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LABORATORY STUDIES ON THE EXCITATION AND COLLISIONAL  
DEACTIVATION OF METASTABLE ATOMS AND MOLECULES IN THE  
AURORA AND AIRGLOW

A Proposal for a Supplement to NASA Grant NGL 39-011-030  
submitted by

The University of Pittsburgh  
Department of Physics  
Space Research Coordination Center  
Pittsburgh, Pennsylvania 15260

to

The National Aeronautics and Space Administration  
Edward C. Zipf  
Principal Investigator

February 1974

(NASA-CR-138614) LABORATORY STUDIES ON  
THE EXCITATION AND COLLISIONAL  
DEACTIVATION OF METASTABLE ATOMS AND  
MOLECULES IN THE AURORA AND (Pittsburgh  
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## A. INTRODUCTION

The aeronomy group at the University of Pittsburgh is actively engaged in a series of coordinated satellite, sounding rocket, and laboratory studies designed to expand and clarify our knowledge of the physics and chemistry of planetary atmospheres. These research activities have been carefully coordinated in order to maximize the productivity of our small group and optimize the use of our limited financial resources.

The remarkable effectiveness of this approach is apparent. Within the last ten months alone we have made three major discoveries in our NASA supported laboratory studies that will lead ultimately to a complete and dramatic revision of our ideas on the ionospheres of Mars, Venus, and the earth and on the origin of their vacuum ultraviolet airglows. These results have already suggested a new generation of ionosphere studies which probably can be carried out best by laser heterodyne techniques. Our laboratory studies have also identified, for the first time, the physical mechanism responsible for the remarkable nitric oxide buildup observed by us in some auroral arcs. This development is an important break-through in auroral physics, and has military ramifications of considerable interest to the Department of Defense. This work may also shed some light on related NO and atomic nitrogen problems in the mesosphere.

During this period we have also had the opportunity and satisfaction to witness the first successful flight of an optical mass spectrometer [OMS] on board Nike-Apache rocket 14.512 UA. This is a very sensitive instrument for measuring the concentrations of O, O<sub>2</sub>

N, N<sub>2</sub>, H, H<sub>2</sub> and a variety of other minor constituents at mesospheric altitudes at levels as little as 10<sup>5</sup> atoms/cm<sup>3</sup>. The [OMS] was suggested by our laboratory cross section work in the vacuum ultraviolet wavelength region. This instrument is a very good example of the valuable symbiotic relationship that can be maintained by a well organized laboratory and rocket group.

During the period covered by this report we have published numerous journal articles and presented a number of papers describing our results at professional meetings. A publication list covering these activities has been included as an addendum to this proposal.

In subsequent sections of this proposal we outline a highly specific research program for the coming year and we explicitly indicate the significance to NASA of each experiment that we will carry out. The intent is to document the high degree of productivity of this group and to show how it strives continuously to contribute in a concrete way to the achievement of NASA's goals in the area of planetary atmospheres.

#### SOME RECENT DEVELOPMENTS

"A picture is worth a thousand words!" This proverb is familiar to us all and though well-worn, it nevertheless succinctly describes Figures 1, 2 and 3 of this report. These illustrations show some extraordinary results from our plasma physics studies and our electron scattering experiments. Figure 1 shows the vacuum ultraviolet spectrum of a recombining plasma in which CO<sub>2</sub><sup>+</sup> ions predominate. The results show strong excitation of the CO fourth positive system (A<sup>1</sup>Π → X<sup>1</sup>Σ) as a result of dissociative recombination.



It is very important to note that only the  $v' = 0$  and  $1$  levels of the  $A^1\Pi$  state can be populated if the  $\text{CO}_2^+$  ions are in thermal equilibrium at  $300^\circ\text{K}$ . It is quite clear from the data shown in Figure 1 that vibrational levels up to at least  $v' = 6$  are in fact being populated. Complementary electron heating experiments have shown that process (1) is exciting all of these levels. The implications are quite clear:  $\text{CO}_2^+$  laboratory plasmas, which had previously been thought to be equilibrated at  $300^\circ\text{K}$ , are in fact vibrationally very hot. But there is actually much more to it than this! Figure 1 shows a very intense spectral feature near  $1400 \text{ \AA}$  which does not appear conspicuously in electron impact excitation of CO or  $\text{CO}_2$ . This is the first laboratory observation of the "mystery" spectral feature at  $1400 \text{ \AA}$  which appears so strikingly in the Venus airglow spectra obtained by Rottmann and Moe (JGR 78, 8033, 1973). Our experiment provides virtually conclusive evidence for the presence of substantial concentrations of vibrationally excited  $\text{CO}_2^+$  ions in the Venus ionosphere. The Mars data in the same wavelength region shows a complete absence of this VUV feature implying a relatively cool ionosphere (and  $\text{CO}_2^+$  plasma). It is not clear at this point why the Venus atmosphere is capable of sustaining a vibrationally hot ionosphere while Mars does not or can not.

Figure 1 is surely a striking piece of plasma spectroscopy. Figure 2, however, is actually shocking for it shows that in plasma containing nearly equal concentrations of  $\text{CO}_2^+$  and  $\text{O}_2^+$  ions that a

