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ALTITUDE DISTRIBUTIONS OF AND RADIATIONS FROM CERTAIN OXYGEN AND NITROGEN METASTABLE CONSTITUENTS

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Abstract

The airglow emitted by certain metastable constituents $N(^2D)$, $O(^1D)$, $O^+(^2P)$, and $O^+(^2D)$ in the daytime atmosphere is investigated and their altitude distributions are obtained.

The production of $N(^2D)$ atoms by dissociative recombination of N_2^+ with electrons is considered. Their quenching by collisions with electrons and O_2 molecules is calculated, and it was shown that if quenching by electrons is neglected, the calculated integrated intensity of NI 5199 line agrees with the observed value.

Assuming collisional deactivation of $O(^1D)$ atoms by O_2 molecules, the production rates of $O(^1D)$ by photo-dissociation of O_2 in the Schumann-Runge continuum at low, medium and high activities of the sun are calculated. The $O(^1D)$ distribution and rates of emission of the oxygen red line in the dayglow are also calculated. Calculated intensity at minimum activity agrees with the observed value. An order of magnitude increase in its intensity from minimum to maximum activity cannot be accounted for as due to the variations of molecular oxygen concentration and of solar extreme ultra violet flux incident upon the upper atmosphere. Contributions due to dissociative recombination of O_2^+ and by thermal electron impact at different levels of solar activity cannot be computed as the variation of ion composition of the ionosphere and that of electron temperature with solar cycle are not known.

The production rates of metastable $O^+(^2P)$ and $O^+(^2D)$ ions by photoionization of O atoms are calculated. Their equilibrium distributions are computed after using the recent data of rate coefficients for ion-atom interchange and other ionic reactions. As a check, the zenith intensity of (7319-7330A) multiplet of O^+ in the day airglow is calculated.

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Introduction

Metastable ions and atoms are important for the photochemistry of the ionsophere. They lead to the emission of important radiations in the airglow. Also, the extra energy which they carry makes certain reactions possible which would not have occurred with normal ions and atoms. For example, the $O^+(^2D)$ ions may produce N_2^+ ions in the ionosphere by a simple charge exchange reaction

$$O^+(^2D) + N_2 \longrightarrow N_2^+ + O$$

which, from energy considerations, cannot occur with normal O^+ ions. In Section 1 of this paper, radiations from $N(^2D)$ atoms are considered, those from $O(^1D)$, and from $O^+(^2P)$ and $O^+(^2D)$ are discussed in Sections 2 and 3 respectively.

Section 1

The NI 5199A(^2D-^4S) radiation in the twilight airglow has been detected by many investigators (Courtès, 1950; Dufay, 1952, 1953). In the day airglow, its intensity was first measured by Wallace and Nidey (1964) using a rocket-borne Ebert-Fastie spectrometer which scanned the entire visible region. The measurement was made in the evening for a zenith angle of 76°. It can be seen from Fig. 3 of their paper that observed from the altitude range 150-192 km, the integrated intensity remained constant (about 200 R) indicating that the radiation originates from above this altitude range. Recently, Wallace and McElroy (1966) again measured the intensity of this line in the evening at a zenith angle of 72° with a photometer mounted on a rocket and obtained an integrated intensity of 100 R.

1. Emission Rate of 5199 A photons

It is believed that $N(^2D)$ metastable atoms are produced mainly by dissociative recombination of N_2^+ ions with electrons (Chamberlain, 1961)

$$N_2^+ + e \xrightarrow{K_1} N(^2D) + N \qquad (1.1)$$

One or both of the N atoms may be in the ^2D state. Another reaction, namely

$$NO^+ + e \xrightarrow{K_2} N(^2D) + O \qquad (1.2)$$

may also produce N atoms in the ^2D state (Chamberlain, 1961; Wallace and McElroy, 1966). Reaction (1.2) does not conserve spin and contrary to observations, the reaction would have enhanced the 5199 A emission at lower altitudes. Therefore, the reaction (1.2) is not considered.

For the loss of $N(^2D)$ atoms, we have considered spontaneous transition and super elastic collisions with electrons, namely

$$N(^2D) \xrightarrow{K_3} N(^4S) + h\nu \ (5199\ A) \qquad (1.3)$$

and

$$N(^2D) + e \xrightarrow{K_4} N(^4S) + e \qquad (1.4)$$

The transition probability of reaction (1. 3) and the rate coefficient of reaction (1. 4) are 2. 3x10^{-5}sec^{-1} (Nicholls, 1964) and 2x10^{-9}cm^{3}sec^{-1} (Seaton, 1956) respectively. Quenching of N(^{2}D) by N_2 molecules may be neglected because the corresponding reaction is disallowed by the spin conservation rule. Quenching by O_2 molecules can however occur by the following reaction (Wallace and McElroy, 1966)

$$N(^2D) + O_2(X^3\Sigma_g^+) \xrightarrow{K_5} N(^4S) + O_2(^1\Delta \text{ or } ^1\Sigma_g^+) \qquad (1.5)$$

whose rate coefficient K_5 = 2x10^{-12}cm^{3}sec^{-1}.

The volume emission rate of 5199A photons at an altitude z by the reaction (1. 1) is given by

$$R_{5199,z} = n(^2D)_z\, K_3 = \frac{K_1 n(N_2^+)_z\, n(e)_z}{K_3 + K_4 n(e)_z + K_5 n(O_2)_z}\, K_3 \qquad (1.6)$$

where $n(N^2D)_z$, $n(N_2^+)_z$ $n(e)_z$ and $n(O_2)_z$ are the densities of N(^{2}D) atoms, N_2^+, electrons, and O_2 at an altitude z respectively. For its computation, N_2^+ densities obtained from rocket-borne mass spectrometers are utilized. Their densities and also of electrons are collected in Fig. 1 of Ghosh's paper (1967). O_2 densities for the medium solar activity are obtained from CIRA, 1965. The dissociative recombination coefficient K_1, has been discussed considerably in the literature. We have adopted a coefficient of 2. 8x10^{-7}cm^{3}sec^{-1} obtained recently by Biondi (1964). The volume emission rates with and without electron quenching are shown in Fig. 1. 1. It will be seen that electrons quench N(^{2}D) atoms throughout the 130-280 km altitude range. Due to the high electron density in the F region, N(^{2}D) atoms are quenched considerably.

To calculate the integrated intensity, the given altitude range is divided into thin layers such that in each layer the emission rate is nearly constant. Multiplying the emission rate by the layer thickness and adding the contributions of individual layers, the integrated intensity (24R) is obtained from Equation (1.6). If quenching by electrons is neglected, the integrated intensity comes out to be 228R assuming both N atoms in reaction (1.1) are excited to ^2D state. The emission from below 180 km is only about 1 R which agrees fairly with the integrated intensity obtained by Wallace and Nidey (1964). The $N(^2D)$ number density as a function of height calculated from curve 2 of Fig. 1.1 is shown in Fig. 1.2. It is evident that an increased integrated emission will be obtained if the volume emission rate beyond 280 km is considered. The discrepancy between the observed and calculated emissions arises from the fact that the emissions are observed during morning whereas calculated values are those for daytime for which N_2^+ ion density is available. Furthermore, since $N(^2D)$ atoms have long lifetime, they diffuse downward into the quenching region.

