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EXPERIMENTAL AND THEORETICAL STUDIES
IN PLANETARY AERONOMY

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I. INTRODUCTION

This interim technical report summarizes the work performed under Contract No. NASW-1283 for the period 16 March 1965 through 17 September 1966. The overall objective of the program is the investigation of experimental and theoretical problems associated with the physics of planetary atmospheres. The broad variety of scientific areas which have been considered are discussed most conveniently under the following major categories:

- A. Photochemistry of planetary atmospheres
- B. Theoretical studies
- C. Laboratory investigations in the VUV (2000-1000 $\text{\AA}$) and the EUV (below 1000 $\text{\AA}$) spectral regions
- D. Planetary aeronomy.

During the performance of the subject contract, a number of reports were generated which have been submitted and accepted for publication in accredited journals. In some cases, a more detailed discussion of the material is available in the form of a published GCA Technical Report. In any event, the pertinent information concerning these publications is presented below for each of the categories previously cited:

A. Photochemistry of Planetary Atmospheres

"On the Quenching of 6300 $\text{\AA}$ Airglow," by P. Warneck and J.O. Sullivan, Planet.Space Sci. (to be published).

"Reactions of ^1D Oxygen Atoms III. Ozone Formation in the 1470 $\text{\AA}$ Photolysis of O_2 ," by J. O. Sullivan and P. Warneck, J. Chem. Phys. (to be published).

"Reactions of ^1D Oxygen Atoms IV. Reactions with N_2O , N_2 and CO_2 ," by P. Warneck and J.O. Sullivan, J. Chem. Phys. (to be published).

" CO_2 Actinometer for Argon Source," by P. Warneck, J. Opt. Soc. Am. 56, 408 (1966).

"Studies of Ion-Neutral Reactions by a Photoionization Mass Spectrometer Technique II. Charge Transfer Reactions of Argon Ions at Near Thermal Energies," by P. Warneck, J. Chem. Phys. (to be published).

B. Theoretical Studies

"The Refractive Index of Helium (Rayleigh Scattering by Helium)," by Y.M. Chan and A. Dalgarno, Proc. Phys. Soc. 85, 227-230 (1965); GCA Technical Report No. 65-14-N (Physics of Planetary Atmospheres I).

"The Time-Dependent Coupled Hartree-Fock Approximation," by A. Dalgarno and G.A. Victor, Proc. Roy. Soc. London A291, 291-295 (1966); GCA Technical Report No. 65-24-N (Physics of Planetary Atmospheres III).

"The Fluorescence of Solar Ionizing Radiation," by A. Dalgarno and M.B. McElroy, Planet. Space Sci. 13, 947-957 (1965); GCA Technical Report No. 65-15-N (Physics of Planetary Atmospheres II).

C. Laboratory Investigations in the VUV (2000-1000⁰Å) and the EUV (Below 1000⁰Å) Spectral Regions

"The Total Absorption Cross Sections of H₂, N₂ and O₂ in the Region 550 to 200⁰Å," by J.A.R. Samson and R.B. Cairns, J. Opt. Soc. Am. 55, 1035 (1965).

"The Measurement of the Photoionization Cross Sections of the Atomic Gases," by J.A.R. Samson, Atomic and Molecular Processes (Academic Press, New York, 1966), Editors Bates and Estermann.

"Total Absorption Cross Section of Atomic Oxygen below 910⁰Å," by R.B. Cairns and J.A.R. Samson, Phys. Rev. 139, A1403-A1407 (1965).

"Ionization Potential of O₂," by J.A.R. Samson and R.B. Cairns, J. Opt. Soc. Am. 56, 769-775 (1966); GCA Technical Report No. 65-30-N (Physics of Planetary Atmospheres V).

"Total Absorption Cross Sections of CO and CO₂ in the Region 550-200⁰Å," by R.B. Cairns and J.A.R. Samson, J. Opt. Soc. Am. 56, 526 (1966).

"Ionization Potential of Molecular Xenon and Krypton," by J.A.R. Samson and R.B. Cairns, J. Opt. Soc. Am. 56, 1140 (1966).

The Photoionization Cross Section of Atomic Hydrogen," by R.B. Cairns and J.A.R. Samson, Phys. Rev. (to be published).

"Gas Analysis by Photoionization Mass Spectrometry," by P. Warneck and W. Poschenrieder, J. Appl. Phys. 37, 2812 (1966); GCA Technical Report No. 66-1-N (Physics of Planetary Atmospheres IV).

D. Planetary Aeronomy

"A Satellite Experiment on the Detection of Noctilucent Clouds in the VUV Region," by F.F. Marmo and T.C. Degges, J. Geophys. Res. (to be published).

"Ion Temperatures in the Topside Ionosphere," by A. Dalgarno and J.C.G. Walker, Planet. Space Sci. (to be published).

In addition to the above publications, additional work has been performed which is either incomplete or not appropriate for publication in the open literature. These topic areas are specified below and discussed in greater detail in Section III.

In the area of photochemical investigations, the major incompleted technical area involves the determination of the role of minor constituents in planetary atmospheres.

Two unpublished theoretical investigations involve (1) collision processes in planetary atmospheres and (2) atom-atom collision processes in astrophysics.

The VUV and EUV spectral region laboratory investigations involving the measurement of total absorption and photoionization cross sections for atomic gases have been completed and have resulted in a number of publications as noted above. The important remaining incomplete laboratory investigation involves (1) the determination of the electron energy spectrum due to the VUV and EUV photoionization of selected planetary atmospheric gases. Two other completed (but unpublished) laboratory investigations include (2) the laboratory investigation on the variation of photoionization threshold with temperature and (3) measurement of absorption and photoionization minima in molecular spectra of planetary gases.

The planetary aeronomy effort involved consideration of a large number and variety of scientific problems, a number of which have not reached the stage of publication. Accordingly, the current status of these unreported investigations require some discussion. The following scientific areas have been included in this category: (1) laboratory investigation on the VUV chemiluminescence from selected planetary gases; (2) laboratory measurements of Lyman-alpha absorption of Xe₂ to derive the photon scattering cross section of atomic xenon; (3) laboratory measurements on the VUV fluorescence from planetary gases; (4) theoretical studies on the solar photoionization rates in the Martian ionosphere; and (5) the role of meteoric debris in the Earth atmosphere: simultaneous observation of meteoric debris by employing a rocket-borne mass spectrometric and optical probe.

A significant portion of the research results generated under the subject contract have been presented at various scientific and technical meetings. Here again, the pertinent information is presented in the adopted categorical format.

A. Photochemistry of Planetary Atmospheres

Atmospheric Ion-Molecule Reactions by a Photoionization Mass Spectrometric Technique (P. Warneck and F.F. Marmo) — INVITED PAPER presented by P. Warneck at a Symposium on the Physics and Chemistry of the Lower Atmosphere held at the University of Colorado in Boulder, Colorado, on June 27-29, 1966.

Reactions of ¹D Oxygen Atoms (P. Warneck) — Presented by P. Warneck at the 152nd National Meeting of the American Chemical Society, New York, New York, on September 12-14, 1966.

B. Theoretical Studies

Atom-Atom Collision Processes in Astrophysics (A. Dalgarno) — INVITED PAPER prepared for presentation by A. Dalgarno at the International Astronomical Union Working Group on Collision Processes in Astrophysics held in Boulder, Colorado, on July 11-15, 1966.

Collision Processes in Planetary Atmospheres (A. Dalgarno) — INVITED PAPER prepared for presentation by A. Dalgarno at the International Astronomical Union Working Group on Collision Processes in Astrophysics held in Boulder, Colorado, on July 11-15, 1966.

C. Laboratory Investigations in the VUV (1000-2000⁰Å) and the EUV (Below 1000Å) Spectral Regions

Photoionization Processes (J.A.R. Samson) — INVITED PAPER presented by J.A.R. Samson at the Thirteenth Annual Conference on Mass Spectroscopy and Allied Topics, St. Louis, Missouri, on May 17-18, 1965.

Oscillator Strengths in the Noble Gases (J.A.R. Samson) — INVITED PAPER presented by J.A.R. Samson at the Thirteenth Annual Meeting of the Radiation Research Society in Philadelphia, Pa., on May 25-26, 1965.

The Interaction of Vacuum Ultraviolet Radiation with a Gas (J.A.R. Samson) — INVITED PAPER presented by J.A.R. Samson at the American Physical Society Meeting in Honolulu, Hawaii, on September 2-4, 1965.

A Study of the Kinetic Energies of Electrons Produced by Photoionization (J.A.R. Samson and R.B. Cairns) — Presented by J.A.R. Samson at the Fiftieth Anniversary Meeting of the Optical Society of America held in Washington, D.C., on March 15-18, 1966.

On Ultraviolet and X-ray Spectroscopy of Laboratory and Astrophysical Plasmas (R.B. Cairns and J.A.R. Samson) — Presented at Culham Laboratory, Abingdon, Berkshire, England, on March 29 - April 1, 1966.

The Measured Photoionization Cross Section of Atomic Hydrogen (R.B. Cairns and J.A.R. Samson) — Presented at the 47th Annual American Geophysical Union Meeting held in Washington, D.C., on April 19-22, 1966.

D. Planetary Aeronomy

Scattering Cross Sections for Xenon and Other Rare Gases in the Vacuum Ultraviolet Region (F.F. Marmo and Shardanand) — Presented by J.A.R. Samson at the American Physical Society Meeting in Honolulu, Hawaii, on September 2-4, 1965.

VUV Reflectivity from a Solar-Illuminated Earth Atmosphere (F.F. Marmo and T.C. Degges) — INVITED PAPER presented by F.F. Marmo at International Symposium on Electromagnetic Sensing of the Earth from Satellites held in Miami, Florida, on November 22-24, 1965, who also attended the Second AAS Symposium on Interactions of Space Vehicles with an Ionized Atmosphere held in Miami, Florida, on November 26-27, 1965.

A Satellite Experiment on the Detection of Noctilucent Clouds in the VUV Region (F.F. Marmo and T.C. Degges) — Presented by F.F. Marmo at the 47th Annual American Geophysical Union Meeting held in Washington, D.C., on April 19-22, 1966.

The remaining sections of the report are also presented according to the adapted categorical format. In Section II, brief summaries of the published material are presented in categorical order together with individual listings and shortabstracts of the pertinent papers for ready reference. More detailed technical discussions of the incomplete and unpublished investigations are included in Section III, since the technical details are not available elsewhere. As such, included in the following sections is a concise and encapsulated review of the results which have been achieved under the current program.

II. SUMMARIES, BIBLIOGRAPHIES, AND ABSTRACTS OF INDIVIDUAL PUBLICATIONS ON THE PHYSICS OF PLANETARY ATMOSPHERES

In this section, the results of several planetary physics investigations, which have been published in the open literature under the present contract effort, are presented. These discussions are accordingly brief since a more comprehensive description of the work is available in the cited references. As such, the ensemble of publications are summarized by technical areas, accompanied by a tabulation of the published papers and short technical abstracts. For convenience, a dual reference system is employed in which the published material generated under the current program is indicated by Roman numerals whereas other references are designated by Arabic numerals.

A. Photochemistry of Planetary Atmospheres

The published investigations pertinent to the photochemistry of planetary atmospheres can be discussed in two major categories: (1) solar photolysis of CO₂ including the subsequent dark reactions of O(¹D) with planetary atmospheric gases and (2) investigations of ion-neutral reactions by employing a photoionization-mass spectrometric technique.

1. Solar Photolysis of CO₂ Including the Subsequent Dark Reactions of O(¹D) with Planetary Atmospheric Gases. - The role of CO₂ photolysis in planetary atmospheres has been stressed previously [1,2]* with particular emphasis [3,4] on the action of the metastable O(¹D) produced in the primary VUV solar photodecomposition of CO₂. Additionally, the role of this metastable in subsequent dark reactions with other planetary gases [5] is a vital factor in determining the ambient composition of solar-illuminated planetary atmospheres. Under the current contracts an extensive experimental program was performed to further clarify the role of O(¹D) oxygen atoms in planetary atmospheres [I-IV].

As a consequence of these investigations [1-5] [I-IV], a major portion of the essential data has been acquired and made available to the scientific community so that their application to specific planetary atmospheric problems is now appropriate. Specifically, these overall studies have established the following important factors: (a) the VUV photolysis of CO₂ results in the generation of O(¹D) metastables with a quantum efficiency of about unity; (b) a previously-unexplained observed "oxygen deficiency" in the photolysis mechanism can now be accounted for by the formation of CO₃; (c) for reactions involving O(¹D), the following important rate coefficients prevail: $k(O_2) = 3 \times 10^{-15} \text{ cm}^3/\text{sec}$, $k(N_2) = 1.2 \times 10^{-15} \text{ cm}^3/\text{sec}$, and $k(O_3) = 3 \times 10^{-10} \exp[-2400 \pm 1000/RT]$; (d) the magnitude of He quenching is similar to that due to nitrogen; and (e) self-quenching is not as rapid as that due to N₂O which was found to be the most efficient quencher of those investigated. As a consequence of the above, the following two factors emerge: (1) a serious data gap has been substantially reduced so that (2) it is propitious to employ these new data in the

*Numbers in [] throughout text represent reference numbers.

analysis of a variety of specific problems associated with the atmospheres of the terrestrial planets. For example, application of these data to the problem involving CO₂ reduction in the Martian atmosphere is particularly appropriate in light of the Mariner IV data, which indicate that CO₂ is the major atmospheric constituent. These data were also applied directly to the investigation of the 6300Å airglow in the Earth's atmosphere [I] to demonstrate that the generally-accepted quenching rate is orders of magnitude faster than the measured rate so that an alternative explanation is required to explain this phenomenon. There exists a broad spectrum of additional planetary atmospheric problems in which these data are directly applicable, a number of which are currently being considered.

2. Investigations of Ion-Neutral Reactions by Employing a Photoionization-Mass Spectrometric Technique. - The study of terrestrial ionospheres requires specific knowledge on the rates of a number of ion-neutral reactions. The role which these reactions assume in planetary ionospheres and the requirement for appropriate laboratory measurements are further emphasized in Section III-B. Concerning these laboratory measurements, it became evident that a new experimental technique was available as a natural by-product of the development of a mass spectrometer coupled to a photoionization light source as discussed in Section II C. This instrument was designed and fabricated under the current program for the expressed purpose of performing a mass analysis of photoionization products of selected planetary gases. It turned out that for high (10-100 μ) ion-source chamber pressures, ion-neutral reactions became the dominant process. Accordingly mass analysis experiments were performed only for low (below 10 μ) pressures. However, the high-pressure behavior suggested the application of this technique for performing ion-neutral reaction rate studies. This experimental procedure involves none of the well-known difficulties and disadvantages of conventional electron impact techniques [V]. Although the investigations of ion-neutral reactions between atmospheric gases was not a specific requirement of the current program some effort was directed toward establishing the overall feasibility of the application by successfully measuring a number of rates involving Ar⁺. Specifically, preliminary rate constants were determined [V] for reactions involving Ar⁺ with NO, O₂, CO₂, CO, and N₂. The next logical extension of this phase is to improve upon this novel experimental apparatus in order to optimize its employment in the measurement of a large number of the ion-neutral reactions pertinent to studies of the ionospheres of the terrestrial planets.

Bibliography and Abstracts of Photochemical Investigations Published under the Current Program:

I. "On the Quenching of 6300Å Airglow," by P. Warneck and J.O. Sullivan, Planet. Space Sci. (to be published).

From current interpretation of the 6300Å dayglow observations, it is inferred that the responsible emitter, O(¹D), is rapidly quenched by oxygen and/or nitrogen. However, experimental results from this laboratory do not support this view. These experiments, utilize the photolysis of oxygen at 1470Å to produce O(¹D) simultaneously with O(³P), and the production of ozone in a flow system

is investigated as a function of pressure and other parameters (see Sullivan and Warneck, J. Chem. Phys., "Reactions of $O(^1D)$ Oxygen Atoms III. Ozone Formation in the $1470\text{\AA}$ Photolysis of O_2 "). The results indicate that $O(^1D)$ reacts with ozone 2000 times faster than with either oxygen or nitrogen so that deactivation of $O(^1D)$ in the atmosphere cannot occur upon every collision as it is required in the currently-accepted $6300\text{\AA}$ dayglow mechanism. The need for a reexamination of this mechanism is indicated.

II. "Reactions of 1D Oxygen Atoms III. Ozone Formation in the $1470\text{\AA}$ Photolysis of O_2 ," by J.O. Sullivan and P. Warneck, J. Chem. Phys. (to be published).

The extent of ozone formation in the $1470\text{\AA}$ photolysis of oxygen and 1:1 helium-oxygen mixture has been studied in a flow system as a function of pressure and temperature. A determination of the ozone quantum yield at atmospheric pressure gave $\phi = 2.0 \pm 0.2$ in good agreement with previous values. At lower pressures, the production of ozone was found to decrease with pressure, and this effect has been interpreted as arising from the reaction of $O(^1D)$ with ozone. The quantitative evaluation of the ozone quantum yields in terms of $O(^1D)$ reactions provides ratios of rate constants for the reactions of $O(^1D)$ with ozone, oxygen, and helium. From the temperature dependence, the reaction with ozone is found to have an activation energy of 2.4 ± 1.0 kcal/mole. Absolute rate constant estimates are obtained by the application of independent data.

III. "Reactions of 1D Oxygen Atoms IV. Reactions with N_2O , N_2 and CO_2 ," by P. Warneck and J.O. Sullivan, J. Chem. Phys. (to be published).

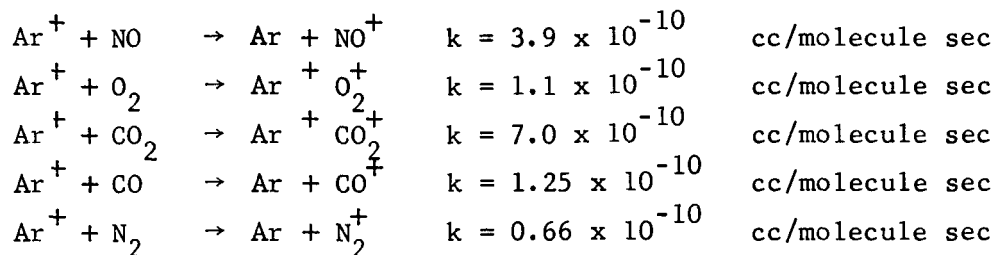
The $1470\text{\AA}$ photolysis of oxygen has been utilized to generate 1D oxygen atoms simultaneously with 3P ground-state oxygen atoms. The quantum yields for ozone formation were measured as a function of pressure in a flow system for mixtures of oxygen with N_2O , N_2 , and CO_2 and compared with quantum yields obtained previously for pure oxygen. The data are evaluated on the basis of a stirred reactor treatment to obtain ratios of rate constants for the involved reactions. It is found that the reactions with N_2O and CO_2 have similar rates, whereas that with N_2 is an order of magnitude slower. All three reactions are slow in comparison to the reaction of $O(^1D)$ with ozone.

IV. " CO_2 Actinometer for Argon Source," by P. Warneck, J. Opt. Soc. Am. 56, 408 (1966).

The argon source with lines at 1048 and $1066\text{\AA}$ was improved by employing LiF windows only 0.25 - 0.5 mm thick, so that the cumulative reduction of LiF transmittance caused by the absorption of argon radiation is slowed down. With this source, the yield for CO formation from the photolysis of CO_2 was explored and found to be unity, independent of pressure or source flux. Thus, the photodecomposition of CO_2 in the 1048 to $1066\text{\AA}$ wavelength region provides a useful actinometer for the argon source.

V. "Studies of Ion-Neutral Reactions by a Photoionization Mass Spectrometer Technique II. Charge Transfer Reactions of Argon Ions at Near Thermal Energies," by P. Warneck, J. Chem. Phys. (to be published).

A photoionization mass spectrometer has been employed to study charge transfer processes involving $2P_{3/2}$ argon ions at ion source pressures of 15 to 60 microns and with a source acceleration potential of 0.5 eV. The average energy of the reacting ions is calculated and is found to be less than 0.17 eV. The following rate constants were obtained:



The theoretical implications are discussed.

B. Theoretical Studies

The theoretical investigations accomplished under the present effort include: (1) UV, VUV, and EUV photon scattering by helium; (2) the time-dependent coupled Hartree-Fock approximation for many-electron systems; (3) intensity estimates of fluorescence from Earth atmospheric constituents (O^+ , O_2^+ and N_2^+) due to EUV solar photoionization; and (4) determination of ion temperatures in the topside ionosphere.

The cross section for photon scattering by an atomic gas may be obtained from its refractive index value; which for helium has been measured with high precision at wavelengths between $2700\text{\AA}$ and $5400\text{\AA}$ [6]. These measurements can be extrapolated to longer wavelengths without serious loss of accuracy. The present program is concerned with obtaining precise photon scattering values for helium in the VUV and EUV wavelength regions. Extrapolations to these spectral regions cannot be achieved with any certainty if current techniques are employed. Accordingly, a new theoretical approach was developed in which the refractive index can be calculated directly at any wavelength by employing variational procedures similar to those employed in the calculation of static polarizabilities and with comparable accuracy [VI]. It was shown that extrapolations of experimental data to the shorter wavelengths can now be accomplished in a very precise manner. Specifically, the calculated helium cross section for scattering of Lyman-alpha radiation is $3.53 \times 10^{-26} \text{ cm}^2$. This value has been employed to establish an absolute basis on which to place the measured relative cross-section values obtained under this program as described in Section III-D.

Time-dependent Hartree-Fock equations have been derived by Dirac [7] and Frenkel [8]. These methods were extended to include external perturbations in the uncoupled case by Karplus and Kolker [9] and for the coupled case by Thouless [10] and McLachlan and Ball. [11] Karplus and Kolker [9] calculated refractive indices and long-range forces for the uncoupled case but were unable to extend their analysis to the coupled case since their approximation did not

lend itself to ready solution. However, Dalgarno [12] has shown that the coupled approximation results in more accurate conclusions. Thus, under the program, a theoretical method was developed [VII] to solve the coupled Hartree-Fock approximation for time-dependent perturbations of many-electron systems. The results were tested by applying the calculations to the frequency-dependent refractive index of helium gas. In this manner, they were compared to the more accurate values obtained by the refined variational calculation [VI] discussed previously. A discrepancy of less than 10 percent was noted; however, it should be emphasized that the coupled Hartree-Fock approximation has a much wider applicability.

The solar EUV photoionization of atomic constituents can generate a positive ion in an excited electronic state which can subsequently fluoresce at longer wavelengths. An estimate has now been obtained [VIII] for the expected intensities due to this type of fluorescence in the Earth's atmosphere. The roles of three Earth atmospheric constituents were considered; namely O^+ , O_2^+ , and N_2^+ . The appropriate ion production and deactivation processes were evaluated as a function of altitude and wavelength and it was concluded that the predicted terrestrial fluorescence signal levels could be observed with present state-of-the-art optical techniques on satellite or rocket platforms. It was also shown that from an Earth-based site, it should be possible to continuously monitor ionospheric behavior in addition to the level and variation of solar UV activity. On the basis of these studies, an experiment has been devised which is to be performed during the forthcoming 12 November 1966 eclipse since it can be shown that only under the unique situation of an overhead total eclipse can this radiation be observed with current instrumentation.

Bibliography and Abstracts of Theoretical Investigations Published under the Current Program:

VI. "The Refractive Index of Helium," by Y.M. Chan and A. Dalgarno, Proc. Phys. Soc. 85, 227-230 (1965); GCA Technical Report No. 65-14-N (Physics of Planetary Atmospheres I).

The refractive index of helium for wavelengths longer than $600\text{\AA}$ is calculated by a variational method from the ground-state representation of Hart and Herzberg. The results agree very well with the observations which refer to wavelengths between $2700\text{\AA}$ and $9000\text{\AA}$.

VII. "The Time-Dependent Coupled Hartree-Fock Approximation," by A. Dalgarno and G.A. Victor, Proc. Roy. Soc. London A291, 291-295 (1966); GCA Technical Report No. 65-24-N (Physics of Planetary Atmospheres III).

A coupled Hartree-Fock approximation for describing the effects of time-dependent perturbations on many-electron systems is presented. It is applied to the calculation of the frequency-dependent refractive index of helium gas with results that differ by between 4 and 8 percent from the accurate values obtained by a refined variational calculation.

VIII. "The Fluorescence of Solar Ionizing Radiation," by A. Dalgarno and M.B. McElroy, Planet. Space Sci. 13, 947-957 (1965); GCA Technical Report No. 65-15-N (Physics of Planetary Atmospheres II).

The mid-day dayglow intensities arising from the fluorescence of solar ionizing radiation are calculated. The predicted overhead intensities above 120 km of the O^+ ($2P - 2D$) lines at $\lambda\lambda$ 7319-7330Å, the Meinel band system of N_2^+ , the first negative system of N_2^+ , the first negative system of O_2^+ , the Hopfield emission system of O_2^+ and the second negative system of O_2^+ are respectively 500R - 1 kR, 9 kR, 600 R, 2 kR, 600 R and 400 R.

C. Laboratory Investigations in the VUV (2000 to 1000Å) and the EUV (below 1000Å) Spectral Regions

Laboratory investigations in the VUV and the EUV spectral regions which have been performed under the current program can be conveniently discussed in two broad categories: (1) measurements of the total absorption and photoionization cross sections for atmospheric gases and (2) mass analysis of the products due to the VUV and EUV photoionization of atmospheric gases.

