AD NUMBER
AD911541
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; 11 JUL 1973. Other requests shall be referred to Office of Naval Research, 875 North Randolph Street, Arlington, VA 22203-1995.**
AUTHORITY
ONR ltr, 8 Oct 1975

Calspan

Technical Report

Calspan Corporation
Buffalo, New York 14221

Formerly Cornell Aeronautical Laboratory, Inc.

Calspan

On November 17, 1972 Cornell Aeronautical Laboratory (CAL) changed its name to Calspan Corporation and converted to for-profit operations. Calspan is dedicated to carrying on CAL's long-standing tradition of advanced research and development from an independent viewpoint. All of CAL's diverse scientific and engineering programs for government and industry are being continued in the aerosciences, electronics and avionics, computer sciences, transportation and vehicle research, and the environmental sciences. Calspan is composed of the same staff, management, and facilities as CAL, which operated since 1946 under federal income tax exemption.

EXPERIMENTAL STUDIES OF PHOTOIONIZATION PROCESSES IN AIR

Calspan Report No. AI-3107-A-3

Principal Investigator: DR. WALTER H. WURSTER (716) 632-7500 ext. 501

Scientific Officer: DIRECTOR, PHYSICS PROGRAM, PHYSICAL SCIENCES DIVISION
OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
800 N. QUINCY STREET
ARLINGTON, VIRGINIA 22217

Code 421

APRIL 1973
CONTRACT NO. N00014-71-C-0387
PROGRAM CODE NO.: 000001E20K21
SEMIANNUAL TECHNICAL REPORT
(SEMIANNUAL REPORTS FOR PERIODS 1 MAY 1972 TO 31 OCTOBER 1972 AND 1 NOVEMBER 1972 TO 30 APRIL 1973 ARE COMBINED HEREIN)

EFFECTIVE DATE OF CONTRACT: MAY 1, 1971

AMOUNT OF CONTRACT: $100,744

Sponsored by:

ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER NO. 1479, AMENDMENT NO. 3/3-11-71

TABLE OF CONTENTS

TECHNICAL REPORT SUMMARY

Technical Problem:

An experimental program to investigate basic vacuum ultraviolet photoionization processes in air is currently underway at Calspan Corporation. Particular emphasis is directed toward the interaction of shock-induced nonequilibrium radiation with gaseous species.

Methodology:

The experimental shock-tube program consists of three tasks;

1. Perform quantitative measurements to determine the contribution of the NO molecule to the nonequilibrium, vacuum ultraviolet emission spectrum from shock-heated air.
2. Obtain quantitative, spectrally resolved measurements of the nonequilibrium, vacuum ultraviolet flux from advancing shock waves to verify previously developed excitation and radiative flux models.
3. Investigate possible excitation mechanisms leading to VUV emission from molecular species pertinent to high-altitude rocket plume radiation.

Technical Results:

Emphasis thus far has been directed toward the first task, that of determining the role of NO in defining the resultant shock-induced vacuum ultraviolet radiative flux. This semiannual report presents a brief review of the problem, and the results of the experimental program to date. Based upon previous computations, an initial series of shock-tube experiments were completed, utilizing the splitter-plate absorption technique. As discussed in the previous semiannual technical report this initial series of experiments utilized a LiF window adapter for the spectrometer, restricting measurements to wavelengths greater than 1050 Å. During the present

reporting period, measurements were obtained in the windowless region of the VUV (i.e., $\lambda < 1050$ Å) utilizing the explosively driven, windowless plunger.

Reflected shock radiation measurements using the splitter-plate technique for absorption were obtained at selected wavelengths over a broad wavelength interval, 706 Å $< \lambda <$ 1200 Å, at a resolution of $\Delta\lambda = 32$ Å. Two test gases were used; a mixture of 10% N_2 + 90% Neon both to confirm previous measurements, and obtain new absorption data for pure N_2 with which to compare data from the total gases; and a 2% N_2 + 8% O_2 + 90% Neon mixture for absorption measurements in a shocked gaseous mixture containing vibrationally excited NO. Preliminary data reduction shows absorption at wavelengths 812 Å $\longleftrightarrow$ 970 Å for the $N_2/O_2/N_e$ mixture. Computations indicate that much of this absorption can be attributed to the presence of NO in the shocked gas.

Comments:

The present report covers two six-month reporting periods; 1 May 1972 to 31 October 1972 and 1 November 1972 to 30 April 1973. During this total interval, the period of performance was extended to 31 August 1973, and the third task which had addressed the area of multiple-step photoionization processes, was redirected toward problems of interest in the ARPA Plume Physics program. In particular, possible excitation mechanisms leading to VUV emission from molecular species pertinent to high-altitude rocket plume radiation will be investigated.

