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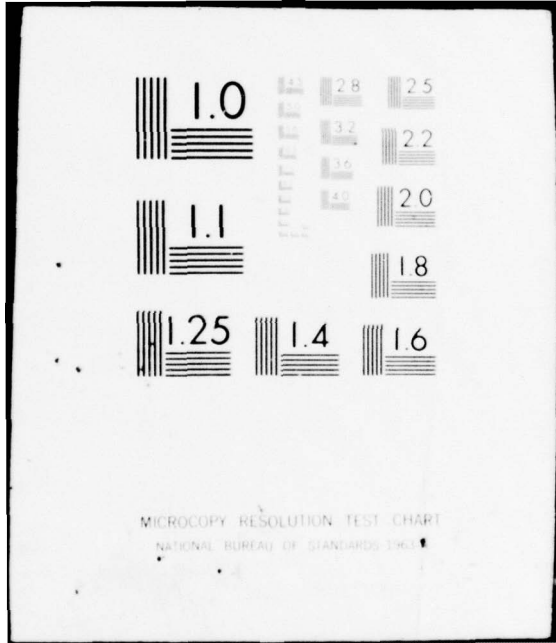
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REACTION RATE DATA.

Number 58.

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ANNUAL SUMMARY OF PROGRESS IN FY 1976 AND 7T DNA REACTION RATE PROGRAM.

Number 58

11 November 1976

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This issue of the DASIAC Reaction Rate Data presents summaries of DNA Reaction Rate Research Programs for FY 1976 and FY 7T.

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**ANNUAL SUMMARY OF PROGRESS IN FY 76 AND FY 77
DNA REACTION RATE RESEARCH PROGRAM**

A. SUBTASK S99QAX HC 064

"Development of a Unified Model"

1. *Improved Models and Fast Running Codes for E,F Regions - M. Scheibe, MRC (Work Unit 33 in FY 76 and FY 77).*

Progress in the area of UHF satellite communications sensitivity calculations has been slow. The original scheme, upon investigation, proved to be too expensive and perhaps technically not feasible. However, within the last few months a satellite communications model has been added to the ROSCOE code. In addition, an unclassified version of ROSCOE has been made available at the AFWL CDC 7600 computer facility. UHF sensitivity calculations will now be initiated using the ROSCOE code.

Our DCHEM coupled reaction rate code has been updated to include the latest data concerning chemical reactions and rate constants. Particular attention was given to the neutral chemistry involving hydrogen and to ion hydration reactions and to ion-ion and electron-ion recombination rate constants. In addition, the code has been revised and will now provide values of the "effective rate constant" at any time desired. This will facilitate use of the code results in modeling efforts and in sensitivity calculations.

The updated DCHEM code and the FIRECHEM code are being used to generate benchmark calculations for the ROSCOE optical development program. In addition, the DCHEM code has been used to provide inputs to VLF and ELF sensitivity calculations and we shall provide more inputs for this purpose in the near future.

B. SUBTASK S99QAX HD 010

"Reaction Rates Critical to Propagation"

1. *Measurement of Rate Coefficients for Two Body Positive Ion-Negative Ion Neutralization J. Peterson, SRI (Work Unit 69 in FY 76; Work Unit 80 in FY 77).*

The merged beam measurements of ion-ion neutralization have been definitive for atomic and small molecular ions. For the less stable hydrated ions, the problem of obtaining adequate beam currents is severe. Several modifications to the apparatus were made to increase its sensitivity for the measurement of clustered ion reactions. The results were somewhat promising, although the increased complexity would cause lengthy measurement times. The need for merged-beam measurements was questioned when results on mixtures of complex ions and hydrates were recently obtained in a flowing afterglow by D. Smith's group in England (Birmingham). They found small rates (3 to 7×10^{-8} $\text{cm}^2 \text{sec}^{-1}$) for combinations of NO^+ , NO_2^+ , NO_3^+ , their hydrates, and halogens, with little variation. In order to determine our future course of action an evaluation of all existing techniques was made. This study was performed by M.N. Hirsch. He analyzed the flowing afterglow, the Dewey stationary

afterglow, and the SRI merged beams experiment, using versions of the AIRCHEM code to model the afterglow experiments. The Dewey results are incompatible with the Birmingham rates; they suggest rate coefficients for recombination with NO^+ as follows (all $\times 10^{-7} \text{ cm}^3/\text{sec}$): NO_2^- : (1-2); NO_3^- : (5-8); $\text{NO}_2^- \cdot \text{H}_2\text{O}$: (0.1-0.5); $\text{NO}_3^- \cdot \text{H}_2\text{O}$: (0.1-1). Complications due to the ion-neutral chemistry impede definitive understanding of the afterglow experiments, the negative ion chemistry being still inadequately understood; this may cause difficulties in the flowing afterglow as long as there is a considerable distance between the positions where the ion density is measured and where the masses are identified. Hirsch concluded that while vibrational excitation is a problem in merged beams experiments, this is presently the only unequivocal method of isolating complex ion reactions in air-like mixtures.

2. *Investigations of Photodissociation and Photodetachment of Negative Ions and Hydrates* – C. Lineberger, JILA (Work Unit 70 in FY 76; Work Unit 80 in FY 77).

The utilization of beam techniques in negative ion photodetachment and photodissociation studies affords considerably enhanced sensitivity, but, to date, ion beam intensity requirements have precluded the use of ion sources for which the ion vibrational state distribution was well characterized. We are completing construction of an intense low-temperature ion source which should produce adequate (10^{-10} to 10^{-11} A) beams of cluster ions at temperatures near thermal. This source will be used in a beam machine where neutrals, charged fragments, and photoelectrons can be detected. The detection systems are working well, as has been demonstrated in calibration and check-out studies on atomic alkali negative ions. The first molecular system to be studied will be electron production from O_3 in the threshold range. Subsequent studies will involve photodetachment and photodissociation of cluster ions, especially hydrates.

3. *Recombination of Electrons with Cluster Ions and Ion-Molecule Reactions* – M.A. Biondi, University of Pittsburgh (Work Unit 71 in FY 76; Work Unit 81 in FY 77).

The rates of recombination of electrons with the ammonium series cluster ions were determined [see Huang, Biondi and Johnsen, *Phys. Rev. A14*, 984, (1976)]. At $T_e = T_+ = T_n = 200, 300,$ and 410 K , respectively, $\alpha(18^+) = (2.5 \pm 1), (1.5 \pm 0.3),$ and $(1.3 \pm 0.2) \times 10^{-6} \text{ cm}^3/\text{sec}$. The very weak electron temperature dependence of cluster ions was verified for $\text{NH}_4^+ \cdot (\text{NH}_3)_{1,2}$ with the finding that (in cm^3/sec) $\alpha(35^+) = 2.82 \times 10^{-6} [300/T_e (\text{K})]^{0.147}$ and $\alpha(52^+) = 2.68 \times 10^{-6} [300/T_e (\text{K})]^{0.050}$, over the range $300 \text{ K} \leq T_e \leq 3000 \text{ K}$, accurate to $\sim \pm 10$ percent. A new recombination mechanism, cluster-detachment recombination is proposed to explain these results. Preliminary results for the hydronium series ion $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_3$ indicate that $\alpha(73^+)$ shows essentially *no* variation ($\sim T_e^{-1}$) with electron temperature.

Problems with operation of the high-temperature drift tube are being overcome, and studies to $\geq 1000 \text{ K}$ of the temperature dependence of the important charge transfer and atom transfer reactions, $\text{O}^+ + \text{O}_2, \text{O}^+ + \text{N}_2, \text{He}^+ + \text{N}_2,$ and $\text{He}^+ + \text{O}_2,$ are in progress. The branching ratio of the $\text{He}^+ + \text{O}_2$ charge transfer reaction has been redetermined at 300 K (in view of conflicting experimental data). We now find, in agreement with the injected ion flowing afterglow results of Birmingham, that essentially all of the reaction goes to the dissociative charge transfer channel to produce O^+ , some in excited $\text{O}^{*+} (^2\text{D})$ state, with little, if any, O_2^+ produced by the primary reaction. Our earlier results were confused by production of O_2^+ by a secondary reaction, the apparently fast charge transfer reaction involving the excited O^{*+} produced in the primary reaction.

4. *Associative Ionization Reactions of Communications Importance* – W. Fite, Extranuclear Labs (Work Unit 72 in FY 76; Work Unit 82 in FY 77).

The study of thermal-energy associative ionization processes has been expanded to include reactions between atmospheric constituents and both debris material and possible fission products.

The total cross sections for reactions of ozone with uranium and thorium are of order 2×10^{-16} cm². Negative ions of O and O₂ are observed only in the thorium-ozone reaction; however, these channels account for less than 1 percent of the total cross section, the major negative product being electrons.

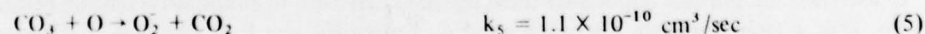
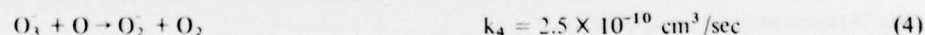
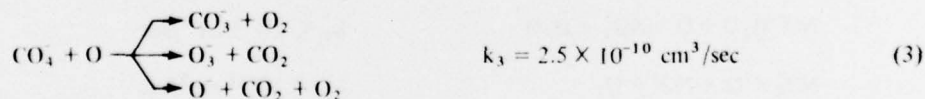
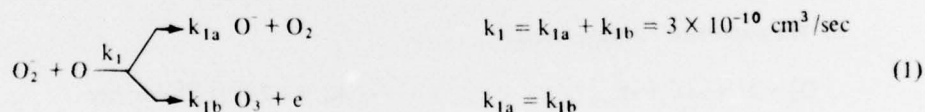
A brief survey of metal oxide-oxygen reactions has been conducted. No reaction products are observed for associative ionization of various oxides of molybdenum, tungsten and titanium with atomic oxygen, indicating that the cross sections for these reactions, if they occur, are less than 10^{-18} cm².

