

The excitation of $O(^1S)$ in the reaction between $N_2(A^3\Sigma_u^+)$ and $O(^3P)$

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The rate constant for the excitation of $O(^1S)$ in the reaction between $N_2(A, v' = 0)$ and $O(^3P)$ has been measured in a discharge-flow reactor at room temperature to be $(2.1 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Combining this measurement with the previously determined rate constant for total quenching of $N_2(A)$ by O shows that the fraction of all quenching events which lead to $O(^1S)$ excitation is 0.75 ± 0.13 . These results are at variance with rate constants estimated from some auroral models and indicate that some revision of auroral models is in order.

I. INTRODUCTION

Following their observation of $O(^1S)$ excitation in laboratory studies on the interaction between $N_2(A)$ and $O(^3P)$, Meyer *et al.*¹ suggested that the energy-transfer reaction between $N_2(A)$ and O was an important mechanism for the production of the auroral green line $O(^1S - ^1D, \lambda = 557.7 \text{ nm})$. Since that work controversy has raged over the relative importance of the $N_2(A) + O$ excitation mechanism compared to other possible green-line excitation channels.²⁻¹⁴ Much of this controversy resulted from a state of ignorance over the magnitude of the rate constant for quenching $N_2(A)$ by O and the fraction of $N_2(A) + O$ quenching events which lead to $O(^1S)$ excitation. A number of years ago Meyer *et al.*¹⁵ and Dunn and Young¹⁶ reported rate constants for the quenching of $N_2(A)$ by O . In addition, Meyer *et al.* estimated that about 25% of the quenching collisions between $N_2(A)$ and O resulted in $O(^1S)$ excitation, although, as they pointed out, this value is in reality a lower bound because they didn't correct for $O(^1S)$ quenching. Although the experimental results of Meyer *et al.* and Dunn and Young agreed, several experimental uncertainties plagued both studies, and neither has been generally accepted by the aeronomic community.

A number of aeronomers⁷⁻¹⁴ have preferred to try to infer the rate constant for quenching $N_2(A)$ by O and for excitation of $O(^1S)$ in the $N_2(A)$ plus O reaction by varying rate constants in an auroral model until the model predictions could be made to coincide with the atmospheric observations. This process is risky, however, because some of the important parameters in the model, such as atomic oxygen number density, usually are quite uncertain.⁹ In addition, some models neglect important processes such as quenching of $N_2(A)$ by NO which can be significant in a strong aurora where NO number densities can build up to levels as high as $10^{11} \text{ molecules cm}^{-3}$.⁹ Therefore, it is not surprising that model-derived rate constants for the $N_2(A)$ plus O reaction vary by more than an order of magnitude, nor that estimates of the fraction of quenching events leading $O(^1S)$ vary between 0.13 and unity.

We have shown recently that the rate constants for quenching $N_2(A)$ by atomic oxygen are 2.8 and $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for vibrational levels 0 and 1, respectively.¹⁷ In this paper we present the results of experi-

mental measurements on the rate constant for excitation of $O(^1S)$ in the $N_2(A)$ plus O reaction which show that 75% of all quenching events lead to $O(^1S)$ excitation.

II. EXPERIMENTAL

The experimental apparatus is a discharge-flow reactor in which $N_2(A)$ number densities are monitored by observing individual vibrational bands of the Vegard-Kaplan ($N_2 A^3\Sigma_u^+ - X^1\Sigma_g^+$) system of nitrogen. The reactor, described in detail previously by Piper *et al.*^{18,19} is a 2 in. diameter quartz tube which is pumped by a Roots blower that is capable of producing linear flow velocities up to $8 \times 10^3 \text{ cm s}^{-1}$ at pressures of 1 Torr. A 0.5 m monochromator (Minuteman) is mounted upon a set of rails parallel to the flow tube. Spectral observations of the luminous gases in the flow tube, therefore, can be made as a function of linear distance along the tube by sliding the monochromator up and down on its rails. The reaction time is the ratio of distance to flow velocity. A thermoelectrically cooled EMI 9558QA photomultiplier and an SSR 1105 photon-counting rate meter measure light intensities photoelectrically.

