Thermospheric Distribution of Fast O(\textit{D-1}) Atoms

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Thermospheric distribution of fast O(1D) atoms

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Detailed calculations are carried out of the sources of energetic metastable O(1D) atoms in the atmosphere at altitudes between 80 km and 200 km, and the corresponding energy distribution functions are derived, taking account of energy transfer and quenching in collisions of the metastable atoms with the ambient atmospheric gas constituents. The energy relaxation of metastable oxygen atoms produced by O_2 and O_3 photolysis and O_2 dissociative recombination is determined by solving the time-dependent Boltzmann equation. The O(1D) thermalization and quenching times are obtained as functions of the altitude. The steady state distributions of metastable O(1D) are computed and used for the determination of the parameters characterizing the nonthermal O(1D) atoms. The nonthermal atoms comprise 4–6% of the distribution, and their effective temperatures are larger by 25–46% than the local temperatures of the ambient gas. The role of hot metastable oxygen atoms in the production of vibrationally excited OH molecules is analyzed.


1. Introduction

Metastable O(1D) atoms constitute a major source of atmospheric heating in the stratosphere, mesosphere and thermosphere. They play an important role in atmospheric chemistry and the red line emission to which they give rise provides a unique diagnostic probe of the environment in which the emission takes place. The atoms are produced by photoabsorption of solar ultraviolet radiation by ozone and molecular oxygen and by dissociative recombination and chemical reactions. The metastable atoms have initial energies much in excess of the thermal energy of the ambient gas atoms and molecules. The energetic atoms relax by elastic and inelastic collisions to an equilibrium velocity distribution. The departure of the velocity distribution from the thermal Maxwellian distribution in the thermosphere at altitudes above 200 km and its influence on the red line profile has been investigated by Schmitt et al. [1981, 1982], Abreu et al. [1982], Yee [1988], Shematovich et al. [1999], and Hubert et al. [2001]. Evidence that the distribution departs from Maxwellian has been provided by observations of an excess intensity of the red lines at high altitudes [Schmitt et al., 1981, 1982] and by apparently anomalous temperatures derived from measurements of red line profiles [Hubert et al., 2001]. In the stratosphere at and below an altitude of 50 km the nonthermal component has been calculated by Takahashi et al. [2002] and Kharchenko and Dalgarno [2004] and its influence on chemical reaction rates has been examined. We consider here the distributions at altitudes between 80 km and 200 km. Shematovich et al. [1999] and Takahashi et al. [2002] adopted collision cross sections based on the hard sphere approximation. We solve the time-dependent Boltzmann equation in which the energy transfer is described by realistic cross sections for collisions of the metastable atoms with the ambient atmospheric atoms and molecules that depend on the collision energy and the scattering angle, and we calculate the evolution with time of the O(1D) velocity distribution function. From these time-dependent distribution functions we determine the rates of thermalization and quenching of metastable O(1D) atoms in the terrestrial atmosphere at altitudes of 80–200 km. We calculate the steady-state distribution functions of the metastable oxygen atoms and we determine the parameters of the non-Maxwellian O(1D) distributions and the effective temperatures and fractions of hot atoms for day and nighttime atmospheric conditions. The role of hot O(1D) atoms in the production of highly excited vibrational OH molecules is discussed.

2. Sources of Energetic O(1D) Atoms

The relative contributions of different sources of nascent metastable oxygen atoms change with the altitude.
In the atmosphere at altitudes below 80 km the major source of \( \text{O}(1^D) \) atoms is the photolysis of ozone

\[
\text{O}_3 + h\nu \rightarrow \text{O}_2(\text{a}^1\Delta_g) + \text{O}(1^D)
\]

\[
\text{O}_3 + h\nu \rightarrow \text{O}_2(\text{X}^3\Sigma_u^+) + \text{O}(1^D).
\]