Studies of associative ionization of O and O₂ with elements in the lanthanide series indicate that many of these metals have significant reaction cross sections. Work is in progress to resolve some experimental discrepancies in the cross sections obtained through different techniques. Preliminary data indicate that many of the cross sections are greater than 10^{-16} cm². Negative ions are observed in one of these reactions, but again, that channel accounts for less than 2 percent of the total cross section.

5. *Investigation of Negative Ion Reaction Rates; Effects of Vibrational Excitation Energy* — E. Ferguson and F. Fehsenfeld et al, NOAA (Work Unit 73 in FY 76; Work Unit 88 in FY 77).

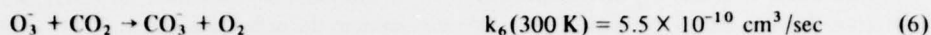
During the past year, the program for measuring ion-molecule reaction rate constants and ion thermochemical values has been involved with a number of current problems of atmospheric ion chemistry under both normal and disturbed conditions. The present investigations include studies carried out as a function of relative kinetic energy in the flow-drift system and temperature in the temperature-variable flowing afterglow, as well as room temperature measurements in the conventional flowing afterglow. Several reaction studies involving unstable neutral reactions were carried out in the flowing afterglow which remains the chief source of information concerning these reactions. Some specific results follow:

1. *A systematic reinvestigation of the negative ion chemistry as it pertains to the D-region has been undertaken.* This study includes important reactions involving atomic oxygen:

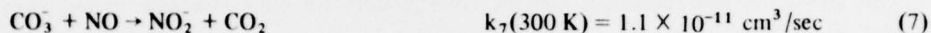


These reaction rate constants have an estimated uncertainty of ± 50 percent, and are in satisfactory agreement with earlier results.

The reactions

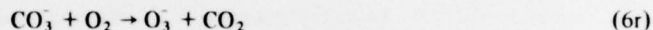


and



have been studied as a function of temperature in the variable-temperature flowing afterglow between 261 K and 629 K and in the flow-drift tube as a function of ion-neutral relative kinetic energy between 0.038 eV and 1.1 eV. These reaction rate constants are quoted with an estimated uncertainty of ± 30 percent. These results are in good agreement with earlier room-temperature determinations.

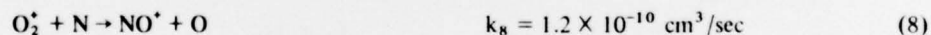
Finally with regards to reaction (6), recent measurements indicate that the energies to dissociate O^- from O_3^- and CO_3^- are similar [i.e., $D(\text{O}^- - \text{CO}_2) = 1.8 \pm 0.1$ eV and $D(\text{O}^- - \text{O}_2) = 1.7 \pm 0.1$ eV]. This, in turn, implies that reaction (6) is almost thermoneutral. As a consequence, the reaction in the reverse direction



could be significant even at low temperatures in the atmosphere, where the concentration of O_2 exceeds the CO_2 concentration by a factor of 10^3 . We have attempted to measure k_{6r} with the following results:

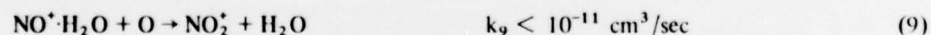
- In the variable temperature flowing afterglow we find $k_{6r} < 5 \times 10^{-16} \text{ cm}^3/\text{sec}$ for $T \leq 600 \text{ K}$.
- In the flow-drift system $k_{6r} < 8 \times 10^{-12} \text{ cm}^3/\text{sec}$ for $\text{K.E.}_{\text{cm}} = 0.5 \text{ eV}$. These results indicate that reaction (2) is of no importance in low-temperature ionized air-like mixtures.

II. The important F-region reaction



was remeasured. This value with an uncertainty of ± 50 percent is in satisfactory agreement with the earlier determination.

III. The reactions



were studied and the upper limits established. These reactions have been discussed in connection with the D-region positive ion chemistry.

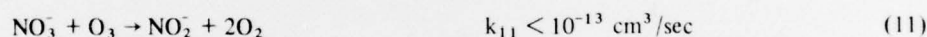
IV. Atmospheric ion reactions involving N_2O have been investigated. These studies were made to ascertain the possible importance these reactions may have to atmospheric ion and neutral chemistry. [For a more complete discussion see F.C. Fehsenfeld and E.E. Ferguson, *J. Chem. Phys.* 64, 1853 (1976).]

V. A systematic study of the effects of ion speed distributions in drift tube studies of ion-neutral reaction has been in progress in the flow-drift system. The first phase of this investigation, the study of the reactions of O^+ with N_2 , O_2 , and NO in rare gas buffers, has been completed. For O^+ ions drifting at nonthermal E/N values in helium and argon, the measured rate constants agree well with theoretical predictions of the effects of non-Maxwellian ion speed distributions, implying that these kinetic effects are properly interpreted and understood and that non-Maxwellian ion speed distributions of atomic ions now pose no problem in the interpretation and application of ion-neutral rate constants measured in drift tubes using atomic buffer gases. [These results along with the theoretical treatment by L.A. Viehland and E.A. Mason and by S.L. Lin and J.N. Bardsley appear as companion articles in the *Journal of Chemical Physics* 66, 410-446, (1977).]

VI. In connection with the D-region negative ion chemistry, we have determined the thermochemical values for NO_3^- ; $H_{298}^{\circ}(NO_3^-) = -74.81 \pm 0.54$ kcal mole $^{-1}$ and $S_{298}^{\circ}(NO_3^-) = 60.0$ cal mole $^{-1}$ deg $^{-1}$. NO_3^- is the terminal negative ion in the atmosphere under most circumstances and the above limits place exact constraints on the reactions that may lead to the formation or destruction of NO_3^- . In addition, we observe that HNO_3 strongly displaces H_2O clustered to NO_3^- . We find that the $NO_3^-HNO_3$ bond is stronger than the $NO_3^-H_2O$ bond by over 0.5 eV. This means that, at stratospheric temperatures and concentrations, HNO_3 will at least partially displace H_2O from NO_3^- .

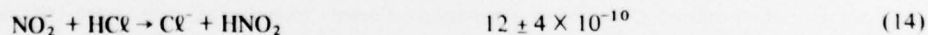
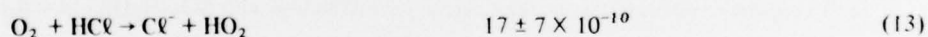
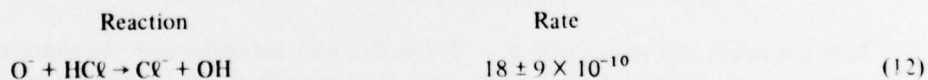
VII. An atmospheric pressure ion source has been placed into operation in the laboratory. This source will be used to investigate ions formed at high pressure (10 to 1000 torr) and the sensitivity of these ions to trace constituents in the gas mixture.

VIII. The reaction between NO_3^- and O_3 was investigated:



The low upper limit quoted above for this rate constant removes this mechanism as a possible loss process for ozone in the stratosphere, as was recently suggested (Ruderman, Foley, and Chamberlain, *Science* 192, 555, 1976).

IX. At present, there is very little information available concerning the negative ion-chemistry of chlorine and its compounds. Although these compounds, Cl^- , HCl^- , and ClO^- , are expected only in trace amounts in the ionosphere ($\sim 10^7$ HCl^- molecules/cm 3 at 60 km), they can nevertheless be important reactant neutrals, because the negative ions produced are quite stable. The following reactions involving HCl^- have been measured in the room temperature flowing afterglow:



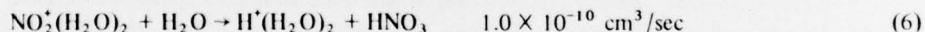
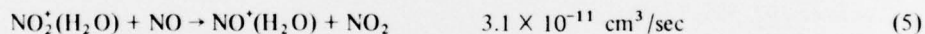
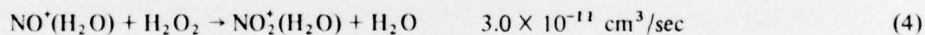
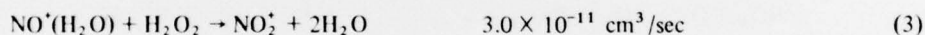
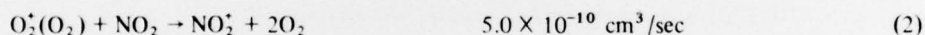
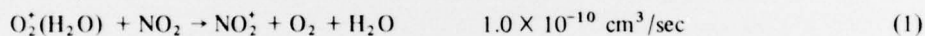
6. *Applications of the AIRCHEM Computer Code — J.M. Heimerl, BRL; and F.E. Niles, ASL/WSMR (Work Unit 74 in FY 76; Work Unit 84 in FY 77).*

A highly disturbed ionosphere which contains sufficiently high electron densities will cause communication links to be severely disrupted for a considerable length of time. Predictive communications codes generally require, as input data, electron density profile information as a function of time, excitation source, and altitude. Since these profiles cannot be determined empirically we have chosen to use the detailed modeling of a multispecies code (AIRCHEM) to compute required electron densities.

During the past year the BRL-originated AIRCHEM code and its auxiliary code, LOADER, were documented. Included as a documenting task was the construction of a program to list the reactions, their rate coefficients and *their references*. This program enables us to keep track of the sources for the values of the many (almost 500) reactions presently employed. Updating these rate coefficients is a continual process and during the past year we have critically analyzed the data available for the collisional dissociation rate coefficients of positive clustered ions of atmospheric importance.

One of the more significant findings to date has been the discovery of a rather strong pre-exponential temperature dependence for such reactions. For a given reaction the temperature dependence is identical for both association and dissociation.

During this year the following NO_2^+ ion sequence was added to the reaction set.



Rate coefficients for reactions 1, 2, 3, 4, together with the temperature dependence of reactions 7 and 8 were estimated. Other reaction rates were taken from the open literature. Also included in this sequence were the rates of the electron recombination with $\text{NO}_2^+(\text{H}_2\text{O})_n$, ($n = 0, 1, 2$).

