Supplement of 1

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Effects of Aerosol Size and Coating Thickness on the Molecular 3 **Detection using Extractive Electrospray Ionization** 4

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(b) Source B



19 Figure S1. (a) EESI-TOF inlet to be coupled to the Tofwerk TOF system. (b) EESI-Orbitrap inlet to be coupled 20 to the Tofwerk TOF system and Thermo Fischer Scientific Orbitrap system. Note: The charcoal denuder is not 21 included in the picture. Both EESI ionization sources were developed by the Laboratory of Atmospheric 22 Chemistry, Paul Scherrer Institute, Switzerland in collaboration with TOFWERK AG, Switzerland and 23 IRCELYON, France (Lopez-Hilfiker et al., 2019; Lee et al., 2020). The approximate distance between the tip of 24 the spray capillary and the heated ion transfer tube at the mass spectrometer interface is shown in the insets. The 25 ESI probes of the both EESI sources have the similar inclination of 30° from the horizontal axis at the mass analyzer 26 capillary. Please note that both EESI sources were deployed on the same mass analyzer with the same sampling 27 flow of 0.8 L min⁻¹.



Figure S2. Schematic of the experimental setup for size dependent sensitivity of the EESI-TOF. Red lines indicate the schematic layout of the EESI-TOF ionization inlet with additional tubing manifolds prior to the electrospray ionization region for three different settings: (1) open straight tube (without denuder and HEPA filter), (2) with charcoal denuder only, (3) with charcoal denuder and HEPA filter. Blue lines indicate the setup, which is

33 used for the size-dependent sensitivity experiment.



Figure S3. Schematic diagram of the CLOUD-14 experiment at CERN, modified from ref. (Kirkby et al., 2011).

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37 CLOUD chamber. The CLOUD facility provides suitable conditions to study new particle formation (NPF) under 38 atmospherically relevant conditions, using the well characterized cylindrical stainless-steel chamber (CLOUD 39 chamber) with ultra-low contamination level and equipped with state-of-the art instrumentation (see Figure S3). 40 The CLOUD chamber is an electro-polished stainless-steel cylindrical chamber of 3 m diameter, ~4 m height and 41 26.1 m³ inner volume, positioned inside a thermal housing (Kirkby et al., 2011). A continuous flow of synthetic 42 air from evaporation of cryogenic liquid nitrogen and liquid oxygen at a volume mixing ratio of 79:21 is injected 43 to the chamber to balance the experiment sample flow. When all the instruments are connected to the CLOUD facility, the total air flow rate is typically 270 L min⁻¹, resulting in a dilution lifetime of 1.6 h in the chamber. 44 45 Humidity of the chamber is adjusted by passing the air through a Nafion® humidifier using ultrapure water (18 46 MΩ cm, Millipore Corporation). 47 The relative humidity of the chamber is determined by dew point mirrors (EdgeTech). Ozone (O₃) is generated by 48 exposing a small fraction of the air through a quartz tube surrounded by UVC lamps (wavelength <240 nm) and 49 added to the inlet chamber flow. For NPF experiments, the chamber is operated at 5 mbar above atmospheric 50 pressure using a pressure regulated valve. Two counter-rotating stainless-steel fans are mounted on the roof and 51 bottom of the chamber to enable a uniform mixing inside the chamber. Under typical NPF experimental conditions,

52 the fans are operated with 12% fan speed, resulting in a wall loss lifetime of 0.002 s^{-1} for sulfuric acid. A typical

53 experiment in CLOUD is running in continuous mode so precursors are constantly injected into the chamber. An

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- 54 experiment starts when the particle concentration inside the chamber is low enough for the measurement and
- 55 precursor gases such as SO₂ and / or volatile organic compounds (VOCs) have reached the intended concentration.
- 56 Chemical reactions start by turning on UV lights or mixing VOCs with oxidants such as ozone.



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Figure S4. Schematic of the experimental setup for coating experiments using α -pinene oxidation products from a flow tube reactor. Inorganic particles ((NH₄)₂SO₄) are injected into the flow tube which act as condensation sink for the low-volatility oxidation products. Red lines indicate the schematic layout of the EESI-TOF ionization inlet with additional tubing manifolds prior the electrospray ionization region for three different settings: (1) open straight tube (without denuder and HEPA filter), (2) with charcoal denuder only, (3) with charcoal denuder and HEPA filter. Blue lines indicate the setup that is used for the coating experiment.





