

AD-A106 231

ALBERTA UNIV EDMONTON DEPT OF CHEMISTRY

F/8 7/4

VIBRATIONAL SPECTROSCOPY OF THE ELECTRODE-ELECTROLYTE INTERFACE--ETC(U)

AUG 81 T DAVIDSON, B S PONS, A BEWICK

N00014-80-6-0107

UNCLASSIFIED

TR-5

NL

1-1
3/2/81



END

12

LEVEL II

k

OFFICE OF NAVAL RESEARCH

Contract # N00014-80-8-0187

Task No. NR 359-718

TECHNICAL REPORT NO. 5

AD A106231

Vibrational Spectroscopy of the Electrode-Electrolyte Interface. Use of Fourier Transform Infrared Spectroscopy.

by

T. Davidson, B. Stanley/Pons, A. Bewick, and P. Schmidt

Prepared for Publication

in

Journal of Electroanalytical Chemistry

University of Alberta
Department of Chemistry
Edmonton, Alberta

DTIC ELECTE
S OCT 27 1981 D

August 4, 1981

B

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

FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 5	2. GOVT ACCESSION NO. AD-A106 231	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Vibrational Spectroscopy of the Electrode-Electrolyte Interface. Use of Fourier Transform Infrared Spectroscopy.		5. TYPE OF REPORT & PERIOD COVERED Technical Report # 5
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) S. Pons, T. Davidson, A. Bewick and P. Schmidt		8. CONTRACT OR GRANT NUMBER(s) N00014-80-8-0107
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Alberta Department of Chemistry Edmonton, Alberta		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS MR 359-7.1, 8/7-22-80
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		12. REPORT DATE August 1st, 1981
		13. NUMBER OF PAGES 19
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
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) Spectroelectrochemistry, Specular Reflectance Spectroscopy, Acetonitrile		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Reported is the first application of Fourier transform infrared spectroscopy as an analytical probe for the <u>in situ</u> monitoring of electrochemical interfacial phenomena. The structure of acetonitrile at the interface is reported.		

Vibrational Spectroscopy of the Electrode-Electrolyte Interface.

Use of Fourier Transform Infrared Spectroscopy.

Timothy Davidson and B. Stanley Pons^{*}
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada
T6G 2G2

Alan Bewick
Department of Chemistry
The University
Southampton, Hampshire SO9 5NH
England

Parbury P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

^{*}To whom correspondence should be addressed.

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
<input checked="" type="checkbox"/>	

The power of electrochemically modulated infrared reflectance spectroscopy (EMIRS) for the elucidation of mechanisms of surface catalyzed reactions at an electrode surface has recently been demonstrated (1-4). We have now successfully used a Fourier transform infrared instrument to obtain spectra under similar conditions. Although the absolute sensitivity is less than that of EMIRS, the speed, spectral range and versatility of FTIR will make it an indispensable tool for the study of electrode solution interfaces. In this initial study, the structure of acetonitrile in the double layer at a platinum electrode was investigated, as well as the effect on that structure of commonly used cations (lithium and tetrabutylammonium). Recent (5) electrochemical investigations have indicated that acetonitrile is strongly adsorbed at a polycrystalline platinum surface over a wide range of potentials. That work also pointed out the non-interference of lithium cation on the strength of this adsorption. Others (6) have indicated, however, disruption of solvent adsorption by specific adsorption of tetrabutylammonium ion. There have also been indications (7) that the water concentration in the interfacial region is affected by these cations. The experiment was designed to see if any of these effects could be sensed with infrared absorption changes at various electrode potentials.

The FTIR spectra were recorded between 4000 and 650 cm^{-1} on a Nicolet 7199 instrument fitted with a polariser. The cell (described elsewhere (8)) had a circular plate window (40 mm diameter; 2mm thickness). The platinum indicating electrode was a disk (1.1 cm^2) mounted in the end of a Kel-F rod, and was

polished to a mirror finish by 0.05 micron alumina. The counter electrode was a platinum wire, and the reference was an Ag/Ag^+ (0.01 M) in acetonitrile containing the same electrolyte as the solution under investigation.

