Semiannual Technical Report No. 1

EXCITATION AND DEEXCITATION OF VIBRATION IN GASES BY OXYGEN AND NITROGEN ATOMS

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EXCITATION AND DEEXCITATION OF VIBRATION IN GASES BY OXYGEN AND NITROGEN ATOMS

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SYNOPSIS

The earth's upper atmosphere continuously emits infrared radiation. Some of this radiation is powered by the energy stored in vibrationally excited nitrogen, which can be produced by a number of exothermic processes. One of these is the reaction of nitric oxide with nitrogen atoms, in which 3.27 eV is available for vibrational and rotational energy of the nitrogen, as well as kinetic energy. The first goal of the current program was to determine the fraction of the energy appearing in nitrogen vibrations, using Raman spectroscopy to determine the population of $N_2(v=1)$ that is produced. The measurements are under way, and a very preliminary result is that 26 ± 8% of the exothermicity of the reaction appears as vibrational energy in the nitrogen.

Once produced, the vibrationally excited nitrogen is deexcited only by collisions. The most important deexcitation mechanisms are energy transfer to CO_2 in the lower E region, the rate for which is moderately well known, and diffusion, electron quenching, and V-T energy exchange with $O(^3P)$ in the upper E region and higher. The rate coefficients for the latter process are not known for the temperatures found in the earth's atmosphere. A second goal of our work (Task II) was, therefore, to measure this rate down to as low a temperature as possible, using a shock tube with ozone as the source of atomic oxygen. Measurements are under way, using the infrared-tracer method first used by R. C. Milliken and D. R. White in 1963, to monitor the vibrational energy of the nitrogen. The initial results are promising, and it is anticipated that measurement of the vibrational-translational energy exchange of $N_2(v=1)$ with $O(^3P)$ can be made to ~1400°K.

INTRODUCTION

In the E region of the earth's atmosphere, a number of exothermic chemical reactions occur that can produce $N_2^{\ddagger}$, vibrationally excited nitrogen. In the lower E region (below 125 km) the major loss of nitrogen vibrational energy is by energy transfer to CO_2,

$$N_2\ (v=1) + CO_2 \rightarrow CO_2\ (\nu_3=1) + N_2 - 18\text{cm}^{-1}\ , \qquad (1)$$

with subsequent radiation in the infrared (principally at 4·3 μ). Processes that excite or deexcite $N_2^{\ddagger}$ are thus of particular interest in connection with some defense problems concerned with atmospheric infrared measurements.

The main processes that have been considered for producing $N_2^{\ddagger}$ are:

$$N(^4S) + NO \rightarrow N_2 + O(^3P) + 3{\cdot}27\ \text{eV} \qquad (2)$$

$$O(^1D) + N_2 \rightarrow N_2 + O(^3P) + 1{\cdot}96\ \text{eV} \qquad (3)$$

$$N_2(A^3\Sigma_u^+) + O(^3P) \rightarrow N_2 + O(^3P, {}^1D, {}^1S),\ \Delta E = 6{\cdot}2,\ 4{\cdot}2,\ 2{\cdot}0\ \text{eV} \qquad (4)$$

$$N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2 + O_2(^3\Sigma, {}^1\Delta, {}^1\Sigma),\ \Delta E = 6{\cdot}2,\ 5{\cdot}2,\ 4{\cdot}6\ \text{eV} \qquad (5)$$

$$e^- + N_2 \rightarrow (N_2^-) \rightarrow N_2^{\ddagger} + e^- \ . \qquad (6)$$

Also, emission of Vegard-Kaplan band radiation by $N_2(A^3\Sigma_u^+)$ will, in most instances, leave N_2 vibrationally excited. Whereas process (6) is certainly important in auroral conditions, it is not important in the undisturbed E region.

If all these processes were equally effective (as a fraction of the energy available) in producing $N_2^{\ddagger}$, then, in the E region, process (3) would produce more $N_2^{\ddagger}$ than process (2) and the latter more than the sum of processes (4) and (5). The first goal of the studies at SRI has, therefore, been investigation of processes (2) and (3).

A second aspect of the atmospheric processes powering emissions through $N_2^‡$ concerns the reactions that can quench it in the upper atmosphere. The most important deexcitation mechanisms have been considered to be energy transfer to CO_2 in the lower E region [process (1)], the rate for which is moderately well known, and diffusion, electron quenching, and V-T energy exchange with $O(^3P)$ in the upper E region and higher. The rate coefficients for the latter process are not known for the temperatures found in the earth's atmosphere. A second goal of our work (Task II) has, therefore, been measurement of this rate for temperatures approaching 1200°K or lower, using a shock tube. (Until now measurements have been made only above 3000°K.[1*])

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[*] References are listed at the end of the report.

RESEARCH PROGRAM AND PLAN

Task I. Vibrational Population Measurements

One aim of the Task I program has been to determine the efficiency with which processes (2) and (3) produce $N_2^{\ddagger}$.