The reaction between metastable $Ar(^3P_{0,2})$ and molecular nitrogen makes the metastable nitrogen molecules.^{20,21} This transfer produces primarily the $C^3\Pi_u$ state of N_2 ²² which quickly cascades radiatively to the metastable $A^3\Sigma_u^+$ state via the $B^3\Pi_g$ state. A cold, hollow-cathode discharge (210 V and 3 mA) through the flowing argon produces the argon metastables. The argon was purified by flowing it through a trap filled with 5 A molecular sieve and cooled with dry ice. Typically, the argon flow rate is $\approx 1600 \mu\text{mol s}^{-1}$, the nitrogen flow rate is $\approx 100 \mu\text{mol s}^{-1}$, the flow tube pressure about 1.3 Torr, and the flow velocities $\approx 1400 \text{ cm s}^{-1}$.

A microwave discharge through a small amount of O_2 in helium (typical flows: $1 \mu\text{mol s}^{-1}$ of O_2 and $100 \mu\text{mol s}^{-1}$ of He) makes atomic oxygen. The oxygen atoms enter the flow tube through a 1 in. diameter loop fabricated from 2 mm o.d. polyethylene tubing. O-atom number densities were determined by measuring the air-after-glow signal at 580 nm,^{23,24} with a 5 nm bandpass as a function of NO number density when NO was injected into the flow tube through a second loop 10 cm downstream from the oxygen injector. Then the slope of the line representing the air-afterglow intensity as a function of

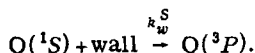
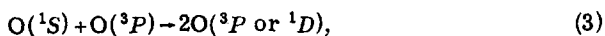
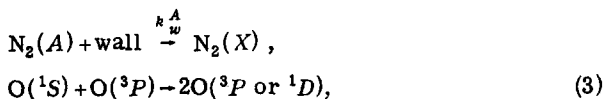
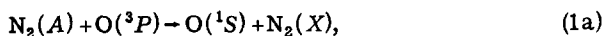
[NO] divided by κ , an apparatus calibration constant, gives [O]. We have discussed in detail previously how to determine κ .^{17,18} Even though small amounts of ozone could be by-products of the O-atom discharge, there can be no interference from the $O_3 + NO$ chemiluminescent reaction in the technique for determining the O-atom number density. The continuum generated from the $O_3 + NO$ reaction has a short wavelength cutoff of 600 nm.²⁵

A series of calibrations taken over a period of time established κ to $\pm 10\%$. The slopes of the $I_{O/NO}$ vs [NO] plots for the determination of [O] had standard deviations less than 5%. Thus, the determination of [O] is in principle accurate to $\pm 12\%$. Because the measurements of [O] were not made simultaneously with the kinetic measurements, it is possible that short-term variations in [O] could lead to differences between the number density of O measured and that actually in the reactor during the kinetic measurements. We shall assume these differences to be random and, therefore, included in the experimental scatter in the data analysis.

The molecular oxygen was purified by pumping on liquid O_2 prior to expanding the middle portion of the liquid O_2 into a 5 l storage bulb. The nitric oxide used in the O-number-density determinations was purified by slowly flowing NO through an ascarite trap, and then a trap at dry ice temperature prior to storage in a 5 l bulb.

III. ANALYSIS AND RESULTS

We have observed variations in the ratio of the intensity of the auroral green line, $O(^1S \rightarrow ^1D)$, at 558 nm to the Vegard-Kaplan 0,6 band as a function of atomic-oxygen number density and time. The processes which must be considered in the data analysis are



The differential equation which describes the change in the $N_2(A)$ number density as a function of time is

$$\frac{d[N_2(A)]}{dt} = -(k_1[O] + k_2[O_2] + k_w^A)[N_2(A)]. \quad (5)$$

Under pseudofirst-order conditions ($[N_2(A)] \ll [O], [O_2]$) it has the solution

$$[N_2(A)] = [N_2(A)]_0 e^{-K_A t}, \quad (6)$$

where $K_A = k_1[O] + k_2[O_2] + k_w^A$.

