

## INTERACTIONS OF EXCITED SPECIES AND ATOMS IN DISCHARGES\*\*

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## ABSTRACT

The influence of atomic nitrogen on the concentration of  $N_2(A^3\Sigma_u^+)$  excited in nitrogen by a weak discharge has been studied. It was found that (1) a high-order process involving atomic nitrogen destroys  $N_2(A^3\Sigma_u^+)$ , (2) a process utilizing species, other than atomic nitrogen, created in the discharge removes  $N_2(A^3\Sigma_u^+)$ , and (3) a process involving atomic nitrogen and another excited species produces  $N_2(A^3\Sigma_u^+)$ .

It was also found that NO rapidly quenches  $N_2(A^3\Sigma_u^+)$  with a rate coefficient of  $3 \times 10^{-11}$  cm<sup>3</sup>/sec. A quarter of the  $N_2(A^3\Sigma_u^+)$  destroyed excites NO to the  $A^2\Sigma^+ v' = 0$  level.

## INTRODUCTION

Nitrogen subjected to an electrical discharge at low pressure has been a subject of study for over 70 years. In general, phenomena occurring in the discharge itself have been studied in static systems, while phenomena caused by long-lived species generated by a discharge have been studied in fast-flow apparatus.

In all these phenomena there are apparently two classes of reactants involved, atomic species and excited molecules. Recombination of atoms accounts for most of the long-lived afterglow phenomena, while the latter are necessary for much that occurs during the discharge and shortly ( $\sim 10$  m sec) after its termination.

In both the discharge and the long-lived afterglow, molecular nitrogen in the  $A^3\Sigma_u^+$  state is suspected of playing an important role. This is because it is metastable, it is the lowest electronic state of  $N_2$ , it is supposedly easily excited in a discharge, and it is a necessary result of atom recombination. However, emission from this state of  $N_2$ , the Vegard-Kaplan bands, is exceedingly difficult to observe in these phenomena. In fact the Vegard-Kaplan bands have never been observed in the long-lived afterglow, and only under very special circumstances in the discharge or in the short afterglow.

Recently<sup>1</sup> we attempted to observe the Vegard-Kaplan bands in the long-lived (Lewis-Rayleigh) nitrogen afterglow. This afterglow is almost entirely due to the first positive bands of  $N_2$  which terminate on the  $A^3\Sigma_u^+$  state. The flux of this radiation represents a minimum rate of production of  $N_2(A^3\Sigma_u^+)$ . From our failure to observe the Vegard-Kaplan bands, from the radiative lifetime of the  $A^3\Sigma_u^+$  state ( $\sim 10$  sec) and from the sensitivity of detection, an upper limit to the actual lifetime of  $N_2(A^3\Sigma_u^+)$  in the afterglow of  $5 \times 10^{-4}$  sec was derived.

This result implied that collision processes were removing  $N_2(A^3\Sigma_u^+)$ . However, it is known that  $N_2$  does not quench  $N_2(A^3\Sigma_u^+)$ . Aside from  $N_2$ , atomic nitrogen is the largest constituent present, and we conjectured that it was responsible for the short lifetime of  $N_2(A^3\Sigma_u^+)$ .

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This paper describes experiments aimed at investigating the hypothesis that atomic nitrogen, as well as several other compounds ( $\text{NO}$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ), effectively destroy  $\text{N}_2(\text{A}^3\Sigma_u^+)$ .

#### EXPERIMENTAL - ATOMIC NITROGEN INTERACTION

Nitrogen was excited by a pulsed or continuous 150 kc, 10 kV oscillator (of the type used in high-voltage supplies) in a 5-liter quartz bulb with simple one-eighth inch tungsten rod electrodes separated by the diameter of the bulb. A one-half-meter Jarrel-Ash Seya-Namioka monochromator was used to scan the discharge spectrum or to isolate bands for decay measurements. Signal levels were very low, and an Enhancetron signal integration unit<sup>2</sup> was used to abstract the decaying signal from the noise.

Prepurified nitrogen was passed through a liquid nitrogen trap, then through heated titanium-zirconium and two additional liquid nitrogen traps, past a microwave excitation section, an NO titration inlet, and finally into the 5-liter observation bulb, from which it was exhausted by a mechanical vacuum pump at approximately 100  $\text{cm}^3/\text{sec}$ . A filtered photomultiplier downstream from the bulb observed the  $\text{N}_2$  first positive bands resulting from atom recombination.<sup>3</sup> This permitted the atom concentration to be computed after calibration against an NO titration.

#### RESULTS INVOLVING ATOMIC NITROGEN

Figure 1 shows spectrometer scans of the discharge. In Fig. 1a the  $\text{N}_2$  second positive and NO  $\gamma$  bands predominate below 3000 A. The  $\beta$  bands were the only other system of NO detected, and these were very weak. If the microwave discharge is adjusted to produce a small quantity of atomic nitrogen, the NO bands can be suppressed almost entirely (Fig. 1b). Although the Vegard-Kaplan bands are also reduced, the second positive bands remain relatively unchanged. Addition of NO causes a large increase in the intensity of the NO  $\gamma$  bands (Fig. 1c).

Figure 2 shows the decay of the (0,5) Vegard-Kaplan band and the (0,3) NO band with the addition of atoms, *i.e.*, when the upstream microwave discharge was on. The decay of the NO  $\gamma$  bands is identical to that of the Vegard-Kaplan bands.

Figure 3 demonstrates the buildup and decay of the (0,5) Vegard-Kaplan band when the 150 kc discharge is turned on and off; the rise and fall of this band involved the same exponential.

Figure 4 indicates the rate of decay of the Vegard-Kaplan bands as a function of pressure without added nitrogen atoms.

Figure 5 shows the dependence of the Vegard-Kaplan decay rate on  $[\text{N}]^2$  derived from the downstream photomultiplier.

Figure 6 illustrates the pressure dependence of the rate coefficient for de-excitation of  $\text{N}_2(\text{A}^3\Sigma_u^+)$  by atomic nitrogen.

Figure 7 is a plot of the growth rate constant of the Vegard-Kaplan bands, after the discharge is turned on, as a function of  $[\text{N}]^2$ .

Figure 8 shows  $(I_0/I)_{vk}$  as a function of atomic nitrogen, where  $I_{ovk}$  is the intensity without added atoms and where  $I_{vk}$  is the intensity with atoms.

Figure 9 indicates the decreased number of nitrogen atoms leaving the quartz bulb due to the discharge.

