

Production of $N_2(A^3\Sigma_u^+)$ in the Low-Pressure Dielectric-Barrier (Ozonizer) Discharge

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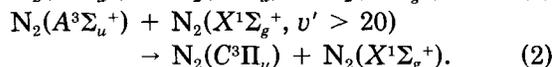
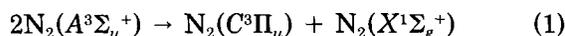
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Several reports in the literature imply that extremely large number densities of metastable nitrogen molecules may be found in the effluents of dielectric-barrier (ozonizer) discharges in flowing nitrogen. We have constructed a dielectric-barrier discharge which operates at 1 to 10 kV in flowing nitrogen or nitrogen mixtures with either argon or helium at total pressures between 0.3 and 6 Torr. Spectroscopic observations in the afterglow of this discharge indicate that virtually all observed excitation between 200 and 850 nm results from discharge streamers. All emissions are quenched upon adding a grounded loop downstream from the discharge. The absence of NO gamma-band emission when NO is added downstream from the grounded loop indicates that $N_2(A)$ number densities in the afterglow are below 10^5 molecules cm^{-3} , some ten orders of magnitude below previous estimates.

Index Headings: Emission spectroscopy; Analytical methods; Spectroscopic techniques; UV-visible spectroscopy.

INTRODUCTION

The dielectric-barrier (ozonizer) discharge is a high-voltage ac discharge. A number of groups have investigated the afterglow of dielectric-barrier discharges through flowing nitrogen for application to spectroscopy¹⁻⁴ and trace analysis.⁵⁻¹² They have reported strong nitrogen second-positive emission, $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$, even at times as long as 100 ms downstream from the discharge. Since the radiative lifetime of $N_2(C^3\Pi_u)$ is 37 ns,¹³ these results suggest that $N_2(C^3\Pi_u)$ is being produced in the discharge afterglow. Ung⁴ postulated that the strong second-positive emission resulted from energy pooling reactions of $N_2(A^3\Sigma_u^+)$ either with itself or with highly vibrationally excited, ground-electronic state nitrogen:



Dodge and Allen,⁶ noting the fall off from linearity of atomic zinc emissions as a function of added [Zn] estimated $N_2(A)$ number densities to be 10^{15} molecules cm^{-3} or about five to six orders of magnitude greater than is produced by microwave¹⁴ or hollow-cathode¹⁵ discharges. Jurgensen and Winefordner¹⁶ have estimated similarly large $N_2(A)$ number densities in a dielectric-barrier discharge afterglow, 10^{16} molecules cm^{-3} .

Intrigued by these reports of large $N_2(A)$ number densities, we undertook a spectroscopic study of the dielec-

tric-barrier discharge afterglow in order to determine number densities of metastable nitrogen quantitatively. Our procedure involves determining absolute photon emission rates of various spectroscopic features. *In situ* calibration of our detection system relies on observations of the air afterglow chemiluminescence under carefully controlled conditions. The absolute photon yields of this reaction at visible wavelengths are well established.¹⁷⁻²⁰

EXPERIMENTAL

Apparatus. The discharge, which is based on Dodge and Allen's design,⁶ consists of two coaxial glass tubes which form an annulus with inside and outside diameters of 8 and 10.8 mm, respectively (see Fig. 1). One electrode is formed by pinching off the bottom of the inner tube, filling it with saturated NaCl solution, and immersing a wire from the power supply in the solution. The second electrode is made by wrapping copper foil tape around the outer tube. The electrodes form a 30-cm-long discharge region.

The ac power supply used with the discharge consists of a 15-kV neon-sign transformer (center tap of secondary grounded) with a variac in the primary circuit to control the output voltage. To reduce interference with nearby electronics, we used only half of the transformer secondary during most of our work. Two 100-k Ω power resistors, placed in the secondary, limited the current.

The afterglow of the discharge was monitored as it passed through a 1-in.-diameter Pyrex[®] flow-tube with quartz windows at various points along its length (see Fig. 2). A wire loop was inserted through a 1/4-in. port at the entrance to the flow-tube. The loop was grounded through a 1-k Ω resistor and served as a groundpoint to ensure that the discharge did not extend into the observation region. A Sargent-Welch No. 1402 (160 Lpm) mechanical pump exhausted the flow tube, maintaining flow velocities of about 300 $cm\ s^{-1}$.

