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Using Coated Black-dyed PSL as a Proxy for Aged Soot to Study Light Absorption Amplification

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Abstract. Quantification of coating-induced absorption amplification of soot is difficult because two processes brought about by the coating process have opposite effects on soot light absorption: (i) collapse of the fractal aggregate resulting in absorption decrease and (ii) the growth of the coating causing absorption increase. In an effort to help elucidate and better quantify the effects that such structural changes may exert on the optical properties of soot, we have initiated a research effort involving the use of black-dyed polystyrene latex (BPSL) spheres as a proxy for collapsed soot on top of which a transparent material is condensed. Utilization of this model system enables absorption amplification as a function of coating thickness to be studied without the complicating effects of aggregate collapse. In the present study, dibutyl phthalate, used as a surrogate for an organic coating, is condensed onto the BPSL spheres and the absorption amplification is measured using the technique of photothermal interferometry. Since the cores are spherical, application of Mie theory can be used to estimate the refractive index of the BPSL core. To the knowledge of the authors this present experimental study represents the first time a model system has been used to study the effects of transparent coatings on particle light absorption. It is expected that the insights gained from these types of studies will impact both interpretation of ambient aerosol measurements as well as those interested in fundamental optical properties of aerosols.

Introduction

As the policymakers push the modeling community for better global climate change forecasting, the modeling community in turn presses the observationalists for improved data on the fundamental properties of aerosols. Soot is one class of particles for which better data is urgently needed because of its role in direct and semi-direct aerosol radiative forcing. However, soot particles are complex and their structure, optical properties and reactivity change with time. Recent articles [*Bond and Bergstrom*, 2006; *Bond et al.*, 2006] capture this complexity where the work from many groups who have examined the optical properties of soot has been reviewed. As discussed in these papers, the variability in B_{abs} (mass absorption cross-section, m^2/g) can be traced back, in part, to the simple fact that optical properties of nascent soot can be quite different

from those of aged soot. Differences between nascent and aged soot include structural changes to the aggregate itself (collapse of the soot aggregate) as well as the encapsulation of the aggregate. From the optical perspective, the aggregate collapse and the encapsulation will have opposite effects on particle absorption. In the former, some spherules that make up the aggregate will inevitably find themselves effectively screened from participating in the light absorption as the nascent aggregate collapses [*Penner*, 1986; *Schnaiter et al.*, 2003; *Saathoff et al.*, 2003]. This screening will result in a decrease in the mass absorption cross-section. In contrast, when soot (or any absorbing particle) is coated with an optically transparent material, the absorption coefficient will increase through a lensing effect [*Ackerman and Toon*, 1981; *Jacobson*, 2000, 2001; *Fuller et al.*, 1999]. Furthermore, there is mounting evidence that encapsulation is neces-

sary to bring about the collapse through surface tension [Mikhailov *et al.*, 2001; Schnaiter *et al.*, 2003; Saathoff *et al.*, 2003], implying that the two processes probably take place simultaneously. Finally, Fuller *et al.* [1999] point out that encapsulation of soot can decrease the interactions between spherules, leading to additional reduction in the absorption. The ramification of these mechanisms is that field measurements of soot absorption will ultimately retrieve an *effective* absorption coefficient; $B_{abs}^{eff} = B_{abs}^{nascent} + \delta B_{abs}^{coating} - \delta B_{abs}^{collapse}$; where $B_{abs}^{nascent}$ represents the absorption cross-section for nascent soot, $\delta B_{abs}^{coating}$ is the increase in absorption due to the coating material and $\delta B_{abs}^{collapse}$ is the absorption decrease due to aggregate collapse. One potential consequence of this is that significant structural changes to the aggregate could take place with little or no change in the measured aerosol absorption. Thus, it is highly desirable to better quantify the effects of these two processes. Towards this end, we have recently initiated an experimental effort to better understand the optical implications of these mechanisms using a model system that would allow us to examine these two effects in isolation. For our first model system we have chosen black-dyed polystyrene latex (BPSL) spheres to serve as a proxy for collapsed soot. The strategy behind the use of BPSL particles is to be able to study the effects of layering an optically transparent coating on top of an absorbing core without having to worry about aggregate collapse. An additional advantage of these particles is that being spherical, Mie theory is rigorous. In this Letter, we present results on the absorption amplification observed when BPSL particles are coated with dibutyl phthalate (DBP).

