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## EXCITATION OF THE AURORAL GREEN LINE BY DISSOCIATIVE RECOMBINATION OF O<sub>2</sub><sup>+</sup>: ANALYSIS OF TWO ROCKET EXPERIMENTS

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ABSTRACT

Analysis from photometric and electron flux data obtained during two sounding rocket auroral experiments has yielded volume emission rates for the  $N_2^+(0-0)$  First Negative Band and the  $OI(^1S - ^1D)$  green line among other emission features. It is shown that excitation of the green line by electrons would require a cross section an order of magnitude larger than expected. From a calculation of the  $O_2^+$  production rate it is shown that dissociative recombination can account for the entire green line emission if one fifth of all  $O_2^+$  recombinations excite the  $^1S$  state. This is the laboratory measured value. Analysis also shows that this mechanism can describe the relative variation of  $\lambda 3914$  and  $\lambda 5577$  in time varying auroras.

## 1. INTRODUCTION

The purpose of this note is to report some evidence we have obtained from rocket experiments that the auroral green line  $\text{OI}(^1\text{S} \rightarrow ^1\text{D})$  [ $\lambda 5577 \text{ \AA}$ ] is produced predominantly as a result of the dissociative recombination of  $\text{O}_2^+$  ions. The evidence to be discussed was obtained on two of a series of rocket flights into auroras above Ft. Churchill, Canada. During these flights data were obtained giving the variation of the brightness of selected lines and bands of  $\text{N}_2$ ,  $\text{N}_2^+$ ,  $\text{O}_2^+$ ,  $\text{O}$  and  $\text{H}$  as the rockets traversed the auroras. Measurements of the flux and energy spectra of auroral electrons were also obtained. Only the results bearing most directly on the problem of the mechanism responsible for the excitation of the green line will be discussed here. We shall reserve to a later detailed paper the analysis of data relating to the processes that lead to excitation of other spectral features of these auroras.

## 2. EXPERIMENTS AND RESULTS

On February 19, 1966 at 23<sup>h</sup>, 30<sup>m</sup> local time Aerobee UA 4.162 was launched from Ft. Churchill into the post breakup phase of a Class II<sup>+</sup> Aurora. The rocket carried filter photometers which continuously measured the overhead brightness of  $\lambda 5577$  [ $\text{OI}(^1\text{S} \rightarrow ^1\text{D})$ ] and  $\lambda 3914$  [ $\text{N}_2^+(\text{B}^2\Sigma_u^+ \rightarrow \text{X}\Sigma_g^{2+})$ ]. It was also equipped with a filter wheel photometer to observe three OI lines at 6300  $\text{\AA}$ , 7774  $\text{\AA}$  and 8446  $\text{\AA}$  as well as two  $\text{N}_2$  LPG bands at 6685  $\text{\AA}$  and 6765  $\text{\AA}$ . Electron spectrometers yielded information concerning the flux of electrons with energy above 100 eV (Doering, 1967).

From the variation of zenith brightness with altitude the rate of emission per unit volume of the lines and bands observed were obtained by differentiation. The resulting rates for the downleg are plotted in Fig. 1. Almost identical results were obtained during ascent even for the details in the structure. The profile of the emission rate of  $\lambda 6765 \text{ \AA} \text{ N}_2^{\circ}$  first positive band is typical for the  $\text{N}_2$  bands and the OI lines at  $7774 \text{ \AA}$  and  $8446 \text{ \AA}$ . The electron flux varied smoothly throughout this portion of the flight. At other times during the flight changes in column emission rates were clearly correlated with changes in electron flux. Because of the appearance of the same bimodal structure in  $\text{N}_2^+$  and  $\lambda 5577$  emission at almost identical altitudes during rocket ascent and descent, because the other emission features have quite another, but common, variation with rocket altitude and because no anomalies were noted in the electron flux we consider the aurora to have been reasonably stable in time during rocket traversal of the 100-130 km region. The observed brightness variations may thus be regarded as spatial, and differentiation with respect to rocket altitude gives the true gradients or volume emission rates.

Aerobee 4.163 was launched February 16, 1967 at  $22^{\text{h}}, 18^{\text{m}}$  local time. The aurora it penetrated was a diffuse glow which changed in brightness several times during the flight. The rocket carried a filter wheel photometer designed to isolate the  $5577 \text{ \AA} \text{ O}^{\circ}$  line, the  $3914 \text{ \AA} \text{ N}_2^{\circ}$  band, a first positive band of  $\text{N}_2$  and two bands of the first negative system of  $\text{O}_2^+$ . It was equipped with electron spectrometers designed to measure the spectrum, the total flux of electrons with energies above 2.0 eV and the

fast, primary flux above 5 keV. On board also was an "up-down photometer" which alternately observed above and below the rocket the brightness of the  $2972 \text{ \AA}$  line ( $^1S \rightarrow ^3P$ ) of atomic oxygen [along with the (2,0) (3,1) and (4,2) second positive bands of  $N_2$ ].

The volume emission rates for the green line and (0-0) first negative band obtained during this flight are plotted in Figs. 2 and 3. With the help of the up-down photometer a small fluctuation observed between 115 km and 125 km during ascent has been removed. During the descent the up-down photometer verified the steadiness of excitation conditions in time down to 105 km where a rapid decrease in the overall excitation rates occurred. The total electron flux  $\Phi_T$  is also plotted in Figs. 2 and 3 as a function of altitude.

It is apparent from the figures that the well known covariability of  $\lambda 5577$  and  $\lambda 3914$  is preserved at all altitudes. This is particularly striking in flight 4.162 where the altitude distribution of excitation for the  $N_2$  first positive bands and the other OI lines was remarkably different from that of the green line and the (0-0)  $N_2^+$  band. This difference between the excitation probability of the (0-0) band on the one hand and the LPG bands and infrared OI lines on the other is ascribable to changes in the electron spectrum and the more rapid variation with energy of the cross sections for excitation of the  $N_2$  and OI levels involved. It is difficult to avoid the conclusion that excitation of the  $5577 \text{ \AA}$  line must involve the same sort of cross section as that of the  $3914 \text{ \AA}$  band both in threshold and energy dependence.

A model atmosphere has been assumed (Table 1) and the efficiencies of excitation for the emission features observed have been calculated as functions of altitude from the relationship

$$P_i = Q_i/n_i \quad (1)$$

where  $Q_i$  is the volume emission rate and  $n_i$  the density of the appropriate atmospheric constituent. The efficiencies calculated for flight 4.162 are plotted in Fig. 4. From the residual overhead brightness at 150 km and the column abundance of constituents in the model the efficiencies for the entire atmosphere above 150 km were also computed and marked on the figure. It is to be noted that the probability of excitation of the 5577 Å line per atom of atomic oxygen is a factor of about 6 higher than that of exciting the 3914 band per nitrogen molecule. The efficiency for 5577 related to  $O_2$  is about five times as large at 110 km as the 3914 efficiency, ten times as large at 130 km, and twenty times above 150 km.