Figure S5. Measured volume-weighted geometric mean diameter by the SMPS as a function of selected size by Aerosol Aerodynamical Classifier for levoglucosan particles. SMPS measurement was corrected by applying ion mobility ratio for air, which is 1.2/1.4. AAC aerodynamic diameter was corrected according to the density of levoglucosan described below. The full width at half maximum (FWHM) of the measured particle size distribution by SMPS is indicated by the *y*-axis uncertainty marker. The blue dotted-line indicates the linear fit with goodness of fit R²=0.999.

For spherical particles, the aerodynamic diameter D_{ae} is defined as

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$$D_{ae} = D_P \sqrt{\frac{\rho_P C_c(D_P)}{\rho_0 C_c(D_{ae})}},$$
 (Eq. 1)

where $C_c(D)$ is the Cunningham Slip Correction Factor applied to diameter D_p , D_p is the diameter measured by a differential mobility particles sizer, $\rho_0 = 1000$ kg m⁻³ and ρ_p the density of the particle. To simplify the relationship shown in Figure S5,

$$\frac{D_P}{D_{ae}} = \sqrt{\frac{\rho_0}{\rho_P}} \tag{Eq. 2}$$

For the case of levoglucosan particles $\rho_P = 1690 \text{ kg m}^{-3}$, the ratio of $\sqrt{\frac{\rho_0}{\rho_P}} = 0.769$. After the correction of the aerodynamical diameters using levoglucosan density, the slope measured in Figure S5 is within 5% of uncertainty.



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82 Figure S6. (a) Brownian coagulation coefficient (BCC) in cm³ s⁻¹ calculated assuming different parent 83 electrospray droplet diameters (D_{ES}). Analyte particle diameter is represented by the x-axis. BCC. The D_{ES} values 84 chosen reflect the extreme (0.5 µm and 5.0 µm) and median (~1.5 µm) sizes of electrospray droplet generated in 85 this study (Table S3). D_{ES} is the electrospray parent droplet diameters that were estimated using scaling laws shown in Figure S7, by assuming that the ES is operating in the Taylor cone jet mode (Gañán-Calvo et al., 2018). As done 86 87 in-text for measured sensitivities, the normalized BCC values (relative to that for 100 nm analyte particle), 88 BCC100nm are also shown. A and B denote the types of the EESI sources used as depicted in Figure S1. (b-d) size-89 dependent sensitivity measurements using individual and internally-mixed (mixture) nebulization solution of 90 different chemical standards, i.e. (b) levoglucosan, (c) NH₄NO₃ and (d) sucrose. The estimated D_{ES} values given 91 the experimental conditions (Table S2) are also shown in the legends. LF, MF and HF denote low, medium and 92 high ES capillary flow as tabulated in Table S2. The mass concentration for internally mixed levoglucosan and NH_4NO_3 particles with $D_p > 100$ nm were measured by an LTOF-AMS. 93



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Figure S7. Scaling laws for predicting the order of magnitude of the size *d* of the emitted ES charged droplets at a certain flow rate *Q* for 39 types of different electrospray working solutions. The predicted diameter *d* is denoted as $d = d_0 \sqrt{Q/Q_0}$.(Gañán-Calvo et al., 2018)

99 D_{ES} shown in Figure S6 is calculated by determining Q, Q_0 and d_0 . Q is the calculated flow rate using Hagen-100 Poiseuille equation:

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$$Q = \frac{\Delta p \pi R^4}{8\mu L},$$
 (Eq. 3)

102 where Δp is the pressure difference applied to the ES bottle reservoir, *R* is the inner radius of the ES capillary, *L* 103 is the length of the ES capillary (80 cm) and μ is the dynamic viscosity of the ES working solution. The dynamic 104 viscosity of H₂O:ACN (50:50 v/v) and H₂O at 25 °C are 0.65 and 0.89 mPa s, respectively. See Table S1 for other 105 variables. Q_0 and d_0 are defined as

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$$Q_0 = \sigma \varepsilon_0 / (\rho K),$$

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$$d_0 = [\sigma \varepsilon_0^2 / \rho K^2]^{1/3}$$
(Eq. 4)

108 where σ is the surface tension, ρ is the density and *K* is the electrical conductivity of the electrospray working 109 solutions.

