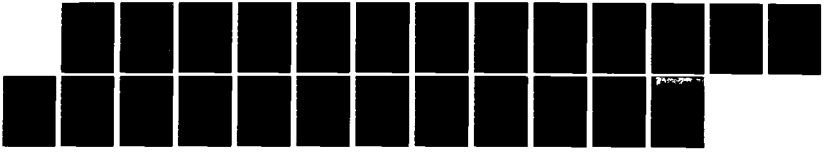
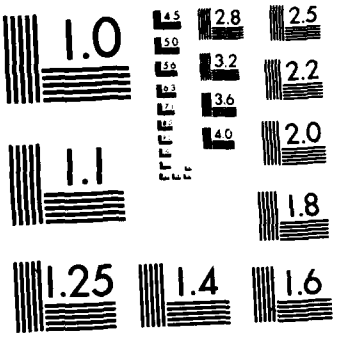
AD-A134 613 COAXIAL MEASUREMENT OF THE TRANSLATIONAL DISTRIBUTION OF CS PRODUCED IN T..(U) HOWARD UNIV WASHINGTON DC LASER CHEMISTRY DIV R LU ET AL. 04 NOV 83 TR-17-ONR 1/1

UNCLASSIFIED N00014-80-C-0305 F/G 7/4 NL





UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR-TR-17	2. GOVT ACCESSION NO. AD-A134 613	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) COAXIAL MEASUREMENT OF THE TRANSLATIONAL DISTRIBUTION OF CS PRODUCED IN THE LASER PHOTOLYSIS OF CS_2 AT 193NM		5. TYPE OF REPORT & PERIOD COVERED TECHNICAL REPORT 17 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Richang Lu, Victor McCrary, David Zakheim and William M. Jackson		8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0305
9. PERFORMING ORGANIZATION NAME AND ADDRESS Laser Chemistry Division Department of Chemistry Howard University Washington, D. C. 20059		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-733
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE November 4, 1983 13. NUMBER OF PAGES 16
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; reproduction is permitted for any purpose of the United States Government; distribution is unlimited.

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

Distribution of this document is unlimited.

18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of Physical Chemistry.

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

Time-of-flight photolysis, excimer laser, CS_2

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

The coaxial translational time of flight (TOF) distributions of CS radicals produced in the 193nm laser photolysis of CS_2 have been measured. The population of CS with low translational energy is higher in the coaxial TOF measurements than it is with perpendicular measurements. These distributions have been analyzed using the Kresin-Lester adiabatic theory of photodissociation to obtain an upper limit for the $S(^3P)/S(^1D)$ branching ratio of 2.1. If this analysis is correct it also suggests that significant amounts of CS radicals are produced in vibrational levels as high as v"=12 and that there

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

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

are angular momentum constraints in the photodissociation process.

Accession For	
NTIS GRA&I	X
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

OFFICE OF NAVAL RESEARCH

Contract N00014-80-C-0305

Task No. NR 051-733

TECHNICAL REPORT NO. 17

COAXIAL MEASUREMENT OF THE TRANSLATIONAL DISTRIBUTION OF CS PRODUCED IN THE LASER PHOTOLYSIS OF CS_2 AT 193NM

BY

Richang Lu, Victor McCrary, David Zakheim
and William M. Jackson

Prepared for Publication in the Journal of Physical Chemistry

Laser Chemistry Division
Department of Chemistry
Howard University
Washington, D. C. 20059

November 4, 1983

COAXIAL MEASUREMENT OF THE TRANSLATIONAL DISTRIBUTION OF CS PRODUCED IN THE LASER PHOTOLYSIS OF CS_2 AT 193nm

Richang Lu, Victor McCrary, David Zakheim, and William M. Jackson

Laser Chemistry Division

Chemistry Department

Howard University

Washington, D.C. 20059

ABSTRACT

The coaxial translational time of flight (TOF) distributions of CS radicals produced in the 193nm laser photolysis of CS_2 have been measured. The population of CS with low translational energy is higher in the coaxial TOF measurements than it is with perpendicular measurements. These distributions have been analyzed using the Kresin-Lester adiabatic theory of photodissociation to obtain an upper limit for the $S(^3P)/S(^1D)$ branching ratio of 2.1. If this analysis is correct it also suggests that significant amounts of CS radicals are produced in vibrational levels as high as v"=12 and that there are angular momentum constraints in the photodissociation process.

