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Experimental observation of surface-enhanced coherent anti-Stokes Raman scattering

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Abstract

Surface-enhanced coherent anti-Stokes Raman scattering has been observed on colloidal silver surface from benzene, the mixture of benzene and N,N-dimethylformamide, toluene, and chlorobenzene. Silver colloids which were prepared in organic solvent N,N-dimethylformamide were used as an enhancement medium. The scattered CARS light was collected at right angles with respect to the exciting pump and Stokes laser beams. It was found that not only is the CARS signal significantly enhanced but the signal-to-noise ratio is also improved after addition of the silver sol. An excitation profile study shows a maximum enhancement for the benzene–silver sol system located at about 500 nm pump laser wavelength. This is in good accord with the surface plasmon resonance of the system.

1. Introduction

The discovery of surface-enhanced Raman scattering (SERS) has stimulated enormous interest in Raman spectroscopy of surfaces [1]. The success of the electromagnetic model, which is based on the response of small metal particles to the electromagnetic fields, in accounting for a large number of features of SERS prompted several authors to seek other manifestations of the enhanced electromagnetic fields near metal surfaces. These include enhanced absorption [2], fluorescence [3–5] and photochemistry [6–9] as well as enhanced second harmonic generation (SHG) [10–13], hyper-Raman scattering [14–17] and other nonlinear processes. Nonlinear processes are expected to be greatly enhanced near the surface of a small metal particle as a result of field enhancement. Enhanced SHG by electrochemically roughened silver and silver island films [10–13], four-wave mixing by a regular array of uniformly shaped and sized silver ellipsoidal particles [18] and hyper-Raman scattering on a variety of silver surfaces have been observed [14–17].

The possibility of surface-enhanced coherent anti-Stokes Raman scattering from molecules located near the surface of small colloidal silver particles was theoretically predicted by Chew et al. [19]. Maximum enhancement factors of about 10^4 for a particle radius of 50 nm were estimated in the visible region. However, no experimental verification has been reported so far.

The negative experimental results of surface-enhanced CARS from molecules on colloidal silver were attributed to the small dimension of the metal particles [20,21]. This explanation does not seem reasonable because silver colloids of 10–100 nm in dimension are optimal for electromagnetic enhancement and the CARS field will be resonantly enhanced if any of the frequencies of the pump laser, Stokes laser and the anti-Stokes laser photons is near a resonance fre-

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quency of the particle. Since the CARS process is limited to a coherence length of about 10 μm, we chose the particle density such that the effective distance between two particles was $\leqslant 10$ μm. Under these conditions the molecules between the particles are within the coherence length. The CARS signal should now be larger in the presence of the particles than in their absence.

We report here the observation of surface-enhanced coherent anti-Stokes Raman scattering (SECARS) by silver colloids [1]. Excitation profile and absorption spectral studies are carried out to confirm the electromagnetic field enhancement effect on silver particles.

2. Experimental

Silver colloids (or sol) were prepared by reduction of silver nitrate in the nonaqueous solvent N,N-dimethylformamide (DMF). To 45 ml DMF 39 mg of $AgNO_3$ was added and the mixture underwent supersonic agitation for about 10 min. Afterwards the resulting reaction mixture stood for one to two weeks. The sol obtained in this way is stable and can be stored for at least one year. The pump and Stokes laser beams were from two dye lasers that were pumped by the third harmonic of a Q-switched Nd:YAG laser (Spectra Physics Quanta Ray GCR-4) with 15 Hz repetition rate and 8 ns pulse width. The pulse energy of the pump and Stokes lasers (Molectron DL200 and DL300, respectively) for most of the measurements ranges between 0.02–0.06 mJ. The laser energy (or power) was measured after the recording of each spectrum and was also monitored during the experiment. The two dye laser beams were crossed at a small angle (1–3°) and focused onto the sample. The scattered light was collected at right angles to the two incident laser beams and guided by an optical fibre bundle to a Spex 1680 0.22 m double monochromator equipped with an RCA C31024A photomultiplier. Additionally, the CARS signal could be detected in the usual forward geometry. A detailed description of the CARS setup can be found in Ref. [23].