During the 4.163 flight we have access to the total flux of electrons  $\phi_T$  ( $E > 2$  ev). With the help of the values for this flux an average cross section for excitation may be computed from the relationship

$$Q_i = \bar{\sigma}_i \phi_T n_i \quad (2)$$

or

$$\bar{\sigma}_i = P_i/\phi_T \quad (3)$$

These cross sections are plotted in Fig. 5. The average cross section for excitation of  $\lambda 3914$  ranges between 1 and  $5 \times 10^{-18} \text{ cm}^2$  which is certainly very reasonable. Cross sections for other emission features similarly computed also seem quite normal except those for exciting the  $5577 \text{ \AA}$  line by electron impact on atomic or molecular oxygen. The cross section related to atomic oxygen which is computed to be between 1 and  $3 \times 10^{-17} \text{ cm}^2$  is a full order of magnitude too large to accord with Seaton's (1956) calculated values. For  $\text{O}_2$  the cross section is reasonable at low altitude only if the average cross section for dissociative excitation of the  $\text{O}(^1\text{S})$  state from  $\text{O}_2$  is about equal to the total ionization cross section of  $\text{O}_2$ . But, above 150 km the effective cross section for this process of  $10^{-16} \text{ cm}^2$  seems much too high.

### 3. EXCITATION RATE OF $\text{O}(^1\text{S}_0)$ BY $\text{O}_2^+$ RECOMBINATION

The foregoing results allocate less than 10% of auroral green line excitation to electron impact on atomic oxygen. While not clearly ruling out dissociative excitation of  $\text{O}_2$  by electrons as a major source they render it very unlikely in view of the large cross section required and the strange increase in this effective cross section with altitude relative to that for  $\lambda 3914$  excitation. (The ratio varies from 5 at low altitudes to 25 near 140 km and to 125 above 150 km). The data suggest that green line excitation like  $\lambda 3914$  excitation is closely related to ionization. The process suggested is formation of  $\text{O}_2^+$  by electron impact on  $\text{O}_2$  and by charge transfer from  $\text{N}_2^+$  and  $\text{O}^+$  followed by dissociative recombination of  $\text{O}_2^+$  and an electron into  $\text{O}(^1\text{S})$  and  $\text{O}(^3\text{P})$  atoms. (Dalgarno



and Khare, 1967). To test the adequacy of this mechanism we have computed the rate of production of  $O_2^+$  as a function of altitude and equated one fifth of this rate to the rate of excitation of the ( $^1S$ ) state of atomic oxygen. The branching ratio used is that recently measured in the laboratory by Zipf (1967) who has found that one fifth of all  $O_2^+$  recombinations result in production of a  $^1S$  atom.

The procedure followed in the calculation was to multiply the  $\lambda_{3914}$  emission rate by 14 to obtain  $Q_2$ , the rate of ionization of ionization of  $N_2$ . The rates of ionization of oxygen and  $O_2$  by electrons were assumed to be given by

$$Q_1 = Q_2(n_1/n_2) \quad (4)$$

and

$$Q_3 = Q_2(n_3/n_2) \quad (5)$$

Where  $n_1$ ,  $n_2$ , and  $n_3$  are the  $O$ ,  $N_2$ , and  $O_2$  densities respectively. Of the  $O^+$  ions produced at a rate  $Q_1$  a fraction is converted to  $O_2^+$  by charge transfer with a rate constant  $k_b = 2 \times 10^{-11} \text{ cm}^3/\text{sec}$  while the rest are changed to  $NO^+$  as a result of ion-atom exchange with  $N_2$  with a rate constant  $k_c$  of  $1.8 \times 10^{-12} \text{ cm}^3/\text{sec}$ . The contribution of charge transfer between  $O^+$  and  $O_2$  to the  $O_2^+$  production rate is given by

$$Q_1 \frac{k_b n_3}{k_b n_3 + k_c n_2} = Q_1 [1 + (k_c n_2 / k_b n_3)] \quad (6)$$

(Note that the ratio of the reaction rates and densities rather than absolute values are involved in determining this fraction of  $Q_1$ ). Similarly  $N_2^+$  is rapidly converted into  $O_2^+$  and  $O^+$  by charge transfer with  $O_2$  and ion-atom interchange with  $O$  with rate constants  $k_a$  and  $k_d$  respectively 1 and  $2.5 \times 10^{-10}$   $\text{cm}^3/\text{sec}$ . (Dissociative recombination of  $N_2^+$  is a negligible source of loss. The rates of production calculated in this way for a few selected altitudes in flight 4.162 are given in Table II.

Comparison of the rates of  $^1S$  excitation calculated in this way with the rates of  $\lambda 5577$  emission observed is afforded on the curves of Fig. 1, 2, and 3. At the very lowest altitudes it is necessary to take into account quenching of the  $^1S$  state by  $O_2$  to relate the excitation rate to the emission rate. Use of a rate coefficient of  $2.1 \times 10^{-13}$   $\text{cm}^3/\text{sec}$  (Zipf, 1967) for this deexcitation process leads to a reduction factor of 0.65 at 100 km, 0.81 at 105 km, 0.92 at 110 km and 0.98 at 115 km for converting  $^1S$  excitation to  $\lambda 5577$  emission rates. We do not consider the small divergences near the top and bottom of the layers significant because of the difficulty in determining the slopes of poorly defined curves for column emission rate there.

A similar calculation can be performed relating the residual high altitude  $\lambda 3914$  column emission rates to column production rates of  $N_2^+$ , thence to  $O_2^+$  and  $\lambda 5577$  column emission rates. The predicted overhead brightness at 130 km on ascent (4.163) is 3.0 kR to be compared with 2 kR observed, and at 150 km on descent (4.163) is 2.1 kR compared with 1.2 kR observed. It is to be noticed that the emission rate of  $\lambda 5577$  relative to that of  $\lambda 3914$  should increase slowly with altitude

according to this oversimplified model of ion production, transformation and loss. This is because ionization of O becomes more important relative to that of N<sub>2</sub> and the ratio of rate coefficients  $k_c/k_c$  is 25 times as large as the ratio  $k_a/k_d$ . Thus charge transfer creation of O<sub>2</sub><sup>+</sup> from O<sup>+</sup> more than compensates for the decrease in direct O<sub>2</sub><sup>+</sup> production relative to N<sub>2</sub><sup>+</sup>. At 200 km in the model used the O<sub>2</sub><sup>+</sup> production by charge transfer is 1.33 times the direct N<sub>2</sub><sup>+</sup> production whereas it is only 0.3 times as large at 120 km. The predicted λ5577 volume emission rate is about 4.8 times the λ3914 rate at 200 km compared to 2.5 times at 120 km. However, there are many probable processes neglected in this calculation. Diffusive loss rates which may become competitive with production rates above 150 km are neglected. It is also assumed that the ratio of the rate coefficients for the O<sup>+</sup> loss reactions remains constant. If the N<sub>2</sub> vibrational temperature increases with altitude this will not be correct and the fraction of the O<sup>+</sup> produced which reacts with N<sub>2</sub> to form NO<sup>+</sup> may increase with altitude. The failure of a pronounced F<sub>2</sub> layer to develop during auroras indicates this may well be the case. So our estimates of the O<sub>2</sub><sup>+</sup> production rates may be considerably too high at high altitude. To the extent that ion diffusion and vibrational excitation of N<sub>2</sub> are important between 100 and 130 km these estimates are also excessive.

