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IN ATMOSPHERIC ENVIRONMENTS

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Brief summaries are given for the following topics: radiative properties of simple atoms and molecules for optical discrimination studies; dissociative excitation of CO(A1Π) by electron impact on CO2; infrared emission from recombination and energy transfer processes of air species; clean air chemistry and chemiluminescence; energy partitioning in metal atom chemi-excitation; neutral-neutral reactions in crossed beams; processes involving metastable species; ion-molecule reactions and excitation processes in a fast flow system; reactions of metal atoms with ions in magnetically confined NO+ plasmas; ion-molecule reactions at elevated temperatures; afterglow studies of the population of excited atomic and molecular states by vibrational energy transfer; time of flight experiments; optical interferometer studies of berium releases; optical photometer studies of nightglow ionospheric modification; measurement of the ionized and neutral constituents of the atmosphere; distribution of gases in the mesosphere; and semiempirical methods for estimating reaction rates.

Atomic physics
Molecular processes
Earth atmosphere
Excitation
Recombination reactions

Electron impact
Infrared radiation
Quantum interactions
Chemiluminescence
Upper Atmosphere

Crossed beam studies
Metastable state
Ionization
Plasmas (physics)

Afterglow
Auroras
Ionosphere
Reactions
Pittsburgh Atmospheric Sciences Institute

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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 October 28, 1971).

A. Laboratory Studies


Experimental studies on important diatomic molecules continued in two directions: (a) extension of lifetime measurements as function of accessible parameters; and (b) design and construction of a new fluorescence cell for improved mechanistic studies. Under (a) several large series of experiments were performed with SO₂ excitation at 2800, 2900, 3000, 3100, and 3170Å, all at about 30Å full width at half height, each at many pressures in the $10^{-4}$ to $10^{-2}$ torr range, with incident radiation modulated at 8 or 16 kHz, and with lifetimes calculated both from measurements of the phase angle and of the modulation of the fluorescent signal. Although our as well as other investigators' early results seemed to indicate large changes in radiative lifetime with excitation energy, suggesting two or more excited states, recent experiments have yielded constant lifetimes in the 50-60 μsec range by the
'fraction of modulation' method. The origin of this discrepancy is under further investigation. For (b), a new copper fluorescence cell of 16 cm diameter was fabricated which can be heated or cooled over a large temperature range. The cell is fitted with a detachable end plate and quartz windows, and its internal metal surfaces are about to be gold-plated. Temperature control will be valuable in showing the contribution of vibrationally excited states in the initial excitation process as well as the temperature dependence of subsequent collisional relaxation processes.


Our work on the dissociative excitation of aeronomically important gases by electron impact continues. These molecular studies are complemented by an elaborate series of experiments on reactive gas targets such as O, N, H, and C. We have recently completed a detailed study of CO$_2$ which will appear soon in the Journal of Chemical Physics. The principal results of this work are summarized in the following abstract:

Vacuum ultraviolet multiplets of CI, CII, and OI have been produced by electron impact on CO$_2$. Absolute emission cross sections for these multiplets have been measured from threshold to 350 eV. The electrostatically focussed electron gun used in this series of experiments is described in detail. The atomic multiplets which were produced by dissociative excitation of CO$_2$ and the cross sections at 100 eV are: OI(2p$^4$ 3P$^o$ - 2p$^3$3s 3S) 1304 Å - 1.04 x 10$^{-18}$ cm$^2$ ± 18%; CI(2s$^2$2p$^2$ 3P$^o$ - 2s2p$^3$ 3P$^0$) 1329 Å - 2.67 x 10$^{-19}$ cm$^2$ ± 21%; CI(2s$^2$2p$^2$ 3P$^o$ - 2s2p$^3$ 3D$^0$) 1561 Å - 7.50 x 10$^{-19}$ cm$^2$ ± 30%;
CI(2p² ³P - 2p3s ³P⁰) 1657Å - 1.45 x 10⁻¹⁸ cm² ± 23%;
CII(2s²²p ⁵P⁰ - 2s2p² ⁵D) 1335Å - 7.60 x 10⁻¹⁹ cm² ± 22%;
and CII(2s²p² ⁵D - 2p3 ⁵P⁰) 1324Å - 1.33 x 10⁻²⁰ cm² ± 23%.
The dependence of the excitation functions in electron energy shows
that these multiplets are produced by electric dipole-allowed transitions in CO₂.

Corroborative studies on CO and CO₂ have revealed new complications that are of particular importance to aeronomists studying CO₂ atmospheres.

1b. Dissociative Excitation of CO(A¹Π) by Electron Impact on CO₂
(E. C. Zipf) (Tasks a and d).

The CO fourth positive band system (A¹Π - X¹Σ) has been excited by electron impact on CO₂ and the shapes of specific vibrational bands have been measured at various electron energies (20 - 300 eV). The observed band shapes show that the CO(A¹Π, J') fragment is produced with a non-thermal rotational distribution cannot be characterized by a single rotational temperature for all J' levels, but a typical "effective temperature" is ~ 1500ºK for J' ~ 20. Furthermore, the rotational distribution is found to vary strongly with the incident electron energy below ~ 40 eV, and also exhibits a dependence on the vibrational level (v'). It is expected that fourth positive bands (v', v'' ≠ 0) which are produced by dissociative excitation of CO₂ by photoelectron impact will not be subject to appreciable resonance trapping because the ambient CO is predominantly v'' = 0. Our data show that this conclusion applies to the bands (v', 0) as well. Thus, attempts, to derive the column density of CO will lead to an upper limit only.

Our work on the H₂ Werner-band system has just been published
in the Journal of Chemical Physics. Our studies on nitric oxide have also been accepted for publication and will appear soon in JCP. To complement this work we are actively studying $N_2O$ and NO$_2$ both optically and in time-of-flight experiments.