Section 2

Brandt (1958) predicted that the intensity of the red oxygen line in the day airglow should be of the order of 50 KR. Noxon and Goody (1962) and Jarrett and Hoey (1963) obtained values comparable to that predicted by Brandt. However, later measurements (Zipt and Fastie, 1963; Wallace and Nidey, 1964; Nagata et al, 1965) yielded values almost an order of magnitude smaller. Noxon (1964) carried out measurements by a ground-based apparatus from June, 1962 through December, 1963 and observed that the intensity of this line has a pronounced variation from day to day and even in the course of a single day. He obtained values ranging from 5 to 50 KR and observed that day to day fluctuations were superimposed over a smooth decrease of intensity.

In this Section, the altitude distribution of $O(^1D)$ atoms and changes in the intensity of the red oxygen line due to changes in the composition of the upper atmosphere and that of the flux in the extreme ultraviolet at different levels of solar activity are considered.

2.1 Production of $O(^1D)$ atoms

$O(^1D)$ atoms are produced mainly through photo-dissociation of O_2 by the Schumann-Runge continuum (1350-1750A)

$$O_2 + h\nu \ (1350\text{-}1750A) \xrightarrow{K_6} O(^3P) + O(^1D) \qquad (2.1)$$

The rates of production of $O(^1D)$ atoms at various altitudes and at different levels of solar activity are calculated by the method outlined in Section 3.1. In this case, O_2 is the only absorbing constituent in the above spectral range. As representatives of atmospheric composition at low, medium and high solar activities, models 2, 6 and 10 from CIRA, 1965, have been adopted. Assuming the EUV fluxes reported by Hinteregger et al (1965) to be characteristic of the solar minimum condition (their measurements were carried out in July, 1963), EUV fluxes at the top of the atmosphere at medium and high solar activities are obtained by multiplying these fluxes by 2.5 and 6 respectively.

The indices of solar activity (S) used in the computation of densities in CIRA, 1965, are the solar radio wave fluxes at 10.7 cm (2800 Mc/s) in radio astronomy units (IRAU = $10^{-22} W/m^2$ c/s). Harris and Priester (1963) and Anderson (1964) however showed that the variation of the radio wave fluxes at 10.7 cm does not correctly represent the variations of EUV fluxes during a solar cycle. Anderson (1965) showed that both radio wave and the EUV fluxes have quiet sun and active region components whose variations are quite unrelated though may be regular. He showed that the radio wave fluxes at 10.7 cm may be regarded as an index of EUV only near the solar minimum and introduced a new parameter S' which represents variations of EUV fluxes. S' varies roughly by a factor of six from the solar minimum to maximum condition. Calculated rates of production of $O(^1D)$ atoms for the three levels of solar activities are shown in Fig. 2.1.

2.2 Deactivation of $O(^1D)$ atoms.

The deactivation of $O(^1D)$ atoms has been considerably discussed in the literature. Bates and Dalgarno (1953) pointed out that $O(^1D)$ atoms should be very rapidly deactivated by the following reaction

$$O(^1D) + O_2(X^3\Sigma_g^- \; v = 0) \xrightarrow{K_7} O(^3P_2) + O_2(b^1\Sigma_g^+ \; v = 2) \qquad (2.2)$$

as this reaction is nearly in exact resonance. Deactivation by N_2 namely

$$O(^1D) + N_2(X^1\Sigma_g^+) \xrightarrow{K_8} O(^3P) + N_2(X^1\Sigma_g^+) \qquad (2.3)$$

is disallowed by the spin conservation rule. From an analysis of amount emission, Wallace and Chamberlain (1959) concluded that $10^{-10} > K_7 > 5 \times 10^{-12} cm^3 sec^{-1}$. Dalgarno and Walker (1964) have shown that if $K_7 \simeq 10^{-10} cm^3 sec^{-1}$ is assumed, the red line intensity in the day airglow can be explained. DeMore and Raper (1962) have shown that O_2 is approximately 4.5 times faster than N_2 in deactivating $O(^1D)$ atoms.

While discussing the photochemistry of O_3 in an atmosphere of oxygen, Hunt (1966a) concluded that in order to maintain the required concentration of $O(^1D)$ in the ozonosphere, which effectively controls the O_3 abundance, the deactivation of $O(^1D)$ by O_2 and N_2 should be slow. He proposed that $K_7 = 2.5\times10^{-14}cm^3sec^{-1}$ and $K_8 = 5\times10^{-15}cm^3sec^{-1}$. These rate coefficients can be discarded on the ground that the concentrations of $O(^1D)$ derived by them in the lower atmosphere would give an unacceptably large red line intensity in the day airglow. However, in a modified photochemical theory of the ozonosphere (Hunt, 1966b) for an oxygen-hydrogen atmosphere, he finds that if $K_7 = 5\times10^{-12}cm^3sec^{-1}$ is accepted, the calculated O_3 abundance agrees with the observed value, and that $O(^1D)$ concentration lies within the acceptable limits. Warneck and Sullivan (1966) obtained from a laboratory study that $K_7 = 4\times10^{-15}cm^3sec^{-1}$ which also should be discarded as being low. We have assumed its value as $10^{-10}cm^3sec^{-1}$ as given by Dalgarno and Walker.

The deactivation through super elastic collisions with electrons is negligible (Chamberlain, 1961). Neglecting the reaction (2.3), the equilibrium concentration of $O(^1D)$ at an altitude z is given by

$$n(O^1D)_z = \frac{q(O^1D)_z}{K_7 n(O_2)_z + .0091}$$

where $q(O^1D)_z$ is the production rate of $O(^1D)$ atoms at z and $0.0091\ sec^{-1}$ is the combined transition probabilities for emissions of 6300A and 6363A lines and is shown in Fig. 2.2 for low, medium and high solar activities.

The volume emission rate of 6300A line at an altitude z is given by

$$R_{6300,z} = n(O^1D)_z \times .0069$$

Its values for the three levels of activities of the sun are calculated and are shown in Fig. 2. 3. The integrated intensities for the three levels are 4. 0, 5. 5 and 6. 6 KR respectively, which agree for low activity but differs by a factor of 7. 5 for high activity of the sun.

2. 3 Other sources of $O(^1D)$ atoms.

