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, \( N_2(a'1\Sigma_u^+, \nu = 0) \), 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 fluorescence 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 \( \approx 23 \pm 4 \) ms, assuming a radiative lifetime of \( 80 \pm 20 \) ms for \( N_2(a'1\Pi_g) \). Rate coefficients for quenching by NO, CH₄, CO, and N₂O are approximately gas kinetic, those by H₂, O₂, and CO₂ roughly tenth gas kinetic, and that by molecular nitrogen \((1.9 \pm 0.5) \times 10^{-13} \) cm³ molecule⁻¹ s⁻¹. The interaction between \( N_2(a') \) and CO produced CO(\( A'2\Pi-X'1\Sigma \)) emission in about 21 ± 10% 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, makes it difficult to detect optically. Several authors have shown that it is possible for the state to which the much more studied \( N_2(a'1\Pi_g) \) state is quenched.⁴⁻⁸

Golde⁴ developed a discharge technique for studying \( N_2(a', \nu' = 0) \). He showed that this state was coupled kinetically to \( N_2(a, \nu = 0) \) 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 \( a', \nu' = 0 \). Later, Casassa and Golde⁶ studied the spectroscopy of \( N_2(a', \nu' = 0) \), determining the transition moment variation with \( r \) centroid, and reanalyzed the absorption data of Tilford and Benesch³ to estimate a radiative lifetime of about 17 ms for \( N_2(a', \nu' = 0) \). 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 \( N_2(a', \nu' = 0) \) 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 \( N_2(a', \nu' = 0) \) and the equilibrium ratio of \( a \) to \( a' \) emission. We have further determined the rate coefficients for quenching \( N_2(a', \nu' = 0) \) 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 fluorescence from the forbidden \( N_2(a', \nu' = 0 - X, \nu' = 4) \) 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 \( N_2(A'2\Sigma_u^+) \), 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 \( N_2(X, \nu > 8) \). The absence of emission at 346.6 nm, N(\( ^2P \)– \( ^2S \)), 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 Metastable helium Penning ionization measurements on the effluents of this discharge source showed that \( N_2(X, \nu) \) also is absent from the gas stream.¹⁶ Our measurements on \( N_2(A) \) energy pooling indicated very little, if any, singlet metastable formation.¹⁷ Resonance-fluorescence 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 possibility of energy pooling between \(N_2(a') (A')\) and \(N_2^2(D)\) as a source of \(N_2(a')\). Our kinetic observations, however, seem to indicate that this is not the case. For example, \(\text{CO}_2\) quenches \(N_2(a')\) efficiently but quenches \(N_2(A)\) poorly\(^\text{18}\) and reacts fairly slowly with \(N_2^2(D)\).\(^\text{13}\) Another possible downstream source of \(N_2(a')\) could be the three-body recombination of atomic nitrogen.\(^\text{4}\) However, N-atom number densities from this discharge source are below \(10^{12}\) atoms \(\text{cm}^{-3}\), 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 \(\text{cm}^{-3}\) and total pressures below 2 Torr.

III. RESULTS
A. Spectral characterization and radiative lifetime of \(N_2(a' \^1\Sigma_u^+ , \nu = 0)\)

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.\(^\text{19}\) 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 Loththus and Krupenie.\(^\text{20}\) 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 transition moment variation we had determined allow us to fit the two band systems with our synthetic spectral fitting code.\(^\text{11}\) 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 \(\pm\) 0.05 at 300 K.

Golde\(^\text{5}\) 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 \(\text{N}_2\text{O}\) and \(\text{CO}_2\) 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:

\[
\begin{align*}
N_2(a' \ ^1\Sigma_u^-) + \text{Ar} & \xrightarrow{k_1} N_2(a \ ^1\Pi_u) + \text{Ar}, \\
N_2(a \ ^1\Pi_u) + \text{Ar} & \rightarrow N_2(X) + \text{Ar}, \\
N_2(a \ ^1\Pi_u) & \rightarrow N_2(X) + h\nu.
\end{align*}
\]

\(N_2(a)\) is in steady state within our field of view because its radiative lifetime is only 80 \(\mu\text{s}\).\(^\text{21-27}\) 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:

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

Since the ratio of the \(a\) to \(a'\) emission is independent of pressure,\(^\text{6}\) 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,

\[
\frac{k_1}{k_{-1}} = 2e^{-1212 \text{ cm}^{-1}/kT},
\]

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

\[
\frac{I_a}{I_{a'}} = \frac{k_1}{k_{-1} + k_2} \frac{T_{a'}}{T_a}.
\]

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:

\[
T_{a'} \simeq \frac{k_{-1}}{k_1} \frac{I_a}{I_{a'}} \frac{T_a}{T_{a'}}.
\]

The radiative lifetime of \(N_2(a)\) is still somewhat in doubt,\(^\text{21-27}\) but a value of 80\(^\text{49,50}\) \(\mu\text{s}\) apparently encompasses the correct value. Thus we find that

\[
T_{a'} \simeq 23^{+11}_{-6} \mu\text{s}.
\]

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

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

\[ N_2^* + Q \rightarrow N_2(X)Q', \]
\[ N_2^* + \text{wall} \rightarrow N_2(X) + \text{wall}, \]
\[ N_2^* + X_i \rightarrow N_2(X) + X_i^*, \]
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

\[ \frac{d}{dt} [N_2^*] = - \left[ k_0[Q] + \sum k_{it'} [X_i] + k_w \right] [N_2^*]. \]

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):

\[ \ln \left[ \frac{[N_2^*]}{[N_2^*_0]} \right] = - \left[ k_0[Q] + \sum k_{it'} [X_i] + k_w \right] t. \]

