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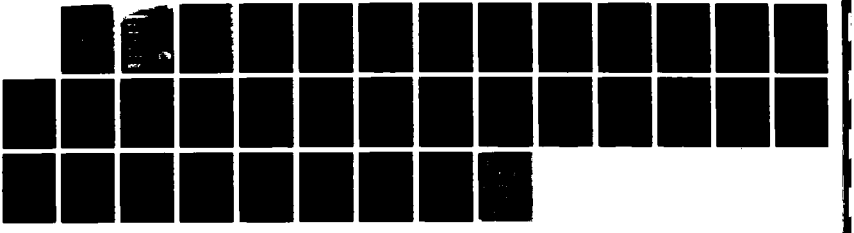

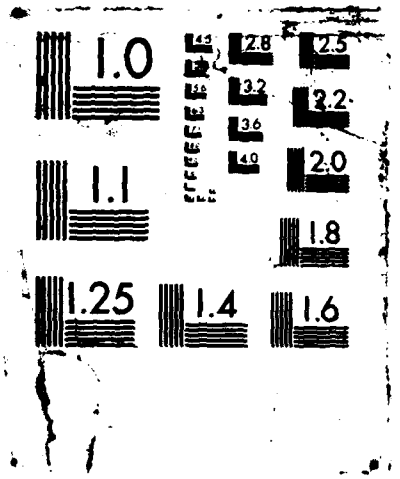
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Room temperature v-level specific bimolecular rate constants for the reaction of $N_2(A\ ^3\Sigma_u^+,\ v \leq 6)$ with efficient (O_2, $O(^3P)$, NO, C_2H_4, N_2O, and CO) and inefficient (H_2, CH_4 and CF_4) electronic quenchers were measured in a rapidly pumped discharge flow reactor at a pressure ~2 torr. $N_2(A,v)$ was produced by the rapid energy transfer reaction $Ar(^3P_{2,0}) + N_2$ or $Xe(^3P_{2,0}) + N_2$ and monitored using laser-excited fluorescence (LEF) detection of $N_2(A,v)$ by excitation in the First Positive system of N_2, B → A.

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For the relatively efficient electronic quenchers of $N_2(A)$ the rate constants are: $k_0 = (2.5 \pm 0.5)$, $k_1 = (4.3 \pm 0.6)$, $k_2 = (5.0 \pm 0.6)$, $k_3 = (5.3 \pm 0.6)$, $k_4 = (4.3 \pm 0.7)$, $k_5 = (3.8 \pm 0.5)$, and $k_6 = (4.5 \pm 0.7) \times 10^{-12}$ $cm^3\ s^{-1}$ for O_2; $k_0 = (3.5 \pm 0.6)$, $k_1 = (4.1 \pm 0.6)$, $k_2 = (4.8 \pm 0.6)$, and $k_3 = (5.2 \pm 0.8) \times 10^{-11}$ $cm^3\ s^{-1}$ for $O(^3P)$; $k_0 = (5.6 \pm 0.9)$, $k_1 = (7.8 \pm 0.9)$, $k_2 = (8.6 \pm 0.9)$, $k_3 = (10.4 \pm 1.3)$, $k_4 = (9.9 \pm 1.2)$, $k_5 = (12.3 \pm 1.6)$, and $k_6 = (11.8 \pm 1.5) \times 10^{-11}$ $cm^3\ s^{-1}$ for NO; $k_0 = (10.2 \pm 1.3)$, $k_1 = (10.5 \pm 1.3)$, $k_2 = (8.9 \pm 1.1)$, $k_3 = (10.0 \pm 1.2)$, $k_4 = (9.2 \pm 1.1)$, $k_5 = (9.5 \pm 1.2)$, $k_6 = (12.0 \pm 1.5) \times 10^{-11}$ $cm^3\ s^{-1}$ for C_2H_4; $k_0 = (6.2 \pm 0.8)$, $k_1 = (12.5 \pm 1.5)$, $k_2 = (14.7 \pm 1.8)$, $k_3 = (14.6 \pm 1.8)$, $k_4 = (12.6 \pm 1.5)$, $k_5 = (12.6 \pm 1.6)$, and $k_6 = (13.6 \pm 1.7) \times 10^{-12}$ $cm^3\ s^{-1}$ for N_2O; and $k_0 = (1.5 \pm 0.2)$, $k_1 = (16.7 \pm 2.1)$, $k_2 = (48.7 \pm 6.1)$, $k_3 = (17.5 \pm 2.4)$, $k_4 = (18.9 \pm 2.4)$, $k_5 = (9.7 \pm 1.5)$, and $k_6 = (14.1 \pm 1.8) \times 10^{-12}$ $cm^3\ s^{-1}$ for CO. These data refer principally to electronic quenching of $N_2(A)$. The v-level dependences are discussed in terms of the probable mechanism for the electronic deactivation of $N_2(A)$.

For CH_4 and CF_4, the rate constants are: $k_1 = (1.2 \pm 0.3)$, $k_2 = (2.5 \pm 0.5)$, $k_3 = (3.0 \pm 0.5)$, $k_4 = (3.8 \pm 0.6)$, $k_5 = (4.0 \pm 0.6)$, and $k_6 = (5.1 \pm 1.0) \times 10^{-12}$ $cm^3\ s^{-1}$ for CH_4; and $k_1 = (0.4 \pm 0.1)$, $k_2 = (1.5 \pm 0.3)$, $k_3 = (4.5 \pm 1.5)$, $k_4 = (6.4 \pm 1.0)$, $k_5 = (13 \pm 2)$, and $k_6 = (22 \pm 4) \times 10^{-12}$ $cm^3\ s^{-1}$ for CF_4. These data refer primarily to vibrational relaxation of $N_2(A,v)$, although electronic quenching may contribute to the removal of high v-levels by CH_4. The v-level behavior is discussed in terms of the energy gap model for the vibrational-to-vibrational (V-V) energy transfer (ET) process. For H_2 and D_2, preliminary rate constants are: $k_1 \sim (2.0)$, $k_2 = (6 \pm 1)$, $k_3 = (14 \pm 4)$, $k_4 = (25 \pm 4)$, $k_5 = (41 \pm 10)$, $k_6 = (70 \pm 10) \times 10^{-14}$ $cm^3 s^{-1}$ for H_2; and $k_1 < 1 \times 10^{-14}$, $k_3 - k_6 \sim 1 \times 10^{-13}$ $cm^3 s^{-1}$ for D_2.