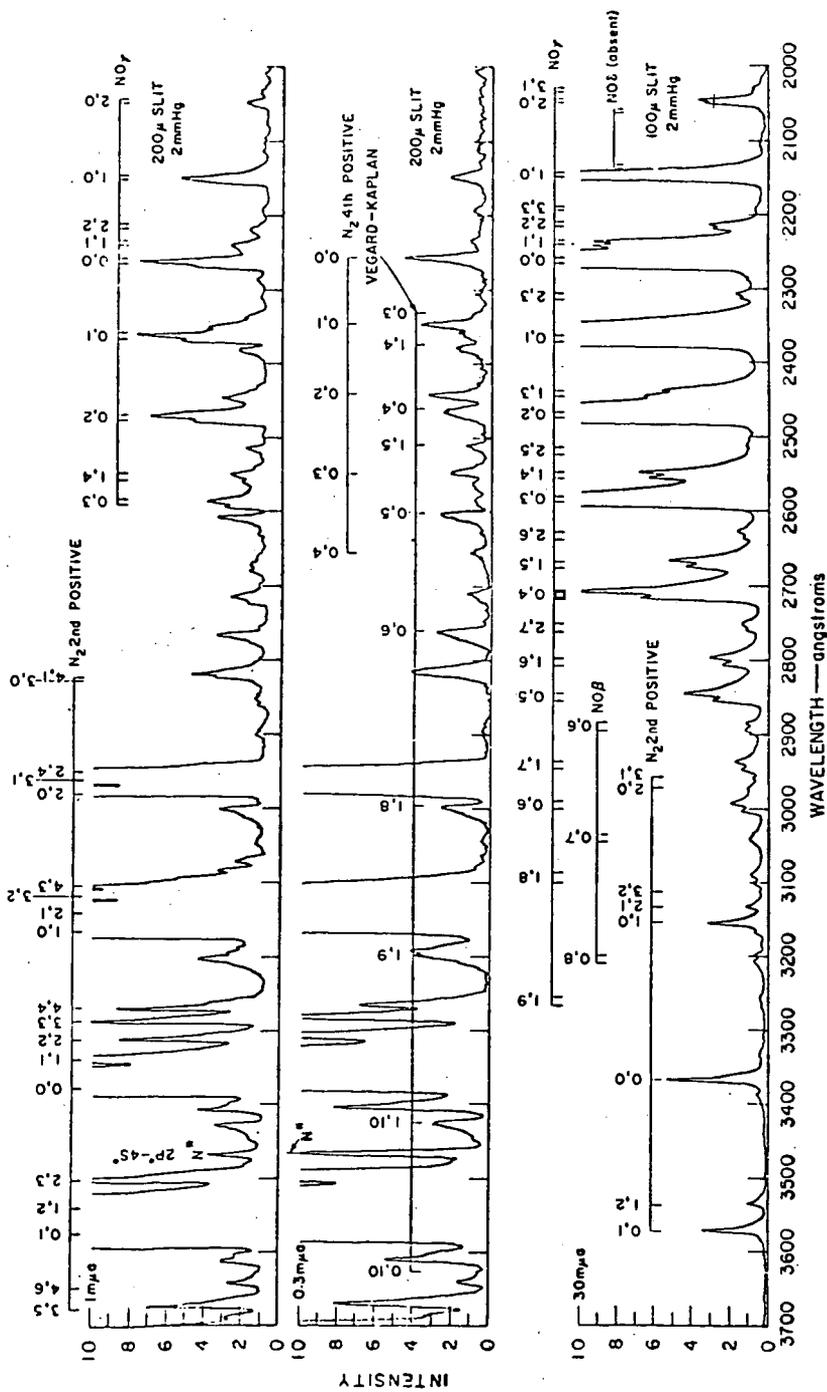
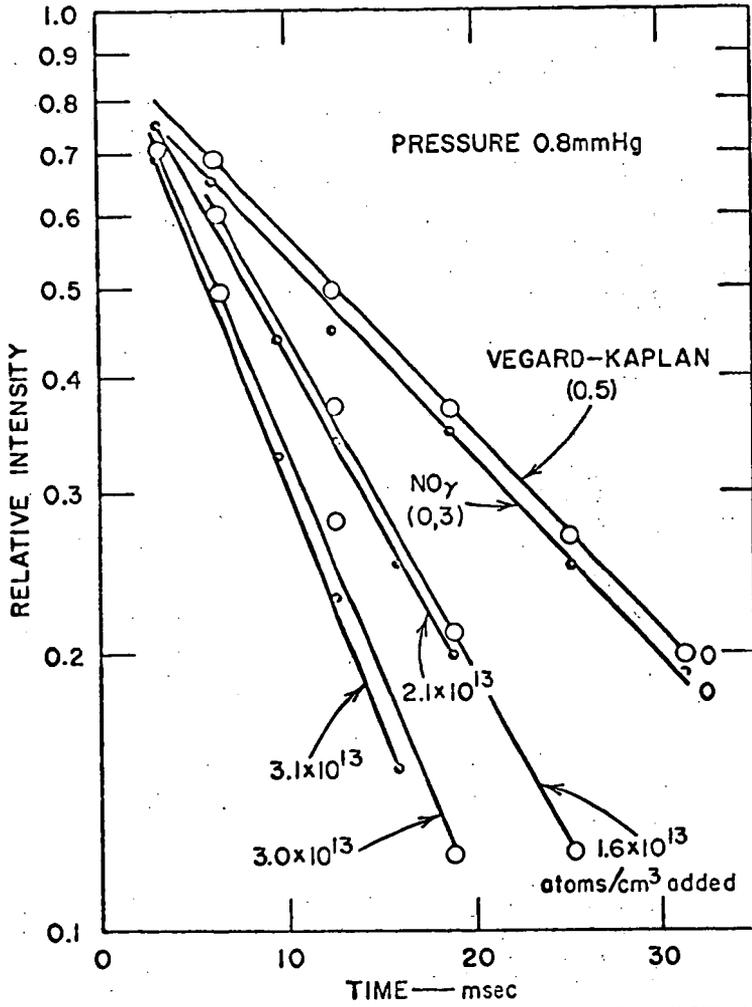


Fig. 1a A characteristic spectrum excited in purified nitrogen by a Tesla-type discharge at 2 mm Hg.

Fig. 1b A spectrum characteristic of purified nitrogen excited by a Tesla-type discharge with a small amount of nitrogen atom added from an upstream microwave discharge. Note how weak the NO bands have become.

Fig. 1c The characteristic spectrum of purified nitrogen with  $\sim 40$  ppm added NO excited by a Tesla-type discharge. Note change in scale from Figs. 1a and 1b.



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Fig. 2

The intensity of the (0,5) Vegard-Kaplan band and the (0,3)  $\gamma$  band as a function of time for various amounts of added atomic nitrogen.

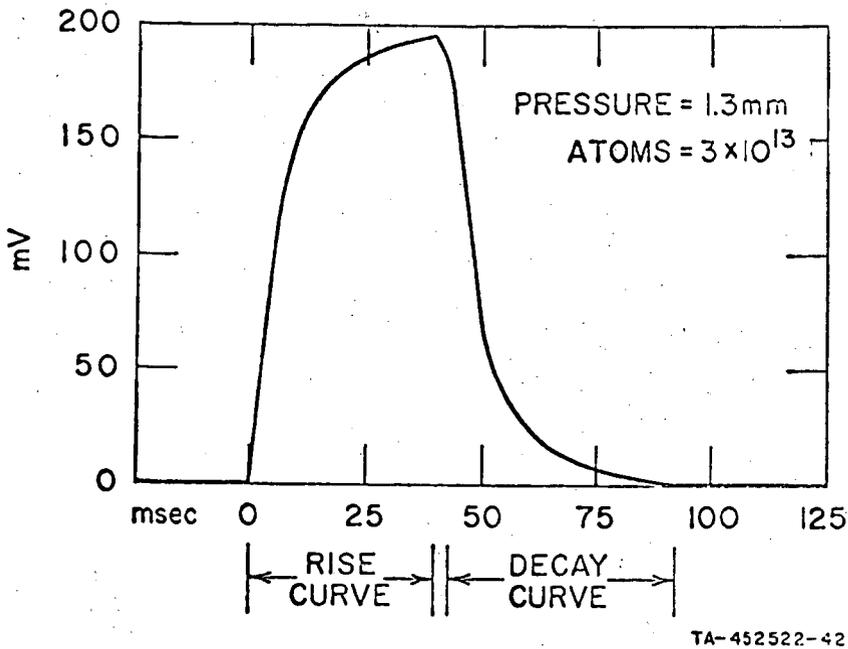


Fig. 3 Buildup and decay of the (0,5) Vegard-Kaplan band when the 150-kc discharge is turned on and off. The curve represents integration of approximately 1000 cycles.