In following the method of calculation used here it is not necessary to compute electron densities and O<sub>2</sub><sup>+</sup> densities nor to use absolute values for the recombination coefficient. Recombination rates - and hence 'S production rates - are directly related to ion production rates. If standard values for recombination rate coefficients are assumed

the ion and electron densities can of course be computed by the methods employed in ionospheric analysis. The predicted profiles of ions and electrons for the 4.162 flight are shown in Fig. 7. The electron densities computed agree in profile quite well with these which have been observed in auroras. So does the correlation between  $n(e)$  and  $\lambda 3914$  brightness.

#### 4. PHASE DIFFERENCE BETWEEN $\lambda 5577$ AND $\lambda 3914$

It has sometimes been argued that phase lags between  $\lambda 5577$  and  $\lambda 3914$  emission measured during fluctuating auroras exclude dissociative recombination as a major source of green line excitation (Omholt, 1967). This does not seem to us to be evident from published data. We have compared the variation of  $\lambda 5577$  brightness and  $\lambda 3914$  brightness given by Evans and Vallance-Jones (1965) with that to be expected on the basis of a recombination mechanism. We find it possible to understand these observations in terms of combined time delays caused by a dissociative type decay of the source of  $0(\frac{1}{2}S)$  and a 0.75 sec lifetime of the  $\frac{1}{2}S$  state. On the other hand it does not seem to us that those data can in fact be fully understood in terms of prompt excitation of the  $\frac{1}{2}S$  state simultaneously with the 1st negative band and exponential decay with the lifetime of 0.75 seconds. A sample of the observed data is illustrated in Fig. 8. It is to be noted that the relative amplitude of the  $\lambda 5577$  brightness is considerably smaller than that of  $\lambda 3914$ . This is to be expected for recombination at reasonable rates but not for prompt excitation. The latter should produce essentially only a phase difference between the  $\lambda 3914$  and  $\lambda 5577$  emissions.

In terms of our proposed mechanism the rate of  $^1S$  decay is given by

$$\frac{dn_1^*}{dt} = \alpha' n_3^+ n_e - \frac{n_1^*}{\tau} \quad (7)$$

or

$$\tau \frac{dQ_1}{dt} = \alpha'_3 n_3^+ n_e - Q_1 \quad (8)$$

Where  $Q_1$  is the  $\lambda 5577$  emission rate,  $\alpha'$  the effective recombination coefficient for  $^1S$  excitation and  $\tau$  is the effective lifetime of the  $^1S$  state (taking into account quenching). The  $n_3^+$  ion production rate is tied to  $Q_2$ , the  $\lambda 3914$  emission rate, by a factor  $k$  so that the continuity equation for  $n_3^+$  is

$$\frac{dn_3^+}{dt} = k Q_2 - \alpha_3 n_3^+ n_e \quad (9)$$

For simplicity we shall assume the relationship

$$\alpha_3 n_3^+ n_e = \alpha n_3^{+2} \quad (10)$$

where  $\alpha$  is an effective rate coefficient. This assumption is not too gross according to the indications of Fig. 7 where the density of  $O_2^+$  dominates that of  $NO^+$ . Using this approximation Eq. (9) may be solved numerically for  $n_3^+$  where the condition

$$\alpha n_3^{+2} = k Q_2 \quad (11)$$

gives the value of  $n_3^+$  when  $Q_2$  has a maximum. With the variation of  $n_3^+$  thus obtained, the rate of 'S excitation may be obtained from the solution of Eq. (8) which is

$$Q_1 = Q_{10} e^{-t/\tau} \left[ 1 + \frac{1}{\tau} \int_0^t (n_3^+/n_{30}^+)^2 e^{\frac{t'}{\tau}} dt' \right] \quad (12)$$

If we assume that  $\alpha n_{30}^+$  is 0.2 (corresponding, say to  $\alpha \approx 3 \times 10^{-7}$  cm<sup>3</sup>/sec and  $n_{30}^+ \approx 6 \times 10^5$  cm<sup>-3</sup>) we predict a variation in  $Q_1/Q_{10}$  very close to that observed. The calculated variation is compared with that observed in Fig. 8. It seems therefore that the observed relative variation of  $\lambda 5577$  and  $\lambda 3914$  emission rates accord well with those expected on the basis of the recombination theory when reasonable values are taken for  $\alpha$  and for the average  $O_2^+$  densities.

On the other hand if the <sup>1</sup>S state is excited directly by electron impact either on O or  $O_2$  the continuity equation becomes

$$\frac{d_1}{dt} = k'Q_2 - Q_1/\tau \quad (13)$$

for which the solution is

$$Q_1 = Q_{10} e^{-\frac{t}{\tau}} \left[ 1 + \frac{1}{\tau} \int_0^t e^{\frac{t'}{\tau}} (Q_2/Q_{20}) dt' \right] . \quad (14)$$

For the variation of  $Q_2$  pictured in Fig. 8 and for  $\tau = 0.75$  seconds the predicted variation of  $Q_1$ , as shown, is quite distinctly different in amplitude and detail from that observed. We consider, therefore, that these observations support the dissociation recombination as the excitation

mechanism as opposed to one in which the excitation is in phase with  $Q_2$ .

## 5. CONCLUSIONS

The results reported here and their interpretation indicate that in the auroras studied almost all of the auroral green line results from dissociative recombination of  $O_2^+$ . We believe that not more than ten percent of the integrated  $\lambda 5577$  emission rate can be attributed to direct excitation of atomic oxygen by electrons. We also believe that dissociative excitation of  $O_2$  is a minor source also at most altitudes. This follows because the dissociative mechanism is adequate almost everywhere to account for the observed emission rates and for the temporal behavior of  $\lambda 5577$  and because the required effective cross section for the direct dissociative process must be large and vary with altitude in a way that is difficult to understand. Our results support the proposal of Dalgarno and Khare (1967) that the dissociative recombination mechanism might be important for  $^1S$  excitation. We would modify their suggestion only to propose that it is the dominant mechanism. The difference between their calculated contribution and ours lies mainly in their taking a branching ratio one fourth as large as the one used here for dissociative recombination into the  $^1S$  state. Their calculated  $\lambda 5577$  rates from dissociative recombination would be 50% higher than ours if we were both to take the same branching ratio. It is not possible for us to determine why this is so in the absence of published details of their method of computing ion densities. In any event we believe that the actual contribution to  $^1S$  excitation by electron impact is no more than half as large as the values they have calculated. For a

Class II aurora their calculations suggest that collisional excitation of atomic oxygen produces about 0.4 times as much  $\lambda 5577$  as  $\lambda 3914$  below 140 km. We suggest that it produces 0.2 times as much or less.