The spin-forbidden channel (2) of \( \text{O}_3 \) photodissociation is the major source of metastable oxygen atoms at altitudes below 20 km, and it yields nascent \( \text{O}(1^D) \) atoms with larger kinetic energies than does channel (1) \([\text{Ravishankara et al., 1998; Taniguchi et al., 2000, 2003; Matsumi et al., 2002; Takahashi et al., 2002; Kharchenko and Dalgarno, 2004}].\) As the altitude increases, channel (1) dominates over (2). \([\text{Takahashi et al., 2002 and Kharchenko and Dalgarno, 2004}].\) have computed the production rates at altitudes of 25 km and 50 km as functions of the \( \text{O}(1^D) \) kinetic energy. Following their procedures at 80 km we obtain a total production rate of \( 5 \times 10^7 \text{ cm}^{-3} \text{s}^{-1} \) for an ozone density of \( 1.3 \times 10^5 \text{ cm}^{-3} \) and an energy distribution of the nascent \( \text{O}(1^D) \) atoms that differs little from that at 50 km \([\text{Kharchenko and Dalgarno, 2004}].\) Above 80 km, even taking into account the enhancement in ozone between 80 km and 90 km \([\text{Marsh et al., 2002}].\) we find that ozone photolysis is negligible compared to that from photoabsorption by molecular oxygen, which is rapidly increasing with altitude. The principal channel is absorption into the Schumann-Runge continuum of the \( \text{B}^3\Sigma_u^- \) state,

\[
\text{O}_2 + h\nu \rightarrow \text{O}_2(\text{B}^3\Sigma_u^-) \rightarrow \text{O}(3^P) + \text{O}(1^D).
\]

As the atoms separate there is a small probability of predissociation leading to a pair of ground state atoms but otherwise the absorption results in \( \text{O}(3^P) \) or \( \text{O}(1^D) \). Branching ratios have been measured by \([\text{Lee et al., 1977}].\) and \([\text{Nee and Lee, 1997}].\) which are in good agreement with the wave packet calculations of \([\text{Balakrishnan et al., 2000a}].\) Total cross sections for absorption in the Schumann-Runge continuum have been measured by \([\text{Yoshino et al., 2005}].\) which when taken in conjunction with the branching ratios yield the source and energy distribution of the \( \text{O}(1^D) \) atoms. The threshold wavelength is 174 nm. The cross section diminishes rapidly at wavelengths shorter than 138 nm and is replaced by absorption into the \( 1^3\Pi_u \) state which dissociates to two ground state oxygen atoms. Between 130 nm and 119 nm there occur weak absorptions that may be due to transitions into higher \( \Sigma_u^- \) states \([\text{Li et al., 1992}].\) and \( 1^3\Pi_u \) states \([\text{Li et al., 1998}].\) which lead to energetic \( \text{O}(1^D) \) atoms \([\text{Lambert et al., 2004}].\) However, in this region the solar spectrum is dominated by Lyman-alpha. For Lyman-alpha the absorption cross section is \( 1 \times 10^{-20} \text{ cm}^2 \) \([\text{LaCoursiere et al., 1999}].\) and the \( \text{O}(1^D)/\text{O}(3^P) \) ratio is 0.56. Below 103 nm, photoionization is energetically allowed. We assume that photoionization is not a direct source of metastable atoms and contributes only through the chemical reactions that it initiates.

\([4]\) Chemical reactions that produce energetic oxygen atoms in the atmosphere have been listed by \([\text{Richards et al., 1994}].\) and \([\text{Hickey et al., 1995}].\) The lists include dissociative recombination of \( \text{NO}^+ \) and \( \text{O}_2 \). The literature on the processes has been reviewed recently \([\text{Sheehan and St.-Maurice, 2004}].\) Dissociative recombination of \( \text{NO}^+ \) is unlikely to be an important source of \( \text{O}(1^D) \) atoms because the process would involve a change in the spin multiplicity \([\text{Dalgarno and Walker, 1964; Vejby-Christensen et al., 1998; Schneider et al., 2000; Hellberg et al., 2003}].\) Dissociative recombination of \( \text{O}_2 \) yields \( \text{O}(1^D) \) and \( \text{O}(1^S) \) atoms. It is the principal source of excited oxygen atoms at night and above 160 km during the day \([\text{Dalgarno and Walker, 1964; Shematovich et al., 1999}].\) The energetically accessible exit channels and the corresponding kinetic energies are

