

Role of Nanoparticle Surface Charge in Surface-Enhanced Raman Scattering

Ramón A. Alvarez-Puebla,[†] Elena Arceo,[‡] Paul J. G. Goulet,[†] Julián J. Garrido,[‡] and Ricardo F. Aroca^{*,†}

Materials and Surface Science Group, Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada, and Department of Applied Chemistry, Universidad Publica de Navarra, Campus Arrosadía, E-31006 Pamplona, Spain

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In this work, the role of nanoparticle surface charge in surface-enhanced Raman scattering (SERS) is examined for the common case of measurements made in colloidal solutions of Ag and Au. Average SERS intensities obtained for several analytes (salicylic acid, pyridine, and 2-naphthalenethiol) on Ag and Au colloids are correlated with the pH and zeta potential (ζ) values of the nanoparticle solutions from which they were recorded. The consequence of the electrostatic interaction between the analyte and the metallic nanoparticle is stressed. The ζ potentials of three commonly used colloidal solutions are reported as a function of pH, and a discussion is given on how these influence SERS intensity. Also examined is the importance of nanoparticle aggregation (and colloidal solution collapse) in determining SERS intensities, and how this varies with the pH of the solution. The results show that SERS enhancement is highest at ζ potential values where the colloidal nanoparticle solutions are most stable and where the electrostatic repulsion between the particles and the analyte molecules is minimized. These results suggest some important criteria for consideration in all SERS measurements and also provide important insights into the problem of predicting SERS activities for different molecular systems.

Introduction

Surface-enhanced Raman scattering (SERS)^{1–3} is a powerful microanalytical technique with several significant advantages for ultrasensitive chemical analysis and interfacial studies.⁴ It provides the high information content of vibrational spectroscopy (yielding a molecular “fingerprint”) while demonstrating detection down to the single molecule level.^{5–7} SERS and surface-enhanced resonance Raman scattering (SERRS) can be achieved by several different experimental methods including dispersing analytes in Langmuir–Blodgett films on nanostructured metal island films,⁷ adsorbing analytes on roughened electrodes,^{8,9} casting analytes on metallic nanostructures,¹⁰ and collecting spectra directly from the analyte in colloidal solutions.¹¹ Metal colloids (sols) have been widely used, in part due to the attractive simplicity of the experiment and because they offer “average” SERS enhancement (up to 10^6) under fairly reproducible experimental conditions. However, this apparent simplicity can be deceiving. Even small changes in the metal particle’s surface charge can have significant ramifications in terms of stability, sensitivity to the environment, and electrokinetic properties, all of which are significant factors governing enhancement in SERS/SERRS experiments with colloidal particles. Colloidal metal particles in contact with solutions develop a charge through the adsorption of ions and the ionization of surface functional groups.¹² This nanoparticle surface charge is of utmost importance, as the adsorption of analyte molecules onto colloidal particles is a primary prerequisite condition for obtaining strong surface enhancement of

Raman signals in SERS measurements. Indeed, when colloidal particles and analyte molecules have charges of the same sign, the adsorption process can be strongly hindered or prevented altogether. Moreover, if colloidal particles fail to exceed a minimum repulsion with one another, they will aggregate and precipitate out of solution. In solution, the development of a net charge at the particle surface affects the distribution of ions in the neighboring interfacial region, resulting in an increased concentration of counterions close to the surface, forming an electrical double layer in the region of the particle–liquid interface. Thereby, the surface charge of colloidal nanoparticles can be monitored by means of a measurement of the potential at the interface between the moving and the stationary solvent layers at their edges (i.e., the slipping plane).¹³ This potential is referred as zeta potential (ζ) and provides useful information about the charge carried by the nanoparticle and, therefore, about its stability and ability to interact with analyte molecules.¹⁴ To date, little work has been done to correlate the electrostatic interactions between colloidal nanoparticles and analyte molecules and their impact on the enhancement of Raman signals in SERS experiments. Lecomte et al.¹⁵ have recently studied the ζ potential of silver colloidal solutions prepared by citrate reduction as a function of the concentration of the analyte added, while Faulds et al.¹⁶ have studied the rate of aggregation of these colloids as a function of ζ potential by altering the same variable.

