Surface Enhanced Raman Scattering by Isomeric Monobromopyridines Adsorbed on Gold and Silver Sol Particles

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SER spectra by 2-, 3-, and 4-bromopyridine (2-BP, 3-BP, and 4-BP) adsorbed on gold and silver sol particles have been studied. When aggregation of the particles proceeds, a new band appears on the long wavelength side of the single sphere plasma resonance band, and the SERS excitation profile peaks at the same wavelength as this new band and moves with this band to longer wavelengths. The maximum enhancement factor of Raman intensity amounts to 10^6. A linear relationship is found to exist between the SERS intensity of the ring breathing vibration of adsorbed bromopyridine (BP) and the absorbance of the gold sol at given excitation wavelengths within the longer wavelength band due to the aggregates. Application of a microfiltering technique to the 4-BP-induced gold particle aggregates suggests that the SERS intensity of the filtrates arises from unfiltered aggregates following the above-mentioned linear relationship. It is concluded from these observations that the aggregation is an essential requirement for observation of SERS in colloidal systems and that the SERS observed here is due to resonant excitation of the surface plasma oscillation in the aggregates of sol particles. Effect of the position of bromine substitution in the pyridine ring on SERS intensity is also discussed.

1. INTRODUCTION

Surface enhanced Raman scattering (SERS) by molecules or ions adsorbed on colloidal gold or silver particles has been a subject of considerable interest for a recent few years.[1,2] Particularly, Creighton *et al.*[3,4] have extensively studied SERS by pyridine adsorbed on gold or silver particles. Takenaka *et al.*[5] have also observed SERS by citrate ions adsorbed on gold particles. In both works, the SERS excitation profiles peaked at the same wavelength as the plasma resonance extinction band due to aggregates of sol particles and moved with this band to longer wavelengths as the aggregation proceeded. Thus it was concluded that the aggregation was an essential requirement for observation of SERS from adsorbates on these colloid particles and that the SERS was associated with the resonant excitation of collective mode of oscillation of the metal conduction electrons.

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On the other hand, Von Raben et al.[6] have reported SERS by cyanide complexes adsorbed on gold colloids of various degrees of aggregation and have pointed out that one of these colloids which containes only 7% aggregates gives rise to a single extinction band at 520 nm and the enhanced Raman scattering at 2138 cm^{-1}. It is a possibility therefore that the Raman scattering for this colloid may have originated predominantly from unaggretated particles. However, from the fact that the Raman excitation profile was found to peak beyond 600 nm, Creighton et al.[4] persisted that the observed Raman scattering was almost entirely contributed by the small fraction of particle aggregates.

Furthermore, Krimm et al.[7] have recently studied SERS by halide ions or pyridine adsorbed on colloidal silver particles and concluded after applying a microfiltering technique to a partially aggregated system that aggregation is not required for SERS by adsorbates on colloidal particles. Therefore, the question of whether aggregation is necessary for the observation of SERS in colloidal systems still remains for solution.

In this paper, we present results of SERS studies on 2-, 3-, and 4-bromopyridine (2-, 3-, and 4-BP) adsorbed on colloidal gold and silver particles. Attemps were made to solve the above-mentioned problem and to explore the mechanism of SERS in the colloidal systems. Effect of the position of bromine substitution in the pyridine ring on SERS intensity was also discussed.

2. EXPERIMENTAL

Chloroauric acid and sodium citrate used in this study were the same as those in the previous work.[5] Specially prepared reagents of silver nitrate and sodium borohydride were supplied by Nakarai Chemicals Ltd. The samples of 2-, 3-, and 4-BP were guaranteed regents of Tokyo Kasei Kogyo Co., Ltd., and used without further purification. Water was purified by a Mitamura Riken model PLS-DFR automatic lab-still consisting of a reverse osmosis module, an ion-exchange column, and a double distiller.

Gold sols were prepared by the sodium citrate method[8] in which aqueous solution of chloroauric acid (2.5×10^{-4} M, 50 ml) was reduced with sodium citrate solution (4.1×10^{-2} M, 1 ml). The concentration of the gold sol was found to be 2.5×10^{-4} M by assuming that all gold introduced as chloroauric acid was converted to colloidal gold. Advantages of this sodium citrate method have been described previously.[1,5] The gold sols thus prepared were red purple color and stable without precipitation on standing for a few weeks.

Silver sols were prepared by reduction of aqueous solution of silver nitrate (1×10^{-3} M, 1 ml) with ice-cold sodium borohydride solution (2×10^{-3} M, 3 ml). Both the solutions were mixed with vigorous stirring to aid monodispersity. The concentration of silver was calculated to be 2.5×10^{-4} M. The silver sols were yellow color and stable in the absence of BP for several days.

Raman spectra were recorded on a JASCO model R-500S spectrophotometer equipped with Spectra-Physics model 164 Ar$^+$ and Kr$^+$ lasers and a model 375 dye laser (Rhodamine 6G) for excitation. Commonly used sample cells were capillary tubes of 1 mm diameter. For the measurements of excitation profiles of Raman scattering, the use was made of a rotating cylindrical cell which was laterally divided into two compartments; the sample solution being in one compartment and the aqueous solution of sodium perchlorate (0.5 M).

in the other as an external standard.   The cell was rotated in the laser beam at *ca.* 3000 rpm, so that the beam off axis passed alternately through the sample and standard solutions. Further details of the cell have been described in the previous paper.[5]   The extinction spectra from 900 to 300 nm were obtained by a Hitachi model 200-10 spectrophotometer using either 0.5 or 1 cm thickness cell.

