# **1** Supplementary Information:

2	Response factor of a Q-ACSM to chamber generated SOA with different average oxygen content
3	Xiaoxiao Li <sup>1</sup> , Yan Ma <sup>2,3*</sup> , Hui Chen <sup>2,3</sup> , Youling Jiang <sup>2,3</sup> , Xin Ma <sup>2,3</sup> , Rujin Yin <sup>1</sup> , Dongsen Yang <sup>2,3</sup> , Xiaowen
4	Shi <sup>2,3</sup> , Jiming Hao <sup>1</sup> , Jingkun Jiang <sup>1</sup> , and Jun Zheng <sup>2,3*</sup>
5	<sup>1</sup> State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment,
6	Tsinghua University, 100084 Beijing, China
7	<sup>2</sup> Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing University
8	of Information Science & Technology, Nanjing 210044, China
9	<sup>3</sup> Joint Laboratory for Air Quality and Climate, Nanjing University of Information Science & Technology,
10	Nanjing 210044, China
11	Corresponding authors: Drs. Jun Zheng and Yan Ma
12	Email: zheng.jun@nuist.edu.cn and mayan@nuist.edu.cn
13	<i>Tel.:</i> +86-18251919852
14	Fax: +86-25-58731090

15 1 Calibration of instruments

# 16 1.1 ACSM RF<sub>NO3</sub>, RIE<sub>NH4</sub> and E<sub>L</sub> Calibrations



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Figure S1. Instrument setup for Q-ACSM RF<sub>NO3</sub> calibration and determination of the aerodynamic lens
 transmission efficiency.

The calibration of  $RF_{NO3}$  (which is also customarily called  $RIE_{NO3}$ ) was conducted by following the procedure recommended in by Jayne et al. (2000), Ng et al. (2011) and the manual of the Q-ACSM. Before the  $RF_{NO3}$  calibration, the sampling flow rate (0.85 LPM) of the Q-ACSM was calibrated with a Gilibrator-2 system (Sensdyne, USA). The nitrogen peak (m/z = 28) and the internal naphthalene standard peak (m/z = 128) were used to do m/z calibration before the experiments. The multiplier gain was set to 20,000 by adjusting the multiplier voltage. The sampling lines to the Q-ACSM and CPC were made as short as possible and were kept at the same length of 25cm. Dry NH<sub>4</sub>NO<sub>3</sub> aerosols with a 300 nm diameter were generated using an atomizer (Model 3076, TSI) followed by a diffusion dryer and size-selected by a DMA. Lens alignment was done using the lens alignment tool prior to the calibration. Different concentrations of NH<sub>4</sub>NO<sub>3</sub> aerosols were achieved by varying atomizer solution concentration (no more than 5 mM to minimize multiple charges) to do the RF<sub>NO3</sub> calibration. A shape factor for NH<sub>4</sub>NO<sub>3</sub> was set to be 0.8 as suggested by Jayne et al. (2000). As a result, RF<sub>NO3</sub> and RIE<sub>NH4</sub> were determined to be  $3.56\pm0.06\times10^{-11}$ , and  $5.54\pm0.25$ , respectively.

32 The lens transmission efficient ( $E_L$ ) of the Q-ACSM was calibrated using the same setup as in Figure S1. The only difference was that the DMA was set to select a variety of particles with diameters ranging from 33 200nm to 600nm instead of a fixed single diameter of 300 nm. The lens pressure was kept at 1.22±0.02 34 throughout the experiment. To minimize multiple charge problem for larger particles, we conducted  $E_L$ 35 calibration under two sets of comparably low NH<sub>4</sub>NO<sub>3</sub> solution concentrations (~2 mM and ~0.5 mM). 36 However, for the set of experiment with extremely low  $NH_4NO_3$  concentration (~0.5 mM), the Q-ACSM 37 38 sensitivity was not high enough to detect NH<sub>4</sub>NO<sub>3</sub> particles, which therefore was not shown here. Consequently, the calibration result of the lens transmission efficiency was shown in Figure S2. 39



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**Figure S2.** Lens transmission efficiency as a function of particle vacuum aerodynamic diameter (d<sub>va</sub>).

