Carbonizable Adsorbate: Ag/Pyridine SERS. The Auger data suggest that the pyridine SERS effect emanates from the relatively minute laser region of the electrode surface which is pure or nearly pure carbon. This is in accord with the previous formulation of the intensely scattering phase as [carbon·pyridine] and not pyridine itself. The enhancement factor (10^4–10^5) for this system is calculated from parameters for the nonilluminated[26] silver surface (viz. pyridine coverage, roughness). The calculation does not consider either pyridine accumulation on laser-zone carbon or resonance (nonsurface) enhancement due to carbon itself.[24,25] Therefore the residual silver-surface enhancement of the [pyridine·carbon] phase is, at present, unknown.

Recent studies[27] have revealed that under typical SERS conditions[28] black laser surface damage spots are visible to the unaided eye for a range of organic adsorbates (pyridine, glycine, ethylenediamine, 4-aminopyridine, etc.). In each case, the observation of the black damage spot is accompanied by the appearance of intense carbon spectral features.

Noncarbonizable Adsorbate: Ag/Cyanide SERS. Extensive laser damage is clearly evident in this case; however, the identity of the intensely-scattering phase is not clearly defined by the Auger data. The data provide some support for both surface phases previously proposed (silver(I) oxide cyanide and silver(I) cyanide complex). For this reason, a mixed formulation is suggested. However, cyanide coverage data based on the nonilluminated surface are unlikely to relate to coverage within the laser (SERS) zone on the surface. Therefore the magnitude of the enhancement factor is again uncertain.

The common factor in both of these systems is the active role of the focussed laser in modifying the local composition of anodized silver surfaces.

Acknowledgment. The authors are grateful to A.R.G.S. for providing Raman spectroscopic and electrochemical equipment, and to Dr. J. A. D. Matthew for helpful advice.

Registry No. Ag, 7440-22-4; KCN, 151-50-8; Na_2SO_4, 7757-82-6; pyridine, 110-86-1.

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(26) Nonilluminated surface: a surface not exposed to laser light or those zones of an illuminated surface outside the (relatively) minute laser zone.

(27) R. A. Kydd and R. P. Cooney, *J. Chem. Soc., Faraday Trans. 1*, in press.

(28) Aqueous KCl electrolyte; ORC: $-0.6\ V \rightleftharpoons +0.2\ V$ at 5 mV s^{-1} and ≤100 mW at 514-nm Ar^+.

Combined Surface-Enhanced and Resonance-Raman Scattering from the Aspartic Acid Derivative of Methyl Orange on Colloidal Silver

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By selecting a chromophore, dabsyl (*N*-4-dimethylaminoazobenzene-4′-sulfonyl) aspartate (DABS–ASP), whose absorption spectrum overlaps with the surface-enhanced Raman scattering (SERS) excitation profile for colloidal silver sols, we have found it possible to study the triple combination of resonant Raman scattering (RRS) of the DABS–ASP in solution and both the combined RRS–SERS (SERRS) and the SERS of DABS–ASP adsorbed on the colloidal silver particles. The SERRS and SERS spectra were distinctly different from each other. The measured surface enhancements were in excess of 10^3. This is less than the values of the order of 10^5 measured earlier for citrate on these silver sols. Just as for citrate, the excitation profiles peaked at about 500 nm whereas the main absorption band was in the region of 400 nm, a disparity from our electrodynamic model for SERS.

Introduction

Surface-enhanced Raman scattering (SERS) studies of species adsorbed to colloidal silver,[1] roughened silver electrodes,[2] and silver films[3] have shown that Raman signals of the adsorbate can be enhanced by as much as 10^5–10^6-fold. Thus, when combined with resonance Raman scattering[4] (RRS) from an appropriate chromophoric adsorbate, total Raman enhancement factors might reach the 10^{10} to 10^{12} range. In those examples, where RRS and SERRS spectra of chromophoric adsorbates have been reported (crystal violet and methyl orange on a Ag electrode,[5a] *p*-nitrosodimethylaniline on Ag and Pt electrodes,[5b] myoglobin and cytochrome *c* on a Ag electrode,[5c] dithizone on a Ag electrode,[5d–f] rhodamine 6G on silver-island

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(1) (a) Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 790. (b) Kerker, M.; Siiman, O.; Bumm, L. A.; Wang, D.-S. *Appl. Opt.* **1980**, *19*, 3253.

(2) (a) Van Duyne, R. P. In "Chemical and Biological Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, p 101. (b) Furtak, T. E.; Reyes, J. *Surf. Sci.* **1980**, *93*, 251. (c) Otto, A. *Appl. Surf. Sci.* **1980**, *6*, 309.

(3) (a) DiLella, D. P.; Moskovits, M. *J. Phys. Chem.* **1981**, *85*, 2042. (b) Murray, C. A.; Allara, D. L. *J. Chem. Phys.* **1982**, *76*, 1290. (c) Chang, R. K.; Furtak, T. E., Ed.; "Surface Enhanced Raman Scattering"; Plenum Press: New York, 1982. (d) Otto, A. In "Light Scattering in Solids"; Cardona, M.; Güntherodt, G., Ed.; Springer: Berlin; Vol. IV, in press.

