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Evaluation on the role of sulfuric acid in the mechanisms of NPF

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Evaluation on the role of sulfuric acid in the mechanisms of new particle formation for Beijing case

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Abstract

New particle formation (NPF) is considered as an important mechanism for gas-to-particle transformation, and gaseous sulfuric acid is believed as a crucial precursor. Up to now few field-based studies on nucleation mechanisms and the role of sulfuric acid were conducted in China. In this study, simultaneously measurements of particle number size distributions and gaseous sulfuric acid concentrations were performed from July to September in 2008. Totally, 22 new particle formation events were observed during the entire 85 campaign days. The results show that the condensation sink of pre-existing particles is one of the limiting factors to determine the occurrence of nucleation events in Beijing. The concentrations of gaseous sulfuric acid show good correlations with freshly nucleated particles (N_{3-6}) and formation rates (J_3 and $J_{1.5}$). The power-law relationship between H_2SO_4 concentration and N_{3-6} or J was adopted to explore the nucleation mechanism. The exponents range from 1 to 5. More than half of the NPF events exhibit an exponent larger than 2.5. For these cases, the thermodynamic process works better than the activation or kinetic nucleation theories to explain the nucleation events in urban atmosphere of Beijing.

1 Introduction

New particle formation (NPF) and the subsequent particle growth have been observed in various environments all over the world (Kulmala et al., 2004; Holmes, 2007). Model results suggest that nucleation may be an important source of condensation nucleus (CN) and cloud condensation nuclei (CCN) in global scale (Spracklen et al., 2008; Merikanto et al., 2009). The particle growth could affect the global climate system by scattering and absorption of solar radiation directly (Stier et al., 2007). Furthermore, these particles may act as CCN and ice nuclei (IN) and influence the climate system indirectly (Lohmann and Feichter, 2005). In order to obtain an improved understanding of the various effects of atmospheric particles, the properties of the nucleation mechanism and growth should be understood completely and validated for different areas.

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Gaseous sulfuric acid has been identified as a key component in the NPF process (Weber et al., 1995; Kulmala, 2003; Berndt et al., 2005; Fiedler et al., 2005) and proposed as a key component in many nucleation theories, such as binary, ternary or ion-induced nucleation (Korhonen et al., 1999; Weber et al., 1999; Yu and Turco, 2000; Napari et al., 2002; Vehkamäki et al., 2002). In order to investigate the role of sulfuric acid in the nucleation process, based on recent observations the relationship between observed nucleation rates and ambient gaseous sulfuric acid concentrations with an exponent between 1 ($J = A^*[\text{H}_2\text{SO}_4]$) and 2 ($J = K^*[\text{H}_2\text{SO}_4]^2$) have been reported (Sihto et al., 2006; Riipinen et al., 2007; Boy et al., 2008; Kuang and McMurry, 2008; Paasonen et al., 2009; Nieminen et al., 2009). In these publications the authors pointed out that the activation and kinetic nucleation maybe the potential formation mechanisms. Meanwhile, the role of low-volatile organic vapors to atmospheric nucleation caused widespread attentions and several recent studies suggested that organic vapors do participate in the nucleation process (Bonn et al., 2008; Paasonen et al., 2009, 2010; Lauros et al., 2011).

However, most of the NPF observations were conducted in a clean environment, results in urban polluted environment are rare. High frequency of NPF event was observed in Beijing based on a one-year statistical analysis (Wu et al., 2007). Yue et al. (2010) pointed out that sulfuric acid plays a dominant role in both the new particle formation and subsequent growth process. Nevertheless, the relationship between sulfuric acid and freshly nucleated particles/formation rates is still unclear.

In this paper, we present the Beijing case for the NPF as an urban polluted atmosphere. Based on simultaneous measurements of particle number size distributions and gaseous sulfuric acid concentrations, the role of sulfuric acid to NPF is explored in order to answer the following questions: (1) what is the limiting factor to determine the occurrence of the NPF events in Beijing, (2) how do the freshly nucleated particles and nucleation rates depend on the sulfuric acid concentrations, and (3) how do the activation and kinetic nucleation theories apply in the urban environment and what are the differences compared with other atmospheric environments.

2 Materials and methods

2.1 Measurements

The measurements were conducted at an urban site, the campus of Peking University (39.99° N, 116.31° E). The observatory is located on the 6th floor of an academic building (about 20 m above the ground level). Detailed descriptions of the measurement site and surrounding environment can be found in Wu et al. (2008). Both particle number size distributions and sulfuric acid measurements were carried out from 12 July to 25 September 2008.