1. Measurements of the total absorption and photoionization cross sections for atmospheric gases. - A broad and systematic experimental investigation has now been completed on the total photoionization and absorption cross section measurements for a large number of atmospheric gases throughout the VUV and EUV spectral regions. The new results [IX-XV] coupled with those obtained in previous studies [13-23] performed under this program have essentially eliminated an important data gap at least for wavelengths above about 200Å. None of the experimental details are repeated here since they are available in the open literature and in pertinent quarterly progress reports. It should be noted that measurements have been performed on both molecular [IX-XII] and atomic [XIII-XV] species. Concerning the former, the true ionization potential for O_2 was established [X] at a value of 12.063 eV to an accuracy of ± 0.001 eV. Ionization was observed at wavelengths below 1046Å due to the process $O_2 + h\nu \rightarrow O_2^+ + O_2^-$. As a bonus effect, since the latter process involves the generation of O_2^- , a new upper limit value was derived for this important atmospheric parameter, that is, the electron attachment probability of O_2 . Additionally, these data were applied to the problem of E-region processes to demonstrate that an important ionization source is due to the presence of two oxygen emission lines spectrally adjacent to the accurately measured ionization threshold. Measurements of the photoionization cross sections of atomic species have been achieved for the first time for atomic constituents: oxygen [XIII, XIV] and hydrogen [XV]. Comparison with theory has indicated that the measured cross sections of both atomic species are in significant disagreement near the ionization threshold where autoionization processes become dominant. Thus the experimental results are especially valuable in these regions, since present theoretical techniques cannot deal adequately with the complex problems associated with autoionization.

2. Mass analysis of the products due to the VUV and EUV Photoionization of Atmospheric Gases. - Total photoionization cross section measurements cannot differentiate between the several additive processes which, in principle, can proceed simultaneously owing to the high energy content of the incident radiation. Alternatively, the cross sections associated with the individual processes are of considerable importance both in terrestrial ionospheric investigations and the proper interpretation of VUV and EUV photolytic experiments of planetary gases. These individual process cross-sections have been obtained by performing a mass analysis on the photoionization products of selected gases. Under the present effort, a 1/2-meter Seya monochromator was coupled to a specifically designed mass spectrometer [XV] to perform mass analyses on the products due to photoionization in the spectral region $\lambda\lambda$ 1200-480 $\text{\AA}$ of the atmospheric gases O_2 , N_2 , and CO_2 . In addition the results indicate that, at these energetic wavelengths, photoionization produces fragment ions which possess significant excess kinetic energy. A detailed literature review has indicated that this factor has not been recognized heretofore. Accordingly, at least two important factors emerge: (1) the results of earlier laboratory investigations should now be viewed with appropriate caution since this important contribution has previously been neglected and (2) the solar VUV photolysis of atmospheric constituents should produce excess ionic temperatures in the topside ionosphere. Similarly, it appears that this effect has not been considered adequately in previous theoretical treatments of this problem. The application of these and future experimental data to a broad spectrum of planetary atmospheric problems will clearly involve some modification of the current equipment in order to measure the individual kinetic energies of specific fragment ions.

Bibliographies and Abstracts of the Laboratory Investigations in the VUV (2000 to 1000 $\text{\AA}$) and the EUV (below 1000 $\text{\AA}$) Spectral Regions:

IX. "The Total Absorption Cross Sections of H_2 , N_2 , and O_2 in the Region 550 to 200 $\text{\AA}$," by J.A.R. Samson and R.B. Cairns, J. Opt. Soc. Am. 55, 1035 (1965).

Values of the total continuum absorption cross sections of H_2 , N_2 , and O_2 have been measured at wavelengths between 550 and 200 $\text{\AA}$ and are tabulated in this article. It was shown that the measured cross sections of the three gases were not pressure dependent. The accuracy of the measurements was ± 10 percent.

X. "Ionization Potential of O_2 ," by J.A.R. Samson and R.B. Cairns, J. Opt. Soc. Am. 56, 769-775 (1966); GCA Technical Report No. 65-30-N (Physics of Planetary Atmospheres V).

The first ionization potential of O_2 has been found to correspond to $1027.8 \pm 0.1\text{\AA}$ (12.063 ± 0.001 eV). Previous determinations of the ionization potential are reviewed and compared with the present result. The photoionization cross section measured from threshold to 993 $\text{\AA}$ reveals vibrational structure superimposed on autoionized absorption peaks. The absorption spectrum illustrates the profuse absorption bands in the vicinity of the ionization threshold. Ionization was observed at wavelengths longer than 1027.8 $\text{\AA}$ and is explained on the basis of the formation of excited O_2 . From the interpretation of the results,

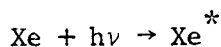
the dissociation energy for the ground state of the ion is 6.669 ± 0.001 eV and the electron affinity of O_2 is ≥ 0.21 eV.

XI. "Total Absorption Cross Sections of CO and CO_2 in the Region 550-2000Å," by R.B. Cairns and J.A.R. Samson, J. Opt. Soc. Am. 56, 526 (1966).

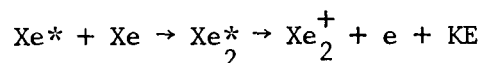
Values of the total continuum absorption cross sections of CO and CO_2 have been measured at wavelengths between 550 and 2000Å. The results are shown graphically. No pressure dependence was observed for the measured cross section values. The estimated accuracy of the results was ± 5 percent between 550 and 3400Å and ± 10 percent at shorter wavelengths.

XII. "Ionization Potential of Molecular Xenon and Krypton," by J.A.R. Samson and R.B. Cairns, J. Opt. Soc. Am. 56, 1140 (1966).

The production of ions in atomic Xe and Kr by resonance-line absorption is described and attributed to the process



followed by



These measurements provided the first ionization potential of Kr_2 at 963.37Å (12.87 eV).

XIII. "Total Absorption Cross Section of Atomic Oxygen below 9100Å," by R.B. Cairns and J.A.R. Samson, Phys. Rev. 139, A1403-A1407 (1965).

The total absorption cross section of atomic oxygen has been measured in the wavelength range 910-5040Å. The results are compared with existing theoretical computations. The source of oxygen atoms was a microwave discharge in a He- O_2 mixture. In addition to the oxygen atoms, excited oxygen molecules in the I_{Δ_g} state and metastable He atoms were formed. The procedure used to extract the oxygen-atom cross section from those of the other neutral and excited species is given.

XIV. "The Measurement of the Photoionization Cross Sections of the Atomic Gases," by J.A.R. Samson, Atomic and Molecular Processes (Academic Press, New York, 1966), Editors Bates and Estermann.

Measurements of the photoionization cross sections of the following atoms have been reviewed: O, H, N, He, Ne, Ar, Kr, Xe, Li, Na, K, Rb, Cs, Ca, Tl, In, Mg, and Cd. A critical analysis of the past and present experimental and theoretical values is given, and the most accurate data were selected and tabulated for wavelengths between 0.1Å and the ionization threshold of each atom.

XV. "The Photoionization Cross Section of Atomic Hydrogen," by R.B. Cairns and J.A.R. Samson, Phys. Rev. (to be published).

The photoionization cross section of H has been measured at many wavelengths in the spectral range 912 to 845Å. The source of H atoms was a microwave discharge in either H₂ or a He-H₂ mixture. At wavelengths shorter than 845Å, values of the cross section could not be obtained since there was appreciable absorption by excited species produced in the discharge. These species were probably H₂ in excited vibrational and rotational levels of its ground electronic state.

XVI. "Gas Analysis by Photoionization Mass Spectrometry," by P. Warneck and W. Poschenrieder, J. Appl. Phys. 37, 2812 (1966); GCA technical Report No. 66-1-N (Physics of Planetary Atmospheres IV).

A photoionization mass spectrometer featuring a special 180-degree magnetic analyzer with inclined pole faces is described and its usefulness as a gas analytical tool explored. Ion-source pressures up to 20μ can be utilized for gas analysis. Higher pressures can be reached, but ion molecule reactions and increasing light absorption cause a nonlinear ion current-pressure relationship. The major advantage of photoionization when compared to electron-impact ionization is the simplicity of fragmentation patterns; the major disadvantage is the lower sensitivity. At 20μ pressure, spark or resonance light sources used in conjunction with a 1/2-m monochromator produced peak ion intensities around 5×10^{-13} A. Although these ion intensities are higher than those reported previously, they are still considerably below the ion intensities commonly produced by electron-impact ion sources.

D. Planetary Aeronomy

A diverse number of planetary aeronomy problems have been investigated during the current contract period. Although considerable progress has been achieved in each case, final analyses and conclusions are not available for many studies so that these are discussed in Section III-D. Alternatively the two important problems which have been completed and published are: (1) a satellite experiment on the detection of noctilucent clouds in the VUV spectral region and (2) a theoretical investigation on the ion temperatures in the top-side ionosphere.

1. A satellite experiment on the detection of noctilucent clouds in the VUV region. - The detection, observation, and characterization of noctilucent clouds on a world-wide basis under conditions other than twilight would afford scientists a long-sought opportunity to perform a systematic study on the nature, distribution and causative mechanism of this phenomenon. Maximum information can be derived from a satellite instrument observing the solar-illuminated cloud residence altitudes in a downward direction. For this geometry, a relatively homogeneous and low background level exists in the VUV region due to oxygen absorption in the Earth's atmosphere. In a sense, this condition is comparable to the twilight or terminator geometry in the visible

region so that the VUV solar illuminated atmosphere may be regarded as affording "permanent twilight". Since this represents the optimum conditions for observing noctilucent clouds, it is evident that such a VUV satellite experiment should be performed. The feasibility of such an experiment has been demonstrated [XVII] using a Fastie-Ebert type spectrometer probing in the relatively narrow spectral region between 1750 and 1850Å. Clearly, the applicability of a similar Martian dust cloud experiment is appropriate in view of the current controversy concerning the role of interplanetary debris and/or dust in the Martian atmosphere.

2. Theoretical investigation on the ion temperatures in the topside ionosphere. - Analysis of backscatter observations [24] has established that the positive ion temperature in the ionosphere exceeds the neutral particle temperature at altitudes above 300 km during the daytime. The results are in general accord with theoretical predictions which assume that the ions are heated by collisions with the hot ambient electrons and cooled by collisions with the neutral particles [25-27]. Since the efficiency of the heating and cooling mechanisms depends upon the nature of the ionic species involved, the individual positive ions may have different temperatures. Theoretical calculations have now been completed [XVIII] which include the cooling due to resonant charge transfer processes as well as the role of near resonance reactions involving H , O^+ , $O(^3P_2)$, $O(^3P_1)$ and $O(^3P_0)$. The important conclusions due to these calculations are: (1) it is sufficient to characterize the ionic temperature distribution by a single ion temperature and (2) the role of He^+ is negligible at all altitudes.

XVII. "A Satellite Experiment on the Detection of Noctilucent Clouds in the VUV Region," by F.F. Marmo and T.C. Degges, J. Geophys. Res. (to be published)

A theoretical investigation has been performed to examine the feasibility of detecting solar-illuminated noctilucent clouds or high-altitude dust particles by employing a satellite-borne spectrometer to measure the VUV backscattered radiation. The solar radiation diffusely-reflected by the earth's atmosphere contributes to the background against which the noctilucent clouds or dust particles must be observed. This part of the background has been computed through second order scattering on the Rayleigh phase function for wavelengths between 1100 and 2000Å where the background radiation is extremely low when compared to wavelengths above 2000Å. Additionally, estimates are made for the contribution of fluorescent scattering in the LBH band system to evaluate their contribution to the diffusely-reflected background intensity. In order to insure proper solar illumination of the noctilucent clouds, it is shown that one must employ wavelengths greater than 1750Å. On the other hand for wavelengths above 2000Å, the background behaves in such a manner as to degrade the system capability. Mie scattering theory is used to estimate the flux backscattered by the solar-illuminated noctilucent cloud particles with a size distribution corresponding to those collected by rocket probes. The backscattered flux from a typical noctilucent cloud display is compared to the diffusely-reflected background flux for the wavelength region between 1750 and 1850Å and its detection by a spectrometer of the Fastie-Ebert type is evaluated.

XVIII. "Ion Temperatures in the Topside Ionosphere," by A. Dalgarno and J.C.G. Walker, Planet. Space Sci. (to be published).

Analysis of backscatter observations has established that the positive ion temperature exceeds the neutral particle temperature at altitudes above 300km during the daytime. Ion temperatures in the topside ionosphere have been calculated with the assumption that the ions are heated by collisions with the hot ambient electrons and cooled by collisions with the neutral particles. Additional cooling occurs through resonant charge transfer processes. Consideration has also been given to the role of near-resonance reactions involving H, O^+ , $O(^3P_2)$, $O(^3P_1)$, and $O(^3P_0)$. The appropriate expressions for the heating and cooling for O^+ , He^+ , and H^+ were derived and equated. On this basis, substantial differences result between the ion temperatures; these are greatly modified due to the long-range Coulomb interaction which closely couples the various ion temperatures to each other. It is shown that the fraction of O^+ ions produced by near resonance reactions is negligible and so accordingly is the heat source; however, near resonance reactions are important sources for H^+ ions. The complete solutions indicate that it is sufficient to characterize the ionic distribution by a single ion temperature. Concerning the flow of heat from electrons to neutrals, at 700 km, the H^+ and O^+ ions are of approximately equal importance. At lower altitudes, the heat flows principally to O^+ and then to O (H^+ loses most of its heat to O^+). At higher altitudes, heat flows principally to H^+ and then to H and He (O^+ receives most of its heat from H^+). Finally, the role of He^+ is shown to be negligible at all altitudes.

III. TECHNICAL SUMMARIES OF UNPUBLISHED RESULTS ON WORK PERFORMED UNDER THE PRESENT CONTRACT EFFORT

In the present section, technical summaries of the unpublished work performed under the present contract effort are presented. In this category, the summaries are necessarily presented in greater detail since the major scientific features are not available elsewhere. The variety of topics included for discussion herein and the adopted presentation format have previously been listed in the Introduction.

A. Photochemistry of Planetary Atmospheres

1. Investigations on the VUV Photolysis of Planetary Gases Designed to Determine the Role of Minor Constituents. - The Mariner IV experimental results have clearly indicated that CO_2 is the major constituent of the Martian atmosphere. Additionally, it is highly suspect that this gas plays a major role in the Cytherean atmosphere. With respect to the Martian case, although other constituent gases are undoubtedly present, their individual identifications and abundances are essentially unknown. The results of laboratory [1-5] [II,III] and theoretical [28] investigations, which have been conducted under this program, have suggested that these other resident species may include O_2 , O_3 , CO and CO_3 . It is also generally recognized that other minor constituents including water vapor, CH_4 , SO_2 , H_2S , C_2H_2 , CH_2O , etc., have a high residence probability in terrestrial planetary atmospheres. In fact, recently Kaplan et al. [29] have identified new absorption bands in a near-infrared spectrum of Mars by Fourier spectroscopy which have been tentatively identified as due partially to reduced gaseous species including substituted methanes. Thus, the performance of laboratory experiments on VUV photolysis of minor constituents in simulated planetary atmospheres is especially timely.

Under the current program, preliminary laboratory investigations were conducted on the VUV photolysis of (1) pure CO_2 and (2) mixtures of $\text{H}_2\text{S} + \text{O}_2$ and $\text{C}_2\text{H}_2 + \text{O}_2$. The initial results indicate that whereas an unidentified photolysis product has been detected in the case of the CO_2 experiments, somewhat more indefinite results were obtained for the gas mixtures.

Of the two experimental configurations which were employed the first involved the coupling of a 1/2-meter Seya monochromator to a 6-inch photolysis cell so that the absorption qualitative analysis and the appropriate photolysis could be performed simultaneously. A hydrogen discharge light source was used for the qualitative analysis absorption measurements for $\lambda\lambda$ 1500 to 3000Å whereas a 1470Å xenon discharge was employed as the photolytic photon source. The second experimental configuration employed a mass spectrometer to perform the required qualitative analysis which was coupled to the same photolysis cell. In this configuration, continuous mass monitoring could be achieved during the entire photolytic period.

Only pure CO_2 measurements were performed on the first experimental setup, whereas the second setup was employed for all three cases. The two experiments and some preliminary results are discussed below.

For the monochromator-photolysis cell configuration involving pure CO_2 , the hydrogen source was operated until its intensity stabilized, which required about two hours. Then the photolysis cell was evacuated and an initial spectrum (I_0) (see Figure 1) was recorded. The CO_2 gas was then admitted at pressures which varied between 10 and 50 mm Hg; an initial (Curve 1) absorption spectrum was recorded. Thereafter during the photolysis process, additional spectra were recorded at periods of 0.5 (Curve 2) and 3.0 (Curve 3) hours, respectively. The results are presented in Figure 1 where the absorption intensity is plotted as a function of wavelength from 1650 $\text{\AA}$ to 2000 $\text{\AA}$. Continued irradiation beyond three hours produced no significant variation in the absorption spectrum so that it was concluded that a steady state had been established at this latter time. A number of auxiliary experiments were performed to eliminate the effects of outgassing or system leaks. On the basis of the observations, it is clear that the photolysis of CO_2 results in one or more unidentified products which absorb radiation of wavelengths of about 1650 to 1900 $\text{\AA}$. The results of previous experiments [1-5] [II,III] have indicated that the most likely candidate end products would include O_2 , CO , O_3 , and CO_3 . Concerning the first two constituents, they are known to absorb discretely in the region 1650 to 2000 $\text{\AA}$. Since their well defined band structure would have been easily identified with the available 5 $\text{\AA}$ resolution capability of this system, they do not appear to be the sought end products. With respect to O_3 , the spectral region around 2500 $\text{\AA}$ was investigated and negative results were obtained. On this basis, it was established that the total ozone concentration must be less than 5×10^{14} molecules per cc so that O_3 could not possibly be a major contributor to the results of Figure 1 since the absorption intensity for O_3 in the spectral region (1650 to 1900 $\text{\AA}$) is at least one order of magnitude less than in the 2500 $\text{\AA}$ region. By the above process of elimination, it appears that the observed absorption is due to either the generation and presence of CO_3 or other unidentified products. Establishment of CO_3 as the responsible product would be a major input to the problem of explaining Mariner IV observations on the degree of reduction of CO_2 in the Martian atmosphere. As far as unambiguous spectral identification of CO_3 is concerned, no previous VUV spectra have been reported. Thus, it appeared that a mass spectrometric technique should be employed; this requirement prompted the second series of experiments described next.

In the mass spectrometer-photolysis setup, a specially-designed mass spectrometer was coupled with an arc liter flask to which the VUV photolytic light source was attached. The 60-degree permanent magnetic-type mass spectrometer performed the scanning operation by variation of the acceleration voltage. It can be shown that the time variation of the product concentration, X , in the vessel is governed by the equation

$$V \frac{dX}{dt} = P - XF$$

where V is the volume of the flask, P is the production rate, and F is the flow rate into the spectrometer. When the X product is not initially present, the solution to the above equation is given by

$$X = \frac{P}{F} \left[1 - \exp\left(-\frac{F}{V} t\right) \right]$$

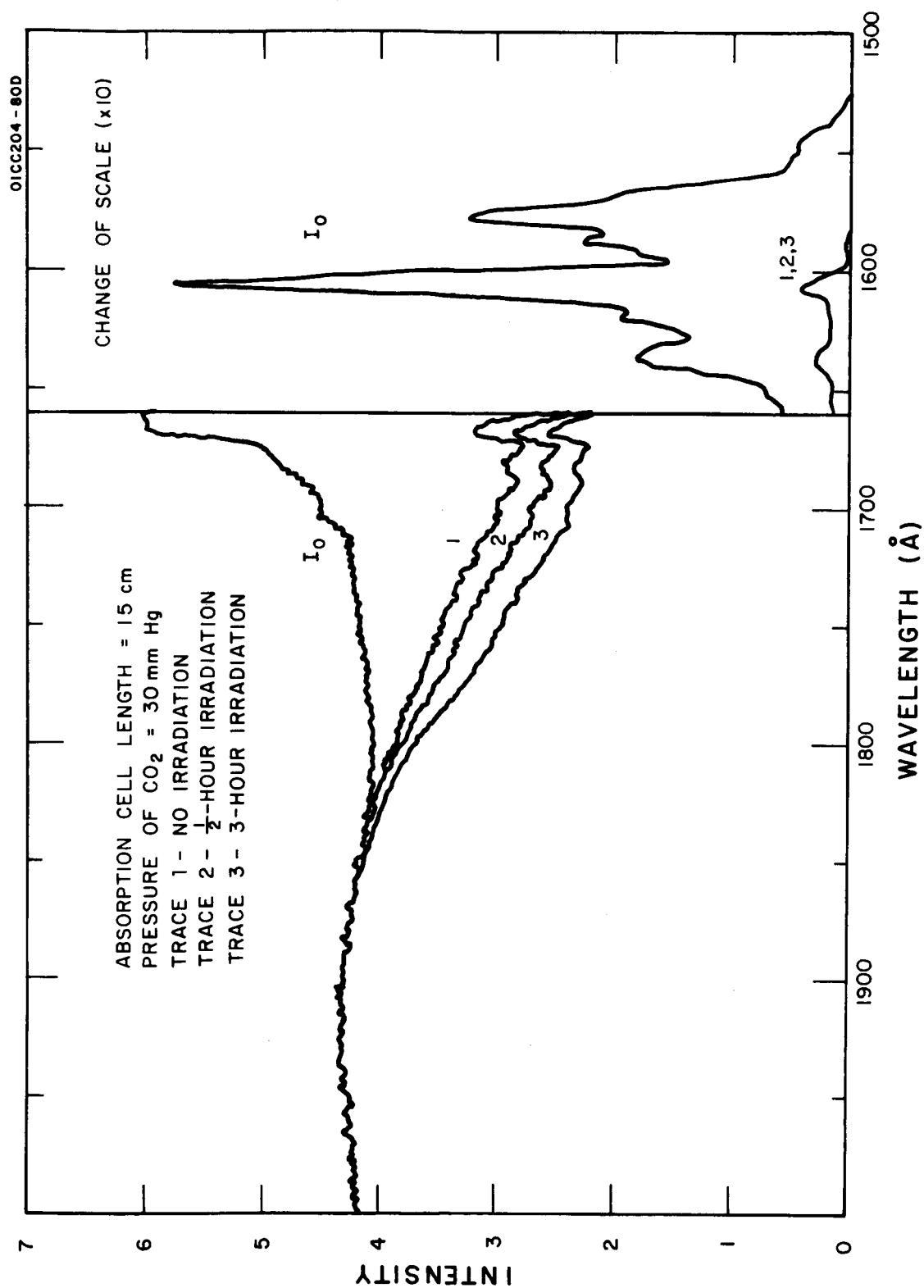


Figure 1. Absorption intensity versus wavelength for CO₂ time-or-photolyses of 0, 1/2 and 3 hours shown by curves 1, 2 and 3 respectively.

indicating that the concentration approaches a steady state. For a flask volume of 1 liter, a flow rate of 0.3 cc/sec steady state is attained in approximately 7×10^3 sec or about two hours regardless of the production rate of the product.

In the case of CO_2 , photolysis was continued for over two hours while the mass spectrum was scanned in 15-minute intervals. While the mass-time variation due to O_2 was observed, the presence of CO at mass 28 could not be verified since it was overlapped by an ionized fragment of CO_2 . Negative results were obtained when the region of mass 62 was probed for CO_3 detection. It turns out that in this region, optimum spectrometer sensitivity is not achieved using the presently-available scanning mode. Thus, it would be desirable to perform the experiments incorporating both magnetic scanning (to enhance higher mass range sensitivity) and a more intense VUV photolytic light source.

In spite of the instrumentation shortcomings, additional survey experiments were performed on two mixtures: (a) 10:1 oxygen-acetylene mixture and (b) 1:1 oxygen- H_2S mixture. In the former, although the methylene radical was qualitatively detected, quantitative measurements could not be obtained. Higher mass number products were not detected for the same reason cited above. In the second mixture, although a significant amount of H_2 was observed, definite identification of sulfur-containing compounds could not be achieved.

It thus appears that improved experimental techniques are required to satisfactorily perform the difficult experiment of identifying constituent end products in the photolysis of planetary gas mixtures. Since gas chromatography may represent a more versatile analytical technique for qualitative analysis, an appropriate instrument has been purchased with GCA funds so that it is now available for future investigations of this nature.

B. Theoretical Studies

The results of two unpublished theoretical investigations are presented herein; namely, (1) collision processes in planetary atmospheres and (2) atom-atom collision processes in astrophysics. As noted previously, the subject materials were prepared as invited presentations at the International Astronomical Union Working Group on Collision Processes in Astrophysics Conference. At present, these papers are not in forms compatible to publication so that they may not appear elsewhere. Since the full text of the second paper is available in Quarterly Progress Report No. 6 (see pp. 29-61) and the topic is somewhat peripheral to the requirements of the current program, a rather brief abstract is presented of this topic. However, owing to the subject matter of (1), it is essentially reproduced in full herein although it also appears in the above-mentioned Quarterly Report.

1. Collision Processes in Planetary Atmospheres. - The proper interpretation of many planetary atmospheric phenomena requires specific knowledge of the rates of the pertinent atomic collision processes. As such, the more significant problems and appropriate collision processes applicable to the Martian and Earth atmospheres are summarized herein.

In the past decade, substantial progress has been achieved in the laboratory determination of the thermal chemical reaction rates which influence the structure of the Earth's atmosphere and ionosphere. In this regard, comprehensive reviews are available of the laboratory measurements of reactions involving oxygen and nitrogen [30] and hydrogen [31]. Most laboratory measurements have been performed over a relatively restricted thermal range about room temperature and efforts to extend the observations over a more applicable ambient range (150°K to 3000°K) are clearly indicated. To date other than the role of O(¹D), [1-5] [I-III], the effects of metastable species on the chemistry of the atmosphere have not been seriously explored, largely because few reaction measurements exist in which the states of the reacting species have been identified.

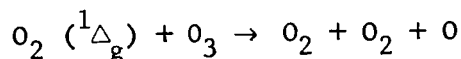
Hunt [32] has recently considered the photochemistry of an oxygen-hydrogen atmosphere and has investigated the diurnal atmospheric ozone concentration. With respect to the former, he has demonstrated that the metastable O(¹D) may play a significant role despite its low concentration to produce free hydrogen atoms in the stratosphere. A major uncertainty in the calculation involves the efficiency of deactivation of the metastable O(¹D) atoms. The ¹D state represents the upper level of the red line of atomic oxygen, which is a familiar airglow emission feature. The observed dayglow intensities are unexpectedly weak, in light of the many prodigious O(¹D) sources, such as photodissociation in the Schumann-Runge continuum of molecular oxygen, recombination of positive ions O₂⁺, (but probably not NO⁺) [33] and collisional excitation by the impact of nonthermal photoelectrons. A quenching rate coefficient of 7 x 10⁻¹¹ cm³ sec⁻¹ is required to explain the dayglow intensity predicated on deactivation by collisions with the major constituent N₂:



Hunt [32] has reproduced the atmospheric ozone profile employing a reaction scheme rate which is about two orders of magnitude smaller than that of Reaction (1) above (see also Refs. I and III).

