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CARS DIAGNOSTICS FOR SOLID PROPELLANT COMBUSTION INVESTIGATIONS

Final Report

J. H. Stufflebeam

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The specific technical achievements of this Army Research Office contract are as follows. Coherent anti-Stokes Raman Spectroscopy (CARS) was first successfully applied to solid propellant combustion at elevated pressure (up to 35 atm) under this project. The high pressure equilibrium chemistry (temperature and multiple species concentration) of nitramine combustion was verified with the CARS measurements. The use of a high pressure, motorized combustion vessel allowed control of the spatial location of the burning propellant surface and data acquisition from the thin (100 micron), near-surface reaction zone. Dual broadband CARS of HCN, H_2CO and CH_4 was utilized to observe the competition between two major reaction mechanisms; they determine the speed of the overall reaction. Resolution of the temperature and species profiles in the reaction zone, required for further insight, was provided by a major advance, the implementation of Line CARS, a 1-D imaging geometry, that allows single shot (10 nsec) measurement of the large temperature and concentration gradients near the surface with a spatial resolution of 25 microns. These milestones have expanded the database of propellant combustion knowledge and provided valuable information for future formulations of energetic materials.

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FOREWORD

This report covers research performed under U. S. Army Research Office Contract DAAL03-87-C-0005 during the period September 1, 1987 to November 29, 1991. The CARS diagnostic technique was developed for the purpose of acquiring temperature and species concentration measurements in high pressure solid propellant flames. This work drew upon earlier ARO support through contract DAAG29-83-C-0001 that supported the basic research necessary to apply this laser diagnostic tool to high pressure environments. Single shot CARS spectra were acquired from nitramine propellant flames at elevated pressure and analyzed with the previously validated computer codes to predict the combustion parameters. A novel technique, the first successful one-dimensional configuration of CARS, was developed under this contract and used to demonstrate the acquisition of gradient features of the temperature and concentration near the combusting surface.

The personnel involved with this contract have had responsibilities for different phases of the work. John H. Stufflebeam performed the experimental investigations into propellant combustion at elevated pressure. A major component of the experimental apparatus, necessary for the near-surface CARS measurements, is the motorized combustion vessel. This was designed by Professor Kenneth Kuo and his group at The Pennsylvania State University, State College, PA. Professor Kuo was also a consultant to this contract, providing timely advice on propellant chemistry, program direction and integration of the results of this contract into the propellant combustion community. Eric B. Cummings, a UTRC summer employee, designed, fabricated and developed the laser diode, servo control circuit for the motorized combustion vessel. His efforts resulted in flawless operation of the propellant strand burner and allowed the acquisition of CARS spectra from within 100 microns of the burning surface. Alan C. Eckbreth provided overall advice on diagnostic techniques for the program and supplied specific solutions to experimental problems that were encountered. This contract was monitored by Dr. Robert W. Shaw, Chief, Chemical Diagnostics & Surface Science Branch and Dr. David M. Mann, Associate Director, Combustion/Propulsion. Both Drs. Shaw and Mann provided invaluable support and suggestions relating to energetic material combustion and guided the direction of this program.

CARS Diagnostics for Solid Propellant Combustion Investigations

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SUMMARY

The specific technical achievements of this Army Research Office contract are as follows. Coherent anti-Stokes Raman Spectroscopy (CARS) was first successfully applied to solid propellant combustion at elevated pressure (up to 35 atm) under this project. The high pressure equilibrium chemistry (temperature and multiple species concentration) of nitramine combustion was verified with the CARS measurements. The use of a high pressure, motorized combustion vessel allowed control of the spatial location of the burning propellant surface and data acquisition from the thin (100 micron), near-surface reaction zone. Dual broadband CARS of HCN, H_2CO and CH_4 was utilized to observe the competition between two major reaction mechanisms; they determine the speed of the overall reaction. Resolution of the temperature and species profiles in the reaction zone, required for further insight, was provided by a major advance, the implementation of Line CARS, a 1-D imaging geometry, that allows single shot (10 nsec) measurement of the large temperature and concentration gradients near the surface with a spatial resolution of 25 microns. These milestones have expanded the database of propellant combustion knowledge and provided valuable information for future formulations of energetic materials.

INTRODUCTION

Solid propellant combustion is an extremely important aspect of propulsion, rocketry and ballistics. Detailed, spatially and temporally precise, diagnostic measurements of temperature and species concentrations is of considerable aid in the development and improvement of these high pressure combustion systems. Understanding the transient, turbulent nature of solid propellant combustion requires measurement technology which has high temporal and spatial resolution and which can handle the severe combustion conditions (*e.g.,* high pressure); such results seek to identify dominant reaction mechanisms that can be affected by parameters such as fluid dynamics, transport properties, or autocatalysis which are usually designed out of the more basic experiments. In particular, information is desired of the regions close to the propellant surface, *i.e.,* the fizz zone or primary reaction zone, which will require a very high spatial resolution technique. Coherent anti-Stokes Raman Spectroscopy (CARS) is a nonintrusive, laser-based spectroscopy with high spatial and temporal resolution used for measurement of temperature and major species concentration. High pressure combustion is not a problem, in fact, it is an advantage from a signal strength standpoint; the CARS signal varies approximately as the square of the gas density.

Various approaches have been pursued to circumvent the experimental complexities of solid propellant combustion at high pressure. In particular, the foam zone and first stage reaction zone are highly inaccessible at moderate pressure (20 atm) because they are extremely small (10–100 microns). Model flames have been used, but they may not have all the critical species present in an actual solid propellant—thus some of the chemistry is missing. Solid propellants have been burned at low pressure with expanded reaction zones, but low pressure combustion may not follow the same rates and branches as at high pressure. Gas sampling methods have been applied (Heller and Gordon, 1955), but there are questions about the validity of this technique. The presence of the sampling probe may alter the flame chemistry or quench the flame and the gas sample itself may not be fully quenched, thus invalidating the results. Imbedded thermocouples have been used (Kubota, 1981), but they also may perturb the flame and give no information about species concentrations. Similarly, some more conventional optical techniques have been applied: emission and infrared absorption. These experiments are line of sight and subject to poor spatial resolution, which makes interpretation difficult. CARS can overcome most of these disadvantages and through its successful use in this research program has yielded some of the quantitative data desired by the propellant community.

In the next section of the report, the results of the work performed under this contract is summarized. The first three appendices list the presentations and publications that arose from the current contract, the personnel involved and, the inventions discovered. The remaining appendices give more details of each of the specific goals achieved during this work, including the verification of the thermo-chemical equilibrium combustion conditions, observation of the two major reaction pathways for nitramine combustion, and the application of Line CARS to acquire data on temperature and concentration gradients near the surface of propellant combustion with high temporal and spatial resolution.

CARS DIAGNOSTICS OF SOLID PROPELLANT COMBUSTION

Introduction

It was the purpose of this contract to demonstrate the application of CARS diagnostic techniques to hostile, high pressure, turbulent propellant flame environments in which few measurements of high accuracy or spatial precision were previously possible. Specific goals to be achieved were the measurement of temperature and species concentrations in the final flame zone of propellant combustion at high pressure, observation of reaction products from the near-surface reaction zones, demonstration of dual broadband CARS for multiple species signatures, and—the most demanding challenge and final goal of this work—the demonstration of Line CARS. Line CARS is a novel, one-dimensional phase-matching geometry that generates a "line" CARS image that is spectrally dispersed and detected on a 2-D array detector, yielding information about the spatial variation of temperature and species concentrations along the line. This valuable tool was then shown capable of measuring the gradients of temperature and concentration near the propellant surface, but only by meeting the stringent requirements of increasing the spatial resolution of CARS to $\sim 25\mu$ while maintaining the high, single shot temporal resolution of 10 nsec. All of these goals were achieved and the details are summarized in the following paragraphs; details are contained in appendices for the reader with specific interests.

Thermo-Chemical Equilibrium

The first experiments undertaken sought to obtain CARS measurements from the final flame zone of nitramine based propellant formulations. A supply of research propellant was acquired from the Air Force Astronautics Laboratory and it proved very reliable throughout the course of this contract. It contained the nitramine HMX, an energetic plasticizer, TMETN, and binder. The early experiments utilized a windowed combustion bomb within which the propellant strand burned cigarette fashion. Initially, the laser beams were aligned close to the surface, but as combustion occurred the propellant surface regressed further and further, so that the CARS experiment sampled the final flame zone during most of the burn. The success of these experiments did lead to quantitative measurements of temperature and species concentration, however, and a more detailed discussion of the verification of the thermo-chemical equilibrium calculations is contained in the paper "CARS Measurements of High Pressure Solid Propellant Combustion," presented at the 25^{th} JANNAF Combustion Meeting in October of 1988, and "CARS Diagnostics of Solid Propellant Combustion at Elevated Pressure," published in Combustion Science and Technology. These are included as Appendices D and E of this report.

Near-Surface Reactions

Due to the nature of solid propellant combustion, namely, its transient nature and regression of the burning surface, a unique facility was designed and implemented for these laser diagnostic experiments. A high pressure combustion vessel was fabricated that housed a motor attached to the propellant strand carrier. A diode-laser, servo system controlled the motor so the strand was advanced at precisely its regression rate to maintain the burning surface fixed in the laboratory frame. This allowed the CARS laser beams to

monitor the all-important surface region, the first few hundred microns above the strand, throughout the combustion process. Using this facility, observation of products from the two major reaction pathways of nitramine combustion was accomplished; additionally dual broadband techniques were applied in this experiment to generate multiple species signatures with each laser shot. This experiment is detailed in Appendix F.

Surface Gradients of Temperature and Concentration

The final goal of this contract was to use CARS to measure the temperature and species *gradients* immediately above the surface during propellant combustion. The small primary reaction zone was expected to be $\sim$ 100–200μ long, about the resolution of current CARS experiments at the start of the work. The servo-controlled combustion vessel was again a requirement for this experimental attempt. In addition, enhanced spatial resolution would be provided by expanding the 150μ diameter CARS focal spot to about 500μ in the direction perpendicular to the surface, thus forming a line focus. This line is imaged through a spectrograph onto a 2-D array detector, providing spectrally dispersed CARS signatures as a function of height in the flame. This severe test of the diagnostic approach was also accomplished. The image can be analyzed for temperature and concentration as a function of height, providing measurement of the spatial gradients, at the high temporal resolution (10 nsec) provided by this coherent laser diagnostic technique. Details of this experiment are included in Appendix G.

Conclusions and Recommendations for Further Work

This contract has shown that CARS may be successfully applied to high pressure solid propellant combustion. The equilibrium chemistry of high pressure nitramine combustion was verified through quantitative CARS measurements of the final flame zone. Use of a motorized combustion vessel was necessary for the majority of the experimental work; it provided access to the important surface region throughout the propellant burn, enabling state-of-the-art experiments. The observation of near-surface reaction products indicated two major reaction pathways in nitramine combustion, one involving HCN and the other, H_2CO. Measurements of the temperature and species concentration gradients adjacent to the surface of the propellant are possible as demonstrated by a novel spatial enhancement scheme called line CARS. Further work is necessary to analyze line CARS spectra, such as in Appendix G, for more quantitative determination of gradients. Thought has to be given to the proper normalization of the data and experiments need to be performed to guarantee the accurate registration of the combustion spectra and normalization data.

The instrumentation technology developed in this program led to successful demonstrations of CARS viability in the solid propellant environment. Even from these demonstration measurements inferences could be drawn regarding mechanisms of combustion. While some incremental improvements are still necessary, it is clear that further application of these methods to a wider variety of propellants and conditions should lead to even more insights into the operative mechanisms. Despite the challenges involved in performing CARS diagnostics, this research has demonstrated that with the right equipment and methodology CARS may be used successfully to obtain quantitative measurements of temperature, species concentrations, and, their gradients.

References

Heller, C.A. and Gordon, A.S. (1955). Structure of the Gas Phase Combustion Region of a Solid Double Base Propellant. *Journal of Physical Chemistry,* Vol. **59**, pp. 773–777.

Kubota, N. (1981). Combustion Mechanisms of Nitramine Composite Propellants. *18^{th} Symposium (International) on Combustion,* The Combustion Institute, pp. 187–194.

APPENDIX A

Publications/Presentations Under ARO Contract DAAL03-87-C-0005

Stufflebeam, J. H., "Progress of CARS Applications to Solid Propellant Combustion", presented at the JANNAF Combustion Subcommittee Panel Meeting on Kinetics and Related Aspects of Propellant Combustion Chemistry, Johns Hopkins University, Applied Physics Laboratory, Baltimore, MD, May 2–4, 1988. CPIA Publication 503, pp. 251–256.

Stufflebeam, J. H., "CARS Applications to Solid Propellant Combustion", presented at the Gordon Conference on the Chemistry of Energetic Materials, New Hampton, NH, June 27–July 1, 1988.

Eckbreth, A. C. and Stufflebeam, J. H., "New Concepts for CARS Diagnostics of Solid Propellant Combustion", invited paper presented at the Gordon Conference on the Chemistry of Energetic Materials, New Hampton, NH, June 27–July 1, 1988.

Stufflebeam, J. H. and Eckbreth, A. C., "CARS Measurements of high Pressure Solid Propellant Combustion", presented at the 25^{th} JANNAF Combustion Meeting, NASA/Marshall, Huntsville, AL, October 24–28, 1988. CPIA Publication 498, Vol. 1, pp. 113–122.

Stufflebeam, J. H. and Eckbreth, A. C., "Multiple Species CARS Measurements of High Pressure Solid Propellant Combustion", Paper No. AIAA-89-0060, presented at the AIAA 27^{th} Aerospace Sciences Meeting, Reno, Nevada, January 9–12, 1989.

Stufflebeam, J. H. and Eckbreth, A. C., "CARS Measurements of High Pressure Solid Propellant Flames", invited paper at the JANNAF Workshop on Advanced Diagnostic Methods for Propellant Combustion, U. S. Army ARDEC, Picatinny Arsenal, Dover, New Jersey, June 13–14, 1989. CPIA Publication 534, pp. 267–301.

Stufflebeam, J. H. and Eckbreth, A. C., "CARS Diagnostics of Solid Propellant Combustion at Elevated Pressures", poster paper presented at the 198 9 Gordon Conference on the Physics and Chemistry of Laser Diagnostics in Combustion, Plymouth State College, Plymouth, NH, July 17–21, 1989.

Stufflebeam, J. H., "Temperature and Multiple Species CARS Measurements of Solid Propellant Flames", presented at the 26^{th} JANNAF Combustion Meeting, JPL, Pasadena, CA, October 23–27, 1989. CPIA Publication 529, Vol. 2, pp. 107–116.

Stufflebeam, J. H., "CARS Measurements of High Pressure Solid Propellant Flames", invited presentation at U.S. Army ARDEC, Picatinny Arsenal, Dover, NJ, November 29, 1989.

Stufflebeam, J. H. and Eckbreth, A. C., "CARS Diagnostics of Solid Propellant Combustion at Elevated Pressure", Combustion Science and Technology, Vol. 66, 1989, pp. 163–179.

Stufflebeam, J. H., "Near Surface CARS and DFWM of Propellant Flames", invited paper presented at the 1990 Gordon Conference on the Chemistry of Energetic Materials, New Hampton School, New Hampton, NH, June 25–29, 1990.

Stufflebeam, J. H., "CARS Measurements in the Near Surface Region of Composite Nitramine Combustion", presented at the 27^{th} JANNAF Combustion Meeting, Warren AFB, Cheyenne, Wyoming, November 5–9, 1990. CPIA Publication 557, Vol. 3, pp. 57–65.

Stufflebeam, J. H., "CARS Diagnostics of Reaction Pathways for Nitramine Combustion", presented at the AIAA/SAE/ASME/ASEE 27^{th} Joint Propulsion Conference, Sacramento, California, June 24–27, 1991.

Stufflebeam, J. H. and Eckbreth, A. C., "Line CARS Experiment for High Pressure Combustion", presented at the 1991 Gordon Research Conference on the Physics and Chemistry of Laser Diagnostics in Combustion, Plymouth, NH, July 15–19, 1991.

Stufflebeam, J. H., "Line CARS Measurements of Nitramine Flame Structure", presented at the 28^{th} JANNAF Combustion Meeting, Brooks AFB, San Antonio, Texas, October 28–November 1, 1991.

APPENDIX B

Participating Scientific Personnel and Degrees Earned During This Contract

J. H. Stufflebeam
A. C. Eckbreth
E. B. Cummings
K. K. Kuo

APPENDIX C

Report of Inventions Under ARO Contract DAAL03-87-C-0005

None

APPENDIX D

CARS Measurements of High Pressure Solid Propellant Combustion

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Presented at

25th JANNAF Combustion Meeting
NASA/Marshall Space Flight Center
Huntsville, Alabama

October 24–28, 1988

CARS MEASUREMENTS OF HIGH PRESSURE SOLID PROPELLANT COMBUSTION *

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ABSTRACT

An experimental program is described that has led to the successful and reliable acquisition of CARS measurements from solid propellant combustion at elevated pressures ($\leq$ 35 atm). HMX/TMETN propellant has been burned in a high pressure combustion vessel and CARS spectra from the CO-N_2 resonant region have been obtained. Sequential laser shots record the temperature and major species concentrations every 100 msec as the propellant strand regresses away from the laser focus. The results show signatures from HCN, CO and N_2 immediately after ignition and spectral features of expected equilibrium products during the hot final flame. The measurement of concentration and temperature is performed by fitting the acquired spectra from computer generated, temperature and concentration dependent, CARS signatures. The data acquired at 23 atm show temperatures up to 2600K with a product distribution of $N_2 \sim 26\%$, CO $\sim 37\%$ and $H_2 \sim 24\%$.

INTRODUCTION

Knowledge of combustion species and temperature is necessary for accurate modeling of solid propellant reaction mechanisms and their effect on the macroscopic characteristics of the propellant. Simultaneous, multiple species measurements provide information on dominant processes and provide data for comparison with combustion models. Diagnostics of solid propellant combustion are extremely difficult because of the transient, turbulent medium and the very thin flame zones.

Little microscopic detail is known experimentally about solid propellant combustion at high pressure[1,2]. The complex flame structure and hostile experimental conditions of solid propellant combustion must be overcome for quantitative data to be obtained on the actual propellant formulation when it burns at the design parameters of temperature and pressure. The combustion is transient and very turbulent, requiring fast diagnostics to avoid averaging over the timescales of turbulence which could mask relevant chemical mechanisms. Various approaches have been pursued to circumvent these experimental complexities. Model flames have been used[3,4] but they may not have all the critical chemical species present in an actual solid propellant, thus some of the chemistry is missing. Solid propellants have been burned at low pressure to expand the reaction zones[5], but low pressure combustion may not follow the same routes and branches as at high pressure[6]. Imbedded thermocouples have been used[7] to measure temperature gradients at fixed points perpendicular to the solid propellant surface but they may perturb the flame and require extensive interpretation to yield valid results[8].

