

## COLLISIONAL QUENCHING OF $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$ PRODUCED BY THE REACTION OF $\text{N}(^2\text{D})$ WITH $\text{N}_2\text{O}^*$

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(Received March 30, 1976)

### Summary

The reaction of  $\text{N}(^2\text{D})$  with  $\text{N}_2\text{O}$  has been used as a source of  $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$ . The effects of added gases on its emission have been used to determine quenching rate coefficients (using a radiative lifetime of  $3 \times 10^{-6}$  s). These coefficients have been compared with rate coefficients for quenching the isoenergetic species  $\text{NO}(\text{A}^2\Sigma^+)_{v'=0,1}$ .

### Introduction

Very little information is available on the quenching of  $\text{NO}(\text{B}^2\Pi_r)$ , largely because the state has not been observed in NO fluorescence [1]. However,  $\text{NO}(\text{B}^2\Pi_r)$  can be made and its quenching studied in many other ways. The  $\beta$  band emission of  $\text{NO}(\text{B}^2\Pi_r)$  is a prominent feature of the recombination of oxygen and nitrogen atoms [2], and there are two published studies of its quenching in this afterglow system [3, 4]. Their results for quenching emission from the  $v' = 0$  level of  $\text{NO}(\text{B}^2\Pi_r)$  by  $\text{N}_2\text{O}$  and  $\text{CO}_2$  were very different. Furthermore, the interpretation of quenching effects in such a system is complicated by the involvement of precursor states of NO between the recombining atoms and the ultimate production of  $\text{NO}(\text{B}^2\Pi_r)$ ; both the  $\text{NO}(\text{a}^4\Pi_i)$  and  $\text{NO}(\text{b}^4\Sigma^-)$  are thought [2] to be involved.

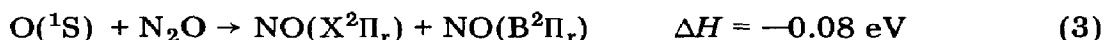
Emission of  $\text{NO}(\text{B}^2\Pi_r)$  in the  $v' = 0, 1, 2,$  and  $3$  levels was observed [5] when  $\text{NO}_2$  was photodissociated with the krypton resonance lines (1165 and 1236 Å). With the 1295 Å xenon resonance line, emission was observed from levels up to  $v' = 2$ . No quenching measurements were made.  $\text{NO}(\text{B}^2\Pi_r)$  is also made by electron collisions with NO [6]. Although this method has been used to obtain the radiative lifetime for  $v' = 0, 1,$  and  $2$ , no quenching information was obtained. Studies in discharge systems [7] have established that addition of NO to a mixture containing  $\text{N}_2(\text{A}^3\Sigma_u^+)$  results in parallel production of  $\text{NO}(\text{A}^2\Sigma^+)$  and  $\text{NO}(\text{B}^2\Pi_r)$ , the B state being excited much less efficiently than the A state. This process:

\*Work supported by Contract DAHCO4-74-C-0003 with the Army Research Office-Durham.



has been confirmed [8] in studies in which photodissociation of  $\text{N}_2\text{O}$  was used as the source of  $\text{N}_2(\text{A}^3\Sigma_u^+)$ . Although this system could be used to study collisional quenching of  $\text{NO}(\text{B}^2\Pi_r)$ , in a similar way to that described below, no such study has been reported.

In the photolysis of  $\text{N}_2\text{O}$  at 1470 Å, the  $\text{NO}$   $\beta$  bands are observed in emission [8 - 12]. Welge [10] proposed that only two reactions could reasonably be expected to form  $\text{NO}(\text{B}^2\Pi_r)$ :



Below 1458 Å,  $\text{N}(^2\text{P})$  production is possible and may lead to  $\text{NO}$   $\beta$  bands by way of:



Our own work [2] showed that reaction (2) was the source of the  $\text{NO}$   $\beta$  bands at 1470 Å and that this was also true for irradiation with a Kr lamp (1165 + 1236 Å), provided the  $\text{O}(^1\text{S})$  was thermalized. We have recently shown [13] this to hold for photodissociation between 1100 and 1250 Å and between 1350 and 1500 Å. Reaction (2) produces most of the  $\text{NO}(\text{B}^2\Pi_r)$  in the  $v' = 0$  level [9] (although the author's unpublished spectra of the  $\text{NO}(\text{B}^2\Pi_r)$  emission obtained from  $\text{N}_2\text{O}$  photolysis at both 1470 Å and 1165 + 1236 Å show  $\text{NO}$   $\beta$  bands up to  $v' = 5$  in the 4200 - 5500 Å region, equivalent to vibrational excitation of the  $\text{NO}(\text{B}^2\Pi_r)$  by 0.6 eV. The  $v' = 5$  population was estimated to be 2% of the total  $\text{NO}(\text{B}^2\Pi_r)$  population.)