We have concluded an intensive study of the excitation of the OI and NI resonance states by electron impact on O, O$_2$, N, and N$_2$. This work is now being prepared for publication. The scope of these experiments is now being expanded to include extreme ultraviolet, visible, and infrared OI and NI emissions features. The intent here is to provide the necessary absolute cross section data needed to support our rocket probings of these spectral regions in the aurora and airglow.

1c. **Infrared Emission from Recombination and Energy Transfer Processes of Air Species (F. Kaufman)**

Quantitative studies of SWIR emissions from 1.2 to 4.4 microns, with emphasis on 2.7 and 4.3 microns, are well under way in a steady-state flow system. Liquid nitrogen cooled PbS and InSb detectors are used, the chemiluminescent radiation passes through a circularly variable filter of 2% spectral bandpass, is modulated at frequencies in the 200 to 300 Hz range and its intensity is measured with a lock-in amplifier. Early experiments have examined the near infrared component of the ubiquitous $O + NO$ radiation when NO is added just upstream of the MgF$_2$ window of the viewing region. The measurements are put on an absolute basis by viewing an accurately constructed black body furnace at known temperature and geometry through the same optical system, and by using a computer program which calculates the total collection efficiency of the diffuse source of radiation in terms
of all geometrical and optical constraints. Initially, quantitative signals due to the \(0 + NO\) recombination were obtained as differences between NO-on and NO-off readings, but an apparent thermal background, probably arising from minor heating of the flow tube by the exothermic recombination reaction, was found to overwhelm the rapidly decreasing chemiluminescent signals beyond 3 microns. A double modulation detection system has therefore been put together in which the main microwave discharge source of O-atoms is square wave modulated at about 1 Hz and the lock-in output is summed on an Enhancetron signal analyzer for long periods. This should remove slow signal drifts as well as heating effects due to exothermic reactions which should quickly approach a steady state.

The spectral distribution of the \(0 + NO\) glow was measured from 1.25 to 3 microns, found to be in good agreement with earlier work by Stair and Kennealy beyond 1.5 microns, but to fall short of their values below 1.5. A tentative value of \(1.0 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ micron}^{-1}\) at 1.3 microns was measured for the radiative rate constant, \(I_o\), in the expression \(I = I_o [0] [NO]\), which is 50 to 60% larger than the early results of Fontijn, Meyer and Schiff. The corresponding \(I_o\) at 2.7 microns is about \(8 \times 10^{-19} \text{ cm}^3 \text{ sec}^{-1} \text{ micron}^{-1}\). These preliminary results will be checked and extended using the double modulation system.

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

(a) The experimental work on the low pressure \(0 + NO\) chemiluminescence in the visible and near infrared was completed, and the resulting Ph.D. thesis by Dr. Regina J. Cody was written and successfully defended. The experimental data fully support the general mechanism of recombination via step-wise vibrational relaxation of an electronically
excited NO$_2$, probably $^2B_1$, from an initial unstabilized collision complex corresponding to the full ON - O bond energy (3.2eV) to the vibrational ground state of NO$_2$ ($^2B_1$) at about 1.5 eV. If the radiative transition probability remains approximately constant over much of this range of excitation, as is suggested by our fluorescence experiments, the observed fall-off of the second order chemiluminescent rate constant, $k_{hv}$, with decreasing total pressure can be interpreted in terms of an average energy transfer and cross section per stabilizing collision. The ratio of high pressure to low pressure limits of $k_{hv}$ rises, as expected, from 1.4 at 4050Å (corresponding to nearly the full ON - O bond energy) to about 8 at 6000 to 8000Å. This reflects the increasing contribution from partially relaxed NO$_2$ ($^2B_1$) to the radiation process. As in the case of our earlier NO$_2$ fluorescence experiments, the cross section for relaxation is large, about half of gas kinetic, and the average amount of energy transferred, which can not be uniquely determined from the fit to experimental data, is in the range 500 to 1000 cm$^{-1}$. The difficulty now arises that O$_2$ which was the only carrier gas used in our O + NO experiments, has a vibration frequency of 1580 cm$^{-1}$ and is therefore unlikely to remove 500 to 1000 cm$^{-1}$ per collision with high efficiency. Further analysis of the data is under way in connection with the preparation of a final publication on this phase of the work. The apparatus is about to be used for a brief study of the important O + CO system over a wide pressure range.

(b) The paper on the kinetics of the O + O$_3$ reaction was revised to take account of the depletion of NO in our steady-state flow experiments where a little NO is added to O plus excess O$_3$ mixtures in
order to measure the O-atom concentration along the flow tube by means of the O - NO chemiluminescence. This depletion comes about by the inability of the $O + NO_2 \rightarrow NO + O_2$ reaction to keep $NO_2$, formed by $NO + O_3 \rightarrow NO_2 + O_2$, in true steady state. Our improved computer analysis of the reaction scheme has slightly decreased the reported $O + O_3$ rate constants whose new Arrehnius expression is $(1.05 \pm 0.18) \times 10^{-11} \exp \left[ (-4.31 \pm 0.10 \text{kcal/mole})/RT \right] \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$. The paper was accepted for publication by J. Chem. Phys.

Excellent progress was made in the study carried out by Dr. J. G. Anderson on the measurement of important atmospheric OH radical reactions using resonance fluorescence in the $(0, 0)$ band of its $^2\Sigma - ^2\Pi$ transition as the method of detection. With a detectability limit of less than $10^{10}$ molecules cm$^{-3}$, relatively slow three-body recombination reactions of OH such as $OH + NO_2 + M \rightarrow$ HNO$_3 + M$ and $OH + NO + M \rightarrow$ HNO$_2 + M$ are being studied under conditions where the parallel second-order $OH + OH \rightarrow H_2O + O$ reaction has become negligibly slow. Over a pressure range from 0.5 to 20 Torr, the rate constant for the important HNO$_3$ reaction has been found to be quite fast, with $k$ decreasing from about $1.7 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$ to $0.8 \times 10^{-30}$ for $M = Ar$ at $298^\circ K$, in agreement with the unimolecular aspects of the recombination. For $M = N_2$, the rate constant is larger by almost a factor of two. The HNO$_2$ reaction with $M = Ar$ is slower than its HNO$_3$ counterpart by about a factor of two. The temperature dependence of these reactions is about to be measured, as is the rate of the $OH + O_3$ reaction.