Number size distributions of atmospheric particles from 3 to 900 nm (mobility diameter) were measured by a TDMPMS (Twin Differential Mobility Particle Sizer) system with 10 min time resolution. It consists of two parallel differential mobility analyzers (DMAs) that classify particles in the size ranges 3–80 nm and 40–900 nm. The relative humidity within the whole system was kept below 30%. The TDMPMS system was described in more detail by Wehner et al. (2008).

The gaseous sulfuric acid concentration was measured by an AP-ID-CIMS, which was developed at Texas A&M University. The time resolution was 12 s, and then the data were averaged to 10 min in order to reduce statistical error and keep consistent with the particle number size distribution. A detailed description of the instrument was introduced by Zheng et al. (2011).

2.2 Data analysis

2.2.1 Time delay Δt and growth rate GR

Recent observations and laboratory calculations imply the diameter of the nucleation particles is around 1.5 nm (Kulmala et al., 2007; Zhang, 2010). The lowest detecting diameter measured by the TDMPMS is however 3 nm. Freshly nucleated particles are thus not observed at the same time of their formation but after a time interval Δt , until

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they grow up to the diameter of 3 nm. This time delay implies that the increase in the concentration of small particles is preceded by the increase in sulfuric acid concentration. Based on this assumption, the growth rate from the nucleation size (1.5 nm in this study) to the detectable size (3 nm) can be expressed as:

$$5 \quad \text{GR}_{1.5-3} = \frac{3 \text{ nm} - 1.5 \text{ nm}}{\Delta t} = \frac{1.5 \text{ nm}}{\Delta t} \quad (1)$$

Here Δt is defined as the time delay between the sulfuric acid concentration and N_{3-6} , where N_{3-6} refers to the particle number concentration in the size range 3–6 nm (covers the five lowest channels of the TDMPs) which could be considered as the freshly nucleated particles to a great extent. For some cases of NPF there was however no time delay observed between N_{3-6} and sulfuric acid concentration. This phenomenon is due to the rapid growth from nucleation size to detectable size and a too long time resolution by the TDMPs. We thus assume that it may take 10 min (time resolution of instruments) for particles to grow up from 1.5 nm to 3 nm pointing to $\text{GR}_{1.5-3}$ equal to 9 nm h⁻¹ (which is (3–1.5) nm/10 min). In these cases, the real growth rate should be larger than 9 nm h⁻¹.

2.2.2 Particle formation rates J_3 and $J_{1.5}$

The time evolution of N_{3-6} is described with a balance equation:

$$20 \quad \frac{dN_{3-6}}{dt} = \text{GR}_3 \cdot n_3 - \text{GR}_6 \cdot n_6 - \text{CoagS}_{3-6} \cdot N_{3-6} \quad (2)$$

Where n is the particle size distribution function, defined as $n_d = dN_d/dd_p$ with the particle diameter d_p and GR_{d_p} is the growth rate of the particles with diameter d_p . The CoagS_{3-6} denotes the average coagulation sink for the 3–6 nm range (Kulmala et al., 2001). Hence, this formula includes terms for the growth into the 3–6 nm range over the 3 nm limit (first term), out of the range over the 6 nm limit (second term) and the loss by coagulation scavenging (third term). By rearranging the terms, and denoting

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the first term on the right hand side of Eq. (2) by J_3 , we get the equation to calculate the particle formation rate at 3 nm:

$$J_3 = \frac{dN_{3-6}}{dt} + \text{CoagS}_4 \cdot N_{3-6} + \frac{1}{3 \text{ nm}} \text{GR}_6 \cdot N_{3-6} \quad (3)$$

The approximations made in Eq. (3) are the following: (i) the CoagS_{3-6} has been approximated by a term representing the loss of 4 nm sized particles (4 nm is approximately the geometric mean of 3 and 6 nm) and CoagS_4 could be calculated directly from the measured particle number size distribution, (ii) the condensation loss out of the size range 3–6 nm is obtained by approximating n_6 by $N_{3-6}/(6 \text{ nm}-3 \text{ nm})$ and the $\text{GR}_6 = \text{GR}$, respectively. Here GR is estimated from the time delay between sulphuric acid and N_{3-6} as shown in the Eq. (1).

