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# VERS UNE MESURE IN-SITU DE LA SURFACE SPECIFIQUE DES NANOPARTICULES EN PHASE AEROSOL PAR L'OPTIQUE NON-LINEAIRE

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## TITLE

## TOWARDS AND IN-SITU PROBING OF THE SPECIFIC SURFACE AREA OF NANOPARTICLES IN THE AEROSOL PHASE BY NON-LINEAR OPTICS

## RESUME

La présente étude quantifie et analyse la production d'effets optiques non linéaires (ONL), tels que la génération de seconde harmonique (SHG), par des particules de carbone noir et par d'autres types de nanoparticules en phase d'aérosol. Les expériences sont réalisées dans une installation optique innovante permettant d'analyser la réponse ONL résolue dans le temps, la longueur d'onde et l'angle, ce qui permet d'isoler la SHG d'autres phénomènes, tels que la filamentation laser. Le signal SHG observé s'avère être non cohérent et donc lié à la diffusion hyper Rayleigh. Le signal SHG détecté augmente linéairement avec la surface des particules, indépendamment de leur forme ou de leur composition. Ces résultats montrent le potentiel de l'ONL, en particulier pour quantifier in situ la surface spécifique d'un aérosol. En donnant accès à cette information qui est cruciale dans l'évaluation de la toxicité des aérosols, le présent travail peut donc ouvrir la voie à une nouvelle classe de diagnostics optiques pour les aérosols.

## ABSTRACT

In the present study the generation of non-linear optical (NLO) effects, such as second harmonic generation (SHG), by black carbon particles and by other types of nanoparticles in aerosol phase is quantified and analysed. The experiments are carried out in an innovative optical setup allowing to analyse the NLO response resolved in time, wavelength and angle, thus having the capability to isolate SHG from other phenomena, such as laser filamentation. The observed SHG signal is shown to be non-coherent and thus related to Hyper Rayleigh Scattering. The detected HRS signal increases linearly with particle surface area, independently of the particle shape or composition. These findings show the potential of NLO, in particular to quantify in situ the specific surface of an aerosol. Giving access to this information which is crucial in the evaluation of toxicity of aerosols, the present work can thus give way to a new class of laser based diagnostics for aerosols.

**MOTS-CLÉS:** Carbone noir, génération de second harmonique, diffusion hyper Rayleigh, optique non linéaire, surface spécifique /**KEYWORDS:** Black carbon, Second harmonic generation (SHG), Hyper Rayleigh scattering (HRS), non-linear optics, Specific surface area

Aerosols of nanoparticles are found in a large variety of natural and human-made processes and act harmfully on the human respiratory and cardiovascular health and contribute to air pollution and global warming (Bond et al. 2013; Jacobson 2010). An example for human-made particles is black carbon (BC - or soot in the combustion field) formed during the incomplete combustion of hydrocarbons, for example in aircraft or car engines, industrial plants and fires. Their experimental in-situ analysis is crucial, either at the source to find ways to reduce their production, in diluted media, as the atmosphere, to study their impact, or to validate theoretical models (formation, aging processes, climate impact,...). Such experiments are however challenging due to the BC particles' complexity and changes during their formation and aging processes. Also, the impact of these particles depends on their structure and composition. In-situ techniques do exist, relying on the particles' optical properties, such as Laser induced incandescence (LII) and light scattering for measuring their volume fraction, size and morphology. Particle structure (i.e. whether the particles are of amorphous, graphitic or organic nature) and morphology can also be studied ex-situ by probing and transmission electron microscopy (TEM) or Raman analysis (Michelsen et al. (2015)). However none of these techniques give access to surface-specific phenomena, which would be extremely interesting for the understanding of particle growth/oxidation phenomena as well as the evaluation of their toxicity, which is directly linked to the particles' specific surface (Al Housseiny et al. (2020)).

An access to these measurands could be offered by non-linear optics (NLO), which have not or very rarely been exploited for the characterization of black/brown carbon aerosols. The physical foundations behind NLO are the following: In general, light interacts with the molecules of a medium, which are excited and themselves emit

and scatter light. With common light sources, the molecules' elastic scattering response is linear to the incident electric field and the scattered light has the same wavelength and polarisation. The term NLO describes the optical response of a medium exposed to very high laser intensities obtained for example by femtosecond lasers (Boyd (2008)). The intensity of the incident light is so high that the medium's response becomes non-linear, leading to effects like the generation of new wavelengths or polarisations, changes in the refractive index of the medium or various multi-photon phenomena (Boyd (ibid.)). One of these effects are second and third harmonic generation (SHG and THG), which are respectively the generation of light at frequencies twice or three times the incident light frequency. While THG can be obtained in all kinds of media, SHG can only be observed in non-centrosymmetric media due to cancellation in symmetric materials or due to symmetry breaking of surfaces. Indeed, in recent studies, SHG has been detected on particles or droplets in aerosol phase due to the prior addition of different types of molecules (Wu et al. (2016)) on their surface. The importance of the surface interactions between the aerosol and the surrounding medium has been confirmed in multiple different studies (Matrokhin et al. 2022)), yet studies directly on black carbon particles in aerosol phase still need to be carried out.

