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SECOND CONFERENCE ON APPLICATIONS OF CHEMISTRY TO NUCLEAR WEAPONS EFFECTS

Abstracts of Papers

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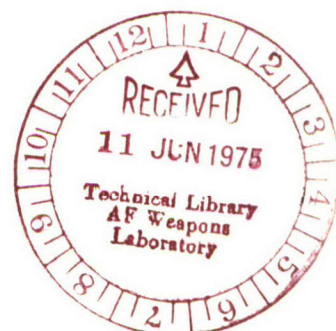
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High altitude nuclear detonation phenomenology, models, and codes

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This document contains unclassified, brief preface, conference agenda and schedule, abstracts, and overall summary addendum of papers submitted and accepted for Hq DNA-sponsored "Second Conference on Applications of Chemistry to Nuclear Weapons Effects".

PREFACE

In April 1970, a conference dealing with "Applications of Chemistry to Nuclear Weapons Effects" was sponsored by the Defense Nuclear Agency (DNA)--formerly the Defense Atomic Support Agency--in cooperation with the Air Force Cambridge Research Laboratories (AFCRL). The significant variety and number of high-quality presentations by attendees at that meeting made it apparent that results obtained from DNA-sponsored research concerning the chemistry and physics of the disturbed upper atmosphere were being widely employed by various governmental agencies and other organizations engaged in the improved comprehension of many facets of nuclear-disturbed ionospheres. This was particularly true for those involved with the formulation of improved models and predictive computer codes required for high priority DOD optical, radar, and communications systems.

Consequently, it was ascertained in early 1972 that the increasingly rapid output of "chemistry" information, since that earlier conference, made it highly desirable to once again convene a similar type of interdisciplinary technical conference for those employing this "chemistry" output in their endeavors, with special emphasis on data of interest to the DNA and DOD code communities. The response to this idea was overwhelming, both from the response of attendees and those desiring to present the latest "chemistry" information and its applications to the nuclear effects community.

As a result, it became mandatory for the DNA Program Committee to regretfully reject a large number of the many papers submitted for presentation, due to overall timing constraints. Even then, those papers chosen were done so with great difficulty by the committee because of the high general level of interest shown by contributing authors and those who attended. As a compromise, the titles and authors of a number of the more significant, unpresented papers were listed on the program and marked with an asterisk; i.e. (*), before and after the title, to indicate the fact that they were not formally presented at the conference but were of interest and concern. The abstracts of such papers are, therefore, included in this document.

Those individuals desiring more information concerning the abstracts of any of the papers listed on the program may wish to contact the authors directly at their own convenience. The understanding and cooperation of all who submitted

papers for this conference are deeply appreciated and sincere thanks are expressed upon behalf of DNA to all attendees whose active participation made this "Second Conference on Applications of Chemistry to Nuclear Weapons Effects", which was indeed a highly informative forum. The tireless efforts of conference administrative personnel are also acknowledged and gratefully appreciated.

DR. CHARLES A. BLANK
DNA Conference Project Officer

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CONFERENCE AGENDA

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                                                            HQDNA
                                                            Conference
                                                            Project Officer

0900-0930   Keynote Address.   W. W. Berning
                                                            Assistant to the
                                                            Deputy Director,
                                                            Science and
                                                            Technology, DNA

SESSION I - Low Altitude Fireball Entrainment and Chemistry

CHAIRMAN: H. C. FITZ, DNA

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               form Mixing on Fireball Chemistry.   Xonics, Inc.

0950-1005   Entrainment by Intermediate Altitude   G. A. Simons
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CHAIRMAN: K. CHAMPION, AFCRL

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CHAIRMAN: F. E. NILES, BRL

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1435-1450	The Vibrational Spectra of Uranium Oxide Vapor Species.	S. Gabelnick G. Reedy M. Chasanov Argonne National Laboratory
	(*) Radiation from Shock-Heated Uranium-Oxygen Mixtures (*).	W. Wurster Calspan Corporation
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1520–1530	Associative Ionization in Uranium–Oxygen Collisions.	W. Fite P. Irving Extranuclear Laboratories
1530–1545	Experimental Rate Measurements in the Uranium–Oxygen System.	J. McKinley NBS
1545–1600	Metal Ion and Atom Reactions in Oxygen.	J. Friichtenicht J. Sellen TRW
1600–1610	Oxidation of Thorium in a Laser Blowoff Experiment.	P. Zavitsanos GE–RESD

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CHAIRMAN: F. GILMORE, R & D ASSOCIATES

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1630–1645	Metal Oxide Releases in the Upper Atmosphere.	G. Best C. Forsberg D. Golomb N. Rosenberg W. Vickery AFCRL
1645–1655	Metal Vaporization by Shock Heating.	R. Fluegge Calspan Corporation
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– END –

SESSION I

LOW ALTITUDE FIREBALL ENTRAINMENT AND CHEMISTRY

CHAIRMAN: DR. H. C. FITZ, DNA

EFFECTS OF TURBULENT ENTRAINMENT AND NONUNIFORM
MIXING ON FIREBALL CHEMISTRY

S. C. Lin†

Xonics, Inc.

The effects of turbulent entrainment and nonuniform mixing on the chemistry and certain observable properties of nuclear fireballs are examined in the light of some small-scale laboratory experiments performed at the University of California, San Diego.[1] These experiments, carried out at thermal energy deposition of the order of 10^3 joule in air at sea-level pressure, indicate that the thermal interface remains very sharp and that large amplitude temperature fluctuations persist at all depths even after the fireball becomes fully turbulent. It is quite clear that mass entrainment of the ambient air into the interior of the fireball is a continuing macroscopic convective mixing process very similar to that occurring in natural atmospheric thermals. In view of the very nonuniform nature of the convective mixing process, one must be very careful in any theoretical treatment of the fireball chemistry problem for the following reasons:

1. For very rapid chemical reactions which tend toward local equilibrium following each change of state resulting from the convective mixing and turbulent cascade process, the local concentrations of dissociation and ionization products (e.g., atoms, free electrons, etc.) are generally very sensitive to the local temperature due to the largeness of D/kT appearing in the Boltzmann factor at late times (where D denotes either the dissociation or ionization energy). Thus. calculation of "averaged concentrations" from statistical mechanics using simple

† Unclassified address: Professor of Engineering Physics and Associate Director, Department of Applied Mechanics and Engineering Sciences and Institute for Pure and Applied Physical Sciences. University of California. San Diego, P.O. Box 109, La Jolla, California 92037.

1   Lin, S. C. , Tsang, L. and Wang, C. P. "Temperature Field Structure in Strongly Heated Buoyant Thermals." Scheduled for publication in The Physics of Fluids, November 1972.

mass-averaged or volume-averaged temperature within the fireball can lead to very large errors.

2. For nonequilibrium endothermic reactions or exothermic reactions with significant activation energies, E^*, calculation of the "averaged rates of formation" of the reaction products from chemical kinetics using "averaged temperature" and "averaged concentrations of reactants" can also lead to serious errors. This is not only due to the largeness of E^*/kT appearing in the temperature-dependent rate constants, but also due to a possible lack of spatial correlation of the reactant concentrations within individual fluid elements.

3. Even for exothermic reactions with negligible activation energies (as in the case of most attachment and recombination reactions in the atmosphere), one still must keep track of the spatial correlation problem among the participating species in order to avoid serious errors in the calculation of averaged reaction rates.

In addition to volume-averaged properties, the spatial distributions and concentration fluctuation spectra of many chemical species relevant to certain gradient-sensitive observables (such as radar scattering, scintillation, etc.) are also of considerable interest in the overall chemistry problem. It is important to note that such fluctuating properties of the fireball generally cannot be obtained by any perturbation method (or as an afterthought), starting from a prematurely smoothed out hydrodynamic calculation. Instead, the macroscopic convective mixing and three-dimensional turbulent cascade nature of the entrainment process must be faced at the outset in any realistic treatment of the fireball chemistry problem.

In the latter part of this paper, the implications of the above-cited effects on the general problem of numerical computation of fireball chemistry and observables will be evaluated. The minimum grid size that would be required in direct numerical computations will be estimated from existing laboratory experiments.[1] The problems of scaling, and possible use of relative small-scale laboratory experiments for statistical modelling of fireball chemistry will be discussed.

ENTRAINMENT BY INTERMEDIATE ALTITUDE FIREBALLS

Girard A. Simons

AVCO-Everett Research Laboratory

A mathematical model is developed to describe the entrainment of ambient air by a rising fireball. It is postulated that entrainment, prior to torus formation, occurs as a result of turbulent mixing at the fireball-atmosphere interface. The interface is Kelvin-Helmholtz unstable over time scales which are several orders of magnitude smaller than the fireball revolution time. The model is valid for the first few revolutions, after which the interface diffuses throughout the fireball.

The inviscid fireball is modeled by Hill's Spherical Vortex. The mixing region separating the fireball from the atmosphere is assumed thin compared to the fireball radius, and the turbulent mixing layer equations are derived. Mathematical closure is achieved by utilizing an eddy viscosity model. A self-similar solution is obtained which describes the density, velocity, and species concentrations on the mixing layer streamlines. The net entrainment of ambient air into the fireball is calculated in terms of the mixing length, and the mixing lengths are inferred from photographs. Hence, the entrainment rates are predicted in a semiempirical method. The model is presently being extended to predict the temperature and density on the fireball streamlines.

PARAMETRIC STUDY OF FIREBALL RISE WITH ENTRAINMENT
AND NONEQUILIBRIUM CHEMISTRY

Robert N. Wilson

Mission Research Corporation

A numerical study is made of a model of nuclear fireball rise in the ambient atmosphere. It is assumed that during the rise and cold air entrainment phase of fireball development, the fireball is in pressure equilibrium with the surrounding ambient atmosphere. The model includes the effects of (1) nonequilibrium chemical composition of the fireball, (2) cold air entrainment by the fireball, and (3) coupling of the equation of motion of the fireball rise to the chemistry and entrainment. The model predicts, as functions of time, the chemical composition, velocity, altitude, volume, pressure, temperature and mass of the fireball.

The equations of hydrodynamics of the fireball are reduced to a one-cell description of the fireball rise under the influence of the buoyant force, aerodynamic drag force, and the force arising from cold air entrainment. This simple characterization results in a rather fast running time for the computer code compared to the more detailed computer codes which make use of the differential equations of hydrodynamics with a difference scheme involving many cells in three-dimensional space. On the other hand, the nonequilibrium chemistry scheme employed in our model includes 37 chemical species and about 300 chemical reactions in the form of a set of coupled rate equations. We have included several species which, although small in number density, are important in certain systems applications.

The model used for the cold air entrainment by the fireball assumes that the mass of cold air entrained per unit time is proportional to the mass of ambient atmosphere swept out by the fireball per unit time; the proportionality factor, α, is called the "mass entrainment" parameter. This model is essentially that introduced by G. I. Taylor* to describe entrainment

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* Taylor, G. I. "Turbulent Gravitational Convection from Maintained and Instantaneous Sources." Proc. Roy. Soc., Series A, 234, p. 1 (1956).

of ambient air by rising buoyant thermals. The cold air entrained is assumed to be instantaneously mixed into the fireball in the sense that the fireball temperature T is assumed to be uniform. We assume that the translational and internal degrees of freedom of the different chemical species are in equilibrium at temperature T, but the concentrations of the different chemical species are not, in general, assumed to have the values which they would have in an equilibrium air mixture at temperature T.

The differential equations governing the thermodynamic behavior of the fireball including nonequilibrium chemical composition effects, are determined by considering an infinitesimal process in which the fireball entrains ambient air and undergoes a change in pressure. It is assumed that Dalton's law of partial pressures is valid for both the fireball gas and the ambient atmosphere. Thus:

$$p_i = n_i kT \tag{1}$$

$$p = \sum_i n_i kT = \sum_k n_k kT_a \tag{2}$$

where p_i is the partial pressure of species i, n_i the number density (concentration) of species i, T the temperature of the fireball and T_a the temperature of the ambient atmosphere. The sum i is over the many species of the fireball while the sum k is over the few species of the ambient atmosphere. The internal energy, ξ, per unit volume is given by:

$$\xi_f = \sum_i n_i \left[f_i(T) + C_i \right] \ , \ \xi_a = \sum_k n_k \left[f_k\left(T_a\right) + C_k \right] \tag{3}$$

for the fireball and ambient atmosphere, respectively. C_i denotes the heat of formation of the species i and $f_i(T)$ is a polynomial fit of the temperature dependence of the internal energy (translational, vibrational, rotational, electronic) of the ith species. The change in the number density n_i, of any given specie in the fireball involves a change due to (1) the addition of ambient air, (2) expansion of the fireball as it rises, and (3) change in the chemical composition.

The model assumes that there is an initial time interval of rise $0 < t < t_t$, during which the fireball has the shape of a sphere and entrains no ambient air. At the time t_t we change the shape of the fireball to that of a torus and "turn on" the entrainment. There is some ambiguity regarding the choice of the time t_t. We have therefore studied numerically the effect of varying t_t.

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The two main parameters whose values are varied in order to fit data are the entrainment parameter, α, and a coefficient, C_D, occurring in the aerodynamic drag, called the "drag" coefficient. We have tried to bracket the data on the BLUE GILL and TIGHTROPE Events by varying the values of α and C_D. Although this parameter study is not completed, the results which we have obtained are in reasonable agreement with the data of the two events mentioned above. We have applied the model to the ORANGE Event using the sets of values of α and C_D which bracket the BLUE GILL and TIGHTROPE data.

SESSION II

NUCLEAR BURST EFFECTS FROM THE TROPOSPHERE

TO THE D-REGION

CHAIRMAN: DR. M. BORTNER, GE

PHOTODETACHMENT BY FIREBALL THERMAL RADIATION

Dale S. Sappenfield

Mission Research Corporation

One of the contributions of the MRC to the analysis of terminal defense antiballistic missile (ABM) systems is the calculation of electron densities produced by high-yield weapons employed as precursors. These calculations were performed by W. A. Schlueter and D. S. Sappenfield.

The effect of fireball thermal radiation on photodetachment rates relative to electron density results will be considered for early times. However, a need exists for certain other atmospheric parametric information in order to improve our current predictive capabilities. These factors will be discussed in detail, and an evaluation of present constraints involved in such calculations will be indicated.

THE ROLE OF NEGATIVE IONS IN LOW ALTITUDE
NUCLEAR BURST PHENOMENOLOGY

Frank P. Hudson

Sandia Laboratories, Albuquerque

The very rapid three-body attachment of free electrons to oxygen molecules at altitudes below 20 kilometers initiates the complex interlinked set of negative ion reactions which compete with the neutralization processes that remove the electrons permanently. The electrons attached to molecules and radicals are potentially readily available as free electrons through low-energy detachment processes. It is through study of the energy, time, altitude, and species dependence of negative ion processes that electron density recovery can be understood.

Calculational models of the chemical kinetics of the recovery from burst induced charge-perturbation of the lower atmosphere have been used to study the above processes as a function of altitude, temperature, energy input, level of detachment, and time. The models include one of 40 species and 200 reactions; an equivalent one using 5 species and 9 reactions; and one incorporating radiation transport and deposition. Results of the calculations will be shown graphically.

NUMBER DENSITIES AND REACTIONS DURING ATMOSPHERIC DEIONIZATION AS PREDICTED BY WEPH D AND AIRCHEM CODES AT 30 KM AND BELOW

B. W. Carney, E. L. Lortie, M. D. Kregel, and F. E. Niles
Ballistic Research Laboratories

The multiple species codes AIRCHEM I and AIRCHEM II were used to solve the rate equations for 59 species involving 523 reactions for a grid of points below and south of a 5-MT nuclear burst at an altitude of 30 km. The values for the rate of ionization at a particular point were obtained from the WEPH D code. The electron density, total positive ion density, and attenuation in db for UHF and S-band radiation were also calculated with WEPH D. The electron density as a function of time predicted by the AIRCHEM codes is less than that predicted by the WEPH D code. Conversely, the total positive ion density as a function of time predicted by the AIRCHEM codes is greater than that predicted by the WEPH D code. There are several reasons for this. First, the numerical solution given by WEPH D is inaccurate. Second, the electron attachment coefficient employed by WEPH D is too small. Third, the dissociative recombination coefficient employed by WEPH D is too small. The AIRCHEM codes reveal that hydrated protons and other cluster ions are the principal positive ions and these have dissociative recombination coefficients greater than 10^{-6} cm^3/sec, whereas WEPH D employs a value of 2.272×10^{-7} cm^3/sec at 20 km. Fourth, WEPH D considers that three-body ion-ion recombination is the major ion-ion recombination process and uses a value of 5.118×10^{-7} cm^3/sec, whereas the AIRCHEM codes did not include three-body ion-ion recombination for cluster ions, and, hence the effective ion-ion recombination coefficient was about 10^{-8} cm^3/sec. Every ion-ion recombination rate coefficient which is important to these calculations has been estimated. Photodetachment and photodissociation were not included in the codes.

REVIEW OF THE CHEMISTRY OF ATMOSPHERIC DEIONIZATION FOR THE D AND SUB-D REGIONS CURRENT STATUS OF KNOWLEDGE AND PROBLEMS REMAINING

F. E. Niles

Ballistic Research Laboratories

Thanks in great measure to the DNA Reaction Rate Program, our knowledge of the rate coefficients for ionospheric and atmospheric reactions has advanced greatly during the past decade. The chemistry of atmospheric deionization for the D and sub-D regions differs from that for the undisturbed regions primarily in that reactions between neutral species are less important. The reaction sequence for positive ions in the undisturbed D region will be given. The species observed with mass spectrometers will be shown for comparison. The complex ions mentioned such as $NO^+\left(H_2O\right)$ and $H^+\left(H_2O\right)$ and $NO^+\left(H_2O\right)_2$ and $H^+\left(H_2O\right)_2$, are indicative of the need in the undisturbed D region of a rapid means of getting from the NO^+ ions to the hydrated protons. Niles and Heimerl (1972) have suggested that reactions of $NO^+\left(H_2O\right)$ or $NO^+\left(H_2O\right)_2$ with either HO_2 or OH may satisfy the need. In the undisturbed D region, an NO^+ sequence (or some as yet undetermined sequence starting with NO^+ and possibly involving water conglomerates) will be found to be more important than the O_2^+ sequence. In the disturbed D region, both sequences are important, but the O_2^+ sequence is the more important. In addition to the reactions, reactions involving N^+ and O^+ are important in the disturbed D region.

Three types of reactions will be indicated; viz, positive ion-neutral association, switching reactions, and positive ion-neutral rearrangement. Laboratory measurements of rate coefficients for positive ion-neutral association for cluster ion breakup, as well as laboratory measurements of rate coefficients for positive ion switching reactions will be enumerated. In addition, laboratory measurements of rate coefficients for positive ion-neutral rearrangement reactions will also be presented.

For the first several hundred seconds the deionization of the atmosphere occurs primarily by dissociative recombination of positive ions and electrons. In the disturbed D region, the recombination occurs initially with N_2^+, next with O_2^+, and then with either NO^+ or one or more of the cluster ions. The

number densities of the positive ions as a function of time in the beta patch at altitudes of 55, 60, 65, and 70 km, respectively, will be presented. The sudden upturn in several of the number densities for an altitude of 70 km around 500 sec is interpreted to reflect a precipitous drop in the number density for atomic nitrogen.

