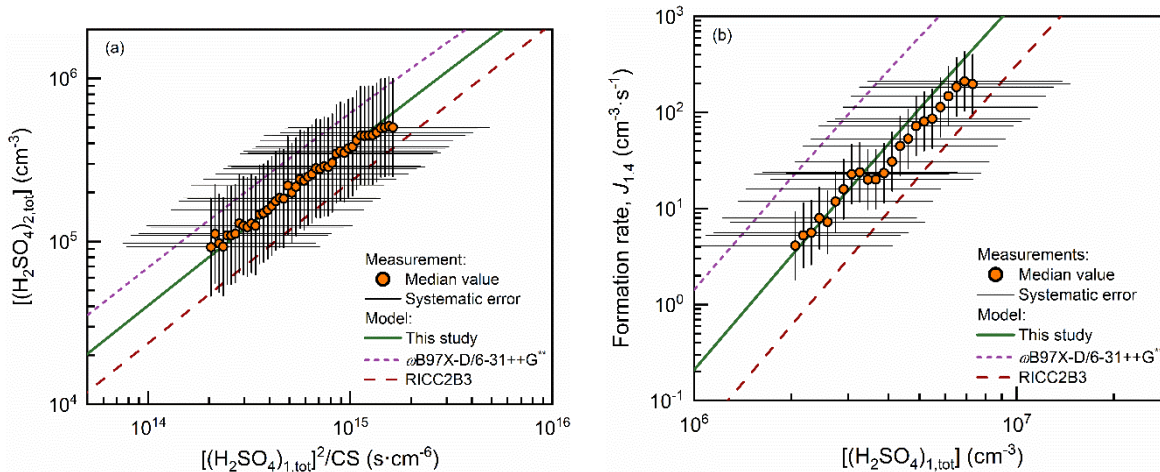
122 The input for Eq. S37 are $[A_{1,tot}]$, $[B]$, and k_1 - k_{13} which are mainly influenced by CS and T. $[A_1B_1]$, $[A]$, $[A_2B_1]$, $[A_2B_2]$, and
 123 $[A_3B_3]$ are given in Eqs. S34, S35, S31, S36, and S33, respectively. The values of k_1 - k_{13} are indicated in Eqs. S1-S13. Equation
 124 S37 is more accurate than Eq. S28 because Eq. S37 does not neglect the sinks due to condensation growth. However, note
 125 that Eq. S37 is derived base on a balance assumption. When the NPF period is shorter than the period for the clusters to reach
 126 their steady-state concentrations, Eq. S37 will overestimate the formation rate.

127 **Supporting figures**



128

129 Figure S1: (a) Time series and (b) a scatter plot of the $(\text{H}_2\text{SO}_4)_{1,\text{tot}}$ concentration measured by a high-resolution ToF-
130 CIMS and a long ToF-CIMS. The ratio of the $(\text{H}_2\text{SO}_4)_{1,\text{tot}}$ concentration measured by the long ToF-CIMS to that of
131 the high-resolution ToF-CIMS is 1.4 ± 0.3 , where 0.3 is the standard deviation. According to (b), the uncertainty of the
132 H_2SO_4 measured in this study was estimated to be 100%.

