Atmospheric Environment 186 (2018) 89–101

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Spectrally resolved light extinction enhancement of coated soot particles

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ARTICLE INFO

Keywords:
Extinction
Coated carbonaceous particles
Brown carbon
Spectral dependence

ABSTRACT

The aim of the present study is to evaluate experimentally the impact of a non-absorbing coating material on the spectral radiative properties of freshly produced carbonaceous aerosols. Once emitted into the atmosphere, carbonaceous particles are prone to interact with organic chemical compounds to acquire a certain amount of non-absorbing or weakly absorbing coating on their surface. In the present study, oleic acid is used as a surrogate for the coating material and applied to aerosols produced by a miniCAST (soot particles of different chemical and morphological properties) and a spark discharge aerosol generator. A simple analytical model is presented to evaluate the coating thickness. Furthermore, the spectrally resolved extinction cross sections of uncoated and coated particles are determined enabling the evaluation of the mass specific extinction coefficient and the extinction enhancement factor over a wide spectral range (200 − 1100nm). Influences of the coating thickness and the type of core carbonaceous particles are also discussed.

1. Introduction

Soot is emitted from a wide variety of combustion processes, such as biomass burning (Unger et al., 2010), and transportation (Kittelson, 1998). Soot plays a major role in the radiative forcing of the Earth because it absorbs strongly the solar radiation and influences the process of cloud formation. Once emitted into the atmosphere, soot particles are subjected to solar radiation and undergo interactions with various compounds in the environment (Bond et al., 2013). During this aging process, soot particles can become partially or even fully coated by organic compounds, which are in general non- or weakly-absorbing in the visible and near infrared spectral range (Jacobson, 2001).

Several experimental studies have found that a coated soot particle with an organic compound can absorb up to twice as much as light as the uncoated soot core (Gangl et al., 2008; Shiraiwa et al., 2010; Bueno et al., 2011; Lack and Cappa, 2010; Khalizov et al., 2009; Bond and Bergstrom, 2006). This absorption enhancement by a factor of two has been confirmed by several numerical studies (Gangl et al., 2008; Soewono and Rogak, 2013; Kahnert et al., 2013). These numerical studies highlight the "lens effect" caused by the coating of a non-absorbing material. Nevertheless, modeling of the radiative properties of coated particles is challenging due to the potential occurrence of morphological restructuration of the fractal soot core when the coating thickness is sufficiently large (Xue et al., 2009; Ghazi and Olfert, 2013; Soewono, 2013; Zhang et al., 2008; Schnitzler et al., 2014; Adachi et al., 2010) and the uncertainty in the spectral dependence of the refractive index of soot core (Schnaiter et al., 2006; Bescond et al., 2016). Despite these difficulties, there is a pressing need for systematic in-depth experimental studies to measure the optical properties of coated soot particles under highly controlled conditions and to obtain reproducible and high quality data, since coating of soot during the atmospheric aging process is an important factor that affects the radiative forcing capabilities of aged soot particles and must be taken into account for modeling the radiative forcing potential of atmospheric aerosols.

Several experiments have been reported in the literature using different experimental apparatuses and approaches. The first kind of device is the aging chamber (Schnaiter et al., 2003, 2006; Saathoff et al., 2003a, 2003b; Henning et al., 2012). This approach enables in situ generation of aged brown carbon particles by heterogeneous nucleation of products from the reactions of $\alpha - pinene$ with ozone. Even if this approach is representative of the atmospheric aging process, the experiments are complex, voluminous, and time-consuming (soot exposure times of several hours). Therefore, it is difficult to use this approach to conduct parametric studies.

The second class of methods involves the interactions between a carrier gas of vaporized organic compounds and an aerosol containing soot particles. This type of technique is largely based on the same design as that of Sinclair and La Mer et al. (1949) (Sinclair and La Mer, 1949) and has been improved over the last few decades (Gangl et al., 2008; Prodi, 1972; Lewitzka and Niessner, 1995; Panne et al., 2000). Such approach makes it possible to generate a layer of coating on the

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https://doi.org/10.1016/j.atmosenv.2018.05.029
Received 16 October 2017; Received in revised form 11 May 2018; Accepted 13 May 2018

Nomenclature

Acronyms

CPC	Condensation Particle Counter
CPMA	Centrifugal Particle Mass Analyzer
DMA	Differential Mobility Analyzer
IR	InfraRed
LII	Laser Induced Incandescence
OC	Organic Carbon
PAH	Polycyclic Aromatic Hydrocarbon
SMPS	Scanning Mobility Particle Sizer
TC	Total Carbon
TEOM	Tapered Element Oscillating Microbalance
UV	UltraViolet
VIS	VISible

