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Kharchenko, V., Dalgarno, A., & Fox, J. L. (2005). Thermospheric Distribution of Fast O(D-1) Atoms. *Journal of Geophysical Research-Space Physics*, 110, A12305.
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Thermospheric distribution of fast O(¹D) atoms

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Received 16 May 2005; revised 27 July 2005; accepted 12 September 2005; published 15 December 2005.

[1] 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 O₂ and O₃ photolysis and O₂⁺ 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.

Citation: Kharchenko, V., A. Dalgarno, and J. L. Fox (2005), Thermospheric distribution of fast O(¹D) atoms, *J. Geophys. Res.*, **110**, A12305, doi:10.1029/2005JA011232.

1. Introduction

[2] 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

[3] 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 O(¹D) atoms is the photolysis of ozone

The spin-forbidden channel (2) of O₃ photodissociation is the major source of metastable oxygen atoms at altitudes below 20 km, and it yields nascent O(¹D) atoms with larger kinetic energies than does channel (1) [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). 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 O(¹D) kinetic energy. Following their procedures at 80 km we obtain a total production rate of $5 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ for an ozone density of $1.3 \times 10^8 \text{ cm}^{-3}$ and an energy distribution of the nascent O(¹D) atoms that differs little from that at 50 km [Kharchenko and Dalgarno, 2004]. Above 80 km, even taking into account the enhancement in ozone between 80 km and 90 km [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 B ³Σ_u⁻ state,

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 O(³P) + O(¹D). Branching ratios have been measured by Lee *et al.* [1977] and Nee and Lee [1997] which are in good agreement with the wave packet calculations of Balakrishnan *et al.* [2000a]. Total cross sections for absorption in the Schumann-Runge continuum have been measured by Yoshino *et al.* [2005] which when taken in conjunction with the branching ratios yield the source and energy distribution of the O(¹D) 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 1³Π_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 ³Σ_u⁻ states [Li *et al.*, 1992] and ³Π_u states [Li *et al.*, 1998] and which lead to energetic O(¹D) atoms [Lambert *et al.*, 2004]. However, in this region the solar spectrum is dominated by Lyman-alpha. For Lyman-alpha the absorption cross section is $1 \times 10^{-20} \text{ cm}^2$ [LaCoursiere *et al.*, 1999] and the O(¹D)/O(³P) 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 Richards *et al.* [1994] and Hickey *et al.* [1995]. The lists include dissociative recombination of NO⁺ and O₂⁺. The literature

on the processes has been reviewed recently [Sheehan and St-Maurice, 2004]. Dissociative recombination of NO⁺ is unlikely to be an important source of O(¹D) atoms because the process would involve a change in the spin multiplicity [Dalgarno and Walker, 1964; Vejby-Christensen *et al.*, 1998; Schneider *et al.*, 2000; Hellberg *et al.*, 2003]. Dissociative recombination of O₂⁺ yields O(¹D) and O(¹S) atoms. It is the principal source of excited oxygen atoms at night and above 160 km during the day [Dalgarno and Walker, 1964; Shematovich *et al.*, 1999]. The energetically accessible exit channels and the corresponding kinetic energies are

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 [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 Pettrignani *et al.* [2005]. Branching ratios at higher electron energies between 0.001 and 0.3 eV have been reported by 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 O(¹S) atoms decay radiatively with a lifetime of 0.79s [Tachiev and Froese Fischer, 2002] and are a minor source of energetic O(¹D) atoms.

[5] Other possible sources are the reactions

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

Shematovich *et al.* [1999] assumed that the preferred reaction path for the quenching of N(²D) atoms by O₂ is (5). Theoretical [Gonzalez *et al.*, 2001; Miquel *et al.*, 2003] and experimental [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 [Piper, 1989; Fell

Figure 1. Energy distribution functions of nascent metastable O(¹D) atoms produced at the altitudes of 80, 160, and 200 km by O₃ and O₂ photodissociation processes. The solar zenith angle is 60 degrees. The dashed curve shows the energy spectra of metastable oxygen atoms in the center of the mass frame of the parent O₂ molecule at the altitude of 200 km. See color version of this figure in the HTML.

et al., 1990]. The branching ratio is uncertain. Bates [1989] argued that reactions (6) is strongly favored but in a review of the measurement data, Herron [1999] concluded that reaction (8) is more probable. The process was not considered by Shematovich *et al.* [1999] but if reaction (6) does occur, the reaction is a significant source of O(¹D) atoms at high altitudes above 200 km. We do not include it in our calculations. The metastable N(²P) atom is a minor product of dissociative recombination of NO⁺ and it produces O(¹D) atoms through the reaction [Rawlins *et al.*, 1989]

The source is small compared to reactions of N(²D). Shematovich *et al.* [1999] included

They pointed out that charge transfer in collisions of metastable ²P and ²D ions of O⁺ with O(³P) atoms is also a potential source of energetic O(¹D) atoms. Reactions of O⁺(²P) with N₂,

produce energetic atoms [Li *et al.*, 1997] though with lower efficiency than equation (4). There are other chemical reactions that may yield energetic O(¹D) atoms such as

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 O(³P) 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 O(³P),

produce mostly thermal O(¹D) atoms but electron impact excitation of O₂ may occur to the continuum of the excited B ³Σ_u⁻ state,

producing energetic O(¹D) 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 $4 \times 10^{-17} \text{ cm}^2$ [Cosby, 1993; Makarov *et al.*, 2003]. We obtain a rate of $40 \text{ cm}^{-3} \text{ s}^{-1}$, small compared to the photodissociation rate of $4000 \text{ cm}^{-3} \text{ s}^{-1}$. 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.