INTRODUCTION

The photolysis of CS_2 in the 180 to 210 nm region has been investigated by a number of workers (1,2,3,4,5) using various techniques including laser induced fluorescence (3), atomic resonance fluorescence (2), and velocity measurement of the fragments (1). Despite the multitude of studies there is still some controversy with respect to the branching ratio between the channels that produce $S(^1D)$ and $S(^3P)$. In particular it has been suggested that the formation of $S(^3P)$(4,5) is the dominant channel, while Yang et.al. (1) suggest that the $S(^1D)$ is dominant. The latter authors argue that very rapid quenching of $S(^1D)$ by CS_2 is the reason that the other techniques detected mostly $S(^3P)$. On the other hand, since Yang et.al. (1) measured the time of flights of the fragments using a perpendicular laboratory geometry there is an experimental bias against fragments with velocities lower than the beam velocity since these can never reach the detector. In the present work we will describe experiments where the time of flight of the fragment is detected coaxially with the beam. In this manner we are able to measure those low energy fragments that can escape detection in the perpendicular arrangement.

EXPERIMENTAL

A schematic diagram of the apparatus is shown in Figure 1. It consists of a pulsed valve source which produces a molecular beam that is crossed 2cm downstream by an ArF laser beam produced by a Lambda Physik EMG 101 excimer laser. The pulsed beam and the

fragments are passed through a skimmer, through the buffer chamber, into a detector chamber, and an ionizer of a quadrupole mass spectrometer. The ionizer is 13.4 cm downstream from the interaction region where the laser and the molecular beam cross each other. The first chamber and the buffer chamber are both pumped by liquid nitrogen trapped six inch diffusion pumps, while the mass spectrometer chamber is pumped by an ion pump along with a titanium getter pump. With this arrangement we are able to obtain pressures of 5 to 6 x 10^{-8} torr in the mass spectrometer chamber with the beam on. Even so, there is still considerable background noise at both the CS and S masses from CS_2 in the beam which undergoes dissociative ionization in the ionizer. To overcome this noise two techniques have been employed. First, the electron energy is lowered to 15 eV to reduce the amount of interference that comes from dissociative ionization of carbon disulfide. Second, the experiment is carried out by pulsing the molecular beam at twice the rate of the laser beam, and counting up in the multichannel analyzer when both the molecular beam and the laser are on, and down when the laser beam is off.

A typical time of flight spectrum is shown in Figure 2. This spectrum exhibits a signal to noise ratio of about 5, which was obtained after 15000 laser shots. The center of mass beam velocity can be determined by measuring the decrease in the CS_2^+ parent peak as a result of the laser photolysis. The time of flight for the ions observed in this study inside the quadrupole was determined by sharply pulsing the extractor electrode and then measuring the time it takes for these ions to reach the electron multiplier.

RESULTS AND DISCUSSION

The measured TOF distributions can be converted to translational energy distributions using the measured beam velocity and time of flight of the ions. These translational energy distributions are shown in Figure 3 along with one from Yang et.al.(1), and one taken in our apparatus for the perpendicular arrangement. In the latter case a single experiment was done to be sure that our apparatus could reproduce their previous result (1). It is clear from Figure 3 that both beam machines yield consistent data. Because of the very poor signal to noise ratio in the perpendicular arrangement in our apparatus the results of Yang et.al. (1) were used in the analysis of the high translational energy regime. It should be noted that the perpendicular geometry has an intrinsically higher resolution at these energies than the coaxial geometry. The two sets of results for the perpendicular geometry curve over at different translational energies. This behavior is a reflection of the different beam velocities that are used in the experiments and further confirms that such a geometry will underestimate the fraction of low velocity fragments produced in the experiment.

The high energy break described by Yang et.al. (1) is more clearly seen in the perpendicular geometry because of it's higher resolution. This high energy break has been ascribed by them to the onset of the $S(^1D)$ channel in the photodissociation process. We agree with this interpretation since, as they pointed out, it occurs at the correct energy for this

process and the analysis (6) of the spectrum at longer wavelengths indicates that there is some mixing of the singlet with the triplet state. This has been further confirmed by a recent report of an analysis of the absorption spectra (7) of CS_2 in pulsed molecular beams in the region around 200nm.

Even though this break probably does correspond to the onset of the production of $S(^1D)$ it is not clear just how the fraction due to $S(^3P)$ can be separated from the fraction due to $S(^1D)$. One way is to follow the earlier procedure (1) and assign all of those molecules with translational energies higher than the break to $S(^3P)$, and all those with translational energies lower than the break to $S(^1D)$. This of course gives a lower limit to the amount of triplet P atoms produced, but the procedure has little justification. An alternate method would be to appeal to theory as a means of unravelling these two distributions.

