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Jane L. Fox

Wright State University - Main Campus, jane.fox@wright.edu

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Effect of H₂ on the Martian ionosphere: Implications for atmospheric evolution

J. L. Fox¹

Institute for Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook, Stony Brook, New York, USA

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[1] Because H₂ reacts efficiently with O⁺, CO₂⁺, CO⁺, and N₂⁺, the molecular hydrogen abundance assumed in models of the Martian ionosphere greatly affects the high altitude density profiles of these ions. We have found that models of the low solar activity Martian ionosphere exhibit much smaller O⁺ densities than the measured values if the adopted H₂ abundance is of the order of 40 ppm, the value proposed in a 1998 model of the Martian atmosphere. For a model based on the recently measured H₂ abundance of 15 ppm [Krasnopolsky and Feldman, 2001a, 2001b], the O⁺ densities are closer to, but still somewhat less than the Viking densities. The O⁺ peak densities of ~600–750 cm⁻³ measured by the retarding potential analyzers on Vikings 1 and 2 [Hanson *et al.*, 1977] are best reproduced with H₂ abundances less than ~4 ppm. We have investigated the effect of various H₂ mixing ratios at the lower boundary of our model, and we find that the high altitude densities of O⁺, CO₂⁺, CO⁺, and N₂⁺ ions decrease as the H₂ abundance increases, and are much less for H₂ mixing ratios greater than 4 ppm than previous models have shown. Moreover, the photochemical escape rates of heavy atoms, such as C and N that are due to reactions of these ions, are also reduced. The Martian atmosphere was probably more reducing in past epochs, and therefore consisted of a larger fraction of H₂. As the abundance of H₂ increases, the composition of the exosphere will also be altered, and the altitude of the exobase will rise. At very large mixing ratios, H and H₂ could potentially dominate the absorption of EUV radiation. Thus the escape of species by other photochemical mechanisms such as photodissociation and photodissociative ionization could also be reduced. If so, the nonthermal escape rates of heavy atoms in past epochs may have been much lower than previous estimates in which it is assumed that the oxidation state of the Martian atmosphere has remained constant over time. *INDEX TERMS:* 5405

Planetology: Solid Surface Planets: Atmospheres—composition and chemistry; 5407 Planetology: Solid Surface Planets: Atmospheres—evolution; 2459 Ionosphere: Planetary ionospheres (5435, 5729, 6026, 6027, 6028); *KEYWORDS:* Martian ionosphere, nonthermal escape, evolution of atmospheres, hydrogen abundance on Mars

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1. Introduction

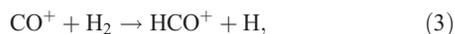
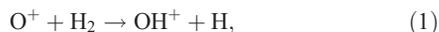
[2] The H densities at high altitudes in the Martian thermosphere and the corresponding escape rates have been inferred from the 1216-Å Lyman alpha dayglow intensities measured by the Mariner spacecraft and by the Hubble Space Telescope (HST). Krasnopolsky *et al.* [1998] [see also Krasnopolsky, 2000] measured the Lyman alpha emission rates from Mars using HST data and derived H density profiles at low solar activity. These data complement the

existing information on H densities and escape rates from Lyman alpha intensities measured by the Mariner 6 and 7 spacecraft, which flew by Mars at higher solar activity, and by Mariner 9, which orbited the planet at moderate solar activity [Anderson and Hord, 1971; Barth *et al.*, 1972; Anderson, 1974]. When this investigation was first presented in May, 2001 [Fox, 2001], and originally submitted for publication, there were no reported measurements of the H₂ abundance on Mars. On July 12, 2001, in an IAU Circular, Krasnopolsky and Feldman [2001a] reported the first detection of H₂ from a UV spectrum taken by the Far Ultraviolet Spectroscopic Explorer. The reported H₂ mixing ratio, ~20 ppm, was subsequently revised to 15 ± 5 ppm [Krasnopolsky and Feldman, 2001b]. Prior to this measurement, H₂ density profiles that were consistent with the upper atmospheric H profiles and with the H₂O abundances in the

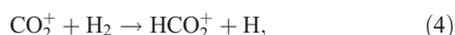
¹Also at Department of Physics, Wright State University, Dayton, Ohio, USA.

lower atmosphere had been modeled by several investigators. Krasnopolsky and co-workers modeled the Martian atmosphere for several levels of solar activity and derived H₂ abundances of 40 ppm [Krasnopolsky *et al.*, 1998; Krasnopolsky, 2000], and 56 ppm [Krasnopolsky, 1993b], compared to values from other models of 36 ppm [Nair *et al.*, 1994], 7.5 ppm [Rodrigo *et al.*, 1990], 10 ppm [Kong and McElroy, 1977], and 20 ppm [Anderson, 1974]. Some of the earlier measurements were based on assumptions that are now known to be inaccurate.