Based on the J_3 values, the nucleation rate $J_{1.5}$ can be estimated using the method presented by Kerminen and Kulmala (2002):

$$J_{1.5}(t) = J_3(t') \exp\left(\gamma \frac{CS'}{\text{GR}} \left(\frac{1}{1.5 \text{ nm}} - \frac{1}{3 \text{ nm}}\right)\right) \quad (4)$$

Here γ is a coefficient with the approximate value of $0.23 \text{ m}^2 \text{ nm}^2 \text{ h}^{-1}$ and CS' is the condensation sink in unit m^{-2} . For the condensation sink CS' we use the median value from the interval $[t, \Delta t]$.

2.2.3 Determination of the nucleation coefficients A and K

In this work, we study two nucleation theories using $J_{1.5}$ estimated from the particle measurement data, the activation theory and the kinetic theory (Kulmala et al., 2006). These theories assume that the nucleation rate should have a power law dependence on the sulfuric acid concentration. In the activation theory, the clusters containing one sulfuric acid molecule will activate for further growth due to heterogeneous nucleation, thus the nucleation rate is directly proportional to the sulfuric acid concentration:

$$J_{1.5} = A[\text{H}_2\text{SO}_4] \quad (5)$$

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where A is the activation coefficient (in unit s^{-1}).

The kinetic theory suggests that critical clusters are formed by collisions of two sulfuric acid molecules. According to kinetic gas theory, the collision frequency of two molecules is correlated with the concentration of both molecules. The nucleation rate can thus be written as:

$$J_{1.5} = K[\text{H}_2\text{SO}_4]^2 \quad (6)$$

where K is the kinetic coefficient (in unit $\text{cm}^3 \text{s}^{-1}$).

According to previous studies (Sihto et al., 2006; Kuang and McMurry, 2008), the relationship between nucleation rate and sulfuric acid concentration is in general within the exponent between 1 and 2 which signifies the reasonability of these two theories. On the other hand, exponents larger than 2 are also observed in some cases (Riipinen et al., 2007), which could indicate that the atmospheric nucleation is thermodynamically limited (Kulmala et al., 2006). In this study, the exponent is set to 3 to represent this case and the nucleation theory is defined as:

$$J_{1.5} = T[\text{H}_2\text{SO}_4]^3 \quad (7)$$

where T is the thermodynamic coefficient (in unit $\text{cm}^6 \text{s}^{-1}$).

3 Results and discussion

3.1 Comparisons of sulfuric acid concentration and condensation sink between the NPF and non-NPF days

The improved air quality during 2008 Olympic Games (UNEP, 2009) with less pre-existing particles enhanced the NPF. The frequency of the NPF event (26 %) was higher than our previous studies in the same period of 2004–2007 (11%–20 %) (Wu et al., 2007; Yue et al., 2009). In total, 22 NPF events were identified out of 85 days from July to September 2008, in which on 17 NPF events both particle number size distributions

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and sulfuric acid concentrations were simultaneously measured. In this paper, freshly nucleated particles in the size range from 3 to 6 nm are chosen to examine its connection with sulfuric acid concentration. Figure 1 displays the temporal variations of the sulfuric acid (H_2SO_4), condensation sink (CS) and 3–6 nm particle number concentrations (N_{3-6}) for the whole measurement period. The N_{3-6} and H_2SO_4 concentration showed similar variation trend on the NPF event days (gray background). During some non-event days however, even the H_2SO_4 concentration went up to equal levels compared to the event days (e.g. 17 August, day 230 and 2 September, day 247). On these days an increase in nucleation mode particles with the H_2SO_4 concentration was not observed. This phenomenon may be due to the high concentration of pre-existing particles, which was also visible in the large CS values. The pre-existing particles could act as a sink to capture for both, condensing vapors and newly formed particles which could prevent the occurrence of NPF events.

Figure 2 shows the comparison between sulfuric acid concentrations and condensation sink values of NPF-event and non-event days before the nucleation events start (08:00–11:00). It can be seen clearly that on average, the event days are associated with lower condensation sinks than the non-event days. The mean CS (during 08:00–11:00) on NPF event days (0.022 s^{-1}) was typically significantly lower than on non-event days (0.045 s^{-1}). Even though during NPF event days, the CS value were higher than other observations in clean environments (Riipinen et al., 2007; Boy et al., 2008) or polluted regions (Kulmala et al., 2005; Hamed et al., 2007). The reasons for the NPF-events in the Beijing case were the abundant SO_2 concentrations and the oxidation capacity, resulting in high concentrations of sulfuric acid (Wu et al., 2007; Yue et al., 2010). These results indicate that the existing aerosol concentration is more likely the key limiting factor to determine the observation of NPF events in Beijing rather than the concentration of gaseous sulfuric acid. This conclusion is consistent with our previous study (Wu et al., 2007).

