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Morphology of the dayside ionosphere of Mars: Implications for ion outflows

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[1] Significant fluxes of tailward streaming ions have been detected in the Martian wake by instruments on spacecraft. Imposing outward fluxes at the top of a model will produce dayside ion density profiles that are characterized by smaller scale heights than those of diffusive equilibrium. We determine the maximum outward fluxes of ions, and those implied by radio occultation data, by constructing ~180 models, with upward velocity boundary conditions in the range from 0 to (7–8) × 10^8 cm s^-1 in small increments. As the upward velocity is increased, the topside ion or electron densities decrease until eventually the computed ion fluxes cease to increase, implying that this is the maximum outward flux that the ionosphere can sustain. By comparison to data, we derive a low solar activity upward flux of O^+ of ~5 × 10^7 cm^-2 s^-1, and a maximum of ~8 × 10^7 cm^-2 s^-1. For O^+, the analogous fluxes are ~4 × 10^4 cm^-2 s^-1 and ~1.1 × 10^7 cm^-2 s^-1. We derive high solar activity upward fluxes of O^+ in the range ~(1.2–1.6) × 10^8 cm^-2 s^-1, and a maximum of 2.4 × 10^8 cm^-2 s^-1. The O^+ derived and maximum fluxes at high solar activity are ~(1.5–2) × 10^7 and 5 × 10^7 cm^-2 s^-1, respectively. If these fluxes are averages over the dayside, we estimate total loss rates of O^+ and O^2+ of (2.8–11) × 10^24 and (3.6–8.7) × 10^25 s^-1, respectively. Our computed escape rates of O^+ are in substantial agreement with the models and data, but our O^2+ escape rates are an order of magnitude larger. We discuss various mechanisms that would bring our O^2+ escape rates or the O^+/O^2+ ratio into agreement with the measurements and models.


1. Introduction

[2] Escape of species as ions is potentially important to the volatile evolution of Mars, Venus, Titan, and other unmagnetized (or weakly magnetized) bodies. Large fluxes of tailward streaming ions at Mars were detected by the Automatic Space Plasma Experiment with a Rotating Analyzer (ASPERA), and toroidal analyzer spectrometer (TAUS) instruments on the Phobos-2 orbiter [e.g., Lundin et al., 1989, 1990a, 1990b; Verigin et al., 1991]. Escape of ions due to the more-or-less direct interaction of the flowing solar wind plasma with ions produced above the ionopause had been predicted earlier [e.g., Cloutier et al., 1969; Michel, 1971; McElroy, 1972; McElroy et al., 1977, 1982]. The proposed process, known as “pickup-ion” escape, begins with ionization of atoms (mostly O) at high altitudes in the hot atom coronas by photoionization, solar wind electron impact ionization, and charge exchange with solar wind protons. The ions thus created are then “picked up” by the convection electric field of the solar wind [e.g., Luhmann, 1990]. Some of the pickup ions may escape from the gravitational field of the planet. Some may, however, reimpact the atmosphere in the region of the exobase, producing loss of neutrals by “sputtering” [e.g., Luhmann, 1990; Luhmann et al., 1992]. The rate of pickup-ion escape is limited by the rate of ionization of the hot atoms in the corona above the ionopause, and possibly by the maximum capacity of the solar wind [Michel, 1971; McElroy et al., 1977; Lundin et al., 1991]. Models of this escape mechanism were initially found not to produce ion fluxes of the magnitudes observed by the Phobos orbiter [e.g., Luhmann and Kozyra, 1991; Luhmann et al., 1992; Zhang et al., 1993]. In addition, measurements by the Phobos-ASPERA instrument showed that, although the major ion detected was O^+, a significant component (up to 50%) of molecular ions was observed [e.g., Lundin et al., 1990a, 1990b; Lundin and Dubinin, 1992].

[3] An additional source of escaping ions is bulk ion outflow, in which ions of ionospheric origin flow upward in the topside ionosphere and outward in the flanks and down the tail of the planet. The rate of ion outflow is limited by the production rate of ions above the photochemical equilibrium (PCE) region [Fox, 1997]. (The PCE region is that in which the photochemical production of a given species is equal to the chemical loss rate.) This source-limited escape process is fundamentally different from the diffusion limited escape of light species, such as H, due to transport from the lower atmosphere and then diffusion across the homopause (where the mixing and diffusion lifetimes are equal) to the...
exobase [cf. Chamberlain and Hunten, 1987; Hunten, 2002]. Because the major ion in the Martian ionosphere is O$_2$, Fox [1993, 1997] predicted that molecular ions could escape from Mars, whereas on Venus, the major ion in the topside ionosphere is O$^+$, and is thus the major escaping ion.

[s] Prior to the Phobos measurements, many modelers had found that they could not reproduce the Viking O$_2$ density profiles [Hanson et al., 1977] without invoking an additional loss process at the top of the models [e.g., Chen et al., 1978; Fox and Dalgarno, 1979; Shinagawa and Cravens, 1989]. Chen et al. [1978] found that they could reproduce the profiles by imposing an upward velocity boundary condition of about $1 \times 10^7$ cm $s^{-1}$ on the O$_2$, which corresponds to an upward flux of $\sim 5 \times 10^7$ cm $s^{-2}$. Fox [1997] found that O$_2$ upward fluxes of the order of $4.7 \times 10^7$ cm $s^{-2}$ reproduced well the Viking lander RPA O$_2$ density profiles, in substantial agreement with the fluxes determined by Chen et al. [1978]. Shinagawa and Cravens [1989] suggested that the loss process is the divergence of horizontal fluxes of ions, by analogy to Venus. Thus large ion escape rates due to ion outflow from the ionosphere are possible, and include molecular ions that are not present in the hot atom coronas.

[s] Duru et al. [2008] have analyzed the high-altitude electron density profiles in situ using the MARSIS instrument on MEX, and showed that the densities above about 300 km are fairly constant from 0 to 80$^\circ$ SZA. They propose that this behavior shows that control of the electron densities has changed from photochemistry to transport by upward diffusion and horizontal convection.

[s] Although the ion acceleration mechanisms have not been well quantified, recent magnetohydrodynamic (MHD) and hybrid simulations have demonstrated that these mechanisms are in general due to pressure gradients and to electromagnetic interactions between the flowing solar wind and the ionosphere [e.g., Kallio et al., 2006a, 2006b; Brecht and Ledvina, 2006; Ma et al., 2002, 2004; Ma and Nagy, 2007]. Dubinin et al. [1993] have suggested that the ions are accelerated by the polarization electric field, while Penz et al. [2004, 2005] have added evidence that at least some of the ions are lost in detached plasma clouds near the terminator that are formed by the Kelvin-Helmholtz or other wave instabilities. Ergun et al. [2006] have proposed that plasma wave heating can lead to escape of O$^+$ ions, and that the present escape rate is source limited. Lundin et al. [2008a] have suggested that the ions are accelerated nighttime by the plasma pressure gradient force.

[s] On Venus, the transequatorial flow of ions is assumed to be produced largely by the plasma pressure gradient force, although detached clouds of scavenged plasma were detected by the Electron Temperature Probe on the Pioneer Venus Orbiter [Brace et al., 1982]. Hartle and Grebowsky [1995] have, however, suggested that escape of light ions on the nightside of Venus is driven by the polarization electric field. Most of the ions accelerated across the terminator on Venus converge and flow downward on the nightside producing a significant nightside ionosphere. Many investigations of the Venus transequatorial ion fluxes, downward flow of ions on the nightside, and the sources of the nightside ionosphere have been carried out (see, for example, the reviews by Kliore and Mullen [1989], Kliore [1992], Knudsen [1992], Fox and Kliore [1997], and the references cited by Fox [2008]).

[s] Models of the ionospheres of Venus have also shown that ion or electron density profiles measured by various instruments on the Pioneer Venus Orbiter cannot be fitted with zero upward flux or velocity boundary conditions [e.g., Brace et al., 1980, 1982; Fox, 2008]. Because the divergence of the flux is a loss process for ions, the imposition of an upward flux or velocity boundary condition at the top of the model may reduce the topside scale height of the predicted ion or electron density profile. Thus, the topside profile of the ion or electron densities may be used as an indicator of the magnitude of the upward flux. Using this method, Fox [2008] derived average upward ion fluxes of $\sim 2 \times 10^7$ cm $s^{-2}$ for a 60$^\circ$ SZA high solar activity model of the Venus ionosphere.

[s] We compute here models of the ionosphere of Mars, with upward velocity boundary conditions on the ions that range from zero to $7 \times 10^6$ cm $s^{-1}$ in small increments for the low solar activity model and from zero to $8 \times 10^5$ cm $s^{-1}$ in small increments for the high solar activity model. The individual ion fluxes are then obtained by multiplying the imposed velocity by the ion densities at the top of the models. We predict the ion and electron density profiles, and the ratios of the electron densities at various altitudes on the topside to the peak electron density for each one of these models. By comparing our results to data, we estimate the implied upward ion fluxes. We also compute the fluxes implied by the maximum velocities, and we thus predict the maximum fluxes that the ionosphere can sustain. Contrary to previous predictions [Fox, 1997], we show here that the predicted maximum fluxes are larger than the upward fluxes implied by the measured ion and electron density profiles.