The major emphasis during the next reporting period will be directed toward final experiments and data analysis on Task I, and installation of the modified optical systems so as to obtain measurements pertinent to both tasks II and III concurrently.

I. INTRODUCTION

The radiative properties of shock-heated gases are much different from those measured at standard conditions, and extrapolations to nonequilibrium situations cannot readily be made. Under strong-shock conditions, vibrational and rotational excited states of the molecular species are populated in nonequilibrium distributions, where different temperatures must be assigned to each of the internal energy modes. The calculation of the ionizing radiative flux emerging from a shock-heated gas has been discussed in Ref. 1, and involves a knowledge of the gas dynamics and chemistry of the flow field, the population of the excited states responsbile for the radiation, the spectral shape and distribution of the radiation in the wavelength region of interest, and a knowledge of the radiation transfer process, including emission and absorption in the shock-heated gas. Examples of such situations are found in areas of nuclear effects as well as reentry physics. The rate of early fireball growth, for instance, involves the interaction of photons with shocked atmospheric gases.

Two of the tasks addressed in the present research program are based on results obtained in the course of a reentry-related research program in which the photoionization of the ambient atmosphere in front of a blunt reentry body was treated.[2, 3, 4] These results were presented in detail in Ref. 1, and will not be discussed here. However, during the course of those experimental studies for N_2 and subsequent computations for air, the question arose as to the contribution of the NO molecule in the determination of the nonequilibrium VUV emissive and absorptive properties of shock-heated air. Based upon available data for cold NO absorption,[5, 6, 7] it may be expected that NO will affect the VUV flux intensity, which highlights the need for absorption coefficient data as a function of temperature.

The experimental research program reported herein is designed to provide data pertinent to vacuum ultraviolet radiation and excitation processes in air. To date, the effort has been directed toward the first task, that of determining the role of NO in the spectral distribution of shock-induced VUV radiation.

II. RESEARCH PROGRAM

II.1 Vacuum Ultraviolet Radiation Measurements

II.1.1 Experiment Description and Definition

A VUV absorption measurement program for the NO molecule, similar in scope to that described in Refs. 1-4 for the N_2 molecule is currently underway. These measurements are obtained using a high-purity shock tube, with two pertinent features for VUV measurements of this type. The first feature of the experimental arrangement is a 3-channel vacuum ultraviolet spectrometer coupled to the shock tube by an explosively driven plunger unit, which serves as a fast-acting valve-shutter combination. This windowless plunger was developed under a research program in which photoionization cross sections for N, O, and C were obtained[8, 9, 10] from emission measurements in the windowless region of the vacuum ultraviolet ($\lambda < 1050$ Å). The second feature is a splitter plate which fits into the shock tube at the reflecting wall. The oncoming incident shock is divided and proceeds down two separate channels. One channel is obstructed and the shock is reflected. This pocket of gas serves as the light source (I_o). The light passes through a small aperture in the splitter plate, continuing through the gas in the second channel and into the spectrometer through the shutter-valve. The gas in this channel has been processed by the incident shock only, and hence is heated to a significantly lesser degree. The operation of the splitter plate is shown in Fig. 1a, with typical radiation data given in Fig. 1b. for the series of N_2 absorption experiments performed at CAL.[2, 3, 4] A test gas mixture of 10% N_2 + 90% Ne was used, giving a reflected-shock temperature of 11,300° K which provided a continuum source of radiation (I_o) over the wavelength region of interest.[8] The absorbing gas gehind the incident shock was at a temperature of 6000° K.

The lower trace in Fig. 1b is from a detector monitoring the total reflected-shock radiation history at a wavelength of about 1300 Å. The upper trace is the recorded signal from one channel of the VUV spectrometer

viewing radiation at 760 Å which has been partially absorbed by the incident shock-heated gas. A comparison of this signal to that obtained with the reflected-shock light source on the spectrometer side of the splitter plate gives the fraction of light transmitted through the heated gas.

This splitter-plate and spectrometer arrangement is being employed for the NO absorption experiments. As discussed in the previous Semiannual Report,[1] prior to initiating the experimental program, several computations had to be completed in order to define the experimental test conditions. Several criteria must be fulfilled in order to obtain suitable absorption data. For example, the test gas mixture, pressure and incident shock speed must be compatible with: (1) attainment of reflected shock conditions (i.e., temperature) so as to obtain a suitably heated, uniform volume of gas to serve as a continuum light source I_o, and (2) incident shock conditions of temperature and species density, so as to obtain a measurable range of absorption in the test gas.