Zeta potential, as one would expect, is closely related to the pH value of the solution for which it is measured, and the fact that the presence of H^+ and other electrolytes affects surface charge, and thus SERS, has been recognized and reported.¹⁷ The aim of this work is to establish the direct correlation between ζ potentials and SERS intensities for three different colloidal solutions commonly used in SERS/SERRS applica-

* To whom correspondence should be addressed: e-mail rarocal@cogeco.ca; fax 1-519-973-7098; tel 1-519-253-3000 (ext. 3528).

[†] University of Windsor.

[‡] Universidad Publica de Navarra.

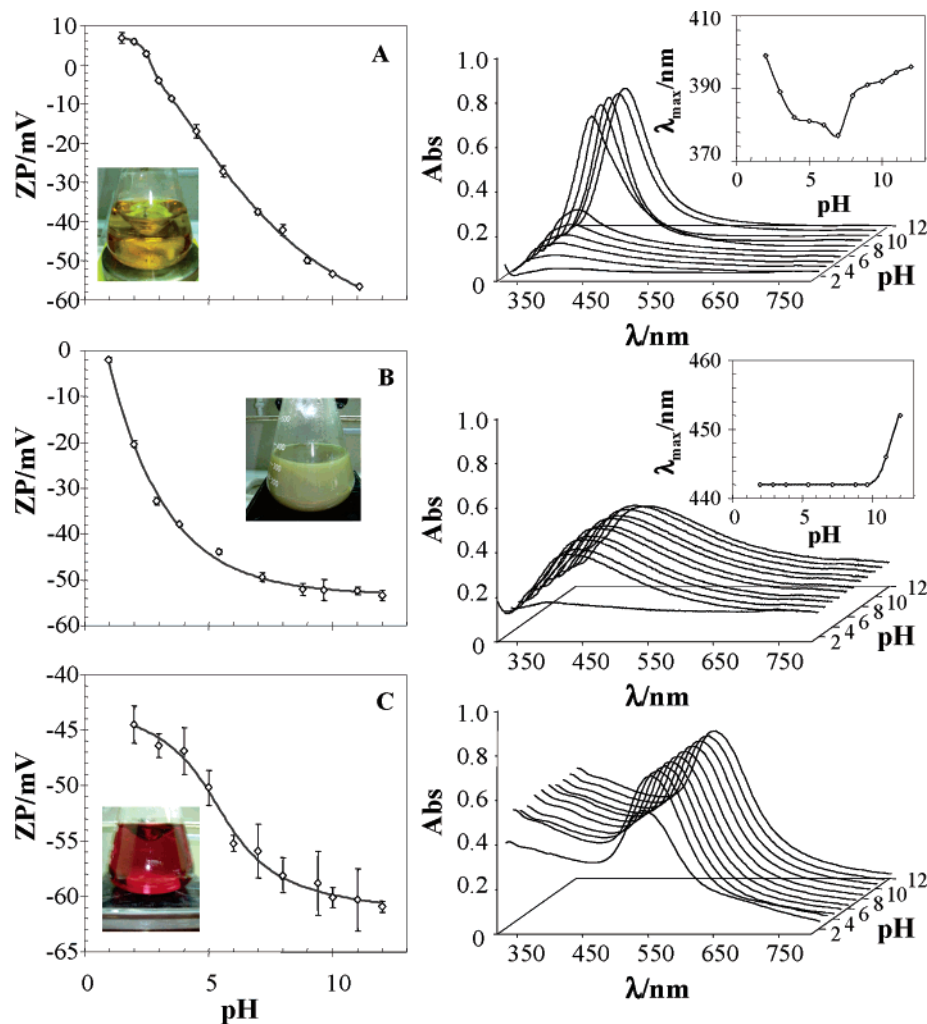


Figure 1. Variation of ζ potential (left) and surface plasmon (right) of (A) silver borohydride, (B) silver citrate, and (C) gold citrate colloids, as a function of the pH of the medium. Insets in the surface plasmon spectra present the behavior of the absorption maximum as a function of pH.

tions. The variation of the ζ potential, as a function of pH, is correlated with the variation of the average SERS intensities observed employing these solutions with three analytes of differing acidic properties at variable pH.

