An *In situ* Raman Spectroscopic Study of Electrochemical Processes in Mercury–Solution Interphases

Alexandre G. Brolo, Marek Odziemkowski and Donald E. Irish*

Guelph–Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada

Electrochemical processes in the mercury–solution interphase were probed by *in situ* spectroelectrochemical micro-Raman spectroscopy. This is the first report of the *in situ* characterization of electrochemical processes for a pure mercury electrode by Raman spectroscopy. Mercury was oxidized in 0.1 M KClO₄ solution, in the presence and absence of pyridine. Raman spectra, at several applied potentials, of the soluble oxidation products present in the mercury/solution interphase were recorded. The aquated Hg²⁺ [mercury(I)] cation was the only product observed for mercury oxidation in the absence of pyridine. This cation was characterized by the Hg–Hg stretch band at ca. 175 cm⁻¹. An Hg³⁺–ClO₄⁻ precipitate was formed on the electrode surface at very anodic potentials. The oxidation of mercury in the presence of pyridine resulted in the formation of soluble mercury(II)–pyridine complexes in the interphase. Characteristic Raman bands of these complexes were observed at ca. 1023 and 1048 cm⁻¹. Solution Raman experiments demonstrated that a mixture of mercury(II)–pyridine complexes [of general formula Hg(py)ₙ²⁺, where 1 < n < 4] was produced in the interphase. © 1998 John Wiley & Sons, Ltd.

INTRODUCTION

The *in situ* characterization of species in the metal–solution interphase can be achieved by surface-vibrational spectroscopy.¹⁻⁴ Surface Raman spectroscopy is probably the most powerful among the vibrational techniques for the *in situ* study of electrochemical processes in aqueous solutions. The weak Raman activity from water allows the spectro-electrochemical studies to be carried out in aqueous solution with minimum solvent interference. However, the intrinsic inefficiency of the Raman effect (only 1 in 10⁶ incident photons result in Raman scattering) is a major limitation for its application to the study of species generated at the metal–solution interface. Nevertheless, there are enhancement mechanisms that, when operative, increase the Raman cross-section by several orders of magnitude.⁵ Surface-enhanced Raman scattering (SERS) is one of these mechanisms. In this case, an unusually high intensity Raman spectrum is obtained from molecules adsorbed on certain rough metallic surfaces (mainly Ag, Cu and Au).⁶ The majority of the *in situ* Raman studies of species adsorbed on electrode surfaces have been performed using the SERS technique; consequently, they are restricted to those SERS-active metal surfaces. Recently, with the advent of a new generation of highly sensitive Raman spectrometers, Raman scattering from molecules adsorbed on ‘smooth’ polycrystalline⁷ and single crystal⁸ electrodes has been observed. It is also possible to obtain spectra from molecules adsorbed on unusual SERS substrates, such as platinum and nickel,⁹ using these new Raman systems.

Mercury is the most studied working electrode. The electrochemical behaviour of mercury in several media has been studied.¹⁰ However, few *in situ* spectroscopic observations of electrochemical processes in the mercury interphase have been reported.¹¹⁻²¹ The experimental difficulties of dealing with a liquid electrode in the spectroelectrochemical cell are probably the main limitation for these kinds of study. Most of the spectro-electrochemical measurements on mercury which have been reported utilized a deposit of mercury in a solid electrode matrix, rather than the pure metal.¹¹⁻¹⁵ For instance, UV–visible absorption and transmission spectroelectrochemical measurements have been reported for electrode processes on the Hg–Pt optically transparent electrode (OTE),¹¹⁻¹² Hg–Au and Hg–Ni minigrid electrodes¹³,¹⁴ and mercury thin films deposited on Pt electrodes.¹⁵ An *in situ* Fourier transform IR study of the electroreduction of flavin adenine nucleotide (FAD) on an Hg–Au electrode has been reported.¹⁶ *In situ* spectroelectrochemical experiments using pure mercury as the working electrode are much less common.¹⁷⁻¹⁹ A pure bubble mercury electrode has been used to study organic radical formation by electrode spin resonance.²⁰ A study of electron transfer involving organic compounds using *in situ* spatially resolved UV–visible spectroscopy to monitor a spherical mercury electrode has recently been conducted.²¹ The potential-dependent reorientation of isoquinones at a stationary mercury electrode has also been probed by...
subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS).\(^{19}\) Raman spectra from mercury deposited on Pt\(^{20}\) and Au\(^{21}\)-solution interphases have been reported. The mercury-deposited electrodes utilized in these Raman experiments were prepared in order to take advantage of any increase in the signal from the adsorbate by SERS. We are not aware of any report of the direct observation of electrochemical processes in a pure mercury electrode–solution interphase by Raman spectroscopy.

