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The Aeronomy of Vibrationally Excited Ozone

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Abstract

Theoretical calculations show that above 80 km in the earth's atmosphere the production of vibrationally excited ozone by chemical processes leads to number densities which are usually larger than those expected for local thermodynamic equilibrium. Quenching of highly excited molecules produced in $O + O_2 + M \rightarrow O_3 + M$ provides a significant source of the lower lying states above the mesopause while the 9.6μ emission of $O_3(0,0,1)$ is a major sink. Analysis of available laboratory results implies that reactions involving excited ozone play a significant role in the global ozone balance despite the relatively small abundance of the molecule. However, this effect is implicit in many of the rate coefficients currently used in stratospheric calculations. In the upper mesosphere and lower themosphere, where the excited state populations differ from those for thermal equilibrium, published reaction rate data are not necessarily applicable to aeronomic calculations.

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THE AERONOMY OF VIBRATIONALLY EXCITED OZONE

Introduction

The aeronomic importance of electronically excited species is well-known. Prominent examples are reactions of the metastable oxygen atom, $O(^1D)+H_2O \rightarrow OH+OH$ and $O(^1D)+N_2O \rightarrow NO+NO$, which provide stratospheric sources of odd hydrogen and odd nitrogen, while excited states of molecules such as $O_2(^1\Delta_g)$ and $OH(v' > 0)$ lead to airglow emissions that act as remote sensors of conditions in the mesosphere and lower thermosphere (Llewellyn et al., 1973; Noxon, 1978; Frederick et al., 1978; Frederick, 1979). Cvetanovic (1974) has given an overview of the species mentioned above and their role in upper atmospheric processes. Recently, attention has focused on the potential significance of electronically excited ozone even though there is doubt concerning the very existence of bound excited states below the dissociation limit. (Hay et al., 1973, 1975; Wraight, 1977; Prasad and Burton, 1979). On the other hand, experimental evidence for the chemical production of vibrationally excited ozone in the atmosphere appears definitive (von Rosenberg and Trainor, 1974, 1975). This paper combines the available data pertaining to production and loss of vibrationally excited ozone so as to estimate its abundance in the earth's atmosphere. Given this information, together with published laboratory results concerning the influence of vibrational excitation on reaction rate coefficients (Gordon and Lin, 1973; Kurylo et al., 1975), one can estimate the potential significance of excited O_3 in the chemical processes which occur in the upper atmosphere.

Aeronomic Significance of Excited States

In a number of known cases, reactions involving excited species proceed more rapidly than when the reactants are in the ground state. Specific examples are the processes:

$$O(^3P) + O_3 \rightarrow O_2 + O_2 \qquad k_1 \qquad\qquad (R1)$$

$$O(^1D) + O_3 \rightarrow O_2 + O_2 \qquad k_{2a} \qquad\qquad (R2a)$$

$$\rightarrow O_2 + O(^3P) + O(^3P) \quad k_{2b} \qquad\qquad (R2b)$$

where $k_1 = 1.5 \times 10^{-11} \exp(-2218/T)$ cm^{3}s^{-1} but $k_2 = k_{2a} + k_{2b} = 2.4 \times 10^{-10}$ cm^{3}s^{-1}, and

$$N(^4S) + O_2 \rightarrow NO + O_2 \qquad\qquad k_3 \qquad\qquad\qquad\qquad (R3)$$

$$N(^2D) + O_2 \rightarrow NO + O_2 \qquad\qquad k_4 \qquad\qquad\qquad\qquad (R4)$$

with $k_3 = 4.4 \times 10^{-12} \exp(-3220/T)$ and $k_4 = 6 \times 10^{-12}$. All rate coefficients listed above are as given by the NASA Panel (1979) except for k_4 which is from Lin and Kaufman (1971). The extra 1.97 eV available in R2 over that in R1 leads to a gas kinetic rate coefficient. In the case of R4, the activation energy of R3 is absent but the pre-exponential term is essentially unaltered.

