

Hyper-Rayleigh scattering from silver nanoparticles

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We experimentally demonstrate for the first time the existence of distinguishable contributions to hyper-Rayleigh scattering (HRS) intensities from Ag nanoparticles arising from electric-dipole and electric-quadrupole plasmon resonances at the emitted wavelength. We show that these results can be successfully modeled using an electromagnetic theory of HRS which assumes a surface-induced nonlinear susceptibility. In addition, we show that simple angular distribution measurements may be used to determine the relative sizes of the dipole and quadrupole contributions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1510439]

I. INTRODUCTION

Metallic nanoparticles have attracted substantial interest because of their size and shape-tunable optical and electronic properties.^{1,2} Important applications of metallic nanoparticles to molecular electronics, biosensors, and chemical catalysis have already been realized.^{3,4} Although the linear optical properties have been well investigated, the second-order nonlinear behavior, specifically incoherent second harmonic generation or hyper-Rayleigh scattering (HRS), of metallic nanoparticles remains relatively unexplored.

HRS has been developed as an advantageous technique for studying the second-order nonlinear response of organic molecules, as well as inorganic nanoparticles, in solution.^{5,6} Importantly, metallic nanoparticles, such as gold, silver and copper, exhibit enormous HRS responses, showing their potential to be excellent *coherent* nonlinear scatterers.⁷⁻⁹ For spherical metallic nanoparticles that are small compared to the wavelength of light, several theories of HRS intensities have been developed, including work by Agarwal and Jha (AJ),¹⁰ Hua and Gersten,¹¹ Oestling *et al.*,¹² Martorell *et al.*,¹³ and Dadap, Shan, Eisenthal, and Heinz (DSEH),¹⁴ These theories make different assumptions concerning the origin of the nonlinear processes; for example, the DSEH theory assumes that only surface-induced nonlinear susceptibility contributions exist, while AJ include both surface and bulk terms, but the surface term has a less general form than in DSEH theory. Some of the theories (such as DSEH) predict two leading-order contributions to HRS for spherical metal particles, corresponding to emission at 2ω by electric-dipole (E1) and electric-quadrupole (E2) mechanisms.¹⁴ However, the existence of distinguishable dipole and quadrupole contributions was not considered in some of the earlier theories.^{11,12} Interestingly, these predictions have not yet been tested experimentally.

Here, by measuring the excitation wavelength dependence of hyperpolarizabilities (β'_{silver}), we provide the first experimental demonstration of the existence of distinguish-

able dipole and quadrupole contributions to HRS. We show that these results may be successfully modeled using the DSEH theory in which HRS scattering arises from nonlocal excitation of induced dipole polarization and local excitation of induced quadrupole polarization, with both arising from the surface-induced nonlinear susceptibility.

II. EXPERIMENTAL SECTION

Aqueous silver colloids (32 ± 6 nm) were synthesized according to published procedure.¹⁵ HRS measurements were performed using a previously described instrument.^{7,9} The incident radiation, taken to define the x -axis, was generated by a mode-locked Ti:sapphire laser, having operating wavelengths that are tunable between 760 and 840 nm. The scattered light [collected over an angular range of about 30° centered on the z -axis (90°)] was collimated and focused. The incident polarization vector was chosen to be perpendicular to the plane of the incident and scattered wavevectors (i.e., along the y -axis), and the outgoing polarization vector was not selected.

III. RESULTS

The HRS measurement allows for the assessment of molecular or nanoparticle hyperpolarizabilities, β , in multicomponent systems if one of the components (internal standard) has a known first hyperpolarizability.^{5-7,9} We find that the output signal intensities $I_{2\omega}$ from aqueous suspensions of nominally spherical, silver nanoparticles increase approximately as the square of the intensity of the incident light I_ω .¹⁵ In addition, we observe that the signal at 2ω is nearly monochromatic. This and additional results described below imply that the output signal at 2ω is indeed due to HRS, rather than multiphoton-absorption induced emission or residual coherent second harmonic generation.⁷