For the experiments described here, we have used reaction (2) as the source of  $\text{NO}(\text{B}^2\Pi_r)$ . By studying the effects of added gases on the intensity of the  $\text{NO}$   $\beta$  bands, we have determined collisional quenching rate coefficients for  $\text{NO}(\text{B}^2\Pi_r)$  in the  $v' = 0$  level.

## Experimental

The apparatus for these measurements has been fully described previously [13], so only a brief description will be given here. The light source was a capillary discharge lamp, operated with a low pressure of hydrogen, attached to the entrance slit of a 1-m monochromator (McPherson Model 225). The 0.2 cm slit width provided a bandpass of 16.6 Å. The lamp was operated in the pulsed mode (approximately  $380 \text{ s}^{-1}$ ) using a hydrogen thyratron switch. Light leaving the exit slit passed through a LiF window into the photolysis cell. After traversing the photolysis cell, the light hit a sodium salicylate-coated window. The resulting fluorescence was measured with a photomultiplier and displayed on a pen recorder. The fluorescence excited in the gas in the cell was measured with a cooled photomultiplier

looking through an appropriate filter. The photon counts were then recorded as a function of time by a multichannel analyzer. All the gases used were of 99.99% purity or greater, except N<sub>2</sub>O (Matheson: 98.0% min.), CO (Matheson UHP Grade: 99.8% min.), O<sub>2</sub> (Matheson UHP Grade: 99.95% min.), CH<sub>4</sub> (Matheson UHP Grade: 99.97% min.) and C<sub>2</sub>H<sub>4</sub> (Matheson Research Purity Grade: 99.98% min.). All the gases used were passed through either a dry ice/acetone cooled trap or a liquid N<sub>2</sub> cooled trap and were mixed before entering the photolysis cell. Pressures were read from a Wallace and Tiernan absolute pressure gauge (0 - 20 Torr). Small changes in pressure were measured with a calibrated diaphragm differential pressure transducer.

Previously [13], we had shown that over the region 1100 - 1500 Å, the largest quantum yield of N(<sup>2</sup>D) from N<sub>2</sub>O occurs between 1150 Å and 1200 Å. Most of the measurements were therefore made at 1175 Å. Some of the measurements with CO<sub>2</sub> were made at 1190 Å and 1200 Å so as to minimize the absorption of the photolysis light by CO<sub>2</sub>. All measurements with CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and NH<sub>3</sub> were made at 1470 Å because of the strong absorption by these gases at the shorter wavelengths.

A Wratten No. 18A filter was used to isolate the 3000 - 4000 Å region in which the strongest (0, v'') NO β bands occur. For these measurements, a cooled EMI 9635AM was used (dark count at -20 °C, ~20 counts/s).

The experiments were performed in a very similar way to those described previously [13]. Argon at approximately 3 Torr was always present in the photolysis cell so as to reduce the rate of loss of N(<sup>2</sup>D) by diffusion. To the argon was added a known pressure of N<sub>2</sub>O (pressures from 15 to 760 m Torr were used). The quenching gas would then be added and its pressure noted. The experiment was then started and run until the display of the MCA showed a well defined transient decay. The experiment was then stopped and the time of the experiment (*t* min) noted. The decay of the NO β band (v' = 0) emission was seen on top of a rising base line resulting from photomultiplier dark counts. This base line was subtracted in the MCA memory and the transient signal was then printed out. The experiment was repeated with different additions of the quenching gas. Semilog plots of the signal intensity against time were then made. Figure 1 shows plots obtained for N<sub>2</sub> = 0 and 17.2 Torr.

