FURTHER QUANTIFICATION OF THE SOURCES AND SINKS OF THERMOSPHERIC O(¹D) ATOMS

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Abstract—In this paper we confirm an earlier finding that the reaction

$$N(^2D) + O_2 \xrightarrow{k_1} O + O(^1D)$$

constitutes a major source of OI 6300 Å dayglow. The rate coefficient for this reaction is found to be consistent with an auroral result, namely $k_1 \approx 6 \times 10^{-12} \, cm^3 \, s^{-1}$. We correct an error in an earlier publication and demonstrate that reaction (1) is consistent with the laboratory determined quenching rate for the reaction

$$O(^1D) + N_2 \xrightarrow{k_2} O(^3P) + N_2$$
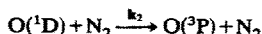
where $k_2 = 2.3 \times 10^{-11} \, cm^3 \, s^{-1}$. Dissociative recombination of O_2^+ with electrons is found to be a major daytime source in summer above ~220 km.

INTRODUCTION AND ANALYSIS

In an accompanying paper, Link *et al.* (1980) re-evaluated the sources and sinks of O(¹D) atoms in the night-time thermosphere. They demonstrated that earlier results of ours (Torr *et al.*, 1980), which indicated that the reaction

$$N(^2D) + O_2 \xrightarrow{k_1} NO + O(^1D) \qquad (1)$$
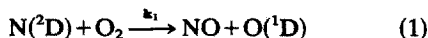
is a major source of OI (6300 Å) dayglow emission, are inconsistent with the aeronomical results of Hays *et al.* (1978). We therefore re-examined our results in detail and have discovered a numerical error which introduced a corresponding error in the value deduced for the rate coefficient for the reaction

$$O(^1D) + N_2 \xrightarrow{k_2} O(^3P) + N_2. \qquad (2)$$
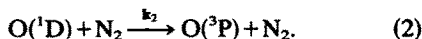
We have corrected this error and also adopted the emission transition probabilities identified by Link *et al.* (1980). The N_2 quenching rate coefficient used to produce the theoretical results in this paper is the corrected value deduced by Link *et al.* (1980) from the night-time data of Hays *et al.* (1978). In addition, we have revised the ionization

and excitation cross sections in the 2-stream photo-electron code developed by Nagy and Banks (1970). The production rate of O(¹D) photoelectron fluxes are ~20% lower than that obtained in our original paper (Torr *et al.*, 1980). The new cross sections for dissociation of N_2 come from Zipf *et al.* (1980) and Zipf and McLaughlin (1978). These cross sections are larger because the $^1\pi_u$ manifold is more efficiently excited by photoelectrons and low energy auroral electrons than previously suspected. The other cross sections come from Porter *et al.* (1976) and Jackman *et al.* (1977). These include cross sections for exciting Rydberg states of O that were not previously included.

In this paper we have chosen not to attempt to specifically reproduce the Atmosphere Explorer (AEC) data for orbit 435 which was analysed by Hays *et al.* (1978), because most of the data were taken at equatorial latitudes, whereas our theoretical model applies to midlatitudes. Instead, we have examined midlatitude data from four 1974 winter orbits (491, 533, 596 and 597) and three 1974 summer orbits (1808, 1823, 1853) (see Hays *et al.* (1973) for a description of the visible airglow experiment-VAE). Within each group the volume emission rates are remarkably similar, but there is a large increase in the summer emission rates over the winter rates above 250 km which has not been theoretically investigated previously.

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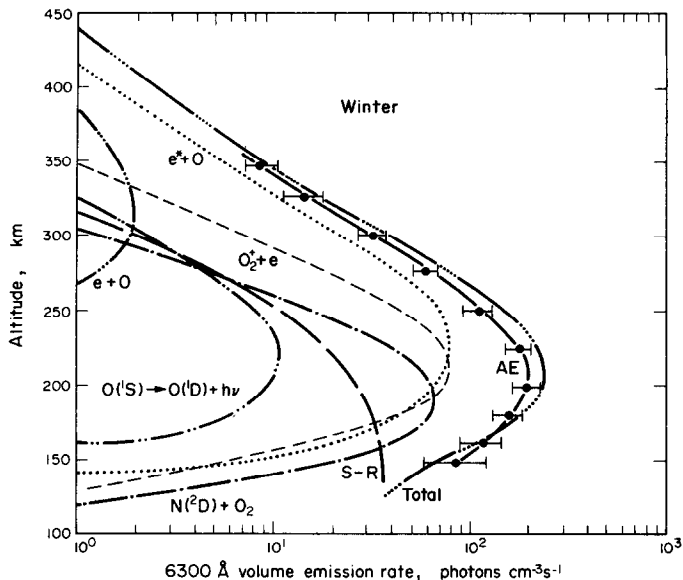
Fig. 1. Daytime OI 6300 Å volume emission rates as a function of altitude for winter 1974.
Total: · · · · ——— · · · ·; N(^{2}D)+O$_2$: ——— · —; e^*+O: · · · · O$_2^+$+e: ——— ——— ———; $h\nu$+O$_2$: ——— ———
; O(^{1}S) → O(^{1}D)+$h\nu$ ——— · · ———; e+O ——— · · · ———. Measurements from 4 winter orbits in 1974
:———; Error bars represent the spread in the data for the 4 orbits.

