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TITLE OF WORK: ATOMIC AND MOLECULAR PROCESSES
IN ATMOSPHERIC ENVIRONMENTS

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* To September, 1971
** Summer 1971 only
+ To September, 1971
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, 1971).

A. Laboratory Studies


A large number of experiments were performed with modulated or steady excitation of $SO_2$ to its excited singlet ($^1B_1$) at incident wavelengths of 2800, 2900, 3000, 3100, and 3170Å, at about 25Å full width at half maximum. Lifetimes and quenching constants were measured at $SO_2$ pressures from 0.5 to about 30 millitorr which permits extrapolation to zero pressure and determination of the radiative lifetime. The radiative lifetime appears to decrease from more than 100 μsec at 2800Å to about 25 μsec at 3170Å excitation. Neither the $1/τ$ vs. $p$ plots nor the $p/I$ vs. p (Stern-Volmer) plots are linear, indicating that both vibrational and electronic energy transfer processes are occurring and that possibly more than one electronically excited state may be populated in the initial absorption process. This would be in some conflict with the presently available spectroscopic
information and will be checked carefully. From the slopes of the \( \frac{1}{t} \) vs. \( p \) plots it appears that quenching processes are very efficient, nearly gas kinetic, and that stepwise vibrational relaxation in the electronically excited state is important, as had been found earlier to be the case for \( \text{NO}_2 \).


Substantial progress has been made during this report period on several electron scattering experiments. These results are summarized below. The Werner band measurements are particularly important because they permit the molecular branching-ratio technique to be used in absolute VUV calibration work at wavelengths as short as 1100Å.

A paper describing this work has been submitted to The Physical Review. In this paper we also describe the first successful observation of a rotational-intensity perturbation predicted on quantum mechanical grounds by Julienne. We have continued with our studies of electron impact on reactive atomic species such as \( \text{N} \) and \( \text{O} \) and we have been able to evaluate the importance of atomic nitrogen as a source of airglow and auroral emission features. We have also made a detailed study of electron-impact excitation of \( \text{NO} \). These studies were prompted by our auroral mass spectrometer observations and a paper describing this work has been submitted to the Journal of Chemical Physics.

(a) **Electron Impact Excitation of the Werner Bands of \( \text{H}_2 \).**

The Werner band system of molecular hydrogen (\( \text{C}^1\Pi_u \rightarrow \text{X}^1\Sigma^+ \)) was excited by electron impact on \( \text{H}_2 \) and studied in the wavelength region 1100Å - 1250Å with sufficient instrumental resolution to resolve much of the rotational
structure of the bands. The absolute cross section for
the excitation of the Q1 line of each of the prominent
bands in this wavelength region was determined. The
absolute spectral sensitivity of the apparatus was deter-
mained by observing the dissociative excitation of Lyman-
Alpha in H₂ and Lyman-band fluorescence in HD. It was
found that the Werner bands are a satisfactory basis for
a spectral sensitivity determination only if the intensity
measurements are made with sufficient resolution (FWHM ≤ 0.44).
The perturbation interaction between the B and C states of
the hydrogen molecule was clearly observed in the rotational
intensity distribution in one set of bands; these results
will be discussed in detail.

(b) Electron Impact Excitation of Atomic Nitrogen. The absolute
cross sections for the excitation of five NI vacuum-ultra-
violet multiplets by electron impact on atomic nitrogen were
measured from threshold to 350 eV. The following results
were obtained:

<table>
<thead>
<tr>
<th>Multiplets</th>
<th>λ(Å)</th>
<th>Q(max; cm²)</th>
<th>E(max; eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI(3s²P → 2p³²P)</td>
<td>1743</td>
<td>1.8 x 10(-17)</td>
<td>17</td>
</tr>
<tr>
<td>NI(3s²D → 2p³²D)</td>
<td>1243</td>
<td>1.7 x 10(-17)</td>
<td>17</td>
</tr>
<tr>
<td>NI(3s¹P → 2p³¹S)</td>
<td>1200</td>
<td>5.5 x 10(-16)</td>
<td>25</td>
</tr>
<tr>
<td>NI(3s²D → 2p³¹D)</td>
<td>1164</td>
<td>4.0 x 10(-17)</td>
<td>18</td>
</tr>
<tr>
<td>NI(2p⁴P + 2p³¹S)</td>
<td>1134</td>
<td>4.8 x 10(-16)</td>
<td>22</td>
</tr>
</tbody>
</table>

The use of VUV absorption techniques to measure the absolute
nitrogen density provided an opportunity to measure the
oscillator strength of the NI(2p⁴P → 2p³¹S) transition.
The branching ratio for the NI(λ1164Å/λ1311Å) multiplets
was also determined. These results will be discussed in detail.

