MEASUREMENT OF ABSORPTION AMPLIFICATION OF COATED PARTICLES USING PHOTOTHERMAL INTERFEROMETRY

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Introduction

Growth of a transparent coating on top of an absorbing core can result in an increase in the measured mass absorption cross-section for the core. In the case of soot, quantification of the coating-induced amplification is difficult because two processes brought about by the coating process itself have opposite effects on light absorption by the particle: (i) collapse of the fractal aggregate resulting in absorption decrease and (ii) the growth of the coating causing absorption increase. In order to help elucidate and to quantify these effects, we have initiated experiments using a model system that enables us to separately study the coating effect on absorption without the complication of aggregate restructuring. For the model system, we have elected to use black-dyed PSL (BPSL) particles as a proxy for collapsed soot over which transparent material is condensed. By utilizing these commercially available BPSL particles, experiments have been carried out where the change in the absorption coefficient is measured as a function of coating thickness using photothermal interferometry (PTI).

Material and Methods

In this investigation, the technique of photothermal interferometry was used to measure the effects of transparent coatings on absorbing particles[1-4]. Photothermal interferometry, as its name implies, combines photothermal spectroscopy with the technique of interferometry to measure the heat dissipated by the particle following light absorption. The degree of absorption by the particle is measured by monitoring the shift in the interference pattern brought about when the *optical* pathlength of the probe arm is altered due to the change in the refractive index of air surrounding during the energy transfer. PTI directly measures aerosol absorption and does not suffer interferences from aerosol scattering.

For the present study, commercially available BPSL particles (Duke Scientific, Polysciences Inc.) with diameters ranging from nominally 100 - 400 nms were used. The monodispersed distribution of particles is generated using an atomizer (TSI, model number 3076) followed by diffusion drying, before being directed into one end of a coating chamber. Nitrogen entrained with dibutyl phthalate (DBP) is then brought into the middle of the chamber by bubbling nitrogen in DBP at a nominal flow rate of 0.5 liter per min (lpm). The DBP-Coated BPSL is sized selected using a differential mobility analyzer (TSI long column DMA, model 3081) and number densities estimated with a condensation particle counter (CPC, TSI model 3025A).

A typical experiment involves injecting the coated BPSL particles into the PTI unit and recording the PTI signal as a function of particle number density. From the slope of the data the absorption cross-section (cm^2/particle) for that given particle diameter can be readily measured. This procedure is then carried out for a series of core+shell diameters (Dp).

Results and Discussion

Shown in Figure 1 are absorption amplification values measured for various DBP coating thicknesses condensed on top of a 233 nm BPSL particle. Here absorption amplification is defined as the ratio of the absorption cross-section for a coated particle to the cross-section for the uncoated particle. As

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can be readily seen, coating BPSL particle results in a significant enhancement of the absorption cross-section. Even at the thinnest coating studied (13.5 nm), a 28% increase in BPSL absorption is observed. It is interesting to note that while a direct comparison with studies that examined coated soot is not possible (or appropriate), similar levels of enhancement has been observed for organic coated soot[5,6]. However, equally interesting to note is that in contrast to these levels of enhancement, Davidovits and coworkers[7] recently reported no observable increase in particle light absorption with 10 nm of oleic acid condensed onto flame-generated soot. This disagreement is puzzling given that oleic acid has a refractive index nearly identical to α-pinene (1.458 vs. 1.466)[8] and that both studies coated similarly sized soot particles with similar thicknesses.

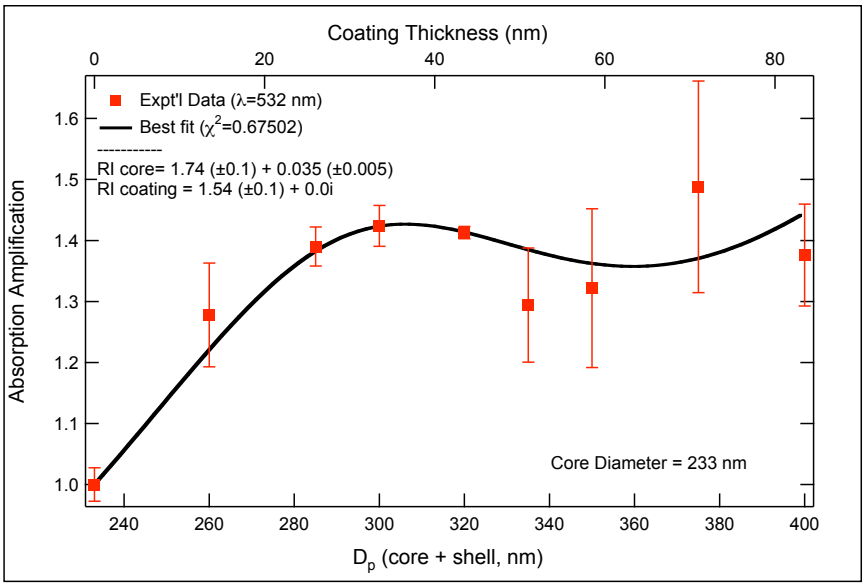

Figure 1.

