Hot carbon densities in the exosphere of Mars

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Abstract. Theoretical results of hot carbon densities in the exosphere of Mars are presented. The calculation is a two-step process: First a two-stream transport code is used to solve for the distribution function at the exobase, and then these results are used in a Liouville equation solution above the exobase. It is found that photodissociation of carbon monoxide is the largest source of hot carbon atoms in the upper atmosphere of Mars, larger than dissociative recombination of CO^+ and much larger than the creation of hot carbon through collisions with hot oxygen atoms. It is also found that the high solar activity densities are about an order of magnitude larger than those for the low solar activity case.

1. Introduction

The changes in the carbon dioxide content of the atmospheres of Mars and Venus over time are determined either by the atmospheric escape of carbon via CO₂, CO, or C or by the surface processes associated with carbon-bearing materials in the regolith and carbonate deposits (and the polar cap at Mars). The escape energies of ${}^{12}C$ at Venus and Mars are ~6.38 and 1.48 eV, respectively. The presence of a hot carbon exosphere at Venus has been established [Paxton, 1983] by the UV spectrometer, carried aboard the Pioneer Venus orbiter [e.g., Stewart, 1980], but it has been shown that the ¹²C escape fluxes at Venus are negligibly small. However, because of the lower escape energy at Mars, an examination of this issue is in order. The observed emissions at 165.1 nm have been identified as coming from hot carbon atoms, and an exobase mixing ratio of C/O was estimated to be on the order of 1% at Venus. There is no observational information regarding hot carbon densities at Mars available at this time.

There are three potentially important sources of hot carbon at Venus and Mars: They are the photodissociation of CO, the dissociative recombination of CO^+ , and the collisions of hot oxygen atoms with cold, thermal carbon. In this brief note we present the results of our calculation of hot carbon densities at Mars, due to all three of these source mechanisms.

2. Calculated Densities and Escape Fluxes

The photodissociation of CO,

$$CO + hv(< 1116 \text{ \AA}) \to C + O, \tag{1}$$

results in excess kinetic energy becoming available to the atomic products, the amount of which depends on the wavelength of the dissociating photon and the electronic state of the dissociation products. The hot C production rates caused by this photodissocia-

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Paper number 2001JA000007. 0148-0227/01/2001JA000007\$09.00 tion process were calculated by assuming that the products were in their ground state and by using the photodissociation cross sections presented by *Fox and Black* [1989]. The solar flux values used were the 79050 and the SC21REFW *Hinteregger et al.* [1981] EUV fluxes, for high and low solar activity, respectively, combined with the X-ray values given by *Ayres* [1997]. The thermospheric models used were similar to those used previously [e.g., *Fox*, 1997; *Kim et al.*, 1998]. The high solar activity model is based on the Mars Thermospheric General Circulation Model (MTGCM) of *Bougher et al.* [1990], and the specific values used were for near the equator at 1600 LT. The low solar activity, neutral atmosphere is that from the Viking neutral mass spectrometer results, which correspond to a solar zenith angle of 44° [*Nier and McElroy*, 1977; *Fox and Dalgarno*, 1979].

The dissociative recombination of CO⁺,

$$CO^+ + e \to C({}^{3}P) + O({}^{3}P) + 2.90 \text{ eV},$$
 (2a)

$$CO^+ + e \to C(^1D) + O(^3P) + 1.64 \text{ eV},$$
 (2b)

$$CO^+ + e \to C(^3P) + O(^1D) + 0.94 \text{ eV},$$
 (2c)

$$CO^+ + e \to C(^1S) + O(^3P) + 0.22 \text{ eV},$$
 (2d)

$$CO^+ + e \to C(^1D) + O(^1D) - 0.33 \text{ eV},$$
 (2e)

results in an excess kinetic energy, the amount of which depends on the electronic excitation state of the products, as indicated above. In a recent paper, Fox and Hac [1999] have carried out detailed Monte Carlo calculations of the altitude-dependent velocity distributions of the C atoms resulting from reaction (2), for both high and low solar cycle conditions. In these calculations they used the latest available rate coefficients and branching ratios [Rosen et al., 1998]. The total dissociative rate coefficient used was $2.76 \times 10^{-7} (300/T_e)^{0.55}$. At 0-eV relative energy the branching ratios given by Rosen et al. [1998] are 0.761, 0.145, 0.094, and 0.0 for channels (2a)–(2e), respectively. At 0.4 eV the endothermic channel (2e) is now energetically possible, and the measured branching ratios are 0.53, 0.34, 0.08, 0.0, and 0.05, respectively. In the calculations below, a linear interpolation between these branching ratio values was used, which depended on the temperatures corresponding to a given altitude. Fox and Hac [1999] assumed that the rotational and vibrational temperatures were the same as the adopted ion temperatures. They did take into account the decrease in the cross section for dissociative recombination due to the relative velocity of the ions and electrons [*Rosen et al.*, 1998]. The assumed ionospheric densities for the low and high solar activity conditions are presented by *Fox and Hac* [1999], and the electron and ion temperatures can be found in the work of *Kim et al.* [1998].

Collisions between energetic oxygen atoms and cold, thermal carbon atoms can result in hot carbon production:

$$O_{hot} + C_{cold} \rightarrow C_{hot} + O_{cold}.$$
 (3)

We used the hot oxygen distribution functions calculated for Mars [*Kim et al.*, 1998] to obtain the production rate of hot carbon due to this process. We adopted a cross-section value of 1.2×10^{-15} cm², a reasonable choice based on the calculations of *Kharchenko et al.* [1997].

