Fractionation of hydrogen and deuterium on Venus due to collisional ejection

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Abstract. The fractionation factor $f$ is important for interpreting the current escape fluxes of H and D on Venus and how the D/H ratio has evolved. The escape flux is currently governed by the two processes of charge exchange and collisional ejection by fast oxygen atoms. Using a best-fit parameterized equation for the O–H scattering angle phase function, more accurate branching ratios for the oxygen ion dissociation and including the effects of the initial energy and momentum of the ions and electrons, as well as for the hydrogen and deuterium gas, we have reanalyzed the collisional ejection process. Our analysis produces improved values for the efficiency of H and D escape as a function of the ionospheric temperature. From our results we propose the reduction of the hydrogen flux for collisional ejection from 8 to $3.5 \times 10^{6}$ cm$^{-2}$ s$^{-1}$. Assuming that collisions leading to escape occur mostly in the region between 200 and 400 km, the revised D/H fractionation factor due to collisional ejection is 0.47, where previously the process had been considered completely discriminating against deuterium escape (or $f \approx 0$). The resulting deuterium flux is $3.1 \times 10^{4}$ cm$^{-2}$ s$^{-1}$, roughly 6 times the flux due to charge exchange, making collisional ejection the dominant escape mechanism for deuterium on Venus.

Introduction

The processes controlling the escape of hydrogen from Venus have been discussed by many authors, and there is a general agreement that currently the most important mechanisms are charge exchange and collisional ejection by fast oxygen. Past analyses have given different estimates of how important each process is. McElroy et al. (1982) placed the collision process as the primary controller of hydrogen escape. More recent work has suggested quite convincingly, however, that charge exchange is the more important hydrogen escape mechanism (Kumar et al., 1983; Rodriguez et al., 1984; Rodriguez, 1986; Hodges and Tinsley, 1986). Knowledge of the escape flux of hydrogen is important for understanding the structure and chemistry of the thermosphere and for interpreting the evolution of the D/H ratio of the Venus atmosphere.

Venus has a well-established lack of water. In comparison with the Earth’s global average ocean of roughly 2.7 km depth, Venus has the equivalent of 2–10 cm of water in its atmosphere (Donahue and Hodges, 1992). This, coupled with Venus’ extremely high deuterium to hydrogen ratio (~ 100 times the Earth’s D/H ratio), has been an attractive hint that Venus may have had the equivalent of at least 100 times more water than its present reservoir (McElroy et al., 1982; Kumar et al., 1983).

In a simple Rayleigh fractionation model of the evolution of the D/H ratio, the global average escape rates of hydrogen and deuterium are proportional to the total atmospheric abundances of H and D:

$$\frac{dH}{dt} = -AH, \quad (1a)$$

$$\frac{dD}{dt} = -A/fD, \quad (1b)$$

where $f$ is the fractionation factor describing the general efficiency of escape of deuterium compared with hydrogen. For $f = 1$ the escape process is not fractionating and D/H remains constant, while for $f = 0$ only H can escape and the D/H ratio will evolve at the fastest possible rate. The above equations are valid when escape has occurred at a rate near the diffusion limit, and when integrated give a solution of:

$$[D/H](t) = [D/H](0) \left( \frac{H(0)}{H(t)} \right)^{1/f}. \quad (2)$$

This equation was derived previously in a discussion of oxygen isotopes on Mars (McElroy and Yung, 1976). This assumes that both $A$ and $f$ are constant over time. Hence, given the current and initial D/H ratios, the current hydrogen abundance $H(t)$ and the fractionation factor $f$, the equation can be rearranged to solve for the initial abundance of hydrogen $H(0)$ and, by extension, the initial abundance of deuterium $D(0)$.
abundance of water. Note that for $f = 0$ the factor of $D/H$ increase is the factor of hydrogen (or water) decrease. If we assume that Venus initially had a $D/H$ ratio similar to Earth's, this factor is roughly 100. For $f$ greater than zero, the factor can be much greater.

Other authors have pointed out that this simple model neglects additions to hydrogen and deuterium over time. Models have been presented which describe the effect of the injection of water into the atmosphere by outgassing (Krasnopolsky, 1985) and cometary impact (Grinspoon, 1987; Grinspoon and Lewis, 1988).

Grinspoon and Lewis argue that hydrogen is roughly in a steady state, with impacts by comets transporting enough water to balance the escape of hydrogen. They find, assuming an escape rate for hydrogen of $2 \times 10^7$ cm$^{-2}$ s$^{-1}$, that the current water abundance would be depleted in only 100 million years. They believe that, in view of this, the best interpretation of the current hydrogen abundance is that it is in a steady state. In its simplest form, the injection is treated as a constant source $\phi$ and the time-dependent solution given by Grinspoon (1987) is:

$$[D/H](t) = [D/H]_0 e^{-\phi t} + (\phi f)(1-e^{-\phi t}),$$  

where $t = H/\phi f$ and $f$ is the $D/H$ ratio of the source. The first term represents the decaying signature of the initial $D/H$ ratio, while the second term is the asymptotic solution for large $t$. For $t$ much greater than $\tau$, the $D/H$ ratio approaches the steady-state solution $z/f$. They note that for small $\tau$ the steady-state solution is appropriate, and a high $D/H$ can be reached if $z$ is large and $f$ is small. Grinspoon and Lewis assert that it is therefore not necessary to have had a large initial reservoir of water to obtain the current high $D/H$ ratio, but that processing of a quasi-continuous influx of cometary or outgassed hydrogen over time can also produce the observed enrichment of $D/H$.

Donahue and Hodges (1992) disagree with this interpretation, objecting to the large hydrogen escape flux and the small hydrogen abundance used to argue for a steady-state hydrogen abundance. They prefer a depletion time of 0.4–5 billion years for the current reservoir of hydrogen and argue that hydrogen is not in a steady state. They assert that a $D/H$ ratio near 10$^{-6}$ implies that the present inventory of atmospheric water vapor is the remnant of an early reservoir at least 100 times greater.

