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RAMAN SPECTROSCOPY OF ADSORBATES ON THIN FILM ELECTRODES DEPOSITED ON SILVER SUBSTRATES

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ABSTRACT

Is is shown that enhanced Raman spectra can be detected for CN^- adsorbed on thin Ni, Co, Cu and Zn layers deposited from cyanide plating baths onto silver substrate electrodes roughened in a preceding controlled oxidation–reduction cycle; adsorption of CN^- on Ag stabilises the roughened substrate structure during the electroplating step. Mechanisms for the generation of enhanced spectra at such composite layered electrodes are discussed briefly.

INTRODUCTION

The Surface Enhanced Raman Scattering (SERS) of CN^- and of pyridine adsorbed on silver surfaces has been extensively investigated mainly with the aim of determining the mechanisms causing the enhancement (for recent summaries and references to work on CN^- see refs. 1 and 2 and to work on pyridine see ref. 3). It has been shown that the high intensity of the signals for physisorbed pyridine on electrodes roughened in Oxidation–Reduction Cycles (ORC) is markedly and irreversibly diminished by cathodic polarisation [4,5] (e.g. at -1.6 V vs. SCE) giving Diminished Surface Enhanced Raman Scattering (DSERS); this reduction in intensity has been attributed to the removal of adatoms or of clusters of atoms formed in the ORC, structures which make a special contribution to SERS. On this view DSERS is due to the enhancement of the electromagnetic field by roughness features of larger scale (typically 10–100 nm). Comparable losses in intensity have been observed for adsorption from the vapour phase on annealing imperfections formed in thermally quenched evaporated silver films [6]. Raman spectra of physisorbed pyridine on silver showing the intensity expected for species having the normal Raman scattering cross section have been observed both for adsorption from the gas phase [7] and at electrode–solution interfaces [5] (Surface Unenhanced Raman Scattering, SUERS). The SER, DSER and SUER spectra of pyridine on silver electrodes are closely similar indicating that SERS samples the whole surface.

The spectra of CN^- adsorbed at silver electrodes have been attributed to the adsorption of two [2,8] or more than two [1,9] CN^- ions at each adsorption site. The intensity, frequencies and line shapes (as well as the spectrum of coadsorbed water molecules [8]) change in a characteristic way with electrode potential. It is a feature of this system that spectra of stable intensity can be measured even at very negative potentials (below −1.7 V vs. SCE).

The effects of the Underpotential Deposition (UPD) of a number of metals (Pb, Tl, Cu and Cd) on the SERS of a number of species (pyridine, benzotriazole, acetate and halide ions) have been investigated (for a summary and references see ref. 10). A recent study has shown that markedly enhanced Raman spectra can still be observed for appropriate systems even on surfaces covered by monolayers of the UPD metals as well as for some thicker Overpotential Deposited (OPD) films. The decrease in the intensity of enhanced Raman spectra due to the repeated deposition and removal of UPD (and OPD) layers has been attributed to the restructuring of the silver substrate, the signals on the silver electrodes having intensities comparable to those of DSERS [5]. This restructuring of the Ag substrate has been shown to be catalysed by Cl^- [10] which is a constituent of many electrolytes used in investigations of SERS.

The stability of SERS at markedly negative potentials of CN^- adsorbed at silver electrodes coupled to the ready formulation of metal plating baths for a wide range of metals in cyanide media [11] suggests that the plating of foreign metals in such media onto silver should allow the deposition of metal films with retention of the underlying roughened substrate structure (prepared by appropriate ORCs either *in-situ* or *ex-situ*). In the light of the previous investigation [10] such electrodeposited films should show some degree of enhancement of the spectra of species adsorbed at the electrode–solution interfaces. In this paper we report on the UPD and OPD films of Zn, Ni, Co and Cu using the spectra of adsorbed CN^- and of pyridine to monitor the effects of the deposition of the layers.

EXPERIMENTAL

The experimental procedures were identical to those which have been described in the preceding paper [10].

RESULTS AND DISCUSSION

The effects of the deposition of Zn on the spectra of anions adsorbed on Ag

The negative sweeps of cyclic voltammograms in cyanide solutions show the UPD of a single layer of Zn followed by bulk deposition. Figures 1a–c illustrate the stripping voltammetry for deposits where the negative sweep was stopped at various potentials and for various times. The formation of a partial monolayer, Fig. 1a, is followed by that of a complete monolayer, Fig. 1b, in turn followed by bulk deposition, Fig. 1c. The stripping voltammetry of the thicker bulk deposits evidently takes place in at least two stages (compare dissolution in alkaline solutions [12]). It

