Quenching rate coefficients for $N_2(a'\ ^1\Sigma_u^-)$

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We have studied the kinetics of the lowest excited singlet state of molecular nitrogen, $N_2(a'\ ^1\Sigma_u^-, v = 0)$, in a discharge flow reactor. The metastables were generated in a hollow cathode dc discharge through molecular nitrogen highly diluted in argon, and detected by VUV flourescence of the forbidden $N_2(a'\ ^1\Sigma_u^- - X\ ^1\Sigma_g^+)$ band system. Observations of the equilibrium between the $N_2(a\ ^1\Pi_g)$ and $N_2(a'\ ^1\Sigma_u^-)$ states in our reactor indicate that the metastable has a radiative lifetime $\gtrsim 23\,^{+11}_{-6}$ ms, assuming a radiative lifetime of $80\,^{+40}_{-20}\mu s$ for $N_2(a\ ^1\Pi_g)$. Rate coefficients for quenching by NO, CH_4, CO, and N_2O are approximately gas kinetic, those by H_2, O_2, and CO_2 roughly tenth gas kinetic, and that by molecular nitrogen $(1.9 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The interaction between $N_2(a')$ and CO produced $CO(A\ ^1\Pi - X\ ^1\Sigma)$ emission in about $21\,^{+10}_{-8}\%$ of the quenching events.

I. INTRODUCTION

Although the lowest excited singlet state of molecular nitrogen, $N_2(a'\ ^1\Sigma_u^-)$, is potentially an important energy carrier in systems involving excited nitrogen, such as nitrogen discharges and aurorae, it has been studied only sparingly. This is probably because its long radiative lifetime, estimated to be between 13 and 500 ms,[1–4] makes it difficult to detect optically. Several authors have shown that it probably is the state to which the much more studied $N_2(a\ ^1\Pi_g)$ state is quenched.[4–8]

Golde[6] developed a discharge technique for studying $N_2(a', v' = 0)$. He showed that this state was coupled kinetically to $N_2(a, v' = 0)$ which is 1212 cm^{-1} higher in energy. The fact that he could see none of the higher vibrational levels of $N_2(a')$ he took as evidence that the a and a' states were efficiently coupled throughout the nested manifold, and that during the few millisecond transit time between his discharge and his observation vessel all of the higher lying a'-state vibrational levels had relaxed to a-state vibrational levels. Radiation or further quenching deactivated these levels so that some fraction of them ultimately ended in a', $v' = 0$. Later, Casassa and Golde[4] studied the spectroscopy of $N_2(a', v' = 0)$, determining the transition moment variation with r centroid, and reanalyzed the absorption data of Tilford and Benesch[3] to estimate a radiative lifetime of about 17 ms for $N_2(a', v' = 0)$. In comparing the ratio of intensities of the a and a' emissions, they estimated a lower limit to the a' lifetime of about 31 ms.

We have studied the kinetics of reactions of $N_2(a', v' = 0)$ with a number of molecules in a discharge-flow reactor. A cold-cathode discharge source similar to Golde's produced the metastables. Our observations confirm those of Casassa and Golde regarding the transition-moment variation of $N_2(a', v' = 0)$ and the equilibrium ratio of a to a' emission. We have further determined the rate coefficients for quenching $N_2(a', v' = 0)$ by a variety of molecules, and have determined the efficiency with which $N_2(a')$ excites the $CO(A-X)$ bands in an energy-transfer reaction with CO.

II. EXPERIMENTAL

The apparatus used in these studies has been described in some detail in several previous publications.[9–13] Basically it is a 2 in. diameter discharge-flow reactor which incorporates a moveable injector for varying the reaction time between the metastables and the quenchers. A cold-cathode discharge operating at about 390 V through molecular nitrogen highly diluted in argon produces the metastables. Observations of flourescence from the forbidden $N_2(a', v' = 0 - X, v'' = 4)$ transition at 171 nm was our primary diagnostic for the metastable number density. Because molecular nitrogen is a reasonably efficient quencher of $N_2(a')$, the mole fraction of nitrogen in the discharge and the total system pressure must be kept low, and transit times between the discharge and the observation region need to be minimized. Typically we operated at a pressure of about 0.95 Torr with a nitrogen mole fraction of about 0.007 and a total transit time between the discharge and the detection region of about 13 ms.