[6] We have constructed neutral particle model atmospheres based on the MSIS model of Hedin [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 O(¹D) atoms from photodissociation of O₃ and O₂ at 80, 160 and 200 km at a solar zenith angle of 60 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.

[7] The total energy distribution function of nascent O(¹D) 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 O(¹D) 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 O(¹D) atoms are mostly produced by the photodissociation of O₂

Figure 2. Energy distribution function of nascent metastable O(¹D) atoms produced at 200 km by O₂ photo-dissociation (PD) is shown by the curve with circles. The dash-dotted curve is the spectrum of the nascent atoms arising in the dissociative recombination of atmospheric O₂⁺ ions. The *a*, *c* and *d* maxima correspond to the *a*, *c* and *d* channels of equation (4). The energy distribution of fast metastable atoms produced in O(³P) + N₂ charge-transfer collisions is given by the dashed curve (IR). The total energy spectrum of nascent O(¹D) atoms is shown by the thick solid curve. See color version of this figure in the HTML.

molecules, and dissociative recombination of O₂⁺ ions dominates above 180 km.

3. Loss of Energetic Atoms

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

resulting in energetic O(³P) atoms, and by quenching in collisions with O, O₂, N₂, and electrons,

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].

[9] Energetic O(¹D) atoms are slowed by elastic and inelastic collisions with the ambient atoms and molecules O, N₂ and O₂. A fast O(¹D) atom colliding with a thermal O(³P) atom can undergo excitation transfer,

producing a thermal O(¹D) atom and a fast O(³P) atom. The cross sections for excitation transfer and for elastic collisions have been reported by Yee and Dalgarno [1987] and the cross sections for elastic and inelastic collisions of O(¹D) atoms with O₂ and N₂ have been assembled by Kharchenko and Dalgarno [2004].

4. Velocity Distributions

[10] 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 ϵ is the kinetic energy of the atom. The equation for the energy relaxation of the fast O(¹D) atoms has the form

$$\frac{\partial f(\epsilon, t)}{\partial t} = \int_0^\infty B(\epsilon|\epsilon') f(\epsilon', t) d\epsilon' - \omega(\epsilon) f(\epsilon, t) - [\gamma(\epsilon, T) + A] f(\epsilon, t) + Q(\epsilon, t), \quad (22)$$

where $Q(\epsilon, t)$ is the production rate of atoms with energy ϵ , $B(\epsilon|\epsilon')$ 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

$$\omega(\epsilon) = \int_0^\infty B(\epsilon'|\epsilon) d\epsilon'. \quad (23)$$

A detailed description of the procedures used to construct the kernel $B(\epsilon|\epsilon')$ and to solve the Boltzmann equation is

Table 1. O(¹D) Production Rates

Altitude, km	Photodissociation O ₃ and O ₂ , 10 ³ cm ⁻³ s ⁻¹	Dissociative Recombination and Ion Reactions, 10 ³ cm ⁻³ s ⁻¹
80	500	0.0
100	740	1.4
120	95	0.9
140	13	0.7
160	3.9	1.1
180	1.5	1.3
200	0.7	1.4

Figure 3. Evolution of the energy distribution function of an ensemble of O(¹D) atoms produced in the terrestrial atmosphere at the altitude of 150 km by O₂ 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 0.3 s (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.

given by Kharchenko and Dalgarno [2004]. The angular and energy dependence of differential cross sections are important for the accurate evaluation of the energy relaxation in collisions of the atmospheric gases [Yee and Dalgarno, 1987; Yee et al., 1990; Sun and Dalgarno, 1992; Balakrishnan et al., 1998a, 1998b, 1999, 2000b; Kharchenko et al., 1997, 1998, 2000; Kharchenko and Dalgarno, 2004]. We found in direct solutions of the Boltzmann equation that our numerical results on the rate of energy relaxation and quenching may be approximately reproduced using a hard-sphere model with effective cross sections. The parameters of the hard sphere model, determined from these comparisons, are in good agreement with the experimental data on quenching and relaxation of O(¹D) in atmospheric gases [Matsumi et al., 1994; Matsumi and Chowdhury, 1996; Taniguchi et al., 2000; Takahashi et al., 2002]. Effective cross sections, describing the translational energy relaxation of O(¹D) atoms in both elastic and inelastic collisions with N₂ and O₂ molecules, are, respectively, $3.0 \times 10^{-15} \text{ cm}^2$ and $2.8 \times 10^{-15} \text{ cm}^2$. The O(¹D) quenching cross sections are $0.7 \times 10^{-16} \text{ cm}^2$ in collisions with N₂ and $0.9 \times 10^{-16} \text{ cm}^2$ with O₂. Hard-sphere cross sections for the energy relaxation and quenching of O(¹D) atoms in atomic oxygen collisions are, respectively, $2.2 \times 10^{-15} \text{ cm}^2$ and $0.7 \times 10^{-17} \text{ cm}^2$.

