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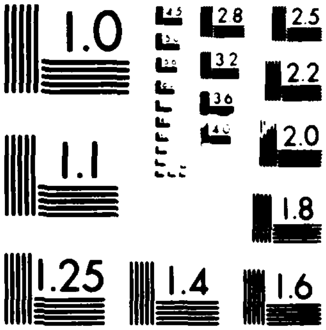
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Energy Transfer Processes of Important Atmospheric Species

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Investigation of quenching of N_2A and v-level dependence of NO product yields.

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Room temperature v-level specific bimolecular rate constants for the reaction of $N_2(A\ ^3\Sigma_u^+, v < 6)$ with efficient (O_2, $O(^3P)$, NO, C_2H_4, N_2O, and CO) and inefficient (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, $B \leftarrow A$.

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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 the inefficient electronic quenchers of $N_2(A)$ the rate constants are: $k_1 = (1.5 \pm 0.3)$, $k_2 = (3.1 \pm 0.6)$, $k_3 = (4.9 \pm 0.8)$, $k_4 = (7.3 \pm 0.9)$, $k_5 = (9.6 \pm 1.1)$, and $k_6 = (8.8 \pm 1.1) \times 10^{-12}$ $cm^3\ s^{-1}$ for CH_4; and $k_1 = (0.47 \pm 0.09)$, $k_2 = (1.8 \pm 0.4)$, $k_3 = (5.5 \pm 0.8)$, $k_4 = (9.1 \pm 0.9)$, $k_5 = (13.0 \pm 1.5)$, and $k_6 = (30.0 \pm 3.8) \times 10^{-12}$ $cm^3\ s^{-1}$ 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. The curvature observed in the vibrational relaxation studies is used to estimate the relative $N_2(A, v)$ population distribution.

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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AFGL (LIU) FINAL TECHNICAL REPORT

Energy Transfer Processes of Important Atmospheric Species

I. INTRODUCTION

The understanding and modeling of normal and 'perturbed' atmospheres requires a knowledge of production and removal processes of energetic species, both electronically charged and neutral. In the context of satellite surveillance problems and of the work currently under way in our laboratory, the emphasis is on neutral electronically excited molecular species whose importance arises in two contexts: (i) as precursors in ionization chemistry, and (ii) as emitters or emitter-precursors of radiation in the infrared or visible, particularly in the short wavelength infrared from 2 to 6 μm. There, the important emitters are NO, CO, CO_2, H_2O, N_2O, and O_3, and the radiation involves vibrational excitation processes, either by collisional energy transfer (ET) or by chemical reactions that produce the emitter in non-thermal distributions such as the steps $N_2(A, v) + CO(X, u''=0) \rightarrow N_2(X, v'') + CO(a, u')$ followed by $CO(a, u') \rightarrow CO(X, u'') + h\nu$ or $N_2(A, v') + O(^3P) \rightarrow NO(X, u'') + N(^4S, ^2D)$. The symbol 'u' will be used to denote the vibrational energy of a chemical species other than $N_2(A)$. The characterization and modeling of the radiative processes then not only requires a knowledge of the rate parameters for the production steps but also for all major loss processes such as ET and chemical removal.

Recent work in our laboratory has concentrated on the kinetics of metastable molecular nitrogen, $N_2(A\ ^3\Sigma_u^+)$. Investigations have included measuring v-level specific bimolecular rate constants for the reactions of $N_2(A, v\leq6)$ with relatively efficient electronic quenchers (O_2, NO, CO, N_2O, and C_2H_4) and inefficient electronic quenchers (CH_4 and CF_4). The latter set of quenchers has provided information on the relative $N_2(A, v)$ population distribution in the discharge flow reactor for various $N_2(A\ ^3\Sigma_u^+)$ generating reactions and N_2 concentrations. In addition, we have measured v-level specific rate constants for the reaction $N_2(A, v \leq 3) + O(^3P)$ and measured the absolute nitric oxide product yield in the reaction $N_2(A) + O_2/O(^3P)$ as a function of the relative $N_2(A, v)$ population distribution using calibrated NO LEF.

