

SECURITY CLASSIFICATION OF THIS PAGE

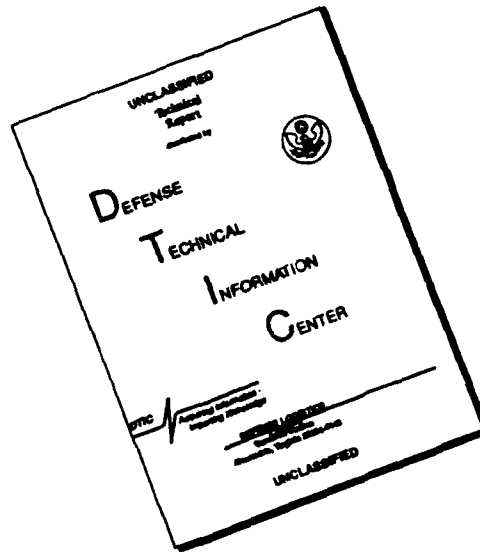
Form Approved
OMB No. 0704-0188

REPORT DOCUMENTATION PAGE

(4)

1a. REPORT SECURITY CLASSIFICATION General distribution		1b. RESTRICTIVE MARKINGS None	
AD-A209 952		3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited	
		5. MONITORING ORGANIZATION REPORT NUMBER(S) N00014-88-J-1005	
6a. NAME OF PERFORMING ORGANIZATION University of Southampton	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, University of Southampton, SO9 5NH, England		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincey Street, Arlington, Virginia, 22217 5000, U.S.A.	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincey Street, Arlington, Virginia, 22217 5000, U.S.A.		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	TASK NO.
		PROJECT NO.	WORK UNIT ACCESSION NO.
End of Year Report on the contract			
12. PERSONAL AUTHOR(S) P.J. Hendra and M. Fleischmann			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM Oct 87 TO May 89	14. DATE OF REPORT (Year, Month, Day) 19th June 89	15. PAGE COUNT 24
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
DTIC ELECTE JUN 26 1989 S E D			
20. DISTRIBUTION AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL DR. P.J. HENDRA		22b. TELEPHONE (Include Area Code) 0703 595000	22c. OFFICE SYMBOL

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST
QUALITY AVAILABLE. THE COPY
FURNISHED TO DTIC CONTAINED
A SIGNIFICANT NUMBER OF
PAGES WHICH DO NOT
REPRODUCE LEGIBLY.

AD A 209 952

REPORT TO OFFICE OF NAVAL RESEARCH

from

Department of Chemistry
University of Southampton
Southampton SO9 5NH, U.K.

Grant Period: 1-10-87 ---- 30-9-89

Grant No. N00014-88-J-1005

Report covers period 1 October 1987 to 31 May 1989

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	(25)

QUALITY
INSPECTED
2

May 1989

P J Hendra
&
M Fleischmann

89 6 26 062

1. Development of F.T. Raman Spectroscopy

Following feasibility studies in the winter of 86/87 it was clear that it was possible to record first class F.T. Raman spectra using a small analytical grade infrared interferometer modified to operate in the near infrared^{1.1,2}. Perkin Elmer (UK) Ltd therefore placed a basic interferometer at Southampton in August 1987 and the Southampton group embarked on a development programme to produce a fully operational spectrometer capable of running in the open laboratory on a routine basis. The first model was shown at the first meeting dedicated to F.T. Raman spectrometry held at Southampton in April 1988. By September 1988 the machine was ready to show at an international conference in London and a review of the technique had appeared^{1.3}. Perkin Elmer had built their own prototype by this time and progress on this and the Southampton machine was reported^{1.3}, whilst the details of the spectrometer were submitted to an analytical journal^{1.5} and the instrumental physics elsewhere^{1.5}.

The subject as a whole has recently been reviewed^{1.7}. Several other reviews have been produced by the Southampton group including the application in the chemical industry^{1.8} and an account in French^{1.9} and another in Spanish^{1.10}.