Certainly, a key component in interpreting the $D/H$ ratio on Venus and how it has evolved is the fractionation factor $f$. The value of $f$ is dependent upon the relative importance of all the escape processes and on the efficiency of D escape relative to H escape for each process. In addition, since the relative importance of each escape process may evolve, the fractionation factor is a function of time. Evolutionary studies of the atmosphere have found that it is possible that a large amount of water may have been lost early through a runaway greenhouse boiling primordial "oceans", photodissociating the water vapor and leading to a massive hydrodynamic escape of hydrogen (Kasting and Pollack, 1983; Kumar et al., 1983). During the proposed hydrodynamic escape phase, the escape rate should have been high enough that little fractionation (i.e. $f = 1$) would have occurred (Hunten et al., 1989). Therefore, the present D/H enrichment (assuming that Earth and Venus initially had similar D/H ratios) is mostly the result of the nonthermal processes of charge exchange and collisional ejection by fast oxygen, occurring since the end of the hydrodynamic escape phase.

Krasnopolsky (1985) has determined that currently $f = 0.022$ for the charge exchange process, correcting an earlier estimate of $f = 0.08$ given by Kumar et al. (1983). McElroy et al. (1987) assumed that for the collision process $f \approx 0$, meaning that essentially no deuterium escapes through this mechanism. Based on these fractionation factors and hydrogen escape fluxes of $1.2 \times 10^7$ and $8 \times 10^6$ cm$^{-2}$ s$^{-1}$ for charge exchange and collisions, respectively, Hunten et al. (1989) derived a value of $f = 0.013$ as a weighted fractionation factor for both processes.

In this paper we will show that the collision process is much more efficient at ejecting deuterium than has been considered in the above work. The use of more accurate dissociation branching ratios for $O_2^+$, the main source of fast oxygen in the Venus thermosphere, as well as the inclusion of the initial ion thermal energy increase the high-velocity tail of light particles after collision. The implication is that deuterium is not completely discriminated against for escape by this process. The derived fractionation factor $f$ must correspondingly be increased, altering models of at least the recent evolution of deuterium and hydrogen on Venus.

The O–H collision process

Collision between light atoms and fast oxygen atoms as an escape mechanism was first proposed by Knudsen (1973) for helium and hydrogen in the Martian atmosphere. McElroy et al. (1982) invoked this mechanism as the primary hydrogen escape process on Venus, with a global average flux of $8 \times 10^6$ cm$^{-2}$ s$^{-1}$. The process involves the dissociative recombination of $O_2^+$, producing fast moving oxygen atoms:

$$O_2^+ + e \rightarrow O^+ + O^*.$$

which may collide with lighter atoms, such as H or D, in the upper atmosphere:

$$O^+ + H \rightarrow O^* + H^*.$$

While the fast oxygen atom never has enough energy to escape, the light atom may be accelerated in the collision to above the escape speed of the planet. If this light atom avoids further collision and is moving in the upward direction, it will escape.

As a model, consider the collision of fast atoms of mass $M$ and speed $V$ with stationary atoms of mass $m$ (corresponding to a gas of H or D approaching 0K). The final speed $v_f$ of a particle initially at rest is given by (see Appendix; also presented in McElroy et al., 1982):

$$v_f = \frac{2}{M+m} \sqrt{\frac{MV}{2}},$$  

where $\Theta$ is the scattering angle in the center of mass frame. Note that this gives an upper limit to the final speed $v_{\text{max}} = 2MV/(M+m)$, corresponding to a "head-on" collision. For collisions between stationary hydrogen or deuterium and fast oxygen, $v_{\text{max}}$ is approximately $2V$. 

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McElroy et al. assumed that the fast oxygen would be the result of O\textsuperscript{3} disassociating into O(D) + O(P), which liberates 5.02 eV and produces two oxygen atoms with speeds of 5.5 km s\textsuperscript{-1}. Using equation (5), \( t_{\text{max}} = 10.35 \) and 9.78 km s\textsuperscript{-1} for H and D, respectively. The escape velocity for Venus at 200 km is 10.2 km s\textsuperscript{-1}, so in this model only hydrogen can escape. This analysis therefore yields \( f = 0 \) for the collision process on Venus. Note, however, that for an oxygen atom with an initial speed greater than 5.74 km s\textsuperscript{-1}, \( t_{\text{max}} \) for D will exceed the escape velocity and some D will escape. Processes which affect the distribution of oxygen speeds will therefore dramatically affect the relative escape efficiency of D compared with H and will have an impact on the fractionation factor \( f \).

Finally, to roughly gauge the impact of the initial thermal energy of the H and D on the limiting final velocity, consider the restricted case of a head-on collision between oxygen and H or D. The light atoms are constrained to have an initial velocity \( v_i \) only along the same line as the oxygen velocity \( V \), but its magnitude can be either positive or negative. The final velocity of the light atom is:

\[
\frac{V}{V - v_i} = \frac{2M}{M + m} + \frac{m - M}{M + m} v_i. \tag{6}
\]

Note that this is approximately \( 2V - v_i \) for H or D collisions with oxygen. This shows that \( V \) is roughly twice as important as \( v_i \) in determining the final speed of the particle. The light particle speed can be set at \( \sqrt{k_B T/m} \), a characteristic thermal one-dimensional velocity, and its direction to be toward the incoming oxygen atom (\( v_i = -\sqrt{k_B T/m} \)). Taking the oxygen speed \( V = 5.5 \) km s\textsuperscript{-1} and using a typical thermospheric temperature of 300K (giving \( v_i = 1.58 \) and 1.12 km s\textsuperscript{-1} for H and D), equation (6) yields final velocities of 11.74 and 10.65 km s\textsuperscript{-1} for H and D, respectively. This quantitatively shows that some D may escape in collisions with O due to the thermal energy of the deuterium. However, any corrections to the initial velocity of the oxygen atoms will have a stronger impact upon the escape rate.

The fraction of collisions leading to final speeds above the escape speed is a complicated function of several parameters. The post-collision distribution of speeds is dependent upon the scattering phase function \( \Omega(\Theta) \), the velocity distribution of the fast oxygen atoms and the thermal energy of the light atoms. The total effect of all of these considerations is considerably more complex than is given in equations (5) and (6) and will be developed sequentially in the next sections.

