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REACTION RATE DATA

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# RESUME OF FY 78 DNA-SPONSORED CHEMISTRY PHYSICS REACTION RATE RESEARCH PROGRAMS

Number 63

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This issue of the DASIAC Reaction Rate Data presents brief resumes of DNAsponsored Chemistry/Physics Reaction Rate Research efforts for FY 1978.

Since information in this document is considered to be preliminary in nature and may be subject to possible future revision and/or changes, it is requested that recipients do not cite or reference the contents in other media without receipt of prior specific approval of the Defense Nuclear Agency.

Future editions of the DASIAC Reaction Rate Data will contain related progress reports concerning the DNA-sponsored efforts described herein.

Submission of other pertinent information of a related nature deemed appropriate for publication in future editions of the DASIAC Reaction Rate Data is welcome and should be addressed to DASIAC, General Electric Company-TEMPO, 816 State Street, Santa Barbara, California 93102, which is contractually engaged by the Defense Nuclear Agency for this purpose.



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# RESUME OF FY 78 DNA-SPONSORED CHEMISTRY/PHYSICS REACTION RATE RESEARCH PROGRAMS

#### A. SUBTASK S99QAXHD411

### "Reaction Rates Essential to Propagation."

- 1. Electron and Cluster Ion Recombinations and Temperature Coefficients M. Biondi, University of Pittsburgh, Ends 30 September 1978 (Work Unit 03).
  - a. Ion-Molecule Reactions: The rates of formation and equilibrium constants for precursor ions such as [NO<sup>+</sup> H<sub>2</sub>O] and [NO<sup>+</sup> CO<sub>2</sub>] will be determined with the new variable temperature drift tube (~80 K to ~500 K capability). Ions such as these are thought to be critical intermediaries in the conversion of D-region NO<sup>+</sup> to the hydronium series ions 37<sup>+</sup>, 55<sup>+</sup>, etc, and little is known of their formation rate or stability under ionospheric conditions.
  - b. Electron-Ion Recombination: A new variable temperature microwave afterglow apparatus will be built with sensitive optical absorption and resonance fluorescence capabilities for two purposes:
    - (1) To determine the rates of recombination of the weakly stable precursor ions such as  $[NO^+ \cdot H_2O]$  and  $[NO^+ \cdot CO_2]$  with electrons under D-region conditions.
    - (2) To determine the yield of energy storing, metastable atoms resulting from the dissociative recombination of atmospheric ions with electrons. Specifically, the yield of final state products for the reactions

 $NO^+ + e \rightarrow (NO^*) \rightarrow N^*(^2D) + O(^3P)$ 

and

$$N_2^+ + e \rightarrow (N_2^*) \rightarrow N^*(^2D) + N$$
,

will be determined. They are of importance, respectively, in the normal ionosphere and in disturbed ionosphere produced by nuclear detonations.

# 2. Three Body Debris Metal Ion Interactions-W. Fite, Extranuclear Corp. Ends 30 September 1978 (Work Unit 04).

Laboratory investigations begun in 1977 of two- and three-body reactions of debris metal ion species with atmospheric D-region constituents will be completed. Specifically, the rate coefficients for the reactions  $A\ell^+ + O + M \rightarrow A\ell O^+ + M$  and  $Fe^+ + O_3 \rightarrow FeO^+ + O_2$  will be measured. Such reactions are important in late time debris effects since they influence the energies, distribution and total concentrations of ionospheric free electrons. These reactions thus affect the refractive indices of disturbed D-regions and hence, EM wave propagation.

## 3. Photodissociation and Photodetachment of Negative Ions and Hydrates-C. Lineberger, JILA. Ends 30 September 1978 (Work Unit 05).

In order to predict electron densities (lower D region), it is necessary to obtain photoproduction rates of electrons from terminal negative ions and their hydrates. Tunable laser photodetachment techniques will be utilized to obtain photoproduction rates and electron affinities of terminal negative ions, and their low hydrates in the spectral region 600-250 nm. Emphasis will be placed on  $O_3^-$ ,  $NO_3^-$ ,  $[NO_2^- \cdot H_2O]$  and  $CO_3^-$  ionic hydrates. The technique of laser photoelectron spectrometry, which has been previously utilized on smaller negative ions, will be employed to verify the above results and to obtain complementary bond energy information from these ions. In addition, exploratory investigations of possible metal oxide negative ions will be undertaken to determine the possibility of high electron affinity species forming an electron sink.

