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Surface -enhanced Raman spectroscopic studies of organonitriles on copper colloids

Candace Mikki Coyle
West Virginia University

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**Surface-Enhanced Raman Spectroscopic Studies of Organonitriles
on Copper Colloids**

Candace Mikki Coyle

Dissertation Submitted to the College of Arts and Sciences
at West Virginia University
In Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy
in
Chemistry

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ABSTRACT

Surface-Enhanced Raman Spectroscopic Studies of Organonitriles on Copper Colloids

Candace Mikki Coyle

Dramatic differences are observed between the surface-enhanced Raman spectra (SERS) of organonitriles mixed with copper colloids, the Raman of the free parent molecules, and the SERS for adsorption on a gold colloid. Specifically, $\nu(\text{C}\equiv\text{N})$ is missing in the SER spectra involving the copper colloid. The data are adequately explained by a transition metal assisted borohydride reduction of the cyano group to an amino group. SER spectra of the reduction products of the organonitriles in the presence of copper colloids are identical within experimental error. The $\nu(\text{C}\equiv\text{N})$ signal was observed when a gold colloid was prepared by borohydride reduction, thereby indicating the metal selectivity of the reaction. Adsorption on silver colloids exhibit a complete disappearance of the nitrile stretching normal mode. The absence of the nitrile stretching signal is not due to a metal-assisted reduction of the nitrile group to an amino group. The observation of no nitrile stretching band for the silver colloids indicates that the silver metal is distinct from the copper and gold. SERS data collected for the isomeric forms of cyanopyridine (4-CP, 3-CP and 2-CP) mixed with the copper and gold colloids supports the theory that the degree of surface enhancement is lowered by the loss of molecular symmetry. Addition of selected sodium salts were used to determine the role of aggregation and co-adsorption in surface enhancement. Our SERS data demonstrate that the increase in surface enhancement is primarily influenced by the chemical interaction between the adsorbate and the metal surface. Although the molecular symmetry of the adsorbate, as well as the affects of aggregation, affect the degree of enhancement observed, the chemical adsorption onto the metal dominates the enhancement mechanism.

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This dissertation is dedicated to the memory of Dr. Therese M. Cotton.

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CHAPTER 1

Introduction

Surface-enhanced Raman spectroscopy (SERS) links the structural information of vibrational spectroscopy with the sensitivity and surface specificity of the enhancement mechanism.^{1,2} The vibrational information contained in the Raman spectra provide the molecular signature required to characterize adsorbate/surface interactions. This technique is applicable to surfaces of free-electron metals, although methods have been developed to overcome this limitation.¹

Since the discovery of SERS^{3,4}, numerous methods have been suggested for the preparation of active sites.⁵ Both metal colloids and roughened metal electrodes are commonly used as substrates.³⁻⁵ Other methods including chemical etching, laser ablation, and mechanical polishing have been used to prepare surfaces for SERS.⁶⁻⁸ In almost all cases, careful control of the experimental conditions is important for obtaining reproducible and reliable data.

The electrochemical method of inducing roughness has become the most common preparation of active surfaces for SERS.^{3,4} However, intensities of the SERS scattering of molecules adsorbed on an electrochemically roughened metal surfaces undergo a potential-induced irreversible decay.⁹ These irreversible changes are most pronounced at very negative electrode potentials and have been ascribed to the disappearance of the so-called “active sites”, which are incorporated into the bulk metal after desorption of their ligand.⁹ While

control of the surface morphology on electrodes is nearly impossible to achieve, colloidal particles with nearly spherical shapes can easily be prepared.¹⁰ Studies of Raman scattering by colloidal dispersions may serve as a guide to understand the SER effect at the surface of an isolated particle which has been suggested to be due to the same phenomenon as at a roughened macroscopic surface.¹¹

Colloidal metals have been used in SERS experiments because adsorbed molecules exhibit strong enhancement and colloids are relatively easy to prepare by chemical reduction methods.¹²⁻¹⁶ Additionally, studies indicate that strong molecular mechanisms exist in colloidal systems. The advantages of colloids over electrodes are: (1) ease of formation and manipulation; (2) possibility of continuous renewal of sample by flowing through the light beam; (3) ability to control and vary particle size and shape; (4) more easily defined surface area; and (5) more tractable morphology for theoretical analysis.¹¹

SER scattering from molecules on silver and gold electrodes and colloids have been extensively studied; however, copper colloids have received less attention due to their inherent instability.^{1,13,14,17,18} Given the potential applications of copper as an inexpensive sensor material or catalyst, it is important that the surface reactivity be explored. A few reports have appeared indicating that there is an effort to develop and study copper colloids.^{15,19-23} Therefore, we are investigating the adsorption of organonitriles on copper colloids. These molecules are important because they provide insight into the selectivity of adsorption sites of metal surfaces as well as the underlying reasons for the SER effect.

Prior studies by Van Duyne^{17,24} showed that there was a decrease in intensity of $\nu(\text{C}\equiv\text{N})$ as the nitrile was moved from the 4- to the 3- to the 2- positions for 4-

cyanopyridine (4-CP), 3-cyanopyridine (3-CP), and 2-cyanopyridine (2-CP) on silver electrodes. This was interpreted as an enhancement controlled by the interaction of the nitrile moiety with the metal surface as determined by its position on the pyridine ring (see Figure 1-1). That is, greater interaction between the nitrile group and the surface leads to lower intensity for $\nu(\text{C}\equiv\text{N})$. It was assumed that adsorption was occurring primarily through the lone pair electrons of the nitrogen in the aromatic ring as had been previously reported.^{3,14}

In another series of studies, it was determined that the intensity of $\nu(\text{C}\equiv\text{N})$ was proportional to the applied potential as well as surface concentration when 4-CP was adsorbed onto copper and silver electrodes.^{25,26,27} As the concentration of the adsorbate at the surface was decreased, the molecules were reported to lie flat-on relative to the electrode surface and $\nu(\text{C}\equiv\text{N})$ was found at 2140 cm^{-1} (see Figure 1-2). At higher concentrations the molecules lie end-on and give rise to $\nu(\text{C}\equiv\text{N})$ at 2238 cm^{-1} . Both orientations give rise to $\nu(\text{C}\equiv\text{N})$ values lower than that of the parent molecule (2246 cm^{-1}). These reports also indicate that as the potential becomes more negative, the donor character of the active site on the copper electrode increases and shifts $\nu(\text{C}\equiv\text{N})$ to lower wavenumbers as a result of the perturbation of a partial charge transfer reaction (the charged radical gives rise to a band at 2090 cm^{-1}). The authors indicate that coordination through the nitrile substituent should give rise to a band above that observed for the parent compound.^{25,26,27} It was found that as the concentration of the adsorbate was decreased the A_1 modes located at 2240 cm^{-1} and 1195 cm^{-1} decreased in intensity and the B_2 modes located at 1217 cm^{-1} and 1420 cm^{-1} increased in intensity.²⁶ This was correlated with a change in adsorbate orientation from an end-on (adsorption through the nitrogen on the aromatic ring) to a flat-on adsorption.

Figure 1-1 Orientation of cyanopyridines (4-CP, 3-CP and 2-CP) adsorbed onto a metallic surface.

Figure 1-2 Orientation of cyanopyridines (4-CP, 3-CP and 2-CP) adsorbed onto a metallic surface [$\nu(\text{CN})$ is indicated].

The debate concerning the foundations of the SER effect is still in the process of being defined.²⁸ The theoretical approaches to SERS consists of two different ideas, the electromagnetic mechanism (EM) and chemical/molecular interactions (CM).^{29,30} Contributions from these effects are contained in the equation for the induced dipole moment (μ), as shown below.

Induced Molecular Dipole (μ)

$$\mu = \alpha E_{\text{local}}$$

<p>CM: Molecular polarizability(α) is increased due to a charge transfer during the formation of a metal-molecule complex.</p>	<p>EM: Local electromagnetic field increases due to excitation of the surface plasmons by both the incident and scattered light.</p>
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EM theory is based on the idea that an enhancement of the electromagnetic field near the metal surface occurs when an incident photon interacts with the EM field.^{29,30} This process is affected by the radius and shape of the metal particles and the spectral effects are similar to those of resonance Raman spectra (i.e., an enhancement of intensity). The CM theory states that enhancement occurs due to a change in the molecular polarizability of the adsorbate caused by physical or chemical interactions between the adsorbate molecule and the surface.^{30,31} This theory is more sensitive to the nature of the adsorbate molecule and explains the observation that SERS differs from the spectra of the same species in solution.

Different metals in metal colloids have differing contributions from each component in the SERS mechanism.^{11,23,32} The EM is primarily a characteristic of the colloidal metals and leads to an enhancement that is nearly independent of the adsorbed molecule.³³ The distinguishing features of each type of metallic colloid include the area of contact between the dispersed colloidal particles and the dispersion medium, as well as the energy associated with creating and maintaining these interfaces. The CM exploits a resonance in the molecule-metal effective polarizability.²³ This mechanism is sensitive to the presence of “active sites” on the metal and provides details of the molecule-metal bond. The actual charge transfer during the adsorption of organonitriles on the different metal surfaces and the resulting orientation, symmetry and chemical interaction will contribute to an understanding of the contributors to surface enhancement.

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CHAPTER 2

4-Cyanopyridine Adsorbed on Copper Colloids

2.1 INTRODUCTION

We have collected SERS for 4-cyanopyridine (4-CP) adsorbed on copper colloids (see Figure 2-1). Our SERS data for substituted pyridines mixed with copper colloids are significantly different from that observed with gold, silver, and copper electrodes. Studies of cyanopyridines on silver electrodes indicate an enhancement of the $C\equiv N$ stretching normal mode signal [$\nu(C\equiv N)$] that is dependent upon the position of the substituent on the aromatic ring.¹⁻³ Further studies showed that there is a dependence of the SERS intensity on the applied potential when isomeric forms of cyanopyridine are adsorbed on silver electrodes.⁴ Similar trends were observed for the adsorption of 4-CP on gold and copper electrodes.⁵ Spectra obtained for pyridine adsorbed onto copper colloids and electrochemically roughened copper electrodes are similar, although a greater enhancement was observed with the electrodes.⁶ We began our studies of cyanopyridines on copper colloids to investigate the differences in the SER spectra and adsorption mechanisms for gold and copper colloids and electrodes.

We present herein the results for non-labeled and isotopically labeled 4-cyanopyridines (4-CP, 4-CP-¹⁵N) mixed with copper and gold colloids. The SER spectra for the copper colloids are markedly different from those obtained when 4-CP is adsorbed onto copper, gold and silver electrodes.¹⁻⁵ It is proposed that excess borohydride used in the

Figure 2-1 Molecular structures for 4-cyanopyridine (4-CP), 4-cyanopyridine-¹⁵N (4-CP-¹⁵N) and 4-aminomethylpyridine (4-AMP).

preparation of the colloid reduces 4-CP to 4-aminomethylpyridine (4-AMP) and that the observed SERS is of 4-AMP on the colloidal surface.

2.2 EXPERIMENTAL

Colloid Preparation

The preparation of the copper colloids is based on the borohydride reduction of Cu^{2+} .⁶ An aqueous solution of copper (II) sulfate (Aldrich Chemical Co., Milwaukee, WI; 99.99%) (2×10^{-2} M, 0.15 mL) was added to a trisodium citrate solution (Aldrich; 99%) (2.8×10^{-3} M, 2.0 mL) followed by the addition of a freshly prepared solution of sodium borohydride (Aldrich; 99%) (2×10^{-2} M, 1.0 mL) in 1.9×10^{-2} M sodium hydroxide (Fisher Scientific Co., Pittsburgh, PA; 98%). All colloidal solutions were prepared in disposable borosilicate glass culture tubes with water passed through a Barnstead/Thermolyne (Dubuque, IA) Nanopure Water Model D4541 purification system. The colloid, which starts as a pale yellow-brown color becomes a dark reddish-brown. The red color is indicative of particle sizes ranging from 10 to 20 nm and gives rise to an absorption band at 564 nm.⁷ After the colloid was allowed to age for two hours, an aqueous solution of the 4-CP (Aldrich; 98%) (1×10^{-3} M, 0.30 mL) was added to the culture tube. The final concentration of the 4-CP was approximately 9×10^{-5} M. Upon addition of the 4-CP, the colloid changes to a dark grey-brown color due to aggregation and has an absorption band at 570 nm. A band at 296 nm indicative of the adsorbate is also observed. The copper colloid with 4-CP-¹⁵N has absorption bands at 571 nm and 305 nm. These shifts in the spectra are indicative of molecule-surface interaction in the colloidal system.⁸ Previous work indicates that the addition of the adsorbate

before or after aging of the colloid results in no significant difference in the SER spectra.⁶ Both procedures have been followed and no differences were observed for the current system. The excess borohydride provides a buffer against oxidation of the copper particles. The high pH of the colloid solution stabilizes the borohydride ions, while the trisodium citrate minimizes colloid precipitation. The copper colloids are stable for approximately 24 hours if stored in a well-stoppered container. Data collection of the SER spectra of the cyanopyridines adsorbed onto the copper colloids was begun 80 minutes after the addition of the adsorbate solution to the colloid.

The preparation of the gold colloid began with the dissolution of HAuCl_4 (Aldrich, 99.99%) (240 mg) in 500 mL of water which was then heated to boiling.⁹ A solution of 1% w/w sodium citrate (Aldrich, 99%) (50 mL) was added. Immediately after the addition of the sodium citrate the solution changed from a pale to a bright yellow color and then to a dark red wine color (absorption band at 523 nm).⁷ The solution was maintained at boiling for 2 hours. Raman samples were prepared by adding 4-CP (0.3 mL, 1×10^{-3} M) to 2.7 mL of the gold colloid solution in a disposable borosilicate glass culture tube. The color changed to a dark violet/purple with an absorption maxima at 563 nm indicative of aggregation due to the presence of the adsorbate. The SER spectra were collected starting 80 minutes after the addition of the cyanopyridine.

4-Aminomethylpyridine (Aldrich, 98%) was adsorbed onto copper colloids using the procedures described above. Spectra of the parent compound were collected as the neat liquid contained in standard melting point capillary tubes.

In order to investigate the potential oxidation of the copper systems, the colloids were also studied under anaerobic conditions. Anaerobic preparation of the copper colloids was performed using the same chemical ratios as listed above with the following differences in treatment. The components of the copper colloids were permitted to set in an argon atmosphere while argon gas at 7 psi was bubbled through the solutions. The initial solutions were treated with argon gas for 3 hours to provide sufficient deoxygenation prior to preparation of the copper colloid. The argon gas was also bubbled through the aging copper colloid and for approximately 1 hour after addition of the 4-CP before sealing the sample in preparation for spectral collection.

In order to investigate the oxidation state of copper required for the reduction process, copper colloids were prepared using different initial states of copper. Colloids were prepared using the methods described above, but with different copper salts [copper (II) sulfate (Aldrich; 99.99%) and copper (I) chloride (Aldrich; 97%).

Spectra Collection

Raman data was collected using two spectrometers. One system consisted of a Coherent Inc. (Santa Clara, CA) Kr⁺ laser operating at 647.1 nm which provided 20 mW at the sample. A 270° geometry was used for collection of the scattered radiation which was analyzed with a Spex Industries (Edison, NJ) Triplemate system equipped with a 1200 grooves/mm grating and a Princeton Instruments CCD detector operating at 115 K. The second system consisted of a Lexel (Fremont, CA) Ramanion Kr⁺ laser operating at 647.1 nm which provided 20 mW at the sample. A Spex Industries Triplemate system equipped with a 600 grooves/mm grating and an Oxford CCD detector operating at 135 K was used for

detection. A 90° geometry was used for collection of scattered radiation. The instruments were calibrated with indene and benzonitrile and reported frequencies are accurate to $\pm 5 \text{ cm}^{-1}$.¹⁰ The absorption spectra were recorded with a Perkin Elmer (Norwalk, CT) Lambda-6 UV-VIS spectrophotometer.

Preparation of isonicotinamide-¹⁵N

Ammonia-¹⁵N (Aldrich, 98%) (20 mmol) was introduced over 2 hours into a solution of isonicotinoyl chloride – hydrochloride (Aldrich, 95%) (2.0 g, 10 mmol) in 100 mL of ethyl ether/THF cooled in an acetone/dry ice bath.¹¹ After 2 hours, a white solid formed, and the mixture was allowed to cool to room temperature with stirring. The mixture was filtered, the solid (ammonium chloride-¹⁵N) was washed with ethyl ether (5 x 15 mL) and the filtrate was concentrated until crystallization occurred. The crystals were treated with benzene (100 mL) and heated until the product dissolved. The mixture was allowed to cool and recrystallize overnight at 10° C. The crystals of isonicotinamide-¹⁵N (0.422 g) were obtained by filtering and washing with cold benzene (5 x 10 mL). Percent yield: 21.18%. NMR- ¹H 5.64-5.96 (2H,d), 7.65 (2H, d), 8.7 (2H, d).

Preparation of 4-Cyanopyridine-¹⁵N

Isonicotinamide- ^{15}N (0.2 g, 1.7 mmol) and phosphorous pentoxide (0.24 g, 1.7 mmol) were carefully mixed in a 50 mL round bottom flask equipped with a distillation head.¹² The mixture was rapidly melted with a flame until effervescence ceased. Heating was continued until distillation of the 4-cyanopyridine- ^{15}N was completed (0.0655 g). Percent yield: 32.75%. NMR- ^1H 7.5 (2H, d, $J = 5.9$ Hz), 8.82 (2H, d, $J = 7.6$ Hz).

Isonicotinamide- ^{15}N and 4-cyanopyridine- ^{15}N were characterized with NMR spectra as reported above. The Raman spectrum of the 4-CP- ^{15}N shows a shift in the nitrile stretching signal from 2246 cm^{-1} to 2218 cm^{-1} (see Figure 2-2).

2.3 RESULTS AND DISCUSSION

The SER spectra obtained when 4-CP and 4-CP- ^{15}N are mixed with copper colloids and the normal Raman spectrum of 4-CP are shown in Figures 2-2 and 2-3. The observed frequencies with tentative assignments are presented in Table 2-1. Upon adsorption, $\nu(\text{C}\equiv\text{N})$ at 2246 cm^{-1} is not observed even though this is the most intense signal in the spectrum of the parent molecule. In addition, the bands at 776 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 550 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 461 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 365 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive) and 169 cm^{-1} [$(\text{C}\equiv\text{N})$] are all absent.¹³ The 1194 cm^{-1} band [$\beta(\text{CH})$] on the SER spectrum is observed with a partner of equal intensity near 1215 cm^{-1} in the spectrum of the adsorbed species. The disappearance of $\nu(\text{C}\equiv\text{N})$ was unexpected because it was observed in previous studies of 4-CP on silver and copper electrodes.²⁻⁵

Comparison of the collected data for 4-CP adsorbed onto a copper colloids [i.e., complete loss of $\nu(\text{C}\equiv\text{N})$] with previous reports (see Chapter 1) suggests that 4-CP is not

Figure 2-2 Raman spectra of 4-cyanopyridine (4-CP) and isotopically labeled 4-cyanopyridine-¹⁵N (4-CP-¹⁵N) in aqueous solution.

Figure 2-3 SERS of 4-cyanopyridine (4-CP) and isotopically labeled 4-cyanopyridine-¹⁵N (4-CP-¹⁵N) adsorbed onto copper (/Cu) colloids.

TABLE 2-1: Raman Frequencies (cm⁻¹) of 4-Cyanopyridine (4-CP) and 4-Cyanopyridine-¹⁵N (4-CP-¹⁵N) in Aqueous Solution (2.0 M) and Adsorbed onto Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	4-CP (2.0 M)	4-CP- ¹⁵ N	4-CP/Cu	4CP- ¹⁵ N/Cu	4-CP/Au	4-CP- ¹⁵ N/Au
$\gamma(\text{C}\equiv\text{N})$	169	162	-	-	-	163
$\text{C}\equiv\text{N}$ sensitive	-	-	-	-	-	265
$\text{C}\equiv\text{N}$ sensitive	365	385	-	-	384	381
$\text{C}\equiv\text{N}$ sensitive	461	461	-	-	-	-
-	-	-	500	-	485	475
$\text{C}\equiv\text{N}$ sens, $\delta(\text{C}\equiv\text{N})$	550	491	-	-	-	-
$\phi(\text{CC})$	560	563	-	-	-	557
-	-	-	605	608	-	-
$\alpha(\text{CCC})$	664	671	668	665	665	643
-	-	-	-	-	-	726
$\text{C}\equiv\text{N}$ sensitive	776	778	-	-	792	782
-	-	-	797	806	-	-
$\gamma(\text{CH})$	-	-	841	843	839	826
-	-	957	-	-	-	-
ring breathing	1001	1003	1018	1019	1022	1018
$\beta(\text{CH})$	1068	1078	1065	1065	1063	1060
-	-	1120	-	-	-	1111
-	-	-	1148	-	-	1157
$\beta(\text{CH})$	1194	1194	1212	1209	1198	1192
$\beta(\text{CH}), \alpha(\text{CC})$	-	-	1216	1220	1217	1212

TABLE 2-1: *(Continued)*

Assignment	4-CP (2.0 M)	4-CP- ¹⁵ N	4-CP/Cu	4CP- ¹⁵ N/Cu	4-CP/Au	4-CP- ¹⁵ N/Au
-	-	-	-	-	-	1221
-	-	-	-	1267	-	1255
-	-	1308	-	-	-	1310
β(CH)	1327	-	1339	1339	-	-
-	-	-	-	1355	-	-
-	1412	-	1423	1423	1420	1411
v(CC,CN)	1492	-	1498	1494	-	1505
v(CC)	1549	1547	1552	1554	-	-
v(CC)	1601	1604	1609	1608	1611	1605
-	-	-	-	-	-	1686
v(C≡N)	2246	2218	-	-	2238	2211

a. Based on Ref. 13.

lying flat-on when adsorbed to the copper colloids because the 2240 cm^{-1} , 1420 cm^{-1} , 1217 cm^{-1} , and 1195 cm^{-1} bands do not change intensities as expected relative to spectra bands of the free molecule. It is anticipated that the primary interaction will occur through the nitrogen in the pyridine ring. In order to understand the observed spectrum of 4-CP with the copper colloids we have collected SER spectra of 4-CP adsorbed onto gold colloids, and have prepared 4-CP- ^{15}N and collected SER spectra for it with copper and gold colloids.