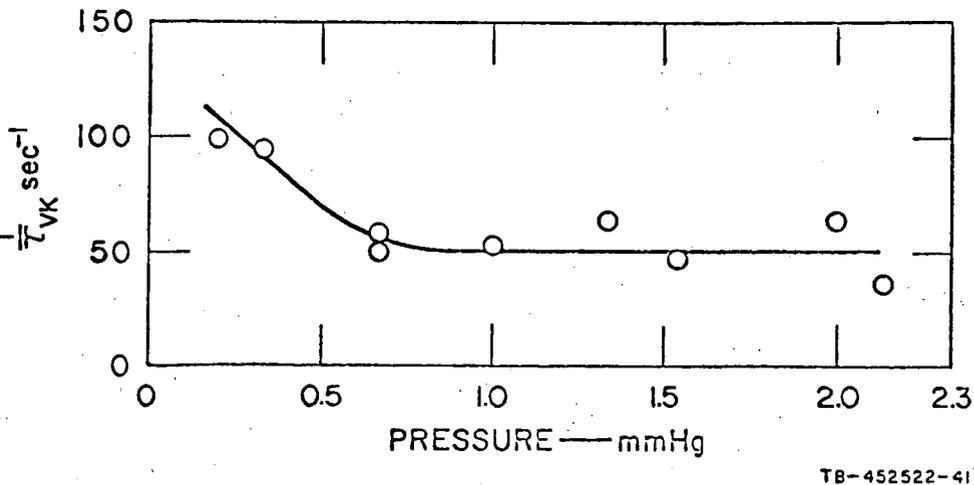
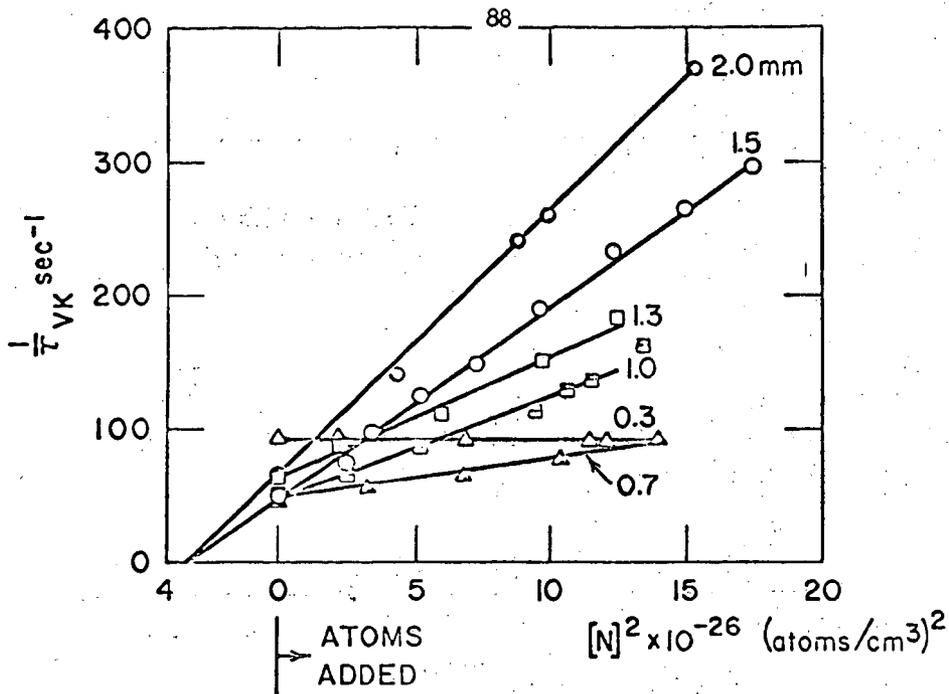
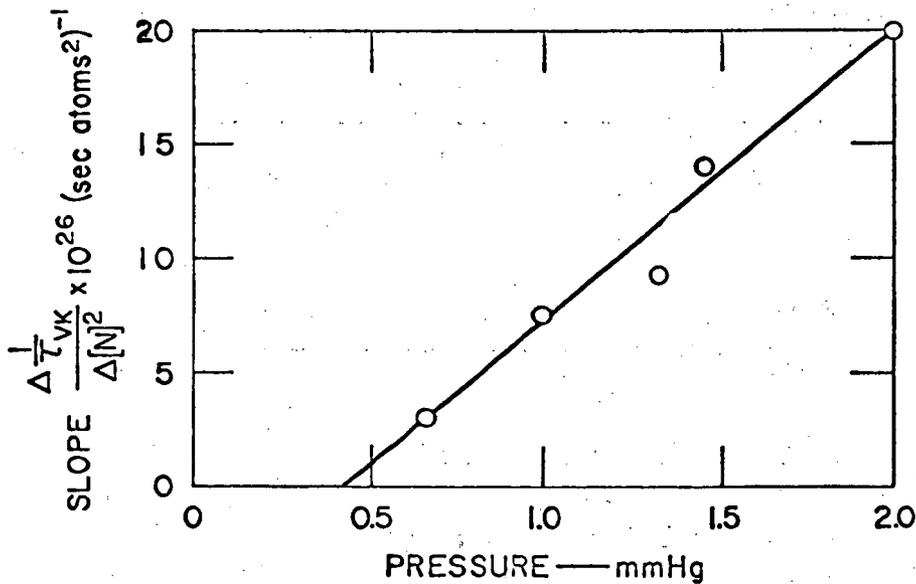


Fig. 4 The dependence of the rate of decay of the Vegard-Kaplan bands as a function of pressure without added nitrogen atoms.



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Fig. 5 The rate of decay of the Vegard-Kaplan bands as a function of the square of the nitrogen atom concentration.



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Fig. 6 The pressure dependence of the rate coefficient for atom destruction of the  $N_2(A^3\Sigma_u^+)$  state.

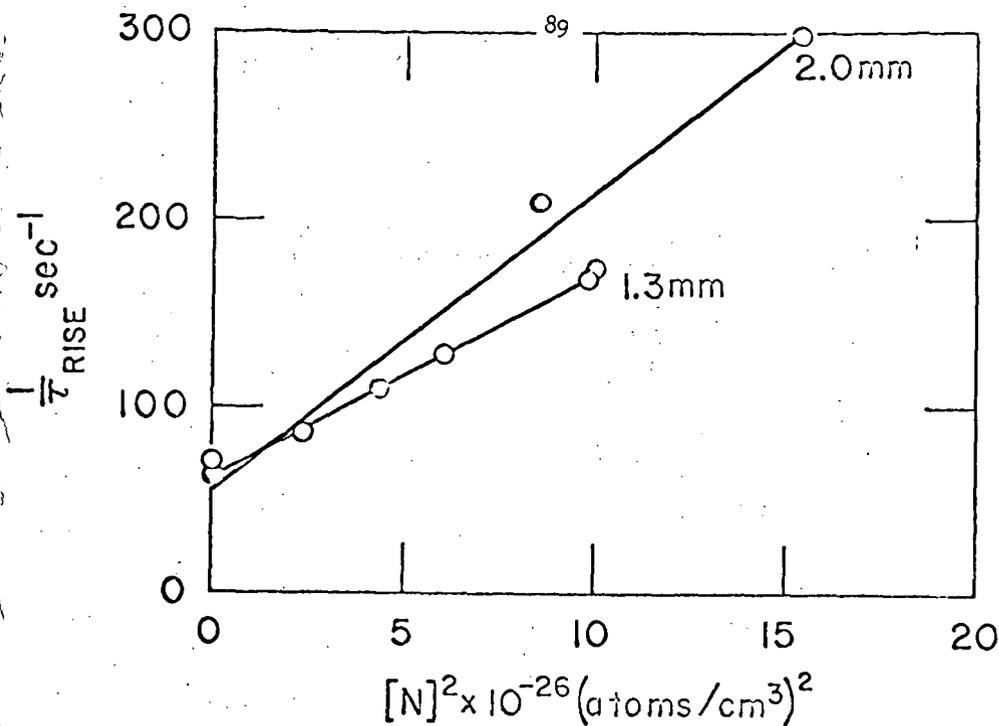


Fig. 7 The buildup rate of the Vegard-Kaplan bands during the excitation discharge as a function of the square of the atomic nitrogen concentration.