## Results and Discussion

In all cases, single exponential decays were observed covering at least one decade change in intensity. Figure 1 shows two effects of adding N<sub>2</sub> — the decay rate increases and the intercept decreases.

The increasing decay rate with quenching gas addition has previously been used [12, 14, 15] to determine rate coefficients for quenching N(<sup>2</sup>D). The decay rates shown in Fig. 1 give a rate coefficient of  $1.96 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the quenching of N(<sup>2</sup>D) by N<sub>2</sub>. All the N<sub>2</sub> measurements could be represented by a rate coefficient of  $(1.9 \pm 0.2) \times 10^{-14} \text{ cm}^3 \text{ mole-}$

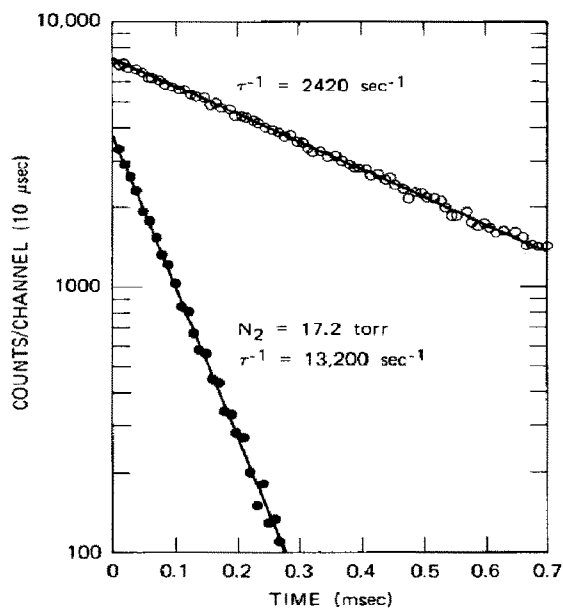


Fig. 1.  $N_2$  quenching of  $N(^2D)$  and  $NO(B^2\Pi_r)_{v'=0}$ . Ar = 3 Torr;  $N_2O$  = 28 mTorr. 20 min experiments at  $1175 \text{ \AA}$ .

cule $^{-1} \text{ s}^{-1}$ , which is in good agreement with the two most recently reported [15, 16] values of  $(1.5 \pm 0.1) \times 10^{-14}$  and  $(1.85 \pm 0.15) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We were also able to put a new upper limit of  $6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  on the rate coefficient for quenching  $N(^2D)$  by both He and Ar (substantially lower than our previous [12] upper limit). Our rate coefficients for quenching  $N(^2D)$  by the other gases were in reasonable agreement with values previously reported by Husain *et al.* [16] for those gases studied in both laboratories ( $N_2$ ,  $CO_2$ ,  $O_2$ ,  $CO$ ,  $NO$ ,  $N_2O$ , and  $H_2$ ) and in agreement with previous work [12] in our laboratory for  $CH_4$ ,  $C_2H_4$ , and  $NH_3$ . However, our values tended to be consistently  $\sim 25\%$  higher than those reported by Husain *et al.* [16]. Although this difference is almost within the error bars of the two measurements, it may be real and arise from two causes. Our values may be too high because of impurity effects. For example, we have shown [15] that a recently published [13] value of  $k_{N_2O}$  ( $2.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) was high, because the  $N_2O$  cylinder used in obtaining it contained some impurity not condensable at 195 K. However, the values obtained by Husain *et al.* may all be slightly too low, because they used the Beer-Lambert law:

$$I_{tr} = I_0 \exp(-\epsilon cl) \quad (5)$$

rather than the modified form [17]:

$$I_{tr} = I_0 \exp[-\epsilon(cl)^\gamma] \quad (6)$$

because of the severe experimental difficulties encountered in determining  $\gamma$

in their system. The use of  $\gamma = 0.8$  would raise their rate coefficients by 25%. Further work would be required to resolve these issues.

