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Enhanced four-wave mixing from silver particles

D. S. Chemla, J. P. Heritage, P. F. Liao, and E. D. Isaacs
Bell Laboratories, Holmdel, New Jersey 07733
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Four-wave mixing from a regular array of uniformly shaped and sized silver particles has been observed. The measured conversion efficiency yields an enhancement in the particles' third-order polarizability by a factor of 900 over that of the bulk metal, and is found to be in satisfactory agreement with the enhancement of the spontaneous Raman scattering from molecules adsorbed on the same samples.

I. INTRODUCTION

Following the discovery of surface-enhanced Raman scattering[1] (SERS) a number of nonlinear optical effects associated with roughened metal surfaces have been observed and discussed.[2,3] Several sources of enhancement have been suggested to contribute to the total enhancement of the Raman scattering by molecules on roughened surfaces.[4] The electromagnetic models ascribe the enhancement to localized plasmon resonances and to the large local fields at the surface microprotrusions. The molecular models consider the enhancement which arises from the modification of the molecular-energy spectra and polarizabilities that is caused by the interaction between the metal and the molecule.

In order to separate the contributions of these two sources of enhancement we have measured the "Raman-type" third-order nonlinearity of microscopic metal particles in air *without* intentionally chemisorbed or adsorbed molecules to compare it to that of bulk metal. Our experimental results indicate that the majority of the Raman enhancement is due to electromagnetic effects, in agreement with the measurements of Chen *et al.*[2] who determined the enhancement of surface second-harmonic generation from electrochemically roughened silver. The present study reports four-wave mixing (FWM) from regular arrays of silver particles produced by microlithographic techniques, and makes a direct comparison with the SERS from molecules adsorbed onto the same arrays. The FWM signal is due to the third-order susceptibility $\chi^{(3)}(-\omega_3;\omega_1,-\omega_2,\omega_1)$ of the bulk metal.[5] It serves as an excellent probe of the magnitude of local field within the microscopic particles. Conversely, second-harmonic generation is only due to the metal surface.[6] Its magnitude may therefore be somewhat dependent on the precise surface preparation. In addition, in the case of second-harmonic generation, the wavelengths of the photons involved are widely separated, and hence raises a problem with assigning the contributions from the enhancement at each wavelength to the total enhancement. In contrast we can choose the wavelengths in FWM to be nearly the same, and hence each will experience a fairly similar enhancement.

The article is divided in three sections. In Sec. II third-order nonlinear optical effects from regular arrays of uniformly shaped metal particles are analyzed, and in Sec. III our experimental setup and data are presented. Finally, in Secs. IV and V our results are compared to SERS and to theoretical prediction of an electromagnetic model.

II. NONLINEAR OPTICAL EFFECTS FROM REGULAR ARRAYS OF METAL PARTICLES

In order to obtain results which could be directly compared with theory, our experiments utilize a planar array of uniformly sized and shaped silver particles. This particle array is obtained on a microstructure produced by microlithography. The fabrication of this microstructure has been described elsewhere.[7] It consists of SiO_2 microposts, about 5000 Å high with a 500-Å radius of curvature at the tip, regularly ordered in a planar lattice of parameter $d \simeq 3000$ Å. By evaporating metal onto the posts, uniform and regularly shaped particles with dimensions in the (500–3000)-Å range are produced.[7] These particles are approximately ellipsoidal with an aspect ratio which can be modified by varying the evaporation angle. Because of the uniformity of the distribution of the particles, the coherently excited nonlinear dipoles induced by the FWM process generate a well-collimated signal beam. Such a beam is not generated in randomly roughened surface.