\[
\text{O}_2^+ + e \rightarrow \text{O}(3^P) + \text{O}(1^D) + 4.99\text{eV}, \quad (4a)
\]

\[
\text{O}_2^+ + e \rightarrow \text{O}(3^P) + \text{O}(1^S) + 2.77\text{eV}, \quad (4b)
\]

\[
\text{O}_2^+ + e \rightarrow \text{O}(1^D) + \text{O}(1^D) + 3.02\text{eV}, \quad (4c)
\]

\[
\text{O}_2^+ + e \rightarrow \text{O}(1^D) + \text{O}(1^S) + 0.80\text{eV}, \quad (4d)
\]

\[
\text{O}_2^+ + e \rightarrow \text{O}(3^P) + \text{O}(3^P) + 6.65\text{eV}. \quad (4e)
\]

if the ion is in the lowest vibrational level. The corresponding branching ratios of the dissociative channels \( a, b, c \) and \( d \) are 0.42, 0.00, 0.31 and 0.05 \([\text{Kella et al., 1997; Peverall et al., 2000, 2001}].\) at electron collision energies below 1 meV. The vibrationally resolved branching ratios have been measured by \([\text{Pettrignani et al., 2005}].\) Branching ratios at higher electron energies between 0.001 and 0.5 eV have been reported by \([\text{Peverall et al., 2001}].\) We averaged them over a thermal velocity distribution to determine the small variation of the branching ratios with electron temperature in the atmosphere. The \( \text{O}(1^S) \) atoms decay radiatively with a lifetime of 0.79s \([\text{Tachiev and Froese Fischer, 2002}].\) and are a minor source of energetic \( \text{O}(1^D) \) atoms.

\([5]\) Other possible sources are the reactions

\[
\text{N}(2^D) + \text{O}_2 \rightarrow \text{NO} + \text{O}(1^D) + 1.79\text{eV} \quad (5)
\]

\[
\text{N}(2^D) + \text{O}(3^P) \rightarrow \text{N}(4^S) + \text{O}(1^D) + 0.42\text{eV}. \quad (6)
\]

The \( \text{N}(2^D) \) atoms are a product of the dissociative recombination of \( \text{NO}^+ \) with a branching ratio of nearly unity \([\text{Hellberg et al., 2003}].\) The \( \text{N}(2^D) \) atoms may also be removed by the reaction

\[
\text{N}(2^D) + \text{O}_2 \rightarrow \text{NO} + \text{O}(3^P) \quad (7)
\]

\[
\text{N}(2^D) + \text{O}(3^P) \rightarrow \text{N}(4^S) + \text{O}(3^P). \quad (8)
\]

\([6]\) Shematovich et al. \([\text{1999}].\) assumed that the preferred reaction path for the quenching of \( \text{N}(2^D) \) atoms by \( \text{O}_2 \) is \( (5) \). Theoretical \([\text{Gonzalez et al., 2001; Miquel et al., 2003}].\) and experimental \([\text{Shihira et al., 1994; Miller and Hunter, 2004}].\) studies suggest otherwise and we assume the preferred path is \( (7) \). The sum of the rate coefficients of reactions \( (6) \) and \( (8) \) has been measured \([\text{Piper, 1989; Fell}].\)
Reaction (12) is important in the destruction of NO. There is no information on the state of the product atom and we assume that the reaction leads exclusively to \( \text{O}(^3\Pi) \) atoms. There remains to be considered fluorescence of solar radiation [Dalgarno and Walker, 1964] and photoelectron impact [Shematovich et al., 1999]. Fluorescence and electron impact excitation of \( \text{O}(^3\Pi) \),

\[
e + \text{O}(^3\Pi) \rightarrow e + \text{O}(^1\Delta),
\]

produce mostly thermal \( \text{O}(^1\Delta) \) atoms but electron impact excitation of \( \text{O}_2 \) may occur to the continuum of the excited \( B \left(^3\Sigma_u^+\right) \) state,

\[
e + \text{O}_2 \rightarrow e + \text{O}_2(B^3\Sigma_u^+) \rightarrow e + \text{O}(^3\Pi) + \text{O}(^1\Delta),
\]