The SER spectrum collected for 4-CP adsorbed on a gold colloid is shown in Figure 2-4 (with the spectrum of the parent 4-CP and 4-CP with a copper colloid), and the frequencies and tentative assignments are presented in Table 2-1. In the gold colloid system, $\nu(\text{C}\equiv\text{N})$ is present and shifted down by 10 cm^{-1} to 2236 cm^{-1} . This observed frequency matches that reported by Rubim and coworkers when 4-CP was adsorbed onto a copper electrode in an end-on orientation.⁵ The ring modes at 1605 cm^{-1} , 1195 cm^{-1} , and 1017 cm^{-1} shift to higher wavenumbers which is consistent with adsorption through the nitrogen in the ring.^{4,5} This suggests that the nitrile group experiences only minor interaction with the surface and undergoes very little change upon adsorption.

The Raman frequencies and tentative assignments of 4-CP- ^{15}N are presented in Table 2-1. Isotopic shifts are observed for $\nu(\text{C}\equiv\text{N})$, $\beta(\text{CH})$, $\delta(\text{C}\equiv\text{N})$, and the $\text{C}\equiv\text{N}$ sensitive bands at 664 cm^{-1} , 550 cm^{-1} , and 365 cm^{-1} in the spectrum of the parent molecule. The SER spectra of 4-CP- ^{15}N mixed with copper and gold colloids are shown in Figures 2-3 and 2-5, respectively, and the frequencies and tentative assignments are presented in Table 2-1. Shifts attributed to isotopic substitution are observed for $\nu(\text{C}\equiv\text{N})$, $\delta(\text{C}\equiv\text{N})$, and the weak ring mode at 1490 cm^{-1} in the spectrum of 4-CP- ^{15}N on gold colloids. In addition, new bands are

Figure 2-4 Raman spectra of 4-cyanopyridine (4-CP) and SERS of 4-CP adsorbed onto copper (/Cu) and gold (/Au) colloids.

Figure 2-5 SERS of 4-cyanopyridine (4-CP) and isotopically labeled 4-cyanopyridine- ^{15}N (4-CP- ^{15}N) adsorbed onto gold (/Au) colloids.

observed at 1310 cm^{-1} and 1255 cm^{-1} in the SER spectrum of 4-CP- ^{15}N . The spectra observed for 4-CP and 4-CP- ^{15}N with the gold colloids are consistent with adsorption of the molecule in an end-on orientation with primary interaction through the nitrogen in the ring. However, virtually identical spectra are observed for 4-CP and 4-CP- ^{15}N on copper colloids. These experiments were carefully repeated and are reproducible. In addition, the spectra observed with the copper colloids contain no signals from modes that contain significant contributions from the $\text{C}\equiv\text{N}$ group. The fact that no isotopic frequency shifts are observed indicates that the $\text{C}\equiv\text{N}$ stretching normal mode does not couple with the ring modes and also indicates that the $\text{C}\equiv\text{N}$ moiety does not become a $\text{C}=\text{N}$ moiety and appear below 1700 cm^{-1} .

The disappearance of the nitrile stretching signal in the SER spectra of 4-CP with copper colloids could be the result of observing the spectra of other species (not 4-CP) in the solution. For instance, we could observe the spectra of the colloid or its components.¹⁶ Raman spectra of copper colloids that we have collected show no observable bands. Garrell¹⁷ and coworkers reported that interferences due to borohydride would give rise to bands at 610 cm^{-1} and 920 cm^{-1} , but with no observation of SERS. Although a band at 608 cm^{-1} in the spectrum of 4-CP with a copper colloid is reported, this signal is not observed in the spectrum of 4-CP- ^{15}N , and a SER spectrum is observed. Therefore it is assumed that interference by borohydride is not occurring.

Chemical removal of the nitrile group with subsequent adsorption of a pyridine-like species is possible. The observed spectra does not support the possibility of a pyridine-like species since the collected spectrum is significantly different from the spectra observed for pyridine on copper surfaces.^{2,6,18}

We believe that a reduction of the nitrile group by excess sodium borohydride from the colloid preparation is a reasonable explanation for the data observed when 4-CP interacts with a copper colloid mixture.¹⁹ We propose that a transition metal assisted borohydride reduction of the nitrile to an amine with the product (4-aminomethylpyridine) adsorbing to the colloid surface adequately accounts for the observed spectra.²⁰ The reaction is depicted as follows.

The spectra of 4-aminomethylpyridine (4-AMP), 4-AMP adsorbed onto a copper colloid and 4-CP mixed with a copper colloid are shown in Figure 2-6. It can be seen that 4-AMP on a copper colloidal surface and 4-CP mixed with a copper colloid solution generate identical spectra within experimental error. The observed Raman frequencies and tentative assignments for neat 4-AMP, and 4-AMP and 4-CP with the copper colloids are presented in Table 2-2.

Our spectral patterns and frequencies are in agreement with the SER spectra collected for 4-AMP on silver electrodes²¹. This includes the doublet near 1210 cm⁻¹ which is a distinguishing feature in the spectrum. This would indicate that the adsorbate is not altered

Figure 2-6 Raman spectra of 4-aminomethylpyridine (4-AMP) and SERS of 4-AMP and 4-CP adsorbed onto copper (/Cu) colloids.

TABLE 2-2: Raman Frequencies (cm^{-1}) of Neat 4-Aminomethylpyridine (4-AMP) and Adsorbed on Copper (/Cu) Colloids and 4-Cyanopyridine (4-CP) Adsorbed on Copper Colloids.

Assignment ^a	4-AMP liquid	4-AMP/Cu	4-CP/Cu
S	415	-	-
Ring deformation	490	500	500
$\gamma(\text{NH}_2)$	592	606	605
S	667	664	668
$\gamma(\text{CH})$	736	-	-
$\nu(\text{CC})$	788	796	797
S	-	841	841
$\beta(\text{CH})$	876	-	-
Ring breathing	994	1017	1018
$\beta(\text{NH}_2)$, $\beta(\text{CH})$	1067	1064	1065
S	-	-	1148
$\beta(\text{CH})$	1206	1210	1212
$\beta(\text{CH})$, $\alpha(\text{CC})$	1219	1215	1216
S	1232	-	-
$\beta(\text{CH})$	-	1340	1339
S	1416	1420	1423
$\nu(\text{CC})$	1447	-	-
$\nu(\text{CC})$	1497	1497	1498
$\nu(\text{CC})$	1560	1552	1552
$\nu(\text{CC})$	1602	1610	1609

a. Based on Ref. 21 and 22.

upon adsorption, and that the SERS is of 4-AMP on the surface of the copper surface. It is noted that 4-AMP adsorbs to the surface through the nitrogen in the pyridine ring as expected.

The gold colloids in the previously described experiments are prepared without borohydride as a reducing agent. The overall SER spectrum is consistent with adsorption through the nitrogen in the pyridine ring. We have prepared gold colloids using borohydride and have found that the signal due to $\nu(\text{C}\equiv\text{N})$ is still present. These results indicate that borohydride ions must act in concert with the copper metal and thus, the nature of the metal is important in the nitrile reduction process.

Deoxygenated copper colloids were utilized to determine whether oxidation of the copper surface is occurring and if this facilitates the reduction process. Copper colloids were prepared under anaerobic conditions (argon atmosphere) and the spectrum of 4-CP adsorbed onto these deoxygenated colloids is shown in Figure 2-7. The observed wavenumbers and tentative assignments are presented in Table 2-3. The aerobic and anaerobic samples give similar spectra. There are little to no shifts in the reported frequencies and the spectral patterns are identical. Based on these results, it can be stated that the presence or absence of oxygen does not facilitate nor hinder the transition metal-assisted reduction process.

The proposed reduction mechanism does not specify the oxidation state of the copper required for the reduction to occur. In order to address this issue, the preparation of copper colloids was performed using various forms of copper (Cu^{+2} , and Cu^{+1}). The SERS collected for the different oxidation states of copper are shown in Figure 2-8. The observed wavenumbers and tentative assignments are reported in Table 2-3. Based on the spectral

Figure 2-7 SERS of 4-cyanopyridine (4-CP) adsorbed onto copper colloids prepared under aerobic (/Cu) and deoxygenated (/Cu (d)) conditions.

TABLE 2-3: Raman Frequencies (cm^{-1}) of 4-Cyanopyridine (4-CP) Adsorbed on Copper Colloids Prepared From Cu^{+2} ($/\text{Cu}^{\circ}(\text{II})$), Cu^{+1} ($/\text{Cu}^{\circ}(\text{I})$) and Under Deoxygenated Conditions ($/\text{Cu}(\text{d})$).

Assignment ^a	4-CP/ $\text{Cu}^{\circ}(\text{II})$	4-CP/ $\text{Cu}^{\circ}(\text{I})$	4-CP/ $\text{Cu}(\text{d})$
S	-	390	385
Ring deformation	500	505	492
$\gamma(\text{NH}_2)$	605	611	607
S	-	649	-
S	668	665	-
$\nu(\text{CC})$	797	799	797
S	841	842	-
Ring breathing	1018	1017	1016
$\beta(\text{NH}_2)$, $\beta(\text{CH})$	1065	1064	1064
S	1148	1154	1151
$\beta(\text{CH})$	1212	1208	1207
$\beta(\text{CH})$, $\alpha(\text{CC})$	1216	1219	1219
S	-	1261	1263
$\beta(\text{CH})$	1339	1340	1343
S	1423	1424	1422
$\nu(\text{CC})$	1498	1495	1496
$\nu(\text{CC})$	1552	1553	1553
$\nu(\text{CC})$	1609	1608	1608

a. Based on Ref. 21 and 22.

Figure 2-8 SERS of 4-cyanopyridine (4-CP) adsorbed onto copper colloids prepared from Cu⁺¹ (/Cu (I)) and Cu⁺² (/Cu (II)) reduction.

data for the preparation using Cu^{+2} and Cu^{+1} the initial state of the copper used is not important. We should also note that the excess of borohydride in solution precludes the existence of copper ions in the colloidal media; i.e., reduction of all copper ions occurs.²³ Thus, the reduction is facilitated by Cu^0 in the colloidal state.

In order to verify that colloidal copper metal is required for the reduction of the nitrile group, a series of experiments in which we added gold colloid to the 4-CP/copper colloid system and copper (II) colloid to the 4-CP/gold colloid system were completed. The SERS collected in these experiments are seen in Figures 2-9, 2-10, 2-11 and 2-12. Initially, 4-CP was adsorbed onto the surface of a gold colloid (this being the point of reference with the observation of a nitrile stretching band at 2243 cm^{-1}). In order to determine if the presence of Cu^{+2} facilitates the reduction of the nitrile group, Cu(II)SO_4 was added to the 4-CP/Au (as seen in Figure 2-9). The resulting SER spectrum is identical to 4-CP/Au. An increase in SERS intensity is observed upon the addition of the Cu(II)SO_4 is due to SO_4^{2-} ions. The presence of SO_4^{2-} ions has been known to promote aggregation of colloidal systems which causes an increase in the observed SER signal.²⁴ In order to further determine that the Cu^{+2} is not an important factor, BH_4^- was added to 4-CP/Au containing Cu(II)SO_4 . As shown in Figure 2-9, the SERS are identical for all three cases and so the addition of Cu^{+2} with borohydride plays no role in the metal-assisted reduction of the nitrile group of 4-CP. Thus, the presence of Cu^{+2} and BH_4^- does not catalyze the reduction of the nitrile group. This is consistent with prior studies involving Cu^{+2} .²⁵

Figure 2-9 SERS of 4-cyanopyridine (4-CP) adsorbed onto a gold colloid (/Au), a gold colloid with CuSO₄ added (/Au/CuSO₄), and a gold colloid with CuSO₄ and borohydride added (/Au/CuSO₄/BH₄⁻).

Figure 2-10 SERS of 4-cyanopyridine (4-CP) adsorbed onto a gold colloid (/Au) and after the addition of a copper colloid (/4-CP/Au/Cu).

Figure 2-11 SERS of 4-aminomethylpyridine (4-AMP) adsorbed on gold (Au/) and copper (/Cu) colloids.

Figure 2-12 SERS of 4-cyanopyridine (4-CP) adsorbed onto a copper colloid (/Cu) and after the addition of a gold colloid (/4-CP/Cu/Au).

The role of Cu° in the colloidal form in the reduction of the nitrile group was investigated and the results are shown in Figures 2-10, 2-11 and 2-12. 4-CP was adsorbed onto a gold colloid (see Figure 2-10). To this system, a copper colloid (consisting of Cu° and BH_4^-) was added. The resulting SERS shows a disappearance of $\nu(\text{C}\equiv\text{N})$ and produces a spectrum identical to that collected for 4-CP mixed with a copper colloid. This indicates that the presence of Cu° in colloidal form is necessary for reduction of the nitrile substituent. This does not, however, indicate whether we are observing the reduction product of 4-CP on the surface of a copper colloid or a gold colloid. In order to determine this, 4-AMP was adsorbed on a gold colloid for comparison with 4-AMP on a copper colloid (see Figure 2-11). The spectral patterns show distinct differences which suggest that the SERS observed for 4-CP adsorbed on a gold colloid and copper colloid mixture is that of 4-AMP on a copper colloid (refer back to Figure 2-10). The opposite experiment was carried out and the results are shown in Figure 2-12. For this particular case, 4-CP was mixed with a copper colloid and then a gold colloid was added to the system. There was no observable change in the SERS. This indicates that the addition of a gold colloid does not reverse the reduction of the nitrile substituent or remove the 4-AMP from the copper colloidal surface. Thus, colloidal Cu° facilitates reduction of the nitrile group with no indications of a reversible process.

The issue of timing of the reaction was addressed. In prior investigations utilizing an electrode surface, a reduction of 4-cyanopyridine to 4-aminomethylpyridine was performed.⁴ The reduction reaction involved a step in which the molecule was adsorbed flat onto the metal surface before the complete transfer of an electron from the molecule to the metal could occur. In the explanation of that reaction, the molecule must first interact with the metal

surface in a flat-on orientation, then subsequently undergo a reduction of the nitrile substituent to an amino group. Thus, the reduction involves a step in which the molecule is adsorbed before the complete transfer of an electron occurs between the metal and the molecule.

A series of concentration experiments were performed to investigate the orientation of the 4-CP mixed with both gold and copper colloids. The SERS for these experiments are shown in Figures 2-13, 2-14 and 2-15. The observed Raman frequencies and tentative assignments are reported in Table 2-4. The adsorbate concentrations were varied from 0.2 M to 1×10^{-6} M and the same preparation methods were used for the colloidal samples. The detection of Raman bands of the free molecule in aqueous solution begins at concentrations of 1×10^{-2} M. Based on the SERS of 4-CP on a gold colloid, the $\nu(\text{C}\equiv\text{N})$ band present at 2238 cm^{-1} is indicative of an end-on orientation. Since the 4-CP undergoes a reduction of the nitrile substituent upon adsorption onto a copper colloid, $\nu(\text{C}\equiv\text{N})$ is not observed and the orientation is assumed to be in a flat-on fashion based on prior discussion (*vide supra*).

The SER spectra of the various concentrations of 4-CP mixed with copper colloids demonstrate a difference in spectral pattern and frequencies at higher concentrations. The differences in SER spectra begin at adsorbate concentrations of 5.7×10^{-2} M. At this particular solution, the concentration of the 4-CP is equivalent to that of the borohydride in the colloidal system. At concentrations of 4-CP above that of the borohydride, a band in the nitrile stretching region is still not detected until a concentration of 4-CP at 2.9×10^{-2} M is

Figure 2-13 Raman spectra of 4-cyanopyridine (4-CP) in aqueous solutions: (a) 0.2 M, (b) 0.1 M, (c) 6.56×10^{-2} M, (d) 0.01 M, (e) 1×10^{-3} M, (f) 1×10^{-4} M, and (g) 1×10^{-6} M.

Figure 2-14 SERS of 4-cyanopyridine (4-CP) adsorbed onto copper colloids at various concentrations: (a) 0.2 M (600 μL), (b) 0.2 M (300 μL), (c) 0.1 M (300 μL), (d) 6.56×10^{-2} M (300 μL), (e) 0.01 M (300 μL), (f) 1×10^{-3} M (300 μL), (g) 1×10^{-4} M (300 μL), and (h) 1×10^{-6} M (300 μL).

Figure 2-15 SERS of 4-cyanopyridine (4-CP) adsorbed onto gold colloids at various concentrations: (a) 0.2 M (600 μL), (b) 0.2 M (300 μL), (c) 0.1 M (300 μL), (d) 6.56×10^{-2} M (300 μL), (e) 0.01 M (300 μL), (f) 1×10^{-3} M (300 μL), (g) 1×10^{-4} M (300 μL), and (h) 1×10^{-6} M (300 μL).

TABLE 2-4: Raman Frequencies (cm⁻¹) of 4-Cyanopyridine (4-CP) Adsorbed onto Copper (/Cu) Colloids at Various Concentrations.

Assignment ^a	4-CP/Cu (2.9 x 10 ⁻² M) ^b (0.2 M)	4-CP/Cu (1.7 x 10 ⁻² M) (0.2 M)	4-CP/Cu (8.7 x 10 ⁻³ M) (0.1 M)	4CP/Cu (5.7 x 10 ⁻³ M) (6.56 x 10 ⁻² M)	4-CP/Cu (8.7 x 10 ⁻⁴ M) (0.01 M)	4-CP/Cu (8.7 x 10 ⁻⁵ M) (1 x 10 ⁻³ M)
S	-	298	303	-	-	-
C≡N sensitive	386	386	387	391	-	-
Ring deformation	-	-	-	-	502	499
γ(NH ₂)	-	-	-	-	604	608
γ(CH)	835	834	838	834	-	-
S	898	895	895	893	-	-
ring breathing	998	998	998	998	1012	1020
β(NH ₂), β(CH)	-	-	-	-	1065	1069
S	-	1107	1109	-	-	-
S	1150	-	1151	-	-	-
β(CH)	1204	1203	1204	1201	1208	1213
β(CH), α(CC)	-	-	-	-	1217	1220
S	1270	1268	1275	-	-	-
S	1312	1310	1310	1307	-	-
β(CH)	-	-	-	-	1340	1342
ν(CC,C≡N)	1395	1394	1394	1391	-	-
S	-	-	-	-	1421	1423
ν(CC)	1453	1451	1451	1447	-	-
ν(CC)	-	-	-	-	-	1496
ν(CC)	1600	1600	1598	1600	1607	1610
ν(C≡N)	2238	-	-	-	-	-

a. Based on Ref. 13, 21, and 22.

b. Final concentration of 4-CP in copper system.

present. The appearance of new SER bands and frequencies in the spectra could be due to two possibilities. First, the increase in adsorbate concentration and resulting change in surface orientation (flat-on to end-on) would cause the enhancement of new SER bands (based on symmetry rules). Second, the nitrile reduction ceases due to lack of copper and borohydride ions and the observed SERS is of both 4-CP and 4-AMP adsorbed on the copper surface. Bands at 391 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 834 cm^{-1} ($\gamma(\text{NH}_2)$), 895 cm^{-1} , 1307 cm^{-1} , 1391 cm^{-1} ($\nu(\text{CC},\text{C}\equiv\text{N})$), and 1447 cm^{-1} ($\nu(\text{CC})$) indicate the presence of both 4-CP and 4-AMP on the metal surface. The disappearance of bands associated with 4-AMP at 502 cm^{-1} (Ring deformation), 604 cm^{-1} ($\gamma(\text{NH}_2)$), 1065 cm^{-1} ($\beta(\text{NH}_2)$, $\beta(\text{CH})$), 1217 cm^{-1} ($\beta(\text{CH})$, $\alpha(\text{CC})$), 1340 cm^{-1} ($\beta(\text{CH})$), 1421 cm^{-1} , and 1496 cm^{-1} ($\nu(\text{CC})$) suggest that the observed molecule on the surface is no longer predominantly the amino species. The shifts to lower energies in the modes associated with the aromatic ring at 998 cm^{-1} (ring breathing), 1201 cm^{-1} ($\beta(\text{CH})$), and 1600 cm^{-1} ($\nu(\text{CC})$) would indicate a change in surface orientation to an end-on alignment.

The SER spectra of the various concentrations of 4-CP adsorbed onto gold colloids demonstrate no changes in spectral pattern or frequencies as concentration is increased. The increase in adsorbate concentration contributes to an increase in the SERS intensity, but with no shift in the nitrile stretching band found at 2238 cm^{-1} ($\nu(\text{C}\equiv\text{N})$). These results verify that the adsorption of 4-CP at any concentration occurs in an end-on fashion on gold colloids.

