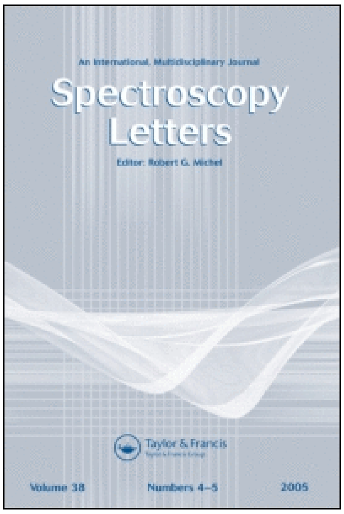

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Surface Enhanced Raman Spectroscopy - Vibrational Spectroscopy of Adsorbates at the Metal-Electrolyte Interface

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SURFACE ENHANCED RAMAN SPECTROSCOPY--VIBRATIONAL SPECTROSCOPY OF ADSORBATES AT THE METAL-ELECTROLYTE INTERFACE

Key Words: Surface Enhanced Raman Spectroscopy,
Vibrational Spectroscopy at Interfaces,
Pyridine and Cyanide Adsorption on Cu, Ag, and Au

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ABSTRACT

Surface enhanced Raman spectroscopy has been used to study the adsorption of pyridine and cyanide on Cu, Ag, and Au electrodes. The Raman spectra for pyridine on these three substrates closely resembled each other, and the Raman peaks exhibited small shifts from the corresponding peaks in an aqueous pyridine solution. The low frequency vibrational modes in the region 200-250 cm^{-1} are attributed to the metal-pyridine stretches, namely, ν[Cu-N(pyridine)] = 241 cm^{-1}, ν[Ag-N(pyridine)] = 237 cm^{-1}, and ν[Au-N(pyridine)] = 232 cm^{-1}. The energies of the metal-pyridine stretches were quite insensitive to the kind of substrate the molecule was on. We report also the surface enhanced Raman scattering from cyanide adsorbed on Au. The CN stretching frequency was at 2109 cm^{-1}, which was attributed to that of the adsorbed $Au(CN)_2^-$ complex. In addition, three low frequency modes were observed at 88, 228, and 325 cm^{-1}. Cyanide adsorption on Cu and Ag electrodes was also investigated. For the Cu/cyanide system, Raman shifts at 175, 312, 434, and 2089 cm^{-1} were observed. They are due to the presence of the complex ions, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. For the Ag/cyanide system, Raman shifts at 143, 218, 303, and 2104 cm^{-1} were observed. They are due to the presence of $Ag(CN)_3^{2-}$ complex.

1. INTRODUCTION

Surfaces play a crucial role in many chemical processes, ranging from corrosion to catalysis. In recent years intense research activities have been devoted to the fundamental studies of surface and interfacial phenomena.[1-9] Physicists and chemists have made important contributions in developing and applying physical methods to the study of surface interactions, particularly at the solid-gas (vacuum) interface. The interactions at the solid-liquid interface, in which electrochemical reactions occur, have not been well understood comparatively. This is partly because most of the surface sensitive techniques--such as Auger electron spectroscopy (AES), ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS), secondary ion mass spectrometry (SIMS), low energy electron diffraction (LEED), and high resolution electron energy loss spectroscopy (EELS)--require ultra high vacuum environments, thus precluding in situ characterization of the electrode surfaces during electrochemical reactions.

The solid-liquid interface refers to the very thin boundary where the solid and the liquid are in contact. This thin boundary is in the order of a few angstroms. The solid could be a metal, a semiconductor or an insulator, the liquid could be an aqueous electrolyte, a nonaqueous solvent or a molten electrolyte. In this study we are primarily concerned with the metal-aqueous electrolyte interface.

A particularly interesting and intriguing aspect of the solid-liquid interface is the presence of high electric fields (field strength $\sim 10^7$ V cm^{-1}) and large surface charges. Electrochemistry is concerned with chemical reactions which involve transfer of electric charge at the interface. Thus, the solid-liquid interface exerts great influence on many electrochemical processes. Given the important role played by the interface in electrochemistry, a better understanding of it is both necessary and essential.[10-12] However, information pertaining to the electronic and surface properties of electrode materials, the chemical identity, the structure and orientation of the adsorbed species or reaction intermediates sometimes cannot be easily obtained by traditional electrochemical methods. Thus optical characterization becomes a necessity.[13] There are some drawbacks for the *ex situ* optical characterization techniques, mainly because of the potential structural changes, contamination and oxidation of electrode surfaces during the transfer between the electrochemical and high vacuum environments.[10] *In situ* optical characterization techniques are superior in these aspects. Some of the most useful techniques are: (1) electroreflectance,[14-16] (2) ellipsometry,[17-20] (3) photoemission-into-electrolyte,[21-24] (4) photoacoustic spectroscopy and photothermal spectroscopy[25-30] (5) infrared spectroscopy[31-33] and (6) Raman spectroscopy.[34,35] Of the six *in situ* optical techniques listed, only the infrared and Raman spectroscopies are capable of providing direct and detailed information such as the structure, the orientation and the nature of the chemisorption bonding on the surface species. *In situ* infrared studies have been carried out using the multiple internal reflection technique and infrared transparent electrode substrate, but have not yielded much information concerning surface adsorbed species. Water absorption and sensitivity have been serious problems.[8]

In surface Raman spectroscopy, one measures the inelastic collisions of the incident photons with the adsorbed surface species or reaction products on the surface. The energy difference between the incident and scattered radiation corresponds to a molecular transition of the surface species. The vibrational transition provides the most useful information on the adsorbed species. Vibrations of the surface species on incidence of electromagnetic radiation give rise to characteristic frequencies that serve as fingerprints for the identification of surface species.