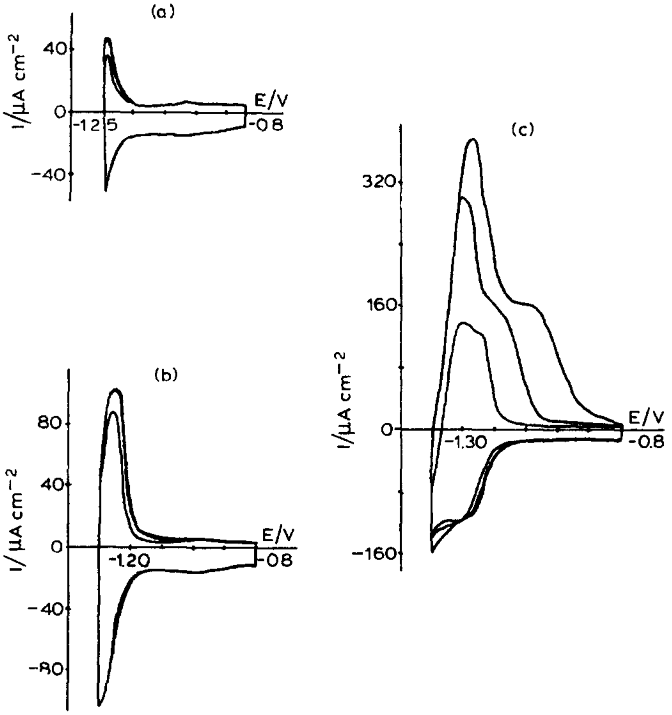

Fig. 1. Stripping voltammetry for Zn deposits in a solution of 0.01 *M* $ZnSO_4$, 0.05 *M* KCN and 0.1 *M* K_2SO_4; the negative sweep was stopped at various times (0.1 and 4 min) and various potentials (a) -1.25 V, (b) -1.30 V, (c) -1.40 V. Sweep rate 25 mV s^{-1}.

has been shown that surface alloys are formed during bulk deposition from zincate solutions [12] but the stripping voltammetry of these alloys could not be observed here in view of the restriction of the accessible potential range by the dissolution of the silver substrate.

At potentials positive to that for the deposition of Zn, a simple spectrum is observed, Fig. 2a, which is due to the ν(CN) frequency of CN^- adsorbed on Ag (the solution contained excess CN^-). Following the deposition of a partial UPD layer of Zn (conditions corresponding to Fig. 1a) the spectrum Fig. 2b was observed. This spectrum was stable with time (cf. Fig. 2c) and showed a new ν(CN) vibration at ~ 2127 cm^{-1} in addition to the original band. On completion of the UPD process, only the new band could be detected, Fig. 2d. It follows that this new band must be attributed either to a zinc cyanide complex or to cyanide ions adsorbed on the partial or complete UPD layers (Fig. 2b–d).

Figures 2e–h show the effects of OPD of zinc on the spectra; at 3 min the deposit thickness was in the range 10–20 layers. It can be seen that the intensity of the spectra decreases progressively with the deposit thickness; after 16 min the intensity