Our main purpose here is to determine rate coefficients for quenching  $\text{NO}(\text{B}^2\Pi_r)$  from the decrease in the intercept with quenching gas addition (Fig. 1). [Recently, we used similar measurements [18] to study the quenching of  $\text{Se}_2(\text{B}^3\Sigma_u^-)$ .] Absorption by the added gas was always negligible over the  $\sim 10$  cm from the LiF window to the center of the region viewed by the photomultiplier. Therefore, for plots like those shown in Fig. 1 (*i.e.* experiments performed at the same wavelength, for the same time, with the same argon and  $\text{N}_2\text{O}$  pressures, and with the same photolysis light intensity), we can write:

$$\frac{I_0}{I} = \frac{\tau k_Q [\text{Q}]}{1 + \tau k_{\text{Ar}} [\text{Ar}] + \tau k_{\text{N}_2\text{O}} [\text{N}_2\text{O}]} \quad (7)$$

where  $I_0$  is the intercept at time zero (the time the lamp is pulsed) with no quenching gas,  $I$  is the intercept with quenching gas addition [Q],  $\tau$  is the radiative lifetime of  $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$  ( $3.0 \times 10^{-6}$  s) [6], and  $k_Q$ ,  $k_{\text{Ar}}$ , and  $k_{\text{N}_2\text{O}}$  are the rate coefficients for quenching  $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$  by Q, Ar, and  $\text{N}_2\text{O}$ , respectively.

Figure 1 gives  $I_0/I = 1.91 \pm 0.09$  for  $\text{N}_2 = 17.2$  Torr. This point and values of  $I_0/I$  at several other nitrogen pressures are shown plotted as suggested by eqn. (7) in Fig. 2. The straight line predicted by eqn. (7) is indeed observed. The slope  $S$  of this Stern-Volmer plot can be written:

$$S = \frac{\tau k_{\text{N}_2}}{1 + \tau k_{\text{Ar}} [\text{Ar}] + \tau k_{\text{N}_2\text{O}} [\text{N}_2\text{O}]} \quad (8)$$

To determine  $k_{\text{N}_2}$ , we must know  $k_{\text{Ar}}$  and  $k_{\text{N}_2\text{O}}$ . (The quenching rates by the argon and  $\text{N}_2\text{O}$ , although small compared with the radiative rate, do contrib-

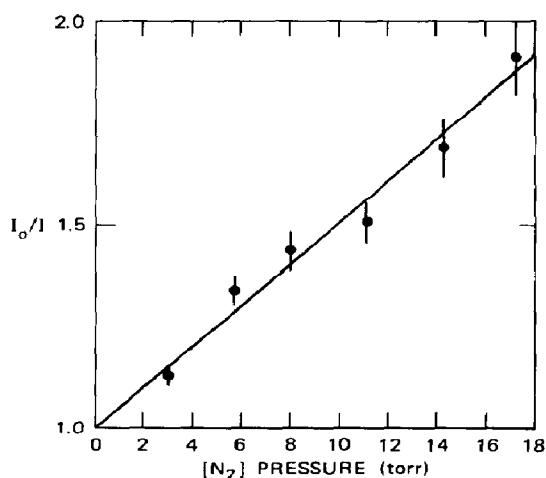


Fig. 2. Stern-Volmer plot for  $\text{N}_2$  quenching of  $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$ . Ar = 3 Torr;  $\text{N}_2\text{O} = 28$  mTorr.

ute to the loss of  $\text{NO}(B^2\Pi_r)$ . We will show that 3 Torr of argon and 28 mTorr of  $\text{N}_2\text{O}$  each add less than 10% to the radiative loss rate.) The rate coefficient  $k_{\text{Ar}}$  was determined with sufficient accuracy for substitution in eqn. (8) by making measurements similar to those described above in argon- $\text{N}_2\text{O}$  mixtures containing  $\text{N}_2\text{O} = 15$  mTorr and neglecting quenching by  $\text{N}_2\text{O}$  (we will show that this introduces a less than 5% error in  $k_{\text{Ar}}$  and hence a less than 0.5% error in the denominator of eqn. (8)). Below, we describe how  $k_{\text{N}_2\text{O}}$  was determined.