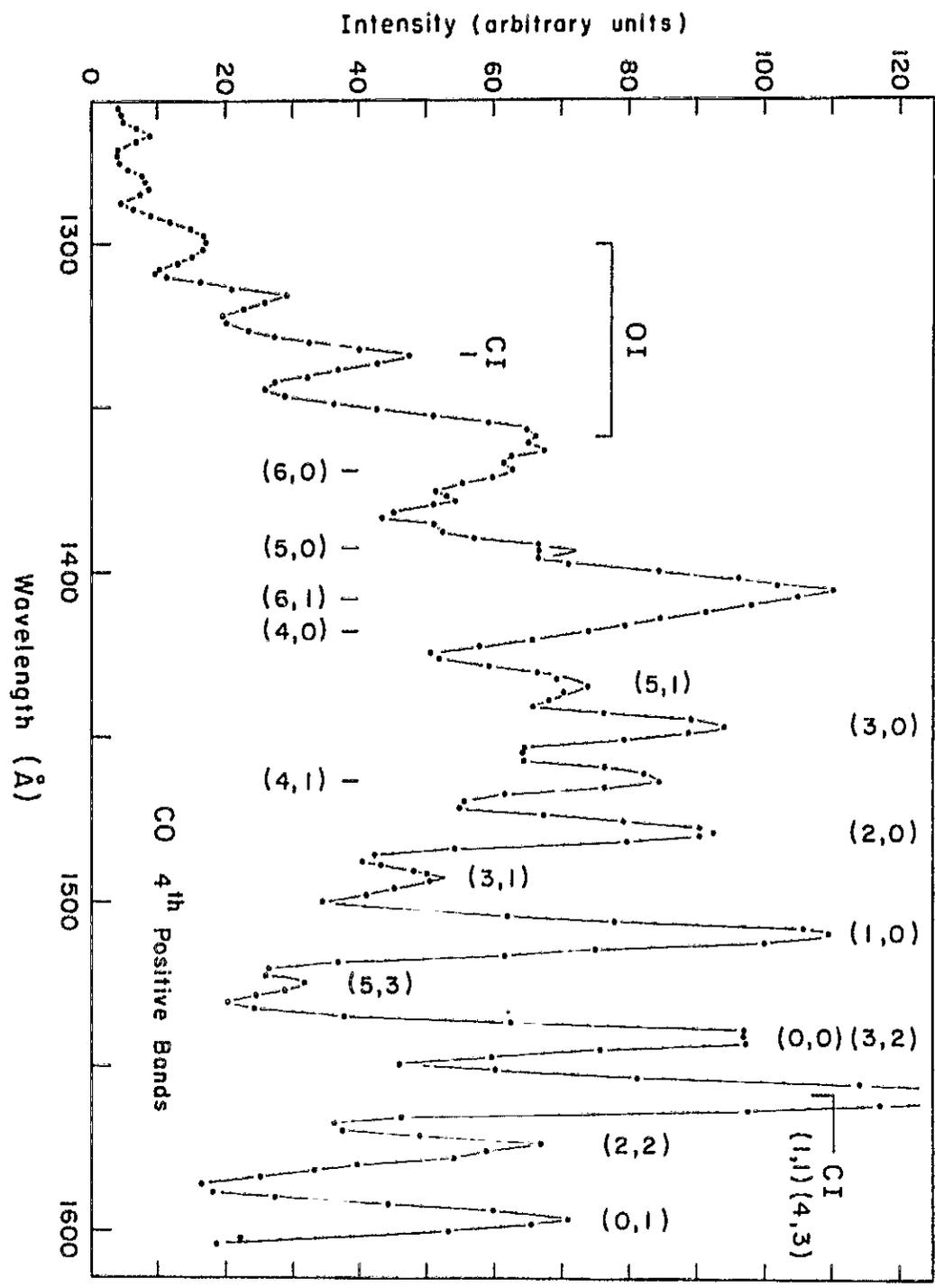
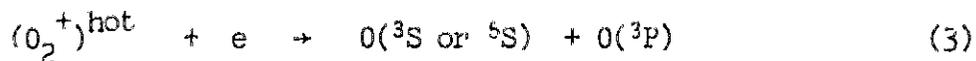
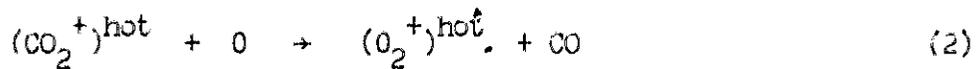


Figure 1

number of carbon and oxygen lines are produced by dissociative recombination. In fact the OI resonance lines at  $1304 \overset{\circ}{\text{A}}$  and the OI metastable feature are nearly equal in intensity and just about as bright as the CO fourth positive system. This development permits a relatively simple explanation of why these features appear so intensely in the Venus airglow and why they are nearly equal in magnitude, an aspect of the Venus spectra that is not duplicated in the data from Mars and has been very baffling to aeronomers. The  $1304 \overset{\circ}{\text{A}}$  emission implies that highly excited  $\text{O}_2^+$  ions also exist in our plasma. We believe that this comes about by exactly the same reaction sequence that takes place on Venus:



Just about the same amount of energy is required for exciting the OI resonance lines by process (2) and (3) as is required for the excitation of the CO 4th positive bands by process (1). This suggests that the vibrationally hot  $\text{O}_2^+$  and  $\text{CO}_2^+$  ions are in good thermal contact with one another. The absence of anomalous  $1304 \overset{\circ}{\text{A}}$  and  $1356 \overset{\circ}{\text{A}}$  signals from Mars is a direct consequence of the absence of vibrationally hot  $\text{CO}_2^+$  ions which are the energy precursors in the formation of hot  $\text{O}_2^+$  ions.

We are not sure at this point just how efficient processes (2) and (3) are. This will be one of our major goals during the coming year.

