

# **Velocity distributions of energetic atoms in planetary exospheres from dissociative recombination**

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Short title: VELOCITY DISTRIBUTIONS OF HOT ATOMS

**Abstract.** A kinetic theory description of translational energetic atoms in the upper planetary atmosphere is presented. A new analytical result for the velocity distribution of the products of reactive collisions is described. Our calculation takes into account different temperatures of the reactants and arbitrary dependence of the cross section on the relative velocity of the colliding particles. The final result is applied to the production of hot oxygen and carbon by dissociative recombination of  $O_2^+$  and  $CO^+$ , respectively. The nascent distribution of hot atoms generated in this way are compared with the earlier Monte-Carlo calculations. We use the Boltzmann equation to study the thermalization of the hot oxygen via collisions with the thermal oxygen population. The results of this calculation demonstrate quasi-steady state velocity distribution of high-energy oxygen atoms near the exobase of Venus for day time conditions.

## 1. Introduction

There are numerous processes in the terrestrial atmosphere and in the atmospheres of other planets, notably Mars and Venus, which involve the production of translational energetic atoms with energies considerably above thermal values. These “hot” atoms can play an important role in enhanced reaction rates [*Logan and McElroy, 1977; Shizgal and Lindenfeld, 1979; Lie-Svendsen et al., 1991*], nonthermal emissions [*Whipple et al., 1975; Yee, 1988; Armstrong et al., 1994*] and in particular the enhanced nonthermal escape of atmospheric species [*Shizgal and Arkos, 1996; Hunten, 1991*]. Energetic  $O(^1S)$  atoms are produced by dissociative recombination of  $O_2^+$ . Metastable  $O(^1S)$  atoms are the source of the 5577 Å green line emission in the F-region of the thermosphere [*Hays and Walker, 1971; Guberman, 1997*]. Similarly, ion-molecule reactions can produce energetic nitrogen atoms and these can play an important role in atmospheric nitrogen chemistry [*Lie-Svendsen et al., 1991; Kharchenko et al., 1997; Gérard et al., 1997*]. Exothermic chemical reactions in an atmosphere can produce nonthermal distributions of oxygen and nitrogen atoms and lead to enhanced escape of these species [*Fox, 1993; Fox and Hać, 1997b; Hodges, 2000*]. The extent of the departure of the distribution functions from Maxwellian depends on the strengths of the production of nonthermal atoms relative to the rate of collisional relaxation with ambient gases.

On the terrestrial planets, there are several processes that lead to the production of substantial populations of energetic atoms that can have energies above the escape speed of the planet. These nonthermal escape mechanisms play an important role in the evolution of the atmospheres of these planets [*Shizgal and Arkos, 1996*]. The charge exchange process of energetic  $H^+$  or  $D^+$  in collision with neutral H can produce a significant population of H and D atoms with energies well above thermal [*Chamberlain, 1977; Shizgal and Lindenfeld, 1982; Hodges and Breig, 1993; Hartle et al., 1996*]. The dissociative recombination of  $O_2^+$  can produce energetic oxygen atoms on all three terrestrial planets and substantial coronae of hot oxygen exist on Earth, Mars and Venus

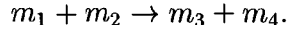
[*Nagy and Cravens*, 1988; *Ip*, 1988]. Similar coronae of hot atoms may exist at some satellites in the Solar System, such as Europa [*Brown and Hill*, 1996]. These energetic oxygen atoms can transfer their energy to H and D and create additional energetic populations of H and D [*Cooper et al.*, 1984; *Gurwell and Yung*, 1993; *Shizgal*, 1999].

The main objective of this paper is to describe a kinetic theory formalism that can be used to determine these nonthermal hot atom distributions. The emphasis is on the development of kinetic theory methods which involve the direct solution of the Boltzmann equation for the velocity distribution function. An alternate approach that is widely used is based on Monte Carlo simulations [*Barakat and Lemaire*, 1990; *Lammer and Bauer*, 1991; *Demars et al.*, 1993; *Hodges*, 1993; *Shematovich et al.*, 1994]. Direct solutions of the Boltzmann equation are an important complement to these Monte Carlo simulations.

In section 2, we derive a new analytical result for the velocity distributions of the product of inelastic collisions, such as dissociative recombination reaction  $O_2^+ + e \rightarrow O^* + O^*$ . This result is quite general and holds for the reactants with Maxwellian distributions at two different temperatures. The final answer is expressed as a single integral over the velocity dependent collision cross section and compliments the previous work by *Whipple* [1974]. Similar distributions were computed before using Monte Carlo techniques by *Gurwell and Yung* [1993]; *Fox and Hać* [1997b]; *Hodges and Breig* [1993]. In section 3, we demonstrate that our analytical calculation agrees very well with the earlier Monte Carlo simulations, requiring insignificant computer resources relative to the Monte Carlo simulations. Finally, in section 4, we use a simplified Boltzmann equation to study the thermalization of the hot oxygen produced by dissociative recombination via collisions with the background thermal oxygen population. As an example, we calculate the hot oxygen distribution function for typical conditions near the day-side exobase of Venus.

## 2. Product velocity distribution functions

Here we treat the general problem of the velocity distributions of the products of bimolecular reactions, depicted as the reaction of species 1 and 2 leading to products 3 and 4, that is,



We study this problem for arbitrary dependence of the total cross section,  $\sigma(g)$  on the relative velocity of the reactants,  $g$ , and we assume the scattering to be isotropic in the center of mass frame. The reaction energy,  $E$ , (the difference between the kinetic energies of the products and the reactants) can be either positive or negative depending on whether the reaction is exothermic or endothermic. We assume that the velocity distributions of particles 1 and 2 are Maxwellian at two different temperatures,  $T_1$  and  $T_2$ . The change of the distribution function  $f_3$  of a product of this reaction can be written as follows [*Chapman and Cowling*, 1961]

$$\left(\frac{\delta f_3}{\delta t}\right)_r d\mathbf{v}_3 = \sigma(g') |\mathbf{v}_1 - \mathbf{v}_2| f_1(\mathbf{v}_1) f_2(\mathbf{v}_2) d\Omega d\mathbf{v}_1 d\mathbf{v}_2 \quad (1)$$