The v-level dependences of the NO product yields in the reactions of $N_2(A)$ with $O(^3P)$ and O_2 were investigated using a calibrated NO LEF.

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Introduction

In the Earth's thermosphere, under conditions of low pressure and high solar flux, metastable atomic and molecular species acquire increased importance, particularly under conditions of natural or artificial perturbation. For molecules, the excitation can be either electronic or vibrational, and it is estimated that ~40% of thermospheric solar UV energy is channeled through metastables.[1] The effect of vibrational excitation on the reactivity of a given species is poorly understood at present. The purpose of this project was to obtain relevant data, both for direct input to models of perturbed atmospheres, and to yield new insight into the effects of vibrational excitation.

This study has concentrated on the reactions of the lowest electronically excited state of N_2, the metastable $N_2(A^3\Sigma_u^+)$ state, in its lowest seven vibrational levels. The reagents O_2, NO, CO, N_2O and C_2H_4 were chosen for their atmospheric relevance, but also exhibit an interesting variety of properties. Dissociation of C_2H_4, N_2O and O_2 is energetically possible. This channel appears to be dominant in the reaction with N_2O[2] and is an important, but not the sole, channel in the reaction with O_2.[2,3] However, dissociation to C_2H_3 + H is a minor channel in the very rapid reaction with C_2H_4. Dissociation of CO and NO is endothermic in reaction with the lowest vibrational levels of $N_2(A)$, and excitation transfer to yield $CO(a^3\pi)$ and $NO(A^2\Sigma^+)$ has been extensively studied.[4-6]

The study was extended to include two inefficient electronic quenchers, CH_4 and CF_4, which are shown to deactivate $N_2(A)$ principally via vibrational relaxation. As well as providing a means of modifying the vibrational distribution in the $N_2(A)$ state, study of the effect of these reagents allows estimation of the vibrational distribution in $N_2(A)$ in a given reaction system.[7]

Preliminary data on two other inefficient quenchers, H_2 and D_2, are also included in this report, as are results on product analysis of the related reac-

tion of $N_2(A)$ with $O(^3P)$ atoms.

The only previous study of a wide range of vibrational levels of $N_2(A)$ was that of Dreyer, Perner and Roy,[8,9] which employed pulse radiolysis to generate $N_2(A)$ and time-resolved absorption spectrometry to monitor v = 0 to 8 in the presence of N_2, C_2H_6, C_2H_4, O_2, CO, CO_2, NO, and NH_3. Unfortunately, due to effects of vibrational cascade or deviations from Beer's Law behavior, the quoted rate constants for low levels differ in several instances from other data by a factor of 2 or more.

A brief description of the experimental technique is presented in Section II. Sections III and IV contain a brief summary and discussion of the projects completed during this contract. For brevity, we have omitted presentation of the representative semi-log plots of $N_2(A, v)$ LEF signal vs. [Q].[10]

II. EXPERIMENTAL

The discharge flow reactor consists of three main sections: the N_2 metastable generation and reagent inlet region, the reaction zone, and the detection cell. The reaction zone consists of a ~2.54 cm i.d. pyrex tube with a maximum reaction distance of ~40 cm (~10 ms reaction time at full pumping). Downstream of the reaction zone is a modular stainless steel detection cell which consists of three permanent observation ports separated by an axial distance of ~5 cm and a chemiluminescence viewing region located above the uppermost fixed observation port. The uppermost permanent observation port is used to monitor the relative concentration of $N_2(A, v)$ by laser-excited fluorescence (LEF). The middle observation port is used for the detection of atomic species by either resonance fluorescence (RF) or resonance absorption (RA) spectrophotometry. The lower port is used to monitor the absolute concentration of $NO(X\ ^2\pi, v = 0)$ by LEF. The chemiluminescence PMT located above

the first observation port is used to measure the absolute [$O(^3P)$] via a calibrated 'air afterglow' intensity.

$N_2(A, v)$ was generated using one of three techniques: (i) the $Ar(^3P_{2,0})$ + N_2 reaction, (ii) the $Xe(^3P_{2,0})$ + N_2 reaction, or (iii) by a low power d.c. discharge in an N_2/Ar mixture. Ar and Xe metastables were generated by passing a pure Ar flow or a Xe/Ar mixture (~0.2%) through a low power d.c. discharge. The initial product of the ET reaction (i and ii)[11] and the discharge in the N_2/Ar mixture[2] is electronically excited molecular N_2. $N_2(A, v)$ is produced in large yield from the resulting cascade in the triplet manifold of electronically excited N_2. Method (ii) was particularly useful for the study of high levels, $v > 3$, of $N_2(A)$. Method (iii) generated appreciably larger concentrations of $N_2(A,v)$ than the other two methods, but also small concentrations of $N(^4S)$ and $N(^2D)$ atoms. Consistent rate data were obtained from the three generating processes.

The $N_2(A, v)$ and $NO(X, v = 0)$ LEF excitation source was a computer controlled (Tandy, Model TRS-80 Model II) N_2-laser-pumped dye laser (Lambda Physik, Models M1000 and FL2000). To monitor $N_2(A, v)$, the dye laser was operated with either Rhodamine 610 ($N_2(A, v\leq2)$) or Rhodamine 590 ($N_2(A, 3\leq v\leq6)$). These seven vibrational levels of $N_2(A)$ were monitored by laser excitation of the First Positive System ($B\ ^3\Pi_g \leftarrow A\ ^3\Sigma_u^+$) at the P_1 band heads of the $\Delta v = 4$ transitions, e.g., $N_2(B, v' = 4) \leftarrow N_2(A, v'' = 0)$ with $\lambda_0 = 617.3$ nm. Fluorescence was collected to the red of the pump wavelength using a dry-ice cooled red sensitive PMT (RCA, Model C31034A) with scattered light from the excitation source eliminated using a sharp cut-off filter. The observed fluorescence signal was due to the $\Delta v = v'' - v' = 0, -1, -2,$ and -3 transitions of the First Positive System ($B \rightarrow A$).