Although the discharge source produces some atomic nitrogen, both $N(^4S)$ and $N(^2D)$, and $N_2(A\ ^3\Sigma_u^+)$, none of these species should affect our kinetic results. In principle, $N_2(A)$ could be collisionally excited to $N_2(a')$ in energy pooling reactions involving other metastables which supply at least 2.23 eV. This means $N(^2D)$, $N(^2P)$, $N_2(A)$, and $N_2(X, v \geqslant 8)$. The absence of emission at 346.6 nm, $N(^2P-^4S)$, shows that $N(^2P)$ number densities are less than 10^6 atoms cm^{-3}. At higher pressures (> 5 Torr) and longer flow times from the discharge, we do see some (N^2P) emissions from this source. Presumably, the $N(^2P)$ is excited by the efficient energy transfer between $N_2(A)$ and $N(^4S)$.[14,15] Mestastable helium Penning ionization measurements on the effluents of this discharge source showed that $N_2(X, v)$ also is absent from the gas stream.[16] Our mesurements on $N_2(A)$ energy pooling indicated very little, if any, singlet metastable formation.[17] Resonance-flourescence measurements in the vacuum ultraviolet, however, do indicate the presence of $N(^2D)$ metastables at number densities which could be as high as 10^{10} atoms cm^{-3}. Thus we cannot so

easily rule out the possibiltiy of energy pooling between $N_2(A)$ and $N(^2D)$ as a source of $N_2(a')$. Our kinetic observations, however, seem to indicate that this is not the case. For example, CO_2 quenches $N_2(a')$ efficiently but quenches $N_2(A)$ poorly[18] and reacts fairly slowly with $N(^2D)$.[13] Another possible downstream source of $N_2(a')$ could be the three-body recombination of atomic nitrogen.[8] However, N-atom number densities from this discharge source are below 10^{12} atoms cm^{-3}, a number density too small to produce significant $N_2(a')$ emission via three-body recombination at pressures below a Torr. We verified this point by failing to find $N_2(a')$ in the afterglow of a microwave-discharge source of atomic nitrogen with atom number densities on the order of 10^{12} atoms cm^{-3} and total pressures below 2 Torr.

III. RESULTS

A. Spectral characterization and radiative lifetime of $N_2(a'\ ^1\Sigma_u^-, v'=0)$

Figure 1 shows the spectrum observed in our reactor. The only significant emissions between 140 and 180 nm are transitions from the lowest vibrational level of the a and a' states. We estimated a relative monochromator response function from the intensities of the various Lyman–Birge–Hopfield bands [$N_2(a-X)$; LBH] assuming a constant transition moment for the $a-X$ emission.[19] With this response function, we could then estimate the relative transition-moment variation for the Ogawa, Tanaka, Wilkinson, Mulliken bands [$N_2(a'-X)$; OTWM] using the Franck–Condon factors given in Lofthus and Krupenie.[20] Not surprisingly, our results agree quite well with those of Casassa and Golde who used a similar procedure. The relative response function, and the transition probabilities calculated with the transi-
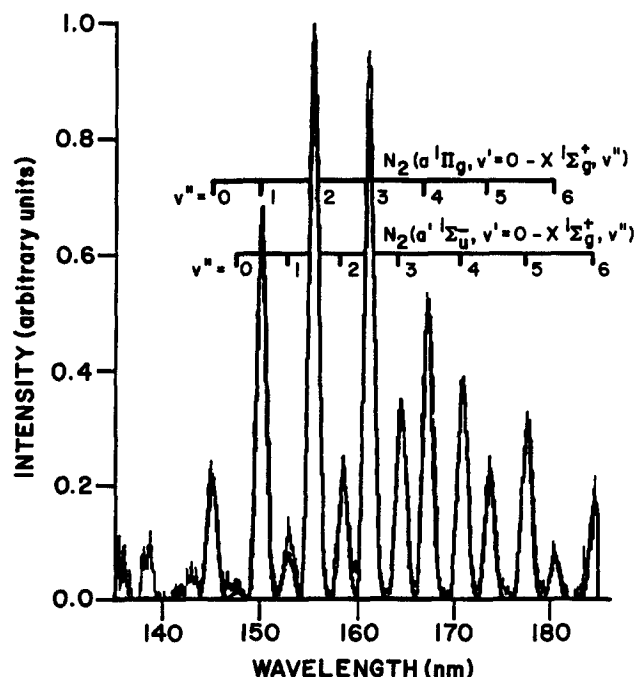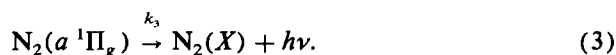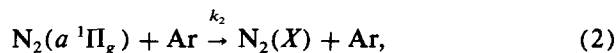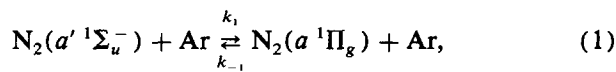
tion moment variation we had determined allow us to fit the two band systems with our synthetic spectral fitting code.[11] The heavy line in Fig. 1 shows the results of the fit compared to the experimental observations which are shown with the light line. Spectral fits to a number of spectra showed that the ratio of the intensities of the LBH to the OTWM bands is 1.71 ± 0.05 at 300 K.