Electron micrographs of the sol particles were observed by the same procedure as that given in the previous paper.[5]

3. SOL PARTICLES

3.1. Gold sol particles

Figure 1 (A) shows an electron micrograph of the fresh gold sol particles observed immediately after the preparation, indicating fairly good sphericity with the uniform particle diameter about 19 nm.   It consists mainly of the single particles with some binary and slightly higher aggregates.   The specific surface area of the particles is calculated to be about $16 \, m^2/g$.   The concentration of adsorbed BP is estimated to be $4.4 \times 10^{-6} \, M$ by assuming monolayer coverage, each molecule occupying an area of $30 \, Å^2$.   Twenty four hours after the addition of 4-BP ($2 \times 10^{-5} \, M$), aggregation had proceeded to give large networks of strings of particles as shown in Fig. 1 (B).   The shape and size of the primary particles had remained unchanged.   This mode of aggregation has been reported by Creighton *et al.*[4] for pyridine-containing sols, and was accounted for in terms of the opposing effects of short range attractive force and the relatively longer range Coulomb repulsive force between the aggregating primary particles.

Figure 2 represents a series of the extinction spectra of gold sol at various growing stages of aggregation by adding 4-BP ($2 \times 10^{-5} \, M$).   As shown previously,[5] freshly prepared sol has a single extinction maximum at 520 nm due to the resonant excitation of dipolar plasma oscillations in the confined electron gas of the isolated gold spheres which
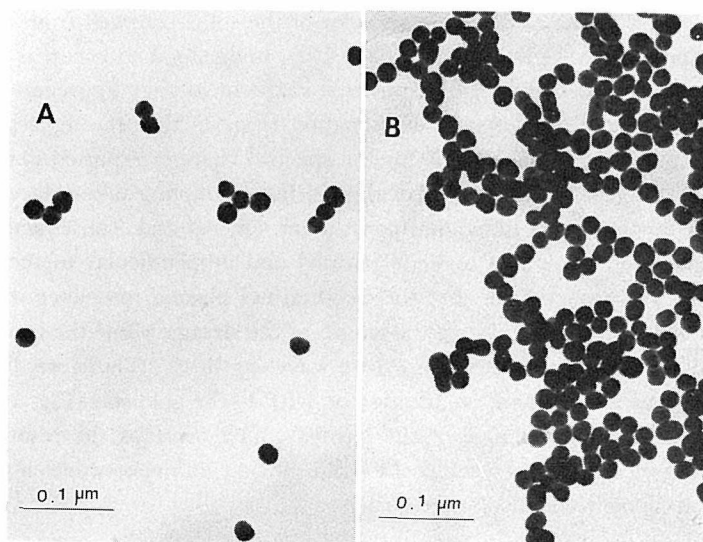

Fig. 1.   Electron micrographs of gold sol particles that are (A) freshly prepared and (B) 24 h after addition of 4-BP (2×10^{-5} M).

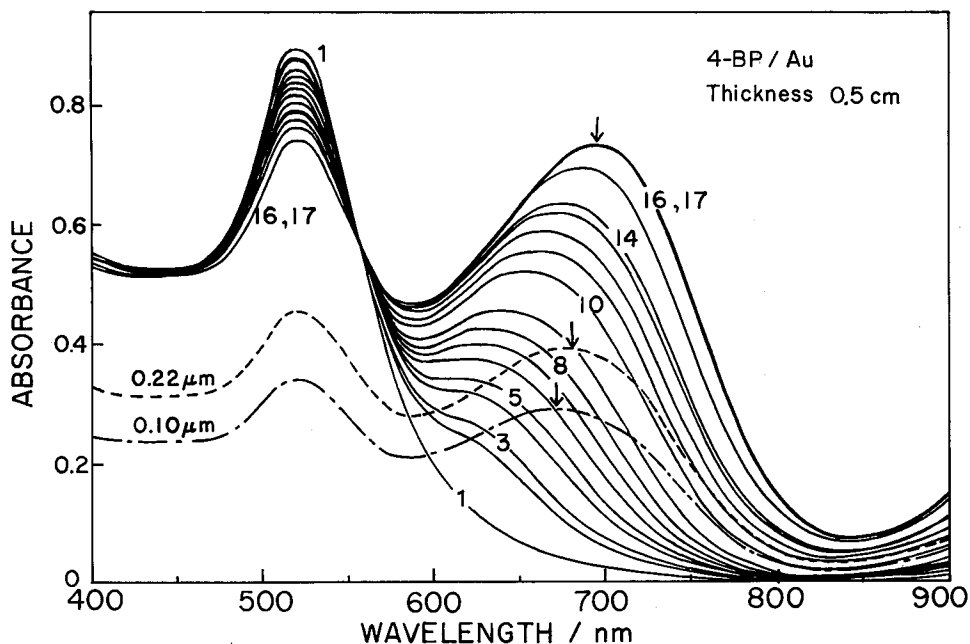T. TAKENAKA, K. EDA, M. MABUCHI, Y. FUJIYOSHI, and N. UYEDA

Fig. 2. Changes in extinction spectra of gold sol at various stages of aggregation. (1) Before addition, and (3) 50 min, (5) 80 min, (8) 200 min, (10) 270 min, (14) 530 min, and (17) 1020 min after addition of 4-BP (2×10^{-5} M). The broken and chain lines are the extinction spectra after filtration with 0.22 and 0.10 μm pore size filters, respectively.

are substantially smaller than the wavelength of light (within the Rayleigh limit). On addition of the adsorbate, a new band appears on the long wavelength side at the expense of the 520 nm band and moves to longer wavelengths with increasing band intensity over the course of 17 h. At the same time, the color of the sol is changed from red purple to blue. These spectral changes of the sol have been understood to occur as the particles become larger or as they deform from spherical shape or as they aggregate.[1] It is apparent from the electron microscopic examination (Fig. 1) that the aggregation of the particles to the networks is responsible for the spectral changes reported above.