We have employed a version of the AIRCHEM code with a 64-species set and a 495-reaction set to obtain species densities as a function of time. Two general cases were considered: (1) the ionization level was specified and the response of the ionosphere examined as a function of altitude and (2) the altitude was specified and the response of the ionosphere examined as a function of ionization level. In case (1) prompt ionization, $N_e = 10^{11} \text{ cm}^{-3}$ and delayed ionization is given by

$$Q(t) = Q_0 (1 + t)^{-1.2}$$

where t is the time in seconds and $Q_0 = 10^8$ ion-pairs $\text{cm}^{-3} \text{sec}^{-1}$. The altitude range considered is 10 to 80 km daytime conditions and 30 to 80 km nighttime conditions. Computations were made every 5 km. In case (2) the altitude is fixed at 60 km and N and Q varied subject to the constraint that $|\dot{O}| < |\dot{N}|$.

Partitioning of the charge closely follows other work by Gilmore, except that $\text{N}_2(\text{A}^3\Sigma)$ is not carried, $[\text{O}_2(^1\Delta)]$ is taken as 0.24 and $[\text{O}]$ is 1.28. Cases for daytime and nighttime conditions are reported; the calculations correspond to about a three-hour interval centered around noon and midnight. Positive ion photodestruction has *not* been considered in the reaction set. Appropriate neutral densities are taken from CIRA 1972, U.S. Standard Atmosphere 1962 and other literature sources and extrapolations.

Two preliminary reports concerning case (1) and case (2) have been published. These reports

- a. Display selected computed species densities as a function of time and altitude or ionization conditions
- b. Show the results of comparison and sensitivity studies of a limited nature and
- c. Report the computed variation of the *Effective Rate Coefficients* (ERCs) as a function of time and altitude or ionization conditions.

These reports should be consulted for details, but the results obtained are summarized as follows.

Case 1

The electron density is computed as a function of time for both current BRL present results (BRL-76) and earlier DCHEM results of Scheibe for *nighttime* conditions. Comparisons made for *daytime* conditions, and for fixed ionization conditions with altitude as a parameter, indicate a basic overall agreement between Scheibe's results and our own for the computation of the electron density as a function of altitude, excitation, and time.

Case 2

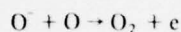
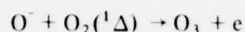
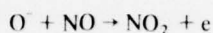
The temporal variation of effective electron-ion recombination coefficient, α_d , for *daytime and nighttime* conditions ranges from values characteristic of electron-ion recombination with diatomic ions at early times to values characteristic of recombination with clustered ions after a natural disturbance at late times. The return to the quiescent clustered ion condition seems to be dominated by the delayed electron production, Q_0 . To wit, for $Q_0 = 10^6$ ion-pairs $\text{cm}^{-3} \text{sec}^{-1}$ the cluster ions seem to be reestablished after about 100 seconds. For $Q_0 = 10^8$ ion-pairs $\text{cm}^{-3} \text{sec}^{-1}$, this time is greater than 10^4 seconds during the day and about 10^3 seconds at night. For $Q_0 = 10^{10}$ ion-pairs $\text{cm}^{-3} \text{sec}^{-1}$ this time is even longer.

Analysis of the AIRCHEM computations show that the detachment processes



is the dominant electron production mechanism at all altitudes (10 to 80 km) and under all ionization conditions studied. This reaction was assigned the upper limit of $1 \times 10^{-12} \text{ cm}^3/\text{sec}$. To test the sensitivity of the computed results to this reaction, computations were made at 80 and 60 km for *daytime* conditions, $Q_0 = 1 \times 10^8$ ion-pairs/ $\text{cm}^3\text{-sec}$ and $N_0 = 1 \times 10^{11} \text{ cm}^3$ with this rate coefficient set to $1 \times 10^{-14} \text{ cm}^3/\text{sec}$ and zero. These changes produced no significant alterations of the electron density at 80 km and at most a 20 percent decline at 60 km. The value of the effective electron detachment coefficient declined by about 30 percent in all these cases, and other computed results were essentially unchanged.

A reason why the removal of an important reaction produces trivial changes in the interesting parameters can be seen by examining the following group of reactions at 80 km:



It was observed that the electron production rate of the *sum* of these reactions was constant within 1 percent regardless of the value for the first rate coefficient.

The 80-km case suggests that the AIRCHEM code contains a sufficient number of reactions (i.e., charge flow paths) that the elimination of one simply raises the "pressure head" through those paths which remain. In short the AIRCHEM code results tend to resemble the chemistry in the atmosphere which can suffer a wide range of perturbations and still remain stable.

Of the 210 ion-ion recombination reactions used in this AIRCHEM code only 8 have been measured in the laboratory. The remaining 202 were assigned a value of $2.0 \times 10^{-7} (T/300)^{-5} \text{ cm}^3 \text{ sec}^{-1}$. Since there is some discussion even as to the order of some of the measured reactions, computations were made for the two cases wherein all of the ion-ion recombination rate coefficients, α_i 's, are multiplied by 10^{-1} and by 10^{+1} . Calculations were carried out at 60 km and during nighttime conditions. Results show that though there are large changes in both the total positive ion and total negative ion densities, the change in the electron density barely exceeds a factor of two for a factor of 100 change in α_i . For these circumstances it is more important to include the correct processes, rather than have very accurate rate coefficients.

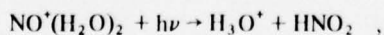
Case 3

The AIRCHEM code, tailored for quiet conditions, was run for Wallops Island, Virginia, 31 Jan 72 conditions. Charged particle profiles were computed at 5-km intervals from 90 to 20 km for both near noon and near midnight conditions.

The computed daytime profiles can be compared with rocket measurements taken around noon. The computed total positive ion profile compares favorably with Pennsylvania State University data over their altitude range of 30 to 80 km. At 65 km the computed density lies about a factor of three lower than the measured density; the agreement improves significantly at both higher and lower altitudes.

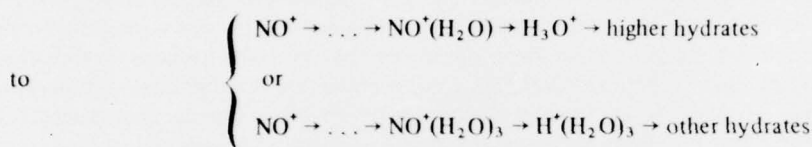
The computed electron density profile agrees with that of the University of Illinois measurements within about a factor of three over their altitude range of 60 to 90 km. The Pennsylvania State University electron density measurements, taken over the altitude range 40 to 80 km and corrected, exhibit a shape and magnitude which is difficult to reconcile with either the Illinois measurements or the AIRCHEM results.

For positive ions, the AIRCHEM computations show that between 80 and 90 km NO^+ is the dominant ion while below 70 km (down to 20 km) the hydrated protons are dominant. The level of hydration is mainly controlled by the temperature profile employed. Code predictions also show that for altitudes above about 75 km the path for the formation of H_3O^+ is



when an assumed cross section of 10^{-18} cm² is used across the solar spectrum, $125 < \nu < 730$ nm.

We find that the assumed cross section could be reduced by a factor of 500 and the reaction would still contribute about 50 percent of the charge flow to the hydrated protons. Since this reaction appears dominant we tested the sensitivity of the computed results to its removal by setting the cross section equal to zero. Insignificant changes occurred in the computed results such as electron, total positive ion, total negative ion densities, and the ERCs. Though the relative populations of the hydrated proton species were shuffled, the same species remained dominant. A more detailed examination of the AIRCHEM results showed that the main charge flow ($90 \leq \text{altitude} \leq 70$ km) changed from

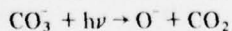


when this cross section was set equal to zero. Again the AIRCHEM code exhibits a resiliency to change characteristic of the atmosphere.

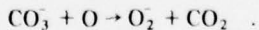
In contrast to the positive ion profiles, the AIRCHEM computations for negative ions showed that the identity of the dominant negative ion changes with altitude. The predicted dominant negative ions are shown as follows:

DAY		NIGHT	
Altitude (km)	Dominant Negative Ion	Altitude (km)	Dominant Negative Ion
90 to 85	O ⁻	90 to 80 km	NO ₃ ⁻
80 to 70	O ₂	75 to 65	NO ₃ (H ₂ O)
65 to 55	CO ₃ ⁻	60 to 25	CO ₃ (H ₂ O)
50 to 35	NO ₃ (H ₂ O)	20	CO ₄ (H ₂ O)
30 to 20	NO ₃ (HNO ₃)		

As seen above, there is a dramatic change in negative ion composition from day to night. (The negative ion chemistry does not yet include multiple clusters.) This suggests that characterization of the negative ions by a single species, X⁻, as is commonly done in "lumped parameter" models, may be too simple an approach. Further, the computed negative ion results showed that between ~55 and 65 km the photodestruction of CO₃ via



was less than 10 percent of the main loss channel



A six-ion species code O₂⁺, O₄⁺, NO⁺, H⁺(H₂O), e⁻, O₂⁻, and X⁻ is under development for use over the altitude region 20 to 90 km and we are using the results of the multispecies code AIRCHEM as a

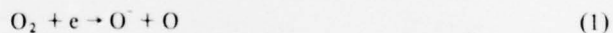
guide to constructing the six-ion code. Difficulties are being encountered in the definition of the detachment rate of X^- , mainly due to the assumption that X^- is a single entity. Further efforts are in progress.

7. *Positive and Negative Ion Reactions, Photodissociation Reactions Hindering Cluster Ions* – J.A. Vanderhoff, BRL; F.E. Niles, ASL/WSMR (Work Unit 75 in FY 76; Work Unit 85 in FY 77).

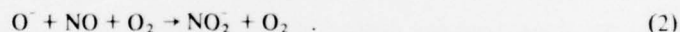
Highly disturbed, ionized regions in the upper atmosphere can seriously degrade the propagation of electromagnetic radiation at communications frequencies. Atmospheric models may be constructed to calculate the electromagnetic radiation attenuation as a function of time and should include all processes important to the transient charged particle density. The interaction of photons (from sunlight) with atmospheric ions can substantially alter the charged particle density and has been an area little studied. To accumulate pertinent data in this area a drift tube mass spectrometer system coupled with a laser photon source was designed and constructed to measure photodestruction (photodetachment and/or photodissociation) cross sections for both positive and negative atmospheric ions and their clusters. The drift tube technique was chosen so that the photodestruction cross section values obtained for molecular ions would be representative of thermalized (ground state) ions. By using a laser photon source much better energy resolution than in prior work is attained, which enables one to observe structure, if it is present, in the photodestruction cross sections.