3. Energy Partitioning in Metal Atom Chemi-Excitation (M. A. Biondi and F. Kaufman)

Early difficulties with our commercial piezoelectric scanning
Fabry-Perot interferometer which were due to a succession of faulty components were finally overcome and successful, stable operation of the two inch aperture system at total finesse values of 20 to 25 has been achieved reproducibly since the beginning of this reporting period. A small, inexpensive, multi-mode He-Ne laser which is used continually to tune the interferometer does so with only slight degradation of the observed finesse compared to that measured with a much more expensive single-mode He-Ne laser.

Several series of experiments were performed in our heated stainless steel chemiluminescence cell in which a discharged gas stream of \( \text{N}_2 \) or \( \text{N}_2/\text{Ar} \) intersects and mixes with Na in Ar carrier coming from a sodium oven at controlled temperature at total pressures from 2 to 10 Torr and temperatures of 450 to 600°K. The intersection region is viewed by the interferometer through a large pyrex window on which condensation of Na is prevented by a tangential Ar stream.

Measured small flows of other gases (NO, CO\(_2\), CO, NH\(_3\)) may be added 25 cm downstream of the microwave discharge (15 cm upstream of the observation region). A glass wool plug, which is known to remove much of the vibrationally excited \( \text{N}_2^\ast \), can be inserted between the discharge and the added gas inlet. Results so far indicate that most of the observed Na D-line chemiluminescence results from reactions of N-atoms or their highly excited association products rather than from \( \text{N}_2^\ast \) produced in the discharge, in some disagreement with earlier published data. Thus, the introduction of the glass wool plug has little effect on the Na intensity, addition of NO decreases it to about 1/20 at the titration endpoint, NH\(_3\) also quenches it sharply, about 1/4 as effectively as NO, whereas CO\(_2\) and CO are two orders of magnitude less effective than NO.
Neither \( \text{NH}_3 \), \( \text{CO}_2 \) nor \( \text{CO} \) substantially decrease the Lewis-Rayleigh afterglow (N-atom density). When their quenching of the sodium chemiluminescence is interpreted in terms of a steady-state \( \text{N}_2 \) A-state model, reasonable quenching rate constants of A-state by \( \text{NH}_3 \) and \( \text{CO} \) are obtained, but \( \text{CO}_2 \) appears to be more efficient than has been reported elsewhere. The line shape of the emitted D-line glow corresponds to a doppler profile at about 1500\(^\circ\)K, i.e. 3kcal of translational energy in Na \((3^2\text{P})\). A removable copper coil has also been used to recombine N-atoms upstream of the sodium addition, and it was found to decrease the D-line intensity by factors of 20 to 40. Experiments are in progress to determine whether the weak residual glow in the absence of N-atoms is due to \( \text{N}_2 \) and to reconcile the present results with those of other workers who have reported chemiluminescent reactions at 300\(^\circ\)K to be entirely due to \( \text{N}_2 \).

4. **Neutral-Neutral Reactions in Crossed Beams (W. L. Fite) (Tasks a and d).**

\( \text{Ba} + \text{O}_2 \rightarrow \text{BaO} + \text{O} \). This reaction, on which considerable data have been obtained in the crossed beam experiment, has been studied in a beam-through-gas-cell configuration in order better to estimate the total cross section for reaction than was possible in the crossed beam experiment. The second measurement was not fully satisfactory, the suggestion was that the reaction cross section for groundstate barium atoms is somewhat smaller than had been believed by us previously, i.e., more like one \( \times 10^{-16} \text{ cm}^2 \) rather than several \( \times 10^{-16} \text{ cm}^2 \). Most disappointing in the second experiment was the failure of the barium beam source upon heating to very high temperatures. It had been hoped that heating the source to around 3000\(^\circ\)K would permit the observation of the difference in reaction cross section between groundstate \( \text{Ba}(^1\text{S}) \) and
metastable Ba ($^3D$). It became necessary to build a better source if the effect of the internal energy on the reaction cross section was to be observed.

**$U + O_2$ and other gases.** It was recently found in another laboratory that Uranium atoms undergo association ionization reactions at thermal energies with both atomic and molecular oxygen, i.e.,

$U + O \rightarrow UO^+ + e$ and $U + O_2 \rightarrow UO_2^+ + e$, both with large (but as yet unmeasured) cross sections. Since the reaction $U + O_2 \rightarrow UO + O$ can occur, it became of immediate interest to measure the branching ratio between the associative ionization and the neutral reaction between $U$ and $O_2$. It is of special interest since both the $UO$ and the $UO_2^+$ are potentially radiators in the infrared. The crossed beam experiment was quickly reinstalled and the experiment was attempted by just replacing the Barium source with Uranium source. It was found that associative ionization with residual gases in the vacuum chamber gave intolerable noise signals with the previously used mounting configuration of the mass filter detector. Before altering the configuration, a series of experiments were run to determine how extensive the associative ionization of Uranium with other gases actually is. It was found that ions are not produced when uranium atoms collide with hydrocarbons, CO, N$_2$, but that the following reactions do proceed: $U + NO \rightarrow UNO^+ + e$ and $U + SF_6 \rightarrow UF_2^+ + SF_4 + e$, or possibly $U + SF_6 \rightarrow UF_2^+ + SF_4^-$. Ions were observed when CO$_2$ and NO$_2$ were added, but the particular ions observed, $UO_2^+$ and UNO$^+$, suggest that the ionization was made from impurity gases rather than the intended gas.

The configuration of the experiment is being changed to avoid the noise from associative ionization and another attempt at measuring
the reaction $\text{U} + \text{O}_2 + \text{UO} + 0$ will be undertaken shortly.