The concentration of the product NO was measured by LEF at ~226.3 nm using frequency doubled (Lambda Physik, FL33T KPB Crystal) Coumarin 450 dye (Exciton) radiation, causing excitation of the (0,0) band of the NO(A → X) γ system at its Q_1 band head. Scattered light from the excitation radiation was not observed and all fluorescence within the observation window (160 - 320 nm) of the solar blind PMT (Hamamatsu R821) was collected. The NO LEF signal was calibrated absolutely using an NO mixture in He. Typically a detection limit of ~2 x 10^7 cm^{-3} was achieved.

The flow rate of the stable reactant (O_2, CO, NO, C_2H_4, N_2O, H_2, CH_4, and CF_4) was determined from the measured pressure rise in a calibrated volume. The concentration of atomic oxygen was measured using either calibrated RF or chemiluminescence, depending on the total concentration of atomic oxygen. For the $N_2(A)$ + O-atom kinetic studies where $[O(^3P)] > \sim 5 \times 10^{11}$ cm^{-3}, the $[O(^3P)]$ was measured using a calibrated O + NO 'air afterglow'. Absolute concentrations of Ar*, Xe* and $N_2(A)$, typically $<1 \times 10^{11}$ cm^{-3}, were measured by calibrated O-atom RF of the products of the reactions of the appropriate metastable with O_2.[12]

In the work reported here, the v-level specific bimolecular rate constants and product yields for the reactions of $N_2(A, v)$ with efficient and inefficient electronic quenchers were measured in the presence of excess Q at a fixed reaction time (distance). The bimolecular rate constants were calculated from the slopes of semi-log plots of $N_2(A, v)$ LEF signal vs. [Q] using $k_v = -(\alpha v/z) \times d\ln(I_{LEF})/d[Q]$, where α is the correction factor for the development of laminar flow,[13] v is the average flow velocity in the reaction zone, z is the reaction distance (z/v is the plug flow reaction time), and $d\ln(I_{LEF})/d[Q]$ is the slope of the semi-log plot. The slope is calculated using either a linear least-squares or a non-linear least-squares computer algorithm.

In the experiments with CH_4 and CF_4, many of the semilog plots exhibited curvature due to formation of the observed v level via cascade from higher levels. Analysis of these curved plots, necessary for deriving valid rate constants, was hampered by significant background contributions to the LEF signal, probably mainly from steady-state emission from the discharged gases. These experiments were, therefore, repeated on a separate flow system of comparable design, but serviced by an excimer pumped dye laser system (Lambda-Physik 101E, 2002E). This more sensitive system was almost background-free under the conditions used, and allowed a more reliable analysis of the curved semilog decay plots.

III. RESULTS

In the reactions of $N_2(A, v)$ with O_2, O atoms, CO, C_2H_4, NO and N_2O the plots of $\ln I_{LEF}$ vs [Q] appeared linear in all cases. This indicates that cascade formation of level v by collisional deactivation of higher levels is unimportant, and the loss of $N_2(A, v)$ was ascribed to electronic quenching. This conclusion was supported by modeling calculations on the $N_2(A) + O_2$ reaction. In contrast, the analogous plots for the reactions of $N_2(A)$ with CH_4 and CF_4 showed negative curvature, indicating formation of level v by collisional vibrational relaxation of higher levels. Indeed the concentration of $N_2(A, v = 0)$ <u>increased</u> with reagent concentration and this level showed no quenching even at the highest reagent concentrations used. It was concluded that electronic quenching is less important than vibrational relaxation for these reagents. Modeling studies suggest that vibrational relaxation by CH_4 and CF_4 occurs mainly by $\Delta v = -1$ transitions in $N_2(A)$.

1. $N_2(A\ ^3\Sigma_u^+,\ v\leq 6) + O_2 \rightarrow$ Products

A summary of the v-level specific bimolecular rate constants for the reaction of $N_2(A,\ v\leq 6) + O_2$ reported in the literature and those measured in the present investigation is presented in Table 1. Although not shown in Table 1, Dreyer et al.[9] measured v-level specific rate constants for the reaction of $N_2(A) + O_2$ up through v = 8. For $N_2(A,\ v=7) + O_2$ they reported $k = (7.5 \pm 3.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; and for $N_2(A,\ v=8)$ they reported $k = (5.1 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Very good agreement is found for k_0 and k_1 with the work of Iannuzzi and Kaufman,[13] Piper et al.,[14] Zipf,[15] and De Souza et al.[16] Our v = 0 measurement is also in good agreement with Dreyer et al.[9] and Dunn and Young.[17] None of the reported investigations confirm the relative maximum in rate constant observed by Dreyer et al. at v = 1.

The bimolecular rate constants for the interaction of $N_2(A,\ v) + O_2$ appear to be well characterized. An average set of bimolecular rate constants can be calculated using the values reported in the literature and those measured in the present investigation: $\langle k_0 \rangle = (2.4 \pm 0.2)$, $\langle k_1 \rangle = (4.1 \pm 0.1)$, $\langle k_2 \rangle = (4.7 \pm 0.3)$, and $\langle k_{3,4,5,6} \rangle = (4.7 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

The lack of curvature observed in the plots of $\ln(I_{LEF})$ vs $[O_2]$ suggests that the major deactivation mechanism involves the electronic deactivation of $N_2(A,\ v)$ by O_2. The observed rise in rate constant with vibrational energy is consistent with work reported by Golde and Moyle[2] in which they compared the yields of $O(^3P)$ product from the reactions of $N_2(A,\ v = 0) + O_2$ and $N_2(A,\ v>0) + O_2$. They also deduced an increase in the $O(^3P)$ branching fraction with v in $N_2(A)$.

2. $N_2(A\ ^3\Sigma_u^+, v<3) + O(^3P) \rightarrow$ Products

A summary of the v-level specific bimolecular rate constants reported in the literature and those measured in the present investigation for the reaction of $N_2(A, v<3) + O(^3P)$ is presented in Table 2. Our values for k_0 and k_1 are in good agreement with those of Piper et al.[18] and De Souza et al.[19] Agreement with the less direct measurements of Meyer et al.[20] and Dunn and Young[17] is not as good. The value reported by Meyer et al. was measured relative to the rate constant for the deactivation of $N_2(A)$ by O_2, which they took to be $\sim 6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and it should be reduced by approximately a factor of 2 to conform with the currently accepted value for the latter reaction (See Table 1).

