Second Harmonic Scattering from Metallic Nanoparticles in a Random Medium

Naima Khebbache,[1,2] Anthony Maurice,[1] Smail Djabi,[2] Isabelle Russier-Antoine,[1]

Christian Jonin,[1] Sergey E. Skipetrov,[3,4] Pierre-François Brevet[1]

[1]*Univ. Lyon, Institut Lumière Matière, ILM UMR CNRS 5306, Université Claude Bernard Lyon 1, Campus LyonTech - La Doua, 10 Rue Ada Byron, 69622 Villeurbanne, France*

[2]*Institut d'Optique et Mécanique de Précision, Université de Sétif 1, Algérie*

[3]*Université Grenoble Alpes, LPMMC, F-38000 Grenoble, France*

[4]*CNRS, LPMMC, F-38000 Grenoble, France*

Transmission Electron Microscopy (TEM) and size distribution of 80 nm diameter silver nanoparticles :

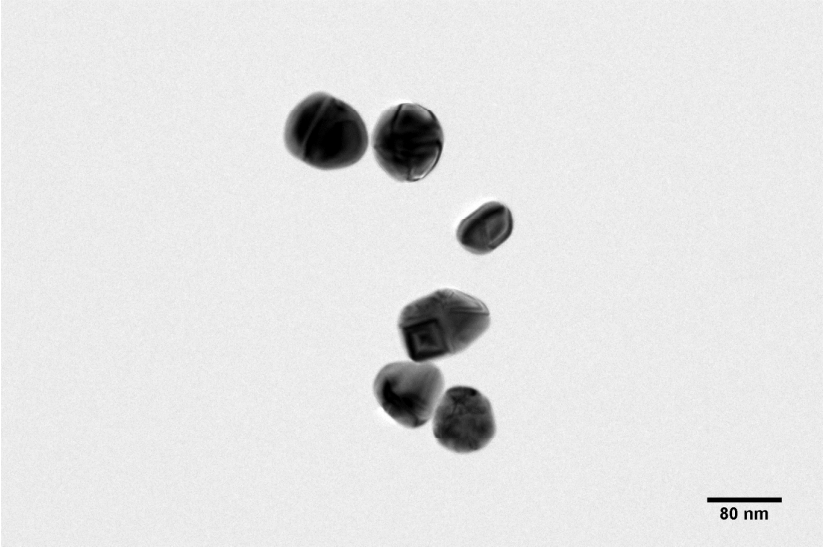

Figure S1 : Transmission Electron Microscopy (TEM) of the silver nanoparticles.

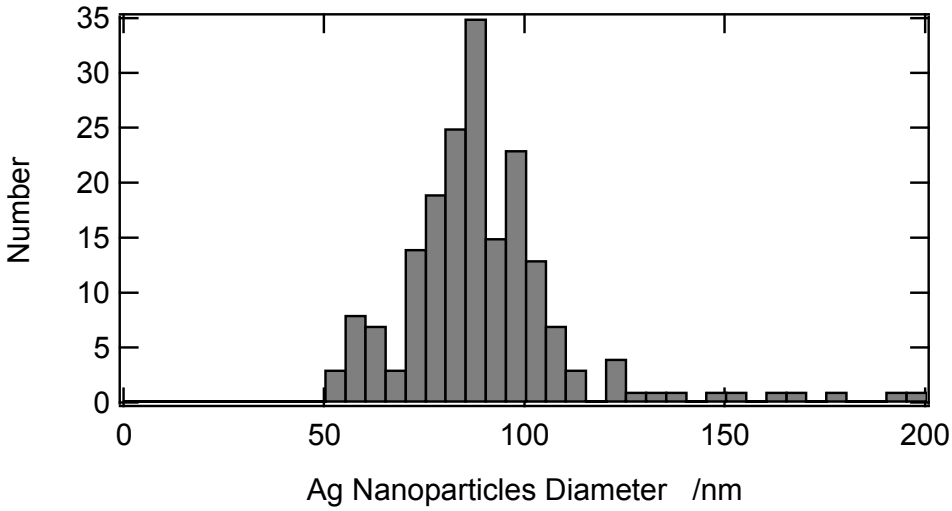

Figure S2 : Size distribution of the silver nanoparticles as measured from the TEM images using 189 nanoparticles.