2. Calculations

[10] We construct models of the Martian thermosphere for low and high solar activities and a solar zenith angle (SZA) of 60$^\circ$. These models comprise 12 background species, including CO$_2$, Ar, N$_2$, O, CO, N, C, NO, O$_2$, He, H and H$_2$ over the altitude range 80 to 700 km. The low solar activity model is based on the measured neutral density profiles of Viking [e.g., Nier and McElroy, 1977]. The high solar activity model is based on a vertical cut through the Mars Thermospheric Global Circulation Model (MTGCM) of Bouger et al. [2000, 2006; also S. W. Bouger, private communication, 2000]. The O mixing ratio in the high solar activity model has been multiplied by a factor of 2 so that its value at 130 km (3.3%) is larger than that of the low solar activity model (2%). Other details of the models are given by, for example, Fox [2004]. The adopted neutral density profiles from 80 to 400 km are shown in Figure 1. All 12 species interact with solar photons and photoelectrons.

[11] The adopted low solar activity neutral temperature ($T_N$) profile is a smoothed version of those that were derived from the Viking 1 lander neutral mass spectrometer neutral density profiles [e.g., Nier and McElroy, 1977]; the high solar activity $T_N$ profiles were taken from the MTGCM. For the low solar activity model, the ion temperatures $T_i$ were adopted from a smoothed profile measured by the Viking 1 retarding potential analyzer (RPA) up to about 300 km [e.g.,
The ion temperatures diverge from the neutral temperatures near 180 km. The electron temperatures, $T_e$, were adopted from the model of Rohrbaugh et al. [1979] up to about 200 km, and from the Viking RPA measurements of Hanson and Mantas [1988] above that altitude. The latter measurements showed that the values of $T_e$ varied from about $\sim 2000$ K just above 200 km to 3000–4000 K near 330 km. At altitudes above 300 km, the ion temperatures were assumed to vary somewhat like the electron temperatures, with the additional requirement that they always be less than the electron temperatures. This assumption introduces a slope discontinuity into the ion temperature profile near 300 km, which is reflected in the ion density profiles. For high solar activity, the ion and electron temperatures were arbitrarily increased by the difference between the high and low solar activity neutral temperatures. This method, while somewhat arbitrary, results in ion and electron temperatures that are everywhere larger than or equal to the neutral temperatures, but which do not vary greatly with solar activity. There have been no measurements or calculations of plasma temperatures in the Martian ionosphere at high solar activity. In fact, neither the measured $T_n$ nor the $T_i$ profiles at low solar activity have been successfully modeled without either imposing an arbitrary source of heat at the top of the ionosphere, or by reducing the thermal conductivity, due possibly to the presence of small fluctuating magnetic fields [e.g., Chen et al., 1978; Johnson, 1978; Choi et al., 1998]. Altitude profiles of the values of $T_n$, $T_i$, and $T_e$ adopted in this study are shown in Figure 2.

We model the ionosphere from 80 to 380 km for low solar activity, and from 80 to 400 km for high solar activity conditions on a 1 km grid. We compute the steady state density profiles for 14 ions, including O$_2$, CO$_2$, N$_2$, Ar, O({}^3S), O({}^3D), O({}^1P), CO$, C$, N$, N$O$, O$^+$, He$^+$, and H$^+$. Diffusion and eddy diffusion are included for the neutrals, and ambipolar diffusion is included for the ions. We also include thermal diffusion of the ions, as formulated by Schunk and Walker [1969]. We determine these densities using an implicit scheme that employs the Newton-Raphson technique. We impose the convergence criterion that the relative changes in the densities of all species at all altitudes from one iteration to the next are required to be less than $8 \times 10^{-5}$ for the zero upward velocity models. For the finite upward velocity models the convergence criterion had to be relaxed, and gradually increased to the requirement that the relative change for all species from one iteration to the next must be less than $5.3 \times 10^{-4}$. (The smoothness of the curves in Figures 5–7, which will be Figure 2. Adopted values of the neutral ($T_n$), ion ($T_i$), and electron ($T_e$) temperature profiles. The solid curves are for low solar activity, and the dashed curves are for high solar activity.
The topside boundary conditions on the ions are upward velocities, except for O\(^{+}\), which is assumed to be in PCE. At the lower boundaries, the ions are assumed to be in PCE. The minor neutrals are assumed to be in diffusive equilibrium at high altitudes, except for H and H\(_2\), for which upward diffusion velocities were imposed. The diffusion velocities are the Jeans velocities multiplied by 0.5 to account for the suppression of the tail of the Maxwell-Boltzmann distribution, as suggested by the calculations of Shizgal and Blackmore [1986]. The lower boundary conditions for the species O(\(^{1}\)D), O(\(^{3}\)S), N(\(^{2}\)D), and N(\(^{2}\)P) are assumed to be PCE. For H\(_2\), a mixing ratio of 10 ppm is assumed, which is within the range of the mixing ratio of 15 ± 5 ppm derived by Krasnopolsky and Feldman [2001] from the Far Ultraviolet Spectroscopic Explorer (FUSE) measurements of a few of the prominent H\(_2\) Lyman bands in the Martian dayglow. Since we do not yet model the chemistry of H completely, the density of H at the lower boundary is fixed so that the densities near 250 km at high solar activity, ~2(4) × 10\(^{4}\) cm\(^{-3}\), are similar to those inferred by Anderson [1974] from the Lyman alpha dayglow of Mars as measured by the Mariner 6, 7, and 9 ultraviolet spectrometers. At low solar activity, the high-altitude H densities are predicted to be larger by an order of magnitude due to the smaller Jeans escape rate [e.g., Levine et al., 1978; Krasnopolsky, 2002]. Zero-flux lower boundary conditions are assumed for atomic carbon. Downward transport of thermospheric N and NO is a source of odd nitrogen to the lower atmosphere. Thus for NO and N, downward fluxes of 2 × 10\(^{2}\) and 1 × 10\(^{3}\) cm\(^{-2}\) s\(^{-1}\), respectively, are imposed at the lower boundary of the low solar activity model; downward fluxes of 7 × 10\(^{2}\) and 1 × 10\(^{4}\) cm\(^{-2}\) s\(^{-1}\), respectively, are imposed at the lower boundary of the high solar activity model. Because we do not model the lower atmosphere, we do not attempt to optimize the values of these fluxes.

The cross sections and rate coefficients adopted are similar to those of Fox and Sung [2001] for the Venus ionosphere, with a few updated rate coefficients [e.g., Fox, 2003, 2004]. A total of 220 reactions were included. We have adopted here the Solar2000 (S2K) v2.22 solar flux model from Tobiska [2004; also W. K. Tobiska, private communication, 2002]. For high solar activity, we adopt the 99178 fluxes, which correspond to day 178 (27 June) of 1999, for which the value of F\(_{10.7}\) adjusted to 1 AU was 214. For low solar activity, we have adopted the 76200 fluxes, which correspond to day 200 (18 July) of 1976, for which the F\(_{10.7}\) adjusted to 1 AU was 70.6. The S2K v2.2 spectra are normalized to early measurements from the Solar EUV Experiment (SEE) on the Thermosphere Ionosphere Meso-Sphere Energetics and Dynamics (TIMED) spacecraft. The SEE instrument has measured solar irradiances in the range 1 to 1940 Å in 10 Å intervals from 2002 to the present [e.g., Woods et al., 2005, 2009] (see also the instrument Web site at http://lasp.colorado.edu/see, which also contains a list of references). The format of the solar flux model that we use is that first proposed by Hinteregger et al. [e.g., 1981; also H. E. Hinteregger, private communication, 1979], in which the continuum fluxes are given in 1 Å intervals, and the strong solar lines are assumed to be delta functions at their central wavelengths, for a total of more than 1800 wavelengths from 18 to 2000 Å. For harder X rays below 18 Å we adopt the solar fluxes from Ayres [1997; also T. Ayres, private communication, 1996].

It should be noted that the use of the S2K v2.22 solar fluxes in ionospheric models has been shown to yield electron density peaks for Mars and Venus that are somewhat smaller than the experimentally determined peaks, and smaller than those in which the S2K v1.24 solar fluxes or the Hinteregger SC#21REFW or 79050 fluxes are adopted [e.g., Fox and Sung, 2001; Fox, 2003, 2004; Fox and Yeager, 2006; Fox, 2007, 2008].

We begin by constructing low and high solar activity ionospheric models with zero upward velocity boundary conditions imposed on the ions at the tops of the models. We then vary the models by imposing increasingly larger upward velocity boundary conditions on 13 of the ions, beginning with a value for which there is no noticeable change in the ion density profiles, 1.0 × 10\(^{3}\) cm\(^{-3}\). The upward velocities are gradually increased until the upward fluxes of the major ions cease to increase significantly with increasing upward velocity. This phenomenon will be explained in detail later. For low solar activity, a total of 84 models were constructed, for upward velocity boundary conditions of zero to ~7.0 × 10\(^{5}\) cm\(^{-3}\). For high solar activity, a total of 93 models were constructed, for upward velocities from zero to ~8 × 10\(^{5}\) cm\(^{-3}\). For each model, we construct ion density profiles, and compute the upward flux at the top of the model for each ion. All the ions are assumed to have the same upward velocities, although small differences would be expected. We also note that in these calculations we assume that the ions are moving through a stationary neutral atmosphere; in fact, the neutrals are probably dragged along somewhat by collisions with the moving ions [e.g., Schunk and Nagy, 2000].

