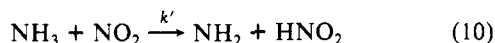


who found $k = 10^{12.6} \exp(-115.7/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction



From the vapor-pressure measurements of Feick¹⁷ we can estimate the concentration of ammonia in our capillary tubes and calculate the concentration of nitrogen dioxide required to consume ammonia by eq 10 at the initial rate that we observe. For a temperature of 370 °C and a capillary containing 5×10^{-5} mol of ammonium nitrate in a volume of 4×10^{-5} L we find an initial rate of 6×10^{-6} mol/s ($k = 0.12 \text{ s}^{-1}$). The initial rate of eq 7 at 370 °C with $[\text{NH}_3] = 0.057 \text{ M}$ and $V = 4 \times 10^{-5}$ L is $3.1 \times 10^{-6}[\text{NO}_2] \text{ mol/s}$. A match of rate requires $[\text{NO}_2] = 2 \text{ M}$. By trial we have found that nitrogen dioxide at a concentration of 0.05 M in a capillary tube shows a distinct red-brown color. According to our visual observations and color video recordings, however, the nitrogen dioxide is either absent or on the threshold of visibility throughout the decomposition reaction. It appears that eq 10 is too slow to account for the main reaction, but it could perhaps be involved in the side reaction leading to N_2 . The absence of a primary H/D kinetic isotope effect is also evidence against its participation. One final point is that reaction 10 is the slow step in the sequence of reactions and its activation energy is 116 kJ/mol. It would be difficult to account for the observed E_{act} of 193 kJ on this basis.

Trapping of Intermediates. Ammonium nitrate was decomposed in the presence of toluene in the high-temperature regime (340 °C) in an effort to trap and identify reactive intermediates. The two most abundant products were benzaldehyde and phenylnitromethane followed by nitrobenzene, benzyl alcohol, and benzonitrile. It seems clear that hydrogen atoms are abstracted from toluene to form benzyl radicals, which combine with NO_2

to form phenylnitromethane and with some other oxygen-containing intermediate to form benzyl alcohol. Benzaldehyde probably results from further oxidation of benzyl alcohol. Benzonitrile is probably the dehydration product of phenylnitrosomethane via benzaldehyde oxime. The origin of nitrobenzene is unclear. It is interesting that 2- and 4-nitrotoluene, the normal products of reaction of toluene with nitronium ion, are absent.

Conclusion. Various lines of evidence indicate that the well-established ionic mechanism for decomposition of ammonium nitrate at temperatures below 300 °C is supplanted by a rate-controlling homolysis of nitric acid at higher temperatures. The observed activation energy changes continuously from 118 kJ at low temperature to 193 kJ at high temperature. The enthalpy of homolysis of nitric acid is nearly equal to the latter. The change of E_a strongly implies a change of mechanism, although it does not prove it conclusively. At the highest temperatures it appeared that ammonium nitrate in large containers was completely vaporized and yet gave the same products at the same rate as in small tubes containing liquid ammonium nitrate. Reaction in the vapor phase could not occur by the ionic mechanism. Added H_2O , NH_3 , and HONO_2 strongly influence the rate at low temperatures because of their effects on nitronium ion concentration, but the effects fade out at high temperature. ND_4NO_3 shows no primary kinetic isotope effect at high temperature. This is appropriate to homolysis of HONO_2 but inappropriate to a chain reaction involving NH_3 and NO_2 . The presence of radical intermediates was demonstrated by trapping with toluene as scavenger.

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Registry No. NH_4NO_3 , 6484-52-2; D_2 , 7782-39-0; H_2O , 7732-18-5; NH_3 , 7664-41-7.

Excitation of $\text{IF}(\text{B}^3\Pi_0^+)$ by Active Nitrogen

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Active nitrogen, or the effluents of microwave discharges in flowing N_2/Ar or He mixtures, excites $\text{IF}(\text{B}^3\Pi_0^+)$ strongly in a discharge-flow apparatus. The distribution of $\text{IF}(\text{B})$ vibrational levels in helium is characterized roughly by an 1150 K Boltzmann temperature and is somewhat hotter in an argon buffer. Excitation rates are as high as 1 photon $\text{cm}^{-3} \text{ s}^{-1}$ per IF molecule cm^{-3} and vary with the number density of $\text{N}_2(\text{B}^3\Pi_g)$. That species, however, is much too sparsely populated to be directly responsible for the excitation. Estimates of number densities of metastables that persist in the afterglow longer than 10 ms indicate that species such as $\text{N}(\text{D})$, $\text{N}(\text{P})$, $\text{N}_2(\text{A}^3\Sigma_u^+)$, and $\text{N}_2(\text{a}^1\Sigma_u^-)$ are too low in number density to account for the observed excitation rates. We conclude, therefore, that the IF is excited by $\text{N}_2(\text{X}, v > 9)$, a species that is abundant in the flow.