# Positive Ion-Negative Ion Recombination Rate Coefficients for the Lower D Region-J. Peterson, SRI International. Ends 30 September 1978 (Work Unit 06).

Rate coefficients for positive ion-negative ion, complex and water-cluster ion specie interactions which occur in the lower D region at late times after an atmospheric nuclear burst are quite sparse and generalized procedures for laboratory measurements are not available.

In FY 78, a reevaluation of the method employed at the University of Birmingham, England, for a few of these reactions will be conducted with a view toward obtaining improved confidence levels in data produced, and extension of this method to reactions of interest to DNA in the lower D region.

Interacting ions at temperatures from 100-600 K, and the products which result will be measured. Ions such as NO<sup>+</sup>;  $[H_3O^+ \cdot nH_2O]$ ;  $O^-$ ;  $[NO_3^- \cdot nH_2O]$ ;  $[CO_3^- \cdot nH_2O]$ ; and  $[CO_4^- \cdot nH_2O]$  will be investigated. Unambiguous methods to create such species for subsequent interactions will also be sought.

## 5. Atmospheric Chemical Sensitivity and Modeling Investigations-M. Scheibe, MRC. Ends 30 September 1978 (Work Unit 09).

Mission Research Corporation will:

- a. Use the ROSCOE code to complete UHF communications chemistry sensitivity studies using techniques developed previously and having the concurrence of the DNA/COR.
- b. Use the results of the above UHF chemistry sensitivity studies, if fruitful, to define those areas of ionospheric chemistry where further research is needed and would be most effective.
- c. Supply chemistry inputs to other DNA contractors as requested, with prior coordination and approval of the DNA/COR.
- d. Construct, improve, and validate chemistry models simulating nuclear environments for communications systems codes. Particular attention will be paid to the approach to ambient and field data.
- e. Maintain and update DCHEM and FIRECHEM codes for use in benchmark and sensitivity calculations and model construction and improvement.
- f. Consult and interact with the COR and DNA chemistry *ad hoc* panels to make the various sensitivity and benchmark calculations responsive to their current needs.
- 6. Low Energy Cross Sections for Debris Metal Ions-R. Neynaber, D. Vroom, and J.A. Rutherford, IRT, Inc. Ends 30 September 1978 (Work Unit 12).

IRT Corporation will obtain data needed for codes to model upper atmospheric disturbances. The following tasks will be included:

### a. Investigation of the reaction

$$N^+ + 0 \rightarrow N + 0^+$$

will be completed using crossed beam techniques. The cross section or an upper limit on the cross section will be determined at the lowest possible energy obtainable.

b. The reactions

$$A\ell^+ + O_2 \qquad \stackrel{\rightarrow}{\leftarrow} \qquad A\ell O^+ + O_2 \\ \rightarrow \qquad A\ell + O_2^+ \\ \rightarrow \qquad A\ell + O + O_2^+ \\ \rightarrow \qquad A\ell + O + O_2^+ \\ \rightarrow \qquad A\ell + O + O_2^+ \\ \rightarrow \qquad A\ell + O_2 \\ \rightarrow \qquad A\ell$$

and

$$A\ell^{+} + N_{2} \qquad \stackrel{\rightarrow}{\mapsto} \qquad A\ell N^{+} + N_{2} \\ \rightarrow \qquad A\ell + N_{2}^{+} \\ \rightarrow \qquad A\ell + N + N$$

will be investigated using crossed beam techniques. The energy range of the measurements will be 1 to 5000 eV.

E and F Region Rate Coefficients for Excited Positive Ions-J. Paulson and E. Murad, AFGL. Ends 30 September 1978 (Work Unit 14).

Specific tasks to be accomplished will include direct laboratory measurements of the absolute cross sections for photodissociation of important atmospheric positive complex ions, such as  $O_3^+$ ;  $[NO^+ \cdot H_2O]$ ; and  $[NO^+ \cdot CO_2]$  in the wavelength range from 300 to 650 nm. Cross section values for the reaction of  $O^+$  with vibrationally excited N<sub>2</sub> up to v = 3 will also be completed.

8. Improved Master/Simple Code Applications to E, F Regions-W. Ali, NRL. Ends 30 September 1978 (Work Unit 15).

NRL will:

7.

