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Surface-Enhanced Raman Scattering of 4-Picolylamine and Its $[\text{Fe}(\text{CN})_5]^{3-}$ Complexes

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The SER spectra of the complexes $[\text{Fe}(\text{CN})_5(4\text{-picolylamine})]^{3-}$ and $[\text{Fe}_2(\text{CN})_{10}(4\text{-picolylamine})]^{6-}$ adsorbed on a silver electrode were investigated. The analysis of the frequency shift of the CN stretching mode indicated that both molecules adsorb via one or more CN ligand groups. For potentials more positive than 0.0 V the CN stretching frequency for both complexes moves towards higher wavenumbers characterizing the presence of Fe(III) over the surface. The SER spectra of 4-picolylamine adsorbed on a silver electrode in solutions of pH 2.8, 6.5 and 10.3 were also investigated. From the data obtained it was concluded that 4-picolylamine in solution at pH 6.5 and 10.3 adsorbs on the electrode through the nitrogen of the pyridine ring.

INTRODUCTION

Recent interest in the chemical and physical properties of chemically modified electrodes stems from the concept that a molecular species with desirable properties can be immobilized on a solid surface, conferring those properties on the new surface. Surface modification techniques can thus be utilized to convert relatively inexpensive, poor electrode materials into useful electrodes. Anodization of metal or semiconductor electrodes in the presence of cyanometallate complexes such as hexacyanoferrate(III) produces mixed metal cyanometallate complexes of the general formula $[\text{M}(\text{NC})\text{M}'(\text{CN})_n\text{L}_n]^{n-}$ (where M and M' are transition metals and L is a donor ligand).^{1–3} These types of derivatized surface reactions can stabilize an electrode against considerable surface reactions such as oxide formation, without inhibiting desirable interfacial charge-transfer processes. They are also useful as electrocatalysts and in sensor applications. Electrochemical and spectroscopic investigations of these metal-metalloacyanide surface complexes are therefore desirable.

Complexes of the pentacyanoferrate(II) moiety with aromatic *N*-heterocycles have been extensively studied. The isolation and characterization of 4-picolylamine (4-picam) derivatives of pentacyanoferrate(II) as the sodium salts of mononuclear $[\text{Fe}(\text{CN})_5(4\text{-picam})]^{3-}$ and binuclear, 4-picam-bridged $[\text{Fe}_2(\text{CN})_{10}(4\text{-picam})]^{6-}$ has been reported.⁴ The dissociative behaviour and the redox properties of these complexes have been reported, in addition to the correlation properties with similar complexes of related ligands.^{5–7}

Surface-enhanced Raman scattering (SERS) has been used in adsorption studies of metallic complexes on silver electrodes.^{8–11} This technique also provides valu-

able information on redox reactions of complexes adsorbed on a silver electrode.^{12–16}

In this work, using the SERS technique, it was possible to monitor the electrochemical processes of adsorption and oxidation–reduction processes of the $[\text{Fe}(\text{CN})_5(4\text{-picam})]^{3-}$ and $[\text{Fe}_2(\text{CN})_{10}(4\text{-picam})]^{6-}$ complexes. In order to obtain additional information, the SER spectra of the ligand were also obtained at several pH values.

EXPERIMENTAL

The instruments used to obtain the Raman and SER spectra and electrochemical measurements have been described elsewhere.¹⁷

4-Picam (Reily Tar and Chemical) was used after distillation. Mononuclear $[\text{Na}_2\text{Fe}(\text{CN})_5(4\text{-picam})] \cdot 5\text{H}_2\text{O}$ and binuclear $[\text{Fe}_2(\text{CN})_{10}(4\text{-picam})] \cdot 5\text{H}_2\text{O}$ were prepared according to the reported method.⁴

All the SER spectra were obtained for a concentration of the complexes of 10^{-4} M. Working solutions were prepared with doubly distilled water. 4-Picam solutions at pH 2.8, 6.5 and 10.3 were prepared by the careful addition of 1 M HCl and 1 M NaOH to an aqueous solution of the ligand. Solutions of the complexes were prepared by the dissolution of the substances in borate buffer solution (pH 8.4).