Dissociative recombination of  $O_2^+$  as the dominant mechanism for green line excitation has also been advanced by Romick and Belon (1967) as the most natural one to account for their observations of the relative lateral and vertical distribution of  $\lambda 3914$  and  $\lambda 5577$  in auroras. They have not been able to suggest an alternative explanation but have rejected the one based on dissociative recombination on the grounds that it would require an atmosphere too rich in  $O_2$  and that the observations of time lags between  $\lambda 3914$  and  $\lambda 5577$  are not compatible with it. In this paper we believe we have shown that neither of these objections is compelling. We regard the observations of Romick and Belon as strong support for the evidence introduced in this paper in favor of dissociative recombination as the principal mode of auroral green line excitation.



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## FIGURE CAPTIONS

- Fig. 1. Volume emission rates and electron flux  $\phi$  (greater than 0.1 Kev) for downleg in 1966. Circles are the calculated rates for  $\lambda 5577$ . Arrows show correction for quenching.
- Fig. 2. Volume emission rates and total electron flux  $\phi$  (greater than 2eV) for upleg in 1967. Circles are the calculated rates for  $\lambda 5577$ . Arrows show quenching correction.
- Fig. 3. Volume emission rates and total electron flux  $\phi$  (greater than 2eV) for downleg in 1967. Circles are the calculated rates for  $\lambda 5577$ . Arrows show quenching correction.
- Fig. 4. Excitation efficiency during upleg in 1966. Values for the residual emission above 150 km are shown on the right.
- Fig. 5. Effective cross sections for excitation during upleg in 1967. Values for the residual emission above 130 km are shown on the right.
- Fig. 6. Effective cross sections for excitation during downleg in 1967. Values for the residual emission above 140/km are shown on the right.
- Fig. 7. Calculated ion densities for the 1966 flight.
- Fig. 8. Brightness in  $\lambda 3914$  and  $\lambda 5577$  reported by Evans and Vallance-Jones (1965). Circles are  $\lambda 5577$ . Values calculated on the basis of the dissociative recombination mechanism. Crosses are values calculated for the mechanism in which excitation of  $O(^1S)$  is proportional to the  $\lambda 3914$  function and emission decays with a time constant of 0.75 sec.

TABLE II

Production Rates in  $10^4$  per  $\text{cm}^3$  per sec

Altitude	$Q_2$	$Q_3$	$Q_1$	$Q_3'$	$Q_3''$	$\int Q_3$	$[0.2 \int Q_3]$	$Q_{\text{obs}}$
km				$\text{N}_2^+ + \text{O}_2$	$\text{O}^+ + \text{O}_2$			$\lambda 5577$
112	2.5	0.63	0.57	0.77	0.42	1.8	0.36	0.35
120	0.31	0.093	0.12	0.07	0.09	0.25	0.50	0.50
130	0.98	0.27	0.53	0.16	0.39	0.83	0.16	0.15
135	0.17	0.05	0.1	0.02	0.07	0.14	0.04	0.05

TABLE I

Model Atmospheric Densities and Column Densities above 150 km

Altitude km	Densities in particles per cm <sup>3</sup>		
	N <sub>2</sub>	O <sub>2</sub>	O
105	3(12)	8(11)	2.8(11)
110	1.1(12)	2.8(11)	2(11)
120	2(11)	6(10)	8(10)
130	6.5(10)	1.8(10)	3.5(10)
140	3(10)	7.6(9)	2.1(10)
150	1.5(10)	1.5(9)	8(9)
>150	3(16)cm <sup>-2</sup>	2.7(15)cm <sup>-2</sup>	2(16)cm <sup>-2</sup>

## TABLE CAPTIONS

Table I. Model Atmospheric Densities and Column Densities above  
150 km.

Table II. Ion Production Rates and  $\lambda 5577$  emission rates during the  
1966 experiment.