- a. Maintain and update the NRL "MASTER" and "SIMPLE" computer codes through use of new and/or updated ionospheric reaction rate information.
- b. Participate in DNA sponsored "benchmark" activities designed to acquire improved effective rate coefficients for use of ionospheric chemistry/communications codes sensitivity assessments.
- c. Provide essential reaction rate information to other DNA-sponsored NRL activities engaged in improvement to the present UV-fireball and other elements in NRL communications/ optical predictive computer models/codes, all in support of ROSCOE code improvements and applications.
- 9. Applications of the AIRCHEM Code to the Lower D Region-F. Niles and M. Heaps, AASLNM. Ends 30 September 1978 (Work Unit 16).

Specific tasks to be accomplished are:

- a. Compare calculated ionic number densities with experimental laboratory measurements to improve lower D region atmospheric deionization.
- b. Attempt to construct a reasonable model to describe lower D region ionospheric ionization processes.

c. Carry out calculations to improve the reference data base through so-called "benchmark" exercises within the D region reaction rate community in order to improve lower D region modeling efforts relevant to ELF/VLF predictive propagation codes.

### 10. Photodissociation of Atmospheric Cluster Ions-F. Niles and J. Vanderhoff, AASLNM and BRL. Ends 30 September 1978 (Work Unit 17).

Efforts in FY 78 will include the laboratory measurement of positive and negative ion reaction rates and photodestruction cross sections in highly disturbed environments, such as the lower D region, which can seriously affect ELF/VLF propagation. The absolute photodissociation cross sections for atmospheric D region cluster ions as a function of input photon energies ranging from 1.4 to 3.5 ev will be ascertained, and identification of the resultant photofragments will be attempted.

## 11. Measurements of Selected Lower D-Region Reactions-E. E. Ferguson, et al., NOAA. Ends 30 September 1978 (Work Unit 18).

Selected laboratory investigations and measurements of reaction rates of high priority interest to DNA/DoD will be performed using the improved flowing afterglow and flow-drift tube technology developed at NOAA in recent years with DNA assistance. In previous years, the NOAA efforts have been concentrated on ion-molecule type reaction rate measurements which have been widely used by the DNA model/predictive computer code community. In FY 78 these laboratory measurement techniques and their range of applicability will be extended to investigations which are outlined below. In addition, as new and urgent problems arise during the year they will be dealt with. Specific efforts will include the following:

- a. Both the flowing afterglow and the flow-drift tube will be modified to allow the injection of ions of a selected type, in the absence of the parent neutral gas of this ion. This modification will facilitate the measurement of branching ratios and will reduce the complications of parallel and/or secondary reactions. Furthermore, an atmospheric-pressure ion source, whose properties have already been examined with a direct-coupled mass spectrometer, will be added to the flow systems. These new ion sources will extend the laboratory's capabilities by greatly increasing the species of ions that can be studied, particularly cluster ions, and electronically excited ions.
- b. Electronically excited positive ions play an important role in atmospheric ion chemistry, particularly above 80 km. In this regard, the metastable (triplet) NO<sup>+</sup> ion has an energy several electron volts higher than that of the ground-state (singlet) NO<sup>+</sup> ions. Therefore, it can react with many neutrals with which the ground state is endothermic. Because of the role that this metastable ion may play in excitation processes in air, the rate constants of the reactions of these ions with a variety of neutrals (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, etc.) will be measured in the flow-drift tube. The relative roles of reaction and quenching will be assessed.
- c. Investigations of the reactions of  $N_2O_5$  in the flowing afterglow and the flow-drift tubes will be extended since these reactions have important implications relevant to electromagnetic wave propagation in the very low D region ion chemistry and perhaps for neutral chemistry. This work will continue with emphasis on the reaction of the hydrated ions, both positive and negative, with  $N_2O_5$ .
- d. The work directed toward the study of atomic oxygen and vibrational excited nitrogen reaction in the flow-drift system will continue, being aided by the apparatus modifications described above. The energy dependences of the reactions involving these species are among the most important in understanding the ion chemistry in disturbed atmospheric conditions.