**Scattering phase function effects**

In their initial proposal of the collision process as an important hydrogen escape mechanism, McElroy et al. assumed that the scattering phase function was isotropic in the center of mass frame. More recently, calculations of the elastic scattering cross-section for O–H collisions have been made by Cooper et al. (1984) using interaction potentials for four molecular symmetry states arising in the approach of ground-state oxygen and hydrogen atoms. The calculations were made for a range of relative impact velocities, all of which found extreme forward scattering for the collision. As the differential elastic scattering cross-sections they obtained were quite similar over a relatively wide range of velocities, we adopted the solution, weighted for the symmetry states, corresponding to a relative impact energy of 0.15 eV and equivalent to an initial oxygen velocity of around 5.5 km s\textsuperscript{-1} (see their Fig. 2). A normalized phase function for the center of mass scattering angle was obtained by dividing this angular distribution function by the total elastic cross-section and then differentiating with respect to the cosine of the scattering angle. This phase function is shown in Fig. 1.

In an effort to describe the scattering phase function in a simple way, we attempted to fit the Cooper et al. calculation with a parameterized phase function. The Henyey–Greenstein (HG) phase function, in terms of \( \cos \Theta \) (where \( \Theta \) is the scattering angle), is given by:

\[
\Phi_{\text{HG}}(g, \cos \Theta) = \frac{(1-g^2)}{(1+g^2-2g \cos \Theta)^2}, \tag{7}
\]

where \( g \) is a parameter between –1 and 1 describing the anisotropy of the phase function (Goody and Yung, 1989). For \( g = 0 \), the phase function is isotropic; for positive values it is forward scattering and for negative values it is backward scattering. This function is normalized such that the integral over \( \cos \Theta \) from –1 to 1 is equal to 2. Scattering is usually considered azimuthally symmetric and the integrated azimuthal angle phase function is \( 2\pi \); together the two give a total phase function integrated over both angles of \( 4\pi \).

The O–H scattering phase function derived by Cooper et al. proved difficult to fit accurately with a single phase function, so a weighted pair of HG phase functions was used. The best-fit phase function for the center of mass frame scattering angle is:

\[
\Phi(\cos \Theta) = \frac{1}{2} [\Phi_{\text{HG}}(g_1, \cos \Theta) + (1-a)\Phi_{\text{HG}}(g_2, \cos \Theta)], \tag{8}
\]

with \( a = 0.4 \), \( g_1 = 0.18 \) and \( g_2 = 0.95 \) (see Fig. 1). In our application it is more convenient to use a scattering phase function normalized such that the integral over \( \cos \Theta \) is normalized to 1. For this reason the parameterized phase function we use is given by introducing a factor of 1/2 to the traditional HG phase function. The values for \( a, g_1 \) and \( g_2 \) show that O–H scattering is 60% extreme forward scattering and 40% near isotropic. Equation (5) shows that forward scattering results in less energy transfer from the moving particle to the stationary particle, while the implication of the best-fit phase function is that O–H scattering will be less efficient at ejecting hydrogen than isotropic scattering, a result which Cooper et al. described. The inaccuracy of the fit in the forward scattering part of the phase function is not important for escape, since only collisions of strong backward scattering will result in the high H and D speeds necessary for escape.

Calculations for O–D collisions were not done by Cooper et al., but differences between the two must be very minor. Therefore, for the remainder of this work, we will assume that the scattering phase function for O–D collisions is the same as that for O–H in the center of mass frame.
Fig. 1. Oxygen–hydrogen scattering angle phase function. The dashed line is derived from the calculations of Cooper et al. (1984) and the solid line is a best fit two-term parameterized phase function, as described in equation (8) of the text.

It is shown in the Appendix that for the model OK gas discussed earlier an analytic formulation for the final speed distribution can be obtained in terms of the scattering phase function. The probability distribution \( P(v_f) \) for the speed of particles, initially at rest, after collision with particles of speed \( V \) is given by:

\[
P(v_f) = \frac{2\Phi(\Theta)}{\sqrt{v_{\text{max}}^2 - v_f^2}},
\]

with \( v_{\text{max}} \) as given earlier. The distribution is zero for \( v_f > v_{\text{max}} \). For the integral of \( \Phi(\Theta) \) normalized to one, the integral of \( P(v_f) \) from 0 to \( v_{\text{max}} \) is also normalized to one.

Figure 2 shows the speed distribution for hydrogen and deuterium after collision with oxygen at 5.5 km s\(^{-1}\). Hydrogen has \( v_{\text{max}} = 10.35 \) km s\(^{-1}\) and deuterium has \( v_{\text{max}} = 9.78 \) km s\(^{-1}\). Distributions are given for our parameterized scattering function and also for isotropic scattering, as assumed by McElroy et al. Isotropic scattering produces a distribution dominated by high speeds, while the more accurate anisotropic scattering produces a distribution dominated by a peak at low speeds and a long tail extending to high speeds. This shows the strong depletion which anisotropic scattering produces in the population at high speeds in relation to isotropic scattering. The efficiency of escape by collisions is correspondingly much reduced for hydrogen. As discussed earlier, deuterium does not escape in this model.

Dissociative recombination branching ratios and ionospheric temperature effects

The dissociative recombination of \( \text{O}_2^+ \) can proceed along a number of branches. The energetically allowed branches all release some quantity of energy, which is equally divided between the two product oxygen atoms as translational energy. The allowed branches, along with the velocity each oxygen atom will obtain (in a center of mass frame) are:

\[
\text{O}_2^+ + e \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P}) + 6.98 \text{ eV}, \quad v_o = 6.49 \text{ km s}^{-1}
\]

(10a)

\[
\rightarrow \text{O}(^1\text{D}) + \text{O}(^3\text{P}) + 5.02 \text{ eV}, \quad v_o = 5.50 \text{ km s}^{-1}
\]

(10b)

\[
\rightarrow \text{O}(^1\text{S}) + \text{O}(^1\text{P}) + 2.79 \text{ eV}, \quad v_o = 4.10 \text{ km s}^{-1}
\]

(10c)

\[
\rightarrow \text{O}(^1\text{D}) + \text{O}(^1\text{D}) + 3.05 \text{ eV}, \quad v_o = 4.29 \text{ km s}^{-1}
\]

