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CONTAMINATION OF THE SPACE STATION ENVIRONMENT BY VENTED CHEMICALS

Paul A. Bernhardt

Geophysical and Plasma Dynamics Branch
Naval Research Laboratory
Washington, D.C. 20375

Abstract. Gaseous materials vented from the Space Station may have noticeable effects on the optical or plasma environment. The magnitude of the effects depends on: (1) rarefied gas dynamics, (2) photochemical reactions, and (3) airglow excitation mechanisms. In general, the effects from atomic species can be mitigated, but the disturbances resulting from venting of molecules like SF₆, CO₂, and C₂H₂ can be significant. The interaction of molecules with the ambient plasma at orbital velocities should be studied with laboratory or space experiments.

Introduction

In this work, we will discuss the environmental effects from vapor substances vented during materials science and life science experiments on the Space Station. These effects can be transient or long-lived depending on the duration of the venting and the type of interaction. Both transport and chemical reactions of the released materials will disturb the neutral and plasma densities of the background atmosphere. The injected atoms may become collisionally or chemically excited to yield enhanced airglow. Procedures for estimating the magnitude of the airglow and density perturbations are described.

As a baseline, we are considering a Space Station orbit at 450 km altitude where, during solar maximum, the neutral density will be about $4 \times 10^8 \text{ cm}^{-3}$ and the neutral temperature may be as high as 2000° K. During solar minimum, the orbit altitude could be reduced to 320 km where neutral densities and temperatures are as low as $1.3 \times 10^8 \text{ cm}^{-3}$ and 705° K, respectively.

The materials considered in this study are listed in Table 1. The atomic species from the materials science experiments are released at rates of 10^{15} to 10^{17} atoms s⁻¹ for several days. The life science experiments deposit atomic or molecular species in 1 to 500 g bursts.

Table 1. Space Station Vented Species.

Vapor	Molecular Weight	Release Amount
<u>Atoms</u>		
Helium	4	7.5×10^{25a}
Neon	20	3.0×10^{24a}
Argon	40	1.5×10^{24a}
Aluminum	27	10^{15} to 10^{17b}
Phosphorous	31	"
Manganese	54.9	"
Gallium	69.7	"
Arsenic	74.9	"
Cadmium	112.4	"
Indium	114.8	"
Tin	118.7	"
Tellurium	127.6	"
Mercury	200.7	"
Lead	207.2	"
<u>Molecules</u>		
Carbon monoxide	28	2.1×10^{22c}
Nitrogen	28	1.1×10^{25c}
Oxygen	32	9.4×10^{24c}
Carbon dioxide	44	1.4×10^{24c}
Acetylene	26	2.3×10^{22c}
Sulfur hexafluoride	146	4.0×10^{23c}

^aatoms

^batoms s⁻¹

^cmolecules per run

Gas Dynamics of Vented Species

The Space Station will be moving supersonically with respect to the ambient atmosphere. At 450 km altitude, the orbital velocity is 7.6 km s^{-1} . The exospheric neutral temperature range of 700 to 2000° K and an average molecular weight of 16.4 amu gives a sound speed of about 10^3 m s^{-1} . Moving at Mach 7 or greater, the mean times between collisions of a single particle will be dependent on the mean free path in the atmosphere, λ_a .

The type of flow for the vented gases will depend on the relationship between the gas cloud size (L), the mean free path inside the cloud (λ_c), and the atmospheric mean free path (λ_a). Figure 1 illustrates these relationships for self-continuum flow ($\lambda_c < L < \lambda_a$), collisionless flow ($L < \lambda_c < \lambda_a$), and diffusive flow ($\lambda_a < L < \lambda_c$). Each one of these phases occurs during the gas expansion process.