Kresin and Lester (8,9,10,11) have recently published an adiabatic theory of photodissociation that can be used to unravel these two distributions. The theory can be used to derive an expression for the probability, P(i,v"), that a S atom in the ith state will be accompanied by a CS radical in the v" level is given by,

$$P(i,v") = K(i)\exp(C(E_{trans}/E_{vib})v") \qquad (1.)$$

The value of ,C, can be calculated using the vibrational frequencies of the excited state of CS_2 and the ground state of CS. Recent measurements (7) of the absorption spectra show that even though the excited state of CS_2 is bent, the absorp-

tion at 193nm leads to a quasi-linear excited state. The symmetric frequency of this state is 392cm^{-1}. Nothing is known about the asymmetric frequency, but assuming that it has decreased to about 1000cm^{-1} because of the decrease in bonding one can calculate a value of C of about 2.. By taking the observed probabilities for the translational energies from 18 to 38 Kcal/mol corresponding to the production of only S(^{3}P) and transforming these into the probability for a given vibrational quantum number we obtain the results shown in Figure 4. Extrapolating this curve out to v"=12, the probability distribution curve for the S(^{3}P) is obtained. This probability curve can be combined with the observed curve to obtain the probability curve for S(^{1}D) atoms which is also shown in Figure 4.

By summing these probability distributions, one can calculate the S(^{3}P)/S(^{1}D) branching ratio at this wavelength. The derived branching ratio is 2.1:1, which can be considered an upper limit. This is considerably larger than the ratio of 0.25:1 computed by Yang (1) but as Table 1 shows they would have obtained an even larger ratio of 5.6:1 if they had used the present method. A branching ratio this large for the production of ^{3}P to ^{1}D sulfur atoms implies that spin conservation is not important in this particular dissociation process. Since the ground state of CS_2 is a singlet, the triplet sulfur atoms must be produced by the upper excited state crossing over to a triplet state before or during dissociation. Evidently the sulfur atom is large enough that spin-orbit interaction breaks the selection rule that prevents a change in the multiplicity

during a transition. A similar conclusion was reached earlier (4,5) using methods that are entirely different from those used in these experiments. It is important to reiterate that the present experimental results demonstrate that a substantial fraction of the CS radicals are produced with low translational velocities and would not be detected in a perpendicular arrangement. Thus, despite which method is used to separate the two channels, the coaxial arrangement will result in the detection of a higher fraction of $S(^1D)$ atoms.

In addition to obtaining branching ratios the probabil y curves can also be used to obtain the value of the ratio fc E_{trans}/E_{vib} for the two channels. The values of this ratio that are obtained are 0.09 and 0.3 for the triplet P and singlet D sulfur atoms channels respectively. In both cases this ratio is less than one which states that more energy goes into the vibrational degrees of freedom than into the translational recoil energy between the two fragments. Thus, in the triplet P atom 10 times as much energy appears in vibration as compared to translation while in the singlet D atom slightly less than 3 times as much energy appears in vibration. Evidently in the latter case some of the energy that would have gone into vibration has appeared as electronic excitation of the sulfur.

The analysis of the data using the theory as a guide has suggested that the CS fragment that is produced together with $S(^3P)$ should have a great deal of vibrational energy. Yet when laser induced fluorescence studies (3) are used to measure the quantum state distribution of the fragments, no evidence is found for vibrational levels above v"=6. However, in the parti-

cular vibrational sequence used the Franck-Condon factors were rapidly decreasing for transitions from the expected higher vibrational levels of the ground state. Because of this, different regions of the spectra have to be probed if these upper vibrational levels are to be detected.[12] In principle the flash photolysis kinetic absorption studies (4) should have been able to detect the higher vibrational levels but the studies were done at very high pressures, and with flash lamps with a large pulse width. Both of these factors could have precluded the detection of the upper vibrational states.

In all of the above discussion no account has been taken of the rotational distribution of the CS fragment. The justification for this is that the measured rotational distribution (3) suggest that only 2 to 2.5 Kcal/mole of the 45 Kcal/mole of available energy goes into internal rotational excitation of the fragment. An examination of the curves of the ln of the probability versus the vibrational quantum number shows that the curves roll off at low vibrational quantum numbers. .This can possibly be explained by invoking an angular momentum constraint in the photodissociation process. It is known that the upper state of CS_2 is bent (6,7) so that some of the excess energy must go into rotation of the fragment even though the molecule is quasi-linear when it is excited. If the amount of the energy that goes into rotation is constrained by conservation of angular momentum and the translational recoil is constrained by the repulsive force at low vibrational levels, the probability for producing these low levels will be lower since progressively fewer and fewer molecules will have the necessary energy to meet both conditions.

CONCLUSIONS

The coaxial and perpendicular time of flight distributions for the CS fragment have been analyzed using the adiabatic photodissociation theory (8). The results indicate that the branching ratio for the triplet to singlet channel is about 2:1. This is in agreement with earlier results obtained using both the kinetic absorption flash photolysis method (4) and product analysis (5). Most of the available energy appears to go into internal energy of the CS fragment and there appears to be a strong angular momentum constraint on the photodissociation process. The analysis suggests that CS radicals should be formed in vibrational levels up to v"=13, and work is currently underway to determine whether this is the case. Finally, the coaxial time of flight arrangement has been shown capable of detecting fragments that are produced with low translational recoil energies in the center of mass system.

