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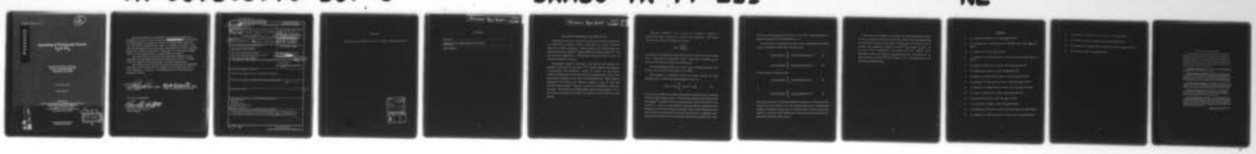

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REPORT SAMSO-TR-77-211

Quenching of Vibrationally Excited N_2 by SO_2

Chemistry and Physics Laboratory
The Ivan A. Getting Laboratories
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El Segundo, Calif. 90245

9 November 1977

Interim Report

Prepared for
SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

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This interim report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. [redacted] with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by S. Siegel, Director, Chemistry and Physics Laboratory. Lieutenant A. G. Fernandez, SAMSO/ YAPT, was the project officer for Advanced Space Programs.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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A photoionization detection technique has been used to measure the rate of quenching of vibrationally excited N_2 by SO_2. The quenching rate coefficient was determined to be $(6 \pm 2.3) \times 10^{-16}$ cm^3/molecule^{-1} sec^{-1}.

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PREFACE

The authors are indebted to Dr. P. F. Zittel for helpful discussions.

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CONTENTS

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QUENCHING OF VIBRATIONALLY EXCITED N_2 BY SO_2

Considerable effort has been expended in recent years to determine energy transfer rate coefficients for processes relevant to high power laser systems, atmospheric radiance, and acoustic propagation. Numerous studies of SO_2 relaxation have been reported using acoustic dispersion[1-7] and laser-induced fluorescence techniques.[8-11] This note reports the application of a photoionization detection technique to study the vibrational quenching of N_2 by SO_2.

The apparatus employed to study $N_2(v = 1)$ quenching has been described in its application to CO_2, H_2O, NO, H_2O, and O.[12-16] A flowing afterglow system coupled to a photoionization mass spectrometer comprised the reaction zone and detector. Detection was based upon the fact that the onset of photoionization of $N_2(v = 1)$ lies toward longer wavelengths than the $N_2(v = 0)$ photoionization limit. Signals caused by photoionization at 80.04 nm were attributed exclusively to $N_2(v = 1)$, based upon previously reported evidence.[12] The $N_2(v = 1)$ was formed in a discharge in a flowing He-N_2 mixture. Flow velocities were typically 20m/sec, and total system pressures ~ 2 Torr. The amount of N_2 present in the system was varied from 3.3% to 35% of the total pressure.

Quenching measurements were performed by observing the decrease in photoionization signal at 28 amu as a function of SO_2 concentration. This decrease defined a simple first order quenching rate coefficient,

$$k_{obs} = \frac{\ln I_o/I}{[SO_2\, t]} \quad ,$$

where $[SO_2]$ is the concentration of SO_2 added to the flow system and t is the reaction time. A correction due to repopulation of $N_2(v = 1)$ from $N_2(v > 1)$ increased k_{obs} by a factor of 1.25 to give the quenching rate coefficient k_q.[13]

The experimentally measured value of k_q for $N_2(v = 1)$ quenched by SO_2 was found to be $k_q = (6 \pm 2.3) \times 10^{-16}$ cm^3 $molecule^{-1} sec^{-1}$ at 300^oK.

This quenching rate coefficient represents the balance between the overall quenching of $N_2(v = 1)$ and reverse process population of $N_2(v = 1)$,

$$N_2(v = 1) + SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2(v = 0) + SO_2^{\dagger} \quad . \qquad (1)$$

In order for k_q to equal k_1, any excited SO_2 produced in process (1) must be deactivated before the reverse reaction can occur. Vibrational self-relaxation times for SO_2 measured by Earl <u>et</u> <u>al</u>.[10] and others[5] indicate that SO_2 vibrational relaxation times for this work vary from ~ .5 msec to 5 msec, assuming that self-quenching for $SO_2(200)$ and other populated levels is at least as rapid as for $SO_2(100)$. Typical experimental reaction times were ~ 80 msec, which indicates that reverse processes should not be a significant effect. Experimental confirmation of this was obtained by varying the N_2 pressure from .15 Torr to .5 Torr and the SO_2 pressure from .06 Torr to .6 Torr, with no observable change in the measured value of k_q. Thus we conclude that $k_q \cong k_1$.

The most likely V-V transfer processes which could be responsible for this quenching of $N_2(v = 1)$, based upon energy defect considerations, are

$$N_2(v=1)+SO_2(000) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} N_2(v=0)+SO_2(100)+1180\ cm^{-1}, \quad (2)$$

$$N_2(v=1)+SO_2(000) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} N_2(v=0)+SO_2(001)+969\ cm^{-1}, \quad (3)$$

or the two quantum excitation processes

$$N_2(v=1)+SO_2(000) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} N_2(v=0)+SO_2(200)+29\ cm^{-1}, \quad (4)$$

or

$$N_2(v=1)+SO_2(000) \underset{K_{-5}}{\overset{k_5}{\rightleftharpoons}} N_2(v=0)+SO_2(002)-393\ cm^{-1}. \quad (5)$$

This experiment provides no information regarding the actual process occurring, since only the loss of $N_2(v=1)$ is monitored, nor is there a reliable theoretical way of calculating the reaction rate coefficients for $N_2 - SO_2$ V-V transfer processes. All that can be said with certainty is that simple theory[17] predicts that all four processes be much slower than a single-quantum resonant transfer process.

The value of the quenching rate coefficient for the $N_2(v=1)-SO_2$ system reported here may be compared to that for the $CO(v=1)-SO_2$ system, in which the energy defects for the processes involved are very similar to those shown in eq. (2) to (5). The CO quenching rate coefficient is reported by Kovacs[18] and Hancock _et_ _al._[8] to be $(1.9 \pm .7) \times 10^{-15}$ cm^3 molecule^{-1}sec^{-1} and $(3.6 \pm .1) \times 10^{-16}$ cm^3 molecule^{-1} sec^{-1}, respectively, which is very similar to our reported value of k_1. We conclude that the reported value, $k_1 = (6 \pm 2.3) \times 10^{-16}$ cm^3 molecule^{-1}sec^{-1}, is a reasonable value for the $N_2(v=1)-SO_2$ quenching process.

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