

The rate coefficient for quenching $N(^2D)$ by $O(^3P)$

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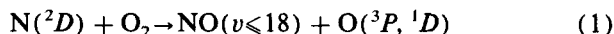
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We have studied the quenching of $N(^2D)$ by atomic oxygen in a discharge-flow reactor. Vacuum ultraviolet resonance fluorescence is used to detect the metastables. Three different discharge-based sources provide the atomic oxygen: discharged O_2/Ar , discharged N_2O/Ar , and the reaction of N with NO . Results from the three different approaches are congruent and indicate the lack of significant systematic errors in the study. The rate coefficient at 300 K is $(1.06 \pm 0.26) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

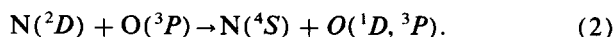
I. INTRODUCTION

The reaction of $N(^2D)$ with O_2 ,

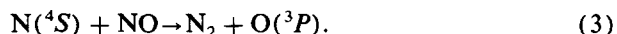


is the major source of NO in the upper atmosphere.¹ Radiation from vibrationally excited NO is one of the primary pathways for cooling the upper atmosphere. Collisions with translationally hot O atoms and absorption of earth shine radiation are the primary mechanisms for exciting $NO(v)$ in the quiescent atmosphere, whereas reaction (1) is the primary source of $NO(v)$ under auroral conditions. Because $N(^2D)$ controls NO production rates in the upper atmosphere, understanding $N(^2D)$ chemistry is essential to understanding upper atmospheric radiative transport.

Caledonia and Kennealy have shown that one of the controlling factors of $N(^2D)$ number densities in the upper atmosphere is the quenching of $N(^2D)$ by atomic oxygen



Efficient quenching by O will reduce $N(^2D)$ number densities and thereby those of NO . Conversely, inefficient quenching will result ultimately in increased NO production. Reaction (2) also affects the total atmospheric NO in that efficient quenching of $N(^2D)$ by O not only reduces the total NO by moderating its production via reaction (1), but also it generates² $N(^4S)$ which is a sink for atmospheric NO via reaction (3)



The magnitude of the rate coefficient for reaction (2) has been the subject of considerable controversy over a number of years and is considered to be uncertain to within at least a factor of 3. This uncertainty in the quenching rate coefficient, therefore, lends considerable uncertainty to efforts to model NO in the upper atmosphere as well as radiative cooling of the atmosphere.

In 1976, Davenport *et al.*³ used vacuum ultraviolet (VUV) resonance absorption to monitor $N(^2D)$ number densities in a discharge-flow reactor to determine a ratio $k_1/k_2 = 3.0 \pm 0.5$. Assuming a value for k_1 of $5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, they reported $k_2 = (1.8 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Several years later, Iannuzzi and Kaufman⁴ monitored $N(^2D)$ in the presence of atomic oxygen with a VUV resonance-fluorescence diagnostic and

reported an upper limit to reaction (2) which agreed with the value given by Davenport *et al.*

Modeling studies, on the other hand, generally have favored values for k_2 which are factors of 2 or more lower than those proposed by Davenport *et al.* and by Iannuzzi and Kaufman. Frederick and Rusch,⁵ e.g., modeled $N(^2D)$ profiles from airglow measurements taken by Atmospheric Explorer C and D and concluded that k_2 must be $4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A similar modeling effort by Richards *et al.*² concluded that Frederick and Rusch underestimated $N(^2D)$ production rates and revised their value upwards slightly to $6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Cravens *et al.*⁶ and Strobel *et al.*⁷ modeled NO profiles in the upper atmosphere and concluded that $k_2 = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas similar modeling efforts by Oran *et al.*⁸ concluded $k_2 < 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Fensen *et al.*⁹ recently modeled the altitude profiles of $N(^2D)$, $N(^4S)$, and NO simultaneously and found their model best matched airglow data for $k_2 = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Recently Jusinski *et al.*¹⁰ reported a laboratory measurement of $(2.1 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for this reaction at room temperature. This value is an order of magnitude greater than previous laboratory measurements and even more discordant with the estimates derived from atmospheric modeling.

The discrepancies between the various laboratory and aeronomic results are such that additional laboratory investigations of this reaction were imperative. We have studied this reaction in a discharge-flow reactor using a sensitive resonance-fluorescence diagnostic for the $N(^2D)$ atoms. We used three different sources for the atomic oxygen to try to reduce systematic errors. In each of these sources, the atomic oxygen is prepared separately from the $N(^2D)$ and then mixed only subsequently. The three different sets of experiments give consistent results and indicate that the two old laboratory measurements of the rate coefficient are about a factor of two too large.

II. EXPERIMENTAL

A. Apparatus

The experiments were carried out in the 2-in. diameter discharge-flow reactor shown schematically in Fig. 1. The $N(^2D)$ was generated at the upstream end of the reactor in a

