

Relative Humidity Dependence of Soot Aggregate Restructuring Induced by Secondary Organic Aerosol: Effects of Water on Coating Viscosity and Surface Tension

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Supporting Information

ABSTRACT: Soot aggregates have a significant warming effect on climate, and their structural and optical properties may evolve in the presence of coatings. Here, the relative humidity (RH) dependence of soot aggregate restructuring induced by secondary organic aerosol (SOA) coatings was investigated in a series of photo-oxidation experiments. Burner-generated soot aggregates were classified by mobility diameter and injected into a smog chamber, where they were exposed to oxidation products of *p*-xylene; coated aggregates were subsequently conditioned at one of the following RHs: <12%, 20%, 40%, 60%, or 85%. Changes in diameter and mass were monitored using differential mobility and centrifugal particle mass



analyzers, respectively. At RH < 12%, the SOA coating was too viscous to induce restructuring, so the particle diameter increased uniformly with coating mass. At RH \ge 20%, the SOA coating induced restructuring, and the degree of restructuring increased with RH, indicating that the decreased viscosity and increased surface tension of SOA have significant implications on SOAinduced restructuring of soot aggregates. At RH \ge 60%, appreciable water uptake occurred, and the hygroscopicity parameter of the SOA coating was derived. Our results provide crucial insights into the complex interactions between soot, SOA, and water in the atmosphere.

INTRODUCTION

Soot aggregates are composed of primary particles of elemental carbon, and they are generated, for example, from the combustion of hydrocarbon fuels^{1,2} and biomass.^{3,4} Since elemental carbon strongly absorbs all visible wavelengths of light, soot aggregates have a significant warming effect on global climate.^{5,6} During combustion, incipient primary particles undergo random Brownian motion and collide with other primary particles to form branched, fractal-like aggregates.⁷ The aggregates can become more compact through restructuring caused by internally mixed liquids, such as water $^{8-10}$ and sulfuric acid.^{9,11} Soot aggregate restructuring due to liquid coatings has been shown to depend on the coating mass (or volume)¹² and surface tension, σ .¹³ The morphological evolution of soot aggregates affects their optical properties, which have been investigated both experimentally¹⁴⁻¹⁶ and theoretically.^{17,18}

In the atmosphere, soot aggregates may be coated by mixtures of many species. Secondary organic aerosol (SOA)—generated from the photo-oxidation of biogenic and/or anthropogenic volatile organic compounds (VOCs)—is a representative mixture, consisting of many semivolatile oxygenated organic species.^{19,20} In the laboratory, soot aggregate restructuring has been induced by coatings of SOA derived from both biogenic (isoprene²¹ and α -pinene^{22,23}) and

anthropogenic (benzene,²⁴ toluene,^{24,25} ethylbenzene,²⁴ and *m*- and *p*-xylene^{24,26,27}) VOCs. Recently, the viscosity of SOA derived from isoprene and toluene has been shown to vary significantly with relative humidity (RH);^{28,29} for example, when poked with a needle, toluene-derived SOA, collected in a large droplet on a slide, shatters at 16.5% RH but returns to its original shape at 39.5% RH, with a characteristic flow time.²⁸ If an SOA coating is a solid at a certain temperature and RH, it would not be expected to restructure soot aggregates under these conditions. In previous studies, SOA-coated soot has been investigated at only low ($\leq 20\%$) and high (90%) RH.^{21,24–27} Studies at intermediate RHs are necessary to fully understand the effects of water on SOA coating mass, viscosity, and surface tension, and their bearing on SOA-induced soot

Here, we report smog chamber experiments in which monodisperse soot aggregates, generated by ethylene combustion in a McKenna premixed burner, were coated with *p*-xylene derived SOA and then exposed to a controlled RH. Particle diameter and mass were monitored using a differential mobility

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analyzer (DMA; TSI, 3081) and a centrifugal particle mass analyzer (CPMA; Cambustion), respectively. Trends in humidified mobility diameter with dry particle mass are evaluated to determine how RH affects SOA viscosity and surface tension and, in turn, SOA-induced soot aggregate restructuring.