[3] H₂ interacts with O⁺, N₂⁺, CO⁺ and CO₂⁺ through the reactions



and



which are destruction mechanisms both for the ions and for H₂, as well as production mechanisms for H. The rate coefficients for reactions (1–4) are very large: 1.35×10^{-9} [Li *et al.*, 1997], 1.52×10^{-9} [Uiterwaal *et al.*, 1995], 1.5×10^{-9} , and 8.7×10^{-10} cm³ s⁻¹ [Scott *et al.*, 1997], respectively. The dominant ion O₂⁺ does not react with H₂, and its density profile is not much impacted by changes in the H₂ abundance.

[4] Most of the existing models of the Martian atmospheric hydrogen have considered to some extent the interaction of ions with H and H₂. The early ionospheric models of Krasnopolsky [1993a, 1993b] were photochemical equilibrium models, which could not be expected to produce realistic O⁺ profiles. Nair *et al.* [1994] noted some differences in their ion density profiles with the Viking measured values [Hanson *et al.*, 1977], but attributed them to their rudimentary reaction set and to the conditions in their model, which were somewhat different from those of Viking 1. Rodrigo *et al.* [1990] used the CO₂⁺ profiles measured by Viking in their model to determine the source of H from reaction of H₂ with CO₂⁺, but did not compute the O⁺ density profiles. Krasnopolsky and Feldman [2001a, 2001b] recently constructed an updated ionospheric model and reported H and H₂ profiles. More details were provided in a presentation by Krasnopolsky [2002].

[5] In our recent low and high solar activity models of the thermosphere/ionosphere [cf. Fox and Bakalian, 2001], we tentatively adopted the H₂ mixing ratio of 40 ppm at 80 km that was suggested by Krasnopolsky *et al.* [1998]. We have also constructed a low solar activity model with 15 ppm H₂. These models are based on the revised set of chemical reactions for the thermospheres/ionospheres of oxidizing atmospheres presented by Fox and Sung [2001]. Figure 1 shows the density profiles of the neutral species in our 40 ppm and 15 ppm H₂ standard models. In the 40 ppm H₂ model, the computed O⁺ peak density of ~ 300 cm⁻³ is less than half of the values of ~ 600 – 750 cm⁻³ implied by