In the case of linear strings of spherical particles, a coupling takes place between the dipolar plasma modes of the individual constituent spheres and, consequently, they are split into two components which oscillate parallel and perpendicular to the string axes, respectively. It has been known that the longitudinal plasma resonance moves rapidly to longer wavelengths with increase in the length of the strings, while the transverse mode remains at roughly the single sphere resonance wavelength.[1,4] Therefore, the extinction band which remains near 520 nm on addition of 4-BP to the gold sols (Fig. 2) is identified as the transverse dipole resonance of the strings which overlaps the resonance of any remaining unaggregated spheres, while the band moving to longer wavelengths is due to the longitudinal dipole resonance of the strings.

3.2. Silver sol particles

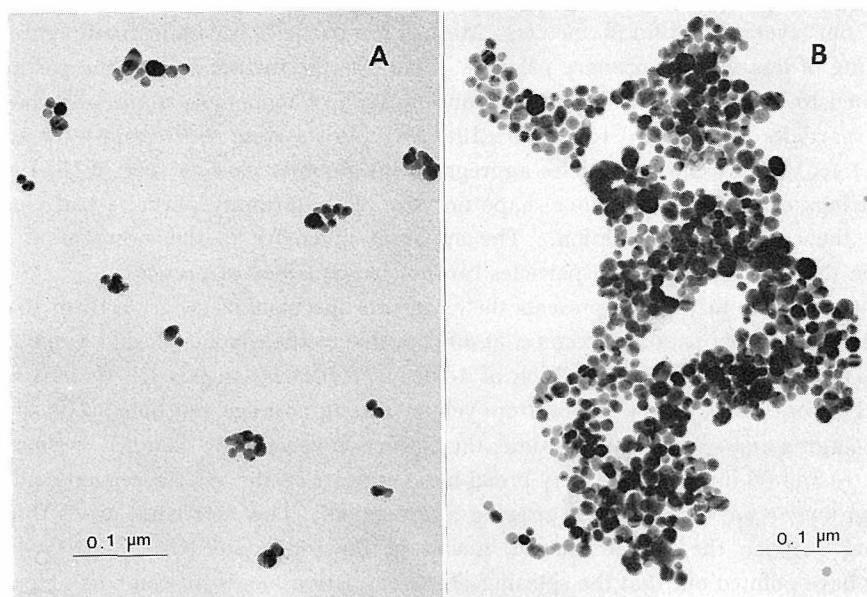Electron micrograph of the fresh silver sol is shown in Fig. 3 (A). It comprises

Fig. 3. Electron micrographs of silver sol particles that are (A) freshly prepared and
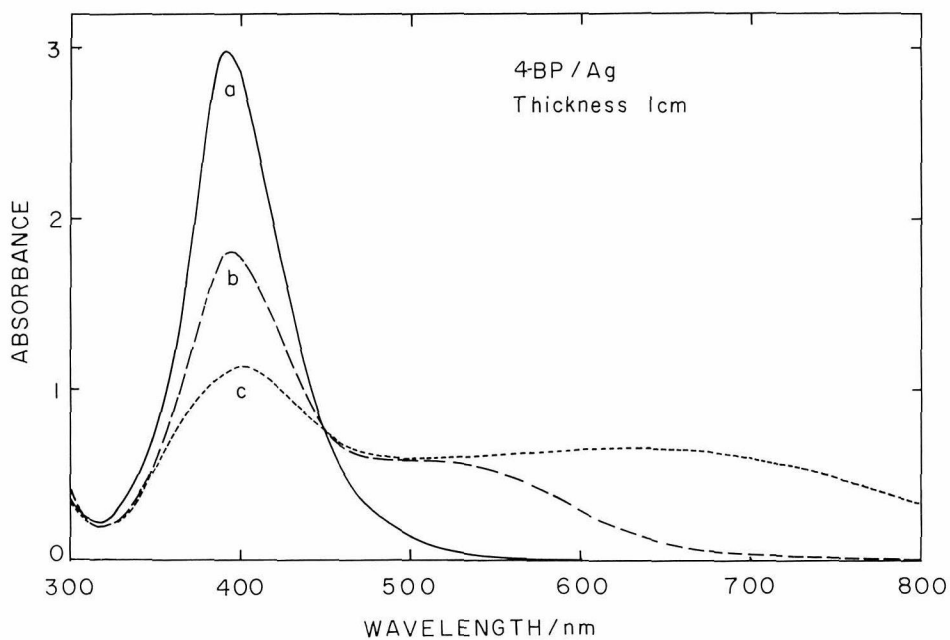(B) 20 min after addition of 4-BP $(1.1 \times 10^{-2} M)$.