Golde[6] has already shown that this ratio is independent of argon pressure over the range 0.5 to 4 Torr. Our observations show that quenching the bands significantly by adding N_2O and CO_2 also does not change this ratio. The two emissions are therefore in a steady-state ratio in our reactor. We can use this observation to estimate a lower limit to the lifetime of the $N_2(a')$ state. We need consider only the following three reactions:

$$N_2(a'\ ^1\Sigma_u^-) + Ar \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2(a\ ^1\Pi_g) + Ar, \tag{1}$$

$$N_2(a\ ^1\Pi_g) + Ar \overset{k_2}{\rightarrow} N_2(X) + Ar, \tag{2}$$

$$N_2(a\ ^1\Pi_g) \overset{k_3}{\rightarrow} N_2(X) + h\nu. \tag{3}$$

$N_2(a)$ is in steady state within our field of view because its radiative lifetime is only 80 μs.[21-27] The kinetic rate expressions derived from reactions (1) through (3) can be combined, therefore, to give the ratio of number densities of the two singlet metastables:

$$\frac{[N_2(a)]}{[N_2(a')]} = \frac{k_1[Ar]}{(k_{-1}+k_2)[Ar]+k_3}. \tag{4}$$

Since the ratio of the a to a' emission is independent of pressure,[6] quenching must dominate radiation and the radiative-decay rate, k_3, can be dropped from Eq. (4). The number density is the observed intensity multiplied by the radiative lifetime. The ratio of the rate coefficients k_1/k_{-1} is the Boltzmann equilibrium ratio,

$$\frac{k_1}{k_{-1}} = 2e^{-1212\ \text{cm}^{-1}/kT}, \tag{5}$$

where the factor of 2 accounts for the lambda doubling in the pi state. With these last three points in mind, we can rearrange Eq. (4) to get

$$\frac{I_a}{I_{a'}} = \frac{k_1}{k_{-1}+k_2}\frac{\tau_{a'}}{\tau_a}. \tag{6}$$

In the limit that deactivation to the a' state is the only significant pathway for a-state quenching, we can set a limit on the radiative lifetime of the a' state in terms of that of the a state:

$$\tau_{a'} \geqslant \frac{k_{-1}}{k_1}\frac{I_a}{I_{a'}}\tau_a. \tag{7}$$

The radiative lifetime of $N_2(a)$ is still somewhat in doubt,[21-27] but a value of 80^{+40}_{-20} μs apparently encompasses the correct value. Thus we find that
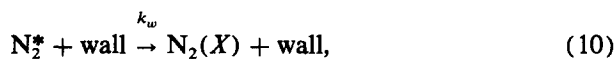
$$\tau_{a'} \gtrsim 23^{+11}_{-6}\ \text{ms}. \tag{8}$$

This analysis is similar to that given by Casassa and Golde.[4] They used a different lifetime for $N_2(a\ ^1\Pi_g)$, however, and reported $\tau_{a'} \geqslant 32$ ms. Their reanalysis of the experiments of Tilford and Benesch[3] yielded a lifetime of 17 ms. Thus they

FIG. 1. Spectrum of $N_2(a'\ ^1\Sigma_u^-)$ and $N_2(a\ ^1\Pi_g)$ 13 ms downstream from the discharge. The light line shows the experimental spectrum, the heavy line the synthetic best fit to the data.