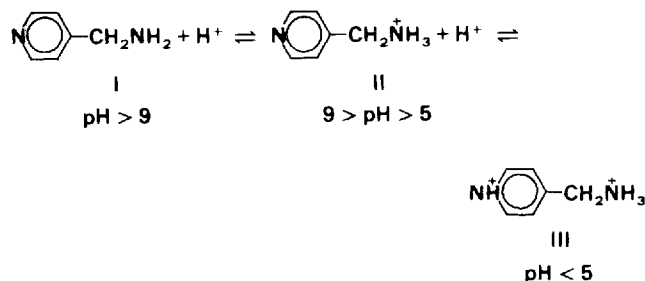
The working electrode was a silver rod (99.99% pure) with a geometric area of 0.20 cm² inserted in acrylic resin. A platinum foil of large area was used as an auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. Before each experiment the working electrode was polished with 600-mesh sandpaper and rinsed with doubly distilled water and the working solution was deaerated for 10 min with nitrogen. The same solutions were used to obtain cyclic voltammograms.

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RESULTS AND DISCUSSION

SERS of 4-picam adsorbed on a silver electrode in solutions of different pH

4-Picam has three different structures, depending on the pH of the solution:



The SERS spectra of 4-picam adsorbed on the silver electrode in 0.1 M KCl solutions at three different pH values and the indicated applied potentials are displayed in Fig. 1, together with the spectrum of a 0.05 M solution of the free ligand at pH 6.5. The normal Raman spectrum shows characteristic bands at 1220,

Table 1. Raman shifts (cm^{-1}) from SERS spectra of 4-picolyamine adsorbed on a silver electrode at -0.6 V from 0.1 M KCl solutions of different pH

10.3	pH 6.5	2.8	0.05 M 4-picam solution	Assignment
		235		$\nu_{\text{Ag-Cl}}$
			791	H_2NCH_2 group
965	965	965		Skeletal py- CH_2NH_2
1005	1010	1010	1009	Py group
1215	1215	1215	1220	Py group
1465	1465	1445		H_2NCH_2 group
1522	1525	1525		Py group + ν_{CN}
1605	1605	1605		Py group
		1636		PyH^+ group
			1630	$\delta_{\text{H}_2\text{O}}$

1009 and 791 cm^{-1} (see Table 1), while the SERS spectra show a greater number of bands and the best signal-to-noise ratio, which are well known characteristics of the SERS effect.¹⁸ It must be mentioned that the resulting spectra of the 4-picam solutions at pH 2.8 and 10.3 were of poorer quality than those at pH 6.5.

Table 1 gives the SERS signals observed for a potential of -0.6 V. A tentative assignment was made based

