

AD-A192 809

THE INFRARED SPECTRA OF SURFACE METAL ATOM VIBRATIONS
SNIFTIRS STUDIES IN. (U) UTAH UNIV SALT LAKE CITY DEPT
OF CHEMISTRY S PONS ET AL. 30 JUL 86 TR-59

1/1

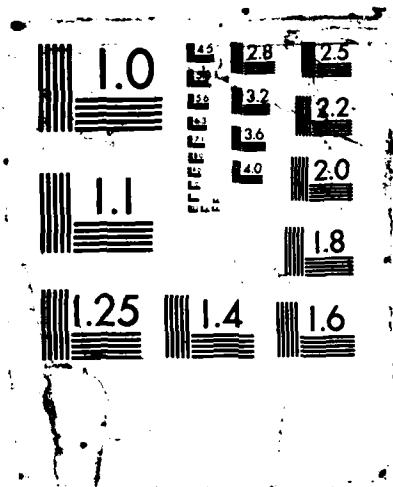
UNCLASSIFIED

N00014-83-K-0470

F/G 20/5

NL





4

DTIC FILE COPY

AD-A192 809

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470-P00003

Task No. NR 359-718

TECHNICAL REPORT # 59

The Infrared Spectra of Surface Metal Atom Vibrations.
SNIFTIRS Studies in the Far Infrared Region using
Time Resolved FTIR Techniques

By

Stanley Pons, J. Li, J. Daschbach, J. Smith, M. Morse

Prepared for Publication in

Journal of Electroanalytical Chemistry

University of Utah
Department of Chemistry
Salt Lake City, Utah 84112

July 30, 1986

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
S APR 14 1988 D
H

1054

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 59	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Infrared Spectra of Surface Metal Atom Vibrations. SNIPTIRS Studies in the Far Infrared Region using Time Resolved FTIR Techniques		5. TYPE OF REPORT & PERIOD COVERED Technical Report # 59
7. AUTHOR(s) Stanley Pons, J. Li, J. Daschbach, J. Smith, M. Morse		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Utah Department of Chemistry Salt Lake City, UT 84112		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0470-P0003
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 359-718
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE July 30, 1986
		13. NUMBER OF PAGES
		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) IR spectroelectrochemistry, Time Resolved Spectroscopy, Metal Atom Spectroscopy, infrared radiation ←		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) IR spectra of metal atoms on electrodes is discussed.		

23A

4

H

J. Electroanal. Chem., 00 (1986) JEC08616
Elsevier-Quoia S.A., Lausanne - Printed in The Netherlands

AUTHOR

Short communication

**THE INFRARED SPECTRA OF SURFACE METAL ATOM VIBRATIONS
SNIFTIRS STUDIES IN THE FAR INFRARED REGION USING TIME
RESOLVED FTIR TECHNIQUES**

DASCHBACH

JIANGUO LI, JOHN DASCHBACH, JERRY J. SMITH*, MICHAEL D. MORSE
and STANLEY PONS**

Department of Chemistry, University of Utah, Salt Lake City, UT 84112 (U.S.A.)

(Received 16th April 1986; in revised form 28th May 1986)

Studies of the vibrations of pure metals have historically been pursued by inelastic neutron scattering (which is sensitive to vibrations of the bulk crystal) and more recently by high-resolution electron energy loss spectroscopy, HREELS (which is more sensitive to vibrations of the metal surface). Direct infrared absorbance techniques provide advantages over both of these methods, since they may be used in more hostile environments (such as at the interface between metal and chemical solutions). They have rarely been applied with much success, however, because of the very effective shielding of the electromagnetic radiation by the metal conduction electrons. This results in an exponential damping of the radiation field as it enters the metal phase, with typical skin depths ($1/e$ damping distances) of only a few tens of nm. This damping improves the sensitivity of infrared absorption measurements to the surface vibrations as opposed to bulk phonons, but limits the magnitude of the absorbance considerably. In this report we demonstrate that reflection infrared vibrational spectroscopy may be used to observe the vibrational structure of metallic species deposited on a metal surface which is under electrochemical control.