110 **Table S1.** Physical properties of the electrospray solvents.

Physical Properties of the Electrospray Solvents							
Types of ES	Surface tension σ (N	Volumetric Density ρ	Electrical Conductivity K				
Solvent	m ⁻¹)	(kg m ⁻³)	(S m ⁻¹)				
H ₂ O:ACN (50:50	0.0514	842.54	0.000252				
v/v)							
H ₂ O	0.072	997	0.0005				

112 When all the variables are determined, *D_{ES}* is estimated as (Gañán-Calvo et al., 2016, 2018)

$$D_{ES} = d_0 \sqrt{Q/Q_0}.$$
 (Eq. 5)

Index no.	EESI Source Designs	ES voltage (kV)	ES pressure (mbar)	ES capillary inner diameter (um)	ES solution	Nebulization solution	ES Flow, Q (nl min ⁻¹)
Levol	А	2.8	120 - 250	75	H ₂ O:ACN (50:50 v/v)	Single	1075- 2240
Levo2	А	3	120 - 250	75	H ₂ O:ACN (50:50 v/v)	Single	1075- 2240
Levo3	А	3	120 - 250	75	H ₂ O:ACN (50:50 v/v)	Single	1075- 2240
Levo4	A	2.9	120 - 250	75	H ₂ O:ACN (50:50 v/v)	Single	1075- 2240
Levo5	A	2.9	120 - 250	75	H ₂ O:ACN (50:50 v/v)	Single	1075- 2240
Levo6	В	2.6	200	50	H ₂ O:ACN (50:50 v/v)	Mixed with AN1	354
Levo7	В	2.9	800	100	H ₂ O:ACN (50:50 v/v)	Mixed with AN2	22655
Levo8	В	2.95	200 - 400	75	H ₂ O:ACN (50:50 v/v)	Single	1792- 3584
Levo9	В	2.88	200 - 400	75	H ₂ O	Single	1309- 2617
AN1	В	2.6	200	50	H ₂ O:ACN (50:50 v/v)	Mixed with Levo6	354
AN2	В	2.9	800	100	H ₂ O:ACN (50:50 v/v)	Mixed with Levo7	22655
AN3	В	2.95	200 - 400	75	H ₂ O:ACN (50:50 v/v)	Single	1792- 3584
AN4	В	2.9	600	75	$H_2O:ACN$ (50:50 v/v)	Mixed with Suc1	5375
AN5	В	2.9	600	75	$H_2O:ACN$ (50:50 v/v)	Single	5375
Suc1	В	2.8	200 - 400	75	H ₂ O:ACN (50:50 v/v)	Mixed with AN4	5375

115 **Table S2.** Size dependence experiments for different chemicals, EESI source and ES operating parameters.

116 Levo#, AN# and Suc# indicate different levoglucosan, NH₄NO₃ and sucrose experiment runs, respectively.

- 118 **Table S3.** Estimation of electrospray (ES) parent droplet size and number concentrations using the median of the
- 119 ES Flow. The estimated ES parent droplet number was used for estimation of coagulation rates between analyte
- 120 and ES charged droplets.

Index	ES Flow, Q (nl	Estimated ES Parent	Estimated ES Parent Droplet
no.	min ⁻¹)	Droplet Size, <i>D_{ES}</i> (µm)	Number Flux N _{ES} , Q/D _{ES} (s ⁻¹)
Levo1	1075-2240	1.53	$9.6 - 20 \cdot 10^6$
Levo2	1075-2240	1.53	$9.6 - 20 \cdot 10^6$
Levo3	1075-2240	1.53	$9.6 - 20 \cdot 10^6$
Levo4	1075-2240	1.53	$9.6 - 20 \cdot 10^6$
Levo5	1075-2240	1.53	$9.6 - 20 \cdot 10^6$
Levo6	354	0.70	$32.9 \cdot 10^{6}$
Levo7	22655	5.66	$4 \cdot 10^{6}$
Levo8	1792-3584	1.59	$14.2 - 28.3 \cdot 10^6$
Levo9	1309-2617	1.45	$13.7 - 27.3 \cdot 10^6$
AN1	354	0.70	$32.9 \cdot 10^{6}$
AN2	22655	5.66	$4 \cdot 10^6$
AN3	1792-3584	1.59	$14.2 - 28.3 \cdot 10^6$
AN4	5375	2.76	8.1·10 ⁶
AN5	5375	2.76	8.1·10 ⁶
Suc1	5375	2.76	$8.1 \cdot 10^{6}$

