

Further Observations on the Excitation of IF(B³Π₀⁺) in Active Nitrogen

Lawrence G. Piper

*Physical Sciences Inc., 20 New England Business Center, Andover, Massachusetts 01810
(Received: July 27, 1990; In Final Form: December 14, 1990)*

We have used a clean source of N₂(X,v) to investigate the excitation of IF(B) by N₂(X,v''=9-15). We find very little excitation even though the partial pressures of N₂(X,v=9-15) are on the order of 5 mTorr. The upper limit to the rate coefficient for IF(B) excitation by N₂(X,v=9-15) is $2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Introduction

In previous studies we inferred the likely role of N₂(X,v''>9) in exciting IF(B³Π₀⁺) in active nitrogen.¹ At the time of those studies, we had neither a clean source of N₂(X,v) that was free from other metastable species nor a clear diagnostic for the higher vibrational levels of N₂(X,v). Recently we developed such a clean source of N₂(X,v) and a diagnostic for v' = 5-15.² This report details our application of this source to the study of IF(B) excitation by N₂(X,v).

The N₂(X,v) source we use in discharge-flow studies involves two steps. A microwave discharge of N₂ dilute in argon or helium generates active nitrogen. The active nitrogen then flows through a nickel screen before entering the flow reactor. The screen recombines most of the atoms exiting the discharge and deactivates electronically excited metastables. However, copious amounts of N₂(X,v) pass through the screen. The N₂(X,v) diagnostic technique is to add metastable nitrogen molecules, N₂(A³Σ_u⁺), to the flow and to observe the resultant nitrogen first-positive emission, N₂(B³Π_g-A³Σ_u⁺). This diagnostic is sensitive to vibrational levels of N₂(X,v) between about 5 and 15.

We have looked for IF(B³Π₀⁺) excitation in the presence of N₂(X,v) generated by this clean source, using downstream addition of N₂(A) to confirm the presence of the N₂(X,v) and to provide an estimate of the N₂(X,v) number density. In addition we studied IF(B) excitation in active nitrogen with the nickel screen removed and confirmed our previous results on the energy-transfer reaction between N₂(A) and IF.³

Experimental Section

The experimental apparatus was the 4.6 cm inside diameter quartz flow reactor that has been described previously (see Figure 1).^{2,4} The N₂(X,v) is generated at the upstream end of the flow reactor in a microwave discharge through a flow of nitrogen dilute in helium. The discharge effluents flow through a nickel screen prior to turning a right angle and entering the flow reactor. At the downstream end of the flow reactor, two injectors, spaced 10 cm apart, introduce first IF and then N₂(A).

The IF is generated in the upstream injector from the reaction between CF₃I and F atoms. The F atoms are produced in a microwave discharge through a mixture of CF₄ in helium at the upstream end of the injector. Downstream from this discharge, CF₃I is added to the injector, and the F atoms and CF₃I flow together for several milliseconds before exiting the injector into the main flow reactor. The residence time in the injector is adjusted to ensure complete reaction of the F with the CF₃I.⁵ The walls of the injector are Teflon coated to retard heterogeneous destruction of the IF.

The N₂(A) is generated in the downstream injector from the reaction between metastable argon atoms and nitrogen molecules.^{6,7} The argon metastables are produced in a hollow-cathode

dc discharge sustained in a mixture of about 5% argon in helium. Nitrogen enters just downstream from the discharge. The N₂(A) number densities at the exit of the injector are fairly modest, roughly 10⁸ molecules cm⁻³, but these number densities are more than adequate for the experimental measurements.

Spectral observations of emissions inside the flow reactor used a 0.5-m monochromator in combination with a thermoelectrically cooled R943-02 photomultiplier tube. This system is sensitive between 200 and 900 nm. All spectra were taken several centimeters downstream from the N₂(A) injector. Scans of the nitrogen Vegard-Kaplan bands, N₂(A³Σ_u⁺-X¹Σ_g⁺), between 250 and 370 nm revealed the number densities of N₂(A). The ratio of the intensities of the nitrogen first-positive bands, between 550 and 900 nm to those of the Vegard-Kaplan bands, allowed estimation of the N₂(X,v) number densities.² Finally we scanned the region between 400 and 650 nm to observe the IF(B³Π₀⁺-X¹Σ⁺) system.