Lens transmission efficiencies for 300~600nm particle were nearly unity, which was in reasonable accordance with some previous studies (Jayne et al., 2000; Knote et al., 2011; Hu et al., 2018), but the diameter range with a unity lens transmission efficiency was much broader than that reported by Liu et al. (2007). The blue line in Figure S2 was used to modify size distribution in our experiments (i.e., 0% transmission for  $d_{va}$  below 40 nm; linear increase in transmission vs log( $d_{va}$ ), from 0% to 100% at  $d_{va}$ =100 nm; 100% transmission efficiency from  $d_{va}$ =100 nm up to  $d_{va}$ =550 nm; 100% transmission between 100 nm and 580 nm; linear decrease in transmission vs log( $d_{va}$ ) from 100% at 580 nm to 0% at 1200 nm). For E<sub>L</sub> below 49 300 nm, we used the results reported by Knote et al. (2011) indicated by the red dashed line in Figure S2. 50 About 10% of uncertainty (shaded area) was applied to the  $E_L$  used in this study as indicated by the blue curve 51 in Figure S2.

# 52 **1.2 APM Calibration**



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#### Figure S3. Instrument Setup for APM calibration.

The calibration of the APM followed the procedures of Ehara et al. (1996) and the APM manual (Figure 55 S2). Three sizes of polystyrene latex spheres (PSL),  $81 \pm 3$  nm,  $147 \pm 3$  nm, and  $269 \pm 5$  nm) were used for 56 size calibration of the the SMPS and mass calibration of the APM. Effective density of the standard PSL 57 spheres was 1.05 g cm<sup>-3</sup>, the measured values were  $1.046 \pm 0.005$  g cm<sup>-3</sup>,  $1.056 \pm 0.006$  g cm<sup>-3</sup> and  $1.067 \pm$ 58 0.008 g cm<sup>-3</sup> for PSL spheres with the size of 81 nm, 147 nm, and 269 nm, respectively. The results indicated 59 that the APM measured slightly lower values of effective density for smaller particles and slightly higher 60 values for larger particles. Nevertheless, the overall bias of the APM measurements were within  $\pm 3\%$  of the 61 62 standard values.

#### 63 2 Uncertainty Analysis

In this work, the reported quantity was considered as a function (y) of measured variables (x<sub>1</sub>, x<sub>2</sub>, x<sub>3</sub>...x<sub>n</sub>)
in the form of f(x<sub>1</sub>, x<sub>2</sub>,..., x<sub>n</sub>). The uncertainties associated with measured x<sub>1</sub>, x<sub>2</sub>, x<sub>3</sub>...x<sub>n</sub> were σ<sub>1</sub>, σ<sub>2</sub>,...σ<sub>n</sub>,
respectively. Accordingly, the mean value of y (y) and its uncertainty (σ<sub>y</sub>) were calculated using Eq. (S1) and
Eq. (S2) as following:

$$\overline{y} = f(\overline{x_1}, \overline{x_2}, \dots, \overline{x_n}) \tag{S1}$$

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$$\sigma_y = \sqrt{\left(\frac{\partial y}{\partial x_1}\right)^2 \sigma_1^2 + \left(\frac{\partial y}{\partial x_2}\right)^2 \sigma_2^2 + \dots + \left(\frac{\partial y}{\partial x_n}\right)^2 \sigma_n^2}$$
(S2)

## 70 2.1 PM<sub>SMPS</sub> uncertainty

71  $PM_{SMPS}$  was calculated using Eq. (3) in the main text. Theoretically, the uncertainty of  $PM_{SMPS}$  ( $\sigma_{PM-SMPS}$ )

72 was associated with  $d_{m,i}$ ,  $dN_i$ ,  $\rho_{eff,i}$ ,  $E_L(d_{m,i})$ , and  $E_{s,i}$ . As discussed in the instrument calibration in Section 1, uncertainties of  $d_{m,i}$  ( $\sigma_{dm}$ ) and  $\rho_{eff}$  ( $\sigma_{\rho}$ ) were within  $\pm 4\%$  and  $\pm 3\%$ , respectively. The uncertainty of E<sub>L</sub> ( $\sigma_{EL}$ ) in 73 the range of 40-600 nm ( $d_{va}$ ) was estimated to be ±10% according to Figure S2. The uncertainty of  $dN_i$  ( $\sigma_N$ ), 74 which was the combination of the uncertainties of particle charging efficiency ( $\sigma_{char}$ ), diffusion loss ( $\sigma_{diff}$ ), and 75 CPC counting efficiency ( $\sigma_{count}$ ) (Buonanno et al., 2009), was assigned to be ±10% for particles with a 76 diameter of 20-200 nm and  $\pm$  20% for 200-800 nm (Wiedensohler et al., 2012; Wiedensohler et al., 2018). The 77 78 uncertainty of  $E_s$  ( $\sigma_{ES}$ ) was estimated to be ±5%. The uncertainty of PM<sub>SMPS</sub> was hence estimated by Eq. (S3) using the averaged sized distribution (as shown in Figures S4 and S6) and  $\rho_{eff}$  in each experiment: 79