The quenching of the intercept by  $\text{CO}_2$  was studied at several  $\text{N}_2\text{O}$  pressures from 40 to 760 mTorr. For these experiments, eqn. (8) was rearranged:

$$S^{-1} = \frac{1}{\tau k_{\text{CO}_2}} + \frac{k_{\text{Ar}}[\text{Ar}]}{k_{\text{CO}_2}} + \frac{k_{\text{N}_2\text{O}}[\text{N}_2\text{O}]}{k_{\text{CO}_2}} \quad (9)$$

where  $S^{-1}$ , the reciprocal of the slope of the Stern-Volmer plots, is the half-quenching pressure. The data for the  $\text{CO}_2$  experiments are shown plotted as suggested by eqn. (9) in Fig. 3. The slope of this graph gives  $k_{\text{N}_2\text{O}}/k_{\text{CO}_2} = 4.5 \pm 0.5$ , and the intercept, after correcting for the small argon contribution, gives a "true" half-quenching pressure (the pressure at which the rate of quenching by  $\text{CO}_2$  equals the rate of radiation) for  $\text{CO}_2$  of  $1.47 \pm 0.2$  Torr. Hence,  $k_{\text{CO}_2} = (7.0 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (since  $\tau = 3.0 \times 10^{-6} \text{ s}$ ) and  $k_{\text{N}_2\text{O}} = (3.2 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Table 1 shows true half-quenching pressures and corresponding rate coefficients for several gases, together with the values of Campbell and Thrush [4] for  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{N}_2\text{O}$ . The Table shows the Melton and Klemperer value [19] for the quenching of  $\text{NO}(B^2\Pi_r)_{v'=0}$  by  $\text{NO}$ . Quenching by  $\text{NO}$  could not be studied in this experi-

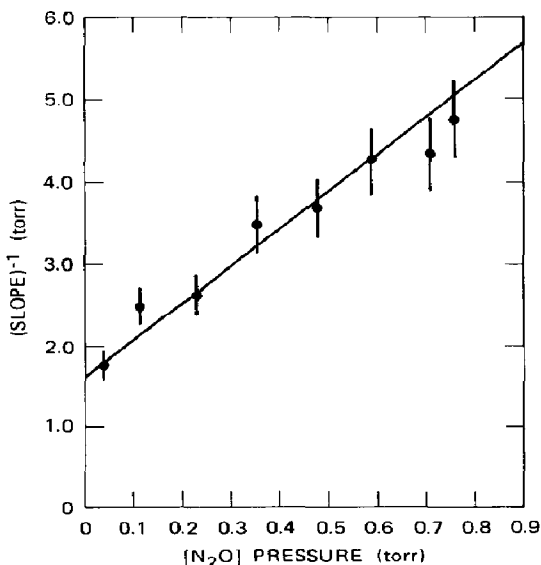


Fig. 3.  $\text{CO}_2$  quenching data. The reciprocal of the slope of Stern-Volmer graphs vs.  $[\text{N}_2\text{O}]$ . Ar = 3 Torr.

TABLE 1

Quenching of  $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$  at 298 K. Half-quenching pressures and rate coefficients.

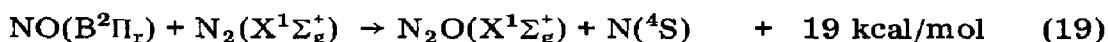
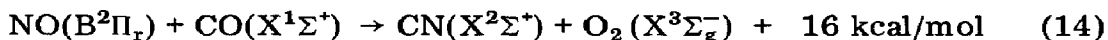
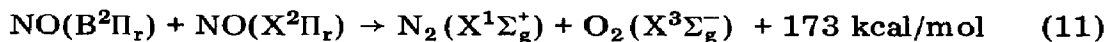
Gas	Half-quenching pressure (Torr)	Rate coefficient ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Other values [4, 19] ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
He	$36 \pm 6$	$(2.9 \pm 0.5) \times 10^{-13}$	
Ar	$36 \pm 5$	$(2.9 \pm 0.4) \times 10^{-13}$	
$\text{N}_2$	$17 \pm 3$	$(6.1 \pm 1.1) \times 10^{-13}$	
$\text{CO}_2$	$1.47 \pm 0.2$	$(7.0 \pm 1.0) \times 10^{-12}$	$1.0 \times 10^{-11}$
$\text{H}_2$	$1.0 \pm 0.25$	$(1.03 \pm 0.26) \times 10^{-11}$	$2.0 \times 10^{-11}$
$\text{CH}_4$	$0.41 \pm 0.09$	$(2.5 \pm 0.6) \times 10^{-11}$	
CO	$0.36 \pm 0.04$	$(2.9 \pm 0.3) \times 10^{-11}$	
$\text{N}_2\text{O}$		$(3.2 \pm 0.8) \times 10^{-11}$	$4.5 \times 10^{-11}$
NO			$(1.4 \pm 0.1) \times 10^{-10}$
$\text{O}_2$	$0.064 \pm 0.013$	$(1.6 \pm 0.3) \times 10^{-10}$	
$\text{NH}_3$	$0.038 \pm 0.009$	$(2.7 \pm 0.6) \times 10^{-10}$	
$\text{C}_2\text{H}_4$	$0.032 \pm 0.008$	$(3.2 \pm 0.8) \times 10^{-10}$	

