The excitation of N(^2P) by N$_2$(A $^3\Sigma_u^+$, $v'=0,1$)

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We have studied the electronic energy transfer reaction between N$_2$(A $^3\Sigma_u^+$, $v' = 0,1$) and N(^4S) in a discharge-flow reactor. Monitoring the decay of the forbidden Vegard–Kaplan emission, N$_2$(A $^3\Sigma_u^+ - X$ $^1\Sigma_g^+$), as a function of time and of atomic nitrogen number density allows determination of the total reaction rate coefficients for removal of vibrational levels 0 and 1 by N(^4S). Simultaneously observing the temporal profiles of the Vegard–Kaplan bands and of the forbidden N($^2P - {}^4S$) line at 346.6 nm allows the branching fraction into atomic nitrogen excitation to be determined. The total quenching rate coefficient for both $v' = 0$ and 1 is $(4.0 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K. The apparent rate coefficient for exciting N(^2P) by N$_2$(A, $v' = 0$) is $(19 \pm 3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, at 300 K, while that for excitation by N$_2$(A,$v = 1$) is $(5 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We interpret the large discrepancy between the N(^2P) excitation and N$_2$(A) destruction rate coefficients as evidence that the currently accepted value for the N($^2P - {}^4S$) transition probability is a factor of 4 to 5 too small, or else that our source of N$_2$(A) metastables, energy transfer from metastable argon atoms to molecular nitrogen, is contaminated by the presence of a second nitrogen metastable species with an energy in excess of 3.6 eV.

I. INTRODUCTION

Metastable N(^2P) atoms are commonly observed constituents in nitrogen discharge afterglows[1-3] and in the aurorally disturbed upper atmosphere.[4-6] In spite of this, their chemistry has been little studied, probably because N(^2P) reacts slowly with most molecules.[7,8] The reaction of N(^2P) with O$_2$ has been invoked as a source of vibrationally excited nitric oxide with accompanying hot-rotational band heads ($T_{\text{rot}} \sim 10^4$ K).[9] In addition, the ratio of the intensity of the N(^2P–^2D) transition at 1040 nm to the N$_2^+$ (A $^2\Pi_u$, $v' = 0$–$^2\Sigma_g^+$, $v'' = 0$) transition at 1109 nm has been used to monitor the depth of penetration of auroral electrons.[10] The intensity ratio becomes smaller for deeper auroral penetration because N(^2P) is quenched by O atoms efficiently.[8]

Several years ago we attempted to measure rate coefficients for quenching N(^2P) by a variety of atmospheric constituents. We used a microwave discharge through a mixture of nitrogen dilute in argon or helium as our N(^2P) source, and monitored N(^2P) unequivocally by vacuum ultraviolet resonance fluorescence. In most instances we observed multiexponential quenching behavior. This behavior suggested that we were observing not only quenching of N(^2P) generated in the discharge, but also quenching of discharge-produced precursors which were coupled kinetically to N(^2P) along the length of the flow reactor. We concluded that a nitrogen/argon discharge didn't provide a clean source of N(^2P) and that reliable kinetic studies could not be pursued using such a source.

The interaction between N$_2$(A) and N excites N(^2P).[11,12] Because N(^2P) is inefficiently quenched by atomic nitrogen,[1,8] this reaction might provide a relatively clean source of N(^2P) for kinetic studies in a flow system. Before such studies can be pursued, the N$_2$(A) + N reaction must be characterized. This report details such a quantitative characterization.

The rate coefficient for quenching N$_2$(A $^3\Sigma_u^+$) by N was first estimated by Wray[13] to be about 5×10^{-11} cm^3 molecule^{-1} s^{-1}. Subsequent work by Young and St. John,[14] Meyer et al.,[11] Vidaud et al.,[15] and Dunn and Young[12] all have concurred with Wray's estimate, obtaining values between 3 and 5×10^{-11} cm^3 molecule^{-1} s^{-1}. Meyer et al.[11] and Young and Dunn[8] both showed that N(^2P) was a product from this quenching reaction but neither group made any quantitative estimates of the efficiency of the energy transfer.

II. EXPERIMENTAL

The experiments were carried out in a 2 in. diameter discharge flow apparatus which is shown schematically in Fig. 1. The apparatus is in two parts. The upstream section is where the N$_2$(A) and N are produced and subsequently mixed. Observations occur in the downstream section. It has been manufactured from quartz so as to transmit ultraviolet radiation.

