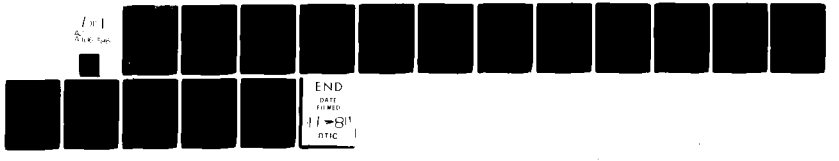
AD-A106 396 IBM THOMAS J WATSON RESEARCH CENTER YORKTOWN HEIGHTS NY F/G 7/3
VIBRATIONAL OVERTONE SPECTROSCOPY OF BENZENE AND PYRIDINE ON AG--ETC(U)
SEP 81 P AVOURIS, J E DEMUTH N00014-77-C-0366
UNCLASSIFIED TR-17 NL



END
DATE FILMED
11-81
DTIC

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0366

Task No. NR 056-123

TECHNICAL REPORT NO. 17

VIBRATIONAL OVERTONE SPECTROSCOPY OF BENZENE AND PYRIDINE ON Ag(111)

by

Ph. Avouris and J. E. Demuth

Prepared for Publication

in

Chemical Physics

IBM T.J. Watson Research Center
Yorktown Heights, NY 10598
September, 1981

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: Technical Report No. 17 — 2. GOVT ACCESSION NO.: AD-A106 396	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Vibrational Overtone Spectroscopy of Benzene and Pyridine on Ag(111).	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER: 14 TR-17
7. AUTHOR(s): Ph. Avouris [redacted] J. E. Demuth	8. CONTRACT OR GRANT NUMBER(s): N00014-77-C-0366
9. PERFORMING ORGANIZATION NAME AND ADDRESS: IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Chemistry Program Office, Arlington, VA 22217	12. REPORT DATE: Sep[redacted] 1981; 13. NUMBER OF PAGES: (12) 17
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)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Preprint; to be published in Chemical Physics.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Overtone Spectroscopy, Pyridine, Pyrazine, Silver, Electron Scattering.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We present electron energy-loss results which permit the detection of up to the fourth vibrational state of the CH stretching vibrations of benzene and pyridine adsorbed on Ag(111). A reduced anharmonicity is observed for adsorbed benzene while both α and β,γ-CH groups for pyridine can be observed. The lifetime for the V=0→4 vibrational excitation of benzene is estimated to be 2×10^{-14} sec.

DD FORM 1 JAN 73 1473

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Vibrational Overtone Spectroscopy of Benzene and Pyridine on Ag(111)†

Ph. Avouris and J. E. Demuth

IBM Thomas J. Watson Research Center

P. O. Box 218

Yorktown Heights, New York 10598

Typed by Janet L. McHale

† Work partially supported by the Office of Naval Research

Vibrational overtone spectroscopy of polyatomic molecules has received considerable attention[1] due to its importance in understanding the character of higher vibrational states and its direct relevance to gas phase studies of single-photon[2] and multiphoton[3] vibrational chemistry. Similarly overtone spectroscopy of adsorbed molecules is important in understanding vibrational photochemistry on (metal) surfaces[4-9] and more importantly in probing changes in intramolecular bonding upon binding to the surface.[10,11] However, such spectroscopy has not been experimentally possible because of the small cross sections for optical excitation and the low density of adsorbed species on surfaces.

In this Communication we present the first electron scattering study which allows the detection of vibrational overtones for monolayer coverages of adsorbed species. We present results on the C-H overtones of pyridine and benzene adsorbed under UHV conditions on a Ag(111) surface. We observe these optically forbidden overtones by utilizing short-range, non-dipolar, electron scattering mechanisms, i.e. impact[12] and resonance scattering via temporary negative ion states.[13] The electron energy loss spectrometer used in these studies (with ~20meV resolution) and the details of the preparation of the Ag surface are described elsewhere.[14]

In Fig. 1 we show the overtone spectra of pyridine at a saturation monolayer coverage. We note that, while the lineshape of the $|0\rangle \rightarrow |2\rangle$ transition is almost symmetric, a distinct shoulder appears in the $|0\rangle \rightarrow |3\rangle$

transition, and, finally, the $|0> \rightarrow |4>$ transition is clearly split. The splitting of the pyridine overtones can be explained on the basis of inequivalent α and β,γ groups of C-H oscillators. On the basis of the relative integrated intensities we assign the lower frequency peak to the β,γ-CH oscillators. The spectra for benzene show only a single peak up to $|4>$ and are not displayed here.

