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Effects of Volatile Coatings on the Morphology and Optical Detection of Combustion-Generated Black Carbon Particles

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Abstract

We have measured time-resolved laser-induced incandescence (LII) from combustion-generated mature soot extracted from a burner and (1) coated with oleic acid or (2) coated with oleic acid and then thermally denuded using a thermodenuder. The soot samples were size selected using a differential mobility analyser and characterized with a scanning mobility particle sizer, centrifugal particle mass analyser, and transmission electron microscope. The results demonstrate a strong influence of coatings particle morphology and on the magnitude and temporal evolution of the LII signal. For coated particles higher laser fluences are required to reach LII signal levels comparable to those of uncoated particles. This effect is predominantly attributable to the additional energy needed to vaporize the coating while heating the particle. LII signals are higher and signal decay rates are significantly slower for thermally denuded particles relative to coated or uncoated particles, particularly at low and intermediate laser fluences.

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NOMENCLATURE

CPMA	Centrifugal Particle Mass Analyzer
CW	Continuous Wave
DMA	Differential Mobility Analyzer
DOE	Department of Energy
ID	Inner Diameter
LII	Laser-Induced Incandescence
PMT	Photomultiplier Tube
slm	Standard Liters per Minute
SMPS	Scanning Mobility Particle Sizer
SNL	Sandia National Laboratories
TEM	Transmission Electron Microscopy

1. INTRODUCTION

Current climate models suggest that black-carbon particles, i.e., soot particles, contribute significantly to global warming and climate change because they absorb strongly in the visible and infrared regions of the solar spectrum [1]. Estimates of their impact on climate have large uncertainties, however, because their optical properties are not well represented in climate models, and their atmospheric abundance and distribution are not well known [2]. Reducing these uncertainties will require a detailed understanding of their optical properties, reliable measurements of their atmospheric abundance, and better estimates of their emissions. Reduction in soot emissions has been proposed as a near-term climate-change mitigation approach [3]. This mitigation approach will require a better understanding of soot formation processes during combustion and reliable measurements of soot in combustors and exhaust streams.

Laser-induced incandescence (LII) is a technique that has been developed over decades to measure soot particle abundances and physical properties in combustors, such as engines [4-10] and flames [11-17], and in combustion exhaust streams [18-21]. More recently it has been applied to measurements of ambient atmospheric black-carbon particles [22-29]. The implementation of this technique involves heating soot particles in an intense laser field and measuring the incandescence from the hot particles. The magnitude of the signal is correlated with the particle volume fraction or mass if the density is constant (see [30] and references therein).

Soot particle coatings can have a strong effect on the optical properties of the particle. A non-absorptive coating on a spherical soot particle is predicted to increase the scattering cross section, particularly forward scattering [21, 31-33]. Such a coating is also expected to increase the absorption cross section because of a refractive focusing effect of the coating [32-39]. These effects will have a significant influence on (1) the impact of black carbon on the Earth's climate and (2) the application of optical techniques, such as LII, to measure it under conditions in which it is expected to be coated, e.g., in combustors, exhaust streams, and the atmosphere.

Coatings can also influence soot particle morphology, which has additional effects on its optical properties. Mature uncoated soot aggregates have a dendritic, branched-chain morphology described by a fractal dimension of ~ 1.7 - 1.9 [40-51]. Numerous studies have shown that this aggregate morphology can become substantially compressed when the particles are coated with oxygenated hydrocarbons [48, 51-61] or sulfuric acid [21, 56, 62-64]. This morphology restructuring may persist even when the coating is removed in a thermodenuder [51, 53, 55, 56, 60, 63, 64].

The predicted effect of the coating-induced restructuring of the particle on its optical properties is unclear; some theories predict that the increased scattering interactions between primary particles should lead to an increase in the scattering cross section with increasing fractal dimension [65, 66], whereas other studies indicate that the scattering cross section should decrease with fractal dimension because of either the reduction in the aggregate size or destructive interference of multiply scattered waves at the core of the aggregate [21, 32, 45, 49]. The coating-induced particle compression is predicted to reduce the absorption cross section for particles with a fractal dimension below ~ 2 because of increased shielding of the primary

particles [32, 45, 67]. At fractal dimensions above 2 the absorption cross section is predicted to increase with fractal dimension [65]. Over the range of fractal dimension change induced by coatings (e.g., 1.78 to 2.50 [49], 1.7 to 2.7 [21], 1.9 to 2.1 [54], 1.72 to 1.87 [48], 1.88 to 2.34 [51]), however, the calculated dependence of the absorption cross section on fractal dimension is not strong [65, 67, 68].

The predicted net effect of volatile coatings on soot optical properties is an enhancement in both scattering and absorption cross sections [21]. These predictions are supported by experimental studies, which have demonstrated large enhancements in soot scattering and absorption cross sections attributable to coatings [21, 50, 54-56, 59, 62, 63, 69, 70].

Volatile coatings can also have an effect on the radiative emission from laser-heated soot and graphite particles, and, thus, on LII signals [21, 50, 71]. Considerable work has been devoted to modelling the particle laser heating, cooling, and mass-loss processes in an attempt to understand and predict the effects of ambient conditions and particle characteristics on the LII signal (see [72] and references therein). Relatively little work, however, has addressed the impact of volatile coatings on LII. Using an energy- and mass-balance model, Michelsen and co-workers [21, 73] predicted that, at low laser fluences from a nanosecond pulsed laser, volatile coatings will have a large effect on the magnitude of the LII signal, but this effect nearly disappears at high laser fluences. This behavior is caused by the requirement for additional energy to vaporize the coating before the core refractory particle can reach its peak temperature, which determines the peak LII signal. At laser fluences high enough to drive off the coating and heat the particle to sublimation temperatures, the peak temperature of ~ 4450 K will be reached whether the particle is initially coated or not, and the peak LII signal will thus be insensitive to particle coating. They confirmed these model predictions with preliminary experimental studies of coatings of sulfuric acid on mature soot extracted from a flame [73]. The results are inconsistent with the experimental results of [74], which indicate that differences in LII signal between coated and uncoated particles are insignificant at all laser intensities.

Moteki and Kondo [71] used an approach similar to that of Michelsen and co-workers [21, 73] to model LII signal from coated graphite particles. Moteki and Kondo [71] modelled an experimental configuration in which a particle drifts through a CW laser beam. Their system was similar to that of Michelsen and co-workers [21, 73] for a high-intensity laser ($\sim 3\text{-}30$ J/cm²) with a long pulse duration ($\sim 20\text{-}30$ μ s). Their model predicted that the evaporative heating of the particle coating should delay the appearance of the LII signal. This result is qualitatively consistent with the experimental results of Moteki and Kondo [71] and Slowik et al. [50], which showed that the delay of the onset of the LII signal, once the particle has intersected with the laser beam, increased with increasing coating thickness.

[75]

None of these studies directly addressed the impact of coating-induced restructuring of the particle. Several studies have targeted the effects of aggregate size on LII signals via its influence on particle conductive-cooling rates [76-80] and optical properties [81, 82], but none of these studies has addressed the effects of fractal dimension on LII.

In this report we present results of experiments focused on determining the effects of coatings of oleic acid on the morphology of combustion-generated mature soot particles [51] and on the

magnitude and temporal response of LII signal from these particles [75]. Our results demonstrate that, for oleic-acid coatings, the dendritic soot particles become more compact when the coating is applied. This restructuring is largely reversible if the coating is removed by laser irradiation but is irreversible if the coating is removed in a thermodenuder [51]. The particle maintains its restructured morphology after the coating is removed in a thermodenuder, even if the particle is laser heated after the thermodenuder. In addition, our results demonstrate a strong dependence of the LII signal magnitude on particle coating at low and intermediate laser fluences. This result is consistent with the predictions of Michelsen and co-workers [21, 73] but inconsistent with the results of Schwarz et al. [74]. The LII excitation curve (peak LII versus fluence) shifts to higher fluence with increasing coating at moderate coating thickness but shifts back to lower fluences with heavy coating thicknesses. In addition, the rising edge of our LII temporal profiles is sensitive to coating thickness, i.e., the onset of the signal for coated particles appears later in time than for uncoated particles. This result is qualitatively similar to the results of Moteki and Kondo [71] and Slowik et al. [50]. The decay rate of the LII signal also appears to be sensitive to particle coating, but the main effect observed is likely attributable to a coating-induced increase in the fractal dimension of the particle and its effects on the conductive cooling rate

2. EXPERIMENTAL APPROACH

2.1. Soot Generation, Coating Application, and Thermal Denuding

A schematic diagram of the experimental apparatus is shown in Fig. 1. We generated soot in an ethylene-air flame from a coflow diffusion burner. The burner had a central fuel nozzle (0.5 cm in diameter) protruding 15 mm above a honeycomb structure (44 mm in diameter), which conducted the air coflow [43, 83, 84]. A mass flow controller (MKS Type 1479A) held the ethylene flow rate at 0.220 standard liters per minute (relative to 0°C and 760 Torr) (slm-MKS). A second flow controller (MKS Type 1559A) held the air coflow at 14 slm-MKS. A brass mesh tube of 1-cm diameter surrounded the flame to a height of 25 mm and helped to stabilize the flame. The flame and air coflow were completely enclosed in a modular flow tube constructed from 50-mm-ID tubing components (Kwik-Flange NW50). The visible flame height in the flow tube was approximately 100 mm. The flame was cut at ~65-mm height above the burner by a horizontal nitrogen cross flow of 50 slm-MKS, which quenched the combustion and carried the soot to the sampling tube approximately 45 cm downstream. A Venturi pump (Vaccon JS-40UM) extracted the soot from the center of the cross-flow tube through a 1/4-inch stainless steel tube with a sample flow rate of 0.38 slm-MKS and a dilution flow rate of 1.2 slm-MKS, which corresponded to a dilution ratio of ~4:1.