The other mechanisms for the production of $O(^1D)$ atoms is the dissociative recombination of O_2^+ ions with electrons

$$O_2^+ + e \longrightarrow O + O(^1D)$$

(Ghosh and Sharma, 1961), and

$$NO^+ + e \longrightarrow N + O(^1D)$$

as pointed out by Chamberlain (1961). For the latter reaction, the spin conservation rule does not hold good. Noxon (1964) pointed out that the variability of the red line intensity in the day airglow may be attributed to the excitation of oxygen atoms by impact of thermal and high energetic photo-electrons. Obviously, for the latter, there is no correlation between their energies and solar activities. Excitation by thermal electrons depends on the electron temperature. Rate coefficients for electron excitation at different electron temperatures have been calculated by Seaton (1956). Fournier and Nagy (1965) have calculated the contribution of photo-electron excitation to red line intensity and have shown that it is significant.

Using ion densities reported by Holmes et al (1963) which are taken at the solar minimum condition, the intensity of the red oxygen line due to dissociative recombination of O_2^+ with electrons is calculated and is found to be 0. 5 KR. No data regarding the variation of ion composition of the ionosphere with solar activity are available. It is unlikely that ionic densities vary by a factor more than 2 or 3. It therefore appears that the dissociation recombination of O_2^+ ions with electrons is a minor source of $O(^1D)$ atom compared to that by photo-dissociation of O_2.

The variation of electron temperature with solar activity is not definitely known. From the rate coefficients calculated by Seaton, (1956) the red line intensities due to thermal electron excitation for the electron temperature 2000-3000°F are calculated. It is assumed that the mechanism in operative only in the altitude range 200-300 Km. It has been found that the intensity varies from about 100 R at $Te = 2000^{o}K$ to about 5 KR at $Te = 3000^{o}K$. It is obvious from the above that though this process significantly affects the intensity, it does not affect the nature of the intensity variation due to photodissociation.

Section 3

In this Section, the calculated densities of metastable $O^+(^2P)$ and $O^+(^2D)$ ions in the daytime ionosphere are presented.

3.1 Production Rates of $O^+(^2P)$ and $O^+(^2D)$ Ions.

$O^+(^2P)$ and $O^+(^2D)$ metastable ions are produced by the following photoionization processes:

$$O(^3P) + h\nu \ (\lambda \lesssim 663A) \longrightarrow O^+(^2P) + e \qquad (3.1)$$

$$O(^3P) + h\nu \ (\lambda \lesssim 732A) \longrightarrow O^+(^2D) + e \quad . \qquad (3.2)$$

The rates of production of these ions are calculated as follows. The production rate of $O^+(^2P)$ ions at an altitude z by radiations of a frequency ν is given by

$$q(O^{+2}P)_z = \Upsilon_\nu \ n(h\nu)_z \ n(O)_z$$

where

Υ_ν — photoionization cross section of O atoms at a frequency ν to $O^+(^2P)$state

$n(h\nu)_z$ — solar photon flux density for a frequency ν at an altitude z

$n(O)_z$ — O atom number density at an altitude z.

To calculate the rate of production of $O^+(^2P)$ ions at z for all wavelengths below the threshold, $q_1(O^{+2}P)$, the solar spectrum is divided into small wavelength intervals such that the cross section within an interval remains nearly constant. The contributions of different wavelength intervals are then summed up. Hence,

$$q(O^{+2}P)_z = n(O)_z \sum_\nu \Upsilon_\nu \ n(h\nu)_z$$

The photon flux density is calculated from the expression

$$n(h\nu)_z = n(h\nu)_\infty \exp\left[-\sum \frac{n_{iz} H_{iz} \ \sigma_{\nu i}}{\mu}\right]$$

where

$n(h\nu)_\infty$ — photon flux for a frequency ν at the top of the atmosphere.

n_{iz} — number density of the ith absorbing constituent at an altitude z.

H_{iz} — scale height of the ith atmospheric constituent at z.

$\sigma_{\nu i}$ — absorption cross section of a frequency ν for the ith constituent.

μ — cosine of zenith angle of the sun.

The summation under the exponential is carried over the three main constituents (O, O_2 and N_2) of the atmosphere. Photoionization cross sections for reaction (3. 1) calculated by Dalgarno et al (1964) are used. Similarly, the production rate of $O^+(^2D)$ by photoionization, $q_2(O^{+2}D)$, can be calculated. Calculated rates of production of $O^+(^2P)$ and $O^+(^2D)$ at noontime are shown in Fig. 3. 1. It will be seen that the maximum rates of production of these ions occur at about 150 km.

3. 2 Equilibrium $O^+(^2P)$ Ion Density.

In addition to the reaction (3. 1), $O^+(^2P)$ ions may be produced when inner shell electrons of O atoms are knocked out (Dalgarno et al, 1963). However, since the photoionization cross sections of such reactions are small (Dalgarno et al, 1964), their contributions are neglected.

$O^+(^2P)$ ions undergo spontaneous transition to ^2D and ^4S states, i. e.,

$$O^+(^2P) \xrightarrow{A_1} O^+(^2D) + h\nu \quad (7330A) \tag{3. 3}$$

$$O^+(^2P) \xrightarrow{A_2} O^+(^4S) + h\nu \quad (2470A) \tag{3. 4}$$

or, can be de-excited by superelastic collisions with electrons

$$O^+(^2P) + e \xrightarrow{K_9} O^+(^2D) + e \tag{3. 5}$$

$$O^+(^2P) + e \xrightarrow{K_{10}} O^+(^4S) + e \tag{3. 6}$$

The transition probabilities A_1, A_2 of reactions (3.3) and (3.4) are respectively 0.318 sec^{-1} and 0.080 sec^{-1} (Nicholls, 1964). The rate coefficients K_9 and K_{10} of reactions (3.5) and (3.6) are $1x10^{-7} cm^3 sec^{-1}$ and $2x10^{-8} cm^3 sec^{-1}$ respectively (Dalgarno et al, 1963).

Also, these ions suffer ion-atom interchanges with atmospheric molecules

$$O^+(^2P, ^2D) + O_2 \xrightarrow{K_{11}} O_2^+ + O \qquad (3.7)$$

$$O^+(^2P, ^2D) + N_2 \xrightarrow{K_{12}} NO^+ + N \qquad (3.8)$$

Hence, the equilibrium concentration of $O^+(^2P)$ ions is given by

$$n_1(O^{+2}P) = \frac{q_1(O^{+2}P)}{(A_1+A_2)+(K_9+K_{10})n(e)+K_{11}n(O_2)+K_{12}n(N_2)} \qquad (3.9)$$