Here  $g' = |\mathbf{v}_1 - \mathbf{v}_2|$ ,  $d\Omega$  is an element of the solid angle in the center of mass reference frame, and  $f_1$  and  $f_2$  are the distribution functions of species 1 and 2. If equation (1) is integrated over all  $\mathbf{v}_1$  and  $\mathbf{v}_2$  such that  $\mathbf{v}_3 = \text{const}$ , we get the production rate of species 3 as a function of velocity  $\mathbf{v}_3$ . Thus, the key to performing this integration is the transformation from the initial velocities  $\mathbf{v}_1, \mathbf{v}_2$  to the product velocities  $\mathbf{v}_3, \mathbf{v}_4$ . In the case of elastic collisions, the Jacobian of this transformation is 1, which is not true for reactive (inelastic) collisions [*Whipple*, 1974].

We define the center of mass and relative velocities (before collision) as

$$\mathbf{G} = M_1 \mathbf{v}_1 + M_2 \mathbf{v}_2$$

$$\mathbf{g}' = \mathbf{v}_1 - \mathbf{v}_2$$

Here  $M_k = m_k/m_0$ ,  $m_0 = m_1 + m_2 = m_3 + m_4$ . It is easy to check that the Jacobian

$$\frac{\partial(\mathbf{G}, \mathbf{g}')}{\partial(\mathbf{v}_1, \mathbf{v}_2)} = -1.$$

Because of momentum conservation,  $\mathbf{G}$  does not change during a collision. The relation between the relative speed before the collision,  $g' = |\mathbf{v}_1 - \mathbf{v}_2|$ , and that after,  $g = |\mathbf{v}_3 - \mathbf{v}_4|$ , is given by conservation of energy

$$\frac{1}{2}\mu_{12}g'^2 + E = \frac{1}{2}\mu_{34}g^2 \quad (2)$$

where  $\mu_{12}$  and  $\mu_{34}$  are the reduced masses of particles 1,2 and 3,4, respectively.

Transformation from  $(\mathbf{G}, \mathbf{g}')$  to  $(\mathbf{G}, \mathbf{g})$  may be thought as consisting of two parts: rotation of the vector of the relative velocity from the direction of  $\mathbf{g}'$  to the direction of  $\mathbf{g}$  and the change of the magnitude from  $g'$  to  $g$ . The rotation is given by a unitary matrix whose contribution to the Jacobian is multiplication by 1. Therefore

$$\frac{\partial(\mathbf{G}, \mathbf{g}')}{\partial(\mathbf{G}, \mathbf{g})} = \frac{dg'}{dg} = \frac{m_3m_4}{m_1m_2} \frac{g}{g'}$$

Finally, the transformation from the center of mass reference frame (after the collision) to the laboratory frame gives another factor of -1. Thus, the total Jacobian of the transformation from  $\mathbf{v}_1, \mathbf{v}_2$  to  $\mathbf{v}_3, \mathbf{v}_4$  is

$$\frac{\partial(\mathbf{v}_1, \mathbf{v}_2)}{\partial(\mathbf{v}_3, \mathbf{v}_4)} = \frac{m_1m_2}{m_3m_4} \frac{g'}{g}.$$

Therefore, we can write equation (1) as

$$\left(\frac{\delta f_3}{\delta t}\right)_r = \frac{m_1m_2}{m_3m_4} \int_{\mathbf{v}_4} \int_{\Omega} \sigma(g') \frac{g'^2}{g} f(\mathbf{v}_1) f(\mathbf{v}_2) d\Omega d\mathbf{v}_4 \quad (3)$$

This equation is true for arbitrary distribution functions, however below we will assume Maxwellian distributions  $f_1^M$  and  $f_2^M$ . In order to proceed with the integration, let us define  $\psi$  to be the angle between  $\mathbf{v}_4$  and  $\mathbf{v}_3$ , and hence  $d\mathbf{v}_4 = v_4 dv_4 d(\cos \psi) d\phi$ . We can express the center of mass and relative speeds as

$$G^2 = M_3^2 v_3^2 + M_4^2 v_4^2 + 2M_3M_4 v_3 v_4 \cos \psi$$

$$g^2 = v_3^2 + v_4^2 - 2v_3v_4 \cos \psi$$

and calculate the Jacobian of transformation from  $(v_4, \cos \psi)$  to  $(g, G)$

$$\frac{\partial(v_4, \cos \psi)}{\partial(g, G)} = \frac{gG}{M_4 v_3 v_4^2}$$

We define  $d\Omega = d\varepsilon d(\cos \theta)$ , and then express  $v_1, v_2$  in terms of  $g', G$  as

$$v_1^2 = G^2 + M_2^2 g'^2 - 2M_2 g' G \cos \theta$$

$$v_2^2 = G^2 + M_1^2 g'^2 + 2M_1 g' G \cos \theta$$

We substitute for  $v_1, v_2$  into (3), change the integration variables to  $G, g$  and use the assumption of Maxwellian distributions for both species

$$f^M(v_k) = n_k (m_k / 2\pi k T_k)^{3/2} \exp(-m_k v_k^2 / 2k T_k)$$

Performing the trivial integrations in  $\phi$  and  $\varepsilon$ , we get

$$\left( \frac{\delta f_3}{\delta t} \right)_r = \frac{m_1 m_2}{m_3 m_4} 4\pi \left( \frac{\sqrt{\lambda_1 \lambda_2}}{\pi} \right)^3 \frac{1}{M_4 v_3}$$

$$\int_g \int_G \int_{-1}^1 \sigma(g') \exp \left[ -(\lambda_1 + \lambda_2) G^2 - (M_1^2 \lambda_2 + M_2^2 \lambda_1) g'^2 + 2(M_2 \lambda_1 - M_1 \lambda_2) g' G \cos \theta \right] g'^2 G d(\cos \theta) dG dg$$