The differential equation for the temporal history of $O(^1S)$ is

$$\begin{aligned} \frac{d[O(^1S)]}{dt} = & k_{1a}[O][N_2(A)] - (k_3[O] + k_4[O_2] \\ & + k_w^S)[O(^1S)]. \end{aligned} \quad (7)$$

The analytical solution to this equation is

$$[O(^1S)] = \frac{k_{1a}[O][N_2(A)]_0}{K_S - K_A} \{e^{-K_A t} - e^{-K_S t}\}, \quad (8)$$

where $K_S = k_3[O] + k_4[O_2] + k_w^S$. Using the result in Eq. (6) and rearranging slightly gives

$$\frac{[O(^1S)]}{[N_2(A)]} = \frac{k_{1a}[O]}{K_S - K_A} \{1 - e^{-(K_S - K_A)t}\}. \quad (9)$$

This result ignores differences in decay rate between the different vibrational levels of $N_2(A)$. Allowing for the vibrational-level effect gives

$$\begin{aligned} \frac{[O(^1S)]}{[N_2(A)]_{v'=0}} = & \frac{k_{1a}^{v'=0}[O]}{K_S - K_{A,v'=0}} \{1 - \exp[-(K_S - K_{A,v'=0})t]\} \\ & + \frac{k_{1a}^{v'=1}[O]}{K_S - K_{A,v'=1}} \{1 - \exp[-(K_S - K_{A,v'=1})t]\} \\ & \times \frac{[N_2(A)]_{v'=1}^0}{[N_2(A)]_{v'=0}^0} \exp\{-\Delta k_1[O_2] + \Delta k_2[O]t\}, \end{aligned} \quad (10)$$

where $K_{A,v'=0,1}$ are as given above but with state-specific rate constants k_1 and k_2 , Δk_1 and Δk_2 are the differences in the respective rate constants between $v'=1$ and 0, respectively, and the super 0 on the $N_2(A)$ number densities represent initial conditions.

Our experimental observations consisted of measurements of the decay of the 0,6 Vegard-Kaplan band and of the $O(^1S)$ 558 nm line as a function of time over a range of O-atom number densities of $0.16 - 3.9 \times 10^{12}$ atoms cm^{-3} and effective reaction times of 18–29 ms, and a spectral scan over the Vegard-Kaplan bands at the beginning of each run to obtain a value for the ratio of $[N_2(A)]_{v'=1}^0/[N_2(A)]_{v'=0}^0$. Although the data showed only a small or negligible change in the ratio $I_{O(^1S)}/I_{0,6}$ as a function of time, the exponential term in Eq. (10) did contribute significantly to the overall kinetics so that a complete analysis of the data according to Eq. (10) was necessary.

Only two of the rate constants in Eq. (10) are unknown k_{1a} the subject of this investigation, and k_3 . Several values have been published for k_3 ^{26–28} spanning a range of several orders of magnitude. Slanger and Black²⁹ have shown recently, however, that some of these measurements were marred by the presence of $O_2(a^1\Delta)$ in the reactor in addition to atomic oxygen. $O_2(a^1\Delta)$ quenches $O(^1S)$ at a gas kinetic rate.²⁹ $O_2(a^1\Delta)$ was undoubtedly present in our measurements also, but at number densities so low that we would not have been able to measure them by conventional methods. However, Orgyzo has shown that the ratio of $[O_2(a^1\Delta)]/[O]$ produced in a discharge containing traces of molecular oxygen in argon or helium is constant at constant pressure, being independent of $[O_2]$.³⁰ Thus $[O_2(a^1\Delta)] \propto [O]$,

TABLE I. Rate constants used in data analysis.

Reaction	Rate constant ^a	Reference
(1) N ₂ (A) + O → products	2.8 × 10 ⁻¹¹ (v' = 0) 3.4 × 10 ⁻¹¹ (v' = 1)	17
(2) N ₂ (A) + O ₂ → products	2.3 × 10 ⁻¹² (v' = 0) 4.1 × 10 ⁻¹² (v' = 1)	19, 31, 32
(3) O(¹ S) + O(³ P) → products	< 10 ⁻¹¹	29
(4) O(¹ S) + O ₂ (X ³ Σ) → products	(3 ± 1) × 10 ⁻¹³	33–35
(5) O(¹ S) + O ₂ (α ¹ Δ) → products	1.7 × 10 ⁻¹⁰	29

^aRate constants are at 238 K and are in units of cm³ molecule⁻¹ s⁻¹.

and we can treat k_3 as an effective atomic-oxygen quenching rate constant which must be determined.