ment, because of the strong  $\beta$  band signal generated by reaction (1) on NO addition (because  $\text{N}_2\text{O}$  photodissociation, in addition to giving  $\text{N}(^2\text{D})$ , also yields  $\text{N}_2(\text{A}^3\Sigma_u^+)$  throughout the 1100 - 1500 Å region [13]). All the rate coefficients have an additional 20% uncertainty introduced by the error bar on the radiative lifetime [6]. The probability of quenching  $\text{NO}(\text{B}^2\Pi_r)$  per collision ranges from  $\sim 10^{-3}$  for He and Ar to  $\sim 1$  for  $\text{NH}_3$  and  $\text{C}_2\text{H}_4$ . The agreement between the two values for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  is satisfactory, but the  $\text{H}_2$  values differ by a factor of 2. All the earlier values are higher. Since we used the same value for the radiative lifetime as Campbell and Thrush [4], the differences between the rate coefficients cannot arise from this source but may reflect a contribution from precursor quenching in the afterglow experiments. Evidence for this viewpoint is that precursor quenching has been invoked [20] to explain the earlier [3], very different results on  $\text{N}_2\text{O}$  and  $\text{CO}_2$  quenching of the NO  $\beta$  bands, which were also made in an afterglow experiment.

The slow quenching of  $\text{NO}(\text{B}^2\Pi_r)$  by argon compared with nitrogen is largely, if not completely, responsible for the slightly increased chemiluminescence intensity of the  $\beta$  bands when replacing nitrogen by argon [3, 20], despite the smaller rate coefficient for  $\text{O} + \text{N} + \text{M} \rightarrow \text{NO}(\text{B}^2\Pi_r) + \text{M}$  with  $\text{M} = \text{Ar}$  compared with  $\text{M} = \text{N}_2$ . The previous interpretation [20] of this observation was that  $\text{N}_2$  quenched a precursor of  $\text{NO}(\text{B}^2\Pi_r)$  in the afterglow.

The products of these quenching reactions were discussed by Campbell and Thrush [4] for quenching with  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{N}_2\text{O}$ . Since the  $v' = 0$  level of  $\text{NO}(\text{B}^2\Pi_r)$  possesses 130 kcal/mol, dissociative quenching is possible for these gases and also for  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{NH}_3$ , and  $\text{C}_2\text{H}_4$  studied in our current experiments.

Dissociative quenching is not energetically allowed for NO, CO, and N<sub>2</sub>. Chemical quenching is possible, however, by the following exothermic channels, even though processes (12), (15), and (19) are spin-forbidden:



Processes (11) and (12), or both, and process (13) have been shown by Macdonald [21] to occur for NO quenching NO(B<sup>2</sup>Π<sub>r</sub>)<sub>v'=5</sub>, although his conclusions have recently been questioned [19]. Because Macdonald used a high pressure of nitric oxide (in excess of 70 Torr), processes (11) and (12) were indistinguishable because any O<sub>2</sub> produced by process (11) would react with NO to yield NO<sub>2</sub>:



whereas, for process (12), the exchange reaction would occur:



followed by:



In either case, one molecule of N<sub>2</sub> and two molecules of NO<sub>2</sub> are the products.

The quenching by N<sub>2</sub> may also arise from collision-induced transitions to other excited electronic states of NO with approximately the same energy (we have recently shown [22] the similar process CO(d<sup>3</sup>Δ)<sub>v=7</sub> + M → CO(e<sup>3</sup>Σ<sup>-</sup>)<sub>v=4</sub> + M to occur in ~100 collisions with M = N<sub>2</sub> or Ar). This type of process is required to explain the quenching by He and Ar. The available states are the A<sup>2</sup>Σ<sup>+</sup>, a<sup>4</sup>Π<sub>i</sub>, and possibly the b<sup>4</sup>Σ<sup>-</sup> states. Production of the latter two states from NO(B<sup>2</sup>Π<sub>r</sub>) represents a reversal of the processes thought to produce NO(B<sup>2</sup>Π<sub>r</sub>) in the recombination of nitrogen and oxygen atoms [3].