Fig. 4. Changes in extinction spectra of silver sol at various stages of aggregation. (a) Before
addition, and (b) 2 min and (c) 20 min after addition of 4-BP $(1.7 \times 10^{-2} M)$.

smaller size primary particles (as compared with the gold sol) with the distribution from 6 to 17 nm (average 10 nm) diameters. Most of the particles occurs in small aggregates consisting of less than 10 primary particles. The specific surface area of the particles is calculated to be about 57 m^2/g and the concentration of monomolecularly adsorbed BP on the particles is estimated to be 7.3×10^{-6} M. On standing for 20 min after adding 4-BP (1.1×10^{-2} M), silver particles aggregate into globular clusters (Fig. 3 (B)) rather than strings of particles. Neither shape nor size of the primary particles had changed during the course of aggregation. The apparent difference in the aggregation mode between the gold and silver sol particles can not be explained at present.

The curve (a) in Fig. 4 represents the extinction spectrum of the fresh silver particle, showing a single extinction maximum at 390 nm due to the dipolar plasma resonance of the isolated particles. Upon addition of 4-BP (1.7×10^{-2} M) to this sol, there is a substantial change in color over 30 min from yellow, through orange and blue, to bluish grey due to aggregation. At the same time, the extinction spectra are changed as shown by curves (b) and (c) in Fig. 4. A very broad band appears on the long wavelength side and shifts to longer wavelengths with growing aggregation. This new band arises from the coupling between the dipolar plasma modes of the individual particles.[1,4,5] Clippe et al.[9] have pointed out that the splitting of the extinction bands for compact aggregates is less than that for linear strings. However, the splitting in Fig. 4 for the globular clusters of the silver particles is comparable to that in Fig. 2 for the linear strings of the gold particles. This may be mainly due to the larger number of aggregated silver particles as well as to the smaller size of primary silver particles. The broadness of the long wavelength band in Fig. 4 as compared with that in Fig. 2 may be also due to the globular shape of the silver particle aggregates.

4. SER SPECTRA OF ADSORBED BP'S

Figure 5 shows SER spectra of 2-, 3-, and 4-BP adsorbed on aggregated gold sols. Each spectrum is similar to that of the same molecule in aqueous solution except for small frequency shifts (up to 20 cm^{-1}) and relative intensity changes. The similar spectral features are also found for BP's adsorbed on silver sols. The spectral changes observed may be interpreted as due to adsorption of the BP molecules through the nitrogen atoms on metal surface.

The Raman excitation profiles for the ring breathing vibration at 1021 cm^{-1} of 4-BP adsorbed on gold sols are given by the broken lines in Fig. 6. The ordinate is the intensity ratio of this band to the 935 cm^{-1} band of the sodium perchlorate solution used as the external standard. The wavelength dependence of the monochromator and the detection system has also been corrected. The extinction spectra of the gold sols are also shown by the solid lines for reference. Fig. 6(A) refers to the gold sol standing for 3 h after adding 4-BP (2×10^{-5} M) and (B) to that standing for 24 h. The SERS intensity maxima are apparently coincident with the extinction maxima of the longitudinal plasma resonance of the gold particle aggregates, and moves with this band to longer wavelengths as the aggregation proceeds. Furthermore, following the strengthening of the longitudinal extinction band, the SERS intensity increases. The same situation is also found not only for 2- and 3-BP adsorbed on gold sols but also for the all BP's adsorbed on silver sols.
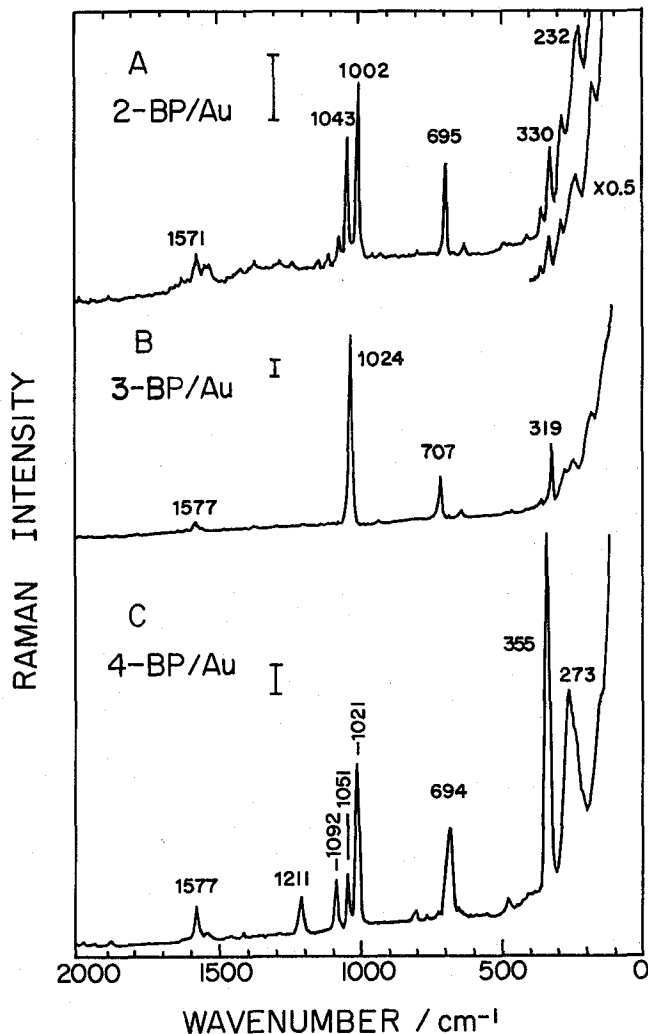
Fig. 5.   SER spectra by (A) 2-BP, (B) 3-BP, and (C) 4-BP adsorbed on gold sols.   Instrumental
condition; 676.4 nm excitation and laser output power 100 mW.

