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THE EFFECTS OF THE UNDERPOTENTIAL AND OVERPOTENTIAL DEPOSITION OF LEAD AND THALLIUM ON SILVER ON THE RAMAN SPECTRA OF ADSORBATES

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ABSTRACT

It is shown that the underpotential deposition (UPD) and dissolution of monolayers of Pb and Tl onto Ag surfaces roughened in a controlled oxidation–reduction cycle produces a Ag surface which shows diminished surface enhanced Raman scattering (DSERS). Significantly enhanced Raman spectra can still be obtained from electrodes covered by complete UPD and overpotential deposited (OPD) layers of the metals. Correct choice of electrolytes for the UPD of the metals reduces the loss of enhanced Raman scattering; chloride ions, constituents of many electrolytes used in the investigation of surface enhanced Raman scattering (SERS), are shown to be especially active in causing the loss of SERS.

INTRODUCTION

The effects of the deposition of thin films of metals on Surface Enhanced Raman Scattering (SERS), has been investigated for a number of systems including the underpotential deposition (UPD) of submonolayer and monolayer quantities of Pb, Tl, Cu and Cd [1–5] and the vapour phase deposition of Pd and Al on Ag [6–8]. The effects of the deposition of such foreign metals on the "tell-tale" adsorbate pyridine has been widely used as a probe of these systems. These investigations have led to the general conclusions that:

(a) deposition of the foreign metals reduces markedly or eliminates the spectrum of the adsorbate,

(b) only a small proportion of the original SER signal can be regenerated by the anodic removal of the UPD layers; in some cases none of the original signal is recovered.

The aim of most of these investigations has been the testing of the various proposed mechanisms of SERS. The design and interpretation of such experiments must take into account numerous factors including:

(i) UPD layers may remove SERS active sites either by displacing adatoms and/or clusters of the SERS active substrate or by catalysing the recrystallisation of the microstructure of this metal: the removal of these sites and/or the recrystallisation of the SERS substrate could be inhibited by strong adsorption of ionic or neutral species,

(ii) statements about the effects of the deposition and removal of UPD layers depend both on the surface treatment used in first generating SERS and on the sensitivity of the spectroscopic instrumentation,

(iii) the bonding of the absorbate (e.g. pyridine) to the surface may be markedly modified by thin film deposits (e.g. by the deposition of a sp- on a d-metal),

(iv) the optical properties of the electrode and therefore the extent of the electromagnetic enhancement of scattering will be changed by the deposition of thin films.

Interpretations of the effects of such surface modifications of SERS have been based on (i) and (iv). However, in our view the interplay of all the factors (i) to (iv) is illustrated by a comparison of several results obtained so far. Thus the quenching of the signal due to pyridine by the UPD of Tl is virtually complete whereas the signal is only partially quenched for the UPD of Pb [5] (effects (i) and (iii)); in fact the deposition of submonolayer amounts of Tl can quench the SERS of pyridine (effect (i)) but by contrast the Raman spectrum of the strongly adsorbed species benzotriazole (BTA) is only partially quenched by the deposition of this metal (effects (ii) and (iii)); vapour phase deposition of monolayer amounts of Ag on a Ag–Pd substrate leads to the regeneration of SERS (effects (iii) and (iv)) [6-8].

It is well known that the final stage of UPD is the complete coverage of low index faces such as of Ag (111) and (100) by incommensurate close-packed layers of the UPD metal [9,10]. In this paper we show that controlled roughening of Ag electrodes leads to the development of a low index faceted structure; deposition and removal of UPD deposits leads to the generation of a stable substrate showing Diminished Surface Enhanced Raman Scattering (DSERS). We extend measurements of the effects of the UPD of Tl in the presence of BTA and pyridine, compare the effects of the UPD of Pb on the spectra of acetate ions and pyridine and show that the results for both metals are dependent on the nature of all anionic species present. Retention of significantly enhanced Raman spectra on fully formed UPD layers leads to new strategies for the design of electrodes consisting of relatively thick films of metals deposited on SER or DSER substrates which show enhanced Raman spectra for the deposited metal. In this paper we report measurements for overpotential deposits of Pb and Tl on Ag. In succeeding papers we report *inter alia* on spectra for Ni, Co and Zn deposited on Ag and compare these spectra to those for Cu on Ag [11]; we show further that it is possible to induce strong Raman scattering e.g. for Ni by depositing this metal on smooth Ag which does not give SERS before this deposition [12].