In Fig. 2 we show the fit of the overtone energies of adsorbed benzene, about half a monolayer on Ag(111), to the Birge-Sponer relationship[1]: $\Delta E_v \cdot v^{-1} = A + B \cdot v$, where ΔE_v is the $|0> \rightarrow |v>$ transition energy, A is the local mode frequency, and B is the diagonal anharmonicity. A linear plot is obtained, giving $A = 3095 cm^{-1}$ and $B = -48 cm^{-1}$. The corresponding values for liquid benzene[15] are $A = 3095 cm^{-1}$ and $B = -58.4 cm^{-1}$. The Birge-Sponer plot for β,γ-CH oscillators of adsorbed pyridine gives $A = 3092 cm^{-1}$ and $B = -51 cm^{-1}$; while for liquid pyridine[16], $A = 3094 cm^{-1}$ and $B = -56 cm^{-1}$. It appears that, upon adsorption, there is a minimal change in A but B is reduced significantly. This fact implies a higher C-H dissociation energy for the adsorbed molecule.

These changes can be the result of both a change of phase and of the involvement of specific metal-molecule interactions. In this respect the liquid-to-solid phase change in 3-methylpentane has been reported to result in a $5 cm^{-1}$ reduction in the C-H anharmonicity.[17] Bond dipole-image dipole coupling could also be involved. In the case of benzene, which lies flat on the

Ag surface[14], we estimate a decrease of B by ~3cm^{-1} due to this type of coupling. The smaller reduction in B for pyridine may reflect the fact that it is bonded by the nitrogen lone pair rather than π-bonded (as benzene is) to Ag(111) under our conditions.[18] More experiments are needed to verify if the observed reduction is anharmonicity is a general occurrence among physisorbed molecules.

In Fig. 2 we also show the variation of the width (corrected for instrumental broadening) of the overtone states of adsorbed benzene as a function of v (dotted line). The corresponding widths for pyridine (α and β,γ peaks) are smaller (~360cm^{-1} for $|4\rangle$ of the β,γ-CH mode) and do not follow a linear dependence. The observed linewidths can have contributions from lifetime broadening, librational broadening[19], and inhomogeneous broadening. Because of the expected steeper librational potential in the adsorbed state (vs. the liquid) and the low surface temperature the contribution from librational broadening is expected to be minimal. Similarly, we expect minimal contribution from inhomogeneous broadening, as we have an idealized, clean and annealed single crystal surface upon which the molecules are weakly adsorbed ($\lesssim$10kcal/mole). In the gas phase the homogeneous linewidth of $|4\rangle$ is calculated to be ~130cm^{-1}.[20] In the liquid state (~300K) where librational broadening occurs the $|4\rangle$ linewidth of benzene is ~180cm^{-1}.[21] The linewidth of $|4\rangle$ for benzene on Ag is significantly larger, ~630cm^{-1}. Thus a lower limit to the total relaxation time T_2 ($T_2^{-1} = (2T_1)^{-1}$ (population

relaxation) + $T_2'^{-1}$ (phase relaxation)) of $|4\rangle$ can be obtained as $T_2 = (\pi\Delta\nu)^{-1} \cong 2\times10^{-14}$ sec .

Several non-radiative mechanisms have already been discussed which can greatly shorten the T_1 of an excited molecule near a metal surface.[22,24] Since overtone transitions have very small dynamic dipoles, relaxation must proceed primarily via mechanisms involving non-dipolar coupling.[24] In the case of the dipole-allowed $^1B_{2u} \leftarrow {}^1A_{1g}$ electronic transition of pyrazine on Ag(111), we have deduced[14,25] an even shorter total relaxation time $T_2 \cong 5\times10^{-15}$ sec . The fast relaxation of the overtones of adsorbed molecules suggested by our data will severely limit any selective multiphoton vibrational chemistry for molecules adsorbed on metals.

We would like to thank Professor A. C. Albrecht for a useful discussion.