The surface FTIR spectroscopic technique SNIFTIRS [1] has been shown to be useful for the observation of the vibrational structure of monlayer (or less) quantities of materials adsorbed at the surface of metal electrodes while under electrochemical control. We have now extended the method by modifying the cell and detector design to permit observations in the far infrared region, even below 100 cm^{-1} . In addition, a signal/timer/controller/sequencer and associated software has been developed to allow time resolved infrared spectral measurements to be recorded with $10 \mu\text{s}$ resolution [2].

Keywords:

* Permanent address: Naval Weapons Center, Physics Division, China Lake, CA 93555, U.S.A.

** To whom correspondence should be addressed.

to p. 1

①

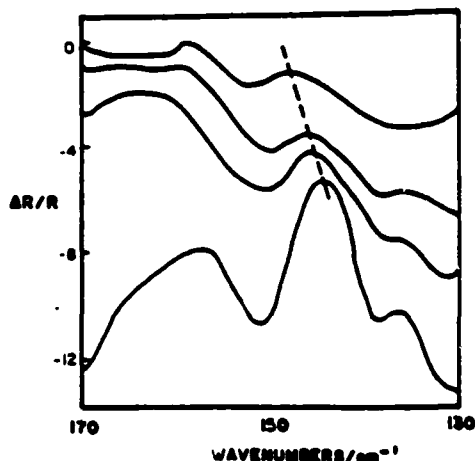


Fig. 1. Surface far infrared difference spectrum of the system described on 130–170 cm^{-1} region as a function of electrode potential. The curves represent potentials of (top to bottom) -1.70 V, -1.90 V, -2.60 V, and -2.90 V respectively. Reference potential -1.50 V.

Underpotential, solid solution, alloy formation, and bulk metal deposition studies were made for lithium deposited on gold from acetonitrile solution. At potentials between -2.40 and -2.60 V, lithium adatoms are underpotentially deposited on a polycrystalline gold surface where they are oxidized rapidly by trace water to solid lithium hydroxide. Between -2.60 and -2.80 V, this insulating precipitate is reduced to lithium atoms in solid solution with gold, and between -2.80 and -3.10 V a chemically resistant gold + lithium alloy is formed. At potentials more negative than -3.10 V, bulk lithium is formed and reduction of solvent proceeds spontaneously.

Figure 1 shows the SNIFTIRS difference spectrum in a region where one would expect to observe the gold-gold fundamental stretch. Diatomic gold has a vibration frequency of 190.9 cm^{-1} , with a reduced mass of 98.5 amu [3]. If the gold atom were vibrating with the same force constant against an infinite mass the reduced mass would be 197 amu, and a vibrational frequency of 135 cm^{-1} would be expected. As the potential is made more negative we observe that the intensity of a band at 145 cm^{-1} increases. At these potentials, the surface is being increasingly covered with underpotentially deposited lithium. Due to the sign convention used in these spectra the increase in intensity is an indication of the loss of absorption by a species, here the gold adatom on the gold surface. The close correspondence between the observed 145 cm^{-1} frequency and that calculated for a gold atom vibrating against an infinite mass suggests that the adatom is bonded to a single surface atom, that most of the motion involved in the optically active vibration occurs on the adatoms, and that the force constant is nearly the same on the surface as the gas-phase dimer.

At 440 cm^{-1} (Fig. 2), a simultaneous and parallel increase in absorbance occurs. This compares to a vibrational frequency of matrix-isolated $^{197}\text{Au}^{7}\text{Li}$ of 705 cm^{-1} . [4]

