

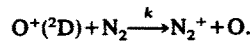
CHARGE EXCHANGE OF METASTABLE 2D OXYGEN IONS WITH N_2 IN THE THERMOSPHERE

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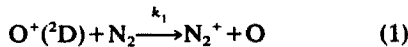
Abstract—Measurements of N_2^+ and supporting data made on the Atmosphere Explorer-C satellite in the ionosphere are used to study the charge exchange process



The equality $k = (5 \pm 1.7) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value lies close to the lower limit of experimental uncertainty of the rate coefficient determined in the laboratory. We have also investigated atomic oxygen quenching of $O^+(^2D)$ and find that the rate coefficient is $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ to within approximately a factor of two.

1. INTRODUCTION

Dalgarno and McElroy (1963) pointed out that charge exchange of $O^+(^2D)$ with N_2 should constitute an important sink for $O^+(^2D)$ in the atmosphere. They indicated that since 38% of the O^+ ions in the thermosphere are produced in the 2D state this could also be an important source of N_2^+ . Thus, accurate knowledge of the rate at which the reaction



proceeds is important for aeronomic studies. Stebbings *et al.* (1966), in a crossed beam experiment, identified the products of charge exchange with N_2 as being primarily N_2^+ , whereas ground state $O^+(^4S)$ reacts with N_2 to produce NO^+ . This result was confirmed by Rutherford and Vroom (1971) whose cross-section measurements indicate that $k_1 = 1 \pm 0.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Ferguson, 1974). In this paper we use ionospheric measurements made by the Atmosphere Explorer-C satellite (AE-C) to make an *in situ* determination of k_1 .

We use the fact that (1) is an important source of N_2^+ to determine the concentration of $O^+(^2D)$ ions from the photochemistry of N_2^+ . A serious problem that we have to deal with is the fact that the dissociative recombination rate coefficient of N_2^+ ,

α , is uncertain. We have discussed this in detail in an earlier paper (Orsini *et al.*, 1977). To summarize the current situation, Mehr and Biondi (1969) have inferred an expression of the form

$$\alpha = 1.8 \times 10^{-7} (T_v/T_e)^{0.39} \quad (2)$$

from various laboratory measurements of α , where T_v is the N_2^+ vibrational temperature and T_e the electron temperature. Equation (2) is derived assuming that the N_2^+ ions are in thermal equilibrium in the laboratory experiments. This assumption has been seriously questioned by Gutcheck and Zipf (1973). To overcome the problem of uncertainties in α we take advantage of the fact that the AE-C database comprises measurements of aeronomic parameters made over three years covering a wide variety of geophysical conditions. With the large dynamic range that is found in most of the parameters measured, it is possible to select the data in such a way as to simulate laboratory-type-control of variables. For example, we can choose conditions so that the dependence of our determination of k_1 on α is minimized, i.e. we can choose data so that recombination is small compared with the reaction of N_2^+ with O. Under these conditions it then becomes possible to solve for k_1 without having to know α .

2. THEORY AND MEASUREMENTS

The photochemistry of $O^+(^2D)$ has been discussed in detail by Orsini *et al.* (1977) and Oppenheimer *et al.* (1976). The relevant chemistry is

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given in Tables 1–3. From this scheme we arrive at the following expressions for the concentration of $O^+(^2D)$

$$[O^+(^2D)] = \frac{(J_{2uv} + J_{2e})[O] + k_9[O^+(^2P)][N_e] + \beta_1[O^+(^2P)]}{k_1[N_2] + k_{12}[O] + k_{13}[N_e]} \quad (3)$$

From the photochemistry of N_2^+ we are able to arrive at an independent expression for the $O^+(^2D)$ density, which arises from its role as a major sink of N_2^+ .

$$[O^+(^2D)] = \frac{[N_2^+](k_5[O] + k_6[N_e]) - (J_{uv} + J_{1e} + k_4[O^+(^2P)])[N_2]}{k_1[N_2]}, \quad (4)$$

where $[O^+(^2P)]$ is given by

$$[O^+(^2P)] = \frac{(J_{3uv} + J_{3e})[O]}{k_{16}[N_2] + k_{18}[O] + (k_9 + k_{19})[N_e] + \beta} \quad (5)$$

