State-to-state excitation of NO ($A\ ^2\Sigma^+$, $v' = 0,1,2$) by N_2($A\ ^3\Sigma_u^+$, $v' = 0,1,2$)

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We have determined that the rate coefficient for quenching N_2($A\ ^3\Sigma_u^+$, $v' = 0$) by NO is $(6.6 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Higher levels of $N_2(A)$ appear to be quenched with a similar rate coefficient. Separate studies show that the rate coefficient for the excitation of NO($A\ ^2\Sigma^+$, $v' = 0 - 2$) by N_2($A\ ^3\Sigma_u^+$, $v' = 0$) is $(10 \pm 3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The apparent discrepancy between the quenching and excitation rate coefficient measurements most likely results from an error in the accepted value of the lifetime $N_2(A)$. Our studies indicate that this lifetime is probably about 30% longer than currently believed. We also report rate coefficients for excitation of each of the vibrational levels 0–2 of NO(A) by each of the vibrational levels 0–2 of $N_2(A)$ relative to the rate coefficient for excitation of NO(A, $v' = 0$) by N_2(A, $v' = 0$).

I. INTRODUCTION

The excitation of the NO γ bands in the energy-transfer reaction between $N_2(A)$ and NO is now well established.[1-4] What is not well established is the fraction of total $N_2(A)$ quenching which results in NO(A) excitation. The published values of the rate coefficient for excitation of NO(A) by $N_2(A)$[1,2] are both a factor of 2 greater than most of the measurements of the rate coefficient for the destruction of $N_2(A)$ by NO.[2,3,5,6] The magnitude of this discrepancy demands further investigation. In addition, the state-to-state partitioning between vibrational levels of the $N_2(A)$ pumping reagent and the NO(A) is uncertain. Callear and Wood[3] claim a strong difference in the ratio of NO(A) $v' = 0$ to $v' = 1$ excited by N_2(A, $v' = 0$) (9.8:1) compared to that excited by N_2(A, $v' = 1$) (1.9:1). Some preliminary results from a Physical Sciences Inc. (PSI) study a number of years ago aimed at using NO γ bands as a monitor of system purity[4] indicate a much smaller difference (7:1 and 4:1, respectively). It is also not clear if there is a strong difference in the quenching rate coefficients for the different $N_2(A)$ vibrational levels. Dreyer *et al.*[6] found NO quenched $N_2(v' = 1)$ almost 70% faster than N_2(A, $v' = 0$) while Clark and Setser[1] and Young and St. John[2] say both $N_2(A)$ levels are quenched by NO with equal efficiency. Consequently, we undertook a careful investigation which we report here.

II. EXPERIMENTAL

The apparatus is a 2 in. flow tube pumped by a Leybold–Heraeus Roots blower/forepump combination capable of producing linear velocities up to 5×10^3 cm s^{-1} at pressures of 1 Torr. The flow tube design is modular (see Fig. 1), with separate source, reaction, and detection sections which clamp together with O-ring joints. We have previously described this apparatus in various configurations.[7-10] The detection region is a rectangular stainless steel block bored out internally to a 2 in. circular cross section and coated with Teflon (Dupont Poly TFE #852-201) to retard surface recombination of atoms.[11-14] Use of a black primer prior to the Teflon coating reduces scattered light inside the block dra-

matically. The block has two sets of viewing positions consisting of four circular ports each on the four faces of the block. These circular ports accommodate vacuum–ultraviolet resonance lamps, VUV and visible monochromator interfaces, laser delivery side-arms, and a spatially filtered photomultiplier/interference filter combination.

In these experiments a suprasil lens collected light from the center of the flow tube and focused it on the entrance slit of a 0.5 m Minuteman monochromator which is outfitted 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. A laboratory computer system digitized the analog output from the rate meter and stored the information on floppy disks for further processing. The computer system comprises an IBM PC with 512K of RAM, two 360K diskette drives, a monochrome monitor, and a 160 cps dot-matrix printer with graphics capability. The data are acquired via a Data Translation I/O system (DT2801A), which features 16 channels of A/D inputs, two channels of D/A output, two 8-bit digital I/O ports, software programmable gain, single-ended or differential input, and data acquisition rates as fast as 14 kHz. The acquisition is interfaced to the computer by a Laboratory Technologies Inc. software package, REAL-TIME LABORATORY NOTEBOOK, which organizes data in a form compatible for analysis using the LOTUS 123 business spreadsheet software or for sending to the PRIME 400 computer in PSI's computer center for analysis there. Much of the analysis revolves around least-squares fitting of spectra. Our procedure[9] is to generate basis functions consisting of a synthetic electronic spectrum for a unit population in each vibrational level of each electronic state appearing in the spectral region of interest. A linear least-squares routine then finds the populations of each vibronic band which, when multiplied by the appropriate basis function and summed with overlapping bands, gives a composite spectrum most nearly matching the experimental spectrum.

Standard quartz–halogen and D_2 lamps were used to calibrate the spectral system for relative response as a function of wavelength. Excellent agreement between observed and calculated intensities of a number of bands of the
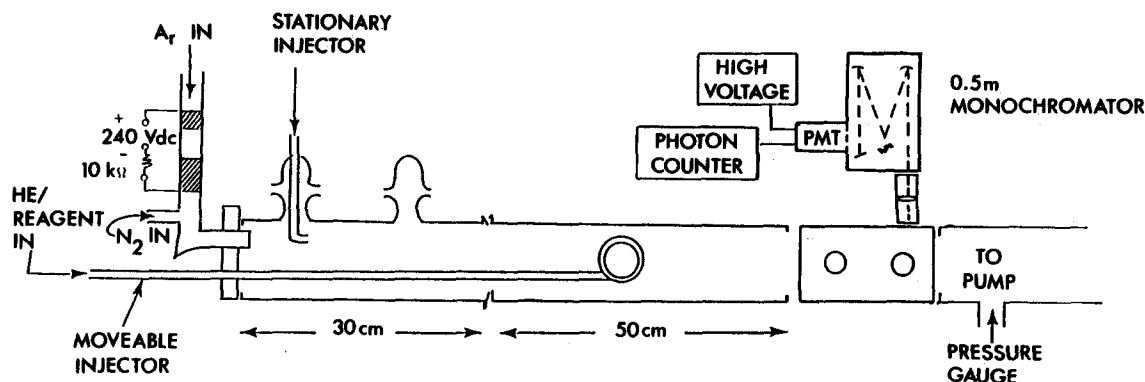
FIG. 1. Flow tube apparatus configured for $N_2(A)$ decay kinetics measurements.

$N_2(A\ {}^3\Sigma_u^+ - X\ {}^1\Sigma_g^+)$ system between 220 and 400 nm confirmed the reliability of the UV calibration.

The reaction between metastable $Ar({}^3P_{0,2})$ and molecular nitrogen produces the metastable nitrogen molecules, $N_2(A\ {}^3\Sigma_u^+)$.[15,16] This transfer excites $N_2(C\ {}^3\Pi_u)$[17] which quickly cascades radiatively to the metastable $A\ {}^3\Sigma_u^+$ state via the $B({}^3\Pi_g)$ state. A hollow-cathode discharge source operating at 240 Vdc and 3 mA produces the argon metastables. The argon and nitrogen are purified by flowing them through traps filled with 5 A molecular sieve.