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3.2 Correlation between freshly nucleated particles and sulfuric acid concentration

The concentrations of newly formed particles and sulfuric acid are obviously correlated on the 17 NPF event days. Figures 3a and 4a show two typical cases of the NPF events observed on 15 August (day 228) and 12 September (day 256), respectively. In both cases a significant nucleation mode was formed around 10:00 and followed by particle growth until the next day. The condensational sink of pre-existing particles before the nucleation event on 15 August ($CS = 0.014 \text{ s}^{-1}$) was lower than that on 12 September ($CS = 0.038 \text{ s}^{-1}$). The initial concentration of pre-existing particles may affect the nucleation process and will be discussed later.

Figures 3b and 4b display the diurnal variations of N_{3-6} and sulfuric acid concentrations in two cases, respectively. Unlike other studies (Riipinen et al., 2007; Kuang and McMurry, 2008; Paasonen et al., 2009), a time shift between the rise of N_{3-6} and sulfuric acid concentrations in both cases was not observed. As discussed before, this might be due to the rapid growth from cluster size to detectable size and the limitation of instrument time response. The growth rate in the size range from 3 to 10 nm are 20.1 nm h^{-1} (15 August) and 34.2 nm h^{-1} (12 September), respectively. The best correlations are 0.90 on 15 August with the exponent 1.62 and 0.92 on 12 September with the exponent 4.5, respectively (see Figs. 3c and 4c).

In order to compare our results with the other studies, we choose the same classification as described in Riipinen et al. (2007). The statistic results are shown in Table 1. The mean value of the correlation coefficient is 0.86 (R in the range 0.66–0.96) which reflects a good correlation between N_{3-6} and sulfuric acid. Different from the other studies, with exponents between 1 and 2, the NPF event days of this study, lead to exponents more concentrated between 2.5 and 5 (53% in 17 investigated days). In addition, we find the exponents of sulfuric acid increase with the CS values in these four categories of Beijing. The mean CS values (08:00–11:00 during nucleation days) are 0.009 ($n \sim 1$), 0.014 ($n \sim 1.5$), 0.020 ($n \sim 2$) and 0.025 ($n > 2.5$), respectively. The

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exponent in the correlation of N_{3-6} and sulfuric acid concentrations might be related to the background particle concentration and atmosphere nucleation precursors. Therefore, more information on the nucleation process and chemical composition of freshly formed particles is needed.

3.3 Correlation between particle formation rates and sulfuric acid concentration

The formation rates are calculated based on the particle number size distributions using Eq. (2). Figure 5 shows the diurnal variations of J_3 values and sulfuric acid concentrations during the two selected days. A good correlation is observed between J_3 and sulfuric acid and for the N_{3-6} and sulfuric acid.

The formation rates J_3 and $J_{1.5}$ are plotted versus the sulfuric acid concentrations in Fig. 6. It is obviously that the exponents in the relationships between particle formation rates (both J_3 and $J_{1.5}$) and sulfuric acid concentrations are mostly between 1 and 5 in Beijing. It is hard to distinguish the dominative nucleation theories depend on the scatter data plots. The average slopes for the 17 days data set are 2.1 (J_3) and 2.8 ($J_{1.5}$), respectively. These values are higher than obtained during the studies in Hyytiälä, Heidelberg or other stations, where the exponents are always between 1 and 2 (Riipinen et al., 2007; Nieminen et al., 2009; Sipila et al., 2010). This results indicate that in the polluted urban environment of Beijing, higher H_2SO_4 concentrations are needed to form new particles and avoid the capture by the existing particles.

3.4 Nucleation coefficients

Two cases of the NPF events were observed in Beijing, as mentioned above: (1) the exponent in the correlation of the formation rate and sulfuric acid between 1 and 2, which implies that activation or kinetic nucleation is the possible main nucleation mechanism; (2) the exponent larger than 3 indicates that thermodynamic nucleation is the dominate mechanism. The first case is similar with the observations in clean environments (Sihto

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et al., 2006; Riipinen et al., 2007). In the polluted urban environment of Beijing, more than half of the NPF events (53%) belong to the second case.