Experimental Section

Salicylic acid, pyridine, and 2-naphthalenethiol were purchased from Aldrich and were used without further purification. Silver colloids were obtained employing common sodium borohydride¹⁸ and citrate¹⁹ reduction methods widely reported in SERS literature. Gold nanoparticles were also produced employing citrate reduction, according to Camafeita et al.²⁰ All colloidal solutions were diluted (1:5) in MilliQ-distilled water to reduce their particle concentration and, thus, their tendency toward aggregation. Aliquots of 50 mL were adjusted to desired pH values, ranging from 1 to 13, by addition of 2 M solutions of NaOH or HNO₃ with a Metrohm Titrino 702SM autoburet. Zeta potential values were determined by injecting 10 mL aliquots of the colloidal solutions into a Malvern Zetasizer HS3000 photon correlation spectrometer with an applied voltage of 100 V and a 5-cm quartz cell.^{21,22} To ensure reproducibility, two subsamples were studied, and three measurements were coadded for each one. The UV–visible absorption spectra (190–1100 nm) of colloidal solutions were recorded, without dilution, in a Varian Cary 50 UV–visible spectrophotometer.

Samples for SERS were prepared by adding 10 μ L of 10⁻², 10⁻³, and 10⁻⁴ M solutions of salicylic acid, pyridine, and

2-naphthalenethiol, respectively, per milliliter of the pH-adjusted colloidal metal solution. Spectra were recorded after 3 h and checked again after 24 h to ensure that thermodynamic equilibrium had been reached. SERS spectra were collected on a Renishaw Invia system equipped with a Peltier cooled CCD detector and a Leica microscope. The spectrograph employs an 1800 g/mm grating and additional band-pass filter optics. For all measurements, laser excitation at 633 nm was used, and spectra were collected in Renishaw's continuous collection mode, with accumulation times of 10 s and with coaddition of five spectra.

Results and Discussion

In Figure 1, the variation, with pH, of ζ potential and surface plasmon maximum is shown for three colloidal solutions, including two silver nanoparticle sols prepared by reduction with sodium borohydride and sodium citrate, respectively, and one colloidal gold solution prepared by reduction with sodium citrate. The variation of ζ potential with pH is shown in Figure 1A for a silver borohydride colloidal solution. Zeta potential is seen to range from 6.5 mV at pH 2 to -56 mV at pH 11, with an isoelectric point at pH 2.7. Silver borohydride colloids dissolve at pH = 1 and precipitate at pH = 12, likely as a silver oxide. The consequence of high ζ potential values, in this case, is the partial aggregation and collapse of the colloidal silver solution from pH 6 to 2, as can be observed in the UV–visible absorption spectra. Proceeding from pH 6 to 2, the intensity of