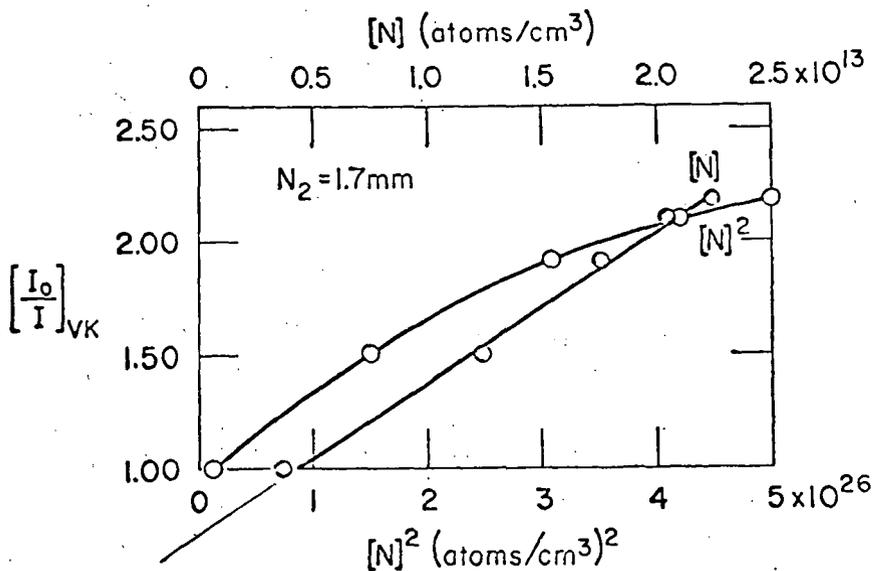
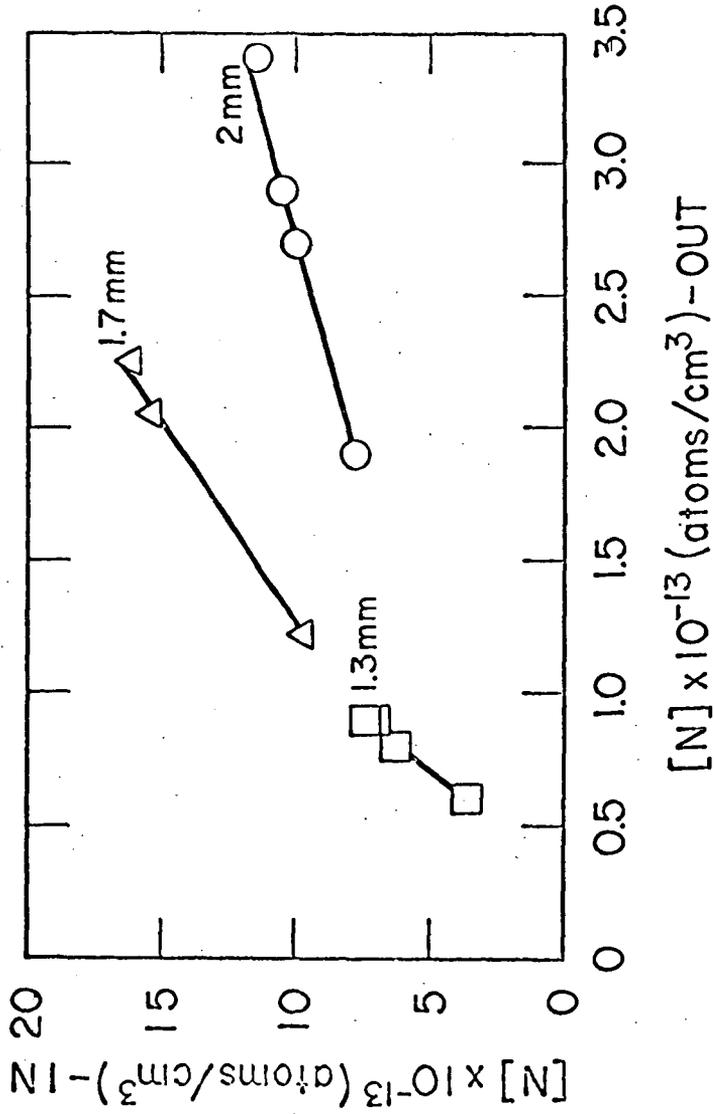


Fig. 8 The normalized inverse intensity of the Vegard-Kaplan bands during the excitation discharge as a function of added atomic nitrogen. The discharge was run continuously.

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Fig. 9 The reduction in the atom concentration produced by the excitation discharge as a function of the atom concentration leaving the excitation bulb. The discharge was run continuously.

## DISCUSSION OF RESULTS PERTAINING TO ATOMIC NITROGEN

The observations indicate that during decay

$$[N_2(A^3\Sigma_u^+)] = [N_2(A^3\Sigma_u^+)]_0 e^{-t/\tau_a} \quad (1)$$

where

$$\frac{1}{\tau_a} = \frac{1}{\tau_0} + K[N]^2 [M] \quad (2)$$

with  $K \approx 4 \times 10^{-42}$  cm<sup>9</sup>/sec. Neither  $\tau_a$  or  $\tau_0$  can be the radiative lifetime of  $N_2(A^3\Sigma_u^+)$  which is  $\approx 10$  sec.

The differential equation describing the time dependence of  $[N_2(A^3\Sigma_u^+)]$  is

$$\frac{d[N_2(A^3\Sigma_u^+)]}{dt} = P - L[N_2(A^3\Sigma_u^+)] \quad (3)$$

where  $L$  contains all factors other than  $[N_2(A^3\Sigma_u^+)]$  such as collision partner concentrations, rates of radiation or diffusion, etc., that are involved in processes removing  $N_2(A^3\Sigma_u^+)$ , and where  $P$  is the rate of production. Substituting Eq. (1) in Eq. (3) gives

$$[N_2(A^3\Sigma_u^+)]_0 e^{-t/\tau_0} (L - \frac{1}{\tau_a}) = P \quad (4)$$

Then either

$$L = \frac{1}{\tau_a} \quad \text{and} \quad P = 0 \quad (5)$$

or

$$\frac{P}{(L - \frac{1}{\tau_a}) [N_2(A^3\Sigma_u^+)]_0} = e^{-t/\tau_a} \quad (6)$$

In the latter eventuality  $L > 1/\tau_a$ , since neither  $P$  nor  $e^{-t/\tau_a}$  can be negative. If  $L$  is comparable to  $1/\tau_a$ , it must be essentially constant in time, while if it is large compared to  $1/\tau_a$ ,

$$\frac{P}{L [N_2(A^3\Sigma_u^+)]_0} = e^{-t/\tau_a} \quad (7)$$

Since all constituents of the system probably decay when the power input is stopped,  $\tau_a$  would be characteristic of the decay of a reactant concentration involved in  $P$  to a higher power than in  $L$ , while other reactant concentrations are either constant or common to both  $P$  and  $L$ . The previous statement would be true if a product of reactant concentrations replaces a single reactant concentration.