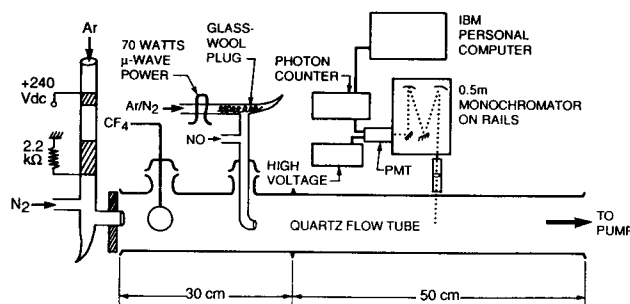The interaction between metastable argon atoms, produced in a dc discharge, and molecular nitrogen[16,17] gener-
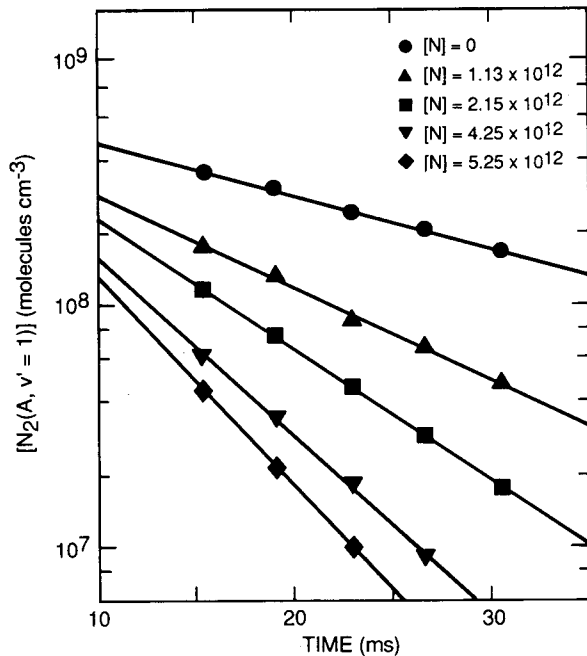

FIG. 1. Schematic of discharge flow reactor.

FIG. 4. Decay of N$_2$(A $^3\Sigma_u^+$, $v' = 1$) as a function of time and of N(^4S) number density.

FIG. 6. N$_2$(A, $v' = 1$) decay rates as a function of [N].

certainty of about 12%. We therefore quote a rate coefficient for N$_2$(A, $v' = 0,1$) removal by N of $(4.0 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The number densities of N$_2$(A, $v' = 2$) were so small as to limit decay measurements to a range of less than a factor of 3 to 5. This small range is insufficient for measuring reliable rate coefficients. In general, $v' = 2$ disappeared at about the same rate as the other vibrational levels, indicating that the rate coefficient for its removal is of similar magnitude.

B. The excitation of N(^2P) by N$_2$(A)

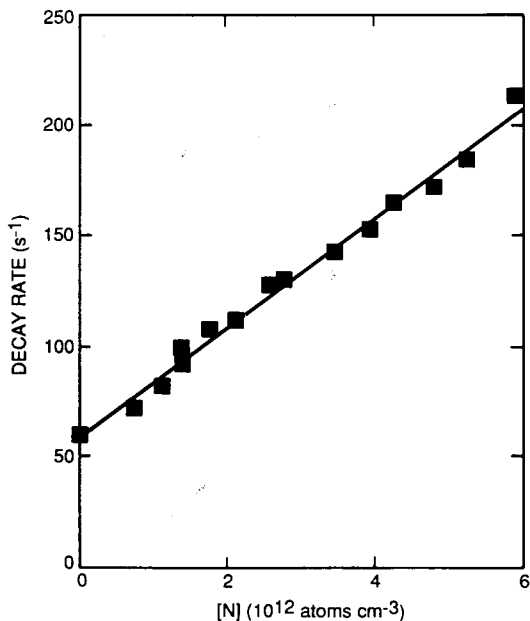The rate equation for the formation and removal of N(^2P) in our reactor is

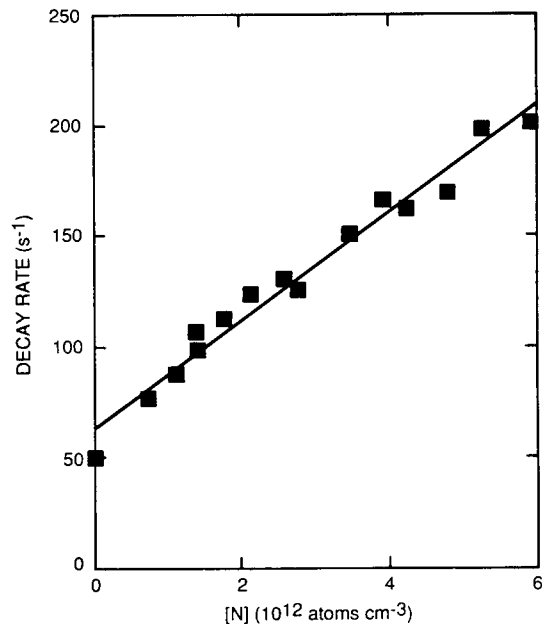FIG. 5. N$_2$(A, $v' = 0$) decay rates as a function of [N].