We substitute (4) in (3) and solve for k_1 .

$$k_1 = \frac{A(k_{12}[O] + k_{13}[N_e])}{[N_2](Q - A)} \quad (6)$$

where

$$A = [N_2^+](k_5[O] + k_6[N_e]) - (J_{uv} + J_{1e} + k_4[O^+(^2P)])[N_2] \quad (7)$$

$$Q = (J_{2uv} + J_{2e})[O] + k_9[O^+(^2P)][N_e] + \beta_1[O^+(^2P)] \quad (8)$$

TABLE 1. RATE CONSTANT UNITS $cm^3 s^{-1}$

N_2^+ Sources	
1. $N_2 + O^+(^2D) \xrightarrow{k_1} N_2^+ + O$	$k_1 = (5.0 \pm 0.3) \times 10^{-10}$, see text
2. $N_2 + h\nu \rightarrow N_2^+ + e$	see text
3. $N_2 + e \rightarrow N_2^+ + 2e$	see text
4. $N_2 + O^+(^2P) \xrightarrow{k_4} N_2^+ + O$	$k_4 = 4.8 \pm 1.4 \times 10^{-10}$ *
N_2^+ Sinks	
5. $N_2^+ + O \xrightarrow{k_5} NO^+ + N$	$k_5 = 1.4 \pm 0.2 \times 10^{-10}$ $\times (T/300)^{-0.44\dagger}$ $\times (1.0 - 0.07(T/300)0.21)$
6. $N_2^+ + e \xrightarrow{k_6} N + N$	see text

*Rusch *et al.* (1977).

†McFarland *et al.* (1974); Torr *et al.* (1977).

TABLE 2. RATE CONSTANT UNITS $cm^3 s^{-1}$

$O^+(^2D)$ sources	
7. $O + h\nu \rightarrow O^+(^2D) + O$	see text
8. $O + e \rightarrow O^+(^2D) + 2e$	see text
9. $O^+(^2P) + e \xrightarrow{k_9} O^+(^2D) + e$	$k_9 = 1.5 \times 10^{-7}$ $\times \sqrt{(300/T_e)^*}$
10. $O^+(^2P) \xrightarrow{\beta_1} O^+(^2D) + h\nu$	$\beta_1 = 0.171 s^{-1}\dagger$
$O^+(^2D)$ sinks	
11. $O^+(^2D) + N_2 \xrightarrow{k_1} N_2^+ + O$	$(5.0 \pm 0.3) \times 10^{-10}$ (this paper)
12. $O^+(^2D) + O \xrightarrow{k_{12}} O^+(^4S) + O$	$k_{12} = \sim 2 \times 10^{-11}$ (this paper)
13. $O^+(^2D) + e \xrightarrow{k_{13}} O^+(^4S) + e$	$k_{13} = 7.8 \times 10^{-8}$ $\times \sqrt{(300/T_e)^*}$

*Henry *et al.* (1969).

†Seaton and Osterbrock (1957).

and J_{uv} and J_e are altitude dependent ionization frequencies for photons and electrons.

In equation (6) k_6 is the major uncertain quantity, but as mentioned above we place constraints on the data used so that the quantity $k_6 N_e$ is reduced to as small a value as possible as is described in Section 4. Before proceeding further with the analysis we describe the measurements of aeronomic parameters and the uncertainties in rate coefficients used.