producing energetic \( \text{O}(^1\Delta) \) atoms. A probable upper limit to the rate of production in the midlatitude thermosphere can be obtained by adopting the photoelectron flux, measured at 167 km [Lee et al., 1980; Solomon et al., 2001], and an excitation cross section of \( 4 \times 10^{-17} \) cm\(^2\) [Cosby, 1993; Makarov et al., 2003]. We obtain a rate of 40 cm\(^{-3}\) s\(^{-1}\), small compared to the photodissociation rate of 4000 cm\(^{-3}\) s\(^{-1}\). The contribution of the electron-impact mechanism to production of metastable oxygen atoms may be larger in polar regions because of the presence of auroral electrons.

[4] We have constructed neutral particle model atmospheres based on the MSIS model of Hedlin [1991] for a F10.7 of 200 and the solar ultraviolet spectrum of Hinteregger et al. [1981]. We determined the corresponding altitude distributions of the positive ions using a modified version of the model ionosphere calculations of Fox and Dalgarno [1985] with some limited updating of the rate coefficients [Fox and Sung, 2001]. The distributions of nascent energetic \( \text{O}(^1\Delta) \) atoms from photodissociation of \( \text{O}_2 \) and \( \text{O}_3 \) at 80, 160 and 200 km at a solar zenith angle of 60 degrees are presented in Figure 1. The structures in the energy spectra of nascent atoms in the center of mass frame are a consequence of strong lines in the solar spectra. When the center of mass motion is taken into account the sharp structures are smoothed.

[5] The total energy distribution function of nascent \( \text{O}(^1\Delta) \) atoms and the contributions from photodissociation, dissociative recombination and ionic reactions at 200 km are shown in Figure 2. The peaks \( a, c, \) and \( d \) are labeled by the product distribution occurring in dissociative recombination with the channels described by equation (4). Photodissociation produces atoms with a kinetic energy peaking at 0.5 eV and dissociative recombination is the source of atoms with energies centered at 0.4, 1.5 and 2.5 eV. The ionic reaction (IR) source, described by equation (11), yields hot \( \text{O}(^1\Delta) \) atoms with energy around 0.74 eV. The production rates from photodissociation, dissociative recombination and ionic reactions are presented in Table 1 for altitudes above 80 km for a solar zenith angle of 60 degrees. At low thermospheric altitudes, ozone photodissociation is the major source of metastable oxygen atoms. In the intermediate region between 100 and 180 km, hot \( \text{O}(^1\Delta) \) atoms are mostly produced by the photodissociation of \( \text{O}_2 \) atoms.
molecules, and dissociative recombination of O$_2^+$ ions dominates above 180 km.

3. Loss of Energetic Atoms

Energetic O(1D) atoms are lost by spontaneous emission,

$$O(1D) \to O(3P) + \nu,$$

resulting in energetic O(3P) atoms, and by quenching in collisions with O, O$_2$, N$_2$, and electrons,

$$O(1D) + O(3P) \to O(3P) + O(3P),$$

$$O(1D) + O_2 \to O(3P) + O_2,$$

$$O(1D) + N_2 \to O(3P) + N_2,$$

$$O(1D) + N_2 \to N + NO,$$

$$O(1D) + e \to O(3P) + e.$$  

The rate of (15) is 0.0088 s$^{-1}$ [Tachiev and Froese Fischer, 2002]. The cross sections for equation (16) are given by Yee et al. [1990], Sun and Dalgarno [1992], and Jamieson et al. [1992]. The cross section for equation (18) has been inferred from fluorescence experiments [Matsumi et al., 1994; Matsumi and Chowdhury, 1996; Chowdhury, 1999; Taniguchi et al., 2000; Kharchenko and Dalgarno, 2004]. Reaction (19) is endothermic but may be an additional sink for energetic O(1D) atoms. Its effect is minor compared to that of the quenching reaction (18). The cross sections for equation (20) have been calculated by Berrington and Burke [1981] and an analytical form for the rate coefficient has been given by Pequignot [1990].