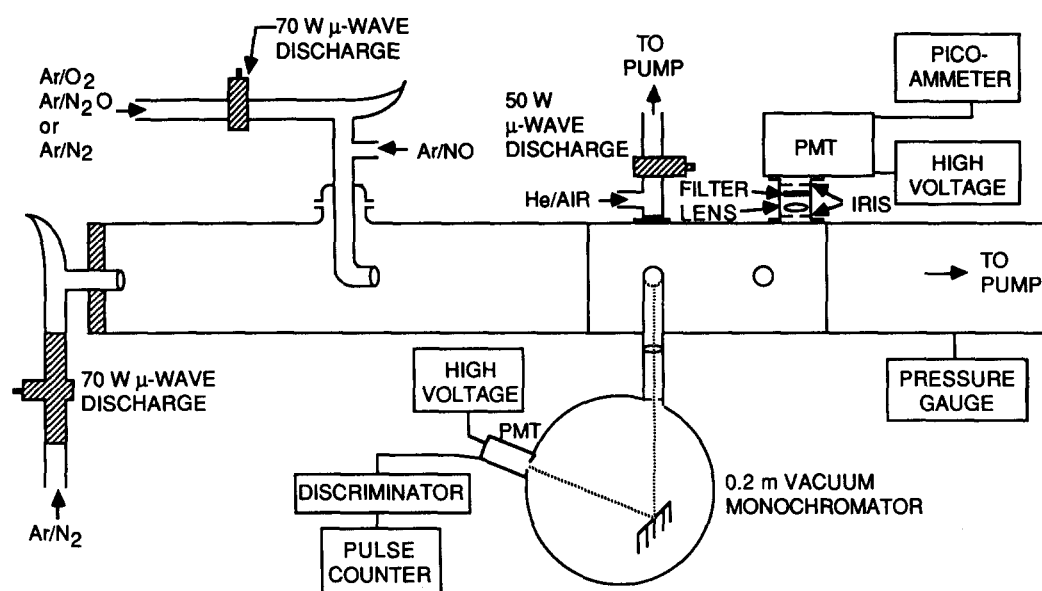


FIG. 1. Apparatus for studying the kinetics of $N(^2D)$ with $O(^3P)$.

70 W microwave discharge of 1% to 2% nitrogen in argon. Further downstream, a flow of atomic oxygen enters the reactor through a hook-shaped injector. At the extreme downstream end of the reactor, $N(^2D)$ number densities are monitored by vacuum-ultraviolet resonance fluorescence. We have detailed out general procedures for monitoring $N(^2D)$ and measuring its kinetics previously.¹¹

The three different sources of atomic oxygen are all microwave-discharge based, the discharge being upstream in the hook-shaped injector. One source consists of discharging mixtures of argon and molecular oxygen. In some cases, small amounts of SF_6 were added to the discharge to enhance the oxygen dissociation. Adding SF_6 to the discharge in the absence of oxygen had no effect on the $N(^2D)$ number densities. The principal effluents of this discharge will be O , $O_2(X^3\Sigma_g^-)$, and $O_2(a^1\Delta_g)$. We describe tests for the effects of $O_2(a)$ below.

The second source of atomic oxygen was a microwave discharge through a mixture of argon and nitrous oxide, or in some instances argon, nitrogen, and nitrous oxide. We have shown previously¹² that at low mole fractions of nitrous oxide this discharge produces oxygen and nitrogen atoms, with the oxygen generally being at least an order of magnitude more abundant than the nitrogen. The small N-atom flows do not affect our kinetic measurements because atomic nitrogen is not a significant quencher of $N(^2D)$. At higher mole fractions of nitrous oxide, nitric oxide accompanies the atomic oxygen out of the discharge. Since NO reacts readily with $N(^2D)$,^{13,14} such conditions are to be avoided. Adding molecular nitrogen to the discharge defers the production of nitric oxide to larger nitrous oxide mole fractions. Undissociated N_2O , and perhaps O_2 or $O_2(a)$, which might be produced by recombination in the active discharge, are also effluents of this discharge source.

Our third source of atomic oxygen was to titrate N atoms with NO in the injector, upstream from its opening into the main flow tube. In this case, we discharged mixtures of N_2 and SF_6 in Ar. The SF_6 greatly enhanced N_2 dissociation.¹⁵ For some experiments we placed a glass-wool plug

downstream from the discharge, but upstream from the NO injector to ensure removal of excited states of atomic and molecular nitrogen produced in the discharge.¹⁶ The presence of the glass-wool plug had no effect on results.

We studied the conditions under which the $N + NO$ titration was complete within the injector by replacing the microwave discharge with an $N_2(A)$ generator and looking for the escape of NO from the injector. $N_2(A)$ excites strong NO γ -band fluorescence,¹⁷ $NO(A^2\Sigma^+ - X^2\Pi)$ in an electronic energy-transfer reaction. Observing γ -band fluorescence, therefore, signals the escape of unreacted NO from the injector. We failed to observe significant γ -band intensities until the NO flow approached the titration end point. Chemiluminescence monitoring with a downstream photometer determined the titration end point unambiguously (*vide infra*).

Turning on the secondary discharge to make the atomic nitrogen increased the resonance fluorescence signals between 5% and 30%, depending upon conditions, i.e., N-atom number density and total pressure. Apparently $N(^2D)$ is formed in an atom recombination process similar to that which is known to generate $N(^2P)$ (*vide infra*). This additional contribution to the resonance-fluorescence signal varied with the amount of NO added to the injector flow and had to be subtracted, therefore, from the signal due to metastables produced in the primary discharge. Ignoring it would have resulted in rate coefficients that were too large.