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

II. EXPERIMENTAL

The discharge flow reactor consists of three main sections: the reaction zone, the detection cell, and the main gas flow inlets/metastable generation region. 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 the modular stainless steel detection cell. The detection cell 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 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.

$N_2(A, v)$ is generated using one of three techniques: (i) $Ar(^3P_{2,0}) + N_2$, (ii) $Xe(^3P_{2,0}) + N_2$, or (iii) a low power d.c. discharge in an N_2/Ar mixture. Ar and Xe metastables are 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) and the discharge in the N_2/Ar mixture 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. As an internal sensitivity check, the v-level specific bimolecular rate constants were measured as a function of $N_2(A)$ generating reaction and N_2 fraction. There was no evidence of a systematic error being introduced into our measurements from the method used to generate $N_2(A\ ^3\Sigma_u^+)$ or from the relative $N_2(A, v)$ population distribution which resulted from variations in the N_2 fraction used.

The $N_2(A, v)$ and $NO(X, v = 0)$ LEF excitation source consists of a computer controlled (Tandy, Model TRS-80 Model II) N_2 laser pumped dye laser (Lambda Physik, Models M1000 and FL2000). To monitor the relative concentration of the $N_2(A, v)$, the dye laser is operated with either Rhodamine 610 ($N_2(A, v<2)$) or Rhodamine 590 ($N_2(A, 3<v<6)$). The dye laser is operated with Coumarin 450 dye to measure the absolute concentration of the product NO.

The relative concentrations of the lowest seven vibrational levels of $N_2(A)$ are 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 is 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 is due to the $\Delta v = v'' - v' = 0, -1, -2$, and -3 transitions of the First Positive System ($B \rightarrow A$).

The absolute concentration of the product NO is 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 of the solar blind PMT was collected. The NO LEF signal is calibrated using an NO mixture in He. Typically a detection limit of $\sim 2 \times 10^7$ cm^{-3} was achieved.

The concentration of the stable reactant (O_2, CO, NO, C_2H_4, N_2O, CH_4, and CF_4) is determined from the measured pressure rise in a calibrated volume. The concentration of atomic oxygen is 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 $[O(^3P)]$ is measured using a calibrated O + NO 'air afterglow'. The 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.

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 are 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, 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. For the inefficient electronic quenchers, the data at large [Q] were used to calculate the slope where interference due to cascade from the higher vibrational levels is negligible.

III. RESULTS AND DISCUSSION

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] were linear in all cases. This indicates that cascade formation of level v by collisional deactivation of higher levels is unimportant, and the processes were 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 all showed negative curvature, indicating formation of level v by collisional vibrational relaxation of higher levels. Indeed the concentration of $N_2(A, v = 0)$ increased 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, mentioned briefly later in this report, suggest that vibrational relaxation by CH_4 and CF_4 occurs mainly by $\Delta v = -1$ transitions in $N_2(A)$.

A. Ineffîcient Electronic Quenchers.

A summary of the bimolecular rate constants reported in the literature and those obtained in the present investigation for the reaction of $N_2(A\ ^3\Sigma_u^+) + CH_4$ is presented in Table 1. Our observation of a very slow electronic quenching of $N_2(A, v = 0)$ by CH_4, i.e., growth in the $N_2(A, v = 0)$ LEF signal with added CH_4, is in full agreement with Clark and Setser[1] who reported an upper limit of 1×10^{-14} cm^3 molecule^{-1} s^{-1} and with other investigators,[2-6] particularly with Slanger et al.[6] who studied the temperature dependence of the reaction and reported a $k_0 = 3.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K. For $N_2(A\ v = 1) + CH_4$ our measured $k = (1.5 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is in excellent agreement with that reported by Piper et al.[7] These results are in satisfactory agreement with the k_1 reported by Clark and Setser,[1] and Taylor and

Setser,[8] for the same process, particularly since they did not correct for the development of a parabolic velocity profile, whereas we use a value of $\alpha = 1.34$. Very good agreement for k_3 is found between the two segments of our investigation (Entries h and i in Table 1). We are unaware of any previous work reported in the literature for $N_2(A, v>1) + CH_4$.