EXPERIMENTAL SECTION

Soot aggregates were generated by a McKenna premixed burner, in which ethylene was used as fuel. The experimental setup for treatment and injection of soot is depicted in Figure S1a, and it is similar to that used earlier.¹³ Briefly, the equivalence ratio of the burner was set to two, using ethylene and air flow rates of 1.1 and 8.0 L min⁻¹, respectively. Soot was sampled 27 cm above the flame and fed into an ejector dilutor (Air-Vac, AVR038H), which was set to a dilution ratio of three, using 210 kPa of nitrogen. To remove particulate water and semivolatile organic compounds, we then passed the aggregates through a diffusion drier and a thermo-denuder set to 573 K.

After treatment, the soot aggregates were neutralized using an X-ray source (TSI, 3087) and directed into a DMA, which was set to classify predominantly singly charged particles 250 nm in mobility diameter, at sample and sheath flow rates of 1.0 and 10.0 L min⁻¹, respectively. The classified aggregates were then injected into a 1.8 m³ perfluoroalkoxy film (Ingeniven) smog chamber, which was described earlier.^{24,30} A deuterium lamp (Ocean Optics, D-2000-S) and a spectrometer (Ocean Optics, HR 2000+) were used to measure *p*-xylene concentrations by differential optical absorption spectroscopy.³⁰

Once the soot aggregate injection was completed (typically, at a particle concentration >1000 cm^{-3}), aggregates were sampled from the chamber into parallel DMA-condensation particle counter (CPC; TSI, 3776) and CPMA-CPC (TSI, 3771) systems. Aggregates were monitored for approximately 1 h after injection to confirm there was no background change in mobility diameter or mass before p-xylene (Fisher, 99.9%) was injected into the chamber to a concentration of ~ 2 ppm. Hydrogen peroxide (Sigma, 30% w/w in water) was then injected into the chamber, and UV radiation was applied to produce hydroxyl radicals. Though water was introduced along with hydrogen peroxide, the chamber RH was <12% throughout each experiment. In all experiments, the CPMA was operated at the chamber RH; in contrast, the DMA was operated at different controlled RHs: <12%, 20%, 40%, 60%, and 85%. For each experiment at $RH \ge 20\%$, the DMA sample was conditioned by a Nafion membrane humidifier (Perma Pure, PD-625-24SS). The RH in the conditioning train and DMA was monitored using a series of RH and temperature probes (Sensirion, SHT75), placed as shown in Figure S1b.

RESULTS AND DISCUSSION

To facilitate comparisons between experiments, the measured mobility diameters and masses were divided by their initial values to give normalized mobility diameter and mass growth factors, Gfd and Gfm, respectively. Trends in Gfd with increasing Gfm are plotted in Figure 1. The values of Gfd shown in Figure 1 were derived from diameters measured downstream of the RH-controlled conditioning train, so they include contributions from soot, SOA, and any condensed water. In contrast, the values of Gfm were derived from masses measured upstream of the conditioning train, so they include



Figure 1. RH-dependent trends in diameter growth factor with increasing mass growth factor, which reflect the morphological evolution of the soot aggregates during photo-oxidation.

contributions from only soot and SOA. By design, this arrangement prevented partial evaporation of any condensed water in the CPMA, where temperature fluctuates periodically with rotational speed. At each RH, two different sample flow rates, 0.3 and 1.5 L min⁻¹, of the DMA were used to vary the residence time of the aggregates in the RH-controlled conditioning train. Despite small discrepancies, reflected in the scatter in Figure 1, no systematic dependence of the aggregate evolution on the residence time was observed. Therefore, trends in Gfd measured at both flow settings, distinguished only by RH, are shown in Figure 1. At RH < 12%, Gfd increases uniformly with Gfm, suggesting that there is little or no soot aggregate restructuring to compensate for the coating thickness.

At $RH \ge 20\%$, the evolution of aggregate morphology occurs in three stages. In the first, SOA thinly coats the soot aggregates while they retain their initial structures, and Gfd increases slightly with Gfm. During the second stage, the aggregates begin to restructure under the influence of the SOA coating, more than compensating for the coating thickness, and Gfd decreases as Gfm increases. At RHs of 20% and 40%, the decrease in Gfd begins at a Gfm between two and three, leading to a local minimum in Gfd of about unity; at RHs of 60% and 85%, the decrease in Gfd begins at a smaller Gfm, \sim 1.5, leading to a local minimum in Gfd of ~0.95. In the third stage, aggregate restructuring is no longer significant enough to outweigh the contribution of the coating to the mobility diameter, and Gfd again increases with Gfm. The Gfm at which this stage begins also depends on RH. At RHs of 20% and 40%, the third stage begins at a Gfm of about four, and at RHs of 60% and 85%, it begins at a Gfm between two to three.