Experimental

To ensure that the optical properties of the particle are not modified or influenced by the measurement process itself, we used the technique of photothermal interferometry (PTI) recently developed in our laboratory [Sedlacek and Lee, 2007]. Since the PTI technique is discussed in detail elsewhere [Sedlacek, 2006] only a brief outline will be given here. Photothermal interferometry combines photothermal spectroscopy with interferometry to measure the heat dissipation by a particle following light absorption from the 2nd-harmonic of a Nd:YAG laser (532 nm). The degree of light absorption 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 the particle during

heat dissipation. This technique is fast, offers high sensitivity, does not suffer interferences from aerosol light scattering.

Dyed polystyrene latex (PSL) particles are commercially available in a variety of diameters and colors (Duke Scientific, Polysciences Inc.). For the current experiment, we used black-dyed PSL particles with diameters ranging from nominally 100 - 400 nms. A couple of items to take note of when using these PSL particles include the presence of multimers (e.g., dimers and trimers, etc.) and the effects of nonuniform dye penetration in different particle diameters. The consequence of this latter issue is that particle absorption as a function of diameter will not necessarily follow behavior typified by an homogeneously absorbing particle. However, for the present experiments this is not an issue since we are interested in the absorption amplification induced by a transparent coating for a given particle diameter.

A monodispersed distribution of particles is generated using an atomizer (TSI, model 3076) and, following diffusion drying, directed into one end of a coating chamber where the BPSL particles are then coated with DBP. Since DBP has a low vapor pressure (3.5×10^{-4} bar at 400 K), dry nitrogen is bubbled at a nominal flow rate of 0.5 liter per minute through DBP contained in a Pyrex reservoir placed in an oil bath. The nitrogen entrained DBP is injected into the coating chamber where the DBP can condense onto the BPSL particles. The coated BPSL particles and unused DBP exit the coating chamber and are sent to the DMA (TSI long column DMA, model 3081) for size selection and then to either a condensation particle counter (CPC, TSI model 3025A) or the interferometer. Coating thickness was controlled through oil bath temperature and overall flow rate in the mixing chamber. The CPC was also used on the DBP entrained N₂ stream devoid of BPSL and no measurable particle count was observed thus indicating the absence of DBP particles.

Shown in Figure 1 is the monodispersed size distribution for uncoated BPSL along with the observed size distributions at 2 different oil bath temperatures. As can be readily observed, there is a shift in the count mean diameter to high values along with a commensurate increase in the geometric standard deviation as the oil bath temperature is increased [CMD = 385 nm, GSD=1.039 (uncoated); 479 nm, 1.184 (383 K); and 521 nm, 1.345 (423 K)]. Three items are to be noted upon inspection of Figure 1. First the monodispersed size distribution for the uncoated BPSL is centered at 385 nm. Use of these monodispersed commercial particles eliminated the requirement for a second DMA to

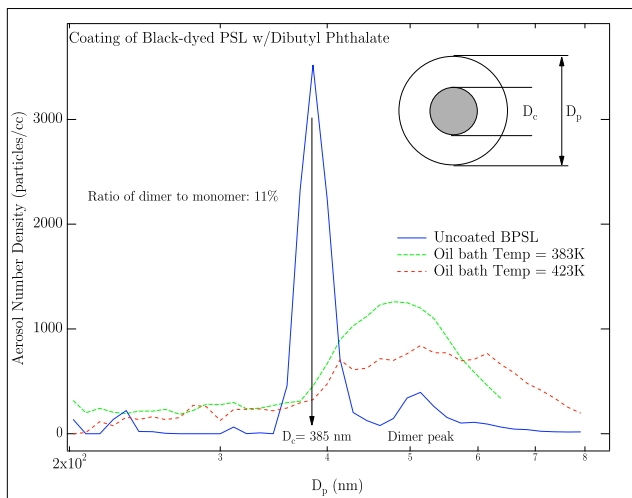


Figure 1. Measured particle size distribution. The mobility diameter of BPSL (core) was found to be 385 nm. In addition, dimer particles were also observed at 514 nm. As the temperature of oil bath increases, size distribution gets broader and a shift in the mean diameter towards higher D_p occurs due to the coating. Note the absence of a 385 nm peak at elevated bath temperatures indicating nearly complete coating of the BPSL particles.