We consider the geometry illustrated in Fig. 1. The position $\vec{r}_l$ of each metal particle is labeled by a double integer index $l=(l_x,l_y)$ such that $\vec{r}_l=(l_x\hat{x}+l_y\hat{y})d$. Let the effective third-order polarizability of the metal particle be γ. Under excitation by two laser fields E_1 and E_2 of frequencies ω_1 and ω_2, each particle acquires a dipole moment oscillating at $\omega_3=2\omega_1-\omega_2$,

$$\vec{\mu}(\vec{r}_l)=\mu(\vec{r}_l)\hat{u}=\hat{u}\gamma E_1^2(0)E_2^*(0)\times\exp[i(2\vec{k}_l-\vec{k}_2)\cdot\vec{r}_l]\ . \quad (1)$$

The particle dipoles result in a field at a point $\vec{R}=R\hat{s}$ ($R\gg|\vec{r}_l|$), which is given by

$$\vec{E}(\vec{R})\simeq k_3^2\frac{e^{ik_3R}}{R}\gamma E_1^2(0)E_2^*(0)(\hat{s}\times\hat{u})\times\hat{s}\sum_l\exp[i(2\vec{k}_1-\vec{k}_2-k_3\hat{s})\cdot\vec{r}_l]\ , \quad (2)$$

where $k_3=\omega_3/c$ and the sum is to be carried over the area of the sample irradiated by the lasers. For simplicity we assume uniform excitation, but the main results of our discussion are still valid if the fields amplitudes are not uniform. The fields radiated by all the particles are in phase in the direction $\hat{s}$, if for all l,

$$\exp[i(2\vec{k}_1-\vec{k}_2-k_3\hat{s})\cdot\vec{r}_l]=1\ .$$

This phase-matching condition yields the relationship

$$\left[\frac{2\sin\theta_1}{\lambda_1}-\frac{\sin\theta_2}{\lambda_2}-\frac{\sin\theta\cos\phi}{\lambda_3}\right]l_y-\frac{\sin\theta\sin\phi}{\lambda_3}l_x=\frac{m}{d}\ , \quad (3)$$

where m is an integer and the angles are defined by

$$\vec{k}_{1,2}=\sin\theta_{1,2}\hat{y}+\cos\theta_{1,2}\hat{z}\ ,$$

$$\hat{s}=\cos\theta\hat{z}+\sin\theta\cos\phi\hat{y}+\sin\theta\sin\phi\hat{x}\ .$$

Since the divergence of the exciting-laser Gaussian beams is limited by diffraction, we can expect a strongly peaked signal emission in the direction satisfying Eq. (3) which is also diffraction limited. When the condition given by Eq. (3) is satisfied, the sum in Eq. (2) reduces to the number of particles in the area excited by the laser, i.e., NA, where A is this area and $N=d^{-2}$ is the particle surface density. Then ΔP_3, the power at ω_3 emitted in such direction within the solid angle $\Delta\Omega$, can be easily evaluated. Let us consider for simplicity the case of common incidence and specular reflexion, $\theta_1=\theta_2=\theta$, $\phi=0$, and $m=0$,

$$\frac{\Delta P_3}{\Delta\Omega}=\left[\frac{(2\pi)^3}{c}\frac{|\gamma|P_1\cos2\theta}{\lambda_3^2d^2}\right]^2\frac{P_2}{A}\ , \quad (4)$$

where P_1 and P_2 are the incident laser power at ω_1 and ω_2, respectively. Equation (4) will be used to deduce γ from the experimental data.

For an isolated particle of dimensions smaller than the optical wavelength, the fields inside the particle are different from the applied fields. To account for this difference it is customary to introduce the so-called "local-field factors" $f(\omega)$, which are such that $E_{\rm loc}(\omega)=f(\omega)E(\omega)$. In the case of a few simple geometrical shapes, analytical expressions can be found for the local field factors.[8] These factors can be large at localized plasmon resonances,[9] which, in the case of silver, occur in the visible. The hyperpolarizability of an isolated particle is then[9]

$$\gamma=Vf^2(\omega_1)f^*(\omega_2)f(\omega_3)\chi^{(3)}(-\omega_3;\omega_1,-\omega_2,\omega_1)\ ,$$

where V is the particle volume. With the use of the value $\chi^{(3)}=17\times10^{-12}$ esu measured by Bloembergen *et al.*[10] for bulk silver and particle volume $10^{-15}\lesssim V\lesssim10^{-16}$ cm^3, one finds that even at laser intensities of 50 MW/cm^2, the conversion efficiency is extremely small for a nonenhanced interaction ($10^{-14}\lesssim P_3/P_2\lesssim10^{-12}$) and it remains small even in the case of substantial local-field enhancement such as those encountered with silver particles ($1\lesssim|f|\lesssim10$).