$$\frac{d[N(^2P)]}{dt} = k_{1a}[N_2(A)][N]$$
$$- (k_W^P + k_3[N])[N(^2P)]. \tag{9}$$

Using the exponential form of Eq. (6) above for the number density of N$_2$(A), allows Eq. (9) to be solved, giving

$$[N(^2P)] = \frac{0.62k_{1a}[N][N_2(A)]_0}{K_P - K_A}$$
$$\times \{ e^{-K_A z/\bar{v}} - e^{-K_P z/\bar{v}} \}. \tag{10}$$

Equation (10) has the visually simplifying substitutions

$$K_A = 0.62(k_W^A + k_1[N]) \tag{11}$$

and

$$K_P = 0.62(k_W^P + k_3[N]). \tag{12}$$

The terms K_A and K_P are the pseudo first-order decay rates for N$_2$(A) and N(^2P), respectively. The factors of 0.62 are included to account for the fluid mechanical affects. The corrections have been derived in detail by Shaw and Stock[41] and by DeSouza et al.[42] and their derivation need not be repeated here.

Rearranging Eq. (10) leads to the result

$$\frac{[N(^2P)]}{[N_2(A)]} = \frac{0.62k_{1a}[N]}{K_P - K_A}$$
$$\times \{ 1 - e^{-(K_P - K_A)z/\bar{v}} \}. \tag{13}$$

By knowing K_A and K_P, we can extract the desired rate coefficient k_{1a} from least squares fits to the ratio $[N(^2P)]/[N_2(A)]$ as a function of [N] and of time. The values of K_A result directly from the measurements described in the previous section. K_P is determined by using k_3 values from the literature[1,8] and k_W^P values determined from the least-squares fits. We can check the reasonableness of the

resulting $k\,^P_W$ by comparing with data already in the literature.

Figure 7 shows how the ratio of the number densities of $N(^2P)$ to $N_2(A, v' = 0)$, for the data taken in the presence of CF_4, vary with N-atom number density at three different reaction times. The best fit of Eq. (13) to these data, shown by the solid lines in Fig. 7, as well as to additional data taken at two other reaction times, results in a value for k_{1a} of $(1.9 \pm 0.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and $k\,^P_W$ of (75 ± 10) s⁻¹. The uncertainty in the fit reflects sensitivity to variations in the value determined for $k\,^P_W$ and for the effective mixing length. This latter quantity is a correction to the distance between the injector and the detection region needed to account for imperfect mixing at the injector. Analysis of the decay plots of $\ln[N_2(A)]$ vs reaction distance indicated that the lines intersected at a common value of 4 ± 2 cm. This value was used to correct for mixing effects.

Equation (13) was also used to analyze the data taken in the absence of CF_4. As in the previous case, the data were fit to the ratio of $[N(^2P)]/[N_2(A, v' = 0)]$ (see Fig. 8). The effective excitation rate coefficient determined from this fit is

$$k_{1a}^{\text{eff}} = k_{1a}^{v' = 0} + k_{1a}^{v' > 0}\frac{[N_2(A, v' > 0)]}{[N_2(A, v' = 0)]}. \quad (14)$$

The number density ratio, which comes from the spectral fits, is 0.78 ± 0.08. The effective k_{1a} from the fits without CF_4 is $(2.3 \pm 0.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ from which we derive that $k_{1a}^{v' > 0} = (0.5 \pm 0.1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

Determining N-atom number densities by monitoring the intensity of the N-atom recombination chemiluminescence should be accurate to $\pm 5\%$ except at low N-atom number densities when the raw signal and the background become comparable. This problem was most severe in the measurements in the presence of CF_4 with $[N] < 3 \times 10^{12}$

FIG. 8. $N(^2P)$ excitation by $N_2(A, v' = 0,1,2)$. The curves through the data points show the results of the fit of Eq. (13) to the data.

atoms cm⁻³ where the monochromator was used to monitor chemiluminescence. All other measurements relied on the photometer which is an order of magnitude more sensitive.