Although water absorption is not a problem, the normal surface Raman still suffers from low sensitivity. Nontheless, useful information has been obtained on the surface corrosion products of Pb[36-38] in electrochemical environments using the normal surface Raman technique. The low sensitivity of the normal surface Raman scattering is primarily due to the weak interaction between the surface species and the incident radiation that is usually used.[34] Scattering processes such as resonance Raman and coherent anti-Stokes Raman (CAR) will increase the Raman scattering efficiency by several orders of magnitude. We do not discuss these processes here. Instead, we describe a new Raman scattering process, known as Surface Enhanced Raman Scattering (SERS). We will demonstrate that SERS can be very useful in the study of surface processes at the metal-electrolyte interface. Specifically, we use Surface Enhanced Raman Spectroscopy to study the adsorption of pyridine and cyanide on Cu, Ag, and Au electrodes. A brief overview of Surface Enhanced Raman Spectroscopy is given below.

2. SURFACE ENHANCED RAMAN SCATTERING (SERS)

Surface enhanced Raman scattering is a process in which the Raman scattering intensity by molecules adsorbed on microscopically rough metal surfaces is enhanced by factors of 10^4-10^6 compared to the intensity expected for nonadsorbed species at the same concentration. Such enormous enhancements totally overcome the traditional low sensitivity problem associated with the normal Raman scattering process, thus enabling researchers to characterize *in situ* the chemical identity, structure and orientation of surface species in an electrochemical environment without much difficulty.

In 1974, Fleischmann, Hendra, and their coworkers[39] first demonstrated surface Raman of pyridine on a silver electrode which has been electrochemically processed to increase the surface area. However, the surface enhancement effect was not realized until 1977, in the work of Jeanmaire and Van Duyne,[40] Albrecht and Creighton.[41] They independently repeated the experiment and reported that the Raman signal for the adsorbed molecule ($\frac{d\sigma}{d\Omega} = 10^{-23}$ cm^2/steradian-molecule) was many times more intense than the Raman signal due to the solution pyridine at the same concentration level ($\frac{d\sigma}{d\Omega} = 10^{-29}$ cm^2/steradian-molecule). This increase in intensity, an enhancement of 10^6 (also known as the "Giant Raman Effect"[35]) cannot simply be due to the surface area increase after the electrochemical treatment. We will not dwell on the theoretical aspects because this anomalously intense Raman signal is still a matter of considerable discussion and dispute. An excellent review of various theories has been provided.[42]

Only the Group IB elements, namely, Cu, Ag, and Au have shown unambiguous SERS. Numberous molecules and ions have been reported to show SERS effects on these metals under potentiostatic conditions (see TABLE 1). Most studies were done on Ag electrode and a few on Cu and Au electrodes. Other metals such as Pt[43-45], Ni[45-47], and Hg[48,49] also appear to show SERS. Recently, Sanchez et al.[50] have confirmed that Hg exhibits SERS. Surface Enhanced Raman scattering has also been observed from pyridine adsorbed on a Cd electrode.[51] In addition to the metal-electrolyte interface, the SERS effects have also been

TABLE 1

Molecules and Ions That Show SERS Eeffects on Cu, Ag, and Au Electrodes Under Potentiostatic Controls

Substrate	Adsorbate	Reference
1. Cu	pyridine	52-55,118, this work
	cyanide	56, this work
	halides	57,58
	H_2O	59
	benzotriazole	57,60
2. Ag	pyridine	39-41,61
	cyanide	62-66
	SCN^-	67,68
	pyrazine	69
	2,6-lutidine	70
	N-heterocycles, amines	40
	isoquinoline	71
	methyl-pyridines	72
	azide ions	73
	cobalt phthalocyanine	74
	nucleic acid components	75
	p-NDHA	76
	carbon, hydrocarbon	77,78
	cyano-pyridines	79
	OH^-/OD^-, halides	58,80-83
	EDTA(di-Na), nitrate	121
	N-heptyl-viologen	122
3. Au	pyridine	53,55, this work
	cyanide	this work
	halides	57

TABLE 2

Environments in Which the SERS Effect Has Been Observed

Environment	Adsorbate/Substrate	Reference
1. Electrode-electrolyte interface	(see Table 1)	
2. Metal-vacuum, -air interface	pyridine/Ag	85-90
	CN/Ag	90-94
	CO/Ag	95
	ethylene, propylene/Ag	96
	C/Ag	97
	4-pyridine-carboxylic acid/Ag, Au	98,99
	benzoic Acid/Ag, Au	98
	fluorescein, isothiocyanate/Ag, Au	98
	4-nitro-, 4-amino-benzoic acids/Ag	99
	polystyrene/Ag	100
	CN/Cu	101
	CO/Ni	47
	butenes/Ag	102
	benzene/Ag	103
	pyridine, benzene, cyclohexande/Hg	49
3. Metal-insulator-metal tunnel junctions (Raman + inelastic electron tunneling spectroscopy)	4-pyridine-carboxylic acid	104,105
	4-pyridine carboxaldehyde	104,105
	4-amino-benzoic acid	104,105
	4-acetyl-benzoic acid	104,105
	p-nitrobenzoic acid	106
	poly(p-nitro-styrene)	106
4. Colloidal suspensions, precipitates	pyridine/Ag, Au	107,108,112
	halides/Ag, Au	108
	formate, acetate/Ag	109,110
	citrate/Ag	111
	benzene/Ag	112
	acetonitrile/Ag	112
	N, N'-dimethyl-aniline/Ag	112
	biliverdine, pyrromethenone/Ag	113
	$Au(CN)_2^-$	114

observed in different environments. The results are summarized in TABLE 2.