The very difficult experimental problems posed by solid propellant combustion environments challenge even the most modern diagnostic techniques. The transient, turbulent nature of solid propellant combustion dictates a diagnostic with high temporal resolution and also one that is applicable to actual combustion conditions (*e.g.*, high pressure) so that results will reflect dominant reaction mechanisms. Optical techniques offer the greatest potential for these studies but even their qualities of high spatial resolution and non-perturbation are strained for applications such as this. Some optical techniques have been applied, largely emission[9] and infrared absorption[10]. These experiments are line of sight and therefore have poor spatial resolution which makes interpretation difficult. The identification of some radicals has been achieved using laser-induced fluorescence (LIFS)[11,12]. LIFS interrogates only one species at a time and is used to measure minor constituents. Analysis of LIFS data is difficult because quenching rates are often not known to sufficient accuracy for the high pressure environments typical of solid propellant combustion.

Of the various optical techniques, CARS is best suited to solid propellant combustion. CARS is fast (10^{-8} second), non-intrusive, spatially and temporally precise, able to measure temperature and major species concentrations simultaneously with each laser pulse and its signal strength increases at more than a linear rate as the pressure increases above $\sim$ 1 atm due to constructive interference between neighboring, overlapping transitions.

This paper presents the preliminary results of experiments that apply CARS diagnostics to solid propellant combustion. The next section briefly reviews the principles of CARS, followed by an outline of the experimental arrangement. Selected CARS spectra are presented and estimates of temperature and major species concentration are obtained from comparisons with computer predictions. A discussion of the results follows and the major findings are summarized in the final paragraph.

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HIGH PRESSURE CARS SPECTROSCOPY

CARS results from a laser photon at frequency ω_1 scattering off an excited Raman coherence, ω_R, of the probed medium. The excitation of the medium is supplied by an additional laser ω_2, acting in concert with ω_1, which provides a frequency difference that is resonant with the Raman transition (*i.e.* $\omega_R=\omega_1-\omega_2$). The CARS frequency, ω_3, is given by:

$$\omega_3 = \omega_1 + (\omega_1 - \omega_2). \tag{1}$$

The CARS intensity is:

$$I(\omega_3) = \left(\frac{4\pi^2\omega_3}{c^2}\right)^2 I(\omega_1)^2 I(\omega_2)|\chi|^2 z^2 \tag{2}$$

where $I(\omega_i)$ is the intensity at ω_i, z is the interaction length and χ is the third order nonlinear susceptibility. The CARS intensity scales as $I(\omega_1)^2$ but is generally limited at elevated pressure by the gas breakdown threshold for $I(\omega_1)$. The effects of temperature and concentration on the CARS spectrum are contained in χ. Changes in temperature and concentration markedly alter the shape of CARS spectra and form the basis for measurements.

CARS exhibits a nonlinear dependence on molecular number density and increases rapidly in signal strength as the gas density is elevated. The intensity of CARS, however, is quite linewidth dependent. Collision processes alter the spectra by perturbing the rovibronic linewidth thus complicating the calculation of the CARS spectrum. For CARS, the collisional narrowing phenomenon is important for pressures above one atmosphere. Collisional narrowing occurs when adjacent Raman transitions have been pressure broadened to the extent that they overlap. The overlap allows communication between lines and they subsequently coalesce or collapse to a narrower bandwidth. Accurate modeling of high pressure, high temperature CARS spectra is necessary to extract temperature and density information and thus, is fundamental to the deployment of the technique as a diagnostic. Measurements of temperature and concentration rely on accurate models of the third order susceptibility, χ.

A precise model of the susceptibility, accurate at high pressure, has been developed[13] but requires extensive computer time because large matrices have to be inverted at each frequency. The size of the matrix depends on the number of active transitions in the molecule and thus increases with temperature. A less time consuming technique[14], requiring just a single inversion per spectrum has recently been incorporated in CARS calculations. To further simplify the evaluation, linewidth parameters which govern the pressure effects in the susceptibility (and are largely unknown), are modeled by an algorithm called the modified energy gap model[15]. The fitting parameters used in this model have been determined from very high resolution Raman spectra taken under controlled experimental conditions[15]. The predicted CARS spectrum is then obtained by a convolution of the pump laser linewidth with the calculated susceptibility. Early CARS codes employed convolutions published by Yuratich[16] but more recent experiments have determined a more accurate solution called the Kataoka-Teets (K-T) convolution[17,18]. The experimental conditions presented by solid propellant combustion and the laser sources used for these experiments require the use of the K-T convolution for analysis of the CARS spectra. A computer code[19] that embodies all the features previously mentioned was employed for the current analysis. It is used to generate single spectra that are visually compared with the experimental data to determine best estimates of temperature and concentration. A second feature of the code, least squares fitting of experimental data, was not used in this work.

The approach to CARS measurements in solid propellant combustion involves analyzing the CARS spectral distribution. A CARS spectrum is composed of resonant and nonresonant contributions. The resonant parts (i.e. CO, H_2 and N_2) are functions of the resonant molecule number density, temperature, resonant molecular constants, and pressure, through the rovibrational linewidths of the molecule. The nonresonant contribution is dispersionless, a function of total gas density and implicitly temperature, through the ideal gas law. Assuming the pressure is independently measured and accurate values of molecular constants are available, the CARS data contain information on the concentrations of CO, H_2, and N_2, the total gas density, and the gas temperature. In mathematical terms the data are represented by the squared modulus of the third order, nonlinear susceptibility,

$$|\chi|^2 = \chi'^2 + 2\chi'\chi^{nr} + \chi^{nr2} + \chi''^2| \tag{3}$$

where χ' and χ'' are the real and imaginary parts of the resonant susceptibility and χ^{nr} is the nonresonant part. Examination of Eqn. (3) can guide data analysis. For instance, it is clear that even when there is no resonant response in the sampled frequency interval *i.e.* χ', $\chi'' = 0$, there is still a CARS signal represented by χ^{nr} which is proportional to total gas density and, by invoking the ideal gas law, temperature. If a molecule has a resonance in the frequency window but is in low concentration such that $(\chi^{resonant})^2 \ll (\chi^{nr})^2$, a modulation of the nonresonant spectrum is predicted through the $2\chi'\chi^{nr}$ term. For this low concentration region, the spectral shape is density and temperature dependent and potentially useful for measurements of these parameters. CARS is a unique spectroscopy in this regard, in that concentration can be measured from spectral shape in certain density ranges.[20] This approach is limited to relatively low concentration, approximately less than 40%, and yields a concentration relative to the total density represented by the nonresonant susceptibility. The accuracy of the measurement depends on how well the nonresonant susceptibility of the total gas density can be determined. In many combustion applications the accuracy is $\sim$ 10%. It is this spectral shape sensitivity that allows estimates of the major species concentration in solid propellant combustion of nitramine propellants. For higher concentration of a resonant species the spectral shape concentration sensitivity is lost and concentration measurements must rely on an absolute measurement. For molecules in very high concentration, the background (nonresonant) signal is lost and the pure resonant response is most evident.

EXPERIMENTAL APPARATUS

CARS DIAGNOSTIC FACILITY

A schematic layout of the optical configuration is shown in Fig. 1. The primary pump, ω_1, is a 10 nanosecond pulse of radiation from a Q-switched Nd:YAG laser operating at 10 Hz with an average output of 2.2 Watts at 532 nm. The pulse width is short enough to freeze the effect of any flame turbulence which could interfere with data interpretation. A folded BOXCARS[21] phase-matching geometry is used to probe the flame structure of solid propellant combustion at elevated pressure. A beamsplitter separates 40% from ω_1 to pump the broadband Stokes dye laser oscillator and amplifier. This Stokes source allows interrogation of Raman resonances with shifts from 1850–2350 cm^{-1} which includes the molecular response of NO, H_2, HCN, CO, N_2, and N_2O. The primary pump is subsequently passed through a polarizer then divided into two pump beams for the folded BOXCARS phase-matching geometry by a beamsplitter/mirror combination. The polarization of each beam is independently controlled by half-wave plates. Galilean telescopes are provided to control beam waists and the focal zone locations of ω_2 and the ω_1's. CARS, at $\omega_3 = 2\omega_1 - \omega_2$, is produced in the propellant exhaust by focussing the pump beams to a cylindrical interaction region ($\sim$ 200 μ diameter by 3 mm long). The CARS frequency is spatially filtered and sent to a 0.6 m spectrograph where it is dispersed and imaged onto a 1000 channel intensified diode array. A spectrograph slit width of 50 μ results in a spectral resolution of $\sim$ 2.8 cm^{-1}. The detector is gated on for 100 nsec during the experiment to record the CARS spectrum and to suppress interferences from flame luminosity. The spectra are acquired at the laser repetition frequency and subsequently stored in a computer for analysis at a later time. A He-Ne laser is shown whose output is coincident with the ω_2 path and used for optical alignment. A beamsplitter in the ω_3 leg provides a reference signal to a photomultiplier which is used to monitor the spectrally-integrated CARS signal strength. Not shown in Fig. 1 is a video camera and recording system used to review each propellant burn for signs of abnormal combustion (*i.e.*, burning down the side of the strand).

SOLID PROPELLANT COMBUSTION VESSEL

The combustion vessel is a closed bomb with provision for pressurization with a background gas up to $\sim$ 50 atm. The bomb has three BK-7 windows for optical diagnostics, two are used for CARS and the third for video recording the combustion. The windows have a 40 mm clear aperture and are 38 mm from the center of the propellant strand. The 12.5 mm strands have a 6 mm square cross section and are ignited with nichrome wire. The fixed laser beams are initially focussed $\sim$ 1 mm above the strand and the propellant regresses away as it burns. CARS spectra are acquired every 100 msec during the burn and form a record of the temperature and major species of the flame structure.

RESULTS

Strands of HMX/TMETN were burned at pressures up to 35 atm in a flowing background gas of helium. Helium is chemically inert and has a low nonresonant susceptibility, adding negligible signal to the CARS spectra. A 12.5 mm strand has a burn rate of $\sim$ 2 mm/sec at 23 atm, where much of the data has been acquired, and results in the acquisition of approximately 60 single-shot CARS spectra. Steering of the laser beams due to refraction through the high pressure, hot gas was not a problem. However, some spectra, perhaps 1 or 2 out of the 60, exhibit interference from laser-induced gas breakdown or scattering from particulates in the flame. The spectra are of high quality with low noise and well defined modulations from the resonant species.

CARS SPECTRA

Figure 2 is a single pulse CARS spectrum from HMX/TMETN propellant burning at 23 atm pressure. The spectrum is taken immediately after ignition when the laser focus is $\sim$ 1 mm above the surface. HCN and CO predominate the spectrum and there is a lesser amount of N_2. The gas appears relatively cool in this data. N_2O is also resonant in this spectral region (2223 cm^{-1}) but no signatures from this molecule have been observed in our experiments. Similarly, experiments that used a slightly different ω_2 spectrum detected no NO (1877 cm^{-1}). Figure 3 is a spectrum later in the burn when the strand has regressed $\sim$ 2.4 mm away from the laser focus. In this case the gas shows considerable heating, as evidenced by significant population of high vibrational states, the absence of HCN, increased concentration of CO and N_2, and the presence of strong signals from the pure rotational transitions of H_2. At the end of propellant combustion, Fig. 4, the gas has started to cool down and again H_2, CO and N_2 are detected. Analysis of these data involves comparison with computer generated spectra to determine the concentration and temperature from the molecular signatures contained in the data.

TEMPERATURE AND SPECIES MEASUREMENTS

The CARS data are visually compared to computer generated spectra for estimates of temperature and species concentration. Shown in Fig. 5 is a comparison of a theoretical spectrum (solid line) to the experimental CARS data (open circles) immediately after ignition (Fig. 2). The experimental data was divided by the broadband Gaussian Stokes laser profile to yield the experimental data set. This technique removes the apparent variation in nonresonant susceptibility and results in resonant signatures that modulate the constant background signal. The modulation is only moderate for the spectra from HMX/TMETN and affords the opportunity to predict relative concentration from spectral shapes[20], in addition to measurement of the gas temperature. The data in Fig. 5 show resonant modulations from HCN, CO and N_2. The computer program does not contain the molecular constants for HCN, so the theory does not predict the feature at 2090 cm^{-1}. Work is currently in progress to incorporate this molecule in the UTRC CARS code at which time estimates of its concentration can be made from the experimental data. The theoretical spectrum is seen to fit the CO and N_2 portions of the data very well with parameters of T = 700K, C_{N_2} = 8.8%, C_{CO} = 17.4%. A higher temperature data set is shown in Fig. 6, again the dye laser profile has been divided into the experimental data (Fig. 3). The best theoretical fit represents T = 2600K, C_{N_2} = 25.9%, C_{CO} = 37.5% and C_{H_2} = 23.6%. Similarly, Fig. 7 shows the data of Fig. 4 together with the best fit parameters of T = 1900K, C_{N_2} = 21.6%, C_{CO} = 40.6% and C_{H_2} = 25.7%.

DISCUSSION

The agreement between theory and experiment demonstrated in the last three figures is impressive. However the analysis of the data is preliminary and further efforts should refine the measurements. A fact worthy of mentioning again is that no signatures from NO or N_2O were observed in our experiments to date, although they are expected for some chemical mechanisms[22] that may occur near the propellant surface.

Except for the first few laser shots ($\sim$ 300 msec), where HCN is detected, the CARS spectra contain only signatures from expected equilibrium products[11], CO, H_2 and N_2. The other major products are CO_2 and H_2O. The assumption that the remaining gas is CO_2 and H_2O determines the nonresonant susceptibility used in the computer generated spectra according to Eq. 4.

$$\chi^{nr}_{mix} = n \sum c_i \chi^{nr}_i \tag{4}$$

The spectra from the hot final flame indicate CO, H_2 and N_2 account for 87% of the total gas mixture. It is the remaining 13% that is undetermined and has an unknown susceptibility that can affect the accuracy of the CARS measurements. If the remaining 13nonresonant susceptibility that varied by 50% from the values for CO_2 and H_2O, the concentration estimates for H_2, CO and N_2 would change by only 10%. The uncertainty in estimates from Fig. 5 (near the propellant surface) is larger because the resonant species account for a lower fraction of the total gas density.

The visual fitting process showed significant departures from the experimental data for temperatures that varied $\pm$ 50K and this uncertainty should be reduced upon further work.

Time has not allowed comparisons with the equilibrium product distribution predicted for this propellant formulation from the Gordon-McBride[23] computer code but the analysis will be done in the near future.

A question arises from this experiment as to whether the HCN, seen in the first few spectra results from a thin steady-state flame zone near the propellant surface or if it merely results from an ignition transient. An experiment is being designed that utilizes a motorized strand burner and should help to answer this question.

FUTURE IMPROVEMENTS

Future improvements include use of a motorized strand burner[24] to hold the burning propellant surface fixed in space and fast response pressure transducers to record the pressure history during the burn. The experiments will be enhanced by multi-color CARS techniques[25] to acquire more resonant signatures, simultaneously with each pulse. Additionally, enhanced resolution techniques[26] will be developed to probe regions close to the propellant surface and provide data of temperature and concentration gradients.

SUMMARY

CARS has been successfully applied to solid propellant combustion at elevated pressure and single pulse acquisition of spectra is reliable. The results show signatures from HCN, CO, and N_2 in the ignition phase of the combustion ($\sim$ 700 K) and spectral features of expected equilibrium products during the hot final flame. A few of the spectra have been analyzed for temperature and species concentration, and show temperatures as high as 2600K with N_2 concentration of $\sim$ 26% and CO $\sim$ 37%. Analysis is continuing as well as comparison with predictions of equilibrium products, their concentrations, and temperatures from the Gordon McBride computer code.

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HIGH PRESSURE, HIGH TEMPERATURE CARS FACILITY

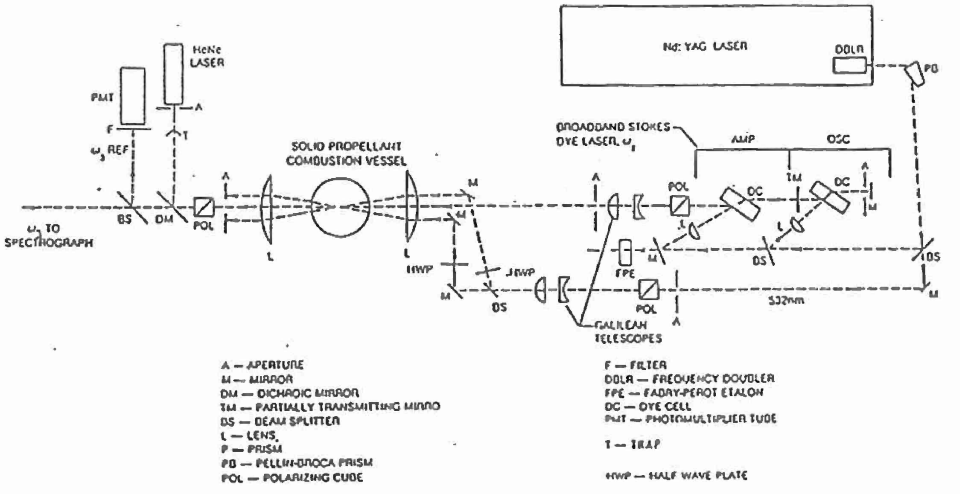


Figure 1.

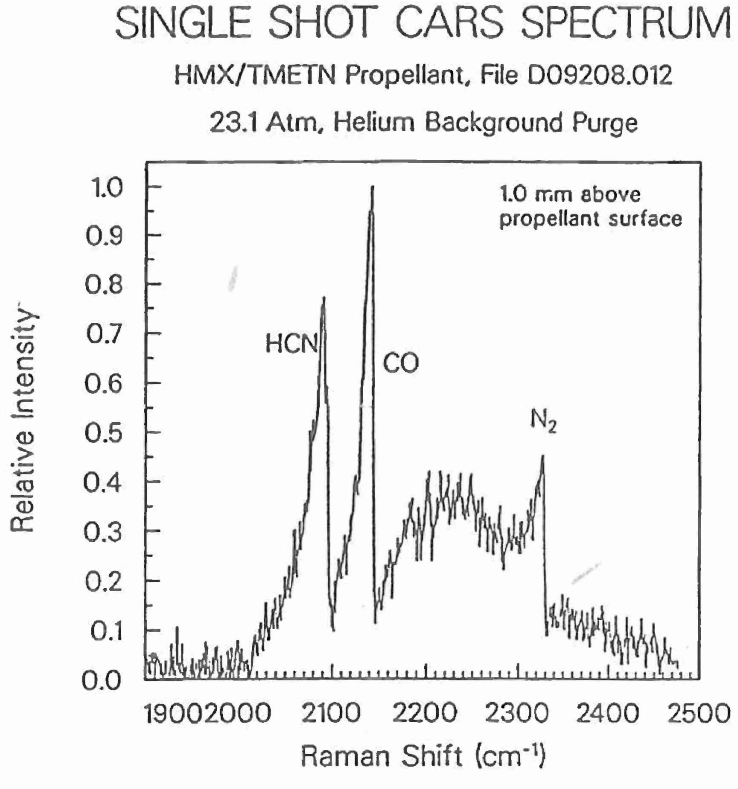


Figure 2.

