

## Electric dipole origin of the second harmonic generation of small metallic particles

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Polarization-resolved hyper Rayleigh scattering experiments were performed on gold metallic nanoparticles. These results unambiguously indicate that the second harmonic generation process of a nanoparticle is of pure electric dipole origin for the smallest particles as opposed to pure electric quadrupole, and that retardation effects come into play for larger sizes. It is furthermore demonstrated that this electric dipole emission at the harmonic frequency is due to a deviation of the particle shape from that of a perfect sphere and not from defects in the crystalline structure of the particle.

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Optical properties of coinage-metal nanoparticles have been extensively investigated over the past years. The main reason for such an extensive use is the domination of the optical spectra of these nanoparticles by the collective excitation of the free conduction-band electrons, known as the surface plasmon (SP) resonance. This is indeed true in linear optics for the photoabsorption spectrum, for instance, but is also valid in nonlinear optics for the first and the second hyperpolarizability of the particles.<sup>1-3</sup> The SP resonance enhancement hence yields large values for the measured hyperpolarizabilities of the nanoparticles. Measurements of the absolute magnitude of the first hyperpolarizability of silver and gold nanoparticles have thus received a lot of attention, since the phenomenon whereby two photons at the fundamental frequency are converted into one photon at the harmonic frequency is forbidden in media with inversion symmetry. The question of the origin of the first hyperpolarizability from small metallic particles has been raised in the past with, to date, no definitive experimental answer. Theoretical calculations, based on the assumption of nanoparticles of finite size with a perfect spherical shape, have been proposed, supporting an origin of the response of an electric quadrupole nature due to the combined centrosymmetry of the crystalline structure of the material and the centrosymmetry of the nanoparticle shape.<sup>4-8</sup> The main result of this theoretical description is the excitation of an effective dipole, along the direction of the propagation of the incident light beam, and of an effective vector quadrupole, along the direction of the incoming fundamental field. Both contributions arise from retardation effects, the effective dipolar one from the nonlocal excitation of the surface nonlinearity and the effective quadrupolar one from the nonlocal radiation of the surface nonlinearity. Both contributions scale with the 3rd power of the diameter of the nanoparticles, and as a result, the second harmonic (SH) intensity from a single nanoparticle scales with the 6th power of the nanoparticle's diameter. This overall quadrupole origin of the SH intensity with two contributions implies further dedicated patterns as a function of the azimuth angle of collection and the input polarization angle. Indeed, one of the interesting features of this theoretical model is that even though the two contributions have the same comparable weight, their origins are different, and in particular their resonance frequencies are different. The first

effective dipole contribution is intrinsically of electric dipole nature in radiation at the harmonic frequency, and therefore its resonance is located at the frequency  $\Omega = 2\omega$  such that the real part of the quantity  $l\varepsilon(\Omega) + (l+1)\varepsilon_m(\Omega)$  with  $l=1$  vanishes. In this expression,  $\varepsilon(\Omega)$  is the dielectric constant of the metal at the frequency  $\Omega$ ,  $\varepsilon_m(\Omega)$  is that of the surrounding medium at the same frequency, and  $l$  is the order of the mode, namely,  $l=1$  for the dipole mode and  $l=2$  for the quadrupole mode. Hence, the second effective quadrupole contribution, which is of quadrupole origin in radiation, is slightly shifted towards higher energies. Spectra recorded for gold nanoparticles by hyper Rayleigh scattering (HRS) or second harmonic generation (SHG) have all exhibited the dipolar Mie resonance. For gold nanoparticles in an aqueous solution, the location of the dipolar SP resonance is observed around 2.38 eV, with small shifts attributable to small changes in the environment or the particle sizes. Recently, experiments on larger silver nanoparticles dispersed in an aqueous solution have been performed by HRS.<sup>2</sup> The data clearly showed the dipolar SP resonance as well as the quadrupolar SP resonance, located at a slightly higher energy, in agreement with the theoretical predictions. Further experimental evidence of these observations was obtained using a slit arrangement modulating the azimuth angle dependence of the HRS intensity integrated over a large solid angle. These results have reinforced the validity of the assumptions of the model based on the perfect spherical shape of the particles and a nonlinearity arising from the breakdown of the centrosymmetry at the surface of the particles. There still remains a discrepancy between the theory and the experimental data regarding the dependence of the first hyperpolarizability with the diameter of the nanoparticles.<sup>9</sup>

In order to resolve these ambiguities, we undertake HRS experiments on gold nanoparticles monodispersed in an aqueous solution and use a complete polarization resolution of the HRS signal instead of an azimuth angle dependence. Indeed, different patterns are expected as a function of the incident polarization angle for a dipole or a quadrupole origin of the HRS signal. As opposed to the previous theoretical predictions, we demonstrate below that the new data unambiguously support the origin of the HRS signal arising from an electric dipole. However, it is shown that there exists no

contradiction with the measurements performed in the past, and it explains the size dependence observed in the range of 8–22 nm for gold nanoparticles.

