Size dependence of the surface plasmon enhanced second harmonic response of gold colloids: towards a new calibration method

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Hyper Rayleigh scattering in solution is used for the determination of the first order hyperpolarizability β_{colloid} of gold colloids in the size range 5–22 nm; these hyperpolarizabilities are found to range from 0.60×10^{-25} esu for 5 nm diameter colloids to up to 16.6×10^{-25} esu for 22 nm diameter colloids at the second harmonic wavelength of 532 nm; the strong size dependence of the hyperpolarisabilities reported here suggests that hyper Rayleigh scattering experiments can efficiently be used to calibrate the particle diameter of colloidal suspensions.

Gold colloids have been extensively investigated in the past owing to the potential applications of these particle suspensions. As a result, a wide range of techniques has been used for their characterisation, and in particular optical and microscopy techniques. For example, UV–VIS absorption spectroscopy and IR spectroscopy have been used to investigate the electronic properties of the particles. Also, transmission electron microscopy (TEM) measurements for deposited particles were performed to determine both the mean diameter and the size distribution of the preparations.[1,2] Recently, we have used the technique of optical surface second harmonic generation (SSHG) as a new technique for the study of noble-metal nanoparticles in diverse environmental conditions.[3,4] Indeed, it has been shown that this nonlinear optical technique is very sensitive to the surface plasmon excitation, the second harmonic signal being resonantly enhanced when the harmonic wavelength is tuned in the vicinity of the plasmon resonance. The hyper Rayleigh scattering (HRS) technique has already been used in the past for the determination of the absolute hyperpolarisability of compounds, in particular silver and gold colloids as well as SiO_2 particles.[5–7] Here, we report the use of the technique of HRS to investigate the size evolution of the first hyperpolarisability β_{colloid} for colloids with sizes ranging from 5 to 22 nm. Within this size range, no significant surface plasmon peak shift occurs, a necessary requirement for single wavelength measurements. From the measurements and the simplicity of the experimental arrangement, we also propose this second order nonlinear technique as an efficient calibration technique for the determination of the size of nanoparticles in solution.

Colloidal gold nanoparticles with a mean particle diameter of 19 and 22 nm were prepared using the method of Turkevich *et al.*[8] Gold colloids of mean diameter 4.9 and 8.6 nm were purchased from Sigma.[9] TEM photographs of each colloidal preparation were taken and the average particle diameter along with the standard deviation were determined from at least 200 particles. The UV–VIS absorption spectrum of the gold colloid solutions presented a strong absorption band with a maximum at *ca.* 520 nm except for the 4.9 nm diameter one. Indeed, for this particle diameter, the plasmon resonance is damped owing to the size effects and therefore swamped by the sharp increase of the absorbance due to interband transitions, appearing as a mere shoulder blue shifted with respect to the true resonance location. Table 1 gives the size and the linear optical characteristics of the four gold colloidal solutions used.

The light source for the HRS experiments consisted of a Q-switched Nd : YAG laser providing pulses of 5 ns and < 4 mJ, at a repetition rate of 10 Hz at 1064 nm. The beam was focused into a 1 × 1 cm spectrophotometric cell and the experiments were performed well below the threshold for any undesirable adverse effects. A small fraction of the incident beam was directed onto a fast photodiode to monitor the intensity stability. The HRS light was collected at an angle of 90° from the incident direction by a lens and a mirror. Spectral discrimination of the second harmonic light from its linear counterpart was accomplished by two low-pass BG38 near IR filters and a 3 nm bandwidth interference filter peaked at 532 nm. The second harmonic light was then detected with a photomultiplier tube and the signal was integrated with a boxcar averager. The quadratic dependence of the HRS signal from the gold colloid solutions with the incident light intensity was always checked beforehand and the experimental conditions were first assessed on *p*-nitroaniline (pNA) in methanol. With the known value of $\beta_{\mathrm{MeOH}} = 0.69 \times 10^{-30}$ esu, we extracted an absolute value of $\beta_{\mathrm{pNA}} = (31 \pm 7) \times 10^{-30}$ esu in very good agreement with previous HRS measurements giving a value of $\beta_{\mathrm{pNA}} = (34 \pm 4) \times 10^{-30}$ esu.[10]

The HRS signal $S_{2\omega}$ dependence on the incident light intensity I_0 is given according to

$$S_{2\omega} = GB^2 I_0\, 10^{-A} \tag{1}$$

where G is a proportionality constant and A the absorbance at the harmonic wavelength. For the two component system at hand:

$$B^2 = \langle N_{\mathrm{colloid}}\, \beta_{\mathrm{colloid}}{}^2 + N_{\mathrm{H_2O}}\, \beta_{\mathrm{H_2O}}{}^2 \rangle \tag{2}$$

where N_{colloid} and β_{colloid} are respectively the number density and the first hyperpolarisability of the aqueous colloids and $N_{\mathrm{H_2O}}$ and $\beta_{\mathrm{H_2O}}$ respectively the number density and the first hyperpolarisability of water. The factor 10^{-A} accounts for the losses due to linear absorption of the scattered light by the colloidal solution at 532 nm and was determined from the UV–VIS spectra.

