Metastable O⁺ ions in Martian atmosphere

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ABSTRACT. Production rates of atomic oxygen ions in the metastable states (${}^{2}P$ and ${}^{4}D$) by photo-ionization have been calculated. Equilibrium distributions of these species have been calculated using recently measured ratecoefficients of ion-atom interchange and other ionic reactions. Finally, the zenith intensity of the (7318.6-7330A) multiplet of 0+in the dayglow has been calculated and found to be approximately in the range 4.5-8.0 R.

1. Introduction

For the ionospheric chemistry of the Martian atmosphere, metastable ions are of importance as they carry extra energy with them. Because of this extra energy, some reactions may occur which are not possible for the normal states. For instance, $O^+(^2D)$ ions may produce a simple charge exchange reaction $O^+ + CO_2 \rightarrow O + CO_2^+$ which is energetically possible.

In this paper, metastable ions $O^+(^2P)$ and $O^+(^2D)$ in the day-time Martian atmosphere have been computed.

2. Models for the ionosphere of Mars

Three different models, namely, F_2 , F_1 and E analogous to terrestrial ionosphere have been proposed by different investigators for the Martian ionosphere (Chamberlain and McElroy 1966; Donhaue 1966; McElroy 1967; Fjeldbo *et al.* 1968; and McElroy 1969). These models are shown in Figs. 1, 2 and 3 respectively. The density of respective neutral gas constituents are tabulated in Tables 1 to 3.

The critical question is the temperature distribution and photochemistry of CO_2 in Martian atmosphere. The temperature structure for these models are given in Fig. 4. It is evident from this figure that F_2 model requires a cold temperature profile which is not at all close to radiative balance and this cold profile is also not consistent with the measured amount of water vapour (Goody 1968). Further, the F_2 model gives no appreciable differences between temperature of electrons, ions and neutrals at this level, whereas detailed calculations and experience with earth's ionosphere suggest that pronounced differences should indeed exist. Because of these limitations, it is doubtful to follow the F_2 model of the Martian ionosphere.

The possibility of an F₁ layer is also ruled out

because the number density required at 125 km are inconsistent with McElroy's (1967) radiativediffusive equilibrium calculations by a quite wide margin.

Existence of an E layer seems to be favourable as it would not require a low temperature profile. But all E region theories encounter particular difficulties. If E layer does exist, the dissociative recombination of CO_2^+ must have a rate coefficient of 10^{-5} which is very high and a laboratory investigation is clearly indicated.

Thus an appropriate model of the Martian ionosphere is in doubt as yet. So, in the present calculations, we have calculated the equilibrium distributions of $O^+(^2P)$ and $O^+(^2D)$ ions for all the three models mentioned above.

3. Froduction rates

The photo-ionization reactions by which the metastable $O^+(^2P)$ and $O^+(^2D)$ ions may be produced are —

$$O(^{3}P) + P \ (\lambda \leq 663 \text{ A}) \rightarrow O^{+}(^{2}P) + e \quad (1)$$

$$O(^{3}P) + P (\lambda \leq 732 \text{ A}) \rightarrow O^{+}(^{2}D) + e$$
 (2)

At an altitude z, the rate of production of the ions due to photo-ionization is given by-

$$q(0)_{\lambda_z} = \gamma_\lambda \ n(P)_{\lambda_z} \ n(0)_z \tag{3}$$

where,

- $\gamma_{\lambda} = \text{photo-ionization cross-section of O at}$ the wavelength λ ,
- $n(P)_{\lambda_z}$ = photon flux density for the wavelength λ at the altitude z and

 $n(0)_z$ = concentration of 0 atoms at altitude z.

The productin rate of these ions for all wavelengths below the threshold is obtained by calculating the $q(O)_{\lambda_2}$ at the small wavelength intervals of the

