

AD-A118 706

ALBERTA UNIV EDMONTON DEPT OF CHEMISTRY

F/G 7/4

VIBRATIONAL SPECTROSCOPY OF THE ELECTRODE-SOLUTION INTERPHASE. --ETC (11)

AUG 82 S PONS. T DAVIDSON, A BEWICK

N00014-82-G-0017

UNCLASSIFIED

TR-10

NL

10-1

4-1

11-706

END
9 82
DTIC

AD A118706

DTIC FILE COPY

(12)

OFFICE OF NAVAL RESEARCH
Contract N00014-82-G-0017
Task No. NR 359-718
TECHNICAL REPORT NO. 10

Vibrational Spectroscopy of the Electrode-Solution Interphase.
III. Use of FTIR Spectroscopy for Observing Double Layer Reor-
ganization.

By
Stanley Pons, Timothy Davidson, and Alan Bewick*
Prepared for Publication in
Journal of Electroanalytical Chemistry

University of Alberta
Department of Chemistry
Edmonton, Alberta, Canada
T6G 2G2

*Department of Chemistry
The University
Southampton, U.K.

August 18, 1982

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited.

DTIC
ELECTE
AUG 31 1982
H

REPORT DOCUMENTATION PAGE		DTIC ACQUISITION POINT DEPARTMENT & OFFICE SYMBOL
1. REPORT NUMBER 10	2. GOVT ACCESSION NO. AD A118706	3. DEPARTMENT & OFFICE SYMBOL 706
4. TITLE (and Subtitle) Vibrational Spectroscopy of the Electrode Solution Interphase. III. Use of FTIR for Observing Double Layer Reorganization.	5. TYPE OF REPORT & PERIOD COVERED Technical Report # 10	
7. AUTHOR(s) Stanley Pons, Timothy Davidson, and Alan Bewick	8. PERFORMING ORG. REPORT NUMBER N00014-82-G-0017	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Alberta Edmonton, Alberta, Canada T6G 2G2	10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 359-718	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217	12. REPORT DATE August 18, 1982	13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electrochemistry, FTIR, Reflection Spectroscopy, Double Layer		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Results are presented for experiments designed to observe structural changes in the electrical double layer under different potential modulations. Results are presented for non-aqueous systems in this report.		

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE
3/74 DIB: 01 014-6681
Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (from Data Entered)

82 8 27 055

ABSTRACT

Potential dependent Fourier transform infrared spectra recorded in situ at a polarized platinum electrode in acetonitrile solutions clearly show the interplay between adsorbed acetonitrile and preferentially adsorbed anions. Water in at least two forms is observed as independent structures in the system.

VIBRATIONAL SPECTROSCOPY OF THE ELECTRODE-SOLUTION INTERFACE.

III. USE OF FOURIER TRANSFORM SPECTROSCOPY FOR
OBSERVING DOUBLE LAYER REORGANIZATION

Stanley Pons* and T. Davidson
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada
T6G 2G2

and

A. Bewick
Department of Chemistry
The University
Southampton, Hampshire
SO9 5NH
U.K.

* To whom correspondence should be sent.

In situ infrared spectroscopy of the electrode-solution interface has recently been used to characterize a variety of electrochemical phenomena (1-6). Basically, three successful techniques exist for obtaining such spectra: (a) electromodulated specular reflectance (5), (b) Fourier transform infrared spectroscopy at differentially polarized surfaces (2), and (c) polarization modulation specular reflectance (6). In this paper, we look at the changes in the composite structure of the double and diffuse layers of a platinum electrode in acetonitrile solutions. It is shown that the technique is sensitive enough to observe the spectral differences in adsorbed and bulk acetonitrile, as well as the differences in the solution structure as anions are specifically adsorbed at potentials positive to the potential of zero charge. Absorbance changes due to water molecules associated with the anion and acetonitrile are also observed.