The integration in  $\cos \theta$  is elementary. The limits of integration in  $G$  are determined by expressing  $\mathbf{G}$  in terms of  $\mathbf{v}_3$  and  $\mathbf{g}$

$$\mathbf{G} = \mathbf{v}_3 - M_4 \mathbf{g}$$

Therefore, the limits of integration in  $G = |\mathbf{G}|$  are given by

$$|v_3 - M_4 g| \leq G \leq v_3 + M_4 g.$$

However, the integrand is odd in  $G$  (after the integration in  $\cos \theta$  it has a general form  $\exp(-G^2) \sinh G$ ), therefore the sign of the lower limit of the integration does not make

any difference. Writing  $\sinh G$  as a difference of two exponentials, we split the integral into two integrals of the form

$$\int \exp(-\alpha G^2 + 2\beta G + \gamma) dG = \frac{1}{2} \sqrt{\pi/\alpha} \exp(\beta/\alpha - \gamma) \operatorname{erf}(G\sqrt{\alpha} + \beta/\sqrt{\alpha})$$

Using this formula, we can perform the integration in  $G$  to get the final result

$$\left(\frac{\delta f_3}{\delta t}\right)_r = \frac{n_1 n_2}{4\sqrt{\pi}} \left(\frac{m_3 m_4}{m_1 m_2}\right)^2 \lambda_*^{3/2} \frac{\lambda_1 + \lambda_2}{(M_2 \lambda_1 - M_1 \lambda_2) M_4 v_3} \exp\left(\lambda_* \frac{2E}{\mu_{12}}\right) \times \quad (4)$$

$$\int \sigma(g') \exp(-\lambda_* g'^2) g' [\operatorname{erf}(a + b - c) - \operatorname{erf}(a + b + c) + \operatorname{erf}(a - b + c) - \operatorname{erf}(a - b - c)] dg$$

where

$$a = v_3 \sqrt{\lambda_1 + \lambda_2},$$

$$b = g M_4 \sqrt{\lambda_1 + \lambda_2},$$

$$c = g' \frac{M_2 \lambda_1 - M_1 \lambda_2}{\sqrt{\lambda_1 + \lambda_2}},$$

$$\lambda_* = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} = \frac{\mu_{12}}{2kT^*},$$

and  $T^* = M_1 T_2 + M_2 T_1$  is an effective temperature, and  $E$  is given by (2). The limits of integration are from  $\sqrt{2E/\mu_{34}}$  to infinity if  $E > 0$  and from 0 to infinity if  $E < 0$ . Note that this integral is in  $g$ , the relative speed after the collision while the integrand depends on  $g'$ , the relative speed before the collision. The relation between  $g'$  and  $g$  is given by (2). This integral can be easily done numerically for arbitrary dependence of the cross section  $\sigma$  on the relative velocity,  $g'$ .

It is worth comparing the results of our calculation with the earlier analytical results. For example, *Fitzpatrick and Shizgal* [1975] derived velocity dependent collision frequencies for elastic hard sphere collisions for the two constituents with different temperatures. In this case,  $E = 0$ ,  $g' = g$ ,  $\sigma = \sigma_0 = \text{const}$ ,  $m_1 = m_3$  and  $m_2 = m_4$ . The integration limits in (4) are from 0 to infinity and the integral can be evaluated analytically

$$\left(\frac{\delta f_3}{\delta t}\right)_r = \frac{\sigma_0 n_1 n_2}{4M_1 M_2 \tau \lambda_1 v_3} \exp(-\lambda_1 v_3^2) \left[ h_2 \exp(h_1 \lambda_1 v_3^2) \operatorname{erf}(h_2 \sqrt{\lambda_2} v_3) - \operatorname{erf}(\sqrt{\lambda_2} v_3) \right]$$

where

$$\begin{aligned} h_1 &= 4M_1M_2\tau/(1 + 4M_1M_2\tau) \\ h_2 &= (1 + 2M_1\tau)/\sqrt{1 + 4M_1M_2\tau} \\ \tau &= T_2/T_1 - 1 \end{aligned}$$

*Whipple* [1974] studied the velocity distribution function for the case  $T_1 = T_2 = T$  but  $E \neq 0$ . In this case  $M_2\lambda_1 - M_1\lambda_2 \rightarrow 0$ , so first we need to apply l'Hopital's rule to get rid of the apparent singularity (this singularity appeared when we performed the integration in  $\cos\theta$ ). This removes the error functions in the expression (4) and allows us to perform the final integration in  $g$  (for hard spheres,  $\sigma = \sigma_0$ ). Upon doing so we recover the result obtained by *Whipple* [1974], that is

$$\left(\frac{\delta f_3}{\delta t}\right)_r = \frac{4\sigma_0 n_1 n_2 m_3^2}{\pi\sqrt{2kTm_1m_2m_4}v_3} \exp(-m_3v_3^2/2kT + E/kT) F(x_3, x_0)$$

where

$$\begin{aligned} F &= \frac{\sqrt{\pi}}{2}(1/2 + x_3^2 - x_0^2)(\operatorname{erf}(x_3 + x_0) + \operatorname{erf}(x_3 - x_0)) + \\ &\frac{1}{2}(x_3 + x_0) \exp(-(x_3 - x_0)^2) + \frac{1}{2}(x_3 - x_0) \exp(-(x_3 + x_0)^2) \end{aligned}$$

for  $E > 0$  and

$$F = \frac{\sqrt{\pi}}{2}(1 + 2x_3^2 - 2x_0^2)\operatorname{erf}(x_3) + x_3 \exp(-x_3^2)$$

for  $E < 0$ . Here

$$\begin{aligned} x_3 &= v_3 \sqrt{\frac{m_4}{2kT}} \\ x_0 &= \frac{1}{M_3} \frac{E}{kT}. \end{aligned}$$

Finally, we can use our result (4) to evaluate the total reaction rate,  $K_r(T_1, T_2)$ , (once again, for hard spheres)

$$K_r(T_1, T_2) = \frac{1}{n_1 n_2} \int_0^\infty \left(\frac{\delta f_3}{\delta t}\right)_r dv_3$$