Equilibrium shock wave computations[11] were initiated for various test gas mixtures and reported in Ref. 1. Based on the previous N_2 experiments, a test gas mixture consisting of 90% neon as the carrier gas, at a total pressure of 2 torr was used in the computations. Neon is used to obtain high reflected shock temperatures and is optically inactive in the wavelength range of interest, $800 < \lambda < 1100$ Å. Both incident and reflected shock conditions, over a range of shock strengths, were calculated for the following gas mixtures:

90% Neon + 10% NO
90% Neon + 10% Air (8% N_2 + 2% O_2)
90% Neon + 5% N_2 + 5% O_2
90% Neon + 2% N_2 + 8% O_2.

The results of these calculations were presented in detail in Ref. 1. On the basis of these computations, the series of absorption experiments was initiated utilizing the 2% N_2 - 8% O_2 - 90% Neon test gas mixture. The

possible absorbing species in the incident-shocked gas are then, the molecular species N_2, O_2 and NO, and the atomic species O and N. However, the NO concentration, for the shock speeds under consideration, is approximately an order of magnitude greater than that of O_2. But the absorption characteristics of the abundant atomic species must be taken into account. The presence of the N atom at these temperatures for example, leads to absorption below 850 Å, which is the absorption edge of the ground state $N \longrightarrow N^+ + e$ transition. This was observed experimentally during the previous program directed at N_2 absorption coefficients.[2, 3, 4] Calculations for the present gas mixture, however, at a shock velocity of 3.8×10^5 cm/sec, indicate an absorption of only about 8% for $\lambda \leq 850$ Å due to the rather low N atom concentration. Similarly, the presence of the O atom will lead to absorption for wavelengths below 911 Å, which is the absorption edge of the ground state $O \rightarrow O^+ + e$ transition. Similar calculations indicate approximately 50% absorption for $\lambda \leq 911$ Å, due to the large number of O atoms present in the incident-shocked gas. (For these computations, the absorption cross-sections given in Ref. 12 were used). On the basis of these atomic absorption calculations, it can be seen that the molecular NO absorption measurements should be directed toward wavelengths greater than 911 Å.

For the 2% N_2 - 8% O_2 - 90% Ne gas mixture, and a nominal shock velocity of 3.8×10^5 cm/sec to be used in the experiments, the reflected shock temperature is 11,300° K, and the absorbing gas behind the incident shock is at a temperature of 5000° K.

II. 1. 2 Experimental Results

An initial test series of shock-tube splitter-plate experiments has been completed. For the first part of this series, the explosively driven plunger which couples the VUV spectrometer to the shock tube was replaced with a LiF window adapter. Thus, wavelengths greater than about 1050 Å were observed during these tests. The primary purpose of these tests (discussed in detail in Ref. 1) was to establish shock-tube performance and

and radiation characteristics of the various test gas mixtures and to compare these characteristics with measurements from a simple N_2 - Neon test gas. Figure 2 shows a schematic of the experimental arrangement employed for the experiments, showing three possible endwall configurations, and either a LiF window or explosively driven plunger coupling the spectrometer to the shock tube. The primary diagnostic for the shock radiation is the three-channel vacuum-ultraviolet spectrometer.[8, 9, 10] A small mirror inside the spectrometer arm was used to permit a photomultiplier-filter combination to view 5100 Å radiation through the same optical path. On the opposite side of the shock tube another photomultiplier-filter assembly viewed 2300 Å radiation, and a thin-film heat transfer gauge was used to display the wall temperature rise (ΔT) due to the incident and reflected shock waves.

Approximately six feet upstream of the reflecting endwall, several detectors were used to monitor the radiation from the hot gas behind the incident shock wave. Here, two photomultiplier-filter combinations were used to view radiation at 2500 Å and 6600 Å, and an EMR solar-blind PMT was utilized to view radiation in the 1300 Å wavelength range. In addition, a thin-film wall ΔT gauge was also displayed to aid in the determination of the incident-shock test time. All of the wavelength intervals chosen for measurements correspond to emitting transitions in the shock heated gas mixture. Spectral intensities from these transitions have previously been recorded and used to monitor the state of the shocked gases. Similarly, the sidewall heat transfer data are used to monitor shock tube operation and repeatability.

The test gas mixtures were admitted to the shock tube through a pumping/loading manifold to an initial pressure of 2 torr. Room temperature hydrogen, at pressures from 650 - 1350 psi, was used as the driver gas. Resultant shock speeds in this test series ranged from approximately 11,500 - 14,000 ft/sec.

The first part of the test series utilizing the LiF window adapter was described in detail in the previous semi-annual report (Ref. 1). However, a brief discussion of the wavelengths investigated and preliminary results are included herein since additional measurements were obtained using the

the explosively driven plunger adapter. For the LiF window experiments, the grating setting was adjusted such that 1110 Å, 1180 Å and 1625 Å radiation was monitored in first order, with a bandpass of ± 16 Å. However, the detector response has dropped considerably at the longest wavelength (1625 Å) and no radiation data was obtained.