<u>Equilibrium $O^+(^2D)$ Ion Density</u>

$O^+(^2D)$ ions may be produced by reaction (3.2), and from spontaneous transition (3.3) or by superelastic collisions

$$O^+(^2D) + e \xrightarrow{K_{13}} O^+(^2S) + e \qquad (3.10)$$

whose rate coefficient $K_{13} \simeq 3x10^{-8} cm^3 sec^{-1}$ (cf. Dalgarno et al, 1963) and also through the ion-atom interchange collisions (3.7) and (3.8). Since the transition probability of $O^+(^2D - ^4S)$ is only about $1.7x10^{-4} sec^{-1}$ (Nicholls, 1964), the loss of $O^+(^2D)$ ions through spontaneous transitions to ^4S state is negligible. Hence, the equilibrium concentration of $O^+(^2D)$ ions is given by

$$n_2(O^{+2}D) = \frac{q_2(O^{+2}D)+A_1n_1(O^{+2}P)+K_9n_1(O^{+2}P)n(e)}{K_{13}n(e)+K_{11}n(O_2)+K_{12}n(N_2)} \qquad (3.11)$$

Swider (1965) has shown that if $K_{11} \simeq 3\times10^{-12}\mathrm{cm}^3\mathrm{sec}^{-1}$ and $K_{12} \simeq 3\times10^{-13}\mathrm{cm}^3\mathrm{sec}^{-1}$ for nighttime ionosphere are assumed, results in agreement with the ionospheric composition determined by rocket-borne spectrometers are obtained. Recently, Ferguson <u>et</u> <u>al</u> (1965) showed that for ions in the ground state $K_{11} = 4\times10^{-11}\mathrm{cm}^3\mathrm{sec}^{-1}$ and $K_{12} = 3\times10^{-12}\mathrm{cm}^3\mathrm{sec}^{-1}$ at 300°K. Ionospheric calculations indicate that these coefficients are temperature dependent. We have assumed the following coefficients (Ghosh, 1967),

$$K_{11} = 8\times10^{-12}\left(\frac{1200}{T}\right)^{\frac{1}{2}}$$

and

$$K_{12} = 4.2\times10^{-12}\exp\left(-\frac{470}{RT}\right)$$

where T is the absolute temperature at the altitude under consideration.

Using these values of K_{11} and K_{12}, the equilibrium concentrations of $n_1(O^{+2}P)$ and $n_2(O^{+2}D)$ are calculated from Equations (3.9) and (3.11) and are shown in Figure 3.2. As a check, the intensity of the $O^+(^2P - {}^2D)$ multiplet (7319 - 7330A) in the day airglow is calculated. The volume emission rate of these radiations at an altitude z is given by

$$R = n_1(O^{+2}P)_z \times A_1 \tag{3.13}$$

and is shown in Figure 3.3. From the procedure outlined in Section 1.1, an integrated intensity $\simeq$1.24 KR is obtained. No experimental measurement of the intensity of these radiations is available. However, this value is in fair agreement with that obtained theoretically by Dalgarno and McElroy (1965).

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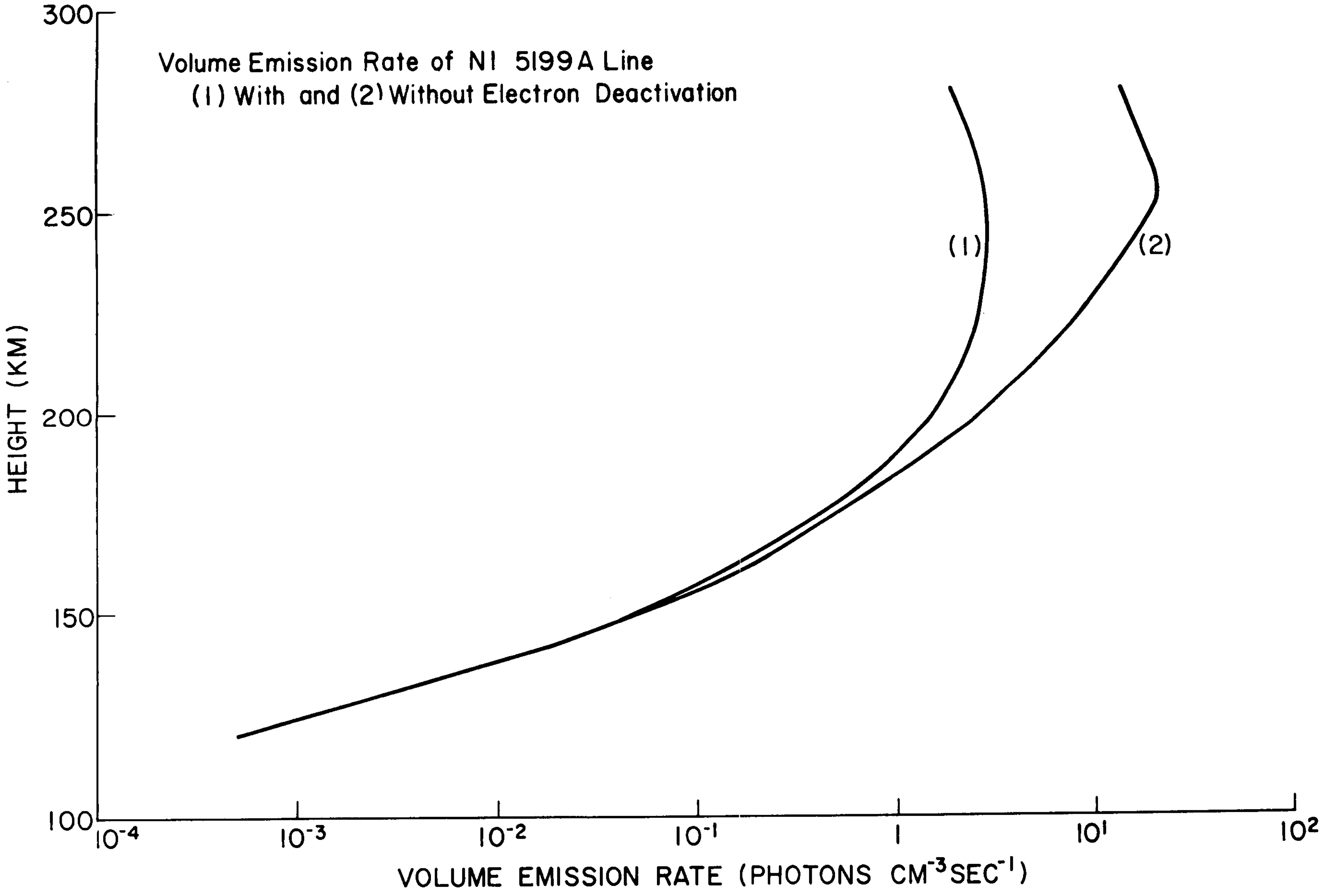

Fig. 1.1 The volume emission rate of NI 5199A line (1) with and (2) without electron deactivation as a function of height.