We analyzed all spectra with the spectral fitting procedure we have documented previously.⁸ This procedure corrects for spectral overlap from different emission bands and gives the number densities of all emitting states contributing to the spectrum. Einstein coefficients used in the spectral analysis were those of Shemansky⁹ for N₂(A-X), Piper et al.⁸ for N₂(B-A), and Marinelli and Piper¹⁰ for IF(B-X).

Typical conditions include a total pressure of 1 Torr, primarily He with about 5% N₂, and bulk flow velocity around 5000 cm s⁻¹.

Results

Our experimental approach involves comparing the rate of IF(B) excitation by N₂(X,v) to that for excitation by N₂(A). The excitation rate is the product of the excitation rate coefficient, *k*_{ex}, times the exciting metastable number density. IF(B) is in steady state within the monochromator's field of view. As a result its formation and decay rates, *k*_{rad}, will be equal:

$$k_{\text{ex}}[\text{IF}][\text{N}_2^*] = k_{\text{rad}}[\text{IF}^*] = I_{\text{IF}^*} \quad (1)$$

We have neglected electronic quenching, because it is minimal under our conditions.¹¹ The excitation rate is the slope of a plot of IF(B) intensity as a function of IF(X) number density, i.e.,

$$dI_{\text{IF}^*}/d[\text{IF}] = k_{\text{ex}}[\text{N}_2^*] \quad (2)$$

In practice, we set the monochromator to observe a single IF(B-X) band and measured how its intensity varied with IF(X) number density. We then scanned the total IF(B-X) system at a fixed [IF(X)] so that we could correct the data to convert the peak intensity to integrated band intensity and to account for the fraction of the total band system intensity contained in the single band observed.

(1) Piper, L. G.; Marinelli, W. J. *J. Phys. Chem.* **1989**, *93*, 4033.
(2) Piper, L. G. *J. Chem. Phys.* **1989**, *91*, 864.
(3) Piper, L. G.; Marinelli, W. J.; Rawlins, W. T.; Green, B. D. *J. Chem. Phys.* **1985**, *83*, 5602.
(4) Piper, L. G.; Marinelli, W. J. *J. Chem. Phys.* **1988**, *89*, 2918.
(5) Morris, R. A.; Donohue, K.; McFadden, D. L. *J. Phys. Chem.* **1989**, *93*, 1358.
(6) Stedman, D. H.; Setser, D. W. *Chem. Phys. Lett.* **1968**, *2*, 542.

(7) Sadeghi, N.; Setser, D. W. *Chem. Phys. Lett.* **1981**, *82*, 44.
(8) Piper, L. G.; Holtzclaw, K. W.; Green, B. D.; Blumberg, W. A. M. *J. Chem. Phys.* **1989**, *90*, 5337.
(9) Shemansky, D. E. *J. Chem. Phys.* **1979**, *51*, 689.
(10) Marinelli, W. J.; Piper, L. G. *J. Quant. Spectrosc. Radiat. Transfer* **1985**, *34*, 321.
(11) Wolf, P. J.; Davis, S. J. *J. Chem. Phys.* **1985**, *83*, 91.

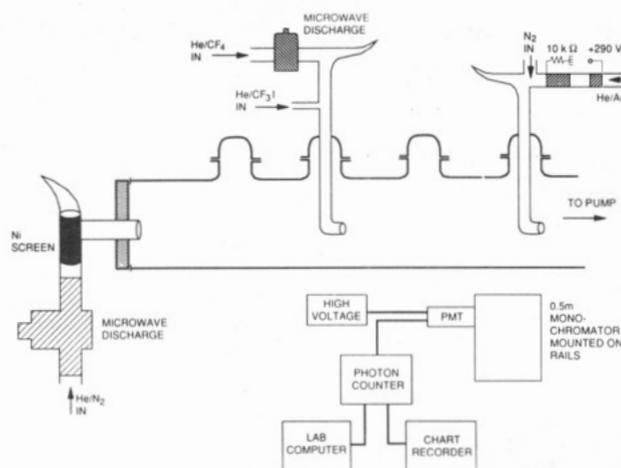


Figure 1. Flow reactor for studying the excitation of IF(B) by $N_2(X,v)$.

