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Fox, J. L. (1993). On the Escape of Oxygen and Hydrogen from Mars. *Geophysical Research Letters*, 20 (17), 1747-1750.

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On the Escape of Oxygen and Hydrogen from Mars

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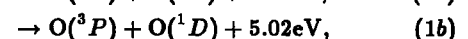
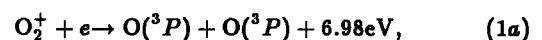
Abstract. Escape rates of oxygen atoms from dissociative recombination of O_2^+ above the Martian exobase are computed in light of new information from ab initio calculations of the dissociative recombination process, and our recently revised understanding of the Martian dayside ionosphere. Only about 60% of the dissociative recombinations occur in channels in which the O atoms are released with energies in excess of the escape velocity. Furthermore, we find that the computed escape fluxes for O depend greatly on the nature of the ion loss process that has been found necessary to reproduce the topside ion density profiles measured by Viking. If it is assumed that the ions are not lost from the gravitational field of the planet, as required by an analysis of nitrogen escape, the computed average O escape rate is $3 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, much less than half the H escape rates inferred from measurements of the Lyman alpha dayglow, which are in the range $(1-2) \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Suggestions for restoring the relative escape rates of H and O to the stoichiometric ratio of water are explored. The final resolution of this problem may have to await a future aeronomy mission to Mars.

INTRODUCTION

Recent models of the Martian ionosphere have shown that the ion densities measured by Viking cannot be reproduced if high electron temperatures, such as those derived recently from Viking retarding potential analyzer (RPA) data [Hanson and Mantas, 1988] are employed, unless a loss process for ions is imposed at the upper boundary of the ionosphere [Shinagawa and Cravens, 1989, 1992; Fox, 1993]. Shinagawa and Cravens [1989] have suggested that this loss process is the divergence of the horizontal ion fluxes at high altitudes, by analogy to the Venus ionosphere, where large antisolar ion fluxes were measured by the Pioneer Venus RPA [e.g. Knudsen et al., 1980]. Fox [1993] has found that such a loss process is also required on Mars to reduce the nitrogen escape rates to values that can reproduce the measured $^{15}\text{N}/^{14}\text{N}$ ratio [Nier and McElroy, 1977]. The nitrogen escape rates are sensitive to the ion density profiles because a large fraction of the N escape is due to dissociative recombination of N_2^+ and to ion-molecule reactions involving N_2^+ . The ultimate fate of the ions that are lost from the dayside is unknown, but the Martian $^{15}\text{N}/^{14}\text{N}$ ratio argues against complete loss of the ions from the gravitational field of the planet. Because of diffusive separation above the homopause, which is near 120 km, the $^{15}\text{N}/^{14}\text{N}$ ratio also would be increased by total loss of N_2^+ . We have com-

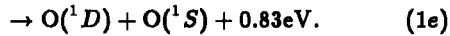
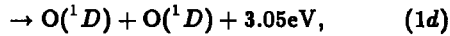
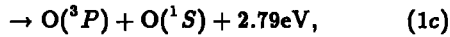
puted the O_2^+ fluxes by fitting the one-dimensional model O_2^+ density profiles to the Viking measured values [Hanson et al., 1977]. The nitrogen and other ion fluxes were then determined by requiring their upward velocities to be the same as that of the O_2^+ ions. On Venus the antisolar fluxes of ions on the dayside converge and flow downward on the nightside, contributing, along with impact of electrons that have been observed at high altitudes in the umbra [e.g., Gringauz, 1979; Knudsen and Miller, 1985] to the production of the nightside ionosphere [e.g., Spenner et al., 1981; Cravens et al., 1983; Kliore et al., 1991; Fox, 1992]. The imposition of an upward flux boundary condition reduces both the O_2^+ densities at high altitudes and the escape fluxes of oxygen atoms.