Results and Discussion

The difference spectra obtained using "anhydrous" acetonitrile containing (a) 0.1 M lithium perchlorate and (b) 0.1 M tetrabutylammonium fluoroborate are shown in Figure 1 for a potential step experiment from 0.00 V to 2.00 V vs the Ag/Ag^+ reference. The spectrum from the lithium perchlorate solution clearly shows the appearance of a $\text{C}\equiv\text{N}$ stretch band at 2325 cm^{-1} . This band is strongly shifted from the $\text{C}\equiv\text{N}$ stretch for bulk acetonitrile and it corresponds to the formation of a new species at 2.0 V, oriented to give the $\text{C}\equiv\text{N}$ band a component perpendicular to the electrode surface as would be expected for bonding to the surface via the nitrogen. Little or no CH_3 stretch is observed indicating little perturbation of this part of the molecule. Also noted is the band near 1650 cm^{-1} , the water bending region, indicating perturbation of the residual water in the interfacial region. The magnitude and shape of this band is strongly dependent on the amount of water present in the system and there is also a broad feature in the corresponding OH stretch region. In the case of tetrabutylammonium tetrafluoroborate the spectrum is very different. In the $\text{C}\equiv\text{N}$ stretch region, there is a broad feature on which is superimposed a sharp band, at exactly the bulk acetonitrile position, but of opposite sign to

that of the C≡N band for the lithium perchlorate solution. It would appear, therefore, that there is a small decrease in the amount of acetonitrile present in the double layer at the more positive potential. In all cases, there is also a strong band near 1200 cm^{-1} and work is continuing to identify its origin.

If acetonitrile- d_3 is substituted for acetonitrile in the above experiments, the results are similar. Figure 2 represents the spectrum obtained between 0.00 and 2.50 V using lithium perchlorate in the deuterated solvent.

Experiments performed over a range of electrode potentials show that acetonitrile or acetonitrile- d_3 adsorbed onto the surface of the platinum electrode from perchlorate solutions gives an almost normal vibrational spectrum when the electrode potential is not far removed from E_{pzc} . However, with more extreme conditions of high positive potentials, the C≡N stretching frequency is strongly blueshifted (Figure 3). A shift in this direction is interesting and is indicative of the bonding of the molecule to the surface. Red-shifting is commonplace in molecules with polarizable bonds which form adducts and complexes with strongly electronegative species (9,10). The blue-shifting which occurs in acetonitrile, however, is entirely consistent with the behaviour of this molecule as a Lewis base. It has been known for some time that the C≡N stretch in acetonitrile is blue-shifted upon the formation of adducts with a variety of Lewis acids. This blueshifting, however, is not substantially influenced by the formation of an adduct bond. Purcell and Drago (9) showed that the kinematic coupling of the C≡N and N-acid

bonds can, at best, account for about 10 cm^{-1} of the increase in the vibrational frequency. These authors determined that the major contribution to the blue-shift occurred through the strengthening of the C≡N bond. And, in particular, they found that although the adduct may lead to a slight decrease in the strength of the π -bonding system, the increase in strength in the σ -bond between C and N more than compensated any effects of polarization. Thus, the C≡N stretching force constant is increased simply because the strength of the bond is increased.

Similar conclusions were reached by Sadlej and Kecki (10). Purcell and Drago (9) based their analysis on calculations using the extended Huckel method. Sadlej and Kecki (10) made use of a modified CNDO scheme. In both sets of analyses it was possible to choose two π orbitals and one σ orbital as being responsible for the majority of the bonding between C and N in acetonitrile. Furthermore, both sets of authors concluded that in the presence of an adduct a certain level of re-hybridization occurs on the N atom. In particular, Sadlej and Kecki state that the $2p\sigma$ and $2s$ atomic orbitals on nitrogen essentially describe the lone-pair orbital on nitrogen. The formation of the complex with a positively charged Lewis acid appears to increase the $2p\sigma$ character of the lone-pair molecular orbital. At the same time, there appears to be a more pronounced $2s_N$ participation in the formation of the C≡N σ bond. The strength of the bond is observed to increase under these conditions.