In the figure axes: INTENSITY (arbitrary units), WAVELENGTH (nm), with labels $N_2(a\ ^1\Pi_g, v'=0 - X\ ^1\Sigma_g^+, v'')$ and $N_2(a'\ ^1\Sigma_u^-, v'=0 - X\ ^1\Sigma_g^+, v'')$

concluded that the true lifetime probably lay between 17 and 40 ms. We feel that the analysis of the ratio of a to a' intensities should give a more accurate assessment of the radiative lifetime than does the VUV absorption measurement of Tilford and Benesch which involves a comparison of densitometer tracings of $a'\,{}^1\Sigma_u^-$ and $A\,{}^3\Sigma_u^+$ absorptions rather than a direct curve-of-growth measurement. The major uncertainty in the present approach is the radiative lifetime of $N_2(a\,{}^1\Pi_g)$. Clearly what is needed is a good determination of that value.

B. Quenching rate measurements

The reactions important in our kinetic analysis involve quenching of the $N_2(a')$ by the species of interest, Q, diffusion to the walls of the reactor with subsequent deactivation, and quenching by the N_2 and Ar bath gas:

$$N_2^* + Q \rightarrow N_2(X)Q', \tag{9}$$

$$N_2^* + \text{wall} \xrightarrow{k_w} N_2(X) + \text{wall}, \tag{10}$$

$$N_2^* + X_i \rightarrow N_2(X) + X_i^*, \tag{11}$$

where X_i represents other quenching species such as N_2, Ar, etc. The differential equation describing the rate of change in the number density of the metastables with time is

$$\frac{d[N_2^*]}{dt} = -\left\{ k_9[Q] + \sum_i k_{11}^i[X_i] + k_w \right\}[N_2^*]. \tag{12}$$

Because the number density of the quenchers is much larger than that of the metastables, it remains constant (it would in any event if the reaction involves energy transfer rather than reaction). Thus we can solve Eq. (12):

$$\ln \frac{[N_2^*]}{[N_2^*]_0} = -\left\{ k_9[Q] + \sum_i k_{11}^i[X_i] + k_w \right\}t. \tag{13}$$

Keeping the reaction time fixed and varying the number density of the quencher gives the decay coefficient Γ defined by

$$\frac{d\ln[N_2^*]}{d[Q]} = -k_9 z/\bar{v} = \Gamma(z), \tag{14}$$

where the reaction time is given by the ratio of the distance from the injector to the observation region z, to the bulk flow velocity $\bar{v}$. Finally, the rate coefficient results from the slope of a plot of Γ vs z

$$k_9 = -\bar{v}\frac{d\Gamma}{dz}. \tag{15}$$

This procedure corrects for imperfect mixing at the injector. Figure 2 shows semilog plots according to Eq. (14) for the quenching of $N_2(a')$ by NO at three different reaction times. Figure 3 shows plots of decay coefficient vs z for three different quenchers.

The above analysis assumes plug flow. The rate coefficients derived from plots according to Eqs. (14) and (15) must be divided by 0.62 to correct for the coupling of a radial density gradient in the metastable number density with a parabolic velocity profile. A number of papers in the literature discuss this effect in detail.[28–31]
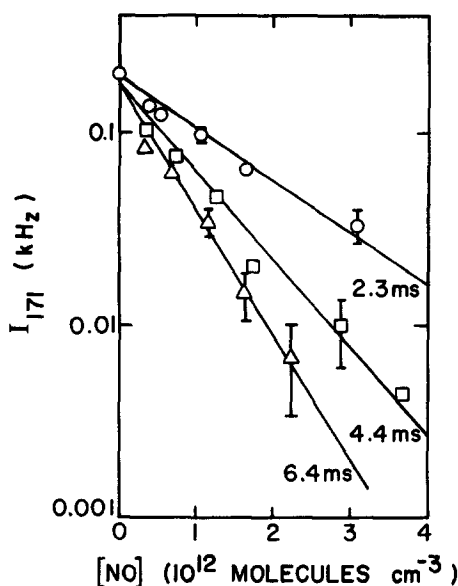
FIG. 2. The decay of $N_2(a'\,{}^1\Sigma_u^-)$ with added [NO] for three different reaction times.