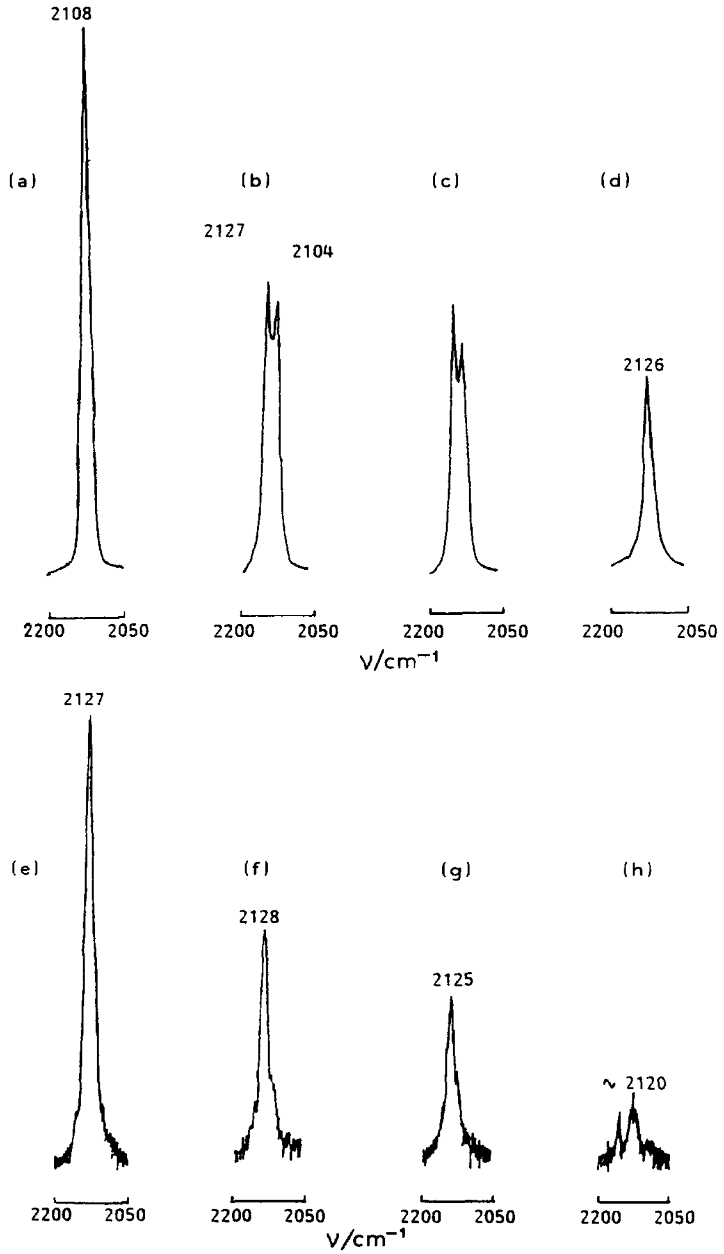

Fig. 2. Raman spectra in the C–N stretch region 2050–2200 cm^{-1} before and after zinc deposition onto a silver electrode from a solution of 0.01 *M* $ZnSO_4$, 0.05 *M* KCN and 0.10 *M* K_2SO_4 at the potentials (a) −1.2 V, (b) −1.25 V, (c) −1.25 V, after 3 min, (d) −1.30 V, (e) −1.4 V, (f) −1.4 V after 1 min, (g) −1.4 V after 3 min, (h) −1.4 V after 16 min.

of the surface band becomes comparable to that of $Zn(CN)_4^{2-}$ complex in solution (2150 cm^{-1}). However, enhanced spectra can readily be measured even on such relatively thick deposits.

Figure 3 compares the spectra in the low frequency region for solutions containing no Zn (Fig. 3a, c) with those containing the complex (Fig. 3b, d). It can be seen

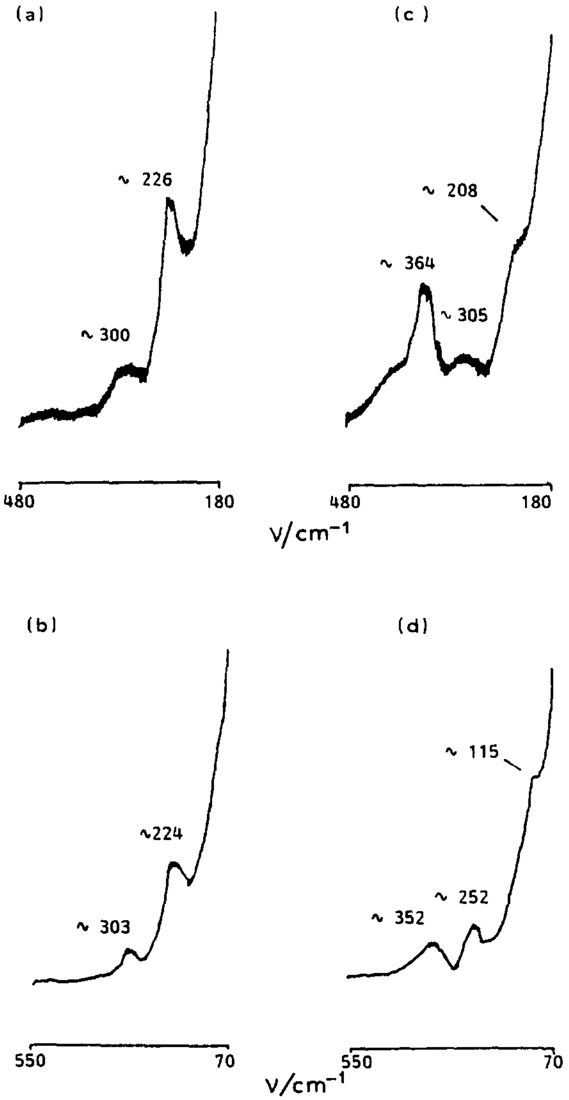

Fig. 3. Raman spectra in the low wavenumber region for solutions (a, c) 1 M KCN + 0.1 M K_2SO_4 and (b, d) 0.1 M $ZnSO_4$ + 0.5 M KCN + 0.1 M K_2SO_4 at the potentials (a, b) -1.0 V and (c, d) -1.4 V.

that before UPD the spectra are idential indicating that CN^- is the adsorbed species. However, marked differences are observed in the spectra following UPD (the potential for UPD is shifted compared to that for the data in Fig. 2 in view of the higher concentrations). Here again we are observing the adsorption of cyano species on the zinc UPD layer, Fig. 3d.

The effects of the deposition of Ni and Co on the spectra of anions adsorbed on Ag

Figure 4 shows that there is an onset of electrodeposition of Ni at ~ −1.3 V. The magnitudes of the currents are small indicating that deposition is markedly hindered, probably by the slow dissociation of the $Ni(CN)_4^{2-}$ complex to form the electroactive species (compare ref. 13). This interpretation is consistent with the high stability constant of this species ($K = 10^{-31}$ mol^4 l^{-4} [14]); direct reduction of this complex could be initiated only at much more negative potentials. Similar comments apply to the deposition of the other metals investigated here. The peak at ~ −1.1 V corresponds to the deposition of monolayer quantities of a solid phase.