Measurements of the photodestruction cross section for O_2^- and CO_3^- had essentially been completed at the start of this time frame. These measurements were conducted mainly to test the experimental apparatus, although the photon energies available with the krypton ion laser represented new data. The results for the photodetachment of O_2^- were in excellent agreement with earlier published work and the photodestruction cross section measurements for CO_3^- agreed with those of Moseley *et al.* In addition, we observed O^- photofragment ions at 514.5 nm, which is consistent with the finding of Moseley *et al.* that most, if not all, of the photodissociation of CO_3^- is due to photodissociation into O^- and CO_2 . Results of this work were reported elsewhere.

The NO_2^- ion was next investigated. By using gas mixtures of oxygen and nitric oxide (100 mtorr), where O_2 comprised 98 percent or more of the mixture, NO_2^- was produced through the reactions



and then



Since there was no published mobility value for NO_2^- drifting in O_2 , measurements were made to determine this using a two drift distance technique. The reduced mobility (K_0) was measured to be $2.85 \text{ cm}^2/\text{V-sec}$ with a probable error of 10 percent. The E/N dependence of the NO_2^- mobility was also determined. As a comparison, a value of $2.63 \text{ cm}^2/\text{V-sec}$ was obtained when mass scaling from the mobility value of $2.50 \text{ cm}^2/\text{V-sec}$ for CO_3^- in O_2 , as measured by Snuggs *et al.*

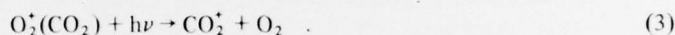
Photodestruction measurements for NO_2^- , $NO_2^-(H_2O)$, and $NO_2^-(H_2O)_2$ have been made at several photon energies and differing E/N values. The photon energy at 2.41 eV is close to the reported electron affinity of NO_2^- .

Recent calculations by Herbst *et al.* in 1974 show that the photodetachment cross section for NO_2^- is sensitive to ion temperature in this region. By increasing E/N the ion temperature can be increased, and this increases the photodetachment cross section. However, photodetachment cross section measurements reported were not made as a function of pressure and drift distance and therefore it cannot be stated that all of the NO_2^- ions were in the ground state. In addition, evidence for

an isomeric form of NO_2 has been reported in the literature, and since we have no detailed knowledge of the structure of NO_2 produced in our system these results on NO_2 cannot be assigned uniquely to the normal form of NO_2 .

Atmospheric positive ion clusters were studied next. These investigations revealed that many species readily dissociate in the presence of visible light. Photodissociation cross section measurements were first taken on $\text{O}_2^+(\text{H}_2\text{O})$. The cross section smoothly increases from $0.6 \times 10^{-18} \text{ cm}^2$ at 1.83 eV to $6 \times 10^{-18} \text{ cm}^2$ at 2.73 eV. These cross section values are the largest reported for a positive cluster ion of atmospheric importance. Details of the experimental apparatus and results are reported in a BRL Memorandum Report No. 2642, June 1976 and *Chem. Phys. Lett.* **38**, 532 (1976).

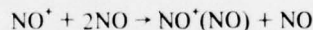
Substantial photodissociation cross sections were found for $\text{O}_2^+(\text{H}_2\text{O})_2$, $\text{O}_2^+(\text{O}_2)$, and $\text{O}_2^+(\text{CO}_2)$. In addition, the $\text{O}_2^+(\text{CO}_2)$ cluster exhibited a photon-associated charge transfer reaction,



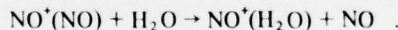
By detecting the CO_2^+ photofragment an upper limit on the bond energy of $\text{O}_2^+(\text{CO}_2)$ was determined to be 0.46 eV. The $\text{H}^+(\text{H}_2\text{O})_{n=1-4}$ ions were investigated for photodissociation at several photon energies. No evidence of photodissociation was observed and consequently upper limits were placed on the photodissociation cross sections. A manuscript describing these photodissociation cross section results has been accepted for publication in the *J. Chem. Phys.*

In May 1976 a high-power krypton ion laser was incorporated into the experimental apparatus. This larger photon source allowed probing photodestruction cross sections in the violet (413.1 nm and 415.4 nm) and UV (350.7 nm and 356.4 nm) portion of the photon energy spectrum. Photodestruction cross section measurements are being made with this new facility.

Studies on the positive ion cluster of nitric oxide have just begun. $\text{NO}^+(\text{NO})$ and $\text{NO}^+(\text{H}_2\text{O})$ were produced in NO gas with a trace of H_2O . The ion NO^+ is made by electron impact and $\text{NO}^+(\text{NO})$ and $\text{NO}^+(\text{H}_2\text{O})$ are produced by



and



8. *Chemistry and Spectroscopy of Optical Emitters* – D.E. Snider and F.E. Niles, *ASL/WSMR (Work Unit 76 in FY 76; Work Unit 86 in FY 77)*.

The goal of this work is to increase our knowledge of the distribution of neutral minor constituents for use as inputs into weapons phenomenology codes and to identify the processes which give rise to infrared emissions in the earth's upper atmosphere under normal or nuclearly perturbed conditions. The approach has been to quantitatively analyze infrared emission measurements and long path transmission measurements which have been obtained with balloon-borne spectrometers and filter radiometers.

Necessary for interpreting transmission and emission spectra in terms of number density profiles for a species is the ability to quantitatively compute the infrared absorption for that species. The most accurate way of doing this is the so-called "line-by-line" technique. If the strength, position, and half-width of all spectral lines within the wavelength of interest are known, this technique can be used to compute the absorption. For most of the major bands of the well known atmospheric constituents this information has been tabulated on a computer tape by the Air Force Geophysics Laboratory (AFGL). For lesser known species, the trace gases which may also be important in the chemistry and physics of the atmosphere, this information is often not available. Therefore, a major part of this year's effort was devoted to generating these line parameters for species of interest.

The molecules NO_2 , SO_2 , HNO_2 , NO_2 , and H_2O_2 have been examined for possible detection in the stratosphere using long-path infrared spectroscopy from balloons. Line parameters for computing synthetic spectra were generated for three bands of NO_2 and for three bands of SO_2 . These were tabulated on a magnetic tape. This tape contains approximately 1700 lines in the AFGL format and has been transmitted to AFGL for distribution to other users. Line parameters for HNO_2 and HO_2 have been computed from known and estimated spectroscopic constants. They are therefore suitable only for preliminary detection of the species. When more accurate laboratory data become available, these parameters will be updated. H_2O_2 was examined for possible detection since many neutral chemistry codes predict its abundance to be nearly as great as HNO_3 . Unfortunately the strongest infrared bands of H_2O_2 correspond to O-H bending and stretching and will be masked by the stronger bands of H_2O since the concentration of H_2O in the stratosphere is a factor of 10^3 greater than H_2O_2 is predicted to be.

9. *Improved Master/Simple Codes for E,F. Regions* – W. Ali, NRL (Work Unit 77 in FY 76; Work Unit 81 in FY 77).

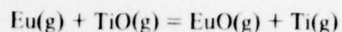
The ionization and deionization processes in the disturbed E- and F-regions of the ionosphere are important areas which have profound effects on all aspects of communications. A realistic, up-to-date, description of these phenomena requires a detailed understanding of its physics and chemistry. This, in general, is accomplished by detailed multispecies and simpler codes. These codes, NRL Master and Simple codes, are kept current with up-to-date reaction rates and are utilized for sensitivity studies. These studies are carried out to assess the impact of individual reactions on ionization and deionization processes. In addition to these studies, physical processes which may be important in the nuclear disturbed ionosphere are pointed out in several reports. In addition to these, analysis of the sensitivity studies in the disturbed D-region are continuing with the General Electric group.

10. *Ion-Neutral Investigations* – J. Paulson and E. Murad, AFGL (Work Unit 78 in FY 76; Work Unit 83 in FY 77).

Beams of such species as CO_3^- , CO_4^- , and NO_3^- used in studying collisional dissociation reactions in our double mass spectrometer system were found to contain ions in excited states. Predissociation and collisional dissociation of these states lead to broad dissociation thresholds from which it is impossible to extract the parameters of real interest, i.e., the dissociation energy and the cross section for collisional dissociation of the ground state near threshold. Nonetheless, the observed cross sections for collisional dissociation at higher energies are not dominated by the presence of small amounts of the excited states, and we have measured some of these cross sections for CO_3^- , CO_4^- , and NO_3^- . In the case of CO_3^- colliding with O_2 , the cross section for dissociation to $\text{O}^- + \text{CO}_2$ reaches a value of about $5 \times 10^{-16} \text{ cm}^2$ at 15 eV (lab) and about $26 \times 10^{-16} \text{ cm}^2$ at 50 eV. This reaction channel is significantly more probable than the reaction leading to $\text{O}_3^- + \text{CO}_2$, for which the cross section shows an onset at about 3 eV and rises to a value of $0.6 \times 10^{-16} \text{ cm}^2$ at 15 eV. The cross section for O_2^- production from $\text{CO}_4^- + \text{N}_2$ is $18 \times 10^{-16} \text{ cm}^2$ at 15 eV, while that for NO_2^- from $\text{NO}_3^- + \text{N}_2$ is about $8 \times 10^{-16} \text{ cm}^2$ at 15 eV.

Studies were completed on the photodissociation of N_2O^+ using a frequency doubled tunable dye laser in the wavelength range from 295 to 340 nm. The photodissociation spectrum in this region is highly structured, with the largest peaks at about 323, 337, and 339 nm, reaching cross sections of 6 to $7 \times 10^{-19} \text{ cm}^2$. The observed peak wavelengths are in good agreement with the spectrum calculated from reported spectroscopic constants. The apparatus is now being modified to allow studies on photodissociation of positive cluster ions.