The efficiency of a reaction depends on details of molecular scale interactions and one cannot necessarily assume that additional vibrational and electronic energy enhances the rate coefficient. Nonetheless, the above reactions clearly show that there are cases where excited states are aeronomically relevant. A process of particular importance to the stratosphere is the reaction of nitric oxide with ozone. Studies of the reaction:

$$NO + O_3(0,1,0) \rightarrow NO_2 + O_2 \qquad\qquad k_5 \qquad\qquad\qquad\qquad (R5)$$

by Gordon and Lin (1973) and Kurylo et al. (1974) show k_5 to be a factor of 22 larger than the rate coefficient, k_6 of:

$$NO + O_3(0,0,0) \rightarrow NO_2 + O_2 \qquad\qquad k_6 \qquad\qquad\qquad\qquad (R6)$$

at a temperature of 350°K. This is approximately the relationship one would expect of the vibrational energy of $O_3(0,1,0)$ were used to overcome the activation energy of R6, that is $k_5 \approx k_6 \exp[hc\nu(010)/kT]$ where ν is the term value of the excited state. In the presence of a Boltzmann distribution of vibrational levels the exponential scaling of rate coefficients, which in this case has empirical justification, then implies:

$$k_5 [O_3(0,0,0)] \, [NO] \approx k_6 [O_3(0,1,0)] \, [NO]$$

The rate of odd oxygen loss in reactions of NO with ground state ozone is equal to that when the excited (0,1,0) state is involved. Hence, despite the small number densities, reactions involving excited vibrational states of ozone can play an important role in certain upper atmospheric chemical processes. If the rate coefficients for the reaction of NO with $O_3(0,0,1)$ and $O_3(1,0,0)$ scale as does

that for $O_3(0,1,0)$, then R5 is of minor importance compared to reactions involving excited ozone. Similarly, studies of R1 with $O_3(0,0,1)$ as a reactant indicate a room temperature rate coefficient 150 to 1500 times faster than when ground state ozone is involved provided the process proceeds by reaction producing O_2 rather than vibrational deactivation (West et al., 1976).

Given that reactions of excited ozone are significant in some circumstances, it becomes important to consider that published rate coefficients refer to the particular vibrational distributions present in the laboratory. If one considers the series of processes:

$$X + O_3(i) \rightarrow XO + O_2 \qquad k_i$$
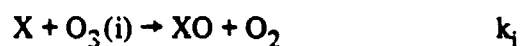
where i refers to a specific state, the rate coefficient determined in the laboratory, $\bar{k}$, is:

$$\bar{k} = \sum_i k_i \frac{[O_3(i)]}{[O_3]}$$

Only a limited number of terms contribute to the sum since k_i can increase with i to at most a gas kinetic value while $[O_3(i)]/[O_3]$ decreases to a negligible value for sufficiently large i. If the fractional population of the excited states are identical in the laboratory and atmosphere, then the effects of the vibrational levels are implicit in the measured rate coefficient. A Boltzmann distribution of vibrational levels prevails at the pressures where most laboratory studies of aeronomic reactions have been made. Yet, above some altitude in the mesosphere or lower thermosphere, the vibrational states of ozone display a non-thermal population. At these altitudes the use of published rate coefficients, especially those involving appreciable activation energies, is likely to be incorrect.

Production and Loss Processes

Vibrationally excited ozone is formed in the atmosphere by the reaction

$$O + O_2 + M \rightarrow O_3 + M \qquad k_7 \qquad \text{(R7)}$$

where M is either O_2 or N_2, and by excitation in collisions with molecules in the high energy tail of the thermal distribution. The products of R7 have 1.08 eV, the dissociation energy of ozone, available for distribution among excitation and translation. The experiments of von Rosenberg and Trainor (1974) imply that half of the exothermicity of R7 lies in vibrational modes of the ozone

molecule, where on the average, the ν_1 and ν_3 modes combined receive 1.6 quanta of energy and the ν_2 mode contains 3.7. Table 1 lists 19 vibrational states plus their wavenumbers and energies which can be excited with a maximum of one quantum each in the ν_1 and ν_3 modes and up to four quanta in the ν_2 mode. For an average initial energy of 0.54 eV, states higher than those listed in Table 1 are likely excited while collisional excitation preferentially populates the lowest lying states. As will be evident, the available data do not merit a detailed treatment of all states and we therefore adopt the simplified method described below to estimate the atmospheric abundance of vibrationally excited ozone.