It is interesting to compare the quenching of NO(B<sup>2</sup>Π<sub>r</sub>) with that of NO(A<sup>2</sup>Σ<sup>+</sup>), which has about the same energy (the v' = 0, 1, 2, and 3 levels have 126, 133, 139 and 146 kcal/mol, respectively). Table 2 shows the quenching rate coefficients. The rate coefficients for quenching NO(B<sup>2</sup>Π<sub>r</sub>)<sub>v'=0</sub> and NO(A<sup>2</sup>Σ<sup>+</sup>)<sub>v'=0 and 1</sub> by He, Ar, N<sub>2</sub>, CO, NO, O<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> are very similar,



TABLE 2

Quenching rate coefficients for  $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$  and  $\text{NO}(\text{A}^2\Sigma^+)$  at 298 K.

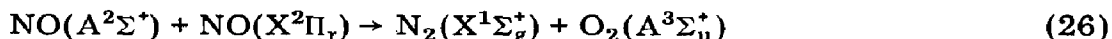
Gas	Rate coefficient for quenching $\text{NO}(\text{B}^2\Pi_r)_{v'=0}$ (this work)	Rate coefficient for quenching $\text{NO}(\text{A}^2\Sigma^+)$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reference
He	$(2.9 \pm 0.5) \times 10^{-13}$	$8 \times 10^{-14}$ at 400 K ( $v' = 0$ and 1)	23
Ar	$(2.9 \pm 0.4) \times 10^{-13}$	$< 8.3 \times 10^{-14}$ ( $v' = 0$ )	24
		$\sim 2.6 \times 10^{-13}$ ( $v' = 1$ )	24
		$\sim 2.6 \times 10^{-13}$ ( $v' = 2$ )	24
		$\sim 4.5 \times 10^{-13}$ ( $v' = 3$ )	24
$\text{N}_2$	$(6.1 \pm 1.1) \times 10^{-13}$	$\sim 8.3 \times 10^{-14}$ ( $v' = 0$ )	24
		$4.3 \times 10^{-13}$ ( $v' = 1$ )	24
		$8.0 \times 10^{-13}$ ( $v' = 2$ )	24
		$2.3 \times 10^{-12}$ ( $v' = 3$ )	24
$\text{CO}_2$	$(7.0 \pm 1.0) \times 10^{-12}$	$(4.0 \pm 0.4) \times 10^{-10}$ ( $v' = 0$ )	24
		$(4.3 \pm 0.4) \times 10^{-10}$ ( $v' = 1$ )	24
		$(3.8 \pm 0.6) \times 10^{-10}$ ( $v' = 2$ )	24
		$(3.7 \pm 0.9) \times 10^{-10}$ ( $v' = 3$ )	24
$\text{H}_2$	$(1.03 \pm 0.26) \times 10^{-11}$	$1.7 \times 10^{-13}$ at 400 K ( $v' = 0$ and 1)	23
		$4.8 \times 10^{-11}$ ( $v' = 0$ and 1)	25
$\text{CH}_4$	$(2.5 \pm 0.6) \times 10^{-11}$	$< 1.7 \times 10^{-12}$ ( $v' = 0$ and 1)	26
		$1.3 \times 10^{-10}$ ( $v' = 0$ and 1)	25
CO	$(2.9 \pm 0.3) \times 10^{-11}$	$2.2 \times 10^{-11}$ ( $v' = 0$ )	24
		$6.9 \times 10^{-11}$ ( $v' = 3$ )	24
$\text{N}_2\text{O}$	$(3.2 \pm 0.8) \times 10^{-11}$	$5.5 \times 10^{-10}$ ( $v' = 0$ )	27
NO	$(1.4 \pm 0.1) \times 10^{-10}$ (Ref. 19)	$(2.3 \pm 0.2) \times 10^{-10}$ ( $v' = 0$ )	19 & 28
		$(1.6 \pm 0.2) \times 10^{-10}$ ( $v' = 1, k' = 13$ )	19 & 28
		$(2.6 \pm 0.3) \times 10^{-10}$ ( $v' = 1, k' = 29$ )	19 & 28
		$(2.2 \pm 0.3) \times 10^{-10}$ ( $v' = 2$ )	19 & 28
		$(2.3 \pm 0.3) \times 10^{-10}$ ( $v' = 3$ )	19 & 28
$\text{O}_2$	$(1.6 \pm 0.3) \times 10^{-10}$	$(1.6 \pm 0.2) \times 10^{-10}$ ( $v' = 0$ )	29
		$(1.7 \pm 0.2) \times 10^{-10}$ ( $v' = 1$ )	29
		$(1.6 \pm 0.2) \times 10^{-10}$ ( $v' = 3$ )	29
$\text{C}_2\text{H}_4$	$(3.2 \pm 0.8) \times 10^{-10}$	$1.7 \times 10^{-10}$ ( $v' = 0$ and 1)	26