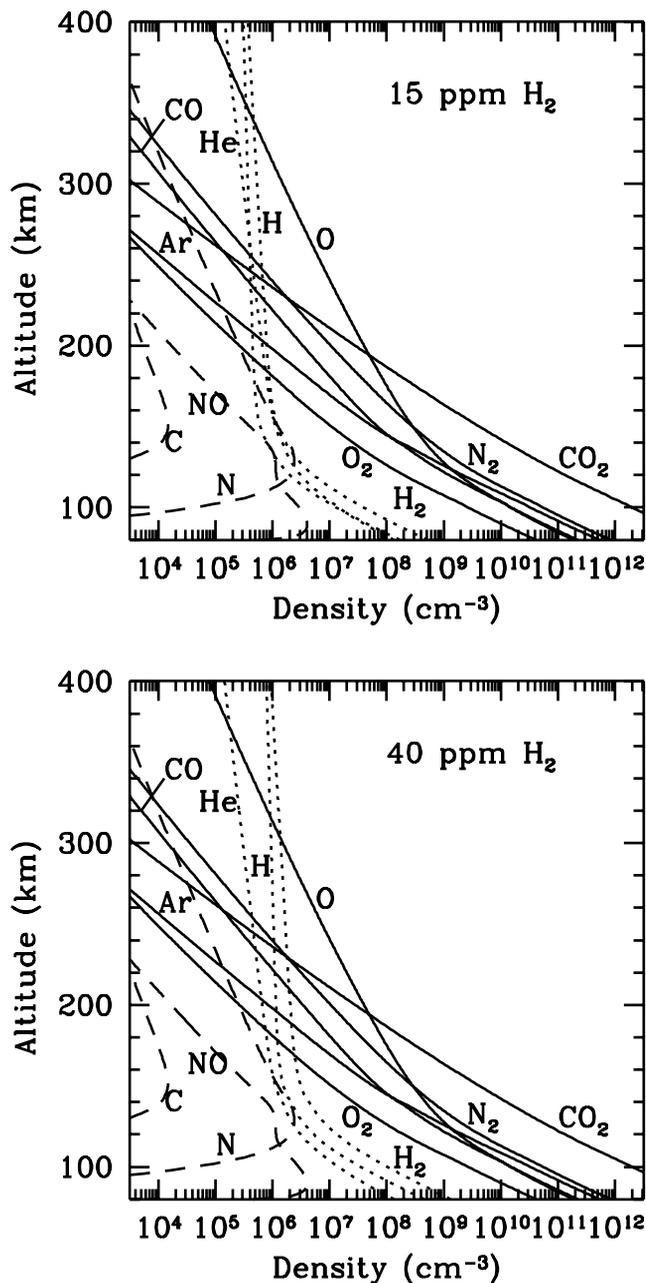


Figure 1. Density profiles of neutral species in the low solar activity model of the Martian thermosphere for H₂ mixing ratios at the lower boundary of (top) 15 and (bottom) 40 ppm.

the Viking RPA measurements, and for the 15 ppm H₂ model, the O⁺ peak density is ~ 430 cm⁻³, which is also significantly less than the Viking measured values. Previous low solar activity models, which did not include H₂, had shown excellent agreement with the Viking measured values [e.g., Fox, 1993a, 1997]. Figure 2 shows the ion density profiles for our standard models, with a comparison to the Viking O⁺ profile. The O mixing ratio at 130 km for the low solar activity models is inferred from the Viking RPA densities of O₂⁺ and CO₂⁺ at 130 km, and is different from the Mariner 9 ultraviolet spectrometer measurements of the 1304 Å emission [Stewart *et al.*, 1992], which are a

