

AD-A107 067

CALIFORNIA UNIV IRVINE DEPT OF CHEMISTRY

F/8 7/4

THE NATURE OF THE PHASE TRANSITION OBSERVED FOR MONOLAYERS OF A--ETC(U)

OCT 81 D DAHLGREN, J C MENNINGER

N00014-79-C-0648

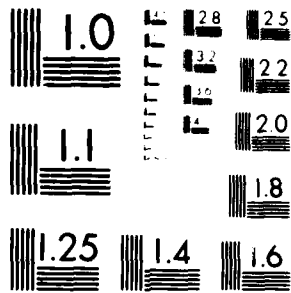
NL

UNCLASSIFIED

TR-2

1
2
3
4
5
6
7
8
9
10
11
12

END
DATE
FILMED
12 81
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A107067

DTIC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

12

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER No. 2.	2. GOVT ACCESSION NO. ADA107067	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Nature of the Phase Transition Observed for Monolayers of Azulene on Pt(111).	5. TYPE OF REPORT & PERIOD COVERED Interim report	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) David Dahlgren and John C. Hemminger	8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0648	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of California Irvine, California 92717		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy 800 N. Quincy Street Arlington, CA 22217	12. REPORT DATE October 1981	
	13. NUMBER OF PAGES 10	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Western Regional Office 1030 E. Green Street Pasadena, CA 91106	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release: distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC NOV 9 1981		
18. SUPPLEMENTARY NOTES To be published in the Journal of Chemical Physics		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Phase transitions Azulene Platinum (111) Low Energy Electron Diffraction		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A model is presented for the reversible phase transition observed for azulene monolayers on Pt(111). Below the transition temperature the overlayer LEED pattern consists of (3x3) aligned with the substrate and (3x3) rotated by 30°. Above the transition temperature the LEED pattern is a (3x3) aligned with the substrate. The model attributes the phase transition to an order-disorder transition of the rotational orientation of azulene molecules with the molecular plane parallel to the surface.		

LEVEL 1

81 10 28 080

DD FORM 1473 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE S N 0102-LF-014-6601

45641 DTIC SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract NO0014-79-C-0648

TECHNICAL REPORT NO. 2

The Nature of the Phase Transition Observed
for Monolayers of Azulene on Pt(III)

by

David Dahlgren and John C. Hemminger

Prepared for Publication

in the

Journal of Chemical Physics

University of California, Irvine

Department of Chemistry

Irvine, California

October 1, 1981

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

The Nature of the Phase Transition Observed
for Monolayers of Azulene on Pt(111)^a

David Dahlgren and John C. Hemminger

Department of Chemistry
University of California, Irvine, California 92717

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Special
A	

Abstract

A model is presented for the reversible phase transition observed for azulene monolayers on Pt(111). Below the transition temperature the overlayer LEED pattern consists of (3x3) aligned with the substrate and (3x3) rotated by 30° . Above the transition temperature the LEED pattern is a (3x3) aligned with the substrate. The model attributes the phase transition to an order-disorder transition of the rotational orientation of azulene molecules with the molecular plane parallel to the surface.

Low energy electron diffraction and other surface sensitive probes have been used to observe many order transitions with temperature for chemisorbed molecular monolayers adsorbed on transition metal surfaces.¹ Unlike the cases of physisorbed overlayers these transitions invariably have been observed to be irreversible and in most cases are due to chemical modifications of the adsorbed molecule. Recently we reported the first observation of a reversible transition in the LEED pattern of a chemisorbed hydrocarbon monolayer adsorbed on a transition metal. The system is azulene ($C_{10}H_8$) chemisorbed on Pt(111).² In this communication we indicate that this transition can be ascribed to an order-disorder transition of the rotational orientation of molecules with the molecular plane parallel to the surface.

When azulene is adsorbed on Pt(111) at room temperature and at coverages which lead to C/Pt atom ratios (from Auger electron spectroscopy) in the range of $1 \leq C/Pt \leq 1.3$ the ordered overlayer of interest is obtained. Following formation of an overlayer in this coverage range the observed LEED pattern consists of a bright 1/3 order ring. This indicates a well defined intermolecular spacing three times the Pt surface unit cell vector. Domains with random orientation with respect to the Pt surface lead to the ring pattern. If this overlayer is annealed at $\sim 125^\circ\text{C}$ an overlayer which exhibits a reversible temperature dependence is observed. Figure 1 shows the LEED pattern obtained from this overlayer below and above the transition temperature. There is no change in the Auger spectrum and no hydrogen evolu-

tion associated with the transition. The facts that the transition is reversible and the sample may be cycled through the transition many times with no change in the behavior of the LEED pattern is strong evidence that the transition is not associated with any chemical modification of the adsorbed azulene.

