

AD-A233 508

DTIC FILE COPY



TECHNICAL REPORT BRL-TR-3212

BRL

FOURIER TRANSFORM INFRARED SPECTROSCOPY
OF NITRIC OXIDE DURING EXPOSURE TO
VACUUM ULTRAVIOLET RADIATION

KEVIN L. McNESBY
ROBERT A. FIFER

DTIC
ELECTRONIC
MAR 26 1991
S

MARCH 1991

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

U.S. ARMY LABORATORY CO' MAND

BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

91 3 21 052

NOTICES

Destroy this report when it is no longer needed. DO NOT return it to the originator.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commercial product.

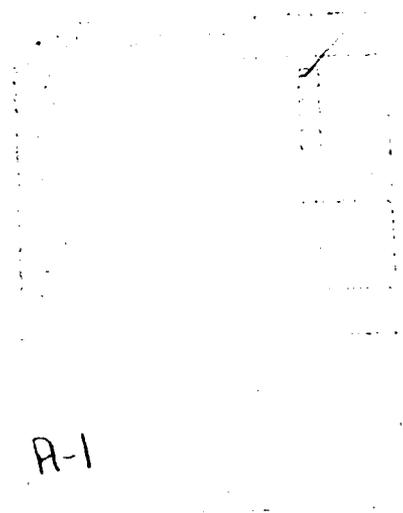
UNCLASSIFIED

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE March 1991	3. REPORT TYPE AND DATES COVERED Final Jan 88 - Jan 90		
4. TITLE AND SUBTITLE FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NITRIC OXIDE DURING EXPOSURE TO VACUUM ULTRAVIOLET RADIATION			5. FUNDING NUMBERS 1L161102AH43	
6. AUTHOR(S) Kevin L. McNesby and Robert A. Fifer				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Ballistic Research Laboratory ATTN: SLCBR-DD-T Aberdeen Proving Ground, MD 21005-5066			10. SPONSORING / MONITORING AGENCY REPORT NUMBER BRL-TR-3212	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The FTIR spectrum of chemically pure (CP) NO was obtained while the gas was being irradiated by radiation at 121.5 nm. A novel cell design allows the ultraviolet radiation and the infrared probe beam to be colinear. The exposure time of the gas to the UV radiation ranged from 0 to 100 minutes. Spectra were collected at evenly spaced time intervals during irradiation by the UV radiation. The composition of the gas changed as a function of irradiation time. Experimental results were compared with the calculated change in the composition of the gas by solving a set of simultaneous differential equations based on a kinetic model, giving good agreement. It is shown that the cell may also be used as an actinometer, and may be used as a check on the applicability of some rate equations to reacting systems.				
14. SUBJECT TERMS Infrared Spectroscopy, Ion Chemistry, Photoionization			15. NUMBER OF PAGES 19	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

INTENTIONALLY LEFT BLANK

TABLE OF CONTENTS

	<u>PAGE</u>
LIST OF FIGURES	v
I. INTRODUCTION	1
II. BACKGROUND	1
III. EXPERIMENTAL	1
IV. RESULTS AND DISCUSSION	3
V. CONCLUSION	7
REFERENCES	9
DISTRIBUTION LIST	11



A-1

INTENTIONALLY LEFT BLANK

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	The Apparatus Used in These Experiments Which Enabled the Infrared Spectrum of a Gas to be Collected While that Gas Was Being Exposed to Vacuum Ultraviolet Radiation	2
2	Integrated Absorbance Vs. Time Curves for the Gas Sample Used in this Experiment	3
3	Pressure Vs. Time Curves for the Gas Sample Used in These Experiments	4
4	Output of the ACUCHEM Program Using Reactions from Table 1 for the Gas Sample During Exposure to Radiation at 121.5 nm	5
5	Infrared Spectra Corresponding to the First (Upper Spectrum) and Last (Lower Spectrum) Data Points in Figures 2 and 3	7

INTENTIONALLY LEFT BLANK

I. INTRODUCTION

The decomposition of energetic nitramines has been the subject of hundreds of articles over the past 50 years.¹ To our knowledge, however, there has been no investigation into the importance of molecular ions in the thermal degradation process. The ionization of NO when exposed to vacuum ultraviolet radiation has been well documented,² and is an appropriate starting point since NO has been observed as a product in thermal degradation studies on the nitramines RDX and HMX.³

We have designed and constructed an infrared spectral cell which fits in the bay of most standard FTIR spectrometers and enables the infrared spectrum of a gas to be collected while that gas is being exposed to the output of an electrodeless rare gas resonance lamp. The cell has been tested using nitric oxide as the gas which is exposed to the lamp output.

II. BACKGROUND

The spectrum of nitric oxide in the infrared and vacuum ultraviolet has been well characterized.²⁻⁵ The molecule is the simplest of the oxides of nitrogen, and has historical significance as the first diatomic to exhibit a Q-branch in the fundamental infrared absorption. Although much of what is known about the photochemistry of the oxides of nitrogen is due to their importance in understanding air pollution,⁴ to our knowledge, there has been no successful study of the gas phase spectroscopy of the nitrosyl ion, NO⁺.

III. EXPERIMENTAL

The vacuum ultraviolet-ir spectral cell apparatus is shown in Figure 1. The spectral cell consists of two equal length chambers in series, separated by a common window. All windows are of LiF. The total VUV-IR cell length is 15 centimeters. The first chamber is a microwave discharge flow lamp.⁶ The second chamber contains the gas whose IR spectrum is desired and may be operated as either a static or flow cell. It is necessary that the central window transmits vacuum ultraviolet and infrared radiation while it is sufficient for the outer two windows to transmit only in the infrared. Contained within this second chamber and out of the VUV light path are a pair of parallel plate electrodes, separated by 1.5 cm, which are used to monitor ion production at low plate voltages, or to increase ion production by accelerating photolytically produced electrons to ionizing potential energies at higher voltages. The infrared beam from the spectrophotometer is incident on and normal to the LiF window of the first chamber and is colinear with the cell cavity axis. Advantage is taken of the fact that the species in the first chamber (in this case D₂ in He because it was available) are transparent to infrared radiation.