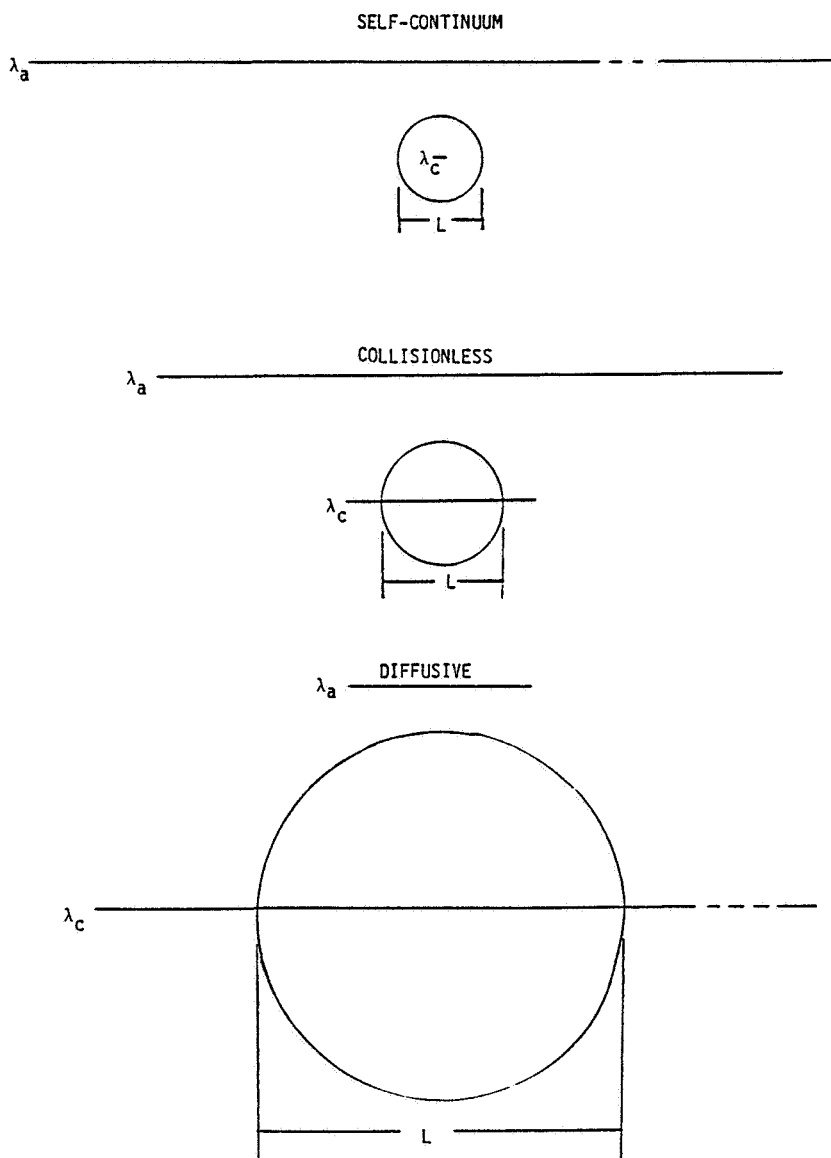


Fig. 1. Relationships between atmospheric mean-free-path, cloud diameter, and cloud mean-free-path for different flow descriptions.

A sample calculation for the self-continuum phase is illustrated in Figure 2. The motion of 0.1 kg of CO₂ released from a point moving at 4.7 km s⁻¹ is simulated using the Los Alamos multi-fluid flow-model (Bernhardt et al., 1988). This type of interaction with the upper atmosphere is representative of venting from the life science experiments on the Space Station. The background atmosphere is assumed to be uniform with $m_a = 16.4$ amu, $T_a = 705^\circ$ K, $n_a = 1.3 \times 10^8$ cm⁻³, and $\gamma_a = 1.5$ based on a thermospheric model for a 317 km release altitude. The core of the injected material is heated to a few thousand Kelvin above ambient. The background atmosphere - ions, electrons, and neutrals - is swept up by the fast moving release.

