

STUDIES OF ATMOSPHERIC PROCESSES

by

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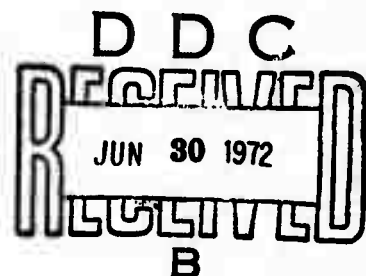
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13. ABSTRACT

The research described in this report is aimed at characterizing the non-equilibrium flow and coupled chemistry associated with the interaction of rocket exhaust effluents in the upper atmosphere. Several aspects of current study should be noted. Although continuum fluid descriptions based on the Navier-Stokes equations are valid at low altitudes, at high altitudes rarified effects must be considered. To investigate this transition and the ultimate analytical modeling of rarified flows, a Monte Carlo technique applied to a Boltzmann equation formulation is being studied.

The major observable from rocket exhaust-atmospheric interactions is radiation in various wavelength regions. To understand the origin of this emission we have focused attention on the emissions as generated from the exothermicity of chemical reactions involving unburned fuel species and O and OH radicals.

Lastly, in order to characterize the non-equilibrium chemistry in expanding gas flow fields, a detailed knowledge of relaxation processes must be obtained. Together with available information, both theoretical calculations and laboratory measurements are herein described to characterize the relaxation processes pertinent to expanding combustion products in a rarified atmosphere.

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The research described in this report is aimed at characterizing the non-equilibrium flow and coupled chemistry associated with the interaction of rocket exhaust effluents in the upper atmosphere. Several aspects of the current study should be noted. Although continuum fluid descriptions based on the Navier-Stokes equations are valid at low altitudes, at high altitudes rarified effects must be considered. To investigate this transition and the ultimate analytical modeling of rarified flows, a Monte Carlo technique applied to a Boltzmann equation formulation is being studied. The technique is described in this report, together with the progress to date.

The major observable from rocket exhaust-atmospheric interactions is radiation in various wavelength regions. To understand the origin of this emission we have focused attention on the emissions as generated from the exothermicity of chemical reactions involving unburned fuel species and O and OH radicals. These experimental studies have shown significant emissions, particularly in the infrared, as a result of direct product vibrational excitation of such species as OH, H<sub>2</sub>O and CO<sub>2</sub>. The specific measurements and results are described in Section II of this report.

Lastly, in order to characterize the non-equilibrium chemistry in expanding gas flow fields, a detailed knowledge of relaxation processes must be obtained. Together with available information, both theoretical calculations and laboratory measurements are herein described to characterize the relaxation processes pertinent to expanding combustion products in a rarified atmosphere.

## PREFACE

The research described in this report falls into four main categories, identified in the contractual work statement as follows:

- a) Calculate the continuum flow structure and rate chemistry of high altitude plumes.
- b) Calculate the vibrational excitation cross-sections for plume relevant species using available interaction potential data.
- c) Measure the quantum yields in the infrared region for the chemi-excitation involving O or OH and plume species.
- d) Measure the inter-molecular potential between atomic oxygen and various plume species as an input to the calculation of vibrational excitation cross sections.

Items (a) and (b) are discussed in Section I, item (c) in Section II, and item (d) in Section III.

TABLE OF CONTENTS

	page
ABSTRACT	i
PREFACE	ii
SECTION I	1
SECTION II	20
SECTION III	36
CONTRIBUTORS TO RESEARCH	37
REPORTS AND PAPERS	38

III a

## SECTION I

### Fluid dynamics

In this portion of the research we are concerned with developing and testing procedures for computing the flow fields of high-altitude rocket exhaust plumes and of atmospheric releases which may be of interest in connection with simulations of plume effects. The major portion of an exhaust plume from a typical large rocket (thrust about  $10^5$  lb) is in a continuum flow regime at altitudes below about 160 km. At altitudes below about 110-120 km., the mixing of the exhaust gases with air is turbulent. At higher altitudes a reverse transition occurs, and the plume becomes essentially laminar, although developing instabilities may persist for a few seconds. At these altitudes the Navier-Stokes equations are presumed to be sufficient to describe local conditions in the exhaust plume flow field. Procedures for solving these equations for thrusting plumes with zero angle of attack are available as the result of previous investigations<sup>1,2</sup> and exemplificative calculations are available<sup>3</sup>. Under the current contract, work has been directed at examining the deviations from this description at altitudes where rarefaction effects become important, and also at developing some comparisons with recent experimental data<sup>4</sup>. The procedures for examining rarefaction effects have been formulated and coded for computer solution, but have as yet produced no significant results. The comparison with experiment has just been initiated.

To describe rarefaction effects, we are making use of an ingenious and physically appealing approach to numerical solution of the Boltzmann equation developed by Bird<sup>5</sup>. The approach used is reminiscent of the molecular dynamics studies of Alder and Wainwright<sup>6</sup>, in that the solution is developed as the solution to a Liouville equation for a small sample of

test particles which represent the actual particles in the real situation. Alder and Wainwright evaluated the macroscopic properties of their systems by computing in detail the microscopic motions of an assembly of molecules with prescribed intermolecular forces. Macroscopic properties were evaluated by averaging over a number of realizations of the microscopic system. The power of available computers (this work was performed in the 1950's) and the necessity for following the motion in detail, even during collisions where rapid changes in velocity occur, limited the scope of Alder and Wainwright's work primarily to consideration of phase transitions in systems of two space dimensions, and to a small sample size.

Bird's approach is similar to that of Alder and Wainwright, in that the motion of a set of test particles is followed in detail between collisions, but differs in that collisions are not evaluated in detail. Instead, Bird assumes that collisions are very short-lived on the time scale of interest for the overall solution, and evaluates their effects by a random sampling procedure or Monte Carlo technique. (He calls his procedure the "Monte Carlo direct simulation method.") The procedure is best illustrated by an example.

Suppose that we wish to calculate conditions in a rarefied gas in a region lying within a bounding surface at which the state of the gas (i.e., the local density and velocity distribution function) is prescribed. The region within the bounding surface is divided into a number of cells whose dimensions are of the order of a mean free path. Initial conditions are prescribed in each cell, and each is assigned a set of particles representing the gas molecules. The number of these particles in each cell depends upon the assigned density. Their positions within the cell are assigned at random, and their velocities are chosen by a random sampling procedure consistent with the initially assigned velocity distribution. The motion of these particles is then followed over a succession of time steps.

At the beginning of each time step, changes in the velocities of the individual particles due to collisions are evaluated. A particle is selected at random from those in a given cell. A second particle is chosen at random from the same cell as the first. This pair of particles is either assumed to collide or assumed not to collide; the probability of collision is proportional to the relative velocity of the collision partners. If the pair are to collide, a set of collision parameters is chosen at random and the resulting new velocities after this collision are evaluated. The colliding partners are assigned these new velocities. A new set of collision partners is then chosen in that cell, and the calculation of collisions is carried on in this fashion until a number appropriate to the local collision frequency and the time step have occurred. One then proceeds to the next cell and repeats this process. When an appropriate number of collisions in each cell have been evaluated, all the particles are moved through a distance given by the product of their velocities and the time step. If a particle crosses a cell boundary, it is removed from the calculation. New particles enter the calculation at random from points on the boundary at an average rate and with properties determined from the local boundary conditions. The calculation of collisions, new positions, particle losses, and particle gains is repeated at each time step.

Periodically, the calculation is sampled. The density in a cell is proportional to the number of test particles it contains and inversely proportional to its volume. The velocity distribution function is developed as a histogram of the velocities of the test particles. No information is requested on a scale smaller than the cell size.

Two kinds of problems can be treated with this method. Steady rarefied flows can be computed by imposing constant boundary conditions and allowing the steady-state solution to evolve as the long-time limit of a time-dependent calculation. In any particular sample, the deviation of the density and velocity distribution from their average values may be large; more correct values are obtained by time-averaging these properties in each cell after a (statistically) steady state has been attained. Unsteady flows are treated as time-dependent calculations, and the scatter of the results is reduced by averaging over a number of successive calculations for the same problem.