The NO used in these experiments was chemically pure (C.P.) and was obtained from Matheson and used without further purification. Analysis of the gas by FTIR spectroscopy showed the main impurities to be NO₂ (~3%) and N₂O (~5%). The Deuterium-Helium mixture (0.1% D₂ in He) used in the microwave discharge lamp⁷ was

obtained from Spectra Gas Inc. Typical pressure in the microwave lamp was 2.3 torr with the flow rate adjusted to give maximum ion current across the parallel plate electrodes when a small (~ 1 V) potential was applied during irradiation of a few torr of NO. Microwave power was supplied by a Raytheon Physicians Diathermy Unit using a Broida-Evenson type cavity. The absence of a photoelectric effect was demonstrated by zero current flow during exposure of the evacuated IR chamber to the radiation at 121.5 nm while a small voltage was applied across the plates. At low sample gas pressures (~ 1 torr), ion current vs. voltage curves during exposure of nitric oxide to the VUV radiation agreed well with previous experiments performed on similar systems.⁸

The experimental procedure was as follows. A 0.1% D₂ in He gas mixture was allowed to flow through the lamp (left side in Figure 1) side of the cell. A needle valve upstream from the cell was used to adjust the flow of gas to give a reading of ~ 2.3 torr on an MKS Instruments capacitance manometer located between the needle valve and the cell. A Broida-Evenson microwave cavity was placed around the 13 mm quartz tubing on the lamp side of the cell. Using a Tesla coil, a 20 watt air cooled discharge was then initiated in the lamp side of the cell. With the sample side of the cell evacuated, a background spectrum was collected. The sample side of the cell was then filled with between 10 and 50 torr of NO. After one or two minutes, an IR spectrum of the gas was obtained, and ratioed against the background spectrum obtained previously. Spectra were collected and ratioed every 15 minutes, with the total exposure time always greater than 90 minutes. Exposure times longer than this produced only slight additional changes in products. No water or hydrocarbon peaks were observed in the spectra of any of the gas samples used in these experiments.

The quantities of NO, N₂O, and NO₂ in the right (sample) side of the cell during an experiment were determined using the integrated absorbance over the wavenumber regions, respectively, 1780-1960, 2125-2280, and 1500-1770. The integration region for NO₂ included the absorption regions for NO₂ and N₂O₄. At the low pressures used in these experiments, the N₂O₄ integrated absorbance was much smaller than the NO₂ integrated absorbance. No correction was made to account for differing oscillator strengths or mass balance between the equilibrium pair. Integrated absorbances were converted to pressures using a linear fit to integrated absorbance vs. pressure plots for pure samples of each gas in the discharge cell when no discharge was occurring. For these calibrations, the NO was the same as that used in these experiments. The NO₂ and N₂O were chemically pure and obtained from Matheson. No correction was made to account for contamination of the oxides of nitrogen by other oxides of nitrogen in the Beer's law

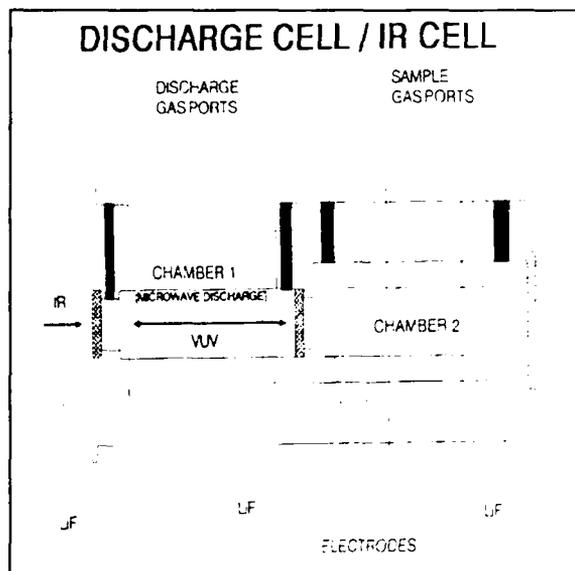


Figure 1. The Apparatus Used in These Experiments Which Enabled the Infrared Spectrum of a Gas to be Collected While that Gas was Being Exposed to Vacuum Ultraviolet Radiation

plots, even though these contaminants were present (evident from IR spectra) in small amounts in each gas sample.

The output of rare gas resonance lamps powered by microwave discharges has been shown to be of high intensity and purity.⁷ The resonance emission for Deuterium atoms occurs at 121.5 nm. To achieve maximum chromatic purity, it is necessary that the lamp be equipped with a getter to remove impurities, particularly water vapor, from the discharge gas. Our cell does not use a getter, so some error is introduced by assuming the output of the lamp to be monochromatic. No filter was used between the left (lamp) and right (sample) chambers of the cell to remove unwanted radiation.

IV. RESULTS AND DISCUSSION

Figure 2 shows a plot of integrated absorbance ($A \cdot \text{cm}^{-1}$) vs. time for NO, N_2O , and NO_2 when 15 torr of NO is exposed to the lamp output for 100 minutes. Figure 3 shows the experimental data reduced to pressure using the calibration curve for each oxide of nitrogen. The overall effect of exposure of the NO sample used in these experiments to radiation at 121.5 nm was decomposition of NO with subsequent formation of NO_2 . N_2O concentration decreased slightly throughout the course of the experiment.

Commercial grade NO always contains significant amounts of N_2O and NO_2 . Because of this, any model of the experiment described here must also take into account photolysis of N_2O and NO_2 .