EXPERIMENTAL

Spectroscopy and Electrochemistry

Spectra were recorded on a Nicolet 7199 FTIR system. Potential step programs were provided by a HI-TEK Instrument DP2101 potentiostat and PPR1 waveform generator. The waveform generator was triggered by a TTL signal from the Nicolet computer denoting the beginning of data acquisition. For

1. A. Bewick, K. Kunitatsu, and S. Pons, *Electrochimica Acta* **25** (1980) 465.
2. T. Davidson, S. Pons, A. Bewick, and P.P. Schmidt, *J. Electroanal. Chem.* **125** (1981) 237.
3. A. Bewick and J. Russell, *ibid* **122** (1982) 329.
4. B. Boden, A. Bewick, K. Kunitatsu, and C. Lamy, *J. Electroanal. Chem.* **121** (1981) 361.
5. A. Bewick and K. Kunitatsu, *Surface Science* **101** (1980) 131.
6. J. W. Russell, J. Overend, K. Scandala, M.W. Severson and A. Bewick, *J. Phys. Chem.*, in press.

sequential potential steps, various delay time sequences were used to record spectra at the same times after the potential was changed so that signal averaging could be used to increase signal-to-noise ratio (7). The spectra herein are the difference between 40 averaged spectra at the same and base potential. The base potential of -0.50 V vs Ag/Ag^+ (0.01 M in 0.1 M tetrabutylammonium tetrafluoroborate or lithium perchlorate in acetonitrile) reference was chosen because of its proximity to the pzc of platinum in the chosen electrolytes.(8)

Chemicals

Acetonitrile (Caledon, HPLC grade, 0.003% water) was distilled twice from calcium hydride, and stored before use in sealed containers over Merck alumina (Super grade I). The cells were dried in a vacuum oven at $150^{\circ}C$ before use, and dry argon admitted to the oven as the vacuum was released. Transfer of solvent/electrolyte to the cell was made in an argon filled glove bag. Electrolytes were purified (7) and dried similarly in a vacuum oven before use.

Cells, Mountings, and Electrodes

The description of the cell construction and the mounting for the Nicolet sample cavity has been described elsewhere (7). The electrode used was a platinum mirror that had been polished with 0.05 μm alumina and dried in a vacuum oven immediately before use. Solution thickness in the optical path was determined by use of the integrated extinction coefficient method as previously described (7).

7. S. Pons, T. Davidson, and A. Bewick, *Anal. Chem.*, in press.
8. D.A. Pettit and I.G. Khamisbakhshi, *J. Electroanal. Chem.* **128**, 277 (1982)

A	Dist	Availability C	Unannounced	Justification	Accession For	DTIC COPY INFORMED
	Special	AVAIL AND	Distribution/	DTIC GRAI	DTIC TAB	

RESULTS

Differential spectra of a 0.10 M solution of tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile as a function of applied potential are shown in Figure 1. The base potential of each spectrum is -0.50 V vs the Ag/Ag⁺ reference electrode. Peaks extending downward correspond to increased absorption of radiation at the sample potential (less absorbance at the base potential of -0.50 V). The converse is true for peaks extending upwards. Figure 2 shows the spectra from the same system after it is made 0.10 M in water. Most noticeable are new absorbance changes in the region from about 3200 cm⁻¹ to 3700 cm⁻¹, around 1650 cm⁻¹, and broadening in the band around 1070 cm⁻¹. Spectra from the same experiment performed on an anhydrous solution of 0.10 M lithium perchlorate are presented in Figure 3, and Figure 4 gives the corresponding spectra after addition of water, as in the tetrafluoroborate system. The solution thickness between the window and the electrode of 0.75 mm was the same in all four experiments.

The C-H stretch region between 2200 cm⁻¹ and 2400 cm⁻¹ is observed to be blue shifted at potentials positive to the base potential in all cases. The perchlorate asymmetric stretch fundamental region (1102 cm⁻¹) is not shifted at positive sample potentials, but is broadened. Further broadening is noticed in the presence of water. The same is true of the tetrafluoroborate anion asymmetric stretch region (1060 cm⁻¹), and some fine structure appears on the band. Normal transmission spectra of perchlorate and tetrafluoroborate anion in acetonitrile show no fine structure in this region.

DISCUSSION

The spectra contain a considerable number of complex bands and clearly their interpretation will give detailed information on the changes in the

number and the nature of various species on the electrode surface and in the double layer. Certain aspects are readily explained: the increasing adsorption of acetonitrile with increasing positive potential beyond -0.5 V is clear from the progressively increasing intensity of the downward extending band at about 2350 cm⁻¹ which is strongly blue shifted by the perturbation of the molecule due to adsorption (2) (bulk acetonitrile gives a -C≡N fundamental at 2220 cm⁻¹); the increasing amount of anion in the double layer is shown by the other dominant downward bands at 1102 cm⁻¹ and 1060 cm⁻¹ for perchlorate and tetrafluoroborate respectively. The upward extending fine structure on the -OH band between 200 cm⁻¹ and 2400 cm⁻¹ is due to decreased absorption by bulk acetonitrile.

