ATOMIC AND MOLECULAR PROCESSES IN ATMOSPHERIC ENVIRONMENTS

M. A. Biondi
Pittsburgh University

Prepared for:
Army Research Office (Durham)
Advanced Research Projects Agency

23 October 1972

DISTRIBUTED BY:
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151
ORDER NUMBER: The Advanced Research Projects Agency ARPA Order No. 826

NAME OF CONTRACTOR: Departments of Physics and Chemistry University of Pittsburgh Pittsburgh, Pennsylvania 15213

DATE OF CONTRACT: April 8, 1970

EXPIRATION DATE: June 30, 1973

CONTRACT NUMBER: DA-31-124-ARO-D-440

PROJECT SCIENTIST: M. A. Biondi, Director Professor of Physics

Telephone: Area Code 412 621-3500 Ext. 7571

TITLE OF WORK: ATOMIC AND MOLECULAR PROCESSES IN ATMOSPHERIC ENVIRONMENTS

October 23, 1972

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Faculty Members:

- J. N. Bardsley
- M. A. Bjondi
- L. T. Brackmann (To August 1972)
- T. M. Donahue
- W. L. Fite
- E. Garjuoy
- R. Johnsen
- F. Kaufman
- E. C. Zipf

Post-Doctoral Personnel:

- J. G. Anderson (Since September 1972)
- J. W. Bozzelli
- E. Enemark
- F. H. Faisal
- T. Finn
- R. G. Ganu (To July 1972)
- B. Guenther
- R. A. Catchick
- M. A. Hender (To August 1972)
- B. R. Junker
- T. Kondow
- H. H. Lo
- R. Nieman
- D. E. Shemansky
- D. Slpler
- E. J. Stone (Since May 1972)
- B. K. Thomas
- R. Thomas
- W. C. Wells

Graduate Research Assistants:

- R. Bain
- V. M. Bierbaum
- D. Brocklebank
- H. L. Brown
- B. Carnahan
- Y. P. Chong
- F. Erdman
- R. J. Girnius
- B. Kim

- S. Z. Levine
- S. C. Liu
- J. J. Margitan
- R. Myers
- C. V. Sukumar
- B. K. Thomas (To May 1972)
- G. Unger
- B. Wasser

Visiting Faculty:

NONE
I. Summary of Research

The following research projects are identified by title, senior investigator(s) in charge of the work, and task designation(s) in the ARPA work statement. This summary only covers advances during the period since our last progress report (dated April 28, 1972).

A. Laboratory Studies


Although some additional fluorescence measurements on NO₂ in a large new coolable cell are still contemplated it is now thought that these as well as the SO₂ fluorescence measurements which are about to be completed should be phased out of the ARPA program into whose principal areas of interest they do not fit sufficiently closely. Our earlier NO₂ studies (J. chem. Phys. 54, 355 (1971)) have greatly clarified the overall mechanism by showing the great importance of efficient, nearly gas-kinetic vibrational energy transfer in an electronically excited state of NO₂. The SO₂ work with excitation at 2800 to 3200Å in 100Å steps and radiative and collisional lifetime measurements by phase shift as well as by attenuation of the extent of modulation has shown large discrepancies between the results of the two methods which suggest the presence of two or more excited states of different radiative lifetimes. The lifetime measured by the phase shift method was also found to be
strongly dependent on modulation frequency, an additional indication that more than one excited state is involved in the process. This complication had not been encountered in NO₂ and can not be clearly resolved by phase shift methods which can only give weighted averages of the various lifetimes.

Flash excitation experiments, preferably highly monochromatic yet tunable (which are experimentally difficult in this wavelength range) and with sufficient intensity to show clearly the contributions of several distinct processes, could provide some of the answers, but can not now be undertaken.


We have largely completed our work on the direct and dissociative excitation (by electron impact on O, N, O₂, N₂, etc) of vacuum ultraviolet emission features in the important wavelength region 1100 - 2000Å which is surveyed by VELA-type satellites. Approximately 50 percent of this work has now been published; the remainder is being prepared or has been submitted for publication. The availability of these absolute cross sections combined with a specific determination of the electron energy degradation profiles from our sounding rocket work in auroras permits a virtually unique interpretation of terrestrial radiation in this wavelength region under disturbed conditions.

We are now concentrating our attention in the 500 - 1100Å wavelength region, which has been largely overlooked for surveillance purposes. A cursory look at absorption work in this region suggests that vast amounts of radiation will be radiated in this domain under disturbed conditions. Our own preliminary laboratory measurements suggest that this is so, and recent auroral measurements indicate that the total
intensity of the radiation emitted in the wavelength interval may be as much as 50 to 100 times the brightness of the OI λ5577 Å emission [which, of course, is the brightest visible feature in the aurora]. If, in fact, this view of the disturbed atmosphere is substantiated by our laboratory studies, it will show that, unfortunately, we have largely misdirected the emphasis of our satellite surveillance programs. In view of these implications, we are pursuing our EUV studies very actively.

**Infrared Emission from Recombination and Energy Transfer Processes of Air Species (F. Kaufman).**

Very good progress was made in our infrared measurements of the O + NO chemiluminescence from 1.2 to about 4.4 µm, the range of our first circularly variable filter, using either our PbS or In Sb nitrogen-cooled detectors. To cancel thermal backgrounds above 3 µm a double modulation system is employed in which, in addition to the 280 Hz modulation of the IR detectors, the O-atoms discharge source is modulated at 1 Hz, two phase sensitive lock-in amplifiers are used, and the signal is integrated for 50 to 100 seconds. The O + NO emission spectrum was found to drop sharply in intensity out to 3.2 µm where it increased to a maximum at 3.7 µm and then drops rapidly to very small values past 4 µm, in good agreement with earlier work by Stair and Kennealy. The 3.7 µm peak is possibly due to an overtone or combination band in the vibrational spectrum of NO₂ in either its ground or electronically excited state. A second CVF for the range 3.2 to 6.4 µm is also now being put into operation.

