Photochemical escape of oxygen from early Mars

CrossMark

Jinjin Zhao, Feng Tian *

Ministry of Education Key Laboratory for Earth System Modeling, Center for Earth System Science, Tsinghua University, Beijing 100084, China

ARTICLE INFO

ABSTRACT

Photochemical escape is an important process for oxygen escape from present Mars. In this work, a 1-D Monte-Carlo Model is developed to calculate escape rates of energetic oxygen atoms produced from O_2^+ dissociative recombination reactions (DR) under 1, 3, 10, and 20 times present solar XUV fluxes. We found that although the overall DR rates increase with solar XUV flux almost linearly, oxygen escape rate increases from $1\times$ to $10\times$ present solar XUV conditions but decreases when increasing solar XUV flux further. Analysis shows that atomic species in the upper thermosphere of early Mars increases more rapidly than O_2^+ when increasing XUV fluxes. While the latter is the source of energetic O atoms, the former increases the collision probability and thus decreases the escape probability of energetic O. Our results suggest that photochemical escape be a less important escape mechanism than previously thought for the loss of water and/or CO_2 from early Mars.

1. Introduction

Atmosphere escape is important for the evolution of Mars and could have contributed to its long term climate change (Tian et al., 2013). On present Mars, the exobase temperature is too low for thermal escape of heavy atoms, such as oxygen, to be efficient (Gröller et al., 2014; Johnson et al., 2008; Lammer et al., 2008). Nonthermal escape processes do not depend on exobase temperature and rely on sources of energetic atoms or ions. Dissociative recombination (DR) reaction of O_2^+ (see the following list) is one such source (Fox and Hać, 2009):

		Branching ratio
(A) $O_2^+ + e^- \rightarrow O(^3P) + O(^3P) + 6.99$ eV		26.5%
(B) $O_2^+ + e^- \rightarrow O(^1D) + O(^3P) + 5.02$ eV		47.3%
(C) $O_2^+ + e^- \rightarrow O(^1D) + O(^1D) + 3.06$ eV		20.4%
(D) $O_2^+ + e^- \rightarrow O(^1D) + O(^1S) + 0.83$ eV		5.8%

Because of the low mass of Mars (escape energy of 1.9 eV, 9.7 eV and 8.6 eV are needed for oxygen atoms to escape from Mars, Earth and Venus respectively) (Shizgal and Arkos, 1996), energetic oxygen atoms produced from branches A, B, and C can escape from the planet. This type of photochemical escape is potentially important for the evolution of volatile inventories on Mars (Lammer et al., 2003).

Because energetic O atoms are produced mainly in the collisional regions of martian upper atmosphere, these particles need to overcome collisions with background gases in order to escape. Many workers have studied photochemical escape of oxygen from present Mars (Chassefière et al., 2013; Cipriani et al., 2007; Fox, 1993; Fox and Hać, 2009, 2014; Gröller et al., 2014; Hodges, 2000; Kim et al., 1998; Krestyanikova and Shematovich, 2006; Lammer and Bauer, 1991; Shematovich, 2013; Valeille et al., 2010; Yagi et al., 2012; Zhang et al., 1993).

Fox and Hać (2009) considered isotropic and forward scattering in the center-of-mass frame in a 3D Monte Carlo Model. A constant total cross section of 3×10^{-15} cm^2 and differential cross sections from Kharchenko et al. (2000) are used for O–CO_2, O–CO, and O–O collisions. The escape rates in their forward scattering model are 1.44×10^{26} s^{-1} and 2.1×10^{26} s^{-1} for low and high solar activity situations respectively, one order of magnitude greater than those in the isotropic model (Fox and Hać, 2009). The small difference between the low and high solar activity in the forward scattering model is caused by the opposite changing trends of O_2^+ DR rate and escape probability of energetic oxygen in different solar activity situation (Fox and Hać, 2009).

