FINAL TECHNICAL REPORT

on

KINETICS OF NITRIC OXIDE FORMATION AND DECOMPOSITION

NASA Grant NGR-05-020-583

covering the period

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by

Co-Principal Investigators:

Professor C. H. Kruger

Dr. R. K. Hanson

Department of Mechanical Engineering
Stanford University
Stanford, California 94305

NASA Technical Officer: Dr. Chul Park
NASA-Ames
Moffett Field, California

1. Summary

This grant was initiated by the Physics Branch at NASA Ames on December 1, 1971, and has been supported since December 1, 1972, by the Physical Gas Dynamics and Lasers Branch, also at Ames. Originally there were two research topics:

a. Nonequilibrium Shock-Wave Structure

b. Kinetics of Nitric Oxide Formation and Decomposition

Work on the first topic, nonequilibrium shock-wave structure, continued for only one year and resulted in two publications, but was not considered of sufficient interest to NASA to merit further support.

During the last two years of the grant, our research has centered entirely on the second topic dealing with the kinetics of nitric oxide. This work was motivated by the need for improved kinetics data for use in modeling NO production in the space shuttle flow field. Our activities included assembly of a shock tube facility, development of suitable diagnostics, and finally a series of experiments to measure appropriate rate constants. Most of this work has been completed and reported in the open literature. One project on NO formation kinetics is still in progress and will be completed later.

2. Publications

During the 3-year period of this grant, the following papers have been presented or published:

1. R. K. Hanson, "Experimental Study of Shock-Wave Reflection from a Thermally Accommodating Wall", Physics of Fluids, 16, 369 (March 1973).

2. G. S. Deiwert and R. K. Hanson, "The Reflection of a Thick Planar Shock Wave from a Coplanar Surface", Proceedings of the Eighth International Symposium on Rarified Gas Dynamics, K. Karamcheti, editor (Academic Press, 1973).

3. R. K. Hanson, "The Dissociation of Shock-Heated Carbon Monoxide", Recent Developments in Shock Tube Research, D. Bershader and W. Griffith, editors (Stanford University Press, 1973), p. 365.

4. R. K. Hanson and W. Flower, "Verification of a Simple Relationship for Shock-Wave Reflection in a Relaxing Gas", AIAA Journal, 11, 1777 (December 1973).

5. R. K. Hanson, "Shock Tube Study of Carbon Monoxide Dissociation Kinetics", Journal of Chemical Physics, 60, 4970 (June 1974).

6. R. K. Hanson, W. L. Flower and C. H. Kruger, "Determination of the Rate Constant for the Reaction $O + NO \rightarrow N + O_2$", Journal of Combustion Science and Technology (December 1974).

7. W. L. Flower, R. K. Hanson and C. H. Kruger, "Investigation of Nitric Oxide Decomposition in the Temperature Range 2500-4100°K, paper presented at the Spring 1974 Meeting of the Western States Section of the Combustion Institute, Pullman, Wash., May 6-7, 1974.

8. W. L. Flower, R. K. Hanson and C. H. Kruger, "Kinetics of the Reaction of Nitric Oxide with Hydrogen", Fifteenth Symposium (International) on Combustion, (The Combustion Institute, 1974).

9. R. K. Hanson, W. L. Flower, J. P. Monat and C. H. Kruger, "Decomposition of NO Studied by Infrared Emission and CO Laser Absorption", submitted for presentation at the Tenth International Shock Tube Symposium, Tokyo, August 1975.

3. Discussion of Work Completed or in Progress

In this section we present a summarized account of all research conducted under support of this grant.

During the first year of the grant, while the Physics Branch was still functioning, work was conducted both at Stanford and at Ames. Experiments on shock-wave structure were conducted at Ames, in the 12-inch shock-tube facility, while research on NO kinetics was performed at Stanford University.

The experiments on shock structure involved simultaneous observations of pressure and temperature on the end wall of the shock tube during reflection of normal shock waves in inert gases. The data were compared with Monte Carlo calculations of the reflection process to infer parameters both for the gas-surface collision model and for the intermolecular potential used to specify collisions in the gas phase. These data made an essential contribution to the verification of Monte Carlo computational techniques under development at Ames.