Serveral characteristics are associated with SERS, and they are:

(1) The appearance of the low frequency vibrational mode(s) which is (are) absent in the Raman spectra of nonadsorbed solution species.

(2) The appearance of a broad luminescence continuum background.

(3) The depolarization of the SER signals.

(4) The deviation of ω^4 law that holds for normal Raman scattering.

(5) Voltage dependence of the SER signals in electrochemical systems.

3. EXPERIMENTAL

The experimental set up for the in situ Raman experiments consisted of an electrochemical cell and a laser Raman spectrometer with the necessary detection system. The electrochemical cell consisted of a working electrode, a Pt counter electrode, and a saturated calomel reference electrode (SCE). The working electrode was either Cu, Ag, or Au. The Cu, Ag, and Au electrodes were polished successively with 1.0, 0.3, and 0.5 μm Al_2O_3 abrasives. Before the experiments, the Cu electrode was lightly etched with a dilute solution of HNO_3; the Ag electrode was etched with $H_2O_2:NH_4OH = 1:1$ solution; the Au electrode was treated with chromic acid. These electrodes were then thoroughly rinsed with triply distilled water before they were transferred into the electrochemical cell. In the pyridine experiments, the solution was 0.1 M KCl + 0.05 M pyridine. In the cyanide experiments, the solution was 0.1 M KCl + 0.01 M KCN. All potentials are reported with respect to SCE. All solutions were made with reagent grade chemicals and deoxygenated with nitrogen.

Spectra were obtained with a Spex 1402 double monochromator or with a Jarrel-Ash 25-400 Raman spectrometer. Either the 647.1 nm line or the 676.4 nm line of a Kr^+ laser (Spectra Physics 171) was used as the excitation source. The laser power used was typically 100 mW. The angle of incidence of the exciting light was 70°. The detection system consisted of a cooled photomultiplier tube (RCA C31034A) and a standard photon counting system.

4. RESULTS AND DISCUSSION

(A) Pyridine Adsorption on Cu, Ag, and Au

Since the first report of a Raman signal from pyridine on a Ag electrode in an electrochemical environment,[39] the Ag/pyridine experiment has been repeated numerous times.[34,35] On the other hand, Cu/pyridine and Au/pyridine systems have not been well studied. We present here some new results on these two systems. The Ag/pyridine experiment was repeated in order to provide a comparison with the Cu/pyridine and Au/pyridine systems under similar experimental conditions.

Figure 1 Shows the surface enhanced Raman (SER) spectra for pyridine adsorbed on Cu, Ag, and Au electrodes at −0.8 V, −0.7 V, and −0.6 V, respectively, using the 676.4 nm red line of a Kr^+ laser. The spectra were obtained after the electrodes had undergone oxidation-reduction cycles. For Cu, the oxidation potential was 0.2 V vs SCE; for Ag, it was 0.2 V; for Au, it was 1.0 V. No SER spectra could be obtained for pyridine on Cu and Au substrates when using 488 or 514.5 nm line of an Ar^+ laser. This is in agreement with earlier results.[53,54] With 676.4 nm excitation, the enhancement factor for Au was one order of magnitude smaller than that for Cu, whereas the enhancement factors for Cu and Ag were comparable.

The frequency shifts and the assignments of the major Raman peaks for pyridine on Cu, Ag, and Au in the range 100-1600 cm^{-1} are tabulated in TABLE 3, along with those for 2.54 M aqueous pyridine.[40]

An interesting feature in the SER spectra was the appearance of low frequency modes, in the region 200 to 250 cm^{-1}, which were absent in the Raman spectrum of solution pyridine. We assigned these modes to the metal-pyridine

TABLE 3

Vibrational Frequencies (cm^{-1}) for Pyridine

Aqueous Solution	Cu(−0.8 V)	Ag(−0.8 V)	Au(−0.6 V)	Assignment*
			232 s	Au-N stretch
		237 s		Ag-N stretch
	241 s			Cu-N stretch
655	638 s	636 s	643 m	ν_{6b}
1005	1009 vs	1010 vs	1009 vs	ν_1
1037	1036 vw	1036 w	1036 vw	ν_{12}
1221	1214 m	1212 m	1205 vw	ν_{9a}
1598	1589 w	1592 s	1598 m	

*L. Corrsin, B. J. Fax, and R. C. Lord, J. Chem. Phys 21, 1170 (1953).