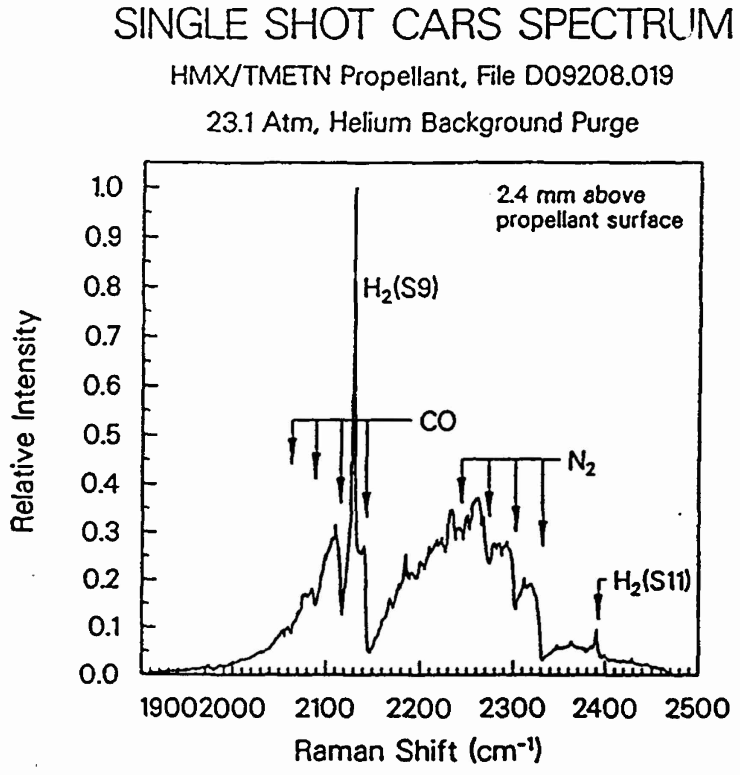
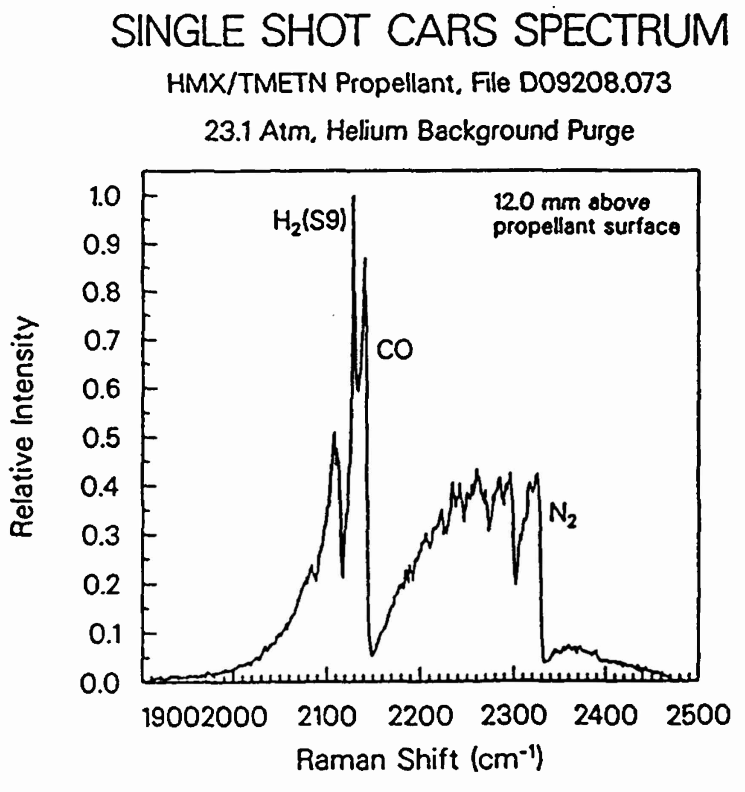


Figure 3.



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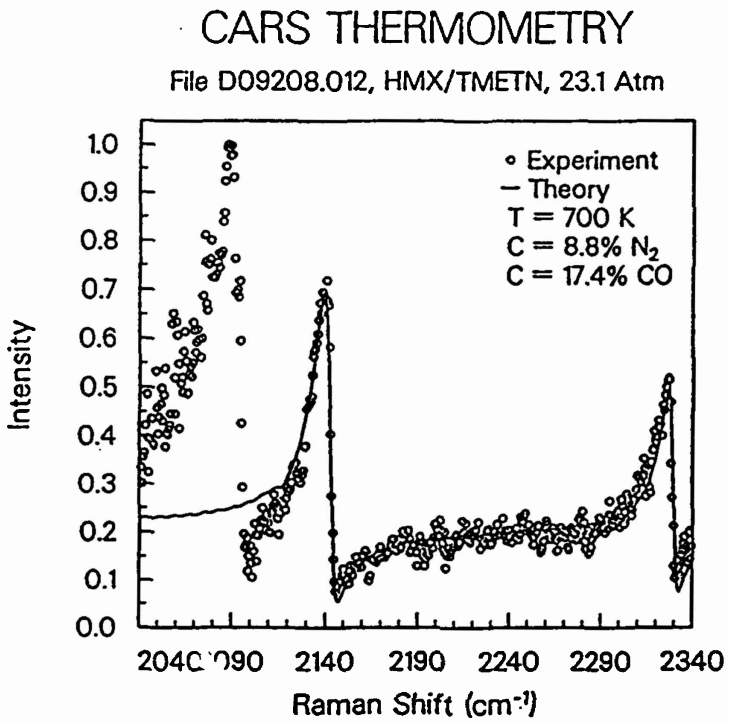
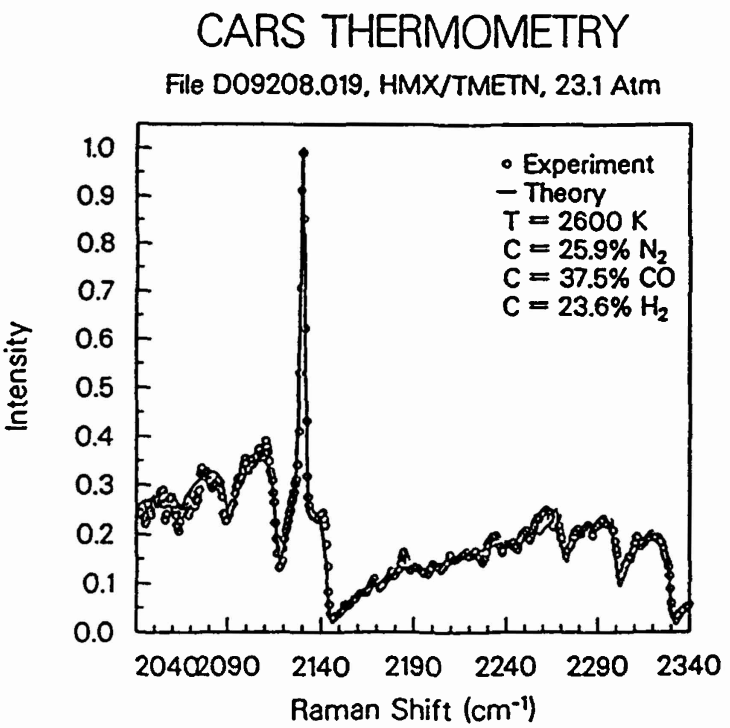


Figure 5.



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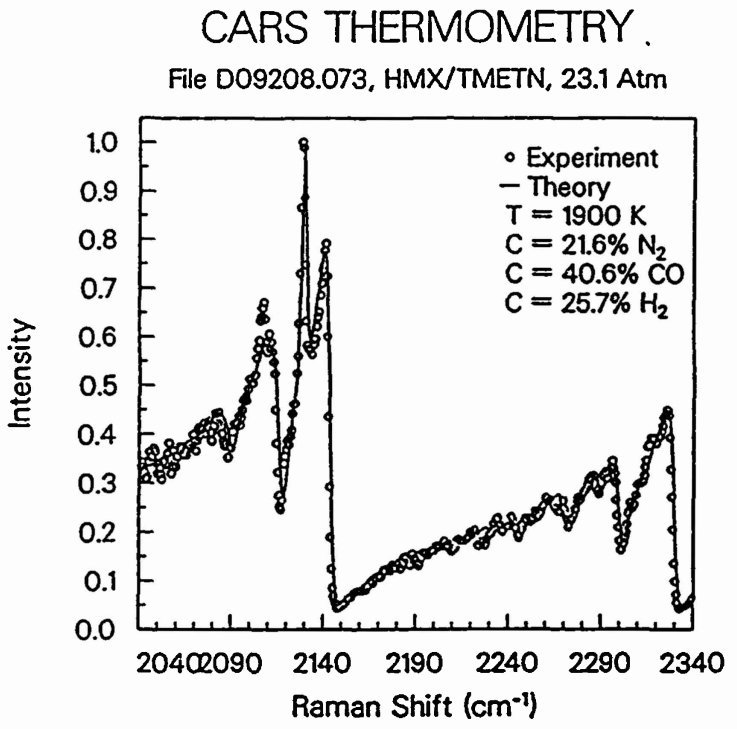
CARS THERMOMETRY
File D09208.073, HMX/TMETN, 23.1 Atm
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
2040
2090
2140
2190
2240
2290
2340
Raman Shift (cm-1)
o Experiment
— Theory
T = 1900 K
C = 21.6% N2
C = 40.6% CO
C = 25.7% H2

Figure 7.

APPENDIX E

CARS Diagnostics of Solid Propellant Combustion at Elevated Pressure

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CARS Diagnostics of Solid Propellant Combustion at Elevated Pressure

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Abstract—The first CARS measurements of temperature and species concentrations in the exhaust of solid propellants burning at elevated pressure (≤ 35 atm) are reported. Multiple species data are acquired at high temporal (10 ns) and spatial resolution from both a homogeneous, double-base and a composite nitramine propellant. CARS spectra have been obtained from three spectral regions that encompass the signatures of the major combustion products, CO_2, CO–N_2, and H_2O. The CARS data are analyzed by comparison with computer synthesized spectra generated at various temperatures and species concentrations. Results in the postflame zone from nitramine combustion at 23 atm indicate temperatures as high as 2600 K with species concentrations of $N_2 \sim 23\%$, CO $\sim 36\%$, and $H_2 \sim 23\%$. These results compare favorably with predictions of temperature and concentration from a chemical equilibrium code that simulates the combustion parameters. Utilization of dual broadband approaches will allow the simultaneous acquisition of data from the three spectral regions with each laser pulse.

INTRODUCTION

Knowledge of combustion species and temperature is necessary for accurate modeling of solid propellant reaction mechanisms and their effect on the macroscopic behavior of the propellant. Simultaneous, multiple species measurements provide information on dominant kinetic processes and provide data for comparison with combustion models. Diagnostics of solid propellant combustion are extremely difficult because the process is transient, the combustion gases are turbulent, often particle-laden and the flame zones are very thin.

Various approaches have been pursued to circumvent the experimental complexities presented by solid propellant combustion. Model flames have been used (Branch *et al.*, 1987; Thorne *et al.*, 1986; Vanderhoff *et al.*, 1986) but they may not precisely simulate an actual burning solid propellant. Propellants have been burned at low pressure to expand the reaction zones (Aron and Harris, 1984), but low pressure combustion may not follow the same routes and branches as at high pressure (Westbrook, 1984). Considerable benefit is likely to be derived from experiments on solid propellants burning under actual design conditions. Initial diagnostics included imbedded thermocouples (Kubota *et al.*, 1974) to measure temperature gradients at fixed points perpendicular to the solid propellant surface. They may perturb the flame, require extensive interpretation to yield valid results (Miller *et al.*, 1984), and moreover, provide no information about the molecular constituents. Optical techniques offer the greatest potential for these studies, but even their qualities of high spatial resolution and potential multiple species measurements are strained for applications such as this. Emission (Edwards *et al.*, 1986a; Mal'tsev *et al.*, 1973) and absorption (Vanderhoff, 1988; Bent and Crawford, 1959) experiments are line of sight which makes interpretation difficult. Laser-induced fluorescence (LIFS) has been used for identification of select radicals (Parr and Hanson-Parr, 1987; Edwards *et al.*, 1986b) but generally only one species at a time is interrogated. Analysis of LIFS data is difficult because quenching rates are often not known to sufficient accuracy for the high pressure

environments typical of solid propellant combustion. Nevertheless, it is the preferred approach for measurement of the minor constituents. Of the various laser-optical techniques for major species, CARS appears best suited to solid propellant combustion and, indeed, has been applied to low pressure solid propellant studies (Aron and Harris, 1984). CARS is not affected by quenching, is fast (10^{-8} s), non-intrusive, spatially precise and able to measure temperature and major species concentrations simultaneously with each laser pulse.

This paper presents the initial results of experiments that apply CARS diagnostics to elevated pressure solid propellant combustion and describes measurements of temperature and species concentrations from such data. The next section briefly reviews the principles of CARS, followed by an outline of the experimental arrangement. Selected CARS spectra are presented and estimates of temperature and major species concentration are obtained from comparisons with computer synthesized spectra. A discussion of the results then follows and future directions for this research are indicated.

TECHNICAL BACKGROUND

Solid Propellant Combustion

Solid propellant combustion presents unique experimental challenges. Unlike gas or liquid fuel combustion, there is no control of stoichiometry after ignition, nor is there any control of fuel or oxidizer flow rate. The sample consumes itself in a relatively short time, restricting the data acquisition process. The data are then compared to predictions based on the components used to prepare the propellant formulation. Theoretical mechanisms (Fifer, 1984; Melius, 1988) predict what the products should be and form the basis for experimental design. The propellants investigated in our experiments produced equilibrium products such as CO_2, CO, N_2, H_2 and H_2O. Additionally chemical mechanisms may be inferred if some intermediate species are observed and insight is obtained as well, if particular molecules are not observed. Some of the intermediate species that are predicted for the propellants studied here are NO_2, NO, HCN, N_2O and H_2CO. The major Raman resonant frequencies for these molecules are listed in Table I. The experiment should be designed to observe as many of these species as possible, all simultaneously.

It is also necessary to execute the experiments at elevated pressure, for the reasons already cited. Chemical equilibrium codes (Gordon and McBride, 1976) are useful for predicting the temperature and final product distributions at pressures of interest. This has been done for the propellants used in our studies and the results are presented

TABLE I
Raman resonances

NO_2	1320 cm^{-1}
CO_2	1388
NO	1876
HCN	2097
CO	2143
N_2O	2223
N_2	2331
H_2CO	2780
H_2O	3657
H_2	4161

TABLE II
Equilibrium calculations of propellant combustion

Propellant	Pressure (atm)	Temperature (K)	Mole fraction (%)				
			CO_2	CO	H_2	N_2	H_2O
NOSOL 436	20	2405	8.6	41.2	17.3	11.2	21.1
HMX/TMETN	20	2627	5.0	34.2	18.8	23.9	17.6

in Table II. The NOSOL 436 is a homogeneous double-base propellant and HMX/TMETN is a composite nitramine. Calculations are presented for just one pressure, close to that of our experiments. The equilibrium values are quite insensitive to variation of this parameter; changes in pressure by a factor of 2 have little effect ($\leqslant 0.5\%$) on the results in the table.

High Pressure CARS

CARS results from a laser photon at frequency ω_1 scattering off an excited Raman coherence, ω_R, of the probed medium. The excitation of the medium is supplied by an additional laser ω_2, acting in concert with ω_1, which provides a frequency difference that is resonant with the Raman transition (*i.e.*, $\omega_R = \omega_1 - \omega_2$). The CARS frequency, ω_3, and intensity are given by:

$$\omega_3 = \omega_1 + (\omega_1 - \omega_2) \tag{1}$$

$$I(\omega_3) = \left(\frac{4\pi^2\omega_3}{c^2}\right)^2 I(\omega_1)^2 I(\omega_2)|\chi|^2 z^2 \tag{2}$$

where $I(\omega_i)$ is the intensity at ω_i; z, the interaction length; and χ the third order nonlinear susceptibility. The CARS intensity scales as $I(\omega_1)^2$ but is generally limited at elevated pressure by the gas breakdown threshold for $I(\omega_1)$. The effects of temperature and concentration on the CARS spectrum are contained in χ. Changes in temperature and concentration markedly alter the shape of CARS spectra and form the basis for measurements (Hall and Eckbreth, 1984).

CARS measurements in solid propellant combustion involve analyzing the CARS spectral distribution. The spectrum is composed of resonant and nonresonant susceptibility contributions. The resonant parts are functions of the molecular number density being probed (N_2, CO, H_2, etc.), temperature, pressure and various molecular parameters, *e.g.*, the rovibrational linewidths of the molecule. The nonresonant contribution is dispersionless, a function of total gas density and composition, and, implicitly, temperature, through the ideal gas law. Assuming the pressure is independently measured and accurate values of molecular properties are available, the CARS data contain information on the concentrations of the resonant constituents, the total gas density, and the gas temperature. In mathematical terms, the data are represented by the squared modulus of the third order, nonlinear susceptibility, which for a single resonance, may be written as (Eckbreth, 1988)

$$|\chi|^2 = \chi'^2 + 2\chi'\chi^{nr} + \chi^{nr2} + \chi''^2 \tag{3}$$

where χ' and χ'' are the real and imaginary parts of the resonant susceptibility and χ^{nr} is the nonresonant part. Similar to their refractive index counterparts, χ' has a

dispersive shape (goes from negative to positive through line center) and χ'' exhibits lineshape behavior. Examination of Eq. (3) illustrates data analysis. For instance, it is clear that even when there is no resonant response in the sampled frequency interval, *i.e.*, χ', $\chi'' = 0$, there is still a CARS signal represented by χ^{nr} which is proportional to total gas density and, by invoking the ideal gas law, temperature. If a molecule has a resonance in the frequency window but is in low concentration, such that $(\chi', \chi'')^2 \ll (\chi^{nr})^2$, a modulation of the nonresonant spectrum is predicted through the $2\chi'\chi^{nr}$ term. For this low concentration region, the spectral shape is density and temperature dependent and useful for measurements of both these parameters. CARS is a unique spectroscopy in this regard, in that concentration can be measured from the spectral shape in certain density ranges. This approach is limited to relatively low concentration, approximately less than 40%, and yields a concentration relative to the total density represented by the nonresonant susceptibility. The accuracy of the measurement depends on how well the nonresonant susceptibility of the total gas mixture can be determined. In many combustion applications, the relative accuracy is $\sim \pm 10\%$. It is this spectral shape sensitivity that allows estimates of the major species concentrations in solid propellant combustion. For molecules in very high concentration, the background (nonresonant) signal is obscured by the more evident, pure resonant response. At these higher concentrations, the spectral shape concentration sensitivity is lost and concentration measurements must rely on an absolute intensity measurement. At very low concentrations, $\lesssim 0.5\%$, the shape sensitivity is lost in the nonresonant background, which must be suppressed for a species to be detectable (Rahn *et al.*, 1979).

CARS exhibits a nonlinear dependence on molecular number density and increases in signal strength as the gas density is elevated. The intensity of CARS, however, is quite linewidth dependent. Collision processes alter the spectra by perturbing the rovibronic linewidths thus complicating the calculation of the spectrum. For CARS, collisional narrowing is generally important for pressures above one atmosphere (Hall *et al.*, 1980). Collisional narrowing occurs when adjacent Raman transitions have been pressure broadened to the extent that they overlap. The overlap allows communication between lines and they subsequently coalesce or collapse to a narrower bandwidth. Accurate modeling of high pressure, high temperature CARS spectra is necessary to extract temperature and density information and thus, is fundamental to the deployment of the technique as a diagnostic. Measurements of temperature and concentration rely on accurate models of the third order susceptibility, χ.