After completing the study of shock reflection, using monatomic gases (see publications 1 and 2 in Section 2), we proposed a study of shock structure in diatomic gases where inelastic collision processes, particularly involving rotational excitation, would play a major role. Again the objective was to compare experimental data with Monte Carlo calculations. Several months were spent in formulating an experimental technique capable of providing time histories of population density in particular rotational quantum states through the shock, an experiment not previously attempted. Our proposal involved use of a tunable infrared laser. Unfortunately, at about this time the Physics Branch was disbanded and it was necessary to terminate this promising project.

Fortunately, our work on NO kinetics was of more general interest to workers at Ames and received continued support from the Physical Gas Dynamics and Lasers Branch after support from the Physics Branch was lost. During the first year

of this grant, we performed a literature survey of related past work and began to plan experiments. There were major gaps in knowledge of NO kinetics particularly at high temperatures where most NO formation and decomposition occurs, and we set out to close these gaps with some careful experiments. Following selection of shock-wave heating as the most useful method for testing, we acquired a shock tube on loan from Ames and completed the necessary installation and modifications at Stanford by January, 1973.

An important aspect throughout our research has been the development of suitable diagnostic techniques: a laser-schieren system for monitoring post-shock density gradients (pub. 4 in Sec. 2), an infrared emission system for monitoring concentrations of NO and N_2O (pub. 6), and most recently, a tunable CO laser for resonance absorption measurements of NO (pub. 9).

Utilizing particularly the IR emission system, we studied, in the second year of the grant, the kinetics of NO decomposition in an extensive series of tests. Although many reactions occur during decomposition of NO, the rate-limiting step is often

$$O + NO \rightarrow N + O_2, \qquad (1)$$

the well-known Zel'dovich reaction. We determined the rate constant for this reaction over the temperature range 2500-4100°K by shock heating mixtures of NO, N_2O and Ar (or Kr) and comparing observed the predicted NO concentrations behind the shock. The purpose of the added N_2O was to serve as a source of O atoms for reaction (1), the atoms being produced by the rapid reaction

$$N_2O + M \rightarrow N_2 + O + M \qquad (2)$$

Our results for the rate constants of reactions (1) and (2) were presented in publications (6) and (7) of section 2.

After completing our work on NO decomposition kinetics, and before turning to a study of NO formation kinetics, we asked for and obtained approval to

renew a study of CO kinetics which had been initiated under NASA support during 1968-1970. A principal motivation for returning to this project was the recognition of the similarity between the reaction mechanisms important in NO and CO decomposition; our experience with NO kinetics having provided important new insight into our earlier CO data. The project on CO kinetics was completed within 6 months by September, 1973, and was reported in publications (3) and (5).

This last year of the grant, under reducing funding, we've concentrated on development of tunable laser spectroscopy as a technique for studying NO formation kinetics. Finally, within the last few months we've completed construction and checkout of a CO laser and successfully identified several spectral coincidences between CO and NO suitable for shock-tube absorption measurements. This work is still in progress, and will be continued without NASA support. We report here our most recent results with the laser.

The governing equation for absorption of radiation is Beer's Law

$$I = I_o \exp(-\beta\, n_{NO}\, L)$$

where I_o and I are the incident and transmitted radiation fluxes, n_{NO} is the number density of NO (cm^{-3}), L is the path length through the absorbing gas (15 cm in our shock tube) and β is the absorption coefficient or cross-section (cm^2). The absorption coefficient is related to the line strength S and the line-shape function ϕ through the relation

$$\beta = S\phi$$

where

$$\int \phi d\nu = 1.$$

Our measurements of β for a range of temperatures are shown in Fig. 1, all for $\nu = 1935.5\ cm^{-1}$, produced by V = 7→6, J = 12→13 laser line of CO. Note that all the results are for a static pressure of about 0.4 atm. The data were obtained by shock heating known mixtures of NO and Ar (or Kr) and

recording the fractional absorption. For purposes of an approximate calculation, $\beta \simeq 10^{-19}$cm, $n_{NO} = \chi_{NO} n \simeq \chi_{NO}\ 10^{18}/cm^3$, where χ_{NO} is the mole fraction of NO, and L = 15cm; therefore

$$\beta\ n_{NO}\ L \simeq 1.5\ \chi_{NO}.$$

Thus a 1% concentration of NO gives 1.5% absorption and so on. The method of CO laser absorption is therefore sufficiently sensitive to measure NO concentrations below 1%, since absorptions of 1% are straightforward to measure and absorptions of 0.1% are within reason.

