SECURITY CLASSIFICATION OF THIS PAGE DTIC FILE COPY

REPORT DOCUMENTATION PAGE

(2)

DTIC
ELECTE
DEC 1 3 1988
D
D

AD-A202 159

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution is unlimited.

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 88-1149

6a. NAME OF PERFORMING ORGANIZATION
Stanford University

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NA

6c. ADDRESS (City, State, and ZIP Code)
Department of Mechanical Engineering
Stanford, CA 94305

7b. ADDRESS (City, State, and ZIP Code)
Building 410, Bolling AFB DC
20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
AFOSR/NA

8b. OFFICE SYMBOL (If applicable)
NA

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR 87-0057

8c. ADDRESS (City, State, and ZIP Code)
Building 410, Bolling AFB DC
20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2308	A3	

11. TITLE (Include Security Classification)
Modern Shock Tube Methods For Chemical Studies In High Temperature Gases

12. PERSONAL AUTHOR(S)
Ronald K. Hanson, A. Y. Change, and D. F. Davidson

13a. TYPE OF REPORT
Journal Reprint

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT (Year, Month, Day)
June 1988

15. PAGE COUNT
4

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Laser, Photolysis, Shock Tube, Absorption

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Recent improvements in shock tube methods will allow more quantitative and direct determinations of high temperature chemical reaction rate coefficients than were previously possible. In this paper we discuss and illustrate two particular improvements, namely laser-based absorption diagnostics for sensitive and accurate species detection, and laser-photolysis of shock-heated gases for direct preparation of molecular and atomic radicals.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Julian M. Tishkoff

22b. TELEPHONE (Include Area Code)
(202) 767-~~[illegible]~~ 0465

22c. OFFICE SYMBOL
AFOSR/NA

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted.
All other editions are obsolete.

88 1011 196

SECURITY CLASSIFICATION OF THIS PAGE

AIAA'88

AFOSR-TR- 88-1149

AIAA-88-2712

Modern Shock Tube Methods for Chemical Studies in High Temperature Gases

R.K. Hanson, A.Y. Chang, and D.F. Davidson, High Temperature Gasdynamics Laboratory, Stanford Univ., Stanford, CA

AIAA THERMOPHYSICS, PLASMADYNAMICS AND LASERS CONFERENCE

JUNE 27-29, 1988/San Antonio, Texas

MODERN SHOCK TUBE METHODS
FOR CHEMICAL STUDIES IN HIGH TEMPERATURE GASES

R. K. Hanson,* A. Y. Chang,† D. F. Davidson**
High Temperature Gasdynamics Laboratory
Stanford University, Stanford, CA

Abstract

Recent improvements in shock tube methods will allow more quantitative and direct determinations of high temperature chemical reaction rate coefficients than were previously possible. In this paper we discuss and illustrate two particular improvements, namely laser-based absorption diagnostics for sensitive and accurate species detection, and laser-photolysis of shock-heated gases for direct preparation of molecular and atomic radicals.

Background

Shock tube measurements are the primary source of chemical kinetic data for gases at high temperature, particularly above the temperature limit of heated steady-flow reactors (about 1500 K). During the past few years significant advances have been made in shock tube methods which enable more direct and quantitative measurements of elementary reactions than previously reported. Such refinements will lead to an improved kinetic data base useful, for example, in modeling nonequilibrium flows of air and combustion gases associated with advanced high-speed aircraft and transatmospheric vehicles. Here we discuss two areas of continuing activity in our laboratory, namely the development of improved diagnostic methods based on cw dye laser absorption spectroscopy and the development of a new laser-photolysis shock tube for direct studies of reactions involving reactive radical species. [illegible]

CW Dye Laser Absorption

The development of laser absorption as a shock tube diagnostic for reaction kinetics began about 10 years ago.[1,2] In that early work, the laser source was a discretely-tunable cw CO electric-discharge infrared laser, and fortuitous coincidences between CO laser lines and NO absorption lines formed the basis of the measurement. Subsequently other fortuitous coincidences were identified to enable quantitative detection of H_2O[3] and N_2O using the same laser source tuned to other emission transitions; detection of excited-state populations of CO was also demonstrated[4] in our laboratory and subsequently utilized in a number of kinetics studies at the Naval Research Laboratory by Lin and co-workers (e.g., see Ref. 5). The critical advantages provided by laser absorption in these various studies were the improved sensitivity and accuracy of the species concentration measurements relative to conventional broadband absorption and emission measurements.