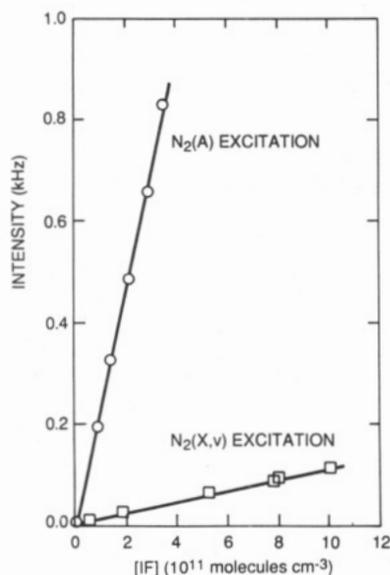


Figure 2. Excitation of the IF(B) 0,4 band by $N_2(A)$ and $N_2(X,v)$.

To check our experimental system, we first looked at the excitation of IF(B) by $N_2(A)$. We have studied this system in some detail previously.³ Cha and Setser¹² subsequently confirmed our results. Mixing IF and $N_2(A)$ together excited the IF- ($B^3\Pi_0^+ - X^1\Sigma^+$) system. The relative vibrational distribution in these experiments is slightly more relaxed than we had reported previously. Our previous experiments used an argon buffer, while the present ones used a helium buffer. Helium is roughly 5 times more efficient than argon at relaxing vibrational energy in IF(B).¹³

Figure 2 shows how the intensity of the IF($B, v''=0 - X, v''=4$) band varied as a function of IF number density. The linear dependence expected from eq 1 is indeed obtained. After the appropriate corrections are made, the slope of this plot gives a rate coefficient for exciting IF(B) by $N_2(A)$ of 7×10^{-11} cm^3 molecule⁻¹ s⁻¹. This agrees excellently with our previously reported³ value of 8×10^{-11} cm^3 molecule⁻¹ s⁻¹.

Figure 2 also shows the variation in IF(B) intensity as a function of added IF number density for excitation by $N_2(X,v)$. The ratio of the slopes of the lines for $N_2(A)$ excitation to $N_2(X,v)$ excitation is 22. This result suggests that the product $k_{ex}^X[N_2(X,v)]$ is much smaller than the product $k_{ex}^A[N_2(A)]$. The superscripts A or X on k_{ex} indicate the different excitation rate coefficients for the two nitrogen electronic states. Alternatively, a small number density of $N_2(A)$ might persist downstream from the nickel screen, and this residual $N_2(A)$ number density is 22 times less than the number density of the $N_2(A)$ that was added through the $N_2(A)$

injector. Such a small $N_2(A)$ number density would have been below our detection limit for observing $N_2(A-X)$ emission.

We estimated our number density of $N_2(X, v''=9-15)$ to be 1.3×10^{14} molecules cm^{-3} based upon the $N_2(B-A)$ intensities we observed when known amounts of $N_2(A)$ were added to the $N_2(X,v)$. For excitation by $N_2(X, v=9-15)$, therefore, this number density and the slope of the line in Figure 2 indicate that the rate coefficient for exciting IF(B) by $N_2(X,v)$ can be no more than 2×10^{-18} cm^3 molecule⁻¹ s⁻¹. This number is an upper limit since excitation by residual $N_2(A)$ in the afterglow was not included in its derivation.

Two pieces of evidence point to the likelihood that a small number density of $N_2(A)$ persists downstream from the discharge. The microwave discharge makes a small amount of NO from impurities in the gases used. $N_2(A)$ excitation of NO results in fluorescence of the NO γ bands,¹⁴ $NO(A^2\Sigma^+ - X^2\Pi)$. The intensity of the NO γ bands can be used as a tracer for $N_2(A)$. We find that the ratio of intensities of the NO γ bands in the presence of $N_2(A)$ to that with the $N_2(A)$ off, i.e., in the presence only of the screened discharge effluent, is 20. This is essentially the same ratio as found for the two cases of IF(B) excitation. Additionally, we observed a weak residual fluorescence from $N_2(B)$ when the $N_2(A)$ was turned off. The most likely source of this $N_2(B)$ is excitation of $N_2(X,v)$ by $N_2(A)$. Here again the ratio of the $N_2(B)$ with the $N_2(A)$ on to that with it off was 22. These observations point to the persistence of residual $N_2(A)$ downstream from the nickel screen and indicate that any excitation of IF(B) by $N_2(X, v=9-15)$ is insignificant.