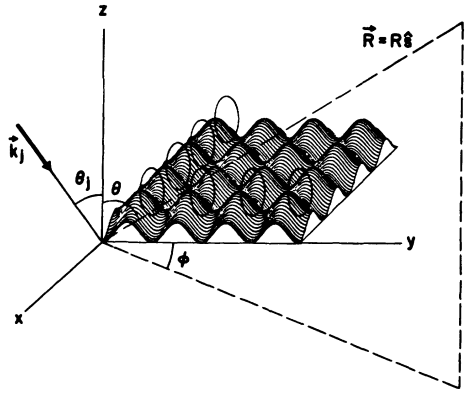

FIG. 1. Geometry of our samples and configuration of FWM. Silver particles are approximately shaped as ellipsoids of revolution with semiaxes $b=1500$ Å and $a=500$ Å. They are arranged on a planar double-square array of silicon-oxide microposts. Incident wave vectors are $\vec{k}_j$ and the direction of observation given by the vector $\vec{R}$ is $R\hat{s}$.

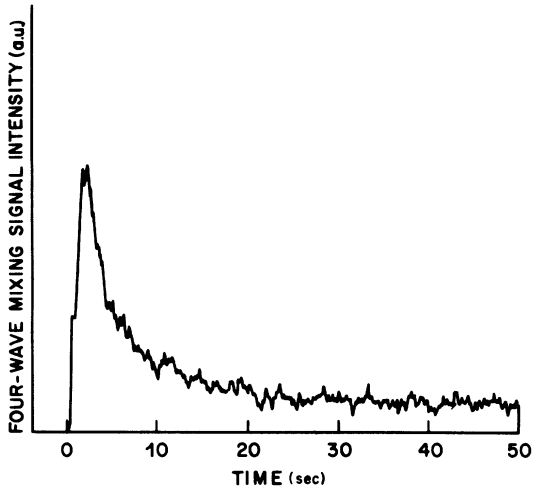

FIG. 2. Time dependence of the signal intensity at $\omega_3=2\omega_1-\omega_2$ when a "fresh" spot on the sample is exposed to the lasers at ω_1 and ω_2. A large signal is first observed for 2 to 3 sec. It then decays in about 20 sec to a constant plateau which lasts for several minutes.

III. EXPERIMENTAL SETUP AND RESULTS

In order to obtain the sensitivity sufficient for the measurement of γ it is necessary to deliver high peak intensities without destroying the sample. We have used a system of two synchronously mode-locked and cavity-dumped dye lasers.[11] The two lasers are simultaneously pumped by a mode-locked Spectra-Physics 171-19 Ar^+-ion laser. Each cavity has a four-mirror folded configuration with two beam waists. The dye jet is located at one beam waist and the acoustic-optic deflector for cavity dumping is located at the other. For a 150-nsec dumping period, 8-psec [full width at half maximum (FWHM)] pulses are obtained with an energy per pulse in the $(2-5)\times10^{-9}$ J range. Tuning over 5700–6100 Å and 6200–6600 Å is achieved with the use of, respectively, Rodamine-6G (R6G) and DCM as dyes.

The samples studied were obtained by evaporating silver onto the lithographic structure to produce approximately ellipsoidal particles with dimensions $2b=3000$ Å and $2a=1000$ Å. The output of the lasers were recombined through a dichroic mirror and focused on the sample in "p" polarization and at an incidence angle $\theta\simeq60°$. The spot diameter on the sample varied from 15 to 40 μm according to the microscope objective used. Another microscope objective was used to collect the reflected beams, which were then passed through a monochromator and dielectric filters before being detected by a photomultiplier. The overall band pass of the detection system when the slits of the monochromator were wide open (2.5 mm) was about 120 Å. The DCM laser was chopped at a low frequency, $\simeq10^3$ Hz, and lock-in detection was used.