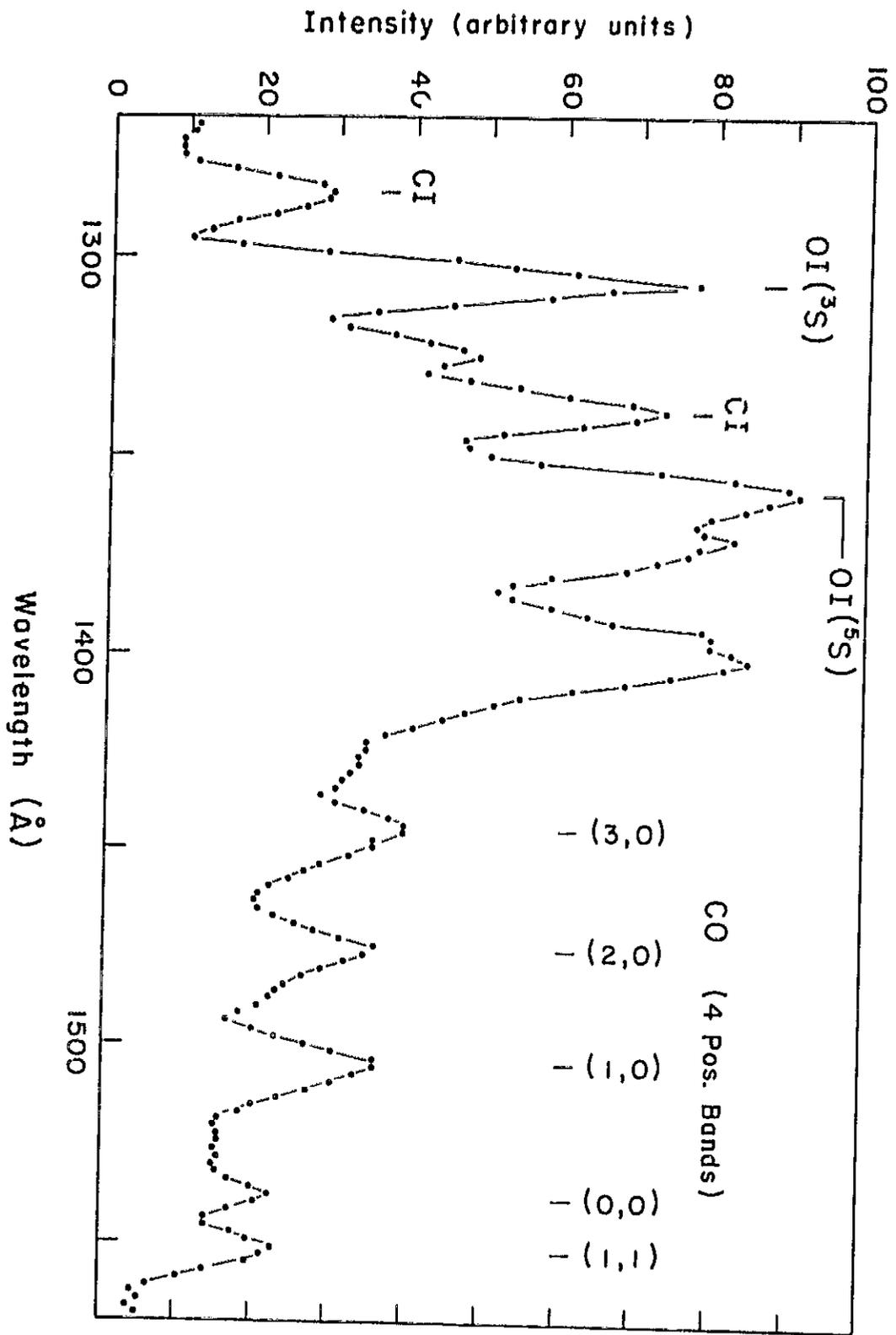


Figure 2

The data, however, speak for themselves: the recombination process seems to be very efficient indeed! There are numerous related questions raised by these results - How are these hot ions made? Why are they excited on Venus and not on Mars? Is the earth's ionosphere filled with hot ions as well? Our preliminary results raise more questions than they answer, but clearly suggest an entirely new view of Venus.

### TERRESTRIAL PROBLEMS

Figure 3 focusses our attention on our earthbound problems. It shows that vacuum ultraviolet spectrum of  $N_2$  excited by electron impact in the 900 - 1100Å. These data are a beautiful illustration of how sometimes a major geophysical process is discovered because laboratory data does not contain certain anticipated emission features. Figure 3 makes 2 important points: (1) Nitrogen is a copious source of EUV photons which are capable of photoionizing and photodissociating the upper atmosphere to a significant degree in an auroral arc. (2) with the exception of the  $v' = 1$  levels of the  $b^1\Pi_u$  state only radiation from  $1/2_u^+$  states is observed. All  $\Pi_u$  symmetry states are found to predissociate producing  $N(^2D)$  atoms by the process:



The failure to observe the expected radiation from  $\Pi_u$  symmetry states is the key to the auroral nitric oxide problem!

We have pondered the implications of Figure 3 and we have distilled these thoughts into 3 papers. The abstracts of these papers speak