2.4 CONCLUSIONS

Dramatic differences are observed between the SER spectrum of 4-CP mixed with a copper colloid and the spectrum of 4-CP on a gold colloid. Specifically, the nitrile stretching band is missing in the SERS involving the copper colloid. 4-CP-¹⁵N was prepared and the SER spectrum collected. This spectrum indicates that the nitrile stretching band is not coupled with the ring modes or shifted to lower wavenumbers as a -C=N moiety. The data are adequately explained by a transition metal-assisted borohydride reduction of 4-CP to 4-AMP. SER spectra of these molecules in the presence of copper colloids are identical within experimental error. The nitrile stretching signal was observed when a gold colloid was prepared by borohydride reduction, indicating the metal selectivity of the reaction. Experiments utilizing deoxygenated solutions and different copper salts for the preparation of the copper colloids showed no effect on the reduction mechanism. Concentration experiments with gold and copper colloids indicate that the orientation upon adsorption is metal dependent. Upon adsorption onto gold colloids, the 4-CP aligns in an end-on fashion, while studies on copper indicate that the orientation goes from a flat-on to an end-on orientation as concentration of 4-AMP is increased. At higher concentrations of 4-CP mixed with the copper colloids, the presence of both 4-CP and its' reduction product, 4-AMP, is observed in the SERS. Additionally, the mixing of copper and gold colloids with 4-CP showed that the molecules undergo the reduction process due to the interaction of colloidal Cu⁰ with the 4-CP, even after adsorption onto gold colloids.

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CHAPTER 3

Isomeric Effects of 4-, 3-, and 2-Cyanopyridines Adsorbed onto Copper Colloids

3.1 INTRODUCTION

In the original study of surface enhanced Raman (SER) scattering from pyridine adsorbed on silver electrodes it was noted that some vibrational modes were enhanced more than others.¹⁻⁵ The reason for this is that vibrational modes are enhanced due to the direction of the induced dipole moment change with respect to the metal surface.

Using the image dipole model of SERS, predictions can be made about the dependence of enhancement on molecular orientation.⁶ If the Raman scattering is treated semi-classically, then the Raman shifted light is seen as arising from an oscillating electric dipole in the molecule. To a first approximation this dipole is oriented along the bond axis for a bond stretching motion. When such a dipole is brought near a metal surface, classical electrostatics predicts that the dipole will induce an image dipole in the metal surface.⁶ For dipoles parallel to the metal surface, this image dipole is opposite in direction and cancellation occurs. However, if the dipole is perpendicular to the metal surface then addition is constructive. Based on this classical model, it is predicted that vibrations parallel to the metal surface should show smaller enhancements than those perpendicular to the surface. Thus, modes which are normal to the adsorption surface would demonstrate the greatest amount of enhancement upon attachment.⁷ Additionally, the more symmetric a vibrational normal mode, the greater the amount of observed enhancement.^{3,8} Based on these premises, normal

modes which have a dipole moment charge normal to the metal surface would show the largest enhancement whether they are classified as symmetric or antisymmetric modes. Thus, relative enhancement intensities can be used to determine the orientation of the molecule on the surface.

Previous studies by Van Duyne and Rubim of cyanopyridines adsorbed onto silver electrodes indicate a surface enhancement of the nitrile stretching normal mode that is dependent upon the position of the nitrile substituent on the aromatic ring.^{3,5,6,9} Van Duyne showed that there was a decrease in intensity of $\nu(\text{C}\equiv\text{N})$ as the nitrile was moved from the 4- to the 3- to the 2-positions for 4-CP, 3-CP, and 2-CP on silver electrodes (see Figure 3-1). This was interpreted as an enhancement controlled by the interaction of the nitrile moiety with the metal surface as determined by its position on the pyridine ring and hence orientation with respect to the metal surface. As the molecule tends to a flat-on orientation the intensity of $\nu(\text{C}\equiv\text{N})$ is lowered. It was assumed that adsorption was occurring primarily through the lone pair electrons of the nitrogen in the aromatic ring as had been previously reported.^{3,5,6,9}

Rubim later found that the orientation of the molecule was dependent upon the applied potential and at certain potentials, an actual reduction of 4-CP to 4-aminomethylpyridine (4-AMP) would occur.^{5,9} Subsequent studies showed the dependence of SERS intensity on the applied potential for different vibrational modes of 4-CP molecules adsorbed onto a silver electrode.^{5,9,10} This was based on the idea that at different applied potentials the concentration of the adsorbate on the surface would increase with steric effects forcing part of the molecules to be adsorbed end-on (σ -interaction; i.e. changed from flat-on orientation). This

4-CP

3-CP

2-CP

4-AMP

3-AMP

2-AMP

Figure 3-1 Molecular structures for the isomeric forms of cyanopyridine (4-CP, 3-CP, and 2-CP) and the isomeric forms of aminomethylpyridine (4-AMP, 3-AMP, and 2-AMP).

causes selected vibrational modes to change from parallel to perpendicular relative to the metal surface, resulting in an increase in SER effect observed for those motions.

In those studies, it was consistently found that the more symmetric the form of cyanopyridine (4-CP>3-CP>2-CP) the greater the SERS effect and the less complicated the spectra since some modes experience very strong enhancement. The more asymmetric forms of CP produced spectra that were more complicated due to the appearance of both the symmetric and asymmetric SERS bands. The generation of particular bands in SERS provides insight into the orientation and site of attachment for each isomeric form of the molecule on the metal surface.¹¹⁻¹⁴

These investigations indicate that the mode of bonding for all three isomers is via the nitrogen in the aromatic ring, however in the case of 2-CP, coordination also occurs via the nitrile nitrogen.^{3,6,15-18} The different bonding interaction of the nitrile group in 2-CP is responsible for a different bonding geometry that results in the enhancement of antisymmetric vibrational modes.

We have extended the study of 4-CP mixed with copper colloids to include isomeric forms of the cyanopyridine. Isomers of cyanopyridine provide different orientations of the nitrile group with respect to the plane of the metal surface (assuming pyridine nitrogen coordination). Determination of whether the transition metal-assisted borohydride reduction proceeds regardless of the nitrile position relative to the surface will provide insight into steric inhibition of the reduction process and the necessity of surface adsorption prior to reduction. SERS of the isomeric forms of CP will provide insight into the mechanism of surface-

enhancement through the degree of enhancement observed and the nature of the spectral bands that are enhanced (symmetric vs. antisymmetric vibrational modes).

3.2 EXPERIMENTAL

Colloid Preparation

The preparation of the copper colloids is based on the borohydride reduction of Cu^{2+} as described in Chapter 2.2.¹⁹ All colloidal solutions were prepared in disposable borosilicate glass culture tubes with water passed through a Barnstead/Thermolyne (Dubuque, IA) Nanopure Water Model D4541 purification system. The colloid, which starts as a pale yellow-brown color becomes a dark reddish-brown. The red color is indicative of particle sizes ranging from 10 to 20 nm and gives rise to an absorption band at 564 nm.²⁰ After the colloid was allowed to age for two hours, an aqueous solution of the CP (4-CP, 3-CP, and 2-CP) (Aldrich; 98%; Aldrich; 98%; Aldrich; 99%) (1×10^{-3} M, 0.30 mL) was added. The final concentration of the CP was approximately 9×10^{-5} M. Upon addition of the CP, the colloid changes to a dark grey-brown color due to aggregation and has an absorption band at 570 nm. A band at 296 nm indicative of the adsorbate is also observed. The shifts in the spectra are indicative of aggregation and molecule-surface interaction in the colloidal system.²¹ Data collection of the SER spectra of the cyanopyridines adsorbed onto the copper colloids was begun 80 minutes after the addition of the adsorbate solution to the colloid.

The preparation of the gold colloid is described in Chapter 2.2.²² Raman samples were prepared by adding CP (4-CP, 3-CP, and 2-CP) (0.3 mL, 1×10^{-3} M) to 2.7 mL of the gold colloid solution in borosilicate glass culture tubes. The color changed to a dark

violet/purple with an absorption maxima at 563 nm indicative of aggregation due to the presence of the adsorbate. The SER spectra were collected starting 80 minutes after the addition of the cyanopyridine.

Aminomethylpyridines (4-AMP, 3-AMP, and 2-AMP) (Aldrich; 98%; Aldrich; 99%; Aldrich; 99%) were adsorbed onto copper colloids using the procedures described above. Spectra of the parent compounds were collected as the neat liquid contained in standard melting point capillary tubes.

Anaerobic preparation of the copper colloids was performed using the same chemical ratios as listed above with the same procedure described in Section 2.2.

Additional copper colloids were prepared using methods described above, but with different initial states of copper salts for reduction [copper(II) sulfate (Aldrich; 99.99% and copper(I) chloride (Aldrich; 97%).

Experimental parameter for collection were identical to those described in Section 2.2.

3.3 RESULTS AND DISCUSSION

The SER spectra of the three isomers of cyanopyridine (4-CP, 3-CP, and 2-CP) mixed with copper colloids are shown in Figure 3-2. The observed wavenumbers with tentative assignments for 3-CP and 2-CP are presented in Tables 3-1 and 3-2. Upon adsorption, the $\nu(\text{C}\equiv\text{N})$ stretching band is not observed within the 2000 cm^{-1} to 2300 cm^{-1}

Figure 3-2 SERS of cyanopyridines (4-, 3-, and 2-CP) adsorbed onto copper colloids (/Cu).

TABLE 3-1: Raman Frequencies (cm^{-1}) of 3-Cyanopyridine (3-CP) in Aqueous Solution (2.0M) and Adsorbed on Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	3-CP (2.0 M)	3-CP/Cu	3-CP/Au
C $\equiv$ N sens, δ (CN)	172	-	189
ϕ (CC), C $\equiv$ N sens, γ (CN)	360	-	362
S	-	347	-
ϕ (CC), C $\equiv$ N sens, γ (CN)	399	-	400
S	-	414	-
C $\equiv$ N sens, δ (CN)	475	-	474
ϕ (CC), C $\equiv$ N sens, γ (CN)	554	-	539
S	-	620	-
α (CCC)	635	644	643
S	-	699	-
C $\equiv$ N sensitive	782	797	792
S	-	820	-
S	-	928	-
S	994	983	-
Ring	1032	1030	1028
β (CH)	1039	1045	1052
S	1060	-	-
S	-	1098	-
S	1127	1120	1119
β (CH)	1192	1188	1192
C $\equiv$ N sensitive	1216	1216	1211
α (CC)	1241	-	-
S	-	-	1296
β (CH)	1342	1334	-
S	-	-	1369
ν (CC, CN)	1423	1426	1425
ν (CC, CN)	1477	1478	1474
ν (CC)	1572	1581	1566
ν (CC)	1593	1595	1598
ν (CN)	2240	-	2235

a. Based on Ref.23.

TABLE 3-2: Raman Frequencies (cm^{-1}) of 2-Cyanopyridine (2-CP) in Aqueous Solution (2.0M) and Adsorbed on Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	2-CP (2.0 M)	2-CP/Cu	2-CP/Au
C $\equiv$ N sens, δ (CN)	175	-	-
ϕ (CC), C $\equiv$ N sens, γ (CN)	364	-	375
S	402	410	-
S	-	-	449
C $\equiv$ N sens, δ (CN)	482	-	488
S	-	501	-
C $\equiv$ N sens, δ (CN)	554	-	546
S	-	614	-
α (CCC)	636	637	634
S	741	750	-
C $\equiv$ N sensitive	779	-	775
S	-	807	-
Ring	1001	1011	1019
β (CH)	1048	1052	1070
β (CH)	1095	-	-
S	-	1105	-
β (CH)	1161	1153	-
C $\equiv$ N sensitive	1206	-	1228
S	1234	1235	-
α (CC)	1258	1259	-
β (CH)	1295	-	1292
S	-	1314	-
S	-	-	1377
S	-	1383	-
ν (CC,CN)	1437	-	-
ν (CC,CN)	1469	1475	1464
S	-	-	1512
ν (CC)	1573	1563	1565
ν (CC)	1587	1594	1613
ν (C $\equiv$ N)	2243	-	2226

a. Based on Ref. 23.

region for any of the isomers. Therefore, reduction of the nitrile group is occurring despite orientation on the surface.

The absence of the $\nu(\text{C}\equiv\text{N})$ band is due to the proposed metal-assisted borohydride reduction of the nitrile group to an aminomethyl substituent during the adsorption process. For verification of this reduction, the isomeric forms of the reduction products (3-AMP and 2-AMP) were collected on copper colloids.

The SER spectrum of 3-AMP adsorbed on a copper colloidal surface, as well as the Raman spectrum of the parent are shown in Figure 3-3. The observed wavenumbers and tentative assignments are presented in Table 3-3. It can be seen that 3-CP mixed with a copper colloid and 3-AMP adsorbed onto a copper surface generate identical spectra within experimental error. In the Raman of the parent 3-AMP, the strongest band is associated with the ring breathing vibration (1030 cm^{-1}). In the SERS of 3-AMP on copper and 3-CP mixed with a copper colloid, the bands at 1594 cm^{-1} ($\nu(\text{CC})$), 1578 cm^{-1} ($\nu(\text{CC})$), 1095 cm^{-1} ($\beta(\text{CH})$), 1046 cm^{-1} ($\beta(\text{NH}_2)$, $\beta(\text{CH})$), and 1029 cm^{-1} (ring breathing) show the greatest amount of enhancement.^{24,25} These bands are all associated with the symmetric ring modes of the reduction product and coincide with adsorption via the pyridine nitrogen.⁹

The SER spectrum of 2-AMP adsorbed on a copper colloidal surface and the corresponding Raman spectrum of the parent are shown in Figure 3-4. The observed wavenumbers and tentative assignments are presented in Table 3-4. It can be seen that 2-CP mixed with a copper surface and 2-AMP adsorbed onto a copper surface generate identical spectra within experimental error. In the Raman of 2-AMP, the strongest Raman bands are

Figure 3-3 Raman spectra of neat 3-aminomethylpyridine (3-AMP) and SERS of 3-AMP and 3-CP adsorbed onto copper colloids (/Cu).

TABLE 3-3: Raman Frequencies (cm⁻¹) of Neat 3-Aminomethylpyridine (3-AMP) and Adsorbed on Copper (/Cu) Colloids and 3-Cyanopyridine (3-CP) in Aqueous Solution (2.0 M) and Adsorbed on Copper Colloids.

3-AMP Assignment ^a	3-AMP liquid	3-AMP/Cu	3-CP/Cu	3-CP liquid	3-CP Assignment ^a
S	167	-	-	172	C≡N sens, δ(CN)
S	-	344	347	-	-
S	-	-	-	360	φ(CC), C≡N sens, γ(CN)
S	404	407	414	399	φ(CC), C≡N sens, γ(CN)
S	-	-	-	475	C≡N sens, δ(CN)
Ring deformation	493	491	-	-	-
S	-	-	-	554	φ(CC), C≡N sens, γ(CN)
γ(NH ₂)	598	-	-	-	-
S	-	625	620	-	-
α(CCC)	633	645	644	635	α(CCC)
S	-	698	699	-	φ(CC)
S	716	-	-	-	-
v(CC)	788	799	797	782	C≡N sensitive
S	811	819	820	-	-
S	932	928	928	-	-
α(CC)	954	-	-	-	-
S	994	980	983	994	-
Ring breathing	1030	1029	1030	1032	Ring
β(NH ₂), β(CH)	1038	1046	1045	1039	β(CH)
S	-	-	-	1060	-
S	1102	1095	1098	-	-

TABLE 3-3: (Continued)

3-AMP Assignment ^a	3-AMP liquid	3-AMP/Cu	3-CP/Cu	3-CP liquid	3-CP Assignment ^a
S	1126	1121	1120	1127	-
$\beta(\text{CH})$	1191	1189	1188	1192	$\beta(\text{CH})$
S	-	-	-	1216	C $\equiv$ N sensitive
$\beta(\text{NH}_2)$, $\beta(\text{CH})$	1224	1218	1216	-	-
S	-	-	-	1241	$\alpha(\text{CC})$
$\beta(\text{CH})$	-	1336	1334	1342	$\beta(\text{CH})$
S	1350	-	-	-	-
S	1387	1386	-	-	-
S	1428	1426	1426	1423	v(CC, CN)
v(CC)	1454	-	-	-	-
v(CC)	1479	1476	1478	1477	v(CC, CN)
v(CC)	1577	1578	1581	1572	v(CC)
v(CC)	1592	1594	1595	1593	v(CC)
v(CC)	1657	-	-	-	-
S	-	-	-	2240	v(CN)

a. Based on Ref. 23, 24 and 25.

Figure 3-4 Raman spectra of neat 2-aminomethylpyridine (2-AMP) and SERS of 2-AMP and 2-CP adsorbed onto copper colloids (/Cu).

TABLE 3-4: Raman Frequencies (cm^{-1}) of Neat 2-Aminomethylpyridine (2-AMP) and Adsorbed on Copper (/Cu) Colloids and 2-Cyanopyridine (2-CP) in Aqueous Solution (2.0 M) and Adsorbed on Copper Colloids.

2-AMP Assignment ^a	2-AMP liquid	2-AMP/Cu	2-CP/Cu	2-CP liquid	2-CP Assignment ^a
S	194	-	-	175	C $\equiv$ N sens, δ (CN)
S	-	-	-	364	ϕ (CC), C $\equiv$ N sens, γ (CN)
S	407	412	410	402	-
S	437	-	-	-	-
S	-	-	-	482	C $\equiv$ N sens, δ (CN)
Ring deformation	500	500	501	-	-
S	-	-	-	554	C $\equiv$ N sens, δ (CN)
γ (NH ₂)	603	611	614	-	-
α (CCC)	627	639	637	636	α (CCC)
S	768	751	750	741	-
S	-	-	-	779	C $\equiv$ N sensitive
ν (CC)	791	809	807	-	-
S	812	-	-	-	-
S	-	884	-	-	-
S	927	935	-	-	-
Ring breathing	994	1013	1011	1001	Ring
β (NH ₂), β (CH)	1048	1055	1052	1048	β (CH)
S	1094	-	-	1095	β (CH)
S	-	1110	1105	-	-
β (CH)	1152	1154	1153	1161	β (CH)
S	-	-	-	1206	C $\equiv$ N sensitive

TABLE 3-4: (Continued)

2-AMP Assignment ^a	2-AMP liquid	2-AMP/Cu	2-CP/Cu	2-CP liquid	2-CP Assignment ^a
$\beta(\text{NH}_2)$, $\alpha(\text{CC})$	1224	1235	1235	1234	-
$\alpha(\text{CC})$	-	1262	1259	1258	$\alpha(\text{CC})$
S	-	-	-	1295	$\beta(\text{CH})$
S	-	1315	1314	-	-
S	-	1388	1383	-	-
$\nu(\text{CC})$	1436	1436	-	1437	$\nu(\text{CC}, \text{CN})$
$\nu(\text{CC})$	1475	1478	1475	1469	$\nu(\text{CC}, \text{CN})$
$\nu(\text{CC})$	1570	1565	1563	1573	$\nu(\text{CC})$
$\nu(\text{CC})$	1593	1596	1594	1587	$\nu(\text{CC})$
S	-	-	-	2243	$\nu(\text{C}\equiv\text{N})$

a. Based on Ref. 23, 24 and 25.

1048 cm^{-1} ($\gamma(\text{NH}_2)$, $\beta(\text{CH})$), 994 cm^{-1} (ring breathing), 791 cm^{-1} ($\nu(\text{CC})$), and 627 cm^{-1} ($\gamma(\text{NH}_2)$).^{24,25} In the SERS of 2-AMP on copper and 2-CP mixed with copper, the bands associated with the amino group at 1235 cm^{-1} ($\beta(\text{NH}_2)$, $\alpha(\text{CC})$), 1055 cm^{-1} ($\beta(\text{NH}_2)$, $\beta(\text{CH})$), and 611 cm^{-1} ($\gamma(\text{NH}_2)$) undergo shifts to higher frequencies due to interaction via both the ring nitrogen and the amino nitrogen.¹⁵ In the SERS, the bands at 1596 cm^{-1} ($\nu(\text{CC})$), 1565 cm^{-1} ($\nu(\text{CC})$), 1478 cm^{-1} ($\nu(\text{CC})$), 1013 cm^{-1} (ring), and 639 cm^{-1} ($\alpha(\text{CCC})$) exhibit the greatest amount of surface enhancement. The SER spectra of 2-AMP are more complex than the other isomeric forms of AMP which is due to additional modes of the molecule (probably antisymmetric) having a dipole charge perpendicular to the surface. The SER signals also demonstrate that the enhancement factor is less for 2-AMP than 4-AMP and 3-AMP presumably due to lower molecular symmetry.

Deoxygenated copper colloids were used to determine whether oxidation of the copper surfaces is occurring and if this facilitates the reduction process. The copper colloids were prepared and mixing with 3-CP and 2-CP was carried under argon atmosphere. The spectral results for 3-CP and 2-CP mixed with the deoxygenated colloids are shown in Figures 3-5 and 3-6. The observed wavenumbers and tentative assignments are presented in Tables 3-5 and 3-6. As shown, the spectra for both conditions give similar spectra. There are no shifts within experimental error in the observed frequencies and the spectral patterns are identical. Based on these results it was determined that the presence or absence of oxygen does not facilitate nor hinder the borohydride reduction mechanism for these two forms of cyanopyridine.