Little information is available concerning vibrational relaxation in O_3, however, the laboratory results of Rosen and Cool (1975) allow one to divide the process into four classes which operate on different time scales. The quenching of excited O_3 proceeds via a rapid exchange of energy between nearly resonant ν_1 and ν_3 modes, a slower transfer from ν_1 and ν_3 states into ν_2, followed by a still slower quenching of ν_2 modes to the ground state. The quenching of ν_1 and ν_3 modes to $O_3(0,0,0)$ is much less efficient than that of ν_2. The quenching rate $k_Q = 2.4 \times 10^{-14}$ cm^{-3}s^{-1} appropriate for an O_2–N_2 atmosphere has been reported by Rosen and Cool (1973) and is in good agreement with the result of von Rosenberg and Trainor (1974). Analysis of relaxation mechanisms in ozone by Rosen and Cool (1975) implies that this k_Q value refers to the quenching:

$$O_3(0,1,0) + M \rightarrow O_3(0,0,0) + M \tag{R8}$$

Processes of the form:

$$O_3(0,0,1) + M \rightarrow O_3(0,0,0) + M \tag{R9}$$

and

$$O_3(1,0,0) + M \rightarrow O_3(0,0,0) + M \tag{R10}$$

are much slower. We here adopt a rate coefficient of 0.1 k_Q for R9 and R10, although this value is very uncertain. Energy transfers of the form

$$O_3(0,0,1) + M \rightarrow O_3(0,1,0) + M \tag{R11}$$

and

$$O_3(1,0,0) + M \rightarrow O_3(0,1,0) + M \qquad\qquad \text{(R12)}$$

proceed at an approximate rate $3 k_Q$ while the near-resonant energy exchange

$$O_3(1,0,0) + M \rightarrow O_3(0,0,1) + M \qquad\qquad \text{(R13)}$$

has a rate coefficient of at least $54 k_Q$ (Rosen and Cool, 1975). Figure 1 summarizes the above discussion by giving a schematic representation of the coupling which exists between the three lowest excited levels and the ground state. Table 2 lists the adopted rate coefficients for each of the four classes of exothermic reaction. Rate coefficients of endothermic processes have the same pre-exponential factors listed in Table 2 for the corresponding exothermic reaction plus an additional attenuation of the form $\exp(-E/kT)$ where E is the energy difference between the upper and lower states obtained from Table 1.

In the altitude region where a thermal distribution exists, the lowest lying states, $O_3(0,1,0)$, $O_3(0,0,1)$, and $O_3(1,0,0)$ account for essentially all of the vibrational excitation and we treat these states explicitly in the calculation. The scarcity of data concerning relaxation of the highly excited states produced in R7 makes it impossible to give a detailed treatment. We here divide all vibrationally excited states higher than $O_3(1,0,0)$ into two classes denoted by $O_3(\nu_2)$ and $O_3(\nu_1,\nu_3)$, collectively denoted by O_3^*. Class $O_3(\nu_2)$ consists of ozone in the form $O_3(0,v_2,0)$ where $v_2 > 1$. Based on the results of Rosen and Cool (1975) for $O_3(0,1,0)$, we assume that rate coefficients for reactions of $O_3(\nu_2)$ have the same pre-exponential factors as the corresponding process involving $O_3(0,1,0)$ as defined in Table 2. Similarly, $O_3(\nu_1,\nu_3)$ consists of all states, $O_3(v_1,v_2,v_3)$, not included above. The adopted rate coefficients are analogous to those of $O_3(1,0,0)$ and $O_3(0,0,1)$. This division of O_3^* into two classes is based on the observed behavior of the lower states, that the reactive properties of the ν_2 excited mode differ from those of ν_1 and ν_3. In particular, energy originally distributed into ν_1 and ν_3 is preferentially channelled into ν_2 and the final quenching to the ground state occurs via a ν_2 mode.

The abundance of each class of vibrationally excited ozone is computed under chemical equilibrium conditions in the following manner. We assume that R7 produces $O_3(\nu_2)$ and $O_3(\nu_1,\nu_3)$ only, consistent with the large amount of energy stored in vibrational excitation (von Rosenberg and

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Trainor, 1974). Based on the number of individual states contained in the two classes we assume that one molecule in five is produced as $O_3(\nu_2)$ with the remainder in $O_3(\nu_1, \nu_3)$. Each of the five subsets of excited ozone is connected to all others and to the ground state by collisional deactivation and excitation with the appropriate rate coefficient from Table 2. An additional process included for each state is dissociation by solar visible and ultraviolet radiation based on the cross sections of Ackerman (1971) and irradiance from Nicolet (1975). In practice, the absorption cross section for an excited molecule is shifted slightly in energy with respect to that for the ground state, however, this has a negligible effect on the dissociation rate calculation. The only significant infrared radiative process is the 9.6μ emission by $O_3(0,0,1)$ and the subsequent excitation of $O_3(0,0,0)$ when the photon is reabsorbed. The Einstein transition frequency for the process:

$$O_3(0,0,1) \rightarrow O_3(0,0,0) + h\nu \ (9.6\mu) \tag{R14}$$

is $A = 13.47 s^{-1}$ (Yamamoto, 1977). To compute the absorption rate J, in s^{-1}, for:

$$O_3(0,0,0) + h\nu \ (9.6\mu) \rightarrow O_3(0,0,1) \tag{R15}$$

we assume a blackbody radiation field, $B_\nu(T)$, at frequency ν and temperature T. The absorption cross section $\sigma(\nu)$ is assumed concentrated at the single frequency ν_0 so that:

$$\sigma(\nu) = \frac{\pi e^2}{mc} f \ \delta(\nu - \nu_0)$$

where δ is the Dirac delta function and $f = 1.915 \times 10^{-5}$ is the band oscillator strength (Yamamoto, 1977). The absorption rate is then

$$J = 2\pi \int d\nu \ \sigma(\nu) \ B_\nu(T)$$

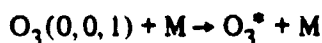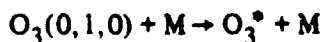$$= \left(\frac{2\pi}{c}\right)\left(\frac{\pi e^2}{me^2}\right) f \frac{\nu_0^2}{\exp(h\nu_0/kT) - 1}$$

Numerical evaluation yields values in the range $1.1 \times 10^{-3} - 1.1 \times 10^{-2} s^{-1}$ between the mesopause and stratopause. The 14.1μ emission of $O_3(0,1,0)$ is sufficiently weak to be negligible. Finally, transitions of the form:

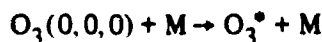$$O_3(v_1, v_2, v_3) \rightarrow O_3(v_1, v_2, v_3-1) + h\nu$$
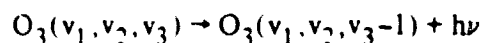
will have Einstein coefficients comparable to that for $O_3(0,0,1)$. However, these merely transform one member of the O_3^* class into another and are therefore not considered here.

Numerical Results

In altitude regions where the atmosphere is sufficiently dense, collisional excitation and de-excitation of a given vibrational level balance to an excellent approximation and a Boltzmann distribution is maintained. The processes which tend to destroy this local thermodynamic equilibrium are the chemical formation of highly excited ozone in R7 and the emission and absorption of 9.6μ radiation. Figure 2 presents the computed production rates of O_3^*. Above 90 to 95 km chemical formation of O_3^* in R7 is the most efficient process. This source exceeds that due to collisional excitation of the ground state above 70-75 km and, above 90-95 km is greater than that due to further excitation of lower lying vibrational levels. Note that the source of O_3^* due to the sum of processes

$$O_3(0,1,0) + M \rightarrow O_3^* + M$$
$$O_3(0,0,1) + M \rightarrow O_3^* + M$$
$$O_3(1,0,0) + M \rightarrow O_3^* + M$$

exceeds that due to:

$$O_3(0,0,0) + M \rightarrow O_3^* + M$$

at all altitudes despite the small relative abundance of the excited states. This is due to the strong coupling of $O_3(0,0,1)$ and $O_3(1,0,0)$ to $O_3(\nu_1,\nu_3)$ and of $O_3(0,1,0)$ to $O_3(\nu_2)$ where resonant transfers of energy are possible. Figures 3 and 4 present the production and loss rates of $O_3(0,0,1)$ respectively. Formation of $O_3(0,0,1)$ due to quenching of higher excited states and by collisional excitation of $O_3(0,1,0)$ are the major sources at all altitudes. However, absorption of 9.6μ radiation upwelling from below is of the same order of magnitude as these processes above 90-95 km. Figure 4 shows that 9.6μ emission exceeds collisions as a loss mechanism for $O_3(0,0,1)$ between 90 and 95 km. Once this occurs the assumption of a blackbody radiation field, used in computing

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the rate of R15, becomes invalid. However, since R15 is never the major source of $O_3(0,0,1)$, the use of the Planck radiation function at all altitudes causes negligible error in comparison to the other uncertainties inherent in the calculations.