The presence of O(¹D) atoms may also have important consequences on the nitrogen oxide atmospheric chemistry, although the pertinent reaction rates, which are largely unknown, must be obtained before a realistic analysis can be performed.

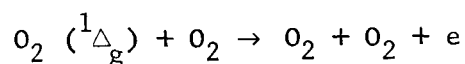
The presence of metastable species of molecular oxygen in the atmosphere may also affect the hydrogen-oxygen and nitrogen oxide chemistries. Molecules of O₂ in the ¹Δ_g state are produced by a number of processes, the most prominent of which is probably photodissociation in the Hartley continuum of ozone. Metastable molecules have been detected in the twilight and day airglow [34] while the appropriate production and loss mechanisms have also been investigated [34, 35]. Schiff and Megill [35] have drawn attention to the possible effect of the reaction



on the ozone chemistry. Although a list of reactions involving $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ is available [32], the identification of the important reactions is somewhat tentative and the magnitudes of the rate coefficients are highly uncertain. Recently, pertinent laboratory work on $O_2(^1\Delta_g)$ has been reported [36].

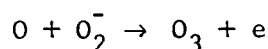
The observed twilight emission of the (0-1) O_2 band of the $^1\Delta_g - ^3\Sigma_g^-$ system is much weaker than predicted on theoretical grounds. Furthermore, the seasonal, annual and evening-morning variations are essentially unexplained [34].

The chemistry of the metastable $^1\Delta_g$ states of O_2 requires clarification in connection with a suggestion [37] that the detachment reaction



may be significant in the D-region both during a polar cap absorption event and possibly under undisturbed conditions.

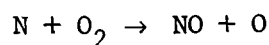
The process of associative detachment



may also be significant. An early theoretical suggestion that the pertinent rate coefficient may be as high as $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ has been confirmed recently by laboratory measurements [38].

Analysis of D-region phenomena suggests that detachment does not occur rapidly enough so that it appears necessary to transform O_2^- into some other negative ion which cannot participate in an apparent associative detachment process. Some potential applicable and relevant chemical reactions have been presented by Dalgarno [39], Whitten and Popoff [40] and Branscomb [41].

It is now firmly established that photoionization of nitric oxide by solar Lyman-alpha is the principal source of electrons in the undisturbed upper D-region. Barth [42] has detected NO fluorescence in the dayglow and has derived a total abundance of $1.1 \times 10^{14} \text{ cm}^{-2}$ below 85 km. Recent studies of NO production [43] have yielded a list of probable pertinent reactions and estimates of the associated rate coefficients. Further laboratory study of the reaction



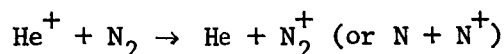
is indicated. Since the above reaction is highly temperature sensitive, extrapolation to other thermal regions may produce misleading results. Another source of NO is provided by the ionic reaction



Although rate coefficient upper limits have been derived from laboratory measurements [44,45], its actual value at D-region temperatures is unknown. Reaction (2) is also important in the chemistry of ionic species, as discussed most recently by Donahue [46], who presents an extensive list of the chemical reactions affecting the major ions O^+ , O_2^+ , N_2^+ , and NO^+ . Most of the relevant rate coefficients have been measured [45,47] over a narrow thermal range centered about room temperature. There is reasonable agreement between the theoretical and observed ion concentrations above 90 km [46] although the situation is somewhat more ambiguous at lower levels. According to Donahue [46], it is difficult to reconcile the reaction scheme selected for the E and F regions with the large O_2^+ concentrations which have been measured in the D-region by mass spectrometric techniques [48]. It should be noted that the metastable $O_2^+(^4\Pi)$, which is produced in the atmosphere [IX] has not been discussed herein. What sparse information is available of the responsible removal reactions has been discussed briefly by Hunten and McElroy [49]. More general reviews of atmospheric deactivation processes [49,50] are also available. Reactions which involve the metastable $O^+(^2D)$ ion may also affect the ionic chemistry [51].

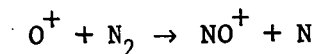
A number of problems involving specification of responsible reactions have been raised by recent spectrometer measurements [48,52] which indicate that complex ions, consisting possibly of water vapor clusters, are the dominant ionic species in the lower D-region.

The most serious difficulty in interpreting ionospheric composition involves the observed high abundance of positive helium ions in the topside ionosphere. The measured rate coefficients [45,53] for



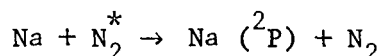
appear to be too high [54]. Either an abundant and unrecognized source of He^+ exists or the laboratory measured rate coefficient is not applicable to ambient ionospheric conditions. It has been suggested [55] that the degree of vibrational excitation may be relevant, but further study of this point is necessary. The above process may also be pertinent to both the problems of neutral helium escape from the atmosphere and the production of N_2^+ and N^+ at high altitudes.

The degree of vibrational excitation of atmospheric molecules merits further study especially since it has recently been demonstrated in the laboratory [56] that the rate of



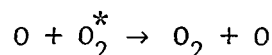
increases rapidly at higher vibrational temperatures. This may explain the diminution in electron density in the vicinity of red arcs and during disturbed ionospheric conditions. Vibrationally excited molecules can be produced by electron impact and possibly by the $O(^1D)$ deactivation process specified in Reaction (1).

It has been suggested [57] that vibrational excitation may be the energy source for excitation of the lines due to NaD according to



Additionally, Hunten [58] has shown that this reaction occurs in low altitude aurora. Pertinent laboratory results have also recently become available [59].

Experimental measurements of vibrational excitation and de-excitation processes and of the effect of excitation on reaction rates would be of considerable value. Bates [60] has argued that the atom-atom interchange process



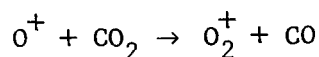
may be an efficient mechanism for O_2^* deactivation. If this is not the case, a substantial atmospheric population of O_2^* must result necessarily through production processes such as fluorescence in the discrete Schumann-Runge system. In addition to its diverse effects on atmospheric chemistry, O_2^* can be ionized by long wavelength solar radiation resulting in a corresponding modification of Lyman-alpha absorption.

The reactions discussed above involve thermal collision processes. Non-thermal heavy particle collision processes involve fast protons and hydrogen atoms resulting from electron capture by the protons in collisions with ambient constituents. The atmosphere is bombarded by protons during auroras and, in particular, during polar cap auroras. Unfortunately, only sparse information is available regarding the cross sections for the various possible processes [61,62].

A similar situation exists for the case of electron impact. Electron impact excitation and ionization investigations have assumed added significance, since it has been recognized that photoelectrons contribute substantially to dayglow excitation. Successful observation of this phenomenon [63] provides a valuable technique of investigating atmospheric properties.

Determination of the ionospheric electron and ion temperatures requires knowledge of the pertinent electron collision processes. Most of the important processes are known to sufficient accuracy [64] with the exception of vibrational and rotational excitation of molecular oxygen. Recently, studies on the cooling of electrons colliding with O_2 have been performed [65,66,67].

The results of the Mariner IV occultation experiment have presented a number of basic interpretive problems. The rates of reactions involving CO_2 and its dissociation and ionization products are vital to a proper understanding of the structure of the Martian atmosphere. Since the ambient temperature may be very low, measurements down to temperatures as low as 50°K are desirable. The reaction

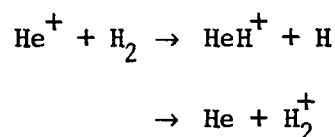


is important in the Martian ionosphere. Although the rate coefficient has been measured at room temperature [38,68], similar observations do not exist at 80°K, a temperature suggested [69,70] as appropriate to a Martian altitude of 120 km. An argument that such a low temperature is not prevalent [71] is predicated on the assumption that CO_2^+ recombines rapidly with electrons. Therefore, laboratory measurements are required on the rate of dissociative recombination of CO_2^+ and identification of the resultant products.

With respect to radiation losses, it has been assumed [71] that the rate coefficient for vibrational deactivation of CO_2 varies as $\exp(-82.8T^{-1/3})$. This specification reproduces the high temperature data adequately but it is uncertain whether it remains appropriate over the possible range of Martian temperatures.

Because of the low Martian atmospheric densities, two-body collision processes assume greater importance than in the terrestrial atmosphere. As such, radiative association, about which only sparse quantitative information is available, may be the major recombination mechanism.

With respect to other planets, there exists some limited discussions of the upper atmospheres of Venus [72] and Jupiter [73]. Reactions involving the dissociation and ionization products of CO_2 and N_2 are significant for Venus, and of H_2 and He for Jupiter. Of particular relevance to a prediction of the composition of the Jovian ionosphere are the rates of the reactions

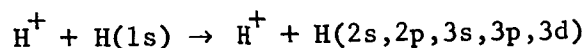


which, though slow, are probably responsible for the removal of He^+ ions.

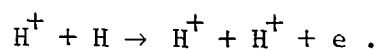
2. Atom-Atom Collision Processes in Astrophysics. - Atom-atom collision processes which are relevant to astrophysical problems occur either at very high energy levels or at thermal energies. With the exception of rearrangement processes, the former can be described by the standard Born approximation whereas for the latter case, specific theoretical treatments are required for individual problems. In the present discussion, both cases are considered for the purpose of defining the relevant problems in each and for presenting appropriate reviews of current knowledge in the defined areas.

a. High energy collisions. - Owing to the occurrence of cosmic rays, high energy collisions of protons and neutral hydrogen atoms with hydrogen and possibly helium assume special importance. On this basis, some of the relevant processes have been defined as follows:

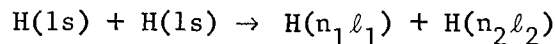
Excitation and ionization of H by H^+ :



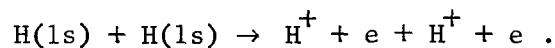
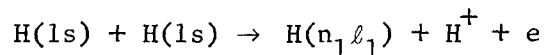
and the ionization process:



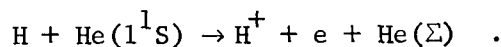
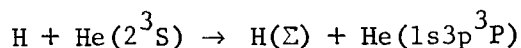
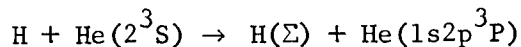
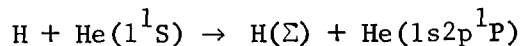
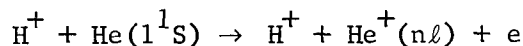
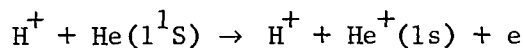
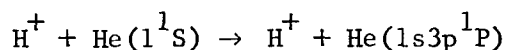
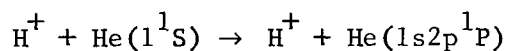
Excitation of H by H:



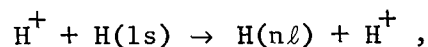
and the ionization processes:



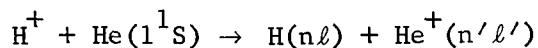
The corresponding excitation and ionization processes for He by H^+ and H include:



In addition, charge transfer processes for these species have also been considered. As examples, the charge transfer of H^+ in H is described by



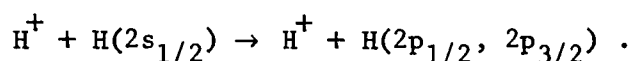
while the associated charge transfer process of H^+ in He is expressed by:



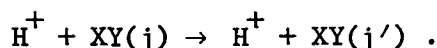
for various excited states of end products. Associated problems which have been considered involve the stopping power of H^+ in H (i.e., the efficiency

with which a beam of protons is slowed down in a gas of ground-state hydrogen atoms) and the stopping power of H^+ in a plasma of H^+ and electrons (i.e., the energy loss of fast protons in an ionized hydrogen plasma). In the above cases, critical evaluations were performed to derive the most current acceptable cross sections.

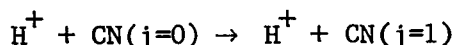
b. Low energy collisions. - In the case of low energy collisions, the electron impact excitation cross section increases rapidly from threshold to a maximum, which occurs at an impact velocity corresponding to about twice the threshold energy; thereafter, it decreases asymptotically either as $E^{-1} \ln E$ for optically-allowed transitions or as E^{-1} for optically-forbidden transitions. Thus, electron impact excitation is usually more efficient than proton impact excitation except when the threshold energy represents a small fraction of the thermal plasma energy. An example of an important excitation process in which proton impact is more efficient than electron impact is the 2s-2p transition in atomic hydrogen



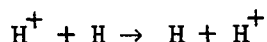
This reaction plays an important role in reducing the intensity of the two-quantum emission from $H(2s)$. A similar reaction which may be important is the proton impact excitation of molecule reactions such as:



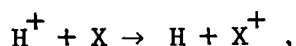
The particular case



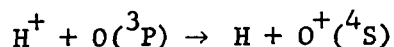
has been investigated in connection with cosmic microwave radiation at a wavelength of 2.63 mm. Other relevant low energy collisional processes include symmetrical and asymmetrical charge transfer processes such as



and



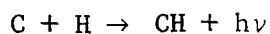
respectively. A specific example of the latter reaction is



which may affect the ratio of the O to O^+ densities in the Cassiopeia radio source. A number of other processes of interest include radiative charge transfer such as



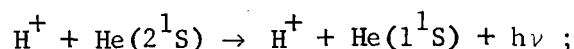
radiative association, such as



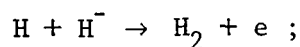
or



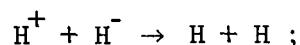
collision-induced radiative deactivation, such as



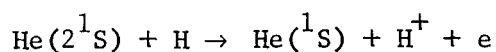
associative detachment, such as



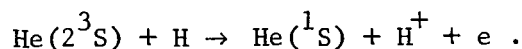
mutual neutralization, such as



and penning ionization in which a radiationless transition occurs, such as



and



Finally, other processes of interest to astrophysics were also identified and discussed. These included spin change processes, the role of quenching collisions, and finally a number of pertinent chemical reactions. The reader is directed toward Quarterly Report No. 6 for a more detailed discussion of this topic.

C. Laboratory Investigations in the VUV (2000 to 1000Å) and the EUV (below 1000Å) Spectral Regions

With respect to unpublished material in the VUV and EUV laboratory investigation category, three scientific areas are discussed herein: (1) the electron energy spectrum due to the VUV and EUV photoionization of O₂, N₂, CO, and CO₂; (2) the variation of the photoionization threshold with temperature; and (3) absorption and photoionization minima in molecular spectra of planetary gases.

1. Laboratory Determination of the Electron Energy Spectrum Due to the VUV and EUV Photoionization of O₂, N₂, CO, and CO₂. - Recently, it has been shown [74,75] [IX] that a proper understanding of the behavior of electron temperature and fluorescence in the Earth's upper atmosphere requires accurate knowledge of both the cross sections and geometric distributions of photoelectrons produced by VUV and EUV solar photoionization of atmospheric gases. Since accurate theoretical determinations are precluded owing to the complexity of the involved processes, the required data could only be obtained experimentally. Under the current contract, considerable progress has been achieved in the experimental determination of the electron energy spectrum due to the VUV and EUV photoionization of several planetary gases including O₂, N₂, CO, and CO₂ as described below.

The general experimental setup involves the use of a suitable electron analyzer coupled to a 1/2-meter Seya monochromator so that the electron energy and geometric distribution can be monitored continuously as a function of the narrow bandpass flux emerging from the exit slit of the monochromator. A preliminary electron energy analyzer was developed, consisting of three concentric cylindrical grids surrounded by a cylindrical collector plate as described in the First Quarterly Progress Report. Although the general performance of this analyzer was encouraging, the observed departure from ideal behavior precluded quantitative measurements involving the fine structure expected for molecular ions such as N₂⁺ and O₂⁺. Accordingly, it was decided that a further instrumental design refinement was required.

On the basis of a systematic design analysis predicated on the performance of the above cylindrical analyzer, a spherical electron energy analyzer was constructed as shown in Figure 2. Although details are not indicated here, most of the major problems encountered in the cylindrical configuration have been eliminated so that acceptable experimental results, with an energy resolution of approximately 3 percent, are now obtained on a routine basis. This resolution is sufficient to identify most of the significant electronic states of a molecule and in some cases even the vibrational states. An important bonus feature of this new configuration is that a 5Å monochromatic bandpass can be employed to produce VUV or EUV photoelectrons within the analyzer. Thus, the combination of high (3 percent) resolution and narrow band (5Å) monochromatic bandpass made it possible for the first time, in any laboratory, to measure the probability of a photon (of given energy) being absorbed into a particular molecular electronic (and even vibrational) state. For example, the raw data obtained directly from the analyzer in the measurement of the individual absorption processes for the calibration test gas, xenon, are shown

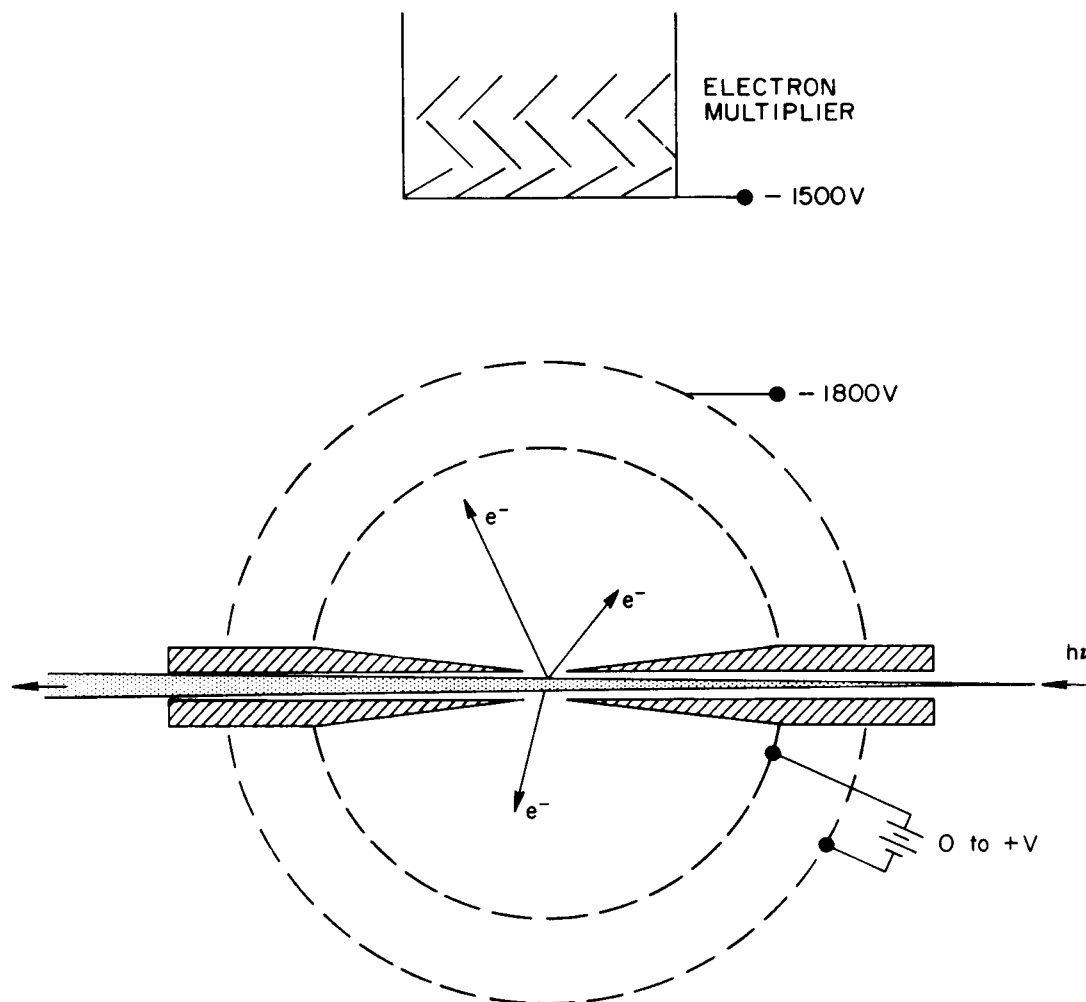


Figure 2. Spherical electron energy analyzer.

in Figure 3. Two steps in the electron current are revealed as the retarding potential is increased. The ratio of the magnitudes of these steps is equivalent to the ratio of the absorption cross sections for the two processes resulting in the ionic $2P_{3/2}$ ground state and $2P_{1/2}$ excited state. The results are presented in Figure 4 as a function of wavelength down to $400\text{\AA}$, where the symbols $\sigma_{1/2}$, $\sigma_{3/2}$, and σ_t refer to the specific absorption cross sections for producing the $2P_{1/2}$, $2P_{3/2}$ states and the total absorption cross section, respectively.

Although the above experiments yielded highly encouraging results, preliminary measurements on selected molecular species indicated that the presence of the Earth ambient magnetic field constituted a limiting experimental factor. Specifically, significant magnetic effects are observed when the electron energy is investigated at wavelengths near the threshold for any given electronic transition. As a result, ambiguous results were obtained initially due to magnetic trapping. To minimize this defect, a Helmholtz coil was employed to produce a uniform field which was then oriented in a direction opposite to the ambient field and adjusted in magnitude to produce a field-free region in the vicinity of the electron analyzer. A view of the Seya monochromator, Helmholtz coil, and analyzer housing is shown in Figure 5 where it can be noted that the coil is inclined perpendicular to the ambient magnetic field. The required bucking field is produced by two coils of radius, a cm, separated by an equivalent distance, and having n turns of wire with a current of I amps flowing through each coil, so that the field at the center of the coil is given by $H = 0.285 \pi I/a$ Gauss. For the design parameters employed herein, $a = 51$ cm and $n = 100$ turns; thus, to produce a field of 0.5 Gauss, a current of 280 mA completely neutralized the contribution of the ambient magnetic field. With this problem solved and a suitable analyzer available, the task of performing quantitative measurements on specific atmospheric gases was then resumed.

Employment of the spherical analyzer results in reduced electron currents so that it was necessary to devise the most efficient photoelectron collection system. For this purpose, a systematic investigation was performed to devise an optimum electron focusing system so that most of the electrons leaving the analyzer could be collected on the finite area of the electron multiplier cathode. The detailed analysis is available in Quarterly Progress Report No. 6.

Although the focusing device may not be optimum, when employed in conjunction with the above over-all experimental configuration, sufficient sensitivity was available for the performance of preliminary measurements at $584\text{\AA}$, for O_2 , N_2 , CO , and CO_2 . Typical results for N_2 and CO_2 are shown in Figures 6 and 7. The improved resolution of these results is demonstrated in Figure 6 where the vibrational structure of the $A^2\Pi_u$ state of the molecular nitrogen ion is indicated. These states are separated by only 0.22 eV which establishes that the present energy resolution of the analyzer is at least 3.7 percent.

Values of the total and individual photoionization cross sections are listed in Table 1 for O_2 , N_2 , CO , and CO_2 at $584\text{\AA}$ where the photoionization yield for these gases is 100 percent. Thus, the tabulated data provide new information on the identification of individual photoionization processes and their associated cross sections for absorption of $584\text{\AA}$ radiation.

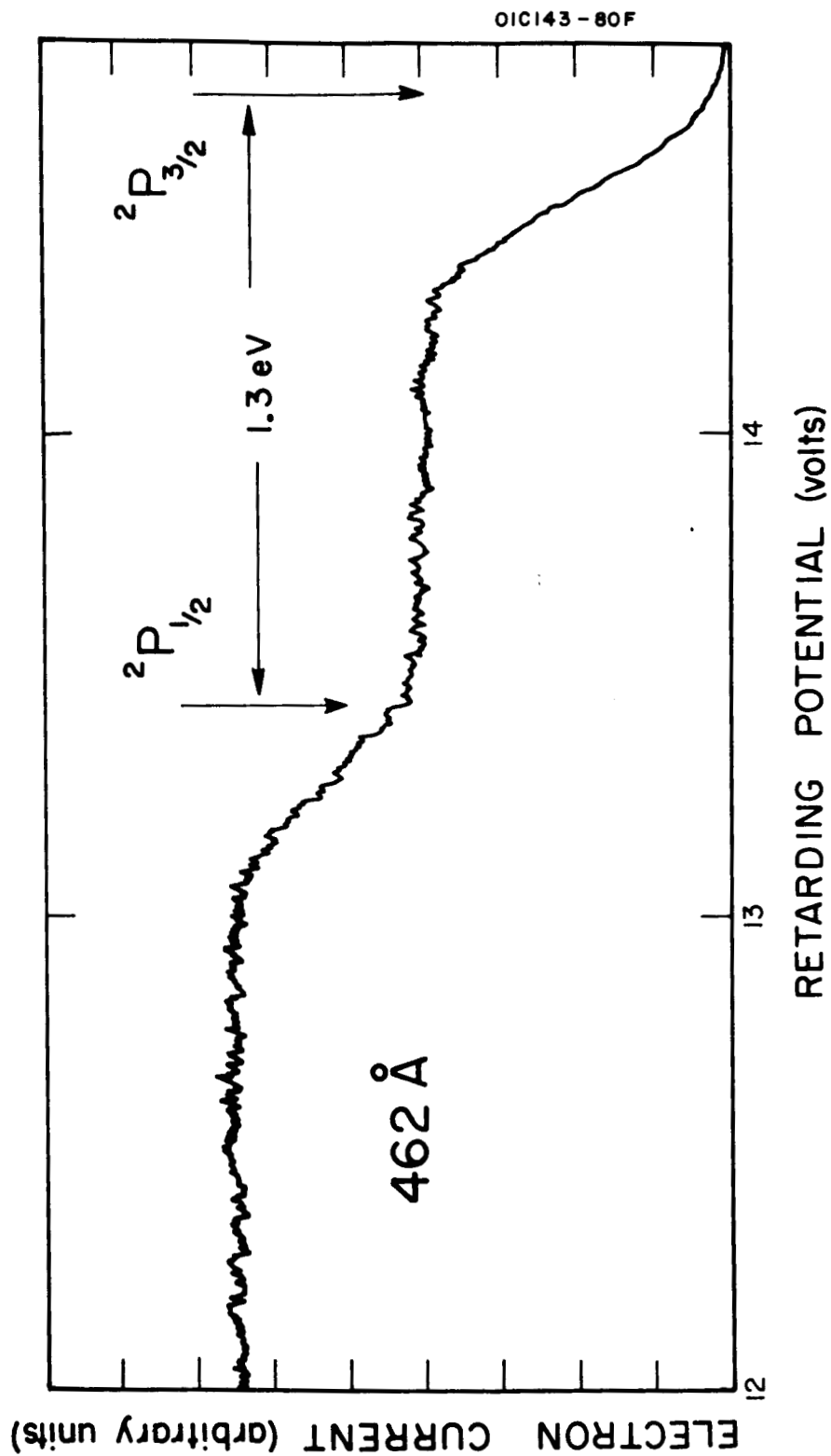


Figure 3. Electron current as a function of retarding potential for electrons produced by the photoionization of xenon at a wavelength of 462 Å.