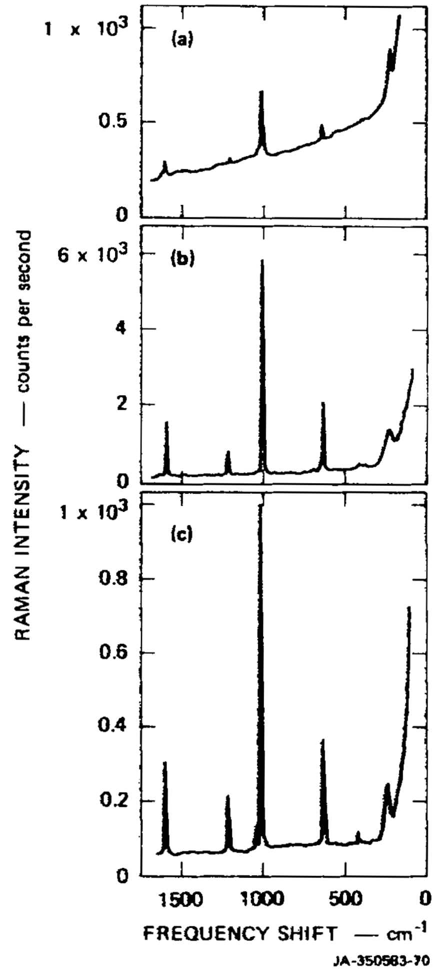

FIGURE 1 SURFACE ENHANCED RAMAN SPECTRA FOR PYRIDINE MOLECULE ADSORBED ON (a) Au ELECTRODE AT -0.6 V VERSUS SCE; (b) Cu ELECTRODE AT -0.8 V; (c) Ag ELECTRODE AT -0.7 V

The electrolyte was 0.1 M KCl + 50 mM pyridine. The excitation source was the 676.4 nm line of a Kr ion laser.

vibrations.[115] The bonding between the pyridine molecule and the metal substrate was through the nitrogen lone-pair electrons to the empty orbitals (5s or 4d) of the metal atoms on the surface. The Au-N(pyridine) stretch was 241 cm^{-1}; the Ag-N(pyridine) stretch, 237 cm^{-1}; the Au-N(pyridine) stretch, 232 cm^{-1}. We note that the ratio ν[Cu-N(pyridine)]/ν[Ag-N(pyridine)] was 1.02. A similar result was found from the SER spectra of benzotriazole on Cu and Ag electrodes;[57] the ratio ν[Cu-N(benzotriazole)]/ν[Ag-N(benzotriazole)] = 224 cm^{-1}/242 cm^{-1} = 1.01. These results are in a marked contrast to those for halides on Cu and Ag. For Ag,[58] ν(Ag-Cl) = 246 cm^{-1} , ν(Ag-Br) = 166 cm^{-1}, ν(Ag-I) = 117 cm^{-1}; for Cu,[57] ν(Cu-Cl) = 297 cm^{-1}, ν(Cu-Br) = 204 cm^{-1}, ν(Cu-I) = 147 cm^{-1}. The ratios, ν(Cu-Cl)/ν(Ag-Cl) = 1.21, ν(Cu-Br)/ν(Ag-Br) = 1.23, and ν(Cu-I)/ν(Ag-I) =1.26, are comparable to the value $(m_{Ag}/m_{Cu})^{1/2}$ = 1.30.

For halides on Cu and Ag, one can readily invoke the role of ad-atoms.[66,28,110,116,117] In this model the low frequency vibrational modes are very sensitive to the masses of the ad-atoms to which the molecules are bonded, since only a single metal atom and not the bulk metal is involved in the bonding. We observed that, in the case of Cl^-, Br^-, and I^-, the frequency shifts in the prominent peak positions were roughly proportional to the square root of the mass ratios of the surface ad-atoms (Cu and Ag). On the other hand, the small frequency shifts in the low frequency modes for pyridine and benzotriazole on different metal substrates implied that the role of ad-atoms might not be important in these cases.

The Raman peaks for pyridine on Cu, Ag, and Au substrates exhibited small shifts from the corresponding peaks in an aqueous solution containing 2.54 M pyridine.[40] This showed that the substrates exerted very small distortion on the pyridine molecule. Additionally, the energies of the vibrational modes for pyridine were quite insensitive to the kind of substrate the molecule was on.

All the major peaks in the region 100-1600 cm^{-1} for the Ag/pyridine/Cl^- system with a red excitation, except the 636 cm^{-1} line, showed small shifts from their counterparts with a green excitation.[40] A line at 623 cm^{-1} in lieu of the 636 $cm^{-1}$was observed with a green excitation. Similar observations were also noted by others.[55,118] Corresponding lines at 638 and

643 cm^{-1} were observed for the Cu/pyridine/Cl^- and Au/pyridine/Cl^- systems, respectively. We correlate these lines with the 655 cm^{-1} mode(ν_{6b}) in the Raman spectrum of 2.54 M pyridine solution. The 623 cm^{-1} line was correlated with the 618 cm^{-1} mode.[40]

The observed frequencies (241, 638, 1009, 1036, 1214, and 1589 cm^{-1}) for the Cu/pyridine/Cl^- system agreed reasonably well with those (233, 630, 1008, 1038, 1213, and 1594 cm^{-1}) reported by Temperini et al.[118] One feature needed to be mentioned here and it concerns the characteristic ring breathing modes. Allen et al., found them to be at 1015 and 1037 cm^{-1} for an anodized Cu electrode, and at 1008 and 1038 cm^{-1} for an unanodized Cu electrode.[54] This result is different from our's (1009 and 1036 cm^{-1}) and Temperini's (1008 and 1038 cm^{-1}) for anodized Cu electrodes. It is interesting to note that the 1015 cm^{-1} band was observed on a Cu electrode which was covered with passivation layers as a result of anodic polarization.[52]

The frequencies for the prominent peaks in the region 100-1600 cm^{-1} for the Au/pyridine/Cl^- systems were 232, 643, 1009, 1036, 1205 and 1598 cm^{-1}. The Au/pyridine/Cl^- system was not well investigated, only two line frequencies (1015 and 1040 cm^{-1}) were reported previously.[53,55] Since Au does not support the enhancement with 514.5 nm excitation, no comparison can be made with regard to the frequency shifts due to the green and red excitations.

