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MODELS OF IONOSPHERIC RELEASE EXPERIMENTS

Part I. SF_6 Releases
Part II. CO_2 Releases

J. Vincent Eccles
Russell A. Armstrong

Mission Research Corporation
One Tara Blvd., Suite 302
Nashua, NH 03062-2801

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PHILLIPS LABORATORY
AIR FORCE SYSTEMS COMMAND
HANSCOM AIR FORCE BASE, MASSACHUSETTS 01731-5000

"This technical report has been reviewed and is approved for publication"

Donald E Hunton
DONALD E. HUNTON
Contract Manager

John F. Paulson
JOHN F. PAULSON, Chief
Ionospheric Interactions Branch

William K Vickery
WILLIAM K. VICKERY, Director
Ionospheric Effects Division

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Russell A. Armstrong

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Nashua, NH 03062-2801

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High-altitude chemical releases are investigated with the use of several numerical models of chemistry, dynamics, and electrodynamics. The specific releases investigated were SF_6 and CO_2 releases in the F-region of the ionosphere.

The chemistry for reproducing observations from the CRRES-at-Kwajalein SF_6 release must include oxidation reactions of ions and neutrals. The dominant negative ion observed, F^-, was modeled well with $SF_5^- + O \longrightarrow SOF_4 + F^-$ as the dominant production mechanism. SOF_3^- is potentially an important negative ion resulting from electron attachment of SOF_4. The electrodynamics model of the SF_6 release did not produce a plasma depletion plume as was hoped. The electrodynamic perturbation is small and short-lived. It will not produce large-scale plume structure associated with equatorial spread-F.

The modeling of CO_2 releases produced too much 6300A airglow when compared with REDAIR experimental results. The conflict between simulation and experiment requires reduction of $CO_2 + O^+$ reaction rates or inclusion of a CO_2 removal mechanism such as freezing. Modeling also shows that the two CO_2 releases of the REDAIR experiment may have spatially mixed airglow signatures.

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PART I. SF_6 RELEASES

1. INTRODUCTION

Sulfurhexafluoride (SF_6) chemistry has been extensively studied for thirty-five years as a gaseous insulator in high-voltage systems. The insulation ability comes from the fast removal of free electrons through electron attachment. The reduced negative charge mobility provides increased resistance to electrical discharges.

The interest in SF_6 as a release chemical in the earth's ionosphere has grown, flagged, and grown. With each SF_6 release the modeling of the SF_6-ionosphere chemistry becomes more complex. This study is no exception to the trend. In the Project Firefly campaign during the early 1960's *Rosenberg* [1964] assumed that the electron attachment ability of SF_6 dominated the physics. The study discussed an electron hole and negative-positive ion plasma. In 1983, Project IMS (Ionospheric Modification Studies) brought about more detailed chemistry: electron attachment, dissociative electron attachment, and subsequent negative-positive ion recombination [*Mendillo and Forbes*, 1982; *Bernhardt*, 1984]. *Mendillo and Forbes* [1982] assumed the major ion would be SF_6^-, while *Bernhardt* [1984] predicted SF_5^- would dominate due to the high ambient temperature [*Fehsenfeld*, 1970]. Experimental results from an SF_6 release in the E-region provided insight into the importance of F^- [*Hunton et al.*, 1987].

The most recent ionospheric releases of SF_6 were performed as part of the CRRES (Combined Release and Radiation Effects Satellite) program. The results of CRRES-at-Kwajalein show that F^- is a dominant product of the SF_6 chemistry in F-region releases (D. E. Hunton, private communication).

Beyond the chemical aspect of the SF_6 release in the ionosphere, there are electrodynamic and transport considerations that must be taken into account. Indeed, the primary goal of the CRRES releases of SF_6 was the study of the artificial perturbation to the electrodynamics of the evening equatorial ionosphere. Barium and water releases in the evening equatorial ionosphere were used in the Coloured Bubbles Experiment and the Brazilian Ionospheric Modification Experiment (BIME) to alter electrodynamics of the ionosphere [*Haerendel et al.*, 1983] and possibly initiate Equatorial Spread-F (ESF). The study of the artificially-initiated ESF will hopefully illuminate the natural causes of ESF.

1.1 Ambient Conditions

There were two SF_6 releases of the CRRES project flown during the summer of 1990. The studies presented here focus on the second release. Prior to the investigation of the perturbed environment, the baseline ambient environment must be modeled. The atmospheric and ionospheric conditions used as a background for the modeling studies reflect the estimated conditions of the CRRES rocket launch from Kwajalein during August 1990. Table 1 compiles the geographic, solar, and atmospheric conditions for the equatorial launches. Both flights released approximately 35 kg of SF_6 (1.4×10^{26} molecules) through a nozzle at a temperature of 320K. The release took about 3 to 7 s.

Table 1. CRRES-at-Kwajalein release conditions.

Launch	15 August 1990
10.7 cm Flux	193
< 10.7 cm Flux >	200
Sunspot Number (R_a)	218
Geo-Longitude	167 East
Geo-Latitude	10 North
Magnetic Dip	0 degrees
A_p Index	26
K_p Index	29
Release Altitude	429 km
Local Solar Time	20.30

It is estimated that 40% of the SF_6 freezes in the release expansion [*Bernhardt*, 1987] and does not participate in the chemistry in a significant way. Figures 1 and 2 present the atmospheric constituents and temperature, respectively, as predicted by the MSIS86 neutral atmospheric model [*Hedin*, 1987]. Figure 3 shows the ionospheric constituent densities obtained by combining the measured electron density and a steady-state chemistry model.

1.2 Electrodynamics Considerations

The interaction of the magnetic field, neutral atmosphere, and ionosphere produces the global electric field system. The large-scale electric field provides the zeroth-order motion of the ionosphere. The primary ionospheric current system is the Solar Quiet (Sq) system. The Sq system is modeled with reasonable success using solar-driven, tidal-mode wind models and an E-region conductivity model [*Richmond et al.*, 1976].

General trends of the equatorial electric fields are reviewed in *Fejer* [1981]. During the day the ionospheric plasma near the equator rises at 10 ms^{-1} due to the eastward electric field created by the Sq current divergences. The F-region profile appears to remain stationary due to the continual production of plasma in the F_1-region. However, after sunset the production ceases and the F-region profile rises.

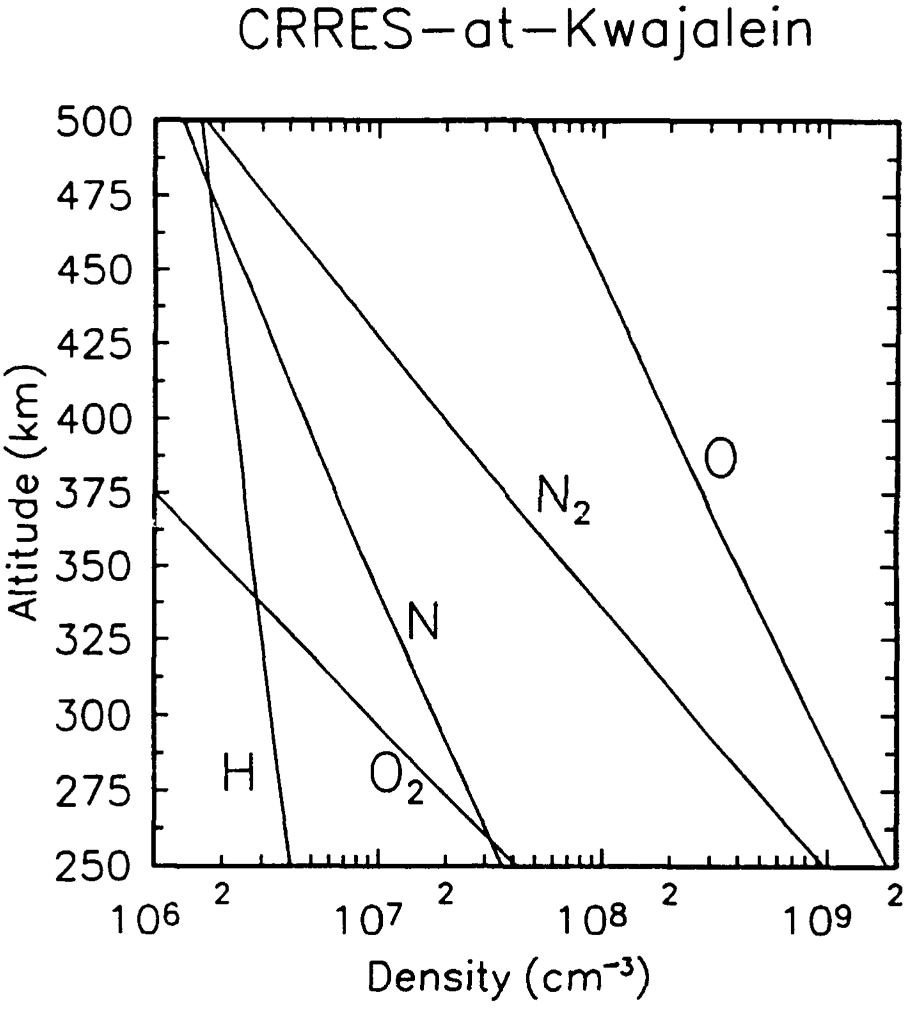

Figure 1. The neutral constituents predicted for the equatorial evening atmosphere in July and August of 1990 by MSIS86 [*Hedin*, 1987].

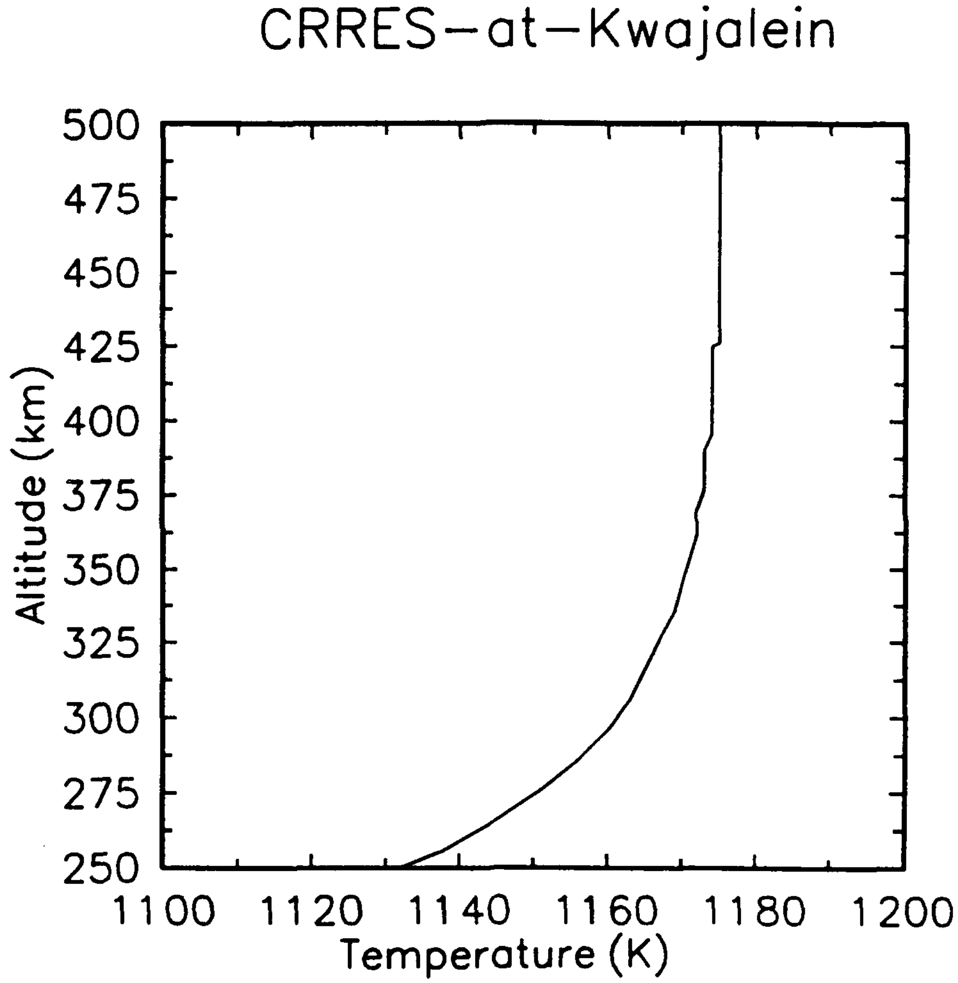

Figure 2. The neutral temperature of the equatorial evening atmosphere as determined for July and August of 1990 by MSIS86 [*Hedin*, 1987].

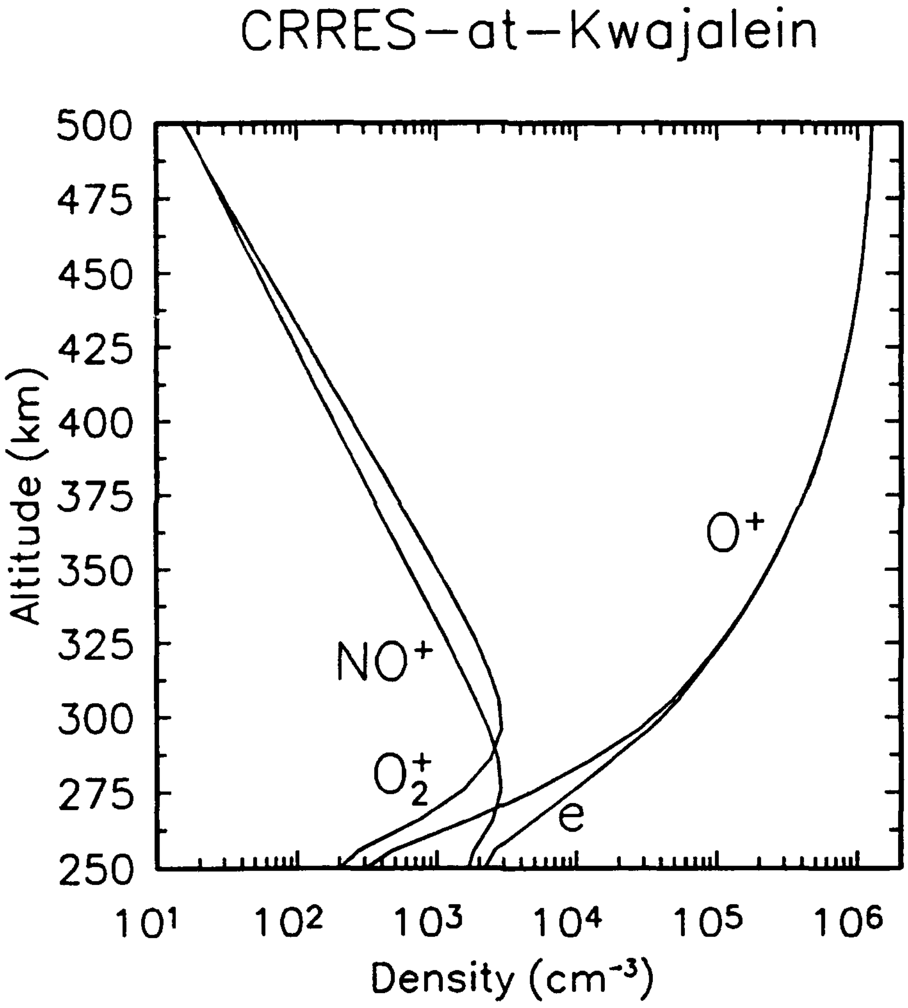

Figure 3. The plasma density measured by Altair radar for the equatorial evening ionosphere of 15 August 1990.

The evening F_1-region chemically decays causing the bottomside F-region ledge to steepen. The evening decay of E- and F_1-region plasma reduces conductivity and causes an increase in polarization electric fields after sunset [*Rishbeth*, 1971]. At sunset the enhancement of the downward-directed electric field drives the plasma eastward at about the same velocity as the thermospheric winds (100 to 200 ms^{-1}). The F-region horizontal drift is fairly constant from night to night and easily predicted from a knowledge of conductivities and the neutral wind magnitude. Unfortunately, a self-consistent electric field model is computer intensive and does not give the desired detail needed for the evening region of the ionosphere. A simplified predictive model of the equatorial electric fields can be obtained from input of average ambient conditions (neutral densities, neutral winds, plasma densities, F- and E-region conductivities) [*Haerendel et al.*, 1991]. The calculation of large-scale electric fields (> 5 km) can be treated as a two-dimensional problem where the important ionospheric quantities are integrated along flux-tubes. The vertical electric field is approximately given by

$$E_z = -(\int u_n \sigma_p \, dl)/\Sigma_p + \Sigma_h E_x/\Sigma_p \qquad (1.1)$$

[*Haerendel et al.*, 1991; *Anderson and Mendillo*, 1983]. E_z is the vertical electric field, E_x is the west-to-east electric field, u_n is the west-to-east neutral wind, σ_p is the local Pederson conductivity, Σ_p is the integrated Pederson conductivity, and Σ_h is the integrated Hall conductivity. Integrations are performed along the magnetic field line (*dl*). Figure 4 shows the integrated conductivities of the evening ionosphere. Figure 5 shows the resulting E_z given a neutral wind of 150 ms^{-1}, $E_x = 1$ mVm^{-1} and $B = .25 \times 10^{-4}$ T. The resulting horizontal motion has a shear at the F-region ledge. Above the shear the velocity is eastward and below it is westward.

Throughout the day the F-region plasma moves upward at about 10 ms^{-1}. Near sunset the plasma vertical velocity (horizontal electric field) grows in magnitude to 30-70 ms^{-1} for about 1 to 2 hours. After the enhancement, the ionosphere drops rapidly (20 ms^{-1}) and continues to have a downward velocity through the remainder of the night (Figure 6). The evening enhancement of the rise velocity has been the focus of scientific study due to its correlation with the occurrence of ESF. Unfortunately, the vertical rise velocity is extremely variable from night to night and difficult to predict. Preliminary determinations of plasma motion for the CRRES-at-Kwajalein launches show that the ionosphere was rising rapidly during the release (50 ms^{-1}).

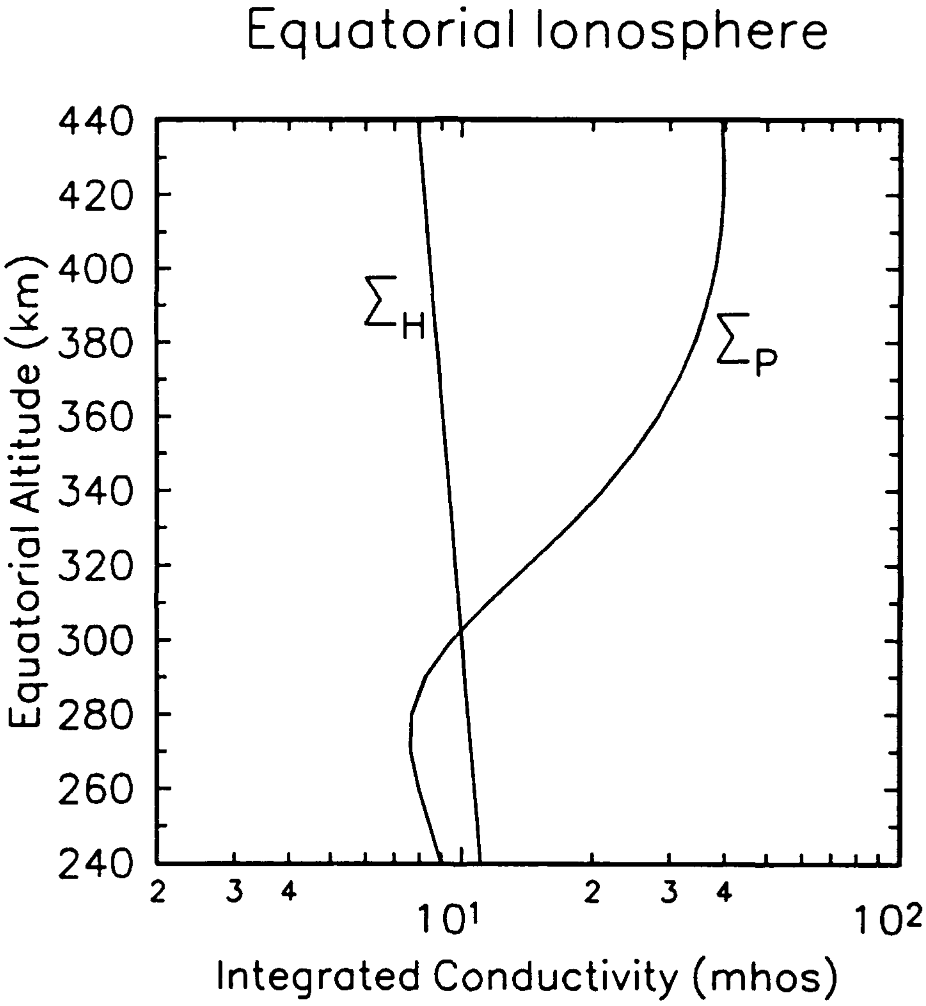

Figure 4. Integrated conductivities of the evening ionosphere.

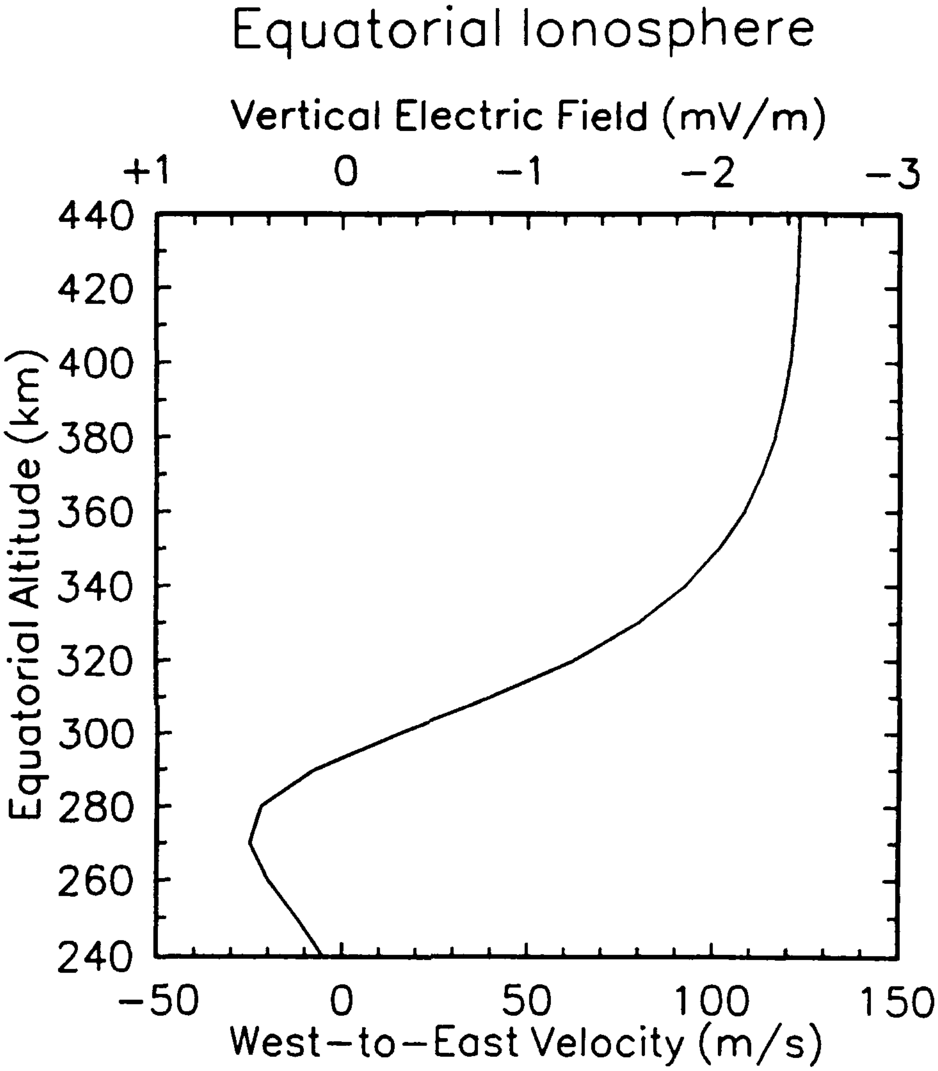

Figure 5. The shear of the horizontal plasma motion derived from the ionospheric conductivities shown in Figure 4. The corresponding vertical electric field strength is shown on the top axis.

The time history of the horizontal electric field can be modeled given integrated ionospheric quantities and $E_x(t)$ (rise velocity) [*Haerendel et al.*, 1991]. The horizontal electric field moves the F-region upward. The rise alters the conductivity-weighted neutral wind in equation (1.1). The shear feature in the horizontal velocity rises (and falls) with the F-region. The above electric field model completes the necessary picture of the ambient conditions of neutral atmosphere, ionosphere, and associated electric fields. One can now introduce chemical perturbations to the background to study resulting composition and electrodynamics changes.

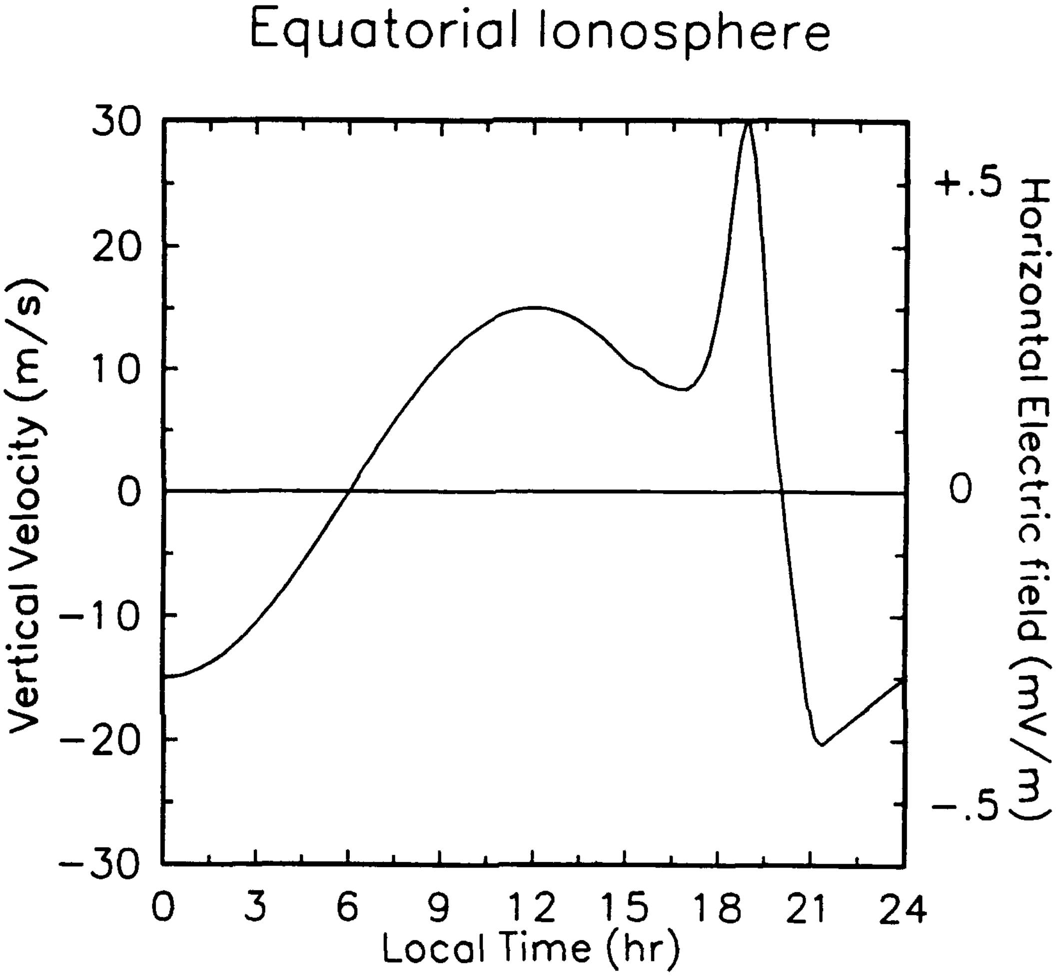

Figure 6. The vertical plasma velocity for typical day during solar maximum [*Fejer*, 1981]. The corresponding vertical electric field st with the corresponding horizontal electric-field strength is shown on the right axis.

2. CHEMISTRY

2.1 Reaction Set

Mendillo and Forbes [1982] and *Bernhardt* [1984; 1987] review important ion chemistry of ionospheric SF_6 releases. Several important reactions are added by *Hunton et al.* [1987]. It is apparent from previous and present SF_6-ionospheric chemistry studies that there is still an element of unknown in the set of chemical reactions. We have attempted, first, to assemble an SF_6 chemistry database, second, to solve the time-dependent chemical system, third, to solve chemistry and transport in a multi-dimensional model, and finally, to indicate directions for future investigation.

SF_6 Ionospheric Chemistry

Initially, the dominant reaction is SF_6-e attachment, which proceeds at a rate $k_c = 2.2\times10^{-7}\ cm^3s^{-1}$ for low energy electrons ($T_e \sim 0.1$ eV) [*Fehsenfeld*, 1970; *Mothes et al.*, 1972; *Spence and Schnultz*, 1973; *Phelps and Van Brunt*, 1988]

$$SF_6 + e \xrightarrow{k_c} \text{products}$$

The cross section dramatically drops off with increasing electron energies [*Mullen et al.*, 1971; *Kline et al.*, 1979; *Phelps and Van Brunt*, 1988]; only the lowest energy electrons have a significant attachment cross section with SF_6. For the low electron temperature of the ionosphere, k_c can be considered constant. If the electron temperature is high, the vibrational states of SF_6 provide a deep energy sink to cool electrons through inelastic collisions. Thus, low-energy electrons should always be present for attachment in an ionospheric release of SF_6.

The products of the electron attachment reaction depend upon the vibrational state of the parent SF_6 molecule prior to attachment. The branching of SF_6 attachment chemistry can be modeled with a ground state SF_6^- and a vibrationally excited SF_6^{-*}. SF_6^{-*} represents all SF_6^- molecules with vibrational energy below the F-SF_5^- dissociation energy. *Bernhardt* [1984] uses three vibrationally excited species, SF_6^{-*}, SF_6^{-**} and SF_6^{-***}, but the two additional excited species dissociate almost instantaneously into end products.

The three main branches of the attachment process

$$SF_6 + e \xrightarrow{k_1} SF_6^{-*} \tag{2.1a}$$

$$SF_6 + e \xrightarrow{k_2} SF_5^- + F \quad (2.1b)$$

$$SF_6 + e \xrightarrow{k_3} F^- + SF_5 \quad (2.1c)$$

have coefficients satisfying $k_1 + k_2 + k_3 = k_c$. Reaction (2.1*c*) is negligible at ionospheric temperatures.

The vibrationally excited state SF_6^{-*} can autodetach, radiatively stabilize, or collisionally stabilize, as illustrated in the following reactions.

$$SF_6^{-*} \xrightarrow{\alpha_a} SF_6 + e \quad (2.2a)$$

$$SF_6^{-*} \xrightarrow{\alpha_s} SF_6^- + h\nu \quad (2.2b)$$

$$SF_6^{-*} + M \xrightarrow{k_m} SF_6^- + M \quad (2.2c)$$

The reactions (2.1*a,b,c*) provide the initial competition for negative charge species dominance with corrections through (2.2*a,b,c*). Autodetachment of SF_6^{-*} is very rapid ($\alpha_a = 11000\ s^{-1}$) when compared to radiative stabilization ($\alpha_s = 100\ s^{-1}$). Collisional loss (Equation 2.2*c*) can be neglected above 200 km. Thus, the net production of SF_6^- through the combined reactions of (2.1*a*), (2.2b), and (2.2*c*) is

$$SF_6 + e \xrightarrow{k_a} SF_6^- \quad (2.3)$$

where

$$k_a = \frac{(\alpha_s + k_m[M])}{(\alpha_a + \alpha_s + k_m[M])} k_1 \simeq \frac{\alpha_s}{(\alpha_a + \alpha_s)} k_1 \simeq 0.01\ k_1$$

Along with fast attachment reactions, SF_6 reacts with the dominant positive ion of the F-region, O^+, via

$$SF_6 + O^+ \rightarrow SF_5^+ + F + O \quad (2.4)$$

(products suggested by E. E. Ferguson (private communication)). Other SF_n fragments can charge exchange with O^+ by

$$SF_4 + O^+ \rightarrow SF_4^+ + O \qquad (2.5)$$

$$SF_5 + O^+ \rightarrow SF_5^+ + O \qquad (2.6)$$

and alter the positive ion composition. The presence of positive ions also provides for an eventual decay of plasma density through ion-ion mutual neutralization.

$$SF_n^- + M^+ \rightarrow \text{neutrals} \qquad (2.7)$$

Two major adjustments to the negative ion populations result from the dominance of O in the upper atmosphere:

$$SF_6^- + O \rightarrow O^- + SF_6 \qquad (2.8)$$

$$SF_5^- + O \rightarrow F^- + SOF_4 \qquad (2.9)$$

Reaction 2.9 was suggested by *Hunton et al.* [1987]. It is shown in the present work to be the most important source of F^- in the ionospheric release of SF_6.

In addition to the above reactions, *Hunton et al.* [1987] suggest collisionally induced detachment and dissociation. Recent investigations [*Wang et al.*, 1989; *Olthoff et al.*, 1989] of collisionally induced detachment reactions,

$$SF_6^- + M \rightarrow SF_6 + e + M \qquad (2.10a)$$

$$SF_5^- + M \rightarrow SF_5 + e + M \qquad (2.10b)$$

$$F^- + M \rightarrow F + e + M \qquad (2.10c)$$

and collisionally induced dissociation reactions,

$$SF_6^- + M \rightarrow SF_5^- + F + M \qquad (2.11a)$$

$$SF_6^- + M \rightarrow F^- + SF_5 + M \qquad (2.11b)$$

$$SF_5^- + M \rightarrow F^- + SF_4 + M \qquad (2.11c)$$

show that these reactions are slow ($< 10^{-12}$ cm^{3}s^{-1}), therefore, they probably have limited influence on the chemical perturbation except during late times after the release.

Potentially important neutral reactions are missing in the review papers of ionospheric release of SF_6. The neutral reactions may influence the late-time development of an ionospheric perturbation. Due to the dominance of O at F-region altitudes, the oxidation of SF_n molecules leads to several SO_mF_{n-1} neutrals [*Van Brunt*, 1985; *Van Brunt and J.T. Herron*, 1990]. In addition, the ion-ion recombination as well as the charge interchange chemistry given above produces many contaminant neutral species within the chemically perturbed region. Some contaminant species are electron attachers (SF_4, SF_5, SO_2F, SO_2F_2, SOF_4). At the high altitude (425 km) and low initial release temperature (320K), the net SF_6 attachment process is slow because SF_6^{-*} auto-detaches before stabilization occurs. Thus, electrons can remain to participate in attachment to products of the slower neutral and ion chemistry. In addition, in regions where $[SF_6] < n_e$, products of the slower ion and neutral chemistry can participate in electron attachment.

In the CRRES-at-Kwajalein SF_6 release, the SF_4^- was detected at about the same density levels as SF_6^- and SF_5^-. Previous studies did not allow for SF_4^- production. SF_4 attachment chemistry is similar to SF_6 chemistry with attachment branches

$$SF_4 + e \rightarrow SF_4^{-*} \tag{2.12a}$$

$$SF_4 + e \rightarrow F^- + SF_3 \tag{2.12b}$$

and stabilization reactions

$$SF_4^{-*} + M \rightarrow SF_4^- + M \tag{2.12c}$$

$$SF_4^{-*} \rightarrow SF_4^- + h\nu \tag{2.12d}$$

and the auto-detachment reaction

$$SF_4^{-*} \rightarrow SF_4 + e. \tag{2.12e}$$

The rates for the above loss reactions are nearly identical with SF_6 loss reactions but the attachment is probably an order of magnitude slower (J. F. Paulson, private communication). The neutral species, SF_4, is a product of positive-negative ion recombination [*Bernhardt et al.*, 1984]

$$SF_6^- + SF_5^+ \rightarrow SF_4 + SF_6 + F \tag{2.13}$$

$$SF_5^- + SF_5^+ \rightarrow SF_4 + SF_6, \tag{2.14}$$

although *Kline* [1986] suggested products of

$$SF_5^- + SF_5^+ \rightarrow SF_5 + SF_5. \tag{2.15}$$

In addition, some neutral chemistry produces SF_4 as well:

$$SF_5 + H \rightarrow SF_4 + HF. \tag{2.16}$$

The charge interchange reaction (2.9) produces SOF_4 in sufficient quantities for the dissociative attachment reaction

$$SOF_4 + e \rightarrow SOF_3^- + F \tag{2.17}$$

to be important for late observation times.

SF_6-H_2O Chemistry

An extended chemistry reaction set is necessary to predict what experimentalists will see in the SF_6 release experiment of the CRRES investigation. The rocket outgassing of imbedded atmospheric gases is primarily H_2O. The outgassed H_2O competes with SF_6 in the positive-ion chemistry. H_2O and O^+ charge exchange and subsequent hydration chemistry occur:

$$H_2O + O^+ \rightarrow H_2O^+ + O \tag{2.18}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \tag{2.19}$$

The increase of molecular ions leads to increased recombination of the plasma.

$$H_2O^+ + e \rightarrow OH + H \tag{2.20}$$

$$H_3O^+ + e \rightarrow H_2O + H. \tag{2.21}$$

Within the SF_6 induced perturbation the electron density is reduced and ion-ion mutual neutralization will be the avenue for H_2O^+ and H_3O^+ loss.

$$H_2O^+ + M^- \rightarrow H_2O + M \tag{2.22}$$

$$H_3O^+ + M^- \rightarrow H_2O + H + M \tag{2.23}$$

A further complication of the SF_6 release chemistry is the possibility of water clustering of the negative ions.

$$SF_n^- + H_2O + M \rightarrow SF_n^-(H_2O) + M \tag{2.24}$$

However, a third-body is required for hydration to proceed. Hydration will only be important for releases below 100 km and in the first moments after a release.