[1] Preliminary results are reported in Ref. [22].

3. Results and discussion

In Figs. 1A–1D we show the signal at the anti-Stokes frequency of 2 ml benzene before (a) and after (b) addition of 3 drops of the silver sol for different pump laser wavelengths. From these spectra we can see that the signals from pure benzene are weak and it is difficult to obtain a spectrum with high signal-to-noise ratio. After addition of the organosol, not only is the signal obviously enhanced but the signal-to-noise ratio is also improved considerably.

The absence of either the pump or the Stokes laser beam causes the signal to vanish completely. This suggests that the observed signal results from a coherent optical process. The observed signal in a direction perpendicular to the laser beams may result from the optical inhomogeneity of the sample. Ishibashi and Hamaguchi [24] have also observed such a phenomenon in pure benzene as well as in the mixture of benzene and other liquids. The authors named this effect partially coherent anti-Stokes Raman scattering (PCARS), which may have some important spectroscopic applications. However, because of the weakness of the PCARS signal it is difficult to obtain a spectrum with a high signal-to-noise ratio using a conventional CARS setup. It is clear that the difficulty can be overcome with the help of silver sol.

We also noticed that with different pump and Stokes laser wavelength excitation, the enhancements are different. Around 500 nm pump laser excitation, an enhancement factor of more than 100 can easily be obtained. We believe that the resonant excitation of surface plasmons of the silver particles mainly accounts for the large enhancement of the coherent anti-Stokes Raman scattering. As other surface-enhanced optical processes, the CARS field will also be resonantly enhanced by the resonant excitation of surface plasmons if any of the frequencies of the pump laser (ω_1), the Stokes laser (ω_2) and the CARS signal (ω_3) are near a resonance frequency of the silver particle. According to the electromagnetic theory [19], the surface plasmon resonance condition for a small sphere in the Rayleigh limit is reached when $\mathrm{Re}[\epsilon(\omega_i)] = -2\epsilon_0(\omega_i)$, and $\mathrm{Im}[\epsilon(\omega_i)]$ is small, $\epsilon(\omega_i)$ and $\epsilon_0(\omega_i)$ ($i=1$, 2, or 3) being the dielectric constant of the bulk metal and the surrounding medium, respectively. For silver, the resonance condition is reached in the blue-green light region.

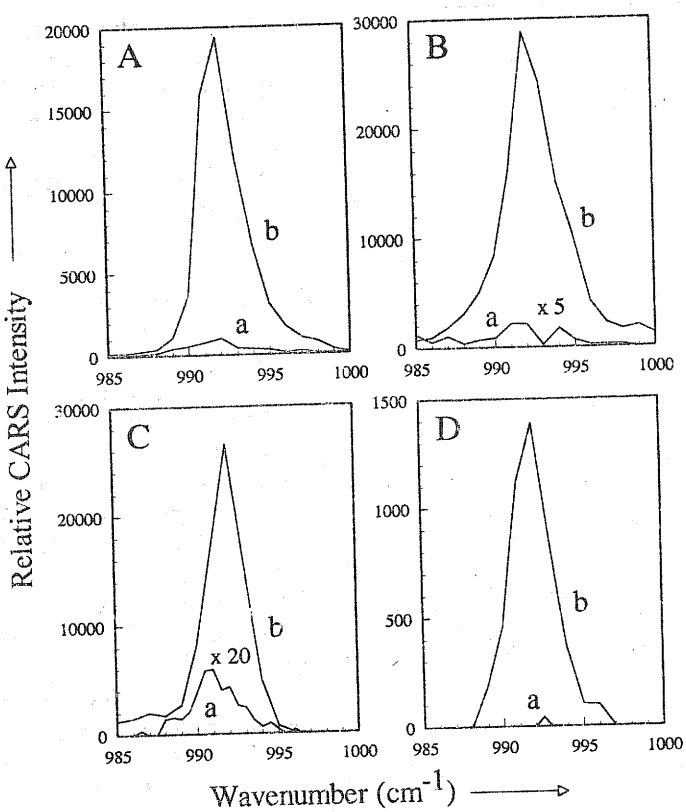

Fig. 1. CARS signal from benzene (a) before and (b) after addition of 3 drops of silver sol with (A) 458, (B) 501, (C) 511, and (D) 521 nm pump-laser excitation, respectively.