Previous measurements[2, 3, 4] for N_2 and calculations indicated that the incident-shocked gas should be transparent at the wavelengths investigated during this test series (1110 Å, 1180 Å). However the splitter-plate data obtained for both the 2% N_2/8% O_2 and the 10% N_2 mixtures indicated a substantially lower signal when the reflected pocket is on the opposite side of the shock tube, i.e., $I / I_o \approx .25$. Earlier experiments[8, 9, 10] indicated that there could be substantial absorption in the boundary layer near the explosively driven plunger entrance, if sufficient care were not taken to pump away the boundary layer. To determine if this was the cause of the reduced signals, the same wavelengths were investigated early in the explosively driven plunger test series described below.

Following preliminary experiments to validate the sequencing of the plunger open time, the VUV spectrometer grating was adjusted to monitor the wavelength intervals noted earlier; 1110 Å, 1180 Å and 812 Å. The third wavelength region was viewed in second order, i.e., 1625 Å first order, 812 Å second order) since the LiF window which had previously restricted the measurements to wavelengths > 1050 Å had been removed. In this windowless coupled configuration, the preliminary measurements indicated the following for the 2% N_2/8% O_2/90% Neon gas mixture at a shock speed of 3.8×10^5 cm/sec:

wavelength	1110 Å	1180 Å	812 Å
I / I_o experiment	~ 0.94	~ 0.94	~ 0.22
I / I_o calculated	0.95 (N_2 only)	1.0 (N_2 only)	0.35 (O + N only)

At the wavelengths of 1110 Å and 1180 Å, these later experiments indicated that the gas is essentially transparent, as opposed to the I/I_o value of ≈ 0.25 obtained when the LiF window adapter was used. These results are in substantial agreement with measurements obtained earlier[8, 9, 10] which indicated that there could be a substantial effect of the boundary layer on the measurements if sufficient care were not taken to pump it away.

Also indicated in the table are approximate calculated values of I/I_o. At wavelengths of 1110 Å and 1180 Å, the calculations assumed that only N_2 was responsible for absorption; the experiments are in substantial agreement with the calculations indicating that the presence of NO had no effect on the measurements. At 812 Å, the calculations were performed with O and N atoms as the principal absorbing species. At this wavelength the experimental value was smaller, indicating that the NO molecule may be contributing to the absorption process.

Additional experiments were performed at various VUV spectrometer grating settings as follows for the same mixture and shock speed:

wavelength	895 Å	970 Å	706 Å
I/I_o experiment	~ 0.13	~ 0.22	~ 0.30
I/I_o calculated	0.20 (N_2 + O alone)	0.535 (N_2 alone)	0.25 (O + N alone)

Again, the calculations at each wavelength were performed for the dominant absorbing species (other than NO) as indicated. At 895 Å and 970 Å, the experimental values are considerably smaller than the calculated values, again indicating that the NO molecule may be contributing to the absorption process.

These results are shown in Figure 3, which presents the ratio I/I_o as a function of wavelength for both the experimental and calculated values. Shown for the calculations are the contributions for each specie as indicated, and the overall computed absorption for the incident-shocked gas mixture, excluding the presence of NO. As noted earlier, the presence of O atoms

must be taken into account for wavelengths below 911 Å, and below 850 Å, the N atoms contribute approximately 8% to the absorption process. The experimental data can be compared with the computed values, and any substantial deviation may be attributed in part to absorption from the NO molecules present in the shocked gas.

For wavelengths greater than about 1100 Å, the gas is essentially transparent, with no substantial absorption from either N_2 or NO. Also, at the shortest wavelength investigated to date, 706 Å, there appears to be no substantial NO absorption and the O and N contributions can essentially account for the measured data. However, at wavelengths of 812 Å, 895 Å, and 970 Å, the experimental results are substantially below the calculations, and NO absorption may play a major role in this wavelength region.

At 895 Å, for example, if the difference between the calculated and measured values of I/I_o were attributed only to vibrationally excited NO, an absorption coefficient of $k_{NO} \approx 9,900\ cm^{-1}$ is obtained. This can be favorably compared with a measured value in cold NO of[5, 6] approximately $9000\ cm^{-1}$ at 898 Å. However, at the 812 Å and 970 Å wavelengths, if the indicated difference were ascribed only to NO, the absorption coefficients obtained are too high: at 812 Å, $k_{NO} \approx 13,000\ cm^{-1}$ and at 970 Å, $k_{NO} \approx 24,000\ cm^{-1}$. Although there is a peak in the cold NO absorption coefficient near 810 Å, i.e., $k_{NO} \approx 3000\ cm^{-1}$, the experimentally determined value is much greater than this.