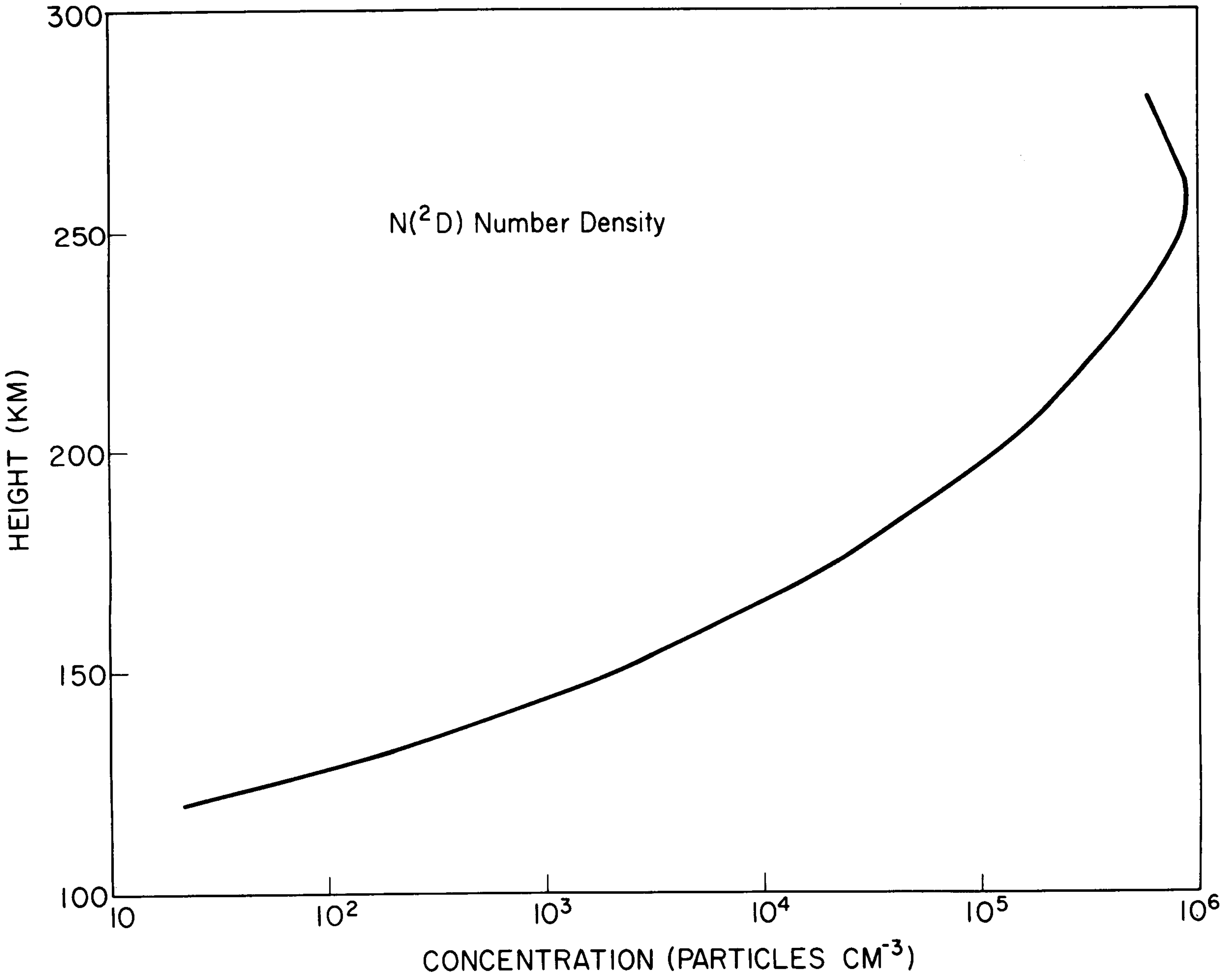

Fig. 1.2 The $N(^2D)$ number density as a function of height calculated from curve 2 of Fig. 1.1.

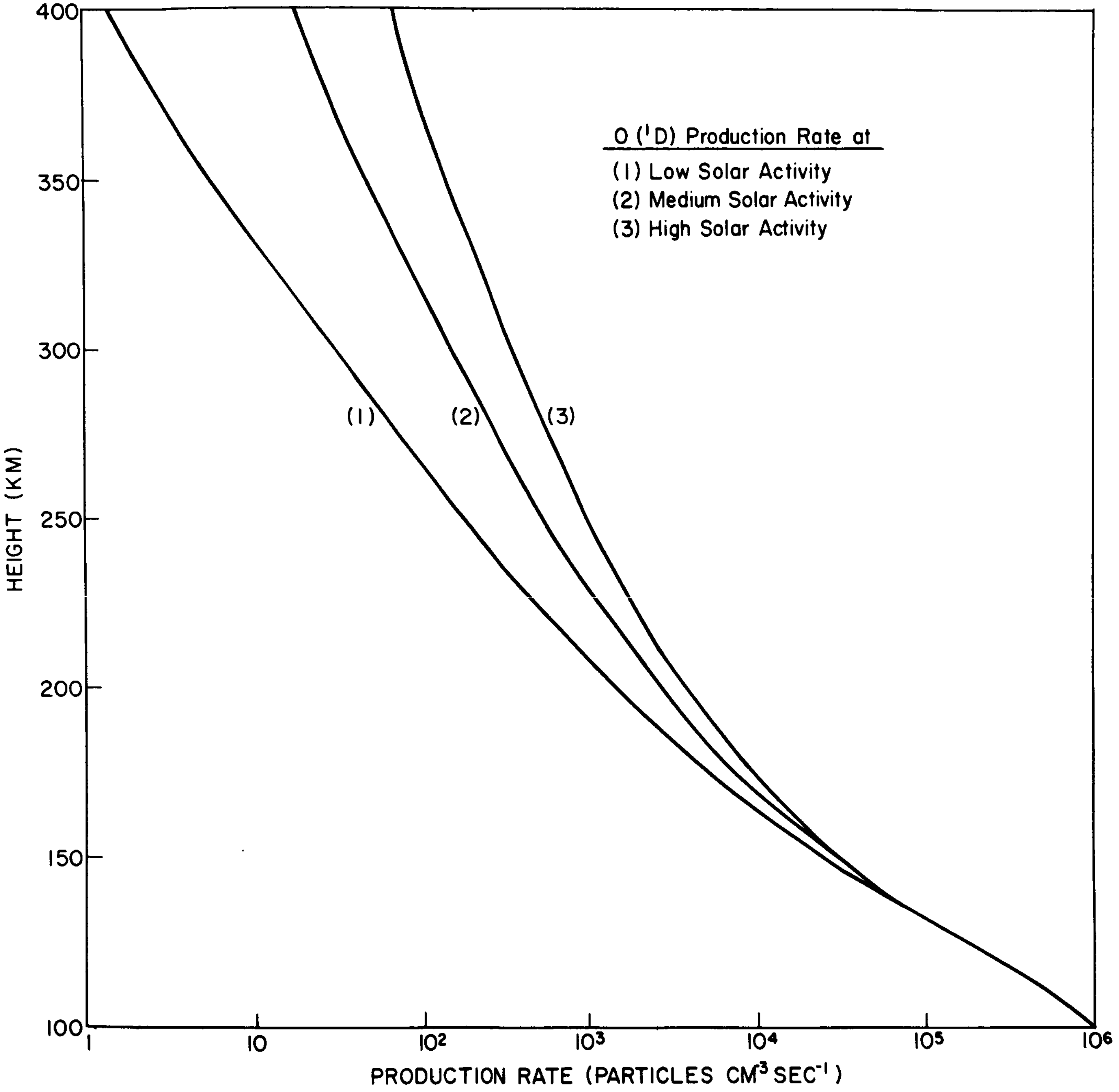

Fig. 2.1 Calculated rates of production of $O(^1D)$ atoms with height for the low, medium and high solar activities.