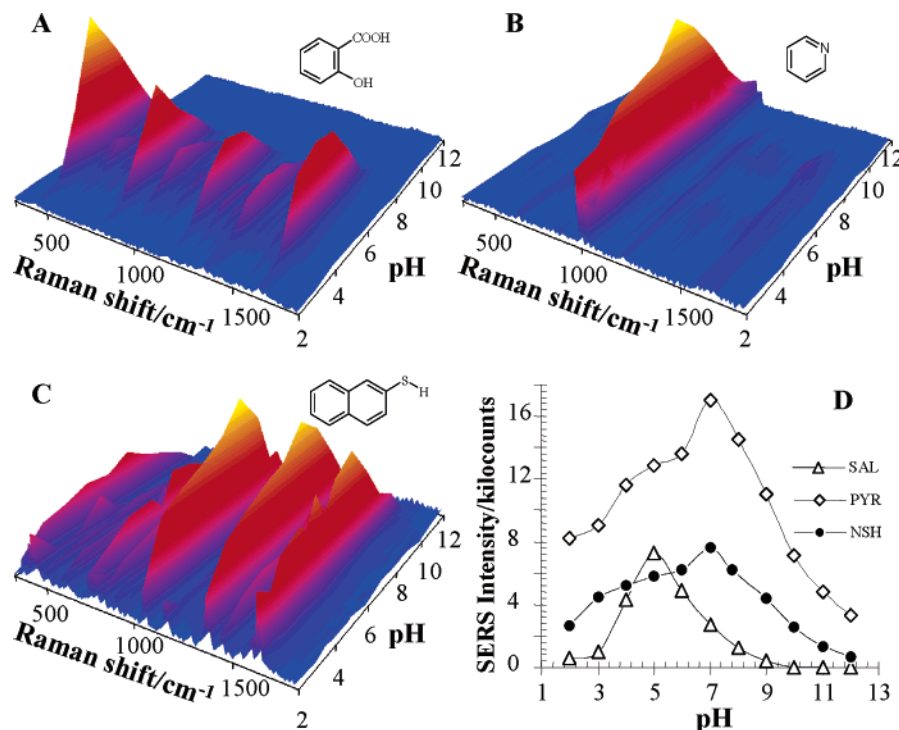


Figure 2. SERS spectra of (A) salicylic acid, (B) pyridine, and (C) 2-naphthalenethiol on silver borohydride colloids as a function of pH. (D) Variation of the intensity of 806, 1008, and 1378 cm^{-1} bands of salicylic acid, pyridine, and 2-naphthalenethiol, respectively, with pH.

the surface plasmon absorption strongly decreases due to the partial precipitation of the Ag nanoparticles, while the extinction intensity remains relatively stable from pH 7 to 11. The position of the surface plasmon maximum, however, is not consistent. The maximum decreases from pH 2 to 7 and then increases until pH 11. These changes may be interpreted as resulting from aggregation processes between pH 2 and 7 and the growth of a silver oxide layer on the surface of the colloids from pH 8 upward, ending finally with the precipitation of the nanoparticles.

Silver citrate colloids (Figure 1B) are stable in a much wider range of pH values, extending from pH 2 to 12. As with silver borohydride colloids, these colloids dissolve at pH 1, giving rise to Ag^+ ions, and precipitate at pH 12, again likely due to the formation of an oxide. The ζ potential of the silver citrate colloid decreases sharply from pH 2 (-20 mV) to 6 (-48 mV) and then more slowly from pH 6 to 10 (-52 mV). From pH 10 to 12, the value of ζ remains relatively constant. Notably, all of these values are in good agreement with those previously reported by Faulds et al.¹⁶ Variation of pH between 2 and 10 appears only to modify the surface charge of the silver citrate colloids, as the surface plasmon absorption maximum remains constant at 442 nm in this range. However, the UV–visible extinction spectrum of these colloids at pH 2 shows an appreciable decrease in intensity, related to an increase in the surface charge of the nanoparticles and consequently to a decrease in their stability, leading to precipitation of some of the particles of the suspension. From pH 10 to 12, the surface plasmon maximum increases, probably as a result of an increase in the size of particles due to the formation of a surface oxide layer. Accordingly, it can be concluded that citrate confers superior stability to silver colloids over those produced by borohydride reduction methods.