The objective of this work was to introduce a new micro-Raman spectroelectrochemical set-up that can be used for the *in situ* characterization of the mercury–solution interphase. Both soluble species in the interphase and film formation on the electrode surface can be detected by this technique. Mercury oxidation in aqueous KClO\(_4\) solutions, in the presence and absence of pyridine, was investigated as a first example.

**EXPERIMENTAL**

**Solutions**

All solutions were prepared using Milli-Q water. Electrochemical and Raman measurements were made on solutions containing 0.1 M KClO\(_4\), with and without pyridine. The KClO\(_4\) was purified by calcinating at 300°C, recrystallizing twice from Milli-Q water and then drying. Analytical-grade pyridine from BDH was used without further purification.

**Cell and electrodes**

A three-electrode spectroelectrochemical cell previously used for micro-Raman studies of the lithium–organic electrolyte interphase\(^{22}\) was modified, as shown in Fig. 1. An Ag/AgCl|Cl\(_{sat}\) reference electrode was used. The reference electrode was sealed into a Luggin capillary by means of a Teflon plug (TP) and O-ring. To avoid any possible contamination of the electrode by Cl\(^-\) ions, the Luggin capillary ended with a second glass-sealed asbestos frit. A platinum ring (Pt) sealed into glass was used as the counter electrode. The counter electrode was isolated from the working solution by a porous glass frit. The working electrode was assembled by filling a 2 mm glass capillary (GC) with Hg. The area of the capillary exposed to the electrolyte was flat polished, while the second end terminated in an internally threaded glass connector (ITGC). Electrical contact to the mercury working electrode was made by a stainless-steel rod (SSR), terminating in an externally threaded rod (ETR). In this way, the working electrode was sealed into the main cell body by a Kalrez O-ring. One filling of the glass capillary usually allowed 4–6 independent measurements on fresh Hg half drops to be performed. The assembled cell was purged with ultra-pure N\(_2\). The solution was then injected into the cell through the injection port (Fig. 1) and further deaerated for 15 min.

**Instrumentation**

The spectroelectrochemical cell was connected to an EG&G PAR Model 273 potentiostat/galvanostat interfaced to a PC operated by M270 version 4.1 electrochemical software. Raman spectra were obtained with a Renishaw 1000 Raman microscope system. The instrument consists of an Olympus microscope, a single spectrograph fitted with holographic notch filters for the spectroscopy mode and an 1800 grooves mm\(^{-1}\) holographic grating and a Peltier-cooled CCD detector. The optical throughput of the instrument is high, as is its sensitivity. The detection of a very weak signal (1 photon s\(^{-1}\)) is therefore possible. Excitation was achieved using 632.8 nm line radiation from a Melles Griot 35 mW He–Ne laser. All Raman measurements were carried out using the backscattering geometry. The long-working-length objective lens, used in the spectral analysis, was essential for the backscattering geometry.
studies, has an objective magnification of 50 x. The high sensitivity of the Raman system permits the locations of the Hg electrode to be further away from the optical window (OFW), allowing the Luggin capillary to be situated 2 mm from the Hg working electrode.

Test for impurities

The Hg half-drop was subjected to continuous cleaning cycles between the limits +0.1 and −1.0 V at 20 mV s⁻¹. This cycling persisted until a cyclic voltammogram reproduced itself; this was usually achieved after the second cycle. No peaks characteristic of oxygen reduction were observed, indicating proper deaeration of the electrolyte.

RESULTS AND DISCUSSION

Oxidation of mercury in 0.1 M KClO₄ aqueous solution

Figure 2 shows the cyclic voltammogram for a mercury electrode in 0.1 M KClO₄ solution (at 20 mV s⁻¹). The curve shows that the mercury electrode was very stable in this medium. Oxidation started to occur at ca. +0.8 V. An anodic peak, formed at ca. +1.2 V, and the anodic current remained practically constant until ca. +1.6 V. The current rose very sharply after this potential. A cathodic peak at +1.4 V was observed in the reverse scan (Fig. 2).

