# THE REACTION OF $N(^2D)$ WITH O_2 AS A SOURCE OF $O(^1D)$ ATOMS IN AURORAE

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Abstract. We have investigated the source of $O(^1D)$ atoms in the auroral ionosphere using sounding rocket data. Previously, it has been shown that the conventional sources of $O(^1D)$ atoms in the aurora, dissociative recombination of O_2^+ and electron impact excitation of atomic oxygen, fail to explain the measured 6300Å volume emission rate profile. We suggest that the atom-atom interchange reaction of $N(^2D)$ with O_2 can be the major source of auroral 6300Å emission if $O(^1D)$ is created with high efficiency.

Introduction

In a series of papers by Rees et al. [1977] and Sharp et al. [1978], an extensive examination of simultaneous rocket and satellite measurements has been undertaken. These data represent the most extensive set of observations of a given auroral event to date. One of the conclusions of their studies is that the accepted sources of $O(^1D)$, dissociative recombination of O_2^+ and electron impact excitation of O, are inadequate to explain the 6300Å volume emission rate profile deduced from the column intensity measurements. The measurements along with the above sources of $O(^1D)$ are shown in Figure 1. The curves for O_2^+ recombination, electron impact excitation calculated from the HARP measurement of secondary electron fluxes [Sharp et al., 1978] are shown as is the 6300Å volume emission rate porfile. The sum of the two sources falls far below the measured volume emission rate.

The atom-atom interchange reaction of $N(^2D)$ with O_2, Reaction 5 of Table 1, results in the production of a vibrationally excited NO, and an $O(^3P)$ atom or an $O(^1D)$ atom. The energy budgets for production of NO in the vibrational ground state are

$$N(^2D) + O_2 \rightarrow NO(v=0) + O(^3P) + 3.77 \text{ eV}$$

$$N(^2D) + O_2 \rightarrow NO(v=0) + O(^1D) + 1.81 \text{ eV}$$
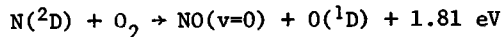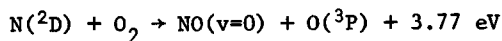
If $O(^3P)$ is formed, NO may be vibrationally excited to the v=18 level. If $O(^1D)$ is the product, the highest level which can be populated is v=8. In a careful laboratory study of the resulting vibrational population of NO, Kennealy et al. [1978] have found that the vibrational population of the NO formed by Reaction 5 is nearly constant for vibrational levels 1 to 8, the population then decreases monotonically to near zero at v=12. They have no information on the state of the product O atom, but if we assume that $O(^1D)$ is created whenever energetically possible, their results imply Reaction 5 would be 87% efficient

in producing $O(^1D)$. The measurements of Kennealy et al. [1978] only establish that some of the reaction goes to form $O(^3P)$. The NO vibrational distribution does strongly indicate the presence of more than one reactive channel, but there is no way to quantitatively assess the relative importance of those two channels. It does, however, seem reasonable that $O(^1D)$ be a significant, albeit not necessarily dominant, product.

Analysis

We have calculated the altitude profiles of the chemical sources and sinks of the metastable $N(^2D)$ atom using the data from the Sharp et al. [1978] paper and their neutral atmosphere. The neutral atmosphere was derived from satellite measurements of O, N_2 and O_2 and has a pronounced decrease in atomic oxygen density compared to the MSIS model predictions. The chemical reaction scheme adopted is given in Table 1. The rates are essentially those shown to be consistent with the AE measurements of $N(^2D)$ densities [see Frederick and Rusch, 1977]. The ionization rate of N_2 is derived from the measured 3914Å profile by assuming 14.7 N_2^+ ions are created for every 3914Å photon [Vallance-Jones, 1974]. The dissociation rate of N_2 by electron impact is set equal to the N_2 ionization rate since the two cross-sections have very similar peak values [Winters, 1966; Zipf and McLaughlin, 1978], and we include the contribution from dissociative ionization excitation in the $N(^2D)$ production rate. Further, the branching ratio of 0.6 for the production of $N(^2D)$ for this reaction is the minimum value consistent with an analysis of the E-region nitric oxide content by Cravens et al. [1979]. The results are shown in Figure 2a. The major sources of $N(^2D)$ are the electron impact dissociative excitation processes and dissociative recombination of NO^+, Reaction 2. The ion-atom interchange of N_2^+ with O, Reaction 3, contributes about 10% to the source of $N(^2D)$. Using the model atmosphere of Sharp et al. [1978], we find the major chemical loss process at all altitudes to be Reaction 5, $N(^2D) + O_2$. The resulting $N(^2D)$ density profile is shown in Figure 2b. Note that the shape of the $N(^2D)$ profile is similar to the 6300Å volume emission rate profile in Figure 1.