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

We continued with our studies of argon atoms in the metastable $\text{Ar}(^{3}\text{P}_{0,2})$ state and nitrogen molecules in the $\text{A}^{3}\text{E}_{u}^{+}$ state. A considerable amount of data on the quenching of these species by atmospheric gases has been obtained and we are currently preparing several papers describing this work. Our attention has now turned to a specific reaction of major geophysical interest: namely, the excitation of the atomic oxygen green line due to the collisional deactivation of these states by $0$ and $\text{O}_2$. These studies are prompted in part by two recent rocket experiments which we carried out at under dawn and twilight conditions in order to separate spatially various chemical reactions, plasma processes (electron-ion recombination) and collision processes involving photoelectrons which contribute to the production of $\text{O}(^{1}\text{S})$ atoms.

In a related series of experiments we have begun a study of metastable $\text{NO}^{+}$ ions in the $\text{a}^{1}\text{Σ}$ state. This state is rapidly populated by electron impact on neutral NO and possibly by $[\text{N}_2^{+} + \text{NO}]$ charge transfer. Although ground-state $\text{NO}^{+}$ ions can not energetically produce $\text{O}(^{1}\text{S})$ atoms by dissociative recombination, $\text{NO}^{+}$ ($\text{a}^{1}\text{Σ}$) ions can. In fact the $^{1}\text{S}$ state is a preferred by-product. The suggestion made here is that many $\text{NO}^{+}$ ions found in auroral arcs are in fact electronically excited and contribute significantly to the production of the auroral green line and produce $\text{O}_2^{+}$ ions as well as charge transfer. These reaction schemes are currently under study.
A number of experimental modifications and improvements in the flowing afterglow apparatus were made during the reporting period:

(1) Construction and testing of a new movable water injector which gives much better mixing of the added He-H$_2$O stream with the main gas flow;

(2) Reconstruction of the upstream water mixing system and recalibration of water hygrometer and pressure transducers; (3) Factory rejuvenation of the electron multiplier (at no cost) and re-assembly of the ion detection and analysis system.

About 60 additional experiments were performed in the O$_2^+$ + N$_2$ + H$_2$O system in order to remove certain inconsistencies in the interpretation of data in terms of the additional reaction path

\[ \text{O}_2^+ + \text{N}_2 + \text{M} \xrightarrow{2a} \text{O}_2^+ \cdot \text{N}_2 + \text{M} \]

\[ \text{O}_2^+ \cdot \text{N}_2 + \text{H}_2\text{O} \xrightarrow{3a} \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{N}_2. \]

In our earlier work, the analysis had neglected the collisional redisassociation of \( \text{O}_2^+ \cdot \text{N}_2 \), -2a, compared to the "switching" reaction, 3a, but for this weakly-bound complex such an assumption is no longer justified. Yet, when the more rigorous steady-state analysis is carried out, the resulting values for \( k_{2a} \), which had formerly been thought to be about \( 8 \times 10^{-31} \) cm$^6$ sec$^{-1}$, now range from 2 to \( 20 \times 10^{-31} \), and \( k_{3a} \) ranges from 3 to \( 6 \times 10^{-9} \) cm$^3$ sec$^{-1}$, i.e. is excessively large. The rate constant of the first clustering reaction, N$_2^+$ + H$_2$O + M + N$_2^+ \cdot \text{H}_2\text{O} + \text{M}$, is \( 2.5 \times 10^{-28} \) cm$^6$ sec$^{-1}$ which is in good agreement with other M-gas data.
and with other investigators' results. The origin of the scatter in the $O_2^+ N_2$ processes, which have not been reported heretofore by others and which may be important since $N_2$ is the most abundant M-gas, is under further investigation.

A small effort has also gone into preliminary quantum-theoretical calculations of bond energies of ion-neutral complexes using the MINDO approximation (modified intermediate neglect of differential overlap), a semi-empirical SCF-MO calculation of ground-state properties of molecules in which all valence electrons are taken into account. An existing computer program of Prof. Ellison's quantum chemistry group is used, and the NO$^+ H_2O$ and $O_2^+ H_2O$ energies are to be calculated.

7. Reactions of Metal Atoms with Ions in Magnetically Confined NO$^+$ Plasmas (W. L. Fite) (Tasks b and j).

Major activity in this experiment during the past six months has been to reshape the magnetic field and to introduce inhomogeneities in the magnetic field that confines the photo-ionization-produced NO$^+$ plasma. In particular the field was strengthened slightly downstream of the point where the photo-ionization occurs. The effect of this will be to limit the pitch angles to fairly small angles, and then ensure that the primary ions will see a "thin" metal atom beam when they cross it. (In the absence of this strengthening, ions with very large pitch angles can interact with the atom beam and although the density of atoms is very small the distance can be very large and the thick target analysis must apply.) The field is made to weaken again further downstream and the atom beam crossed the plasma on the other side of the bump in the magnetic field from where the light beam crosses. The effect
of this is to ensure that ionic products of the reaction which have initial motion upstream away from the mass filter detector will be reflected by the field in the bump and enhance the secondary ion efficiency. Mathematical analyses of the experiment with improved field shapes have been carried out, and experimentation with the new field geometry has begun. Some changes in the field are still called for, we find, but the idea of putting a bump in the field strength appears to be a major improvement that will make analysis of the experiment much easier and yield much better absolute cross sections for the thermal energy processes that occur between NO\(^+\) ions and metals that would be put into the atmosphere by a nuclear explosion.

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

The considerable interest in the reaction of neutral uranium vapor with molecular oxygen led us to repeat some of the earlier measurements on this reaction. While a drift tube is not the ideal apparatus to investigate neutral reactions, it did permit us to answer the question of whether or not this reaction would produce ionized products. In order to increase the detection efficiency of our apparatus a special low frequency rf supply for the quadrupole mass spectrometer was borrowed from Dr. Fite which completely eliminated the previously encountered problem of electrical breakdown in the mass filter which had caused a high noise level at high masses. In the new experiments the small orifices which connect the ion source and drift tube were replaced by a single larger opening of 4 mm diameter, thus allowing a much higher flux of uranium vapor into the drift tube. After these changes had been made, UO\(_2^+\) ions were observed when the source was operated in such a way
that only neutral particles were able to leave the source region. The total absence of ions other than $\text{UO}_2^+$ confirmed the conclusion that these ions indeed were produced by the reaction $\text{U} + \text{O}_2 \rightarrow \text{UO}_2^+ + e$ and not by other sources of ionization such as surface ionization on hot electrodes.