ACKNOWLEDGEMENTS

We are grateful to the Division of Basic Energy Sciences of the Department of Energy for their support in construction of part of this beam apparatus and for their support of Richang Lu under grant E-40-1-505. We are also grateful to NASA for their support of some of the equipment and Victor McCrary under grant number NSG-5071 and William Jackson on grant number NAG W446 for one (1) month summer salary. Finally, William M. Jackson acknowledges the support of the Office of Naval Research for the balance of the equipment used in this project and for his summer salary under contract number N00014-80-C-0305. We would also like to thank Dr. William Lester for his helpful comments and Dr. Richard Bersohn for his discussions during the course of this work.

REFERENCES

1. S. Yang, A. Freedman, M. Kasakawi, and R. Bersohn, J. Chem. Phys. 72, 4058 (1980).

2. M.C. Addison, C.D. Bryne and R.J. Donovan, Chem. Phys. Letters, 64, 57 (1979).

3. J.E. Butler, W.S. Drozdoski, and J.R. McDonald, Chem. Phys. 50, 413 (1980).

4. A.B. Callear, Proc. R. Soc. London, Ser. A 276, 401 (1963).

5. M. deSorgo, A.J. Yarwood, O.P. Strausz and H.E. Gunning, Can. J. Chem. 43, 1886, (1965).

6. F.R. Greening and G.W. King, J. Mol. Spectrosc. 59, 312 (1976).

7. R.J. Hemley, D.G. Leopold, J.L. Roebber, and V. Vaida to be published.

8. V. Kresin, and W.A. Lester, Jr., Int. J. Quantum Chem. Quantum Symp., 15, 703 (1981).

9. V. Kresin, and W.A. Lester, Jr., J. Phys. Chem. 86, 2182 (1982).

10. V. Kresin, and W.A. Lester, Jr., Chem. Phys. Letters, 87, 392 (1982).

11. V. Kresin, and W.A. Lester, Jr., Chem. Phys. Letters, 92, 214 (1982).

12. T. Bergeman and D. Cossart, J. Mol. Spectrosc. 87, 119 (1981).

TABLE 1

BRANCHING RATIO OF TRIPLET P AND SINGLET D SULFUR ATOMS

	$[^3P]/[^1D]$	
	LOWER LIMIT*	UPPER LIMIT**
THIS WORK	0.18	2.1
YANG et.al.(1)	0.25	5.6

* Using the method of Yang et.al. to determine this ratio.
** Using the method described in this paper to determine the ratio.

Figure Captions

Figure 1. Schematic of molecular beam photolysis apparatus for TOF measurement on coaxial geometry.

Figure 2. A typical TOF spectrum of CS fragments on coaxial geometry.

Figure 3. Translational energy distribution of photo-fragmentation of CS_2 193nm from conversion of TOF spectra. Comparison of the results of coaxial to perpendicular detection is shown: (●)----From coaxial detection averaged over 5 measurements; (0)----from Yang, et.al. [1]; and (□)----one measurement at right angle in this work. There is a break that occurs at E_T = 18 Kcal/mol. The error bars refer to the coaxial detection arrangement.

Figure 4. Inferred vibrational population of CS_2 fragments produced in processes: (a). $CS_2 + h\nu \rightarrow CS\ (X^1\Sigma, v'') + S\ (^3P)$ represented by 0; (b). $CS_2 + h\nu \rightarrow CS\ (X^1\Sigma^+, v'') + S\ (^1D)$ represented by