The nucleation activation coefficients A and kinetic coefficient K are calculated by using the Eqs. (5) and (6). The formation rates ($J_{1,5}$) calculated from particle number size distributions and the sulfuric acid concentrations are compared in Fig. 7. It illustrates the correlation between the results from particle size distribution and sulfuric acid measurements on two cases of NPF event days: the exponent between 1 and 2 on 15 August, while greater than 3 on 12 September. On 15 August, the correlation coefficients between activation nucleation and kinetic nucleation are almost the same and the difference is negligible. The kinetic nucleation theory fits better than the activation theory on 12 September. In contrast, the thermodynamic process seems more reasonable than the other two theories (thermodynamic coefficient T are calculated by using the Eq. 7).

The results in this and other studies are summarized in Table 2. During the 17 NPF event days, the mean values of the activation coefficient was $1.56 \times 10^{-6} \text{ s}^{-1}$ ranging from $0.59 \times 10^{-6} \text{ s}^{-1}$ to $4.00 \times 10^{-6} \text{ s}^{-1}$, and the mean values of kinetic coefficient was $2.72 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ varying from $0.86 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ to $5.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. Compared to the coefficients A and K calculated at Hohenpeissenberg, in Hyytiälä, and in the Rocky Mountains, the A values are between 10^{-8} and 10^{-6} s^{-1} and the K values are between 10^{-14} and 10^{-12} s^{-1} , which is in the same order as chemical reaction rate coefficients in the gas phase (Sihto et al., 2006).

4 Conclusions

This paper focuses on the Beijing case of the NPF in the polluted urban environment. Field-based discussion is made to explore the nucleation mechanism and the role of sulfuric acid. The following conclusions are made.

The mean CS during the time period of 08:00–11:00 on the NPF event days is about half of that in non-event days. The results reveal that besides abundant gaseous

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sulfuric acid, a low CS of pre-existing particles is one of the limiting factors to determine the occurrence of a nucleation event.

Good correlation ($R = 0.86$) between N_{3-6} and sulfuric acid was observed in Beijing. The correlation coefficient values varied from 0.66 to 0.96. Due to the rapid growth from nucleation size to detectable size, most of the NPF events in Beijing were observed without a time delay between the detection of freshly formed particles and the occurrence of sulfuric acid, which was rarely observed previously. The exponent is larger in other studies, more than half of them are located between 2.5 and 5. Meanwhile, the exponents of sulfuric acid increasing with the CS values were observed in Beijing case.

Formation rates of 3 nm and 1.5 nm particles estimated from particle measurements are correlated with sulfuric acid concentration to the power from 1 to 5 in this study. The mean slopes for the 17 days data set are 2.1 (J_3) and 2.8 ($J_{1.5}$), respectively. In more than half of all cases, the thermodynamic process works better than the activation and kinetic nucleation theories, which is different from the previous literatures. The mean values of activation and kinetic coefficient are $1.56 \times 10^{-6} \text{ s}^{-1}$ and $2.72 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, respectively. The values of A and K are in the same order as the previous studies.

The larger exponent between particle formation rates and sulfuric acid concentrations implies that besides H_2SO_4 , also other species such as low-volatility organic vapors might be involved in the early stage of NPF events in Beijing. Future investigations on the role of organic compounds in the initial nucleation process are required and the comparison with previous studies in other atmosphere environment are very important.

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Table 1. Comparisons of the exponent in the correlation of N_{3-6} and sulfuric acid concentrations with other studies. R refers to the correlation coefficient. N (%): N is the number of nucleation event and the value in bracket indicates the percentage accounting for.

	Hyytiälä QUEST II	Heidelberg QUEST III	Hyytiälä BACCI/QUEST IV	Beijing CAREBeijing 2008
$n \approx 1$	6 (38 %)	6 (60 %)	9 (45 %)	3 (18 %)
$n \approx 1.5$	4 (25 %)	3 (30 %)	2 (10 %)	1 (6 %)
$n \approx 2$	5 (31 %)	1 (10 %)	6 (30 %)	4 (23 %)
$n > 2.5$	1 (6 %)	–	3 (15 %)	9 (53 %)
Mean R	0.85	0.75	0.82	0.86
Ref.		Riipinen et al. (2007)		This study