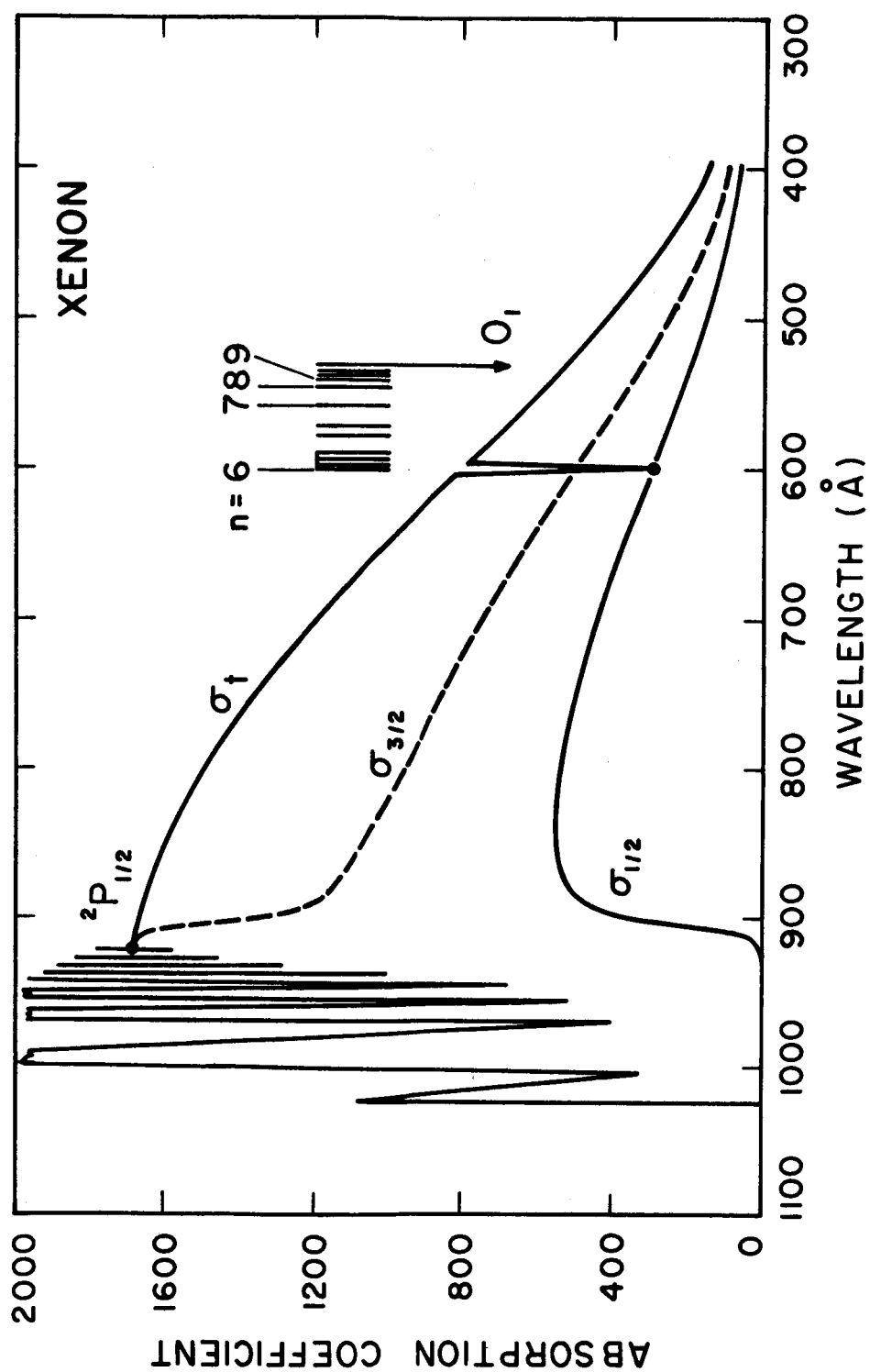


Figure 4. The specific absorption coefficients for xenon. σ_t denotes the total absorption coefficient.

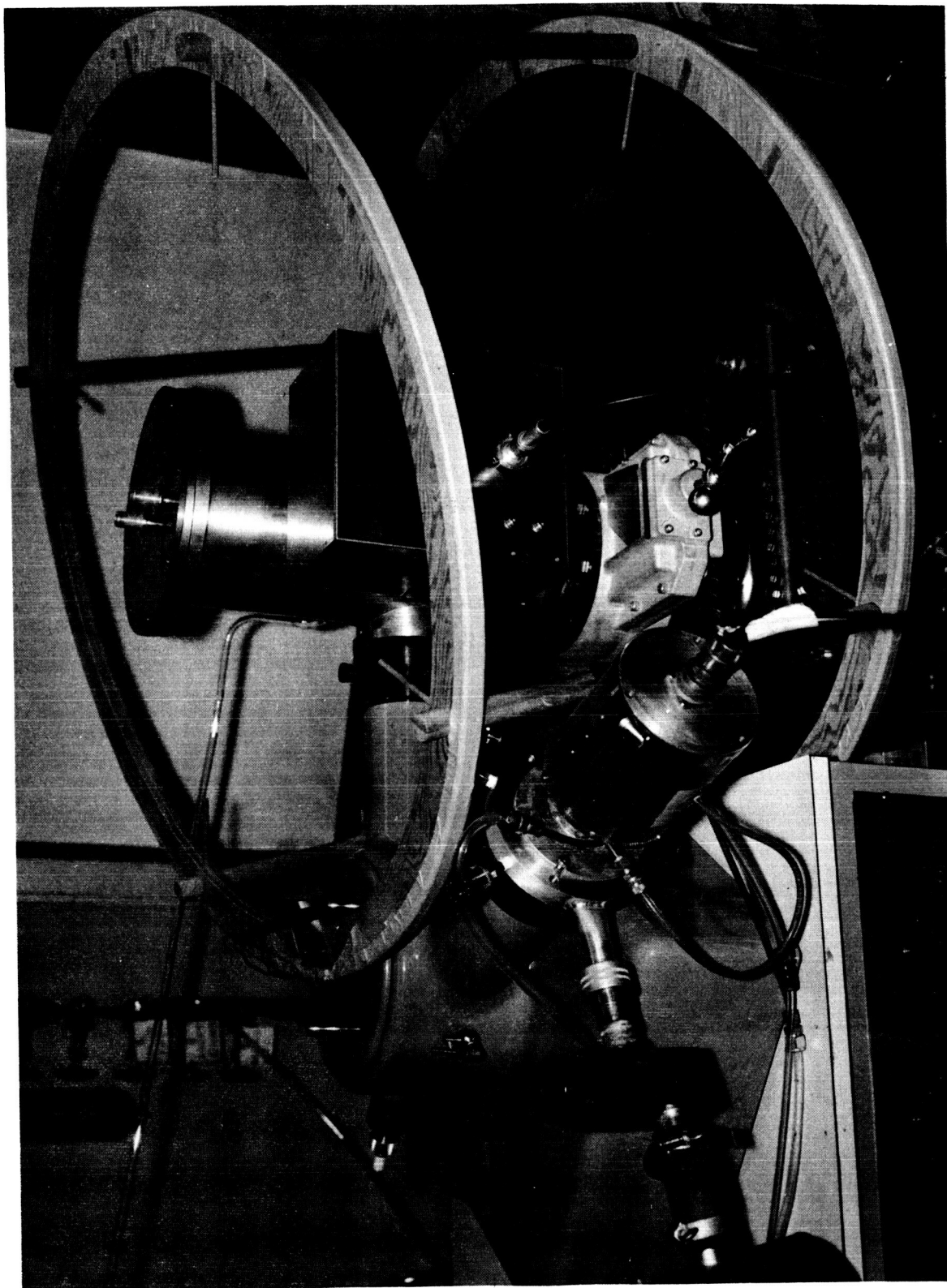


Figure 5. View of Seya monochromator, helmholtz coil, and analyzer housing.

N_2 $\lambda = 584 \text{ \AA}$
 $= 21.21 \text{ eV}$
 IP = 15.58 eV

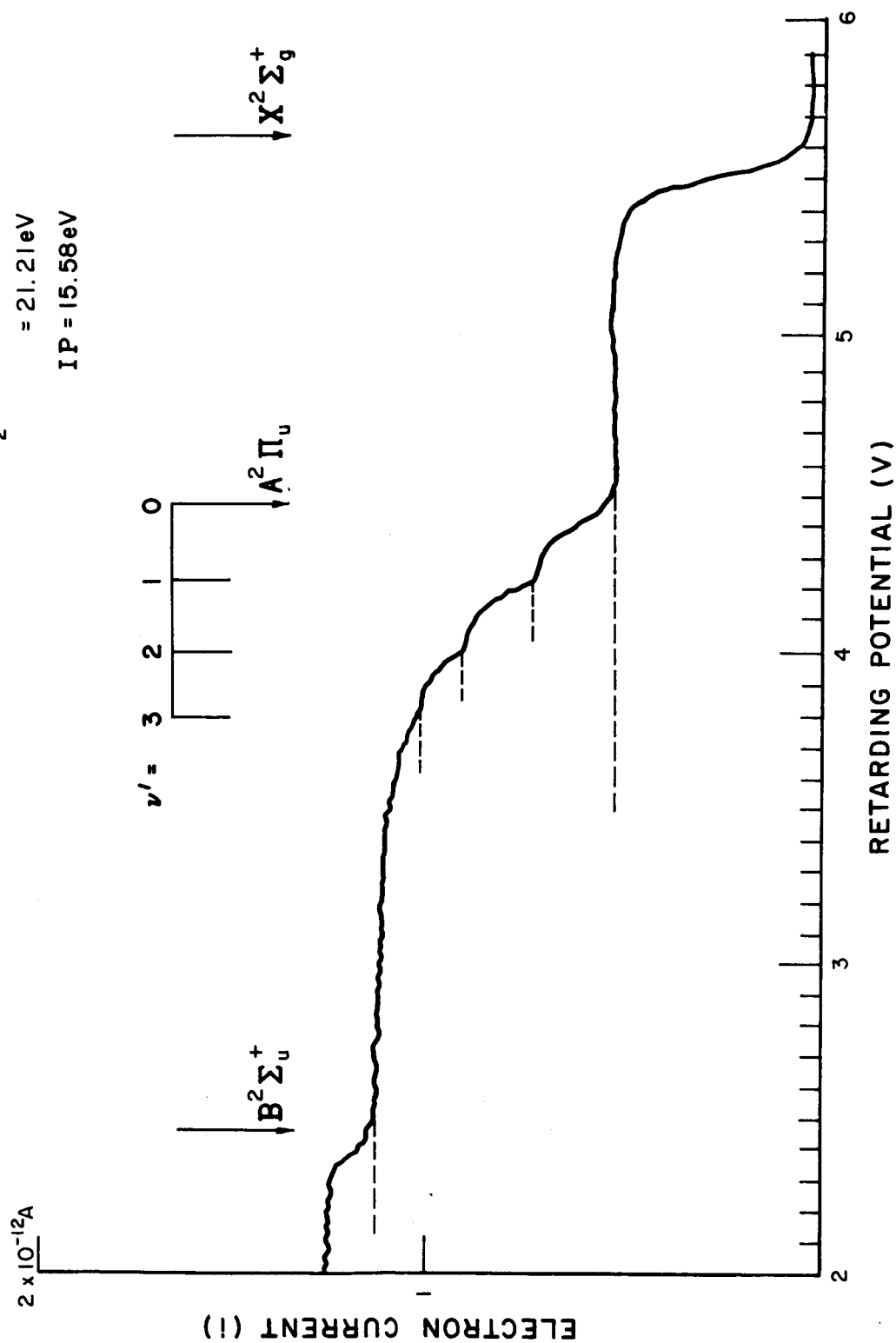


Figure 6. Electron energy groups in N_2 revealing vibrational structure in the $A^2\Pi_u$ state of the ion.

CO₂
 $\lambda = 584 \text{ \AA}$
 $\nu = 21.21 \text{ eV}$
 $IP = 13.77 \text{ eV}$

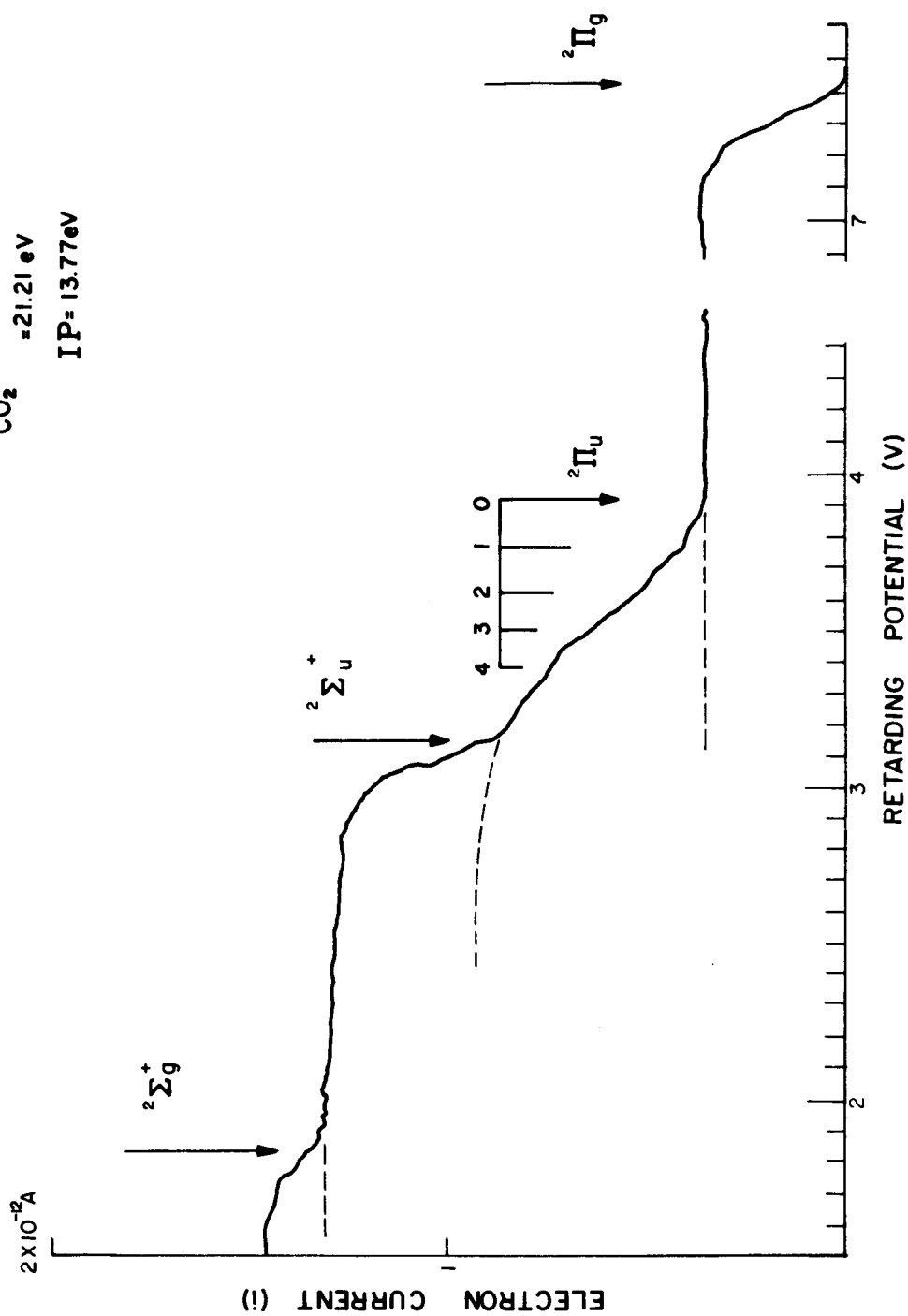


Figure 7. Electron energy groups in CO₂. The electronic state of the ion are clearly visible.

TABLE 1

THE INDIVIDUAL PHOTOIONIZATION CROSS SECTIONS FOR
VARIOUS GASES MEASURED AT 5848 Å

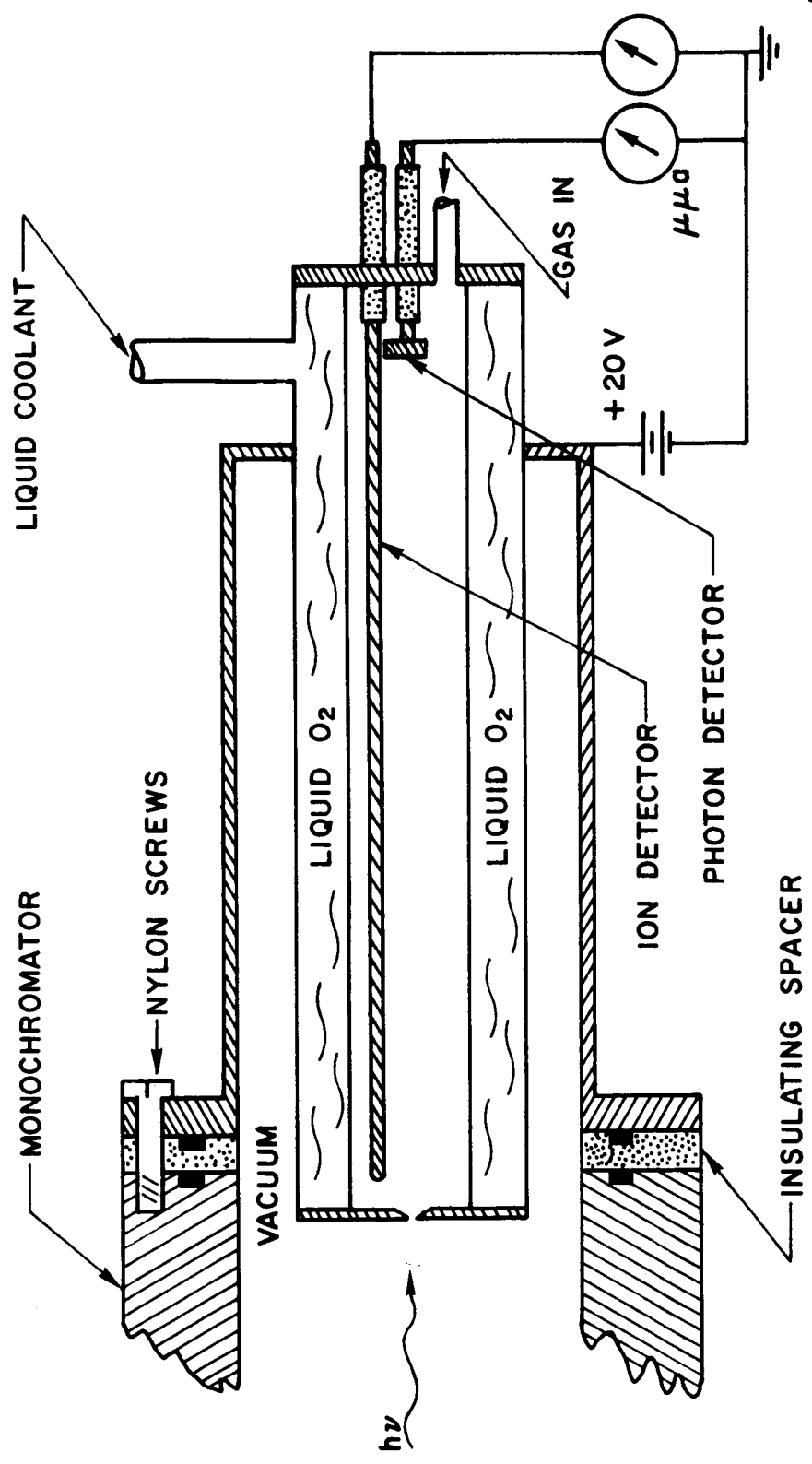
Gas and Transition	Total Photoionization Cross Section	Specific Photoionization Cross Section	Ionization Potential	
	(cm ²)	(cm ²)	(eV)	(Å)
$O_2 \ X^3\Sigma_g^- \rightarrow X^2\Pi_g$	23×10^{-18}	3.7×10^{-18}	12.063	1027.8
$\left. \begin{array}{l} a^4\Pi_u \\ A^2\Pi_g \\ b^4\Sigma_g^- \\ 2\Sigma_g^- \end{array} \right\}$		6.9×10^{-18}	16.107	769.740
			16.812	737.474
		5.5×10^{-18}	18.173	682.217
		6.9×10^{-18}	20.308	610.493
$N_2 \ X^1\Sigma_g \rightarrow X^2\Sigma_g^+$	23×10^{-18}	9.0×10^{-18}	15.580	795.755
$A^2\Pi_u$		11.2×10^{-18}	16.704	742.225
$B^2\Sigma_u^+$		2.8×10^{-18}	18.750	661.231
$CO \ X^1\Sigma^+ \rightarrow X^2\Sigma^+$	22×10^{-18}	6.8×10^{-18}	14.013	884.73
$A^2\Pi$		9.9×10^{-18}	16.536	749.74
$B^2\Sigma^+$		5.3×10^{-18}	19.674	630.15
$CO_2 \ ^1\Sigma_g^+ \rightarrow ^2\Pi_g$	34×10^{-18}	8.8×10^{-18}	13.769	900.414
$^2\Pi_u$		13.6×10^{-18}	17.312	716.158
$^2\Sigma_u^+$		8.8×10^{-18}	18.076	685.871
$^2\Sigma_g^+$		2.7×10^{-18}	19.392	639.345

2. Laboratory Investigation on the Variation of Photoionization Threshold with Temperature. - Many ionospheric physics problems require precise knowledge of both the ionization thresholds of atmospheric gases and their variation with temperature. Under the present contract, the variation of the first ionization potential of O_2 with temperature was investigated experimentally so that the precise threshold value of $1027.8 \pm 0.1 \text{ \AA}$ corresponding to $12.063 \pm 0.001 \text{ eV}$ could be established. The application of the technique described below is clearly applicable to other gases at wavelengths in the vicinity of their ionization potentials. In the present discussion, the variation of ionization threshold with temperature is stressed since a more complete discussion of the basic threshold experiment is available elsewhere [X]. The photoionization onset potential of O_2 at room temperature has been measured previously by Inn [76] and by Watanabe and Marmo [77] who observed ions at wavelengths as long as $1029 \text{ \AA}$ and $1030.8 \text{ \AA}$, respectively. Watanabe and Marmo [77] ascribed an observed long wavelength tail to the presence of excited vibrational states. As a consequence, the true ionization onset potential was established at $1026.5 \pm 1 \text{ \AA}$ corresponding to $12.08 \pm 0.01 \text{ eV}$. Since more sensitive techniques were employed in the present experiments, ionization currents were observed at wavelengths as long as $1046 \text{ \AA}$. With respect to vibrationally-excited O_2 , it has been shown [X] that only about 0.06 percent can reside in the first vibrational state at room temperature. Therefore, by cooling the gas to the temperature of liquid oxygen (-188°C), the role of vibrational states could essentially be eliminated since, at this temperature, the population would be reduced by a factor of 10^9 compared to the condition at room temperature. Thus, if vibrational states indeed contribute significantly, a substantial decrease in current would be observed at this low temperature.

For the above purpose, an appropriate ion chamber was designed and constructed to perform the indicated measurements at two reduced temperatures: dry ice (-80°C) and liquid oxygen (-188°C). A general configuration of the cell is presented in Figure 8. A detailed discussion of the experimental procedures employed herein is available elsewhere [X] so that no further description is required. Since no variation in the photoionization current was observed at either low temperature (that is, -80°C or -188°C), it was concluded that the observed long-wavelength (above threshold) ions were not attributable to the ionization of vibrationally-excited O_2 .

Additional experiments, performed on the variation of ion current with pressure, indicate that the observed ion currents at wavelengths longer than $1027.8 \text{ \AA}$ could be ascribed to collisional processes involving O_2^+ and O_2 to produce O_2^- and O_2^+ . Finally, interpretation of these data resulted in the important conclusion that the dissociation energy of the ion is $6.669 \pm 0.001 \text{ eV}$ and the electron affinity of O_2 is $\geq 0.21 \text{ eV}$. This latter value is especially pertinent to the problems involving the presence and role of O_2^- in the lower ionosphere.

3. Measurement of Absorption and Photoionization Minima in Molecular Spectra of Planetary Gases. - The VUV and EUV solar emission spectrum contains a number of discrete radiation features. As such, when dealing with problems which involve absorption of this radiation, one must utilize absorption and



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Figure 8. Ion chamber suitable for measurements at low temperature.

photoionization data of sufficient spectral resolution to assure that the appropriate cross-section value is employed at the specific wavelength of interest. Unfortunately, in the VUV and EUV spectral regions, the absorption processes display absorption continua superimposed on discrete band features. For this reason, it is highly important to obtain minimum cross sections at given wavelengths in order to establish the magnitude of the continuum contribution. Experimentally, this can be achieved by either (a) measuring the variation of the absorption cross section with pressure for wavelengths between absorption bands or (b) employing sufficiently-high spectral resolution to insure that the measurements are performed at precise wavelengths between the known discrete features.