Introduction

The molecule IF and other interhalogens have been the subject of considerable interest in recent years because their compressed electronic energy manifold and intense radiative transitions make them ideal candidates for visible molecular lasers.¹ Clyne and co-workers studied the radiative and collisional properties of IF , BrCl , and BrF , and showed that these species were highly suitable for forming an electronic transition laser operating on the $\text{B}(\text{B}^3\Pi_0^+) \rightarrow \text{X}(\text{X}^1\Sigma^+)$ transition²⁻⁷ because the upper states have short radiative and long electronic-quenching lifetimes. Davis and Hanco⁸ excited ground-state IF , formed in an I_2/F_2 flame, with a pulsed dye laser and demonstrated optically pumped lasing action on the $\text{IF}(\text{B} \rightarrow \text{X})$ transition. Efficient chemical (kinetic) means for pumping the $\text{IF}(\text{B})$ state remain to be determined.

Clyne et al.,⁹ Whitefield et al.,¹⁰ and Davis et al.¹¹ all found that singlet molecular oxygen, both a $^1\Delta$ and $^1\Sigma$, excited $\text{IF}(\text{B})$

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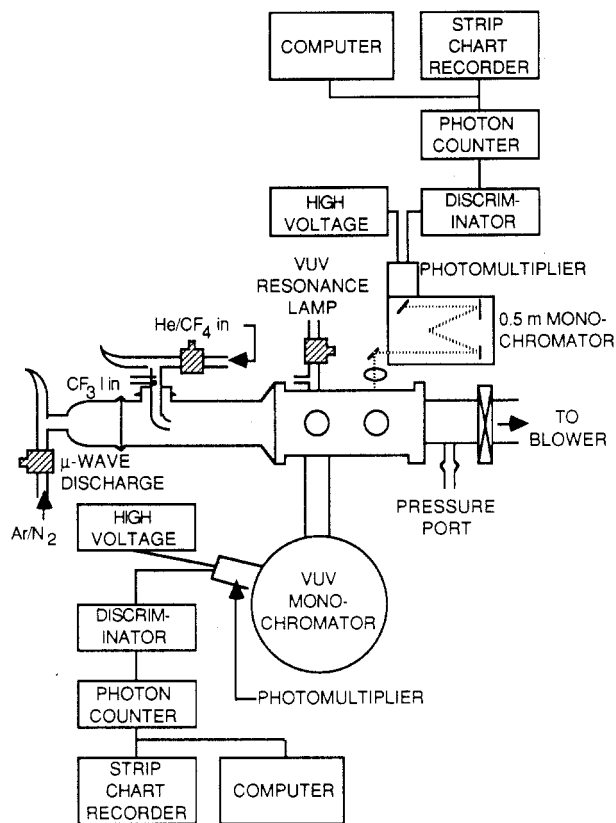


Figure 1. Flow-tube apparatus for studying reactions of $N_2(v)$ and $N^*(^2D,^2P)$ with IF.

strongly. This excitation is even more robust when the ground electronic state of IF is vibrationally excited.¹¹ Davis and co-workers¹² observed IF(B) excitation when the effluents of microwave discharges in He/ N_2 mixtures interacted with the I_2/F_2 mixing zone of their reactor. This excitation was much stronger than they had observed from singlet-oxygen excitation.¹⁰ They did not identify which species in their active nitrogen was responsible for the IF excitation but speculated it might be the $A^3\Sigma_u^+$ state of N_2 .

