NEWMAN deHAAS, ROBERT M. FRISTROM, MILTON J. LINEVSKY, and DAVID M. SILVER

SMOKE SCAVENGING BY ATMOSPHERIC OZONE AS A POSSIBLE FACTOR IN THE NUCLEAR WINTER PROBLEM

A nuclear exchange would probably start catastrophic fires, producing such massive amounts of smoke that the sun would be blotted out for periods of months to years. Such a catastrophe is commonly called "nuclear winter." The factors usually thought to limit its lifetime are physical—fallout, rain, and agglomeration—but we predict that chemical factors may also play a role. We have made theoretical estimates for three limiting conditions under which smoke might be scavenged by high-altitude ozone have been investigated. We conclude that if the reaction probability is high, the rate of smoke removal will be limited by atmospheric mixing, but if a chemical barrier exists, scavenging will be limited by the chemical rate. To test our hypothesis, a laboratory experiment has been set up to examine the smoke/ozone chemical reaction. Preliminary measurements provide evidence for the existence of atmospheric chemical scavenging of smoke by ozone and indicate that the rate is significant for understanding the dynamics of nuclear winter.

INTRODUCTION

Massive cyclonic fire storms and conflagrations would be expected to follow a major nuclear attack.[1] Fires ignited by thermal-radiation pulses would feed on blast debris and propagate to surrounding undamaged areas. Since fire-fighting capabilities would be damaged and, in any case, inadequate to fight massive multiple fires, the spread of fires would be limited primarily by natural barriers. Areas affected by fires would be much larger than those affected by blast and primary induced radioactivity.

The nature of such massive fires will depend not only on their extent but also on details of local combustion, including the local weather; the character, dispersion, and composition of the combustibles; the presence or absence of species, such as halogens, that promote smoke production; and local air access, which controls oxygen availability.

Smoke has been suggested as a major contaminant from the fires.[1,2] Smoke production, its size distribution and dispersion, and subsequent fallout rate depend on the combustion factors. The distribution, both vertical and horizontal, of the generated smoke depends on local weather and the character of the fire. Wind-driven conflagrations tend to produce low-lying smokes, while fire storms produce massive circulating plumes that would lift smoke to high altitudes. Successive explosions could drive combustion products to almost any altitude. Humidity also plays a role in the rates of fire propagation and smoke production.

When smoke particles with sizes on the order of 1 micron or less are lofted into the upper troposphere or lower stratosphere, they absorb incoming sunlight in the visible spectrum but are transparent to outgoing radiation in the infrared. This produces an inverse greenhouse effect leading to global climatic cooling (nuclear winter). If smoke were a chemically inert material, its persistence in the atmosphere would be governed by physical scavenging mechanisms such as settling out. It has been assumed that these mechanisms are slow, and therefore the duration of nuclear winter has been predicted to have a time scale of months to years.[1-4]

The atmospheric chemical reactions resulting from massive intrusion of ground-fire combustion products are relevant. As these products, both gaseous and solid, rise through various layers of the atmosphere, interactions occur with preexisting reactive species such as ozone, nitric oxide, and atomic oxygen. At the altitudes corresponding to the upper troposphere or lower stratosphere, smoke is exposed to both actinic ultraviolet light and significant concentrations of reactive species, notably ozone. This might result in a reaction that could chemically scavenge the smoke, reduce the ozone, or both.

Little is known about this reaction. Smoke clouds from massive fires have been observed for a few weeks, but they generally cannot be followed for longer periods because of dilution, settling, and, perhaps, chemical scavenging. This article outlines a preliminary investigation[5-7] of the importance of chemical scavenging.

SMOKE AND OZONE

Smoke quenched from fire is not a homogeneous substance of fixed chemical composition. It can take on various molecular structures and shapes depending on the nature of the fuel from which it is derived, the

combustion conditions under which it is formed, and the ensuing environment through which it passes. The predominant chemical element in smokes is carbon in graphitic or polyacetylenic structures and possibly in some unsaturated rings and chains. The particles can agglomerate forming clumps or chains of spherules. Other elements such as hydrogen, oxygen, nitrogen, and the halogens may be included in the structure. In addition, various airborne materials may condense or adsorb onto the surface of smoke particles. Even "clean" smoke shows electron spin resonance signals that indicate the presence of unpaired electrons and, therefore, potentially reactive sites.