The introduction of H_2O will affect SF_6 chemistry through competition for O^+ ions and through indirect reaction of H_2O chemistry products (OH, H) with SF_n fragments.

F-region chemistry

The model includes background ionospheric chemistry to set up initial ambient conditions and to follow ambient species variation. The species and the reactions are extensive and were obtained from the ARCHON-D2 database of atmospheric-ionospheric reactions [*Kennealy et al.*, 1989]. Some reduction of the reaction set was done to reflect the altitude of the release (e.g., no three-body reactions).

2.2 ARCHON Chemistry Investigation

To include an extensive set of reactions is not a burden for the chemistry kinetics program ARCHON [*Kennealy et al.*, 1989]. Including an extensive set will insure that the effects of catalytic and minor constituents are taken into account. Appendix A lists reactions that are potentially active in an SF_6 release in the F-region. The solution of the chemical system is then evaluated by a diagnostic program (DIG) to determine the relative importance of the reactions. With DIG the number of reactions and species can be reduced to include only important reactions and species necessary to model a particular event. However, if important species or reactions are missing from the initial input then ARCHON will not reproduce the "real" results. Differences between experiment and ARCHON results allow deductions to be made on what reactions or species are absent from the analysis.

All studies of the perturbed F-region presented below have identical ambient conditions at $t = 0$ s. The densities of ambient ground state constituents were obtained from the MSIS86 neutral atmosphere [*Hedin*, 1987] and PSU Mark III ionosphere (O^+ 98%, H^+ 2%). These ground state densities were input into ARCHON with the extensive ambient chemistry reaction set to obtain excited species and minor species concentrations. The chemistry was allowed to progress for 1000 s to obtain a near equilibrium situation. The near stationary result was used as the initial condition of the following simulations. Some species were not in equilibrium at the end of the 1000 s. Likewise, the evening F-region is not in chemical equilibrium at the altitude and time of the release.

SF_6 Release

Transport is not explicitly followed in ARCHON. This is a drawback but it can be minimized by making appropriate assumptions on SF_6 diffusion in the F-region. The average density of a 35 kg SF_6 release with a 30 km radius is 10^6 cm^{-3}.

The model uses two populations of the SF_6 species. One is a cold (320K) release, which reacts with all species, but is not produced through any reaction. The other is a hot (1000K) SF_6 species, which results as a product of ion-neutral chemistry and collisional heating of the cold population

$$SF_6(\text{cold}) + M \rightarrow SF_6(\text{hot}) + M. \qquad (2.25)$$

This is necessary because the two populations have very different rates in reactions (2.1). Initially, all SF_6 is cold. The cold SF_6 is removed from the chemical system with a rate that simulates the diffusion of the release cloud. All species, other than the original cold SF_6, remain in the chemical system with transport ignored. This is not a problem since the plasma constituents remain bound on one magnetic flux tube. The net removal of neutrals from the average position within the plasma perturbation is slow. This allows for confidence in the solution for the first 100 s after the release. After this time, the contaminant neutral densities should begin to be altered by gravitational settling.

Figure 7*a,b* uses an initial density of cold SF_6, which is greater than the ambient electron density. This approximates the region near the release point, that is, within 20 km of the release point. The electron depletion is deep in this region. The chemistry kinetics code ARCHON predicted the initial dominance of SF_5^- production over SF_6^- and F^- (Figure 7). This agrees with *Bernhardt*'s [1984] predictions, though there is probably a core region where SF_6^- dominates. F^- dominates at later times due to the charge interchange mechanism of *Hunton et al.* [1987]. The positive ions (Figure 7*b*) show the expected O^+ and SF_5^+ dominance but SF_4^+ is at measurable densities.

Figure 8*a,b* uses an initial density of hot SF_6, which is less than the ambient electron density. This approximates the very large region influenced by the release but far from the release point, that is, greater than 50 km from the release point. The obvious changes in results from the previous simulation are the early domination of F^- and the potential importance of SOF_3^-. SOF_3^- is produced primarily through dissociative electron attachment of SOF_4. This attachment rate was estimated to be 10^{-8} cm^3s^{-1} (absolute cross sections have not been reported in literature).

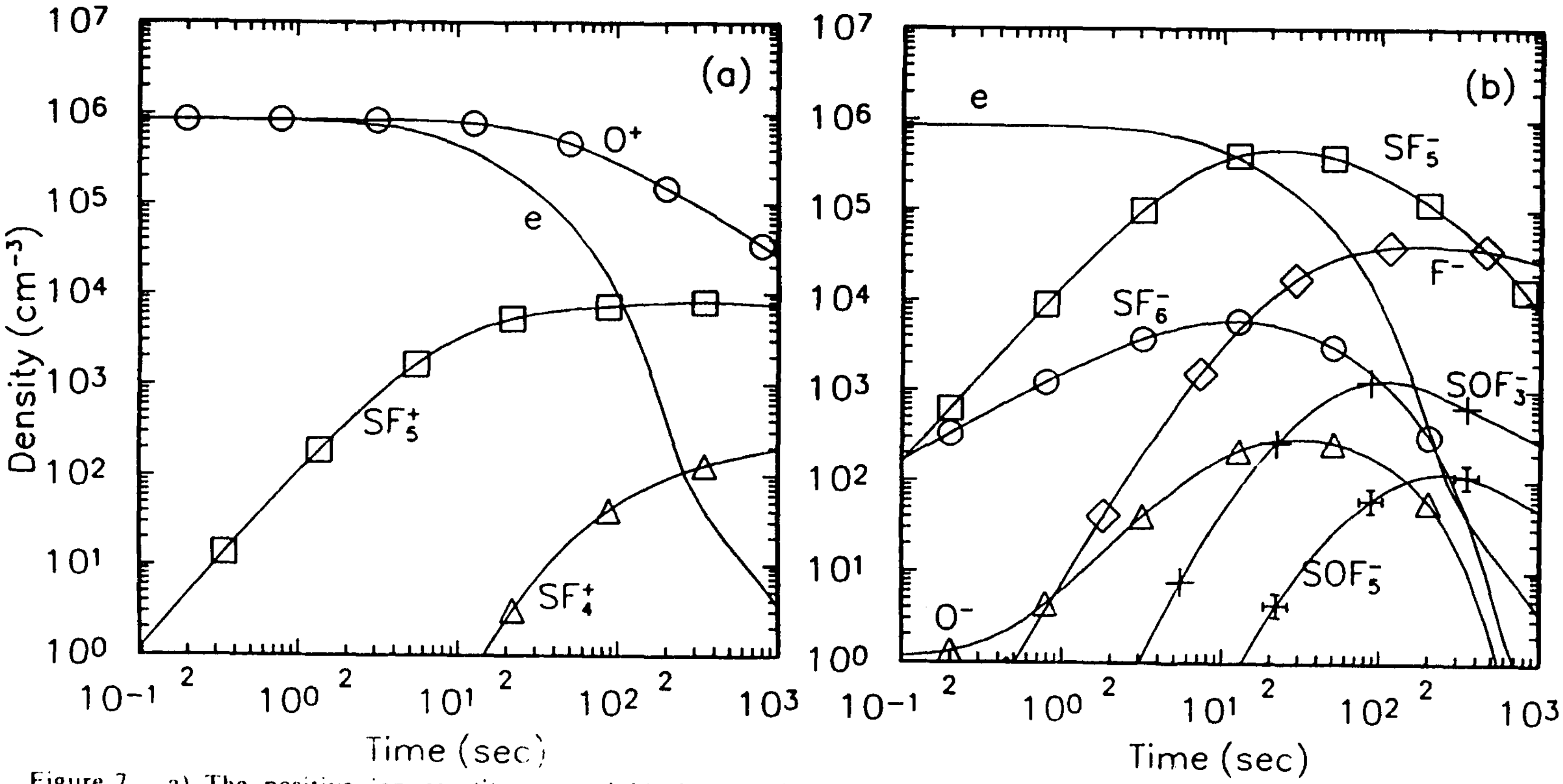

Figure 7. a) The positive ion constituents and b) the negative ion constituents of an average flux tube within the SF_6 release in the evening equatorial F-region. Since a flux tube is followed and the plasma velocity is derivable from a potential function and the neutral constituents lose chemical influence on the plasma composition after about 200 s, the Lagrangian solution to the plasma constituents is well represented for the entire 1000 s. The neutral constituents are overestimated after about 200 s because gravitational settling is not modeled.

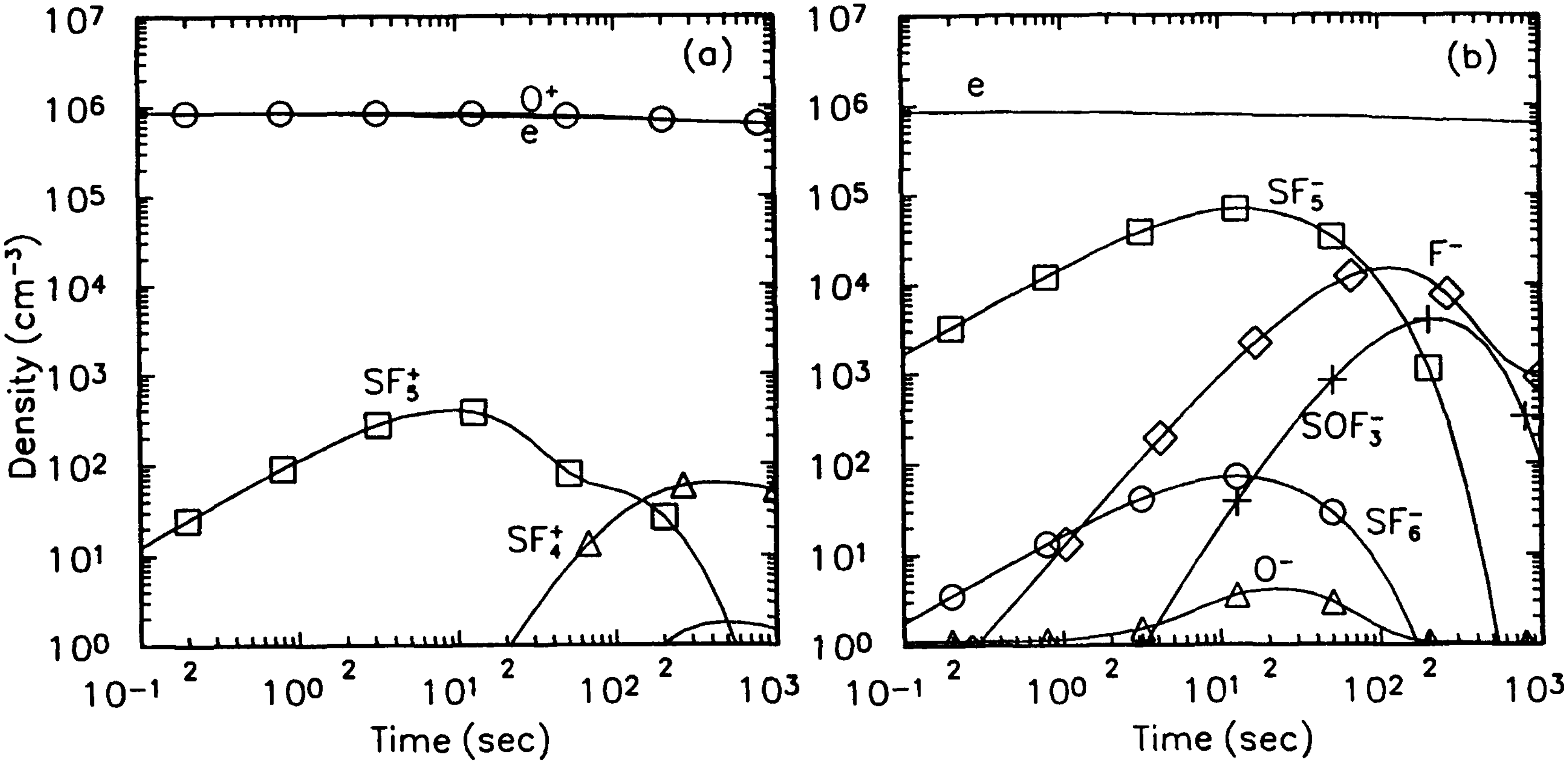

Figure 8. a) The positive ion constituents and b) the negative ion constituents of an average flux tube within the an SF_6 release in the evening equatorial F-region. The initial density of SF_6 is less than the electron density. This reflects chemistry far away from the release point.

In all simulations, there were no significant amounts of SF_4^- produced. This differs from the actual experiment where SF_4^- was observed. Electron attachment of SF_4 is the only avenue of production included in the ARCHON simulations. The difference between simulation and experiment suggests there is another avenue of production for SF_4^- or the electron attachment rate has been underestimated. However, the mass of SOF_3^- (105 amu) is only 3 amu lower than SF_4^- (108 amu). The Mass Spectrometer resolution of the CRRES-at-Kwajalein experiment was about 3 amu, thus SF_4^- and SOF_3^- would be combined in the measurement (D. E. Hunton, private communication). The measurement might suggest the presence of SOF_3^-. The simulation results would then agree qualitatively with the experimental observations.

To estimate the effects of rocket outgassing on an SF_6 release, H_2O chemistry was included in the reaction set. The initial H_2O density of 10^5 cm^{-3} corresponds to a diffuse H_2O cloud created by typical outgassing rates [*Narcisi*, 1987]. Figure 9 shows the alteration of the SF_6-ionospheric chemistry due to the presence of H_2O outgassing. The negative ion composition did not change. The H_2O contaminant affects mainly the positive ion composition.

The ARCHON simulation of the SF_6 release does reflect the experimental results of the CRRES releases in several respects. D. E. Hunton (private communication) indicates that the dominant ion is F^- while SF_4^-, SF_5^- and SF_6^- are present in roughly equivalent quantities (though SOF_3^- and SF_4^- are indistinguishable in the measurements). It is probable that the observation rocket did not pass through the small region of the deep electron hole. This region would be identified by the dominance of SF_6^- and SF_5^- and a reduced plasma density. The observing rocket did pass through the broader region of the SF_6 release chemistry.

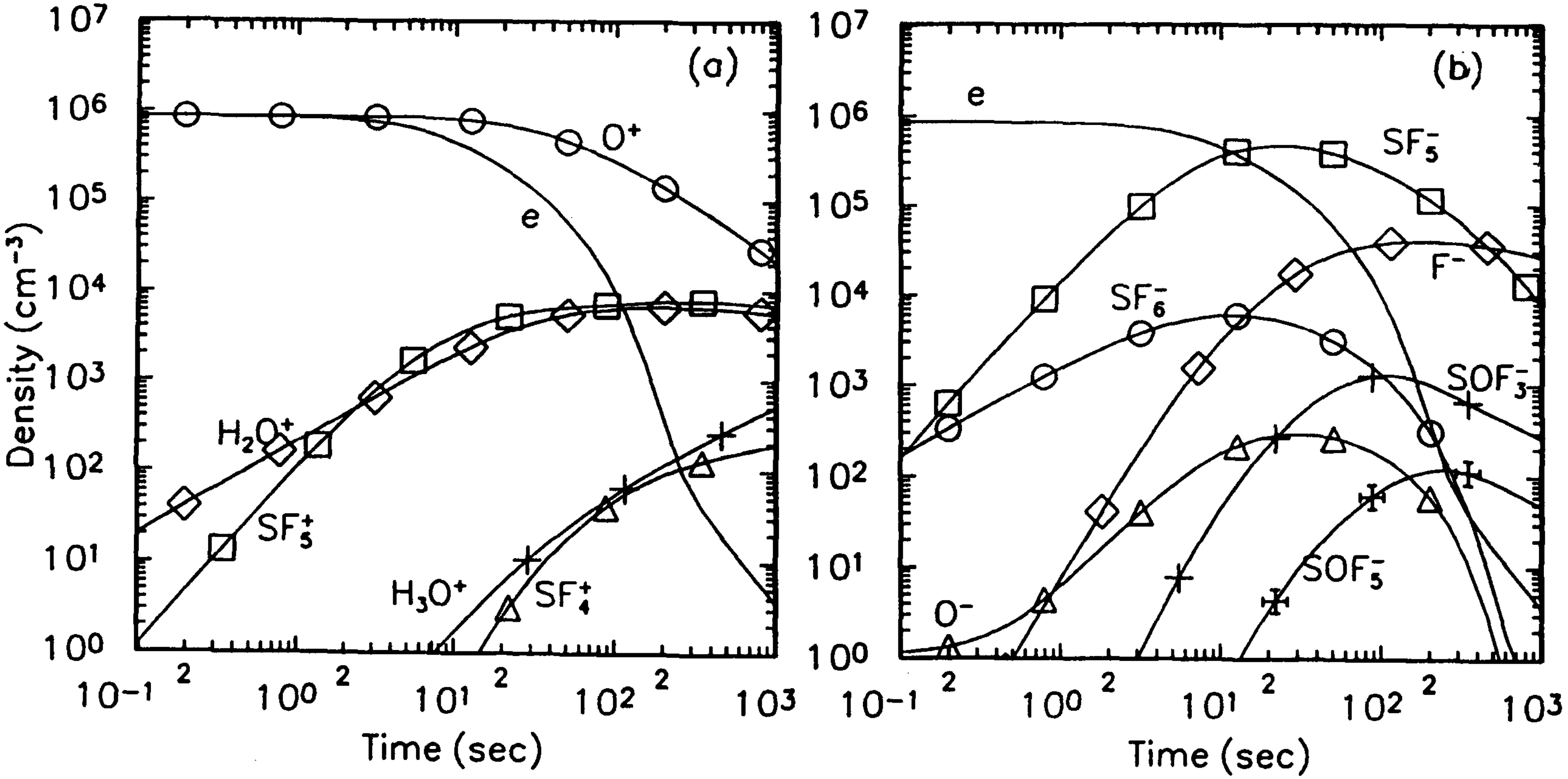

Figure 9. a) The positive ion constituents and b) the negative ion constituents of an average flux tube within the an SF_6 release in the evening equatorial F-region. The results reflect the presence of H_2O outgassing as a contaminant to the experiment.

3. RELEASE DYNAMICS

The resulting SF_6-ionospheric chemistry creates four categories of alterations to the ambient conditions:

1. Electron depletion. This interesting perturbation alters electromagnetic wave scattering and propagation.
2. Negative-positive ion plasma. The replacement of electrons by heavy negative ions alters the transport properties along magnetic field-lines, increases cross field conductivity, and increases the gravitationally-induced current.
3. Plasma depletion through negative-positive ion mutual recombination. The plasma reduction takes place on the time scale of minutes and eventually decreases conductivities.
4. Neutral composition perturbation. There are several metastable constituents that participate in airglow enhancements.

The study of the SF_6 release cannot be done exclusively with models of the chemical perturbation. Comparison of simulation and experiment would have only limited validity. To obtain more quantitative comparisons, the dynamics and electrodynamics of the CRRES-at-Kwajalein release were modeled.

3.1 SF_6 Neutral Cloud Motion

A simple and computationally fast release cloud model was developed to predict approximate position, density and size of a neutral release cloud (ignoring chemistry). The basic assumption is that the cloud limbs maintain Gaussian shapes

$$n(x,y,z,t) = n_o(t)\ \exp[-((x-x_o)^2/r_x^2 + (y-y_o)^2/r_y^2 + (z-z_o)^2/r_z^2)] \qquad (3.1)$$

where x, y, z represent eastward, northward and vertical directions, n is density, and n_o is peak density. An implicit assumption is that the n_o/e radius of the cloud grows at the rate defined by the velocity of the gas at that radius. The velocity and position equations of the three unique radii (the horizontal radii, r_x, and the upper and lower radii, r_{z+} and r_{z-}, respectively) are solved

$$d\mathbf{u}/dt = \mathbf{g} - m(\mathbf{u}-\mathbf{u}_n) - kT\nabla n/mn \qquad (3.2)$$

$$d\mathbf{x}/dt = \mathbf{u} \qquad (3.3)$$

where $\mathbf{u}$ is velocity, $\mathbf{g}$ is gravitational acceleration, m is mass, and T is temperature. Subscripted variables (m_n, u_n, T_n) refer to background atmospheric parameters. It is assumed that $r_x = r_y$. Notice that the pressure term of Equation (3.2) can be determined explicitly by differentiating Equation (3.1). In addition the cloud temperature changes can be determined through

$$dT/dt = mm_n/(m_n+m)[(T_n - T) + m_n(u_n-u)^2/3k](C_p/C_v) \tag{3.5}$$

The solutions assume that the background gases are unchanged by the release. This is true for the large scale problem. Only at early times ($t < 10$s) will the release affect the background densities and temperatures.

The release of August 1990 took place at the apogee of the rocket flight (427km). The rocket velocity at the release was $u_x = -34$ ms^{-1}, $u_y = 130$ ms^{-1} and $u_z = 0$ (D. E. Hunton, private communication). Figure 10 gives the expansion history of the cloud limbs determined through the solution of Equations (3.1-3.5). Figure 11 shows density, temperature and position of the SF_6 cloud center for the conditions of the August 1990 launch. The temperature increase is slow due to the internal energy capacitance of SF_6. The slow increase in temperature of the SF_6 allows SF_6^- to be produced as the dominant ion for a significant period. The cloud moves initially with the rocket trajectory and expands adiabatically for one mean free path (~ 50 km). After two minutes diffusion controls the motion. Within five minutes the release cloud has the same horizontal motion and temperature as the background atmosphere. The region of chemical influence of the cloud has a radius greater than 100 km.

A two-dimensional contour plot (*Figure 12a,b*) shows the cloud at $t = 1,5,10$, and 15 minutes in the *x-y* and *x-z* planes. The horizontal extent is very large due to the high altitude of the release point. In contrast, the differential neutral drag force on the top and bottom limbs of the cloud causes the cloud to flatten.

3.2 Plasma Perturbation Motion

A two-dimensional, electrodynamic model was developed to solve for the motion of the perturbed plasma region. The electrodynamics model is reduced to a potential equation with source terms. The source terms are determined by gravitationally-generated and neutral-wind-generated currents perpendicular to the magnetic field. The method used is similar to that described in *Haerendel et al.* [1991] and *Cakir et al.* [1991]. The background ionosphere is modeled with field-line integrated quantities excluding the 30 km slice containing the main perturbation of the SF_6 release.

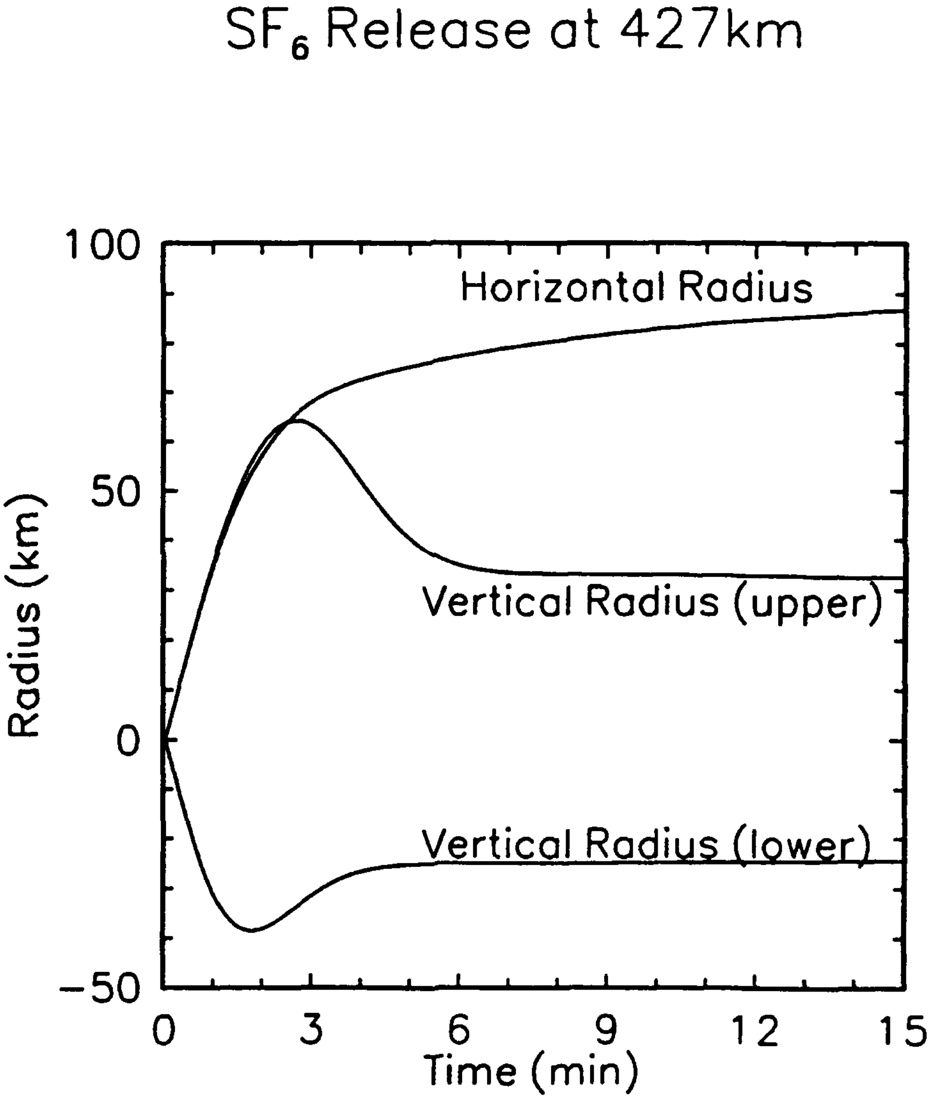

Figure 10. The time history of the release cloud limbs (conditions for August 1990 in Table 1).

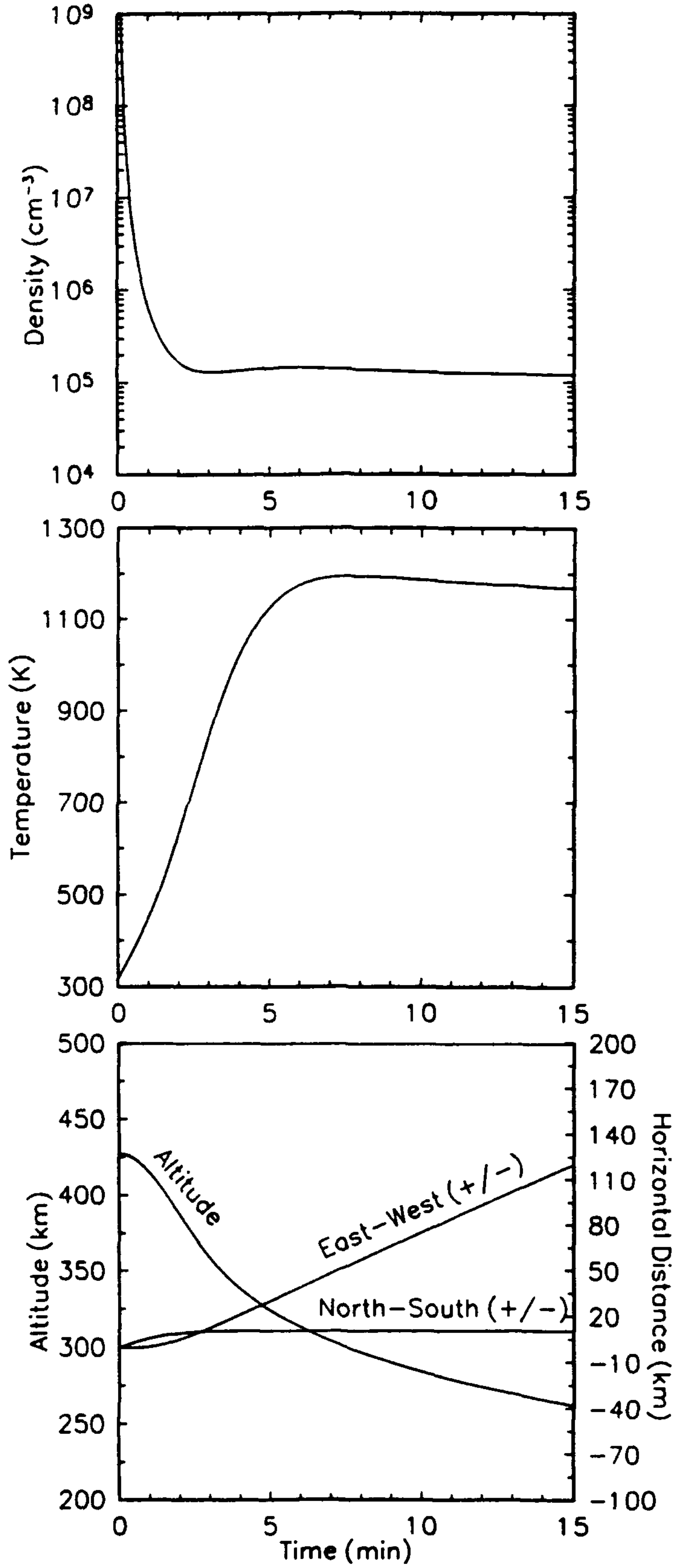

Figure 11. a) Position, b) velocity and c) temperature of a release cloud (conditions for August 1990 in Table 1).

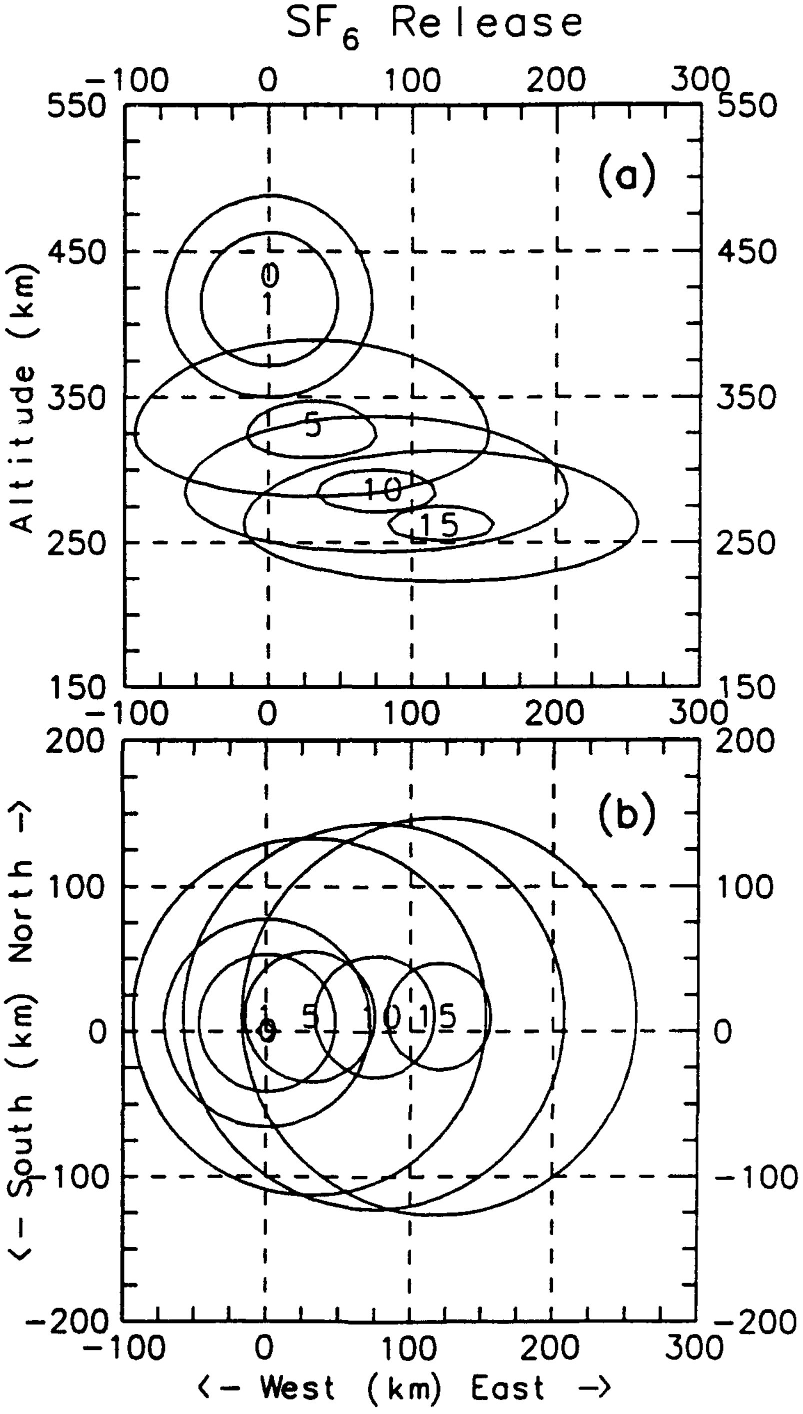

Figure 12. a) *x-y* visual projection, b) *x-z* visual projection of a release cloud (conditions for August 1990 in Table 1).

The chemistry and motion of the cloud are followed using local quantities. The reaction set used is simplified in order to reduce the number of species in the two-dimensional calculation. The reduced reaction set only models the deep electron hole well. The extended chemical perturbation will not be modeled well with the limited chemistry. This chemical approximation is appropriate for determining the electrodynamic effect of the SF_6 release. The background ionosphere is connected to the slab containing the cloud via equipotential magnetic field-lines.

The resulting perturbation of the integrated Pederson conductivity shown in Figure 13*a*, is very small due to the low collision frequencies at the high altitude of the release. The largest electrodynamic perturbation is due to the mass loading of the field-lines. This generates greater gravitational current in the region of dense SF_6^- (Figure 13*b*). The mass of the SF_6^- plasma is still only a fraction of the integrated mass of the flux tube. However, it is sufficient to cause an electrodynamic perturbation. The horizontal plasma velocity perturbation is largest in the vertical direction (horizontal electric field perturbation) (Figures 13*c*), because the gravitationally-generated current is horizontal. The vertical velocity perturbation is significant up to 60 s after the release and should be greater in the early seconds of the release (Figure 13*d*). However, due to the rapid decay of the molecular negative-positive ion plasma within the cloud region, the velocity perturbation also will decay rapidly. This is not true of an atomic ion perturbation.

The electrodynamics within the SF_6^- cloud causes the plasma cloud to drop in altitude. A net drop in the plasma flux tube containing the ion cloud causes adjacent regions to rise. Any plume development comes from these adjacent regions of the SF_6^- cloud. As the negative-positive plasma recombines, the net plasma loss causes the perturbed region to slow. It could eventually rise when the mass in the perturbed region is less than the surrounding region.

The quick decay of the velocity field perturbation suggests that the SF_6 release will not stimulate large-scale plume structures associated with ESF. However, the steep sides of the plasma perturbation in the local release volume provide a free-energy source from which small-scale irregularities can grow. The short wavelength perturbations can develop without coupling to the extended ionosphere.

The horizontal velocity perturbation always remains small and the perturbation region moves at nearly 99% of the ambient horizontal velocity. The expected position of the plasma perturbation can be determined by simply following the ambient motions of the ionosphere from the initial release position.

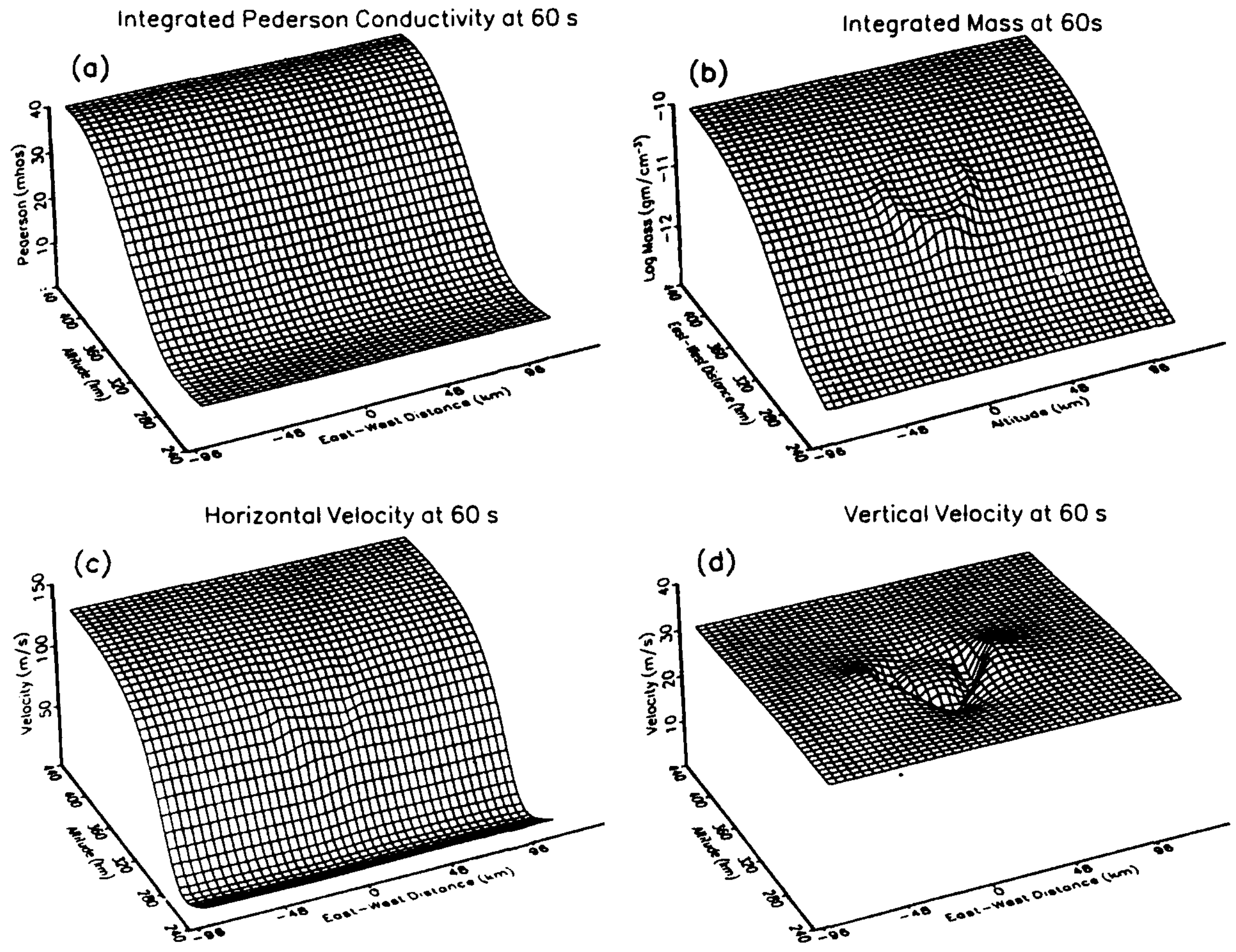

Figure 13. a) The field-line integrated Pederson conductivity. b) The field-line integrated ion mass. c) The horizontal plasma velocity. d) The vertical plasma velocity. The time is 60 s after the SF_6 release.

