Plasma Resonance Enhancement of Raman Scattering by Pyridine Adsorbed on Silver or Gold Sol Particles of Size Comparable to the Excitation Wavelength

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Intense Raman scattering by pyridine molecules adsorbed on silver or gold aqueous sol particles of dimensions comparable to the wavelength is reported. The degree of intensity enhancement is strongly dependent on the excitation wavelength, with a sharp resonance Raman maximum for excitation at the wavelength of the Mie extinction maximum of the metal particles, and for the silver sols the Raman maximum is shown to follow the extinction maximum to longer wavelengths with increase in particle size. A new resonance Raman phenomenon is thus proposed which is the Raman component of resonant Mie scattering, and in which the polarizability of the metal particles is modulated by the vibrations of the adsorbed molecules. These observations confirm that surface plasma oscillations are involved in the intense Raman scattering already reported for molecules adsorbed at roughened silver surfaces. The metal dielectric function requirements for resonant Mie scattering enable the optimum excitation wavelength for plasma resonance-enhanced Raman studies at the surface of other metals to be estimated.

The anomalously intense Raman spectrum of pyridine and other molecules adsorbed at silver surfaces in contact with aqueous or other liquid media has been reported by several observers.1-5 The degree of Raman intensity enhancement depends on the state of division of the metal surface and is greatest for surfaces which have been electrochemically roughened. The enhanced Raman scattering for silver surfaces prepared in this way shows a marked increase with increase in the wavelength of the exciting radiation through the visible region,6 with a maximum for red excitation.7

It has been suggested1,6 that the electronic excitation responsible for this resonantly enhanced Raman scattering is the excitation of collective oscillations of the conduction electrons of the metal surface by the incident electromagnetic wave. For plane (evaporated and unroughened) silver surfaces in contact with aqueous media these surface plasma oscillations have a resonance maximum at \( \approx 2.8 \times 10^4 \text{ cm}^{-1} \),8 at a substantially higher frequency than the reported optimum Raman excitation frequency for the electrochemically roughened surfaces.6,7 However, microscopic examination of the roughened silver electrodes has shown them to be highly uneven, with nodular formations and cavities,9 and it is known that finely divided surfaces show surface plasmon absorption maxima at lower frequencies than those of plane surfaces.10 It is thus important that absorption measurements be carried out at the silver-aqueous interface in order to determine the position of the plasmon absorptions, in parallel with Raman intensity studies.

Measurements of this kind are particularly easy for dispersions of finely divided metal particles, yet the Raman spectra of metal sols do not appear to have been investigated previously. The colour of metal dispersions is due to extinction bands associated with excitation of plasma resonances and the colour is dependent on the particle size for particles of size comparable to the wavelength of visible light.11 It is possible by choice of preparation conditions to control the particle size and disper-
sicity, and there is thus the opportunity, perhaps unique in resonance Raman spectroscopy, to choose the frequency of the electronic excitation band. In this paper we report the enhanced Raman scattering by pyridine molecules adsorbed on colloidal silver and gold particles in aqueous sols of various colours, and the relationship between the Raman excitation profiles and the transmission spectra of the sols is explored.

**EXPERIMENTAL AND RESULTS**

All aqueous solutions were prepared using triply-distilled water. Pyridine and Ag[NO₃] were analytical grade, and the pyridine was further purified by fractionally distilling under nitrogen from zinc dust and stored under nitrogen over fresh silver powder. The silver powder was prepared by treating zinc dust with silver nitrate solution. Raman spectra were recorded in the normal way for liquid samples, using a Coderg PH1 spectrometer, which collected scattered light with an f/1.8 collection lens whose axis was at 90° to the incident light beam.

![Absorbance vs Wavelength](image)

**Fig. 1.** (a) Extinction spectrum of silver sol (1.5 cm³) (i) freshly prepared; (ii) 5 min after adding 0.25 cm³ 10⁻² mol dm⁻³ pyridine; (iii) 1 min and (iv) 5 min after adding 0.1 cm³ 10⁻¹ mol dm⁻³ pyridine. (b) Extinction spectrum of gold sol (1.5 cm³) (i) freshly prepared; (ii) 3 h after adding 0.05 cm³ 0.1 mol dm⁻³ pyridine. For concentrations of sols see text.