3. INPUT DATA

The solar flux used is a reference spectrum compiled by Hinteregger *et al.* (1973, 1976) from measurements made on the AE satellites. The fluxes given in this reference spectrum are in good agreement with the photoionization frequency for $O^+(^2P)$ determined from aeronomic data by Rusch *et al.* (1976). The ionization and absorption cross sections used for O and N_2 were compiled by G. Victor (private communication, 1976) from data acquired from many sources. These are considered to be established to within 30%. Since measurements of the photoelectron spectrum were not always available, this source function was simulated by increasing the photoionization rate of N_2^+ by 27% and that of $O^+(^2D)$ and $O^+(^2P)$ by 15%. The latter value is based on observations by Hays *et al.* (1975) that 7320 Å $O^+(^2D - ^2P)$ auroral emission is not as bright as that expected from the measured

TABLE 3. RATE CONSTANT UNITS cm³ s⁻¹

O ⁺ (² P) Sources	
14. O + hν → O ⁺ (² P) + e	see text
15. O + e → O ⁺ (² P) + 2e	see text
O ⁺ (² P) Sinks	
16. O ⁺ (² P) + N ₂ $\xrightarrow{k_{16}}$ N ₂ ⁺ + O	4.8 ± 1.4 × 10 ⁻¹⁰ (* in Table 1)
17. O ⁺ (² P) + e $\xrightarrow{k_9}$ O ⁺ (² D) + e	1.5 × 10 ⁻⁷ √300/T _e
18. O ⁺ (² P) + O $\xrightarrow{k_{18}}$ O ⁺ + O	5.2 ± 2.5 × 10 ⁻¹¹ (* in Table 1)
19. O ⁺ (² P) + e $\xrightarrow{k_{19}}$ O ⁺ (⁴ S) + e	4.0 × 10 ⁻⁸ √300/T _e (* in Table 2)
20. O ⁺ (² P) $\xrightarrow{\beta}$ O ⁺ + hν	β = 0.218 sec ⁻¹ († in Table 2)

energy influx and the electron impact ionization cross-sections of Dalgarno and Lejeune (1971). Fifteen percent represents an upper limit for the auroral study and is also an approximate lower limit for the results of Dalgarno and Lejeune [1971] for the cross-sections. The electron quenching rates of O⁺(²P) and O⁺(²D), k₉ + k₁₉ and k₁₃, respectively, were computed theoretically by Henry *et al.* (1969) and are believed to be accurate to within ±30%. Orsini *et al.* (1977) have determined that the oxygen quenching rate of O⁺(²D), k₁₂, is less than 3 × 10⁻¹¹ cm³ s⁻¹. We discuss this further in Section 4. Torr *et al.* [1977] have determined that k₅ = 1.1 × 10⁻¹⁰ ± 15% at 650 K. This is in excellent agreement with the laboratory results of McFarland *et al.* [1974] which we adopt here. Rusch *et al.* (1977) have determined both the N₂ and O quenching rates of O⁺(²P) using AE-data. These are considered to be established to within ±30%.

The database that we use for this analysis has already been used in several other analyses (cf., e.g. Torr *et al.*, 1976, 1977; Orsini *et al.*, 1977). The data were taken at invariant latitudes less than 55° and at solar zenith angles less than 80°. The neutral densities were measured by the open source mass spectrometer (OSS) (Nier *et al.*, 1973), the N₂ densities by the Bennett ion mass spectrometer (BIMS) (Brinton *et al.*, 1973). The electron density and temperature was measured by the cylindrical electrostatic probe (CEP) (Brace *et al.*, 1973) and the ion temperature by the retarding potential analyzer (RPA) (Hanson *et al.*, 1973).