The chemistry for the negative ions is much more uncertain than that for the positive ions. Number densities of the negative ions and the electron as a function of time in the beta patch at altitudes of 55, 60, 65, and 70 km, respectively, will also be presented. In these calculations $NO_2^-(H_2O)$ was the terminal negative ion and as such is a collective representation of all hydrated negative ions except $O_2^-(H_2O)$. A great deal of research remains to be done before we can adequately model the chemistry of the negative charged, cluster ions.

The chemistry of the sub-D region is very similar to that of the D region except that the time constants for many of the reactions are much shorter. Consequently, both positively charged and negatively charged cluster ions become important sooner.

Some of the problems remaining are these:

1. Rate coefficients for the formation and breakup of cluster ions are needed. Those for positive ions need to be measured at the temperatures of the D region. Those for negative ions are needed at room temperature as well as at the temperatures of the D region. Breakup of the ions by photodissociation, associative detachment of the neutral molecule from the central ionic core, and unreacting collisions need to be studied.

2. Switching and ion-neutral rearrangement rate coefficients are needed for the reactions involving cluster ions.

3. Measurement of the photodetachment cross section as a function of wavelength for the negatively charged cluster ions and for NO_3^-, CO_3^-, and CO_4^- is needed.

4. Rate coefficients for both two-body and three-body ion-ion recombination are needed for cluster ions. These reactions control the late-time deionization.

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D-REGION ANALYTICAL CHEMISTRY FOR EARLY TIMES FOLLOWING X-RAY ENERGY DEPOSITION

B. F. Myers

Science Applications, Inc.

At early times following energy deposition by X-rays at altitudes below 100 km, the initial high level of ionization resulting from the deposition rapidly decays; accurate numerical computation of the time profiles of species involved in this decay could require more computer time than one would normally allot per unit problem-time interval. In anticipation of this possibility with the HAIR code, a full code developed at SAI, an early-time analytical chemistry scheme was devised. Subsequent experience with the analytical scheme demonstrated that the computer time required could be a factor of five hundred smaller when calculations with the analytical scheme were made compared to calculations with the full code. Furthermore, the agreement between the codes was very good in calculating the major species densities.

The mechanism on which the analytical scheme was based consisted of the following nine reactions involving 13 species:

$$e + N_2^+ \left(X^1\Sigma_g^+\right) \rightarrow \alpha N \left(^4S^o\right) + \beta N \left(^2D^o\right)$$

$$e + O_2^+ \left(X^2\Pi_g\right) \rightarrow \gamma O \left(^3P\right) + \delta O \left(^1D\right)$$

$$N_2^+ \left(X^1\Sigma_g^+\right) + O_2 \left(X^3\Sigma_g^-\right) \rightarrow N_2 \left(X^1\Sigma_g^+\right) + O_2^+ \left(X^2\Pi_g\right)$$

$$N \left(^2D^o\right) + O_2 \left(X^3\Sigma_g^-\right) \rightarrow NO \left(X^2\Pi_r\right) + O \left(^3P\right)$$

$$N_2 \left(A^3\Sigma_u^+\right) + O_2 \left(X^3\Sigma_g^-\right) \rightarrow N_2 \left(X^1\Sigma_g^+\right) + 2O \left(^3P\right)$$

$$O \left(^1D\right) + N_2 \left(X^1\Sigma_g^+\right) \rightarrow O \left(^3P\right) + N_2 \left(X^1\Sigma_g^+\right)$$

$$O\left(^{1}D\right) + O_{2}\left(X^{3}\Sigma_{g}^{-}\right) \rightarrow O\left(^{3}P\right) + O_{2}\left(b^{1}\Sigma_{g}^{+}\right)$$

$$O_{2}\left(a^{1}\Delta_{g}\right) + O_{2}\left(X^{3}\Sigma_{g}^{-}\right) \rightarrow 2O_{2}\left(X^{3}\Sigma_{g}^{-}\right)$$

$$O_{2}\left(a^{1}\Delta_{g}\right) \rightarrow O_{2}\left(X^{3}\Sigma_{g}^{-}\right) + h\nu$$
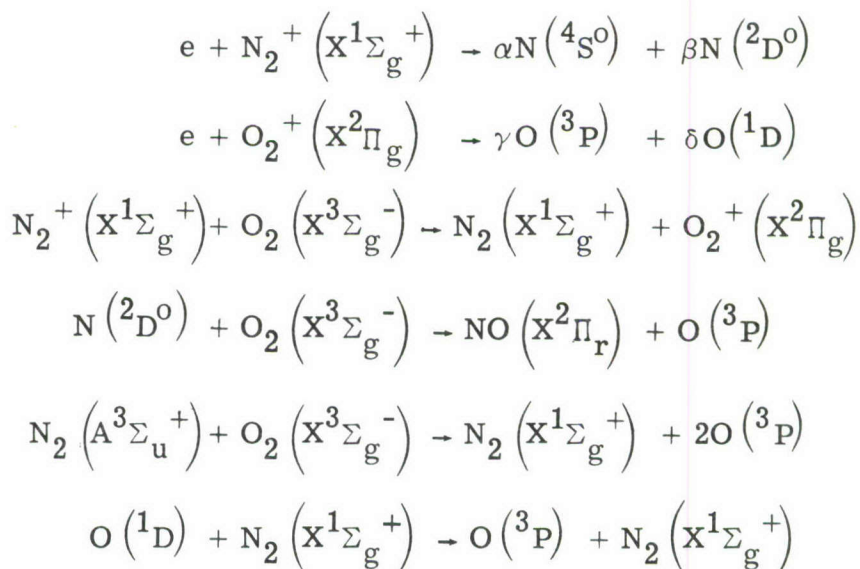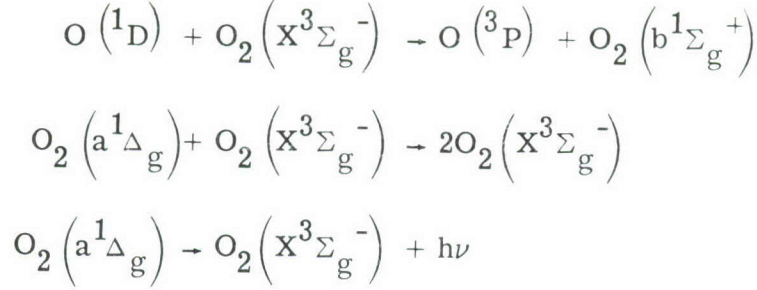
The quantities of α, β, γ, and δ are parameters to be specified. This scheme appears to valid for $t \leq 1$ sec and for initial levels of ionization corresponding to ion-pair densities less than 10^{12} cm^{-3}. The justification for omitting negative ions, atomic ions, and certain reactions can be established for the altitude range from 60 to 100 km. An exact mathematical solution of the rate equations governing this approximate mechanism has been obtained.

The analytical scheme (DACET) and the HAIR code have been compared for an X-ray energy deposition involving an initial density of 10^{9} ion-pairs cm^{-3} with the following results at 0.1 sec. Differences are due to the fact that HAIR contains many additional reactions of lesser importance in this time period.

	Number, Density, cm^{-3}			
	Alt. = 60.92 km		Alt. = 90.7 km	
Species	HAIR	DACET	HAIR	DACET
$O\left(^{3}P\right)$	2.92(9)	2.99(9)	1.46(11)	1.46(11)
$O\left(^{1}D\right)$	8.70(2)	8.04(2)	1.27(5)	7.93(4)
$O_{2}\left(X^{3}\Sigma_{g}^{-}\right)$	1.23(15)	1.23(15)	1.17(13)	1.17(13)
$O_{2}\left(a^{1}\Delta_{g}\right)$	1.67(9)	1.67(9)	6.12(9)	6.13(9)
$O_{2}\left(b^{1}\Sigma_{g}^{+}\right)$	1.26(8)	1.32(8)	3.35(8)	3.10(8)
$O_{2}\left(X^{2}\Pi_{g}\right)$	4.32(7)	4.11(7)	4.80(7)	3.69(7)

| | Number, Density, cm^{-3} (Continued) | | | |
| | Alt. = 60.92 km | | Alt. = 90.7 km | |
Species	HAIR	DACET	HAIR	DACET
$N\left(^4S^0\right)$	1.84(8)	1.83(8)	1.97(9)	1.69(9)
$N\left(^2D^0\right)$	1.17(3)	---	8.43(6)	7.40(6)
$N_2\left(X^1\Sigma_g^+\right)$	4.57(15)	4.57(15)	4.34(13)	4.34(13)
$N_2\left(A^3\Sigma_u^+\right)$	---	---	5.79(6)	1.54(7)
$NO\left(X^2\Pi_r\right)$	2.61(8)	2.58(8)	2.41(9)	2.46(9)
$N_2^+\left(X^3\Sigma_g^+\right)$	---	---	5.34(-1)	6.5(-7)
e	4.44(7)	4.11(7)	5.23(7)	3.69(7)

AN ANALYTIC MODEL FOR NUCLEAR-INDUCED
D-REGION CHEMISTRY

Murray Scheibe

Mission Research Corporation

During the last few years it has become apparent that the processes governing the chemistry in the D-region are extremely complicated. Up to 60 different chemical species have been identified as being involved.

The numerical integration of all the differential equations which are needed, many of which become stiff, has thus become impractical for fast or even comparatively slow systems codes in which one wishes to include the effects of nuclear weapons. A simplified model of D-region chemistry is needed and if the systems code is not forward running, an analytic model is preferable.

We have divided the chemical and ionization phenomena following a nuclear burst into four phases. The first phase involves the initial ionization, dissociation and excitation of air by the X-ray pulse. The second phase involves the subsequent charge transfer, recombination, and other neutral and ion reactions leading to the production of the species N, O, and NO. After this phase, the neutral chemistry uncouples from the charged particle chemistry, and the third phase deals with the decay of the N, O, NO, and $O_2\left(^1\Delta\right)$ formed in the first two phases. The fourth phase, concurrent in time with and dependent on the results of the third phase, involves the late-time deionization.

We have given the second and third phases the greatest emphasis because neutrals such as NO, O_3, and NO_2 are strong infrared emitters, and the neutral chemistry is therefore important for optical systems as well as for radar systems. In addition, lumped-parameter models which attempt to solve essentially the fourth part of the problem need solutions for the neutral species production and decay as inputs.

The initial distribution of species formed by the X-ray pulse was taken from the work of Ory and Gilmore[1]. The second phase was treated by solving for the branching ratios of charge transfer (with or without rearrangement) to

1. Ory, H. A. and Gilmore, F. R. "The Chemistry of Nitrogen Oxides and Ozone in the Disturbed D-Region" DNA 2835T, September 1971.

electron recombination for the initial ions present. The third phase behavior was obtained, to a large extent, by solving individually for the $O - O_3$, the early-time $N - NO$, and the late-time $NO - NO_2$ systems and accounting for the interaction between the systems as small correction factors. The final phase, the deionization process was obtained by assuming the charged-particle densities are in a steady state. At early times, when the steady-state assumption does not apply, a simple transient solution was used for the electron density and several of the positive ion species.

The analytic solutions obtained by the methods described were applied to a number of cases at 40 to 80 km altitudes and the results compared with those obtained using a coupled reaction rate code which numerically integrates the nonlinear differential equations. The general agreement was fairly good. The largest disagreements occurred when the initial ionization levels were low and also at the 40-km-altitude cases. The main reason for this was that the assumed small correction terms used to account for the interaction between chemically reacting systems became the dominant terms. In addition, at 40 km, ion clustering was dominant during the charged-particle transient period, and this was not included in the transient solution. The ion clusters were included only in the steady-state solution.

Future work will include extending the model to low altitudes and ionization levels and to daytime effects. This is not expected to be too difficult. The extension of the model to multiburst effects is also contemplated, and this may entail some loss in accuracy.

ERRORS ASSOCIATED WITH RANC AND WEPH CODE LUMPED-PARAMETER CHEMISTRY MODELS

W. S. Knapp

General Electric—TEMPO

Delayed radiation is a major source of atmospheric free electrons following a nuclear burst. Comparisons are presented of the electron density due to delayed radiation calculated with a multispecies chemistry model and with the lumped-parameter chemistry model used in the RANC and WEPH codes. The multispecies model includes effects of prompt radiation on the minor neutral species concentrations and effects of cluster ions. Results are presented as a function of altitude and delayed-radiation source strength for parametric values of initial ionization. Current modifications of the lumped-parameter model to reduce errors are described.

CALCULATIONS OF ATMOSPHERIC IONIZATION
PRODUCED BY SPRINT BURSTS AT VARIOUS ALTITUDES

William B. Maier II

Los Alamos Scientific Laboratory, University of California

A high-speed digital computer has been used to calculate the time dependence and spatial extent of ionization produced by Sprint bursts at 3, 10, 20, and 26 km. Contours of electron concentration and absorption of 3 GHz radar signal are given. At 20 and 26 km, the electron densities and radar absorption contours are asymmetric about the burst point. For 3 and 10 km bursts, radar absorption and electron densities are only slightly asymmetrically distributed around the burst point. Up to 1 sec after a burst, CO_4^- constitutes a significant fraction of the negative ions, but after 1 sec, CO_3^-, NO_2^-, and NO_3^- are the only abundant negative ions. Ionized regions are larger at the higher altitudes than at the lower altitudes.

SESSION III

NUCLEAR BURST EFFECTS IN THE D- AND E-REGIONS

CHAIRMAN: DR. F. E. NILES, BRL

WORRY INFRARED CHEMISTRY AND
LOW ALTITUDE PROBLEMS

W. A. Whitaker
Air Force Weapons Laboratory, AFSC

WORRY is an infrared and optical systems code corresponding to RANC IV. The chemistry pertinent for optical emissions is much more complex than that assumed for the normal procedures on electron densities. WORRY therefore demands much more detailed physical input and must solve much more elaborate chemistry equations.

This paper will discuss the WORRY chemistry, its solution in direct integration and analytic fits which are used for swift systems runs. The analytic chemistry modeling is fairly general, and a procedure has been adapted which allows rapid addition of large classes of additional reaction rates and species. The procedure may therefore have more general application.

Checks are given against full numerical integration on the chemistry and against hydrocode calculations on the phenomenological model. Suggestions will be made on the basis of systems runs, what physical parameters seem to be the most significant, and those that seem to be the least well known at this time.

PREDICTION OF THE NO CHEMILUMINESCENCE
IN THE STARFISH EVENT

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Science Applications, Inc.

We have applied our recently developed IR models and codes to predicting the NO chemiluminescence from the STARFISH Event. This application was made because (1) it affords an opportunity to compare predictions with experimental data and with other code predictions, and (2) we have improved the description of the phenomenology by explicitly computing both the source function and deposition of the charge-exchange (CHEX) particles emitted from the debris-air piston.

The deposited X-ray energy was computed by standard techniques. The resulting initial species were those recommended by Ory and Gilmore modified above 100 km to account for a changing composition and excited states. The angle-dependent CHEX-particle energy spectra were obtained from our debris-air coupling (DAC) code. The CHEX particles were slowed according to a velocity-dependent stopping power. The deposited CHEX energy was divided into elastic and inelastic portions; the latter is associated with ionization which was partitioned among various species, with account of dissociation. Partitioning of the elastic portion, in the absence of relevant information, was done with a simple model developed to obtain a distribution of species, including dissociated and excited states for molecular targets. By combining the species and energies from the X-ray and CHEX-particle energy depositions, we obtained inputs to our chemistry codes, DACET and HAIR.

Comparison of the results of the calculation with the field data for the spectral interval 4.8 to 5.5 μm shows good agreement. On the basis of the volume emission rates, as a function of altitude and time, one can show the relative importance of the energies deposited by X-rays and by CHEX particles. By combining these results with an inspection of the rates of reactions that lead to NO formation, we find that (1) for t > 2 sec, 78 percent of the signal results from the reaction $N\left(^4S\right) + O_2 \xrightarrow{k_1} NO + O$, while (2) for t < 2 sec, 72 percent of the signal results from the reaction $N\left(^2D\right) + O_2 \xrightarrow{k_2} NO + O$.

In view of the importance of reaction (1), we have examined the effect of the initial NO vibrational distribution on the results. Three distributions have been used. Distributions A and C have been derived by analyzing experimental data and differ only in the (experimentally-undetermined) initial fractional populations assigned to levels $v = 0$ and 1. Distribution B represents the equal population assumption and gives a greater signal, being larger by a factor of 3.5 at 70 sec than the signal represented by Distribution C.

The present calculations differ from recent calculations in important respects; however, we consider the conclusions to be tentative until further calculations have been made which include the effects of atmospheric heave and to explore the assumptions involved in the CHEX-particle energy deposition.

(*) THE ROLE OF ELECTRIC FIELDS IN HIGH ALTITUDE
REACTION RATE MODELS (*)

C. M. Crain

The Rand Corporation

The degree to which electric fields can affect reaction rates in the lower D-region appears poorly resolved. This matter and its practical implications are discussed.

SESSION IV

NUCLEAR BURST EFFECTS IN THE E- AND F-REGIONS

CHAIRMAN: Lt Col W. WHITAKER, USAF

SHOCK ENHANCED LWIR AT 15μ FROM THE CO_2-N_2 SYSTEM

T. I. McLaren

Mount Auburn Research Associates, Inc.

The problem considered is the enhancement of the 15μ radiation band from the ν_2 (bending) mode of CO_2 due to the passage of a strong shock wave through the atmosphere at 100 km. Such shock waves are characteristic of a ballistic detonation.

The model used considers the CO_2-N_2 system and includes energy exchange processes to account for T-V and V-V excitation and deexcitation, absorption, and induced and spontaneous emission. Estimates of shock wave parameters were based on the COWL calculation for the TEAK Event.

A number of cases have been run, including:

1. Ambient conditions at 100 km (no shock).
2. Postshock conditions where the nitrogen vibrational temperature was much less than the kinetic temperature for times of interest (Mach 6 shock).
3. Postshock conditions where nitrogen vibrational and kinetic temperatures were equilibrated (Mach 8 shock).
4. Conditions corresponding to the late-time adiabatic relaxation of the shock-treated atmosphere.

Results of these calculations showed that, for the cases treated, the radiance level is insensitive to the value of nitrogen vibrational temperature, the main effect being due to the enhanced T-V reaction rates behind the front. In cases (2) and (3) above, the 15μ-radiance levels were increased 2-3 orders of magnitude above the corresponding ambient levels.

CHECKMATE OPTICAL OUTPUT CALCULATIONS

Paul C. Kepple and A. W. Ali
Naval Research Laboratory

The visible $\left(3800 \text{ to } 7600\overset{\circ}{A}\right)$ radiation from the early expansion phase $\left(3.02 \times 10^{-3} \leq \text{to} \leq 3.52 \times 10^{-1} \text{ sec}\right)$ of the CHECKMATE Event is computed.

The temperatures and densities were taken from the tapes of CHECKMATE runs of the TIGHT code which include N, O, and Al. The total energy radiated in the visible is only 4 percent of that in the ultraviolet (UV), thus justifying the uncoupling of the visible radiation calculations from those of the dynamics of UV.

Comparison with existing data shows fair agreement in certain aspects of the total power radiation.