This procedure was originally applied by Bird to calculating flow conditions in shock waves and to calculations of drag coefficients in the transition flow regime. It has been used by Vogenitz, et al.<sup>7,8</sup> for calculating drag coefficients on high-altitude bodies and to investigate some aspects of the transition from continuum to rarefied flow on simple shapes. The procedure can be regarded as an algorithm for solving the Boltzmann equation. The arguments for regarding it as such have been put forward by Bird in a recent paper. Basically, the procedure gives one all the information which one asks from the Boltzmann equation to an accuracy which depends upon the sample size, including the number of test particles and the length of the interval over which a time average is taken. The random sampling of collisions is consistent with the level of information contained in solutions to the Boltzmann equation so long as this sampling is done in a way consistent with collision probabilities in the real flow being simulated.

We are in the process of adapting Bird's procedure to calculating flows in high-altitude atmospheric releases and (in the small-disturbances approximation) to rocket exhaust plumes. The procedure will ultimately be used as a time-dependent

calculation in one space and two velocity dimensions. (At the present time, the applications have been limited to steady-state flows.) A computer code has been prepared to evaluate the Monte Carlo solution of rarefied flow problems. The code in its current form is described below. Following this description we discuss planned improvements which will allow us to investigate upper-atmosphere releases and chemical reactions.

We initiate the calculation by specifying cell boundary positions along the x axis. The cell dimensions are currently selected to make them of the order of the expected mean free path in that location after the calculation has achieved the statistically steady state. Each cell is assigned an initial temperature, number density, and mean velocities parallel and transverse to the x axis. The calculation assigns to each cell a number of particles proportional to the assumed number density. The particles are located at random between the boundaries of the cell. The code assigns these positions by calling a random number generator subroutine (RANDU on the IBM 360) which produces a random number between 0 and 1; the position is thus

$$x_p = x_1 + R(x_2 - x_1)$$

where  $x_2$  and  $x_1$  are the upper and lower boundaries of the cell and  $R$  is the random number. The initial velocities assigned are selected at random in a manner consistent with a Maxwellian distribution at the local temperature and with the mean velocities. Thus if the local temperature is  $T$  and the mean velocity is  $\vec{u} = \hat{i}u_x + \hat{j}u_y + \hat{k}u_z$ , the velocities of the particles may be assigned by using the IBM subroutine GAUSS, which produces random numbers with a Gaussian distribution about a specified mean value with a specified standard deviation - in this case,  $\sigma^2 = kT/m$ .

The temperatures and velocities outside of the first and last cells in the calculation are assumed constant. These boundary conditions complete the specification of the problem. The location of the boundaries is chosen far enough from the region of interest so that their effects are minimal. (For example, consider a normal shock wave. Here we may assign at the upstream boundary  $T_1$ ,  $\rho_1$ , and  $u_1$ , and at the downstream boundary  $T_2$ ,  $\rho_2$ , and  $u_2$  according to the Rankine-Hugoniot relations. If the boundaries are chosen too close together, the shock wave will be distorted. As the boundaries are moved further apart, the solution approaches more closely the solution obtained when the boundary conditions are imposed only at great distances from the shock. A reasonable compromise between computation time and accuracy is usually necessary.)

The calculation is initiated by calculating collisions in the first cell. A "molecule" is chosen at random from those in the cell, and a second molecule is also selected at random. The probability that these two molecules will collide is proportional to their relative velocity, which can be determined from the assigned velocity components. Thus if

$$|v_r| > v_0 R,$$

where  $v_0$  is a large velocity and  $R$  a random number, the pair is allowed to collide. If not, a second pair is chosen and the process is repeated. When a pair has been selected, the collision dynamics are calculated for a randomly selected impact parameter.

In the current version of the code, a hard-sphere potential has been chosen for simplicity. Since the scattering of hard spheres is isotropic, the orientation of the new relative velocity is a random function of  $\theta$  and  $\phi$  on the unit sphere. New velocity vectors relative to the center of mass for each particle can be calculated in terms of two random numbers,  $R_1$  and  $R_2$ , by setting

$$\varphi = 2\pi R_1$$

and

$$\sin \theta = 4R_2(1 - R_2)$$

and calculating new velocity components

$$v_x = v_{cm,x} \pm \frac{1}{2}v_r \sin \theta \cos \varphi$$

$$v_y = v_{cm,y} \pm \frac{1}{2}v_r \sin \theta \cos \varphi$$

$$v_z = v_{cm,z} \pm \frac{1}{2}v_r \cos \theta$$

where the + sign is chosen for one particle and the - sign for the other.

At each collision in a particular cell a time counter  $t_c$  is advanced by the amount

$$\delta t_c = 2/(N_i \pi a_0^2 n_i v_r)$$

where  $n_i$  is the number density in the  $i^{\text{th}}$  cell,  $N_i$  is the actual number of particles in the simulation calculation, and  $\pi a_0^2$  is the collision cross-section. The calculation of collisions in the cell is continued until the time counter  $t_c$  exceeds  $t_n$ , a pre-selected value which is small compared to the mean collision time. (In practice, we examine the chances of  $t_c$  exceeding  $t_n$  before each collision. If  $t_c + \delta t_c > t_n$ , we allow the final collision if

$$\frac{t_n - t_c}{\delta t_c} > R$$

and disallow it otherwise.) When  $t_c$  exceeds  $t_n$ , the calculation proceeds to the next cell.

After all collisions have been calculated, in all cells, each particle is moved through a distance

$$\delta x_i = v_{x,i} t_n$$

If the new value of  $x_i$  lies within another cell, the particle is removed from the list of particles contained in the cell it left and added to the list of particles contained in the cell it entered. If the particle has crossed one of the boundaries, it is removed from the calculation.

New particles are allowed to enter the calculation from upstream and downstream, using a procedure developed by Haviland<sup>9</sup>. The number flow of particles into the region of calculation across the upstream boundary is

$$\dot{n}_1 = \int_0^{\infty} dv_x v_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z f_1(v_x, v_y, v_z)$$

where  $f_1$  is the velocity distribution function imposed at the upstream boundary. In our calculation the velocity distribution is currently a Maxwellian about the mean velocity  $U_1$ , so that

$$\dot{n}_1 = \int_0^{\infty} dv_x v_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \frac{n_1}{\pi^{3/2} c_1^3} e^{-\frac{(v_x - U_1)^2 + v_y^2 + v_z^2}{c_1^2}}$$

where  $c_1 = (2kT_1/m)^{1/2}$ , and  $n_1$  is the number density. The integrals are easily evaluated to give

$$\dot{n}_1 = n_1 c_1 \left[ \frac{1}{2\sqrt{\pi}} e^{-U_1^2/c_1^2} + \frac{U_1}{2c_1} \left\{ 1 + \operatorname{erf}\left(\frac{U_1}{c_1}\right) \right\} \right]$$

Likewise, the number flow into the region of calculation across the downstream boundary is

$$\dot{n}_2 = n_2 c_2 \left[ \frac{1}{2\sqrt{\pi}} e^{-U_2^2/c_2^2} - \frac{U_2}{2c_2} \left\{ 1 + \operatorname{erf}\left(\frac{U_2}{c_2}\right) \right\} \right]$$

Since particles enter at random across the upstream boundary, the probability that  $N$  particles enter during a time  $t_n$  across the  $j^{\text{th}}$  boundary is

$$P_{n,j} = \sum_{i=0}^N \frac{(t_n \dot{n}_j)^i}{i!} e^{-t_n \dot{n}_j}$$

so that the number of new particles to be added can be calculated by setting  $B_{n,j}$  equal to a random number  $R$ .