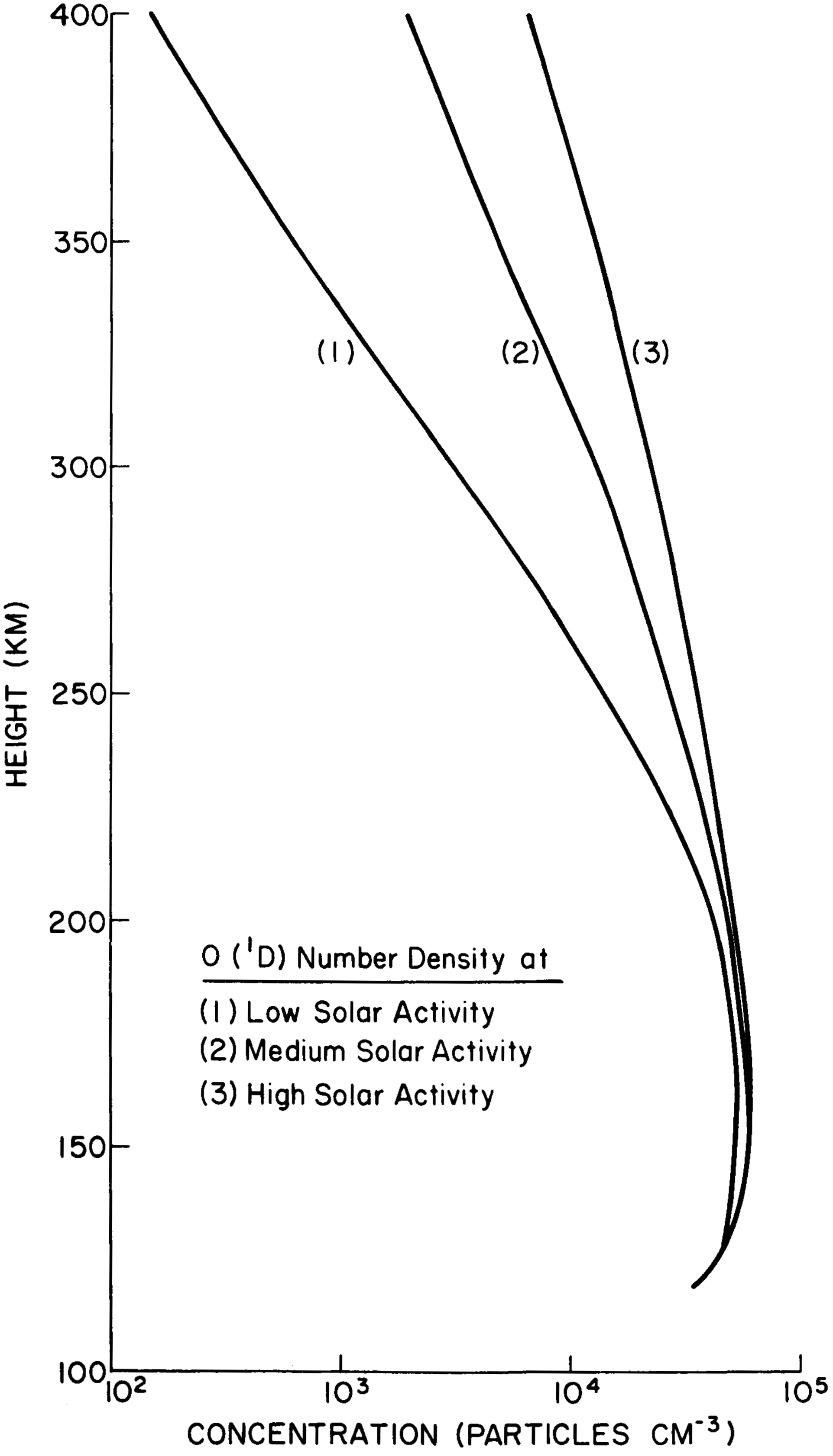

Fig. 2.2 The O(^{1}D) number density as a function of height at the low, medium and high solar activities.