Nitrogen flow rates ranged from 20 to 200 $\mu moles^{-1}$, and total pressures varied between 0.5 and 6 Torr. Most spectra were taken 28 cm (~ 100 ms) downstream from the discharge terminus. These conditions were picked to reproduce those of Dodge and Allen⁶ and of Jurgensen *et al.*¹²

Spectra were taken with the use of a Spex No. 1269 (1.26-m) monochromator (1 to 3 mm slits) and a Hamamatsu No. R955 photomultiplier tube. The photomultiplier tube was cooled to $-40^\circ C$ and operated at a gain of 1.7×10^6 . The output of the photomultiplier tube was measured with a Keithley picoammeter, which fed into a strip-chart recorder.

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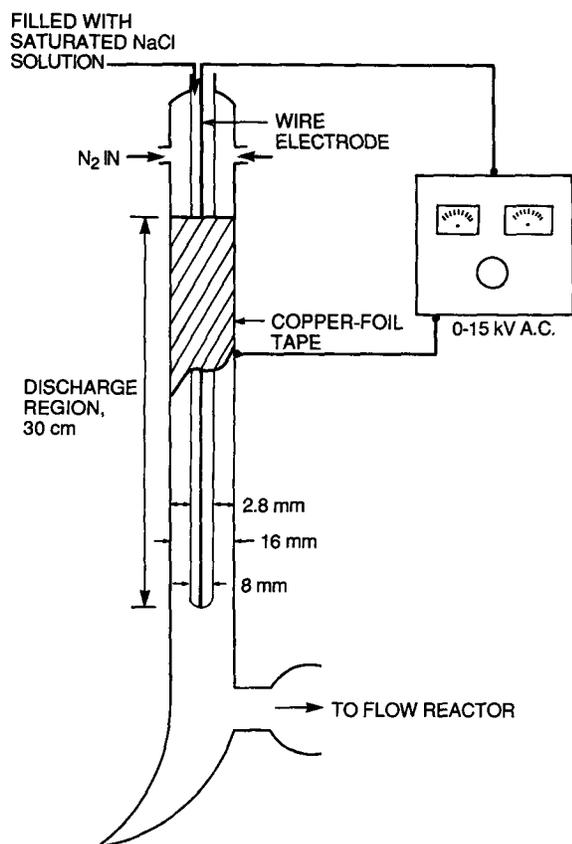
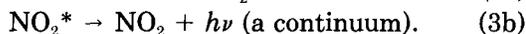
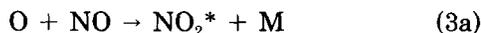


FIG. 1. Details of dielectric-barrier discharge. Although the figure indicates N_2 as the discharge gas, some experiments used mixtures of N_2 in either Ar or He.

Photometric Calibrations. Calibrating the apparatus for absolute photon-emission rates was done in two steps. First, the relative response function (R_λ) of the monochromator was measured with an ultraviolet irradiance standard (a D_2 discharge lamp from Optronic Laboratories) between 200 and 400 nm and the O/NO air afterglow continuum between 400 and 800 nm (reaction 3).¹⁷⁻²⁰ This relative response function corrects for wavelength variations in detector efficiency and the transmission of the optical system. Second, the absolute response at 580 nm was established with the use of an O/NO air-afterglow titration.

Mixing oxygen atoms and nitric oxide generates a continuum emission that extends from 375 nm to beyond 3000 nm:



The intensity of the emission is

$$I_\lambda^{O/NO} = k_\lambda [O][NO]\Delta\lambda \quad (4)$$

where k_λ is the air afterglow rate coefficient ($k_\lambda = 1.25 \times 10^{-19}$ photon $cm^{-3} s^{-1} nm^{-1}$ at 580 nm)¹⁷ and $\Delta\lambda$ is the monochromator bandwidth. Measuring the air-afterglow intensity at a fixed wavelength under conditions of known $[O]$ and $[NO]$ fixes the relative response function absolutely.

Known number densities of O atoms can be generated by titrating N atoms, produced by passing nitrogen gas

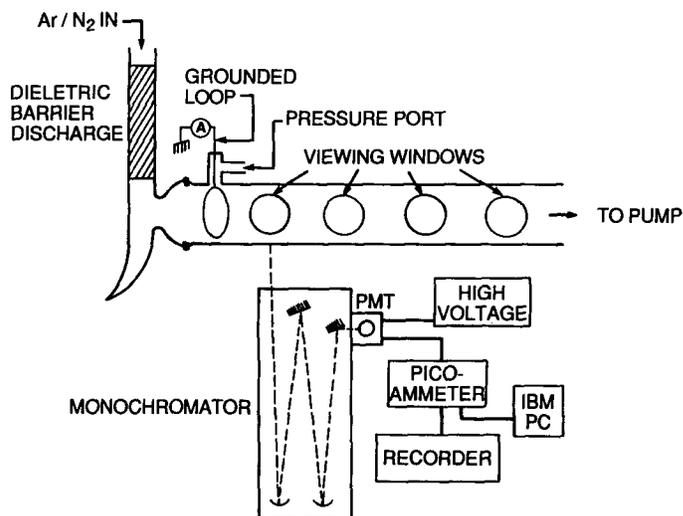


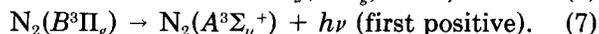
FIG. 2. Schematic diagram of apparatus used to study dielectric-barrier discharge afterglows. Although N_2 /Ar mixtures are indicated as the discharge gas, some experiments used N_2 /He mixtures or just N_2 .