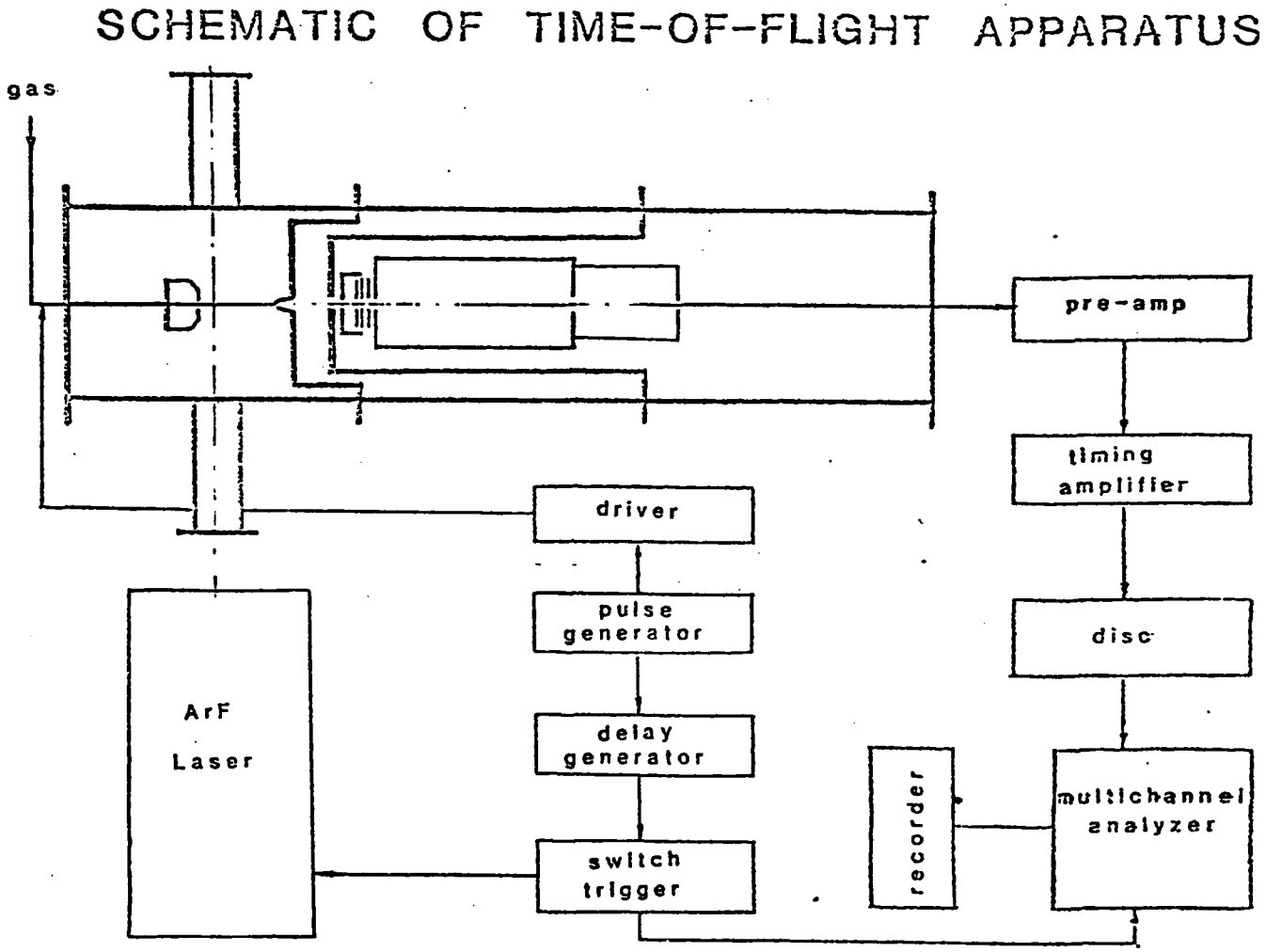

SCHEMATIC OF TIME-OF-FLIGHT APPARATUS
gas
D
pre-amp
timing amplifier
driver
pulse generator
disc
ArF Laser
delay generator
recorder
multichannel analyzer
switch trigger