ATMOSPHERIC ELECTRON DENSITIES AND TEMPERATURES FROM A HIGH ALTITUDE SPARTAN DEVICE

Carl A. Rouse, John P. Wondra, W. B. Lindley, and W. G. Vullier
Intelcom Rad Tech

We report preliminary calculations that approximate the heating of ambient air at high altitudes by a Spartan device. The objective is to roughly anticipate the two-dimensional energy deposition that will be predicted later using the asymmetric radiant flux from current Intelcom Rad Tech late-time, two-dimensional calculations of a Spartan device. We are interested in the asymmetric radiant energy deposition in air and the resulting electron and ion densities and temperature under conditions of local thermal equilibrium (LTE) and non-LTE due to the asymmetric properties of the ambient atmosphere. We consider the previous one-dimensional calculations that simulate the deposition of a Spartan device in regard to the low frequency spectrum. We also use a Spartan spectrum previously reported. The absorption coefficients for nitrogen were obtained from other literature sources. Using the Intelcom Rad Tech FHUFF code, we perform various one-dimensional, time-independent, radiative-transfer calculations assuming constant densities at altitudes of 200 km and 400 km. The results are applied to radiative transfer in the horizontal, upward, and downward directions using the appropriate optical depths. The atmospheric heating will be discussed, and estimates of the electron and ion densities and temperature as functions of space will be given.

EFFECTS OF CHEMISTRY ON ELECTRON DENSITIES
IN THE REFRACTIVE REGION

J. I. Valerio

Science Applications, Inc.

After a nuclear burst of intermediate yield at 150 km altitude, the electron density just outside the fireball is found to decay more rapidly than ionization at larger radial distances. Within 15 seconds, a spatial structure is introduced in the 10^6 and 10^7 cm^{-3} electron density contours of possible importance to the refraction analysis of radar signals. Electron density contours illustrating the structure are shown in the below figure for 60 seconds after the burst.
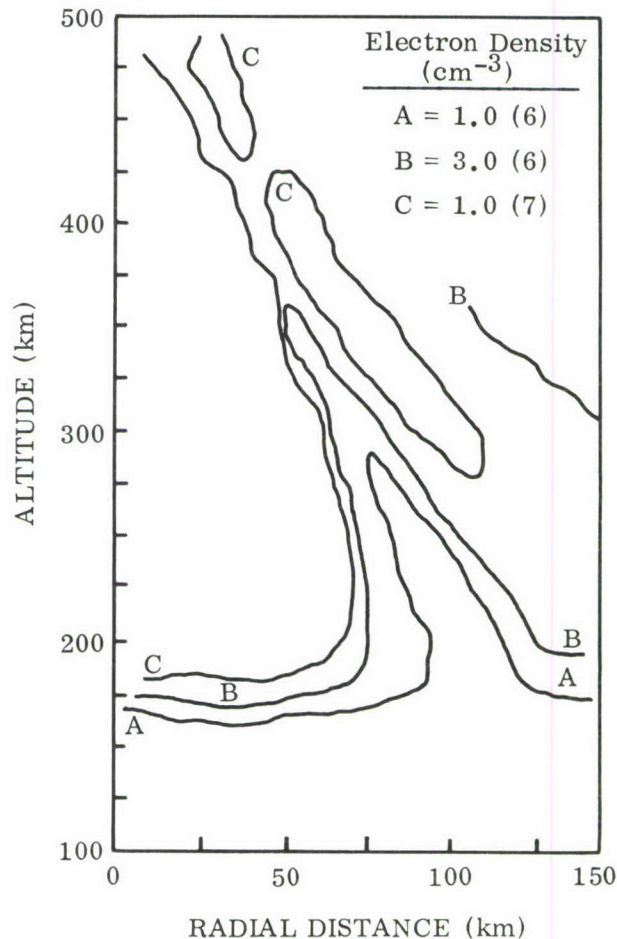
Deionization of the disturbed atmosphere was computed by the CHIEF chemistry code both with and without the burst induced shock wave at a number of locations. Density variations produced by the passage of the shock wave were found to increase the chemical rates by only a small amount and thereby showing the radial dip in electron density to be primarily a chemical effect.

Outside of the initial species composition, the major factor governing the deionization rate was found to be the radial gradients in the heavy particle temperature T and N_2-vibrational temperature θ_v. These gradients determine the relative importance of the rate coefficients k_1 and k_2 for the competing reactions:

$$O^+ + N_2 \rightarrow NO^+ + N \qquad k_1 = k_1(T, \theta_v) ; \quad 4^{-13} \lesssim k_1 \lesssim 10^{-10} \qquad (1)$$

$$O^+ + O_2 \rightarrow O_2^+ + O \qquad k_2 = k_2(T) ; \quad 3^{-11} \lesssim k_2 \lesssim 10^{-10} \qquad (2)$$
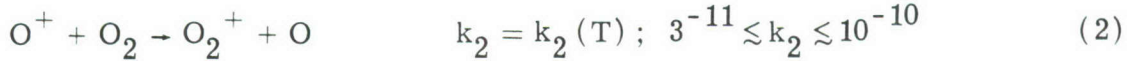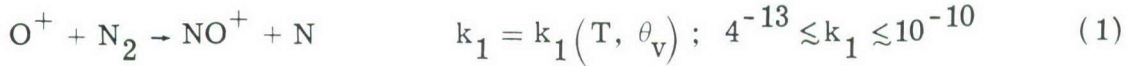
Immediately outside the fireball region of persistent ionization, reaction (1) is by far the more important because of the high N_2-vibrational temperature. Here, the depletion of O^+ proceeds with a relatively short characteristic time. At larger radial distances, θ_v falls to such low values that k_2 exceeds k_1 making reaction (2) the dominant process. Since the characteristic decay time $\left(k_2\left[O_2\right]\right)^{-1}$ for reaction (2) is longer than the decay time just outside the fireball, a dip in the electron density is obtained at intermediate distances.

An approximate analytical solution can be obtained for the electron density outside the fireball that closely agrees with the more complex CHIEF calculation. In addition to reactions (1) and (2), we consider the dissociative recombination reactions:

$$NO^+ + e \rightarrow N + O \qquad (3)$$

$$O_2^+ + e \rightarrow O + O \qquad (4)$$

with a single average rate coefficient k_3 and assume that $\left[N_2\right]$ and $\left[O_2\right]$ remain constant in time. The resulting solution for the electron density is:

$$[e] = \frac{[e]_o \, e^a \, \exp\left(-a \, e^{-\lambda t}\right)}{1 + \dfrac{[e]_o \, k_3}{\lambda} \, e^a \left[E_1\left(a \, e^{-\lambda t}\right) - E_1(a)\right]}$$

where

$$\lambda = k_1 \left[N_2 \right] + k_2 \left[O_2 \right]$$

$$a = k_3 \left[O^+ \right]_o / \lambda$$

$$E_1(x) = \int_x^\infty du \, \frac{e^{-u}}{u}$$

with $[e]_o$ and $\left[O^+ \right]_o$ denoting concentrations at the initial time $t = 0$.

HIGH ALTITUDE FIREBALL IR EMISSION STUDY

Paul G. Fisher

Mission Research Corporation

The uncertainties associated with high altitude fireball infrared (IR) emission chemistry and their relation to the overall phenomenology problem are. as will be discussed, in the light of certain requirements and needs for various types of DOD defensive systems.

(*) OPTICAL AND IR EMISSION FROM DISTURBED E AND F LAYERS (*)

Joan L. Lewis

Science Applications, Inc.

A. W. Ali

Naval Research Laboratory

A review of NRL's effort in the Optical and IR emission calculations is given with emphasis on all possible sources of radiation. Areas of uncertainty and relevant reactions are pointed out for future experimental or theoretical evaluations.

Using NRL's Master Code Optical and IR emission's along a given ray are calculated for a Spartan burst and the results are discussed.

OPTICAL AND IR RADIATION FROM PHENOMENOLOGY
RESULTS OF HIGH ALTITUDE NUCLEAR BURSTS

Ellis Hyman
Science Applications, Inc.

A. W. Ali and T. P. Coffey
Naval Research Laboratory

A computer code is developed to calculate the radiant energy incident on arbitrarily placed cameras or sensors following high altitude nuclear bursts. It utilizes the results of NRL's hydrocodes. Thus the calculated time-dependent irradiances are directly tied to phenomenological outputs. The irradiance contours give both space and time resolution of the high altitude event in specified wavelength bands (3800Å - 50μ). The emission processes included are line, band, free-free, free-bound, bound-bound, chemiluminescence, etc. transitions arising from dominant and minor atmospheric species and their ions.

Using NRL's hydrocode results for CHECKMATE calculations, contour plots are exhibited and some preliminary comparisons to CHECKMATE optical data are made.

UNCERTAINTIES IN THE FORMATION OF METAL OXIDES FROM DEBRIS DEPOSITED IN THE E-REGION BY HIGH ALTITUDE NUCLEAR EXPLOSIONS

A. Kaufman

Mission Research Corporation

The problem of metal oxide formation from debris which escapes the burst region in a Zinn loss cone is considered. In particular, an attempt is made to estimate horizontal column densities of AlO or AlO^+ which may have been formed as a result of the STARFISH explosion.

The major uncertainty centers around the charge state of the aluminum atoms when they come to rest. Neutral aluminum may form the oxide via the reaction:

$$Al + O_2 \rightarrow AlO + O + .1 \text{ eV}$$

Assuming a rate coefficient of 10^{-11} cm^3/sec, the oxide can be formed in about .3 seconds at deposition altitudes between 102 and 110 km.

Formation of an oxide by the singly charged ion proceeds endothermically:

$$Al^+ + O_2 + 3.5 \text{ eV (c.m.)} \rightarrow AlO^+ + O$$

The 3.5 eV in the center of mass system can be supplied by the slowing Al^+ ions with energies above 6.5 eV. Friichtenicht has observed that the cross section for this reaction is about 1 percent of the elastic cross section over a range of energies centered at 30 eV. Using this information we have estimated that about .5 percent of the Al^+ ions can be converted to AlO^+, but, because AlO^+ has a binding energy of only 1.6 eV, it is likely that some collisional dissociation of these molecules may occur before thay are brought to rest.

The ratio $[Al]$ / $\left[Al^+\right]$ in the beam is determined at the point at which the mean free path for charge exchange and ionization of Al^+ and Al, respectively, become larger than the residual particle range. This happens at velocities under 10^7 cm/sec for which there is no data on charge exchange or ionization cross sections.

Critical column densities of the oxide seem to be around 3×10^{10} molecules cm^2. In STARFISH, column densities of deposited aluminum in excess of 10^{13} atoms/cm^2 were calculated between 102 and 107 km. Thus formation of only

small percentages of the oxide can yield critical results. An experiment which measured metal oxide formation by fast metal ions stopped by thick air targets would be helpful in reducing the uncertainties cited above.

CONJUGATE IONIZATION FROM HIGH ALTITUDE X-RAY DEPOSITION

Cullen M. Crain
The Rand Corporation

Warren Knapp
General Electric—TEMPO

A source of significant energy deposition and ionization in the conjugate
region of high altitude nuclear detonations burst above about 100 km is photo-
electrons which are produced by X-ray interactions with the atmosphere in the
burst region and which escape the burst region and travel along the earth's
magnetic field lines to the conjugate region. This phenomena is not, at present,
included in our weapons effects codes. The magnitude and spatial extent of the
energy deposited in the conjugate region--as indicated by the calculations which
have been made and which are presented in the paper--are significant to both
the radio and optical effects areas. Full understanding of observations in the
conjugate region at various altitudes and distances from the conjugate ground
zero require knowledge of all the energy sources which may contribute. Con-
jugate energy sources previously identified and analyzed include fission-debris
betas, fission debris, Compton-betas from prompt and delayed gammas, and
neutron-decay betas and protons. It turns out that for altitudes in the conjugate
region from about 100 and 250 km and at distances equal to the burst horizon at
about a 100 km altitude, the energy deposited in the conjugate region due to
X-ray photoelectrons can be sizably greater than that from any of the other
identified sources. Many examples of the magnitude and extent of the energy
deposition are presented for various burst altitudes, yield and bomb radiating
temperature. In a report to be published soon, the details of the calculation
procedures are given including X-ray deposition parameters, the energy dissi-
pation of the escaping fast electrons, and the time and altitude characteristics
of the energy deposition in the conjugate region. Also, comparative values of
energy deposition from other conjugate sources are presented.

As an example of the results presented, the electron density 600 km from the
conjugate ground zero of a large nuclear burst detonated at 150 km altitude has
a peak value of 10^6 electrons per cm at an altitude of 120 km. This value greatly
exceeds the ambient day or night electron density in this altitude region and will

affect radio transmission at frequencies into the VHF band. The energy deposition at 600 km range is approximately that of an intense aurora for about 200 seconds; hence, the optical aspects are expected to be quite significant but have not been adequately examined in the work to date.

(*) CHARGE EXCHANGE COUPLING BETWEEN ION
AND NEUTRAL FLUIDS (*)

R. W. Kilb

Mission Research Corporation

In striation analysis or in two fluid MHD simulations of nuclear bursts, the plasma is represented by a neutral fluid and an ion-electron fluid:

$$\rho_0 \frac{d\vec{V}_0}{dt} = -\nabla P_0 + \rho_0 \vec{g} - A\left(\vec{V}_0 - \vec{V}_1\right) \tag{1}$$

$$\rho_1 \frac{d\vec{V}_1}{dt} = -\nabla P_1 + \vec{J} \times \vec{B} + \rho_1 \vec{g} + A\left(\vec{V}_0 - \vec{V}_1\right) \tag{2}$$

where $A\left(\vec{V}_0 - \vec{V}_1\right)$ represents the momentum coupling. For example, if oxygen atoms constitute the neutral fluid and O^+ ions compose the ion fluid, then:

$$A = s\rho \ (O) \ \rho\left(O^+\right) \tag{3}$$

where s is the coupling coefficient between O atoms and O^+ ions, and $\rho(O)$ and $\rho\left(O^+\right)$ are, respectively, the mass densities of oxygen atoms and ions. If additional species are present in the neutral or ion fluid, then additional similar terms with appropriate s coefficients must be added to Equation 3.

The coupling coefficient s arises from elastic collisions and from charge exchange. At temperatures below 1 eV, the elastic collisions are mainly due to polarization forces with an interaction potential $V(r) = e^2 \alpha_\rho / 2r^4$. Langevin (Reference 1) has shown that the polarization coupling s_ρ is:

$$s_\rho \ \frac{e\sqrt{4\pi\alpha_\rho}}{0.505} \ \frac{1}{\sqrt{m_1 m_0 \left(m_1 + m_0\right)}} \tag{4}$$

where m_1 is the mass of the ion and m_0 is the mass of the neutral, and α_ρ

is the polarizability of the neutral. Table 1 gives appropriate values of α_ρ (Reference 2). For O and O^+, $s_\rho = 1.53 \times 10^{13}$ cm^3/gm sec; for Ba^+ in air, $s_\rho = 0.24 \times 10^{13}$ cm^3/gm sec.

Table 1. Polarizability of some atoms and molecules.

NEUTRAL	$\alpha_\rho \left(cm^3\right)$	NEUTRAL	$\alpha_\rho \left(cm^3\right)$
N	11.3×10^{-25}	NO	18×10^{-25}
N_2	17.5	Ne	3.96
0_2	7.7	A	16.54
0_2	16.2		

However, charge exchange can also lead to substantial transfer of momentum between the ions and neutrals, especially at $T > 0.01$ eV for resonant charge exchange, and at $T > 1$ eV for nonresonant charge exchange. We approximate the coupling arising from charge exchange by assuming it is equal to that of hard spheres with a collision cross section πr_m^2 equal to σ_x, where r_m is the minimum distance of approach of the centers of the hard spheres and σ_x is the charge-exchange cross section. Using Langevin's result for hard spheres, we then have for the charge-exchange coupling s_x:

$$s_x = \frac{r_m^2}{0.75} \sqrt{\frac{8\pi kT}{m_1 m_0 \left(m_1 + m_0\right)}} = \frac{\sigma_x}{0.75\pi} \sqrt{\frac{8\pi kT}{m_1 m_0 \left(m_1 + m_0\right)}} \qquad (5)$$

The total coupling is then given by the sum of the polarization and charge-exchange coupling $\left(s = s_\rho + s_x\right)$.

For the resonant $\sigma_x \left(O^+ \to O, N^+ \to N, NO^+ \to NO\right)$ we use 40×10^{-16} cm^2 at $T = 0.01$ eV, and 15×10^{-16} cm^2 at $T = 1000$ eV. For nonresonant $\sigma_x \left(O^+ \to N, N^+ \to O, O^+ \to O_2, N^+ \to N_2, \text{etc.}\right)$ we use 1×10^{-16} cm^2 at $T = 1$ eV, and 5×10^{-16} cm at $T = 1000$ eV. For ionized air plasmas the approximate total s for the resonant s_{res} and nonresonant s_{non} are then:

$$s_{res} = \left[1.5 + (100T)^{0.375}\right] \times 10^{13} \; cm^3 / gm \; sec \qquad (6)$$

$$s_{non} = \left[1.6 + 0.3T^{2/3}\right] \times 10^{13} \; cm^3 / gm \; sec \qquad (7)$$

These values are believed to be correct to within a factor of two in the range $0.01 \; eV < T < 1000 \; eV$.

The above procedure may be checked by comparing with ion mobilities K in gases because $s = e/m_1\rho_0 K$. Agreement to within 10 percent of the observed value is found for Ne^+ ions in neon, and for A^+ ions in argon.

(*) THE POSSIBLE ROLE OF METASTABLE MINOR CONSTITUENTS IN THE DISTURBED UPPER ATMOSPHERE (*)

Henry Miranda

Epsilon Laboratories, Inc.

The existence of noble gas compounds was first established a decade ago with the successful synthesis of $Xe\ F_4$ and $Xe\ O_3$. Since then, other stable compounds such as $Xe\ F_2$, He_2, and others have also been reported. Additionally, the likelihood of reactions resulting in the formation of HeO and NeO has been speculated upon in the literature.

Metastable species are believed to play an important role in the formation of these molecules, as is evidenced by the fact that a gaseous discharge appears to be a necessary ingredient for most of these reactions to proceed. This suggests, that under disturbed upper atmospheric conditions, the excitation of noble gas metastable atoms by energetic particle deposition might lead to the ıormation of relatively stable molecules. The emission of vibrational relaxation radiation in the infrared region by these molecules is considered here.

Using an electron impact excitation cross section inferred from available data for helium and argon, an upper limit emission rate is calculated for such a molecule formed by collisions between some appropriate atmospheric constituent and argon, the major E-region noble gas constituent. A potential well of about 1V is taken as a reasonable value, and it is assumed that the molecules are found in the uppermost possible vibrational level upon formation. For those molecules whose characteristic vibrational frequency lies in the 10 micron regime, a maximum of 10 photons can be emitted in cascade for every molecule formed.

Using this model, it is shown that under typical artificially disturbed E-region conditions, the maximum limb radiance observable by an exoatmospheric sensor viewing the 90-km level tangentially is about six orders of magnitude greater than the sensitivity threshold of present state-of-the-art LWIR instrumentation.