Bibliography Development of F.T. Raman Spectrometry

Papers actually published:-

- 1.1 S F Parker, K P J Williams, P J Hendra & A Turner. J.App Spect. 42 1988
796.
- 1.2 S F Parker, K P J Williams, P J Hendra & A Turner. Microchim Acta 11
(1988) 23.
- 1.3 D J Cutler, P J Hendra, H M Mould & R A S Spragg ICORS 1988 Proceedings
P.953 Sec 19.14.
- 1.4 P J Hendra & H M Mould, International Laboratory 34 Sept (1988)

Papers in press:-

- 1.5 P J Hendra, H M Mould & A J Turner. J.Raman Spect (1989)
- 1.6 G Ellis, P J Hendra, C M Hodges, T Jawhari, C H Jones, P Le Barazer,
C Passingham, I A M Royaud, A Sanchez & G M Warnes. The Analyst (1989)
- 1.7 P J Hendra, U.S. Naval Reviews. Submitted May 1989.
- 1.8 S Church, P J Stephenson, P J Hendra & D Bourgouis. Analyst (1989)
- 1.9 M Hanniet, T Jawhari & I A M Royauld. J de Chim Phys. (1989)
- 1.10 A Sanchez Blasquez. Optica Pura y Aplicada (1989)

2. Applications of F.T. Raman Spectroscopy to Chemistry

2.1 Introduction

The Southampton group have had a first class (probably unequally so) F.T. Raman instrument available since January 1988. The group is large (currently 2 Physicists and 12 Chemists) and all to varying degrees are involved in the F.T. Raman programme. As a result we are in a quite unique position to develop application across a wide range of chemistry. We have involved numerous collaborators, several of which have either started to support students or have agreed to do so in the Fall. It is amusing for that papers are still appearing describing new instruments and offering odd spectra proving their frequently abysmal performance [c.f F J Purcell Spectroscopy Current Edition 4 24-33 (1989)] while we left this stage behind months ago and are developing the applications and have been doing so for 1-1/2 years.

The survey of applications is very abbreviated due to lack of space. If any readers would appreciate further details, we would be delighted to supply them.

2.2 Inorganic Species +

Many deeply coloured inorganic materials impossible or difficult to study by conventional methods appear to be easy using nmr/F.T. methods. We have had conspicuous success with a range of tetroxy anions including KMnO_4 - a novel result^{2,4}. It has also been possible to show that the literature is in some disarray over the biologically interesting complex Ni Dimethyl Glyoxime. This

material contains a very strong hydrogen bond (possibly a symmetrical O--H---O moiety). The resonance Raman spectrum has been recorded previously and assigned on the basis that it is a resonance enhanced spectrum. We have shown this is not the case and are very unhappy about the assignment of vibrational bands to the vibrations of the OHO group. The work nears completion.

We have examined a range of tellurium organometallics and their complexes. The high quality of the data has enabled us to clear up an anomaly in the literature where it is suggested that R_3Te might be linear. It is not, and the work is being prepared for publication.

Many other inorganic components have been examined with the conclusion that the method is a little suspect for transition element chemistry. High oxidation states of Mo, V^{IV} , Mn^{VI} , Cu^{II} , Fe^{III} and several others have been identified as problematic since absorption of the laser occurs. Clearly this problem needs further clarification.

- Collaborators - Universities of South Africa (Pretoria) and Reading (UK),
Departments of Chemistry.

2.3 Synthetic Polymers +

A huge number of specimens have been examined under this heading and numerous papers are either in press or publication. Completed work includes -

Crystallinity determinations in polyether ketone and polyether ether ketones. We are reporting some success in homopolymer and glass fibre filled composites^{2,4}. The analysis of Aryl ether sulphone/ether ether sulphone copolymers is regarded as difficult but is facile using F.T. Raman techniques^{2,3}.

William is preparing describing in some detail the Raman and infrared spectra of single number nylons^{2,15}.

Partial analyses of the spectra of polyphenylene sulphide^{1,10} and modified P.P.O.^{1,10} are in preparation for publication or in press whilst work on liquid crystal polymers is in hand. In these, spectral changes through and above the melting point are of interest.

Several fibre systems have been studied including acrylonitrile copolymers. It has been possible to examine the undyed fibre, the dyed one and subtract out the features due to the dye. Shifts due to dye/polymer surface or bulk interactions are of interest. A preliminary report has been made^{1,8}. Other fibres are also accessible including natural, bleached and dyed cotton.

A highly important part of the Polymer Industry is the manufacture of paints. The study of the mechanism of 'curing' processes is

normally carried out using infrared measurements on varnishes. Pigments cause severe scattering problems spoiling the infrared spectra thus the use of varnishes, yet it is known that the pigments play a vital role in accelerating and/or altering curing reactions. We have been able to record superb spectra on several paint systems involving alkyd resins and are in process of investigating the kinetics of curing. A preliminary publication is ready for submission.