(c) Electron-Impact Excitation of Atomic Nitrogen in the Terrestrial Airglow. The absolute cross sections for the excitation of NI transitions in the vacuum ultraviolet due to the impact of low-energy electrons on atomic nitrogen have been measured in the laboratory. The cross sections for the resonance transitions at 1134Å and 1200Å are quite large \[ Q(\text{max}) \sim 5 \times 10^{-16} \text{ cm}^2 \] while the excitation cross sections for other NI transitions in the VUV are comparatively small. When the absolute cross sections for the direct excitation of N are compared with the corresponding cross sections for dissociative excitation of \( \text{N}_2 \), striking differences in shape and magnitude are found to exist. In principal, these differences permit one to estimate the density of atomic nitrogen in the upper atmosphere from an examination of VUV spectra obtained by satellites and sounding rockets. All data published up to the present indicate that the observed NI emissions in the day airglow and aurora are predominantly molecular in origin, and imply very low atomic nitrogen densities above 140 km.

(d) Electron-Impact Excitation of Nitric Oxide. The absolute cross sections for the excitation of the \( \text{NO}^+ \) Beer-Miescher bands \((A^1\Pi_u \rightarrow X^1\Sigma_g^+)\), two nitric oxide \( \beta' \) bands \((\beta' ^2\Delta \rightarrow X^2\Pi_g^-)\), and several atomic nitrogen multiplets in the vacuum ultraviolet by electron impact on NO have been measured over an
energy range extending from threshold to 300 eV. The variation of the dipole transition moment for the NO* 
\((A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^-)\) band system was also determined.

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

(a) In order to obtain strictly comparable values for the \(0 + NO\) radiative rate constant as function of pressure and wavelength, the OI resonance light source (He plus trace \(O_2\) discharge) and detector (NO photoionization) were extensively calibrated by producing known concentrations of \(O\) in the flow tube from excess \(N\) with a small, measured flow of added \(NO\) and comparing the experimentally observed absorption with a computer calculation. In this calculation Doppler-shaped lines of the emitted triplet, whose intensity ratios range from 5:3:1 for negligible optical depth in the source to lower ratios consistent with any given optical depth, are absorbed by the three J-states of atomic oxygen in thermal equilibrium in the large flow tube. In this manner, a given \(O\)-concentration (measured by \(N + NO\)) and measured light absorption (integrated over the triplet) uniquely determines the extent of source "broadening", i.e. the \(O\)-concentration in the source. It is this latter parameter which is quite variable and almost impossible to set experimentally with any degree of reliability, probably because of slight oxygen evolution from the glass walls in the discharge region. The problem is thus subverted by calibrating the light source/absorption system immediately before and after each experiment in the above manner. An extensive, new series of radiative rate constant measurements at pressures from 0.5 to 100 millitorr and wavelengths from 4000 to 7800Å were carried out, and were properly corrected for source broadening. They show the predicted
decrease of the pseudo-bimolecular rate constant, $I_o$ from the higher to the lower pressures, and they also show that the ratio $I_o^{\text{high}} / I_o^{\text{low}}$ decreases sharply from about 6 at and above 6000Å to about 1.5 at 4050Å. This arises from the fact that 4050Å is close to the high energy threshold of the chemiluminescence ($\sim 3975Å$) so that virtually every collision which results in some vibrational relaxation (and these occur with roughly gas-kinetic cross section) removes the emitting NO$_2$, i.e. the emitters at the wavelength are mainly unstabilized collision complexes, whereas at longer wavelengths they include many, partially vibrationally relaxed NO$_2$ molecules. The recent experiments bear out very nicely the correctness of our general mechanism. Miss Cody has completed all necessary experiments and most of her Ph.D. dissertation which she is expected to defend within one to two months.

(b) The completed experimental study of the important $O + O_3 \rightarrow 2O_2$ reaction was fully analyzed and written up as a Ph.D. dissertation by Mr. McCrumb. The best least squares computer fit to all data points from 296 to 4096K gave an Arrhenius expression of $1.78 \times 10^{-11} \exp (-4.46 \text{kcal/RT}) \text{cm}^3\text{sec}^{-1}$, slightly different from the earlier expression which was based on a graphical fit. Mr. McCrumb successfully passed his Ph.D. final examination and is now preparing a condensed version of his work for publication in the Journal of Chemical Physics.

