# Energy transfer studies on $N_2(X\,^1\Sigma_g^+,v)$ and $N_2(B\,^3\Pi_g)$

Lawrence G. Piper
*Physical Sciences Inc., 20 New England Business Center, Andover, Massachusetts 01810*

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We have developed a novel discharge–flow technique for studying the quenching of $N_2(X\,^1\Sigma_g^+,v''\geqslant 5)$ and $N_2(B\,^3\Pi_g)$ by a variety of molecules. The technique involves adding small number densities of $N_2(A\,^3\Sigma_u^+)$ to a flow of $N_2(X,v)$ producing, thereby, $N_2(B)$. By comparing $N_2(B)$ fluorescence intensities generated when a quencher is added to the $N_2(X,v)$ flow 2–3 ms before $N_2(A)$ addition with intensities observed after the $N_2(X,v)$ and quencher have been mixed for times of 10–30 ms, we can separate the effects of $N_2(B)$ fluorescence quenching from effects of $N_2(X,v)$ quenching. Our results indicate that $CH_4$, $CO_2$, CO, $O_2$, and $N_2O$ quench $N_2(B)$ at rates approaching gas kinetic while $H_2$, $N_2$, $SF_6$, and $CF_4$ are about ten times slower. Rate coefficients for $N_2(X,v''\geqslant 5)$ quenching by $H_2$ and $N_2$ are on the order of $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, those for $CO_2$, $CH_4$, and $CF_4$ roughly an order of magnitude faster, and CO and $N_2O$ yet another order of magnitude faster.

## I. INTRODUCTION

We have developed a technique for determining global quenching rate coefficients for $N_2(X,v'')$ in vibrational levels $v''\geqslant 5$. This technique involves monitoring nitrogen first-positive fluorescence, $N_2(B\,^3\Pi_g\text{–}A\,^3\Sigma_u^+)$, excited in the energy transfer reaction between $N_2(A)$ and $N_2(X,v'')$. The first-positive emission intensity is proportional to the number density of $N_2(X,v'')$.[1] Molecules added to the reactor can quench both the $N_2(X,v'')$ and the first-positive emission. This paper describes techniques for separating the two processes.

Vibrationally excited, ground–electronic state nitrogen plays an important role in a number of areas including laser excitation,[2] discharge physics,[3] semiconductor processing,[4] and upper atmospheric chemistry.[5] Determining the role of $N_2(X,v)$ in these various processes is difficult, however, due to $N_2(X,v)$'s diabolical resistance to detection. A number of laser-based techniques for detecting $N_2(X,v)$ have been developed in recent years,[6] but these techniques tend to be prohibitively expensive for most budgets, insensitive ($\gtrsim 10^{14}$ molecules cm$^{-3}$), or they defy ready quantification. The technique we have developed is sensitive ($\gtrsim 10^{11}$ molecules cm$^{-3}$) and easy to implement. Although our approach cannot quantify $N_2(X,v)$ number densities exactly, it can specify them within factors of 2 or 3.

## II. EXPERIMENT

These experiments used the 4.6 cm i.d., quartz, discharge–flow reactor we have described in detail previously[1] (see Fig. 1). Briefly, the $N_2(X,v'')$ is generated in a microwave discharge through a flowing mixture of nitrogen dilute in helium. The effluents from the discharge pass through a nickel screen prior to entering the upstream end of the flow reactor. The screen removes the atoms and deactivates electronically excited metastables, but has relatively little effect on vibrationally excited $N_2$.

$N_2(A)$ enters at the downstream end of the flow reactor through an axial injector. The $N_2(A)$ is prepared in a side arm off the flow tube from the reaction between metastable $Ar(^3P_{2,0})$ and $N_2$.[7,8] A hollow cathode, dc discharge in a flow of a few percent Ar in He makes the $Ar(^3P_{2,0})$. Nitrogen intercepts the argon metastables just after they flow out from the cathode. A loop injector that can be moved along the length of the flow tube adds the quenching reagent.