It is interesting to note that the location of the shifted C≡N vibrational stretch is potential-dependent, Figure 3. Again,

this observation is entirely consistent with that which is known from the behaviour of acetonitrile in the free, solution phase. The potential dependence of the frequency for the adsorbed acetonitrile reflects the fact that a variety of electronegative adducts lead to the same behaviour for acetonitrile in the solution phase.

It is apparent from these initial experiments that a standard FTIR instrument may be used quite effectively in the investigation of electrochemical interfacial phenomena. Work is in progress to increase the sensitivity of the technique and to apply it to aqueous systems.

Acknowledgements

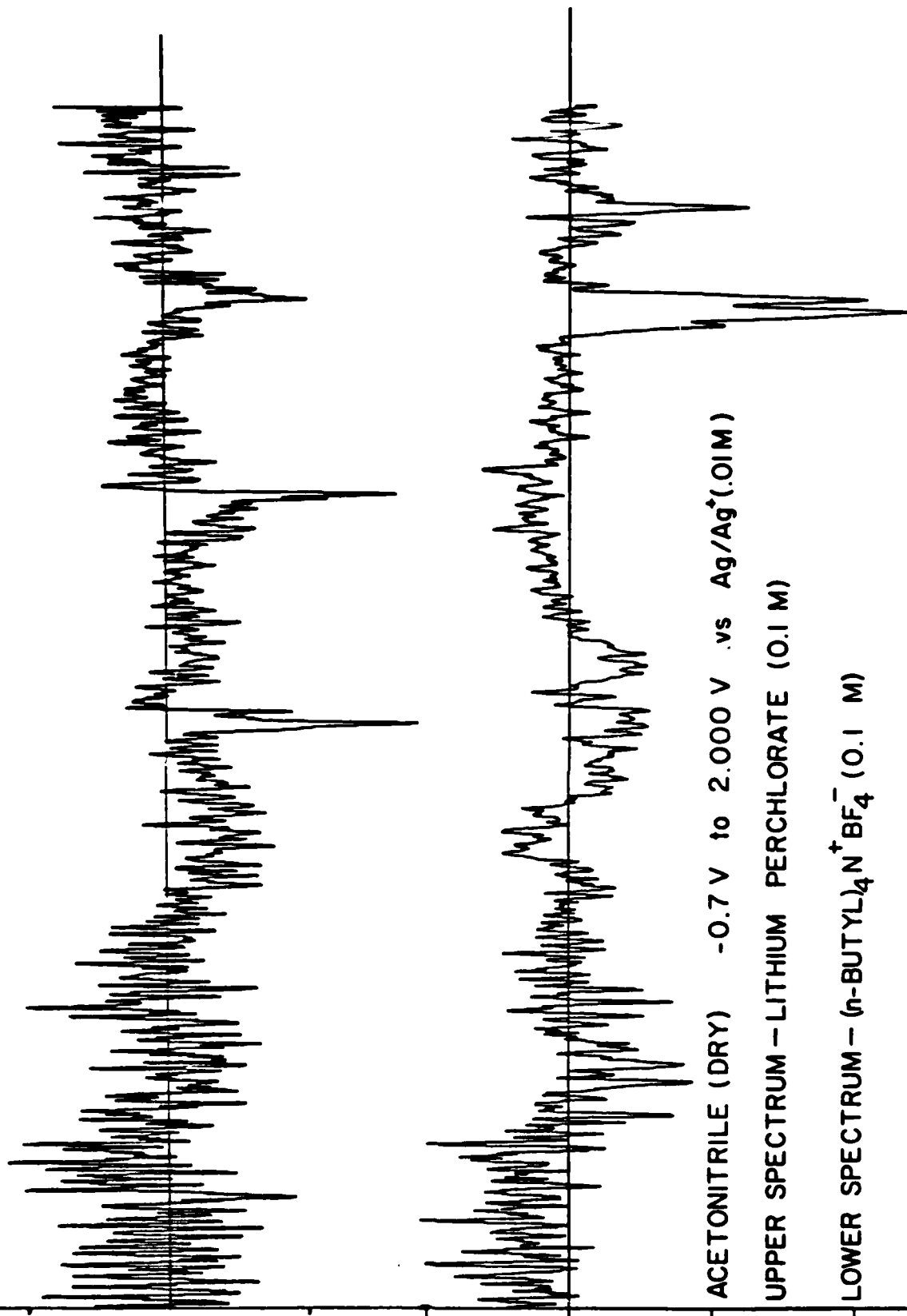
This work was supported in part by the Office of Naval Research, Washington, D.C. The authors would like to thank Dr. Keiji Kunimatsu for providing electrochemical information, and Professor John Bertie for his advice and consultations on the use of the Fourier transform and polarization techniques.