(10d)

\[
\rightarrow \text{O}(^1\text{S}) + \text{O}(^1\text{D}) + 0.83 \text{ eV}, \quad v_o = 2.24 \text{ km s}^{-1}
\]

(10e)

It is immediately clear that the relative weights of these channels will dramatically affect the escape of hydrogen and deuterium, because of the differences in obtained oxygen speeds. In particular, the first two branches allow for the possible ejection of hydrogen, while only the first branch allows for the possible ejection of deuterium (using equation 5). As stated above, McElroy et al. (1982) assumed that all dissociations went along the second branch. However, it has been shown that the branch along which the dissociative recombination proceeds depends strongly on the vibrational state of the ion. Fox and Bougher (1991) present a brief overview of recent work.
Fig. 2. Normalized probability distributions for the speed of hydrogen and deuterium atoms initially at rest (corresponding to a gas at 0K) after collision with oxygen atoms at 5.5 km s$^{-1}$. The triangular distributions are for isotropic scattering, while the distributions with dominant peaks at low speeds are for the anisotropic phase function shown in Fig. 1.

on yields for the above branches. This overview provides a table of the yields for the five branches used in four different studies of the hot oxygen coronas, which is reproduced in Table 1.

The yields found by Fox (column d) and Rohrbaugh and Nisbet (1973, column a) agree surprisingly well. The values found by Paxton (1983, column b) are somewhat less in agreement, while the assumed values of McElroy et al. are quite different from those in the other three. It is notable that although there is a large disagreement among the various presented sets of yields, the average energy of the product O atoms is fairly similar for all.

Table 1. Yields for branches in the dissociative recombination of O$_2^-$ assumed or computed in calculations of hot oxygen coronas. After Fox and Bougher (1991).

<table>
<thead>
<tr>
<th>Branch</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3_P + ^1_P$</td>
<td>0.325</td>
<td>0.22</td>
<td>0.0</td>
<td>0.334</td>
</tr>
<tr>
<td>$^1_D + ^3_P$</td>
<td>0.30</td>
<td>0.55</td>
<td>1.0</td>
<td>0.393</td>
</tr>
<tr>
<td>$^1_S + ^1_P$</td>
<td>0.05</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$^1_D + ^1_D$</td>
<td>0.275</td>
<td>0.13</td>
<td>0.0</td>
<td>0.233</td>
</tr>
<tr>
<td>$^1_S + ^1_D$</td>
<td>0.05</td>
<td>0.10</td>
<td>0.0</td>
<td>0.038</td>
</tr>
</tbody>
</table>

(a) Derived by Rohrbaugh and Nisbet (1973) from data of Zipf (1970).
(b) Found by Paxton (1983) from a best fit to the PV OUVS (Pioneer Venus Orbiter Ultraviolet Spectrometer) hot oxygen data.
(c) Assumed by McElroy et al. (1982).
(d) Derived by Fox from calculations by Guberman (1987, 1988) and the measurements of Mul and McGowan (1979).

will be discussed below, this rough agreement in average energy is important in determining the escape efficiency of hydrogen and deuterium in collisions with oxygen.

No clear consensus exists as to which branching ratios are most consistent with the actual conditions on Venus, although the presumed ratios of McElroy et al. are probably quite inaccurate. We have therefore modeled the effects of all four branching ratios presented in Table 1 in order to determine the sensitivity of hydrogen and deuterium escape (and hence the fractionation factor $f$) to changes in the relative importance of each branch.

Until this point it has been assumed that the oxygen atoms created during the dissociative recombination of O$_2^-$ obtain the speeds shown above. The speed distribution of the product oxygen would therefore be described by delta functions of varying strengths at 2.24, 4.10, 4.29, 5.50 and 6.49 km s$^{-1}$, and all collisions with a model 0K gas of hydrogen and deuterium would occur at these speeds. However, this neglects the initial ion and electron energies.

Measurements made by the Pioneer Venus Orbiting Retarding Potential Analyzer (ORPA) show that the peak O$_2^-$ number densities occur near 150–160 km in the atmosphere, with values of roughly $10^5$ cm$^{-3}$. The O$_2^-$ density falls off steadily with altitude above that to values of around $10^6$ cm$^{-3}$ at 200 km and $10^2$ cm$^{-3}$ at 350 km (Miller et al., 1984). These values are fairly constant over the dayside, but drop sharply to low levels on the nightside. Over this distribution, the ion temperature varies from near 350K at 150 km to over 2000K at 350 km for the dayside. Nightside values can be even more extreme, with $T_i$ rising to roughly 5000K at 350 km. The most
probable speed for $O_2^-$, assuming a Maxwellian distribution of velocities at the ionospheric temperature, ranges from 0.7 km s$^{-1}$ at 1000K to 1.6 km s$^{-1}$ at 3000K, which represents a significant source of initial momentum and energy which should be accounted for. Similar measurements of electron temperature by the ORPA show that there is little diurnal variation of $T_e$. The electron temperature rises quickly from roughly 500K at 150 km to over 4000K at 350 km (Miller et al., 1980; Miller et al., 1984).

To investigate the effect of electron and ion energies on the speed distribution of product oxygen atoms, a Monte Carlo computer simulation was performed. It was assumed that the electron and ion temperatures were representative of Maxwellian distributions and ion velocities in the ionosphere. Test ions were created with randomly chosen $x$-, $y$- and $z$-velocities according to a Maxwell distribution based on the temperature $T_e$ and test electrons were created with velocities based upon $T_e$. Since the mass of the electron is much less than the mass of the oxygen ion, it was assumed that the ion determined the center of mass. In the center of mass frame the ion was dissociated along one of the five branches, and the center of mass frame translational energy of the electron was added to the dissociation energy for that branch. The dissociation was assumed to be isotropic in the center of mass. The $x$-, $y$- and $z$-velocities of the product O atoms were determined for the center of mass frame from the equally divided energy of dissociation and random angles following isotropy. Translation back to the initial frame gave final product oxygen speeds. Statistical distributions were obtained by simulating a large number of dissociations. Distributions for $T_e = 400$, 1000, 2000, 3000, 4000 and 5000K were obtained: for each distribution $T_e$ was held at 3000K.