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TABLE 1

F2 Model of the Martian atmosphere

Altitude	Temperature	[CO2]	[CO]	[0]	
(km)	(°K)	(cm ⁻³)	(cm-3)	⁻³) (cm ⁻³)	
240	395	1890	4.68×10^{7}	$8\cdot 2 imes 10^7$	
230	385	· · · · · · · · · · · · · · · · · · ·	$5.30 imes 10^{7}$	1.2×10^{8}	
220	365		6.60×10^{2}	3.0×10^{8}	
210	350		$8.60 imes 10^{7}$	$7 \cdot 0 imes 10^8$	
200	330		$1 \cdot 10 imes 10^{8}$	$9\cdot8 imes10^8$	
190	300		$1.40 imes 10^{8}$	$1 \cdot 2 \times 10^{9}$	
180	260		$1\cdot70 imes10^8$	2.8×10	
170	220	$3\cdot 0 imes 10^6$	$2\cdot90 imes10^8$	$5.0 imes 10^{4}$	
160	190	$6 \cdot 0 \times 10^{6}$	$3.70 imes 10^{8}$	8.0×10^{10}	
150	150	$1\cdot 2 imes 10^7$	4.80×10^{8}	$1.0 imes 10^{1}$	
140	120	$3 \cdot 2 imes 10^7$	$6 \cdot 20 \times 10^{8}$	$2 \cdot 1 \times 10^{10}$	
130	110	$4 \cdot 1 \times 10^{7}$	$7 \cdot 10 imes 10^{8}$	$3.5 imes 10^{1}$	
120	100	$4 \cdot 4 \times 10^{7}$	1.80×10^{9}	5.0×10^{-3}	
110	100	$2.0 imes 10^{9}$	$4 \cdot 80 \times 10^{9}$	7.2×10^{-10}	
110	92	$3.6 imes 10^{10}$	$1.70 imes 10^{10}$	8.0×10	
90	80	$3 \cdot 2 imes 10^{11}$	$4 \cdot 40 imes 10^{10}$	$9\cdot2 imes10^4$	
80	60	$2 \cdot 1 \times 10^{12}$	$9\cdot 20 imes 10^{10}$	1.0×10^{1}	
70	50	$1\cdot 2 imes 10^{13}$	$4 \cdot 00 \times 10^{11}$	4.0×10^{10}	
60	50	$6.0 imes 10^{13}$			
50	90	$2 \cdot 8 \times 10^{14}$		-	
40	115	$2 \cdot 1 imes 10^{15}$			
30	160	$4 \cdot 8 imes 10^{15}$		the second second	
20	160	$1\cdot 8 imes 10^{16}$		12 - C	
10	160	$5\cdot 8 imes 10^{16}$	and the second second	1	
	160	$1.7 imes 10^{17}$			

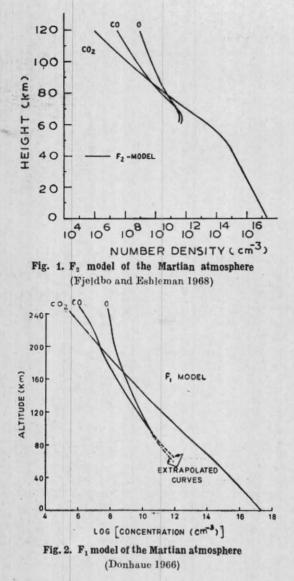
TALBE 2

F, Mcdel of the Martian atmosphere

Altitude	Temperature	[CO ₂]	[CO]	[0]
(km)	(°K)	(cm-3)	(cm ⁻³)	(cm ⁻³)
240	485	$3 \cdot 10 \times 10^{5}$	$2\cdot 80\! imes\!10^6$	9.0×107
230	480	$1\cdot 30 imes 10^{a}$	$6.30 imes 10^{6}$	$1.0 imes 10^{8}$
220	475	$3 \cdot 20 \times 10^{6}$	$-1.00 imes 10^{4}$	$1\cdot 3 imes 10^8$
210	470	$8\cdot90 imes10^6$	$1.60 imes 10^{2}$	$1.6 imes 10^{8}$
200	465	$2.50 imes 10^{7}$	$2\cdot 20 imes 10^7$	$2\cdot0 imes10^8$
190	460	$9\cdot 60 imes 10^7$	$4.00 imes 10^{4}$	$2\cdot8 imes10^8$
180	450	$2\cdot 00 imes 10^8$	$8 \cdot 20 \times 10^{8}$	$4.0 imes 10^{8}$
170	445	$7\cdot 30 imes 10^8$	1.40×10^{8}	6.3×10^{8}
160	420	$1.60 imes 10^{9}$	$2 \cdot 80 imes 10^{8}$	1.0×10^{9}
150	390	$4.60 imes 10^{9}$	$6 \cdot 10 \times 10^{8}$	1.6×10 ⁹
140	350	$1 \cdot 60 imes 10^{10}$	$1.30 imes 10^{9}$	$2 \cdot 9 \times 10^{9}$
130	300	$5.00 imes 10^{10}$	$2.60 imes 10^{9}$	5.0×10 ⁹
120	270	1.70×10^{11}	$6.30 imes 10^9$	8.0×10 ⁹
110	230	$6\cdot 30 imes 10^{11}$	1.40×10^{10}	$1.3 imes 10^{10}$
100	220	$2.00 imes 10^{12}$	$3.00 imes 10^{10}$	$3.0 imes 10^{10}$
90	190	$7.10 imes 10^{12}$	$7.00 imes 10^{10}$	$7 \cdot 0 imes 10^{10}$
80	160	$2.80 imes 10^{13}$	2.00×10^{11}	$2 \cdot 2 \times 10^{11}$
70	150	$1.00 imes 10^{14}$	5.00×10^{11}	4.0×10 ¹¹
60	130	$3.20 imes 10^{14}$		
50	120	1.00×10^{15}	소문 영향을 다 가격하게	10
40	125	$4 \cdot 00 imes 10^{15}$		State of the second
30	130	$1.00 imes 10^{16}$	지수는 전화에 관고 전에 가지 않는다.	· · · · · · · · · · · · · · · · · · ·
20	140	$3 \cdot 20 imes 10^{16}$		
10	150	1.00×10^{17} ·	1 1 1 1 1	
10	160	$2.00 imes 10^{17}$		Section 1. Section 1.