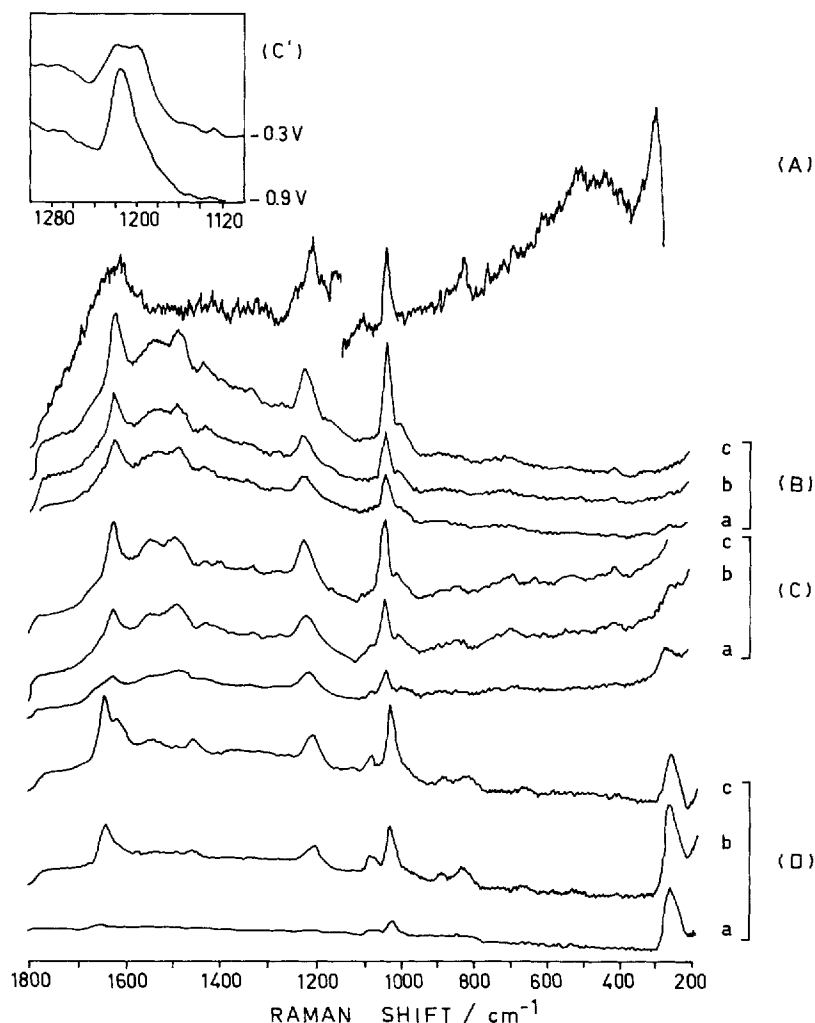


Figure 1. Raman spectra: (A) 0.05 M aqueous 4-picolyamine solution; (B), (C), (C') and (D) 4-picolyamine adsorbed on a silver electrode in KCl solution of pH 10.3, 6.5 and 2.8, respectively. Applied potential: (a) -0.2 ; (b) -0.4 ; (c) -0.8 V. $\lambda_L = 514.5$ nm.

on 4-picolyamine, 4-methylpyridine, pyridinium ion and ethylenediamine.¹⁹⁻²³

On comparing the spectra of the 4-picam in solution at pH 6.5 and 10.3 no substantial changes in the relative intensities are observed. These results indicate that the same adsorbed species exists at both pH values. For pH 10.3 and 6.5 the dominant species are I and II, respectively. As in both cases the only unprotonated nitrogen corresponds to that in the pyridine ring, it can be concluded that the interaction of the molecule with the surface is through the aromatic nitrogen.

Considering the SER spectra of the adsorbed 4-picam on the silver electrode in a solution of pH 6.5, an increase in the signal and no significant frequency shifts were observed as the applied potential became more negative. It is interesting to note the changes in the relative intensities of the bands at 1200 and 1215 cm^{-1} , attributed to a_1 and b_2 modes of the pyridine moiety, as shown in the inset in Fig. 1. The maximum intensity of the 1200 cm^{-1} band occurs at more positive potentials while the intensity of the 1215 cm^{-1} peaks at more negative potentials. This behaviour was also observed in the SERS effect of 4-methylpyridine and 4-cyanopyridine,^{24,25} which was attributed to changes in the orientation of the molecule, via the nitrogen atom, at less negative potentials, or via π bonding at more negative potentials.

The SERS effect of the pyridinium ion was studied by Sun *et al.*²² and its characteristic bands have been assigned at 1196 and 1630 cm^{-1} . In the spectra of the 4-picam at pH 2.8, bands at 1200 and 1636 cm^{-1} were observed, among others, indicating the presence of 4-picamH⁺. The band at 1636 cm^{-1} is assigned as a $\nu\text{C}-\text{C}$ mode of the 4-picam²⁺ ion (species III). Since the SER spectrum at -0.6 V shows bands at 1636 and 1605 cm^{-1} , it can be inferred that protonated and non-protonated species exist on the electrode surface. The adsorption of protonated species is favoured by ion-pair formation with Cl⁻. The adsorption of the chloride anion is characterized by the band at 235 cm^{-1} , which decreases in intensity for potentials more negative than -0.6 V owing to the desorption of the chloride anion.