Furthermore, these facts have already been reported for pyridine adsorbed on gold and silver sols[1,3,4] and citrate ion adsorbed on gold sols.[5]   It can be said therefore that this similarity between the longitudinal extinction band and the SERS excitation profile is not characteristic of particular metal particle and adsorbate but is general nature reflecting the mechanism of SERS in colloidal systems.   The maximum enhancement factors for the ring breathing band amount ot 4×10^5 to 1×10^6 for all the three BP's.

In order to look more closely at the above-mentioned relation, the SERS intensities for the ring breathing vibration of adsorbed BP are plotted as a function of the absorbance of the gold sol at given excitation wavelengths (676.4 and 647.1 nm) within the longitudinal extinction band at various growing stages of aggregation shown in Fig. 2.   Here, the contribution from the single particle extinction band (peaked at 520 nm) to the absorbance
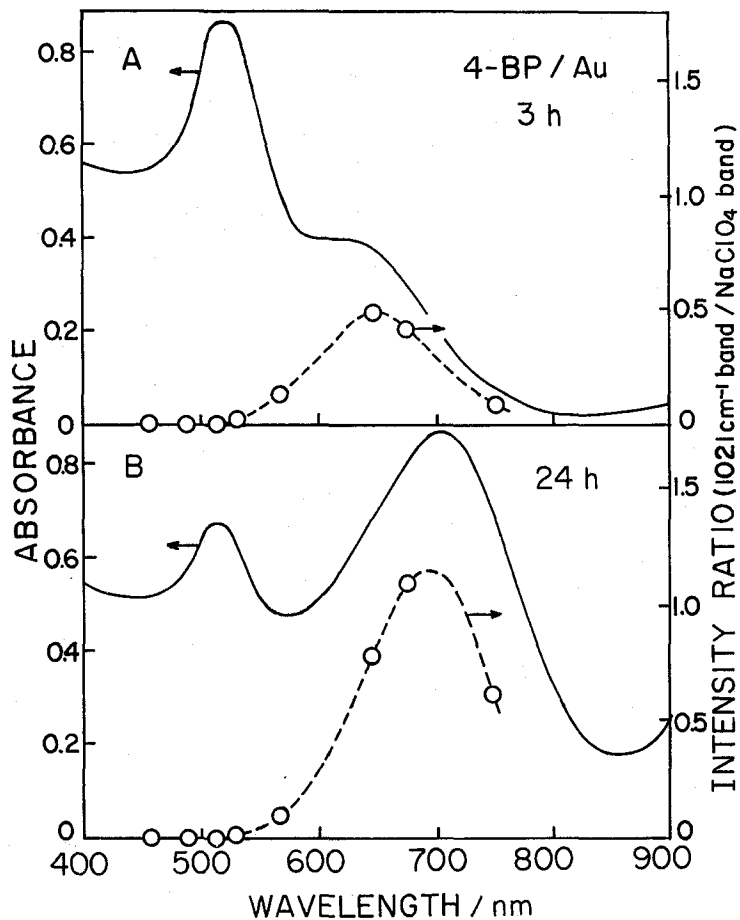
Fig. 6. Extinction spectra (———) of gold sol and the excitation profiles (————) for the
1021 cm⁻¹ Raman band of adsorbed 4-BP. (A) 3 h and (B) 24 h after addition
of 4-BP.

at the two excitation wavelengths is eliminated. Results are shown in Figs. 7, 8, and 9
for 2-, 3-, and 4-BP adsorbed on gold sols, respectively, indicating good linear relationships.
However, Creighton et al.[4] have reported that there is a near-quadratic relationship
between the SERS intensity of adsorbed pyridine and the absorbance of a gold sol. The
reason for this disagreement is not clear at present, but may be found partly in the above-
mentioned elimination of the contribution of the single particle extinction band in this
work. Further, it should be noted that Figs. 7, 8, and 9 include the experimental data
over wider range of aggregation degrees than Fig. 7(B) of Ref. (4) does, as is easily seen
from comparison of wavelength and relative intensity of the longitudinal extinction band
between Fig. 2 in this paper and Fig. 7(A) in Ref. (4).