Figure 3-5 SERS of 3-cyanopyridine (3-CP) adsorbed onto copper colloids prepared under aerobic (/Cu) and deoxygenated (/Cu (d)) conditions.

Figure 3-6 SERS of 2-cyanopyridine (2-CP) adsorbed onto copper colloids prepared under aerobic (/Cu) and deoxygenated (/Cu (d)) conditions.

TABLE 3-5: Raman Frequencies (cm^{-1}) of 3-Cyanopyridine (3-CP) Adsorbed on Copper Colloids Prepared From Cu^{+2} ($/\text{Cu}^{\circ}(\text{II})$), Cu^{+1} ($/\text{Cu}^{\circ}(\text{I})$) and Under Deoxygenated Conditions ($/\text{Cu}(\text{d})$).

Assignment ^a	3-CP/ $\text{Cu}^{\circ}(\text{II})$	3-CP/ $\text{Cu}^{\circ}(\text{I})$	3-CP/ $\text{Cu}(\text{d})$
S	347	344	-
S	414	-	-
S	620	623	616
$\alpha(\text{CCC})$	644	648	644
S	699	704	700
S	797	800	796
S	820	825	824
S	928	-	930
$\alpha(\text{CC})$	-	949	-
S	983	984	983
Ring breathing	1030	1031	1029
$\beta(\text{NH}_2)$, $\beta(\text{CH})$	1045	1048	1047
S	1098	1100	1099
S	1120	1122	1123
$\beta(\text{CH})$	1188	1188	1188
$\beta(\text{NH}_2)$, $\alpha(\text{CC})$	1216	1222	1219
S	-	1261	1262
$\beta(\text{CH})$	1334	1330	1328
S	-	1385	-
$\nu(\text{CC})$	1426	1427	1426
$\nu(\text{CC})$	1478	1475	1475
S	-	-	1550
$\nu(\text{CC})$	1581	1575	1577
$\nu(\text{CC})$	1595	1595	1595

a. Based on Ref. 24 and 25.

TABLE 3-6: Raman Frequencies (cm^{-1}) of 2-Cyanopyridine (2-CP) Adsorbed on Copper Colloids Prepared From Cu^{+2} ($/\text{Cu}^{\circ}(\text{II})$), Cu^{+1} ($/\text{Cu}^{\circ}(\text{I})$) and Under Deoxygenated Conditions ($/\text{Cu}(\text{d})$).

Assignment ^a	2-CP/ $\text{Cu}^{\circ}(\text{II})$	2-CP/ $\text{Cu}^{\circ}(\text{I})$	2-CP/ $\text{Cu}(\text{d})$
S	410	411	412
Ring deformation	501	-	-
$\gamma(\text{NH}_2)$	614	607	605
$\alpha(\text{CCC})$	637	638	637
S	750	748	747
$\nu(\text{CC})$	807	810	811
Ring breathing	1011	1014	1014
$\beta(\text{NH}_2)$, $\beta(\text{CH})$	1052	1054	1054
S	1105	1110	1110
$\beta(\text{CH})$	1153	1155	1155
$\beta(\text{CH})$, $\alpha(\text{CC})$	1235	1234	1234
$\alpha(\text{CC})$	1259	1267	1266
S	1314	1318	1317
S	1383	1388	1388
$\nu(\text{CC})$	-	1434	-
$\nu(\text{CC})$	1475	1477	1476
$\nu(\text{CC})$	1563	1564	1564
$\nu(\text{CC})$	1594	1597	1597

a. Based on Ref. 24 and 25.

In order to confirm the state of copper that is required in the borohydride reduction, and that the isomer differences play no role in the reduction reaction, 3-CP and 2-CP were mixed with copper surfaces prepared using different oxidation states of copper (Cu^{+2} , and Cu^{+1}). The SERS collected for $\text{Cu}^{\circ}(\text{I})$ and $\text{Cu}^{\circ}(\text{II})$ with 3-CP and 2-CP are shown in Figures 3-7 and 3-8, respectively. The observed wavenumbers and tentative assignments are reported in Table 3-5 and 3-6. Based on the data, the initial state of the copper used in the preparation of the copper colloid is not important since identical spectra were collected for all three isomers adsorbed onto the different copper colloids. Thus, the presence of a copper colloid (assumed to be Cu°) and borohydride is required for the reduction reaction to proceed (just as we found for 4-CP) and the differences in isomeric form plays no role in the process.

The SER spectra obtained when 3-CP is mixed with gold and copper colloids and the normal Raman spectrum of 3-CP are shown in Figure 3-9. The observed wavenumbers and tentative assignments are presented in Table 3-1. Upon adsorption onto a copper colloid, the $\nu(\text{C}\equiv\text{N})$ at 2240 cm^{-1} is not observed and the nitrile sensitive bands at 1216 cm^{-1} , 782 cm^{-1} , 554 cm^{-1} , 475 cm^{-1} , 399 cm^{-1} , 360 cm^{-1} , and 172 cm^{-1} are absent.²³ The bands associated with the symmetric ring modes of the parent 3-CP are the most enhanced in the SERS on copper colloids. These are found at $1032\text{ cm}^{-1}(\text{ring})$, $1039\text{ cm}^{-1}(\beta(\text{CH}))$, $1192\text{ cm}^{-1}(\beta(\text{CH}))$, and $1593\text{ cm}^{-1}(\nu(\text{CC}))$. The 1216 cm^{-1} band ($\text{C}\equiv\text{N}$ sensitive) in the Raman spectrum is of equal intensity to the $1192\text{ cm}^{-1}(\beta(\text{CH}))$, however, in the SERS the 1216 cm^{-1} band is absent. This indicates that the nitrile substituent is no longer present. Additionally,

Figure 3-7 SERS of 3-cyanopyridine (3-CP) adsorbed onto copper colloids prepared from Cu^{+1} (/Cu(I)) and Cu^{+2} (/Cu (II)) reduction.

Figure 3-8 SERS of 2-cyanopyridine (2-CP) adsorbed onto copper colloids prepared from Cu^{+1} (/Cu(I)) and Cu^{+2} (/Cu (II)) reduction.

Figure 3-9 Raman spectra of 3-cyanopyridine (3-CP) and SERS of 3-CP adsorbed onto copper (/Cu) and gold (/Au) colloids.

the 1572 cm^{-1} ($\nu(\text{CC})$) in the Raman is enhanced to almost equal intensity to the 1595 cm^{-1} ($\nu(\text{CC})$) in the SERS. These features support adsorption occurring via the pyridine nitrogen as seen in prior studies.^{3,6} Relative to the SERS collected for 4-CP mixed with a copper colloid, the amount of enhancement observed for the 3-CP is less. Two insights are gained from the adsorption of 3-CP in compared to 4-CP: (1) the adsorption is based on a weaker interaction with the metal surface as indicated by the weaker surface enhancement; and (2) the lower the molecular symmetry, the lower the surface enhancement observed.

In the SER spectrum of 3-CP adsorbed on a gold colloid, a $\nu(\text{C}\equiv\text{N})$ signal is present and shifted to the red by 5 cm^{-1} to 2235 cm^{-1} . This observed wavenumber coincides with values reported when 3-CP is adsorbed onto copper and silver electrodes in an end-on configuration with adsorption via the pyridine nitrogen.^{3,6} The most significant change in relative intensity of SERS for 3-CP adsorbed onto a gold colloid is that the 1032 cm^{-1} ring breathing mode dominates over the other modes associated with the aromatic ring. This would indicate that the interaction between the molecule and the colloidal surface is an end-on orientation causing this particular mode to become aligned perpendicular relative to the metal surface, and thus, resulting in the greatest surface enhancement. The ring modes at 1595 cm^{-1} , 1192 cm^{-1} , 1052 cm^{-1} , and 1028 cm^{-1} shift to higher wavenumbers, which is consistent with adsorption via the nitrogen on the aromatic ring.^{3,5,6,9} These observations confirm that the primary adsorption site for 3-CP is via the nitrogen on the aromatic ring.

The SERS of 2-CP mixed with gold and copper colloids and the Raman spectrum of 2-CP are shown in Figure 3-10. The observed Raman frequencies and tentative assignments

Figure 3-10 Raman spectra of 2-cyanopyridine (2-CP) and SERS of 2-CP adsorbed onto copper (/Cu) and gold (/Au) colloids.

are reported in Table 3-2. The Raman of 2-CP appears more complex than 4-CP and 3-CP due to lower molecular symmetry. The SERS of 2-CP mixed with a copper colloid shows the absence of the 2243 cm^{-1} ($\nu(\text{C}\equiv\text{N})$) band. The nitrile sensitive bands at 1206 cm^{-1} , 779 cm^{-1} , 554 cm^{-1} , 482 cm^{-1} , 364 cm^{-1} , and 175 cm^{-1} disappear in the SER spectrum.²³ The relative shifts of the ring modes to 1594 cm^{-1} , 1563 cm^{-1} , 1475 cm^{-1} and 1011 cm^{-1} from 1587 cm^{-1} , 1573 cm^{-1} , 1469 cm^{-1} , and 1001 cm^{-1} , respectively, all correspond to adsorption occurring via the pyridine nitrogen.⁶ The observation of large positive shifts in the ring modes has been interpreted as being indicative of nitrile bonding.¹⁵ The complexity of the SERS for 2-CP and observed blue shifts would indicate that the bonding of 2-CP when mixed with the copper surface involves coordination via both the pyridine and nitrile nitrogens.³ The complexity of the SERS in comparison with 4- and 3-CP mixed with copper is due to the proximity of the substituent group relative to the metal surface. The SER spectrum shows the appearance of more asymmetric modes which means that the dipole change of these modes are oriented perpendicular to the surface. The overall enhancement factor of the 2-CP is considerably less than observed for 4-CP and 3-CP.

In the SER spectrum of 2-CP adsorbed on a gold colloid, a signal due to $\nu(\text{C}\equiv\text{N})$ is present and shifted 17 cm^{-1} to 2226 cm^{-1} . This suggests that the orientation of the molecule is partially a flat-on orientation due to interaction between the gold surface and both nitrogen adsorption sites.^{15,18} Coordination via the nitrile band should give rise to a signal above that of the parent $\nu(\text{C}\equiv\text{N})$ mode²⁶⁻²⁸ and adsorption via the nitrile nitrogen in a flat-on orientation results in bands lower than the parent $\nu(\text{C}\equiv\text{N})$.^{29,30} The intensity of the nitrile band for 2-CP on the gold colloid is weak with respect to the other primary ring modes present in the SER

spectrum which indicates weak interaction between the nitrile nitrogen and the metal surface. The nitrile sensitive bands undergo shifts in the SERS to 1464 cm^{-1} , 1228 cm^{-1} , 775 cm^{-1} , 546 cm^{-1} , 488 cm^{-1} , and 375 cm^{-1} which are indicative of adsorption via the nitrile nitrogen.²³ Due to the weak conjugation of the nitrile group with respect to the aromatic ring, shifts in the nitrile sensitive bands represent interactions of the cyano group with the surface. The dominant bands in the SERS found at 1613 cm^{-1} ($\nu(\text{CC})$), 1292 cm^{-1} ($\beta(\text{CH})$), 1228 cm^{-1} ($\text{C}\equiv\text{N}$), and 1019 cm^{-1} (ring) are shifted to higher frequencies which are indicative of adsorption via both nitrogens present in the molecule.³

Based on the SERS collected for all three forms of the adsorbates and their respective counterparts, we can report that the reduction is consistent for all forms of cyanopyridine. The Raman frequencies for all three isomers of cyanopyridine with the respective reduction products are reported in Table 3-7. It can be seen that all three isomers produce SERS with the strongest enhanced modes being associated with the symmetric ring modes. The spectral pattern appears to become more complicated as the substituent moves from the 4- to 3- to 2- position on the ring. This is indicative of the symmetry of the molecule and the adsorption occurring primarily through the nitrogen on the ring for 4-CP and 3-CP and through both nitrogens for 2-CP.

Based on the symmetry rules of SERS theory, one would expect that the more symmetric the adsorbate/molecule the greater the SER enhancement observed.^{3,6,9} Consistent with this theory, the adsorption of 4-CP shows greater enhancement than 3-CP, and 3-CP greater than 2-CP. When comparing the cyanopyridines (4-CP to 3-CP to 2-CP) we find an increase in enhancement of antisymmetric modes compared to the symmetric

TABLE 3-7: Raman Frequencies (cm⁻¹) of Cyanopyridines (4-, 3-, and 2-CP) and Aminomethylpyridines (4-, 3-, and 2-AMP) Adsorbed onto Copper (/Cu) Colloids.

Assignment ^a	4-CP/Cu	4-AMP/Cu	3-CP/Cu	3-AMP/Cu	2-CP/Cu	2-AMP/Cu
S	371	-	347	347	-	-
$\gamma(\text{C-NH}_2)$	-	-	414	407	410	412
Ring deformation	500	500	-	491	501	500
$\gamma(\text{NH}_2)$	605	606	620	625	614	611
$\alpha(\text{CCC})$	668	664	644	645	637	639
S	-	-	-	-	-	-
S	-	-	699	698	-	-
$\gamma(\text{CH}), \text{NH}_2$ sens.	-	-	-	-	750	751
$\nu(\text{CC})$	797	796	797	799	-	-
S	-	-	-	-	807	809
$\gamma(\text{CH})$	-	-	820	819	-	-
S	841	841	-	-	-	-
S	-	-	-	-	-	884
$\beta(\text{CH})$	-	-	928	928	-	935
S	-	-	983	980	-	-
Ring breathing	1018	1017	1030	1029	1011	1013
$\beta(\text{NH}_2), \beta(\text{CH})$	1065	1064	1045	1046	1052	1055
S	-	-	1098	1095	-	-
$\beta(\text{CH})$	-	-	-	-	1105	1110
S	-	-	1120	1121	-	-
S	1148	-	-	-	1153	1154

TABLE 3-7: (Continued)

Assignment ^a	4-CP/Cu	4-AMP/Cu	3-CP/Cu	3-AMP/Cu	2-CP/Cu	2-AMP/Cu
$\beta(\text{CH})$	1212	1210	1188	1189	-	-
$\beta(\text{CH}), \alpha(\text{CC})$	1216	1215	1216	1218	-	-
S	-	-	-	-	1235	1235
$\alpha(\text{CC})$	-	-	-	-	1259	1262
S	-	-	-	-	1314	1315
$\beta(\text{CH})$	1339	1340	1334	1336	-	-
S	-	-	-	1386	1383	1388
S	1423	1420	1426	1426	-	-
$\nu(\text{CC})$	-	-	-	-	-	1436
S	-	-	-	-	1475	1478
$\nu(\text{CC})$	1498	1497	1478	1476	-	-
$\nu(\text{CC})$	1552	1552	1581	1578	1563	1565
$\nu(\text{CC})$	1609	1610	1595	1594	1594	1596

a. Based on Ref. 24 and 25.

modes of the molecules. The complexity of the spectra of the 2-CP adsorbed on the metal colloids would indicate possible interactions of both the nitrogens with the surface.

It can be imagined that the relative enhancements might be a function of the distance of the substituent from the metal surface, although if there is a strong electronic “communication” between the amino group and the pyridine ring, one would expect that the distance of the amino group from the surface would not affect the SERS intensity.³¹ Since any distance dependence would reduce the intensity of 4-CP relative to 2-CP, it appears that any distance effects are much weaker than the orientation effects.

3.4 CONCLUSIONS

The SERS collected for the three cyanopyridines adsorbed onto the surface of copper colloids exhibit a complete disappearance of the nitrile stretching normal mode which is due to a metal-assisted reduction of the nitrile group to an amino group. Adsorption of the reduction products (aminomethylpyridines) occurs primarily through the pyridine nitrogen. The SERS of 2-AMP exhibit strong contributions due to the interaction of the amino substituent with the metal surface, thus indicating adsorption via both nitrogens.

The orientation specificity of SER scattering has been demonstrated. The SER spectra for all three isomeric forms of cyanopyridines adsorbed onto copper colloids supports the theory that the normal modes with substantial perpendicular components relative to the surface show the largest enhancement. In addition, the 4-cyanopyridine spectrum shows generally greater surface enhancement than the SERS of 3- and 2-cyanopyridine. Thus, observation of specific SER bands can provide insight into the orientation of the adsorbates

relative to the colloidal surfaces as well as the identity of the molecular moiety that attaches to the surface.

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CHAPTER 4

Other Nitrile Adsorbates on Copper Colloids

4.1 INTRODUCTION

In order to distinguish whether the reduction mechanism is unique for the case of cyanopyridines mixed with copper colloids (as shown in Chapters 2 and 3), other nitrile containing molecules were mixed with both copper and gold colloids. The molecules included in this study are benzonitrile (BN), 1,4-dicyanobenzene (1,4-DCB), acetonitrile (AN) and hexanenitrile (HN) (see Figure 4-1). These molecules were chosen to delineate the importance of two molecular characteristics in the reduction process. These characteristics are the presence of a pyridine moiety and the proximity of the cyano group to the ring. These results will help define the generality of the reduction process in the copper colloidal system.

4.2 EXPERIMENTAL

Colloidal Preparation

The copper and gold colloids were prepared as follows. The preparation of the copper colloids is based on the borohydride reduction of Cu^{2+} as described in Chapter 2.2.¹ The copper colloid, which starts as a pale yellow-brown color becomes a dark reddish-brown indicative of particle sizes ranging from 10 to 20 nm and give rise to an absorption band at 564 nm.³ The copper colloids were allowed to age for two hours prior to adsorption of the organonitriles. The preparation of the gold colloid by citrate reduction is described in

Figure 4-1 Molecular structures for benzonitrile (BN), benzylamine (BA), 1,4-dicyanobenzene (1,4-DCB), xylenediamine (XY), acetonitrile (AN), ethylamine (EA), hexanenitrile (HN) and hexylamine (HA).

Chapter 2.2.² The gold colloid exhibits an absorption band at 523 nm upon aging.³ All colloidal solutions were prepared in disposable borosilicate glass culture tubes with water passed through a Barnstead/Thermolyne (Dubuque, IA) Nanopure Water Model D4541 purification system.

The samples were prepared by adding 0.300 mL of each adsorbate to 3.150 mL of each of the aged colloids. The following adsorbates were used without further purification: benzonitrile (Aldrich chemical Co., Milwaukee, WI; 99.9%), benzylamine (Aldrich; 99%), 1,4-dicyanobenzene (Aldrich; 98%), xylylenediamine (Aldrich; 99%), acetonitrile (Aldrich; 99.9%), ethylamine 97%), hexanenitrile (Aldrich; 98%), and hexylamine (Aldrich; 99%). Data collection of the SER spectra of the organonitriles adsorbed onto the copper colloids was begun 80 minutes after the addition of the adsorbate solution to the colloid.

Data collection parameters are also defined in Chapter 2.2.

4.3 RESULTS AND DISCUSSION

Spectra were collected for all adsorbates on copper and gold colloids, and for the parent compounds and possible reduction products.

Benzonitrile and Benzylamine

The SER spectra obtained when benzonitrile (BN) is mixed with gold and copper colloids and the Raman spectrum of the parent BN are shown in Figure 4-2. The observed wavenumbers and tentative assignments are presented in Table 4-1. Upon mixing with a copper colloid, the $\nu(\text{C}\equiv\text{N})$ disappears, although it is the strongest band in the Raman

Figure 4-2 Raman spectra of neat benzonitrile (BN) and SERS of BN adsorbed onto copper (/Cu) and gold (/Au) colloids.

TABLE 4-1: Raman Frequencies (cm⁻¹) of Neat Benzonitrile (BN) and Neat Benzylamine (BA) and Adsorbed onto Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	BN liquid	BN/Au	BN/Cu	BA/Cu	BA/Au	BA liquid	Assignment ^a
$\gamma(\text{C}\equiv\text{N})$	169	-	-	-	-	-	-
S	-	244	-	-	238	-	-
$\text{C}\equiv\text{N}$ sensitive	378	-	-	-	343	-	-
S	-	-	-	-	399	402	-
$\text{C}\equiv\text{N}$ sensitive	459	439	455	454	-	-	-
S	-	-	-	-	-	484	CH_2NH_2 sensitive
$\text{C}\equiv\text{N}$ sensitive	547	-	-	-	-	-	-
S	-	-	599	604	601	-	-
$\alpha(\text{CCC})$	622	-	-	-	-	621	$\alpha(\text{CCC})$
$\gamma(\text{CH})$	749	-	747	744	-	736	$\gamma(\text{CH})$
$\text{C}\equiv\text{N}$ sensitive	761	-	-	-	-	-	-
Ring	-	-	791	793	803	791	CH_2NH_2 sensitive
S	-	-	-	831	-	-	-
$\gamma(\text{CH})$	927	-	937	-	-	-	-
S	-	-	981	984	983	-	-
Ring breathing	1001	998	1000	997	-	1003	Ring breathing
$\beta(\text{CH})$	1024	1020	1028	1028	-	1030	$\beta(\text{CH})$
$\beta(\text{CH})$	1068	-	-	-	-	-	-
S	1096	-	-	-	-	-	-
$\beta(\text{CH})$, Ring	1178	-	-	-	-	1164	$\beta(\text{CH})$
$\text{C}\equiv\text{N}$ sensitive	1192	-	-	-	-	1186	$\beta(\text{CH})$, Ring

TABLE 4-1: *(Continued)*

Assignment ^a	BN liquid	BN/Au	BN/Cu	BA/Cu	BA/Au	BA liquid	Assignment ^a
S	-	-	1203	1202	1207	1208	$\gamma(\text{CH}_2)$
S	1287	-	-	-	-	-	-
S	1319	-	-	-	-	-	-
S	1335	-	1348	1343	-	-	-
S	1373	-	-	-	1381	-	-
$\nu(\text{CC})$	1448	1449	-	-	1440	-	-
S	-	-	-	-	-	1465	$\nu(\text{CC})$
S	1492	-	-	-	-	-	-
S	-	-	-	-	-	1591	$\nu(\text{CC})$
$\nu(\text{CC})$	1600	1608	1602	1600	1601	1607	$\nu(\text{CC})$
$\nu(\text{C}\equiv\text{N})$	2229	2131	-	-	-	-	-

a. Based on Ref. 4-8.

spectrum of the parent molecule (2229 cm^{-1}). Additionally, the bands 1192 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 761 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 547 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 459 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 378 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), and 169 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive) all disappear.⁴⁻⁷ The strongest bands in the SERS are associated with the symmetric modes of the pyridine ring; 1602 cm^{-1} ($\nu(\text{CC})$) and 1000 cm^{-1} (ring breathing). These modes are also the strongest bands in the Raman spectrum of BN. The appearance of a band at 1203 cm^{-1} ($\gamma(\text{CH}_2)$) indicates that a reduction of the nitrile substituent has occurred. The disappearance of the nitrile band was unexpected based on previous investigations of BN on other metal surfaces⁹⁻¹², but easy to explain based on our recent work.