The final results are given in Figure 5 as ratios of the number density of an excited state to that which would exist if a Boltzmann distribution prevailed. Below 74 km the standard ozone profile adopted was the rocket model of Krueger and Minzner (1976) and above 86 km ozone was derived from the atomic oxygen profile of the U.S. Standard Atmosphere 1976 assuming a balance between R7 and photodissociation. Between 74 and 86 km a smooth curve was drawn even though there are indications of a secondary maximum in this region (Park and London, 1974). However, for the present work, which considers only ratios of excited states, the details of $[O_3]$ in the 74 to 86 km region are not critical. Figure 5 shows that below 80 km all vibrational levels are populated according to a Boltzmann distribution. The highly excited states, O_3^*, have the greatest deviation, due to the increasing influence of chemical production with altitude. Between 95 and 110 km the population of these vibrational levels exceeds that expected for collisions alone by a factor of three or more. Quenching of these states tends to increase the abundance of the $(0,1,0)$, $(0,0,1)$, and $(1,0,0)$ levels, however, the 9.6μ emission tends to counteract this. Above 95 km the abundance of $O_3(0,0,1)$ is less than expected from collisions alone. The efficiency of the 9.6μ emission as a loss process for excited ozone affects all vibrational levels such that above 105 km all ratios in Figure 5 decrease with altitude despite the efficiency of chemical production of O_3^*. Note, however, that below 110 km the abundances of $O_3(0,1,0)$ and O_3^* remain larger than predicted by a Boltzmann distribution.

Concluding Remarks

Laboratory studies show that each ozone molecule produced in the earth's atmosphere has an average vibrational energy near 0.5 eV. Insufficient information exists with which to perform accurate calculations of the vibrational relaxation, however, the semi-quantitative results obtained here show that excited ozone deviates significantly from a Boltzmann distribution in the uppermost

mesosphere and lower thermosphere. Since the rate coefficients of several aeronomically important reactions vary with vibrational excitation, further laboratory studies of these processes and of vibrational relaxation would be valuable in defining the role of excited ozone in the upper atmosphere.

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Table 1

Vibrational States of Ozone, $O_3(v_1, v_2, v_3)$
Which Can Be Excited With v_1, $v_3 \leq 1$ and $v_2 \leq 4$

$O_3(v_1, v_2, v_3)$	Wavenumber (cm^{-1})	Energy (eV)
010	701.42	.087
001	1042.10	.129
100	1103.16	.137
020	1402.84	.174
011	1743.52	.216
110	1804.58	.224
030	2104.26	.261
101	2145.25	.266
021	2444.94	.303
120	2506.00	.311
040	2805.68	.348
111	2846.67	.353
031	3146.36	.390
130	3207.42	.398
121	3548.09	.440
041	3847.78	.477
140	3908.84	.485
131	4249.51	.527
141	4950.93	.614

Table 2

Adopted Rate Coefficients for Exothermic Energy Exchange
Between Vibrational States of Ozone

Process Type	Description	Example in Text	Rate Coefficient
I	Quenching of ν_2 modes to the ground state	R8	$k_Q = 2.4 \times 10^{-14} \, cm^3 s^{-1}$
II	Quenching of ν_1 and ν_3 modes to the ground state	R9,R10	$0.1 \, k_Q$
III	Transfer to energy from ν_1 and ν_3 into ν_2 modes	R11,R12	$3 \, k_Q$
IV	Transfer of energy from ν_1 to ν_3	R13	$54 \, k_Q$