The SER signals were voltage dependent, which indicates the Raman signals were due to the adsorbed species. The intensity of the ring breathing mode of pyridine, corresponding to the 1005 cm^{-1} of 2.54 M aqueous pyridine, on Cu, Ag, and Au electrodes as a function of the applied potential is shown in Figure 2. The potential at which the maximum SER intensity was attained did not correspond to the potential of zero charge (pzc), the potential at which the charge on the electrode is zero. The potentials of zero charge for pollycrystalline Cu, Ag, and Au are -0.21, -0.94, and -0.01 V vs SCE, respectively.[119,120] The absence in the pzc correlations and the presence of

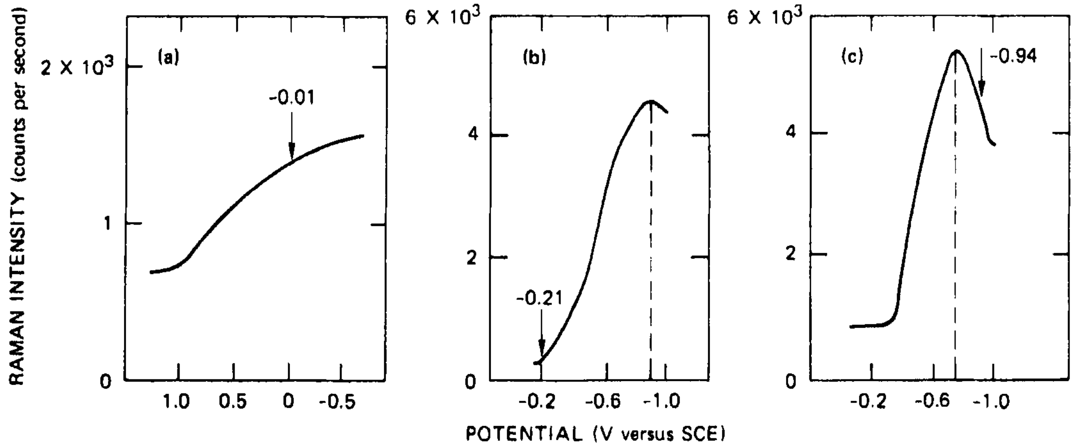

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FIGURE 2 SER INTENSITY OF THE RING BREATHING MODE (corresponding to the 1005 cm^{-1} band of 2.54 M aqueous pyridine) DUE TO ADSORBED PYRIDINE ON (a) Au ELECTRODE, (b) Cu ELECTRODE; AND (c) Ag ELECTRODE AS A FUNCTION OF APPLIED POTENTIAL

The arrows indicate the potentials of zero charge. The electrolyte was 0.1 M KCl + 50 mM pyridine. The excitation source was the 676.4 nm line of a Kr ion laser, and the laser power was 100 mW. The bandpass was 17 cm^{-1}. The electrode potential was scanned cathodically at a rate of 0.1 V min^{-1}.

the low frequency modes, the metal-N(pyridine) stretches, clearly indicate the occurrence of chemisorption rather than physisorption.

(B) Cyanide Adsorption on Cu, Ag, and Au

Cyanide adsorption on a Ag electrode has been well studied.[39-41,61] However, only one study has been made on the cyanide adsorption on a Cu electrode,[56] and no report has been made on the cyanide adsorption on a Au electrode. We report here the CN stretching frequency due to cyanide adsorption on a Au electrode. Comparisons were made with those due to cyanide adsorption on Cu and Ag electrodes, obtained under similar experimental conditions. In addition, we report the low vibrational frequency modes for all three systems, which have not been reported before.

The CN stretches for cyanide on Cu, Ag, and Au are tabulated in TABLE 4, together with their assignments and the observed half widths. For Cu, the CN stretch was at 2089 cm^{-1}; for Ag, 2104 cm^{-1}; for Au, 2109 cm^{-1}. The half width for the CN stretch on Cu substrate is twice the half width for the CN stretch on Ag, and the half width for the CN stretch on Ag substrate is about twice the half width for the CN stretch on Au. It is known that for Group IB elements, the heavier element forms a stronger bond.[123] This trend probably can be correlated with the observed half widths of the CN stretches on these three substrates; the larger the natural line width, the shorter the lifetime of the vibrationally excited state.[124]

Figure 3 shows the SER spectrum for cyanide adsorbed on a Au electrode at -0.7 V (SCE), using the 676.4 nm line of a Kr^+ laser as the excitation source. The Au electrode was first anodized at 1.0 V in an electrolyte containing 0.1 M KCl + 0.01 M KCN. In addition to the CN stretching mode, three low frequency modes were observed at 83, 228, and 325 cm^{-1}. Again, no Raman signals can be obtained with the 514.5 nm or the 488 nm line of an Ar^+ laser.