The colloidal nanoparticle solutions obtained by citrate reduction of gold (Figure 1C) present the most negative ζ potential values of the three tested, and they are also of the highest stability. Observed absorption spectra show no shifts

in the wavelength corresponding to the plasmon absorption (maximum at 532 nm) of the Au nanoparticles from pH 2 to 12, but the intensity of the plasmon band is demonstrably lower at pH 2 than at pH 3, and this is likely due to the partial dissolution of gold. In addition, these gold colloids do not exhibit oxidation with pH variation, as is consistent with the high reduction potential of this metal (1.50 V).

Figure 2 shows the average SERS spectra for three analytes, salicylic acid (SAL), pyridine (PYR), and 2-naphthalenethiol (NSH), on silver borohydride-reduced colloids, as a function of pH. We use here, and recommend the use of, the term “average SERS/SERS” to refer to common enhancement factors in the 10^3 – 10^7 range obtained in ensemble measurements such as sols, films, or electrochemical measurements. The latter helps to focus on the parameters affecting these experiments and separate the discussion of single particle–single molecule and hot-spot experiments where the spatial resolution is of primary importance. Enhanced vibrational spectra for all of these molecules are shown in Figure A of the Supporting Information and have been discussed in detail elsewhere (SAL,^{23,24} PYR,²⁵ and NSH²⁶). In all the experiments reported here the commonly used excitation line at 633 nm, within the tail of the plasmon resonance absorption, was selected. Salicylic acid (Figure 2A) shows an increase in the average SERS intensity as the pH decreases, until a maximum in intensity is observed at pH 5 (Figure 2D). From this pH downward, SERS signals decrease abruptly, which can be explained by the fact that SAL is a moderately strong acid, characterized by an acid dissociation constant ($\text{p}K_a$) of 2.98,²⁷ and also by the fact that increases in ζ potential values result in an increased tendency toward colloidal aggregation and flocculation, as shown in Figure 1A. The average SERS signal also decays noticeably from pH 5 upward, as a result of the surface potential of the silver colloids becoming more negative, while the rate of ionization of SAL increases. This leads to increased repulsion between the nanoparticles and the analyte molecules and, thus, a hindered adsorption process. Importantly, the SERS intensity for SAL