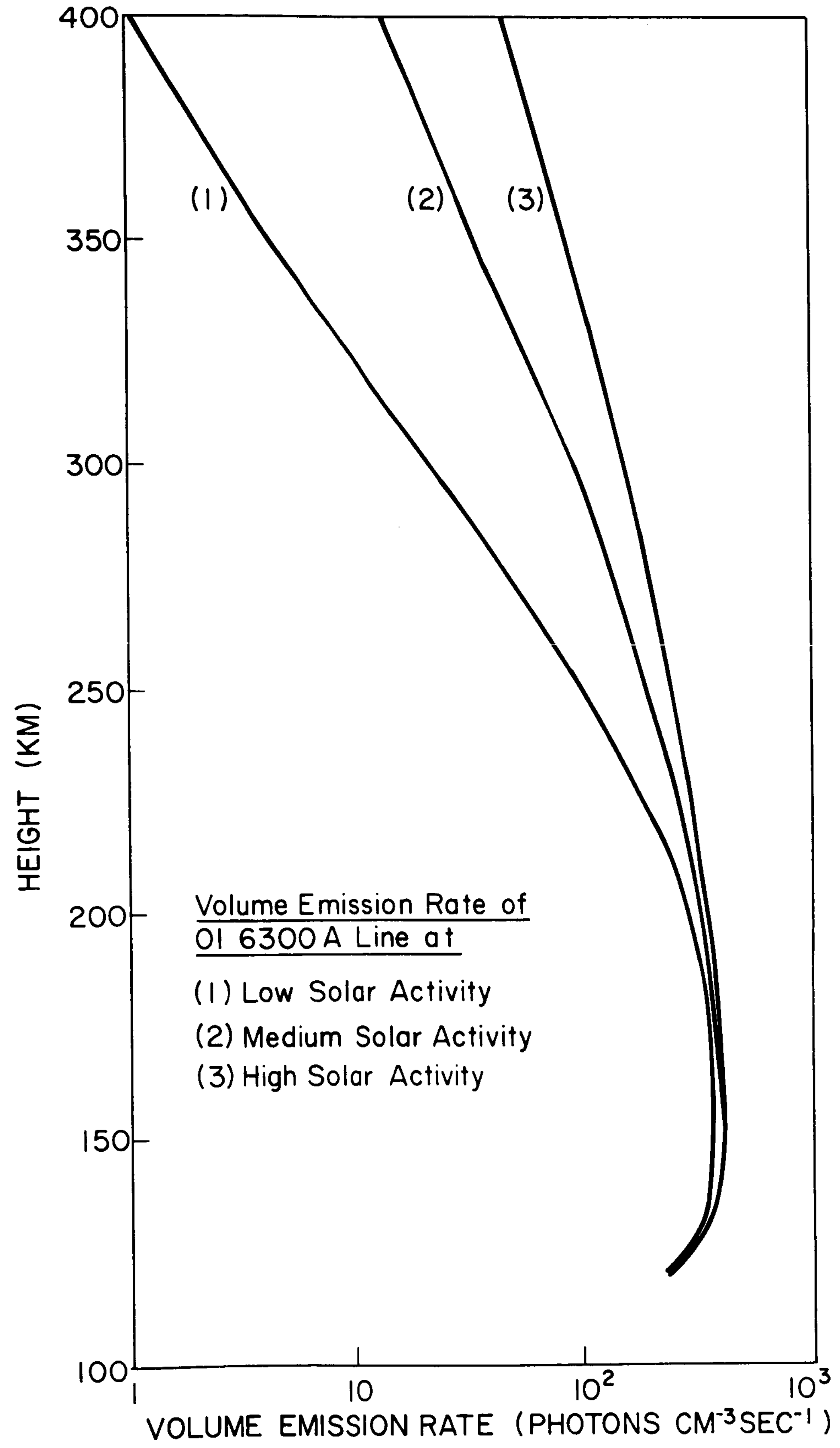

Fig. 2. 3 The volume emission rate of OI 6300A line at low, medium and high solar activities as a function of height.

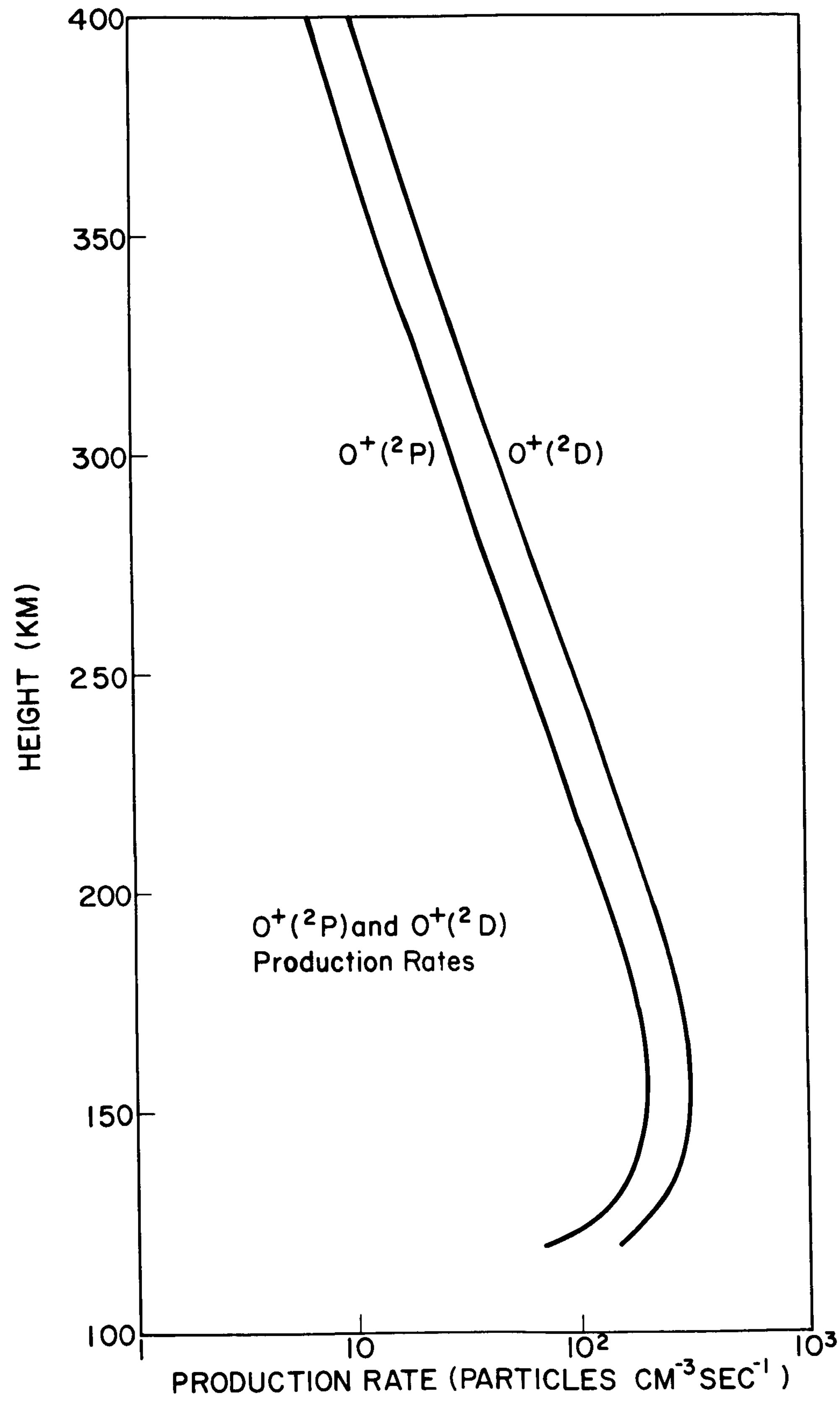

Fig. 3.1 Calculated rates of production of $O^+(^2P)$ and $O^+(^2D)$ with height at noontime.