3.3 Chemical Perturbation

Due to the quick coupling of the cloud to the neutral background and the lack of any significant perturbed plasma motion, a simplified "3D" model of chemistry and dynamics can be used to simulate the chemical perturbation of the SF_6 release. A cylindrical geometry in the frame of the ambient neutral wind can model the 3D aspects of the neutral constituents. Because the plasma is bound to the magnetic field lines, its only motion is parallel to the magnetic field. This cannot be properly modeled in the cylindrical geometry. However, it can be modeled by solving plasma motion in the plane containing the magnetic field and altitude directions with rectangular coordinates. The combined cylindrical-rectangular two-dimensional model effectively reproduces a three-dimensional transport result. This simplified transport allows one to use large chemistry sets with less computational demand. The present simulations use the chemistry set proposed by *Bernhardt* [1986] and *Hunton et al.* [1987] with SF_4^- production through attachment included.

Figures 14*a,b,c,d* provide a quick overview of the history of the dynamics and chemistry at 100 s, 300s, 600s, and 900s, respectively. An interesting feature of the SF_6 release is the shape of the neutral clouds at 100 and 300 s. The rapid chemistry of the electron attachment has shaped the early expansion of the SF_6. In addition, the deep electron hole region provides a suspended source point for various SF_n neutrals, which adds topside structure to the profile of the neutral clouds. The ion chemistry shows interesting spatial structure due to the chemical shaping and motion of the SF_6 cloud. The SF_5^+ distribution in space is structured.

The observation rocket trajectory is used to obtain density profiles to compare to IMS data. The double hump SF_5^- and F^- profiles (Figures 15*a,b*) reveal active chemistry in two altitude ranges: (1) the release altitude region and (2) the altitude of the remaining SF_6 cloud that has fallen to lower altitudes.

The shape and magnitude of the F^- density profile agree well with the rocket observation of F^-. The mechanism suggested by *Hunton et al.* [1987] appears sufficient for the F^- densities seen by the IMS (D. E. Hunton, private communication).

SF_5^- concentrations are two orders of magnitude larger in the simulation than observed by the IMS. The inclusion of dynamics did not improve the predicted SF_5^- over the previous single cell calculation. Experimental observations of F^- and SF_5^- present a paradox since SF_5^- + O is the main avenue of F^- production.

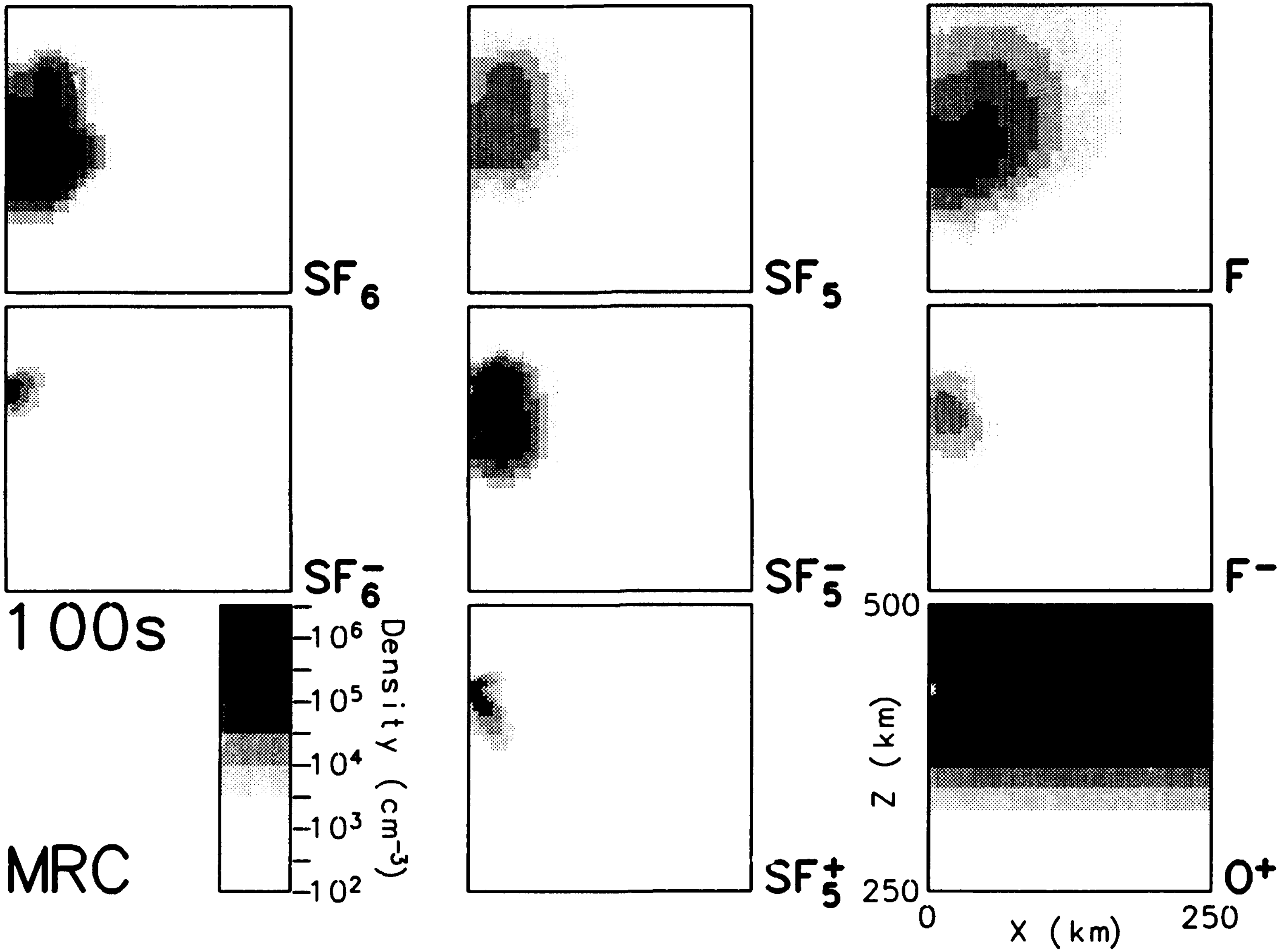

Figure 14. a) A grayscale overview of neutral and plasma constituents at 100s.

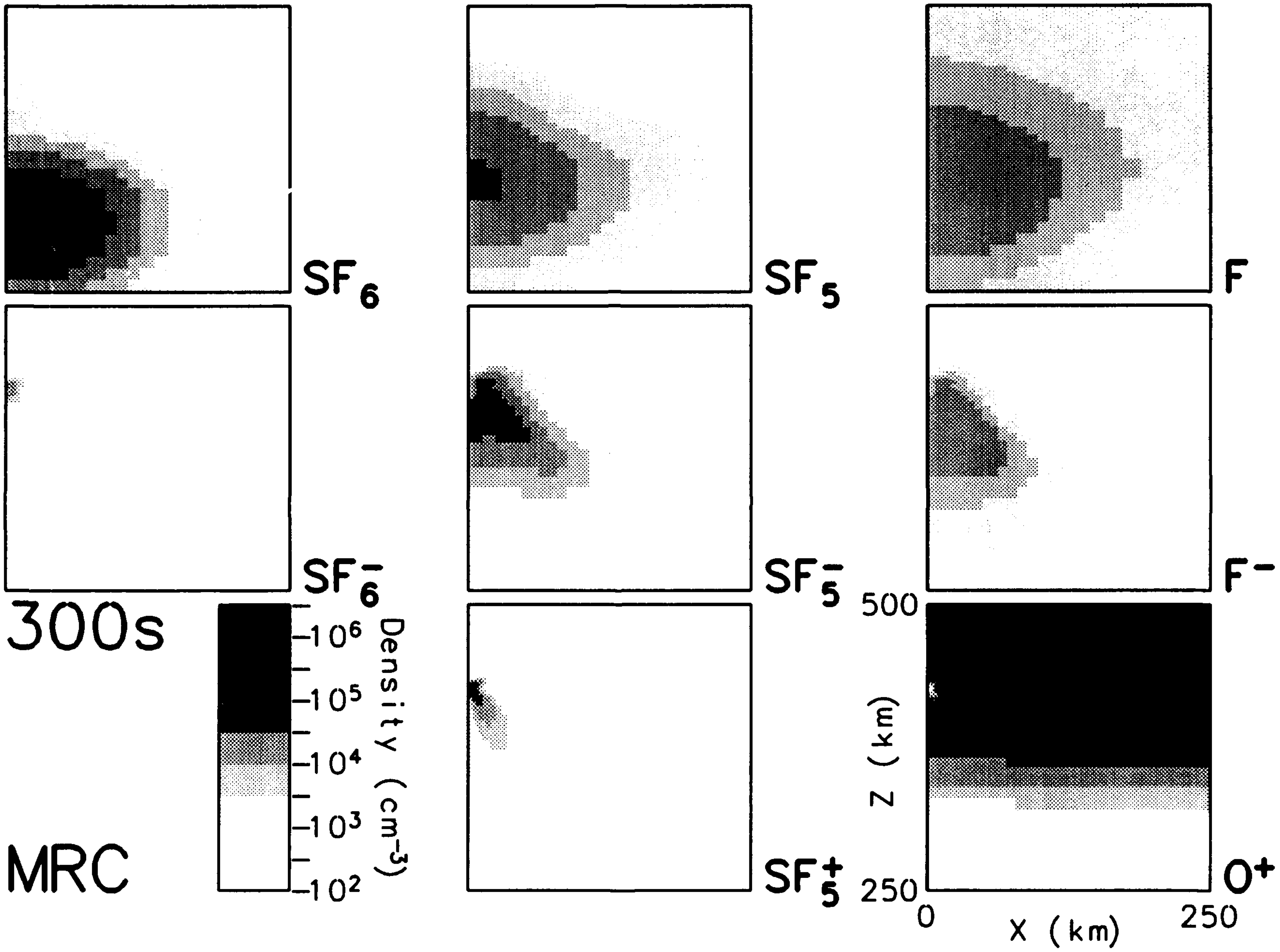

Figure 14. b) A grayscale overview of neutral and plasma constituents at 300s.

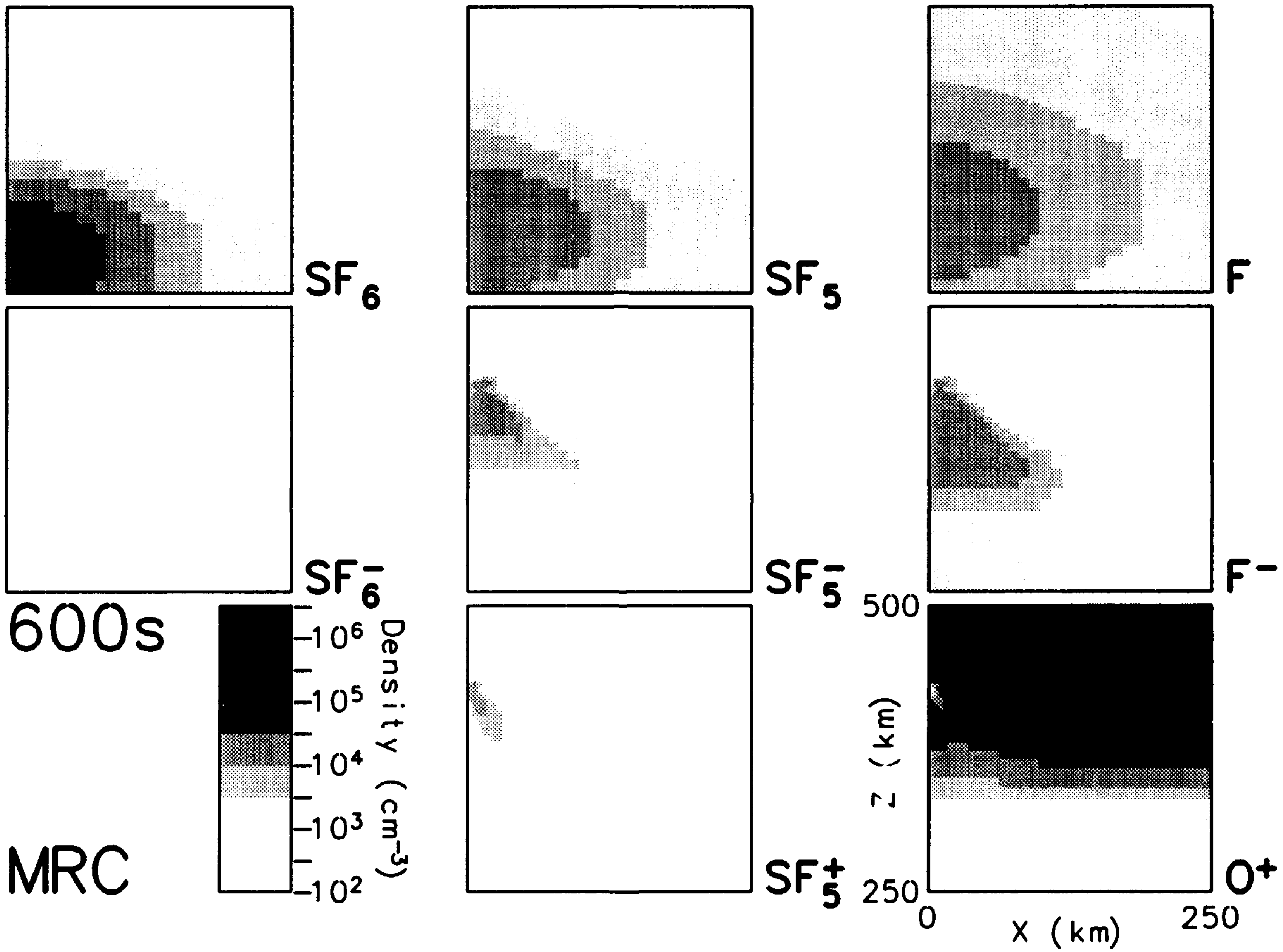

Figure 14. c) A grayscale overview of neutral and plasma constituents at 600s.

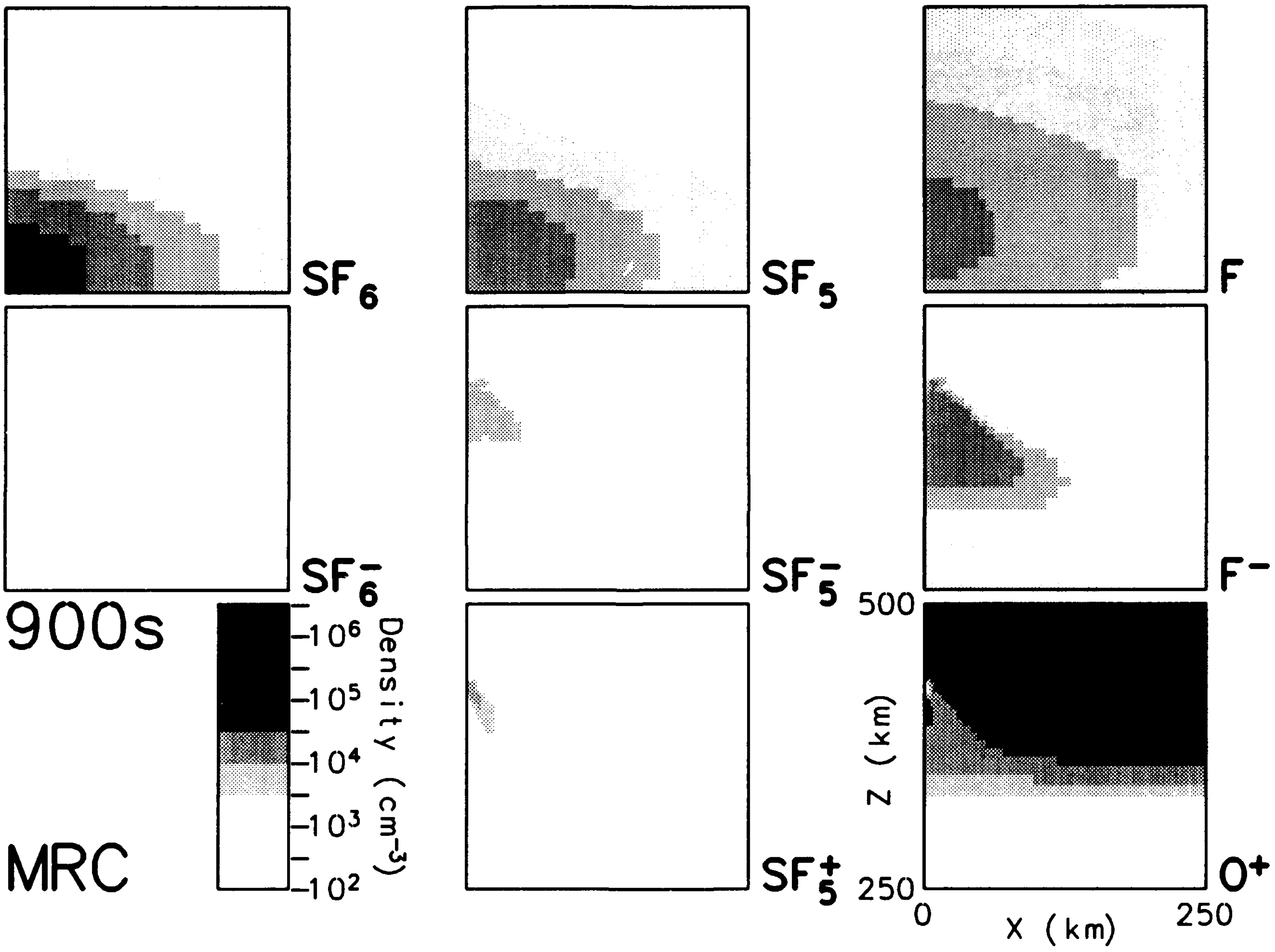

Figure 14. d) A grayscale overview of neutral and plasma constituents at 900s.

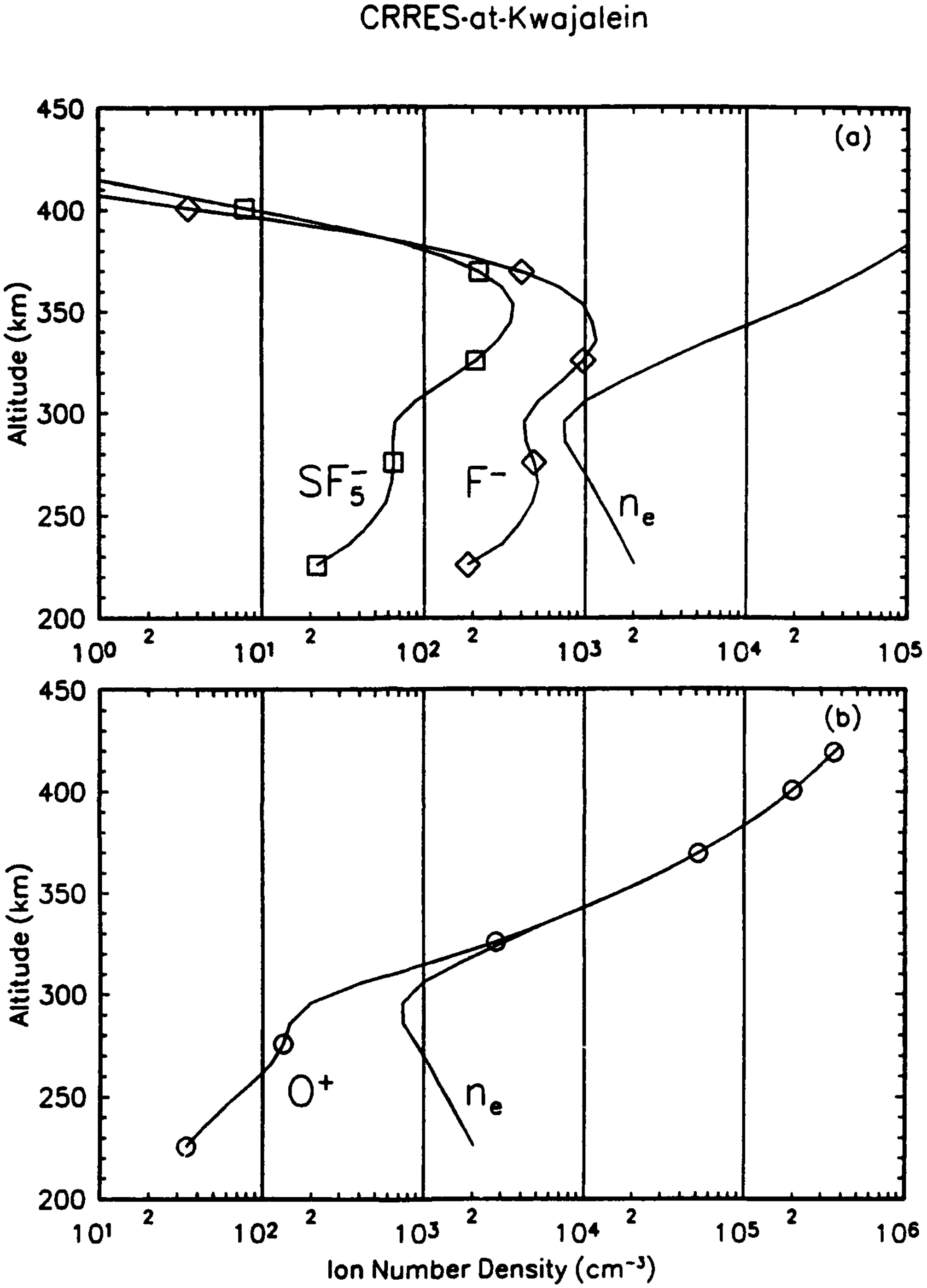

Figure 15. Numerical predictions of density observations on rocket ascent for a) negative ions and b) positive ions.

In addition, the simulation has almost no observable SF_4^-. The experimental observations of SF_4^- number density suggested that SF_4^-, SF_5^- and SF_6^- were present in approximately equal amounts (D. E. Hunton, private communication). As stated earlier, the IMS SF_4^- measurement also may include SOF_3^-. Thus, SF_4^- may indeed not be present in the release and SOF_3^- may be a measurable negative-ion product in an SF_6 release.

The SF_5^- density in the simulation is much too large in comparison to experimental observation. Because SF_5^- is the precursor of F^-, one would expect it to have a significant density and have a similar altitude profile to F^-. This was not observed in the experiment and is observed in the simulation. Possibly, there are transport effects that have not been taken into account.

The electron depletion is observable in the simulation on the downleg of the observing rocket. However, this is not the deep central hole near the release point but the column of depletion caused by gravitational settling of the SF_6. The downleg is closer to the center of the release point.

The positive ion plots of Figure 16*a,b* show predictions of O^+ and SF_5^+ profiles. These compare favorably with IMS measurements in shape and density. The O^+ profile in the simulation is altered very little between the up and down leg of the rocket trajectory even when the electron depletion is observable.

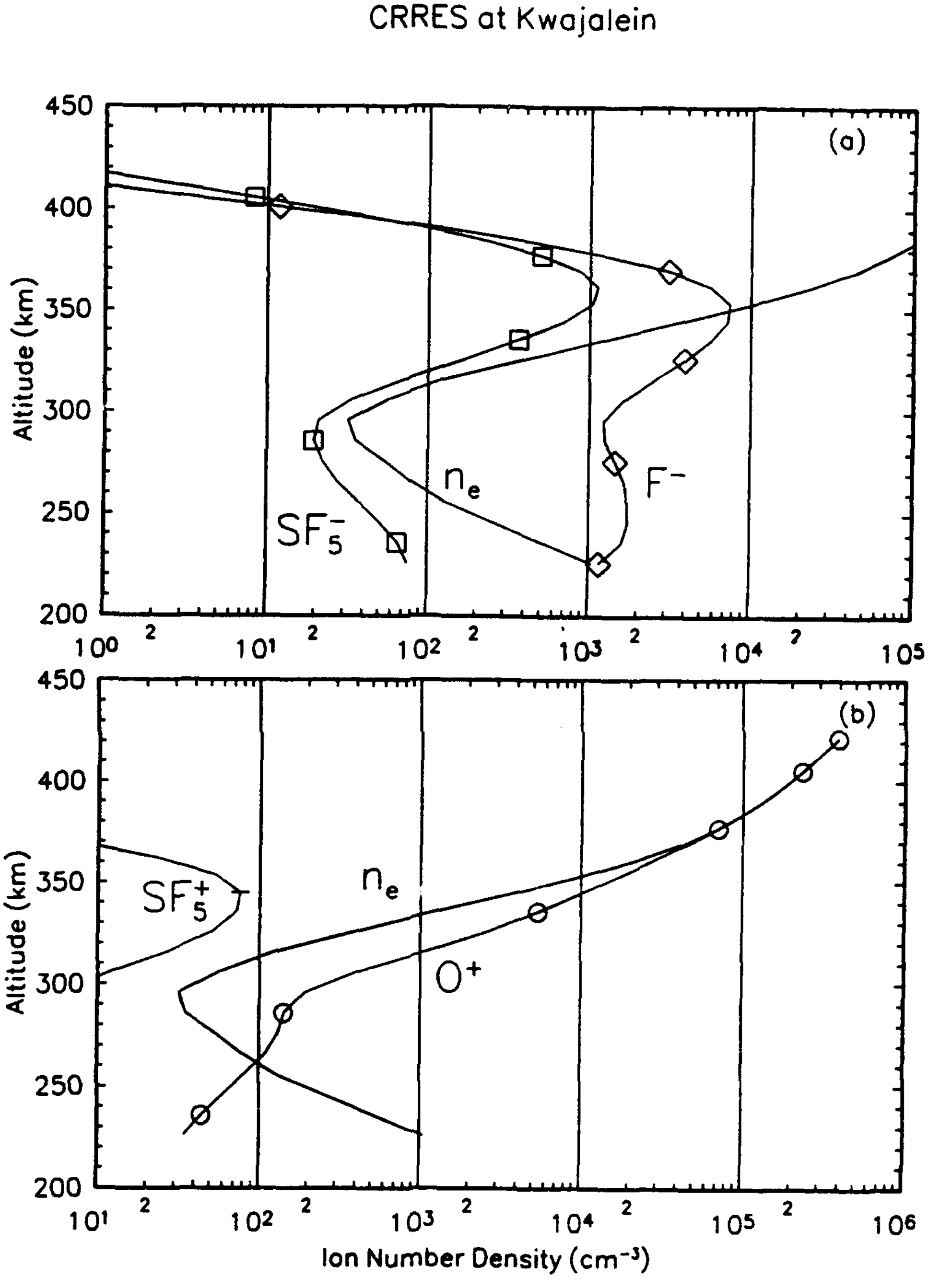

Figure 16. Numerical predictions of density observations on rocket descent for a) negative ions and b) positive ions.

4. AIRGLOW SIGNATURE

Airglow observations were made during the CRRES-at-Kwajalein campaign. An all-sky camera was used to observe the spatial distribution of the expected 7774Å enhancement from the SF_6 release. The enhancement is primarily from the ion-ion recombination

$$SF_6^- + O^+ \rightarrow SF_6 + O^{**} \tag{4.1}$$

which produces highly excited states of atomic oxygen O^{**}. These excited states decay in multiple steps. The specific excited states of interest and their associated emission lines are:

$$O(3p^5P) \rightarrow O(3s^5S) + h\nu(7774\text{Å}) \tag{4.2}$$

$$O(4p^3P) \rightarrow O(3s^3S) + h\nu(4368\text{Å}) \tag{4.3}$$

$$O(3p^3P) \rightarrow O(3s^3S) + h\nu(8446\text{Å}) \tag{4.4}$$

The lower states relax to ground state via

$$O(3s^5S) \rightarrow O(2p^3P) + h\nu(1356\text{Å}) \tag{4.5}$$

$$O(3s^3S) \rightarrow O(2p^3P) + h\nu(1304\text{Å}) \tag{4.6}$$

The branching ratios for the excited states of O produced in the recombination have been approximated by using the O^+-e recombination branching ratios [*Bernhardt et al.*, 1986]. The branching ratios are similar to O^--O^+ recombination branching ratios but there are some differences that suggest the SF_6^--O^+ recombination may differ. For 7774Å production the O^+-e and O^--O^+ recombination models will give almost identical results. Other ion-ion recombinations involved in the airglow production are:

$$SF_6^- + O^+ \rightarrow SF_6 + O + 13.06\text{ eV} \tag{4.7}$$

$$SF_4^- + O^+ \rightarrow SF_4 + O + 12.11\text{ eV} \tag{4.8}$$

$$F^- + O^+ \rightarrow F + O + 10.20\text{ eV} \tag{4.9}$$

$$SF_5^- + O^+ \rightarrow SF_5 + O + 9.91\text{ eV} \tag{4.10}$$

The energetics do not allow F^--O^+ or SF_5^--O^+ recombinations to populate higher energy states of O higher than $O(3s^5S)$ and $O(3s^3S)$. This allows for interesting spatial structure of the airglow in different wavelengths. In the region where SF_6^- densities are high, 7774Å is bright, but in the broader region where SF_5^- and F^- dominate, 1356Å is important. The pseudo-three-dimensional model described in Section 3.3 was used to predict airglow intensities. Figure 17 shows the time history of 7774Å airglow at a range of radii from the vertical line intersecting the release point. There is an apparent doughnut shape to the airglow pattern. The peak airglow occurs at 8 km from the center line and 50 s after the release. This is seen clearly in the gray scale plot of the airglow versus radius and time (Figure 18). One can see the expansion of the SF_6 cloud in the line made by the lower edge of the airglow gray scale. The reason for the reduced airglow in the center is that the O^+ density is reduced through charge exchange with SF_6 producing SF_5^+. The different chemistry of regions near and far from the release point can be seen in the 1356Å and 1304Å airglow histories. Figure 19 shows several lines of airglow as measured in the vertical line through the release point. During the early moments after the release (less than 30 s) the cool SF_6 cloud expands and produces SF_6^-. As the cloud heats, SF_5^- becomes more dominant and O^{**} production ceases. Thus, 7774Å just decays away evenly after 30 s. However, the SF_5^- continues to produce O^*, therefore, 1356P and 1304P continue to increase beyond a minute in time.

It would be instructive to measure 7774Å and 8446Å or 1304Å and 1356Å lines together. The comparisons could show whether the O^+-e recombination branching or the O^+-O^- recombination branching would serve as a better model for the O^+-M^- recombination. A comparison of Figures 19 and 20 illustrates the differences. Notice that the 7774Å predictions are nearly identical for either model of branching.

A direct comparison of the all-sky camera measurements and the simulation result has yet to be done. The all-sky camera did show high 7774Å airglow production. Unfortunately, the center of the image saturated the instrument sensitivity limit of 300 Rayleighs for several minutes (M. Mendillo, private communication). The simulation prediction of kilo-Rayleighs of 7774Å airglow agrees with the saturation qualitatively. It is anticipated that the limb of the airglow measurements will allow direct comparison between simulations and experiment.

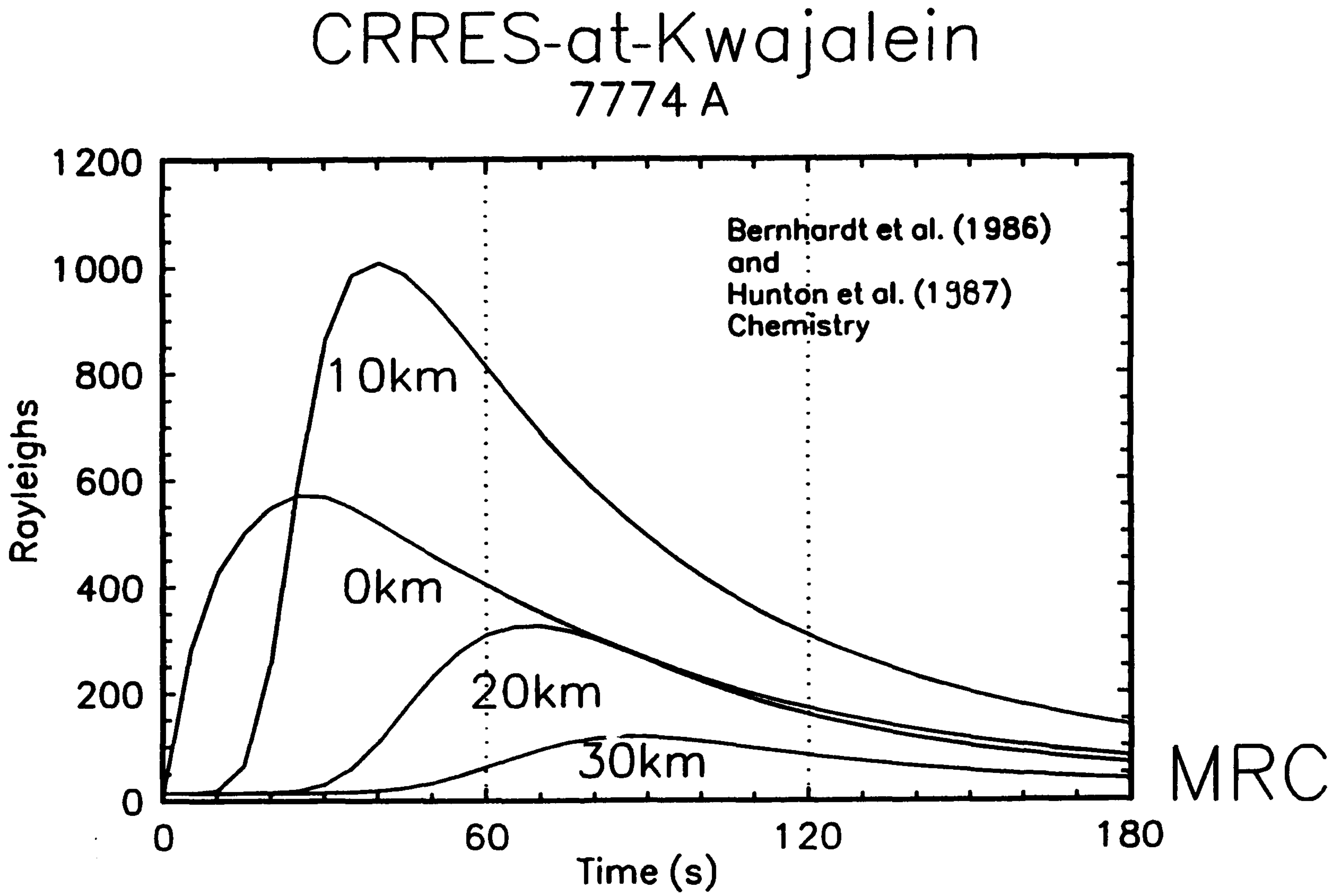

Figure 17. Time history of the vertically integrated 7774A airglow produced by the SF_6 release at 0km, 10km, 20km and 30km horizontal radius from the release point.

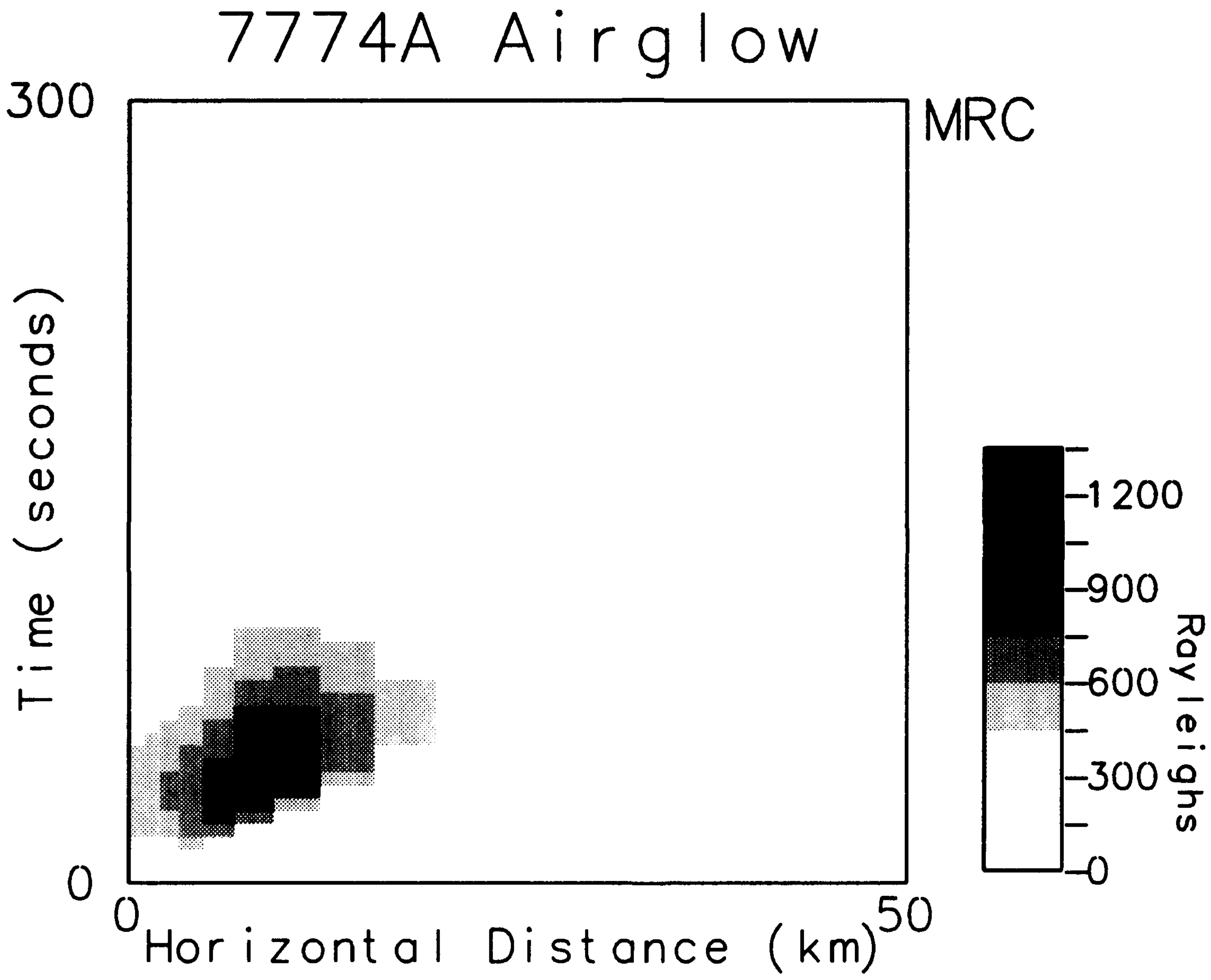

Figure 18. Time versus radial distance from release point versus line-of-signt integrated airglow intensity shows where the maximum airglow is expected.