* The number density of (CO] and [O] have been extrapolated after 100 km

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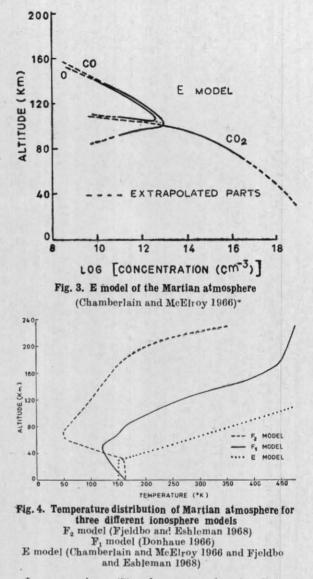
solar spectrum below the threshold and by summing over all the calculated values, *i.e.*,

$$q(\mathbf{O})_z = \Sigma \,\, \boldsymbol{\gamma}_\lambda \,\, n(P)_{\lambda_z} \,\, n(\mathbf{O})_z \tag{4}$$

The photon flux density at an altitude z can be obtained by —

 $n(P)_{\lambda_z} = n(P)_{\lambda_{\infty}} \exp\left[-\Sigma_i n_{iz} H_{iz} \sigma_{i\lambda}\right]$ (5)

- where, $n(P)_{\lambda\infty} =$ photon flux density at the top of the atmosphere at the wavelength λ ,
 - $n_{iz} =$ number density of i^{th} absorbing constituent at the altitude z,
 - $H_{iz} = \text{scale height of } i^{\text{th}} \text{ constituent at}$ the altitude z and
 - $\sigma_{i\lambda} = ext{absorption cross-section for } i^{ ext{th}} ext{ constituent-at the wavelength } \lambda.$



In expression (5), the summation in the exponential is carried out over three main absorbing constituents of the Martian atmosphere, viz., CO₂, CO, O2 and O. The vertical distribution of these constituents were taken from Tables 1 to 3 for different models. O2 profiles were taken from Chamberlain and McElroy's (1965) paper. Absorption cross-sections for CO2 and CO were obtained from tabulations of Sun and Weissler (1957). For O2 and O; the absorption cross-sections were taken from the data of Hinteregger et al. (1965). The photon flux density at different wavelengths were taken from the data of Hinteregger after multiplying each by 0 44, the dilution factor. The photon flux density at the top of the Martian atmosphere and photoionization cross-section of neutral particles used here are given in Table 4 as a function of wavelength band. The calculated rates of production for the two ionic species $O^+(^2P)$