Under the assumption of the electron plasma resonance model for SERS on silver-
island films, Weitz et al.[10] have proposed that the relative SERS intensity $I(\omega_E)$ at the
excitation frequency ω_E can be expressed by the product of absorbances of the films
$A(\omega_E)A(\omega_R)$ at the excitation and Raman frequencies ω_R, as follows.[10]
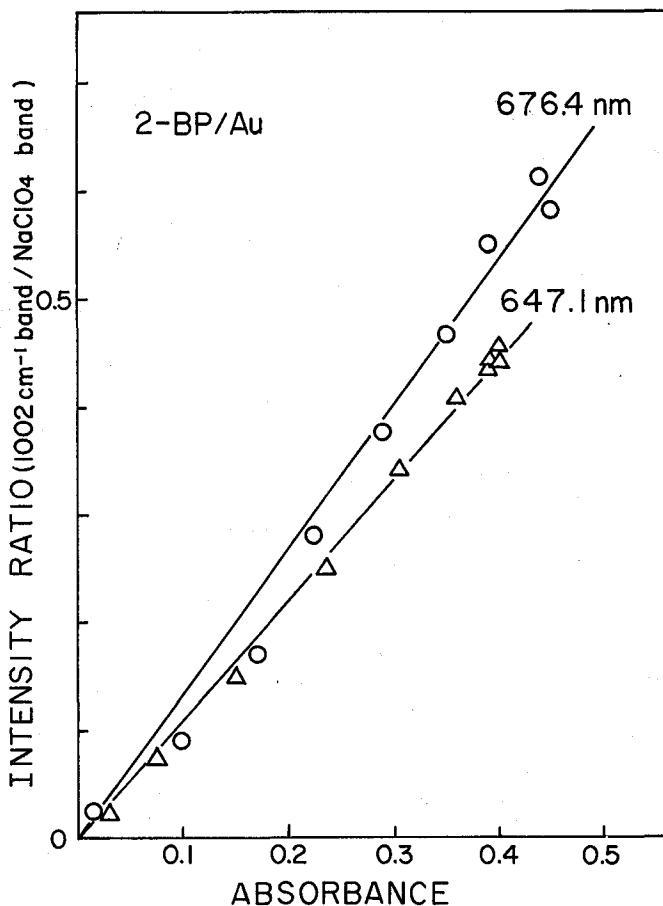
Fig. 7. The Raman intensity for the ring breathing vibration of 2-BP adsorbed on gold sol as a function of the absorbance of the sol at given excitation wavelengths (676.4 and 647.1 nm) within the longitudinal extinction band.

$$I(\omega_E) \simeq k \frac{|\varepsilon(\omega_E)|^2 |\varepsilon(\omega_R)|^2}{\omega_E \omega_R \varepsilon_2(\omega_E)\varepsilon_2(\omega_R)} A(\omega_E)A(\omega_R) \qquad (1)$$

where k is a constant concerning the film thickness etc. and $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$ is the dielectric constant of bulk metal. On the basis of this equation, Creighton et al.[4] have accounted for their empirical observation that $I(\omega_E)$ varies as $[A(\omega_E)]^2$ with increase in aggregation, since $A(\omega_E)$ and $A(\omega_R)$ are approximately equal for relatively small Raman shifts. However, Weitz et al. have pointed out that eq. (1) is valid only if the spectral dependence of the electronic plasma resonances is the same on the individual islands of the film and that the use of $A(\omega_R)$ in eq. (1) is incorrect in the case of colloidal systems, in which the above spectral homogeneity probably does not exist because of much larger inter-particle separations. This may resut in a possibility of a linear relationship between $I(\omega_E)$ and $A(\omega_E)$ as shown in Figs. 7, 8, and 9.

The much larger Raman enhancement for excitation under the longitudinal than

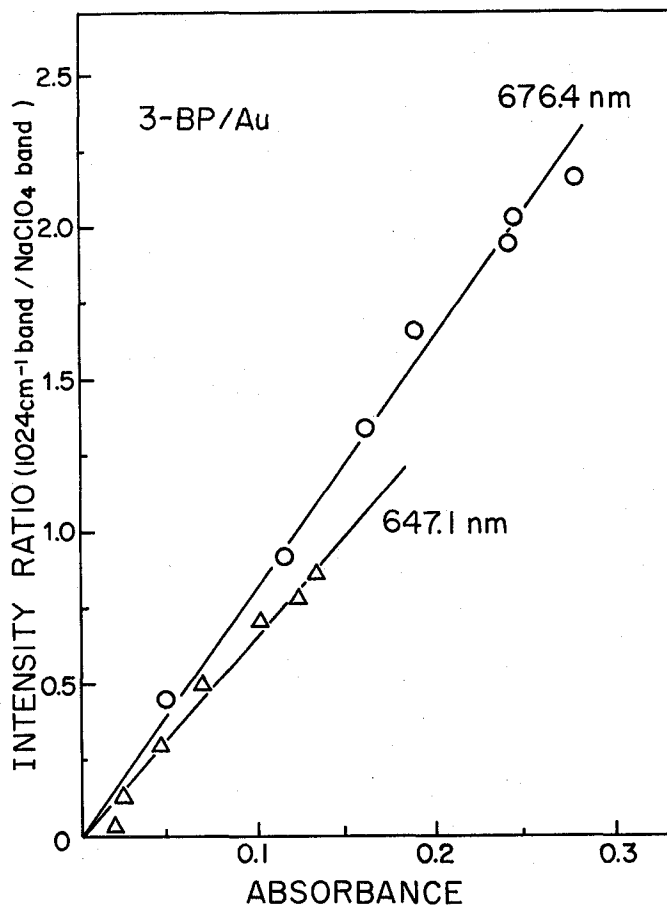T. TAKENAKA, K. EDA, M. MABUCHI, Y. FUJIYOSHI, and N. UYEDA

Fig. 8. The Raman intensity for the ring breathing vibration of 3-BP adsorbed on gold sol as a function of the absorbance of the sol at given excitation wavelengths (676.4 and 647.1 nm) within the longitudinal extinction band.

under the transverse plasma resonance shown in Fig. 6 has been interpreted as due principally to the steep rise in a fractional part in eq. (1) for silver and gold particles with increase in wavelength in the visible region.[4,10)