Other Symbols

Δm	Added mass of coating material (g)
λ	Wavelength (nm)
λ_{ref}	Reference wavelength (nm)
ρ_c	Density of coating material ($kg.\ m^{-3}$)
ρ_p	Bulk density ($kg.\ m^{-3}$)
σ_g	Geometric standard deviation of primary particle diameter distribution
$\sigma_{s,ref}$	Mass specific extinction at the reference wavelength ($m^2.\ g^{-1}$)
σ_s	Mass specific extinction coefficient ($m^2.\ g^{-1}$)
ξ	Ångström exponent (based on absorption)
ξ_{ext}	Extinction based Ångström exponent
C_{abs}	Absorption cross section (m^2)
C_{ext}	Extinction cross section (m^2)
C_s	Mass concentration ($kg.\ m^{-3}$)
D_c	Diameter of a sphere whose volume correspond to the coating volume V_c (m)
D_f	Fractal dimension
D_m	Mobility diameter (nm)
$D_{p,geo}$	Median primary particle diameter (nm)
D_p	Primary particle diameter (nm)
e	Coating thickness (nm)
EEF	Extinction Enhancement Factor
f_v	Soot volume fraction
I_s and I_0	Experimentally measured transmitted light with and without the particle-laden aerosol
K_{ext}	Extinction coefficient (m^{-1})
K_e	Dimensionless extinction coefficient
k_f	Prefactor
L	Length of extinction cell (m)
M	Mass of the deposited particles on TEOM filter (kg)
m	Mass of the core soot particle (g)
N_0	Total number concentration of particles generated by miniCAST ($part.\ m^{-3}$)
$N_{p,modal}$	Modal number of primary particles of a lognormal distribution
N_p	Number of primary particles
N_p^*	Mass equivalent number of primary particles
N_{tot}	Total number concentration of particles in extinction cell ($part.\ m^{-3}$)
p	Parameter quantifying the coating thickness (%)
Q_v	Sampling flow rate of TEOM (lpm)
S_c	Surface of core soot (m^2)
T	Temperature of coating device (C)
V_c	Volume of coating material (m^3)
V_s	Volume of core soot (m^3)

soot particles rapidly, namely in few seconds. However, precaution must be taken to avoid the generation of droplets formed by the coating material, i.e., droplets without the soot core.

The last class of devices for the rapid generation of coating is based on the design of Moteki and Kondo (2007) (Moteki and Kondo, 2007). This design, chosen in the present study, has been commonly used in laboratory experiments in recent years (Shiraiwa et al., 2010; Xue et al., 2009; Ghazi and Olfert, 2013; Soewono, 2013; Slowik et al., 2007; Bambha et al., 2013; Cross et al., 2010). In this technique, a freshly generated soot aerosol flow is delivered through a heated chamber containing the supersaturated vapor of the coating material. Varying the temperature in the coating device (chamber), which is generally maintained by an oil bath, makes it possible to control the vapor concentration of coating material and thus the amount of coating material deposited on the soot particle surface.

It is important to establish a quantitative relationship between the change in the radiative properties of soot in the presence of coating material to a parameter that quantifies the amount of added material. The coating thickness has been shown to be a useful and convenient parameter for such purpose and commonly used, e.g. (Liu et al., 2016). Different methods have been used to estimate the coating thickness. One approach is based on the measurement of particle diameter before and after coating (Gangl et al., 2008; Shiraiwa et al., 2010; Bueno et al., 2011; Zhang et al., 2008; Abo Riziq et al., 2008). However, the difference in diameter between the coated and uncoated particles allows the determination of coating thickness only for monodisperse spherical particles (Abo Riziq et al., 2008). Indeed, for soot fractal aggregates, the interpretation of electrical mobility diameter is not straightforward (Sorensen, 2011), in particular if the restructuration phenomenon occurs during the coating process.

Another approach to estimate the coating thickness is to determine the change in particle mass with the addition of coating material (Xue et al., 2009; Moteki and Kondo, 2007; Bambha et al., 2013; Cross et al., 2010; Petersson, 2016). Nevertheless, to evaluate the coating thickness certain hypotheses about the morphology of soot particle have to be made. The simplest approach is to assume that the particles are spherical (Slowik et al., 2007). Although this assumption may be reasonable when the volume of coating material is large compared to the volume of the core particle, especially when the restructuration phenomenon occurs, it is hardly applicable to thinly coated particles, which are relevant to the early stage of the aging process, since the fractal morphology of the particles is still highly perceptible. One of the major concerns of the present study is the quantification of the coating thickness by preserving the aggregate nature of soot particles.

The relationship between the amount of coating added to the particle and the particle absorption cross sections has been experimentally evaluated using Laser Induced Incandescence (LII) (Moteki and Kondo, 2007; Bambha et al., 2013), the photoacoustic methods (Shiraiwa et al., 2010; Bueno et al., 2011; Cross et al., 2010; Lack et al., 2009), or derived from the difference between the measured extinction and total scattering (Gangl et al., 2008; Khalizov et al., 2009; Xue et al., 2009; Abo Riziq et al., 2008). These studies have generally been performed for a limited number of size-selected particles with the use of a differential mobility analyzer (DMA). The selection in size leads to a dramatic decrease in the particle number concentration, implying that a sensitive optical measurement technique, such as the cavity ring-down extinction, must be employed. Therefore, a clear drawback of this approach is the significantly reduced number concentration of size-selected particles and the selected working wavelengths λ. To overcome these limitations, in the present study, the extinction enhancement factors will