Observations of strong Vegard–Kaplan, $N_2(A\ {}^3\Sigma_u^+ - X\ {}^1\Sigma_g^+)$, emission downstream of the Ar/N_2 mixing zone confirms the production of the nitrogen metastables (Fig. 2). Codischarging the nitrogen with the argon increases the $N_2(A)$ yield by a factor of about 6[18] but we have found that this procedure also produces some atomic nitrogen, vibrationally excited N_2, and metastable $N_2(a'\ {}^1\Sigma_u^-)$.[19] Unequivocal measurements on $N_2(A\ {}^3\Sigma_u^+)$

reactions, therefore, demand that the nitrogen be added downstream from the discharge. In the absence of vibrational relaxation partners the initial $N_2(A)$ vibrational distribution is a function of nitrogen mole fraction, total pressure, and transit time between the discharge and the observation region. Under conditions of short transit time, low pressure, and low nitrogen mole fraction, we have observed emission from levels as high as $v' = 4$. More typically, because of vibrational relaxation by N_2 and Ar during the ≈ 25 ms transit time between the discharge and the observation region, we observe only levels 0–2 with a distribution of 1:0.7:0.2, respectively.

Nitric oxide enters the flow tube through a 1 in. diam loop injector seated on the end of a 1/4 in. diam tube which slides along the bottom of the flow tube and parallel to its axis. This allows a variety of reaction distances for accurate kinetic studies. Adding CH_4, CF_3H, or CF_4 to the gas stream through a fixed, hook-shaped injector just downstream from
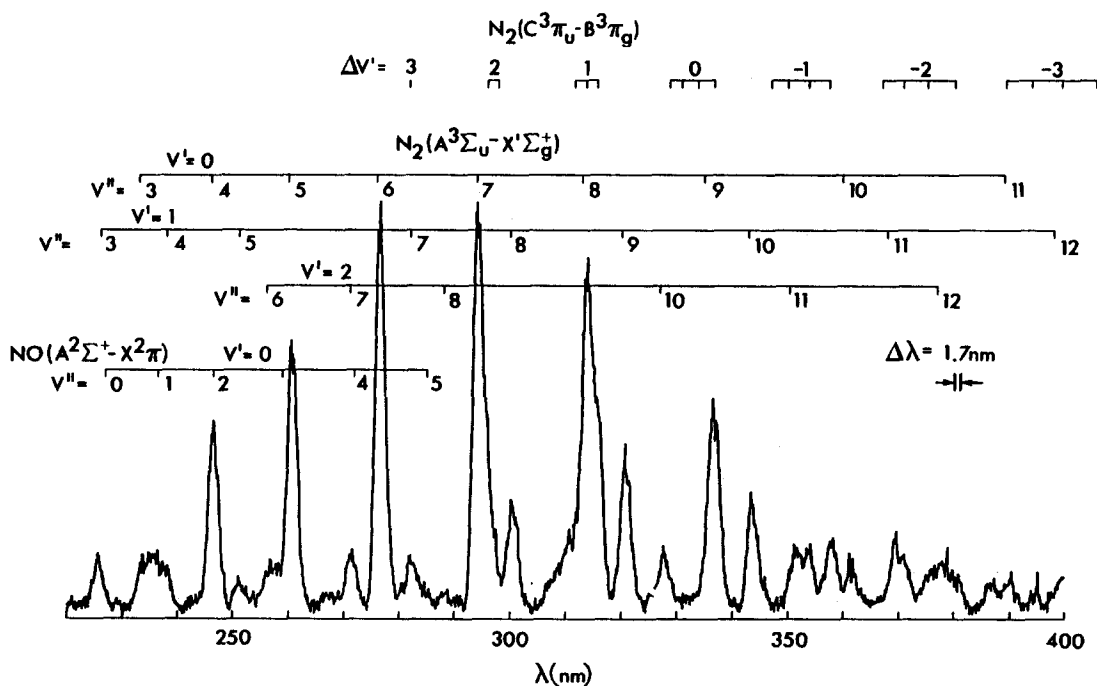

FIG. 2. Vegard–Kaplan emission in flow reactor 9 ms downstream from the discharge.
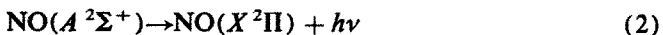
where the $N_2(A)$ entered the flow reactor, relaxes $N_2(A)$ vibrational excitation without significant electronic quenching.[9,20]

Mass-flow meters or rotameters monitor gas flow rates. All flow meters are calibrated by measuring rates of increase of pressure with time into 6.5 or 12 ℓ flasks, using appropriate differential pressure transducers (Validyne DP-15) which themselves have been calibrated with silicon oil or mercury manometers. Typical flow rates for argon, nitrogen, and helium through the injector are 2000–5000, 100–500, and 50 μmol s^{-1}, while the NO flow rate ranges between 0 and 1 or 0 and 0.01 μmol s^{-1} for decay or excitation rate measurements, respectively. Total pressures, as measured by a Baratron capacitance manometer, range from 0.3 to 10 Torr, and flow velocities vary from 500 to 5000 cm s^{-1}.

Nitric oxide is purified by slowly flowing it at atmospheric pressure through an Ascarite trap and then through a cold finger surrounded by a methanol/ℓN$_2$ slush bath ($-100\,°$C). The NO is then diluted in argon and the mixtures stored in 5 ℓ Pyrex flasks. Mixtures of 5% to 8% NO sufficed for decay rate measurements while the excitation rate determinations required NO mole fractions $\lesssim 10^{-3}$.

III. RESULTS

Complete characterization of the energy-transfer reaction between $N_2(A)$ and NO.

$$N_2(A\,^3\Sigma_u^+) + NO(X\,^2\Pi) \rightarrow NO(A\,^2\Sigma) + N_2(X) \quad (1a)$$

$$\rightarrow \text{other channels}, \quad (1b)$$

$$NO(A\,^2\Sigma^+) \rightarrow NO(X\,^2\Pi) + h\nu \quad (2)$$

involves measuring both the rate coefficient for removal of $N_2(A)$ by NO and the rate coefficient for the excitation of the NO γ bands in the energy-transfer reaction. The rapid vibrational relaxation of $N_2(A)$ by molecules such as CF_4, CF_3H, and CH_4, with no accompanying electronic quenching[9,20] allows us to alter the vibrational distribution of the $N_2(A)$. This makes state-to-state measurements possible.

A. The quenching of N₂($A\,^3\Sigma_u^+$, $v' = 0$) by NO

Measurements of the rate of removal of $N_2(A)$ by NO are not so straightforward as corresponding measurements of $N_2(A)$ quenching by other molecules. Ordinarily, one follows $N_2(A)$ number density decays by monitoring the Vegard–Kaplan emission.[7,9,21] The extremely bright NO γ band emission in the same region of the spectrum, however, masks the Vegard–Kaplan bands. Fortunately γ band emission is a sensitive tracer of the $N_2(A)$ number density.