Since  $1/\tau_a$  changes by almost a factor of 10 over the range of  $[N]$  used, either  $L \gg 1/\tau_a$  for small  $[N]$  and hence  $P/L [N_2(A^3\Sigma_u^+)]_0 = e^{-t/\tau_a}$ , or  $L$

closely follows  $1/\tau_a$  in dependence on  $[N]$ , *i.e.*,  $L \propto 1/\tau_a$ . Discussion of the last possibility will be deferred. In the former case  $L$  must be very large indeed and  $[N_2(A^3\Sigma_u^+)]$  must be essentially in a quasi-steady state with its production rate, *i.e.*,  $\tau_a$  refers to the decay of  $P$ . Since  $[N_2(A^3\Sigma_u^+)]$  is not strongly deactivated by pure  $N_2$ ,  $L$  would certainly not increase when the energy of the system dissipates as would be necessary if  $P$  did not decay. Because the decay of  $[N_2(A^3\Sigma_u^+)]$  appears to remain exponential for all values of  $[N]$  and because  $\tau_a$  is a smooth function of  $[N]$ , then  $L > 1/\tau_a(\max)$  if the data are interpreted as the decay of  $P$  with  $[N_2(A^3\Sigma_u^+)]$  in a quasi-steady state. For this to be true some species capable of deactivating  $N_2(A^3\Sigma_u^+)$  must be generated in the discharge and remain constant for times long compared to those where  $[N_2(A^3\Sigma_u^+)]$  is detectable. The most abundant chemical species generated by the discharge is  $N$ ; the most abundant excited molecule is  $N_2(A^3\Sigma_u^+)$  -- except possibly for the  $^3\Delta$  state of  $N_2$  which has not yet been directly detected. Only atomic nitrogen appears to be a realistic choice for the species which decays slowly and would keep  $L \gg 1/\tau_a$ .

However, a difficulty arises in the interpretation with  $L \gg 1/\tau_a$  if we consider the observed behavior of  $[N_2(A^3\Sigma_u^+)]$  when the discharge is turned on. The rise of  $[N_2(A^3\Sigma_u^+)]$  to a steady state is describable by

$$[N_2(A^3\Sigma_u^+)] = [N_2(A^3\Sigma_u^+)]_0 (1 - e^{-t/\tau_a}) \quad (8)$$

If this is substituted into Eq. (3), we obtain

$$[N_2(A^3\Sigma_u^+)]_0 ((1/\tau_a) - L) e^{-t/\tau_a} = P - L [N_2(A^3\Sigma_u^+)]_0 \quad (9)$$

If  $1/\tau_a = L$ , then  $P = L [N_2(A^3\Sigma_u^+)]_0 = P_0$ , a constant in time. When  $t = 0$ ,  $P = P_0 = ([N_2(A^3\Sigma_u^+)]_0/\tau_a)$  if  $L \neq (1/\tau_a)$ ; and if  $P = P_0 + P'$ , we obtain

$$P' = [N_2(A^3\Sigma_u^+)]_0 (1/\tau_a - L) (e^{-t/\tau_a} - 1) \quad (10)$$

If  $L \gg 1/\tau_a$ ,  $P'$  is positive; and if  $L \ll 1/\tau_a$ ,  $P'$  is negative and  $P$  ranges from  $P_0$  to 0. A decrease of  $P$  from  $P_0$  is not expected during the discharge and certainly not with an exponential behavior identical to that which occurs when the discharge is turned off. Hence of the two possibilities, when  $L \neq 1/\tau_a$ ,  $L \gg 1/\tau_a$  is the only one tenable during the excitation discharge.

Since  $P_0$  follows the discharge transients, it must become zero when the discharge is turned off, so that  $P$  changes rapidly compared with  $\tau_a$  from  $P_0 + P'$  to  $P'$ . But this is inconsistent with the interpretation of the decay of  $[N_2(A^3\Sigma_u^+)]$  previously given on the assumption that  $L \gg 1/\tau_a$  because this rapid fall in  $P$  would be reflected in a rapid fall of  $[N_2(A^3\Sigma_u^+)]$  which is not observed. Hence this contradiction forces  $L = 1/\tau_a$  and  $P = P_0$ , a constant, during the discharge and  $L = 1/\tau_a$  and  $P = 0$  after the discharge.

During the excitation discharge a steady state is reached, and

$$\bar{P} = \bar{L} [N_2(A^3\Sigma_u^+)] \quad (11)$$

where the bar indicates values constant in time. Then indexing all quantities with a subscript 1 when atoms are not added and with N when they are added, we obtain

$$\frac{I_1(\text{VK})}{I_N(\text{VK})} = \frac{\bar{P}_1}{\bar{P}_N} \frac{\bar{L}_N}{\bar{L}_1} = 0.75 + \alpha[N] \quad (12)$$

where the last equality uses the results of Fig. 8. Hence  $\bar{L}_N$  involves  $[N]$  to a higher power than does  $\bar{P}_N$ . Thus  $\tau_a$  cannot refer to the decay of  $[N]$ . This is consistent with the usual slow decay of  $[N]$ .

Since  $\bar{L}_N$  is essentially proportional to  $[N]^2$ , these results imply that  $\bar{P}_N$  is proportional to  $[N]$ . If this additional production of  $N_2(A^3\Sigma_u^+)$  utilizes nitrogen atoms on a one-for-one basis,  $[N]$  must decrease in passing through the discharge, i.e.,

$$[N]_{\text{in}} - L[N]_{\text{out}} \Delta t = [N]_{\text{out}} \quad (13)$$

where  $\Delta t$  is an average residence time, where  $L[N]_{\text{out}}$  represents the rate of atom removal, and where mixing is rapid compared with reaction. This leads to

$$[N]_{\text{in}} = [N]_{\text{out}} (1 + L\Delta t) \quad (14)$$

or

$$[N] = [N]_{\text{out}} L\Delta t \quad (15)$$

which is the general form observed.

From Fig. 9 we can obtain  $L$  (using  $\Delta t \approx 50$  sec), and from Fig. 8 with a slope of  $(K\tau_0 P_0 [N_2]/L)$ , we can also obtain  $L$  if  $K\tau_0 P_0 [N_2]$  can be found. A comparison of  $L$  derived from Fig. 9 and Fig. 8 is then possible. Since  $P = [N_2(A^3\Sigma_u^+)]/\tau_0$ , absolute measurements of  $[N_2(A^3\Sigma_u^+)]$  derived from  $I(\text{VK}) = ([N_2(A^3\Sigma_u^+) ]/\tau_r)$  where  $\tau_r$  is the radiative lifetime of the excited state give  $\tau_0 P$ .

The absolute intensity of the 0,5 Vegard-Kaplan band in the discharge bulb can be roughly obtained by measuring its signal and calibrating the spectrometer response using the NO  $\gamma(0,3)$  band excited by the chemiluminescent association of N and O in conjunction with measurements of  $[N]$  and  $[O]$  and the known rate coefficient for these processes.<sup>4</sup> In general, the comparisons of  $L$  derived from Figs. 8 and 9 show that if nitrogen atoms are consumed in the excitation of  $N_2(A^3\Sigma_u^+)$ , then several hundred times more atoms need to disappear than in fact are destroyed. This implies that nitrogen atoms are not consumed but catalyze the production of  $N_2(A^3\Sigma_u^+)$  in conjunction with other species generated in the discharge.

