Surface-enhanced parametric scattering of light by silver clusters

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Theoretical considerations predict a surface enhancement of intrinsic optical nonlinearities of metallic clusters. A surface-enhanced parametric scattering of light by clusters in a colloidal solution of silver has been observed experimentally.

The unique optical properties of fractals (or fractal clusters), which are distinct from the properties of both gases and condensed media, are described in Refs. 1 and 2. Surface-enhanced nonlinear susceptibilities were predicted in Ref. 2 for impurity molecules associated with a fractal.

In the present paper we work from theoretical considerations to predict a surface-enhanced nature of the intrinsic nonlinear susceptibilities of fractals. We also report an experimental observation of a surface-enhanced parametric scattering of light (in the phase-conjugation geometry) by clusters in colloidal solutions of silver.

The surface-enhanced nature of the susceptibilities stems from the existence near the particles (monomers) constituting the fractal of strong local fields E_i, which are considerably stronger than the average (macroscopic) field E. Let us find the ratio $\Lambda_i = E_i/E$ for clusters in which the monomers are metal spheres of radius R_m, separated by a characteristic distance R_0, under the conditions $R_0, R_m \ll \lambda$, where λ is the wavelength of the light.

For arbitrary monomer i we have $\Lambda_i \sim d_i/R_0^3 E \sim \chi_i/R_0^3$, where d_i is the dipole moment induced at the monomer by the field. The susceptibility of monomer i of the cluster χ_i is given by

$$\Lambda_r \sim (1 - \Delta_r)^{-1} R_m^3 R_0^{-3} \, | \, (\epsilon - 1)/\epsilon'' \, | \sim (\epsilon' - 1)^2/\epsilon'' \, . \tag{1}$$

where $\epsilon = \epsilon' + i\epsilon''$ is the dielectric constant of the metal, χ_0 is the susceptibility of the isolated monomer, and the real quantity Δ_i incorporates the shift due to the dipole interaction. For "resonant" monomers $\Delta_i = \Delta_r = (\epsilon' + 2)/(\epsilon' - 1)$ the value of Λ_i is at a maximum:

$$\chi_i = R_m^3 (R_m^3 \chi_0^{-1} - \Delta_i)^{-1}, \quad \chi_0 = R_m^3 (\epsilon - 1)/(\epsilon + 2), \tag{2}$$

Using the Drude formula $\epsilon = \epsilon_0 - \omega_p^2 [\omega(\omega + i\gamma)]^{-1}$ and values of the constants for silver [$\epsilon_0 = 6$, $\omega_p = 1.4 \times 10^{16} \, \text{s}^{-1}$, and $\gamma = 10^{14} - 10^{15} \, \text{s}^{-1}$ (Ref. 3) (the width γ depends strongly on the presence of impurities)], we find that at $\lambda \approx 500$ nm the factor by which the local field is enhanced is $\Lambda_r \sim 10$–100.

Let us estimate the enhancement factor G for degenerate parametric four-wave mixing. The factor G is the ratio of the intensity of the light excited as a result of the four-wave mixing at a monomer of the cluster and that at an isolated monomer. The amplitude of the light excited at the monomer is evidently proportional to the third power of the local field E_i. Furthermore, in degenerate four-wave mixing the excited wave has the same frequency as the pump, so its amplitude $E_i^{(s)}$ may also be enhanced in comparison with the "seed" value $E^{(s)}$. As a result, we find the estimate $G \sim |\langle (E_i/E)^3 \times (E_i^{(s)}/E^{(s)}) \rangle|^2$, where $\langle ... \rangle$ means an average over the ensemble of fractals (i.e., over various realizations of the cluster).

This mean value can be estimated as the value for a resonant monomer multiplied by the fraction of such monomers, Λ_r^{-1}; as a result we find

$$G \sim | \Lambda_r^4 \Lambda_r^{-1} |^2 \sim [(\epsilon')^2 / \epsilon '']^6 \sim 10^6 \div 10^{12} . \tag{3}$$

The numerical estimate was found for $\lambda \approx 500$ nm and $\gamma = 10^{15} - 10^{14}$ s^{-1}.