In Figure 3 we present examples of the most important ion density profiles for the low solar activity models for upward velocity boundary conditions of zero, 1 × 10\(^{5}\), 3 × 10\(^{5}\), and 6 × 10\(^{5}\) cm\(^{-3}\). In Figure 4, we present examples of the ion density profiles for the high solar activity models for upward velocity boundary conditions of zero, 2 × 10\(^{5}\), 4 × 10\(^{5}\), and 7 × 10\(^{5}\) cm\(^{-3}\). Note the change of density scale for the high solar activity models, which was introduced so that the H\(^{+}\) and He\(^{+}\) profiles, as well as that of O\(_{2}\), would be visible on the plots. In these models, the curves labeled O\(^{+}\) are the sum of all forms of O\(^{+}\), including O(\(^{3}\)S), O(\(^{3}\)D), and O(\(^{2}\)P). It can be seen easily that the upward fluxes imposed on the models do not affect the ion density peaks, which are in the PCE region. The predicted F\(_{1}\) peak electron densities are 8.8 × 10\(^{5}\) cm\(^{-3}\) at 135 km at low solar activity, and 1.33 × 10\(^{5}\) cm\(^{-3}\) at 137 km at high solar activity.

Above 300 km all the ions appear to take on the same scale height. In a stationary ionosphere, the ion density scale height \(H_i\) and plasma pressure scale height \(H_p\) of the major ion are related by

\[
\frac{1}{H_i} = \frac{1}{H_p} + \frac{1}{\frac{dH_p}{dz}},
\]

The predicted F\(_{1}\) peak electron densities are 8.8 × 10\(^{5}\) cm\(^{-3}\) at 135 km at low solar activity, and 1.33 × 10\(^{5}\) cm\(^{-3}\) at 137 km at high solar activity.
where $T_p = (T_e + T_i)$ is the plasma temperature. At altitudes where the plasma temperatures are increasing, the ion density scale heights will be substantially smaller than the “diffusive equilibrium” scale height $H_p = kT_p/m_i g$, even in the absence of the assumed upward fluxes. [cf. Banks and Kockarts, 1973; Schunk and Nagy, 2000; Ma et al., 2004]. The only requirement for the dominance of the second term in equation (1) is that there be significant gradients in $T_e$ or $T_i$, as there are in all the existing models and measurements of the plasma temperature profiles. As a result, the ions in models are never characterized by a “diffusive equilibrium” scale height of $kT_p/m_i g$ at high altitudes even for an assumed upward velocity boundary condition of zero.

For each model, we compute the ratio of the electron density at 200, 250, and 300 km to that at the peak. If there is a neutral model associated with the measured ion density profiles, we can model the ion densities using these background neutral densities, and increase the upward velocity boundary conditions until we obtain agreement with the measured ion density profiles. This is the procedure that we carried out with the Viking ion density profiles. If there are no simultaneous measurements of neutral density profiles, as is the case for electron densities derived from radio occultation data, we must adopt the neutral density profiles from models, such as the MTGCM of Bouger et al. [2000, 2006]. We can estimate the upward fluxes by determining the ratio of the electron densities at specific altitudes above the peak to that at the peak. These values can be compared with the ratios derived from our models. Obviously, this method works best when the measured peak electron density is of a similar magnitude and at a similar altitude as that of the model.

There are very few available Martian electron density profiles from periods of high solar activity. The Mariner 6 and 7 immersion radio occultation electron density profiles were measured on 31 July 1969 and 5 August 1969, respectively, at 56–57° SZA. Mariner 6 probed the ionosphere near a latitude of 4°N, and a longitude of 5°W, at a local time of 1544 in early fall. The Mariner 7 profile was obtained near a latitude of 58°S, 30°E longitude, at a local time of 1432 in early spring. This is well outside the region of the remanent crustal magnetic fields, which are concentrated in the southern hemisphere, between ~140 and 240°E. longitude [e.g., Connerney et al., 2001]. Ness et al. [2000] have shown that

Figure 3. Representative ion density profiles for the low solar activity model. Each panel is labeled by the upward velocity boundary condition assumed. The major ions are shown with solid curves, $C^+$ and $N^+$ are shown with dashed curves, $He^+$ and $H^+$ are shown with dot-dashed curves, $N_2^+$ is shown with a dotted curve, and $CO^+$ is shown as a long-dashed curve. The total electron density $n_e$ is shown with a dotted curve.
the MGS electron density scale heights were much larger above regions of locally vertical magnetic fields.

3. Results

3.1. Maximum Fluxes and Loss Rates

In Figures 5 and 6 we present upward fluxes for O$_2^+$, O$^+$, CO$_2^+$, N$_2^+$, C$^+$, H$^+$, and N$^+$ as a function of assumed upward velocity at the top of the 60° solar zenith angle low and high solar activity models, respectively. For small upward velocities, the implied upward fluxes of the ions increase nearly linearly, but eventually the rate of increase of the upward fluxes of the major ions, including O$_2^+$, O$^+$, and CO$_2^+$ begins to decrease as the upward velocity boundary condition is increased. This behavior is observed when the outward flux is large enough to reduce the densities at the upper boundary of the model. Eventually we would expect no increase in the fluxes at all as the ion densities at the boundaries of the models decrease enough to compensate for the increasing velocities. These limiting upward ion fluxes can be interpreted as the largest fluxes that could be sustained by the ionosphere. These values are relevant to, for example, extreme solar wind conditions.

This limiting flux appears to be $\sim (7.7-24) \times 10^7$ cm$^{-2}$ s$^{-1}$ for O$_2^+$, where the range quoted here and below is from the low to high solar activity. The limiting upward fluxes of O$^+(^4S)$ and O$^+(^3D)$ appear to be $\sim (7.1-33) \times 10^6$ and $\sim (4.0-17) \times 10^6$ cm$^{-2}$ s$^{-1}$, respectively, for a total limiting upward flux of O$^+$ in all forms of $\sim (1.1-5) \times 10^7$ cm$^{-2}$ s$^{-1}$. The limit to the upward flux of CO$_2^+$ is about $\sim (1.1-2.6) \times 10^7$ cm$^{-2}$ s$^{-1}$. The maximum total flux for all ions is $\sim (1.0-3.4) \times 10^8$ cm$^{-2}$ s$^{-1}$. These limiting fluxes for O$_2^+$ and total ions are larger than those reported by Fox [1997], of $(4.7-13.5) \times 10^6$ and $(6-20) \times 10^6$ cm$^{-2}$ s$^{-1}$, respectively. We attribute this difference to the more stable numerical procedure we have implemented here. The predictions for the maximum upward flux of O$^+$, however, are smaller here than those reported by Fox [1997], largely because in the current low solar activity model the O$^+$ density profiles are smaller than those of previous models, and smaller than the Viking RPA data indicate [e.g., Hanson et al., 1977]. It appears that as more complicated ion chemistry is included in the model, the smaller the predicted O$^+$ density profiles become. For example, a major loss mechanism for several ions, including O$^+$, is reaction with H$_2$ [e.g., Krasnopolsky, 2002; Fox,
In addition, the use of the S2K v2.22 solar flux model of Tobiska is also a factor because it leads to smaller solar ionization rates. We will address this discrepancy briefly below and in detail in a future study.

In Figures 5 and 6 (middle and bottom), we present some of the minor atomic ion upward fluxes as a function of upward velocity, for low and high solar activities, respectively. The curves do not appear to flatten out at the same upward velocities as the major ions. Indeed, there is no a priori reason to expect that all the ions reach their limiting fluxes at the same velocities, unless their densities are tied photochemically to those of the major ion. Figures 5 and 6 show that the upward fluxes of the atomic ions C⁺, H⁺, and N⁺ are still increasing for upward velocities of \((7-8) \times 10^5 \text{ cm s}^{-1}\).

In Table 1, we present the maximum upward fluxes of 12 ions for low and high solar activities in columns 2 and 4. If we assume that our 60° SZA models are averages over the dayside, then we can predict the maximum loss rates of the ions from the dayside ionosphere. This loss rate may include total loss by ion outflow and also transport to the nightside, where the ions may converge and flow down, contributing to the maintenance of a nightside ionosphere. The resulting loss rates are shown in Table 2 for the ions that have been detected, including O⁺, O₂⁺, CO₂⁺, and H⁺. It can be seen that the predicted maximum loss rates for O₂⁺ ((5.5–17) \times 10^{25} \text{ s}^{-1}), where the range is from low to high solar activity, are larger than those for O⁺ by factors of 7 at low solar activity and by a factor of 5 at high solar activity. More accurate O⁺ density profiles could increase the low solar activity O⁺ flux by a factor of 2 or so, but it would not result in loss rates for O⁺ that are larger than or comparable to those of O₂⁺. The maximum loss rates for CO₂⁺ ((~7.9–19) \times 10^{24} \text{ s}^{-1}) are comparable to those for O⁺, and the maximum loss rates for H⁺ (~(1.2–1.7) \times 10^{23} \text{ s}^{-1}) are an order of magnitude or more smaller than those for the other ions. The maximum total ion loss rates are \((7.2–24) \times 10^{25} \text{ s}^{-1}\).