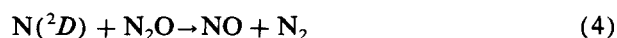
Atomic oxygen number densities were monitored by measuring the O/NO air afterglow when nitric oxide was added to the flow reactor with the $N(^2D)$ discharge off. A photometer consisting of an interference filter centered at 580 nm, with a full width at half-maximum bandpass of 10 nm, and an HTV R-955 photomultiplier detected the air-afterglow fluorescence. O-atom number densities were determined for each flow rate of O_2 or N_2O , and the photometer calibration was checked after each run under the identical flow and pressure conditions of the run. Previous reports detail our procedures for measuring O-atom number densities from air-afterglow observations as well as our pho-

tometer-calibration procedures.^{12,18}

Typical conditions in the reactor include main argon and nitrogen flow rates of 1500–4000 and 25–75 $\mu\text{mol s}^{-1}$, respectively, argon and nitrogen flows through the injector discharge of 200–700 and 15–100 $\mu\text{mol s}^{-1}$, respectively, reagent O_2 , N_2O , or NO flows of 0–8, 0–20, and 0–6 $\mu\text{mol s}^{-1}$, respectively, SF_6 flow rates less than or equal to 0.05 $\mu\text{mol s}^{-1}$, and total pressures between 0.8 and 3 Torr. The fixed injector was situated either 34 or 44 cm from the observation region. Effective reaction times were varied by altering the total flow rate and the pumping speed of the system. These times ranged between 4.5 and 21 ms.

B. Experimental technique

In addition to reactions (1) and (2), important processes for removing $N(^2D)$ in our reactor are



and



For the case of using O_2 as a source of atomic oxygen, the differential equation describing the rate of change in the $N(^2D)$ number density with time is

$$\frac{d[N(^2D)]}{dt} = -\{k_5 + k_1[O_2]\}[N(^2D)], \quad (6)$$

for the case where the injector discharge is off, and

$$\frac{d[N(^2D)]}{dt} = -\{k_5 + k_2[O] + k_1[O_2]\}[N(^2D)] \quad (7)$$

when the injector discharge is on. Because the number density of $N(^2D)$ is much smaller than that of either O or O_2 , these two differential equations are effectively first order and can be solved analytically. The resulting solutions become

$$\ln\left\{\frac{[N(^2D)](t)}{[N(^2D)](t=0)}\right\} = -\{k_5 + k_1[O_2]\}t \quad (8)$$

with the discharge off, and

$$\ln\left\{\frac{[N(^2D)](t)}{[N(^2D)](t=0)}\right\} = -\{k_5 + k_2[O] + k_1[O_2]\}t \quad (9)$$

with the discharge on.

The decay coefficient Γ is minus one times the variation in the natural log of the $N(^2D)$ number density as a function of molecular oxygen number density at a fixed time. With the discharge off, we have

$$\Gamma_{\text{off}} = -\frac{d \ln I_{\text{off}}}{d[O_2]} = k_1 t, \quad (10)$$

where we have exploited the fact that the $N(^2D)$ number density is directly proportional to the resonance-fluorescence intensity I .¹¹

When the discharge is on, some of the molecular oxygen is dissociated to make atomic oxygen. The relationship between the number densities of the two species is

$$[O] = 2\alpha[O_2]_0 \quad (11)$$

and

$$[O_2] = (1 - \alpha)[O_2]_0, \quad (12)$$

where the subscript 0 indicates the number density which would have been obtained in the absence of dissociation, i.e., the number density with the discharge off, and α is the fractional dissociation. In terms of experimentally measured quantities

$$\alpha = \frac{[O]}{2[O_2]_0}. \quad (13)$$

When the molecular-oxygen mole fraction in the discharge region is on the order of 1% or less, α is invariant to changes in the oxygen flow rate. This allows the decay coefficient with the discharge on to be expressed as

$$\Gamma_{\text{on}} = -\frac{d \ln I_{\text{on}}}{d[O_2]_0} = \{2\alpha k_2 + (1 - \alpha)k_1\}t. \quad (14)$$

The basic experimental approach is to determine decay coefficients with the discharge on and with it off. Any differences between the two measurements result from differences between the rate coefficients for reactions (1) and (2). Ratiating Eqs. (10) and (14) gives

$$\frac{\Gamma_{\text{on}}}{\Gamma_{\text{off}}} = 2\alpha \frac{k_2}{k_1} + 1 - \alpha. \quad (15)$$

Equation (15) can be solved to give the ratio of the rate coefficients k_2 to k_1 in terms of the experimentally measured quantities α and the ratio of the decay coefficient with the discharge on to that with it off. Since we have previously established¹¹ that the rate coefficient for reaction (1) is $(4.6 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, k_2 can be determined unambiguously.

A similar approach results from using discharged N_2O as the atomic-oxygen source. In this case, the relevant data-analysis equation is

$$\frac{\Gamma_{\text{on}}}{\Gamma_{\text{off}}} = \alpha \frac{k_2}{k_4} + 1 - \alpha, \quad (16)$$

where we have assumed that undissociated nitrous oxide is the primary effluent, in addition to atomic oxygen, exiting the discharge. If instead of N_2O the other effluent from the discharge is molecular oxygen, the analysis equation becomes

$$\frac{\Gamma_{\text{on}}}{\Gamma_{\text{off}}} = \frac{1}{k_4} \left\{ \alpha k_2 + \frac{1 - \alpha}{2} k_1 \right\}. \quad (17)$$

Given that the ratio of the rate coefficients $k_1/k_4 = 2.1 \pm 0.3$, Eq. (17) will give similar results to those derived using Eq. (16). Here again we determine k_2 from the ratio of two rate coefficients. We have shown previously¹¹ that $k_4 = (2.2 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Generating O atoms from the reaction between N and NO results in a much simpler analysis. The basic measurement is of the decay coefficient, determined similarly to Eq. (10), but as a function of added nitric oxide number density [i.e., the number density of nitric oxide which would be obtained in the absence of reaction (3)]. This analysis relies on the fact that reaction (3) is stoichiometric.¹⁹ In addition, we assume that none of the atomic oxygen recombines on the injector walls prior to injection into the flow reactor. Given

that the injector was Teflon coated, this is a reasonable assumption. In order to avoid the uncertainties of mixing and flow development, we divided the decay coefficients we obtained by decay coefficients for molecular oxygen removal of $N(^2D)$ measured under identical conditions. This result again gives the ratio of rate coefficients k_2/k_1 .