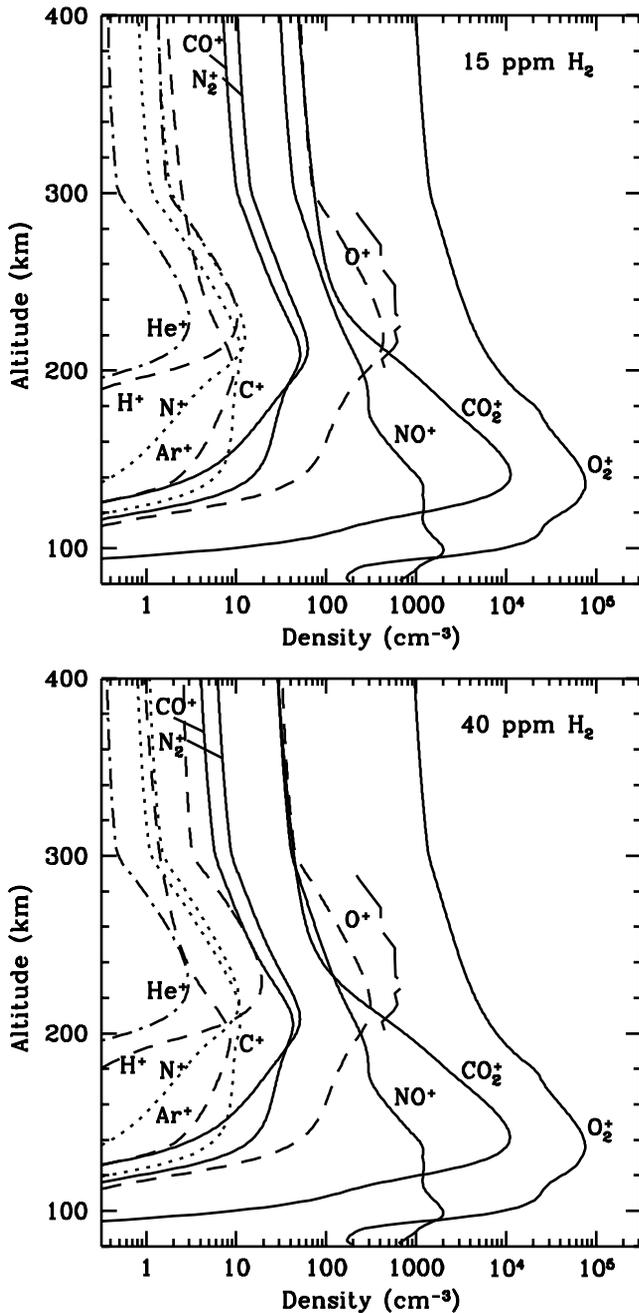


Figure 2. The computed ion density profiles for the neutral density models shown in Figure 1. The Viking 1 O⁺ density profile (long dashed curve) from *Hanson et al.* [1977] is also shown for comparison.

factor of 2–3 less than those assumed here. The difference between our computed O⁺ densities and the density profile measured by Viking is large even though our H₂ density profile for the 40 ppm model falls off more rapidly with altitude than that presented by *Krasnopolsky et al.* [1998]. The H₂ density at 250 km in our 40 ppm model is 1.6×10^6 cm⁻³, compared to 6×10^6 cm⁻³, determined by *Krasnopolsky et al.* [1998]. The difference in the shape of the H₂ profiles is difficult to determine, but is probably due in part to the larger rate coefficient for reaction of H₂ with CO₂⁺ that we have adopted, and may also be due to differences in

the eddy diffusion coefficient profiles in the models. For the 15 ppm H₂ model, the H₂ density at 250 km is 6×10^5 compared to about 4×10^5 cm⁻³ in the model by *Krasnopolsky and Feldman* [2001a, 2001b]. The model density is now larger than that of *Krasnopolsky and Feldman*, but the difference is smaller and than in the previous models.

[6] We have constructed models of the Martian thermosphere/ionosphere for H₂ mixing ratios of 4, 10, 15, 40 and 100 ppm at the lower boundary (80 km). For the calculations presented here, we employed upward flux boundary conditions on H₂, since it is transported from the lower atmosphere, and destroyed in the thermosphere. The results are nearly identical for fixed density lower boundary conditions on H₂, because even if the density is fixed, an upward flux exists in order for steady state to be achieved. Although larger H₂ abundances imply larger H densities, the relationship is not straightforward and accurate modeling requires the inclusion of the chemistry of HCO⁺, HCO₂⁺, OH⁺, and N₂H⁺. Furthermore, thermospheric production is a source of H to the lower atmosphere. In these models, we made the simplification that the bottom boundary condition for H was fixed to the about 1/3 the density of H₂ at that altitude, which was the ratio that reproduced the density of H at 250 km (about 1.4×10^6 cm⁻³) implied by the HST Lyman alpha measurements, as modeled by *Krasnopolsky et al.* [1998]. Thus since the H density profiles are not modeled, a high level of accuracy is not assigned to them. In any case, the H densities are not central to the conclusions we draw here. The H₂ density profiles, which were computed self-consistently with the ion and neutral density profiles, for the five models are shown in Figure 3, along with the background density