EXPERIMENTAL

The cells used in the Raman spectroscopic studies and the associated electronics have been described previously [13]. In these cells the flat working electrodes can be placed in contact with optically flat windows, thereby forming a thin layer cell to minimise the solution volume sampled by the laser beam as well as minimising contact with the bulk of the solution in the cell. Spectra were obtained using a modified Coderg T800 spectrometer having an additive triple dispersion monochromator. Samples were excited using a Coherent Radiation Model 52G Argon ion laser. Radiation was filtered, prior to use, by a premonochromator. The laser was operated normally at 514.5 with ~ 70 mW power at the sample. The Raman signals were processed by a Brookdeal Ortec 5C1 photon scalar counting system using a bandpass of 5 cm^{-1}, a counting time of 10^{-1} s and single scans to acquire the spectra.

Working electrodes were constructed from a 5 mm diameter Specpure polycrystalline silver rod (Johnson Matthey) and unfocussed radiation was used to minimise any possible photolysis. Activation of the silver electrodes was carried out through an ORC in 1 *M* KCl solution. The potential was pulsed to +0.15 V (SCE) for a time such that the reformation charge reached ~ 200 mC cm^{-2}; this was followed by a constant current reduction at 7.5 mA cm^{-2} which was terminated when the potential reached −0.25 V and the electrode was then maintained at this potential. Before activation the electrode was polished to a mirror finish using alumina powder of 0.05 μm average diameter.

Solutions were prepared using AnalaR grade reagents in triply distilled water. All potentials are quoted on the saturated calomel electrode scale (SCE).

RESULTS AND DISCUSSION

The effects of cathodic polarisation and of UPD of metals on the SERS of silver

The characteristics of UPD on roughened Ag surfaces prepared according to the procedure outlined in the experimental section are illustrated in Fig. 1 for one system, the deposition of Pb from acetate solutions. It can be seen that the surface area of the polished electrode is increased by a factor of ~ 2.2 by the roughening process. The most striking change in the cyclic voltammograms is the development of sharp deposition and dissolution peaks which are similar to those observed on well defined Ag (111) single crystal faces. The shape of the voltammograms is independent of the number of cycles and similar results are obtained for other solution compositions as well as for the UPD of Tl. It follows that the surface develops well defined (111) facets whereas the area of other crystal faces is small.

The silver surfaces roughened according to the procedure outlined in the Experimental Section show very strong SERS; cathodic polarisation at very negative potentials (e.g. −1.7 V for 10 min) diminishes the SERS intensity irreversibly. However, the residual intensity remains high compared to that obtained using other ORC procedures. The intensity of the DSERS signals produced from such cathodi-