A precise model of the susceptibility, accurate at high pressure, has been developed (Hall *et al.*, 1980) but requires extensive computer time because large matrices have to be inverted at each frequency. The size of the matrix depends on the number of active transitions in the molecule and thus increases with temperature. Koszykowski *et al.* (1985) recently incorporated a less time consuming approach for such CARS calculations, requiring just a single inversion per spectrum. To further simplify the evaluation, linewidth parameters, which govern the pressure effects in the susceptibility (and are largely unknown), are modeled by an algorithm called the modified energy gap model (Rahn and Palmer, 1986). The fitting parameters used in that model have been determined from very high resolution Raman spectra taken under controlled experimental conditions (Rahn and Palmer, 1986). The predicted CARS spectrum is then obtained by a convolution of the pump laser linewidth with the calculated susceptibility (Kataoka *et al.*, 1982; Teets, 1984) through an expression popularly called the Kataoka–Teets (K–T) convolution. The experimental conditions presented by solid propellant combustion and the laser sources used for these experiments require the use of the K–T convolution for analysis of the CARS spectra. A computer

code (Clark, 1986) that embodies all the features previously mentioned has been employed for the current analysis. It is used to generate spectra that are visually compared with the experimental data to determine best estimates of temperature and concentration. A second feature of the code, least-squares fitting of experimental data, has also been used for portions of this work although it requires many hours of computer time per spectrum (*e.g.*, up to 40 hours of CPU time on a Convex C220).

EXPERIMENTAL APPARATUS

Optical Configuration

A three-dimensional folded BOXCARS (Shirley *et al.*, 1980) phase-matching geometry was used to probe the flame structure of solid propellant combustion at elevated pressure. The configuration is shown schematically in Figure 1. The primary pump, ω_1, is a 10 ns pulse of 532 nm radiation from a Q-switched Nd : YAG laser operating at 10 Hz. The pulse width is short enough to freeze the effect of any flame turbulence which could interfere with data interpretation. A broadband Stokes dye laser is pumped by a portion of the 532 nm beam and forms the ω_2 laser. CARS, at $\omega_3 = 2\omega_1 - \omega_2$, is produced in the propellant exhaust by focussing the pump beams to a cylindrical interaction region ($\sim 200\,\mu$ diameter by 3 mm long). The CARS frequency is spatially filtered and sent to a 0.6 m spectrograph where it is dispersed and imaged onto a 1000 channel intensified diode array. The measured spectral resolution is 2.8 cm^{-1}. Single pulse spectra are acquired at the laser repetition frequency and subsequently stored in a computer for analysis at a later time.

Three different Stokes sources were used for the CARS experiments. A dye laser employing Rhodamine 590 and 610, centered at 1300 cm^{-1} from the pump, excited resonances in the CO_2 region. Kiton Red 620 and Rhodamine 640 provide a laser that allows interrogation of Raman resonances with shifts from 1850–2350 cm^{-1} which includes the molecular responses of NO, H_2, HCN, CO, N_2, and N_2O. The laser used for the H_2O region was achieved with the dye DCM dissolved in DMSO.

Solid Propellant Combustion Vessel

The combustion vessel is a closed bomb with provision for background gas purge at pressures up to ~ 50 atm. The bomb has three BK-7 windows for optical diagnostics; two are used for CARS and the third for video recording of the combustion. The windows have a 40 mm clear aperture and are 38 mm from the propellant strand. The 12.5 mm long strands of nitramine propellant have a 6 mm square cross section and are ignited with NiChrome wire. The double base propellant is a cylinder, 11 mm in diameter. The fixed laser beams are initially focussed 1 mm above the strand and the propellant surface regresses as it burns. CARS spectra are acquired every 100 ms during the burn and form a record of the temperature and major species of the flame structure.

RESULTS

CARS Spectra

Single shot CARS spectra have been acquired from the exhaust of combusting solid propellant and the data have been analyzed to determine the temperature and species

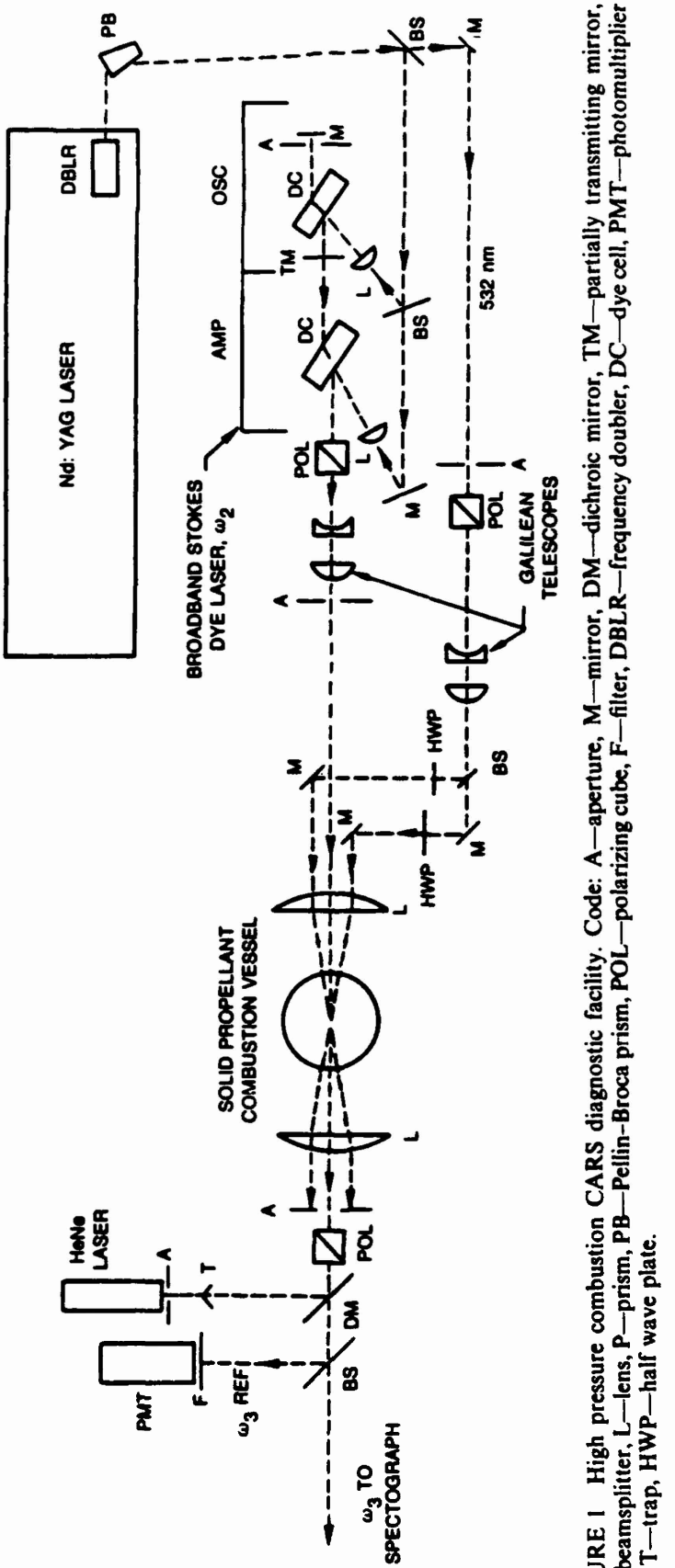

FIGURE 1 High pressure combustion CARS diagnostic facility. Code: A—aperture, M—mirror, DM—dichroic mirror, TM—partially transmitting mirror, BS—beamsplitter, L—lens, P—prism, PB—Pellin-Broca prism, POL—polarizing cube, F—filter, DBLR—frequency doubler, DC—dye cell, PMT—photomultiplier tube, T—trap, HWP—half wave plate.

concentration of the major molecular constituents. The propellants are burned with a background of helium which is chemically inert and has a low nonresonant susceptibility, adding negligible signal to the CARS spectra. A typical experiment lasts 5 or 6 s and results in 50–60 single shot CARS spectra. The experiments have been performed with a composite nitramine, HMX/TMETN, and a homogeneous, double-base propellant, NOSOL 436.

HMX/TMETN The highest pressure that has been employed to date in the propellant studies is 35 atm and Figure 2 is a representative single pulse spectrum from that combustion environment. The spectrum was acquired at a distance of 5.5 mm above the surface of the burning propellant and exhibits species signatures from CO, N_2 and H_2. Most of the experiments were performed at 23 atm so that they would be compatible with the LIF and emission spectroscopy work performed on an identical propellant (Edwards *et al.*, 1986a, b). A video record of each propellant burn was made to provide a means for measuring the distance between the laser focus and the propellant surface as it regressed. Mie scattering of the laser beams shows up clearly on the video tape and provides a reference for distances to the moving surface. Shown in Figure 3 are the data derived from the video record of the experimental run that provided the CARS spectra of HMX/TMETN combustion at 23 atm presented in the remainder of this paper. The lasers were initially focussed 1.7 mm above the strand and ignition occurred at $t = 0$ seconds. There is an ignition transient of ~ 0.6 s during which the flame spreads across the propellant surface but the strand does not regress. After the transient, the strand regresses with a nearly constant burn rate of 2.1 mm/s and is totally consumed after 6.4 s. Figure 4 is a single pulse CARS spectrum from the nitramine propellant burning at 23 atm pressure. The spectrum is taken immediately after ignition when the laser focus is ~ 1.7 mm above the surface. The

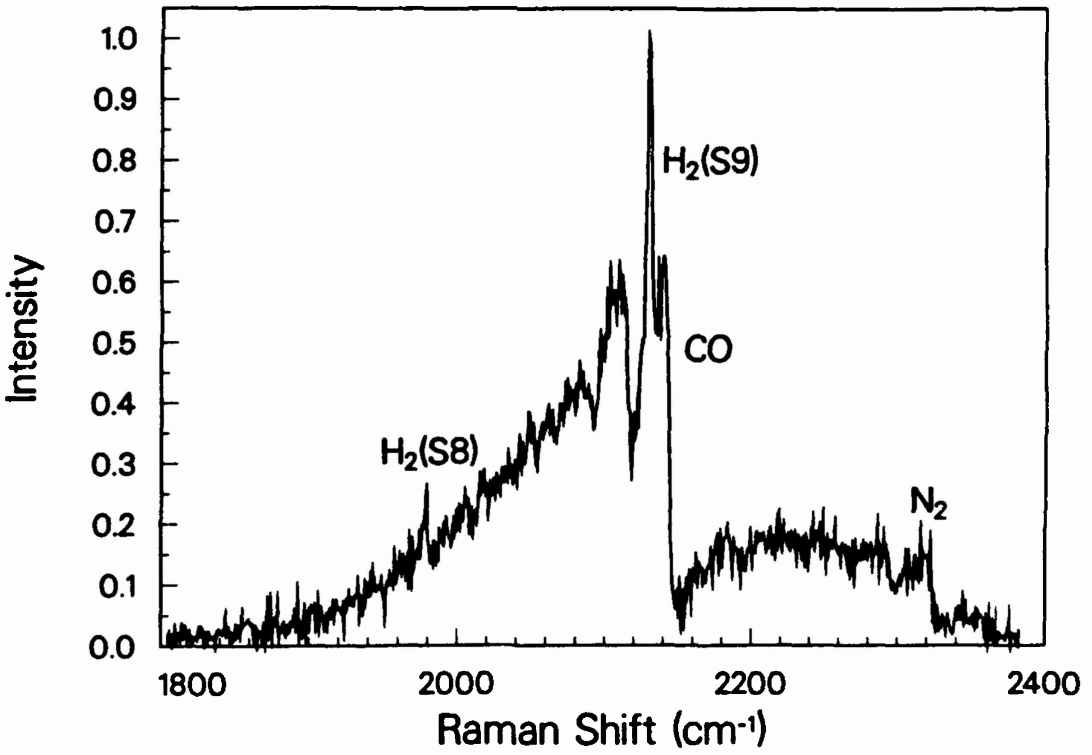

FIGURE 2 CARS spectrum from HMX/TMETN propellant burning at 35.0 atm of helium background pressure, 5.5 mm above propellant surface.

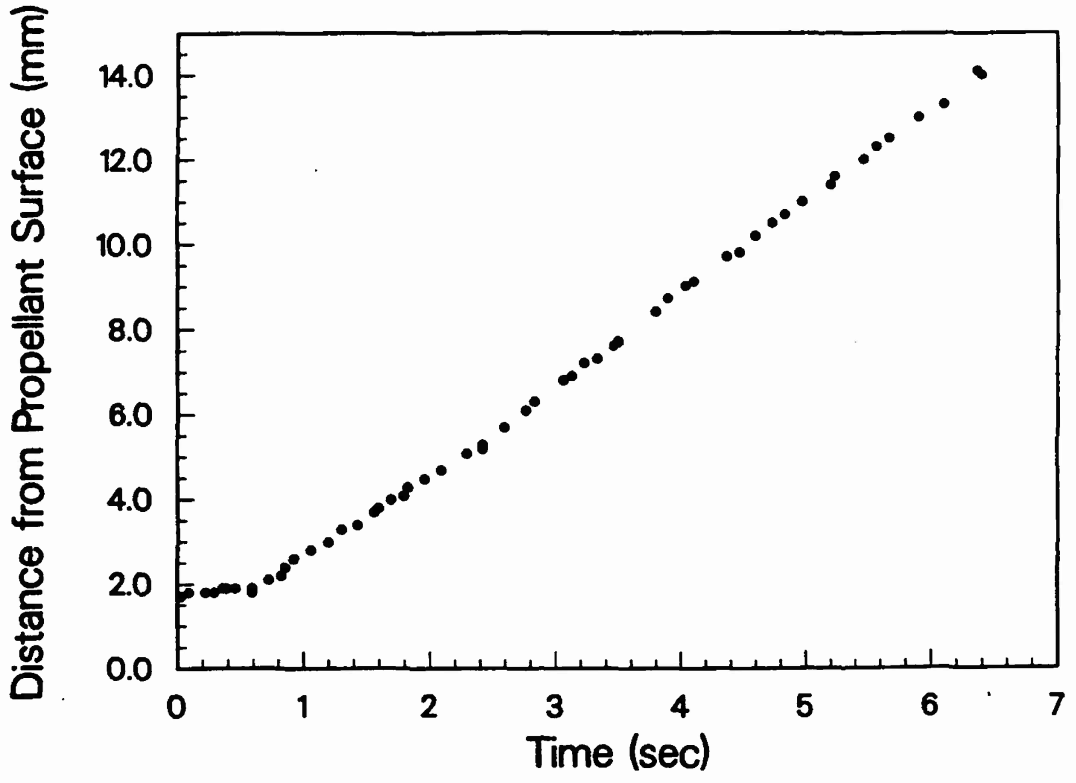

FIGURE 3 Burn rate measurements of HMX/TMETN at 23.1 atm of helium background pressure determined from video observations.

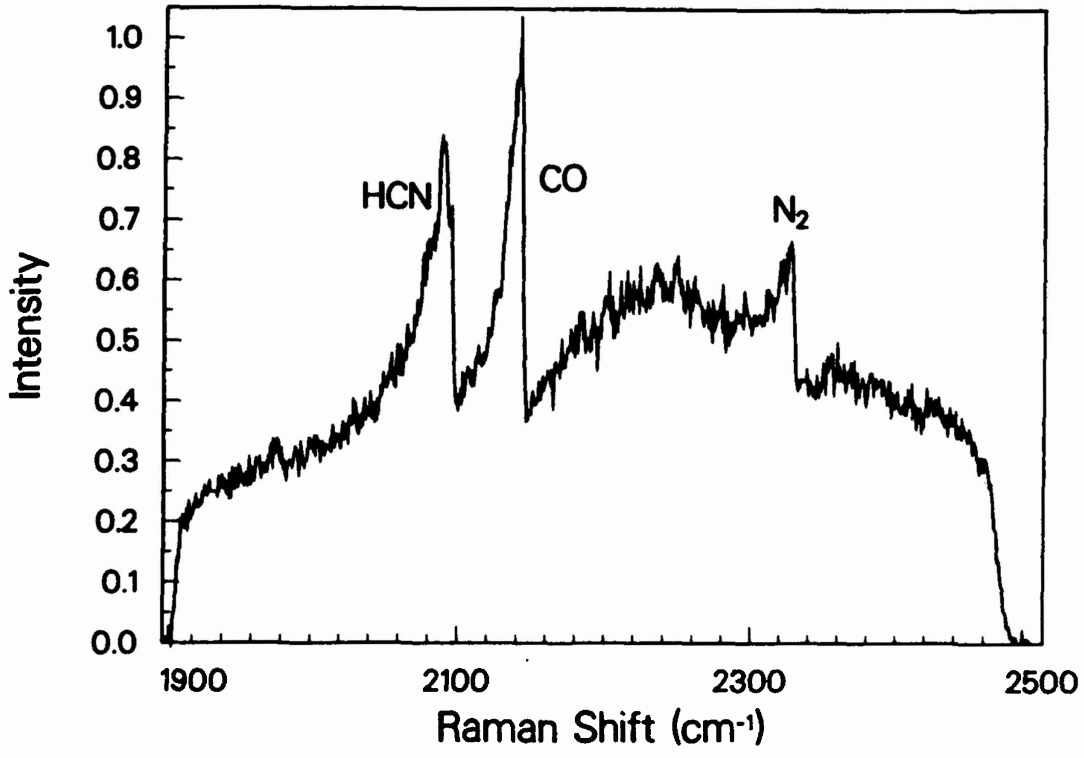

FIGURE 4 CARS spectrum from HMX/TMETN propellant at 23.1 atm of helium background pressure and 1.7 mm above propellant surface.