Last year our measurements were confined to reaction (3)--the quenching of $O(^1D)$ by nitrogen. The vibrationally excited nitrogen was measured by Raman spectroscopy. During the period of that experimental program, a theoretical study by E. R. Fisher and E. Bauer concluded that less than 5% of the $O(^1D)$ electronic energy is channeled into the vibrational levels of N_2. Our experimental findings supported the estimate. Our results gave an efficiency of 8.3 ± 6.5% for the conversion of $O(^1D)$ electronic energy to N_2 vibrational energy. The total uncertainties in this measurement exceeded the 6.5% statistical error indicated above and made further work on this reaction desirable. An objective of the current program has been to perform such measurements by using CO as an infrared-emitting tracer of the $N_2^{\ddagger}$.

Measurements of process (2) a decade ago[2-4] indicated that about 30% of the exothermicity of the reaction appears in $N_2^{\ddagger}$. If this is true, and if the efficiency of (3) is as low as was indicated by both the theoretical study and our initial experimental results, then process (2) is much more important than (3) as a source of $N_2^{\ddagger}$. For these reasons, we proposed that a measurement of the efficiency of production of $N_2^{\ddagger}$ in process (2) should be a primary part of the present program.

We had intended to make measurements of process (2) also by the infrared-tracer technique with CO. Unknown to us at the time of writing the proposal, such a program was already under way at Air Force

Cambridge Research Laboratories. That program revealed serious problems in interpretation when the infrared-tracer technique was applied to process (2). Early in March 1972, the Optical Physics Group of A. T. Stair at AFCRL discussed their findings with us. The problems have also been discussed with Drs. Gilmore and Bauer. In all these discussions it has generally been agreed that process (2) should be given high priority and that the preferable technique for studying it would be the Raman scattering technique for measuring $N_2^‡$. It was anticipated that the Raman technique would be easier to apply to process (2) than it was, in our earlier work, to process (3), both because much higher initial populations of N atoms could be created than was possible with $O(^1D)$ and because of the expectation[2-4] that about 30% of the reaction energy would appear as vibrations in N_2.

Although the main goal of the measurements was to obtain reliable information on the N + NO reaction, it was hoped that the use of the Raman technique for reaction (2) would reveal the causes of the difficulties encountered at AFCRL in using the infrared-tracer technique on that reaction. In this way it should be possible to improve the reliability of the infrared technique.

Task II. Deexcitation of $N_2(v=1)$ by $O(^3P)$

The objective of Task II was to extend to significantly lower temperatures the shock-tube measurements of the V-T transfer between $N_2^‡$ and $O(^3P)$ made by Breshears and Bird[1] in the temperature range $3000 < T < 4500^oK$. To accomplish this, we adapted the infrared-tracer method, in which the 4.7-micron radiation from (typically) 1% added CO is proportional to the vibrational energy of the N_2. The $O(^3P)$ is generated by thermal dissociation of O_3 behind the shock wave.

Last year we developed the infrared measurement technique and made measurements of N_2 - CO and N_2 - CO - O_2 mixtures. During the reporting period we made additional N_2 - CO - O_2 measurements, as well as a number of N_2 - CO - O_3 measurements. In these experiments we showed that infrared intensity histories can be obtained that are free of interference from extraneous sources, such as radiation from CO_2 formed by reaction of CO and O. We also investigated the influence of the presence of such species as CO, O_2, and CO_2 on the results. Finally, we undertook examination of the errors introduced by uncertainties in rates of thermal dissociation of ozone. On the basis of our findings, we anticipate being able to determine the V-T rate for N_2 - $O(^3P)$ energy transfer, at least down to 1500^oK.

ACCOMPLISHMENTS

Task I. Vibrational Population Measurements

The reaction

$$N(^4S) + NO \rightarrow N_2\ (v=n) + O(^3P) \qquad (2)$$

is fast ($\approx 2 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1} at room temperatures[5,6]) and is sufficiently exothermic (3·27 eV) to produce $N_2^{\ddagger}$ up to n=12. It is expected[2-4,7-12] that the initial vibrational distribution will be rapidly degraded by vibrational exchange collisions of the type

$$N_2(v=n) + N_2(v=0) \rightarrow N_2(v=n') + N_2(v=n-n') \qquad (7)$$

to produce a higher-temperature Boltzmann population of $N_2(v=1)$. Hence a measurement of thermalized $N_2(v=1)$ should be sufficient to determine the fraction of the exothermicity of reaction (2) that appears as vibrational energy. During the reporting period such measurements were undertaken by observing Raman scattering of 4880 Å Ar^+ laser radiation. The intensity of the Q-branch of the anti-Stokes transition (at 4382 Å) is being measured, because the anti-Stokes spectra are free from Raman transitions due to the $N_2(v=0)$ level [whereas the Stokes transitions from $N_2(v=1)$ lie in the rotational structure of the Stokes lines from $N_2(v=0)$].