5. EFFECT OF THE POSITION OF BROMINE SUBSTITUTION IN THE PYRIDINE RING ON SER SPECTRA

To examine the SERS intensity of the C-Br stretching band near 700 cm^{-1} semi-quantitatively, we compare the intensity ratios of this band to the totally symmetric ring breathing band near 1010 cm^{-1} for the three BP's in bulk solution and on the colloid surface. The results summarized in Table I reveal that the changes in the intensity ratios with changes in the molecular environment of BP's from the aqueous solution to the metal surface show the same trend for gold and silver particles; a two or threefold increase for 2-BP, a slight increase for 4-BP, and a slight decrease for 3-BP. Under the assumption that adsorption occurs through an interaction of the metal with the nitrogen lonepair
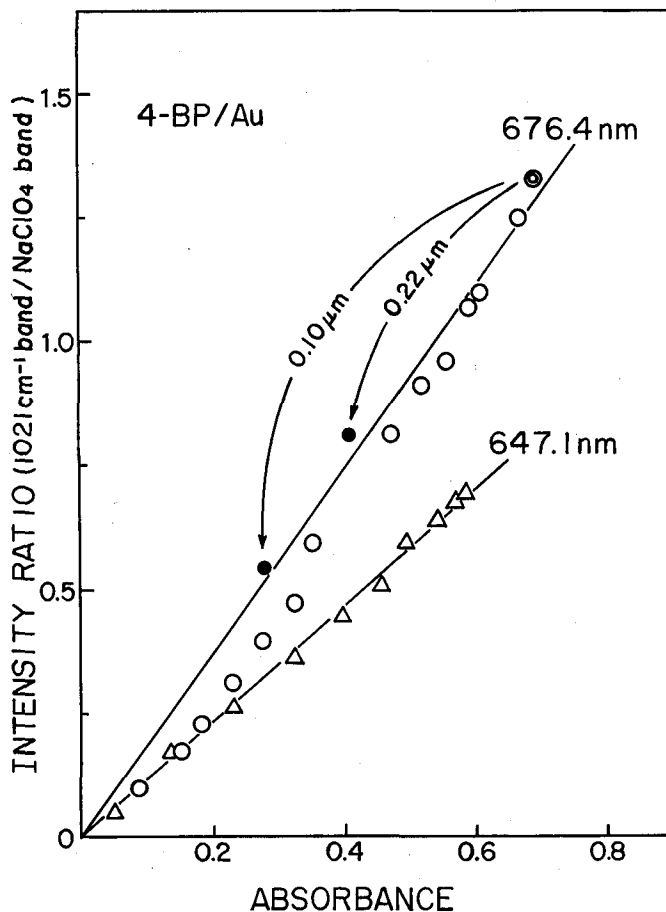
Fig. 9. The Raman intensity for the ring breathing vibration of 4-BP adsorbed on gold sol
as a function of the absorbance of the sol at given excitation wavelengths (676.4 and
647.1 nm) within the longitudinal extinction band. Two black points are the experi-
mental ones obtained after filtration with 0.22 and 0.10 μm pore size filters.

electrons, with the plane of the molecule perpendicular to the surface, these results show
the definitive deviation from the prediction of the image-dipole model for enhancement
which is one of various theories proposed to explain SERS.[11,12] On the other hand, the
electronic theory in organic chemistry suggests that the charge density on the nitrogen atom

Table I. Raman intensity of the C-Br stretching vibration relative to the ring
breathing vibration for bromopyridines in various environments

	I_{CBr}/I_{ring}			R_{Ag}/R_0	R_{Au}/R_0
	Aq. solution (R_0)	SERS on Ag (R_{Ag})	SERS on Au (R_{Au})		
2-BP	0.19	0.54	0.41	2.8	2.2
3-BP	0.18	0.12	0.16	0.7	0.9
4-BP	0.27	0.32	0.36	1.2	1.3

of the three BP's decreases in the order of 2-BP>4-BP>3-BP, which is just the same as that mentioned above.   It seems therefore that the difference in the charge density on the nitrogen atom due to the difference in the position of bromin substitution in the pyridine ring exerts significant influence upon the modulation of the surface plasma oscillation of the metal particle aggregates by the C-Br stretching vibration of adsorbed BP's.[13]

6. APPLICATION OF A MICROFILTERING TECHNIQUE TO AGGREGATED GOLD SOLS

In order to solve the above-mentioned question of whether aggregation is required for the observation of SERS in colloidal systems, recently Krimm *et al.* have applied a microfiltering technique to pyridine-induced silver aggregates.[7]   They used polycarbonate, 0.05 μm pore size filters to remove aggregates consisting of primary particles with 5–13 nm (average 7.5 nm) diameters (the ratio of the pore size to the average particle diameter is about 7 : 1).   From observations that SERS intensity of adsorbed pyridine before and after the filtration showed only a 20% decrease, it was believed that molecules adsorbed on unaggregated particles were responsible for the most of SERS intensity.   They declared the nearly complete removal of aggregates by filtration from electron microscopic examination of the filtrate, however, it is essential to definitely indicate the degree of removal by presenting electron micrographs and/or extinction spectra of the sol systems before and after the filtration.   But they presented neither in their paper.[7]