There is evidence that soot restructuring can occur by two mechanisms: coating condensation or evaporation. For example, decreases in Gfd were observed for aggregates thinly coated with pure liquids, including sulfuric acid and oleic acid;^{9,12} in contrast, light scattering by aggregates injected into bulk water implied that the aggregates restructure only upon coating evaporation.³¹ One criterion for SOA-induced soot restructuring to be broadly atmospherically relevant is that it must occur while the coating is present since the coatings are not expected to evaporate significantly. It is therefore interesting to note that, in the present experiments, restructuring occurs while the coating is still present, leading to the local minima in Figure 1.

The above differences reveal a significant dependence of aggregate evolution on RH. In the past, SOA-induced restructuring of soot aggregates was investigated at RHs of $\leq 20\%$ and 90%,^{24–26} and water was shown to be important only to the extent that it increased the coating mass (or volume).²⁵ Here, by investigating intermediate RHs, we demonstrate that water is important also for its effects on the viscosity and surface tension of the coatings. These effects are discussed in the context of Figure 2, which shows the evolution



Figure 2. RH-dependent trends in shape factor with increasing mass growth factor.

in shape factor, χ , with increasing Gfm. The shape factor, χ , is calculated as

$$\chi = \frac{d_{\rm m}C_{\rm c}(d_{\rm ve})}{d_{\rm ve}C_{\rm c}(d_{\rm m})} \tag{1}$$

where C_c is the slip correction, and d_{ve} is the volume-equivalent diameter, calculated as

$$d_{\rm ve} = \left[\frac{6}{\pi} \left(\frac{m_{\rm soot}}{\rho_{\rm soot}} + \frac{m_{\rm p} - m_{\rm soot}}{\rho_{\rm SOA}}\right)\right]^{1/3}$$
(2)

where $m_{\rm soot}$ is the mass of the aggregates after injection and before photo-oxidation, $m_{\rm p}$ is the combined mass of the aggregates and coatings during photo-oxidation, and $\rho_{\rm soot}$ and $\rho_{\rm SOA}$ are the material densities of soot and *p*-xylene SOA, 1.8 and 1.46 g cm^{-3,32,33} respectively. Initially, the aggregates have a shape factor of ~2.4, which begins to decrease as Gfm increases.

First, we consider the experiment at RH < 12%. Since toluene SOA, collected in a large droplet on a slide, was observed to shatter when poked at 16.5% RH and not flow at all after 6.5 h of observation,²⁸ the *p*-xylene SOA is likely a solid at RH < 12%. Consequently, it is too viscous to induce restructuring, consistent with the uniformly increasing Gfd noted above. Thus, the decrease in shape factor shown in Figure 2 results solely from accumulation of the SOA coating that would lead eventually, at a Gfm of about eight,²⁴ to a spherical particle encapsulating the unchanged soot aggregate. In earlier experiments performed at low RH, Gfd also increased uniformly with SOA coating mass (or thickness);^{24,25} none-theless, restructuring was inferred from a decrease in mobility

diameter upon thermo-denuding the coated aggregates.^{24,25} Our results indicate that the restructuring observed for coateddenuded particles likely occurred in the thermo-denuder, where the elevated temperature caused the solid SOA to melt, restructure the soot cores, and then evaporate. These results also relate to a recent estimation of SOA surface tension, based on the extent of soot aggregate restructuring because an increase in temperature corresponds to a decrease in surface tension.¹³