The effect of the ion and electron initial energies on the speed distribution of product oxygen atoms is shown in Fig. 3a and b. Figure 3a is for $T_e = 3000K$ and shows the individual contributions of each branch to the total distribution following the yields given by Fox. The inclusion of electron and ion energies spreads the “delta function” of each branch into Gaussian-like speed distributions and pushes the peak due to each branch to higher speeds. Note that a significant fraction of the distribution is above 5.75 km s$^{-1}$, the minimum oxygen speed at which model OK hydrogen and deuterium can be accelerated to speeds greater than the escape speed.

Figure 3b presents the total product oxygen speed distributions for the four branching ratio groups in Table 1. From the similarities in the distributions it is evident that the inclusion of electron and ion energies partially compensates for the differences among the branching ratio groups. In particular, all the distributions have maxima at just under 6 km s$^{-1}$ and all extend to speeds greater than 8 km s$^{-1}$. The similarities of the distributions are the result of the similar mean energies for the branching ratio groups and the smearing of speeds caused by the electron and ion energies. From this we can predict that hydrogen escape efficiencies will be quite similar for the four branching ratio groups. We can also predict that deuterium will escape by the collision process, since substantial fractions of the oxygen distributions are at $r > 5.75$ km s$^{-1}$.

This is true even for the assumed branching ratio of McElroy et al., which had previously been considered 100% selective against deuterium escape.

The analytic probability function $P(t)$ can now be used to generate speed distributions for H and D after collision with fast oxygen given these speed distributions. The results are shown in Fig. 4a for hydrogen and 4b for deuterium. The ion and electron temperatures were both 3000K. Note that a logarithmic scale has been used for the normalized weight axis to accentuate the small differences between the four distributions. Even with this scale the differences are quite small, validating our earlier intuition that the distributions would be quite similar. The distribution for deuterium includes some fraction in the high-speed tail, at speeds greater than 10.2 km s$^{-1}$, showing that D can escape by the collision process. In fact, there exists a marked similarity between the hydrogen and deuterium distributions computed from the same oxygen distribution. This similarity qualitatively shows that the efficiency of deuterium escape relative to hydrogen escape on a per collision basis, under the conditions assumed, will be quite high compared with that of charge exchange.

**Neutral gas temperature effects**

The final component to be considered is the inclusion of the initial thermal energy and momentum of the hydrogen and deuterium. Exospheric temperatures on Venus range from roughly 300K on the dayside to below 120K on the nightside and represent a significant source of initial light particle velocity. For our model we assume that the hydrogen and deuterium gases have Maxwellian speed distributions given by the exospheric temperature $T_{exo}$. With this inclusion, however, the favorable geometry of the OK gas discussed above is lost and it was found necessary to develop a Monte Carlo algorithm to compute the hydrogen and deuterium speed distributions after collision with fast oxygen.

The Monte Carlo simulations were performed as follows. An oxygen velocity was chosen to be used for an entire run, consisting of several tens of thousands of simulated collisions. For each collision, the $x$-, $y$- and $z$-component velocities for the light particle were determined randomly assuming Maxwellian distributions at $T_{exo}$. The frame was then shifted to the center of mass of the oxygen-light particle system. In the center of mass frame, the angles of scattering were randomly determined according to the scattering phase function $P(\theta)$, and the new center of mass velocities were then calculated. Translating back into the initial frame gave the final, post-collision speed of the light particle. By calculating in this manner for each of the collisions, a statistical distribution was formed. Each run was done for only one oxygen speed, thus it was necessary to do many runs in order to span the range of possible oxygen speeds. The final distributions were obtained by weighting the hydrogen and deuterium speed distributions found for each oxygen speed by the probability of that speed, given by the distributions of fast oxygen (i.e. those shown in Fig. 3b).

In addition to determining the elastic scattering cross-sections for O–H collisions, Cooper et al. (1984) presented...
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Fig. 3. The normalized probability distribution for the speed of product oxygen atoms from the dissociative recombination of \( \text{O}_2^+ \) is given in (a). The dashed lines represent the contributions from each of the branches following the branching ratios of Fox and the solid line is the sum of the contributions, giving the total oxygen speed distribution. A is the distribution for \( \text{O}_2^+ + e \rightarrow \text{O}(^1\text{P}) + \text{O}(^1\text{P}) \); B: \( \text{O}(^1\text{D}) + \text{O}(^1\text{P}) \); C: \( \text{O}(^3\text{D}) + \text{O}(^3\text{D}) \); and D: \( \text{O}(^3\text{S}) + \text{O}(^3\text{D}) \). (b) Shows the normalized probability of the speed of product oxygen atoms following the branching ratios suggested in four sources: \( F = \) Fox, presented in Fox and Bougher (1991), \( M = \) McElroy et al. (1982), \( P = \) Paxton (1983) and \( R = \) Rohrbaugh and Nisbet (1973). Branching ratios are given in Table 1. The distributions in both (a) and (b) are for ion and electron temperatures of 3000K.

A formula for determining the rate coefficient for the production of particles with a specific energy in an elastic collision with the atoms of a thermal gas. They used this formula to determine the fraction of hydrogen atoms which have velocities greater than the escape velocity on Venus after collision with hot oxygen atoms moving at 5.6 km s\(^{-1}\). They calculated that for hydrogen initially at 300K the fraction with speeds in excess of the escape speed...
would be 8.5%. A similar calculation made assuming isotropic scattering gave the result that 18.8% would be faster than the escape speed. The calculations of McElroy et al. (1982) gave the result of 15% for the same conditions and assuming isotropic scattering. Using our model, we find that for oxygen at 5.6 km s\(^{-1}\), hydrogen at 300K and isotropic scattering, 15.8% are above the escape speed, which agrees with the value found by McElroy et al., more so than with that of Cooper et al. When we perform the calculation assuming the forward scattering phase function (based upon the elastic scattering cross-sections determined by Cooper et al.) we find that 4.6% are above the escape speed, which is just over half of that found by Cooper et al. The phase functions used are nearly identi-
ical, especially for angles of strong backscattering which produce the fastest hydrogen and deuterium after collision and therefore lead to escape, so this discrepancy is somewhat puzzling. However, since we verify the results of McElroy et al., assuming isotropic scattering, we believe that our calculations yield the more correct results in comparison with those of Cooper et al.