We combined these three hot C production rates as a function of altitude and energy. We then used these production rates in our two-stream model to calculate the hot C fluxes as a function of altitude. This two-stream model [cf. Schunk and Nagy, 2000] has been used widely and successfully to calculate electron, ion, and neutral particle fluxes [e.g., Cravens et al., 1980a; Nagy and Cravens, 1988; Kim et al., 1998]. Specifically, it has been used to calculate hot oxygen densities at both Venus and Mars; the calculated densities at Venus agreed well with the observed values, and the Mars results [Nagy and Cravens, 1988; Kim et al., 1998] are in reasonably good agreement with the values calculated by Lammer and Bauer [1991] and Hodges [2000], who used a Monte Carlo method. (There is a factor of ~ 13 difference in the escape fluxes given in Table 1 of Kim et al. [1998] and Hodges [2000], which is due to an error in compiling that table; the densities and the distribution function presented by Kim et al. [1998] are correct.) Using these calculations, we obtained the hot C fluxes at the exobase. The classical definition of the exobase, namely, the location where the mean free path equals the scale height, places it at \sim 195 and 215 km for low and high solar cycle conditions, respectively. The exact choice of the exobase altitude does not impact our calculated densities to any significant degree, as long as that choice is "reasonable" (see Figure 5 and two paragraphs below). The calculated energy distribution functions at the nominal exobases, for the two solar cycle conditions, are shown in Figure 1. The upward, downward, and escape hemispheric fluxes are plotted in Figures 2a and 2b, for the high and low solar activity cycle conditions, respectively.



Figure 1. Hot carbon differential number density versus energy for the high and low solar activity cases. Spectra are for the 192-km altitude bin, and each energy "box" has a width of 0.02 eV.



Figure 2. Hot carbon number flux versus altitude for (a) high solar activity conditions and (b) low solar activity conditions. Upward and downward flux values are integrated over all energies, while the escaping upward flux values are integrated above 1.48 eV.

Having calculated the distribution functions at the exobase, we used Liouville's theorem [cf. *Schunk and Nagy*, 2000] to calculate the hot carbon densities in the exosphere of Mars, as we have done for hot hydrogen and oxygen cases before [e.g., *Cravens et al.*, 1980b; *Nagy and Cravens*, 1988]. The resulting hot carbon densities are shown in Figure 3. The density values decrease from $\sim 4.7 \times 10^3$ and 3.6×10^2 cm⁻³ near the exobase for the high and low solar activity conditions, respectively, and remain a minor constituent throughout the exosphere, compared to hydrogen and oxygen.

We found that photodissociation is the most important source mechanism, followed by dissociative recombination, while the hot oxygen impact source appears to be negligibly small at Mars. To demonstrate this conclusion we plotted in Figures 4a and 4b, for the high solar activity conditions, the exospheric densities and hemispheric escape fluxes, respectively, due to the three possible sources separately. In Figure 5 we plotted the calculated high solar activity densities, as a function of altitude, for four different assumed exobase altitudes, in order to demonstrate that the choice of the exobase altitude has only a small influence on our calculated hot carbon densities.

We also calculated the hemispheric escape fluxes and found them to be 7.7×10^6 and 5.3×10^5 cm⁻² s⁻¹ for high and low solar cycle conditions, respectively. Note that the escape flux



Figure 3. Hot carbon densities in the exosphere of Mars versus altitude for the high and low solar activity cases. The exobase altitude was chosen to be 192 km for these calculations.

values are obtained directly from the two-stream calculations and thus do not depend on the choice of the exobase location. This calculated escape flux can be compared to the sputtering rate of CO_2 , CO, and C by O^+ ions, which is estimated to fall somewhere



Figure 4. Altitude dependence of hot carbon (a) exospheric density and (b) escaping upward number flux, calculated by assuming different source terms. These values are for the high solar activity case.



Figure 5. Hot carbon densities in the exosphere of Mars for the high solar activity case using various altitudes for the exobase height.

between $1-5 \times 10^5$ cm⁻² s⁻¹ [Luhmann et al., 1992; Jakosky et al., 1994; Kass, 1999]. There are indirect indications of "heavy" ion escape (O⁺, O₂⁺, CO₂⁺, CO⁺, and C⁺) from the ionosphere of Mars by measurements from the Phobos spacecraft [Lundin et al., 1990; Verigin et al., 1991] and by model calculations [Fox, 1997; Liu et al., 1999, 2001]. These direct ion escape fluxes may carry more carbon than the escape due to hot carbon, but both the measurements and three-dimensional models can only provide an estimate of the total ion escape flux (3–14 × 10²⁵ s⁻¹).

The various possible escape mechanisms must have certainly changed over the history of the planet. It has been suggested that the escape due to sputtering was more than 3 orders of magnitude larger than the present rate 3.5 Gyr before the present [*Luhmann et al.*, 1992; *Kass and Yung*, 1995, 1996], but of course large uncertainties are associated with these estimates. The currently calculated escape fluxes would also have been greater in an earlier epoch when the solar fluxes were higher. The ion escape mechanism must also have been significantly different, because of the presence of an intrinsic magnetic field. This all means that while these calculated escape fluxes are of intellectual interest, it is difficult to estimate their significance in terms of the overall evolution of the atmosphere of Mars, especially since some of the atmospheric carbon may be tied up in carbon-bearing materials in the regolith and carbonate deposits.

Our calculations are one-dimensional and assumed mean ionospheric conditions. If one assumes that this result is a good representation of daytime fluxes and that the nighttime escape is negligibly small, then the estimate of the total escape rate originating from the dayside of the planet is $\sim 6.3 \times 10^{24}$ and 4.3×10^{23} atoms s⁻¹ for the high and low solar activity cases, respectively.

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