 $\sigma_{PM-SMPS}$ 

$$= \sqrt{\sum_{i=1}^{n} PM_{SMPS}^{2}(d_{m,i}) + \sum_{i=1}^{n} PM_{SMPS}^{2}(dN_{i}) + \sum_{i=1}^{n} PM_{SMPS}^{2}(\rho_{eff,i}) + \sum_{i=1}^{n} PM_{SMPS}^{2}(E_{L}(d_{m,i})) + \sum_{i=1}^{n} PM_{SMPS}^{2}(E_{s,i})}$$
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(S3)

82 where  $PM_{SMPS}(x_i)$  is the product of the uncertainties of each bin  $x_i$  ( $\sigma_{x,i}$ ), and the corresponding sensitivity 83 coefficient  $\frac{\partial PM_{SMPS,i}}{\partial x_i}$ , as shown in Eq. (S4):

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$$PM_{SMPS}(x_i) = \frac{\partial PM_{SMPS,i}}{\partial x_i} \cdot \sigma_{x,i}$$
(S4)

85 Then, Eq (S3) can be simplified as Eq. (S5):

$$\sigma_{PM-SMPS} = \sqrt{\sum_{i=1}^{n} (9\sigma_{dm,i}^{2} + \sigma_{dN,i}^{2} + \sigma_{\rho_{eff,i}}^{2} + \sigma_{EL,i}^{2} + \sigma_{ES,i}^{2}) P M_{SMPS,i}^{2}} = \sqrt{\sum_{i=1}^{n^{*}} 0.0378 P M_{SMPS,i}^{2} + \sum_{i=n^{*}}^{n} 0.0678 P M_{SMPS,i}^{2}}}$$
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(S5)

where n\* corresponds to the bins with  $d_m$  larger than 200 nm. Overall, the uncertainty of PM<sub>SMPS</sub> was estimated to be between  $\pm 19.4\%$  and  $\pm 26.0\%$  with the exact value depending on the size distribution (Figures S4 and S6).

# 91 **2.2 RRF uncertainty**

92 RRF was calculated with Eq. (2) in the main text. The uncertainty of RRF ( $\sigma_{RRF}$ ) was related to PM<sub>ACSM</sub>

and  $PM_{SMPS}$  and was calculated using Eq. (S6).  $PM_{SMPS}$  uncertainty obtained from Section 2.1 of the SI was used to calculate the RRF uncertainty, instead of using the standard deviations of the  $PM_{SMPS}$  measured in the "relative stable state" of chamber studies. While for the case of Q-ACSM, the standard deviation in the stable state was used to evaluate the RRF uncertainty.

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$$\sigma_{RRF} = \sqrt{\left(\frac{\partial RRF}{\partial PM_{ACSM}}\right)^2} \sigma_{PM-ACSM}^2 + \left(\frac{\partial RRF}{\partial PM_{SMPS}}\right)^2 \sigma_{PM-SMPS}^2 = \sqrt{\left(\frac{\sigma_{PM-ACSM}}{PM_{SMPS}}\right)^2 + \left(\frac{PM_{ACSM}\sigma_{PM-SMPS}}{PM_{SMPS}^2}\right)^2}$$
(S6)

#### 98 2.3 CE uncertainty

For the experiments using AS seeds, the collection efficiencies before and after SOA coating were
calculated using Eq. (S7) and Eq. (S8), respectively:

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$$CE_{AS} = \frac{0.5PM_{ACSM-AS1}}{PM_{SMPS-AS}}$$
(S7)

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$$CE_{org} = \frac{0.5PM_{ACSM-AS2}}{PM_{SMPS-AS}}$$
(S8)

103 where,  $PM_{ACSM-AS1}$  and  $PM_{ACSM-AS2}$  represents average Q-ACSM measured mass 104 concentrations before and after SOA coating, respectively.  $PM_{SMPS-AS}$  was the mass concentration of AS 105 measured by SMPS before SOA coating. The default CE is 0.5. The uncertainties of CE<sub>AS</sub> and CE<sub>org</sub> were 106 calculated with the Eq. (S9) and Eq. (S10), respectively.