A brief discussion of the product channels for the reaction of $N_2(A, v) + O(^3P)$ is presented in the following section.

3. $N_2(A, v) + O(^3P)/O_2 \rightarrow NO + N/NO$

The corrected NO + NO product yield in the reaction of $N_2(A, v) + O_2$ represents <0.1% of the total $N_2(A\ ^3\Sigma_u^+)$ present at the O_2 inlet. This quantity is independent of the relative $N_2(A, v)$ population distribution and represents the upper limit of the uncertainty of a null quantity. Although this null result was as expected, it was necessary to rule out possible interference with the NO product yield measurements in the reaction of $N_2(A) + O(^3P)$.

The corrected NO + N product yield in the reaction of $N_2(A, v<2) + O(^3P)$ accounts for <1% of the total $N_2(A\ ^3\Sigma_u^+)$ present at the $O(^3P)/O_2$ inlet. As in the NO + NO product yield measurement for the reaction of $N_2(A\ ^3\Sigma_u^+) + O_2$, this quantity represents the upper uncertainty limit of a null quantity. When the relative $N_2(A, v)$ population distribution was shifted to higher v by reducing the total $[N_2]$, a small NO LEF signal was observed above the background. The product NO observed when the relative $N_2(A\ ^3\Sigma_u^+)$ v-level distribution is shifted

to high-v represents ~5.7% of the total $N_2(A\ ^3\Sigma_u^+)$ when corrected for competing $N_2(A\ ^3\Sigma_u^+)$ loss processes.

To further investigate the existence of a v-level dependence of the NO + N product yield, the product NO was monitored as a function of added CH_4. With enough CH_4 added upstream of the O/O_2 inlet to vibrationally relax $N_2(A, v>3)$ into $N_2(A, v\leq 3)$ the NO LEF signal was reduced by a factor of ~2.

The present investigation has answered two questions. First, the NO + NO product yield in the reaction of $N_2(A, v) + O_2(X)$ represents less than 0.1% of the total $N_2(A)$ present at the O_2 inlet, independent of the relative $N_2(A)$ vibrational level distribution for $v\leq 6$. Second, the NO + $N(^4S, ^2D)$ product yield accounts for less than ~2% of the $N_2(A, v\leq 2) + O(^3P)$ interaction. This is qualitatively consistent with the high $O(^1S)$ yields observed previously, but somewhat lower than suggested by the results of those studies. Our investigation, while ruling out the formation of NO + N from the low vibrational levels of $N_2(A)$, raises the question of a possible v-level dependence for the NO + N product yield in the reaction of $N_2(A)$ with $O(^3P)$.

4. $N_2(A, v\leq 6) + NO \rightarrow$ products

A summary of the bimolecular rate constants reported in the literature and those measured in the present investigation for the reaction of $N_2(A)$ with NO is presented in Table 3. We observe an increase in quenching rate with v for $0\leq v\leq 3$ followed by an apparent leveling off for $3\leq v\leq 6$. Taking an average of the rate constants for $3\leq v\leq 6$, we obtain a value of $(11.1 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, ~40% of gas kinetic. Although not presented in Table 3, Dreyer et al.[9] measured v-level specific rate constants for the $N_2(A)$ + NO interaction up through v = 8. For $N_2(A, v = 7)$ they reported a $k = (8.9 \pm 3.5) \times 10^{-11}$ cm^3

molecule^{-1} s^{-1}; and for N_2(A, v = 8) they reported a k = (6.7 ± 0.5) x 10^{-11} cm^3 molecule^{-1} s^{-1}.

For v ≥ 2, our measurements are in good agreement with the measurements of Dreyer et al., but we do not confirm the small decrease in quenching rate at high v, which they observed. Our rate constant for v = 0 is in satisfactory agreement with the less direct, but state-specific measurement of Piper et al., but a factor of ~2 larger than that measured by Dreyer et al. No other studies have yielded direct, state-specific rate data, because N_2(A, v-X) emission, used in other direct studies of N_2(A) quenching, is obscured by the very strong NO(A-X) emission produced by this reaction. By using the NO emission to monitor N_2(A), effective rate constants, averaged over the experimental vibrational distribution, have been obtained: published values range from 2.8 to 15 x 10^{-11} cm^{3}s^{-1}. We can determine an effective removal rate constant for our system using $k_T = \Sigma(f_v \times k_v)$. With 20% N_2 in the flow reactor, the relative concentrations of N_2(A), f_v, are: ~0.61, ~0.29, and ~0.11 for v = 0, 1 and 2, respectively. This would give a total removal rate of (6.6 ± 0.6) x 10^{-11} cm^3 molecule^{-1} s^{-1} in satisfactory agreement with recent work by Shibuya et al.[21]

5. N_2(A, v<6) + C_2H_4 → products

A summary of the reported bimolecular rate constants and those measured in the present investigation for the electronic deactivation of N_2(A, v) by C_2H_4 is presented in Table 4. Previous work, with the exception of Dreyer and Perner,[8] has been limited to v<1. For N_2(A, v = 1) our results are in very good agreement with the results of Callear and Wood[4] and Dreyer and Perner. Our results do not confirm the k_0 obtained by Dreyer and Perner but are in good agreement with the rate constant reported by Callear and Wood for the electronic deactivation of N_2(A, v = 0) by C_2H_4. For N_2(A, v<2) our v-level specific rate

constants are ~16% lower than the values reported by Dreyer and Perner but still quite fast, i.e., ~30% of gas kinetic.

The products from the reaction $N_2(A) + C_2H_4$ have been investigated by Meyer et al.[22] The only condensable product observed in their system was C_2H_2, suggesting that a major reaction channel is $N_2(A) + C_2H_4 \rightarrow N_2(X) + C_2H_4^*$, followed by $C_2H_4^* \rightarrow C_2H_2 + H_2$, or $\rightarrow C_2H_2 + 2H$ (exothermic for $N_2(A, v>1)$). More recently, Golde and Moyle (unpublished data) measured a yield of (0.20 ± 0.07) H atoms per reactive event, implying that the latter channel, or more likely, dissociation to $C_2H_3 + H$, occurs to a small but significant extent.