A monochromator sensitive to radiation between 200 and 900 nm detects emissions diagnostic of $N_2(X,v'')$ and $N_2(A)$. The important spectral features are the $N_2$ first-positive bands, $N_2(B\,^3\Pi_g\text{–}A\,^3\Sigma_u^+)$ between 560 and 900 nm, excited in the $N_2(A)$ plus $N_2(X,v'')$ energy-transfer reaction, and the $N_2$ Vegard–Kaplan bands, $N_2(A\,^3\Sigma_u\text{–}X\,^1\Sigma_g^+)$, between 250 and 370 nm. The $N_2(X,v'')$ number density is proportional to the ratio of the first-positive to Vegard–Kaplan intensities.[1] A least-squares, spectral fitting procedure, that we have described in some detail previously,[9] determines band intensities from the spectra.

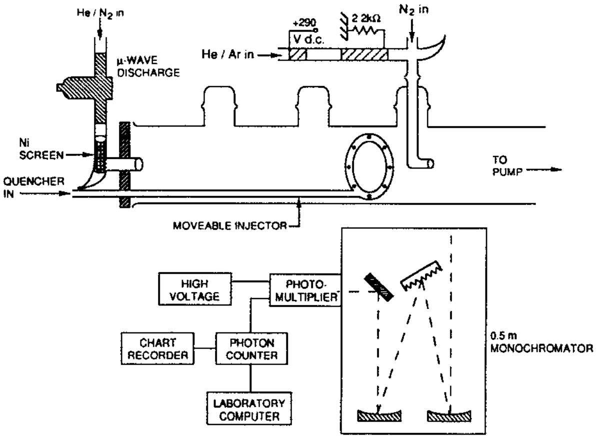

FIG. 1. Discharge–flow reactor for studying $N_2(B)$ and $N_2(X,v)$ quenching.

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## III. EXPERIMENTAL TECHNIQUE

When quencher is injected immediately behind the $N_2(A)$ inlet, the number density of $N_2(X,v'')$ remains essentially unchanged. This is because vibrational quenching is a relatively slow process ($k_v \lesssim 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and reagents are mixed for too short a time ($\approx 2$ ms) to effect significant quenching. Any diminution in the first-positive emission, therefore, results from quenching $N_2(B)$, or, in some cases, $N_2(A)$. Injecting the reagent into the upstream end of the flow reactor allows adequate time ($\sim$10–30 ms) for some of the $N_2(X,v'')$ to be quenched, unless its quenching rate coefficients are exceedingly small. Any difference in diminution of the first-positive emission with the injector in the upstream position as compared to the downstream position can be attributed to quenching of the $N_2(X,v'')$ by added reagent.

These concepts are described mathematically as follows. In the absence of added quencher, the intensity of the $N_2$ first-positive emission is given by[1]

$$I_0 = k_r[N_2(B)] = k_{ex}[N_2(X,v'')][N_2(A)], \qquad (1)$$

where, $k_{ex}$ is the rate coefficient for $N_2(B,v'' \geqslant 1)$ excitation in the reaction between $N_2(A)$ and $N_2(X,v'')$, $3.5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (see below), and $k_r$ is the $N_2(B)$ radiative decay rate, taken here for the global measurements to be $1.5 \times 10^5$ s$^{-1}$.[9] These experiments were run at low pressures ($\sim$1 Torr), primarily of helium. This reduces bath-gas quenching of $N_2(B)$ in the flow tube to less than a 20% effect.[10] We have neglected bath-gas quenching, therefore, in Eq. (1).

When the quencher is introduced into the flow reactor with the injector in the downstream position, the first-positive emission intensity is given by

$$I = k_r[N_2(B)] = \frac{k_{ex}[N_2(A)][N_2(X,v'')]}{1 + k_Q[Q]/k_r}, \qquad (2)$$

where $k_Q$ is the rate coefficient for $N_2(B)$ quenching by the quencher $Q$. For the moment we ignore quenching of the $N_2(A)$. Taking the ratio of the first-positive intensity in the absence of quencher to that in the presence of quencher gives the classical Stern–Volmer formula[11] for electronic quenching, viz.,

$$\Gamma = I_0/I = 1 + k_Q[Q]/k_r. \qquad (3)$$

The rate coefficient for $N_2(B)$ quenching is given, therefore, by the product of the $N_2(B)$ radiative decay rate times the slope of a plot of $\Gamma$ vs $[Q]$ for data taken with the injector in the downstream position.