(4) (a) Behringer, J. In "Raman Spectroscopy. Theory and Practice"; Szymanski, H. A., Ed.; Plenum: New York, 1967; Vol. 1, p 168. (b) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1. (c) Carey, P. R.; Salares, V. R. In "Advances in Infrared and Raman Spectroscopy"; Clark, R. J. H.; Hester, R. E., Ed.; Heyden: London, 1980; Vol. 7, p 1.

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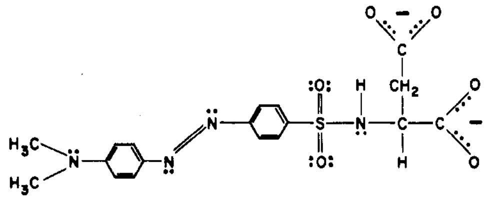
films[5g]), the Raman band positions and relative intensities appear to be identical in almost all cases. Only intensification of the original RRS spectrum was observed. However, the SERS spectrum of methyl orange[5a] on a Ag electrode and the RRS spectrum in solution[6] were different, a case that needs to be confirmed.

The triple combination of RRS in solution, combined RRS–SERS of this species adsorbed on a metal surface, and SERS from this adsorbate on the same surface at a frequency where there is no RRS has not been studied. In such an experiment, if the concentration of adsorbed molecules is determined, it is possible to estimate the absolute contribution of SERS to the combined RRS–SERS signals and compare this with earlier estimates of normal SERS. In RRS–SERS experiments the Raman bands are *both* resonance- and surface-enhanced. This should give rise to the same selective Raman spectrum that is observed in the resonance Raman spectrum of the pure chromophoric molecule. On the other hand, the SERS spectrum of the chromophore, when excited in a spectral region that does not give RRS, should resemble its normal Raman spectrum.

In SERS experiments with adsorbates on electrode surfaces it has not been possible to control the size and shape of the surface protrusions that give rise to the roughness nor even to describe these deterministically. Yet, the roughness determines the shape and intensity of the SERS excitation profile. This major disadvantage in SERS work with electrodes can be overcome in the study of adsorbates on colloidal metal particles over which a considerable degree of control of size and shape can be exercised. Some control over the shape and size of silver island films which can be thought of as two-dimensionally supported colloids can also be exercised, and recent work in this field has been discussed in several review articles[2b,3d] or collections of articles[3c] that indicate the scope of the SERS field.

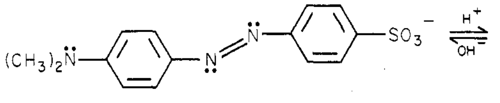
Colloidal dispersions also have the advantage that, in addition to techniques such as electron microscopy, the particle morphology can be monitored by optical techniques such as absorption spectroscopy. For example, small (diameter < 20 nm) silver spheres dispersed in water show a narrow absorption band centered at about 380–390 nm which broadens and develops longer wavelength shoulders or secondary peaks as the particles become larger or as they deform from spherical shape or as they aggregate. SERS effects have been observed to be associated with these spectral effects.[1a,7] Indeed, the electrodynamic model which has been developed to account for SERS by molecules adsorbed on spheres,[8] spheroids,[9] and concentric spheres[10] delineates a direct relationship between the particle absorption spectrum and the SERS excitation profile on the one hand and the particle morphology on the other.

Scheme I

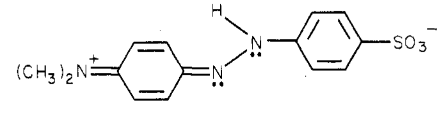


This work is a study of the triple combination of RRS in solution and RRS–SERS and SERS of a chromophore adsorbed on colloidal silver particles. The chromophore chosen is a methyl orange derivative, dabsyl aspartate (DABS–ASP), *N*-((4-((4-(dimethylamino)phenyl)azo)phenyl)sulfonyl) aspartate (*N*-4-dimethylaminoazobenzene-4′-sulfonyl aspartate, see Scheme I). In neutral or basic solutions its absorption band, centered at 472 nm, overlaps with the SERS excitation profile of citrate adsorbed on colloidal silver which peaks at 490 nm[7] so that when DABS–ASP is either coadsorbed or displaces adsorbed citrate, RRS–SERS should be observed. Furthermore, since the SERS profile extends to lower energies where the chromophore no longer absorbs, particularly when the sol is aggregated, the signal in this region should be mainly SERS. There is the added advantage that DABS–ASP in neutral and basic solutions does not fluoresce.

The parent acid–base indicator, methyl orange, changes color from yellow-orange to red in pH 3.1–4.4 range.[11,12] The yellow-orange, alkaline form absorbs maximally at 464 nm while the red, acid form absorbs at 508 nm.[6b] The color change is accompanied by the following structural change:



alkaline form



acid form

RRS of both alkaline and acid forms have been reported[6b] and agree with the above structural assignments. Similar structural changes may be expected in DABS–ASP on going from the alkaline to the acid form.