The output signal shows a linear dependence on silver atom concentration after correction for self-absorption, and from the slope, the first hyperpolarizability of the silver particles can be calculated using water as internal standard, $\beta_{\text{water}} = 0.56 \times 10^{-30}$ esu.⁷ On this basis, we find that β'_{silver} [defined as $(\beta_{\text{particle}}^2/\text{atom})^{1/2}$] is about 5000 esu at an excitation wavelength of 820 nm. This value, which is consistent

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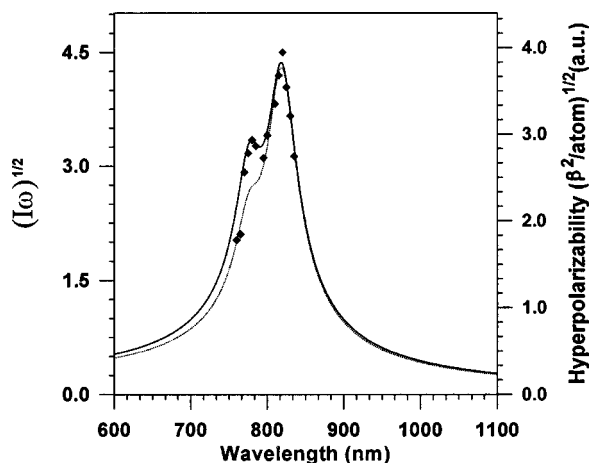


FIG. 1. The hyperpolarizabilities of silver colloid as a function of the incident wavelengths (cone experiment). Solid squares are the experimental data. The solid line is a fit to the DSEH theory obtained using the parameters $A=1$ and $B=6.2$. The dashed line represents the predictions from the Agarwal and Jha theory.

with earlier measurements from this laboratory,^{7,9} very substantially exceeds the normalized values found for organic molecular superchromophores. At this wavelength a potentially important contributing factor is the resonance between the nonlinearly scattered radiation at 2ω and the silver dipole plasmon absorption ($\lambda_{\text{max}}=408$ nm).

To further elucidate plasmon resonance contributions to the hyperpolarizabilities, we have measured HRS excitation profiles. Figure 1 shows the hyperpolarizabilities of the 32 nm silver colloid as a function of the incident wavelength. Here we see maxima at around 820 and 780 nm, corresponding, as we shall show below, to double the dipole and quadrupole plasmon wavelengths, respectively.

Although the data in Fig. 1 imply the existence of two distinct contributions to HRS, it is essential to examine angular distributions to demonstrate that they are consistent

with dipole and quadrupole emission. To do this, we take advantage of the theory of DSEH¹⁴ who give explicit expressions for the differential cross section for HRS. According to this theory, which we describe in greater detail later, the HRS signal arises from emission by an induced dipole at 2ω , that is aligned along the direction of the incident light (\hat{k}_1), and also an induced vector quadrupole, that is aligned along the polarization direction of the incident light ($\hat{\epsilon}_0$). The electric dipole at 2ω arises from two excitation mechanisms associated with the incident radiation: $E1+E2$ and $E1+M1$ ($M1$ is the magnetic dipole excitation). The electric quadrupole arises from $E1+E1$ excitation. Figure 2 shows angular distributions associated with the induced moments at 2ω based on DSEH theory, with Fig. 2(a) showing the pure electric dipole distribution and Fig. 2(b) the pure electric quadrupole distribution. The coordinates used are x,y,z as described in the experimental section. Figure 2(c) shows the effect of adding the dipole and quadrupole contributions, here taken to have equal amplitudes.

Figure 2 shows that if the outgoing direction \hat{n} is chosen perpendicular to $\hat{\epsilon}_0$, (i.e., \hat{n} is in the $\hat{u}\hat{k}_1$ (xz) plane where $\hat{u}=\hat{k}_1\times\hat{\epsilon}_0$) the HRS response will only come from the dipole term. However, if \hat{n} is in the $\hat{u}\hat{\epsilon}_0$ (yz) plane, both dipole and quadrupole mechanisms are present, but with the electric quadrupole contribution maximized. In order to collect the HRS response in the $\hat{u}\hat{\epsilon}_0$ plane or in the $\hat{u}\hat{k}_1$ plane, we add a narrow slit (~ 2 mm) in front of the convex lens, blocking the rest of the lens. We refer to these experiments as “slit” experiments with slit 1 referring to $\hat{u}\hat{k}_1$ and slit 2 to $\hat{u}\hat{\epsilon}_0$. Our experiments with no slit will be referred to as a “cone” experiment.