A well-collimated signal was observed. When a fresh spot of the sample was exposed a strong signal was detected for about 2.5 sec. This signal decayed in about 20 sec to a plateau, 8 times smaller, which then lasted for several minutes. A recording of this unusual time dependence is shown in Fig. 2, which was obtained for an average power of 4 mW for each laser on the sample, focused on a 15-μm-diameter spot. It was checked that the signal existed only when the two lasers actually overlapped in time and space. Its monochromaticity was verified and found to be comparable to that of the incident lasers, i.e., $\delta\lambda\simeq0.5$ Å, and by tuning the dye lasers it was verified that the signal frequency varied according to $\omega_3=2\omega_1-\omega_2$. The $P_3\propto P_1^2P_2$ dependence was also verified down to our detection limits. Finally two sets of experiments at $\omega_1-\omega_2\simeq1500$ cm^{-1} and $\omega_1-\omega_2\simeq2000$ cm^{-1}, each one consisting of the examination of about a dozen of samples, were performed reproducing essentially the same results. No FWM signal could be detected from smooth silver surface, e.g., on a nonpatterned area of our substrate. A typical example of a recording of the signal from the grating and from the smooth silver is shown in Fig. 3 as a function of the wavelength of the R6G laser.

In order to elucidate the origins of the time decay of the FWM signal we have exposed different spots of a freshly prepared sample to the lasers for periods of time varying from 30 sec to 5 min under the same

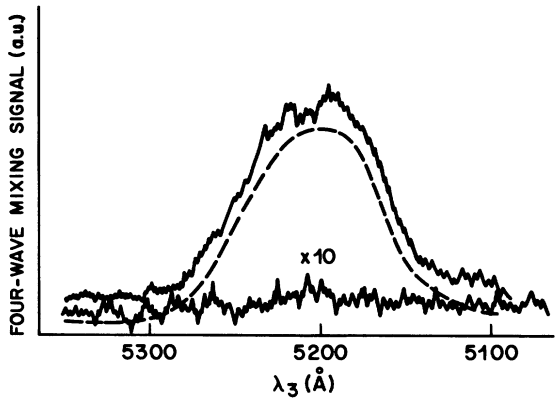

FIG. 3. Variation of the signal intensity observed through a monochromator and a dielectric filter as the wavelength of one of the exciting lasers was tuned. Dashed line shows the band pass of the detection channel. At the center of the spectrum, $\lambda_1=0.58$ μm, $\lambda_2=0.656$ μm, and $\lambda_3=0.52$ μm. Lower track shows a similar recording with a sensitivity 10 times better, obtained when the lasers are focused on a smooth silver surface.