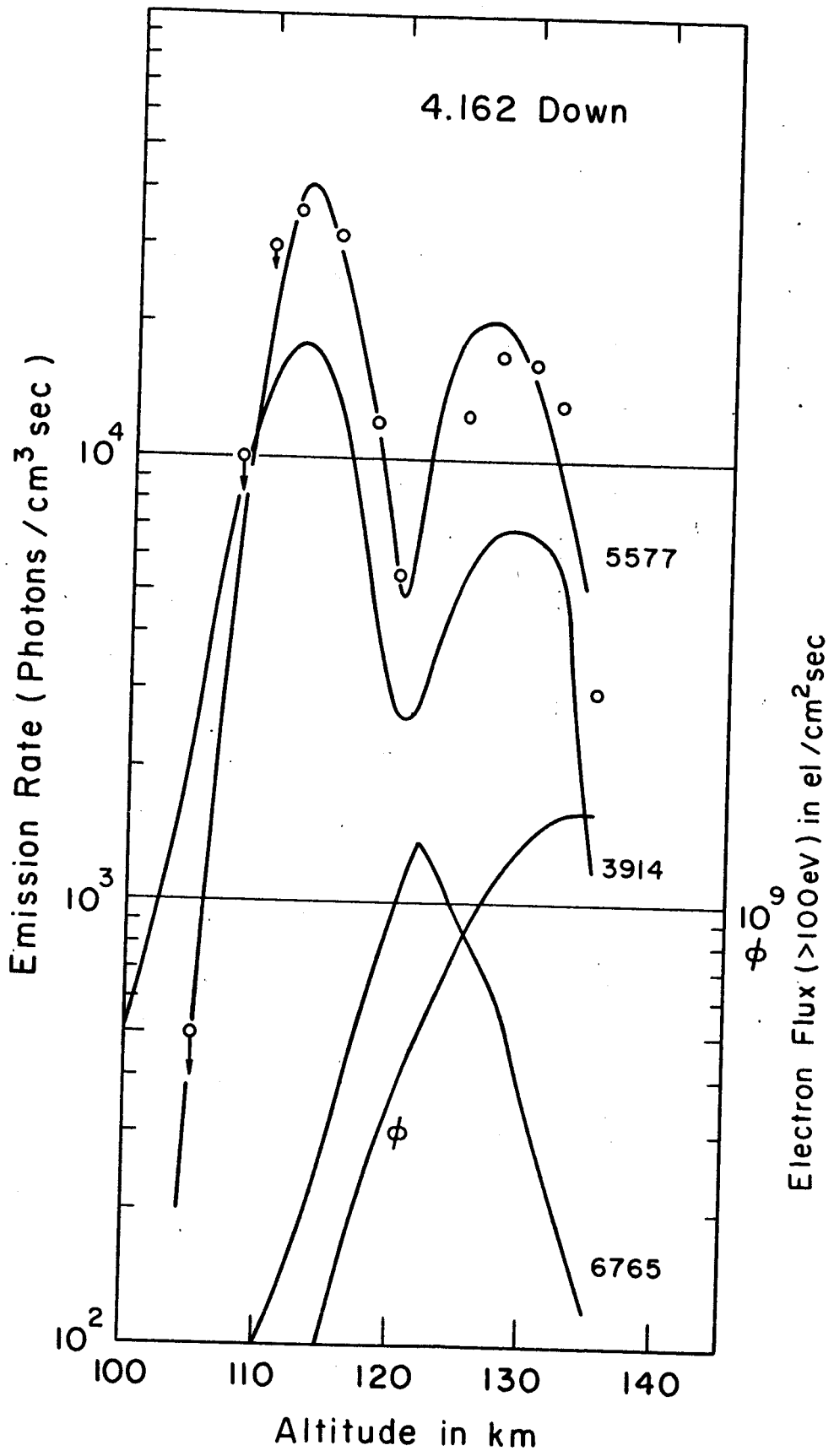


Fig. 1

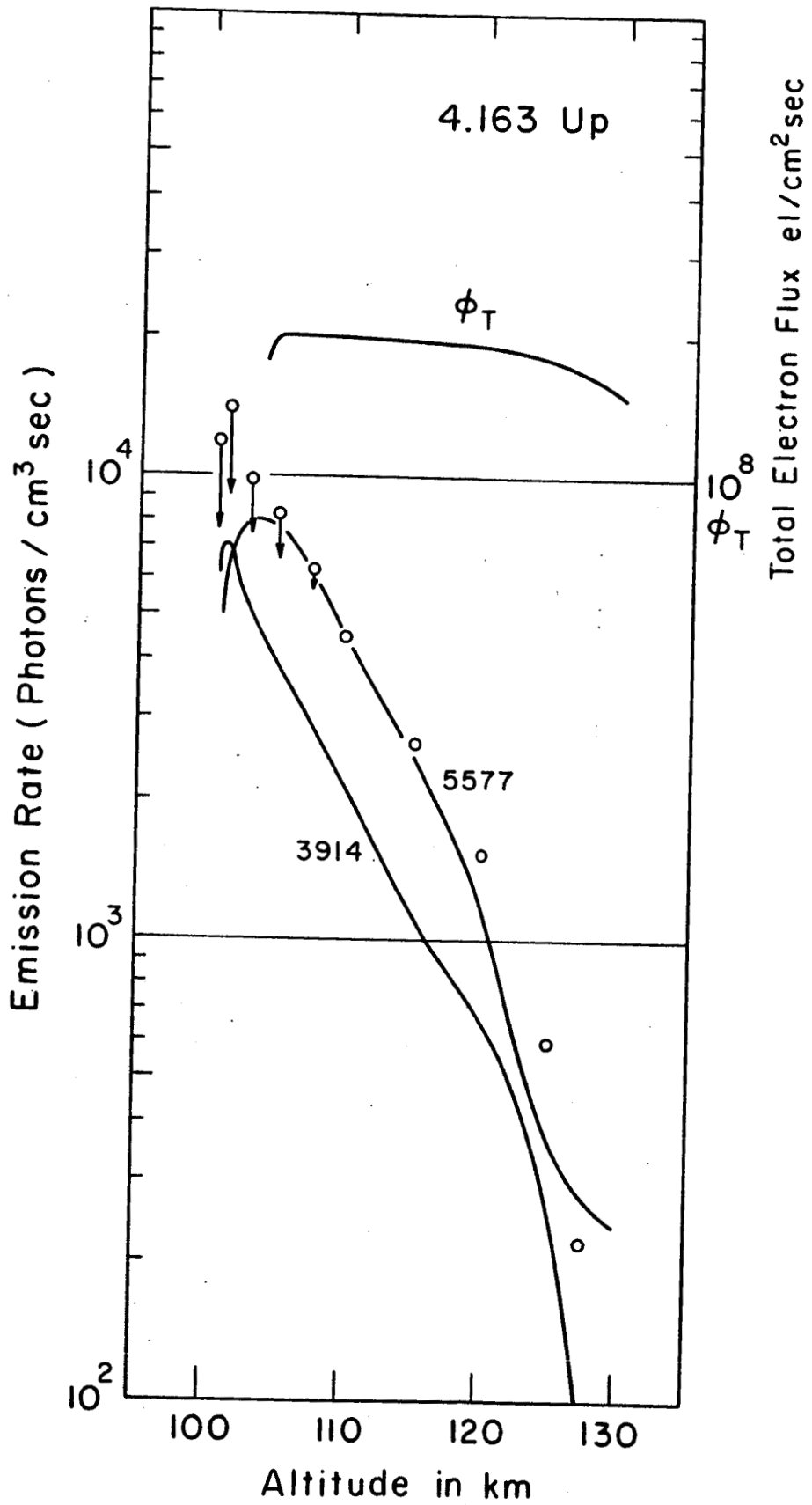


Fig. 2