The flow apparatus has been substantially modified by Dr. J. O. Anderson for the study of OH reactions of stratospheric and mesospheric importance such as $OH + O_3$, $OH + NO_2 + M$, $OH + NO + M$, etc. This is accomplished by placing a fixed fluorescence cell downstream of the heated or cooled reaction section and adding the stable reactant
(NO₂ or O₃) through a movable inlet tube. Excellent sensitivity and dynamic range have been achieved for the OH density measurement, and the desired reaction rates will soon be measured.

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

A new experimental system was designed and built for the study of the translational energy release in sodium atom excitation reactions by means of line shape studies using a Fabry-Perot interferometer. Much difficulty was encountered with a commercial, piezoelectric scanning interferometer which did not meet specifications in various ways and several of whose components had to be returned for repair or replacement. An overall finesse of 20 to 25 was finally obtained with good reproducibility, but the stability and drift problem is not yet fully under control. Experiments could be performed successfully for two systems, Na + Cl₂ and Na + "active nitrogen". The latter is the more important, because it has direct bearing on the question of energy transfer from vibrationally excited N₂ to Na. It is also experimentally easier to study, since sufficiently bright light emission is observed at Na temperatures as low as 180°C (where the optical depths is reasonably low) whereas the Na + Cl₂ glow is until now observed only above about 280°C. A computer program was developed which generates Doppler-shaped Na line profiles (including hyperfine structure) as function of temperature, and folds in the desired experimental finesse. Preliminary results for the Na + N system indicate a normal (unreversed) line-shape and a relatively low translational temperature (< 1000°K). It has not yet been determined whether the excitation is due to N-atoms, i.e. to the highly excited N₂ species.
formed early in the recombination, or to $N_2^\ast$ from the discharge at more moderate excitation energies (~2 eV, near $V=8$ or 9). The $N_2$ discharge flow line has a titration inlet upstream of the emission cell, and in future experiments it will be possible to add "titrant" species such as NO, which removes $N$ and produces $N_2^\ast$, or CO$_2$, which relaxes $N_2^\ast$ but does not react with $N$, in order to clarify the precursor species in this energy transfer.

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

The crossed beam studies of the reaction $\text{Ba} + \text{O}_2$ has proceeded well during the past six months. Signal quality has improved and a very satisfactory curve of angular distribution of BaO has at last been obtained. Estimates of the reaction cross section have increased slightly, to a few times $10^{-16} \text{cm}^2$. Phase spectrometry measurements, used to determine the mean velocity of the reaction products have been confusing. Although the data appears reasonably satisfactory, we have not been able to reconcile in detail the data with any of the standard simple models of the reaction dynamics. Of particular concern is the fact that at some laboratory angles, the signal phases as a function of modulation frequency suggest that the reaction products emitted transversely to the line of centers of the reactants in center-of-mass coordinates have a total kinetic energy of about 0.3 eV (therefore, leaving about 0.3 eV in internal energy in the BaO), but that at other angles the division of energy between kinetic and internal energy changes.

Variation of temperature of the Ba did not reveal discernible changes in apparent rate coefficients, which permits the estimate that cross section for the triplet Barium metastable atom's reaction...
cross section is not more than about one order of magnitude greater than the groundstate Barium atom's.

Attempts are currently being made to obtain a better absolute value for the groundstate atom's reaction cross section.

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

We have continued with our studies of argon atoms in the metastable $\text{Ar}^{(\text{3P}_0,2)}$ state with special emphasis on airglow and auroral applications. This work has yielded a number of interesting results which are summarized below:

(a) Collisional Deactivation of Metastable $\text{Ar}^{(\text{3P}_0,2)}$ Atoms and $\text{N}_2(\text{A}^3\Sigma_u^+)$ Molecules. In a series of afterglow experiments, we measured the rate coefficients for the collisional depopulation of argon atoms in the metastable $\text{3P}_0,2$ state by $\text{Ar}$, $\text{CO}$, $\text{N}_2$, and $\text{O}_2$. and we found that $k(\text{Ar}) = 2.2 \times 10^{-15}$ cm$^3$/sec, $k(\text{CO}) = 1.5 \times 10^{-11}$ cm$^3$/sec, $k(\text{N}_2) = 2.8 \times 10^{-11}$ cm$^3$/sec, and $k(\text{O}_2) = 1.2 \times 10^{-10}$ cm$^3$/sec. Inelastic collisions between metastable argon atoms, resulting in the ionization of one collision partner, were also observed and from simultaneous electron density measurements we obtained a tentative value of $5 \times 10^{-10}$ cm$^3$/sec for the corresponding rate coefficient. The excitation of the 2nd Positive System of $\text{N}_2(\text{C}^3\Pi_u + \text{B}^3\Pi_g)$, produced by the depopulation of metastable argon atoms by $\text{N}_2$, was studied in detail and the specific rate coefficient for this important process was found to have a value of $1.2 \times 10^{-13}$ cm$^3$/sec. The collisional deactivation of
metastable $\mathrm{N}_2(A^3\Sigma_u^+)$ molecules by CO, O$_2$, and Ar was also studied, and the following rate coefficients were obtained: $k(\text{CO}) = 1.7 \times 10^{-12}$ cm$^3$/sec, $k(\text{O}_2) = 3.0 \times 10^{-12}$ cm$^3$/sec, and $k(\text{Ar}) < 8 \times 10^{-17}$ cm$^3$/sec.