Calculating the final hydrogen and deuterium speeds given the oxygen speed distribution and assuming a 300K gas as outlined above, we find that the resulting distributions are similar in form to those found for a 0K gas, but there are important differences. Figure 5 compares the final distribution of speeds for a hydrogen gas initially at 0K with that for a hydrogen gas initially at 300K. The gas particles were in collision with oxygen atoms found from assuming the branching ratios of Fox and ion and electron temperatures of 3000K. The general characteristics of the distributions are similar, including a pronounced peak at low speeds and a long higher speed tail. The inclusion of modeling the initial hydrogen temperature effects manifests itself in a shift to higher speeds of the low-speed peak and a slight increase in the high-speed tail.

The distribution for the hydrogen initially at 300K can be fitted extremely well by a two-temperature Maxwellian distribution. Shown in Fig. 5 is a best-fit distribution, with roughly 60% at 365K and 40% at 2540K. Previous observations have shown that the Venus hydrogen distribution can be described by a two-component model. The "cold" component represents the main exospheric hydrogen reservoir accommodated to the exospheric temperature. The "hot" component represents suprathermal atoms, which probably do not have a Maxwellian velocity distribution, but through the observed scale height can be assigned a temperature. The dayside cold component has been found to be at roughly 300K and the dayside hot component to be from 900 to 1400K (Wallace, 1969; Anderson, 1976; Takacs et al., 1980; Bertaux et al., 1982). The two temperatures found from Fig. 5 are not in tremendous agreement with these observed values, especially for the hot component. This may be the result of the collision process not being a major source of the hot hydrogen exosphere, which then must be populated by some other mechanism such as charge exchange. It is also possible that the loss of particles with speeds above the escape velocity depletes the tail enough to mimic hot component distributions at temperatures more in line with those observed.

Discussion

For distributions such as that shown in Fig. 5, a small but significant fraction $F$ of atoms lie at speeds greater than the escape speed. The efficiency of atoms which actually escape the atmosphere will be some further fraction of $F$. For example, particles in the high-speed tail of the distributions for hydrogen and deuterium are only produced in collisions of strong backward scattering, those of scattering angles approaching 180° [see equation (5)]. Therefore, anisotropy in the initial oxygen velocity distribution will lead to anisotropy in the final H or D velocity distribution, being most important in the high-speed tail. This is important because only those particles scattered.
into the “up” hemisphere can escape (assuming no further collisions and no reflection of downward moving particles off the exobase). Consider the extreme anisotropic case of fast oxygen atoms only moving downward (perhaps in the region of 30 km altitude near the 03 ionospheric peak), the fraction of H or D atoms with post-collision speeds exceeding the escape speed and moving upwards will be much less than for the reverse case of oxygen atoms only moving upward. In the case of an isotropic distribution of oxygen velocities, however, the resultant H and D distributions will also be isotropic immediately following collision, and the escaping fraction will then be 1/2 (as half the atoms are moving up and half are moving down). Again, this assumes no further collisions nor reflections of downward moving H or D from the exobase.

Figure 6a plots the value of $F$ for both H and D as a function of ionospheric temperature. Results determined using the four groups of branching ratios (from Table 1) are shown, giving slightly different but comparable results. The electron temperature was held at 300K and the neutral temperature was held at 300K for all cases. As can be seen, the value of $F$ for the collision process is only 5–7.5% for H and 2.5–5% for D. The results for the branching ratios of McElroy et al. are the most sensitive to the ionospheric temperature. The value of $F$ for deuterium is greater than zero, showing that deuterium will escape by this process over the range of ionospheric temperatures appropriate for Venus.

Rearrangement of equations (1a) and (1b) leads to a mathematical description of the fractionation factor $f$ in terms of the globally averaged H and D escape fluxes and the bulk atmospheric D/H ratio:

$$f = \frac{\phi_H/\phi_D}{D/H}.$$  

(11)

This is the important parameter when dealing with the evolution of D/H. The value of $\phi = F_0/F_E$, shown in Fig. 6b, is the efficiency of D escape relative to H escape on a per collision basis. The two are not, in general, equivalent. Above the homopause the D/H ratio is constantly decreasing with altitude, as D has a scale height of half that of H. As the D/H ratio decreases, the escaping flux of D relative to H will decrease, all other parameters being equal, simply due to the decrease in available D atoms. Hence the value of $f$ is dependent upon the (variable) D/H ratio through the region where most of the collisions leading to escape occur, as well as on $\phi$. If it can be shown that escape by collisions is well-confined to a particular region in altitude $z_{ref}$, then:

$$f \sim D/H(z_{ref}).$$  

(12)

where $D/H$ is the mean D/H ratio of the entire atmosphere, approximately $1.9 \times 10^{-3}$ (de Bergh et al., 1991).

A corrected flux due to collisional ejection of hydrogen can now be determined, and a weighted mean $\bar{f}$ can be found for the two processes of charge exchange and collisional ejection. The global average flux from charge exchange has been calculated as $1.2 \times 10^3$ cm$^{-2}$ s$^{-1}$ (Kumar et al., 1983) and as $2.8 \times 10^2$ cm$^{-2}$ s$^{-1}$ (Hodges and Tinsley, 1986). In a more recent paper (Donahue and Hodges, 1992), the authors state that these are rather high escape fluxes, and that a flux between 0.4 and $1 \times 10^2$ cm$^{-2}$ s$^{-1}$ as determined by Rodríguez et al. (1984) is more accurate.

The global average flux due to collisional ejection was calculated by McElroy et al. (1982) to be $8 \times 10^2$ cm$^{-2}$ s$^{-1}$ assuming isotropic scattering, fast oxygen only at 5.6 km s$^{-1}$ (a minor discrepancy in the energy of dissociation leads to differences between the center of mass speeds of the product oxygen used by McElroy et al. and by ourselves), and cold component H at 300K. They found, and we have verified using our model, that given these assumptions roughly 15% of the scattered H will have speeds greater than the escape speed. Utilizing the anisotropic scattering function and the inclusion of initial ion and electron energy and momentum, we find that for $I_{dec} = 3000$K and cold component H at 300K, the fraction of scattered H that will have speeds greater than the escape speed is roughly 6.5% (see Fig. 6a), or 0.43 times that determined by McElroy et al. We therefore argue that their estimate for the global average hydrogen flux due to collisional ejection by fast oxygen should correspondingly be reduced to $3.8 \times 10^2$ cm$^{-2}$ s$^{-1}$, which is about 30% of the flux due to charge exchange found by Kumar et al. (1983) or about 12.5% of that found by Hodges and Tinsley (1986).