As noted in Chapter 3, when the nitrile frequency is lower than the free molecule, then the orientation is assumed to be in a flat-on configuration. When the nitrile frequency is higher or near the free molecule, then the orientation is assumed to be in an end-on configuration. The SERS of BN adsorbed onto a gold colloid shows the presence of a nitrile stretching signal at 2131 cm^{-1} . This frequency indicates that adsorption is occurring via the nitrogen on the cyano group in a flat-on configuration.¹³⁻¹⁵ The band at 449 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive) undergoes a shift to a lower frequency, while the ring modes of 1608 cm^{-1} ($\nu(\text{CC})$), 1449 cm^{-1} ($\nu(\text{CC})$), 1020 cm^{-1} ($\beta(\text{CH})$), and 998 cm^{-1} (ring breathing) undergo very little shift.⁴⁻⁸ This would indicate that the interaction occurs between the metal surface and the ring. The relative enhancement of both the symmetric and antisymmetric modes¹⁶, specifically the detection of the SER band at 1449 cm^{-1} ($\nu(\text{CC})$)⁹ indicates that the orientation of the molecule is in a flat-on fashion which is consistent with the lowered $\nu(\text{C}\equiv\text{N})$.

The SERS collected is relatively weak for the adsorption of BN onto both the copper and gold colloids. This is due to the fact that the interaction between the substituent and the metal surface is relatively weak.¹⁷ The gold colloid does not aggregate well upon adsorption of BN. Regardless of the weak aggregation, a nitrile band is still present in the SERS. The copper colloids mixed with BN show weak signs of aggregation (slight color change), and so the relative intensity of the SER bands are greater for copper than for gold.

The SER spectra obtained when benzylamine (BA) and BN are adsorbed onto copper colloids and the Raman spectrum of BA are shown in Figure 4-3. The observed wavenumbers and tentative assignments are presented in Table 4-1. The SERS of BA and BN with copper colloids are identical in spectral pattern and frequencies (within experimental error). In addition, the Raman bands of 1607 cm^{-1} ($\nu(\text{CC})$), 1208 cm^{-1} ($\gamma(\text{CH}_2)$), 1030 cm^{-1} ($\beta(\text{CH})$), and 1003 cm^{-1} (ring) in the spectrum of BA are all shifted to lower frequencies in the SERS relative to the parent molecule.^{4,8} This indicates adsorption via the nitrogen on the amino group with an orientation in a flat-on fashion relative to the metal surface based on the shifts to lower frequencies.

The SERS of BN mixed with a copper colloid demonstrates that a transition metal-assisted borohydride reduction of the nitrile group to an amino group occurs. Therefore, adsorption in a flat-on configuration involving the nitrile interacting with the surface does not hinder the reaction. In addition, a pyridine ring is not essential for the reaction to proceed.

Figure 4-3 Raman spectra of neat benzylamine (BA) and SERS of BA and BN adsorbed onto copper (/Cu) colloids.

1,4-Dicyanobenzene and Xylylenediamine

The SER spectra obtained when 1,4-dicyanobenzene (1,4-DCB) is mixed with gold and copper colloids and the Raman of 1,4-DCB are shown in Figure 4-4. The observed wavenumbers and tentative assignments are presented in Table 4-2. Upon mixing with a copper colloid, the $\nu(\text{C}\equiv\text{N})$ band disappears. In addition, the bands of 1234 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 1211 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 517 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 378 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), and 208 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive) are absent in the SER spectra.¹⁸ The strongest signals in the SERS are associated with the symmetric modes of the aromatic ring: 1613 cm^{-1} ($\nu(\text{CC})$), 1203 cm^{-1} ($\beta(\text{CH})$), 1186 cm^{-1} ($\beta(\text{CH})$, ring), 831 cm^{-1} (ring, $\gamma(\text{CH})$) and 804 cm^{-1} (ring, $\gamma(\text{CH})$). It is interesting to note that the bands at 831 cm^{-1} and 1203 cm^{-1} are correlated with Raman-inactive but infrared-active vibrations. This occurrence has been reported frequently¹⁹⁻²² and has been attributed to a symmetry reduction of the adsorbed molecules.²³⁻²⁵ The disappearance of the nitrile stretching signal would suggest that a reduction of the nitrile groups of 1,4-DCB is occurring.

1,4-DCB transforms according to the D_{2h} point group. The two $-\text{C}\equiv\text{N}$ stretching motions will be classified as symmetric (A_{1g}) and antisymmetric (B_{1g}). Selection rules show that only the A_{1g} mode will be Raman active and so only one band will be observed in the $\nu(\text{C}\equiv\text{N})$ region. If both $-\text{C}\equiv\text{N}$ groups are reduced then no signals are expected in the $\nu(\text{C}\equiv\text{N})$ region. If only one $-\text{C}\equiv\text{N}$ group is reduced then the resultant molecule will possess C_s point group symmetry and a signal due to the remaining $-\text{C}\equiv\text{N}$ group should be observed. The data indicates that both $-\text{C}\equiv\text{N}$ groups are reduced since no signals are observed in the $\nu(\text{C}\equiv\text{N})$ region.

Figure 4-4 Raman spectra of 1,4-dicyanobenzene (1,4-DCB) in aqueous (2.0 M) and SERS of 1,4-DCB adsorbed onto copper (/Cu) and gold (/Au) colloids.

TABLE 4-2: Raman Frequencies (cm⁻¹) of 1,4-Dicyanobenzene (1,4-DCB) (2.0 M) and Xylylenediamine (XY) (2.0 M) and Adsorbed onto Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	1,4-DCB (2.0 M)	1,4-DCB/Au	1,4-DCB/Cu	XY/Cu	XY/Au	XY (2.0 M)	Assignment ^a
$\gamma(\text{C}\equiv\text{N})$	208	234	-	-	239	-	-
S	-	-	313	315	-	-	-
S	-	409	-	-	350	-	-
C $\equiv$ N sensitive	378	-	-	-	-	384	CH ₂ NH ₂ sensitive
S	483	-	-	-	-	-	-
C $\equiv$ N sensitive	517	-	-	-	-	-	-
S	-	-	-	-	577	-	-
S	-	-	-	-	618	-	-
$\alpha(\text{CCC})$	631	629	636	639	-	640	$\alpha(\text{CCC})$
$\gamma(\text{CC})$	701	720	-	-	-	-	-
S	-	796	804	802	804	804	CH ₂ NH ₂ sensitive
Ring, $\gamma(\text{CH})$	811	-	-	-	-	-	-
S	-	-	831	832	829	826	$\nu(\text{C-NH}_2)$
S	-	-	-	-	921	-	-
S	-	-	948	948	955	949	$\gamma(\text{CH})$
S	-	-	977	978	-	-	-
Ring breathing	-	992	-	-	1001	1002	Ring breathing
$\beta(\text{CH})$	-	-	1099	1099	-	1072	$\beta(\text{CH})$, $\beta(\text{NH}_2)$
S	-	1113	1120	-	1114	-	-
S	-	-	1154	1157	-	-	-
$\beta(\text{CH})$, Ring	1173	1177	1186	1186	1190	1185	$\beta(\text{CH})$, Ring

TABLE 4-2: (Continued)

Assignment ^a	1,4-DCB (2.0 M)	1,4-DCB/Au	1,4-DCB/Cu	XY/Cu	XY/Au	XY (2.0 M)	Assignment ^a
S	-	-	1203	1202	1198	1198	$\gamma(\text{CH}_2)$
C $\equiv$ N sensitive	1211	-	-	-	-	-	-
C $\equiv$ N sensitive	1234	-	-	-	-	-	-
S	-	1255	1268	1267	-	1276	CH ₂ NH ₂ sensitive
S	-	1289	-	-	1292	-	-
$\beta(\text{CH})$, $\nu(\text{CC})$	1315	-	-	-	-	-	-
S	-	1346	1340	1343	-	1357	$\gamma(\text{CH}_2)$
S	-	1375	1380	1382	1374	1389	$\beta(\text{CH}_2)$
$\nu(\text{CC})$	1405	-	-	-	-	-	-
$\nu(\text{CC})$	-	1464	-	-	1430	1461	$\nu(\text{CC})$
S	1499	-	-	-	-	1511	-
$\nu(\text{CC})$	1526	1533	-	-	-	-	-
S	-	-	-	-	1565	1578	$\nu(\text{CC})$
$\nu(\text{CC})$	1609	1643	1613	1613	1611	1615	$\nu(\text{CC})$
$\nu(\text{C}\equiv\text{N})$	2234	2246	-	-	-	-	-

a. Based on Ref. 4,5 and 18.

The signals which undergo enhancement are all associated with the symmetric ring modes. The lack of strong signals due to antisymmetric modes indicates that the orientation of the molecule with respect to the colloidal surface permits optimal enhancement of the symmetric modes. This would suggest that the molecule is oriented in an end-on fashion.

A very weak signal for $\nu(\text{C}\equiv\text{N})$ is observed when 1,4-DCB is adsorbed on a gold colloid. The band is blue shifted by 12 cm^{-1} to 2246 cm^{-1} . This shift to a higher frequency is indicative of adsorption via a nitrile nitrogen.^{13,14} Considering the rigidity of the molecular frame of 1,4-DCB, end-on coordination via a nitrogen lone pair would allow only one of the two nitrile groups to interact effectively with the metal. In other SER studies of 1,4-DCB on metal electrodes, two $\nu(\text{C}\equiv\text{N})$ signal were observed; one was due to an end-on coordinated $-\text{C}\equiv\text{N}$ group while the other was due to the free ligand.^{26,27} The observation of a single broad $\nu(\text{C}\equiv\text{N})$ band in the SERS indicates that the two nitrile groups exist in a similar chemical environment on the metal surface. Thus, both of the nitrile groups interact effectively with the surface and the molecular plane lies flat with respect to the surface.

The disappearance of the nitrile stretching signal in the SERS of 1,4-DCB mixed with a copper colloid is due to a transition metal-assisted borohydride reduction described in Chapter 2. In order to verify this reaction, the SERS for the reduction product, xylylenediamine, has been collected.

The SERS collected when xylylenediamine (XY) and 1,4-DCB are mixed with copper colloids and the Raman spectrum of XY are shown in Figure 4-5. The observed wavenumbers and tentative assignments are reported in Table 4-2. The adsorption of both

Figure 4-5 Raman spectra of xylylenediamine (XY) in aqueous (2.0 M) and SERS of XY and 1,4-DCB adsorbed onto copper (/Cu) colloids.

XY and 1,4-DCB mixed with copper colloids generate identical spectra. Additionally, the SERS is very similar to the Raman of the free molecule of XY. The bands 1267 cm^{-1} (CH_2NH_2 sensitive), 832 cm^{-1} ($\nu(\text{C-NH}_2)$), and 802 cm^{-1} (CH_2NH_2 sensitive) all undergo shifts (as seen in Table 4-2) indicative of interactions between the amino group(s) and the metal surface.²⁸ The dominant signals present in the SERS are 1613 cm^{-1} ($\nu(\text{CC})$), 1343 cm^{-1} ($\gamma(\text{CH}_2)$), 1202 cm^{-1} ($\gamma(\text{CH}_2)$), 1186 cm^{-1} ($\beta(\text{CH}_2)$, ring), 832 cm^{-1} ($\nu(\text{C-NH}_2)$), and 802 cm^{-1} (CH_2NH_2 sensitive).^{4,5,18} The observed red-shifts of the modes associated with the aromatic ring indicate adsorption via the amino moiety in a flat-on orientation.¹⁸ The shifts observed for those bands associated with the $-\text{NH}_2$ group indicate an interaction between the amino group and the metal surface. The simplicity of the SERS and the observation of no additional bands associated with the amino group indicate that identical behavior is occurring for both amino substituents. The similarities in the spectra of the parent XY and the SERS of XY adsorbed onto copper colloids indicates attachment on the surface via both of the amino groups in a flat-on configuration.

The SERS of 1,4-DCB mixed with copper colloids demonstrates a transition metal-assisted borohydride reduction of the nitrile groups. The spectra also exhibit characteristics indicative of adsorption via both of the amino groups in a flat-on arrangement with respect to the metal surface.

Acetonitrile and Ethylamine

The SER spectra obtained when acetonitrile (AN) is mixed with gold and copper colloids and the Raman of AN are shown in Figure 4-6. The observed wavenumbers and tentative assignments are presented in Table 4-3. The Raman of AN exhibit strong bands at 2290 cm^{-1} ($\nu(\text{CH}_3)$, $\text{C}\equiv\text{N}$ sensitive), 2252 cm^{-1} ($\nu(\text{C}\equiv\text{N})$), 1375 cm^{-1} ($\nu(\text{CH}_3)$), 919 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), and 376 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive).^{29,30} Upon adsorption to a copper colloid, the SERS of AN shows no $\nu(\text{C}\equiv\text{N})$ signal and very little indication of any SERS. The lack of surface enhancement indicates a weak interaction between the molecule and the metal surface. Due to the lack of SERS observed, it is hard to predict if any reduction of the nitrile group is occurring with this data alone.

A signal for $\nu(\text{C}\equiv\text{N})$ is observed at 2129 cm^{-1} when AN is adsorbed to a gold colloid. This shift to a lower frequency is indicative of adsorption via the nitrile nitrogen in a flat-on orientation.¹³⁻¹⁵ The SERS is relatively weak with bands exhibited at 1613 cm^{-1} , 1292 cm^{-1} , 1019 cm^{-1} , and 450 cm^{-1} . The SERS of AN on gold is very different from the NR of the free molecule. The lack of surface enhancement signifies the weak adsorption of the AN molecules with the gold surface.

Based on the disappearance of the nitrile stretching signal in the SERS of AN mixed with a copper colloid and the weak surface enhancement it is difficult to determine whether a transition metal-assisted borohydride reduction occurs. SERS for the potential reduction product, ethylamine has been collected in order to address this issue.

Figure 4-6 Raman spectra of neat acetonitrile (AN) and SERS of AN adsorbed onto copper (/Cu) and gold (/Au) colloids.

TABLE 4-3: Raman Frequencies (cm^{-1}) of Neat Acetonitrile (AN) and Neat Ethylamine (EA) and Adsorbed onto Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	AN liquid	AN/Au	AN/Cu	EA/Cu	EA/Au	EA liquid	Assignment ^a
S	-	221	-	-	225	-	-
C $\equiv$ N sensitive	376	-	-	-	-	-	-
S	-	-	-	-	-	416	$\beta(\text{C-NH}_2)$
S	-	450	450	-	449	-	-
S	744	-	-	-	-	-	-
S	-	797	-	-	-	-	-
S	-	-	-	-	-	882	$\nu(\text{CC})$
C $\equiv$ N sensitive	919	-	-	-	-	-	-
S	-	-	983	976	986	-	-
S	-	1019	-	-	1010	1004	$\delta(\text{CH}_3)$
$\beta(\text{CH}_3)$	1034	-	-	-	-	1051	NH_2 sensitive
S	-	-	1073	1062	-	1079	NH_2 sensitive
S	-	1226	-	-	-	1129	$\beta(\text{CH}_3)$
S	-	-	-	-	1234	1237	-
S	-	1292	-	-	1290	1298	$\beta(\text{NH}_2), \beta(\text{CH}_2)$
S	-	-	-	-	-	1359	$\beta(\text{CH}_2)$
$\nu(\text{CH}_3)$	1375	1368	-	-	1374	-	-
$\delta(\text{CH}_3)$	1444	-	-	-	-	1455	$\delta(\text{CH}_3)$
S	-	-	-	-	1530	-	$\nu(\text{CC})$
S	-	1613	1610	1610	1610	-	$\nu(\text{CC})$
H ₂ O	-	-	1627	1625	-	-	H ₂ O

TABLE 4-3: *(Continued)*

Assignment ^a	AN liquid	AN/Au	AN/Cu	EA/Cu	EA/Au	EA liquid	Assignment ^a
S	2200	-	-	-	-	-	-
$\nu(\text{C}\equiv\text{N})$	2252	2129	-	-	-	-	-
$\nu(\text{CH}_3), \text{C}\equiv\text{N}$ sens.	2290	-	-	-	-	-	-

a. Based on Ref. 29-32.

The SERS collected for ethylamine (EA) and AN mixed with copper colloids and the Raman spectrum of EA are shown in Figure 4-7. The observed wavenumbers and tentative assignments are reported in Table 4-3. The adsorption of both EA and AN mixed with copper colloids generate very weak SERS. The SERS bands detected are 1625 cm^{-1} (water), 1610 cm^{-1} ($\nu(\text{CC})$), 1062 cm^{-1} (NH_2 sensitive), and 976 cm^{-1} are very similar to the bands that occur in the SERS of AN mixed with copper colloid, namely 1627 cm^{-1} (water), 1610 cm^{-1} ($\nu(\text{CC})$), 1073 cm^{-1} ($\nu(\text{NH}_2)$ sensitive), and 983 cm^{-1} . The subtle differences in the SERS bands for AN and EA mixed with copper colloids indicate that the molecules are similar in nature but oriented in two different configurations onto the copper surface. However, due to the lack of surface enhancement in the SERS, which provides information pertaining to whether a reduction reaction is occurring, we cannot report that a reduction is occurring.

The weak interaction between AN and EA on copper and gold colloids demonstrate that the chemical mechanism plays a dominant role in surface enhancement. Although significant aggregation was observed during the adsorption process, the resulting SERS was weak as a result of the minimal interaction between the substrate and the colloidal surface. Thus, the chemical interaction between the adsorbate and the metal surface limits the observation of the SER effect.

The SERS of AN with both copper and gold colloids indicate that the absence of the aromatic ring limits the ability of the molecule to sufficiently interact with the metal surface.

Figure 4-7 Raman spectra of neat ethylamine (EA) and SERS of EA and AN adsorbed onto copper (/Cu) colloids.

Hexanenitrile and Hexylamine

The SER spectra obtained when hexanenitrile (HN) is mixed with gold and copper colloids and the Raman of HN are shown in Figure 4-8. The observed wavenumbers and tentative assignments are presented in Table 4-4. Upon mixing with a copper colloid, the SERS of HN shows no $\nu(\text{C}\equiv\text{N})$ signal. The Raman of HN exhibit strong Raman bands at 2245 cm^{-1} ($\nu(\text{C}\equiv\text{N})$), 1146 cm^{-1} ($\delta(\text{CH}_2)$), 1307 cm^{-1} , 1114 cm^{-1} , 1068 cm^{-1} ($\beta(\text{CH}_2)$), 831 cm^{-1} , and 368 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive).^{29,30} In the SER spectrum, the nitrile sensitive modes associated with the HN molecule are absent. The strongest bands in the SERS consist of the vibrations associated with the bending motions of the alkyl chain: 1595 cm^{-1} ($\beta(\text{CH}_2)$) and 1004 cm^{-1} ($\beta(\text{CH}_3)$). The nitrile group nitrogen is assumed to be the only point of adsorption onto the copper surface. The absence of the nitrile stretching signal indicates that a reduction of the cyano group to an amino group has occurred.

A signal for $\nu(\text{C}\equiv\text{N})$ at 2130 cm^{-1} is observed when HN is adsorbed to a gold colloid. This shift to a lower frequency is indicative of adsorption via the nitrile nitrogen in a flat-on orientation.¹³⁻¹⁵ The SERS for adsorption onto gold colloids demonstrates stronger surface enhancement which indicates a stronger interaction between HN and the gold surface. The strongest bands observed in the SERS are 1380 cm^{-1} ($\nu(\text{CH}_3)$), 1015 cm^{-1} ($\beta(\text{CH}_3)$), and 247 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive).^{29,30} The shifts in these bands from those observed for the free molecule (see Table 4-4) confirm that the orientation of the HN molecules are flat-on relative to the metal surface with coordination via the nitrile nitrogen.^{15,28}

Figure 4-8 Raman spectra of neat hexanenitrile (HN) and SERS of HN adsorbed onto copper (/Cu) and gold (/Au) colloids.