We can roughly compare the maximum fluxes to the production rates above the PCE boundaries for the major ions. The PCE boundaries are located roughly where the time constants against loss by diffusion, \(\tau_D\), are equal to the time constants against loss by chemical reactions, \(\tau_c\). The former is usually estimated as \(H^2/D_i\), where \(D_i\) is the diffusion coefficient of an ion, and \(H\) is the average scale height of...
loss rate due to dissociative recombination. As the PCE boundary is driven down, the production rates of ions available for transport increase. The PCE boundary for an atomic ion stops decreasing when collisions with neutrals become more important than collisions with ions in determining the diffusion coefficient of the ion.

[27] Because the rate of direct production of O$_3^+$ is negligible, it is difficult to determine what species to include in computing the maximum escape fluxes. O$_2^+$, CO$_2^+$, and O$_2^+$ are transformed in reactions, such as

$$\text{CO}_2^+ + O \rightarrow \text{O}_2^+ + \text{CO},$$

(3)

$$\text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO},$$

(4)

and

$$\text{CO}_2^+ + O \rightarrow \text{O}^+ + \text{CO}_2.$$  

(5)

The production rate of CO$_2^+$ + O$^+$ above the lowest O$_3^+$ PCE boundary of 185–210 km (from low to high solar activity) is $(3–9) \times 10^{24}$ s$^{-1}$ compared to our model O$_2^+$ loss rates of $(5.5–17) \times 10^{25}$ s$^{-1}$, which are thus in agreement to within a factor of 2.  

[28] The rate of production of O$_3^+$ above its lowest PCE boundary is in the range $(2.6–15) \times 10^{24}$ s$^{-1}$, which is in fair agreement with the model values of $(8–36) \times 10^{23}$ s$^{-1}$. If we add the O$_3^+$ production rates above the O$_3^+$ PCE boundary, we obtain production rates of $(4.5–26) \times 10^{24}$ s$^{-1}$, in better agreement with the model maximum loss rates. The rate of production of CO$_2^+$ above its PCE boundary of 216–261 km is $(1.1–2.9) \times 10^{24}$ s$^{-1}$, which is somewhat less than its maximum model fluxes of $(7.9–19) \times 10^{24}$ s$^{-1}$. CO$_2^+$ is produced at high altitudes by the reaction with O$_3^+$(D) with CO$_2$:

$$\text{O}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{O}.$$  

(6)

If we add the direct production rate of O$_3^+$(D) to that of CO$_2^+$, we obtain $(2.8–11) \times 10^{24}$ s$^{-1}$, in better agreement. For H$^+$, the direct production rates above the PCE boundaries of 218–261 km are in the range $(2.3–2.6) \times 10^{23}$ s$^{-1}$, and are slightly larger than our model maximum escape rates of
We note here that $H^+$ is transformed to $O^+$ by near resonance charge transfer reaction 

$$H^+ + O \rightarrow O^+ + H$$

(7)

and thus the maximum escape rates predicted by our model are expected to be somewhat smaller than the values estimated from the direct production rates of $H^+$ above the PCE boundary. While we recognize that we have double counted some of the production rates in this analysis, we have not included all the processes that contribute to production of the major ions. These species are subject to significant chemical transformations.

3.2. Upward Fluxes Implied by the Measured Electron or Ion Density Profiles

As indicated earlier, a simple indicator of the major ion upward flux implied by a measured electron density profile is given by the ratio of the electron number density at a given altitude substantially above the peak to the electron density at the peak. In Figure 7, we present the computed ratio of the electron number densities at 200, 250, and 300 km to the peak electron number densities as a function of total upward ion flux for the low and high solar activity models.

It is apparent that the ratio decreases slowly for small upward fluxes but decreases more rapidly for fluxes that are larger than $\sim 1 \times 10^7$ cm$^{-2}$ s$^{-1}$, at low solar activity, and for fluxes that are larger than $\sim 3 \times 10^7$ cm$^{-2}$ s$^{-1}$ at high solar activity. By comparing the computed electron or total ion density profiles to those of measurements, we can estimate the implied upward fluxes. To demonstrate the method, we consider three profiles here: the ion density profiles obtained from Viking 1 for low solar activity [Hanson et al., 1977] and the Mariner 6 and Mariner 7 ingress radio occultation profiles for high solar activity [Fjeldbo et al., 1970].

The Viking $O_2$ profile, for which there are measurements of the underlying neutral densities, is well fit by an upward velocity of about $1 \times 10^5$ cm$^{-2}$ s$^{-1}$, as shown in Figure 8. This velocity and the implied upward $O_2^+$ flux of $5 \times 10^7$ cm$^{-2}$ s$^{-1}$ are consistent with those determined by Chen et al. [1978]. Contrary to the conclusion of Fox [1997], this value is smaller than the computed limiting upward flux of $\sim 8 \times 10^7$ cm$^{-2}$ s$^{-1}$. Assuming that the ions all have the same upward velocity, we compute the implied upward fluxes for 12 ions, and the total fluxes, which are also shown in column 3 of Table 1. According to our calculations, the implied upward flux for the sum of $O^+(2S)$ and $O^+(2D)$ is $3.9 \times 10^6$ cm$^{-2}$ s$^{-1}$. This is expected to be an underestimate because our model $O^+$ densities are smaller than the Viking measured densities by a factor of about 2. The predicted upward $CO_2^+$ flux at low solar activity is $3.6 \times 10^6$ cm$^{-2}$ s$^{-1}$.
Figure 9. Electron density profiles measured by the Mariner 6 and 7 radio occultation experiment. The bold black curve is the Mariner 6 ingress profile, and the gray shaded curve is the ingress Mariner 7 profile. After Fjeldbo et al. [1970].

[32] There are very few measurements available for high solar activity. Mariners 6 and 7 flew by Mars at a time of moderately high solar activity. At the time of the Mariner flybys (31 July to 5 August 1969), Mars trailed the Earth in its orbit by only 23–24°, and therefore it viewed almost the same face of the Sun as the Earth. The $F_{10.7}$ solar flux parameter on 31 July 1969 was 167, which is high, but somewhat less than the value of ~200 that characterizes our solar flux model. The $F_{10.7}$ solar flux parameter on 5 August 1969 was 187.7, and thus pertains to fairly high solar activity. The Mariner 6 and 7 electron density profiles, which are shown overplotted here in Figure 9, are thus not strictly comparable to our high solar activity model. The peak electron densities in the Mariner 6 and 7 profiles are $1.58 \times 10^6$ and $1.7 \times 10^5$ cm$^{-3}$, respectively, and are somewhat larger than our model peak density of $1.33 \times 10^5$ cm$^{-3}$, although the altitudes of the peaks are comparable to those in our models. We can attribute at least part of the discrepancy in the peak electron densities to the use of the S2K v2.22 solar fluxes. For the 99178 S2K v1.24 solar flux model of Tobiska [2001], we find that the peak electron density is $1.68 \times 10^5$ cm$^{-3}$ near 137 km, and thus is slightly larger than that for the Mariner 6 profile of $1.58 \times 10^5$ cm$^{-3}$, but is comparable to that of the Mariner 7 profile, which peaks at ~137 km, with a density of $1.7 \times 10^5$ cm$^{-3}$. An additional uncertainty is introduced by the necessity of determining the electron densities by visual inspection of Figure 9.

[33] It appears from the Mariner 6 profile that the electron density at 200 km is $\sim4.4 \times 10^4$ cm$^{-3}$, although there is some noise evident at that altitude, which prevents the determination of a precise density. The implied upward velocity is of the order of $4 \times 10^4$ cm s$^{-1}$. Figure 9 shows that at 250 km, the Mariner 6 electron density profile is very noisy and it is difficult to assign a value at that altitude. We estimate a “mean” electron density of $\sim1.3 \times 10^6$ cm$^{-3}$, which implies an upward velocity of $6 \times 10^4$ cm s$^{-1}$, but the uncertainty in this value is considerable. For the Mariner 7 profile, it appears that the electron density at 200 km is $\sim4.5 \times 10^4$ cm$^{-3}$, which implies an upward velocity of $\sim7 \times 10^3$ cm s$^{-1}$. Above 200 km, this profile is also very noisy; we estimate an average density of $\sim1.7 \times 10^5$ cm$^{-3}$ at 250 km, which corresponds to an upward velocity of $\sim3 \times 10^4$ cm s$^{-1}$, but the uncertainty in this value, as is that for 250 km in the Mariner 6 profile, is considerable. The limitations of this procedure are obvious, and for high solar activity we therefore derive a range of upward velocities of $(4–7) \times 10^3$ cm s$^{-1}$, and a range of predicted (or implied) upward fluxes, rather than a single value. The predicted fluxes for 12 ions for low and high solar activities are shown in columns 3 and 5 in Table 1. For the high solar activity model, the upward velocity implied by the data are smaller than that of the low solar activity model. In addition, the ratio of the implied total ion escape flux to the maximum escape flux is smaller at high solar activity (0.51) than at low solar activity (0.60). Thus, it appears that the ionosphere at high solar activity is not as eroded as that at low solar activity. This may imply that the high solar activity ionospheric pressure can “stand off” the solar wind more effectively than that of the low solar activity ionosphere.