The ionization potential and bond energy (D_0) for nitric oxide are 9.266 eV⁹ and 6.496 eV,¹⁰ respectively. Absorption of radiation at 121.5 nm by NO produces the nitrosyl ion,⁷ NO^+ :

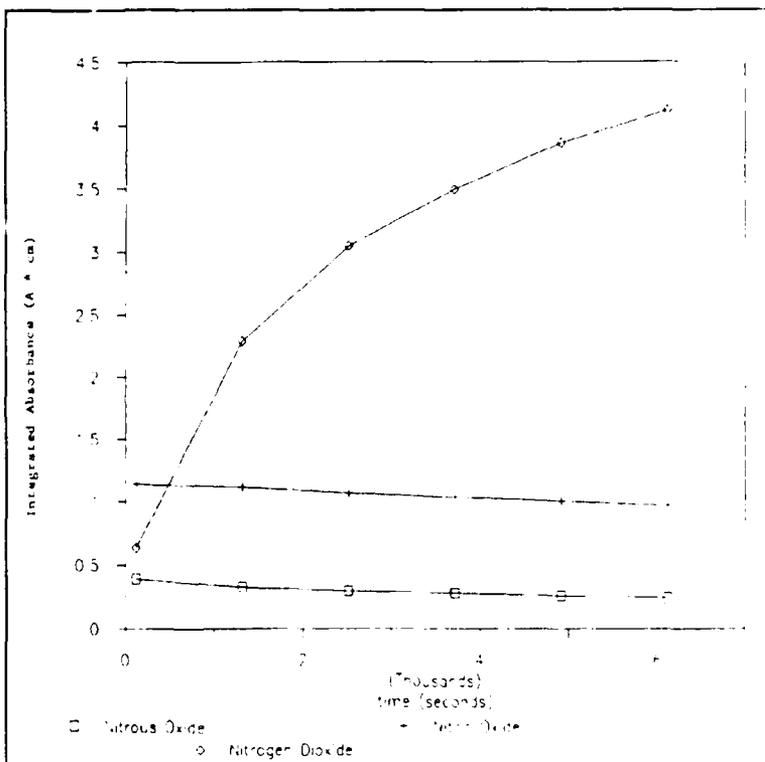
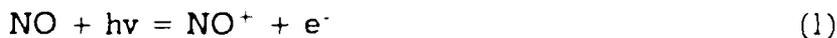


Figure 2. Integrated Absorbance Vs. Time Curves for the Gas Sample Used in this Experiment

The absorption coefficient at 121.5 nm is approximately $40 \text{ atm}^{-1} \text{ cm}^{-1}$. The photolysis of the nitric oxide was entered into the kinetic scheme as follows. Watanabe¹¹ has determined the photoionization cross section of NO at 121.6 nm to be approximately $10^{-18} \text{ cm}^2 \text{ mol}^{-1}$. In general,¹² electrodeless rare gas resonance lamps for photochemistry as used here have an output on the order of $10^{14} \text{ quanta cm}^{-2} \text{ sec}^{-1}$. The lamp used in these experiments is ungettered, so it is assumed that output is approximately decreased by an order of magnitude to $10^{13} \text{ quanta cm}^{-2} \text{ sec}^{-1}$. Since the lamp output is assumed to be constant, then:

$$[\text{NO}] = [\text{NO}_0] \exp(-kx t) \quad (2)$$

Since kx must have units of $1/\text{time}$, k must have units of area. The area used is the photoionization cross section derived from Beer's law, yielding for these experiments an effective rate constant for NO ionization of 10^{-4} sec^{-1} . The gradient of nitrosyl ion concentration in the cell with respect to path length has not been considered.

At low pressures the main deactivation pathway of the nitrosyl ion is dissociative recombination⁸ to give N (^4S , ^2D) and O (^3P) atoms:



The rate constant for the recombination process (Eq. (3)) has been measured¹³ and found to be approximately equal to $1 \times 10^{16} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.

For N_2O , the absorption coefficient at 121.5 nm is approximately¹⁴ $100 \text{ atm}^{-1} \text{ cm}^{-1}$. Bond dissociation energies are⁷ $D_0(\text{N}_2\text{-O}) = 1.67 \text{ eV}$ and $D_0(\text{N-NO}) = 4.99 \text{ eV}$. Photolysis of N_2O in the vacuum ultraviolet is not completely understood. Experimentally,¹² metastable species produced by photolysis of N_2O at wavelengths greater than 120 nm are O atoms (^1D , ^1S), N atoms (^2D , ^2P), and N_2 ($\text{B}^2\Pi$). At 123.6 nm, the ratio of quantum yields N_2/O_2 for N_2O photolysis is approximately 6. Products of photolysis of N_2O at 121.5 nm which are energetically possible are N_2 , NO, and N and O atoms, in their ground and excited state:

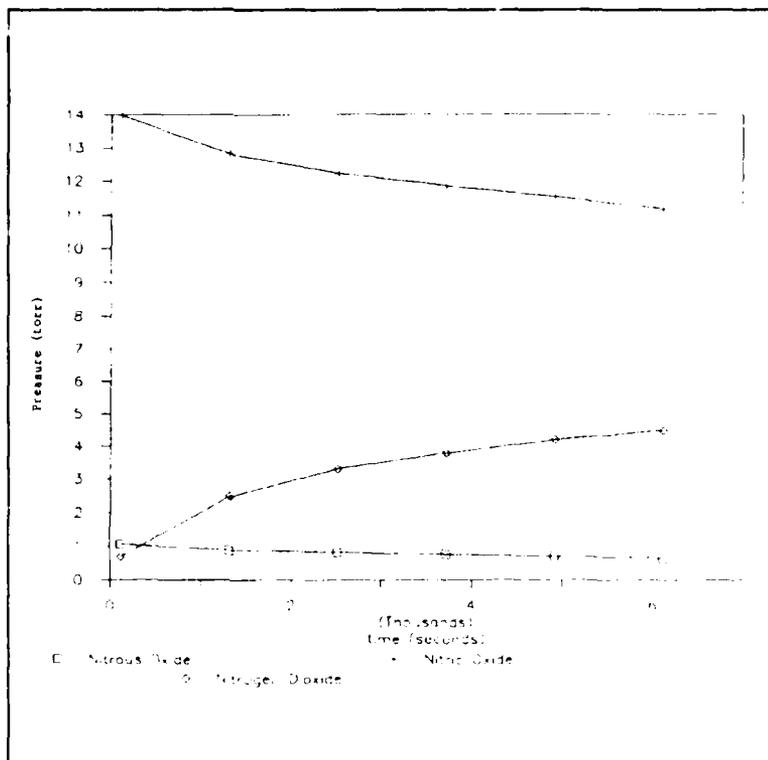


Figure 3. Pressure Vs. Time Curves for the Gas Sample Used in These Experiments. This graph was produced using pressure vs. absorbance curves for each oxide of nitrogen.



It was assumed that the effective rate constant for N_2O photolysis to give N_2 and O atoms was greater than the rate constant for NO photolysis by a factor equal to the ratio of the absorption coefficients for each oxide of nitrogen at 121.5 nm (approximately 2.5). For N_2O photolysis to give NO and N, the effective rate constant was made equal to one sixth of that for the photolysis which yields N_2 and O. The choice of this factor was somewhat arbitrary and based on the quantum yields mentioned above. It seems reasonable in light of the bond dissociation energies. Using the ratio of the bond dissociation energies instead of the quantum yield ratio had no apparent effect on the outcome of the kinetic calculation.

For NO_2 , the absorption coefficient at 121.5 nm is approximately⁷ $300 \text{ atm}^{-1}\text{cm}^{-1}$. The bond dissociation energy $D_0(\text{ON-O}) = 3.12 \text{ eV}$. Photodissociation in the vacuum ultraviolet produces NO ($A^2\Sigma^+ + B^2\Pi$) and O atoms ($^3P, ^1D$):



Similar to N_2O photolysis, the effective rate constant used for photolysis of NO_2 was increased over that for NO by a factor equal to the ratio of the absorption coefficients at 121.5 nm (7.5).

Table 1 shows the individual reactions which were assumed to be important for photolysis by radiation at 121.5 nm and subsequent reaction of the gas mixture used in these experiments. The set of simultaneous differential equations resulting from the reactions in Table 1 was solved using the ACUCHEM and ACUPLOT programs developed by Braun, Herron and Kahaner.¹⁵ Figure 4 shows the output of the ACUCHEM modeling program for the reactions listed in Table 1.

The results of the ACUCHEM program and the experimental results agree to within the experimental error of the pressure calibration, which we believe to be within 10% of actual based on slight curvature of the Beer's law plots. The main

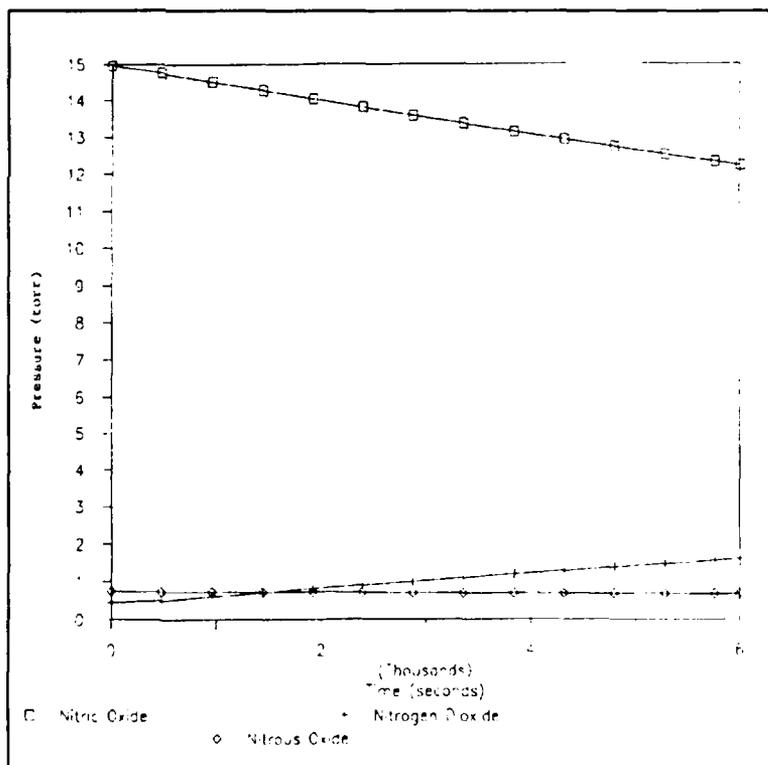


Figure 4. Output of the ACUCHEM Program Using Reactions from Table 1 for the Gas Sample During Exposure to Radiation at 121.5 nm

discrepancies between the experimental and calculated results are that in the experimental results the NO_2 concentration overtakes that of N_2O faster than that calculated using ACUCHEM and that the overall rate of disappearance of NO and appearance of NO_2 is faster experimentally than the calculated rate. This is probably due to the lamp output being slightly underestimated, since increasing the lamp output used in the ACUCHEM program by an order of magnitude moves the cross over point closer to that observed experimentally. Another source of the discrepancy may be that the lamp is emitting light at wavelengths other than 121.5 nm capable of photolyzing the sample gas. This has not been taken into account here. For the experiment reported here, spectra were collected at 4 cm^{-1} resolution for 250 scans. Scan time was 2 minutes 20 seconds. During the course of the experiment, the pressure in the cell increases a few percent, depending on initial pressure. We believe this is caused by heating from the discharge lamp. A stream of room temperature nitrogen is blown around the lamp during the experiment to minimize this effect. Figure 5 shows spectra from the beginning and end of a typical experiment. Depletion of NO and enrichment of NO_2 is evident, even without taking into account differing oscillator strengths in the infrared. Finally, we observed no evidence of NO disproportionation to N_2O and NO_2 as was recently reported in the literature.¹⁶