After we change the order of integration and integrate over  $v_3$ , multiple cancellations occur (due to the symmetry of the integrand) yielding

$$K_r(T_1, T_2) = 4\pi \left(\frac{\lambda_*}{\pi}\right)^{3/2} \sigma_0 \int \exp(-\lambda_* g'^2) g g'^2 dg$$

The limits of integration are the same as for (4): 0 to infinity if  $E < 0$  and  $\sqrt{2E/\mu_{3A}}$  to infinity if  $E > 0$ . Thus, for  $E > 0$  the reaction rate is

$$K_r(T_1, T_2) = \frac{2\sigma_0}{\sqrt{\pi\lambda_*}}$$

independent of the value of  $E$ , as expected. For  $E < 0$ , we get a well-known result for reactions with a threshold energy

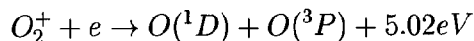
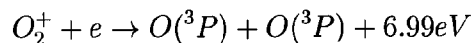
$$K_r(T_1, T_2) = \frac{2\sigma_0}{\sqrt{\pi\lambda_*}} \left(1 + \frac{|E|}{kT^*}\right) \exp\left(-\frac{|E|}{kT^*}\right)$$

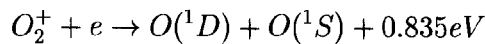
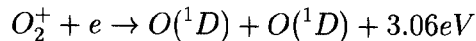
These two temperature rate coefficients are the same as those obtained by, for example, *Light et al.* [1969].

### 3. Comparison with Monte-Carlo simulations

One of the main sources of the translationally energetic atoms in the upper planetary atmosphere is dissociative recombination of ions, such as  $O_2^+$ ,  $CO^+$ ,  $N_2^+$ . The problem of the velocity distributions of the products of dissociative recombination was addressed for example by *Fox and Hać* [1997a, b, 1999] who used Monte Carlo methods. Our analysis of section 2 shows that this problem can be reduced to a single integral which can be evaluated efficiently and precisely using standard methods, such as Laguerre integration.

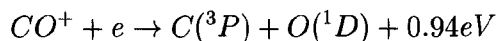
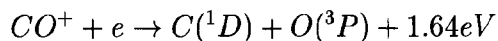
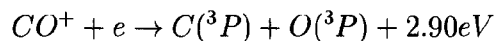
Dissociative recombination of  $O_2^+$  can proceed according to the following channels





Another channel giving  $O(^1S) + O(^3P)$  is energetically possible, but according to both calculations and measurements has zero quantum yield. *Kella et al.* [1997] recommend the yields of 0.22, 0.42, 0.31, and 0.05 for the four branches of the reaction, respectively. These yields were measured for the  $O_2^+$  in the ground vibrational state. It is certain that these yields are affected by the vibrational states of the oxygen ion, but no detailed information about the change in the yields is yet available. In our computations, we have used the same vibrational distribution as *Fox and Hać* [1997b] which is based on the measurements of *Hunton et al.* [1991]. We have also used the same ion and electron temperatures of 500 K and 3000 K, respectively, as *Fox and Hać* [1997b] which are typical for the Venus exobase [*Nagy and Cravens*, 1988]. Although there are recent quantum mechanical calculations of the dissociative recombination cross-sections [*Guberman*, 1997] which agree with the experiment, we have used a simpler analytic cross section  $\sigma \sim g'^{-2.3}$  based on the work of *Walls and Dunn* [1974] for the purpose of comparison with *Fox and Hać* [1997b].

For the conditions typical for Mars, the dissociative recombination of  $CO^+$  may follow one of the three following routes [*Fox and Hać*, 1999]



We have assumed the velocity dependence of the reactive cross section  $\sigma \sim g'^{-1.1}$  used by *Fox and Hać* [1999] based on the measurements of *Rosén et al.* [1998]. The electron and ion temperatures were taken to be 3000 K and 500 K, respectively.

Figure 1 presents the comparison of our calculations using equation (4) (solid lines) with those of *Fox and Hać* [1997b] (dashed lines) for conditions typical of the

Venus exobase. The nascent distributions of  $^{16}\text{O}$  and  $^{18}\text{O}$  resulting from dissociative recombination of  $\text{O}_2^+$  are shown. For the comparison purposes we have used the same normalization for the distribution function as *Fox and Hać* [1997b] (probability per velocity bin of the Monte-Carlo simulation). One can see a perfect agreement between the two methods of calculation of the nascent distribution of the products of dissociative recombination of  $\text{O}_2^+$ , except that the Monte Carlo simulation is fairly noisy.

**Figure 1.**

Figure 2 presents the comparison of the nascent velocity distributions of  $^{12}\text{C}$  and  $^{13}\text{C}$  produced by dissociative recombination of  $\text{CO}^+$  at the exobase of Mars for low solar activity. The results of our calculations are shown by continuous lines and those of *Fox and Hać* [1999] by dashed lines. Once again, we have used exactly the same conditions as *Fox and Hać* [1999] and we have achieved essentially perfect agreement.

**Figure 2.**

#### 4. Thermalization of the hot oxygen

In the previous sections, we have calculated the velocity distribution of the hot oxygen atoms produced by dissociative recombination of  $\text{O}_2^+$ . A complete description of the nonthermal oxygen should take into account the thermalization of these hot atoms via collisions with ambient species, notably thermal oxygen, the diffusion to different altitudes and the escape to space. In general, this is a complicated problem which involves the solution of the Boltzmann equation in both physical and velocity spaces. This may be done either directly or with Monte-Carlo methods. However, we believe that important insights into the distribution of the hot oxygen can be obtained using a simple one dimensional local Boltzmann equation.