4. ANALYSIS AND RESULTS

The major difficulty to be overcome in this analysis is the uncertainty in the N₂⁺ recombination rate. In principle it is a straightforward matter to select data so that the term k₆[N_e] is small compared with k₅[O] in equation (7). However, this generally occurs at low altitudes when charge exchange of O⁺(²D) with N₂ is the only major removal process of the former. Under these conditions Q ≈ A and equation (6) becomes indeterminate. Thus it is necessary to introduce an additional constraint. Charge exchange must not be the only removal process of O⁺(²D). There must be at least one other loss process competing for destruction of O⁺(²D) to be able to determine k₁. The term A given by equation (7) is equal to production of N₂⁺ due to charge exchange of O⁺(²D) with N₂. We therefore introduce the constraint 0.3 ≤ A/Q ≤ 0.7 where Q (given by equation 8) is the total production rate of O⁺(²D). This ensures that charge exchange of O⁺(²D) with N₂ is a significant source of N₂⁺, but at the same time is not the only loss process of O⁺(²D). These constraints remove the occurrence of the singularity in (6) discussed above. Values of k₁ were computed from (6) applying these constraints. We searched through the AE data until a sample size of at least 500 was obtained. The data were then sorted as a function of the ratio R = k₆[N_e]/k₅[O]. The range in R was divided into bins. The bin size was defined by ΔR = 0.1. An average value and standard deviation for k₁ was calculated for each bin. Values obtained for k₁ as a function of R are shown in Fig. 1 for three values of the recombination rate coefficient, k₆. As is to be expected the results for lower values of k₆ extend to lower values of R. For k₆ = 2.5 × 10⁻⁷ cm³ s⁻¹ the data run out at R = 0.33. Although there is an approximate difference of 40% between the values of k₁ for k₆ = 1 × 10⁻⁷ and k₆ = 2.5 × 10⁻⁷ cm³ s⁻¹, it is clear that we obtain significantly lower values for k₁ than 1 × 10⁻⁹ cm³ s⁻¹, the laboratory determined value (Ferguson, 1974; Rutherford and Vroom, 1971). We believe that the values obtained for k₁ at the higher end of the range of values used for k₆ are more likely to be the correct ones. Our reasons for this are as follows. Orsini *et al.* (1976, 1977) have studied N₂⁺ recombination in the ionosphere using AE data. They find that when N_e is low (such as in this analysis) the recombination rate coefficient of N₂⁺ appears to increase. They attribute this to a dependence of k₆ on N₂⁺ vibrational excitation. The dependence is such that k₆ increases with vibrational excitation. Thus when N_e is high, the

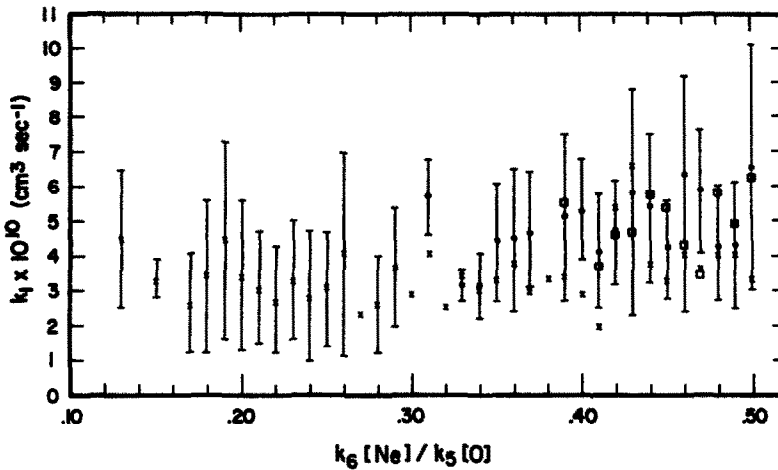


FIG. 1. THE RATE COEFFICIENT k_1 AS A FUNCTION OF THE RATIO $k_6[N_e]/k_5[O]$ FOR SEVERAL VALUES OF k_6 ; X: $k_6 = 1 \times 10^{-7}$, ●: $k_6 = 2 \times 10^{-7}$, □: $k_6 = 2.5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$; $k_{12} = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.
The average sample size for each data point shown is 25.

relative population of high vibrational levels of N_2^+ is depleted in comparison with cases when N_e is low. This gives rise to an effective value for the recombination coefficient which is larger when N_e is depressed. Orsini *et al.* (1977) estimated k_6 to be $2.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for electron densities which correspond to values of R lying between 0.3 and 0.5 in this study. This would yield values for k_1 of $\sim 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, a value which lies within the limits of

experimental error of Rutherford and Vroom (1971).