In order to make an absolute, spectrally resolved measurement of the second-order emission rate constant, \( I_o \) (\( \text{cm}^3 \text{ sec}^{-1} \text{ µm}^{-1} \)) = \( I/([O] [NO]) \), it became necessary to modify the pumping line and O-atom
titration system so that \( I_0 \) could be measured over a sufficiently wide pressure range (0.3 to 3 torr) without appreciable degradation of the square wave modulated emission wave form at the \( \text{Ca F}_2 \) window where the IR radiation is detected. This was successfully accomplished and the final, absolute results await only some modification of the reference black body whose internal temperature differences had been found to be too wide. The importance of these measurements lies not only in the need for having data on this IR chemiluminescence, but in their special usefulness as a secondary standard for laboratory measurements of other IR emissions in the 1 to 5\( \mu \)m range if the \( O + NO \) glow can be produced in the same system with similar optics and \([O]\) and \([NO]\) can be measured by standard techniques. This method is entirely analogous to that based on the absolute measurement of the \( O + NO \) glow in the visible by Fontijn, Meyer, and Schiff which has been used as a secondary standard by many investigators for the absolute actinometry of glows in the visible or near ultraviolet. Upon completion of this work a number of processes involving reactive and vibrational energy transfer to \( CO_2, H_2O, \) and \( NO \) will be examined.

2. **Clean Air Chemistry and Chemiluminescence** (F. Kaufman) (Tasks a and d).

(a) Both the low pressure visible/near infrared chemiluminescence kinetics of \( O + NO \) and the kinetic studies of the important atmospheric \( 0 + O_3 + 2 O_2 \) reaction were successfully completed and are now phased out. The results of the latter were published in J. Chem. Phys. in August (57, 1270 (1972)) and the former is being written up for publication and for presentation at the International Conference on Chemiluminescence in October 1972.

(b) Rapid progress continues to be made in our study of \( OH \)
reactions which are of great importance in the understanding of the natural stratospheric and mesospheric background. The reactions include the three-body processes \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \) and \( \text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \) and the slow two-body step \( \text{OH} + \text{O}_3 \rightarrow \text{H}_2\text{O} + \text{O}_2 \). They are studied by resonance fluorescence of OH near 3090Å in the \((0,0)\) band of OH \( ^2\Sigma-^2\Pi \) at the downstream end of a one-inch diameter flow tube, one meter long, with temperature controlled over the range -200 to 500°K, and with variable injection of stable reactant species.

Measured three-body rate constants of \( 1.0 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \) for \( \text{OH} + \text{NO}_2 + \text{Ar} \) and \( 2.0 \times 10^{-30} \) for \( \text{M} = \text{N}_2 \) have been obtained at 1-4 torr, 298°K, and some fall-off is observed in \( k \) between 4 and 10 torr. The expected negative temperature dependence is also observed and a preliminary value of \( m \approx 3 \) can be reported for \( k \propto T^{-m} \). The \( \text{OH} + \text{NO} + \text{Ar} \) reaction is somewhat slower than its \( \text{NO}_2 \) counterpart, with \( k = 0.5 \times 10^{-30} \) at 298°K and \( m \) is again found to be around 3 in a \( T^{-m} \) temperature dependence expression. The great sensitivity of the experimental method and its easy extension to the measurement of other species such as \( \text{O}, \text{N}, \text{H}, \text{CH}, \text{NH}, \text{etc.} \) in ground or electronically excited states makes this a particularly valuable tool for kinetic flow-tube studies. A preliminary account of our HNO\(_3\) work was submitted to and accepted by Chem. Phys. Letters for publication.


Much additional experimental work was done on our interferometric line shape studies of Na excitation to its \( 3p \, ^2P_3/2 \) state by active nitrogen and on the related studies of precursor quenching by added gases. Our initial observations were fully borne out by these experiments, i.e. the principal species responsible for the excitation
under our conditions (T=400°K, p=3.10 torr) are not vibrationally excited nitrogen, $N_2^+$, nor N-atoms by direct recombination, but some other electronically excited states. These conclusions are based on the fact that insertion of a glass wool plug between the microwave discharge and the Na mixing point had no effect on the D-line emission whereas NO-addition or insertion of a copper coil reduced its intensity by a factor of $\sim 20$, which rules out $N_2^+$; and small additions of NH$_3$ and somewhat larger ones of CO and CO$_2$ also quenched the Na glow severely without decreasing the nitrogen afterglow whose intensity is proportional to $[N]^2$ which rules out direct N-reactions. On the assumption that $N_2(A)$ is the main precursor and is removed either by the known quenching reaction with N or by reaction with the added species, Q, one can obtain $k_Q$'s of $-2 \times 10^{-10}$, $-5 \times 10^{-12}$, and $-5 \times 10^{-12}$ cm$^3$ sec$^{-1}$ for Q=NH$_3$, CO, and CO$_2$, respectively. The first two are in agreement with recent literature values, but the third appears to be too large. The measured Doppler temperature of $1500 \pm 200^\circ$K for the Na emission corresponds to a translational energy release of about 6 kcal/mole in a Na-$N_2^+$ collision which shows that close internal energy resonance is not an important consideration in the process. Our preliminary work was submitted to and accepted by Chem. Phys. Letters for publication.