The in situ surface micro-Raman spectra from the mercury electrode in 0.1 M for several applied potentials, are presented in Fig. 3. It is important to point out that no surface-enhancement contribution is expected from a smooth liquid mercury electrode. A peak at ca. 175 cm⁻¹ was first observed when the potential was set to +0.8 V. The intensity of this peak increased as the potential became more positive. Only bands due to perchlorate anion in the solution were observed in other spectral regions.

The oxidation of mercury may yield either mercury(I) or mercury(II) derivatives. Mercury(I) exists as a diatomic cation (Hg₂²⁺), and it is the oldest known and most common of the metal polycations. Mercury(I) cation is barely stable in aqueous solution, and can readily disproportionate into metallic mercury and mercury(II), according to the equation:

\[
\text{Hg}_2^{2+} \rightarrow \text{Hg} + \text{Hg}^{2+}
\]

Therefore, any species that decreases the concentration of free mercury(II), by complexation or precipitation, causes the equilibrium to shift in favour of the disproportionation.

The oxidation of mercury in non-complexing media (perchlorate is a weak ligand) has been reviewed and mercury(I) was found to be the predominant species in these situations. Therefore, we can assign the 175 cm⁻¹ band, presented in Fig. 3, as an Hg–Hg stretch vibration of the electrochemically formed aquated cation [Hg₂(aq)²⁺], present in the diffusion layer (i.e. in the solution, not adsorbed on the electrode). A normal Raman spectrum of 0.01 M Hg₂(NO₃)₂ solution was also measured for comparison. A band at ca. 180 cm⁻¹ was observed from the Hg₂(NO₃)₂ aqueous solution, which confirmed the assignment for the potential-dependent peak presented in Fig. 3. In fact, the Hg–Hg stretching wavenumber appears in all mercury(I) compounds, and it can be easily observed by Raman spectroscopy. The wavenumber for this Hg–Hg mode ranged between 113 and 207 cm⁻¹, depending on the strength (or the electronegativity) of the ligand bound to the mercury(I) cation. The position of this Raman band has been correlated with the Hg–Hg interatomic distance in different mercury(I) compounds.

When the applied potential was stepped to +2.0 V, the amount of mercury(I) formed was very high, and the solubility limit of mercury(I) perchlorate salt was attained. The in situ unenhanced Raman spectrum of the precipitate formed on the electrode surface was recorded and is presented in Fig. 4. Note that in the case of the film formation, the spectral features correspond mainly to the species adsorbed on the electrode surface. The Raman wavenumbers and assignments are presented in Table 1. Multiple bands for both the Hg–Hg (around 180 cm$^{-1}$) and the ClO$_4^-$ (around 930 cm$^{-1}$) stretching regions are present. The 175 and 934 cm$^{-1}$ bands are from the solution, and the 192 and 924 cm$^{-1}$ bands correspond to the Hg–Hg and ClO$_4^-$ stretching modes, respectively, in the solid phase. The shoulders at 187 and 908 cm$^{-1}$ may be due to some distortion in the structure of the precipitate. The ClO$_4^-$ ion has $T_d$ symmetry, and the coordination of this ion with metal should decrease its overall symmetry to either $C_{3v}$ (undentate complex) or $C_{2v}$ (bidentate or bridged complex). These direct consequences of the symmetry lowering would be a split in the $v_2$, $v_3$ and $v_4$ ClO$_4^-$ modes. These splits were not observed in Fig. 4 (except for a weak shoulder on $v_3$ at 1075 cm$^{-1}$), which indicates that the effect of the Hg$^{2+}$ cation on the perchlorate ion is very small. Other Raman bands, which are possibly not due to ClO$_4^-$ vibrations, are observed at 221, 365, 433 and 502 cm$^{-1}$. These low-wavenumber bands can be tentatively assigned to the aquamercury(I) complex. Perchlorate is a poor ligand, hence it is plausible that the solid is a hydrate containing Hg$_2$(H$_2$O)$_2^{2+}$ aqua cations. In fact, a weak, but defined, peak was observed at 3486 cm$^{-1}$, which is characteristic of the H–O stretch of water of hydration in solids. The coordinated water may exhibit other modes in the low-wavenumber region. Normal coordinate analyses have been performed on aquo complexes of metals containing both four ($D_{4h}$ symmetry) and six ($T_h$ symmetry) waters of hydration.