SESSION V

ATMOSPHERIC DYNAMICS

CHAIRMAN: DR. K. S. W. CHAMPION, AFCRL

(*) TURBULENCE IN THE UPPER ATMOSPHERE (*)

Ernest Bauer
Institute for Defense Analysis

The nature and scales of diffusion in the normal atmosphere will be discussed with reference to the effective diffusivity for different scales of motion. It will also be indicated in qualitative terms how the characteristics of ambient turbulence can affect the effective rate of specific chemical reactions.

MEASURED UPPER ATMOSPHERE
TRANSPORT COEFFICIENTS

Samuel P. Zimmerman

Air Force Cambridge Research Laboratories

The minimum vertical turbulent diffusivity in the upper atmosphere, as measured during the ALADDIN experiment, is determined from the simultaneous measurements of temperature, or density, and the rate of viscous dissipation of turbulent kinetic energy (ϵ). This diffusivity is approximated by $\nu_B = K\alpha^{1/2} \epsilon N^{-2}$ where: ν_B is the buoyance limited turbulent diffusivity,

α is the one dimensional Kolmogoroff constant,

K is a constant of order unity,

$N^2 = \frac{g}{T}\left(\frac{\partial T}{\partial z} + \Gamma\right)$ is the Brunt-Vaissala frequency,

T is the temperature,

$\frac{\partial T}{\partial z}$ is the vertical temperature gradient,

Γ is the adiabatic lapse rate,

and g is the gravitational acceleration.

The technique of measurement of the rate of dissipation and its uncertainties, as well as the derived spatial distribution and amplitude of the vertical turbulent diffusivity, will be discussed.

CHEMICAL REACTIONS IN NONHOMOGENEOUSLY
MIXED TURBULENT FLOWS

Coleman duP. Donaldson and G. Hist
Aeronautical Research Associates of Princeton, Inc.

Recently, both theoretical and some experimental studies of turbulent chemistry in the atmosphere and in chemical lasers have shown that conventional methods of computing reactions in such flows can be inadequate. The problem lies in treating the time-averaged concentrations as though they were mixed on the molecular level at a temperature equal to the time-averaged temperature. When chemical reaction rates are fast and turbulent scales are large; a calculation of this type is valid only after mixing has been complete for some time. In the present paper, a theoretical approach is developed which will enable one to compute chemical reactions in nonhomogeneously mixed turbulent flows. With the aid of the equations developed, the three characteristic times which are involved in this problem are derived. These times are the residence time, the reaction time, and the diffusion time. It is shown, that for some turbulent calculations in the atmosphere, conventional chemical techniques are inadequate. A formula is also derived for the scaling of turbulent flows in devices so that the rates of reaction are not diffusion-limited.

SESSION VI

PROPERTIES OF THE IONOSPHERE

CHAIRMAN: DR. K. S. W. CHAMPION, AFCRL

SATELLITE STUDIES OF THE DISTURBED D-REGION

J. N. Bradbury, W. L. Imhof, R. G. Johnson, and J. B. Reagan
Lockheed Palo Alto Research Laboratory

Simultaneous satellite measurements of energetic particle fluxes which precipitate into the D-region and the resulting radio-wave absorption have been made during a variety of magnetically disturbed conditions in 1971-1972. The STP-71-2 polar orbiting satellite at an altitude of about 800 km carries both an array of particle detectors which provide high spectral and spatial/temporal resolution of proton, electron, and α-particle fluxes and a multifrequency earth reflecting ionospheric sounder which yields the radio absorption. Correlation of the data produces information on the height variation of the D-region electron loss coefficient during disturbed conditions. The experimental technique will be described and results presented.

EFFECTIVE RECOMBINATION COEFFICIENTS AND LUMPED PARAMETERS IN THE D-REGION DURING SOLAR PARTICLE EVENTS

James C. Ulwick

Air Force Cambridge Research Laboratories

Rocket and satellite measurements were made during the 2 November 1969 solar particle event of the proton spectra, for the determination of the rate of ion production, and of the altitude profiles of electron and ion concentrations. The effective recombination coefficient and the effective positive-ion recombination coefficient, determined from the measurements for nighttime and daytime conditions, are compared and discussed. The daytime effective recombination coefficients obtained over the 3-day period, where the ion production rate changed by almost 2 orders of magnitude, differ by less than a factor ot two. Variations of the coefficients with solar zenith angle for both sunrise and sunset are shown. Lumped parameters are derived and compared to parameters derived from the output of the Keneshea code which preserves the detailed chemistry.

APPLICATIONS OF VLF/ELF TECHNIQUES TO EVALUATION
OF IONOSPHERIC DISTURBANCES

V. Hildebrand

Naval Electronic Laboratory Center

Wideband VLF/ELF propagation measurements provide a good means for evaluating methods for modeling ionosphere parameters used in communications coverage prediction calculations. Highlights of ongoing investigation are presented. Also examples of significant problem areas are described in order to illuminate requirements for further investigation.

D AND E REGION COMPOSITION AND CHEMISTRY

R. S. Narcissi

Air Force Cambridge Research Laboratories

A fast reaction which can convert NO^+ to water-cluster ions is being sought to explain the quiescent D region. Ion composition measurements during a total solar eclipse have given evidence for the existence of such a reaction, although the actual process could not be determined. The large electron loss rates observed near 87 km during an eclipse and near sunset are presently unexplained and indicate the need for new and more efficient electron attachment mechanisms. A maximum concentration of heavy negative ions is measured in a layer centered near 87 km. These and other observations have led to the suggestion that water containing conglomerates are playing an important role in determining both the positive and negative ion composition in the D region. The reaction,
$$NO^+ E \left(H_2O \right)_x - H^+ \left(H_2O \right)_y + \text{products,}$$
where E is a binding embryo, has been proposed as a possible solution to the D region positive-ion composition problem. At the same time, these conglomerates may be the efficient bodies for electron attachment. Smaller concentrations of other species are found in the D region. A group of ions identified as sulfur, its oxides and possible acids is being consistently measured. Ion species which could be identified as NO_3^- and its hydrate have also been measured. In view of the current interest of metal oxide chemistry and metal releases, the results of two flights are presented in which Al^+ and AlO^+ ions resulting from trimethyl aluminum releases were measured in the E region. Atmospheric chemical and ionization processes of the TMA are discussed.

D AND E REGION COMPOSITION DURING PCA
AND AURORAL DISTURBANCES

R. S. Narcissi

Air Force Cambridge Research Laboratories

Positive- and negative-ion composition measurements in the D and E regions during a PCA have aided in clarifying several aeronomical processes but have also generated some problem areas. The positive-ion measurements have allowed a modeling of the disturbed D region by revealing the ionospheric chemistry of O_2^+ and its importance as a source of water-cluster ions. The negative-ion measurements have shown a predominance of O^- at night and O_2^- during the day between 75 and 94 km; however, the relatively large concentrations measured cannot be explained since the destruction rates of these ions by associative detachment reactions with atomic oxygen are apparently very large. Mesospheric NO concentrations do not exhibit much change during a PCA, but very large enhancements seem to occur in the lower thermosphere during auroral events. Analysis of measurements from six flights in auroral forms ranging from IPC I to II^+ indicates that a high O_2^+ to NO^+ conversion rate is needed which increases with the strength of the aurora. If this process depends solely on the NO concentrations, then the upper limits of NO required between 110 and 120 km varies from about 4×10^8 cm^{-3} for Class I to 1.5×10^9 cm^{-3} for Class II^+.

D-REGION NEGATIVE ION CHEMISTRY

Eldon Ferguson

NOAA Environmental Research Laboratories

The present status of D-region negative ion chemistry will be reviewed with emphasis on the most recent laboratory determinations of reaction rate constants and electron affinities. The initially formed negative ion O_2^- is either associatively detached by O, collisionally detached by $O_2\left(^1\Delta_g\right)$, or charge transfers with O_3 or clusters to form O_4^-. By a somewhat complex series of steps, the ion chemistry eventually leads to NO_3^-, which with its hydrates, is believed to be a "terminal" negative ion. A recent addition to this chemistry is the finding that the reaction $NO_2^- + H \rightarrow OH^- + NO$ is rapid. This is of importance because the OH^- electron is efficiently detached by both O and H. It has also been found that OH^- associates with CO_2 with an unusually large rate constant to form HCO_3^-. It has also been recognized that two distinct forms of NO_3^-, presumably geometrical isomers, play a role in D-region negative ion chemistry. The two NO_3^- species have quite different reactivities and electron binding energies. The electron affinities of NO_2 and NO_3 have recently been determined, $EA\left(NO_2\right) = 2.38 \pm 0.06$ eV and $EA\left(NO_3\right) = 3.9 \pm 0.2$ eV. These energies are critical in determining both photodetachment rates and chemical reactivities in the D-region.

RESULTS OF GROUND-BASED STUDIES OF
THE LOWER IONOSPHERE

G. Falcon

Institute for Telecommunications Sciences

Recent results of ground-based studies of the lower ionosphere (by means of partial reflection technique), using the DNA-owned mobile experimental system, are presented. Highlights of the joint ground-based and rocket-launched winter anomaly study at White Sands Missile Range during January-February 1972 are discussed. Recent application of the technique at higher altitudes (to 110 km) and its comparison with other measurements are described.

DIGISONDE OBSERVATION OF AUGUST 1972 SOLAR FLARES

Bodo W. Reinisch

Lowell Technological Institute Research Foundation

On Friday, 4 August 1972, radio wave absorption in Maynard, Massachusetts (42.4°N, 71.5°W geographic) increased by 35 dB within half an hour starting at 0530 UT. After 0300 UT, several short lasting amplitude recoveries by up to 20 dB were recorded. The absorption event lasted until Wednesday morning, 16 August, when the absorption level reached its normal value. On Saturday, 12 August, the absorption was still 10 dB above normal.

Disappearance of the F-echoes at the high frequency end of the ionogram was the first indication of the upcoming event, as if the F-region had dissolved. Then the lower frequencies disappeared due to nondeviative absorption in the D-region.

Strong Z-type returns at the low frequency end of the F-trace on 9 August indicate oblique echoes from the south along the geomagnetic field lines. This could be caused by a high north-south electron density gradient.

E-REGION CHEMICAL TIME CONSTANTS AS MEASURED BY THE CHATANIKA INCOHERENT SCATTER RADAR

Walter G. Chesnut, Murray J. Baron
and Charles L. Rino
Stanford Research Institute

The Defense Nuclear Agency's Incoherent Scatter Radar was relocated from Stanford, California to Chatanika, Alaska in July 1971. Since then the radar has been measuring the ionospheric electron density, ion and electron temperatures, ion drifts, and ionospheric currents in the auroral ionosphere. During periods of auroral precipitation, the radar has measured the rapid electron density variations produced by time varying particle precipitation over the height range of 90 to 150 km. A technique is being developed to determine, from the temporal behavior of ionospheric electron density, the characteristic chemical time constant as a function of altitude in this height region. Preliminary findings are very encouraging concerning the eventual success of the technique. A description of the technique with early results will be presented.

CHEMISTRY OF THE E- AND F-REGIONS

William Swider

Air Force Cambridge Research Laboratories

Rate coefficients for the major E- and F-region processes appear to be fairly well known near $300°K$. Further laboratory work is required to define the processes $O^+ + O_2 \rightarrow O_2^+ + O$ and $O^+ + N_2 \rightarrow NO^+ + N$ at temperatures of 500 to $1500°K$, the normal F-region temperature range. Information on other oxygen-nitrogen ion molecule reactions may be sufficient except for the temperature dependence of $N_2^+ + O \rightarrow NO^+ + N$. The change of the dissociative recombination rates $NO^+ + e$ and $O_2^+ + e$ with electron, T_e, and ion T_i, temperature must be further studied. These processes may possess a simple T_e^{-1} behavior, but a factor like $T_e^{-1/2}\left(1-e^{-T_v/T_i}\right)$, where T_v is the equivalent temperature of the first vibrational level of the diatomic ion, may better accommodate auroral results.

The production of excited molecules in aeronomic reactions is also of vital interest. Laboratory results indicating that about 50 percent of all $O_2^+ + e$ recombinations yield $O\left(^1D\right)$ appear consistent with F-region studies of the $6300/6360\text{Å}$ airglow. The $N\left(^2D\right)$ yield of $NO^+ + e$, $N_2^+ + O$ and $N_2^+ + e$ has yet to be measured in the laboratory. The aeronomic production of $N\left(^2D\right)$, which reacts rapidly with O_2 to form NO, is critical to E-region chemistry since $O_2^+ + NO \rightarrow NO^+ + O_2$ is important. A rapid substantial buildup of NO in an aurora requires an equally substantial production of $N\left(^2D\right)$ from N_2 because (a) only $N\left(^2D\right)$ reacts rapidly with O_2 to yield NO, and (b) N_2 is the only appreciable nitrogen species in the ionosphere. Since the formation of NO will be suppressed by the rapid processes $N\left(^2D\right) + NO \rightarrow N + NO$ and $N + NO \rightarrow N_2 + O$, about 1 percent of the N_2 must be dissociated per cm^3 sec^{-1} with 12.12 eV being required per dissociation to yield $N\left(^2D\right) + N$, or about 18 ergs cm^{-3} sec^{-1} at 110 km in order to attain NO $\sim 10^{11}$ cm^{-3}. Other phenomena should be expected besides a buildup of NO, if it occurs. Thus, substantial dissociation of O_2 and presumably considerable $O\left(^1S\right)$ production with subsequent 5577Å emission should be expected.

SATELLITE OBSERVATIONS OF ENERGETIC HEAVY IONS

R. G. Johnson

Lockheed Palo Alto Research Laboratory

Large fluxes of energetic heavy ions ($m/q \approx 16$) have been observed in the inner magnetosphere with a set of energetic ion mass spectrometers on board the Air Force polar orbiting satellite STP71-2 at altitudes near 800 km. The heavy ions have been observed throughout the spectrometer energy range from 0.7 to 12 keV, and during the geomagnetic storm of 17 December 1971, the heavy ion fluxes frequently exceeded the proton fluxes in the same energy range. The heavy ions were observed over a wide latitudinal range ($2.4 < L < 12$), and the spectrums were highly variable. The peak energy flux of these ions was about 0.4 $ergs/cm^2$-sec-sr, which is substantial in terms of the expected observable ionospheric effects. The source of the energetic ions is inferred to be the ionosphere and thus a form of extreme heating in the upper ionosphere is inferred.

SESSION VII

CHARGED PARTICLE REACTION RATES

CHAIRMAN: DR. E. FERGUSON, NOAA

ENERGY LOSSES OF LOW-ENERGY ELECTRONS AND NEGATIVE ION FORMATION IN ATMOSPHERIC GASES

G. J. Schulz

Yale University

It has been known for some time that vibrational excitation of diatomic molecules at low energy proceeds, predominantly, through the formation of an intermediate state, called a "compound state" or "resonance". Also, it has been suspected that many electronically excited states are affected by the presence of compound states. As a result of recent work in this and other laboratories, it is now possible to obtain a much clearer overview of inelastic processes and of negative-ion formation. This significant advance in our understanding of collision processes is a result of the discovery of large numbers of compound states in various molecules and the classification of these states. For example, in the case of N_2 we now know of three progressions of shape resonances,[1,2] each progression consisting of 8 to 18 vibrational members. These three progressions of shape resonances are centered near 2.3, 9.0, and 10.0 eV, and they dominate the excitation of vibrational levels of the $X^1\Sigma_g^+$ ground state, and the $A^3\Sigma_u^+$ and $B^3\Pi_g$ excited states of N_2. Shape resonances in the 12 eV region also exist. A number of Feshbach resonances, connected with excited Rydberg states, span the region from 11.48 eV to 15 eV.

In the case of O_2, a similar situation prevails. Of particular interest is the low-lying $^2\Pi_g$ compound state which is responsible for the vibrational excitation of O_2 and for three-body attachment.[3] The attachment cross section to a number of complex molecules and their temperature dependence also has been investigated.

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NUMBER DENSITIES, WALL CURRENTS, AND PRINCIPAL REACTIONS IN IONIZED AIR CONTAINING WATER VAPOR

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Ballistic Research Laboratories

A multiple species computer code, LABCHEM, has been developed which models the chemistry and physics occurring in a controlled laboratory experiment simulating the disturbed sub-D region. The experiment is being conducted at the Dewey Electronics Corporation where air containing either 6 ppm or 0.6 ppm water vapor is ionized either continuously or repetitively by high-energy electrons. The code models the experiment by dividing the reaction chamber into concentric zones and calculating the concentrations of each species at the center of each zone and the transport of particles by diffusion from one zone to the next. The wall currents of the charged species from the outermost zone are calculated and may be compared directly with the measured wall currents. The chemistry set in the LABCHEM code is the same as the chemistry set in our AIRCHEM I and AIRCHEM II codes. Consequently, a comparison of the calculated wall currents and the measured wall currents for the principal ions should produce an excellent check on the adequacy of the chemistry set used in making atmospheric deionization calculations.

RECENT FLOWING AFTERGLOW RESULTS ON IONOSPHERIC
ION-NEUTRAL REACTIONS

F. C. Fehsenfeld

NOAA, Environmental Research Laboratories

The reaction:

$$NO^+ + O_3 \rightarrow NO_2^+ + O_2 \tag{1}$$

has been studied in the NOAA flowing afterglow system at $300°$ K and found to have a rate constant less than 10^{-14} cm^3 sec^{-1}. This reaction was of potential importance as an NO^+ loss process, as an NO_2^+ source, and as a potential $O_2\left(^1\Delta_g\right)$ source. Additional NO^+ loss processes are required, the origin of large $O_2\left(^1\Delta_g\right)$ concentrations in disturbed conditions remains puzzling and NO_2^+ has been reported so that this reaction is of considerable potential importance. Some theoretical justification for the inefficiency of this reaction will be presented. The charge transfer of O^+ with NO is also found to not be efficient.

$$O^+ + NO \rightarrow NO^+ + O \tag{2}$$

with $k_2 < 10^{-12}$ cm^3 sec^{-1}. This is of importance in the E-region under disturbed conditions, because of the grossly enhanced nitric-oxide concentrations which have been found. The behavior of doubly charged-ion charge transfer with molecules at thermal energy has been investigated for several cases. An empirical relationship between rate constant and curve crossing distance (which can be deduced from the reactant parameters) is found which may be useful for predictive purposes. Further work on ion-neutral clustering has been carried out in this laboratory which gives some insight into the nature of the bonding forces involved.

(*) CLUSTERING OF ATMOSPHERIC GASES TO NO^+ (*)

J. M. Heimerl and J. A. Vanderhoff

Ballistic Research Laboratories

A stationary afterglow has been used to measure the room temperature rate coefficients for the clustering of atmospheric gases to NO^+. The reactions studied were of the form:

$$NO^+ + X + M \xrightarrow{k} NO^+(X) + M$$
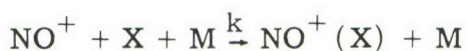
where $X = N_2$, O_2, CO_2, CO, N_2O, and SO_2. Except for the case of SO_2, $X \approx M$. With respect to the O_2 reaction only an upper limit could be obtained. The room temperature clustering rate coefficients are:

$$X = N_2 \qquad k = 2.4 \times 10^{-31} \ cm^6/sec$$
$$X = O_2 \qquad k < 4 \times 10^{-32} \ cm^6/sec$$
$$X = CO_2 \qquad k = 2.4 \times 10^{-29} \ cm^6/sec$$
$$X = CO \qquad k = 1.9 \times 10^{-30} \ cm^6/sec$$
$$X = N_2O \qquad k = 2.5 \times 10^{-29} \ cm^6/sec$$
$$X = SO_2 \qquad k = 2.5 \times 10^{-28} \ cm^6/sec$$

The collisional breakup reaction:

$$NO^+(N_2) + M \rightarrow NO^+ + N_2 + M$$
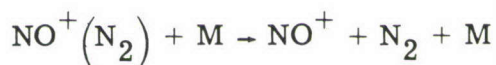
has been investigated and limits for the rate coefficient will be discussed.