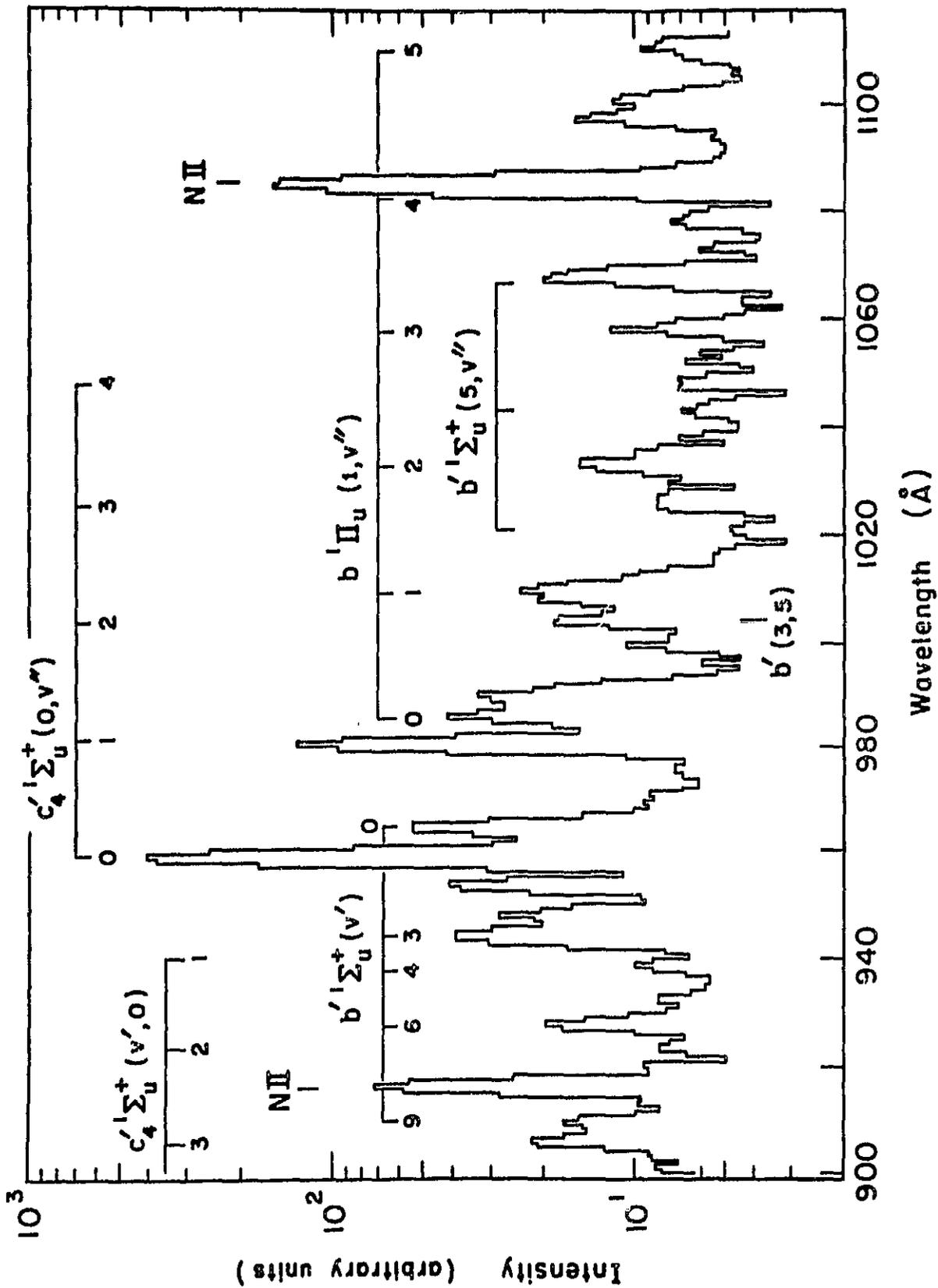


Figure 3

for themselves:

Photodissociation of  $O_2$ : A Major Source of the Auroral Green Line. Numerous theories have been proposed to account for the excitation of the OI  $5577\overset{\circ}{\text{Å}}$  line in auroras and to explain its remarkable covariation with the 1st. NEG. bands of  $N_2^+$ . These auroral models generally assume that the  $^1S$  state is quenched (weakly) below 100 km by  $O_2$ , and that at higher altitudes the  $O(^1S)$  production rate is essentially equal to the  $\lambda 5577\overset{\circ}{\text{Å}}$  volume emission rate. Recent laboratory studies, however, show that the  $^1S$  state is efficiently quenched by  $O(^3P)$  atoms, so that at 105 km, for example, only one  $O(^1S)$  atom in four actually survives to radiate. Thus the  $^1S$  source implied by the  $\lambda 5577\overset{\circ}{\text{Å}}$  auroral data is considerably larger in magnitude than previously realized. None of the excitation mechanisms proposed up to this point can create  $O(^1S)$  atoms at the required rate with an altitude profile consistent with ground-based and rocket data. In this paper we show that photodissociation of  $O_2$  by extreme-ultraviolet photons produced in the aurora itself is the dominant source of the OI  $5577\overset{\circ}{\text{Å}}$  emission and that this mechanism readily accounts for the observed  $\lambda 5577\overset{\circ}{\text{Å}}/3914\overset{\circ}{\text{Å}}$  intensity ratio and behavior. The reaction  $N_2(A^3\Sigma_u^+) + O \rightarrow O(^1S) + N_2$  is also shown to be important and to have an efficiency-rate coefficient product  $ek \sim 1.5 \times 10^{-11} \text{ cm}^3/\text{sec}$ .  $\lambda 5577\overset{\circ}{\text{Å}}/3914\overset{\circ}{\text{Å}}$  intensity ratios of 1 or less are attributed to additional  $^1S$  quenching by nitric oxide.

Comment on the Role of Photoionization in Auroral Arcs.

Very large fluxes of extreme ultraviolet [EUV] radiation have been observed in-situ by Paresce et al (1972) in an otherwise weak auroral display ( $\lambda 5577\text{\AA}$  intensity of 5 kR or less). Their measurements, as well as independent ground-based and rocket observations of the  $c' \ ^1\Sigma_u^+ \rightarrow a' \ ^1\Pi_g$  intercombination bands, suggest that the total EUV production rate in an auroral arc is comparable in magnitude to the total  $N_2$  ionization rate. The observational data are shown to be consistent with recent laboratory measurements of the absolute cross sections for exciting EUV radiation by electron impact on atmospheric gases, and with in-situ electron-energy distribution measurements. Below 120 km locally excited EUV photons are readily absorbed and efficiently photoionize the neutral constituents of the auroral arc. Radiation entrapment is important for some of these EUV transitions and the concomitant flux enhancement which occurs within the optically thick medium, increases the net photoionization rate. Because the bulk of the EUV radiation is emitted in the 800 - 1000  $\text{\AA}$  region, preferential photoionization of O,  $O_2$ , and NO occurs. This selective ionization alters the ion chemistry in an auroral arc, changes the  $NO^+/O_2^+$  ratio in a complex manner depending on the local NO abundance, and may explain some compositional anomalies observed by mass spectrometers.