In this approximation, the relaxation of a distribution function in time is governed by the equation

$$\frac{\partial f(v, t)}{\partial t} = \int_0^\infty K(v', v) f(v', t) dv' - Z(v) f(v, t) + K_r n_e^2 S(v) \quad (5)$$

Here  $K(v', v)$  is the collision kernel,  $Z(v) = \int_0^\infty K(v', v) f^M(v') dv' / f^M(v)$  is the velocity

dependent collision frequency, and  $S(v)$  is the source term. For the hard sphere cross section for particles with equal masses  $K(v', v)$  and  $Z(v)$  have a particularly simple form [Hoare and Kaplinsky, 1970] (Wigner-Wilkins kernel for equal masses)

$$\begin{aligned} K(x, y) &= A\sqrt{\frac{\pi}{x}}\text{erf}(\sqrt{y}) & y < x; \\ K(x, y) &= A\sqrt{\frac{\pi}{x}}\exp(x-y)\text{erf}(\sqrt{x}) & y > x \end{aligned} \quad (6)$$

$$Z(x) = A \left\{ (2\sqrt{x} + 1/\sqrt{x})\frac{\sqrt{\pi}}{2} + \exp(-x) \right\} \quad (7)$$

Here  $x = mv^2/2kT$ ,  $y = mv'^2/2kT$  and  $A = n_0\sigma(kT/2m)^{1/2}$ .  $T$  and  $n_0$  are the temperature and density of the ambient gas and the source term is proportional to the  $(\delta f/\delta t)_r$  calculated in section 2, that is  $S(v) = 4\pi v^2(\delta f/\delta t)_r$ .

It is quite easy and straightforward to discretize equation (5) and solve it forward in time using, for example, Euler's method. We performed the actual calculation in dimensionless units where the velocity is normalized with the thermal velocity of the ambient gas  $\sqrt{2kT/m}$ , and time with  $t_0 = A/K_e n_e^2$ .

We expect that the details of the realistic O-O differential cross section would not have a large effect on the distribution of hot atoms [Kharchenko *et al.*, 1997]. Consequently, we have taken the O-O collision cross section to be  $\sigma = 10^{-14}$  cm<sup>2</sup> [Kharchenko *et al.*, 2000],  $K_r = 10^{-7}$  cm<sup>3</sup>s<sup>-1</sup> [Hodges, 2000],  $T = 327$  K and  $n_0 = 3 \times 10^8$  cm<sup>-3</sup> which are a typical day-time exospheric parameters at Venus [Nagy and Cravens, 1988; Fox and Hać, 1997b].

We would like to point out that there is no steady state solution for (5). It is easy to see by integrating the distribution function over velocity. The equation for particle density has the form

$$\frac{\partial n}{\partial t} = S_{total}$$

which solution grows linearly with time. This is an obvious result – there is no loss mechanism in the system. In reality, the loss of particles is achieved through drift upward and eventually escape from the exosphere. This problem is, however, quite

complicated and its solution is unnecessary for some simple predictions about the distribution of hot oxygen. Drift velocities on the order of meters per second can noticeably affect only the low energy thermal oxygen. The main loss mechanism for the high energy atoms is scattering by collisions to lower energies. This mechanism is adequately described by the Wigner-Wilkins collision kernel (6).

The formal solution of equation (5) may be written as follows

$$f(v, t) = U_1(v)[q_1 + s_1 t] + \sum_{j=2}^{\infty} U_j(v) \left[ q_j e^{-\lambda_j t} + s_j \frac{1 - e^{-\lambda_j t}}{\lambda_j} \right] \quad (8)$$

where  $U_j(v)$  are the eigenfunctions of the integral operator of the Boltzmann equation,  $\lambda_1 = 0 < \lambda_2 < \lambda_3 < \dots$  are the corresponding eigenvalues and  $q$  and  $s$  are the coefficients of the expansion of the initial condition and the source function in terms of the eigenfunctions. The spectrum of this operator was analyzed on many occasions [*Shizgal et al.*, 1981; *Kryszewski and Gondek*, 1997] and is well-known. The eigenfunction corresponding to  $\lambda_1 = 0$  is the Maxwellian, it is the only steady solution in the absence of the source term. The expansion (8) shows that as  $t \rightarrow \infty$  the density of the thermal population grows linearly in time, while the distribution of the hot atoms (which we define as everything but the Maxwellian part) tends to a steady state determined by

$$f(v, t = \infty) = \sum_{j=2}^{\infty} U_j(v) \frac{s_j}{\lambda_j} \quad (9)$$

independent of the initial conditions. However, in this paper we choose to integrate equation (5) in time with an Euler method, which is equivalent to the iterated kernel method.

For small dimensionless times, some evolution of the distribution function takes place after which a state of dynamic equilibrium is reached. This is the equilibrium at which the number of high-energy atoms produced by the source term  $S(v)$  equals to the number of atoms scattered to the lower energy by collisions (described by the  $Z(v)$  and integral terms). As a result, the low energy (thermal) part of the distribution function

grows linearly in time, while the high energy tail does not change. The time evolution of the velocity distribution function is illustrated in figure 3. The dash-dotted line shows the distribution used as a source function (same as  $^{16}\text{O}$  in figure 1 corresponding to the altitude of 210 km); the thin solid lines marked 1,2, and 3 are the distribution function for dimensionless times 0.2, 0.4, and 0.8, respectively; the thick dashed line corresponds to the dimensionless time 60 and the thin dashed line is the Maxwellian at the ambient temperature. In agreement with the formal solution (8), the time evolution shows the convergence to a steady state for high energy part of the distribution function. At the same time, the Maxwellian part of the distribution grows linearly in time. One can see that the higher energy parts of the distribution function reach the equilibrium faster than the lower energy parts. These velocity distributions are qualitatively similar to those computed by *Yee* [1988] and *Hodges* [1993] using Monte-Carlo simulations.

**Figure 3.**

We can subtract out the Maxwellian part of the distribution function to get the steady state distribution of the hot oxygen. The result is shown in figure 4 (solid lines) for two different temperatures of  $\text{O}_2^+$ . The bold line corresponds to  $T_i = 500$  K,  $z=210$  km and the thin line to  $T_i = 2000$ ,  $z=300$  km which are based on the in situ measurements reported by *Miller et al.* [1980]. The electron temperature remains essentially the same for these two altitudes [*Miller et al.*, 1980], and so does the neutral temperature [*Shizgal*, 1999]. The corresponding dashed lines on figure 4 show the source functions for the two different ion temperatures. Because of the higher ion temperature, the source function at the higher altitude is broader and does not exhibit distinct maxima corresponding to the different dissociative recombination channels.