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Figure 1. Schematic of the coupling between the three lowest vibrationally excited levels of ozone and the ground state. The thickness of the lines connecting the various levels indicates the magnitude of the associated reaction rates.
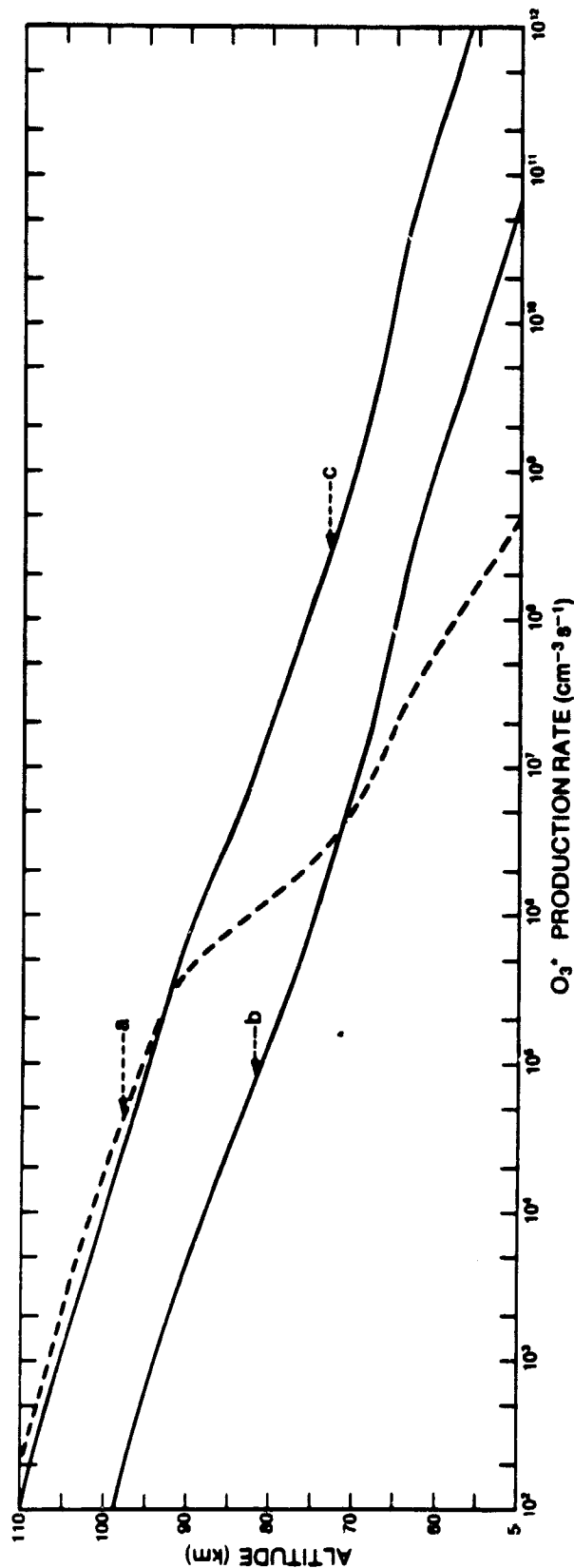
Figure 2. Production rates of highly excited states of ozone by chemistry and collisional processes. Curves refer to the production of states with energy greater than that of $O_3(1,0,0)$.

Curve a. Chemical production in reaction R7.
Curve b. Excitation of $O_3(0,0,0)$ by collision.
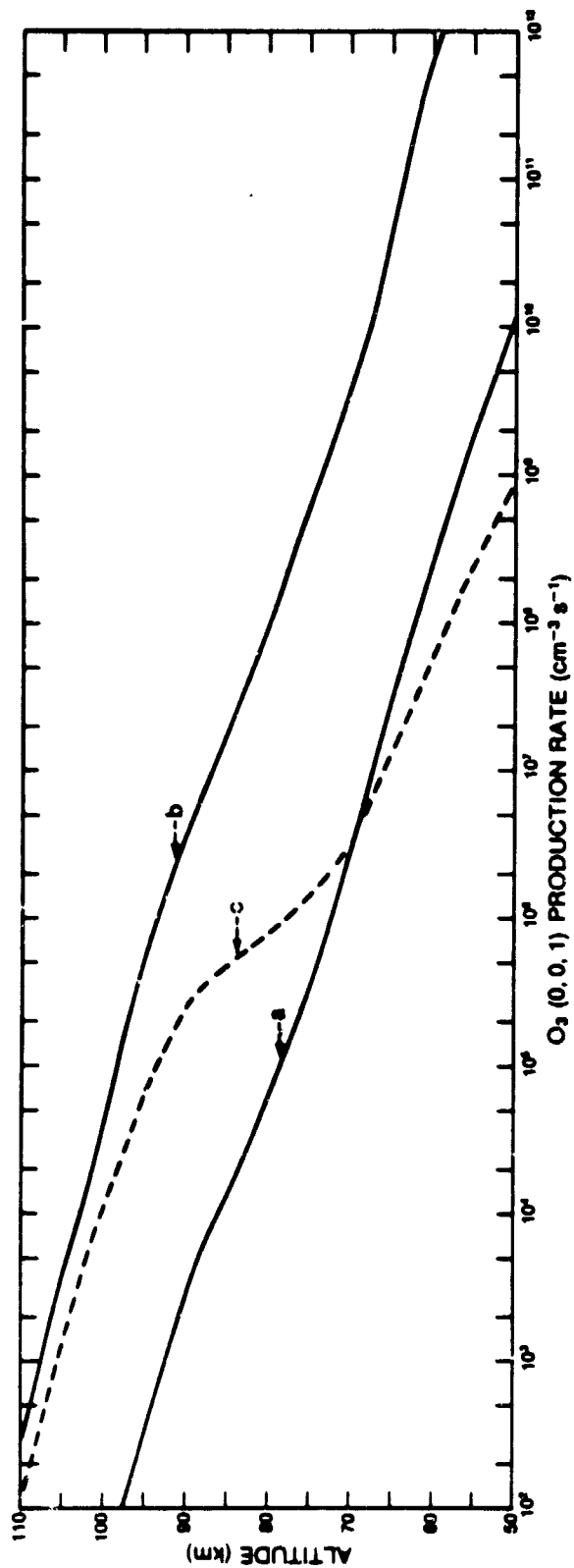Curve c. Further excitation of low-lying states by collision.