---

### Table 1: Vibrational wavenumbers ($\tilde{\nu}$) and assignments for mercury perchlorate deposited on a mercury electrode

<table>
<thead>
<tr>
<th>$\tilde{\nu}$ / cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>$\tilde{\nu}$ Hg–Hg</td>
</tr>
<tr>
<td>187</td>
<td></td>
</tr>
<tr>
<td>192</td>
<td></td>
</tr>
<tr>
<td>221</td>
<td>$\nu_{\text{sym}}$ Hg–OH$_2$ (?)</td>
</tr>
<tr>
<td>365</td>
<td>$\nu_{\text{sym}}$ Hg–OH$_2$</td>
</tr>
<tr>
<td>433</td>
<td>$\rho_\omega$ (H$_2$O)</td>
</tr>
<tr>
<td>459</td>
<td>$v_3$ ClO$_4^-$</td>
</tr>
<tr>
<td>502</td>
<td>$\rho_\omega$ (H$_2$O)</td>
</tr>
<tr>
<td>624</td>
<td>$v_4$ ClO$_4^-$</td>
</tr>
<tr>
<td>908</td>
<td>$\nu_1$ ClO$_4^-$</td>
</tr>
<tr>
<td>924</td>
<td></td>
</tr>
<tr>
<td>934</td>
<td></td>
</tr>
<tr>
<td>1076</td>
<td>$v_3$ ClO$_4^-$</td>
</tr>
<tr>
<td>1102</td>
<td></td>
</tr>
<tr>
<td>3486</td>
<td>$\nu$ H$_2$O (lattice)</td>
</tr>
</tbody>
</table>

---

Oxidation of mercury in 0.1 M KClO$_4$ aqueous solution in the presence of pyridine

Cyclic voltammograms of mercury in 0.1 M KClO$_4$ and 0.05 M pyridine (py) are shown in Fig. 5. These voltammograms were obtained for different switching potentials ($E_s$) and at a sweep rate of 20 mV s$^{-1}$. First, one can observe that the mercury oxidation started at potentials more negative than in the absence of py (Fig. 2). This is an indication that py forms complexes with the mercury oxidation products. The stability constants of Hg$^{2+}$–py complexes have been reported. The return sweep, presented in Fig. 5, shows a convoluted cathodic peak, which indicates the reduction of more than one oxidation product. The cathodic peak shifted to more negative potentials as the anodic limit was made more positive. The anodic current in the reverse scan was always higher than the current at the switching potential (in the anodic part of the voltammogram). This behaviour suggests that the surface was blocked.

---

**Figure 4.** In situ Raman spectra of mercury– perchlorate precipitate, formed during mercury oxidation at +2.0 V. Spectrum obtained using a 10 s acquisition time and 10 accumulations. The insets show enlargements of the regions between 120 and 230 cm$^{-1}$ and between 900 and 950 cm$^{-1}$. The wavenumbers in cm$^{-1}$ for the main Raman bands are indicated.

**Figure 5.** Cyclic voltammograms of a mercury electrode in 0.1 M KClO$_4$ and 0.05 M pyridine solution for several reverse potentials. Scan rate, 20 mV s$^{-1}$. Note that the anodic current in the forward scan is smaller than the anodic current in the reverse scan.
during the forward scan. Pyridine adsorbs on a mercury surface at negative potentials, and a significant amount of py may remain on the surface at positive potentials. In this case, py would remain adsorbed on the electrode during the mercury oxidation in the forward scan, blocking the surface for the anodic dissolution process. As mercury dissolution occurs, the pyridine molecules are expelled from the surface; they are consumed to form soluble Hg$_2^{2+}$–py complexes (see below). Therefore, in the reverse scan, the anodic dissolution current is always larger than in the forward scan. One would expect that this effect should be minimized in a steady-state type of experiment, because, in this case, the equilibrium $p_{\text{py(ads)}} \Leftrightarrow p_{\text{py(sol)}}$ would have time to be established at each potential. This prediction is confirmed by Fig. 6, which shows the cyclic voltammograms for the same conditions as in Fig. 5, but swept at 0.02 mV s$^{-1}$ (steady-state situation). In this case, the forward and reverse curves are superimposed. Experiments for different switching potentials also yielded superimposed curves. An anodic peak at ca. +0.5 V is present in Fig. 6, but no cathodic peak was observed at this slow scan rate. Both the absence of the cathodic reduction peak and the superimposition of forward and reverse polarization curves in the steady-state experiment indicate that oxidation products or a surface film (if formed) are soluble.