The gold nanoparticles are purchased from Sigma-Aldrich (USA, gold nanoparticles, 10 and 20 nm diameter) and British Biocell International (United Kingdom, gold nanoparticles, 50, 80, 100, and 150 nm diameter) and are used as received. The HRS experimental apparatus consists of a femtosecond Ti:Sa oscillator delivering at a fundamental wavelength of 800 nm pulses with a duration of 150 femtoseconds and operating at a repetition rate of 76 MHz. The fundamental beam is focused by a microscope objective into a quartz spectrophotometric cell containing the monodispersed nanoparticles, and the HRS light is collected at a right angle by a 5-cm-long focal-length lens through a monochromator and detected with a cooled photomultiplier in photon counting mode. Filters are used to remove any unwanted light at the fundamental or the harmonic frequency. All data are corrected for any laser-power drifts, and the duration of the laser pulses are always checked. Finally, the fundamental beam is chopped at 100 Hz to enable gated photon counting, allowing automatic subtraction of the noise level. The fundamental input beam is linearly polarized and the input angle of polarization  $\gamma$ , defined as the angle between the direction of the electric field and the  $x$  axis, is selected with a rotating half-wave plate. The configuration of the experimental setup is such that the fundamental beam is propagating in the  $z$  direction with the electric field polarized in the  $\{x, y\}$  plane with the polarization angle  $\gamma$ . The harmonic light is collected along the  $y$  direction, at a right angle from the propagation direction of the fundamental beam and after passing through an analyzer selecting the output polarization state.

The initial experiments consist of the measurement of the linear dependence of the HRS intensity with the number density of particles in the solution and with the square of the fundamental intensity. Indeed, the HRS intensity is given by

$$I_{\text{HRS}} = G(N_S \beta_S^2 + N \beta^2) I^2 \exp(-\epsilon N l), \quad (1)$$

where  $I$  is the fundamental intensity,  $N$  and  $\beta$  are the number density and the hyperpolarizability of a nanoparticle, respectively, and  $\epsilon$  is the molecular extinction coefficient due to the self-absorption of the HRS signal in the cell, the width of which is  $l$ .  $G$  is a general factor embedding all geometrical factors as well as absolute constants. The measurement of the HRS intensity in the absence of the nanoparticles provides an internal reference for the extraction of the absolute values of the first hyperpolarizabilities, knowing  $N_S$  and  $\beta_S$  as the number density and the hyperpolarizability of the solvent molecules. In order to achieve this absolute calibration, the spectrum around the HRS line is first determined to subtract the photoluminescence background, which could account for up to 50% of the total photon counts collected at the SH frequency. This subtraction procedure is valid since HRS and photoluminescence are two incoherent processes. For the polarization-resolved HRS intensity measurements, a similar procedure was performed. Because of the photoluminescence background, a polarization curve is registered off the HRS line, 20 nm on the blue side of the HRS line, in order to subtract the input polarization dependence of the photolumi-