The curing of other bulk polymer systems such as epoxy resins is also facile using F.T. Raman measurements and some results have been included in talks given recently.

Collaborators ICI Petrochemicals & Polymers Div (Wilton UK) ICI Paints Div. (Slough UK) & Courtaulds Plc (Coventry UK)

2.4 Drugs and Explosives +

Working with the Hampshire County Constabulary and assisted by the Home Office Forensic Science Lab Aldermaston we have been able to show that F.T. Raman methods enable us to identify dangerous drugs including heroine, cocaine, amphetamines and morphine. The experimental arrangements are most attractive to the Police because no scientific skill is required in loading the sample cavity and placing it in the instrument. Further, software helps the diagnosis so the method can be applicable in operational police work not only as a Court acceptable Forensic tool. The Police tell us that this facility opens up a whole new vista for them and considerable interest is being generated^{2,6}.

Similar comments can be made regarding explosives. We have been

able to record superb spectra of all the significant explosives as pure compounds, mixtures/blends except for the dark coloured propellants. We are told by the Ministry of Defence with whom we are collaborating that coupled with their existing identification methods F.T. Raman is likely to be invaluable in diagnosis. The current methods involve solution/extraction, separation and chromatographic analysis and are very slow. F.T. Raman can either provide results on 'as supplied' specimens or on separated or extracted materials. One of the outstanding features of this work is that we have been able to study minute samples (down to ~ 5 microgrammes).

Some of the completed work in this continuing programme is in press.

- Collaborators Hampshire County Constabulary (Winchester UK) & the Royal Military College of Science (Shrivenham UK).

2.5 Surfaces Surface Enhanced Raman Spectroscopy (SERS)

One of our early successes was the demonstration of SERS spectra. In fact it was this success that enabled us in March 1988 to obtain from the Science and Engineering Research Council Funds to develop a second F.T. Raman instrument. Our original work centred on the familiar Pyridine: Ag, Cu and Au systems and has been published^{2,3}. Of particular interest is that the 'white' background familiar in all SERS studies is remarkably strong in the near infrared. The Surface Enhancement is unexpectedly high (10¹⁰) and that spectra are recorded so easily and quickly

that detailed chemical work is now possible. Studies on the equilibria at electrochemical surfaces have become possible since sets of spectra over wide ranges of pH, electrolyte conc. or temperature are facile. A detailed programme in this area is in progress. In addition, a programme on the Ferri/Ferro cyanide/gold system is awaiting publication^{2,6}, whilst others on Au/CNS⁻ and Cu/polyethylene glycol will be complete and publishable in the Autumn. In all cases superbly detailed spectra at various potentials and electrolyte concentrations have enabled us to give a detailed insight into the reactions occurring at the electrode/electrolyte interfaces.

In the late sixties we showed that Raman spectra could be recorded on some catalyst systems and that the adsorbed organic molecules could be readily observed as they sorbed and reacted. The technique did not however develop because in chemically useful systems (e.g. cracking catalysts) fluorescence made measurement impossible. By 1975 the technique had been rejected almost everywhere when it was realised that all efforts to reduce fluorescence had in effect failed.

We have re-investigated this area and as we expected to do, have shown considerable progress. The area in which we have concentrated involves the zeolites. We have sorbed pyridine to a range of zeolites (acidic and sodium treated) and made assays of the surface activity. We have then extended our work to include the de-aluminated materials and have examined samples

exposed to pyridine at high temperatures. Current methods of assaying zeolites involve the use of infrared methods and are far from satisfactory. Our collaborators describe the new F.T. method as outstanding - the first really useful technique for doing this vital job. A note on this subject has been submitted for publication^{2,9}, whilst a full paper is in preparation. The work, of course, continues.

Zeolitic catalysts are tonnage materials in the chemical industry and are used in a wide range of reactions. We have started work on certain isomerization reactions and will publish this data shortly. The interest here is to test the feasibility of following this type of reaction using F.T. Raman methods and then to explore mechanisms, types of acid sites involved and the role of temperature.

