Journal of Quantitative Spectroscopy & Radiative Transfer 172 (2016) 134–145

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

On the radiative properties of soot aggregates – Part 2: Effects of coating

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ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form
26 July 2015
Accepted 12 August 2015
Available online 20 August 2015

Keywords:
Radiative properties
Coated soot aggregates
DDA
RDG-FA

ABSTRACT

The effects of weakly absorbing material coating on soot have attracted considerable research attention in recent years due to the significant influence of such coating on soot radiative properties and the large differences predicted by different numerical models. Soot aggregates were first numerically generated using the diffusion limited cluster aggregation algorithm to produce fractal aggregates formed by log-normally distributed polydisperse spherical primary particles in point-touch. These aggregates were then processed by adding a certain amount of primary particle overlapping and necking to simulate the soot morphology observed from transmission electron microscopy images. After this process, a layer of WAM coating of different thicknesses was added to these more realistic soot aggregates. The radiative properties of these coated soot aggregates over the spectral range of 266–1064 nm were calculated by the discrete dipole approximation (DDA) using the spectrally dependent refractive index of soot for four aggregates containing $N_p=1$, 20, 51 and 96 primary particles. The considered coating thicknesses range from 0% (no coating) up to 100% coating in terms of the primary particle diameter. Coating enhances both the particle absorption and scattering cross sections, with much stronger enhancement to the scattering one, as well as the asymmetry factor and the single scattering albedo. The absorption enhancement is stronger in the UV than in the visible and the near infrared. The simple corrections to the Rayleigh–Debye–Gans fractal aggregates theory for uncoated soot aggregates are found not working for coated soot aggregates. The core–shell model significantly overestimates the absorption enhancement by coating in the visible and the near infrared compared to the DDA results of the coated soot particle. Treating an externally coated soot aggregate as an aggregate formed by individually coated primary particles significantly underestimates the absorption enhancement by coating in the visible and the near infrared.

1. Introduction

Soot particles are emitted primarily from various combustion systems and biomass burning. Due to their black carbon content, soot aerosols have been recognized as a major contributor to global warming due to their strong ability to absorb solar radiation. The current estimate of various light absorbing components in the atmosphere put soot aerosols as the second largest contributor just after carbon dioxide in terms of radiative forcing [1,2]. However, the estimate of the role of soot aerosols to radiative forcing is subject to large uncertainties. One of the main reasons for such large uncertainty is due to our relatively poor quantitative understanding of the radiative properties of

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http://dx.doi.org/10.1016/j.jqsrt.2015.08.005

soot aerosols. It has been well established that fresh soot particles can be described as fractal aggregates formed by fairly spherical primary particles or monomers with a certain degree of overlapping and necking between neighbouring primary particles. After emitted from various combustion devices and fires, the fresh soot particles undergo the so-called 'aging' process during which soot aerosols are mixed with various materials in the atmosphere and often become coated or partially coated by organic aerosols, sulphate, water, and sea salt, see [3,4] and references cited therein. These liquid or crystal materials are characterized by very weak absorption in the visible spectrum. In this study, the various materials acquired by soot aggregates during aging are collectively called weakly absorbing materials (WAM). The radiative properties of coated soot aerosol particles depend on many factors, such as the original soot particle (freshly emitted and uncoated) morphology, the coating materials and thickness, the mixing state, and the refractive indices of soot and the host particle. Studies conducted so far have established that coating of soot aggregates by WAM leads to significantly enhanced absorption cross section by up to about a factor of 2 [5–7], even though these coating materials are weakly- or even non-absorbing. This enhanced absorption due to coating is often referred to as the lensing effect [8–10].

Various mixing states between soot particle and other WAM aerosol compounds have been observed in the transmission electron microscopy (TEM) images of sampled aerosol particles [5,6]. It has been made clear that the internal mixing situation, where the soot aggregate is fully embedded by WAM, leads to the most enhancement in the coated particle absorption cross section [1,6] and has drawn much of the research attention recently.