The differential equation describing the rate of change in the $NO(A\,^2\Sigma^+)$ number density with time is

$$\frac{d[NO(A)]}{dt} = k_{1_a}[N_2(A)][NO(X)] - k_2[NO(A)]. \quad (3)$$

The $NO(A)$ is in steady state in the observation volume because the lifetime of $NO(A)$ is short compared to the time a molecule resides within the field of view of the detector. Thus the intensity of the γ band emission is

$$I_{NO*} = k_2[NO*] = k_{1_a}[N_2(A)][NO]. \quad (4)$$

Upon rearranging this equation, we relate the number density of $N_2(A)$ in the observation volume to the ratio of the γ band emission intensity and the NO number density:

$$[N_2(A)] = \frac{I_{NO*}}{k_{1_a}[NO]}. \quad (5)$$

The differential equation describing the decay of $N_2(A)$ in the reactor is

$$\frac{d[N_2(A)]}{dt} = -(k_1[NO] + k_{wall})[N_2(A)], \quad (6)$$

where k_{wall} is the first-order (pressure dependent) rate coefficient for $N_2(A)$ quenching in wall collisions. Because the NO number density is typically several orders of magnitude greater than the $N_2(A)$ number density, we can assume that the NO number density is a constant (the pseudo-first-order approximation). This approximation leads to an analytical solution to Eq. (6), viz.,

$$\ln\frac{[N_2(A)]}{[N_2(A)]^0} = -(k_1[NO] + k_{wall})z/\bar{v}. \quad (7)$$

We have replaced the reaction time by the ratio of the distance z, from flow tube injector to the observation point, to the bulk velocity in the reactor $\bar{v}$. Inserting Eq. (5) into Eq. (7) gives

$$\ln\left\{\frac{I_{NO*}/[NO]}{I_{NO*}^0[NO]^0}\right\} = -k_1[NO] + k_{wall}z/\bar{v}. \quad (8)$$

The above equation shows that measurements of the logarithm of the ratio of γ band intensity to NO number density as a function of NO number density but with fixed reaction time will give a linear relationship with a slope of $-k_1z/\bar{v}$. Such measurements at several different reaction distances, under otherwise constant conditions of pressure, temperature, total flow rate, etc., will correct for noninstantaneous mixing at the injector. The results must further be corrected by a factor of $(0.62)^{-1}$ to correct for the coupling of a radial density gradient in $N_2(A)$ number density with a parabolic velocity profile.[22–29]

We have shown previously[7] that rate coefficients measured using a tracer can be seriously in error if the tracer is sensitive to several different $N_2(A)$ vibrational levels each of which quenches at significantly different rates. For this reason we have relaxed the $N_2(A)$ vibrational distribution to only $v' = 0$. CF_3H, CF_4, and CH_4 all were used to relax $N_2(A)$ to $v' = 0$. As expected, the results were invariant with relaxation partner.

Figure 3 shows a plot of the ratio of the natural log of the γ band intensity to the NO number density as a function of the NO number density for several different distances between the injector and observation volume. The linearity of these plots is quite good, extending over more than two orders of magnitude. Figure 4 shows a plot of the slopes of the lines in Fig. 3 and two other sets of data plotted as a function of the reaction time. The slope of this plot, when divided by the radial-profile correction factor, 0.62, gives the rate coefficient for quenching $N_2(A)$ by NO. Note the non-
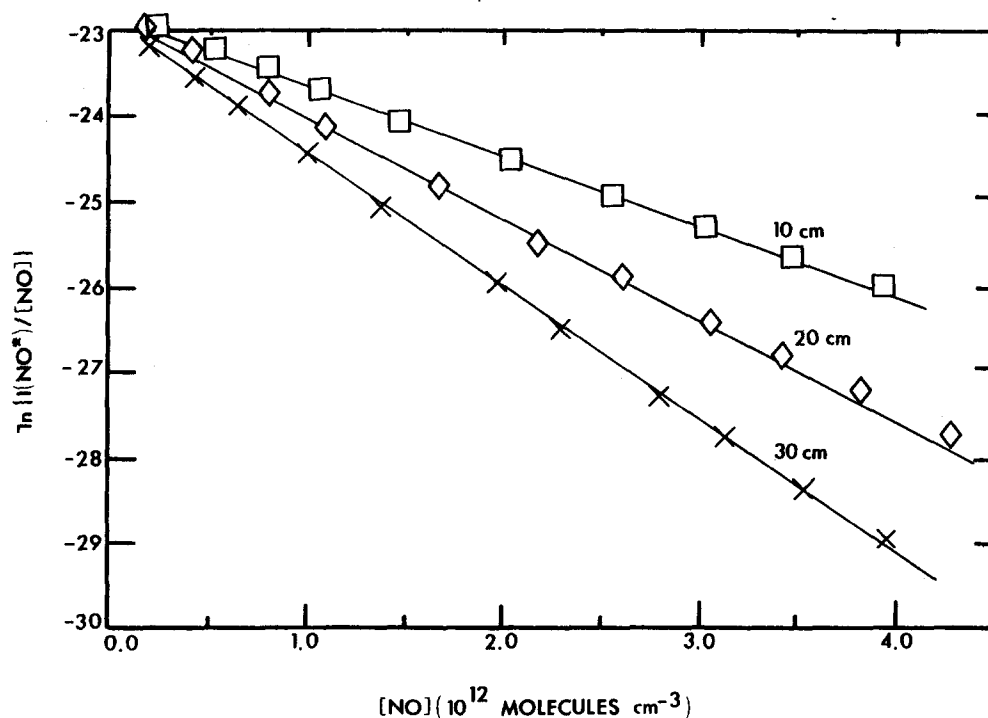
FIG. 3. Decay in the natural log of the $N_2(A, v' = 0)$ number density as a function of NO number density at three different reagent mixing distances.

zero intercept, indicative of the finite time required for complete reagent mixing.

A number of experiments spanning a range in total gas pressures from 0.7 to 3.7 Torr and reaction times from 11 to 124 ms, and using several different NO/Ar gas mixtures all gave consistent results for the rate coefficient for $N_2(A, v' = 0)$ quenching by NO of $(6.6 \pm 0.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The quoted error estimate is one standard deviation in the averaging process. The total experimental uncertainty, including estimates in the uncertainties in the calibrations of the flow meters, pressure gauges, etc., is about 15%. A few decay measurements in which the $N_2(A)$ was

not vibrationally relaxed gave decays only slightly larger ($\lesssim 5\%$) than those measured for the relaxed $N_2(A)$. Thus we infer that NO quenches vibrationally excited $N_2(A)$ at a rate similar to that for quenching $v' = 0$.