Collaborators Crossfield Chemicals Ltd (Warrington UK) and University of Reading (UK)

2.6 Elastomers +

Progress in this area has been so rapid that we have deliberately separated it from "polymers". Superb analytical data is now available on acrylonitrile butadiene copolymers, butadiene styrene copolymers - there is no doubt that as an analytical procedure the method will prove valuable in assaying cis: trans vinyl and A:B copolymer concentrations¹⁴. Crosslinking reactions and the ~~mechanism and kinetics thereof is still of considerable relevance~~ significance to the rubber industry. We have recorded specific results on a variety of sulphur vulcanization reaction curves of natural rubber and other elastomers. We see 'new'

II

bands due to sulphidic constituents and are deeply involved in an extended programme in this area. A preliminary report has been submitted for publication^{2,10} and another will follow surveying progress in this field in September.

When crosslinked elastomers are extended, orientation and crystallization occurs. The experiment can very conveniently be carried out in the sample area of the F.T. instrument and has yielded some superb data. We clearly see the appearance of bands in the spectrum at high strains originating in oriented crystalline material. We are now involved in assaying the bands, studying temperature effects and the interconnection with X-ray data. A publication is about to be submitted.

Collaborators Malaysian Rubber Producers Research Association
(Hertford UK)

2.7 Raman Intensities

Due to the coaxial nature of the sample area developed at Southampton, intensities of Raman scatter are very reproducible. This observation has been exploited, corrections made for instrument sensitivity across the spectral range and adsorption of the Raman scatter by the sample producing spectra against a meaningful intensity scale. We have suggested that in future all liquid phase results should be acceptable for publication only if the intensity scale is understandable and reproducible^{2,11}. Our work and reasoning is being prepared for rapid publication.

This exciting development raises the possibility that in future,

a Raman "equivalent" to the extinction coefficient will be available to all consultors of the literature or spectra collections with enormous benefit to industrial and other analysts.

Biosystems +

A vast range of biologically derived molecules have been studied including foodstuffs, enzymes, carbohydrates, polypeptides, wood and natural fibres. In the solid phase good spectroscopic results are usually produced but in aqueous solution the outcome is disappointing. Some spectra can be obtained but only at concentration of little interest to the biochemical fraternity.

Some of our results have been prepared for publication^{2,12} and a collection of results is in preparation for inclusion in a special edition of *Spectrochimica Acta* to be devoted to F.T. Raman spectroscopy and its applications.

Biomedical samples such as drugs (indomethacin for example) are more promising. We have accumulated detailed spectra showing spectral characteristics indicative of conformation in drugs sorbed into lattices e.g. cyclodextrin which are sure to be of value. This work has been written up and is about to be submitted for publication.

Collaborators: University of Nottingham, Department of Pharmacological
Science

Subject: F.T. Raman

References that have appeared

1. J. Le Barazer and A. Crookell, *J. Raman* 20 (1989)

2,2 A Crookell, M Fleischmann, M Harriet and P J Hendra. Chem Phys Letts 149 123-127 (1988)

2,1 J M Chalmers, J G Eaves, J Howard, A Sanchez Blasquez & P J Hendra. Proceedings ICORS London Sept 88, 19,15 p965,6

Papers in Press

2,4 K Kruger, A Sanchez Blasquez, P J Hendra & H A Willis, Polymer (1989)

2,5 I A M Royauld, P J Hendra, H A Willis & W Maddams. J. Raman Spect (1989)

2,6 P J Hendra, C M Hodges, H A Willis & T Farley. J. Raman Spect (1989)

2,7 J Akhavan, C M Hodges & P J Hendra. J. Raman Spect. (1989)

2,8 R Lowry. Ph.D Thesis, Southampton 1988

2,9 R Durr, D Rawlence, C Fassingham & P J Hendra. J. Catal (1989)

2,10 G Ellis, P J Hendra, C H Jones, K D O Jackson & M J R Loadman. J. Raman Spect (1989)

2,11 H A Willis, P J Hendra & T Jawhari. Spectroscopy International (1989)

2,12 D Gani, P J Hendra, W Maddams, I A M Royauld, H A Willis, V Zichy & M E A Cudby. J. Raman Spect (1989)

3. Polymer Research not involving F.T. Raman Studies

3.1 During the grant period we have finished several programmes of polymer research whilst others are approaching completion. Thus:-

(a) An investigation into the structural changes that occur below the M.Pt.^{3,4} and the multiple endotherm peaks typical of isotactic polypropylene has shown that the situation is far simpler than suspected. Only one phase is involved, the multiple peaks arising from continuous annealing near the melting point. This work is in press^{3,6}. P.E.E.K. behaves in a similar way and is being investigated at this time.