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TABLE 3

E Model of the Martian atmosphere

Altitude (km)	Temperature (°K)	[CO ₂] (cm ⁻³)	[CO] (cm ⁻³)	[O ₂] (cm ⁻³)	[O] (em ⁻³)
120	500	1. <u>1</u> . 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.	$1.0 imes 10^{12}$		4 · 1 × 1012
110	470	8.0×1011	$4 \cdot 2 imes 10^{12}$	$2 \cdot 1 \times 10^{11}$	$4 \cdot 1 \times 10^{12}$
100	430	1.8×10^{13}	$2 \cdot 0 imes 10^{13}$	1.0×1012	8.1×10 ¹¹
90	390	$7 \cdot 0 imes 10^{14}$	1.0×10^{13}	8 · 0 × 10 ¹¹	$5 \cdot 3 imes 10^{10}$
80	350	1.0×10^{15}	$7\cdot0 imes10^{12}$	$6.5 imes 10^{10}$	$3\cdot2\! imes\!10^9$
70	310	$4 \cdot 0 \times 10^{15}$	$3 \cdot 1 \times 10^{12}$	$2\cdot 1 imes 10^8$	$1\cdot 6 imes 10^8$
60	270	$7\cdot0 imes10^{15}$	6.2×10^{11}	1 · 0 × 10 ⁶	$5\cdot7 imes10^7$
50	230	$8.5 imes 10^{15}$			72 ····
40	190	1.0×10^{16}			- · · ·
30	150	$3.5 imes 10^{16}$		The state of the state	alesta -
20	150	$5 \cdot 1 \times 10^{16}$		and - the	1. State -
10	150	8·3×1016			-
0	150	1.4×1017		23 ·	

TABLE 4

Photon flux density at the top of the Martian atmosphere and photo-ionization cross-section of CO_2 , CO_2 , O_2 and O at different wavelength bands

			Photo-ionization c	ross-section for	
Wavelength Band $(\lambda \pm 25 A^\circ)$	Photon flux density at the top of the Martian atmosphere	O ₂ (cm ²)	0 (cm ²)	CO (cm ²)	CO ₂ (cm ²)
(F	hontons cm ⁻² sec ⁻¹ (50A°			A STATE OF A	1.00
50A	$0.00456 imes 10^{10}$	0.165×10^{-18}	0.22×10^{-18}	2·1 ×10-19	$3 \cdot 2 \times 10^{-1}$
100A	$0.0152 imes 10^{10}$	0.66×10^{-18}	$0.65 imes 10^{-18}$	7.5 ×10-19	1.8×10^{-1}
150A	0.0269 ×1010	2.60×10^{-18}	1·1 ×10-18	$1.15 imes 10^{-18}$	$4 \cdot 2 \times 10^{-1}$
200A	0.0556×10^{10}	6.82 ×10-18	3·2 ×10-18	$2.61 imes 10^{-18}$	1-9×10-4
250A	0.0724×10^{10}	10.5 ×10.18	5.7 ×10.18	3.6 ×10-18	2.6×10^{-3}
300A	0.0465×10^{10}	15.7 ×10.18	8·1 ×10-18	5.0 ×10.18	1.5×10-
350A	0.0189×10^{10}	20·3 ×10-18	8.7 ×10.18	1.0 ×10-17	$2 \cdot 6 \times 10$
400A	0.0216 ×10 ¹⁰	22.5×10^{-18}	10.8 ×10.18	1.5 ×10.17	$2 \cdot 2 \times 10$ -
450A	0.0243 ×1010	24·1 ×10-18	11.1 ×10.18	2.0 ×10-17	$2 \cdot 4 \times 10$ -
500A	0.0303 ×1010	26.5 ×10-18	12.9 ×10.18	1.9 ×10-17	2.7×10-
550A	0.0357 ×1010	26.5 ×10-18	13.0 ×10.18	1.9 ×10-17	$2 \cdot 9 \times 10$
600A	0.0390×10^{10}	27.6 ×10.18	13.0 ×10-18	$1.8 imes 10^{-17}$	3.0×10^{-1}
650A	0.0422 ×10 ¹⁰	31.6 ×10-18	11.8 ×10-18	1.7 ×10-17	$2 \cdot 2 \times 10$ -
700A	0.0456×10^{10}	$26 \cdot 2 \times 10^{-18}$	8.6 ×10-18	1.6 ×10-17	1.8×10-
750A	0.0487 ×10 ¹⁰	21.4 ×10-18	5.6 ×10-18	1.3 ×10.17	3.0×10-
800A	0.0693 ×10 ¹⁰	12.9 ×10.18	3.3 ×10.18	1.6 ×10.17	1.5×10-
800A 850A	0.0033×10^{10} 0.276×10^{10}	8·2 ×10-18	3.2 ×10-18	1.8 ×10.17	$1\cdot 1 \times 10$
900A	0.326 ×10 ¹⁰	5.6 ×10-18	3.1 ×10.18	$2\cdot 3 \times 10^{-17}$	5.0×10-
	0.0969 ×10 ¹⁰	3.4×10^{-18}	0.56×10^{-18}	1.3 × 10-16	6.6×10-
950A 1000A	0.0369 ×10 ¹⁰	1.9×10^{-18}	0.00×10-18	2.8 × 10.17	3.4×10-