Experiments were performed on the reactions of Ba and U atoms with O$_2$. $\text{Ba} + \text{O}_2 \rightarrow \text{BaO} + \text{O}$. This study is very nearly completed at this point. Improved angular distribution measurements agree with those previously determined in our laboratory. Particular attention was given to measurements of both BaO$^+$ and Ba$^+$ ions. The phase
differences of the signals were also studied in order to determine the extent to which Ba\textsuperscript{+} signals came from dissociative ionization of product BaO or from simple ionization of scattered Ba. In principle, such data can give a ratio of reactive to elastic scattering cross sections. Both can then be assigned from performing a separate experiment to measure the total cross section (i.e., reactive plus elastic scattering). The analysis of the experimental data is proceeding slowly but some progress in interpretation is being made.

The total cross section data indicates that the cross section is about $1 \times 10^{-16} \text{ cm}^2$ for ground state barium colliding with oxygen molecules. This is a slightly lower value than that given by the earliest data $\text{U} + \text{O}_2 \rightarrow \text{UO} + \text{O}$. This process is competitive with the associative ionization process, i.e., $\text{U} + \text{O}_2 \rightarrow \text{UO}_2^+ + e$. Attempts to examine the neutral reaction channel were not successful because of background provided by the associative ionization channel and it is evident that the mass filter configuration will have to be changed for the experiment to be fully successful. It was ascertained during the first attempts at this experiment that UO impurity coming from the U beam source will be more troublesome than the BaO impurity from the Ba source, and observing the product UO over the impurity UO may be very difficult. Some possible improvements in the uranium atom source are being considered.

5. Processes Involving Metastable Species (E. C. Zipf) (Tasks c and d).

We continue with our afterglow studies of metastable atoms and molecules of aeronomic importance. Although a variety of processes are currently under investigation, the most interesting experiment involves the dissociative recombination of CO\textsubscript{2}\textsuperscript{+} leading specifically to the
production of CO(A^1Π) molecules:

\[ \text{CO}_2^+ + e + \text{CO}_2^* \rightarrow \text{CO(A^1Π)} + O(3P) \]

which subsequently emit the Fourth Positive bands [CO(A^1Π) + CO(X^1Σ) + hv]. Our preliminary results show that this process has a net efficiency of several percent. This is quite surprising since this particular process would not be expected on the basis of the conventional theory of dissociative recombination. The reaction requires 13.7 eV, only 0.15 eV less than the ionization potential, so that conventional repulsive curves crossing the CO_2^+ potential well in the v' = 0 Franck-Condon region and leading to the observed separated states are not available.

A clue to what happens comes from our electron-impact studies on CO_2. Here an analogous process is observed.

\[ e + \text{CO}_2 \rightarrow \text{CO}_2^*(^1Σ) + \text{CO(A^1Π)} + O(3P) \]

The intermediate state has been identified, and pre-dissociation has been shown to be the basic mechanism involved. Presumably, the [CO_2^+ + e] reaction we have been studying also involves pre-dissociation. The experiment suggests that a variety of excited product states, which might not have been expected on the basis of the traditional theory of dissociative recombination, can be excited nonetheless with considerable efficiency. More experiments are planned.
6. **Ion Molecule Reactions and Excitation Processes in a Fast Flow System (F. Kaufman) (Tasks a and b).**

Additional series of experiments were performed on the formation and switching reactions of water cluster ions formed from $O_2^+$, especially in $N_2$ carrier gas, where the importance of $O_2^+\cdot N_2$ as an intermediate in the initial formation of $O_2^+\cdot H_2O$ was discovered by us. Although it was found to be of only marginal importance in our work at 296 K, it would be of increasing importance in the lower D-region. Our data in all four M-gases, He, Ar, $N_2$, and $O_2$ were analyzed and a total of 17 rate constants were obtained either directly from parent ion decays or indirectly by computer analysis of the known scheme of coupled pseudo-first-order rate equations involving $O_4^+$, $O_2^+\cdot N_2^+$, $O_2^+\cdot H_2O$, $H_3O^+\cdot OH$, and $H_3O^+\cdot H_2O$. These results show the expected range of $10^{-27}$ to $10^{-31}$ for the three-body formation rate constants of cluster ions and $10^{-9}$ to $10^{-11}$ for two body switching and rearrangement rate constants.

The relatively small k's of $10^{-20}$ to $10^{-31}$ for the formation of $O_4^+$ or $O_2^+\cdot N_2$, which are weakly bonded, can be understood in terms of a much smaller than Langevin cross section for the formation of the initial, energetic collision complex such as $O_2^+ + N_2 \rightarrow (O_2^+\cdot N_2)^*$, because angular momentum conservation requires the collision complex to have amounts of rotational energy, when the $O_2^+\cdot N_2$ distance has decreased to the $-2\text{Å}$ bonding range, which are of the order of total binding energy of the stabilized species. This greatly shortens the lifetime of the excited collision complex and thereby decreases the overall three-body rate constant. The same effect also requires that the process become second-order at a higher pressure and show a smaller second-order rate constant at the high pressure limit, a matter which has been confirmed experimentally for a number of known ion-molecule recombination processes.
Our work was submitted to and accepted by J. Chem. Phys. and will appear in the October 15, 1972 issue.

7. Reactions of Metal Atoms with Ions in Magnetically Confined NO\textsuperscript{+} Plasmas (W. L. Fite) (Tasks b and j)

The present reporting period has been given over primarily to improving the apparatus and techniques of this novel method of studying thermal ion-atom collision processes. Construction, testing and evaluation of the following items have consumed the major effort: (1) The magnetic field power supply and the field coils were modified so as to place a variable magnetic field "hill" between the light and the atom beam locations, (2) The Lyman-alpha radiation source was rebuilt so as to permit its easier removal and disassembly for maintenance and cleaning; (3) The insertion of a liquid-nitrogen-cooled trap for the atom beam was made, in order to minimize surface scattering and condensation onto the grounded inner shield of the experiment, where such condensation alters the work function over a small region of the shield and imposes a serious electric field problem.