The tabulations given in Ref. 12 indicate several strong lines of the O atom particularly in the 970 Å bandpass, and to a lesser extent, in the 812 Å bandpass. The 895 Å bandpass is relatively free of strong lines, and the additional absorption observed may in fact, be attributed to the NO molecule. The experimental data at 812 Å and 970 Å, however, is compromised due to the presence of strong lines. Thus, attributing the additional absorption at these wavelengths only to the NO molecule would lead to extremely large absorption coefficients, as indicated previously.

III. CURRENT STATUS AND FUTURE PLANS

The initial test series for the NO splitter-plate experiments has been completed, with preliminary measurements obtained for the wavelength interval $700\ \text{Å} \leq \lambda \leq 1200\ \text{Å}$. Final splitter-plate experiments will be performed with a smaller bandpass to enable absorption measurements to be made in regions free of strong lines. The gas mixture and shock speed discussed in this report will be used for the final experiments.

After completion of the splitter-plate tests, the high-resolution optics will be installed for the excitation measurements, and Task II and III experiments will be performed concurrently.

ACKNOWLEDGEMENT

The work reported herein was performed by Dr. P. V. Marrone and Mr. J. E. Stratton.

REFERENCES

1. Experimental Studies of Photoionization Processes in Air; Semi-annual Technical Report for Period 1 November 1971 to 1 May 1972. Cornell Aeronautical Laboratory Report No. AI-3107-A-2, May 1972. Submitted by W. H. Wurster.

2. Marrone, P.V. and Wurster, W.H.: Reentry Precursor Plasma-Determination of the Vacuum Ultraviolet Photoionizing Radiative Flux. Paper Presented at the 4th Entry Plasma Sheath Symposium. NASA Langley Research Center. October 13-15, 1970.

3. Precursor Ionization From Blunt Body Shock Waves: Annual Technical Report. Prepared by W.H. Wurster, Cornell Aeronautical Laboratory Report No. AF-2581-A-2, July 1970.

4. Edwards, K.R., Marrone, P.V., Olson, G.E. and Wurster, W.H. The Photoionized Precursor Plasma and Its Effect on Blunt Body Radar Observables (U). Presented at the AIAA Joint Strategic Missile Sciences Meeting. U.S. Naval Academy, Annapolis, Maryland. 10-12 May, 1971 (SECRET).

5. Watanabe, K., Matsunga, F.M. and Sakai, H.: Absorption Coefficient and Photoionization Yield of NO in the Region 580-1350 A. Applied Optics, Vol. 6, No. 3. March 1967. pp. 391-396.

6. Cook, G.R. and Ching, B.K.: Absorption, Photoionization, and Fluorescence of Some Gases of Importance in the Study of the Upper Atmosphere. Aerospace Corporation Report No. TDR-469(9260-01)-4. January 1965.

7. Watanabe, K. Marmo, F.F. and Inn, E.C.Y.: Photoionization Cross Section of Nitric Oxide. Physical Review, Vol. 91, 1953, p. 1155.