TABLE 4-4: Raman Frequencies (cm^{-1}) of Neat Hexanenitrile (HN) and Neat Hexylamine (HA) and Adsorbed onto Copper (/Cu) and Gold (/Au) Colloids.

Assignment ^a	HN liquid	HN/Au	HN/Cu	HA/Cu	HA/Au	HA liquid	Assignment ^a
S	183	-	-	-	-	-	-
C≡N sensitive	208	-	-	-	-	-	-
S	-	247	-	-	253	-	-
S	-	-	-	-	-	308	-
S	322	-	-	-	-	-	-
C≡N sensitive	368	-	-	-	-	355	-
S	-	-	-	-	-	400	$\beta(\text{C-NH}_2)$
S	449	449	448	450	450	434	-
S	-	-	-	526	-	499	NH ₂ sensitive
$\delta(\text{CH})$, $\nu(\text{CC})$	555	-	-	-	-	-	-
S	-	600	-	-	-	-	-
S	-	637	628	621	-	-	-
S	766	-	-	-	-	-	-
S	-	806	-	-	810	811	-
S	831	-	-	-	-	848	$\nu(\text{C-NH}_2)$
S	-	-	-	-	-	883	$\delta(\text{CH}_3)$
S	900	-	-	-	-	-	-
S	-	-	-	-	-	917	$\gamma(\text{CH})$
S	930	-	-	-	-	-	-
S	979	-	-	978	-	973	-
$\beta(\text{CH}_3)$	1028	1015	1004	-	1015	1022	$\beta(\text{CH}_2)$

TABLE 4-4: (Continued)

Assignment ^a	HN liquid	HN/Au	HN/Cu	HA/Cu	HA/Au	HA liquid	Assignment ^a
$\beta(\text{CH}_2)$	1068	1035	1062	1066	-	1068	$\beta(\text{CH}_2)$, NH_2 sensitive
S	1114	1119	-	1129	-	1118	$\beta(\text{CH}_2)$
S	-	-	-	-	1151	1169	$\beta(\text{CH}_2)$
S	1196	-	1204	-	-	-	-
$\nu(\text{CH}_2)$	1223	-	-	1217	-	-	-
S	-	1243	-	-	-	-	-
S	1280	-	-	-	-	-	-
S	1307	-	1308	1311	1308	1298	$\beta(\text{NH}_2)$, $\beta(\text{CH}_2)$
S	-	1322	-	-	-	-	-
S	-	-	-	-	-	1349	$\gamma(\text{CH}_2)$
$\nu(\text{CH}_3)$	1372	1380	-	-	1377	-	-
$\delta(\text{CH}_3)$	1446	-	1432	1448	1437	1438	$\delta(\text{CH}_3)$
S	-	1540	-	-	1550	-	-
S	-	1577	-	-	-	-	-
$\beta(\text{CH}_3)$	-	1599	1595	1615	1607	1605	$\nu(\text{CC})$
S	-	-	1633	-	-	-	-
$\nu(\text{C}\equiv\text{N})$	2245	2130	-	-	-	-	-

a. Based on Ref. 29, 30 and 33.

The disappearance of the nitrile stretching signal in the SERS of HN mixed with a copper colloid suggests the nitrile reduction. In order to determine whether a transition metal-assisted borohydride reduction occurs, the SERS for the potential reduction product, hexylamine, has been collected.

The SERS collected when hexylamine (HA) and HN are mixed with copper colloids and the Raman spectrum of HA are shown in Figure 4-9. The observed wavenumbers and tentative assignments are reported in Table 4-4. The adsorption of both HA and HN mixed with copper colloids generates weak SERS. The enhancement of HA is considerably less than that collected for HN with copper colloids. The bands at 1615 cm^{-1} ($\nu(\text{CC})$), 1448 cm^{-1} ($\delta(\text{CH}_2)$), 1066 cm^{-1} ($\beta(\text{CH}_2)$, NH_2 sensitive), and 450 cm^{-1} ($\beta(\text{C-NH}_2)$) are all associated with the amino component of HA.^{29,30,33} The blue shifts in the bands (compared to the parent frequencies) at 1615 cm^{-1} ($\nu(\text{CC})$), 1448 cm^{-1} ($\delta(\text{CH}_3)$), 1311 cm^{-1} ($\beta(\text{CH}_2)$, $\beta(\text{NH}_2)$), 1129 cm^{-1} ($\beta(\text{CH}_2)$), 1066 cm^{-1} ($\beta(\text{CH}_2)$, NH_2 sensitive)), 978 cm^{-1} , 526 cm^{-1} (NH_2 sensitive), and 450 cm^{-1} indicate end-on adsorption to the colloidal surface.^{13-15,28} The SERS bands detected at 1615 cm^{-1} ($\nu(\text{CC})$), 1448 cm^{-1} ($\delta(\text{CH}_3)$), 1311 cm^{-1} ($\beta(\text{CH}_2)$, $\beta(\text{NH}_2)$), 1066 cm^{-1} ($\beta(\text{CH}_2)$, NH_2 sensitive)), 621 cm^{-1} and 450 cm^{-1} are very similar to the bands that occur in the SERS of HN mixed with copper colloid, namely 1595 cm^{-1} ($\nu(\text{CC})$), 1432 cm^{-1} ($\delta(\text{CH}_3)$), 1308 cm^{-1} ($\beta(\text{CH}_2)$, $\beta(\text{NH}_2)$), 1062 cm^{-1} ($\beta(\text{CH}_2)$, NH_2 sensitive), 628 cm^{-1} and 448 cm^{-1} .^{29,30,33} The red shifts in the SERS bands for HN mixed with copper colloids at 1595 cm^{-1} ($\nu(\text{CC})$), 1432 cm^{-1} ($\delta(\text{CH}_3)$), 1308 cm^{-1} ($\beta(\text{CH}_2)$, $\beta(\text{NH}_2)$), 1062 cm^{-1} ($\beta(\text{CH}_2)$, NH_2 sensitive)), and 1004 cm^{-1} ($\beta(\text{CH}_2)$) indicate a flat-on configuration to the metal surface. These subtle

Figure 4-9 Raman spectra of neat hexylamine (HA) and SERS of HA and HN adsorbed onto copper (/Cu) colloids.

differences in the SERS bands for HN and HA mixed with copper colloids and the disappearance of the $\nu(\text{C}\equiv\text{N})$ suggest that the molecules are the same, but oriented in two different configurations on the copper surface. The HN adsorbs onto the copper surface in a flat-on configuration prior to reduction, whereas the HA orients in an end-on fashion.

The SERS of HN and HA mixed with copper colloids demonstrates that a transition metal-assisted borohydride reduction occurs for HN mixed with copper colloids. The weak interaction between HN and HA on copper and gold colloids demonstrates that the chemical mechanism reflects the degree of surface enhancement observed. The differences in the resulting SERS when HN and HA are mixed with copper colloids indicates dissimilar orientations onto the copper surface. This data indicates that an alkyl chain may provide an alternative to a ring system.

4.4 CONCLUSIONS

The SERS collected for organonitriles adsorbed onto the surface of copper colloids exhibit a complete disappearance of the nitrile stretching normal mode. The absence of the nitrile stretching signal for the organonitriles is due to a metal-assisted reduction of the nitrile group to an amino group. Adsorption of alkyl organonitriles onto copper colloids demonstrate weak surface enhancement when compared with SERS of the aromatic organonitriles mixed with a copper colloid. The SERS of the alkyl organonitriles with both copper and gold colloids indicate that the absence of the aromatic ring plays a significant role in the ability of the molecule to sufficiently interact with the metal surface.

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CHAPTER 5

Effects of Colloid Aggregation on the Surface Enhanced Raman Effect

5.1 INTRODUCTION

Aggregation of colloidal particles provides a great deal of insight into the nature and level of surface-enhancement observed during adsorption processes. Since the studies of Faraday¹, the addition of salts to metal sols resulted in color change and this was attributed to the aggregation of what were initially individual particles.² Investigations have utilized the addition of salts to initiate aggregation of metallic colloids.³⁻⁷ Salts may cause aggregation of the metal colloids, may co-adsorb with the adsorbate or may promote desorption of the adsorbates from the metal surfaces. The response of the colloid and the adsorbate to the addition of salts can be used to characterize colloidal self-assembly and adsorbate/surface interactions.⁸

The dependence of the SER enhancement mechanism on the aggregation of colloidal systems has been an issue since the discovery of surface enhancement.⁹⁻¹¹ The response of the system to the addition of salts can provide insight into adsorbate orientation.^{3,12,13} Results that permit a comparison of the electromagnetic (plasmon) enhancement mechanism and the adsorbate/surface chemical interaction mechanism can be obtained. This is due to the fact that the SER effect changes based on the metal/adsorbate interactions during the adsorption process.

Sodium salts were utilized to promote increased aggregation, co-adsorption, and desorption of the adsorbates from the colloidal surfaces. We have investigated the effects of sodium sulfate (aggregation), sodium chloride (co-adsorption), and sodium sulfide (desorption) on mixing of 4-, 3- and 2-cyanopyridines with copper and gold colloids.^{6,7,10} These results will be used to determine if the metal influences the degree of aggregation as well as the amount of enhancement observed.

5.2 EXPERIMENTAL

Colloid Preparation

The preparation of the copper colloids is based on the borohydride reduction of Cu^{2+} as described in Chapter 2.2.¹⁴ All colloidal solutions were prepared in disposable borosilicate glass culture tubes with water passed through a Barnstead/Thermolyne (Dubuque, IA) Nanopure Water Model D4541 purification system. The colloid, which starts as a pale yellow-brown color becomes a dark reddish-brown upon aging. The red color is indicative of particle sizes ranging from 10 to 20 nm and give rise to an absorption band at 564 nm.¹⁵ After the colloid was allowed to age for two hours, an aqueous solution of CP (4-CP, 3-CP, and 2-CP) (Aldrich; 98%; Aldrich; 98%; Aldrich; 99%) (1×10^{-3} M, 0.30 mL) was added. Upon addition of the CP, the colloid changes to a dark grey-brown color due to aggregation and has an absorption band at 570 nm. A band at 296 nm indicative of the adsorbate is also observed. The shifts in the spectra indicate aggregation and molecule-surface interactions in the colloidal system.¹⁶ Data collection of the SER spectra of the cyanopyridines adsorbed

onto the copper colloids was begun 80 minutes after the addition of the adsorbate solution to the colloid.

The preparation of the gold colloid is described in Chapter 2.2.¹⁷ Raman samples were prepared by adding CP (4-CP, 3-CP, and 2-CP) (0.3 mL, 1×10^{-3} M) to 2.7 mL of the gold colloid solution in borosilicate glass culture tubes. The color changed to a dark violet/purple with an absorption maxima at 563 nm indicative of aggregation due to the presence of the adsorbate. The SER spectra were collected starting 80 minutes after the addition of the cyanopyridine.

The colloidal samples of the cyanopyridines were prepared and then 0.03 mL of 0.1 M of sodium salt was added to each sample after SERS (sans salt addition) were collected. The sodium salts utilized for these experiments were sodium sulfate (Aldrich; 99.99%), sodium chloride (Aldrich; 99%), and sodium sulfide (Aldrich; 99.99%). Color changes were observed after each addition of each salt. Raman spectra were collected immediately after salt addition and for intervals up to a week after addition for the gold samples.

Experimental parameters of collection were identical to those described in Section 2.2.

5.3 RESULTS AND DISCUSSION

The SER spectra of the isomeric forms of cyanopyridine (4-CP, 3-CP, and 2-CP) mixed with copper colloids upon addition of the various salts are presented in Figures 5-1, 5-2, and 5-3. In each of these cases, 4-AMP showed the slowest rate of aggregation prior to and after salt addition, whereas 2-AMP showed the fastest rate of aggregation. The color

Figure 5-1 (a) SERS of 4-cyanopyridine (4-CP) adsorbed onto a copper colloid (/Cu), (b) SERS of 4-CP/Cu after the addition of Na_2SO_4 , (c) SERS of 4-CP/Cu after the addition of NaCl , and (d) SERS of 4-CP/Cu after the addition of Na_2S .

Figure 5-2 (a) SERS of 3-cyanopyridine (3-CP) adsorbed onto a copper colloid (/Cu), (b) SERS of 3-CP/Cu after the addition of Na_2SO_4 , (c) SERS of 3-CP/Cu after the addition of NaCl , and (d) SERS of 3-CP/Cu after the addition of Na_2S .

Figure 5-3 (a) SERS of 2-cyanopyridine (2-CP) adsorbed onto a copper colloid (/Cu), (b) SERS of 2-CP/Cu after the addition of Na_2SO_4 , (c) SERS of 2-CP/Cu after the addition of NaCl , and (d) SERS of 2-CP/Cu after the addition of Na_2S .

of copper colloids changed from dark red to a dark brown-grey upon increased aggregation due to salt addition. Despite the indication of additional aggregation and expected increase in the surface-enhancement, the SER spectra were generally identical in intensity and pattern before and after addition of sodium sulfate and sodium chloride for all three isomers. Sodium sulfide removed the adsorbates which resulted in the complete loss of any SER spectra.

Although prior investigations indicate that the addition of sodium sulfate and sodium chloride should increase the degree of surface-enhancement, the copper systems deviate from predicted behavior.^{4,5,12,13} Given the results of the anaerobic experiments involving the copper systems (see Chapters 2 and 3), we can eliminate the possibility that the presence of oxygen facilitates immediate aggregation since no decrease in enhancement was observed in anaerobic conditions.

Although the addition of the SO_4^{2-} or the Cl^- ions causes aggregation and concomitant color change, no additional surface enhancement is observed. This is due to the fact that the copper colloids are prepared via the borohydride reduction of copper (II) sulfate. The colloidal solution contains SO_4^{2-} prior to adsorption of the cyanopyridines. Thus, aggregation of the colloids is manifested prior to the addition of the sodium salts. The lack of enhancement produced by the addition of the Cl^- ions provides information concerning the effects of co-adsorption in copper colloidal systems. The SERS data indicate that co-adsorption of Cl^- ions with the cyanopyridines does not affect aggregation or enhancement of SERS signals for the copper colloidal system.

In order to verify this fact, the SER spectra of 4-AMP adsorbed onto copper colloids prepared by borohydride reduction of Cu^{+1} under conditions of salt addition are reported in

Figure 5-4. The color of the adsorbed 4-AMP adsorbed onto the copper colloid changes from a faint dark red to a dark grey. Despite the indication of additional aggregation and expected increase in the surface-enhancement, the SER spectrum after the addition of the sodium sulfate was less than the original spectrum. This would indicate that aggregation occurs during the adsorption process due to the presence of Cl^- ions during the preparation of the copper colloid. The SER spectrum after the addition of the sodium chloride demonstrate no change in intensity of the spectral pattern or observed frequencies. This would indicate that co-adsorption does not affect the level of enhancement observed in the SERS.

The SER spectra of 4-CP, 3-CP, and 2-CP adsorbed onto gold colloids under conditions of salt addition are reported in Figures 5-5, 5-6, and 5-7. Upon salt addition, a color change indicative of aggregation is observed for all three salts. SER spectra of the cyanopyridines adsorbed onto gold colloids indicate that there is a dependence of the enhancement mechanism on the effects of aggregation and salt co-adsorption upon addition of sodium sulfate and sodium chloride. An increase in enhancement of the SER signal is observed upon addition of these salts. This is in contrast to the results for the copper colloids where SO_4^- was initially present in the colloidal solution. Although there appears to be greater aggregation (darker color change) due to the sodium sulfate, there is a larger enhancement due to the addition of sodium chloride. This would indicate that the co-adsorption of Cl^- contributes more to the enhancement effect than the aggregation caused by SO_4^- . In the case of sodium sulfide, the successful removal of the adsorbates is observed by a complete loss of any SER spectra.

Figure 5-4 (a) SERS of 4-cyanopyridine (4-CP) adsorbed onto a copper colloid (/Cu(I)) prepared by borohydride reduction of Cu^{+1} , (b) SERS of 4-CP/Cu(I) after the addition of Na_2SO_4 , and (c) SERS of 4-CP/Cu(I) after the addition of NaCl.

Figure 5-5 (a) SERS of 4-cyanopyridine (4-CP) adsorbed onto a gold colloid (/Au), (b) SERS of 4-CP/Au after the addition of Na_2SO_4 , (c) SERS of 4-CP/Au after the addition of NaCl , and (d) SERS of 4-CP/Au after the addition of Na_2S .

Figure 5-6 (a) SERS of 3-cyanopyridine (3-CP) adsorbed onto a gold colloid (/Au), (b) SERS of 3-CP/Au after the addition of Na_2SO_4 , (c) SERS of 3-CP/Au after the addition of NaCl , and (d) SERS of 3-CP/Au after the addition of Na_2S .

Figure 5-7 (a) SERS of 2-cyanopyridine (2-CP) adsorbed onto a gold colloid (/Au), (b) SERS of 2-CP/Au after the addition of Na_2SO_4 , (c) SERS of 2-CP/Au after the addition of NaCl , and (d) SERS of 2-CP/Au after the addition of Na_2S .

The effects of aggregation caused by the addition of SO_4^- ions are related to the electromagnetic field mechanism proposed for SERS.^{9,13} This mechanism supposes that as the surface is aggregated and 'roughened' and the particle size and shape leads to a larger enhancement. This is exhibited in the case of all three isomeric forms of aminomethylpyridine adsorbed onto both copper and gold colloids. Although the SERS of the copper systems indicate no signs of increased enhancement, the presence of SO_4^- in the colloidal system (from Cu(II)SO_4) facilitates additional aggregation prior to salt addition.

The co-adsorption of sodium chloride onto the surface of the copper and gold colloids with AMP provides insight into the chemical mechanism of SERS. In the case of copper colloids, the adsorption of Cl^- ions on the metal surface does not promote any additional enhancement compared to that provided by aggregation. This would indicate that the molecule/adsorbate interaction in the case of copper is optimized without the addition of subsequent molecules. However, in the case of the gold colloids this is not true. A greater degree of enhancement is observed upon addition of sodium chloride compared to the addition of sodium sulfate. This would indicate that for gold colloids aggregation is not as effective as both aggregation with Cl^- co-adsorption in increasing the enhancement. The fact that the addition of Cl^- ions promotes additional enhancement indicates that the chemical interaction between the co-adsorbed molecules with the metal surface plays a significant role in the SER effect.

In order to elucidate the effects of Cl^- co-adsorption on the SERS intensity, a series of experiments were performed using 4-CP adsorbed onto a gold colloid with addition of various amounts of NaCl. The resulting SERS are shown in Figure 5-8. Sodium chloride

Figure 5-8 SERS of 4-cyanopyridine (4-CP) adsorbed onto a gold colloid (/Au) with the addition of various concentrations of NaCl: (a) 4-CP/Au with no NaCl, (b) 4-CP/Au with 0.05 M NaCl, (c) 4-CP/Au with 0.1 M NaCl, (d) 4-CP/Au with 0.5 M NaCl, (e) 4-CP/Au with 0.75 M NaCl, (f) 4-CP/Au with 1.0 M NaCl, and (g) 4-CP/Au with 3.0 M NaCl.

was added to gold colloids with adsorbed 4-CP with final NaCl concentrations in the range 0.05 M to 3.0 M. The resulting spectra show an increasing intensity with increasing concentration of sodium chloride added. The integrated intensity of the 1605 cm^{-1} line of 4-CP adsorbed on gold colloids was monitored and was found to increase with the concentration of the sodium chloride added to the sample (see Figure 5-9). This dependence of enhancement on salt concentration supports the importance of chemical interaction in the surface enhancement mechanism. This would indicate that in the case of gold colloids the chemical interaction between the adsorbed molecules and the metal surface dominate over the effects generated by aggregation.

In order to measure the degree of influence that aggregation plays in surface enhancement, similar experiments were performed using 4-CP adsorbed onto a gold colloid with the addition of sodium sulfate. The resulting SERS are shown in Fig. 5-10. The spectra show an increasing intensity with the addition of sodium sulfate with increasing concentrations up to 0.1 M. The addition of sodium sulfates above 0.1 M results in a significant decrease in surface enhancement (see Figure 5-9). This decrease is due to precipitation of the colloid caused by fast aggregation.

Figure 5-9 Dependence of relative integrated intensities of the 1605 cm^{-1} line as a function of concentration of NaCl and Na_2SO_4 in a sample of 4-CP/Au.

Figure 5-10 SERS of 4-cyanopyridine (4-CP) adsorbed onto a gold colloid (/Au) with the addition of various concentrations of Na_2SO_4 : (a) 4-CP/Au with no Na_2SO_4 , (b) 4-CP/Au with 0.05 M Na_2SO_4 , (c) 4-CP/Au with 0.1 M Na_2SO_4 , (d) 4-CP/Au with 0.5 M Na_2SO_4 , (e) 4-CP/Au with 1.0 M Na_2SO_4 , and (f) 4-CP/Au with 3.0 M Na_2SO_4 .

5.4 CONCLUSIONS

The addition of sodium sulfate and sodium chloride appears to have no effect on the SERS enhancement mechanism of 4-, 3-, and 2-aminomethylpyridines (4-AMP, 3-AMP, and 2-AMP) on copper colloids. In the addition of sodium sulfate, aggregation is already promoted by the presence of SO_4^{2-} ions present in the original copper colloid solution. The lack of intensity enhancement upon addition of Cl^- ions indicates that co-adsorption plays no significant role in the degree of enhancement observed in the SERS for these systems.