Figure 1. Experimental Setup. Soot was generated in a coflow diffusion ethylene-air flame at atmospheric pressure. Combustion was quenched with a cross flow of nitrogen. Part of the flow was extracted and size selected with a DMA. The size-selected soot could be sent through a condenser and coated with oleic acid. The coated or uncoated soot could also be sent through a thermodenuder to remove coating. The uncoated, coated, or denuded soot was sent into an optical cell, where the particles were heated with pulsed 1064-nm laser beam with a homogeneous spatial profile. The LII signal was detected with a photomultiplier tube attached to an oscilloscope. The particles were characterized by SMPS measurements of mobility size, CPMA measurements of mass, and TEM imaging of morphology.

A differential mobility analyser (DMA) (TSI 3081) selected soot in a narrow size range for use in the subsequent coating, denuding, and measurement sections. The DMA was set to select aggregates of mobility diameter 150 nm using a sample flow rate of 0.2 standard liters per minute (relative to 21°C and 1 bar) (slm-TSI) and a sheath flow of 2.0 slm-TSI.

The coating condenser consisted of a straight section of 50-mm-ID stainless steel tubing 14 cm long with tapered ends that allowed the particles to flow through continuously to mitigate the effects of multiple residence times. The condenser was wrapped in heating tape and insulated, and a type-K thermocouple provided the feedback for a temperature controller. The coating material used in the experiments was oleic acid ($\geq 99\%$, Sigma Aldrich). The temperature of the oleic acid was measured with a thermocouple inside the chamber immersed in the liquid. The flow rate of the aerosol was 0.200 slm-MKS for all experiments, and the volume of the chamber was 400 ml, which resulted in a residence time of approximately 2 min in the coating chamber. Immediately downstream of the coating chamber a room-temperature denuder containing activated carbon strips (Sunset Laboratory) trapped coating vapour leaving the condenser but allowed the coated particles to pass. The condenser temperatures and the nomenclature for the coatings associated with these temperatures are given in Table 1.

Table 1. Coating and Denuding Conditions

Coating	Condenser temp (°C)	Laser fluence coated (J/cm ²)	Laser fluence denuded (J/cm ²)	Ave mass coating ratio ^a	Ave coating mass fraction ^b	Coating mass fraction ^c
Uncoated	20	0.15	0.15	1.00	0.00	0.00
Very light	40	0.15	0.15	1.02	0.02	0.05
Light	60	0.17	0.15	1.25	0.20	0.27
Moderate light	70			1.76	0.43	0.47
Moderate	80	0.20	0.15	2.85	0.65	0.72
Moderate heavy	90			7.26	0.86	0.89
Heavy	95	0.20	0.15	12.6	0.92	0.94
Very heavy	105	0.20, 0.27	0.15	37.4	0.97	0.98
Extreme heavy	110	0.20	0.15	70.2	0.99	0.99

^aThe mass coating ratio averaged over the full mass distribution (all three modes) is given by (Total particle mass / Uncoated particle mass).

^bThe coating mass fraction averaged over the full mass distribution (all three modes) is given by (Total particle mass - Uncoated particle mass)/Total particle mass.

^cThe coating mass fraction for just the singly charged mode (i.e., Peak 1) is given by (Coated particle median mass - Uncoated particle median mass)/Coated particle median mass.

Coatings could be removed from the particles using a thermodenuder. Our thermodenuder design achieved the two important criteria suggested by Fierz et al. [85] of avoiding strong temperature gradients and maintaining elevated gas temperatures in the absorption section. We achieved the desired behavior using two temperature-controlled sections as opposed to the three sections in the Fierz et al. [85] design. The overall length of the thermodenuder was 100 cm with the initial 70 cm heated in two zones, each 35 cm in length. The aerosol flowed through 12-mm ID tubing,

the first 40 cm of which was solid-walled stainless steel tubing, and the last 60 cm of the tubing was fine stainless steel mesh surrounded by activated charcoal contained within a 25-mm ID stainless steel tube. The initial 90 cm of the denuder was surrounded by 50-mm thick fiberglass insulation, and over the last 10 cm the stainless steel tubing was left exposed. In the initial heated section intended to desorb coatings the tubing was heated to 410°C, while the second heated section, which included 30 cm of the activated carbon, was heated to 170°C. The peak temperature in the aerosol stream was 400°C, approximately in the middle of the initial heated section, and the temperature gradually transitioned down to approximately room temperature at the exit of the denuder.

2.2. Coating Removal by Laser Heating

Laser heating was performed using pulsed 1064-nm radiation formatted with a top-hat spatial profile to provide uniform irradiation on the aerosol in a desorption cell. A ceramic iris with a 3-mm aperture selected a portion of the ~5-mm diameter output beam from the Nd:YAG laser (Continuum NY81C) to produce a top-hat profile that was then relay imaged with demagnification to produce a ~2.4-mm top-hat spatial profile along the path where laser desorption was performed. A half-wave plate and thin-film polarizer provided laser power adjustment without changing the laser profile. The uniformity of the laser spatial profile was measured using a beam profiling camera (Dataray WinCamD), and the beam diameter was found to be 2.3-2.5 mm in diameter along the desorption path with maximum intensity excursions of $\pm 20\%$ around the mean.

The laser desorption cell (not shown in Fig. 1) consisted of a straight section of aluminium tubing with Brewster-angled borosilicate glass windows on both ends providing optical access along the full axis of the tube, and fittings adjacent to the windows served as the aerosol inlet and outlet ports. The combination of desorption cell length (8 cm), inner diameter (2.4 mm), flow rate (0.2 slm-TSI), and laser profile and repetition rate (10 Hz) ensured that the vast majority of the particles studied would be exposed to comparable laser fluence.

Soot particles were laser-heated to a temperature of ~3000 K. This temperature was derived from peak LII measurements for which the signal depends on the laser fluence and can be associated with a core particle temperature under low-fluence conditions (see Eq. (8)). A description is given in Section 3.1.

2.3. Particle Characterization by SMPS, CPMA, and TEM

Mobility-size distributions were recorded using a scanning mobility particle sizer (SMPS), which consisted of an electrostatic classifier (TSI 3080 with TSI 3081 DMA) and the condensation particle counter controlled by a computer. The sample flow in the SMPS was 0.2 slm-TSI, and the sheath flow was 2.0 slm-TSI. The input and output flows of the DMA were balanced, giving a theoretical mobility resolution of 10% of the measured mobility size [86]. An impactor with a 0.0457-mm orifice at the SMPS limited the maximum sampled particle diameters to approximately 800 nm.

Particle masses were monitored with a centrifugal particle mass analyser (CPMA) (Cambustion). Results of the mass measurements are summarized here; more details are given in [51].

Soot particles were collected on TEM grids down stream of the condenser, denuder, and laser-heating cell. The grids were a copper mesh substrate covered with a layer of Formvar and stabilized with silicon monoxide (Ted Pella, 01830). The TEM grids were analyzed using a JEOL 1200 EX TEM (120 kV). The images were collected at a magnification of 250,000 using a CCD camera with a scaling of approximately 0.4 nm/pixel.

2.4. Laser-Induced Incandescence Measurements

The optical arrangement used for LII is shown in Figure 1. A Nd:YAG laser (Continuum NY81C) generated 17 ns (full width at half max) unseeded pulses at 1064 nm and a repetition rate of 10 Hz. A top-hat intensity distribution was generated by placing a 3-mm iris in a uniform section of the ~5-mm laser output beam. The top-hat profile was relay imaged and demagnified to 1-mm diameter using two lenses (152.5-cm and 50-cm focal length). A camera (DataRay WinCam-D) profiled the beam, as shown in Fig. 2, and the intensity profiles were measured and adjusted to have root-mean-squared variations of approximately 14% in the soot LII detection region. A first thin-film polarizer ensured the beam had a well-defined vertical polarization, and the power was adjusted by rotation of a half-wave plate, which was followed by two fixed thin-film polarizers. The average laser pulse energy was measured using a power meter (Coherent PM3 or PS19).