There are three commonly known gold cyanides, namely AuCN, $Au(CN)_2^-$ and $Au(CN)_4^{3-}$. Infrared studies[125] showed that the CN stretching frequency for AuCN was at 2261 cm^{-1}, and the Raman studies showed those for $Au(CN)_2^-$ and

TABLE 4

Vibrational Frequencies for CN Stretches of Cyanide Complexes on Au, Ag, and Cu Electrodes

Substrate	CN Stretch	Half Width	Assignments
Au	2109 cm^{-1}	17 cm^{-1}	$Au(CN)_2^-$
Ag	2104	40	$Ag(CN)_3^{2-}$
Cu	2089	80	$Cu(CN)_3^{2-}$ + $Cu(CN)_4^{3-}$

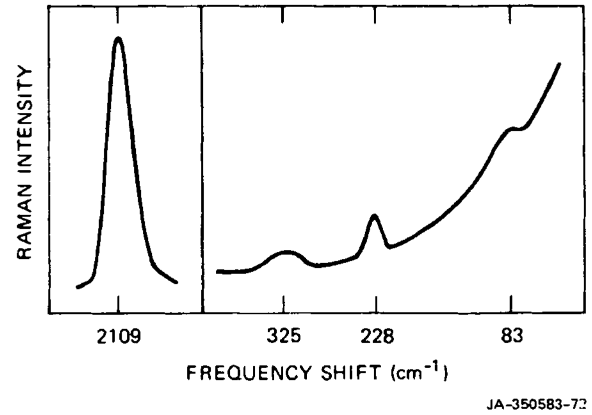

FIGURE 3 SURFACE ENHANCED RAMAN SPECTRUM FOR CYANIDE ADSORBED ON GOLD ELECTRODE AT -0.7 V VERSUS SCE

The electrolyte was 0.1 M KCl + 0.01 M KCN, and the excitation source was the 676.4 nm line of a Kr ion laser.

$Au(CN)_4^{3-}$ were at 2164 and 2207 cm^{-1}, respectively.[126,127] The $Au(CN)_4^-$ complex is known to be unstable with respect to $Au(CN)_2^-$. $Au(CN)_2^-$ is the only complex anion of gold(I), and the stability of which forms the basis for the cyanide process for the extraction of gold. AuCN is formed on the gold electrode surface before the dissolution of gold occurs in cyanide solution as $Au(CN)_2^-$.[128,129] Thus the most likely species on the Au electrode that give the enhanced Raman signals is AuCN or $Au(CN)_2^-$. Based on the frequency shift of the observed CN stretch and the appearance of more than one low frequency vibrational mode, we believe the SERS signal is due to the $Au(CN)_2^-$ complex adsorbed on the Au electrode. Even though $Au(CN)_2^-$ was formed at low overpotentials,[128,129] we did not detect any enhanced Raman signal before the Au electrode had undergone an oxidation-reduction cycle.

The big red shift in frequency (55 cm^{-1}) from the reported value probably indicates the weakening of the CN bond.[130] This is probably caused by a stronger interaction between the gold substrate and the adsorbed gold cyanide complex resulting in a stronger Au-C π bond. A smaller red shift (26 cm^{-1}) was also found by van Raben et al.,[144] for $Au(CN)_2^-$ ions adsorbed on Au colloids. They observed the CN stretching frequency at 2138 cm^{-1}.

The cyclic voltammogram of a Au electrode in 0.1 M KCl + 0.01 M KCN solution is shown in Figure 4, and the Raman intensity of the 2109 cm^{-1} band as a function of the applied potential is shown in Figure 5. The Au electrode was first anodized at 1.0 V. The Raman intensity-voltage curve clearly reveals several things on the surface dynamics: (1) surface coverages of $Au(CN)_2^-$ on the Au electrode were different for the cathodic and the anodic scans, (2) cathodic deposition of $Au(CN)_2^-$ on the Au electrode occurred at about -0.7 V, (4) on the anodic scan the $Au(CN)_2^-$ complex was formed at low overpotentials (~ -0.8 V), which provided a spectroscopic confirmation for earlier electrochemical results,[128,129] (5) anodic dissolution of the Au electrode as $Au(CN)_2^-$ solution species started at about -0.2 V, which was marked by the onset of the decrease in the Raman signal at this potential. Thus the anodic peak in the cyclic voltammogram centered at about 0.05 V was due to the dissolution of the Au electrode as $Au(CN)_2^-$.

In cyanide solutions, copper forms complexes $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$, and the Raman studies showed the CN stretches for these complexes in aqueous solution to be at 2106, 2094, and 2079 cm^{-1}, respectively.[131] Our experimental results show a strong band at 2089 with a shoulder at its low frequency side. We assign the strong band at 2089 cm^{-1} to the CN stretch of $Cu(CN)_3^{2-}$ complex adsorbed on the Cu electrode, whereas the shoulder at its

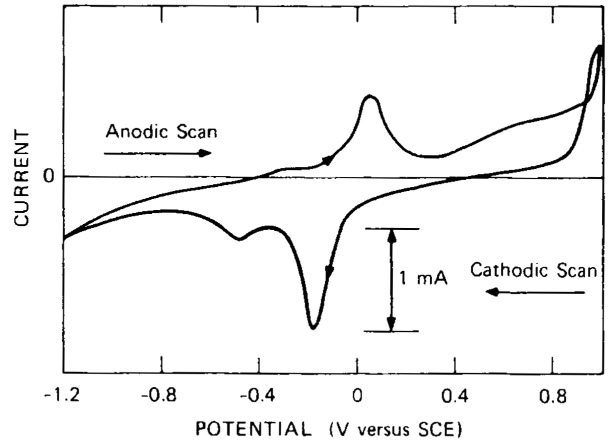

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FIGURE 4 CYCLIC VOLTAMMOGRAM FOR Au IN 0.1 M KCl + 0.01 M KCN SOLUTION

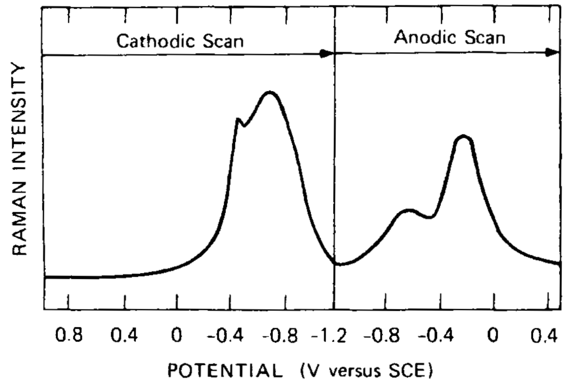

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FIGURE 5 SER INTENSITY OF THE 2109 cm^{-1} BAND DUE TO ADSORBED CYANIDE ON GOLD ELECTRODE AS A FUNCTION OF APPLIED POTENTIAL.