Our apparatus is not suitable for determining the rate constant of this process. However, an estimate was obtained of the total loss rate of uranium vapor in the presence of $\text{O}_2$, which includes not only chemi-ionization but also oxidation,

$$\text{U} + \text{O}_2 \rightarrow \text{UO}_2^+ + e \rightarrow \text{UO} + \text{O}$$

Our estimate of the total reaction rate was obtained from the observed variation of the $\text{UO}_2^+$ count rate with the $\text{O}_2$ density and an estimate of the diffusion coefficient of $\text{U}$ in helium. Rate constants of the order of $2 \times 10^{-11}$ cm$^3$/sec were inferred from these measurements. There is reason to believe that the actual rate constant is higher than this value since to some degree the uranium source pumps oxygen (acting as a getter pump), with the result that the actual $\text{O}_2$ density is reduced in the vicinity of the source.

A second investigation carried out during this report period involved determination of the ionic mobility of barium ions in nitrogen and in oxygen. Since the diffusion coefficient of $\text{Ba}^+$ ions in $\text{N}_2-\text{O}_2$ atmospheres can be calculated from the measured mobilities, these measurements have direct application in model calculation of barium
ion cloud experiments.

The value obtained from these studies is

\[ \mu_0^{(\text{Ba}^+ \text{in N}_2)} = (2.0 \pm 0.1) \text{ cm}^2/\text{V-sec} \]

in the limit of small \( E/P \) at 300°K, (\( \mu_0 \) refers the mobility to a standard density of \( 2.96 \times 10^{19} \text{ cm}^{-3} \)). The corresponding mobility of \( \text{Ba}^+ \) ions in oxygen need not be determined as accurately, since the density of \( \text{O}_2 \) at altitudes where barium release experiments are carried out is much smaller than that of \( \text{N}_2 \). This is fortunate, inasmuch as the experimental determination is seriously hampered by the rapid destruction of the barium source by oxygen. Some data have been obtained in \( \text{O}_2 \) yielding a mobility,

\[ \mu_0^{(\text{Ba}^+ \text{in O}_2)} = (1.9 \pm 0.2) \text{ cm}^2/\text{V sec} \]

Since the mobilities are not expected to depend on ion energy, the ionic diffusion coefficient in the \( \text{N}_2-\text{O}_2 \) mixture corresponding to the upper atmosphere temperature and composition ratio can be calculated by use of Blanc's law and the Einstein relation \( D_+ = (kT/e)\mu_+ \).

9. **Afterglow Studies of the Population of Excited Atomic and Molecular States by Vibrational Energy Transfer** (E. C. Zipf) (Task d).

Preliminary work has been done on the excitation of the Lyman-Birge-Hopfield system of \( \text{N}_2 \) by electron impact on vibrationally excited nitrogen. The results appear to be consistent with the simplest view of this important collision process; the dipole transition moment exhibits little or no dependence on \( r_{o,v} \) and the band intensities can
be calculated in a straight-forward manner if the vibrational temperature is known. These laboratory results, when taken in conjunction with satellite and rocket studies of LBH emission features in aurora, reinforce the view that nitrogen molecules in auroral arcs retain a near thermal vibrational temperature distribution in spite of the fact that the higher vibrational levels (e.g. v' > 5) are very efficiently excited by electron impact. Additional relaxation channels, not currently included in routine auroral theory, remain to be identified.

10. **Time of Flight Experiments (E. C. Zipf) (Tasks b and d).**

We continue to investigate the properties of metastable atoms and molecules and Rydberg states using translational-energy spectroscopy. During this report period these studies have led to a measurement of the radiative lifetime of the elusive $^5S$ state of atomic oxygen which is excited efficiently in the aurora, in the normal airglow, and in the equatorial anomaly. The lifetime measurement now permits an accurate accessment of the absolute magnitude of the dissociative excitation cross section of the $^5S$ state due to electron impact on $O_2$ and $CO_2$:

**Abstract**

**Absolute Cross Sections for the Dissociative Excitation of $OI(^5S_0)$ and its Radiative Lifetime.** Past attempts to determine absolute cross sections for the $OI(^5S_0)$ production have been hindered by the absence of an experimental measurement of the radiative lifetime. To this end the radiative lifetime has been measured in a time of flight experiment and found to be $189 \pm 50$ µsec which is a factor of 3 shorter than Garstang's previously accepted theoretical value of 595 µsec. This lifetime has also been measured concurrently by C. E. Johnson in a similar experiment.
with the result $\tau = 185 \pm \mu$sec. These results are in excellent agreement with each other. With the radiative lifetime established it was possible to revise the previously deduced cross sections for dissociative excitation of $\text{OI}(5g^0)$ by electron impact on $\text{O}_2$ and $\text{CO}_2$ resulting in $\sigma = 3.5 \times 10^{-18} \text{ cm}^2 (100 \text{ eV})$ and $\sigma = 2.2 \times 10^{-18} \text{ cm}^2 (100 \text{ eV})$ respectively.

Comprehensive sets of time-of-flight spectra for the principal atmospheric gases (e.g. $\text{N}_2$, $\text{O}_2$, $\text{CO}$, $\text{CO}_2$, $\text{CH}_4$, $\text{NO}$, $\text{N}_2\text{O}$) have also been obtained as a prelude to a new series of experiments studying the interaction of "hot" atoms ($0.1 \rightarrow 200 \text{ eV}$) with atmospheric gases. As the result of these studies, we have developed a controllable source of hot atoms, which can be used to simulate disturbed atmospheres and to study the production of NO by kinetically active species. The time-of-flight data are currently being analyzed and the results prepared for publication.