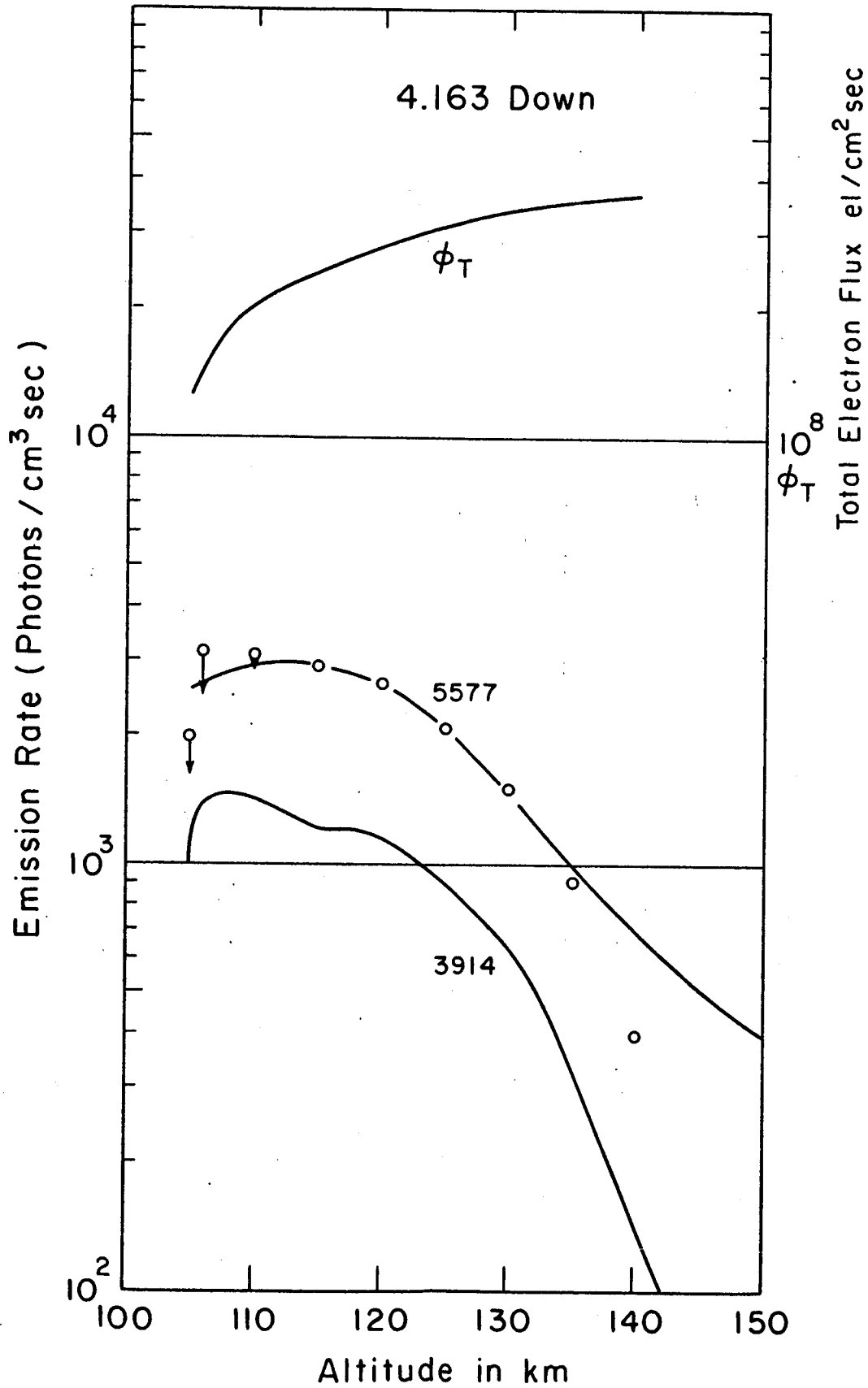


Fig. 3

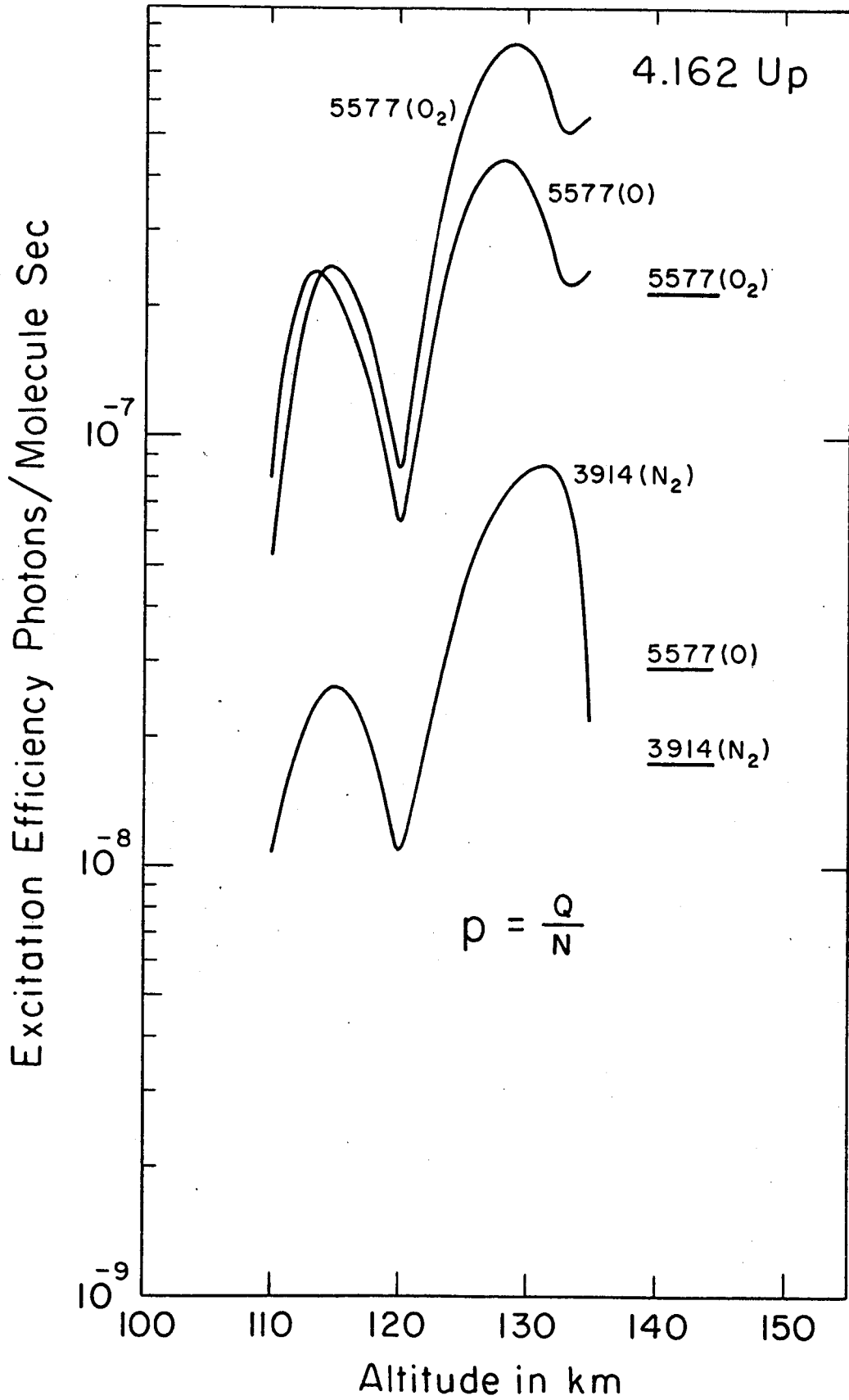


Fig. 4