through a microwave discharge, with NO. The titration reaction,



quantitatively converts the N to O.²¹ Upon adding an excess of NO, therefore, the O-atom number density will equal the initial N-atom number density, while the NO number density in the reactor will be the difference between the NO number density that would have been obtained in the absence of reaction 5 and the initial N-atom number density.

N-atoms recombine in a chemiluminescent reaction which results in the generation of the nitrogen first-positive bands:



The intensity of this first-positive emission, therefore, can be used as an indicator of atomic nitrogen. As NO is added to the reactor, the intensity of the first-positive emission drops. At the titration end point, no first-positive emission is observed and the O-atom number density is equal to the initial N-atom number density. Adding excess NO generates the greenish O/NO air afterglow. The air-afterglow intensity varies linearly with the number density of NO added,

$$I_\lambda^{O/NO} = \kappa [N]_0 ([NO] - [N]_0), \quad (8)$$

where subscript 0 refers to the N-atom number density determined from the titration end point. Equation 8 shows that κ can be determined by the ratio of the square of the slope to the intercept of the line determined by the variation in intensity of the air afterglow as a function of added NO number density.

Combining Eqs. 4 and 8 converts the observed intensities (in nA) to absolute photon emission rates:

$$I_{\text{true}} = I_{\text{obs}} k_{580} \Delta\lambda R_{580} / (\kappa R_{\lambda_{\text{obs}}}) \quad (9)$$

where I_{obs} is the total integrated band intensity of the spectral feature of interest.

RESULTS

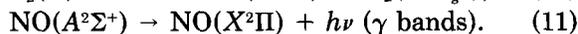
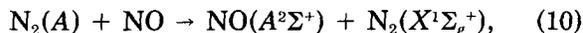
General Observations. A number of spectra were taken in the afterglow region with the loop floating and with it grounded. With the loop floating, the second-positive bands ($N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$) are by far the strongest system. Other observed systems include the first-positive system of nitrogen between 500 and 800 nm ($N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)$); N_2^+ first-negative bands at 391 and 428 nm ($v', v'' = 0, 0$ and $0, 1$ of $N_2^+(B^2\Sigma_u^+) \rightarrow N_2^+(X^2\Sigma_u^+)$); and a relatively weak NO γ system between 230 and 300 nm ($NO(A^2\Sigma^+) \rightarrow NO(X^2\Pi)$). We did not observe the nitrogen Vegard-Kaplan bands, $N_2(A^3\Sigma_u^+ - X^1\Sigma_g^+)$, that would have demonstrated conclusively the presence of $N_2(A)$ in the afterglow. These weak bands appear in the same spectral region as the NO γ -bands, and generally are masked by the much stronger NO emissions.

With the loop grounded, the afterglow intensities downstream from the groundpoint decreased by three orders of magnitude. The residual emissions under these conditions merely were traces of scattered light from the discharge. This was verified when the flow tube was modified to position the groundpoint upstream from the light trap.

The output of the discharge was observed for pressures ranging from 0.3 to 6 Torr and supply voltages from 1 to 10 kV. The observed intensities were roughly proportional to the voltage. Variations in pressure, however, seemed to have the most effect on the discharge output. At low pressure the discharge output was bright pink and uniform, whereas at higher pressures the output became purplish in color and also very unsteady. The intensities of all band systems were greatest at low pressure. At higher pressures the intensities of the first- and second-positive systems were greater, relative to the first negative system, than at low pressure.

Measurements of the current flowing out of the groundpoint were made by monitoring the voltage drop across a 1-k Ω resistor between the groundpoint and ground. At 6 Torr the current was about 60 mA (with 5400 V across the discharge). At lower pressures the current rose to around 400 mA.