Silver sols were prepared by reduction of 10⁻³ mol dm⁻³ Ag[NO₃] (1.0 cm³) with excess ice-cold 2 × 10⁻³ mol dm⁻³ Na[BH₄] solution (3 cm³). The solutions of these salts were mixed rapidly with vigorous shaking to aid monodispersity. The sols were yellow and showed a single visible extinction band near 400 nm (fig. 1), characteristic of silver particles substantially smaller than the wavelength of light. This was
verified by transmission electron microscopy which showed the particles to be roughly spherical with diameters in the range 1-50 nm, and for some preparations 1-10 nm. The sols were stable in the absence of pyridine, and there was no precipitation or change in colour on standing for several weeks.

Upon the addition of pyridine (100 mm$^3$ of 0.1 mol dm$^{-3}$ aqueous solution) to a fresh silver sol (1.5 cm$^3$) particle growth or coagulation occurred as shown by the immediate appearance of a shoulder on the long-wave side of the 400 nm band. This new band moved quickly to longer wavelengths, increasing in area at the expense of the 400 nm band (fig. 1), and there was a substantial change in the colour of the sol over $\approx$10 min through orange and red to blue-grey.

The initial colour changes for sols prepared in this way were too rapid to permit Raman measurements on sols of intermediate colour. However, particle growth, as indicated by the appearance and movement of this new extinction band, was less rapid when pyridine was added to silver sols which had been aged for several hours and for smaller additions of pyridine. For Raman measurements fresh silver sols (4.0 cm$^3$) were therefore aged for 1-2 h and varying amounts of pyridine (50-200 mm$^3$ of 0.1 mol dm$^{-3}$ aqueous solution) were added to give, after standing for 30 min, a series of sols ranging in colour from orange to blue-grey. These had extinction maxima at various wavelengths in the range 500-620 nm (fig. 3) and their transmission spectra changed negligibly in the time ($\approx$3 h) required for the Raman intensity measurements.

A gold sol was prepared similarly by reduction of $2.5 \times 10^{-3}$ mol dm$^{-3}$ K[AuCl$_4$] (1.0 cm$^3$) with $10^{-3}$ mol dm$^{-3}$ Na[BH$_4$] solution (3.0 cm$^3$). The sol was purple and showed an extinction maximum at 525 nm (fig. 1) characteristic of gold particles substantially smaller than the wavelength.$^{11}$ Addition of pyridine (125 mm$^3$ of 0.1 mol dm$^{-3}$ aqueous solution) to this sol (4.0 cm$^3$) caused rapid particle growth or coagulation, and this band moved quickly to 750 nm to give a blue sol.

Although the silver sols were only 0.002-0.007 mol dm$^{-3}$ in total pyridine, their Raman spectra (fig. 2) showed remarkably strong bands at 1038, 1014 and 260 cm$^{-1}$ characteristic of adsorbed pyridine, and similar in frequencies to strong bands reported for pyridine adsorbed on silver electrodes in 0.1 mol dm$^{-3}$ KCl electrolyte.$^{2, 3, 6}$ The 1010 cm$^{-1}$ band was up to $\approx$5 times more intense than the corresponding 1003 cm$^{-1}$ band of 0.1 mol dm$^{-3}$ aqueous pyridine solution (depending on the excitation wavelength, see below) and there is thus a substantial Raman intensity enhancement for pyridine adsorbed on the silver sols, as was found$^{1, 3}$ for the roughened silver electrodes. In addition to their high intensities the 1038 and 1010 cm$^{-1}$ bands of the silver sols were also found to have surprisingly high depolarization ratios ($\rho = 0.53$). This is also similar to observations reported in the electrode studies, where the 1036 and 1008 cm$^{-1}$ bands were reported$^{3, 6}$ to have $\rho > 0.5$, whereas for aqueous pyridine the corresponding 1035 and 1003 cm$^{-1}$ bands are almost completely polarized ($\rho < 0.05$).