At RH \geq 20%, soot aggregate restructuring without denuding is unambiguous, but the effects of coating viscosity, surface tension, and mass (or volume) must be distinguished to better understand the dependence of restructuring on RH. If the extent of restructuring were limited by water diffusivity or particle viscosity, a longer residence time in the RH-controlled conditioning train would be expected to allow more restructuring to occur. That there is no dependence on residence time in the conditioning train suggests that water partitions into the particle phase, and the soot-coating interface relaxes, to a similar extent at both flow rates. At the low and high flow rates (0.3 and 1.5 L min⁻¹, respectively), the residence times in the conditioning train are about 75 and 15 s, respectively. The latter is comparable to the experimental flow time of toluene SOA measured by Song et al. at 40% RH (τ = 13.75 s).²⁷ On the other hand, the residence time is significantly less than the flow time measured by Song et al. at their lowest RH (30%), which was on the order of 10^{3} s.²⁷ At RHs of 20% and 40%, the extent of soot aggregate restructuring is similar, indicated by their overlapping trends in shape factor with Gfm in Figure 2. The Gfm required for the shape factor to converge to unity decreases from eight to about five because the encapsulated soot core itself is more compact. At 60% RH, the role of restructuring increases, such that shape factor decreases toward unity even more sharply. At both RHs of 40% and 60%, the soot-coating interfaces have enough time to approach equilibrium, so the difference in extent of restructuring must be due to a difference in the surface tensions of the coatings. Since coatings of higher surface tension result in a greater extent of restructuring,¹³ the SOA coating likely has a greater surface tension at 60% RH than at 40% RH.

This difference in extent of restructuring suggests appreciable water uptake at RH \geq 60%. Another indication of water uptake is that the values of Gfd at all RHs do not converge at high Gfm because the CPMA measurements of particle mass do not include the contribution of water, as described above. For spherical particles, the differences in Gfd can be used to quantify the volume of particle-bound water. Measurements at a Gfm > 6 were used to fit logarithmic curves, as shown in Figure S2, from which the respective values of Gfd at a Gfm of exactly 8.5 were calculated. These values of Gfm were selected because the particles were spherical, as indicated by their shape factors (Figure 2). Gfd_{20%} is assumed to be that of only soot and SOA. For higher RHs, the hygroscopic diameter growth factor, hGfd, is calculated as Gfd_{RH}/Gfd_{20%}; in turn, the hygroscopic volume growth factor, hGfv, is calculated as (hGfd)³. The values of hGfv at RHs 20-85% are shown in Figure S3. At all RHs, coated aggregates were 325 nm or greater in mobility diameter at a Gfm of 8.5, so the Kelvin effect was negligible.

 κ -Köhler theory relates hGfv to the fractional RH, f_{RH} , ^{34,35} as follows:

$$hGfv = \frac{\nu_{soot} + \nu_{SOA} + \nu_{w}}{\nu_{soot} + \nu_{SOA}} = \kappa \left(\frac{f_{RH}}{1 - f_{RH}}\right) + 1$$
(3)

where v_{soot} , v_{SOA} , and v_W are the volumes of soot, SOA, and particle-bound water, respectively, and κ is the hygroscopicity parameter. Using hGfv from the 85% RH experiment results in a κ value of 0.062 for the SOA-coated aggregates. Since soot is hydrophobic, $\kappa_{soot} = 0$, and division of κ by the volume fraction of SOA (0.91) at a Gfm of 8.5 gives v_{SOA} of 0.068. Accounting for the uncertainty in hGfv and the accuracy of the RH probes (1.8%), v_{SOA} is 0.07 ± 0.02. This value is comparable to that of phthalic acid, 0.059, 35,36 which is similar to the ring-retaining products of *p*-xylene photo-oxidation.³⁷ Furthermore, our value falls in the range recently reported for SOA particles derived from biogenic and anthropogenic precursors and their mixtures: ~0.04-0.10.37 As described in the Supporting Information, our value of κ_{SOA} was used to calculate the total mass of the particles (soot, SOA, and water) for the duration of the 85% RH experiment (Figure S4). We note that the value of Gfd at the local minimum is not affected by the correction for the mass of water; in other words, water uptake certainly affects the surface tension of the coating, as discussed above.