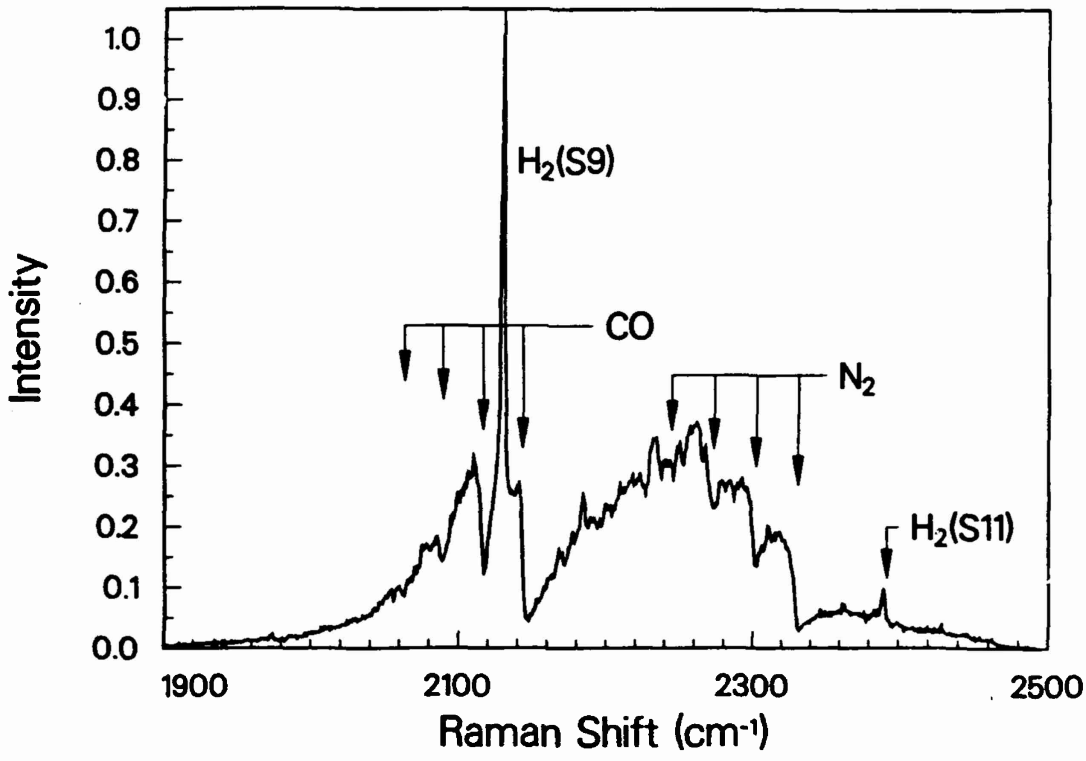

FIGURE 5 CARS spectrum from HMX/TMETN propellant at 23.1 atm of helium background pressure and 2.4 mm above propellant surface.

CARS signatures are superimposed on a pedestal of incoherent emission due to laser breakdown of the gas. Figure 4 is one of three CARS spectra, from a total of sixty acquired during the burn, that exhibited the incoherent pedestal. HCN and CO dominate the spectrum and there is a lesser amount of N_2. The gas appears relatively cool in this data based upon the N_2 CARS spectral width. Figure 5 is a spectrum later in the burn when the strand has regressed ~ 2.4 mm away from the laser focus. In this case the gas shows considerable heating, the absence of HCN, the signatures of CO and N_2, and the presence of strong signals from the pure rotational transitions of H_2. The combustion products heat up very fast and Figure 5 is typical of most of the spectra obtained during the propellant burn.

The CARS data were first visually compared to computer generated spectra for estimates of temperature and species concentration. Shown in Figure 6 is a comparison of a theoretical spectrum (solid line) to the experimental CARS data (open circles) immediately after ignition (Figure 4). A scaled, breakdown emission spectrum was subtracted from the experimental data and it was then divided by the broadband Gaussian Stokes laser profile to yield the reduced experimental data set. This technique removes the incoherent emission pedestal and the apparent variation in nonresonant susceptibility and results in resonant signatures that modulate the constant background signal. The modulation is moderate for the spectra from HMX/TMETN and affords the opportunity to predict relative concentration from spectral shapes (Hall and Eckbreth, 1984), in addition to measurement of the gas temperature. The data in Figure 6 show resonant modulations from HCN, CO and N_2. The computer program does not currently contain the molecular constants for HCN, so the theory does not predict the feature at 2095 cm^{-1}. Work is currently in progress to incorporate this molecule into the UTRC CARS code at which time estimates of its concentration can be made. The theoretical spectrum fits the CO and N_2 portions of the data very well

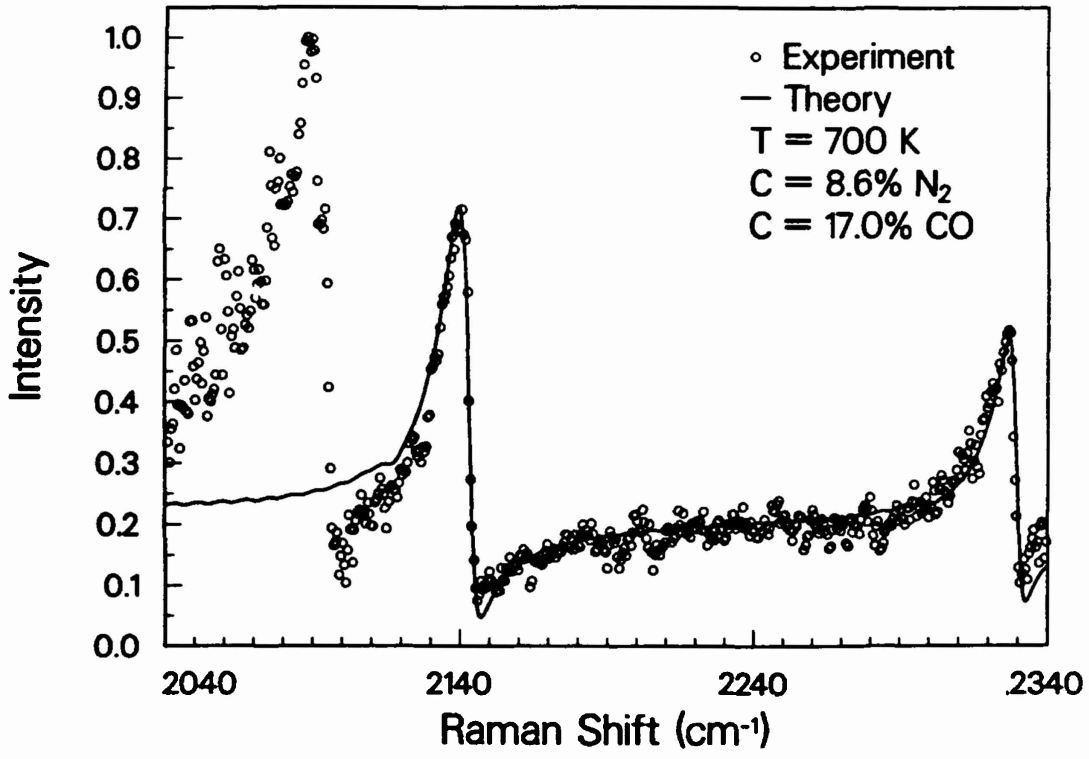

FIGURE 6 Comparison of theoretical and experimental CARS spectra. Experimental data are from Figure 4. The unfitted feature is from HCN, currently not included in the CARS computer codes.

with parameters of $T = 700\,\text{K}$, $C_{N_2} = 8.6\%$, $C_{CO} = 17.0\%$. A higher temperature data set is shown in Figure 7; again the dye laser profile has been divided into the experimental data (Figure 5). The theoretical calculation represents a temperature of 2600 K and concentrations of $N_2 = 25.3\%$, $CO = 36.6\%$ and $H_2 = 23.0\%$.

Based upon the encouraging results of the visual overlay technique, a second, albeit time-consuming, feature of the code was utilized to least-squares fit several spectra from the experimental data set for temperature and species concentration. The experimental conditions of high temperature and high pressure require the program to use the exponential gap model of collisional narrowing and the K–T convolution over extended spectral regions ($\sim 300\,\text{cm}^{-1}$). To conserve computer resources, the program treats only one species at a time with the exponential gap model. Consequently, the spectra were first fit for temperature and N_2 concentration using the exponential gap parameters for nitrogen, then those values were input back to the code to fit the CO/H_2 portion for concentration, using appropriate exponential gap parameters for CO. H_2 was treated with the isolated line model because its transitions are so widely separated. The results of this procedure are presented in Figure 8 where gas temperature and species concentrations are presented as a function of distance above the burning propellant. The distance measurement was made from the video record for this run (Figure 3), the successive laser shots were easily identifiable on sequential video frames. The predicted equilibrium values are shown as thick, solid horizontal lines above the flame parameter they represent. The longer, thin solid lines are least-squares fits to the data points. The H_2 concentration results are divided by two for this presentation because their full scale values confuse visualization of the N_2 data. The data in Figure 8 represent fits to 24 individual spectra. The first few laser shots reflect the ignition transient through the initial steep rise of the temperature and concentrations. During the transient, the flame merely spreads over the surface and

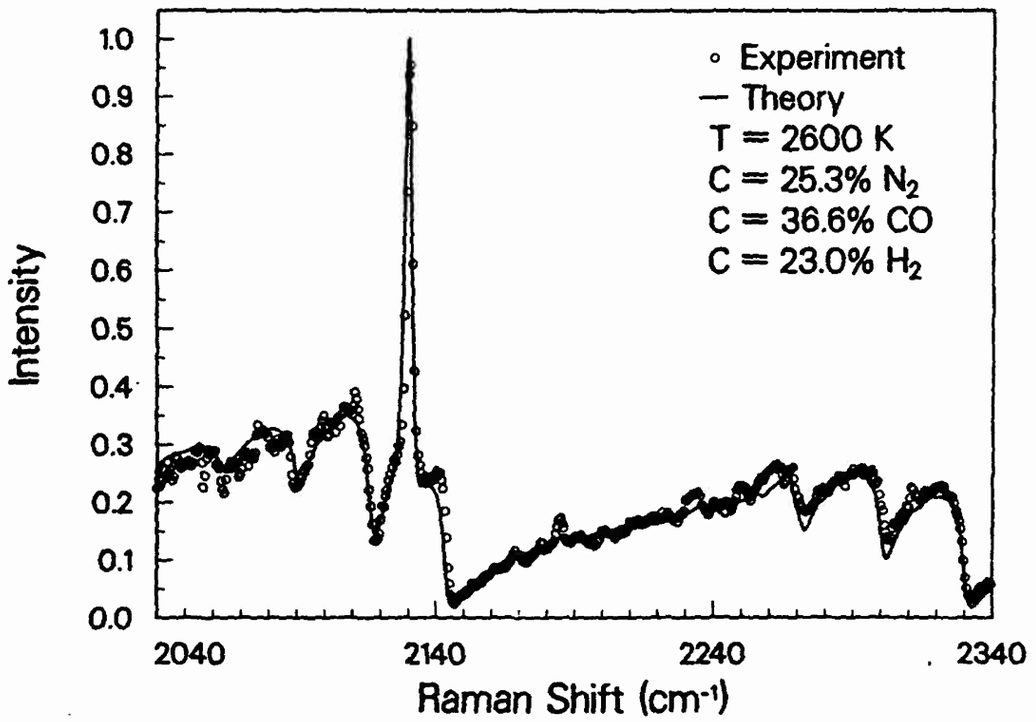

FIGURE 7 Comparison of theoretical and experimental CARS spectra. Experimental data are from Figure 5.

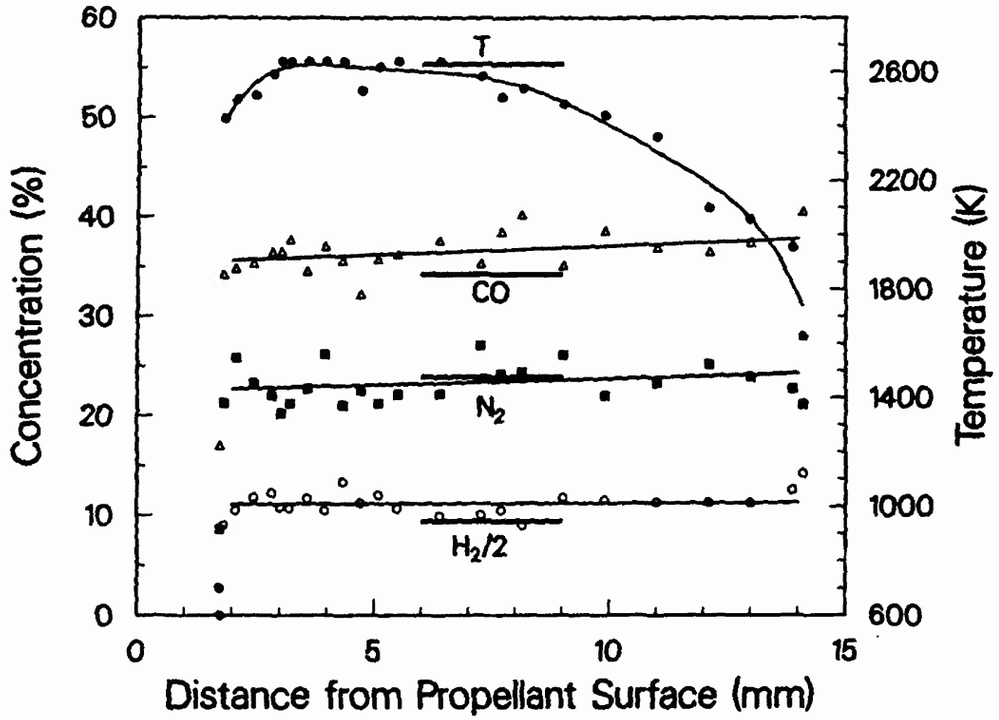

FIGURE 8 Summary of CARS measurements from HMX/TMETN combustion at 23.1 atm. ●—Temperature, △—CO concentration, ○—H_2 concentration, ■—N_2 concentration. The thick horizontal bars above each experimental parameter represent the value predicted from chemical equilibrium calculations. The thin lines are least-squares fits to the data points.

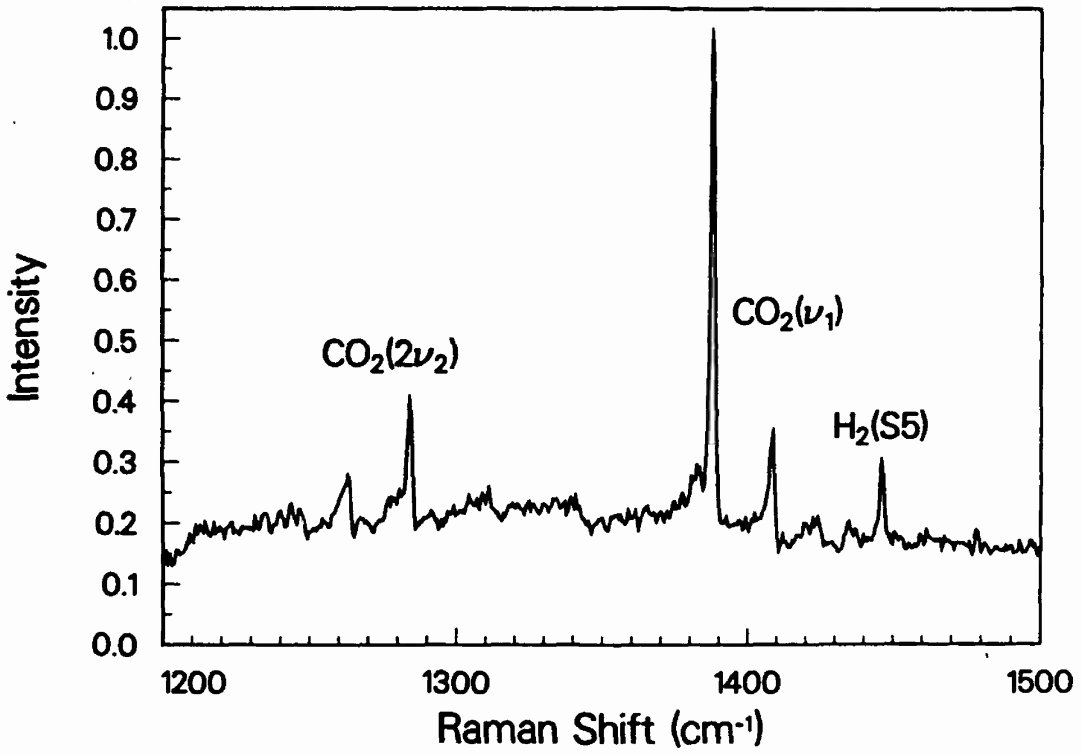

FIGURE 9 CARS spectrum from NOSOL 436 propellant at 18.7 atm of helium background pressure, 0.1 s after propellant ignition.

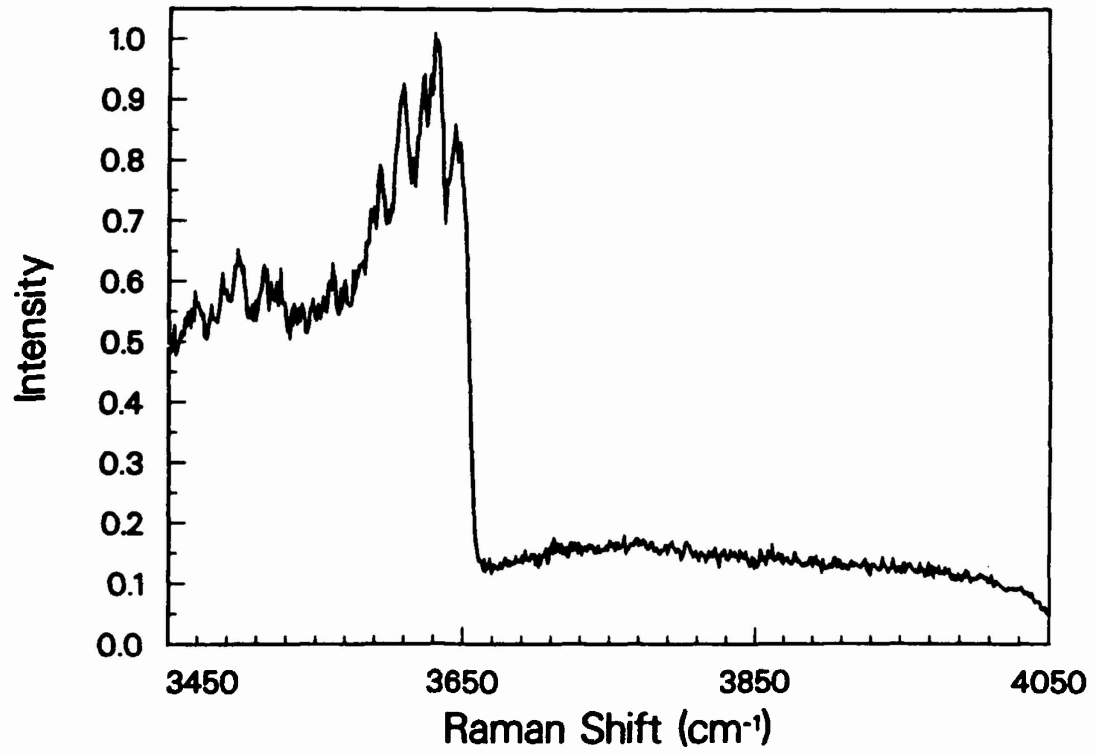

FIGURE 10 CARS spectrum from NOSOL 436 propellant at 21.4 atm of helium background pressure, 0.1 s after propellant ignition.