FIGURE 1

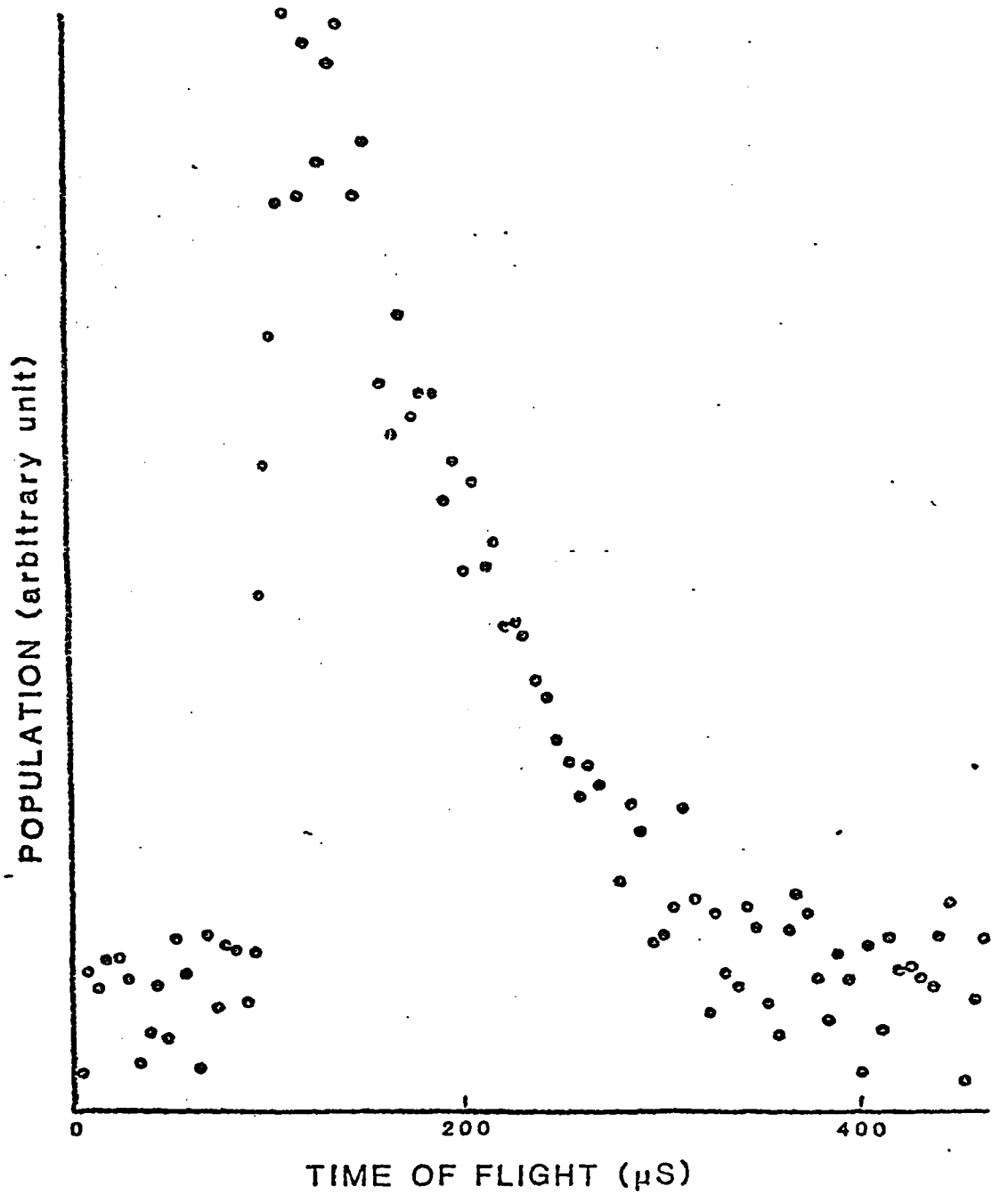
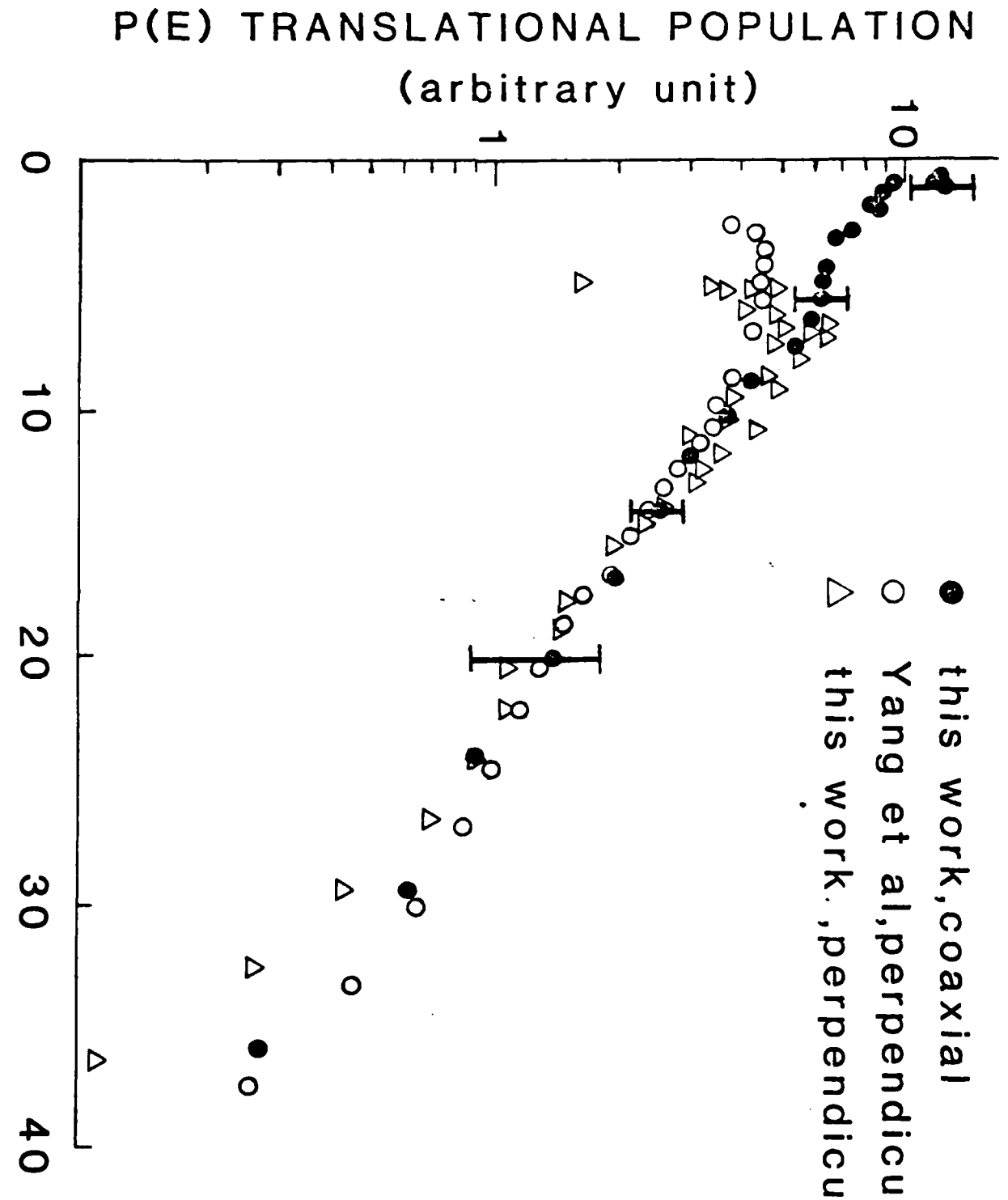