Figure 2. Laser Beam Spatial Profile. The image of the 1064-nm laser beam was taken using a camera with a pixel size of $6.7 \mu\text{m} \times 6.7 \mu\text{m}$. The beam diameter was 0.99 mm with a spatial variability of ~14% (one standard deviation) over the entire beam profile. The lines represent vertical and horizontal cross sections through the beam profile shown.

The laser irradiation of the soot for LII was performed in a flow cell shown in Fig. 1. Windows on the cell provided optical access for the LII measurements and the laser input. Soot entered the cell through a 5-mm ID tube and flowed through the center of the cell surrounded by a sheath of clean air along a path perpendicular to the laser beam. A lens (25-mm focal length) placed one focal distance from the center of the cell collected the incandescence and directed it through two filters (Schott RG610 long-pass and Thorlabs FES0900-1 900 nm short-pass) to a second lens (75 mm focal length) that imaged the incandescence onto the face of a photomultiplier tube (PMT) (Hamamatsu R7400-20). The filters blocked the 1064-nm laser scatter and passed incandescence from 610 – 900 nm.

3. ANALYSIS APPROACH

3.1. Inference of Maximum Particle Temperatures

Maximum particle temperatures were estimated from the peak LII signal using an expression based on the Planck function. The LII signal from X aggregate particles at the detection wavelength λ_s is given by the Planck function modified by the emissivity to correct for deviations from perfect blackbody emission, i.e.,

$$S = XN \frac{2\pi^2 d_p^3 hc^2 E(m)}{\lambda_s^6} \frac{1}{\exp\left(\frac{hc}{\lambda_s kT}\right) - 1} \Omega \Sigma_\lambda, \quad (1)$$

where N is the number of primary particles in the aggregate, d_p is the primary-particle diameter, h is the Planck constant, c is the speed of light, and k is the Boltzmann constant. The spectral response and efficiency of the detector are represented by Σ_λ . The solid angle element Ω is determined by the detector configuration, which, for cylindrically symmetric collection optics and detector, is given by

$$\Omega = 2\pi(1 - \cos\theta), \quad (2)$$

where θ is the acceptance angle of the detection system. The dimensionless refractive-index function for absorption $E(m)$ is given by

$$E(m) = -\text{Im}\left(\frac{m^2 - 1}{m^2 + 2}\right) = \frac{6nk}{(n^2 - k^2 + 2)^2 + 4n^2k^2} \quad (3)$$

for a complex refractive index $m=n-ki$. $E(m)$ is calculated to be 0.373 using a value for the refractive index of $1.75-1.03i$ measured by Williams et al. [87] at 635 nm in Eq. (3). Previous work has suggested deviations from the $1/\lambda$ dependence of the emissivity [88-93], which can be accounted for by assuming a wavelength dependence for $E(m)$. The wavelength dependence derived from the work of Köylü and Faeth [89, 94] can be expressed as

$$E(m) = \frac{\lambda_s^{1-\xi} \beta}{6\pi}, \quad (4)$$

where $\xi=0.83$ [89]. A value for the scaling factor β of $36.34 \text{ cm}^{-0.17}$ allows $E(m)$ in Eq. (4) to match the value of $E(m)$ given by Eq. (3) with the refractive index from Williams et al. [87] at 635 nm.

We used the same detection optics for all of the experiments described here, which ensured that λ_s , Ω , and Σ_λ did not change between measurements. We also used the same soot-generation and size-selection process. Monitoring of particle characteristics using TEM imaging confirmed that

the primary-particle size of the core soot particles did not vary over the course of these measurements, and monitoring using an SMPS and a CPMA ensured that the aggregate size did not change. We can also assume that the fine structure of the core soot particles is unlikely to vary during these experiments, and therefore the values of $E(m)$ and the sublimation temperature T_{sub} should not change. As long as the number of particles in the detection volume X does not vary over a fluence sweep (a scan in fluence), we can normalize the signal over the entire fluence sweep such that the peak LII signal at high fluences is normalized to one.

Given the above conditions, Equation (1) can be simplified to

$$S = \frac{A}{\exp\left(\frac{B}{T}\right) - 1} - C, \quad (5)$$

where $B=hc/\lambda_s k$. Our peak LII signal is scaled from 0 at room temperature to a maximum of 1 at high fluence. C accounts for scaling the signal to zero at 298 K. A encompasses a host of constants; for our normalized LII signal, assuming that the particle does not surpass T_{sub} (~4450 K) [95] at high fluences, A is given by

$$A = \left[\frac{1}{\exp\left(\frac{B}{4450}\right) - 1} - \frac{1}{\exp\left(\frac{B}{298}\right) - 1} \right]^{-1}, \quad (6)$$

which equals 113.6 for $\lambda=682$ nm. Likewise C is given by

$$C = \frac{A}{\exp\left(\frac{B}{298}\right) - 1}, \quad (7)$$

which equals 2.019×10^{-29} for $\lambda=682$ nm.

Figure 3 shows a plot of the signal calculated using Eq. (5) as a function of temperature. This equation estimates the signal at a single wavelength (682 nm). Our experiments, however, were performed with broadband collection from 610 nm to the PMT wavelength limit of ~890 nm. Figure 3 also shows the signal calculated using Eq. (1) with the true PMT spectral response function and integrated over the wavelength range of 610-900 nm. The comparison in Fig. 3 demonstrates that the approximation of single-wavelength detection leads to a very small systematic error in calculated signal.

The maximum particle temperature T_{max} at a particular fluence can then be calculated from the peak LII signal S_{pk} by solving Eq. (5) for temperature, which yields

$$T_{\max} = \frac{B}{\ln\left(\frac{A}{S_{\text{pk}} + C} + 1\right)}. \quad (8)$$

The small bias in calculated signal caused by the approximation of single-wavelength detection (Fig. 3) corresponds to a bias in the inferred temperature of less than 50 K.

Figure 3. Temperature Dependence of the LII Signal. The solid curve represents the signal calculated using Eq. (5), which corresponds to detection at a single wavelength. The calculated signal is normalized to unity at a temperature of 4450 K and to zero at 298 K. The dotted curve represents the similarly normalized signal calculated using Eq. (1) integrated over a wavelength range of 610-900 nm.

3.2. Factors Influencing Maximum Particle Temperature

The particle-heating rate and the ultimate temperature reached by the particle are controlled by the balance of gain of energy as the particle absorbs laser radiation or is oxidized with the loss of energy by conduction, radiation, core sublimation, and coating vaporization. During the laser pulse, the rate of heating by absorption greatly exceeds the oxidative heating rate and the conductive and radiative cooling rates by orders of magnitude at atmospheric pressure [94]. Sublimation rates are negligible at low fluences. Neglecting oxidative heating and conductive, radiative, and evaporative (core sublimation) cooling, the energy-balance equation can be approximated by

$$\left[Mc_s(T) + M_{\text{coat}}c_{\text{coat}}(T)\right]\frac{dT}{dt} = \dot{Q}_{\text{abs}} - \dot{Q}_{\text{coat}}, \quad (9)$$

where M is the particle mass, c_s is the specific heat of the core particle, M_{coat} is the mass of the particle coating, c_{coat} is the specific heat of the coating (2.046 J/g K for oleic acid), T is the particle temperature, and t is time. $\dot{Q}_{\text{abs}}$ is the heating rate by absorption of laser radiation and is given by

$$\dot{Q}_{\text{abs}} = \sigma_{\text{abs}}F_Lq_n(t), \quad (10)$$

where σ_{abs} is the absorption cross section, F_L is the laser fluence, and $q_n(t)$ is the normalized laser temporal profile, which yields a value of one when integrated over the laser pulse in time. $\dot{Q}_{\text{coat}}$ is the cooling rate by evaporation of the volatile coating and is given by

$$\dot{Q}_{coat} = \frac{\Delta H_{coat}}{W_{coat}} \frac{dM_{coat}}{dt}, \quad (11)$$

where ΔH_{coat} is the enthalpy of vaporization of the coating at its boiling point (1.356×10^5 J/mol for oleic acid [96]), and W_{coat} is the molecular weight of the coating (282.47 g/mol for oleic acid). Integrating Eq. (9) over the laser pulse gives

$$M \int_{T_0}^{T_{max}} c_s dT + M_{vap} c_{coat} (T_{boil} - T_0) = \sigma_{abs} F_L - M_{vap} \frac{\Delta H_{coat}}{W_{coat}}, \quad (12)$$

assuming that some amount of coating M_{vap} vaporizes after being heated from the initial particle temperature T_0 to the boiling point T_{boil} (658.5 K for oleic acid). If all of the coating vaporizes, $M_{vap} = M_{coat}$. Assuming that c_s is approximately constant with temperature, performing the integration, and rearranging Eq. (12) yields

$$T_{max} = \frac{\sigma_{abs} F_L}{M c_s} - \frac{M_{vap}}{M c_s} \left[\frac{\Delta H_{coat}}{W_{coat}} + c_{coat} (T_{boil} - T_0) \right] + T_0. \quad (13)$$

In these studies the average coating mass M_{coat} was determined by integrating over the entire mass distribution for the coated particles.