Estimates of the quantity of smoke expected to be produced in fires attending a nuclear exchange span a wide range. The TTAPS (the initials stand for the authors' names, Ref. 2) baseline smoke injection consists of a smoke generation of 225 million tons, with 5 percent (5.6×10^{35} atoms of carbon) persisting into the stratosphere.

In the altitude range of interest, 8 to 12 kilometers, ozone is present[8,9] at concentration levels of 1 to 2×10^{12} molecules per cubic centimeter. The specific global distribution of ozone varies with location, altitude, and season. Nevertheless, the existing global inventory of ozone, in a 1-kilometer layer at an 8- to 12-kilometer altitude, is comparable to the postulated levels of injected smoke, and it could scavenge the smoke through the reaction

$$O_3 + C \text{ (solid)} \rightarrow CO + O_2 + 60 \text{ kcal/mole}.$$
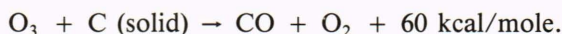
Since the reaction is strongly exothermic, the reaction could be rapid, but this speculation requires experimental verification.

THEORETICAL ESTIMATES OF LIFETIME

Several upper bounds for the chemical reaction rate of smoke with ozone can be derived from fundamental considerations; three limiting conditions are considered below. For convenience, a list of symbols is provided in Table 1, and some assumed properties of the atmosphere are listed in Table 2. The calculations use a smoke particle diameter of 1 micron (10^{-4} centimeter). The dependence on diameter is indicated in the equations given in Tables 3 and 4.

Case 1 (collision limited) assumes (a) that the reaction is controlled by collisions of active species with the particle surface and (b) that the local concentration of active species is not affected by reaction and is continuously renewed (Fig. 1). This serves to establish an upper limit for the smoke-removal process. The results are given in Table 3. This case predicts a very short life, on the order of minutes, for a smoke particle at altitude. The effect of a reasonable activation energy is also considered. These conditions are not usually met because diffusion is often important and turbulent mixing is limited.

Case 2 (diffusion limited) assumes that the reaction is controlled by the diffusion of reactive species to the surface of an isolated smoke particle (Fig. 2). The characteristic diffusion length is taken to be 10

Table 1—Glossary of symbols.

C	Average molecular speed (centimeters per second)
d	Particle diameter (centimeters)
d_E	Eddy scale length (centimeters)
D	Diffusion coefficient (square centimeters per second)
E	Activation energy (calories per mole)
f	Smoke concentration in cloud as a mole fraction
L	Characteristic diffusion length (centimeters)
M_C	Atomic weight of carbon
N_C	Number of carbon atoms (number per cubic centimeter)
N_{O_3}	Number of ozone molecules (number per smoke particle)
N_T	Total number of species (number per cubic centimeter)
P	Pressure (atmospheres)
R	Chemical rate probability (dimensionless) $R \le \exp(-E/2T)$
T	Temperature (kelvin)
$t_{1/2}$	Half-life (seconds)
V_D	Diffusion velocity (centimeters per second)
V_E/A_E	Volume-surface ratio of eddy
Γ	Collision rate (per second)
ν	Number diffusing to surface per unit time (per second)
ρ	Density (grams per cubic centimeter)

Table 2—Properties assumed for the atmosphere as a function of altitude.

Altitude (km)	P (atm)	T (K)	C (cm/sec)	N_{O_3} (molecules/cm³)	N_T (molecules/cm³)
0	1	300	3.4×10^4	($\approx 10^{12}$)	(2.4×10^{19})
8	0.45	236	3.1×10^4	6.5×10^{11}	1.09×10^{19}
10	0.36	223	3.0×10^4	1.1×10^{12}	8.6×10^{18}
12	0.27	217	2.9×10^4	2×10^{12}	6.49×10^{18}

Table 3—Collisional and reaction barrier limits for isolated particles (Case 1).