Spectroelectrochemical behaviour of $[\text{Fe}(\text{CN})_5(4\text{-picam})]^{3-/2-}$ and $[\text{Fe}_2(\text{CN})_{10}(4\text{-picam})]^{6-/5-}$ complexes

This study could not be done in KCl solution as the oxidation of the complexes occurs simultaneously with the oxidation of the silver electrode and in addition rapid decomposition of the complexes in this medium occurs.

Figure 2 presents the cyclic voltammograms of the complexes using a silver working electrode and borate buffer (pH 8.4) as the supporting electrolyte. For the mononuclear complex the oxidation of Fe(II) to Fe(III) is characterized by a potential peak at 0.22 V with a corresponding reduction peak at -0.05 V. For the binuclear complex the voltammogram shows two oxidation waves prior to that of the silver electrode, with potential peaks at 0.18 and 0.28 V. These peaks can be attributed to the oxidation of the species $[\text{Fe}^{\text{II}}(\text{CN})_5(4\text{-picam})\text{Fe}^{\text{II}}(\text{CN})_5]$ and $[\text{Fe}^{\text{III}}(\text{CN})_5(4\text{-picam})\text{Fe}^{\text{II}}(\text{CN})_5]$, respectively. The reduction of these species gives two

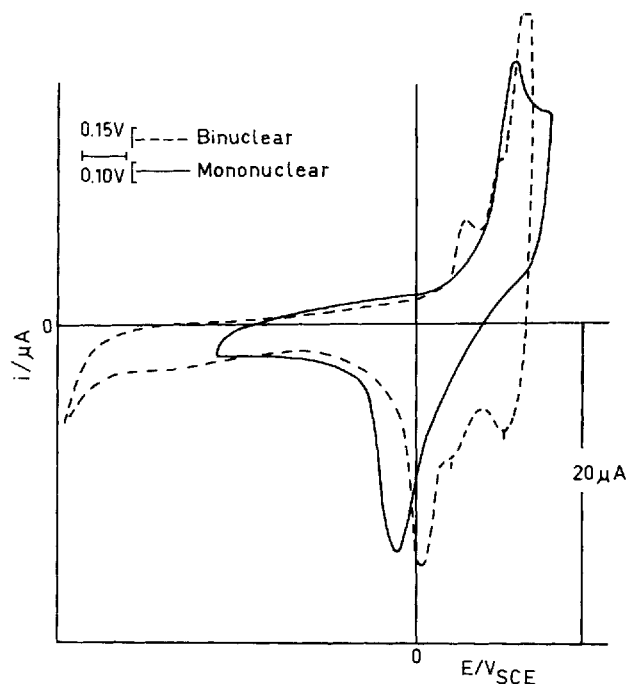


Figure 2. Cyclic voltammograms at a silver electrode of 5×10^{-4} M solutions of the mononuclear (solid line) and binuclear complexes (dashed line) in borate buffer solution (pH 8.4).

waves at 0.08 and 0.02 V, respectively. The cathodic peak at 0.30 V corresponds to the reduction of the silver which was oxidized at 0.45 V.

Figure 3 shows the SER spectra of the mononuclear complex adsorbed on a silver electrode, recorded during an anodic sweep. The same SER spectra (not included in Fig. 3) were obtained during a cathodic sweep, showing the reversibility of the oxidation-reduction process.

By comparison of these spectra with the SER spectra of 4-picam at pH 6.5, it can be seen that the regions below 1700 cm^{-1} in both spectra are very similar and so are the variations of the relative intensities with the applied potentials. Unfortunately, the low- and high-frequency regions could not be analysed owing to the low intensity of the bands.