3.3. Inferring Coating Effects on LII Signal and Absorption Cross Section

Particles with the same volume fraction, size, fine structure, and morphology that reach the same T_{max} will produce the same maximum LII signal for a particular detection system. For fluences at which coated particles give the same peak LII signal as uncoated particles, from Eq. (13) we can assume that

$$\frac{\sigma_{coat} F_L(\text{Coated})}{M c_s} - \frac{M_{vap}}{M c_s} \left[\frac{\Delta H_{coat}}{W_{coat}} + c_{coat} (T_{boil} - T_0) \right] = \frac{\sigma_{uncoat} F_L(\text{Uncoated})}{M c_s}, \quad (14)$$

where $F_L(\text{Coated})$ gives the same peak LII signal for coated particles as does $F_L(\text{Uncoated})$ for uncoated particles, σ_{uncoat} is the absorption cross section for uncoated particles, and σ_{coat} is the corresponding absorption cross section for coated particles. Simplifying and rearranging Eq. (14) yields

$$F_L(\text{Coated}) = \frac{\sigma_{uncoat}}{\sigma_{coat}} F_L(\text{Uncoated}) + \frac{M_{vap}}{\sigma_{coat}} \Gamma, \quad (15)$$

where

$$\Gamma = \left[\frac{\Delta H_{coat}}{W_{coat}} + c_{coat} (T_{boil} - T_0) \right]. \quad (16)$$

Equation (15) suggests that a plot of $F_L(\text{Coated})$ as a function of $F_L(\text{Uncoated})$ will give a line with a slope that depends on the coating enhancement for absorption, i.e.,

$$\frac{1}{\text{Slope}} = \frac{\sigma_{\text{coat}}}{\sigma_{\text{uncoat}}}. \quad (17)$$

From the ratio of the intercept to the slope, we can estimate how much coating was evaporated from the particle, i.e.,

$$M_{\text{vap}} = \frac{\text{Intercept}}{\text{Slope}} \frac{\sigma_{\text{uncoat}}}{\Gamma}. \quad (18)$$

For oleic acid at $T_0=298$ K, $\Gamma=1217.6$ J/g. We can estimate σ_{uncoat} using the equation for a particle in the Rayleigh regime [45], i.e.,

$$\sigma_{\text{uncoat}} = N \frac{\pi^2 d_p^3 E(m)}{\lambda_L}, \quad (19)$$

where λ_L is the laser wavelength (1064 nm), and d_p is the primary-particle diameter (11 nm for this study). The number of primary particles N can be determined according to

$$N = \frac{6M}{\pi d_p^3 \rho}, \quad (20)$$

where the average uncoated particle mass over the entire mass distribution was determined from CPMA measurements to be 1.321 fg [51], and ρ is the density for polycrystalline graphite assumed to be 1.8 g/cm³. Combining Eqs. (4), (19), and (20) gives an expression for the uncoated aggregate absorption cross section in terms of the uncoated aggregate mass, i.e.,

$$\sigma_{\text{uncoat}} = \frac{\beta M}{\rho \lambda_L^{\frac{3}{2}}}, \quad (21)$$

which gives an average value for σ_{uncoat} of 5.29×10^{-11} cm² at 1064 nm.

3.4. Soot Characterization by TEM

The fractal dimension D_f of the soot aggregates was inferred from these images by assuming that [97]

$$N = k_0 \left(\frac{R_g}{a} \right)^{D_f}, \quad (22)$$

where N is the number of primary particles, R_g is the radius of gyration of the aggregate, a is the primary particle radius (5.5 nm for our particles), and k_0 is a prefactor that depends on the

overlap between primary particles in the TEM image. When the overlap is small, e.g., for uncoated particles, $k_0=1.3$, and when the overlap is large, e.g., for fully collapsed particles, $k_0=2.6$ [97]. For the intermediate case of very lightly coated particles, we used $k_0=1.8$ [97]. Solving for D_f yields

$$D_f = \frac{\ln\left(\frac{N}{k_0}\right)}{\ln\left(\frac{R_g}{a}\right)}. \quad (23)$$

We estimate N according to [97]

$$N = k_a \left(\frac{A_c}{A_a} \right)^\alpha, \quad (24)$$

where A_c is the projected area of the soot aggregate, A_a is the projected area of the primary particle (assuming here a radius of 5.5 nm), and k_a and α are constants that depend on the overlap between the primary particles. When the overlap is small, e.g., for the uncoated particles, $k_a=1.15$ and $\alpha=1.07$, and, when the overlap is large, $k_a=1.65$ and $\alpha=1.16$ [97]. For the very lightly coated particles we used $k_a=1.37$ and $\alpha=1.11$ [97].

3.5. Soot Characterization by SMPS and CPMA

The mobility size distributions were recorded using a scanning mobility particle sizer (SMPS), which consisted of an electrostatic classifier (TSI 3080 with TSI 3081 DMA) and a condensation particle counter (CPC) controlled by a computer. The sample and sheath flows in the SMPS were 0.2 and 2.0 slm-TSI, respectively, and the input and output flows of the differential mobility analyser (DMA) were balanced. The expected mobility resolution was 10% of the measured mobility size, where the resolution is defined at the full-width-half-maximum (FWHM) of the DMA's triangular mobility transfer function [86]. An impactor with a 0.0457-mm orifice at the SMPS limited the maximum sampled particle diameters to approximately 800 nm.

Mass distributions were acquired using a Centrifugal Particle Mass Analyzer (CPMA) (Cambustion CPMA) interfaced to a CPC (TSI 3776). The mass resolution was typically set to 5.5%, where the resolution is defined analogously to the DMA resolution as the ratio of the FWHM of the mass to the peak mass of the triangular transfer function [98]. Corrections to the mass distributions for multiply charged particles [99] were performed using our measured mobility distributions and the charge distribution approximations [100]. The coating masses corresponding to the condenser temperatures are given in Table 1.

The mobility-size and mass distributions were well described by a sum of log-normal distribution functions, i.e.,

$$W(\log x) = W_1(\log x) + W_2(\log x) + W_3(\log x), \quad (25)$$

where the first mode W_1 represents particles that were singly charged in the neutralizer before the size-selecting DMA, W_2 represents the particles that were doubly charged, W_3 represents the particles that were triply charged, and x represents either the particle mobility diameter D_m or the particle mass M . The measured number concentrations were fit using Eq. (5) with each mode represented by a log-normal distribution given by [101]

$$W_i(\log x) = \frac{n}{\sqrt{2\pi} \log \sigma} \exp \left\{ -\frac{\left[\log \left(\frac{x}{x_0} \right) \right]^2}{2 \log^2 \sigma} \right\}, \quad (26)$$

with mode-specific values for the median (or geometric mean) x_0 , geometric standard deviation σ , and scaling factor n . Coating fractions were calculated using average masses over the entire multi-modal distributions for the coated particles and the uncoated particles, i.e.,

$$\overline{M} = \frac{\int MW(\log M)d(\log M)}{\int W(\log M)d(\log M)}, \quad (27)$$

and the results are compared in Table 1 with values derived from the mean and median values for the singly charged mode.

Mobility-fractal dimensions were estimated for the uncoated and denuded particles from the mobility-size and mass distributions for comparison with the fractal dimensions derived from the TEM images. Previous work has shown that the mobility radius R_m is related to R_g according to

$$R_m = k_R R_g^\beta \quad (28)$$

where k_R is a proportionality constant, $\beta=0.79$ in the free-molecular-flow regime, i.e., when the Knudsen number Kn (the ratio of the gas mean free path to a characteristic length) is much greater than one, and $\beta=1$ in the continuum regime where $Kn \ll 1$ [97, 102]. Equation (2) can be rewritten with respect to the mobility radius or mobility diameter $D_m (=2R_m)$, i.e.,

$$N = k_0 \left(\frac{R_m^{1/\beta}}{a k_R^{1/\beta}} \right)^{D_f} = k_0 \left[a (2k_R)^{1/\beta} \right]^{-D_f} D_m^{D_f/\beta}, \quad (29)$$

The number of primary particles can be estimated from the particle mass M , i.e.,

$$N = \frac{3M}{4\pi a^3 \rho}, \quad (30)$$

where ρ is the density of the primary particles, which can be estimated from the density of polycrystalline graphite ($\sim 1.8 \text{ g/cm}^3$). Substituting Eq. (30) into Eq. (29), rearranging, and simplifying yields the following relationship between particle mass and mobility diameter

$$D_m = C_m M^{\beta/D_{fm}}, \quad (31)$$

where $D_{fm}=D_f$ and

$$C_m = 2k_R a^\beta \left(\frac{3}{4\pi a^3 \rho k_0} \right)^{\beta/D_{fm}}. \quad (12)$$

We have substituted D_{fm} for D_f in Eqs. (31) and (32) to distinguish it from the fractal dimension derived directly from TEM images.