Altitude (km)	$t_{1/2}$ (E = 0) (sec)	$t_{1/2}$ (E = 4000 cal/mole) (sec)
8	160	8×10^5
10	100	8×10^5
12	60	6×10^5

$$t_{1/2} = \frac{1}{2} N_C / \Gamma R$$

$$N_C = (\pi d^3/6) \rho_C M_C^{-1} \times 6.02 \times 10^{23}, \quad \rho_C = 2.3 \text{ gm/cm}^3$$

$$\Gamma = \pi d^2 (C/4) N_{O_3}$$

$$t_{1/2} = 3.3 \times 10^{22} \frac{d}{C N_{O_3} R}$$

particle diameters. The results appear in Table 4. Again, calculated lifetimes are short.
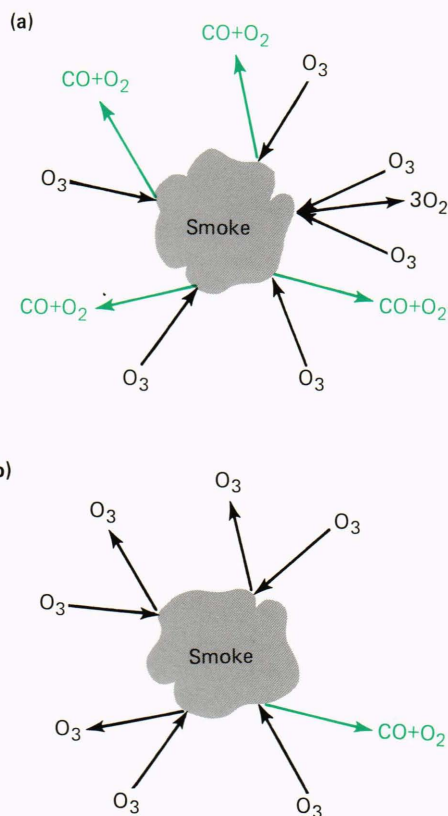
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Figure 1—Case 1. Excess ozone surrounds each smoke particle, and the process is not limited by diffusion: (a) No chemical reaction barrier; every collision of an ozone molecule with the surface of a smoke particle results in reaction. (b) Chemical reaction barrier; limited probability of a reaction for each collision of ozone with smoke.

Table 4—Diffusion-controlled limit for isolated particles (Case 2).

Altitude (km)	$t_{1/2}$ (sec)
8	220
10	160
12	100

$$t_{1/2} = \tfrac{1}{2}N_C / \nu R$$

$$N_C = (\pi d^3/6)\rho_c M_C^{-1} \times 6.02 \times 10^{23}, \quad \rho_C = 2.3 \text{ gm/cm}^3$$

$$\nu = \pi d^2 V_d N_{O_3}$$

$$V_D = \frac{D}{X}\frac{dx}{dz} \approx 2D/L, \qquad L \approx 10d$$

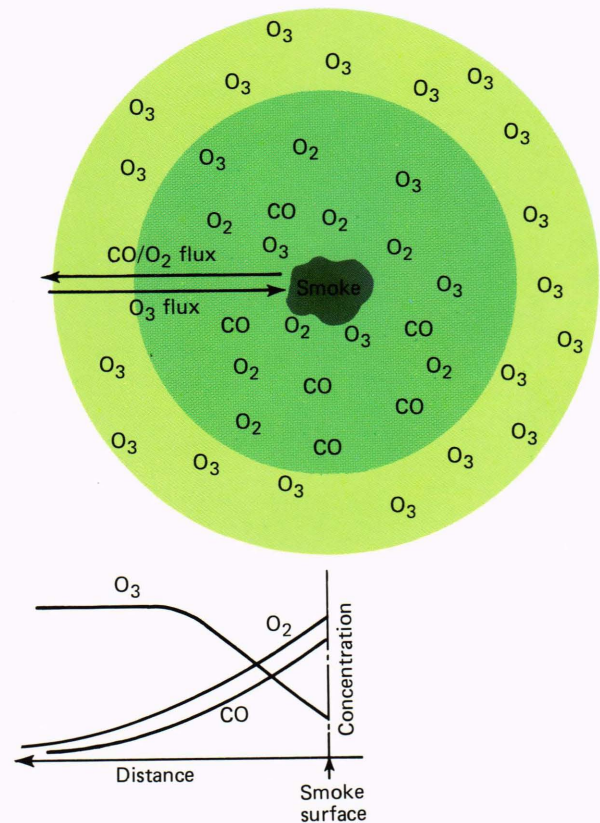$$D = D_O P^{-1}(T/300)^{1.67}, \qquad D_O \approx 0.2$$

$$t_{1/2} = 2.08 \times 10^{22}\ \frac{Pd^2}{N_{O_3} R}\left(\frac{300}{T}\right)^{1.67}$$