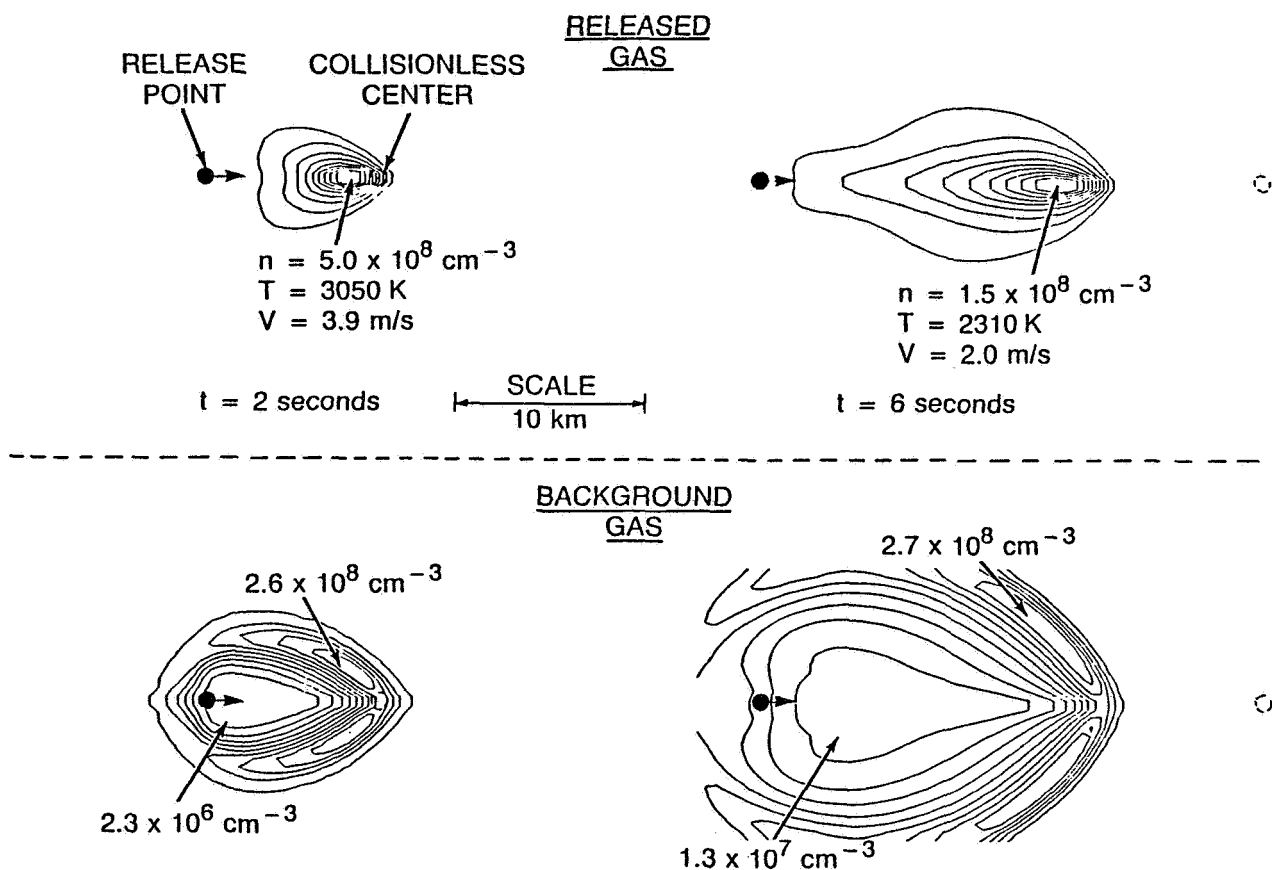
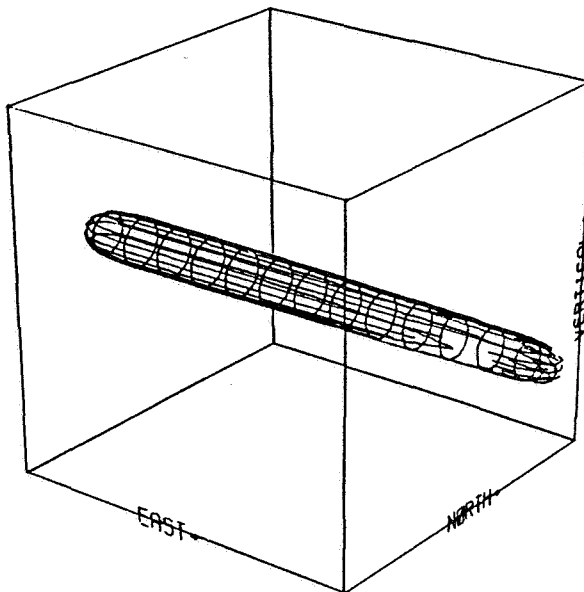


Fig. 2. Neutral gas distribution from the release of 0.1 kg of vented CO₂ at 317 km altitude. The solid circle is the release location. The dashed circle shows the center of the release for collisionless motion. An elongated cavity is formed in the background.