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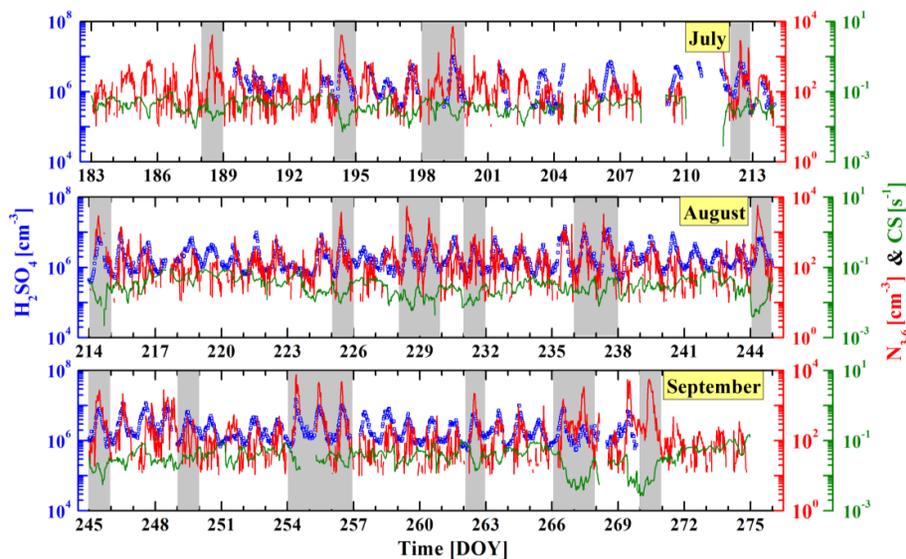


Fig. 1. Time series for the sulfuric acid (H_2SO_4 , blue), condensation sink (CS, green), and 3–6 nm particle number concentrations (N_{3-6} , red) for the whole measurement period. The NPF event days are presented on gray background. The x-axis is presented by DOY (day of year), 1 January is defined as day 1.

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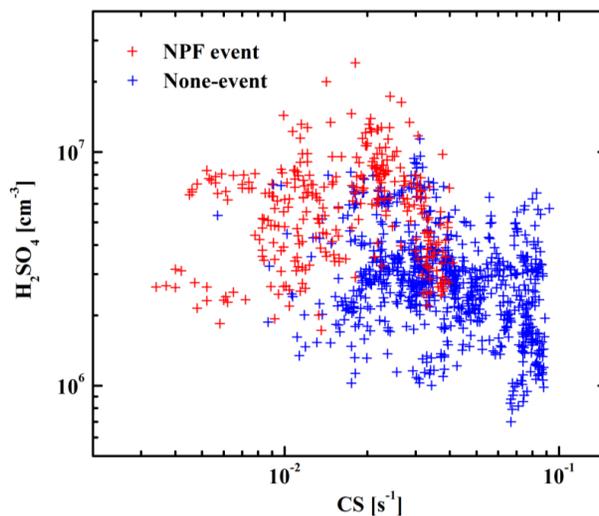


Fig. 2. The 10 min integrated sulfuric acid concentrations and condensation sink values for all data between 08:00 and 11:00. NPF event days (red), Non-event days (blue).

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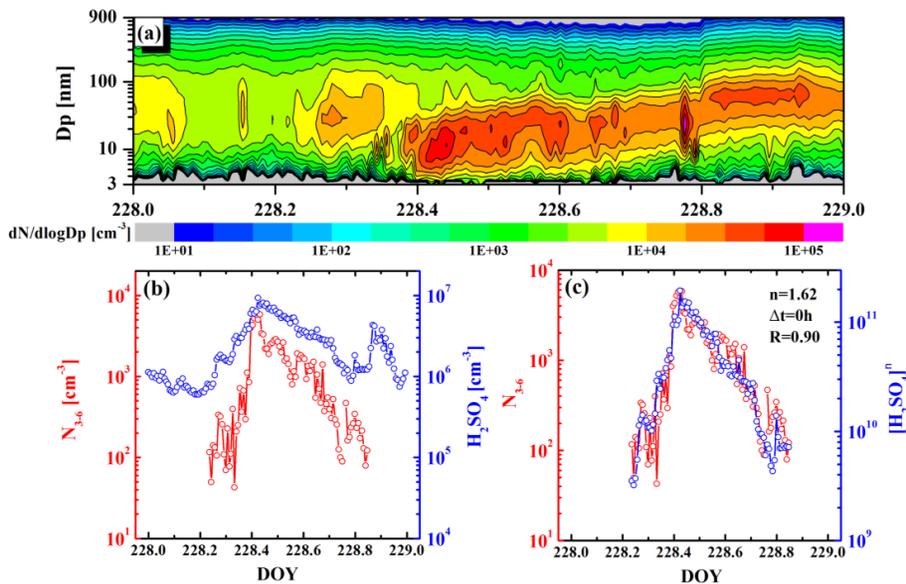


Fig. 3. An example of new particle formation day on 15 August 2008 (day 228) in Beijing. **(a)** particle number size distribution, **(b)** the number concentration of 3–6 nm particles (red) and the sulfuric acid concentration (blue), **(c)** the number concentration of 3–6 nm particles and the sulfuric acid concentration delayed by the time shift ($\Delta t = 0$ h) and raised to the fitted power ($n = 1.62$) with the best correlation ($R = 0.90$).

