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An experimental and numerical study of the light scattering properties of ice crystals with black carbon inclusions

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ABSTRACT

We investigate the optical properties of ice crystals nucleated on atmospheric black carbon (BC). The parameters examined in this study are the shape of the ice crystal, the volume fraction of the BC inclusion, and its location inside the crystal. We report on new spectrometer measurements of forward scattering and backward polarization from ice crystals nucleated on BC particles and grown under laboratory-controlled conditions. Data from the Cloud and Aerosol Spectrometer with Polarization (CASPOL) are used for direct comparison with single-particle calculations of the scattering phase matrix. Geometrical optics and discrete dipole approximation techniques are jointly used to provide the best compromise of flexibility and accuracy over a broad range of size parameters. Together with the interpretation of the trends revealed by the CASPOL measurements, the numerical results confirm previous reports on absorption cross-section magnification in the visible light range. Even taking into account effects of crystal shape and inclusion position, the ratio between absorption cross-section of the compound particle and the absorption cross-section of the BC inclusion alone (the absorption magnification) has a lower bound of 1.5; this value increases to 1.7 if the inclusion is centered with respect to the crystal. The simple model of BC-ice particle presented here also offers new insights on the effect of the relative position of the BC inclusion with respect to the crystal's outer surfaces, the shape of the crystal, and its size.

1. Introduction

The aerosol direct effect is the radiative forcing that results from both enhanced backscattering and absorption of solar radiation by particles in the atmosphere. The challenge in predicting the radiative forcing of compound aerosol particles depends on understanding how their different components are combined. At one extreme, each aerosol component can be assumed to be physically separated from the others, therefore creating an external mixture of chemically pure modes. At the other extreme, each particle can be assumed to be internally mixed in the limit of a homogeneous material representing the chemical and physical average of all the contributing components. Correct mixing rules becomes particularly important when ice crystals nucleate on atmospheric soot – the small, carbonaceous particles produced during incomplete combustion and henceforth referred to as black carbon (BC). BC is the dominant light-absorbing aerosol particulate in the visible spectrum and causes positive radiative forcing (warming) in the atmosphere [10,58].

In current estimates, the absorption of internally mixed, BC-containing particles is found to be greater than the absorption of the corresponding external mixture, therefore suggesting an "enhancement" of the BC absorption properties [8,28]. This occurs because in weakly absorbing spheres radiation focuses near the sphere's center, enabling more absorption if the inclusion resides there [15]. Absorption estimates are often carried out by assuming that a compact, spherical BC core is located at the center of a homogeneously mixed shell, following the core-shell (CS) approach by Toon and Ackerman [62]. For instance, using a model of BC core coated by an aqueous solution of sulfuric acid, Jacobson [29] found an enhancement factor between two and four with respect to the estimate from the corresponding external mixture. The enhancement was lower (2.5) for larger-sized uncoated BC particles (120 nm diameter) and larger for smaller particles (40 nm and 80 nm).

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While computationally very convenient, it has been pointed out that the CS approach could overestimate the enhancement factor. With randomized BC inclusions, Fuller et al. [18] found that the averaged absorption enhancement factor was in the range 2.5–4 for water droplets, but that it could be appreciably larger when a concentric carbon sphere was assumed. Cappa et al. [11] compared measurements of particle absorption enhancement from two field campaigns in California with CS calculations, concluding that the latter overestimated absorption enhancement and pointing out that BC inclusions are often found at the edge of collected particles rather than deeply embedded in a coating material.

Internal BC can be modeled as multiple inclusions at any location using the dynamic effective medium approximation (DEMA). For an ice grain radius of 100 µm and monodisperse BC size distribution, Chýlek et al. (1984) predicted a factor of about 1.7. Flanner et al. [15] found the enhancement to be in the range of 1.8–2.1 at 460 nm; the BC effective radius was indicated as the dominant cause of variation in the results, more than ice grain size and BC volume fraction. Using a geometric-optics, surface-wave approach, Liou et al. [37] explored the optical properties of BC inclusions for a sphere, a pristine plate, and a plate with rough surface; compared to external mixing, the single-scattering co-albedo was enhanced by a factor of 1.9 and displayed a slight dependence on shape.

Rather than compact spheres, depending on their photochemical age soot particles may appear as open, chainlike structures. Electron tomography of sampled soot particles embedded in organic material was used by Adachi et al. [1] as an input to three-dimensional calculations carried out by Discrete Dipole Approximation (DDA); it was found that the CS model overestimated absorption by 30% with respect to the DDA calculations. In another example, Mishchenko et al. [49] modeled soot inclusion as a fractal aggregate with varying compactness that was either embedded or externally mixed with respect to a micrometer-sized spherical water droplet. Using the extended superposition T-matrix method, the results revealed that absorption could vary by a factor as high as 6.5, depending on the mode of soot-water mixing.