We fit Eq. (31) to the singly, doubly, and, when available, triply charged peaks of the mobility-size and mass distributions to infer D_{fm} and C_m , which were used in the multiple-charge corrections for the mass distributions. The characteristic sizes of the aggregates yield values for Kn in the range of 0.1-0.5, indicating that they are not safely in the continuum-regime values. If the primary particles size is the relevant characteristic size for determining Kn , the value for Kn is ~ 6 , suggesting that conditions for the non-restructured aggregates may be close to the free-molecular flow regime. We found that $\beta=0.90$ gave good agreement with fractal dimensions derived from TEM images for the restructured particles and that $\beta=0.87$ gave good agreement for the less compact particles, allowing us to correct for flow conditions in the slip-flow regime (in between the free-molecular and continuum flow regimes). We will refer to D_{fm} as the mobility-fractal dimension to distinguish it from similarly derived mass-mobility exponents [56, 60], also known as mass-fractal dimensions [55], which have historically neglected the correction for the flow regime. Because we correct for the flow conditions, our values of D_{fm} tend to be lower than previously reported mass-fractal dimensions [55, 56, 60] and more consistent with the fractal dimensions measured via TEM. Fitting results are given for uncoated and coated particles in Table 2 and for denuded particles in Table 3. With the above assumptions we find that

$$C_m = (365 \pm 16) - (95.8 \pm 7.1)D_f, \quad (33)$$

where $D_{fm} \approx D_f$.

For the charge corrections, we used values of $\beta=0.87$, $D_{fm}=1.88$, and $C_m=184 \text{ nm fg}^{-0.456}$ (derived from uncoated particles) for the laser-heated and then denuded particles, values of $\beta=0.90$, $D_{fm}=2.43$, and $C_m=141 \text{ nm fg}^{-0.371}$ for denuded and then laser-heated particles, and values of $\beta=0.90$, $D_{fm}=2.7$, and $C_m=129 \text{ nm fg}^{-0.333}$ for heavily coated particles. We used the values in Tables 2 and 3 for all other conditions.

Mass distributions were inferred from mobility-size distributions and measured fractal dimensions using the expression

$$M = \left(\frac{D_m}{C_m} \right)^{D_f/\beta} \quad (34)$$

for the mass scaling and multiplying the mobility-size distribution by

$$\frac{d \log D_m}{d \log M} = \frac{\beta}{D_f}. \quad (35)$$

Table 2. Summary of Results for Uncoated and Coated Particles^a

Coating	Median D_m (nm) Peak 1	Median D_m (nm) Peak 2	Median M (fg) Peak 1	Median M (fg) Peak 2	Fractal dim D_f	D_{fm}	C_m (nm fg ^{-βD_{fm}})
Uncoated	152	234	0.659	1.67	1.88	1.88	184
Very light	135	203	0.695	1.66	2.16	2.00	160
Light	130	189	0.901	2.19	2.34	2.13	136
Moderate light	126	178	1.24	2.84		2.14	115
Moderate	158	192	2.33	4.35	2.31	2.95	122
Moderate heavy	220	249	6.14	9.01		2.69	120
Heavy	270	314	10.7	14.1	2.30		
Very heavy	420	470	34.9	42.1	2.34		
Extreme heavy	509	648	66.6	79.7			

^aThe standard deviation is estimated to be 7.5% for median particle mass [103], ≤3% for median mobility diameter, and ≤6% for mean fractal dimension with ≥13 particles analyzed for each coating.

Table 3. Summary of Results for Denuded Particles^a

Coating before denuding	Median D_m (nm) Peak 1	Median D_m (nm) Peak 2	Median M (fg) Peak 1	Median M (fg) Peak 2	Fractal dim D_f	D_{fm}	C_m (nm fg ^{-βD_{fm}})
Uncoated	154	240	0.665	1.73	1.88	1.87	186
Very light	143	224			2.15		
Light	124	175	0.738	1.79	2.36	2.28	139
Moderate light	122	173	0.689	1.67		2.30	142
Moderate	122	171	0.686	1.70	2.36	2.40	140
Moderate heavy	123	173	0.725	1.77		2.37	139
Heavy	117	163	0.721	1.78	2.33	2.44	1.2
Very heavy	119	170	0.712	1.75	2.39	2.25	137
Extreme heavy	118	163	0.712	1.73		2.43	134

^aThe standard deviation is estimated to be 7.5% for median particle mass [103], ≤3% for median mobility diameter, and ≤8% for mean fractal dimension with ≥13 particles analyzed for each coating.

4. RESULTS AND DISCUSSION

4.1. Effects of Coatings on Particle Morphology

Figure 4 shows a TEM image of a typical uncoated soot particle produced by the ethylene flame and sampled in the particle stream after size selection using a DMA set to 150 nm. The particle demonstrates the branched-chain morphology and fractal dimension (1.72 ± 0.10) characteristic of mature soot particles generated in a flame [40-50, 104, 105]. When coated with oleic acid, the particles collapse, as demonstrated in Fig. 5a for a particle with a very light coating of oleic acid, in Fig. 5c for a moderate oleic acid coating, and in Fig. 5e for a heavy oleic acid coating. This restructuring is represented by a substantial increase in fractal dimension (from 1.88 for an uncoated particle to a maximum of ~ 2.31 for a moderate to heavily coated particle). The fractal dimension change is summarized in Table 2. This change is consistent with previous studies that have shown coating-induced fractal dimension changes of 1.78 to 2.50 [49], 1.7 to 2.7 [21], 1.9 to 2.1 [54], and 1.72 to 1.87 [48]. During this coating-induced restructuring, the stringy branched limbs of the particles fold on themselves and draw in toward the particle center. With a very light coating, some pockets or voids are still observable (Fig. 5a), and the fractal dimension is smaller than for the more heavily coated particles. Particle collapse is more complete, and the pockets disappear when the particle is moderately or heavily coated (Figs. 5c and 5e). TEM images of heavily coated particles showed oleic acid wetting the surface when the grids were first mounted in the microscope. The particles were already restructured with the oleic acid surrounding them and did not change when the coating evaporated during TEM imaging. The images shown for the coated particles may be partially or fully denuded during TEM imaging, but this process did not change the morphology of the particles.

Figure 4. TEM Image of an Uncoated Soot Particle. The particles were size selected with the DMA set to 150 nm. The scale is indicated in the lower left corner. The TEM image was recorded at a magnification of 250,000.

The mobility diameter is correlated with the radius of gyration of a particle [102, 106-109]. A reduction in mobility diameter without a reduction in particle mass is consistent with particle restructuring. Figure 6a shows the mobility size distribution for uncoated particles. The largest peak in the size distribution (at 152 nm) corresponds to size-selected particles that passed through the DMA with a single charge. The peak at 234 nm corresponds to particles that were doubly charged when passing through the DMA, and the peak at 310 nm is associated with triply

charged particles. The small peak at 100 nm is attributable to particles that were singly charged in the first DMA and became doubly charged in the neutralizer before the second DMA, which is part of SMPS. The SMPS charge-correction software removes most (but not all) of this peak. These modes appear in all of the size distributions presented here. Similar modes are demonstrated in the mass distributions.

Figure 5. TEM Images of Coated and Thermally Denuded Soot Particles. The scale is indicated in each figure. The TEM images were recorded at a magnification of 250,000. The particles were (a) very lightly coated with oleic acid, (b) very lightly coated and then denuded, (c) moderately coated with oleic acid, (d) moderately coated and then denuded, (e) heavily coated with oleic acid, and (f) heavily coated and then denuded. In all cases, the particles were size selected (DMA set to 150 nm) prior to coating.

Figure 6a also shows mobility-diameter size distributions corresponding to the very lightly and lightly coated particles, compared with the distribution for the uncoated particles, and Fig. 6b shows the associated mass distributions. The mobility size distribution is significantly smaller for the very lightly and lightly coated particles. These results show that the mobility size decreases with increasing coating thicknesses for light and moderate coatings. Although the mobility diameter decreases with increasing coating, the mass increases measurably with increasing coating for all coating thicknesses. The coating on the very lightly coated particles is so small that the mass change is not resolved with the CPMA, but nevertheless the mobility diameter is significantly smaller for the lightly coated particle than for the uncoated particle, which is consistent with the change in fractal dimension shown by the TEM images.

Figure 6. Mobility-Diameter Size and Mass Distributions of Coated Soot Aggregates. The uncoated particles were size selected with a DMA set to 150 nm prior to coating. Particles that were not coated were also size selected. (a) The size distribution of the uncoated particles is compared with those of particles that have been very lightly and lightly coated with oleic acid. The units on the y-axis are normalized values of number of particles per unit volume in each mobility size bin ($dW/d\log D_m$). (b) The mass distributions of the very light and lightly coated particles are compared with the mass distribution for the uncoated particles. The units on the y-axis are normalized values of number of particles per unit volume in each mass bin ($dW/d\log M$). (c) The size distribution of the uncoated particles is compared with those of particles that have been moderately, heavily, and very heavily coated with oleic acid. (d) The mass distributions of the moderately, heavily, and very heavily coated particles are compared with the mass distribution for the uncoated particles. Curves are scaled to the top of each graph and identified in the legend.