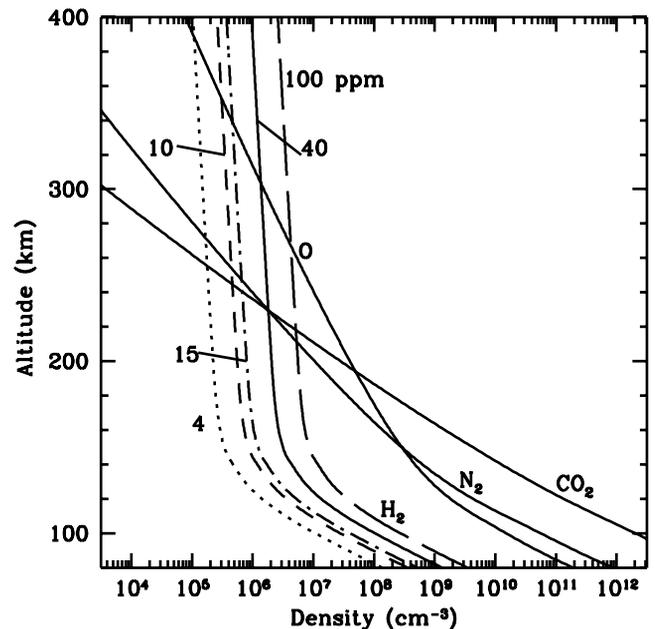
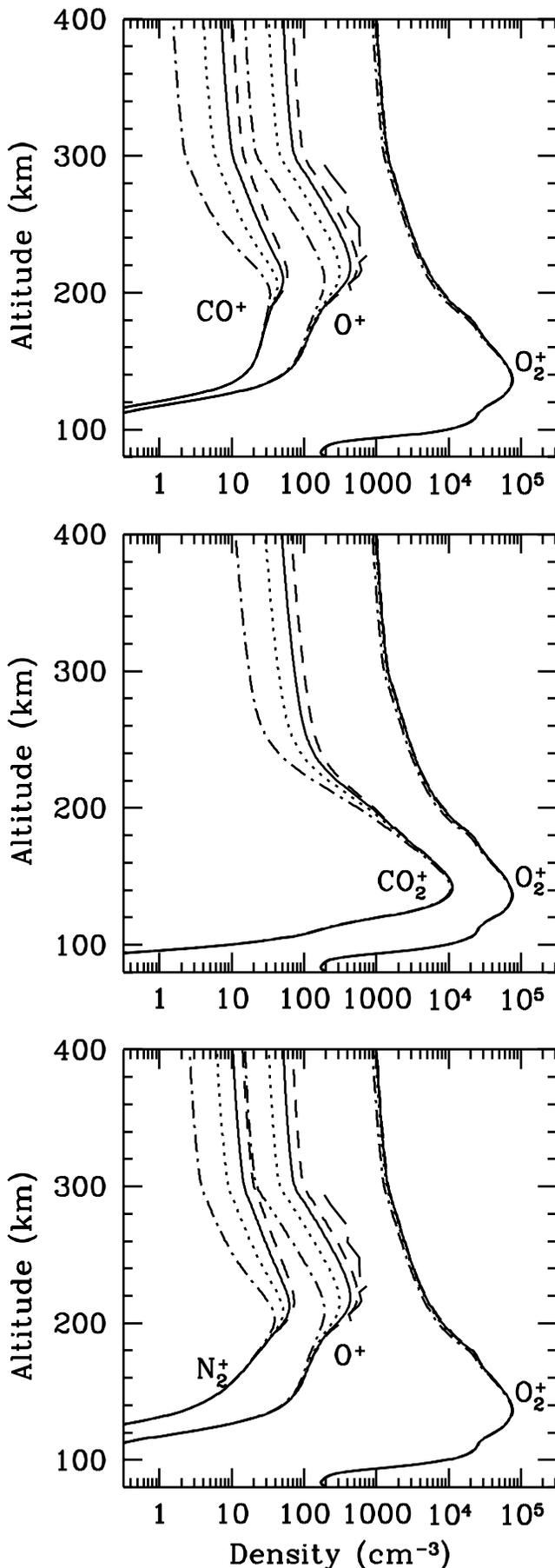


Figure 3. Density profiles of H₂ for models with mixing ratios of 4, 10, 15, 40 and 100 ppm H₂. The CO₂, N₂, and O profiles are shown for reference. The H₂ density profiles were computed self-consistently with the ion density profiles.



profiles of CO₂, N₂, and O for comparison. In the three panels of Figure 4, we present the density profiles of O⁺, CO₂⁺, N₂⁺, and CO⁺ for mixing ratios of 4, 15, 40 and 100 ppm H₂, compared to the O⁺ profiles measured by Viking. As Figure 4 shows, the Viking measured peak O⁺ density can only be approached with mixing ratios of the order of 4 ppm or less, and the high altitude densities of CO₂⁺, N₂⁺, and CO⁺ are also significantly depleted as the assumed H₂ abundance increases.