WINTER RESULTS

The results obtained for winter using the revised theory are shown in Fig. 1 where the error bars on the experimental data represent the spread of the volume emission rates over the four orbits. The winter theory and data agree reasonably well at all altitudes, but the theory tends to overestimate the volume emission rate by up to 30%.

Above 250 km altitude, there are only two major sources of O(^{1}D) in winter. These are recombination of O$_2^+$, and photoelectron excitation of atomic oxygen, with a small contribution from thermal electron excitation of O. Of these three sources, thermal electron excitation of O is the least reliable production rate in Fig. 1 due to its very strong temperature dependence. We have used the expression derived by Rees *et al.* (1967) which gives more than a factor of 2 change in the excitation rate when the electron temperature increases by only 200 K from 2000 K to 2200 K. Nevertheless, the electron temperature and density were too low on the winter orbits to produce significant thermal excitation of O. Diffusion of O(^{1}D) is included in the calculations, but the production rate from the divergence of the flux is not shown since this term only becomes important above ~350 km where it contributes less than 15% to the total volume emission rate.

Figure 1 suggests that the N(^{2}D) source of O(^{1}D) from reaction (1) is needed below 175 km to compensate for the difference between the high O$_2$ dissociation rate used by Hays *et al.* (1978) and the lower rate that we have obtained using the results of Torr and Torr (1980). Elimination of the N(^{2}D)+O$_2$ source does not produce better overall agreement, as becomes clearly evident from the summer results discussed in the next section.

SUMMER RESULTS

The results obtained for summer are shown in Fig. 2. The agreement between the summer theory and data is excellent below 225 km where the new source dominates. The agreement is poor above 225 km where the discrepancy amounts to almost a factor of 2. A comparison with the measured source due to O$_2^+$ recombination, which is discussed further below, has shown that the theoretical results are too small in summer for all orbits examined. However, we regard this as a separate problem pertaining to the chemistry of O$_2^+$ which is currently under investigation.

We note that, while the total theoretical volume emission rate exhibits a small seasonal variation, that does not mean that the individual sources do not change significantly from summer to winter. For example, the N(^{2}D) source is much larger in
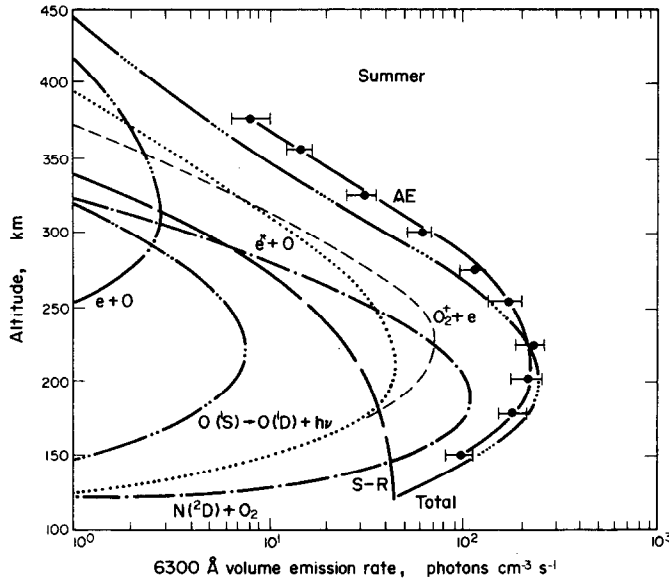
FIG. 2. SAME AS FIG. 1 FOR JULY 1974.

summer than in winter. This is mainly due to the increased densities of N(^{2}D) and O$_2$. Reaction (1) is the dominant source of O(^{1}D) below 170 km. If this source were not present the theoretical volume emission rate would be too low by almost a factor of 2.