Velocities are assigned to the new particles according to the distribution function at the boundary at which they entered. For a Maxwellian distribution about a mean velocity  $U_1$  at the upstream boundary, the components in the  $y$  and  $z$  directions are assigned by using GAUSS. The value of  $u_x$  is determined by solving the equation

$$\begin{aligned} R &= \frac{\int_{u_x}^{\infty} v e^{-\left(\frac{v-U_1}{c_1}\right)^2} dv}{\int_0^{\infty} v e^{-\left(\frac{v-U_1}{c_1}\right)^2} dv} \\ &= \frac{e^{-\left(\frac{U_1-u_x}{c_1}\right)^2} + \frac{\sqrt{\pi} U_1}{c_1} \left\{ 1 + \operatorname{erf}\left(\frac{U_1-u_x}{c_1}\right) \right\}}{e^{-\left(\frac{U_1}{c_1}\right)^2} + \frac{\sqrt{\pi} U_1}{c_1} \left\{ 1 + \operatorname{erf}\left(\frac{U_1}{c_1}\right) \right\}} \end{aligned}$$

where R is a random number and the solution can be obtained by a Newton-Raphson iterative procedure starting with the initial guess

$$U_x^0 = \frac{U_1}{2} + \left( \frac{U_1^2}{4} + \frac{c_1^2}{2} \right)^{1/2}$$

At the downstream boundary, a like procedure is followed with  $U_1$  replaced by  $-U_2$  and  $c_1$  by  $c_2$ . The solution is then multiplied by  $-1$  to give the correct direction. The position of each newly added particle is determined by letting

$$x_i = x_j + R U_{x,i} t_m.$$

The above procedure has been coded for the IBM 360 and is currently being checked out. At the current time, we are applying the procedure to the calculation of a steady, one-dimensional plane shock wave. We have as yet been unable to achieve convergence to the final result (attainment of a statistically steady state). The running time on our computer (IBM 360-75) is rather long. The shock calculation comprises 20 cells and about 500 particles, and at one hours' running time had not yet relaxed to statistically steady densities, mean velocities, and temperatures. No extensive attempts to optimize the code have yet been made, although it is clear that to obtain a calculation which results in convergence of high moments of the distribution function (a necessary condition for investigation of effects on chemical reactions of a non-continuum environment) such optimization will be needed. We are now in the process of making it possible to write out intermediate output on tape, so that a calculation may be run in several steps of moderate individual length rather than in one very long step.

We plan to employ the foregoing procedure to assess the effects of rarefaction upon reaction and excitation processes in high-altitude plumes. The calculation (in cylindrical geometry) is actually a small-disturbance approximation to the plume flow field; in comparing results with the plume calculation, this must be taken into account. In order to be able to assess the effects on reactions independently of the effects of the small-disturbance calculation, we felt it desirable to develop a small-disturbance code for the continuum flow. This code should also be useful for calculating conditions in high-altitude releases. The code is based upon a Lagrangian finite-difference procedure very similar to that employed in MULTITUBE, and essentially is an adaptation of MULTITUBE to a one-dimensional unsteady flow.

The equations of overall continuity, momentum, energy and species conservation are

$$\frac{d\rho}{dt} + \rho(\nabla \cdot \vec{v}) = 0$$

$$\rho \frac{d\vec{v}}{dt} = -\nabla P - (\nabla \cdot \underline{\tau})$$

$$\rho \frac{dE}{dt} = -\nabla \cdot \vec{q} - \nabla \cdot \sum_i \bar{H}_i \vec{J}_i - P \nabla \cdot \vec{v} - \underline{\tau} : \vec{v}$$

$$\rho \frac{dc_i}{dt} = -\nabla \cdot \vec{J}_i + \dot{w}_i$$

Here the time derivative  $\frac{d}{dt}$  is taken following a fluid element. The heat flux  $\vec{q}$  is  $-k\nabla T$ , and other quantities are defined in the table of nomenclature.

We now specialize to a system in one space dimension  $r$ , and introduce a metric coefficient  $j$ , which takes on the values 0, 1, and 2 for planar, cylindrical, or spherical symmetry, respectively. All fluxes and velocities are zero except in the radial direction and we let  $v = v_r$ ,  $q = q_r$ , and  $J_i = J_{i,r}$ . The non-vanishing parts of the stress tensor are the diagonal components

$$\tau_{rr} = -\mu \left[ 2 \frac{\partial v}{\partial r} - \frac{2}{3} \nabla \cdot \vec{v} \right]$$

and

$$\tau_{\theta\theta} = \tau_{\phi\phi} = -\mu \left[ 2 \frac{v}{r} - \frac{2}{3} \nabla \cdot \vec{v} \right]$$

Then

$$\nabla \cdot \underline{\tau} = \frac{1}{r^j} \frac{\partial}{\partial r} (r^j \tau_{rr}) - \frac{j}{r} \tau_{\theta\theta}$$

and

$$\tau : \nabla \vec{v} = \tau_{rr} \frac{\partial v}{\partial r} + j \frac{v}{r} \tau_{\theta\theta} .$$

We can then write the governing equations in terms of a "radial" normal stress  $\tau_{rr}$  and an "angular" normal stress  $\tau_{\theta\theta}$  as

$$\frac{d\rho}{dt} = - \frac{\rho}{r^j} \frac{\partial}{\partial r} (r^j v)$$

$$\rho \frac{dv}{dt} = - \frac{\partial P}{\partial r} - \frac{1}{r^j} \frac{\partial}{\partial r} (r^j \tau_{rr}) - \frac{j}{r} \tau_{\theta\theta}$$

$$\begin{aligned} \rho \frac{dE}{dt} &= - \frac{1}{r^j} \frac{\partial}{\partial r} \left[ r^j \left( q + \sum_i H_i J_i \right) \right] - \frac{P}{r^j} \frac{\partial}{\partial r} (r^j v) \\ &\quad - \tau_{rr} \frac{\partial v}{\partial r} - \frac{jv}{r} \tau_{\theta\theta} \end{aligned}$$

$$\rho \frac{dc_i}{dt} = - \frac{1}{r} \frac{\partial}{\partial r} \left[ r^j J_i \right] + \dot{w}_i$$

We will develop the Lagrangian finite-difference approximation to these equations in terms of a model consisting of an array of expandable cells, with movable boundaries separating them. It is natural to define some quantities as cell quantities and others as boundary quantities. The Lagrangian velocity  $v$  is naturally associated with a moving boundary, for example, while the pressure and the internal energy are naturally associated with a cell. We can then use the momentum equation to describe

the motion of the cell boundaries, and the remaining equations to describe the properties of the fluid in the cells. Formally, we proceed by introducing a coordinate transformation

$$dy = c_j r^j dr \quad ,$$

where  $y$  has the dimensions of a  $(j+1)$ -dimensional volume and  $c_j$  is  $1$ ,  $2\pi$ , or  $4\pi$  as  $j$  is  $0$ ,  $1$ , or  $2$ . Then

$$\frac{\partial}{\partial r} \rightarrow c_j r^j \frac{\partial}{\partial y}$$

and the equations become

$$\frac{d\rho}{dt} = -c_j \frac{\partial}{\partial y} (r^j v)$$

$$\rho \frac{dv}{dt} = -c_j r^j \frac{\partial p}{\partial y} - e_j \frac{\partial}{\partial y} (r^j \tau_{rr}) - \frac{j}{r} \tau_{\theta\theta}$$

$$\begin{aligned} \rho \frac{dE}{dt} = & -c_j \frac{\partial}{\partial y} \left[ r^j \left( q + \sum_i H_i J_i \right) \right] - p c_j \frac{\partial}{\partial y} (r^j v) - c_j r^j \tau_{rr} \frac{\partial v}{\partial y} - \\ & - \frac{jv}{r} \tau_{\theta\theta} \end{aligned}$$

$$\rho \frac{dc_i}{dt} = -c_j \frac{\partial}{\partial y} (r^j J_i) + \dot{w}_i$$