Experiment

The experimental arrangement is shown schematically in Fig. 1. Molecular nitrogen is partially dissociated by a microwave discharge in a flow system having a linear flow velocity of about 400 cm sec^{-1}. The nitrogen atom can be titrated with NO at any of six fixed inlet jets at 8, 15, 30, 42, 65, and 100 cm from the pyrex cell (referred to as inlets 1 through 6, respectively). The output of an Ar^+ ion laser traverses

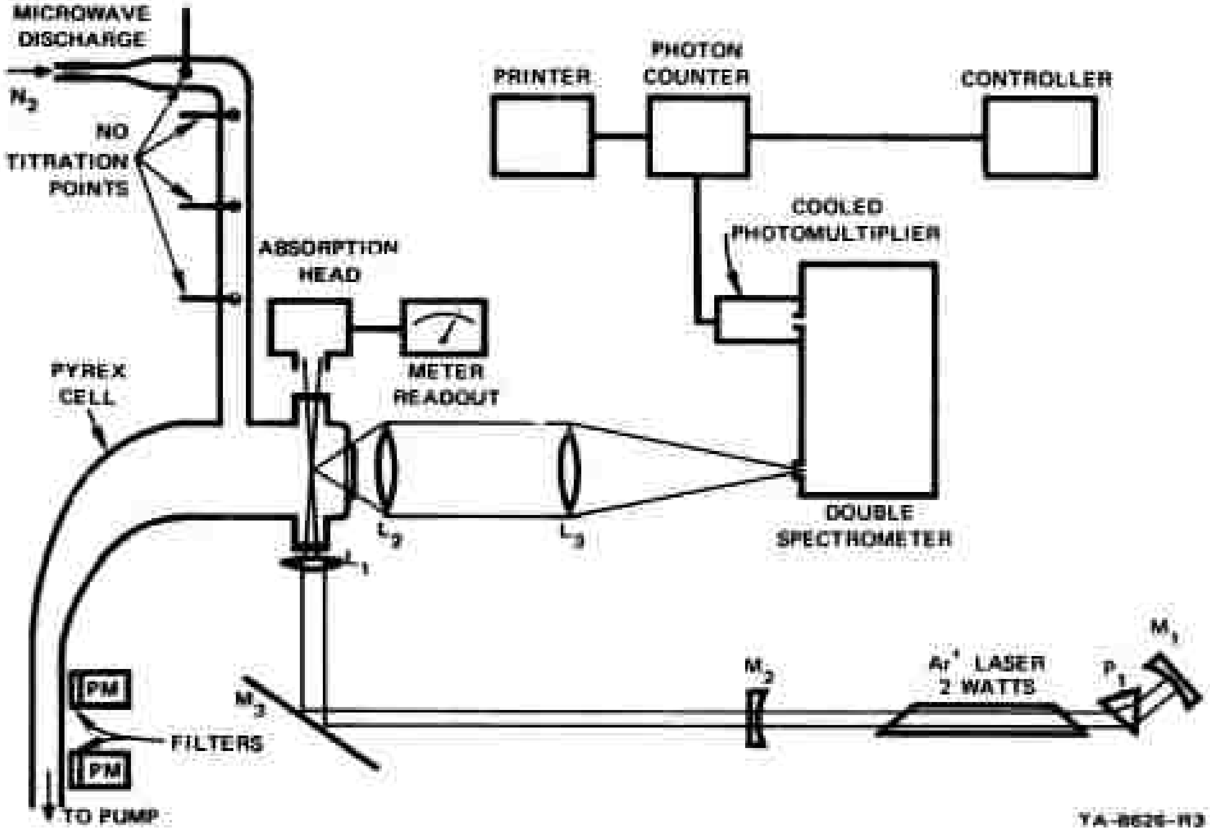

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FIGURE 1 EXPERIMENTAL ARRANGEMENT FOR RAMAN SPECTROSCOPY. The lens L_2, which has an aperature ratio of f/0.95 and a focal length of 5 cm, collects the Raman-scattered light over a large solid angle.

this cell and is focused to a point within it. This focal point is imaged on the slit of a spectrometer by a second optical system. The light passing through the exit slit of this spectrometer is imaged on the photocathode of a photomultiplier. Its output is measured in a pulse-counting system and then printed out after a predetermined counting time (governed by the setting of the controller).

The first experiments were made without the laser, to determine the magnitude of the interference from emissions of the titrated afterglow. The nature of this problem can be seen in Fig. 2, which shows the light signal at 4382 Å from the afterglow as a function of NO addition. The signal reaches a minimum of ~10 counts $\sec^{-1}$ (which includes a dark count of ~5 $\sec^{-1}$) when the NO is just sufficient to remove the N atom by process (2) (called "null"). Further addition of NO generates the NO_2 continuum by the reaction of the excess NO with the oxygen atoms, that is,

$$NO + O + M \rightarrow NO_2 + M^* \quad , \tag{8}$$

followed by

$$NO_2^* \rightarrow NO_2 + h\nu \; (3875\text{-}14{,}000 \text{ Å}) \quad . \tag{9}$$

Thus when NO is in excess, radiation from process (9) is transmitted by the filter at 4382 Å.