Figure 3(a) presents the hyperpolarizability (β'_{silver}) for the slit 1 experiment, while Fig. 3(b) presents the corresponding results for the slit 2 experiment. The results of these experiments are clear-cut: the slit 1 result only shows a peak at 820 nm, while slit 2 shows both the 780 and 820 nm

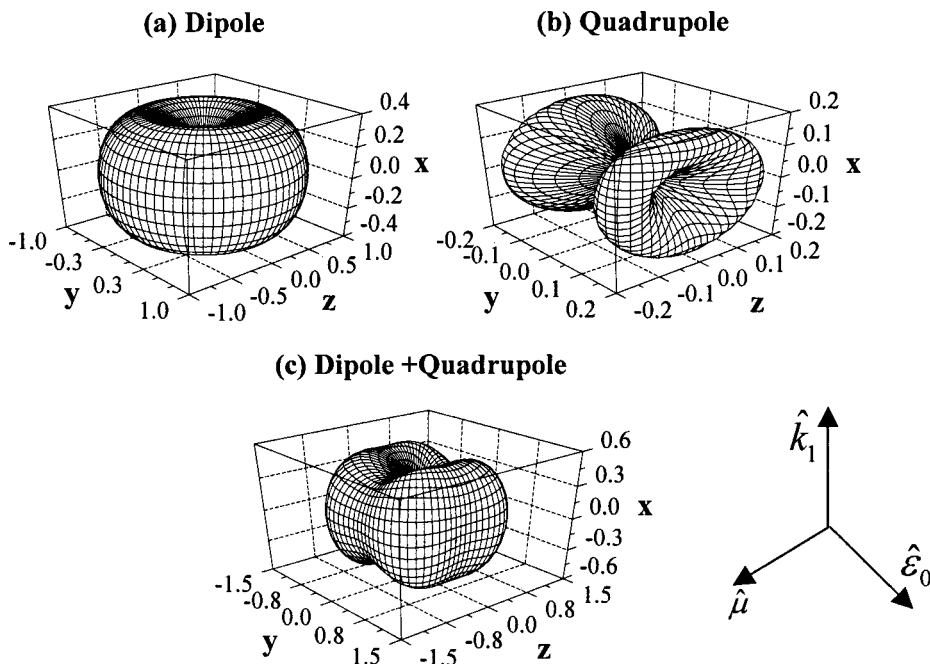


FIG. 2. DSEH angular distribution for three choices of the induced moments at 2ω . (a) pure dipole emission ($\alpha=1$), (b) pure quadrupole emission ($\eta=1$), and (c) equal contributions of dipole and quadrupole emission ($\alpha=\eta=1$).