size select particles for coating. Second the presence of a second peak around 514 nm, which is assigned to a BPSL dimer. And third, is that at elevated DBP oil bath temperatures, the 385 nm peak is no longer observed indicating that all BPSL particles entering the coating chamber are coated.

For a given experiment, the size-selected, coated particles are injected into the PTI instrument for measurement of the absorption cross-section. This measurement is carried out by recording the PTI signal as a function of particle number density for a given D_p (core diameter + 2x shell thickness) where particle number density was controlled via standard gas mixing techniques. This same procedure is then followed for a variety of D_p s. The absorption cross-section for the uncoated core is also measured the same way. Typical particle number densities used in these experiments ranged from about 50 particles cm^{-3} up to a several thousand particles cm^{-3} .

Results and Discussion

Absorption amplification is defined as the ratio of the measured absorption cross-section for a coated particle

to that for the uncoated particle. Shown in Figure 2 are absorption amplification values measured for various DBP coating thicknesses on 385 nm BPSL particles. With a DBP coating of 55 nm thick, a 15% increase in BPSL absorption is observed while at 83 nm the amplification increases to almost 40%. Similarly for 233 nm particles (not shown), a 28% enhancement is observed at the thinnest coating studied, 14 nm, and an enhancement approaching 45% with thicker coatings. Interestingly, similar levels of enhancement have been observed for organic-coated soot [Schnaiter *et al.*, 2003; Saathoff *et al.*, 2003].

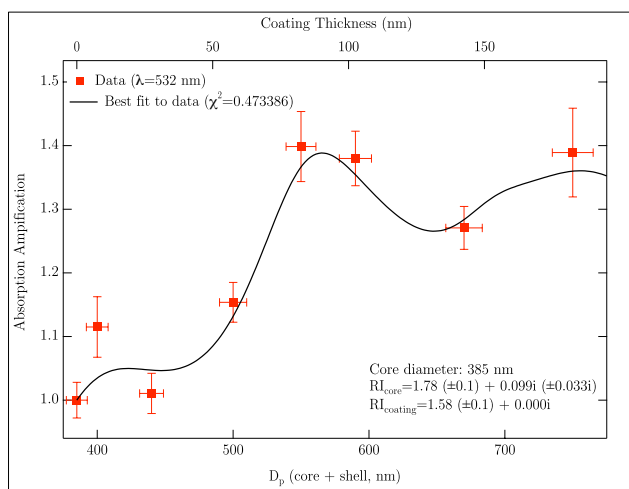


Figure 2. Observed absorption amplification for a DBP-coated, 385 nm BPSL core as a function of D_p (absorbing core diameter + 2x transparent shell thickness). The absorption enhancement induced by DBP coating ranges between 1.1 - 1.4, depending on the coating thickness. Also shown is the best fit curve using Mie theory for coated sphere. Through curve fitting, the RI for the core can be estimated. From this analysis, the imaginary part of RI for the core is estimated to be 0.099 (± 0.033), in close agreement with that obtained from bulk measurement. The same analysis for 233 nm BPSL cores gives 0.035 (± 0.023).