When insufficient NO is added, the signal arises from the generation of NO β-bands by the chemiluminescent recombination of oxygen and nitrogen atoms, that is,

$$N + O + M \rightarrow NO\,(B^2\Pi_r) + M \tag{10}$$

$$NO(B^2\Pi_r) \rightarrow NO\,(X^2\Pi_r) + h\nu(\beta\text{-bands}) \quad . \tag{11}$$

The light being transmitted by the spectrometer at 4382 Å is in the tail of the (0,13) band, with its head at 4309·7 Å (the bands are degraded to

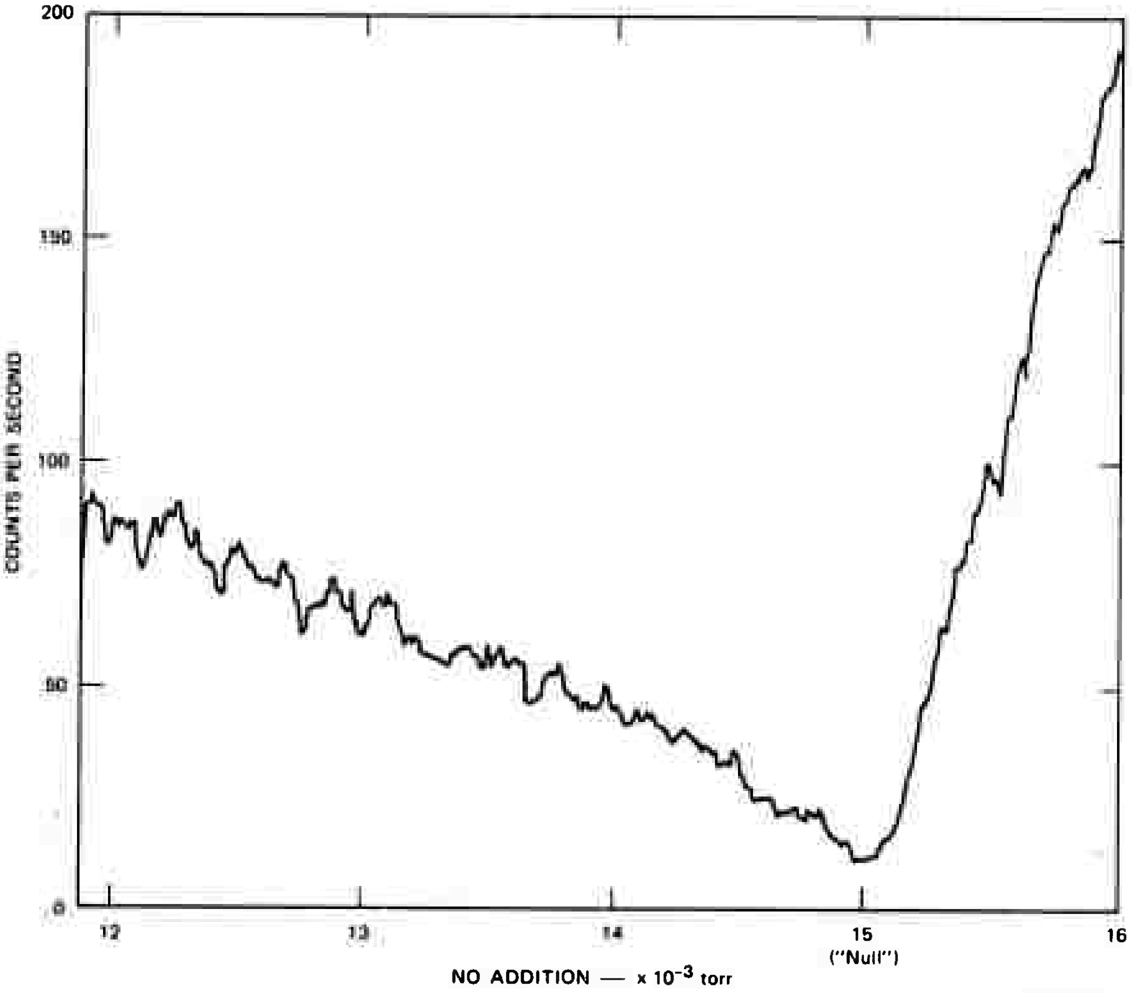

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FIGURE 2 LIGHT SIGNAL AT 4382 Å FROM MICROWAVE-DISCHARGED N_2 AT 3 TORR AS A FUNCTION OF NO ADDITION CLOSE TO THE EQUIVALENCE POINT ("NULL"). Spectrometer band pass ~1.1 Å. Titration performed 100 cm (~0.25 second flow time) from cell.

longer wavelengths). [The bandpass of the spectrometer (~1·1 Å) was such as not to transmit any of the short wavelength head of the (1,14) band at 4385·7 Å.]