With the injector in the upstream position, quenching of the $N_2(X,v'')$ also becomes possible, and the first-positive emission intensity becomes

$$I = k_r[N_2(B)] = \frac{k_{ex}[N_2(A)][N_2(X,v'')]_0 e^{-k_v[Q]\Delta t}}{1 + k_Q[Q]/k_r}, \qquad (4)$$

where $k_v$ is the rate coefficient for $N_2(X,v'')$ quenching, $\Delta t$ is the time the quencher and the $N_2(X,v'')$ are mixed, and the subscript $o$ refers to conditions in the absence of added quencher. The $N_2(X,v'')$ quenching rate coefficients can be determined, therefore, from the natural log of the ratio of Stern–Volmer factors, $\Gamma$, at long to short delay times divided by quencher number density and reaction time:

$$k_v = \frac{\ln(\Gamma_u/\Gamma_d)}{[Q]\Delta t}, \qquad (5)$$

where the subscripts $u$ and $d$ refer to intensity measurements with the injector in the upstream and downstream positions, respectively.

These formalisms presume that the added $N_2(A)$ is not diminished upon injecting the quencher. This is not necessarily always the case. When the $A$ state also is quenched, the actual $A$-state number density must be determined by measuring Vegard–Kaplan intensities for each set of experimental conditions, and then divided into the corresponding first-positive intensities. This procedure corrects for $A$-state quenching, and therefore makes this technique applicable for studies of quenchers which react rather efficiently with $N_2(A)$, e.g., $N_2O$. Because of the rather short time that $N_2(A)$ is actually in the flow reactor before the fluorescence is observed, $A$-state quenching generally is not large even for efficient $A$-state quenchers.

## IV. RESULTS

Figure 2 shows typical spectra generated in the quenching of $N_2(B)$ and $N_2(X,v)$ by $CO_2$. Clearly the longer mix-

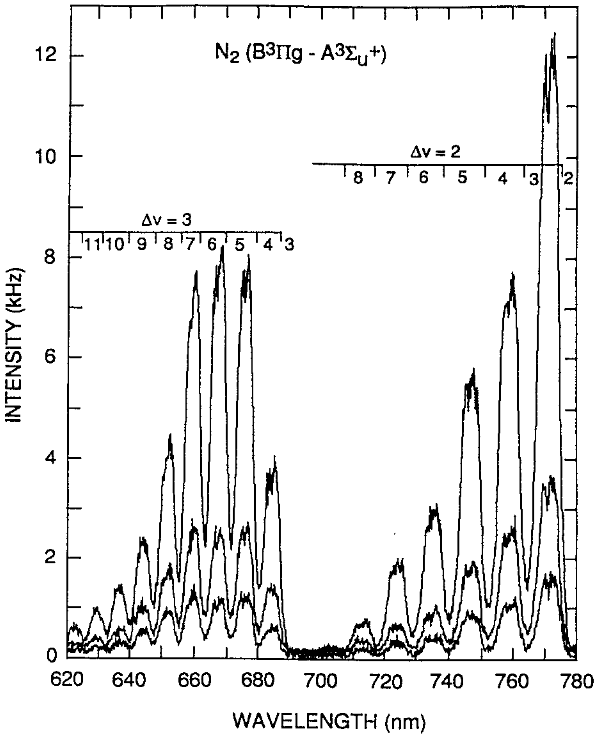

FIG. 2. $N_2(B\,^3\Pi_g - A\,^3\Sigma_u^+)$ spectra excited in the energy transfer reaction between $N_2(A)$ and $N_2(X,v)$ at different number densities of added $CO_2$ and varying reaction times. In order of decreasing intensity the conditions are $[CO_2] = 0$, $\Delta t = 2.5$ ms; $[CO_2] = 9.6 \times 10^{14}$ molecules cm$^{-3}$, $\Delta t = 2.5$ ms; $[CO_2] = 9.6 \times 10^{14}$ molecules cm$^{-3}$, $\Delta t = 19.4$ ms. The spectra are not corrected for monochromator spectral response.