The addition of sodium sulfate and sodium chloride to gold colloids with adsorbed cyanopyridines leads to an increase in the surface enhancement. The addition of Cl^- ions promotes a larger surface enhancement than produced by the addition of SO_4^{2-} ions. This indicates that the chemical interaction between the adsorbed molecules and the gold surface plays a dominant role in the SER mechanism compared to the plasmon/electromagnetic field mechanism.

The addition of sodium sulfide to both copper and gold colloids successfully desorbs the adsorbates from the metal surfaces resulting in no observable SERS.

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CHAPTER 6

Cyanopyridines Adsorbed onto Silver Colloids

6.1 INTRODUCTION

The surface potential of the different metals in metal colloids affect the contribution of the electromagnetic (EM) and chemical (CM) mechanisms to surface enhancement in SERS. The EM is primarily a characteristic of the colloidal metals and leads to an enhancement that is nearly independent of the adsorbed molecule.¹ The distinguishing features of each type of metallic colloid include the area of contact between the disperse colloidal particles and the dispersion medium, as well as the energy associated with creating and maintaining these interfaces. The CM exploits a resonance in the molecule-metal effective polarizability. This mechanism is sensitive to the presence of “active sites” on the metal and provide details of the molecule-metal bond.¹ The actual charge transfer of the adsorption of organonitriles onto the different metal surfaces and the resulting orientation, symmetry and chemical interaction will dispense understanding as to the contributing influences which generate surface enhancement.

The role of the metal in the amount of SERS observed and relative surface potential for SERS will be determined by the collection of the three isomeric forms of cyanopyridine on silver colloids prepared by borohydride and citrate reduction of AgNO_3 . This data will be compared to that collected on the copper and gold congeners (see Chapters 2 and 3).

6.2 EXPERIMENTAL

The preparation of the citrate reduced silver colloids involves the dissolution of AgNO_3 (Aldrich, 99.99%; 90 mg) in 500 mL of water followed by heating until boiling.² A solution of 1% w/w sodium citrate (Aldrich 99%) (10 mL) was added. Immediately after the addition of the sodium citrate the solution changed to a yellowish brown color (absorption band at 390 nm).³ The solution was maintained at boiling for 2 hours. Raman samples were prepared by adding cyanopyridine (0.3 mL, 1×10^{-3} M (aq.)) to 2.7 mL of the silver colloid solution. The color changed to a grey/green with an absorption maxima at 394 nm indicative of aggregation due to the presence of the adsorbate. The SER spectra were collected starting 80 minutes after the addition of the cyanopyridine in the borosilicate glass culture tube.

The preparation of the borohydride reduced silver colloids involves the dissolution of AgNO_3 (Aldrich, 99.99%; 17 mg) in 100 mL of water.³ A solution of sodium borohydride (Aldrich; 99%; 300 mL of 2×10^{-3} M (aq.)) was added rapidly and the solution stirred vigorously for 2 hours at room temperature. The colloid was allowed to sit for several hours without stirring prior to collection of spectra. Raman samples were prepared by adding cyanopyridine (0.3 mL, 1×10^{-3} M (aq.)) to 2.7 mL of the silver colloid solution in a borosilicate glass culture tube. The SER spectra were collected starting from 80 minutes after addition of the cyanopyridine up to 2 months after addition for aged samples.

6.3 RESULTS AND DISCUSSION

The SER spectra of 4-cyanopyridine (4-CP) adsorbed on each type of silver colloid are presented in Figure 6-1. The vibrational frequencies and tentative assignments are

Figure 6-1 Raman spectra of 4-cyanopyridine (4-CP) and SERS of 4-CP adsorbed onto silver colloids prepared by citrate reduction (Ag_{cit}) and borohydride reduction ($\text{Ag}_{\text{BH}_4^-}$).

TABLE 6-1: Raman Frequencies (cm^{-1}) of 4-Cyanopyridine (4-CP) and Adsorbed on Silver Colloids Prepared by Borohydride Reduction ($\text{Ag}^{\circ}_{\text{BH}_4}$) and Citrate Reduction ($\text{Ag}^{\circ}_{\text{cit}}$) and a Silver Electrode (Ag_{elec}).

Assignment ^a	4-CP (2.0 M)	4-CP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	4-CP/ $\text{Ag}^{\circ}_{\text{cit}}$	4-CP/ Ag_{elec} ^b
$\gamma(\text{C}\equiv\text{N})$	169	-	-	-
S	-	-	211	210
$\text{C}\equiv\text{N}$ sensitive	365	-	383	376
$\text{C}\equiv\text{N}$ sens, $\phi(\text{CC})$	-	390	392	396
$\text{C}\equiv\text{N}$ sensitive	461	483	432	469
$\text{C}\equiv\text{N}$ sens, $\delta(\text{C}\equiv\text{N})$	550	-	520	553
$\phi(\text{CC})$	560	-	-	-
S	-	601	600	-
$\alpha(\text{CCC})$	664	-	-	666
S	-	713	714	-
$\text{C}\equiv\text{N}$ sensitive	776	-	-	785
$\gamma(\text{CH})$	-	-	-	823
S	-	857	853	-
S	-	-	863	-
$\gamma(\text{CH})$	-	-	-	961
ring breathing	1001	1008	1006	1006
$\beta(\text{CH})$	1068	-	1075	1063
S	-	1105	-	-
S	-	-	1133	-
S	-	-	1161	-
$\beta(\text{CH})$	1194	-	-	1191
$\beta(\text{CH}), \alpha(\text{CC})$	-	-	-	1212
$\text{C}\equiv\text{N}$ sensitive	-	1237	1237	1225
S	-	1265	1277	-
$\beta(\text{CH})$	1327	-	1314	-
S	-	1391	1391	1380
S	1412	-	-	-
$\nu(\text{CC}, \text{CN})$	1492	-	1455	1517
$\nu(\text{CC})$	1549	-	1561	1572
$\nu(\text{CC})$	1601	1605	1589	1601
$\nu(\text{C}\equiv\text{N})$	2246	-	-	2238

a. Based on Ref. 4.

b. Based on Ref. 5.

reported in Table 6-1. The SERS of 4-CP adsorbed on silver colloids exhibit no $\nu(\text{C}\equiv\text{N})$ signal. The disappearance of this mode differs from previous studies of cyanopyridines adsorbed on silver electrodes.⁶⁻⁹

The adsorption of 4-CP on the borohydride colloids demonstrates very weak surface enhancement. Even upon sample aging (up to 2 months) with signs of increased aggregation, no increase in enhancement was observed in the SERS. This would indicate a weak interaction between the silver borohydride colloids and the adsorbate molecules.

The SERS of 4-CP adsorbed onto borohydride-based silver colloids do not contain bands due to modes that are sensitive to the nitrile substituent; 2246 cm^{-1} ($\nu(\text{C}\equiv\text{N})$), 1492 cm^{-1} ($\nu(\text{CC}, \text{C}\equiv\text{N})$), 776 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 550 cm^{-1} ($\delta(\text{C}\equiv\text{N})$), 461 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 365 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), and 169 cm^{-1} ($\gamma(\text{C}\equiv\text{N})$).⁴ The bands that were found at 1605 cm^{-1} ($\nu(\text{CC})$), 1008 cm^{-1} (ring), and 390 cm^{-1} ($\text{C}\equiv\text{N}$ sens., $\phi(\text{CC})$) are similar to those found when 4-CP was adsorbed onto a silver electrode.⁷⁻⁹ Adsorption occurs via the nitrogen on the pyridine ring based on previous reports.⁶⁻⁹

The disappearance of the nitrile frequency could suggest a reduction similar to that proposed with the copper colloids. In order to verify adsorption of 4-CP onto silver colloids without nitrile reduction we studied 4-CP adsorbed on citrate-based silver colloids. The study of 4-CP adsorbed on citrate-based colloids would assist in determining whether the presence of borohydride play a significant role in the adsorption process.

The SERS of 4-CP adsorbed onto silver colloids prepared by citrate reduction demonstrate strong surface enhancement. The disappearance of $\nu(\text{C}\equiv\text{N})$ is observed. The bands 1455 cm^{-1} ($\nu(\text{CC}, \text{C}\equiv\text{N})$), 1237 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 520 cm^{-1} ($\delta(\text{C}\equiv\text{N})$), 432 cm^{-1}

(C≡N sensitive), 392 cm^{-1} (C≡N sens., $\phi(\text{CC})$), and 383 cm^{-1} (C≡N sensitive) indicate the presence of a nitrile group with significant shifts in frequency.⁴ The spectral pattern of 4-CP adsorbed on the citrate-based silver colloids is similar to that found for adsorption on a silver electrode with the exception of the missing of $\nu(\text{C}\equiv\text{N})$.^{5,7} The variation between the frequencies of 4-CP adsorbed on citrate-based silver colloids and a silver electrode are due to the potentials applied to the electrode.⁷⁻⁹ Systematic studies of the dependence of the SERS intensity and spectral pattern on the potential applied to a silver electrode have shown that at various potential regions the orientation changed based on the increase or decrease of surface coverage (concentration) of the 4-CP at the electrode surface.^{8,9} The differences in our data with that reported for 4-CP on a silver electrode provide insight into the molecular orientation on the colloidal surface. The shifts to lower frequencies represent a flat-on orientation with adsorption occurring via the nitrogen on the pyridine ring.^{10,11}

The loss of the $\nu(\text{C}\equiv\text{N})$ signal could be due to a few possibilities. First, the conjugation of the nitrile group with the pyridine ring is insignificant and hence $\nu(\text{C}\equiv\text{N})$ simply may not be observed in the SER spectrum. The only bands enhanced in this particular case are those modes associated directly with the pyridine ring. The observation of modes sensitive to the nitrile substituent would still be observed since they are primarily ring modes. Another possibility is that we are observing a different species or resonance form of 4-CP on the silver surface.

In order to determine the role of the nitrile group in the observation of SERS, 3-CP and 2-CP were adsorbed onto each type of silver colloid. The idea is that enhancement of the

nitrile modes occur as the nitrile group gets closer to the metal surface and the point of adsorption (pyridine nitrogen).

The SERS of 3-cyanopyridine on both types of silver colloids are presented in Figure 6-2. The vibrational frequencies and tentative assignments are reported in Table 6-2. The SERS for 3-CP adsorbed on the silver colloids still exhibits no $\nu(\text{C}\equiv\text{N})$ signal.

The SERS of 3-CP on the borohydride-based colloid exhibits slightly better surface enhancement than that observed for adsorption of 4-CP. This would signify a stronger (yet still weak) interaction between the silver borohydride colloids and the adsorbate molecules. This increase in surface enhancement could be provided by possible interaction between the nitrile group and the metal surface.

The SERS of 3-CP on borohydride-based colloids exhibits a complete disappearance of the nitrile stretching signal. The bands 787 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive) and 464 cm^{-1} ($\delta(\text{C}\equiv\text{N})$) indicate the presence of the nitrile substituent.⁴ The bands at 1594 cm^{-1} ($\nu(\text{CC})$), 1391 cm^{-1} ($\beta(\text{CH})$), 1030 cm^{-1} (ring), and 1006 cm^{-1} ($\gamma(\text{CH})$) indicate adsorption via the nitrogen on the pyridine ring based on silver electrode results.^{5,7} The shifts to lower frequencies for the primary ring modes and the appearance of antisymmetric modes suggest a flat-on configuration.^{5,7,10,11}

SERS of 3-CP adsorbed on citrate reduced colloids was also collected (as shown in Figure 6-2). The SERS of 3-CP adsorbed on these silver colloids demonstrate strong surface enhancement. The disappearance of the $\nu(\text{C}\equiv\text{N})$ is observed. The bands at 1455 cm^{-1} ($\nu(\text{CC}, \text{C}\equiv\text{N})$), 392 cm^{-1} ($\phi(\text{CC}), \text{C}\equiv\text{N}$ sens., $\gamma(\text{C}\equiv\text{N})$), and 383 cm^{-1} ($\phi(\text{CC}), \text{C}\equiv\text{N}$ sens., $\gamma(\text{C}\equiv\text{N})$)

Figure 6-2 Raman spectra of 3-cyanopyridine (3-CP) and SERS of 3-CP adsorbed onto silver colloids prepared by citrate reduction (Ag_{cit}) and borohydride reduction ($\text{Ag}_{\text{BH}_4^-}$).

TABLE 6-2: Raman Frequencies (cm^{-1}) of 3-Cyanopyridine (3-CP) and Adsorbed on Silver Colloids Prepared by Borohydride Reduction ($\text{Ag}^{\circ}_{\text{BH}_4}$) and Citrate Reduction ($\text{Ag}^{\circ}_{\text{cit}}$) and a Silver Electrode (Ag_{elec}).

Assignment ^a	3-CP (2.0 M)	3-CP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	3-CP/ $\text{Ag}^{\circ}_{\text{cit}}$	3-CP/ Ag_{elec} ^b
C $\equiv$ N sens, $\delta(\text{CN})$	172	-	-	-
S	-	219	-	208
S	-	-	313	-
$\phi(\text{CC})$, C $\equiv$ N sens, $\gamma(\text{CN})$	360	-	383	360
$\phi(\text{CC})$, C $\equiv$ N sens, $\gamma(\text{CN})$	399	-	392	402
C $\equiv$ N sens, $\delta(\text{CN})$	475	464	-	475
S	-	-	504	-
S	-	-	520	-
$\phi(\text{CC})$, C $\equiv$ N sens, $\gamma(\text{CN})$	554	-	-	548
S	-	-	600	-
$\alpha(\text{CCC})$	635	-	-	641
$\phi(\text{CC})$	-	-	713	696
C $\equiv$ N sensitive	782	787	-	790
S	-	-	853	-
S	-	-	861	-
$\gamma(\text{CH})$	994	1006	1007	960
Ring	1032	1030	-	1030
$\beta(\text{CH})$	1039	-	-	1040
S	1060	-	1076	-
S	-	-	-	1094
$\beta(\text{CH})$	1127	-	1131	-

TABLE 6-2: (Continued)

Assignment ^a	3-CP (2.0 M)	3-CP/Ag [°] _{BH4}	3-CP/Ag [°] _{cit}	3-CP/Ag _{elec}
S	-	-	1158	-
β(CH)	1192	-	-	1192
C≡N sensitive	1216	-	-	1208
α(CC)	1241	-	1239	-
S	-	1267	1278	-
S	-	1299	1299	-
S	-	-	1315	-
β(CH)	1342	-	-	-
β(CH)	-	1391	1392	1380
v(CC, CN)	1423	-	-	1419
v(CC, CN)	1477	-	1455	-
v(CC)	1572	-	1561	1567
v(CC)	1593	1594	1590	1589
v(CN)	2240	-	-	2237

a. Based on Ref. 4.

b. Based on Ref. 5.

indicate the presence of a nitrile group (refer to Table 6-2).⁴ The reduction of the nitrile would be unlikely based on the observed frequencies and since borohydride ions are not present in solution. The strong SERS bands at 1392 cm^{-1} ($\beta(\text{CH})$), 1239 cm^{-1} ($\alpha(\text{CC})$), 1131 cm^{-1} ($\beta(\text{CH})$), 1007 cm^{-1} ($\gamma(\text{CH})$), 713 cm^{-1} ($\phi(\text{CC})$), 392 cm^{-1} ($\phi(\text{CC})$, $\text{C}\equiv\text{N}$ sens., $\gamma(\text{C}\equiv\text{N})$), and 383 cm^{-1} ($\phi(\text{CC})$, $\text{C}\equiv\text{N}$ sens., $\gamma(\text{C}\equiv\text{N})$) indicate adsorption via the pyridine nitrogen in a flat-on configuration.^{5,7,10,11} These frequencies coincide with those of 3-CP adsorbed onto a silver electrode (with the exception of the absence of $\nu(\text{C}\equiv\text{N})$) supporting a flat-on orientation.

It is interesting to note that the spectral pattern of 3-CP adsorbed on the citrate-based colloids is almost identical to that found of 4-CP adsorbed on citrate-based silver colloids. This could be due to two possibilities. First, the binding and orientation of the two different isomers is identical in nature and independent of the $-\text{C}\equiv\text{N}$ group and this leads to similar SERS. Another probability is that we are observing interfering species or co-adsorption of citrate on the silver surface.¹²⁻¹⁵ The collection of 2-CP on these silver colloids would provide a complete insight as to whether we are observing either of these possibilities due to isomeric differences in the CP molecules.

The SERS of 2-cyanopyridine on both types of silver colloids are presented in Figure 6-3. The vibrational frequencies and tentative assignments are reported in Table 6-3. The SERS of 2-CP adsorbed on the silver colloids contain no $\nu(\text{C}\equiv\text{N})$ signal. This would indicate that for all three isomeric forms of cyanopyridine, the binding and orientation of the molecules onto the silver surfaces prevent detection of the nitrile group.

The adsorption of 2-CP on the borohydride-based silver colloids demonstrates

Figure 6-3 Raman spectra of 2-cyanopyridine (2-CP) and SERS of 2-CP adsorbed onto silver colloids prepared by citrate reduction (Ag_{cit}) and borohydride reduction ($\text{Ag}_{\text{BH}_4^-}$).

TABLE 6-3: Raman Frequencies (cm^{-1}) of 2-Cyanopyridine (2-CP) and Adsorbed on Silver Colloids Prepared by Borohydride Reduction ($\text{Ag}^{\circ}_{\text{BH}_4}$) and Citrate Reduction ($\text{Ag}^{\circ}_{\text{cit}}$) and a Silver Electrode (Ag_{elec}).

Assignment ^a	2-CP (2.0 M)	2-CP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	2-CP/ $\text{Ag}^{\circ}_{\text{cit}}$	2-CP/ Ag_{elec} ^b
C $\equiv$ N sens, $\delta(\text{CN})$	175	-	-	-
S	-	-	209	220
C $\equiv$ N sensitive	-	-	-	334
$\phi(\text{CC})$, C $\equiv$ N sens, $\gamma(\text{CN})$	364	-	381	-
S	-	-	394	-
S	402	-	408	-
S	-	-	433	440
C $\equiv$ N sensitive	-	-	-	468
C $\equiv$ N sens, $\delta(\text{CN})$	482	486	-	496
S	-	-	-	515
C $\equiv$ N sens, $\delta(\text{CN})$	554	-	-	551
S	-	600	600	-
$\alpha(\text{CCC})$	636	-	635	658
$\phi(\text{CC})$	-	-	670	689
S	-	-	704	-
S	-	713	713	-
S	741	-	752	740
C $\equiv$ N sensitive	779	-	-	-
S	-	-	825	-
C $\equiv$ N sensitive	-	856	842	856
S	-	-	927	-
S	-	-	978	-
Ring	1001	1006	1012	1017

TABLE 6-3:

(Continued)

Assignment ^a	2-CP (2.0 M)	2-CP/Ag [°] _{BH4}	2-CP/Ag [°] _{cit}	2-CP/Ag _{elec}
β(CH)	-	-	1031	1042
β(CH)	1048	-	1051	1050
β(CH)	1095	-	1091	1098
S	-	-	1110	-
S	-	1132	1132	-
β(CH)	1161	-	1168	1157
β(CH)	-	-	-	1179
C≡N sensitive	1206	-	-	1203
S	1234	1237	1231	-
α(CC)	1258	-	1257	1254
S	-	-	1277	-
β(CH)	1295	-	1299	1282
β(CH)	-	-	-	1354
β(CH)	-	1395	1381	1397
S	-	-	1403	-
v(CC,CN)	1437	-	1439	-
v(CC,CN)	1469	-	1475	1475
S	-	-	1539	-
v(CC)	1573	-	1574	1560
v(CC)	1587	-	1594	1595
v(CC)	-	-	-	1611
v(C≡N)	2243	-	-	2255

a. Based on Ref. 4.

b. Based on Ref. 5.

comparable surface enhancement to that observed of the adsorption of 4-CP. This would indicate similar interaction between each of these cyanopyridines and the borohydride colloids. This weak surface enhancement suggests that possible interaction between both nitrogens of 2-CP and the metal surface does not generate surface enhancement greater than that observed for 4-CP and 3-CP adsorbed on these silver colloids. Therefore, observation of weak surface enhancement for all three isomers indicates weak interactions between the CP's and the borohydride-based silver colloids.