A SIMPLE METHOD OF ESTIMATING THE RATES OF FORMATION OF SINGLY-CHARGED, METALLIC POSITIVE CLUSTER IONS

L. M. Colonna-Romano and G. E. Keller

Ballistic Research Laboratories

Time constants for the formation of singly-charged, metallic positive ions may easily be estimated using a contour map representation of drift tube clustering studies. The contour map presents minimum values for three-body rate constants for the initial clustering of gas molecules to positive ions. The contour map has been used to estimate the time constants for N_2 clustering to Fe^+, Al^+, Li^+, Na^+, and Si^+ at 60 to 120 km. Additional calculations show that this clustering can provide an important method for neutralization of the ions.

Of the ions considered, clustering to Li^+ is the fastest, with time constants for initial clustering ranging from 2×10^{-2} sec at 60 km to 2×10^6 sec at 120 km. The clustering to Fe^+ is slowest, with time constants from 3 sec at 60 km to 4×10^8 sec at 120 km. When these time constants are compared with those that could be expected for mutual neutralization, clustering is found to be faster for all cases except Fe^+ at or above 100 km, where the rates are about equal. Further, clustering should be faster than radiative recombination for all ions at 100 km or lower, and for Li^+ at all altitudes considered. Collisional breakup of the N_2 clusters has been compared to switching with CO_2 to form more tightly bound clusters; viz,

$$X^+\left(N_2\right) + CO_2 \rightarrow X^+\left(CO_2\right) + N_2.$$
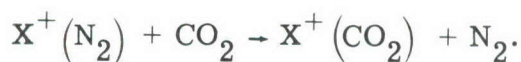
These considerations show switching faster for $Li^+\left(N_2\right)$, about equally as fast as breakup for $Si^+\left(N_2\right)$, $Al^+\left(N_2\right)$, and $Na^+\left(N_2\right)$, and collisional breakup faster for $Fe^+\left(N_2\right)$. Further switching with H_2O can occur at the lower altitudes. Dissociative recombination of the cluster ions eventually results in their neutralization.

LABORATORY STUDIES ON ION-NEUTRAL REACTIONS

John F. Paulson

Air Force Cambridge Research Laboratories

A double mass spectrometer system has been used to study several reactions of positive and negative ions with neutral species. Reactant ion kinetic energies ranged from a few tenths of an eV to about 30 eV. Results on $O_2^+(NO, O_2)NO^+$; i.e., $O_2^+ + NO \rightarrow O_2 + NO^+$, show that the rate constant is independent of ion energy from 0.4 to 6 eV and has the value 8.5×10^{-10} cm^3 sec^{-1}. A similar result was obtained for $N_2^+(NO, N_2)NO^+$, for which the rate constant is 7.5×10^{-10} cm^3 sec^{-1}. Time-of-flight (TOF) analysis on the latter process shows that the NO^+ has only thermal kinetic energy. The reaction is therefore nearly exactly resonant and probably leads to $N_2\left(A^3\Sigma_u^+, v = 1\right)$. TOF studies on $N_2^+(O_2, N_2)O_2^+$ indicate that the product ion here also has only thermal kinetic energy.

Several reactions of negative atomic sulfur ions with N_2, O_2, N_2O, and CO_2 have been studied. In all cases examined, the reactions appear to be endothermic, showing cross sections below 0.05×10^{-16} cm^2 at the lowest interaction energies. In the case of the nominally exothermic process $S^-(N_2O, N_2)SO^-$, the occurrence of an onset in the excitation function suggests that the N_2 is vibrationally excited. A similar result had been previously obtained for the analogous reaction $O^-(N_2O, N_2)O_2^-$. Other negative ion-neutral processes studied have included the reactions $O^-(H_2O, OH)OH^-$, $OH^-(D_2O, HDO)OD^-$, and $D^-(H_2, HD)H^-$. The last of these was investigated in order to determine whether the observation of onsets in the excitation functions for several nominally exothermic negative ion-neutral reactions might be due to the occurrence of a fast associative detachment channel at low energies.

EFFECTS OF INTERNAL ENERGY ON ION-NEUTRAL REACTIONS

J. A. Rutherford, D. A. Vroom, and R. H. Neynaber
Intelcom Rad Tech

Crossed ion-neutral beam techniques have been employed to study the effects of the addition of internal energy to the neutral partner of an ion-neutral reaction. Noteworthy among the processes that show an effect are $O^+ + N_2 \rightarrow NO^+ + N$, $N^+ + N_2 \rightarrow N + N_2^+$, and $N_2^+ + O_2 \rightarrow N_2 + O_2^+$. In these cases, the cross sections for reaction were found to increase at low energies with the addition of internal energy to the neutral reactant by either thermal or rf discharge methods. In some instances, these changes can be related to the mechanism for reaction and, as a consequence, lead to indications of the states of the product particles and hence the overall reaction kinetics. For example, in the third reaction above, addition of vibrational energy to the O_2 decreases the energy defect for formation of the O_2^+ in the $\left(a^4\Pi_u\right)$ state. This is the probable reason for the increase in the cross section at low energies and would indicate that for O_2 with sufficient vibrational energy to react by this channel, there would be no kinetic energy of the resultant particles. Reactions of N^+ with O_2 to form O^+, NO^+, and O_2^+ showed no dependence on the internal energy of the O_2 molecule. Preliminary results obtained using an oxygen atom beam will also be presented.

MULTICHARGED ATMOSPHERIC AND DEBRIS-ION CROSS SECTIONS

J. N. Bradbury and T. E. Sharp
Lockheed Palo Alto Research Laboratory

The current status of cross-section information on the interaction of multicharged atmospheric and debris ions with electrons and gases is briefly reviewed. Potentially important gaps in the existing data on excitation, ionization, and charge-transfer processes are noted. Some recent measurements on the cross section for the excitation of the 2p level of N^{4+} (1240Å) by electron impact in the collisional energy range 100 to 400 eV are presented.

TRANSITION PROBABILITIES OF HIGHLY STRIPPED
IONS OF NITROGEN AND OXYGEN

A. Dalgarno

Harvard University

Some theoretical methods are described for the calculation of transition probabilities between discrete levels, photoionization cross sections and radiative and dielectronic recombination coefficients. Results are presented for highly stripped ions of nitrogen and oxygen.

ION-ION RECOMBINATION

J. R. Peterson, J. T. Moseley, and R. E. Olson
Stanford Research Institute

The two-body mutual neutralization reaction $A^+ + B^- \rightarrow A + B$ terminates the sequence of positive- and negative-ion mulecule reactions in the D region. The uncertainty of two orders of magnitude in the rate coefficients that existed 5 years ago has been reduced, by laboratory measurements, to about 30 percent for most atmospheric species.

Reaction cross-section measurements on the merged beam apparatus at SRI have been carried out on various combinations of the positive ions O^+, N^+, NO^+, N_2^+, He^+, and H^+ and the negative ions O^-, O_2^-, NO_2^-, NO_3^-, N^-, and D^-, at well-defined energies between about 0.1 eV and several hundred eV (c.m.). A low-energy form of the Landau-Zener theoretical cross section is fitted to the low-energy portion of the data to obtain reaction rate coefficients as functions of temperature. The 300° K rates are generally found in the region 1-5 x 10^{-7} cm^3/sec. The thermal rates approach a $T^{-1/2}$ dependence toward low temperatures. Theoretical work has been carried out with fairly good success on atomic species, using a Landau-Zener theory. An "absorbing sphere" theoretical model has been used for reactions between molecules.

(*) THE PLASMA CHROMATOGRAPH^{TM} - AN ION-MOLECULE REACTOR AND ION-MOBILITY SPECTROMETER (*)

M. G. Cohen

Franklin GNO Corporation

The Plasma Chromatograph is an ion-molecule reactor and ion-mobility spectrometer which operates normally at atmospheric pressure with air as an all-electronic, high-speed chemical analyzer. The instrument can be used in the range of 0.1 to over 1 atmosphere to study positive or negative sequences of ion-molecule reactions initiated by a radioactive source. In chemical applications for single chemicals, the ion-mobility spectrometer produces a characteristic signature from which molecular weight can be determined to ± 2 percent in the mass range from below 100 amu to above 10,000 amu. The response can be obtained for concentrations in the ion-molecule reactor on a volume basis of as low as 10^{-11} parts. The instrument and both typical and potential applications will be described.

SESSION VIII

COMPUTER CODE DEVELOPMENT

CHAIRMAN: DR. F. E. NILES, BRL

THE BRL MATRIX FORMULATION TECHNIQUE FOR NUMERICAL INTEGRATION OF RATE EQUATIONS

M. D. Kregel

Ballistic Research Laboratories

The Ballistic Research Laboratories has for the past few years utilized a very large atmospheric deionization code named AIRCHEM I. Paralleling the utilization of this code has been the development of various refined methods for numerical integration, particularly methods which employ a matrix formulation approach. This work has resulted in a new code named AIRCHEM II. The chemistry set employed in both codes currently includes 523 reactions involving 59 interconverting species.

In a recent study using AIRCHEM II, this chemistry set was integrated out to 1,000 seconds for different altitudes following a nuclear burst at an altitude of 30 km. For AIRCHEM II the following run times were required: 20 km required 90 minutes, 25 km required 65 minutes, and 30 km required 30 minutes. All computations were done to an accuracy within ± 1 percent. For comparison purposes, a CDC 6600 computer is about four times faster than the machine on which these computations were performed.

The matrix formulation is based on the matrix equation written in terms of the predicted value of the ith species, y_i, the corrected value y_i^C, and is of the form

$$y_i^P - y_i^C \approx f \cdot \sum_{j=1}^{n} \left(\frac{\partial y_i^{P\,'}}{\partial y_j} - \frac{\delta_{ij}}{f} \right) d_j,$$

where the superscript prime denotes differentiation with respect to time, f a weight which is a function of the integration step size, and d_j a correction factor to the predicted value of the jth species.

An iterative scheme based on the Gauss-Seidel technique for solving matrix equations is employed to solve for the correction factors d_j. This scheme permits the exploitation of the fact that most of the off-diagonal elements of the matrix are zero. In addition, special coding is employed which permits the subscripts of all the remaining nonzero elements of the matrix to be written for the computer in terms of absolute machine locations which makes the

elements appear as if they were not subscripted to the machine. Also, special tests have been developed to determine if a "full" matrix approach is required in the iteration or if only the diagonal elements are required, and to indicate when the iteration on selected species have converged sufficiently to withdraw them from continued iterations. As a consequence, the machine deals with only those species for which convergence has not yet taken place. The result of this is an extremely fast matrix manipulation scheme which significantly improves the speed of the integration method. Charge balance and chemistry balance are preserved automatically in a final step in which the corrections to the predicted values are incorporated into a final value through a classical predictor-corrector formula.

This type of matrix method is equally suited to chemistry sets with only a few number of species. In this case, the direct inversion of the matrix may offer attractive alternatives to the iterative scheme employed when the number of species is large.

CHEMICAL KINETICS CALCULATIONS

Gerhard Rohringer

General Electric–TEMPO

General Electric–TEMPO has developed a computer code to numerically solve problems arising in chemical kinetics. This code currently solves problems consisting of up to 49 species and 300 reactions. The species rate equations are integrated by either explicit or implicit integration. The latter method is used when formation and removal rates for any participating species become comparable.

Inputs to the program are the reactions of interest and the initial concentrations of the participating species. Reactions can proceed in the forward and reverse directions or in the forward direction only, as determined by the specification of the reaction rate coefficients. The rate of formation and removal of any given species is computed by superposition of the forward and reverse rates of the individual reactions. Evaluation of the elements of the Jacobian matrix relies upon an efficient scheme of using analytical rather than numerical differentiation. No separate programming is required to obtain rates of change or the Jacobian matrix, since all necessary information is obtained from the reactions written in their chemical form.

The code has been tested on various problems. One of these was a hypothetical chemistry problem in which 24 species participating in 18 reactions, all proceeding in the forward and reverse directions, achieved their correct thermal equilibrium concentrations starting from nonequilibrium concentrations. The reactions very nearly achieved detailed balance in spite of very widely varying rates. This demonstrates that the described analysis can properly handle problems close to equilibrium in which all species are formed as rapidly as they are removed. Our previous experience has shown that by using special equilibrium assumptions, it has not been possible to solve this problem successfully. Special equilibrium assumptions must be made in all codes not using an implicit method to overcome the problem of stiffness.

Another important test was conducted by duplicating one daytime, 65-km-altitude run originally made by Dr. Murray Scheibe of MRC. Dr. Scheibe's

chemistry model uses 39 species participating in 280 reactions, which all proceed only in the forward direction. The general-purpose code described here has obtained essentially the same solution as the special-purpose, D-region chemistry code of Dr. Scheibe. This shows that complex chemistry problems can now be solved with a high degree of confidence.

We shall briefly describe our methods of numerical analysis and the results of sample computations.

SESSION IX

NEUTRAL ATMOSPHERES INCLUDING OPTICAL EMISSIONS

CHAIRMAN: DR. F. BIONDI, UNIVERSITY OF PITTSBURGH

REVIEW OF THE 1972 ADVANCED STUDY INSTITUTE

B. M. McCormac and R. N. Varney
Lockheed Palo Alto Research Laboratory

The subject of the 1972 Advanced Study Institute was "Physics and Chemistry of the Upper Atmosphere." Selected topics of potential interest, presented at the Institute, to the DOD community will be discussed. These include recent developments in the areas of atmospheric composition and temperature, D-region chemistry, excited-state quenching rate coefficients, solar UV fluxes, and IR emissions in quiet and disturbed atmospheres. Outstanding problems in key areas will be reviewed.

COSPAR INTERNATIONAL REFERENCE ATMOSPHERES 1972

K. S. W. Champion

Air Force Cambridge Research Laboratories

The COSPAR International Reference Atmospheres (CIRA) 1972 will contain three sections of models plus two major reviews as appendices.

One set of models is for lower altitudes and was prepared by Dr. G. V. Groves while working at AFCRL. The models include tables of temperature, pressure and density for altitudes from 25 to 110 km and for latitudes between 0 and 70° N for each month of the year. There are also models for average E-W winds for altitudes between 25 and 130 km at latitudes from 80° S to 80° N for each month of the year. There are gaps in the models for regions for which data were not available.

The high-altitude models were prepared by Dr. L. G. Jacchia, and tables are presented giving temperature, density and composition for altitudes between 110 and 2,500 km for exospheric temperatures ranging from 500 to 1900 K at 100-K intervals. Formulae and auxiliary tables are included to provide for diurnal, seasonal, latitudinal, semiannual, and geomagnetic variations. In the models, the O/O_2 ratio at 120 km is approximately 2.69. It should be noted that the low- and high-altitude models are not continuous.

Finally, the Mean CIRA 1972 model was prepared by the author. It was developed for the altitude range 25 to 500 km and contains tables of temperature, density and pressure for the whole range. Composition (major constituents and some minor constituents) is given for the range 75 to 500 km. The model represents mean annual and solar cycle conditions for latitudes near 30°.

NUMERICAL MODEL OF THE ALADDIN I EXPERIMENT

Thomas J. Keneshea and S. Zimmerman

Air Force Cambridge Research Laboratories

A coupled set of one-dimensional time-dependent equations of conservation of mass and momentum are solved for 13 neutral atmospheric species. The numerical solution of a finite-difference approximation to these partial-differential equations produces time histories of the vertical distribution of Ar, He, $O(^3P)$, $O(^1D)$, $O_2(^3\Sigma)$, $O_2(^1\Delta)$, O_3, OH, H, HO_2, H_2O, H_2O_2, and H_2. Measured turbulent and molecular diffusion coefficients, total mass density and temperature as obtained from the ALADDIN I experiment along with current chemical reaction rates are used as input data to a computer code that solves these transport equations. Detailed computations of the absorption of energy in the Schumann Runge bands provide more accurate values for the photodissociation rates of O_2, O_3, and H_2O. Appropriate initial and boundary conditions which take into account the dissociation of molecular oxygen above the upper boundary are imposed upon the solutions. The computed results for the distribution of these species are compared to the measured neutral species profiles at the experiment time.

ATMOSPHERIC OZONE AND OXYGEN MEASUREMENTS

Lawrence H. Weeks

Air Force Cambridge Research Laboratories

Midlatitude observations of the daytime ozone distribution from 50 to 75 km show density variability of less than a factor of five and the results generally agree with the more recent models. The few nighttime measurements that are available illustrate the expected increase above about 55 km. However, above 70 km there is still considerable uncertainty as to the magnitude of this increase.

At higher latitudes the ozone is much more variable, in part due to the greater variability of the total atmospheric density. Too few measurements exist here to obtain an adequate picture of the variability to be expected. A pronounced decrease in ozone has been observed in conjunction with a solar proton event.

The latest results on molecular oxygen in the 110 to 180 km region are reviewed. At the lower altitudes, winter midlatitude densities are larger than summer values, and there is an overall density increase at high latitudes. Comparisons with the Jacchia (1971) model show some significant deviations, especially at 180 km. Here no clear latitude dependence is observed except during disturbed magnetic conditions.

O_3 CHEMILUMINESCENCE IN THE ATMOSPHERE
UNDER AMBIENT AND DISTURBED CONDITIONS

D. A. Hamlin and B. F. Myers

Science Applications, Inc.

Gilmore has estimated the importance of the O_3 ν_3-mode chemilumi-nescence from the reaction $O + O_2 + M \xrightarrow{k_1} O_3 + M$. Prediction of this chemiluminescence is extremely difficult, in the absence of experimental data. By using different modeling of the O_3 chemiluminescence and quenching, we obtain different estimates of the O_3 radiance in the atmosphere under ambient and disturbed conditions. These differences are a partial measure of the uncertainties in such predictions.

Our main assumptions for O_3 ν_3-mode chemiluminescence in Reaction 1 are:

1. O_3 is formed in its ground electronic state.

2. Essentially all of the dissociation energy, $D = 1.05$ eV, appears as vibrational energy.

3. The vibrational energy levels are predicted by the formula for a nonlinear triatomic molecule having no degenerate vibrations [He-45], and that the best values of fundamental frequencies and anharmonic constants are given by McCaa and Shaw [MS-68a].

4. Each of the possible 47 sets of states $\left(v_1 \leq 7, v_2 \leq 12, v_3 \leq 9 \right)$ with energy below D by less than one vibrational quantum, is equally probable. (This assumption leads to relative probabilities of 8, 7, 7, 6, 5, 4, 4, 3, 2, and 1 for initially exciting the ν_3 mode from $v_3 = 0$ to $v_3 = 9$. Gilmore equally populates the 10 ν_3-mode levels.)