The studies of water cluster formation rates of NO$^+$ and O$_2^+$ were successfully concluded. In the NO$^+$ work the mechanism involves the steps

$$\text{NO}^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}^+. \text{H}_2\text{O} + \text{M}$$

$$\text{NO}^+. \text{H}_2\text{O} + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}^+. \text{2H}_2\text{O} + \text{M}$$

$$\text{NO}^+. 2\text{H}_2\text{O} + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}^+. 3\text{H}_2\text{O} + \text{M}$$

$$\text{NO}^+. 3\text{H}_2\text{O} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightarrow \text{2H}_2\text{O} + \text{HONO}$$

all of which were measured directly and/or by consistent computer fit for four M, He, Ar, O$_2$ and N$_2$, i.e. a total of 21 rate constants were obtained, since $k_4$ does not involve M and should therefore be identical for all M within the error bars of the data. This was found to be the case. A paper describing this work was submitted to and accepted by the Journal of Chemical Physics.

The O$_2^+$ clustering sequence was studied in M = He, Ar, and N$_2$. It consists of the steps

$$\text{O}_2^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{O}_2^+. \text{H}_2\text{O} + \text{M}$$
\[ \text{O}_2^+ + \text{H}_2\text{O} + \text{H}_2\text{O} \xrightarrow{26} \text{H}_3\text{O}^+ + \text{OH} + \text{O}_2 \]

with additional routes to form \( \text{O}_2^+ \cdot \text{H}_2\text{O} \) in the presence of much \( \text{O}_2 \) or \( \text{H}_2 \) via

\[ \text{O}_2^+ + \text{O}_2 + M \xrightarrow{\text{-3}} \text{O}_4^+ + M \]

\[ \text{O}_4^+ + \text{H}_2\text{O} \xrightarrow{\text{4}} \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{O}_2 \]

or

\[ \text{O}_2^+ + \text{N}_2 + M \xrightarrow{\text{-5}} \text{O}_2^+ \cdot \text{N}_2 + M \]

\[ \text{O}_2^+ \cdot \text{N}_2 + \text{H}_2\text{O} \xrightarrow{\text{6}} \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{N}_2 \]

These latter steps lead to an inverse dependence of the apparent pseudo-first-order rate constant for \( \text{O}_2^+ \) decay on the concentration of added \( \text{H}_2\text{O} \). This makes possible the indirect measurement of very slow reaction rate constants such as \( k_3 \) and \( k_5 \) which were found to be \( 2.5 \times 10^{-30} \) and \( 8 \times 10^{-31} \text{cm}^3/\text{sec} \), respectively. Consistent computer fits to the above reaction scheme were again obtained.

A publication describing this work is in preparation.

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

Progress in this experiment has been relatively slight during the past six months since during this period the graduate student (L. N. Clendenning) was writing his thesis based on this experiment. It did become apparent during the course of his thesis writing, that the slight inhomogeneities in the magnetic confining
field introduce considerable complications into the analysis of results that lead to absolute cross sections. Rather than attempt to go through the detailed analysis, the results of which would always contain considerable uncertainties, it was decided to alter the apparatus in such a way as to reduce the magnetic field inhomogeneities and make the analysis required more simple. This work has been going on since Mr. Clendenning left.

Interestingly enough, the field inhomogeneities work in such a way as to bias the results for the ratio of ion-atom reaction to charge transfer reaction in the positive direction, i.e., detection of ion atom reaction is more sensitively done than detection of charge transfer. This implies that our previous statements that charge transfer strongly dominates over ion-atom reaction can be made even more strongly.

8. Ion-Molecule Reactions at Elevated Temperature (M.A. Biondi) (Tasks b and d)

The drift tube measurements of the reaction

\[ U^+ + O_2 \rightarrow UO^+ + O \]

have been completed. A rate constant of \( 8.5 \times 10^{-10} \text{ cm}^3/\text{sec} \) has been found at thermal energy (300°K) decreasing to \( 7 \times 10^{-10} \text{ cm}^3/\text{sec} \) at a mean kinetic ion energy of 11 eV (in lab frame). The experimental uncertainty of these rate constants is estimated to be about ± 20%.