Two reactions were investigated as possible sources of $O(^1D)$ atoms:

$$N(^2D) + O \rightarrow N(^4S) + O(^1D) \qquad \text{S1}$$

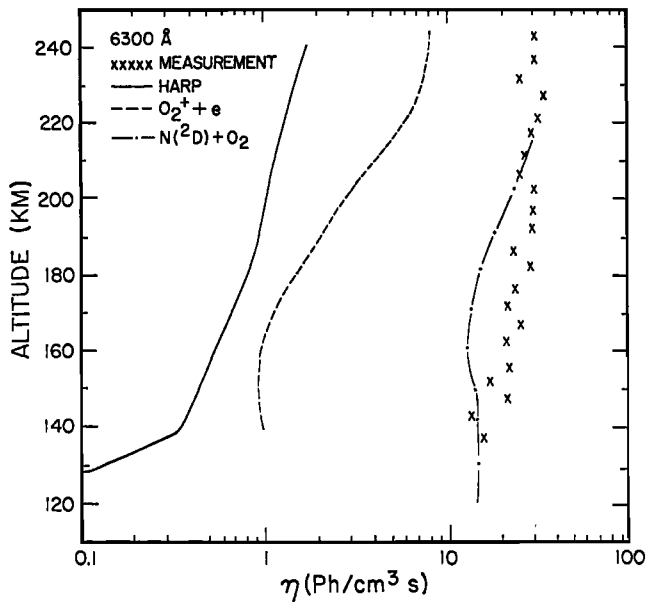$$N(^2D) + O_2 \rightarrow NO + O(^1D) \qquad \text{S2}$$
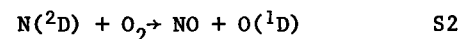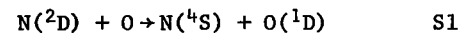
Fig. 1. The volume emission rate profiles of 6300Å emission due to the sources discussed in the text. The curve marked HARP is calculated from the measured fluxes. The curve labeled $O_2^+ + e$ is calculated from measured ion and electron densities. A comparison is given by Sharp et al. [1978].

We can write the volume emission rate of 6300Å photons for S1 as

$$n_{6300} = \frac{0.0069 \; k_4 \; [N(^2D)][O]}{k_6[N_2] + 0.0091}$$ (1)

where 0.0069 is the Einstein coefficient for the $OI(^3P - {}^1D)$ transition and 0.0091 is the inverse lifetime of the $O(^1D)$ state. The result is given in Table 2 under the column labeled S1. The reaction can be eliminated as a significant source of $O(^1D)$ in this case because of its small magnitude.

The source of 6300Å photons from S2 can be written as

$$n_{6300} = \frac{0.0069 \; k_5 \; [N(^2D)][O_2]}{k_6[N_2] + 0.0091}$$ (2)

The calculated 6300Å volume emission rates for S1 and S2 are given in Table 2 as S2 and shown in

Figure 1. This source is sufficient to explain the measurement if it operates with near unit efficiency. It provides a source of 6300Å photons which is nearly constant with altitude and the source of ^1D atoms is as large as the total ionization rate in the aurora, as required by the measurement.

Excitation of auroral $O(^1D)$ by Reaction 5 implies that the ratio of the 6300Å to 5200Å emissions is given by

$$\frac{n_{6300}}{n_{5200}} = 1.4 \times 10^2 \; [O_2]/[N_2]$$ (3)

where n_{5200} is the volume emission rate of 5200Å photons.

$$n_{5200} = A \cdot [N(^2D)]$$

where A is the Einstein coefficient for $N(^2D)$ and is equal to 1.07×10^{-5} s^{-1} [Garstang, 1956]. The $N(^2D)$ densities are given in Table 2.