As a final check of our laser absorption method, before undertaking a study of NO formation, we've made comparative measurements of NO concentrations using both laser absorption and IR emission. For simplicity, these measurements were made behind strong shocks in NO-Kr mixtures, where NO decomposition is the dominant process. The experimental setup is shown schematically in Fig. 2; good agreement is obtained between both measurement techniques and kinetic calculations, thereby validating, we feel, the new laser absorption technique. Some of this work will be reported at the forthcoming International Shock Tube Symposium (see pub. 9).

Our next objective will be to apply the technique of laser absorption to a study of NO formation kinetics. Sample calculations have been made and the work is now underway. Although our grant has expired, we plan to complete this work with partial support from the National Science Foundation.

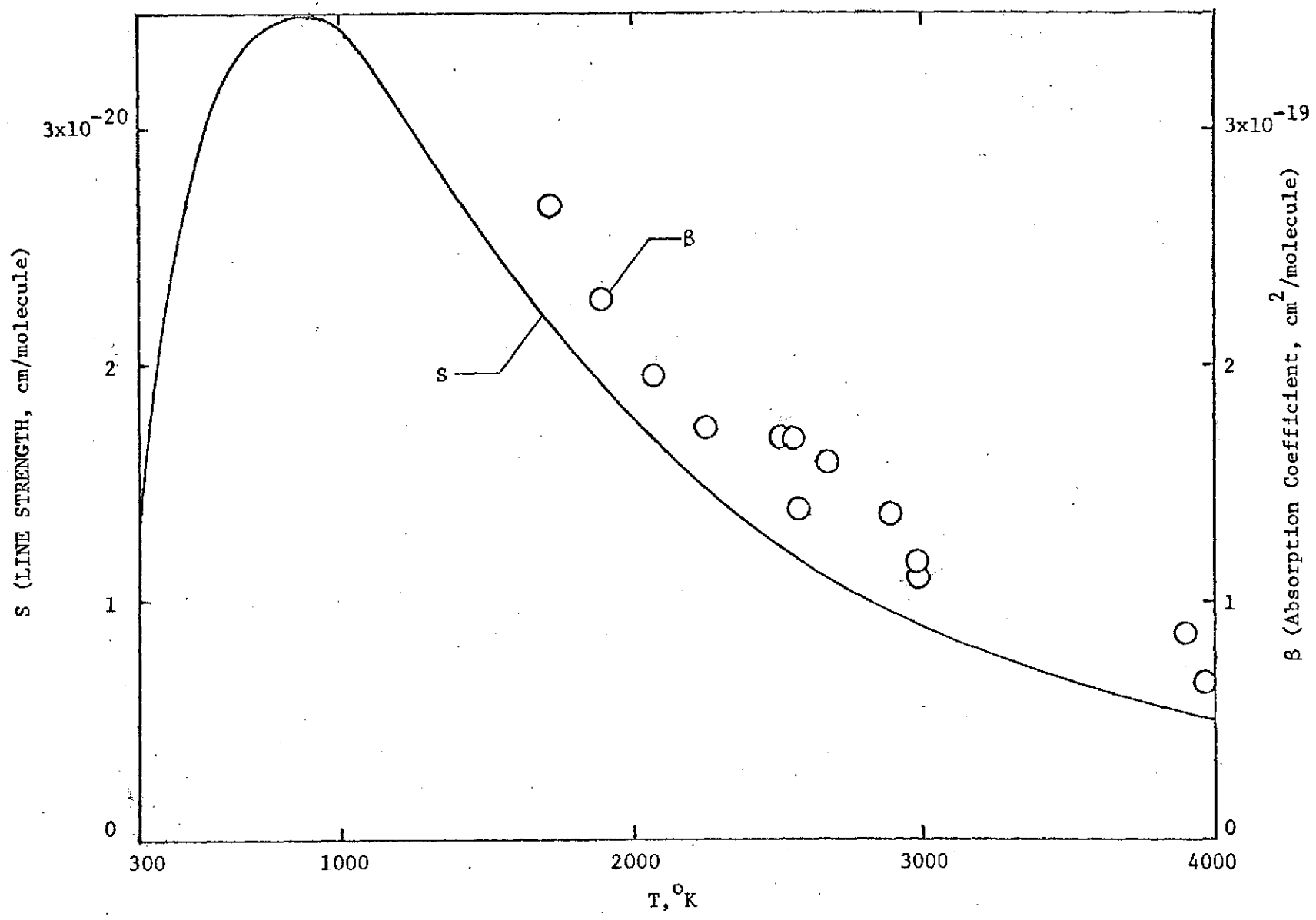

Fig. 1 Calculated line strength S and measured absorption coefficient β in NO for the ground state $^2\Pi_{3/2}$, R(J=18.5) at ν=1935.5 cm^{-1}. The post-shock pressure is about 0.4 atmospheres in all cases.