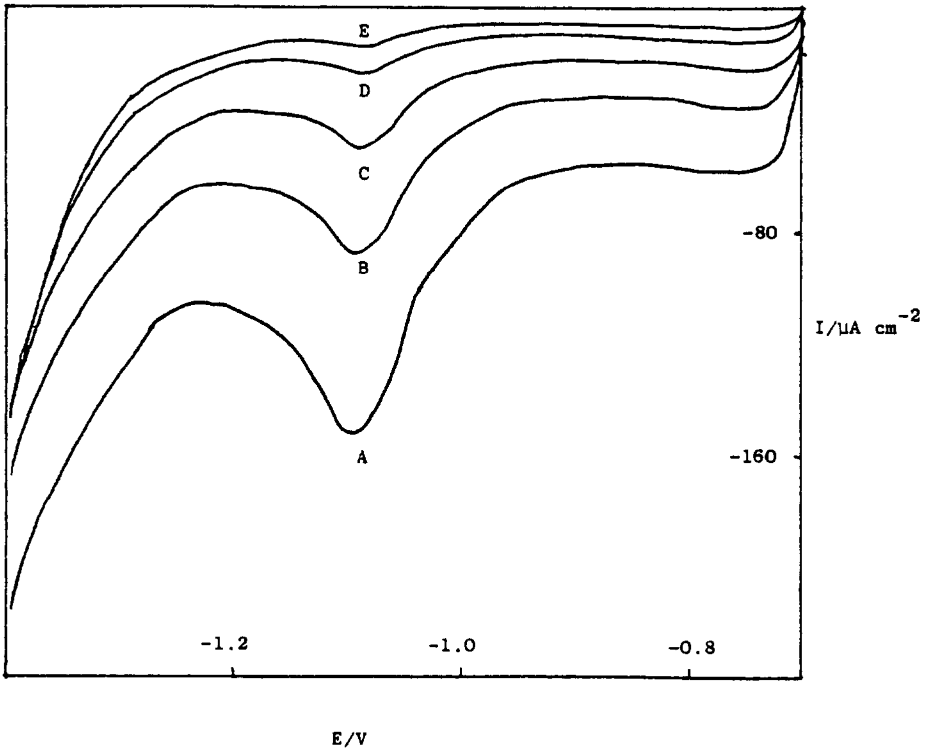

Fig. 4. Linear sweep voltammograms for the electrodeposition of nickel onto a silver electrode from a solution of 0.01 *M* $NiSO_4$, 0.04 *M* KCN and 0.10 *M* K_2SO_4. The sweep rates are (A) 150, (B) 100, (C) 50, (D) 20, (E) 10 mV s^{-1}.