Our result disagrees markedly with Dreyer and Perner's reported value of 2.8×10^{-11} cm³ molecule⁻¹ s⁻¹ for $v' = 0$.[6] We agree excellently with the recent result of Shibuya et al.,[30] $(6.9 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and also quite well with early measurements by Callear and Wood,[3] 8.0×10^{-11}, Young and St. John,[2] 7.0×10^{-11}, Hill et al.,[5] 7.5×10^{-11}, and Piper[31] at 196 K $(9 \pm 2) \times 10^{-11}$. Mandel and Ewing's[32] rate coefficient, 4.3×10^{-11}, appears
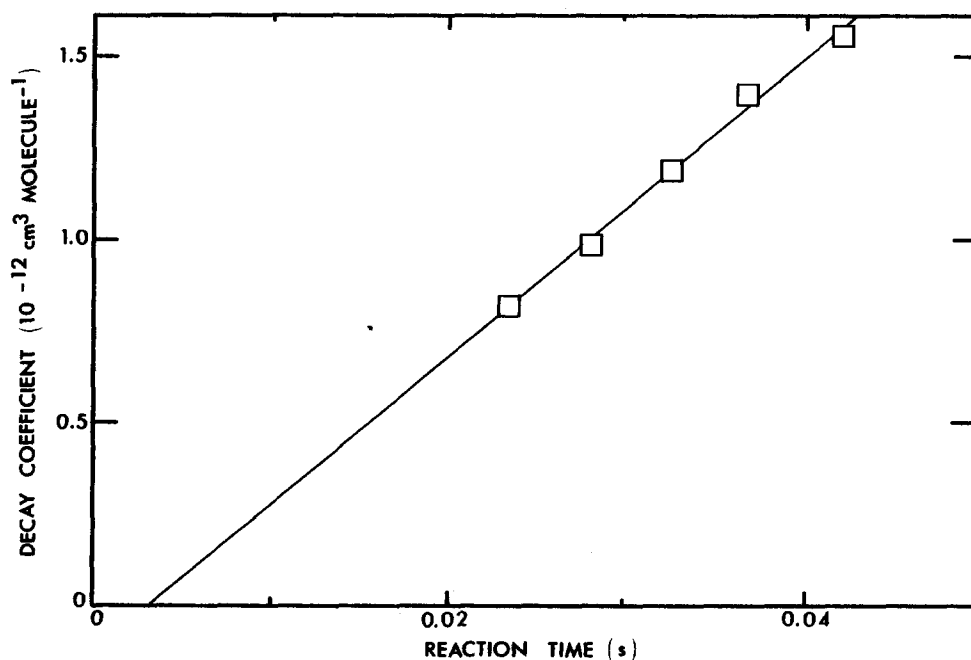

FIG. 4. $N_2(A, v' = 0)$ decay constants in NO as a function of reaction time.

to be discordant with the rest of the literature. All the above rate coefficients are in units of cm^3 molecule^{-1} s^{-1}. All measurements excepting Dreyer and Perner's used tracer techniques, and were not state specific. As we have pointed out, however, our measurements indicate that the quenching of N$_2$(A) by NO does not appear to show a strong dependence on the N$_2$(A) vibrational level. Callear and Wood[3] also reached this conclusion when they attempted to relax N$_2$(A) vibration with large additions of helium to their flash photolysis system.

B. The excitation of NO(A $^2\Sigma^+$, v' = 0) by N$_2$(A $^3\Sigma_u^+$, v' = 0)

We have determined the rate coefficient for excitation of NO(A $^2\Sigma^+$, v' = 0) by measuring the increase in the intensity of several bands originating from NO(A, v' = 0) as a function of added NO number density but for constant N$_2$(A) number density. If we note that the N$_2$(A) number density is the intensity of the Vegard–Kaplan bands divided by the Einstein coefficient[33] for spontaneous radiation, we can rearrange Eq. (5) to give the working equation for our analysis

$$I_{\text{NO}^*} = k_{1_a} \frac{I_{\text{VK}}}{A_{\text{VK}}}[\text{NO}] . \tag{9}$$

One convenient feature of this analysis is that the absolute calibrations for photon-emission rate measurements of the two intensities cancel and only the relative spectral response is important. Thus the intensity measurements do not introduce significant potential sources of systematic error. In practice, we determined total Vegard–Kaplan intensity from a spectral fit to the whole band system. We then measured the change in the peak intensity of one of the bands of NO(A) as a function of added NO number density, being careful to keep added NO number densities below the range giving significant N$_2$(A) quenching. Multiplying the peak

intensity by a correction factor gave the total integrated intensity under that specific band. Dividing the integrated intensity by the appropriate branching ratio which we reported elsewhere[34] determined the total emission from NO(A). We observed the 0,1, 0,4, and 0,5 γ bands. Under our experimental resolution, the 1,5 and 1,6 bands overlap the 0,4 and 0,5 γ bands and thus contribute to the observed emission intensity. We subtracted out this small contribution from our data. All three of the observed γ bands gave excitation rate coefficients which were identical within experimental error.

Figure 5 shows that the intensity of the 0,1 band increases linearly with added NO number density in accord with Eq. (9). A number of such experiments yielded a rate coefficient for exciting NO(A, v' = 0) by N$_2$(A, v' = 0) of (9.0 ± 2.7) × 10^{-11} cm^3 molecule^{-1} s^{-1}, where the error bars represent the total estimated statistical and systematic error. The major contribution to the uncertainty is in the 20% uncertainty quoted for the N$_2$(A) Einstein coefficient.[33] Variations of greater than a factor of 5 in pressure, and of more than an order of magnitude in N$_2$(A) number density gave consistent results. We also varied the distance between the NO injector and the observation region to ensure that the NO was fully mixed. In addition, using Xe* + N$_2$ as the N$_2$(A) source, and using several different NO/Ar gas mixtures did not change the results.

Relatively high resolution scans over the 0,6 and 1,7 bands as a function of pressure between 0.4 and 10 Torr showed that the ratio of NO(A, v' = 1) to NO(A, v' = 0) excitation by N$_2$(A, v' = 0) was 0.094 ± 0.006, Fig. 6, and that this ratio was independent of pressure. Spectral scans between 200 and 400 nm indicated that excitation of NO(A, v' = 2) and NO(B, v' = 0) were both ≲ 0.003 as compared to NO(A, v' = 0). Thus the total rate coefficient for NO excitation by N$_2$(A, v' = 0) is (10 ± 3) × 10^{-11} cm^3 molecule^{-1} s^{-1}.
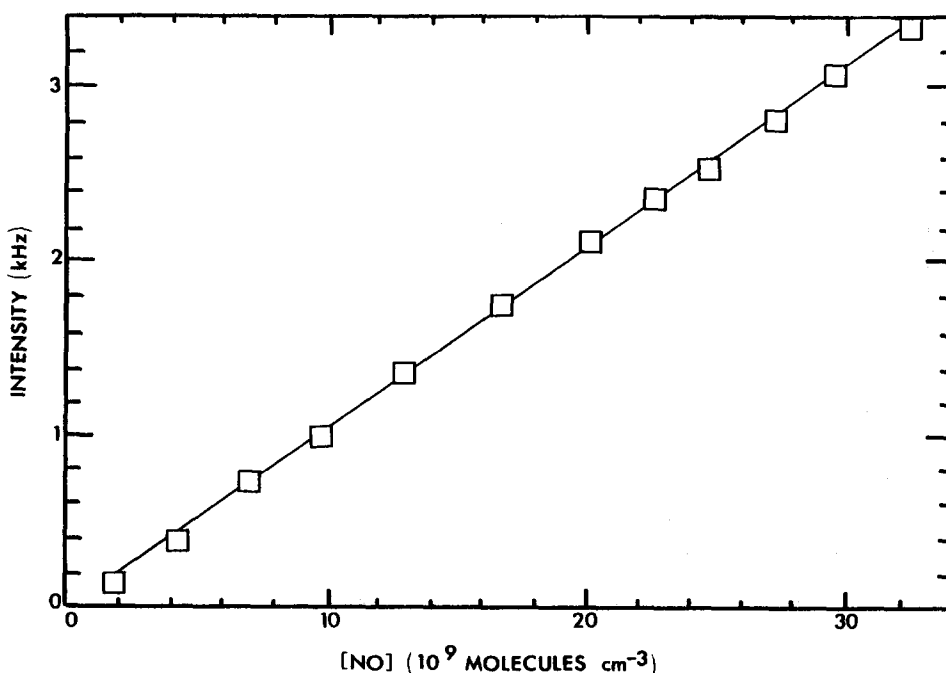

FIG. 5. Variation in the peak intensity of the NO(A–X, 0,1) band as a function of added NO number density.