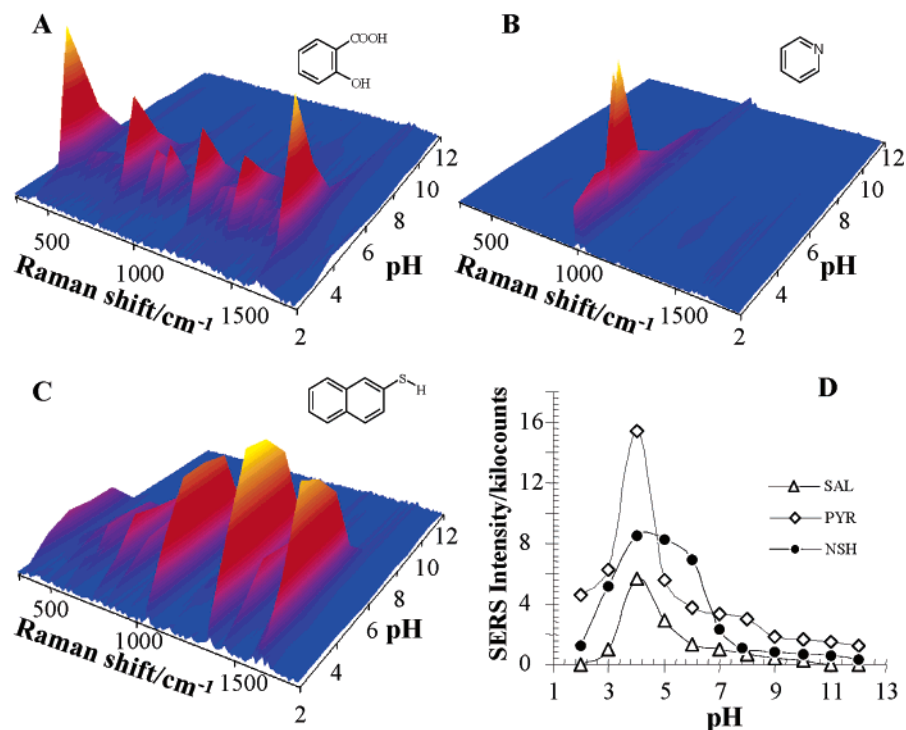


Figure 3. SERS spectra of (A) salicylic acid, (B) pyridine, and (C) 2-naphthalenethiol on silver citrate colloids as a function of pH. (D) Variation of the intensity of 806, 1008, and 1378 cm^{-1} bands of salicylic acid, pyridine, and 2-naphthalenethiol, respectively, with pH.

at pH 5 is 3.5 times greater than it is at pH 7 (the normal pH of these colloids after synthesis is 7–8), stressing the importance of such factors in SERS experiments.

As pH is varied, the SERS intensities for PYR (Figure 2B), and NSH (Figure 2C) change in similar ways. Both analytes show increasing SERS intensity as pH decreases, until a maximum is reached at pH 7 (Figure 2D). This maximum coincides with the stabilization of the surface plasmon intensity (Figure 1A) and confirms that SERS intensities are also largely dependent on the particle concentration of the suspension. Proceeding from pH 7 to 2, SERS signals decay progressively as a consequence of the aggregation and flocculation of the system. However, the silver borohydride colloids show a wider pH range for effective surface enhancement of Raman signals for PYR and NSH than they do for SAL. This can be explained by the lower acidity of PYR ($\text{pK}_a = 5.19^{28}$) and NSH ($\text{pK}_a = 8.20^{29}$) when compared to SAL, making their positively charged and neutral species, respectively, more stable in a wider range of pH and thus decreasing the electrostatic repulsion between the colloids and the analytes. Additionally, N and S have a higher affinity for binding Ag atoms than O,^{30,31} and this also may contribute to reduced SERS intensities for SAL on Ag nanoparticles.

Figure 3 shows the SERS spectra for SAL, PYR, and NSH on silver citrate colloids as a function of pH. In this case, SAL (Figure 3A) and PYR (Figure 3B) show a similar pattern of behavior, both maximizing their SERS intensity at pH 4. Abrupt decreases in SERS intensity resulting from electrostatic repulsions are observed with increased pH, while decreasing pH values also lead to reduced signals as a result of aggregation and flocculation phenomena induced by adsorption of the analytes onto the particles. Notably, SERS signals, for both SAL and PYR, are ca. 5 times stronger at the maximum pH 4 than they are at pH 6, with 6 being the pH of the colloids after their synthesis. The NSH SERS results also show a maximum intensity at pH 4, with an abrupt decrease in signal going down to pH 2 (Figure 3C). However, the behavior of NSH as pH

increases is different from the other analytes. In this case, the decrease in the SERS signal is much slower and does not dip strongly until pH 6. This is likely due the lower acidity of the naphthalenethiol, which remains a neutral species until nearly pH 6. From this pH upward the signal decays abruptly due to the electrostatic repulsion between the analyte and the colloidal particle.

Figure 4 shows the SERS spectra for SAL, PYR, and NSH on gold citrate colloids, as a function of pH. These colloids present the most negative ζ potential values of all those studied, down to -45 mV at pH 2. This large negative charge makes the adsorption of SAL on the gold surface impossible, as emphasized by the lack of SERS signals at any pH value (Figure 4A). PYR and NSH, in contrast, do show some SERS activity (Figure 4B,C), due to their lower acidity and higher b character (as defined by Pearson's hard–soft acid–base theory^{30,31}), but it is quite weak in comparison with the results obtained for silver colloids (Figure 4D). In addition, the maximum SERS intensities for these molecules are obtained at pH 3, when ζ values are less negative and hindrance to analyte adsorption is reduced. As can be supposed, intensities progressively decrease with increases in pH, due to decreased ζ values and consequent increases in electrostatic repulsion. Noteworthy, also, is that both PYR and NSH present intensities 2 and 1.4 times higher, respectively, at pH 3 than they do at pH 8, which is the normal pH of the colloids after their synthesis.