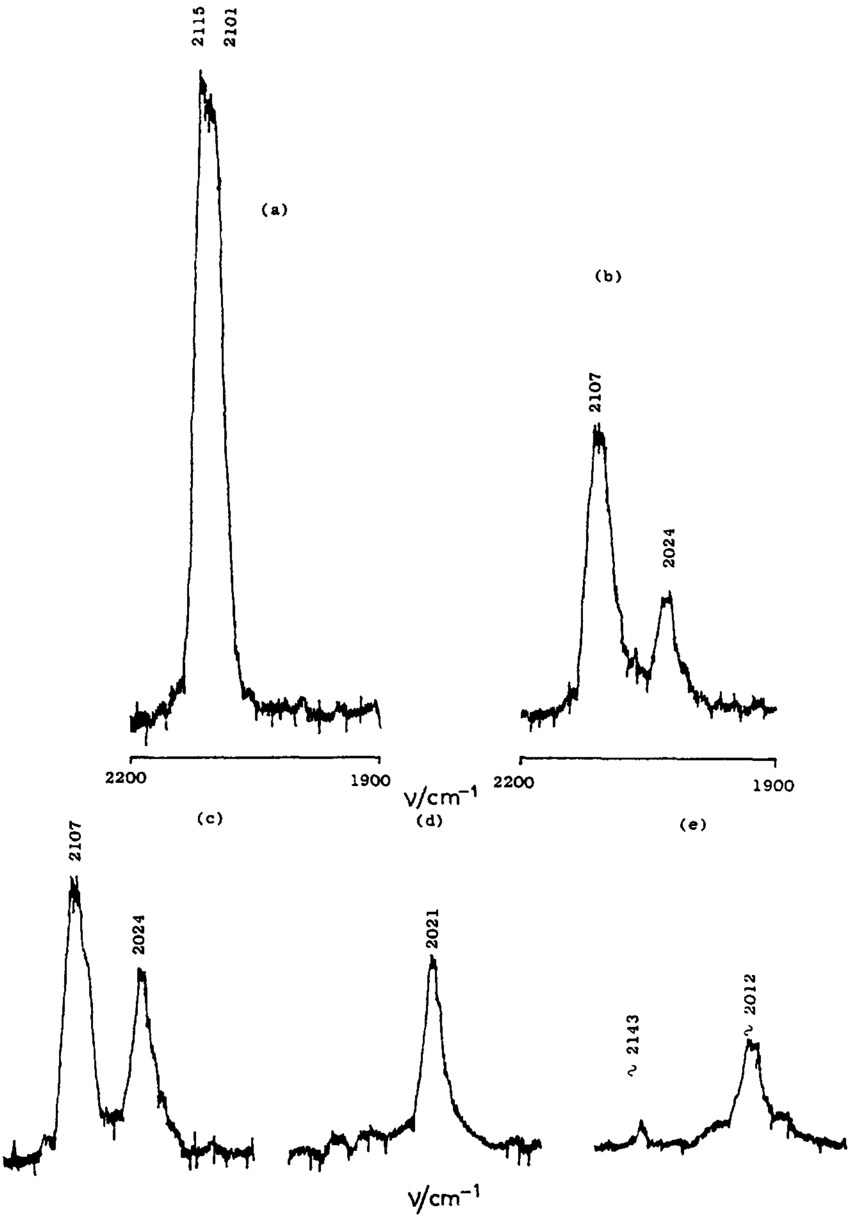

Fig. 5. Raman spectra of the C–N stretch region for a solution of 0.01 *M* $NiSO_4$, 0.04 *M* KCN and 0.10 *M* K_2SO_4 at a potential of (a) −0.8 V, (b) −1.0 V, (c) −1.0 V, after 20 min, (d) −1.2 V, (e), −1.4 V. The bandpass is 5 cm^{-1}.

TABLE 1

Raman band frequencies in the ν(CN) region of solution phase and adsorbed species

Species	Aqueous solution ν/cm^{-1}	Ref.	$\nu(\text{CN})/\text{cm}^{-1}$ of adsorbed species (E/V)
$[\text{Ni(CN)}_4]^{2-}$	2138, 2144	17	2101, 2115 (−0.8) 2018 (−1.2)
$[\text{Zn(CN)}_4]^{2-}$	2152	18	2112 (−0.8) 2125 (−1.4)
$[\text{Cu(CN)}_2]^-$	2106	18	2126 (−0.2)
$[\text{Cu(CN)}_3]^-$	2094	18	2101 (−1.2)
$\text{K}_3\text{Co(CN)}_6$	2139, 2152	19	2098, 2115 (−0.8) 1991, 2070 (−1.2)

The spectra observed at potentials positive to the deposition potential (see Fig. 4) are broad compared to those for the adsorption on CN$^-$ on Ag [8], Fig. 5, suggesting that the bands are due to several adsorbed species. The band at ~2101 cm^{-1} can be assigned to CN$^-$ while that at ~2115 cm^{-1} is probably due to Ni(CN)_4^{2-}, the CN stretch frequency being appreciably reduced compared to those for the solution free species, Table 1. This reduction must be due to the interaction of the square planar complex via one (or two) N atoms with the surface. Deposition of Ni at −1.0 V leads to a new band (here at ~2024 cm^{-1}) which increased progressively in intensity relative to that due to the adsorbed complex and adsorbed CN$^-$, here at ~2107 cm^{-1}, Fig. 5 (separate bands for the adsorbed complex and CN$^-$ cannot be resolved). We assign the band at ~2024 cm^{-1} to ν(CN) of CN$^-$ adsorbed at the nickel–electrolyte interface. Figure 5 also shows the effect of potential on this species. In view of the thin-layer configuration used in these experiments (the electrode was pushed against the optical flat cell window) the nickel cyanide complexes are completely reduced and their spectra are not detected. The very low frequency of the ν(CN) band due to the adsorbed species on the negatively polarised electrode (~2012 cm^{-1} at −1.4 V) may be compared with that observed in the zero valent complex Ni(CN)_4^{4-}, ~1985 cm^{-1} [15].

The behaviour of the Co(CN)_6^{4-} system (in the presence of a small excess of CN$^-$) is broadly similar to that of the Ni(CN)_4^{2-} system. At potentials positive to that for the reduction of the anion to the metal, bands due to adsorbed CN$^-$ and Co(CN)_6^{4-} can be detected, Fig. 6, whereas at more negative potentials bands due to species adsorbed on the Co surface are observed. The low frequency of the CN vibration is close to that which has been observed for CN bonded to zero valent Ni [15]. CN frequencies in a comparable region have also been detected for adsorbed CN$^-$ on Ag electrodes at very negative potentials [18]. It may be noted however that CN$^-$ is desorbed from Ag electrodes at potentials as negative as that for the measurements in Fig. 6c. Shifts in the CN$^-$ frequency with changes of potential can