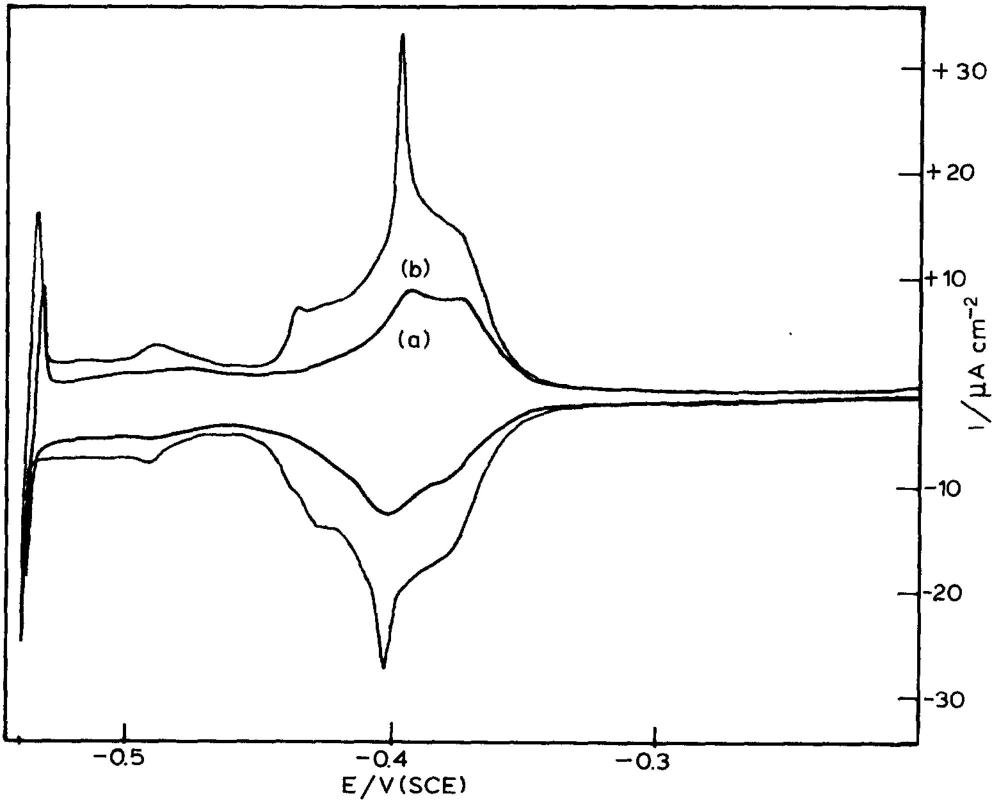

Fig. 1. Cyclic voltammograms for underpotential deposition of lead from a solution of 0.005 *M* $Pb(OAc)_2$, 0.01 *M* HOAc and 0.50 *M* NaOAc onto (a) a mechanically polished silver electrode, (b) an ORC roughened silver electrode; sweep rate 5 mV/s.

cally treated surfaces is relatively stable with time and to further cathodic polarisation. Successive deposition and dissolution of UPD layers of metals such as Pb or Tl produces some further decrease in the intensity of the Raman signals of the silver electrode. The effect of UPD alone is illustrated in Figs. 2a–c. The changes in intensity are reversible up to the onset of UPD, Fig. 2a, but UPD causes an irreversible loss of intensity following the first deposition/dissolution cycle; the intensities for subsequent cycles are essentially constant provided a complete layer is deposited in the first cycle. The enhanced Raman spectra produced by these surfaces have an intensity comparable to that of DSERS obtained by cathodic polarisation at very negative potentials (see above). Moreover, the intensities given by the UPD treated surfaces are stable with time; intensity changes with changes of potential are reversible, Fig. 2d, and also reversible to further underpotential and overpotential deposition and dissolution cycles. Cathodic polarisation of SERS surfaces at very negative potentials and UPD of Pb from acetate solutions therefore produce similar changes in the roughened silver surfaces, presumably by the