2. Martian Atmosphere at Previous Epochs

[7] The theory that O and H escape from Mars in the stoichiometric proportions of water, the “balanced escape” hypothesis, which was proposed by *McElroy* [1972] and *McElroy et al.* [1977], was almost universally accepted for two decades. It is interesting to note, however, that the inspiration for the hypothesis was an erroneous estimate for the escape rate of O in dissociative recombination of O₂⁺, which was accidentally approximately equal to half the estimated H escape rate. Recently the escape rates of atomic oxygen have been found to be much smaller than half the H escape rates, and the balanced escape hypothesis has thus been called into question [*Lammer and Bauer*, 1991; *Fox*, 1993b; *Zhang et al.*, 1993; *Luhmann*, 1997; *Lammer et al.*, 1996]. (It should be noted, however, that these small O escape rates have been disputed recently by *Hodges* [2000].) It is also possible that the imbalance in the O and H escape rates may be temporary; *McElroy* [1972] and *McElroy et al.* [1977] proposed that the balance is achieved on a timescale of 10⁵ years. Direct escape of O in ions may provide the missing escape flux, but the magnitude of the ion escape flux can only be estimated at this time [*Fox*, 1997; *Liu et al.*, 2001; *Ma et al.*, 2002]. It has been suggested that oxidation of the surface supplements the escape to space, and that the total imbalance may be small or zero. Even a small imbalance, will, however, change the oxidation state of the atmosphere over timescales of billions of years. That the atmosphere of Mars was reducing at earlier times is, in any case, quite likely, just as was the primordial atmosphere of the Earth [e.g., *Sagan and Chyba*, 1997; *Kasting*, 1997]. A reducing atmosphere on early Mars seems necessary to provide a greenhouse effect capable of raising the temperature of atmosphere to a value sufficient to support liquid water on the surface [e.g., *Squyres and Kasting*, 1994; *Sagan and Chyba*, 1997]. If so, the H₂ abundance in the bulk atmosphere will have been larger in past epochs.

[8] The effect of H₂ on the model ion density profiles implies that if the H₂ densities were larger in the past, the escape rates of heavy atoms due to reactions of these ions would also be reduced. For example, decreased densities of

Figure 4. (opposite) The density profiles of molecular ions and O⁺ for various abundances of (top) H₂: CO⁺ and O⁺; (middle) CO₂⁺; and (bottom) N₂⁺ and O⁺. In all three panels the H₂ abundances are represented as follows: 4 ppm H₂ (dashed curves), 15 ppm H₂ (solid curves), 40 ppm H₂ (dotted curves), and 100 ppm (dash-dot curves). The O⁺ density profile measured by Viking 1 [*Hanson et al.*, 1977] is shown as a long dashed curve.

Table 1. Exobase Altitude as a Function of H₂ Mixing Ratio

H ₂ Mixing Ratio, ppm	Exobase Altitude, km
4	188
10	189
15	190
40	193
100	206

CO⁺ and N₂⁺ lead to smaller rates of dissociative recombination of these ions:



which are major sources of escaping N and C atoms [e.g., *Fox*, 1993a, and references therein; *Fox and Hać*, 1997; *Fox and Bakalian*, 2001]. Furthermore, as the H₂ abundances increase, the altitude of the exobase will rise, and the escape fluxes due to processes such as photodissociation also will be smaller.

[9] To illustrate this effect, we have adopted the simple, but traditional assumption that the exobase is located where the total column density is $3.3 \times 10^{14} \text{ cm}^{-2}$, which corresponds to a collision cross section of $3 \times 10^{-15} \text{ cm}^2$, and we have identified the altitude of the exobase for the 5 models described above. The results in Table 1 show that the exobase rises from 188 to 206 km as the H₂ mixing ratio increases from 4 to 100 ppm. We have also computed the global average escape fluxes of C for these four models due to photodissociation of CO, electron-impact dissociation of CO, and dissociative recombination of CO⁺; the results are given in Table 2. Near the exobase, the dissociative recombination of CO⁺ is assumed to produce C atoms with energies in excess of the escape energy 63% of the time [cf. *Fox and Hać*, 1999]. The global average escape fluxes of N due to photodissociation of N₂ and to dissociative recombination of N₂⁺ are given in Table 3. In computing the escape flux due to dissociative recombination of N₂⁺, a fraction 0.20 of the dissociative recombinations reactions were assumed to produce N atoms with energies in excess of the escape energy [cf. *Fox and Hać*, 1997]. For photodissociation, the major impact is from the increase in the exobase altitude, so the effects on the escape fluxes are moderate except for the 100 ppm model. As the mixing ratio of H₂ in the model increases from 4 to 100 ppm, the escape fluxes due to photodissociation decrease by a factor of