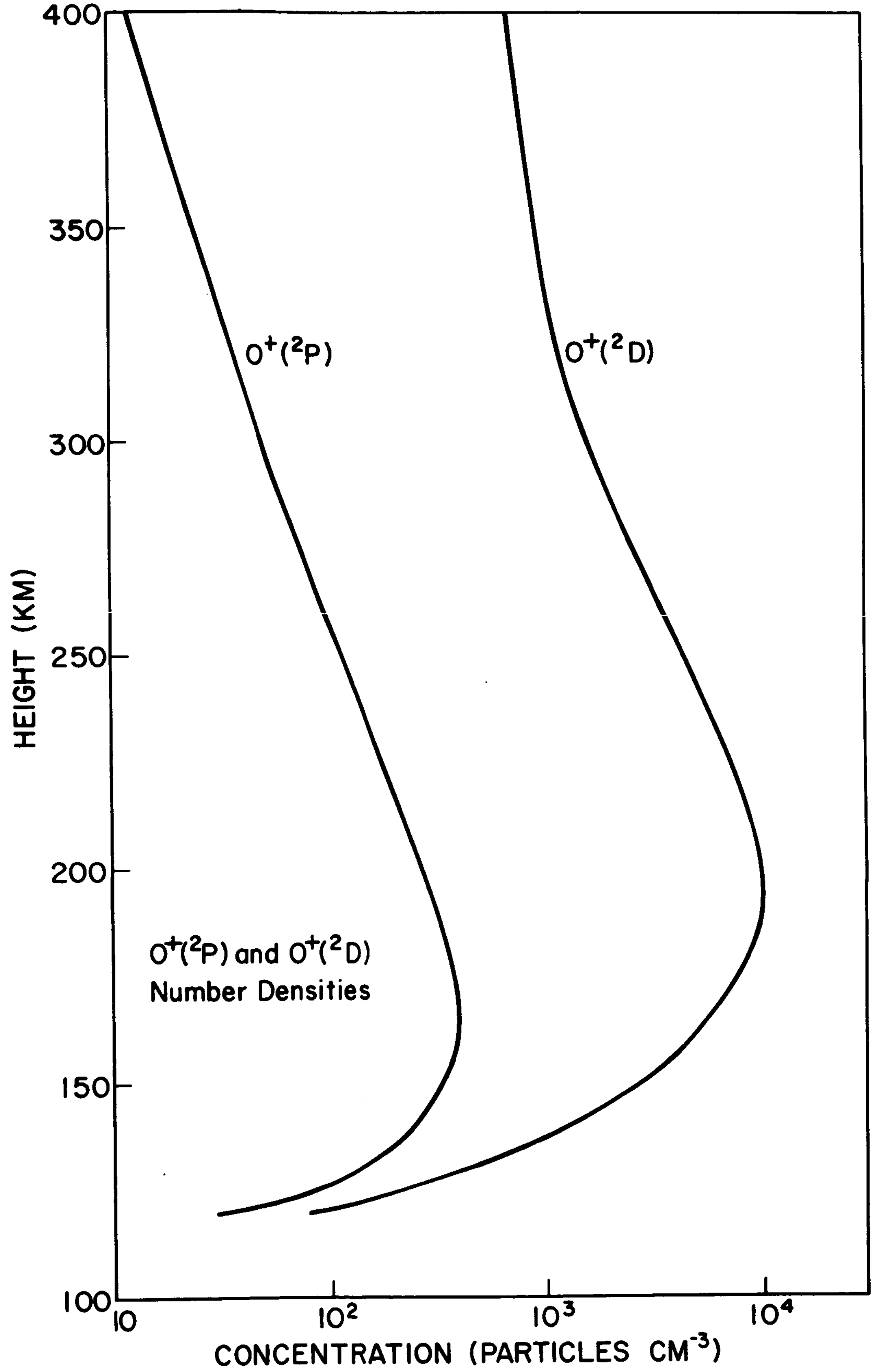

Fig. 3.2 The equilibrium concentrations of $O^+(^2P)$ and $O^+(^2D)$ ion densities as a function of height.

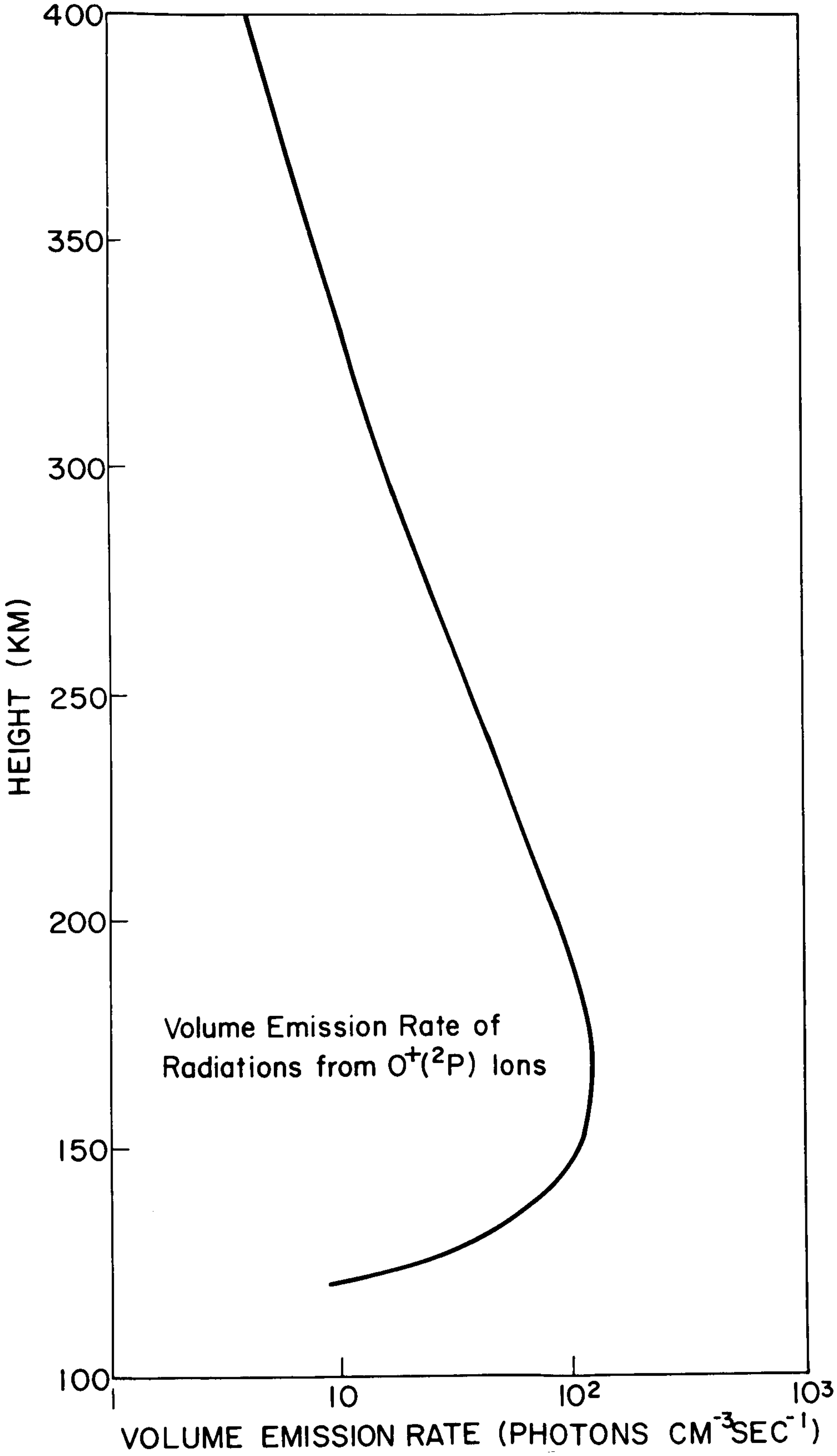

Fig. 3.3 The volume emission rate of $O^+(^2P-^2D)$ multiplet (7319-7330A) with height in the day airglow.