Determination of $N_2(A)$ Number Density. Failure to observe Vegard-Kaplan emission indicated that the $N_2(A)$ number density was below about 10^{10} molecules cm^{-3} , because we had previously detected $N_2(A)$ number densities of this magnitude using the same detection system.²² Lower $N_2(A)$ number densities may be determined by adding NO to the reactor and observing NO(A-X) emission produced in the energy-transfer process:



The differential equation governing the number density of NO($A^2\Sigma^+$) is

$$\frac{d[NO(A)]}{dt} = k_{ex}[N_2(A)][NO] - k_{rad}[NO(A)],$$

where k_{ex} (7×10^{-11} cm^3 molecule $^{-1}$ s $^{-1}$)²³ is the excitation rate coefficient and k_{rad} is the radiative decay rate.²⁴ NO(A) is in steady state in our reactor because its radiative lifetime is short (~ 200 ns) compared to the time

the gas resides within the monochromator field of view (~ 1 ms). This means that

$$I_{NO(A)} = k_{rad}[NO(A)] = k_{ex}[N_2(A)][NO], \quad (13)$$

so that

$$[N_2(A)] = \frac{1}{k_{ex}} \frac{dI_{NO(A)}}{d[NO]}.$$

We looked for emission from the 0, 1 γ -band at 235 nm when we added NO to the reactor. We could detect no changes in emission intensity as the NO number density was increased to 10^{14} molecules cm^{-3} . We estimate a minimum detectable signal increase of 2×10^{-3} nA, which, when converted for absolute system response, corresponds to an absolute photon emission rate of 1.6×10^9 photons cm^{-3} s $^{-1}$. Using this value in Eq. 14 along with the NO number density and k_{ex} implies an upper limit to the $N_2(A)$ number density of 2.3×10^5 molecules cm^{-3} . This number is some ten orders of magnitude below previous estimates that were based upon indirect evidence.

DISCUSSION

The termination of the afterglow at the groundpoint, the relatively large electron currents observed at the groundpoint, and the lack of measurable $N_2(A)$ in the afterglow suggest that the afterglow is actually an extension of the discharge. The $N_2(C^3\Pi_u)$, observed by others and by us in the afterglow region when the loop is floating, is formed continuously by electron impact excitation of N_2 by discharge streamers rather than by energy-pooling reactions such as 1 and 2.

The lack of $N_2(A)$ under the conditions employed actually is not particularly surprising. $N_2(A)$ is well known to be quenched with unit efficiency in collisions with reactor walls.¹⁵ In order to transport $N_2(A)$ for any appreciable distance, therefore, either one must work at quite high pressure and, thereby, slow diffusion to the reactor walls, or else one's observations must be made only a few milliseconds downstream from the discharge.

Noxon³ was successful in detecting $N_2(A)$ in the afterglow of a dielectric-barrier discharge. He worked at pressures on the order of an atmosphere and could observe Vegard-Kaplan emission for times up to a second in the afterglow. The configuration of Rice *et al.*¹¹ for exciting analyte spectra in the afterglow of a dielectric-barrier discharge also employs pressures on the order of an atmosphere and, in addition, quite high nitrogen flow rates. Although these authors do not report having observed Vegard-Kaplan emission, their conditions should be favorable for the presence of $N_2(A)$ in the afterglow. One sign that $N_2(A)$ exists in their afterglow is their observation of atomic oxygen emission at 557.7 nm. This emission is excited in the energy-transfer reaction between $N_2(A)$ and O atoms.²⁵

We moved our dielectric-barrier discharge to a 2-in.-diameter flow reactor with significantly enhanced pumping capabilities²³ to see whether $N_2(A)$ would indeed persist in the discharge afterglow. We observed Vegard-Kaplan emission quite readily upon discharging mixtures of nitrogen in argon at pressures on the order of 5 to 10 Torr and times on the order of 10 ms downstream from

the grounded loop. Absolute photometric observations of Vegard-Kaplan emission established the $N_2(A)$ number densities in the observation region to be about 10^{10} molecules cm^{-3} . This number density is comparable to what is produced by other laboratory sources. The dielectric-barrier discharge, therefore, does not seem to offer significant advantages over other discharge-flow methods of $N_2(A)$ generation. Its one advantage appears to be the ability to generate $N_2(A)$ at pressures on the order of an atmosphere.

SUMMARY AND CONCLUSIONS

The dielectric-barrier discharge, as commonly configured for analytical applications, is not an efficient source of $N_2(A)$, as has been reported previously. Observed spectra in these systems appear to be excited by direct electron impact by discharge streamers. $N_2(A)$ may be generated if the discharge is configured for atmospheric pressure operation with short transit times between the discharge and the observation region. In such a system one could generate analytically useful spectra from $N_2(A)$ energy-transfer reactions. This high-pressure configuration might prove efficacious for exciting spectra of molecules separated by a gas chromatograph column.

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