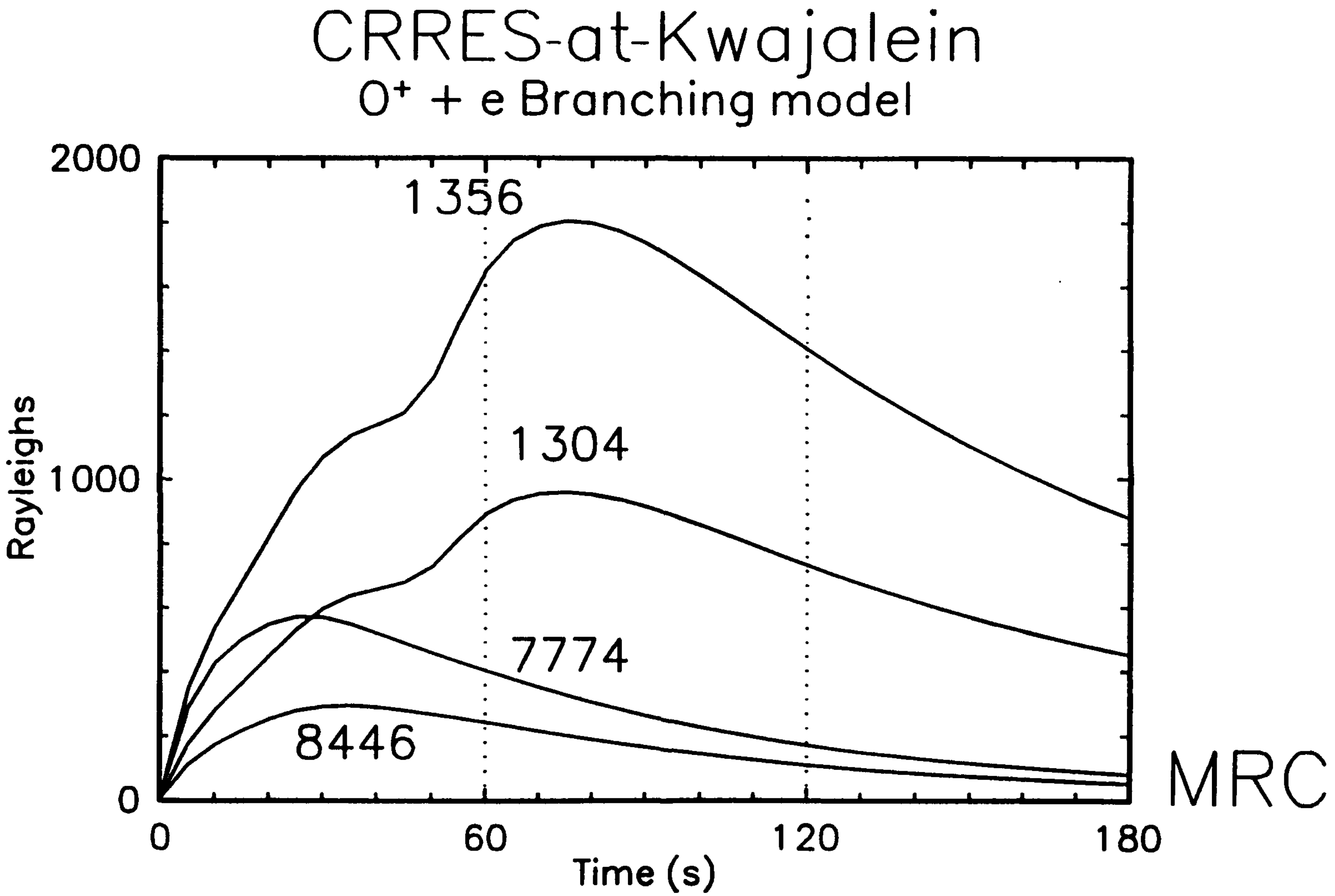

Figure 19. Time history of the vertically integrated 7774A, 8446A, 1304A, and 1356A airglow produced by the SF_6 release through the release point. O^+,e recombination branching model is used for the predictions.

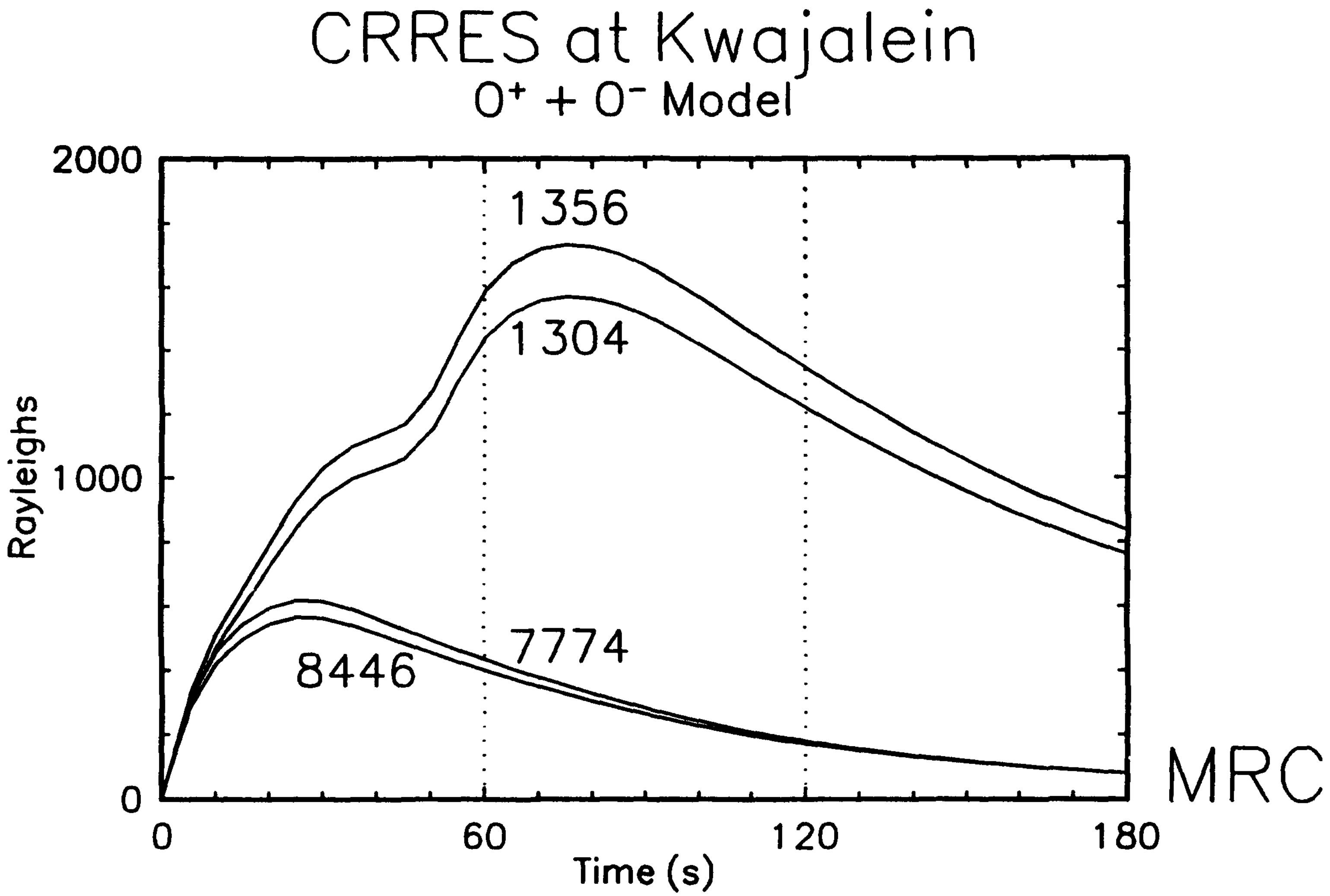

Figure 20. Time history of the vertically integrated 7774A, 8446A, 1304A, and 1356A airglow produced by the SF_6 release through the release point. O^+,O^- recombination branching model is used for the predictions.

5. SUMMARY

5.1 Observations

A thorough examination of the possible chemistry associated with an SF_6 release in the ionosphere has been performed. In making comparisons of simulations and field experiments it was necessary to simulate dynamics, electrodynamics and experimental measurement procedures in the numerical calculations. Favorable comparisons between the experiment and simulation of the SF_6 release give greater confidence in interpreting the simulation and experimental data. Any differences between the simulation results and experimental observation of the SF_6 release could reside in the oversight of significant reactions, ignorance of temperature dependences of known reactions, and/or difficulties in combining complex chemistry with geometrically realistic transport models.

One important result of the detailed modeling effort is a suite of computer programs that can be readily applied to investigate the chemical, dynamic and electrodynamic effects of upper atmosphere chemical releases. The findings obtained during this contract period pertaining to the release of SF_6 in the ionosphere as reported above are summarized below:

1. Before the rocket flight CRRES investigators were provided with (a) predicted ambient conditions of the atmosphere, electrodynamics, and ionosphere, and (b) predicted size and motion of SF_6 perturbation.

2. The results of an electrodynamic model suggest that the large scale (> 5 km) electric field perturbations induced by an SF_6 release are small in magnitude and short in duration. The large-scale electric fields are determined by the field-line integrated quantities and the induced perturbations to these integrated quantities are small. Thus, it is concluded that the perturbed plasma region moves approximately with the background plasma. In addition, the artificial seeding of equatorial spread F is unlikely to cause large-scale plasma plumes. Small-scale irregularities (< 1 km) can still form on the sharp gradients in the local quantities of plasma density, conductivity, etc.

3. The extent of the electrodynamic perturbation region perpendicular to the magnetic field is approximately 30 km in radius. This is the region of the deep electron hole. The extent of the chemically perturbed region was determined to be very large (r > 200 km). This is due to the high altitude of the release point, which allows a broad expansion of the SF_6 cloud. Examination of the IMS data indicates that the observation rocket flew through the larger region of chemical disturbance.

4. Previously suggested SF_6 chemistry [*Mendillo and Forbes*, 1982; *Bernhardt*, 1984; *Hunton et al.*, 1987] appears to be sufficient for the initial chemistry of an SF_6 release (near the release point). The pseudo three-dimensional model of the chemistry as well as the single cell chemical calculations illuminated the expected and unexpected findings of the CRRES release experiment. SF_6^- production is large in central region. The saturation of the all-sky camera measurement of 7774Å airglow is an evidence for the production of SF_6^- near the release point. The unexpected dominance of F^- is explained well by the charge interchange mechanism given in *Hunton et al.* [1987]. Both the shape and magnitude of the F^- density profile as measured by the IMS on the observation rocket are matched in the simulations.

5. Chemistry simulations indicated that in the late time (>5 min), oxidation of SF_n is potentially important. Several neutral species produced later in the SF_6-ionospheric chemistry are electron attachers. SOF_3^- is probably an important late time negative ion. In addition, several SF_n and SOF_n neutrals can participate in positive ion chemistry. The IMS did measure an unexpected heavy positive ion other than SF_5^+ (D. E. Hunton, private communication). This is not predicted with the present chemical reaction set.

6. The differences between simulation and experiment may provide interesting avenues for continued investigation of SF_6-ionospheric chemistry. SF_4^- densities in experimental observations are much higher than simulation predictions. However, the mass spectrometer resolution does not have the necessary resolution to separate the masses of SOF_3^- and SF_4^-. Therefore, the measurable density of SOF_3^- predicted in the simulation may be combined into the measurement of SF_4^- density. SF_5^- densities are still much lower in the simulation when compared to the observed densities. Possibly, chemical reactions are missing or the observation rocket position relative to the release point is not as predicted.

7. There are differences in the O^+-e and O^+-O^- recombination branching models used to model O^+-SF_n^- recombination. Both models give nearly identical intensities for 7774Å emissions. Examination of other lines will indicate which model better describes the O^+-SF_n^- recombination.

5.2 Recommendations

The findings of the simulation and experiment comparisons can be used to suggest directions for the continued cooperation of simulation, field and laboratory experiments. The recommendations below focus on the attempt to resolve the apparent differences between simulation and experiment of the CRRES SF_6 release of August 1990. Implications for future experiments are also enumerated.

1. The observed low density of SF_5^- is the most disconcerting difference between experiment and simulation. SF_5^- is an initial product of the attachment chemistry and is the avenue for F^- creation. To model an SF_6 release with confidence one must have correct predictions of the SF_5^- densities. Continued simulation studies can be performed to determine the importance of collisionally induced dissociation and detachment of SF_5^-.

2. The absolute electron-attachment cross section of SF_4 and SOF_4 need to be measured in a laboratory investigation.

3. The positive-ion chemistry resulting from SF_n oxidation and fragmentation is unknown.

4. While the large-scale electric fields are not perturbed greatly by an equatorial release of SF_6, small scale irregularities can be formed and observed. Simulations of the development of the small scale irregularities would provide insight into the timing of probable observations of the irregularity onset in a positive-negative ion plasma.

5. The dynamic and electrodynamic implications of the negative-positive ion plasma in the F-region are still unexplored. The late-time modeling of the depleted plasma tube can be examined in simulation to determine the time constant for refilling of the electron hole and plasma hole. Questions about the extent of the depletion along a magnetic field line could have possible ramifications on how big the long term electrodynamic perturbation is. If the perturbation has a long life, then a release of SF_6 on the F-region ledge prior to the pre-reversal enhancement may have a more destabilizing effect than a later release. The present models can suggest optimal altitudes and times for a release to seed ESF phenomenon.

6. The simulations of the airglow produced by the SF_6 release show that identical 7774Å emission is predicted by both O^+-e and O^+-O^- recombination branching models for O^+-M^- recombination. The observation of 8446Å and 7774Å simultaneously would provide information to indicate preference of the O^+-e or O^+-O^- model. Observation of the spatial distribution of 1304Å and 1356Å emissions along with 8446Å and 7774Å emissions would provide strong indicators of the regions where SF_6^- or SF_5^- production is taking place. The 1304Å and 1356Å emissions must be observed from a space-based platform since the atmosphere is optically thick for these emissions.

PART II. CO2 RELEASES

6. INTRODUCTION

CO_2-ionospheric chemistry is important in rocket plumes and in the ionospheres of Mars and Venus. Releasing CO_2 in the upper atmosphere provides controlled insight into CO_2 chemistry. Boston University's REDAIR (Release Experiments to Derive Airglow Inducing Reactions) Program investigates CO_2-ionospheric chemistry by observing the induced airglow emissions.

The main effects of CO_2 release in the F-region are: (1) atomic-ion concentration reduction, (2) plasma reduction via dissociative recombination, and (3) enhanced 6300A airglow through the production of $O(^1D)$. The main reactions in the CO_2-ionospheric reaction set are

$$CO_2 + O^+ \qquad O_2^+ + CO \tag{1}$$

$$CO_2 + O^+ \qquad CO_2^+ + O \tag{2}$$

$$O_2^+ + e \qquad O + O(^1D) \tag{3}$$

$$CO_2^+ + e \qquad CO + O \tag{4}$$

$$O(^1D) + e \qquad O + h\,\nu(6300A) \tag{5}$$

The combined reaction rate for reaction channels (1) and (2) is 9.4×10^{-10} cm^3s^{-1} with little temperature variation. The branching of the CO_2-O^+ reaction varies strongly with energy [*Fehsenfeld et al.*, 1966; *Paulson et al.*, 1966; *Dunkin et al.*, 1968; *Mosesman and Huntress*, 1970; *Johnsen et al.*, 1970; *Lindinger et al.*, 1974; *Jaffe and Klein*, 1974; *Viggiano et al.*, 1990*a*; *Viggiano et al.*, 1990*b*]. The importance of reaction (1) is demonstrated by comparing the reaction rate to the rates of O^+ reacting with O_2 and N_2, which are 2 and 3 orders of magnitude slower than reaction (1), respectively.

Implications of the branching energy dependence for ionospheric release of CO_2 have been discussed in *Caledonia et al.* [1987] and *Hunton et al.* [1990]. At low energies the interchange branch (Reaction (1)) is dominant and produces O_2^+ and, eventually, 6300A airglow. At higher energies the charge exchange branch (Reaction (2))dominates. The same branching trends are observed with CO_2 vibrational energy and translational energy (A.A. Viggiano, private communication). The population distribution of the vibrational states of the produced O_2^+ varies with temperature [*Viggiano et al.*, 1990*a*]. A change in the vibrational state population of O_2^+ alters the branching ratios of dissociative recombination [*Guberman*, 1988].

Due to the rarified conditions of an upper atmospheric release of CO_2, NLTE (non-local thermal equilibrium) conditions hold. Under such conditions the vibrational state populations of molecular neutrals and ions can depart from Boltzmann distributions. Chemical rate coefficients obtained under LTE conditions may be a misrepresentation within models of chemical release. Explicit vibrational dependencies in rate coefficients and products are potentially important in modeling such NLTE environments.

The release of CO_2 in the ionosphere is useful as a control experiment to single out the effects of CO_2 from the complex chemistry of plumes. CO_2-ionospheric chemistry without explicit vibrational states has been used to model 6300Å airglow production in CO_2 releases from exhaust plumes [*Mendillo and Baumgardner*, 1982]. There were indications that the observed 6300Å intensity was less than the value predicted by the chemistry model.

There are also indirect questions of importance that can be answered through CO_2 releases in the high ionosphere. If published CO_2-O^+ reaction rates are accurate, then a high-altitude CO_2 release can be used to find quenching rates of $O(^1D)$ by ground state O. This quenching reaction, first suggested by *Yee and Dalgarno* [1985], could alter predicted airglow profiles for daytime, nighttime and auroral ionospheres. Some investigators suggest that quenching by O is not needed to explain experimental observations [*Link and Cogger,* 1988] (also see, *Bates* [1989]). A high-altitude release of CO_2 would produce $O(^1D)$ above regions of quenching by N_2 and O_2. This would leave O as the dominant quenching species.

The REDAIR Campaign attempted to place CO_2 release above and below the F peak. For these two release points, the electron densities would be similar but the neutral background would give different characteristics in diffusion and chemical constituent concentrations. M. Mendillo (private communication) has reported preliminary results indicating a peak 6300Å enhancement of 80 Rayleighs over the background for the upper release. The enhancement was immediate (< 1 minute) and decreased approximately as a simple decay curve, though the decay curve had a "hump" suggesting the presence of other processes beyond simple CO_2-ionospheric chemistry. The low-altitude release produced a peak enhancement of 25 Rayleighs over the background. The enhancement time history had a slow rise time when compared to the upper release but decayed at approximately the same time constant.

In this investigation, two questions are studied through numerical simulations of the REDAIR CO_2 release experiment. First, how does the introduction of explicit vibrational states of CO_2 (A. A. Viggiano, private communication) and O_2^+ [*Guberman*, 1988; *Queffelec et al.*, 1989] into the chemistry change the simulated 6300Å airglow production from a CO_2 release. Second, what are the important effects of species transport. The first question is investigated with the chemical kinetic code, ARCHON, to identify differences in chemical reaction sets. The second question is examined with the use of a multi-dimensional simulation of a CO_2 release to identify dynamic and spatial effects on the observed airglow.

The reaction set necessary for ambient $O(^1D)$ production and loss is reviewed in *Torr and Torr* [1982], *Link and Cogger* [1988], *Solomon et al.* [1988], and *Solomon and Abreu* [1989]. The ambient reactions used to model airglow production are given in Appendix B. The reactions are generally those of *Solomon and Abreu* [1989]. Appendix C contains relevant reactions for single state representations of CO_2 and O_2^+ and Appendix D for explicit vibrational states. The rates of reactions (1) and (2) are given as a function of vibrational states of CO_2 using unpublished data of A. A. Viggiano (private communication). There has been no attempt to extrapolate the data up to the high ionospheric temperatures, thus, data for T_{CO2} = 500K is used. Rates for vibrational quenching and excitation of CO_2 are taken from *Archer* [1990]. The production rates of vibrational states of O_2^+ is taken from *Viggiano et al.* [1990*a*]. These rates are based on data taken in the temperature range of 88K to 300K. This is a limitation on the NLTE investigation but the results will indicate trends. Quenching rates of $O_2^+(\nu)$ are estimated. Further laboratory studies are necessary to provide proper rates for the chemical models.

7. MODELING RESULTS

7.1 REDAIR Ambient Conditions

Computations were performed using a single-cell Lagrangian chemical-kinetics code to investigate the possible differences in the chemistry sets of standard CO_2 reactions (Appendix C) and explicit vibrational CO_2-O_2^+ reactions (Appendix D). For the investigation of the REDAIR CO_2 releases, ambient atmospheric conditions were determined from MSIS86 [*Hedin*, 1987] using Geo-solar conditions listed in Table 2. The electron density was obtained from experimental measurements (M. Mendillo, private communication).

Table 2. Release Conditions (estimates).

Launch	3 April 1989
10.7cm Flux	184
< 10.7cm Flux >	196
Sunspot Number (R_a)	218
Geo-Longitude	284.6 East
Geo-Latitude	37.8 North
A_p Index	21
K_p Index	27
Release Altitude	379 km and 253 km
Local Solar Time	21:30

7.2 REDAIR Chemistry Investigation

Figure 21 compares the plasma constituents resulting from the two chemistry sets for the high altitude release. Very little compositional difference is seen between the results of the two chemistry sets. The CO_2^+ density is increased when using the vibrational states reactions. The first vibrational state is populated at a sufficiently fast rate to allow for increased charge exchange with O^+ for the CO_2^+ production. The resulting decrease in ion-molecule interchange reduces $O(^1D)$ densities only slightly. With the $O(^1D)$ densities given by the model one can estimate the Rayleigh production of a release. For a region of 30 km where dense CO_2 chemistry takes place, the peak enhancement is approximately 900 Rayleighs. This is 10 times larger than observed for the release.

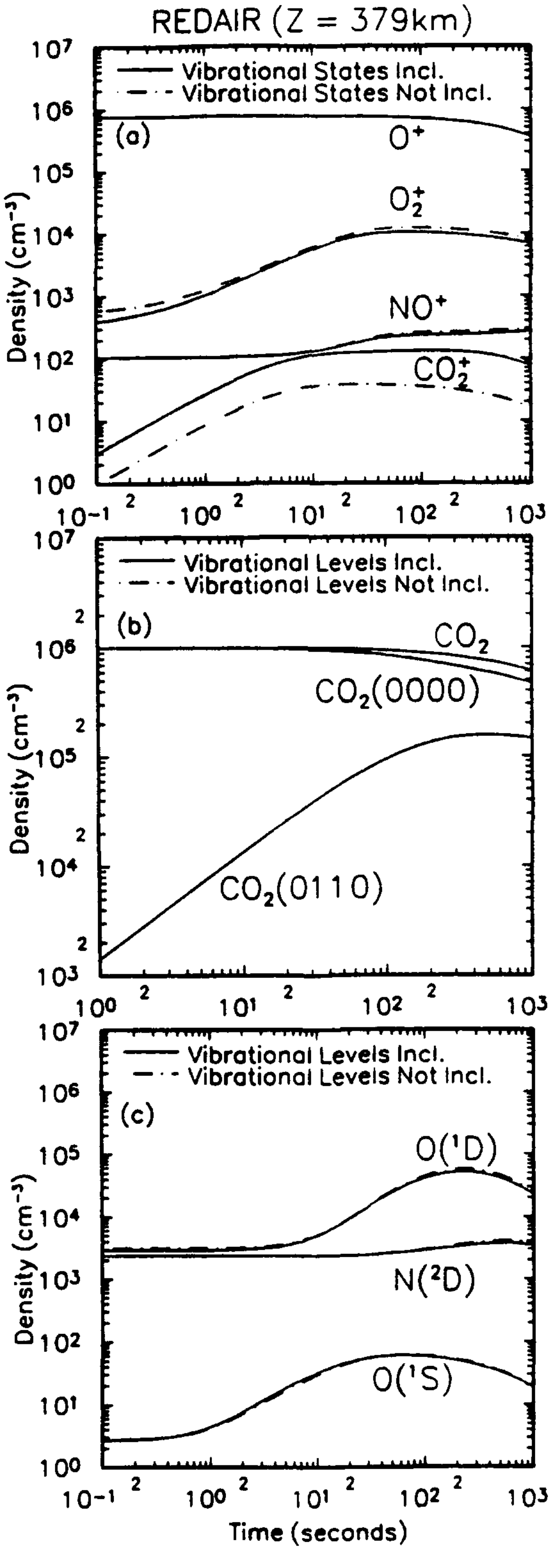

Figure 21. a) Plasma constituent densities, b) CO_2 vibrational distribution and c) metastable species densities for CO_2 release at 379 km altitude. Solid lines use vibrationally explicit chemistry.

The lack of dynamics or spatial modeling makes it difficult to obtain absolute comparisons to the airglow measurements. However, when these effects are modeled (results in Section 3), the predicted airglow is still four times higher than observed.

The modeling of the low-altitude release (Figure 22) gives very different results from the high-altitude release. Very little $O(^1D)$ is produced in the release due to the low O^+ density. The local 6300Å emission is enhanced slightly over the background (5 Rayleighs). These results are intriguing: the high-altitude simulation overestimates the 6300Å production and the low-altitude simulation underestimates the production.

One candidate for the discrepancy is the electron density profile obtained from digisonde measurement for the REDAIR experiment. The factor of two reduction of the O^+ at the release point reduces the local airglow emission proportionally (Figure 23).

Computations using the two different chemistry sets of CO_2 (with and without vibrational states) give the same results. There is presently no advantage to using explicit vibrational levels of CO_2 and O_2^+ in the chemistry. This does not say that vibrational level chemistry is not important in the modeling of the NLTE conditions in CO_2 releases. A possible explanation is that the rates for reactions containing CO_2 and O_2^+ were obtained from low temperature measurements ($T <$ 545K and 300K, respectively). Laboratory experiments with higher temperature environments could give reaction rates that would alter results of subsequent simulations.

7.3 REDAIR Spatial Modeling

The CO_2 releases at 253km and 379km gave 6300Å airglow enhancements that differ with each other in magnitude, rise time, and decay shape. The differences are not simply explained by the chemistry results in the above section. Modeling the REDAIR experiment requires simulation of the spatial and dynamic effects of the CO_2 release and the observation methods. As will be seen, the geometry of the line-of-sight integration of the airglow played a role in the magnitude and time history of the 6300Å measurement. The REDAIR experiment was modeled by assuming cylindrical symmetry thereby reducing the three-dimensional problem to a two-dimensional numerical grid. It is assumed that the magnetic field is vertical and the horizontal rocket motion is negligible. Plasma motion is only vertical. The two releases are modeled with separate simulations.

Figure 24 depicts the 6300Å enhancement image from the all-sky Camera at 100 s after release. The all-sky Camera view has the zenith in the center of the circle and the horizon on the perimeter.

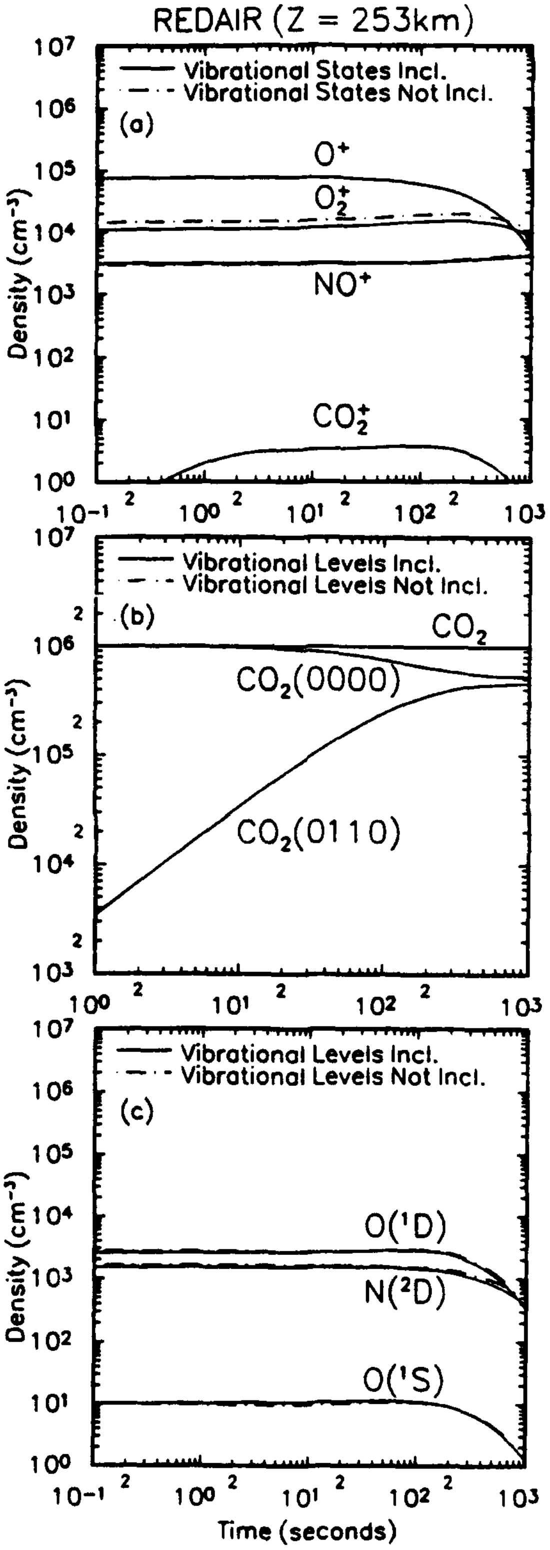

Figure 22. a) Plasma constituent densities, b) CO_2 vibrational distribution, and c) metastable species densities for CO_2 release at 253 km altitude. Solid lines use vibrationally explicit chemistry.

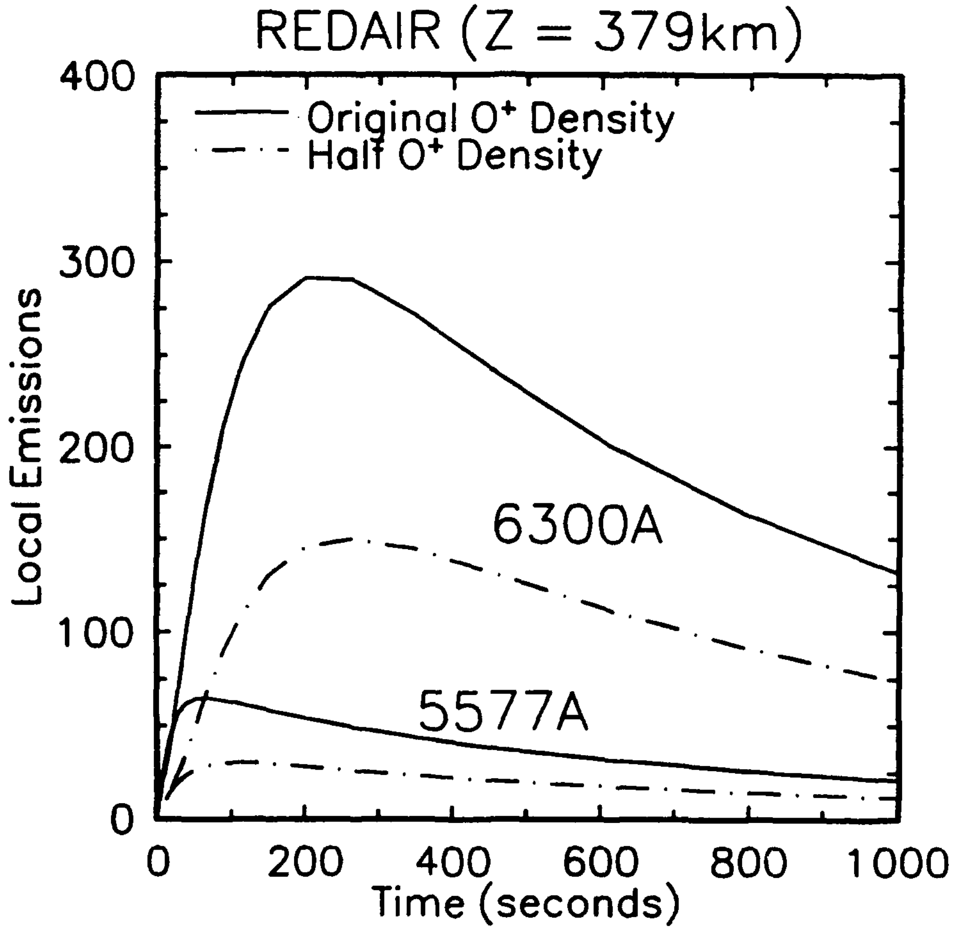

Figure 23. Local emission from O(^{1}D) and O(^{1}S) for measured n_e and half measured n_e for CO_2 release at 379 km altitude.

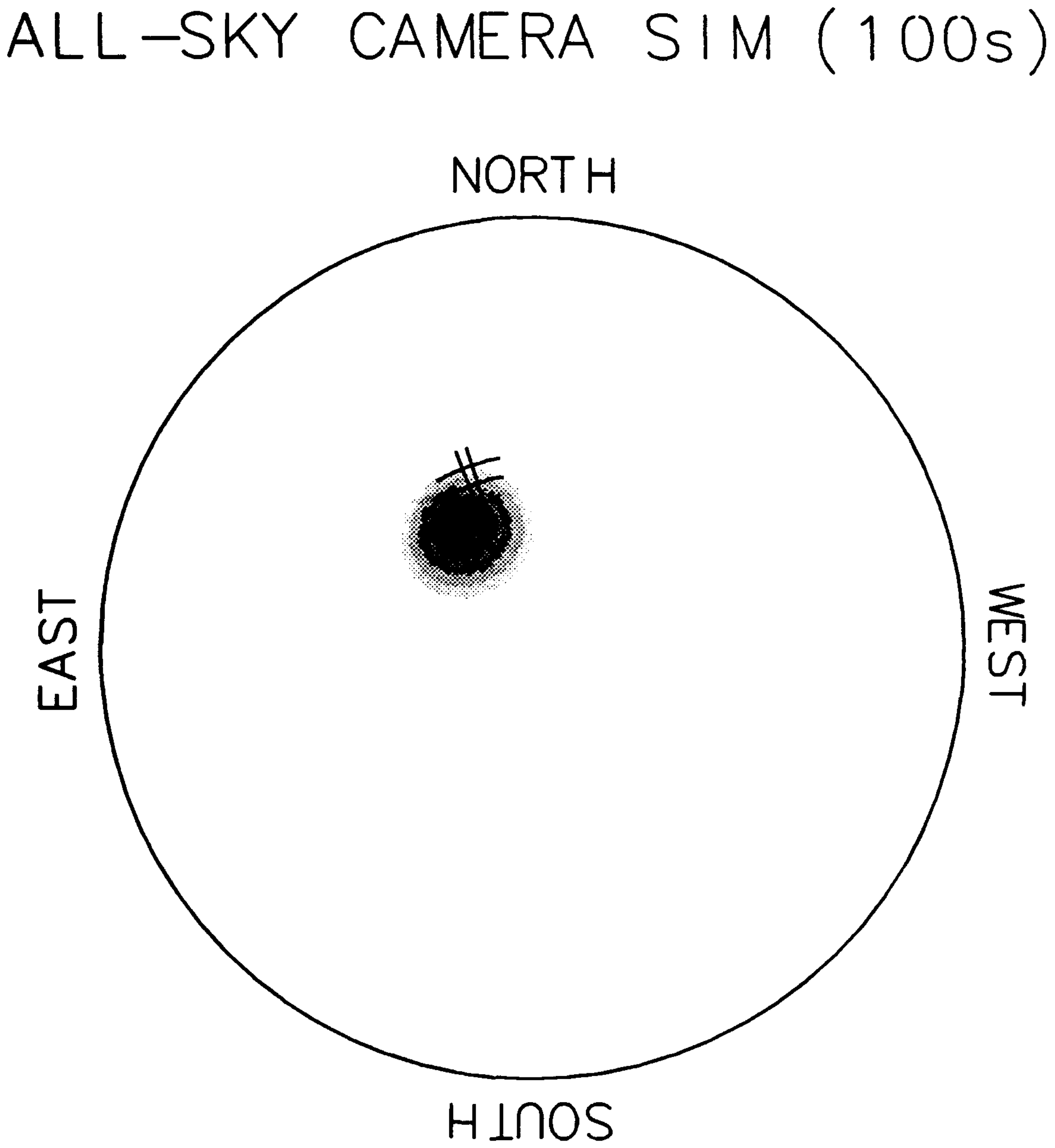

Figure 24. All-sky Camera image simulation. The two regions bound by cross hatches are the regions of measurement for the upper and lower release. Only the airglow from the upper release upper release is plotted. The region of measurement for the lower release is under the influence of the upper release airglow enhancement at t = 100 s.

Using the region within the lines shown at the center of the enhancement, an average Rayleigh value is obtained to compare with REDAIR data. The simulated airglow peak is four times too large (Figure 25). This suggests that there are missing or misrepresented processes in the present model or the ambient conditions are not well represented. The process could be chemical or thermodynamic. In addition, the shape of the enhanced airglow curve of the simulation is a simple decay structure and not the double hump of the REDAIR data.