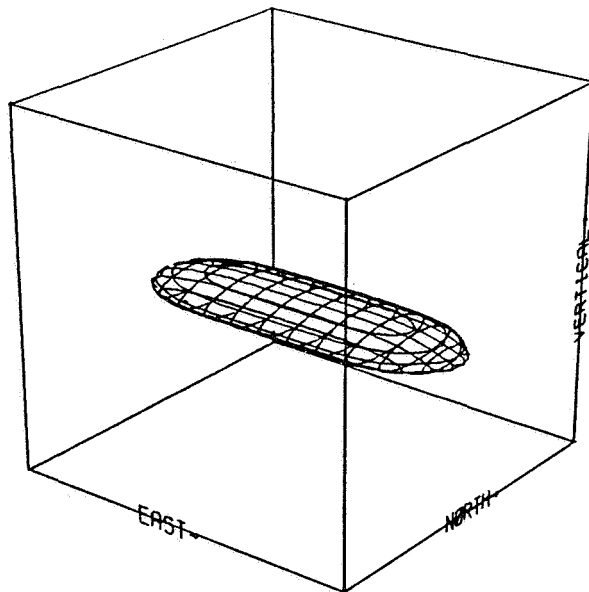
The diffusive-expansion phase is shown in Figures 3 and 4. Molecules are released from a source moving horizontally at 7.6 km s^{-1} . The release rate is $10^{17} \text{ atoms s}^{-1}$ lasting 150 s. The calculation uses the three-dimensional diffusion model described by Bernhardt (1979). The neutral scale height at the 400 km release altitude is 57 km. Relatively larger diffusion at higher altitudes causes the cloud to settle and to dissipate.



1638 km CUBE CENTERED AT 400.0 km ALTITUDE
 TIME AFTER RELEASE: 25.8 sec $\frac{1}{4}$
 H_2O CONCENTRATION AT SURFACE: $5.7 \times 10^4 \text{ m}^{-3}$

Fig. 3. Cylindrical cloud of H_2O to illustrate molecular diffusion.

One half hour after the release, the maximum density of the cloud has been reduced by a factor of 11 and the peak has fallen to 220 km altitude. When the Space Station crosses a release point after one orbit of 1.5 hours, the original release will be dissipated. Recontamination does not seem to be a problem.



2560 km CUBE CENTERED AT 400.0 km ALTITUDE
 TIME AFTER RELEASE: 1736.5 sec
 H_2O CONCENTRATION AT SURFACE: $3.3 \times 10^{-3} \text{ m}^{-3}$

Fig. 4. Late-time, pancake distribution of the diffusing gas.

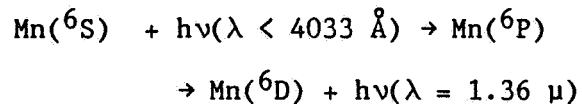
Chemistry of the Vented Species

Chemical reactions may determine the fate of the vented species. Should the vapors become ionized, they will become trapped in magnetic flux tubes and their dispersal will be limited by one-dimensional diffusion along B . The materials may become ionized by photo-processes, collisional processes, charge exchange with ambient O^+ ions, or by electron attachment. Table 2 lists the ionization potentials of the vented atoms. All of the ionization potentials are less than their kinetic energy at orbital velocity. Consequently, collisional ionization or critical-velocity ionization may be important. Photoionization by single photon events takes about 10^6 s for substances like Al, Ga, and In which have ionization potentials near 6 eV.

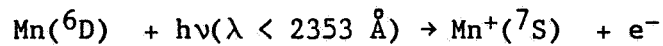
Table 2. Atomic Species Release.

Name	Symbol	IP (eV)	λ_0 (Å)
Helium	He	24.6	591
Neon	Ne	21.6	626
Aluminum	Al	6.0	3944
Argon	Ar	15.8	894
Phosphorous	P	10.5	1788
Manganese	Mn	7.4	4034
Gallium	Ga	6.0	4173
Arsenic	As	9.8	1973
Cadmium	Cd	9.0	3261
Indium	In	5.8	4513
Tin	Sn	7.3	3035
Tellurium	Te	9.0	--
Mercury	Hg	10.44	2536
Lead	Pb	7.42	3685

Atoms with metastable states may be ionized more rapidly by a two photon process. The first photon populates the metastable state and the second photon ionizes the material from this state. Consequently, lower-energy, more-abundant solar photons are used. Manganese may be a candidate for two photon ionization. The Mn(⁶D) level can be populated as follows

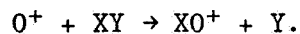


The ionization then only requires 5.27 eV.