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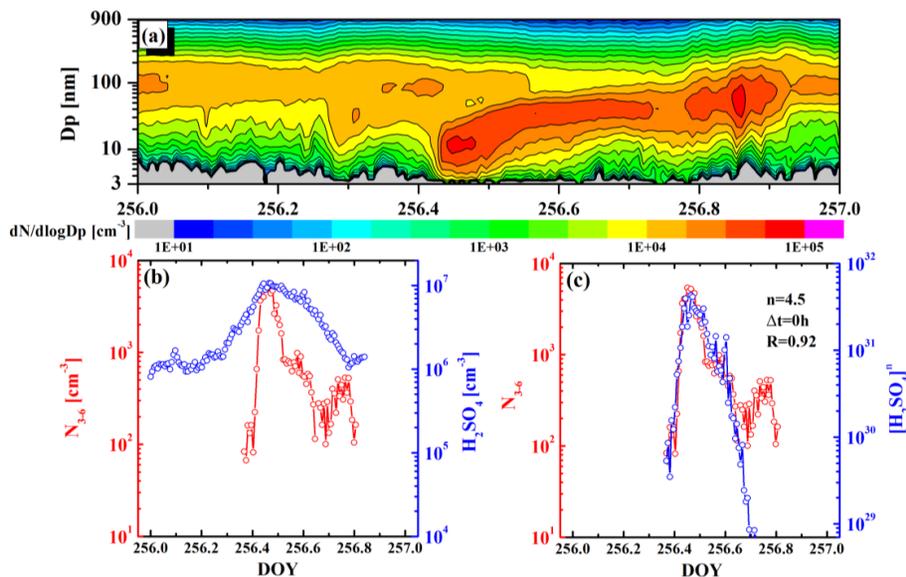


Fig. 4. An example of new particle formation day on 12 September 2008 (day 256) in Beijing. **(a)** Particle number size distribution, **(b)** the number concentration of 3–6 nm particles (red) and the sulfuric acid concentration (blue), **(c)** the number concentration of 3–6 nm particles and the sulfuric acid concentration delayed by the time shift ($\Delta t = 0\text{h}$) and raised to the fitted power ($n = 4.5$) with the best correlation ($R = 0.92$).

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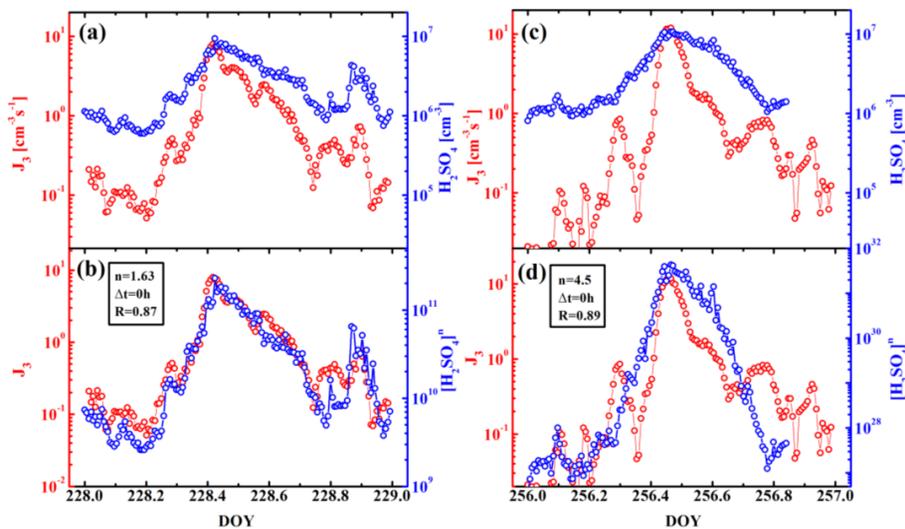


Fig. 5. The correlation of J_3 values (red) and sulfuric acid concentrations (blue) on 15 August (left panel) and 12 September 2008 (right panel) in Beijing. **(a)** and **(c)** the diurnal variation of J_3 values and the sulfuric acid concentrations, **(b)** and **(d)** the J_3 values and the sulfuric acid concentrations delayed by the time shift and raised to the fitted power with the best correlation.