The fractionation factor $f$ has not been computed for the charge exchange flux found by Hodges and Tinsley. For the flux determined by Kumar et al., the weighted mean $f$ is given by:

$$f = 0.77f_{[\text{charge exchange}]} + 0.23f_{[\text{collisional ejection}]}.$$  

(13)

Krasnopolsky (1985) found $f = 0.022$ for charge exchange based on the flux determined by Kumar et al. For $T_i = 3000$K we find $\phi$ to be approximately 0.64 (almost 30 times $f$ due to charge exchange). Using the VIRA thermospheric model (Keating et al., 1985) for hydrogen distribution and a homopause near 140 km, the D/H ratio at 200 km is roughly $1.6 \times 10^2$, at 300 km is $1.1 \times 10^2$, and at 400 km is $8 \times 10^1$ for the dayside. An average of the D/H ratio over the region, weighted by the hydrogen density, is $1.4 \times 10^2$. This leads to a fractionation factor for collisional ejection of $f = 0.47$ for the assumed conditions. The mean fractionation factor for both charge exchange and collisional ejection is estimated to be $f = 0.125$, which is almost an order of magnitude larger than that found by Hunten et al. (1989).

The globally averaged deuterium escape flux due to collisional ejection is therefore estimated, by rearrangement of equation (11), to be $3.1 \times 10^1$ cm$^{-2}$ s$^{-1}$. A similar estimate for charge exchange yields a flux of $2.5 \times 10^1$ cm$^{-2}$ s$^{-1}$, a factor of more than 6 below that for collisional ejection. We therefore find that, far from being an unimportant source of deuterium escape, collisional ejection is the dominant loss process for D on Venus.

We must point out that no effort has been made to model the effects of multiple scattering of the fast oxygen. Our model includes only oxygen “fresh” from dissociative recombination. Any oxygen scattering previous to collision with hydrogen or deuterium will necessarily decrease the mean energy of the overall oxygen distri-
Fig. 6. (a) The fraction $F$ of H and D atoms with speeds greater than the escape speed of 10.2 km s$^{-1}$ after collision with fast oxygen, as a function of the ionospheric temperature. The electron temperature is 3000K and the neutral temperature is 300K. (b) Shows the relative escape efficiency per collision, $\phi = F_D/F_H$, as a function of the ionospheric temperature. The results are calculated assuming the branching ratios of: F = Fox, presented in Fox and Bougher (1991), M = McElroy et al. (1982), P = Paxton (1983) and R = Rohrbaugh and Nisbet (1973).
Conclusions

The current escape flux of hydrogen is governed by the processes of charge exchange and collisional ejection by fast oxygen atoms. The D/H ratio on Venus is roughly 100 times that on Earth and, together with a comparatively small current inventory of water, this indicates that a significant amount of water may have been lost since the initial formation of the atmosphere. In order to interpret the current D/H ratio and formulate models of the evolution of the D/H ratio it is necessary to understand the fractionating effects of the escape processes. We have reanalyzed the collisional process, bringing together several important complexities, to examine the efficiency of D escape relative to H escape. The process had, in more simplified models, been considered to be completely discriminating against deuterium escape.

Our models include four estimates of the branching ratios in the dissociative recombination of O\(_3\), which is the source of the fast oxygen leading to hydrogen escape. In addition, the initial energy and momentum of the ions and electrons are accounted for, which leads to oxygen atom speed distributions dependent upon the ionospheric temperature. These distributions include a significant fraction of atoms at speeds above 5.75 km s\(^{-1}\), the minimum speed necessary, in a head-on collision, to accelerate both H and D atoms initially at rest to above the escape speed.

Assuming hydrogen and deuterium gases initially at 300K, calculations were made to determine the H and D speed distributions after collisions with fast oxygen atoms. Using the results of Cooper et al. (1984) for the elastic scattering cross-sections in O–H collisions, we determined a best-fit parameterized scattering angle phase function. This function was used to determine the H and D speed distributions. Due to the extreme forward scattering properties of the phase function, the fraction of atoms accelerated to speeds greater than the escape speed is significantly less than if isotropic scattering had been assumed. This reduction in efficiency leads to a correction in the hydrogen escape flux determined by McElroy et al. (1982), with the flux falling from 8 to 3.5 \(\times 10^9\) cm\(^{-2}\) s\(^{-1}\).

The hydrogen and deuterium post-collision speed distributions were used to determine a fractionation factor \(\phi\), which is the efficiency of escape of D relative to H on a per collision basis. For an ionospheric temperature of 3000K, we calculate \(\phi = 0.64\), which is quite significant since the collision process was previously assumed not to be a mechanism for deuterium escape (i.e. \(\phi = 0\)). Using the VIRA thermospheric model for hydrogen distribution and assuming that collisions leading to escape occur over a region with a mean D/H ratio of 1.4 \(\times 10^{-2}\), we estimate the current fractionation factor to be \(f = 0.47\) for the collision process.

By weighting the effects of fractionation due to charge exchange and collisional ejection, a mean fractionation factor for both processes was determined to be \(f = 0.125\). This is an order of magnitude greater than that found by Hunten et al. (1989). The collision process, previously considered an effective process for the fractionation of H and D on Venus, must now be considered to be the principal source of deuterium escape and is, in comparison with charge exchange, a very inefficient fractionating process.

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References

Mul, P. M. and McGowan, J. W., Temperature dependence of


Appendix: speed distributions for gases initially at 0K

(A) Speed of particle initially at rest as a function of colliding particle speed and scatter angle

Consider particle 1 with mass $M$ and speed $V$ in an elastic collision with stationary particle 2 of mass $m$. Take $V$ to lie along the $x$-axis of this initial frame. The center of mass therefore only has an $x$-component of velocity, which is given by $v_{cm} = MV/(M+m)$.