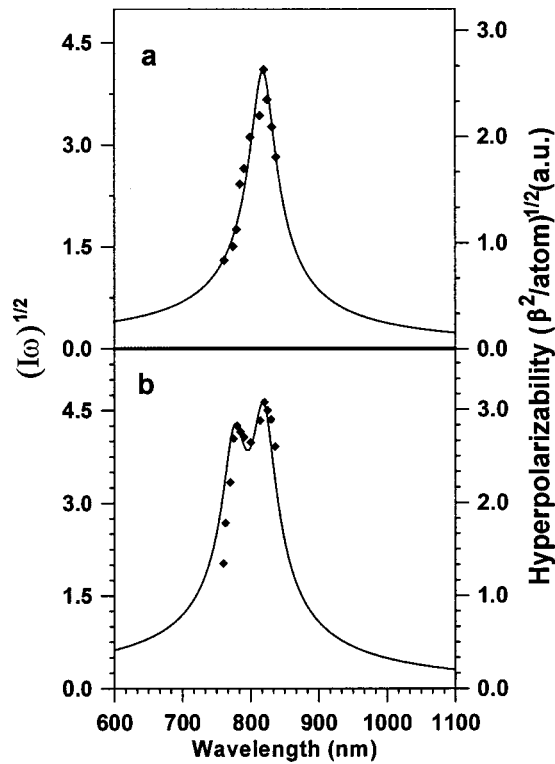


FIG. 3. The hyperpolarizabilities of silver colloid as a function of the incident wavelengths for the slit 1 experiment (a) where the HRS response is collected in the $\hat{u}\hat{k}$ plane and the slit 2 experiment (b) in which the HRS response is collected in the $\hat{u}\hat{\epsilon}_0$ plane. Solid squares are the experimental data. The solid line is based on the DSEH theory using $A=1$, $B=6.2$.

peaks, with the 780 nm peak enhanced compared to what we observed in the cone experiment in Fig. 2.

IV. THEORY AND DATA ANALYSIS

To analyze the data just presented, we now examine the DSEH theory¹⁴ in more detail. This theory shows that the HRS arises from an induced electric-dipole moment (P) and an induced vector quadrupole moment [$Q(\hat{n})$]. The radiated power at 2ω per unit solid angle is given by

$$\frac{dP_{2\omega}}{d\Omega_s} = \frac{cK_1^4}{2\pi[\epsilon_1(2\omega)]^{3/2}} \left\{ |P|^2 + \left(\frac{K_1}{6}\right)^2 |Q(\hat{n})|^2 + \frac{K_1}{3} \text{Im}[(\hat{n} \cdot P)(\hat{n} \cdot Q(\hat{n}))^*] \right\}, \quad (1)$$

where K_1 is the magnitude of the wave vector at 2ω .

As described in the experimental section, the nonlinear scattered signal in the cone experiment was collected over a wide cone angle centered along the vector \hat{u} . In this case, it is convenient to express the angular distribution in polar coordinates. In this coordinate system, the radiated power at 2ω per unit solid angle can be written in the following form:

$$\frac{dP}{d\Omega} = \alpha \cos^2 \theta + (\alpha + \eta) \sin^2 \theta \sin^2 \phi - \eta \sin^4 \theta \sin^4 \phi + \gamma \sin^3 \theta \cos \phi \sin^2 \phi, \quad (2)$$

where α , η , and γ are parameters that refer to the pure electric-dipole, pure electric quadrupole, and interference terms, respectively. Although α , η , and γ have a complex dependence on wavelength in general, for wavelengths where only the plasmon resonances at 2ω are important, the dominant resonant parts can be expressed as

$$\alpha = A \left| \frac{1}{\epsilon(2\omega) + 2} \right|^2, \quad (3)$$

$$\eta = B \left| \frac{1}{\epsilon(2\omega) + 3/2} \right|^2, \quad (4)$$

$$\gamma = \text{Im} \left\{ \frac{C}{[\epsilon(2\omega) + 2][\epsilon(2\omega) + (3/2)]} \right\}, \quad (5)$$

where A , B , and C are constants. Now let us analyze this expression for the cone and slit experiments defined earlier.

A. Cone experiment

The intensity of overall nonlinear scattering can be given by integrating over all ϕ and for θ between 0 and an angle that we denote by c . In our experiments, c is equal to 30° . To integrate over ϕ , we get,

$$H = \frac{1}{2\pi} \int_0^{2\pi} \frac{dP}{d\Omega} d\phi = \alpha \left\{ \cos^2 \theta + \frac{1}{2} \sin^2 \theta \right\} + \eta \left\{ \frac{1}{2} \sin^2 \theta - \frac{3}{8} \sin^4 \theta \right\}. \quad (6)$$

After that,

$$I_s = \frac{\int_0^c H \sin \theta d\theta}{\int_0^c \sin \theta d\theta} = \frac{1}{1 - \cos c} \left\{ \frac{\alpha(1 - \cos^3 c)}{6} + \frac{\alpha(1 - \cos c)}{2} + \frac{1}{2} \eta \left[\frac{1 - \cos c}{4} + \frac{1 - \cos^3 c}{6} - \frac{3(1 - \cos^5 c)}{20} \right] \right\} = 0.936\alpha + 0.0559\eta. \quad (7)$$

We see that only pure dipole and pure quadrupole terms contribute.