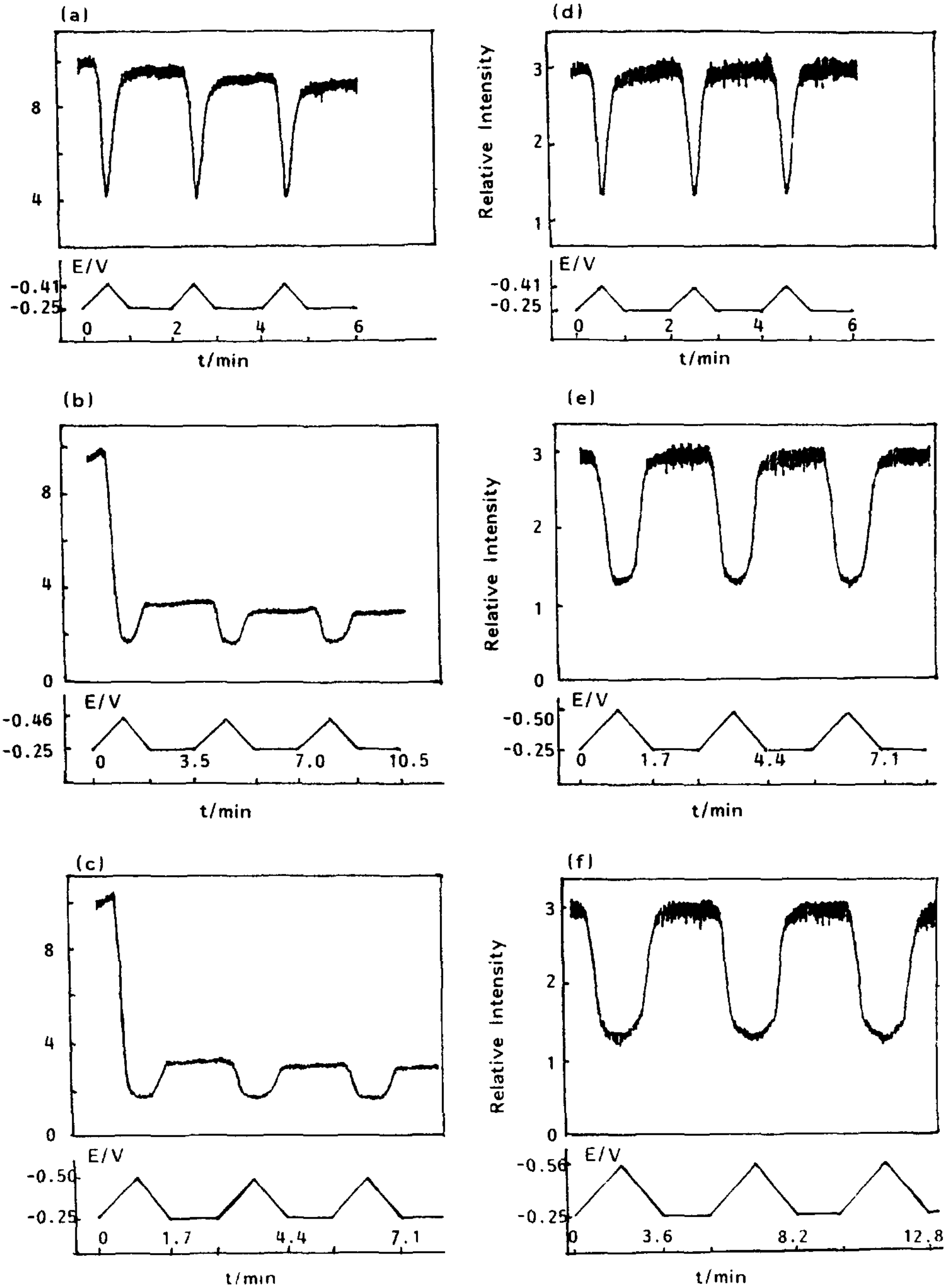

Fig. 2. Irreversible potential dependence of the 1007 cm^{-1} ring breathing mode of pyridine in a solution of 0.005 *M* $Pb(OAc)_2$, 0.05 *M* Py and 0.20 *M* NaOAc for a silver electrode subjected to a controlled ORC (a–c). Reversible potential dependence of the 1007 cm^{-1} mode for an electrode previously treated with 3 underpotential deposition/dissolution cycles (d–f).

removal of adatoms or clusters of atoms of Ag which make a special contribution to the total intensity of the Raman signal.

In view of the stability of the DSERS signals from surfaces treated by the underpotential deposition/dissolution of metals, we have used such Ag substrates for all the measurements reported in the following sections.