A similar argument can be used to show that atomic nitrogen is not consumed in destroying  $N_2(A^3\Sigma_u^+)$ . For example, there are often as many  $N_2(A^3\Sigma_u^+)$  molecules as N atoms; these would be seriously depleted during the decay of  $N_2(A^3\Sigma_u^+)$  and thus would lead to a nonexponential behavior.

The short lifetime of  $N_2(A^3\Sigma_u^+)$  in the discharge (Fig. 4) cannot be due to atoms because their concentration, as inferred from downstream chemiluminescence measurement, is too small. Furthermore, the pressure dependence of  $\tau_0$  is incompatible with atom

deactivation. Hence, some species is produced in the discharge in addition to atomic nitrogen which is capable of rapidly deactivating  $N_2(A^3\Sigma_u^+)$ . This species persists for times long compared to  $\tau_0$ .

The results of these experiments indicate that several unusual processes are occurring: (1) a high-order process destroying  $N_2(A^3\Sigma_u^+)$  which involves atomic nitrogen; (2) a process utilizing species, created in a discharge other than atomic nitrogen, which removes  $N_2(A^3\Sigma_u^+)$ ; and (3) a process involving atomic nitrogen and another species generated in the discharge which produces  $N_2(A^3\Sigma_u^+)$ . These processes are in addition to electron excitation and radiative destruction of  $N_2(A^3\Sigma_u^+)$ . Several possible reaction schemes can be constructed which are consistent with our observations. However, without positive identification of all the species created in the discharge and the intermediaries necessarily involved in high-order processes, these reaction schemes are speculative. It seems best to postpone discussions of these until more experimental information is available.

#### EXPERIMENTAL REACTIONS INVOLVING NO

For experiments on the effect of NO on  $N_2(A^3\Sigma_u^+)$ , three photomultipliers were installed downstream from the RF excitation bulb to observe chemiluminescence. One photomultiplier had an interference filter centered on the strong bands of  $N_2$  at 5800 Å, a second (called the yellow detector) observed radiation at wave lengths longer than 5200 Å, and a third (called the ultraviolet detector) observed emission between 3800 Å and the pyrex cutoff. The first two photomultipliers are sensitive to the  $N_2$  first positive bands excited by recombination of atomic nitrogen and to the  $NO_2$  continuum excited by reactions of O with NO, while the ultraviolet photomultiplier is mainly sensitive to the NO,  $\beta$  bands excited in the association of atomic nitrogen and oxygen.<sup>4</sup> These photomultipliers were calibrated by generating nitrogen atoms in the microwave discharge and titrating them with NO. It should be remembered that all emission observed in the downstream bulb is of chemiluminescent origin.

#### RESULTS

Figure 10 shows the decay rate when the exciting discharge is turned off from the 0,3 NO  $\gamma$  band, and the 0,5 Vegard-Kaplan band as a function of atomic nitrogen added by the upstream microwave discharge.

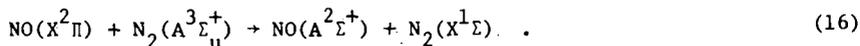
Figures 11 and 12 show the intensity of the 0,5 Vegard-Kaplan band, the 0,3 NO  $\gamma$  band and the 0,6 NO  $\beta$  band in the discharge bulb as a function of the NO concentration that would have existed in the stream if no destruction of NO occurred. Also shown are the responses of the yellow photomultiplier and the ultraviolet photomultiplier, both of which are located at the downstream bulb.

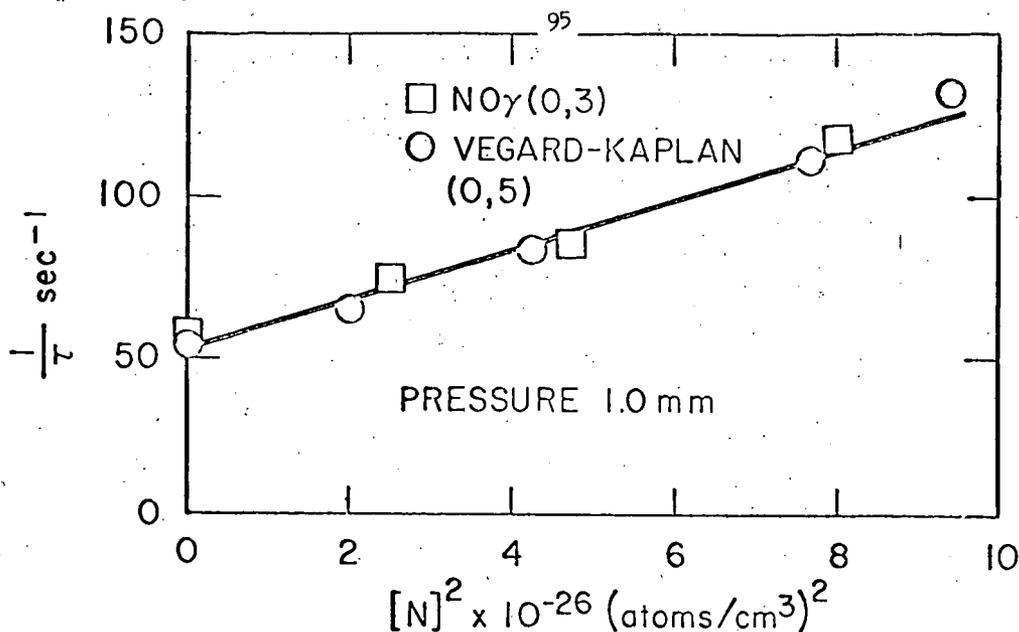
Spectrometer scans of the discharge without adding NO and on the plateau of Figs. 11 and 12 are shown in Fig. 1.

Figure 13 is a plot of the area intensity ratio of 0,3 NO  $\gamma$ /0,5 Vegard-Kaplan bands as a function of NO added beyond the null and as a function of the relative response of the yellow phototube to the  $NO_2$  continuum. Figure 14 is similar to Fig. 13 but involves the 1,10 Vegard-Kaplan band and the 3,0 NO  $\gamma$  band.

#### DISCUSSION

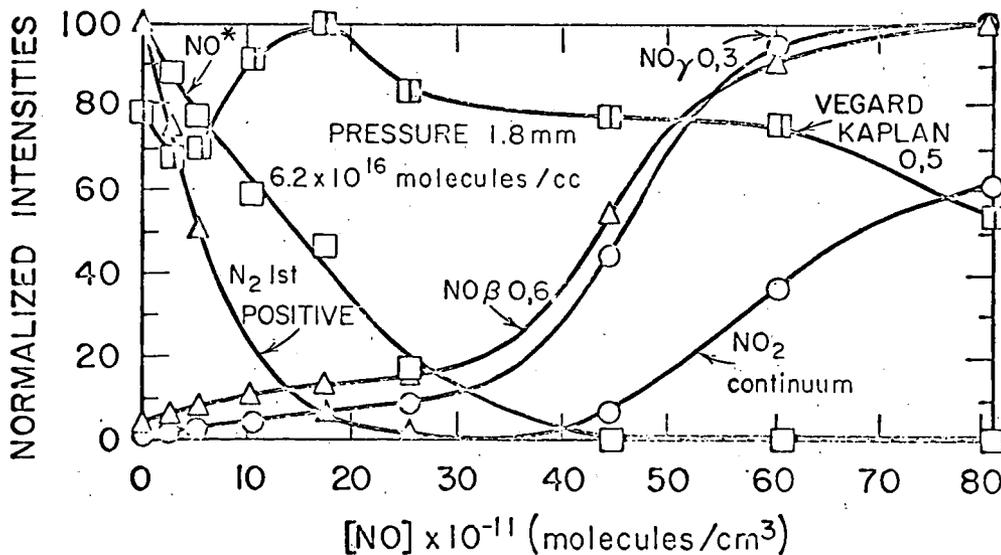
The simultaneous decay of  $N_2(A^3\Sigma_u^+)$  and  $I_\gamma$ , the intensity of the NO  $\gamma$  bands, suggests that NO is excited in the process<sup>5</sup>