HRS measurements at different number density of the 22 nm diameter colloids by dilution of the initial solution were first performed and the results are displayed in Fig. 1. A linear

Table 1 Size (mean diameter $\langle D \rangle$ and dispersion), initial concentration, maximum of linear absorbance $\lambda_{\max}$ and first hyperpolarizability β_{colloid} of gold colloids

Gold colloid	$\langle D \rangle$/nm	Dispersion/nm	Initial concentration/colloid dm^{-3}	$\lambda_{\max}$/nm	$\beta/10^{-25}$ esu
a	4.9	0.7	4.4×10^{16}	508[a]	0.60 ± 0.09
b	8.6	1.0	6.9×10^{15}	518	2.0 ± 0.3
c	19.0	1.5	6.4×10^{14}	520	13.1 ± 2.0
d	22.0	1.7	4.6×10^{14}	520	16.6 ± 2.5

[a] Location of the shoulder of the absorbance spectrum (see text).

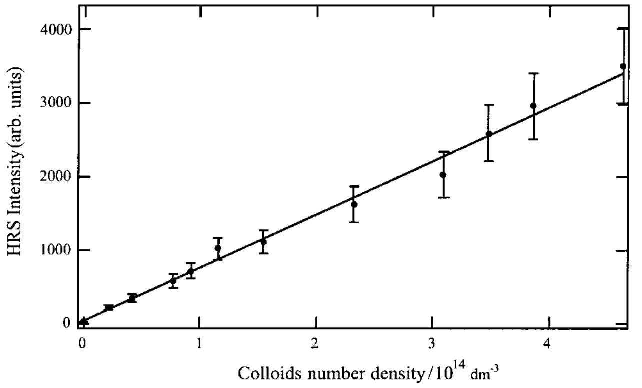

Fig. 1 HRS signal corrected for the linear absorbance at the harmonic wavelength *versus* the number density of the 22 nm gold colloids (sample d).

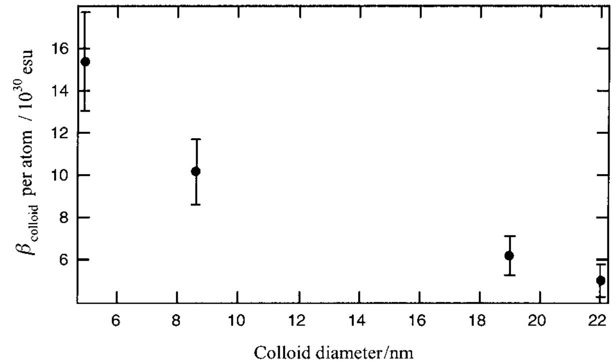

Fig. 2 Absolute value of the first hyperpolarizability $\beta_{colloid}$ calculated per gold atom in the colloid *versus* the mean diameter of the gold colloids.

behaviour is observed as expected after the correction for the absorption, and from the slope, the first hyperpolarisability of the 22 nm colloids $\beta_{colloid}$ is calculated to be $(16.6 \pm 2.5) \times 10^{-25}$ esu on the basis of $\beta_{H_2O} = 0.56 \times 10^{-30}$ esu.[7] Then, using this solution as an external reference, the first hyperpolarisability of the other colloids of size 4.9, 8.6 and 19 nm were obtained using the concentration of the initial solutions. The data are reported in the last column of Table 1. A 30-fold increase in the magnitude of the first hyperpolarisability is observed for a five-fold increase in diameter only. Such a large magnitude is however expected as it stems from the coupling between the SH field with the surface plasmon.[4] These values are rather different from the ones recently reported for 13 nm diameter gold colloids but are of the same order of magnitude as that obtained near resonance for silver colloids.[5,7] Fig. 2 shows the size dependence of the hyperpolarisability as calculated per atom, obtained dividing the value given in Table 1 by the number of gold atoms in the colloid. It is observed that the hyperpolarisabilities per atom decreases by a factor of 10 over the five-fold increase of the particle in diameter. The origin of such a behaviour may stem from the saturation of the collective effect contribution to the nonlinear optical activity when the colloid diameter gets too large.

These experiments emphasise the strong dependence of the first hyperpolarisability of the gold colloids on the particle diameter. As a result, the SH signal exhibits a 1000 fold increase in intensity for a five-fold increase in particle diameter only. For instance, for the 19 and 22 nm diameter colloids, the reported increase in the HRS signal is *ca.* 50% for a mere 16% increase in diameter. Therefore, in view of the simplicity of the experimental apparatus for these experiments, the HRS technique offers an efficient alternative to particle size determination with an external reference.

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