The photoelectron source remains the same at high altitudes but decreases to 60% of the winter value near 200 km. The decrease at low altitudes results from a seasonal decrease in the O density in summer while the photoelectron flux remains approximately the same. The dissociation of O$_2$ by solar radiation in the Schumann–Runge continuum is a larger source in summer due to a seasonal increase in the O$_2$ density. The O$_2^+$ recombination source does not change much below 250 km where the theoretical results are reliable. There is a small increase in the theoretical O$_2^+$ source in summer at higher altitudes, but this is not sufficient to account for the observed volume emission rates. This source is investigated further below. Despite a seasonal decrease in both the electron and O densities, the theoretical thermal electron excitation production rate is larger in summer due to an increase in electron temperature. This seasonal variation is also seen in the data. However, it is partly due to an increase in the measured electron density in summer not reproduced by the model. An important consequence of the above seasonal changes, is that, whereas in winter photoelectron excitation is a dominant source of O(^{1}D) above 250 km, in sum-

mer O$_2^+$ recombination, N(^{2}D)+O$_2$, and thermal electron excitation all compete effectively with the photoelectron source.

Although it is possible that errors in several sources might combine to account for the high altitude discrepancy, we demonstrate below that if the measured source due to O$_2^+$ recombination is added to the other theoretically deduced sources, good agreement with the data is obtained as in the case of winter.

For convenience we have referred to the above problem as being seasonal. However, we have identified some winter orbits that display summer-like behavior, but we have found no cases of summer orbits with the low winter-type volume emission rates. The winter orbit 666 which occurred on 14 February 1974, for example, and which was studied by Roble *et al.* (1978) has large volume emission rates which are similar to the summer orbits.

In order to determine the cause of the discrepancy between experiment and theory above ~220 km in summer we have calculated the production rate due to recombination of O$_2^+$ using the AE measurements of the O$_2^+$ and the electron densities and the electron temperature to evaluate this source experimentally. In Fig. 3, we have plotted the total volume emission rate measured by the VAE experiment on orbit 1823 of AE-C on day 74142. We have also plotted the volume emission rates due to recombination and thermal electron excitation of O. These were obtained by using
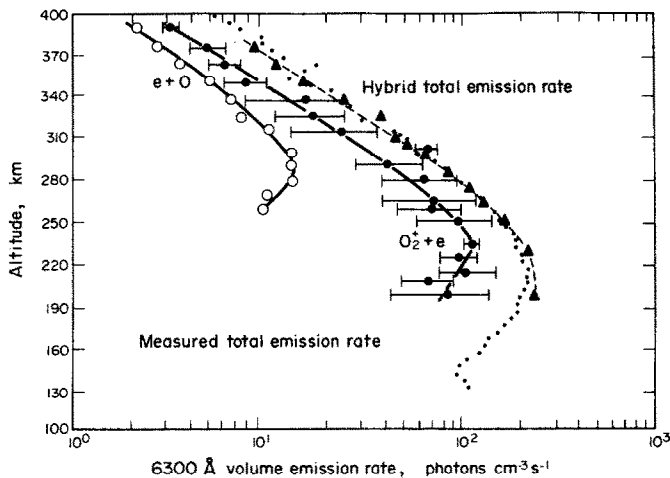
FIG. 3. MEASURED 6300 Å TOTAL VOLUME EMISSION RATE ON ORBIT 1823 DAY 74142 (DOTS).
Also shown are the $O_2^+ + e$ production rate (full circles) and thermal electron excitation rates (circles) calculated using AE–C measurements. The full triangles represent the sum of the recombination and thermal electron excitation rates of Fig. 3 plus the other theoretical production rates from Fig. 2.

measurements of O_2^+ made independently by two ion mass spectrometers (BIMS—Brinton et al., 1973; MIMS—Hoffman et al., 1973), measurements of electron density made independently by two instruments (RPA—Hanson et al., 1973; CEP—Brace et al., 1973), and the electron temperature. The O densities were not measured on this orbit and MSIS (Hedin et al., 1977 a,b) model O densities were used. The error bars on the full circles represent estimated uncertainties of measurement. To avoid confusion we have not included error bars on the thermal electron excitation points, but the errors associated with these points are of similar magnitude.

It is clear from Fig. 3, that the recombination source can account for the much larger volume emission rate on this orbit. This is also true for all other summer orbits for which we have data. On the other hand, with the exception of orbit 435, the measured production rates due to O_2^+ recombination agree with theory on all the other winter orbits analysed. Thermal excitation of O is also a negligible source of $O(^1D)$ for the winter orbits.

In Fig. 3, the broken line and the full triangles represent the total volume emission rate calculated by adding the theoretical volume emission rate for the photoelectron excitation, $N(^2D) + O_2$, and O_2 dissociation sources in Fig. 2, to the experimentally deduced production rates of Fig. 3. It is readily seen that the fit to the experimental total volume emission rate is excellent.

We do not know why the present theory fails to reproduce the high electron and O_2^+ densities seen on the summer orbits, but we are exploring various mechanisms. Any successful explanation has to account for the simultaneous occurrence of high O_2^+ and electron densities.