The LEED pattern obtained from the lower temperature phase (α -phase), Figure 1a, consists of (3×3) domains aligned with the substrate plus (3×3) domains rotated by 30° with respect to the substrate. In addition, some intensity still exists as a $1/3$ order ring. The LEED pattern of the higher temperature phase (β phase) is a (3×3) aligned with the substrate. The transition temperature $T_{\alpha \rightarrow \beta}$ is coverage dependent. $T_{\alpha \rightarrow \beta}$ increases with coverage from a value of $T_{\alpha \rightarrow \beta} \sim 100^\circ \text{C}$ for $\text{C/Pt} \sim 1$ to $T_{\alpha \rightarrow \beta} \sim 150^\circ \text{C}$ for $\text{C/Pt} \sim 1.3$.

Any microscopic explanation for the $\alpha \rightarrow \beta$ transition must explain the driving force for domain formation in the α phase. We propose that the $\alpha \rightarrow \beta$ transition corresponds to an order-disorder transition of the rotational orientation of azulene molecules bound to the Pt with the molecular plane parallel to the surface. Our model of the ordering of azulenenes in the α phase is shown in Figure 2. Only one domain (aligned with the substrate) is shown. Two phenomena will exist for such ordered overlayers which will lead to a driving force for domain formation. An ordered domain such as that shown in figure 2 will have a strain field associated with it if the Pt atoms below each azulene are moved even slightly from their clean surface equilibrium positions. The total strain energy of the system can be

minimized by domain formation. This has been postulated recently by King, et. al. as the driving force for domain function in the reconstruction of W(001) following adsorption of N.³ The minimization of the strain energy is balanced by the energy required to form the domain wall as well as the energy required to form the slightly less stable domains rotated by 30° with respect to the Pt. This energy balance results in a finite domain size. Above the transition temperature (β phase) the azulenes are rotationally disordered leading to the (3x3) LEED pattern.

The other, less likely, driving force for domain formation in the α phase is the existence of an electrostatic field associated with the ordered domain. Azulene has a dipole moment of .8 Debye. Since the molecule is not well described by a point dipole model, the molecular dipole will not be totally screened by its image. Thus there will be a field associated with such a domain. The interaction of the fields of neighboring domains may lead to stabilization of domains, not aligned with the substrate. This effect will again be balanced by the domain wall energy and the instability of the domains not aligned with the Pt. Modeling this effect with a two point charge model of the molecular dipole indicates that it will be minor compared to the strain energy. However, a sophisticated model is required to totally eliminate this possibility.

Within this model the barrier to rotation of an azulene molecule is on the order of 1 kcal/mole. At present we are

taking LEED intensity data in an attempt to measure the critical exponent for this transition.⁴ A detailed discussion of the strain energy will be included in the publication of these results.

We wish to thank D.L. Mills and J. Lawrence for several discussions.