6. $N_2(A, v<6) + N_2O \rightarrow$ products

A summary of the reported bimolecular rate constants and those measured in the present investigation for the deactivation of $N_2(A, v)$ by N_2O is presented in Table 5. Excellent agreement is found for k_0 with the work of Young et al.,[23] Callear and Wood,[4] and Slanger et al.[24] For $N_2(A, v = 1)$, our bimolecular rate constant is approximately a factor of 2 less than that reported by Meyer et al.[22] for the same process. For $N_2(A, v>1) + N_2O$, we are unaware of any previous measurements reported in the literature.

For $N_2(A, v>3) + N_2O$ an average bimolecular rate constant of $(13.6 \pm 0.6) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, ~5% of gas kinetic, is obtained.

7. $N_2(A\ ^3\Sigma_u^+, v<6) + CO \rightarrow$ Products

A summary of the bimolecular rate constants reported in the literature and those measured in the present investigation for the electronic deactivation of $N_2(A, v)$ by CO is presented in Table 6. Previous work, with the exception of Dreyer et al.,[9] has been limited to $v<1$. For $N_2(A, v = 0)$ our results are in excellent agreement with the results of Callear and Wood,[4] Slanger et al.,[24] and Dreyer et al. Comparison with the k_0 reported by Young et al.[23] is

complicated by the fact that their measurement was made relative to the quenching of $N_2(A)$ by NO and they used a value that is ~25% larger than recent measurements made in our lab (See Table 3) and by Piper et al.[5] For $N_2(A, v = 1)$ + CO our k_1 is in very good agreement with that reported by Dreyer et al., but ~30% lower than that reported by other investigators. For $N_2(A, v>1)$ our measurements are in very good agreement with those reported by Dreyer et al. with the exception of k_5 where our measurement is ~40% lower than that reported by those investigators.

From the observed behavior of the bimolecular rate constants, i.e., a maximum in rate constant at v = 2, the deactivation process appears to have the characteristics of an electronic-to-electronic (E-E) ET with a resonant or near resonant transfer of energy at $N_2(A, v= 2)$ + CO(X, u" = 0). In agreement, the major product in the reaction of $N_2(A)$ + CO appears to be CO(a, u').[25,26] As first suggested by Dreyer et al.,[9] the observed behavior can be explained on the basis of preferred vertical transitions in both the Vegard-Kaplan (VK) system of molecular nitrogen and the Cameron system of CO, and minimum energy defects for the respective ET processes. While $N_2(A, v' = 0)$ + CO(X, u" = 0) has very poor Franck-Condon (FC) overlap in the VK system and an energy defect of ~1285 cm^{-1}, the transfer of energy between $N_2(A, v' = 2)$ and CO(X) has good FC overlap in both molecular systems and is near energy resonant, i.e., ~82 cm^{-1} exoergic, if the final products are CO(a, u' = 1) and $N_2(X, v" = 1)$.

Meyer et al.[22] and Clark and Setser[27] have suggested that the rate constant k_0 obtained by Callear and Wood,[4] and Dreyer et al.,[9] is too small, due to interference from the reverse reaction CO(a, u' > 0) + $N_2(X, v" = 0)$ + CO(X, u") + $N_2(A, v' = 0)$. To investigate the effect of this reaction on our measurements, the concentration of $N_2(A, v'>0)$ (the source of CO(a, u'>0)) was varied by varying the N_2 fraction. The v-level specific rate constants appear

to be invariant to changes in the $N_2(A)$ state vibrational distribution. To further investigate the effect of the reverse reaction on our measured rate constants, the concentration profiles of $N_2(A, v')$ and $CO(a, u')$ were simulated. Even if the above process occurs, it would not significantly affect the $N_2(A, v = 0)$ decay under the present conditions.

We conclude that the ratio k_1/k_0 obtained in our measurements and those reported by Callear and Wood, and Dreyer et al. are valid. It is possible that there is a systematic error in the measurements reported by Meyer et al. and Clark and Setser. Setser has reported v-level specific rate constants for other reactions that appear to be faster than measurements reported from our lab and other labs, e.g., $N_2(A\ ^3\Sigma_u^+)$ + NO (Table 3), $N_2(A\ ^3\Sigma_u^+)$ + C_2H_4 (Table 4), $N_2(A\ ^3\Sigma_u^+)$ + N_2O (Table 5) and $N_2(A\ ^3\Sigma_u^+)$ + O_2 (Table 1).

8. <u>$N_2(A, v = 1\text{-}6) + H_2, D_2$</u>.

A summary of rate constants reported in the literature and preliminary results obtained in this lab is presented in Table 7. As can be seen, previous work is limited to $v < 1$ for the reaction with H_2. In the current study, the maximum amount of quenching of each level was too small to distinguish definitely between vibrational relaxation and electronic quenching. If vibrational relaxation is dominant, the values in Table 7 are lower limits to the true deactivation rate constants. Levron and Phelps[28] ascribed deactivation of $N_2(A, v = 1)$ by H_2 to vibrational relaxation, and we observed enhancement of $N_2(A, v = 0)$ when H_2 was added. However, product studies of the $N_2(A) + H_2$ reaction revealed a small but significant yield of H atoms, implying that electronic quenching is also contributing. It is possible that a transition from vibrational relaxation at low v to electronic quenching at higher v occurs, as observed recently in the reactions with D_2O and CF_2HCl.[29] D_2 is clearly much

less efficient than is H_2 at deactivating $N_2(A)$. No quenching of $N_2(A, v = 0-2)$ was observed, and very weak quenching of higher levels, with no apparent dependence of quenching rate constant on v.

9. $N_2(A, v = 1-6) + CH_4, CF_4$.