We have studied the excitation of IF(B) by energy-transfer processes between metastable nitrogen species and ground-state IF. A previous paper detailed the excitation of IF($B^3\Pi_0^+$) by $N_2(A^3\Sigma_u^+)$.¹³ These experiments showed that the energy-transfer reaction between $N_2(A^3\Sigma_u^+)$ and IF($X^1\Sigma^+$) is essentially gas kinetic ($k_{\text{total}} = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and that 40% of the quenching collisions result in the production of IF(B). The reaction populates all IF(B) vibrational levels below the predissociation limit, $v' = 9$, and produces $v' = 0-6$ with about equal probability. The vibrational distribution relaxes rapidly, however, in collisions with the reactor bath gas even at pressures of a few Torr. We found the vibrational relaxation rate coefficients for levels 3-6 to about $3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. More extensive measurements by Wolf and Davis on IF(B) vibrational relaxation confirmed these findings.¹⁴ Although we did not study it explicitly, electronic quenching of IF(B) in our reactor must have been much slower because we observed strong IF(B) excitation by $N_2(A)$ at pressures up to 10 Torr. Wolf and Davis also corroborate the less efficient electronic quenching of IF(B).¹⁵

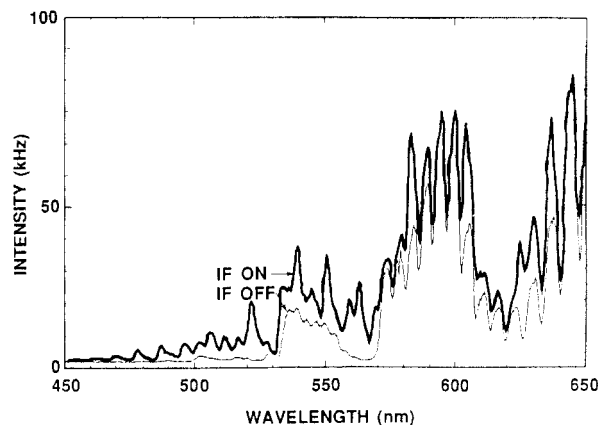


Figure 2. Spectrum of active nitrogen between 480 and 780 nm in the absence and presence of IF.

This paper describes the excitation of IF by the nitrogen metastables present in active nitrogen—the effluents of microwave discharges in Ar/ N_2 or He/ N_2 mixtures. The intensity of the IF(B) excitation and its vibrational distribution, however, are quite different from those observed from $N_2(A)$ excitation. Our results indicate that the primary species responsible for the IF(B) excitation in the active nitrogen is not $N_2(A)$ but probably $N_2^-(X, v > 9)$.

Experimental Section

The apparatus is a 2-in.-diameter discharge-flow reactor pumped by a Leybold-Heraeus Roots blower/forepump combination capable of producing linear velocities up to $5 \times 10^3 \text{ cm s}^{-1}$ at pressures of 1 Torr. The flow-tube design is modular (see Figure 1), with separate source, reaction, and detection sections that clamp together with O-ring joints. We have described it in detail previously.¹³

Discharging about 70 W of microwave power through a flowing mixture of nitrogen in argon or helium generated the active nitrogen. Reagents were then injected downstream from the primary discharge, and the resulting fluorescence was monitored downstream from the injector.

A suprasil lens collected light from the center of the flow tube and focused it on the entrance slit of the monochromator, which is a 0.5-m Minuteman instrument equipped with a 1200 groove mm^{-1} grating blazed at 250 nm. A thermoelectrically cooled photomultiplier (HTV R943-02) detected photons with the aid of an SSR 1105 photon-counting rate meter interfaced to a laboratory computer system and strip-chart recorder.

The spectral system was calibrated for relative response as a function of wavelength by using a standard quartz-halogen or D_2 lamp. Absolute response calibrations were made in situ by observing the air afterglow under carefully controlled conditions.^{16,17}

IF entered the flow tube through a hook-shaped injector whose outlet orifice is coaxial with the main flow tube. This injector has a relatively large diameter (10-mm o.d.) and is Teflon coated to inhibit IF wall recombination. IF was produced in this injector by the reaction between CF_3I and F atoms, the F atoms having been produced in a microwave discharge through CF_4/He mixtures further upstream in the injector. We have detailed the characterization of this IF source previously.^{13,18}

Mass-flow meters or rotameters monitored gas flow rates. All flow meters were calibrated by measuring rates of increase of pressure with time into 6.5- or 12-L flasks, by using appropriate differential pressure transducers (Validyne DP-15) that themselves

