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Optical properties of soot nanoparticles

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Abstract

In this paper, the dipole–dipole approximation is used to characterize the dynamical electromagnetic properties of two types of carbonaceous nanoparticles modelling the basic constituents of aircraft soot particles. The corresponding polarizability per unit volume is then compared with the one calculated for equivalent defect-free structures and with the one resulting from a continuum model. It is found that the polarizability per unit volume strongly depends on the details of the structure of the nanoparticle, and that this dependence could be used to discriminate between different carbonaceous particles using optical scattering experiments in the visible or near-UV domain.

Keywords: Carbon soot; Fullerenes; Light diffusion; Dielectric susceptibility; Polarizability; Dipole–dipole approximation

1. Introduction

The contribution of soot particles emitted by aircraft to atmospheric chemistry and greenhouse effect is highly uncertain and becomes a focal point in recent atmospheric research [1,2]. Indeed, in the upper troposphere, water vapor can condense around soot and freeze to form ice particles, thereby producing a visible condensation trail (a *contrail*). These contrails may be persistent and lead to the formation of artificial cirrus clouds, that add to the natural cirrus clouds [2,3]. In addition to their contribution to greenhouse warming [1,4,5], these artificial clouds could also modify the chemical equilibrium of the atmosphere by favoring heterogeneous chemical processes such as, for example, the conversion of HNO_3 to NO_x [6,7].

A quantitative characterization of the impact of soot in the upper troposphere/lower stratosphere (UTLS) requires a preliminary characterization of the soot particles, on both morphological and chemical points of view. Indeed, recent studies of the adsorption of water on various soot particles have shown that the hydration properties of these particles depend on their nanoscopic structure as well as on the presence of functional groups which can form hydrogen bonds with water molecules [2,8–19].

Recent transmission electron microscopy (TEM) studies have shown that soot emitted by aircraft is made of nanocrystallites containing graphite-type layers arranged in an onion-like structure. Soot nanoparticles are thus of quasi-spherical shape, with diameters ranging between 10 and 50 nm [20]. Results of recent Raman spectroscopy measurements have also shown that these graphite layers are partially oxidized, and that they

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contain a certain number of oxygen atoms sites [21]. Although these experiments can give very useful details on the nanoscopic structure and chemical composition of the soot, they are very scarce in the literature mainly due to the difficulty of collecting real soot. Moreover, Raman spectroscopy or electron microscopy are absolutely impractical for routine monitoring of soot particles in our environment.

To tackle this problem, spectroscopy and scattering of electromagnetic waves are thus highly used, aiming at obtaining an *in situ* characterization of the soot particles [22]. The use of optical methods for this characterization is based on the broad-band light absorption of these graphite-like particles. Indeed, in the literature, soot particles are often included in the more general term of "black carbon" [22]. However, carbonaceous particles with a potentially significant absorption in the UV have also been recently discovered in atmospheric aerosol [23,24] and this so-called "brown carbon" certainly covers a wide range of particles with chemical and physical properties which are difficult to characterize [22]. The discovery of this "brown carbon" emphasizes the fact that there actually exists nearly as many types of carbonaceous particles as there are ways to produce them, and a direct relation between the optical properties of these atmospheric carbonaceous particles and their nanoscopic structure is certainly lacking.

In the present paper, we calculate the effective polarizability per unit volume of different kinds of carbonaceous nanoparticles, in order to find correlations between their structure and their optical properties. We adopt here a bottom-up approach and compute the effective polarizabilities of the carbonaceous nanoparticles directly from the polarizability of their constituent atoms. Then, we compare the results obtained for different types of soot nanoparticles with those calculated for perfect fullerene onions structures. Indeed, such perfect onions are suspected to be responsible for the 217.5 nm interstellar extinction feature [25–28], and thus correspond to particles which can be found outside of laboratories.

The present approach is based on the point dipole interaction (PDI) model [29] which comes from seminal works of Silberstein [30–32]. The interest of this PDI model is that it is used at the nanoscopic scale with atomic dynamic polarizabilities. Note that the PDI model is very similar to the discrete dipole approximation (DDA) [33] although references from one domain are largely ignored in the other domain. The DDA is, however, used at the microscopic scale with effective polarizabilities that are derived from the multiplication of the material local dielectric susceptibility by the volume of discretization elements [34]. The DDA is thus based on a Clausius–Mossotti-like relation between the relative dielectric constant of the material and the effective polarizability of the discretization volumes. This relation depends on the shape of the discretization volumes which are most often defined as homogeneous isotropic spheres. Note that in the numerically exact T-matrix method [35], the atomistic structure of the monomers constituting the soot aggregates is similarly disregarded.

Our model of soot particles is described in Section 2. Then, the basics of our DDA-like method applied at the nanoscopic scale is briefly recalled in Section 3, with an emphasis on the setting of the parameters for the carbon anisotropic atomic dynamical polarizabilities. In Section 4, the accuracy of these parameters is checked by comparison with experimental results obtained for the C_{60} molecule, and these parameters are used to calculate the polarizabilities of the model soot particles. In the same section, the results for these soot particles are also compared to those calculated for a continuum model and for well-characterized fullerene single-shell molecules and fullerene onions. Finally, conclusions and perspectives on further developments of this work are given in Section 5.

2. Soot nanoparticle models

Two types of soot nanoparticles are considered in the present study.

The first one is built empirically, similarly to the soot nanoparticle modelled in our previous study devoted to the adsorption of water molecules on soot [17]. This soot nanoparticle is generated by replicating a small cluster of 19 carbon atoms on concentric spheres arranged in an onion-like structure. This small cluster is made of five fused benzene rings and will be referred below as the C_{19} unit. One hundred and thirteen of these C_{19} units have been randomly scattered on the surface of four concentric spheres of radii ranging from 9.8 to 20.0 Å. The separation of two successive spheres is thus equal to 3.4 Å, i.e., close to the distance between two layers in pure graphite. For the scattering of the C_{19} units on the surface of these spheres, a minimum distance of 3.80 Å has been imposed between the nearest neighboring carbon atoms of two adjacent units on the same sphere. Note that this distance is slightly larger than the Lennard-Jones (LJ) parameter for the dispersion