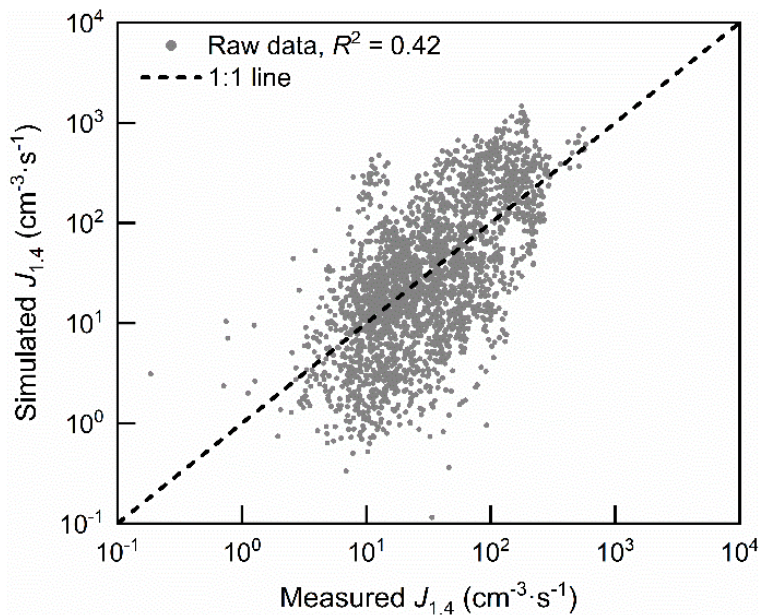


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134 Figure S2: The potential systematic errors for (a) Fig. 1a. and (b) Fig. 1b. The error bar indicates the standard deviation
 135 of data due to systematic errors. The uncertainties of CS, $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]$, $[(\text{H}_2\text{SO}_4)_{2,\text{tot}}]$, and $J_{1,4}$ are detailed in the main
 136 text. The uncertainty of $[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]^2/\text{CS}$ was estimated according to the formula for error propagation,

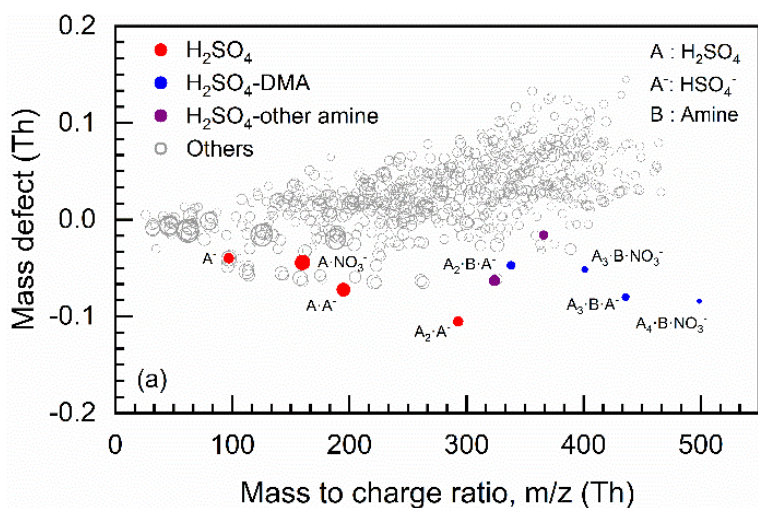
$$137 \quad \sigma \left\{ \frac{[(\text{H}_2\text{SO}_4)_{1,\text{tot}}]^2}{\text{CS}} \right\} = \sqrt{(2\sigma\{(\text{H}_2\text{SO}_4)_{1,\text{tot}}\})^2 + (\sigma\{\text{CS}\})^2},$$

138 where σ indicates the relative error. The uncertainty range of simulation was estimated using the evaporation rate of
 139 $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$ from different literature (Ortega et al., 2012; Myllys et al., 2019). $\omega\text{B97X-D/6-31++G}^{**}$ and
 140 RICC2B3 indicate the evaporation rates therein. The uncertainty in the amine measurement is included in the simulation,
 141 i.e., the higher simulation curve uses $[\text{amine}] \times (1 + \sigma_{\text{amine}})$ as the model input while the low curve uses $[\text{amine}] \times (1 - \sigma_{\text{amine}})$.

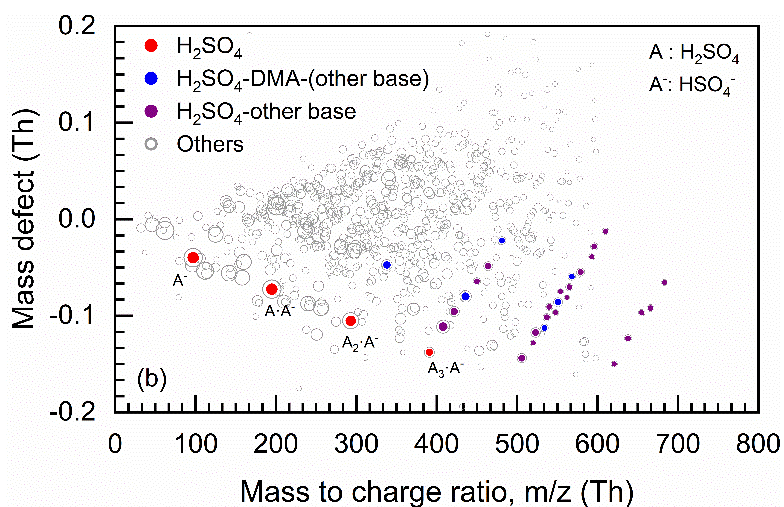


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143 Figure S3: The correlation between the simulated and measured particle formation rates ($J_{1,4}$). The R^2 value was calculated
144 using logarithmic values. This figure uses the same dataset as Fig. 3b. The temporal resolution of the raw data is 5 min, which
145 is determined by the aerosol size spectrometers.