In their analysis Orsini *et al.* (1977) determined that $k_{12} < 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. However, their results are presented in a way which suggests that k_{12} might be zero or very small. This analysis offers an opportunity to narrow down still further the uncertainty on k_{12} . The reason for this is that as R tends to zero, the term $k_{12}[O]$ in the numerator of (6)

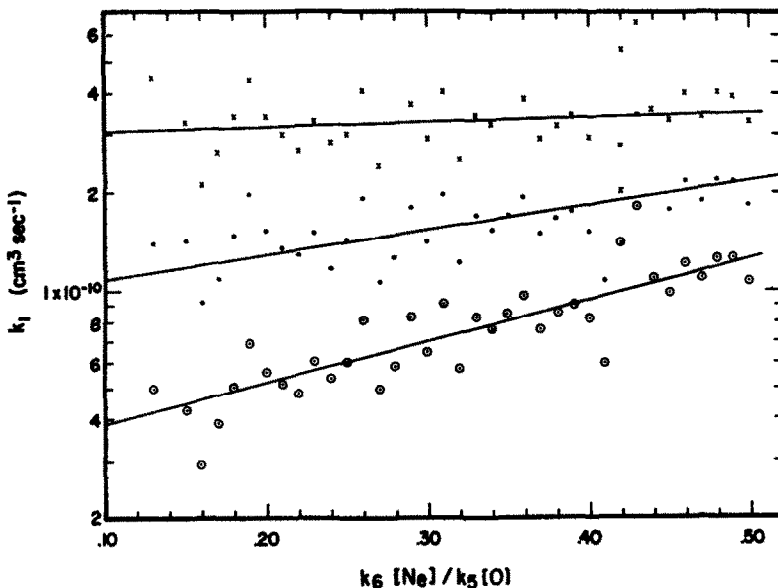


FIG. 2. THE RATE COEFFICIENT k_1 AS A FUNCTION OF THE RATIO $k_6[N_e]/k_5[O]$ FOR SEVERAL VALUES OF k_{12} ; X: $k_{12} = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, ●: $k_{12} = 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, ○: $k_{12} = 0 \text{ cm}^3 \text{ s}^{-1}$, $k_6 = 1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$.
The average sample size for each data point shown is 25.

becomes increasingly important in determining the correct value for k_1 . We should not expect k_1 to vary significantly as a function of R . The rate coefficient is large, and temperature dependences are generally not significant for gas kinetic rates. Therefore if k_1 varies strongly with R when the latter is small, we must attribute this effect to an incorrect choice of k_{12} . For the data we have already presented, this did not happen. In Fig. 2 we show the effect of setting k_{12} to zero, 1×10^{-11} , and $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The results show a clear increase of k_1 with R for $k_{12} < 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, which does not occur for $k_{12} = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Orsini *et al.* (1977) determined the upper limit for the ratio k_{12}/k_1 to be 2×10^{-2} . Using our value for k_1 , i.e. $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ we find $k_{12} \leq 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for their data. Although our analysis of k_{12} is not a sensitive one, a value of $k_{12} = 3 \times 10^{-11}$ is preferred to $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Therefore we draw the conclusion that k_{12} is not zero, and that a value of $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ is probably correct to within a factor of 2.

5. CONCLUSIONS

We have used measurements of aeronomic parameters made by the Atmosphere Explorer-C satellite to study reactions with the neutral atmosphere which result in the destruction of O⁺(²D). We have determined rate coefficients for charge exchange of O⁺(²D) with N₂, and quenching of O⁺(²D) by atomic oxygen. We find the former to be $5 \times 10^{-10} \pm 0.3 \times 10^{-10}$ and the latter to be $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (within about a factor of 2). The charge exchange rate is about a factor two lower than the preferred laboratory value of Rutherford and Vroom (1971), but lies within their limits of experimental error. The oxygen quenching rate coefficient improves an earlier determination by Orsini *et al.* (1977) which placed an upper limit on its value of $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

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