Under the present contract, the above refinements were incorporated into all the absorption and photoionization measurements reported previously in Section II [IX,XI] so that these data could be employed to assess the continuum in these spectral regions. Specifically, the absorption and photoionization measurements have been performed for $\lambda\lambda$ 550 to 2000^oÅ for O₂, N₂, and H₂ [IX] and for CO₂ and CO [XI]. For these cases, it was concluded that the major absorption intensity was attributable to the underlying continuum while only a minor contribution was due to discrete absorption.

D. Planetary Aeronomy

In this section, the unpublished work performed under the current contract is discussed in five categories: (1) laboratory investigation on the VUV chemiluminescence from selected planetary gases; (2) laboratory measurements of Lyman-alpha absorption of Xe_2 to derive the photon scattering cross section of atomic xenon; (3) laboratory measurements on the VUV fluorescence from planetary gases; (4) theoretical studies on the solar photoionization rates in the Martian ionosphere; and (5) the role of meteoric debris in the Earth atmosphere: simultaneous observation of meteoric debris by employing a rocket-borne mass spectrometric and optical probe.

1. Laboratory Investigation on the VUV Chemiluminescence from Selected Planetary Gases. - Recently, Kaplan et al. [29] have identified absorption bands in the near infrared spectrum of Mars employing Fourier spectroscopic techniques. The bands have been tentatively identified as due to reduced organic gaseous species possibly including sulfur-containing compounds. Additionally, due to photodissociation of the major constituent, CO_2 , other resident species may include O_2 , O_3 , CO , CO_3 , and O . Other minor constituents could include the atomic species H , N , C and a variety of chemically-reactive radicals. The hypothetical presence of such a species ensemble results in a large number of possible highly-reactive chemical processes so that the question of VUV Martian atmospheric chemiluminescence arises. Recently, laboratory studies by Jonathan, Marmo, and Padur [78] resulted in the observation of VUV chemiluminescence (due to the fourth positive band of CO) for the first time in the "cold" chemical reaction between atomic oxygen and acetylene. Since appropriate data did not exist, a laboratory survey experiment was performed in order to evaluate the possibility of VUV chemiluminescence (airglow) in the Martian atmosphere. The results are applicable to either (1) the specification of a definitive in situ VUV Martian airglow experiment or (2) take appropriate accounting of the VUV background airglow contribution in other optical measurement programs.

The preliminary survey work reported herein is spectrally limited to the region $\lambda\lambda$ 1050 to 1340 $\text{\AA}$, since the photoionization photon counter employed in the measurement program was filled with nitric oxide (photoionization threshold 1340 $\text{\AA}$) and utilized a LiF window (transmission cutoff 1050 $\text{\AA}$). The chemiluminescence investigations were performed to examine the reactions between the fifteen molecular species shown in the first column of Table 2 and atomic O , N , and H resulting in a total of forty-five reactions.

A block diagram of the over-all apparatus manifold is shown schematically in Figure 9. A detailed account of the fast-flow system employed and the data reduction technique are described elsewhere [78] so that no additional details are presented here. Atomic oxygen and hydrogen were produced by passing 99:1 mixtures of oxygen-argon and hydrogen-argon, respectively through a discharge while the production of N was achieved by a discharge through pure N_2 . The atomic oxygen content was measured quantitatively by the classical NO_2 titration test whereas the quantitative abundances of atomic hydrogen and atomic nitrogen were estimated on the basis of the discharge characteristics.

TABLE 2

REACTIONS OF ATOMIC OXYGEN WITH VARIOUS COMPOUNDS

Reactant	Observed Counting Rate cps	Flux photons $\text{cm}^{-3} \text{sec}^{-1}$	Photon Production Reaction Rate Constant $\text{cm}^3 \text{sec}^{-1}$
Ammonia	3-4	$2-3 \times 10^5$	10^{-24}
Ethane	10^2	7×10^6	3×10^{-23}
Ethylene	10^3	7×10^7	3×10^{-22}
Allene	$2-3 \times 10^4$	$1-2 \times 10^9$	10^{-20}
Methyl Acetylene	$3-4 \times 10^4$	$2-3 \times 10^9$	10^{-20}
Acetylene	$1-2 \times 10^5$	10^{10}	10^{-19}
Carbon Dioxide	.1	$< 10^4$	$< 10^{-25}$
Carbon Monoxide	.1	$< 10^4$	$< 10^{-25}$
Carbonyl Chloride	.1	$< 10^4$	$< 10^{-25}$
Carbonyl Sulfide	.1	$< 10^4$	$< 10^{-25}$
Hydrogen Sulfide	.1	$< 10^4$	$< 10^{-25}$
Methane	.1	$< 10^4$	$< 10^{-25}$
Nitric Oxide	.1	$< 10^4$	$< 10^{-25}$
Nitrogen Dioxide	.1	$< 10^4$	$< 10^{-25}$
Sulfur Dioxide	.1	$< 10^4$	$< 10^{-25}$
Background	.1	$< 10^4$	$< 10^{-25}$

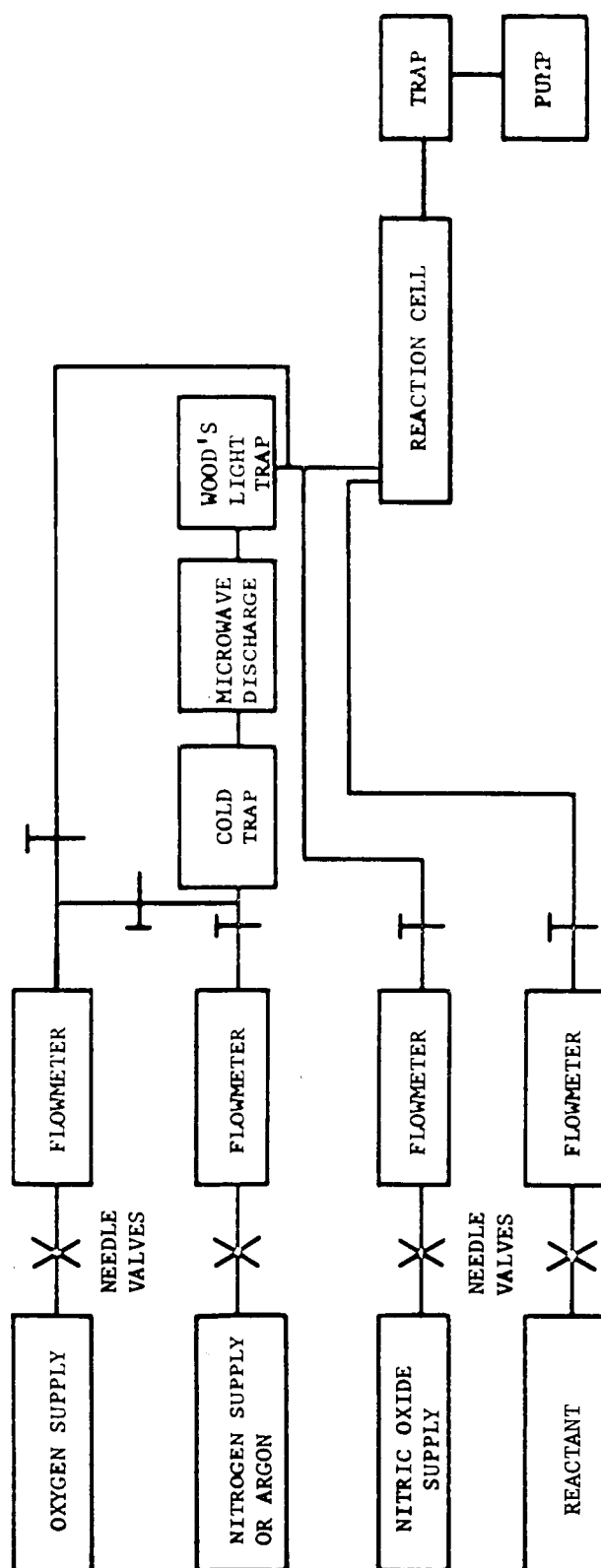


Figure 9. Block diagram of apparatus for observing chemiluminescence.

All the reactions were performed at a total cell pressure of one atmosphere consisting of atomic and molecular species partial pressures of 7 and 18 microns, respectively, and argon as the remainder filler gas. Proper experimental performance was predicted on absolute calibration of the photon counter which was accomplished on the McPherson monochromator utilizing a GCA standard VUV hydrogen discharge. For the particular photon counter employed in this investigation, it was ascertained that an incident flux of 2.6×10^3 photons sec^{-1} resulted in a counting rate of 1 count per second. Additionally, the experimental geometry must also be considered in the determination of the absolute photon flux. As shown in Quarterly Progress Report No. 2, the calibrated counter intercepted only 3.4×10^{-3} of the total radiation flux emitted by the chemiluminescent cell.

Employing the known concentrations of atomic and molecular species and the calibrated VUV photon counter, it was a straightforward task to survey the reactions for radiation in the 1050 to 1340 Å region, as described briefly below.

Negative results were obtained for all reactions involving atomic nitrogen and atomic hydrogen with the molecular species of Table 2. Accordingly, only an upper limit value of 10^{-25} $\text{cm}^3 \text{ sec}^{-1}$ could be ascribed to the corresponding photon production rate constants for these cases. With respect to the atomic oxygen case, positive results were obtained for the six molecular species indicated in Table 2, of which the $\text{O-C}_2\text{H}_2$ reaction resulted in the most intense photon flux. For the other atomic oxygen cases, negative results were obtained so that the 10^{-25} $\text{cm}^3 \text{ sec}^{-1}$ upper limit value was pertinent to these reactions. It should be noted that the convolved product of applicable photon production reaction rate constant and the number densities of the two involved reactants is the rate of production of photons $\text{cm}^{-3} \text{ sec}^{-1}$. As such the planetary VUV airglow can be calculated from the results of this investigation when the appropriate species number densities become available.

2. Laboratory Measurement of Lyman-Alpha Absorption by Xe_2 to Derive the Photon Scattering Cross Section of Atomic Xenon. - Relative photon scattering cross-section measurements at Lyman-alpha have been determined experimentally by Gill and Heddle [79] for Ar, H_2 , N_2 , Xe and Kr. In a subsequent program, Marmo *et al.* [80] employed an improved experimental procedure to measure the low (relative) cross sections of Ne and He. The latter measurement was of particular significance since Chan and Dalgarno [81] calculated an accurate absolute value for He at Lyman-alpha of 3.5×10^{-26} cm^2 which could then be employed to place the experimentally-measured relative values on an absolute basis. For the cases of Ar, H_2 and N_2 , the measured relative scattering cross-section values of Marmo *et al.* [80] compared favorably with those of Gill and Heddle [79]. However, for the cases of Xe and Kr, Marmo *et al.* observed significantly lower values by at least an order of magnitude. Furthermore, comparison of the experimental results for these gases was precluded for several additional reasons. First, the preliminary measurements of Marmo *et al.* indicated the presence of significant attenuation amounting to as much as 76 percent for Xe and

10 percent for Kr for cm^2 -column count values comparable to those employed by Gill and Heddle. However, the latter apparently did not recognize the importance of attenuation since they employed formulae appropriate to a non-absorbing medium. Further, Marmo *et al.* noted that the observed attenuation cross section did not obey Beer's law; i.e., it was not constant with pressure. In fact, a linear pressure dependence was observed which suggested: (a) that the attenuation could not be attributed to impurities and (b) the possibility of the formation of the diatomics; i.e., Xe_2 and Kr_2 .

On this basis, a series of experiments were devised and performed to determine the photon scattering cross sections at Lyman-alpha for atomic Xe and Kr by measuring the variations in attenuation with temperature and pressure due to the presence of the diatomic species and extrapolating these data to zero pressure. Additionally, it was possible to derive the heat of dissociation from the temperature dependence experiment as described briefly below.

In the present investigation, considerable experimental improvement was achieved by utilizing monochromatic radiation which was made available through the use of a 2-meter McPherson ultraviolet spectrometer and a hydrogen discharge light source. This improvement eliminated a number of problems associated with the use of undispersed radiation [79,80]. An additional experimental capability was achieved by employing an attenuation cell which was operable over a broad temperature range. Other pertinent experimental details have been described previously [80] and are not repeated here.

In the basic experimental procedure, the unattenuated intensity (I_0) was recorded and the transmitted intensity (I) was measured as a function of pressure. These data were utilized to calculate the attenuation cross section [$\sigma(\text{cm}^2)$] using the expression

$$\sigma = \frac{1}{nL} \log_e \frac{I_0}{I} \quad (1)$$

where n is the number density (cm^{-3}) reduced to STP and L is the pathlength in centimeters. As noted previously, the σ -values were observed to increase linearly with pressure as shown in Figures 10 and 11 for xenon and krypton, respectively. In addition, the temperature dependence of the measured attenuation cross section for Xe was also obtained as shown in Figure 12. The corresponding temperature dependence results for the case of Kr were experimentally imperceptible using the present apparatus.

The formation of the diatomic species, Xe_2 and Kr_2 , has been deduced from the following arguments. When the chemical process



prevails, it can be shown that

$$I = I_0 \exp [-(n_1\sigma_1 + Kn_1^2\sigma_2)L] \quad (2)$$

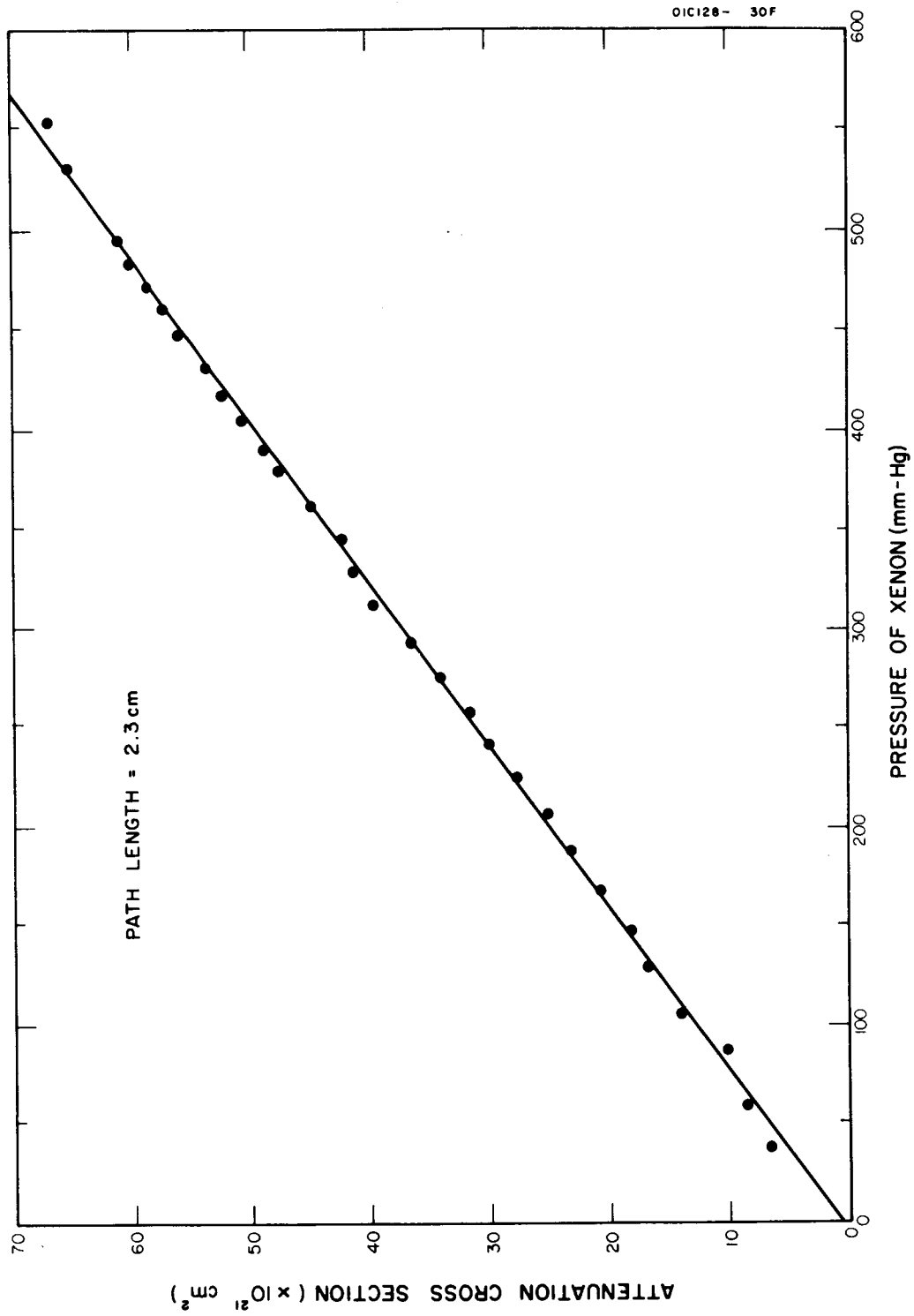


Figure 10. Pressure dependence of the attenuation cross section of xenon at 1215.7 Å.

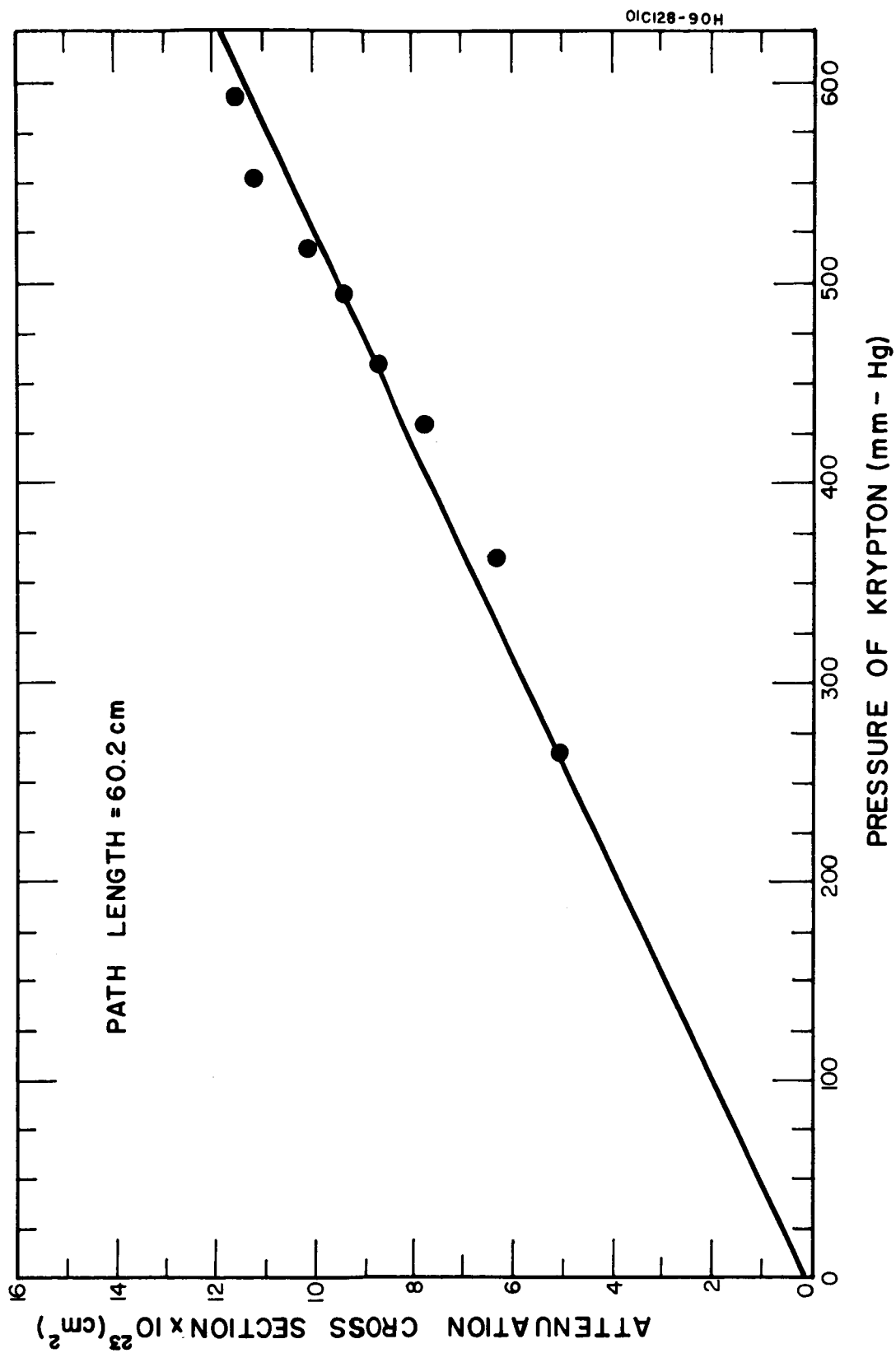


Figure 11. Pressure dependence of attenuation cross section of krypton at 1215.7 Å.

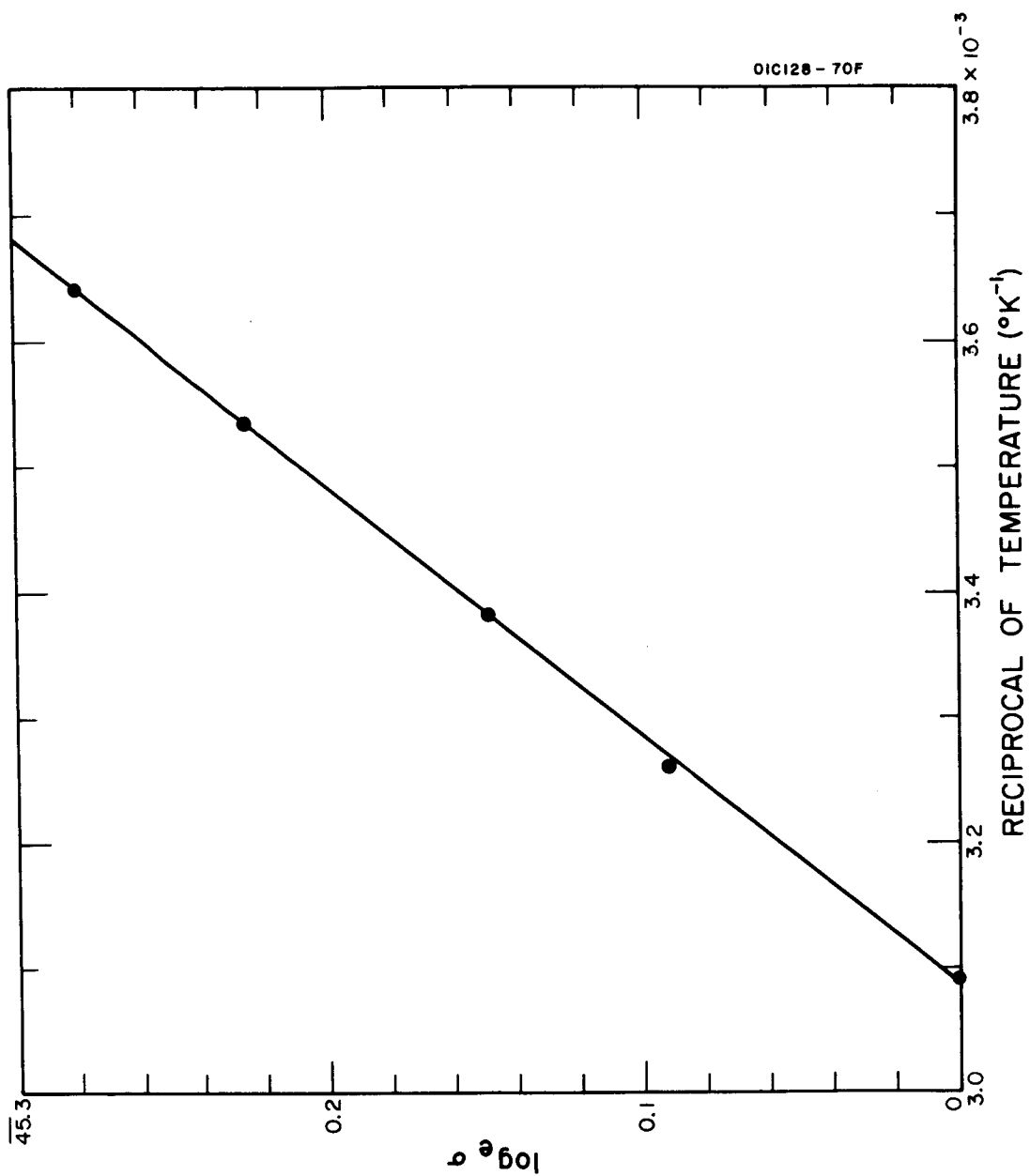


Figure 12. Temperature dependence of attenuation cross-section of xenon at 1215.7Å.

where

- σ_1 = scattering cross section for Xe
- σ_2 = absorption cross section for Xe_2
- K = equilibrium constant
- n_1 = number density of Xe atoms

For the present measurements, $n_1 \approx n$ where n = total number density of $\text{Xe}_2 + \text{Xe}_1$ so that

$$\sigma = \frac{1}{nL} \log_e \frac{I_0}{I} = \sigma_1 + K\sigma_2 n \quad (3)$$

From the above expression, the measured cross section (σ) would be expected to vary linearly with pressure when relatively-strong attenuating diatomic species are present in the experimental mixture. Additionally, the zero intercept yields the absolute value of the scattering cross section for the atom at that wavelength. From the data shown in Figures 10 and 11, respectively, the following σ_1 -values are obtained: $\sigma_1 (\text{Xe}) = 5 \times 10^{-22} \text{ cm}^2$ and $\sigma_1 (\text{Kr}) = 1 \times 10^{-24} \text{ cm}^2$.