122 The coagulation coefficients K_{12} were calculated using the Fuchs form of the Brownian coagulation

$$K_{12} = 2\pi (D_1 + D_2)(D_{p1} + D_{p2}) \left(\frac{D_{p1} + D_{p2}}{D_{p1} + D_{p2} + 2(g_1^2 + g_2^2)^{1/2}} + \frac{8(D_1 + D_2)}{(\bar{c}_1^2 + \bar{c}_2^2)^{1/2}(D_{p1} + D_{p2})} \right)^{-1}$$
where
$$\bar{c}_i = \left(\frac{8kT}{\pi m_i} \right)^{1/2}$$

$$\ell_i = \frac{8D_i}{\pi \bar{c}_i}^a$$

$$(Eq. 6)$$

$$g_i = \frac{\sqrt{2}}{3 D_{pi} \ell_i} \left[(D_{pi} + \ell_i)^3 - (D_{pi}^2 + \ell_i^2)^{3/2} \right] - D_{pi}$$

$$D_i = \frac{kTC_c}{3 \pi \mu D_{pi}}$$

$$D_{pl}$$
 is denoted as D_{ES} (Table S2) with the density of the electrospray solution and D_{p2} is denoted as the mid-size of

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125 D_{p1} is denoted as D_{ES} (Table S2) with the density of the electrospray solution and D_{p2} is denoted as the mid-size of 126 the measured *j*-th bin of the size-selected particle size distribution with the density of the analyte particle. For 127 clarity, K_{12} is referred to as $K_{ES,J}$ in the following.

128 The coagulation rate J_{12} between the ES parent droplets and the size distribution of the size selected particles was 129 calculated as

$$J_{12} = N_{ES} \sum_{j=1}^{\infty} K_{ES,j} N_j , \qquad (Eq. 7)$$

131 where N_{ES} is the estimated number concentration of electrospray parent droplets (Table S2), $K_{ES,J}$ is the calculated

132 Brownian coagulation coefficient described above and N_j is the number concentration of the measured *j*-th bin of

133 the size-selected particle size distribution.





Figure S8. Particle growth experiments in the CLOUD chamber. (a) SMPS measurements of the numberweighted size distribution. (b) Raw EESI-TOF total ion counts (TIC) after high-resolution peak fitting and total mass concentrations measured by SMPS with effective mass density of 1.3 g cm⁻³. (c) EESI-TOF TIC normalized by mass concentrations measured by the SMPS and geometric mean diameter. (d) EESI-TOF TIC normalized by mass concentrations measured by SMPS and full width at half maximum (FWHM) of the volume-weighted size distribution. Shaded areas depict the new particle formation events that are included for the size-dependent sensitivity measurements shown in Figure 3a.





143Figure S9. (Top sub-panel) SMPS size distributions and (bottom sub-panel) sum of the high-resolution fitted144ions of EESI- normalized by the mass concentration measured by the SMPS for α-pinene (AP) SOA formation145experiments in the CLOUD chamber at four different conditions. (a) AP SOA formation at -30°C with low relative146humidity (RH). (b) AP SOA formation at -50°C with low RH. (c) AP SOA formation at -50°C with high RH. (d)147AP SOA formation at -30°C with high RH.



149 Figure S10. Measurements of C₁₀H₁₆O₃₋₈ in the particle phase. EESI-TOF to FIGAERO-CI-ToF-MS normalized

150 sensitivity for AP SOA formation experiments in the CLOUD chamber at four different conditions.



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Figure S11. Coating of NH₄NO₃ particles using oxidation products from α -pinene ozonolysis. (a) Size distribution of the coated NH₄NO₃ particles. (b) Volume weighted geometric mean diameter and mass concentration measured by the SMPS. (c) Signals of NH₄NO₃ particles and particle-phase C₁₀H₁₆O₃ molecules. (d) Signals of NH₄NO₃ particles and particle-phase C₁₀H₁₆O₈ molecules.



157 Figure S12. Absolute changes of NH₄NO₃ and C₁₀H₁₆O₆₋₈ for two different core size of NH₄NO₃ particles as a

158 function of the coating thickness (a) 156 nm and (b) 226 nm after normalization to the most abundant electrospray

159 ion NaINa⁺.

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