Keeping the reaction time fixed and varying the number density of the quencher gives the decay coefficient \(\Gamma\) defined by

\[ \frac{d \ln [N_2^*]}{d [Q]} = - \frac{k_0z/A^2}{d} = \Gamma(z), \]
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 \(A\). Finally, the rate coefficient results from the slope of a plot of \(\Gamma\) vs \(z\)

\[ k_0 = - \frac{A}{d} \frac{d\Gamma}{dz}. \]

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.\[28-31\]

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**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

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**FIG. 3.** Decay coefficients plotted against reaction time for \(N_2(a' 1\Sigma^-_u)\) quenching.
TABLE I. Results of \( N_2(a' \Sigma_u^-) \) quenching studies.

| Molecule | Quenching rate coefficient 
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( N_2 )</td>
<td>((1.9 \pm 0.5) \times 10^{-13})</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>((2.8 \pm 0.6) \times 10^{-11})</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>((2.5 \pm 0.6) \times 10^{-11})</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>((3.6 \pm 0.8) \times 10^{-10})</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>((1.7 \pm 0.4) \times 10^{-10})</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>((3.0 \pm 0.8) \times 10^{-10})</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>((1.1 \pm 0.3) \times 10^{-10})</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>((2.6 \pm 0.6) \times 10^{-11})</td>
</tr>
<tr>
<td>( \text{CF}_4 )</td>
<td>((2.4 \pm 1.0) \pm 10^{-13})</td>
</tr>
<tr>
<td>( \text{SF}_6 )</td>
<td>((7.8 \pm 1.8) \pm 10^{-14})</td>
</tr>
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</table>

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 \( N_2(a') \). The decrease in the effective argon decay coefficient with increasing reaction time indicates this assumption is valid. The molecules \( N_2, \text{CF}_4, \) and \( \text{SF}_6 \) were corrected in this manner. This large addition of gas was still \( \lesssim 7\% \) 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 reproducibility 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 \( \text{CO}(A) \) by energy transfer from \( N_2(a') \)

When carbon monoxide is added to the metastables, emission from the CO fourth-positive system, \( \text{CO}(A \, \Pi^+ \rightarrow \chi \, \Sigma^-) \), is observed. Golde and Thrush\(^32,33\) have shown that CO fourth-positive emission is excited in the energy transfer between \( N_2(a) \) and CO. In our system, however, the low steady-state number density of the \( N_2(a) \) precludes that state as being the source of the observed \( \text{CO}(A) \) emission (see below). We conclude therefore, that it arises from energy transfer from \( N_2(a') \):

\[
\text{CO}(\chi \, \Sigma^-) + N_2(a' \Sigma_u^-) \rightarrow \text{CO}(A \, \Pi^+) + N_2(\chi \, \Sigma_u^+) ,
\]

\[
\text{CO}(A \, \Pi^+) \rightarrow \text{CO}(\chi \, \Sigma^-) + hv .
\]

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

\[
\frac{[\text{CO}(A)]}{[N_2(a')] = \frac{k_{16}}{k_{17}} \tau_{a'} .
\]

We scanned the spectrum between 140 and 185 nm for varying amounts of added CO. We determined the number density of the emitting \( \text{CO}(A) \) molecule and the \( N_2(a') \) and \( N_2(a) \) 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 \( \text{CO}(A) \). Excitation-rate coefficients derived from the slopes of the lines in Fig. 5, assuming a radiative lifetime of \( N_2(a') \) of \( 23 \pm 11 \) ms, are given in Table II. The results indicate that only \( 21 \pm 10\% \) of the quenching events between \( N_2(a') \) and CO result in CO electronic excitation.

If the \( a \) state rather than the \( a' \) state were responsible for exciting \( \text{CO}(A \, \Pi^+) \), then our data would indicate an excitation rate coefficient of \( 5 \times 10^{-9} \) \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), more than ten times gas kinetic. Golde and Thrush\(^33\) previously

![FIG. 4. Spectrum of CO(A \, \Pi) excited by energy transfer from N2(a' \Sigma_u^-). The experimental spectrum is the light line, the synthetic best fit to the experimental data is the heavy line.](image)

![FIG. 5. Excitation of CO(A \, \Pi) by N2(a' \Sigma_u^-).](image)
TABLE II. Results of CO(A' \Pi) excitation by N_2(a' \Sigma^-_g).

<table>
<thead>
<tr>
<th>(v')</th>
<th>(k_a \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>((11.7_{-2.8}^{+1.5}) \times 10^{-12})</td>
</tr>
<tr>
<td>1</td>
<td>((6.6_{-3.9}^{+2.2}) \times 10^{-12})</td>
</tr>
<tr>
<td>2</td>
<td>((3.8_{-1.6}^{+1.5}) \times 10^{-12})</td>
</tr>
<tr>
<td>3</td>
<td>((0.8_{-0.5}^{+0.3}) \times 10^{-12})</td>
</tr>
<tr>
<td>Total</td>
<td>((23.1_{-4.3}^{+6.0}) \times 10^{-12})</td>
</tr>
</tbody>
</table>

* Assumes lifetime of 23 \(s\) ms for \(N_2(a' \Sigma^-_g)\).

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

IV. DISCUSSION

Dreyer and Perner\(^5\) 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 \((2.21 \pm 0.14) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) in excellent agreement with our value. Van Veen et al.\(^1\) used a laser to excite \(N_2(a' \Pi_\Sigma_g a' = 0.1)\) 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 \((2.3 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), 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 \(117 \pm 20\). 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 quenching by \(N_2\). Our results give a ratio of the CO\(_2\) rate coefficient to that for \(N_2\) of 129 \pm 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.

ACKNOWLEDGMENTS

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\(^17\) L. G. Piper, PSI TR-593 and (in preparation).