*not by missing
from lead.
Please
insert.*

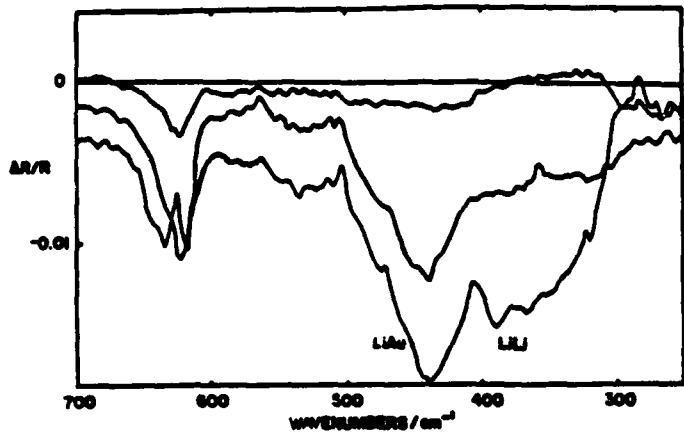


Fig. 2. Surface far infrared difference spectrum of the system described in Fig. 1 in the 200–700 cm^{-1} region as a function of electrode potential. The curves represent potentials of (top to bottom) -1.70 V , -2.90 V , and -3.0 V respectively. Reference potential -1.50 V .

and probably corresponds to a gold-lithium surface species. The diatomic gold-lithium molecule probably derives much of its high vibrational frequency and large bond strength (2.92 eV) [5] from ionic interactions, $\text{Li}^+ \text{Au}^-$. This is expected since apart from the halogen atoms, gold has the highest electron affinity of any element (2.31 eV) [6]. On a surface or in the bulk, the electron donated to gold may be delocalized into the gold conduction band, resulting in a smaller Coulombic force between the atoms in Li–Au (surface) than in diatomic Li–Au. Other explanations are possible, of course, but this does explain the lower than expected value for the Li–Au vibrational frequency, however.

No bands attributed to Li–Li vibrations are observed at potentials more positive than those required for bulk deposition of lithium. As soon as three dimensional growth of lithium begins, however, a band at 395 cm^{-1} rapidly grows in. This may be compared to the $^7\text{Li}_2$ vibrational frequency of 351 cm^{-1} in the gas phase [3]. The shift of 44 cm^{-1} to higher frequency is relatively small considering that it corresponds to condensation of a dimer onto a solid surface. It is therefore probable that the 395 cm^{-1} peak does correspond to a surface vibration of Li–Li.

A cell was equipped with a very small electrode (0.5 mm diameter) so that the time constant of the cell could be decreased to suitably small values, and time resolved spectra were obtained for the fast nucleation and growth process of lithium on gold. Figure 3a shows the time and wavenumber resolved spectral response obtained at 10 ms intervals following application of the potential. The time profile alone is shown in Fig. 3b. The growth of the absorption transient follows a t^3 dependence (a plot of absorbance/ t^3 vs. t is linear with a correlation coefficient = 0.9989). With this information, one may consider various models of nucleation and crystal growth to determine which possibilities are consistent with this time depend-

Session For	
S	GRA&I <input checked="" type="checkbox"/>
T	TAB <input type="checkbox"/>
U	Unannounced <input type="checkbox"/>
V	Classification <input type="checkbox"/>

Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



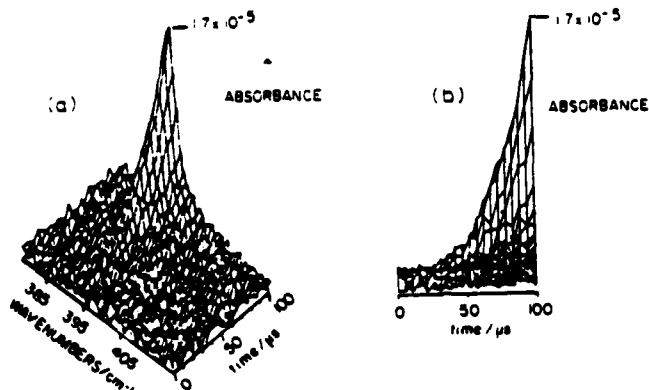


Fig. 3. Time resolved surface far infrared difference spectrum of lithium nucleation and growth. Total experimental time is 100 ms; spectral width is 45 cm^{-1} , peak is at 396 cm^{-1} . (a) 3-dimensional plot; (b) time profile of 395 cm^{-1} peak.

ence. In this particular example, one finds that a mechanism involving instantaneous nucleation of lithium atoms followed by three dimensional growth is consistent with the observed time dependence. One also notes that the absorption peak broadens as it grows, as a result of lateral interactions and surface defects which are incorporated into the new-grown crystallite.