5. The ν_3-mode, with integrated band strength for fundamental vibrations being over an order of magnitude larger than those for modes ν_1 and ν_2, relaxes by successive emission of fundamental-sequence photons $\left(\Delta v_3 = 1 \right)$ from the ν_3-mode while modes ν_1 and ν_2 are frozen at their initial values. Thus we, as well as Gilmore, have neglected combination and difference bands, effects of perturbations due to Fermi resonances, and overtones from the ν_3-mode. (The main effect of Assumptions 4 and

5 is to produce a considerably softer spectrum than that from the $\left(O,\ O,\ v_3 \to O,\ O,\ v_3\text{-}1\right)$ - sequence computed by Gilmore.)

6. The collision-induced quenching probability is given by a theoretical v^3-dependence instead of Gilmore's assumed v-dependence.

We have used our model to compute (a) the limb radiance in an ambient atmosphere for 80- and 100-km-tangent altitudes and (b) both limb and vertical-path radiances in an atmosphere disturbed by the X-rays from a megaton-range burst at 150-km altitude. These results for the ambient atmosphere, with and without quenching, are shown in Figure 1; also shown are Gilmore's (quenching) results. Our spectral shape differs from Gilmore's mainly because of our Assumptions 4 and 5. The effect of Assumption 6 is to flatten the spectrum and, hence, to reduce the difference in spectral shapes.

In obtaining these results, we have used the rate coefficient given by Kaufman and Kelso, and by Bortner, et al., $k_1 = 5.5 \times 10^{-34}\ (T/300)^{-2.6}$, which facilitates comparisons with Gilmore. Use of the rate coefficient of Johnston which becomes $k_1 = 1.85 \times 10^{-35}\ \exp\ (1057/T)$ when account is taken of relative efficiencies of third bodies, increases the limb radiance for the 80-km-tangent altitude (where $T \approx 186°$ K) by a factor of about three.

In addition to the uncertainties in our assumptions and rate coefficient, the radiance will be affected by variations of the atomic oxygen density in the proximity of 80-km altitude. There seems to be no measurement of $[O]$ in this altitude region. We have used the CIRA-1965 atmospheric properties, but theories indicate diurnal variations of one-to-one and one-half orders of magnitude, seasonal variations of an order of magnitude, variations of one-to-two orders of magnitude due to different treatments of eddy and molecular diffusion and assumed heights of the turbopause, and variations with solar flux.

Limb and vertical-path radiances for an X-ray disturbed atmosphere will be presented.
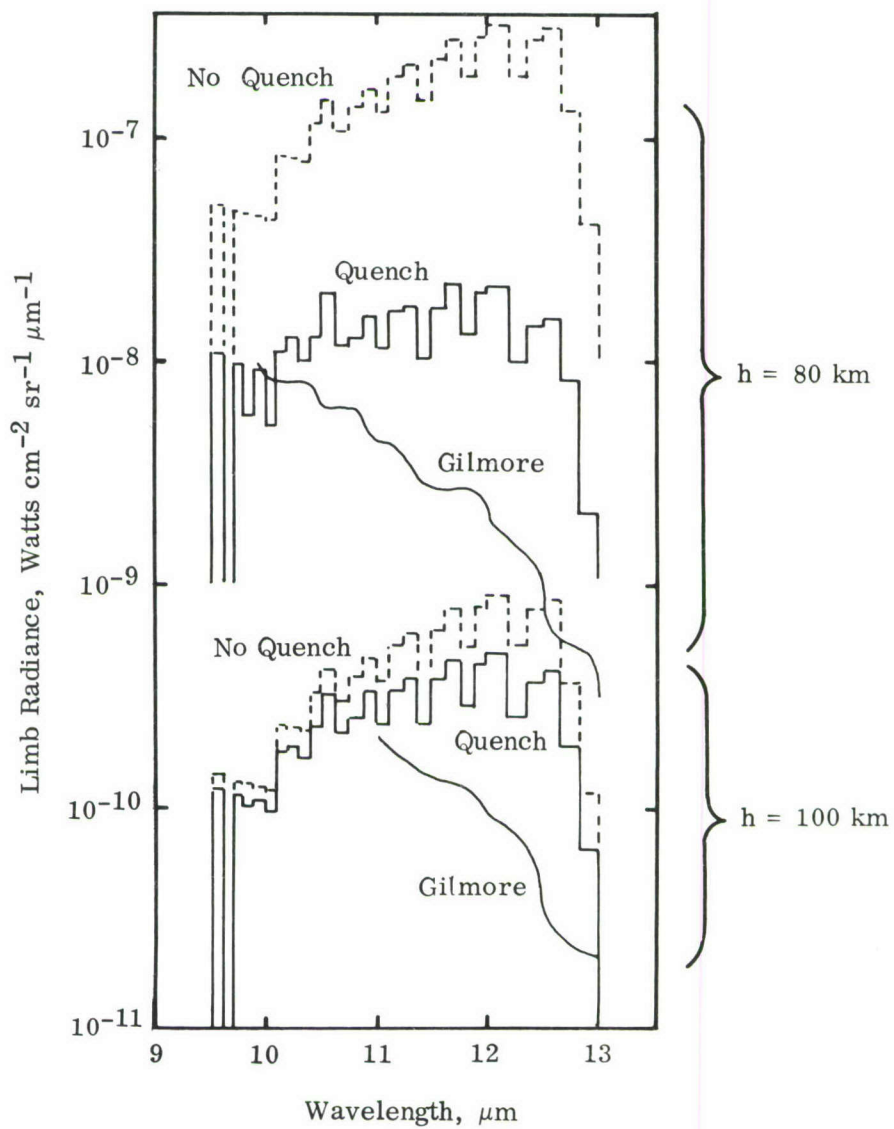
98

Figure 1. Limb Radiance of O_3 Chemiluminescence.

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IR MEASUREMENTS IN AURORAS

A. T. Stair and J. C. Ulwick

Air Force Cambridge Research Laboratories

In March 1972, three rockets with instruments to measure emissions in the short wave infrared region (SWIR) were flown to Poker Flat, Alaska as part of the DNA ICE CAP 72 program. An Astrobee "D" rocket launched during low-level auroral activity carried a nitrogen-cooled dual channel radiometer for measurements in the 1.4 to 1.65 μ and 1.85 to 2.12 μ ranges to a predicted 90 km. A second Astrobee "D" rocket carried a nitrogen-cooled spectrometer (circular variable filter (CVF)) to 90 km that measured emissions from 1.5 to 5.3μ. This rocket was fired after an auroral breakup into a region that had been subjected to long-time electron bombardment. The third rocket, a Black Brant VA, carried a multiexperiment payload (21 experiments) to measure production sources, positive-ion composition, ionization, heating, and emissions in the visible and SWIR. This rocket was fired towards a bright $\left(\text{Class II}^{+}\right)$ auroral form. On all three rockets, radiations were observed in the wavelength region of the first overtone of OH. The measured height profiles suggest that more than one mechanism is important in producing hydroxyl molecules. The Black Brant results showed interesting spatial structure not observed in the other two flights. Approximately 700 spectra were obtained from the CVF spectrometer flight. Tentative identification of molecular species responsible for the observed emission bands is made and aeronomic implications are discussed.

MEASUREMENT OF NO CONCENTRATIONS IN EXCITED AIR FROM γ-BAND EMISSION

I. L. Kofsky

Photometrics, Inc.

The concentrations of NO molecules following irradiation of the upper atmosphere have proven difficult to measure by optical spectroradiometry. However, the $A^2\Sigma^+$ state of NO, which is the upper state of the ultraviolet A-X γ-band system, is efficiently excited (with known rate coefficient) by the metastable $A^3\Sigma_u^+$ state of N_2, which is the lower state of the strong N_2 First Positive bands. Therefore the intensity in the permitted γ-bands of NO, taken with intensities in the N_2 First Positive and N_2^+ First Negative bands, whose fluorescence efficiencies and excitation cross-sections are known, along with that of the N_2 Vegard-Kaplan (A-X) bands, can provide a measure of the concentration of NO in excited air. We have constructed synthetic auroral spectra for the ultraviolet wavelength region 2000 to 3200Å, using measured or calculated N_2 V-K, Second Positive, and L-B-H band intensities; the relative probabilities of exciting vibrational states of NO from the different vibrational states of N_2(A); and the transition probabilities in the γ-band system. These spectra serve in the design of ultraviolet spectrometers for measuring upper-atmosphere NO concentrations from rockets and aircraft.

(*) APPLICATIONS OF ADVANCED PHOTOMETRIC AND IMAGE INTENSIFIED TV INSTRUMENTATION TO ENERGY INPUT MEASUREMENTS ON ICE CAP '72 (*)

Robert D. Sears

Stephen B. Mende

Lockheed Palo Alto Research Laboratories

Two types of advanced auroral photometric and image intensified TV instrumentation have been developed at Lockheed Research Laboratories and applied to measurements of the spatial and temporal variations of auroral and airglow emissions. These instruments were used at Poker Flats, Alaska during ICE CAP '72 operation in March 1972, to measure the energy deposited in the atmosphere by precipitating energetic particles.

The three-color photometer, operated at $4278\overset{\circ}{A}$, $4861\overset{\circ}{A}$, and $6300\overset{\circ}{A}$, was intended to monitor the energy flux and spectral hardness of precipitating particles. Total energy deposited by electrons and/or protons within the photometer field of view can be determined from the N_2^+ 1N band at $4278\overset{\circ}{A}$. The total number flux of the protons may be determined from the $4861\overset{\circ}{A}$ intensity. The intensity of the OI $6300\overset{\circ}{A}$ line, and its ratios with $4278\overset{\circ}{A}$ and $4861\overset{\circ}{A}$ intensities, provides rough information on the hardness of the precipitating particle flux, in that a soft spectrum will deposit more of its energy at high altitudes where the $6300\overset{\circ}{A}$ emission will be radiated.

An example of the digital data plotted from the computer will be given. After editing raw data plots and applying calibration factors, the data output in terms of energy flux, intensity in Rayleighs, and the relative intensity ratios between different colors has been computed and will be illustrated. For ICE CAP '72, three-color or three-beam photometer data were obtained on a sample interval of 1 second. Approximately 50 hours of useful data were obtained.

Results obtained with the IITV and photometer operations during ICE CAP '72 are summarized as follows: the three-beam photometer, operating in the $5890\overset{\circ}{A}$, $6300\overset{\circ}{A}$, and $5577\overset{\circ}{A}$ wavelength regions observed small wavelike motions at ionospheric altitudes before and during the launch of 6 March 1972 (0214 local time). Because of a temperature drift problem, observations of Na line intensity at $5890\overset{\circ}{A}$ could not be made, but 15 to 40 R of residual emission were

measured on the branch of the N_2 1PG (9-5) band overlapping the filter passband centered at 5875Å. These measurements were confirmed on later nights. Peak energy flux deduced during the auroras present based upon the 5577Å intensity peak was 2 ergs/cm^2 sec from precipitating electrons and protons. At launch time, the energy flux level was approximately 0.2 ergs/cm^2 sec in the spatial region surrounding the rocket trajectory through the E-region. High 6300Å emission intensity was observed with intensity peaks exceeding 1 kR. This implies a relatively soft precipitating electron/energy spectrum at least at times, but the possibility of heat conduction from the magnetosphere cannot be ruled out as a background phenomena.

Operation of the three-color photometer before and during the launch of 9 March (0052 local time) showed active auroras present for at least 20 minutes before launch, with a total energy input of about 4000 ergs/cm^2 during this time. in the field of view of the photometer.

Unfortunately, the Black Brant instrumentation carrying rocket was launched into an active aurora through fairly opaque cloud cover, such that the instrumentation did not distinguish any spatial or temporal emission features which could be attributable to the auroral variations alone.

SESSION X

AIR EMISSION AND QUENCHING RATES

CHAIRMAN: DR. A. T. STAIR, AFCRL

OSCILLATOR STRENGTHS OF ATOMIC OXYGEN AUTOIONIZED LINES

R. A. Van Tassel and R. E. Huffman
Air Force Cambridge Research Laboratories
and
J. L. Roebber
Northeastern University

In order to determine the characteristics of the photon absorption process of atomic oxygen in the ionization continuum region, a technique has been developed for measuring oscillator strengths of its autoionized lines. This technique was used to obtain the oscillator strength and other line parameters of the transition $2p\ ^3P_2 \rightarrow 5s'\ ^3D^0$ at 775.3Å. The curve-of-growth method was used, since the spectral width of the lines is far less than the spectrometer bandwidth. In order to remove possible interference from excited states, the atomic oxygen was made by pyrolysis of ozone in a flow system. The concentration was determined by means of the $O - NO_2$ titration. The absorption of the line was observed against the helium continuum background in the vacuum ultraviolet.

Sets of curves-of-growth were computed on the basis of the observed separation of the three levels, $^3D^0_3$, 2, 1, tabulated values of relative line strengths based on L-S coupling, and various line profiles. The following parameters were determined by comparison of the experimental curve-of-growth with the computed curves: the oscillator strength, f, equals 0.0021; the autoionization lifetime, τ, equals 2.0×10^{-11} sec.; and the line width, Γ, equals 0.01 Å. A value for the Fano line profile index q equal to 16 was derived by consideration of the total photoionization cross section to the continuum. This technique is being applied to a number of other autoionized multiplets of series converging to the ^2D and ^2P states of the ion.

EXCITED STATE PHOTOIONIZATION CROSS SECTIONS AND MODIFIED EMISSION COEFFICIENTS FOR OI AND NI PLASMAS

J. Davis

Science Applications, Inc.

The Quantum Defect Method is developed to obtain photoionization cross sections for some 40 (50) levels of OI (NI) over a range of electron energies from threshold to 1 Rydberg. For those levels where a comparison can be made, the agreement is good. The only exception being the ^{3,5}S series of OI where severe matrix element cancellation causes a gross underestimation of the cross sections. Corrected values are obtained by employing a Scaled Thomas Fermi model.

These cross sections are then used to predict the total radiative output in Saha equilibrium resulting from radiative recombination and bremsstrahlung in the field of a singly ionized oxygen (nitrogen) plasma. Modified emission coefficients are presented for the wavelength region extending from the visible to the infrared for a variety of temperatures. Comparison with hydrogenic models is shown to be good in the infrared but becomes progressively poorer in the visible due to difference in atomic structure.

FREE-FREE RADIATION FROM ELECTRON-NEUTRAL COLLISIONS—THEORY AND EXPERIMENT

A. V. Phelps

Joint Institute for Laboratory Astrophysics

Comparisons will be made of experimental measurements and theoretical calculations of the intensity of free-free radiation produced in collisions between electrons and neutral atoms or molecules. The experimental data is obtained from published measurements using shock tubes and electric discharges. Recent theoretical calculations show a considerable discrepancy with experiment.

(*) ELECTRON EXCITATION OF N_2 METASTABLE STATES AND N_2 IR EMISSION BANDS UNDER AURORAL CONDITIONS † (*)

D. C. Cartwright

Space Physics Laboratory, Aerospace Corporation

and

S. Trajmar and W. Williams

Jet Propulsion Laboratory

A combination of experimental and theoretical cross sections for the electron-impact excitation of six triplet states of N_2 (A, B, W, C, E, and D) has been utilized to predict the vibrational population of each electronic state. Secondary electron fluxes appropriate to an IBC II normal aurora were used in the calculations. The cascade contributions coupling the various electron states were included as well as the most important quenching processes. The results indicate that the B ⟶ A and W ⟶ B cascade processes, which are important in determining the vibrational population of the A, B, and W states, produce appreciable radiation in the 1-5 μm wavelength region. The calculations indicate that an appreciable number density of metastable $A^3\Sigma_u^+$ ($v' \leq 7$), $W^3\Delta_u$ (0) and $E^3\Sigma_g^+$ (0) molecules may exist under auroral conditions. An outline of the IR emissions to be expected from analogous intrasystem cascade processes, and metastable molecules formation, within the singlet system will be discussed.

(*) ADDITIONAL INFORMATION FROM THE MEASUREMENTS BY
HUSHFAR, ROGERS, AND STAIR OF THE INFRARED
CHEMILUMINESCENCE FROM THE REACTION
$$NO + O_2 \rightarrow NO + O \quad (*)$$

D. A. Hamlin and B. F. Myers
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Hushfar et al. measured the chemiluminescent first-overtone radiation at 2.7 μm from the reaction $N + O_2 \xrightarrow{k_1} NO + O$, followed by the fast quenching reaction $N + NO \xrightarrow{k_2} N_2 + O$. They reported (Reference 1) that (a) 1.5×10^{-6} overtone photons per second were produced per O_2 molecule, and (b) the low-resolution spectrum could be approximated by a Boltzmann-type distribution at 5000° K. Later, they (Reference 2) used these data to compute the first-overtone photon efficiency, ξ_2; i.e., the number of overtone photons per reaction forming a NO molecule, in the low-density limit when no quenching occurs. We show that ξ_2 is (to within a few percent) independent of Datum (b), infer the limits on the fundamental-band photon efficiency, ξ_1, and obtain the initial population distribution of NO ($2 \le v \le 6$).

By starting with the differential equation for the population of the v-th vibrational level, $[NO(v)]$, assuming no vibrational deactivation of NO(v) by collisions (as justified by the observed linear variation of intensity with $[O_2]$), and dropping four radiative terms because quenching by Reaction 2 is much faster than radiative decay, we find for the steady-state conditions obtaining in the experiment that the measured emission rate of first-overtone photons from levels $2 \le v \le 6$, per O_2 molecule, can be written as:

$$(1.5 \pm 0.5) \times 10^{-6} = \frac{1}{[O_2]} \sum_{v=2}^{6} A_{v-2}^{v} [NO(v)] = \frac{k_1}{k_2} \sum_{v=2}^{6} \frac{f_v}{k_2(v) \cdot k_2} A_{v-2}^{v} \quad (1)$$

where $f_v \equiv k_1(v)/k_1$. By using $k_1 = (1.08 \pm 0.10) \times 10^{-16}$ cm^3 sec^{-1} (Reference 3), $k_2 = (2.2 \pm 0.6) \times 10^{-11}$ cm^3 sec^{-1} (Reference 4), and Datum (c), we find from Equation (1) that:

$$\sum_{}^{6} \frac{f_v}{k_2(v)/k_2} \; A_{v-2}^{v} = 0.31 \text{ sec}^{-1}. \tag{2}$$

A unique distribution of initially populated levels cannot be determined from Datum (a) alone, but we consider two extreme cases, realizing there are all possible mixes in between. For Case 1, in order for equal-population of levels to obtain: i.e., $f_v = 1/7$, we must have k_2 (v$\geq$2) $= 26.2$ k_2 (v=0)/(7 x 0.31) = 12.1 k_2 (v=0) $= 2.7 \times 10^{-10}$ cm^3 sec^{-1}, an improbably large-rate coefficient since it implies that every gas-kinetic collision between N and NO (v$\geq$2) results in a reaction. We regard Case 1 as improbable. In evaluating the Einstein coefficients, we used the harmonic oscillator approximation for the higher levels, $A_o^2 = 0.819$ sec^{-1} (Reference 5), and (as needed below) $A_o^1 = 12.6$ sec^{-1} (Reference 6).