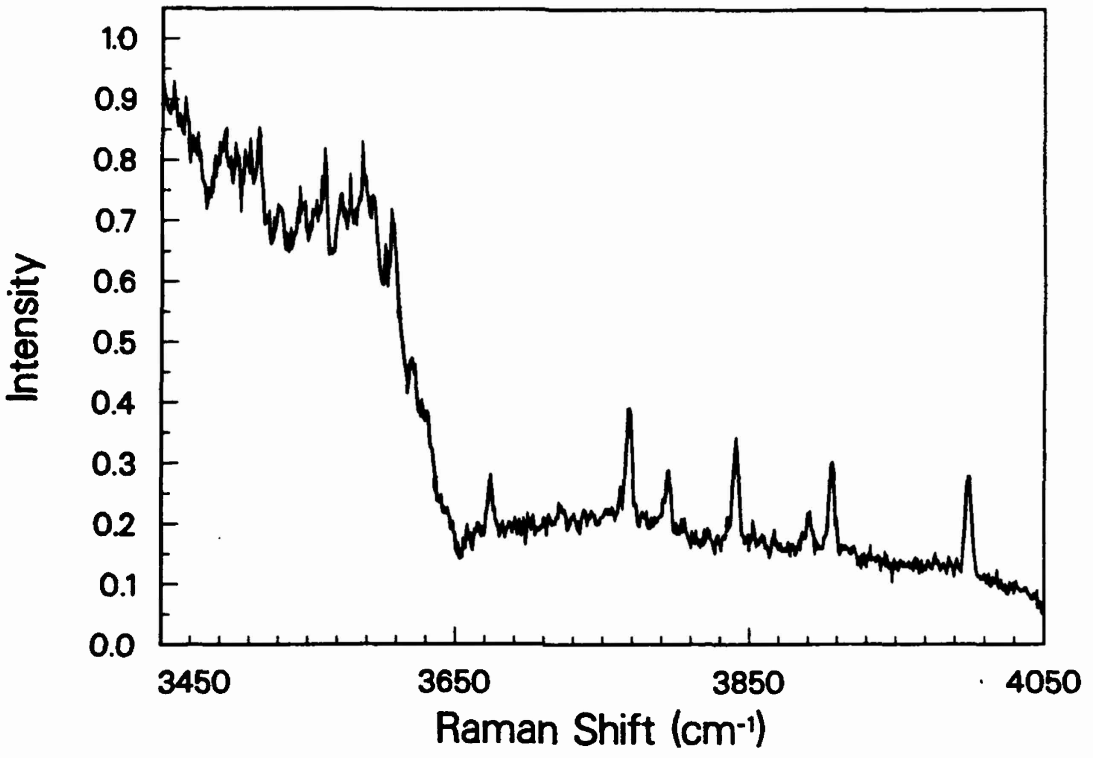

FIGURE 11 CARS spectrum from NOSOL 436 propellant at 21.4 atm of helium background pressure, 1.1 s after propellant ignition.

the propellant does not regress. It is apparent that the propellant is already burning near its equilibrium parameters once the ignition transient is over and the data are not indicative of any reaction zones close to the surface. After the ignition phase, the parameters remain reasonably constant until the flame starts to cool off after ~ 7 mm above the surface. The cooling may be the result of helium diffusion into the flame. The agreement between the equilibrium values and experimental measurements is very good for T, N_2, and CO. The concentration of H_2 is uniformly higher than the equilibrium prediction and this point is discussed in a later section.

NOSOL 436 In an effort to investigate other propellants, NOSOL 436 was also burned. Spectra acquired from the combustion of NOSOL 436 include the CO_2 resonant region as shown in Figure 9. This spectrum was obtained 100 ms after ignition, near the propellant surface. The two resonant modes of CO_2 are evident as well as a small signal from the rotational H_2(S5) transition.

The H_2O resonant region was also probed during the NOSOL combustion. Shown in Figure 10 is a single shot spectrum 100 ms after propellant ignition. The resonant H_2O signal dominates this spectral region. One second later in the burn (Figure 11), the gases have heated up considerably, the H_2O signal is reduced and there are multiple H_2 Q-branch transitions present.

DISCUSSION

CARS Measurements

A comparison between the experimental CARS measurements and the calculated equilibrium product distribution is presented in Table III. The CARS measurements

TABLE III
CARS measurements of HMX/TMETN combustion

	Pressure (atm)	Temperature (K)	Mole fraction (%)		
			CO	H_2	N_2
Equilibrium prediction	23.1	2629	34.2	18.8	23.9
CARS measurement	23.1	2600	35.8	22.5	22.9

are an average of the data between the ignition transient and onset of flame cooling (2.1–7.2 mm in Figure 8). The average measurements for CO and N_2 are within 5% of the predictions and temperature is within 2%. The measurement for H_2 concentration is 20% above the predicted value and may reflect the use of improper linewidths for this molecule; a more recent version of the code with more accurate H_2 linewidths is being acquired. The computer fitting procedure also requires an estimate of the nonresonant susceptibility for the remaining constituents of the gas mixture. Since the resonant species in the spectra account for most of the total mixture, the estimate for the remaining χ^{nr} will not have a large impact on the results. A value that represents the contribution from CO_2 and H_2O in proportion to the predictions of the equilibrium code was assumed for these measurements. Variations of 50% in this value have only a 10% effect on the concentration results in Table III. If there is significant helium dilution of the flame products, as perhaps indicated by the flame cooling, the CARS concentration estimates for this region high in the flame may be inaccurate. The concentration measurements are relatively insensitive to this particular background gas because its nonresonant susceptibility is so low. In effect, the helium is transparent to the CARS process even though the partial pressure of helium affects the partial pressure of the other constituents; the CARS spectrum and thus concentration measurement remain essentially unchanged. The temperature measurement would be unaffected, however. The agreement between theory and experiment for HMX/TMETN is encouraging and indicates the applicability of CARS for quantitative assessment of high pressure solid propellant combustion.

A fact worth mentioning is that no signatures were observed for NO or N_2O in the nitramine experiments although they are expected for some chemical mechanisms (Melius, 1986, 1988) that may occur near the propellant surface. HCN is expected near the propellant surface and was observed there; however, it may have been due to the ignition transient rather than a steady state flame zone. We will be conducting further experiments that should help discern chemical mechanisms near the propellant surface, and the question of these intermediate species still remains open.

The more recent results from NOSOL 436 have not been analyzed yet. The predictive code for CO_2 (Hall and Stufflebeam, 1984) will be incorporated in the UTRC fitting algorithm soon and then measurements of CO_2 temperature and concentration may be obtained from the data. Similarly, work has been done at our laboratory on a code for H_2O (Hall, 1983) that may be incorporated in fitting routines.

Future Directions

Data have been presented that cover the three major frequency intervals of interest for solid propellant CARS. These three separate regions contain the molecular resonances of all the major combustion products and intermediates (see Table I). The next step in our propellant combustion studies will be to obtain all major resonant

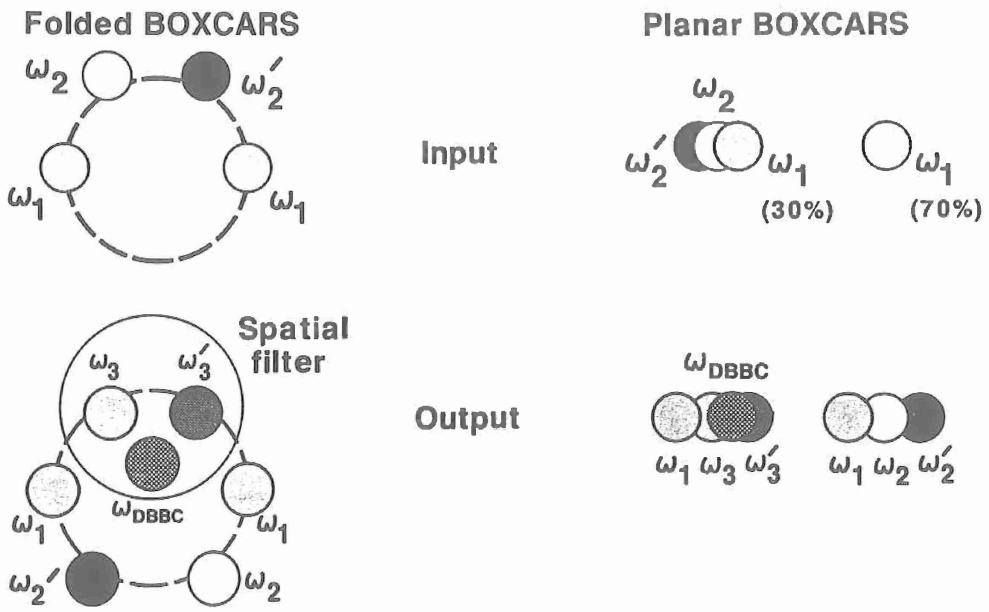

FIGURE 12 Phase-matching geometries for preferred dual broadband CARS approaches to solid propellant combustion. Beams are viewed along the optical axis against the propagation direction.

signals simultaneously with each laser shot. This will be accomplished with dual broadband CARS (Eckbreth and Anderson, 1985). With this technique, two broadband Stokes lasers are employed together with the normal 532 nm, primary pump. CARS signals are generated in normal 2-color processes from ω_1, ω_2 and ω_1, $\omega_{2'}$. In addition, a three-color CARS process is active through ω_1 scattering off resonances excited by the difference of ω_2 and $\omega_{2'}$. Either planar or folded BOXCARS phase-matching geometries can be employed as depicted in Figure 12. For solid propellant combustion, appropriate choices are ω_2–CO_2, $\omega_{2'}$–H_2O, then ω_2–$\omega_{2'}$ is centered in the CO–N_2 region and will be very broad. The particular folded BOXCARS phase matching geometry shown in Figure 12 is advantageous because of the spatial location of the generated CARS signals. Notice that all the CARS beams are spatially isolated from the ω_1 pump beams. This arrangement allows for easy spatial filtering and manipulation of the CARS beams for simultaneous incidence on the spectrograph. The intensity of the two ω_1 beams can be adjusted to increase the 3-color signal while minimally impacting the 2-color intensities, as indicated in the planar BOXCARS configuration of Figure 12. Normally the total ω_1 intensity is split equally between the pump beams. If the total ω_1 intensity is instead split 70/30, then the 2-color process is reduced to 80% of normal but the intensity of the 3-color process is increased 40%. It is clear such adjustments in ω_1 intensity can enhance the dual broadband sensitivity.

Additional improvements include use of a motorized strand burner (Field *et al.*, 1988) and fast response pressure transducers to record the pressure history during the burn. The servo-controlled strand burner will hold the burning propellant surface reasonably fixed in space and thus enable measurements very close to the surface throughout the combustion process. It is in this region near the propellant surface that the interesting chemistry occurs and it is here we need to concentrate our measurement efforts. An approach to high spatial resolution measurements near the surface, using the all planar BOXCARS geometry of Figure 12, has been suggested which may yield a resolution of 50 μm or better (Stufflebeam, 1986).

SUMMARY

The results reported herein represent the first successful CARS measurements of solid propellant combustion at elevated pressure. Single shot spectra were acquired from both double-base and composite nitramine propellants at pressures up to 35 atm. The CARS spectral quality was sufficient to determine temperature and the major species concentrations. For the composite nitramine propellant at a pressure of 23 atm, the measured temperature (2600 K) and species concentrations (N_2–23%, CO–36% and H_2–23%) compared favorably with predictions from chemical equilibrium calculations. Techniques that employ an additional Stokes source to obtain more resonant signatures simultaneously with each laser pulse were outlined. Our proposed implementation of these three color (dual broadband) processes and a motorized strand burner for solid propellant measurements is in progress and will be reported in future publications.

ACKNOWLEDGEMENTS

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APPENDIX F

CARS Measurements in the Near-Surface Region of Composite Nitramine Combustion

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Cheyenne, Wyoming

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CARS MEASUREMENTS IN THE NEAR-SURFACE REGION OF COMPOSITE NITRAMINE COMBUSTION*

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ABSTRACT

Knowledge of combustion species and temperature is necessary for accurate modeling of solid propellant reaction mechanisms and their effect on the combustion characteristics of the propellant. Simultaneous, multiple-species and temperature measurements are required to elucidate the dominant chemical processes by comparison with model predictions. Experimental investigation of these combustion mechanisms is reported. The most important measurements to make in the nitramine combustion experiments are temperature and species concentrations of the products of the intermediate chemical reactions. These reactions occur very close to the propellant surface for combustion at elevated pressure. Diagnostics that couple temperature with species concentration measurements are preferred, *e.g.*, CARS. CARS is a nonintrusive, laser-based spectroscopy with high spatial and temporal resolution used for measurement of temperature and major species concentration. Results are presented from CARS experiments that utilize single shot, multiple-species measurements near the burning surface of an HMX/TMETN propellant at elevated pressure. A Nd:YAG pumped, broadband Stokes system is resonant with transitions of NO, HCN, H_2, CO, N_2O, N_2, CH_2O and CH_4. Dual broadband approaches add resonances of N_2O, CO_2 and H_2O. The CARS spectra are dispersed and imaged onto a 1000-intensified channel, diode array detector. A motorized strand burner, servo-controlled by a diode laser, is used to maintain the burning surface fixed relative to the focal region of the CARS beams. By minimizing the distance between the CARS focus and the propellant surface, interrogation of intermediate species is accomplished throughout the combustion process.

NITRAMINE COMBUSTION

There has been considerable recent interest and activity in the nitramine class of energetic materials because of their formulations that provide minimum smoke and low vulnerability propellants. HMX and RDX are the prominent nitramines that have received attention and have been studied through theoretical and experimental programs on decomposition, pyrolysis, ignition, gas- and solid-phase reactions. To understand the combustion of these nitramines, their microscopic chemical pathways need to be investigated.[1,2] HMX and RDX are cyclic nitramines formed from the basic nitroformimine, CH_2NNO_2. It is believed the initial decomposition step is N–NO_2 bond scission and subsequent fragmentation of the remaining ring structure.[3]

$$n(CH_2NNO_2) \rightarrow H_2CN + NO_2 + (n-1)CH_2NNO_2 \begin{cases} n = 4 & \text{for HMX} \\ n = 3 & \text{for RDX} \end{cases} \quad (1)$$

$$H_2CN \rightarrow HCN + H \quad (2)$$

The early decomposition studies[4] indicated the formation of CH_2O from the nitramines so pathways were determined based on the rapid, exothermic reaction of CH_2O with N_2O.

$$CH_2NNO_2 \rightarrow CH_2O + N_2O \quad \text{(low temperature, bimolecular)} \quad (3)$$

$$CH_2O + N_2O \rightarrow CO + H_2O + N_2 \quad (4)$$

Later pyrolysis experiments,[5] at higher temperatures and heating rates, more reflective of actual combustion conditions, showed that HCN and NO_2 were important decomposition products.

$$CH_2NNO_2 \rightarrow H_2CN + NO_2 \quad \text{(high temperature)} \quad (5)$$

* Supported in part by the U. S. Army Research Office.
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Thus, there appear to be two competing decomposition pathways. Melius[3] was successful in modelling an RDX propellant flame and comparing his predictions to data[6] obtained at 0.5 atm. Eq. 3 was a minor pathway in his model of RDX combustion. On the other hand, models of HMX combustion[7,8] had to include Eq. 3 in the initial decomposition mechanism to correctly predict measured burn rates; in fact it accounted for half of the decomposition. Thus one difference between HMX and RDX propellant flames is the nitramine decomposition pathway.

for HMX:

$$(C_4H_8N_8O_8) \rightarrow 2NO_2 + 2HCN + 2H + 2CH_2O + 2N_2O \quad (6)$$

$$2CH_2O + 2N_2O \rightarrow 2CO + 2H_2O + 2N_2 \quad (7)$$

for RDX:

$$(C_3H_6N_6O_6) \rightarrow 3NO_2 + 3HCN + 3H \quad (8)$$

$$2HCN + 3NO_2 \rightarrow 2CO + 3NO + H_2O + N_2 \quad (9)$$

Detection and measurement of intermediate species concentrations and temperature from reactions close to the surface may help to resolve these important reaction pathways that ultimately determine propellant performance.

EXPERIMENTAL APPARATUS

A comprehensive review of CARS is given by Eckbreth[9] and this diagnostic has been successfully applied to nitramine combustion.[10] The experiment uses a Nd:YAG laser operating at a 10 Hz rate with 10 nsec pulses. A folded BOXCARS configuration is utilized for high spatial resolution. The propellant burns are monitored by a video camera that gives a quantitative measure of the distance between the laser focus and propellant surface for the sequential laser pulses. The propellant used for these measurements is a composite nitramine that contains 73% HMX, 17% TMETN and 10% polyester binder. The propellant is burned with a background of helium which is chemically inert and has a low nonresonant susceptibility, adding negligible signal to the CARS spectra. To address the problem of measurements near the surface, the experiment was upgraded to include a motorized combustion vessel.[11] It has a stepper motor to advance the propellant as it regresses, maintaining the burning surface fixed relative to the laboratory reference frame. It is capable of burning strands up to 3 inches long so more data can be collected during each combustion event.

The motor is controlled by the servo system depicted in Fig. 1 which utilizes a laser diode and a phototransistor array to sense the burning surface location. The diode laser is modulated at 20 KHz to discriminate against flame luminosity. The detection system demodulates the signal and logic circuits determine the location of the surface. An error signal is generated, based upon the difference from a manually supplied reference position. The error signal is transformed through the PID (proportional, integral, derivative) electronics into a train of variable frequency pulses that drive the stepper motor through the translator. The amount of proportional, integral, or derivative feedback supplied is manually adjusted depending on experience with the device. Preliminary experiments indicate the HMX/TMETN propellant surface can be controlled to within $\sim 100\mu$ jitter from the reference position. In addition to the servo-controlled burner, the phase matching geometry of the experiment was changed from folded BOXCARS to planar BOXCARS. This allows positioning of the laser focus closer to the propellant surface, without impinging on the surface, than the 3-D configuration.

EXPERIMENTAL RESULTS

TWO COLOR CARS

An example of the acquisition of CARS spectra from the near-surface region of solid propellant combustion at elevated pressure is shown in Fig. 2.

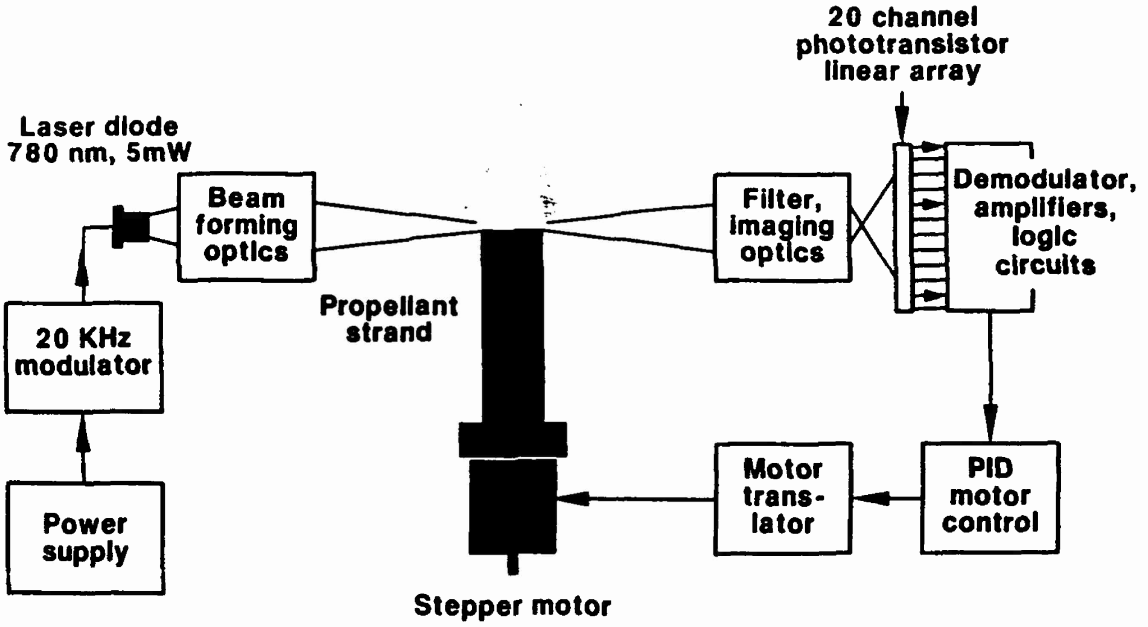

Figure 1. Laser servo system for the motorized propellant combustion vessel.