The populations of $N_2(A)$ and $N(^2P)$ determined from the spectral fitting procedure are also generally accurate to $\pm 5\%$. In some of the fits at low N-atom number densities in the presence of CF_4, the $N(^2P)$ population may be more uncertain. In these fits the 346.6 nm emission is weak relative to the Vegard–Kaplan emission. Any errors in determining the baseline will contribute to a larger error in determining $N(^2P)$ number densities compared to those for $N_2(A)$. For the data taken without the CF_4, the $N_2(A)$ emissions were reduced by about a factor of 2 and could be monitored on a lower amplifier scale setting. In this case, the $N(^2P)$ emission was relatively stronger and baseline errors affected $N_2(A)$ and $N(^2P)$ number density determinations by comparable amounts.

These larger experimental errors at low N-atom number density affect the fits to Eq. (13) only weakly. The fits are more strongly influenced by the data at higher N-atom number densities which are inherently more precise.
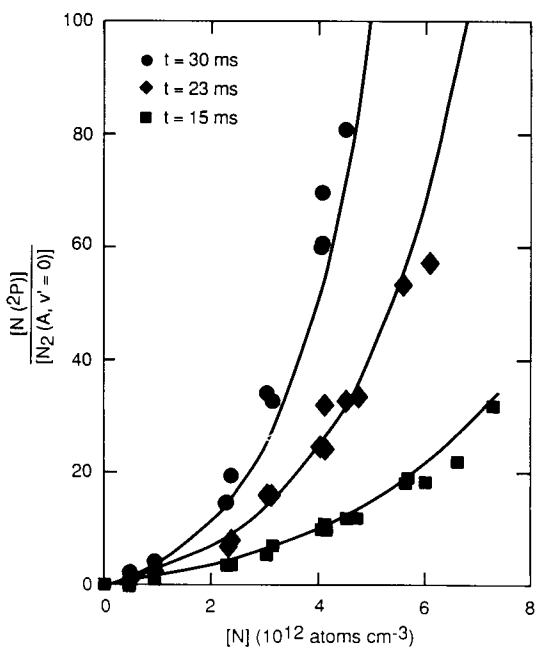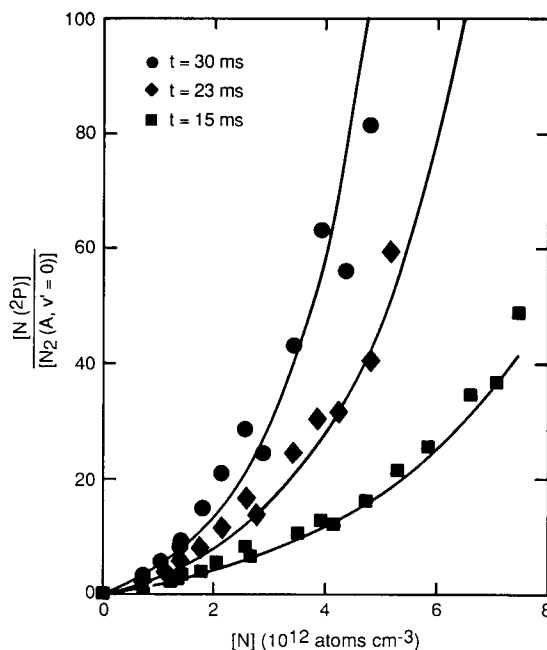
Table I summarizes our experimental results.

FIG. 7. $N(^2P)$ excitation by $N_2(A\ ^3\Sigma_u^+, v' = 0)$. The curves through the data points show the results of the fit of Eq. (13) to the data.

TABLE I. Rate coefficients for $N_2(A) + N$ interaction.

Process	Rate coefficient $(10^{-11}$ cm³ molecule⁻¹ s⁻¹$)$	
$N_2(A, v' = 0) + N \rightarrow$ products	3.8 ± 0.3	with CF_4
	4.1 ± 0.2	no CF_4
$N_2(A, v' = 1) + N \rightarrow$ products	3.9 ± 0.2	no CF_4
Average	4.0 ± 0.5	
$N_2(A, v' = 0) + N \rightarrow N(^2P) + N_2(X)$	19 ± 3	
$N_2(A, v' > 0) + N \rightarrow N(^2P) + N_2(X)$	5 ± 1	