The effects of the UPD and OPD of Pb on the Raman spectra of adsorbed species

The effect of the UPD of Pb on the Raman spectra of acetate ions adsorbed on Ag substrate electrodes is illustrated in Fig. 3. At the most positive potentials, the

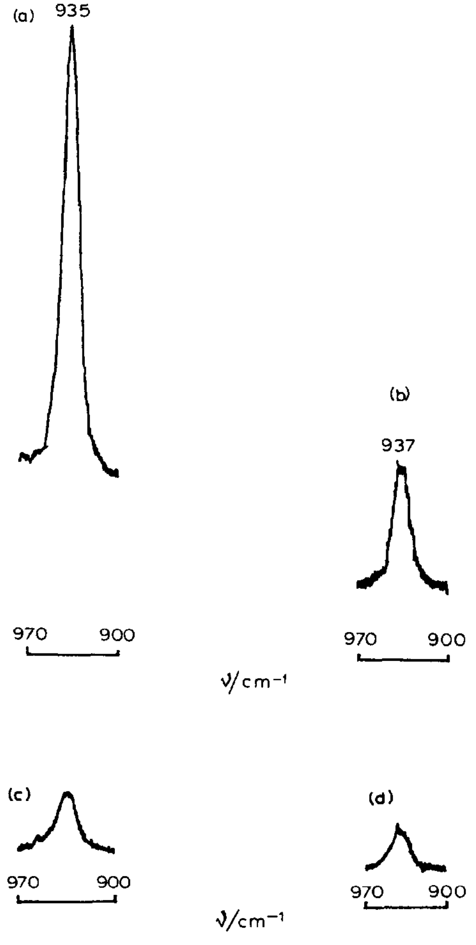

Fig. 3. The ν_4 mode of OAc^- for adsorption on a roughened silver electrode in a solution of 0.005 *M* $Pb(OAc)_2$, 0.01 *M* HOAc and 0.50 *M* NaOAc at (a) −0.25 V, (b) −0.47 V, (c) −0.55 V and (d) −0.55 V after 10 min.

SERS of adsorbed acetate on Ag is observed (the strongest ν_4 band is illustrated in Fig. 3 [14,15]). The main effect of increasing coverage by Pb in the UPD region is the decrease in the intensities of all bands which nevertheless can still be clearly detected with our instrumentation even on completion of the UPD layer, Fig. 3b. A further marked change is the decrease in the background intensity and the associated background noise: this has been observed for all the other systems we have studied. Our observations of the retention of enhanced Raman signals in this system even for complete UPD layers may be contrasted with previous statements that UPD of such sp metals leads to the complete quenching of SERS (see e.g. ref. 1)

