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Effects of aggregate morphology and size on laser-induced incandescence and scattering from black carbon (mature soot)

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ABSTRACT

We have used a Single-Particle Soot Photometer (SP2) to measure time-resolved laser-induced incandescence (LII) and laser scatter from combustion-generated mature soot with a fractal dimension of 1.88 extracted from a burner. We have also made measurements on restructured mature-soot particles with a fractal dimension of 2.3–2.4. We reproduced the LII and laser-scatter temporal profiles with an energy- and mass-balance model, which accounted for heating of particles passed through a CW-laser beam over laser–particle interaction times of $\sim$10 μs. The results demonstrate a strong influence of aggregate size and morphology on LII and scattering signals. Conductive cooling competes with absorptive heating on these time scales; the effects are reduced with increasing aggregate size and fractal dimension. These effects can lead to a significant delay in the onset of the LII signal and may explain an apparent low bias in the SP2 measurements for small particle sizes, particularly for fresh, mature soot. The results also reveal significant perturbations to the measured scattering signal from LII interference and suggest rapid expansion of the aggregates during sublimation.

1. Introduction

Mature-soot particles absorb strongly over broad regions of the solar spectrum, and recent climate assessments indicate that these particles contribute significantly to global warming and climate change (Bond et al., 2013; IPCC, 2013). In addition, numerous studies have indicated that these particles can have adverse effects on cardiopulmonary health (Anenberg et al., 2012; Janssen et al., 2011; Pope & Dockery, 2006). Hydrocarbon combustion is the dominant source of atmospheric-soot emissions, and reducing the impact of combustion-generated particles on global climate and human health through emissions reductions will require a much better understanding of soot formation and oxidation mechanisms over a wide range of combustion conditions. Development of such an improved description of soot chemistry will depend on enhanced diagnostics to measure and characterize soot particles in the combustor and exhaust stream. In addition, improving the accuracy of predictions of the impact of soot emissions reductions requires narrowing the uncertainties of the abundance, distribution, and physical characteristics of these particles in the atmosphere, which also relies on improvements in soot measurement techniques.

Mature soot is composed of primary particles 10–50 nm in diameter with fine structure similar to polycrystalline graphite and low hydrogen-to-carbon ratios (Chen & Dobbins, 2000; Köylü & Faeth, 1992; Lahaye & Prado, 1981).

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These primary particles are covalently bound into aggregates of varying size ranging from tens to hundreds of nanometers. Mature-soot aggregates have branched-chain structures that are typically characterized by fractal dimensions in the range of 1.7–1.9, e.g., (Charalampopoulos & Chang, 1991; Oh & Sorensen, 1997; Sorensen, 2001). Atmospheric scientists refer to mature soot as "black carbon" because it absorbs strongly over a broad spectral range covering ultraviolet, visible, and infrared wavelengths (Bond et al., 2013; Lack, Moosmüller, McMeeking, Chakrabarty, & Baumgardner, 2014; Petzold et al., 2013). Mature soot is also a refractory material with a sublimation point above 4000 K, and it is insoluble in polar and non-polar solvents, further meeting the criteria established for designation as "black carbon". Less mature soot particles have higher hydrogen-to-carbon ratios, less graphitic fine structure (i.e., less sp^2 hybridization), and absorption cross sections shifted to shorter wavelengths, which may make them appear brown rather than black (Bond & Bergstrom, 2006; Dalzell & Sarofim, 1969; Habib & Vervisch, 1988; Hopkins et al., 2007; López-Yglesias, Schrader, & Michelsen, 2014; Minutolo, Gambi, & D'Alessio, 1996; Siddall & McGrath, 1963).

Laser-induced incandescence (LII) is a diagnostic technique that has been used extensively to measure soot-particle abundances and physical properties under a wide range of conditions, e.g., in engines, flames, exhaust streams, and the ambient atmosphere (see Michelsen, Schulz, Smallwood, & Will, accepted for publication; Schulz, Kock, Hofmann, Michelsen, & Will, 2006 and references therein). The implementation of LII exploits the refractory nature of soot and involves heating soot particles in an intense laser field to temperatures that may be as high as 4450 K (Goulay, Schrader, López-Yglesias, & Michelsen, 2013) and measuring the resulting incandescence from the hot particles. The signal magnitude is related to the particle-volume fraction or mass (see Michelsen et al., accepted for publication; Schulz et al., 2006 and references therein).