Figure Captions

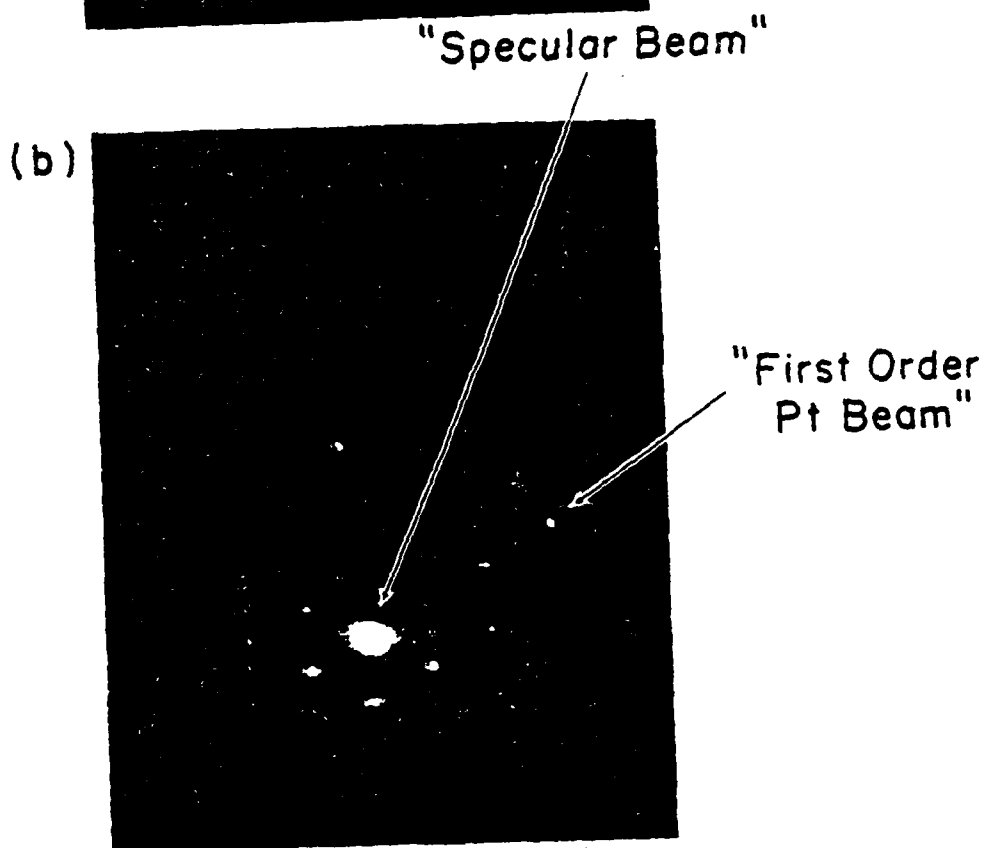
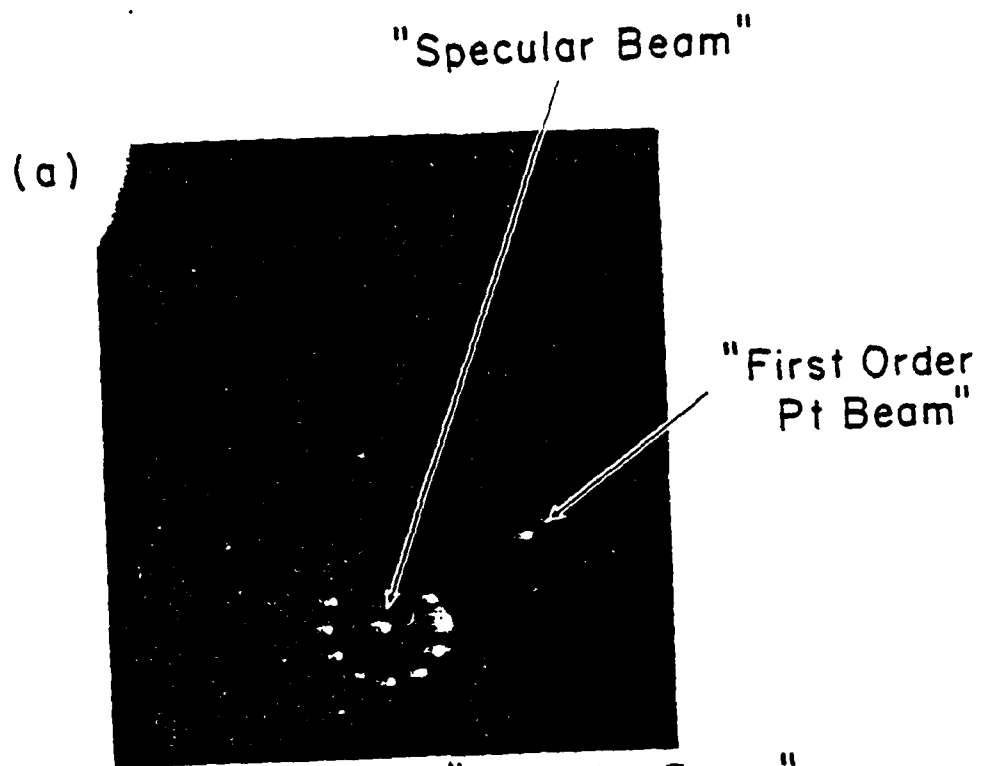
Figure 1