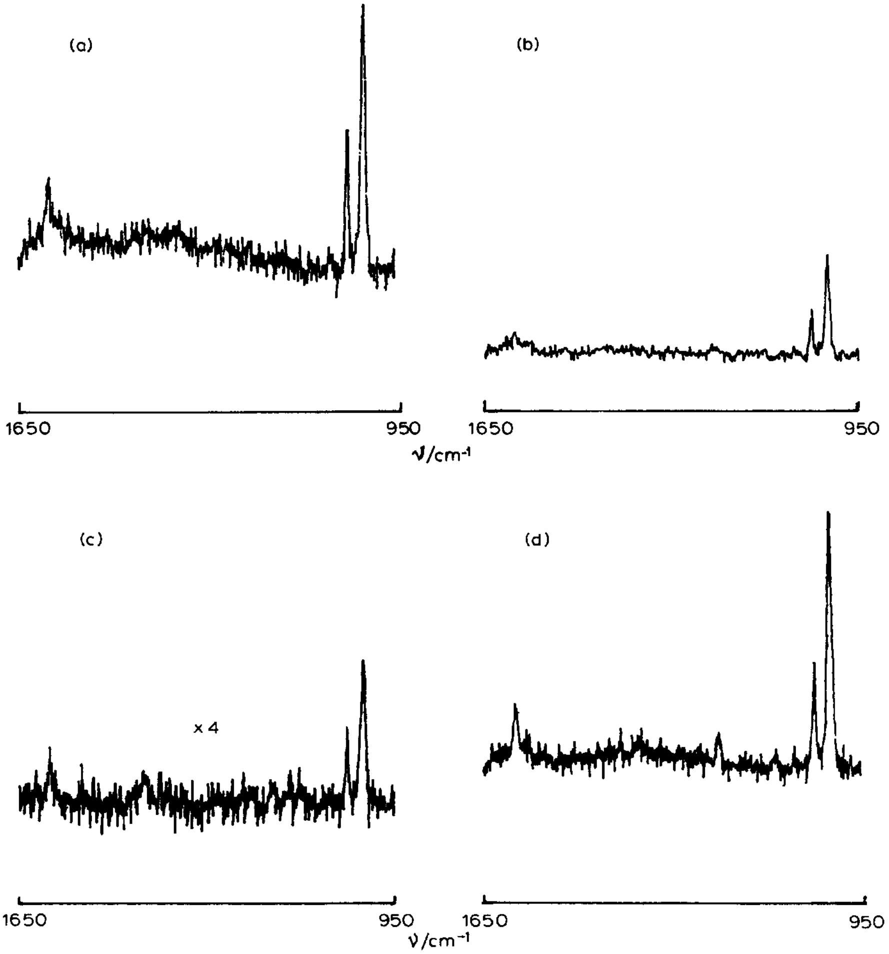

Fig. 4. Raman spectra of pyridine from a silver electrode roughened and processed by three cycles of deposition and dissolution of a monolayer of lead from −0.25 V to −0.50 V. (a) −0.25 V, (b) −0.48 V, (c) −0.54 V and (d) back to −0.25 V. Solution, 0.005 *M* $Pb(AOc)_2$, 0.05 *M* Py and 0.20 *M* NaOAc.

(see further below). Indeed enhanced Raman spectra are still observed on OPD layers, e.g. Fig. 3c. The intensity of these signals decreases progressively with increasing average thickness of the deposits, e.g. Fig. 3d.

