Classic paper

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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.

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

2. Experimental

The spectra were recorded using a Cary 82 Raman 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.

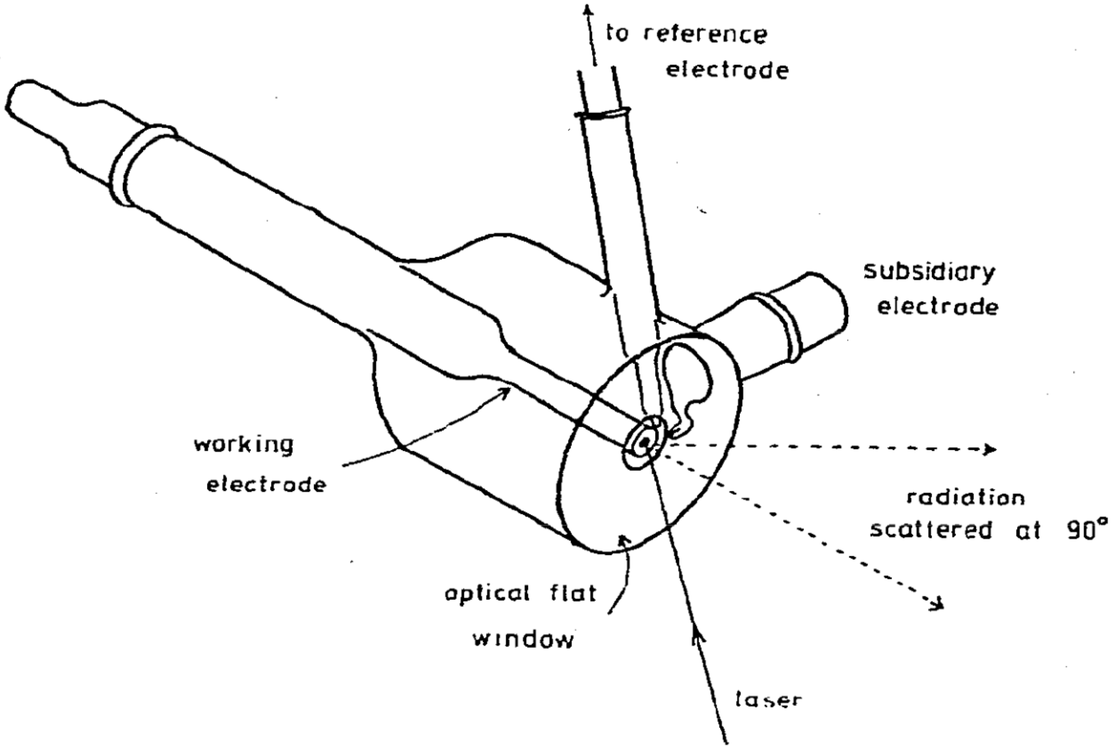


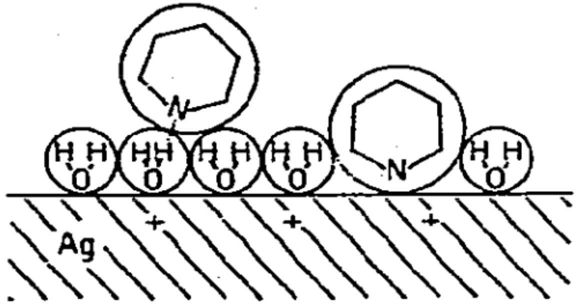
Fig. 1. The electrochemical cell used for the Raman experiments.

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.