In the course of these and other improvements, experiments on reactions of NO\textsuperscript{+} with Na, Ca, and Mg have been examined several times. While the later data seem to indicate smaller cross sections than were first estimated by Clendenning who did the early work on this experiment, Clendenning's observations that charge transfer greatly dominates over ion-atom reaction are confirmed.

8. Ion Molecule Reactions at Elevated Temperatures (M. A. Biondi) (Tasks b and j).

The work on the reaction of uranium ions with oxygen and of neutral uranium with oxygen has been finished and an article describing these measurements has been published in the Journal of Chemical Physics.
Further experiments, however, are planned on possible reactions of UO+ with O2 and U+ with nitric oxide. New electronic components for the RF mass spectrometer have been purchased that will permit us to operate the mass spectrometer at high masses without the previously encountered noise problems (due to electrical breakdown in the mass filter).

It was found that our earlier determination of the ionic mobility of uranium ions in the helium buffer gas was in error because of unforeseen ion injection effects (the mobility of the parent ion in the buffer gas determines the energy scale of ion molecule reactions measured in a drift tube and must therefore be known accurately). We have remeasured the mobility of uranium ions in helium and found a value of 16.0 x 0.5 cm²/V sec (at 300 K and a standard density of 2.69 x 10⁻¹⁹ cm⁻³). To test the validity of our experimental technique we also remeasured the mobility of mercury ions in helium and obtained excellent agreement with published data. A paper describing the results of these measurements has been accepted for publication in The Journal of Chemical Physics.


We continue to investigate the properties of metastable atoms and molecules, and Rydberg states using translational-energy spectroscopy. During this report period we have explored the implications of some of these results. Briefly:

(a) Emission Line-Shapes Produced by Electron Impact Dissociative Excitation of Atmospheric Gases. Emission line-shapes for the OI(⁵S⁰-³P) transition have been computed from previously reported¹ time of flight spectra
of \(O(5s^0)\) atoms excited by electron impact on \(O_2\), \(CO\), and \(CO_2\). The profiles exhibited a characteristic flat-topped appearance; the line widths were found to increase as a function of the incident electron beam energy reaching a maximum around 150 eV. Computed line-shapes at these energies are compared to Doppler line profiles with temperatures ranging up to 50,000 K. It is quite likely that allowed transitions produced by dissociative excitation would display broad line-shapes similar to those of the forbidden 1356 Å transition. These results have far ranging implications concerning radiative transfer calculations in planetary atmospheres where dissociative excitation plays a major role.


(b) **Lifetime and Cross Section of an Unidentified Metastable State in Carbon Monoxide.** The electron impact excitation function and radiative lifetime of an unidentified metastable state in CO has been investigated from threshold (~10 eV) to 45 eV using a time-of-flight apparatus. The measured lifetime at the peak of the excitation function (15 eV) was found to be 97 ± 15 usec. The absolute cross section at 15 eV was estimated to be \(3 \times 10^{-18}\) cm\(^2\) to within a factor of 2. Other investigators who have observed this 10 eV state\(^1,2\) have tentatively identified it as the \(b\ 3\ell^+\) state. This assignment is inconsistent with the fact that the observed lifetime
reported here is three orders of magnitude longer than that for the \( \text{b} \ 3\Sigma^+ \) state. The shape of the cross-section does suggest, though, that the state is a triplet.


We continue to develop a controllable source of kinetically energetic atoms (0.1 - 200 eV) in order to study hot atoms and molecules collision processes of importance in the upper atmosphere. In the aurora, in particular, dissociative processes produce copious fluxes of kinetically energetic atoms which may react with \( \text{O}_2 \) and \( \text{N}_2 \) to form NO molecules. The collision chamber and accessory mass spectrometer that will be used in these experiments are nearing completion so that the actual experiment should be underway shortly.

B. Ground Based Observations, Rocket and Satellite Measurements, and Aeronomy Calculations.

10. Optical Interferometer Studies of the Upper Atmosphere (M. A. Biondi) (Task 8).

The 150 mm aperture Fabry-Perot interferometer, intended as a back-up for the 100 mm FP used in the barium release studies, has been completed (under another contract) as a substitutional instrument in the 100 mm FP telescope and scanning mount. As part of the PASI program, we are also completing the 150 mm FP as an independent interferometer instrument to permit studies of chemi-excitation processes in the upper atmosphere. When completed and installed in the Airglow Observatory at Laurel Ridge, the 150 mm FP will be used to measure the profiles of the Na D_2 (and D_1) lines emitted faintly from the night-time ionosphere. These studies will clarify the source
of the radiation, which is believed to be one of several possible chemi-excitation reactions.

11. Optical Photometer Studies of Nightglow Ionospheric Modification (M. A. Biondi) (Task g).

An article detailing our O(1D) quenching determinations in the F-region from analyses of the 6300Å intensity enhancements produced by the Platteville transmitter has been accepted for publication in the Journal of Geophysical Research.

In May we achieved first success in detecting similar 6300Å intensity transients produced by the Arecibo heating transmitter (of smaller power-aperture product than that of Platteville). Optical experiments at Arecibo are greatly enhanced in value by the simultaneously recorded radar backscatter observations of plasma line (energy absorption) heights, T_e, T_i, etc. Considerable time has been spent in reducing the optical photometer data, and O(1D) lifetimes have been obtained from the better quality runs which will permit a determination of the optical emitting heights for comparison with the enhanced plasma line heights.