Comment on the Production of  $N(^2D)$  Atoms by Photoabsorption Processes and by Electron-Impact Excitation of  $N_2$ . Laboratory

studies on the production of extreme ultraviolet radiation by electron-impact excitation of  $N_2$  show that  $N(^2D)$  atoms are produced very efficiently by the predissociation of  $N_2$  Rydberg and valence states with  $^1\Pi_u$  symmetry. This dissociation process involves a non-radiative transition to the  $C' \ ^3\Pi_u$  continuum:  $e + N_2 \rightarrow N_2(^1\Pi_u) + e$  followed by  $N_2(^1\Pi_u) \rightarrow N_2(C' \ ^3\Pi_u) \rightarrow N(^2D) + N(^4S)$ . Under auroral conditions these predissociating  $^1\Pi_u$  states are populated by electron-impact at a rate comparable to the  $N_2^+$  ionization rate. Thus, the total  $N(^2D)$  population rate from dissociative excitation, from dissociative recombination of  $NO^+$  ions, and from ion molecule reactions could be as much as 50-100 times the  $\lambda 3914$  volume emission rate. This excitation rate would suffice to account for the large  $N(^2D)$  concentrations observed recently by Rusch and Sharp in an IBC  $1^+$  aurora, and for the production of unusually large nitric oxide densities in some auroral forms as a result of the  $[N(^2D) + O_2]$  quenching reaction. Under daytime conditions these same  $N_2(^1\Pi_u)$  states are populated by absorption of solar photons and the  $N(^2D)$  production rate from this process is shown to be comparable to that from photoelectron impact and from the dissociative recombination of  $NO^+$  ions.

We believe that the broad outlines of a solution to the NO question have been delineated by our preliminary laboratory work. In Section B of this report we outline our plans for the coming year; plans which are strongly influenced by the events of a truly remarkable year.

During this report period we have also made substantial progress

in our studies of methane and ammonia. This time-of-flight work has been stimulated by our interest in the atmosphere of Jupiter and in complex molecules observed in comets and in interplanetary space. Two papers describing these results are in preparation.

Our laboratory work on EUV radiation has also contributed to the development of an auroral payload containing a scanning concave grating monochromator (500 - 1300<sup>o</sup>Å), which in conjunction with visible photometers and a double-mode ion/neutral mass spectrometer, will allow us to test out the ideas discussed in the above abstracts.

## B. CURRENT PROGRAM

### Specific Plans for the Period 1 May 1974 to 30 April 1975

In the paragraphs that follow we outline our research program for the coming year. A highly diversified program is proposed involving several complex experiments stimulated by recent airglow, auroral and ionospheric data from Earth, Mars, and Venus.

#### 1. Program: Plasma Physics Studies and Afterglow Measurements

Our plans for the immediate future are strongly influenced by the discovery of evidence for vibrationally hot ions in the ionosphere of Venus and the strong suspicion that similarly "hot" ions exist in our own atmosphere especially under disturbed conditions. Five separate questions will be investigated: (1) We need to determine where all this extra energy is being stored. Are we dealing only with vibrationally hot ions or are metastable ions also involved? (2) How does our laboratory plasma and the Venus ionosphere manage to maintain such large equilibrium concentrations of these excited species? (3) What final products (or photons) are produced when these excited ions recombine dissociatively? (4) What are the specific recombination rate coefficients? And finally (5) To what extent are the UV photons produced by recombination a result of predissociation rather than a conventional curve crossing process? Our efforts will be strongly focused on the following major atmospheric ions:  $\text{NO}^+$ ,  $\text{O}_2^+$ ,  $\text{N}_2^+$  and  $\text{CO}_2^+$ .

NASA Significance: (1) Atoms and molecules excited by dissociative recombination constitute a major source of photons in the martian, cytherean, and terrestrial airglows. Accurate specific yield measure-

ments are needed to provide a quantitative basis for a detailed physical description of planetary airglow phenomena. (2) Observation of the radiation resulting from dissociative recombination by sounding rockets, satellites, or spacecrafts is the basis of a simple, but powerful, optical technique for determining the ionic and neutral composition of a planetary atmosphere. (3) Dissociative recombination is a source of kinetically "hot" atoms. In the F region kinetically energetic atoms have an increased escape probability which Nisbet (1973) has shown leads to an unexpected modification of the atomic oxygen distribution above 300 km. Detailed information on the specific atomic yields are needed in order to calculate the initial velocity distribution of the dissociative fragments. (4) Our recent studies on  $\text{CO}_2^+$  recombination have shown that laboratory plasma generally contain a substantial percentage of vibrationally excited ions. This raises serious questions about previous total recombination-coefficient measurements and their applicability in the analysis of ionospheric. Several apparent ion-chemistry anomalies may be traceable to this problem. (5) We have obtained preliminary data showing the "mystery" feature visible in the Venus spectrum at  $1400\overset{\circ}{\text{A}}$  as well as the OI  $1304$  and  $1356\overset{\circ}{\text{A}}$  lines. We have been able to demonstrate that the laboratory spectra results from positive ion recombination and we believe that future laboratory work on this mechanism will resolve the vexing questions posed by the Venus data.

## 2. Program: Electron Scattering Experiments

We plan to continue with our detailed studies of airglow and auroral

radiation produced by electron impact. These experiments will include (1) Absolute cross section measurements in the extreme ultraviolet [EUV] and infrared wavelength regions. The targets of interest are O, O<sub>2</sub>, N, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, C, NH<sub>3</sub>, and CH<sub>4</sub>. (2) Further attempts to measure with very high resolution the inelastic electron loss spectrum of N and O so that electron degradation calculations can be placed on a firm quantitative foundation and the electron, F-region thermal economy problem straightened out. And (3) we are especially anxious to attempt to measure the total cross section for atomic nitrogen production as the result of dissociative electron impact. This, we believe, is the key NO mechanism.

NASA Significance: Our previous laboratory work in the VUV and EUV spectral regions has led to three proposals concerning the role of electron scattering in the upper atmosphere. We have suggested (1) that EUV photons produced as precipitating electrons degrade in an aurora profoundly effect the ion chemistry of an auroral arc through preferential photoionization of O<sub>2</sub> and NO, (2) that these same photons also photodissociate O<sub>2</sub> and very effectively excite the OI green line (λ5577Å), which is the brightest visible feature in the aurora, and (3) that the excitation processes leading to this EUV emission also result in the predissociation of N<sub>2</sub> into N(<sup>2</sup>D) atoms which ultimately lead to enhanced NO concentrations. Our laboratory work is thus directed at three pivotal questions in auroral physics with related applications in the quiet ionosphere.