The trace on Fig. 2 clearly demonstrates the need to maintain the NO addition as close to the null point as possible. To do this the valve controlling the NO addition was coupled to a servo-controlled motor. The inputs to the motor controller were derived from two 1P21 photomultipliers viewing the afterglow downstream of the pyrex cell. One photomultiplier "sensed" the continuum through a 5622 Å interference filter (10 Å half-width), while the other viewed the afterglow through a Kodak 18A filter and was therefore sensitive only to the NO β-bands. With this arrangement it was possible to maintain the NO addition within 1% of null. Therefore, for Raman measurements on the titrated afterglow, the servo-controlled motor was always used to regulate the NO addition.

The measurements during the reporting period were made with an EMI 6256S phototube with 20-dB attenuation inserted in the line between the photomultiplier base and the photon counter, to provide the greatest freedom from rf pickup. The best signal-to-dark count was obtained with 1200 V on the photomultiplier, which resulted in a 75% counting efficiency and a dark count of ~5 sec^{-1}.

Before making any Raman measurements, the position of lenses L_1 and L_2 was adjusted to provide the biggest Rayleigh-scattered light signal (with N_2 at 600 torr in the cell) using the 4579 Å laser line (the shortest wavelength laser line and hence that closest in wavelength to the position of the anti-Stokes line at 4382 Å). This focus was periodically checked but was found to require very little adjustment on a daily basis. The wavelength error in the readout of the spectrometer was periodically checked with the 4358·3 Å line of Hg. It did not change during the course of these measurements.

Because of the scattered light from both the afterglow and the laser,* the Raman signal had to be extracted from the counts C_i obtained in four consecutive counting periods of equal length. From such a sequence, which we define as an "experiment," the Raman signal is obtained from

$$\text{Raman counts} = C_2 + C_4 - C_1 - C_3 \quad , \tag{12}$$

where C_2 is the count obtained with the microwave discharge and laser on (and hence includes the Raman signal together with the scattered light from both sources and the dark count); C_4 is the photomultiplier dark count (microwave discharge and laser off); C_1 is the count with only the microwave discharge on; and C_3 is the count with only the laser on. For most of the experiments, the counting period has been 5 minutes.

Theory

The partial pressure of $N_2(v=1)$, $P_{N_2(v=1)}$, that can be produced by a partial pressure P_N(torr) of nitrogen atoms reacting with NO is given by

$$P_{N_2(v=1)} = 12\, P_N\, f \quad , \tag{13}$$

where f is the fraction of the exothermicity of the reaction (3·27 eV) that is converted to vibrational energy in N_2, and the factor of 12 is introduced because each reaction can populate up to $N_2(v=12)$. Collisions will then rapidly convert the initial distribution to a Boltzmann one which, for vibrational temperatures $<600^{\circ}$K, will have over 99% of the vibrationally excited molecules in v=1.

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* The small scattered light signal from the laser arises from the 4379·7 Å argon line emitted by the discharge in the laser cavity.

Because of the flow time from the titration point to the cell, some vibrational energy may be lost prior to the measurement of $N_2(v=1)$ in the cell. For this reason a number of titration points were provided. The signal could then be measured as a function of distance from the titration point to the cell and extrapolated to zero distance.

Results

Prior to commencing actual experiments, we measured the intensity of the anti-Stokes line at 4382 Å with nitrogen alone in the cell (heated to 220°C). Such measurements provide a convenient means[13] for determining the conversion factor from Raman counts/sec to partial pressure of $N_2(v=1)$. Our measurements established that, depending mainly on the spectrometer settings (slit width and length), the sensitivity was from 10 to 100 counts sec^{-1} $[torr\ N_2(v=1)]^{-1}$.

The initial measurements soon established that a large Raman count and hence a large pressure of $N_2(v=1)$ existed in the microwave-discharged N_2, even without titrating the N atoms. The magnitude of this signal as a function of N_2 pressure is shown in Table 1. The pressure of $N_2(v=1)$ in the last column is obtained by dividing the Raman counts/sec by the sensitivity for the spectrometer settings used--in this case 40 counts sec^{-1} $[torr\ N_2(v=1)]^{-1}$.