During this report period we have continued to analyze the results of four highly successful sounding rocket experiments: (1) Aerobee rocket 13.46 UA was launched into a developing, dawn ionosphere above White Sands, N. M. on January 1971. This flight was a joint effort with the Johns Hopkins University and it achieved several important goals. Firstly, it provided a direct, in-situ test under quiet atmospheric conditions of our double-mode mass spectrometer and showed conclusively that the instrument functioned properly in both
modes. No ion punch-through was observed that could have accounted for the large amounts of nitric oxide observed by us [Aerobee 4.309 UA] in an intense auroral arc above Fort Churchill. Secondly, the flight took place in the aftermath of a very large solar flare (class 3) which was accompanied by large X-ray and proton fluxes, and ultimately produced a PCA event lasting 3 days. The flare occurred at 4:30 MST the evening preceding the launch. We believe now that the hard X-rays ($\lambda < 20\text{Å}$) created large quantities of $O^{++}$ during the twilight period and that these ions persisted throughout the night. The ion mass spectrometer on board 13.46 UA detected large concentrations of these ions ($\approx 10^{4}$ cm$^{-3}$) above 200 km the following morning. This is the first observation of such large quantities of $O^{++}$ ions at these altitudes.

We are now studying this problem in detail.

The time of launch (7:25 MST) had been selected with considerable care so that the various excitation mechanisms contributing to the emission of $\lambda 5577$ and $\lambda 6300$ in the dawn airglow would be spatially separated; photoelectron impact at high altitudes ($> 220$ km), dissociative recombination of $O_2^+$ ion in the mid-altitude range (180 - 220 km), and the Chapman mechanism at low altitudes (below 110 km). This separation, which allows a more detailed study of these processes, was observed as planned. The data, however, clearly revealed the presence of an additional source of $O(1S)$ atoms in the region from 100 - 180 km. A detailed study of the results (submitted for publication) shows conclusively that photodissociation of $O_2$ by solar photons in the 1244Å and 1292Å region is largely responsible for the $\lambda 5577$ signal in this altitude region. This is the first direct experimental confirmation of the important role played by
photodissociation as a green line source in the dayglow.

(2) On 25 June 1971 an Aerobee 350 rocket (17.09 UA) was launched from Wallops Island, Va. during twilight. This experiment, conducted jointly with the Johns Hopkins University, complemented our dawn experiment at White Sands. In addition to providing data on the brightness and altitude distribution of many airglow features in the visible and vacuum ultraviolet region, simultaneous measurements of the ion, electron and neutral composition of the upper atmosphere (from approximately 120 - 300 km) were obtained. Once again the double-mode instrument performed flawlessly. This was most encouraging since this was a new instrument with a more advanced design which would be flown ultimately into auroral arcs on two rockets [Nike Apache 14.486 UA and Aerobee 4.320 UA] during February and March of 1972.

(3) After a delay of two years we resumed our auroral studies and our search for enhanced nitric oxide concentrations in bright auroral arcs. Two payloads were prepared and subsequently flown on a Nike Apache rocket (14.486; launched 14 February 1972) and an Aerobee 150 rocket (4.320 UA; launched 16 March 1972). The Aerobee experiment was conducted in collaboration with the Johns Hopkins University. Both vehicles were launched into bright auroral forms (class II+ aurora) which were strikingly different in three respects. The Nike Apache payload was launched into an active arc which was characterized by a large magnetic bay (- 400 gammas) and a very low $\lambda_{5577}/\lambda_{3914}$ ratio (- 1); the experiment took place in the pre-midnight magnetic quadrant. This form was quite similar to the arc studied by Aerobee rocket 4.309 (28 March 1970) and the mass spectrometer once again
observed a substantial NO enhancement. This form was quite structured so that the vehicle moved through patches of NO as it traversed the arc. The ion composition was observed to vary in a manner reflecting the nitric oxide buildup.

The Aerobee experiment provided a remarkable contrast. First of all, the aurora occurred in the post-midnight magnetic quadrant and exhibited little magnetic activity ($\Delta H < 25$ gammas). Further, the $\lambda 5577/\lambda 3914$ ratio was approximately 2 and strikingly constant with altitude. Finally, the neutral mass spectrometer did not detect any significant quantities of nitric oxide. We are now in the process of carefully organizing the data from these highly successful flights focusing our attention particularly on the NO and $\lambda 5577A$ problems which continue to be enigmas. A sample of the neutral mass spectrometer data from the Nike Apache experiment is shown in the accompanying figure.

The analytic phase of our work has been balanced by the feverish activity surrounding the preparation and planning of six rocket payloads which are scheduled for launching during the next twelve months: (1) We are preparing (jointly with the aeronomy group at Johns Hopkins University) an Aerobee 170 payload to be launched from White Sands, N. M. in support of Apollo 17. The experiment will involve simultaneous measurements of pertinent solar EUV fluxes, terrestrial airglow features, ion, neutral and electron concentrations and temperatures. (2) We are re-furbishing our Nike Apache auroral payload and are scheduled to return to Fort Churchill for a launching during the last week of February (1973). This flight will continue our study of anomalous nitric oxide production in auroral arcs.
(3) We are in the final stages of preparing a new payload to be launched in late spring (1973) under daytime conditions on board a Javelin rocket. The primary objectives of this experiment are to study atomic oxygen resonance radiation in the dayglow and to test an entirely new type of mass spectrometer which uses optical techniques and is largely free of the sampling problems that plague conventional mass spectrometers. This is basically a high-altitude experiment (250 – 800 km) which is essential for a clearer understanding of the radiation entrapment problem in a planetary atmosphere. (4) A new mesospheric payload has been developed for measuring the composition of the atmosphere at altitudes above 50 km. The first flight for this payload is scheduled during August 1973. (5) We have initiated a joint auroral program with G. Shephard and R. A. Young of York University, Toronto. This effort will involve two Black Bryant-5 rockets that will be elaborately instrumented for auroral studies and will be flown early in the fall of 1973. The firings will be coordinated. The first rocket will be fired into an active aurora exhibiting the characteristic diagnostic signs associated with anomalous NO concentrations. The second rocket will be launched after the auroral activity has subsided in order to study the temporal characteristics of this problem.