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Figure 3. Production rates of $O_3(0,0,0)$.

Curve a. Collisional excitation of $O_3(0,0,0)$.
Curve b. Collisional excitation and quenching of all other excited states.
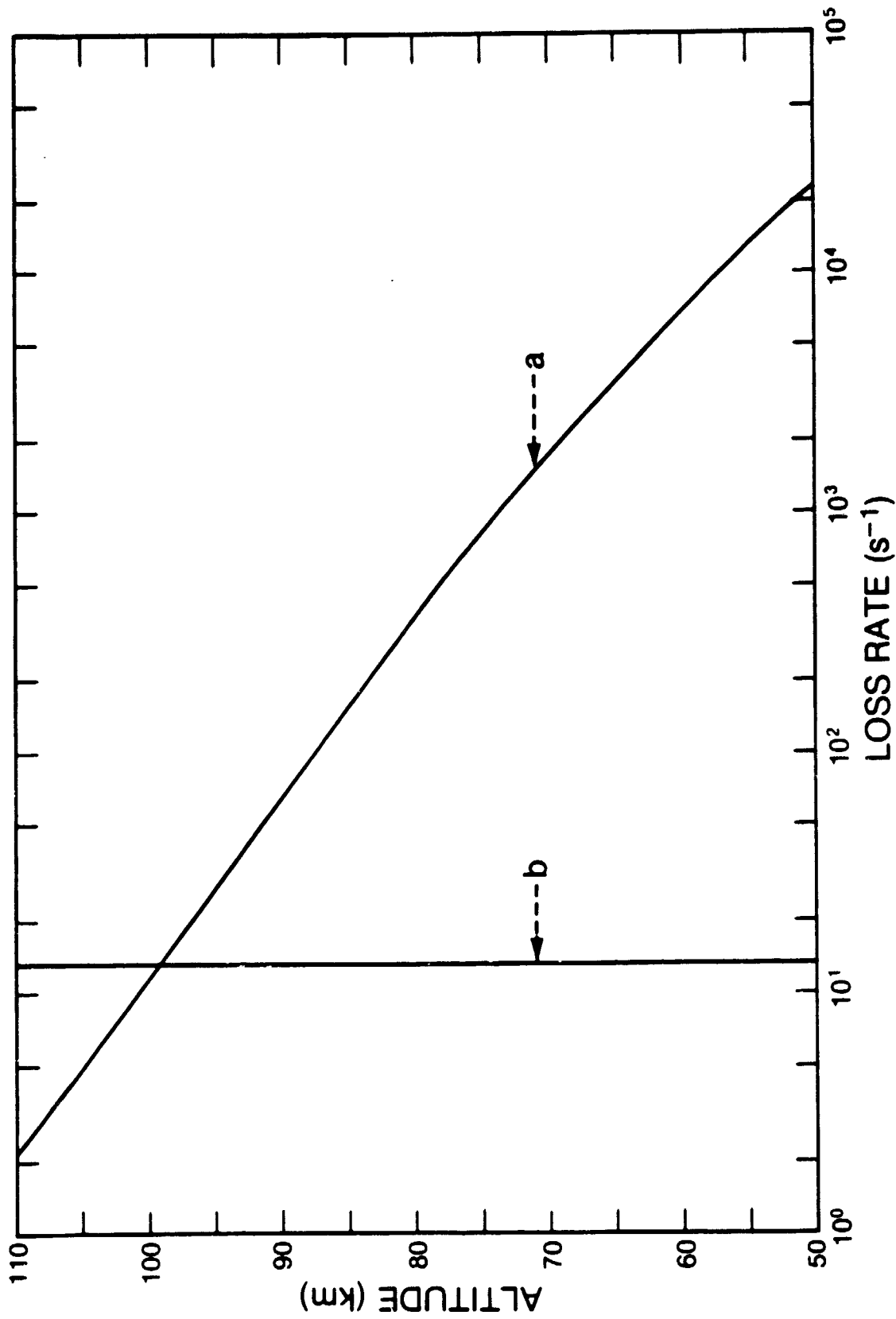Curve c. Absorption of 9.6μ radiation.