Experimental Procedures

For the initial stages of this work, DABS–ASP was prepared on a micromole scale by condensation of DABS–Cl in acetone (Pierce Chemical Co.) with L-aspartic acid in 0.1 M $NaHCO_3$, as previously described.[13] After reaction the residual mixture, however, was applied on a column (15 cm × 7 cm) packed with MN silica Gel 60, 200 mesh (Brinkmann) or on a column (30 cm × 3 cm) packed with Bio-Sil A, 200–400 mesh (Bio-Rad Laboratories). The solvent system, toluene–pyridine–acetic acid, was used to develop the column. First, a solvent mixture, 16:4:1, v/v/v, was used to elute a narrow red fraction. The bulk of the colored material remained near the top of the column. Second, a red-orange band representing most of the product was eluted slowly with a solvent mixture, 3:3:2, v/v/v, collected, evaporated to dryness, and dried in vacuo over P_2O_5. This fraction was identified as DABS–ASP by its 472-nm absorption band maximum in a basic solution of 0.01 M aqueous sodium citrate and by its infrared

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spectrum (KBr disk). A third yellow band that was eluted very slowly showed a 420-nm absorption peak in ethanolic solution and an infrared spectrum[6a] characteristic of methyl orange.

Most of this work utilized a larger scale synthesis of DABS–ASP. DABS–Cl was prepared by the reaction of methyl orange (DABS–ONa) with phosphorus pentachloride as described by Lin and Chang.[13]

The reactants, L-aspartic acid and DABS–Cl, were scaled up to the 1-g DABS–Cl level and refluxed for 2 h in an acetone–0.1 M $NaHCO_3$ solvent mixture. Acetone was subsequently stripped under reduced pressure from the mixture. Solid sodium chloride was added to saturate the remaining aqueous solution. An equal volume of 1-pentanol was then added and DABS–ASP was extracted into the pentanol layer. The solvent was stripped in a rotatory evaporator and the dark red solid that remained was dried in vacuo under P_2O_5. Recrystallization of the crude DABS–ASP was carried out in acetone–diethyl ether mixtures.

Silver hydrosols stabilized by adsorbed citrate were prepared by an improved Carey Lea[14] procedure in which flocculation and repeptization of the initial crude sol was repeated three times with 0.5 and 0.01 M sodium citrate, respectively, instead of potassium nitrate. The larger particles of the sol were centrifuged down at 10 000 rpm ($8.1 \times 10^3 g$) for 5 min and the centrifugate retained. This preparation, which will be called sol 3 as in an earlier report,[7] has a clear solutionlike yellow appearance. Electron microscopic examination showed it to consist mainly of spheres in the 5–10-nm range with a small number of globular clusters. It showed a SERS excitation profile peaking near 500 nm.

A second preparation was formed by applying 20 cm^3 of a 10:1 dilution of sol 3 to a Bio-Gel P-6 polyacrylamide, 100–200 mesh, column (3.0 cm × 85 cm). Tenth molar sodium citrate was used to wash the column initially and develop the silver sol bands. Two bands were produced. The first orange-red one was broad and eluted with the solvent head; the second dark red band was sharp and eluted slowly. A large amount of sol remained adsorbed tightly to the top of the column and could not be eluted. Only the second fraction was used in this work. Samples were pooled, dialyzed twice against 2 L of distilled water overnight, and then dialyzed against 0.01 M sodium citrate. This preparation will be called sol 6 as in the earlier report.[7] It had a reddish tinge. Electron microscopic examination showed large clusters which were presumably aggregates of the primary particles of sol 3. It showed a broad SERS excitation profile peaking near 490 nm which was similar to that of sol 3.

The sols were treated with DABS–ASP as follows. In one case 2.0 cm^3 of 6.6×10^{-5} M DABS–ASP in 0.01 M sodium citrate (pH ~9.0) was added to 10 cm^3 each of sol 6 and distilled water giving a total DABS–ASP concentration of 1.1×10^{-5} M in each sample. In a second case 1.0 cm^3 of 1.16×10^{-3} M DABS–ASP in 0.01 M sodium citrate was added to 10.0 cm^3 each of sol 3 (dialyzed once or twice against 2 L of distilled water) and of distilled water giving a total DABS–ASP concentration of 1.05×10^{-4} M. This sample was then diluted tenfold.

It took several days for the adsorbed citrate and DABS–ASP to equilibrate. Though weak citrate SERS bands could still be detected in these stock silver sol mixtures with DABS–ASP shortly after mixture, none were observed after several days. On the other hand, the DABS–ASP SERS band intensities increased by a factor of ten during this period.

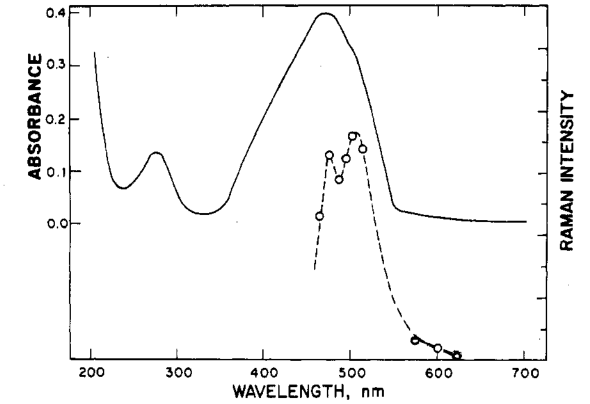

Figure 1. Absorption spectrum of DABS–ASP (1.08×10^{-4} M) in 0.01 M Na_3cit, solid line; resonance Raman excitation profile of DABS–ASP (1.08×10^{-4} M) vs. Na_2SO_4 (0.9 M) internal standard, $I_{\text{DABS-ASP}}$ (~1400 cm^{-1})/$I_{SO_4^{2-}}$ (985 cm^{-1}), dashed line.