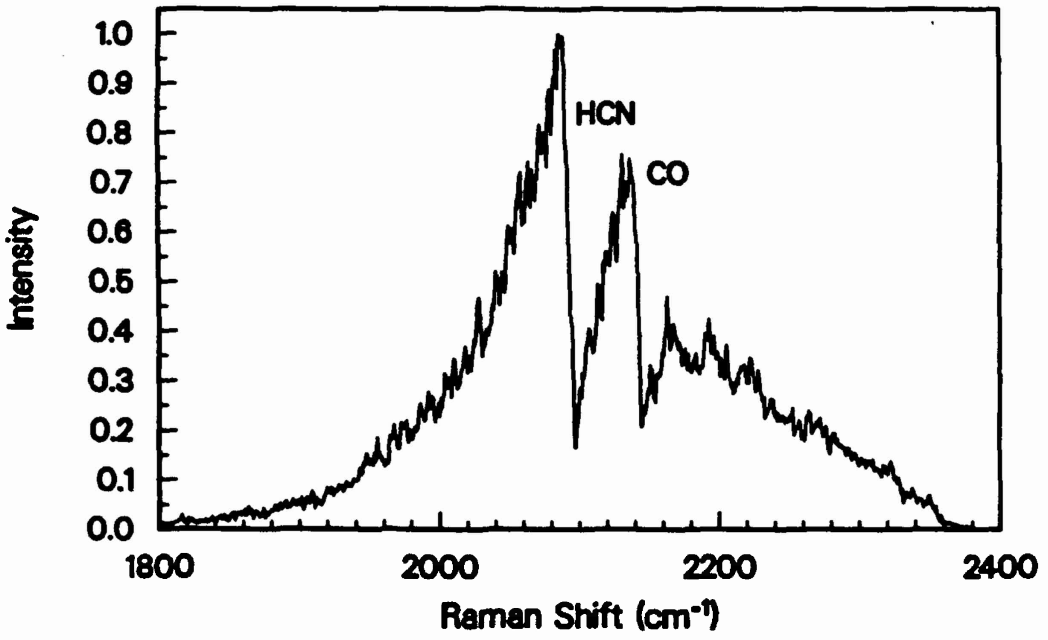

Figure 2. Single shot CARS spectrum from solid propellant combustion in the servo-controlled burner. This data was acquired approximately 100 μ from the surface.

Figure 2 was acquired at 9.8 atm. It shows resonant modulations from HCN and CO, at low temperature. This is expected from propellant flame models that predict intermediate chemical species such as HCN and low temperature near the surface. We have previously seen and reported HCN spectra from propellant flames[12] but those signatures were from an ignition transient, not indicative of the reactions close to the propellant surface such as the case for Fig. 2. There are also indications from some of the spectra that trace amounts of N_2, NO, and N_2O may be present near the surface, further experimental data is necessary for definitive observation however. Propellant has also been burned at other pressures as shown in Fig. 3,

acquired at 18.4 atm. Again the gas is low temperature, well below the adiabatic temperature of ~2600 K. CO dominates this spectrum and N_2 is present in addition to HCN.

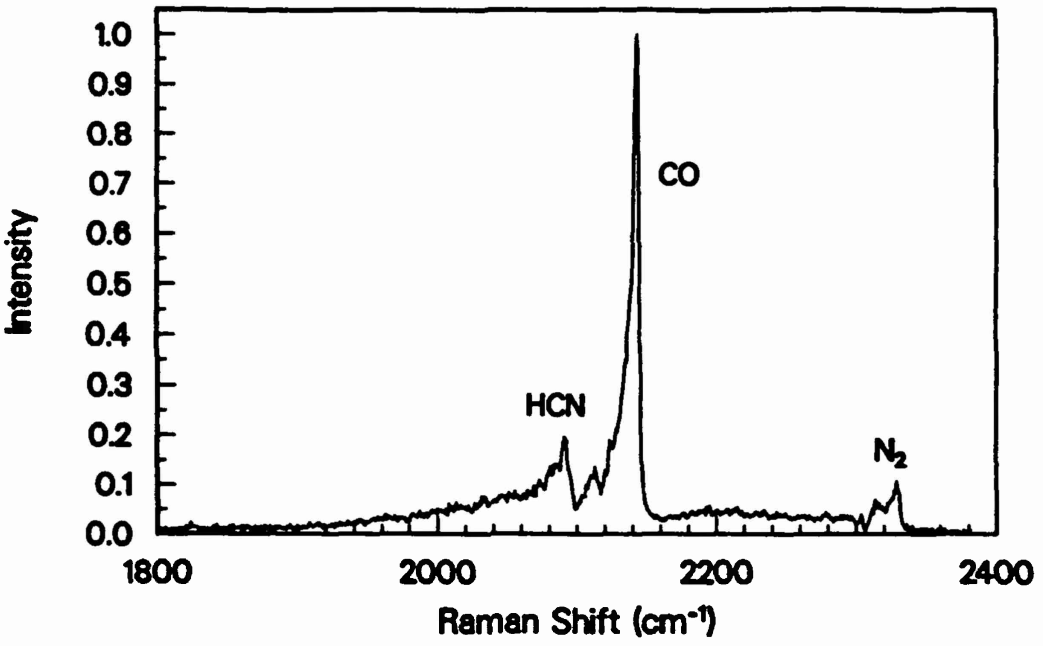

Figure 3. Single shot CARS spectrum from solid propellant combustion in the servo-controlled burner. This data was acquired approximately 100 μ from the surface.

The observation of CH_2O is an important step toward discerning reaction pathways in nitramine combustion and Fig. 4 demonstrates this achievement. It is a single shot spectrum from the near-surface region that shows signatures from CH_2O and CH_4. The binder chemistry may be responsible for some of the resonant signatures.

DUAL BROADBAND CARS

Dual broadband CARS[13] allows the simultaneous acquisition of several more signatures with the addition of one more Stokes dye laser. In addition to the two-color process with the extra Stokes laser, dual broadband signatures derive from molecules resonant with the frequency difference between the broadband dye lasers mixing with the 532 nm pump, a three-color CARS process. The CO-N_2 region was chosen for a test of dual broadband CARS because previous results had shown these molecules were in relatively high concentration for HMX combustion. To achieve dual broadband resonances with this Raman shift the Stokes dye lasers were tuned for H_2O and CO_2.

The acquisition of single-shot dual broadband CARS spectra from the near-surface region of solid propellant combustion at elevated pressure is shown in Fig. 5. Figure 5 was acquired at 15.6 atm, it shows resonant modulations from HCN, CO and N_2. This is expected from propellant flame models that predict intermediate chemical species such as HCN and low temperature near the surface.

Another example is shown in Fig. 6, from the same burn. This spectrum shows CO and N_2, but no HCN. I believe the absence of HCN is due to the thin reaction zone at this pressure and the normal jitter ($\pm 100\mu$) of the propellant surface as the burn progresses. Spectra from lower pressure combustion should be more consistent since the reaction zone will be wider.

These dual broadband spectra clearly show resonant modulations and could be used to determine concentration and temperature. The signal to noise ratio is not as good as observed in two-color processes but is within about a factor of two. I don't think the signal to noise ratio can be improved to the level of the two-color spectra but some enhancements are possible. In particular, incorporation of a 70/30 beamsplitter

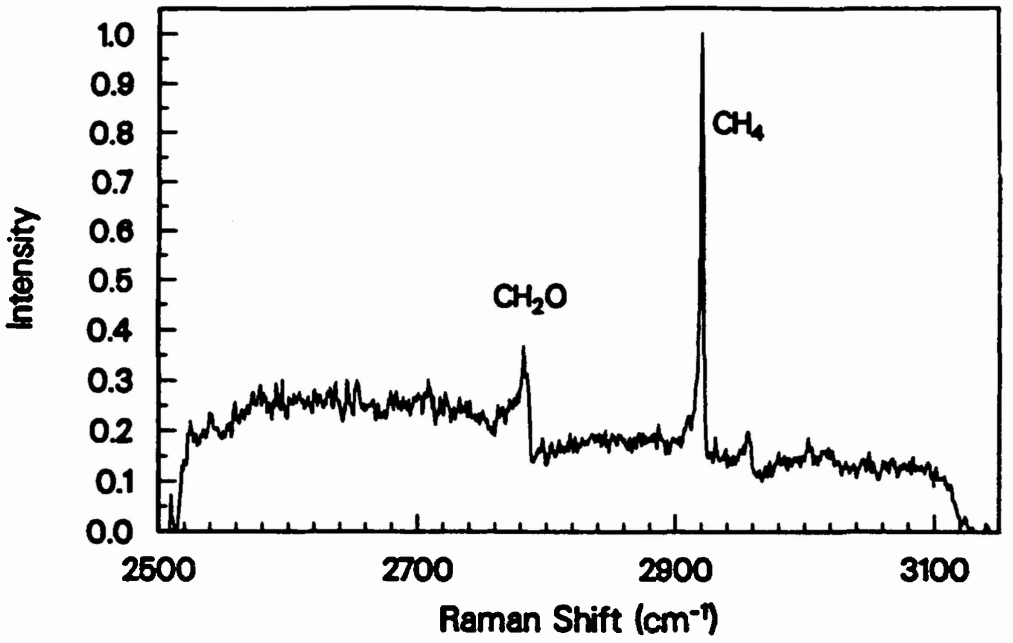

Figure 4. Single shot CARS spectrum from solid propellant combustion in the servo-controlled burner. The pressure was 12.8 atm, with a helium background purge. The signature of CH_2O is clearly evident.

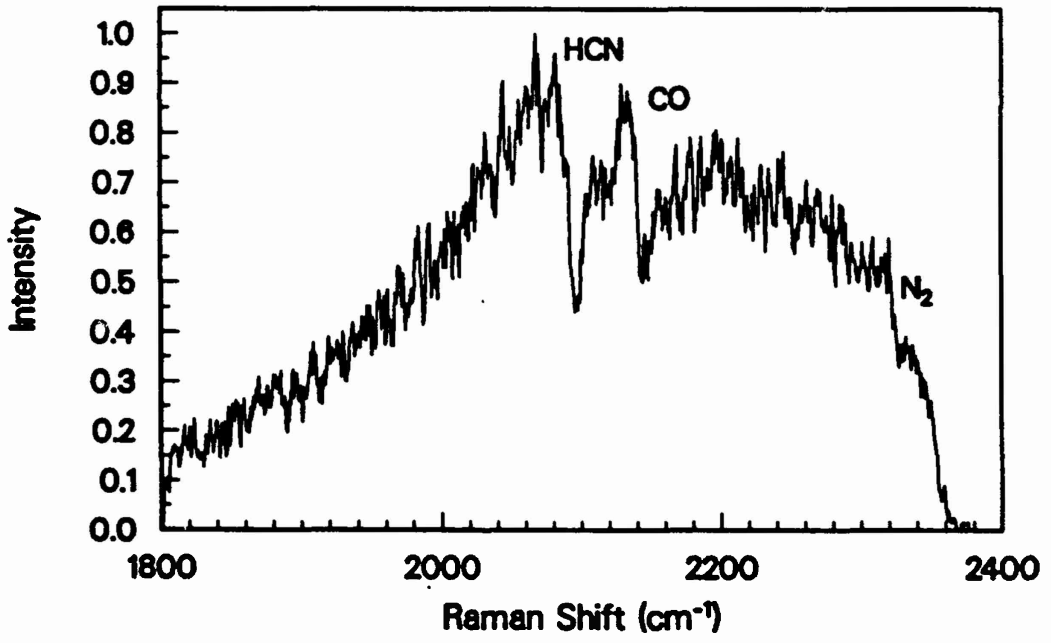

Figure 5. Single shot, dual broadband CARS spectrum from solid propellant combustion in the servo-controlled burner. This data was acquired approximately 100 μ from the surface.

for the two green beams to replace the 50/50 used for the current work should enhance the three-color process by 40%. Additional improvement may be realized through higher magnification of the Stokes beams which will increase the focal intensity and thus the signal to noise ratio.

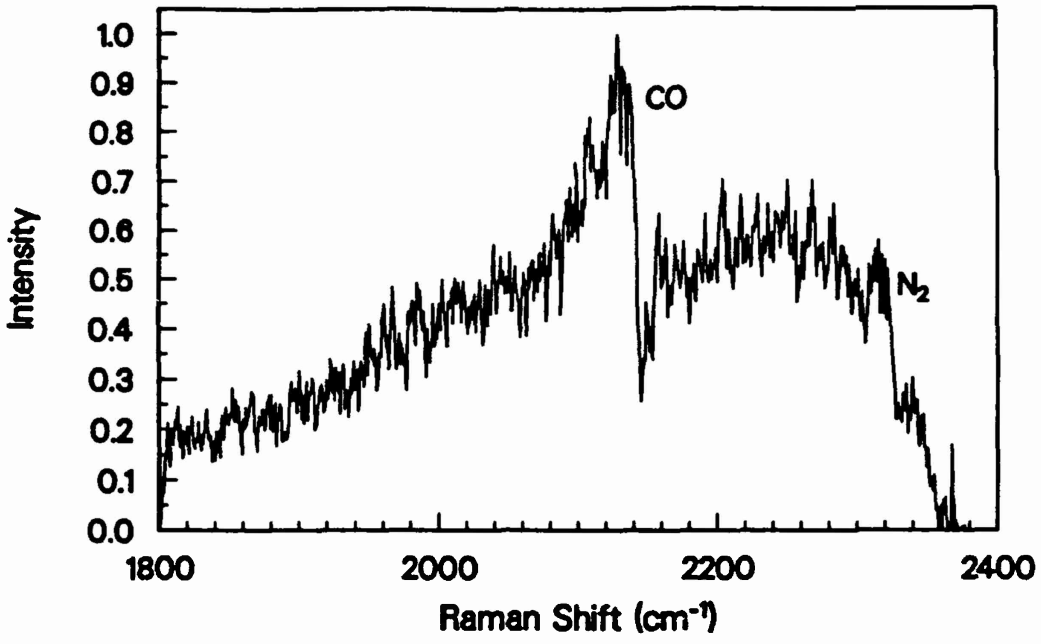

Figure 6. Single shot, dual broadband CARS spectrum from solid propellant combustion in the servo-controlled burner.

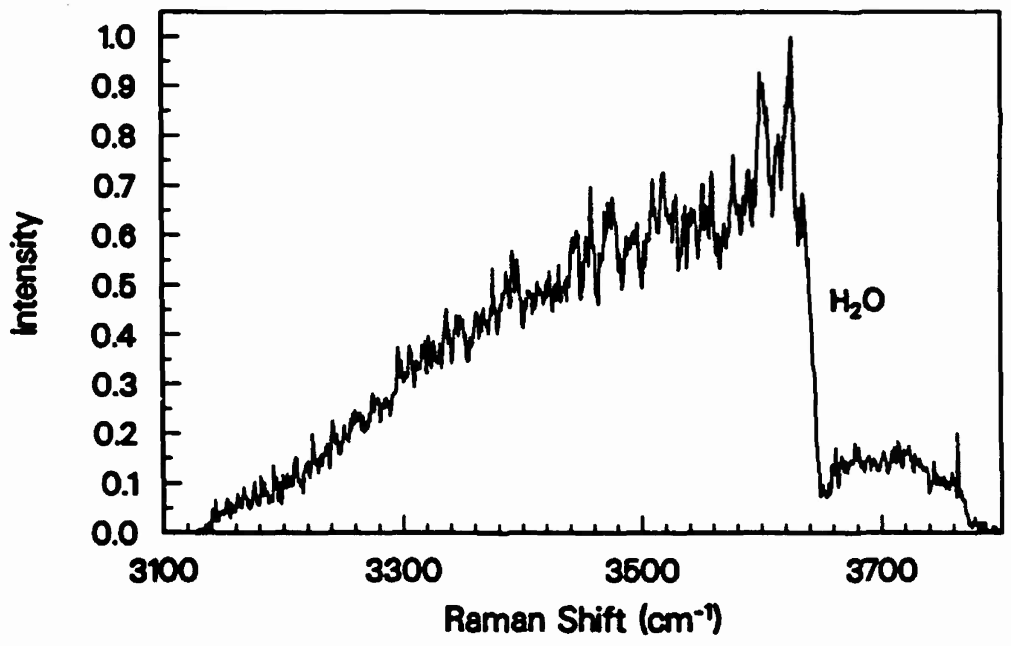

Figure 7. Single shot CARS spectrum from solid propellant combustion in the servo-controlled burner.

The H_2O dye laser produces spectra such as Fig. 7 during propellant combustion. The H_2O resonance is very clear and the gas appears cool, indicative of regions close to the propellant surface. There is also an HCN resonance in this region, HCN(ν_1) at 3312 cm^{-1}, but its Raman cross section is much weaker than the HCN(ν_3) signature seen in Figs. 2, 3 and 5; apparently it is below the sensitivity of my apparatus. The

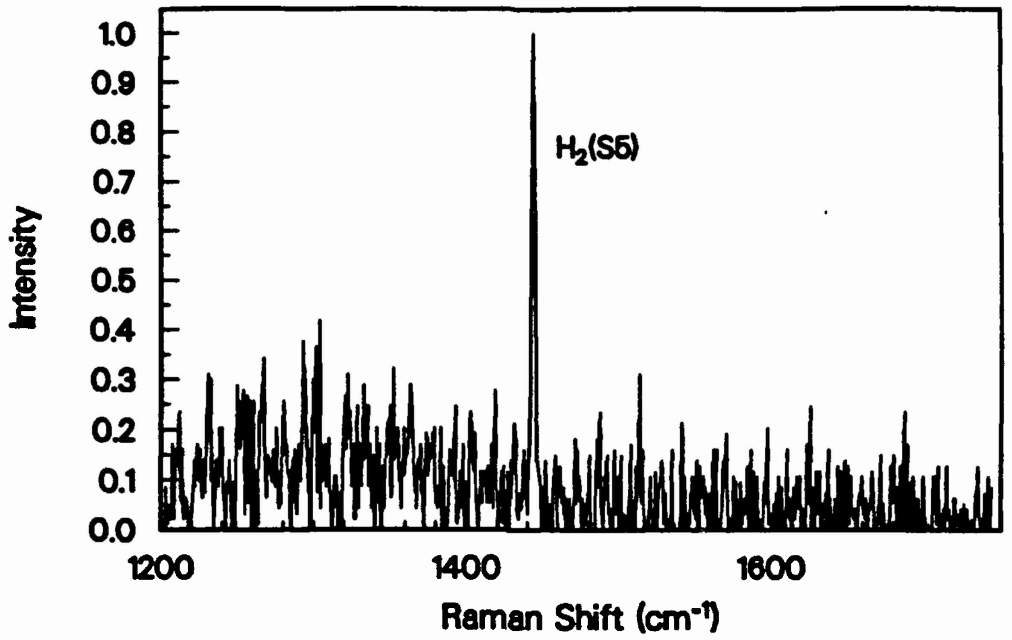

Figure 8. Single shot CARS spectrum from solid propellant combustion in the servo-controlled burner.

other two-color process occurs for molecules resonant in the CO_2 region; a representative spectrum is shown as Fig. 8.