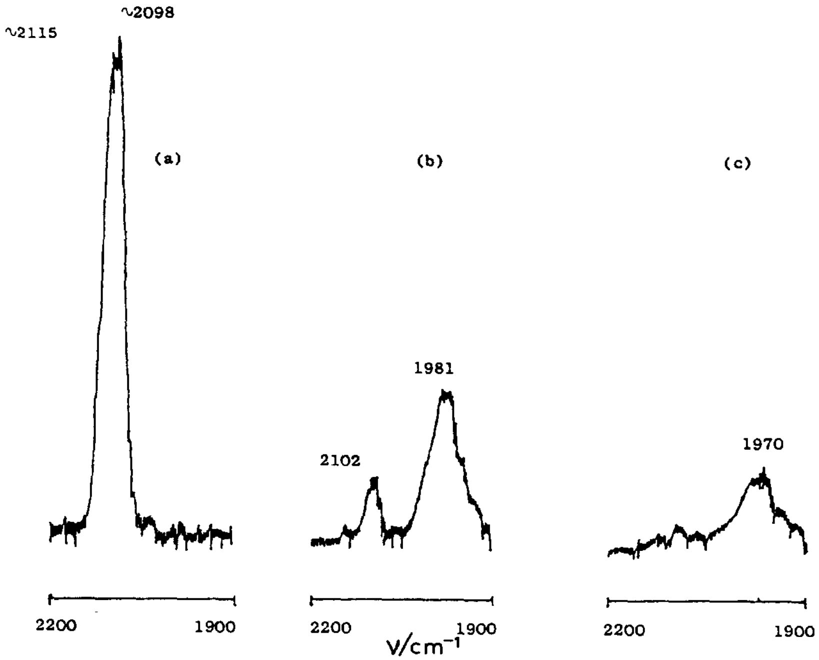

Fig. 6. Raman spectra in the region 1900–2200 cm^{-1} for 0.005 *M* $CoSO_4$, 0.03 *M* KCN and 0.10 *M* K_2SO_4 before and after the deposition of cobalt on silver at (a) −0.8 V, (b) −1.4 V, (c) −1.6 V.

be interpreted in terms of back donation from the metal to the antibonding $2p\ \pi^*$ orbital of the anion.

The effects of the deposition of Cu on the spectra of anions adsorbed on Ag

Figure 7 and Table 1 show that ν(CN) of the adsorbed complex prior to Cu deposition is higher than that of any copper complex present in solution. In this case therefore it is likely that the complexes are adsorbed via π interaction of the CN groups with the surface rather than through coordination via the terminal N atoms. Figure 7 shows that following deposition of a thin layer of Cu, adsorbed CN^- is detected at a frequency close to that for CN^- adsorbed on Ag. It should be noted that although Cu itself shows SERS with red excitation, these spectra were measured with 514.5 nm radiation so that the mechanism of enhancement is similar to that observed in the case of Ni, Co and Zn and the intensities are indeed comparable (compare ref. 16).

The effects of the deposition of Ni on the spectrum of adsorbed pyridine

Layers of the metal were deposited from a sulphate/chloride bath containing pyridine onto Ag electrodes roughened according to the ORC described in the Experimental Section. Measurements of the spectra of adsorbed pyridine were then

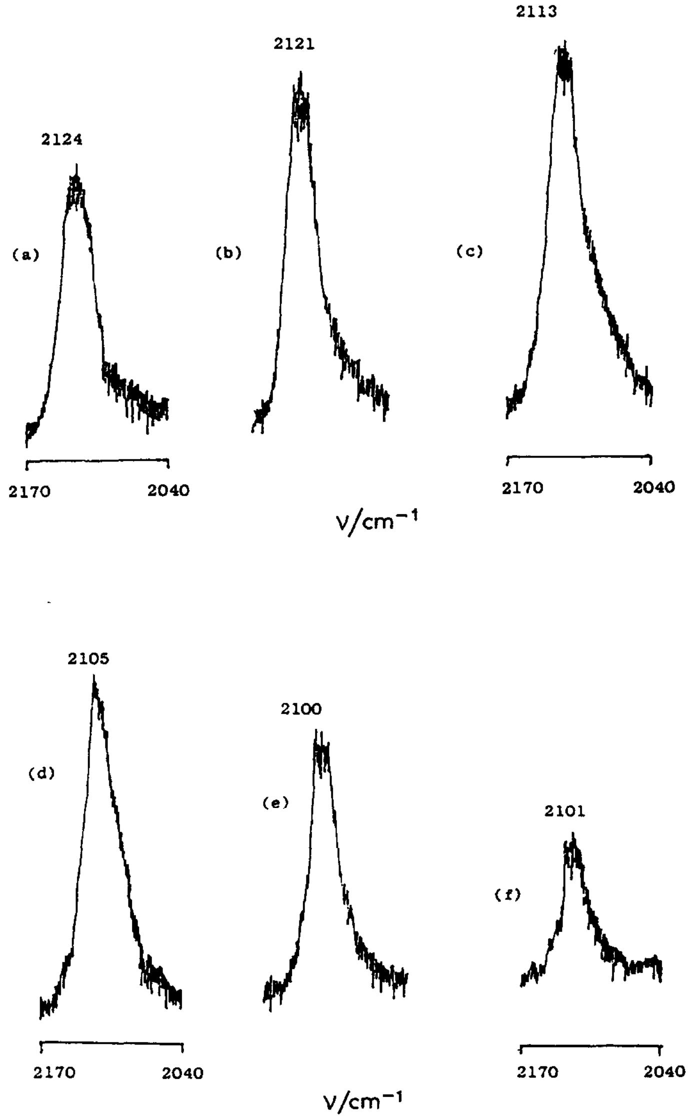

Fig. 7. Raman spectra in the C–N stretch region before and after copper deposition onto a silver substrate from a solution of 0.01 *M* $CuSO_4$, 0.04 *M* KCN and 0.10 *M* K_2SO_4 at the potentials (a) −0.3 V, (b) −0.5 V, (c) −0.7 V, (d) −0.9 V, (e) −1.1 V, (f) −1.2 V.