We now pass from this transformed set of equations to the finite-difference equations. Let the flow be divided into a number of cells, and define the boundary of each cell in such a way

that the total mass within each cell does not change with time. The cell boundaries are then identifiable as mean particle trajectories in the moving fluid. While individual species may pass across the mean trajectory by diffusion, no net transfer of mass occurs. The mean trajectories are analogous to streamlines in flows with two space dimensions. It is natural to define the fluid velocity at the cell boundaries, and thermodynamic state properties (temperature, pressure, composition, internal energy, density) within the cells. The heat and mass fluxes are also conveniently defined at the boundaries. The stresses, which are in effect additional pressure terms, are more conveniently defined in the cells. We introduce two difference operators,  $\Delta_k$ , which takes the difference in boundary properties across the  $k^{\text{th}}$  cell, and  $\delta_k$ , which takes the difference in cell quantities across the  $k^{\text{th}}$  boundary. We then adopt the convention that the  $k^{\text{th}}$  boundary bounds cell  $k$  on the "outside," i.e., the direction of increasing  $r$ . Then if we set the mass of a cell  $m_k = \rho_k \Delta_k V$ , the equations for the rates of change of the cell quantities become

$$m_k = \text{constant}$$

$$m_k \frac{dE_k}{dt} = -c_j \left[ \Delta_k \left\{ r^j \left( q + \sum_i H_i J_i \right) \right\} + p_k \Delta_k (r^j v) + r^j \tau_{rr,k} \Delta_k v \right] - j \left( \frac{v}{r} \right) \tau_{\theta\theta,k}$$

$$m_k \frac{dc_{i,k}}{dt} = -c_j \Delta_k (r_k^j J_i) + \dot{w}_i \frac{m_k}{\rho_k}$$

where  $\overline{r_k^j} = \frac{1}{2}(r_k^j + r_{k-1}^j)$  and  $\left(\overline{\frac{v}{r}}\right)_k = \frac{1}{2}\left(\frac{v_k}{r_k} + \frac{v_{k-1}}{r_{k-1}}\right)$ . The

momentum equation and the definition of the velocity describe the motion of the cell boundaries:

$$\overline{m_k} \frac{dv_k}{dt} = -c_j \left[ r_k^j \delta_{kP} + \delta_k (\overline{r_k^j} \tau_{rr}) \right] + \frac{j}{r_k} \overline{\tau_{\theta\theta,k}}$$

$$\frac{dr_k}{dt} = v_k$$

where  $\overline{m_k} = \frac{1}{2}(m_k + m_{k+1})$  and  $\overline{\tau_{\theta\theta,k}} = \frac{1}{2}(\tau_{\theta\theta,k} + \tau_{\theta\theta,k+1})$ .

The above equations provide the changes in cell boundary position and velocity, and the changes in composition and internal energy within a cell, over a small time increment. The thermal and caloric equations of state

$$E = E(T, \rho)$$

and

$$P = P(T, \rho)$$

provide the remaining information required for a complete specification of state properties in the expanding flow. In general we will consider ideal mixtures of perfect gases, so that these equations become

$$E = \sum_i c_i \left\{ \int_0^T c_{v,i} dT + E_{i0} \right\}$$

and

$$\rho RT = \left( \sum_i \frac{c_i}{M_i} \right)^{-1} P .$$

A solution to this set of equations consists of the positions and velocities of the cell boundaries, together with the state properties in the cells, as functions of time following some prescribed initial condition. The procedure for evaluating the solution is the following: Using the initial velocities and state properties, the stresses, the heat and mass fluxes, and the reaction rates within the cells are evaluated. From the calculated stresses and the known pressures, the accelerations of the cell boundaries are calculated, using the equations of motion. After a small time step  $\delta t$ , new positions of the cell boundaries are computed and, from the new cell volumes and the constant cell masses, new cell densities are evaluated. The changes in composition within the cells is then evaluated from the previously calculated mass fluxes and reaction rates, and the internal energies within the cells are computed using the energy equation. Finally, from the now known density, internal energy, and composition, the state properties are determined using the equations of state. The flow field at the end of a time step  $\delta t$  is now completely specified, and the calculation is repeated at the next time step. The calculation marches in time in this fashion until the entire flow has been evaluated.

One can show by summation over all the cells that the difference scheme identically satisfies the integral conservation equations of mass and energy.

The foregoing procedure has been coded and initial computer calculations are now being performed for simple free expansions with cylindrical and spherical symmetry. In preparing the code, we have made considerable use of routines from MULTITUBE. Because of the considerable similarity between these problems, most of the FORTRAN statements from MULTITUBE could be used directly in the new 1-D unsteady code with some redefinition of the variables. Some reprogramming was necessary in order to account for differences in handling of shocks and stresses. Since the new code is still being checked out, we shall not present a complete description here; we expect to document the code at a future date.

The third effort under the fluid mechanics effort is the comparison of exhaust plume calculations made with MULTITUBE to experiments<sup>4</sup> recently performed at AEDC. Specifically, a calculation is currently under way for the test conditions IC5 of Reference 4, which consisted of a helium plume for a 1.61:1 area ratio nozzle injected into an N<sub>2</sub> free station at Mach 18.15. These calculations and the comparison with experiment (impact pressure and species density) will be the subject of a separate report.

### Literature Cited

1. F.P. Boynton and A. Thomson, "Numerical Computation of Steady, Supersonic, Two-Dimensional Gas Flow in Natural Coordinates", J. Comput. Phys.
2. F.P. Boynton, "The MULTITUBE" Supersonic Flow Computer Code", General Dynamics/Convair Report GDC-DBE67-003, February 1967.
3. F.P. Boynton, "Numerical Calculations of Viscous High-Altitude Exhaust Plume Flow Fields", Research Institute for Engineering Sciences, Wayne State University, Report RIES 70 - , November 1970.
4. W. Norman, M. Kinslow, and J.W.L. Lewis, "Experimental Study of Simulated High Altitude Rocket Exhaust Plumes", AEDC-TR-71-25, July 1971.
5. G.A. Bird, "Aerodynamic Properties of Some Simple Bodies in the Hypersonic Transition Regime", AIAA J. 4, 55-60 (1966).
6. B.J. Alder and T.E. Wainwright, "Studies in Molecular Dynamics I. General Method", J. Chem. Phys. 33, 1439-51 (1960).
7. F.W. Vogenitz, G.A. Bird, J.E. Broudwell, and H. Rungaldier, "Theoretical and Experimental Study of Low Density Supersonic Flows About Several Simple Shapes", AIAA J. 6, 2388-94 (1968).
8. F.W. Vogenitz and G.Y. Takata, "Rarefied Hypersonic Flow about Cones and Flat Plates by Monte Carlo Simulations", AIAA J. 9, 94-100 (1971).
9. J.K. Haviland, "The Solution of Two Molecular Flow Problems by the Monte Carlo Method", Methods in Computational Physics, v. 4 (Academic Press, New York, 1965), pp.109-210.

## SECTION II

### Introduction/Summary

Prior to quantitative model predictions on the radiative properties of exhaust products in the upper atmosphere, several important chemical reaction rate coefficients must be determined. In particular, our studies have focussed on simple exothermic oxidation reactions involving O and OH attack on various hydrocarbon fuel species and accompanying vibrational relaxation processes.

The interest in simple exothermic reactions is directed toward the release of the available energy of the reaction into radiative modes of the product molecules. Measurements in our laboratory have been made from 2000 Å to 25μ in an attempt to determine the reaction mechanism and available radiative modes.

OH is a strong emitter at 3064 Å ( $\text{OH } A^2 \Sigma^+ \rightarrow X^2 \Pi$ ) as well as in the Meinel Bands from 7000 to 9000 Å and in the near IR at 2.7μ. OH emission has been observed as a result of O atom attack on virtually all hydrocarbons tested to date. In addition, we find that the subsequent OH attack on  $\text{CH}_2\text{O}$  results in strong  $\text{H}_2\text{O}$  emission at 2.7μ as well as some 6.3μ radiation.

Our early results have focused on the identification and determination of concentration values through the visible chemiluminescence associated with the attack of O atoms and OH on reactive hydrocarbons. Preliminary survey measurements have, however, been made out to 25μ and the results from these measurements are discussed herein. As the mass spectrometer system is completed and fully incorporated into the flow system, the current stress on visible emission will no longer be necessary.