### 3. Program: Time of Flight Experiments [TOF]

In these experiments we are probing three major problem areas:

- (1) We are attempting to determine the ultimate fate of the energetic (both kinetically and electronically) atoms and molecules produced by dissociative processes in planetary atmospheres. In this study we use a novel source of "hot" atoms (0.1 - 200 eV) and observe their interaction with atmospheric gas targets by exploiting TOF techniques. Our initial interest is in the magnitude of the inelastic cross sections involved in such interactions and in identifying the specific products [e.g., NO] that result from these collisions.
- (2) We plan to study collision processes involving vibrationally and kinetically excited ions. This study is prompted by the theoretical work of Cole on the role of Joule heating and electric fields in auroral arcs.
- (3) We are attempting to obtain detailed potential surface curves from our TOF spectra and to test the so-called "ion-core model" which is frequently invoked in dissociative excitation studies. This aspect of our work is of fundamental interest to molecular theoreticians and has additional life sciences applications.

NASA Significance: A extraordinary, but largely overlooked fact, is that the total cross section for producing "hot" atoms by dissociative electron impact on  $N_2$  and  $O_2$  is twice as large as the total ionization cross section. Hence, a large amount of the energy deposited initially in an auroral arc by primary and secondary electrons is channeled ultimately into a "hot" atomic gas. Our own studies show that on the average atomic fragment produced by dissociative excitation possesses 3 - 5 eV in the form of kinetic energy (or an equivalent temperature

of about 60,000°K). We have no knowledge, as yet, of the kinds of chemical interaction possible to such energetic atoms. All manners of reaction which are slow at 300°K because of 1 to 2 eV activation energies, are highly exothermic to kinetically excited atoms. It is the purpose of our TOF experiments to explore this virgin territory and to determine what role hot atom chemistry may have in planetary atmospheres.

### C. PERSONNEL

As in the past a number of young people have received part of their training by participating in the research work described in this report. They have contributed substantially to its success:

Thomas Finn	-	Postdoctoral Research Associate
Edward J. Stone	-	Postdoctoral Research Associate
Robert A. Gutcheck	-	Postdoctoral Research Associate

#### Graduate Research Assistants

G. Unger  
P. Erdman  
B. Carnahan  
R. McLaughlin

From time to time we have employed (on a part time basis) undergraduate students who have expressed an interest in geophysics or in environmental research. This arrangement has proven to be mutually beneficial.

#### D. BACKGROUND AND RESOURCES

Since 1959 Edward C. Zipf has been engaged in laboratory studies of atomic and molecular collision processes that play an important role in the physics of the upper atmosphere. His laboratory work has been complemented by numerous field experiments in which he has studied the radiation emitted in auroras and in the day and night airglow with both ground-based and rocket-borne instrumentation. He has been active in studies of the ion and neutral composition of the upper atmosphere and he has developed a programmable quadrupole mass spectrometer that permits simultaneous ion and neutral density measurements during the same rocket flight. This instrument has been flown successfully into auroral arcs where, on several occasions, it observed large quantities of nitric oxide, and into the dawn and twilight airglow where it observed the birth and death of the daytime ionosphere as solar EUV radiation first reached and then receded from the F region. These transient experiments have been complemented by day and night airglow flights under quiet conditions. Most recently, in collaboration with the Johns Hopkins University and the University of Colorado, he participated in a multiple rocket experiment supporting the Apollo 17 mission. His research group has developed numerous flight instruments as the result of their deep involvement in complementary laboratory experiments. This includes cylindrical and planar probes for electron temperature and density measurements in the upper atmosphere, the only double mode mass spectrometer currently in systematic use, and now an entirely new device, an optical mass spectrometer [OMS], for use at mesospheric altitudes (and above). An

[OMS] payload was flown successfully at mesospheric altitudes on 14 August 1973 from the White Sands Missile Range, where it measured the concentrations of O, O<sub>2</sub>, N, N<sub>2</sub>, H, and H<sub>2</sub> from 85 to 115 km.

His work has also included measurements of airglow radiation emitted during two total solar eclipses and during auroral displays both from the ground and from a jet aircraft. In the laboratory he has used modern data processing techniques in afterglow studies and in electron scattering experiments. This has permitted on-line control and review of the data and the data acquisition process and has resulted in a substantial improvement in the quality of the data and a reduction in the amount of time, manpower and cost required to achieve our objectives. The laboratory program has made important contributions to the study of dissociative recombination of molecular ions of aeronomic interest, to the study of metastable lifetimes, transport properties and quenching coefficients, to the study of dissociative excitation of atomic species by electron impact on molecular or polyatomic targets and to the study of atomic oxygen and nitrogen emission lines excited by electron impact on O and N. This systematic and mission-oriented approach to a variety of important aeronomy problems has resulted in the measurement of more than 200 absolute excitation cross sections, and to the publication of more than 70 papers in the short period of 4 years. In the areas of specific recombination measurements and electron scattering off reactive targets such as O and N, this team is the sole contributor in the world. His research group has also been involved in ground-based interferometric studies of mid-latitude red arcs and the airglow from an observatory maintained by the University

of Pittsburgh on Laurel Mountain.

E. C. Zipf received his Ph.D from the Johns Hopkins University in 1961. From 1961 to 1963 he was on the staff of the Johns Hopkins University as a Research Associate and an Instructor of Physics. During 1963 - 1964 he was a visiting fellow at the Joint Institute for Laboratory Astrophysics. He joined the faculty of the University of Pittsburgh in 1964; he is currently a Professor of Physics. In all phases of his research work he will be able to call upon his colleagues in the Space Research Coordination Center for technical assistance. The University of Pittsburgh maintains a modern computing center which we use extensively in our data reduction and analysis work. This includes a time-sharing computer terminal in our laboratory that services our laboratory and sounding rocket experiments.

A list of our publications for the current year is attached.