The corresponding reaction of \( U^+ \) with nitrogen has also been investigated. No reaction is observed to occur in the energy range from thermal to 11 eV indicating that this (endothermic) reaction is probably very slow (less than \( 10^{-11} \text{ cm}^3/\text{sec} \)).

In the course of the uranium experiments it was discovered
that some neutral uranium vapor diffused from the ion source into the drift tube. While this was of little consequence for the reaction rate measurements, this effect also provided a simple way to test if a reaction of neutral uranium with $O_2$ would produce uranium oxide in ionized form, as suggested by some investigators. The fact that no ionized products were observed when the ion source was biased such that no ions could enter the drift cell is a strong indication that a reaction of neutral uranium with $O_2$ is not likely to result in ionized products. The results of the uranium experiments were presented by R. Johnsen at the 24th Gaseous Electronics Conference.

The evaporative ion source developed for uranium ions is also found to be suitable for production of aluminum ions when the uranium metal is replaced by aluminum. The reaction of aluminum ions with $O_2$

$$Al^+ + O_2 \rightarrow AlO^+ + O,$$

is endothermic by about 3.5 eV and cannot be expected to occur at energies available in a drift tube experiment. In agreement with this expectation, no reaction products from $Al^+$ were found when $O_2$ was admitted to the drift cell.

A recurring problem in interpreting drift tube data is that of specifying the drifting ions' velocity distribution. Without this knowledge the conversion of the measured rate constants to the more basic reaction cross sections is not possible. Since very little progress has been made in the theory of ion energy distributions in the last twenty years (following O. H. Wannier's contribution) we have decided to investigate the problem experimentally. To study the feasibility of employing a retarding potential technique, we have placed
a fine grid between the drift tube's exit orifice and the mass spectrometer and have taken a number of retarding potential curves at various values of \( E/p \) and for a number of ions with different masses (\( \text{He}^+, \text{O}^+, \text{O}_2^+, \) and \( \text{Xe}^+ \)). The results are in qualitative accord with our expectations. Gross features such as the shift in the mean energy and the increasing width of the distributions with increasing \( E/p \) can be read easily from the retarding potential curves. However, a more careful design of the retarding electrodes to avoid problems with contact potentials will be needed before this technique can be used to provide quantitative data on ion energy distributions. A means of experimentally determining velocity distributions should be of particularly great value in cases that are theoretically difficult to treat such as the drift of molecular ions in molecular gases, including the effect of inelastic collisions and related effects at very high values of \( E/p \).

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

Our efforts in this area have been directed into two channels:

1. Measurements of the absolute cross sections for the excitation numerous airglow and auroral emission features due to electron impact on vibrationally excited \( \text{O}_2^- \) and \( \text{N}_2^- \). These experiments are important in our auroral work and central to the magnetic-cusp rocket experiments (see item 14) that we will launch from Greenland. (2) We have been studying the process

\[
(\text{O}_2^+)^* \rightarrow \text{O}_2 + \text{O}_2^0 (\frac{3}{2}) + \text{O}_2^+
\]

which has been proposed by Walker to explain the anomalous excitation of the \( \frac{3}{2} \) state in the auroral zone and we have obtained preliminary
evidence which supports Walker's contention that this process
proceeds very rapidly \( (k \sim 10^{-10} \text{ cm}^3/\text{sec}). \)


We have continued to investigate the properties of metastable
atoms and molecules and Rydberg States using translational-energy
spectroscopy. These studies lead to cross section values for the
basic collision processes, to the identification and location (in
absolute energy as a function of the internuclear separation) of
hitherto unknown molecular states, to the evaluation of radiative
lifetimes, to the determination of the Auger \( \gamma \)-coefficient for a
variety of detector surfaces (at room and elevated temperature),
and to the measurement of quenching coefficients for excited states
at relative impact velocities (effective temperatures) not observable
in conventional many-body experiments. The latter studies are
particularly interesting in the light of our in situ auroral studies.