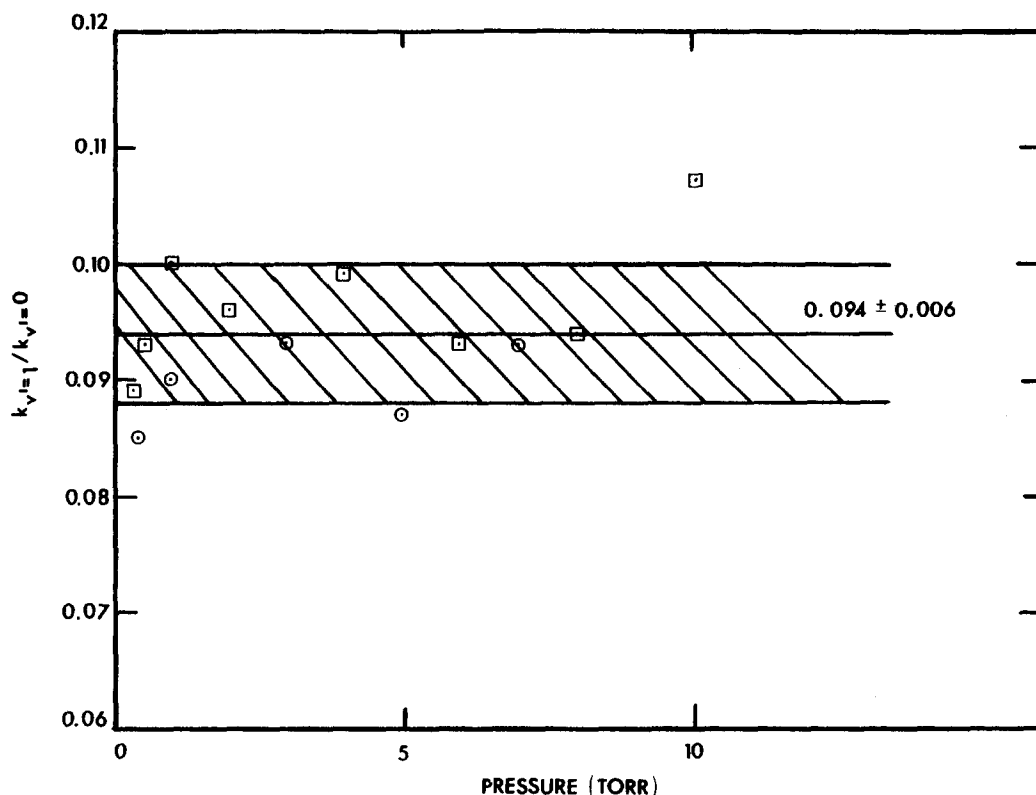FIG. 6. Ratio in the rate coefficients for exciting NO($A, v' = 1$) to NO(A, $v' = 0$) by N₂(A, $v' = 0$) as a function of argon pressure.

C. State-to-state excitation of NO(A, $v' = 0,1,2$) by N₂(A, $v' = 0,1,2$)

We scanned a number of spectra of the NO γ bands and N₂ Vegard–Kaplan bands with fixed NO number density but with varying CF₄ number density, and thus varying N₂(A) vibrational distribution (Figs. 7 and 8). The total N₂(A) number density changed little over the series of experiments, but the vibrational distribution changed from one in which more than half of the N₂(A) was vibrationally excited to one in which well over 80% of the N₂(A) was in

$v' = 0$. These measurements therefore tracked how the NO(A) vibrational distribution changed with changes in N₂(A) vibrational distribution. We can express the observed intensity of a given NO(A) vibrational level by Eq. (10),

$$I_{NO_v^*} = \{k_{0v}[N_2A]_0 + k_{1v}[N_2A]_1 + k_{2v}[N_2A]_2\}[NO] ,$$
(10)

where the subscripts on the k's represent the vibrational level of the N₂(A) and NO(A), respectively. CF₄ vibrationally relaxes N₂(A) in $\Delta v = 1$ transitions, and relaxes $v' \geqslant 2$ much
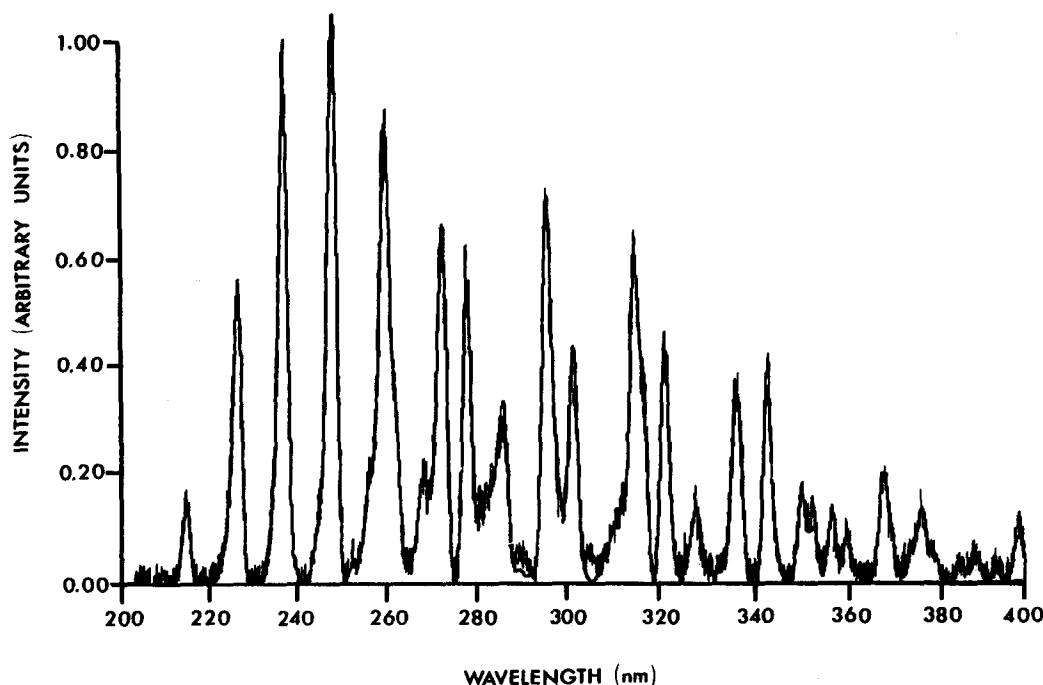