An important further improvement in the laser absorption approach was provided in 1983 (e.g., see Ref. 6) when a cw UV dye laser was first coupled to a shock tube to enable measurements of the OH radical. This work was significant for two reasons: (1) it demonstrated feasibility for accessing the larger absorption coefficients which apply in the UV (electronic rather than vibrational transitions), thereby lowering the species detection limits considerably; and (2) it confirmed the ability to monitor OH, which is a critical species for a number of important combustion reactions. Even in this initial demonstration, the use of laser absorption enabled substantial improvements in OH detection accuracy and sensitivity over previous diagnostic methods. These diagnostics improvements have already resulted in improved rate coefficient determinations.

More recently, also in our laboratory, extensions of this same general approach have been carried out to enable cw dye laser absorption measurements of CH (at 431 nm),[7] NCO (440 nm),[8] NH_2 (597 nm), and NH (336 nm).[9] Unfortunately, each of these measurements requires a different dye laser arrangement, either in terms of frequency-doubling crystal, laser dye, or laser optics, and hence it is not always easy to change from detecting one species to another. Also, it is necessary to perform supporting spectroscopic calculations, and supporting laboratory validations, for each species to provide the absorption coefficient as a function of temperature at the chosen transitions (wavelengths). Progress in developing and validating these new species diagnostics thus requires a substantial effort, but the long-term advantages of the improved methods in determining reaction rate coefficients clearly justifies the effort involved.

A schematic diagram of the experimental arrangement employed for cw dye laser absorption of NH at 336 nm is shown in Fig. 1. In this case, a 5 W argon-ion laser is used to pump a single-frequency ring dye laser which emits about 0.5 W at 672 nm. This light is frequency-doubled external to the ring cavity in a $LiIO_3$ crystal, yielding a final output power of about 5 microwatts at 336 nm. The UV light is single-passed through the 14.3 cm diam shock tube about 1.9 cm from the end wall, and low levels of absorption are monitored using a two-beam differencing scheme.[9] The nominal laser wavelength is monitored with a wavemeter, but the final wavelength selection is made by peaking the absorption signal of a small fraction of the beam passed through a flat flame burner which produces NH. Further details of the experimental arrangement and strategies are given in recent papers;[7-9] here we will focus on the detection sensitivity which can be achieved with this measurement technique.

The single-frequency laser absorption is governed by Beer's law evaluated at the center of a Voigt-broadened line in the electronic absorption spectrum of the species under study. The relevant equation for the fractional transmission of the laser light is

$$T_v = (I/I_o)_v = \exp(-\beta_v P X_i L)$$

where β_v is the spectral absorption coefficient (cm^{-1}-atm^{1}), P is the static pressure of the gas mixture (atm), L is the optical pathlength (one or two passes of the tube diam, 14.3 cm), and X_i is the mole fraction of the absorbing species. The absorption coefficient is simply the product of an integrated line strength (cm^{-2}-atm^{-1}) and the line-center value of the lineshape function (cm); the former can be calculated directly from the electronic oscillator strength of

---

*Professor, Mechanical Engineering Department; Member, AIAA

†Research Assistant, Mechanical Engineering Dept.

**Research Associate, Mechanical Engineering Dept.

the molecule and the latter can be calculated using a Voigt lineshape function. Measurements of the collision-broadening coefficient, needed for the Voigt calculation, are made separately. The data reduction process is quite simple and involves converting each local value of the transmission directly to a value for the mole fraction of the species using Beer's law and the known values of L, P and β_v. The value of P is found from the initial pressure and standard shock wave calculations in terms of the measured shock speed; the same calculations yield the post-shock temperature needed to specify the absorption coefficient. In general, the accuracy of the inferred mole fraction is limited primarily by knowledge of the relevant oscillator strength, which is typically 5%.