IV. DISCUSSION

A. N$_2$(A)+N removal

Our determination of the total rate coefficient for quenching N$_2$(A) by N, $(4.0 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, agrees well with most other determinations. In some instances, the agreement can be considered fortuitous. Neither Wray[13] nor Vidaud et al.[15] observed N$_2$(A) directly, but had to make inferences based upon indirect measurements. In particular, agreement with Vidaud et al.'s[15] experiment is somewhat puzzling. They used both photoionization and isothermal calorimetry as their metastable-nitrogen diagnostics. Neither of these diagnostics is specific to N$_2$(A). In addition to obtaining an N-atom quenching-rate measurement, they determined a wall-quenching probability for their metastable of 10^{-5}. Flow-tube measurements both in our laboratory as well as others[43] show conclusively that N$_2$(A) is deactivated with essentially unit probability in wall collisions. Thus Vidaud et al. must have been observing some other metastable in their experiment. One possibility is vibrationally excited nitrogen which is known to deactivate somewhat more slowly than N$_2$(A) in wall collisions.[20]

Meyer et al.[11] reported two separate determinations of the rate coefficient for N$_2$(A) quenching by N. One measurement was made relative to the quenching rate of N$_2$(A) by O$_2$. Using an assumed value for this latter quenching rate coefficient of 6.0×10^{-12} cm^3 molecule^{-1} s^{-1}, they reported a value for k_1 of 5.1×10^{-11} cm^3 molecule^{-1} s^{-1}. Since the O$_2$ quenching rate coefficient is now known to be about half of the value chosen by Meyer et al. [assuming a typical distribution of N$_2$(A) vibrational levels in their discharge flow system],[44–46] their reported value for k_1 must be reduced accordingly. A second determination by them resulted from observing the quenching of Hg 253.7 nm emission in their reactor as a function of added atomic nitrogen number density. The mercury emission was excited by transfer from N$_2$(A) and thereby served as a tracer of the N$_2$(A) number density. The result from that study gave a value for k_1 of 4.3×10^{-11} cm^3 molecule^{-1} s^{-1}. They made no corrections for imperfect mixing or for fluid dynamical effects.

Young and St. John[14] and Dunn and Young[12] excited N$_2$(A) in a Tesla discharge. While this type of discharge tends to dissociate nitrogen inefficiently, it is a source of other nitrogen metastables which could be kinetically coupled to N$_2$(A). Young and St. John reported a 30% increase for quenching N$_2$(A, $v' = 1$) compared to the rate coefficient for quenching N$_2$(A, $v' = 0$) whereas Dunn and Young reported no difference between the two vibrational levels.

B. N(^2P) product formation

Our measurements result in an excitation rate coefficient for N(^2P) by N$_2$(A, $v' = 0$) which is five times greater than the total quenching rate coefficient. Part of this discrepancy may result from errors in the published values for the transition probabilities of N$_2$(A) and N(^2P). A 30% to 40% decrease in the Einstein coefficient for N$_2$(A)[26] would reduce this discrepancy somewhat, but even so would require that the Einstein coefficient for the N(^2P–^4S) transition calculated by Garstang could be as much as a factor of 4 too

small. If the excitation probability were significantly less than unity, then this transition probability would be even larger. Godefroid and Froese Fischer's[31] calculation appears to confirm Garstang's result. We think, however, that this aeronomically important transition probability merits an experimental confirmation.

Another possibility for the discrepancy between N(^2P) excitation and N$_2$(A) decay rate coefficients is that a significant fraction of the observed N(^2P) is generated in an N-atom recombination process. Taghipour and Brennen[1] have demonstrated that N(^2P) is produced in active nitrogen by a two-step process. In the first step the three-body recombination of atomic nitrogen makes N$_2$(A). The N(^2P) then is excited by energy transfer between N$_2$(A) and N(^4S) (reaction 1a). This process is unimportant under our conditions. When we extinguish the N$_2$(A), the N(^2P) signal vanishes. For typical pressures and flow times in our reactor, the signal generated by N-atom recombination is less than 10% that excited in reaction (1a), even for N-atom number densities of 1×10^{13} atoms cm^{-3}. The N(^2P) number density that is made via N-atom recombination scales approximately as the cube of the N-atom number density at low number densities. Because our maximum N-atom number density is about 7×10^{12} atoms cm^{-3}, our N(^2P) signal will be contaminated by this extraneous source by no more than a few percent. This alternative N(^2P) source, therefore, does not appear to be responsible for our puzzling results.

A third explanation would be that N$_2$(A) isn't the only molecular-nitrogen metastable present in our flow reactor. Energy transfer from metastable argon to molecular nitrogen might also produce a companion metastable to N$_2$(A) which has unobservable radiation between 200 and 900 nm. This companion metastable would have to have a number density several times greater than that of the N$_2$(A) to explain our results.