(b) A study of the paraffins below C₃₆ near their melting points has yielded evidence for the conversion to a one chain/unit cell morphology. Further, the melt crystallized and solution crystallized materials differ. This work is being prepared for publication. This work has relevance to the 'freezing' of diesel fuel.

(c) A study has been initiated into the processes that occur during welding of polymers and the reasons behind their mechanical weakness. The weakness is related to poor mixing and the lack of longitudinal motion in the polymer chains. This work is ready for submission as a preliminary note.

— — — — — A re-appraisal has been made of the well known and transition in low crystallinity polyethylenes near -18°C. We feel it is in fact a first order transition and that it is caused by the crystallization (or at least the local

ordering) of parts of the disordered phase. Again this work is about ready for submission.

- (e) Over the last four years an extended programme has been continuing at Southampton involving research into the structure of flowing melts. We have convincing data from i.r., Raman and X.R.D. to show that orientation is minimal even when die swell is pronounced. The work is now collected and ready for submission (only parts have been published to date). When crosslinked polyethylene rubber (i.e. Polyethelene crosslinked with dicumyl peroxide and maintained above its Melting Point) is examined, like a flowing melt, which in some respects it models, it shows little or no orientation. On cooling whilst elongated, oriented crystallization occurs due to oriented nucleation. The orientation of the solid does not imply orientation in the rubber (or melt, of course). This work has been submitted^{3,7}.

- (f) As part of our investigation into heat treatments and the molecular processes that occur therein, we have been examining the state of the disordered material in ultra highly cold drawn polyethylenes. This phase behaves very peculiarly and it is heated and does so irreversibly. This work is in press^{3,5}.

g An extended study has been made on the mechanism at the molecular level of plastic deformation of semicrystalline

polymers. The report has appeared^{3.1}.

- (h) The morphology and its relationship to the branch content in L.L.D.P.E.s has been reported^{3.2} and the morphology of linear polyethylene crosslinked in their melts has also been appraised^{3.3}. The result of these reports is to contribute to our knowledge of the structure of melt crystallized polymers.

3.2 Bibliography

Papers that have appeared

- 3.1 P J Hendra, J Hammond, B G Lator, W F Maddams & H A Willis. Polymer 29 49-53 (1988)
- 3.2 C France, P J Hendra, W F Maddams & H A Willis. Polymer 28 710-712 (1987)
- 3.3 P J Hendra, A J Peacock & H A Willis. Polymer 28 705-709 (1987)
- 3.4 L Hanna, P J Hendra, V Zichy, W F Maddams, H A Willis & M E A Cudby. Polymer 29 1843-1847 (1988)

Papers in Press

- 3.5 A Sanchez Blasquez, K N Kruger, V Zichy & P J Hendra. Polymer (1989)
- 3.6 C Passingham, P J Hendra, M E A Cudby & H A Willis. Eur.Pol.J. (1989)
- 3.7 G Ellis, D Hodgson, P J Hendra. H A Willis, M A Taylor & L Hanna. Polymer (1989)

4. Electrochemical Research

4.1 Introduction

The programme of research on Electrochemical processes continues both at Southampton and also in liaison with the University of Utah. In addition to students working at Southampton several visitors have joined the group for extended periods increasing the output of work. Research success has been achieved in several areas including X-ray diffraction of electrode electrolyte interfaces, micro and ultramicro electrode processes and S.E.R.S. studies.

A major review of in situ measurements in electrochemical systems has been presented at one of the Welch Meetings held in Houston, Texas (1987)^{4,5} whilst another on processes in small systems has been presented at one of the Surface Science Meetings held on Campobello Island, New Brunswick and is to be published by Springer Verlag.

One of the principal investigators (Prof M Fleischmann) has recently been honoured* for his work on in situ techniques and particularly the development of the SERS process and of X-ray diffraction from electrode surfaces; much of the work mentioned in the citations was funded by O.N.R.

~~Award of the Palladium-Medal of the American Electrochemical Society. Elected to the Royal Society, Bruno-Breyer-Medal of the Australian Chemical Society.~~

Further plenary papers on electrochemical processes, at the molecular level have been presented at the Electrochemistry Conference of the Royal Australian Chemical Society (February 1988), held in Sydney and at the 39th Meeting of the International Society for Electrochemistry held in Glasgow in September 1988.