A summary of the bimolecular rate constants reported in the literature and those obtained in the present investigation for the reaction of $N_2(A\ ^3\Sigma_u^+) + CF_4$ is presented in Table 2. As in the case of the CH_4 investigation, our observation of a very slow electronic quenching of $N_2(A, v = 0)$ by CF_4 is consistent with Piper et. al.[7] who reported an upper limit of 1×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. For $N_2(A, v = 1)$ our result is in satisfactory agreement with Piper et al.[7]. As in the CH_4 investigation, we are unaware of any previous work reported in the literature for $N_2(A, v>1) + CF_4$.

The observed vibrational level behavior of the bimolecular rate constants for the vibrational relaxation of $N_2(A)$ by CH_4 and CF_4 is consistent with the 'Energy Gap' model for pure vibrational-to-vibrational (V-V) ET. The acceptor modes are assumed to be the triply degenerate C-H bend, $\nu_4 = 1306$ cm^{-1}, and the triply degenerate C-F stretch, $\nu_3 = 1283$ cm^{-1}. Other fundamental frequencies are too low for CF_4 and too high for CH_4.

The curvature observed in the $N_2(A, v) + CH_4/CF_4$ plots of $\ell n I_{LEF}$ vs [Q] was used to extract the relative $N_2(A, v)$ population distributions for various generating reactions and N_2 concentrations. These population distributions compare satisfactorily with those determined directly from corrected $N_2(B-A)$ LEF signal intensities, and with predictions made using models developed in our lab of the radiative and collisional processes in the triplet manifold of electronically excited N_2, as shown in Table 10 for an N_2 fraction of ~20% of the total flow. With the exception of $N_2(A, v = 4$ and $5) + CH_4$ the curvature observed in the plots can be explained on the basis of the $\Delta v = -1$ relaxation of $N_2(A)$. At present, the deviation from the expected behavior for these levels has not been explained.

B. Efficient Electronic Quenchers

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

A summary of the v-level specific bimolecular rate constants for the reaction of $N_2(A, v<6) + O_2$ reported in the literature and those measured in the present investigation is presented in Table 3. Although not shown in Table 3, Dreyer et al.[13] 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,[9] Piper et al.,[10] Zipf,[11] and De Souza et al.[12] Our v = 0 measurement is also in good agreement with Dreyer et al.[13] and Dunn and Young.[14] None of the reported investigations confirm the relative maximum in rate constant observed by Dreyer et al.[13] 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[15] in which they monitor the formation of $O(^3P)$ for the reaction of $N_2(A, v = 0) + O_2$ and the reaction of $N_2(A, v>0) + O_2$. They also observe an increase in the $O(^3P)$ branching fraction when the population distribution $N_2(A)$ is shifted to favor v>0.

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 4. Our values for k_0 and k_1 are in good agreement with those of Piper et al.[16] and De Souza et al.[17,18] Agreement with the less direct measurements of Meyer et al.[19] and Dunn and Young[14] 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 ~6×10^{-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 3).

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,[20] it was necessary to verify that the reaction of $N_2(A)$ with undissociated O_2 did not produce NO which could interfere 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 $N_2(A, v<3)$ the NO LEF signal was reduced by a factor of ~2, down into the noise in the NO background signal from the microwave discharge in the O_2/He mixture.

