RAMAN SPECTRA OF PYRIDINE ADSORBED AT A SILVER ELECTRODE

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Raman spectroscopy has been employed for the first time to study the role of adsorption at electrodes. It has been possible to distinguish two types of pyridine adsorption at a silver electrode. The variation in intensity and frequency of some of the bands with potential in the region of the point of zero charge has given further evidence as to the structure of the electrical double layer; it is shown that the interaction of adsorbed pyridine and water must be taken into account.

1. Introduction

In recent years, electronic spectroscopic methods have been increasingly employed to study species adsorbed to or in the proximity of electrode surfaces. Although vibrational spectroscopy (i.e., infrared and Raman spectroscopy) has made important contributions to many areas of chemistry because of its highly specific nature and its sensitivity to the molecular environment, there have only been a few applications to electrochemical systems, e.g., refs. [1—4]. Infrared absorption [5] and, to a lesser extent, Raman spectroscopy [6] have been more extensively employed to investigate the nature of adsorption at the solid—gas interface. Raman spectroscopy has promise in the study of electrode surfaces in aqueous solution as water gives only very weak Raman scattering. The development of infrared methods will be more taxing experimentally because water and most useful polar solvents absorb very strongly.

Our initial work [3] was confined to solid phases electrochemically deposited on mercury electrodes. Raman spectra were obtained from multilayer films of mercurous chloride, mercurous bromide and mercuric oxide deposited on an electrode consisting of small mercury droplets supported on a platinum foil. Sensitivity limitations are such that monolayer deposits do not give useful spectra with existing spectrometers, even though mercurous halides are very strong Raman

scatterers. Subsequent experiments [7] have confirmed that the limits of detection found in our initial work are close to those found when using a mercury single drop electrode, i.e., when applying Raman methods to planar metal electrodes one is limited to detecting a few molecular layers of strongly scattering substances.

In order to study the behaviour of species adsorbed at about monolayer coverage with Raman techniques it has been found necessary therefore to prepare solid metal electrodes with high surface areas. We report here the Raman spectra of pyridine adsorbed at a silver electrode. Pyridine was chosen as a suitable adsorbate because it is a strong Raman scatterer and because its adsorption at the solid—gas interface has been investigated fully using both infrared and Raman spectroscopy [6]. Silver is a typical "soft" metal electrode which is expected to have a high "adsorbtivity" [8]. The point of zero charge, in the vicinity of which the adsorption of neutral species is expected to be at a maximum, has been determined [9] and this lies in a region of potential in which electrochemical experiments can readily be carried out. Adsorption of pyridine on silver electrodes has also been investigated [10].

2. Experimental

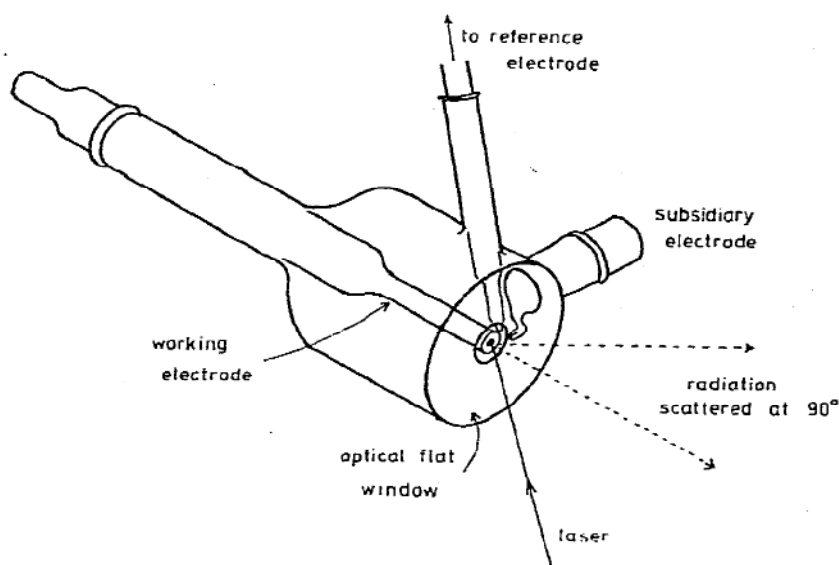The spectra were recorded using a Cary 82 Raman

Fig. 1. The electrochemical cell used for the Raman experiments.

spectrometer operating at 2 cm^{-1} slits and with 5000 counts/sec full scale sensitivity. A Spectra Physics 164AC Ar$^+$ laser, operating at 514.5 nm with ca. 100 mW power, was used in the experiments.

The electrochemical cell is illustrated in fig. 1. Both the incident laser beam and the radiation scattered at 90° are transmitted through the optical flat glass window. The working electrode consisted of a rod of Johnson Matthey Specpure silver sheathed in polytetrafluoroethylene. The subsidiary electrode, a ring of platinum wire, and the Luggin capillary from the saturated calomel reference electrode (S.C.E.) were outside the optical path. The potential of the silver electrode was controlled by a Chemical Electronics potentiostat type TR 70/2A and a Chemical Electronics waveform generator type RB1 was employed during the electrode preparation.