Figure 2—Case 2. Ozone in local excess, but the reaction is limited by the diffusion of ozone to the smoke particle surface.

Case 3 (*turbulent mixing and entrainment limited*) pertains to a cloud or plume of smoke particles where the reaction is assumed to be controlled by the penetration of ozone into the plume (Fig. 3). In this case, two processes are involved: (a) turbulent entrainment mixing that is relatively rapid and is assumed to proceed down to a smallest level of turbulent eddy size, and (b) diffusion into the eddy. Since reaction requires mixing at the molecular level, final penetration below the turbulence level must be by diffusion, which is normally the rate-limiting process. Spherical symmetry is assumed, and calculations are made for two minimum eddy scales that are believed to bracket the eddy scales of meteorological interest. The characteristic diffusion length is taken to be the distance required to penetrate to the half-volume surface. The results appear in Table 5. These calculations give half-lives comparable to observed smoke-cloud lifetimes but the half-lives are somewhat on the short side. Of course, if a chemical barrier exists, that would affect the smoke lifetime.

The effect of reaction probability is shown explicitly in Case 1 (Table 3). A comparable dependence on reaction probability is present in Cases 2 and 3, as is indicated in the equations given in Tables 4 and 5. It can be concluded that if the chemical reaction probability is high, the rate will be limited by atmospheric mixing. If, however, there is a chemical barrier (greater than 4 kilocalories per mole), scavenging will be limited by the chemical rate rather than by mixing. Case 3 should be taken as being the closest to reality, assuming suffi-

Table 5—Smoke cloud scavenging (limited by turbulent entrainment that, in turn, is diffusion limited below the minimum mixing scale length) (Case 3).

Altitude (km)	$t_{1/2}$ (sec) (scale, 1 m)	$t_{1/2}$ (sec) (scale, 10 m)
8	1170	1.2×10^5 (33 hours)
10	500	5×10^4 (14 hours)
12	160	1.6×10^4 (5 hours)

$$t_{1/2} = \frac{\frac{1}{2}fN_TV_E}{A_EV_DN_{O_3}R}$$

$$f = 4.8 \times 10^{-3} \text{ (Ref. 10)}$$

$$V_E/A_E = d_E/6$$

$$V_D \approx 2D/L = \frac{2D_o}{PL}\left(\frac{T}{300}\right)^{1.67}, \; L \approx d_E$$
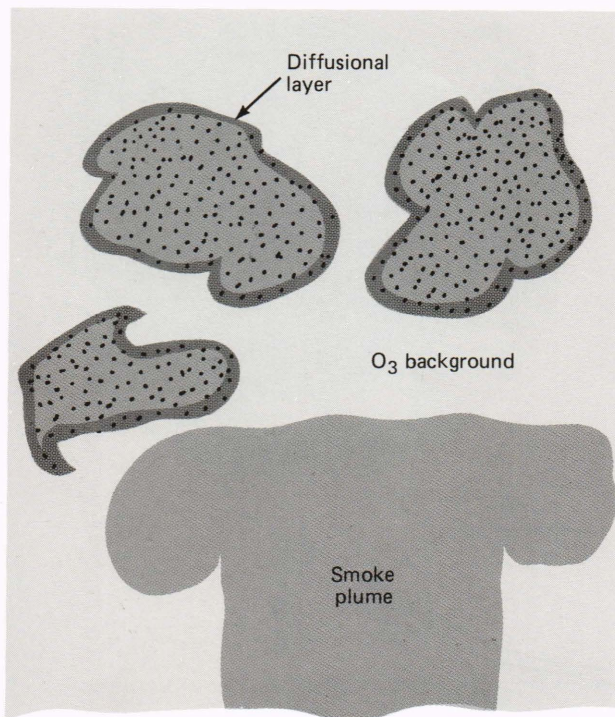
$$t_{1/2} = 1 \times 10^{-4}\frac{PN_Td_E^2}{N_{O_3}R}\left(\frac{300}{T}\right)^{1.67}$$