Figure 2 presents calculated values of the absorption coefficient for several species of interest. These coefficients were evaluated at line center (or at the peak absorption in the case of overlapping lines) using a Voigt profile and an assumed pressure of 1 atm. Note that larger absorption coefficients lead to better species detection limits, and hence diatomic species can generally be monitored at lower levels than triatomic species. In most cases, our detection limit is about 0.1% absorption (SNR = 1), and hence it is easy to estimate the lower level of detection for a given species once the appropriate absorption coefficient has been calculated. For example, in the case of NH at 3000 K, and using the curve in Figure 2, the detection limit for single-pass absorption (14.3 cm) is seen to be less than 0.1 ppm at a total pressure of 1 atm. By the way of comparison, the detection limit for OH near 2000 K is below 1 ppm. These examples of detection limits illustrate clearly the high sensitivity of the laser-absorption method. Such high sensitivity allows study of very dilute systems which are relatively free of the complications which arise when several reactions are active simultaneously.

*An example data trace for NH absorption in a shock-*heated NH_3-Ar mixture near 2700 K is shown in Fig. 3. The initial mole fraction of NH_3 is 0.13%, leading to a peak post-shock NH level of about 34 ppm. In this case, the early-time profile is sensitive to the unimolecular decomposition reaction for NH_3 and the subsequent reaction $H + NH_3 \rightarrow NH_2 + H_2$. At somewhat later times, near the peak level of NH, other formation and decomposition reactions of NH come into play. By controlled variation of temperature, pressure and initial level of NH_3, several separate elementary reaction rate coefficients can be determined in these experiments.

At present we are engaged in several studies which involve the application of laser-based absorption to determine rate coefficients of elementary combustion reactions. These same methods should also be useful for studying high temperature reactions of air.

Laser-Photolysis Shock Tube

The second experimental technique to be covered in this paper is a new type of chemical kinetics shock tube. The objective is to provide improved capability for generating reactive radical species in shock tube experiments. This goal is motivated by the strong current interest in obtaining rate coefficient data for elementary reactions involving these species (e.g., radical-molecule and radical-radical reactions). At present the shock tube method employed in generating radical species involves use of a precursor molecule which decomposes by thermal reaction to produce the radical of interest. Unfortunately, this process often is coupled to many other simultaneous pyrolysis reactions, with the result that interference reactions often obscure the reaction of interest. In our new approach, an intense pulse of UV laser light is used to photolyze the precursor molecules, thereby instantly converting a fraction of these molecules to the radical of interest. In general this is done in the reflected shock region of a shock tube, following shock heating, so that the subsequent reactions of the radical species occur at the high temperature of interest.

The method under development is similar in many respects to that used by reaction kineticists working with low temperature static cells. The major difference is that the shock tube provides a transient high temperature environment, and because the experiment is a single-shot event the diagnostics employed cannot be signal averaged as is often done in low temperature work. Although our work is apparently the first based on laser photolysis in a shock tube, there has been previous work in the shock tube community in which a flashlamp was used to photolyze molecules in shock-heated gases. Our hope is that the greater monochromaticity and higher spectral intensities available with laser sources will provide much more efficient photolysis and less ambiguity in the identity and quantum states of the photofragments produced.

The experimental arrangement employed in our initial studies is shown schematically in Fig. 4. The photolysis source is an argon fluoride excimer laser which provides up to 100 mJ of 193 nm radiation in a 25 nsec pulse. The radiation is introduced coaxial with a probe laser beam used to monitor the time history of reactant or product species in the photolysis volume. Typical fluence levels are 10 to 25 mJ/cm^2 in this transverse illumination mode. (Illumination along the shock tube axis is an alternative scheme which can be employed when the absorption at photolysis wavelengths is suitably strong.)