Therefore, the intensity ratio should remain relatively constant in different auroras. This is in agreement with ground-based observations of Gerard and Harang [1973] showing that under steady auroral conditions the 6300Å/5200Å ratio is 20 ± 10 over more than two orders of magnitude change in the incident energy flux. The scatter in the observed ratio may be explained by variations in the $[O_2]/[N_2]$ ratio similar to those observed on Atmosphere Explorer at high latitudes [Potter et al., 1977].

Effects on the Day Airglow

In a recent paper, Hays et al. [1978] conducted a comprehensive survey of the day and night midlatitude 6300Å airglow. The results confirmed the low quenching rate of $O(^1D)$ by N_2. Reaction 5 would contribute 43 ph cm^{-3} s^{-1} at 200 km in the fully illuminated ionosphere, approximately equivalent to the Schumann-Runge source and about one-third of the photoelectron impact source. At 160 km Reaction 5 contributes 34 ph cm^{-3} s^{-1} compared to a total volume emission rate of 100 ph cm^{-3} s^{-1}. Inclusion of this source would require an increase in the derived quenching rate of $O(^1D)$ by N_2 of about 30%. This is within the error quoted by Hays et al. [1978]. This impact of the new source on the derived daytime $O(^1D)$ chemistry is, therefore, small.

TABLE 1. Chemical Reactions

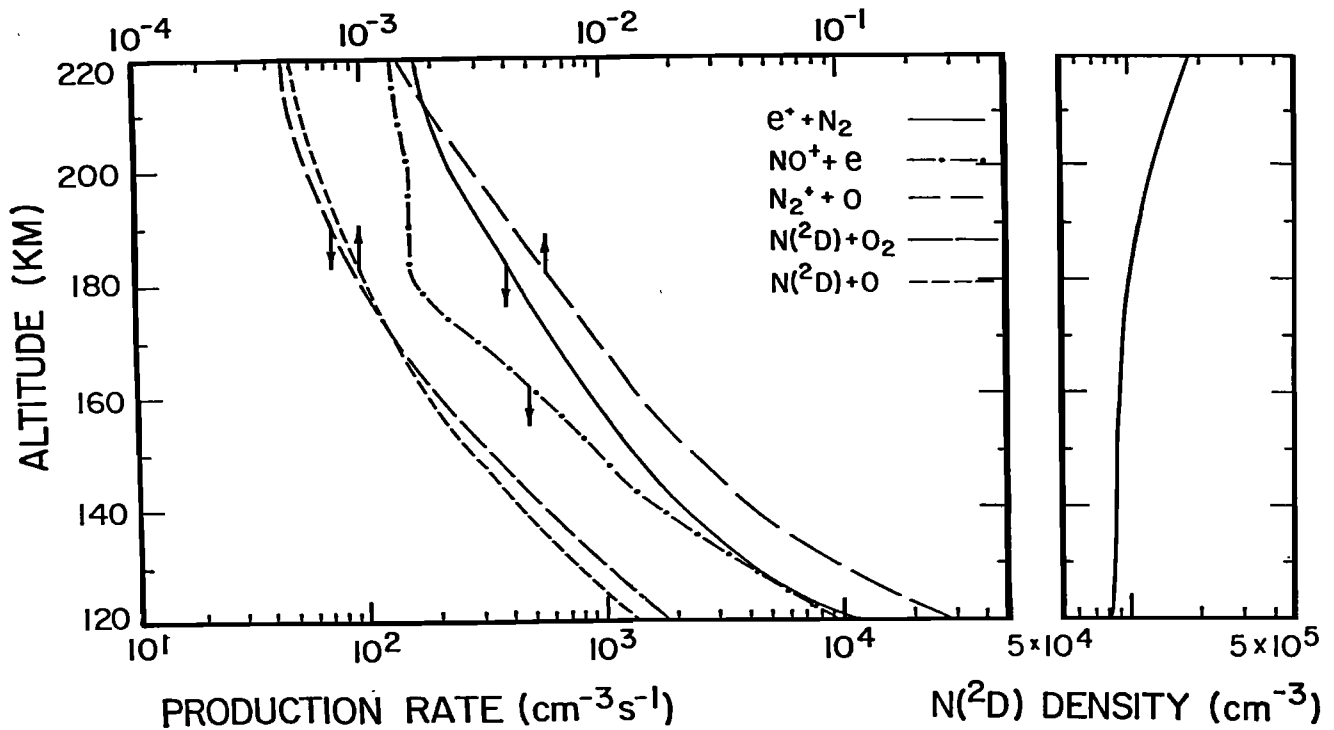| Reaction	Rate (cm^{-3}s^{-1})	Source
1. $e^* + N_2 \rightarrow N(^2D) + N(^4S) + e$	$f = 0.6$	See text
2. $NO^+ + e \rightarrow N(^2D) + O$	$4.3 \times 10^{-7}(T_e/300)^{-0.83}$, $f=0.8^*$	Walls and Dunn [1974]
3. $N_2^+ + O \rightarrow N(^2D) + NO^+$	$1.4 \times 10^{-10}(T/300)^{-0.44}$, $f=1.0^*$	McFarland et al. [1974]
4. $N(^2D) + O \rightarrow N(^4S) + O$	5×10^{-13}	Frederick and Rusch [1977]
5. $N(^2D) + O_2 \rightarrow NO + O(^1D, {}^3P)$	6×10^{-12}	Lin and Kaufman [1971]
6. $O(^1D) + N_2 \rightarrow O(^3P) + N_2$	3×10^{-11}	Hays et al. [1978]