References

1. A. Bewick, K. Kunimatsu, and B. Stanley Pons, *Electrochim. Acta*, 25, (1980) 465.
2. A. Bewick, K. Kunimatsu, Jim Robinson, and J.W. Russell, *J. Electroanal. Chem.*, 119, (1981) 175.
3. A. Bewick and K. Kunimatsu, *Surf. Sci.*, 101, (1980) 131.
4. B. Beden, A. Bewick, K. Kunimatsu, and C. Lamy, *J. Electroanal. Chem.*, 121 (1981) 343.
5. O.A. Petrii and I.G. Khomchenko, *J. Electroanal. Chem.*, 106, (1980) 277.
6. See for example J.P. Billon, *J. Electroanal. Chem.*, 1, (1960) 486.
7. See for example L. Horner in B. Baizer, Ed., "Organic Electrochemistry", Marcell Dekker, New York, p. (1973) 430.
8. A. Bewick, K. Kunimatsu and B. Stanley Pons: in preparation.
9. K.F. Purcell and R.S. Drago, *J. Amer. Chem. Soc.*, 88, (1967) 919.
K.F. Purcell, *J. Amer. Chem. Soc.* 89, (1967) 247.
10. J. Sadlej and Z. Kecki, *Roczniki Chemii*, 43, (1969) 2131.

Figure Legends

- Figure 1. FTIR spectra of the Pt/CH₃CN interface.
- Figure 2. FTIR spectra of the Pt/CD₃CN interface.
- Figure 3. C=N vibrational fundamental location for acetonitrile (AN) and acetonitrile-d₃ (DAN) as a function of potential.