The solution in contact with the silver electrode during the experiments was aqueous 0.1 M analytical grade KCl containing 0.05 M of British Drug Houses Analar grade pyridine. Before assembling the cell, the planar surface of the silver electrode was polished with fine emery paper. The electrode was then subjected in the cell to cyclic linear potential sweeping for about 15 minutes at 0.5 V sec^{-1} between +200 mV and −300 mV relative to the saturated calomel potential.

The formation and reduction of silver chloride during each cycle of this treatment resulted in considerable etching of the silver surface which at the end of the pre-treatment appeared pale cream in colour. Some preliminary electrochemical experiments have shown that the surface area increases by at least a factor of 10 during this treatment.

3. Results and discussion

Hendra and co-workers, in a study of pyridine sorbed to acidic oxide surfaces, have found that the most prominent Raman bands for the sorbate occur around $\Delta\nu = 1000$ and 3000 cm^{-1} and that these bands are sensitive to the nature of adsorption. As the lower frequency region is better characterised, the spectra which appear in fig. 2 (spectra C–H correspond to several potentials of the silver electrode) were recorded in the region 990–1050 cm^{-1}.

The characteristics of the ring breathing modes of pyridine in different environments are illustrated in table 1. It can be seen from fig. 2 that the Raman spectrum changes considerably when pyridine is examined close to the surface of a silver electrode. There is a strong band at 1025 cm^{-1} which decreases
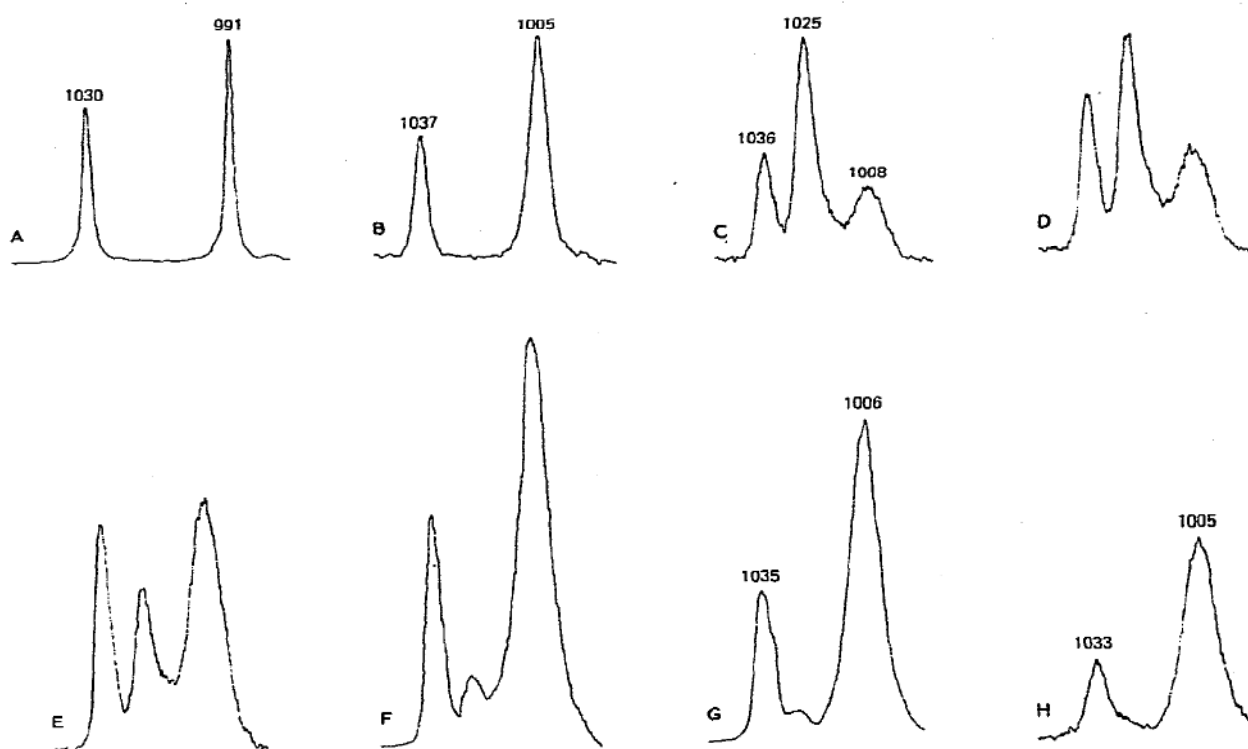
Fig. 2. Raman spectra of pyridine in solution and at the silver electrode. (A) liquid pyridine; (B) 0.05 M aqueous pyridine; (C) silver electrode 0 V (S.C.E.); (D) −0.2 V; (E) −0.4 V; (F) −0.6 V; (G) −0.8 V; (H) −1.0 V.