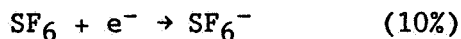


the time constant for photoionization of Mn will be about 10^5 s.

Reactions with the ambient ionospheric constituents will ionize the vented species. In the ionosphere, most ion-molecule reactions have the form



Thermal-energy rate constants for reactions between the vented molecules and ambient O^+ ions are given in Table 3. The rates and reaction products can be substantially different for orbital velocity interactions (Caledonia et al., 1987). Also listed in Table 3 is the electron attachment rate for SF_6 for the reactions



Subsequent chemical reactions of the newly created ions will deplete the ambient plasma and may leave the reaction products in excited states to produce airglow.

Table 3. Molecular Species Releases.

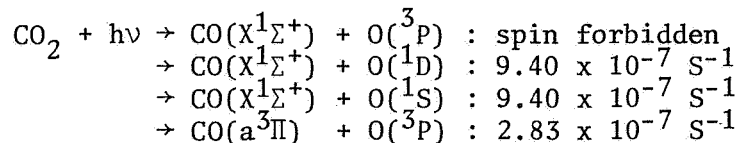
NAME	IP(eV)	$t_I(10^6 \text{ s})$	$D_0(\text{eV})$	$t_D(10^6 \text{ s})$	$k_{O^+}(\text{cm}^3 \text{ s}^{-1})$	$k_{e^-}(\text{cm}^3 \text{ s}^{-1})$
Carbon monoxide	14.014	3.2	11.09	3.6	5.0×10^{-13}	0.0
Nitrogen	15.581	2.9	9.76	1.5	1.2×10^{-12}	0.0
Oxygen	12.071	2.0	5.116	0.24	1.9×10^{-11}	0.0
Carbon dioxide	13.769	1.5	5.45 (CO-O)	0.82	9.4×10^{-10}	0.0
Acetylene	11.42	1.3	5.38 (C ₂ H-H)	0.03	10^{-9}	0.0
Sulfur hexafluoride	15	---	3.95	0.3	1.5×10^{-9}	2.2×10^{-7}

Airglow Production by the Vented Species

Airglow enhancements may be excited by solar photons or by chemical reactions. Resonance fluorescence occurs by absorption of a solar photon and subsequent re-radiation at the same wavelength in an arbitrary direction. Table 2 lists the wavelengths for ground state transitions of vented atoms. Emissions from these substances occur in the ultraviolet and visible spectrum. A radiometric standard for acceptable radiance ($W \text{ sr}^{-1} \text{ m}^{-2}$) should be established for line emissions.

Atomic species can react with neutrals to produce molecules which fluoresce in sunlight. Atomic aluminum reacts with oxygen (O_2) to produce AlO . Bands of AlO at 4842 (0,0), 5080 (0,1), 4648 (1,0), and 5337 (0,2) have been measured after releases between 80-140 km. Simultaneous releases of Al and O_2 at 450 km probably should be avoided to prevent production of the fluorescent aluminum monoxide.

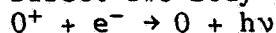
Excited states are produced during photodissociation of molecular species. For example, Huebner and Carpenter (1979) list the following products for photolysis of CO₂ in sunlight:



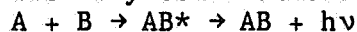
where the rate constants are given. The excited states O(¹D), O(¹S), and CO(a³Π) radiate at 6300, 5577, and 2054 Å, respectively. The dissociative energies and rate constants for photolysis of the molecules are given in Table 3.

Excited states may be produced without sunlight by collisional or chemiluminescent processes. The types of chemiluminescent reactions which yield excited species are listed below.