4.2 X-Ray Diffraction at the electrode-electrolyte interface

Progress in this experimentally difficult area has been significant. The technique is fairly well developed and the applications are now of prime interest. Thus, studies have been completed at the surfaces of platinum electrodes over a range of potentials, the differences in the diffractograms at two potentials being compared over long data accumulation periods^{4.4}. The technique has also been applied to the under potential deposition of thallium onto silver and gold electrodes^{4.5} and the effect of weakly adsorbed hydrogen on the surface structure of platinum electrodes^{4.6}.

In principle one does not need to confine oneself to metal electrodes in this type of study. Recently X-ray transmission and reflection diffractograms have been recorded off polyaniline electrodes in several electrolytes^{4.7}. This work opens up several new avenues of research particularly in view of the increasing interest in electrically conducting polymers.

Research into Surface Enhanced Raman Spectroscopy in Electrochemical Systems

This work has involved the use of visible lasers (more recent work

on SERS using near-infrared lasers and F.T. Raman methods is

covered in section 2.5). Working with smooth silver electrodes Fleischmann and Tian induced SERS by depositing Nickel and Cobalt layers^{4,8} whilst the same authors explored the effect of underpotential and overpotential deposition of lead and thallium on the underlying silver electrode using the SERS method^{4,9,10}. The possibility of obtaining SERS from iron electrodes has also been investigated. A theoretical analysis of the Ferri/Ferrocyanide system at electrode surfaces has also appeared^{4,11} of relevance to the new experimental work described in section 2.5.

In many cases, the use of a wide range of laser wavelengths is highly beneficial and our ability to cover the range 400nm - 1µm is particularly valuable.

4.4 Microelectrodes

Very rapid progress has taken place in this field and a large amount of work has been published as follows:

Voltametric methods have been applied in low conductivity electrolytes by using the unique potential gradients typical of microelectrodes^{4,12}. Work on the lead-acid battery has been continued by using mercury ultramicroelectrodes to determine Pb^{2+} concentrations^{4,13} and progress has been reviewed^{4,14}. Most recently the nucleation of α PbO_2 on carbon microelectrodes has been investigated at the molecular level^{4,15}.

The value of microelectrodes as sensors and detectors has been

explored^{4,15} and the details of the mercury-ultramicroelectrode investigated in detail^{4,17}. The authors have pointed out that measurements on the properties of the double layer with particular reference to its structure and on coupled chemical reactions are in prospect using the ultramicroelectrode.

Several other systems have been studied including the $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}$ equilibrium^{4,18} and the material is in press whilst Fleischmann and Pons have reported on the A.C. impedance of microelectrodes relating the diffusional impedance of micro discs, rings, spheres and cylinder electrodes to that of planar systems^{4,19,20,30,34}.

In a series of papers Fleischmann, Pons et al have described work on microdisc and microring electrodes including experiments and analyses in the steady state,^{4,21,22} and in the unsteady state for chronopotentiometry^{4,21,23,24}. Chronoamperometry^{4,21,25,26}, linear sweep amperometry^{4,21,24} and coupled chemical reactions in solution^{4,21,27}. A further series of papers giving more exact methods of analysis of these topics is in course of publication^{4,28,29,30,31,32}.

4.5 Miscellaneous Electrochemical Results

Several other fields have been investigated and reports made including an observation of surface species on platinum colloids^{4,33} using ¹⁹⁵Pt NMR. The authors showed that the resonance is altered by the addition of species to the solution known to adsorb to the platinum surface. Clearly this exciting observation will open up a new field of research on in-situ

investigations of electrode-solution interfaces.