The electrode was anodized at 1.0 V and the electrode potential was then swept cathodically from this potential at a rate of 0.1 V min^{-1}. The sweep was reversed at -1.2 V to begin the anodic scan. See Figure 4 for the corresponding cyclic voltammogram. The electrolyte was 0.1 M KCl + 0.01 M KCN. The excitation source was the 676.4 nm line of a Kr ion laser.

low frequency side is due to that of $Cu(CN)_4^{3-}$ on the surface. The assignments are made on the basis of the closeness between our observed frequency shifts and the reported values. Benner et al,[56] studied the cyanide adsorption on Cu and found a broad peak centered at 2100 cm^{-1}. They attributed this Raman band to a mixture of $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$.

The cyclic voltammogram of a Cu electrode in 0.1 M KCl + 0.01 M KCN solution is shown in Figure 6. The Raman intensity of the 2089 cm^{-1} band as a function of the applied potential is shown in Figure 7. The Cu electrode was first anodized at 0.4 V. The voltage dependence of the Raman signal was recorded when the electrode potential was swept cathodically from 0.4 V. The Raman intensity shows a maximum at about -0.65 V during the cathodic scan, a potential which is close to the maximum of the second reduction peak in the cyclic voltammogram. The Raman signal became barely visible at about -1.0 V. On the anodic scan, the maximum Raman intensity occurred at about -0.5 V. In addition to these, we observed two small maxima on the cathodic and anodic scans, centered at about -0.25 and 0 V, respectively. This signal may be due to the CN stretch of the species CuCN. The CN stretch of a CuCN 2170 cm^{-1} was observed at these potentials.[56] The bandpass used in recording the Raman intensity-voltage curve was wide, and probably it overlapped partially with the CN stretching mode for CuCN.

The surface enhanced Raman scattering from cyanide on Ag has been well investigated.[62-66,90-94] Our results are in agreement with those obtained under similar experimental conditions. We observed the CN stretch at 2104 cm^{-1} (at -0.8 V versus SCE). Billman et al.,[63] observed two lines for CN stretches at 2102 and 2141 cm^{-1}. They attributed these lines to the CN stretches of complexes $Ag(CN)_3^{2-}$ and $Ag(CN)_2^-$, respectively, based on steric hinderance and the known Raman data. These assignments are reasonable. In cyanide solutions, silver forms complexes $Ag(CN)_2^-$, $Ag(CN)_3^{2-}$, and $Ag(CN)_4^{3-}$. Raman studies showed that the CN stretching frequency for $Ag(CN)_2^-$ was at 2141 cm^{-1};[126] $Ag(CN)_3^{2-}$, 2108 cm^{-1};[131] $Ag(CN)_4^{3-}$, 2097 cm^{-1}.[131] In addition, solid AgCN gives the CN stretch at 2167 cm^{-1}.[132]

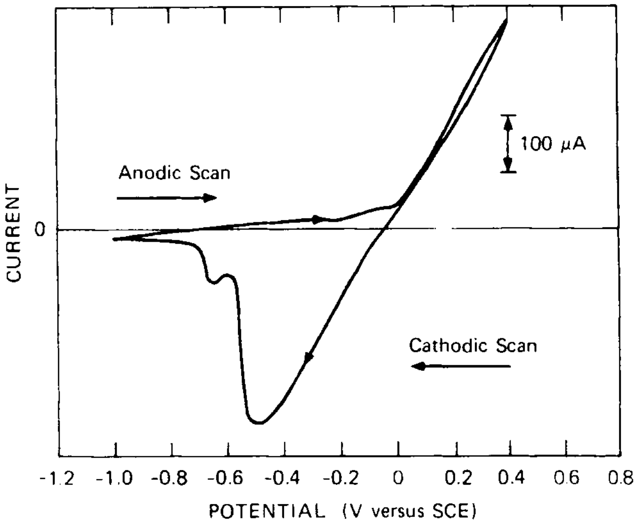

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FIGURE 6 CYCLIC VOLTAMMOGRAM FOR Cu IN 0.1 M KCl + 0.01 M KCN SOLUTION

One of the interesting features in the SER spectra of cyanide on Cu, Ag, and Au is the appearance of the low frequency vibrational modes (LFVM). The presence of more than one LFVM (See Figure 3 and Figure 8) indicates that more than one cyanide group are involved in the complex formation. Three LFVM are observed for cyanide on Cu, Ag, and Au, and they are tabulated in TABLE 5. For Cu, they are at 175, 312 and 434 cm^{-1}; for Ag, they are at 143, 218, and 303 cm^{-1}; for Au, they are at 83, 228, and 325 cm^{-1}.