It was observed that the addition of NO to the "null" titration point, instead of increasing the above signals [by producing more $N_2(v=1)$], actually reduced them. The reduction was greater the further the titration point was from the pyrex cell--ranging from 25 to 30% for titration 15 cm from the cell (inlet No. 2) to ~90% when the titration was performed 100 cm from the cell (inlet No. 6). A likely explanation for this is that the catalytic activity γ of the walls for removing $N_2(v=1)$ is higher downstream from the titration point (where the walls are in contact with oxygen atoms)

Table 1

PRESSURE OF $N_2(v=1)$ IN MICROWAVE-DISCHARGED N_2

(No NO titration)

N_2 Pressure (torr)	Raman Signal Counts/sec	$N_2(v=1)$ Pressure (torr)
1·4	~ 0·4	~ 0·01
3	2·5	0·063
6·2	8·5	0·21
12	16·9	0·42
18	14·4	0·36

than before the titration point (where the walls are in contact only with nitrogen atoms). We can rule out the gas phase relaxation of $N_2(v=1)$ by oxygen atoms, since the rate for this reaction is certainly too low to be important ($<10^{-21}$ cm^3 $molecule^{-1}$ sec^{-1}).[1,14]

On the assumption that $N_2(v=1)$ is removed only by wall deactivation and under conditions where the production of $N_2(v=1)$ (by the N + NO reaction) at the titration point can be neglected compared to the amount already present, we can calculate the increase in the rate of wall loss (Δk sec^{-1}) downstream from the titration point, in the presence of oxygen atoms, from the expression

$$\frac{N}{N_o} = e^{\Delta k \cdot t} , \tag{14}$$

where N and N_o are the Raman signals before and after titrating, and t is the elapsed time from the titration point to the cell in which the Raman signal is measured. For the signal reductions observed, $\Delta k = 8{\cdot}6 \pm 0{\cdot}9\ \mathrm{sec}^{-1}$.

In the absence of oxygen atoms (without titration), the rate of wall loss for pyrex ($k\ \mathrm{sec}^{-1}$) can be calculated from the expression

$$k = \frac{\bar{c}\gamma}{2r} \quad , \tag{15}$$

where $\bar{c}$ is the average N_2 thermal velocity ($5{\cdot}2 \times 10^4$ cm sec^{-1} at 300°K); γ is the surface deactivation coefficient for $N_2(v=1)$, which has been previously determined[2-4] to be $4{\cdot}5 \times 10^{-4}$; and r is the radius of the tube (1.1 cm). Hence $k = 10.6\ \mathrm{sec}^{-1}$. Therefore, in the presence of oxygen atoms, the rate of loss on the walls increases to $k + \Delta k = 19{\cdot}2 \pm 0{\cdot}9\ \mathrm{sec}^{-1}$.

To increase the detectability of the $N_2(v=1)$ produced in the N + NO reaction, it was decided to remove or at least minimize the $N_2(v=1)$ originating in the discharge. The first approach tried was to use 1% N_2 in argon as the source of atoms. This did indeed remove the $N_2(v=1)$ originating in the discharge but at the expense of a reduced pressure of nitrogen atoms. The second approach tried was to insert a glass-wool plug between the discharge and the NO-inlet position. The logic behind this approach, which has been used before,[2-4] is that the deactivation of $N_2(v=1)$ on pyrex surfaces ($\gamma = 4{\cdot}5 \times 10^{-4}$) is much more efficient than the removal of nitrogen atoms ($\gamma = 2 \times 10^{-5}$).[15-17] The first two trials of a glass-wool plug confirmed this situation, reducing the $N_2(v=1)$ in N_2 at 6 torr by factors of 3 and 5, while reducing the nitrogen atoms by 10 and 25%, respectively. Under these conditions the Raman signal no longer decreased when the nitrogen atoms were titrated with NO but the increase observed was not statistically significant. [For example, in a 5-minute counting period, 758 ± 31 counts were obtained (from 25 experiments) for the untitrated discharge and 801 ± 27 counts (from 16 experiments) for the titrated discharge (titrating ~15 cm from the pyrex cell). The uncertainties are the estimated errors of the means, obtained by dividing the standard deviations of the individual counts by the square root of the number of measurements.] The next experiments will use a larger glass-wool plug to further reduce the background from the untitrated discharge.

The above results, although very preliminary and still beset with background, can be used to estimate the efficiency of reaction (2) in the following manner. By using the wall deactivation rate coefficients estimated previously, we can correct the above signals for the different decays between the titration point and the cell. For the untitrated discharge ($k = 10{\cdot}6\ \text{sec}^{-1}$), no decay between inlet No. 2 and the cell (flow time 0·0375 sec) would have given a Raman signal of 1128 ± 46 counts in a 5-minute period, whereas for the titrated discharge ($k' = 19{\cdot}2 \pm 0{\cdot}9\ \text{sec}^{-1}$) no decay would have given a signal of 1648 ± 111 counts. The Raman signal is therefore 520 ± 157 counts in a 5-minute period or $1{\cdot}73 \pm 0.52\ \text{sec}^{-1}$.