In the presented context, the present study demonstrates and quantifies for the first time with the help of an innovative experimental setup for the possibility of SHG measurements on different types of nanoparticles in aerosol phase due to an exposure to highly intense femtosecond laser light, to put forward the importance of surface related phenomena. It gives way to new potential class of diagnostics allowing to study surface related phenomena in black carbon particles, especially during their formation and aging in the atmosphere or when analysing their toxicity. Indeed, previous studies have shown the importance of the reaction surface on black carbon nanoparticles' on the particle toxicity (Al Housseiny et al. (2020)), and the combination of specific surface area measurement by SHG together with toxicologic measurements as carried out by Juarez-Facio et al. (2022) could be used to directly investigate the link between these two parameters.

## 1. Experiments

The experimental setup is explained in detail by Joret et al. (2025). The non linear optical response of multiple types of carbonaceous nanoparticles in aerosol phase is analysed in the present study, featuring different types of internal structures, different size distributions and particle morphologies. Three types of aerosol generators are used: A miniCAST 5201c soot generator which generates the particle by burning a fuel-rich mixture of propane, nitrogen and air. The particles properties, such as size distribution and internal structure are altered by varying the different gas flows, resulting in the operating points names CAST1, CAST2 and CAST3, that are known as reference particles in the soot community (Bescond et al. (2016)).

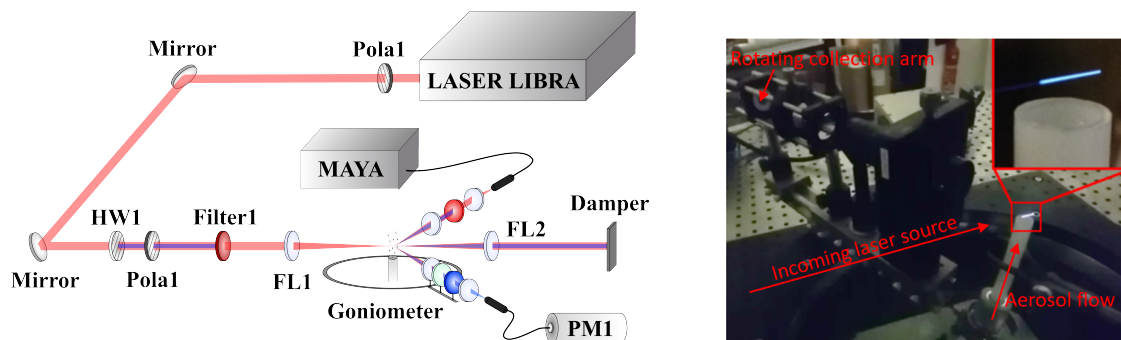


Figure 1. Left: Optical setup using a photomultiplier (PM) tube as a detection. HW: Half-wave plate, FL: Focusing lens, Pola: Polariser, DM: Dichroic mirror. Right: Photograph of interaction between particle jet coming out of the white nozzle and femtosecond laser (800 nm) focused on the nozzle exit. One can see a strong laser filament.

The analysis itself is carried out by the optical setup shown in figure 1, which aims at focusing the high intensity laser beam in the measurement volume and collecting the SHG and other signals resulting from the laser/particles interaction in an angularly, spectrally and temporally resolved way. The setup is motivated by multiple theoretical and experimental studies that have demonstrated an angular dependence of SHG (Wunderlich et al. (2012)) as well as an angular and spectral dependence of other femtosecond laser induced phenomena, such as laser filamentation (Durand (2011)), also shown in figure 1. The used laser source is a Coherent Libra II femtosecond laser, producing a 800 nm linearly (vertical to the laboratory reference frame) polarised light with a pulse duration of 100 fs, at a frequency of 1 kHz and a maximum energy of 3.5 mJ. In order to ensure a stable laser power, the laser is set to its standard working current of 20 A, generating around 1 W of average power. The beam traverses a Half wave plate and polariser assembly (HW1 & Pola1), in which the half wave

plate is rotated to fine-tune the incident laser power on the sample in order to avoid significant ionization in the interaction region. A filter of 800 nm central wavelength and 12 nm spectral width ensures that no SHG results from the light-matter interaction in the half wave plates, as observed in Clark et al. (2014). The beam is then focused by a convex lens of 300 mm focal length into a region of a jet of generated particles, as shown in figure 1. The different mirrors are ultrafast dielectric mirrors, in order to avoid a spectral broadening of the laser beam. The detection is carried out by Hamamatsu - H3378-50 photomultiplier, which features a time response in the order of a few ns, with a fibered end that is mounted on a motor controlled rotation system. An 800 nm IR-blocking filter as well as a filter of either 400 nm or 532 nm is mounted, allowing to obtain quantitative data on SHG and other filament induced phenomena. In parallel, a compact Maya spectrometer is installed at 35 degrees (at the other side of the optical path relative to the rotating detection) and centered at 800 nm with the aim to measure an elastic scattering reference signal.