Considering the CARS process which is due to the nonlinear interaction of four photons, two pump photons with frequency ω_1, one Stokes photon with frequency ω_2 and one CARS photon with frequency ω_3, we expect the optimal enhancement to appear at such frequencies, at which the pump photon is in optimal resonance with the surface plasmons. In order to confirm this point, we carried out the excitation profile and absorption spectral measurements. The results are shown in Figs. 2 and 3, respectively.

The excitation profile study shows that the maximum enhancement for the benzene–DMF silver sol system is at about 500 nm pump laser wavelength. With either longer or shorter pump laser wavelength, the enhancement decreases. The absorption spectrum of pure silver sol has a single band with a maximum at about 437 nm which is a characteristic of the plasma resonance absorption of silver spheres. The resonance absorption shifts to longer wavelength for the benzene–silver sol mixture. We noticed that this band is much broader than that of the pure silver sol. This broad band has two components, one from the pure silver sol and another from the benzene–colloidal silver complexed system. As in the case of SERS, the latter contributes to the observed enhancements. A comparison of the excitation profile and absorption spectra shows that the wavelength at which the optimal enhancement appears is in good accordance with that of the surface plasmon resonance.

We would like to point out that the observed excitation profile is much narrower than the surface plasmon resonance. This can be understood by the resonance conditions of the four photons involved in the CARS process [25]. If the pump photons have a wavelength longer than the optimal resonance wavelength, the Stokes photon wavelength will be further

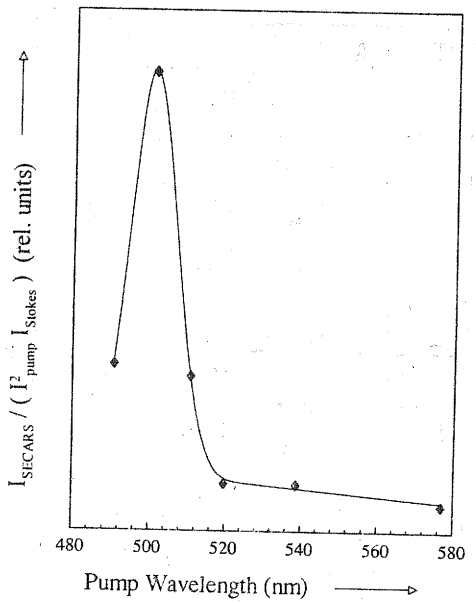

Fig. 2. Excitation profile of surface-enhanced CARS (SECARS) from benzene. The points are experimental values. The line is to guide the eye.

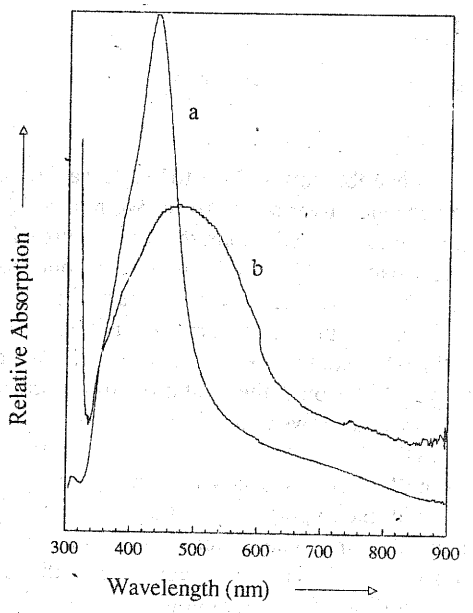

Fig. 3. Absorption spectra of (a) pure silver sol prepared in N,N-dimethylformamide and (b) a mixture of 2 ml benzene and 0.05 ml silver sol.

away from the optimal resonance wavelength. This will cause the enhancement to decrease quickly with increasing of the wavelength difference relative to the optimal resonance wavelength. Following this discussion, we also expect the excitation profile for SECARS to be much narrower than that for SERS. This is easily understandable from the electromagnetic theories of SERS and SECARS.