The results for the gold sol with added pyridine (total pyridine concentration 0.003 mol dm$^{-3}$) were closely similar. Strong Raman bands were observed at 1038, 1014 and 260 cm$^{-1}$ (fig. 2), and the 1014 cm$^{-1}$ band was $\approx$3 times more intense than the 1003 cm$^{-1}$ band of 0.1 mol dm$^{-3}$ aqueous pyridine for 632.8 nm excitation. This is the first report of surface-enhanced Raman scattering at a gold surface. The gold sol particles were sufficiently large to settle out completely on allowing the sol to stand for a few days. The Raman spectrum of the settled particles was identical to that of the dispersed sol, whereas no Raman bands were detectable from the remaining colourless aqueous solution, thus verifying that for the dispersed sol the intense Raman bands are due entirely to pyridine adsorbed on the sol particles.
The dependence on the excitation wavelength of the intensities of the 1038 and 1010 cm\(^{-1}\) Raman bands of pyridine adsorbed on silver and gold sols was investigated using argon, krypton and helium-neon lasers. The incident electric vector was set parallel to the direction of collection of scattered light so as to effectively eliminate contributions from the strongly polarized 1035 and 1003 cm\(^{-1}\) bands of solution pyridine. The 1003 cm\(^{-1}\) band of a 0.1 mol dm\(^{-3}\) aqueous pyridine solution was used as an external intensity standard at each excitation wavelength, and since this is more strongly polarized than the sol bands it is important that a polarization scrambler was fitted in front of the spectrometer slit. The relative intensities of these two bands, corrected for extinction losses in the sols, are plotted against excitation wavelength for several silver sols in fig. 3, where they are superimposed on the extinction spectra of the sols. These excitation profiles show that there is a fairly sharp resonance Raman maximum for each of the sols. Of particular interest, however, is the observation that this Raman maximum is coincident with the extinction maximum for each sol, and moves with this band to longer wavelengths as the particle size increases. The results for the gold sol are less complete since the extinction maximum (750 nm) lies outside the range of our available excitation wavelengths, but the Raman intensity is seen to rise sharply as the excitation wavelength approaches the extinction maximum (fig. 4).

![Raman spectra](image-url)
**FIG. 3.**—Absorbances (—) and Raman excitation profiles (-----) for silver sols with added pyridine. ○ and × denote the experimental points (arbitrary linear intensity scale) for the 1038 and 1010 cm⁻¹ Raman bands of adsorbed pyridine.
DISCUSSION

The colour of metal sols is due to the sum of the effects of visible light absorption and scattering, and the dependence of these on the particle size and the dielectric function of the metal for a wide range of particle sizes is given by the Mie theory. The particular case of gold sols was treated in detail in the original paper of Mie, where it was shown that for spherical gold particles of radii \( \lesssim \lambda/20 \) the wavelength \( \lambda \) of the extinction maximum near 525 nm is to a good approximation independent of particle size, whereas for particles larger than this the extinction maximum becomes wavelength-dependent. This result is illustrated in fig. 5, where the total extinction
for gold particles of various sizes, and the separate contributions from scattering and absorption, are plotted against wavelength from Mie's calculated data. Mie's extinction data may be used to estimate particle sizes in gold sols, and the positions of the extinction maxima for the gold sol with added pyridine (fig. 4) show that it contained particles in two size ranges, those with radii >90 nm and giving rise to the extinction maximum at 750 nm, and residual primary particles with radii <30 nm for which the extinction maximum is at 525 nm.

Of particular interest in relation to the Raman excitation profiles for pyridine adsorbed on the sols are the Mie scattering against wavelength curves in fig. 5. Thus the Raman intensity measurements on the gold sols (fig. 4) show that for excitation on the side of the extinction band of the larger gold particles the Raman intensity is relatively high, whereas for excitation near the small-particle extinction maximum the Raman scattering was immeasurably weak. For the silver sols the large-particle extinction maximum is more favourably placed in relation to available laser wavelengths, and it is seen from fig. 3 that there is a pronounced resonance Raman maximum for excitation under the large-particle extinction band. The wavelength of this maximum coincides within experimental error with that of the extinction band centre, shifting with this band and increasing substantially in height with increase in particle size. Reference to fig. 5 now shows that these results are similar to the variations in the Mie scattering of gold sols with change of particle size and wavelength. Thus for the gold sol the Mie scattering for particles with radii >90 nm at wavelengths near their extinction band centre is relatively large, whereas scattering by small particles at wavelengths within the small-particle extinction band is of low intensity. The similarity between the Mie scattering curves for the gold sols and the Raman excitation profiles of the silver sols is particularly striking, however. There unfortunately appears to be no published calculation of the Mie scattering against wavelength for silver sols from accurate dielectric function data, but there can be little doubt from the similarity in the dielectric functions of silver and gold in the visible regions \(^{13}\) that the scattering curves for silver sols are similar to those for gold in fig. 5 except for a shift of \(\approx 150 \text{ nm}\) to shorter wavelengths.