III. RESULTS

Figures 2 and 3 show examples of data taken using O_2 and N_2O , respectively, as atomic-oxygen sources. These figures show clearly that the effect of turning on the discharge is to *reduce* the effective decay coefficient. This can be so only if some discharge-produced species has a *smaller* rate coefficient than does either O_2 or N_2O . Since the major discharge-produced species in both cases is atomic oxygen, it follows that k_2 must be less than either k_1 or k_4 .

Another significant discharge effluent from both sources, but especially from the molecular oxygen source, is electronically excited $O_2(a^1\Delta_g)$. In several experiments, we tried to enhance the production of $O_2(a)$ by placing a nickel screen downstream from the discharge in the injector. The screen recombines some of the atoms into molecular electronic states which readily quench to $O_2(a^1\Delta)$ in the presence of O_2 .²⁰ The rate coefficients obtained for O-atom quenching agreed within experimental error to those obtained without the presence of the screen, but under otherwise similar conditions. This suggests that $O_2(a^1\Delta)$ quenching of $N(^2D)$ is similar to $O_2(X)$ quenching.

Figure 4 shows the results of two different experiments using the reaction between N and NO as the O-atom source. In both cases, the decay is relatively slow, but as the lower curve shows conclusively, the decay rate increases dramatically past the N-atom titration end point when NO is allowed to enter the flow reactor. Clearly the NO reacts much

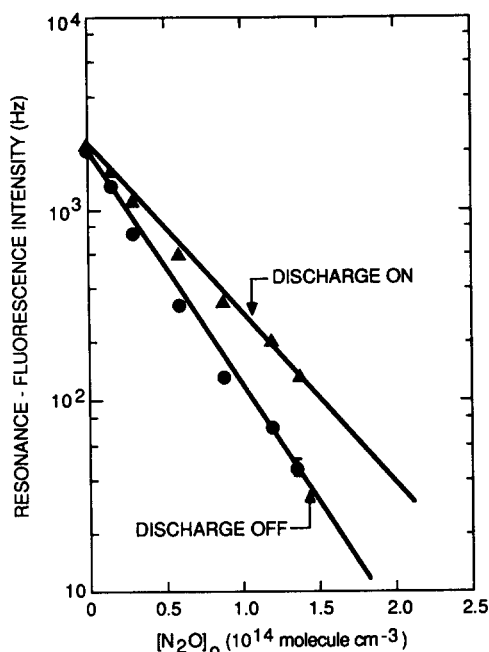


FIG. 3. Decay of $N(^2D)$ resonance-fluorescence intensity as a function of the number density of discharged and undischarged N_2O .

more rapidly with the $N(^2D)$ than does the atomic oxygen. The much greater number densities of ground-state nitrogen atoms than $N(^2D)$ in the flow reactor do not remove the NO by reaction (3) fast enough to protect $N(^2D)$ from NO quenching. One must be careful, therefore, to prepare the atomic oxygen reagent in the injector, removed from the $N(^2D)$ reactant.

Our approach for determining k_2 has the distinct advantage that by determining it from the ratio of two rate coefficients, one of which is already well established, uncertainties introduced by poor mixing or incompletely developed laminar flow conditions are eliminated. This is an important

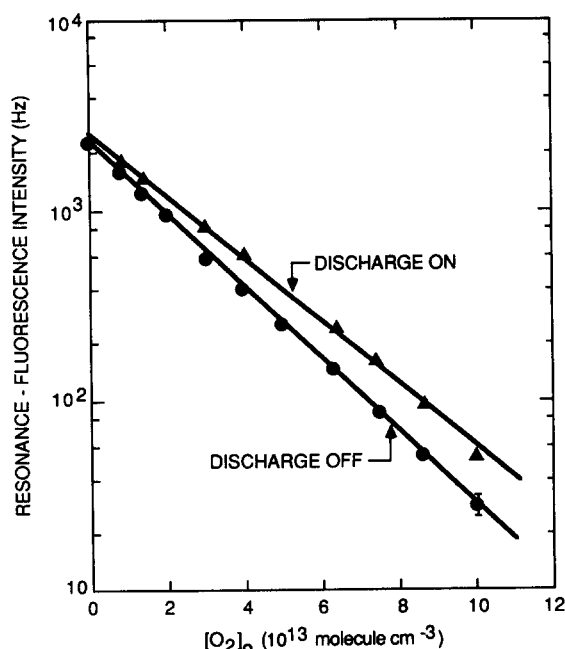


FIG. 2. Decay of $N(^2D)$ resonance-fluorescence intensity as a function of the number density of discharged and undischarged O_2 .