Table 1. Reactions Used as Input to the ACUCHEM Program

	Mechanism	Rate Constant at 300 K
a*	$\text{NO} = \text{NO}^+ + \text{e}$	$1 \times 10^{-4} \text{ sec}^{-1}$
b**	$\text{NO}^+ + \text{e} = \text{N} + \text{O}$	$1 \times 10^{16} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
c*	$\text{NO}_2 = \text{NO} + \text{O}$	$7.5 \times 10^{-5} \text{ sec}^{-1}$
d*	$\text{N}_2\text{O} = \text{N}_2 + \text{O}$	$2.5 \times 10^{-5} \text{ sec}^{-1}$
e*	$\text{N}_2\text{O} = \text{NO} + \text{N}$	$4.0 \times 10^{-6} \text{ sec}^{-1}$
f	$\text{NO} + \text{O} = \text{NO}_2$	$5 \times 10^7 \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
g	$\text{O} + \text{NO} + \text{M} = \text{NO}_2 + \text{M}$	$4.6 \times 10^{16} \text{ cm}^6\text{mole}^{-2}\text{sec}^{-1}$
h	$\text{NO} + \text{N} = \text{N}_2 + \text{O}$	$1.6 \times 10^{13} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
i	$\text{NO}_2 + \text{N} = \text{N}_2\text{O} + \text{O}$	$1.1 \times 10^{13} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
j	$\text{NO}_2 + \text{N} = \text{NO} + \text{NO}$	$3.6 \times 10^{12} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
k	$\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$	$3.68 \times 10^{12} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
l	$\text{O}_2 + \text{N} = \text{NO} + \text{O}$	$5.28 \times 10^7 \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
m	$\text{NO} + \text{NO} + \text{O}_2 = \text{NO}_2 + \text{NO}_2$	$7.2 \times 10^9 \text{ cm}^6\text{mole}^{-2}\text{sec}^{-1}$
n	$\text{O} + \text{O}_2 = \text{O}_3$	$2.0 \times 10^{14} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
o	$\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$	$1.03 \times 10^{10} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$

*Calculated in text.

**See Reference 13.

Unless otherwise indicated, all rate constants taken from:

D.L. Baulch, D.D. Drysdale, and D.G. Home, "Evaluated Kinetic Data for High Temperature Reactions", CRC Press, Vol. 2, Cleveland, OH, 1973.

V. CONCLUSION

The combined rare gas resonance lamp - infrared cell has been used to monitor the effect of exposure of a sample of mixed oxides of nitrogen to radiation from a Deuterium atom resonance lamp. By assuming the output of the lamp to be monochromatic at 121.5 nm, a kinetic scheme has been devised which correctly predicts the behavior with time of the species being exposed to the lamp output. The electron-ion dissociative recombination mechanism for NO photolysis has been shown to account for the observed behavior of commercial grade NO during exposure to radiation at 121.5 nm. The development of the VUV-IR cell used in these experiments should enable the examination of infrared spectra of reacting chemical systems without the need for drastic modifications to conventional FTIR instrumentation.

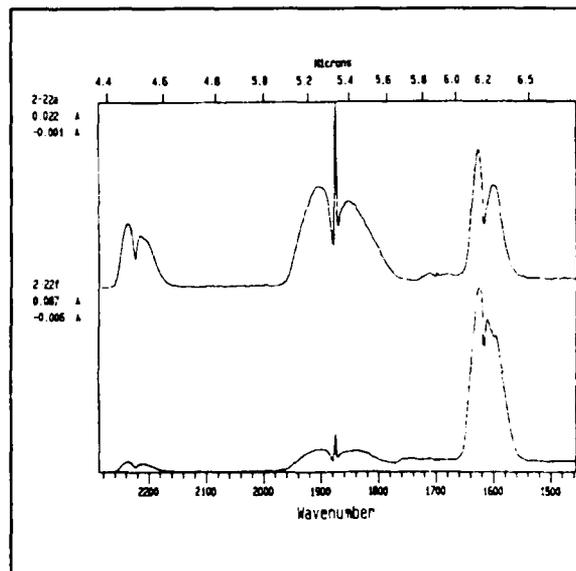


Figure 5. Infrared Spectra Corresponding to the First (Upper Spectrum) and Last (Lower Spectrum) Data Points in Figures 2 and 3. The spectra are not in scale to each other.