Figure 3 also shows the SER spectra of the mononuclear complex in the CN region (2000–2300 cm^{-1}). These spectra were obtained by varying the potential from positive to negative values. For potentials more negative than -0.4 V, ν_{CN} is observed at ca. 2110 cm^{-1} , and this band shifts towards higher wavenumbers at less negative potentials. At 0.16 V this band shifts to 2130 cm^{-1} and at more positive potentials the signal disappears owing to the oxidation of the electrode. The ν_{CN} modes for cyano complexes of Fe(II) and Fe(III) are observed at 2050–2090 and 2100–2150 cm^{-1} , respectively.²⁶ In complexes where the CN group is a bridged ligand its frequency occurs at ca. 2150 cm^{-1} .³

In the SER spectra the ν_{CN} band is observed at 2110 cm^{-1} , at potentials where the Fe(II) species has to be the more stable. This indicates that the complex is adsorbed through one or more CN groups. An explanation of the increase in CN force constant due to its coordination with the group was given by Billman and Otto.²⁷

In the mononuclear complex the oxidation of the

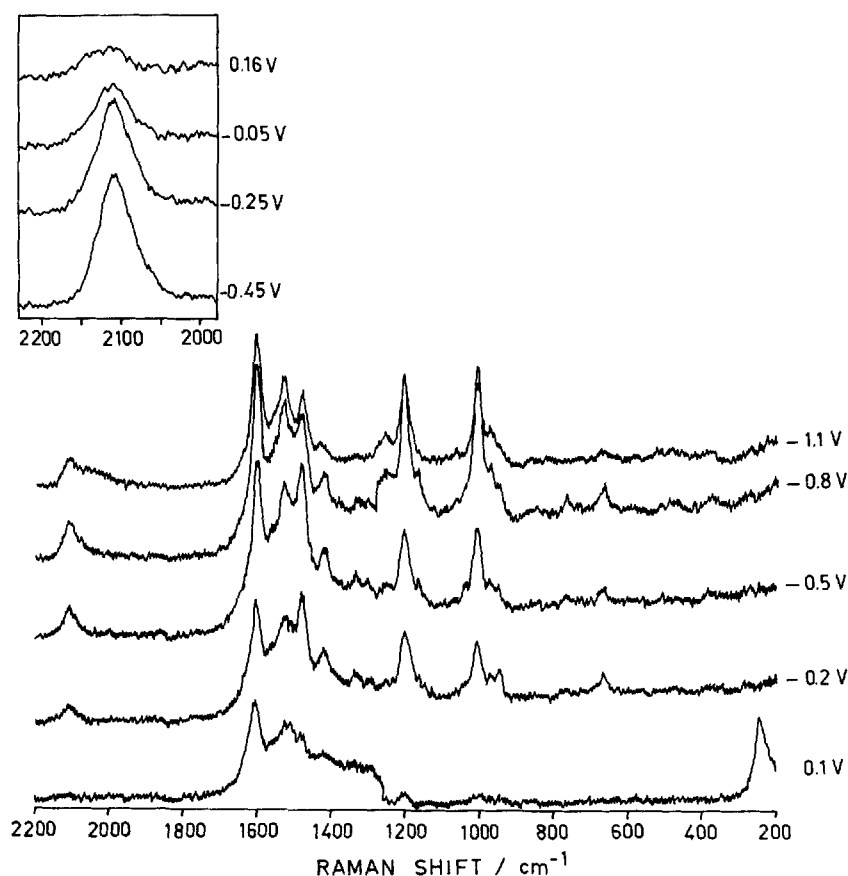


Figure 3. SER spectra at a silver electrode of 4×10^{-4} M $[\text{Fe}(\text{CN})_5(4\text{-picam})]^{3-}$ in borate buffer solution (pH 8.4) at the indicated potentials. $\lambda_L = 514.5$ nm.