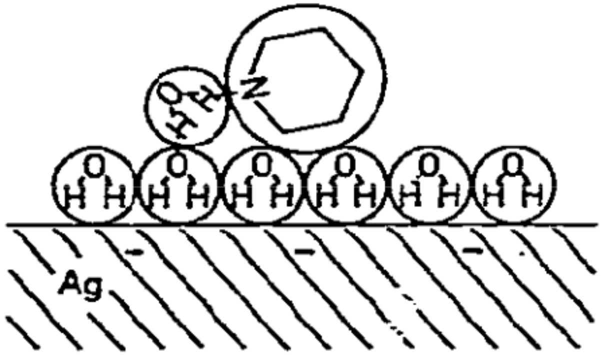
The solution in contact with the silver electrode during the experiments was aqueous 0.1 M analytical grade KCl containing 0.05 M of British Drug Houses Analar grade pyridine. Before assembling the cell, the planar surface of the silver electrode was polished with fine emery paper. The electrode was 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.

3. Results and discussion

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 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.



(a)



(b)

Table 1

Raman bands of pyridine in different environments

	Δν (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	

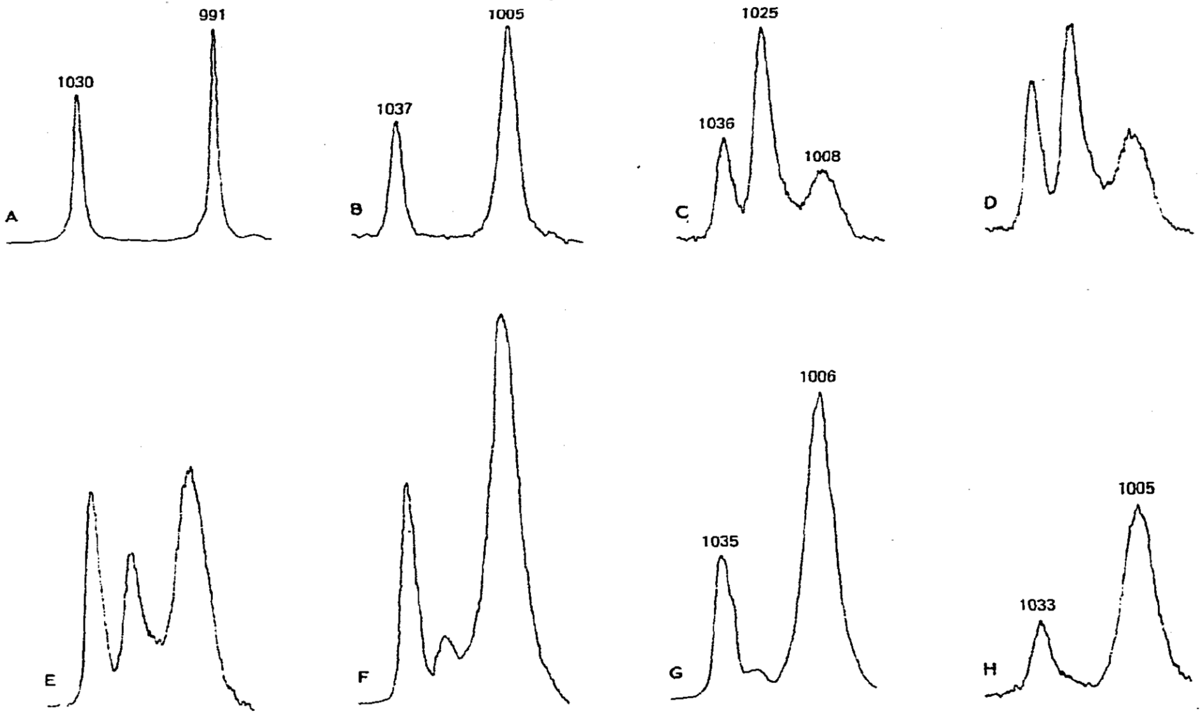
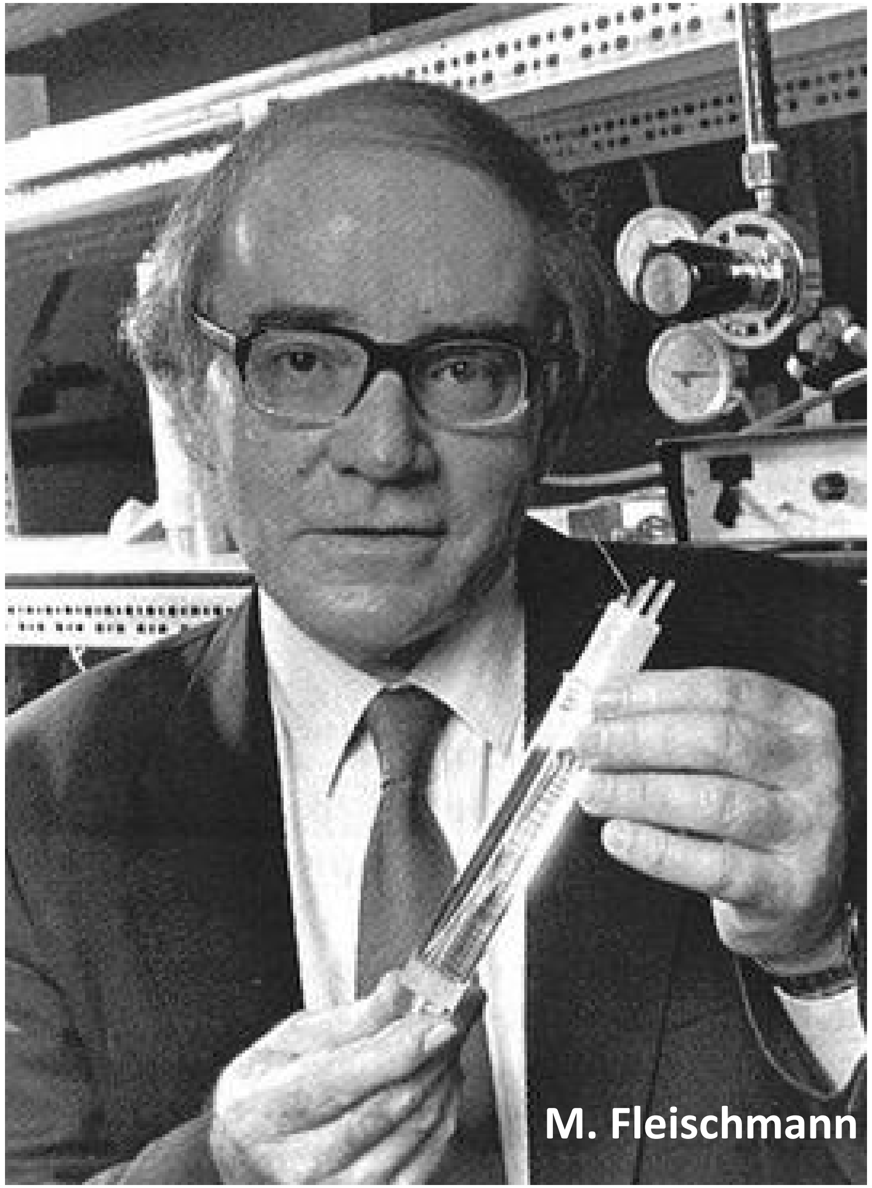
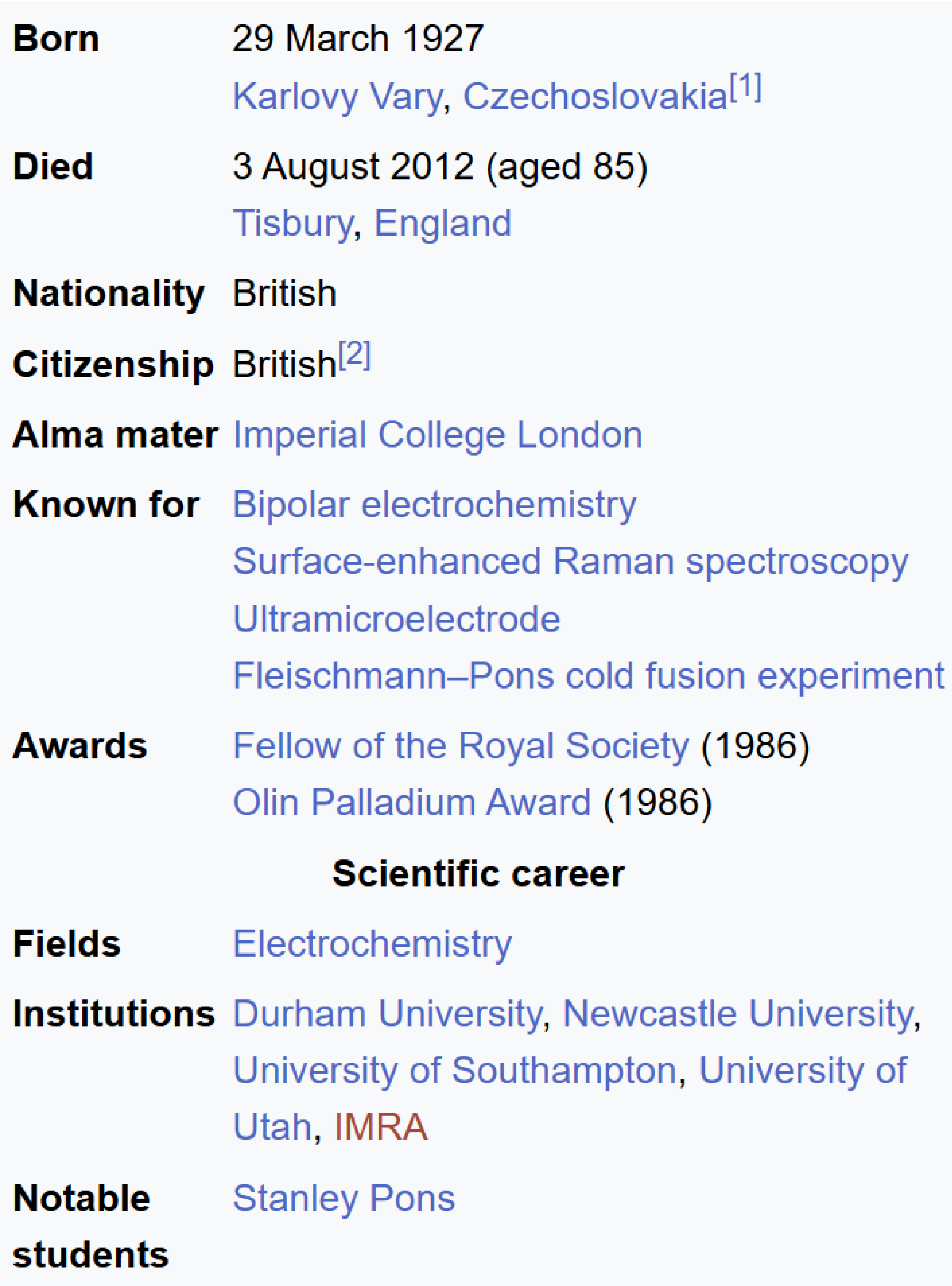


Fig. 2. Raman spectra of pyridine in solution and at the silver electrode. (A) liquid pyridine; (B) 0.05 M aqueous pyridine; (C) silver electrode 0 V (S.C.E.); (D) −0.2 V; (E) −0.4 V; (F) −0.6 V; (G) −0.8 V; (H) −1.0 V.



M. Fleischmann

Thank you



Born	29 March 1927 Karlovy Vary, Czechoslovakia[1]
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Citizenship	British[2]
Alma mater	Imperial College London
Known for	Bipolar electrochemistry Surface-enhanced Raman spectroscopy Ultramicroelectrode Fleischmann–Pons cold fusion experiment
Awards	Fellow of the Royal Society (1986) Olin Palladium Award (1986)
	Scientific career
Fields	Electrochemistry
Institutions	Durham University, Newcastle University, University of Southampton, University of Utah, IMRA
Notable students	Stanley Pons