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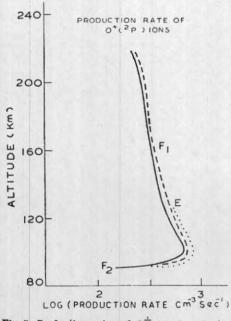


Fig. 5. Production rates of $O^+(^2P)$ ions in the Martian atmosphere

and $O^+(^2D)$ are shown in Figs. 5 and 6 respectively. These figures show that the maximum rates of poduction for both the species occur at about 100 km.

4. Equilibrium concentrations

4.1. $O^+(^2P)$ ions — These ions are produced, as mentioned before, by the photo-ionization and also by the spontaneous transitions from excited states of O^+ ions, which are produced when inner electrons are knocked out (Dalgarno *et al.* 1963). However, the later ones can be neglected because of its small cross-sections. $O^+(^2P)$ ions undergo spontaneous transitions to 2D and 4S states by —

$$O^{+}(^{2}P) \xrightarrow{A_{6}} O^{+}(^{2}D) + P (\lambda 7330 \text{ A})$$
(6)

$$O^{+}(^{2}D) \xrightarrow{A_{7}} O^{+}(^{4}S) + P(\lambda \ 2440 \ \text{A})$$
(7)

The transition probability A_6 and A_7 are 0.318/sec and 0.080/sec respectively (Nicholls 1964). These can be de-excited by super-elastic collisions with electrons, *i.e.*,

$$O^+(^{2}P) + e \xrightarrow{k_8} O^+(^{2}D) + e \tag{8}$$

$$O^+(^2D) + e \xrightarrow{\mu_0} O^+(^4S) + e \tag{9}$$

The rate coefficients k_8 and k_9 are 1×10^{-7} cm³ sec⁻¹ and 2×10^{-8} cm³ sec⁻¹ respectively (Seaton and Osterback 1957). Also, these ions

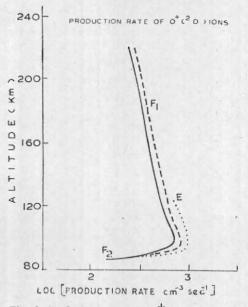


Fig. 6. Production rates of $O^+(^2D)$ ions in the Martian atmosphere

will undergo ion-atom interchange with atmospheric molecules, namely,

$$0^+ + 0_2 \xrightarrow{k_{10}} 0_2^+ + 0$$
 (10)

$$\mathbf{O}^{+} + \mathbf{CO}_2 \xrightarrow{k_{11}} \mathbf{O} + \mathbf{CO}_2^{+} \tag{11}$$

Loss of O+ ions also occurs through the radiative recombination

$$0^+ + e \xrightarrow{k_{13}} 0 + P \tag{12}$$

However, it may be neglected because, $k_{12} = 4 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ (Biondi 1964) and electron concentrations over whole of the ionospheric altitudes are small, for it will be an effective loss mechanism.

Hence, if q_1 (O⁺) denotes the rate of production of O⁺(²P) due to photo-ionization and n_1 (O⁺) its equilibrium concentrations, we have at the equilibrium

$$n_{1}(O^{+}) = \frac{q_{1}(O^{+})}{(A_{6}+A_{7}) + (k_{8}+k_{9})n(e) + k_{10} n(O_{2}) + k_{11} n(CO_{2})}$$
(13)

4.2. $O^+(^2D)$ ions — These ions may be produced by reaction (2), by spontaneous transition (reaction 6) or by super-elastic collision (reaction 8) from 2P states.