The solid line in the plot is the best-fit generated using Mie theory for a concentric core-shell sphere [Mätzler, 2002] where the adjustable parameters are the refractive indices (RI) of the absorbing core and the coating material. The curve fitting employed a reduced chi-square minimization routine where the core RI was first adjusted until a minimal value for χ^2 was found and then the DBP RI was adjusted. The convergence criterion was $\chi^2 \leq 0.0001$. The real and imag-

inary parts of the RI obtained for the 385 nm BPSL using this fitting procedure was found to be $1.78 (\pm 0.1) - 0.099i (\pm 0.033i)$ and for DBP the RI is estimated to be $1.58 (\pm 0.1) - 0.0i$, a value about 6% larger at 532 nm than that reported for DBP at 589 nm ($1.49 + 0i$). The same type of measurement and analysis procedure used on 233 nm BPSL gives $1.74 (\pm 0.06) - 0.035i (\pm 0.023i)$ and $1.54 (\pm 0.1) - 0.0i$ for DBP. Quoted uncertainty is 1σ . The larger relative error in the imaginary part for the smaller BPSL particles is due to the presence of a high fraction of BPSL dimers and trimers and the smaller absorption cross-section.

An independent verification of the absorption index (imaginary part of the core's RI) estimated via Mie theory-based curve fitting routine described above can be conducted by measuring the visible transmission of a known concentration of a BPSL-water solution with a commercial spectrometer (Perkin-Elmer model 320 UV/VIS). From this bulk measurement, the mass absorption cross-section for 385 nm BPSL was found to be $2.27 (\pm 0.08) \text{ m}^2/\text{g}$. The absorption index, k , can be readily calculated via Eq. 1 [Bohren and Huffman, 1983], which relates k to the mass absorption cross-section B_{abs} , the BPSL density ($\rho = 1.05 \text{ kg/m}^3$) and the wavelength of light ($\lambda = 532 \text{ nm}$).

$$k = \frac{B_{abs}\rho\lambda}{4\pi} \quad (1)$$

Using this expression, the absorption index is calculated to be $0.101 (\pm 0.004)$, a value in good agreement with that estimated by curve fitting the coated BPSL data to the concentric core-shell model. As an additional check, the mass absorption cross-section was also calculated from the PTI measured absorption cross-section for the uncoated BPSL sphere and found to be $2.45 (\pm 0.14) \text{ m}^2/\text{g}$, which translates to an absorption index of $0.109 (\pm 0.006)$, in good agreement with values obtained from the other two measurements described above. Table 1 summarizes the measured optical properties of the two BPSL cores studied (233 nm and 385 nm). It is to be noted that the RI is not constant for these dyed particles. This variability is most likely due to the dye not uniformly penetrating to the same depth in the different particles [Lack et al., 2006].

The use of the model system approach presented here enables subtle aspects of amplification brought about by layering a transparent material on top of an absorbing core, to be studied without the complications associated with restructuring. An example is readily revealed upon further examination of Figure 2, which shows that the absorption enhancement brought about by an

ever-thickening layer of DBP is not a smooth function of coating thickness but has structure. This structure is presumably due to the DBP reaching its dipole resonance [Fuller et al., 1999]. It is in this way that information about the refractive index of the encapsulating material can be retrieved since it is the coating material that dictates the frequencies of these oscillations [Redemann et al., 2001; Fuller et al., 1999]. To the knowledge of the authors, this is the first time such structure in aerosol absorption amplification has been experimentally observed.

Our results suggest that while the degree of amplification will depend upon core size, core and coating RIs, and coating thickness even at the thinnest coatings (14 nm for 233 nm core and 7.5 nm for 385 nm core), some degree of absorption enhancement will take place. Put another way, if no absorption amplification is observed for a coated absorbing particle, then an additional mechanism(s) that can counteract the coatings lensing effect is (are) likely to be present. In the case of soot, one potential candidate is aggregate restructuring to more compact form. Such morphological changes in soot has been documented for organic-coated soot [Schnaiter et al., 2003; Saathoff et al., 2003] and soot-water agglomerates [Mikhailov et al., 2006, 2001]. Optically this coating-induced restructuring means that fewer spherules participate in light absorption due to screening by other spherules [Penner, 1986] and, as discussed by Fuller et al. [1999] and Bond et al. [2006], can also lead to a reduction in spherule interaction. Both of these effects lead to reduced light absorption.