We have reported previously the rate constant k_1 ¹⁷ and our value for k_2 ¹⁹ agrees well with the other recent literature^{31,32} (see Table I). The rate constant k_4 ^{33–35} may safely be neglected compared to k_3 . The wall-loss rate constants k_w can be calculated from the known diffusion coefficients of N₂(A)^{36–38} and O(¹S)^{39,40} in argon since both species are quenched with unit efficiency at the reactor walls:

$$k_w = \frac{0.62 D_0}{\Lambda^2 P}, \quad (11)$$

where $\Lambda^2 = (a/\lambda_0)^2$ with λ_0 being the first root of the Bessel function J_0 , a the flow tube radius, D_0 the diffusion coefficient in argon, and the factor of 0.62 is included to correct for the coupling of the parabolic velocity profile with the radial density gradient of diffusing species. Corney and Williams³⁹ and Zipf⁴⁰ both have measured the diffusion coefficient of O(¹S) in argon at 298 K obtaining 268 ± 10 and 260 ± 6 cm² s⁻¹ at 1 Torr, respectively. We have analyzed our data with the value 265 cm² s⁻¹ at 1 Torr. Brömer and Spieweck,³⁷ Zipf,³⁸ and Levron and Phelps³⁸ all have determined the diffusion coefficient of N₂(A) in nitrogen to be 153 cm² s⁻¹ at 1 Torr while Levron and Phelps have also measured

the diffusion coefficient of N₂(A) in argon to be 153 ± 10 and 169 ± 6 cm² s⁻¹ at 1 Torr for $v' = 0$ and 1 of N₂(A), respectively. We have chosen to use the value 155 cm² s⁻¹ at 1 Torr for both vibrational levels. The diffusion coefficient of O(¹S) in argon is 15% larger than the diffusion coefficient of O(³P) in argon measured by Morgan and Schiff,⁴¹ while the N₂(A) diffusion coefficient is 8% larger than that for ground-state nitrogen.⁴²

The raw data in the form of an intensity ratio had to be corrected by the factor γ which relates intensities to populations

$$\gamma = \frac{R_{\lambda}^{1S} A_{1S} \beta}{R_{\lambda}^{0,6} A_{0,6}}, \quad (12)$$

where R_{λ}^i is the relative monochromator response function and A_i is the Einstein coefficient of species i [(0.163 for the 0,6 Vegard-Kaplan band⁴³ and 1.18 for the O(¹S – ¹D) transition⁴⁴), β is a correction factor relating the measured peak height of the 0,6 band to the integrated band intensity.

The reaction time is given by $(z - z_0)/\bar{v}$ where z is the distance from the injector to the observation region, z_0 is a mixing correction of 10%–15%, and \bar{v} is the bulk flow velocity. The analysis of the N₂(A) + O rate constants¹⁷ showed that $z_0 = 4.5$ cm under our experimental conditions.

We analyzed all our data using a nonlinear least-squares program based on Eq. (10) and the input parameters just discussed. The ratio k_{1a}/k_1 was assumed to be the same for both vibrational levels, even though the rate constants differ by about 20%. This assumption does not introduce significant uncertainties in the final value obtained for k_{1a} . The two parameters to be determined in the fit were $k_{1a}^{v'=0}$ and k_3 .

The results of the fit gave $k_{1a}^{v'=0} = (2.1 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $k_3 = (5.7 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where the quoted uncertainty is one standard deviation from the least-squares fit. The O(¹S) production ef-

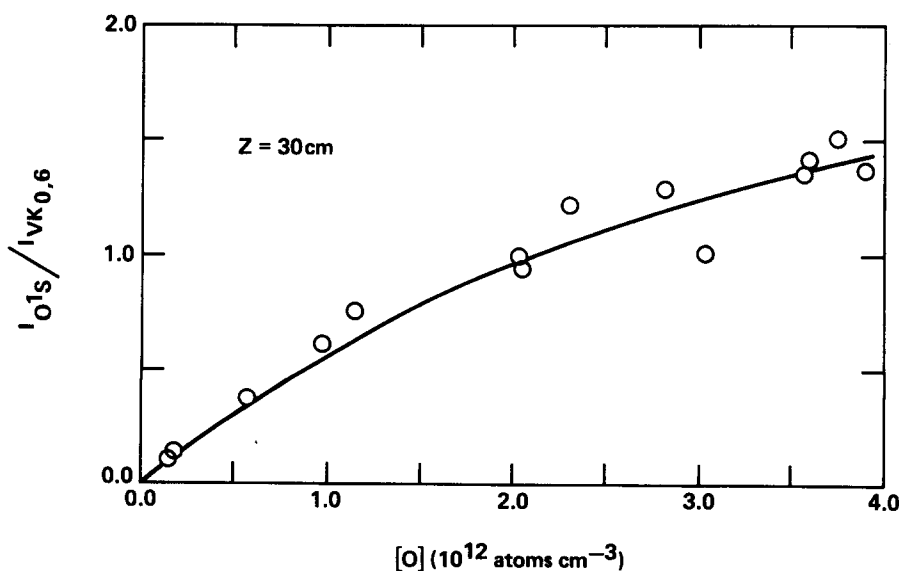


FIG. 1. Variation in ratio of O(¹S) emission intensity to that of Vegard-Kaplan 0,6 band as a function of [O] for a mixing distance of 30 cm.