[34] The fluxes implied by the data are significantly less than the maximum values. The largest implied fluxes are those for O$_2^+$, with values of $5 \times 10^5$ cm$^{-2}$ s$^{-1}$ at low solar activity, and a range of $(1.2–1.6) \times 10^6$ cm$^{-2}$ s$^{-1}$ for high solar activity. The sum of the O$^+$(4S) and O$^+$(2D) fluxes are $3.9 \times 10^6$ cm$^{-2}$ s$^{-1}$ and in the range $(1.5–2.1) \times 10^6$ cm$^{-2}$ s$^{-1}$ for low and high solar activities, respectively. The CO$_2^+$ fluxes implied by the data are $3.6 \times 10^6$ at low solar activity, and in the range $(5.4–8.4) \times 10^6$ cm$^{-2}$ s$^{-1}$ at high solar activity. The maximum fluxes are larger than the implied fluxes by factors of 1.5 to 3.

[35] If we assume that the predicted upward fluxes for our 60° SZA model are averages over the dayside, we can estimate the total rates of tailward flowing ions by multiplying the fluxes by the surface area of the dayside hemisphere. The results for 4 ions for which there are model or measured values, O$^+$, O$_2^+$, CO$_2^+$, and H$^+$ are shown in Table 2. For the high solar activity model, we have used the smaller value of the implied fluxes. The range of predicted O$^+$ loss rates from low to high solar activity is $(2.8–11) \times 10^{24}$ s$^{-1}$; for O$_2^+$, the range is $(3.6–8.7) \times 10^{25}$ s$^{-1}$; for CO$_2^+$, the range is $(2.6–3.9) \times 10^{24}$ s$^{-1}$; and for H$^+$, the range is $(5.1–8.8) \times 10^{22}$ s$^{-1}$. The predicted loss rate of H$^+$ is larger at low solar activity than at high solar activity because the H densities at high altitudes are predicted to be larger at low solar activity, as explained previously. The implied total ion escape rate is in the range $(4.3–11) \times 10^{25}$ s$^{-1}$ from low to high solar activity.

4. Discussion
4.1. Sources of Uncertainties

[36] We begin the discussion by enumerating some of the sources of uncertainties in our model results. First, our models were constructed for the average Sun-Mars distance for a solar zenith angle of 60°. Mars has a significantly eccentric orbit, and is tilted on its axis by about 24°. Thus there may be large seasonal, solar zenith angle, latitudinal,
and possibly local time variations that we do not take into account here.

[37] The ion escape rates have been shown to be significantly anisotropic [e.g., Kallio et al., 2006a; Brecht and Ledvina, 2006]. Kallio et al. [2006a] have shown that there is a dawn/dusk asymmetry in the O\textsubscript{2} escape fluxes. Thus the use of a single profile, or even two profiles, is a potentially important source of error here.

[38] The solar fluxes that we assume may not be comparable to the actual fluxes for the dates of the profiles. Although the Viking 1 profile occurred quite near day 200 of 1976, there is a large difference among the different versions of the 76200 SZK fluxes of Tobiska [e.g., 2004] (e.g., v1.24 and v2.22), and the SC\#21REFW fluxes of Hinteregger. In addition, the Viking low solar activity neutral and ion density profiles may not be representative of low solar activity conditions. Since there are no other profiles from in situ measurements available, however, this is a common assumption.

[39] The neutral thermospheric profiles adopted in the high solar activity models, which are used to compute the Mariner 6 and 7 electron density profiles, may not be appropriate to the conditions for those profiles. As mentioned previously, there is substantial error introduced into the procedure by manually digitizing the Mariner 6 and 7 electron densities. It would be better, certainly, to analyze multiple electron density profiles, or average profiles, such as those that were used for Venus by Fox [2008]. The availability of simultaneous (or near simultaneous) ion and neutral density profiles would certainly improve the situation. This may have to await an aeronomy mission that involves in situ measurements in the Martian thermosphere/ionosphere, such as the MAVEN mission planned for 2013–2014.

### 4.2. Comparison to Measurements

[40] A summary of the measurements made by instruments on the Phobos-2 and Mars Express (MEX) orbiters is shown in Table 4. The Phobos spacecraft sampled the Martian atmosphere at high solar activity. Measurements of escaping ions by the Phobos-ASPERA instrument lead to an estimated magnitude of the loss of oxygen in ions of 3 \times 10\textsuperscript{25} s\textsuperscript{-1}, or a hemispheric average flux of 4 \times 10\textsuperscript{17} cm\textsuperscript{-2} s\textsuperscript{-1}, referred to the surface [Lundin et al., 1990a, 1990b].

[41] Lundin et al. [1990a] suggested that the loss of ions was by solar wind pick-up at high altitudes, as indicated by early models of ion escape [e.g., Cloutier et al., 1969; Michel, 1971; McElroy, 1972; McElroy et al., 1977]. The major ion detected was O\textsuperscript{+}, but a significant component (∼50%) of molecular ions were observed. Lundin et al. [1990a, 1990b] identified two regions of ion outflow: an outer region of “cold” ions which originate in the dayside ionosphere and flow outward across the terminator in the flanks, and a region in the optical shadow of the planet in which very energetic ions, which they referred to as “ion beams” were detected [cf. Lundin and Dubinin, 1992]. H\textsuperscript{+} pickup ions were also detected [Barabash et al., 1991]. Heavy ions of ionospheric origin were detected in the magnetosphere [Lundin et al., 1990b]. Lundin and Dubinin [1992] suggested that the observation of a substantial fraction of molecular species implies that escape must originate at fairly low altitudes in the ionosphere, which are not accessible by the pickup ion process, as traditionally defined [cf. Kallio et al., 1995].

[42] The TAUS instrument on Phobos-2 detected energetic ions with only crude mass resolution in the central region of the plasma sheet. The investigators assumed that the ion loss rates from Mars using instruments on spacecraft because of the asymmetric and time-dependent way the ions are predicted to be lost from Mars. Such an asymmetry was also shown by the hybrid simulations of Kallio et al. [2006b].

[43] The difference between the escape fluxes derived from the ASPERA and TAUS instruments may also relate to the different ion energetic ranges that the instruments detected. The ASPERA detected ions with nominal energy to charge ratios of 0.5 eV−24 keV, while the range of energy for the TAUS instrument was 0.03−6 keV [e.g., Vaisberg, 1992]. We can compare these escape rates to our high solar activity predictions of 1.1 \times 10\textsuperscript{25} s\textsuperscript{-1} of O\textsuperscript{+}, and 8.7 \times 10\textsuperscript{25} s\textsuperscript{-1} for O\textsubscript{2}. As mentioned earlier, some of these loss rates may represent ions that flow across the terminator, converge, and flow downward on the nightside. Ma et al. [2004] used a multispecies MHD model in which they computed the transterminator escape fluxes and the escape fluxes for each of their four models. The ratios of the transterminator fluxes to the escape fluxes were of the order of 1.75 for the high
solar activity models, and ranged from 1.7 to 2.4 for the low solar activity models. Therefore, a reduction of our escape rates by factors of ~2 are appropriate. If we add these rates together and divide by 2 to account for the downward fluxes on the nightside, we obtain a total loss rate of $5 \times 10^{23}$ s$^{-1}$, which is in fair agreement with the measurements of the Phobos-ASPERA instrument. The identification of the major ion as O$^+$ in the measurements is, however, inconsistent with our identification of the major escaping ion as O$_2^+$ in our models.

[44] Recently, a large number of measurements at low solar activity of escaping ions with better mass resolution has been made with the ASPERA-3 instrument on board the MEX spacecraft, which entered into orbit around Mars in 2004. The ASPERA-3 has been described by Lundin and Barabash [2004]. Lundin et al. [2004] reported the first measurements of ion escape from Mars detected by the ASPERA-3 Ion Mass Analyzer (IMA). Outward flowing heavy ions, including O$^+$, O$_2^+$, and CO$_2^+$ were detected, which indicates that the ions are of ionospheric origin, and thus can be attributed in large part to ion outflow, rather than to pickup ion escape.