The SERS of 2-CP on borohydride-based silver colloids exhibits a complete disappearance of the nitrile stretching signal (refer to Figure 6-3 and Table 6-3). The bands at 1237 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 856 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), 486 cm^{-1} $\text{C}\equiv\text{N}$ sens., $\delta(\text{C}\equiv\text{N})$) indicate the presence of the nitrile substituent.⁴ The shift to higher frequencies in the SERS indicates adsorption via both the nitrile nitrogen and the pyridine nitrogen, in similar fashion to the adsorption of 2-CP onto a silver electrode in an end-on configuration.^{5,7,10,11}

It is interesting to note that the spectral pattern of 2-CP adsorbed on the borohydride-based silver colloids is almost identical to that found of 4-CP adsorbed onto borohydride colloids. This would suggest that the binding and orientation of the two different isomers is identical in nature and results in similar SERS. It is not possible that we are observing an interference or co-adsorption of borohydride on the silver since borohydride would give rise to bands at 610 cm^{-1} and 920 cm^{-1} with no observation of SERS.¹⁴

The adsorption of 2-CP on silver colloids prepared by citrate reduction exhibit SERS with no indication of $\nu(\text{C}\equiv\text{N})$. The bands at 1475 cm^{-1} ($\nu(\text{CC}, \text{C}\equiv\text{N})$), 1439 cm^{-1} ($\nu(\text{CC}, \text{C}\equiv\text{N})$), 842 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), and 381 cm^{-1} ($\phi(\text{CC}), \text{C}\equiv\text{N}$ sens., $\gamma(\text{C}\equiv\text{N})$) signify the

presence of a nitrile group.⁴ The strongest SERS bands at 1594 cm^{-1} ($\nu(\text{CC})$), 1574 cm^{-1} ($\nu(\text{CC})$), 1439 cm^{-1} ($\nu(\text{CC}, \text{C}\equiv\text{N})$), 1381 cm^{-1} ($\beta(\text{CH})$), 1168 cm^{-1} ($\beta(\text{CH})$), 1051 cm^{-1} ($\beta(\text{CH})$), 1381 cm^{-1} ($\beta(\text{CH})$), 1012 cm^{-1} (ring), 842 cm^{-1} ($\text{C}\equiv\text{N}$ sensitive), and 635 cm^{-1} ($\alpha(\text{CCC})$) indicate adsorption via both the pyridine and nitrile nitrogens in an end-on configuration.^{5,7,10,11} These frequencies correspond to those of 2-CP adsorbed onto a silver electrode (with the exception of the absence of $\nu(\text{C}\equiv\text{N})$) indicating an end-on orientation.

The spectral pattern of 2-CP adsorbed on the citrate-based silver colloids is clearly different than that found of either 3-CP or 4-CP adsorbed on citrate-based silver colloids. This suggests that the binding and the orientation of 2-CP upon adsorption is different from the other isomeric forms of cyanopyridine. The SER spectra of 4-CP and 3-CP support adsorption via the nitrogen on the aromatic ring with a flat-on configuration relative to the metal surface.^{5,7,10,11} The SERS of 2-CP exhibit Raman bands associated with adsorption via both the pyridine and nitrile nitrogens in an end-on fashion.^{5,7,10,11}

The similarity in the SERS of 4-CP and 3-CP adsorbed on citrate-based silver colloids could be attributed to an interference or co-adsorption of citrate on the silver surface.¹²⁻¹⁵ The SER scattering by citrate on colloidal silver is shown in Figure 6-4. The Raman frequencies and tentative assignments are presented in Table 6-4. The spectral pattern and the reported frequencies are different than those for the three isomeric forms of cyanopyridine adsorbed onto the citrate-based silver colloids. The bands at 1396 cm^{-1} ($\nu_{\text{as}}(\text{COO}^-)$), 1147 cm^{-1} ($\nu_{\text{as}}(\text{C}_4\text{O})$), 1025 cm^{-1} ($\nu_{\text{s}}(\text{C}-\text{C})$), 948 cm^{-1} ($\nu_{\text{s}}(\text{C}-\text{C})$), 835 cm^{-1} ($\nu_{\text{as}}(\text{C}_4\text{O})$), and 799 cm^{-1} ($\nu_{\text{s}}(\text{C}_4\text{O})$) indicate adsorption of the citrate onto the colloidal surface.^{12,15} There appears to be no similarity between these spectral pattern or frequencies

Figure 6-4 SER scattering by trisodium citrate (CIT) in aqueous solution (2.0 M) and adsorbed on colloidal silver surfaces (/Ag).

TABLE 6-4: Raman Frequencies (cm^{-1}) of Trisodium Citrate (CIT) in Aqueous Solution (2.0 M) and Adsorbed onto Silver Colloids.

Assignment ^a	CIT (2.0 M)	CIT/Ag
$\nu(\text{Ag-O})$	-	217
$\nu(\text{Ag-O})$	-	289
$\rho(\text{COO}^-)$	398	397
S	550	-
$\pi(\text{COO}^-)$	-	597
$\delta(\text{COC})$	-	674
$\nu_s(\text{CCO}^-)$	-	735
S	765	-
$\nu_s(\text{C}_4\text{O}), \nu_{\text{as}}(\text{C}_4\text{O})$	801	799
$\nu_s(\text{C}_4\text{O})$	839	836
$\nu_s(\text{C}_4\text{O})$	909	902
$\nu_s(\text{C-C})$	951	950
$\nu_s(\text{C-C})$	-	1024
$\nu_s(\text{CCO})$	1039	-
$\nu_{\text{as}}(\text{CCO})$	1087	1091
$\nu_{\text{as}}(\text{CCO})$	-	1143
S	1210	1203
S	1254	-
S	1304	1298
$\nu_s(\text{CCO}^-)$	1414	1396
S	-	1483

a. Based on Ref. 12 and 15.

with those collected for the cyanopyridines. Thus, the observed surface enhancement is not due to an interference or co-adsorption of the citrate ions on the silver surface.

In order to facilitate comparison, the SERS of the three isomers on silver colloids prepared by borohydride and citrate reduction are shown in Figures 6-5 and 6-6. The tabulated Raman frequencies and tentative assignments are shown in Table 6-5. The common characteristic of all the SER spectra is the absence of the $\nu(\text{C}\equiv\text{N})$ stretching signal. The observation of nitrile sensitive Raman signals with shifts in frequency signify the presence of the nitrile substituent. The adsorption of the cyanopyridines on the silver surfaces occur primarily through the nitrogen on the pyridine ring, although the SERS of 2-CP contains Raman bands that indicate an additional interaction between the nitrile nitrogen and the metal surface. The SERS suggests that the molecular orientation of 4-CP and 3-CP are a flat-on configuration, while the 2-CP orients in an end-on fashion. The possibility of interferences or co-adsorption by borohydride or citrate ions are excluded based on the absence of Raman bands indicative of each species in previous reports.^{13,14} The enhanced Raman bands coincide with previous reports of these molecules on silver electrodes.^{5,7,10,11} Thus, the only remaining issue is the absence of the nitrile stretching signal of each isomer.

Based on the disappearance of the nitrile stretching signal in the SERS of the CP's adsorbed on the silver colloids, and the weak display of surface enhancement for the borohydride colloids, it is enigmatic to conclude whether a transition metal-assisted borohydride reduction is occurring. In order to determine if this reaction takes place, the SERS for the potential reduction product, aminomethylpyridine, has been collected.

Figure 6-5 SERS of cyanopyridines (4-, 3-, and 2-CP) adsorbed onto silver ($\text{Ag}_{\text{BH}_4^-}$) colloids prepared by borohydride reduction.

Figure 6-6 SERS of cyanopyridines (4-, 3-, and 2-CP) adsorbed onto silver (/Ag_{cit}) colloids prepared by citrate reduction.

TABLE 6-5: Raman Frequencies (cm^{-1}) of Cyanopyridines (4-, 3-, and 2-CP) Adsorbed on Silver Colloids Prepared by Borohydride Reduction ($/\text{Ag}^{\circ}_{\text{BH}_4}$) and Citrate Reduction ($/\text{Ag}^{\circ}_{\text{cit}}$).

Assignment ^a	4-CP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	3-CP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	2-CP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	4-CP/ $\text{Ag}^{\circ}_{\text{cit}}$	3-CP/ $\text{Ag}^{\circ}_{\text{cit}}$	2-CP/ $\text{Ag}^{\circ}_{\text{cit}}$
S	-	219	-	211	-	209
S	-	-	-	-	313	-
C $\equiv$ N sensitive	-	-	-	383	383	381
C $\equiv$ N sens, $\phi(\text{CC})$	390	-	-	392	392	394
S	-	-	-	-	-	408
S	-	-	-	432	-	433
C $\equiv$ N sensitive	483	464	486	-	-	-
S	-	-	-	-	504	-
S	-	-	-	520	520	-
S	601	-	600	600	600	600
$\alpha(\text{CCC})$	-	-	-	-	-	635
$\phi(\text{CC})$	-	-	-	-	-	670
S	-	-	-	-	-	704
$\phi(\text{CC})$	713	-	713	714	713	713
S	-	-	-	-	-	752
C $\equiv$ N sensitive	-	787	-	-	-	-
S	-	-	-	-	-	825
C $\equiv$ N sensitive	857	-	856	853	853	842
S	-	-	-	863	861	-
S	-	-	-	-	-	927
S	-	-	-	-	-	978

TABLE 6-5: (Continued)

Assignment ^a	4-CP/Ag [°] _{BH4}	3-CP/Ag [°] _{BH4}	2-CP/Ag [°] _{BH4}	4-CP/Ag [°] _{cit}	3-CP/Ag [°] _{cit}	2-CP/Ag [°] _{cit}
Ring	1008	1006	1006	1006	1007	1012
β(CH)	-	1030	-	1075	1076	1031
β(CH)	-	-	-	-	-	1051
β(CH)	-	-	-	-	-	1091
S	1105	-	-	-	-	1110
S	-	-	1132	1133	1131	1132
β(CH)	-	-	-	1161	1158	1168
C≡N sensitive	1237	-	1237	1237	1239	1231
S	-	-	-	-	-	1257
α(CC)	1265	1267	-	1277	1278	1277
β(CH)	-	1299	-	1301	1299	1299
S	-	-	-	1314	1315	-
S	1391	1391	1395	1391	1392	1381
S	-	-	-	-	-	1403
ν(CC,CN)	-	-	-	1455	1455	1439
ν(CC,CN)	-	-	-	-	-	1475
S	-	-	-	-	-	1539
ν(CC)	-	-	-	1561	1561	1574
ν(CC)	1605	1594	-	1589	1590	1594

a. Based on Ref. 4.

SERS for the isomeric forms of aminomethylpyridine (4-AMP, 3-AMP, and 2-AMP) on silver colloids prepared by borohydride and citrate reduction is shown in Figures 6-7 and 6-8. The tabulated Raman frequencies and tentative assignments are shown in Table 6-6. The SERS for the AMP's exhibit different spectral patterns and frequencies than those observed for the CP's on the same types of silver surfaces. This shows conclusively that reduction of the nitrile group in the isomers of CP is not occurring on the silver colloids.

The SERS of the AMP's on borohydride reduced silver colloids demonstrate an increase in surface enhancement from 4-AMP to 2-AMP. This observation is opposite to that observed for adsorption of these molecules on copper and gold colloids (see Chapters 2 and 3). This would indicate that the interaction between the 2-AMP and the borohydride-based silver colloid is significantly stronger than 4-AMP.

The SERS of AMP's on citrate-based silver colloids display strong surface enhancement. The complexity of the SER spectra increase in the series of 4- to 3- to 2-position. This coincides with previously reported SERS for isomeric forms of CP on silver electrodes which display modes associated with the antisymmetric vibrations of the molecule.^{5,7,10,11}

It is interesting to note that the SERS for 4-AMP and 3-AMP adsorbed on citrate-based silver colloids demonstrate similar spectral patterns. This could be attributed to an interference or co-adsorption of citrate on the silver surface. The SERS bands detected for 4-AMP/3-AMP adsorbed on these silver colloids at $1397\text{ cm}^{-1}/1391\text{ cm}^{-1}$, $844\text{ cm}^{-1}/835\text{ cm}^{-1}$, and $804\text{ cm}^{-1}/801\text{ cm}^{-1}$ ($\nu(\text{CC})$)^{5,16} are very similar to the bands that occur in the SERS of

Figure 6-7 SERS of aminomethylpyridines (4-AMP and 2-AMP) adsorbed onto silver ($\text{Ag}_{\text{BH}_4^-}$) colloids prepared by borohydride reduction.

Figure 6-8 SERS of aminomethylpyridines (4-, 3-, and 2-AMP) adsorbed onto silver (Ag_{cit}) colloids prepared by citrate reduction.

TABLE 6-6: Raman Frequencies (cm^{-1}) of Aminomethylpyridines (4-, 3-, and 2-AMP) Adsorbed on Silver Colloids Prepared by Borohydride Reduction ($/\text{Ag}^{\circ}_{\text{BH}_4}$) and Citrate Reduction ($/\text{Ag}^{\circ}_{\text{cit}}$).

Assignment ^a	4-AMP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	4-AMP/ $\text{Ag}^{\circ}_{\text{cit}}$	3-AMP/ $\text{Ag}^{\circ}_{\text{cit}}$	2-AMP/ $\text{Ag}^{\circ}_{\text{BH}_4}$	2-AMP/ $\text{Ag}^{\circ}_{\text{cit}}$
$\nu(\text{Ag-N})$	-	214	221	233	213
S	-	-	-	-	381
S	-	393	-	-	393
S	-	-	409	411	414
S	-	-	-	-	460
Ring deformation	482	488	-	500	-
S	-	-	-	527	528
S	-	-	-	-	580
$\gamma(\text{NH}_2)$	-	592	-	-	600
$\gamma(\text{NH}_2)$	-	615	-	613	-
$\alpha(\text{CCC})$	-	-	624	633	632
S	-	-	-	655	-
S	-	666	-	-	-
S	-	-	707	-	701
S	-	-	-	-	713
$\nu(\text{CH})$	-	746	-	746	-
S	-	-	-	768	777
$\nu(\text{CH})$	798	804	801	-	814
S	831	844	834	825	-
S	-	-	-	855	852
$\beta(\text{CH})$	-	877	-	-	-
S	-	-	-	906	906
S	-	-	-	929	-
S	-	983	1001	995	-
Ring breathing	1007	1002	1033	1006	1004

TABLE 6-6: (Continued)

Assignment ^a	4-AMP/Ag [°] _{BH4}	4-AMP/Ag [°] _{cit}	3-AMP/Ag [°] _{cit}	2-AMP/Ag [°] _{BH4}	2-AMP/Ag [°] _{cit}
S	-	1015	-	-	1022
β(NH ₂), β(CH)	-	1069	1050	1056	1058
S	1100	1097	1104	1106	-
S	-	-	-	1115	-
S	-	-	-	-	1133
β(CH)	-	-	-	1157	-
S	-	-	-	-	1170
β(CH)	-	1212	1197	1212	1196
β(NH ₂), β(CH)	-	-	1230	1232	1239
α(CC)	1267	1269	1268	1270	1279
S	-	1310	-	-	1317
S	-	1331	-	-	1334
S	-	1352	1360	-	1349
S	1393	1397	1391	1390	1392
S	-	1426	-	-	-
v(CC)	-	-	1448	1440	1446
v(CC)	-	1463	1481	1476	1475
S	-	-	-	-	1496
S	-	1531	1522	1533	-
v(CC)	-	1555	-	1569	1578
v(CC)	-	-	1581	1594	-
v(CC)	1612	1614	1600	1607	-
S	-	-	1624	1626	-

a. Based on Ref. 5,16.

citrate mixed with a silver colloid, namely 1396 cm^{-1} ($\nu_{\text{as}}(\text{COO}^-)$), 835 cm^{-1} ($\nu_{\text{as}}(\text{C}_4\text{O})$), and 799 cm^{-1} ($\nu_{\text{s}}(\text{C}_4\text{O})$).^{12,15} Therefore, SERS collected for the AMP's adsorbed on the citrate-based silver colloids show bands that could indicate of co-adsorption of citrate on the silver surface.

The reduction of the nitrile substituent to an amino group upon adsorption of the cyanopyridines onto the silver colloids does not occur. The observation of no nitrile stretching band for the citrate reduced silver colloids indicates that the silver metal is distinct from the copper and gold. The silver colloid experiments complicate the matter and further investigation needs to be performed to elucidate the nature of the cyanopyridine-silver colloid interactions.

6.4 CONCLUSIONS

The SERS collected for cyanopyridines (4-CP, 3-CP, and 2-CP) adsorbed onto the surface of silver colloids prepared by borohydride and citrate reduction exhibit a complete disappearance of the nitrile stretching normal mode. The absence of the nitrile stretching signal is not due to a metal-assisted reduction of the nitrile group to an amino group. Adsorption on borohydride-based silver colloids demonstrate weak surface enhancement when compared with SERS of adsorption on citrate-based silver colloid. The observation of no nitrile stretching band for the silver colloids indicates that the silver metal is distinct from the copper and gold. The silver colloids require further investigations in order to elucidate the nature of the SERS collected.

The SER spectra of each of the three isomeric forms of cyanopyridine adsorbed onto copper, gold and silver colloids are shown in Figures 6-9, 6-10, and 6-11. The gold colloids demonstrate “ideal” behavior with adsorption via the pyridine nitrogen in an end-on configuration. The copper colloids demonstrate a transition metal-assisted borohydride reduction of the nitrile substituent to an amino group with primary interaction occurring through the pyridine nitrogen in a flat-on orientation. The silver colloids demonstrate no reduction of the nitrile substituent to an amino group with no observed $\nu(\text{C}\equiv\text{N})$.

All three metal colloids display SER signals indicative of adsorption primarily through the pyridine nitrogen. Interaction between both the nitrile and pyridine nitrogens with the colloidal surfaces are observed in the SERS for 2-CP. Previous studies would indicate that the degree of surface enhancement would be increasing in the series of copper to gold to silver.^{17,18} Our SERS data concurs with prior results with the exception of borohydride-based silver colloids.

The isomeric effects on enhancement observed for adsorption onto the three metals obey anticipated behavior except in the case of silver. The aggregation of the adsorbates on all three metals increases from 4-CP to 3-CP to 2-CP. The loss of molecular symmetry as the substituent is moved from the 4- to 3- to 2- position also plays a role in the degree of surface enhancement observed.⁷⁻⁹ Our data for the CP's mixed with the copper and gold colloids supports the theory that the degree of surface enhancement is lowered by the loss of molecular symmetry.

Figure 6-9 SERS of 4-cyanopyridine (4-CP) adsorbed onto silver (Ag_{cit}), copper (Cu), and gold (Au) colloids.

Figure 6-10 SERS of 3-cyanopyridine (3-CP) adsorbed onto silver (/Ag_{cit}), copper (/Cu), and gold (/Au) colloids.

Figure 6-11 SERS of 2-cyanopyridine (2-CP) adsorbed onto silver (/Ag_{cit}), copper (/Cu), and gold (/Au) colloids.

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CHAPTER 7

Conclusions

Dramatic differences are observed between the SER spectrum of 4-CP mixed with a copper colloid, the spectrum of 4-CP, and the spectrum of 4-CP on a gold colloid. Specifically, $\nu(\text{C}\equiv\text{N})$ is missing in the spectrum involving the copper colloid. 4-CP- ^{15}N was prepared and the SER spectra collected. Data for that isotopic species indicates that $\nu(\text{C}\equiv\text{N})$ is not coupled with the ring modes and hence shifted to lower wavenumbers when 4-CP is mixed with copper colloids. The data are adequately explained by a transition metal assisted borohydride reduction of 4-CP to 4-AMP. SER spectra of these molecules and their reduction products in the presence of copper colloids are identical within experimental error. The $\nu(\text{C}\equiv\text{N})$ signal was observed when a gold colloid was prepared by borohydride reduction, thereby indicating the metal selectivity of the reaction.

SER spectra for two additional isomers of cyanopyridine (3-CP, and 2-CP) adsorbed onto the surface of copper colloids also exhibit a loss of the nitrile stretching band. Based on studies of the corresponding reduced molecules (3-AMP, and 2-AMP) adsorbed onto copper colloids, the SERS verifies the transition metal-assisted reduction of the nitrile group with the subsequent products being adsorbed on the copper surfaces.

The SERS collected for other organonitriles adsorbed onto the surface of a copper colloids exhibit a complete disappearance of the nitrile stretching normal mode in most cases. The absence of the nitrile stretching signal for the organonitriles is due to a metal-assisted

reduction of the nitrile group to an amino group. Adsorption of alkyl organonitriles onto copper colloids demonstrate weak surface enhancement when compared with SERS of the aromatic organonitriles mixed with a copper colloid. The SERS of the alkyl organonitriles with both copper and gold colloids indicate that the absence of the aromatic ring plays a significant role in the ability of the molecule to sufficiently interact with the metal surface.

The addition of selected salts (sodium chloride, sodium sulfate, sodium sulfide) was used to explore the effect of aggregation, co-adsorption, and desorption of the adsorbates on the observed SERS. This work demonstrates the roles of the chemical and electromagnetic field mechanism in the observation of surface enhancement. For the case of the copper colloids, the use of aggregation and co-adsorption played no significant role in the degree of surface enhancement detected. For the SERS of the cyanopyridines adsorbed onto the gold colloids, the co-adsorption of sodium chloride made a stronger contribution than sodium sulfate. Thus, the role of chemical interaction dominates over the electromagnetic mechanism in the observation of surface enhancement for our systems. The addition of sodium sulfide to both copper and gold colloids successfully desorbs the adsorbates from the metal surfaces indicated by no observable SERS.

The surface potential of the different metals in metal colloids reflect the contributions of the possible mechanisms giving rise to the Raman enhancement. The argument concerning the origin of the surface enhancement mechanism is based on the dominant roles of chemical and electromagnetic field interactions at the metal surface. Our SERS data demonstrate that the increase in surface enhancement is primarily influenced by the chemical interaction between the adsorbate and the metal surface. Although the molecular symmetry of the

adsorbate, as well as the affects of aggregation, affect the degree of enhancement, the chemical adsorption onto the metal dominates the enhancement mechanism.

The potential use of this reduction reaction can be of utmost significance in the modification of surfaces in the fields of self-assembly and colloidal chemistry. Additionally, the significance of molecule-surface interactions provides insight into energy-related issues, such as field stable chemical probes, deleterious corrosion processes, and catalysis.

VITA

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