The quantity G increases rapidly with the wavelength (in proportion to λ^6) by virtue of the increase in ϵ' (cf. the Drude formula). For a bulk metal, the increase in ϵ' with λ leads to an increase in the reflection coefficient, while for a monomer it leads to an increase in the quality factor of the resonance, (2). The increase in G predicted by (3) might thus be called a "luster effect."

A theory of intrinsic susceptibilities of fractals derived on the basis of Refs. 1 and 2 shows that the quantity G contains the large factor in (3), multiplied by a smooth function of the frequency which depends strongly on the fractal dimensionality D. At $D = 1.7$, which is a value characteristic of clusters in colloidal solutions (cf. Ref. 4), this smooth function is on the order of unity in the absorption band of the cluster, and expression (3) yields a correct estimate of G. For a fractal which is approximately a trivial fractal $(D \to 3)$, the spectra of the individual monomers are blurred, and the large enhancement disappears. On the basis of the estimates above we would expect a large enhancement of degenerate parametric four-wave mixing for the clusters which were studied in the experiments reported below.

We studied the efficiency of degenerate parametric four-wave mixing in a silver colloid as a function of the degree of clustering of the hydrosol. The degree of clustering was monitored by measuring the extinction spectra of the hydrosol (Fig. 1). A hydrosol with a low degree of clustering, consisting primarily of spherical monomers of diameter $a \sim 10$ nm, corresponds to an absorption spectrum with a high-contrast peak (which is at $\lambda \approx 400$ nm for silver).[5] As the clustering of the hydrosol proceeds, a long-wavelength wing appears in the spectrum.

Two methods were used to prepare a hydrosol. The first method, a borohydride method, corresponded to the procedure described in Ref. 6. The extinction spectrum of the freshly prepared hydrosol is shown by curve 1 in Fig. 1. The hydrosol clusters after a few days (curve 2). In some of the experiments we added polar solvents and impurities to accelerate the clustering (curve 5). In the second method, the monomers were produced by dissolving a mixture of silver with proteins (8.5 mg of a collargol preparation in 85 ml of doubly distilled water). The solution was then heated to 90° and agitated for 30 min. These proteins stabilized the hydrosol. Its extinction (curve 3
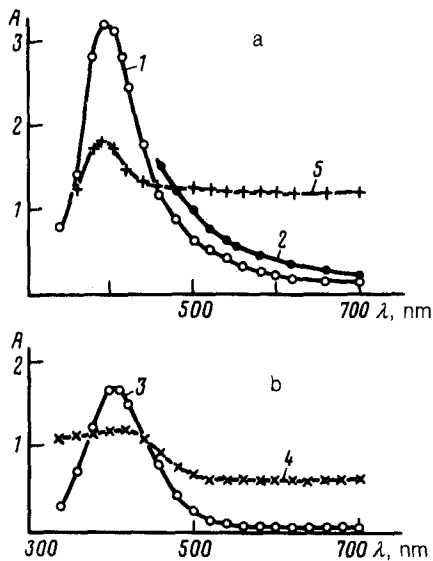
FIG. 1. Extinction spectra of hydrosols. a: Borohydride method. 1—Thirty minutes after preparation; 2—in 2 days; 5—in the presence of 3 μM of rhodamine 6 G and 0.5 M of ethanol. b: Collargol. 3—Stabilized monomers; 4—with a NaOH admixture.

in Fig. 1) remains the same for a month. Its coagulation can be caused by adding 0.6 ml of a 10% NaOH solution to 6 ml of the hydrosol (curve 4). The coagulation process continues for one or two weeks.

We used light with $\lambda = 532$ nm, with a power $P_0 \lesssim 40$ kW in the pulse, and with a pulse length of 15 ns. The probing beam was directed into the cell containing the hydrosol, 1 or 3 mm thick, at an angle of 7×10^{-2} rad with respect to the counterpropagating reference waves. When the light beams were focused, the intensities of these reference waves reached $I_0 \approx 1$ GW/cm^2; in the case of unfocused beams, we have $I_0 \approx 1$MW/cm^2. The intensity of the probing wave was $I_p \approx 0.1 \cdot I_0$.