For a sensitivity of 40 counts sec^{-1} [torr $N_2(v=1]^{-1}$, this corresponds to $P_{N_2(v=1)} = 0{\cdot}043 \pm 0{\cdot}013$ torr. For $P_N = 0{\cdot}014$ torr, Eq. (13) can then be used to determine that 26 ± 8% of the exothermicity of the reaction appeas as vibrational energy in the nitrogen. The measurements to be made during the next period should considerably improve the accuracy of our results.

Task II. Deexcitation of $N_2(v=1)$ by $O(^3P)$

The work on Task II, which involves the measurement in a shock tube of the influence of atomic oxygen on the vibrational relaxation of nitrogen, is a continuation of work carried out in 1970-71 under ARPA Contract

DAHC04-70-C-0036. The details of the experimental technique and the status of the work accomplished under that contract were given in a final report,[13] and only a brief review follows. The objective of these experiments has been the determination of the rate of vibrational relaxation of N_2 by atomic oxygen, by shock tube techniques over a temperature range from approximately 1,000° to greater than 3,000°K, to provide overlap with the data of Breshears and Bird[1] in the range from 3,000° to 4,500°K. It was determined that measurement techniques relying on changes in density, such as interferometry or the laser schlieren method, were not sufficiently sensitive for these experiments.

Efforts have therefore been concentrated on the infrared-tracer method, by which a close resonance in the vibrational energies of N_2 and CO ensures rapid energy transfer and consequent vibrational equilibrium between these species; the subsequent infrared radiation from the CO near 5 microns is then proportional to the vibrational energy of the N_2. Atomic oxygen is generated by thermal dissociation of ozone in the test gas mixture behind the shock wave, according to the reaction scheme

$$O_3 + M \rightarrow O + O_2 + M \tag{16}$$

$$O + O_3 \rightarrow O_2 + O_2 \quad , \tag{17}$$

where M is any species (primarily N_2). Nitrogen is then vibrationally excited by vibration-translation (V-T) energy exchange from any of the species N_2, O, O_2 or CO, as well as by vibration (V-V) exchange with O_2 or CO. The V-T and V-V rates for N_2 with CO and O_2 are reasonably well known, so the presence of these species in the gas mixture can be taken into account. We made measurements in N_2 - O_2 - CO mixtures to confirm these rates and verify our measurement technique. The results of these measurements were reported[13] for the temperature range $1200 \leq T \leq 1800$°K. At higher temperatures, extraneous radiation was found to obscure the desired infrared signal and thus prevent the taking of useful data. For those experiments, the infrared radiation to the detector was limited by a filter with a bandpass from 4.71 to 4.78 microns, which is near the center of the fundamental CO infrared band but which we felt was outside the wings of the CO_2 band centered at 4.3 microns. However, the results of Malkmus[18] indicate that considerable CO_2 radiation could pass through this filter at the elevated temperatures typical of the shock-tube experiments, particularly if the CO_2 were formed in high vibrational levels by the reaction

$$CO + O_2 \rightarrow CO_2^{\pm} + O \quad . \tag{18}$$

To verify this supposition, we recently obtained a filter that passes $5.05 \leq \lambda \leq 5.15$ microns, and repeated a series of tests on the 94% N_2 - 5% O_2 - 1% CO mixture. These new tests showed that the extraneous radiation was indeed eliminated and that useful data can be obtained for temperatures up to at least 4000°K.

During the reporting period, major effort was devoted to the generation and handling of ozone mixtures and to the completion of a series of tests with 1% O_3 and 1% CO in N_2. In previous work,[19-21] as well as in this program, a significant decomposition of O_3 was found to occur in the storage vessel with CO in the gas mixture. Although surface reaction had been suspected, evidence indicated that the O_3 - CO reaction was catalyzed by an impurity, probably methane, present in the CO gas supply.[21] We examined the decrease of O_3 and the rate of formation of CO_2 in an initial mixture of 1% CO - 1% O_3 - 98% N_2 in our gas mixing and storage vessel by infrared absorptivity techniques. We found as much as 40% decomposition in 1 hour at room temperature and 20% decomposition in 1 hour at dry ice temperature. The study showed that approximately 20% of the decomposing O_3 reacted to form CO_2 at 300°K, increasing to 30% CO_2

formation at dry ice temperature. The presence of CO_2 in the test gas mixture, even in small amounts, must be taken into account, since CO_2 - N_2 V-V exchange can provide an alternative path for N_2 vibrational excitation (the rates for CO_2 - N_2 V-V exchange are also known).