FIG. 7. Spectrum NO(A–X) in the absence of CF₄. The light line shows the experimental data, while the heavy line shows the synthetic best fit to the data.
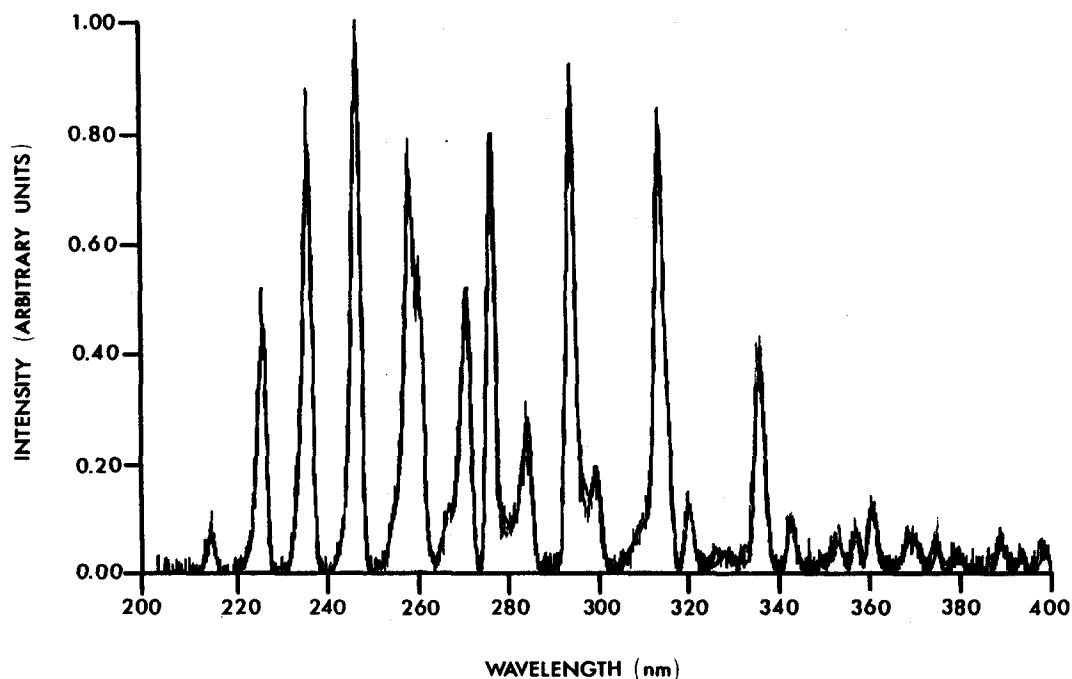
FIG. 8. Spectrum of $NO(A-X)$ and $N_2(A-X)$ in presence of CF_4 which relaxes most of the $N_2(A)$ vibrational energy. The light line is the experimental data while the heavy line shows the synthetic best fit.

more efficiently than it does $v' = 1$.[20] Thus for small CF_4 additions, the $v' = 1$ number density stays relatively constant, and primarily $v' \geqslant 2$ is quenched. For example, while the fraction of total $N_2(A)$ in $v' \geqslant 2$ drops from 0.20 to < 0.05, the fraction in $v' = 1$ changes from 0.34 to 0.31. For moderate to high amounts of vibrational relaxation, therefore, only $N_2(A)$ $v' = 0$ and 1 remain in the reactor and further relaxation beyond that point changes only the ratio of $v' = 1/v' = 0$; thus Eq. (10) can be simplifed and rearranged to give

$$\frac{I_{NO_v^*}}{[N_2A]_0} = \left\{ k_{0v} + k_{1v} \frac{[N_2A]_1}{[N_2A]_0} \right\} [NO] . \qquad (11)$$

The ratio of the slope to intercept of the linear plot implied by Eq. (11) will give the ratio of the rate coefficients k_{1v}/k_{0v}. Figure 9 shows that this linear relationship does indeed obtain for $NO(A, v = 0)$.

Using the results for $v' = 1$ excitation derived from the moderate to high relaxation data, we can subtract out the contribution to observed excitation from $v' = 1$ for the data showing little relaxation and thereby probe contributions from $v' \geqslant 2$. A small amount of $N_2(A)$, $v' = 3$ was observed in our reactor in the absence of CF_4 [$< 4\%$ of total $N_2(A)$], but we observed no emission from higher levels under the conditions of these experiments. With the addition of CF_4, the ratio of $v' = 3$ to $v' = 2$ was less than 0.1. Thus the relatively
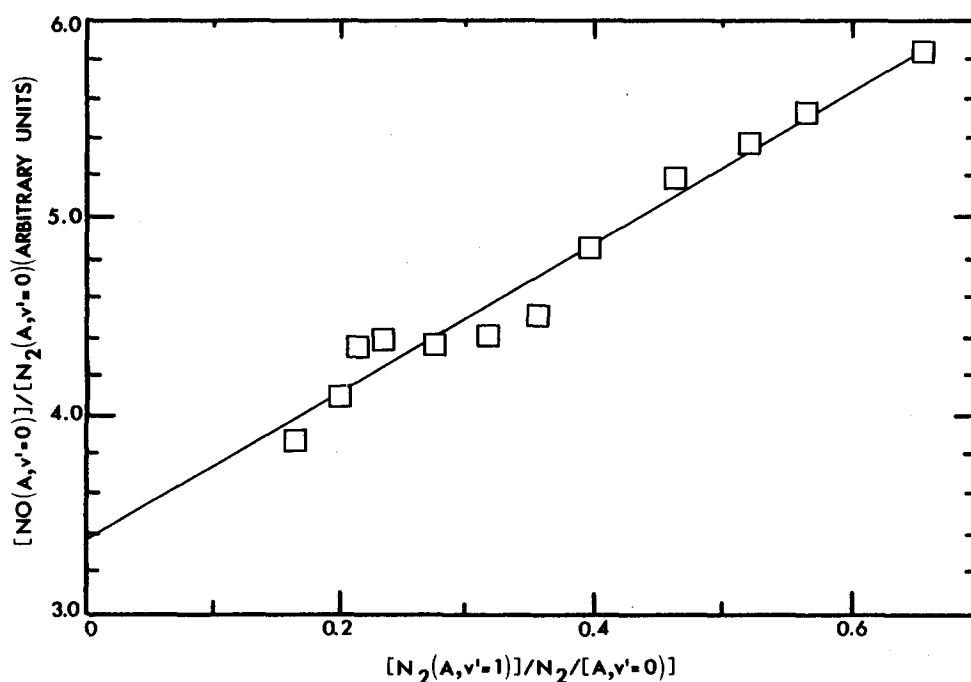