ing time further decreases the first-positive emission intensities from the levels at short mixing times. Most of our observations were survey measurements designed primarily to determine relative quenching efficiencies. Thus the majority of $N_2$ ($B$) and $N_2$ ($X,v''$) quenching rate coefficients were determined by monitoring changes in the $N_2$ ($B$) band intensities in the presence and absence of a single quencher number density at the two different injector positions. In a few cases, spectra were taken at two different quencher number densities with agreement between the two sets of data better than 20%.

To assess the validity of our procedure, we studied the quenching of $N_2$ ($B$) by $CH_4$ in more detail than the other molecules investigated. Figure 3 shows the Stern–Volmer quenching plot for two of the four bands of the first-positive system that were monitored as a function of added $CH_4$. The rate coefficients for quenching $N_2$ ($B$) by $CH_4$ range from about $3\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, for $v' = 2$ and 3, to 4 and $5\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $v' = 6$ and 8, respectively. The good linearity of these Stern–Volmer plots indicates that the two- or three-point measurements for all other quenchers should not give grossly inaccurate results.

Table I summarizes the global quenching rate coefficient measurements. Since we were interested primarily in relative quenching efficiencies, the experimental values can have absolute uncertainties up to a factor of 2. In relative terms, the numbers should be good to ±25%. Table II shows that rate coefficients for quenching individual vibrational levels of $N_2$ ($B$) can vary considerably for some molecules.

The values reported for $N_2$ ($X,v$) quenching (also Table I) are not state specific. The energetics of the $N_2$ ($A$) plus $N_2$ ($X,v$) reaction restrict $N_2$ ($X,v$) to vibrational levels no smaller than five for $N_2$ ($B,v = 1$) excitation, and at least as great as 13 to excite $N_2$ ($B,v = 12$). Undoubtedly each $B$-state vibrational level is excited by several $X$-state levels.

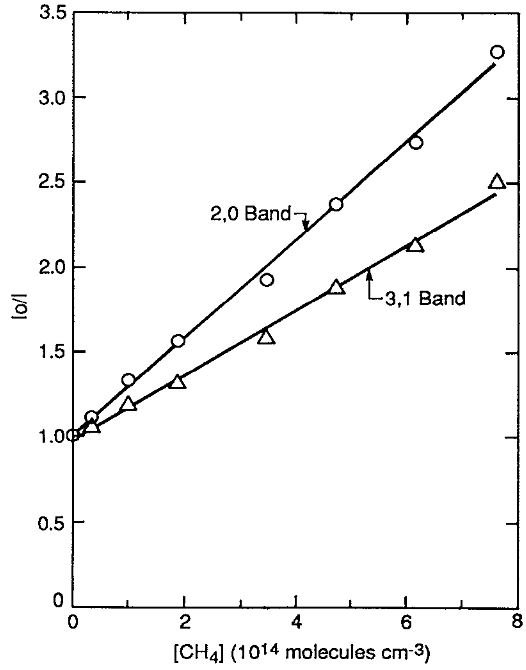

FIG. 3. Stern–Volmer plot for $N_2$ ($B$) quenching by $CH_4$.