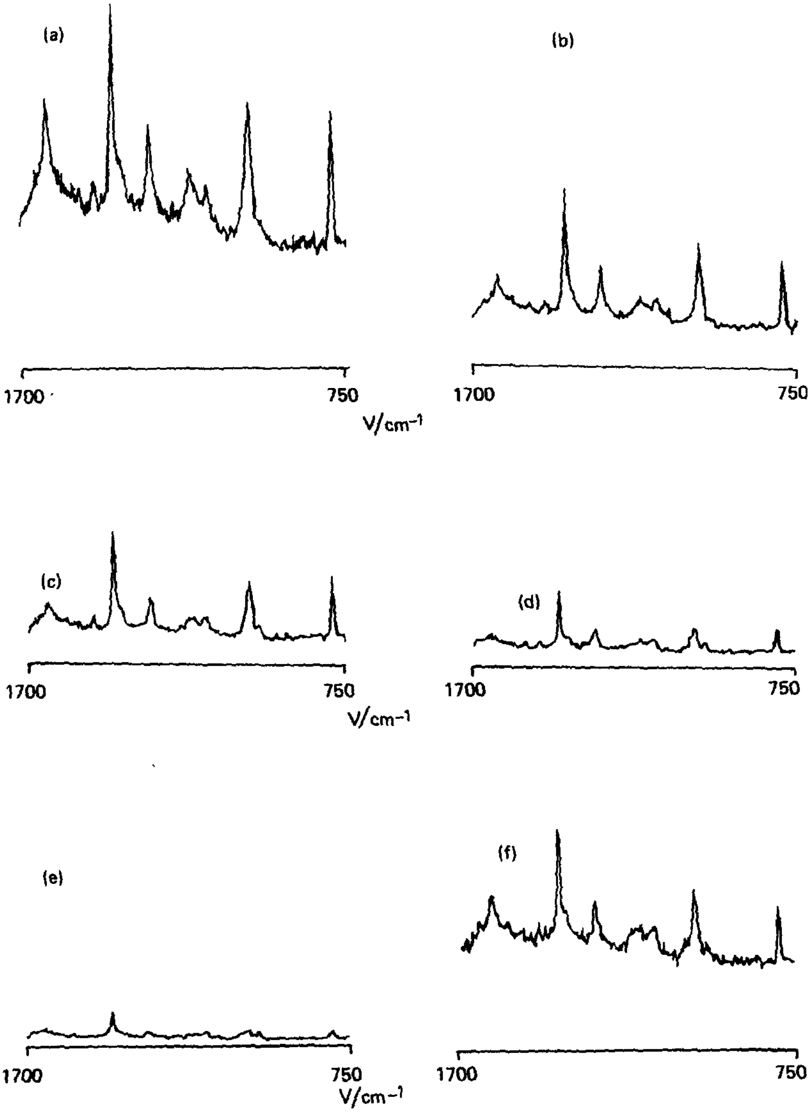

Fig. 5. Raman spectra of BTA from a roughened silver electrode treated by three cycles of deposition and dissolution of a monolayer of thallium from −0.25 V to −0.79 V. (a) −0.25 V, (b) −0.76 V, (c) −0.80 V, (d) −0.8 V, after 15 min, (e) after 38 min, and (f) −0.25 V. Solution of 0.001 *M* Tl_2SO_4, 0.001 *M* BTA and 0.10 *M* K_2SO_4.

The effects of the UPD and OPD of Pb in acetate solutions containing pyridine are illustrated in Fig. 4. We note in the first place that the strongest bands detected before UPD are due to the DSERS of pyridine; weak bands of acetate species are due to the solution, Fig. 4a. Evidently pyridine is much more strongly adsorbed than the acetate species. Weaker spectra due to adsorbed pyridine are observed on the complete UPD layer, Fig. 4b, as well as for OPD layers, e.g. Fig. 4c. The intensity of these spectra decreases progressively with increasing thickness of the deposit. Evidently, as in the case of Ag, pyridine is more strongly adsorbed than the acetate species on both the UPD and OPD layers. Finally, comparison of Figs. 4a and 4d shows that the DSERS of pyridine on silver is stable even following dissolution of OPD layers.

The effects of the UPD and OPD of Tl on the Raman spectra of adsorbed species

The spectra observed on the Ag substrates in the presence of BTA were similar to those which have been reported for other systems containing this species [2,5]. The intensity decrease due to repeated deposition and dissolution of Tl UPD layers was much less marked than for the case of pyridine; Fig. 5a illustrates the spectra obtained following three such deposition/dissolution cycles. Evidently, BTA stabilises the substrate structure during the UPD process (compared to the situation in the presence of pyridine, see below). Moderately intense spectra of BTA could still be observed on fully formed UPD layers, Fig. 5b, and, as in the other systems investigated, the OPD of Tl led to the progressive decrease in the intensity of these spectra, Figs. 5c–e. Dissolution of the OPD layer gave a Ag surface which showed a further weakening of the DSERS signals as compared to the initial substrate, Figs. 5a and f. BTA cannot therefore stabilise the substrate completely to the effects of recrystallisation induced by Tl.

In contrast to the effects of the UPD and OPD of Tl on the Raman spectra of BTA, the effects of the deposition of Tl on the spectrum of pyridine were much more pronounced. There was a marked and irreversible decrease in the intensity of all bands, this decrease being much larger than for the UPD and OPD of Pb. Evidently the extent of the retention of enhanced Raman signals is dependent on the competitive effects of the stabilisation of the substrate by adsorption of the neutral species and the recrystallisation of the SERS surface induced by the UPD process.

The effect of Cl^- ions

The results obtained in this study using sulphate and acetate electrolytes differ markedly from those reported previously. The earlier studies used Cl^- based electrolytes and in these systems deposition of Tl or Pb layers has invariably led to the quenching of the SERS of pyridine; retention of reduced SERS signals has been reported only for the strongly adsorbed species BTA. It appears therefore that loss of SERS due to UPD is enhanced in the presence of Cl^- ions and this can be readily demonstrated by the controlled addition of Cl^-, Fig. 6. It should also be noted that addition of Cl^- leads to displacement of acetate ions so that the