[11] In Figure 3 we show the evolution with time from $t = 0$ of the energy distribution function at 150 km at times of 0.01, 0.05, 0.10 and 0.30 s. The dimensionless distribution function of nascent O(¹D) atoms at $t = 0$ is normalized to unity, and the translational kinetic energies are given in units of the thermal energy $k_B T$. The high energy tail gradually disappears and after 0.30 s the distribution is

Figure 4. Evolution of the relative energy $E(t)/E_0$ and number $N(t)/N_0$ of metastable O(¹D) 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(¹D) atoms produced by photodissociation of O₂ molecules at $t = 0$.

Maxwellian at the temperature $T_{150} = 740 \text{ K}$ of the ambient atmosphere. In Figure 4 the time evolution of the kinetic energy $E(t)$ and the number $N(t)$ of O(¹D) atoms are shown as functions of time for an ensemble of metastable O(¹D) atoms produced by photodissociation of O₂ atmospheric 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 τ_{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 τ_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(¹D) 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(¹D) Atoms for the Daytime Atmosphere

Altitude, km	Thermalization, time τ_{th} [s]	Quenching, time τ_q [s]	Hot O(¹ D) Fraction, ξ [%]	T_{eff}/T , %	O(¹ D) Density, 10^3 cm^{-3}
80	$1.1 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	5	138	0.24
100	$2.6 \cdot 10^{-3}$	0.035	4.3	146	8.2
120	0.047	0.6	4.9	133	18.3
140	0.17	2.18	4.7	125	9.5
160	0.39	4.9	4.8	129	8.0
180	1.0	8.4	5.1	132	7.7
200	1.1	13.5	5.5	137	8.9

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 O₂ 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.

and we may put $\partial f / \partial t = 0$ 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 cm³, and the distribution produced by the photodissociation of O₂ molecules (the curve PD) provides 9×10^3 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 ξ 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 ϵ_S ,

$$\xi = \frac{\int_{\epsilon_S}^{\infty} [f(\epsilon) - f_M(\epsilon)] d\epsilon}{\int_0^{\infty} f(\epsilon) d\epsilon}. \quad (24)$$

Both distributions, $f(\epsilon)$ and $f_M(\epsilon)$, are normalized to the same number of particles. The fractions of suprathermal atoms with energies above $\epsilon_S = 3 k_B T$ 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

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. Production rate R_l [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.

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

Altitude	v	1	2	3	4
80 km	Hot O(¹ D)	0.38	0.25	0.008	0.0009
	Maxwellian	0.37	0.24	0.003	0.0004
100 km	Hot O(¹ D)	0.37	0.24	0.007	0.0012
	Maxwellian	0.36	0.24	0.0022	0.0003

daytime. At 200 km the midnight rate of O(¹D) production is $400 \text{ cm}^{-3} \text{ s}^{-1}$ 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 O₂⁺ ions, is 1.96 eV. This energy is 25 times larger than the nighttime atmosphere thermal energy $k_B T_{200}$. Figure 7 shows the calculated steady state distribution for midnight at 200 km. The density of metastable oxygen atoms is $2.3 \times 10^3 \text{ cm}^{-3}$. 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

[13] 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 N₂O [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 O₃ 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

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) + H₂O 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) + H₂O 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]

and by photodissociation of H₂O

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

[14] 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 O₂⁺ ions have higher effective temperatures than distributions produced by photoabsorption, and their effective temperatures are 50% higher than local atmospheric temperatures. Photon sources of O(¹D) dominate below 160 km, and dissociative recombination of O₂⁺ molecules is a major source above 160 km. O₂⁺ dissociative recombination and charge transfer collisions of O⁺(²P) ions with N₂ produce hot metastable oxygen atoms in the nighttime terrestrial thermosphere, and the nighttime distributions of O(¹D) are hotter than in the

daytime. At 200 km the effective temperature of the midnight O(¹D) distribution is 52% larger than the atmospheric 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($v = 3,4$) 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(¹D) and O(³P) atoms.

[15] **Acknowledgment.** The work has been supported by the NASA Office of Space Science through grant NAG5-11857 to V. K. and grant NAG5-12755 to J. L. F. and by the National Science Foundation through grant ATM-0430506 to A. D. and grant AST-0315053 to J. L. F.

[16] Arthur Richmond thanks Valery Shematovich and Tom Slanger for their assistance in evaluating this paper.

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