Figure 5 shows the SERS intensity of SAL, PYR, and NSH adsorbed on the three colloids as a function of their ζ potential. Salicylic acid shows two different maxima for silver colloids reduced with borohydride and citrate (Figure 5A). The fact that the maxima do not coincide is due to the precipitation of silver citrate colloids at pH values of 2 and 3, due to decreases in their stability resulting from the adsorption of salicylic acid. SERS measurements of salicylic acid in gold colloids do not show any discernible signal, likely because the molecule is not able to adsorb on the highly negatively charged nanoparticles. In the case of pyridine (Figure 5B), however, the maxima for

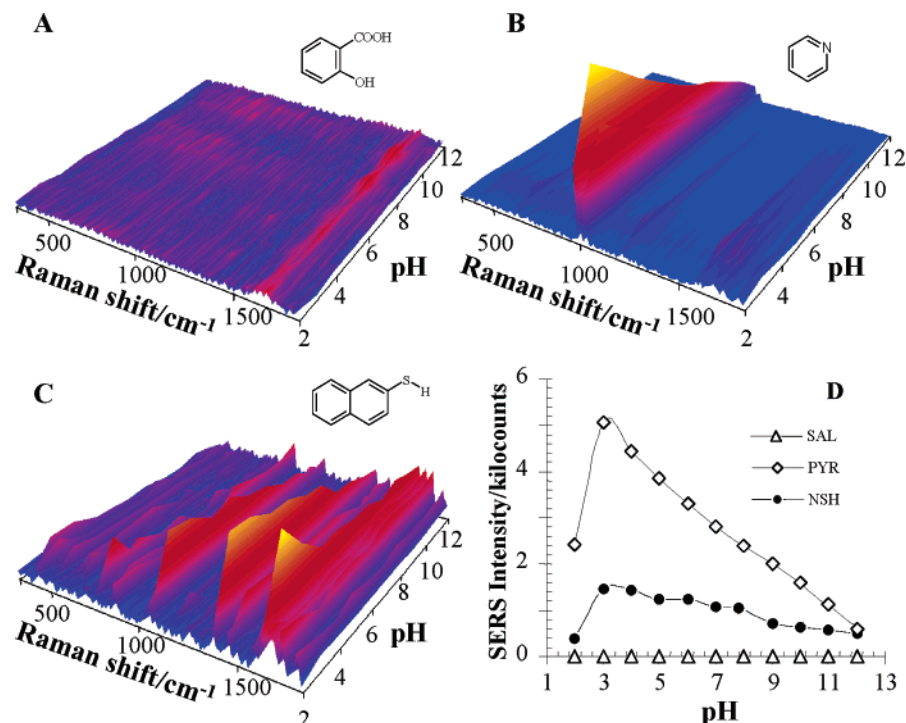


Figure 4. SERS spectra of (A) salicylic acid, (B) pyridine, and (C) 2-naphthalenethiol on gold citrate colloids as a function of pH. (D) Variation of the intensity of 806, 1008, and 1378 cm⁻¹ bands of salicylic acid, pyridine, and 2-naphthalenethiol, respectively, with pH.