Thus far we have investigated: NH_3 as a source of H, NH and NH_2; H_2O as a source of H and OH; O_2 as a source of O; *HNCO as a source of NH and* NCO; and NO as a source of N and O. Critical elements in planning laser-photolysis shock tube experiments are knowledge of the absorption coefficient of the dissociating species and the quantum yield (i.e., the fraction of absorbed photons which yield dissociated products). In most cases the absorption coefficient data are not available at high temperatures and must first be measured prior to reaction kinetics experiments. An example survey of the H_2O absorption coefficient for 193 nm radiation is shown in Fig. 6. Note that the absorption is quite low at low temperatures but increases to a value of about 1 cm^{-1}-atm^{-1} at temperatures above 2000 K. With the absorption coefficient known, it is then fairly straightforward to select the appropriate test conditions.[10]

An example data trace for the OH time history following pulsed illumination of a shock-heated H_2O-Ar mixture (about 1% H_2O) is shown in Fig. 7. The OH was monitored by cw dye laser absorption of the $R_1(6)$ line near 306.6 nm. In the case shown, the post-shock temperature and pressure were 1810 K and 1.22 atm respectively, and the laser pulse was fired about 60 microseconds following shock reflection. The absorbed photons lead to instantaneous production of about 13 ppm of OH; an equal level of H-atoms is formed simultaneously. Subsequently, the OH undergoes additional formation owing primarily to the reaction of the H-atoms with residual H_2O. Thus the final level of OH is nearly twice that formed initially.

Owing to the low concentrations of all species except H, OH and H_2O at early times, the dominant single reaction is $H + H_2O \rightarrow H_2 + OH$, and hence the measured OH time history can be used to provide a direct, accurate value of the rate coefficient which affects the level of OH for this reaction. The conventional form for plotting rate coefficient data is an Arrhenius diagram, and the results from our initial laser-photolyis experiments are plotted on such a diagram in Fig. 8. The least-squares fit to the data shown is in good agreement with the limited data previously available for the reaction. (The previous data were actually measured for the reverse direction of the reaction and converted through use of the known equilibrium constant.)

Conclusions

In this paper we have demonstrated the power of laser methods for shock tube experimentation of reaction kinetics, both for controlled production of reactant species and for their detection. The combination of shock wave heating with laser pump/probe strategies offers prospects for detailed study of chemical reactions and nonequilibrium phenomena at high temperatures of interest to the aerospace community.

Acknowledgements

This work was supported by the Air Force Office of Scientific Research, Aerospace Sciences Directorate.

References

1. R. K. Hanson, J. P. Monat, W. L. Flower and C. H. Kruger, "Decomposition of NO Studied by Infrared Emission and CO Laser Absorption," *Modern Developments in Shock Tube Research*, ed. G. Kamimoto, Kyoto Univ. Press (1976), pp. 536-543.

2. R. K. Hanson, J. P. Monat and C. H. Kruger, "Absorption of CO Laser Radiation by NO," J. Quant. Spectrosc. Radiat. Trans. 16, 705 (1976).

3. S. Salimian and R. K. Hanson, "Absorption Measurements of H_2O at High Temperatures Using a CO Laser," J. Quant. Spectrosc. Radiat. Trans. 30, 1 (1983).

4. M. Y. Louge and R. K. Hanson, "Shock Tube Study of Cyanogen Oxidation Kinetics," I. J. Chem. Kin. 16, 231 (1984).

5. D. S. Y. Hsu, C. Y. Lin and M. C. Lin, "CO Formation in Early Stage High Temperature Benzene Oxidation Under Fuel Lean Conditions: Kinetics of the Initiation Reaction, $C_6H_6 \rightarrow C_6H_5 + H$" *Twentieth Symposium (International) on Combustion*, The Combustion Institute (1985), p. 623.

6. R. K. Hanson, S. Salimian, G. Kychakoff and R. A. Booman, "Shock Tube Absorption Measurements of OH Using a Remotely Located Dye Laser," App. Opt. 22, 641 (1983).