The temperature dependence results of Figure 12 were obtained by measuring the attenuation in the Xe-filled cell at a constant pressure of 215 mm Hg and at temperatures of 25°C, 36°C, 45°C and 56°C. The observed inverse variation of the measured attenuation coefficient with temperature can be ascribed to the presence and role of Xe_2 molecules as described below. The equilibrium constant of Equation (2) is related to the temperature (T) and the heat of reaction (ΔH) by $K = A \exp [\Delta H/RT]$ where A is essentially constant over the relatively-small temperature range under investigation. From Equation (3) it follows that

$$\sigma = \sigma_1 + \sigma_2 n A \exp \left[\frac{\Delta H}{RT} \right] \quad (4)$$

Additionally, since σ_1 is $\ll \sigma$, one may write

$$\log_e \sigma = \frac{\Delta H}{RT} + \text{constant}$$

The results of Figure 12 show that the measured $\log_e \sigma$ -values vary inversely with temperature. Additionally, the slope of the line on the semi-log plot is equal to $\Delta H/R$ so that an estimated value of 0.029 eV was obtained for ΔH , the heat of dissociation of the Xe_2 molecule as measured from the first vibrational state. Recently, Paul *et al.* [82] measured the isotopic thermal diffusion factor for xenon to derive an ϵ -value of 0.022 eV which represents the depth of the potential well in Xe_2 at the equilibrium internuclear distance. Although the ϵ -value does not account for the zero-point energy involved in the first vibrational state, it does offer some basis of comparison with the ΔH -value derived in the present experiment.

Since the zero-point energy is low, its consideration would result in a slightly larger discrepancy between the two independent experimental determinations. On the other hand in view of the relatively-large error sources involved in each investigation, better agreement cannot be justifiably expected. Specifically, with respect to the present experiment, a more precise ΔH -value could be obtained by extending the investigation of a wider temperature range.

The experimental techniques described above are clearly applicable to other planetary gaseous species where the tendency for dimerization exists i.e., the other rare gases and O_2 , NO , H_2O , N_2^+ , etc. In this regard, it is interesting to note that the measured absorption cross section of O_2 at $1215.7\text{\AA}$ was observed [83] to decrease linearly with decreasing pressure. This anomolous behavior could not be ascribed to lack of resolution and no satisfactory explanation has been offered to date. In any event, an empirical value of the absorption cross section was derived by extrapolating these data to zero pressure. Clearly, then, a test for the presence of O_4 would be to measure the cross-section variation with temperature. Similar experiments could also be performed for O_2 in specific regions between 2000 and $3000\text{\AA}$ where weak absorption has been observed experimentally at a pressure of about one atmosphere.

3. Laboratory Measurements on the VUV Fluorescence from Planetary Gases. — Fluorescence in the VUV may assume a number of different forms predicated on the energetic source function and the gaseous constituent under consideration. In the present laboratory investigation, two types of fluorescence were studied: (a) fluorescence from molecular oxygen excited by Lyman-alpha radiation and (b) fluorescence from molecular nitrogen excited by electron bombardment.

a. Fluorescence from molecular oxygen excited by Lyman-alpha radiation. — Under the current program, a brief investigation was performed to evaluate one of the many alternative schemes which have been proposed to explain the oxygen airglow in the Earth's atmosphere. Specifically, an attempt was made to produce the Hertzberg emissions by measuring fluorescence from molecular oxygen excited by Lyman-alpha radiation. Since negative and inconclusive results were obtained, the experiment is described only briefly below.

The GCA VUV monochromator was coupled to an intense hydrogen light source to yield about 10^9 photons sec^{-1} at Lyman-alpha ($1215.7\text{\AA}$) at the exit slit where an O_2 gas-filled cell with LiF windows was attached. An appropriate photomultiplier detector was employed to detect broad-band fluorescence emitted from the O_2 -filled cell when excited by monochromatic Lyman-alpha radiation. A relatively-broad pressure range was investigated between a few millimeters to one atmosphere. Quantitative calibration of the system indicated that a fluorescence photon flux as low as 10^5 photons sec^{-1} could be detected. In spite of this high overall system sensitivity, negative results, that is no observable fluorescence, were obtained at all pressures. The experimental data have established an upper limit value on the fluorescence of O_2 in the upper atmosphere excited by solar Lyman-alpha radiation. This appears to be incompatible with in situ observations so that another mechanism is required to explain the observed Hertzberg emissions.

b. Fluorescence from molecular nitrogen excited by electron bombardment. — The VUV fluorescence of atmospheric gases can be examined experimentally using the well-known technique of afterglow generation by microwave discharge. Under the current program, a laboratory investigation yielded results which have been interpreted in terms of a detailed mechanism due to Bayes and Kistiakowsky [84, 85]. On this basis, self-quenching cross sections of about 10^{-18} cm^2 were derived for the quenching of the Lyman-Birge-Hopfield (LBH) VUV bands. Since the value is directly applicable to the study of atmospheric aurora, detailed discussions of the experimental results and data interpretation are presented below.

The various characteristics of the Lewis-Rayleigh nitrogen afterglow have been reviewed extensively [86-88]. Previously, only first positive bands ($\text{B}^3\Pi_g - \text{A}^3\Sigma_u^+$) were observed in its spectrum. An anomalous intensity distribution has been reported for these bands indicating maximum excitation of the 12th, 11th, and 6th vibrational levels of the $\text{B}^3\Pi_g$ state. A new band system ($\text{y}^3\Sigma_u^- - \text{B}^3\Pi_g$) was subsequently found [89-91] in the near infrared region of the spectrum. In contrast to the above two visible and infrared band systems Tanaka et al. [92] have reported the presence of the weak LBH system ($\text{a}^1\Pi_g - \text{x}^1\Sigma_g^+$) in the VUV region.

Berkowitz *et al.* [93] have shown that the recombination of $N(^4S)$ atoms is responsible for the characteristic first positive bands emitted in the Lewis-Rayleigh afterglow of nitrogen and postulated further that $5\Sigma_g^+$ nitrogen molecules are in equilibrium with nitrogen atoms. On the basis of extensive observations of the bands of $B^3\Pi_g - A^3\Sigma_u^+$ and $y^3\Sigma_u^- - B^3\Pi_g$, Bayes and Kistiakowsky [84, 85] concluded that the resultant emissions are mainly due to the collision-induced transition of nitrogen molecules from the $5\Sigma_g^+$ level to the $B^3\Pi_g$ and $y^3\Sigma_u^-$ states. Although direct kinetic evidence for the elucidation of the excitation mechanism of the LBH system is not available, the above mechanism has also been assumed [85-92] for the LBH excitation based on the observed predissociation in the $a^1\Pi_g$ state of N_2 . The results of the present investigation of the VUV emission support the above assumption and also provide information regarding self-quenching of the N_2 $a^1\Pi_g$ state which can be used to determine the optimum conditions for excitation of the LBH bands.

The visible and VUV afterglow emission intensities were measured simultaneously under various conditions. The low pressure (below 1 mm Hg) nitrogen afterglow was produced in the conventional fast flow system depicted in Figure 13. Control of the flow was maintained by a needle valve and measured by a capillary flow meter, while the pressure in the afterglow tube was monitored by a McLeod gauge.

The visible radiation intensity (predominantly due to the first positive bands of N_2) was measured by a 1P28 photomultiplier tube whose output was fed to a micro-microammeter. The VUV radiation (due to the LBH system [92]) was observed on an oscilloscope fed by a Geiger counter VUV radiation detector similar to that employed by Chubb *et al.* [94]. The counter was filled with 10 mm Hg of nitric oxide, and a lithium fluoride window was employed so that the useful operating spectral range included wavelengths between 1050 and 1340 Å. When operating between 570 and 590V, the response was observed to be linear to an accuracy of about 1 percent over the range between 100 and 3000 counts per second.

The nitrogen flow rate was adjusted to obtain a suitable pressure in the afterglow tube whereupon the microwave discharge was initiated which resulted in the characteristic straw-yellow afterglow. After the system reached equilibrium, the intensities of the visible and VUV emissions were measured. The procedure was subsequently repeated so that experimental observations could be obtained as a function of pressure. A plot of the observed visible intensity against the VUV intensity is shown in Figure 14 where a departure from linearity is observed at high intensity. The ratio of the visible to VUV intensities is illustrated in Figure 15 as a function of pressure. It is apparent that the ratio is linear at pressures below about 250 microns while at higher pressures, the relationship is clearly nonlinear. The reasons for this behavior are discussed in greater detail subsequently.

The detailed excitation mechanism of the various spectral features in the emission of Lewis-Rayleigh afterglow of nitrogen has been presented by Bayes and Kistiakowsky [85] as follows:

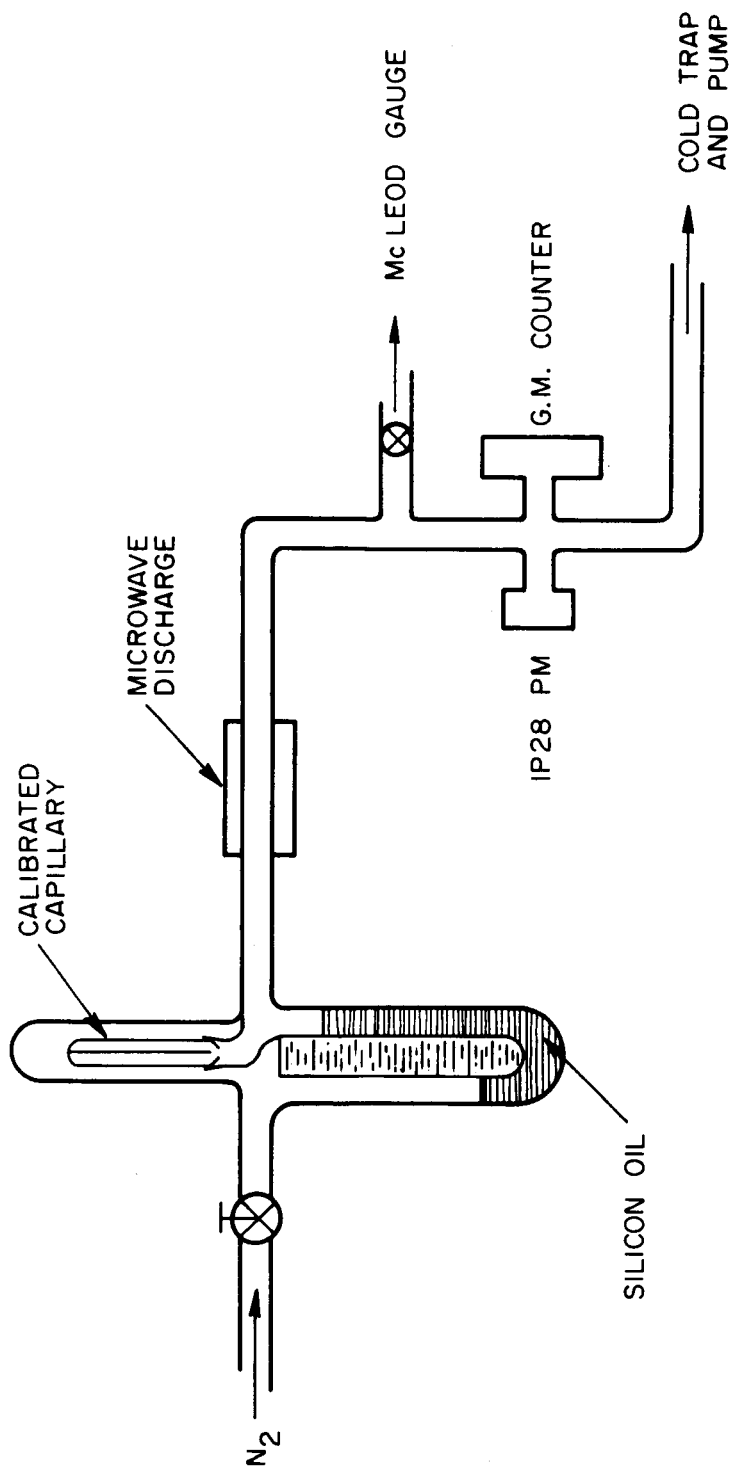


Figure 13. Conventional fast flow system for production of low pressure nitrogen afterglow.

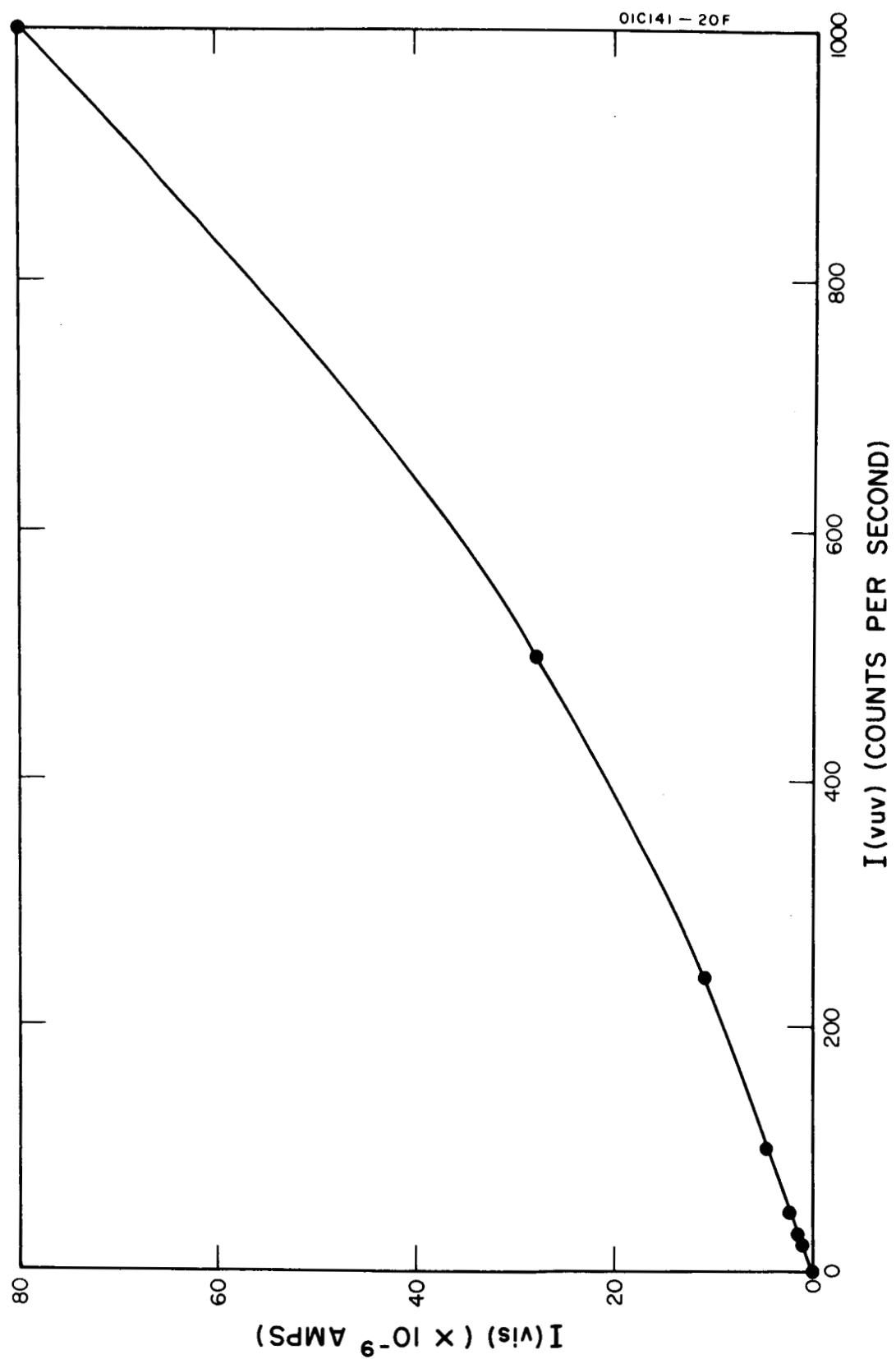


Figure 14. Observed visible intensity against VUV intensity.

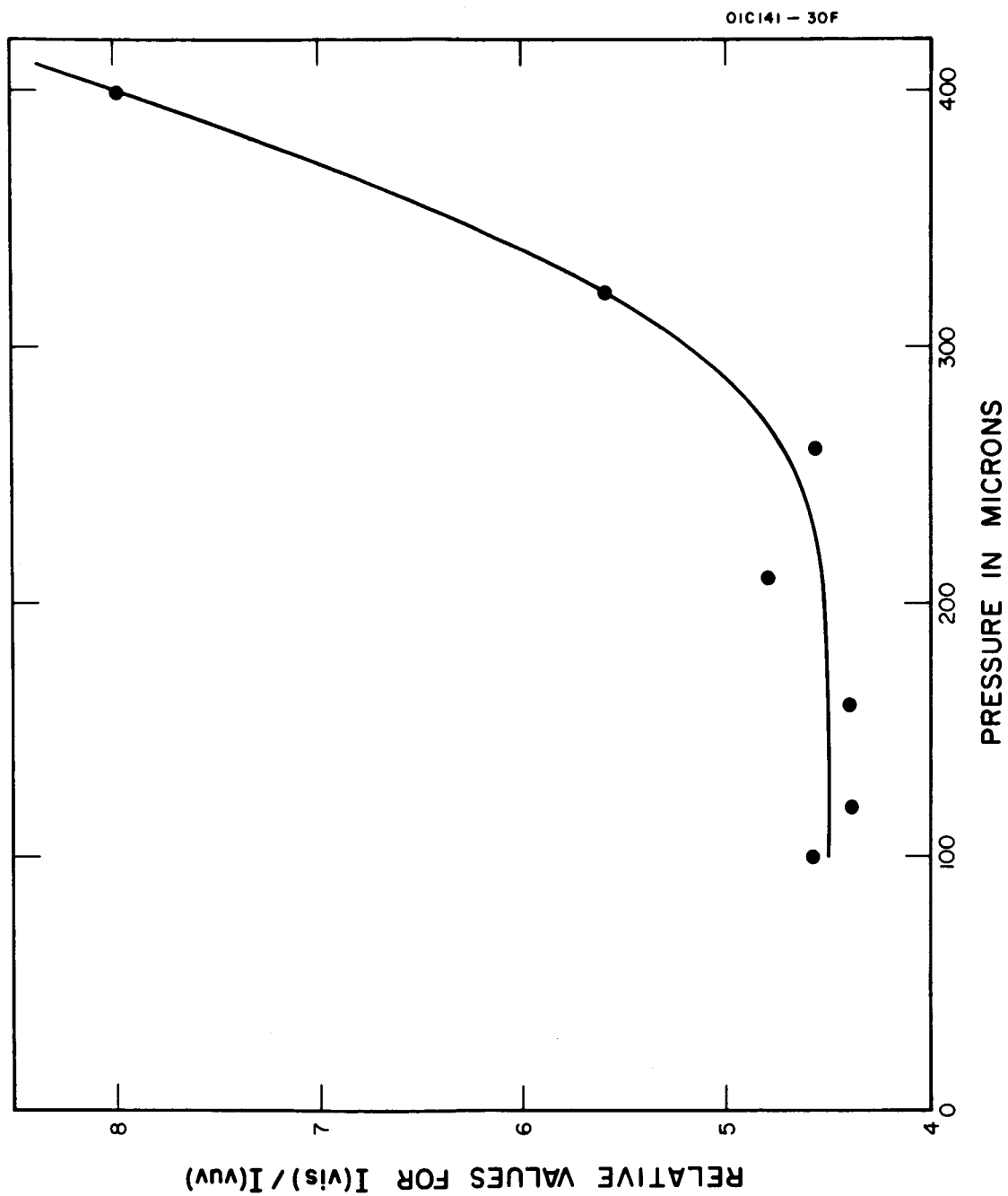
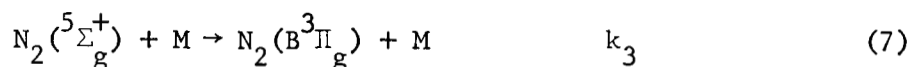
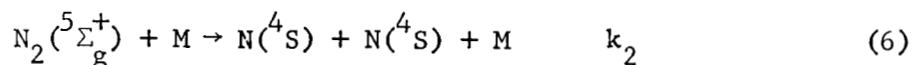
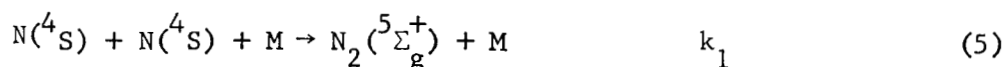


Figure 15. Ratio of visible to VUV intensities as a function of pressure.



where the k -values are rate coefficients and the A -values are radiative transition probabilities. The emitted radiation from (13) lies in the far infrared so that it does not contribute directly to the observed I(vis). On the other hand, (13) can act as a source function [85] for (11) so that it can contribute indirectly to the observed spectrum of the nitrogen afterglow.

The $N_2(^5\Sigma_g^+)$ molecules are assumed to be in equilibrium with nitrogen atoms covered by reaction (1) and reactions (6-10) so that

$$k_1 [N]^2 [M] = [N_2(^5\Sigma_g^+)] [k_2 + k_3 + k_4 + k_5 + k_6] [M]$$

where $[M]$, $[N]$ and $[N_2(^5\Sigma_g^+)]$ indicate the concentrations of the respective species. In the present case, the N_2 molecule acts as a third body, M . The equilibrium concentration of the $[N_2(^5\Sigma_g^+)]$ molecule is, therefore, given by

$$[N_2(^5\Sigma_g^+)] = \frac{k_1}{k_2 + k_3 + k_4 + k_5 + k_6} [N]^2 \quad (15)$$

The formation of N_2 in the $B^3\Pi_g$, $y^3\Sigma_u^-$ and $3\Delta_u$ states is responsible for the long wavelength end of the Lewis-Rayleigh afterglow spectrum whose observed emission intensity is given by

$$I(\text{vis}) = K_1 [N_2(^5\Sigma_g^+)] [N_2] (k_3 + k_4 + k_5) \quad (16)$$

where K_1 is a constant which depends on the units, sensitivity, and geometry of the photometric system. Substituting the value of $[N_2(^5\Sigma_g^+)]$ from Equation (15) into Equation (16)

$$I(\text{vis}) = \frac{K_1 k_1 [N]^2 [N_2] (k_3 + k_4 + k_5)}{k_2 + k_3 + k_4 + k_5 + k_6} \quad (17)$$

which shows that the visible intensity is directly proportional to the number density, $[N_2]$ and the square of the nitrogen atom concentration $[N]$. Rayleigh [95] observed a linear pressure dependence of the visible emission in the 10^{-2} to 10^{-1} mm Hg pressure region while Kash [96] obtained similar results between 4 and 50 mm Hg pressure. Additionally Berkowitz *et al.* [93] have verified that the visible intensity is directly proportional to the square of the nitrogen atom concentration.

It can also be shown that the VUV intensity is given by

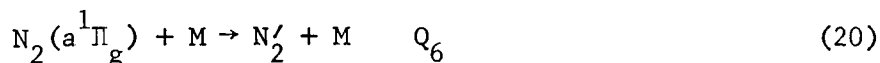
$$I(\text{vuv}) = K_2 \frac{k_1 k_6 [N]^2 [N_2]}{k_2 + k_3 + k_4 + k_5 + k_6} \quad (18)$$

where K_2 is a constant similar to K_1 . According to the above mechanism, the ratio of visible to vuv intensities can be expressed as

$$\frac{I(\text{vis})}{I(\text{vuv})} = \frac{K_1}{K_2} \left(\frac{k_3 + k_4 + k_5}{k_6} \right) \quad (19)$$

which indicates a linear relationship. As discussed previously, the relationship of the $I(\text{vis})/I(\text{vuv})$ ratio with pressure is observed to be non-linear above about 250 microns as shown in Figure 15. At higher pressures the ratio is observed to increase, indicating a decreased relative intensity of vuv radiation which can be explained by the following argument. The upper electronic states ($B^3\Pi_g$, $y^3\Sigma_u^-$, and $3\Delta_u$) responsible for the visible emission are non-metastable with a lifetime of $\leq 10^{-6}$ sec, while the upper electronic state ($a^1\Pi_g$) involved in the vuv emission is a metastable with a lifetime of about $1.7 \pm 0.3 \times 10^{-4}$ sec [97]. As such, the $a^1\Pi_g$ state is more readily quenched than the upper states

responsible for the visible emission. Incorporation of the quenching effect of the $a^1\Pi_g$ state is accomplished by the addition of the following process:



where Q_6 is the quenching rate coefficient and M represents the third body (in this case, the N_2 molecule). The intensity of the vuv radiation can now be expressed as

$$I(\text{vuv}) = K_2 \frac{k_1 k_6 [N]^2 [M]}{k_2 + k_3 + k_4 + k_5 + k_6} \left(\frac{A_6}{A_6 + Q_6} \right) \quad (21)$$

and the intensity ratio as

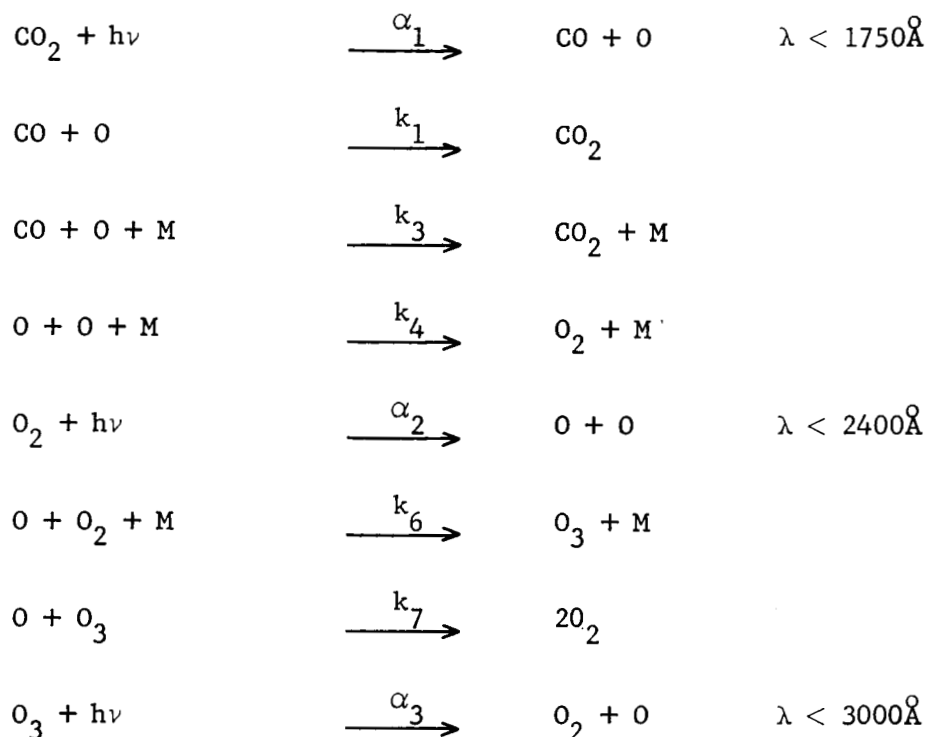
$$\frac{I(\text{vis})}{I(\text{vuv})} = \frac{K_1}{K_2} \left(\frac{k_3 + k_4 + k_5}{k_6} \right) \frac{A_6 + Q_6}{A_6} \quad (22)$$

This indicates that at low pressures where A_6 is $\gg Q_6$, the intensity ratio should be independent of pressure as specified by Equation (19) while at higher pressures, the ratio should increase linearly with pressure as specified by Equation (22). Application to the data results in an experimental average value for Q_6 of about $2 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ which corresponds to a quenching cross-section value of only about 10^{-18} cm^2 . This low quenching value is directly applicable to theoretical considerations on Earth airglow and aurora problems.