INTENTIONALLY LEFT BLANK

REFERENCES

1. M.A. Schroeder, "Critical Analysis of Nitramine Decomposition Data: Activation Energies and Frequency Factors for HMX and RDX Decomposition", Proceedings, 17th JANNAF Combustion Meeting, CPIA Publication No. 329, Vol. II, pp. 493-508, November 1980; also Proceedings, 16th JANNAF Combustion Meeting, CPIA Publication No. 308, Vol. II, pp. 17-34, December 1979; see also Reference 3.
2. S. Cieslik and M. Nicolet, "The Aeronomic Dissociation of Nitric Oxide", Planet. Space Sci., Vol. 21, p. 925, 1973.
3. R.A. Fifer, "Chemistry of Nitrate Ester and Nitramine Propellants", in Fundamentals of Solid Propellant Combustion, edited by K. Kuo and M. Summerfield, Vol. 90 of Progress in Astronautics and Aeronautics, 1984.
4. A.C. Stern, R.W. Boubel, D.B. Turner, and D.L. Fox, Fundamentals of Air Pollution, Academic Press, Inc., London, p. 164, 1984.
5. A.H. Nielson and W. Gordy, "The Infrared Spectrum and Molecular Constants of Nitric Oxide", Phys. Rev., Vol. 56, p. 781, 1939.
6. D. Davis and W. Braun, "Intense Vacuum Ultraviolet Line Sources", Applied Optics, Vol. 7, p. 2071, 1968.
7. H. Okabe, Photochemistry of Small Molecules, Wiley-Interscience, New York, NY, 1978.
8. M. Zelikoff and L. Aschenbrand, "Vacuum Ultraviolet Photochemistry. Part IV. NO at 1236Å", J. Chem. Phys., Vol. 25, p. 674, 1956.
9. K. Watanabe, "Photoionization and Total Absorption Cross Section of Gases. I. Ionization Potentials of Several Molecules. Cross Sections of NH₃ and NO", J. Chem. Phys., Vol. 22, p. 1564, 1954.
10. A.G. Leiga and H.A. Taylor, "Far-Ultraviolet Photolysis of Nitric Oxide", J. Chem. Phys., Vol. 42, p. 2107, 1963.
11. K. Watanabe, F.M. Matsunaga, H. Sakai, "Absorption Coefficient and Photoionization Yield of NO in the Region 580-1350Å", Applied Optics, Vol. 6, p. 391, 1967.
12. J.R. McNesby and H. Okabe, "Vacuum Ultraviolet Photochemistry", in Advances in Photochemistry, Vol. 3, edited by W.A. Noyes, G.S. Hammond, and J.N. Pitts, Jr., Interscience Publishers, New York, NY, 1964.
13. C. Huang, M. Biondi, and R. Johnson, "Variation of Electron-NO⁺-Ion Recombination Coefficient with Electron Temperature", Phys. Rev. A, Vol. 11, p. 901, 1975.

14. M. Zelikoff, K. Watanabe, and E.C.Y. Inn, "Absorption Coefficients of Gases in the Vacuum Ultraviolet. Part II. Nitrous Oxide", J. Chem. Phys., Vol. 21, p. 1643, 1953.
15. W. Braun, J.T. Herron, and D.H. Kahaner, "ACUCHEM: A Computer Program for Modeling Complex Chemical Reaction Systems", Int. Journal of Chemical Kinetics, Vol. 20, p. 51, 1988.
16. D.M. Smith, W.F. Welch, S.M. Graham, A.R. Chughtai, B.G. Wicke, and K.A. Grady, "Reaction of Nitrogen Oxides with Black Carbon: An FTIR Study", Applied Spectroscopy, Vol. 42, p. 674, 1988.

No of Copies	<u>Organization</u>	No of Copies	<u>Organization</u>
2	Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station Alexandria, VA 22304-6145	1	Commander U.S. Army Missile Command ATTN: AMSMI-RD-CS-R (DOC) Redstone Arsenal, AL 35898-5010
1	HQDA (SARD-TR) WASH DC 20310-0001	1	Commander U.S. Army Tank-Automotive Command ATTN: AMSTA-TSL (Technical Library) Warren, MI 48397-5000
1	Commander U.S. Army Materiel Command ATTN: AMCDRA-ST 5001 Eisenhower Avenue Alexandria, VA 22333-0001	1	Director U.S. Army TRADOC Analysis Command ATTN: ATRC-WSR White Sands Missile Range, NM 88002-5502
1	Commander U.S. Army Laboratory Command ATTN: AMSLC-DL 2800 Powder Mill Road Adelphi, MD 20783-1145	(Class. only) 1	Commandant U.S. Army Infantry School ATTN: ATSH-CD (Security Mgr.) Fort Benning, GA 31905-5660
2	Commander U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-IMI-I Picatinny Arsenal, NJ 07806-5000	(Unclass. only) 1	Commandant U.S. Army Infantry School ATTN: ATSH-CD-CSO-OR Fort Benning, GA 31905-5660
2	Commander U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-TDC Picatinny Arsenal, NJ 07806-5000	1	Air Force Armament Laboratory ATTN: AFATL/DLODL Eglin AFB, FL 32542-5000
1	Director Benet Weapons Laboratory U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-CCB-TL Watervliet, NY 12189-4050		<u>Aberdeen Proving Ground</u>
1	Director Benet Weapons Laboratory U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-CCB-TL Watervliet, NY 12189-4050	2	Dir, USAMSAA ATTN: AMXSY-D AMXSY-MP, H. Cohen
1	Commander U.S. Army Armament, Munitions and Chemical Command ATTN: SMCAR-ESP-L Rock Island, IL 61299-5000	1	Cdr, USATECOM ATTN: AMSTE-TD
1	Director U.S. Army Aviation Research and Technology Activity ATTN: SAVRT-R (Library) M/S 219-3 Ames Research Center Moffett Field, CA 94035-1000	3	Cdr, CRDEC, AMCCOM ATTN: SMCCR-RSP-A SMCCR-MU SMCCR-MSI
		1	Dir, VLAMO ATTN: AMSLC-VL-D
		10	Dir, BRL ATTN: SLCBR-DD-T

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
4	Commander US Army Research Office ATTN: R. Ghirardelli D. Mann R. Singleton R. Shaw P.O. Box 12211 Research Triangle Park, NC 27709-2211
2	Commander US Army, ARDEC ATTN: SMCAR-AEE-B, D. S. Downs SMCAR-AEE, J. A. Lannon Picatinny Arsenal, NJ 07806-5000
1	Commander US Army, ARDEC ATTN: SMCAR-AEE-BR, L. Harris Picatinny Arsenal, NJ 07806-5000
1	Commander US Army Missile Command ATTN: AMSMI-RD-PR-E, A. R. Maykut Redstone Arsenal, AL 35898-5249
1	Office of Naval Research Department of the Navy ATTN: R. S. Miller, Code 432 800 N. Quincy Street Arlington, VA 22217
1	Commander Naval Air Systems Command ATTN: J. Ramnarace, AIR-54111C Washington, DC 20360
1	Commander Naval Surface Warfare Center ATTN: J. L. East, Jr., G-23 Dahlgren, VA 22448-5000
2	Commander Naval Surface Warfare Center ATTN: R. Bernecker, R-13 G. B. Wilmot, R-16 Silver Spring, MD 20903-5000