Valeille et al. (2010) considered different solar zenith angle in a 2-D Direct Simulation Monte Carlo (DSMC) model and obtained oxygen escape rate between 3.8–14×10^{25} s^{-1}. It is also shown that the oxygen escape rates change from 3×10^{25} to 5×10^{25} s^{-1} between different seasons of Mars (Yagi et al., 2012). Shematovich (2013) considered the collisions between energetic oxygen and hydrogen and calculated oxygen escape rate of 1.5×10^{25} s^{-1}.

* Corresponding author.
   E-mail address: tianfengco@tsinghua.edu.cn (F. Tian).

More recently Fox and Hać (2014) updated their model with larger O–CO_2 and O–CO collision cross sections (2.0×10^{-14} and 1.8×10^{-14} cm^2 respectively) and energy dependent on O–O collision cross section which used by Kharchenko et al. (2000). Because of CO_2 is the main component of modern martian atmosphere below about 200 km altitude, new collision cross sections decrease oxygen photochemical escape rates to 6.5×10^{24} s^{-1} and 1.6×10^{25} s^{-1} for low and high solar activity situations respectively (Fox and Hać, 2014).

Another recent work including DR of O_2^+ and CO_2^+ in a 1-D Monte Carlo Model (Gröller et al., 2014) found oxygen escape rates at exobase from DR of O_2^+ to be 1.5×10^{25} s^{-1} and 2.1×10^{25} s^{-1} for low and high solar activity conditions respectively. In comparison, oxygen escape rates at exobase from DR of CO_2^+ are found to be 1.3×10^{25} and 1.1×10^{25} s^{-1} for low and high solar activity conditions respectively (Gröller et al., 2014). Note that DR of CO_2^+ has been deemed unimportant in most previous works on photochemical escape of oxygen.

Despite the differences between models, the calculated photochemical escape rates of oxygen are on the order of 10^{25} s^{-1} for present Mars. In comparison, there are fewer works discussing photochemical escape of O atoms from early Mars. The pioneer work of Zhang et al. (1993) suggested that photochemical oxygen escape rate from ancient martian atmosphere under 1, 3 and 6 times present solar XUV flux were 7×10^{25} s^{-1}, 4×10^{26} s^{-1} and 1×10^{27} s^{-1} respectively (Zhang et al., 1993). Lammer et al. (2003) scaled oxygen DR escape rate of 6×10^{24} s^{-1} for present Mars to 3×10^{25} s^{-1} at 2.5 Ga ($3 \times$ XUV) and 8×10^{25} s^{-1} at 3.5 Ga ($6 \times$ XUV) respectively. It is a general consensus that oxygen photochemical escape rate from Mars should increase monotonically with increasing solar XUV.

Tian et al. (2009) proposed that the upper atmosphere of early Mars was highly expanded (exobase moves to a few martian radii) during the early Noachian and that a CO_2 atmosphere of early Mars was unstable against solar XUV driven thermal escape (Tian et al., 2009). No previous work has modeled photochemical escape in such a scenario.

In this work a 1-D Monte Carlo Model is used to investigate the oxygen photochemical escape from a highly expanded atmosphere. We found that photochemical escape of oxygen from early martian atmosphere does not increase with solar XUV monotonically. Instead there is a threshold beyond which the expansion of the upper atmosphere, mainly consists of atomic species, exceed the increase of O_2^+ and thus escape rate of energetic O atoms decreases with increasing XUV beyond that threshold. The next section describes the model. Section 3 is the results and discussion for early Mars.

2. Model description

The neutral and electron temperature profiles, as well as the density profiles of O, CO, CO_2, O_2^+, and e$^-$, used in this work (shown in Figs. 1 and 2) under $1\times$, $3\times$, $10\times$ and $20\times$ XUV conditions are based on Tian et al. (2009). The top of the upper atmosphere are set to 300 km, 500 km, 1200 km and 10,000 km respectively. At the altitudes for which Tian et al. (2009) model does not provide data, densities and temperatures are extrapolated. The rate coefficient for the O_2^+ DR reaction is set to 1.95×10^{-7} $(300/T_e)^{0.7}$ cm^3 s^{-1} for $T_e < 1200$ K and 7.39×10^{-8} $(1200/T_e)^{0.56}$ cm^3 s^{-1} for $T_e > 1200$ K (Fox and Hać, 2009).