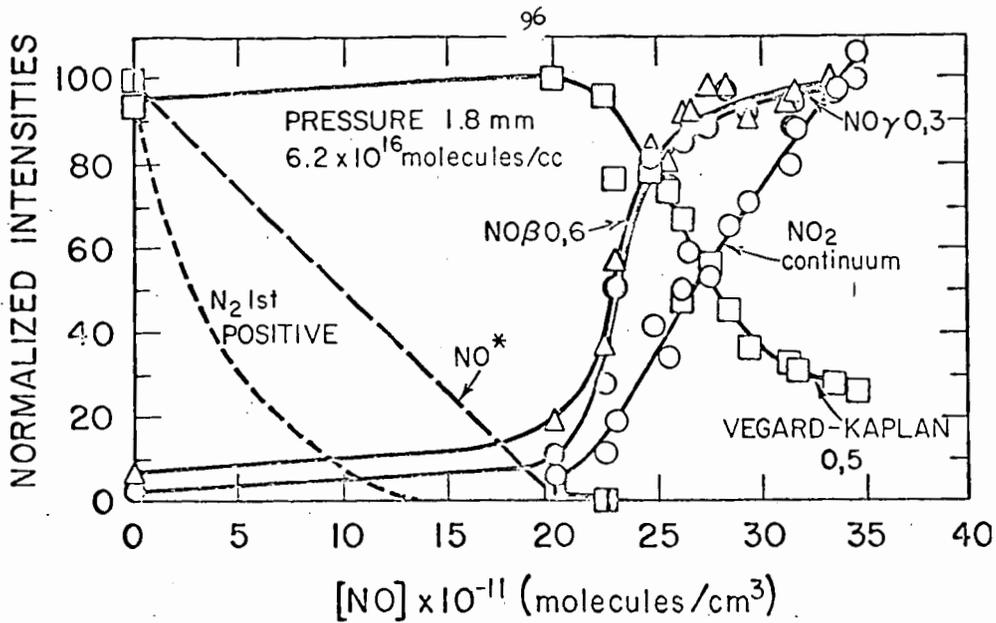
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Fig. 10 The dependence of the rate of decay of  $N_2(A^3\Sigma_u^+)$  and  $NO(A^2\Sigma^+)$  as a function of the square of the atomic nitrogen concentration.



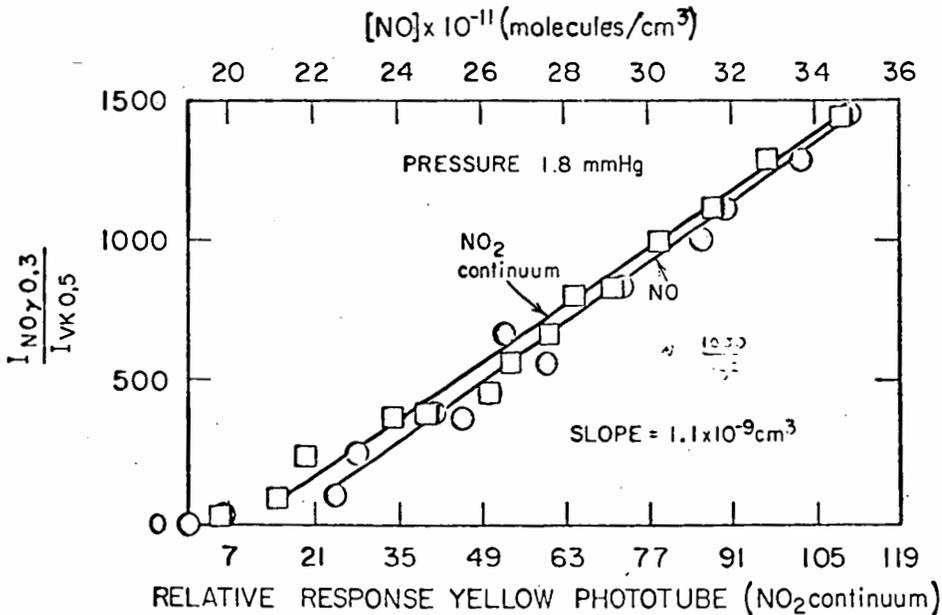
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Fig. 11 The dependence of emission intensities on NO concentration:  $\square$  - the  $NO \beta$  bands,  $\Delta$  - the  $N_2$  first positive bands,  $\circ$  - the  $NO_2$  continuum -- all excited in the downstream observation bulb;  $\circ$  - the 0,3  $NO \gamma$  band,  $\Delta$  - the 0,6  $NO \beta$  band, and  $\square$  - the 0,5 Vegard-Kaplan band excited in the Tesla discharge bulb.



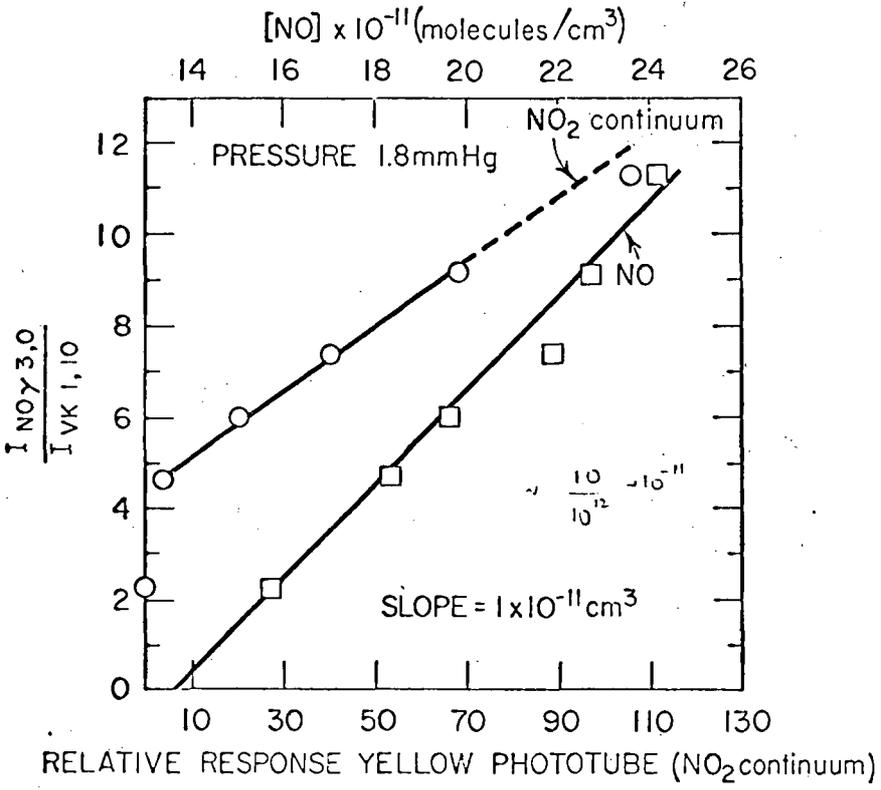
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Fig. 12 The dependence of emission intensities on NO concentration:  $\square$  - the NO  $\beta$  bands,  $\circ$  - the NO<sub>2</sub> continuum -- both excited in the downstream observation bulb;  $\circ$  - the 0,3 NO  $\gamma$  band,  $\Delta$  - the 0,6 NO  $\beta$  band; and  $\square$  - the 0,5 Vegard-Kaplan band excited in the Tesla discharge bulb.