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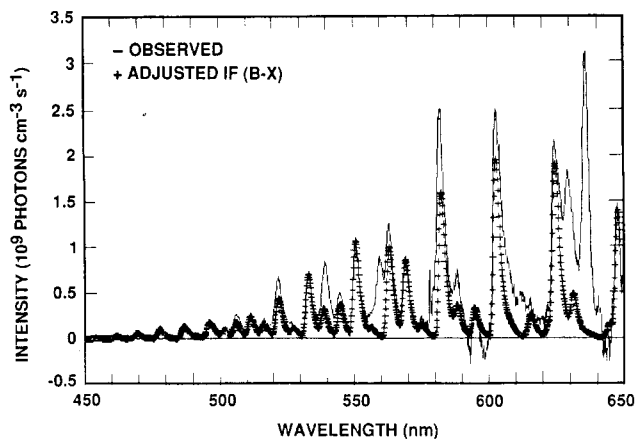


Figure 3. Spectrum between 450 and 650 nm from active nitrogen/IF mixture with the $N_2(B)$ spectral features subtracted. The underlying spectrum shows the contributions from the IF(B-X) system.

have been calibrated with silicon oil or mercury manometers. Typical flow rates for argon or helium buffer, nitrogen, and helium through the injector were 2000–5000, 100–500, and 200–500 $\mu\text{mol s}^{-1}$, respectively, while CF_4 and CF_3I flow rates range between 0 and 1 $\mu\text{mol s}^{-1}$. Total pressures, as measured by a Baratron capacitance manometer, ranged from 0.4 to 9 Torr, and flow velocities varied from 500 to 5000 cm s^{-1} .

Tetrafluoromethane (CF_4) is obtained 99.5% pure from Matheson and, due to the small amount employed, was used without further purification. Trifluoroiodomethane (CF_3I) is obtained 99% pure from PCR Research Chemicals. The major impurity, I_2 , is removed by distilling CF_3I from a trap at -115°C followed by storage in a dark bulb.

Results

Emission from Active N_2 /IF Mixtures. Figure 2 displays spectra of active nitrogen between 450 and 650 nm in the absence and presence of added IF. To characterize the spectra better, we normalized them to the 8,5 first-positive band between 643 and 646 nm, a region where no significant IF(B) emission exists. Then the active nitrogen spectrum was subtracted from that with active nitrogen plus IF. Figure 3 shows the result. The IF($B^3\Pi_0^+-X^1\Sigma^+$) system is prominent and, in addition, spectral features belonging to two other band systems appear in the spectrum. One of the other spectral systems in Figure 3 is the $\text{CF}_2(3B_1-1A_1)$ system;¹⁹ we have not identified the remaining system. By measuring the band spacings, we have determined that one of the two states in the unknown transition (either the upper or lower) has an effective ω_e of $587 \pm 10 \text{ cm}^{-1}$. This value is not greatly different from those for some of the known states of IF or IN, but the spectrum does not correspond to any known transitions of these two molecules.

We could not fit the observed spectrum by the normal least-squares approach.¹³ We have not developed the capability to simulate the emission from polyatomic molecules at present, and one of the three band systems in Figure 3 is unknown. We have determined the contributions to the spectrum from IF(B) by fitting individual IF(B) basis functions by trial and error until an adequate agreement is obtained with the obvious IF(B) features. The features plotted as crosses in Figure 3 illustrate the final result of this procedure.

We fit the spectrum piecewise over three consecutive wavelength regions after first subtracting the N_2 first-positive contributions. The spectral region between 450 and 500 nm contains mostly bands of the IF(B \rightarrow X) system from vibrational levels $v' = 3-8$. The populations of these vibrational levels, therefore, can be determined fairly cleanly in this spectral region. The contributions of these levels to the spectrum at longer wavelengths will then be reasonably well determined from these values.