C. Model Calculations of Atmospheric Composition and Response

13. Composition of the Mesosphere and Lower Thermosphere (T. M. Donahue) (Task b).

As a result of partial analysis of airglow and auroral emission data obtained with the University of Pittsburgh photometer experiment aboard OGO-6 we have definitive proof that the southern polar atmosphere is drastically different from the northern polar
atmosphere. In northern winter at high northern latitudes there is almost twice as much atomic oxygen near 100 km as there is at comparable southern latitudes. On the other hand during southern winter there is little excess (atomic) oxygen at southern latitudes over northern latitudes. This is probably the result of a different seasonal variation in eddy diffusivity in the two hemispheres. Turbulent mixing in the mesosphere and lower thermosphere appears to vary seasonally by a factor of two in the south (K Dec ≈ K May/2) but not in the north. The evidence has been obtained by measurements based on the vertical profile of the atomic oxygen green line (5577 Å) in the day and night airglow. The implications of this result could be profound for the distribution of major (O₂ & O) as well as minor species: NO, NO₂, CO, OH, HO₂, H, O₃ and H₂O, and for auroral and airglow emissions in the visible and IR. Results on atmospheric properties obtained at high northern latitudes where most have been accumulated are not necessarily applicable to southern latitudes.

We propose to continue to analyze other airglow and auroral data from that satellite experiment with a view to extracting all of the important information concerning hemispherical asymmetries. We also plan to develop models for atmospheric composition in the southern summer stratosphere, mesosphere and thermosphere and to predict natural airglow and auroral emission properties that will result.

We also plan to begin adapting one of our Nike Apache auroral aeronomy payloads for possible launch in the southern auroral zone.

Another important discovery with the OGO-6 photometer was
a dense but geometrically thin layer of aerosols (50 cm\(^{-3}\) ice crystals 1500Å in radius in a layer 1-5 km wide at 85 km) which develops near the summer polar mesopause. This is an extension of noctilucent clouds into the daylit polar atmosphere where they are about 50-100 times as thick optically. These aerosols could be strong IR emitters. We plan to develop techniques for further study of these layers.

D. Theoretical Studies


(a) Glauber Theory Calculations. Our calculations of charged particle-neutral atom collision cross sections using the Glauber approximation continue, and continue to excite interest. Our results on closed-form expressions for Glauber \(e-H(1s)\) cross sections, and our inferred asymptotic low energy and high energy limits—described in our previous Technical Progress Summary No. 12—has been written up and accepted for publication by the Journal of Applied Physics. More recently, Dr. Thomas has begun an examination of the possibility of extending our methods to more complex atoms. As we have explained in previous Technical Progress Summaries, making the Glauber calculations for more complicated atoms feasible without excessive use of computer time remains the major task of the theory, if the Glauber is to have any use in such atoms more complex than hydrogen. In particular, Dr. Thomas is programming what seems to be a practical reduction of the Glauber integrals in \(e-He\) collisions, and expects to generalize this reduction to \(e-Li\) collisions as soon as the \(e-He\) program is completed. A student (Dave Brocklebank) is continuing some \(e-H(1s)\) Glauber calculations designed to elucidate,
if possible, the regimes in which the Born, Vainshtein and Glauber approximations differ and agree. Specifically, he is computing the angular correlation between scattered electrons and emitted photons in $e$-$H(1s)$ excitation, to the $n = 2$ and $n = 3$ levels of hydrogen, using the Born, Vainshtein and Glauber approximations.

We add that the continued interest in our Glauber work is indicated by the following two invitations: (i) E. Gerjuoy, to give an invited talk on Glauber theory at the American Physical Society Division of Electron and Atomic Physics (DEAP) meeting November 1972, Palo Alto, California, and (ii) to E. Gerjuoy and Brian Thomas, to write a review on Glauber theory for the prestigious British Journal Reports on Progress in Physics.

(b) Rotational Excitation Studies. We have continued our studies of the cross sections for rotational excitation of molecules by slow collisions with neutral particles, whose initiation was described in our last Technical Progress Summary. This work is being done in collaboration with Dr. Faisal, and recently has received partial support from NASA. As explained in our previous Technical Progress Summary, a main objective of this work is to examine the applicability of Chase's so-called adiabatic approximation to rotational excitation by molecules. If it is applicable, Chase's method would offer a significant advance in the theory of such collisions, which presently usually are treated by the very arduous close-coupling method. To evaluate the adiabatic method, it is necessary to compare with reasonably reliable close coupling results. The only collisions fitting this category are $H_2$ rotational excitation by atomic hydrogen, and perhaps by helium. But even for these
comparatively simple collisions discordant close-coupling results have been reported in the literature. We are pursuing this subject vigorously, and are endeavoring to get some other groups, notably at Rice Institute (Prof. Lane) to independently repeat the close coupling calculations on $\text{H}_2$ rotational excitation.