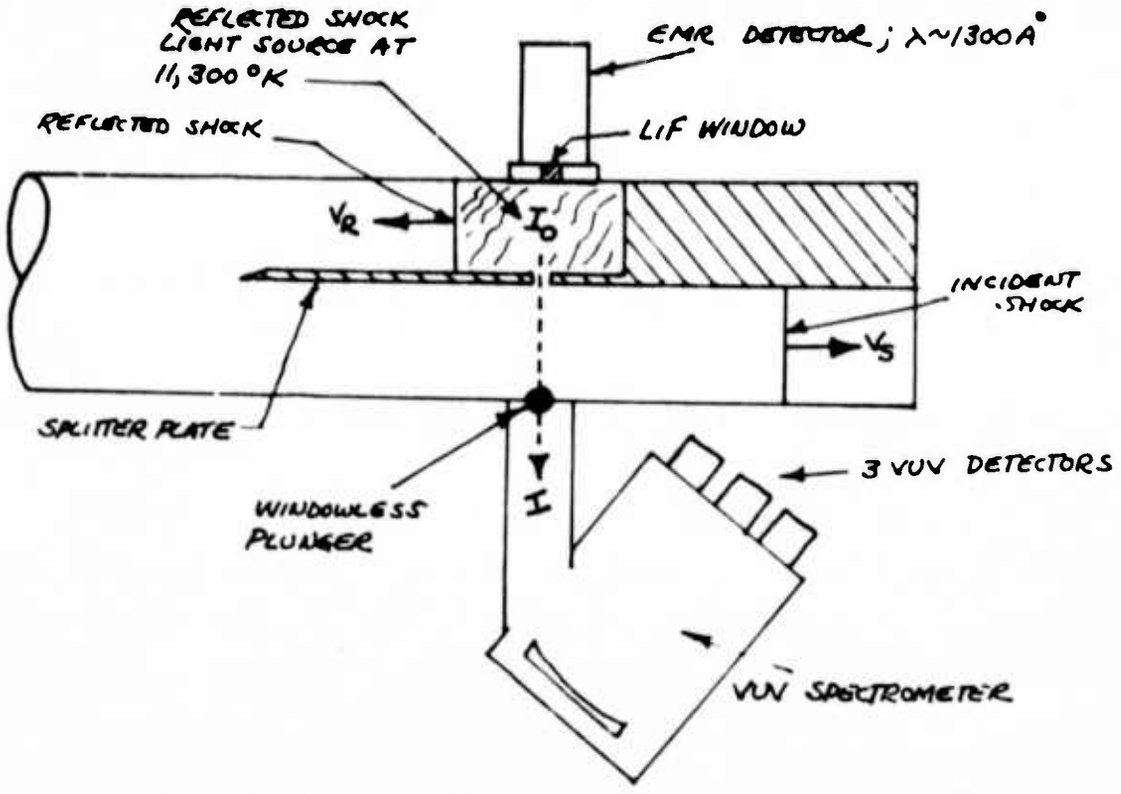
8. Marrone, P.V., Wurster, W.H. and Stratton, J.E.: Shock-Tube Studies of N^+ and O^+ Recombination Radiation in the Vacuum Ultraviolet. Cornell Aeronautical Laboratory Report No. AG-1729-A-7. June 1968.

9. Marrone, P.V. and Stratton, J.E.: Vacuum Ultraviolet C^+ Recombination Radiation from Shock Heated CO/Ne Mixtures. Cornell Aeronautical Laboratory Report No. RH-2786-A-1. March 1970.

10. Marrone, P.V. and Wurster, W.H.: Measurement of Atomic Nitrogen and Carbon Photoionization Cross Sections Using Shock Tube Vacuum Ultraviolet Spectroscopy. JQSRT, Vol. 11, No. 4. April 1971. pp. 327-349.

11. Williams, M. J. and Garr, L. J.: A Description of the CAL Equilibrium Normal Shock Program. Cornell Aeronautical Laboratory Internal Memorandum, September, 1966.

12. Wilson, K. H. and Nicolet, W. E.: Spectral Absorption Coefficients of Carbon, Nitrogen, and Oxygen Atoms. JQSRT. Vol. 7, No. 6. November/December 1967 (pp. 891-943).