B. Slit 1 experiment

Taking the slit to be parallel to the $\hat{u}\hat{k}_1$ plane, the radiated power at 2ω is obtained by taking $\phi=0$ and π in Eq. (2). This gives

$$\frac{dP}{d\Omega} = \alpha \cos^2 \theta, \quad I_{s1} = \frac{\int_0^c \frac{dP}{d\Omega} \sin \theta d\theta}{\int_0^c \sin \theta d\theta} = \frac{\alpha}{3} (1 + \cos c + \cos^2 c) = 0.872\alpha. \quad (8)$$

C. Slit 2 experiment

In this experiment, the HRS response is collected in the $\hat{u}\hat{\varepsilon}_0$ plane, for which $\phi = \pi/2$ or $3\pi/2$. From Eq. (2), the scattering radiated power at 2ω per solid unit angle is given by

$$\begin{aligned}\frac{dP}{d\Omega} &= \alpha(\cos^2 \theta + \sin^2 \theta) + \eta \sin^2 \theta \cos^2 \theta \\ &= \alpha + \eta \sin^2 \theta \cos^2 \theta, \\ I_{s2} &= \frac{\int_0^c \frac{dP}{d\Omega} \sin \theta d\theta}{\int_0^c \sin \theta d\theta} \\ &= \frac{1}{1 - \cos c} \left\{ \alpha(1 - \cos c) \right. \\ &\quad \left. + \eta \left[\frac{1 - \cos^3 c}{3} - \frac{1 - \cos^5 c}{5} \right] \right\} = \alpha + 0.1064\eta. \quad (9)\end{aligned}$$

Note that like the cone expression [Eq. (7)] this result has both dipole and quadrupole contributions, but the quadrupole contribution here is about double that for the cone experiment. This means that comparison of the cone and slit 2 experiments should provide a clear signature of the enhanced quadrupole term, and indeed this is what is seen in comparing Fig. 1 and Fig. 3(b).

To quantify the comparisons between theory and experiment, we have evaluated the cone, slit 1 and slit 2 expressions [Eqs. (7), (8), and (9)], using the expressions for α and η in terms of the parameters A and B noted above. Note that the square root of the intensity expressions is used in comparing with the β'_{silver} values. Dielectric constants from Innes and Sambles¹⁶ were used that include finite size corrections following standard procedure.^{17,18} Figures 1 and 3 show results based on $A = 1$, $B = 6.2$ that were determined by fitting only the information in Fig. 1. We see that the match with all figures is excellent, indicating that the dipole and quadrupole contributions in all the slit and cone experiments are consistent with the DSEH expression.

For comparison, we also present results in Fig. 1 based on the Agarwal and Jha (AJ) formula¹⁰ (that we have converted from the integral cross section expression which they provide to a differential cross section expression that has the same form as our cone expression above). The AJ formula contains dipole and quadrupole terms like the DSEH formula, but the physical mechanism underlying these terms is somewhat different as described in the Introduction. The AJ formula contains no adjustable parameters, so there is no fitting, but what we see is that the AJ formula seriously underestimates the size of the quadrupole term relative to the dipole term. This is not surprising, as the AJ expression is based on a simple free electron model for the nonlinear optical response.

V. CONCLUSION

The leading-order contribution to the incoherent second harmonic generation of silver nanoparticles has been studied both theoretically and experimentally. By measuring the excitation wavelength dependence of β'_{silver} , we have experimentally demonstrated for the first time that there are distinguishable dipole and quadrupole plasmon contributions to hyper-Rayleigh intensities. These two contributions have different angular distributions, and we show that DSEH theory in conjunction with simple angular distribution measurements may be used to determine the relative sizes of the dipole and quadrupole contributions.

DSEH theory has proven to be successful for the present application, but it is to be noted that the materials dependent expressions in this theory are not known, and we have simply fit them to one experiment and then demonstrated consistency with the rest. The AJ theory gives us a parameter free result, however, this provides a less quantitative match with experiment than the DSEH result.

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