made using the solution which has been frequently used previously (0.05 *M* pyridine + 0.1 *M* KCl). Figures 8a and b compare the spectra of pyridine at Ag and Ni electrode–solution interfaces. It can be seen that the spectra are markedly different for example in the ratio of the intensities of the ν_1 (1007 cm^{-1}) and ν_{12}

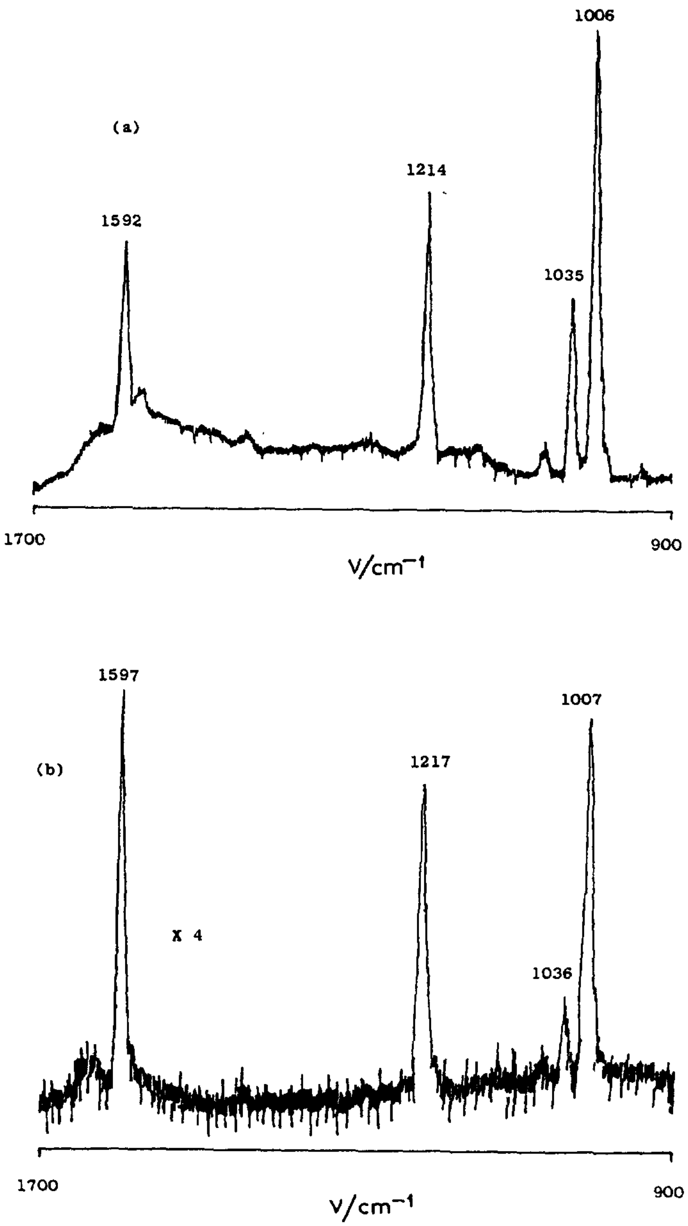

Fig. 8. Raman spectra of pyridine at −0.9 V on (a) a silver electrode, (b) a thin nickel layer on the silver substrate. The solution is 0.05 *M* pyridine +0.10 *M* KCl.

(1036 cm^{-1}) ring breathing modes. The particularly high intensities of the ν_{9a} ($\sim$ 1216 cm^{-1}) and ν_{8a} ($\sim$ 1596 cm^{-1}) ring deformation modes for adsorption onto Ni as compared to those observed for adsorption onto Ag indicate that there is a marked difference in orientation: pyridine must be adsorbed more nearly perpendicularly to the surface in the case of Ni than in the case of Ag (an increase of intensity of these modes relative to those of the ring breathing modes at particular potentials as the potential is made more negative has been observed for the adsorption onto Ag and has been interpreted as being due to a change of orientation from an essentially flat π-coordinated structure to adsorption via the N atom [5]). It is of interest that stable spectra of adsorbed pyridine can be recorded at much more negative potentials on this surface than in the case of Ag. The deposition of the transition metal layer onto the silver SERS substrate evidently produces a surface at which pyridine is still adsorbed and which maintains conditions for the observation of enhanced Raman spectra.