In addition to the metal stretch bands reported in this note, we point out that there are other bands observed in other regions of the infrared spectrum. These correspond to adsorbed supporting electrolyte and solvent, as is evidenced by changing the system components. The behavior and nature of these vibrations will be the subject of a forthcoming report.

In conclusion, we have shown that two new powerful variations of infrared spectroelectrochemistry may be used for the study of a fast reactions at metal surfaces involving direct bonding to the metal surface. Finally, we report the direct observation of metal atom vibrations at surfaces by reflection FTIR spectroscopy.

ACKNOWLEDGEMENT

We thank the Office of Naval Research for support of this work.

REFERENCES

- 1 J.W. Foley, C. Korzeniewski, J. Daschbach and S. Pons in A.J. Bard (Ed.), *Electroanalytical Chemistry*, Marcel Dekker, New York, in press.
- 2 J. Daschbach, D. Heisler and S. Pons, *Appl. Spectrosc.*, in press.
- 3 K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
- 4 H.R. Ihle, E. Langenscheidt and B. Zmbora, *J. Chem. Phys.*, 66 (1977) 5105.
- 5 A. Neubert and K.F. Zmbor, *J. Chem. Soc. Faraday Trans.*, 70 (1974) 2219.
- 6 H. Hotop and W.C. Lineberger, *J. Phys. Chem. Ref. Data*, 4 (1975) 539.

DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southampton SO9 5NH
United Kingdom

Dr. J. Driscoll
Lockheed Palo Alto Research
Laboratory
3251 Hanover Street
Palo Alto, California 94304

Dr. D. N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, Utah 84602

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. J. J. Auburn
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135

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

Dr. Manfred Breiter
Institut für Technische Elektrochemie
Technischen Universität Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
Science Department
Lawrence Livermore National Laboratory
Livermore, California 94550

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. B. Brummer
EIC Incorporated
111 Downey Street
Norwood, Massachusetts 02062

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706

Library
Duracell, Inc.
Burlington, Massachusetts 01803

Electrochimica Corporation
20 Kelly Court
Menlo Park, California 94025-1418

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. M. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
Room 5E036 Forrestal Bldg., CE-14
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. John Wilkes
Air Force Office of Scientific
Research
Bolling AFB
Washington, D.C. 20332

Dr. R. Nowak
Naval Research Laboratory
Code 6171
Washington, D.C. 20375

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. B. P. Lever
Chemistry Department
York University
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
and Power Sources Division
Naval Weapons Support Center
Crane, Indiana 47522

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson
NAVSEA-56Z33 NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Dr. Carl Kannewurf
Department of Electrical Engineering
and Computer Science
Northwestern University
Evanston, Illinois 60201

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

DL/413/83/01
359/413-2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Robert Somoano
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus
NASA Headquarters
M.S. RTS-6
Washington, D.C. 20546

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. H. Tachikawa
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Dr. Theodore Beck
Electrochemical Technology Corp.
3935 Leary Way N.W.
Seattle, Washington 98107

Dr. Farrell Lytle
Boeing Engineering and
Construction Engineers
P.O. Box 3707
Seattle, Washington 98124

Dr. Robert Gotscholl
U.S. Department of Energy
MS G-226
Washington, D.C. 20545

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402

Dr. Martha Greenblatt
Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Dr. John Wasson
Syntheco, Inc.
Rte 6 - Industrial Pike Road
Gastonia, North Carolina 28052

Dr. Walter Roth
Department of Physics
State University of New York
Albany, New York 12222

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymer Science and Standards
Division
National Bureau of Standards
Washington, D.C. 20234

Ms. Wendy Parkhurst
Naval Surface Weapons Center R-33
R-33
Silver Spring, Maryland 20910

DL/413/83/01
359/413-2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. John Owen
Department of Chemistry and
Applied Chemistry
University of Salford
Salford M5 4WT ENGLAND

Dr. O. Stafsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

Dr. Boone Owens
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. S. G. Greenbaum
Department of Physics
Hunter College of CUNY
New York, New York 10021

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531
S-751 21 Uppsala, Sweden

Dr. Menahem Anderman
W.R. Grace & Co.
Columbia, Maryland 20144

END

DATE

FILMED

6-1988

DTIC