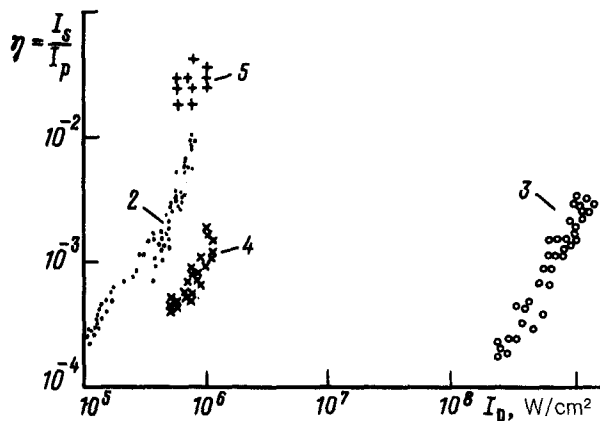Figure 2 shows the results of measurements of the conversion coefficient

FIG. 2. The conversion coefficient in the degenerate parametric four-wave mixing versus the intensity of the reference waves for hydrosols with various degrees of clustering. Groups of points 2, 3, 4, and 5 have the same meaning as in Fig. 1.

$\eta = I_s/I_p$, where I_s is the intensity of the signal wave, as a function of I_0 for the initial solutions (monomers) and for the coagulated hydrosols. We see that values of η, which are the same in order of magnitude, are attained in the case of the clustered hydrosols at reference-wave intensities lower by a factor of 10^3 than in the colloid consisting of monomers. It follows that during clustering in the hydrosol we have $G \sim 10^5$–10^6 (here we are using the relation $I_s \propto I_0^3$ for degenerate parametric four-wave mixing). The dependence $I_s(I_0)$ found from Fig. 2 and other experiments is approximately cubic: $I_s \propto I_0^q$, where $q = 2.3$–3.5 (under various conditions). When a phase object is placed in the probing beam, the wavefront in the signal beam is reconstructed.

Let us examine the kinetics of the growth of the degenerate parametric four-wave mixing (in time). At $I_0 = 1\text{MW/cm}^2$, for a freshly prepared hydrosol ($t \lesssim 30$ min) prepared by the borohydride method, we have $\eta < 2 \times 10^{-5}$. After 1 h we measured $\eta \approx 4 \times 10^{-5}$, and after 2 days we measured $\eta \approx 10^{-2}$. In the most coagulated hydrosol (point groups 5 in Figs. 1 and 2), the value $\eta = 0.04$ was reached.

Let us compare the value of G measured for phase conjugation with some estimates. If we take γ to be the width of the monomer absorption band (10^{15} s^{-1}; cf. Fig. 1), we find $G \approx 10^6$ from (3), in agreement with experiment.

These results clearly demonstrate the promising outlook for metal clusters as a nonlinear-optics medium. The value $G \sim 10^6$ has been achieved, and values $G \gg 10^6$ are possible in principle. The nonlinearity here differs from that in other nonlinear-optics media (in particular, liquid crystals and atomic vapor) in its short response time (relaxation time is $\tau \sim \gamma^{-1}$) and its broad-band nature.

[1]V. M. Shalaev and M. I. Shtokman, Zh. Eksp. Teor. Fiz. **92**, 509 (1987) [Sov. Phys. JETP **65**, 287 (1987)].
[2]A. V. Butenko, V. M. Shalaev, and M. I. Shtokman, Zh. Eksp. Teor. Fiz. **94**, 109 (1988) [Sov. Phys. JETP **67** (to be published)].
[3]U. Kreibig and L. Genzel, Surface Science **156**, 677 (1985).
[4]D. A. Weitz and M. Oliveria, Phys. Rev. Lett **52**, 1433 (1984).
[5]Surface-Enhanced Raman Scattering [Russ. transl., Mir, Moscow, 1984].
[6]J. A. Creighton, C. G. Blatchford, and M. G. Albreht, J. Chem. Soc. Faraday II **75**, 790 (1979).