Some of our current results and their implications are summarized below:

(a) Translational Spectroscopy of Fast Metastable Frag-
ments Produced by Electron Impact Dissociation of
Atmospheric Gases. Atmospheric gases \( (O_2, N_2, CO, CO_2) \) have been bombarded by a pulsed electron beam
in the 0 - 300 eV energy range and the resulting
metastable fragments were detected by means of Auger
ejection of secondary electrons from a metal surface
in a time of flight experiment. The velocities of the
dissociatively excited fragments were found to be non-
thermal, with some fragments having as much as 10 eV
in kinetic energy. Cross sections for the production
of slow (0.1 – 0.3 eV) fragments rapidly reached their maximum values in the 20 – 30 eV region and fell off slowly out to 300 eV whereas the cross sections for the production of fast (1 – 10 eV) fragments rose steadily from threshold to a peak around 100 eV and then fell off. These cross sections are large and imply that the presence of fast excited atoms must be taken into account in the upper atmosphere, particularly under auroral conditions where dissociative excitation plays a major role.

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

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

The observations of neutral barium spectral line profiles and intensities obtained in Alaska in 1969 and in Florida in 1971 yield information on the initial photoionization history of sunlit barium clouds. During the report period, a fairly simple computer program dealing with the time history of ten "species" – 6 states of neutral barium, the barium ion (electron), and barium oxide – has been developed which includes relevant populating and depopulating mechanisms for each of the "species". Radiation transport effects are neglected in this approximation. The qualitative features of some of our interferometer observations of the neutral barium behavior are reproduced when values for the relevant atomic collision rates, such as those postulated by G. Best, are used. The computer code appears useful for fixing allowable values for some of the key reaction rates.

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

Using our observations of the 6300 intensity transients
induced in the F-region of the ionosphere by the turning on and off of a 1.6 MW ground-based transmitter we have been able to determine the in-situ lifetime of the $0(^1D)$ atoms as a function of altitude over the range 225-300 km. The natural lifetime ($\sim 110$ sec) of the $0(^1D)$ state is reduced by $N_2$ quenching at these altitudes. Using a model atmosphere for the $N_2$ density, we obtain a value for the quenching coefficient, $k_{\text{quench}} \approx (5 \pm 2) \times 10^{-11} \text{ cm}^3/\text{sec}$, independent of altitude. This value is in excellent agreement with laboratory values.


We continue with our analysis of two highly successful sounding rocket studies of the transient ionosphere. The instrumentation on board both vehicles included a quadrupole mass spectrometer that measured the local ion and neutral composition of the upper atmosphere, two hemispherical analysers for measuring the photoelectron energy distribution in the dawn and twilight ionosphere, a cylindrical probe for electron temperature and density measurements, and a planar total positive ion probe. These particle experiments were complemented by a 1/4-meter Ebert monochromator that scanned the VUV dayglow spectrum from 1150Å to 1500Å and six filtered photometers that measured the overhead intensity of a variety of airglow features.

The dawn experiment (Aerobee 170 rocket 13.46 UA) was particularly interesting because it took place during a major solar flare and revealed the presence of substantial concentrations of $O^{++}$ ions in the F region. This ion is not a normal F region constituent, although it has been observed occasionally by high-altitude satellites. Our data suggest that heavy particle bombardment may be the source
of this ion.

By contrast our twilight experiment (Aerobee 350 rocket 17.09 UA), which carried a payload weighing nearly 700 lbs. to 350 km, was performed under very quiet conditions. All instruments on board worked to perfection and we are studying these results now.

Our analytic activities are balanced by the intensive preparations for our return to Fort Churchill to study the aurora and to attempt to verify our earlier NO observation. Two rockets are being prepared for this task: an Aerobee 150 and a Nike-Apache. Both rockets will carry a dual mode mass spectrometer equipped with complementary cylindrical and planar probes. The Aerobee payload will also include a liquid nitrogen cooled 1/4-meter monochromator for infra-red out to 5 microns. The normal complement of visible VUV instruments that we have flown in the past are an important part of both payloads.

During this same time window we are also preparing a new payload that will be launched next summer from Wallops Island, Va. on board a Javelin rocket. We anticipate a minimum peak altitude of 800 km. This experiment will provide the first test of a new type of optical mass spectrometer which we have developed as the result of our laboratory experiments (item lb).

We have also embarked on a new series of rocket experiments that will be launched from Greenland in collaboration with the Danish Space Agency to study the unusual atmospheric conditions that occur in the region of the earth's magnetic cusp. This is a natural extension of our auroral and disturbed ionosphere work and
ties in very well with our laboratory studies of hot atom chemistry (item 9 and 10).

14. **Distribution of Gases in the Mesosphere** (T.M. Donahue and E.C. Zipf) *(Task f)*

Our analysis of OGO-6 photometer data continues. A paper describing OI λ5577 measurements is being prepared and will be submitted for publication shortly. The data relating to the excitation of sodium D lines and the noctilucent clouds is being analyzed and reviewed.