#### E. RECENT PUBLICATIONS AND TECHNICAL PRESENTATIONS

1. W. C. Wells, W. L. Borst and E. C. Zipf, "Production of  $\text{CO}(a^3\Pi)$  and Other Metastable Fragments by Electron Impact Dissociation of  $\text{CO}_2$ ", J. Geophys. Res., 77, 69, 1972.
2. E. J. Stone and E. C. Zipf, "Excitation of the Werner Bands of  $\text{H}_2$  by Electron Impact", J. Chem. Phys., 56, 4646, 1972.
3. E. J. Stone and E. C. Zipf, "Electron-Impact Excitation of Nitric Oxide", J. Chem. Phys., 56, 2870, 1972.
4. W. C. Wells and E. C. Zipf, "Excitation of Vacuum Ultraviolet Radiation by Electron Impact on Carbon Monoxide: Some Unresolved Questions Near Threshold", J. Chem. Phys., 57, 3583, 1972.
5. R. C. Schaeffer, P. D. Feldman, and E. C. Zipf, "The Dayglow [OI]  $\lambda\lambda$  6300 and 5577 $\text{\AA}$  Lines in the Early Morning Ionosphere", J. Geophys. Res., 77, 6828, 1972.
6. M. J. Mumma, E. J. Stone, W. L. Borst and E. C. Zipf, "Dissociative Excitation of Vacuum Ultraviolet Emission Features by Electron Impact on Molecular Gases III.  $\text{CO}_2$ ", J. Chem. Phys., 57, 68, 1972.
7. W. L. Borst, W. C. Wells, and E. C. Zipf, "Excitation of the Metastable  $\text{E}^3\Sigma_g^+$  State of  $\text{N}_2$  by Electron Impact", Phys. Rev. A, 5, 1744, 1972.
8. E. C. Zipf, "Comment on the Role of Photoionization in Auroral Arcs", Trans. Am. Geophys. Union 54, 403, 1973.
9. E. J. Stone and E. C. Zipf, "Excitation of the  $\text{OI}(^3S^0)$  and  $\text{OI}(^5S^0)$  States by Electron Impact on Atomic Oxygen", submitted to J. Chem. Phys., 1973
10. R. A. Gutcheck and E. C. Zipf, "The Excitation of the CO Fourth Positive System by the Dissociative Recombination of  $\text{CO}_2^+$  Ions", J. Geophys. Res., 78, 5429, 1973.
11. W. C. Wells, W. L. Borst, and E. C. Zipf, "Electron Impact Excitation of Metastable States in Carbon Monoxide", Proceedings Eight International Conference on the Physics of Electronic and Atomic Collisions, Belgrad, 1973.
12. W. C. Wells, W. L. Borst, and E. C. Zipf, "Excitation of Higher Lying Metastable States in Carbon Monoxide by Electron Impact: Cross Section and Lifetime Measurements", accepted by Phys. Rev., 1973.
13. E. J. Stone and E. C. Zipf, "Excitation of Atomic Nitrogen by Electron Impact", J. Chem. Phys., 58, 4278, 1973.

14. E. C. Zipf, "Photodissociation of  $O_2$ : A Major Source of the Auroral Green Line", Trans. AGU 54, 1155, 1973.
15. E. C. Zipf, P. W. Erdman and T. G. Finn, "A New Instrument for Mesospheric Composition Measurements", Trans. AGU 54, 1151, 1973.
16. E. C. Zipf, "On the Role of Photoionization in Auroral Arcs", submitted to J. Geophys. Res., 1973.
17. W. C. Wells and E. C. Zipf, "Lifetime of the Metastable  $5s^0$  State of Atomic Oxygen", accepted by Phys. Rev., 1973.
18. E. C. Zipf, "Comment on the Production of  $N(^2D)$  Atoms by Photoabsorption Processes and by Electron-Impact Excitation of  $N_2$ ", Trans. AGU 55, XXXX, 1974.
19. B. L. Carnahan, T. G. Finn and E. C. Zipf, "Dissociation of  $CH_4$  by Electron Impact: Production of Metastable Hydrogen and Carbon Fragments", submitted to J. Chem. Phys., 1974.

## F. BUDGET

A detailed budget is presented for the current year (1 May 1974 - 30 April 1975) covering the research activities outlined in the preceding sections. In previous years this program has been step-funded. This arrangement has contributed significantly to its success and we request continuance of this form of support. A step-funded budget is also presented.

PROPOSED BUDGET

Year I: 1 May 1974 to 30 April 1975

"Laboratory Studies on the Excitation and Collisional Deactivation of Metastable Atoms and Molecules in the Aurora and Airglow"

E. C. Zipf

	<u>Total Research</u>	<u>University Contribution</u>	<u>Research Requested</u>
<u>Salaries</u>			
Edward C. Zipf, Principal Investigator*	\$ 6,098	\$ 2,904	\$ 3,194
Postdoctoral Research Associate (Full Time)	11,500		11,500
Secretary (Part Time)	2,800		2,800
Graduate Student Research (Full Time)	4,500		4,500
	<hr/>	<hr/>	<hr/>
TOTAL SALARIES	24,898	\$ 2,904	\$21,994
<u>Fringe Benefits</u> (13.5% of Salaries except Graduate Student Researcher)	2,754	392	2,362
<u>Overhead</u> (70.3%) of Salaries	17,504	2,042	15,462
<u>Electronic &amp; Machine Shops</u>	4,000		4,000
<u>Expendable Material &amp; Supplies</u>	3,952		3,952
<u>Publication &amp; Reports</u>	2,500		2,500
<u>Travel</u>	1,500		1,500
<u>Communication</u>	500		500
<u>Permanent Equipment</u> (Details on separate budget sheet)	11,230		11,230
<u>Computer Terminal Rental</u>	2,500		2,500
	<hr/>	<hr/>	<hr/>
TOTALS	\$71,338	\$ 5,338	\$66,000
Allowance from Step Funding			\$44,000
1st year Additional Funds Requested			\$22,000

\*See Salary Schedule Attached to Letter of Transmittal

PROPOSED BUDGET

Year II: 1 May 1975 to 30 April 1976

"Laboratory Studies on the Excitation and Collisional Deactivation of Metastable Atoms and Molecules in the Aurora and Airglow"

E. C. Zipf

	<u>Total Research</u>	<u>University Contribution</u>	<u>Research Requested</u>
Anticipated Expenditures	\$ 71,338	\$ 5,338	\$ 66,000
Allowance from Step Funding			22,000
			<u>\$ 44,000</u>
Step Funding Requested 1/3 x 66,000			<u>\$ 22,000</u>

Full Budgetary details will be provided with the renewal proposal to be submitted prior to the next grant anniversary date.