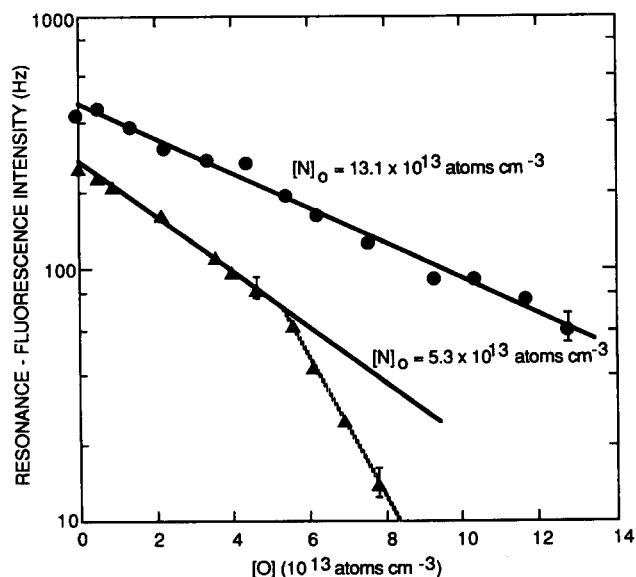


FIG. 4. Decay of $N(^2D)$ resonance-fluorescence intensity as a function of atomic-oxygen number density.

point because hook-shaped injectors generally do not give the good mixing that results from using loop injectors. Furthermore mixing corrections cannot be explored easily using a fixed injector. We have shown previously that such corrections can at times be considerable in studies of metastable kinetics.¹¹

The problem with mixing in our system is not associated with the reliability of decay coefficient measurements, but rather with estimating the effective reaction time. The two orders of magnitude linearity of our decay plots ensures absence of secondary processes or uneven mixing. A few milliseconds are required, however, before the injected quenchers are distributed uniformly throughout the reactor. This finite time to achieve a uniform distribution means that the effective reaction time may be somewhat different from that calculated from the ratio of the distance between the injector and observation region to the average flow velocity. By making decay measurements on a molecule whose quenching rate coefficient is already well known, we effectively calibrate the injector for imperfect mixing. In these experiments, the mixing correction generally amounted to a 20% to 30% reduction in the effective reaction time. Ignoring it would result in the measurement of rate coefficients which were *too small* by that amount. Note that the correction enters the data analysis explicitly only in the runs using the $N + NO$ source. The other two sources result in the direct determination of a rate coefficient ratio and the effective reaction time does not enter the analysis. All three approaches give the same result. The results were invariant, furthermore, to changes in reactor pressure or effective reaction time. We are confident, therefore, that major systematic errors have been eliminated from our measurements.

Table I summarizes our results for the various experimental runs. The error bars represent 1σ standard deviations. The error bars on the weighted averages include the uncertainties in the reference rate coefficients and the weighted average of the three sets of data include an additional 10% uncertainty to account for possible determinate errors. At the 95% confidence level, 2σ , our experiments indicate that k_2 is $(1.06 \pm 0.26) \times 10^{-12} \text{ molecule}^{-1} \text{ s}^{-1}$.

IV. DISCUSSION

A. Comparison with the literature

Our results are somewhat lower than the two earliest experimental studies,^{3,4} but do agree with them within the limits of experimental error. Agreement with the aeronomically derived values of Cravens *et al.*,⁶ of Strobel *et al.*,⁷ and Fensen *et al.*⁹ is very good, and agreement with Richards *et al.*² model-derived value is acceptable.

The major disagreement with the recent results of Jusinski *et al.*¹⁰ indicates the likelihood of a large systematic error in those experiments. The basis of their experiment was to add NO directly to the flowing stream of active nitrogen, and to rely on the much greater number density of ground-state nitrogen atoms than of metastable nitrogen atoms to convert the NO to atomic oxygen before the NO had a chance to diminish the $N(^2D)$ number density significantly.

TABLE I. Results of $N(^2D) + O$ studies.

O-atom source	Run number	α	k_2 ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Weighted average ^a k_2 ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
O_2	1	0.16	1.56 ± 0.78	1.21 ± 0.18
	2	0.30	1.61 ± 0.69	
	3	0.61	1.06 ± 0.32	
	4	0.57	0.92 ± 0.32	
	5	0.34	0.55 ± 0.46	
	6	0.37	1.43 ± 0.18	
	7	0.15	0.92 ± 0.67	
N_2O	1	0.34	0.88 ± 0.13	0.90 ± 0.13
	2	0.27	0.68 ± 0.12	
	3	0.26	0.77 ± 0.17	
	4	0.46	1.19 ± 0.25	
	5	0.40	1.32 ± 0.11	
	6	0.41	0.70 ± 0.11	
$N + NO$	1		1.10 ± 0.064	1.15 ± 0.13
	2		1.19 ± 0.064	
	3		1.17 ± 0.074	
				1.06 ± 0.13^b

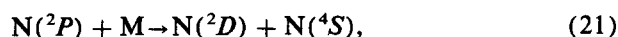
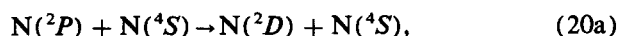
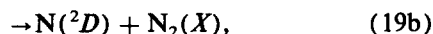
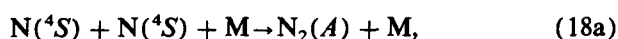
^a Includes uncertainties in reference rate coefficients.

^b Includes estimated 10% uncertainty for systematic errors.

In principle, this approach should work provided that the difference in number densities between $N(^4S)$ and $N(^2D)$ is sufficiently great and provided that mixing is instantaneous and uniform. In practice, the approach does not work. Figure 4, as well as the results of similar experiments by Iannuzzi and Kaufman,⁴ shows that adding NO to a stream of active nitrogen greatly enhances the rate of removal of $N(^2D)$ over that due to atomic oxygen.