References

1. For reviews see B. R Henry, Acc. Chem. Res. **10**, 207 (1977); A. Albrecht in **Advances in Laser Chemistry**, A. H. Zewail, Editor (Springer-Verlag, Berlin, 1978) p. 235.
2. K. V. Reddy, R. G. Bray and M. J. Berry, in **Advances in Laser Chemistry**, A. H. Zewail, Editor (Springer-Verlag, Berlin, 1978) p. 48, and references therein.
3. P. A. Schulz, Aa. S. Sudbo, D. J. Krajonovich, H. S. Kwok, Y. R. Shen and Y. T. Lee, Ann. Rev. Phys. Chem. **30**, 379 (1979).
4. M. E. Umstead and M. C. Lin, J. Phys. Chem. **82**, 2047 (1978); M. E. Umstead, L. D. Talley, D. E. Tevault and M. C. Lin, Opt. Eng. **19**, 94 (1980).
5. C. T. Lin and T. D. Z. Atvars, J. Chem. Phys. **68**, 4233 (1978).
6. A. V. Khmelev, V. V. Apollonov, V. D. Berman, B. I. Nikolaev, A. A. Sazykin, V. I. Troyan, K. N. Firsov and B. A. Frolov, Sov. J. Quantum Electron. **7**, 1032 (1977).
7. T. J. Chuag, to be published.
8. J. Lin and T. F. George, Surf. Sci. **100**, 381 (1980); J. Phys. Chem. **84**, 2957 (1980); J. Chem. Phys. **72**, 2554 (1980).
9. M. S. Dzhidzhoev, A. I. Osipov, V. Ya. Panchenko, V. T. Platonenko, R. V. Khokhlov and K. V. Shaitan, Sov. Phys. JETP **47**, 684 (1978).

10. Th. N. Rhodin and G. Ertl, Editors, **The Nature of the Surface Chemical Bond** (North Holland, Amsterdam, 1979).

11. R. Gomer, Solid State Physics (H. Ehrenreich, F. Seitz and D. Turnbull, Editors), Academic Press, New York **30**, 93 (1975).

12. R. J. Celota and R. H. Huebner, in **Electron Spectroscopy - Theory, Techniques and Applications, Vol. III**, C. R. Brundle and A. D. Baher (Academic Press, New York, 1979), p. 41.