TABLE I. Global rate coefficients[a] for quenching of $N_2$ ($B$) and $N_2$ ($X,v''$).

| Quencher | $N_2$ ($B$) | $N_2$ ($X,v''$) |
|---|---|---|
| $CH_4$ | $3\times10^{-10}$ | $1\times10^{-14}$ |
| $H_2$ | $5\times10^{-11}$ | $2\times10^{-15}$ |
| $CO_2$ | $2\times10^{-10}$ | $4\times10^{-14}$ |
| $N_2$ | $3\times10^{-11}$ | $2\times10^{-15}$ |
| $CF_4$ | $4\times10^{-11}$ | $1\times10^{-14}$ |
| $SF_6$ | $\sim1\times10^{-11}$ | ··· |
| $N_2O$ | $4\times10^{-10}$ | $3\times10^{-13}$ |
| CO | $2\times10^{-10}$ | $7\times10^{-14}$ |
| $O_2$ | $2\times10^{-10}$ | ··· |

[a] Units of cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K.

In our initial studies on the reaction between $N_2$ ($A$) and $N_2$ ($X,v''$), we studied the variation in $B$-state excitation as a function of $A$-state vibrational level.[1] We added $CH_4$ to our reactor to relax the vibrational energy in the $A$ state. In our analysis, we included the effects of some vibrational relaxation of the $N_2$ ($X,v''$) by the $CH_4$, but presumed no electronic quenching of the $N_2$ ($B$) state. The current studies show that this supposition was in error and that, in fact, $CH_4$ is quite efficient at quenching first-positive emission.

Correcting the data of Ref. 1 for $N_2$ ($B$) quenching by $CH_4$ has only a small effect on the rate coefficient for exciting $N_2$ ($B,v' = 1$–$12$) in the reaction between $N_2$ ($A$) and $N_2$ ($X,v' = 5$–$15$). The revised value for this rate coefficient is $(3.5 \pm 1.5)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, a 16% increase over the value reported previously.

## V. DISCUSSION

### A. $N_2$ ($B$) quenching

Most gases studied quenched $N_2$ ($B$) quite strongly, with rate coefficients for quenching by $CH_4$, CO, $CO_2$, $O_2$, and $N_2O$ being roughly gas kinetic. $N_2$, $H_2$, $CF_4$, and $SF_6$ quenched $N_2$ ($B$) about 10 times more slowly.

TABLE II. Vibrational level dependent $N_2$ ($B$) quenching rate coefficients.[a]

| $v'$ | $N_2$ | CO | $CO_2$ | $N_2O$ | $CH_4$ | $CF_4$ | $SF_6$ | $H_2$ | $O_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.16 | 2.1 | 2.0 | 3.1 | 2.3 | 0.29 | 0.08 | 0.34 | 1.5 |
| 2 | 0.21 | 2.0 | 2.0 | 4.6 | 2.5 | 0.59 | ··· | 0.39 | 1.5 |
| 3 | 0.29 | 1.7 | 1.8 | 4.5 | 1.6 | 0.20 | 0.53 | 0.50 | 1.5 |
| 4 | 0.31 | 1.2 | 2.1 | 5.1 | 1.6 | 0.14 | 0.23 | 0.48 | 1.7 |
| 5 | 0.35 | 0.7 | 2.5 | 6.5 | 2.0 | 0.16 | 0.66 | 0.54 | 1.6 |
| 6 | 0.35 | 1.0 | 2.3 | 6.6 | 2.4 | 0.59 | 0.33 | 0.56 | 2.2 |
| 7 | 0.36 | 1.1 | 1.6 | 5.2 | 2.3 | 0.23 | ··· | 0.50 | 2.3 |
| 8 | 0.39 | ··· | 1.4 | 5.8 | 2.7 | 0.65 | ··· | 0.57 | 2.7 |
| 9 | 0.36 | 0.5 | 2.1 | 7.4 | 3.1 | 0.73 | 0.38 | 0.73 | 1.9 |
| 10 | 0.29 | 1.6 | 2.0 | 7.5 | 3.6 | 0.60 | 0.20 | 0.69 | 4.0 |
| 11 | 0.30 | 0.7 | 1.7 | 9.1 | 4.9 | 0.45 | 0.39 | 0.82 | 3.2 |
| 12 | 0.22 | 3.0 | 1.6 | 7.4 | 5.1 | 1.3 | 0.28 | 0.61 | 2 |