7. M. Y. Louge and R. K. Hanson, "Shock Tube Study of High Temperature Absorption Spectroscopy of CH at 431 nm," *Shock Waves and Tubes*, ed. D. Bershader and R. K. Hanson, Stanford Press (1986), pp. 827-833.

8. M. Y. Louge, R. K. Hanson, E. C. Rea, Jr., and R. A. Booman, "Quantitative High Temperature Absorption Spectroscopy of NCO at 305 and 440 nm," J. Quant. Spectrosc. Radiat. Transf. 32, 353-362 (1984).

9. E. C. Rea, Jr., A. Y. Chang and R. K. Hanson, "Rapid-Tuning Laser Absorption Diagnostics for Shock Tube Flows," *Shock Tubes and Waves*, ed. H. Gronig, Weinheim, New York (1988), pp. 863-869.

10. D. F. Davidson, A. Y. Chang and R. K. Hanson, "Laser-Photolysis Shock Tube for Combustion Kinetics Studies," submitted to 22nd Combustion Symposium (International) on Combustion, Aug. 14-19, 1988, Seattle.

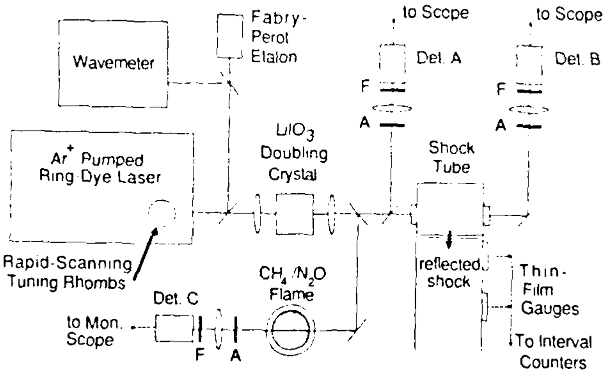

Fig. 1. Experimental arrangement for cw dye laser absorption measurements in a shock tube.

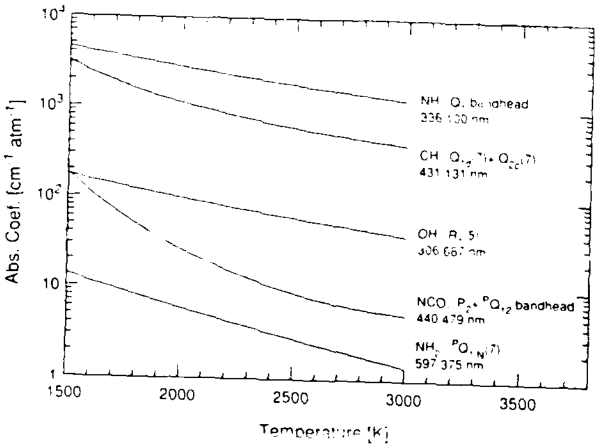

Fig. 2. Spectral absorption coefficients as a function of temperature for several radical species.

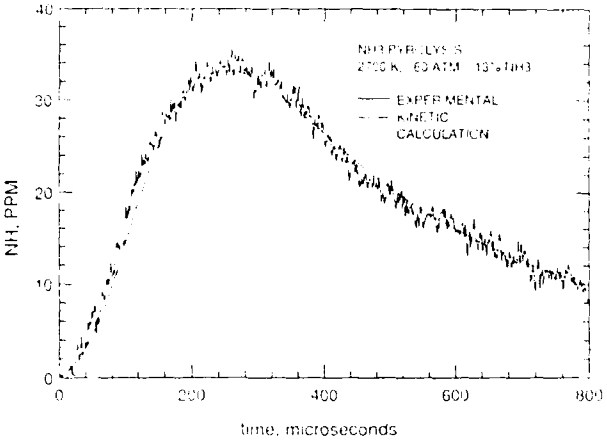

Fig. 3. Comparison of measured and calculated NH time histories in a reflected shock experiment.