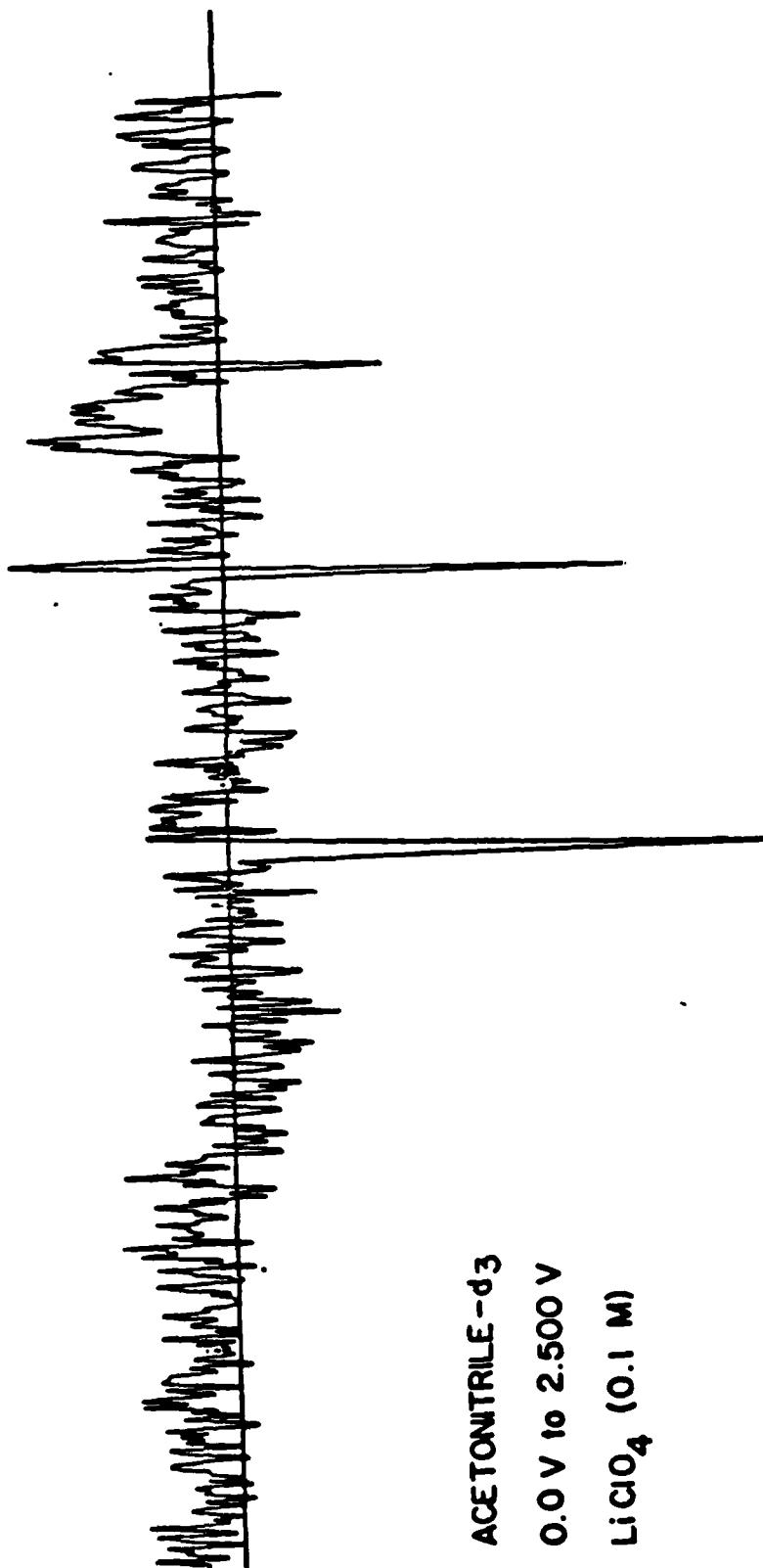


ACETONITRILE (DRY) -0.7 V to 2.000 V vs Ag/Ag⁺ (0.1 M)

UPPER SPECTRUM - LITHIUM PERCHLORATE (0.1 M)

LOWER SPECTRUM - (n-BUTYL)₄N⁺BF₄⁻ (0.1 M)

4000 3600 3200 2800 2400 2000 1600 1200 800 400
VOLTAGE (V)