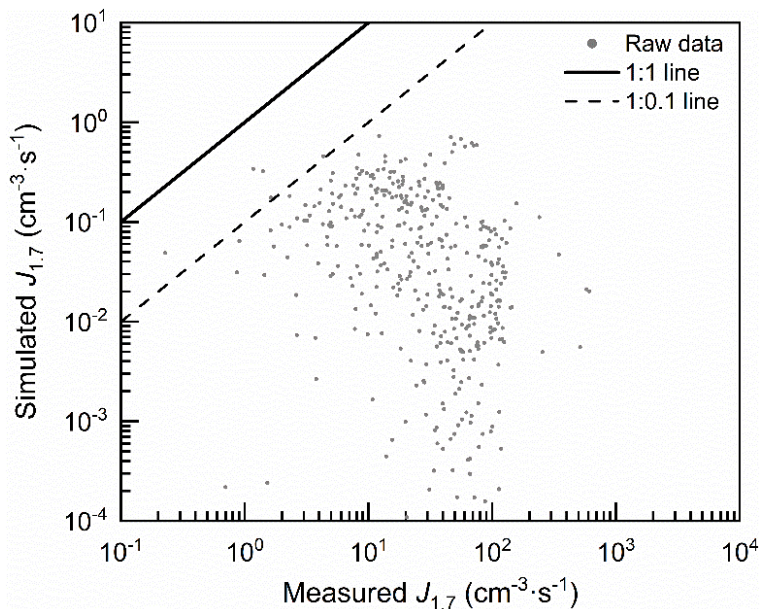


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148 Figure S4: Mass defect plots of (a) neutral clusters measured by a ToF-CIMS and (b) naturally charged clusters measured by
 149 an Api-ToF-MS on Feb. 24, 2018. The dot size indicates the ion count number of each corresponding peak per unit volume.
 150 The ion counts were averaged between 11:30 and 12:30. The neutral clusters in (a) were charged using a nitrate source and
 151 only the chemical species after charging are shown. The red dots represent the measured H_2SO_4 clusters without amine, while
 152 the blue and purple dots represent H_2SO_4 clusters with amines (or NH_3 in (b)). In addition to $\text{H}_2\text{SO}_4\text{-C}_2\text{H}_7\text{N}$ cluster, $\text{H}_2\text{SO}_4\text{-}$
 153 CH_5N and $\text{C}_4\text{H}_{11}\text{N}$ clusters were observed for H_2SO_4 trimers. NH_3 was not detected in the neutral clusters in (a). Note that
 154 due to the ionization, evaporation, and fragmentation, the amine molecule in a stable neutral $\text{H}_2\text{SO}_4\text{-amine}$ cluster may detach
 155 during the detection by the mass spectrometer (ToF-CIMS). For instance, although $(\text{H}_2\text{SO}_4)_1(\text{DMA})_1$ is thought to be
 156 relatively stable, the charged $(\text{HSO}_4^-)_1(\text{DMA})_1$ is unstable and hence only HSO_4^- and $\text{H}_2\text{SO}_4\text{NO}_3^-$ were detected. In addition,
 157 although a variety of organics were detected, the concentrations of extremely low volatile organic compounds are limited (~ 1
 158 order of magnitude lower compared to Finnish boreal forest). The volatility of organic compounds was estimated from their
 159 molecular formula using the volatility basis set (Donahue et al., 2011; Donahue et al., 2012). Considering the uncertainties
 160 in this estimation, the contributions of organic compounds to nucleation and the very initial steps of particle growth are
 161 thought to be minor compared to the fast $\text{H}_2\text{SO}_4\text{-amine}$ clustering process.