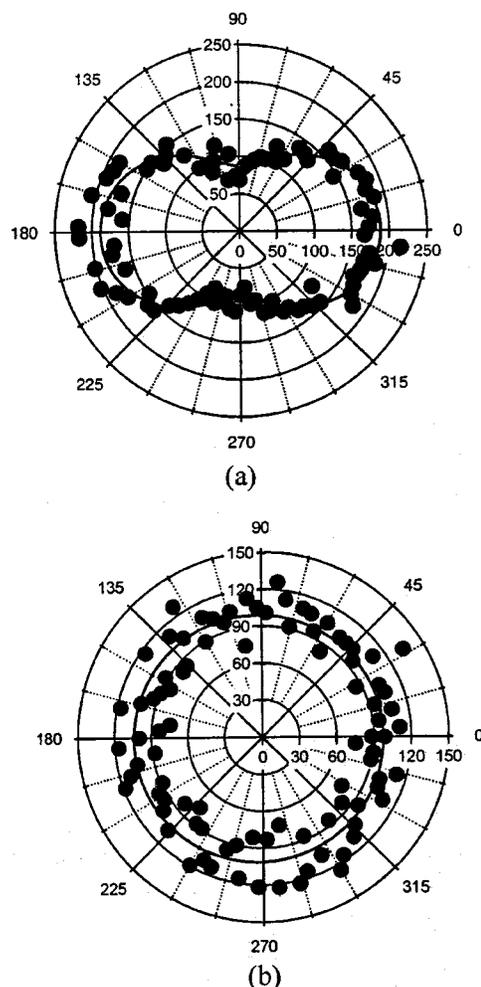


FIG. 1. Polar plot of the input-polarization-angle dependence of the output-HRS intensity from 20-nm-diameter gold nanoparticles polarized (a) along the  $x$  direction and (b) along the  $z$  direction. The solid line is a fit to Eq. (2).

nescence. Figure 1 reports the polarization-resolved HRS intensity for the 20-nm-diameter gold nanoparticles for the output harmonic light polarized along the  $x$  direction. The pattern observed is that of the classical emission pattern of an electric dipole as a function of the polarization of the excitation field. This pattern is in complete disagreement with the theoretical calculations which predicted for the  $x$  polarized output curve a quadrupolar-type pattern with four lobes.<sup>8</sup> Indeed, for a geometrical configuration where the collection is at a right angle to the excitation, the expected  $x$ -polarized output is solely a function of the effective quadrupolar contribution. The data presented in Fig. 1 can be fitted with the classical polarization dependence expected for an electric dipole radiation at the harmonic frequency, as for molecular systems,

$$I_{\text{HRS}}^{\Gamma}(\gamma) = a_{\Gamma} \cos^4 \gamma + b_{\Gamma} \cos^2 \gamma \sin^2 \gamma + c_{\Gamma} \sin^4 \gamma, \quad (2)$$

where  $a_{\Gamma}$ ,  $b_{\Gamma}$ , and  $c_{\Gamma}$  are real coefficients. In Eq (2),  $\Gamma$  is defined as the outgoing direction, namely,  $\Gamma = X(V), Z(H)$  for the vertically and horizontally polarized light, respectively.

The equality  $a_x + c_x = b_x$  also applies because of the isotropy of the liquid phase and the cylindrical symmetry of the experimental configuration. The pattern observed for the 20-nm-diameter gold nanoparticles is similar to the pattern observed for molecular systems.<sup>10,11</sup> Quadrupolar molecular systems have also been described in the past, but the expected patterns for these systems do not follow the one reported here.<sup>12</sup> It is therefore concluded that the origin of the HRS signal from small metallic nanoparticles is of pure electric dipole origin. The depolarization ratio is found to be  $c_x/a_x = 0.47 \pm 0.03$ . For the SH output polarized along the horizontal direction, one also finds  $2a_z = 2c_z = b_z$  with  $c_x = c_z$ , in agreement with the pure dipole nature of the SH radiation (see Fig. 1).

There are two main possibilities for such a dipolar origin of the HRS signal from nanoparticles. First, the assumption of a perfect spherical shape for the particles may not be valid, and this deviation from the perfect case yields a breaking of the centrosymmetry of the particles. As a result, the nanoparticle can radiate at the harmonic frequency like a dipole. It is important to stress here that in principle any phenomena destroying the perfect spherical symmetry of the particles are allowed. From transmission electron microscopy, it is rather obvious that metallic particles are not strictly spherical. However, surface states arising from surface defects or from an organic layer adsorbed at the surface of the particles would be an equally valid source of the destruction of the pure spherical symmetry. Second, the gold nanoparticles are not perfect nanocrystals, and therefore they contain defects in their crystalline structure. The assumption of particles made of centrosymmetric material is therefore no longer valid, and the particles radiate like dipoles at the harmonic frequency. The polarization-resolved HRS intensity observed in the two cases is similar, but a way to distinguish between the two origins is the size dependence of the first hyperpolarizability. Indeed, if the origin of the signal is a deviation from a perfect sphere, then the hyperpolarizability will scale with the square of the particle diameter, since the nonlinearity arises from the surface. On the other hand, if the origin of the signal arises from defects within the nanocrystal, then a scaling with the volume of the particle is expected, at least for small-diameter particles when the defects do not start to counteract themselves because of a random orientation. Figure 2 gives the size dependence of the square root of the HRS intensity for the input fundamental beam polarized along the  $x$  direction as a logarithmic plot. A linear fitting procedure yields a slope of  $1.9 \pm 0.2$ . This result thus supports an origin of the electric dipole hyperpolarizability arising from a deviation of the nanoparticle shape from that of a perfect sphere. This power dependence of the HRS intensity on the diameter of the nanoparticles is now in agreement with previous data obtained in the range of 8–22 nm diameter.<sup>9</sup>