In summary, we have investigated the RH-dependence of soot aggregate restructuring induced by SOA coatings, and we have demonstrated that water has significant effects on the coating viscosity and surface tension, in addition to mass (or volume). At RH < 12%, SOA is too viscous to induce soot aggregate restructuring, and the coated aggregates become spherical only as the coating fills the voids of the unchanged aggregates. At RH \geq 20%, water uptake decreases the viscosity of SOA sufficiently to induce soot aggregate restructuring, and the coated aggregates become spherical through a combination of collapse of the aggregates and accumulation of the coating. Since ambient RH is typically greater than 20%,²⁷ SOA-induced restructuring is an important mechanism in the morphological and optical evolution of soot aggregates. Furthermore, at RHs of 60% and 85%, water uptake significantly increases the surface tension of the SOA coating, leading to incrementally greater soot aggregate restructuring, which may occur in very humid regions with soot sources—for example, coastal cities with active commercial harbors.³⁸⁻⁴⁰ Future studies should investigate the effects of water on SOA coatings derived from other precursors. For example, at a given RH, SOA from isoprene is less viscous than that from toluene,^{27,28} so it may cause restructuring at all ambient RHs. If so, water would affect restructuring only by increasing the coating mass²¹ and surface tension. Also, the increase in surface tension could be lessened by the presence of surface active species, which would enhance the ability of the particles to act as cloud condensation nuclei.⁴ Our results provide crucial insights into the interactions between soot, SOA, and water that partly govern the complex climate effects of soot aggregates.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00298.

Figures of experimental setup, logarithmic fits to humidity data, hygroscopic volume growth factors of coated soot, trends in diameter growth factors and corrected growth factors, and text discussing correction for mass of particulate water. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Olfert, J. S.; Symonds, J. P. R.; Collings, N. The Effective Density and Fractal Dimension of Particles Emitted from a Light-Duty Diesel Vehicle with a Diesel Oxidation Catalyst. *J. Aerosol Sci.* **2007**, *38*, 69– 82.

(2) Park, K.; Cao, F.; Kittelson, D. B.; McMurry, P. H. Relationship between Particle Mass and Mobility for Diesel Exhaust Particles. *Environ. Sci. Technol.* **2003**, *37*, 577–583.

(3) Keywood, M.; Kanakidou, M.; Stohl, A.; Dentener, F.; Grassi, G.; Meyer, C. P.; Torseth, K.; Edwards, D.; Thompson, A. M.; Lohmann, U.; et al. Fire in the Air: Biomass Burning Impacts in a Changing Climate. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 40–83.

(4) Schwarz, J. P.; Gao, R. S.; Spackman, J. R.; Watts, L. A.; Thomson, D. S.; Fahey, D. W.; Ryerson, T. B.; Peischl, J.; Holloway, J. S.; Trainer, M.; et al. Measurement of the Mixing State, Mass, and Optical Size of Individual Black Carbon Particles in Urban and Biomass Burning Emissions. *Geophys. Res. Lett.* **2008**, *35*, L13810.

(5) Bond, T. C.; Bergstrom, R. W. Light Absorption by Carbonaceous Particles: An Investigative Review. *Aerosol Sci. Technol.* 2006, 40, 27–67.

(6) Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Berntsen, T.; DeAngelo, B. J.; Flanner, M. G.; Ghan, S.; Kärcher, B.; Koch, D.; et al. Bounding the Role of Black Carbon in the Climate System: A Scientific Assessment. J. Geophys. Res. Atmos. 2013, 118, 5380–5552.

(7) Sorensen, C. M. The Mobility of Fractal Aggregates: A Review. *Aerosol Sci. Technol.* **2011**, *45*, 765–779.

(8) Mikhailov, E. F.; Vlasenko, S. S. Structure and Optical Properties of Soot Aerosol in a Moist Atmosphere: 1. Structural Changes of Soot Particles in the Process of Condensation. *Izv. Atmos. Ocean. Phys.* **2007**, 43, 181–194.

(9) Pagels, J.; Khalizov, A. F.; McMurry, P. H.; Zhang, R. Y. Processing of Soot by Controlled Sulphuric Acid and Water Condensation—Mass and Mobility Relationship. *Aerosol Sci. Technol.* **2009**, 43, 629–640.

(10) Miljevic, B.; Surawski, N. C.; Bostrom, T.; Ristovski, Z. D. Restructuring of Carbonaceous Particles upon Exposure to Organic and Water Vapours. J. Aerosol Sci. 2012, 47, 48–57.

(11) Khalizov, A. F.; Xue, H.; Wang, L.; Zheng, J.; Zhang, R. Enhanced Light Absorption and Scattering by Carbon Soot Aerosol Internally Mixed with Sulfuric Acid. *J. Phys. Chem. A* **2009**, *113*, 1066–1074.