Plans for an elaborate mesospheric rocket experiment which would measure the concentration of $\text{H}_2$, $\text{O}_2$, $\text{N}$, $\text{O}$, $\text{NO}$, $\text{OH}$, $\text{O}_2(^1\text{D})$, $\text{O}_2(^3\Sigma)$, $\text{H}_2\text{O}$ and $\text{CO}_2$ at D region altitudes have been finalized and portions of the payload constructed.

C. **Theoretical Studies**


(a) Our calculations of charged particle-neutral atom collision cross sections using the Glauber approximation continue. The papers by Thomas and Franco, and by Thomas and Gerjuoy, mentioned in our last technical report as having been submitted for publication, now have appeared. In addition, we have completed some rather detailed calculations on the polarization of the radiation following electron excitation as computed in the Glauber approximation. A paper on this subject, whose initiation and motivation was explained in our last technical report, has been submitted for publication. Since our last technical report we also have published (in a Letter to the Editor by Thomas, Sheorey and Gerjuoy) careful comparisons of angular distributions and total cross sections for electron-hydrogen collisions
computed in both the Glauber and Vainshtein approximations; the Vainshtein approximation has been favored by several groups, including an atomic collision group in Moscow, who developed the approximation. It was found that for integrated (over angle) elastic or inelastic cross sections the Glauber approximation is at least as good as any of the many (there are at least six) versions of the Vainshtein approximation, while the Glauber differential cross sections are markedly superior to the Vainshtein results. For computing the polarization of the radiation following electron excitation, the Glauber, Born and Vainshtein are about equally good, and are quite close to the observations (by Fite and co-workers here at PASI) in the energy range 30 eV - 700 eV. There are some discrepancies between the computations and observations at the higher energies (500 - 700 eV) measured, which suggest further experimental and theoretical work on these polarizations may be instructive. As a result, a student (D. Brocklebank), has been assigned the task of computing the angular correlation between the photons following excitation and the outgoing scattered electron, in the Born, Vainshtein and Glauber approximations. It is our hope that these predictions will be sufficiently different to provide (after comparison with hoped-for observations) a very sensitive test of the comparative validity of the three approximations.

We are proceeding with our attempts to extend the applicability of the Glauber approximation to the scattering of electrons and protons by atomic systems more complicated than hydrogen. A suggested procedure on this extension, based on the closed form Glauber amplitudes derived and published by Genjuoy and Thomas, has appeared (in Physical Review Letters by V. Franco). However, we believe that Franco's procedure
still involves far too much computational effort, and we are continuing to seek a method which—for these more complicated collisions—requires not much more computer time than do the electron-hydrogen Glauber calculations.

We are pleased to report that our work on the Glauber approximation was the subject of an invited paper (by E. Gerjuoy) at the VIIth International Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, July, 1971.

(b) The work on the theoretical studies of ionization and excited state populations in Ba plasmas continues, but reliable numerical results are disappointingly slow, and we are considering terminating these calculations.

(c) The quantum defect calculations by V.B. Sheorey, whose submission for publication was mentioned in our last Technical Summary Report, has appeared.

(d) A thorough review of the theory of rotational excitation of homonuclear diatomic molecules by slow electrons (by E. Gerjuoy with D. Golden, Neal Lane and A. Temkin) has been completed and accepted for publication by the Reviews of Modern Physics.

(e) Our studies of the effects of potential barriers on thermal collisions have been concentrated on the processes leading to the formation of molecules. We have shown that the presence of a high barrier does not necessarily prevent molecular formation. Indeed in some cases the reaction rate may be enhanced, as, for example, for CH formation by radiative association, and H₂ formation by three-body recombination.

(f) Our calculations on dielectronic recombination involving
electrons and highly charged ions have been completed and the results have been accepted for publication. We concluded that experimental studies of these reactions are feasible and would be useful as a check on the theory of this important recombination process.

(g) Our program for calculating cross sections for electron-atom collisions using variational techniques is being continued. In collaboration with Drs. Temkin and Bhatia of the Goddard Space Center, in Maryland, we have been studying resonant scattering of electrons by helium. This work, which is essentially completed, has involved extension of the theory of projection operators, and has given numerical results to compare with the experimental work which is at the forefront of high resolution electron collision studies. We have obtained the physical parameters of the well-known resonance at 19.3 eV. We have strong evidence that some other oscillations which have been observed in the cross section near 19.5 eV cannot be due to a resonance, and must be caused by some spurious experimental effect. We intend to study the 19.3 eV resonance further, using the complex energy method, since reliable theoretical results on this resonance are needed. This is because the resonance is used for calibrating the average energy of electron beams, and could possibly also be used for studying the energy profile of high resolution beams.