Year III: 1 May 1976 to 30 April 1977

	<u>Total Research</u>	<u>University Contribution</u>	<u>Research Requested</u>
Anticipated Expenditures	\$ 71,338	\$ 5,338	\$ 66,000
Step Funding Requested 1/3 x 66,000			<u>\$ 22,000</u>

Summary of Funds Requested

Year I	-	1 May 1974 to 30 April 1975	\$ 22,000
Year II	-	1 May 1975 to 30 April 1976	\$ 22,000
Year III	-	1 May 1976 to 30 April 1977	\$ 22,000
GRAND TOTAL			<u>\$ 66,000</u>

#### G. PERMANENT EQUIPMENT BUDGET (Some Comments)

In the detailed budget presented in Section F we request permission to purchase some capital equipment that will substantially expand our capacity to investigate aeronomic and ecological problems of particular importance in planetary atmospheres. Some of the factors that helped guide us in formulating our equipment requests are the following:

From the inception of this program our laboratory facility has been noted for the remarkably large number of experiments (a dozen or more) that it has been able to carry out simultaneously with only a limited amount of equipment and personnel. This effectiveness can be traced to three factors (1) choosing the correct contemporary problems to work on; problems that are important and solvable using state of the art techniques, (2) the use of a central data-processing facility which services all of these experiments through a time-sharing scheme. This system permits us to control and review the data, and in real time to continually modify the data acquisition process itself. This, of course, substantially improves the quality of the primary data and decreases the amount of time, manpower and cost to achieve our objectives, and (3) wherever possible each apparatus is constructed using common building blocks. For example, conflat-style vacuum plumbing, standardized pulse amplifiers-discriminators, power supplies, etc. This allows us to borrow equipment from one apparatus, if the situation warrants, without encountering a compatibility or interfacing problem. In this manner we avoid having to maintain a large equipment reserve that is ineffectively used.

One acceptable consequence of the continuous use of our capital equipment is that it simply wears out, and in this budget we make a specific request (items II 5(a,b)) to purchase vacuum valves to replace existing but worn components in several of our experiments. This will assure continued peak utilization of our laboratory facility.

Up until now our attempts to study aeronomically important infrared emission features, which are excited by electron impact, have been hampered by the lack of a suitable photomultiplier tube with sufficient IR quantum efficiency and gain. RCA has now developed a new photomultiplier tube using a gallium-arsenide photocathode which is ideal for our purposes. Selected photomultiplier tubes of this type have quantum efficiencies as much as 30% at 8000 Å and when properly cooled residual background counting rates of only several counts/sec. Possession of such a tube would improve our experiments considerably and make it possible to extend the scope of the work substantially. In view of the numerous advantages that would accrue, we request permission to purchase a selected RCA photomultiplier tube.

We are the only group to my knowledge to attempt two very difficult experiments of central importance to the aeronomy community. The first experiment is concerned with measuring the inelastic collision cross sections for electrons impacting on atomic oxygen (the principal photoelectron cooling mechanism at F region altitude). The second study addresses itself to the role of hot atoms in the formation of nitric oxide under disturbed conditions, and involves painfully difficult (from the signal point-of-view) source-target problems. In both of these experiments we are in very great need for a sensitive

and accurate pressure measuring device which is "inert". Ionization gauges and other similar instruments create havoc in our apparatus because they are copious sources of x-rays, charged particles, metastable atoms, and just general electrical noise. In our judgment a well designed capacitance manometer is the best choice for this application. We need such an instrument to place our studies on an absolute footing and we request permission to purchase a Baratron capacitance manometer (Items II - 1a, b, c).

In the course of our preliminary work we have also found that many of our problems (e.g. the development of charging spots, contamination from the background gas, excessive outgassing, etc) could be reduced significantly if we increased the effective pumping speed of our vacuum system. We propose to accomplish this through the purchase of Items (II - 2, 3, 4). This modification to our apparatus would result in a nearly five-fold increase in pumping speed with much better baffling against oil backstreaming. Since this would allow us to pursue these experiments under much more favorable conditions, we request permission to purchase this additional equipment.

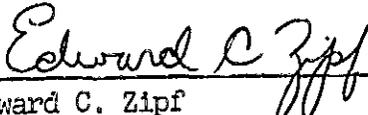
PERMANENT EQUIPMENT BUDGET

Year I: 1 May 1974 to 30 April 1975

"Laboratory Studies on the Excitation and Collisional Deactivation of Metastable Atoms and Molecules in the Aurora and Airglow"

I. Detectors:		
RCA [GaAs] Photomultiplier tube (selected for Q.E. and dark current)		\$ 1,000
II. Vacuum Components:		
1. (a) Baratron pressure head type 90H-1		1,580
(b) Baratron indicator type 100A-XR-2		3,725
(c) Type 1090-2 temperature controller		950
2. Granville Phillips Cryoclean trap		860
3. Varian gate valve with pneumatic control		1,880
4. Varian VHS6 pump		850
5. (a) Granville Phillips Model 202-038 Type C ultrahigh vacuum valve		385
(b) Granville Phillips Model 267-001 Auroseal valve		375
	TOTAL	<hr/> \$11,250

Submitted by:

  
\_\_\_\_\_  
Edward C. Zipf  
Principal Investigator

  
\_\_\_\_\_  
Philip Stehle, Chairman  
Department of Physics

Approved by:

\_\_\_\_\_  
Jerome L. Rosenberg, Dean  
Faculty of Arts and Sciences

\_\_\_\_\_  
Paul Solyan  
Comptroller and Assistant Treasurer