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 $v<6$. Second, the NO + $N(^4S, ^2D)$ product yield accounts for less than ~2% of the $N_2(A, v<2) + O(^3P)$ interaction. This is qualitatively consistent with the high $O(^1S)$ yields observed previously,[18,21] 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. $N_2(A, v<6) + NO \rightarrow$ 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 5. We observe an increase in quenching rate with v for $0<v<3$ followed by an apparent leveling off for $3<v<6$. Taking an average of the rate constants for $3<v<6$, 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 5, Dreyer et al.[13] 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 = $(6.7 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

A majority of the previous measurements have been indirect and/or limited to v = 0 and 1 (See Table 5). For $v>3$, our measurements are in good agreement with the measurements of Dreyer et al.[13] We do not confirm the small decrease in quenching rate at high v observed by Dreyer et al. For $N_2(A, v<2)$, there have been many measurements reported in the literature with rate constants ranging from 2.8 to 15 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Most of the measurements have involved systems where the quenching rate constant for v = 0 and 1 were not resolvable because of the use of tracer emission to monitor $N_2(A)$. Our rate constant for v = 0 is in satisfactory agreement with the less direct measurements of Piper et al.[22] but a factor of ~2 larger than that measured by Dreyer et al. We can determine a total removal rate 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.[23] This would give a total removal rate of $(6.6 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} in satisfactory agreement with recent work by Shibuya et al.[24]

The observed increase in k_v between v = 0 and 3 can be explained in two ways. First, the energy released in the vertical (Franck-Condon favored) transitions from $N_2(A, v)$ to $N_2(X, v)$[25] increases from ~4.6 eV for v = 0 to ~5.9 eV for v = 2. The dominant reaction channel

$$N_2(A, v') + NO(X, u'') \rightarrow N_2(X, v'') + NO(A, u')$$

requires transfer of at least 5.5 eV of energy, i.e., $NO(X, u'' = 0) + 5.5\ eV \rightarrow NO(A, u' = 0)$. Although the Franck-Condon overlap does not appear to be a dominant factor in the deactivation of $N_2(A, v<2)$ by NO, i.e., $k_0 \sim 20\%$ of gas kinetic, the presence of favorable Franck-Condon overlap, which increases with v' in the Vegard-Kaplan $A \rightarrow X$ system, does seem to enhance the energy transfer process, i.e., $k_1 \sim 26\%$ of gas kinetic and $k_2 \sim 30\%$ of gas kinetic. And second, for $N_2(A, v<2)$, a second reaction channel is energetically accessible, i.e., $N_2(A, v<2) + NO(X) \rightarrow N_2(X) + N + O$. A previous study has provided indirect evidence for this channel.[26]

5. $N_2(A, v<6) + C_2H_4 \rightarrow$ 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 6. Previous work, with the exception of Dreyer and Perner,[27] has been limited to v<1.[1,2,3,4,27,28] For the electronic deactivation of $N_2(A, v = 1)$ by C_2H_4, our results are in very good agreement with the results of Callear and Wood[2] and Dreyer and Perner.[27] Our results do not confirm the k_0 obtained by Dreyer and Perner[27] but are in good agreement with the rate constant reported by Callear and Wood[2] 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[27] 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.[4] 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_2 is presented in Table 7. Excellent agreement is found for k_0 with the work of Young et al.,[3] Callear and Wood,[2] and Slanger et al.[6] For the electronic deactivation of $N_2(A, v = 1)$ by N_2O our bimolecular rate constant is approximately a factor of 2 less than that reported by Meyer et al.[4] 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. The observed v-level behavior of the bimolecular rate constants for the E-E energy transfer between $N_2(A, v)$ and N_2O appears qualitatively to track predictions derived from considering the Franck-Condon weighted $N_2(A, v' - X, v'')$ transitions.[29,30]

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 8. Previous work, with the exception of Dreyer et al.,[13] 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,[2] Slanger et al.,[6] and Dreyer et al.[13]. Comparison with the k_0 reported by Young et al.[3] 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 5) and by Piper et al.[22] For $N_2(A, v = 1) + CO$ our k_1 is in very good agreement with that reported by Dreyer et al.,[13] but ~30% lower than that reported by other investigators.[1,2,4,5] For $N_2(A, v>1)$ our measurements are in very good agreement with those reported by