While laser absorption is responsible for heating the particle, conductive heat transfer is the dominant cooling mechanism under non-vacuum conditions when sublimation can be ignored, i.e., when the particle is below the sublimation temperature (Michelsen, Liu et al., 2007). For pulsed LII using lasers with pulse durations of 5–10 ns, the signal-decay rate after the laser pulse is related to the conductive-cooling rate when the particles are heated with a laser fluence that is insufficient to heat the particles to the sublimation temperature. Because the conductive-cooling rate depends on the surface-area-to-volume ratio, the signal-decay rate can be used to infer primary-particle sizes (Michelsen et al., accepted for publication; Schulz et al., 2006). Inferring primary-particle sizes from pulsed-LII signal-decay rates requires a model that accounts for a wide range of factors that influence the particle-cooling rate, including particle maturity (Bladh, Johnsson, & Bengtsson, 2009; López-Yglesias et al., 2014) and aggregation effects involving primary-particle polydispersity (Bladh, Johnsson, & Bengtsson, 2008; Johnsson, Bladh, & Bengtsson, 2010; Liu, Daun, Snelling, & Smallwood, 2006; Liu & Smallwood, 2010; Liu, Yang, Hill, Snelling, & Smallwood, 2006), bridging between primary particles (Johnson, Hilton, Waterman, & Black, 2003), aggregate size (Bladh et al., 2008; Bladh et al., 2011; Filippov, Zurita, & Rosner, 2000; Johnsson, Bladh, Olofsson, & Bengtsson, 2013; Kuhlmann, Reimann, & Will, 2006; Liu, Smallwood, & Snelling, 2005; Liu, Yang et al., 2006), and aggregate morphology (Bambha, Dansson, Schrader, & Michelsen, 2013b).

The particle maturity influences the thermal-accommodation coefficient (Bladh et al., 2009; López-Yglesias et al., 2014), i.e., the average energy-exchange rate during collisions of the bath gas with the particle surface. Aggregation effects, on the other hand, modify the average particle-surface area available to interact directly with the bath gas. Shielding of some primary particles within an aggregate by other primary particles is predicted to cause large aggregates to have lower effective surface areas per primary particle than smaller aggregates (Bladh et al., 2008; Bladh, Johnsson, Rissler et al., 2011; Daun, 2010; Filippov et al., 2000; Johnsson et al., 2013; Kuhlmann et al., 2006; Liu et al., 2005; Liu, Yang et al., 2006; Snelling, Liu, Smallwood, & Gülder 2004). Experiments by Kuhlmann et al. (2006) to confirm these effects demonstrated only small changes to the decay rate with increasing aggregate size. Experimental confirmation of these effects performed by Bladh, Johnsson, Rissler et al. (2011), in contrast, demonstrated more significant changes to the decay rate than anticipated or explained by aggregate size. Bladh, Johnsson, Rissler et al. (2011) suggested that additional effects could be related to aggregate morphology. Bambha et al. (2013b) experimentally demonstrated significant reductions in pulsed-LII signal-decay rates with an increase in fractal dimension. The behavior can be explained by lower conductive-cooling rates caused by an increase in primary-particle shielding and a decrease in effective-surface area for the restructured (i.e., collapsed) particle.

Particle aggregation may also affect light absorption cross sections, absorptive-heating rates, and radiative-emission rates, and hence, LII signals. Rayleigh–Debye–Gans (RDG) theory suggests that, to a first approximation, the absorption cross section scales linearly with the number of primary particles and is independent of morphology (Sorensen, 2001). Studies using more accurate methods for calculating absorption by non-spherical particles indicate that aggregates with a more compact morphology should have a smaller absorption cross section than loose, dendritic particles when the fractal dimension is below ~2 because of increased shielding of the primary particles (Liou, Takano, & Yang, 2011; Mackowski, 1995; Sorensen, 2001). At fractal dimensions above 2 the absorption cross section is predicted to increase with fractal dimension (Liu, Mishchenko, & Arnott, 2008). Studies have also shown that, for small particle sizes at mid to near infrared wavelengths, the absorption cross section should be enhanced above the RDG approximation and that this enhancement increases as the aggregate size increases (Liu & Smallwood, 2010, 2011; Mackowski, 2006; Yon et al., 2014; Yon, Therssen, Liu, Bejaoui, & Hebert, 2015). At larger particle sizes (> ~100 primary particles), the absorption cross section is predicted to scale linearly with number of primary particles at these wavelengths (Mackowski, 2006; Yon et al., 2014, 2015). At shorter wavelengths, however, the absorption cross section is predicted to decrease, relative to the RDG approximation, with increasing particle size (Liu & Smallwood, 2010, 2011; Yon et al., 2014, 2015). The LII signal is related to the light absorption