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$$\sigma_{CE-AS} = 0.5 \sqrt{\left(\frac{\sigma_{PM-ACSM-AS1}}{p_{M_{SMPS-AS}}}\right)^2 + \left(\frac{p_{M_{ACSM-AS1}}\sigma_{PM-SMPS-AS}}{p_{M_{SMPS-AS}}}\right)^2}$$

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$$\sigma_{CE-org} = 0.5 \sqrt{\left(\frac{\sigma_{PM-ACSM-AS2}}{PM_{SMPS-AS}}\right)^2 + \left(\frac{PM_{ACSM-AS2}\sigma_{PM-SMPS-AS}}{PM_{SMPS-AS}^2}\right)^2}$$

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(S10)

(S9)

## 111 **3** Size distributions in different experiments



**Figure S4**. Average number size distributions measured with the SMPS as a function of  $d_{va}$  (nm) during the relative stable state for experiments using (a)  $\alpha$ -pinene (b) toluene, and (c) isoprene, respectively.  $d_m$  was converted to  $d_{va}$  via  $d_{va}=d_m \cdot \rho_{eff}/\rho_0$ . Gray lines represent the Q-ACSM aerodynamic transmission efficiency (E<sub>L</sub>) as a function of  $d_{va}$  (nm). For most of the experiments, more than 94% of the total particle mass was transported into the Q-ACSM through aerodynamic lens. While for three of them (Exp. 4, 5, and 7), a portion of particles were too small to pass the lens and only 87-89% of the total mass was transported.

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Figure S5. Geometric mean diameter,  $d_g$  (nm), as a function of experiment duration in the experiments using AS seed particles and  $\alpha$ -pinene (panel a) and toluene (panel b) as precursor gases. The geometric mean diameter increased slightly before the oxidation was initiated because of the coagulation of particles, which could be confirmed by the decreasing total number concentration measured by the SMSP. After the oxidation reaction started,  $d_g$  increased substantially as secondary oxidation products condensed onto the the seed particle surfaces. The downward arrows indicate when SOA was starting to condense on AS cores. The

upward arrows indicate when Q-ACSM measured organic and sulfate concentrations both reached "relatively stable state". The differences in geometric mean diameters between the up and down arrows were used to calculate the average coating thickness. Note that coagulation and wall losses of small particles also increase the geometric mean diameter, this makes the evaluated coating layer a little higher than the real value.

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Figure S6. Average number size distributions ( $d_{va}$ ) measured before (dashed lines) and after (solid lines) SOA (panel a:  $\alpha$ -pinene; panel b: toluene) was coated. Gray lines represent the Q-ACSM  $E_L$  as a function of  $d_{va}$ (nm). Gray lines represent the Q-ACSM aerodynamic transmission efficiency ( $E_L$ ) as a function of  $d_{va}$  (nm). For all the experiments, more than 95% particles were transported through the lens.

## 137 4 f44 variations



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**Figure S7.** Triangle plots for (a)  $\alpha$ -pinene, (b) toluene, (c) isoprene oxidation in pure SOA generation experiments. Different colors of symbols represent different  $f_{44}$  and  $f_{43}$  values of SOA generated in different experiments. Because some O<sub>3</sub> was produced during OH initiated chain reactions, the oxidation state of

isoprene-generated SOA varied more significantly as the experiment proceed than the experiments with a pure OH oxidation experiment. For  $\alpha$ -pinene, however,  $f_{44}$  did not vary considerably as isoprene during one experiment and in between experiments.

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147Figure S8. Triangle plots for SOA coating experiments using (a) α-pinene and (b) toluene. Different symbols148and colors represent different  $f_{44}$  and  $f_{43}$  values of SOA generated in different experiments.

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