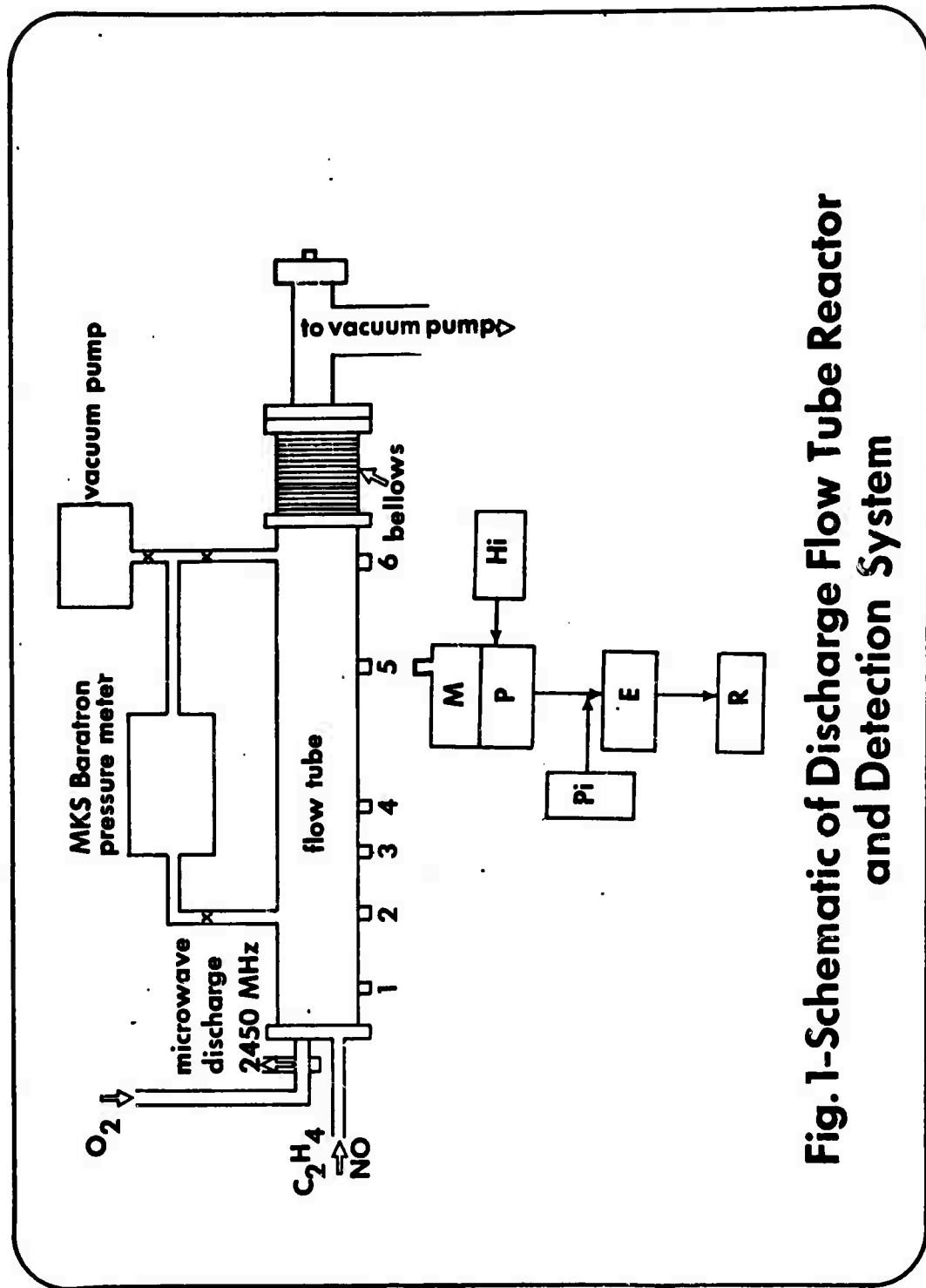
## Experimental

All studies were performed in the discharge flow system shown schematically in Figure 1. Molecular oxygen (American Cryogenics, purity 99.6%) was discharged in an Evenson or Broida Cavity at 2450 MHz using a Raytheon PGM 10x2 diathermy system. The discharge was pulsed at 238 Hz for simultaneous infrared, visible and ultraviolet measurements. The discharged oxygen was passed into the flow tube reactor through a teflon tube with a radially-multiperforated exit stream which permits excellent mixing with a second gas and prevents discharge region radiation from reaching the observation ports. The stainless steel reactor is lined with a teflon sleeve which largely prevents wall recombination of the atomic species. The inside diameter of the reactor is one inch and typical gas velocities are 30 to 40 m/sec through a Heraeus Engelhard E - 225 mechanical pump. Six ports permit radial viewing through KBr windows using an RCA C31025C uncooled photomultiplier on a Jarrell Ash scanning quarter meter monochrometer with a Keithley 602 Electrometer recorded on a Honeywell Electronik 194 recorder. Signal to noise ratios were such that no damping or time integration of signals was necessary in the u.v. and visible. Measurements in the infrared were made using a Santa Barbara uncooled PbS detector (to  $3\mu$ ), Ge:Cu detector (to  $8\mu$ ) and Ge:Cu detector (to  $25\mu$ ). All infrared measurements were made with a PAR HR8 Phase Sensitive Lock In Amplifier.

The hydrocarbons employed as reactant gases were methane, ethane, propane, ethylene, propylene, trans-butene, acetylene and formaldehyde. Linde research grade methane and ethane were employed. Union Carbide chemically pure propane was used. The propylene and trans-butene from Cryogenic Sales had purities of 95% and 99% respectively. Several runs were made with "house" methane with no perceptibly different results.

Figure 1. Schematic of discharge flow tube reactor and detection system. Legend:

- M = Monochromator - Jarrell Ash, quarter meter, scanning.
- P = Photomultiplier - RCA C31025C (uncooled)
- E = Electrometer, D.C. Amplifier - Keithley 602
- Pi = Picoampere source - Keithley 261
- R = Recorder - Honeywell Electronik 194
- Hi = High voltage D.C. power supply - Power Designs Pacific model 2K-10



**Fig. 1-Schematic of Discharge Flow Tube Reactor and Detection System**

Oxygen atom concentrations were determined through gas phase  $\text{NO}_2$  titration; typically 1% atoms were present. The spectral response function for the system was determined using the  $\text{NO} + \text{O}$  chemiluminescence as an actinometric standard (Fontijn, et al., 1964; Keneally, et al., 1967) from 4000 Å to  $3\mu$ .

The  $\text{C}_2\text{H}_4 + \text{O}$  signal was maximized with respect to a set of flow conditions by scanning all wavelengths between 7000 - 9000 Å and monitoring the signal at the contact times determined by the position of the KBr windows (contact time in the system at a given pressure is from 3 to 15 msec, depending on the viewing port). For this total pressure, about 1280  $\mu$ , the first window gave the largest signal at all wavelengths. The signals from the other hydrocarbon plus atomic oxygen reactions were also monitored at the first window and approximately equal concentrations of hydrocarbon (about 20  $\mu$ ) and molecular oxygen (about 1200  $\mu$ ) were employed. Consequently, the intensities may not be the maximum intensities obtainable although the intensities of the signals from the various hydrocarbons correspond to the same experimental conditions.