Figure 3—Case 3. Smoke formed in an ozone-depleted plume; the rate is limited by turbulent mixing that, in turn, is limited by diffusion into the smallest scale eddy.

cient chemical reactivity. Cases 1 and 2 illustrate that rates of scavenging are not limited by local diffusion or ozone concentration when involving individual particles.

SMOKE/OZONE EXPERIMENTS

Smoke lifetimes under conditions present at altitudes of interest are inconveniently long for laboratory experiments. Fortunately, laboratory simulations lie in a more convenient time range (1 second at laboratory conditions can be made equivalent to 10 minutes at high altitude). This is so because of the high ratio of laboratory ozone concentration to atmospheric concentration ($\approx 5 \times 10^4$). The laboratory room-temperature factor favors reaction over lower temperatures at altitude, but temperature can be simulated easily, as can the actinic light bath. Initial experiments (see Figs. 4 and 5) ignore these refinements.

Smoke prepared by using a smoky lantern fueled by toluene or xylene was collected in a large plastic bag. Fines below 1 micron were selected by allowing overnight settling. The size was confirmed by measuring the variation of forward scattering with angle using a helium-neon laser with a sensitive photometer. Other sources of smoke particles used in these experiments were acetylene, cellulose, and polystyrene.

The initial smoke concentration was determined by pumping a known volume of the smoky atmosphere through a filter paper, which, with collected smoke, was weighed on a microbalance. Smoke concentration was monitored by measuring the forward-scattered light at a fixed angle, normalized to beam intensity.

The size and morphology of the smoke particles have been determined using the scanning electron microscope on collected smoke samples. The smoke particles derived from a xylene flame had a crystalline-like graphitic structure. However, smoke particles obtained from a cellulosic source had an amorphous structure. Acetylenic smoke particles had a structure resembling connected spheres.

Ozone concentration was measured by absorption of the Chappuis bands, which peak at the helium-neon laser output. The photometric value was confirmed by a chemical method (iodine formation from aqueous potassium iodide).

A stopped-flow experimental procedure has been developed showing that ozone (without smoke) is stable in the apparatus over a period of hours; smoke (without ozone) is also stable over a period of hours. However, smoke-ozone mixtures begin decaying immediately, and, under the experimental conditions employed, the mixtures have half-lives of one-half to 2 hours depending on the fuel source of the smoke particles. Specifically, the half-life is defined as the time in which the optical extinction at 6328 angstroms is reduced to one-half its initial value. Translating these results to nuclear winter atmospheric conditions yields half-lives in the range of several weeks to several months. These experiments provide evidence for the existence of atmospheric chemical scavenging of smoke by ozone and indicate that the rate is significant for understanding the dynamics of nuclear winter.