Besides the photochemical age of BC and its distribution inside the ice crystal, another cause of uncertainty in estimating absorption enhancement is due to the shape of the particle [30]. Spheroidal or cylindrical approximations are often assumed (e.g., Mishchenko and Sassen [45], Lee et al. [35], and Nicolet et al. [53]). A broader range of regular hexagonal columns, plates, droxtals, hollow columns and bullets was examined by Bi and Yang [5]. But data of airborne particles collected using the Cloud Particle Imager [34] showed that only 3% of the particles were in “pristine” shape, that is, regular column, needle, plate and dendrite geometries. The remaining 97% of crystals were either irregular faceted polycrystallines, sublimating ice particles with smooth curving sides and edges, or aggregates of columns and plates [23,66].

Microscale surface roughness is another challenge specific to ice that affects radiative effects. This effect can be modeled by an assumed probability distribution of crystal face tilt angles [43,64]. Baran and Francis [2] first showed that an ice aggregate model with roughened faces was spectrally consistent with high-resolution data from the radiance values collected above a cirrus cloud. Regular hexagonal ice columns were not spectrally consistent. Studies of the optical properties of ice clouds where the surface roughness of the ice crystals is taken into account can be found in Liu et al. [39] and in Geogdzhayev and van Diedenhoven [19], among others.

Finally, atmospheric ice crystals vary strongly in size depending upon time and location, as shown by data from the International Cirrus Experiment (ICE) and by the First International Satellite Cloud Climatology Project (ISCCP) Regional Experiment (FIRE; [32]). The reader is referred to the studies and reviews of cirrus radiative properties by Liou et al. [36], Lynch et al. [41], Baran [3], and Yang et al. [67].

The approach adopted in this work is different from previous investigations in that ice crystals are grown in laboratory from soot particles under controlled temperature, humidity, and flow conditions; the aerosol spectrometry data obtained at these conditions are then compared with single-particle parametric calculations from models that take into account crystal shape and the BC location. The Cloud and Aerosol Spectrometer with Polarization (CASPOL), manufactured by Droplet Measurement Technologies, is a rather unique measurement tool in that it can measure optical properties of individual particles. The CASPOL, previously used to evaluate the optical scattering signatures of dust particles [20], was placed at the exit of an ice nucleation chamber (the Continuous Flow Diffusion Chamber, or CFDC – [21]) while BC particles of reproducible size were introduced to act as ice nuclei (IN).

On the computational side, the discrete dipole approximation (DDA) and the ray tracing (RT) techniques are used in this work to account for the effects of an arbitrary crystal shape and BC location on particle scattering. Scattering is rather insensitive to shape when the characteristic length D of the particle is smaller than the incident wavelength; when the size parameter $X = \pi D/\lambda > 1$, only the largest-scale deviations from the spherical shape may be significant (e.g., [54]). But, as X increases, the geometrical details of the particle become important. For wavelength-scale compound particles, the properties of internal inclusions become increasingly relevant and justify using a volume-integral method such as DDA; at size parameters of a few hundred, geometrical optics (or RT) techniques become appealing for their comparatively low computational expense [48].

A well-known modeling challenge is the need to explicitly account for wavelength-scale particle details while the particles themselves are considerably larger than the wavelength. The range of size parameters between the resonance and the geometric-optics domains remains a difficult territory to explore (e.g., [55]), although the numerically exact Invariant-Imbedding T-Matrix (II-TM) method [4] promises to bridge that gap. One of the tests presented here consists of a direct comparison between the phase matrices derived from DDA and RT for $X = 50$ to show consistence of the results between the two methods.

In the first part of the paper, CASPOL's scattering data are evaluated to assess the relevant trends in crystal shape, specifically whether differences between needle and plate geometries can be identified from the signals. The analysis is not trivial because of the uncertainty in the actual crystal shape and the noise in the backscattered signals, and it is carried out by comparison with model predictions. The second part of the paper is focused on parametric studies to isolate the effects due to BC volume fraction, inclusion position, and shape of the ice crystal. The study does not take into account effects of aging on the geometrical and optical properties of BC, although this could be relevant in atmospheric soot. Conclusions and a path forward are then discussed.

2. BC inclusion model and crystal shapes

Crystallization of water in the atmosphere occurs through homogenous freezing of liquid droplets or through heterogeneous nucleation processes facilitated by atmospheric particles that act as ice nuclei (IN) [63]. The heterogeneous nucleation of interest in this work occurs through a variety of freezing modes, including those in which ice grows from water vapor (deposition mode) or from a supercooled liquid water droplet [16,25,51].

After being emitted, BC particles are agglomerates of primary spherules forming chain-like structures that can be described as fractal aggregates [9,61]. The morphology of the aggregates evolves in time (“aging”) in a manner that is very relevant to the optical