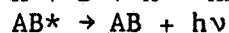
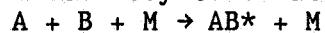
Direct Two-Body Combinations



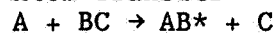
Two-Body Combinations with Preassociations



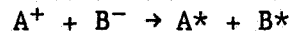
Three-Body Combinations



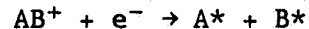
Atom Transfer



Mutual Neutralization

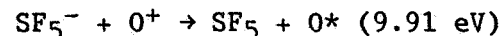
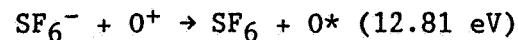


Dissociative Recombination



The excited CH and C₂ spectra from acetylene releases between 90 and 100 km altitude (Rosenberg, 1964) may be a result of photodissociation and atom transfer reactions with O₂.

The mutual neutralization and dissociative recombination reactions are known to yield excited atomic oxygen from SF₆ and CO₂ releases in the ionosphere (Bernhardt, 1987). The negative ions formed by electron attachment to SF₆ react with O⁺ to give excited atoms.



At thermal speeds, only the first reaction has enough energy to populate O(3p³P) and O(3p³P) states which radiate in the visible at 777.4 nm and 844.6 nm, respectively. The thermal, low-speed release of 7.4 x 10²⁵ molecules of SF₆ into the ionosphere was estimated to produce 150 Rayleighs at 777.4 nm (Bernhardt et al., 1986). At orbital velocities, we calculate that the same SF₆ release would produce over 6000 Rayleighs.

Conclusions

In this note, we have tried to identify some upper atmosphere disturbances that are stimulated by the venting of vapors from the Space Station. These disturbances include neutral and plasma density perturbations and airglow enhancements. Modeling efforts should be considered for estimating:

(1) Transient behavior of the release, including gas dynamics, collisional airglow excitation, and chemical reactions.

(2) Long-term, global distribution of the material in neutral and ionized states.

Standards should be established for acceptable levels of line emissions. This would be in addition to the spectral irradiances ($\text{Watts m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$) for particulate and molecular scattering given by the Space Station External Contamination Requirements (JSC 30426, November 19, 1986).

The atoms listed in Table 1 should present no hazard to the Space Station environment. All of the atomic species except helium, neon and argon, can be condensed and prevented from being released as a vapor. The other three atomic vapors (i.e., He, Ne, and Ar) are inert to photochemical process and should not be noticeable.

The molecules listed in Table 1 can be hazardous to both the optical and plasma environment. They are all gaseous at standard temperature and pressure and they all react with O^+ at orbital velocities. Sulfur hexafluoride seems to be the most harmful of these substances because it also interacts with the ambient plasma through dissociative or radiative attachment. The molecular species create excited states by dissociative recombination of positive ions and electrons and by mutual neutralization of negative ions and O^+ . These states radiate line emissions which may interfere with low-light-level observations.

The primary uncertainty in predicting the effects of the vented species is the reactions of ambient O^+ with the high velocity molecules. At orbital velocity, O^+ has 5 eV energy and reaction products and rates are different than at thermal energies. These interactions should be measured with laboratory or space experiments. The Combined Release and Radiation Effects Satellite (CRRES) mission provides an excellent opportunity to measure the interaction of SF_6 and, possibly, CO_2 with O^+ at orbital velocities.

References

- Bernhardt, P.A., Three-dimensional, time-dependent modeling of neutral gas diffusion in a nonuniform, chemically reactive atmosphere, J. Geophys. Res., 84, 793, 1979.
- Bernhardt, P.A., A critical comparison of ionospheric depletion chemicals, J. Geophys. Res., 92, 4619, 1987.
- Bernhardt, P.A., E.J. Weber, J.G. Moore, J. Baumgardner, and M. Mendillo, Excitation of oxygen permitted line emissions by SF_6 injection into the F-region, J. Geophys. Res., 91, 8937, 1986.
- Bernhardt, P.A., B.A. Kashiwa, C.A. Tepley, and S.T. Noble, Spacelab 2 upper atmospheric modification experiment over Arecibo, 1, neutral gas dynamics, Astrophysical Lett. and Comm., in press, 1988.
- Caledonia, G.E., J.C. Person, and D.E. Hastings, The interpretation of space shuttle measurements of ionic species, J. Geophys. Res., 92, 273, 1987.
- Huebner, W.F. and C.W. Carpenter, Solar Rate Coefficients, Los Alamos Report LA-8085-MS, October 1979.
- Rosenberg, N.W., Project Firefly 1962-1963, AFCRL-64-364, May 1964.