4. Velocity Distributions

The energy and momentum relaxation of the initially energetic metastable oxygen atoms is described by the solution $f(\epsilon,t)$ of the time-dependent linear Boltzmann equation where $\epsilon$ is the kinetic energy of the atom. The equation for the energy relaxation of the fast O(1D) atoms has the form

$$\frac{\partial f(\epsilon,t)}{\partial t} = \int_0^\infty B(\epsilon|\epsilon')f(\epsilon',t)d\epsilon' - \omega(\epsilon)f(\epsilon,t)$$

$$- [\gamma(\epsilon,T) + A]f(\epsilon,t) + Q(\epsilon,t),$$

where $Q(\epsilon,t)$ is the production rate of atoms with energy $\epsilon$, $B(\epsilon|\epsilon')$ is the rate of energy transfer in elastic and inelastic collisions with the atmospheric constituents, $\gamma(\epsilon,T)$ is the rate of collisions that remove O(1D) atoms, $T$ is the ambient temperature, $A$ is the spontaneous radiative transition probability, and $\omega(\epsilon)$ is given by

$$\omega(\epsilon) = \int_0^\infty B(\epsilon|\epsilon')d\epsilon'.$$

A detailed description of the procedures used to construct the kernel $B(\epsilon|\epsilon')$ and to solve the Boltzmann equation is
Evolution of the energy distribution function of an ensemble of O(1^D) atoms produced in the terrestrial atmosphere at the altitude of 150 km by O_2 photolysis. The energy distribution of nascent metastable oxygen atoms produced at t = 0 (curve 0) and the time-dependent distribution functions after 0.01, 0.05, 0.1 and 0.3s (curves 1–4) are shown. The dashed curve is the Maxwellian distribution, normalized to unity at the ambient gas temperature of 736 K. See color version of this figure in the HTML.

Figure 4. Evolution of the relative energy E(t)/E_0 and number N(t)/N_0 of metastable O(1^D) atoms as functions of the relaxation time t at the altitude of 150 km. E_0 and N_0 are the initial energy and number of nascent O(1^D) atoms produced by photodissociation of O_2 molecules at t = 0.

Maxwellian at the temperature T_{150} = 740 K of the ambient atmosphere. In Figure 4 the time evolution of the kinetic energy E(t) and the number N(t) of O(1^D) atoms are shown as functions of time for an ensemble of metastable O(1^D) atoms produced by photodissociation of O_2 molecules at the altitude of 150 km. The initial energy of atoms, E_0, is reduced due to elastic and inelastic collisions of nascent fast atoms with the atmospheric gas, and the initial number of atoms N_0 decays due to quenching. The time dependence of the distribution function is characterized by the thermalization time \( t_{th} \), which is the time to reach the Maxwellian form. The time dependence of N(t)/N_0 is exponential. We characterize it by a quenching time \( t_q \) which we define as the time to lose 95% of the metastable atoms. The two times are listed in Table 2 for altitudes between 80 and 200 km. They show that most of the atoms are thermalized before they are lost. Because of the fast thermalization of the nascent energetic atoms, the transport of metastable atoms from other regions of the thermosphere may be neglected. For example, the thermalization time at 200 km is 1.1 s, and the nascent hot O(1^D) atoms are thermalized within a 1-km region around their point of origin. In the atmosphere because of the fast loss rates and the rapid influx of energetic atoms a steady state is reached.