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
5	Commander Naval Research Laboratory ATTN: M. C. Lin J. McDonald E. Oran J. Shnur R. J. Doyle, Code 6110 Washington, DC 20375
1	Commanding Officer Naval Underwater Systems Center Weapons Department ATTN: R. S. Lazar/Code 36301 Newport, RI 02840
2	Commander Naval Weapons Center ATTN: T. Boggs, Code 388 T. Parr, Code 3895 China Lake, CA 93555-6001
1	Superintendent Naval Postgraduate School Dept. of Aeronautics ATTN: D. W. Netzer Monterey, CA 93940
3	AL/LSCF ATTN: R. Corley R. Geisler J. Levine Edwards AFB, CA 93523-5000
1	AL/MKPB ATTN: B. Goshgarian Edwards AFB, CA 93523-5000
1	AFOSR ATTN: J. M. Tishkoff Bolling Air Force Base Washington, DC 20332
1	OSD/SDIO/IST ATTN: L. Caveny Pentagon Washington, DC 20301-7100

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	Commandant USAFAS ATTN: ATSF-TSM-CN Fort Sill, OK 73503-5600
1	F.J. Seiler ATTN: S. A. Shackelford USAF Academy, CO 80840-6528
1	University of Dayton Research Institute ATTN: D. Campbell AL/PAP Edwards AFB, CA 93523
1	NASA Langley Research Center Langley Station ATTN: G. B. Northam/MS 168 Hampton, VA 23365
4	National Bureau of Standards ATTN: J. Hastie M. Jacox T. Kashiwagi H. Semerjian US Department of Commerce Washington, DC 20234
1	Aerojet Solid Propulsion Co. ATTN: P. Micheli Sacramento, GA 95813
1	Applied Combustion Technology, Inc. ATTN: A. M. Varney P.O. Box 607885 Orlando, FL 32860
2	Applied Mechanics Reviews The American Society of Mechanical Engineers ATTN: R. E. White A. B. Wenzel 345 E. 47th Street New York, NY 10017

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	Atlantic Research Corp. ATTN: M. K. King 5390 Cherokee Avenue Alexandria, VA 22314
1	Atlantic Research Corp. ATTN: R. H. W. Waesche 7511 Wellington Road Gainesville, VA 22065
1	AVCO Everett Research Laboratory Division ATTN: D. Stickler 2385 Revere Beach Parkway Everett, MA 02149
1	Battelle Memorial Institute Tactical Technology Center ATTN: J. Huggins 505 King Avenue Columbus, OH 43201
1	Cohen Professional Services ATTN: N. S. Cohen 141 Channing Street Redlands, CA 92373
1	Exxon Research & Eng. Co. ATTN: A. Dean Route 22E Annandale, NJ 08801
1	Ford Aerospace and Communications Corp. DIVAD Division Div. Hq., Irvine ATTN: D. Williams Main Street & Ford Road Newport Beach, CA 92663
1	General Applied Science Laboratories, Inc. 77 Raynor Avenue Ronkonkama, NY 11779-6649

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	General Electric Ordnance Systems ATTN: J. Mandzy 100 Plastics Avenue Pittsfield, MA 01203
2	General Motors Rsch Labs Physics Department ATTN: T. Sloan R. Teets Warren, MI 48090
2	Hercules, Inc. Allegheny Ballistics Lab. ATTN: W. B. Walkup E. A. Yount P.O. Box 210 Rocket Center, WV 26726
1	Alliant Techsystems, Inc. Marine Systems Group ATTN: D. E. Broden/ MS MN50-2000 600 2nd Street NE Hopkins, MN 55343
1	Alliant Techsystems, Inc. ATTN: R. E. Tompkins MN38-3300 5700 Smetana Drive Minnetonka, MN 55343
1	IBM Corporation ATTN: A. C. Tam Research Division 5600 Cottle Road San Jose, CA 95193
1	IIT Research Institute ATTN: R. F. Remaly 10 West 35th Street Chicago, IL 60616

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
2	Director Lawrence Livermore National Laboratory ATTN: C. Westbrook M. Costantino P.O. Box 808 Livermore, CA 94550
1	Lockheed Missiles & Space Co. ATTN: George Lo 3251 Hanover Street Dept. 52-35/B204/2 Palo Alto, CA 94304
1	Los Alamos National Laboratory ATTN: B. Nichols T7, MS-B284 P.O. Box 1663 Los Alamos, NM 87545
1	National Science Foundation ATTN: A. B. Harvey Washington, DC 20550
1	Olin Ordnance ATTN: V. McDonald, Library P.O. Box 222 St. Marks, FL 32355-0222
1	Paul Gough Associates, Inc. ATTN: P. S. Gough 1048 South Street Portsmouth, NH 03801-5423
2	Princeton Combustion Research Laboratories, Inc. ATTN: M. Summerfield N. A. Messina 475 US Highway One Monmouth Junction, NJ 08852
1	Hughes Aircraft Company ATTN: T. E. Ward 8433 Fallbrook Ward Canoga Park, CA 91303