Only a few normal Raman studies have been made on the LFVM of cyanide complexes of Group IB elements. For $Au(CN)_2^-$, two LFVM were reported at 445 (ν_2) and 304 (ν_5) cm^{-1}.[126] These probably can be correlated with our observed values at 325 and 228 cm^{-1}, respectively. No correlation can be made on the LFVM of surface $Ag(CN)_3^{2-}$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$ complexes, because there are no published data. However, LFVM for $Ag(CN)_2^-$ have been reported at 360 (ν_2), 328 (ν_6), 250 (ν_5), and 174 (ν_7) cm^{-1}.[133] Only one low frequency mode at 319 cm^{-1} was observed for CuCN.[101] It is interesting to note that both Cu and Ag electrodes in halide solutions also give multiple

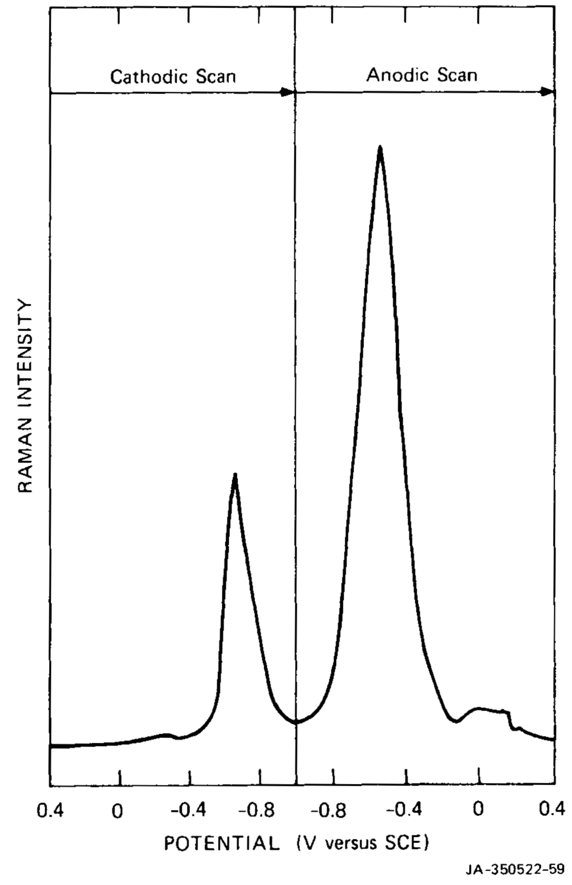

FIGURE 7 SER INTENSITY OF THE 2089 cm^{-1} BAND DUE TO ADSORBED CYANIDE ON COPPER ELECTRODE AS A FUNCTION OF APPLIED POTENTIAL

The electrode was anodized at 0.4 V and the electrode potential was then swept cathodically from this potential at a rate of 0.1 V min^{-1}. The sweep was reversed at -1.0 V to begin the anodic scan. See Figure 6 for the corresponding cyclic voltammogram.

The electrolyte was 0.1 M KCl + 0.01 M KCN. The excitation source was the 676.4 nm line of a Kr ion laser.

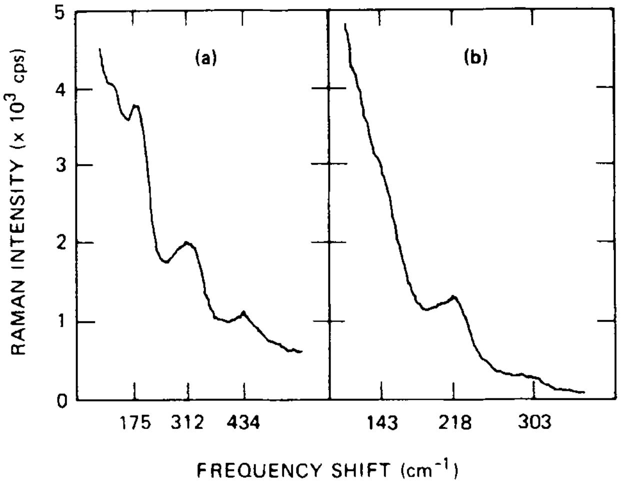

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FIGURE 8 SER SPECTRA FOR CYANIDE ADSORBED ON (a) Cu AT -0.6 V; (b) Ag AT -0.6 V

The electrolyte was 0.1 M KCl + 0.01 M KCN, and the excitation source was the 647.1 nm line of a Kr ion laser.

TABLE 5

Low Frequency Vibrational Modes (in cm^{-1}) for Cyanide Complexes on Cu, Ag, and Au

Cu(-0.6 V)	Ag(-0.6 V)	Au(-0.7 V)
175	143	83
312	218	228
434	303	325

LFVM.[57,58,80,81] These LFVM were attributed to surface complexes of the form MX^{n-}_{n+1} (M = Cu, Ag; X = Cl, Br, I; N = 1, 2,---). There are some indications that the frequency distribution of LFVM may be a function of surface coverage of these ions.[134,135] More experiments are needed in order to provide a better understanding of the LFVM of the surface complexes on Cu and Ag electrodes in the presence of highly complexing ions, cyanide and halide ions.

4. CONCLUSION

Surface enhanced Raman spectroscopy has been demonstrated to be a very useful tool in the study of adsorption. Direct and detailed information on the adsorbate can be easily obtained. Electrode processes such as corrosion, inhibition and passivation that occur at the metal-electrolyte interface can also be investigated by this technique. Corrosion, inhibition and passivation can be regarded simply as processes in which a sequence of breaking and forming of chemical bonds occurs on the surfaces. Thus, the identification of structure and orientation of surface species and the determination of strength and nature of surface chemisorption bonding are of utmost importance in the ultimate understanding of these processes.

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