COMPARISON WITH ORBIT 435

Although our midlatitude model is not well suited for analysis of low latitude orbits like 435, it is interesting to briefly discuss the differences found between our results and those of Hays et al. (1978) to assess whether inclusion of the $N(^2D) + O_2$ source conflicts with the data in this case. Orbit 435 was unusual in that the measured O_2^+ recombination production rates are much lower than the theoretical rates, and also lower than that obtained on other winter orbits. We find that we would obtain an excellent fit to the total volume emission rate profile of orbit 435 if our model reproduced the low measured O_2^+ recombination production rates. Therefore the inclusion of the new $N(^2D) + O_2$ source does not conflict with the data for this orbit. There are two reasons why both the old theory and the new theory appear to agree with the data. Firstly, we have used the lower O_2 dissociation rate of Torr and Torr (1980). Secondly, the old and new photoelectron production rates agree at altitudes above 250 km, but the new production rates are lower at lower altitudes. That is, our calculated profile is much less sharply peaked in shape than that derived from the old theory. We have observed in addition that in an independent
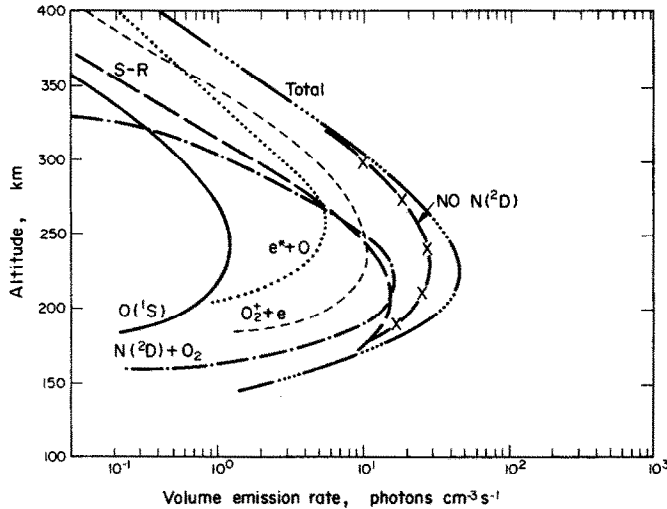
FIG. 4. SAME AS FIG. 1 FOR TWILIGHT, JULY 1974, EXCEPT THAT: ——×—— REPRESENTS RESULTS OBTAINED WITHOUT REACTION (1) —— IS O(^{1}S) → O(^{1}D) + 5577 Å.
The solar zenith angle is 95°.

calculation for February, 1974, Roble et al. (1978) obtained an even flatter photoelectron production rate profile for orbit 666.

TWILIGHT RESULTS

The necessity for a long lived source of 6300 Å emission is evident in the twilight profiles presented by Hays et al. (1978). The effect of reaction (1) on the twilight 5300 Å volume emission rate is shown in Fig. 4. The lifetime of N(^{2}D) at these heights is long enough to provide the correct diurnal variation in the source function. This effect was originally interpreted by Hays et al. (1978) as indicative of a diurnal increase in the O_2 density at twilight.

CONCLUSION

Elimination of a numerical error in our calculations and adoption of O(^{1}D) transition probabilities listed by Link et al. (1980) has resulted in a lower value for N_2 quenching of O(^{1}D) than we reported previously (Torr et al., 1980). The value used in this paper is the laboratory value of $\sim 2.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Davidson et al., 1976, 1977; Amimoto et al., 1979; Streit et al., 1976) which is consistent with that deduced by Link et al. (1980) from the 6300 Å nightglow data of Hays et al. (1978). We find that the lower quenching rate is also consistent with a large daytime production of O(^{1}D) atoms by the reaction

$$N(^2D) + O_2 \xrightarrow{k_1} NO + O(^1D)$$
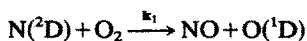
reported previously by Torr et al. (1980) where

$k_1 = 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

We note further that if Link et al. (1980) agree with Rusch et al. (1978) on the auroral ratio

$$\frac{\eta_{6300}}{\eta_{5200}} \approx 130[O_2]/[N_2]$$

where η_{6300} and η_{5200} are the 6300 Å and 5200 Å(N(^{4}S) − N(^{2}D)) volume emission rates, then the importance of reaction (1) in the dayglow is inescapable. Furthermore, Rusch et al. (1978) deduced that $k_1 \approx 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ which is in harmony with our dayglow calculations. This value should not be taken as indicative of an efficiency of 100% for the production of N(^{2}D) by (1), but rather that the efficiency is large, i.e. greater than ~70%. With the corrected value for k_2 and the updated values for the spontaneous Einstein transition probabilities, we agree with a value of 130× $[O_2]/[N_2]$ for the auroral η_{6300}/η_{5200} ratio.

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