McElroy [1972] first suggested that the Martian thermal escape flux of H is constrained, on time scales of the order of 10^5 years, to twice the non-thermal O escape flux in order to maintain the oxidation state of the atmosphere. The mechanism for this relationship was elaborated by McElroy and Donahue [1972] and by Liu and Donahue [1976], who performed model calculations that showed that an increase in the O_2 abundance (presumably from reduced O escape) in the atmosphere results in a decrease in the thermal escape rate of H. McElroy [1972] and McElroy and Yung [1976] suggested that the O escape flux is equal to the ionization rate above the exobase, for which they estimated a value of $(6-7) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. The latter equality arises if the escape of O is assumed to be due mainly to dissociative recombination (DR) of O_2^+ , which is the major ion at the Martian exobase. Although two energetic O atoms are produced in each DR, only the one with its velocity vector oriented in the upward hemisphere is assumed to escape. The H escape flux has been estimated to be in the range $(1-2) \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Anderson and Hord [1971] derived a value of $1.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ from Mariner 6 and 7 Lyman alpha data; Barth et al. [1972] and Anderson [1974] derived values of 2×10^8 and $1.7 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, respectively, from Mariner 9 Lyman alpha profiles. Agreement with these values has been and still is one of the criteria that serves to differentiate and verify photochemical models of the Martian atmosphere. For example, in the recent time-dependent model of Rodrigo et al. [1990], an H escape rate of about $10^8 \text{ cm}^{-2} \text{ s}^{-1}$ was derived. In his recent comparison of several photochemical models of the Mars atmosphere, Krasnopolsky [1993a] computed a value of $1.7 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ for his favored model.

DISSOCIATIVE RECOMBINATION OF O_2^+ DR of O_2^+ can proceed by a number of channels, including

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Paper number 93GL01118
0094-8534/93/93GL-01118\$03.00



Since the escape energy of an O atom at the Martian exobase (about 200 km) is about 1.98 eV, escape is possible only when the reaction proceeds via one of the first two channels. *McElroy* [1972] and *McElroy and Yung* [1976] assumed that all the dissociative recombinations proceed via channel (1b), and thus that all lead to escape. The channel by which the DR proceeds has, however, been found to depend greatly on the vibrational level of the ion [e.g. *Bates and Zipf*, 1980; *Guberman*, 1987; 1988; *Guberman and Giusti-Suzor*, 1992]. Using a procedure similar to that employed by *Fox* [1985; 1986] for the terrestrial and Venusian ionospheres, we have computed the vibrational distribution of O_2^+ in the Martian ionosphere. The results at 200 km are presented in Table 1. We find that O_2^+ is less vibrationally excited at the Martian exobase than at the exobases of the other terrestrial planets, even though the neutral densities are smaller. This is largely because the ion and electron densities are also smaller, resulting in longer ion lifetimes and thus more effective quenching.

Using the rate coefficients for channels (1b), (1d), (1e), computed by *Guberman* [1987, 1988; also *Guberman and Giusti-Suzor*, 1992], along with the measured values for the total rate [*Mehr and Biondi*, 1969; *Alge et al.*, 1983], we have obtained the spectrum of O atoms released in DR of O_2^+ . The results for the ion peak (130 km) and the exobase (200 km) are shown in Figure 1. *Guberman* [1987] showed that the channel leading to $\text{O}({}^1S) + \text{O}({}^3P)$ (1c) is not important. The greatest uncertainty occurs in the calculation of the yield for channel (1a), which is assumed to be the difference between the measured total rate and the computed rates for channels (1b – 1e). The appearance of a negative yield for the 6.98 eV channel at 200 km is a result of this assumption, and could indicate that the total rate coefficient varies with vibrational quantum number, or that the computed rate coefficients for the other channels are too large. *Guberman* [private communication, 1992] has suggested that the rate coefficients for channels (1b) and (1d) will be reduced when the indirect dissociative recombination mechanism is included, but the magnitudes of the changes will probably be small. In any event, the fraction of dissociative recombinations proceeding by channels (1a) and (1b) at 130 km is about 70%; at 200 km the fraction is about 60%. That fact and the imposition of a loss process for O_2^+ at the top of the ionosphere undermines the equality between the total ion production rate and the O escape rate. If the horizontally flowing ions are assumed not to escape