[a] Units of $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Young *et al.*[12] reported the most extensive set of $N_2(B)$ quenching rate coefficients in the literature. Their values, in units of $cm^3$ $molecule^{-1}$ $s^{-1}$, were $4.6\times10^{-11}$, $8.5\times10^{-11}$, $1.5\times10^{-10}$, $2.7\times10^{-11}$, $1.1\times10^{-10}$, and $1.6\times10^{-10}$ for $N_2(B)$ quenching by $H_2$, CO, $CO_2$, $N_2$, $O_2$, and $N_2O$, respectively. Their rate coefficients for quenching by $N_2$ and $H_2$ agree quite well with ours, but their other values are about 50% smaller. Their value for $N_2(B)$ quenching by He, $8\times10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, is similar to that which we reported previously.[10]

Young *et al.*'s rate coefficient measurements were relative to their rate coefficient for $N_2(B)$ quenching by $N_2O$. Since the value for $N_2O$ quenching is about half the one we measured, their rate coefficients should be doubled for proper comparison. Agreement between the two sets of measurements then is quite good for CO, $CO_2$, and $O_2$ while their rate coefficients for quenching by $H_2$ and $N_2$ are roughly double ours.

Both Young *et al.*'s measurements and our global quenching-rate coefficients are not state specific and might, therefore, have been most sensitive to different groups of $N_2(B)$ vibrational levels. This could then explain the reported differences if the individual $N_2(B)$ vibrational levels were quenched at markedly disparate rates. Table II shows that in cases where significant variation with vibrational level exists, the lower levels tend to quench more slowly. Our global quenching rate coefficients are weighted towards the lower vibrational levels, $v'=1$–3, whereas Young *et al.*'s experiment was most sensitive to middle levels, $v'=4$–7. One would expect, therefore, that our results would be smaller than those of Young *et al.* In the present case, however, the average rate coefficients for quenching $v=4$–8 by both $H_2$ and $N_2$ and is essentially the same as the global rate coefficients.

Lee and Suto[13] reported $N_2(B)$ quenching rate coefficients by $H_2$ and $N_2$ to be $2.4\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and $2.1\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively. While their rate coefficient for quenching by $N_2$ is consistent with ours, their $H_2$ quenching rate coefficient is outside the combined uncertainties of the two studies. Their experiment was most sensitive to $N_2(B,v'=6$–$12)$. For this range of vibrational levels, our $H_2$ quenching rate coefficients are two to three times larger than theirs.

Our data for the individual vibrational levels (see Table II) indicate little variation with vibrational level for $N_2(B)$ quenching by $CO_2$ and $N_2$. In contrast, $CH_4$, $CF_4$, $H_2$, $O_2$, and $N_2O$ show a tendency for quenching rate coefficients to increase with increasing vibrational level. The increase between $v'=2$ and $v'=12$ is roughly a factor of 2–3.

Our results on quenching by $N_2$ are consistent with our previous study[14] which indicated $N_2(B)$ quenching rate coefficients by $N_2$ ranged between 2 and $3\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ for most vibrational levels. We had observed previously, however, that vibrational levels 7–9 were quenched two to three times faster than the other vibrational levels. Shemansky reported similar observations.[15] Shemansky's investigation and our earlier studies were more extensive than the current investigation, and should be more reliable.

Global observations cannot provide mechanistic information related to $N_2$ *B*-state quenching. Thus the observed rate of removal of a lower vibrational level of $N_2(B)$ might be moderated by collisional cascade from higher $N_2(B)$ vibrational levels. The measured global quenching rate coefficient for these low $v'$ levels would then be somewhat less than one would measure in a single state selected study. The cascade could be either direct removal of vibrational energy from $N_2$ molecules in the *B* state or it could involve electronic quenching into one or more of the electronic states nested within the $N_2(B)$ manifold, the primary ones being $A(^3\Sigma_u^+,v\geqslant7)$, $B'(^3\Sigma_u^-)$, $W(^3\Delta_u)$, or $X(^1\Sigma_g^+)$, followed by collisional intersystem crossing back to lower vibrational levels of the *B* state. An additional mechanism for quenching by $N_2$ is electronic energy exchange where a molecule in the *B* state transfers some of its electronic energy to a ground state molecule, leaving the receptor molecule in a lower vibrational level of the *B* state. This process has been demonstrated in isotopic studies by Pravilov *et al.*[16] and more recently by us.[17] For most cases of practical interest, e.g., discharge or auroral excitation of $N_2(B)$, the effective, global rate coefficient describes better the overall system behavior.