Wall deactivation and relatively efficient quenching by molecular nitrogen constrained the experimental conditions to fairly low pressures and short reaction times. Several of the most inefficient quenchers, therefore, required fairly large additions of gas to the reactor in order to obtain adequate decays. In order to correct for any possible perturbation to the metastable number densities caused by injecting large mass flow of gas into the main flow, we measured apparent decays when comparable amounts of argon were added through the injector. We then corrected the measured
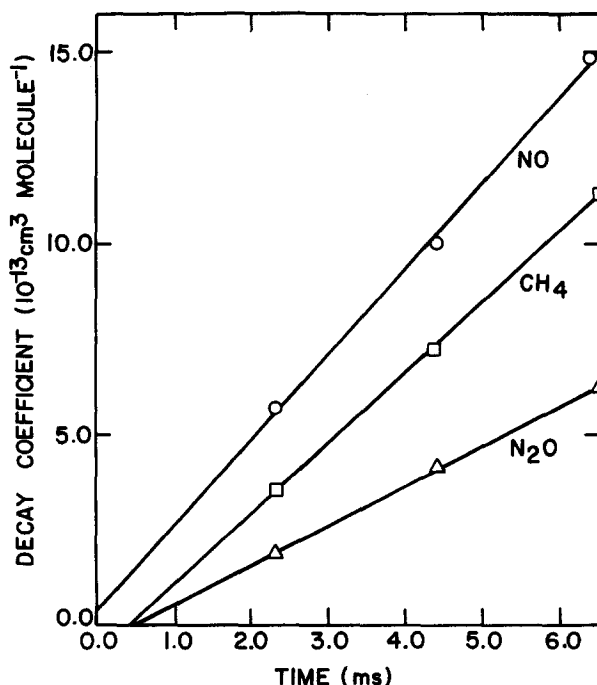
FIG. 3. Decay coefficients plotted against reaction time for $N_2(a'\,{}^1\Sigma_u^-)$ quenching.
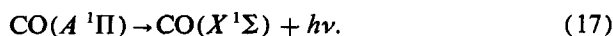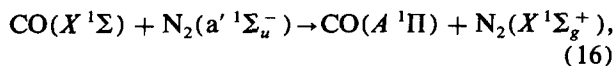
TABLE I. Results of N₂(a' ¹Σ_u⁻) quenching studies.

Molecule	Quenching rate coefficient (cm^3 molecule⁻¹ s⁻¹)
N_2	$(1.9 \pm 0.5) \times 10^{-13}$
O_2	$(2.8 \pm 0.6) \times 10^{-11}$
CO_2	$(2.5 \pm 0.6) \times 10^{-11}$
NO	$(3.6 \pm 0.8) \times 10^{-10}$
N_2O	$(1.7 \pm 0.4) \times 10^{-10}$
CH_4	$(3.0 \pm 0.8) \times 10^{-10}$
CO	$(1.1 \pm 0.3) \times 10^{-10}$
H_2	$(2.6 \pm 0.6) \times 10^{-11}$
CF_4	$(2.4 \pm 1.0) \pm 10^{-13}$
SF_4	$(7.8 \pm 1.8) \pm 10^{-14}$

decay coefficients of the quenchers of interest by subtracting the effective argon decay coefficients from them. This correction procedure assumes that argon is an inefficient quencher of N₂(a'). The decrease in the effective argon decay coefficient with increasing reaction time indicates this assumption is valid. The molecules N₂, CF₄, and SF₆ were corrected in this manner. This large addition of gas was still ≲ 7% of the total gas flow, so it did not perturb the flow field sufficiently to change the flow correction factor.