Table 1. Vibrational Distribution of O_2^+ at the Martian Exobase

Vibrational Quantum Number	Fractional Population
0	0.86
1	0.063
2	0.029
3	0.021
4	0.015
5	0.0095
6	0.0035
7	0.00026

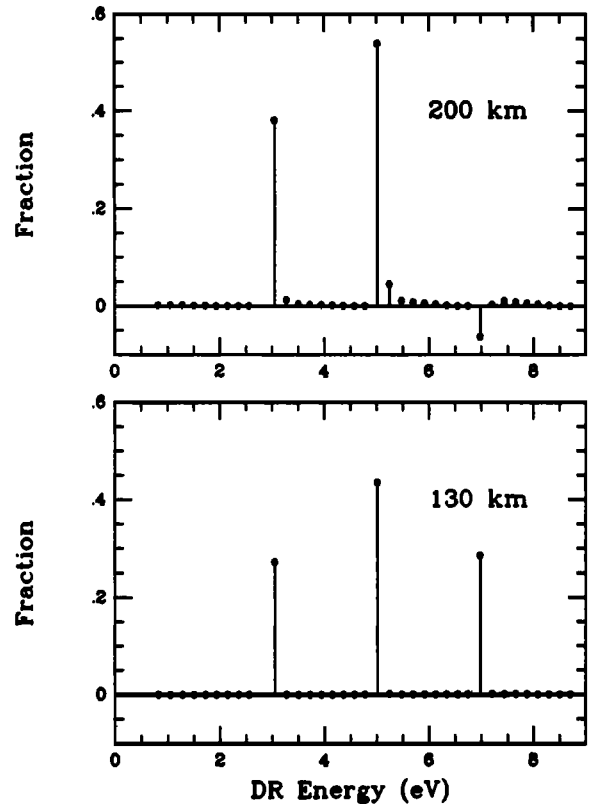


Fig. 1. Fraction of dissociative recombinations vs. exothermicity of the recombination at the Martian exobase, near 200 km, and at the ion peak, near 130 km. Each dissociative recombination produces two O atoms with equal energy. Only those recombinations with energies greater than 3.96 eV can produce an escaping atom.

the gravitational field of the planet, the O escape rate is much reduced. Our calculations indicate that at high solar activity, the integrated rate of O_2^+ DR above the exobase at times of low solar activity is about $5.5 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, and that at high solar activity is $16 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, with an average of about $11 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. Multiplying by 0.5 to account for the fact that escape is negligible at night, and by the fraction 0.6 of DR's that proceed via channels (1a) and (1b), we obtain an O escape rate of about $3 \times 10^6 \text{ atoms cm}^{-2} \text{ s}^{-1}$. This number is smaller by more than an order of magnitude than half the H escape rate inferred from the Mariner 6, 7, and 9 Lyman alpha measurements. A similar value of $6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ was obtained from Monte Carlo calculations of the Martian O escape rates by *Lammer and Bauer* [1991]. They used the O_2^+ profiles computed by *Fox and Dalgarno* [1979] (in which a low electron temperature was employed in order to fit the Viking measured ion densities) with a value of the dissociative recombination coefficient ($1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$) that is appropriate to a high electron temperature. Because they essentially adopted the measured O_2^+ profiles, they did not need to explicitly impose an ion loss processes at the top of the ionosphere.

THE RELATIVE ESCAPE RATES OF O AND H

There are a number of possibilities for restoring the relationship between the O and H escape rates. If it is assumed that the horizontally flowing ions don't converge and flow downward on the nightside, but are lost from the gravitational field of the planet, then the O escape rate is increased

to about $1.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. Because two O atoms are lost for every O_2^+ that escapes, this number is almost twice the ionization rate above the exobase on the dayside, and is about equal to the H escape rate. Another possibility is that the horizontally flowing ions are destroyed en route by DR. In order to verify or refute this hypothesis, it would be necessary to determine the velocities and densities of the ions and electrons at the altitudes of the flow.