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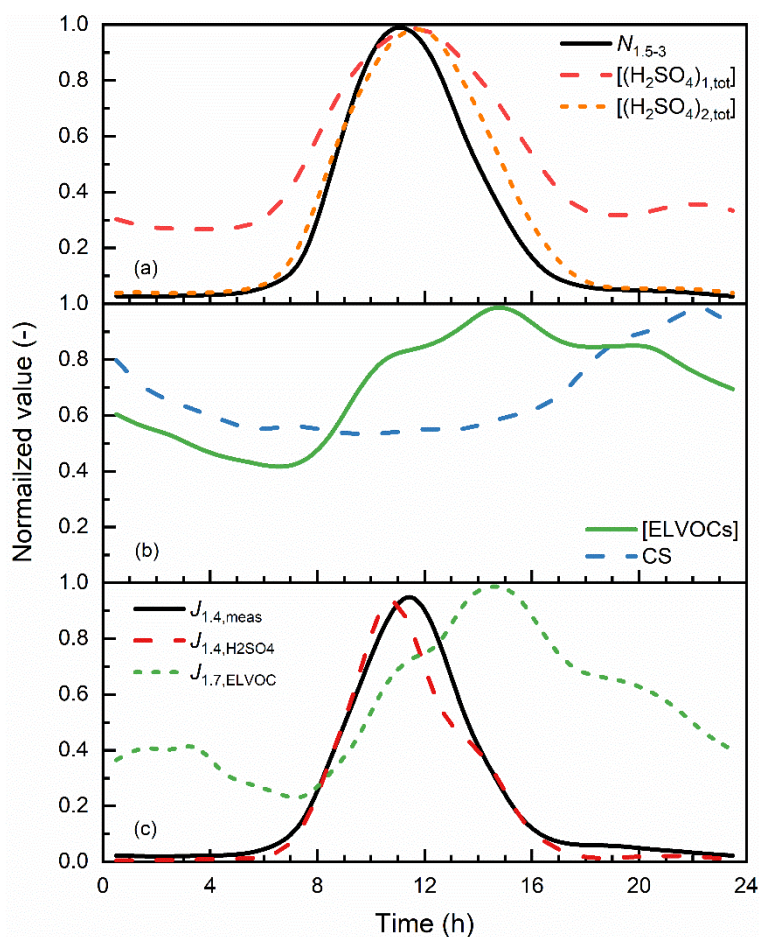
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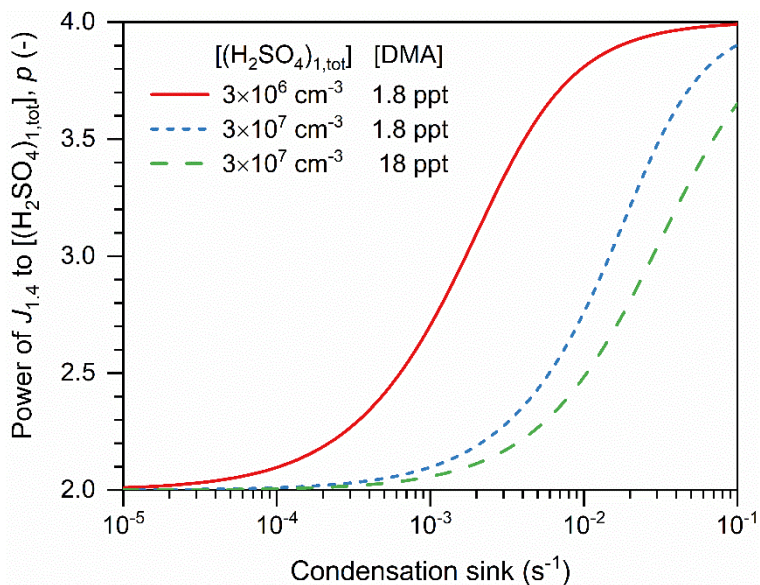
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Figure S5: The measured formation rate of 1.7 nm particles, $J_{1.7}$, and the simulated $J_{1.7}$ using the organics nucleation mechanism. Only the extremely low volatile organic compounds (ELVOCs) measured by the ToF-CIMS was accounted for in the simulation. The volatility was estimated using the volatility basis set (Donahue et al., 2011; Donahue et al., 2012). The $J_{1.7}$ was simulated using the formula proposed in Kirkby et al. (2016). Note that the simulated $J_{1.7}$ from organics nucleation in this figure is overestimated because the CS in urban Beijing is higher than that in the CLOUD chamber, whereas the empirical formula used for this simulation does not account for the influence of CS on $J_{1.7}$. Besides, ion-induced nucleation contributes majorly the simulated $J_{1.7}$ in this figure, whereas its contribution in the polluted atmosphere is thought to be minor. Considering this overestimation and measurement uncertainties, this figure indicates the organics nucleation is insufficient to explain the high nucleation rates observed in urban Beijing.