Table 2. Parameters of Hot O(1^D) Atoms for the Daytime Atmosphere

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>Thermalization, ( \tau_{th} ) [s]</th>
<th>Quenching, ( \tau_{q} ) [s]</th>
<th>Hot O(1^D) Fraction, ( \xi ) [%]</th>
<th>( T_{eff}/T ), %</th>
<th>O(1^D) Density, ( 10^3 \text{ cm}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.1 ( 10^{-2} )</td>
<td>1.5 ( 10^{-3} )</td>
<td>5</td>
<td>138</td>
<td>0.24</td>
</tr>
<tr>
<td>100</td>
<td>2.6 ( 10^{-3} )</td>
<td>0.035</td>
<td>4.3</td>
<td>146</td>
<td>8.2</td>
</tr>
<tr>
<td>120</td>
<td>0.047</td>
<td>0.6</td>
<td>4.9</td>
<td>133</td>
<td>18.3</td>
</tr>
<tr>
<td>140</td>
<td>0.17</td>
<td>2.18</td>
<td>4.7</td>
<td>125</td>
<td>9.5</td>
</tr>
<tr>
<td>160</td>
<td>0.39</td>
<td>4.9</td>
<td>4.8</td>
<td>129</td>
<td>8.0</td>
</tr>
<tr>
<td>180</td>
<td>1.0</td>
<td>8.4</td>
<td>5.1</td>
<td>132</td>
<td>7.7</td>
</tr>
<tr>
<td>200</td>
<td>1.1</td>
<td>13.5</td>
<td>5.5</td>
<td>137</td>
<td>8.9</td>
</tr>
</tbody>
</table>
and we may put $\frac{\partial f}{\partial t} = 0$ in the Boltzmann equation (22). The source functions are additive so we may display the steady-state distributions that result from each source. Figure 5 illustrates them for photodissociation, dissociative recombination and ionic reactions at 140 km and a solar zenith angle of 60. The steady state distribution, arising from dissociative recombination (the curve DR in Figure 5), provides 480 metastable atoms per cm$^3$, and the distribution produced by the photodissociation of O$_2$ molecules (the curve PD) provides $9 \times 10^3$ cm$^{-3}$ atoms. The effective temperatures of the O(1D) distributions, arising from dissociative recombination and photodissociation, are 1005 K and 795 K, respectively, temperatures that are significantly larger than the temperature 644 K of the ambient atmospheric gas. Figure 6 gives the total steady state distribution functions at 80 km, 120 km, 160, and 200 km and compares them with Maxwellian distributions shown by the dashed curves. The equivalent mean temperatures $T$ obtained by expressing the mean energy as $k_B T$ are listed in Table 2, where they are compared with the ambient temperatures.

The fraction $\xi$ of suprathermal atoms is defined as the relative number of atoms in excess of the thermal Maxwellian distributions with energies larger than some selected energy $\varepsilon_S$,

$$\xi = \int_{\varepsilon_S}^{\infty} [f(e) - f_M(e)] de / \int_0^{\infty} f(e) de. \quad (24)$$

Both distributions, $f(e)$ and $f_M(e)$, are normalized to the same number of particles. The fractions of suprathermal atoms with energies above $\varepsilon_S = 3 k_B T$ are included in Table 2. They vary little with altitude, ranging between 4.3% and 5.5%. The fractions are substantially higher than the fractions of energetic ground state atoms [Cotton et al., 1993; Kharchenko and Dalgarno, 2000] because quenching reactions remove the thermalized metastable atoms thereby increasing the mean energy of those remaining.

[12] At night photodissociation is absent but dissociative recombination and ionic reactions are a time-dependent continuing source of energetic atoms with an average energy larger than that due to photodissociation in the thermosphere at 140 km. The populations of metastable oxygen atoms produced by the dissociative recombination (DR) and O$_2$ photodissociation (PD) are shown by dashed curves. The thick solid curve is the steady state distribution of O(1D) atoms produced by all source reactions. The Maxwellian distributions at 140 km are given by dash-dotted curves. The solar zenith angle is 60°, and the latitude is 30°N.

![Figure 5](image1.png)

**Figure 5.** Steady state distributions of metastable O(1D) atoms at 140 km. The populations of metastable oxygen atoms produced by the dissociative recombination (DR) and O$_2$ photodissociation (PD) are shown by dashed curves. The thick solid curve is the steady state distribution of O(1D) atoms produced by all source reactions. The Maxwellian distributions at 140 km are given by dash-dotted curves. The solar zenith angle is 60°, and the latitude is 30°N.

![Figure 6](image2.png)

**Figure 6.** Steady state energy distributions of metastable O(1D) atoms in the thermosphere between 80 and 200 km. Solid curves show the energy distribution at 80, 120, 160, and 200 km, and dashed curves show Maxwellian distributions at the corresponding altitudes. The value of the distribution function at 120 km have been reduced by 10 for convenience in plotting. See color version of this figure in the HTML.