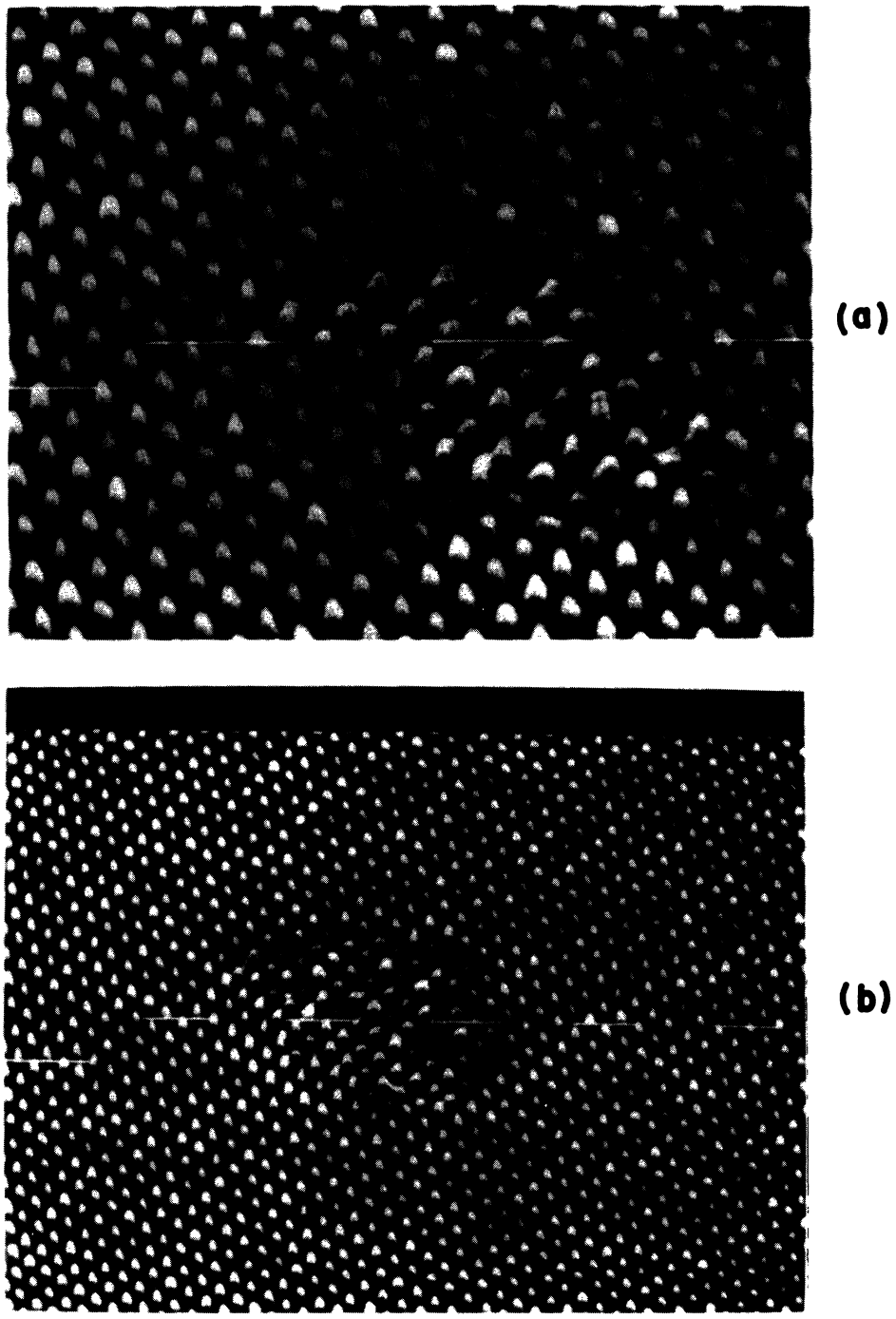

FIG. 4. Scanning electron micrographs of our sample after exposure to the two laser beams (5 mW average power each) focused on a 8-μm-diameter spot. (a) After 1 min exposure, (b) after 2 min exposure, and (c) after 3 min exposure.

configurations as previously described and using our largest magnification objective ($\times 20$). The sample was then examined at the secondary-emission monitor (SEM). Typical micrographs obtained with an average power of 5 mW on each laser focused on a 8-μm-diameter spot for an exposure of 3, 2, and 1 min are shown in Fig. 4. One can see that at the center of the focal spot the silver particles have been rounded. The energy per pulse delivered by each laser is $\simeq 1.5\times 10^{-9}$ J, and although there is 150