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173 Figure S6: The diurnal variations of median (a) number concentration of particle ranging from 1.5 nm to 3 nm ($N_{1.5-3}$)
 174 H_2SO_4 monomer concentration, and H_2SO_4 dimer concentration; (b) ELVOC concentration and condensation sink (CS);
 175 (c) measured particle formation rate ($J_{1.4,\text{meas}}$) and simulated formation rates using the H_2SO_4 -amine nucleation
 176 mechanism and the organics nucleation mechanism in ref. (Kirkby et al., 2016). All the variables are normalized by
 177 dividing them by their daily maximum concentration. The trend of the measured nucleation (indicated by $N_{1.5-3}$ and
 178 $J_{1.4,\text{meas}}$) is consistent with that of H_2SO_4 -amine nucleation (indicated by the measured H_2SO_4 dimer concentration and
 179 the simulated $J_{1.4,\text{H}_2\text{SO}_4}$), whereas it is inconsistent with that of organics nucleation (indicated by the measured ELVOC
 180 concentration and the simulated $J_{1.7,\text{ELVOC}}$). Figures S5 and S6 support that organics nucleation is not the governing
 181 nucleation mechanism in urban Beijing.



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183 Figure S7: The power of the simulated formation rate of ~1.4 nm particles to the total concentration of H₂SO₄ monomers as
 184 a function of condensation sink. The curves are obtained at the steady-state. Under a negligible condensation sink, the
 185 formation rate of a cluster is approximately equal to its growth rate into the next cluster. Thus, the formation rate under such
 186 a condition is approximately equal to that of (H₂SO₄)₂(DMA)₂, which is proportional to the square of (H₂SO₄)_{1, tot}
 187 concentration, i.e., $p = 2$. In contrast, the formation rate of a cluster is approximately equal to its coagulation loss rate under
 188 a high condensation sink. Given a fixed DMA concentration, Eqs. S28 indicates that $p = 4$ when the coagulation sink is the
 189 governing sink for clusters. The solid curve in this figure resembles the typical H₂SO₄ and DMA concentrations during this
 190 measurement in urban Beijing. At the typical condensation sink and temperature during new particle formation in urban
 191 Beijing, e.g., 0.017 s⁻¹ and 281 K, the simulated p on the solid line is approximately 3.6.