## B. $N_2(X,v'')$ quenching

Nitrous oxide and carbon monoxide quench $N_2(X,v)$ rather efficiently, roughly 0.1% gas kinetic. Rate coefficients for quenching by $CO_2$, $CF_4$, and $CH_4$ are roughly an order of magnitude, and $H_2$ and $N_2$ two orders of magnitude smaller than $N_2O$ and CO. The primary mode of de-excitation is undoubtedly $v$–$v$ transfer, although our measurement technique cannot distinguish single quantum from multiquanta relaxation.

The process being identified as vibrational quenching essentially involves the difference between removal of vibrational energy in levels 5–13 to vibrational levels 4 and below and energy resident in vibrational levels greater that 13 into levels 5–13. It is thus a net vibrational quenching, and the reported quenching rate coefficients should be taken to be lower limits to the true values. Because the higher vibrational levels of the *B* state can be excited only from larger vibrational levels of the ground state, one can determine, in a qualitative sense, relative quenching efficiencies for the *X*-state vibrational levels involved by examining changes in the $N_2(B,v)$ distribution under the different sets of conditions.

The $N_2(B,v)$ distributions with the injector placed in the upstream position are essentially identical ($\pm$15%) to those with the injector in the down stream position for $N_2(X,v)$ quenching by $N_2$ and $CO_2$. This result suggests that the relative $N_2(X,v)$ distributions do not change with added $N_2$ or $CO_2$, but that the overall $N_2(X,v)$ number density is diminished.

With $H_2$, $CH_4$, and $CF_4$, quenchers, the relative vibrational distributions of the five lowest $N_2(B,v)$ are similar for both injector positions, as are the relative distributions of the six highest $N_2(B,v)$. Relative to each other, however, the magnitude of the emission from the high vibrational level group diminishes twice as much as the lower vibrational level group when the injector is in the upstream position. The observations suggest that these molecules quench $N_2$ ($X$) vibrational levels greater than about 9 about twice as efficiently as levels 5–9.

On the other hand, $N_2O$ and CO quenchers decrease the relative $N_2$ ($B,v$) more for the lower six vibrational levels than for the higher ones when the reagent injector is moved to the upstream position. Such behavior would result if the $N_2$ ($X,v$) levels most responsible for $N_2$ ($B,v = 1$–$6$) excitation are quenched more rapidly than the higher $N_2$ ($X,v$).

An alternative explanation of our observations might be that the added quenchers just rearrange population within ground state vibrational levels 5–13 from vibrational levels more efficiently excited to the $B$ state by $N_2$ ($A$) into levels that are excited less efficiently. If this were the case, however, one would expect that the quenched $N_2$ ($B$) vibrational distributions with the injector in the upstream position would differ from those with the injector in the downstream position. In reality, as we have mentioned, for some quenchers the $N_2$ ($B,v$) distributions do not vary with injector position while for other quenchers changes are readily apparent.

$SF_6$ and $O_2$ behaved anomalously. In the global sense, $SF_6$ quenched $N_2$ ($B$) only modestly with the injector in the downstream position. With the injector in the upstream position, adding $SF_6$ actually increased the total $N_2$ ($B$) number density. The first-positive vibrational distributions in the absence and presence of $SF_6$ were quite different, however, with some levels increasing in intensity as $SF_6$ was added, while others diminished in intensity. This observation appears to indicate that $SF_6$ relaxes vibrational energy within the $B$-state manifold. The increase in $N_2$ ($B$) with the injector in the upstream position indicates that $SF_6$ relaxes higher vibrational levels of $N_2$ ($X,v$) into those for which our diagnostic is most sensitive, most likely $v' = 5$–$15$. However, $SF_6$ apparently does not relax the observed levels efficiently.