the situation with  $\text{H}_2$  and  $\text{CH}_4$  is unclear, and no rate coefficient could be found for the quenching of the  $\text{NO} \gamma$  bands by  $\text{NH}_3$ . However, the rate coefficients for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  are much larger for quenching  $\text{NO}(\text{A}^2\Sigma^+)$  than  $\text{NO}(\text{B}^2\Pi_r)$ .

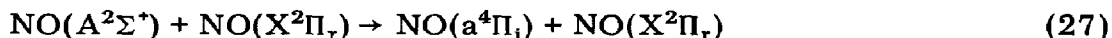
In the self-quenching of  $\text{NO}(\text{A}^2\Sigma^+)$ , Heicklen [25] has found that all the following processes occur:



Reactions (23), (24), and (25) occur in 71%, 19% and 9.6% of the quenching collisions, respectively. Heicklen also investigated the quenching of  $\text{NO}(\text{A}^2\Sigma^+)$  by hydrogen, methane, and ethane but could not distinguish between collisional dissociation and chemical reaction. Callear [30] has shown that  $\text{NO}(\text{A}^2\Sigma^+)$  does not react with  $\text{H}_2$ , but an intermediate formed in the quenching of  $\text{NO}(\text{A}^2\Sigma^+)$  by  $\text{NO}$  does collisionally dissociate  $\text{H}_2$ . This intermediate could be  $\text{O}_2(\text{A}^3\Sigma_u^+)$ , formed by:



or  $\text{NO}(\text{a}^4\Pi_1)$ , formed by:



Quenching of this intermediate could account for the great difference between the results of Heicklen [25] for  $\text{H}_2$  and  $\text{CH}_4$  shown in Table 2 and the results deduced from fluorescence quenching [23, 26].

The quenching of  $\text{NO}(\text{A}^2\Sigma^+)$  by  $\text{CO}_2$  has been shown [31] to involve a chemical reaction:



In this case, the rate coefficient for  $\text{CO}_2$  deduced from this study agreed with those determined from fluorescence studies [23, 24, 26, 27]. Hence, the  $\text{CO}_2$  is interacting with the  $\text{NO}(\text{A}^2\Sigma^+)$  as shown and not with an intermediate.

McGee and Heicklen [32] also examined the products of  $\text{NO}(\text{A}^2\Sigma^+) + \text{C}_2\text{H}_4$ . They found  $\text{H}_2$  and  $\text{C}_2\text{H}_2$  produced by dissociative quenching (analogous to mercury sensitization).



All the above processes involved with quenching  $\text{NO}(\text{A}^2\Sigma^+)$  may also play a role in the quenching of  $\text{NO}(\text{B}^2\Pi_r)$ . Much more work is clearly needed to establish the products of these quenching reactions. It would also be instructive to determine the effect of vibrational energy on the reactivity of  $\text{NO}(\text{B}^2\Pi_r)$  in much the same way as has been done for  $\text{NO}(\text{A}^2\Sigma^+)_{v'=0,1,2,3}$ . Reactions (1) and (2) and the photodissociation of  $\text{NO}_2$  [5] all provide sources of  $\text{NO}(\text{B}^2\Pi_r)$  in a number of vibrational levels.

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