Extinction spectrum of 80 nm diameter silver nanoparticles :

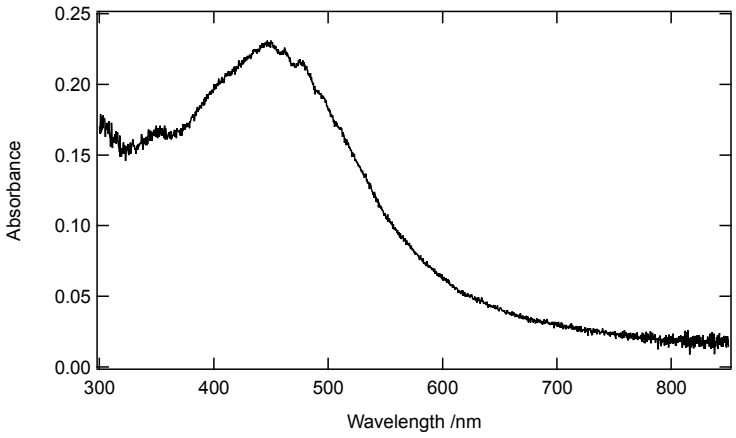

Figure S3 : Extinction spectrum of an aqueous solution of silver nanoparticles with a diameter of 80 nm and a concentration of $7x10^{10}$ cm^{-3}

Dynamic Light Scattering (DLS) determination of the size distribution of 203 nm diameter latex nanoparticles

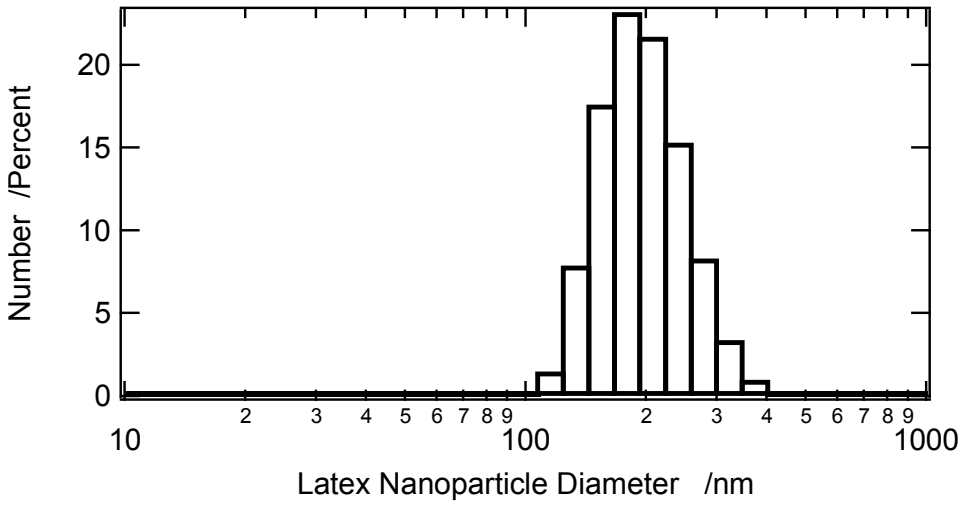

Figure S4 : Size distribution of the latex nanoparticles as measured by Dynamic Light Scattering (DLS).

Decay rates

The SHG intensity $I^{(2\omega)}$ scattered from a suspension of silver nanoparticles with concentration N writes as :

$$I^{(2\omega)} = GN < \beta^2 > \left(I^{(\omega)}\right)^2 exp[-A] \quad \text{(S1)}$$

where G is a general constant, β is the nanoparticles hyperpolarizability and $I^{(\omega)}$ is the input fundamental intensity. The brackets indicate an averaging procedure over all orientation taken by the nanoparticles and A is the decay rate due to extinction, here limited to scattering due to the presence of the latex nanospheres. Hence, A writes simply as :

$$A = \left(\sigma^{(2\omega)} + 2\sigma^{(\omega)}\right)Lc \quad \text{(S2)}$$

introducing the respective extinction cross-sections at the fundamental and harmonic frequency $\sigma^{(\omega)}$ and $\sigma^{(2\omega)}$and the concentration c of latex particles. We can then simply define the latex nanospheres concentration corresponding to an absorbance of unity as

$$c_{decay}^{(2\omega)} = 1/\left[\left(\sigma^{(2\omega)} + 2\sigma^{(\omega)}\right)L\right] \quad \text{(S3)}$$

in order to compare with the different total extinction cross-sections, either obtained from Mie theory or extracted from the fits to experimental data.