![Figure 7](image3.png)

**Figure 7.** Production rate $R_I$[eV$^{-1}$ cm$^{-3}$ s$^{-1}$] of energetic nascent O(1D) atoms in the midnight atmosphere at 200 km are shown by the dashed curve. The steady state energy distribution function of the metastable oxygen atoms is given by the solid curve and the nighttime Maxwellian distribution by the dash-dotted curve. See color version of this figure in the HTML.
daytime. At 200 km the midnight rate of O(1D) production is 400 cm$^{-3}$ s$^{-1}$ for the ionospheric conditions described by the IRI-2001 model [Bilitza, 2001]. The energy spectra of nascent metastable oxygen atoms in the nighttime atmosphere are shown in Figure 7 by the thick dashed curve. The average energy of nascent atoms produced by ionic reactions, mostly by dissociative recombination of O$_2$ ions, is 1.96 eV. This energy is 25 times larger than the nighttime atmosphere thermal energy $k_B T_{300}$. Figure 7 shows the calculated steady state distribution for midnight at 200 km. The density of metastable oxygen atoms is $2.3 \times 10^3$ cm$^{-3}$. The corresponding equivalent temperature is 1371 K, 446 K higher than the ambient temperature of 925 K.

5. Atmospheric Reactions With Hot O(1D) Atoms

Metastable oxygen atoms participate in key atmospheric reactions such as decomposition of the ozone and water molecules, the production of OH and NO molecules and others [Brasseur and Solomon, 1984; Summers et al., 1997; Finlayson-Pitts and Pitts, 2000]. The majority of reactions with metastable oxygen are exothermic, and reaction rates are not sensitive to the translational energies of the O(1D) atoms [Streit et al., 1976; Gericke and Comes, 1981]. Nevertheless, the translational energy is important in determining the distribution of the internal energy of the reaction products [Cleveland and Wiesenfeld, 1992; Tsurumaki et al., 1999; Sayos et al., 2000]. We have investigated the influence of non-thermal O(1D) atoms on the yield of rovibrationally excited NO molecules in the mesosphere from the reaction of O(1D) with N$_2$O [Kharchenko and Dalgarno, 2004]. Unusual rotational distributions of OH have been obtained by Dodd et al. [1994] which they attribute to the reaction of H with O$_3$ and to the transfer of vibrational energy to rotational energies by collisions of OH with oxygen atoms. Some contribution to the enhanced OH excitation may arise from the reaction

$$ O(1D) + H_2O \rightarrow OH + OH, \quad (25) $$

which is an important source of OH in the middle atmosphere [Summers et al., 1997]. The excess kinetic energy of the non-thermal component of O(1D) atoms influences the rovibrational distribution of OH molecules produced in the middle atmosphere. The rotational and vibrational distribution of the hydroxyl molecules produced by O(1D) atoms have been investigated in laboratory measurements [Gericke and Comes, 1981; Cleveland and Wiesenfeld, 1992; Tsurumaki et al., 1999]. The results of ab initio calculations of OH rovibrational distributions carried out by Sayos et al. [2000] at collisional energies of 0.23, 0.30, and 0.43 eV are reasonably close to the recommended experimental values. The relative populations of the different vibrational and rotational states depend on the translational energies of O(1D) atoms and are sensitive to the fraction of non-thermal metastable atoms. To illustrate this, we have calculated the relative populations of different vibrational levels of OH molecules produced in O(1D) + H$_2$O atmospheric collisions. The relative populations P(v)/P(0) of vibrational levels $v = 1$–4 of nascent hydroxyl molecules have been calculated with the non-Maxwellian distributions of O(1D) atoms at altitudes of 80 and 100 km. Data by Sayos et al. [2000] on the dependence of the relative v-populations on the translational O(1D) energy have been linearly extrapolated to the energy interval of 0–2.4 eV and averaged over the energy distribution functions of hot O(1D). The results of our calculations are compared in Table 3 with the results of the calculations with the Maxwellian distribution functions at the temperatures at the altitudes of 80 and 100 km. The production of OH highly vibrational states $v = 3$ and 4 in the O(1D) + H$_2$O reaction is very sensitive to the presence of non-thermal atoms in the atmospheric distributions of O(1D). The relative populations of $v = 3$ and 4 states produced by hot atoms are 2.5–4 times larger than populations produced by a Maxwellian O(1D) gas, whereas the populations of the low vibrational levels are not sensitive to the character of the energy distribution. Vibrationally excited OH molecules are also produced in the reaction [Dodd et al., 1994]

$$ H + O_3 \rightarrow OH + O_2, \quad (26) $$

and by photodissociation of H$_2$O

$$ H_2O + hv \rightarrow OH + H. \quad (27) $$

The specific contributions from reaction (25) in the thermosphere will be difficult to identify but should be apparent at altitudes near 65 km, where it is the major source of OH [Summers et al., 1997].