In those cases where a sol was diluted in order to obtain a Raman spectrum, it was necessary to permit it to stand for at least 2 days in order that the adsorbed DABS–ASP again comes to equilibrium. The Raman signals from the freshly diluted sols decreased with time as the DABS–ASP desorbed from the surface, an indication of course that the adsorbed species gave an enhanced Raman signal.

An assay for the amount of DABS–ASP that adsorbed to the silver particle surface was performed only for the second case. After the sol–DABS–ASP mixture had equilibrated for several days the silver particles were separated by ultracentrifugation at 40 000 rpm ($1.3 \times 10^5 g$) for 55 min. By measuring the difference in absorbance at 472 nm between a blank + DABS–ASP and the supernatant of the sol + DABS–ASP after centrifugation it was found that 35% and 5.9% of the added DABS–ASP had adsorbed to the silver particle surfaces to give an adsorbed DABS–ASP concentration of 3.7×10^{-5} and 6.2×10^{-7} M, respectively, for undiluted and ten times diluted mixtures.

Raman spectra obtained with Spectra-Physics Model 165 Ar^+ and Kr^+ laser and Coherent Model 590-03 dye (rhodamine 6G) laser excitation were measured on a Jarell-Ash 25-500 double Ebert monochromator (f/6.5). A thermoelectrically cooled Hamamatsu R928 PM tube and EG&G Model 112 photon counter/processor were used in detection. Solutions and hydrosols were recirculated with a peristaltic pump (~3 mL/min) through a rectangular quartz flow cell (3 mm × 3 mm cross section) positioned at 90° to the laser beam and monochromator slits which were both vertically arranged. Scattered light was always collected at 90° to the incident beam. The scan speed was 1.0 cm^{-1}/s in all cases.

Absorption spectra were measured on a Cary 14 UV–VIS–NIR spectrophotometer. Ultracentrifugations were performed on a Beckman Model L8-70 with a 70Ti fixed angle rotor.

Results and Discussion

Absorption Spectra. The absorption spectrum of DABS–ASP in 0.01 M sodium citrate, shown in Figure 1, exhibits a band maximum at 472 nm. Curve A in Figure 2 is the absorption spectrum of sol 3 after dialysis against distilled water, but prior to addition of DABS–ASP. It shows the narrow resonance band at about 400 nm characteristic of small unaggregated silver spheres. Curves B and C in Figure 2 are the absorption spectra of sols 6 and 3, respectively, to which DABS–ASP has been added as described above. These sols, which were initially yellow

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[14] (a) Carey Lea, M. *Am. J. Sci.* **1889**, *37*, 476. (b) Frens, G.; Overbeek, J. T. G. *Kolloid Z. Z. Polym.* **1969**, *233*, 922.

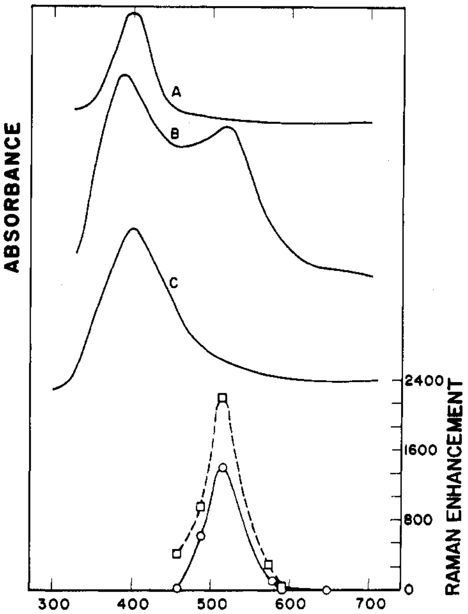


Figure 2. Absorption spectra of A, silver citrate hydrosol, centrifuged sol 3; B, sol 6 with DABS–ASP; C, Sol 3 with DABS–ASP. SERS excitation profiles, absolute surface enhancement for sol 3, solid line; lower limit of enhancement for sol 6, dashed line.

TABLE I: Experimental Conditions for Raman Spectra in Figure 3

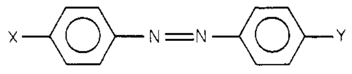
sample in Figure 3	λ_0,[a] nm	laser power, mW	counting interval,[b] s	spectral slit-width,[c] cm^{-1}
A	465.8, Ar$^+$	50	0.30	4.2
B	488.0, Ar$^+$	58	0.012	5.3
C	572.5, dye	30	0.085	5.0
D	591.5, dye	73	0.060	5.0
E	624.7, dye	35	0.40	5.0
F	647.1, Kr$^+$	72	0.40	6.0
G	676.4, Kr$^+$	77	0.50	8.0

[a] Excitation wavelength, laser sources. [b] 10^3 counts full scale. [c] At 1400 cm^{-1}.

and slightly reddish, respectively, were mixed with the reddish DABS–ASP. They rapidly developed a deeper reddish color as indicated by the spectra. Sol 6 showed the greatest change with the formation of two maxima at 385 and 525 nm from the single initial band at 400 nm. For sol 3 there was a significant broadening of the band with a shoulder at 475 nm. Such shifts have been shown in earlier work[7] to be associated with coagulation.