## 2. Results and discussion

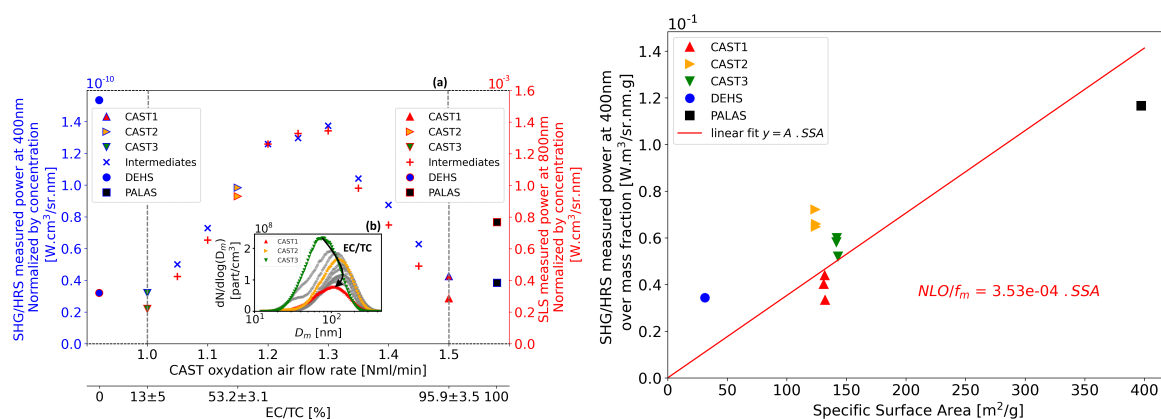


Figure 2. Left: a) SHG/HRS and SLS signal intensity normalised by the particle concentration of CAST soot with different quantities of oxidation air, thus giving a different organic content, carried out at 35 degrees detection angle and 0.2 mJ per pulse laser energy. The figure also includes the signal for PALAS particles, being 100 % amorphous (without any organic compounds) and DEHS being 100 % organic. b) Particle size distributions measured by SMPS for the different studied operating points, including CAST1, CAST2 and CAST3. The black arrow shows the evolution of the size distribution peaks with increasing EC/TC. Right: SHG/HRS signal intensity, normalized by mass fraction, depending on specific surface area, carried out at 35 degrees detection angle and 0.2 mJ per pulse laser energy

The experimental have shown that the present setup is able to measure the incoherent SHG (also called Hyper Rayleigh Scattering - HRS) generated by the interaction between the laser and the particles. The influence of particle inner structure on SHG/HRS intensity is shown in figure 2, depicting the SHG/HRS signal intensity normalised by the particle number concentration for CAST soot with different quantities of oxidation air, thus giving a different organic content, carried out at 35 degrees detection angle and 0.2 mJ per pulse laser energy. The increase of oxidation air flow rate leads to an increase of the elementary carbon to total carbon ratio (EC/TC). The figure also includes the signal for PALAS particles, being 100% amorphous (0 % organic) and DEHS being 100 % organic. While the organic content is only known for CAST1, CAST2 and CAST3 (Bescond et al. (2016)), it is assumed that the CAST points with intermediate oxidation air flow rates in-between will feature organic contents that between the three known points. It can be seen, that both signals, the linear 800 nm signal (SLS - static linear scattering), as well as the non-linear 400 nm signal (SHG/HRS), depend very similarly on the EC/TC ratio, with the maximum being located at around 1.15 Nml/min of air, which corresponds to CAST2. The figure includes a size distribution plot in sub-figure b), which indicates that CAST2 is also the point with the highest aggregate size. Besides, his point also features the highest monomer diameter. It can thus be deduced that the amount of elementary or organic carbon does not have a significant influence on the SHG/HRS, but the increase in SHG/HRS seems to be completely related to an increase in aggregate and/or monomer size. The figure also shows (on the right) the measured SHG/HRS signals for the three CAST points, as well as PALAS and DEHS, all normalized by the nanoparticle mass fraction, are plotted against the specific surface area in figure 2. The different measurements align roughly along a straight line, with a slope of  $3.53 \cdot 10^{-4} W.m/sr.nm.g.m^2$ , independently of the particles' inner structure or morphology. This observation is even more interesting when taking into account the fact that the DEHS particles are particularly large compared to the other studied aerosols. These observations confirm the findings in literature (Beer et al. (2011)) which indicate that SHG in nanoparticles is generated by symmetry breaking on the surface of the nanoparticles and not at the molecular or atomic level.

### 3. Conclusion

The present study allowed to demonstrate the feasibility of an SHG and/or HRS measurement and analysis setup on different types of nanoparticles (black carbon, DEHS droplets, arc generated carbon) in-situ in aerosol phase. The results show that the developed experimental setup is suitable and sufficiently sensitive and robust to analyse the NLO response of aerosols and that the non-linear signals are associated with incoherent SHG, also named Hyper Rayleigh Scattering (HRS). The signals are shown to be proportional to the specific surface area, while the composition does not seem to play a significant role. With the linear dependence on particle surface, the here presented setup can give way to a new class of diagnostics, which are capable of measuring the aerosol's specific surface area and thus help to evaluate the aerosols' toxicity.

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