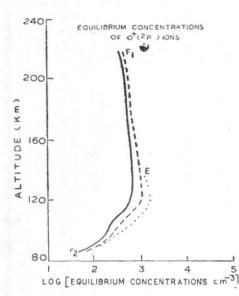


Fig. 7. Equilibrium concentrations of $O+(^{2}P)$ ions

They are lost to the ground state by super-elastic collisions

$$O^{+}(^{2}D) + e \xrightarrow{\kappa_{14}} O^{+}(^{4}S) + e \qquad (14)$$

(Dalgarno et al. 1963), whose rate-coefficient is 3×10^{-8} cm³ sec⁻¹ (Seaton and Osterback 1957) and also through the ion-atom interchange reactions (10) and (11). The loss of $O^+(^2D)$ through spontaneous transitions to the 4S state is negligible since the corresponding transition probability is 1.7×10^{-5} sec⁻¹ (Nicholls 1964).

Hence, if $q_2(O^+)$ denotes the rate of production of $O^+(^2D)$ by photo-ionization and $n_2(O^+)$ its equilibrium concentration, then at equilibrium,

$$n_{2}(O^{+}) = \frac{q_{2}(O^{+}) + A_{6} n_{1}(O^{+})n(e) + k_{8} n_{1}(O^{+}) n(e)}{k_{14} n(e) + k_{10} n(O_{2}) + k_{11} n(CO_{2})}$$
(15)

5. Radiation from $O^+(^2P)$

 $O^+(^2P)$ ions undergo spontaneous transitions to 2D state (reaction 6) radiating the multiplet (7318.6 -7330.7 A), for which the transition probability is equal to $0.318 \sec^{-1}$. Hence, the volume emission at any altitude z is given by ---

$$R_z = n_1(0^+) \times 0.318 \tag{16}$$

The integrated intensity of this radiation is calculated in the following way. The altitude region under consideration is divided into thin layers such that the emission rate in each of them is approximately constant. Intensity from each

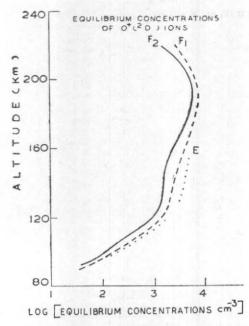


Fig. 8. Equilibrium concentrations of $O+(^{2}D)$ ions

layer is obtained by multiplying mean R_z with the layer thickeness. Summation over all the layers gives the integrated intensity.

6. Results and discussions

Swider (1965) has shown that if $k_{10} = 3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ for night time earth's atmosphere are assumed, results in agreement with the ionospheric composition determined by rocket-borne spectrometers are obtained. Recently, Ferguson *et al.* (1965) showed that for ions in the ground state $k_{10} = 4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K. Ionospheric calculations indicate that these coefficients are temperture dependent. According to Ghosh (1967), k_{10} should be taken as—

$$k_{10} = 8 \times 10^{-12} (1200/T)^{1/2} \text{ cm}^3 \text{ sec}^{-1}$$
 (17)

where, T is the absolute temperature appropriate to the altitude under consideration.

For k_{11} , Norton *et al.* (1966) found it equal to $1 \cdot 2 \pm 0 \cdot 4 \times 10^{-9}$ cm³ sec⁻¹ at $T = 300^{\circ}$ K. As, no other value of k_{11} are available its temperature study could not be done.

Using Eq (17) and $k_{11} = 1 \cdot 2 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ the equilibrium concentrations of $O^+(^2P)$ and $O^+(^2D)$ ions have been calculated and are shown in Figs. 7 and 8 respectively as a function of altitude.

From relation (16), the integrated intensity R for the transition from $O^+(^2P)$ and $O^+(^2D)$ states is calculated and is tabulated in Table 5. From

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REFERENCES

	TABLE 5	
Intensity o	f the radiation from O	+(°P) to 0+ (°D)

F ₂ Model	F ₁ Model	E Model	
(Rayleighs)	(Rayleighs)	(Rayleighs)	
4.60	5.20	7.58	

For E model, the intensity R has been calculated from 120 km-0 km altitude because it is difficult to extrapolate the The production rate in F_3 and F_1 model, the intensity (R) for 240-120 km has been assumed and thus total intensity has been found.

this table, it is evident that the intensity for this radiation lies within the limit 4.6 -8.0 Rayleighs.

Experimental measurements of this radiation have not been carried out till now. Therefore, it is suggested that the temperature dependence of reaction (11) should be carried out and the experimental measurements of R to be done because the experimental observations on this radiation would help in constructing a better theoretical model.

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