Raman Spectra of DABS–ASP in Solution. The resonance Raman spectrum of DABS–ASP, 1.1×10^{-4} M, in 0.01 M aqueous sodium citrate solution is shown as curve A in Figure 3 for λ_0 = 465.8 nm. The experimental conditions for this and the other spectra reported in Figure 3 are listed in Table I. Similar spectra were observed with excitation wavelengths between 457.9 and 622.5 nm.

An excitation profile for the three most intense RR bands near 1400 cm^{-1} was obtained by comparing the integrated band intensities against the intensity of an internal standard (1 M sodium sulfate) Raman band at 985 cm^{-1}. The ratio of the DABS–ASP to Na_2SO_4 intensity was normalized to unity at excitation wavelength λ_{exc} = 622.5 nm. The excitation profile is shown in Figure 1 in arbitrary units. Two peaks appear in the RR profile: one near 475 nm (20800 cm^{-1}); another near 508 nm (19700 cm^{-1}). The difference in energy of 1100 cm^{-1} corresponds to an intense RR band of DABS–ASP in this spectral region. Thus, it is reasonable to associate the maxima in the RR excitation profile with vibrational fine structure. The 475-nm peak may correspond to a 0–n electronic transition while the 508-nm peak would be asssignable to the 0–(n + 1) electronic transition. Raman and/or resonance Raman spectra of azobenzene compounds of the type



have been reported.[15] In addition, the RR spectra of methyl orange (X = $-N(CH_3)_2$, Y = $-SO_3^-Na^+$) in aqueous solution and in the solid state were also obtained.[6] All show RR spectra similar to the one reported herein when excitation into a near-UV absorption band in the 350–500-nm region is used. The most intense RR bands can be associated with vibrations of the azo group and its nearest-neighbor bonds (Ph–N). Raman bands due to the X or Y terminal groups were not observed. The spectrum in Figure 3A also contains no Raman bands that can be assigned to dimethylamino or sulfonyl aspartate groups.

SERS of DABS–ASP on Colloidal Silver. Curves B–G in Figure 3 are the Raman spectra of the mixture of sol 6 and DABS–ASP taken at six different excitation wavelengths, 488.0, 572.5, 591.5, 624.7, 647.1, and 676.4 nm. The total concentration of DABS–ASP (in solution plus that which is adsorbed on silver) is 4.0×10^{-7} M for the first three wavelengths and 1.1×10^{-5} M for the latter three. Spectra with 457.9- and 514.5-nm excitation were identical with the 488.0-nm spectrum. The mixture of sol 3 and DABS–ASP gave similar relative intensities.

Three distinct regions were covered: (1) 457.9-514.5 nm, where the excitation profile of citrate of the original sol and of DABS–ASP in solution overlap giving strong coupling of SERS and RR; (2) 572.5–624.7 nm where the DABS–ASP absorbs weakly giving much weaker RR but where the reddened mixture of the sol to which DABS–ASP has been added absorbs appreciably due to coagulation of the sol; (3) 647.1–676.4 nm where only the reddened sol absorbs weakly.

It is immediately obvious that each of these spectra are surface enhanced. For example, the signal strengths for 465.8-nm excitation of 1.3×10^{-4} M DABS–ASP in solution (curve A) are somewhat weaker than for 488.0-nm excitation of sol 6 to which the *total* added DABS–ASP is only 4.0×10^{-7} M (curve B). Pure DABS–ASP solutions at the highest concentration levels encountered in the sol mixtures (1.1×10^{-5} M) showed no measurable Raman signals at 572.5 nm or higher excitation wavelengths.

The contribution of SERS to the Raman signal from each of the two sols to which DABS–ASP had been added was placed on a quantitative basis by observing the spectrum of the sol and reference solution of DABS–ASP under the same instrument conditions at 457.9, 488.0, and 514.5 nm. For sol 6 the total DABS–ASP concentration was 4.4×10^{-7} M; the reference solution was 1.1×10^{-5} M. For sol 3 these concentrations were 1.1×10^{-5} and 1.1×10^{-4} M, respectively. The relative intensities were obtained by integrating the area under the Raman bands in the 1300–1500-cm^{-1} region and the sol-to-solution ratios are given on lines 1 and 3 of Table II. These ratios, after the intensities have been corrected for absorption and adjusted to the same total DABS–ASP concentration, are shown in lines 2 and 4.

Since only a part of the total DABS–ASP in the sol is adsorbed on the silver particle surface where it is enhanced to give a measurable signal, these ratios represent a *lower*

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[15] Kumar, K.; Carey, P. R. *Can. J. Chem.* **1977**, *55*, 1444.