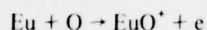
The investigation of the dissociation energy of gaseous europium monoxide was finished. Three independent gaseous equilibria were investigated in a high-temperature mass spectrometer at SRI:



From the heats of reaction of these equilibria and from the known dissociation energies of AlO, BaO, and TiO, a value of $D_0^\circ(\text{EuO}) = 4.85 \pm 0.10$ eV was derived. This dissociation energy is considerably lower than the previous determinations, but it is consistent with the failure to observe emission from EuO when Eu is released in the upper atmosphere. The data indicate that the reaction



is endothermic by 0.26 eV. In addition to the dissociation energy of EuO its ionization potential was measured and found to be 6.3 ± 0.2 eV. These two values indicate that the associative ionization reaction with O:



is endothermic by 1.4 ± 0.3 eV.

During the reporting period a high-temperature mass spectrometer was successfully refurbished and put into operation. This instrument is capable of studying equilibria at temperatures as high as 2800 K and has an ultimate mass resolution of about 2000.

C. Subtask S99QAX HD 028

"Theoretical Investigations of Ionizing Mechanisms in the Upper Atmosphere"

1. *Reaction Rate Sensitivity Assessments* - M. Bortner and T. Baurer, GE/SSL. (Work Unit 36 in FY 76 and FY 77).

Sensitivity Studies

An *Ad Hoc* Panel was established by the DNA (RAAE) Chemistry/Physics Support Program. The Chairman of the Panel is M.H. Bortner of GE/SSL. The general purpose of this group is to monitor sensitivity investigations designed to demonstrate the relationship between ionospheric chemical and physical process input model parameters and predictive communications systems code outputs (in dB), and ultimately to indicate what additional or improved chemical rate data DNA should try to obtain. Under the current contract, the Panel has met as a group, and its members have also been consulted as individual specialists in their respective areas of expertise.

Reaction Rate Handbook

During FY 1976-1977, Revision No. 5 (Revised Chapter 18A and new Chapter 18B) and Revision No. 6 (Errata to Chapters 11 and 16, updatings of Chapters 17 and 19) were issued.

A major portion of the handbook effort was expended at the request of the *Ad Hoc* Sensitivity Panel, in the total reevaluation of the chemical kinetics tables comprising Chapter 24. This work will be completed by the end of the current calendar year, and go out as Revision No. 7 early in CY 1977. In addition, revision efforts are in progress vis-a-vis Chapter 2, 8, 11, 13, and 20. A planned effort to update the Appendices was deferred to the coming year in order to make way for the revision (noted above) of Chapter 24.

2. *Computations of Structure and Transition Probabilities in Atmospheric Molecules – H. Michels, UARL (Work Unit 37 in FY 76; Work Unit 40 in FY 77).*

Theoretical investigations of the electronic structure and radiative transition probabilities of atmospheric and metal oxide species, and of kinetic reaction rates for electron-ion and atom-atom reactions have been carried out. These studies are being performed using quantum mechanical methods and digital computer codes based on both *ab initio* methods, employing configuration-interaction (CI), and density functional methods, employing developments and extensions of models used previously in solid-state calculations.

An extensive analysis of the dipole moment function for the ground state of NO was carried out and computer least-square fits to all the available experimental and theoretical data relating to the dipole moment were obtained. Using this dipole moment function and accurate RKR vibrational-rotational wavefunctions, the integrated band absorption coefficients have been calculated for the fundamental, first, and second overtones of NO as a function of temperature. The calculated absorption indicates a near constancy of the intensity of the fundamental band up to 5000 K, in agreement with recent experimental data.

Density functional calculations were performed for the ground \tilde{X}^2A_1 state of NO₂ at several geometries. The density functional method successfully predicts the bent character of the ground state and the correct orbital occupancy for this molecule. The results were compared with *ab initio* calculations. Additional calculations were carried out for the first excited \tilde{A}^2B_1 state of NO₂. The linear configuration is favored in this excited state. A vertical excitation energy for $\tilde{X}^2A_1 \rightarrow \tilde{A}^2B_1$ of 2.43 eV was obtained, in good agreement with experimental estimates and the best *ab initio* calculations for this system. More detailed calculations of potential energy hypersurfaces, using the density functional method, are clearly indicated as a result of the success of these initial studies.

In addition to these calculations for atmospheric molecules, both *ab initio* and density functional calculations were performed for the electronic structure of TiO⁺. The calculated data on energy levels are in good agreement between the two methods and illustrate the utility of the faster density functional approach for ionic systems. A final report has been prepared for these studies (AFGL-TR-76-0120).

Calculations for the electronic structure, potential energy curves and dipole transition moments of the ground and low-lying excited states of the nitric oxide ion (NO⁺) are now in progress. Singlet, triplet, and quintet states of Σ^+ , Σ^- , Π , Δ , and Φ symmetry will be analyzed and the radiation characteristics for the strongest allowed band systems will be calculated.

3. *Theoretical Aspects of SRI Laboratory Ion-Ion Measurements – F. Smith et al, SRI (Work Unit 38 in FY 76; Work Unit 41 in FY 77).*

For moderately large cluster (hydrated) ions, neutralization by electron transfer is replaced by recombination of the two ions into a larger neutral cluster, stabilized by loss of one or more neutral fragments (H₂O). If the ions come close enough under the Coulomb attraction for a hard (geometrical) impact, the rearrangement occurs rapidly and with high probability; this model gives an estimated lower bound rate coefficient of $\sim 5 \times 10^{-8}$ cm³/sec at 300 K, for typical ions with a hydration number, n, of 6 (and suggests an $n^{-1/5}$ and $T^{-1/2}$ dependence). In somewhat more distant encounters, tidal distortion of the ions can put enough energy into internal modes to initiate trapping in large elliptic orbits, leading to the same stable recombination with some intermediate probability. A simple model for the distortion energies, based on reorientation of H₂O dipoles, suggests an upper bound rate about 10 times the hard impact lower bound (and an $n^{-1/2}$ and T^{-1} dependence). To improve these estimates, and take into account such effects as hydration number, strength of bonding, number of available (low-energy) degrees of freedom, and stiffness of internal bending modes, we are developing and testing classical and semiclassical methods of calculation.

A semiclassical perturbation approach is proving both rapid and reliable. We have tested it against the Born approximation and several numerical quantal methods, including the Glauber approximation, the distorted wave approximation and the close coupling treatment, with very satisfactory results, using a model problem (electron and ion dipole scattering) for which there exist numerical data obtained by these various methods. The semiclassical method is remarkably rapid for calculations, has a much wider range of validity than the Born approximation (to which it gives important corrections), and reproduces most quantum effects very successfully, unlike a purely classical treatment.

4. *Investigations Relevant to the "Twilight Anomaly" and Other Relevant Problems – W. Swider, AFGL (Work Unit 39 in FY 76; Work Unit 42 in FY 77).*

Early in this period, work was completed on "HF/VHF Absorption in the Disturbed D-Region" by W. Swider and L.L. Chidsey, Jr. The results are available in an in-house report, AFGL-TR-76-0053. It was found that standard theoretical methods led to calculations in agreement with the observations. The accord was within about ± 20 percent, less than the estimated error of the electron concentrations used in the absorption calculations. The lesser error apparently derives from integration effects of the computations which smooth out random errors in the electron concentrations and from the zero-reference method adopted for the measurements.

Analysis of the ICECAP 73A ion composition data of 27 March 1973 was found to imply a peak of NO concentration of 10^9 cm^{-3} . The results will be published soon in the *Journal of Geophysical Research* as a paper entitled "Ionic Structure Near an Auroral Arc" by R.S. Narcisi and W. Swider.

Estimated photodetachment rates for several important negative ions were placed in the experimental Keneshea Code for the disturbed D-region. Best comparison with daytime data was attained when rather high cross sections were adopted for photodetachment processes, i.e., cross sections approaching about the maximum possible. However, agreement with the twilight data was poor probably because the effective wavelengths for the photodetachment processes were uncertain and hence the appropriate twilight attenuation conditions for the incident wavelengths. It would appear that there remain too many unknown reaction rates (particularly for negative ions), photodetachment rates, etc., for a theoretical approach to the solution of the twilight anomaly problem.

Recently, investigations of the August '72 SPE have been performed using the latest proposed NO^+ ion clustering chemistry with N_2 and involving switching with CO_2 and H_2O . Using cold mesopause temperatures, 135 K, and a high water vapor mixing ratio, 10^{-5} , we were unable to obtain effective electron loss rates as large as those deduced by the Lockheed group for this event. The disagreement strongly suggests that gas phase chemistry cannot explain the results near 80 km. However, if heterogeneous reactions are responsible, the presence of the necessary particulate matter may have influenced the electron concentration measurements made by the backscatter radar. Hence, in our opinion, an experimental and/or chemical problem may be operative in regards to the 80-km results for the August '72 SPE.

D. **Subtask S99QAX HD 031**

"Determination of Reaction Rates and Ionizing Mechanisms by Use of Natural Disturbances"

1. *Satellite Borne Low Energy Particle Spectrometer – J. Reagan, LMSC (Work Unit 12 in FY 76; not supported by DNA in FY 77).*

A satellite experiment supported by the Office of Naval Research and the Defense Nuclear Agency and designed to measure energetic particle fluxes in the important energy range which provides the bulk of the precipitated energy input to the ionosphere has recently been launched aboard an Air Force satellite, STP 74-2. The experiment is unique in that it includes a type of mass spectrometer allowing the identification of the species of the magnetospheric ions as well as their energy

and angular distributions. The experiment is operating completely successfully and is providing a large body of data on natural phenomena and disturbances which are directly relevant to ionospheric disturbance phenomena of interest to DNA. A major new discovery was made in the examination of the data from the first few orbits. Large fluxes [10^8 (cm²-sec-sterad-keV)⁻¹] of protons and O⁺ ions in the keV range were observed flowing up the field lines from the ionosphere in the auroral and polar regions. The ionospheric/magnetospheric acceleration mechanism which is responsible for these particles is not known but is now under extensive study. Its relationship to ionospheric irregularities and other disturbance phenomena associated with the natural degradation of communications and surveillance systems is obviously of major interest. Its importance in understanding nuclear weapons effects, including late-time debris dispersion and ionospheric effects in the high-altitude magnetosphere cannot be assessed in detail at this time since the basic physical processes are still unknown.