* See text for an explanation of the choices of f.

Fig. 2. a) The altitude profiles of the production and loss rates of $N(^2D)$ in the aurora. b) The calculated density profile for $N(^2D)$ atoms.

Discussion and Conclusion

We have suggested a chemical source for $O(^1D)$ which can explain the observed 6300Å altitude distribution measured in the aurora. The calculated ratio of 6300Å to 5200Å emission in the model is approximately 20 in good agreement with the measurements of Gerard and Harang [1973]. This ratio would be independent of the auroral intensity, but would depend on the $[O_2]/[N_2]$ ratio in the aurora.

A high efficiency for the production of $N(^2D)$ in the aurora by Reaction 1 would lower the required efficiency for the production of $O(^1D)$ by Reaction 5. If Reaction 1 were 100% efficient the required branching ratio for Reaction 5 would be 65% for the production of $O(^1D)$.

The relatively long chemical lifetime of the $N(^2D)$ atom at 180 km (200 s) compared to the $O(^1D)$ atom (3.3 s) would allow $O(^1D)$ atoms to be created at much greater distances from the center of the auroral arc if Reaction 5 is operative. This would explain the discrepancy between the calculated and observed 6300Å emission away from the center of an auroral arc. This emission cannot be accounted for if Reaction 5 is neglected [see Rees et al., 1967].

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TABLE 2. Terms Used in the Calculation of S1 and S2

z (km)	$D \cdot N_2$ $(cm^{-3}s^{-1})$	$K_2[N_2^+][O]$ $(cm^{-3}s^{-1})$	$\alpha[NO^+]e$ $(cm^{-3}s^{-1})$	$k_5[O_2]$ (s^{-1})	$k_4[O]$ (s^{-1})	$[N(^2D)]$ (cm^{-3})	S1 $(cm^{-3}s^{-1})$	S2 $(cm^{-3}s^{-1})$
120	1.2(4)*	2.1(3)	1.0(4)	2.9(-1)	1.4(-2)	8.0(4)	0.75	16.3
140	2.3(3)	5.7(2)	1.7(3)	4.1(-2)	4.3(-3)	9.9(4)	1.5	14.2
160	9.0(2)	1.9(2)	5.2(2)	1.4(-2)	1.7(-3)	8.0(4)	1.5	12.1
180	4.2(2)	1.1(2)	1.7(2)	6.0(-3)	1.0(-3)	9.9(4)	2.7	16.1
200	2.3(2)	6.2(1)	1.6(2)	2.9(-3)	6.5(-4)	1.3(5)	4.9	21.5
220	1.7(2)	4.5(1)	1.3(2)	1.4(-3)	4.9(-4)	1.8(5)	9.6	28.5

*read 1.2(4) as 1.2×10^4

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