$\text{Fe}(\text{II})$ starts at a potential of 0.16 V, hence the value of 2130 cm^{-1} for ν_{CN} indicates that the SER spectrum at this potential corresponds to the complex in its oxidized state.

The SER spectra of the binuclear complex are presented in Fig. 4. The ν_{CN} region is also included. A band

at 2111 cm^{-1} is observed at potentials where the reduced species is the most stable. As mentioned above, this indicates that the binuclear complex is also adsorbed via one or more CN groups.

At a potential of 0.1 V, ν_{CN} is observed at 2135 cm^{-1} and after 30 s (spectrum marked with an asterisk) this

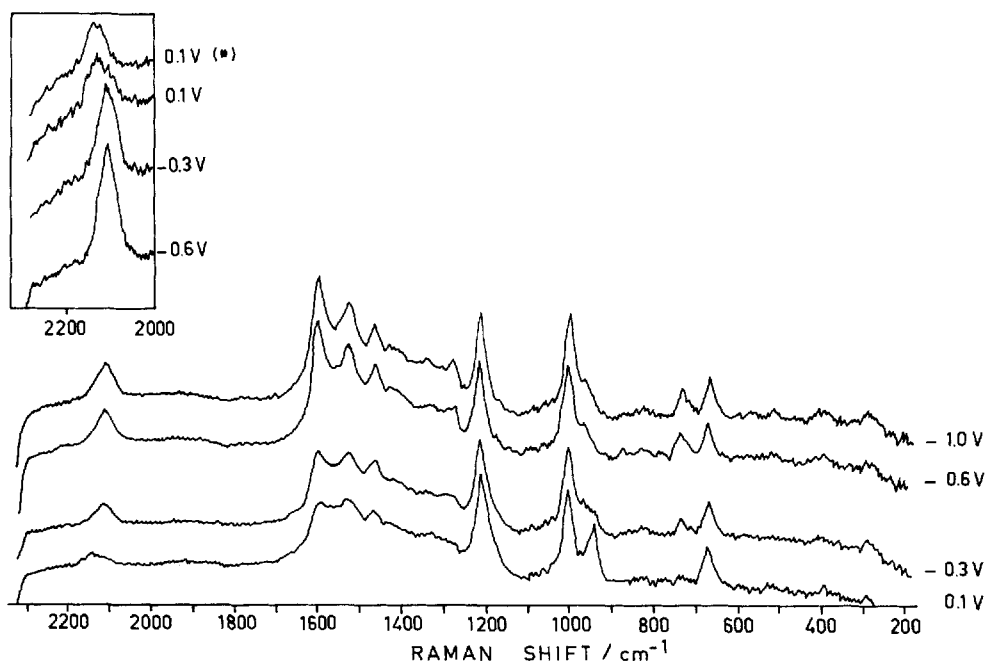


Figure 4. SER spectra at a silver electrode of 5×10^{-4} M $[\text{Fe}_2(\text{CN})_{10}(4\text{-picam})]^{8-}$ in borate buffer solution (pH 8.4) at the indicated potentials (*: 0.1 V after 30 s). $\lambda_L = 514.5$ nm.

band moves towards 2141 cm^{-1} . It can be seen in the voltammogram in Fig. 2 that at this potential the oxidation of the complex starts, forming the species $[\text{Fe}^{\text{III}}(\text{CN})_5(4\text{-picam})\text{Fe}^{\text{II}}(\text{CN})_5]$. It was not possible to obtain the SER spectrum at the second oxidation potential owing to the simultaneous oxidation of the silver electrode.

Bands of the binuclear complex spectra show a different behaviour to those of the mononuclear complex and free ligand with respect to the variation in the relative intensities. Whereas for the mononuclear complex and free ligand the bands at 1605 , 1525 and 1465 cm^{-1} show significant variations of their relative intensity with the applied potential, the same does not hold for the binuclear complex. These results suggest that the

mononuclear complex and the free ligand adsorbed on the electrode can change their orientation with respect to the surface with the applied potential whereas the binuclear complex forms a less flexible adsorption structure.