In most climate models the radiative properties of soot aerosols are modelled using the Mie theory applied to either a core–shell system or a homogeneous sphere with the help of a mixing rule, such as the Maxwell–Garnet effective medium approximation [2,6]. Other extensions of the core–shell type model have been proposed and evaluated by Kahnert and coworkers [11,12]. In general, the performance of such simple mixing models is highly dependent on the mixing states of the coated soot particles [11,12]. For climate modelling the required radiative properties are the mass absorption cross section (MAC), single scattering albedo (SSA), and the asymmetry parameter (g) [6]. Although the Mie theory performs fairly well when the absorbing core is a spherical particle [13] or non-aggregated graphite particles [7] against experimentally measured absorption enhancement, it has been found to significantly overestimate the absorption enhancement in the visible spectrum [14]. The experimental measurements of atmospheric black carbon conducted by Cappa et al. [15,16] also showed that the measured absorption enhancement by WAM coating was much lower than that predicted by the core–shell Mie theory. These inconsistent findings suggest that the effects of WAM coating on soot aggregates deserve further research.

Although the radiative properties of uncoated or dry soot have been extensively studied by using the approximate Rayleigh–Debye–Gans theory for fractal aggregates (RDG-FA) [17–20] and several more advanced numerical methods, e.g. [21–26] among others. However, there have been fewer studies on the radiative properties of coated soot particles employing accurate numerical methods or dealing with realistic soot particle morphology and the mixing state. Due to the limitations of the T-matrix method [27] and the generalized Mie-solution method (GMM) [28], several studies had to use a simplified representation of the coating of WAM over a soot aggregate by an aggregate formed by individually coated primary particles [29–31]. Although such studies are useful to understand the effects of non-absorbing material coating on the radiative properties of soot aggregates, these studies suffer the major drawback that the mixing state considered is unrealistic. Coating of soot aggregates by WAM during aging takes place over the entire outer surface of the aggregates, e.g., [14]. Treating such mixing state between the soot aggregate core and the host coating material as an aggregate of individually coated primary particles is clearly an idealized and over-simplified model. In another recent study, Cheng et al. [32] carried out a numerical study using the updated superposition T-matrix method, MSTS [27], to investigate the effects of atmospheric water coating on the radiative properties of a soot/sulphate system of three different mixing states in the spectral range of 400–1020 nm. Although there are still some limitations with regard to the morphology of the soot/sulphate system dictated by MSTS, the morphology considered by Cheng et al. [32] is much more realistic than the simplified model used in [29–31]. Similar to previous studies, Cheng et al. also observed about a factor of 2 increases in the particle absorption cross section under thick coating conditions.

Besides the few studies of the radiative properties of coated and mixed soot particles using the GMM and T-matrix methods discussed above, several studies have also been carried out using the discrete-dipole approximation (DDA) to handle the complex morphology of internally mixed soot particles with WAM based on TEM images of atmospheric aerosols [11,12,14,33]. Worringen et al. [33] constructed two relatively more realistic internally mixing models between sulphate and soot particles based on the mixing state revealed from TEM images of mixed sulphate and soot particles and calculated the radiative properties of these two models at a wavelength of 550 nm using the DDSCAT code (version 5.9) developed by Draine and Flatau [34]. Using the 3-D shapes of internally mixed soot particles constructed from electron tomography (ET), Adachi et al. [14] performed DDA calculations using DDSCAT version 6.1 for the optical properties of these internally mixed soot particles embedded in WAM host and evaluated the performance of several spherical model particles assumed in climate modelling. Their results showed that coating enhances the absorption cross section of the coated soot particles and the core–shell Mie model in general overestimates the absorption cross section of coated soot particles over a wide range of wavelengths, except at wavelengths below about 350 nm, where the core–shell Mie model underpredicts the absorption cross section. Their numerical experiments also showed that the absorption cross section is enhanced the most when the