13. J. E. Demuth, D. Schmeisser and Ph. Avouris, to be published.

14. Ph. Avouris and J. E. Demuth, J. Chem. Phys., in press.

15. R. L. Swofford, M. E. Long and A. C. Albrecht, J. Chem. Phys. **65**, 179 (1976).

16. Y. Mizugai and M. Katayama, Chem. Phys. Lett. **73**, 240 (1980).

17. W. R. A. Greenlay and B. R. Henry, Chem. Phys. Lett. **53**, 325 (1978).

18. J. E. Demuth, K. Christmann and P. Sanda, Chem. Phys. Lett. **76**, 201 (1980).

19. G. M. Korenowski and A. C. Albrecht, Chem. Phys. **38**, 239 (1979).

20. D. F. Heller and S. Mukamel, J. Chem. Phys. **70**, 463 (1979).

21. C. K. N. Patel, A. C. Tam and R. J. Kerl, J. Chem. Phys. **71**, 1470 (1979).

22. R. R. Chance, A. Prock and R. Silbey, Adv. Chem. Phys. **37**, 1 (1978).

23. B. N. Persson and M. Persson, Surf. Sci. **97**, 609 (1980).

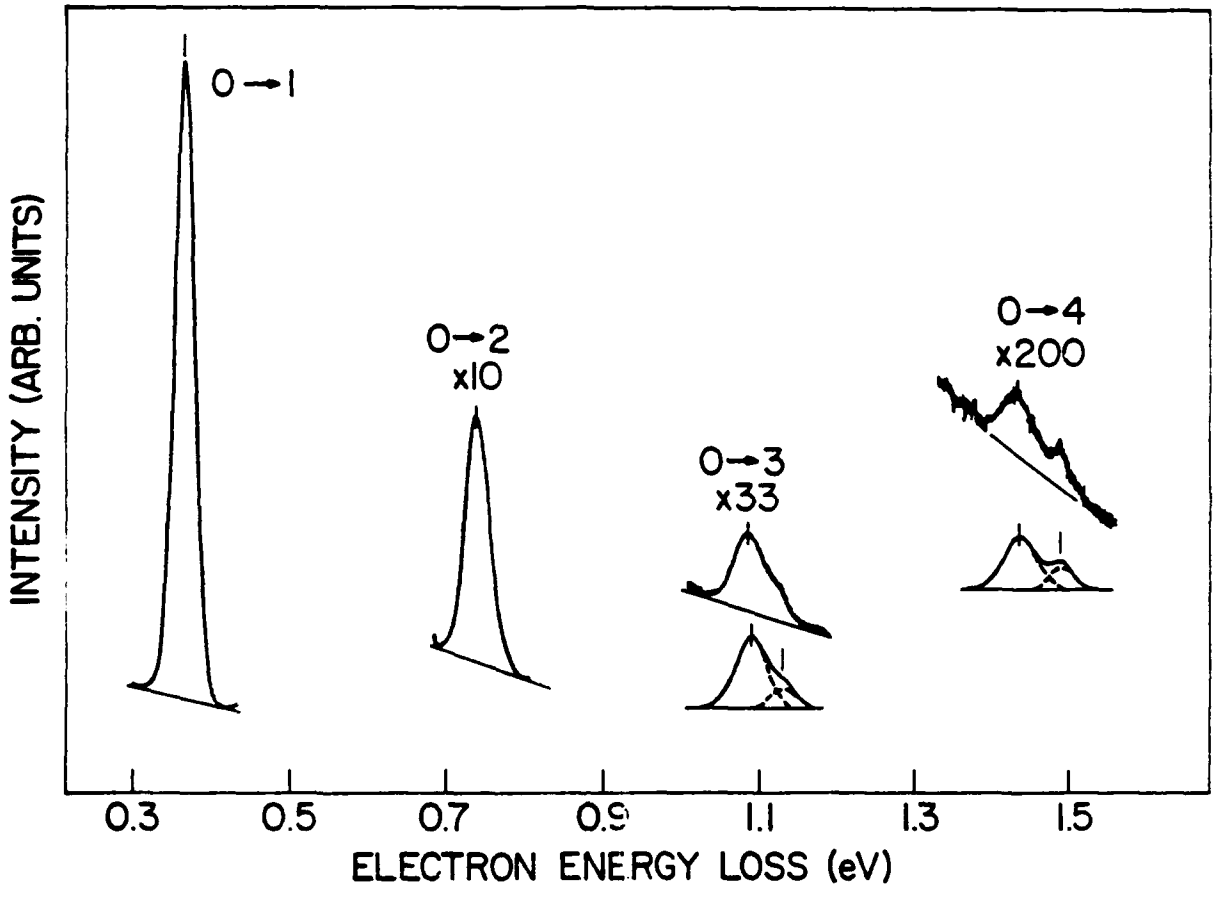
24. B. N. Persson and M. Persson, Solid State Commun. **36**, 175 (1980).