**Figure 2. Intensity of chemiluminescence in the 700-900 nm region from O atom attack on saturated hydrocarbons.**

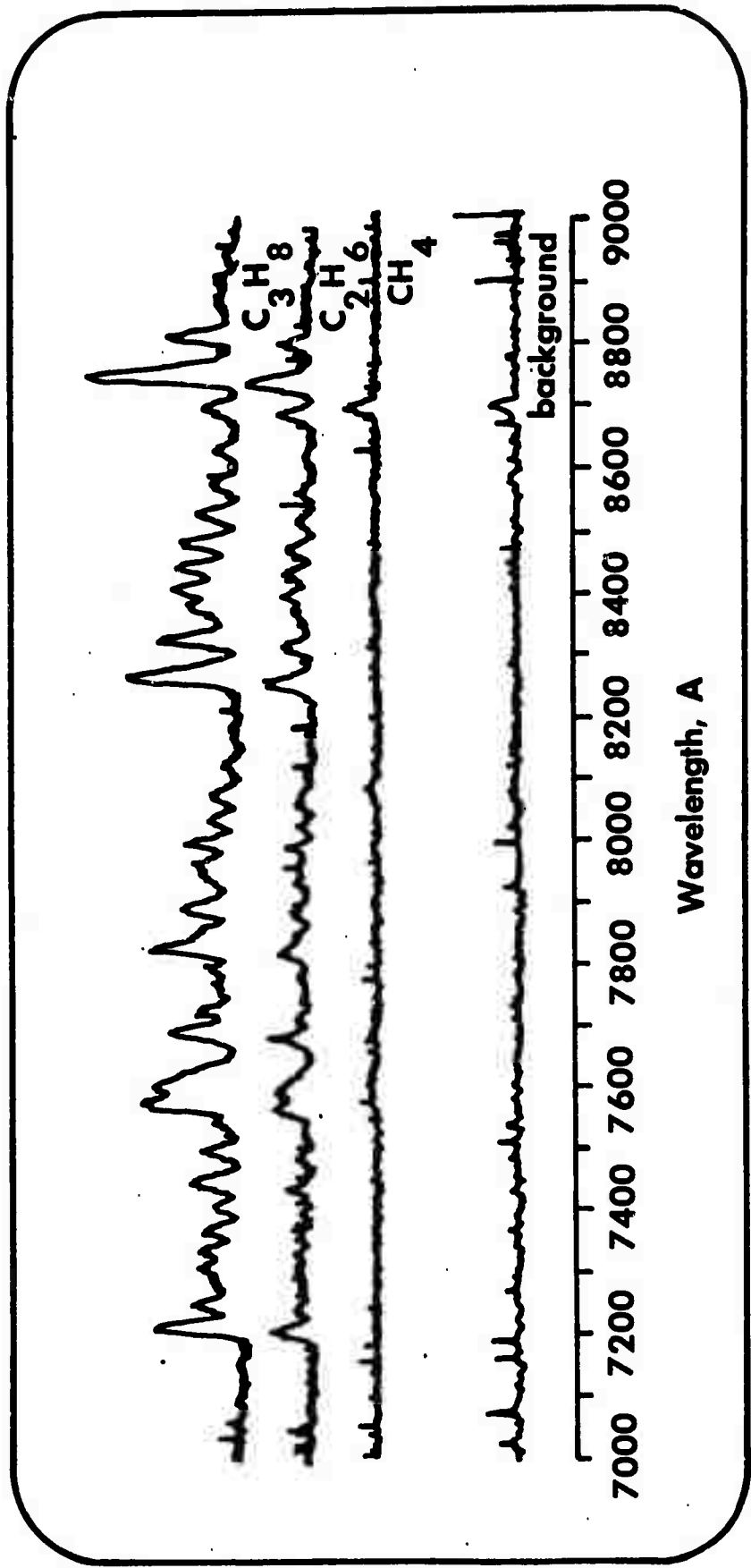


Figure 3. Intensity of chemiluminescence in the 700-900 nm region from O atom attack on unsaturated hydrocarbons.

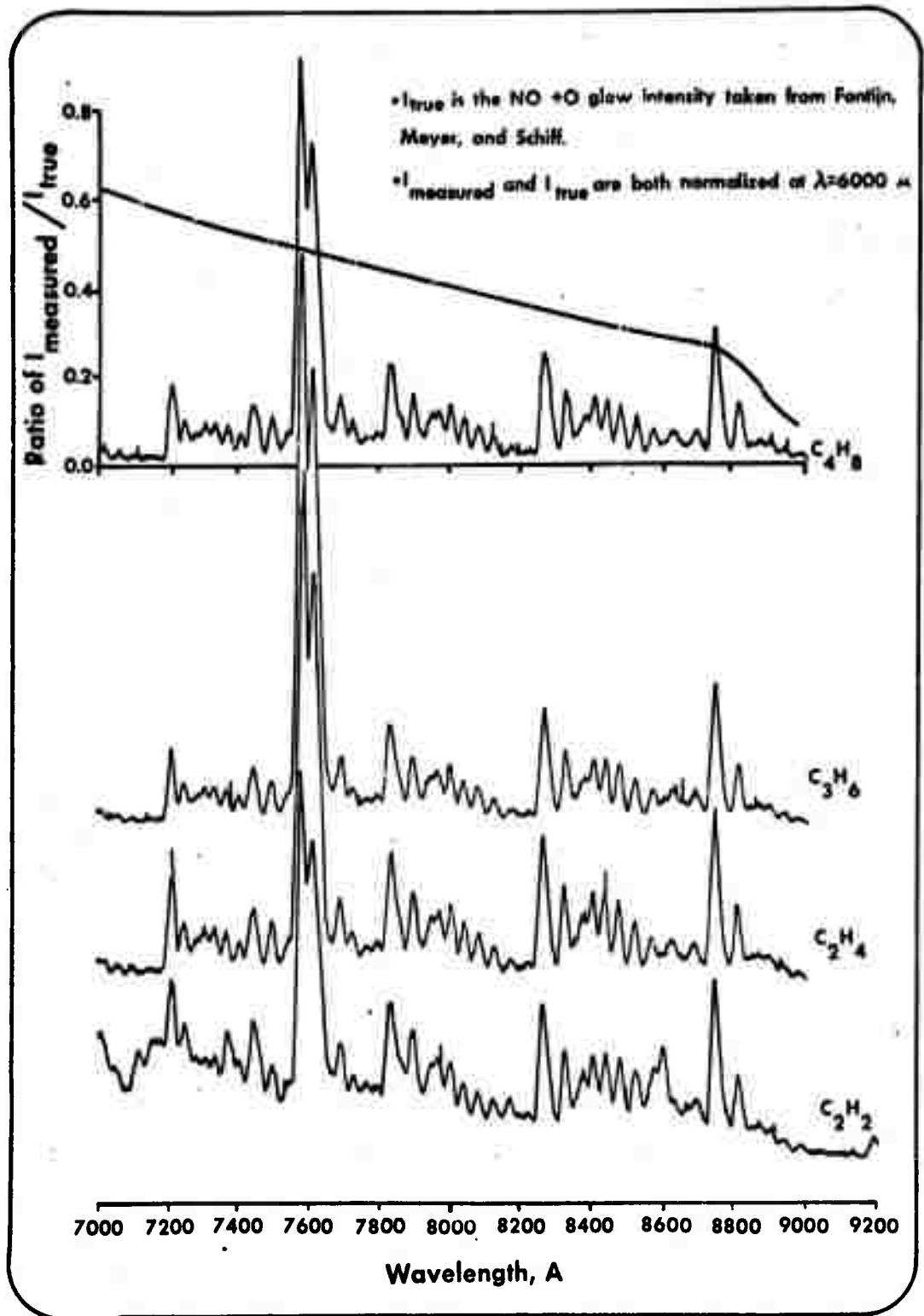
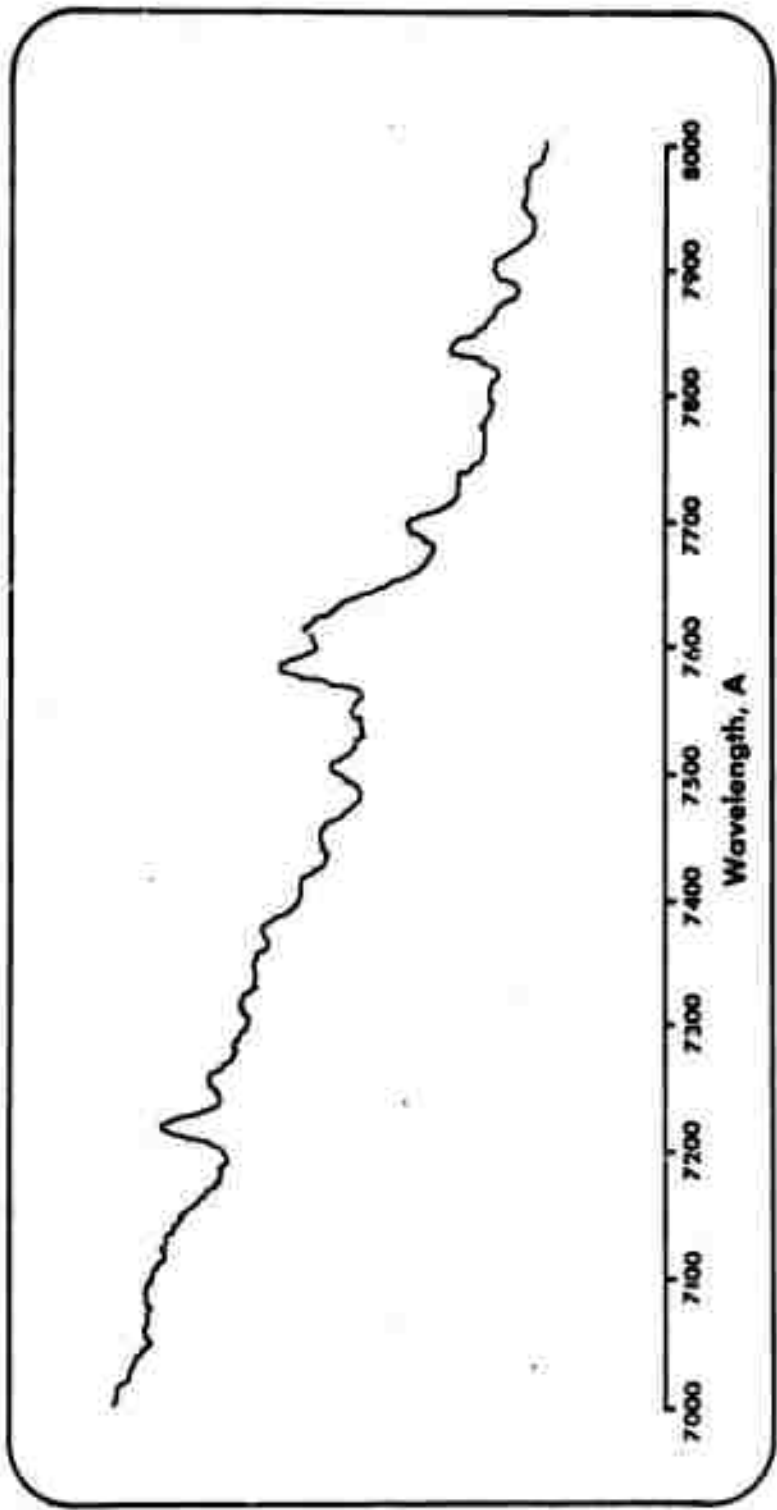