Adding more coating causes the particles to grow in mobility diameter and mass because of the extra material from the coating itself, as shown for moderately to very heavily coated particles in Figs. 6c and 6d. The change in mobility diameter and mass with particle coating is summarized in Table 2.

4.2. Effects of Thermal Denuding on Particle Morphology

Sending coated particles through a thermodenuder to remove the coating appears to have little effect on the particles' collapsed morphology, as shown for a very lightly coated particle in Fig. 5b, for a moderately coated particle in Fig. 5d, and for a heavily coated particle in Fig. 5f. The mobility size distributions shown in Fig. 7a confirm that the particles do not return to their original size when the coatings are removed in a thermodenuder. The thermally denuded particle size distribution is more consistent with that of the restructured lightly coated particles. The thermodenuder itself has a negligible effect on the uncoated particles, as shown by the singly charged mode in Fig. 7; the multiply charged modes are more variable in general than the singly charged mode. The amount of coating the particle originally had seems to increase the amount

the particle collapses, as indicated by the mean mobility diameters given in Table 3. These results are quantitatively consistent with the results of Ghazi and Olfert [60] who demonstrated a similar decrease in mobility diameter of up to ~17% with a mass coating ratio change from 1 (uncoated) to 5 (moderately heavy coating) for particles coated with oleic acid and then denuded. They also observed a saturation of the effect at higher mass coating ratios, which is consistent with our results. These results further support previous work that has shown that restructured soot aggregates coated with oxygenated hydrocarbons or sulfuric acid do not regain their original morphology when the coating is removed with a thermodenuder [53, 55, 56, 63, 64]. The mobility-fractal dimensions inferred from the mobility-size and mass measurements D_{fm} (see Table 3) reproduce the trends observed in the values derived from the TEM images D_f (see Table 3); fractal dimension increases from 2.16 to 2.34 with increasing coating prior to denuding for light and moderate coatings but is independent of original coating for heavier coatings.

Figure 7. Mobility Size and Mass Distributions of Coated and Thermally Denuded Particles. The uncoated particles were size selected with a DMA set to 150 nm. Particles that were not coated were also size selected. (a) The size distribution of the uncoated particles is compared with those of particles that have been coated with oleic acid and then denuded in a thermodenuder. The units on the y-axis are normalized values of number of particles per unit volume in each mobility size bin ($dW/d\log D_m$). (b) The mass distributions of the coated and denuded particles are compared with the mass distribution for the uncoated particles. The units on the y-axis are normalized values of number of particles per unit volume in each mass bin ($dW/d\log M$). Curves are scaled to the top of each graph and identified in the legend.

The mass distributions shown in Fig. 7b and summarized in Table 3 indicate that the denuded particles are slightly heavier than the uncoated particles by 0.05 ± 0.03 fg on average. These results suggest that the denuder as operated in this study may leave a small amount of residual coating on the particles.

4.3. Effects of Laser Heating on Particle Morphology

In contrast to the irreversible restructuring observed when the thermodenuder is used to remove coatings, restructured lightly, moderately, and heavily coated soot returns to a less compact morphology similar to that of uncoated soot when heated with a laser at relatively low fluence. TEM images of individual particles are shown of lightly coated soot in Fig. 8a, moderately coated soot in Fig. 8c, and heavily coated soot in Fig. 8e.

Figure 8. TEM Images of Laser-Heated Particles. The scale is indicated in each figure. The TEM images were recorded at a magnification of 250,000. The particles were (a) lightly coated with oleic acid and then laser heated at a fluence of 0.17 J/cm^2 , (b) lightly coated, denuded, and then laser heated at a fluence of 0.15 J/cm^2 , (c) moderately coated with oleic acid and then laser heated at a fluence of 0.20 J/cm^2 , (d) moderately coated, denuded, and then laser heated at a fluence of 0.15 J/cm^2 , (e) heavily coated with oleic acid and then laser heated at a fluence of 0.20 J/cm^2 , and (f) heavily coated, denuded, and then laser heated at a fluence of 0.15 J/cm^2 . In all cases, the particles were size selected (DMA set to 150 nm) prior to coating, and the laser fluence was selected to heat the particles to $\sim 3000 \text{ K}$.

Laser heating has no effect on the size distribution and fractal dimension of uncoated particles at these low fluences, as demonstrated in Fig. 9a. This observation is consistent with previous results, which demonstrated that uncoated soot does not fragment into primary particles at any fluence and that the particles reach the sublimation temperature without fragmenting [43]. Figure 9a also shows that the effects of laser heating are negligible for very lightly coated particles, and Table 4 shows negligible effects on the fractal dimension by laser heating.

Figure 9. Mobility-Diameter Size Distributions of Laser-Heated Coated Particles. The uncoated particles were size selected with a DMA set to 150 nm. Particles that were not coated were also size selected. Size distributions are shown for (a) uncoated particles, laser-heated uncoated particles, very lightly coated particles, and laser-heated very lightly coated particles, (b) lightly coated particles, laser-heated lightly coated particles, and lightly coated particles heated with the laser and then sent through a denuder, and (c) moderately coated particles, laser-heated moderately coated particles, and moderately coated particles heated with the laser and then sent through a denuder. The units on the y-axis are normalized values of number of particles per unit volume in each mass bin ($dW/d\log D_m$). Curves are scaled to the top of each graph and identified in the legend.

The particle morphology observed in the TEM images for laser-heated lightly coated particles (8a) is manifested in the size distributions shown in Fig. 9b as an increase in the mean mobility size. Figure 9b also shows a broadening of the size distribution of the laser-heated particles to smaller particle sizes. One possible explanation is that oleic acid vaporized from the laser-heated particles re-condenses to form new particles. However, sending the particles through the thermodenuder to remove oleic acid after laser heating returns the same size distribution (shown in Fig. 9b), which demonstrates that these new particles in the size range of ~20-100 nm are not oleic acid. These particles appear to be fragments of the core soot particles. Laser heating more heavily coated particles increases the degree of soot-particle fragmentation, as demonstrated for moderately coated particles in Fig. 9c. The aggregate fragments do not decrease in size, but more of them are generated from the moderately coated particles. In addition, enough coating is vaporized during the laser heating of the moderately coated particles that significant numbers of

oleic acid particles (mobility diameters <50 nm) are also formed. These particles are removed when the sample is passed through a thermodenuder after laser heating, as shown in Fig. 9c.

One explanation for these results is that rapid heating of the particle and vaporization of the coating forcefully opens the particle, breaking off limbs of the soot aggregates in the process. The process may require a minimum amount of coating to build sufficient internal pressure within the aggregate to change its morphology, which may explain why very lightly coated particles (indistinguishable from uncoated by mass) do not undergo such morphology changes when laser heated. This mechanism would also explain why more fragmentation is observed for the moderately coated particles than for the lightly coated particles.

Figure 9c also demonstrates that, when the moderately coated laser-heated particles are sent through the thermodenuder, a peak appears between 110 and 140 nm, whereas particles disappear between 145 and 200 nm. This behavior suggests that the coating is not fully vaporized by the laser under these conditions and that some of the soot particles are still contained in a mantle of oleic acid or large oleic acid droplets. When the remaining oleic acid is removed in the thermodenuder, the measured particle sizes shrink to the size distribution of the core soot particles. This effect is more pronounced for heavily coated particles, which is consistent with recent results based on laser-induced incandescence studies [75].

When the particles are heavily coated, laser heating does not fully vaporize the coating. Figure 10 demonstrates that the size distributions for heavily, very heavily, and extremely heavily coated particles do not change substantially when laser heated. Some aggregate fragment formation is observable in the small size range (20-100 nm), but less fragmentation is obvious with increasing coating thickness. A majority of the oleic acid droplets are left after these heavily coated particles are laser heated. Figure 10 shows that, when the heavily to extremely heavily coated particles are thermally denuded after laser heating, the large droplets disappear, leaving particles with smaller size distributions, i.e., size distributions for the non-volatile core particles. These results suggest that the particles undergo rapid heating, coating vaporization, and fragmentation, but that this heating is not sufficient to vaporize the oleic acid droplet containing the core particle. Although some aggregate fragments escape from the particles, most of the soot particles remain surrounded by a mantle of oleic acid after laser heating.