Our recent study of the various products resulting from the N$_2$(A) interaction with molecular oxygen[47] provided evidence for such a companion metastable. One aspect of those studies was the determination of the amount of atomic oxygen that was produced in the reaction. Our observations indicated that the O-atom yield was a factor of 3 greater than could be accounted for even if every N$_2$(A) molecule dissociated O$_2$. Dreiling and Setser also have reported evidence of a companion metastable to N$_2$(A),[48] which carried at least 6.5 eV internal energy, in their studies on the excitation of mercuric halides by N$_2$(A). The energy of the companion metastable reported in both studies is more than sufficient to excite N(^2P) in an energy-transfer reaction with N(^4S).

In the present study as in the earlier study we were careful to add the nitrogen to the flow of argon metastables downstream from the dc discharge which produced the metastable argon. This ensures that the nitrogen metastables only can be produced in the energy-transfer reaction and not by direct electron impact as could be the case were the nitrogen co-discharged with the argon. This latter configuration generates more N$_2$(A), but we have observed previously that it also generates other nitrogen metastables which enhance N$_2$(B–A) emission in the afterglow far in excess of what would be generated from N$_2$(A) energy pooling.[49] Dreiling

and Setser also were careful to add their nitrogen downstream from the metastable-argon discharge.

We cannot find a satisfactory explanation as to the identity of this companion metastable. Known metastable states of molecular nitrogen below 11.6 eV, which have radiative lifetimes in excess of a millisecond, include a' $^1\Sigma_u^-$, w $^1\Delta_u$, A $^3\Sigma_u^+$, W $^3\Delta_u$, A' $^5\Sigma_g^+$, and N$_2$(X $^1\Sigma_g^+$,v). Some of these states undoubtedly can persist for long times in the afterglow.

Sadeghi and Setser[17] have shown that essentially all of the quenching events between metastable argon and molecular nitrogen result in N$_2$(C $^3\Pi_u$) excitation. A minor fraction of the reaction results in dissociation,[50,51] but N$_2$(C) excitation clearly is the dominant channel. The radiative lifetime of N$_2$(C) is so short, 36 ns,[52] that molecules in this state will undergo only one collision prior to radiation at a pressure of 2 Torr. Thus electronic quenching of this state should be unimportant, and all of the molecules initially in this state will cascade radiatively to the B $^3\Pi_g$ state.

Given the vibrational distribution of N$_2$(C) excited by Ar*($^3P_{2,0}$)[17] and the N$_2$(C--B) Einstein coefficients tabulated in Lofthus and Krupenie,[52] we calculate that about 97% of the radiative cascade from N$_2$(C) will populate N$_2$(B) in vibrational levels 4 and below. Under the conditions of our experiment, some of the molecules in the B state will radiate to the lower vibrational levels of the A $^3\Sigma_u^+$ state. Many of them, however, will be transferred collisionally into lower B-state levels,[53] to other levels of the triplet manifold, principally the A, B' $^3\Sigma_u^-$, and W states,[54-58] or perhaps directly into high vibrational levels of the X $^1\Sigma_g^+$, ground-electronic state. The best available evidence suggests that much of the quenching of the B state is effectively a vibrational relaxation process. Ultimately, $v' = 0$ of the B and W states and $v' = 7$ of the A state are the primary end products of B state quenching.

Heidner et al.[59] have shown that N$_2$(B, $v = 0$) and N$_2$(W, $v = 0$) rapidly establish an equilibrium between themselves, and then, somewhat more slowly, collisions with ground-state nitrogen quench the coupled complex. Under our conditions ([N$_2$] $= 8 \times 10^{15}$ molecules cm^{-3}), the quenching time of the coupled complex will be 60 μs given Heidner et al.'s quenching rate coefficient of 2×10^{-12} cm^3 molecule^{-1}s^{-1}. The most likely product of this quenching is $v' = 7$ of the A state. Dreyer and Perner[60] have shown, however, that this level is relaxed vibrationally by collisions with ground-state nitrogen. Their rate coefficient of 2.4×10^{-12} cm^3 molecule^{-1} s^{-1} implies a relaxation time of 50 μs under our conditions. Thus, the evidence suggests that, even if the B-state levels initially populated in the radiative cascade from the C state are quenched before they radiate, N$_2$(A) still is the ultimate product from the Ar* + N$_2$ energy-transfer reaction.

Were the C state coupled collisionally to the nearby C'' $^5\Pi_u$ state, the A' $^5\Sigma_g^+$ state could be populated by radiative cascade on the Herman infrared system.[61,62] In this event, one would be able to observe Herman infrared emission in the Ar*/N$_2$ flame. One does not observe such emission, however. Direct excitation of either the C'' or A' states is precluded by spin conservation.