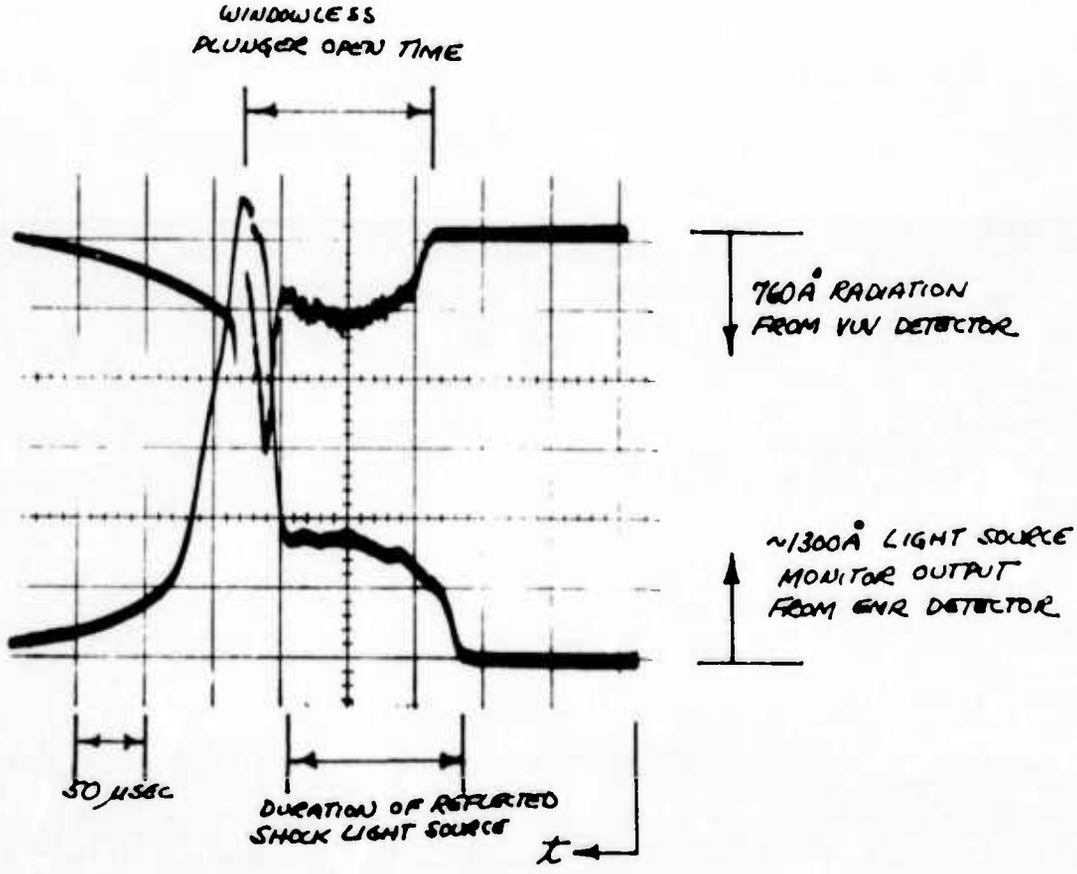


FIG. 1 (a) VUV EXPERIMENT (b) TYPICAL RADIATION DATA

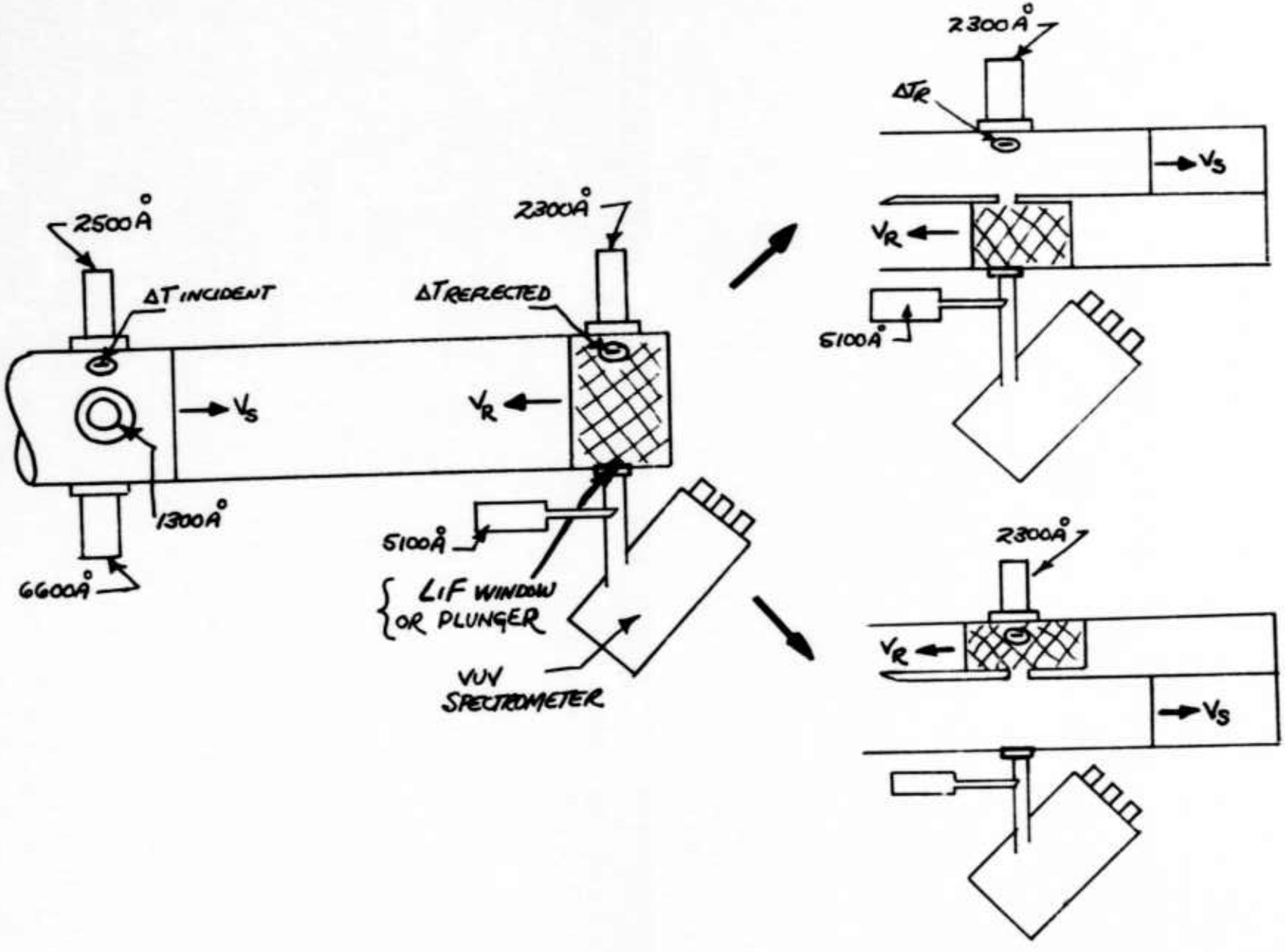