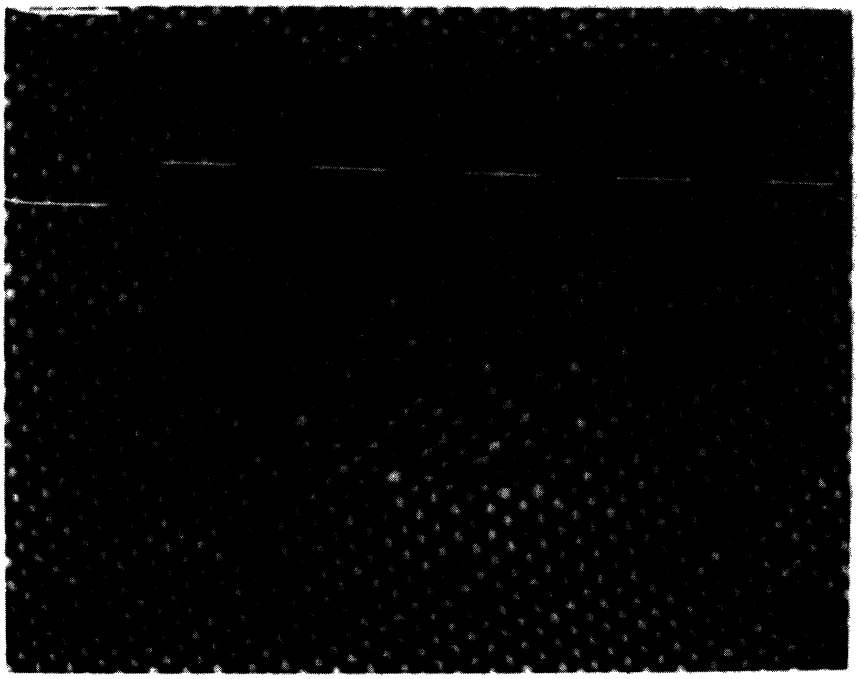

FIG. 4. (*Continued.*)

nsec between each pulse it appears that this is enough for the particles to reshape themselves under the influence of heat and surface tension toward more spherical forms. After cleaning the sample, dissolving the silver, and reevaporating fresh silver, the same particles with a 3:1 aspect ratio were again observed at the location previously exposed to the lasers, attesting that the lithographic structure was not damaged. The only effect of exposure to large light intensities appears to be a mild reshaping of the silver particles. We conclude from these observations that FWM on silver particle is shape dependent with a larger efficiency for ellipsoidal particles than for more spherical ones at $\lambda_1 \simeq 0.58 \mu$m and $\lambda_2 = 0.656 \mu$m. With an average power of each laser of 4 mW focused on a 15-μm-diameter spot on the sample, we have measured a conversion efficiency of $P_3/P_2 \simeq 6 \times 10^{-7}$ at the peak of the signal on a fresh spot and of $P_3/P_2 \simeq 7.5 \times 10^{-8}$ in the steady regime after 40 sec of exposure. We deduced from the peak efficiency a hyperpolarizability,

$$|\lambda| = (2.4 \pm 0.6) \times 10^{-23}$$

in esu. The hyperpolarizability of the same particle in the bulk silver is $\gamma_B = 2.6 \times 10^{-26}$ esu, and the enhancement factor is therefore

$$F = \frac{|\gamma|}{\gamma_B} \simeq 900 . \quad (5)$$

In order to compare this number to that involved in surface-enhanced effects involving molecules, we have attempted to observe FWM from cyanide or PNBA molecules adsorbed on our samples. In both cases we were unable to observe unambiguously a resonance, most likely because the molecules are desorbed by the particle heating. Using very fast scan of the R6G laser (100 Å in 5 sec), changing the exposed spot after each scan, and integrating over four scans, we have been able to identify a very weak structure in our spectra for $\omega_1 - \omega_2 = 2145$ cm^{-1} in the case of a sample exposed to KCN vapor. However, the accuracy of our observations was not sufficient to allow us to make reliable measurements. Nevertheless, observation of enhanced spontaneous Raman scattering from our sample is very easy, with cw rather than pulsed excitation and an enhancement of the scattering efficiency ($10^6 < S < 10^7$) has been measured in agreement with the previous measurements of Liao *et al.*[3,12]

IV. DISCUSSION

In order to make a quantitative comparison with theoretical models we shall assume that the silver particles are isolated perfect ellipsoids. We also assume that the cyanide radicals are perpendicular to the ellipsoid surface which is fully covered. The field inside the ellipsoid is uniform. The enhancement factor for the third-order polarizability is therefore

$$F = |f(\omega_1)|^2 |f(\omega_2)||f(\omega_3)| .$$

Across the surface of the ellipsoid the normal component of the field experiences a discontinuity such that $\epsilon\vec{E}_{in}\cdot\hat{n}=\vec{E}_{out}\cdot\hat{n}$. Since the C≡N radicals are normal to the surface, the local-field factors involved in the Raman scattering at each site are $\epsilon(\omega_{l,s})f(\omega_{l,s})\hat{e}\cdot\hat{n}$, where $\hat{e}$ is the unit vector along the field inside the ellipsoid. The enhancement factor of the scattering efficiency for each molecule is