Table 4. Summary of Results for Particles that were Denuded and Then Laser Heated^a

Coating before denuding	Median D_m (nm)	Median M (fg)	D_f	D_{fm}	C_m (nm fg ^{-βD_{fm}})
Uncoated	154	0.629		1.82	191
Very light			2.17		
Light	119	0.648	2.33	2.47	139
Moderate	117	0.628	2.39	2.27	141
Heavy	117	0.602	2.35	2.56	140
Very heavy			2.37		

^aThe standard deviation is estimated to be 7.5% for median particle mass [103], ≤3% for median mobility diameter, and ≤7% for mean fractal dimension with ≥ 16 particles analyzed for each coating.

If the particle coating is removed in the thermodenuder prior to laser heating, the aggregate does not return to a less compact morphology, and there is no evidence of aggregate fragmentation. A higher-resolution example of a heavily coated, thermally-denuded, and laser-heated particle is shown in Fig. 8f. The image shows a collapsed aggregate that is as compact as the heavily coated and denuded particle shown in Fig. 5f. Similar examples are shown in Fig. 8b for a light coating and in Fig. 8d for a moderate coating. All of these particles are significantly more compact than the uncoated particles or the vast majority of the particles that were laser heated prior to the thermodenuder. The fractal dimensions derived for these particles (given in Table 4) are consistent with those of the coated particles (given in Table 2) and the coated, denuded particles (given in Table 3).

Figure 10. Mobility-Diameter Size Distributions of Laser-Heated Coated Particles. The uncoated particles were size selected with a DMA set to 150 nm. Size distributions are shown for (a) heavily coated particles, laser-heated heavily coated particles, and heavily coated particles heated with the laser and then sent through a denuder (b) very heavily coated particles, laser-heated very heavily coated particles, and very heavily coated particles heated with the laser and then sent through a denuder, and (c) extremely heavily coated particles, laser-heated extremely heavily coated particles, and extremely heavily coated particles heated with the laser and then sent through a denuder. The units on the y-axis are normalized values of number of particles per unit volume in each mass bin ($dW/d\log D_m$). The curves representing particles that have not been laser heated are scaled to the top of the graph, and the other curves are scaled to the non-laser heated curves.

4.4. Effects of Coatings on the LII Signal

Coating the particles with oleic acid has a significant effect on the magnitude of the LII signal at low and moderate laser fluences ($< \sim 0.4 \text{ J/cm}^2$). Figure 11 shows the laser-fluence dependence of the peak of the LII temporal profiles at low to moderate particle coating thicknesses (Fig. 11a) and at moderate to high coating thicknesses (Fig. 11b). At any fluence below 0.4 J/cm^2 the LII signal for the uncoated particles is significantly higher than that associated with the coated particles. The difference between the signals from coated and uncoated particles depends on laser fluence and coating thickness. These differences are qualitatively consistent with the predictions of Witze et al. [21] and are at least partially attributable to the increase in the energy needed to vaporize the volatile coating. The laser energy required to heat the core particle to a particular temperature requires the additional energy needed to vaporize the coating, which increases with the amount of coating, and the peak-LII excitation curves are thus shifted to higher laser fluence, with increasing coating thickness. Figure 11a shows that, as the coating increases from low to moderate coating thicknesses, the amount of additional energy needed to desorb the coating also increases. Table 1 gives the coating mass and coating mass fraction for selected condenser temperatures [51].

Figure 11. Fluence Dependence of the Peak LII Signal. The normalized peak of the LII temporal profile is plotted relative to laser fluence on a log scale for (a) low to moderate coating thickness and (b) high coating thickness, as indicated in the legend. The coating masses and mass fractions corresponding the condenser temperatures shown in the legend are given in Table 1. All curves corresponding to the denuded particles are indicated by dotted lines.

At some moderate coating thickness (condenser temperature of $\sim 85^\circ\text{C}$) the peak-LII excitation curves stop shifting to higher fluences. Figure 11b shows that at higher coating thicknesses the curves start shifting to lower fluence. These effects are summarized in Fig. 12, which shows the difference between the fluence needed to heat the coated particles and the fluence needed to heat

the uncoated particles for different amounts of coating as a function of normalized peak-LII signal, i.e., the y-axis on Fig. 11. The shift increases for condenser temperatures up to 85°C and decreases for condenser temperatures above 90°C. The denuded peaks tend to have a negative shift.

Figure 12. Fluence Shift of the Peak-LII Excitation Curves. This shift represents the increase in fluence required to heat coated particles to a comparable temperature as uncoated particles and is plotted relative to the normalized peak LII signal. For measurements with the same normalized LII signal (x-axis), the fluence difference between coated and uncoated particles is plotted for particles of various coating thicknesses (see legend and Table 1 for coating masses corresponding to the condenser temperatures shown in the legend). The y-axis is the shift in fluence between the coated and uncoated curves in Fig. 11.

These effects can be analyzed with respect to the particle temperature, which is directly related to the LII signal. Figure 13a shows the laser-fluence dependence of the peak of the LII temporal profiles on a linear scale and the temperatures inferred from these data using Eq. (8). The maximum particle temperature increases approximately linearly with fluence at low and intermediate fluences, as suggested by Eq. (13) and shown in Fig. 13b. The peak LII signal increases nonlinearly with temperature, and hence laser fluence, at these fluences, as indicated by Eqs. (1) and (5). The maximum temperature and peak-LII signal are predominantly determined by the initial particle temperature, the amount of energy absorbed by the particle during the laser pulse, the amount of energy needed to desorb the volatile coating, the amount of energy lost by heat conduction to the surrounding atmosphere, and the amount of energy lost to core-particle sublimation. Equation (13) neglects the latter two effects but demonstrates the influence of these other factors. The deviations from a linear dependence on fluence at high fluences demonstrate the effect of core-particle sublimation. At low to moderate fluences sublimation has little effect on the peak temperature.

At high laser fluences the maximum temperature and peak-LII signal approach a plateau. This plateau region is associated with the fluence range in which the particle has sufficient energy to reach the sublimation temperature of the core particle. Because the sublimation temperature of the core particle should be independent of the coating, we assume that the particles all reach the sublimation temperature at high fluences.

Figure 13. Fluence Dependence of the Peak LII Signal and Maximum Particle Temperature. (a) The normalized peak of the LII temporal profile is plotted relative to laser fluence on a linear scale for low to moderate coating thickness, as indicated in the legend. (b) This panel shows the maximum particle temperatures corresponding to the data in the top panel. Temperatures were calculated using Eq. (4). The coating masses and mass fractions corresponding to the condenser temperatures shown in the legend are given in Table 1. All curves corresponding to the denuded particles are indicated by dotted lines.

Equation (13) shows that, at any particular laser fluence below the plateau region, $T_{\max}$ decreases with increasing M_{coat} . It follows that the LII signal decreases with increasing coating thickness, which is shown in Fig. 11a and Fig. 13a for coating thicknesses up to ~75% by mass (~condenser temperature of 85°C). If there is an enhancement in the absorption cross section σ_{abs} with the particle coating, however, an increase in the first term on the right-hand side of Eq. (13) could compensate for an increase in the second term, and $T_{\max}$ could increase with coating thickness, leading to an increase in peak-LII signal with increasing coating thickness and a shift of the excitation curve to lower fluences. Equation (15) suggests that plotting the fluence for coated particles as a function of the fluence at which the uncoated particles reach the same LII signal level will allow us to separate these effects. Figure 14 shows a series of plots of matching fluences and linear fits to the data, and Table 5 summarizes the results. The data were fit in the range of uncoated fluences of 0.126-0.212 J/cm², which corresponds to normalized peak LII signals between 0.05 and 0.4.

The slopes derived for coated (not denuded) particles are ≥ 1 for all coating thicknesses (Table 5), suggesting that the absorption cross section is not enhanced by the coatings but may instead be reduced by the coatings. In our experiments, however, the slope is defined by fluences at which particles reach temperatures (>2000 K) well above the boiling point of oleic acid (658.5 K) (Fig. 13b). Under these conditions coatings may be mostly evaporated in the early part of the laser pulse and thus may not have a significant contribution to the pulse-averaged absorption cross section.

Table 5. Summary of Fits Using Eq. (15) to Data in Fig. 14

Coating	Slope	Slope uncertainty*	Intercept	Intercept uncertainty*
Very light	1.00	0.01	-0.0033	0.0015
Light	1.03	0.06	0.0089	0.0107
Moderately light	1.08	0.03	0.0224	0.0063
Moderate	1.06	0.05	0.0451	0.0087
Moderately heavy	1.06	0.05	0.0503	0.0087
Heavy	1.10	0.02	0.0391	0.0043
Very heavy	1.27	0.07	-0.0084	0.0125
Extremely heavy	1.26	0.06	-0.0210	0.0099
Very light denuded	0.965	0.010	-0.0012	0.0018
Light denuded	0.984	0.028	-0.0078	0.0050
Moderate denuded	0.959	0.006	-0.0006	0.0011
Heavy denuded	0.940	0.018	0.0079	0.0033
Very heavy denuded	0.993	0.004	0.0015	0.0007
Extremely heavy denuded	0.829	0.018	0.0021	0.0032

*Standard deviation of one σ .