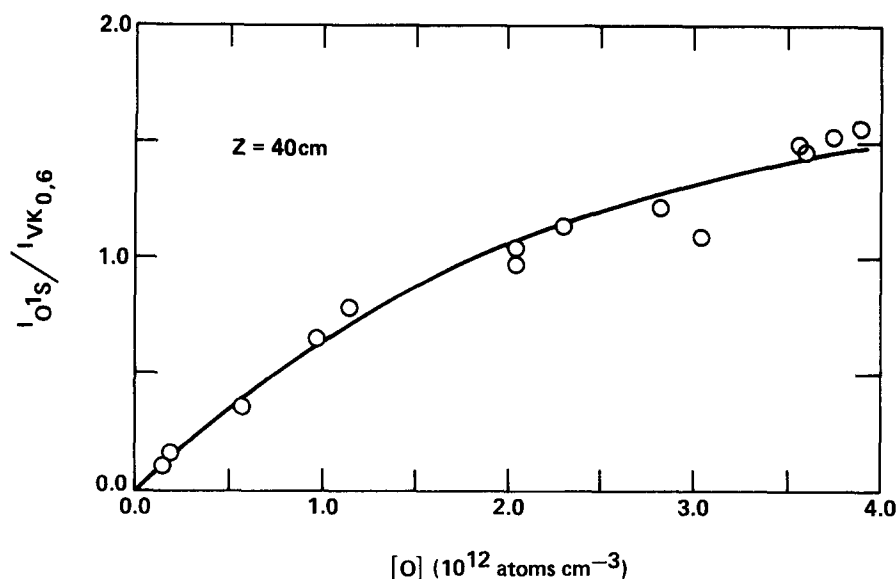


FIG. 2. Variation in ratio of $O(^1S)$ emission intensity to that of Vegard-Kaplan 0,6 band as a function of $[O]$ for a mixing distance of 40 cm.

efficiency η from this fit is 0.75. We did a sensitivity analysis of the data by varying in turn values of the $N_2(A)$ quenching rate constants, the difference between the $O(^1S)$ and $N_2(A)$ wall loss rate constants, the ratio $[N_2(A)]_{v'=1}^0/[N_2(A)]_{v'=0}^0$, and the mixing correction while holding the other parameters fixed at their normal values. The only significant changes came in varying the wall-loss rate-constant difference, where a change of $\pm 12\%$ changed $k_{1a}^{v'=0}$ by $\pm 5\%$, and the ratio $[N_2(A)]_{v'=1}^0/[N_2(A)]_{v'=0}^0$ where a $\pm 20\%$ variation gave a $\pm 7\%$ change in $k_{1a}^{v'=0}$. A complete error analysis in which all experimental uncertainties were estimated indicated a 17% uncertainty in the ratio η if the $\pm 20\%$ uncertainty in the Vegard-Kaplan transition probability is neglected, and a 27% overall uncertainty when the $A_{0,6}$ error estimate is included. The error limits on $k_{1a}^{v'=0}$ ($19\frac{1}{2}\%$ and $28\frac{1}{2}\%$ for neglect and inclusion of $A_{0,6}$ uncertainty, respectively) are slightly larger than those for the rate-constant ratio η due primarily to a cancellation of $[O]$ (12% uncertainty) in determining η .

Data at two reaction times are shown in Figs. 1 and 2. The line through the data is the best fit to Eq. (10) when pressure, flow velocity, and the ratio $[O]/[O_2]$ are assumed to be the same for all points. This fit gives

TABLE II. Excitation of $O(^1S)$ in $N_2(A) + O$ reaction.