[45] Carlsson et al. [2006] used the MEX ASPERA/IMA to determine the ratios of escaping O$^+$, O$_2^+$ and CO$_2^+$ ions. They presented distributions of the ratios O$_2^+$/O$^+$ and CO$_2^+$/O$^+$ for 77 ion beam events. For O$_2^+$/O$^+$ the ratio varied from 0.2 to 2.0 with a 97% confidence interval of 0.4–1.4, and an arithmetic mean of 0.9. Carlsson et al. then used the Phobos-2 ASPERA measurements to normalize the escape rate of CO$_2^+$. Thus they suggested that the rates of escape of O$^+$ and O$_2^+$ were comparable, and the ratio of the escape rate of CO$_2^+$ to that of O$^+$ was about 0.2. Barabash et al. [2007] used the IMA on MEX to estimate averaged escape rates of O$^+$, O$_2^+$, and CO$_2^+$ of $1.6 \times 10^{23}$, $1.5 \times 10^{23}$ s$^{-1}$, and $8 \times 10^{22}$ s$^{-1}$, respectively. The O$_2^+$/O$^+$ ratio of 0.9 is in agreement with the investigation of ion mass ratios of Carlsson et al., although the CO$_2^+$/O$^+$ ratio is larger. This difference has been ascribed to the different methods of mass separation used in the two studies. The ratios of the low solar activity escape rates implied by our models of O$_2$ to O$^+$ and of CO$_2$ to O$^+$ are of the order of 12 and 0.9, respectively. The magnitudes of the escape rates measured by the MEX ASPERA-3 as reported by Barabash et al. [2007], are much smaller than the Phobos values. Some of this decrease can be ascribed to solar activity effects.

[46] A comparison of the measured rates to our predicted ion loss rates in Table 2 shows that the measured escape rates are an order of magnitude smaller than our low solar activity predicted escape rates, which are of the order of a few times $10^{24}$ for O$^+$ and CO$_2^+$ and a few times $10^{25}$ s$^{-1}$ for O$_2^+$. The variability in the model escape rates from low to high solar activity is a factor of ~3.

[47] Lundin et al. [2008a] recently used data from 42 orbits of the MEX spacecraft over 17 months to simulate the escape rates of low-energy (30–800 eV) heavy ions, O$^+$, O$_2^+$, and CO$_2^+$, presumably arising from ion outflow. They found short-term variability of an order of magnitude over periods of hours and days, and suggested that the escape fluxes are directly connected to variability of the solar wind, soft x rays, and solar EUV fluxes. They noted a trend of decreasing ion outflow with EUV during the declining phase of solar cycle 23.

[48] Lundin et al. [2008b] described new settings that allow the ASPERA-3 to cover lower ion energies of 10–100 eV. They proposed two kinds of ion escape: that which is associated with ion energies less than 200 eV, and that for ions with higher energies. The low-energy ions were observed to be expanding symmetrically into the tail in a comet-like manner. They suggested that these ions are probably of ionospheric origin, and that the higher-energy ions are probably pickup ions, accelerated above the magnetic anomalies. They reported a rate of heavy ion escape of $3.3 \times 10^{24}$ s$^{-1}$.

[49] These loss rates are an order of magnitude larger than those proposed by Barabash et al. [2007], but consistent with observations of photoelectrons at high altitudes in planetary wake [e.g., Frahm et al., 2006]. A comparison of the O$^+$ loss rates with our predicted low solar activity loss rate of O$^+$ of $2.8 \times 10^{24}$ s$^{-1}$ are consistent. Our predicted O$_2^+$ loss rates are, again, a factor of 8 larger than those derived from the measurements. Lundin et al. [2008b] also suggested that the loss rates at high solar activity could be of the order of $10^{25}$ s$^{-1}$. This is consistent with our solar maximum predicted O$^+$ loss rate of $1.1 \times 10^{25}$ s$^{-1}$, but our predicted O$_2^+$ and total ion loss rates are an order of magnitude larger.

4.3. Comparison to Models of Escape Fluxes

4.3.1. Pickup Ion Escape

[50] Some of the discrepancy between our models and the measurements may arise from the pickup ion escape process, which discriminates against O$_2^+$ and is not included in our models. The traditional definition of pickup ions are those that are produced at high altitudes by ionization of atoms (predominantly O) in the hot atom coronas. The ionization processes include photoinization, solar wind electron impact, and charge exchange with solar wind protons. Other atoms such as C or N may be subject to the same processes, but their coronal densities are expected to be much smaller than that of O. These pickup ions are subsequently accelerated by the convection electric field of the flowing solar wind plasma [Luhmann, 1990; Luhmann et al., 1992]. Some of the pickup ions escape from the gravitational field of the planet, and some reimpact the atmosphere near the exobase producing additional escape by “sputtering”. Luhmann et al. [1992] suggested that up to 90% of the pickup ion number flux reimpacts the atmosphere. These reimpacting ions may be neutralized by exchange, so that the impinging particles may be energetic neutral O as well as O$^+$. The energy range of pickup O$^+$ ions is ~100 eV to ~10 keV. If the pickup ions are traveling horizontally they can produce escaping neutral species by “knock-on” collisions; if they impinge on the atmosphere more vertically they can cause the ejection of a particle through a cascade of collisions. The results of various models of pickup ion escape are summarized in Table 5.

[51] Luhmann and Kozylar [1991] used a test particle model in which O coronal densities taken from Nagy and Cravens [1988] were combined with the gas dynamic model of Spreiter and Stahara [1980] to investigate the pickup ion escape from Venus and Mars. The ionization mechanism was limited to photoionization. Zhang et al. [1993], however, added electron impact by solar wind electrons and charge exchange with solar wind protons as ionization mechanisms. The computed escape rates of O$^+$
showed that the rate of escape due to sputtering [Luhmann and Kozyra [1991], Lammer et al. [1992]] could potentially increase the O\(^+\) escape rate derived for Mars were (0.8–4) \(\times\) 10\(^{21}\) s\(^{-1}\) [Luhmann and Kozyra, 1991], 6 \(\times\) 10\(^{24}\) s\(^{-1}\) [Luhmann et al., 1992] and 4 \(\times\) 10\(^{25}\) [Zhang et al., 1993]. The calculations of Luhmann et al. [1992] showed that the rate of escape due to sputtering by pickup ions was smaller than direct escape of pickup ions by a factor of about 20 at the current epoch, although at prior epochs, loss due to sputtering is predicted to eventually become comparable to pickup ion escape. The coronal hybrid model of Chafray et al. [2007] showed that the O\(^+\) pickup ion escape flux is smaller than the reimpacting flux, especially at low solar activity.

The rate of loss of neutrals due to energetic O\(^+\)/O sputtering has subsequently been modeled by many investigators, including, for example, Luhmann et al. [1992], Zhang et al. [1993], Jakosky et al. [1994], Johnson and Luhmann [1998], Kass [1999], Johnson et al. [2000], Leblanc and Johnson [2001], Cipriani et al. [2007], and Chafray et al. [2007]. The predicted loss rates due to sputtering at the current epoch are in the range 1 \(\times\) 10\(^{22}\) to 3.7 \(\times\) 10\(^{23}\) s\(^{-1}\). Sputtering is capable of removing any species that is present at the Martian exobase, including molecules [Leblanc and Johnson, 2002]. Since the focus of this study is ion escape, we will not discuss these studies further, except to note that the escape rates of neutrals due to sputtering are potentially comparable to escape rates of volatiles as ions.

Recently, most of the estimates of pickup ion escape have been of the order of a few \(\times\) 10\(^{24}\) for O\(^+\) ions. For example, the MHD test particle model of Jin et al. [2001] predicts a range of loss rates of (7.3–19) \(\times\) 10\(^{23}\) s\(^{-1}\). Ma and Nagy [2007] used an MHD model to estimate the importance of pickup ion escape of O\(^+\) by investigating one model (case 1) in which all escape mechanisms were included, and one model (case 5) in which pickup ion escape was excluded. They found that the rate of escape of O\(^+\) was reduced from 3.3 \(\times\) 10\(^{23}\) s\(^{-1}\) to 1.3 \(\times\) 10\(^{23}\) s\(^{-1}\) from case 1 to case 5. This shows that the rate of pickup ion escape is about 2 \(\times\) 10\(^{23}\) s\(^{-1}\), and is larger than escape by ion outflow. Chafray et al. [2007] used a 3-D hybrid model to predict pickup ion escape rates for low and high solar activities of 2 \(\times\) 10\(^{23}\) and 3 \(\times\) 10\(^{24}\) s\(^{-1}\), respectively. Fang et al. [2008] recently constructed a new test particle model to more accurately resolve the Martian pickup ion distribution in velocity space. They used the 3-D MHD model of Ma et al. [2004] (which will be discussed below) to describe the Martian electromagnetic environment. Their neutral thermospheric model included three species: CO\(_2\), O, and H, and the ionosphere included four species: H\(^+\), O\(^+\), O\(_2\), and CO\(_2\). They launched more than a billion test particles, and their predicted total pickup ion escape rate was 3.7 \(\times\) 10\(^{24}\) s\(^{-1}\). Table 5 shows that only the O\(^+\) pickup ion escape rate predicted by Kallio and Koskinen [1999] of 2 \(\times\) 10\(^{25}\) s\(^{-1}\) could potentially increase the O\(^+\) escape flux enough to explain the low ratio of O\(^+\) to O\(_2\) escape derived from our models, which do not include pickup ion escape.