Spin-conservation rules also proscribe excitation of the singlet nitrogen metastables. These rules again are supported by direct observations in the vacuum ultraviolet which do not find significant emission in the Lyman–Birge–Hopfield bands, N$_2$(a $^1\Pi_g$--X $^1\Sigma_g^+$).[50,63] Were the singlet excitation into the a' or w states, one would still expect to see LBH emission because the three singlet states are efficiently coupled collisionally.[64]

In summary, the available evidence suggests that the quenching of metastable argon by nitrogen ultimately should result in N$_2$(A) production. The only alternative possibility for a long-lived metastable would appear to be N$_2$(X,v). To explain our results, however, would require efficient spin-changing collisions to convert triplet nitrogen into singlet nitrogen in high vibrational levels. Golde and Thrush[65] suggest that efficient manifold switching can result from collisions with nitrogen atoms. In the upstream end of our reactor, however, our atom number density can at most be 10^{10} atoms cm^{-3}. Such low number densities cannot generate sufficient collisions on the required time scale of tens of microseconds to effect triplet-to-singlet manifold switching. Spin changing in collisions with molecular nitrogen or argon should be inefficient. We have failed to find evidence that this N$_2$(A) source produces N$_2$(X,v) in low vibrational levels.[66] This observation doesn't preclude the possibility of anomalous N$_2$(X,v) distributions consisting of molecules containing either 6 eV of vibrational energy or none. It just doesn't seem particularly likely.

C. Other products

Some fraction of the interactions between N$_2$(A) and N probably also results in N(^2D) formation. The low-temperature matrix measurements from Dressler's group[67-70] show that both N(^2P) and N(^2D) are excited in the reaction between N$_2$(A) and N. They also observe the vibrational levels of the ground electronic state which are excited in the N$_2$(A) deactivation. When N(^2P) is the excited product, $v'' = 6$–9 primarily are populated with roughly equal probability. The thermochemical limit for the ground-state N$_2$ is $v'' = 9$. When N(^2D) is the atomic product, most of the ground-state population resides in $v' = 7$–10, although excitation up to $v'' = 13$ was observed. In this case the thermochemical limit would give N$_2$(X, $v'' = 14$). They assumed that the excitation of both states is a direct process.

We see no reason, based upon the evidence reported by Dressler's group, why much of the N(^2D) excitation might not result from lattice-induced radiative cascade from initially excited N(^2P). The N(^2P) radiates in the matrix with a 1 ms lifetime, whereas the effective radiative lifetime of the N(^2D) in the lattice is 37 s. Clearly, some of the N(^2D) excitation must be direct because several vibrational levels of N$_2$(X) are populated above the N(^2P) thermochemical limit. Kunsch[69] states that unpublished results from the group indicate a somewhat greater intensity from N(^2D) than from N(^2P). This observation argues for direct N(^2D) formation.

We looked briefly for N(^2D) using a resonance-fluorescence diagnostic.[40] We observed N(^2D) in our reactor only when both the N$_2$(A) and the N were present together. The

N(^2D) number densities were of the same order of magnitude as those for N(^2P). Because the observations were made after a fairly long reaction time, the N(^2D) could have resulted from N(^2P) quenching by argon rather than from direct excitation by N$_2$(A). Unravelling this issue will require lengthy and detailed measurements.

In our recent studies on the quenching of N(^2D) by atomic oxygen,[71] we observed a resonance–fluorescence signal from N(^2D) that was generated by N-atom recombination. The atoms had been passed through a glass–wool plug prior to flowing into the observation region, so discharge-produced N(^2D) could be discounted as the source of the N(^2D). The intensity of the N(^2D) signal scaled in proportion to the product of the square of the N-atom number density times the total pressure. Such scaling is consistent with N(^2D) production via reaction (1) subsequent to the generation of N$_2$(A) from N-atom recombination. The measurements were not sufficiently extensive, however, to rule out alternative N(^2D) excitation schemes such as N(^2P) quenching by argon or atomic nitrogen.

Superficially, our data indicate that the excitation rate of N(^2P) by vibrationally excited N$_2$(A) is reduced by a factor of 4 in spite of the fact that the total quenching rates are the same for vibrationally excited and relaxed N$_2$(A). Certainly, if the discrepancy between the rate coefficients for N(^2P) excitation by N$_2$(A, $v' = 0$) and for N$_2$(A) quenching by N is caused by inaccuracies in the Einstein coefficients, this would be the surprising result. If the discrepancy is caused by a companion metastable, however, then the data indicate that the branching ratio for N(^2P) excitation by N$_2$(A, $v > 0$) is unity and, furthermore, that CF$_4$ doesn't quench the companion metastable.