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

11. Optical Interferometer Studies of Barium Releases (M. A. Biondi) (Task g).

Work continues on the development of a new, larger aperture (150 mm) interferometer (jointly funded) for future studies of barium releases. The instrument is approximately 70% complete and should be ready for preliminary testing during the next report period.

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

The analysis of in-situ measurements of quenching of metastable atoms by molecules provides important information concerning electronic- to-vibrational energy transfer rates in the upper atmosphere. In the present case the quenching of $\text{O}(1\text{D})$ metastables by $\text{N}_2$ and $\text{O}_2$ molecules
has been determined by a detailed analysis of F-region 6300Å intensity enhancements produced by the I.T.S. Platteville transmitter. The final results are being readied for publication in the Journal of Geophysical Research.

An f/0.7 "camera" has been constructed which should be capable of photographing the enhanced 6300Å intensity region produced by the Platteville transmitter under ideal seeing conditions and large enhancements. Such photographs would provide a more detailed map of the energetic electron region than we currently can obtain with spatial scanning photometers. Preliminary testing of the camera during February 1972 revealed some serious problems in the film advance system. Design changes have been made to minimize these problems.


Our intensive preparations for our return to Fort Churchill to study the aurora and to attempt to verify our earlier NO observation involved two rockets: An Aerobee 150 and a Nike-Apache. Our efforts were rewarded by two highly successful, but very different, flights. The Nike Apache rocket (14.486UA) was launched on 14 February 1972 into a class 2+ auroral arc in the pre-midnight magnetic quadrant. The arc was characterized by an intense westward electrojet that produced a 700 gamma magnetic bay and by a modest amount of NO:

**A Confirmation of Large Concentrations of Nitric Oxide in an Auroral Arc.** Nike-Apache rocket 14.486UA was launched from the Churchill Research Range on 14 February 1972 into an IBC 2+ auroral arc. The payload included a double-mode quadrupole mass spectrometer for ion and neutral composition measurements, a cylindrical
microprobe for electron temperature and density measurements, and a six-channel filter-wheel photometer. Approximately five neutral and ion composition measurements were made before the rocket penetrated the auroral form. No unusual amounts of nitric oxide were observed below the arc on either the upleg or the downleg of the flight. However, inside the arc large quantities of NO were observed. The aurora was highly structured with local regions of marked NO enhancement. In these regions the NO and O₂ densities were comparable in magnitude and NO⁺/O₂⁺ ratios of 20:1 or more were observed. This experiment confirms similar results obtained by us earlier [Aerobee rocket 4.309 UA].

The arc was highly structured and there were striking differences between the NO concentration and the NO⁺/O₂⁺ ratio as the vehicle moved vertically and horizontally through this complex form.

The Aerobee 150 rocket was also launched into a bright class 2+ aurora. This arc was highly stable maintaining an overall green-line brightness of approximately 35kR throughout the flight. This payload was very elaborate consisting of a liquid nitrogen cooled infrared monochromator which scanned to 5.6 microns, a double-mode mass spectrometer for ion and neutral measurements, a cylindrical probe for electron density and temperature measurements, a six-channel tilting-filter photometer, and two deployable hemispherical analyzers for measuring the primary and secondary electron energy distribution and flux up to 30 keV. The Aerobee rocket was launched successfully on 16 March 1972 into the post-midnight magnetic quadrant. The arc exhibited very little magnetic activity (less than 25 gamma, day) in striking contrast to the pre-midnight arcs that we are accustomed to firing into and are characterized
by very large heating currents. Little NO was observed by the Aerobee payload. A positive correlation between the presence of enhanced NO concentrations and the magnitude of the current flowing in a given arc may exist so that simply launching a rocket into a bright aurora as the sole launching critique may not lead to an observation of enhanced NO concentrations. The rocket data suggested several ground-based observations that could be used to study this problem further. This information may already exist in the Churchill Research Range's data bank and we are pursuing this point actively.

In the meantime we are actively preparing a new payload to be launched on 16 August 1972 under daytime conditions on board a Javeline rocket [8:61 UA]. 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.

Preparations are also underway for two rocket experiments which will be launched in conjunction with the Apollo 17 mission in support of an optical experiment on board the lunar spacecraft.


We continue with our development work on an elaborate mesospheric rocket experiment which will measure the concentration of $N_2$, $O_2$, $N$, $O$, $NO$, $OH$, $O_2(1\Delta)$, $O_2(1\Sigma)$, $H_2O$ and $CO_2$ at D region altitudes. The payload will include a liquid nitrogen cooled infrared monochromator that was flown successfully for the first time as part of our second auroral rocket experiment launched from Fort Churchill on 16 March 1972.
The first field test of an optical mass spectrometer, which will work well up to pressures of at least 1 Torr and will be included in the mesospheric payload, will take place this summer as part of a complex airglow experiment to be launched from Wallops Island on 16 August 1972 on board a Javelin rocket (NASA 8:61 UA).