A notable deviation from the pure dipolar pattern for the HRS intensity with the input angle of polarization is observed for large particle diameters, in particular those above 80 nm, where the polarization plots of the HRS intensity with the fundamental angle of polarization clearly exhibit four lobes (see Fig. 3). In this range, the diameters are no longer much smaller than the wavelength of the fundamental

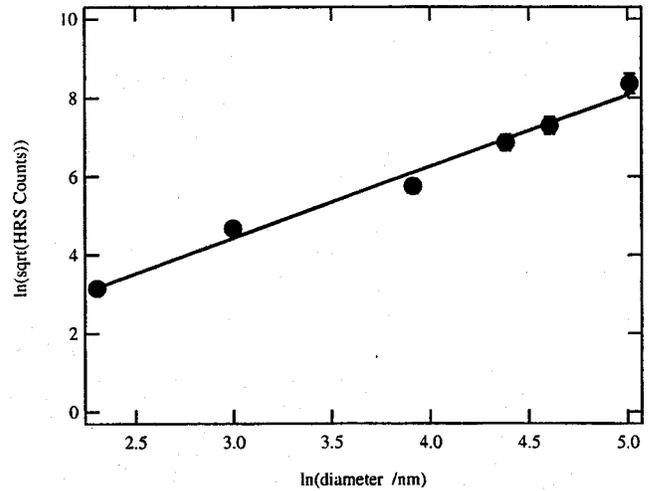


FIG. 2. Logarithmic plot of the square root of the HRS intensity, recorded for both the input fundamental and the output harmonic intensities polarized along the  $x$  direction versus the diameter of the nanoparticles.

light. Indeed, for the 20-nm-diameter particles, this ratio is still of the order of  $\frac{1}{40}$ , whereas for the 80-nm-diameter particles it has increased up to  $\frac{1}{10}$ . Thus retardation effects cannot be discarded anymore. The quadrupolar pattern exhibited by the polarization-resolved curves of the HRS intensity is due to retardation effects with the dipolar contribution still present as observed through the deviation of the four-lobe pattern from that of an exact fourfold quadrupolar symmetry. In order to properly account for this plot, a complete model is derived, encompassing not only the usual response of pointlike dipolar and quadrupolar molecules but also that of larger objects such as nanoparticles. To do so, the electric field collected at position  $\vec{r}$  and radiated by a single nanoparticle is taken as the coherent superposition of the spherical

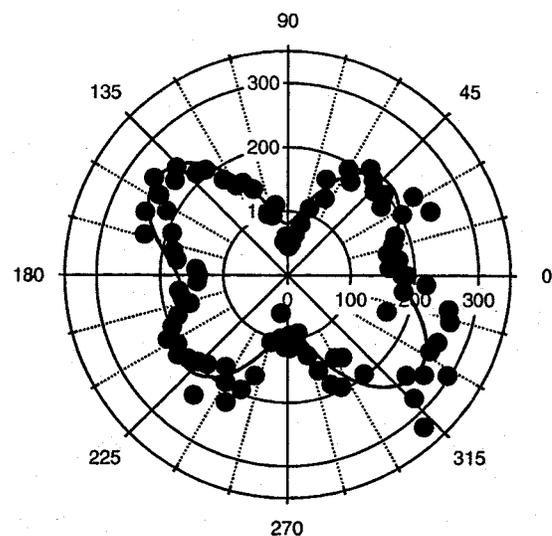


FIG. 3. Polar plot of the input-polarization-angle dependence of the output-HRS intensity from 80-nm-diameter gold nanoparticles polarized along the  $x$  direction. The solid line is a fit to the general form of Eq. (3).