For Case 2, if $k_2(v)$ is independent of v, what are the special values of f_v' -- called f_v' --permitted by Equation (2), if only one vibrational level with v$\geq$2 is populated? Table 1 gives the answers, computed from $f_v' = 0.31/A_{v-2}^v$, along with values of the total number of first-overtone photons per reaction, ξ_{2v}', including cascading and branching but no reaction quenching, as obtains in the low-density limit. From Table 1 we see the surprising result that ξ_{2v}' is very nearly constant, regardless of which vibrational level is populated provided Equation (2) is satisfied.

TABLE 1

v	f_v'	ξ_{2v}'	f_v
2	0.378	0.0123	0.0451
3	0.130	0.0121	0.0267
4	0.0670	0.0120	0.0160
5	0.0415	0.0119	0.0096
6	0.0285	0.0118	0.0058
		$\eta \equiv \sum f_v = 0.1032$	

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Since any set of fractional initial populations, $\{f_v\}$, satisfying Equation (2) will give essentially the same value of ξ_2, we conclude for Case 2 that Datum (a) from the experiment (Reference 1), has in fact determined ξ_2 to be approximately 0.012. This value of ξ_2 is smaller by a factor of 12 than the value resulting from the equal-population assumption, $f_v = 1/7$.

The value of 0.018 for ξ_2 obtained by Hushfar et al. (Reference 2), is larger than ours because they used $3 \times 10^{-11} / \left(1 \times 10^{-16} \right)$ for k_2 / k_1 and 111 instead of our 128 cm^{-2} atm^{-1} for the fundamental band absorption coefficient.

We also infer that the maximum possible value of ξ_1 is 1.35, based on all of the population not in level $v = 2$ being in level $v = 1$, and that the minimum value of ξ_1 is 0.15, based on all of the population not in level 6 being in level $v = 0$. These two extreme values of ξ_1 are smaller than that for the assumption $f_v = 1/7$ by the factors 2.0 and 18.

The absolute value of f_v (for Case 2) can be determined by using Datum (b) and Equation (2). For a Boltzmann-type distribution, $f_v = c \exp\left[-(\epsilon_v - \epsilon_2)/ kT_{vib} \right]$, $2 \leq v \leq 6$. For $T_{vib} = 5000°$ K, and by satisfying Equation (2), we find $c = 0.0451$ and the values for f_v given in Table 1. The corresponding extreme values of ξ_1 are now 1.2 and 0.31.

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OZONE EMISSION EXPERIMENT

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The possibility of infrared emission resulting from the chemiexcitation reaction $O + O_2 + O_2 \xrightarrow{k_1^*} O_3^*$ (00v) $+ O_2$ is to be experimentally determined, where O_3^* denotes vibrationally excited ozone. A flash photolysis experiment has been constructed and is operating. $O_2 + h\nu$ (flash lamps; Schumann-Runge) $\rightarrow O + O$ (ground state) initiates the reaction in 10 μsec; Reaction 1 occurs in 100 to 200 μsec. Absorption of 2537Å light has measured $\left[O_3\right] = 4 * 10^{14}$ cm^{-3} a few msec after the flash and thus confirmed our ability to produce [O] in this same quantity, which is sufficient for the experiment. A state-of-the-art Cu: Ge IR detector, the principal diagnostic, has been delivered and has undergone testing in our laboratory. A detectivity of $D^* = 2.4 * 10^{11}$ cm Hz$^{1/2}$watt^{-1} has been measured both by the vendor and by ourselves under conditions simulating those obtainable in the experiment. The detector operates with a cold-shielded 6 degree field-of-view, a cold filter, a cold-bias resistor, a cold MOSFET preamplifier and requires for its ultimate performance a cold background and cold window. A cold background has been engineered for the photolysis cell and is now operational. Calculations using the measured D^* indicate that a S/N of 6 should be obtainable without cooling the window if Reaction 1 produces one quanta of 10μ excitation in O_3^*. (Energetically, up to 8 quanta are possible.) Initial experiments will be conducted without cooling the detector window. Current developments are concerned with elimination of electrical pickup by the very sensitive detector from the 1000-J-flash lamp discharge. Difficulties with MOSFET source-to-drain punctures have also occurred and are being eliminated in a program of shielding and redundant protection. It is anticipated that meaningful data should be forthcoming within 6 weeks.

A subtask to measure the absorption of CO_2 laser emission by O_3 is also underway in a separate experiment. The laser has just been assembled and is now operating. Next, a grating for single-line operation will be installed in the laser cavity and controlled single-line operation confirmed before introduction of O_3 into an intracavity absorption cell.

BRIEF OUTLINE OF THE COCHISE TANK EXPERIMENT

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The total project objective is to create and exercise a new capability for experimental investigations of chemical processes which can contribute strongly to IR backgrounds of quiescent and disturbed atmospheres, but which cannot be studied satisfactorily with conventional laboratory techniques. Of primary current interest is the recombination of atomic oxygen, with molecular oxygen, which can produce highly vibrationally excited ozone and thereby constitute an important infrared background component in the 10 to 12-micron atmospheric window.

Definitive laboratory studies of this type of problem must be done at relatively low pressures (1 to 10 mTorr) in very fast and large flow systems (contact time: 1 to 10 msec) in order to eliminate energy redistribution due to surface collisions, postexcitation particle collisions, and simple radiative decay. Only under these conditions will the observed emission accurately reflect the degree and nature of the chemistry-induced excitation; significantly, these are also the constraints consistent with any attempt to do limited partial simulations of atmospheric phenomena within this program.

The research to be carried out under Project COCHISE cannot be done within existing programs, because, in the low-pressure and short-contact time regimes, any infrared emissions will be too weak to be studied with conventional laboratory instrumentation. In COCHISE, all spectrometric instrumentation will be operated at temperatures below 20° K and all other components of the experiment will operate below approximately 60° K; by severely limiting the thermal radiation background of the experiment in this manner (ten order of magnitude reduction), an improvement in detection sensitivity of five orders of magnitude will be achieved. Furthermore, since some of the three-body recombinations of most interest have appreciable negative activation energies (e.g., approx. 2 kcal/mole for both $O + O_2 + M$ and $O + NO + M$), operation at reduced temperatures is also favorable to the chemistry. Additionally, by maintaining the walls of the chemistry cell at the proper reduced temperature, those excited species which migrate to the walls will stick there (i.e., cryopumping); inasmuch as the

walls will not be in the field-of-view of the infrared spectroscopic system, surface effects will contribute nothing to the observations. In a very real sense, therefore, this will constitute a wall-less vessel.

BRIEF OUTLINE OF THE LABCEDE EXPERIMENT

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Efforts at AFCRL/Optical Physics Laboratory have recently begun to develop the facilities for the investigation of chemical and radiative phenomena resulting from the impact of 0.2 to 2 keV electrons on airlike mixtures. Interest in this phenomena stems from the X-ray absorption (60 to 90 km) and the production of electrons by a high-altitude nuclear weapon. Measurements on the emission of N_2 - O_2 mixtures followed by the addition of NO, CO, CO_2, and H_2O will be made in the infrared with diagnostic support in the ultraviolet and visible. Metastables and their populations will be determined from their characteristic emissions and reaction paths of the important species followed spectroscopically to obtain intensity, transition probabilities, energy-distribution reaction states, and fluorescent efficiencies.

The system parameters (time, size, energy, pressure, etc.) for the infrared measurements produced by electron impact will be reviewed, and the construction of the apparatus discussed. Anticipated signal levels from N_2, N_2^+, NO, H_2O, CO_2, etc. from direct excitation, chemical reaction, and energy-exchange processes have been obtained from a modified Q-chem calculation which will be presented.

The preliminary measurements of IR measurements from 50-keV electrons impacting on atmospheric species in the 1.6 to 3 μ portion of the spectrum have been performed. The measurements have been made with a cold-circular-variable filter spectrometer and the emissions attributed to $N_2(1P)$ and CO_2.

QUENCHING OF VIBRATIONALLY EXCITED N_2 BY ATOMIC OXYGEN

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and G. R. Cook

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A recently developed photoionization technique for detection of vibrationally excited nitrogen $\left(N_2^*\right)$ has been applied to study of the quenching of N_2^* by O at $300°$ K. The rate coefficient for quenching of N_2^* by 0 is found to be 3.5 ± 1.4 x 10^{-15} cm^3 sec^{-1}. The efficient vibrational relaxation previously observed in the N_2^* - 0 system in shock tubes at high temperatures and attributed to a chemical interaction persists at low temperatures. The implications of this result to upper atmospheric vibrational temperatures will be discussed.

SESSION XI

METAL OXIDES ENERGIES AND REACTION RATES

CHAIRMAN: DR. F. GILMORE. R & D ASSOCIATES

THEORETICAL STUDIES OF POTENTIAL CURVES AND
f-NUMBERS FOR DIATOMIC METAL OXIDES

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Quantum mechanical studies are now in progress at UARL for determining the electronic structure of the ground and low-lying excited states of AlO, FeO, UO and UO^+. Extensive configuration-interaction (CI) wavefunctions are constructed for the electronic states of interest. These wavefunctions yield variational estimates of the potential curves for the diatomic molecule, within the Born-Oppenheimer approximation. These wavefunctions are also used for calculations of dipole moment functions and electronic transition moments. Finally, these calculated electronic properties are combined with accurate vibration-rotation wavefunctions, (obtained from numerical solutions of the Schrödinger equation using Rydberg-Klein-Rees potential functions) to yield band-to-band f-numbers, Einstein transition probabilities and integrated band absorption coefficients.

A description of the current status of each metal oxide system under study is given below.

AlO

Extensive quantum mechanical studies have been performed for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of AlO. These theoretical studies yield an f-number of 0.012 for the strongest (0,0) transition in the blue-green (B-X) system, (Reference 1). Parallel experimental lifetime studies yield a lifetime of 129 nsec for $B^2\Sigma^+(v'=0)$ (Reference 2). This lifetime, uncorrected for the contribution of the B-A band strength, converts to an f-number of 0.021 for the (0,0) transition. A detailed analysis of the B-A band system is now in progress, but preliminary indications are that this is a very weak system. Previous experimental studies of the AlO blue-green oscillator strengths yield lifetimes about an order of magnitude greater than the values reported here (References 3 and 4).

Calculations were also performed for the integrated IR absorption coefficient AlO. The calculations at S.T.P. yield an absorption coefficient of 300 ± 100 cm^{-2} atm^{-1} for the (0,1) fundamental band. A large uncertainty is found for the absorption in the ground state due to an unfortunate sensitivity of the

calculated absorption coefficients to small changes in the dipole moment function. In a separate theoretical study (Reference 5), essentially no IR absorption is predicted from the ground $^2\Sigma^+$ state. Further theoretical studies are underway in an attempt to reduce the uncertainties in the calculations.

FeO

Extensive calculations of the low-lying electronic states of FeO have been carried out. The total study included over 300 electronic states. Symmetries ranging from $^1\Sigma^+$ to $^7\Gamma$ were examined. We find that the ground electronic state has symmetry $^5\Sigma^+$ and that this state connects diabatically to Fe ^5D + O ^1D. An avoided curve crossing with a repulsive $^5\Sigma^+$ state arising from Fe ^5D + O ^3P is evident at about 2 Å. Our calculated dissociation energy for $\chi\,^5\Sigma^+$ is ≈ 3.7 eV, in good agreement with the best experimental value (Reference 6) (3.92). The upper state of the Orange bands is $^5\Sigma^+$ and is strongly predissociated by a $^5\Pi$ state. The near infrared bands (0.67 to 1.4 μ), often called the D system, have origin in a low-lying $^5\Pi$ state which is similar in character to the low-lying B$^2\Pi$ state of AlO. A more complete theoretical study of these band systems appears to be warranted. Our calculated absorption coefficient is 300 ± 100 cm^{-2} atm^{-1} for the fundamental band, a value which appears to be typical for many of the metal oxides (LiO, AlO, FeO, BaO) which have been studied.

UO and UO$^+$

Quantum mechanical studies have been initiated on the low-lying electronic states of UO and UO$^+$. These calculations were carried out assuming L-S coupling and with an effective nuclear charge for the U-core electrons. A complete CI was carried out among the valence electrons of U$^+$ ^5I and O $\left(^3P,\,^1D,\,^1S\right)$ to insure proper limiting behavior at infinite internuclear separation. Tentatively, we find the ground state of UO$^+$ to be $^4\Pi$ but there are low-lying states of $^4\Sigma^+$ and $^6\Sigma^+$ symmetries.

The situation for UO is much more complex. Here the separated atom limits, ^5L, ^5K, ^5I, ^3I, ^5H, ^3H, ^3K, ^5G, ^3G, and ^3L, corresponding to the configuration $7s^25f^36d$ must all be included in the CI calculation. Preliminary calculations indicate that there are many low-lying bound molecular states, and that nearly continuum absorption should be realized.

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MASS SPECTROMETRIC STUDIES OF SOME GASEOUS METAL OXIDES

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Chemical reaction equilibria involving the gaseous monoxides of lithium, iron, and aluminum have been studied by Knudsen cell mass spectrometry, and the measurements have been used to derive the dissociation energies of the metal monoxides. In each instance, the reaction $M + O_2 = MO + O$ was studied, so that $D_0^0(MO)$ was measured directly against $D_0^0(O_2)$. Several other reactions involving the gaseous monoxides were studied as well, giving good internal agreement and leading to $D_0^0(MO)$ values with an accuracy of 0.1 eV or better. Similar data were obtained for the gaseous oxides FeO_2 and Al_2O. The ionization potentials of the oxides were determined by the electron-impact method, also with an accuracy on the order of 0.1 eV, and the results were used to derive the dissociation energies of the positive molecular ions. The data will be reviewed and compared with the results of other studies, including theoretical studies.

SOME INFRARED SPECTRA OF MATRIX ISOLATED URANIUM OXIDES

Stanley Abramowitz

National Bureau of Standards

The results of experiments designed to yield the vibrational frequency of uranium oxide ions in argon matrices at liquid hydrogen temperatures will be given. Some of the results obtained and given previously will be described. Some recent reactions of a clean uranium atom beam and molecular oxygen will be discussed and compared to available results obtained using Knudsen cells.

THE VIBRATIONAL SPECTRA OF URANIUM OXIDE VAPOR SPECIES

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The midinfrared spectra of UO, UO_2, and UO_3 formed by vaporization of $UO_{2 \pm x}$ and trapped in argon and krypton matrices have been obtained. A study of the spectra of the normal ^{16}O and isotopically substituted ^{18}O species, as a function of temperature and composition of the condensed uranium oxide, has led to the following assignments for ^{16}O species: $UO_2 (\nu_3) = 776.1$ cm^{-1}, $UO_3 (\nu_3) = 852.5$ cm^{-1}, and $UO_3 (\nu_1) = 745.6$ cm^{-1}. On the basis of the isotopic data, a bond angle for UO_2 of $180 + 0 - 10°$ and a value of $UO_2 (\nu_1)$ of 765.4 cm^{-1} have been calculated. Calculations of peak intensities for the various UO_2 isotopes, based on the frequency assignments reported, agree well with observed intensities. The observation of a strong peak at 820.0 cm^{-1} above $U-UO_{2-x}$ suggests its assignment to UO.

(*) RADIATION FROM SHOCK-HEATED
URANIUM-OXYGEN MIXTURES (*)

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Calspan Corporation

This paper describes the results obtained to date in a research program designed to measure absolute spectral radiances from uranium-oxygen mixtures. The measurements are made under controlled conditions of temperature and species concentrations and include infrared data between 8 and 14 μm. The objective of the program is to provide a sufficiently broad data base to permit the specification of equilibrium IR radiation from uranium oxides for the conditions of interest to ARPA objectives. The experiment involves the production of an aerosol of uranium in a controlled mixture of oxygen and inert gas such as argon. This aerosol is shock heated, undergoes vaporization and provides a gaseous mixture of U, O_2, and argon at high, equilibrium temperatures. The data comprise absolute measured spectral radiances over wavelength regions of interest. The parameters of the experiment are the temperature relative U/O_2 ratios and wavelength range and resolution. The experimental method will be described briefly and results to date presented. They include data demonstrating the applicability of the technique as well as preliminary radiance measurements near 12 μm. Evidence for identifying the radiation with a molecular oxide source is discussed.

METAL ATOM OXIDATION AND RELEASE STUDIES

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Sybron Corporation

Concentrations of metal oxides in nuclear detonation-induced environments must be known to predict the behavior of certain defensive systems. We have approached this problem in two ways: (1) via laboratory determinations of the (temperature-dependent) rate coefficients of metal atom (particularly Fe and Al) oxidation, suitable for use in modeling studies and computer code formulations, and (2) by experimentally and theoretically investigating means for releasing metal atoms in the upper atmosphere for studying in situ the formation and destruction of metal oxides.

The apparatus used in the rate coefficient determinations is a heated cylindrical fast-flow reactor, suitable for studies of the kinetics of gaseous species at temperatures up to 2000 K (Reference 1). The reactor and vacuum furnace jacket have ports for optical observations. The metal is vaporized and entrained in an inert carrier gas stream: O_2 is introduced into this gas stream at concentrations several orders of magnitude larger than that of the metal atoms. Rate coefficients are obtained from the observed variation in the relative metal atom concentration, (measured in absorption) as a function of reaction time, O_2 concentration, total pressure, and temperature. The gas phase Fe/O_2 reaction at 1600 K has been determined (Reference 2) to be $Fe + O_2 \rightarrow FeO + O(1)$ with a rate coefficient K_1 of $(3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1}. The estimated T-dependent rate coefficient is $k_1(T) = 2.0 \times 10^{-10} \exp(-20,000/RT)$ ml molecule^{-1} sec^{-1}. The $Al + O_2 \rightarrow AlO + O(2)$ reaction is currently being studied. Data obtained over an as yet limited range of reaction conditions yield a rate coefficient k_2 of 4×10^{-11} m. molecule^{-1} sec^{-1} at 1400 K. Future experiments will include the experimental determination of the T-dependence of the rate coefficients of reactions (1) and (2).

AlO and FeO have been produced in the upper atmosphere (by AFCRL for example) by release of trimethyl aluminum and $Fe(CO)_5$, respectively. Additional release and observation methods are needed for evaluation of nuclear detonation effects. Releases of metal atoms would allow a study of upper

atmospheric metal oxide formation and subsequent phenomenology. Several methods for releases of metal atoms are under consideration and will be discussed.

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ASSOCIATIVE IONIZATION IN URANIUM-OXYGEN COLLISIONS

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This report gives the present status of experiments on associative ion in collisions of uranium atoms with oxygen atoms and molecules. Both processes

$$U + O \rightarrow UO^+ + e \qquad (1)$$

and

$$U + O_2 \rightarrow UO_2^+ + e \qquad (2)$$

have been observed in crossed beam experiments at thermal (i.e., hot enough to vaporize uranium) energy. In the first experiment, which was a triple crossed beam experiment involving uranium atoms, oxygen atoms and molecules, and electrons (for diagnosis of the uranium and oxygen beams), the ratio of cross sections, Q_1/Q_2, for processes (1) and (2), was determined to be 97 ± 20. In the second experiment, an absolute measurement of Q_2 is being performed by passing an uranium beam through static oxygen gas in a manner analogous to the condenser method of measuring charge-transfer cross sections. A preliminary value of $Q_2 = 2.65 \times 10^{-17}$ cm^2 has been obtained, but this value is subject to change as possible systematic errors are assessed.