15. **Formal Collision Theory**

(a) **Development of Variational Methods (E. Gerjuoy).** In our last Technical Progress Summary we reported initiation of a study of the utility of variational principles of non-standard type, in collaboration with Prof. L. Spruch at New York University. This work has made very good progress, including acceptance by the J. of Math. Physics of a paper on variational identities which may point the way toward development of techniques for obtaining variational bounds on quantities such as oscillator strengths and polarizabilities; at any rate, this paper generalizes a variational identity (the so-called Kato identity) which has been used to obtain bounds on scattering cross sections. In addition a long paper, really partly a review, on routine procedures for obtaining variational principles for all sorts of quantities both quantum mechanical and classical (e.g., the electric field in the neighborhood of charged conductors of arbitrary shape), is being prepared, still in collaboration with Prof. Spruch. We have high hopes for this work, which we believe has the potential for a significant advance in the computation of many quantities, by making variational estimates of such quantities practical, and perhaps even by furnishing variational bounds within which the quantities will have to lie. In fact, we anticipate that E. Gerjuoy's efforts next year will largely be concentrated on such formal
variational principle theory.

(b) **Minimum-Variance Method (J. N. Bardaley)**. Our tests of this method on a simple potential scatter problem have been completed, and the results accepted for publication. We have shown that accurate estimates of the phase shift can be obtained with very little computation, using a method that is very simple. We also were able to show that for certain potentials rigorous bounds can be obtained on the phase shifts. Further tests on e-H scattering are in progress. We have not yet obtained satisfactory results on this system and are not yet able to decide whether or not this method will be of value for systems of real physical interest.

(c) **Resonances in Electron Scattering (J. N. Bardaley)**. Our investigations into the use of complex coordinates in the determination of the position and width of resonances have continued. We first tried to implement a method suggested by Nuttall, by application to the lowest $^1S$ resonance in e-H scattering. We found the convergence of the calculated values for the width to be unsatisfactory. We, therefore, developed an alternative method in which the integrals over complex coordinates are transformed to integrals involving only real coordinates. Rapid convergence was obtained with this technique and we believe our results to be accurate to about 0.001 eV. Our results are consistent with experiment and most previous theoretical studies. In spite of the success of the method we are as yet unable to construct a formal proof that our procedure should converge to the correct answer. We next plan to apply this technique to e-He scattering, and we are still confident of obtaining results with an error of only a few meV, thus providing an accurate calibration point
for the energy profiles of electron beams.


Our computer code, through which the pseudopotential method can be applied to any atom with a small number of valence electrons, has been completed and applied to several systems. The valence energy of the ground state of Be was calculated using five different forms of the pseudopotential. The largest error obtained was 0.05 eV (0.2%). These results confirm that the results do not strongly depend on the form of potential used, and that the accuracy can be as high as that of ab initio calculations, even for such small systems.

In connection with our Be studies, we have examined the following problem. The spectrum of BeI contains several lines that have been attributed to the (3s) (2p) \(^3\)P state. This state is above the ionization threshold and there are no selection rules which forbid its auto-ionization. It has been recently suggested that several lines, which were previously unassigned or wrongly assigned, may be due to transitions involving the (3s) (2p) \(^1\)P level. This state ought also to auto-ionize rapidly. However, in calculations of the photo-ionization spectrum of Be this singlet state appears as a wide resonance. This latter feature suggests that the lifetime of the state may be less than \(10^{-15}\) sec, in which case it would clearly not be associated with discrete spectral lines. We are currently calculating the lifetime of this state and studying its effect on the photoionization cross section in order to see whether these spectral assignments can be correct.

The electron affinities of the alkalis, Li through Cs, have
been calculated. The value for Li, 0.60 eV, compares well with previous ab initio and model calculations; that for Na, 0.54 eV, is in agreement with both ab initio calculation and experiment. Our results for K, Rb and Cs should be the most reliable values so far obtained, either from theory or experiment.

A similar code for diatomic molecules has been completed. It is being applied to several systems by B. R. Junker, who has recently left the Institute to join the University of Georgia. A simple scattering code is also almost ready and will soon be tested on e-Li scattering. A review article describing the basis of the pseudopotential method and the scope of its applications is presently being prepared.

17. Low Energy Atom-Atom Collision Cross Sections (J. N. Bardley).

After completion of the calculations on Li$^+$-Li scattering, which were described in our last report, studies of the first row hydrides were initiated. Potential curves have been obtained for two excited $^2\Pi$ states of CH. These curves indicate that dissociative recombination of CH$^+$ should occur rapidly, and reveal several reaction paths for electronic excitation in C-H collisions.
II. Publications and Technical Presentations

A. Publications


"Inner Shell Ionization in Ion-Atom Collisions", J. N. Bardsley, Comments on Atomic and Molecular Physics, to be published.


"Measurements of O(1D) Quenching Rates in the F Region", Dwight P. Sipler and Manfred A. Biondi, J. Geophys. Res., to be published.


"New Results on Applications of Glauber Theory to Atomic Collisions", Brian Thomas and E. Gerjuoy, Third International Conference on Atomic Physics, August 7-11, 1972, Abstracts of Papers, pp. 262-264.


B. Technical Presentations


M. A. Biondi presented a colloquium at University of Alabama at Huntsville, Alabama, May 19, 1972.


"Modulated Beam Mass Spectrometry", W. L. Fite, Institute of Chemical Physics, Moscow, September 7, 1972.

"Reactions between Metal Atoms and Gases", W. L. Fite, invited colloquium at Ohio State University, October 13, 1972.

"Recent Progress in the Application of Glauber Theory to Electron-Atom Collisions", E. Gerjuoy, Seminar at Lebedev Institute (Moscow) and at the Ioffe Institute (Leningrad) during May 1972.