4.6 Bibliography

- 4.1 M Fleischmann.
Proceedings of the Meeting of the Welch Society, Houston, Texas.
- 4.3 M Fleischmann.
Proceedings of the 7th Australian Electrochemistry Conference, Sydney, February (1988)
- 4.2 M Fleischmann.
Proceedings of the Surface Science Conference, Campobello Island, New Brunswick, August (1987) To be published by Springer Verlag.
- 4.4 M Fleischmann and B W Mao
X-ray Diffraction Studies of Pt Electrode Solution Interfaces, J. Electroanal. Chem., 229 (1987) 125.
- 4.5 M Fleischmann and B W Mao.
In-Situ X-ray diffraction.
Investigations of the UPD of Tl and Pb on Ag and Au Electrodes. J. Electroanal. Chem., 247 (1988) 297-309.
- 4.6 M Fleischmann and B W Mao. In Situ X-ray Diffraction Measurements of the Surface Structure of Pt in the Presence of "Weakly" adsorbed H.
- 4.7 M Fleischman, N Gerrard, B W Mao and G Mengoli.
J. Electroanal. Chem., in the press.
- 4.8 M Fleischmann and Z Q Tian
The Induction of SERS on Smooth Ag by the deposition of Ni and Co.
J. Electroanal. Chem., 217 (1987) 411.
- 4.9 M Fleischmann, Z Q Tian and L J Li
Raman Spectroscopy of Adsorbates on Thin Film Electrodes Deposited on Silver Substrates.
J. Electroanal. Chem., 217 (1987) 397.
- 4.10 M Fleischmann and Z Q Tian
The Effects of the Underpotential and Overpotential of deposition of Lead and Thallium on Silver on the Raman spectra of Adsorbates. ———
J. Electroanal. Chem. 217 (1987) 385
- 4.11 M Fleischmann and S Pons in (Eds) M Fleischmann, S Pons, D A Holleson and P P Schmidt, Ultramicroelectrodes, Datatech Systems Inc., Morganton N.C. 28655-0435 (1987) 17.
- 4.12 S Pons, M Fleischmann and N Garrard.

Voltammetric Measurements with Microelectrodes in low conductivity Systems.

J. Electroanal. Chem. 220 (1987) 31

- 4.13 L J Li, M Fleischmann and L Peter
In-situ measurements of Pb^{2+} concentration in the lead-acid battery using mercury ultramicroelectrodes.
Electrochim. Acta. 32 (1987) 1585.
- 4.14 L J Li, L M Peter and M Fleischmann,
Microelectrode Studies of the Lead-Acid Accumulator System in L J Pearce (Ed) Power Sources II, International Power Sources Symposium Committee (1986) 83.
- 4.15 M Fleischmann, L J Li and L M Peter,
Electrochimica Acta 34 (1989) 4755-483
- 4.16 R Brina, S Pons and M Fleischmann,
Ultramicroelectrode Sensors and Detectors.
J. Electroanal. Chem., 244 (1988) 81-90.
- 4.17 J M Pons, J Daschbach, S Pons and M Fleischmann.
The Behaviour of the Mercury Ultramicroelectrode.
J. Electroanal. Chem., 239 (1988) 427-431.
- 4.18 S Danieli and M Fleischmann submitted for publication.
- 4.19 M Fleischmann and S Pons,
J. Electroanal. Chem., 250 (1988) 277
- 4.20 M Fleischmann and S Pons, submitted for publication.
- 4.21 M Fleischmann, S Pons, D Rolishu and P P Schmidt,
Ultramicroelectrodes. Datatech, Morganton, N.C. (1987)
- 4.22 M Fleischmann, and S Pons,
J. Electroanal. Chem., 222 (1987) 107.
- 4.23 M Fleischmann and S Pons,
J. Electroanal. Chem., 250 (1988) 257.
- 4.24 L M Abrantes, M Fleischmann, L J Li, M Hawkins, J W Pons,
J Daschbach and S Pons
J. Electroanal. Chem., 262 (1989) 55.
- 4.25 M Fleischmann, J Daschbach and S Pons,
J. Electroanal. Chem., 250 (1988) 269.
- 4.26 L J Li, M Hawkins, J W Pons, J Daschbach, S Pons, M
Fleischmann and L M Abrantes,
J. Electroanal. Chem., 262 (1989) 45.
- 4.27 M Fleischmann and S Pons,
J. Electroanal. Chem., 250 (1988) 285
- 4.28 M Fleischmann, J Daschbach and S Pons,

- J. Electroanal. Chem., 263 (1989) 189,
- 4.29 M Fleischmann, J Daschbach and S Pons,
J. Electroanal. Chem., 263 (1989) 205.
- 4.30 M Fleischmann, D Fletcher, G Denuault, J Daschbach and S
Pons,
J. Electroanal. Chem., 263 (1989) 225
- 4.31 M Fleischmann, D Fletcher, G Denuault, J Daschbach and S
Pons,
J. Electroanal. Chem., submitted.
- 4.32 M Fleischmann, D Fletcher, G Denuault, J Daschbach and S
Pons,
J. Electroanal. Chem., submitted
- 4.33 R D Newmark, M Flesichmann and B S Pons,
J. Electroanal. Chem., 255 (1988) 325.
- 4.34 L M Abrantes, M Fleischmann, L M Peter, S Pons and B P
Scharifker,
J. Electroanal. Chem., 254 (1988) 229.