Process	Value
(1a) $N_2(A)_{v'=0} + O(^3P) \rightarrow O(^1S) + N_2(X)$	$k_{1a} = (2.1 \pm 0.4) \times 10^{-11} \text{ a}$ $= (2.1 \pm 0.6) \times 10^{-11} \text{ b}$
(1b) $N_2(A)_{v'=0,1} + O(^3P) \rightarrow \text{all products}$	$k_1^{v'=0} = (2.8 \pm 0.4) \times 10^{-11} \text{ c}$ $k_1^{v'=1} = (3.4 \pm 0.6) \times 10^{-11} \text{ c}$ $k_{1a} = 0.75 \pm 0.13$ $k_1 = 0.75 \pm 0.20 \text{ b}$

^aRate constants are at 298 K and are in units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

^bThe error estimates of these values include the 20% uncertainty in $A_{VK_{0,6}}$.

^cReference 17.

values of k_{1a} and k_3 about 10% larger than the complete fit. Our results are summarized in Table II.

IV. DISCUSSION

If we assume that some of the $O(^1S)$ quenching is by $O_2(a^1\Delta)$ rather than by O , then the least-squares fit k_3 represents an effective $O_2(a^1\Delta)$ quenching rate constant k_3^{eff} :

$$k_3^{eff} = k_3 + k_5 \frac{[O_2(a^1\Delta)]}{[O]} \quad (13)$$

If k_3 is negligible, Slanger and Black's²⁰ value of k_5 ($1.7 \times 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) along with our experimentally derived k_3^{eff} gives $[O_2(a^1\Delta)]/[O] = 0.34$. We would not have been able to measure such small amounts of $O_2(a^1\Delta)$ in our reactor using conventional techniques.

The presence of $O_2(a^1\Delta)$ in our reactor in no way affects the value obtained for k_{1a} . The reaction between $N_2(A)$ and $O_2(a^1\Delta)$ lacks sufficient energy to give $O(^1S)$ as a product. However, if $O_2(a^1\Delta)$ is a very efficient quencher of $N_2(A)$ (i.e., a rate constant $> 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) then our previously reported rate constant for quenching $N_2(A)$ by O^{17} could be too high as we have already discussed. In this event, the value of η deduced in these studies would be too low and a value closer to unity would be correct. The $[O_2(a^1\Delta)]/[O]$ ratio estimated above and the constraint that $\eta \leq 1$ limits the $N_2(A) + O_2(a^1\Delta)$ rate constant to be less than or equal to $2 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

Within the past ten years, aeronomers have tried to explain auroral observations of Vegard-Kaplan and OI 558 nm emissions by proposing total $N_2(A) + O$ quenching rate constants between 1.5 and $40 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and $O(^1S)$ excitation efficiencies between 0.13 and unity. We feel that the present measurements on $O(^1S)$ excitation and our earlier $N_2(A) + O$ rate constant determination¹⁷ should remove one long standing source of controversy in trying to reconcile auroral models with auroral measurements. Other parameters in auroral models such as atomic oxygen number density, $N_2(A)$

excitation mechanism and O(¹S) quenching rates are now less certain than the kinetics of the N₂(A)+O interaction, and should receive more attention in the future.

Swider⁴⁵ suggested that the reaction between N₂(A) and O could be an important source of NO in auroras and perhaps in the quiet daytime E region. The results of this study indicate that the reactive channel is minor compared to the direct energy-transfer channel. Thus NO production does not appear to be a major consequence of the N₂(A)+O interaction. We do plan to investigate the importance of this reactive channel in the near future, however, as a check on the present results.