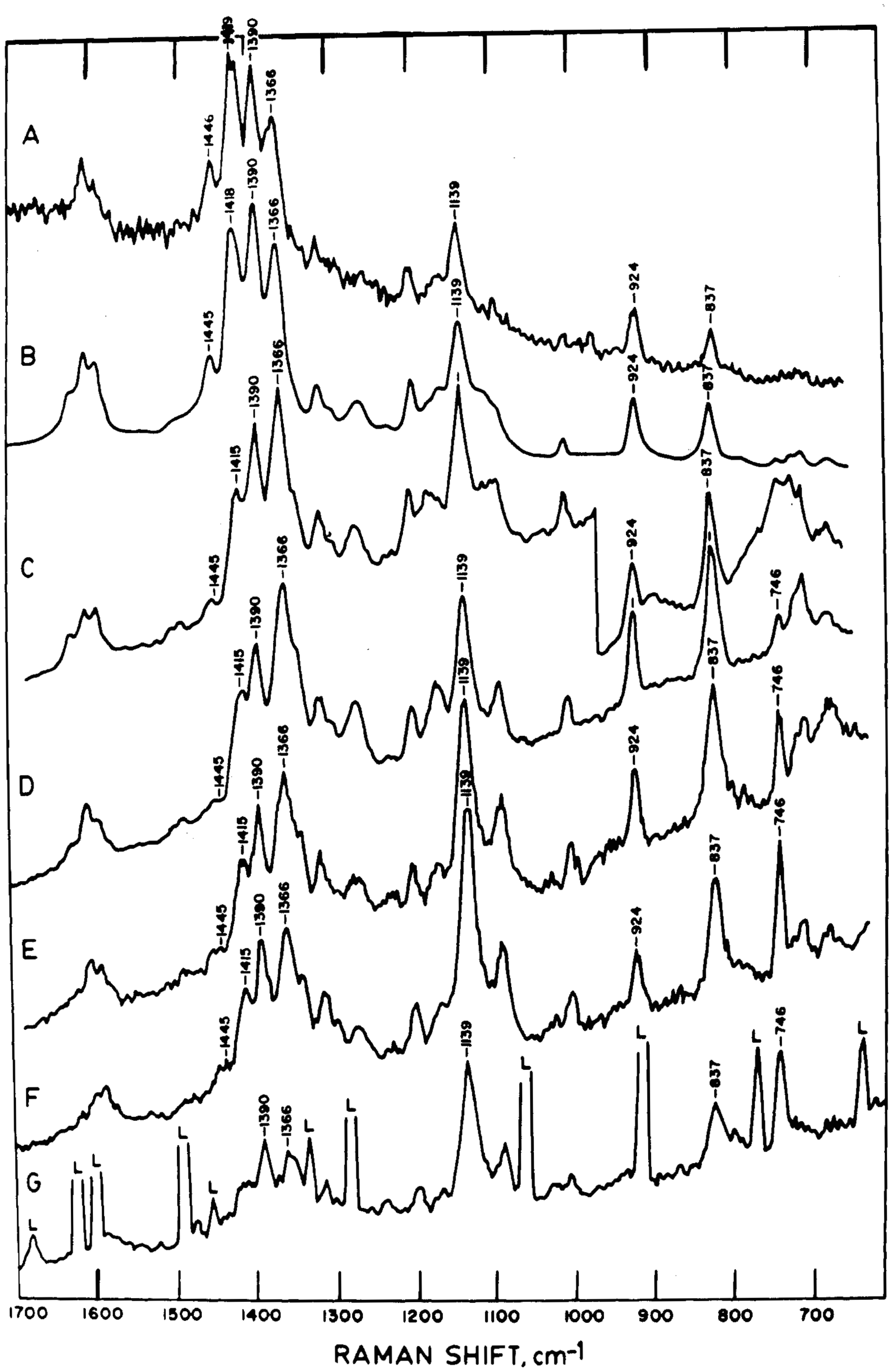

Figure 3. Raman spectra: A, 1.3 × 10^{-4} M DABS-ASP, λ_0 = 465.8 nm; B, C, D, sol 6 with 4 × 10^{-7} M DABS-ASP (total concentration), λ_0 = 488.0, 572.5, 591.5 nm, respectively; E, F, G, sol 6 with 1.1 × 10^{-5} M DABS-ASP (total concentration), λ_0 = 624.7, 647.1, 676.4 nm, respectively. Laser plasma lines in G are denoted L.

limit for the absolute enhancement values. In the case of sol 3 the fraction of surface-bound DABS-ASP was determined to be 0.0586 by the procedure described in the Experimental Section. This permitted obtaining the absolute enhancement shown on line 5.

The following stratagem was used to estimate the enhancement at wavelengths longer than 514.5 nm. Raman signals from both 1.35 M sodium citrate and the sols were measured at 514.5 nm and longer wavelengths from which the ratio of sol to sodium citrate signal corrected for absorption and adjusted for concentration was obtained. By comparing this ratio at 514.5 nm with the ratio for DABS-ASP solution, we obtained a factor for conversion of the sol-to-citrate ratios at higher wavelengths to sol-to-DABS-ASP ratios as shown by the values in parentheses in Table II.

The SERS excitation profiles for sols 3 and 6 to which DABS-ASP had been added are plotted in Figure 2 where

TABLE II: Surface Enhancement of DABS-ASP Raman Signals ($I_{\text{sol}}/I_{\text{soln}}$) at Various Excitation Wavelengths (λ_0)

	$I_{\text{sol}}/I_{\text{soln}}$					
λ_0, nm	457.9	488.0	514.5	572.5, 576.8*	591.5, 590.9*	647.1
sol 6	22	48	104			
sol 6[a]	430	950	2200	(290)	(50)	
sol 3	1.36	29.6	30.7			
sol 3[a]	1.5	36	83			
sol 3[b]	26	610	1400	(85*)	(18*)	(2)

[a] Corrected. [b] Absolute.