As mentioned above, plots of $\ln[N_2(A,v)]$ vs [Q] for Q = CH_4 and CF_4 were curved in most cases, indicating vibrational relaxation as a significant mode of collisional removal of levels $v > 1$. In the initial experiments on levels $v > 3$, as reported in several interim progress reports on this project, rate constants were estimated from data at high [Q], where vibrational cascade was expected to be unimportant. Unfortunately, the net LEF signals under these conditions were very small compared to background signals, leading to great uncertainty in the derived data. Therefore, the study of $N_2(A, v = 1-6) + CH_4$, CF_4 was repeated on a separate discharge-flow apparatus. Curved semilog plots were obtained as in the preliminary experiments. Because of the greatly improved signal-to-noise ratio, detailed analysis of the data, including effects of vibrational cascade, was feasible. The resulting rate constants for deactivation of $N_2(A, v)$ were significantly smaller than those reported earlier, by factors of between 1.3 and 1.7 for most reactions, but by larger factors for $N_2(A, v = 4,5) + CH_4$, which gave excessively curved plots in the earlier study.

Following a re-evaluation of the earlier data, it was concluded that the data are close to consistent with the newer set but that independent analysis is not feasible because of the low signal-to-noise ratio. Therefore, these data should be considered as preliminary, and the rate constants obtained by the more recent experiments are included in this report in Tables 8, 9. CH_4 and CF_4 show rather different behavior, the deactivation rate constants increasing from 1.2×10^{-12} ($v = 1$) to 5.1×10^{-12} ($v = 6$) for CH_4, and from 2.9×10^{-13} ($v = 1$)

to 2.2 x 10^{-11} (v = 6) for CF_4. For CH_4, the value for v = 1 is close to the previous published data,[7] while those for v = 2 and v = 3 are slightly smaller than the earlier values from this lab. For CF_4, the present values for v = 1-3 are systematically smaller than the earlier values from this lab, but that for v = 1 agrees closely with the recent work of Piper et al.[30] At present, average values of (4 ± 1) x 10^{-13}, (1.5 ± 0.3) x 10^{-12} and (4.5 ± 1.5) x 10^{-12} cm^3s^{-1} are recommended for respectively $N_2(A, v = 1-3) + CF_4$.

Strong evidence has been obtained that CF_4 removes $N_2(A, v = 1-6)$ predominantly by vibrational relaxation. In particular, the product yield from reaction of $N_2(A)$ with e.g. NH_3[2] is unchanged by addition of CF_4 upstream, in sufficient quantities for almost complete removal of $N_2(A, v = 1-6)$. For CH_4, similar experiments show that, averaged over the nascent vibrational distribution in $N_2(A)$, approximately 5% of v > 1 is removed by electronic quenching. This is supported, firstly by detection of H atoms from a dissociation pathway, and secondly by decreased curvature of the plots of $\ell n[A, v]$ vs $[CH_4]$ at high v, suggesting that the electronic quenching is most important at the highest levels studied, v = 5 and 6.

IV. DISCUSSION

Except for the pioneering study by Dreyer, Perner and Roy,[9] the current study includes the first direct, state-specific measurements of $N_2(A, v)$ deactivation rate constants. The agreement with Dreyer et al. is remarkably good. The only serious discrepancy concerns v = 0, for which the pulse radiolysis values appear consistently lower than those of other workers.

The reagents used in this study exhibit a variety of behavior. C_2H_4 is a very efficient quencher, with a rate constant which is approximately one-third of the collision number and is nearly independent of v. NO quenches high v with

comparable efficiency to C_2H_4 but low levels, particularly v = 0, are quenched significantly more slowly. N_2O and O_2 show comparable v dependences to NO but the rate constants are an order of magnitude smaller. Finally, CO shows a remarkable v dependence, with a maximum rate constant at v = 2 and apparently a subsequent minimum at v = 5. Two features in the data stand out. The first is the behavior of CO, which has been discussed in terms of the importance of vertical transitions in the molecules. The second is the plateau in the rate constants at high v, at values well below the collision number, especially for N_2O and O_2.

The importance of vertical transitions in N_2 and in the reagent Q in the energy transfer process has been pointed out by several workers. It has been realized for some years that species that have accessible excited states at an energy of about 6 eV or less are generally efficient quenchers of $N_2(A)$, especially if the excited state is dissociative,[2,4,27] and that species that lack such accessible states, such as H_2, CH_4, H_2O, CF_3Cl, and CF_4 quench many orders of magnitude more slowly. More recently, it has been shown that, for some of these "slow" quenchers, the rate constant of electronic quenching increases very sharply with vibration in $N_2(A)$, consistent with improved access to excited states of the quencher.[31] More quantitiative correlations with Franck-Condon factors have been sought,[4,9,32] for instance in the reactions with NO and CO, but appear to require more specific information concerning the relevant interaction potentials.

Less insight concerning the importance of vertical transitions can be obtained from the data for C_2H_4, O_2, and N_2O. For O_2, excitation by between 4.5 and 7.2 eV [the energy released in vertical transitions from $N_2(A, v = 0$ and 6), respectively] corresponds to states of O_2 below and above its dissociation limit, respectively. The measured O yields are consistent with this picture, in

showing a branching fraction for dissociation which is approximately 0.5 for reaction of $N_2(A, v = 0)$ and which increases with v.[2] Moreover, the increase in the rate constant with v is consistent with greatly improved access, via near-vertical transitions, to the excited states of O_2. For N_2O, the large yield of O atoms[2] indicates that excitation to a dissociative state of N_2O is the principal outcome of the reaction with $N_2(A)$. The absorption cross section of N_2O increases strongly with energy around 6 eV, again consistent with the increase in rate constant with v (at low v). Quenching by C_2H_4 has been ascribed to excitation of a readily accessible $\pi\pi^*$ state.[22] The reaction products are not sufficiently characterized to confirm this process, but the large rate constant, essentially independent of v, supports this mechanism.