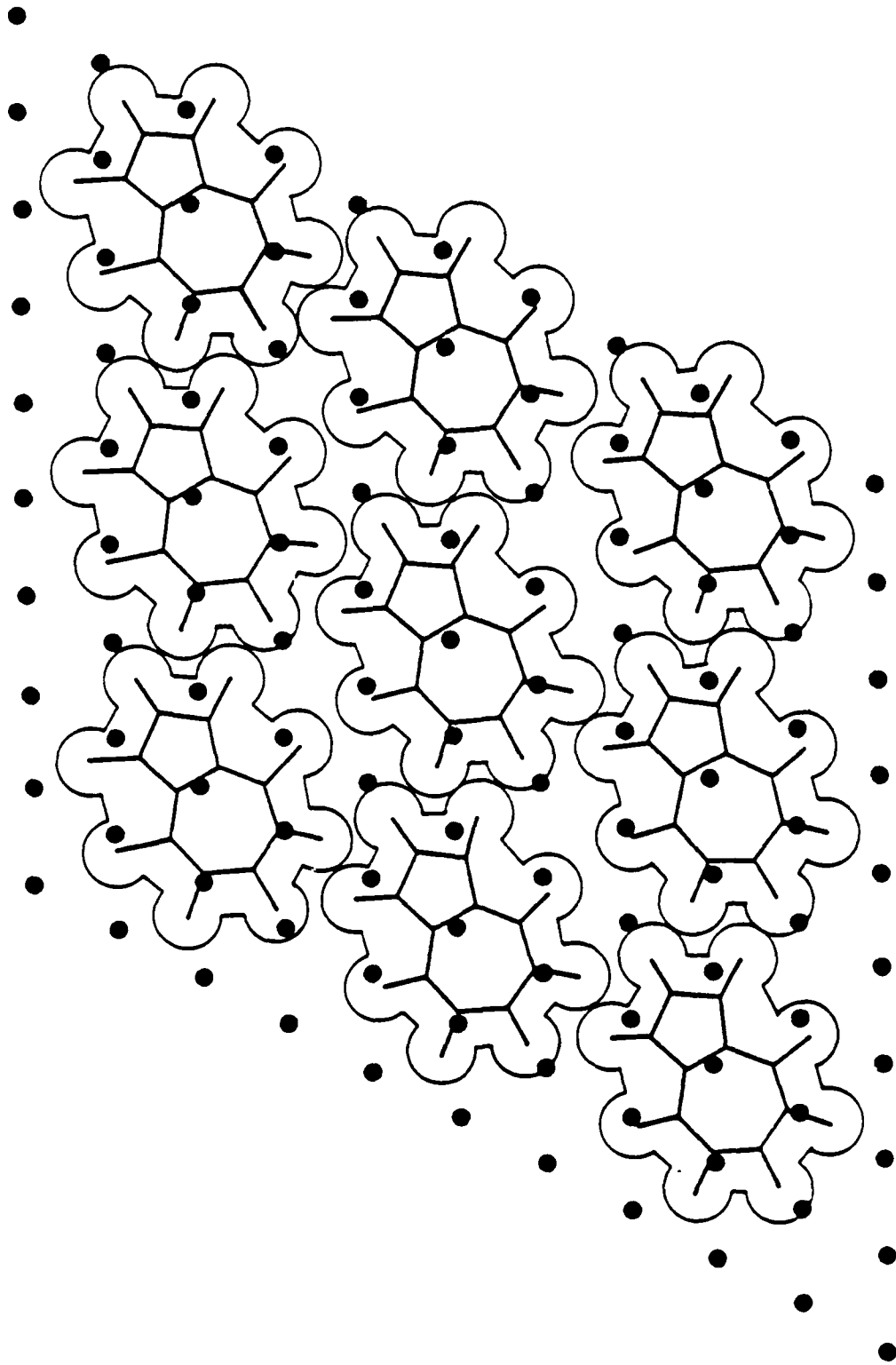
- a) LEED pattern obtained from the α phase of azulene adsorbed on Pt(111).
- b) LEED pattern obtained from the β phase of azulene adsorbed on Pt(111).

Figure 2 Model proposed for the lower temperature (α) phase of azulene adsorbed on Pt(111). Only one domain (aligned with the Pt) is shown. Van der Waal radii are included for the hydrogens to give an indication of the molecular size.