Jusinski *et al.* suggested a number of alternative explanations for their obtaining a rate coefficient a factor of 10 larger than previous investigations suggested. They dismissed them all as unreasonable. We feel, however, that three of their alternative explanations might have more credence than they admitted. These three possibilities are that $N(^2D)$ is created downstream from the microwave discharge via an N-atom recombination process, that downstream $N(^2D)$ production results from the reaction between $N_2(X, v'' \geq 9)$ and $N(^4S)$, or that the $N(^2D)$ reacted with NO before the N atoms in the flow consumed the NO. An additional complication, not discussed by Jusinski *et al.*, is that by adding electron-attaching quenchers, they might have reduced the efficiency of their ion-collection system. An apparent reduction in signal, therefore, might be mistaken for quenching rather than just a change in detection sensitivity.

The first possibility is that $N(^2D)$ might be created in N-atom recombination by a mechanism involving the following sequence of reactions:



Reaction (21) can be neglected for the the Jusinski *et al.* experiment because neither nitrogen nor helium quench $N(^2P)$.^{13,21,22} Had they used an argon carrier, reaction (21) would have had to be considered.⁴

A steady-state analysis using reactions (5), (18), and (19b) gives

$$[N(^2D)] = \frac{k_{18a}}{k_5} \frac{k_{19b}}{k_{19}} [N]^2 [M]. \quad (22)$$

If reaction (20) were responsible for $N(^2D)$ excitation, the relevant steady-state expression would be

$$[N(^2D)] = \frac{(k_{18a}/k_5)(k_{19a}/k_{19})k_{20a}}{k_5 + k_{20}[N]} [N]^3 [M]. \quad (23)$$

Whether or not the two $N(^2D)$ excitation mechanisms described by Eqs. (22) and (23) scale differently with N-atom number density depends upon the relative magnitudes of k_5 and $k_{20}[N]$. The rate of wall quenching k_5 is controlled by diffusion to the walls. Lin and Kaufman²¹ have reported a diffusion coefficient for $N(^2D)$ in helium of $790 \text{ cm}^2 \text{ s}^{-1}$ at one Torr, from which we calculate that in Jusinski *et al.*'s 10 mm diameter reactor $k_5 \sim 1.13 \times 10^4/p$, where p is the pressure in Torr. Taghipour and Brennen²² and Young and Dunn²³ have shown the rate coefficient for $N(^2P)$ quenching by $N(^4S)$ to be $6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For the conditions typical in the Jusinski *et al.* experiment, the ratio $k_{20}[N]/k_5$ will generally be less than 0.3. The mechanism described by Eq. (23), therefore, will scale approximately as the cube of the N-atom number density in contrast to that described by Eq. (22), which scales as the N-atom number density squared. The high N-atom number densities and high pressures in Jusinski *et al.*'s system makes $N(^2D)$ production by these mechanisms likely.

Our recent studies²⁴ on the production of $N(^2P)$ in reaction (19) indicated that $N(^2D)$ was also produced in our reactor. Our observations did not allow us to distinguish direct production of $N(^2D)$ in reaction (19b) from indirect production resulting from $N(^2P)$ quenching by nitrogen atoms or argon, reactions (20a) and (21) [using theoretical arguments, Taghipour and Brennen²² support $N(^2D)$ as the primary product in this quenching reaction]. The present measurements showed quite clearly a residual $N(^2D)$ signal when the primary discharge was turned off. This residual signal was proportional to the product of the square of the N-atom number density and the total pressure. This scaling, as given in Eq. (22), suggests direct $N(^2D)$ production via reactions (18) and (19b).

At 3 Torr, with an N-atom number density of 1.3×10^{14}

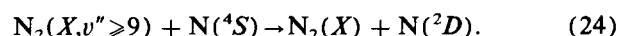
atoms cm^{-3} and a transit time of about 30 ms, only two thirds of our $N(^2D)$ signal was from $N(^2D)$ produced in the primary discharge, the other third was generated by N-atom recombination. One would expect that the conditions of Jusinski *et al.*, N-atom number densities three times greater and total pressures an order of magnitude larger than in our work, would result in roughly two orders of magnitude increased $N(^2D)$ production from N-atom recombination. Diffusion to the walls and quenching by molecular nitrogen result in a two to three e -fold decay in our system between the discharge and the observation region. In the Jusinski *et al.* experiment this decay increases from three to seven e -folds under their typical experimental conditions. Thus one might expect the $N(^2D)$ signal generated by N-atom recombination to dominate that produced directly in the discharge under their conditions.

Apparently, this was not the case. Jusinski *et al.* noted that their $N(^2D)$ signal diminished when they moved the primary discharge further away from the observation region. This indicates that some of the observed $N(^2D)$ is produced directly in their discharge. Their data indicate the presence of a residual component, however, which under some conditions comprised a significant fraction of their $N(^2D)$ signal. Undoubtedly this residual component is produced by N-atom recombination. Adding NO will alter the N-atom number density and, thereby, reduce the residual $N(^2D)$ signal. Because molecular oxygen reacts very slowly with atomic nitrogen,²⁵ it will quench only the $N(^2D)$ produced in the discharge. The decay plot will be curved, therefore, with an eventual plateau corresponding to the $N(^2D)$ which is generated by N-atom recombination. This may explain the curvature in the O_2 quenching plot of their Fig. 2(b).

The NO added by Jusinski *et al.* generally amounted to only about 10% of their N-atom number density. This small fraction would suggest that consumption of atomic nitrogen in their system would account only for about a 20% reduction in their $N(^2D)$ signal. Some further small reduction would be obtained because the atomic oxygen will reduce the steady-state number density of $N_2(A)$ in their system via quenching. This will then further diminish the production of $N(^2D)$ in reaction (19b). N-atom quenching of $N_2(A)$ will still dominate other loss processes, so this additional reduction should amount to no more than an additional 10%.