C. Theoretical Studies


(a) Our calculations of charged particle-neutral atom collision cross sections using the Glauber approximation continue. More and more papers following our lead, and applying our methods to atoms such as He and Li have been appearing. However (as explained in our last progress report), we are not satisfied with these calculations or the procedures they employ, and are still actively pursuing the task of developing new Glauber formulations which will be legitimated applicable to atoms more complicated than hydrogen. In this connection, we now have succeeded in developing convenient closed-form expressions for the integral—over all angles—of the absolute value squared of the Glauber amplitude, elastic or inelastic, in $e^{-}\text{H}(1s)$ collisions; previously, we only had succeeded in finding closed-form expressions for the amplitude. In other words, we now can write—in greatly closed form in terms of a finite number of hypergeometric functions—the $e^{-}\text{H}(1s)$ elastic cross section, $\sigma(1s + 2s)$ cross section, $\sigma(1s + 2p)$ cross section, etc., in the Glauber approximation. These closed formulas have made it possible for us to examine analytically the asymptotic behaviors of these cross sections, a task we previously could not successfully accomplish. To our astonishment, we find that the Glauber elastic cross section in
both $e^- - H(1s)$ and $p - H(1s)$ collisions, has the same extremely simple
limit (proportional to $1/E$) at both low and high energies, and that
the exact calculations differ from this $1/E$ law by no more than a few
percent over the entire energy range of conceivable interest (from
1 eV up in the case of $e^- - H(1s)$ collisions). The algebraic difficulties
involved in extracting the high and low energy limits without error
are severe, and we have not yet succeeded in finding reliable expression
for the high and low energy limits of the inelastic cross sections,
which will not have the same limits at high and low energies. But the
possibility of using these limits as the starting points for very rapid
(involving almost no numerical calculation) extrapolations of the exact
numerical cross sections is intriguing, especially if these procedures
can be extended to more complex atoms. This work is being performed
with Brian Thomas, who has just passed his final oral for the Ph.D.,
and who will stay on as a post-doctoral Research Associate, continuing
to work on these Glauber problems.

(b) As foreshadowed in our last Progress report, we have
terminated our theoretical studies on Ba plasmas. The graduate student
working on this task (P. Buchwalter) is no longer being supported on
this contract. Unfortunately, it was not found possible to obtain
reliable theoretical results, despite the very considerable effort that
was put into this problem. If there are any conclusions to be drawn,
you are that use of quantum defect theory in a three-channel problem
requires a very large amount of accurate data (more data and more
accuracy than usually available) before the reliable quantum defects
and mixing coefficients—needed in the application of the quantum defect
theory to oscillator strengths and collision cross sections—can be obtained.
(c) We have begun a study of the cross sections for rotational excitation of molecules by slow collisions with neutral particles. This is an important problem, having application to various practical problems of interest to ARPA. However, this rotational excitation problem is extremely difficult to treat reliably by present theoretical techniques, though there exist several essentially untested approximate treatments, e.g., classical approximations. It is our intention to examine the use of Chase's so-called adiabatic approximation—discussed in our review paper on rotational excitation by slow electrons (listed under IIA below)—in rotational excitation by neutrals. As always, we are seeking procedures which are reasonably reliable without excessive computation; in our judgment, only in exceptionally important problems would it be worthwhile to support the arduous theoretical effort required for, e.g., a reliable close coupling calculation of rotational excitation of even a small molecule by an incident slow neutral.

(d) We have begun a study of the utility of variational procedures of non-standard type (variational principles applicable to, e.g., computations of oscillation strengths and polarizabilities) to atomic and molecular problems, especially in situations where previously obtained very good (to second order) wave functions yield first order errors in conventionally computed quantities such as oscillator strengths and polarizabilities. This work is being carried on in close collaboration with Professor L. Spruch, at N.Y.U. Results on this program already have been achieved, and will be reported in due course.

(e) As part of our program to study excitation processes in atom-atom collisions, we have performed calculations of the differential cross section for excitation of the first resonance level of Li in
collisions with Li$^+$ ions. We have completed calculations at energies of 25, 50 and 100 eV and obtain very good agreement with the experimental results of the Stanford group. We are presently working at an energy of 2.5 eV to study the low energy region of interest in atmospheric analysis. Our major aims are to test the feasibility of accurate calculations on systems with several electrons, to see whether such excitation processes are likely at energies of a few eV, and to provide accurate data to use in testing models of these processes. One interesting feature of this process is that it occurs through the transfer of angular momentum from the nuclei to the electrons. For such transfer the adiabatic criterion and the Landau-Zener models do not appear to be applicable. We hope to test these models and to look for alternative empirical approaches if these should indeed fail. We also have sufficient data to calculate the charge transfer cross section.

(f) We are continuing our examination of the effects of the formation of collision complexes on the reaction rates for heavy particle collision processes. The results of our work on the formation of molecules have been published in the Journal of Physics. Further major progress in this area is not expected until we begin studies of the effects of spin orbit interactions. An understanding of these interactions may be crucial to the theoretical study of reactions involving C, N or O atoms, and we plan to begin such an investigation in the fall of 1972.

(g) We have been studying some of the properties of highly charged species of the atmospheric atoms. The calculations on the cross section for dielectronic recombination reported in our last technical summary, were published in Physics Letters. We have completed a study
of the spectrum of Auger electrons emitted from highly charged oxygen atoms. Our aim was to assist in the interpretation of some recent beam foil experiments. We found considerable agreement between the theoretical and experimental spectra, although there are differences of 1 or 2 eV in the positions of some lines. We were able to make plausible assignments for all the observed lines.

(h) Our pseudo-potential calculations have been proceeding slowly. A new graduate student has been assigned to this program, and he has been studying the properties of atoms and ions with two valence electrons. Our technique has been tested by a calculation of the electron affinity with a result of 0.57 eV as compared to the ab initio value of 0.62 eV. We searched for an excited state of Li⁺ without success, but confirmed the existence of a low energy resonant state which leads to the large cross section for e-Li collisions near zero energy. We have been studying the spectrum of Be, but found several spectral lines that were incorrectly assigned by the spectroscopists. These difficulties have almost been resolved so that we are in a position to make rigorous tests of our pseudo-potential model. We intend to give this topic the highest priority during the next few months.

(i) Our study of resonant scattering is at a transition stage. Our collaboration with Drs. Temkin and Bhatia at the Goddard Space Center has been completed, and our results have been accepted for publication in the Physical Review. We have just begun an attempt to implement a recent suggestion by Nuttall, that the study of resonant scattering might be greatly facilitated by the use of complex coordinate space. It appears to be possible that this esoteric procedure could simplify the numerical computation. We have encountered some computa-
tion problems in this implementation, but are hopeful that we will soon have results for e-H collisions. If this method is successful, it might be very valuable in the study scattering by molecules. If the method fails we will continue calculations using complex energies, but real coordinates.