Figure 7 shows the in situ unenhanced micro-Raman spectra of the mercury–solution interphase for several applied potentials. Only three Raman bands are observed at +0.3 V [Fig. 7(a)]. The oxidation of the mercury electrode has not started at this potential (Fig. 6). These peaks can be assigned to the ClO$_4^-$ stretch at 934 cm$^{-1}$ and to the ring breathing and the ring stretching py modes at 1002 and 1034 cm$^{-1}$, respectively, from the diffusion layer. As the potential was made more positive mercury oxidation commenced and new peaks at 1023 and 1048 cm$^{-1}$ were observed [Fig. 7(b)–(d)]. The intensities of these two new peaks increased with increasing potential at the expense of the py bands. After recording the spectrum at +0.6 V [Fig. 7(d)], the applied potential was stepped down to +0.4 V. The spectrum obtained at this potential [Fig. 7(e)] reproduces that obtained at +0.4 V on the forward sweep [Fig. 7(b)]. This is a confirmation that the Raman signals presented in Fig. 7 originated from the mercury–solution interphase and not from the bulk solution; the voltage dependence suggests that the species is near the electrode, but the solubility of the species suggests that they are unlikely to be specifically adsorbed. It is known that the ring modes of pyridine in the 1000 cm$^{-1}$ region are sensitive to the coordination of the N electron lone pair by a Lewis acid. For instance, it has been observed, in a previous SERS study of the adsorption of py at different pH values on silver electrodes, that the protonation of the py’s nitrogen (which yields the pyridinium cation, pyH$^+$) shifts these ring bands to 1011 and 1027 cm$^{-1}$, respectively. These results strongly indicate that the two new bands observed from the mercury–solution interphase during the mercury oxidation can be assigned as the modes 1 (ring breathing) and 8 (ring stretching) of py coordinated with a mercury cation. Further experiments involving mixing py and Hg(NO$_3$)$_2$ aqueous solutions were performed. The objective of these experiments was to confirm that the oxidation product was a soluble Hg$_2^{2+}$–py complex.

Figure 6. Cyclic voltammograms of a mercury electrode in 0.1 M KClO$_4$ + 50 mM pyridine solution with several reverse potentials. Scan rate, 0.02 mV s$^{-1}$ (steady-state situation). The curves for different reverse scans are superimposed on each other.

Figure 7. In situ Raman spectra of a mercury–solution interphase at several potentials. Solution, 0.1 M KClO$_4$ + 50 mM pyridine. Each spectrum was obtained using a 10 s acquisition time and 10 accumulations. Potentials: (a) +0.3; (b) +0.4; (c) +0.5; (d) +0.6; (e) +0.4 V. The position of the peaks due to the mercury–pyridine complexes are marked with asterisks.

[and not a mercury(I)–py derivative], and to estimate the speciation in the mercury/solution interphase.

Normal Raman spectra for 0.05 M py aqueous solution containing di†erent amounts of are pre-Hg(NO$_3$)$_2$ presented in Fig. 8. No precipitation was observed in the preparation of the solutions used to generate the data presented in Fig. 8, indicating that the Hg$^{2+}$–py complexes are soluble. This observation conÐrms that no solid surface Ðlm had been formed during the mercury electro-oxidation. The spectra in Fig. 8 are in good agreement with those obtained in Fig. 7. The ‘free’ aqueous py and the Hg$^{2+}$–py complex bands can be observed in both Figs 7 and 8 at the same positions.

The method of continuous variations was used to determine the composition of the Hg$^{2+}$–py complexes in the interphase. This method is a classical procedure to determine the stoichiometry of complexes. The procedure consisted of preparing a series of solutions in which the sum of the concentrations of the two reactants (Hg$^{2+}$ and py in our case) was kept constant (0.005 M) while the ratios of their concentrations di†ered from one solution to another. The Raman spectra of these solutions were recorded, and the area from the Hg$^{2+}$–py complex band (at ca. 1023 cm$^{-1}$) was obtained using band Ðtting procedures. The calculated area of this band (the stretching peak was usedClO$_4$~ as a reference) was plotted against the mole fraction of py in the solution, assuming that the area of the band is proportional to the amount of pyridine bound up in the complex. This graph, known as a Job plot, yielded a bell-shaped curve. The stoichiometry of the complex can be estimated from the mole fraction of py where the curve maximizes (see Refs 31 and 32 for a more detailed description). However, in the case of Hg$^{2+}$–py, a mixture of complexes is expected. It has been demonstrated that complexes of general formula Hg(py)$_n$$^{2+}$ (1 $\leq$ n $\leq$ 4) may be formed for mercury(II)-py mixtures.