The complex bands between 3300 cm⁻¹ and 3600 cm⁻¹ and also near 1600 cm⁻¹ are particularly interesting and they can be ascribed to the stretching modes of water in different environments. The broad band at 3350 cm⁻¹ corresponds to extensively hydrogen-bonded water, possibly associated with the anion, and increasing in intensity as more anions enter the double layer. The sharper bands of opposite sign near 3625 cm⁻¹, 3550 cm⁻¹ and 1625 cm⁻¹ probably arise from water which is less perturbed by hydrogen bonding. A very likely candidate is the symmetrically bonded complex between two acetonitrile molecules and one water molecule. This is a well characterized species for which the ν₃, ν₁ and ν₂ vibrational modes are at the frequencies given above (8-11). The intensities of these bands are seen to decrease as the potential is made more positive indicating a decreasing population of this complex.

These assignments lead to a simple explanation of the spectra in terms of the dependence on the electrode potential of the population of the various species in the optical path. As a consequence of making the electrode potential more positive there is an increased amount of adsorbed acetonitrile

end of anions in the double layer. Movement of anions into the double layer will not, however, deplete the thin layer of electrolyte solution in the optical path because migration of the 0.1 M electrolyte solution will readily replenish the layer; thus there will be a net increase in the total number of anions in the IR beam and also of the water associated with them, as is shown by the spectra. As a result, some acetonitrile, both free and complexed with water, will be displaced from the fixed volume of the thin layer as is observed from changes in the acetonitrile bands and in the bands for complexed water, particularly at high potentials. These changes are summarized in Figure 5.

There are also contributions from the cation. A bipolar band is observed in the region 2900 - 3050 cm^{-1} corresponding to the C-H stretch of TBAF. The major part of the band is upward extending which corresponds to the decrease in the amount of the cation in the double layer with increasing positive potential. The small lobes of opposite sign indicate also that there are changes in the detailed band shape.

It is clear from the data presented here that the method employed will be of great value in probing changes in the structure of the electrical double layer.

References:

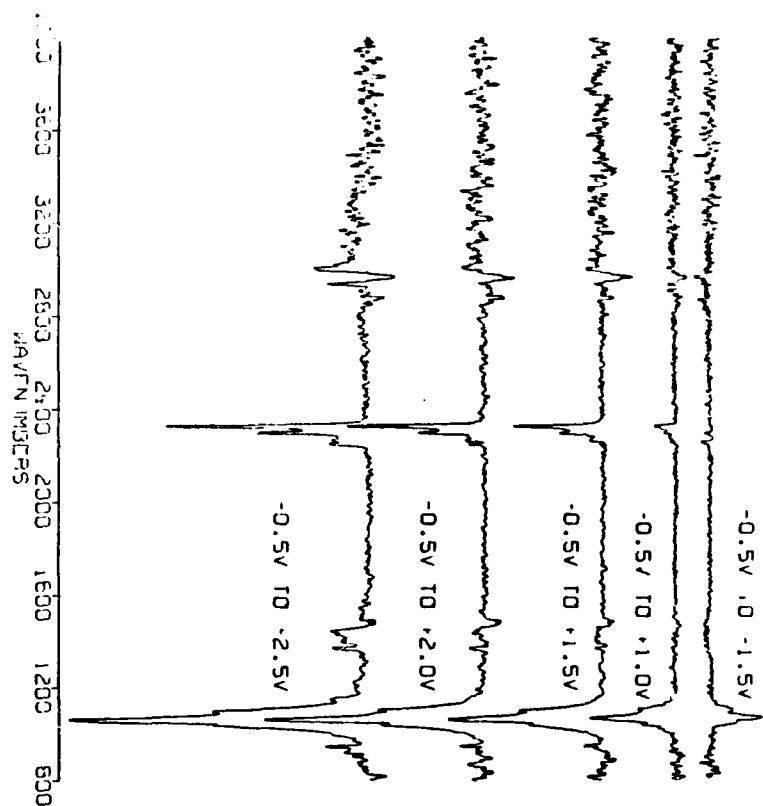
- (9) P. Saumagne, Ph.D. Thesis, Universite de Bordeaux, France, 1961.
- (10) E. Gentric, Ph.D. Thesis, Universite de Bretagne Occidentale, France, 1972.
- (11) P. Saumagne and M.L. Josien, Bull. Soc. Chim. France (1958) 813.