A possible alternative for the first-positive emission observed in the absence of added $N_2(A)$ would be that generated from N-atom recombination. We checked our N-atom number densities downstream from the nickel stream by titrating with NO. NO quantitatively converts any N atoms in the flow to O atoms.¹⁵ In the presence of excess NO, any atomic oxygen in the flow will recombine with the NO to give the well known air afterglow emission.¹⁶⁻²¹ Upon adding excess NO, we did observe the air afterglow very weakly. Its variation in intensity with the number density of added NO indicated an initial N-atom number density downstream from the nickel screen of 1.1×10^{11} atoms cm^{-3} . Our previous experience²² is that such small number densities of N atoms at the low pressures employed, 1.06 Torr, would result in unobservable first-positive emission by our detection system. The nickel screen was quite efficient at removing N atoms from the flow. NO titrations of the discharge afterglow under identical conditions, but with the nickel screen removed, indicated an N-atom number density of 6.4×10^{12} atoms cm^{-3} .

Finally, we removed the nickel screen and looked briefly at the excitation of IF(B) in the microwave-discharge afterglow. In this case the ratio of the rate of excitation of IF(B) by unscreened active nitrogen to that by $N_2(A)$ alone was 14.2. Scans over the $N_2(A-X)$, Vegard-Kaplan, bands, however, showed that the ratio of the $N_2(A)$ number density in the unscreened active nitrogen to that from the $N_2(A)$ source alone was 5.5. Thus only 40% of the excitation in the active nitrogen comes from $N_2(A)$ in the flow.

The IF(B) vibrational distribution excited in active nitrogen is considerably more relaxed than that excited by $N_2(A)$. Figure 3 compares the total IF(B) vibrational distribution excited in the unscreened active nitrogen to that excited by just the $N_2(A)$ component of the active nitrogen. The difference between the two curves gives the IF(B, v) distribution excited by the additional metastable species in the active nitrogen. The fraction of IF(B) excitation by the $N_2(A)$ in the active nitrogen varies from about 30% for the lowest levels to about 75% for the highest levels. The

(14) Piper, L. G.; Cowles, L. M.; Rawlins, W. T. *J. Chem. Phys.* **1986**, *85*, 3369.

(15) Brocklehurst, B.; Jennings, K. R. *Prog. React. Kinet.* **1967**, *4*, 1.

(16) Fontijn, A.; Meyer, C. B.; Schiff, H. I. *J. Chem. Phys.* **1964**, *40*, 64.

(17) Vanpee, M.; Hill, K. D.; Kineyko, W. R. *AIAA J.* **1971**, *9*, 135.

(18) Golomb, D.; Brown, J. H. *J. Chem. Phys.* **1975**, *63*, 5246.

(19) Sutoh, M.; Morioka, Y.; Nakamura, M. *J. Chem. Phys.* **1980**, *72*, 20.

(20) Prvilov, A. M.; Smirnova, L. G. *Kinet. Catal.* **1978**, *19*, 202.

(21) Bradburn, G. R.; Lilienfeld, H. V. *J. Phys. Chem.* **1988**, *92*, 5266.

(22) Piper, L. G. *J. Chem. Phys.* **1989**, *90*, 7087.

(12) Cha, H.; Setser, D. W. *J. Phys. Chem.* **1987**, *91*, 3758.

(13) Wolf, P. J.; Davis, S. J. *J. Chem. Phys.* **1987**, *87*, 3492.

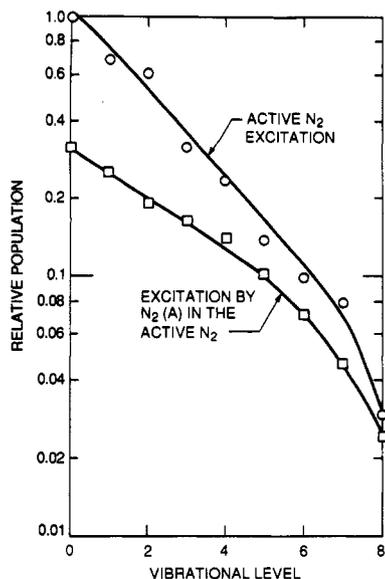


Figure 3. Relative vibrational distribution of IF excited by active N_2 compared to that excited by the $N_2(A)$ component of the active N_2 . The difference between the two curves is the enhancement that active nitrogen contributes to IF(B) excitation above that by $N_2(A)$.