Figure 26 displays the simulated lower release airglow. While the enhancement magnitude is approximately correct, the shape is not at all like the slow rise and fall. The two releases of the REDAIR experiment were performed from a single rocket. This allows for the possibility of mixing the effects of the two releases spatially. To determine if the airglow perturbations of the separate releases were "mixed", the airglow histories of the two simulations are linearly added using the observational geometry of the all-sky Camera. The releases were separated enough to make the linear adding of the airglow effects reasonable. The CO_2 of the lower release may have expanded up to the higher altitude of the second release and vice versa. Figure 27 shows the added effects of the two releases at the airglow measurement point of the high-release altitude. Apparently, the expansion of the lower release cloud is stopped abruptly at the lower altitude. The lower release does not affect the upper release region greatly.

The shape of the time decay of the airglow enhancement measured at the upper release point is still unexplained by the physics of the simulation. Figure 28 shows the airglow magnitudes of the two releases through the point of the lower release altitude.

The higher altitude release has a definite influence on the measurement of the lower release experiment. The upper release expands and falls into the region of the lower release point. The REDAIR airglow measurement has a plateau near the front of the time-airglow curve. This could be the mixing region of the upper and lower cloud effects.

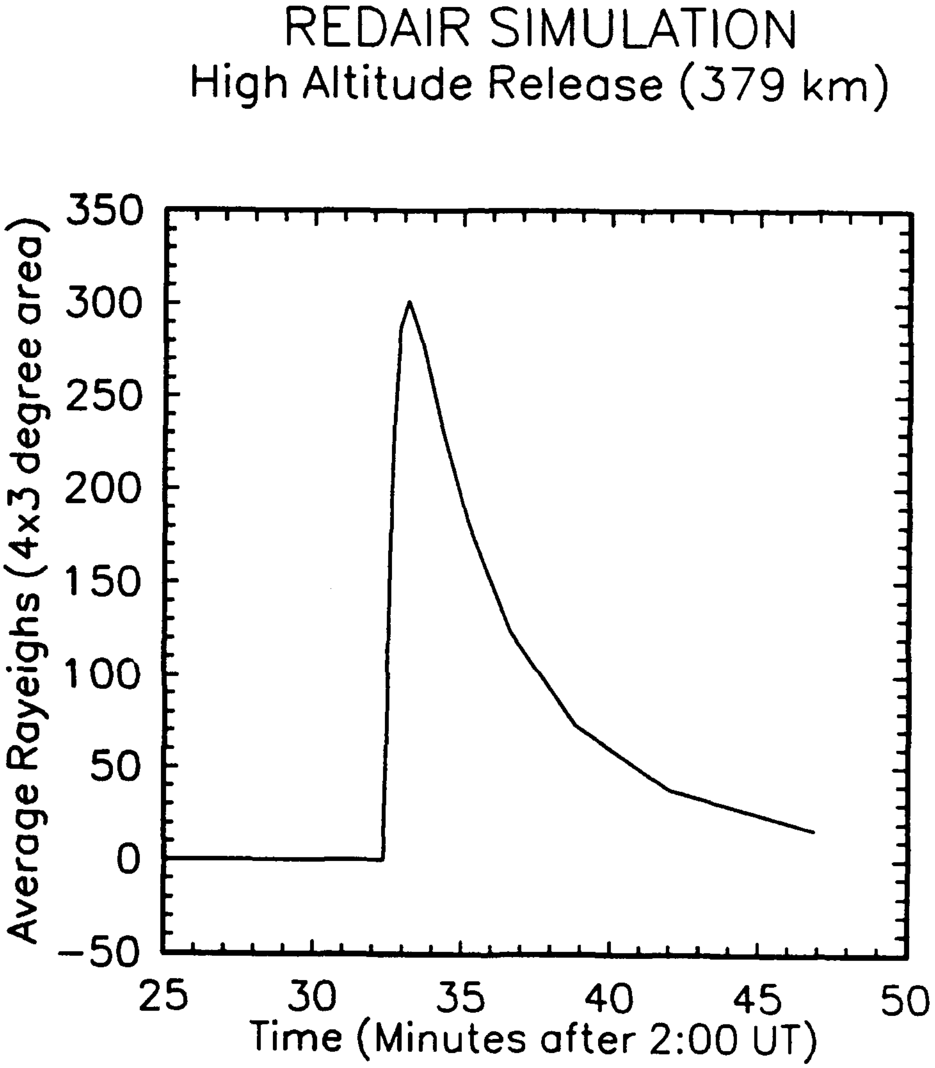

Figure 25. The average airglow from simulation measured within a rectangle centered on the upper release point.

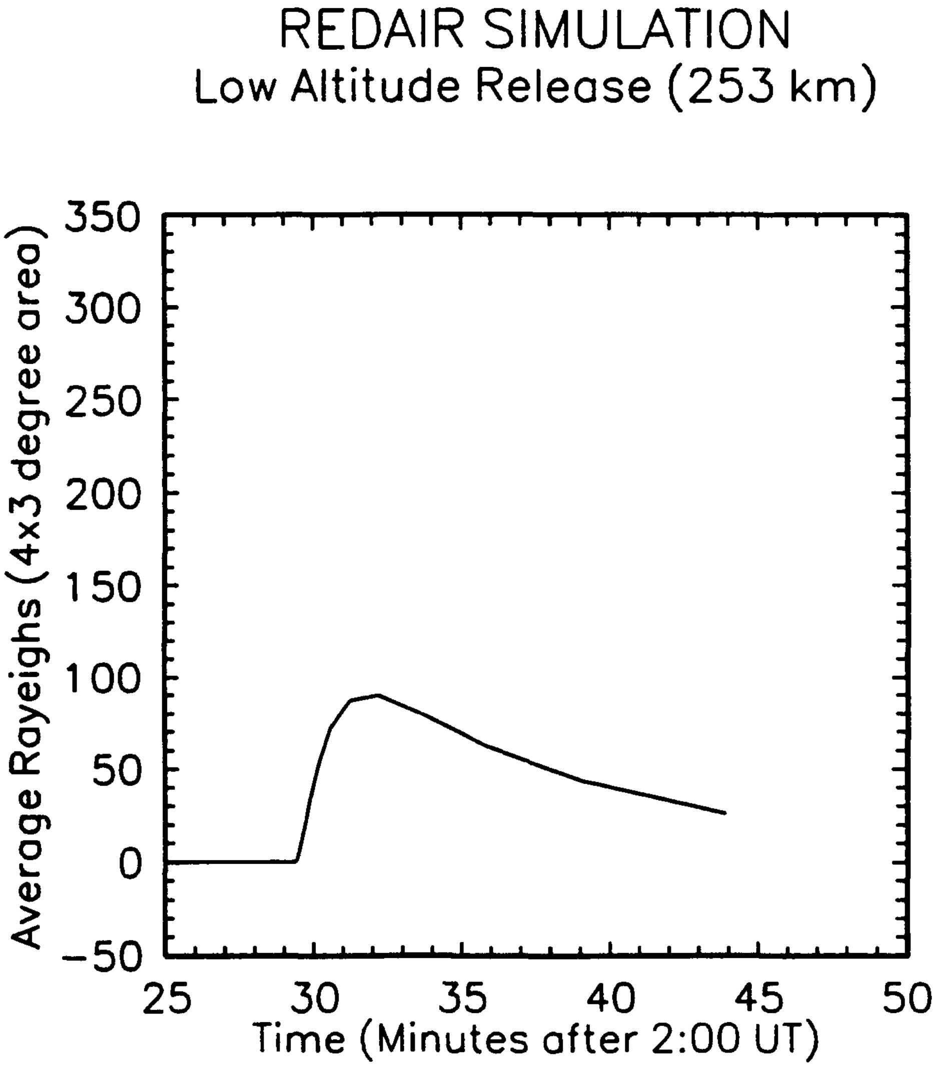

Figure 26. The average airglow from simulation measured within a rectangle centered on the lower release point.

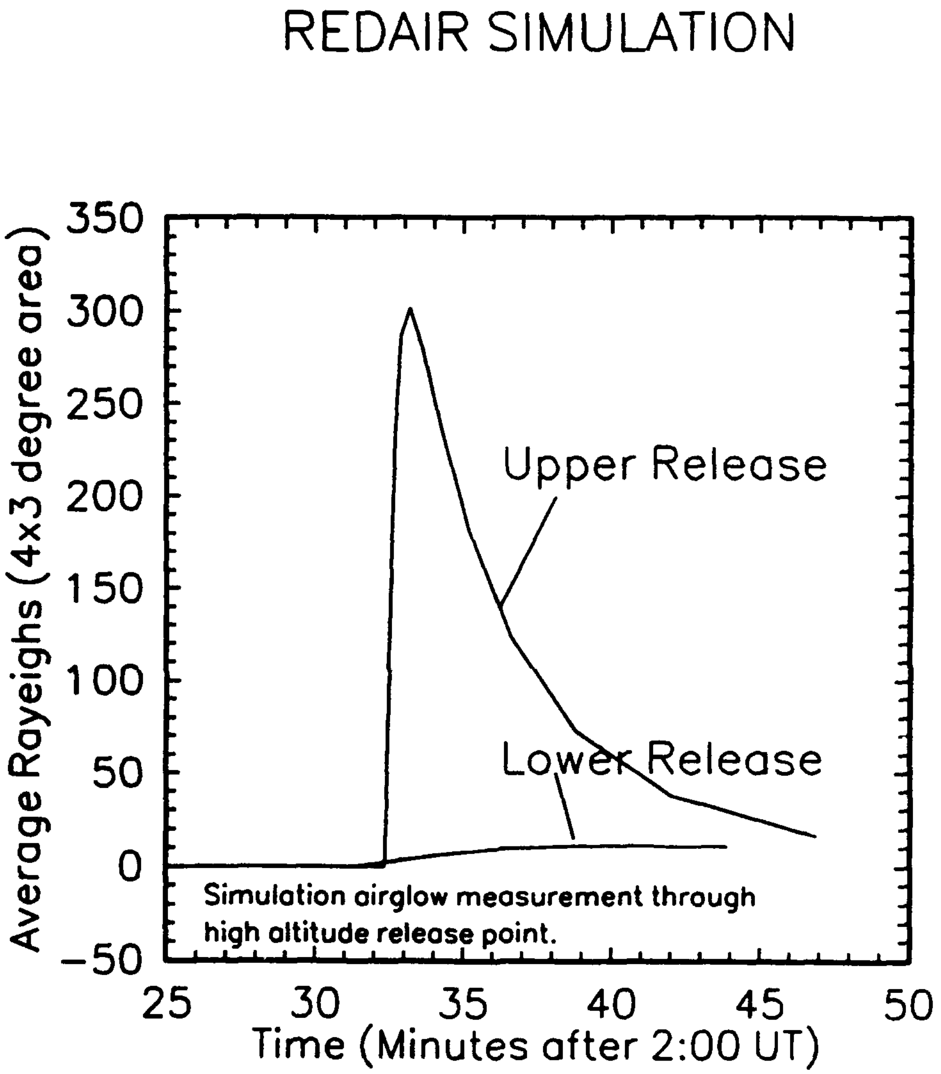

Figure 27. Superposition comparison of the upper release and lower release airglow enhancements measured at the position of the upper release point.

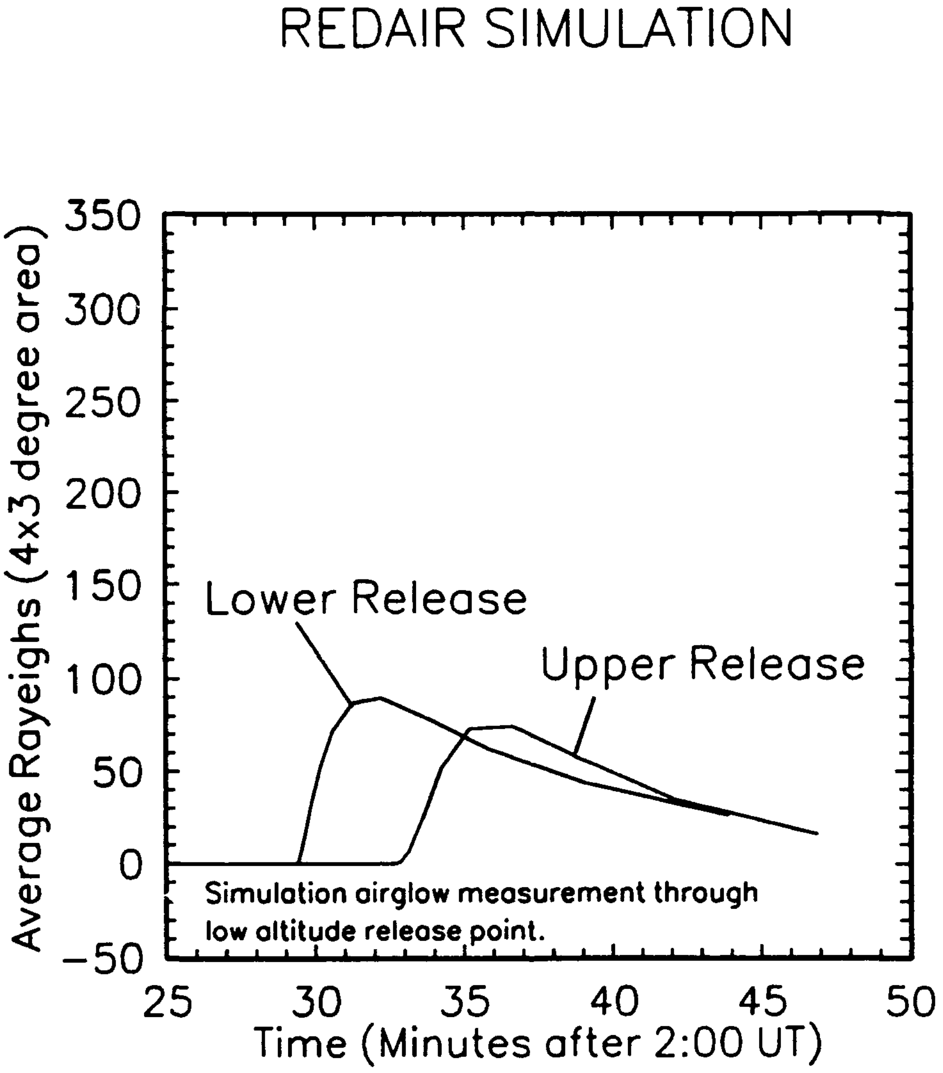

Figure 28. Superposition comparison of the upper release and lower release airglow enhancements measured at the position of the lower release point.

8. SUMMARY

The present knowledge of CO_2-ionospheric chemistry has been tested through simulation comparison to the REDAIR campaign 6300Å airglow measurements. The modeling effort of CO_2 release is still young. The continuing investigation will help find if numerical effects contaminate the prediction. The present state of the investigation is summarized below to provide an overview of initial accomplishments from the effort. With each item of summary a discussion of implications and recommendations for future studies on CO_2-ionospheric chemistry is given.

1. The simulation of the REDAIR experiment with standard CO_2-ionospheric reactions predicts more 6300Å airglow than observed. The simulated airglow is too large by a factor of four for the upper release and a factor of two for the lower release. Not only do the observed and predicted airglow magnitudes differ, but also the shapes of the airglow intensity versus time curves differ. The cause of the magnitude discrepancies could be chemical, *e.g.*, the charge exchange rate of O^+ with CO_2 is larger than the published rate, or mechanical, *e.g.*, freezing of the CO_2 upon release. Due to the lack of laboratory measurements at higher temperatures, the CO_2 vibrational-state chemistry used in this study may not represent CO_2-ionospheric chemistry well. The discrepancy between simulation and experiment also could be in the misrepresentation of the actual ambient conditions. As the simulation in Section 7 showed, variation of the electron density profile has a proportional effect on the 6300Å airglow enhancement for the upper release. In addition, there are other physical processes that are not in the present simulations that may influence the $O(^1D)$ production. Perhaps CO_2 freezes or clusters when released and effectively reduces $O(^1D)$ production. These processes are promising because sublimation or breakup of the bound CO_2 could produce the second hump of the airglow curve of the upper release.
2. The simulation of the low- and high-altitude releases of the REDAIR campaign does indicate that low-altitude release airglow measurement was mixed with the airglow perturbation of the high-altitude release. The upper cloud's airglow pattern was spread over a very wide area while the lower cloud's region of influence was very confined. The mixing of the effects of the two releases has implications for the planning of REDAIR II CO_2 releases.

9. REFERENCES

9.1. References for Part I

Anderson and Mendillo, Ionospheric conditions affecting the evolution of equatorial plasma depletions, *Geophys. Res. Lett., 10,* 541-544, 1983.

Bernhardt, P.A., Chemistry and dynamics of SF_6 injections into the F Region, *J. Geophys. Res., 89,* 3929-3937, 1984.

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,* 8937-8946, 1986.

Bernhardt, P.A., A critical comparison of ionospheric depletion chemicals, *J. Geophys. Res., 92,* 4617-4628, 1987.

Cakir, S., G. Haerendel and J.V. Eccles, Modeling the ionospheric response to artificially produced density enhancements, *J. Geosphys. Res.*, to be published, 1991.

Fejer, B.G., The equatorial ionospheric electric fields: A review, *J. Atmos. Terr. Phys., 43,* 377-386, 1981.

Fehsenfeld, F.C., Electron attachment to SF_6, *J. Chem. Phys., 53,* 2000-2004, 1970.

Haerendel, G., O.J. Bauer, S. Cakir, H. Goppl, E. Rieger, and A. Valenzuela, Coloured Bubbles-An experiment for triggering equatorial spread F, Active Experiments in Space, *Eur. Space Agency Spec. Publ., SP-195,* 295-299, 1983.

Haerendel, G., J.V. Eccles, and S. Cakir, Theory for modeling the equatorial evening ionosphere and the origin of the shear in the horizontal plasma flow, *J. Geophys. Res.*, to be published, 1991.

Hedin, A.E., MSIS-86 thermospheric model, *J. Geophys. Res., 92,* 4649-4662, 1987.

Hunton, D.E., A.A. Viggiano, W. Swider, J.F. Paulson, and C. Sherman, Mass Spectrometric Measurements of SF_6 Chemical Releases, *J. Geophys. Res., 92,* 8827-8830, 1987.

Kennealy, J.P., S.B. Downer, R.J. Larkin, and T.J. Moratz, ARCHON-22, *DNA-TR-89-65-V1,* Defense Nuclear Agency, 1989.

Kline, L.E., Electron and chemical kinetics in the low-pressure RF discharge etching of silicon in SF_6, *IEEE Trans. Plasma Sci., 14,* 145-155, 1986.

Mendillo, M. and J. Forbes, Theory and observation of a dynamically evolving negative ion plasma, *J. Geophys. Res., 87,* 8273-8285, 1982.

Mothes, K.G., E. Schultes, and R.N. Schindler, Application of electron cyclotron resonance technique in studies of electron capture processes in the thermal energy range, *J. Phys. Chem., 76,* 3758-3764, 1972.

Mullen, J.H., J.M. Madson, and L.N. Medgyesi-Mitschang, Measurement of electron attachment processes in a high-temperature plasma, *Proceedings of the IEEE, 59,* 605-607, 1971.

Olthoff, J.K., R.J. Van Brunt, Y. Wang, R.L. Champion, and L.D. Doverspike, Collisional electron detachment and decomposition rates of SF_6^-, SF_5^-, F^- in SF_6: Implications for ion transport and electrical discharges, *J. Chem. Phys., 91*, 2261-2268, 1989.

Phelps, A.V., and R.J. Van Brunt, Electron-transport, ionization, attachment, and dissociation coefficients in SF_6 and its mixtures, *J. Appl. Phys., 64*, 4269-4277, 1988.

Richmond, A.D., S. Matsushita and J.D. Tarpley, On the production mechanism of electric currents and fields in the ionosphere, *J. Geophys. Res., 81*, 547-555, 1976.

Rishbeth, H., Polarization fields produced by winds in the equatorial F-region, *Planet. Space Sci., 19*, 357-369, 1971.

Rosenberg, N.W. (Ed.), Project Firefly 1962-1963, *Environ. Res. Pap. 15, AFCRL-64-363*, Air Force Cambridge Res. Lab., Hanscom Field, Mass., 1964.

Spence, D. and G.J. Schulz, Temperature dependence of electron attachment at low energies for polyatomic molecules, *J. Chem. Phys., 58*, 1800-1803, 1973.

Van Brunt, R.J., Production rates for oxyflourides SOF_2, SO_2F_2 and SOF_4 in SF_6 corona discharges, *J. Res. National Bureau of Standards, 90*, 229-253, 1985.

Van Brunt, R.J. and J.T. Herron, Fundamental processes of SF_6 decomposition and oxidation in glow and corona discharges, *IEEE Transactions on Electrical Insulation, 25*, 75-94, 1990.

Wang, Y., R.L. Champion, L.D. Doverspike, J.K. Olthoff, and R.J. Van Brunt, Collisional electron detachment and decomposition cross sections for SF_6^-, SF_5^-, F^- on SF_6 and rare gas targets, *J. Chem. Phys., 91*, 2254-2267, 1989.

9.2. References for Part II

Archer, D.H., DNA chemistry panel review---CO_2, *DNA-TR-90-92*, Defense Nuclear Agency, 1990.

Bates, D.R., Theoretical considerations regarding some inelastic atomic collision processes of interest in aeronomy: Deactivation and charge transfer, *Planet. Space Sci., 37*, 363-368, 1989.

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.

Dunkin, D.B., F.C. Fehsenfeld, A.L. Schmeltekopf and E.E. Ferguson, Ion-molecule reaction studies from 300 to 600K in a temperature-controlled flowing afterglow system, *J. Chem. Phys., 49*, 1365, 1968.

Fehsenfeld, F.C., E.E. Ferguson, and A.L. Schmeltekopf, Thermal-energy ion-neutral reaction rates. III. The measured rate constant for the reaction $O^+ + CO_2 \dashrightarrow O_2^+ + CO$, *J. Chem. Phys., 44*, 3022, 1966.

Guberman, S.L., The production of $O(^1D)$ from dissociative recombination of O_2^+, *Planet. Space Sci.*, 36, 47-53, 1988.

Hedin, A.E., MSIS-86 thermospheric model, *J. Geophys. Res., 92*, 4649-4662, 1987.

Hunton, D.E., A.A. Viggiano, R.A. Morris, and J.F. Paulson, The $O^+ + CO_2$ reaction: New results and atmospheric implications.

Jaffe, S., and F.S. Klein, An ion cyclotron resonance mass spectrometric study of ion molecule reactions in CO_2 and CO, *Int. J. Mass Spectro. and Ion Phys.*, *14*, 459-466, 1974.

Johnsen, R., H.L. Brown and M.A. Biondi, Ion-molecule reactions involving N_2^+, N^+, O_2^+, and O^+ ions from 300K to 1 eV, *J.Chem. Phys.*, *52*, 5080, 1970.

Kennealy, J.P., S.B. Downer, R.J. Larkin, and T.J. Moratz, ARCHON-22, *DNA-TR-89-65-V1*, Defense Nuclear Agency, 1989.

Lindenger, W. R.C. Fehsenfeld, A.L. Schmeltekopf, and E.E. Ferguson, Temperature dependence of some ionospheric ion-neutral-reactions from 300-900K, *J. Geophys. Res.*, *59*, 4753-4755, 1974.

Link, R. and L.L. Cogger, A reexamination of the OI 6300Å nightglow, *J. Geophys. Res.*, *93*, 9883-9892, 1988.

Mendillo, M. and J. Baumgardner, Optical signature of an ionospheric hole, *Geophys. Res. Let.*, , 215-218, 1982.

Mosesman, M. and W.T. Huntress, On the reaction of O^+ with CO_2, *J. Chem. Phys.*, *53*, 462, 1970.

Narcisi, R. S., Quantitative determination of the outgassing water vapor concentrations surrounding space vehicles from ion mass spectrometer measurements, *Adv. Space Res.*, *2*, 283-286, 1983.

Paulson, J.F. and R.L. Mosher, Reaction $O^+ + CO_2 \rightarrow O_2^+ + CO$, *Bull. Am. Phys. Soc.*, *7*, 633, 1966.

Queffelec, J.L., B.R. Rowe, F. Vallee, J.C. Gomet and M. Morlais, The yield of metastable atoms through dissociative recombination of O_2^+ ions with electrons, *J. Chem. Phys.*, *91*, 5335-5342, 1989

Solomon, S.C., P.B. Hays, and V.J. Abreu, The auroral 6300Å emission: Observations and modeling, *J. Geophys. Res.*, *93*, 9867-9882, 1988.

Solomon, S.C. and V.J.Abreu, The 630 nm dayglow, *J. Geophys. Res.*, *94*, 6817-6824, 1989.

Torr, M.R. and D.G. Torr, The role of metastable species in the thermosphere, *Rev. Geophys. and Space Phys.*, *20*, 91-144, 1982.

Viggiano, A.A., R.A. Morris, F. Dale, and J.F. Paulson, Production of vibrationally excited O_2^+ in the reaction O^+ with CO_2, *J. Chem. Phys.*, *93*, 1681-1688, 1990a.

Viggiano, A.A., R.A. Morris, and J.F. Paulson, Rate constant and branching fraction for the reaction of $O^+(^2D,^2P)$ with CO_2, *J. Chem. Phys.*, *93*, 1483-1484, 1990b.

Yee, J.H., and A. Dalgarno, The quenching of $O(^1D)$ by $O(^3P)$ atoms, *EOS Trans. AGU*, *66*, 993, 1985.