The experiments described herein have been designed to yield values for the half-life of various types of smoke particles in ozone. The work is in a preliminary stage;
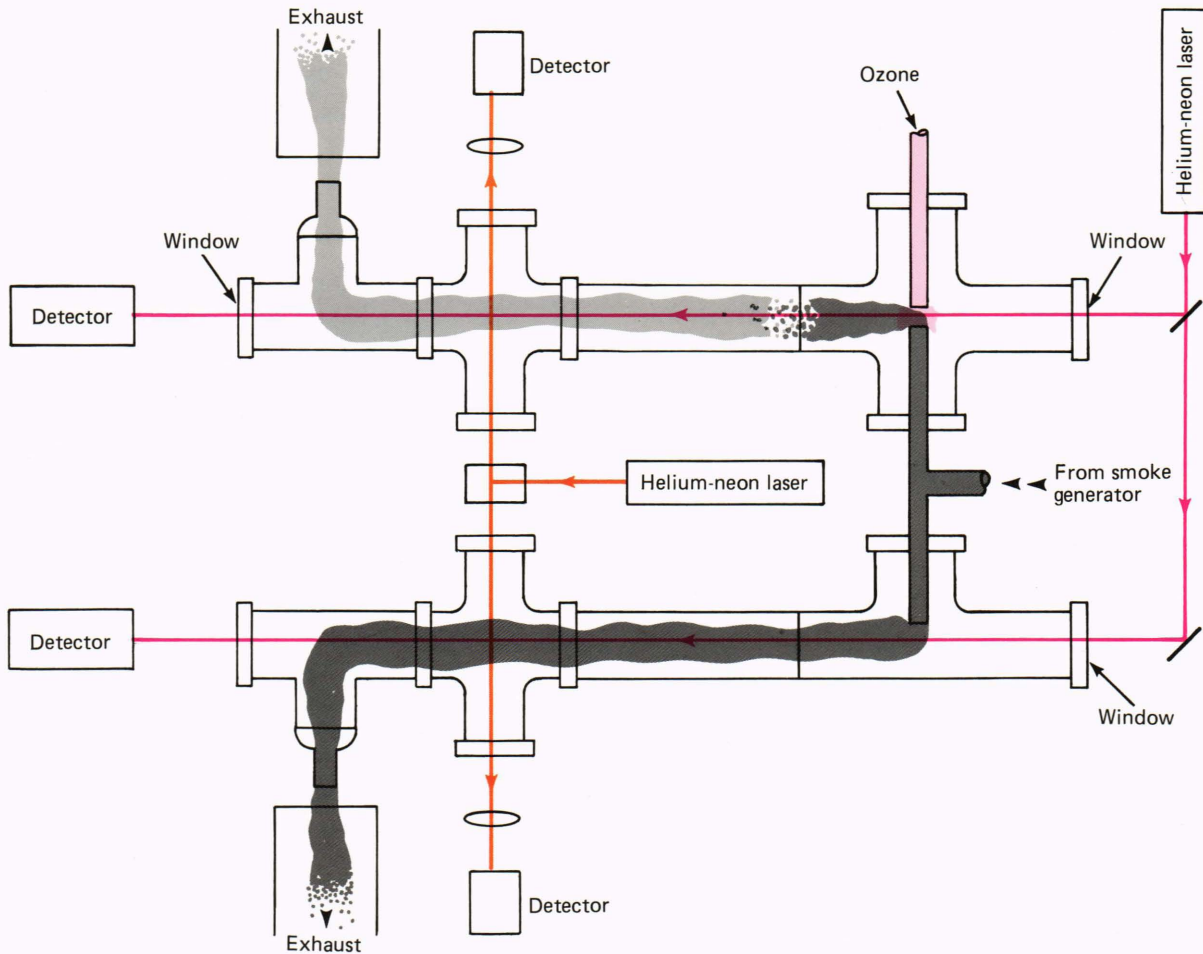
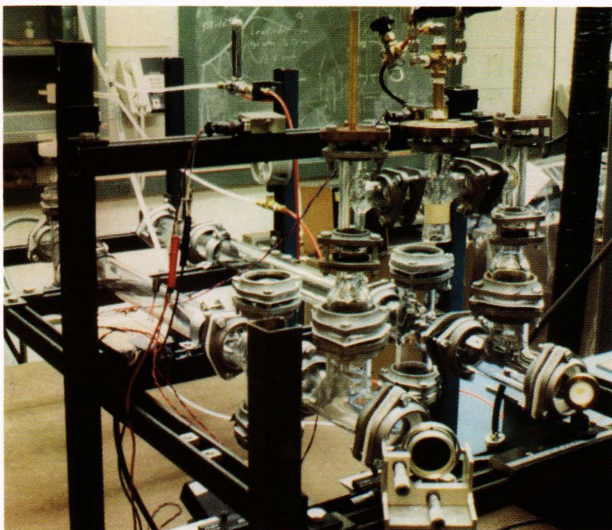**Figure 4**—Schematic of smoke/ozone experimental apparatus.

Figure 5—The laboratory smoke/ozone experiment.

however, when the experimental procedures have been completed, the results should be of direct use in global modeling calculations[11-13] and in assessments[14,15] of the nuclear winter problem.