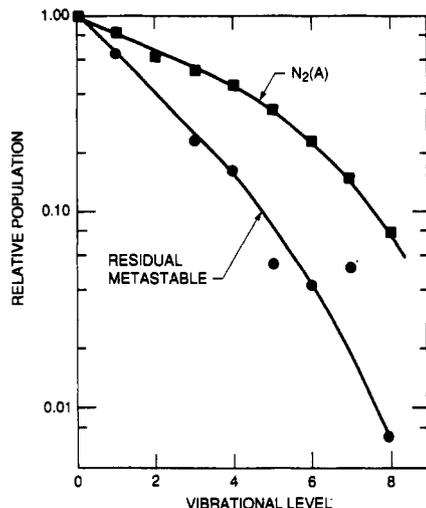


Figure 4. Relative vibrational distributions of IF(B,v) in 1 Torr of helium from $N_2(A)$ excitation compared to that by the residual metastable in active N_2 .

residual excitation comes from some other nitrogen metastable that excites IF with a much more relaxed vibrational distribution than does $N_2(A)$. Figure 4 compares the IF(B) vibrational distribution from $N_2(A)$ excitation to that from excitation by the unidentified metastable. In our previous work, we had speculated that $N_2(X,v)$ might be that additional metastable. The results of this work show conclusively that $N_2(X,v''=9-15)$ is incapable

of exciting IF(B) to any appreciable extent. Conceivably somewhat higher vibrational levels could be involved but we have no readily available, quantitative diagnostic for them. This rationalization does not seem to be particularly likely.

We showed previously⁴ that the number densities of higher electronic states of molecular nitrogen were much smaller than that of the A state. As a result, these states are unlikely to contribute significantly to IF(B) excitation. We have no diagnostic for $N_2(A'^5\Sigma^+)$ and so cannot rule out its role in IF(B) excitation on the basis of our observations. Attempts by two other groups to detect $N_2(A')$ in nitrogen afterglows,^{23,24} using laser-induced fluorescence on the Herman Infrared system, have not been successful. This null result has led to the conclusion that $N_2(A'^5\Sigma)$ is quenched quite efficiently by species in the afterglow. As a result, $N_2(A')$ does not appear to be a likely candidate for the species responsible for the excess IF(B) excitation.

Vibrational levels of $N_2(A)$ greater than or equal to 4 are difficult to detect in emission. Generally vibrational populations decrease as the vibrational energy increases so the populations of these higher levels could account for no more than a small fraction of the excess IF(B) excitation that we observe. Vibrational levels of $N_2(A)$ as high as $v' = 6$ have been observed under some conditions in discharge-flow reactors using a laser-induced fluorescence diagnostic.^{23,25} We never see Vegard-Kaplan emission from $N_2(A)$ vibrational levels above two in a helium buffer, even at pressures and residence times for which emission from $v' = 3$ and 4 is readily observable in an argon buffer. This is because helium is relatively efficient at relaxing the vibrational energy in $N_2(A)$ compared to argon.²⁶ Significant number densities of $N_2(A, v > 2)$, therefore, seems unlikely.

Metastable nitrogen atoms, $N(^2D)$, lack sufficient energy to excite IF($B, v > 0$), unless the IF(X) is vibrationally excited. If the $N_2(X, v)$ in the afterglow transferred vibrational energy to IF(X), then the higher levels of IF(B) could be excited by $N(^2D)$. It is also conceivable, of course, that the rate coefficient for IF(B) excitation by $N_2(A)$ could be enhanced significantly if the IF(X) is vibrationally excited. Davis and Woodward noted large enhancements in IF(B) excitation in oxygen afterglows when the IF(X) was vibrationally excited.²⁷ This possibility merits further study.

Acknowledgment. We appreciate partial financial support from the Air force Weapons Laboratory under Contract No. F29601-87-C-0056. We also appreciate Bill Cummings' contributions to the data analysis. As always the advice, criticisms, and comments of PSI colleagues George E. Caledonia, Steven J. Davis, B. David Green, William J. Marinelli, and W. Terry Rawlins proved beneficial.

Registry No. IF, 13873-84-2; N_2 , 7727-37-9.

(23) Marinelli, W. J.; Kessler, W. J.; Woodward, A. M.; Rawlins, W. T. *J. Chem. Phys.* **1990**, *92*, 1796.

(24) Young, R. A.; Bauer, R. D. *J. Chem. Phys.* **1990**, *92*, 1617.

(25) Thomas, J. M.; Kaufman, F.; Golde, M. F. *J. Chem. Phys.* **1987**, *86*, 6885.

(26) Roy, C. R.; Dreyer, J. W.; Perner, D. *J. Chem. Phys.* **1975**, *63*, 2131.

(27) Davis, S. J.; Woodward, A. M. *J. Phys. Chem.*, in press.