Figure 9 shows the calculated amount of each Hg(py)$_n$$^{2+}$ complex for different mole fractions of py. The stability constants reported in Ref. 27 were used in this calculation. The amount of 1:1 complex is very small over all the range. The 1:2 (Hg:py) complex is the predominant species at high mercury mole fractions, and the 1:4 complex is the predominant species at high py mole fractions. However, the three species (1:2, 1:3 and 1:4 complexes) co-exist in signiÐcant amounts over all the range. The calculated result presented in Fig. 9 was conÐrmed experimentally. The experimental data for the normalized Raman intensity (area of the 1023 cm$^{-1}$ band divided by the area of the perchlorate stretch mode at 934 cm$^{-1}$) obtained for several Hg(NO$_3$)$_2$–py mixtures in 0.1 M KClO$_4$, prepared using the conditions described above for the method of continuous variations, are also presented in Fig. 9. The Raman intensities are compared with the

Figure 8. Raman spectra of aqueous 0.1 M KClO$_4$ solutions containing a mixture of pyridine and Hg(NO$_3$)$_2$. Each spectrum was obtained using a 5 s acquisition time and 10 accumulations. [py] = 50 mM in all spectra. [Hg(NO$_3$)$_2$] = (a) 8; (b) 14; (c) 27; (d) 33 mM. The 1048 cm$^{-1}$ band of NO$_3^-$ is marked with an asterisk.

Figure 9. Calculated concentrations of each Hg$^{2+}$–py complex in aqueous solutions with different mole fractions of py (Job plots). Stability constants used in the calculation (from Ref. 27): $\beta_1$ = 5.1; $\beta_2$ = 4.9; $\beta_3$ = 9.3; $\beta_4$ = 0.3. A comparison between the relative integrated intensity of the ca. 1026 cm$^{-1}$ band, due to the Hg$^{2+}$–py complexes (®lled squares), obtained from the Raman spectra of Hg(NO$_3$)$_2$–py aqueous solutions with different compositions, and the sum of the calculated amount of all py species (dashed line) is also presented.
sum of the calculated amounts of $\text{Hg}^{2+}$-py species in solution (sum of the calculated concentrations of all complexed py at a given mole fraction of py in solution). The experimental points correlate very well with the calculated curve, as can be seen in Fig. 9, indicating that the normal Raman data are in good agreement with the calculated equilibrium constants presented in Ref. 27. The result also shows that the ca. 1023 cm$^{-1}$ band contains contributions from all complexed py species in solution. The amount of py in the mercury–solution during the in situ Raman measurements must be much higher than the amount of $\text{Hg}^{2+}$-cation (mainly from the beginning of the oxidation curve); therefore, the mole fraction of py must be close to unity in this situation. Hence we can conclude that the peak of complexed py formed in situ arises from a mixture of $\text{Hg}^{2+}$-py complexes, where the 1:4 component is the predominant species.

**CONCLUSION**

The unenhanced Raman spectrum of the pure mercury–solution interphase was obtained in situ for the first time. The electro-oxidation of mercury in perchlorate medium, in the absence and presence of pyridine, was studied. The electrochemically generated $\text{Hg}^{2+}$ species was formed in the absence of pyridine. The oxidation of mercury in the presence of pyridine results in the formation of a mixture of $\text{Hg}^{2+}$-py complexes. The composition of these complexes in the interphase was estimated by normal Raman spectroscopy. Comparison between the integrated area of the bound py with the calculated speciation for different mole fractions of py indicates that a mixture of complexes was present in the interphase. The potential for the application of the technique to the study of other mercury electrode processes (such as the reduction of organic molecules on mercury electrodes and film formation processes) is enormous. Mercury is probably the most commonly used working electrode in electrochemical experiments. These electrochemical measurements can now be revisited with a powerful in situ spectroelectrochemical technique for characterization of the processes at a molecular level. However, it is important to point out that these preliminary results indicate that the electrochemical unenhanced Raman spectroscopic technique is still not sensitive enough to study non-faradaic processes (such as adsorption and reorientation).

**REFERENCES**