In the case of $O_2$, the $N_2$ ($B,v$) intensity was reduced by the addition of $O_2$ at both injector positions. However, the diminution was less with the injector in the upstream position. Unlike the case of $SF_6$, $N_2$ ($B,v$) quenching by $O_2$ was fairly uniform over the range of vibrational levels at both injector positions. These observations would suggest that $O_2$ is an inefficient quencher of the $N_2$ ($X,v$) important for $N_2$ ($B$) excitation process, but that it does quench higher $N_2$ ($X,v$).

Morgan and Schiff[18] used a catalytic probe to monitor vibrationally excited nitrogen in a discharge afterglow. They deduced rate coefficients for vibrational relaxation by $N_2$, $CO_2$, and $N_2O$ to be $<5\times10^{-18}$, $7.2\times10^{-15}$, and $2.6\times10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Their results for quenching by $CO_2$ and $N_2O$ are roughly an order of magnitude smaller than what we have determined, while their upper-bound rate coefficient for relaxation by nitrogen is smaller by three orders of magnitude. Their diagnostic was sensitive to all excited vibrational levels of nitrogen, whereas our diagnostic monitors only $v\geqslant5$. Thus our technique in essence monitors relaxation from levels $\geqslant5$ to any of the vibrational levels $v\leqslant4$. Morgan and Schiff's technique, on the other hand measures only quenching to $v'' = 0$. Since the $CO_2$ ($v$) and $N_2O(v)$ that are created from $N_2$ ($v$) quenching can re-excite $N_2$ ($v = 0$) back to $N_2$ ($v = 1$), the overall quenching rates of $N_2$ ($v$) by $CO_2$ and $N_2O$ will be retarded. McNeal *et al.*[19] demonstrated this effect for $CO_2$ by showing that the effective rate of $N_2$ ($v$) quenching diminished as the $N_2$ partial pressure increased.

McNeal *et al.*[19] and Starr and Shaw[20] also reported rate coefficients for $N_2$ ($v$) quenching by $CO_2$ and $N_2O$. Starr and Shaw noted that $N_2$ ($v$) excited atomic potassium fluorescence at a number of wavelengths. They monitored diminution of the 404.4 nm potassium line as a function of increasing $CO_2$ or $N_2O$ number density. This state of potassium can be excited only by $N_2$ ($v\geqslant11$), so their experiment measured quenching of vibrational levels above those for which we are most sensitive. Nonetheless, their values of $8\times10^{-14}$ and $1.4\times10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $CO_2$ and $N_2O$, respectively, are in reasonable accord with our values.

McNeal *et al.*[19] monitored $N_2$ ($v$) by photoionization of $N_2$ at wavelengths too long to ionize $N_2$ ($v = 0$). Although their signals were for ionization of $N_2$ ($v\geqslant1$), their diagnostic was heavily weighted towards $N_2$ ($v = 1$). They measured effective rate coefficients for quenching at a number of $N_2$ partial pressures and found the effective rate coefficients for $N_2$ ($v$) quenching by $CO_2$ and $N_2O$ increased as the $N_2$ partial pressure decreased. In the low $N_2$ partial pressure limit, they determined rate coefficients of $(2\pm1)\times10^{-13}$ and $(9\pm4)\times10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $CO_2$ and $N_2O$, respectively. Since our diagnostic monitors only $N_2$ ($v\geqslant5$), we should not be affected by back relaxation from $CO_2$ ($v$).

In summary, we have presented a novel technique for measuring the quenching of $N_2$ ($X,v''$) and $N_2$ ($B$) by a variety of quenchers. Our observations indicate that most species studied quench $N_2$ ($B$) at near gas-kinetic rates, whereas even efficient vibrational quenching of $N_2$ ($X,v''$) generally proceeds at rates four or more orders of magnitude less than gas kinetic.

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