Dreyer et al.[13] 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 relative 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 $N_2(A, v= 2) + CO(X, u'' = 0)$. The major product in the reaction of $N_2(A) + CO$ appears to be $CO(a, u')$.[31,32] As first suggested by Dreyer et al.,[13] 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.[4,5] and Clark and Setser[1] have suggested that the rate constant k_0 obtained by Callear and Wood,[2] and Dreyer et al.,[13] is too small, due to interference from the reverse reaction $CO(a) + N_2(X, v'' = 0) \rightarrow CO(X, u'') + N_2(A, v' = 0)$, $k = 2.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.[8] This channel represents ~25% of the total CO(a) deactivation by N_2.[8] To investigate the effect of the reverse 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 the $N_2(A, v')$ and $CO(a, u')$ were simulated as a function of k and compared to the observed concentration profiles. From the apparent insensitivity of the bimolecular rate constants to changes in the relative population of $N_2(A, v)$ and the results of the simulations, we conclude that the ratio k_1/k_0 obtained in our measurements and those reported by Callear and Wood,[2] and Dreyer et al.[13] are valid. It is possible that there is a systematic error in the measurements reported by Meyer et al.[4,5] and Clark and Setser.[1] 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 5), $N_2(A\ ^3\Sigma_u^+)$ + C_2H_4 (Table 6), $N_2(A\ ^3\Sigma_u^+)$ + N_2O (Table 7) and $N_2(A\ ^3\Sigma_u^+)$ + O_2 (Table 3).

IV. UNFINISHED WORK AT THE END OF THE CONTRACT

A. $N_2(A, v = 7) + Q$

Efforts have been made to detect $N_2(A, v = 7$ and $8)$ in the discharge flow reactor. Recently, $N_2(A, v = 7)$ has been detected using LEF techniques. Unfortunately, the net LEF signal is ~70 counts in 10 seconds on top of a background of ~12,000 counts in 10 seconds. This signal-to-background could be improved by using narrow band pass interference filters to selectively pass radiation specific to the $N_2(A, v'' = 7)$ and by shortening the $N_2(A)$ residence time in the flow reactor. With a shortened reaction time, we should be able to monitor the relative concentration of $N_2(A, v = 8)$ by LEF.

B. $N_2(A, v) + H_2/H \rightarrow$ Products

A summary of the rate constants reported in the literature and preliminary results of those obtained recently in our lab is presented in Table 9. As can be seen, previous work is limited to $v \leq 1$ for $N_2(A) + H_2$ and $v = 0$ for $N_2(A) + H$. Although the primary goal of the present investigation is to measure the v-level specific bimolecular rate constants and products for the reaction of $N_2(A) + H$, it was first necessary to investigate the interaction of $N_2(A)$ with molecular hydrogen so that corrections to be made for the presence of undissociated H_2 in the flow reactor to the H-atom removal rates.

For the interaction of $N_2(A) + H_2$, there appears to be a very strong v-level dependence on removal rate, i.e., $k_6/k_0 \sim 272$. The only energetically accessible reaction path involves the dissociation of H_2. We have observed no evidence, at least for high-v, for the vibrational relaxation of $N_2(A, v)$ by H_2. We estimate the quenching rate for $N_2(A, v = 2) + H_2O$ to be $\sim 65.0 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}.

For the interaction of $N_2(A, v) + H$, the v-level specific bimolecular rate constants will be measured. In addition, the formation of NH will be studied as a function of vibrational energy.

Table 1: 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
-------	---------	---------	4.8 ± 0.5	7.3 ± 0.9	9.6 ± 1.1	8.8 ± 1.1	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.

b. A. B. Callear and P. M. Wood, Trans. Faraday Soc. 67 (1971) 272.