FIGURE 2

FIGURE 3


P(E) TRANSLATIONAL POPULATION
(arbitrary unit)
10
1
0
10
20
30
40
TRANSLATIONAL ENERGY(kcal/mol)
this work,coaxial
Yang et al,perpendicular
this work.,perpendicular

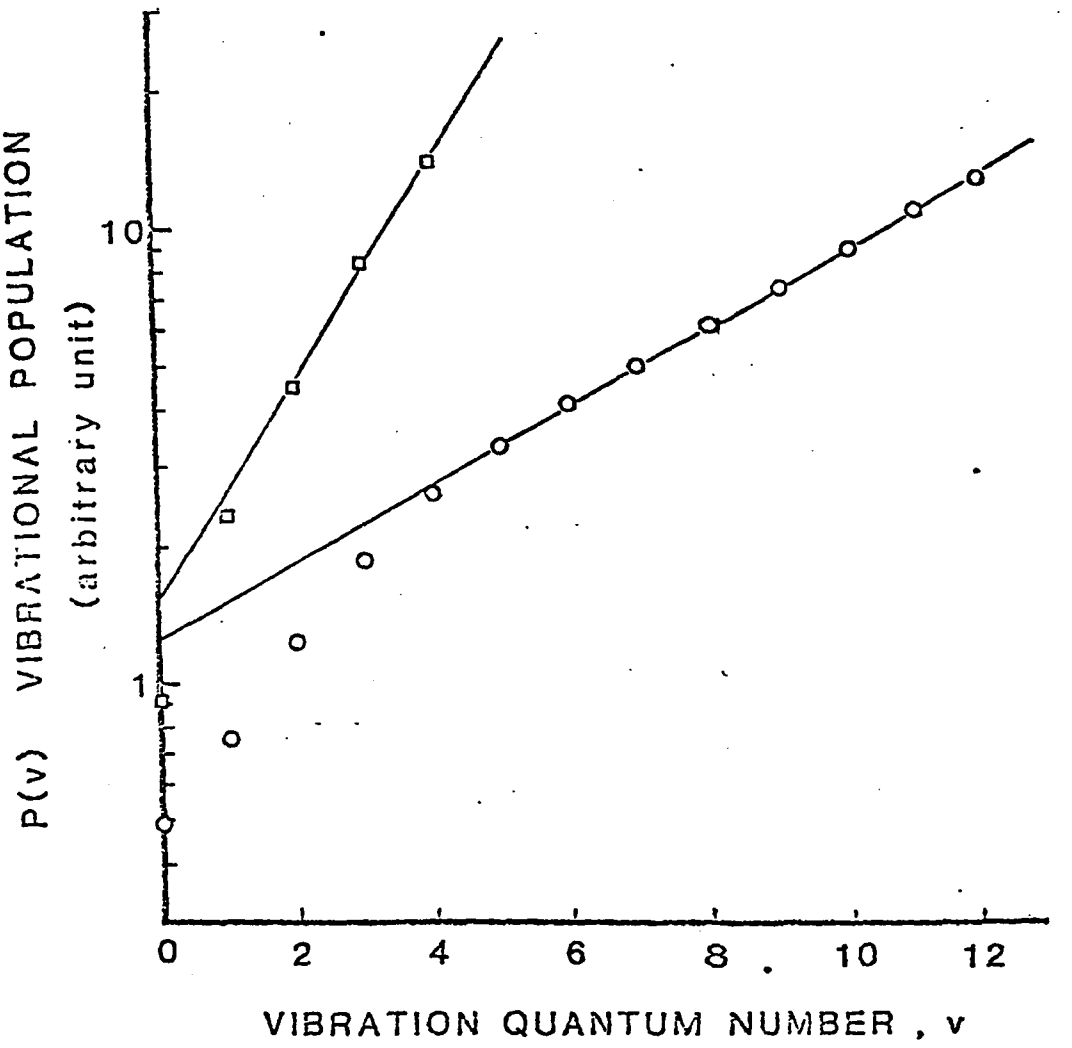

P(v) VIBRATIONAL POPULATION
(arbitrary unit)
10
1
0
2
4
6
8
10
12
VIBRATION QUANTUM NUMBER , v