Another important aspect of the data is the effect on the ionosphere of the precipitation of the measured ions and electrons. This is being addressed by the acquisition of coordinated observations with the Chatanika incoherent scatter radar and with the WIDEBAND satellite-borne electromagnetic wave propagation experiment. The ability to identify the species of the precipitating ions is critical to these coordinated studies. The O⁺ ions deposit their energy at much higher altitudes than protons of equivalent energy and during magnetic storms are expected to produce extremely high heating rates (up to about 1 K/second) at F-region altitudes. The turbulence which is generated by these high heating rates has unknown effects on the ionosphere. Effects such as plasma irregularities leading to ionospheric scintillation will be investigated during magnetically disturbed periods with the coordinated data sets.

2. *Twilight Anomaly Analysis - J. Regan et al, LMSC (Work Unit 14 in FY 76; Work Unit 17 in FY 77).*

Electron loss rate ($\Psi = Q/N_e^2$) altitude profiles have been derived for the intense solar particle event of August 1972 (SPE 72) from electron density (N_e) profiles measured at Chatanika, Alaska by the DNA-sponsored/SRI-managed incoherent backscatter radar and from ionization rate (Q) profiles calculated from ionizing particle fluxes measured by the DNA/ONR payload on the LPARL polar-orbiting satellite 1971-89A. Ψ profiles at altitudes from about 50 to 90 km have been obtained at 28 times during the intense period of the event, 4-6 August. These results have recently been published by Reagan and Watt [*JGR* 81, 4579 (1976)]. Some of the important conclusions from that work are: (1) a strong diurnal dependence of Ψ was observed below 80 km but not above 80 km over a χ range of 50 to 98 degrees; (2) above 70 km the solar summer daytime Ψ values are significantly larger than those measured during the winter daytime of 2 November 1969 (SPE 69); (3) near 80 km these Ψ values are consistent with the dominant ions being H₃O⁺ and H₃O⁺·H₂O. Since these hydrated ions were not dominant during the wintertime SPE in 1969, a strong seasonal dependence of Ψ is indicated.

Based on these experimental results, the ion chemistry and the state of the D-region during this SPE have been studied in detail. A fast operating model of the neutral and ion chemistry of the D-region has been used that represents a good approximation to more complex and slower-operating models in general use. The model has some 22 species and 63 processes and is intended to represent the ion chemistry with only a small number of adjustable altitude-independent parameters. The model is diurnal and requires as inputs time dependences of photodissociation and photodetachment. Laboratory measurements of reaction rates, where available, have been used. A small number of parameters representing lumped processes have been adjusted in the model within reasonable limits to produce a considerable measure of agreement with the experimental daytime and twilight profiles of Ψ measured at altitudes of 60, 70, and 80 km. Some of the finer details of the diurnal dependence of Ψ remains unresolved.

One of the results of the modeling is that considerably higher atmospheric densities and lower temperatures appear to occur near the summer polar mesopause than in winter. This is qualitatively consistent with CIRA 72 but quantitatively higher densities and lower temperatures than found in CIRA 72 are needed to explain the experimental results.

Another result of this study to date is that a strong correlation exists between the behavior of Ψ and the diurnal and SPE-induced variation of the O atom density at altitudes near 60 km. The relationship exists because the effect of O atoms in the detachment process is important to the determination of Ψ . This result, when fully substantiated, will be important in the analysis/prediction of propagation effects in the highly disturbed nuclear atmosphere/ionosphere.

The same model adjusted for season and latitude has been used to derive effective electron loss rates during the wintertime SPE 69. Comparison with the experimental rates reported by Swider ("Composite PCA 69 Study: Final Report," AFGL-TR-75-0149), shows reasonable agreement at altitudes of 60, 70, and 80 km. Processes leading to formation of hydrated protons and the roles of minor species O, NO, and H₂O in those processes are found to be important, as expected.

3. *Assessments of Partial Reflection Ionospheric Sounder Data for Disturbed Ionospheres - G. Falcon, ITS (Work Unit 15 in FY 76; not supported by DNA in FY 77).*

The partial-reflection ionospheric sounder technique was used to develop several daytime and nighttime D-region electron density profiles at Poker Flat Rocket Range (near Fairbanks), Alaska throughout ICECAP 74. Although some experimental difficulties prevented optimum operation of this system at Poker Flat, the numerous observations still produced good results during quiet periods and times of moderate auroral ionospheric disturbances which supplemented data obtained from the Chatanika Radar Facility.

Distinct differences appear between the daytime profiles and the nighttime profiles. The day profiles typically show one of two minima in electron density, with a minimum often appearing in the vicinity of 70 km. Night profiles, which begin at much greater heights, generally increase monotonically. The median lowest height of the profiles is 67 km in daylight hours (before 1830 ADT), 74 km between 1830 and 2200, and 87 km after 2200 ADT. The ionization gradient tends to be relatively low before 1800, higher in the 2000-2300 ADT period, and highest in the nighttime hours after 2300 ADT.

The auroral disturbances observed during ICECAP 74 were neither as frequent nor as extensive as those observed during ICECAP 73. Constraints in the program schedule, however, dictated the specified coordinated period. Electron density data from the partial reflection measurements were obtained at lower altitudes during auroral disturbances than during the corresponding day or night quiet periods. When ionospheric absorption was very high some of the individual daytime results obtained by the 2.24-MHz system during ICECAP 74 were truncated at heights above about 80 km because the transmitter power was limited to 25 percent of its rated value. Unfortunately, the 6.8-MHz system, intended for use during these high absorption periods, was also operating with greatly reduced transmitter power and was thus not able to contribute much useful data.

Comparisons of partial reflection sounder data with those of other ionospheric measurements performed during ICECAP 74 were made where possible. No useful or pertinent satellite or rocket data were available for this purpose. Continuous riometer recordings at College, Alaska, clearly discriminated between geomagnetically quiet and disturbed days. The partial reflection profiles developed in this study show good correspondence with the riometer variations. Ionosonde recordings, while unable to provide limited D-region information, were used (in some instances) to compare estimated electron density values at altitudes near the upper limit of the partial-reflection data, where the agreement is reasonably good. Electron density profiles from the coincident, steep-incidence VLF sounder measurements by NELC personnel were not available at the time of this report.

Several comparisons of ionization density were made, over a limited altitude interval (centered at about 90 km), with data from the Chatanika incoherent scatter radar, which was also operated extensively throughout this period. There was good agreement during certain times, but significant differences during others. The latter case is obviously due to the inherent different operating features (sample duration, ionospheric area sampled, altitude resolution, direction of antenna main-lobe, etc.) and fundamental sensitivity levels of measurement. The minimum sensitivity of 5×10^4 electrons/cm³ for this radar is greater than the maximum value of about 1×10^4 obtainable from the 2.24-MHz partial-reflection system used primarily during ICECAP 74.

The new partial-reflection sounder's control logic and real-time data acquisition system, designed and built by ITS, performed very well and provided an easy and reliable way of monitoring system operation. However, the limited core (4 K) of the minicomputer prevented the real-time computations of electron density that are useful during rocket launch operations.

4. *Vertical Sounder Improvements and Data Analysis – I. Rothmuller, NELC (Work Unit 16 in FY 76; not supported by DNA in FY 77).*

Sounder measurements were made at frequencies of 11.416, 11.935, 12.454, 12.973, 13.492, 20.757, 21.275, 21.794, 22.313, and 22.832 kHz. These were obtained by radiating 160- μ sec pulses at 12.454 and 21.794 kHz with a repetition period of 1920 μ sec (12 pulse widths). The receiver then monitored the center frequency and two spectral lines on either side of each center frequency to obtain the ten frequencies listed. The short radiated pulses yield a ground wave and ionospheric reflected wave which are separated in time. The receiver is synchronously gated with the transmitted signal so that only the wave reflected from the ionosphere is processed by the receiver. The receiver thus measures the reflectivity of the polar D-region without contamination from the ground wave.

The received data were analyzed to yield ionospheric reflection coefficients for both the direct (${}_1R_1$) and converted (${}_1R_H$) components. Both day and night data were recorded. Only the nighttime data, however, had sufficient signal-to-noise ratio for analysis.

Data were obtained for the nights of 12, 13, 14 and 15 April 1974. On the 15th the experiment was terminated due to transmitter malfunction. All data have been reduced and calibrated and are being analyzed.

Preliminary results show that the polar D-region is more variable, even during quiet magnetic periods, than might have been anticipated. Amplitude fluctuations of 10 dB are not uncommon. Phase variations, when translated into reflective height changes, indicate 5- to 6-km fluctuations.

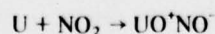
E. **Subtask S99QAX HI 002**

"Atomic and Molecular Physics of IR Emissions"

1. *Fine Definition of IR Spectra for Certain Metal Oxide Species – D.W. Green and G.T. Reedy, Argonne National Laboratory (Work Unit 28 in FY 76; Work Unit 39 in FY 77).*

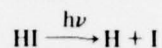
The primary goal of this research is to produce the UO^+ ion in low-temperature Ar matrices and to record its infrared absorption spectrum. Two methods have been employed to achieve this objective: (1) *in situ* reactions of matrix-isolated U atoms with nitrogen oxides, and (2) *in situ* reaction of UO with I atoms produced by photolysis of HI.

Cocondensation of UO or UO_2 in Ar matrices has been demonstrated to produce UO_2^+ and NO_2^- or NO^- in the form of cation-anion pairs. Cocondensation of U atoms with NO_2 in Ar matrices has been studied to see if the following thermodynamically favorable reaction proceeds:

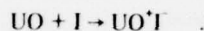


Reaction products observed include nitrides of uranium (UN and UN₂), the neutral oxides of uranium (UO and UO₂), and several unidentified species. None of the unidentified absorption peaks can be attributed to UO^{*}.

Preliminary experiments have been completed with HI and UO. Photolysis of matrix-isolated HI is known to dissociate it.