We can estimate the amount of coating evaporated by combining the intercept with the slope from the fits in Fig. 14 using Eq. (18). Figure 15 shows a plot of the evaporated coating mass inferred from Eq. (18) as a function of the coating mass on the particles derived from the CPMA measurements published recently [51]. At the lower coating thicknesses ($\leq 65\%$ by mass), the mass evaporated is equal to the measured coating mass, suggesting that all of the coating on the particle is evaporated from the particle during laser heating.

Figure 14. Correlations of Coated and Uncoated Fluences at the Same Peak LII Signal. The symbols represent data, and the lines represent fits of Eq. (15) to the data for peak LII signal levels between 0.05 and 0.4, which corresponds to uncoated fluences of 0.126-0.212 J/cm². The results of the fits are summarized in Table 5.

At high coating thicknesses (>65% by mass), on the other hand, the analysis shown in Fig. 15 suggests that the evaporated mass is significantly less than the coating mass, i.e., the laser does not evaporate all of the coating. These results are consistent with conclusions drawn from mobility size distributions of laser-heated coated particles discussed in Section 4.4 [51].

Figure 15. Mass vaporized by the laser plotted as a function of measured mass of the coating. The evaporated masses M_{vap} were derived from the fits shown in Fig. 14 using Eq. (18), and the coating masses M_{coat} were measured using a CPMA. Error bars for M_{coat} represent 1σ uncertainties of the masses of the coated particles and uncoated core particles. Error bars for M_{vap} are estimated uncertainties associated with the density of polycrystalline graphite and $E(m)$ for uncoated particles. The 1:1 line represents perfect agreement between M_{vap} and M_{coat} .

Figure 16 compares temporal profiles for fluences at which uncoated and coated particles reached the same peak temperature and LII signal, i.e., the same y-value on Fig. 11. All curves are scaled to the top of the graph in each panel. Such plots provide information about the conductive-cooling rates and evaporative-mass-loss rates of the laser-heated particles. At each fluence range the decay curves for the coated and uncoated particles are generally independent of coating. This result indicates that, once the particle coating has been vaporized by the laser, the conductive-cooling rate is independent of whether the particle had been coated. Laser vaporization of the coating returns the particles to its original morphology, as shown in Figs. 8a, 8c, and 8e.

Figure 16. LII Temporal Profiles for Coated and Uncoated Particles. Temporal profiles in each panel were recorded at fluences that gave the same LII peak signal. Profiles were recorded for particles that were uncoated and coated at a condenser temperature of 60°C (coating was 20% by mass) or 95°C (coating was 92% by mass). The fluences used were (a) 0.15 J/cm² for the uncoated particles, 0.18 J/cm² for the 60°C coating, and 0.21 J/cm² for the 95°C coating, (b) 0.25 J/cm² for the uncoated particles, 0.28 J/cm² for the 60°C coating, and 0.31 J/cm² for the 95°C coating, and (c) 0.31 J/cm² for the uncoated particles, 0.34 J/cm² for the 60°C coating, and 0.37 J/cm² for the 95°C coating.

4.6. Effects of Morphology on the LII Signal

In contrast to the effects of coatings on the LII peak signal, Figs. 11 and 13a show that the denuded particles require no additional laser energy to reach the same LII signals as the uncoated particles, and the fluence curves are slightly shifted to lower laser fluences than the uncoated particles, i.e., the difference for denuded particles in Fig. 12 is negative. This shift suggests either an enhancement in the absorption cross section for the denuded particles, thereby requiring a lower laser fluence to heat the particles, or a reduction in the cooling rate for these particles, perhaps as a result of a reduction in the conductive cooling rate. The latter explanation is the likely reason. Coating and denuding the particles leads to an irreversible restructuring of the particle that may cause the conductive cooling rate to be significantly reduced [51]. Figure 4 shows a TEM image of an uncoated particle, which has a typical fractal dimension of 1.8. Figure 8b, 8d, and 8f show coated and denuded particles that have been laser heated, demonstrating that these particles stay restructured when laser heated if they have been thermally denuded first. This

collapsed morphology reduces the available surface area for gas-particle collisions, and thus reduces the conductive-cooling rate.

Previous experimental investigations on the relationship between aggregate size and heat transfer have suggested that aggregate size and morphology have an effect on the conductive cooling rate and LII signal decay rate [78, 110, 111]. Reduced conductive cooling is associated with larger particle aggregates because of a shielding effect and effective reduction in surface area. Because of this shielding effect, the fractal dimension also influences the conductive-cooling rate. More compact aggregates have a smaller effective surface area. Our results [112] have shown that the LII signal decay rate can be substantially reduced for aggregates with larger fractal dimensions. Coating and denuding the particles causes the aggregates to become more compact, increasing the fractal dimension from an average of 1.88 for the uncoated particles (Fig. 4) to 2.3-2.4 for the coated particles (Fig. 5f). Figure 17 shows a comparison of LII temporal profiles for uncoated, i.e., Fig. 4, and processed (compact), i.e., Fig. 5f, particles and demonstrates the change in signal decay rate caused by the aggregate-morphology change. The compact particles have a much lower conductive-cooling and signal-decay rate.

Figure 17. LII Temporal Profiles for Aggregates with Different Morphologies. Temporal profiles are shown for aggregates with the same mean number of primary particles and different aggregate morphologies. Particles were heated to the same peak temperature with a laser fluence of 0.15 J/cm^2 at 1064 nm. Profiles were recorded for particles with an average fractal dimension of 1.88, corresponding to the image in Fig. 4, and an average fractal dimension of 2.33, corresponding to the image in Fig. 5f. Modified from [112].

5. CONCLUSIONS

We have used a wide range of techniques to demonstrate that soot is restructured (and the fractal dimension increases from 1.88 to ~ 2.34) when coated with oleic acid and that the restructuring increases with the amount of coating. These results support those from previous studies of coating-induced restructuring of soot [21, 48, 52-64] and also demonstrate that significant restructuring can occur with an extremely small amount of coating. We have also confirmed previous studies that have shown that removing the coatings in a thermodenuder does not return the particle to its original morphology [53, 55, 56, 63, 64] and that the degree of irreversible restructuring increases with increasing coating thickness [60]. In addition, we have shown that removing light (20% by mass) and moderate (65% by mass) coatings by laser heating to ~ 3000 K allows the particle to return to a significantly less compact morphology and leads to some fragmentation of the refractory soot aggregate as the coating forcefully leaves the particle. Laser heating particles with very light coatings causes neither morphology changes nor aggregate fragmentation. Laser heating heavily coated particles does not lead to full vaporization of the oleic acid mantle and causes some soot fragmentation and ejection of aggregate fragments from the oleic acid droplet. Most of the laser-heated soot particles, however, appear to stay associated with the remaining oleic acid droplet when the particle is heavily coated, despite being heated to ~ 3000 K; these particles do not collapse back to the restructured morphology after laser heating. We have further shown that, if the coating is originally removed in a thermodenuder, laser heating leads to neither a less compact morphology nor fragmentation.

These results are relevant to applications of optical diagnostics to measurements of inhomogeneous carbonaceous particles, e.g., in combustion systems or the atmosphere. Non-absorptive coatings are well known to change the optical properties of soot particles and have a strong effect on absorption and scattering cross sections [21, 50, 54-56, 59, 62, 63, 69], but the impact of aggregate morphology and restructuring on the optical properties of soot aggregates is not as well understood. Volatile coatings can also have an impact on the radiative emission from laser-heated soot and graphite particles [21, 50, 71, 75].

The magnitude of the LII signal is very sensitive to coating thickness at fluences below 0.4 J/cm^2 . Signals decrease with increasing coating thickness up to a thickness of $\sim 75\%$ by mass. This effect is attributable to the additional energy needed to vaporize the coating in addition to heating the particle to incandescence temperatures. At higher coating thickness signals increase with increasing coating thickness. This behavior does not appear to be attributable to an increase in the absorption cross section with coating thickness at high coating thicknesses. At these coating thicknesses, the coating is not fully vaporized. Although some small fragments are ejected from the mantle of unvaporized oleic acid, a majority of the particles are contained within the remaining oleic-acid droplet after laser heating. Denuded particles have slightly higher signals at these fluences; this behavior is likely attributable to the reduced conductive-cooling rate because of the irreversible restructuring of the particle in the thermodenuder.

The delay in the onset of the LII signal appears to depend on a range of factors, including coating thickness, coating-induced particle morphology changes, and optical-property changes caused by coating and heating in a thermodenuder. We also expect that other physical characteristics of the coatings, such as the enthalpy of vaporization and density, will influence this signal delay. In

addition, the signal-decay rates appear to be very sensitive to the irreversible restructuring of particles processed in a thermodenuder. The resulting morphology change reduces the exposed surface area, conductive-cooling rate, and LII signal decay rates substantially. Particles that have been coated and not thermally denuded prior to laser heating return to a less compact morphology during the laser pulse and have very similar LII decay rates to uncoated particles.

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