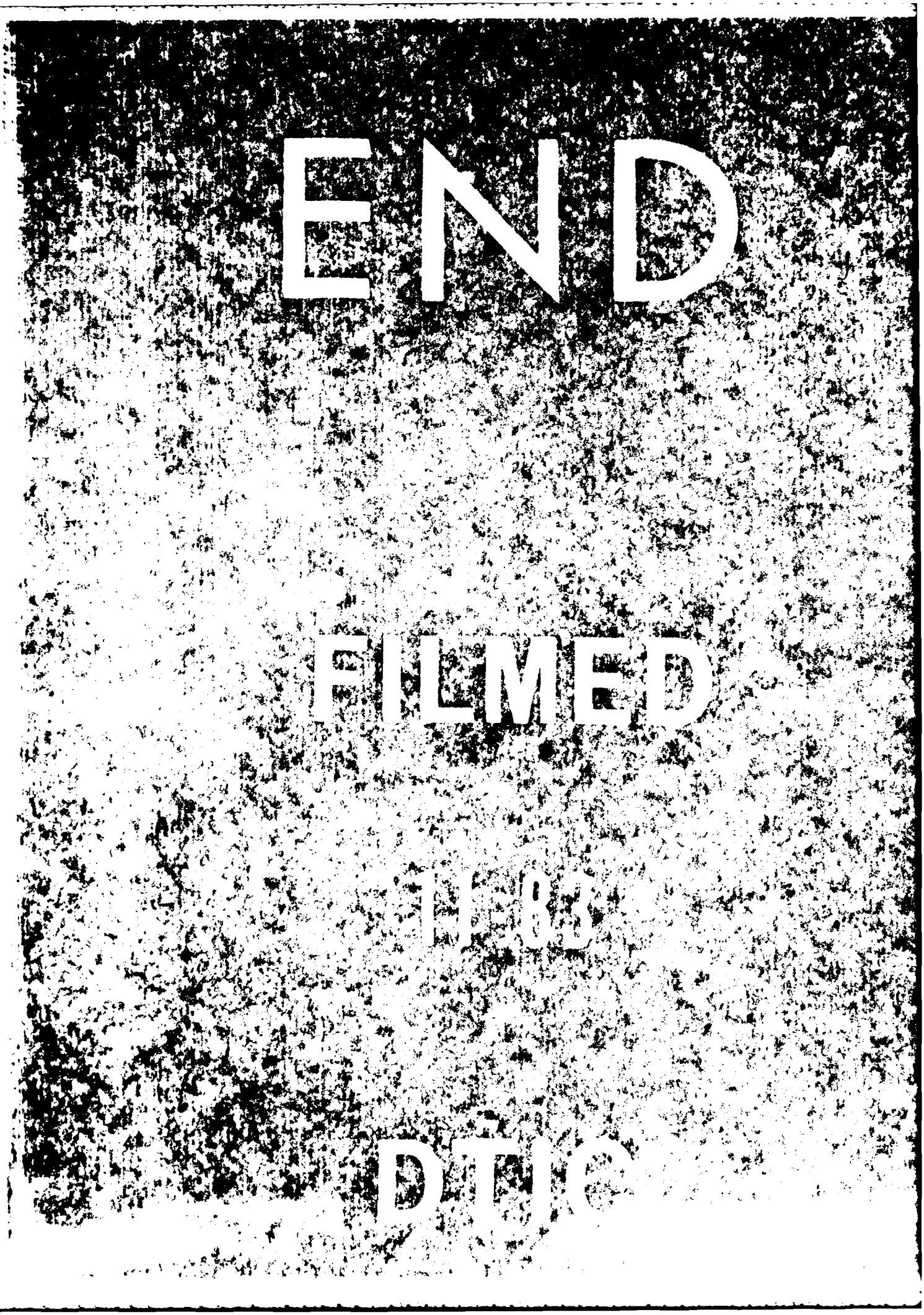
FIGURE 4

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	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 12211 Research Triangle Park, N.C. 27709	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	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
Dean William Tolles 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
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	No. Copies
Dr. M. A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1
Dr. C. A. Heller Naval Weapons Code 6059 China Lake, California 93555	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1
Dr. M. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. A. Paul Schaap Department of Chemistry Wayne State University Detroit, Michigan 49207	1
Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. D. M. Burland IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. William M Jackson Department of Chemistry Howard University Washington, D.C. 20059	1
Dr. George E. Walrafen Department of Chemistry Howard University Washington, D.C. 20059	1
Dr. Joe Brandelik AFWAL/AADO-1 Wright Patterson AFB Fairborn, Ohio 45433	1
Dr. Gary Bjorklund IBM 5600 Cottle Road San Jose, California 95143	1
Dr. Carmen Ortiz Cousejo Superior de Investigaciones Cientificas Serrano 117 Madrid 6, Spain	1


END
FILMED
DTIC