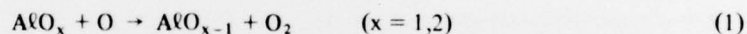


Studies are in progress to determine whether, after photolysis, the following thermodynamically favorable reaction will proceed in an Ar matrix:

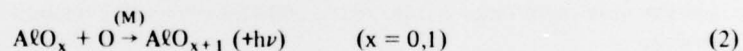


2. *Reactions between AlO_x with O Atoms – A. Fontijn et al. AeroChem (Work Unit 29 in FY 76; Work Unit 40 in FY 77).*

Information on the lifetimes and fates of AlO_x species (Al, AlO and AlO₂) in disturbed atmospheres is needed for evaluation of operations in those environments. In previous DNA-supported work we obtained the rate coefficients of the Al/O₂ and AlO/O₂ reactions in high-temperature fast-flow reactors (HTFFR). The reactions between AlO_x and O should also be considered. Such reactions could be abstraction reactions

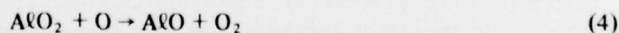
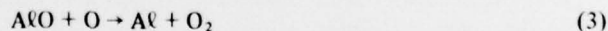


or addition reactions



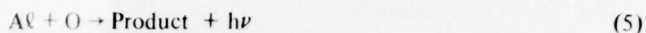
In the present work information on reactions of types (1) and (2) has been obtained in HTFFRs.

Reactions (1) are the reverse of the O₂ oxidation reactions (-1) for which we previously measured the rate coefficients. Thus determination of the equilibrium constants K₁(T) will directly yield the rate coefficients k₁(T). Available values of K₁(T) are uncertain due to uncertainty in D(Al-O). The present work on this problem has concentrated on the determination of a lower limit for this bond energy. From measurements of the activation energy of the Al/SO₂ reaction at 700 K it is concluded that D(Al-O) ≥ 126 kcal mole⁻¹, somewhat higher than the 120 ± 2 kcal mole⁻¹ adopted in the JANAF tables. Our earlier Al/CO₂ measurements also point toward a D(Al-O) higher than 122 kcal mole⁻¹. Assuming the value of D(Al-O) as 126 kcal mole⁻¹, the log K_p(AlO) and (AlO₂) values from the JANAF tables have been recalculated, from which the equilibrium constants for the two reactions of type (1), i.e.,



could also be determined. Combination of these values with the upper limit values of the reverse reactions yields k₃(T) ≤ 1.4 × 10⁻¹¹ exp(-4000/T) and k₄(T) ≤ 5.4 × 10⁻¹² exp(-4000/T), both in ml molecule⁻¹ sec⁻¹ units. These rate coefficients appear too low to significantly influence [AlO_x] in disturbed atmospheres.

Preliminary information on reactions of type (2) has been obtained; i.e., the well known chemiluminescence continuum accompanying Al -oxidation has been studied in atomic Al /atomic O mixtures. From the observed intensity a rate coefficient on the order of 10^{-12} ml molecule $^{-1}$ sec $^{-1}$ was obtained for the *formal* reaction



This rate coefficient is similar to that deduced from earlier, including upper atmospheric, observations and points toward a reaction of type (2) sufficiently fast to affect $[\text{AlO}_x]$ in disturbed atmospheres. A direct observation of the consumption of Al by O atoms also suggests a rapid reaction.

Further work in this area should concentrate on obtaining quantitative information on reactions of type 2, i.e., O -addition reactions.

3. *UV and VUV Photoabsorption and Photoionization Investigations – R.E. Huffman, AFGL (Work Unit 30 in FY 76; Work Unit 35 in FY 77).*

Work has been initiated to explore the relationship of ionospheric irregularities, such as striations, to rocket-borne and ground-based optical and ultraviolet measurements. This work is being pursued with PhotoMetrics, Inc. Rocket photometers offering spatial resolution have been assessed relative to known oxygen ion-electron recombination radiation intensities.

Additional work has involved identification of the predictive and operational defense systems codes that utilize UV spectroscopic inputs and discussion of the adequacy of present information with the technical personnel responsible.

A report has been completed entitled "Nitrogen Dioxide Absorption Coefficients at High Temperatures" by D.E. Paulsen and R.E. Huffman. The temperature range covered is 669 to 1313 K and the wavelength range is from 380 to 760 nanometers. The results are useful in developing fireball models.

4. *Analysis of UV and X-Ray Data for O_2 and O_3 – L. Weeks and A. Faire, AFGL (Work Unit 31 in FY 76; Work Unit 36 in FY 77).*

Two Paiute Tomahawk payloads were fortuitously launched during a solar substorm from the Poker Flat Research Range in conjunction with the ICECAP 76 program in Feb-March 1976. One payload was instrumented with UV and X-ray sensors, while another included a 10-inch sphere as well. In addition to providing general background information on the atmospheric structure associated with the IR measurements, information on geomagnetic storm effects as related to the neutral atmosphere was obtained. Data analysis is in progress, and the overall quality is seen to be excellent.

Significant reductions in the ozone distribution, attributable to a solar proton event, were previously recorded in the rocket measurements during the PCA (SPE) 69 program (Weeks *et al.*, 1972). Subsequent satellite measurements also have shown an ozone reduction that extends well into the upper stratosphere (Heath *et al.*, 1976). There has been an inadequate amount of ozone data, particularly above 60 km, however, to show the extent of the high latitude variability in comparison with the effects associated with solar proton events. The ICECAP 76 ozone data will help to fill this gap and may show if there are geomagnetic storm related perturbations.

Preliminary data reduction has been accomplished on density results acquired by the 10-inch PZL Densitometer (10-inch falling sphere instrumented with triaxial piezoelectric accelerometer system) launched onboard A10.507-1. Excellent data were obtained in the approximate altitude range 50 to 150 km. The density profile shows some interesting departures relative to the USSA-62 and CIRA 72 models that were used for comparison. The observed perturbations which occur above

90 km are probably related to the atmospheric heating associated with an auroral breakup. Work is in progress to finalize these results.

5. *Recombination Rate, Energy Transfer to N₂ and O₂ from Vibrationally Excited NO** M. Camac, F. Bien, *Aerodyne (Work Unit 32 in FY 76, Work Unit 37 in FY 77)*.

Laboratory investigations are in progress to complete the measurement of the dissociative recombination rate of NO*(v) and the transfer of vibrational energy from the v = 1 through v = 4 levels of NO* to N₂. This is done by monitoring the absorption of laser light by various vibration rotation states of NO*. From the absorption, rates for several processes are determined, including the dissociative recombination of the NO* molecule, the formation of complexes of NO* · NO, and the collisional deactivation of the excited state. Since the radiative lifetime of any particular state is long compared to times for the above processes, monitoring the absorption of NO* gives a measure of the above rates.

Work has been centered around measuring the absorption coefficient of NO*(v). NO*(v) is formed in upper vibrational states by photoionizing NO using a 29000 K black-body continuum lamp source. The concentration of particular vibration-rotation levels of NO* formed by photoionization is measured as a function of time. The absorption of light by different vibrational levels determines the initial population of the vibrational level and its relative dissociative recombination rate. By introducing known amounts of N₂, the transfer of energy from NO*(v) to N₂ is also measured. Preliminary measurements show a ground-level integrated absorption coefficient of $S_{\text{Gu}} = 240 \pm 100 \text{ cm}^{-2} \text{ atm}^{-1}$ when extrapolated from the R-3 line of the v = 1 to the v = 2 transition. Preliminary measurements have also indicated a population inversion in the P-6 line of the v = 0 to v = 1 transition of NO* formed by our photoionization technique. The transfer rate of NO*(v = 1) to N₂ is currently being measured. Measurements of the transfer rate of energy from NO* (v = 2, 3, and 4) to N₂ are also planned.

6. *Reactions of Excited Atmospheric Gases - F. Kaufman, University of Pittsburgh (Work Unit 33 in FY 76, Work Unit 38 in FY 77)*.

Water cluster ion formation was studied in our flowing afterglow apparatus. The hydration sequence $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} + \text{He} \rightleftharpoons \text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{He}$ was investigated for n = 1 to 4, rate constants for 3 forward and 1 reverse reactions as well as 2 equilibrium constants were measured at 296 K and some discrepancies in the literature were resolved. It was also possible to measure and/or interpolate values of the mobilities and diffusion coefficients of the hydrated ions. A paper describing this work appeared in the 15 October issue of *J. Chem. Phys.* A paper on two- and three-body processes involving D₂O is in preparation.

Successful infrared chemiluminescence experiments using highly sensitive detection and moderately good spectral resolution in a fast flow apparatus have provided us with two kinds of results: (1) initial vibrational energy distributions as a result of the H + Cl₂ and H + NOCl reactions which show virtually no vibrational relaxation even though the total pressure is about 1 torr, because reactant concentrations are very small (10⁻⁵ to 10⁻⁴ torr) and the inert carrier gas, He, is an inefficient quencher; (2) rate constants for the vibrational relaxation of specific v-states of the excited reaction product (HCl) by other added molecules. N₂, H₂, and CO₂ have been studied so far, with CO₂, the most effective, $k_{\text{CO}_2}^v$ increasing from 2×10^{-12} to $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ as v increases from 2 to 6. This is accomplished through computer analysis of the infrared chemiluminescence spectrum and of its dependence on the amount of added quencher species. Application to other vibrational relaxation processes is under way.

Tunable dye laser fluorescence studies of NO₂ in the 578- to 612-nm region at pressures from 0 to 20 millitorr and with accurately controlled, narrow bandwidth excitation have, at last, resolved

several of the puzzles connected with both the anomalously long radiative lifetime and with the non-exponential decay of the fluorescence. By careful analysis of the fluorescence intensity in known vibronic absorption bands of NO_2 as functions of time, pressure and wavelengths it could be shown (1) that decays corresponding to the strong features of vibronic transitions were the most highly nonexponential but could be fitted to biexponentials; (2) that only the ${}^2\text{B}_2$ state of NO_2 was responsible for this absorption; and (3) that a model which invokes variable vibronic coupling of the ${}^2\text{B}_2$ state with vibrationally and highly excited ${}^2\text{A}_1$ ground state is able to explain all observed data including the lifetime anomaly for that part of the spectrum which lies mainly towards the red of about 500 nm.