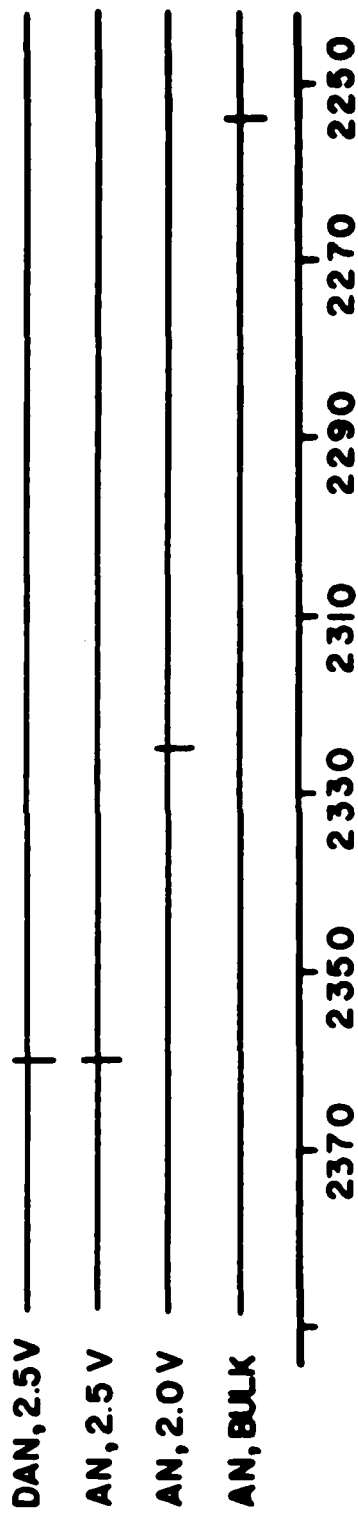
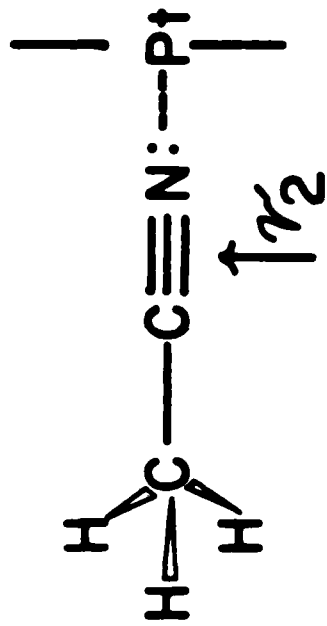
ACETONITRILE - d3

0.0 V to 2.500 V

LiClO₄ (0.1 M)

4000 3600 3200 2800 2400 2000 1600 1200 800 400

CHADWICK INSTRUMENTS



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
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 Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Branch Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

7

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

4

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copie</u>
Dr. Paul Delahay 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. Bennion Chemical Engineering Department University of California Los Angeles, California 90024	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. 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. Auburn 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. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica 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. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02155	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. P. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry Oakland University Rochester, Michigan 48063	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

No.
Copies

Dr. R. Nowak
Naval Research Laboratory
Code 6130
Washington, D.C. 20375

1

Dr. John F. Houlihan
Shenango Valley Campus
Penn. State University
Sharon, PA 16146

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. Novak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NE England	1		
Dr. A. Hiny NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

TECHNICAL REPORT DISTRIBUTION LIST, 051C

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. M. B. Denton Department of Chemistry University of Arizona Tucson, Arizona 85721	1	Dr. John Duffin United States Naval Postgraduate School Monterey, California 93940	1
Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1	Dr. G. M. Hieftje Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. B. R. Kowalski Department of Chemistry University of Washington Seattle, Washington 98105	1	Dr. Victor L. Rehn Naval Weapons Center Code 3813 China Lake, California 93555	1
Dr. S. P. Perone Department of Chemistry Purdue University Lafayette, Indiana 47907	1	Dr. Christie G. Enke Michigan State University Department of Chemistry East Lansing, Michigan 48824	1
Dr. D. L. Venezky Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. Kent Eisentraut, MBT Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433	1
Dr. H. Freiser Department of Chemistry University of Arizona Tucson, Arizona 85721		Walter G. Cox, Code 3632 Naval Underwater Systems Center Building 148 Newport, Rhode Island 02840	1
Dr. Fred Saalfeld Naval Research Laboratory Code 6110 Washington, D.C. 20375	1	Professor Isiah M. Warner Texas A&M University Department of Chemistry College Station, Texas 77840	1
Dr. H. Chernoff Department of Mathematics Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor George H. Morrison Cornell University Department of Chemistry Ithaca, New York 14853	1
Dr. K. Wilson Department of Chemistry University of California, San Diego La Jolla, California	1		
Dr. A. Zirino Naval Undersea Center San Diego, California 92132	1		