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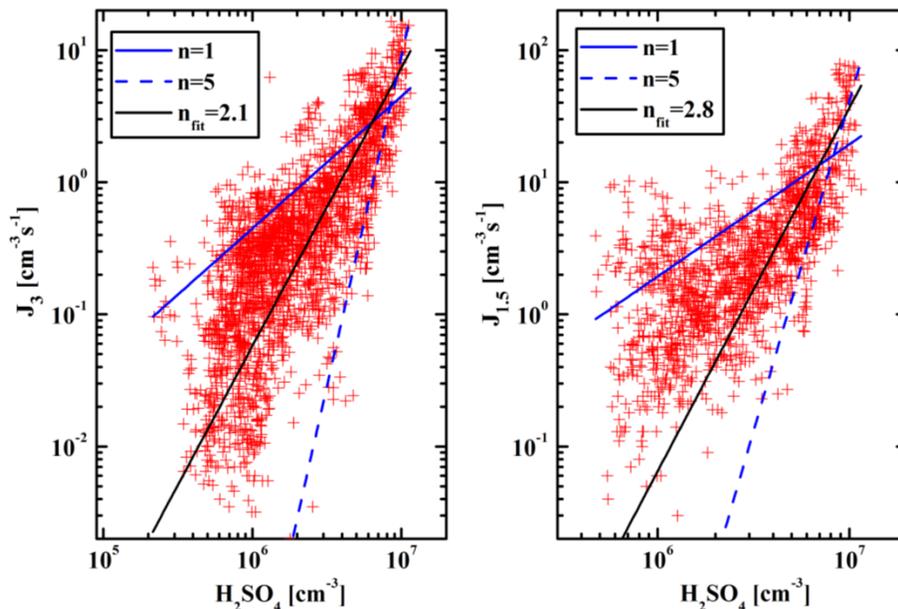


Fig. 6. The formation rate J_3 and $J_{1,5}$ estimated from particle number size distributions versus the sulfuric acid concentrations. Blue lines represent the slopes with $n = 1$ and $n = 5$ in $[H_2SO_4]^n$, Black line represents the average value for the exponent in the entire data set.

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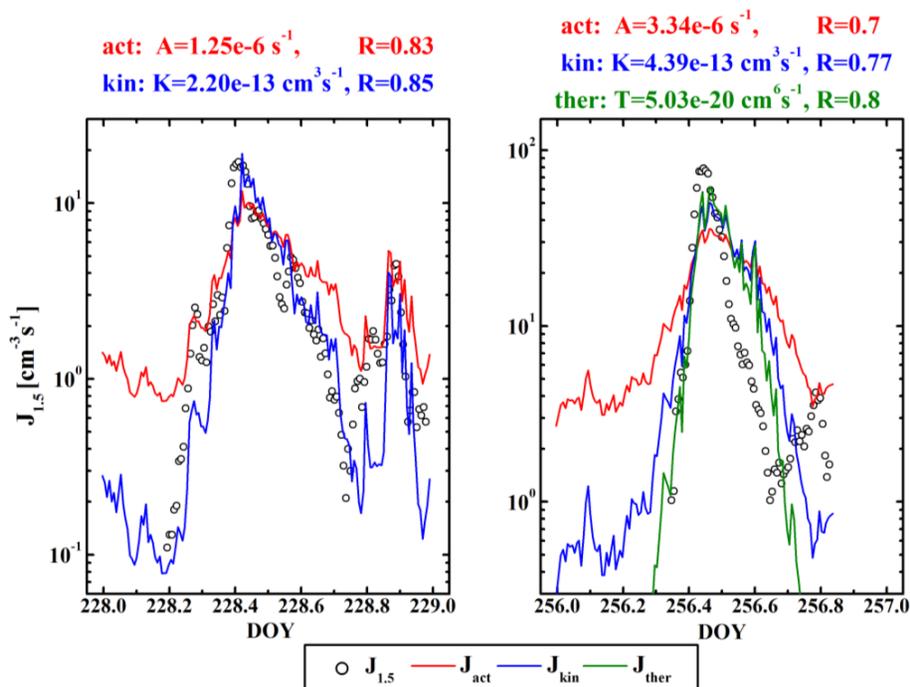


Fig. 7. Nucleation rate ($J_{1.5}$) on 15 August (left panel) and 12 September (right panel) estimated from the particle number size distribution measurements and calculated from the sulfuric acid concentration using the activation and kinetic nucleation mechanisms. Also the thermodynamic coefficient is calculated on 12 September.

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