Over the wavelength region between 500 and 600 nm, the major vibrational levels of IF(B) contributing to the spectrum are $v' =$

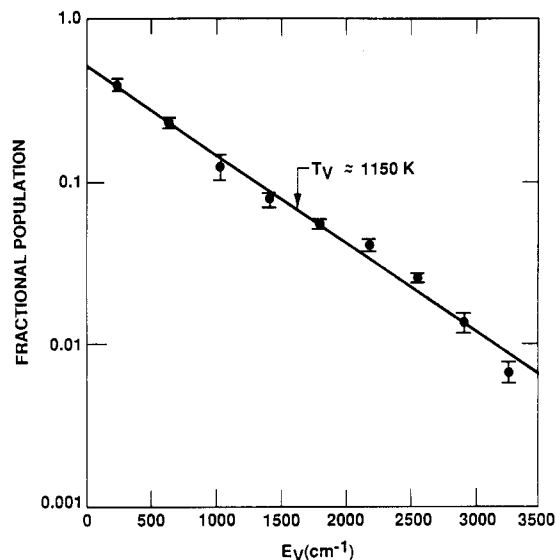


Figure 4. Vibrational distribution of IF($B^3\Pi_0^+$) excited by active nitrogen.

0–2. Fairly isolated bands at 533, 551, and 568 nm determine the $v' = 1$ population reasonably well. In some instances, however, the $v' = 0$ and 2 populations can be determined only by fitting shoulders of bands. By operating at flow conditions that optimize IF(B) emission relative to other emission systems, a good evaluation of the IF($B, v' = 0$) population can be obtained.

Figure 4 summarizes the population distributions determined from fits to several spectra obtained in a helium bath gas at 1.5 Torr. The vibrational distribution is well described by an 1150 K Boltzmann vibrational temperature. In an argon buffer the resulting vibrational distribution is somewhat hotter, $\sim 2000 \text{ K}$. The significance of a Boltzmann distribution in terms of the dynamics of the energy transfer is unclear. In addition, such distributions are somewhat dependent on the conditions of the measurement since IF(B) vibrational relaxation by He, Ar, and N_2 is efficient.^{13,14} In either case, however, the IF(B) vibrational distribution is significantly more relaxed than that obtained from $N_2(A)$ excitation of IF. This suggests that a nitrogen metastable other than $N_2(A)$ is responsible for IF(B) excitation in active nitrogen.

IF* Excitation Rates in Active N_2 . To characterize the energy transfer between active nitrogen and IF, we have measured IF* excitation rates. The IF* will be in steady state because its lifetime ($\sim 8 \mu\text{s}$)⁵ is short compared to residence times in the observation volume. Thus, its formation and destruction rates can be equated. Neglecting IF* electronic quenching¹⁵ gives

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

where k_{ex} is the excitation rate coefficient for IF* excitation by active N_2 , and k_{rad} is the IF* radiative decay rate. Equation 1 shows that without knowing the identity of the precursor for the IF* excitation, the product of the excitation rate coefficient and the number density of the precursor species can be determined.

Figure 5 illustrates one set of measurements on the variation in the intensity of the 5,0 band of IF(B \rightarrow X) as a function of number density of added IF for a number of different initial $N_2(B)$ number densities in the reactor. The $N_2(B)$ number density was varied by changing the angle of rotation of a Ni screen in the flow and was monitored with a photometer centered at $580 \pm 5 \text{ nm}$ that previously had been calibrated against $N_2[(B), v' = 2-12]$. The excitation rates determined from the slopes of the lines in Figure 5, after converting raw intensities to absolute photon emission rates and correcting for the fraction of total IF(B) emission appearing in the 5,0 band are on the order of 0.1 photon $\text{cm}^{-3} \text{ s}^{-1}$ per IF molecule cm^{-3} . These rates vary linearly with the measured $N_2(B)$ number densities (Figure 6), suggesting that $N_2(B)$ and IF(B) share a common excitation source. Figure 7 shows that the CF_2 and unidentified band intensities also vary

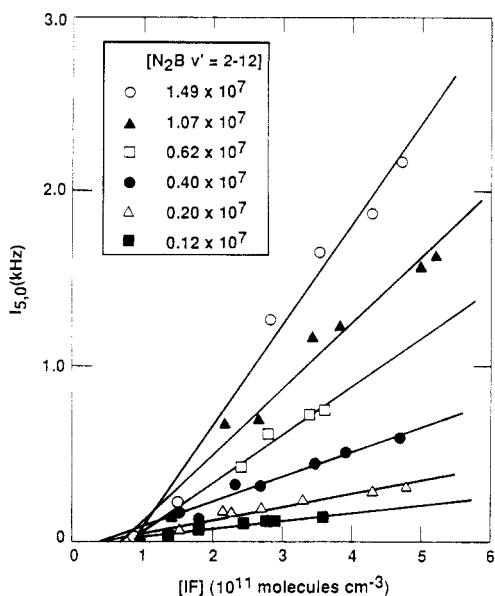


Figure 5. Variation in the intensity of the IF(B,5-0) band as a function of added IF number density for various number densities of $N_2(B)$ in the flow reactor.