Figure 4. Intensity of chemiluminescence from simultaneous O atom attack on  $C_2H_4$  and NO in equal concentrations of  $20\mu$ .



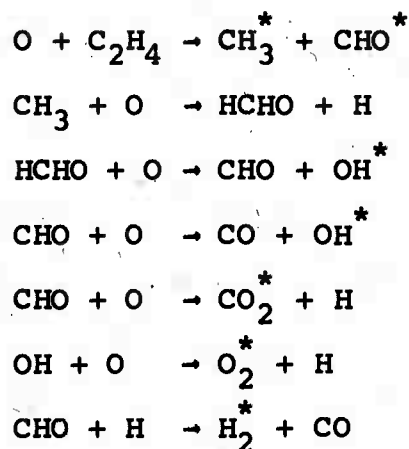
## Results and Discussion

The chemiluminescent spectra generated by the reaction of oxygen atoms with a series of saturated and unsaturated hydrocarbons are presented in Figures 2 and 3 along with the relative spectral response of the photomultiplier - spectrometer system, as determined through calibration with  $\text{NO} + \text{O}$ . At the first window, the signal was scanned over the sensitive wavelength range of the photomultiplier. The spectra of olefin plus oxygen atom reactions exhibited the  $\text{OH}(\text{A}^2\Sigma^+ - \text{X}^2\Pi)$  band at  $3064 \text{ \AA}$  and the emission in the  $7000\text{--}9000 \text{ \AA}$  region was characteristic of the OH Meinel bands plus a strong band near  $7620 \text{ \AA}$  which could be  $\text{O}_2(^1\Sigma)$  emission. The intensity of the Meinel bands is a strong function of the contact time whereas the  $\text{O}_2(^1\Sigma)$  emission is much less sensitive over the contact time range of this experiment.

The O plus reactive hydrocarbon emission is structured, and nearly as strong as the  $\text{NO} + \text{O}$  emission in the wavelength region from  $7000 - 9000 \text{ \AA}$ . Figure 4 presents the spectrum of  $\text{O} + \text{C}_2\text{H}_4 + \text{NO}$  from  $7000 - 8000 \text{ \AA}$ . The  $\text{C}_2\text{H}_4 + \text{O}$  emission peaks are clearly distinguishable superimposed on the  $\text{NO} + \text{O}$  continuum emission.

While acetylene exhibits the same structure in the  $7000$  to  $9000 \text{ \AA}$  region as do olefins, the spectrum from  $2500 - 7000 \text{ \AA}$  is quite different with strong emission near  $6000 \text{ \AA}$ , which should be readily observable in the presence of  $\text{NO}$  as well, provided that appropriate spectral resolution is provided.

Currently, we are examining the reaction mechanism of Niki for consistency with u.v., visible and infrared observations for reaction of  $\text{O} + \text{C}_2\text{H}_4$ :



The OH emission steps can be initiated either using  $\text{C}_2\text{H}_4$  directly or by using HCHO. Both generate strong  $2.7\mu$  emission. HCHO, however, does not seem to lead to strong 3064 Å or Meinel radiation. Installation of our Extranuclear Quadrupole Mass Spectrometer in the next funding period will greatly enhance our capability for interpreting these mechanisms.

In order to generate OH concentrations suitable for reacting and subsequent observation of chemiluminescence,  $\text{H}_2$  is discharged using a 2450 MHz microwave system as outlined in the previous section. The concentration of [H] produced in the discharge can be determined from the  $\text{H} + \text{NO} \rightarrow \text{HNO}^* + \text{h}\nu$  (7460 Å) titration as shown in Figure 5. Normal [H] concentrations in a total pressure of about 1 torr are 3 to 8% (Figure 5 shows a 6% concentration). At the second inlet port  $\text{NO}_2$  is added to produce OH via  $\text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH}$ . Without further addition of reactants, a substantial 2.7 and 6.3 $\mu$  signal is observed; presumably this is due to

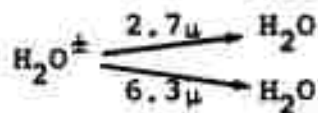
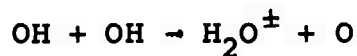