Table 2. Escape Fluxes of C ($10^4 \text{ cm}^{-2} \text{ s}^{-1}$) as a Function of H₂ Mixing Ratio for Various Escape Mechanisms

Mixing Ratio, ppm	CO + hν	CO + e	CO ⁺ + e
4	16.5	0.69	4.8
10	15.7	0.64	4.2
15	14.9	0.60	3.7
40	12.7	0.49	2.4
100	6.4	0.21	0.67

Table 3. Escape Fluxes of N ($10^4 \text{ cm}^{-2} \text{ s}^{-1}$) as a Function of H₂ Mixing Ratio for Two Escape Mechanisms

Mixing Ratio ppm	N ₂ + hν	N ₂ ⁺ + e
4	19	3.6
10	18	3.1
15	17	2.8
40	14	1.9
100	6.2	1.3

almost 3. For larger H₂ abundances, the rates of photodissociation of molecules could be reduced due to absorption of photons by H and H₂, but for H₂ mixing ratios up to 100 ppm, we find that the photodissociation rates of CO and N₂ themselves are reduced very little. The effects of the increase in the exobase altitude and the decrease in the ion densities at high altitudes combine to produce more dramatic effects on the escape flux due to dissociative recombination of molecular ions; the reduction in the escape fluxes as the H₂ abundance increases from 4 to 100 ppm is a factor of 3 for CO⁺ dissociative recombination and a factor of 7 for N₂⁺ dissociative recombination.

3. Summary and Conclusions

[10] We have constructed models of the Martian thermosphere/ionosphere for H₂ mixing ratios of 4, 10, 15, 40 and 100 ppm H₂, and we have calculated the ion density profiles for these models. We find that the density profiles of O⁺, N₂⁺, CO⁺, and CO₂⁺ are greatly influenced by the assumed H₂ mixing ratio in models of the Martian ionosphere. The Viking O⁺ peak densities reported by *Hanson et al.* [1977] cannot be reproduced in our models with H₂ abundances of more than ~ 4 ppm. We have shown that increasing mixing ratios of H₂ lead also to significantly smaller high altitude densities of N₂⁺, CO⁺, and CO₂⁺. The escape fluxes of C and N are reduced as the H₂ abundance increases, owing both to the decrease in the high altitude molecular ion densities and to the rise of the exobase as H₂ and H become more important species in the exosphere.

[11] Our analysis has incorporated many simplifications. For example, we have assumed that the exobase is located at a constant column density, regardless of the identity of the species in the exosphere. We have considered only the low solar activity model, which at present, shows the largest effects. In addition, we have not considered the interaction of the solar wind with the ionosphere. Models of the Viking O₂⁺ densities have shown that there is a loss process for ions at the top of the ionosphere that reduces the scale heights of the ion density profiles and thus influences the escape rates due to ion reactions [*Chen et al.*, 1978; *Fox*, 1997; *Shinagawa and Cravens*, 1989, 1992]. Our models were constructed with zero-flux upper boundary conditions, which do not mimic this effect. Thus the ion densities, including those of O₂⁺ and O⁺ are larger at high altitudes than in models in which the maximum upward flux is imposed at the upper boundary [e.g., *Fox*, 1997].

[12] Because of these considerations, the escape fluxes that we have computed should be considered qualitative rather than quantitative, and are meant only to illustrate the effect. The thermospheric density profiles of neutrals other than H₂ and H might also be affected by larger H₂

abundances. Only more detailed modeling of the lower and upper atmospheric chemistry simultaneously could illuminate all the effects of variations in the H₂ abundances. In spite of these model limitations, it is clear that if the Martian atmosphere contained more H₂ in the past, the nonthermal escape rates of heavy C and N atoms would be smaller than those predicted based on the current oxidation state of the atmosphere.

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J. L. Fox, Department of Physics, Wright State University, Dayton, OH 45435, USA. (fox@platmo.phy.wright.edu)