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Fig. 13 The relative photomultiplier response to the NO  $\gamma$  (0,3) and N<sub>2</sub> (0,5) Vegard-Kaplan bands as a function of both [NO] and the response of the yellow photomultiplier.



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Fig. 14 The relative photomultiplier response to the NO  $\gamma$  (3,0) and N<sub>2</sub>(1,10) Vegard-Kaplan bands as a function of both [NO] and the response of the yellow photomultiplier.

The initial decrease of the signals from the yellow downstream photomultiplier is due to NO titration of nitrogen atoms produced in the exciting discharge, i.e.,



The null point represents the complete conversion of nitrogen atoms to oxygen atoms. The concentration of these atoms derived from the amount of NO added to reach this null is consistent with the intensity of the first positive bands before NO addition. The linear rise of the yellow sensitive photomultiplier after null is due to



and indicates that O is essentially constant.

There is a slow increase of the NO  $\gamma$  and  $\beta$  bands in the excitation bulb because of the slow increase in the actual steady-state concentration of NO which is maintained by



and reaction (16), i.e.,

$$[NO] = \frac{k_{19}}{k_{17}} [O] [M] \quad (22)$$

When [N] goes to zero, this steady state cannot be maintained, and NO in the stream increases as expected for no reaction of NO. In the reaction time available reaction (20) does not significantly alter either [O] or [NO].

As [NO] increases sharply after the removal of N, the NO  $\gamma$  and  $\beta$  bands increase sharply in the discharge and the  $N_2$  Vegard-Kaplan bands decrease rapidly. Since

$$I_{vk} = [N_2(A^3\Sigma_u^+)]/\tau_{vk} \quad (23)$$

$$I_{\gamma} = [NO(A^2\Sigma^+)]/\tau_{\gamma} \quad (24)$$

for excitation in the discharge bulb, and since

$$I_{NO_2} = K_{NO_2} [NO] [O] \quad (25)$$

for chemiluminescent excitation in the downstream bulb, reaction (16) implies

$$I_Y = k_{16} [\text{NO}] [\text{N}_2(\text{A}^3\Sigma_u^+)] = k_{16} [\text{NO}] I_{\text{vk}\tau_{\text{vk}}} = \frac{k_{16} I_{\text{NO}_2} I_{\text{vk}\tau_{\text{vk}}}}{[\text{O}]K_{\text{NO}_2}} \quad (26)$$

if  $\text{NO}(\text{A}^2\Sigma^+)$  is only deactivated by emission.

Since  $\text{O}$  is constant,

$$\frac{I_Y}{I_{\text{vk}}} \propto I_{\text{NO}_2} \quad (27)$$

This is true, as Figs. 13 and 14 show. In these graphs intensities are not absolute, but relative.

To obtain  $k_{16}$  from Eq. (26), we must experimentally relate the emission intensities more directly to the concentration of the emitting state. If  $I_Y(0,3)$  represents the absolute intensity of the 0,3  $\gamma$  band of NO and similarly for the Vegard-Kaplan bands, then Eq. (11) becomes

$$\frac{I_Y(0,3)}{f_Y(0,3)} = \frac{k_{16} [\text{NO}] \tau_{\text{vk}} I_{\text{vk}}(0,5)}{f_{\text{vk}}(0,5) \beta} \quad (28)$$

where  $f_Y(0,3)$  is the fraction of all emission from the  $v' = 0$  level which terminates on the  $v'' = 3$  level and similarly for  $f_{\text{vk}}(0,5)$  and where  $\tau_{\text{vk}}$  is the radiative lifetime of the  $\text{A}^3\Sigma_u^+$  state<sup>6</sup> and  $\beta$  represents the fraction of all  $\text{N}_2(\text{A}^3\Sigma_u^+)$  which are in  $v' = 0$ . Only  $v' = 1$  and 0 are detected by their emission, and  $\beta$  is found to be one half and constant. Then

$$k_{16} = \left( \frac{f_{\text{vk}}(0,5)}{f_Y(0,3) \tau_{\text{vk}}} \right) \frac{\beta I_Y(0,3)}{I_{\text{vk}}(0,5) [\text{NO}]} \quad (29)$$

The parameters in parentheses depend only on the internal characteristics of the molecules and have previously been measured<sup>6</sup> as  $\tau_{\text{vk}} = 20$  sec,  $f_{\text{vk}}(0,5) = 0.17$ , and  $f_Y(0,3) = 0.14$ . Hence

$$k_{16} = \frac{0.03 I_Y(0,3)}{[\text{NO}] I_{\text{vk}}(0,5)} \quad (30)$$

To obtain  $k_{16}$ , only the relative intensity of  $I_Y(0,3)$  and  $I_{\text{vk}}(0,5)$  are required. Since these bands occur very near each other in the spectra of the discharge, their relative intensity is equal to their relative signal level. Hence  $k_{16}$  is 0.03 times the slope of the line in Fig. 13, *i.e.*,

$$k_{16} = 0.03 (1.1 \times 10^{-9}) = 3 \times 10^{-11} \text{ cm}^3/\text{sec} \quad (31)$$

This rate is much larger than that reported by Dugan.<sup>7</sup>

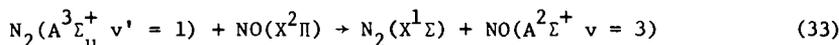
The existence of the  $\beta$  bands and emission from higher vibrational levels of the  $\text{NO}(A^2\Sigma^+)$  state indicate that this rate is a lower bound to the rate of energy transfer from  $\text{N}_2(A^3\Sigma_u^+)$  to  $\text{NO}(X^2\Pi)$ . There are several states of NO accessible in an energy exchange involving  $\text{N}_2(A^3\Sigma_u^+)$  -- the  $a^4\Pi$ ,  $b^4\Pi$ ,  $b^4\Sigma^-$ , as well as the  $A^2\Sigma^+$  and  $B^2\Pi$  which are revealed by their emission.

The total rate of de-excitation of  $\text{N}_2(A^3\Sigma_u^+)$  can be estimated, since we know, in the absence of NO, its deactivation rate is  $1/\tau = 50/\text{sec}$ , and the intensity of the Vegard-Kaplan bands is reduced by half when  $[\text{NO}] \approx 7 \times 10^{11}$  molecules/ $\text{cm}^3$ , i.e.,  $50 = k'_{16}(7 \times 10^{11})$ ; in other words

$$k'_{16} = 7 \times 10^{-11} \text{ cm}^3/\text{sec} \quad (32)$$

or essentially a quarter of all the  $\text{N}_2(A^3\Sigma_u^+)$  deactivated leads to excitation of the  $v' = 0$  level of the  $\text{NO}(A^2\Sigma^+)$ .

It is apparent from the spectra that excitation of the  $A^2\Sigma$  state of NO by  $\text{N}_2(A^3\Sigma_u^+)$  decreases in efficiency as  $v'$  increases in the NO molecule, becoming very small for  $v' = 3$  which is the highest level observed. This level can only be excited by  $\text{N}_2(A^3\Sigma_u^+ v = 1)$ , while the  $v' = 2, 1$ , and 0 levels of the  $\text{NO}(A^2\Sigma^+)$  state can be excited by  $\text{N}_2(A^3\Sigma_u^+ v = 0, 1)$ . Using the data in Fig. 14, we can obtain the rate coefficient of



as  $k_{16}(1,3) = 10^{-13} \text{ cm}^3/\text{sec}$ .

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