The electromagnetic theory predicts an excitation profile of the enhancements with a peak value at about 404 nm [19]. This is, however, quite different from our experimental observations. This difference may result from the simplified theoretical model, which is based on the assumption that the considered molecules are around a single spherical silver particle. The particle–particle interactions are neglected. It fails also to describe inhomogeneous particle size and shape distributions. Besides, the wave-vector-independent bulk dielectric constants for silver are used in the theoretical model.

In the forward direction, the CARS signal in silver colloids could be detected, but with a weaker intensity than in the absence of silver colloids. This result is due to the fact that a fraction of the CARS signal is scattered off its original direction by silver particles.

Finally, we emphasize that the observed surface-enhanced CARS effect is not restricted to benzene only. We have also observed the effect from toluene, chlorobenzene and the mixture of benzene and N,N-dimethylformamide. Therefore, it should be a general effect. In Figs. 4A and 4B we show the results from toluene and chlorobenzene, respectively.

4. Conclusion

The observation of surface-enhanced coherent anti-Stokes Raman scattering (SECARS) on colloidal silver surface is reported. SECARS spectra and excitation profiles could be obtained from benzene, the mixture of benzene and N,N-dimethylformamide, toluene and chlorobenzene in suspensions of silver particles. Silver colloids enhance the CARS signal and improve the signal-to-noise ratio considerably. The maximum enhancement for the benzene–silver sol system appears at about 500 nm pump laser wavelength. At this wavelength, enhancements of two orders of magnitude are easily obtainable. The en-

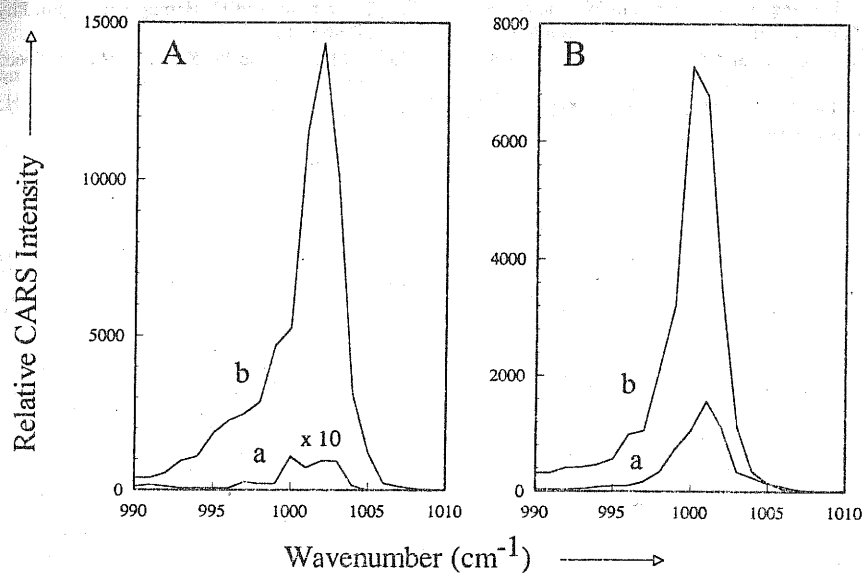

Fig. 4. SECARS signal from (A) toluene and (B) chlorobenzene: (a) and (b) were obtained before and after addition of silver sol, respectively. Pump-laser wavelength: 501 nm.

hancement results mainly from the resonance excitation of the surface plasmons of the silver particles. Further experiments, as well as an interpretation of the SECARS by means of a theoretical model, are in progress.

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