If the apparent difference in N(^2P) excitation rates between vibrationally excited and unexcited N$_2$(A) is real, it might be because the branch to form N(^2P) decreases with increasing vibrational level. Kunsch[70] performed some trajectory calculations on this system. He found that whereas 95% of his trajectories starting with N$_2$(A, $v' = 0$) were effective in exciting N(^2P), only 70% of the trajectories starting from $v' = 1$ succeeded. Trajectories involving N$_2$(A, $v' = 3$) resulted in N(^2P) excitation less than 50% of the time. Kunsch's calculations involving N(^2D) as a product did not address the issue of vibrational excitation in the N$_2$(A). Clearly, additional gas-phase experiments designed to observe both excited-atom products are warranted.

D. N(^2P) quenching

N(^2P) wall loss is diffusion controlled.[37,38] The wall-loss rate, therefore, is

$$k_W^P = \frac{0.62D_0}{\Lambda^2 P},\qquad(15)$$

where D_0 is the diffusion coefficient at 1 Torr, and Λ is the characteristic diffusion length. This value is the ratio of the radius of the flow reactor to the first root of the zeroth-order Bessel function:

$$\Lambda = \frac{r_0}{2.405}.\qquad(16)$$

Iannuzzi and Kaufman[35] obtained a value of 230 cm^2 s^{-1} at 1 Torr for N(^2P) diffusing in argon. Other values reported in the literature are 214 cm^2 s^{-1} by Lin and Kaufman[36] (corrected from 400 K) and 160 $\pm$ 20 cm^2 s^{-1} by Cernogora and Sadeghi.[72]

In addition to diffusion to the walls, a small loss of N(^2P) results from quenching by the argon bath gas. Iannuzzi and Kaufman[35] reported a rate coefficient for this process of 4$\times$10^{-16} cm^3 molecule^{-1} s^{-1}. Lin and Kaufman[36] proposed a similar value, 7$\times$10^{-16} cm^3 molecule^{-1} s^{-1}. Rather than include this quenching term explicitly, we compensated for it implicitly by including it with the effective wall quenching rate. Our effective wall quenching rate, 75 s^{-1}, is compatible with a diffusion coefficient of 210 cm^2 s^{-1} at 1 Torr and an argon quenching rate of 4$\times$10^{-16} cm^3 molecule^{-1} s^{-1}. These values agree quite well with the more direct measurements of Iannuzzi and Kaufman.

Taghipour and Brennan[1] have estimated a rate coefficient for reaction (3) of 6$\times$10^{-13} cm^3 molecule^{-1} s^{-1}. Young and Dunn[8] obtained a similar value, but Golde and Thrush[73] estimated a value considerably larger, 1$\times$10^{-11} cm^3 molecule^{-1} s^{-1}. For additions of large number densities of atomic nitrogen, such that the conversion from N$_2$(A) to N(^2P) is essentially complete in the vicinity of the injector, we see only a small decrease in [N(^2P)] as [N(^4S)] is further increased. The magnitude of this decrease is consistent with the smaller N-atom quenching rate coefficients of N(^2P) given by Taghipour and Brennan and Young and Dunn rather than that estimated by Golde and Thrush.

V. SUMMARY AND CONCLUSIONS

We have shown that the total rate coefficient for quenching N$_2$($A\,^3\Sigma_u^+$) by N atoms is (4.0 $\pm$ 0.5)$\times$10^{-11} cm^3 molecule^{-1} s^{-1} at room temperature. We saw no obvious variation in this value with N$_2$(A) vibrational level. N(^2P) is excited quite efficiently in this reaction, but N$_2$(A, $v' = 0$) appears to be a factor of 4 more efficient in the excitation than is N$_2$(A, $v' > 0$).

The rate coefficient determined for N(^2P) excitation by N$_2$(A, $v' = 0$), based upon currently accepted Einstein coefficients for N$_2$(A) and N(^2P), is five times the total quenching rate coefficient. This indicates that either the accepted value for the N(^2P-^4S) Einstein coefficient is seriously in error, or else that the interaction between metastable argon and molecular nitrogen generates another nitrogen metastable in addition to N$_2$(A). Either possibility could indicate serious misunderstandings of processes important in disturbed atmospheres or nitrogen discharges. Clearly both issues require further investigation.

In spite of the somewhat unsatisfactory situation regarding the discrepancies between N(^2P) excitation and N$_2$(A) destruction rate coefficients, our study shows that our experimental configuration provides a straightforward source of N(^2P) suitable for kinetic studies. Some preliminary investigations of N(^2P) kinetics using this source indicate a freedom from the kinetic complications observed using a microwave discharge in N$_2$/Ar mixtures to generate N(^2P). These studies currently are underway, and will be detailed in a future publication.

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