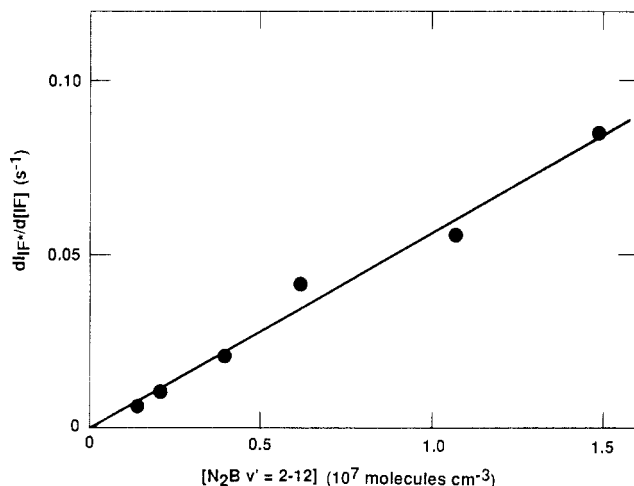


Figure 6. Excitation rates of IF(B) versus $N_2(B)$ number density.

linearly with the $N_2(B)$ number density in the flow reactor when the IF number density is held constant.

If $N_2(B)$ were the species responsible for the IF(B) excitation, the slope in Figure 6 would give the excitation rate coefficient. The value derived, however, is $(5.6 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, more than an order of magnitude greater than gas kinetic, meaning that $N_2(B)$ is an unlikely excitation partner. The data show quite clearly, however, that the excitation rates of IF(B) and the other emissions do vary with $N_2(B)$ number density. Apparently the metastable that excites the IF* and other emissions also is coupled collisionally to the $N_2(B)$ state.

The observations just discussed were made in 1.5 Torr of helium, 22 ms downstream from the microwave discharge, and with a Ni screen in the flow reactor. Observations in argon at much shorter transit times (~ 7 ms) and with no nickel screen in the reactor resulted in IF(B) excitation rates that approached unity, i.e., 1 IF(B) photon $\text{cm}^{-3} \text{ s}^{-1}$ per IF molecule cm^{-3} in the observation region. These experiments also gave a somewhat hotter IF(B) vibrational distribution.

The larger excitation rates in argon buffer suggest that the metastable species responsible for IF(B) excitation is deactivated by collisions with the reactor walls (enhanced in the He measurements both by the longer transit time and by the much more rapid diffusion of species in He compared to Ar) as well as by collisions with the Ni screen. Argon discharges also might generate the metastables more efficiently.

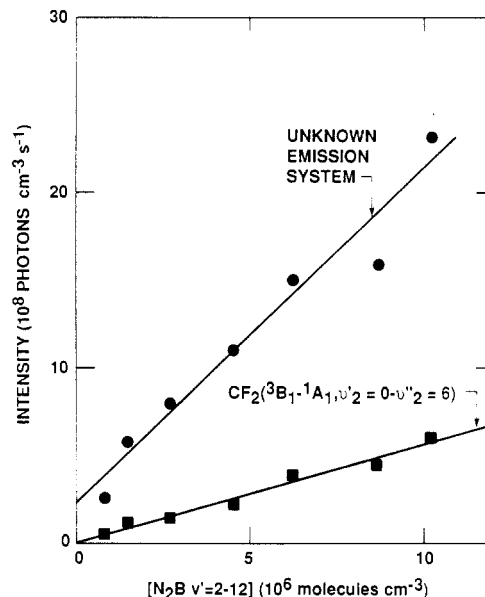


Figure 7. Intensities of unknown and $CF_2(3B_1-1A_1, \nu'_2 = 0-\nu'_2 = 6)$ emissions as a function of $N_2(B)$ number density for constant IF number density.