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- ¹J. A. Meyer, D. W. Setser, and D. H. Stedman, *Astrophys. J.* **157**, 1023 (1969).
- ²T. D. Parkinson and E. C. Zipf, *Planet. Space Sci.* **18**, 895 (1970).
- ³K. Henriksen, *Planet. Space Sci.* **21**, 863 (1973).
- ⁴A. W. Yau and G. G. Shepherd, *Planet. Space Sci.* **27**, 481 (1978).
- ⁵W. E. Sharp and D. G. Torr, *J. Geophys. Res.* **84**, 5345 (1979).
- ⁶R. R. O'Neil, E. T. P. Lee, and E. R. Huppi, *J. Geophys. Res.* **84**, 823 (1979).
- ⁷D. M. Hunten and M. B. McElroy, *Rev. Geophys.* **4**, 303 (1966).
- ⁸W. E. Sharp, *J. Geophys. Res.* **76**, 987 (1971).
- ⁹D. E. Shemansky, E. C. Zipf, and T. M. Donahue, *Planet. Space Sci.* **19**, 1669 (1971).
- ¹⁰A. Vallance-Jones and R. L. Gattinger, *J. Geophys. Res.* **81**, 497 (1976).
- ¹¹M. H. Rees, G. G. Sivjee, and K. A. Dick, *J. Geophys. Res.* **81**, 6046 (1976).
- ¹²A. J. Deans and G. G. Shepherd, *Planet. Space Sci.* **26**, 319 (1978).
- ¹³W. E. Sharp, M. H. Rees, and A. I. Stewart, *J. Geophys. Res.* **84**, 1977 (1979).
- ¹⁴D. G. Torr and W. E. Sharp, *Geophys. Res. Lett.* **6**, 860 (1979).
- ¹⁵J. A. Meyer, D. W. Setser, and D. H. Stedman, *J. Phys. Chem.* **74**, 2238 (1970).
- ¹⁶O. J. Dunn and R. A. Young, *Int. J. Chem. Kinet.* **8**, 161 (1976).
- ¹⁷L. G. Piper, G. E. Caledonia, and J. P. Kenealy, *J. Chem. Phys.* **75**, 2847 (1981).
- ¹⁸G. E. Caledonia, L. G. Piper, W. T. Rawlins, and B. D. Green, PSI TR-233 (1980), available from the authors upon request.
- ¹⁹L. G. Piper, G. E. Caledonia, and J. P. Kenealy, *J. Chem. Phys.* **74**, 2888 (1981).
- ²⁰D. W. Setser, D. H. Stedman, and J. A. Coxon, *J. Chem. Phys.* **53**, 1004 (1970).
- ²¹D. H. Stedman and D. W. Setser, *Chem. Phys. Lett.* **2**, 542 (1968).
- ²²N. Sadeghi and D. W. Setser, *Chem. Phys. Lett.* **82**, 44 (1981).
- ²³F. Kaufman, *Proc. R. Soc. London Ser. A* **247**, 123 (1958).
- ²⁴F. Kaufman, *Chemiluminescence and Bioluminescence*, edited by M. J. Cormier, D. M. Hercules, and J. Lee (Plenum, New York, 1973), pp. 83-100.
- ²⁵P. N. Clough and B. A. Thrush, *Trans. Faraday Soc.* **63**, 915 (1967).
- ²⁶W. Felder and R. A. Young, *J. Chem. Phys.* **56**, 6028 (1972).
- ²⁷T. G. Slanger and G. Black, *J. Chem. Phys.* **64**, 3763 (1976).
- ²⁸For a review of the O(¹S)+O quenching literature see D. R. Bates, *Planet. Space Sci.* **26**, 897 (1978).
- ²⁹T. G. Slanger and G. Black, *Geophys. Res. Lett.* **8**, 535 (1981).
- ³⁰E. A. Ogryzlo (private communication, 1980).
- ³¹E. C. Zipf, *Nature (London)* **287**, 523 (1980).
- ³²M. P. Ianuzzi and F. Kaufman, *J. Phys. Chem.* **85**, 2163 (1981).
- ³³T. G. Slanger, B. J. Wood, and G. Black, *Chem. Phys. Lett.* **17**, 401 (1972).
- ³⁴S. V. Filseth, F. Stuhl, and K. H. Welge, *J. Chem. Phys.* **52**, 239 (1970).
- ³⁵R. Atkinson and K. H. Welge, *J. Chem. Phys.* **57**, 3689 (1972).
- ³⁶E. C. Zipf, *J. Chem. Phys.* **38**, 2034 (1963).
- ³⁷H. H. Brömer and F. Spieweck, *Planet. Space Sci.* **15**, 689 (1971).
- ³⁸D. Levron and A. V. Phelps, *J. Chem. Phys.* **69**, 2260 (1978).
- ³⁹E. C. Zipf, *Bull. Am. Phys. Soc.* **14**, 264 (1969).
- ⁴⁰A. C. Corney and J. Williams, *J. Phys. B* **5**, 686 (1971).
- ⁴¹J. E. Morgan and H. I. Schiff, *Can. J. Chem.* **42**, 2300 (1964).
- ⁴²J. O. Hirschfelder, C. J. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- ⁴³D. E. Shemansky, *J. Chem. Phys.* **51**, 689 (1969).
- ⁴⁴C. Nicolaides, O. Sinanoğlu, and R. Westhouse, *Phys. Rev. A* **4**, 1400 (1971).
- ⁴⁵W. Swider, *Geophys. Res. Lett.* **3**, 335 (1976).