As stated above, a curious feature of the data, particularly for O_2 and N_2O is the leveling off of the rate constants at high v, at values well below the collision number. This implies that these processes are characterized by reduced preexponential factors, only weakly dependent on vibration in $N_2(A)$. This contrasts for instance with vibrational relaxation of HCl and HF by a large number of species,[33,34] for which rate constants rise to the collision number at high v. This finding is consistent with the few measurements of the temperature dependence of $N_2(A)$ quenching. For the reactions with CO, O_2, and N_2O, Slanger et al.[24] obtained activation energies of 1.87 ± 0.40, 0.47 ± 0.32, and 0.24 ± 0.29 kcal/mole, respectively, and preexponential factors of 3.9×10^{-11}, 7.2×10^{-12}, and 9.3×10^{-12} cm^3s^{-1}, respectively. These values agree, within (their) experimental errors, with the largest rate constant for the given reagent obtained here. De Sousa et al.[16] interpreted the $N_2(A, v = 0,1,2) + O_2$ rate data between 80 and 300 K (560 K for v = 0) in terms of $k \propto T^{1/2}$, implying no activation energy in this reaction. It is concluded therefore, that constraints in addition to the Franck-Condon principle operate in these reactions, and

presumably involve restricted geometries of the transition states to achieve favorable overlap of the molecular orbitals involved. This feature is apparently not present in the reactions, for instance, of the ^3P excited states of Ar, Kr, Xe, Hg, and Cd, nor for $CO(a^3\Pi)$. These states feature either a diffuse Rydberg s orbital (Ar*, Kr*, Xe*) or a hole in a near spherically symmetric s or σ orbital (Hg*, Cd*, CO*). In contrast, the quenching of $N_2(A^3\Sigma_u^+)$ involves a $\pi^* \rightarrow \pi$ transition, and the results suggest a tantalizing increase in required geometric specificity of approach of the reagents in this case.

CH_4 and CF_4 cause vibrational relaxation of $N_2(A)$, in contrast to most of the other reagents studied here. A vibration-to-vibration (V-V) energy transfer model for these reagents has been proposed previously[7] on the basis of the small energy defects for transfer to the ν_4 (triply degenerate C-H bend) mode of CH_4 and to the ν_3 (triply degenerate C-F stretch) mode of CF_4. For both species, the energy defect decreases with increasing v; this probably contributes to the observed increases in k(v) with v.

The availability of suitable acceptor modes is a necessary, but not a sufficient condition for efficient V-V transfer; strong coupling of these modes with that of N_2 is also required. The data imply that such coupling exists for CF_4 and CH_4. It is of interest to consider why vibrational relaxation of $N_2(A)$ by O_2, CO and N_2O is <u>not</u> observed; such processes, at rates comparable to those for CH_4 and CF_4, would have been easily observable in the present study. For O_2 and CO, the acceptor frequencies, 1560 cm^{-1} and 2140 cm^{-1}, are too high for near-resonant transfer from $N_2(A, v = 1\text{-}6)$ (vibrational spacings: 1430-1290 cm^{-1}); however, for N_2O, $\nu_3 = 1280$ cm^{-1} and V-V transfer may be expected to be favorable. The measured rate data, Table 5, show that vibrational excitation of $N_2(A)$ has little effect on the rate of <u>electronic</u> quenching, which involves

dissociation of N_2O to N_2 + O. This implies that the coupling between $N_2(A)$ vibration and the NN-O stretch mode is weak, offering a possible explanation for the lack of vibrational energy transfer to the ν_3 mode, which is the low frequency stretch mode in N_2O.

The behavior of H_2 is reminiscent of that of CH_4. The temperature dependence study of Slanger et al.[24] yielded similar Arrhenius expressions for electronic quenching, with E_{act} = 7.0 ± 0.6 kcal/mol (H_2) and 6.3 ± 0.6 kcal/mol (CH_4). For these reagents, N_2 vibration appears to be much less efficient than translational energy at promoting electronic quenching of $N_2(A)$. In addition, vibrational relaxation by H_2 is clearly much slower than by CH_4, probably due to the large energy mismatch for V-V energy transfer. Ab initio calculations, currently underway on this reaction, may give insight into this behavior. End-on approach of $N_2(A)$ to H_2 is strongly repulsive. In contrast, in a parallel configuration, an adiabatic surface leads from $N_2(A)$ + H_2 to $N_2(X)$ + H + H, via an energy barrier, with a saddle point at small N_2-H_2 separations. Translational energy in the reagents can bring about the required close approach, whereas N_2 vibration, in this configuration, does not appear to provide a route towards the saddle point.

Table 1: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+,\ v<6) + O_2$

k_v, 10^{-12} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
3.8	---	---	---	---	---	---	a
3.6 ± 0.2	---	---	---	---	---	---	b
6.5	---	---	---	---	---	---	c
7.6	---	---	---	---	---	---	d
3.3	---	---	---	---	---	---	e
1.9 ± 0.3	7.4 ± 0.7	5.0 ± 0.3	3.4 ± 0.4	6.2 ± 0.9	5.8 ± 0.5	6.5 ± 0.6	f
2.9 ± 0.6	---	---	---	---	---	---	g
4.5	5.1	---	---	---	---	---	h
1.9	4.0	---	---	---	---	---	i
2.5 ± 0.4	3.9 ± 0.6	4.3 ± 0.7	---	---	---	---	j
2.3 ± 0.4	4.1 ± 0.7	---	---	---	---	---	k
2.5 ± 0.4	4.0 ± 0.6	4.5 ± 0.6	---	---	---	---	l
2.5 ± 0.5	4.3 ± 0.6	5.4 ± 0.7	5.7 ± 0.9	---	---	---	m
---	---	4.5 ± 0.5	4.9 ± 0.7	4.3 ± 0.7	3.8 ± 0.5	4.5 ± 0.7	n

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

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Table 2: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+,\ v<3) + O(^3P)$

k_v, 10^{-11} cm^3 s^{-1} vibrational level, v				
0	1	2	3	Ref.
2.2	---	---	---	a
1.5	---	---	---	b
2.8 ± 0.4	3.4 ± 0.6	---	---	c
2.8	3.3	3.6	---	d
3.5 ± 0.6	4.1 ± 0.5	4.6 ± 0.6	5.2 ± 0.8	e