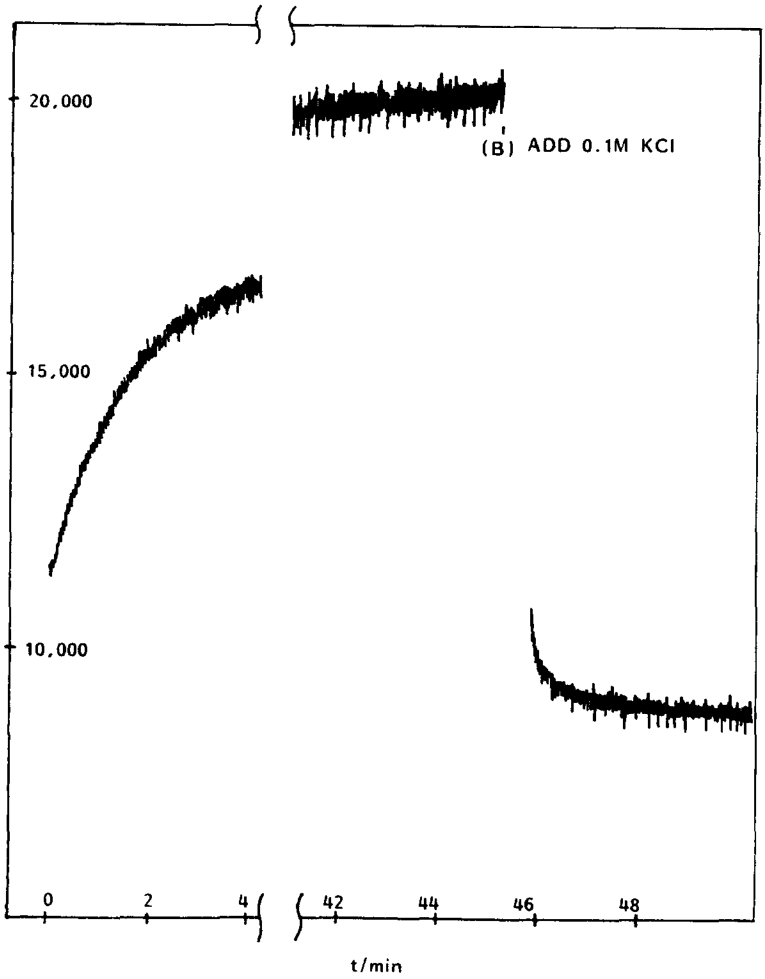

Fig. 6. Time dependence of the 1007 cm^{-1} ring breathing mode of pyridine from a silver electrode in a solution of 0.005 *M* $Pb(OAc)_2$, 0.05 *M* Py and 0.20 *M* NaOAc. At B, 0.1 *M* KCl was added to the cell.

relatively stronger adsorption of Cl^- does not stabilise the SERS substrate during UPD.

CONCLUSIONS

It has been shown that the repeated deposition and dissolution of UPD and OPD layers leads to Ag surfaces giving Raman spectra showing a remarkable stability in intensity and reversibility of the signals for successive depositions and dissolutions. The intensity of the signals following these treatments is comparable to the

Diminished Surface Enhanced Scattering, DSERS, observed following cathodic polarisation of SERS surfaces at very negative potentials [16]. Use of adequately sensitive instrumentation, control of the roughening procedure and the choice of electrolytes which diminish the reconstruction of these SERS substrates during UPD allows the preparation of UPD–electrolyte and OPD–electrolyte interfaces which still give enhanced Raman spectra for appropriate adsorbates. At this stage it is not yet possible to define strategies for optimising the retention of the enhanced signal although it is clear that stabilisation of the SERS substrate structure during the deposition process is essential. Other strategies for the generation of layered electrodes showing enhanced Raman scattering from the metal–electrolyte interfaces will be described elsewhere [11,12].

The enhancement of the spectra observed here must be dominantly due to the generation of high electromagnetic fields at the surfaces of the microstructures rather than by the "chemical" enhancement observed in the full SERS for e.g. Ag substrates alone. This will be discussed further in the following papers.

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