APPENDIX A

DATAFILE OF SF_6 CHEMISTRY

```
*
*      Sections
*
*      1.  Radiative Recombination
*      2.  Photoionization
*      3.  Three-Body Recombination
*      4.  Dissociative Recombination
*      104. Reverse of 4.
*      5.  Ion-Ion Mutual Neutralization
*      105. Reverse of 5.
*      6.  Three-body ion-ion Recombination
*      7.  Radiative Attachment
*      8.  Photodetachment
*      9.  Three-body Attachment
*      10. Collisional Detachment
*      11. Dissociative Attachment
*      12. Associative Detachment
*      13. Positive-Ion Charge Transfer
*      14. Positive-Ion Atom Interchange
*      15. Negative-Ion Charge Transfer
*      16. Negative-Ion Atom Interchange
*      18. Positive-Ion Photodissociation
*      19. Three-Body Positive-Ion/Neutral Association
*      20. Positive-Ion Collisional Dissociation
*      22. Negative-Ion Photodissociation
*      23. Three-Body Negative-Ion/Neutral Association
*      24. Negative-Ion Collisional Dissociation
*      25. Radiation-Stabilized Neutral Recombination
*      26. Neutral Photodissociation
*      27. Three-Body Neutral Recombination
*      28. Neutral Collisional Dissociation
*      29. Neutral Rearrangement
*      30. Radiative Electronic State De-excitation
*      31. Electronic State Photoexcitation
*      32. Collisional Electronic State Quenching
*      132.Reverse reactions of 32.
*      34. Collisional Vibrational State Quenching
*      35. Collisional Vibrational Energy Exchange
*
```

```
*  Format used is:
*
*   reactants   --->  products            rate
*  R1 + R2 + R3 ---> P1 + P2 + P3         A  B  C
*   where
*     1)  k(T) = A*(T/300)**B*EXP(-1000*C/T)
*     2)  Asterisk (*) in the first column denotes a comment.
*           Unused reactions have an asterisk in the first column.
*
*0----------------------------------------------------------------------
*0    SFX-H2O-IONOSPHERIC CHEMISTRY
*0----------------------------------------------------------------------
*
*1----------------------------------------------------------------------
*I. RADIATIVE RECOMBINATION:
*1----------------------------------------------------------------------
*
*2----------------------------------------------------------------------
*II. PHOTOIONIZATION:
*2----------------------------------------------------------------------
*
*3----------------------------------------------------------------------
*III. 3-BODY RECOMBINATION:
*3----------------------------------------------------------------------
*
*4----------------------------------------------------------------------
*IV. DISSOCIATIVE RECOMBINATION
*4----------------------------------------------------------------------
*
 SF5+         + e            ---> SF4       + F          2.00E-07  -0.5
*
*     Biondi, M.A., Comments At. Mole. Phys., D4, p85, 1973.
*                k=2.0(-7)
*
*     Dissociative recombination temperature dependence is inverse
*       Best estimate (JVE)    k=2.0(-7)  (T/300)^-0.5
*       See Biondi, M.A., Charged-Particle Recombination Processes,
*           DNA Reaction Rate Handbook, 1972.
*
*4-----------------------------------------------------------------------
*
 SF4+         + e            ---> SF3       + F          2.00E-07  -0.5
 SF3+         + e            ---> SF2       + F          2.00E-07  -0.5
```

```
*
*    Best Estimate (JVE)
*
*5-------------------------------------------------------------------
*V. MUTUAL NEUTRALIZATION
*5-------------------------------------------------------------------
*
* X+           + Y-          ---> products (probably X + Y) 1.00E-07  -0.5
* X+(cluster) + Y-          ---> products                  5.00E-07  -0.5
* X+           + Y-(cluster)---> products                  5.00E-07  -0.5
* X+(cluster) + Y-(cluster)---> products                  5.00E-07  -0.5
*
*      See Bortner, M.H., R.H. Kummler, and T. Baurer,
*          Summary of suggested rate constants,
*          DNA Reaction Rate Handbook, 1972.
*
*   or
*
* X+           + Y-           ---> X    + Y                 6.00E-07  -0.5
*
*  Mutual Neutralization reactions (cluster or not) were suggested
*  by the DNA Chemistry Committee.  They are based of measurements on
*  several reactions by David Smith in Birmingham, England.
*  The products are estimated.  See ARCHON22-D database.
*
*
 F-            + H2O+        ---> F         + H2O        6.00E-08  -0.5
 F-            + H3O+        ---> F         + H2O   + H  6.00E-08  -0.5
*
*5-------------------------------------------------------------------
*
* F-           + O+          ---> F         + O          6.00E-08  -0.5
*
*  Branching modeled by O+ + e branching and 10.2 eV energy of reaction
*
 F-            + O+          ---> F         + O(5S)      0.38E-08  -0.5
 F-            + O+          ---> F         + O(3S)      0.47E-08  -0.5
 F-            + O+          ---> F         + O          5.15E-08  -0.5
*
*     Bernhardt, P.A., et al.,
*       Excitation of Oxygen Permitted Line Emissions by
*       SF6 Injection into the F region, JGR, 1986.
*  He estimates 5.00e-08 with excitation of O(5S) due to 10.2eV endo.
```

```
*            F- + O+     ---> F + O*
*
*5-----------------------------------------------------------------------
*
 F-            + SF5+          ---> F          + SF5        6.00E-08   -0.5
*
*
*      Bernhardt, P.A., et al.,
*        Excitation of Oxygen Permitted Line Emissions by
*        SF6 Injection into the F region, JGR, 1986.
*
*      He estimates 4.00e-08 because of the measurements of
*        Church and Smith, J. Mass Spectrom. and Ion. Physics, 1977.
*        on reactions of SF5+ + SF6- and SF3+ + SF5-.
*             F- + SF5+ ---> neutrals
*      Also Bernhardt suggests excitation of O(5S) due to 10.2eV endo.
*
*5-----------------------------------------------------------------------
*
* SF5-         + SF5+          ---> SF4        + SF6        6.00E-08   -0.5
 SF5-          + SF5+          ---> SF5        + SF5        6.00E-08   -0.5
*
*      Bernhardt, P.A.,
*        Chemistry and dynamics of SF6 injections into the F region
*        JGR, 1984.
*
*      He estimates 4.00e-08 because of the measurements of
*        Church and Smith, J. Mass Spectrom. and Ion. Physics, 1977.
*        on reactions of SF5+ + SF6- and SF3+ + SF5-.
*
*             SF5- + SF5+ ---> neutrals
*             SF5- + SF5+ ---> SF6 + SF4  are estimated products
*
*        Van Brunt, R.J., and J.T. Herron,
*        Fundamental Processes of SF6 Decomposition and Oxidation in
*        Glow and Corona Discharges,
*        IEEE Transactions on Electrical Insulation, 25, 75-94, 1990.
*
*        They give the neutral products as:
*             SF5- + SF5+ ---> SF5 + SF5
*
*5-----------------------------------------------------------------------
*
```

```
 SF5-         + SF3+         ---> SF4       + SF4        4.00E-08  -0.5
*
*      Church and Smith,
*      Bionic recombination of SF5- and SF6-,
*      J. Mass Spectrom. and Ion. Physics, 1977.
*
*      For
*      SF5-   + SF3+ ---> products       4.0(+/-.5)e-8
*      at T=300K in afterglow experiment (high pressure limit)
*
*      Best Estimate temperature dependence is 4.0e-8(T/300)^-.5
*
*5-----------------------------------------------------------------------
*
* SF5-         + O+           ---> SF5       + O(5S)      6.00E-08  -0.5
*
*  Branching modeled by O+ + e branching and 9.91 eV energy of reaction
*
 SF5-         + O+           ---> SF5       + O(5S)      0.38E-08  -0.5
 SF5-         + O+           ---> SF5       + O(3S)      0.47E-08  -0.5
 SF5-         + O+           ---> SF5       + O          5.15E-08  -0.5
*
*    Mendillo, M, and Forbes, JGR, 1982 because it is close to
*      the recombinations measured by
*      Church and Smith, J. Mass Spectrom. and Ion. Physics, 1977,
*      on reactions of SF5+ + SF6- and SF3+ + SF5-.
*
*5-----------------------------------------------------------------------
*
 SF5-         + O2+          ---> SF5       + O2         6.00E-08  -0.5
 SF5-         + NO+          ---> SF5       + NO         6.00E-08  -0.5
 SF5-         + H2O+         ---> SF5       + H2O        6.00E-08  -0.5
 SF5-         + H3O+         ---> SF5  + H2O        + H  6.00E-08  -0.5
*
*5-----------------------------------------------------------------------
*
 SOF5-        + O+           ---> SOF4   + F   + O       6.00E-08  -0.5
 SOF5-        + O2+          ---> SOF4   + F   + O2      6.00E-08  -0.5
 SOF5-        + NO+          ---> SOF4   + F   + NO      6.00E-08  -0.5
 SOF5-        + SF5+         ---> SOF4   + F   + SF5     6.00E-08  -0.5
 SOF5-        + H2O+         ---> SOF4   + F   + H2O     6.00E-08  -0.5
 SOF5-        + H3O+         ---> SOF4   + F   + H2O + H 6.00E-08  -0.5
*
```

```
*5----------------------------------------------------------------------
*
 SOF3-        + O+           ---> SOF2   + F   + O       6.00E-08  -0.5
 SOF3-        + O2+          ---> SOF2   + F   + O2      6.00E-08  -0.5
 SOF3-        + NO+          ---> SOF2   + F   + NO      6.00E-08  -0.5
 SOF3-        + SF5+         ---> SOF2   + F   + SF5     6.00E-08  -0.5
 SOF3-        + H2O+         ---> SOF2   + F   + H2O     6.00E-08  -0.5
 SOF3-        + H3O+         ---> SOF2   + F   + H2O + H 6.00E-08  -0.5
*
*-----------------------------------------------------------------------
*
* SF4-         + O+           ---> SF4       + O          6.00E-08 -0.5
*
*  Branching modeled by O+ + e branching and 12.5 eV energy of reaction
*     Bernhardt, P.A., et al.,
*       Excitation of Oxygen Permitted Line Emissions by
*       SF6 Injection into the F region, JGR, 1986.
*
 SF4-         + O+           ---> SF4       + O(3p5P)    2.53E-08  -0.5
 SF4-         + O+           ---> SF4       + O(4p3P)    0.03E-08  -0.5
 SF4-         + O+           ---> SF4       + O(3p3P)    0.93E-08  -0.5
 SF4-         + O+           ---> SF4       + O(5S)      0.38E-08  -0.5
 SF4-         + O+           ---> SF4       + O(3S)      0.47E-08  -0.5
 SF4-         + O+           ---> SF4       + O          1.66E-08  -0.5
*
 SF4-         + O2+          ---> SF4       + O2         6.00E-08  -0.5
 SF4-         + NO+          ---> SF4       + NO         6.00E-08  -0.5
 SF4-         + SF5+         ---> SF4       + SF5        6.00E-08  -0.5
 SF4-         + H2O+         ---> SF4       + H2O        6.00E-08  -0.5
 SF4-         + H3O+         ---> SF4       + H2O  + H   6.00E-08  -0.5
*
 SF4(1)-      + O+           ---> SF4       + O          6.00E-08  -0.5
 SF4(1)-      + O2+          ---> SF4       + O2         6.00E-08  -0.5
 SF4(1)-      + NO+          ---> SF4       + NO         6.00E-08  -0.5
 SF4(1)-      + SF5+         ---> SF4       + SF5        6.00E-08  -0.5
 SF4(1)-      + H2O+         ---> SF4       + H2O        6.00E-08  -0.5
 SF4(1)-      + H3O+         ---> SF4       + H2O  + H   6.00E-08  -0.5
*
*5----------------------------------------------------------------------
*
 SF6-         + SF5+         ---> SF6       + SF5        3.90E-08  -0.5
*
*       Church and Smith, J. Mass Spectrom. and Ion. Physics, 1977,
```

```
*       on reactions of SF5+ + SF6- and SF3+ + SF5-.
*             T=300K in afterglow experiment (high pressure limit)
*
*       Temperature dependence is estimated with (T/300)^-0.5.
*
*5----------------------------------------------------------------------
*
* SF6-         + O+           ---> SF6       + O(3p5P)    6.00E-08 -0.5
*
*  Branching modeled by O+ + e branching and 13.06 eV energy of reaction
*
 SF6-         + O+           ---> SF6       + O(3p5P)    2.53E-08  -0.5
 SF6-         + O+           ---> SF6       + O(4p3P)    0.03E-08  -0.5
 SF6-         + O+           ---> SF6       + O(3p3P)    0.93E-08  -0.5
 SF6-         + O+           ---> SF6       + O(5S)      0.38E-08  -0.5
 SF6-         + O+           ---> SF6       + O(3S)      0.47E-08  -0.5
 SF6-         + O+           ---> SF6       + O          1.66E-08  -0.5
*
*     Bernhardt, P.A., et al.,
*       Excitation of Oxygen Permitted Line Emissions by
*       SF6 Injection into the F region, JGR, 1986.
*            SF6- + O+ ---> neutrals
*
*     He estimates 4.00e-08 because of the measurements of
*       Church and Smith, J. Mass Spectrom. and Ion. Physics, 1977.
*       on reactions of SF5+ + SF6- and SF3+ + SF5-.
*
*     Also Bernhardt suggests excitation of O(5S) due to 10.2eV endo.
*            SF6- + O+ ---> SF6 + O(3p5P)       B=.3442
*                SF6- + O+ ---> SF6 + O(3p3P)       B=.1543
*                SF6- + O+ ---> SF6 + O(4p3P)       B=.0047
*       (estimated from e + O+ recombination branches)
*
*       where
*                O(3p5P) ---> O(3s5S) + hv(7774A)       t=1(-8)s
*                O(3p5S) ---> O(2p3P) + hv(1356A)     t=.00019s
*                                           or .0006s (DNA rate book)
*
*       and
*                O(3p3P) ---> O(3s3S) + hv(8446A)       t=1(-8)s
*                O(3s3S) ---> O(2p3P) + hv(1304A)     t=1.8(-9)s
*
*       and
```

```
*                O(4p3P) ---> O(3s3S) + hv(4368A)       t=1(-8)s
*                O(3s3S) ---> O(2p3P) + hv(1304A)     t=1.8(-9)s
*
*5----------------------------------------------------------------------
*
 SF6-         + O2+          ---> SF6       + O2         6.00E-08  -0.5
 SF6-         + NO+          ---> SF6       + NO         6.00E-08  -0.5
 SF6-         + H2O+         ---> SF6       + H2O        6.00E-08  -0.5
 SF6-         + H3O+         ---> SF6  + H2O        + H   6.00E-08  -0.5
*
*5----------------------------------------------------------------------
*
 SF6(1)-      + SF5+         ---> SF6       + SF5        3.90E-08  -0.5
 SF6(1)-      + O+           ---> SF6       + O          5.00E-08  -0.5
 SF6(1)-      + O2+          ---> SF6       + O2         6.00E-08  -0.5
 SF6(1)-      + NO+          ---> SF6       + NO         6.00E-08  -0.5
 SF6(1)-      + H2O+         ---> SF6       + H2O        6.00E-08  -0.5
 SF6(1)-      + H3O+         ---> SF6  + H2O        + H   6.00E-08  -0.5
*
*  same but less important than SF6-    reactions.
*
*5----------------------------------------------------------------------
*
 O-           + SF5+         ---> O         + SF5        6.00E-08  -0.5
 OH-          + SF5+         ---> OH        + SF5        6.00E-08  -0.5
 NO-          + SF5+         ---> NO        + SF5        6.00E-08  -0.5
 O2-          + SF5+         ---> O2        + SF5        6.00E-08  -0.5
*
*5----------------------------------------------------------------------
*
 F-(H2O)      + O+           ---> F    + H2O        + O   6.00E-08  -0.5
 F-(H2O)      + SF5+         ---> F    + H2O        + SF5 6.00E-08  -0.5
 F-(H2O)      + H2O+         ---> F    + H2O        + H2O 6.00E-08  -0.5
 F-(H2O)      + H3O+         ---> F    + H2O  + H2O  + H 6.00E-08  -0.5
 SF4-(H2O)    + O+           ---> SF4  + H2O        + O   6.00E-08  -0.5
 SF4-(H2O)    + SF5+         ---> SF4  + H2O        + SF5 6.00E-08  -0.5
 SF4-(H2O)    + H2O+         ---> SF4  + H2O        + H2O 6.00E-08  -0.5
 SF4-(H2O)    + H3O+         ---> SF4  + H2O  + H2O  + H 6.00E-08  -0.5
 SF5-(H2O)    + O+           ---> SF5  + H2O        + O   6.00E-08  -0.5
 SF5-(H2O)    + SF5+         ---> SF5  + H2O        + SF5 6.00E-08  -0.5
 SF5-(H2O)    + H2O+         ---> SF5  + H2O        + H2O 6.00E-08  -0.5
 SF5-(H2O)    + H3O+         ---> SF5  + H2O  + H2O  + H 6.00E-08  -0.5
 SF6-(H2O)    + O+           ---> SF6  + H2O        + O   6.00E-08  -0.5
```

```
 SF6-(H2O)    + SF5+          ---> SF6   + H2O        + SF5 6.00E-08  -0.5
 SF6-(H2O)    + H2O+          ---> SF6   + H2O        + H2O 6.00E-08  -0.5
 SF6-(H2O)    + H3O+          ---> SF6   + H2O  + H2O  + H 6.00E-08  -0.5
*
*  Higher clustering important only if first-order clustering is
*  significant.
*
*6------------------------------------------------------------------------
*VI. 3-Body Ion-Ion Recombination
*6------------------------------------------------------------------------
*
* X+     + Y-    + M    ---> products (probably X + Y + M) 3.00E-25  -2.5
*    with an M saturation limit of 3.00e-06
* (same for clusters)
*
*       See Bortner, M.H., R.H. Kummler, and T. Baurer,
*           Summary of suggested rate constants,
*           DNA Reaction Rate Handbook, 1972.
*
 SF6-    + O+    + M    ---> SF6   + O   + M   3.00E-25 -2.5 0. 0. 3.00e-06
 SF5-    + O+    + M    ---> SF5   + O   + M   3.00E-25 -2.5 0. 0. 3.00e-06
 SF4-    + O+    + M    ---> SF4   + O   + M   3.00E-25 -2.5 0. 0. 3.00e-06
 SOF5-   + O+    + M    ---> SOF4 + F + O + M 3.E-25 -2.5 0. 0. 3.00e-06
 F-      + O+    + M    ---> F   + O   + M     3.00E-25 -2.5 0. 0. 3.00e-06
*
 SF6-    + SF5+  + M    ---> SF6   + SF5 + M 3.00E-25 -2.5 0. 0. 3.00e-06
 SF5-    + SF5+  + M    ---> SF6   + SF4 + M 3.00E-25 -2.5 0. 0. 3.00e-06
 SF4-    + SF5+  + M    ---> SF4 + SF5   + M 3.00E-25 -2.5 0. 0. 3.00e-06
 SOF5-   + SF5+  + M    ---> SOF4 + F + SF5 + M 3.E-25 -2.5 0. 0. 3.e-06
 F-      + SF5+  + M    ---> F   + SF5   + M   3.00E-25 -2.5 0. 0. 3.00e-06
*
 SF6-    + H2O+  + M    ---> SF6 + H2O   + M 3.00E-25 -2.5 0. 0. 3.00e-06
 SF5-    + H2O+  + M    ---> SF6 + H2O   + M 3.00E-25 -2.5 0. 0. 3.00e-06
 SF4-    + H2O+  + M    ---> SF4 + H2O   + M 3.00E-25 -2.5 0. 0. 3.00e-06
 SOF5-   + H2O+  + M    ---> SOF4 + F + H2O + M 3.E-25 -2.5 0. 0. 3.e-06
 F-      + H2O+  + M    ---> F   + H2O   + M 3.00E-25 -2.5 0. 0. 3.00e-06
*
 SF6-    + H3O+  + M    ---> SF6 + H2O + H + M 3.E-25 -2.5 0. 0. 3.0e-06
 SF5-    + H3O+  + M    ---> SF6 + H2O + H + M 3.E-25 -2.5 0. 0. 3.0e-06
 SF4-    + H3O+  + M    ---> SF4 + H2O + H + M 3.E-25 -2.5 0. 0. 3.0e-06
 SOF5- + H3O+ + M ---> SOF4 + F + H2O + H + M 3.E-25 -2.5 0. 0. 3.0e-06
 F-      + H3O+  + M    ---> F   + H2O   + H + M 3.E-25 -2.5 0. 0. 3.0e-06
*
```

```
*7----------------------------------------------------------------------
*VII. Radiative Attachment
*7----------------------------------------------------------------------
*
*  X + e ---> X- + hv  is very slow.
*
*  With metastable state it can be modeled
*
*  X + e ---> X-*       k = 1.e-7
*
*  without a third body to stabilize is very slow to stabilize.
*
*  X-* ---> X + e       t_a
*  X-* ---> X- + hv     t_s
*
* the net reaction of
*  X + e ---> X- is  k*ta/ts (approximately 1.e-9 at T=300K)
* best to model X-* and X- separately.
*
*
*  Attachment, detachment and stabilization reactions.
*  see SECTION XXXIV for collisional stabilization.
*
*  SF6 attachment ... radiative and dissociative channels
*      with autodetachment processes.
*
 SF6          + e              ---> SF6(1)-                |SF6E1
 SF6          + e              ---> SF5-      + F          |SF6DEA1
*
 SF6(1)-                       ---> SF6       + e           1.10E+04
*
* Basic attachment rate for low energy electrons (Te<.2eV) measured
* to be constant by
*     Fehsenfeld, F.C.,
*       Electron attachment to SF6, J. Chem. Phys., 53, 1970.
*            (300K to 500K)
*       Spence, D. and G.J. Schulz,
*       Temperature dependence of electron attachment at low energies
*       for polyatomic molecules
*       J. Chem. Phys., 58, 1973.
*                (300K to 1200K)
*       Mothes, K.G., E. Shultes, and R.N. Schindler,
*       Application of electron cyclotron resonance technique in
```

```
*       studies of electron capture processes
*       in the thermal energy range,
*       J. Phys. Chem. 76, 3758, 1972.
*
*           SF6 + e ---> SF6-*(all excited states)        k(total)
*
*           k(total) = k1 + k2 + k3 + k4
*
*       k1 and k2 is modeled by
*       Bernhardt, P.A.,
*       Chemistry and Dynamics of SF6 injections into the F region
*       JGR, 1984.
*
*       For Tn<600K k3=0 and k4=0.
*            k2=k(total)/[1.+1.56e-3*exp(4770/T)]
*       and
*            k1=k(total)-k2
*
* also see
*
*       Chen, C.L., and P.J. Chantry,
*       Temperature dependence of SF6-, SF5- and F- production from
*       SF6, Bull. Am. Phys. Soc., 17, 406, 1971.
*
*       Kline, L.E., D.K. Davies, C.L. Chen, and D. J. Chantry,
*       Dielectric properties for SF6 and SF6 mixtures predicted
*       from basic data, J. Appl. Phys., 50, 6789, 1979.
*
*       Mullen, J.H., S.M. Madson, and L.N. Medgysi-Mitschang,
*       Measurement of electron attachment processes in high
*       temperature plasmas, Proc. IEEE, 59, 605, 1971.
*
*B----------------------------------------------------------------------
*
 SF5        + e         ---> F-       + SF4      1.00e-08
*
 SF4        + e         ---> SF4(1)-             9.50e-09
 SF4        + e         ---> SF3-     + F        0.00e-10
 SF4        + e         ---> F-       + SF3      5.00e-10
 SF4(1)-                ---> SF4      + e        1.00E+05
*
 SOF4       + e         ---> SOF3-    + F        1.00e-08
*
```

```
 SOF2         + e           ---> SOF2(1)-                  5.00e-10
 SOF2(1)-                   ---> SOF2      + e             1.00E+05
*
 SO2F2        + e           ---> SO2F2(1)-                 1.00e-08
 SO2F2(1)-                  ---> SO2F2     + e             1.00E+05
*
*       Sauers, I, L.,G. Christophorou, and S.M. Spyrou,
*       Negative ion formation in SF6 spark by products,
*       ??, 1990.
*
*       C.L. Chen and  P.J. Chantry, Electron Attachment in SF4,
*       Bull. Amer. Phys. Soc., 17, 406, 1972.
*
*
*8-----------------------------------------------------------------------
*VIII.  Photodetachment
*8-----------------------------------------------------------------------
*  These values are for normal incidence, unattenuated solar flux
*  at top of earth's atmosphere.
*
 SF4-                       ---> SF4       + e             1.5 |DAY
 SF4(1)-                    ---> SF4       + e             1.5 |DAY
 SF3-                       ---> SF3       + e             0.7 |DAY
 SF-                        ---> SF        + e             0.4 |DAY
 F-                         ---> F         + e             1.0 |DAY
*
*       Simple constant cross section assumed (20e-18 cm2) for
*       wavelengths shorter than threshold based on electron affinity.
*       AE(SF6)=1.0eV           2.
*       AE(SF5)=3.7eV         .15
*       AE(SF4)=1.5eV         1.5
*       AE(SF3)=3.0eV         .7
*       AE(SF )=3.0eV         .4
*       AE(F  )=2.5eV         1.
*       (see  Babcock and G.E. Streit: Negative ion-molecule reactions
*             of SF4, J. Chem. Phys., 75, 1981.)
*     (see Viggiano, A.A., T.M. Miller, A.E.S. Miller, R.A. Morris,
*     J.M. Van Doren, and J.F. Paulson,
*     SF4: Electron Affinity determination
*       by Charge-transfer Reactions,
*     Int. J. Mass Spectrom. Ion Processes, submitted 1991.)
*
*8-----------------------------------------------------------------------
```

```
*
 SF5-                    ---> SF5      + e          0.15 |DAY
 SF6-                    ---> SF6      + e          2.0  |DAY
 SF6(1)-                 ---> SF6      + e          2.0  |DAY
*
*     Bernhardt, P.A.,
*     Ionospheric Depletions Chemicals, JGR, 1987.
*
*       Simple constant cross section assumed (20e-18 cm2) for
*       wavelengths shorter than threshold based on electron affinity.
*       AE(SF5)=3.7eV
*       AE(SF6)=1.0eV
*
*9----------------------------------------------------------------------
*IX. 3-Body Attachment
*9----------------------------------------------------------------------
*
*  X + e + M ---> X- + M
*
*  With metastable state it can be modeled
*
*  X + e ---> X-*        k = 1.e-7
*
*  without a third body to stabilize is very slow to stabilize.
*
*  X-* ---> X + e        t_a
*  X-* + M ---> X- + M   k_s
*  X-* ---> X- + hv
*  X-* ---> Y- + Z  (through dissociation)
*
* the net reaction of
*  X + e + M ---> X- + M is  k*ta if first two reactions most important.
*  It is best to model X-* and X- separately.
*
*
*10---------------------------------------------------------------------
* X. Collisional Detachment (CID)
*10---------------------------------------------------------------------
*
 SF6-         + M        ---> SF6   + e    + M      1.00e-12
 SF5-         + M        ---> SF5   + e    + M      1.00e-13
 F-           + M        ---> F     + e    + M      5.00e-18
 SF6-         + SF6      ---> SF6   + e    + SF6    0.00e-14
```

```
 SF5-         + SF6          ---> SF5    + e    + SF6    0.00e-15
 F-           + SF6          ---> F      + e    + SF6    5.00e-18
*
*   Estimated for T=1000K from:
*   Wang, Y, R.L. Champion, L.D. Doverspike, J.K. Olthoff
*   and R.J. Van Brunt,
*   Collisional electron detachment and decomposition
*   cross sections for
*   SF6-, SF5-, and F- on SF6 and rare gas targets,
*   J. Chem. Phys., 91, p2254-2260, 1989.
*      and
*   J.K. Olthoff, R.J. Van Brunt, Wang, Y, R.L. Champion,
*   L.D. Doverspike,
*   Collisional electron detachment and decomposition rates of
*   SF6-, SF5-, and F- in SF6:
*   Implications for ion transport and electrical discharges,
*   J. Chem. Phys., 91, p2261-2268, 1989.
*
*   Used Maxwellian distribution for F- + SF6 estimation
*   and Kagan-Perel
*   distribution with gamma=1 for others.
*
*12---------------------------------------------------------------------
* XII. Associational Detachment
*12---------------------------------------------------------------------
*
 F-           + H            ---> e         + HF         1.60E-09
*
*     Fehsenfeld, F.C., C.J. Howard, and E.E. Ferguson,
*     J.Chem. Phys., 58, 5841, 1973.
*
*12---------------------------------------------------------------------
*
 O-           + SO2          ---> e         + SO3        2.10E-09
*
*     Lindinger, W., D.L. Albritton, F.C. Fehsenfeld,
*       and E.E. Ferguson,
*     J. Chem.PHys., 63, 3238, 1975.
*
*12---------------------------------------------------------------------
*
 S-           + O2           ---> e         + SO2        4.60E-11 -0.72
*
```

```
*     Fehsenfeld, F.C. , J. Chem. Phys., 63, 1686, 1975.
*
*12---------------------------------------------------------------------
*
 S-          + O3           ---> e          + SO3         1.00E-09
*
*     Lifshitz, C., R.L.C. Wu, J.C. Haartz, and T. O. Tiernan,
*     J. Chem. Phys., 67, 2381, 1977.
*
*12---------------------------------------------------------------------
*
 HS-         + H            ---> e          + H2S         1.30E-09
*
*     Fehsenfeld, F.C., C.J. Howard, and E.E. Ferguson,
*     J.Chem. Phys., 58, 5841, 1973.
*
*13---------------------------------------------------------------------
* XIII. Positive-ion Charge Transfer
*13---------------------------------------------------------------------
*
 F+          + H2           ---> H2+        + F           0.70E-09
 F+          + NO           ---> NO+        + F           8.10e-10
 F+          + N2           ---> N2+        + F           9.00E-10
 F+          + O2           ---> O2+        + F           6.40E-10
*
*     Hamdan, M., N.W. Copp, K. Birkinshaw, J.D.C. Jones,
*       and N.D. Twiddy,
*       Int. J. Mass Spectrom. Ion Processes, 69, 191, 1986.
*
*13---------------------------------------------------------------------
*
 O+          + H2S          ---> H2S+       + O           1.60E-09
 O2+         + H2S          ---> H2S+       + O2          1.40E-09
*
*     Liddy, G.P., C.G. Freeman, and M.J. McEwan,
*     Astrosphy. Lett., 16, 155, 1975.
*
*13---------------------------------------------------------------------
*
 SO2+        + O2           ---> O2+        + SO2         2.80E-10
*
*     Fehsenfeld, F.C. and E.E. Ferguson, J. Geophys. Res.,
*     78, 1699, 1973.
```

```
*
*13---------------------------------------------------------------------
*
 HS+          + NO           ---> NO+       + HS         4.50E-10
 S+           + NO           ---> NO+       + S          3.70E-10
*
*    Smith, D., N.G. Adams, and W. Lindinger,
*      J. Chem. Phys., 75, 3365, 1981.
*
*13---------------------------------------------------------------------
*
 H2O+         + H2S          ---> H2S+      + H2O        8.70E-10
 H2O+         + SO2          ---> SO2+      + H2O        2.00E-09
*
*    Castleman, Jr. et al., 1986?
*
*13---------------------------------------------------------------------
*
 SF4+         + NO           ---> NO+       + SF4        4.20E-10
 SF5+         + NO           ---> NO+       + SF5        0.91E-10
*
*    Fehsenfeld, F.C.,
*    Ion Chemistry of SF6, J. Chem. Phys., 54, 438, 1971.
*
*13---------------------------------------------------------------------
*
 SF5+         + NO2          ---> NO2+      + SF5        2.30E-11
 SF5+         + H2S          ---> H2S+      + SF5        5.60E-11
*
*    Babcock, L.M. and G.E. Streit,
*      J. Chem. Phys., 74, 5700, 1981.
*
*13---------------------------------------------------------------------
*
*  Reactions that should go
 O+           + S            ---> S+        + O          1.00E-10
 O+           + SO           ---> SO+       + O          1.00E-10
 O+           + SF           ---> SF+       + O          1.00E-10
 O+           + SF2          ---> SF2+      + O          1.00E-10
 O+           + SF3          ---> SF3+      + O          1.00E-10
 O+           + SF4          ---> SF4+      + O          1.00E-10
 O+           + SF5          ---> SF5+      + O          1.00E-10
* Estimated rates
```

```
 H2O+          + S          ---> S+        + H2O         1.00E-10
 H2O+          + SO         ---> SO+       + H2O         1.00E-10
 H2O+          + SF         ---> SF+       + H2O         1.00E-10
 H2O+          + SF2        ---> SF2+      + H2O         1.00E-10
 H2O+          + SF3        ---> SF3+      + H2O         1.00E-10
 H2O+          + SF4        ---> SF4+      + H2O         1.00E-10
 H2O+          + SF5        ---> SF5+      + H2O         1.00E-10
*  Estimated rates
 NO+           + SF3        ---> SF3+      + NO          1.00E-10
 SF3+          + NO         ---> NO+       + SF3         1.00E-10
*(possibly accidentally resonant)
*
 O2+           + S          ---> S+        + O2          1.00E-10
 O2+           + SO         ---> SO+       + O2          1.00E-10
 O2+           + SF         ---> SF+       + O2          1.00E-10
 O2+           + SF2        ---> SF2+      + O2          1.00E-10
 O2+           + SF3        ---> SF3+      + O2          1.00E-10
 O2+           + SF4        ---> SF4+      + O2          1.00E-10
 SF4+          + O2         ---> O2+       + SF4         1.00E-10
*(possibly accidentally resonant)
 O2+           + SF5        ---> SF5+      + O2          1.00E-10
*
 SF+           + SF3        ---> SF3+      + SF          1.00E-10
 SF2+          + SF         ---> SF+       + SF2         1.00E-10
 SF2+          + SF3        ---> SF3+      + SF2         1.00E-10
 SF4+          + SF         ---> SF+       + SF4         1.00E-10
 SF4+          + SF2        ---> SF2+      + SF4         1.00E-10
 SF4+          + SF3        ---> SF3+      + SF4         1.00E-10
 SF4+          + SF5        ---> SF5+      + SF4         1.00E-10
 SF5+          + SF         ---> SF+       + SF5         1.00E-10
 SF5+          + SF2        ---> SF2+      + SF5         1.00E-10
 SF5+          + SF3        ---> SF3+      + SF5         1.00E-10
*
*14-----------------------------------------------------------------
* XIV.  Positive-Ion Interchange
*14-----------------------------------------------------------------
*
 HE+           + SO2        ---> SO+     + HE      + O   3.00E-09
 HE+           + SO2        ---> S+      + HE      + O2  0.86E-09
 SO+           + N          ---> NS+     + O             5.00E-11
*2-132
*     Fehsenfeld, F.C. and E.E. Ferguson, J. Geophys. Res.,
*     78, 1699, 1973.
```

```
*
*14-----------------------------------------------------------------------
*
 F+            + H2            ---> FH+       + H            0.50E-09
 F+            + O2            ---> OF+       + O            8.00E-11
 F+            + O2            ---> O+        + OF           8.00E-11
 F+            + NO            ---> NF+       + O            9.00E-11
 F+            + SO2           ---> SO+       + OF           2.20E-09
*4-480
*     Hamdan, M., N.W. Copp, K. Birkinshaw, J.D.C. Jones,
*     and N.D. Twiddy,
*     Int. J. Mass Spectrom. Ion Processes, 69, 191, 1986.
*
*14-----------------------------------------------------------------------
*
 O+            + H2S           ---> HS+       + OH           0.42E-09
 O+            + H2S           ---> S+        + H2O          0.22E-09
*2-2011
*     Smith, D., N.G. Adams, T.M.Miller,
*     J. Chem. Phys., 1978.
*
*14---------------------------------------------------------------------
*
 S+            + H2S           ---> S2+       + H2           1.15E-09
 SO+           + H2S           ---> S2+       + H2O          9.40E-10
*2-4000
*     Liddy, J.P., C.G. Freeman, M.J. McEwan,
*     Int. J. Mass Spectrom. Ion Phys., 23, 153, 1977.
*
*14-----------------------------------------------------------------------
*
 S+            + O2            ---> SO+       + O            2.10E-11
*4-008
*     M. Tichy, A.B. Rakshit, D.G. Lister, and N.D. Twiddy,
*     N.G. Adams, D.Smith,
*       Int. J. Mass Spectrom. Ion Phys., 29, 231, 1979.
*
*14-----------------------------------------------------------------------
*
 HS+           + H2O           ---> H3O+      + S            6.30E-10
*4-055
*     Smith D., N.G. Adams, and W.Lindinger,
*     J. Chem. Phys., 75, 3365, 1981.
```

```
*
*14---------------------------------------------------------------------
*
 SO+          + SF6          ---> SF5+      + SOF        4.50E-10
 SO2+         + SF6          ---> SF5+      + SO2F       2.80E-10
*4-323
*     Babcock, L.M. and G.E. Streit,
*     J. Chem. Phys., 74, 5700, 1981.
*
*14---------------------------------------------------------------------
*
 HE+          + SF6          ---> SF5+      + F      + HE  1.00E-09
 HE+          + SF6          ---> SF4+ + F  + F      + HE  0.60E-09
 HE+          + SF6          ---> SF3+ + F2 + F      + HE  0.40E-09
* estimates at partition of reaction
 N2+          + SF3          ---> SF3+      + N2         1.00E-09
 N2+          + SF4          ---> SF4+      + N2         1.00E-09
 N2+          + SF5          ---> SF5+      + N2         1.00E-09
 N2+          + SF6          ---> SF5+      + F      + N2  1.30E-09
* N+           + SF6          ---> SF5+      + NF        1.40E-09
* see below
* O+           + SF6          ---> SF5+      + OF        1.50E-09
* see below
*2-93
*     Fehsenfeld, F.C.,
*       Ion Chemistry of SF6, J. Chem. Phys., 1971.
*
 N+           + SF6          ---> SF5+      + F        + N 1.40E-09
 O+           + SF6          ---> SF5+      + F        + O 1.50E-09
*
*       Eldon Fergenson at NOAH Boulder, CO: said that SF6(IP) is
*       13.6eV instead of the previously measured 15. eV.  This
*       means that these two reactions (above) are charge exchange
*       (with SF6+ unstable) and not ion interchange reactions.
*
*15---------------------------------------------------------------------
* XV.  Negative-Ion Charge Transfer
*15---------------------------------------------------------------------
*
 F-           + NO2          ---> NO2-      + F          5.00E-12
*2-40
*     F.C. Fehsenfeld and E.E. Ferguson,
*     Planet. Space Sci., 16, 701, 1968.
```

```
*
*15------------------------------------------------------------------
*
 F-          + SF6         ---> SF6-     + F          1.20E-12
*
*    Greenberg and Hargis, Appl. Phys. Lett., 1989.
*    Seppelt, Z. anorg. ally. chem., 1977...has 1.40e-12
*      Olthoff et al., J. Chem. Phys., 91, 2254, 1989
*                      ...estimates >5e-13
*
*15------------------------------------------------------------------
*
 SF5-        + SF6         ---> SF6-     + SF5        2.90E-14
*
*    Seppelt, Z. anorg. ally. chem., 1977.
*      Olthoff et al., J. Chem. Phys., 91, 2254, 1989
*                  ...estimates >3e-16
*
*15------------------------------------------------------------------
*
 SF4-        + NO2         ---> NO2-     + SF4        5.70E-11
 OH-         + SF4         ---> SF4-     + OH         1.30E-09
 HS-         + SF4         ---> SF4-     + HS         9.50E-10
 O-          + SF4         ---> SF4-     + O          1.40E-09
 S-          + SF4         ---> SF4-     + S          1.10E-09
*4-324
*    Babcock and G.E. Streit,
*    J. Chem. Phys., 75, 3864, 1981.
*
*15----------------------------------------------------------------
*
 O2-         + SF4         ---> SF4-     + O2         1.70E-09
 SO-         + SF4         ---> SF4-     + SO         0.11E-09
 SO2-        + SF4         ---> SF4-     + SO2        0.15E-09
*
*    (see Viggiano, A.A., T.M. Miller, A.E.S. Miller, R.A. Morris,
*    J.M. Van Doren, and J.F. Paulson,
*    SF4: Electron Affinity determination by
*      Charge-transfer Reactions,
*    Int. J. Mass Spectrom. Ion Processes, submitted 1991.)
*
*15------------------------------------------------------------------
*
```

```
 NO-          + SF6          ---> SF6-      + NO          1.50E-10
 O-           + SF6          ---> SF6-      + O           2.40E-13
*0-132
*     Lifshitz, C., T.O. Tiernan, B.M. Hughes,
*     J. Chem. Phys., 59, 3182, 1973.
*
*15-------------------------------------------------------------------
*
 O-           + HF           ---> F-        + OH          5.00E-10
*4-360
*     Hamilton, C.E., M.A. Duncan, T.S. Zwier, J.C. Weisshaaar,
*     G.B. Ellison, V.M. Bierbaum, S.R. Leone,
*     Chem. Phys. Lett., 94, 4, 1983.
*
*15---------------------------------------------------------------------
*
 S-           + NO2          ---> NO2-      + S           1.30E-09
*2-124
*     Dunkin, D.B., F.C. Rehsenfeld, and E.E. Ferguson,
*     Chem. Phys. Lett., 15, 257, 1972.
*
*15-------------------------------------------------------------------
*
 S-           + O3           ---> O3-       + S           9.00E-11
 F-           + O3           ---> O3-       + F           2.00E-14
*4-284
*     Lifshitz, C., R.L.C. Wu, T.O. Tiernan, and D.T. Terwilliger,
*     J. Chem. Phys., 68, 247, 1978.
*
*15---------------------------------------------------------------------
*
 HS-          + O3           ---> O3-       + HS          6.00E-11
*4-281
*     Lifshitz, C., R.L.C. Wu, J.C. Haartz, and T.O. Tiernan,
*     J. Chem. Phys., 67, 2381, 1977.
*
*15---------------------------------------------------------------------
*
 O2-          + SF6          ---> SF6-      + O2          7.00E-11
*     Fehsenfeld, F.C.,
*       Ion Chemistry of SF6, J. Chem. Phys., 1971.
*     Streit, J. Chem. Phys., 1982. has 3.e-11
*
```

```
 SF6-         + O            ---> O-         + SF6        5.00E-11
 SF6-         + O3           ---> O3-        + SF6        3.20E-11
*2-93
*     Fehsenfeld, F.C.,
*       Ion Chemistry of SF6, J. Chem. Phys., 1971.
*
*15-------------------------------------------------------------------
*
 O2-          + SO2          ---> SO2-       + O2         1.90E-09
*4-255
*     Fahey, D.W., F.C. Fehsenfeld, E.E. Ferguson, and L. A. Viehland,
*     J. Chem. Phys., 75, 669, 1981.
*
*15---------------------------------------------------------------------
*
 O3-          + SO2          ---> SO3-       + O2         1.70E-09
*4-258
*     Albritton, D.L., I. Dotan, G.E. Streit,
*       D.W. Fahey, F.C. Fehsenfeld,
*     E.E. Ferguson, J.Chem. Phys., 78, 6614, 1983.
*
*15---------------------------------------------------------------------
*
 SF6-         + F2           ---> F2-        + SF6        3.40E-11
 SF6-         + O2           ---> O2-        + SF6        1.00E-17
 SF6-         + NO2          ---> NO2-       + SF6        1.30E-10
*4-144
*     Streit, G.E., J. Chem. Phys., 77, 826, 1982.
*
*16-------------------------------------------------------------------
* XVI. Negative-Ion Atom Interchange
*16-------------------------------------------------------------------
*
 SO-          + SF4          ---> SF3-       + SOF        0.99E-09
 SO2-         + SF4          ---> SO2F-      + SF3        0.85E-09
*
*     (see Viggiano, A.A., T.M. Miller, A.E.S. Miller, R.A. Morris,
*     J.M. Van Doren, and J.F. Paulson,
*     SF4: Electron Affinity determination by
*       Charge-transfer Reactions,
*     Int. J. Mass Spectrom. Ion Processes, submitted 1991.)
*
*16---------------------------------------------------------------------
```

```
*
 SF5-          + O            ---> F-         + SOF4        1.10E-11
*
*     Hunton, D.E., A.A. Viggiano, W. Swider, J.F. Paulson,
*       and C. Sherman,
*     J. Geophys. Res., 92, 8827-8830,1987.

*16-------------------------------------------------------------------
*
 SF6-          + H            ---> SF5-       + HF          2.10E-10
 SF6(1)-       + H            ---> SF5-       + HF          2.10E-10
*2-163
*     Howard, C.J., R.C. Fehsenfeld, and M. McFarland,
*     J. Chem. Phys., 60, 5086, 1974.
*
*16-------------------------------------------------------------------
*
 SF6-          + SO2          ---> SO2F-      + SF5         0.30E-09
 SF6-          + SO2          ---> SF5-       + SO2F        0.30E-09
 SF6-          + SO2          ---> SO2F2-     + SF4         0.30E-09
*4-144
*     Streit, G.E., J. Chem. Phys., 77, 826, 1982.
*
*16-------------------------------------------------------------------
*
 SF6-          + SOF4         ---> SOF5-      + SF5         8.50E-09
*
*     Van Brunt, R.J., L.W. Sieck, I. Sauers, M.C. Siddagangappa,
*     Plasma Chemistry and Plasma Processing, 8, 225, 1988.
*
*16-------------------------------------------------------------------
*
 SF4-          + SF4          ---> SF5-       + SF3         5.40E-10
 SF6-          + SF4          ---> SF5-       + SF5         3.70E-10
*4-324
*     Babcock and G.E. Streit,
*     J. Chem. Phys., 75, 3864, 1981.
*
*17-------------------------------------------------------------------
* XVII.  Radiation-Stabilized Positive-ion Neutral Association
*17-------------------------------------------------------------------
*
*18-------------------------------------------------------------------
```

```
* XVIII.  Positive-ion Photodissociation
*18------------------------------------------------------------------
*
*19------------------------------------------------------------------
* XIX. 3-Body Positive-Ion Neutral Association
*19------------------------------------------------------------------
*
*20------------------------------------------------------------------
* XX. Positive-Ion Collision Dissociation
*20------------------------------------------------------------------
*
*21------------------------------------------------------------------
* XXI. Radiation-Stabilized Negative-Ion-Neutral Association
*21------------------------------------------------------------------
*
*22------------------------------------------------------------------
* XXII. Negative-Ion Photodissociation
*22------------------------------------------------------------------
*
*23------------------------------------------------------------------
* XXIII. 3-Body Negative-ion-Neutral Association
*23------------------------------------------------------------------
*
 F-      + SO2   + M         ---> SO2F        + M      5.50E-28
*2-141
*    Spears, K.G., E.E. Ferguson, J.Chem. Phys.,
*    59, 4174, 1973.
*
*23------------------------------------------------------------------
*
 F-      + SF4   + M         ---> SF5-        + M      1.00E-28  -1.0
 F-      + H2O        + M    ---> F-(H2O)     + M      1.00E-28  -1.0
 SF5-    + H2O        + M    ---> SF5-(H2O)   + M      1.00E-28  -1.0
 SF4-    + H2O        + M    ---> SF4-(H2O)   + M      1.00E-28  -1.0
 SF4(1)- + H2O        + M    ---> SF4-(H2O)   + M      1.00E-28  -1.0
 SF6-    + H2O        + M    ---> SF6-(H2O)   + M      1.00E-28  -1.0
 SF6(1)- + H2O        + M    ---> SF6-(H2O)   + M      1.00E-28  -1.0
*
*    Estimates to compare with DNA rate reaction Handbook
*
*24------------------------------------------------------------------
* XXIV. Negative-Ion collisional Dissociation
*24------------------------------------------------------------------
```

```
*
* SF5-        + SF6        ---> F-     + SF4  + SF6    1.60e-14
* SF6-        + SF6        ---> SF5-   + F    + SF6    1.20e-13
* SF6-        + SF6        ---> F-     + SF5  + SF6    1.20e-13
 SF5-         + M          ---> F-     + SF4  + M      2.00e-14
 SF6-         + M          ---> SF5-   + F    + M      1.00e-13
 SF6-         + M          ---> F-     + SF5  + M      1.00e-13
 SF6(1)-      + M          ---> SF5-   + F    + M      1.00e-13
 SF6(1)-      + M          ---> F-     + SF5  + M      1.00e-13
*
*  Estimated for T=1000K from:
*  Wang, Y, R.L. Champion, L.D. Doverspike, J.K. Olthoff
*  and R.J. Van Brunt,
*  Collisional electron detachment and decomposition cross sections for
*  SF6-, SF5-, and F- on SF6 and rare gas targets,
*  J. Chem. Phys., 91, p2254-2260, 1989.
*     and
*  J.K. Olthoff, R.J. Van Brunt, Wang, Y, R.L. Champion, L.D. Doverspik
*  Collisional electron detachment and decomposition rates of
*  SF6-, SF5-, and F- in SF6:
*  Implications for ion transport and electrical discharges,
*  J. Chem. Phys., 91, p2261-2268, 1989.
*
*  Used Maxwellian distribution for F- + SF6 estimation and Kagan-Perel
*  distribution with gamma=1 for others.
*
*25-------------------------------------------------------------------
* XXV. Radiation-Stabilized Neutral Recombination
*25-------------------------------------------------------------------
*
*26-------------------------------------------------------------------
* XXVI. Neutral Photodissociation
*26-------------------------------------------------------------------
*
 SF6                       ---> SF5       + F          3.00E-06 |DAY
*
*    Bernhardt, P.A.,
*    Ionospheric Depletions Chemicals, JGR, 1987.

*      Simple constant cross section assumed (1e-22 cm2) for
*      wavelengths shorter than threshold based on electron affinity.
*      D(SF5-F)=3.95eV       3.e-6
*
```

```
*26---------------------------------------------------------------------
*
*       Just as in Bernhardt, P.A., JGR, 1987. (above)
*       D(SF5-F)=3.95eV      3.e-6
*       D(SF4-F)=2.30eV      3.e-5
*       D(SF3-F)=3.65eV      3.e-6
*       D(SF2-F)=2.74eV      3.e-5
*       D(SF -F)=3.98eV      3.e-6
*       D(S  -F)=3.52eV      3.e-6
*
*
 SF5                         ---> SF4       + F          3.00E-05 |DAY
 SF4                         ---> SF3       + F          3.00E-06 |DAY
 SF3                         ---> SF2       + F          3.00E-05 |DAY
 SF2                         ---> SF        + F          3.00E-06 |DAY
 SF                          ---> S         + F          3.00E-06 |DAY
*
*27---------------------------------------------------------------------
* XXVII. 3 Body Neutral Recombination
*27---------------------------------------------------------------------
*
*28---------------------------------------------------------------------
* XXVIII. Neutral Collisional Dissociation
*28---------------------------------------------------------------------
*
*       D(SF5-F)=3.95eV
*       D(SF4-F)=2.30eV
*       D(SF3-F)=3.65eV
*       D(SF2-F)=2.74eV
*       D(SF -F)=3.98eV
*       D(S  -F)=3.52eV
*
 SF6          + M            ---> SF5       + F      + M 1.00E-11 0.0 46.
 SF5          + M            ---> SF4       + F      + M 1.00E-11 0.0 27.
 SF4          + M            ---> SF3       + F      + M 1.00E-11 0.0 42.
 SF3          + M            ---> SF2       + F      + M 1.00E-11 0.0 32.
 SF2          + M            ---> SF        + F      + M 1.00E-11 0.0 46.
 SF           + M            ---> S         + F      + M 1.00E-11 0.0 41.
*
*  Estimates.
*
*29---------------------------------------------------------------------
* XXIX. Neutral Rearrangement
```

```
*29----------------------------------------------------------------------
*
 F            + SF            ---> S         + F2         1.00E-11
 F            + SF3           ---> SF2       + F2         1.00E-11
 H            + SF4           ---> SF3       + HF         4.00E-10
 H            + SF5           ---> SF4       + HF         4.00E-10
 O            + SF            ---> SO        + F          1.70E-10
 O            + SF2           ---> SOF       + F          1.10E-11
 O            + SF3           ---> SOF2      + F          1.00E-10
 O            + SF4           ---> SOF2      + F      + F 2.00E-14
 O            + SF5           ---> SOF4      + F          2.00E-11
 O            + SOF3          ---> SO2F2     + F          5.00E-11
 OH           + SF            ---> SOF       + H          1.00E-10
 OH           + SF2           ---> SOF2      + H          1.00E-10
 OH           + SF3           ---> SOF2      + HF         1.00E-10
 OH           + SF4           ---> SOF3      + HF         3.60E-14
 OH           + SF5           ---> SOF4      + HF         2.00E-11
 SF5          + SF5           ---> SF4       + SF6        5.00E-13
 OH           + SOF3          ---> SO2F2     + HF         1.00E-13
*
*
*     Van Brunt, R.J., J.T. Herron,
*     IEEE Transactions on Electrical Insulation, 25, 75, 1990.
*
*29----------------------------------------------------------------------
*
 O2           + SF3           ---> SO2F2     + F          1.00E-11
*GUESSED RATE
*
 H2O          + F             ---> OH        + HF         1.10E-11
 H2O          + SF4           ---> SOF2      + HF    + HF 1.00E-19
 H2O          + SOF4          ---> SO2F2     + HF    + HF 1.00E-21
 H2O          + SOF2          ---> SO2       + HF    + HF 1.20E-23
*
*     Van Brunt, R.J., L.W. Sieck, I. Sauers, and M.C. Siddagangappa,
*       Transfer of F- in the Reaction of SF6- with SOF4,
*       Plasma Chemistry and Plasma Processing, 8, p225-245, 1988.
*
*     Van Brunt, R.J. and M.C. Siddagangappa,
*       Identification of Corona Discharge induced SF6.
*       Plasma Chemistry and Plasma Processing, 8, p207-223, 1988.
*
*29----------------------------------------------------------------------
```

```
*
* O            + SF           ---> SOF                   1.70E-10
* O            + SF2          ---> SOF2                  1.00E-10
* O            + SF3          ---> SOF3                  1.00E-10
* O            + SF4          ---> SOF4                  1.00E-10
*
*  High pressure limits ... use estimated three-body rate
 O      + SF      + M        ---> SOF       + M          1.00E-30
 O      + SF2     + M        ---> SOF2      + M          1.00E-30
 O      + SF3     + M        ---> SOF3      + M          1.00E-30
 O      + SF4     + M        ---> SOF4      + M          1.00E-30
*
 F      + SF      + M        ---> SF2       + M          4.00E-31
 F      + SF2     + M        ---> SF3       + M          2.00E-31
 F      + SF3     + M        ---> SF4       + M          4.00E-31
 F      + SF4     + M        ---> SF5       + M          2.00E-31
 F      + SF5     + M        ---> SF6       + M          3.60E-31
 O2     + SF2     + M        ---> SO2F2     + M          5.00E-29
*GUESSED RATE
*
*     Van Brunt, R.J., J.T. Herron,
*     IEEE Transactions on Electrical Insulation, 25, 75, 1990.
*
*30---------------------------------------------------------------------
* XXX. Radiative Electronic State De-excitation
*30---------------------------------------------------------------------
*
*31---------------------------------------------------------------------
* XXXI. Electronic State Photoexcitation
*31---------------------------------------------------------------------
*
*32---------------------------------------------------------------------
* XXXII. Collisional Electron State Quenching
*32---------------------------------------------------------------------
*
*33---------------------------------------------------------------------
* XXXIII. Radiative Vibrational-state De-excitation
*33---------------------------------------------------------------------
*
 SF6(1)-                     ---> SF6-                   1.00E+02
*
*33-------------------------------------------------------------------
*
```

```
 SF4(1)-                      ---> SF4-                    1.00E+02
*
*34-----------------------------------------------------------------
* XXXIV. Collisional Vibrational-State Quenching
*34-----------------------------------------------------------------
*
* SF6(1)-      + M            ---> SF6-     + M            5.40E-10
 SF6(1)-       + O(1S)        ---> SF6-     + O(1S)        5.40E-10
 SF6(1)-       + O            ---> SF6-     + O            5.40E-10
 SF6(1)-       + O(1D)        ---> SF6-     + O(1D)        5.40E-10
 SF6(1)-       + O2           ---> SF6-     + O2           5.40E-10
 SF6(1)-       + HE           ---> SF6-     + HE           5.39E-10
 SF6(1)-       + N2           ---> SF6-     + N2           5.39E-10
 SF6(1)-       + SF4          ---> SF6-     + SF4          5.40E-10
 SF6(1)-       + F            ---> SF6-     + F            5.40E-10
 SF6(1)-       + H2O          ---> SF6-     + H2O          5.40E-10
*
 SF6(1)-       + SF6          ---> SF6-     + SF6          1.90E-10
*
*  Odom, R.W., D.L. Smith and J.H. Futrell,
*  J. Phys. B, 8, 1349, 1975.
*
*34---------------------------------------------------------------
*
 SF4(1)-       + M            ---> SF4-     + M            5.00E-10
 SOF2(1)-      + M            ---> SOF2-    + M            5.00E-10
 SO2F2(1)-     + M            ---> SO2F2-   + M            5.00E-10
*
**35--------------------------------------------------------------
* XXXV. Collisional Vibrational Energy Exchange
*35--------------------------------------------------------------
```