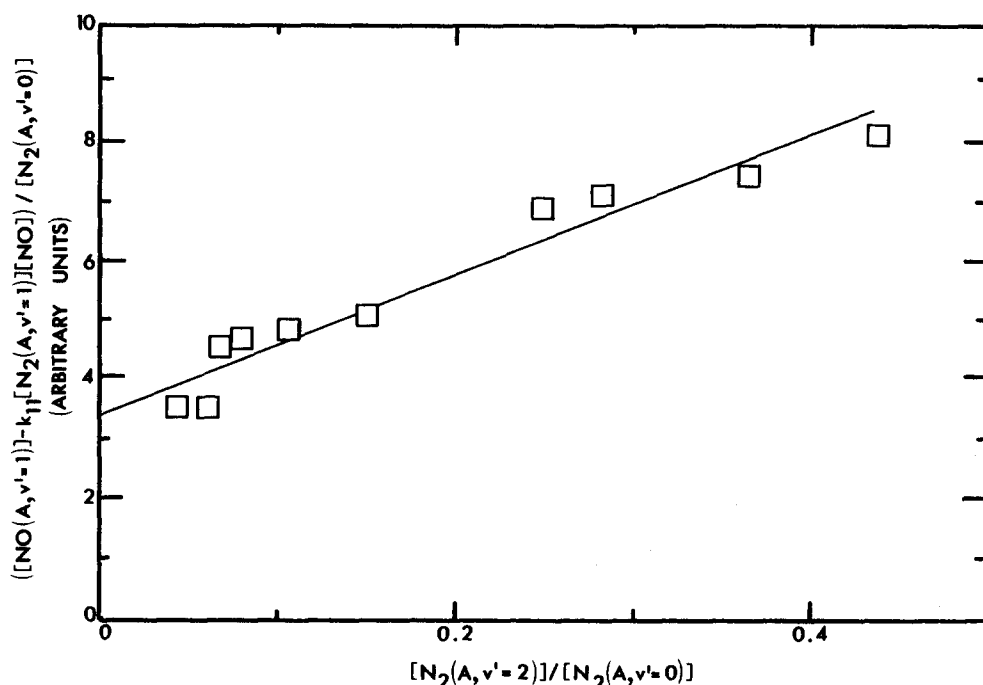FIG. 9. Excitation of $NO(A, v' = 0)$ as a function of the ratio of $N_2(A, v' = 1)$ to $N_2(A, v' = 0)$.

FIG. 10. Variation in the excitation of NO(A, $v' = 1$) as a function of the ratio of $N_2(a, v' = 2)$ to $N_2(A, v' = 0)$.

unrelaxed measurements probe only $v' = 2$. The working equation is

$$\frac{I_{NO_v^*}}{[N_2A]_0} - k_{1v}\frac{[N_2A]_1}{[N_2A]_0}[NO]$$

$$= \left\{k_{0v} + k_{2v}\frac{[N_2A]_2}{[N_2A]_0}\right\}[NO]. \qquad (12)$$

Figure 10 shows the linear relationship implied by this equation for NO(A, $v' = 1$). The ratio of the slope to intercept from this plot and a similar one for NO(A '$v' = 0$) gives the ratio k_{2v}/k_{0v}. Because excitation of NO(A, $v' = 2$) and NO($B, v' = 0$) were such minor channels, we only estimated their contributions to the total excitation by measuring the integrated intensity under the 2,0 gamma band and the 0,7 beta band in several spectra in which the $N_2(A)$ was vibrationally excited and several more in which it was relaxed. Thus we report only an excitation rate coefficient for excited and unexcited $N_2(A)$ for these two states. Table I lists the relative excitation rate coefficients for the state-to-state excitation of NO(A, $v' = 0,1,2$) and NO(B, $v' = 0$) by $N_2(A$, $v' = 0,1,2$).

IV. DISCUSSION

If the energy transfer between $N_2(A)$ and NO proceeds only through exit channels of radiating NO states, then the rate coefficients for $N_2(A$, $v' = 0$) quenching by NO [$(6.6 \pm 1.0)\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹] and for NO(A, B) excitation by $N_2(A$, $v' = 0$) [$(10 \pm 3)\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹] ought to be the same. We are therefore somewhat disturbed by the lack of congruency between the two measurements, even though they do overlap slightly at the extreme limits of their respective error bars. We have cross checked our data very carefully, and varied the experimental conditions over a wide range, thereby hoping to find systematic trends which might explain the discrepancy. We have been unable to find any. Our conclusion, therefore, is that the Einstein coefficient for the $N_2(A–X)$ transition is in error by about 30% (it should be smaller).

The experimental determination of lifetimes on the order of 2 s is extremely difficult and fraught with manifold uncertainties. The accepted value of the Einstein coefficient for the $N_2(A–X)$ transition rests upon absorption measurements by Shemansky in the vacuum ultraviolet[33] and his reanalysis[35] of Carleton and Oldenberg's absorption mea-

TABLE I. State-to-state relative excitation-rate coefficients.

	NO(A) $v' =$			
$N_2(A)$ v'	0	1	2	NO($B, v' = 0$)
0	1[a]	0.094 ± 0.006	0.003	0.0032 ± 0.0007
1	1.11 ± 0.07	0.22 ± 0.03		
			0.024	0.033 ± 0.007
2	0.29 ± 0.07	0.32 ± 0.03		

[a] $1 = 9.0\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

surements of $N_2(A)$ in a discharge.[36] His analysis requires a long extrapolation of the transition-moment function with r-centroid from the region encompassed by his absorption measurements into the region of r-centroid sampled by the strong transitions from the $v' = 0$ level. He tied this extrapolation to the lifetime for the $v' = 0$ level derived from the Carleton and Oldenberg reanalysis. Carleton and Oldenberg[36] attempted to measure simultaneously the absolute photon-emission rate of 0,6 Vegard–Kaplan band and the absolute number density $v' = 0$ level of the A state via resonance absorption on the 1,0 transition of the first-positive system (N_2 B–A). Assuming that the experimental observations of Carleton and Oldenberg are accurate, and that Shemansky's reanalysis of their observations is correct, then their derived lifetime for $N_2(A, v' = 0)$ depends directly upon the accuracy of the lifetime of the $v' = 1$ level of $N_2(B)$. While the recent lifetime measurements of Eyler and Pipkin[37] on the radiative lifetimes of $N_2(B, v' = 5$–$12)$ indicate that the transition probabilities of the first-positive system given by Shemansky[38] are essentially correct for $v' \gtrsim 3$, we do not feel confident that Shemansky's transition probabilities for the three lowest levels are necessarily accurate. The transition probabilities for these three levels depend predominantly upon an extrapolation of the electronic transition-moment function which Shemansky derived from relative intensity measurements of bands with r-centroid values between 1.35 and 1.6 Å out to r-centroid values as small as 1.0. This is generally a risky procedure. The recent *ab initio* calculations of the transition-moment function by Werner *et al.*,[39] Yeager and McKoy,[40] and Weiner and Öhrn[41] all show a much slower increase in the transition moment to smaller r-centroid than is given by Shemansky's extrapolation. The lifetimes Werner *et al.*[39] calculated from their transition-moment function are consistently 16% larger than the lifetimes measured by Eyler and Pipkin,[37] but the relative variation of their calculated lifetimes with vibrational level matches that of Eyler and Pipkin quite well. They also match the relative variation in the lifetimes measured by Jeunehomme,[42] and by Carlson *et al.*[43] and those calculated from Shemansky's transition probabilities for $v' \gtrsim 4$. They deviate markedly from the experimental results, however, for the lowest vibrational levels, with the calculated lifetimes of Werner *et al.*, being somewhat longer. If we reduce the calculated lifetimes of Werner *et al.* by 16% to make them coincide with Eyler and Pipkin's measurements for the high vibrational levels, we obtain a lifetime for $v' = 1$ of $N_2(B)$ of 9.5 μs in contrast to the value of 7.8 μs which results from Shemansky's transition probabilities. This large a change in the lifetime of the B state will reduce the transition probability for $N_2(A, v' = 0)$ from Carleton and Oldenberg's experiment by 20%. This reduction would then bring our quenching and excitation-rate measurements into reasonable agreement. Taking the *ab initio* transition probabilities at face value would result in a Vegard–Kaplan transition probability about 40% smaller than the currently accepted values, and would bring our two measurements into almost perfect congruence. The other theoretical treatments agree with the calculations of Werner *et al.* The lifetime of $N_2(B, v' = 0)$ measured by Heidner *et al.*[44] via resonance fluorescence is also somewhat larger than