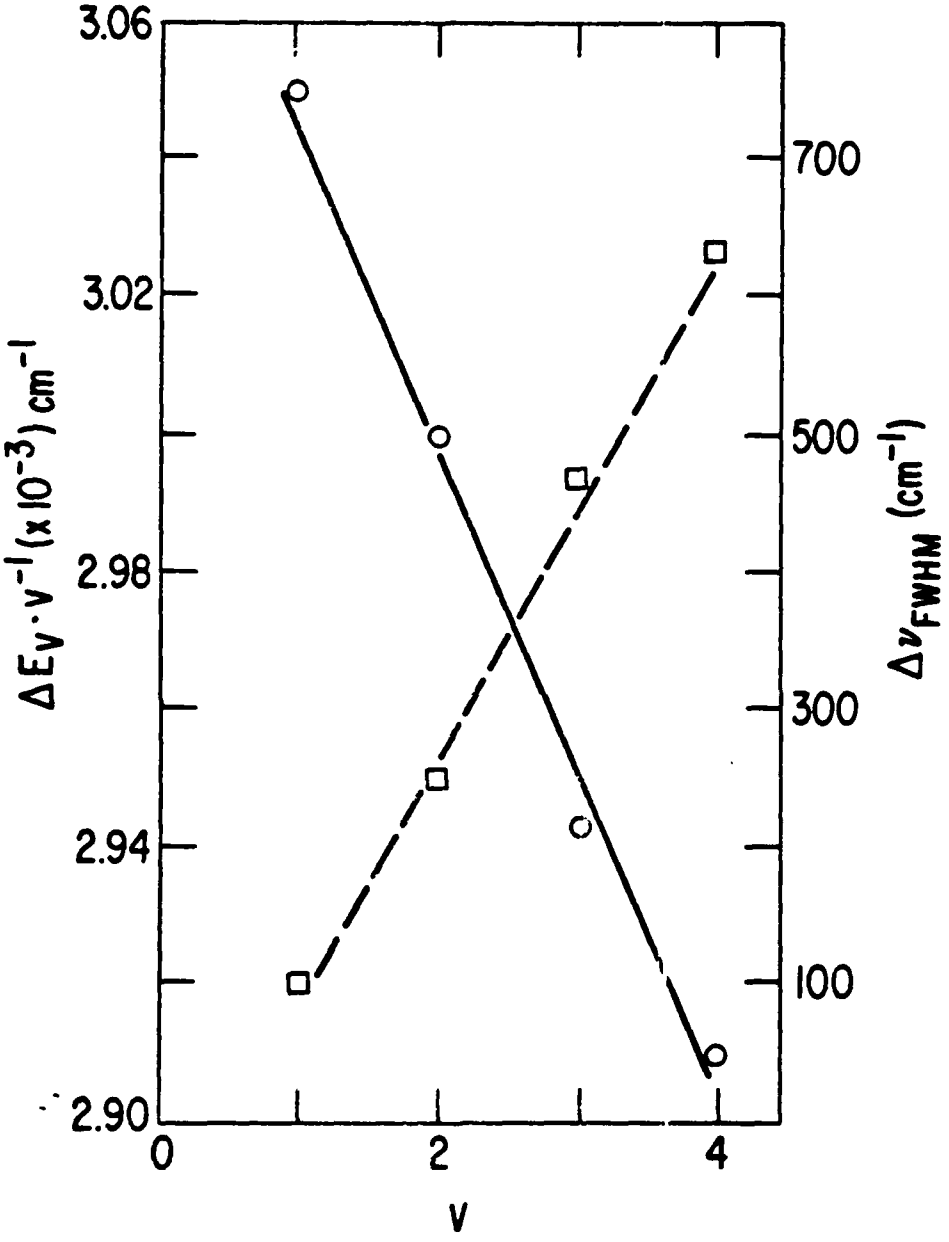
25. J. E. Demuth and Ph. Avouris, Phys. Rev. Lett. **47**, 61 (1981).

Figure Captions

Figure 1 Electron energy loss spectra of the C-H overtones of pyridine (1 Langmuir) on Ag(111) at 140K. Electron beam energy E_B~4eV.

Figure 2 Birge-Sponer plot for the C-H overtones of benzene (1 Langmuir) on Ag(111) at 140K, E_B~3.5eV (solid line); linewidth (full width at half maximum) of these overtones as a function of the vibrational quantum number v (dotted line).


0→1
0→2
x10
0→3
x33
0→4
x200
INTENSITY (ARB. UNITS)
0.3
0.5
0.7
0.9
1.1
1.3
1.5
ELECTRON ENERGY LOSS (eV)


3.06
3.02
2.98
2.94
2.90
0
2
4
v
700
500
300
100
$\Delta E_v \cdot v^{-1} (\times 10^{-3})\ cm^{-1}$
$\Delta \nu_{FWHM}\ (cm^{-1})$

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1
ONR Eastern Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Naval Ship Research and Development Center 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
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

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

TECHNICAL REPORT DISTRIBUTION LIST, 056

	No. Copies
Dr. S. Sibener Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. R. G. Wallis Department of Physics University of California, Irvine Irvine, California 92664	1
Dr. D. Ramaker Chemistry Department George Washington University Washington, D.C. 20052	1
Dr. P. Hansma Chemistry Department University of California, Santa Barbara Santa Barbara, California 93106	1
Dr. P. Hendra Chemistry Department Southampton University England SO9JNH	1
Professor P. Skell Chemistry Department Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. J. C. Hemminger Chemistry Department University of California, Irvine Irvine, California 92717	1
Dr. Martin Fleischmann Department of Chemistry Southampton University Southampton 509 5NH Hampshire, England	1
Dr. J. Osteryoung Chemistry Department State University of New York at Buffalo Buffalo, New York 14214	1
Dr. G. Rubloff I.B.M. Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1
Dr. J. A. Gardner Department of Physics Oregon State University Corvallis, Oregon 97331	1
Dr. G. D. Stein Mechanical Engineering Department Northwestern University Evanston, Illinois 60201	1
Dr. K. G. Spears Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. R. W. Plummer University of Pennsylvania Department of Physics Philadelphia, Pennsylvania 19104	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	2
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. Steckl 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

1-81

DTIC