(12) Ghazi, R.; Olfert, J. S. Coating Mass Dependence of Soot Aggregate Restructuring due to Coatings of Oleic Acid and Dioctyl Sebacate. *Aerosol Sci. Technol.* **2013**, *47*, 192–200. (13) Schnitzler, E. G.; Gac, J. M.; Jäger, W. Coating Surface Tension Dependence of Soot Aggregate Restructuring. *J. Aerosol Sci.* **2017**, *106*, 43–55.

(14) Radney, J. G.; You, R.; Ma, X.; Conny, J. M.; Zachariah, M. R.; Hodges, J. T.; Zangmeister, C. D. Dependence of Soot Optical Properties on Particle Morphology: Measurements and Model Comparisons. *Environ. Sci. Technol.* **2014**, *48*, 3169–3176.

(15) Xue, H.; Khalizov, A. F.; Wang, L.; Zheng, J.; Zhang, R. Effects of Dicarboxylic Acid Coating on the Optical Properties of Soot. *Phys. Chem. Chem. Phys.* **2009**, *11*, 7869–7875.

(16) Cappa, C. D.; Onasch, T. B.; Massoli, P.; Worsnop, D. R.; Bates, T. S.; Cross, E. S.; Davidovits, P.; Hakala, J.; Hayden, K. L.; Jobson, B. T.; et al. Radiative Absorption Enhancements Due to the Mixing State of Atmospheric Black Carbon. *Science* **2012**, *337*, 1078–1081.

(17) Liu, F.; Yon, J.; Bescond, A. On the Radiative Properties of Soot Aggregates – Part 2: Effects of Coating. J. Quant. Spectrosc. Radiat. Transfer 2016, 172, 134–145.

(18) Wu, Y.; Cheng, T.; Zheng, L.; Chen, H. Sensitivity of Mixing States on Optical Properties of Fresh Secondary Organic Carbon Aerosols. J. Quant. Spectrosc. Radiat. Transfer **201**7, 195, 147–155.

(19) Mentel, T. F.; Wildt, J.; Kiendler-Scharr, A.; Kleist, E.; Tillmann, R.; Dal Maso, M.; Fisseha, R.; Hohaus, T.; Spahn, H.; Uerlings, R.; et al. Photochemical Production of Aerosols from Real Plant Emissions. *Atmos. Chem. Phys.* **2009**, *9*, 4387–4406.

(20) Donahue, N. M.; Robinson, A. L.; Stanier, C. O.; Pandis, S. N. Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics. *Environ. Sci. Technol.* **2006**, *40*, 2635–2643.

(21) Khalizov, A. F.; Lin, Y.; Qiu, C.; Guo, S.; Collins, D.; Zhang, R. Role of OH-Initiated Oxidation of Isoprene in Aging of Combustion Soot. *Environ. Sci. Technol.* **2013**, *47*, 2254–2263.

(22) Schnaiter, M. Absorption Amplification of Black Carbon Internally Mixed with Secondary Organic Aerosol. J. Geophys. Res. 2005, 110, D19204.

(23) Saathoff, H.; Naumann, K.-H.; Schnaiter, M.; Schöck, W.; Möhler, O.; Schurath, U.; Weingartner, E.; Gysel, M.; Baltensperger, U. Coating of Soot and $(NH_4)_2SO_4$ Particles by Ozonolysis Products of α -Pinene. J. Aerosol Sci. **2003**, 34, 1297–1321.

(24) Schnitzler, E. G.; Dutt, A.; Charbonneau, A. M.; Olfert, J. S.; Jäger, W. Soot Aggregate Restructuring Due to Coatings of Secondary Organic Aerosol Derived from Aromatic Precursors. *Environ. Sci. Technol.* **2014**, *48*, 14309–14316.

(25) Qiu, C.; Khalizov, A. F.; Zhang, R. Soot Aging from OH-Initiated Oxidation of Toluene. *Environ. Sci. Technol.* **2012**, *46*, 9464–9472.

(26) Guo, S.; Hu, M.; Lin, Y.; Gomez-Hernandez, M.; Zamora, M. L.; Peng, J.; Collins, D. R.; Zhang, R. OH-Initiated Oxidation of *m*-Xylene on Black Carbon Aging. *Environ. Sci. Technol.* **2016**, *50*, 8605–8612. (27) Leung, K. K.; Schnitzler, E. G.; Dastanpour, R.; Rogak, S. N.; Jäger, W.; Olfert, J. S. Relationship between Coating-Induced Soot Aggregate Restructuring and Primary Particle Number. *Environ. Sci. Technol.* **2017**, *51*, 8376–8383.