Mean Free Paths

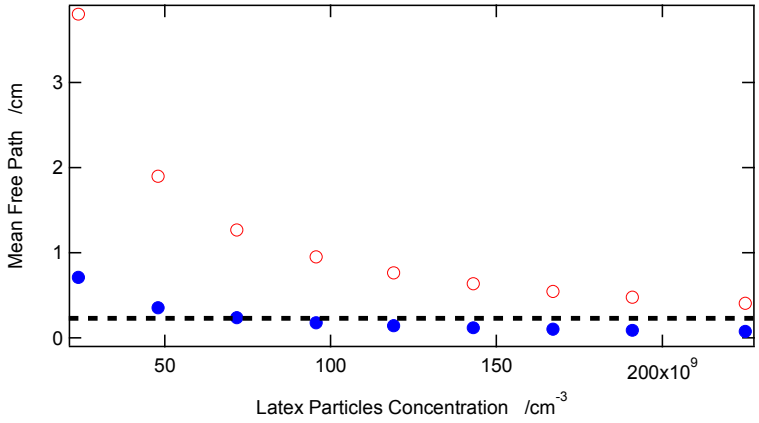

Figure S5 : Photon mean free path as a function of the latex particle concentration (empty disks) at the fundamental wavelength of 800 nm and (filled disks) at the harmonic wavelength of 400 nm. The dashed line indicates the ballistic path length L.

Scattering Cross-Sections for Latex Nanospheres from Mie Theory

The calculation of the latex nanospheres nanoparticles were computed using the following parameters :

Latex nanosphere optical index	1.58
Aqueous solution optical index	1.34
Latex nanospheres diameter	203 nm

The calculations were performed with the standard open source MatLab package *"MatScat", available at https://it.mathworks.com/matlabcentral/fileexchange/36831-matscat*. We disregarded dispersion for the optical indices. The observed values thus obtained are :

Latex nanospheres cross-section at 800 nm : 1.10×10^{-11} cm^2

Latex nanospheres cross-section at 400 nm : 7.37×10^{-11} cm^2

To investigate the variability of the 400 nm Latex nanospheres Cross-section at 400 nm, we performed other calculations with slight changes in the input parameters. For instance, the following set of parameters :

Latex nanosphere optical index 1.57

Aqueous solution optical index 1.34

Latex nanospheres diameter 200 nm

led to the cross-sections below :

Latex nanospheres cross-section at 800 nm : 0.93×10^{-11} cm^2

Latex nanospheres cross-section at 400 nm : 6.28×10^{-11} cm^2

Further refinements can be obtained by introducing the optical index dispersion.

SHG intensity in absence and presence of silver nanospheres

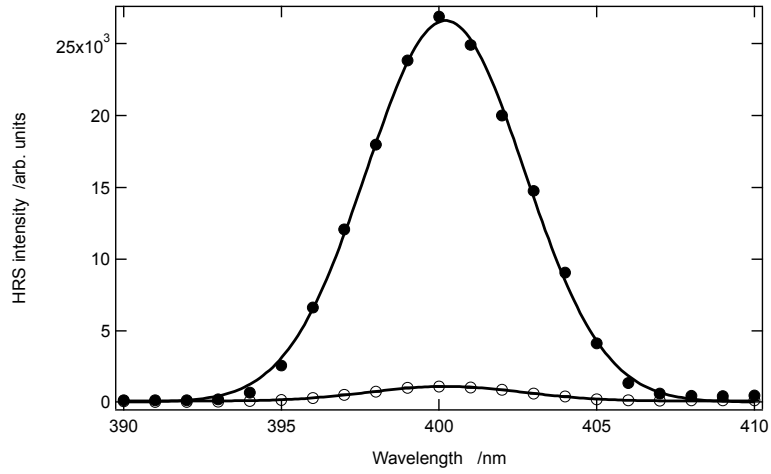

Figure S6 : SHG intensity measured as a function of the detection wavelength for a fundamental wavelength of 800 nm and a 3.1×10^{11} cm^{-3} latex nanospheres concentrations. (Filled disks) in presence of a 7×10^{10} cm^{-3} silver nanospheres concentration, (empty disks) in absence of silver nanoparticles.