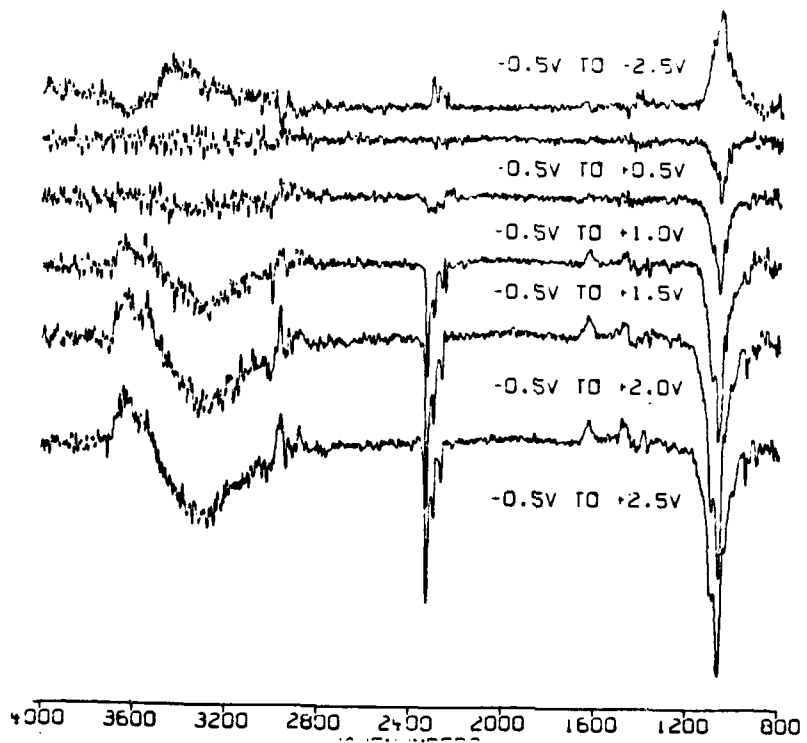
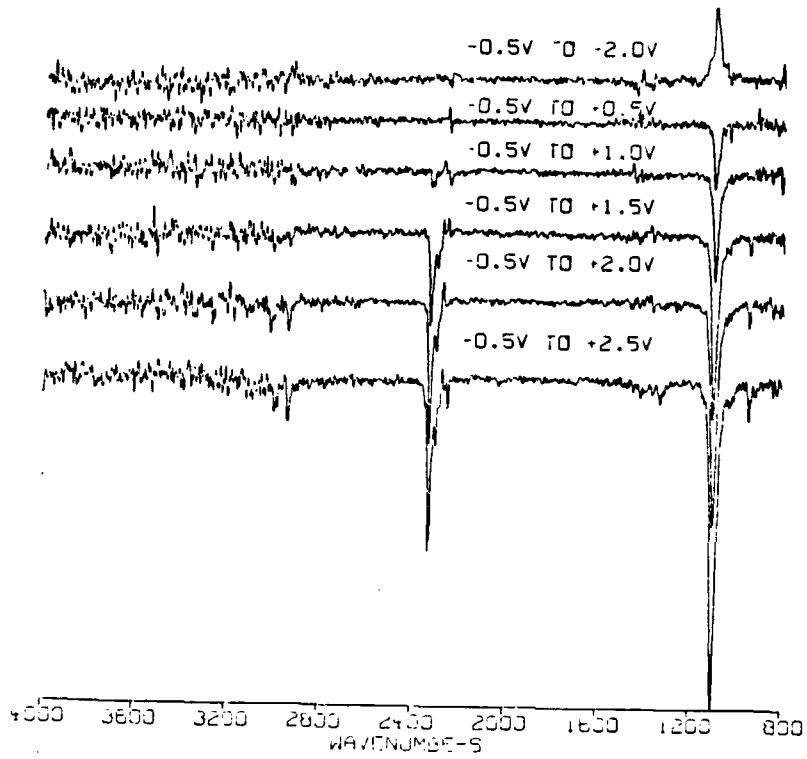
FIGURE LEGEND

- (1) Differential reflectance FTIR spectra of 0.10 M tetrabutylammonium tetrakisborate in anhydrous acetonitrile. Solution thickness = 0.75 microns. Spectra recorded under steady state conditions at each indicated potential. Spectrum at the -0.50 V base potential was always subtracted from those obtained at the other potential.
- (2) Same as Figure 1 except water concentration 0.10 M.
- (3) Differential reflectance FTIR spectra of 0.10 M lithium perchlorate in anhydrous acetonitrile. For other notes, see Figure 1.
- (4) Same as Figure 3 except water concentration 0.10 M.
- (5) Note: see ... account for spectral observations.