The center of mass velocities of the particles only have $x$-components. In addition, in the center of mass frame particles undergoing elastic collision retain their speeds but have their directions altered. Particle 2 has an initial center of mass velocity of $u_x = -v_{cm}$, as shown in Fig. A1.

Let the particles be scattered from their initial directions through an angle $\Theta$, giving for particle 2:

$$u'_x = u_x \cos \Theta, \quad u'_z = u_z \sin \Theta. \quad (A1)$$

The $T$-component is defined as the velocity of particle 2 perpendicular to the $x$-axis. Note that due to the symmetry of the collision orientation, the azimuthal angle of the scattering, which determines the orientation of the scattering plane with respect to the $y$- and $z$-axes, is unimportant for determining the final speed of the particle in the initial frame. The case of particle 2 not initially at rest and having randomly directed speeds destroys this symmetry, and the azimuthal scattering angle becomes important. Transforming back to the initial frame for our simple case gives:

$$v_x = v_{cm}(1 - \cos \Theta), \quad v_T = v_{cm} \sin \Theta. \quad (A2)$$

Finally, taking $v_T = \sqrt{(v_x)^2 + (v_T)^2}$ as the final speed of particle 2, we find:

$$v_T = \frac{MV}{M+m} \sin \left( \frac{\Theta}{2} \right) = \frac{v_{max} \sin \left( \frac{\Theta}{2} \right)}{2} \quad (A3)$$

Note that $v_{max}$ is the maximum speed obtainable by particle 2, corresponding to a “head-on” collision.

(B) Speed distribution as a function of colliding particle speed and scatter phase function

In part (A) of the Appendix, the dependence of the final particle speed on the center of mass frame scattering angle is shown to be relatively simple for a particle initially at rest. This formula can be extended to consider the distribution of speeds which a statistically large set of initially stationary particles will obtain in collisions with particles whose motion is characterized by a single speed $V$.

The scattering cross-section for the elastic collision of two sets of particles can be described by a total cross-section $\sigma$ and a scattering phase function $\Phi$, which describes the probability of scattering through an angle $\Theta$ (measured in the center of mass frame) in a collision. Using the notation from part (A), the speed distribution is:

$$F(v) = \frac{1}{v_{max}} \frac{dv}{dv} \frac{1}{\sin \frac{\Theta}{2}} \quad (B1)$$

Fig. A1. A schematic representation of scattering. The $x$- and $T$-axes are in the center of mass (CM) frame. The $T$-axis is defined such that it is perpendicular to the $x$-axis and lies in the scattering plane. Particle 2 (stationary in the initial frame) has a CM velocity of $u$ and particle 1 has a CM velocity of $U$. After scattering through angle $\Theta$, the final CM velocities are $U'$ and $u'$ for particles 1 and 2, respectively.
distribution for particle 2, \( P(v_i) \), is given by:

\[
P(v_i) = \Phi(\Theta) \left| \frac{d\Theta}{dv_i} \right|.
\]  

(A4)

Here \( \Phi(\Theta) = \sin \Theta \Phi(\cos \Theta) \) is the phase function for scattering in terms of \( \Theta \). If \( \Phi(\Theta) \) is a normalized probability, then \( P(v_i) \) will also be a normalized probability. The derivative is easily evaluated [noting \( \sin (\Theta/2) = \sqrt{1 - \sin^2 \Theta} \)] as:

\[
\frac{d\Theta}{dv_i} = \left[ \frac{d\Theta}{d\cos \Theta} \right]^{-1} = \frac{2}{v_{\text{max}} \cos (\Theta/2)} = \frac{2}{\sqrt{v_{\text{max}}^2 - v_i^2}},
\]  

(A5)

leading to:

\[
P(v_i) = \frac{2\Phi[\Theta(v_i)]}{\sqrt{v_{\text{max}}^2 - v_i^2}}.
\]  

(A6)

In the case that the scattering phase function can be expressed as the weighted sum of \( n \) parameterized phase functions, such that:

\[
\Phi(\Theta) = \frac{1}{2} \sin \Theta \sum_{i=1}^{n} a_i (1 - g_i^2)
\]  

\[
\left[ 1 + g_i^2 - 2g_i \cos \Theta \right]^{-1/2},
\]  

(A7)

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where \( \sum a_i = 1 \), it is relatively straightforward to obtain the speed distribution \( P(v_i) \). Using trigonometric substitutions for \( \cos \Theta \) and \( \sin \Theta \), the speed distribution is expressed as:

\[
P(v_i) = \frac{r_i}{v_{\text{max}}} \sum_{i=1}^{n} a_i (1 - g_i^2)
\]  

\[
\left[ 1 + 4g_i (v_i/v_{\text{max}})^2 \right]^{1/2}.
\]  

(A8)

For the case of isotropic scattering \( (g = 0) \) this reduces to the extremely simple form \( P(v_i) = 2v_i/v_{\text{max}}^2 \). For more elaborate scattering functions, the distribution is somewhat more complicated, yet the overall form is still simple. It is easily shown by integrating over the range of \( v_i = 0 - v_{\text{max}} \) that the distribution is normalized to unity.

Of particular interest is determining the fraction \( F \) of the distribution lying at speeds greater than some speed \( v_{\text{esc}} \), which could correspond to the escape velocity for the planet. This is found by integrating over the range \( v_i = 0 - v_{\text{esc}} \). For the simple case of isotropic scattering \( F = 1 - (v_i/v_{\text{esc}})^2 \); for an arbitrary scattering function as given in equation (A7):

\[
F = \frac{1}{2} \sum_{i=1}^{n} \frac{a_i (1 - g_i^2)}{2g_i \left[ (1 - g_i^2) + 4g_i (v_i/v_{\text{max}})^2 \right]^{1/2}}.
\]  

(A9)

Hence \( F \) can be used to find the fraction of escaping particles. Assuming that the post-collision velocity distribution for the particles is isotropic and that no further collisions occur, the fraction of escaping particles (those headed “up” with speeds greater than the escape velocity) would be \( 1/2 F \).