TABLE III: Resonance- and Surface-Enhanced Raman Band Frequencies (cm^{-1}) of Dabsyl Aspartate from Figure 3 and Tentative Vibrational Assignments

RRS, spectrum A	RRS + SERS, spectrum B	SERS, spectra C-D	SERS, spectra E-G	vibr assgn
	1624 w, sh	1624 w	1624 vw	
1607 m	1607 m	1607 mw	1607 w	
1594 w, sh	1594 w, sh	1594 w	1594 vw	8b[a]
	1490 w	1490 vw	1490 vw	
1446 mw	1445 mw	1445 vw	1445 vw	19b
1419 vs	1418 s	1415 w, sh	1415 w, sh	ν(N=N)
1390 s	1390 vs	1390 s	1390 s	19b
1366 m, sh	1366 s	1366 vs	1366 s	ν(Ph-NMe$_2$)
		1339 vw, sh	1339 w, sh	
1317 w	1317 mw	1317 mw	1317 mw	3
	1300 vw, sh	1300 vw, sh	1300 vw, sh	
1260 vw	1260 w	1260 mw	1260 mw	
1201 mw	1201 mw	1201 mw	1201 mw	7a
1163 vw	1163 vw, sh	1170 mw	1170 w	9a
1139 ms	1139 ms	1139 s	1139 vs	ν(PhN$_2$-)
1096 w	1096 vw, sh	1096 mw	1096 m	18b
1010 vw	1010 w	1010 mw	1010 mw	
924 m	924 m	924 m	924 m	5
837 mw	837 m	837 s	837 s	10a
	746 vw	746 mw	746 s	10a
	724 vw	724 vw, sh		
	717 vw	717 m	717 mw	

[a] Wilson's mode numbering follows.

they can be compared with the absorption spectra. The peak at about 500 nm is consistent with earlier results for citrate adsorbed on colloidal silver. This occurs because the RRS species has been selected so that its excitation profile nearly coincides with the SERS enhancement profile for this colloidal sol.

Just as in the case of the enhancement of the ordinary Raman scattering by citrate adsorbed on the sol,[7b] there is a disparity between location of the Raman peak at 500 and the main sol absorption peak at about 400 nm. The broadening of the absorption spectrum upon addition of DABS-ASP to sol 3 (curve C) and the secondary absorption peak for sol 6 (curve B) are due to formation of aggregates and these can clearly lead to a shift of the Raman enhancement peak to longer wavelengths, particularly if the aggregate was elongated.[9,16] However, the continued presence of the major peak at 400 nm indicates the continued presence of a considerable fraction of small, nearly spherical particles, which according to the electrodynamic model, would result in enhanced-Raman signals in that wavelength region. As we have indicated earlier, morphological changes in this particle size range such as elongation[9] or a layered structure[10] for which the enhancement shifts to longer wavelength, also requires a corresponding shift in the absorption spectrum. The same would be true if the optical constants for the colloidal silver were different from the bulk value due to quantum size or other effects. Also, recent unpublished theoretical work in this laboratory on the effect of intermolecular interactions due to varied surface coverage by the active molecules does not change the shape of the excitation profile.

The second matter to note is that the magnitude of the peak values of the surface enhancement reported in Table II are considerably less than the values of about 3×10^5 observed in the earlier study of citrate on the silver sols which in turn agreed with the peak value of about 5×10^5 predicted by the electrodynamic model. The value of 2200 for sol 6 is a lower limit because it is based upon total DABS-ASP rather than the amount actually adsorbed at the surface. However, even with an order of magnitude increase it would still fall short of the measured value for citrate. The lower value of 1400 for sol 3 was higher than obtained in a parallel run with this sol.

The possibility that these lower enhancement values were due to attenuation of the incident and scattered light by the absorbing layer of DABS-ASP at the surface of the silver particle was ruled out since an estimate based on assumption of a 20 Å thick layer of DABS-ASP on a 100 Å radius particle leads only to about 2% absorption. This would not account for a significant decrease of the SERS.

A more likely possibility is that the lower enhancement may originate from the larger distance separating the chromophoric (CH$_3$)$_2$NPhN=N- group, that gives rise to the SERS, from the silver surface. The electrodynamic model predicts very rapid falloff of SERS with distance.[8,17] Adsorbed citrate is expected to lie within 6 Å of the surface whereas the azobenzene group of DABS-ASP is probably more than 12 Å removed from the surface when the carboxylate groups are attached directly to the particle. If

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(16) Blatchford, C. G., Ph.D. Dissertation, University of Kent, Canterbury, 1981.

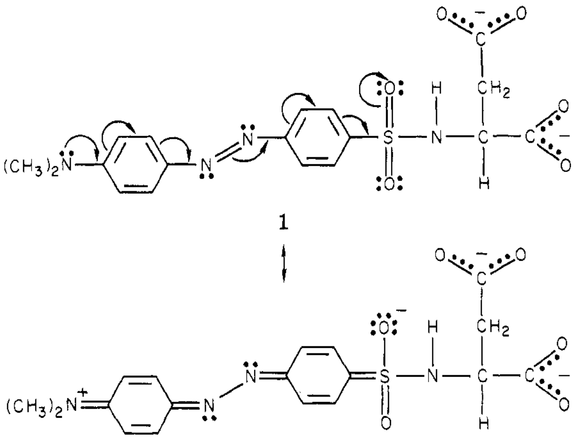
(17) Murray, C. A. In "Surface Enhanced Raman Scattering"; Chang, R. K.; *Furtak, T. E.*, Ed.; Plenum Press: New York, 1982; p 203. Moskovits, M.; DiLella, D. P. *Ibid.* p 243.

the DABS–ASP were not to actually displace citrate from the surface layer but to add on as an overlayer to the adsorbed citrate, the signal would be expected to be still smaller.