Table 1
Raman bands of pyridine in different environments

	$\Delta \nu$ (cm^{-1})	
liquid pyridine	991	1030
0.05 M aqueous pyridine solution	1005	1037
0.05 M aqueous pyridinium ion solution	1011	1029
Lewis acid site on alumina	1019	
Zn (pyridine)$_2$Cl$_2$	1025	

in intensity with shift of the potential of the electrode in the cathodic direction. The evidence in table 1 and the behaviour of the 1025 cm^{-1} band with electrode potential suggest that this band is associated with pyridine coordinated to the metal through the nitrogen atom.

The intensities of the Raman bands, which occur at 1008 and 1036 cm^{-1} when the electrode is at the S.C.E. potential, pass through a maximum at about −0.6 V (S.C.E.). This behaviour is typical of adsorption at electrodes which has been studied by other methods; for an uncharged species the adsorption is at a maximum near the potential of zero charge, (P.Z.C.), which has been reported [9] to be at −0.95 V (S.C.E.). It is generally considered that as the electrode potential is moved, anodically or cathodically, away from the potential of zero charge the replacement of the adsorbate by water, and anions or cations respectively, is increasingly favoured, i.e., desorption takes place as the potential is shifted away from the P.Z.C. These ideas [11] are retained in the most detailed model of the double layer [12].

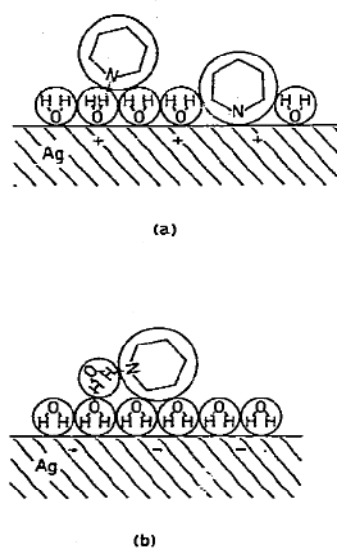The Raman spectra, however, lead to a more detailed picture of the structure of the double layer and

Fig. 3. A possible model of the structure of the double layer between silver and potassium chloride solution containing pyridine. (a) At potentials positive to the P.Z.C. showing pyridine adsorbed to silver via nitrogen and in an "aqueous acidic environment", (b) at potentials negative to the P.Z.C. showing adsorbed pyridine in "aqueous environment".

the interaction between the species. It can be seen from fig. 2 that the frequencies of the bands at the more anodic potentials are intermediate between those observed for the pyridinium ion and those for aquated pyridine indicating that the "adsorbed" pyridine is hydrogen-bonded through the nitrogen atom to a water molecule containing a more acidic H atom than is the case in the bulk of the solution. This suggests that the pyridine is separated from the electrode by a monolayer of water molecules which are oriented and perturbed in the high electric field at the electrode surface. Evidence from the variation in frequency of these bands with potential supports this view. At potentials more cathodic than that for maxi-

mum adsorption, both the 1008 and 1036 cm^{-1} bands shift to slightly lower frequencies. For the 1008 cm^{-1} band the Raman frequency at -1.0 V (S.C.E.) is the same as that for pyridine in the bulk of the solution. Thus the properties of the adsorbed pyridine approach those appropriate to dissolved pyridine. The shift could well be interpreted as being due to the reorientation of the water molecules in contact with the electrode and suggests that there is more than one layer of water between the "physisorbed" pyridine and the silver surface, fig. 3. It must be pointed out, however, that the behaviour of the band at higher frequencies (near 1036 cm^{-1}) does not support this view.

References

[1] A.H. Reed and E. Yeager, Electrochim. Acta 15 (1970) 1345.
[2] W.R. Heineman, J.N. Burnett and R.W. Murray, Anal. Chem. 49 (1968) 1974.
[3] M. Fleischmann, P.J. Hendra and A.J. McQuillan, J. Chem. Soc. Chem. Commun. (1973) 80.
[4] A.J. McQuillan, Faraday Discussion No. 56, to be published.
[5] L.H. Little, Infrared spectra of adsorbed species (Academic Press, New York, 1966).
[6] P.J. Hendra, J.R. Horder and E.J. Loader, J. Chem. Soc. A (1971) 1766;
P.J. Hendra, I.D.M. Turner, E.J. Loader and M. Stacey, J. Phys. Chem. (1974), to be published.
[7] M. Fleischmann, P.J. Hendra and A.J. McQuillan, to be published.
[8] D.J. Barclay and J. Caja, Croat. Chem. Acta 43 (1971) 221.
[9] D.I. Leikis, K.V. Rybalka, E.S. Sevastyanov and A.N. Frumkin, J. Electroanal. Chem. 46 (1973) 161.
[10] R.G. Barradas and B.E. Conway, J. Electroanal. Chem. 6 (1963) 314.
[11] A.N. Frumkin, Z. Physik 35 (1926) 792.
[12] J.O'M Bockris, M.A.V. Devanthan and K. Muller, Proc. Roy. Soc. A274 (1963) 55.