Armed with this insight it is interesting to speculate upon the potential optical implications of both mechanisms during soot aging. If both mechanisms are operating at the same time, as would seem reasonable given that the aggregate collapse requires a coating, the degree of absorption change early in the coating (soot aging) process might be less than expected from a simple core-shell model where the core is assumed static. Furthermore, depending upon the properties of the coating material (e.g., surface tension) it might not be unreasonable to observe no change in particle light absorption early in soot aging, or even a slightly negative change (for example, see Lioussse et al. [1993]), if the rate of aggregate collapse was initially faster than the growth of the coating. Once the aggregate completely collapses, additional coating would result in uncontested absorption amplification to the limits dictated by Mie theory and the properties of the core and coating material.

The importance of trying to quantify the contribution of these two mechanisms on the absorption of

Table 1. Optical Properties of Uncoated Black-dyed PSL Particles

Particle Diameter (nm)	385	233
σ_{abs} (cm ²); Uncoated BPSL	7.7(\pm 0.4) $\times 10^{-10}$	6.4(\pm 0.4) $\times 10^{-11}$
σ_{abs} (cm ²); Coated BPSL & Mie theory	11.6(\pm 1.4) $\times 10^{-10}$	8.8(\pm 0.9) $\times 10^{-11}$
B_{abs}^{Bulk} , (m ² /g)	2.27(\pm 0.08)	0.86(\pm 0.01)
$B_{abs}^{Uncoated}$, (m ² /g)	2.45(\pm 0.14)	0.91(\pm 0.05)
Im{RI}; Bulk	0.101(\pm 0.004)	0.038(\pm 0.001)
Im{RI}; Coated BPSL & Mie theory	0.099(\pm 0.033)	0.035(\pm 0.023)
Im{RI}; Uncoated BPSL particles	0.109(\pm 0.006)	0.041(\pm 0.002)

coated soot is exemplified by comparing two recent laboratory-based studies. On one hand, *Slowik et al.* [2007] reported no observable amplification when 10-nm and 50-nm thick coatings of oleic acid were condensed onto flame-generated soot, whereas *Schnaiter et al.* [2003] reported 35% increase in absorption when SOA from the ozonolysis of α -pinene encapsulated spark-discharge generated soot. Given that oleic acid has a refractive index nearly identical to that estimated for the SOA product (1.458 vs. 1.443) and that both studies examined similarly-sized soot particles coated with similar thicknesses, such differing results are puzzling, especially given that our results suggest some degree of absorption enhancement should occur. If we ignore the presence of organic carbon in the flame-generated soot (due to incomplete combustion [*Slowik et al.*, 2007]), the higher surface tension of oleic acid as compared to α -pinene (32.8 dyne/cm³ @ 293 K vs. 25.3 dyne/cm³ @ 303 K) would suggest that the onset of aggregate restructuring might proceed more readily. If true, a slight restructuring could offset a modest lensing effect early in the coating process leading to no observable change in coated soot absorption.

Conclusion

Soot is known to age through encapsulation and collapse of the nascent aggregate fractal structure. However, while the encapsulation will result in absorption amplification through a lensing mechanism, the aggregate collapse will cause a decrease in the mass absorption cross-section. In an effort to help elucidate and quantify these two contributions on the optical properties of absorbing particles experiments involving use of black-dyed PSL particles as a proxy for collapsed soot upon which a transparent coating is grown have been conducted. This strategy enables the study of absorption amplification brought about by the coating without

complications associated with core restructuring. Absorption enhancement induced by a dibutyl phthalate coating was found to range from 1.1 - 1.4 for 385 nm BPSL core and 1.1 - 1.5 for 233 nm BPSL core. While the degree of absorption enhancement was dependent upon core size and core and coating RI, *amplification was observed for all coating thicknesses*. This result suggests that when a transparent coating is grown onto an absorbing core, some degree of absorption amplification will always be present.

These present *model-system* experiments will be expanded to study the effects of different types of coating material on absorption amplification and experimental designs are currently underway to allow careful examination of absorption decrease due to soot agglomerate collapse. It is expected that the insights derived from such studies will provide valuable guidance towards reducing the uncertainty of aerosol direct forcing.

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