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

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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.


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
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.

\[ \text{H}_2 \] interacts with \( \text{O}^+ \), \( \text{N}_2^+ \), \( \text{CO}^+ \) and \( \text{CO}_2^+ \) through the reactions

\[ \text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}, \]  
\[ \text{N}_2^+ + \text{H}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}, \]  
\[ \text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}, \]  
\[ \text{CO}_2^+ + \text{H}_2 \rightarrow \text{HCO}_2^+ + \text{H}, \]

which are destruction mechanisms both for the ions and for \( \text{H}_2 \), as well as production mechanisms for \( \text{H} \). The rate coefficients for reactions (1–4) are very large: 1.35 \( \times 10^{-9} \) \([\text{Li et al., 1997}]\), 1.52 \( \times 10^{-9} \) \([\text{Uiterwaal et al., 1995}]\), 1.5 \( \times 10^{-10} \) \( \text{cm}^3 \text{s}^{-1} \) \([\text{Scott et al., 1997}]\), respectively. The dominant ion \( \text{O}_2^+ \) does not react with \( \text{H}_2 \), and its density profile is not much impacted by changes in the \( \text{H}_2 \) abundance.

Most of the existing models of the Martian atmospheric hydrogen have considered to some extent the interaction of ions with \( \text{H} \) and \( \text{H}_2 \). The early ionospheric models of Krasnopolsky [1993a, 1993b] were photochemical equilibrium models, which could not be expected to produce realistic \( \text{O}^+ \) 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 \( \text{CO}_2 \) profiles measured by Viking in their model to determine the source of \( \text{H} \) from reaction of \( \text{H}_2 \) with \( \text{CO}_2 \), but did not compute the \( \text{O}^+ \) density profiles. Krasnopolsky and Feldman [2001a, 2001b] recently constructed an updated ionospheric model and reported \( \text{H} \) and \( \text{H}_2 \) profiles. More details were provided in a presentation by Krasnopolsky [2002].

In our recent low and high solar activity models of the thermosphere/ionosphere [cf. Fox and Bakalian, 2001], we tentatively adopted the \( \text{H}_2 \) 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 \( \text{H}_2 \). 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 \( \text{H}_2 \) standard models. In the 40 ppm \( \text{H}_2 \) model, the computed \( \text{O}^+ \) peak density of \( \sim 300 \text{ cm}^{-3} \) is less than half of the values of \( \sim 600–750 \text{ cm}^{-3} \) implied by the Viking RPA measurements, and for the 15 ppm \( \text{H}_2 \) model, the \( \text{O}^+ \) peak density is \( \sim 430 \text{ cm}^{-3} \), which is also significantly less than the Viking measured values. Previous low solar activity models, which did not include \( \text{H}_2 \), 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 \( \text{O}^+ \) profile. The \( \text{O} \) mixing ratio at 130 km for the low solar activity models is inferred from the Viking RPA densities of \( \text{O}_2^+ \) and \( \text{CO}_2^+ \) 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
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 H\(_2\) density profile for the 40 ppm model falls off more rapidly with altitude than that presented by Krasnopolsky et al. [1998]. The H\(_2\) density at 250 km in our 40 ppm model is 1.6 \times 10^6 \text{ cm}^{-3}, compared to 6 \times 10^6 \text{ cm}^{-3}, determined by Krasnopolsky et al. [1998]. The difference in the shape of the H\(_2\) profiles is difficult to determine, but is probably due in part to the larger rate coefficient for reaction of H\(_2\) with CO\(_2\)\(^+\) that we have adopted, and may also be due to differences in the eddy diffusion coefficient profiles in the models. For the 15 ppm H\(_2\) model, the H\(_2\) density at 250 km is 6 \times 10^5 \text{ cm}^{-3}, compared to about 4 \times 10^5 \text{ 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.

We have constructed models of the Martian thermosphere/ionosphere for H\(_2\) 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 H\(_2\), 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 H\(_2\), because even if the density is fixed, an upward flux exists in order for steady state to be achieved. Although larger H\(_2\) abundances imply larger H densities, the relationship is not straightforward and accurate modeling requires the inclusion of the chemistry of HCO\(^+\), HCO\(_2\)\(^+\), OH\(^+\), and N\(_2\)H\(^+\). 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 H\(_2\) at that altitude, which was the ratio that reproduced the density of H at 250 km (about 1.4 \times 10^6 \text{ 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 H\(_2\) 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 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.

Figure 3. Density profiles of H\(_2\) for models with mixing ratios of 4, 10, 15, 40 and 100 ppm H\(_2\). The CO\(_2\), N\(_2\), and O\(^\cdot\) profiles are shown for reference. The H\(_2\) density profiles were computed self-consistently with the ion density profiles.
profiles of CO$_2$, N$_2$, and O for comparison. In the three panels of Figure 4, we present the density profiles of O$^+$, CO$_2^+$, N$_2^+$, and CO$^+$ for mixing ratios of 4, 15, 40 and 100 ppm H$_2$, 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 CO$_2$, N$_2^+$, and CO$^+$ are also significantly depleted as the assumed H$_2$ 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 O$_2^+$, 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 10$^5$ 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 H$_2$ abundance in the bulk atmosphere will have been larger in past epochs.

[8] The effect of H$_2$ on the model ion density profiles implies that if the H$_2$ 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

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Figure 4. (opposite) The density profiles of molecular ions and O$^+$ for various abundances of (top) H$_2$: CO$^+$ and O$^+$; (middle) CO$_2^+$; and (bottom) N$_2^+$ and O$^+$. In all three panels the H$_2$ abundances are represented as follows: 4 ppm H$_2$ (dashed curves), 15 ppm H$_2$ (solid curves), 40 ppm H$_2$ (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.
and Bakalian
Mixing Ratio, Mixing Ratio for Various Escape Mechanisms

Table 2. Escape Fluxes of N (10^4 cm^−2 s^−1) as a Function of H₂ Mixing Ratio for Two Escape Mechanisms

<table>
<thead>
<tr>
<th>Mixing Ratio ppm</th>
<th>N₂ + hν</th>
<th>N₂⁺ + e</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>19</td>
<td>3.6</td>
</tr>
<tr>
<td>10</td>
<td>18</td>
<td>3.1</td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>2.8</td>
</tr>
<tr>
<td>40</td>
<td>14</td>
<td>1.9</td>
</tr>
<tr>
<td>100</td>
<td>6.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

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

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.

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].

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 H$_2$ abundances. In spite of these model limitations, it is clear that if the Martian atmosphere contained more H$_2$ 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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