FIGURE 5

[NO] ~ 100  $\mu$

[H] ~ 60  $\mu$

238 Hz

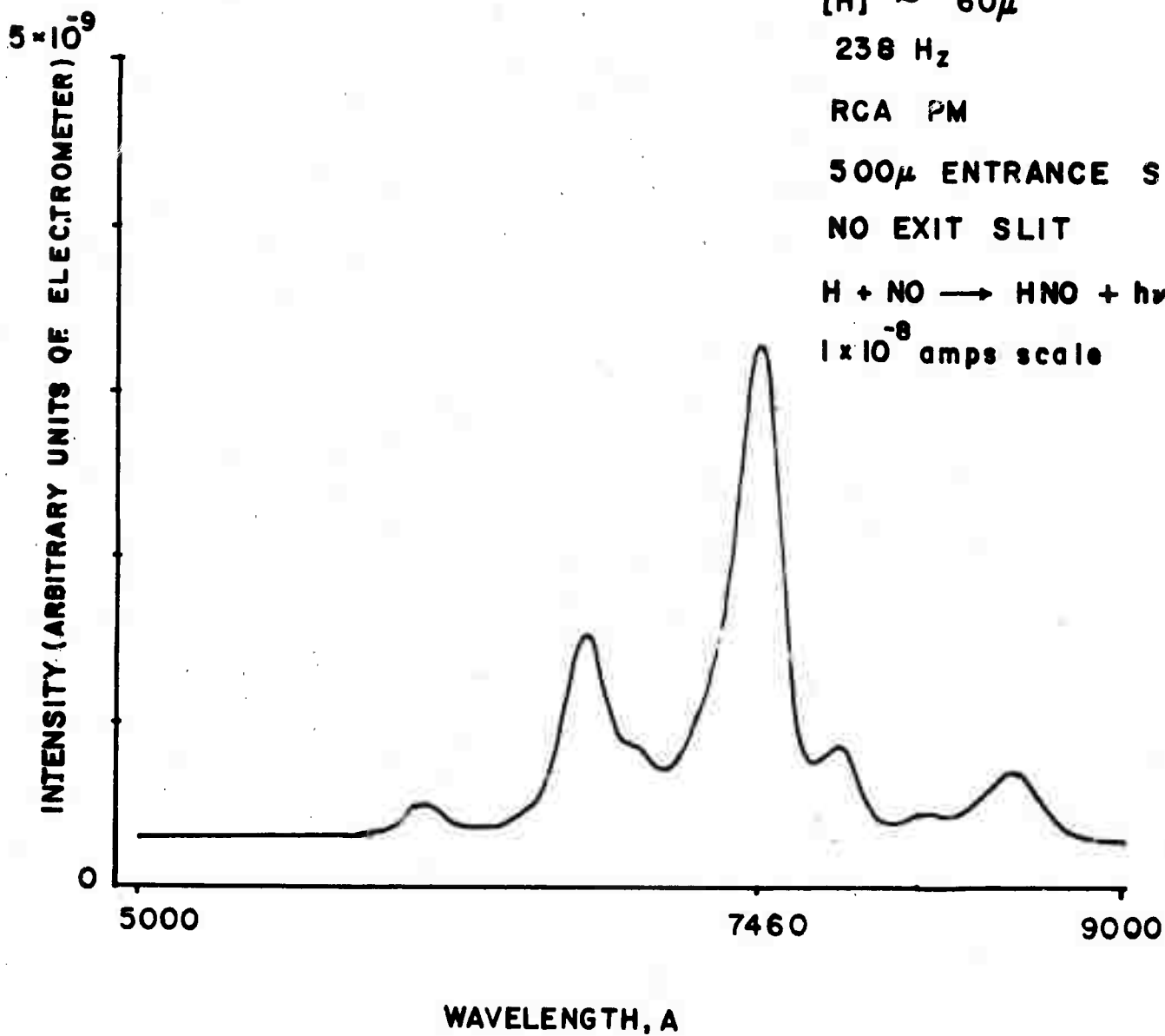
RCA PM

500  $\mu$  ENTRANCE SLIT

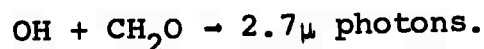
NO EXIT SLIT

H + NO  $\rightarrow$  HNO + h $\nu$

$1 \times 10^{-8}$  amps scale



but some contribution may come from  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O}^\pm + \text{H}$ . Once the OH is generated, various simple hydrocarbons can be added and the chemiluminescence in the IR determined. To date we have done preliminary measurements on the added reactants CO,  $\text{C}_2\text{H}_4$  and  $\text{CH}_2\text{O}$  using IR filters and a range of solid state detectors (described earlier). Our results show that the  $\text{OH} + \text{CH}_2\text{O}$  reaction leads to a large  $2.7\mu$  signal and a somewhat smaller signal in the  $5 - 10\mu$  region (presumably  $\text{H}_2\text{O}$  bending mode). The  $\text{OH} + \text{C}_2\text{H}_4$  gives a rather small  $2.7\mu$  signal but a larger signal in the  $5 - 10\mu$  region than from  $\text{CH}_2\text{O}$ . With  $\text{CO} + \text{OH}$  we have not been able to identify any significant IR radiation although there appeared a hint of a signal in the  $12 - 20\mu$  region ( $\text{CO}_2$  bending mode). Using the available actinometric standard  $\text{O} + \text{NO}$  at  $2.7\mu$ , we have deduced a preliminary rate coefficient for the reaction



Assuming that the  $2.7\mu$  radiation is from  $\text{H}_2\text{O}^\pm$ , we note that the system is radiation limited due to the relatively high concentration of  $\text{H}_2$  (present from the discharge flow) and the very high vibrational relaxation times associated with  $\text{H}_2\text{O}^\pm$  (roughly  $1 \mu\text{sec}$  at 1 torr  $\text{H}_2$ ). Using these numbers, we estimate that the  $2.7\mu$  production from  $\text{OH} + \text{CH}_2\text{O}$  has a rate constant between  $2^{-12}$  and  $5^{-14}$  depending on the  $[\text{OH}]$  concentration in the flow tube. We are currently working on a numerical model for the flow tube chemistry which will enable a considerably more reliable estimate of the  $[\text{OH}]$  and other intermediate species for use in deducing rate constants and photon yields from measured flow tube data.

These studies will continue jointly with the development of the flow tube chemistry code for the interpretation of the chemiluminescence.

## Theoretical Cross Sections

In a series of papers beginning in 1964 and earlier Convair Reports, R. Marriott has generated theoretical cross sections for many vibrational relaxation processes involving  $H_2O$ ,  $CO_2$ ,  $CO$ ,  $N_2$ ,  $H_2$  and  $O$  atoms. To date, many of these theoretical estimates are the only available results to use in model non-equilibrium calculations involving these molecules. Yet these cross sections have not in general been available in a convenient form for use in model calculations.

To eliminate this problem, we have written a simple numerical program to reduce the cross sections calculated for all vibrational processes analyzed by the close coupling method, including excited vibrational state processes, to temperature dependent rate coefficients. The results of this analysis will be described in a forthcoming report where available experimental data will be included.

The results of this analysis, particularly the excited level rate coefficients, should be important in providing scaling information of the relaxation of excited vibrational levels and also provide currently unknown relaxation rates for  $H_2O$  (stretching modes and bending modes) in collision with  $H_2$ ,  $CO_2$  and  $H_2O$  as collision partners. The relaxation processes being calculated are tabulated in the following list.

- |     |                         |   |   |                                    |              |             |   |   |                 |
|-----|-------------------------|---|---|------------------------------------|--------------|-------------|---|---|-----------------|
| 1.* | $CO_2(v_2)$             | } | + | $H_2$<br>$H_2O$<br>$CO_2$<br>$N_2$ | 2.*          | $H_2O(v_2)$ | } | + | $H_2$<br>$H_2O$ |
|     | $CO_2(v_1)$             |   |   |                                    | $H_2O(2v_2)$ |             |   |   |                 |
|     | $CO_2(2v_2)$            |   |   |                                    | $H_2O(v_1)$  |             |   |   |                 |
|     | $CO_2(v_3)$             |   |   |                                    | $H_2O(v_3)$  |             |   |   |                 |
| 3.  | $CO + H_2O, O(^1D), He$ |   |   |                                    | 4.           | $N_2 + Ar$  |   |   |                 |

\*plus all interstate combination processes

Literature Cited

- Fontijn, A., C.B. Meyer and H. Shiff, J. Chem. Phys., 40,  
65 (1964).
- Marriott, R., Proc. Phys. Soc., 83, 159 (1964).
- Marriott, R., Proc. Phys. Soc., 84, 877 (1964).
- Marriott, R., Proc. Phys. Soc., 86, 1041 (1965).
- Marriott, R., Proc. Phys. Soc., 88, 83 (1966).
- Marriott, R., Proc. Phys. Soc., 88, 617 (1966).
- Marriott, R., RIES Report 71-21 (1971).
- Marriott, R., and Kindt, G., RIES Report 71-22 (1971).
- Marriott, R., RIES Report 70-17 (1970).

### SECTION III

#### Molecular Beam Studies

An experimental effort is being initiated to provide input data needed for calculating excitation cross sections. Of particular interest are those with atomic oxygen at energies between a few tenths of an electron volt to several electron volts.

An apparatus designed for this type of experiment, and constructed by High Voltage Engineering Corporation for NASA Lewis Research Center was donated to Wayne State University when the NASA program was discontinued. It is proposed to use this equipment to measure the needed potentials.

The equipment has been transferred to our laboratory, and during the present reporting period work has been carried out to bring the machine back to a functioning level, and to install the necessary modifications for these measurements.

The machine is now almost ready for preliminary experiments. A post-doctoral fellow will join our group in the middle of January to assist in carrying out the research program.

Contributors to the research described in this Report:

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## PREVIOUS CONTRACT AND REPORTS

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The following reports have been sponsored in full or in part by this contract and the previous contract:

"Numerical Calculations of Viscous High-Altitude Exhaust Plume Flow Fields," F.P. Boynton, RIES-70-18.

"Transport Coefficients and Rates of Collisional Energy Transfer of Electrons and Ions in the Upper Atmosphere," A.R. Hochstim, RIES-70-8.

"Quasi-Steady Motions of Weakly Ionized Inhomogeneous Plasma Clouds in a Strong Magnetic Field," J.Alex Thomson, RIES-70-2.

"Energy Deposition in Artificial Ionospheric Heating Experiments," J. A. Thomson, J. Geoph. Res. 75, 6446 (1970), RIES-70-4.

"A Calculation of the Vibrational Excitation of Carbon Monoxide by Collision with Atomic Oxygen in the <sup>1</sup>D State", R. Marriott, RIES-70-17.

"Relaxation Processes in Expanding Flows of Combustion Products," F.P. Boynton and E.R. Fisher, RIES-71-32.

"A Hydrodynamic Analog of Ionospheric Plasma," J. Alex Thomson, invited paper presented at the Fall Meeting of the A.G.U., San Francisco, December 1971.

"Alkali Quenching in High Temperature Environments," E.R. Fisher and G.K. Smith, accepted for publication in Chem. Phys. Letters, 1972.