APPENDIX B

DATABASE FOR AMBIENT IONOSPHERIC CHEMISTRY

```
*
*    Sections
*
*    2.  Photoionization
*    3.  Radiative Recombination
*    4.  Dissociative Recombination
*    5.  Ion-Ion Mutual Neutralization
*    8.  Photodetachment
*    13. Positive Ion Charge Transfer
*    14. Positive Ion Atom Interchange
*    26. Neutral Photodissociation
*    29. Neutral Rearrangement
*    30.  Radiative Electronic State De-excitation
*    31.  Electronic State Photoexcitation
*    32.  Collisional Electronic State Quenching
*    62.  Reverse reactions of 32.
*
* Format used is:
*
*  reactants   --->   products          rate
* R1 + R2 + R3 ---> P1 + P2 + P3         A  B  C
*
*  where k(T) = A*(T/300)**B*EXP(-1000*C/T)
*
*------------------------------------------------------------------
*
*                        AMBIENT CHEMISTRY
*                    simple ionospheric chemistry
*              for F1- and F-regions (altitude 200 to 1000km)
*           (down to 90km if photoionization is modified)
*
*-------------------------------------------------------------------
*                      1  PHOTOIONIZATION
*1------------------------------------------------------------------
*
*    Torr, M.R., D.G. Torr, R.A. Ong, and J.E. Hinteregger,
*      Ionization frequencies for major thermospheric constituents as a
*      function of solar cycle 21,
*      Geophys. Res. Lett. 6, 771, 1979.
```

```
*
*  near solar minimum ionization frequencies obtained from
*  Day 113 1974
*
 O                           ---> O+        + e         1.18E-07 |DAY
 O                           ---> O(2D)+    + e         9.02E-08 |DAY
 O                           ---> O(2P)+    + e         5.28E-08 |DAY
*
 O2                          ---> O2+       + e         4.97E-07 |DAY
*
 N2                          ---> N2+       + e         3.60E-07 |DAY
*
*  near solar maximum ionization frequencies obtained from
*  Day 50 1979
*
* O                           ---> O+        + e        4.17E-07 |DAY
* O                           ---> O(2D)+    + e        3.25E-08 |DAY
* O                           ---> O(2P)+    + e        1.94E-08 |DAY
*
* O2                          ---> O2+       + e        1.73E-06 |DAY
*
* N2                          ---> N2+       + e        1.28E-06 |DAY
*
*1-----------------------------------------------------------------------
*
* nighttime photoionization levels determined from
*
*      Strobel, D.F., C.G. Opal and R.R. Meier,
*      Photoionization rates in the nighttime E and F region ionosphere
*      Planet. Space Sci., 28, 1027-1033, 1980.
*
*  The values below were obtained from a model which incorporates
*  the strobel ionization sources.
*
*    Rasmussen, C.E., R.W. Schunk, and V.B.Wickar,
*    A photochemical equilibrium model for ionospheric conductivity,
*    J. Geophy. Res., 93, 9831-9840, 1988.
*
*  O+ branching given as 43% O+    , 29% O(2D)+, 28% O(2P)+ in:
*
*      Torr, M.R., D.G. Torr, R.A. Ong, and J.E. Hinteregger,
*      Ionization frequencies for major thermospheric constituents as a
*      function of solar cycle 21,
```

```
*       Geophys. Res. Lett. 6, 771, 1979.
*
 O                           ---> O+        + e          8.89E-12
 O                           ---> O(2D)+    + e          6.67E-12
 O                           ---> O(2P)+    + e          6.44E-12
*
 O2                          ---> O2+       + e          1.30E-10
*
 N2                          ---> N2+       + e          3.00E-11
*
*-----------------------------------------------------------------------
*                       2   RADIATIVE RECOMBINATION
*2----------------------------------------------------------------------
*
 N+           + e            ---> N                      1.00E-18
 O+           + e            ---> O                      4.00E-18 -0.70
*
*-----------------------------------------------------------------------
*                       4   DISSOCIATIVE RECOMBINATION
*4----------------------------------------------------------------------
*
*     Queffelec J.L., et al., Planet. Space Sci., 33, 263, 1985.
*
 N2+          + e            ---> N         + N          1.00E-08 -0.40
 N2+          + e            ---> N(2D)     + N(2D)      1.80E-07 -0.40
*
*  Branching of one given by:
*
*     Torr, M.R., and D.G. Torr,
*     The role of metastable species in the thermosphere
*     Rev. Geophys. Space Phys., 20, 91-144, 1982.
*
*  Also see
*
*     Mehr, F.J. and M.A. Biondi,
*     Electron temperature dependence of recombination of O2+ and N2+
*     ions with electrons,
*     Phys. Rev., 181, 264, 1969.
*
*     Frederick, J.E., and D.W. Rusch,
*     On the chemistry of metastable atomic nitrogen in the
*     F region deduced from simultaneous satellite measurement
*     of the 5200A airglow and atmospheric composition,
```

```
*     J. Geophys. Res. 82, 3509, 1977.
*
*  N(2P) is suggested to be a product by:
*     Zipf, E.C., P.S., Espy, and C.F. Boyle,
*     The excitation and collisional deactivation of metastable
*     N(2P) atoms in auroras,
*     J. Geophys. Res. 85, 687, 1980.
*
*------------------------------------------------------------------------
*
*     Alge, E., N.G. Adams and D. Smith,
*     Measurements of the dissociative recombination coefficients of
*     O2+, NO+, and NH4+ in the temperature range of 200-600 K
*     J. Phys. B, 16, 1433, 1983.
*           k = 4.00e-07 -0.9
*
*  This is near the 4.3e-7 -1. given by
*
*     Torr, M.R. and D.G. Torr,
*     Recombination of NO+ in the mid-latitude
*     trough and the polar ionization hole,
*       J. Geophys. Res., 84, 4316, 1979.
*
*  Branching founding in:
*
*     Kley, D., G.M. Lawrence and E. J. Stone,
*     The yield of N(2D) atoms in the dissociative recombination
*     of NO+,
*     J. Chem. Phys., 66, 4157, 1977.
*
 NO+          + e            ---> N         + O           1.00E-07 -0.9
 NO+          + e            ---> N(2D)     + O           3.00E-07 -0.9
*
*------------------------------------------------------------------------
*
*  Rates by measurement found in
*     Alge, E., N.G. Adams and D. Smith,
*     Measurements of the dissociative recombination coefficients of
*     O2+, NO+, and NH4+ in the temperature range of 200-600 K
*     J. Phys. B, 16, 1433, 1983.
*           k = 1.95e-07 -0.7
*
*  Also by
```

```
*     Zipf, E.C., J. Geophys. Res., 85, 4232, 1980.
*           k = 2.00e-7 -0.7
*
*  With branching from:
*     Link, R., J.C. McConnell, and G.G. Shepherd,
*     A self-consistent evaluation of the
*     rate constants for the production of the OI 6300 A airglow,
*     Planet. Space Sci., 29, 589, 1981.
*            to O(1D) b = 1.1
*            to O(1S) b = 0.1
*
O2+        + e            ---> O(1S)     + O(1D)        0.20E-07 -0.7
O2+        + e            ---> O         + O(1D)        1.55E-07 -0.7
O2+        + e            ---> O(1D)     + O(1D)        0.20E-07 -0.7
*
*------------------------------------------------------------------------
*                       5    MUTUAL NEUTRALIZATION
*5-----------------------------------------------------------------------
*
O+            + O-           ---> O         + O         2.37E-07  -0.5
O+            + O-           ---> O         + O(1D)     0.33E-07  -0.5
NO+           + O-           ---> NO        + O         6.00E-08  -0.5
O2+           + O-           ---> O2        + O         6.00E-08  -0.5
*
*------------------------------------------------------------------------
*                       7   RADIATIVE ATTACHMENT
*7-----------------------------------------------------------------------
*
O             + e            ---> O-                    1.30E-15
*
*------------------------------------------------------------------------
*                       8   PHOTODETACHMENT
*8-----------------------------------------------------------------------
*
O-                           ---> O         + e         1.15E+00 |DAY
O-                           ---> O(1D)     + e         6.00E-02 |DAY
*
*------------------------------------------------------------------------
*                       12   ASSOCIATIVE DETACHMENT
*12----------------------------------------------------------------------
*
O-            + O            ---> O2        + e         2.00E-10
*
```

```
*-----------------------------------------------------------------------
*                        13   POSITIVE ION CHARGE TRANSFER
*13---------------------------------------------------------------------
*
 N+            + O             ---> O+        + N          2.00E-12
*
*     Scheibe, M.
*     "Sensitivity of Satellite Communications to the
*     Uncertainties in Selected Chemical Reaction Rate Coefficients",
*     MRC-R-458, May 1979.
*
*13---------------------------------------------------------------------
*
 N+            + NO            ---> NO+       + N         3.00E-10  -0.27
 N+            + NO            ---> NO+       + N(2D)     1.93E-10  -0.27
 N+            + NO            ---> NO+       + N(2P)     1.07E-10  -0.27
*
*  ARCTIC-9
*     Fahey, D.W., I. Dotan, F.C. Fehenfeld, and D.L. Albritton,
*     J. Chem. Phys. 74, 3320 (1981).
*  plus estimate regarding products.
*
*13---------------------------------------------------------------------
*
 N+            + O2            ---> O2+       + N          1.5E-10
 N+            + O2            ---> O2+       + N(2D)      1.5E-10
*
*  ARCTIC-8
*     Howorka, F., I.Dotan, F.C. Fehsenfeld, and D.L. Albritton,
*     J. Chem. Phys. 73, 758 (1980)
*
*  ARCTIC-2
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*  ARCTIC-37
*     Rees, M.H.,
*     Planet. Space Sci. 32, 373 (1984)
*
*  ARCTIC-38
*     Smith, A.M. et. al.,
*     Chem. Phys. Lett. 94, 398 (1983)
*
*13---------------------------------------------------------------------
```

```
*
*
 N(1D)+        + O            ---> O+         + N          1.00E-12
 N(1D)+        + O            ---> O+         + N(2D)      1.00E-12
*
*  ARCTIC-10
*     An estimate, maybe increased based on A. Dalgarno,
*     AE Reaction Rate Data, Air Force Geophysics Laboratory,
*       AFGL-TR_79-0067, March, 1979 (U).
*
*13-------------------------------------------------------------------
*
 N(1D)+        + NO           ---> NO+       + N          4.29E-11  -0.27
 N(1D)+        + NO           ---> NO+       + N(2D)      2.79E-10  -0.27
 N(1D)+        + NO           ---> NO+       + N(2P)      2.79E-10  -0.27
*
*  ARCTIC-13 reference
*  ARCTIC-9 plus estimate regarding
*  effect of metastable reactant,and the effect of spin-conservation
*  rules on ratio of products.
*
*  ARCTIC-9
*     Fahey, D.W., I. Dotan, F.C. Fehenfeld, and D.L. Albritton,
*     J. Chem  Phys. 74, 3320 (1981),
*  plus estimate regarding products.
*
*13-------------------------------------------------------------------
*
*
 N(1D)+        + O2           ---> O2+       + N           1.2E-10
 N(1D)+        + O2           ---> O2+       + N(2D)       1.2E-10
 N(1D)+        + O2           ---> O2+       + N(2P)       1.0E-10
*
*  ARCTIC-11 reference
*  ARCTIC-8 plus estimate regarding effect of metastable reactant.
*
*  ARCTIC-8
*     Howorka, F., I.Dotan, F.C. Fehsenfeld, and D.L. Albritton,
*     J. Chem. Phys. 73, 758 (1980).
*
*  DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*13-------------------------------------------------------------------
```

```
*
 N(1S)+       + O            ---> O+        + N          1.0E-12
 N(1S)+       + O            ---> O+        + N(2D)      1.0E-12
*
*  ARCTIC-10 An estimate, maybe increased based on
*     A. Dalgarno,
*     AE Reaction Rate Data, Air Force Geophysics Laboratory,
*     AFGL-TR-79-0067, March, 1979 (U).
*
*13-----------------------------------------------------------------------
*
 N(1S)+       + N2           ---> N2+       + N(2D)      1.0E-10
*
*  ARCTIC-14 An estimate
*
*13-----------------------------------------------------------------------
*
 N(1S)+       + NO           ---> NO+       + N      4.29E-11   -0.27
 N(1S)+       + NO           ---> NO+       + N(2D)  2.79E-10   -0.27
 N(1S)+       + NO           ---> NO+       + N(2P)  2.79E-10   -0.27
*
*  ARCTIC-13 reference
*  ARCTIC-9 plus estimate regarding effect of metastable reactant,
*  and the effect of spin-conservation rules on ratio of products.
*
*  ARCTIC-9
*     Fahey, D.W., I. Dotan, F.C. Fehenfeld, and D.L. Albritton,
*     J. Chem. Phys. 74, 3320 (1981).
*  plus estimate regarding products.
*
*13-----------------------------------------------------------------------
*
 N(1S)+       + O2           ---> O2+        + N         1.20E-10
 N(1S)+       + O2           ---> O2+        + N(2D)     1.20E-10
 N(1S)+       + O2           ---> O2+        + N(2P)     1.00E-10
*
*  ARCTIC-11 reference
*  ARCTIC-8 plus estimate regarding effect of metastable reactant.
*
*  ARCTIC-8
*     Howorka, F., I.Dotan, F.C. Fehsenfeld, and D.L. Albritton,
*     J. Chem. Phys. 73, 758 (1980).
*
```

```
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*13H--------------------------------------------------------------------
*
 O+           + N            ---> N+        + O     8.23E-12 0.0  9.8
*
*  Reverse reaction calculated by detailed balancing.
*  Keq = 0.243  0.0  -9.8   (JANAF and F. Gilmore)
*
*13---------------------------------------------------------------------
*
 O+           + N(2D)        ---> N+        + O          1.30E-10
*
*13---------------------------------------------------------------------
*
 O+           + NO           ---> NO+       + O          8.00E-13 -0.20
*
*   Based on Data presented in
*     DNA Reaction Rate Handbook Chapter 18A
*
*13---------------------------------------------------------------------
*
*
 O+           + O2           ---> O2+       + O          2.00E-11 -0.70
*
*  Based on Chen, A., R. Johnsen and M. A. Biondi,
*           Measurements of the O+ + N2 and O+ + O2 reaction
*       rates form 300 to 900K,
*     J.Chem. Phys., 69, 2688, 1978.
*
*  Based on data found in
*     "Sensitivity of Satellite Communications to the Uncertainties
*     in Selected Chemical Reaction Rate Coefficients",
*     MRC-R-458, May 1979.
*
*13---------------------------------------------------------------------
*
*
 O(2D)+       + N2           ---> N2+       + O          8.00E-10
*
*     Johnsen R., and M. Biondi,
*     Laboratory measurements of the O+(2D) + N2 and
*     O+(2D) + O2 reaction rate coefficients and their
```

```
*     ionospheric implications
*     Geophys. Res. Lett., 7 401, 1980.
*
*     Johnsen R., and M. Biondi,
*     J. Chem. Phys. 73, 190 (1980);
*
*     B. R. Rowe, D. W. Fahey, F. C. Fehsenfeld, and D. L. Albritton,
*     Rate constants for the reactions of metastable O++ ions
*     with N2 and O2 at collision energies 0.04 to 0.2 eV and
*     the mobilities of these ions at 300K
*     J. Chem. Phys. 73, 194 (1980)
*
*     Oppenheimer, M.A., A. Dalgarno, and H.C. Brinton,
*     Ion chemistry of N2+ and the solar ultraviolet flux in the
*     thermosphere,
*     J. Geophys. Res., 81, 3762, 1976.
*
*     Torr, D.G., and M.R. Torr,
*     Determination of the thermal rate coefficient,
*     products and branching ratios for the reaction
*     of O+(2D) with N2,
*     J. Geophys. Res., 85, 783, 1980.
*
*13-----------------------------------------------------------------------
*
 O(2D)+       + NO          ---> NO+       + O          1.00E-12
 O(2D)+       + NO          ---> NO+       + O(1D)      1.00E-12
 O(2D)+       + NO          ---> NO+       + O(1S)      1.00E-12
*
*  ARCTIC-5 same reference as  ARCTIC-2 plus estimate regarding
*  products and effect of metastable reactant.
*
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*13-----------------------------------------------------------------------
*
 O(2D)+       + O2          ---> O2+       + O          4.00E-10
 O(2D)+       + O2          ---> O2+       + O(1D)      2.00E-10
 O(2D)+       + O2          ---> O2+       + O(1S)      1.00E-10
*
*     Johnsen R., and M. Biondi,
*     Laboratory measurements of the O+(2D) + N2 and
*     O+(2D) + O2 reaction rate coefficients and their
```

```
*     ionospheric implications
*     Geophys. Res. Lett., 7 401, 1980.
*
*     Johnsen R., and M. Biondi,
*     J. Chem. Phys. 73, 190 (1980);
*
*     B. R. Rowe, D. W. Fahey, F. C. Fehsenfeld, and D. L. Albritton,
*     Rate constants for the reactions of metastable O++ ions
*     with N2 and O2 at collision energies 0.04 to 0.2 eV and
*     the mobilities of these ions at 300K
*     J. Chem. Phys. 73, 194 (1980)
*
*13-------------------------------------------------------------------
*
 O(2P)+       + O            ---> O+         + O          5.20E-11
*
*     Rusch, D.W., D.G. Torr, P.B. Hays, and J.C.G. Walker,
*     The OII (7319-7330 A) dayglow,
*     J. Geophys. Phys., 82, 719, 1977.
*
*     Torr, M.R., and D.G. Torr,
*     The role of metastable species in the thermosphere,
*     Rev. Geophys. Space Phys., 20, 91-144, 1982.
*  suggests that the rate should be 15 to 30 percent larger
*
*13-------------------------------------------------------------------
*
 O(2P)+       + N2           ---> N2+        + O          4.0E-10
 O(2P)+       + N2           ---> N2+        + O(1D)      4.0E-10
*
*  ARCTIC-7 same reference as  ARCTIC-3 plus estimate regarding
*  products and effect of metastable reactant.
*
*  ARCTIC-3
*     Johnsen R., and M. Biondi,
*     J. Chem. Phys. 73, 190 (1980);
*
*     B. R. Rowe, D. W. Fahey, F. C. Fehsenfeld, and D. L. Albritton,
*     Rate constants for the reactions of metastable O++ ions
*     with N2 and O2 at collision energies 0.04 to 0.2 eV and
*     the mobilities of these ions at 300K
*     J. Chem. Phys. 73, 194 (1980)
*
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*     Rusch, D.W., D.G. Torr, P.B. Hays, and J.C.G. Walker,
*     The OII (7319-7330 A) dayglow,
*     J. Geophys. Fes., 82, 719, 1977.
*
*     Torr, M.R., and D.G. Torr,
*     The role of metastable species in the thermosphere,
*     Rev. Geophys. Space Phys., 20, 91-144, 1982.
*  suggests that the rate should be 15 to 30 percent larger
*
*13-----------------------------------------------------------------
*
 O(2P)+        + NO           ---> NO+       + O          1.00E-12
 O(2P)+        + NO           ---> NO+       + O(1D)      1.00E-12
 O(2P)+        + NO           ---> NO+       + O(1S)      1.00E-12
*
*  ARCTIC-5 same reference as  ARCTIC-2 plus estimate regarding
*  products and effect of metastable reactant.
*
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*13-----------------------------------------------------------------
*
 O(2P)+        + O2           ---> O2+       + O          2.50E-10
 O(2P)+        + O2           ---> O2+       + O(1D)      2.50E-10
 O(2P)+        + O2           ---> O2+       + O(1S)      2.50E-10
*
*  ARCTIC-7 same reference as  ARCTIC-3 plus estimate regarding
*  products and effect of metastable reactant.
*
*  ARCTIC-3
*     Johnsen R., and M. Biondi, J. Chem. Phys. 73, 190 (1980)
*
*     B. R. Rowe, D. W. Fahey, F. C. Fehsenfeld, and D. L. Albritton,
*     J. Chem. Phys. 73, 194 (1980).
*
*13-----------------------------------------------------------------
*
 N2+           + O            ---> O+        + N2         1.00E-11 -0.23
 N2+           + NO           ---> NO+       + N2(A)      3.30E-10
*
*  The above reaction rate data are found in the
*       DNA Reaction Rate Handbook Chapter 18A.
*
```

```
*13-------------------------------------------------------------------
*
 N2+          + O2          ---> O2+       + N2          5.00E-11 -0.80
*
*    Dunkin et al., J. Chem. Phys. 49, 1365 (1968)
*
*    Biondi et al., J. Chem. Phys. 52, 5080 (1970)
*
*13-------------------------------------------------------------------
*
*
 O2+          + N(2D)       ---> O2        + N+          2.50E-10
 O2+          + NO          ---> NO+       + O2          4.50E-10
*
*  Based on data presented in the
*      DNA Reaction Rate Handbook Chapters 18A and 24
*
*--------------------------------------------------------------------
*                       14    POSITIVE ION ATOM INTERCHANGE
*14-------------------------------------------------------------------
*
*
 N+           + O2          ---> O+        + NO          4.00E-11
 N+           + O2          ---> NO+       + O           2.45E-11
 N+           + O2          ---> NO+       + O(1D)       2.00E-10
 N+           + O2          ---> NO+       + O(1S)       2.20E-10
*
*  The reaction rate data for these reactions are based on informed
*  estimates found in
*     DNA Reaction Rate Handbook
*       Chapters 18A and 24
*
*  The third reaction is referenced by
*     Rees, M. H. et al.,
*     Planet. Space Sci., 32, 373, (1984).
*
*  The fourth is referenced by Smith, A. M.,
*               Chem. Phys. Lett., 94, 398 (1983).
*
*14-------------------------------------------------------------------
*
 N(1D)+        + O2          ---> NO+       + O          1.80E-10
 N(1D)+        + O2          ---> NO+       + O(1D)      1.00E-11
```

```
*
*  ARCTIC-12 reference  ARCTIC-8 plus estimate regarding effect of
*  metastable reactant,
*  and the effect of spin-conservation rules on ratio of products.
*
*  ARCTIC-8
*     Howorka, F., I.Dotan, F.C. Fehsenfeld, and D.L. Albritton,
*     J. Chem. Phys. 73, 758 (1980),
*
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*14-------------------------------------------------------------------
*
 N(1S)+        + O2           ---> NO+     + O        1.80E-10
 N(1S)+        + O2           ---> NO+     + O(1D)    1.00E-11
 N(1S)+        + O2           ---> NO+     + O(1S)    1.00E-11
*
*  ARCTIC-12 reference  ARCTIC-8 plus estimate regarding effect of
*   metastable reactant,
*  and the effect of spin-conservation rules on ratio of products.
*
*  ARCTIC-8
*     Howorka, F., I.Dotan, F.C. Fehsenfeld, and D.L. Albritton,
*     J. Chem. Phys. 73, 758 (1980),
*
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*14-------------------------------------------------------------------
*
 O+           + N2           ---> NO+       + N          1.20E-12 -1.00
*
*  The reaction rate data for these reactions are based on informed
*  estimates found in the
*     DNA Reaction Rate Handbook Chapters 18A and 24
*
*14-------------------------------------------------------------------
*
 N2+          + O            ---> NO+       + N          1.45E-11 -0.46
*
*  The reaction rate data for this reaction is based on informed
*  estimates found in the
*     DNA Reaction Rate Handbook Chapters 18A and 24
*
```

```
 N2+          + O           ---> NO+       + N(2D)      1.40E-10 -0.44
*
*     Frederick, J.E. and D.W.Rusch,
*     On the chemistry of metastable atomic nitrogen in the
*     F region deduced from simultaneous satellite measurement
*     of the 5200A airglow and atmospheric composition,
*     J. Geophys. Res. 82, 3509, 1977.
*
*     McFarland et al.,
*     Energy dependence and branching ratio of the N2+ + O reaction,
*     J. Geophys. Res., 79, 2925, 1974.
*
*14---------------------------------------------------------------------
*
 NO+          + N           ---> O+        + N2     9.30E-11  0.0 5.53
*
*14---------------------------------------------------------------------
*
 O2+          + N           ---> NO+       + O          1.20E-10
 O2+          + N2          ---> NO+       + NO         1.00E-16
*
*  The reaction rate data for these reactions are based on informed
*  estimates found in the
*     DNA Reaction Rate Handbook chapters 18A and 24
*
*----------------------------------------------------------------------
*                       26    NEUTRAL PHOTODISSOCIATION
*26--------------------------------------------------------------------
*
 NO                         ---> N         + O          5.30E-06 |DAY
*
*     Franklin Niles, private communication
*
*26--------------------------------------------------------------------
*
* solar min.
* O2                         ---> O         + O(1D)      1.50E-06 |DAY
* solar max.
 O2                         ---> O         + O(1D)      2.80E-06 |DAY
*
*     Torr, M.R. and D.G. Torr,
*     The role of metastable species in the thermosphere,
*     Rev. Geophys. Space Phys., 20, 91-144, 1982.
```

```
*
*     Torr, M.R., D.G. Torr, and H.E. Hinteregger,
*     Solar flux variability in the Schumann-Runge continuum
*     as a function of solar cycle 21,
*     J. Geophys. Res., 85, 6063, 1980.
*
*-----------------------------------------------------------------------
*                       29   NEUTRAL REARRANGEMENT
*29---------------------------------------------------------------------
*
 N            + NO           ---> O         + N2         3.60E-11
*
*  CODATA(1984) suggests a value of 3.1E-11 over the range 200-400K
*
*  Based on
*     Lee, J. H., Michael, J. V., Payne, W. A., and Stief, L. J.,
*     J. Chem. Phys., 69, 3069 (1978).
*
*  The vibrational distribution is an assumption.
*
*29---------------------------------------------------------------------
*
 N            + O2           ---> O         + NO       4.40E-12 0.0 3.22
*
*  NASA Panel for Data Evaluation, Chemical Kinetics
*  and Photochemical Data
*  for Use in Stratospheric Modeling, Evaluation Number 6, W. B. Demore,
*  M. J. Molina, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo
*  C. J. Howard, and A. R. Ravishankara, JPL Publ 83-62 (1983)
*
*  CODATA Task Group on Gas Phase Chemical Kinetics,
*     D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, J. Troe,
*     and R. T. Watson,
*     J. Phys. Chem, Ref. Data 9 (2), 295-471. (1980)
*
*  For the O2(1) the energy of the v = 1 level (0.19 eV) was  subtracted
*  the exponential factor.
*
*29---------------------------------------------------------------------
*
N(2D)         + NO           ---> N2        + O          3.00E-11
N(2D)         + NO           ---> N2        + O(1D)      2.00E-11
N(2D)         + NO           ---> N2        + O(1S)      1.00E-11
```

```
*
*  ARCTIC-15 Reference  ARCTIC-2, Plus
*     T.G. Slanger and G. Black, J. Chem. Phys. 60, 468, 1974.
*
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*29--------------------------------------------------------------------
*
 N(2D)        + O2            ---> O          + NO          1.60E-12  0.5
*
*  Forest Gilmore, private communication  suggests
*  The value used by ARCHON
*
*     Rusch, D.W., et al.,
*     Geophys. Res. Lett. 5, 1043, 1978.
*  reports  1.60E-12   0.5
*
*  also see
*     Torr, D.G., P.G. Richards, M.R. Torr, and V.J. Abreu,
*     Further qualification of the sources and sinks
*     of thermospheric O(1D) atoms,
*     Planet. Space Sci., 29, 595, 1981.
*
*  others report 6e-12 without branching
*
*     Lin, C.L., and F. Kaufman,
*     Reactions of metastable nitrogen atoms,
*     J. Chem. Phys., 55, 3760, 1977.
*
*     Frederich and Rusch,
*     On the chemistry of metastable atomic nitrogen in the
*     F region deduced from simultaneous satellite measurement
*     of the 5200A airglow and atmospheric composition,
*     J. Geophys. Res., 82, 3509, 1977.
*
*
 N(2D)        + O2            ---> O(1D)      + NO          3.70E-12  0.5
*
*     Rusch, D.W., et al., Geophys. Res. Lett. 5, 1043, 1978.
*  reports 4.85E-12
*  also see
*     Torr, D.G., P.G. Richards, M.R. Torr, and V.J. Abreu,
*     Further qualification of the sources and sinks
```

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*     of thermospheric O(1D) atoms,
*     Planet. Space Sci., 29, 595, 1981a.
*
*  Forest Gilmore, private communication suggests
*  the value used by ARCHON
*
*29---------------------------------------------------------------------
*
 N(2P)        + NO           ---> O         + N2         3.00E-11
 N(2P)        + NO           ---> O(1D)     + N2         2.00E-11
 N(2P)        + NO           ---> O(1S)     + N2         1.00E-11
*
*  ARCTIC-17 Reference  ARCTIC-15 plus estimate regarding products
*  and effect of metastable reactant.
*  ARCTIC-15 Reference  ARCTIC-2, Plus
*     T.G. Slanger and G. Black, J. Chem. Phys. 60, 468, 1974.
*
*     DNA Reaction Rate Handbook, DNA 1948H, 1972.
*
*29---------------------------------------------------------------------
*
 N(2P)        + O2           ---> O(1D)     + NO         3.50E-12   0.5
*
*  The above two reactions are based on Forest Gilmore's private
*  communication and the rates for the two vibrational states of
*  O2 shown is an estimate.
*
*  Suggested rate of 2E-12 by:
*     Young, R.A. and O.J. Dunn,
*     The excitation and quenching of N(2P),
*     J. Chem. Phys., 63, 1150, 1975.
*
*29---------------------------------------------------------------------
*
 O            + N2(A)        ---> N(2D)     + NO         1.00E-13
*
*  An estimate.  Private communication M. Scheibe.
*
*29---------------------------------------------------------------------
*
 O(1S)        + NO           ---> O2        + N(2D)      2.00E-10
*
*  ARCTIC-14 An estimate
```