"The Construction and Use of Variational Principles in Quantum Mechanical Calculations", E. Gerjuoy, Seminar at the Lebedev Institute
(Moscow), at the University of Leningrad and at the Latvian Academy of Sciences Institute (Riga), during May 1972.

"Detailed Balance in the Time-Dependent Impact Parameter Method", E. Gerjuoy, Seminar at the Lebedev Institute (Moscow) and at the University of Leningrad, during May 1972.

"The University of Pittsburgh Atomic and Molecular Physics Program", E. Gerjuoy, colloquium at the Lebedev Institute (Moscow), at the University of Leningrad, and at the Latvian Academy of Sciences Institute (Riga), during May 1972.


"Gas Phase Ion-Molecule Reactions Involving Water", F. Kaufman, invited seminar at Louisiana State University, New Orleans, La., April 28, 1972, and at Ohio State University, Columbus, Ohio, May 22, 1972.

"Absolute Cross Section for the Dissociative Excitation of OI(5S0) and its Radiative Lifetime", W. C. Wells and E. C. Zipf, paper presented at the Spring meeting of the American Geophysical Union, April 1972.


C. Activities Relating to ARPA

M. A. Biondi attended the Secede Final Data Meeting, Washington, D. C., April 11-12, 1972.

M. A. Biondi attended the ARPA Optical Planning Meeting, June 6, 1972, in Washington, D. C.

M. A. Biondi attended the ARPA Arecibo Optical Results Meeting on June 28, 1972 in Washington, D. C.


D. Other Activities

J. N. Bardasley is a member of the program Committee for the American Physical Society Division of Electronic and Atomic Physics.
J. N. Bardsley attended the International Conference on Inner Shell Ionization Phenomena, Atlanta, Georgia, April 17-21, 1972.


J. N. Bardsley is visiting the IBM Research Laboratory in San Jose, California from September 21st to December 20th 1972.


T. M. Donahue, NAIC Advisory Board (Arecibo-Cornell) to President Corson - Arecibo, March 1972 and Ithaca, October 1972.

T. M. Donahue is chairman of the Board of Trustees, Upper Atmosphere Research Corporation

T. M. Donahue was elected vice chairman, Solar Planetary Section, AGU, 1972.


T. M. Donahue was member, NASA SSG for Grand Tour/Mariner-Jupiter-Saturn Mission.
T. M. Donahue attended NASA planning panel meeting to plan a Magnetospheric program, Cornell, July 1972.

T. M. Donahue was appointed member of the NAS Standing Committee on Polar Research, and the NAS Aeronomy Panel. He is already a member of NAS standing committees on Sounding Rocket Research and Potential Contamination and Interference by Space Experiments.

T. M. Donahue completed sabbatical year at Center for Planetary Physics, DEAP, Harvard University, July 1972.

T. M. Donahue is an Associate Editor of Review of Geophysics and Space Physics, and Planetary and Space Science.

W. L. Fite attended the IUPAP U.S. National Committee Meeting, April 27, 1972.

E. Gerjuoy has been serving (since October 1971) as Coordinator (Editor) with Prof. Bederson of New York University, of the Journal "Comments on Atomic and Molecular Physics", published by Gordon and Breach.

E. Gerjuoy spent a month (4/25/72 - 5/26/72) in the Soviet Union as a guest of the Soviet Academy of Sciences, lecturing and visiting laboratories in Moscow (Lebedev Institute), Leningrad (Ioffe Institute) and Riga (Latvian Academy of Sciences Institute). He also spent two days at the University of Warsaw on the way back to the United States.

E. Gerjuoy visited New York University on several occasions, to pursue his collaboration on variational principles with Prof. L. Spruch.

E. Gerjuoy spent the months of July and August at JILA, working on variational Principles and discussing various theoretical problems with members of the ARPA Institute at JILA.

During his residence at JILA, E. Gerjuoy attended the Third International Conference on Atomic Physics, at JILA, August 7-11, 1972.
F. Kaufman, was chairman of a session of the 14th International Combustion Symposium at Penn State University, University Park, Pa., on August 21, 1972.

F. Kaufman agreed to serve as a member of a new Committee of the National Academy of Sciences on the Department of Transportation's Climatic Impact Assessment Program for a three-year term. He also agreed to serve as a member of a new Panel on Aeronomy of the Committee on Solar-Terrestrial Research of the National Academy of Sciences for a three-year term.

E. C. Zipf attended the 3rd International Conference on Atomic Physics at the University of Colorado, Boulder (August 7-11, 1972).

E. C. Zipf attended a planning meeting at York University, Toronto, Canada (September 19, 1972) to initiate a joint Canadian-American auroral program involving the launch of two Black Bryant 5 rockets from Fort Churchill.

III. Visiting Scientists

R. P. Anders, Princeton University

A. L. Broadfoot, Kitt Peak National Observatory

W. Chupka, Argonne National Laboratories

M. A. A. Clyne, Queen Mary College, London, England

A. Dupasquier, Institute for Physics, Milan, Italy

D. G. Horne, The University of Leeds, England

M. Inokuti, Argonne National Laboratories

R. W. Klingensmith, Battelle Memorial Institute

J. E. Mentall, NASA, Goddard Space Flight Center

Warren Moos, The Johns Hopkins University

Jean Pascal, from Saclay, France
Edward Salpeter, Cornell University

G. Sørensen, Institute of Physics, University of Aarhus

L. Spruch, from New York University

P. Thaddeus, from NASA Institute, New York

IV. Degrees Awarded

Brian Thomas, Ph.D, April 1972
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<th>Senior Investigator</th>
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**Total Expended and Committed**

1,963.8

**Available Funds**

2,245.8

**Estimated Remaining Funds as of 10/1/72**

282.0

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**University Accounting of Funds**

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