(28) Song, M.; Liu, P. F.; Hanna, S. J.; Zaveri, R. A.; Potter, K.; You, Y.; Martin, S. T.; Bertram, A. K. Relative Humidity-Dependent Viscosity of Secondary Organic Material from Toluene Photo-Oxidation and Possible Implications for Organic Particulate Matter over Megacities. *Atmos. Chem. Phys.* **2016**, *16*, 8817–8830.

(29) Song, M.; Liu, P. F.; Hanna, S. J.; Li, Y. J.; Martin, S. T.; Bertram, A. K. Relative Humidity-Dependent Viscosities of Isoprene-Derived Secondary Organic Material and Atmospheric Implications for Isoprene-Dominant Forests. *Atmos. Chem. Phys.* **2015**, *15*, 5145–5159.

(30) Parsons, M. T.; Sydoryk, I.; Lim, A.; McIntyre, T. J.; Tulip, J.; Jäger, W.; McDonald, K. Real-Time Monitoring of Benzene, Toluene, and P-Xylene in a Photoreaction Chamber with a Tunable Mid-Infrared Laser and Ultraviolet Differential Optical Absorption Spectroscopy. *Appl. Opt.* **2011**, *50*, A90–A99.

(31) Ma, X.; Zangmeister, C. D.; Gigault, J.; Mulholland, G. W.; Zachariah, M. R. Soot Aggregate Restructuring during Water Processing. J. Aerosol Sci. 2013, 66, 209–219. (32) Park, K.; Kittelson, D. B.; Zachariah, M. R.; McMurry, P. H. Measurement of Inherent Material Density of Nanoparticle Agglomerates. *J. Nanopart. Res.* **2004**, *6*, 267–272.

(33) Nakao, S.; Tang, P.; Tang, X.; Clark, C. H.; Qi, L.; Seo, E.; Asa-Awuku, A.; Cocker, D., III Density and Elemental Ratios of Secondary Organic Aerosol: Application of a Density Prediction Method. *Atmos. Environ.* **2013**, *68*, 273–277.

(34) Kreidenweis, S. M.; Petters, M. D.; DeMott, P. J. Single-Parameter Estimates of Aerosol Water Content. *Environ. Res. Lett.* **2008**, *3*, 035002.

(35) Petters, M. D.; Kreidenweis, S. M. A Single Parameter Representation of Hygroscopic Growth and Cloud Condensation Nucleus Activity. *Atmos. Chem. Phys.* **2007**, *7*, 1961–1971.

(36) Huff Hartz, K. E.; Tischuk, J. E.; Chan, M. N.; Chan, C. K.; Donahue, N. M.; Pandis, S. N. Cloud Condensation Nuclei Activation of Limited Solubility Organic Aerosol. *Atmos. Environ.* **2006**, *40*, 605– 617.

(37) Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. Secondary Organic Aerosol from the Photooxidation of Aromatic Hydrocarbons: Molecular Composition. *Environ. Sci. Technol.* **1997**, *31*, 1345–1358.

(38) Healy, R. M.; O'Connor, I. P.; Hellebust, S.; Allanic, A.; Sodeau, J. R.; Wenger, J. C. Characterisation of Single Particles from in-Port Ship Emissions. *Atmos. Environ.* **2009**, *43*, 6408–6414.

(39) Zhou, X.; Gao, J.; Wang, T.; Wu, W.; Wang, W. Measurement of Black Carbon Aerosols near Two Chinese Megacities and the Implications for Improving Emission Inventories. *Atmos. Environ.* **2009**, *43*, 3918–3924.

(40) Evans, M.; Kholod, N.; Malyshev, V.; Tretyakova, S.; Gusev, E.; Yu, S.; Barinov, A. Black Carbon Emissions from Russian Diesel Sources: Case Study of Murmansk. *Atmos. Chem. Phys.* **2015**, *15*, 8349–8359.

(41) Facchini, M. C.; Mircea, M.; Fuzzi, S.; Charlson, R. J. Cloud Albedo Enhancement by Surface-Active Organic Solutes in Growing Droplets. *Nature* **1999**, 401, 257–259.