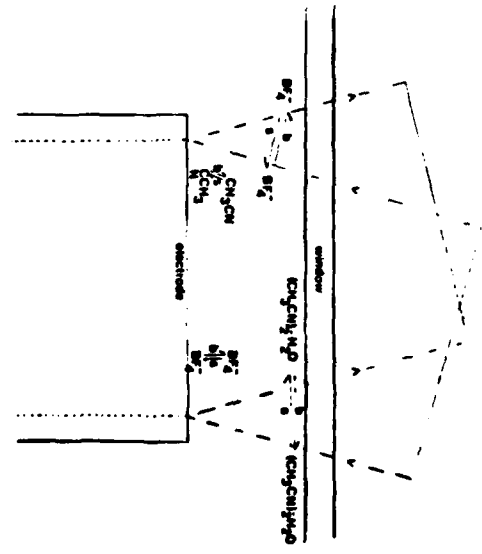
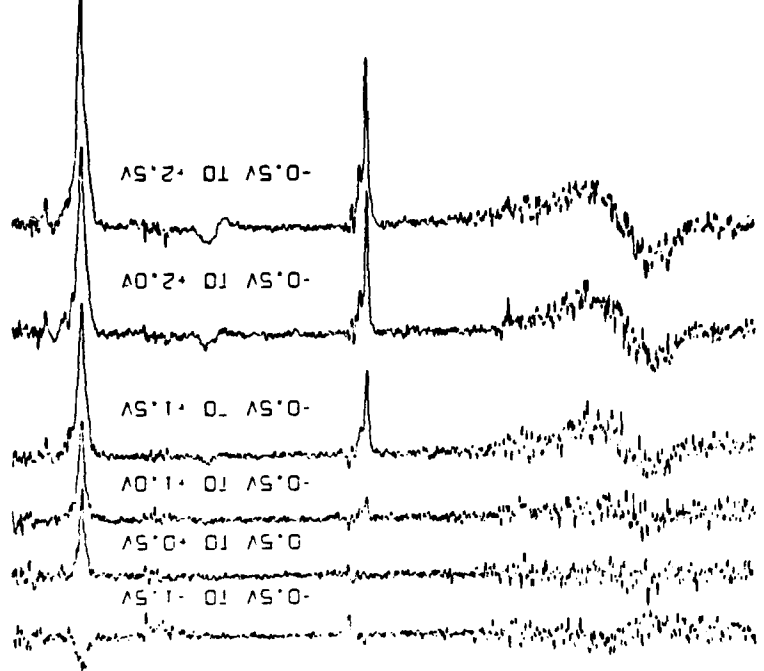
NOTES ON SPECTRA OBSERVATION

Method of spectra was on off the electrode surface and due on out of the thin electrode layer caused by the potential step from the more positive potential to the more negative potential is represented by the arrow included in the figure legends of references and reverse process.





WAVELENGTHS
4000 3600 3200 2800 2400 2000 1600 1200 800



SP472-3/A1

472:GAN:716:enj
78a72-608

SP472-3/A11

472:GAN:716:dc
78a72-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. H. Neables Building 114, Section B 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. S. Anster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. J. Drisko Port Puenome, California 92-01	1
The Assistant Secretary of the Navy (SEA5) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20330	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 113C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22304	12	Naval Ship Research and Development Center Attn: Dr. G. Somanjian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Sealford Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 92132	1
		Mr. John Bowie Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	No. Copies		No. Copies
Dr. Paul Delehav Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Benson Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Boyce M. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27516	1
Dr. E. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Amborn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Eaton Lockheed Missiles & Space Co., Inc. P.O. Box 506 Sunnyvale, California 94088	1	Dr. J. Bouchier Electrochimie Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. S. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. P. Nictel Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. S. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

SP472-3/B17

472:GAN:716:1ab
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>
Dr. Micha Tomkiewicz Department of Physics Brooklyn College Brooklyn, NY 11210	1
Dr. Lesser Blum Department of Physics University of Puerto Rico Rio Piedras, PR 00931	1
Dr. Joseph Gordon II IBM Corporation F33/281 5600 Cottle Road San Jose, CA 95193	1
Dr. Robert Somoso Jet Propulsion Laboratory California Institute of Technology Pasadena, CA 91103	1

END

DATE
FILMED

9 . 8 2

DTI