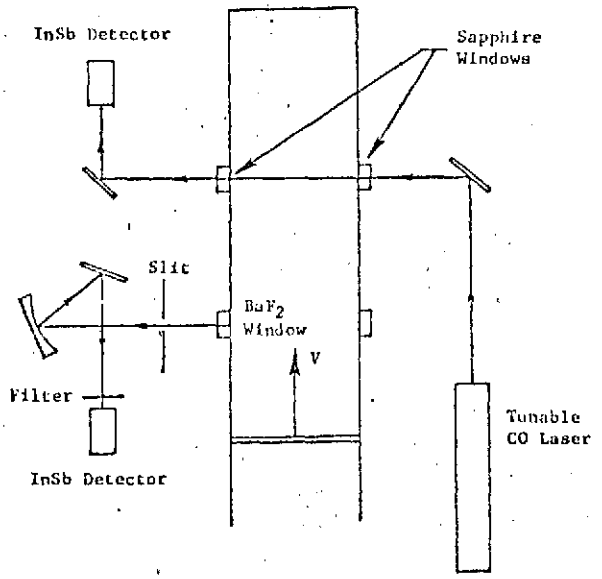

Fig. 2. Experimental Setup

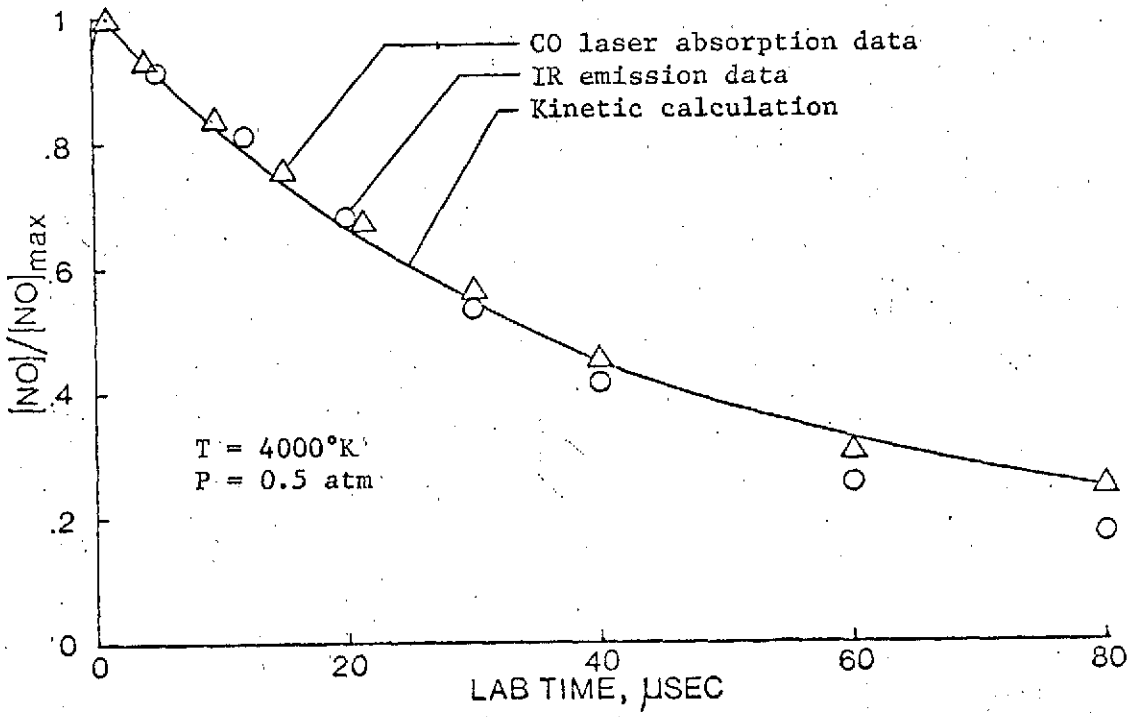

Fig. 3. Absorption and emission data and kinetic calculations of $[NO]/[NO]_{max}$. Shock conditions: P_1=6.94 Torr (N_2O/NO/Kr = 2.2/9.8/88), V = 1.53 mm/μsec.