In view of the reduced decomposition rate of O_3 at dry ice temperature, all shock-tube test gas samples are mixed and stored at the reduced temperature. The actual O_3 concentration in the test gas after introduction into the shock tube is measured by an ultraviolet absorption setup oriented perpendicular to the infrared emission optics at the shock tube test section. The ultraviolet absorption is measured at 2537 Å by using a mercury light source and a narrow-band filter, and the concentration of O_3 is calculated by assuming an absorption cross section of 300/cm-atm. The mole fraction of O_3 in the test gas for each shock-tube run is calculated from the pressure of O_3 determined by the uv absorption, and the total gas pressure is measured with either calibrated Wallace and Tiernan Gauges or a sulfuric acid manometer. A new test gas mixture is prepared daily. Experience during the period indicates somewhat less decomposition than indicated by the measurement, with approximately 10% decomposition after 1 hour, increasing asymptotically to 20% after several hours. A two-stage cold trap filled with alumina pellets and copper wool, as suggested by Millikan,[22] was recently added to the CO supply line in an attempt to remove impurities and thus reduce the decomposition rate even further.

As indicated above, a series of tests covering the temperature range $1000^\circ < T < 4000^\circ K$ and using a nominal gas mixture of 1% O_3 - 1% CO - 98% N_2 was completed, and data reduction was undertaken. Additional tests will be conducted using different O_3 concentrations; the consistency of the results obtained by using different gas mixtures will help to ensure the validity of the rather complicated data reduction process.

It has been noted earlier that the atomic oxygen in these experiments is generated by thermal decomposition of O_3 behind the shock wave following reactions (16) and (17). At high temperatures, reaction (17) becomes negligible, and there is one-to-one ratio of oxygen atom to initial ozone concentrations. At lower temperatures, however, reaction (17) becomes competitive in depleting the O_3, and the net amount of O-atoms formed is reduced. Wray[23] has shown that the mole fractions of O-atoms (Ψ_O) and of initial O_3($\Psi^i_{O_3}$) are related by

$$\Psi_O = (1 - \beta)\, \Psi^i_{O_3} \quad ,$$

where β is given by the solution of the equation

$$\ln[1-G(1-\beta)] + \tfrac{1}{2}G(1-\beta) + \tfrac{1}{2}G = 0 \quad .$$

The parameter G is related to $\Psi^i_{O_3}$ and to the rates for reactions (16) and (17) k_{16} and k_{17} by

$$G = \Psi^i_{O_3}(k_{16}/k_{17}) \quad .$$

Unfortunately, some remaining uncertainty in the values of k_{16} and k_{17} as a function of temperature causes a corresponding uncertainty in Ψ_O. Measurements have been made by Jones and Davidson,[24] Myers and Bartle,[25] Benson and Axworthy,[26] and Michael.[27] There is reasonable consistency in the results for $T < 1000^\circ K$, but Wray[23] and Kiefer and Lutz[28,29] have found that at higher temperatures the ratio k_{17}/k_{16} has varied from 3 to 30 times the values given by extraplating Jones and Davidson's low temperature results.[24] Michael[27] attributes the discrepancy to a change in the value of k_{16} due to the increasing importance of dissociation from excited vibrational levels of O_3 at higher temperatures.

In view of these results, we have adapted Benson and Axworthy's value for k_{17}, which is given in units of liter/mole-sec by

$$k_{17} = 3.27 \times 10^{10} \exp(-5700/RT).$$

Consistency with the results of Michael, Wray, and Kiefer and Lutz is then provided by modifying Jones and Davidson's value of k_{16} by a rather arbitrary factor $(900/T)^2$ to yield in the same units

$$k_{16} = 5.8 \times 10^{11} \exp(-23{,}500/RT)(900/T)^2 \quad .$$

A parametric evaluation of $\psi_O/\psi^i_{O_3}$ as a function of temperature, made by using the various rates, indicated that for $\psi^i_{O_3} = 0.01$ the uncertainty in oxygen atom concentration will be less than ±10% for temperatures above 1500°K but may be as large as ±100% at 1000°K. If $\psi^i_{O_3}$ is reduced to 0.0025, the uncertainty at 1000°K drops to approximately 25%. Thus with a suitable choice of $\psi^i_{O_3}$ the oxygen atom concentration can be reasonably well predicted over the temperature range of these experiments.

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ADDENDUM

Remarks on Recent Paper by McNeal et al

A paper by McNeal, Whitson and Cook[1] on the relaxation of vibrationally excited N_2 by atomic oxygen has just come to the attention of the authors. They have measured a rate coefficient of $3{\cdot}5 \pm 1{\cdot}4 \times 10^{-15}$ cm^3 $molecule^{-1}$ sec^{-1} at 300°K. This result is orders-of-magnitude larger than that quoted on p. 14 of this report. If the results of McNeal et al. are correct then the increased rate of decay of $N_2(v=1)$ after the titration point (described on p. 13 of this report) which we have attributed to a change in the catalytic efficiency of the walls may be due, at least partly, to gas phase relaxation by oxygen atoms. This possibility will be further examined in our experimental program. It does not affect any of our other conclusions.

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[1] "Quenching of Vibrationally Excited N_2 by Atomic Oxygen," by R. J. McNeal, M. E. Whitson, Jr., and G. R. Cook, submitted to Chemical Physics Letters (July, 1972).