- e. Work will be completed concerning the details of the processes leading to the formation of  $[H_3O^+ \cdot nH_2O]$  (where n > 2) in the atmosphere. This work was initiated in FY 77 through the conversion of  $[O_2^+ \cdot O_2]$  to  $[O_2^+ \cdot CO_2]$  and  $[O_2^+ \cdot O_3]$ . Subsequent investigations of reactions of these ions with  $H_2O$  was then begun. Attention in FY 78 will focus on the conversion of NO<sup>+</sup> to the hydrated hydronium ions. These investigations will be carried out in the variable-temperature flowing afterglow.
- f. The flow-drift tube has a unique capability for measuring the mobility of a wide variety of ions in many different gases. Such data, as well as the zero-field diffusion coefficients derived from them, are useful as transport parameters in the many applications involving the motion of ions in electric fields. Furthermore, ion mobilities are now being used in the determination of ion-neutral scattering potentials and the calculation of ion-ion recombination coefficients. The flow-drift tube will continue to be used to measure ion-neutral mobilities. One such investigation will be ions in air, with the long-term goal of developing a means of identifying the ion types in the very low D region.
- g. Evaluations and measurements of the thermochemistry of specific atmospheric ions will be completed if time and resources permit. The determination of the heats of formation of these ions is necessary to place precise constraints on the possible reaction paths leading to the production or destruction of these ions. During the past year, the stabilities of  $[H_3O^+ \cdot rH_2O]$  relative to  $[CH_3O^+ \cdot nH_2O]$  (where n = 0, 1, 2, 3) were determined. Furthermore, the stabilities of  $[O_2^+ \cdot O_3]$  and  $[O_2^+ \cdot CO_2]$  relative to  $[O_2^+ \cdot O_2]$ , and a limit on the heats of formation of CO<sub>3</sub> were established. ("A Study of the Reactions O<sub>3</sub> + CO<sub>2</sub>  $\rightarrow$  CO<sub>3</sub> + O<sub>2</sub> and Its Implication on the Thermochemistry of CO<sub>3</sub> and O<sub>3</sub> and Their Negative Ions." Dotan, Davidson, Streit, Albritton, Fehsenfeld, J. Chem. Phys. accepted for publication.)
- h. The ion-molecule reaction rate constants that have been measured in the flow tubes of the NOAA laboratory, as well as those of six other laboratories, will be collected together in a compendium that will include the rate constants, branching ratios, and energy dependences. It is expected that this will include approximately 1000 reactions, only about one-third of which are presently accessible in review articles.
- 12. Ion Measurements in the Lower D Region-D. Snider and F. Niles, AASLNM. Ends 30 September 1978 (Work Unit 19).

Rocket-borne and balloon-borne instruments will be flown into the very low D region (40-50 km) in order to acquire in situ data concerning ion masses (including cluster ions), ion mobilities, and related upper atmospheric data of importance to ELF/VLF propagation. Data thus obtained will be evaluated against theoretical and laboratory measurements, and subsequently employed to evaluate and improve existing ELF/VLF models employed in applicable predictive computer codes. In FY 78 a new and improved positive ion/negative ion mass spectrometer will be included among the instrumentation employed.

#### B. SUBTASK S99QAXHD028

### "Theoretical Investigations of Ionizing Mechanisms in the Upper Atmosphere"

1. Computations of Molecular Structures and Transition Probabilities-H. Michels, UTRC. Ends 30 September 1978 (Work Unit 44).

Specific tasks will be:

- a. Complete the development and validation of a low energy atom-atom collision code.
- b. Perform detailed calculations of the kinetics of the following charge transfer reactions for collision energies 0-5 eV:

 $N^{+}(^{3}P) + O(^{3}P) \rightarrow N(^{4}S) + O^{+}(^{4}S)$ 

$$N^{+}(^{1}D) + O(^{3}P) \rightarrow N(^{2}D) + O^{+}(^{4}S).$$

c. Collate the calculated kinetic reaction rates with reaction channels for comparison (where possible) with existing experimental cross-section data for the reaction:

 $N^+ + O \rightarrow O^+ + N$ .

2. Theoretical Aspect of Ion-Ion Laboratory Measurements-F. Smith, SRI International. Ends 30 September 1978 (Work Unit 45).

The tasks for FY 78 will be:

- a. Perform theoretical calculations to describe the effects of ion clustering upon the rate coefficients for positive ion-negative ion recombination reactions of interest and concern to ELF/VLF propagation.
- b. Develop and improve existing theoretical methods to permit extension of these calculations for complex species, such as  $[H_3O^+ \cdot nH_2O]$ ;  $[NO_3^+ \cdot nH_2O]$ ;  $[NO_3^- \cdot nH_2O]$ , and  $[CO_3^- \cdot nH_2O]$ , for comparison with laboratory experimental data.
- 3. Theoretical Investigations of Disturbed Ionospheres-W. Swider, AFGL. Ends 30 September 1978 (Work Unit 46).