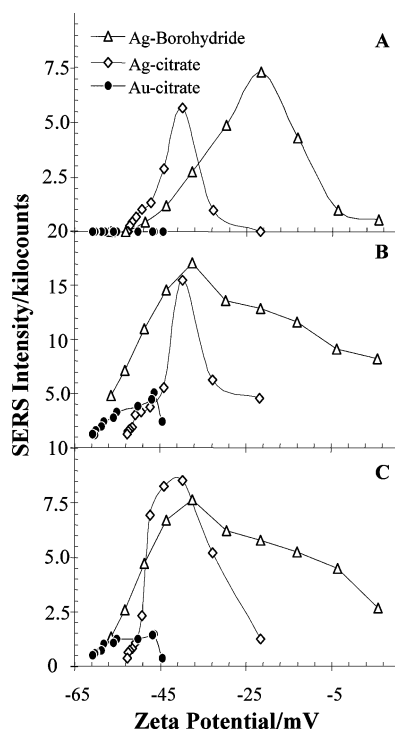


Figure 5. SERS intensity as a function of ζ potential for (A) salicylic acid, (B) pyridine, and (C) 2-naphthalenethiol on silver borohydride, silver citrate, and gold citrate colloids.

the two silver colloids are both near ζ values of -40 mV. For silver borohydride colloids, the SERS signal decrease progressively as ζ increases, because the increased adsorption of PYR molecules onto the surface of the Ag nanoparticles is largely overshadowed by the decreased number of colloidal particles in solution. In the case of silver citrate colloids, on the other hand, the adsorption of the analyte at low pH (2 and 3) leads to flocculation of the nanoparticles, and maximum intensities are seen at ζ values where the colloids are sufficiently stable. Below

these maximum intensity values, SERS signals decrease abruptly due to the repulsion of the colloids and the analyte. With this molecule, notably, SERS signals tend to be quite low when employing gold citrate colloids as the enhancing nanoparticles. Finally, for NSH, the variation of SERS intensities with changing ζ values appears very similar to that of PYR, with minor differences that can be attributed to its different acidic character.

In summary, the sol results show that when colloidal particles and analyte molecules have charges of the same sign, the adsorption process can be strongly hindered or prevented altogether. In addition, each sol presents a peculiar aggregation behavior, and when colloidal metal particles fail to exceed a minimum repulsion with one another, they precipitate out of solution. In a recent study of aggregation of citrate colloids, Faulds et al.¹⁶ have concluded that "This is a major advantage if nanoparticle sensors are to be constructed using SERS because it shows that the effect of aggregation is not required under these conditions." They referred to the advantage of exciting at the center of the plasmon absorption. The average SERS results reported here were obtained with a fixed laser line that is not at the center of the observed plasmon absorption. The ensemble changes due to aggregation are dramatic only at the edges of the pH range. Dynamic light scattering data for the silver citrate colloids (Figure B in Supporting Information) follow the same trend. The effect of aggregation in these experiments is, of course, included in the average SERS. However, it does not seem to play the dramatic role reported in some spatially resolved single-molecule experiments.⁵

Conclusions

Thus, the role of nanoparticle surface charge in surface-enhanced Raman scattering (SERS) has been examined for the common case of measurements made in colloidal solutions of Ag and Au. It has been demonstrated that the average intensities of SERS spectra of several analytes (salicylic acid, pyridine, and 2-naphthalenethiol) are strongly related with the pH and ζ

potential values of the nanoparticle solutions from which they are recorded. Indeed, the ζ potentials of colloidal solutions, and the molecular species present in solution, are shown to be critical factors that determine the average SERS intensity. Moreover, as surface charge determines nanoparticle aggregation (and colloidal solution collapse), as well as possible electrostatic interactions with analytes, it provides an important experimental guide for the optimization of experimental conditions for a successful SERS measurement. Generally, and perhaps not surprisingly, it has been found that SERS enhancement is strongest at ζ potential values where the colloidal nanoparticle solutions are of sufficient stability and where the electrostatic repulsion between the particles and the analyte molecules is minimized. Notably, based on the results of this work, it is concluded that optimum conditions for SERS are not necessarily met by colloidal solutions that are used "as prepared" by synthetic approaches commonly used in the literature. We anticipate that this work can provide some important insights into, and solutions for, problems that are commonly encountered in colloidal solution SERS experiments.

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Supporting Information Available: Figures showing enhanced vibrational spectra for salicylic acid, pyridine, and 2-naphthalenethiol and dynamic light scattering data for silver citrate colloids. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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