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	Rockwell International Corp. Rocketdyne Division ATTN: J. E. Flanagan/HB02 6633 Canoga Avenue Canoga Park, CA 91304
4	Sandia National Laboratories Division 8354 ATTN: R. Cattolica S. Johnston P. Mattern D. Stephenson Livermore, CA 94550
1	Science Applications, Inc. ATTN: R. B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364
3	SRI International ATTN: G. Smith D. Crosley D. Golden 333 Ravenswood Avenue Menlo Park, CA 94025
1	Stevens Institute of Tech. Davidson Laboratory ATTN: R. McAlevy, III Hoboken, NJ 07030
1	Sverdrup Technology, Inc. LERC Group ATTN: R. J. Locke, MS SVR-2 2001 Aerospace Parkway Brook Park, OH 44142
1	Thiokol Corporation Elkton Division ATTN: S. F. Palopoli P.O. Box 241 Elkton, MD 21921
1	Thiokol Corporation Huntsville Division ATTN: J. Deur Huntsville, AL 35807-7501

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
3	Thiokol Corporation Wasatch Division ATTN: S. J. Bennett P.O. Box 524 Brigham City, UT 84302
1	United Technologies Research Center ATTN: A. C. Eckbreth East Hartford, CT 06108
3	United Technologies Corp. Chemical Systems Division ATTN: R. S. Brown T. D. Myers (2 copies) P.O. Box 49028 San Jose, CA 95161-9028
1	Universal Propulsion Company ATTN: H. J. McSpadden Black Canyon Stage 1 Box 1140 Phoenix, AZ 85029
1	Veritay Technology, Inc. ATTN: E. B. Fisher 4845 Millersport Highway P.O. Box 305 East Amherst, NY 14051-0305
1	Brigham Young University Dept. of Chemical Engineering ATTN: M. W. Beckstead Provo, UT 84058
1	California Institute of Tech. Jet Propulsion Laboratory ATTN: L. Strand, MS 512/102 4800 Oak Grove Drive Pasadena CA, 91109
1	California Institute of Technology ATTN: F. E. C. Culick/MC 301-46 204 Karman Lab. Pasadena, CA 91125

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	University of California Los Alamos Scientific Lab. P.O. Box 1663, Mail Stop B216 Los Alamos, NM 87545	1	University of Florida Dept. of Chemistry ATTN: J. Winefordner Gainesville, FL 32611
1	University of California, Berkeley Chemistry Department ATTN: C. Bradley Moore 211 Lewis Hall Berkeley, CA 94720	3	Georgia Institute of Technology School of Aerospace Engineering ATTN: E. Price W. C. Strahle B. T. Zinn Atlanta, GA 30332
1	University of California, San Diego ATTN: F. A. Williams AMES, B010 La Jolla, CA 92093	1	University of Illinois Dept. of Mech. Eng. ATTN: H. Krier 144MEB, 1206 W. Green Street Urbana, IL 61801
2	University of California, Santa Barbara Quantum Institute ATTN: K. Schofield M. Steinberg Santa Barbara, CA 93106	1	Johns Hopkins University/APL Chemical Propulsion Information Agency ATTN: T. W. Christian Johns Hopkins Road Laurel, MD 20707
1	University of Colorado at Boulder Engineering Center ATTN: J. Daily Campus Box 427 Boulder, CO 80309-0427	1	University of Michigan Gas Dynamics Lab Aerospace Engineering Lab ATTN: G. M. Faeth Ann Arbor, MI 48109-2140
2	University of Southern California Dept. of Chemistry ATTN: S. Benson C. Wittig Los Angeles, CA 90007	1	University of Minnesota Dept. of Mechanical Engineering ATTN: E. Fletcher Minneapolis, MN 55455
1	Cornell University Department of Chemistry ATTN: T. A. Cool Baker Laboratory Ithaca, NY 14853	3	Pennsylvania State University Applied Research Laboratory ATTN: K. K. Kuo H. Palmer M. Micci University Park, PA 16802
1	University of Delaware ATTN: T. Brill Chemistry Department Newark, DE 19711	1	Pennsylvania State University Dept. of Mechanical Engineering ATTN: V. Yang University Park, PA 16802

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	Polytechnic Institute of NY Graduate Center ATTN: S. Lederman Route 110 Farmingdale, NY 11735
2	Princeton University Forrestal Campus Library ATTN: K. Brezinsky I. Glassman P.O. Box 710 Princeton, NJ 08540
1	Purdue University School of Aeronautics and Astronautics ATTN: J. R. Osborn Grissom Hall West Lafayette, IN 47906
1	Purdue University Department of Chemistry ATTN: E. Grant West Lafayette, IN 47906
2	Purdue University School of Mechanical Engineering ATTN: N. M. Laurendeau S. N. B. Murthy TSPC Chaffee Hall West Lafayette, IN 47906
1	Rensselaer Polytechnic Inst. Dept. of Chemical Engineering ATTN: A. Fontijn Troy, NY 12181
1	Stanford University Dept. of Mechanical Engineering ATTN: R Hanson Stanford, CA 94305
1	University of Texas Dept. of Chemistry ATTN: W. Gardiner Austin, TX 78712

<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	University of Utah Dept. of Chemical Engineering ATTN: G. Flandro Salt Lake City, UT 84112
1	Virginia Polytechnic Institute and State University ATTN: J. A. Schetz Blacksburg, VA 24061
1	Freedman Associates ATTN: E. Freedman 2411 Diana Road Baltimore, MD 21209-1525

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. BRL Report Number BRL-TR-3212 Date of Report MARCH 1991
2. Date Report Received _____
3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

CURRENT
ADDRESS

Name

Organization

Address

City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the New or Correct Address in Block 6 above and the Old or Incorrect address below.

OLD
ADDRESS

Name

Organization

Address

City, State, Zip Code

(Remove this sheet, fold as indicated, staple or tape closed, and mail.)

-----FOLD HERE-----

DEPARTMENT OF THE ARMY

Director
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-5066
OFFICIAL BUSINESS



NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL
FIRST CLASS PERMIT No 0001, APG, MD

POSTAGE WILL BE PAID BY ADDRESSEE

Director
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-9989



-----FOLD HERE-----