(j) An investigation of the minimum variance method has been initiated for studies of electron-atom collisions. This method has received very little attention in scattering theory, but it is potentially extremely powerful in two respects. Firstly, it could provide rigorous bounds on scattering cross sections, and so could possibly be used to provide definitive answers to some of the more delicate problems in scattering theory. Secondly, it might provide an extremely rapid method of obtaining estimates for cross sections for a wide range of electron collision problems. We are studying both aspects of the method, but with special emphasis on the latter feature.
II. Publications and Technical Presentations

A. Publications


"Collisional Deactivation of Metastable Ar(3P0,2) Atoms and N2(A3Σu+)


B. Technical Presentations

"Applications of Molecular States to Atomic Collisions", J. N. Bardsley, invited talk at the meeting on Potential Energy Surfaces Sponsored by NBS, ARPA and IDA, Gaithersburg, October 5, 1971.


"Determination of the \(0(2D)\) Quenching Coefficient in the F Region", D. P. Sipler and M. A. Biondi, paper presented at the Fall Meeting of the AGU, San Francisco.

"Recombination of Electrons with Positive Ions of the \(H_2O^+(H_2O)_n\) Series" M. T. Leu, M. A. Biondi and R. Johnsen, paper presented at 24th Annual Gaseous Electronics Conference, Oct. 5-8, 1971, Gainesville, Fla.


"Multiple Scattering Approach for Vibrational Excitations of Diatomic Molecules", F. Faisal, invited talk, DEAP Meeting, Atlanta, Georgia, November 30, 1971.


"Reactions of Metal Atoms with Atmospheric Ions and Molecules", W. L. Fite, Colloquium, Rice University, Houston, Texas, February 17, 1972.

"Reactions of Metal Atoms with Atmospheric Ions and Molecules", W. L. Fite, Colloquium, Rice University of Texas, Austin, March 22, 1972.


C. Other Activities

M. A. Biondi, R. Johnsen, M. T. Leu, and H. L. Brown attended and presented papers at the 24th Annual Gaseous Electronics Conference, Oct. 5-8, 1971, Gainesville, Fla.

M. A. Biondi attended meetings of the Advisory Panel on Physics, National Science Foundation, on Oct. 18-19, 1971 and again on March 13-14, 1972, to review the NSF activities in support of Physics research.

T. M. Donahue is a consultant for the Space Science & Applications Steering Committee, National Aeronautics and Space Administration.
T. M. Donahue is a member of the Site Selection Committee, Upper Atmosphere Research Corporation.

T. M. Donahue is a member of the Science Steering Group for Outer Planets Mission.

T. M. Donahue is a member for the advisory Panel for Atmospheric Sciences, Division of Environmental Sciences, National Science Foundation.

T. M. Donahue is an Associate Editor of *Review of Geophysics and Space Physics*.

F. Faisal has made several visits to Goddard Space Flight Center, Washington, for consultation with Dr. Temkin.

W. L. Fite, member Advisory Committee on Research, Office of Aeronautics and Space Technology, Headquarters, N.A.S.A.

W. L. Fite attended meeting Langley Research Center, Virginia, November 18-19, 1971.

E. Gerjuoy participated in the regular annual meeting of the Oak Ridge National Laboratory Health Physics Visiting Committee, Oak Ridge, Tennessee, October 24-26, 1971.


E. Gerjuoy visited New York University approximately once a month (at the invitation of the N.Y.U. Physics Department) during the period of Oct. 1971-Jan. 1972, to collaborate with Professor L. Spruch on research into the applications of variational principles to atomic and molecular physics problems.

E. Gerjuoy, has been serving, since October 1971, as Coordinator (Editor), with Prof. Bederson of N.Y.U., of the Journal "Comments on Atomic and Molecular Physics", published by Gordon and Breach.
F. Kaufman was invited to attend a Survey Conference on the Climatic Impact Assessment Program of the U. S. Department of Transportation at Cambridge, Mass. on February 15-16, 1972.

F. Kaufman attended a meeting of the Executive Committee of the Pittsburgh Section of the American Chemical Society on February 1, 1972.


D. Activities Relating to ARPA

M. A. Blondi participated in the ARPA Workshop on Dissociative Excitation at JILA, March 16-17, 1972.

M. A. Blondi attended a meeting of the ARPA Institute Directors at Washington, D. C., Jan. 20-21, 1972.


F. Kaufman attended the ARPA Plume Physics Meeting at Los Angeles, California, on February 28, 29 and March 1, 1972, chaired a subpanel on Chemistry and Excitation Mechanisms, and wrote a brief subpanel report for ARPA.

F. Kaufman attended the ARPA-IVY OWL Contractors Meeting at Everett, Mass. on March 21-22, 1972 chaired a subpanel on Metal Oxides, and wrote a brief subpanel report for ARPA.

III. Visiting Scientists

Professor M. Deloche, Saclay, France
Dr. L. Doverspike, William & Mary College
Professor Florence Fayard, Université Paris-Sud, Orsay, France, Jan. 13, 1972
Dr. Michael Hender, University of Windsor
Professor D. Holschar, Eindhoven, Netherlands
Dr. Y. Itikawa, Univ. of Tokyo and Argonne National Laboratory, Feb. 11, 1972
Dr. Charles Johnson, University of California at Berkley
Professor J. Macek, University of Nebraska, January 11, 1972
Professor Fredrick McLafferty, Cornell University
Dr. R. Schoen, National Science Foundation, Washington, D. C.
Dr. Vijay Sheorey, University of Windsor, December 20, 1971.
Dr. Ausna Skerbele, Mellon Research Institute

IV. Degrees Awarded

R. J. Cody, Ph.D., January 1972
R. A. Gutcheck, Ph.D., December 1971
C. J. Howard, Ph.D., December 1971
J. L. McCrum, Ph.D., October 1971
B. A. Thomas, Ph.D., April 1972
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