CONCLUSIONS

The marked differences in the spectra of CN^- and of pyridine for adsorption on OPD layers deposited on Ag SERS active substrates as compared to the spectra of these species on the Ag SERS surface itself, Fig. 9, shows that enhanced Raman spectra are being detected at the electrode–solution interfaces. Alternative explanations such as the generation of SERS at gaps in the covering metal layer are not consistent with the marked and stable changes in the spectra caused by electrodeposition of the metal layers nor with the well-known deposition of uniform, coherent deposits from cyanide media. Furthermore stable spectra can be observed from the deposit–solution interfaces at very negative potentials where the silver substrate would show a marked loss of SERS intensity. The deposition of metals from cyanide plating baths onto SERS active substrates therefore appears to offer a ready means of extending the range of electrode–solution interfaces giving enhanced Raman spectra.

The intensity of the spectra observed for adsorbates on the UPD and OPD layers (see also ref. 10) is comparable to that for DSERS on Ag [5] and the Ag substrate also gives DSERS spectra following dissolution of the layers. The enhancement of the spectra of adsorbates on the deposited layers must therefore be due to enhanced electric fields at the metal–solution interfaces. Electrodynamic calculations have predicted such enhancements of the electromagnetic intensity for relatively large ($\sim$ 100 nm) spheroidal particles of transition metals and the intensity passes through a maximum with increasing particle size for a given excitation frequency [19]; electrostatic calculations for thin overlayers of metals on Ag (up to $\sim$ 1 monolayer) indicate an appreciable quenching of the field intensities although the fields remain enhanced even at full coverage [20] (for references to earlier work on spherical and spheroidal particles see refs. 19 and 20). However, the experiments reported here show that the intensities of the spectra are initially high and decrease with increasing thickness of the metal overlayers. Evidently the behaviour is more

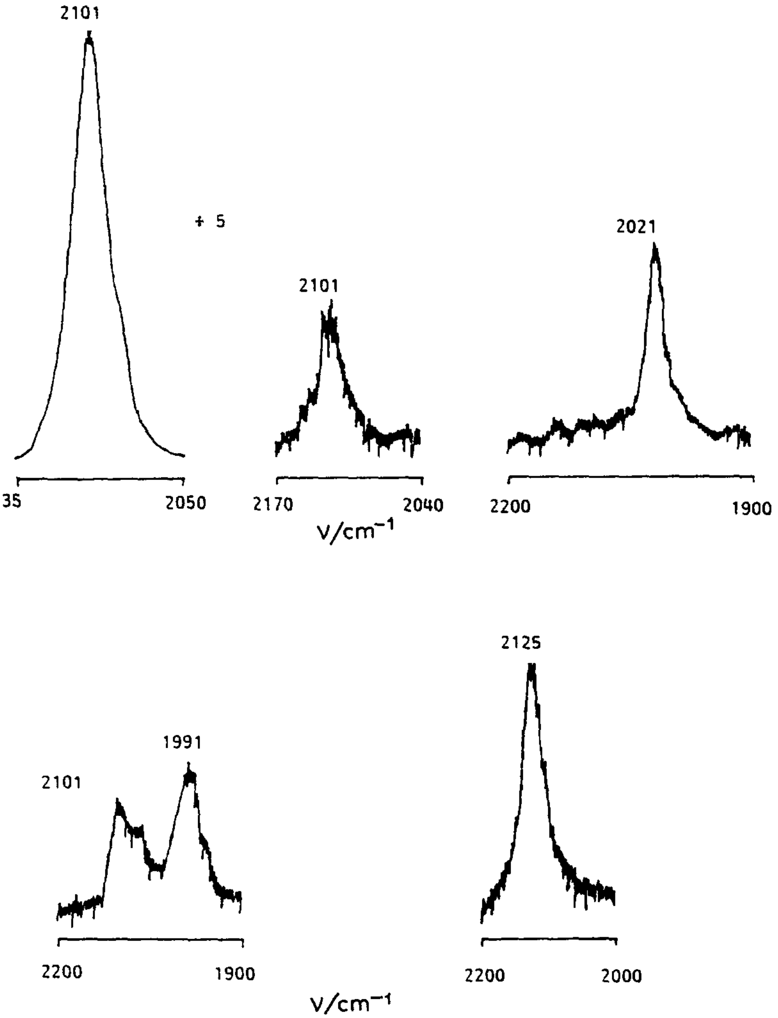

Fig. 9. Raman spectra in the C–N stretch region at −1.4 V from solutions of (a) 0.01 *M* $AgNO_3$ + 0.02 *M* KCN + 0.25 *M* KNO_3, (b) 0.01 *M* $CuSO_4$ + 0.04 *M* KCN + 0.10 *M* K_2SO_4, (c) 0.01 *M* $NiSO_4$ + 0.04 *M* KCN + 0.10 *M* K_2SO_4, (d) 0.005 *M* $CoSO_4$ + 0.03 *M* KCN + 0.10 *M* K_2SO_4, (e) 0.005 *M* $ZnSO_4$ + 0.03 *M* KCN + 0.10 *M* K_2SO_4.

complex than can be explained by existing models (for example the dielectric permittivity of the metal–metal interfacial layer may differ greatly from that derived from the bulk values); the observed behaviour would be more plausibly explained by the penetration through the metal overlayers of high fields generated at the silver surfaces. However, the following paper shows that further phenomena must be taken into account.

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