### 4.3.2. Comparison to 3-D Models of Ion Outflow

The rate of ion outflow from the ionosphere of Mars has been modeled by many investigators, and we summarize the results from the last 5 years in Table 6. These investigations represent several varieties of models, including multispecies spherical MHD models [e.g., Ma et al., 2004; Ma and Nagy, 2007], and hybrid codes, in which the electrons are treated as a fluid, and the ions as particles [Modolo et al., 2005; Kallio et al., 2006a, 2006b; Brecht and Ledvina, 2006] There are also models of the Kelvin-Helmholtz instability, which may produce detached plasma clouds near the terminator of the planet [Penz et al., 2004, 2005], and a model of wave-heating that may lead to accelerations of ions to escape speeds [Ergun et al., 2006]. The predicted escape rates pertain to a variety of solar activities, and the results can be seen to range over 2 orders of magnitude. Brecht and Ledvina [2006] have compared some of these models; Ma and Nagy [2007] have commented on some of the models as well. A detailed comparison is beyond the scope of this investigation; we limit ourselves to the remarks below.

Ma et al. [2004] constructed a spherical 3-D four-species MHD code that included the remanent crustal magnetic fields to study the interaction of the solar wind with Mars. Their model has a spherical grid structure that allows fairly fine resolution (10 km) in the ionosphere. They computed the density profiles of H\(^+\), O\(^+\), O\(_2\), and CO\(_2\) over the region 100 km to 10 Mars radii, and escape rates for the three ions for two low solar activity and two high solar activity models. Their predicted escape rates are shown in Table 6 as a range for these two low and two high solar activity models. Ma and Nagy [2007] improved the model by incorporating the neutral densities from the MTGCM of S. Bougher, rather than assuming that the neutral densities were spherically symmetric. Their computed escape rates are of the order of a few times 10\(^{23}\) s\(^{-1}\) for O\(^+\), and the escape rates of O\(_2\) are only slightly smaller for low solar activity. At high solar activity, the escape rates of O\(^+\) exceed those of the molecular ions significantly. This is a direct reflection of the model ion densities, which predict that O\(^+\) and O\(_2\) are comparable on the topside of the low solar activity model, but O\(^+\) exhibits a prominent peak at high altitudes. In our models, O\(_2\) is the dominant ion at all altitudes at both low and high solar activities.

We can also compare our high solar activity estimated maximum escape rates to those computed by Ma and Nagy [2007] for extreme solar wind conditions. Our maximum ion escape rates at high solar activity are 1.8 \(\times\) 10\(^{23}\), 8.5 \(\times\) 10\(^{22}\),

### Table 5. Model Rates of Pickup Ion Escape From Mars

<table>
<thead>
<tr>
<th>Rate (s(^{-1}))</th>
<th>Species</th>
<th>Model</th>
<th>Reference</th>
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<tr>
<td>(8/22)–(4/23)(^a)</td>
<td>O(^+)</td>
<td>test particle/gas</td>
<td>Luhmann and Kozyra [1991]</td>
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<td>O(^+)</td>
<td>test particle</td>
<td>Luhmann et al. [1992]</td>
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<td>O(^+)</td>
<td>2-stream</td>
<td>Zhang et al. [1993]</td>
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<td>(1.2–17.5)(24)(^b)</td>
<td>O(^+)</td>
<td>gas dynamic</td>
<td>Lichtenegger and Dubinin [1998]</td>
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<tr>
<td>~2(25)</td>
<td>O(^+)</td>
<td>3-D test particle</td>
<td>Kallio and Koskinen [1999]</td>
</tr>
<tr>
<td>7.4(23)–1.9(24)(^c)</td>
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<td>MHD/test particle</td>
<td>Jin et al. [2001]</td>
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<tr>
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<td>gas dynamic/</td>
<td>Lammer et al. [2003]</td>
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<tr>
<td>1.2(25)</td>
<td>H(^+)</td>
<td>test particle</td>
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<td>H(_2)</td>
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<td></td>
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<tr>
<td>2(23)–3.5(24)(^d)</td>
<td>O(^+)</td>
<td>coronal/hybrid</td>
<td>Chafray et al. [2007]</td>
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<td>3.7(24)</td>
<td>O(^+)</td>
<td>MHD/test particle</td>
<td>Fang et al. [2008]</td>
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</table>

\(^a\)Read as 4 \(\times\) 10\(^{23}\).
\(^b\)For variable size obstacle.
\(^c\)Variation of exobase altitudes from 250 to 300 km.
\(^d\)Solar Activity Variation.
\(^e\)Chamberlain (spherically symmetric) coronal model.
\(^f\)The 3-D multispecies single fluid MHD model from Ma et al. [2004].


<table>
<thead>
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<th>Species</th>
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<td>O⁺</td>
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</tr>
<tr>
<td>Total</td>
<td>(1.7–2.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>(2.23–3.24)</td>
<td>K-H instability ²</td>
<td>Penz et al. [2004]</td>
</tr>
<tr>
<td>H⁺</td>
<td>(4.28–1.14)</td>
<td>3-D hybrid model</td>
<td>Modolo et al. [2005]</td>
</tr>
<tr>
<td>O⁺</td>
<td>(0.52–2.37)</td>
<td>low SA–high SA</td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>(5–7)</td>
<td>mostly pickup ions</td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>~1.25</td>
<td>plasma wave heating</td>
<td>Ergun et al. [2006]</td>
</tr>
<tr>
<td>O⁺</td>
<td>1.38(25)</td>
<td>pickup + ion outflow ²</td>
<td>Kallio et al. [2006a]</td>
</tr>
<tr>
<td>O⁺</td>
<td>1.38(24)</td>
<td>ion outflow only</td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>5(25)</td>
<td>hybrid model</td>
<td>Brecht and Ledvina [2006]</td>
</tr>
<tr>
<td>O⁺</td>
<td>1.3(25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>(3.3–7.2)</td>
<td>MHD², low SA</td>
<td>Ma and Nagy [2007]</td>
</tr>
<tr>
<td>O₂</td>
<td>(1–2.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>(0.57–1.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>1.8(24)</td>
<td>high SA</td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>4.1(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.8(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O⁺</td>
<td>2.3(25)</td>
<td>extreme SW⁶ conditions</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>3.3(24)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>4.1(24)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹Read as (2.5–8.4) × 10⁻²⁵.
²Three-dimensional multispecies single fluid MHD; neutral densities are spherically symmetric.
³SA, Solar Activity.
⁴Kelvin-Helmholtz Instability.
⁵Three-dimensional four-species quasi-neutral hybrid model.
⁶Four-species spherical MHD model; neutral densities from MTGC model of Bougher et al. [2006].
⁷SW, Solar Wind.

and 9.5 × 10⁻²⁴ s⁻¹ for O⁺, O₂⁺, and CO₂⁺ escape, respectively. These values include the factor of 0.5 reduction to account for the ions that converge and flow downward over the nightside, presumably producing a nightside ionosphere. Ma and Nagy [2007] computed a maximum escape flux of 2.3 × 10⁻²³ s⁻¹ for O⁺, in substantial agreement with our predicted value, but in contrast to the maximum rate of escape of 3.3 × 10⁻²⁴ s⁻¹ for O₂⁺, which is smaller than our value by a factor of 25. Again, the major difference appears to arise from the ion density profiles of O⁺ and O₂⁺ in our 1-D model and those in the MHD 3-D models. The rates of escape of CO₂ differ from those of Ma and Nagy [2007] by a factor of ~2.

Brecht and Ledvina [2006] constructed a hybrid model in which they used the same neutral density profiles as Ma et al. [2004], the same ionospheric chemical scheme, and an altitude resolution of 20 km in the ionosphere. Their computed escape rates are, however, about an order of magnitude larger than those of Ma et al. [2004], and their total escape fluxes are of the same order of magnitude as our high solar activity values. The ratios of the O⁺ to O₂⁺ fluxes, however, are more like those of Ma et al. [2004] than those we predict. This is a direct reflection of their adoption of thermosphere/ionosphere model of Ma et al. [2004]. Brecht and Ledvina [2006] also showed that the ion escape rates are highly asymmetric in space.

5. Summary and Conclusions

In this investigation, we construct 84 low solar activity and 93 high solar activity models of the Martian ionosphere. These models vary only in the assumed upward velocity boundary condition on the ions, which ranges from 0 to 7 × 10⁵ cm s⁻¹ for the low solar activity model, and from 0 to 8 × 10⁵ cm s⁻¹ for the high solar activity model. The topside scale height in the models is found to decrease as the upward velocity increases. For each model, we compute the upward fluxes by multiplying the ion densities at the top of the model ionosphere by the assumed upward velocity boundary condition. We show that for small upward velocities, the fluxes increase fairly linearly, while for larger upward velocities, the ion densities at the top of the model decrease, partially offsetting the increase in velocities. Eventually the modeled fluxes as a function of velocities for the major ions are observed to “flatten out”, indicating that the increases in the velocities are more or less completely offset by decreases in the ion densities, and that near maximum fluxes are reached. These maximum fluxes are shown in Table 1 for 12 ions for both low and high solar activity models.