$$|\epsilon(\omega_l)|^2|\epsilon(\omega_s)|^2|f(\omega_l)|^2|f(\omega_s)|^2(\hat{e}\cdot\hat{n})^4,$$

so that the enhancement factor averaged over all the molecules on the surface is

$$S=|\epsilon(\omega_l)|^2|\epsilon(\omega_s)|^2|f(\omega_l)|^2|f(\omega_s)|^2\eta,$$

where

$$\eta=\frac{1}{\Sigma}\int(\hat{e}\cdot\hat{n})^4 d\Sigma$$

is a simple integral which accounts for the averaging over the molecular orientation on the surface. If ω_1 and ω_2 are chosen to be equal to ω_l and ω_s, then

$$S=|\epsilon(\omega_1)|^2|\epsilon(\omega_2)|^2\frac{|f(\omega_2)|}{|f(\omega_3)|}\eta F. \quad (6)$$

From our previous measurement of the dispersion of SERS (Ref. 7) we evaluate the ratio $|f(\omega_2)|/|f(\omega_3)|=0.4$ and we calculate that $\eta=2.3\times10^{-2}$ for $b{:}a\sim 3{:}1$. Then using the dielectric constant of silver[13] and our experimental result for F we find $S=7.5\times10^5$, a result slightly smaller than but still in good agreement with the experimental one. This indicates that most of the enhancement of SERS is of electromagnetic origin with a possible contribution, perhaps of one order of magnitude, from other mechanisms.

V. CONCLUSIONS

We have observed FWM from uniformly shaped and ordered silver particles at light intensities where no FWM could be detected from a smooth silver surface. We have found that the FWM efficiency is shape dependent as the heating of our sample by the laser light modified the particle shape. We have measured, for particles having the form of ellipsoids of revolution with semiaxis $b=1500$ Å and $a=500$ Å, an enhancement of the third-order polarizability of 900 Å ±25% over that of the bulk metal. Finally we have found that an analysis based on the electromagnetic model of the SERS gives a relatively good agreement between the enhancement of the nonlinearity of the metal by local-field effects *inside* the particles and the enhancement of the Raman scattering efficiency of the C≡N bond due to local-field effects *on* the surface of the particle. Our measurements indicate an electromagnetic enhancement to SERS slightly smaller than the one we have measured on the same sample. From that we can deduce an upper bound of about 1 order of magnitude to any additional contribution to the enhancement by some other mechanism.