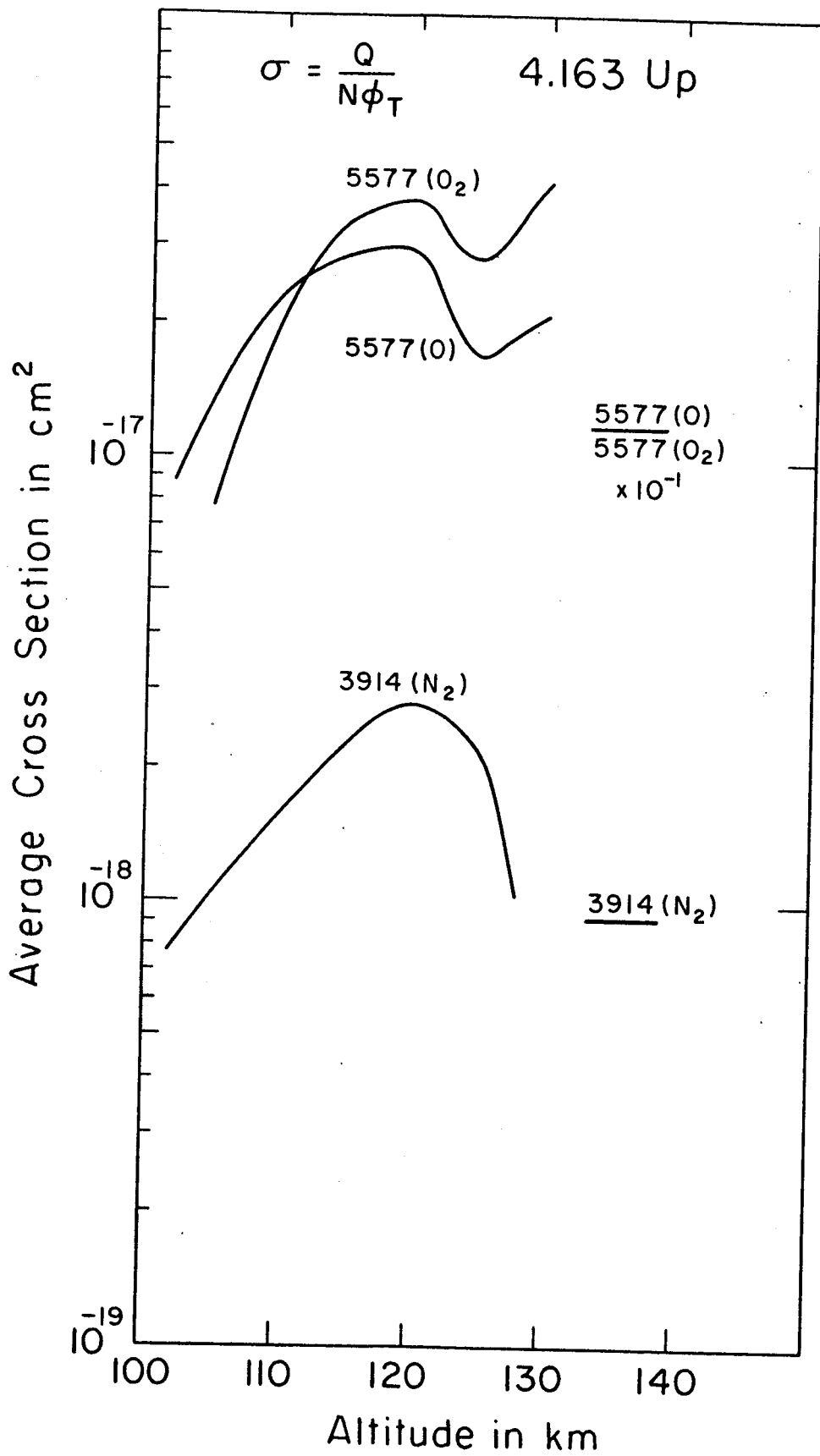


Fig. 5

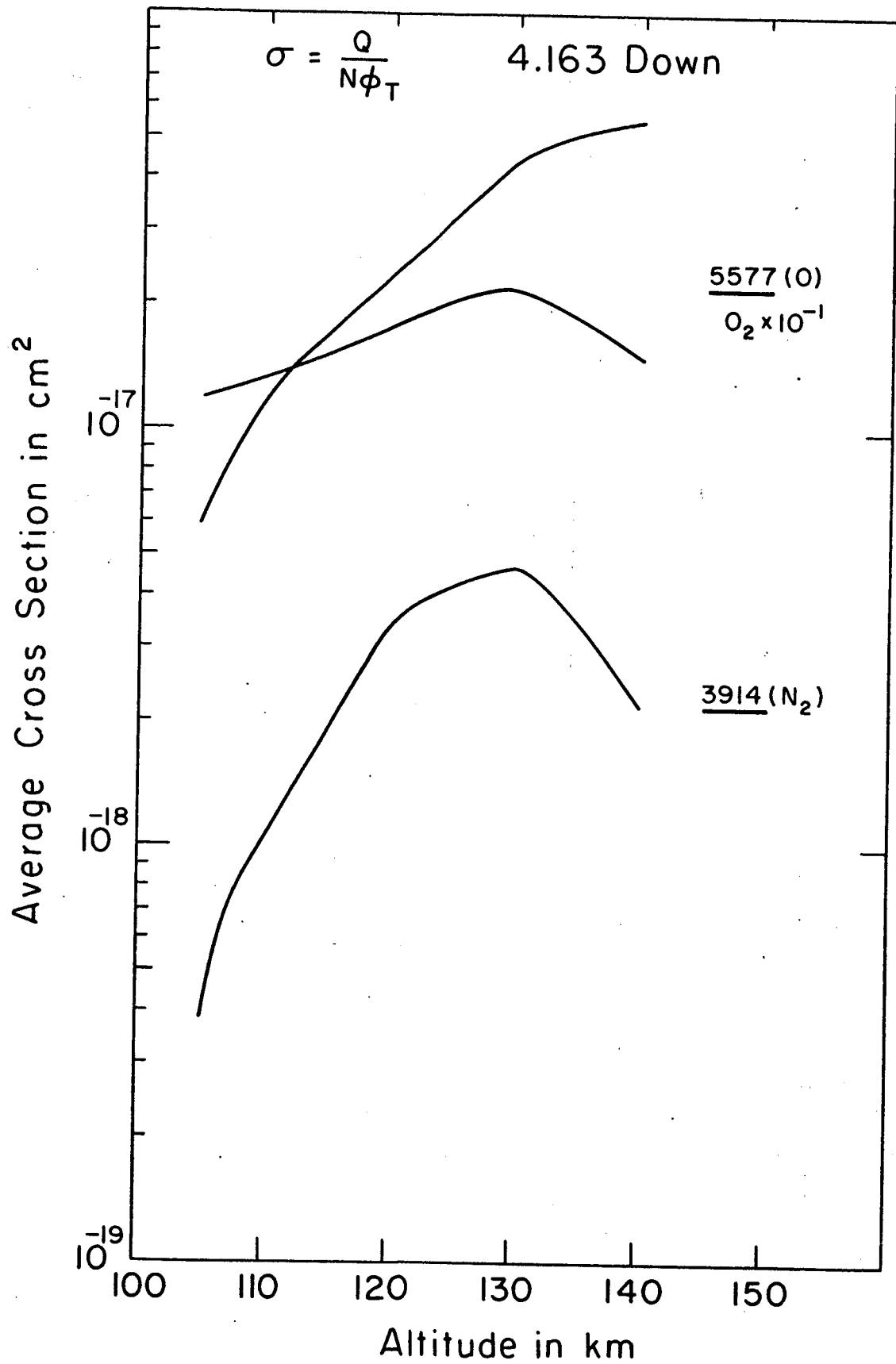


Fig. 6