**Figure 4.**

It is remarkable that the two thermalized distribution functions are essentially identical, the only difference appearing at the very high energy part of the distribution function. This part of the hot oxygen distribution is simply proportional to the source function divided by the velocity dependent collision frequency because the scattering from low to high energies is negligible. At moderately high energies, the contribution

from the integral term of equation (5), which mostly describes scattering from higher to lower energies, becomes significant. For the situation that we have considered, we find a very weak dependence of the steady state hot oxygen distribution on the specific details of the source function.

We would like to point out that the altitude dependence in our simplified model is entirely parametric through constants  $A(z)$  and  $n_e(z)$ . The altitude dependent distribution function can be written as

$$F(v, z) = n_{hot}(z)f(v) = \frac{K_r n_e^2(z)}{n_0(z)\sigma(kT(z)/2m)^{1/2}} f(v)$$

where  $f(v)$  is a steady state solution (9) independently calculated for any given altitude.  $f(v)$  is normalized to 1. The dependence of  $n_e(z)$ ,  $n_0(z)$  and  $T(z)$  on the altitude needs to be provided by an independent model of the vertical structure of Venusian atmosphere, such as *Nagy et al.* [1981] or *Hedin et al.* [1983]. In this paper we focus our attention on the velocity dependent part of the hot oxygen distribution.

One can define the temperature associated with a non-Maxwellian distribution as the average kinetic energy of molecule by

$$\frac{3}{2}kT = \frac{m \langle v^2 \rangle}{2}.$$

Defined in this manner, the temperature for the nascent distribution at 210 km (presented in figure 1) is 20,700 K while for the thermalized hot oxygen distribution at this altitude (figure 4, bold solid line) is it much lower, just 2900 K. The temperatures of the distributions of hot oxygen at 300 km are not that different from those at 210 km: 21,500 K for the nascent distribution and 3080 K for the thermalized one. Although the hot oxygen distribution has a large high energy tail, its center of mass has been shifted towards the lower energies. Of course, it still defines temperature much higher than that of the cold thermal oxygen (which is 327 K).

## 5. Summary

The present paper has described a theoretical approach to the subject of nonthermal or energetic atoms in aeronomy. These hot atoms can play an important role in atmospheric processes, in particular in the direct or indirect escape of atmospheric species. A new analytical result for the velocity distribution of the atoms produced by dissociative recombination of ions has been presented. This result holds for arbitrary energy dependence of the cross-section and accounts for different initial temperatures of the reactants. The results of our analytical calculations were found to be in nearly perfect agreement with the earlier Monte-Carlo calculations. A formal approach to the subsequent thermalization of the hot oxygen atoms in an upper planetary atmosphere based on the solution of the Boltzmann equation for spatially homogeneous systems has been presented. The resulting distribution functions were calculated and compared with the nascent distributions of the hot atoms. It was found that the velocity distribution of hot oxygen atoms varies little with the altitude as long as hot oxygen may be considered to be a minor species compared with the thermal oxygen.