References

- a. This work was supported in part by the Office of Naval Research and the Hooker Chemical Corporation Grant of Research Corporation.
1. G.A. Somorjai, "Chemistry In Two Dimensions: Surfaces," Cornell University Press, 1981. Chapter 5.
2. D. Dahlgren, J.C. Hemminger, submitted to Surface Science.
3. K. Griffiths, C. Kendon, D.A. King, Phys. Rev. Lett. 46, 1584 (1981).
4. L.D. Roelofs, A.R. Kortan, T.L. Einstein, R.L. Parks, Phys. Rev. Lett. 46, 1465 (1981).





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 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. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 00210	1	Naval Weapons Center Attn: Dr. A. B. Amstar, 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. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 3100 (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. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Saalfeld 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 Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. G. A. Somorjai Department of Chemistry University of California Berkeley, California 94720	1	Dr. C. P. Flynn Department of Physics University of Illinois Urbana, Illinois 61801	1
Dr. L. N. Jarvis Surface Chemistry Division 4555 Overlook Avenue, S.W. Washington, D.C. 20375	1	Dr. W. Kohn Department of Physics University of California (San Diego) LaJolla, California 92037	1
Dr. J. B. Hudson Materials Division Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. R. L. Park Director, Center of Materials Research University of Maryland College Park, Maryland 20742	1
Dr. John T. Yates Surface Chemistry Section National Bureau of Standards Department of Commerce Washington, D.C. 20234	1	Dr. W. T. Peria Electrical Engineering Department University of Minnesota Minneapolis, Minnesota 55455	1
Dr. Theodore E. Madey Surface Chemistry Section Department of Commerce National Bureau of Standards Washington, D.C. 20234	1	Dr. Chia-wei Woo Department of Physics Northwestern University Evanston, Illinois 60201	1
Dr. J. M. White Department of Chemistry University of Texas Austin, Texas 78712	1	Dr. D. C. Mattis Polytechnic Institute of New York 333 Jay Street Brooklyn, New York 11201	1
Dr. Keith H. Johnson Department of Metallurgy and Materials Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. Robert M. Hexter Department of Chemistry University of Minnesota Minneapolis, Minnesota 55455	1
Dr. J. E. Demuth IBM Corporation Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, New York 10598	1	Dr. R. P. Van Duyne Chemistry Department Northwestern University Evanston, Illinois 60201	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. S. Sibener Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1	Dr. Martin Fleischmann Department of Chemistry Southampton University Southampton 509 5NH Hampshire, England	1
Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1	Dr. J. Osteryoung Chemistry Department State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1	Dr. G. Rubloff I.B.M. Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1
Dr. R. G. Wallis Department of Physics University of California, Irvine Irvine, California 92664	1	Dr. J. A. Gardner Department of Physics Oregon State University Corvallis, Oregon 97331	1
Dr. D. Ramaker Chemistry Department George Washington University Washington, D.C. 20052	1	Dr. G. D. Stein Mechanical Engineering Department Northwestern University Evanston, Illinois 60201	1
Dr. P. Hansma Chemistry Department University of California, Santa Barbara Santa Barbara, California 93106	1	Dr. K. G. Spears Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. P. Hendra Chemistry Department Southampton University England S09JNH	1	Dr. R. W. Plummer University of Pennsylvania Department of Physics Philadelphia, Pennsylvania 19104	1
Professor P. Skell Chemistry Department Pennsylvania State University University Park, Pennsylvania 16802	1	Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	2
Dr. J. C. Hemminger Chemistry Department University of California, Irvine Irvine, California 92717	1	Professor D. Hercules University of Pittsburgh Chemistry Department Pittsburgh, Pennsylvania 15260	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

No.
Copies

Professor N. Winograd
The Pennsylvania State University
Department of Chemistry
University Park, Pennsylvania 16802 1

Professor T. F. George
The University of Rochester
Chemistry Department
Rochester, New York 14627 1

Professor Dudley R. Herschbach
Harvard College
Office for Research Contracts
1350 Massachusetts Avenue
Cambridge, Massachusetts 02138 1

Professor Horia Metiu
University of California,
Santa Barbara
Chemistry Department
Santa Barbara, California 93106 1

Professor A. Stecki
Rensselaer Polytechnic Institute
Department of Electrical and
Systems Engineering
Integrated Circuits Laboratories
Troy, New York 12181 1

Professor R. D. Archer
University of Massachusetts
Chemistry Department
Amherst, Massachusetts 01003 1

Dr. A. C. Pastor
Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, California 90265 1

END

DATE
FILMED

12-81

DTIC