Completed studies of neutral atom-molecule reactions such as that between N and CO_2 [*J. Chem. Phys.* 64, 1128 (1976)] which use vacuum UV resonance line absorption techniques have led us to investigate the excitation mechanisms and line shape of radio frequency or microwave powered resonance lamps of the type which were used in our successful Apollo-Soyuz ultraviolet absorption experiment. A brief study of the pressure dependence of the inferred line width (i.e., emission "temperature") of such lamps has shown a sharp decrease of this "temperature" with increasing pressure, especially for rf lamps, and has shown microwave lamps to be considerably "cooler" than rf lamps. Cascading from highly excited atomic levels originally populated through dissociative excitation by He metastables appears to be important. The increasing use of such lamps in field and laboratory experiments makes it important to characterize their spectral parameters and to establish their mechanism. This is now being accomplished in preparation to their application in metastable reaction and energy transfer problems such as upcoming studies of $\text{N}({}^2\text{D})$ and $\text{N}({}^2\text{P})$ processes.

7. *High Intensity Ion Source Data - J. Friichtenicht, TRW (Work Unit 34 in FY 76; not supported by DNA in FY 77).*

A high intensity, pulsed beam source was devised to accelerate energetic metallic ions (e.g., Ar^+) into oxygen and nitrogen gaseous mixtures to ascertain the mechanisms by which such species are stopped. It appeared that perhaps more than one-third of such energetic metallic ions are converted into a singly charged metal oxide (ArO^+) which in turn can be readily reunited with available electrons to form neutral oxide species. The data obtained suggest that complicated reaction mechanisms are involved and that the resulting products obtained may be significantly influenced by various components employed in the experimental apparatus. Work was discontinued pending a comparison of the results from other pertinent, independent laboratory experiments which appear to be in conflict.

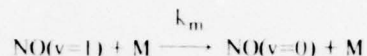
F. Subtask L25BAX HX 632

"IR Phenomenology and Optical Code Data Base"

1. *LABCEDE - Investigations of Irradiated N_2 and O_2 Gas Mixtures - R. Murphy, AFGL. (Work Unit 02 in FY 76; Work Unit 05 in FY 77).*

The primary objective of this work is the study of infrared backgrounds generated in air by electron deposition. We have used both an electron gun injecting a few milliamperes into a target chamber and a hollow cathode discharge which allows currents of the order of amperes to be used. Instrumentation uses both Fourier spectroscopy, particularly in the recently developed time-resolved mode, which gives 2 cm^{-1} , 10^{-5} sec response time, and conventional filter studies.

ζ The rate of quenching of vibrationally excited NO by $\text{O}_2 + \text{N}_2$ has been measured. The NO was formed from air and O_2 plus N_2 mixtures by the electron gun. The characteristic decay times of the reactions



were observed and interpreted as rate constants. It was not possible to determine whether the process was V-V and V-T. The rate constants depend on whether the quenching rates are proportional to v or independent of it, but the effect is not marked.

Assuming rates proportional to V , the ratios for the fundamental were found to be

$$k_{\text{O}_2} = 2.4 \pm 1.5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$$

$$k_{\text{N}_2} = 1.7 \pm 0.5 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$$

and if the rates are independent of v , the rates are 25 percent greater.

Identification of Nuclear Induced Spectra

Spectra of past nuclear burst-disturbed air have shown pertinent emission features of interest but complete evaluation of these data has been extremely difficult to date. Analysis was difficult because the original spectra were taken under low resolution and gave the feature a band-like appearance. The electron beam facility did generate a feature which closely resembled the nuclear-induced one. It was never possible, even with improved resolution, to obtain spectra which enabled a positive identification to be made. Investigation of the pulsed hollow cathode source operating at a few torr with the time-resolved technique showed a series of sharp lines in air and N_2 and O_2 . Both the sharpness and time behavior indicated atomic emitters. The lines were identified as due to both O atoms and N atoms and involved high excitation levels close to the ionization continuum. Specifically, transitions involving 6s, 5d, 5g and 4s, 4p, 4d, 4f levels were observed. For nitrogen many of these can cascade to the metastable ^2D and ^2P levels important in the NO infrared background problem. The lifetimes of the transitions observed were too fast to measure with our electronics which was limited to 2-microsecond resolution.

The cathode source has also been used to study the reaction kinetics of metastable nitrogen atoms. The discharge space, a mesh cylinder ~ 2 cm long and 1 cm in diameter, was probed by a background lamp emitting the $^2\text{D}-^2\text{P}$, 1492A and $^2\text{P}-^2\text{P}$, 1742A multiplets. Absorption due to the generation in the discharge of ^2D and ^2P states was detected by a VUV monochromator and photomultiplier combination. The output was processed as individual counts which were co-added in a multichannel scaler whose time base was synchronized with the pulsed power supply of the hollow cathode. This enabled ^2D and ^2P concentration to be followed as a function of time.

The time behavior of these atoms was translated to kinetic rates with the assumption of no activation energy being involved and the gas being at room temperatures. The following preliminary results have been obtained:

<u>Quenching Process</u>	<u>Rate (cm³ sec⁻¹)</u>
$\text{N}^2\text{D} + \text{N}_2$	2×10^{-13}
$\text{N}^2\text{P} + \text{N}_2$	too slow to measure, thus 10^{14}
$\text{N}^2\text{D} + \text{O}_2$	10^{-11}
$\text{N}^2\text{P} + \text{O}_2$	2×10^{-12}

The rates are in good agreement with flash photolysis work and flow experiments.

Oxides of Nitrogen Emission

The time-resolved observation of the infrared radiation from both the electron beam and the hollow cathode discharge have shown NO emission when O₂ plus N₂ mixtures have been used. Vibrational levels as high as 12 have been observed. The time resolution and comparison experiments with NO in a carrier show that these high levels are associated with the chemistry and not merely due to electron excitation. Late in the afterglow, N₂O has been observed to be formed. This is a very strong emitter in several portions of the IR spectrum.

Oxygen Emission at 1.9 microns

In the electron beam experiments it was noted that oxygen gave an emission at 1.9 microns which was identified as the Noxon bands. The intensity was found to be strongly pressure sensitive. This was interpreted as a relaxation of the forbiddenness of the transition by the presence of a perturbing molecule. From 0.0001 to 300 torr the enhanced radiation was found to be proportional to pressure and the rate constant for nitrogen was found to be

$$3.6 \times 10^{-20} \text{ cm}^3 \text{ sec}^{-1}$$

2. *COCHISE - Ozone and Related Investigations - J.P. Kennealy and F.P. DelGreco, AFGL (Work Unit 03 in FY 76; Work Unit 06 in FY 77).*

During FY 76 the COCHISE facility became meaningfully operational, and excellent progress was made in the study of several different problems.

Briefly, COCHISE provides sufficient detection sensitivity to measure (detect and spectrally resolve) infrared radiation from typical excited species with number densities no greater than 10⁷ to 10⁸ cm⁻³. Measurements are carried out at very low total pressures (0.1 to 10 mtorr) and under very fast flow conditions (contact time 1 to 10 msec), so collisional and radiative relaxation of excited states is generally negligible. In addition, utilization of cryo-pumping on all reaction chamber walls eliminates surface chemistry and relaxation effects. This unique combination of experimental conditions provides, for the first time, a capability to determine excited state distributions, created by chemi-excitation and energy transfer phenomena, unmodified by relaxation processes.

Well resolved emission spectra have been obtained from nitric oxide chemi-excited by the N(²D) + O₂ → NO* + O reaction; these measurements were taken in the Δv=1 sequence in order to get data on the populations of all levels from v=1 on up. The spectra show excitation of all levels up to v=12 or 13, and an analysis is currently being completed to extract the set of relative rates of formation into individual vibrational levels. However, the immediate indication is that there is very little production into vibrational levels beyond v=10, and the maximum of the distribution is well below v=10. Since the reaction is energetically capable of producing nitric oxide excited at least as high as v=18, it appears that approximately 15 to 25 percent of the total available energy is partitioned into vibrational states of nitric oxide by this reaction.

Preliminary experiments have been completed on the chemi-excitation of ozone in the recombination of atomic oxygen (i.e., O + O₂ + M → O₃ + M). Resolved spectra have been recorded of emission from the Δv=1 sequence of the ozone O₃ system, which shows banded structure out to approximately 11 microns and suggests excitation of all levels out to v₃=7. Unfortunately, no data (either experimental or theoretical) exists on the spectroscopic constants and transition coefficients associated with highly excited vibrational states of ozone; consequently, it is difficult at present to be very positive about the interpretation of these spectra. In fact, more intensive and higher resolution studies of the ozone problem with COCHISE will probably yield the first reliable spectroscopic constant data on the higher vibrational levels of ozone; however, determination of the transition coefficients would probably best be done by an independent theoretical effort.

In addition to nitric oxide and ozone work, some experiments were done utilizing the N_2 -CO VV exchange for temperature and wavelength calibrations of the COCHISE system. The experimental conditions were such that only single-step excitation was possible, yet significant excitation of at least $v=2, 3,$ and 4 was evidenced by the highly resolved spectral data. An obvious implication is that multi-quanta VV transfer may be appreciably more important than previously assumed. Further experiments will better define this.

3. *Improved Barium Releases - P. Zavitsanos and E. Alvea, GE/RESO (Work Unit 04 in FY 76; not supported by DNA in FY 77).*

These efforts have been concerned with an updated theoretical evaluation of barium metal vapor release technology. A significant portion of this endeavor was conducted in cooperation with, and support to, the efforts of special DNA Chemistry/Physics *Ad Hoc* Panel No. 3 (concerned with effective use of barium vapor chemical releases) which are currently in progress under the guidance of Dr. E. Bauer, IDA. Subsequent laboratory experiments to improve the capability to disperse barium metal vapor in the upper ionosphere, in desired spatial and temporal configurations, for future applications of interest to DNA are scheduled to be completed in later calendar 1976.

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