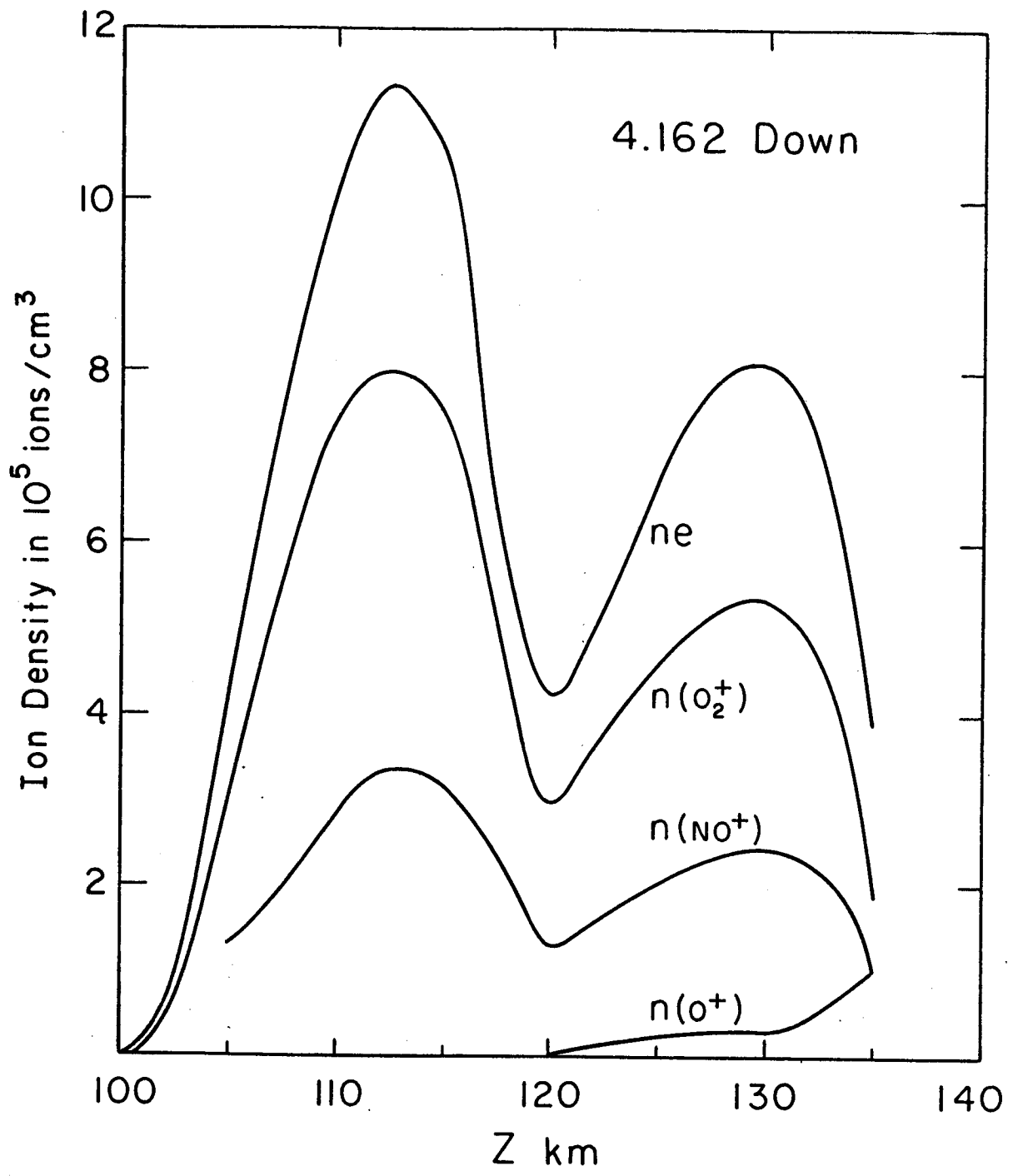


Fig. 7

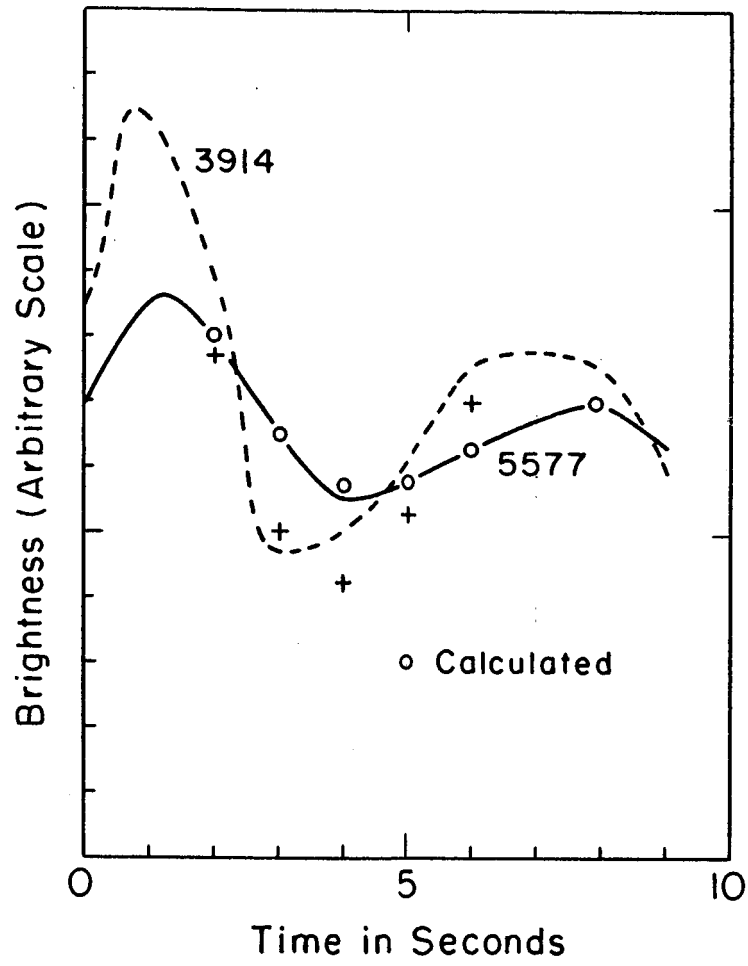


Fig. 8