Using SER spectroscopy it has been possible to characterize the oxidation and reduction forms of $[\text{Fe}(\text{CN})_5(4\text{-picam})]^{3-}$ and $[\text{Fe}_2(\text{CN})_{10}(4\text{-picam})]^{6-}$ complexes.

Acknowledgements

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REFERENCES

1. S. Sinha, B. D. Humphrey and A. B. Bocarsly, *Inorg. Chem.* **23**, 303 (1984).
2. S. Sinha, B. D. Humphrey, E. Fu and A. B. Bocarsly, *J. Electroanal. Chem.* **162**, 351 (1984).
3. G. A. Arbuckle, Y. Chen, C. Hidalgo-Luangdilok and A. Bocarsly, *Solid State Ionics* **32/33**, 941 (1989).
4. P. A. M. Williams and P. J. Aymonino, *Inorg. Chim. Acta* **113**, 37 (1986).
5. P. A. M. Williams and P. J. Aymonino, *Transition Met. Chem.* **11**, 213 (1986), and references cited therein.
6. H. E. Toma and J. M. Malin, *Inorg. Chem.* **12**, 1039 (1973), and references cited therein.
7. M. Li Mihailovic, A. Stajilković and V. Andrejević, *Tetrahedron Lett.* **461** (1961), and references cited therein.
8. J. R. Bertolino, M. L. A. Temperini and O. Sala, *J. Raman Spectrosc.* **20**, 725 (1989).
9. M. J. Weaver, S. Farquharson and M. A. Tadայyoni, *J. Chem. Phys.* **82**, 4867 (1985).
10. J. A. Chambers and R. P. Buck, *J. Electroanal. Chem.* **163**, 297 (1984).
11. R. P. Van Duyne and J. P. Haushalter, *J. Phys. Chem.* **87**, 2999 (1983).
12. J. R. Bertolino, C. O. Della Vedova and O. Sala, *Polyhedron* **8**, 361 (1989).
13. H. R. Virdee and R. E. Hester, *J. Phys. Chem.* **88**, 451 (1984).
14. A. M. Stacy and R. P. Van Duyne, *Chem. Phys. Lett.* **102**, 365 (1983).
15. S. Farquharson, P. A. Lay and M. J. Weaver, *Spectrochim. Acta, Part A* **40**, 907 (1984).
16. S. Farquharson, K. L. Guyer, P. A. Lay, R. H. Magnuson and M. J. Weaver, *J. Am. Chem. Soc.* **106**, 5123 (1984).
17. S. L. F. A. da Costa, S. M. L. Agostinho and J. C. Rubim, *J. Electroanal. Chem.* **295**, 203 (1990).
18. M. Moskovits, *Rev. Mod. Phys.* **57**, 783 (1985).
19. R. Joeckle, E. D. Schmid and R. Mecke, *Z. Naturforsch., Teil A* **21**, 1906 (1966).
20. M. G. Giorgini, M. R. Peletti, G. Paliani and R. S. Cataliotti, *J. Raman Spectrosc.* **14**, 16 (1983).
21. V. I. Berzin and M. D. Elkin, *Opt. Spectrosc.* **34**, 395 (1973).
22. S. C. Sun, I. Bernard, R. L. Birke and J. R. Lombardi, *J. Electroanal. Chem.* **196**, 359 (1985).
23. H. Chang and K.-C. Hwang, *J. Am. Chem. Soc.* **106**, 6586 (1984).
24. J. C. Rubim, PhD Thesis, Instituto de Química, Universidade de São Paulo (1985).
25. J. C. Rubim and O. Sala, *J. Mol. Struct.* **145**, 147 (1986).
26. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Wiley, New York (1986).
27. J. B. Billman and A. Otto, *Surf. Sci.* **138**, 1 (1984).