The solid line in Figure 1 is a best-fit line generated using Mie theory for a concentric core-shell sphere[9,10] where the adjustable parameter is the refractive index (RI) of the absorbing core and the RI for the coating material. Another advantage of using the inherently spherical BPSL particles is that Mie theory can be used rigorously. The curve fitting routine utilized chi-square minimization where the core RI was first adjusted until a minimal value for the reduced χ^2 was found and then the DBP RI was adjusted. This process was repeated until the change in χ^2 dropped below 0.0001. The real and imaginary parts of the RI obtained for the 233 nm BPSL using this fitting procedure was found to be 1.74 (±0.1) - 0.035i (±0.005i) and for DBP the RI is estimated to be 1.54(±0.1) – 0.0i. In the case of DBP, this value is about 3% larger than that commonly cited (1.49+0i).

An independent verification of the absorption index estimated via Mie theory-based curve fitting routine described above can be conducted by measuring the visible transmission of a known concentration of a BPLS-water solution with a commercial spectrometer (Perkin-Elmer model 320 UV/VIS). From this bulk measurement, the mass absorption cross-section for 233 nm BPSL was found to be 2.27 m^2/g. The absorption index can now be readily calculated via Eqn. 1[10], which relates the absorption index to mass absorption cross-section, B_{abs} (m^2/g), the BPSL density, ρ (1.05×10^6 g/m^3), and the wavelength, λ (532 nm)

$$\mathrm{Im}\{RI\} = \frac{B_{abs}\rho\lambda}{4\pi}. \quad (1)$$

Using this expression, the absorption index is calculated to be 0.038 (±0.001) a value in very good agreement with that estimated by curve fitting the coated BPSL data to the concentric core-shell model[9,10]. Table I summarizes the measured optical properties of the two BPSL cores studied thus far (233 nm and 385 nm).

Table I: Optical properties of Uncoated Black-dyed PSL Particles

Particle Diameter (nm)	385	233
Absorption cross-section (cm^2)	7.7(±0.8) x10^{-10}	6.4(±0.6) x10^{-11}
Mass Absorption cross-section, B_{abs}^{Bulk}, (m^2/g)	2.27(±0.08)	0.86(±0.01)
Im{RI}; Bulk	0.101(±0.004)	0.038(±0.001)
Im{RI}; Curve fit (Mie theory/Coated BPSL)	0.099(±0.015)	0.035(±0.005)

Our results suggest that while the degree of amplification will depend upon core size, core and coating RI, and coating thickness, even at the thinnest coatings, some degree of absorption enhancement will take place. Put another way, if no absorption amplification is observed when coating an absorbing core, then an additional mechanism(s) that can counteract the coating's lensing effect must be present. In the case of BC, one potential candidate is the restructuring of the soot aggregate. Restructuring of soot aggregates to more compact forms has been documented during the condensation of organics[5,6]. Optically this restructuring means that fewer spherules can participate in light absorption due to screening by other spherules[5]. The consequence of this is that the mass absorption coefficient will decrease and eventually the soot aggregate will reach a regime where absorption is be dominated by the volume of the collapsed BC particle (as opposed to the individual spherules that make up the aggregate)[7].

Since the aggregate collapse requires a coating, it is interesting to speculate upon the optical implications of having both mechanisms present early in the aging process. If both mechanisms were operating at the same time, then the degree of absorption change early in the coating process might be less than that expected from simple core-shell model simply because the increased spherule screening would offset the lensing effect of the coating. Furthermore, depending upon the properties of the coating material (e.g., surface tension) it might not be unreasonable to observe no change in the absorption during the initial stages of soot aging or even a slightly negative change if the rate of aggregate collapse was initially faster than the growth of the coating. Of course, once the aggregate completely collapses additional coating will result in uncontested absorption amplification. It is conjectured that perhaps such a slight aggregate restructuring might be responsible for the reported absence of absorption amplification when oleic acid was coated on top of flame-generated soot[7].

In an effort to help elucidate the effects of coatings on the optical properties of absorbing particles, a series of experiments have been initiated using a model system approach[11]. Using this strategy, the effects of individual mechanisms on the optical properties of an aerosol can be systematically examined. It is expected that the insights gleaned from such studies will provide valuable guidance towards reducing the uncertainty of aerosol direct forcing.

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