Raman Spectra of Adsorbed DABS–ASP. The Raman spectrum, Figure 3B, observed with 488.0-nm excitation differs considerably from spectra with $\lambda_0 \geq 572.5$ nm in Figure 3, C–G. The $\lambda_0 = 488.0$ nm spectrum resembles very closely the RR spectrum of pure DABS–ASP whereas, with $\lambda_0 \geq 572.5$ nm, the spectra should be more similar to the normal Raman spectrum of DABS–ASP in that additional usually intense phenyl ring Raman bands, albeit still relatively weak when compared to azo group Raman bands, may be observed. With $\lambda_0 = 647.1$ and 676.4 nm and to a lesser degree with $\lambda_0 = 572.5$, 591.5, and 624.7 nm three major changes relative to $\lambda_0 = 488.0$ nm are noted: (1) the 1139-cm^{-1} band has become the most intense one, replacing the 1350–1450-cm^{-1} azo group bands in highest Raman enhancement; (2) a 746-cm^{-1} medium-intensity Raman band has appeared where very weak bands were observed in the RR spectrum of pure DABS–ASP and the $\lambda_0 = 488.0$ spectrum of the silver sol DABS–ASP mixture; (3) the relative intensities of bands in the 1300–1420-cm^{-1} range have changed so that the 1366-cm^{-1} band is now the most intense and a new 1339-cm^{-1} shoulder is present.

A summary of RR and SER band frequencies, their relative intensities, and tentative vibrational mode assignments is found in Table III. These band assignments are on the whole taken from a previous systematic study[15] of Raman and resonance Raman spectra of azobenzenesulfonamides and other derivatives. Although sulfonyl groups have been found[18] to give intense Raman bands in the 1100–1200-cm^{-1} region, none of these bands were detected in this study of DABS–ASP. The intense phenyl group vibrational mode (10a) in the 700–850-cm^{-1} range is substituent sensitive.[18] Since two distinct para-substituted phenyl rings $(CH_3)_2NPhN{=}$ and ${=}NPhSO_2{-}$ are present in DABS–ASP, the intense SERS bands at 837 and 746 cm^{-1} are both assigned to mode 10a.

It appears that the RRS spectrum of DABS–ASP originates from vibrational modes localized mainly in the $(CH_3)_2NPhN{=}N{-}$ portion of the molecule. This may reflect the fact that delocalization does not extend through the carbon–sulfur bond as might be conjectured from resonance forms of the type Form 1 with an electron-donating dimethylamino end, and an electron-withdrawing sulfonyl end suggests that the molecule has a high dipole moment spread over both aromatic groups and thus gives rise to the intense near-UV absorption band. However, other considerations such as the reluctance of C–S bonds to be involved in p_π–p_π bonding or the stability[19] of polarized C–S bonds suggest that delocalization does not extend into the phenyl ring adjacent to the sulfonyl group. This has also recently been concluded in an RR study[20] of the cyclic disulfide cation, 3,5-diphenyl-1,2-dithioylium (I), and its hydrosulfide reduction intermediates. Thus, notable Raman bands that involve the phenyl group = $NPhSO_2NH{-}$ vibrational modes are conspicuously absent in the RRS and SERRS spectra; but, they do appear in the SERS spectra in the form of intensification of the $\nu(Ph{-}N_2)$ band at 1139 cm^{-1}, ν_{10a} at 746 cm^{-1}, and ν_{19b} at 1390 cm^{-1} over ν_{19b} at 1445 cm^{-1}. The most intense RR band, $\nu_{N=N}$ at 1419 cm^{-1}, is observed only weakly at 1415 cm^{-1} in the SERS spectra, Figure 3, C–G.



1

2

Conclusions

Silver sols were prepared for which the surface-bound citrate of a Carey-Lea sol was replaced by DABS–ASP, a methyl orange derivative of aspartic acid.

The solution RRS spectrum of DABS–ASP has been observed as well as both its SERRS and SERS spectrum when adsorbed on colloidal silver. The latter was obtained in a region where the chromophore did not absorb strongly. The transition from RRS to oridinary Raman scattering, each surface enhanced, was observed.

The maximum SERS enhancement for DABS–ASP was about two orders of magnitude less than that of citrate on these silver particles. The loss in SERS intensity may be attributed to the greater distance between the silver particle surface and the chromophoric region in the DABS–ASP molecule. This part of the molecule produces the RR enhanced spectrum that is further enhanced by the SERS effect.

The SERS excitation profiles of the two sols peaked at about the same wavelength, 500 nm, despite the peaking of the absorption spectra at 400 nm.

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Registry No. DABS-ASP, 87667-33-2; Ag, 7440-22-4.

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[18] Dollish, F. R.; Fateley, W. G.; Bentley, F. F. "Characteristic Raman Frequencies of Organic Compounds"; Wiley-Interscience: New York, 1974.

[19] Streitwieser, Jr., A.; Williams, Jr., J. E. *J. Am. Chem. Soc.* **1975**, *97*, 191.

[20] Siiman, O.; Shobsngob, S.; Fresco, J. *J. Am. Chem. Soc.* **1982**, *104*, 5338.