Specific tasks to be accomplished are:

- a. The investigation and documentation of technical information relevant to existing DoD communication and optical satellite problems, as acquired from extensive data of the NASA "Atmospheric Explorer" satellites, will be completed.
- b. A review of the Chatanika backscatter radar data base, in order to determine if additional twilight data are available for utilization in structuring daytime electron density concentration profiles in disturbed lower D-region environments will be conducted.
- c. Cognizance of progress of cluster ion reaction mechanisms and rates will be maintained and assistance in this complex problem area of ELF communications as requested by DNA/COR will be provided.

# 4. Reaction Rate Sensitivities and Assessments-M. Bortner, T. Baurer, GEMSD. Ends 30 September 1978 (Work Unit 49).

Tasks to be accomplished are:

- a. Coordinate completion of identification and assessment of ionospheric chemical and physical parameters which influence the output of computer codes concerned with the operation of DoD communications systems in the ELF, VLF, and UHF bands; develop ion mobility and collisional frequency data applicable to the ELF/VLF calculations.
- b. Coordinate and complete the preparation, editing, and (in cooperation with DASIAC) distribution of the DNA Reaction Rate Handbook, Second Edition (DNA 1948H), as proposed originally and as updated according to subsequently changing concepts.
- c. Maintain an active and continuously updated file of chemical kinetics information relevant to DNA-sponsored model and code work.
- d. Assess the capability for improvement of the so-called "Pocket Manual" (Physical and Chemical Characteristics of the Earth's Atmosphere, DNA 3467H).

#### C. SUBTASK S99QAXHI002

#### "Atomic and Molecular Physics of IR Emissions"

1. UV and VUV Photoabsorption and Photoionization Investigations-R. Huffman, AFGL. Ends 30 September 1978 (Work Unit 42).

Specific tasks to be accomplished are:

- a. The compilation of a revised set of photoionization cross sections and solar flux values will be completed and submitted for inclusion in the DNA Reaction Rate Handbook (DNA 1948H).
- b. These improved cross section data will be employed to recalculate the approximate width and spatial extent of an overionized F region, such as might exist in a highly disturbed ionosphere created by the UV fireball phenomena associated with atmospheric nuclear detonations.
- c. Improved measurements of the complex oxygen Schumann-Runge absorption bands will be made and employed to produce an accurate temperature dependent model for the spectral region where atomic oxygen and nitrogen species have strong emission lines.
- d. Assessments of visible, UV, and VUV techniques for monitoring the ionosphere from satellite and space shuttle platforms in regard to problems of DNA interest (such as applicability to observation of ionospheric irregularities which adversely affect satellite communication systems) will be completed. Determination of inadequacies in present laboratory measurements needed to develop such observational methods for *in situ* use will be delineated.

# 2. Reactions of Excited Atmospheric Gases-F. Kaufman, University of Pittsburgh. Ends 30 September 1978 (Work Unit 44).

Specific tasks to be accomplished are:

- a. Vibrational excitation and collisional relaxation of atmospheric species by IR chemiluninescence in fast flow reactors: The vibrational relaxation of OH<sup>v</sup> in v = 1 to 9 as produced by the H + O<sub>3</sub> reaction will be measured accurately for a variety of quencher molecules including N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, and NO.
- b. Reaction and quenching process of atomic metastables: Work on  $N^{(2D,2P)}$  quenching by  $O_2$  is nearing completion.  $O(^{3P})$  reactions with N\* will be studied by N\* resonance fluorescence.
- c. Laser vibronic excitation and collisional quenching of air triatomics: The highly perturbed vibronic states involved in absorption and fluorescence of  $NO_2$  at 2 to 3 eV are nearly fully mapped. Their collisional relaxation will be investigated in detail as a function of collision partner. Rate constants and the average amount of energy transferred per collision will be measured and interpreted in terms of energy transfer theories.

## 3. Vibrational Energy Transfer Investigations and Spectral Data for UO<sup>+</sup>-F. Bien and M. Camac, Aerodyne Research Laboratories. Ends 30 September 1978 (Work Unit 45).

Specific tasks to be accomplished are:

a. Completion of laboratory measurements of IR spectral data for the UO and UO<sup>+</sup> molecules, with heavy emphasis upon such data for the latter, elusive, singly ionized oxide specie. This information will complete the spectral atlas for uranium oxide species of nuclear debris interest (not available elsewhere). Experimental data for the neutral UO specie, previously measured, will be remeasured for comparison and validation purposes.

- b. Additionally, IR data (e.g., the number) for vibrationally excited NO<sup>+</sup> emissions at 4.3 microns will be investigated to determine vibrational lifetimes and energy transferred to the N<sub>2</sub> molecule.
- 4. Theoretical and Laboratory Investigations of Enhanced SWIR Radiance J. Kumer and T. James, LMSC-PA. Ends 30 September 1978 (Work Unit 48).