Jusinski *et al.*'s observed decays appear to be linear down to about one third of their initial $N(^2D)$ number density. Thus, apparent $N(^2D)$ quenching, resulting from reducing their N-atom number density, can account only for about a third of their observed decay. The additional mechanisms mentioned above must be responsible for the balance.

A second mechanism for producing $N(^2D)$ downstream from the discharge could be the reaction between $N_2(X, v'' \geq 9)$ and $N(^4S)$:



This reaction is not as unlikely as it might seem at first glance. Clearly it must go at some finite rate because the reverse reaction is well known.^{13,21} The quenching of $N(^2D)$ by N_2 is not particularly fast,¹³ $k \simeq 1.5 \times 10^{-14} \text{ cm}^3 \text{ mole}$

cule $^{-1}$ s $^{-1}$, so one might expect that its reverse, reaction (24), would proceed similarly slowly. Reaction (24), however, has many more available channels. All vibrational levels greater than or equal to nine have sufficient energy to react. While the exoergicity of reaction (24) for $v'' = 9$ is almost 4 kT , the reaction becomes resonant within kT for vibrational levels 11 and 12. This more nearly resonant quenching might be substantially more efficient. That these levels are populated significantly in active nitrogen is clear. We have observed recently the excitation of $N_2(B)$ in the energy transfer reaction between $N_2(A)$ and $N_2(X, v)$.²⁶ Those observations required vibrational levels of ground-state nitrogen up to at least $v'' = 14$. Our Penning ionization studies on active nitrogen revealed the presence of $N_2(X, v)$ containing at least 3.8 eV.²⁷ Finally, Black *et al.*²⁸ and Kessler²⁹ have used multiphoton-ionization techniques to detect $N_2(X, v)$ in vibrational levels as high as 25. Some fraction of the apparent $N(^2D)$ quenching observed by Jusinski *et al.* could well actually result from the quenching of $N_2(X, v)$. Such quenching would reduce the $N(^2D)$ production rate and, thereby, its signal.

The production of $N(^2D)$ in reaction (24) potentially could affect our results also. Our much lower number densities of $N_2(X, v)$ and $N(^4S)$, however, would result in a $N(^2D)$ production rate that is several orders of magnitude less than that which would be obtained in Jusinski *et al.*'s experiment. If important, this mechanism would be strongest in the experiments using reaction (3) as the source of O atoms because those experiments had much greater N-atom number densities (still far below those of Jusinski *et al.*, however). Those experiments gave results similar to the ones using the other two O-atom sources. We conclude, therefore, that reaction (24) and its concomitant complications are unimportant under our experimental conditions.

The third mechanism which could contribute to the faster rate coefficient measured by Jusinski *et al.* would be the reaction between $N(^2D)$ and NO. Husain *et al.*¹³ have shown that NO reacts with $N(^2D)$ with a rate coefficient of 6×10^{-11} cm 3 molecule $^{-1}$ s $^{-1}$. Any NO that finds an $N(^2D)$ atom, therefore, will react with it rapidly. Jusinski *et al.* dismiss this possibility by claiming that NO has a chemical lifetime in their system of only 0.1 ms. This calculation, however, assumes perfect, instantaneous mixing of the NO into the gas stream. In fact, the NO is injected from a small ball located on the axis of their flow reactor. The local NO number density in the vicinity of the reagent inlet will be much higher than its asymptotic limit. Even if the asymptotic NO number density were only 10% of the N-atom number density, the local NO number density will not equal the N-atom number density until it has diffused one third of the distance to the reactor walls. While this region contains only 10% of the reactor volume, it contains almost a quarter of the $N(^2D)$ in the reactor because wall quenching causes $N(^2D)$ to have a large radial gradient in number density. By the time NO has diffused halfway to the reactor walls, its number density is still on the order of a third of that of the N atoms, but it has already been in contact with well over half of the $N(^2D)$ in the reactor. Thus the effective chemical lifetime of NO in the reactor must be somewhat longer than

calculated by Jusinski *et al.* It is the combination of the radial number density gradients of NO and $N(^2D)$ in the vicinity of the injector which allows the NO the opportunity to react with $N(^2D)$ prior to being consumed by ground-state nitrogen atoms.

A final possibility for Jusinski *et al.*'s large rate coefficient measurement is a reduction in detection efficiency with the addition of atomic oxygen to their reactor. Atomic oxygen, being an electron attaching gas, can alter the collection efficiency in several ways. One thing that happens is that the negative ions formed by electron attachment take longer to reach the electrodes.³⁰ The temporal pulse of the charges is thereby increased. Since Jusinski *et al.* monitored their signal with a boxcar averager, their gate width might not have been optimized to account for this lengthened temporal pulse. The longer temporal pulse will have the effect of lowering the current collected during a fixed gate width. This reduced signal can be mistaken as quenching.

Neither in the paper under discussion,¹⁰ nor in their earlier papers on multiphoton ionization detection of $N(^2D)$,^{31,32} do Jusinski *et al.* discuss the current vs voltage characteristics of their ion collection electrodes. In general, the ion signal will increase as an increasing potential difference is applied across the electrodes until a plateau is reached. Further increases in the voltage do not result in increasing signals until the voltage becomes high enough to cause secondary ionization of the background gas by collisions with the accelerated ions and electrons. Cool³⁰ has shown that adding an electron attaching gas both delays the onset of the plateau to higher voltages and, in addition, reduces the avalanche effect at the highest voltages. Thus, whether Jusinski *et al.*'s system was biased to be in either the plateau or avalanche region, the addition of an attaching gas could lower their signal. This diminutization in signal would have the appearance of being quenching when in reality it was just a change in detection sensitivity. One might expect similar behavior upon adding molecular oxygen. Atomic oxygen has a much higher electronegativity, however, so it could show a somewhat larger effect.