4. Theoretical Studies on the Solar Photoionization Rates in the Martian Ionosphere. — The Mariner IV occultation experiment has provided new ambient atmospheric parametric data including surface pressure, surface temperature, and atmospheric refractivity. Specifically, the measurements indicate that the atmosphere consists essentially of carbon dioxide with a local number density of about $1.9 \times 10^{17} \text{ molecules cm}^{-3}$ at a temperature of $180 \pm 20^\circ\text{K}$ at the reference level probed which was close to the Martian surface. In addition, no significant change in scale height was observed throughout the lower part of the atmosphere, indicating that the temperature remains essentially constant at least in this altitude regime. The measurements have also provided valuable information concerning the ionospheric peak electron density and altitude. In the light of these new data, it was propitious to modify a previous model atmosphere (see Quarterly Progress Report No. 1) and to derive the solar photoionization rates as a function of altitude for the several ionospheric constituents. Since the experimental temperature data permitted temperatures of 200, 180 and 160°K , these three cases were considered in the present investigation. First, new calculations were performed to determine the neutral particle distribution as established by the solar photodecomposition of CO_2 in the Martian atmosphere. These models were then employed to calculate the corresponding

solar photoionization rates as a function of altitude for the individual constituents as well as the total rate.

For the purpose of establishing the neutral particle distribution, the following chemical reactions were considered:



The values of these reaction rate constants for these reactions and other pertinent parameters employed in this investigation are presented in Table 3. Three different isothermal atmospheres are assumed corresponding to temperatures of 200, 180 and 160°K. It is further assumed that mixing prevails up to the dissociation region and that diffusive equilibrium predominates at higher altitudes where photodissociation is essentially complete. A previously-employed computer program discussed in detail QPR No. 1 was applied to the present investigation. The neutral particle distribution results, shown in Figures 16, 17, and 18, demonstrate that the temperature has a significant influence upon the peak altitude of dissociation.

These model results were then employed to calculate the corresponding solar photoionization rates as a function of altitude for the individual constituents as well as the total rate. For this purpose, a numerical summation technique was applied. The photoionization rate $P(Z)$ (ion-pairs/cm³ sec) at a given altitude was computed from the expression

$$P(Z) = \sum_{\lambda} I(\lambda, Z) \left[\sum \sigma_i(\lambda) n_i(Z) \right]$$

TABLE 3
PERTINENT PARAMETERS AND REACTION RATE CONSTANTS

Parameter	Reference
Surface temperature	[98]
Case I - $T = 200^{\circ}\text{K}$	
Case II - $T = 180^{\circ}\text{K}$	
Case III - $T = 160^{\circ}\text{K}$	
Surface number density - 1.9×10^{17} molecule/cm ³	[98]
Solar flux at the top of the Earth's atmosphere in 50Å intervals:	
Wavelength regions 3000 to 2550Å	[99]
2500 to 1550Å	[100]
1550 to 50Å	[101]
Average dilution factor to account for the diminution of solar flux in the vicinity of Mars, $\mu = 0.444$	
Absorption cross sections	
Carbon dioxide	
Oxygen	[102]
Ozone	
Photoionization cross sections	
Carbon monoxide	[103]
Atomic oxygen	[104]
Carbon dioxide	[105]
	[103]
	[106]
Photodissociation yield factors for oxygen, ozone, and carbon dioxide and photoionization yield factors for carbon monoxide, atomic oxygen, and carbon dioxide are assumed to be unity	
$k_2 = 1.6 \times 10^{-14} \exp\left(-\frac{4000}{RT}\right) \text{ cm}^3/\text{sec}$	[107]
$k_3 = 0$	
$k_4 = 2.8 \times 10^{-33} \text{ cm}^6/\text{sec}$	[108]
$k_6 = 5 \times 10^{-35} \exp\left(\frac{1000}{RT}\right) \text{ cm}^6/\text{sec}$	[109,110]
$k_7 = 5 \times 10^{-11} \exp\left(-\frac{5600}{RT}\right) \text{ cm}^3/\text{sec}$	[109,110]

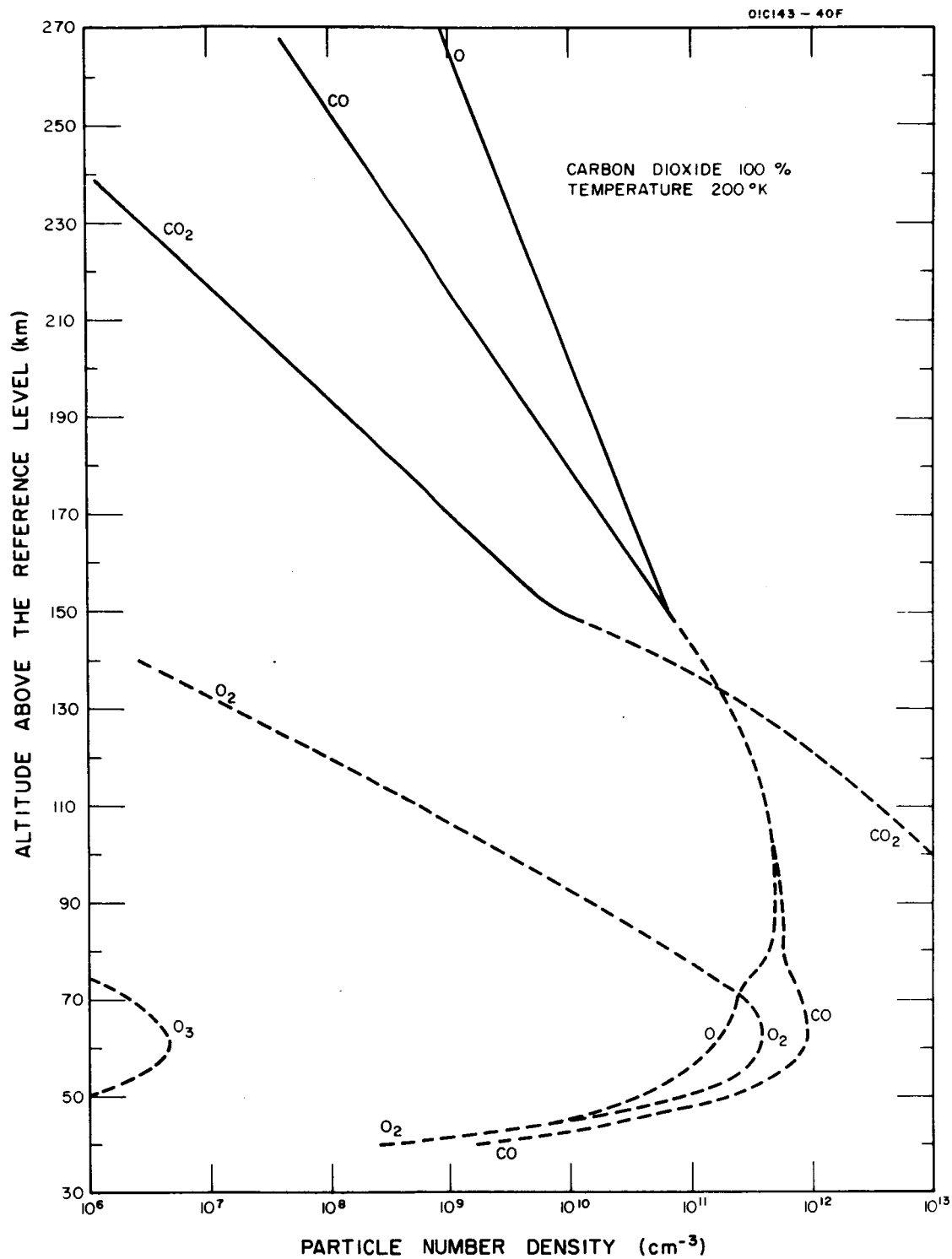


Figure 16. Neutral particle model atmosphere of Mars. Dotted lines are due to photochemical processes and the solid lines indicate the region of diffusion.

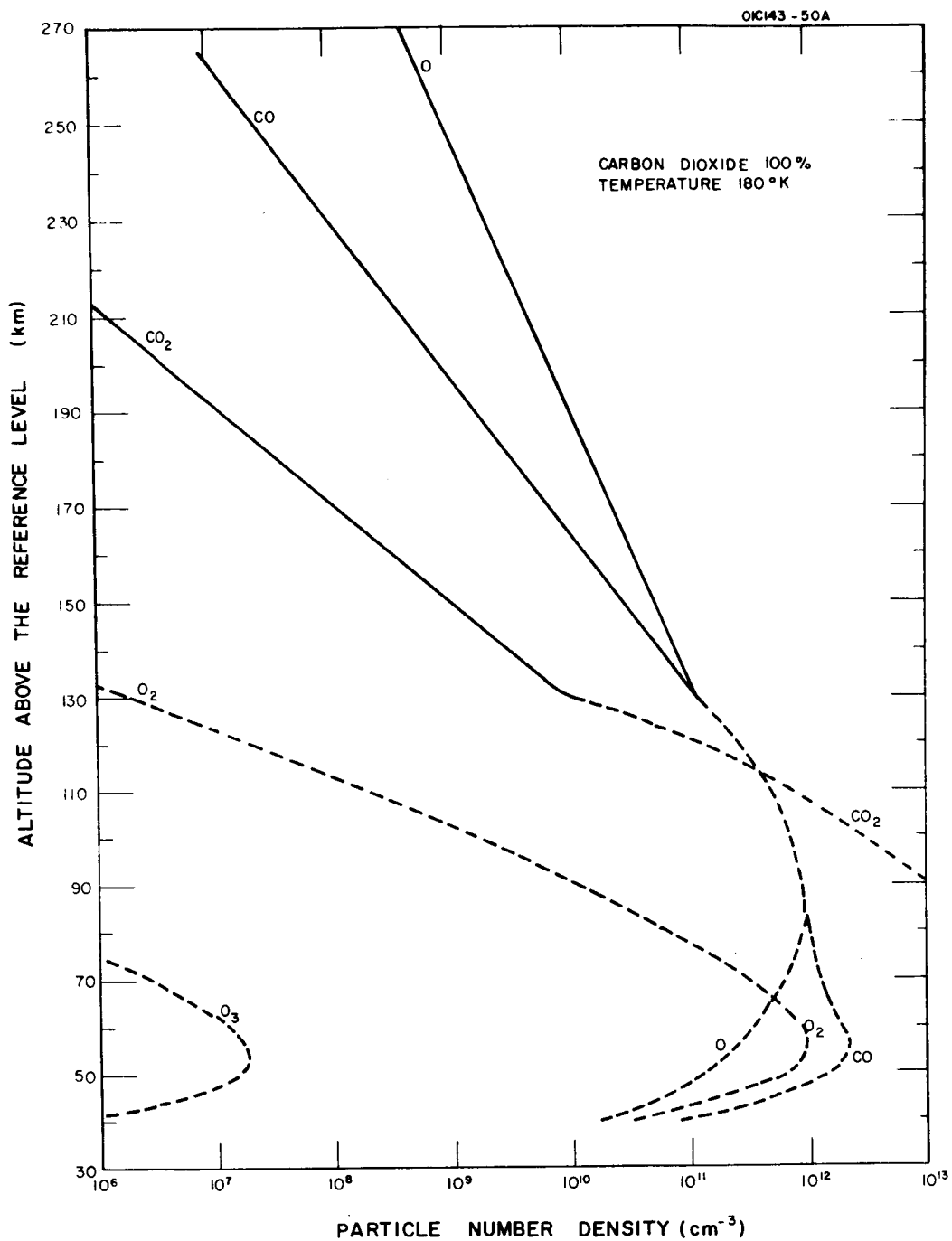


Figure 17. Neutral particle model atmosphere of Mars. Dotted lines are due to photochemical processes and the solid lines indicated the region of diffusion.

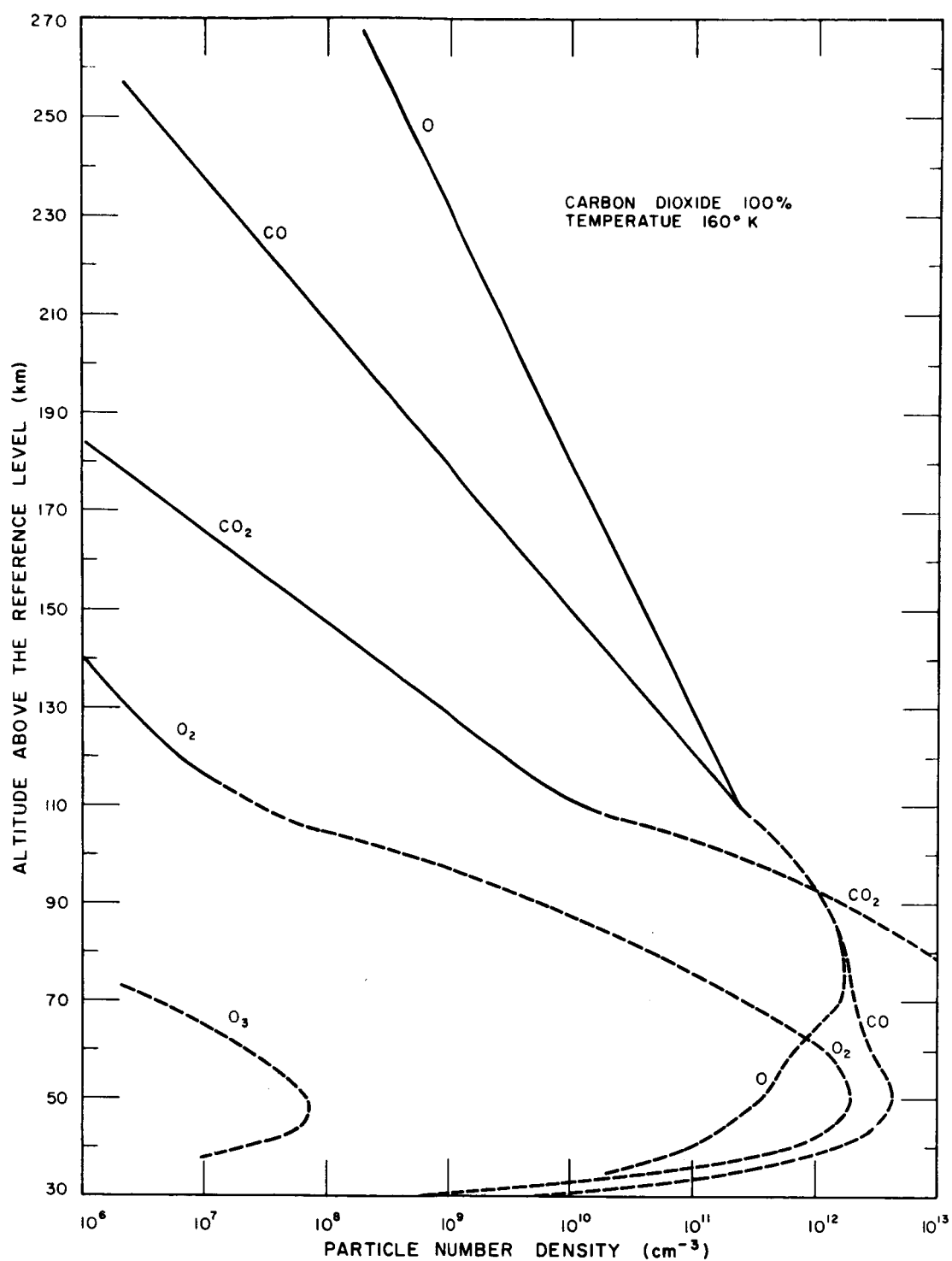


Figure 18. Neutral particle model atmosphere of Mars. Dotted lines are due to photochemical processes and the solid lines indicate the region of diffusion.

where $I(\lambda, Z)$ is the ionizing flux for a given wavelength interval of $50\text{\AA}$ at a given altitude, $\sigma_i(\lambda)$ is the average photoionization cross section for each constituent and wavelength interval, and $n_i(Z)$ is the constituent number density as a function of altitude. The calculated photoionization rates corresponding to the three assumed temperatures are presented as functions of altitude in Figures 19, 20 and 21, respectively. The corresponding ion density peaks can be seen to reside at altitudes of 170, 160, and 145 km for 200, 180, and 160°K, respectively. It is also noted that these peak altitudes are higher than the observed ionization maximum observed between 120 and 125 km in the Mariner IV experiment. This apparent discrepancy may be attributed to a number of shortcomings in the present model which constitutes the subject matter of a current investigation.

5. The Role of Meteoric Debris in the Earth Atmosphere: Simultaneous Observation of Meteoric Debris by Employing a Rocket-Borne Mass Spectrometric and Optical Probe. — Recently, identification and measurement of a considerable number of ambient ion species has been performed by both Narcisi and Bailey [111] and Istomin [112] using mass spectrometric techniques. Certain measurement ambiguities exist due to absolute instrumental calibration and the difficulty of precise mass identification of certain constituents. The results of the present investigation indicate that several meteoric debris species, including the aforementioned and others, may be observed with extremely-high sensitivity by solar resonance scattering. Thus, the use of an appropriate optical instrument, such as a Fastie-Ebert spectrometer or a properly-designed photometer, in addition to a quadrupole mass spectrometer would result in the simultaneous measurement of a number of species by the two independent techniques. Additionally, measurements could be obtained on a number of neutral species not presently observable by mass spectrometry. The incorporation of the optical capability additionally serves to reduce the above-cited experimental ambiguities by acting as an absolute calibration source for the mass spectrometer and by providing specific mass identification criteria for the observed atoms or ions. Thus, the additional and confirmatory optical measurements will provide more satisfactory data upon which to evaluate the role of interplanetary debris in the Earth's atmosphere, especially where the ionic and neutral states of an individual species can be measured simultaneously.

In the present analysis, expected signal intensities from solar-illuminated debris species are calculated on the basis of the reported number density distributions obtained from rocket-borne mass spectrometric [111, 112] and ground-based twilight measurements [113, 114]. These signal intensities are then compared to the Rayleigh-scattered background level to aid in defining the experimental mode and to demonstrate the feasibility of the suggested experiment. Finally, if it is assumed that the abundances of the neutral species are roughly equivalent to their observed ionic counterparts, then a high probability exists for successfully performing the indicated resonance scattering observations as well for these species.

a. Signal characteristics. — In the Earth's atmosphere, trace materials of possible meteoric origin have been detected and measured here by two methods of interest. These involve ion density measurements employing a quadrupole mass

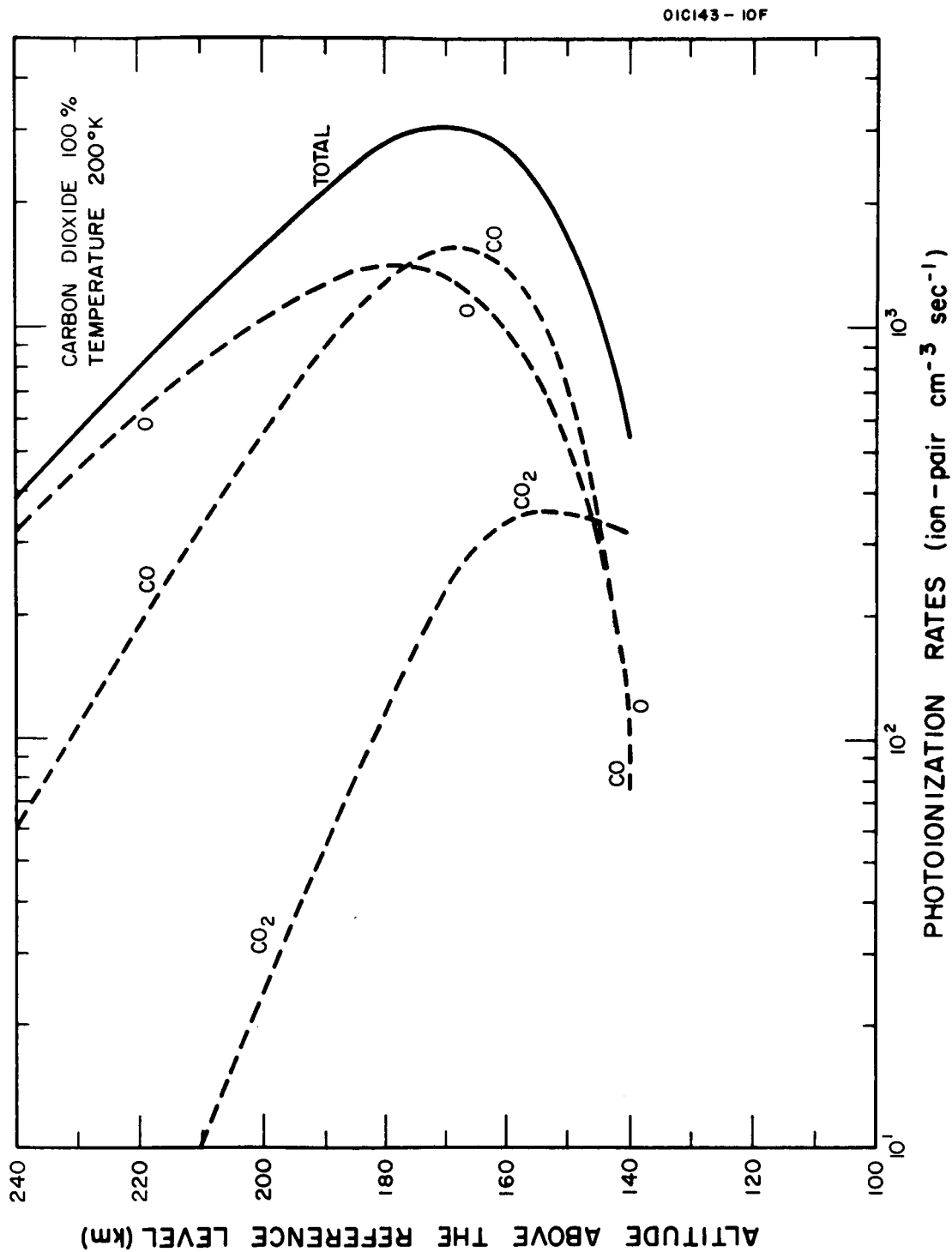


Figure 19. Photoionization rates for the atmosphere of Mars.

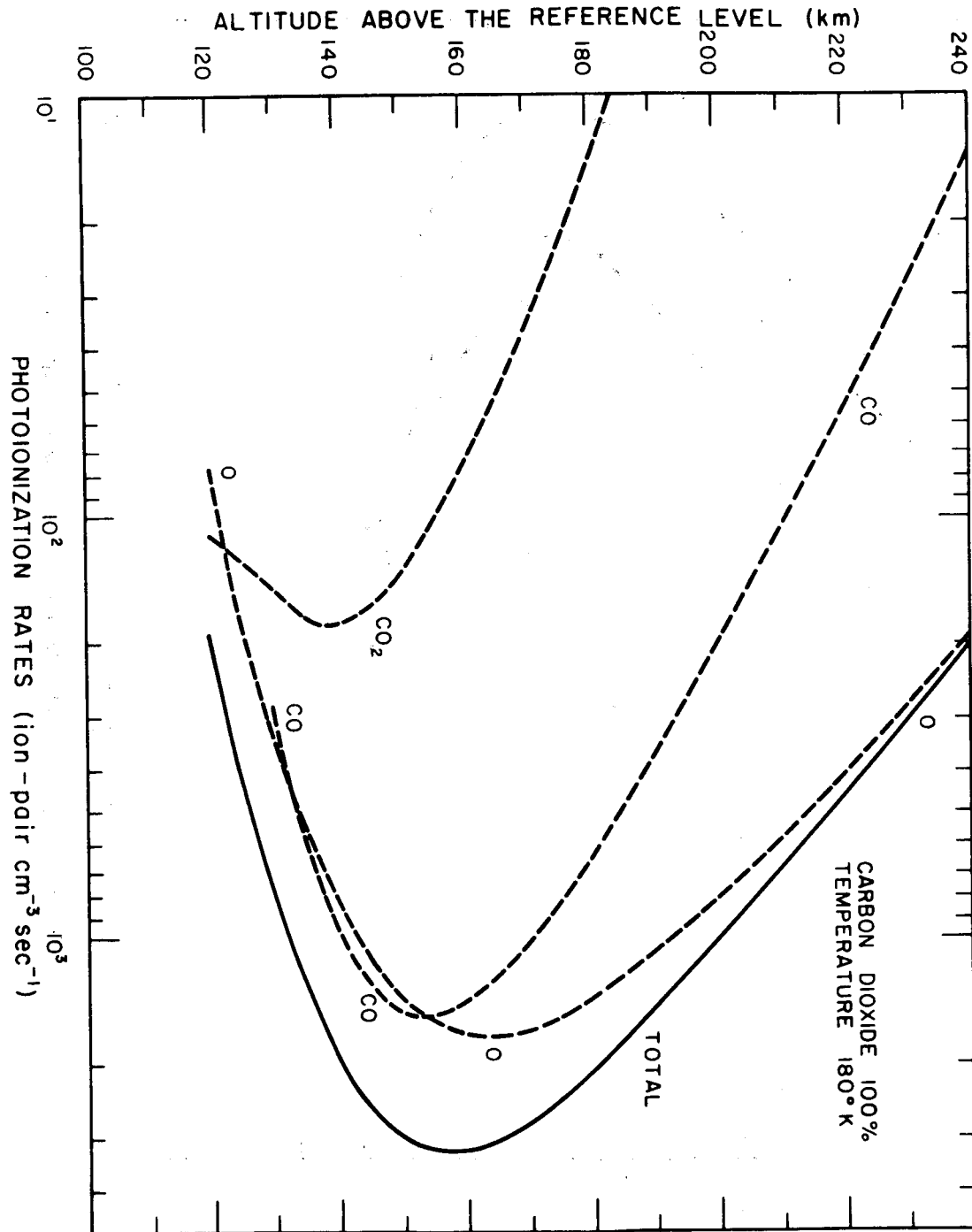


Figure 20. Photoionization rates for the atmosphere of Mars.