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Table 2: 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							
$0^\dagger$	1	2	3	4	5	6	Ref.
<0.01	.30	---------	---------	---------	---------	---------	a
-------	.47 ± .09	1.8 ± 0.4	5.5 ± 1.1	---------	---------	---------	b
-------	---------	---------	5.5 ± 0.6	9.1 ± 0.9	13. ± 1.5	30. ± 3.8	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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Table 3: 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.

a. R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. 50 (1969) 303.
b. A. B. Callear and P. M. Wood, Trans. Farad. Soc. 67 (1971) 272.
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Table 4: 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 5: 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 6: 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.

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Table 7: Electronic Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+,\ v\leq 6) + N_2O$

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

Table 8: 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 9: Quenching Rate Constants for $N_2(A\ ^3\Sigma_u^+, v<6) + H_2$

k_v, 10^{-15} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
3.0	---------	---------	---------	---------	---------	---------	a
<16.6	---------	---------	---------	---------	---------	---------	b
<16.6	---------	---------	---------	---------	---------	---------	c
1.9	---------	---------	---------	---------	---------	---------	d
2.4 ± 0.3	44.0 ± 4.0	---------	---------	---------	---------	---------	e
---------	---------	---------	144. ± 23.	221. ± 29	347. ± 52.	652 ± 111.	f

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

k_v, 10^{-12} cm^3 s^{-1} vibrational level, v							
0	1	2	3	4	5	6	Ref.
3.5	---------	---------	---------	---------	---------	---------	a

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Table 10: Observed and Predicted $N_2(A, v<2)$ Populations for the $Ar^* + N_2$ generating reaction (a).

v-level	Experimental (b)	 (c)	Simulation (d)
0	(0.61±0.05)	(0.63±0.04)	0.57
1	(0.29±0.05)	(0.29±0.05)	0.33
2	(0.11±0.02)	(0.08±0.02)	0.10

a. The population distributions are for t ~ 0.003 ms downstream of the N_2 inlet system. The N_2 fraction is ~20% of the total flow.

b. Population distribution obtained from the analysis of the curvature in the $N_2(A, v) + CH_4$ and CF_4 plots (J. M. Thomas, J. B. Jeffries, and F. Kaufman, Chem. Phys. Letters 102 (1983) 50).

c. Population distributions obtained from the analysis of the curvature in the $N_2(A, v) + CH_4$ and CF_4 plots and reanalyzed using a non-linear fitting routine.

d. Simulation based on radiative $N_2(C-B)$ cascade, radiative $N_2(B-A)$ cascade and $N_2(B-W)$ radiative and collisional coupling.

LIST OF PUBLICATIONS IN REFEREED JOURNALS SINCE 1983

Joseph M. Thomas, Jay B. Jeffries, and Frederick Kaufman, "Vibrational Relaxation of $N_2(A\ ^3\Sigma_u^+$, v = 1, 2, and 3) by CH_4 and CF_4," Chem. Phys. Letters 102 (1983) 50.

J. M. Thomas and F. Kaufman, "Rate constants of the reaction of metastable $N_2(A\ ^3\Sigma_u^+)$ in v = 0, 1, 2, and 3 with ground state O_2 and O," J. Chem. Phys. 83 (1985) 2900.

PUBLICATIONS TO BE SUBMITTED

J. M. Thomas, J. A. McCaulley, and F. Kaufman, "Determination of NO formation in the reaction of $N_2(A\ ^3\Sigma_u$, v) with $O(^3P)/O_2$ at 300 K," to be submitted, Chem. Phys. Letters.

J. M. Thomas, F. Kaufman, and M. F. Golde, "Vibrational relaxation of $N_2(A\ ^3\Sigma_u^+$, $3<v<6$) by CH_4 and CF_4: An extension of previous work," to be submitted, J. Chem. Phys.

J. M. Thomas, F. Kaufman, and M. F. Golde, "Vibrational level specific bimolecular rate constants for the reactions of $N_2(A\ ^3\Sigma_u^+$, $v<6$) with NO, C_2H_4, N_2O, CO, and O_2," to be submitted, J. Chem. Phys.

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