We conclude from these observations that the enhanced Raman scattering by the adsorbed pyridine molecules is associated with the Mie scattering by the metal particles. In the Rayleigh theory of the scattering of light by molecules, the scattering arises from the excitation of oscillating electric dipoles in the molecules by the incident electromagnetic field. As is well known, there is accompanying Raman scattering which is due to the modulation of the polarizability of the molecules, and hence of the induced oscillating dipoles, by the molecular vibrations. Mie's theory extends the Rayleigh theory to larger particles by taking account, not only of electric dipole scattering, but also of scattering by induced magnetic dipoles and electric and magnetic higher multipoles, which become significant for particles of size comparable to or greater than the wavelength.\(^{14}\) Mie scattering thus reduces to Rayleigh scattering for small particles. However, the Raman component of Mie scattering has not previously been recognized as being of any experimental significance. The Raman frequency shifts in the spectra reported here are characteristic of the adsorbed molecules, whereas the Mie scattering is due to electric and magnetic multipoles induced in the metal particles, and thus the dipole or higher multipole polarizabilities of the metal particles are modulated by the vibrations of the adsorbed molecules. The mechanism of this modulation remains to be determined, however.

We thus conclude that an essential feature for the observation of the intense Raman spectra of molecules adsorbed on the sols is that the sols show strong Mie scattering at the Raman excitation wavelength. The strong and relatively narrow...
extinction and scattering bands which silver and gold sols show in the visible region are due to resonant excitation of the dipolar and higher multipolar collective normal modes of the conduction electrons in the metal particles. The condition for resonant excitation of the electric dipole oscillation may be seen from the Lorentz formula for the polarizability of a sphere of radius $a$ in a medium of refractive index $n_0$:

$$\alpha = a^3 \left[ \frac{\epsilon - n_0^2}{\epsilon + 2n_0^2} \right]$$

where $\epsilon = \epsilon_1 + i\epsilon_2$ is the dielectric function of the metal. $\alpha$ has a maximum when $\epsilon_1 = -2n_0^2$, and small metal particles, for which the scattering is entirely via induced dipoles, thus show resonant Mie scattering at wavelengths for which $\epsilon_1$ satisfies this condition ($\epsilon_1 = -3.55$ for aqueous sols), with the resonance band half-width proportional to $\epsilon_2$. For silver and gold $\epsilon_1 = -3.55$ occurs in the visible range, but for many elemental metals this condition is unfortunately only satisfied in the far ultraviolet, and for several of these $\epsilon_2$ at these wavelengths is unfavourably large.

These Raman observations on pyridine adsorbed on metal sols are of considerable significance in relation to the intense Raman spectra of pyridine and other molecules at roughened bulk silver surfaces. Enhanced Raman scattering at metal surfaces is of great potential importance as a technique for in situ electrochemical and other metal surface studies, yet so far the phenomenon has been confined to silver and possibly copper surfaces. It is important that the mechanism of the enhancement and the range of metals to which it is applicable is better understood. The similarity in the high Raman intensity, the strong dependence of this on the excitation wavelength, and the high depolarization ratios of the $a_1$ pyridine modes at silver sols and roughened bulk silver surfaces strongly suggests that the enhanced Raman scattering phenomena at the two types of surface are the same. The sol results thus confirm the previous suggestion that the electronic excitation responsible for the resonantly enhanced Raman scattering at the electrodes are plasma oscillations, and the role of the electrochemical roughening is now seen to be the creation of structures on the surface which are resonant at optical frequencies. The dimensions of the nodules and cavities seen in the electron micrographs of the roughened silver surfaces is consistent with this conclusion.

Of particular practical value however are the conditions for small-particle resonant Mie scattering as a guide to the feasibility of enhanced Raman scattering at roughened surfaces of other metals. For coarsely roughened surfaces the resonance Raman maximum is expected to shift somewhat to longer wavelength than that required by the small particle resonance conditions, but these conditions at least give a guide to the region of the optimum excitation wavelength.

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RAMAN SCATTERING BY PYRIDINE ON Au OR Ag SOLS


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