Figure 4. Loss rates of $O_3(0,0,1)$.

Curve a. Quenching and collisional excitation.
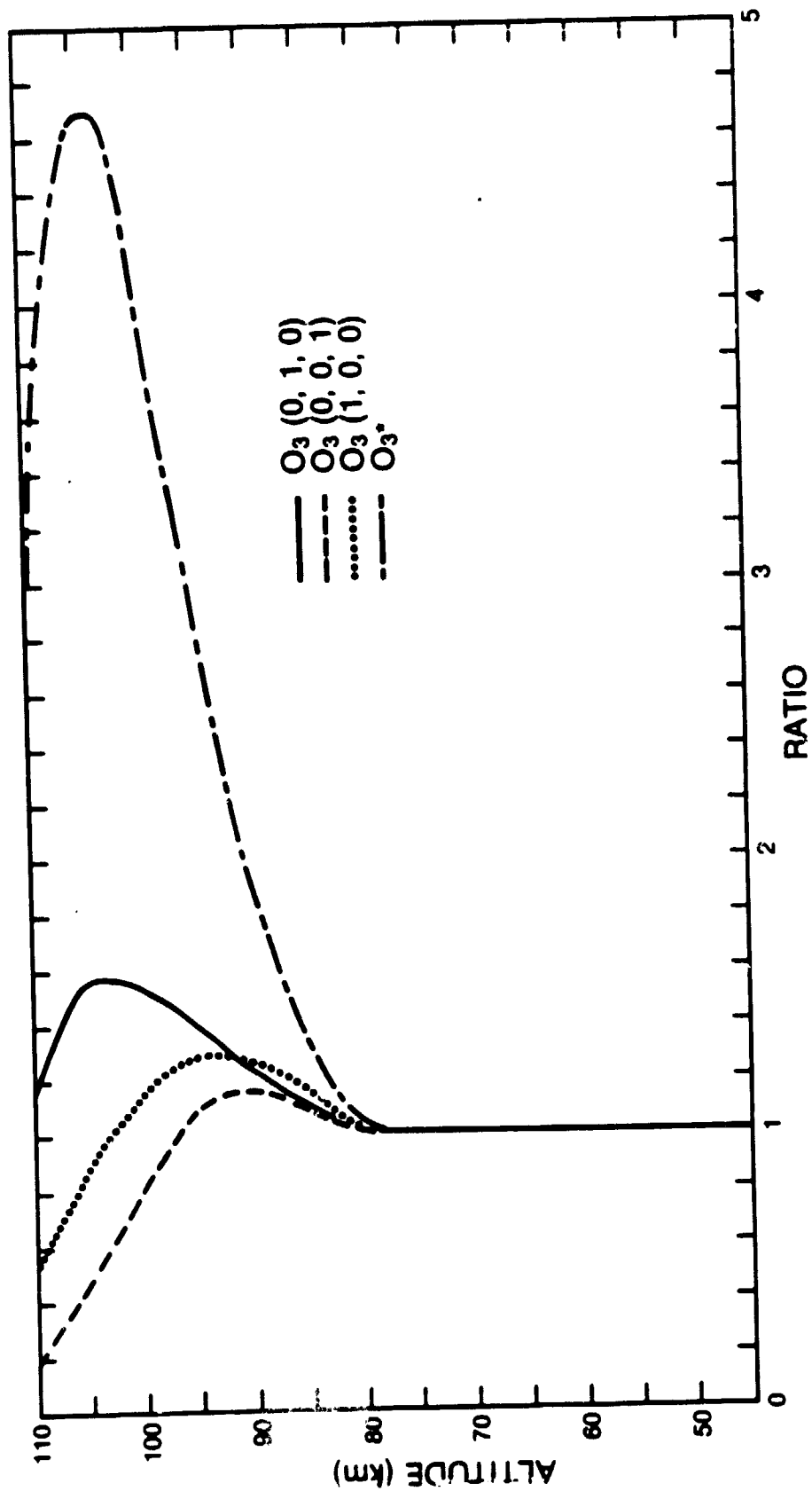Curve b. Emission of 9.6μ radiation.

Figure 5. Ratio of computed number densities to those which would prevail in a Boltzmann distribution.