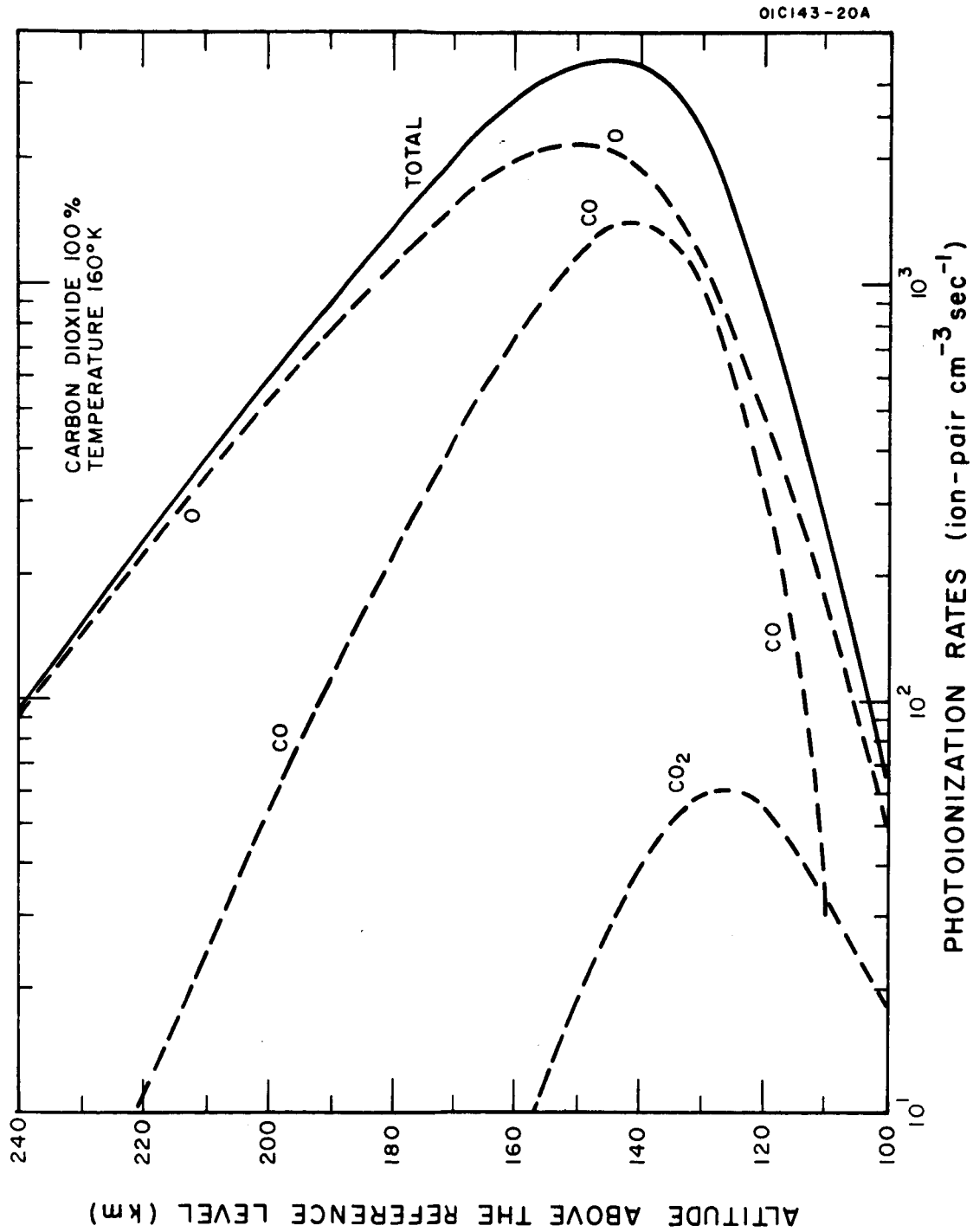


Figure 21. Photoionization rates for the atmosphere of Mars.

spectrometer wherein Narcisi and Bailey [111] have reported observations of Mg^+ , Na^+ and Ca^+ , while Istomin [112] has reported Mg^+ , Ca^+ , Si^+ and Fe^+ . The measured density profiles and the derived integrated vertical column counts for the species are presented in Figures 22 and 23, respectively. As a partial confirmation of the above results, Vallance Jones [113] has reported a column count of Ca^+ of about $4.5 \times 10^8 \text{ cm}^{-2}$ by performing twilight resonance scattering observations from a ground-based photometric site. Additionally, neutral Na, K, and Li twilight photometric measurements have been summarized by Vallance Jones [114]. These photometric data are shown in Figures 22 and 23 in terms of the measured integrated column counts and the derived number-density profiles. To calculate estimates of the overhead signal intensities (I_S) as a function of altitude, due to the solar resonance scatter from these observed constituents, it is necessary to obtain the product of the appropriate solar resonance efficiency per atom or ion, P (photon/sec atom), and the total column counts, N_T ; i.e., $I_S = PN_T$.

The solar resonance efficiency per atom (P) is defined by

$$P = \phi_{\lambda} \alpha \quad (23)$$

where ϕ_{λ} is the incident solar flux and α is given by

$$\alpha = \frac{\pi e^2}{mc} \frac{gf}{g_1} \frac{1}{\lambda_0^2} \quad (24)$$

where e = the unit charge

m = electron mass

gf = the oscillator strength of the particular transition (for the present purpose, the statistical weight of the upper state is incorporated in this value)

g_1 = the statistical weight of the ground level

λ_0 = the wavelength of the resonance line

The P -values for all of the observed neutral and ionic species and their neutral and/or ionic species counterparts have been previously calculated by Marmo and Engelman [115]. In Equation (23), no account has been taken for the increased illumination of the species due to Earth and atmospheric albedo radiation [116].

The resultant overhead signal strengths (I_S) are presented in Figure 24 for all of the observed species having available resonance lines. The summarized data indicate that the expected signal-strength values are essentially constant to about 95 km and decrease, as expected, at higher altitudes.

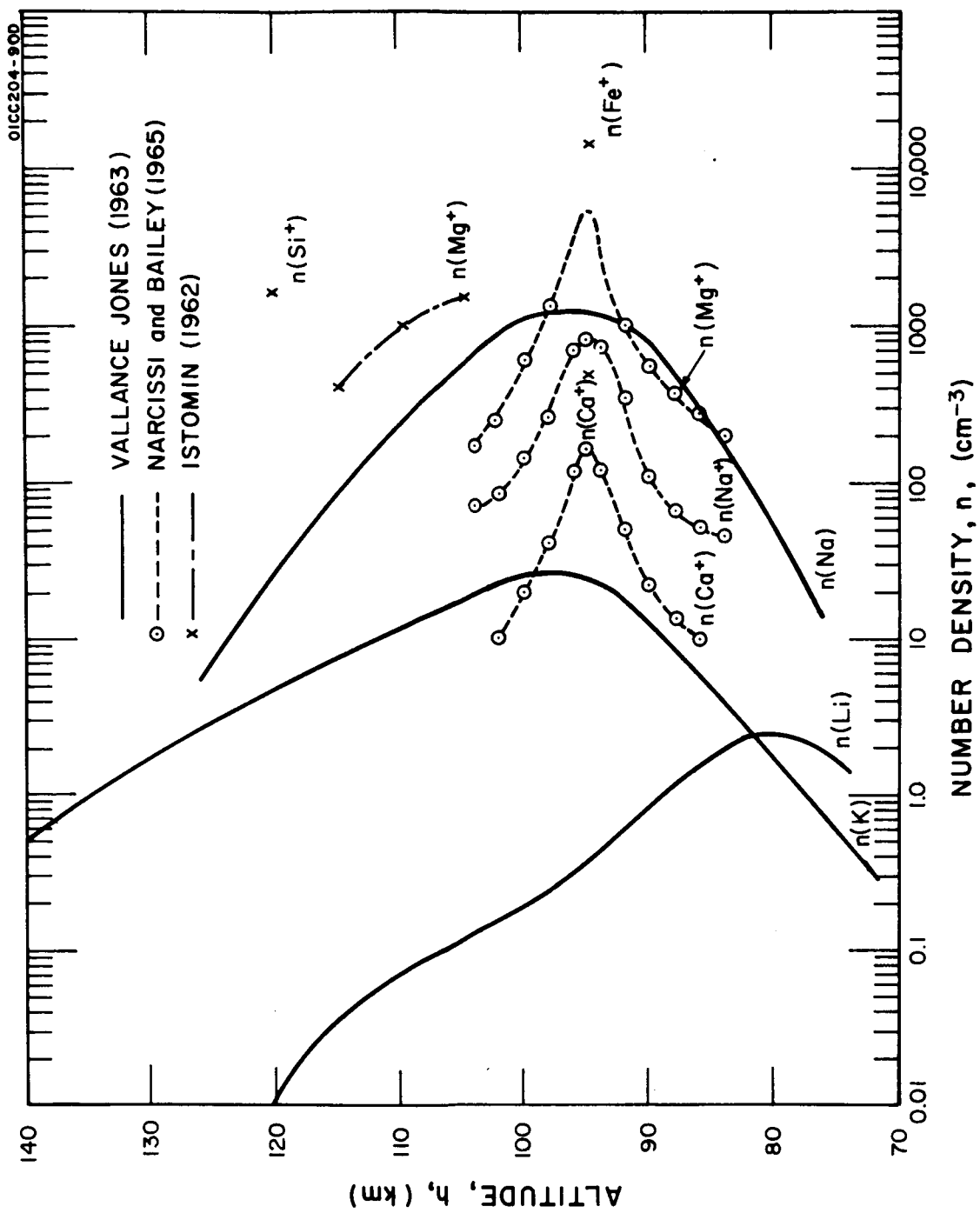


Figure 22. Observed number densities of debris species as a function of altitude.

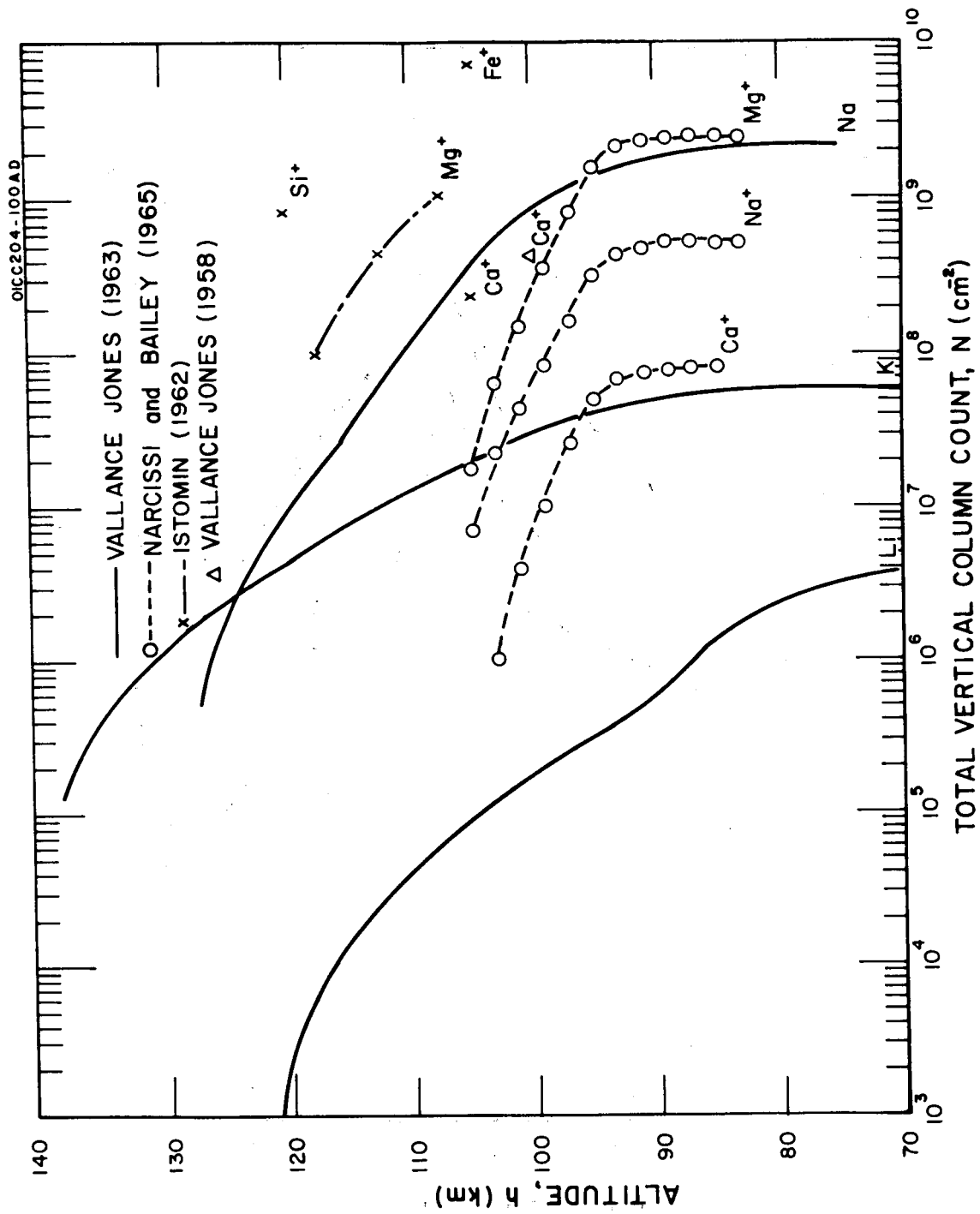


Figure 23. Vertical column counts of debris species as a function of altitude.

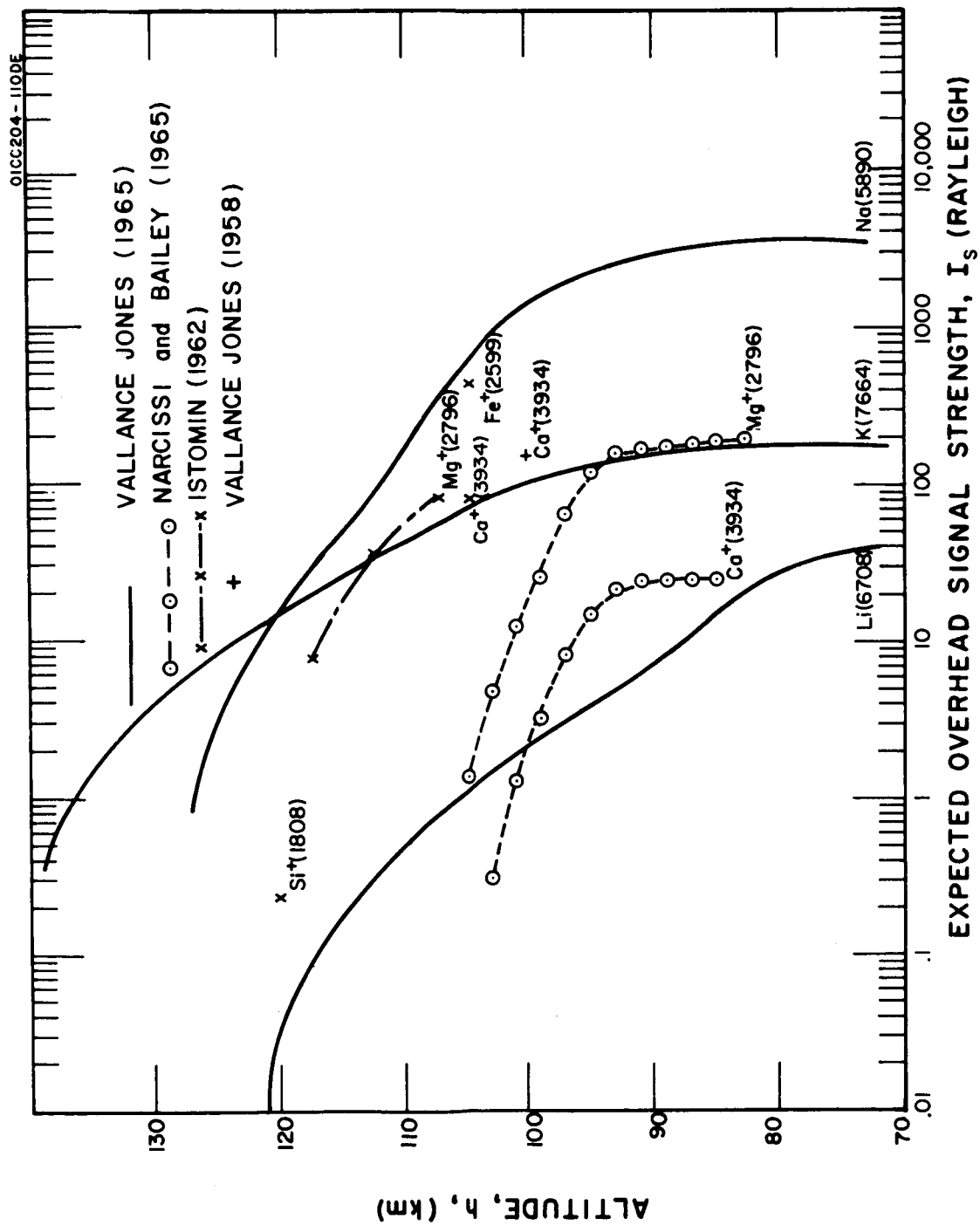


Figure 24. Expected resonance scattering signal levels as a function of altitude.

b. Rayleigh scattered background intensities.— In the rocket experiment discussed above, it is evident that the indicated measurements must be performed against the ambient Rayleigh scattered background evaluated vertically as defined by

$$I_B(\lambda, \psi) = K(\psi) \phi_\lambda \sigma_\lambda n_o H \quad (25)$$

where

$K(\psi)$ = Rayleigh scattering phase function = $\frac{3}{4} (1 + \cos^2 \psi)$

ϕ_λ = solar photon flux (photons $\text{cm}^{-2} \text{sec}^{-1} \text{\AA}^{-1}$)

σ_λ = Rayleigh scattering cross section (cm^{-2})

$n_o H$ = vertical column count of ambient atmospheric constituents (cm^{-2})

The evaluation of background profile with altitude assists in the selection of an optimum probe level. In order to consider a representative case, in Equation (25), a geometrical configuration has been assumed involving a solar zenith angle of 45° and a 0° instrumental zenith angle. This results in a scattering phase function value, $K(\psi) = 1.125$. Here again, no account has been taken of the contribution due to the additional illumination from Earth and atmospheric albedo [116]. The atmospheric column counts were obtained from the 1962 Standard Atmosphere [117]. The results of these calculations are shown in Figure 25 for probe altitudes of 80, 85, 90, 95, and 100 km. The intensity values are presented in units of Rayleighs/ $\text{\AA}$ ($10^6 \text{ photons/cm}^2\text{-sec}\text{\AA}$), so that these backgrounds would be directly applicable to an instrument with a $1\text{\AA}$ resolution capability, viewing vertically at the indicated altitudes and a solar zenith angle of 45° .

c. Suggested experiment. — A summary of the previously discussed signal and background results is contained in Table 4 appropriate to an upward viewing instrument and a 45° solar zenith angle. The tabulated signal levels for Ca^+ and Mg^+ are average values from Figure 24, while the background levels appropriate to rocket viewing altitudes of 80 and 95 km have also been selected. In most instances, it can be seen that the magnitudes of the expected signals (compared to the background levels) indicate that favorable experimental conditions prevail so that positive results could be anticipated. The spectral locations and P-values for neutral Ca, Si, Mg, and Fe are also included in the table to illustrate that since their P-values are either essentially equivalent to or greater than those of their ionic counterparts, at least equivalent favorable experimental performance can be predicted for these hitherto undetected ambient neutrals, provided they exist in roughly equivalent amounts.

It has thus been shown that the simultaneous measurement of possible meteoric debris species by mass spectrometric and optical resonance scattering techniques will both reduce existing constituent abundance uncertainties and eliminate mass determination ambiguities. Furthermore, if the selected rocket-borne optical instrumentation has a broad spectral operational capability, positive identification and measurement of additional constituents appears possible including the neutral counterparts of previously-observed ionic species.

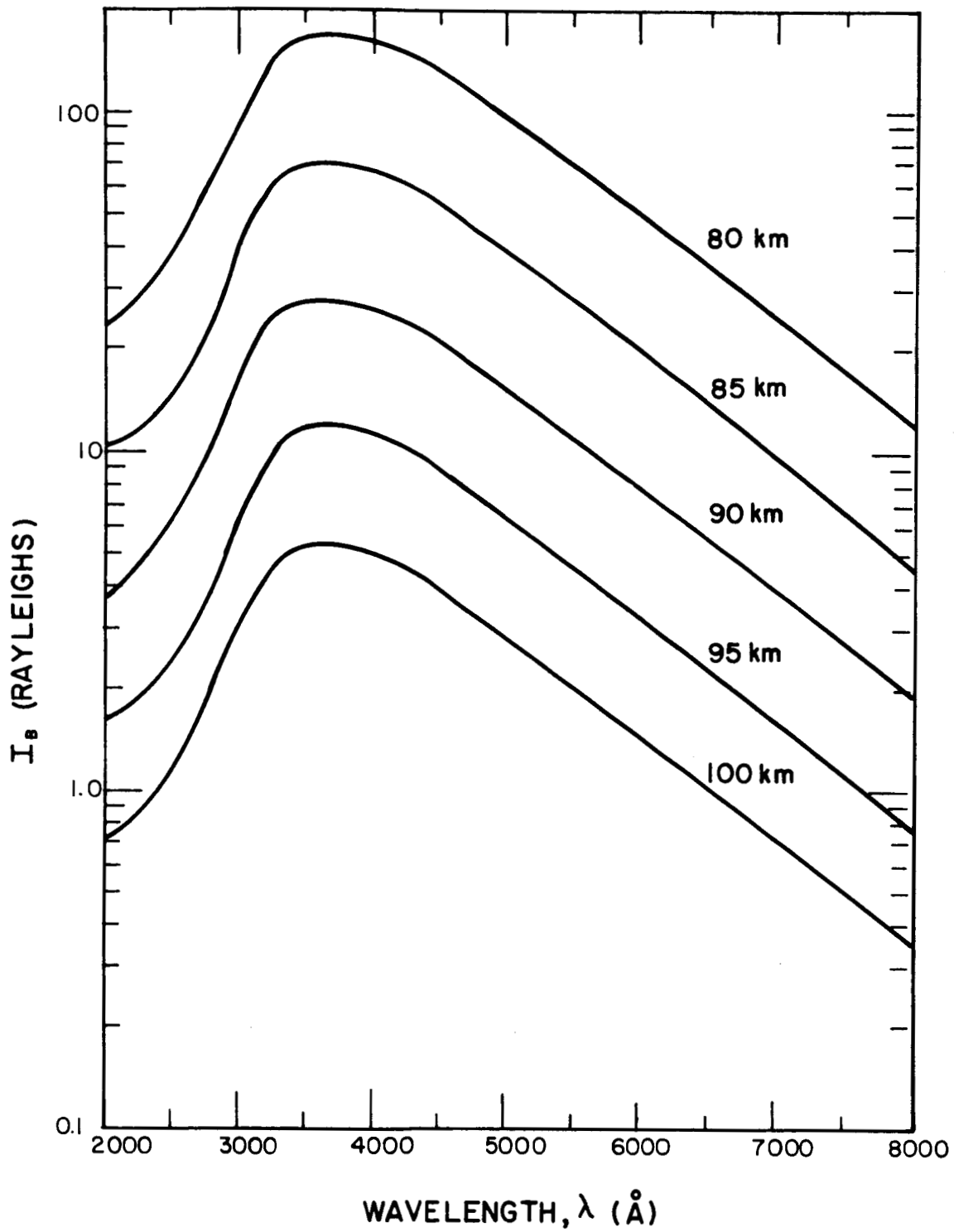


Figure 25. Rayleigh scattered background, I_B , for 45° zenith angle solar illumination and a 0° zenith look angle.

TABLE 4
PREDICTED SIGNAL AND BACKGROUND INTENSITIES

Element	λ ($\text{\AA}$)	P $\frac{\text{photon}}{\text{sec atom}}$	$N_T(\text{observed})$ (cm^{-2})	I_S (Rayleighs)	I_B (Rayleighs/ $\text{\AA}$)	
					k = 80 km	k = 95 km
LiI	6706(d)	1.6×10^1	4×10^6	64	30	2
KI	7665	1.4×10^0	6×10^7	84	20	1
NaI	5890	1.6×10^0	2×10^9	3200	50	4
CaII	3934	3.2×10^{-1}	2.6×10^8	83	140	10
CaI	4227	2.5×10^{-1}	--	--	140	9
SiII	1808	2.7×10^{-4}	8×10^8	0.2	--	--
SiI	2514	1.4×10^{-2}	--	--	30	2
MgII	2796	7.9×10^{-2}	1.8×10^9	140	80	5
MgI	2852	2.6×10^{-1}	--	--	90	6
FeII	2599	6.5×10^{-2}	7×10^9	455	50	3
FeI	3441	1.9×10^{-2}	--	--	170	11

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