TABLE I: Active Nitrogen Constituents in Argon

species	observation band	concn, molecule cm^{-3}	
		1% N_2	80% N_2
$N(^2D)$	vacuum UV resonance fluorescence	1×10^{12}	1×10^{10}
$N(^2P)$	($2P-4S$)	4×10^{10}	1×10^{10}
$N_2(a^1\Pi_g)$	($a^1\Pi_g-X^1\Sigma_g^+$)	5×10^6	none ($<10^6$)
$N_2(a^1\Sigma_u^-)$	($a^1\Sigma_u^-X^1\Sigma_g^+$)	1×10^9	none ($<10^6$)
$N_2(B^3\Pi_g)$	($B^3\Pi_g-A^3\Sigma_u^+$)	8×10^6	6×10^6
$N_2(A^3\Sigma_u^+)$	($A^3\Sigma_u^+X^1\Sigma_g^+$)	1×10^9	1×10^9
$N_2(\nu)$	He* Penning ionization	2×10^{12}	2×10^{14}

Further investigations in Ar/ N_2 afterglows indicated a decline in the effective IF(B) excitation rate of roughly a factor of 2 in changing the N_2 mole fraction from 0.02 to 0.90. Inserting a glass-wool plug into the flow just downstream from the discharge, however, reduced the IF(B) excitation rate to levels comparable to the noise level. The glass-wool plug quenches all electronic and most vibrational excitation in the flow but generally reduces the number density of atoms by only about 20%.²⁰ We discuss the implications of these observations in the next section.

Discussion

The maximum excitation rate of 1 photon $\text{cm}^{-3} \text{ s}^{-1}$ per IF molecule cm^{-3} places a lower limit on the number density of the exciting species. This limit aids in identifying the metastable responsible for the IF excitation. Even if the excitation rate coefficient for the active species were gas kinetic ($\sim 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the concentration of the exciting species could be no smaller than $10^{10} \text{ molecule cm}^{-3}$. A slower excitation rate coefficient would require a more plentiful excitation partner.

Spectroscopic observations between 130 and 850 nm of the discharge effluent helped to characterize the metastable species in the flow. Prominent emissions observed 20 ms downstream from the discharge included the Lyman-Birge-Hopfield ($a^1\Pi_g-X^1\Sigma_g^+$), Ogawa-Tanaka-Wilkinson-Mulliken ($a^1\Sigma_u^-X^1\Sigma_g^+$), Vegard-Kaplan ($A^3\Sigma_u^+X^1\Sigma_g^+$), second-positive ($C^3\Pi_u-B^3\Pi_g$), and first-positive ($B^3\Pi_g-A^3\Sigma_u^+$) systems of N_2 , the NO γ -bands ($A^2\Sigma^+-X^2\Pi$) and $N(^2P-4S, \lambda = 346.6 \text{ nm})$. Under some conditions, when CF_3I or discharged CF_4 was added to the reactor, the CN blue ($B^2\Sigma^+-X^2\Sigma^+$) and red ($A^2\Pi-X^2\Sigma^+$) systems appeared. We have also characterized the $N_2(X,\nu)$ vibrational distributions using a Penning-ionization diagnostic^{21,22} and $N(^2D)$

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by vacuum UV resonance absorption and fluorescence.²³

Table I lists estimates, based on the photonemission rate measurements and the other data, of the likely excited-state species concentrations in active nitrogen for two different compositions at 1 Torr. These estimates show that only N(²P), N(²D), and N₂(*v*) exist in high enough concentrations to excite IF at the rates observed.

N(²D) and N(²P) are unlikely precursors for IF(B) excitation. N(²D) number densities decrease dramatically with increases in nitrogen mole fraction. The IF excitation rates, on the other hand, decreased only slightly. Because N(²P) is quenched by Ar, this metastable tends to be more abundant in helium flows. We found, however, that IF excitation rates were somewhat greater in argon buffers.

We think the most likely excitation species is N₂(X,*v*>9). Extremely high levels of vibrational excitation can survive long into the afterglow because they will not be relaxed efficiently by N₂, Ar, or He. Our Penning-ionization measurements indicate substantial vibrational excitation in N₂(X).^{21,22} In some instances more than two-thirds of the N₂(X) is vibrationally excited,²² and the vibrational excitation extends at least as high as 3.8 eV.²¹ We believe that it is these high vibrational levels of N₂(X,*v*) that are responsible for the excitation of N₂ electronic states in the afterglow as discussed in the previous subsection.