Table I summarizes our results. The error bars on the rate coefficients include the contributions from the standard deviations in the least squares fits according to Eqs. (14) and (15), our estimates of the uncertainties involved in the calibrations of our flow meters, pressure gauge, thermometer etc., and our estimate of the basic repoducibility of our measurements as determined in other kinetic investigations which involved multiple determinations of rate coefficients under a number of different conditions of pressure, total gas flow rate, and flow velocity.[9,12,13]

C. The excitation of CO(A) by energy transfer from N₂(a')

When carbon monoxide is added to the metastables, emission from the CO fourth-positive system, CO(A ¹Π–X ¹Σ), is observed. Golde and Thrush[32,33] have shown that CO fourth-positive emission is excited in the energy transfer between N₂(a) and CO. In our system, however, the low steady-state number density of the N₂(a) precludes that state as being the source of the observed CO(A) emission (see below). We conclude therefore, that it arises from energy transfer from N₂(a'):

$$CO(X\ ^1\Sigma) + N_2(a'\ ^1\Sigma_u^-) \rightarrow CO(A\ ^1\Pi) + N_2(X\ ^1\Sigma_g^+),$$
$$\tag{16}$$

$$CO(A\ ^1\Pi) \rightarrow CO(X\ ^1\Sigma) + h\nu.$$
$$\tag{17}$$

The extremely rapid radiative lifetime of the CO(A)[34] prevents its being deactivated by electronic quenching under our conditions. Thus the CO(A) is in steady state in our observation region, and we can write

$$\frac{[CO(A)]}{I_{N_2(a')}} = \frac{k_{16}}{k_{17}} \tau_{a'}.$$
$$\tag{18}$$

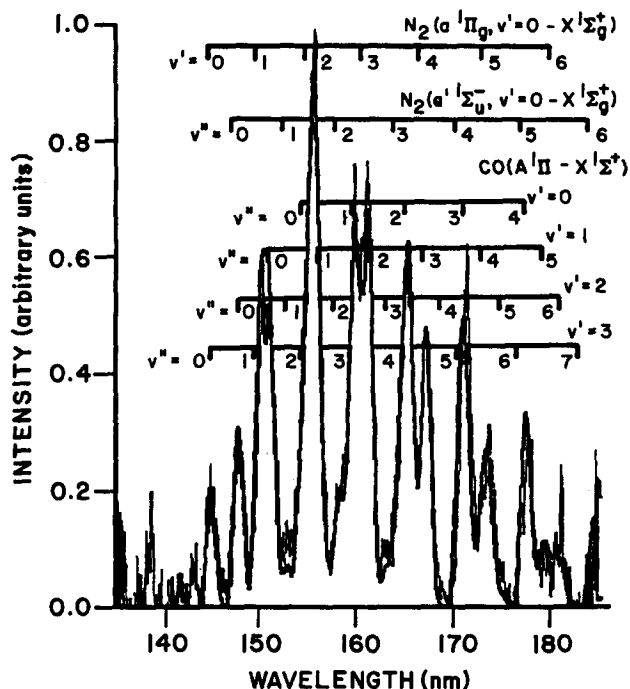We scanned the spectrum between 140 and 185 nm for varying amounts of added CO. We determined the number

FIG. 4. Spectrum of CO(A ¹Π) excited by energy transfer from N₂(a' ¹Σ_u⁻). The experimental spectrum is the light line, the synthetic best fit to the experimental data is the heavy line.

density of the emitting CO(A) molecule and the N₂(a') and N₂(a) emission intensities by spectral fitting. Figure 4 shows one such spectrum with its associated fit. The data derived from the fits are plotted according to Eq. (18) in Fig. 5 for vibrational levels 0–2 of CO(A). Excitation-rate coefficients derived from the slopes of the lines in Fig. 5, assuming a radiative lifetime for N₂(a') of 23 ₋₈⁺¹¹ ms, are given in Table II. The results indicate that only 21 ₋₈⁺¹⁰% of the quenching events between N₂(a') and CO result in CO electronic excitation.