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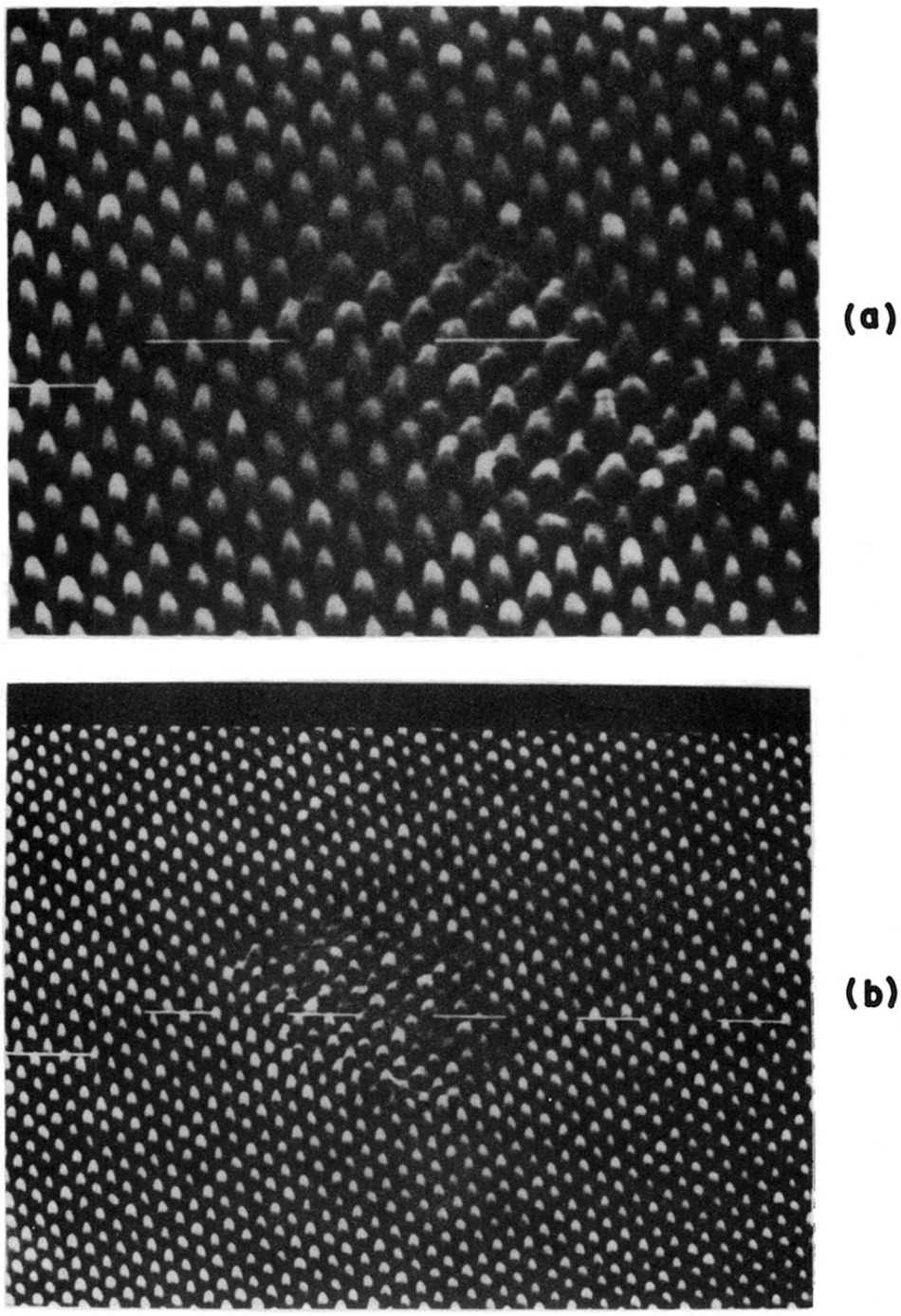

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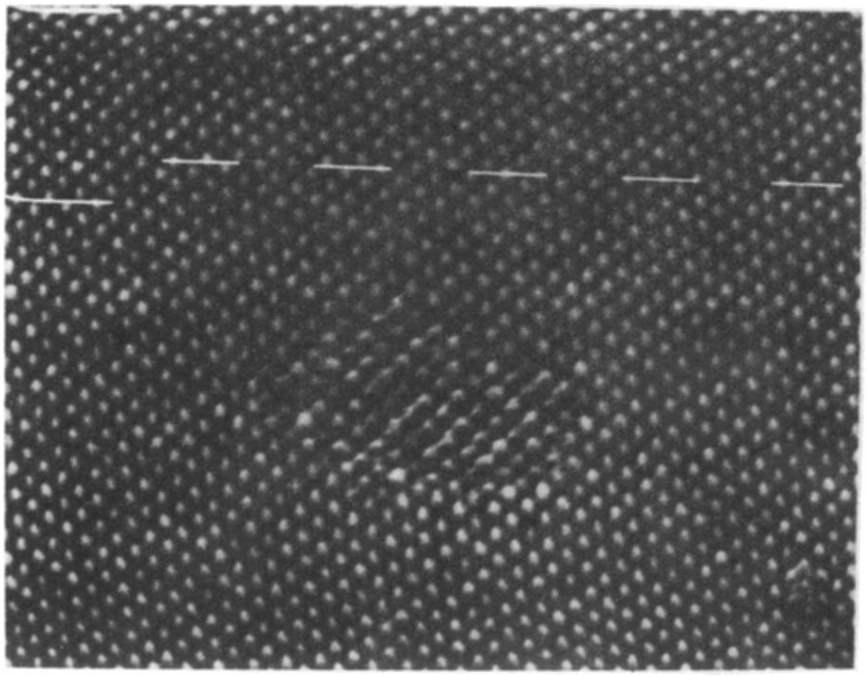

(c)

FIG. 4. (*Continued.*)