Because the measured IF excitation rates vary linearly with the N₂(B) fluorescence intensity, it appears that both species are likely to be excited by the same precursor. The precursor for the N₂(B) emission cannot be N(²P) because that state lacks sufficient energy to excite N₂(B). Thus N₂(X,*v*>9), because it is the only remaining long-lived state in the reactor, appears to be the precursor state for N₂(B) excitation. This excitation could be either direct or indirect through an intermediary state of nitrogen that is excited from the N₂(X,*v*>9) precursor. Inserting the glass-wool plug into the active nitrogen stream eliminates vibrationally excited N₂ and electronically excited atomic and molecular metastables, leaving only N(⁴S). The small residual IF excitation in this case is consistent with expected N₂* number densities created by N-atom recombination.

Grigor and Phillips²⁴ and Phillips²⁵ have studied molecular and atomic emission in active nitrogen flames with added I₂, IBr, ICl, and ICN. They observed emission from electronically excited I and I₂ in all systems and, in addition, some emission from excited IBr, ICl, Br and Cl. They proposed that excitation resulted from energy-transfer reactions involving N₂(A,³Σ_u⁺), N₂(W³Δ_u), or N₂(X¹Σ_g⁺,*v*>0). These metastables were generated from N-atom recombination or the reaction between N and NI and were mixed in N(⁴S)-atom-transfer reactions. The proposed N₂* state mixing effectively renders the three metastables indistinguishable from the standpoint of assigning a specific excitation source.

Our studies indicate that both N₂(A) and N₂(X,*v*>9) can excite IF(B). N₂(W³Δ_u) might also excite IF(B), but it should not be responsible for the IF(B) excitation we observe. N₂(W) is very efficiently coupled to N₂(B) in collisions with N₂, Ar, and He.^{26,27} Its steady-state number densities, therefore, will be similar

to those for N₂(B), and we have shown that N₂(B) is not sufficiently populated to be responsible for the IF(B) excitation that we observe.

In a limited-distribution report, West and Bhaumik²⁸ related observations of IF(B) fluorescence when they added IF or just CF₃I to a flow of active nitrogen. Their active nitrogen was prepared by discharging pure nitrogen at relatively high pressures, 5–20 Torr. They showed that the intensity of IF(B) they observed was proportional to the number density of atomic nitrogen. The nitrogen species exciting their IF(B), therefore, was generated from N-atom recombination. They suggested N₂(*v*) as the exciting species, but given the steady-state number densities of N₂(A) they calculated to be in their system and the efficiency we determined for IF(B) excitation by N₂(A),¹³ their observations are fully compatible with N₂(A) as the excitation source.

More recently, Ongstad et al.²⁹ observed IF fluorescence generated by the addition of CF₃I to active nitrogen. They showed that the active nitrogen dissociated the CF₃I to produce F atoms, with IF generated subsequently in the reaction between F and CF₃I. Inserting a glass-wool plug into their afterglow, downstream from the nitrogen discharge but upstream from the CF₃I inlet, had little effect on their observed IF(B) intensities. Here again, the excited nitrogen molecules that pumped IF(B) were generated by N-atom recombination. In such a case one cannot distinguish between N₂(A) and N₂(X,*v*) as the excitation source.

Davis³⁰ has shown that a steady-state number density of IF(B) of 10¹³ molecules cm⁻³ will be sufficient to achieve an optical gain of 0.1% cm⁻¹. A gain of this magnitude would render laser oscillation easily achievable. Our conditions of relatively mild N₂ excitation, low ground-state IF number density (~10¹¹ molecules cm⁻³), and low total pressure (~1 Torr) produces steady-state IF(B) number densities of 10⁶ molecules cm⁻³. An increase of at least 4 orders of magnitude in IF(B) number density ought to result from easily achieved increases in total pressure and ground-state IF number density. Additional enhancement of the IF(B) number density would require improved N₂* production. This might be accomplished by a higher power excitation source. The phenomenon known as V–V up pumping^{31,32} allows substantial number densities of highly vibrationally excited N₂ to be produced by appropriate discharge sources. This is in contrast to N₂(A³Σ_u⁺), whose maximum number densities will be limited by energy-pooling reactions.^{17,33} The interaction between N₂(X,*v*) and IF therefore shows some promise as a potential chemical laser source.

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