waves radiated by an infinite number of pointlike dipoles at a location  $\vec{r}'$ , radiating at the harmonic frequency  $2\omega$  and sitting at the surface of the particle. These dipoles are excited by the fundamental field taken as the cavity field inside the particle. Furthermore, the field radiated at the harmonic frequency is taken as the superposition of the radiation field produced by the local surface dipole, taking into account the polarization field inside the cavity at the harmonic frequency. (The details of the model will be reported elsewhere.) Doing so, the introduction of the retardation effects at both wavelengths leads to an extended form of the HRS intensity, as given by Eq. (3), where the two last terms must be introduced as compared to Eq. (2):

$$I_{\text{HRS}}^{\Gamma}(\gamma) = a_{\Gamma} \cos^4 \gamma + b_{\Gamma} \cos^2 \gamma \sin^2 \gamma + c_{\Gamma} \sin^4 \gamma + d_{\Gamma} \cos^3 \gamma \sin \gamma + e_{\Gamma} \cos \gamma \sin^3 \gamma. \quad (3)$$

To the first and the second order in the scale factor  $x=R/\lambda$ , where  $R$  is the radius of the nanoparticle and  $\lambda$  the fundamental wavelength, all coefficients have similar expressions, being linear combinations of the fourth and the fifth powers of  $x$ . For instance,  $a_{\Gamma}$  has an expression of the form  $a_{\Gamma} = a'_{\Gamma} x^4 + a''_{\Gamma} x^5$ . However,  $d_{\Gamma}$  and  $e_{\Gamma}$  are proportional to  $x^5$  only. Thus a more correct expression for the form of the HRS intensity with the diameter of the nanoparticles is a combination of the fourth and the fifth powers of the nanoparticle's diameter. In this case, the agreement with the experimental

data is improved for large diameters. Furthermore, the polarization-resolved HRS intensity of the 80-nm-diameter nanoparticles can then be accurately fitted with the extended form of Eq. (3) (see Fig. 3). Because neither the dipolar nor the quadrupolar response dominates, the resulting figure is a mixture of pure dipolar and pure quadrupolar radiation patterns.

In conclusion, it is demonstrated that the first hyperpolarizability of small metallic nanoparticles is of electric dipole origin, and that it arises from a deviation of the shape of the nanoparticles from that of a perfect sphere. A general framework is given that explains all previous data on the size dependence of the absolute values of the hyperpolarizability of the particles as well as the polarization-resolved HRS intensity for small and large diameter particles. In the latter case, retardation effects start to play a dominant role. The general model is also in agreement with the data reported in the past, namely, the wavelength dependence and the size dependence of the hyperpolarizability of the metallic nanoparticles.

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<sup>1</sup>U. Kreibig and M. Vollmer, in *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).

<sup>2</sup>E. C. Hao, G. C. Schatz, R. C. Johnson, and J. T. Hupp, *J. Chem. Phys.* **117**, 5963 (2002).

<sup>3</sup>I. Russier-Antoine, C. Jonin, J. Nappa, E. Benichou and P. F. Brevet, *J. Chem. Phys.* **120**, 10748 (2004).

<sup>4</sup>G. S. Agarwal and S. S. Jha, *Solid State Commun.* **41**, 499 (1982).

<sup>5</sup>D. Oestling, P. Stampfli, and K. H. Bennemann, *Z. Phys. D: At., Mol. Clusters* **28**, 169 (1993).

<sup>6</sup>X. M. Hua and J. I. Gersten, *Phys. Rev. B* **33**, 3756 (1986).

<sup>7</sup>V. Brudny, B. S. Mendoza and W. L. Mochan, *Phys. Rev. B* **62**, 11 152 (2000).

<sup>8</sup>J. I. Dadap, J. Shan, K. B. Eisenthal, and T. F. Heinz, *Phys. Rev. Lett.* **83**, 4045 (1999).

<sup>9</sup>P. Galletto, P. F. Brevet, H. H. Girault, R. Antoine, and M. Broyer, *Chem. Commun. (Cambridge)* **1999**, 581.

<sup>10</sup>K. Clays and A. Persoons, *Phys. Rev. Lett.* **66**, 2980 (1991).

<sup>11</sup>S. Brasselet and J. Zyss, *J. Opt. Soc. Am. B* **15**, 257 (1998).

<sup>12</sup>S. Kielich, M. Kozierowski, Z. Ozgo, and R. Zawodny, *Acta Phys. Pol. A* **45**, 9 (1974).