FIG. 2 SCHEMATIC OF EXPERIMENTAL SHOCK-TUBE CONFIGURATIONS

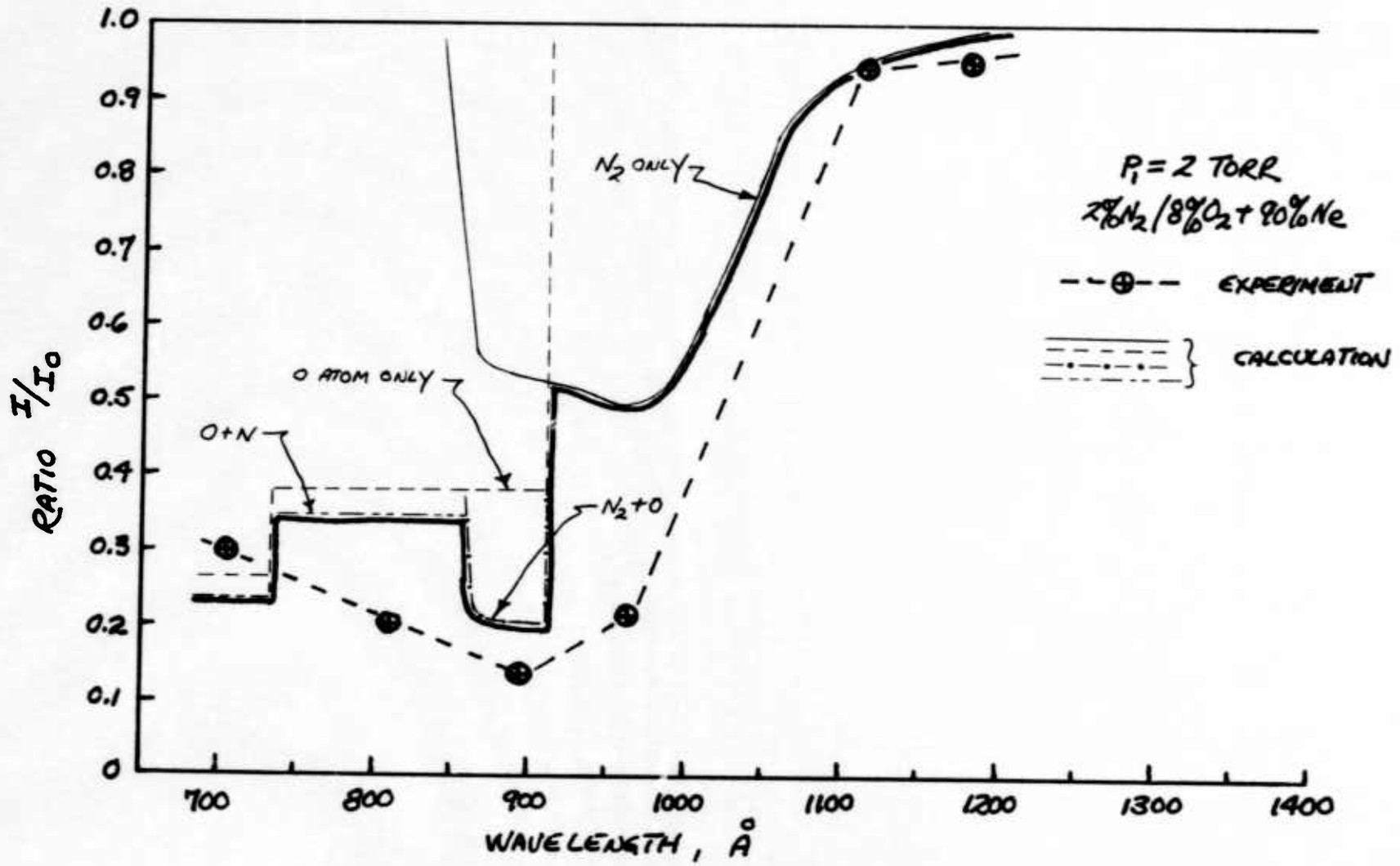


FIG. 3 ABSORPTION AS A FUNCTION OF WAVELENGTH