It is also possible that a part of the upward flux of H derived from the Mariner Lyman alpha emission profiles is due to the day-to-night circulation, rather than to escape. This is the case for Venus, where the escape of H is non-thermal, and the subsolar-to-antisolar circulation is strong [e.g. Hartle et al., 1978; Bougher et al., 1988]. From Pioneer Venus orbiter ultraviolet spectrometer data, Paxton et al. [1988] derived an upward flux of H atoms of about $7.5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ on the Venus dayside, but the non-thermal escape rates are only about $(1 - 2) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ [Rodriguez et al., 1984; Hodges and Tinsley, 1986; Kumar et al., 1983]. Upward velocities near the Martian exobase of about 120 cm s^{-1} have been computed by Bougher et al. [1990; also private communication, 1992] from their Mars Thermospheric General Circulation Model. The range of exobase atomic hydrogen densities inferred from the Mariner Lyman alpha measurements is $(2.5 - 13) \times 10^4 \text{ cm}^{-3}$ [Anderson and Horde, 1971; Liu and Donahue, 1976]. Thus the upward flux due to the circulation is about $(3 - 16) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, which is significant, but not sufficient to account for the imbalance in the O and H fluxes. Larger exobase densities were inferred by Levine et al. [1978], who measured Martian Lyman alpha at a time of low solar activity (1975) using the Copernicus Orbiting Astronomical Observatory. They concluded that the exobase density of H had increased by a factor of 60 over that at the time of the Mariner measurements. The use of such large densities with the velocities computed by Bougher yields a very large upward flux due to the subsolar-to-antisolar circulation. Levine et al., however, interpreted the increase in H densities from high to low solar activity as indicating that the escape of H atoms on Mars is an example of a diffusion-controlled escape process, the theory of which was first put forward by Hunten [1973]. It is difficult to understand how the H thermal escape fluxes could track the non-thermal O escape fluxes if the H escape rate were controlled by the mixing ratio of H-containing species in the lower atmosphere, as it would be for diffusion-limited escape. Moreover, recent photochemical models of the Martian atmosphere have predicted that the H escape fluxes are not diffusion-limited [Krasnopolsky, 1993a,b; Rodrigo et al., 1990].

A third possibility is that loss of O proceeds primarily via another mechanism, such as sputtering or solar wind pick-up [Luhmann et al., 1992; Zhang et al., 1993]. Measurements by instruments on the Phobos spacecraft indicated an O^+ loss rate of about $2 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ [Lundin et al., 1990]. More recently, Verigin et al. [1991] have reported that the O^+ loss rate by this mechanism may be as large as $7 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. If the O^+ loss rates are indeed this large, solar wind pick-up would constitute the major process for oxygen removal from Mars, and would restore the near equality between the O escape rate and half the H escape rate. The Phobos measurements are, however, very uncertain, and cannot be considered definitive.

Although the balanced escape of H and O as articulated by McElroy [1972] and McElroy and Donahue [1972] remains

credible, it is clear that the picture is not as straightforward as they envisioned, and that the mechanism for the escape of O is not simply dissociative recombination of O_2^+ above the dayside exobase. It is possible that a definitive identification of the mechanisms for O and H escape, and a determination of their absolute magnitudes will have to await a future aeronomy mission to Mars. Measurements of the neutral and ion densities, ion fluxes, and emissions of O and H over a range of altitudes both inside and outside the atmosphere could yield quantitative information about the escape mechanisms and fluxes of both H and O.

Acknowledgements. This work was supported in part by the National Aeronautics and Space Administration under grants NAGW-2238 and NAGW-2958 to the Research Foundation of the State University of New York at Stony Brook.

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(Received February 24, 1993;
accepted April 7, 1993)