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THE AUTHORS

NEWMAN deHAAS (right) is now a member of the Materials Science Group of the Milton S. Eisenhower Research Center after working in the Bumblebee Warhead and Propulsion Groups since joining APL in 1951. He received a B.S. degree in physics from Iowa State University (1950) and an M.S. degree in physics from the University of Maryland (1956). In the Research Center, he has been involved in research related to the transport of gases, gas-phase chemical kinetics, and the outgassing of microelectronic materials. His birthplace is Harrison, Ark.

ROBERT M. FRISTROM (center) was born in Portland, Ore., and received degrees in chemistry from Reed College (B.A.), the University of Oregon (M.A.), and Stanford University (Ph.D.). He was a Research Fellow in chemistry at Harvard Unversity from 1948 to 1951. In 1951, he joined APL in the Bumblebee Propulsion Group. Presently he is in the Computational Physics Group of the Milton S. Eisenhower Research Center. His interests at the Laboratory have included propulsion, microwave spectroscopy, flames, fire, molecular beams, and chemical kinetics.

Dr. Fristrom has been awarded the Parsons Fellowship, the Silver Medal of the Combustion Institute, the Hillebrand Award of the Chemical Society of Washington, the Certificate of Achievement from the Armed Services Explosives Safety Board, and one of the first Humboldt Foundation awards (of West Germany) to U.S. scientists. His publications include three books and over 90 technical and review articles.

MILTON J. LINEVSKY (left, standing), who joined APL in 1979 as a member of the Milton S. Eisenhower Research Center, was born in Glen Cove, N.Y. He received the B.S. degree in chemistry (1949) at the Rensselaer Polytechnic Institute and the M.S. and Ph.D degrees (1951,1953) in physical chemistry from the Pennsylvania State University. Prior to joining APL, he was a member of General Electric's Space Sciences Laboratory (1957-79), where he was involved with chemical lasers, high-temperature materials, and spectroscopy. As a member of the Aeronautics Department, his research interests include problems in combustion, chemical kinetics, aeronomy, and turbulence.
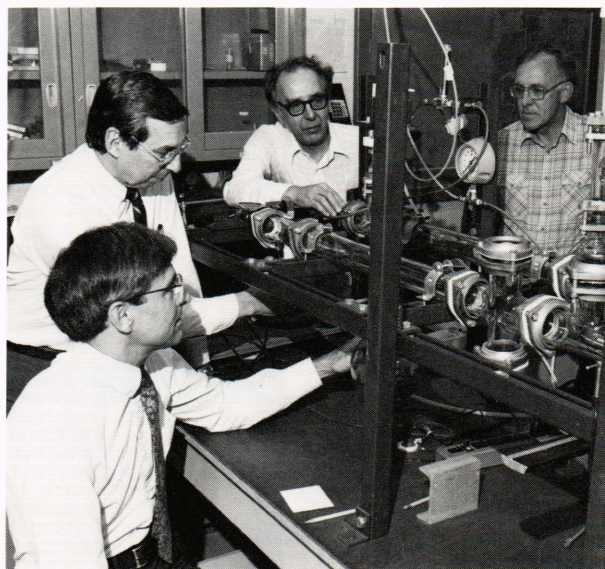
DAVID M. SILVER (left, seated) is a chemist and the supervisor of the Computational Physics Group in the Milton S. Eisenhower Research Center. Born in Chicago, he obtained a B.S. degree from Illinois Institute of Technology, an M.A. degree from The Johns Hopkins University, and a Ph.D degree from Iowa State University. Subsequently, he was a National Science Foundation Fellow at Harvard and a visiting scientist at the Centre Européen de Calcul Atomique et Moléculaire. He joined APL in 1970. Dr. Silver's research interests span the areas of theoretical and physical chemistry, molecular and computational physics, atmospheric chemistry and aeronomy, cryogenics, oceanography, rocket motor technology, and strategic systems. He is a member of the AAAS, the American Chemical Society, the American Geophysical Union, the American Physical Society, the Association of Harvard Chemists, the U.S. Naval Institute, and the United States Strategic Institute.