Thus we also applied the same technique to our 4-BP-containing gold sol.   We used polycarbonate, 0.10 and 0.22 μm pore size filters to remove aggregates consisting of primary gold particle with 19 nm diameter (the ratio of pore size to the particle diameter is about 5 : 1 and 12 : 1, respectively).   A 0.05 μm pore size filter got clogged immediately. Figure 10(A) and (B) are the electron micrographs of the sol before and after the filtration, respectively, by use of the 0.10 μm pore size filter.   Figure 10(A) is almost the same as
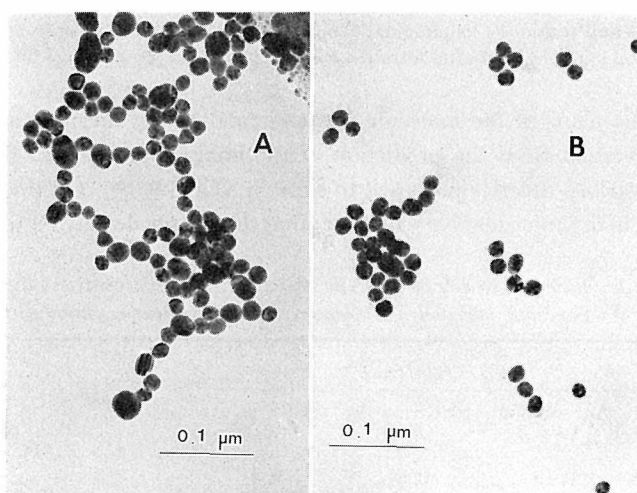

Fig. 10.   Electron micrographs of 4-BP-induced gold sol particles that are (A) before and (B) after filtration with a 0.10 μm pore size filter.

Fig. 1(B), indicating networks of strings. After filtration, the networks completely disappear and single particles and small aggregates consisting of less than 5 primary particles remain as seen in Fig. 10(B). Furthermore, larger aggregates consisting of more than 20 particles exist occasionally.

The same conclusion is also drown from extinction spectra of filtrates shown by the broken and chain curves in Fig. 2. The former refers to filtration by a 0.22 μm pore size filter from an aggregated sol which represents the extinction spectrum No. 17 of Fig. 2 and the latter to that by a 0.10 μm filter. The over-all decrease in the extinction intensity may be due to a reduced number of particles as a consequence of retention of both the aggregated and unaggregated particles in the microfilters. The slight shift of the longitudinal plasma resonance to the short wavelength side is ascribed to the larger degree of removal of higher aggregates. It should be noticed anyhow that the extinction band at longer wavelength side due to the aggregates still remains with considerable intensity. Both observations by the electron micrographs and extinction spectra of our gold sols clearly indicate the presence of fairly large amounts of aggregates after filtration, being contrary to the above-mentioned statement by Krimm et al.[8]

Furthermore, we examined the relationship between the SERS intensities for ring breathing band of adsorbed 4-BP and the absorbance of the sols at 676.4 nm for the filtrates. The results are shown in Fig. 9. The experimental point obtained before filtration moves to the respective black points by filtration with the 0.22 and 0.10 μm pore size filters, the both points lying approximately on the straight line mentioned above. This suggests that by filtration the experimental point moves along this straight line in the opposite direction to that in the growing process of aggregation. It is concluded therefore that the SERS intensity obtained after filtration also follows the linear relationship between that and the absorbance of the extinction band as a measure of the degree of aggregation and consequently the intensity arises entirely from the aggregates of colloidal particles.

7. SUMMARY

SER spectra by 2-, 3-, and 4-BP adsorbed on gold and silver sol particles have been studied. The extinction spectrum of the freshly prepared sol shows a single peak ascribed to the dipolar plasma resonance of isolated particles. When aggregation of the particles starts by addition of adsorbate, a new band appears on the long wavelength side, which is due to a coupling between the dipolar plasma modes of individual constituent particles. At the same time, the Raman intensity of adsorbate is enhanced up to 10^6 time when the new band due to the aggregates is excited. The SERS excitation profile peaks at the same wavelength as the new band and moves with this band to longer wavelengths as the aggregation proceeds.

A linear relationship is obtained between the SERS intensity of the ring breathing vibration (*ca.* 1020 cm^{-1}) of adsorbed BP and the absorbance of the gold sol at excitation wavelengths within the longer wavelength band due to the aggregates. This relationship is interpreted by a theory of Weitz et al.[10] which has been derived under the assumption of electron plasma resonance model for SERS.

A microfiltering technique is applied to the 4-BP-induced gold particle aggregates. On the contrary to a previous finding by Krimm et al.[7] it is proved by electron micrographs

and extinction spectra of the filtrates that the fairly large amounts of aggregates remain after filtration and that the SERS intensity of the filtrates arises from the unfiltered aggregates following the above-mentiones linear relationship between the Raman intensity and the absorbance of the extinction band as a measure of the degree of aggregation.

It is concluded therefore that the aggregation is an essential requirement for observation of SERS in colloidal systems and that the SERS observed in this work is mainly due to resonant excitation of the surface plasma oscillation of the aggregates of sol particles.[1,4,5]

Recently, on the basis of an electromagnetic theory, Inoue and Ohtaka[14] have calculated the absorption spectra by two-, three-, and four-sphere clusters (aggregates) of gold and silver in water and the Raman intensity by adsorbates. It was presented that the absorption spectrum was doubly peaked with a new peak appearing in the long wavelength side and the maximum enhancement factor of Raman intensity amounted to 10^7–10^8 when the longer wavelength peak was excited. This was explained as due to extraordinary strengthening of the local electric field between metal spheres. Their results reproduce the gross features of our experimental observations satisfactorily.

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