If the a state rather than the a' state were responsible for exciting CO(A ¹Π), then our data would indicate an excitation rate coefficient of 5×10^{-9} cm^3 molecule⁻¹ s⁻¹, more than ten times gas kinetic. Golde and Thrush[33] previously
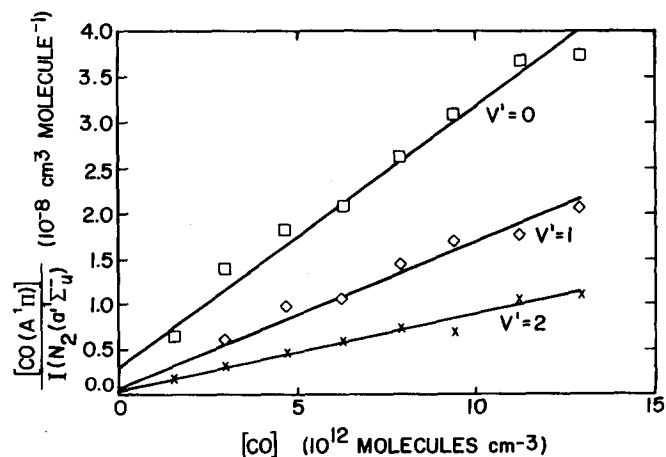
FIG. 5. Excitation of CO(A ¹Π) by N₂(a' ¹Σ_u⁻).

TABLE II. Results of $CO(A \, ^1\Pi)$ excitation by $N_2(a' \, ^1\Sigma_u^-)$.

v'	k_{ex} (cm^3 molecule^{-1} s^{-1})[a]
0	$(11.7^{+5.5}_{-4.4}) \times 10^{-12}$
1	$(\ 6.8^{+3.1}_{-2.5}) \times 10^{-12}$
2	$(\ 3.8^{+1.7}_{-1.4}) \times 10^{-12}$
3	$(\ 0.8^{+0.5}_{-0.4}) \times 10^{-12}$
Total	$(23.1^{+10.8}_{-8.7}) \times 10^{-12}$

[a] Assumes lifetime of 23^{+11}_{-6} ms for $N_2 \, (a' \, ^1\Sigma_u^-)$.

have established that the rate coefficient for exciting $CO(A)$ by $N_2(a)$ is only 1.5×10^{-10} cm^3 molecule^{-1} s^{-1}. Thus we can confidently assign $N_2(a')$ as the precursor for $CO(A)$ excitation in our system.

IV. DISCUSSION

Dreyer and Perner[35] excited $N_2(a')$ with a pulsed relativistic electron beam in nitrogen gas and observed its temporal behavior via resonance absorption on the fifth-positive system of nitrogen. They analyzed their data to determine a rate coefficient for $N_2(a')$ quenching by molecular nitrogen of $(2.21 \pm 0.14) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} in excellent agreement with our value. Van Veen et al.[7] used a laser to excite $N_2(a \, ^1\Pi_g, v' = 0,1)$ via two-photon pumping. The variation in the fluorescence decay lifetimes with nitrogen pressure over the range of 0.05 to 10 Torr indicated complete coupling between $N_2(a)$ and $N_2(a')$ at pressures above 1 Torr, so that observed decays in that pressure region were diagnostic of $N_2(a')$ behavior. They reported a rate coefficient for quenching $N_2(a')$ by nitrogen of $(2.3 \pm 0.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, again in excellent agreement with the present results.

Golde and Thrush[8] observed the behavior of $N_2(a)$ and $N_2(a')$ under various conditions in a flow of recombining nitrogen atoms and concluded that the ratio of the rate coefficients for $N_2(a')$ quenching by Ar to that by N_2 was unity and that the similar ratio for CO_2 quenching to that by N_2 was 117 ± 20. Our results clearly indicate that quenching of $N_2(a')$ by argon must be much less efficient than quenching by nitrogen. If the argon quenching rate coefficient were the same as our nitrogen value, we calculate that the metastables would have a lifetime against quenching of 0.28 ms at the argon number density in our reactor. Thus it would not survive the 13 ms traversal time from the discharge to the observation region. The fact that $N_2(a')$ is observed in the observation region shows that $N_2(a')$ quenching by Ar is more than an order of magnitude slower than is quenching by N_2. Our results give a ratio of the CO_2 rate coefficient to that for N_2 of 129 ± 21 in good agreement with Golde and Thrush's observation.

We are unaware of any other quenching data on $N_2(a')$. Our rate coefficient for quenching by molecular oxygen indicates that quenching would be comparable to radiative decay at an altitude just below 105 km (assuming a radiative lifetime of 23 ms). Thus one cannot neglect the importance of $N_2(a')$ as a metastable energy carrier in modeling energy degradation in the disturbed upper atmosphere.

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