To calculate escape probabilities of energetic oxygen atoms formed at different altitudes with different energies, 6×10^7 test particles, initial kinetic energy uniformly distribute from 0.03 eV to 10.02 eV with 0.03 eV bin size, are launched at each altitude grid. Random collisions between 3 type collision pairs, O–O, O–
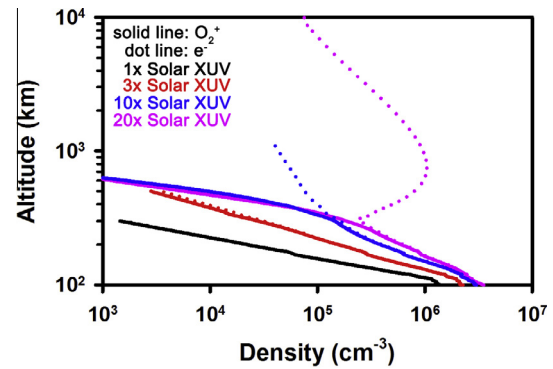

Fig. 1. Density distributions of O_2^+ (solid curves) and e$^-$ (dot curves) in $1\times$ (black), $3\times$ (red), $10\times$ (blue), $20\times$ (purple) solar XUV cases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
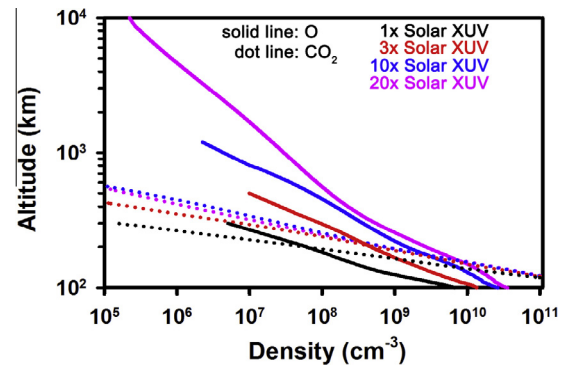

Fig. 2. Density profiles of O (solid curves) and CO_2 (dotted curves) in different solar XUV level.

CO_2 and O–CO, are considered in the simulation. The occurrence of collisions and the target species with which energetic oxygen should collide with are calculated based on the collision probability P_i:

$$P_i = 1 - \exp(-\sigma_i n_i \Delta h)$$

where n_i is the number density of background species i, Δh is the distance the particle traveled, set to be the smaller of 20% of local mean free path and 1 km (Fox and Hać, 2009), σ_i is the collision cross section of the energetic O atoms with background species i. For O–CO_2 and O–CO collisions, the collision cross sections are 2.0×10^{-14} cm^2 and 1.8×10^{-14} cm^2 respectively (Fox and Hać (2014). For O–O collisions, the energy dependent diffusion collision cross sections and differential cross sections in Tully and Johnson (2001) are used. When collisions occur, the energy loss of the projectile is calculated based on the diffusion cross sections in Tully and Johnson (2001) for O–O collisions. For O–CO_2 and O–CO collisions, we assume 100% energy loss for simplicity.

For each test particle, its kinetic energy after each collision is compared with the escape energy of Mars. Particles reaching the top of the atmosphere and still possess kinetic energy exceeding the escape energy contribute to the calculations of escape probability of oxygen atoms from particular altitudes.

Secondary energetic oxygen atoms, background oxygen atoms gaining energy through collisions from the primary energetic oxygen atoms formed directly from the DR reactions, could escape from Mars if their kinetic energy exceeds the local escape energy. To account for them, the model stores the number of the secondary test particles capable of escaping (their initial energy be identical