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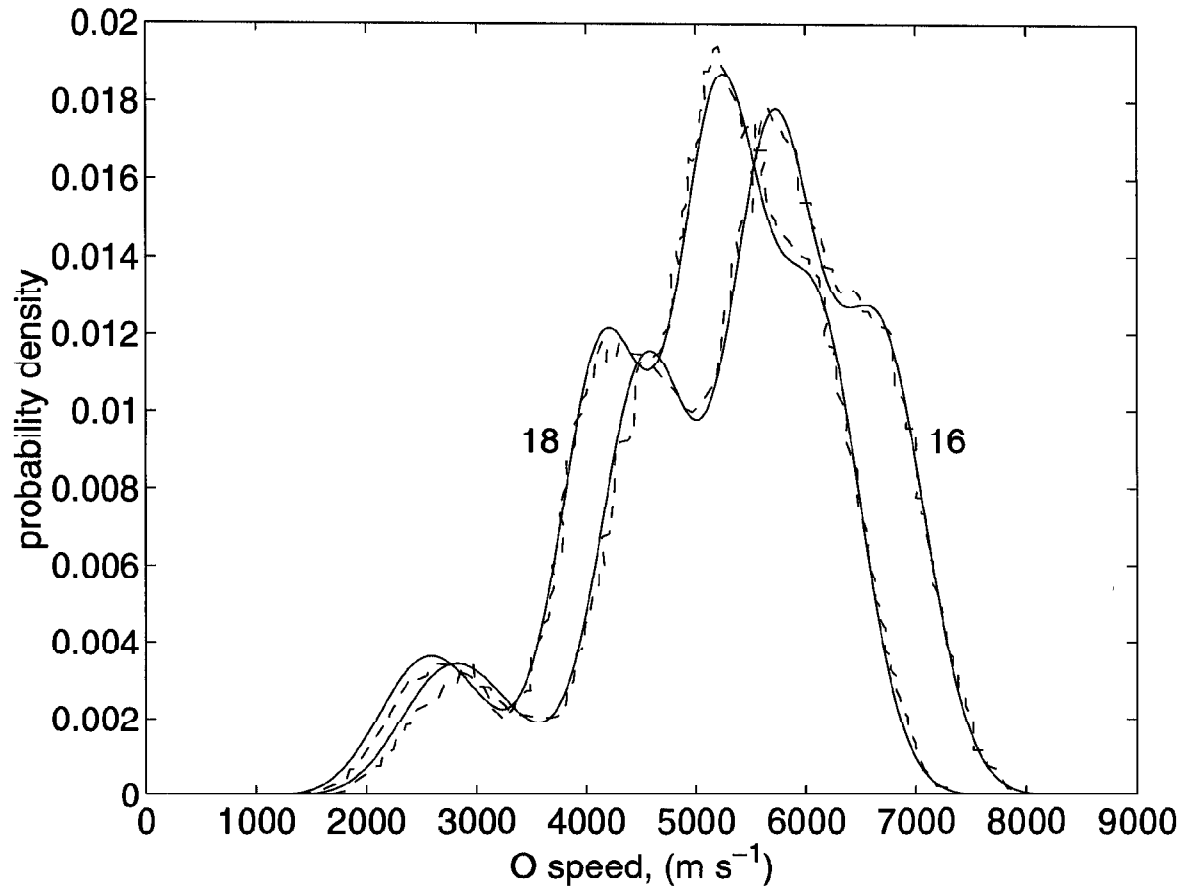
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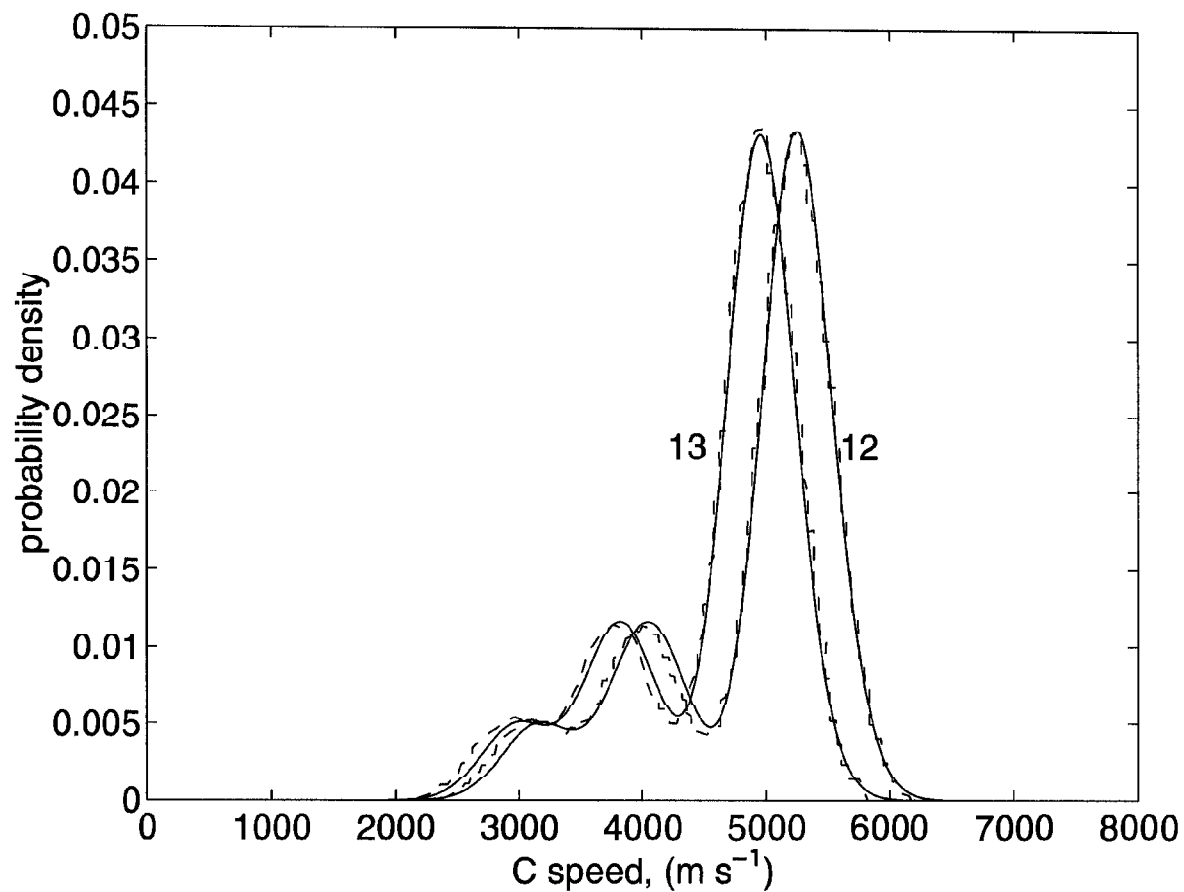
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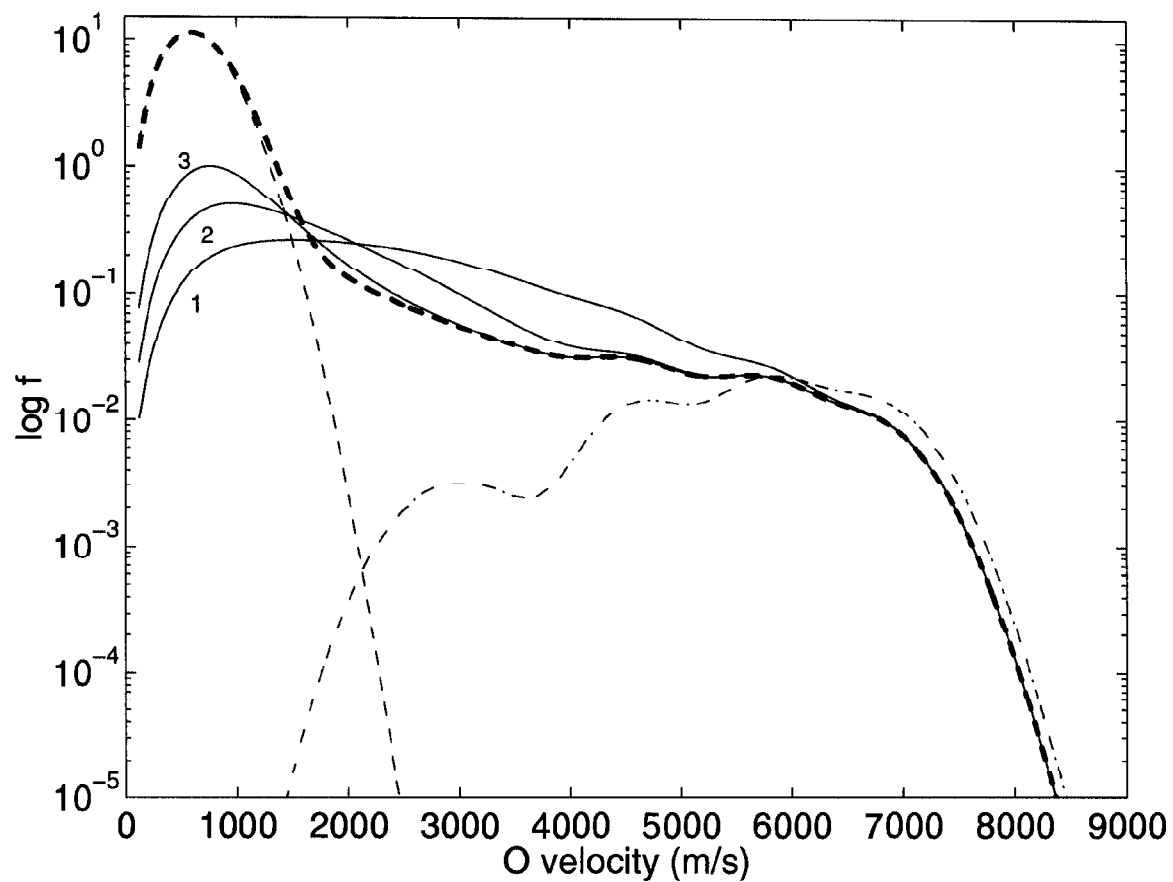
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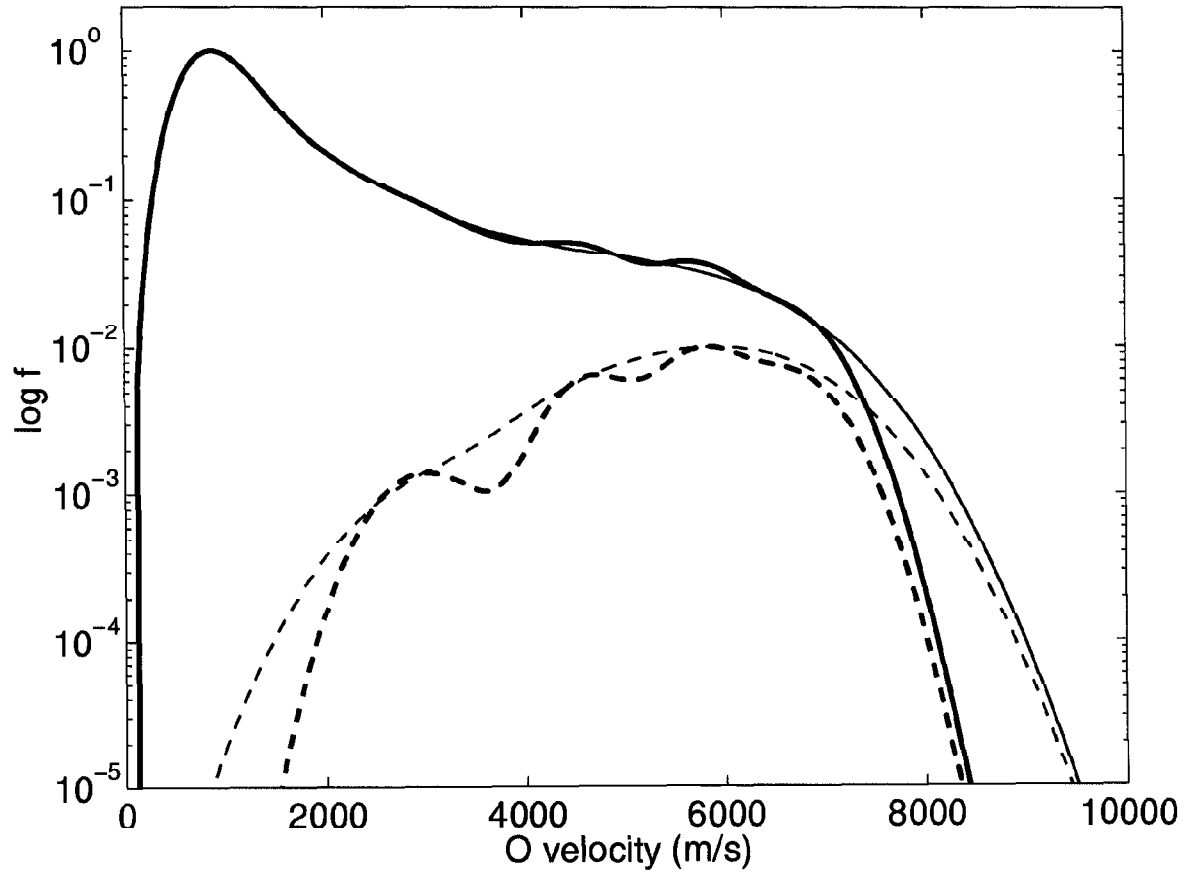
**Figure 1.** Nascent velocity distributions for <sup>16</sup>O and <sup>18</sup>O, compared with the Monte-Carlo simulations of *Fox and Hać* [1997b] (figure 2 of *Fox and Hać* [1997b]) (dashed lines).



**Figure 2.** Nascent velocity distributions for  $^{12}\text{C}$  and  $^{13}\text{C}$ , compared with the Monte-Carlo simulations of *Fox and Hać* [1999] (figure 2(b) of *Fox and Hać* [1999]) (dashed lines).



**Figure 3.** The velocity distribution function at different times. Thin continuous lines correspond to dimensionless times  $\hat{t} = tK_e n_e^2 / A$ : (1)  $\hat{t} = 0.2$ ; (2)  $\hat{t} = 0.4$ ; (3)  $\hat{t} = 0.8$ , bold dashed line  $\hat{t} = 60$ , thin dashed line – Maxwellian, and the dash-dotted line – the nascent distribution used as a source term.



**Figure 4.** The steady-state distribution of the hot oxygen obtained by subtracting the thermal part from the total oxygen distribution. Bold solid line corresponds to the exobase of Venus (210 km), thin solid line corresponds to the altitude of 300 km. Bold dashed line is the nascent distribution of oxygen at 210 km ( $T_i = 500$  K) and thin dashed line at 300 km ( $T_i = 2000$  K).