The research project for FY 78 will be comprised of the following specific tasks:

- a. Use a 2.7  $\mu$ m tunable laser light source to perform a laboratory confirmation of the CO<sub>2</sub> 2.7 to 4.3  $\mu$ m pumping mechanism.
- b. Evaluate the laboratory data obtained on the  $CO_2$  2.7 to 4.3  $\mu$ m pumping mechanism with the blackbody 2.7  $\mu$ m light source. This evaluation will include the effect of multiple photon absorption and re-emission by  $CO_2$  and the effect of photon reflection on the walls of the apparatus.
- c. Include N<sub>2</sub>O, <sup>14</sup>N<sup>15</sup>N and CO in the current model for prediction of spectral radiance in the MWIR region in order to attempt to model the spectral auroral zenith radiance data obtained in the 4.5 to 4.6  $\mu$ m region via a SWIR CVF spectrometer which was launched into an aurora 12 March 1975.
- d. Document the results in progress reports and a final report.

#### D. SUBTASK 125BAXHX632

1.

"IR Phenomenology and Optical Code Data Base"

LABCEDE-Investigations of Irradiated N<sub>2</sub>, O<sub>2</sub>, and Other Gas Mixtures-R. Murphy, AFGL. Ends 30 September 1978 (Work Unit 07).

Specific tasks to be accomplished are:

- a. Acquisition, checkout, calibration and utilization of a new, very effective and powerful electron gun as a source of energetic electrons.
- b. Attention will then be directed to the excitation processes which produce both  $N_2O^{\ddagger}$  and  $NO_2^{\ddagger}$  at such a rapid rate as to preclude the usually considered three-body process. Current data indicate that tracking the production mechanism is possible.  $N_2O$  and  $NO_2$  emission is important to atmospheric chemistry and to potential DSP type future surveillance systems.
- c. The survey of electron induced emission produced in LABCEDE will be continued. After the electron emission from the new source is realized, and the cryogenic spectrometer is mated, the survey of 6-15 $\mu$ m will be completed and evaluated. Physical Sciences, Inc. (Dr. George Calendonia) will continue to assist in the reduction and assessment of data obtained previously from the irradiated N/Ar/He-CO<sub>2</sub> gas mixtures. These data can supply rate information on CO<sup>+</sup> recombination, N<sup>+</sup><sub>2</sub> heating efficiency, CO<sub>2</sub>  $\leftrightarrow$  CO exchange and CO(v) vibrational exchange with parent gases.
- 2. COCHISE-Investigations of Ozone and Other Reactions of E Region Interest-J. Kennealy and F. Del Greco, AFGL. Ends 30 September 1978 (Work Unit 08).

Specific tasks to be accomplished are:

a. Experimental validation of the NO upper level Einstein coefficients. Only theoretical values are currently available, and apparent anomalies approaching an order of magnitude in the

ICECAP and EXCEDE 2.7/5.3 intensity ratios may be reflecting errors in the assumed values for the A's.

- b. Determination of the radiative potential for N<sup>14</sup>N<sup>15</sup>. Preliminary laboratory simulations and allusions in the Soviet literature suggest that the isotopic nitrogen may be a principal 4.3 (and 2.2) micron emission source above 90-100 km in disturbed atmospheres. This is a startling possibility which, if true, could drastically alter much of our understanding of high alt<sup>\*</sup>tude radiative transfer.
- c. Experimental characterization of low pressure 2.7/4.3 micron CO<sub>2</sub> radiation. One explanation proposed to account for the ICECAP 2.7 micron anomalies invokes CO<sub>2</sub> as a major radiator. This will be tested in the COCHISE simulation experiments.
- d. Complete spectral characterization of the ozone 9-12 micron chemiluminescent emission, excited by the recombination of atomic oxygen. Preliminary work on the problem in the COCHISE program has suggested that this phenomenon could severely impact limb-looking surveillance systems operating in the 9-12 micron atmospheric window, unless their spectral bandpasses are carefully selected; such a selection will require far better data than currently exist.
- e. Identification of the source for the rather intense 9.2 micron "mystery" radiation which has now been seen sporadically in both field measurements and laboratory simulations. Although 9.2 microns is not currently considered an important wavelength, the inexplicable nature of this emission demonstrates that there is a major gap in our understanding of atmospheric emissions which may impact other wavelength regions as well (one obvious example: the 4.6 micron "overtone" system).

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