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193 References

- 194 Chan, T. W., and Mozurkewich, M.: Measurement of the coagulation rate constant for sulfuric acid particles as a function of
195 particle size using tandem differential mobility analysis, *Journal of Aerosol Science*, 32, 321-339, 10.1016/S0021-
196 8502(00)00081-1, 2001.
- 197 Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol
198 mixing thermodynamics, *Atmospheric Chemistry and Physics*, 11, 3303-3318, 10.5194/acp-11-3303-2011, 2011.
- 199 Donahue, N. M., Kroll, J. H., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set – Part 2: Diagnostics of
200 organic-aerosol evolution, *Atmospheric Chemistry and Physics*, 12, 615-634, 10.5194/acp-12-615-2012, 2012.
- 201 Halonen, R., Zapadinsky, E., Kurtén, T., Vehkamäki, H., and Reischl, B.: Rate enhancement in collisions of sulfuric acid
202 molecules due to long-range intermolecular forces, *Atmospheric Chemistry and Physics*, 19, 13355-13366, 10.5194/acp-19-
203 13355-2019, 2019.
- 204 Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl,
205 J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke,
206 S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen,
207 T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S.,
208 Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I.,
209 Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y.,
210 Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M.,
211 Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and
212 Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521-526, 10.1038/nature17953, 2016.
- 213 Kuang, C., Riipinen, I., Sihto, S. L., Kulmala, M., McCormick, A. V., and McMurry, P. H.: An improved criterion for new particle
214 formation in diverse atmospheric environments, *Atmospheric Chemistry and Physics*, 10, 8469-8480, 10.5194/acp-10-8469-
215 2010, 2010.
- 216 Kürten, A., Li, C., Bianchi, F., Curtius, J., Dias, A., Donahue, N. M., Duplissy, J., Flagan, R. C., Hakala, J., Jokinen, T., Kirkby, J.,
217 Kulmala, M., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Onnela, A., Rissanen, M. P., Simon, M., Sipilä, M., Stozhkov, Y.,
218 Tröstl, J., Ye, P., and McMurry, P. H.: New particle formation in the sulfuric acid–dimethylamine–water system: reevaluation
219 of CLOUD chamber measurements and comparison to an aerosol nucleation and growth model, *Atmospheric Chemistry and*
220 *Physics*, 18, 845-863, 10.5194/acp-18-845-2018, 2018.
- 221 Lehtinen, K. E. J., Dal Maso, M., Kulmala, M., and Kerminen, V.-M.: Estimating nucleation rates from apparent particle
222 formation rates and vice versa: Revised formulation of the Kerminen–Kulmala equation, *Journal of Aerosol Science*, 38, 988-
223 994, 10.1016/j.jaerosci.2007.06.009, 2007.
- 224 McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala, M., and Vehkamäki, H.: Atmospheric
225 Cluster Dynamics Code: a flexible method for solution of the birth-death equations, *Atmospheric Chemistry and Physics*, 12,
226 2345-2355, 10.5194/acp-12-2345-2012, 2012.
- 227 McMurry, P. H., Fink, M., Sakurai, H., Stolzenburg, M. R., Mauldin, R. L., Smith, J., Eisele, F., Moore, K., Sjostedt, S., Tanner,
228 D., Huey, L. G., Nowak, J. B., Edgerton, E., and Voisin, D.: A criterion for new particle formation in the sulfur-rich Atlanta
229 atmosphere, *Journal of Geophysical Research*, 110, D22S02, 10.1029/2005jd005901, 2005.
- 230 Myllys, N., Kubečka, J., Besel, V., Alfaouri, D., Olenius, T., Smith, J. N., and Passananti, M.: Role of base strength, cluster
231 structure and charge in sulfuric-acid-driven particle formation, *Atmospheric Chemistry and Physics*, 19, 9753-9768,
232 10.5194/acp-19-9753-2019, 2019.
- 233 Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From
234 quantum chemical formation free energies to evaporation rates, *Atmospheric Chemistry and Physics*, 12, 225-235,
235 10.5194/acp-12-225-2012, 2012.
- 236 Stolzenburg, D., Simon, M., Ranjithkumar, A., Kürten, A., Lehtipalo, K., Gordon, H., Nieminen, T., Pichelstorfer, L., He, X.-C.,
237 Brilke, S., Xiao, M., Amorim, A., Baalbaki, R., Baccarini, A., Beck, L., Bräkling, S., Caudillo Murillo, L., Chen, D., Chu, B., Dada,

238 L., Dias, A., Dommen, J., Duplissy, J., El Haddad, I., Finkenzeller, H., Fischer, L., Gonzalez Carracedo, L., Heinritzi, M., Kim, C.,
239 Koenig, T. K., Kong, W., Lamkaddam, H., Lee, C. P., Leiminger, M., Li, Z., Makhmutov, V., Manninen, H. E., Marie, G., Marten,
240 R., Müller, T., Nie, W., Partoll, E., Petäjä, T., Pfeifer, J., Philippov, M., Rissanen, M. P., Rörup, B., Schobesberger, S., Schuchmann,
241 S., Shen, J., Sipilä, M., Steiner, G., Stozhkov, Y., Tauber, C., Tham, Y. J., Tomé, A., Vazquez-Pufleau, M., Wagner, A. C., Wang,
242 M., Wang, Y., Weber, S. K., Wimmer, D., Wlasits, P. J., Wu, Y., Ye, Q., Zauner-Wieczorek, M., Baltensperger, U., Carslaw, K. S.,
243 Curtius, J., Donahue, N. M., Flagan, R. C., Hansel, A., Kulmala, M., Volkamer, R., Kirkby, J., and Winkler, P. M.: Enhanced
244 growth rate of atmospheric particles from sulfuric acid, *Atmospheric Chemistry and Physics Discussions*, in review,
245 10.5194/acp-2019-755, 2019.

246 Thomas, J. M., He, S., Larriba-Andaluz, C., DePalma, J. W., Johnston, M. V., and Hogan, C. J., Jr.: Ion mobility spectrometry-
247 mass spectrometry examination of the structures, stabilities, and extents of hydration of dimethylamine-sulfuric acid
248 clusters, *Physical Chemistry Chemical Physics*, 18, 22962-22972, 10.1039/c6cp03432b, 2016.

249