Probably none of the four possibilities suggested to rationalize Jusinski *et al.*'s obtaining a rate coefficient which we think is too large is a major effect. Each may contribute only 10% or 20% to the reduction of $N(^2D)$. In concert, however, they could easily account for a diminutization in signal of 50% to 70%. The dynamic range in Jusinski *et al.*'s experiment is of comparable magnitude.

Recently, Miller *et al.*³³ have investigated the quenching of $N(^2D)$ upon adding NO to a flow of active nitrogen. In some of their experiments they tried to reproduce the operating conditions of Jusinski *et al.* Using resonance-enhanced multiphoton ionization to detect both $N(^2D)$ and NO, Miller *et al.* found that NO persisted in the afterglow for times much greater than they would expect based upon the rate of consumption of NO by $N(^4S)$ that they calculated to be appropriate to their experimental conditions. They attributed this discrepancy to be due to slow mixing of the NO into the main flow. They noted that the $N(^2D)$ number-density decay was effectively first order in added NO, but that the effective rate coefficient for $N(^2D)$ quenching was much fas-

ter under conditions where significant NO remained at the detection region compared to conditions under which the NO was completely consumed. Their analysis of mixing effects allowed them to uncouple the effects of NO quenching of $N(^2D)$ from those of O quenching. Their data imply a rate coefficient for reaction (2) of $(1.0 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with our results.

B. Other issues

The doublet potential curves which asymptotically correlate to an $N(^2D)$ and an $O(^3P)$ atom have myriad crossings with lower potential curves whose asymptotic limits correlate to $N(^4S)$ and either $O(^3P)$ or $O(^1D)$ atoms. On the basis of spin conservation, one would expect that the favored product would be $O(^3P)$ atoms. Oran *et al.*⁸ on the other hand, speculated that the one-electron spin-orbit matrix elements will couple the incoming doublet states with the quartet states correlating to the production of an $O(^1D)$ atom as readily as to the doublet states correlating to $O(^3P)$ atoms as a product. Davenport *et al.*,³ however, report that unpublished calculations by Olson and Smith show the channel leading to $O(^3P)$ production will be favored.

Sivjee *et al.*³⁴ report anomalies, noted in auroras over Svalbard, in the ratio of emission of the two components of the $N(^2D_{5/2,3/2}-^4S_{3/2})$ doublet at 520 nm. They suggest that these differences might result from the need of reaction (2) to conserve total angular momentum. The $J = 5/2$ sublevel, therefore, could react only with the $J = 1,0$ sublevels of atomic oxygen, producing the $J = 2,1$ sublevels. The $J = 3/2$ sublevel of $N(^2D)$, on the other hand, can react with all three sublevels of $O(^3P)$. Thus, under certain conditions, they would expect to see a depletion in the emission from $N(^2D_{3/2})$. The relatively high pressure in our reactor ensures that the two sublevels of $N(^2D)$ will be in equilibrium. Our measurements, therefore, will be an average of the reactivities of the two sublevels and cannot be used to test Sivjee *et al.*'s hypothesis.

One cannot use the criterion of conserving total angular momentum as an argument against the production of $O(^1D)$ in reaction (2). Both sublevels of $N(^2D)$ can interact with one of the sublevels of $O(^3P)$ to produce $O(^1D_2)$. All that can be argued on this basis, therefore, is that with fewer channels available, $O(^1D)$ production would be expected to be less efficient than that of $O(^3P)$.

In the event that $O(^3P)$ is the favored product, reaction (2) will proceed with the release of 2.38 eV of translational energy. This reaction, therefore, could be a source of translationally hot O and N atoms in the upper atmosphere. The reactions of these hot atoms could be somewhat different from those of thermal atoms. For example, the production of NO from the reaction of $N(^4S)$ with O_2 could be much more efficient if the nitrogen atoms are translationally hot. Solomon³⁵ has discussed the effects of translationally hot atoms on thermospheric chemistry in some detail.

SUMMARY AND CONCLUSIONS

We have shown that the rate coefficient for quenching $N(^2D)$ by atomic oxygen is $(1.06 \pm 0.26) \times 10^{-12} \text{ cm}^3 \text{ mol-}$

ecule⁻¹ s⁻¹ at 300 K. This value is consistent with many of the aeronomically derived quenching rate coefficients. In particular, very recent modeling results of Fesen *et al.*⁹ favor a value of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for k_2 . They show convincingly that a value for k_2 as large as that proposed by Jusinski *et al.*¹⁰ would completely quench all radiation at 520 nm from the $N(^2D-^4S)$ transition and would, furthermore, result in $N(^4S)$ (and NO) number densities that are much larger (or smaller) than has been consistently obtained from numerous aeronomic observations. The atmospheric chemistry of $N(^2D)$, and of NO, now appears to be reasonably well understood.

Agreement with earlier laboratory studies^{3,4} is within experimental error, while that with the most recent experimental effort³³ is excellent. The discrepancies with the Jusinski *et al.*¹⁰ laboratory study, however, indicates a large systematic error in that experiment.

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