Although the standard variational techniques provide the most accurate means of calculating cross sections they do not in general provide an estimate of the error of a particular calculation. This is a serious problem in applications to large systems. We have begun an
investigation of the minimum variance technique, which not only gives an indication of the error inherent in a trial wave function, but also gives a simple prescription for choosing between trial wave functions of different types.

(h) Our studies of atom-atom and ion-atom interactions are continuing. We aim to calculate the cross sections for charge transfer and electronic excitation in Li⁺-Li collisions, and have obtained the potential curves and interaction matrix elements needed in this calculation. We are now studying the particle trajectories and will then solve the coupled differential equations which govern the states of the atoms as they move along those trajectories.

Our computer program for applying the pseudopotential method to the calculation of interatomic potentials has been written, but it has not yet been fully tested. Calculation of electron impact cross sections for Be⁺, Mg⁺, Ca⁺ and Ba⁺ will soon be initiated by this technique, and a graduate student is being trained to carry through this project.
II. Publications and Technical Presentations

A. Publications


"Excitation of a D-line Radiation in Collisions of Sodium Atoms with Internally Excited H₂, D₂ and N₂", W. L. Fite, J. Fricke and H. F. Krause, to be published.


B. Technical Presentations

"Recombination of Electrons with Positive Ions of the \( \text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} \) \( \text{n} \) Series", invited paper presented by R. Johnsen at the COSPAR Symposium on the D and E Regions of the Ionosphere, Urbana, Illinois.
"Reactive Scattering of Ba by O\( _2 \) in a Crossed Beam Experiment", W. L. Fite, Seventh International Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, 1971.
"Thermal Energy Reactions between NO \(^+\) Ions and Metal Atoms", W. L. Fite, invited paper at the DASA High Altitude Nuclear Effects Symposium, Stanford Research Institute, September, 1971.


"NO \(_2\) Fluorescence and O + NO Chemiluminescence", F. Kaufman, Seminar, Georgetown University, Washington, D.C., April 8, 1971.


C. Other Activities

J.N. Bardsley and B. R. Junker have continued the collaboration with the Goddard Space Center's group for Theoretical Studies, and have made several visits to Washington for consultations.


M.A. Biondi participated as a member, Advisory Committee on Physics of the National Science Foundation in April, 1971.

T.M. Donahue, Trustee, Upper Atmosphere Research Corp.


T.M. Donahue, Member, Science Steering Group for Outer Planets Mission.

T.M. Donahue, Member, Advisory Panel, for Atmospheric Sciences, Division of Environmental Sciences, National Science Foundation.
W.L. Pite is co-authoring a chapter of the DASA Reaction Rate Handbook entitled "High Energy Heavy Particle Collisions", with A. W. Ali and J. Greene.  
W.L. Pite attended meeting of Research Advisory Committee for Office of Advanced Research and Technology at NASA.  
F. Kaufman was invited to attend an AROD Review "Gaseous Interactions and Plasma Physics", at El Paso, Texas on April 21 and 22, 1971 and chaired one of its technical sessions.  
F. Kaufman was outside examiner at the Ph.D. thesis examination of Mr. George Spindler at York University, Toronto, on May 3, 1971.  
F. Kaufman was an invited member of the ad hoc Panel on the (NOx)-Ozone Problem of the National Academy of Sciences on July 29, 1971.  
F. Kaufman attended the DMA High Altitude Nuclear Effects Symposium at the Stanford Research Institute on August 10-12, 1971.  
F. Kaufman was invited to attend the General Motors Symposium on Emissions from Continuous Combustion Systems at Warren, Michigan on September 27 and 28, 1971, and to be the discussor of one of its papers.  
F. Kaufman attended meetings of the Executive Committee of the Pittsburgh Section of the American Chemical Society on June 28 and September 8, 1971.  

III. Visiting Scientists  
Dr. David Spence, Argonne National Laboratory  
Professor Ugo Fano, University of Chicago  
Dr. R. Schoen, National Science Foundation
Professor Dr. J. Kistemaker, FOM Laboratory for Atomic and Molecular Physics, Amsterdam.

Dr. M. F. R. Mulcahy, CSIRO, Chatswood, N.S.W., Australia,


Dr. Robert Schaeffer, Johns Hopkins University.

IV. Degrees Awarded

D.P. Sipler, Ph.D., September, 1971.

B. Guenther, Ph.D., September, 1971.

R. Nieman, Ph.D., September, 1971.

L.M. Clendenning, Ph.D., August, 1971. (Subject to revisions in thesis).

E.J. Stone, Ph.D., June, 1971.
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**University Accounting of Funds**

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