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

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Table 3: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+, v<3) + NO$

k_v, 10^{-11} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
7.0	---	---	---	---	---	---	a
7.0	---	---	---	---	---	---	b
8.0 ± 0.4	---	---	---	---	---	---	c
11.	---	---	---	---	---	---	d
2.8 ± 0.5	6.6 ± 1.2	---	---	---	---	---	e
2.8 ± 0.5	4.0 ± 0.3	6.8 ± 0.8	12. ± 1.0	11. ± 1.0	10 ± 1.0	9.6 ± 0.7	f
7.5 ± 1.0	---	---	---	---	---	---	g
4.3 ± 0.5	---	---	---	---	---	---	h
11.	---	---	---	---	---	---	i
15.0 ± 3.0	---	---	---	---	---	---	j
9.0 ± 2.7	---	---	---	---	---	---	k
6.9 ± 0.9	---	---	---	---	---	---	l
6.6 ± 0.8	---	---	---	---	---	---	m
5.6 ± 0.9	7.8 ± 0.9	8.6 ± 0.9	10.4 ± 1.3	9.9 ± 1.2	12.3 ± 1.6	11.8 ± 1.5	n

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

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Table 4: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+, v<6) + C_2H_4$

k_v, 10^{-11} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
15.	---	---	---	---	---	---	a
16.	---	---	---	---	---	---	b
11. ± 1.0	---	---	---	---	---	---	c
12.	---	---	---	---	---	---	d
6.4 ± 0.6	10.8 ± 4.0	10.9 ± 0.6	11.1 ± 1.1	11.9 ± 1.1	10.9 ± 2.1	14.5 ± 2.9	e
12.0	14.0	---	---	---	---	---	f
18.0	---	---	---	---	---	---	f
10.2 ± 1.3	10.5 ± 1.3	8.9 ± 1.1	10.0 ± 1.2	9.2 ± 1.1	9.5 ± 1.2	12.0 ± 1.5	g

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

a. R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. 50 (1969) 303.

b. J. A. Meyer, D. H. Klosterboer, and D. W. Setser, J. Chem. Phys. 55 (1971) 2084.

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Table 5: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+,\ v<6) + N_2O$

k_v, 10^{-12} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
6.4	---	---	---	---	---	---	a
6.1 ± 0.9	---	---	---	---	---	---	b
14.3	---	---	---	---	---	---	c
19.9	23.2	---	---	---	---	---	d
6.4	---	---	---	---	---	---	e
7.7	---	---	---	---	---	---	f
6.2 ± 0.8	12.5 ± 1.5	14.7 ± 1.8	14.6 ± 1.8	12.6 ± 1.6	12.6 ± 1.6	13.6 ± 1.7	g

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

a. R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. 50 (1969) 303.

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f. W. G. Clark and D. W. Setser, J. Phys. Chem. 84 (1980) 2225.

g. This Lab, J. M. Thomas, F. Kaufman, and M. F. Golde, private communication.

Table 6: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+, v<6) + CO$

k_v, 10^{-12} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
2.5	---	---	---	---	---	---	a
1.5 ± 0.2	14.0 ±0.5	---	---	---	---	---	b
---	22.0	---	---	---	---	---	c
---	23/22	---	---	---	---	---	d
1.7	---	---	---	---	---	---	e
1.8 ± 0.5	18.0 ± 1.0	46.0 ± 4.0	21.0 ± 3.0	19.0 ± 2.0	16.0 ± 1.0	17.0 ± .20	f
5.0	25.0	---	---	---	---	---	g
1.5 ± 0.2	16.7 ± 2.1	48.7 ± 6.1	17.5 ± 2.4	18.9 ± 2.4	9.7 ± 1.5	14.1 ± 1.8	h

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

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Table 7: Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+,\ v\leq 6) + H_2, D_2$

	k_v, 10^{-15} cm^3 s^{-1} vibrational level, v							
	0	1	2	3	4	5	6	Ref.
H_2	3.0	---	---	---	---	---	---	a
H_2	<16.6	---	---	---	---	---	---	b
H_2	<16.6	---	---	---	---	---	---	c
H_2	1.9	---	---	---	---	---	---	d
H_2	2.4 ± 0.3	44.0 ± 4.0	---	---	---	---	---	e
H_2	---	~20	60 ± 10	140. ± 40.	250. ± 40	410. ± 100	700 ± 100.	f
D_2	---	<10	---	~100	~120	~120	~100	f

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Table 8: Vibrational Relaxation Rate Constants for $N_2(A\ ^3\Sigma_u^+,\ v<6) + CH_4$

k_v, 10^{-12} cm^3 s^{-1} vibrational level, v							
0†	1	2	3	4	5	6	Ref.
<0.007	---	---	---	---	---	---	a
<0.0017	---	---	---	---	---	---	b
<0.017	---	---	---	---	---	---	c
<0.017	---	---	---	---	---	---	d
0.0032	---	---	---	---	---	---	e
<0.01	1.1	---	---	---	---	---	f
---	1.4	---	---	---	---	---	g
---	1.5 ± 0.3	3.1 ± 0.6	5.0 ± 1.0	---	---	---	h
---	1.2 ± 0.3	2.5 ± 0.5	3.0 ± 0.5	3.8 ± 0.6	4.0 ± 0.6	5.1 ± 1.0	i

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

†Electronic Quenching.

a. R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. 50 (1969) 303.
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h. This lab, J. M. Thomas, Jay B. Jeffries, and F. Kaufman, Chem. Phys. Lett. 102 (1983) 50.
i. This lab, G. H. Ho, W. Tao, and M. F. Golde, private communication.

Table 9: Vibrational Relaxation Rate Constants for $N_2(A\ ^3\Sigma_u^+, v<6) + CF_4$

k_v, 10^{-12} cm^3 s^{-1} vibrational level, v							
0†	1	2	3	4	5	6	Ref.
<0.01	.30	---	---	---	---	---	a
---	.47 ± .09	1.8 ± 0.4	5.5 ± 1.1	---	---	---	b
---	0.29 ± .05	1.2 ± 0.2	3.4 ± 0.7	6.4 ± 1.0	13. ± 2	22. ± 4	c

The uncertainty limits reflect the 1σ uncertainties of the slopes and the estimated uncertainties of the experimental variables added in quadrature.

†Electronic Quenching.

a. L. G. Piper, W. J. Marinelli, W. T. Rawlins, and B. D. Green, J. Chem. Phys. 83 (1985) 5602.

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