This paper describes both experiments, discusses the physics of the processes and describes planned future studies on associative ionization and other uranium atom reactions.

EXPERIMENTAL RATE MEASUREMENTS IN THE
# URANIUM-OXYGEN SYSTEM

John D. McKinley

National Bureau of Standards

A molecular beam containing uranium and uranium oxides is exposed to room temperature oxygen at concentrations of 10^{11} - 10^{12} molecules cm^{-3}. The beam consists initially of U, UO, and UO_2 at concentration of about 10^8 molecules cm^{-3}. Chemical reactions with oxygen lead to changes in the beam composition. Mass spectrometric analysis of the beam, before and after oxygen exposures, serves to identify these reactions and permits an estimate to be made of their rates. Reaction of U to form UO_2^+, and of UO and UO_2 to form UO_3 have been observed. The evidence is consistent with the view that these processes are very rapid; the rates being comparable to the bimolecular collision frequencies. This suggests that at higher oxygen pressures, conversion of uranium to its oxides would occur in a few milliseconds.

METAL ION AND ATOM REACTIONS IN OXYGEN

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TRW Systems Group

Reactions of uranium, thorium, aluminum, and iron with oxygen have been examined. The energy range for metal ions or atoms is from 1 eV to 100 eV. Target oxygen molecules have been provided in either a low density $\left(\sim 10^{11}\right.$ molecules/cm^3) "extended" (1 meter length) target or a pulsed nozzle high-density beam $\left(\sim 10^{15}\right.$ molecules/cm^3, 3 centimeter thickness). Metal ions or atoms are produced by focusing the output of a Q-switched ruby laser (1 to 2 joules, 50 nanoseconds) upon the surface of the host metal. Diagnosis of the resulting metal ion plasma has utilized Faraday Cups, Langmuir probes, and Quadrupole Mass Analyzers. Metal particle energy is determined by particle time-of-flight from the surface to the detectors. Burst dynamics indicate the formation of a Maxwellian ion velocity distribution through a collisional phase followed by a free expansion of the ion cloud. Electron temperatures in the expanding cloud appear to be at extremely low values. Leading portions of the ion flow appear to be highly laminar, while trailing portions of the flow may have some particle scattering during the cloud expansion. For uranium and thorium, particle dynamics allow a total reaction cross section to be determined. Data will be presented for

$$U^+ + O_2 \rightarrow UO^+ + O$$

and

$$Th^+ + O_2 \rightarrow ThO^+ + O$$
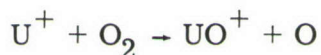
for the energy range 1 to 100 eV. At increased O_2 density in the gas targets, formation of UO_2^+ is observed. Estimates of cross sections for the dioxide formation will be given. For reactions of Al^+ and Fe^+ with oxygen, particle dynamics require measurements of differential reaction cross sections. Values of $d\sigma/d\Omega$ will be compared to gas kinetic scattering cross sections of Fe^+ and Al^+ on O_2. Reaction of neutral uranium with oxygen has also been observed in the 1 to 100 eV energy range. Estimates of reaction cross sections for

$$U + O_2 \rightarrow UO + O$$

will be given.

OXIDATION OF THORIUM IN A LASER BLOWOFF EXPERIMENT

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The oxidation of metal vapors is being studied by combining laser vaporization techniques and time-of-flight mass spectrometry. Metal atoms are generated by laser vaporization and further oxidized by oxygen. Mass spectrometric analysis of the metal/metal oxide ratio as a function of oxygen pressure and reaction time provides information on mechanisms and rates of oxidation.

Mass spectrometric analysis of the vaporization products (as a function of power input) as well as preliminary data on reaction products will be presented for the oxidation of thorium.

SESSION XII

METAL RELEASES

CHAIRMAN: DR. F. GILMORE, R & D ASSOCIATES

A THEORETICAL COMPARISON OF METAL RELEASES
WITH NUCLEAR BURSTS

F. R. Gilmore

R & D Associates

Metal releases by chemical or explosive means produce initial clouds of
neutral metal atoms (or sometimes metal oxides), usually mixed with hydrogen,
carbon, and other species, which later become diluted with ambient air. In
contrast, nuclear bursts produce metal vapors which initially are highly ionized
and expand with velocities corresponding to kilovolt energies per ion, and
generally mix with many times as much air before they slow down and cool
enough to form molecules. At low altitudes the metals deionize and thermalize
rapidly, so that the ordinary metal-air reactions can occur, but at higher alti-
tudes ionic reactions are important, while at very high altitudes reactions at
eV or keV energies are also significant. Moreover, even at low altitudes the
air into which these metals mix has been disturbed by X-rays, beta rays,
ultraviolet radiation, etc. from the nuclear burst, so that it generally contains
above-ambient amounts of O, NO, O_3, and excited species that may effect the
chemistry.

It follows that the early chemistry of metal releases is significantly different
from that of high-altitude nuclear bursts. Only at rather late times, after the
bomb debris has come to rest and been dispersed into relatively undisturbed air,
may it be approximately simulated by a metal release, provided that its earlier
history did not leave it in a permanently different state. Thus, a release pro-
ducing a metal oxide (by any means) probably will not indicate whether the same
metal in a nuclear weapon will become oxidized, but if it does, the release can
reveal the subsequent late-time fate of the oxide. For example, the recent
AFCRL releases of iron and nickel carbonyl produced FeO and NiO which were
then rapidly converted to atomic Fe and Ni, presumably by the exothermic
reaction $FeO + O \rightarrow Fe + O_2$ (and similarly for Ni). These results suggest
that these oxides, and other metal monoxides having a dissociation energy less
than O_2, like LiO, MgO, and CuO, play a minor role in nuclear bursts.

Recent laboratory measurements answer some of the questions concerning
early-time metal-air reactions. This progress increases the priority of

questions concerning late-time reactions which might be answered by metal or metal-oxide releases.

There remain a number of early-time questions which can be more readily answered by laboratory experiments than by atmospheric releases. Besides several reactions which are currently under laboratory investigation, these include the cross section for charge transfer between U and O^+ below 0.5 eV, the rates of reaction of Ti and Ti^+ with O_2, and several cross sections connected with the final fate of fast metal ions stopped in air. The latter might be attacked by a laboratory simulation experiment in which kilovolt Al^+ ions are stopped in air at a density low enough to minimize three-body reactions. The products $\left(Al, Al^+, AlO, \text{ and } AlO^+\right)$ could be detected at low concentrations by laser-excited fluorescence.

METAL OXIDE RELEASES IN THE UPPER ATMOSPHERE

G. T. Best, C. A. Forsberg, D. Golomb,
N. W. Rosenberg, and W. K. Vickery
Air Force Cambridge Research Laboratories

The release of iron carbonyl in the upper atmosphere has been recently reported [previous HANE symposium and J. Geophys. Res. 77, 1677 (1972)]. It was found that FeO rapidly formed in the altitude region 130 to 150 km. In a sunlit release, the FeO bands appeared both in fluorescence and in chemiluminescence. Within a few seconds the orange FeO bands disappeared, and only a bluish afterglow remained. With the equipment available in that experiment it was not possible to determine if this afterglow was due to resonance scattering by Fe(I) atoms. The experiment has been repeated in May 1972 with ultraviolet optics including a 372 nm filter-camera, from which we found that the blue glow is due to the Fe(I) resonance line at 372 nm and that it persists for many minutes. Additional confirming evidence was obtained using a new reflective-grating UV slitless spectrograph which showed that the 372 nm radiation is the only persistent spectral feature in the afterglow. The release (like the experiment reported earlier) terminated with an expanding halo, which was more intense in the red than in the blue, and which we attribute to solar scattering by particulate condensed matter.

A release of nickel tetracarbonyl had a similar appearance, except that only the headglow was visible and photographable. The slitless spectrum showed only a relatively structure-free continuum, which is expected since the strongest system (a - X) of NiO lies at wavelengths beyond 790 nm. However, a ~ 2 nm band-pass filter centered at 614 nm showed the headglow while one at 611 nm did not. It is probable that the two strongest bands of the b - X system afterglow was visible in the NC release, probably because the longest wavelength resonance lines of Ni(I) are at 352.4 and 343.7 nm where the atmospheric transmission is about half that at 372 nm, the wavelength of the Fe(I) resonance line.

The dissociation energy of NiO and FeO are similar, about 4.3 eV, and both oxides appear to be reduced to metallic atoms in the atomic-oxygen rich environment of the upper atmosphere, $MO + O \rightarrow M + O_2$. Apparently, only metal oxides with dissociation energies greater than O_2 are likely to persist above 90 km, such as AlO and oxides of some heavy metals.

METAL VAPORIZATION BY SHOCK HEATING

Robert A. Fluegge

Calspan Corporation

An experimental and analytical program that will determine the parameters that control vaporization processes under shock-heating conditions is being conducted at the Cornell Aeronautical Laboratory. It is under ARPA sponsorship. The program has just began, but the overall goals and experimental approach will be described along with a summary of similar work that has been performed at the Max Planck Institute.

CONFERENCE CONCLUDING REMARKS

Charles A. Blank
Defense Nuclear Agency

The technical and general comments made by the authors are, in large measure. included in the Addendum of this conference document. This Addendum was prepared in final form by Dr. F. Gilmore. It summarizes to a more detailed extent the brief remarks in this closing paper, coupled with pertinent remarks and tentative conclusions reached by those members of the ROSCOE Chemistry Research Unit as a result of the foregoing papers and comments presented during this conference.

ADDENDUM

SUMMARY OF THE ROSCOE CHEMISTRY RESEARCH

UNIT MEETING OF 15 SEPTEMBER 1972

SUMMARY OF THE ROSCOE CHEMISTRY RESEARCH
UNIT MEETING OF 15 SEPTEMBER 1972 †

F. Gilmore

R & D Associates

and

C. A. Blank

Headquarters, Defense Nuclear Agency

1. A meeting of the ROSCOE Chemistry Research Unit was held at Headquarters, Defense Nuclear Agency (HQDNA), Arlington, Virginia on Friday, 15 September 1972, from 0900 to 1600 hours. The objectives of the meeting were:

    a. To briefly review the present overall status of the ROSCOE effort.

    b. To summarize specific progress toward fulfillment of the ROSCOE chemistry requirements, as set forth in the previous meeting.

    c. To identify and elucidate any new ROSCOE chemistry requirements, or areas where increased effort is required on a priority basis.

    d. To produce an updated version of the priority listing of specific, unfulfilled ROSCOE chemistry requirements.

    e. To discuss other matters of importance and relevance to the future activities of this research unit.

2. The program began with a summary by P. Fleming (DNA) of the DNA-sponsored ROSCOE effort. ROSCOE is a Radar and Optical Systems Code to be developed over the next 3 years by Science Applications, Inc. (SAI) (phenomenology portions) and General Research Corporation (GRC) (systems portions). It is intended that the code accuracy be "balanced" between radar and optical effects, and between the different atmospheric regions of interest. H. C. Fitz (DNA) added that DNA is also supporting a HARC code effort at Mission Research Corporation (MRC). This code, the groundwork for which has already been laid at MRC under Bell Telephone Laboratories (BTL) sponsorship, will take a more physical approach to phenomenology problems as compared to the modelling approach of ROSCOE.

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† Includes technical information developed at the DNA-sponsored "Second Conference on Applications of Chemistry to Nuclear Weapons Effects", 12-14 September 1972, Institute for Defense Analysis (IDA) auditorium, Washington, D.C.

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3. C. A. Blank (DNA) announced that the Reaction Rate Handbook is in press, and he hoped it would be in the mail soon. T. Baurer, General Electric Space Sciences Laboratory (GE SSL) stated that two additional chapters and a list of errata would be distributed soon thereafter.

4. F. Gilmore (RDA) announced that, since the meeting immediately followed the DNA Chemistry Conference, a number of laboratory reaction-rate investigators were present, so it seemed appropriate to spend most of the time on updating the reaction-rate requirements for ROSCOE and for the more-detailed chemistry codes used to derive and check the models in ROSCOE. Accordingly, several weapons-effects workers had been asked to summarize the additional reaction-rate data that they felt were needed in order to predict radar and optical effects in various atmospheric regions.

5. F. Niles, Ballistic Research Laboratories (BRL) discussed the data needed for low-altitude weapons effects (0 to 30 km):

   I. Negative Species

      A. Identity of important negative species $\left(\text{probably e, } O_2^-, CO_3^- \cdot nH_2O, CO_4^- \cdot nH_2O, NO_3^- \cdot nH_2O\right)$.

      B. Formation processes and rate constants.

      C. Photodetachment cross sections.

   II. Positive Ions

      A. Identity $\left(\text{probably } O_2^+, O_2^+ \cdot H_2O, H^+ \cdot nH_2O\right)$.

      B. Dissociation of clustered ions by reaction with O or $O_2\left(^1\Delta\right)$.

      C. Photodissociation of clustered ions.

  III. Clustered Ion-Ion Recombination

      A. Rate constants.

      B. Identity of neutral products.

Measurements around 250° K are especially needed, but measurements of the thermal breakup of clusters at temperatures up to about 1000° K are also desired for shock-heating problems.

In the discussion that followed, Lieutenant Colonel W. Whitaker, USAF stated that determination of the neutral products of reactions like $H^+ \cdot 5H_2O + NO_3^- \cdot nH_2O$ is important, but nobody is really working on such questions. F. Gilmore mentioned that H. Foley and M. Ruderman (IDA P-894, August 1972) argued that the low-altitude megaton nuclear tests in the 1961-1962 injected as much NO_x into the stratosphere as would a fleet of SST's; hence, many of the

reactions just discussed may also be pertinent to the stratospheric polution problem.

6.   F. Hudson (Sandia) listed over 30 neutral species produced in the 20 to 30 km region by solar UV. Besides the usual nitrogen and oxygen species, these included 5 metastable excited states, and species like N_2O_5, HO_2, HNO_3, and CH_3O. Some species last only ~0.1 sec, but others have a much longer lifetime. Many of the pertinent cross sections or even the reaction products are not known.

7.   F. Niles began the discussion of the 30 to 90 km region by mentioning the need for determining the products of the recombination $H^+.nH_2O + e$, and also the importance of associative detachment. F. Gilmore stated that we still needed more information on most of the reactions listed by him at the December 1971 Chemistry Research Unit meeting. (Many of these involve the state of excitation of reaction products, which are experimentally difficult to determine.) Especially important is the ozone chemiluminescence (i.e., vibrational excitation when formed), which is being investigated at AVCO, but at high pressures and hence stronger quenching than in the upper atmosphere. Also very important is the NO chemiluminescence $(from\ N + O_2)$. This has been measured at Air Force Cambridge Research Laboratories (AFCRL), but only for ground-state N atoms, and only under conditions such that chemical quenching of the excited NO is more important then in the upper atmosphere.

8.   Major W. Whitaker emphasized the need for data that can go immediately into weapons effects codes. This includes the ambient atmospheric concentrations of H_2O, OH, HNO_3, and perhaps HO_2 (the ambient concentration of O_3 is quite well established). Also needed are quantitative yields for the species N, N_2^+, N^+, O_2^+, $N(^2D)$, etc., produced directly when air is bombarded by gammas, neutrons, debris, UV (including nonionizing UV), etc. For these processes and for the "fast chemistry" like $N_2^+ + e \rightarrow N + N^*$, it is important to learn the excitation of the products. Electronic excitation can affect subsequent reaction rates, while vibrational excitation can lead directly to infrared emission. Quenching-rate constants are also required, and radiative decay rates (f-numbers). Some of the quenching rates being measured by laser scientists may be relevant to nuclear problems.

9.   A member of the group asked that standardized rate constants be made available on punched cards. A brief discussion of the desirability and preferred format ensued. M. Bortner (GE SSL) stated that the forthcoming edition of the Reaction Rate Handbook would contain a large compilation of rate constants.

10. R. Lowen (SAI) discussed the region above 90 km. He said that more information is needed on the details of the slowing down of fast electrons and heavy particles. These include the energy partition in charge exchange, large-angle scattering, and knock-on reactions. For UV fireball problems it would be good to have a standard set of cross sections.

It was suggested that R. Huffman (AFCRL), as a measurer of UV absorption cross sections, and D. Hamlin (SAI), as a user, get together to compile a table of the important values. A. Phelps, Joint Institute for Laboratory Astrophysics (JILA), added that L. Kieffer, (JILA) and R. Hudson, National Aeronautics and Space Administration (NASA), Houston, were also measuring UV cross sections; JILA is compiling some on punched cards.

11. J. Cooper, National Bureau of Standards (NBS) led the discussion on electron-ion emission processes in air plasmas. He and others concluded that free-free on ions is in good shape, but free-free on neutral atoms could use more work, as could free-bound on ions. Free-bound on neutrals (to form negative ions) is controversial, but for nitrogen and oxygen probably does not extend into the LWIR. Bound-bound is dominant in several practical situations and definitely needs more theoretical and experimental work. Some theoretical calculations are being made by J. Davis (SAI).

12. It was suggested that since $O_2\left(^1\Delta\right)$ is very prevalent, transfer of its energy to vibrational excitation of CO_2, O_3, or NO_2 might be important. Also, since no reasonable explanation of the large amounts of NO observed in some auroras is known, further auroral work by DNA is desirable, together with global (partial simulation) experiments.

13. F. Gilmore discussed the important metal oxide reactions. Rate constants at upper-atmospheric temperatures are needed for reactions like

$$Al + O_2 \rightarrow AlO + O$$
$$U + O_2 \rightarrow UO + O$$

At these and somewhat higher temperatures, data are needed for

$$U + O^+ \rightarrow U^+ + O$$

It should also be determined whether the reaction

$$Ti + O \rightarrow TiO^+ + e$$

will occur at atmospheric temperatures.

The wavelengths of the vibrational bands of UO^+, UO_2^+, and TiO^+ (if the above reaction goes) are needed, and the controversy about the UO and UO_2 wavelengths needs to be resolved. The vibrational and electronic f-numbers for these molecules are also required.

An important question which might be resolved by a global experiment concerns the final products (ions, atoms, and oxides) when fast debris ions (especially aluminum ions) are stopped in low-density air. Titanium and silicon are also of some interest in this connection.

The rapid disappearance of FeO when produced in the upper atmosphere by rocket releases suggests that a lower priority be assigned to investigating reactions involving iron, and those involving metals like lithium, magnesium and copper that like iron have monoxide dissociation energies less than that of O_2.

A very important and little-investigated question concerns the further oxidation of the metal monoxides, involving reactions such as

$$AlO + O_2 \rightarrow AlO_2 + O$$

$$UO + O_2 \rightarrow UO_2 + O$$
$$UO^+ + O_2 \rightarrow UO_2^+ + O$$
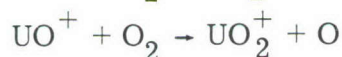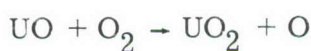
Thermodynamic data on these gaseous dioxides (or any higher oxides) would be helpful here.

Another reaction that may be important is

$$UO^+ + N \rightarrow U^+ + NO.$$

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