```
*
*29---------------------------------------------------------------------
*
 O(1S)        + O2(1D)       ---> O         + O2         1.10E-10
*
*  Estimate.
*
*-----------------------------------------------------------------------
*                       30   RADIATIVE ELECTRONIC STATE DE-EXCITATION
*30---------------------------------------------------------------------
*
 N(2D)                       ---> N                      1.28E-05
*
*  Producing 5200A
*     Garstang, R.H.,
*     Transition probabilities in auroral lines,
*     in Airglow and the Aurora,
*     Ed. by E. B. Armstrong and A. Dalgarno,
*     pp. 324-327, Pergamon, New York, 1956.
*
 N(2P)                       ---> N                      5.40e-03
*
*  producing 3466A
*     Chamberlain, J.W.,
*     Physics of the Aurora and Airglow,
*     p579, Academic, New York, 1961.
*
 N(2P)                       ---> N(2D)                  7.90e-02
*
*  producing 10400A
*     Chamberlain, J.W.,
*     Physics of the Aurora and Airglow,
*     p579, Academic, New York, 1961.
*
*30---------------------------------------------------------------------
*
 O(1D)                       ---> O                      6.80E-03
*
*     Kernahan, J.H. and H.L. Pang,
*     Experimental determination of absolute A coefficients for
*     "forbidden" atomic oxygen lines,
*     Can. J. Phys. 53, 455 (1975)
*
```

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*30----------------------------------------------------------------------
*
 O(1S)                        ---> O(1D)                  1.06E+00
*
*     Kernahan, J.H. and H.L. Pang,
*     Experimental determination of absolute A coefficients for
*     "forbidden" atomic oxygen lines,
*     Can. J. Phys. 53, 455 (1975)
*
*30----------------------------------------------------------------------
*
 O(1S)                        ---> O                      4.50E-02
*
*     Kernahan, J.H. and H.L. Pang,
*     Experimental determination of absolute A coefficients for
*     "forbidden" atomic oxygen lines,
*     Can. J. Phys. 53, 455 (1975)
*
*30----------------------------------------------------------------------
*
 O(2D)+                       ---> O+                     7.72E-05
*
*  Radiates 3914A at 7.72e-05 s-1
*
*     Garstang, R.N.,
*     Transition probabilities in auroral lines,
*     in The Airglow and the Aurora,
*     ed. E. B. Armstrong and A Dalgarno,
*     pp. 324-327, Pergamon, New York, 1956.
*
*30----------------------------------------------------------------------
*
 O(2P)+                       ---> O+                     4.77E-02
*
*  Radiates 2470A at .219x.218 s-1
*
 O(2P)+                       ---> O(2D)+                 1.71E-01
*
*  Radiates 7320-7330A at .781x.218 s-1
*
*     Seaton, M.J. and Osterbrock, D.E.,
*     Relative OII intensities in gaseous nebulae,
*     Astrophys. J., 125, 66, 1957.
```

```
*
*30----------------------------------------------------------------------
*
 N2(A)                       ---> N2                     1.10E+00
*
*  The DNA Reaction Rate Handbook with the product estimated.
*
*     Zipf, E. C.
*     Can. J. Chem. 47, 1863 (1969)
*
*     Shemansky, D.
*     J. Chem. Phys. 51, 689 (1969) and 5487 (1969)
*
*30----------------------------------------------------------------------
*
 O2(1S)                      ---> O2                     8.30E-02
*
*     Nicholls, R.,
*     Ann. Geophys. 20, 144 (1964)
*
*     Childs, W., and R. Mecke,
*     Zeits. Phys. 68, 344 (1931)
*
*     Miller, J.H., R.W. Boese, and L.P. Giver,
*     J. Quant. Spectry. Rad. Trans. 9, 1507 (1969)
*
*------------------------------------------------------------------------
*                       31    ELECTRONIC STATE PHOTOEXCITATION
*31----------------------------------------------------------------------
*
 O2                          ---> O2(1D)                 1.00E-10  |DAY
 O2                          ---> O2(1S)                 7.30E-09  |DAY
*
*     Franklin Niles, private communication
*
*------------------------------------------------------------------------
*                       32   COLLISIONAL ELECTRONIC STATE QUENCHING
*32----------------------------------------------------------------------
*
*------------------------------------------------------------------------
*                       32   COLLISIONAL ELECTRONIC STATE QUENCHING
*32----------------------------------------------------------------------
*
```

```
 N(2D)        + O            ---> N         + O      1.00E-11  0.  0.50
*
*  The review article reference for this reaction is
*     Schofield, J. Phys. Chem. Ref. Data, 8, 723 (1979)
*
*  The data presented here is different than originally presented as
*     4.00E-12  0.0  .25
*
*32---------------------------------------------------------------------
*
 N(2D)        + N2           ---> N         + N2     9.40E-14  0. -0.51
*
*     Schofield, J. Phys. Chem. Ref. Data, 8, 723 (1979)
*  With the products estimated.
*
*32---------------------------------------------------------------------
*
 N(2D)        + O2           ---> N         + O2         5.30E-12
*
*     no reference
*
*32---------------------------------------------------------------------
*
 N(2D)        + e            ---> N         + e          2.40E-10  0.7
*
*  This reaction a reverse reaction, the forward found in category 62.
*  The rate data is formed by detailed balancing with a
*                 Keq = 2.50  0.0  -27.67.
*
*  The reference for the forward reaction is:
*     Slinker and Ali, NRL Memorandum Report 4756 (1982)
*
*  Also see
*     Frederick, J.E., and D.W. Rusch,
*     On the chemistry of metastable atomic nitrogen in the
*     F region deduced from simultaneous satellite measurement
*     of the 5200A airglow and atmospheric composition,
*     J. Geophys. Res. 82, 3509, 1977.
*  They suggest 3.6-6.5E-10 0.5
*
*32---------------------------------------------------------------------
*
 N(2P)        + O            ---> N         + O          1.00E-11
```

```
*
*  ARCTIC-14'
*     Young, R.A. and O.J. Dunn,
*     The excitation and quenching of N(2P),
*     J. Chem. Phys., 63, 1150, 1975.
*
*     Zipf, E.C., P.S. Espy, and C. F. Boyle,
*     The excitation and collisional deactivation of
*     metastable N(2P) atoms in auroras,
*     J. Geophys. Res., 85, 678, 1980.
*
*32--------------------------------------------------------------------
*
 N(2P)        + O            ---> N(2D)    + O          5.00E-12
*
*     Schofield, J. Phys. Chem. Ref. Data, 8, 723 (1979)
*
*32--------------------------------------------------------------------
*
 N(2P)        + NO           ---> N         + NO        2.80E-11
*
*  ARCTIC-14'
*     Young, R.A. and O.J. Dunn,
*     The excitation and quenching of N(2P),
*     J. Chem. Phys., 63, 1150, 1975.
*
*32--------------------------------------------------------------------
*
 N(2P)        + e            ---> N        + e          5.00E-10  0.50
*
*  This reaction is a reverse reaction, the forward found in category 62
*  The rate data is formed by detailed balancing with a
*  Keq = 1.50  0.0  -41.49.
*  The reference for the forward reaction is:
*     Slinker and Ali, NRL Memorandum Report 4756 (1982)
*
*32--------------------------------------------------------------------
*
 N(2P)        + e            ---> N(2D)    + e          2.30E-09   0.50
*
*  This reaction is a reverse reaction found in category 62.
*  The rate data is formed by detailed balancing with a
*  Keq = 0.60  0.0  -13.82
```

```
*  The reference for the forward reaction is:
*     Slinker and Ali, NRL Memorandum Report 4756 (1982)
*
*32---------------------------------------------------------------------
*
 N(1D)+       + e            ---> N+        + e          2.97E-7  -0.5
 N(1S)+       + e            ---> N+        + e          1.96E-7  -0.5
 N(1S)+       + e            ---> N(1D)+    + e          2.04E-7  -0.5
*
*  ARCTIC-32
*     Ali, A.W., Electron Impact Rate Coefficients for the Low Lying
*     Metastable States of O, O+, N, and N+,
*     Navel Research Laboratory, NRL
*
*32---------------------------------------------------------------------
*
 O(1D)        + O            ---> O         + O          8.00E-12
*
*32---------------------------------------------------------------------
*
 O(1D)        + N2           ---> O        + N2    2.00E-11 0.0 -0.1118
*
*     Forrest Gilmore, April 9, 1985 letter.
*
*32---------------------------------------------------------------------
*
 O(1D)        + NO           ---> O         + NO         4.20E-11
*
*     Heidner, R. F. III, and Hussain, D.,
*     "Electronically Excited Oxygen Atoms, O(1D).
*     A Time-Resolved Study of the Collisional Quenching by the
*     Gases H2, D2, NO, N2O, CH4, and C3O2 Using Atomic Absorption
*     Spectroscopy in the Vacuum Ultraviolet,"
*     Int. J. Chem. Kinet. 5, 819-831 (1973)
*
*     Hampson, R. F.,
*     "Chemical Kinetic and Photochemical Data Sheets for
*     Atmospheric Reactions,"
*     National Bureau of Standards, Washington, D. C., April 1980
*
*32---------------------------------------------------------------------
*
 O(1D)        + O2           ---> O2        + O  2.90E-11  0.0 -0.0675
```

```
*
* Data sheet for this reaction appears in earlier evaluation,
*    J. Phys. Chem. Ref. Data 11, 327 (1982)
*
*    Amimoto, et al., J. Chem. Phys. 71, 3640 (1979)
* reports an overall rate of [4.2+-0.2]E-11 at 295K
*
*    Brock et al., at NATO Advanced Study Institute on
*      Atmospheric Ozone,
*    Portugal (1979).
*
* Also see
*    Moortgat's Review FAA-EE-20 (1980)
*    reports [4.0+-0.6]E-11 at 298
*
*    Lee, L.C. et al., J. Chem. Phys, 69, 4053 (1978)
* reports a branching ratio for the products above to be 0.77+-0.2
*
* The recommended temperature range is given to be 200 to 350 Kelvin.
* Reliability is delta log(k) = +-0.05 at 298K and
* delta (E/R) = +- 100K
*
*32---------------------------------------------------------------------
*
 O(1D)        + e            ---> O         + e          2.87E-10  0.91
*
*    Berrington, K.A. and P.G. Burke,
*    Effective collision strengths for forbidden transitions
*    in e-N and e-O scattering,
*    Planet. Space Sci., 29, 377, 1981.
*
* The reverse reaction is found in category 62.
*
*32---------------------------------------------------------------------
*
 O(1S)        + O            ---> O         + O          1.80E-13
*
*    DNA Reaction Rate Handbook
*
*32---------------------------------------------------------------------
*
 O(1S)        + O            ---> O(1D)     + O          2.00E-13
*
```

```
*  ARCTIC-35
*     Slanger, L.G., and G. Black, J. Chem. Phys. 64, 3763, 1976.
*
*32--------------------------------------------------------------------
*
 O(1S)        + NO           ---> O(1D)     + NO          3.50E-10  0.5
 O(1S)        + NO           ---> O         + NO          2.00E-10  0.5
*
*     Schofield, K., "Rate Constants for the Gaseous Interactions of
*     O(1D) and O(1S) - A critical Evaluation,"
*     J. Photochem. 9, 55-68 (1978)
*
*     Slanger, T. G., and Black, G.
*     "Temperature Dependence for Quenching of O(1S) by N2O,"
*     J. Chem. Phys. 65, 2025-2026 (1976b)
*
*     Slanger, T. G., and Black, G.
*     "O(1S) Interactions - The Product Channels,"
*     J. Chem. Phys. 68, 989-997 (1978a)
*
*     Hampson, R. F.,
*     "Chemical Kinetic and Photochemical Data Sheets for
*     Atmospheric Reactions,"
*     National Bureau of Standards, Washington, D. C., April 1980
*
*  The product distribution is estimated
*
*32--------------------------------------------------------------------
*
 O(1S)        + O2           ---> O(1D)     + O2      1.30E-12 0.0 0.85
 O(1S)        + O2           ---> O         + O2      7.00E-12 0.0 0.85
*
*
*     Hampson, R. F.,
*     "Chemical Kinetic and Photochemical Data Sheets for
*     Atmospheric Reactions,"
*     National Bureau of Standards, Washington, D. C., April 1980
*
*32--------------------------------------------------------------------
*
 O(1S)        + e            ---> O         + e           7.00E-10  0.50
 O(1S)        + e            ---> O(1D)     + e           6.00E-09
*
```

```
*  The two forward and two reverse reactions (in category 62) are
*  referenced by
*
*     Slinker and Ali, NRL Memorandum Report 4756 (1982)
*
*  With the data for the reverse reactions formed via detailed balancing
*  the first reaction has a Keq = 0.11  0.0  -48.62.  With the second
*  Keq = 0.20  0.0  -25.79.
*
*32---------------------------------------------------------------------
*
*  Quenching through resonant charge exchange is possible though
*  probably small
*     Oppenheimer, M.A., A. Dalgarno, and H.C. Brinton,
*     Ion chemistry of N2+ and the solar ultraviolet flux in the
*     thermosphere,
*     J. Geophys. Res., 81, 3762, 1976.
*
*     Orsini, N, et al.,
*     Quenching of metastable 2D oxygen ions in the
*     thermosphere by atomic oxygen,
*     J. Geophys. Res., 82, 4829, 1977.
*
*     Torr, D.G., and M.R. Torr,
*     Determination of the thermal rate coefficient,
*     products and branching ratios for the reaction
*     of O+(2D) with N2,
*     J. Geophys. Res., 85, 783, 1980.
*
 O(2D)+       + O            ---> O+        + O            1.00E-11
*
*32---------------------------------------------------------------------
*
 O(2D)+       + e            ---> O+        + e            7.85E-08 -0.5
 O(2P)+       + e            ---> O+        + e            3.94E-08 -0.5
 O(2P)+       + e            ---> O(2D)+    + e            1.47E-07 -0.5
*
*  ARCTIC-31
*     Ali, A.W., Electron Impact Rate Coefficients for the Low Lying
*     Metastable States of O, O+, N, and N+,
*     Naval Research Laboratory, NRL
*     Memorandum Report 3371, September 1976.
*
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```
*     Torr, M.R., D.G. Torr, and R.A. Ong,
*     Comparison of the N2+ photochemistry at different phases of
*     the solar cycle,
*     J. Geophys. Res., 85, 2171, 1980.
*
*     Henry, R.J.W., P.G. Burke, and A.L. Sinfailam,
*     Scattering of electrons by C, N, O, N+, O+, and O++,
*     Phys. Rev., 178, 218, 1969.
*
*32------------------------------------------------------------------------
*
 N2(A)        + N              ---> N2         + N(2P)       5.00E-11
*
*  ARCTIC-14 An estimate
*
*32------------------------------------------------------------------------
*
 N2(A)        + O              ---> O          + N2          3.47E-11
 N2(A)        + O              ---> O(1S)      + N2          5.30E-12
*
*  ARCTIC-24
*     Piper, L.C. et al.,
*     J. Chem. Phys. 75, 2847, 1981;
*
*     J.A. Meyer et al.,
*     Astrophys. J. 157, 1023, 1968;
*  plus inferences from ICECAP data and
*  estimates regarding vibrational excitation of product.
*
*  ARCTIC-39
*     Piper, L.C. et al.,
*     J Chem. Phys. 77,2373, (1982)
*
*32------------------------------------------------------------------------
*
 N2(A)        + NO             ---> N2         + NO          8.00E-11
*
*  ARCTIC-25
*     Black G. et al.,
*     J. Chem. Phys. 51, 116, 1969;
*  plus estimate regarding vibrational excitation of product.
*
*32------------------------------------------------------------------------
```

```
*
N2(A)        + O2            ---> N2         + O2(1D)      3.15E-12 0.50
*
*     Piper, L.G. and G.E. Caledonia,
*     J. Chem. Phys. 74,2888, 1981.
*
*  The vibrational distribution is an estimate.
*
*32----------------------------------------------------------------------
*
O2(1D)       + NO            ---> O2         + NO          2.50E-17
*
*  ARCTIC-14 An estimate
*     Memorandum Report 3371, September 1976.
*
*32----------------------------------------------------------------------
*
O2(1D)       + O2            ---> O2         + O2          1.70E-18 0.80
*
*     P. Borrell, P. M. Borrell, and M. D. Pedley,
*     Chem. Phys. Lett. 51, 300 (1977)
*
*     A. Liss, U. Schurath, K. H. Becker, and E. H. Fink,
*     J. Photochem. 16, 211 (1978)
*
*  The two preceding references give the rate coefficient at 300 K
*  while the following two references where used to estimate the
*  temperature dependence:
*
*     The DNA Reaction Rate Handbook
*
*     Hampson, R. F.,
*     "Chemical Kinetic and Photochemical Data Sheets for
*     Atmospheric Reactions,"
*     National Bureau of Standards, Washington, D. C., April 1980
*
*32----------------------------------------------------------------------
*
O2(1D)       + O2(1D)        ---> O2         + O2(1S) 1.80E-18 3.8 -0.7
*
*     Cohen and Westberg,
*     J. Phys. Chem. Ref. Data, 12, 531 (1983)
*
```

```
*32-----------------------------------------------------------------------
*
 O2(1D)      + e          ---> O2       + e        2.31E-12  1.50
*
*  This is the reverse reaction, hence reaction rate coefficient data is
*  formed by detailed balancing with a Keq = 0.66  0.0  -11.34.
*
*32-----------------------------------------------------------------------
*
 O2(1D)      + N2         ---> O2       + N2       1.40E-19
*
*     Hampson, R. F. (editor),
*     "Survey of Photochemical and Rate Data for Twenty-Eight
*     Reactions of Interest in Atmospheric Chemistry,"
*     J. Phys. Chem. Ref. Data 2, No 2.
*     pg. 267-312 (1973).
*
*     Collins, R. J., Husain, D., and Donovan, R. J.,
*     Kinetics and Spectroscopic Studies of O2(1D)
*     by Time-Resolved Absorption Spectroscopy in the Vacuum
*       Ultraviolet,
*     J. Chem. Soc., Faraday Trans. II, 69, 145-157 (1973)
*
*32-----------------------------------------------------------------------
*
 O2(1S)       + O         ---> O        + O2       8.00E-14
*
*  This is an estimate.  Private communication M. Scheibe.
*
*32-----------------------------------------------------------------------
*
 O2(1S)      + N2         ---> O2       + N2       2.00E-15
*
*     Martin, L.R., Cohen, R.B., and Schatz, J. F.,
*     Chem. Phys. Lett. 41, 394 (1976)
*
*     Catha, J.P.S., Arora,P. K., Nalini Raja, S. M. T,
*     Kulkarni, P. B., and Vohra, K. G.,
*     Int. J. Chem. Kinet. 11, 175 (1979)
*
*     Hampson, R. F., et al.,
*     J. Phys. Chem. Ref. Data 2, 267 (1973)
*
```

```
*32-------------------------------------------------------------------
*
 O2(1S)       + O2            ---> O2         + O2          5.60E-18
 O2(1S)       + O2            ---> O2(1D)     + O2          5.04E-17
*
*     Knickelbein, M., Marsh, K., Ulrich, O.,Busch, G.,
*     J. Chem. Phys. 87, 4 (1987).
*  This follows from their minimum estimate of k2/(k1+k2) = 0.9 and
*  k1+k2 = 5.6E-17.
*
*32-------------------------------------------------------------------
*
 O2(1S)       + e             ---> O2         + e           3.80E-11  0.6
*
*  The source of the data is unknown.
*
*--------------------------------------------------------------------
*                    62    REV RSE OF 32
*62---------------------- ------------------------------------------
*
 N            + e             ---> N(2D)      + e      6.00E-10 0.7 27.67
 N            + e             ---> N(2P)      + e      7.50E-10 0.5 41.49
 N(2D)        + e             ---> N(2P)      + e      1.38E-09 0.5 13.82
*
*     Slinker and Ali,
*     NRL Memorandum, Report 4756 (1982)
*
*62-------------------------------------------------------------------
*
 N+           + e             ---> N(1D)+     + e      1.67E-07 -.5 22.016
 N+           + e             ---> N(1S)+     + e      2.19E-08 -.5 46.989
 N(1D)+       + e             ---> N(1D)+     + e      4.10E-08 -.5 24.973
*
*  ARCTIC-32
*     Ali, A.W.,
*     Electron Impact Rate Coefficients for the Low Lying
*     Metastable States of O, O+, N, and N+,
*     Naval Research Laboratory, NRL
*     Memorandum Report 3371, September 1976.
*
*62-------------------------------------------------------------------
*
 O            + e             ---> O(1D)      + e      1.79E-10 0.6 22.83
```

```
 O            + e            ---> O(1S)     + e     7.78E-11 0.5 48.62
 O(1D)        + e            ---> O(1S)     + e     1.20E-09 0.0 25.79
*
*     Slinker and Ali,
*     NRL Memorandum, Report 4756 (1982)
*
*62---------------------------------------------------------------------
*
 O+           + ehot-        ---> O(2D)+    + ehot-      2.00E-08
 O+           + ehot-        ---> O(2P)+    + ehot-      5.00E-09
 O(2D)+       + ehot-        ---> O(2P)+    + ehot-      1.00E-08
*
*62---------------------------------------------------------------------
*
 O+           + e            ---> O(2D)+    + e   1.96E-07 -.5 38.529
 O+           + e            ---> O(2P)+    + e   5.77E-08 -.5 58.157
 O(2D)+       + e            ---> O(2P)+    + e   8.66E-08 -.5 19.625
*
*  ARCTIC-31
*     Ali, A.W.,
*     Electron Impact Rate Coefficients for the Low Lying
*     Metastable States of O, O+, N, and N+,
*     Naval Research Laboratory,
*     NRL Memorandum Report 3371, September 1976.
*
*62---------------------------------------------------------------------
*
 N2           + e            ---> N2(A)     + e   6.00E-10 .25 71.59
 O2           + e            ---> O2(1D)    + e   1.54E-12 1.5 11.34
*
*     Slinker and Ali, NRL Memorandum, Report 4756 (1982)
*
*62---------------------------------------------------------------------
*
 O2           + e            ---> O2(1S)    + e   1.41E-11 0.6 18.88
*
*  The source of the data is unknown.
*
*-------------- -------------------------------------------------
```

APPENDIX C

DATABASE FOR CO_2-IONOSPHERIC CHEMISTRY

```
*
*     Table of Sections
*
*     2.  Photoionization
*     3.  Radiative Recombination
*     4.  Dissociative Recombination
*     5.  Ion-Ion Mutual Neutralization
*     8.  Photodetachment
*     13. Positive Ion Charge Transfer
*     14. Positive Ion Atom Interchange
*     26. Neutral Photodissociation
*     29. Neutral Rearrangement
*     30.  Radiative Electronic State De-excitation
*     31.  Electronic State Photoexcitation
*     32.  Collisional Electronic State Quenching
*     62.  Reverse reactions of 32.
*
*----------------------------------------------------------------------
*
*                              CO2 Chemistry
*        CO2 chemistry to be added to ambient F-region chemistry
*
*----------------------------------------------------------------------
*                        4   DISSOCIATIVE RECOMBINATION
*4---------------------------------------------------------------------
*
 CO2+         + e           ---> O         + CO         3.80E-07 -0.5
*
*     Weller, C.S. and M.A. Biondi,
*     Measurements of Dissociative Recombination of CO2+ Ions
*     with electrons",
*     Phys. Rev. Lett. 19, 59 (1967).
*
*----------------------------------------------------------------------
*                        13   POSITIVE ION CHARGE TRANSFER
*13--------------------------------------------------------------------
*
 N+           + CO2         ---> CO2+      + N          7.50E-10
*
```

```
*     Smith, D. et al.,
*     "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*       O2+, and NO+ ions with several molecules at 300 K"
*     J. Chem. Phys. 69, 308, (1978).
*
*     Tichy, M. et al.
*     A study of the reactions of the ground and metastable
*     states of C+, N+, S+ and N2+ at 300K,
*     J. Chem. Phys. 69, 308 (1978).
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*13--------------------------------------------------------------------
*
O+           + CO2          ---> CO2+      + O      8.00E-10 0.0 5.0
*
*     Smith, D. et al.,
*     "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*     O2+, and NO+ ions with several molecules at 300 K"
*     J. Chem. Phys. 69, 308, (1978).
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*13--------------------------------------------------------------------
*
N2+          + CO2          ---> CO2+      + N2         7.70E-10
*
*     Smith, D. et al.,
*     "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*       O2+, and NO+ ions with several molecules at 300 K"
*     J. Chem. Phys. 69, 308, (1978).
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
```

```
*13---------------------------------------------------------------------
*
 CO2+         + O            ---> O+        + CO2        9.60E-11
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*13---------------------------------------------------------------------
*
 CO2+         + NO           ---> NO+       + CO2        1.20E-10
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*13---------------------------------------------------------------------
*
 CO2+         + O2           ---> O2+       + CO2    3.00E-11 2.89 -1.7
*
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*     Miller, T.M. et al.,
*     Temperature Dependence of the ion-molecule
*     reactions N+ + CO, C+ + NO, and C+, CO+, CO2+ with
*     O2 from 90-450K,
*     J. Chem. Phys., 80, 4922 (1984).
*
*-----------------------------------------------------------------------
*                       14    POSITIVE ION ATOM INTERCHANGE
*14---------------------------------------------------------------------
*
```

```
N+          + CO2          ---> CO+       + NO         2.50E-10
*
*    Smith, D. et al.,
*    "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*      O2+, and NO+ ions with several molecules at 300 K"
*    J. Chem. Phys. 69, 308, (1978).
*
*    Tichy, M. et al.
*    A study of the reactions of the ground and metastable
*    states of C+, N+, S+ and N2+ at 300K,
*    J. Chem. Phys. 69, 308 (1978).
*
*    Albritton, D.L.,
*    "ion-Neutral Reaction-rate constants measured in flow
*    reactors through 1977",
*    Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*14---------------------------------------------------------------------
*
O+          + CO2           ---> O2+       + CO         9.46e-10
*
*  |OCO2A      k = [(10.1-T/2320) - 8exp(-5000./T)]x10-10 cm3/s
*
*    Smith, D. et al.,
*    "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*       O2+, and NO+ ions with several molecules at 300 K"
*    J. Chem. Phys. 69, 308, (1978).
*
*    Dunkin, D.B. et al.,
*    Ion-molecule reaction studies from 300 to 600K in a temperature
*    controlled flowing afterglow system,
*    J.Chem. Phys. 49, 1365, (1968).
*
*    Albritton, D.L.,
*    "ion-Neutral Reaction-rate constants measured in flow
*    reactors through 1977",
*    Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*    Johnsen, R. H.L. Brown and M.A. Biondi,
*    Ion-molecule reactions involving N2+, N+, O2+ and O+ ions
*    from 300K to 1eV,
*    J. Chem. Phys., 52, 5080, (1970)
*
```

```
*     also see,
*     Hunton, D.E., A.A. Viggiano, R.A. Morris and J.F. Paulson
*     The O+ + CO2 reaction: New results and atmospheric implications.
*
*14--------------------------------------------------------------------
*
 CO2+         + O            ---> O2+       + CO        1.60E-10
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*----------------------------------------------------------------------
*                       32  NEUTRAL REARRANGMENT
*29--------------------------------------------------------------------
*
 N(2D)        + CO2         ---> N         + CO2   2.50E-10 0.0 .8
*
*     Husain, D et al.,
*     Kinetic study of electronically excited nitrogen atoms
*     N(2D,2P) by attenuation of atomic resonance radiation in
*     the vacuum ultra-violet,
*     J.Chem. Soc. Farad. 2, 70, 1721 (1974)
*
*     Schofield, K.,
*     Critically evaluated rate constants for gaseous reactions of
*     several electronically excited species,
*     J. Phys. Chem. Ref. Data 8, 724, (1979)
*
*----------------------------------------------------------------------
*                       32  COLLISIONAL ELECTRONIC STATE QUENCHING
*32--------------------------------------------------------------------
*
 O(1D)        + CO2         ---> O         + CO2        3.00E-12
*
*     DNA Reaction Rate Handbook, 1972
*
 O(1S)        + CO2         ---> O         + CO2        3.30E-13
*
*     DNA Reaction Rate Handbook, 1972
*
*----------------------------------------------------------------------
```

APPENDIX D

DATABASE FOR CO_2-IONOSPHERIC CHEMSITRY
WITH IMPLICIT VIBRATION STATES

```
*     WITH IMPLICIT CO2 and O2+ VIBRATIONAL STATES
*
*     Table of Sections
*
*     2.  Photoionization
*     3.  Radiative Recombination
*     4.  Dissociative Recombination
*     5.  Ion-Ion Mutual Neutralization
*     8.  Photodetachment
*     13. Positive Ion Charge Transfer
*     14. Positive Ion Atom Interchange
*     26. Neutral Photodissociation
*     29. Neutral Rearrangement
*     30.  Radiative Electronic State De-excitation
*     31.  Electronic State Photoexcitation
*     32.  Collisional Electronic State Quenching
*     62.  Reverse reactions of 32.
*
*------------------------------------------------------------------------
*
*                               CO2 Chemistry
*        CO2 chemistry to be added to ambient F-region chemistry
*                               CO2(v) and O2(v)+
*
*------------------------------------------------------------------------
*                        4   DISSOCIATIVE RECOMBINATION
*4-----------------------------------------------------------------------
*
 CO2+          + e            ---> O          + CO          3.80E-07 -0.5
*
*     Weller, C.S. and M.A. Biondi,
*     Measurements of Dissociative Recombination of CO2+ Ions
*     with electrons",
*     Phys. Rev. Lett. 19, 59 (1967).
*
*------------------------------------------------------------------------
*                        13   POSITIVE ION CHARGE TRANSFER
*13----------------------------------------------------------------------
```

```
*
 N+            + CO2(0000)    ---> CO2+      + N           7.50E-10
*
*     Smith, D. et al.,
*     "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*       O2+, and NO+ ions with several molecules at 300 K"
*     J. Chem. Phys. 69, 308, (1978).
*
*     Tichy, M. et al.
*     A study of the reactions of the ground and metastable
*     states of C+, N+, S+ and N2+ at 300K,
*     J. Chem. Phys. 69, 308 (1978).
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*13---------------------------------------------------------------------
*
 O+            + CO2(0000)    ---> CO2+      + O           3.88E-11
 O+            + CO2(0110)    ---> CO2+      + O           1.26E-10
*
*     Viggiano et al.,
*     Personal Communication
*     (1991)
*
*13---------------------------------------------------------------------
*
 N2+           + CO2(0000)    ---> CO2+      + N2          7.70E-10
 N2+           + CO2(0110)    ---> CO2+      + N2          7.70E-10
*
*
*     Smith, D. et al.,
*     "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*       O2+, and NO+ ions with several molecules at 300 K"
*     J. Chem. Phys. 69, 308, (1978).
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
```

```
*13-------------------------------------------------------------------
*
 CO2+         + O             ---> O+        + CO2(0000)  9.60E-11
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*13-------------------------------------------------------------------
*
 CO2+         + NO            ---> NO+       + CO2(0000)  1.20E-10
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*13-------------------------------------------------------------------
*
 CO2+         + O2           ---> O2(0)+  + CO2(0000) 3.00E-11 2.89 -1.7
*
*
*     Albritton, D.L.,
*     "ion-Neutral Reaction-rate constants measured in flow
*     reactors through 1977",
*     Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*     Fehsenfeld, F.C. et al.,
*     Rate constants for the reaction of CO2+
*     with O, O2 and NO,
*     Planet. Space Sci. 18, 1267 (1970).
*
*     Miller, T.M. et al.,
*     Temperature Dependence of the ion-molecule
*     reactions N+ + CO, C+ + NO, and C+, CO+, CO2+ with
*     O2 from 90-450K,
*     J. Chem. Phys., 80, 4922 (1984).
*
*--------------------------------------------------------------------
*                      14    POSITIVE ION ATOM INTERCHANGE
*14-------------------------------------------------------------------
*
```

```
N+           + CO2(0000)    ---> CO+       + NO         2.50E-10
*
*    Smith, D. et al.,
*    "A laboratory study of the reactions of N+, N2+, N3+, N4+, O+,
*      O2+, and NO+ ions with several molecules at 300 K"
*    J. Chem. Phys. 69, 308, (1978).
*
*    Tichy, M. et al.
*    A study of the reactions of the ground and metastable
*    states of C+, N+, S+ and N2+ at 300K,
*    J. Chem. Phys. 69, 308 (1978).
*
*    Albritton, D.L.,
*    "ion-Neutral Reaction-rate constants measured in flow
*    reactors through 1977",
*    Atomic Data and Nucl. Data Tables 22, 1 (1978)
*
*14---------------------------------------------------------------------
*
O+           + CO2(0000)     ---> O2(0)+    + CO        2.14E-10
O+           + CO2(0110)     ---> O2(0)+    + CO        1.94E-10
O+           + CO2(0000)     ---> O2(1)+    + CO        4.19E-10
O+           + CO2(0110)     ---> O2(1)+    + CO        3.80E-10
O+           + CO2(0000)     ---> O2(2)+    + CO        2.98E-10
O+           + CO2(0110)     ---> O2(2)+    + CO        2.70E-10
*
*    A.A. Viggiano, R.A. Morris, F. Dale, and J.F. Paulson
*    Production of vibrationally excited O2+ in
*    the reaction of O+ with CO2,
*    J. Chem. Phys. 93, 1681, 1990.
*
*    Hunton, D.E., A.A. Viggiano, R.A. Morris and J.F. Paulson
*    The O+ + CO2 reaction: New results and atmospheric implications.
*
*14---------------------------------------------------------------------
*
CO2+         + O             ---> O2(0)+    + CO        1.60E-10
*
*    Fehsenfeld, F.C. et al.,
*    Rate constants for the reaction of CO2+
*    with O, O2 and NO,
*    Planet. Space Sci. 18, 1267 (1970).
*
```

```
*----------------------------------------------------------------------
*                       29   NEUTRAL REARRANGEMENT
*29--------------------------------------------------------------------
*
 N(2D)        + CO2(0000)    ---> NO        + CO      2.50E-10 0.0 .8
 N(2D)        + CO2(0110)    ---> NO        + CO      2.50E-10 0.0 .8
*
*    Husain, D et al.,
*    Kinetic study of electronically excited nitrogen atoms
*    N(2D,2P) by attenuation of atomic resonance radiation in
*    the vacuum ultra-violet,
*    J.Chem. Soc. Farad. 2, 70, 1721 (1974)
*
*    Schofield, K.,
*    Critically evaluated rate constants for gaseous reactions of
*    several electronically excited species,
*    J. Phys. Chem. Ref. Data 8, 724, (1979)
*
*----------------------------------------------------------------------
*                       32  COLLISIONAL ELECTRONIC STATE QUENCHING
*32--------------------------------------------------------------------
*
 O(1D)        + CO2(0000)    ---> O         + CO2(0110)  3.00E-12
 O(1D)        + CO2(0110)    ---> O         + CO2(0110)  3.00E-12
*
*    DNA Reaction Rate Handbook, 1972
*
 O(1S)        + CO2(0000)    ---> O         + CO2(0110)  3.30E-13
 O(1S)        + CO2(0110)    ---> O         + CO2(0110)  3.30E-13
*
*    DNA Reaction Rate Handbook, 1972
*
*----------------------------------------------------------------------
*                       35   COLLISIONAL VIBRATIONAL ENERGY EXCHANGE
*35--------------------------------------------------------------------
*
 CO2(0110)    + N2           ---> CO2(0000) + N2       3.04E-13
 CO2(0000)    + N2           ---> CO2(0110) + N2       2.73E-13
 CO2(0110)    + O2           ---> CO2(0000) + O2       5.62E-13
 CO2(0000)    + O2           ---> CO2(0110) + O2       5.05E-13
 CO2(0110)    + O            ---> CO2(0000) + O        1.52E-12
 CO2(0000)    + O            ---> CO2(0110) + O        1.36E-12
 CO2(0110)    + e            ---> CO2(0000) + e        6.24E-09
```

```
CO2(0000)     + e          ---> CO2(0110) + e      1.18E-09
*
*    Archer, D.H.,
*    DNA Chemistry Panel Review---CO2,
*    dna-tr-90-92, (1990).
*
*-----------------------------------------------------------------------
*-----------------------------------------------------------------------
*------------------------ O2(vib)+ reactions -------------------------
*-----------------------------------------------------------------------
*-----------------------------------------------------------------------
*
 O2(0)+       + e          ---> O(1S)     + O(1D)     2.20E-08 -0.46
 O2(1)+       + e          ---> O(1S)     + O(1D)     1.82E-08 -0.49
 O2(2)+       + e          ---> O(1S)     + O(1D)     1.17E-08 -0.42
 O2(0)+       + e          ---> O         + O(1D)     1.98E-07 -0.46
 O2(1)+       + e          ---> O         + O(1D)     1.64E-07 -0.49
 O2(2)+       + e          ---> O         + O(1D)     1.05E-07 -0.42
*
*    Guberman, S.L.,
*    The production of O(1D) from dissociative recombination of O2+
*    Planet. Space Sci. 36, 47-53, (1988)
*
*-----------------------------------------------------------------------
*                       5    MUTUAL NEUTRALIZATION
*5----------------------------------------------------------------------
*
 O2(0)+       + O-         ---> O2        + O           6.00E-08  -0.5
 O2(1)+       + O-         ---> O2        + O           6.00E-08  -0.5
 O2(2)+       + O-         ---> O2        + O           6.00E-08  -0.5
*
*-----------------------------------------------------------------------
*                       13   POSITIVE ION CHARGE TRANSFER
*13---------------------------------------------------------------------
*
 O2(0)+       + N(2D)      ---> O2        + N+          2.50E-10
 O2(0)+       + NO         ---> NO+       + O2          4.50E-10
 O2(1)+       + N(2D)      ---> O2        + N+          2.50E-10
 O2(1)+       + NO         ---> NO+       + O2          4.50E-10
 O2(2)+       + N(2D)      ---> O2        + N+          2.50E-10
 O2(2)+       + NO         ---> NO+       + O2          4.50E-10
*
*  Based on data presented in the
```

```
*       DNA Reaction Rate Handbook Chapters 18A and 24
*
*-----------------------------------------------------------------------
*                       14    POSITIVE ION ATOM INTERCHANGE
*14---------------------------------------------------------------------
*
 O2(0)+         + N            ---> NO+        + O            1.20E-10
 O2(0)+         + N2           ---> NO+        + NO           1.00E-16
 O2(1)+         + N            ---> NO+        + O            1.20E-10
 O2(1)+         + N2           ---> NO+        + NO           1.00E-16
 O2(2)+         + N            ---> NO+        + O            1.20E-10
 O2(2)+         + N2           ---> NO+        + NO           1.00E-16
*
*  The reaction rate data for these reactions are based on informed
*  estimates found in the
*     DNA Reaction Rate Handbook chapters 18A and 24
*
*34---------------------------------------------------------------------
*                       34   COLLISIONAL VIBRATIONAL STATE QUENCHING
*34---------------------------------------------------------------------
*
 O2(1)+         + M            ---> O2(0)+     + M      2.00E-14  0.5
 O2(2)+         + M            ---> O2(1)+     + M      2.00E-14  0.5
 O2(0)+         + M            ---> O2(1)+     + M      2.00E-14  0.5  2.78
 O2(1)+         + M            ---> O2(2)+     + M      2.00E-14  0.5  2.66
*
*     Estimated
*
*-----------------------------------------------------------------------
```