We also compare the computed ion and electron density profiles with existing measurements to estimate the actual upward fluxes of ions. To demonstrate the method, the profiles we have analyzed here are limited to the Viking 1 ion density profile for low solar activity, and the Mariner 6 and 7 radio occultation electron density profiles for high solar activities. The predicted upward velocities are 1 × 10⁵ cm s⁻¹ at low solar activity, and (4–7) × 10⁵ cm s⁻¹ at high solar activity. The upward fluxes for 12 ions implied by these velocities are also shown in Table 1 as “predicted” fluxes. These fluxes may contribute to ion outflow, and/or to the formation of the nightside ionosphere by ion transport.
If we make the assumption that our 60° SZA models are averages over the dayside, we can compute the total loss rate of ions by multiplying the fluxes by the area of the dayside hemisphere. A comparison of our predicted and maximum loss rates for O\(^+\), O\(_2\), CO\(_2\), and H\(^+\) are shown in Table 2. These “loss rates” may not represent true escape because some of the ions, especially at low altitudes, may flow across the terminator, where they converge and flow downward, producing a nightside ionosphere. Ma et al. [2004] have provided predictions of the fraction of the transterminator fluxes of ions that leads to escape, and values of the order of ~5% were reported. When we compared the predicted escape rates to measurements or models, we find that the values for O\(^+\) escape are similar to those derived from measurements and models. Our predicted O\(_2\) escape rates are, however, larger that those for O\(^+\) by an order of magnitude.

Investigations based on the data measured by instruments on the Phobos-2 spacecraft and the ASPERA/IMA on MEX generally showed that the loss rates of O\(^+\) are larger than or comparable to those of O\(_2\) [e.g., Carlsson et al., 2006; Barabash et al., 2007; Lundin et al., 2008a, 2008b]. Some of the IMA mass spectra presented by Lundin et al. [2006] show that O\(_2\) is the dominant ion detected, although O\(^+\) and CO\(_2\) are comparable. Lundin et al. [2008a, 2008b; also R. Lundin, private communication, 2009] have examined 800 individual samples, however, and although the average densities of O\(^+\) and O\(_2\) detected by the ASPERA/IMA slightly favor O\(^+\), the median values indicate that the O\(_2\)/O\(^+\) ratio is about 2.

There are several possibilities for explaining the discrepancy between the measured densities, those of MHD and hybrid models, and our model escape fluxes. We noted that pickup ion escape favors O\(^+\), and effectively discriminates against O\(_2\). Modeled values of the rates of O\(^+\) pickup ion escape, which are summarized in Table 5, are significant. If these values are added to our estimated escape rates of O\(^+\) by ion outflow, however, the total O\(^+\) escape rates are still much less than our estimates of the O\(_2\) ion outflow rates. We also describe the 3-D quasi-neutral hybrid model of Kallio et al. [2006a, 2006b], which showed that the total emission rate from the Martian “obstacle” boundary of O\(^+\) and O\(_2\) were comparable, ~1.4 × 10\(^{-3}\) s\(^{-1}\) and ~2 × 10\(^{25}\) s\(^{-1}\) respectively. In addition, the O\(^+\) escape rate originating from the corona was computed as ~2.7 × 10\(^{25}\) s\(^{-1}\). The computed average total ion loss rates, however, were 1.4 × 10\(^{-3}\) s\(^{-1}\) for O\(^+\) and 1.4 × 10\(^{-24}\) O\(_2\) ions. Kallio et al. thus suggested that almost all the O\(_2\) ions emitted from the Martian obstacle return to the obstacle. They proposed that this difference in the behavior of the O\(^+\) and O\(_2\) ions is the result of differences between the masses and gyroradii of the two ions. If this analysis is valid, it could aid in explaining the discrepancy in the computed loss rates of O\(_2\) and the observed loss rates. We do not here postulate a loss mechanism; our goal is to estimate the outward fluxes from the morphology of the Martian dayside ionosphere, and we do not distinguish between ion outflow and fluxes that converge and flow downward on the nightside of the plant. This explanation is inconsistent, however, with the results of the MHD model of Ma et al. [2004], which suggested that the ratios of the transterminator fluxes to the escape fluxes are of the order of two, and do not vary significantly for O\(^+\), O\(_2\), and CO\(_2\).

Another possibility to reconcile our model with the observed fluxes is that the acceleration mechanism, which we do not address here, is mass-selective. This has been suggested also by Carlsson et al. [2006], and by Ergun et al. [2006], who have adduced evidence that plasma wave heating in the upper ionosphere can lead to loss of ~10\(^{-25}\) s\(^{-1}\) O\(^+\) ions from Mars. Since the heating rate is inversely proportional to the mass, and O\(_2\) requires twice the energy to escape from Mars, this mechanism discriminates against O\(_2\) to an unknown extent.

We note here, however, that the model ionosphere that Ergun et al. [2006] use is similar to that proposed by Penz et al. [2005], Penz et al. [2005] obtained their neutral thermospheric model from Shinagawa and Cravens [1989] and coupled it with the chemistry scheme of Terada et al. [2002]. Their model ionosphere for the subsolar point showed that O\(^+\) densities exceed those of O\(_2\) near 250 km, and that the O\(^+\) peak density is ~2000 cm\(^{-3}\) near 300 km.

The photochemical model of Ma et al. [2004] also shows that O\(^+\) dominates at high altitudes at high solar activity. In two of the models, a prominent F\(_2\) peak is observed. Brecht and Ledvina [2006] used the same thermosphere/ionosphere model as that of Ma et al. [2004]. These models are in many ways unlike our 1-D photochemical/diffusion models, in which we find that the O\(_2\) densities exceed those of O\(^+\) over the entire ionosphere, including in the region of the O\(^+\) peak. In our high solar activity models, the O\(^+\) peak density is ~1600–2500 cm\(^{-3}\), in quite good agreement with these models, but the peak is near 260 km in our model, and between 300 and 400 km in the models of Penz et al. [2005] and Ma et al. [2004]. The O\(^+\) peak in our model appears roughly at the altitude where the time constant for chemical loss is equal to that for loss by diffusion, that is, at the O\(^+\) PCE boundary. Our PCE boundary is apparently lower than those of the models of Ma et al. [2004] and Penz et al. [2005]. It is possible that this is due to vertical diffusion due to the presence of magnetic fields, or other phenomena that are not included in our 1-D models. We note, however, that the Mariner 6 and 7 ion density profiles do not exhibit clear evidence of an F\(_2\) peak. Fjeldbo et al. [1970] noted that the scale height of the electron density profiles seemed to increase above an altitude of 250 km, and our models also show this effect, which is due to the large gradient in the plasma temperature profiles.

In our models, the O\(_2\) density exceeds that of O\(^+\) up to at least 400 km. Although we reproduced the Viking O\(^+\) density profiles quite well in the past, [cf. Fox, 1993], as the chemistry of the models has become more complicated, the O\(^+\) densities have been reduced. Additional loss processes for O\(^+\) have been included in our current model, such as reactions with H and H\(_2\). These reactions are more important at low solar activity than at high solar activity, because the H densities are larger at low solar activity. We also note that the predicted high-altitude densities of H and H\(_2\) are greatly dependent on the adopted eddy diffusion coefficients.

As we pointed out previously, the S2K v2.24 solar fluxes of Tobiska [2001, 2004] that we use have been found to produce smaller ionization rates of all species than the S2K v1.24 solar fluxes. We have tested different solar flux spectra by computing ionospheric models using the S2K
the atomic O mixing ratios have been predicted from the ratio of O\textsuperscript{2} to CO\textsubscript{2} in the model compared to the measured value [Hanson et al., 1977]. Values of 1–2% near 130 km have been proposed [Hanson et al., 1977; Fox and Dalgarno, 1979]. Figure 8 shows that our current model, in which the O mixing ratio is 2% near 130 km, reproduces quite well the CO\textsubscript{2} and O\textsubscript{2} densities measured by the Viking I RPA. There is little support for larger O mixing ratios. In fact, Stewart et al. [1992] derived an even smaller O abundance of 0.7% at the ion peak from an analysis of intensities of the O 1304 Å triplet, as measured by the Mariner 9 ultraviolet spectrometer.

It appears that we must both increase the altitude of the O\textsuperscript{2} peak, and increase the loss rates of O\textsuperscript{2} in order to produce densities that are less than that of O\textsuperscript{2} at high altitudes. One such mechanism, but not one that we would favor, would be to reduce the electron temperatures near 200 km. This would have the effect of increasing the loss rate of O\textsuperscript{2} by dissociative recombination, which has an inverse temperature dependence. Since the electron temperatures reported by Hanson and Mantas [1988] were confined to high altitudes, and were admittedly subject to some error, there is some flexibility in this area, although not a great deal. It is possible that the discrepancies between the ion density profiles of the 3-D models and those in our 1-D models are due to horizontal motions, restricted vertical motions, or magnetic fields, that are not included in our 1-D models. We will address the differences between our photochemical/diffusion models and the three dimensional ionospheric models in a future investigation.

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