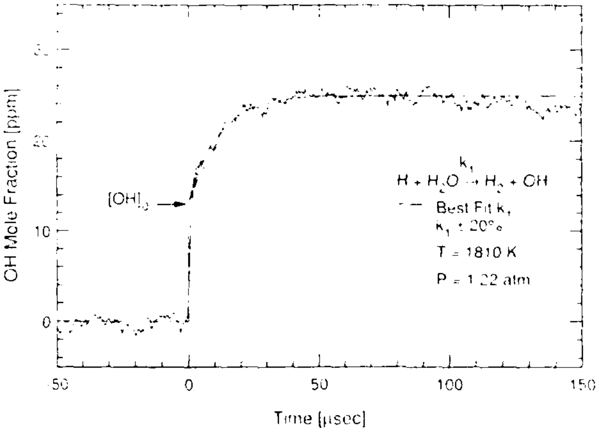

Fig. 6. Comparison of measured and calculated OH time histories following laser photolysis of shock-heated H_2O.

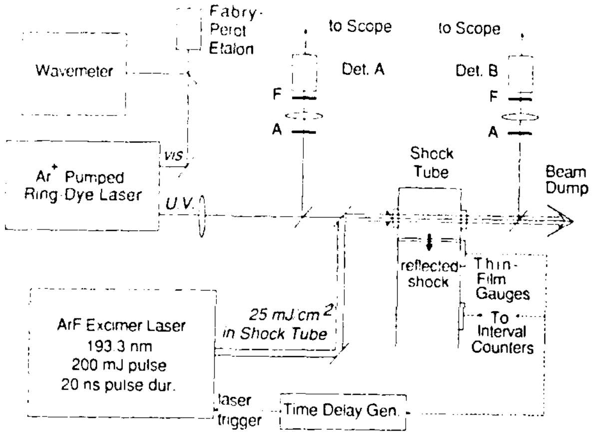

Fig. 4. Experimental arrangement for the laser photolysis shock tube in the transverse illumination mode.

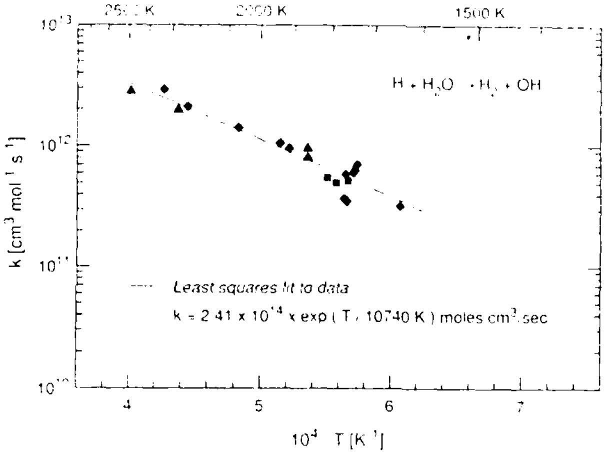

Fig. 7. Arrhenius diagram for the reaction $H + H_2O \quad H_2 + OH$.

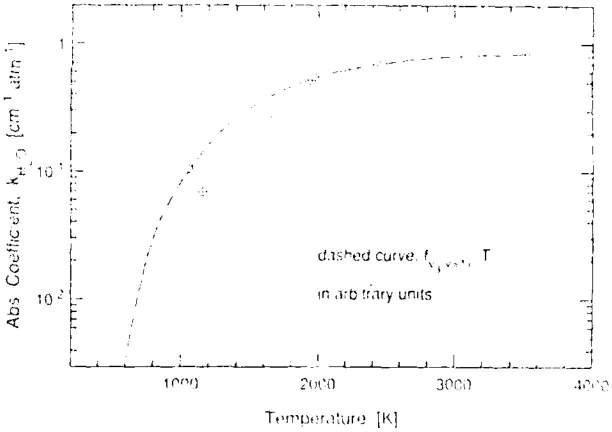

Fig. 5. Absorption coefficient of H_2O for excimer laser radiation at 193 nm.