given by Shemansky's extrapolation.

A reduction in the transition probability of the $N_2(A)$ state on the order of 20% to 30% would still give a variation in the absolute transition moment of the A–X transition fully consistent with the absolute measurements of Shemansky that sampled smaller values of the r-centroid, and the relative transition-moment measurements of Broadfoot and Maran[45] which sampled larger r-centroid values, those sensitive to the Vegard–Kaplan transitions from $v' = 0$. Clearly, this issue needs further investigation.

Our measurements on the vibrational-level dependence of NO excitation by $N_2(A)$ show that $N_2(A, v' = 1)$ excites NO(A, B) about 25% more efficiently than does $N_2(A, v' = 0)$. $N_2(A, v' = 2)$ however, is somewhat less efficient at exciting NO transitions. The reduction in observed intensity of NO(A, B) from excitation by $N_2(A, v' = 2)$ could result from one of three possibilities. First, the quenching efficiency could be smaller. Second, the more highly excited $N_2(A)$ can access higher lying levels of NO(A, B) which might be collisionally coupled into other states of NO which do not radiate or emit outside our spectral bandpass, such as the b $^4\Sigma^-$ or a $^4\Pi$ states. The third possibility is that some of the encounters between $N_2(A, v' = 2)$ and NO end up dissociating the NO. Only vibrational levels of $N_2(A)$ greater than or equal to two have sufficient energy to dissociate the NO. We have not yet attempted to look for atom production from this interaction, but such measurements would confirm this possibility.

The difference between the excitation rates of $N_2(A, v' = 1)$ and $N_2(A, v' = 0)$ is not sufficiently great for us to observe significant changes in decay-rate measurements involving vibrationally excited and unexcited $N_2(A)$. Given a typical $v' = 1/v' = 0$ ratio of 0.6, we compute that the effective decay rate would increase by only 10% when both $N_2(A)$ vibrational levels were present. Within experiment error, this small enhancement is consistent with our observations.

In order to investigate more completely the energy disposal in the reaction, we scanned the 0,6 an 1,7 bands of NO(A–X) under moderate resolution ($\Delta\lambda \approx 0.20$ nm) at pressures between 0.4 and 9 Torr. This resolution was adequate to resolve partially the rotational structure. We then adjusted rotational temperatures in our fitting program until we could match our observations. At 0.4 Torr, Boltzmann rotational temperatures of 1400 and 800 K fit the emission from $v' = 0$ and 1, respectively, quite well. At higher pressures, however, the band and contours were decidedly non-Boltzmann. Collisions with the argon bath gas relaxed the lower rotational levels much more efficiently than they did the higher rotational levels. For example, at 4.0 Torr a rotational temperature of 600 K fit region around the heads of the 0,6 band quite well, while the high rotational levels in which are prominent the short-wavelength tail of the band followed an 1100 K Boltzmann distribution. Assuming a hard-sphere model with a 40 Å^2 collision cross section, we calculate that an excited NO molecule will experience 1.5 collisions during a radiative lifetime at 1 Torr. Thus at 0.4 Torr most of the NO(A) molecules will not experience a collision prior to radiation, whereas at 4 Torr they will expe-

rience an average of six collisions. Thus the rotational relaxation of NO(A) by Ar is a relatively efficient process, requiring only a few collisions to remove most of the rotational energy. The efficient rotational relaxation of low J levels of NO(A) by argon and the correspondingly much smaller efficiency for high-J level relaxation has been studied in some detail by Ebata et al.[46]

The efficient transfer of vibronic energy from $N_2(A)$ to NO may occur by a Franck–Condon type of mechanism. Deperasinska et al.[47] have calculated Franck–Condon factors for the transitions relevant to the transfer of energy from $N_2(A, v' = 0)$ to NO. The Franck–Condon factors for producing NO(A) are three orders of magnitude greater than those for producing NO(B), which they claim is reflected in the much smaller efficiency for producing NO(B) relative to NO(A). Their calculated Franck–Condon factors, however, would predict roughly equal probabilities for producing vibrational levels $v' = 0$ and 1 of NO(A). In contrast, our observations show that NO($A, v' = 0$) is produced ten times more efficiently than NO($A, v' = 1$). They have not performed the relevant Franck-Condon calculations for $N_2(A, v' = 1, 2)$.

The kinetics of the $N_2(A)$ + NO energy transfer have been studied by several other investigators. Callear and Wood[3] estimated rate coefficient ratios from their work of $k_{01}/k_{00} = 0.105$ in reasonable agreement with our value of 0.094 ± 0.006 and $k_{11}/k_{10} = 0.53$ in disagreement with our value of 0.20 ± 0.03. Clark and Setser[1] determined a population ratio for NO($A, v' = 0,1,2$) of 1.0:0.15:0.014, respectively, from excitation by $N_2(A)$ with the ratio $v' = 1/v' = 0$ of 0.61. With the same $N_2(A)$ vibrational distribution, we calculate an NO(A) vibrational distribution from our excitation rate coefficients of 1.0:0.14:0.011, respectively, in excellent agreement with Clark and Setser's observations. More recently Golde and Moyle[48] have measured vibrational distributions of NO(A) from $N_2(A)$ excitation of 1.00:0.083:0.002 for excitation by $N_2(A, v' = 0)$ and 1.00:0.17:0.025 for excitation by $N_2(A)$ with a vibrational distribution of 1.00:0.48:0.19:0.14 for $v' = 0$–3, respectively. Our rate coefficients would predict an NO(A) vibrational distribution of 1.00:0.19:0.13 given the same initial $N_2(A)$ vibrational distribution. In order to make this comparison, we assumed $v' = 2$ and $v' = 3$ had the same excitation rates. Golde and Moyle's data show a 7% decrease in total NO(A) intensity for the vibrationally excited case whereas our results would indicate that the intensities of the NO(A) produced from vibrationally excited and unexcited $N_2(A)$ would be within 2% of each other. Our error limits encompass a range from a 6% decrease in intensity to a 3% increase with some additional uncertainty added by our having treated $N_2(A)$ vibrational levels 2 and 3 the same. They are therefore fully consistent with Golde and Moyle's result.

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