6. Conclusions

The energy distribution functions of metastable O(1D) atoms in the thermosphere have been calculated at altitudes of 80–200 km. We have determined the thermalization and quenching times, the densities of O(1D) atoms in the steady state distributions, and the effective temperatures. At all altitudes, 4–6% of O(1D) atoms are hot, which increases the effective temperatures of metastable oxygen atoms by 30–50% above the local temperatures of the atmospheric gas. Several mechanisms of production of metastable oxygen atoms and their efficiency as functions of the altitude have been investigated. We have found that steady state distributions of O(1D) atoms produced by dissociative recombination of molecular O$_2$ ions have higher effective temperatures than distributions produced by photodissociation, and their effective temperatures are 50% higher than local atmospheric temperatures. Photon sources of O(1D) dominate below 160 km, and dissociative recombination of O$_2$ molecules is a major source above 160 km. O$_2$ dissociative recombination and charge transfer collisions of O$^+$ ions with N$_2$ produce hot metastable oxygen atoms in the nighttime terrestrial thermosphere, and the nighttime distributions of O(1D) are hotter than in the

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Table 3. Relative Population P(v)/P(0) of OH(v) Vibrational States

<table>
<thead>
<tr>
<th>Altitude</th>
<th>v</th>
<th>P(v)</th>
<th>P(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>0.38</td>
<td>0.0009</td>
</tr>
<tr>
<td>80 km</td>
<td>2</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>100 km</td>
<td>1</td>
<td>0.37</td>
<td>0.0004</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.37</td>
<td>0.0012</td>
</tr>
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<tr>
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<td>4</td>
<td>0.0003</td>
<td></td>
</tr>
</tbody>
</table>
daytime. At 200 km the effective temperature of the midnight O(1D) distribution is 52% larger than the atmosphere temperature. The distributions of the metastable oxygen atoms modify the rates of chemical reactions involving O(1D) atoms. Hot O(1D) atoms may enhance the production of highly excited vibrational states of OH(ν = 3, 4) molecules by a factor of 2–4 in reactions with water molecules. Metastable oxygen atoms are a significant source of the hot ground state O(3P) atoms, and the parameters of the O(1D) distributions could be important in developing a self-consistent description of the upward fluxes of energetic O(3P) and O(1D) atoms.

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References


Balakrishnan, N., V. Kharchenko, and A. Dalgarno (1999b), Slowing of energetic O(1D) atoms in collisions with N2, J. Geophys. Res., 103, 23393.


Bates, D. R. (1989), Rapid deactivation of N(3D) by O(1D) and 630 nm emission, Planet. Space Sci., 37, 1145.


Chowdhury, A. M. (1999), Studying of the competing collisional relaxation reactions of O(1D) atoms. Hot O(1D) atoms may enhance the production of highly excited vibrational states of OH(ν = 3, 4) molecules by a factor of 2–4 in reactions with water molecules. Metastable oxygen atoms are a significant source of the hot ground state O(3P) atoms, and the parameters of the O(1D) distributions could be important in developing a self-consistent description of the upward fluxes of energetic O(3P) and O(1D) atoms.

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Bates, D. R. (1989), Rapid deactivation of N(3D) by O(1D) and 630 nm emission, Planet. Space Sci., 37, 1145.


Cotton, D. M., G. R. Gladstone, and S. Chakrabarti (1993), Sounding rock-


Yee, J.-H., S. L. Guberman, and A. Dalgaro (1990), Collisional quenching of O(1D) by O(3P), Planet. Space Sci., 38, 647.


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