The only resonance observed in Fig. 8 is from H_2(S5), not an unexpected result. The dye laser is peaked close to 1300 cm^{-1}, in the hope of observing CO_2 at 1285 and 1388 cm^{-1} and possibly NO_2 at 1320 cm^{-1} or the bending mode of N_2O at 1285 cm^{-1}. Apparently the concentration of CO_2 is below the sensitivity of my apparatus, the equilibrium concentration in the final flame should be only 5%, and near the surface the concentration is expected to be much lower. NO_2 should be in adequate concentration (~5%) near the surface but I think it must absorb the CARS signal because of its huge cross section in the visible region. I have not clearly observed the ν_3 mode of N_2O near the surface in earlier propellant combustion so I am not surprised at the absence of ν_1 at 1285 cm^{-1} in Fig. 8. However, it would be spectrally efficient to pick up signatures from N_2O, NO_2, CO_2 and H_2 in the same image.

FUTURE WORK

Future work will concentrate on 'line' CARS images above burning propellants. This is a novel spatial enhancement technique that is being developed to apply the simultaneous species acquisition of dual broadband CARS[13,14] to the fizz zone of the burning propellant. For this technique the motorized combustion vessel is employed with two broadband dye lasers and the 532 nm pump focussed as sheets (1-2 mm high) in a planar BOXCARS geometry immediately over the solid propellant surface, as shown pictorially in Fig. 9.

The surface is rough with features (hills and valleys) approximately 10 microns in dimension so that the fizz zone should be in the laser 'line of sight.' The focal zone where the CARS is generated will then be a line perpendicular to the propellant surface and extending up about 1–2 mm. Upon exiting from the burner vessel, the pump beams can be blocked and the 1 mm CARS image will be incident on a very narrow slit. The CARS that passes through the slit will be spectrally dispersed and detected on an OMA in the usual fashion. The minimum slit width that results in usable CARS signal strength (*e.g.* a signal to noise ratio of say, 10) will define the spatial resolution. It is anticipated that the slit width can be made as small as 20 microns which is adequate resolution to resolve the fizz zone. The entire 1mm line CARS element can be interrogated for chemical species and temperature with a spatial resolution of about 20 microns by moving the slit with a stepper motor drive. A further step is to image the entire line, thereby acquiring data of temperature and concentration gradients with each laser shot. Previous experiments[15,16] used two dimensional vidicon detectors upon which the entire 'line' CARS was imaged on the 2-D array. However, the cross-talk between adjacent channels of the vidicon interfered with or limited the spatial resolution. New CCD detectors can now be employed for these imaging experiments, they have virtually no crosstalk, high dynamic range and very low dark current which decreases noise. UTRC has a 2-D CCD detector for

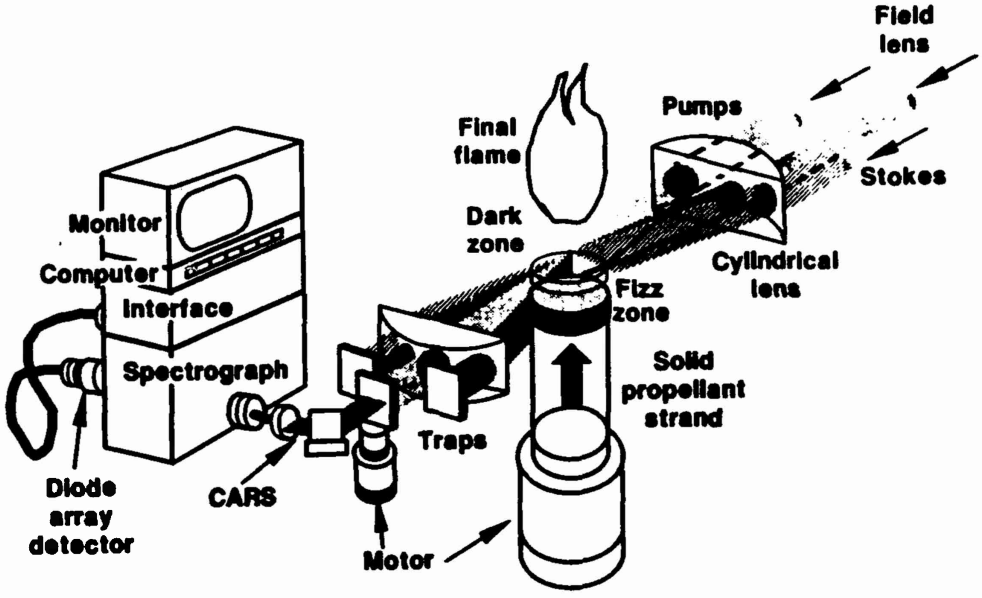

Figure 9. Linear CARS imaging geometry for gradient measurements near the propellant surface.

application to the 'line' CARS imaging. Imaging the entire line acquires all species, temperature, and thus, their gradients simultaneously. The experiments will strive to attain the highest resolution, so that the propellant flame zones can be resolved.

SUMMARY

CARS spectra have been obtained from the near surface region of solid propellant combustion at elevated pressure. Both normal two color CARS processes and dual broadband geometries have been used to excite the resonant molecules. Planar BOXCARS was used for these experiments because it provides high spatial resolution and allows the laser focus to be placed very close to the propellant surface. The spectra show the gas is cooler than the adiabatic flame limit and resonances from HCN, CH_2O, CO, N_2, H_2, CH_4, and H_2O are seen in this region. These results demonstrate the applicability of our apparatus to study the near surface region of propellant combustion at elevated pressure and probe the intermediate chemical species that may help determine chemical mechanisms. Further analysis can yield concentration and temperature from the data.

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APPENDIX G

Line CARS Measurements of Nitramine Flame Structure

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San Antonio, Texas

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LINE CARS MEASUREMENTS OF NITRAMINE FLAME STRUCTURE*

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ABSTRACT

The very difficult experimental problems posed by solid propellant combustion environments challenge even the most modern diagnostic techniques. CARS is a nonintrusive, laser-based spectroscopy with high spatial and temporal resolution used for measurement of temperature and major species concentration. Prior CARS measurements at our laboratory confirmed the equilibrium chemistry (temperature and species concentration) of nitramine propellant formulations burning at elevated pressures. To investigate intermediate chemical reactions and their contribution to the flame structure, high spatial resolution capability is required very close to the burning surface.

A motorized strand burner, servo-controlled by a diode laser, advances the regressing propellant strand at its burn rate to maintain the surface fixed in the laboratory frame. CARS spectra can be acquired arbitrarily close to the burning surface with this facility. A Nd:YAG pumped, broadband Stokes system is resonant with transitions of HCN, H_2, CO, N_2O, and N_2, although all of these molecules may not be present near the burning surface. To enhance the spatial resolution and provide 1-D spectra of temperature and species concentration, a planar BOXCARS phase matching geometry is employed with cylindrical optics to form a 'line' focus perpendicular to the surface. The CARS spectra, when imaged on a 2-D detector, provide visualization and data for measurements of temperature and concentration profiles on a single shot (10 nsec) basis. Results are presented from CARS experiments that utilize single shot, species and temperature measurements near the burning surface of an HMX/TMETN and XM39 (LOVA), an RDX based, propellant at elevated pressure.

NITRAMINE CHEMISTRY

There has been considerable recent interest and activity in the nitramine class of solid propellants because of their formulations that provide minimum smoke and low vulnerability propellants. HMX and RDX are the prominent nitramines that have received attention and have been studied through theoretical and experimental programs on decomposition, pyrolysis, ignition, gas- and solid-phase reactions. To understand the combustion of these nitramines, their microscopic chemical pathways need to be investigated. Excellent reviews of this subject are given by Fifer[1] and Schroeder[2]. HMX and RDX are cyclic nitramines formed from the basic nitroformimine, CH_2NNO_2. It is believed the initial decomposition step is $N-NO_2$ bond scission and subsequent fragmentation of the remaining ring structure[3].

$$n(CH_2NNO_2) \rightarrow H_2CN + NO_2 + (n-1)CH_2NNO_2 \begin{cases} n = 4 & \text{for HMX} \\ n = 3 & \text{for RDX} \end{cases} \quad (1)$$

$$H_2CN \rightarrow HCN + H \quad (2)$$

The early decomposition studies[4] indicated the formation of H_2CO from the nitramines so pathways were determined based on the rapid, exothermic reaction of H_2CO with N_2O.

$$CH_2NNO_2 \rightarrow H_2CO + N_2O \qquad \text{(low temperature, bimolecular)} \quad (3)$$

$$H_2CO + N_2O \rightarrow CO + H_2O + N_2 \quad (4)$$

Later pyrolysis experiments[5], at higher temperatures and heating rates, more reflective of actual combustion conditions, showed that HCN and NO_2 were important decomposition products.

* Supported in part by the U. S. Army Research Office.

$$CH_2NNO_2 \rightarrow H_2CN + NO_2 \quad (5)$$

Thus, there appear to be two competing decomposition pathways. Hatch[6] and Price *et al.*[7] modelled HMX combustion and to correctly predict measured burn rates, they had to include Eq. 3 in the initial decomposition mechanism; in fact it accounted for half of the decomposition.

for HMX:

$$(C_4H_8N_8O_8) \rightarrow 2NO_2 + 2HCN + 2H + 2H_2CO + 2N_2O \quad (6)$$

$$2H_2CO + 2N_2O \rightarrow 2CO + 2H_2O + 2N_2 \quad (7)$$

for RDX:

$$(C_3H_6N_6O_6) \rightarrow 3NO_2 + 3HCN + 3H \quad (8)$$

$$2HCN + 3NO_2 \rightarrow 2CO + 3NO + H_2O + N_2 \quad (9)$$

Thus more HCN and NO is expected from RDX based propellants, whereas HMX should produce more H_2CO.

CARS MEASUREMENTS

The most important measurements to make in the nitramine combustion experiments are temperature and species concentrations of the products of the intermediate chemical reactions. Diagnostics that couple temperature with species concentration measurements are preferred, *i.e.*, CARS.

A comprehensive review of CARS is given by Eckbreth[8] and this diagnostic has been successfully applied to nitramine combustion[9]. The experiment uses a Nd:YAG laser operating at a 10 Hz rate with 10 nsec pulses. A folded BOXCARS configuration is utilized for high spatial resolution. The burns were monitored by a video camera that gave a quantitative measure of the distance between the laser focus and propellant surface for the sequential laser pulses. The propellant used for these measurements was a composite nitramine that contains 73% HMX, 17% TMETN and 10% polyester binder[10]. The propellant was burned with a background of helium which is chemically inert and has a low nonresonant susceptibility, adding negligible signal to the CARS spectra.

NEAR-SURFACE RESULTS

The early data[9] indicate that the experiment measured equilibrium product distributions and while the data are useful for confirming this portion of the combustion, the more revealing chemical reactions near the propellant surface were not interrogated. To address the problem of measurements near the surface, the experiment was upgraded to include a motorized combustion vessel[11]. It has a stepper motor to advance the propellant as it regresses, maintaining the burning surface fixed relative to the laboratory reference frame. The motor is controlled by the servo system depicted in Fig. 1 which utilizes a laser diode and a phototransistor array to sense the burning surface location.

The diode laser is modulated at 20 KHz to discriminate against flame luminosity. The detection system demodulates the signal and logic circuits determine the location of the surface. An error signal is generated, based upon the difference from a manually supplied reference position. The error signal is transformed through the PID (proportional, integral, derivative) electronics into a train of variable frequency pulses that drive the stepper motor through the translator. The amount of proportional, integral, or derivative feedback supplied is manually adjusted depending on experience with the device. Experiments indicate the HMX/TMETN propellant surface can be controlled to within $\sim 100\mu$ jitter from the reference position. In any case, the distance from the laser volume to the burning surface can be measured from the video record for each individual CARS spectrum.

An example of the acquisition of CARS spectra from the near-surface region of solid propellant combustion at elevated pressure is shown in Figs. 2.

It is a single shot spectrum from the near-surface region of HMX burning at 12.8 atm. It shows signatures from H_2CO and CH_4. As discussed in the previous section, the observation of H_2CO is an important step toward discerning reaction pathways in nitramine combustion. CH_4 has also been observed in pyrolysis experiments on HMX, but the binder chemistry may additionally be responsible for some portion of the resonant signatures.

LINE CARS IMAGES

Attempts to quantify the relative importance of the two reaction pathways requires higher spatial resolution measurements because the CARS focal diameter is $\sim 150\mu$ and may sample the entire reaction zone at elevated pressure. To enhance the resolution and provide 1-D spectra of temperature and species concentration, a planar BOXCARS phase matching geometry is employed with cylindrical optics to form a 'line' focus perpendicular to the surface. This is a novel spatial enhancement technique that is being developed to apply CARS to the fizz zone of the burning propellant[12]. For this technique the motorized combustion vessel is employed with the dye laser and the 532 nm pump focussed as sheets (0.5-1.0 mm high) in a planar BOXCARS geometry immediately over the solid propellant surface, as shown pictorially in Fig. 3.

The surface is rough with features (hills and valleys) approximately 10 microns in dimension so that the fizz zone should be in the laser 'line of sight.' The focal zone where the CARS is generated will then be a line perpendicular to the propellant surface and extending up about 0.5 mm. Upon exiting from the burner vessel, the pump beams can be blocked and the 0.5 mm CARS image will be incident on the slit of the spectrograph. Previous experiments[13,14] used two dimensional vidicon detectors upon which the entire 'line' CARS was imaged on the 2-D array. However, the cross-talk between adjacent channels of the vidicon interfered with or limited the spatial resolution. New CCD detectors can now be employed for these imaging experiments, they have virtually no crosstalk, high dynamic range and very low dark current which decreases noise. The CARS spectra, when imaged on a 2-D detector, provide visualization and data for measurements of temperature and concentration profiles on a single shot (10 nsec) basis.

Preliminary data from this experiment is presented in the accompanying figures. The line CARS spectra are dispersed along the horizontal axis and vertical distance is indicated along the y-axis. The distance scale is arbitrary at this point, requiring further experiments to determine its range and resolution. Figure 4 was obtained from a thermoelectrically cooled, CCD camera. It is a CARS spectrum of N_2 from air at STP and allows evaluation of the detector optical configuration. Data like Fig. 5 are also necessary for normalizing propellant data to account for the spatial variation of the pump beam intensities in the focal volume. The CARS image was formed by orthogonal cylindrical field lenses, 250 mm focal length in the horizontal plane and 600 mm in the vertical plane. This resulted in a CARS line (focal image) of 150μ $\times$ 400μ. The collection optics map the CARS image onto the slit of the 0.6 m spectrograph forming a line on the detector that is 3 channels wide and 70 channels high. The image quality appears good, with little aberration introduced by the optics or spectrograph. The next experiment was to image the CARS from propellant combustion. The sensitivity of this detector required averaging for 600 laser shots (1 minute) to obtain the spectrum shown in Fig.6. The image shows the resonant signature of CO but no HCN is evident. The quality of the image is low because of the low sensitivity of this detector.

The next experiment employed an intensified CID detector that has lower spatial resolution and dynamic range than the CCD but has high enough sensitivity to allow single shot data acquisition. The results are displayed in Fig. 5. The 3-D rendition more clearly displays the species profiles although this data has not been normalized by the pump beam intensity distribution. This spectrum was obtained early in the burn and may reflect ignition phenomena. It clearly indicates the presence of HCN and CO. Their spatial distributions are different, HCN peaks closer to the surface where there is little CO. The spectra appear to broaden at their base as the distance increases, an indication that the gas is getting hotter further from the surface. Refinements to the experiment will produce more quantitative results.

Most recent experiments have employed an intensified CCD camera to detect Line CARS images from an RDX based propellant, XM39 (LOVA). The results are shown in Fig. 6.

SUMMARY

CARS spectra have been obtained from the near surface region of solid propellant combustion at elevated pressure. The spectra show the gas is cooler than the adiabatic flame limit and resonances from HCN, CH_2O, CO, and CH_4, are seen in this region. They represent activity from the two major decomposition pathways in nitramine combustion. An enhanced spatial resolution technique, 'line' CARS, has been demonstrated and preliminary data demonstrated single shot capability for high pressure propellant

combustion. These results demonstrate the applicability of our experiment to study the near surface region of propellant combustion at elevated pressure and probe the intermediate chemical species that may help determine chemical mechanisms. Further analysis can yield concentration, temperature, and their gradients from the data.

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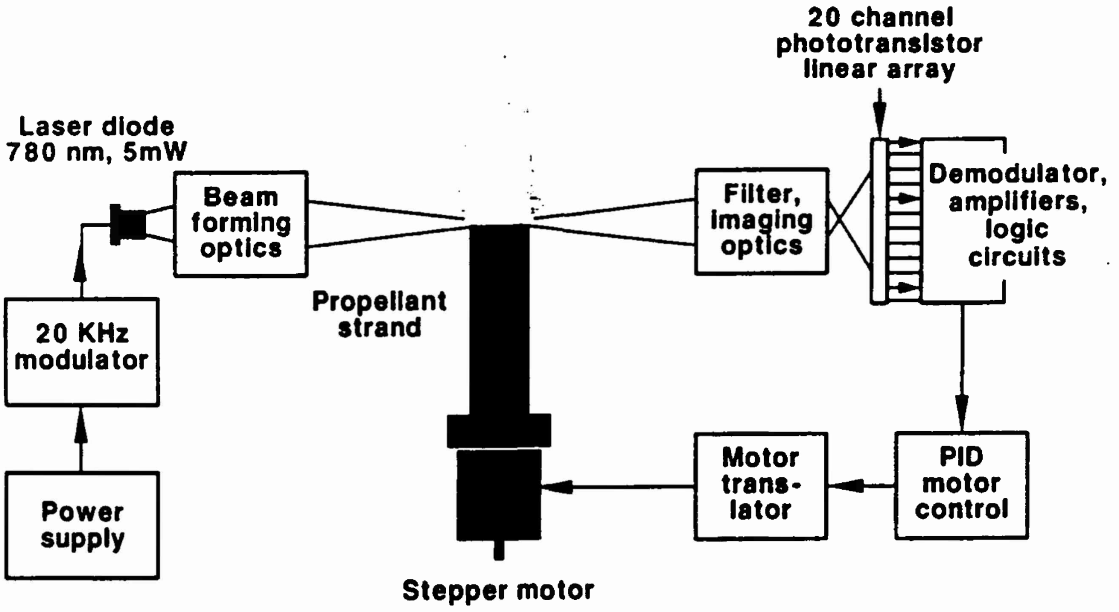


Figure 1. Laser-Servo controlled combustion chamber for high pressure solid propellant combustion.

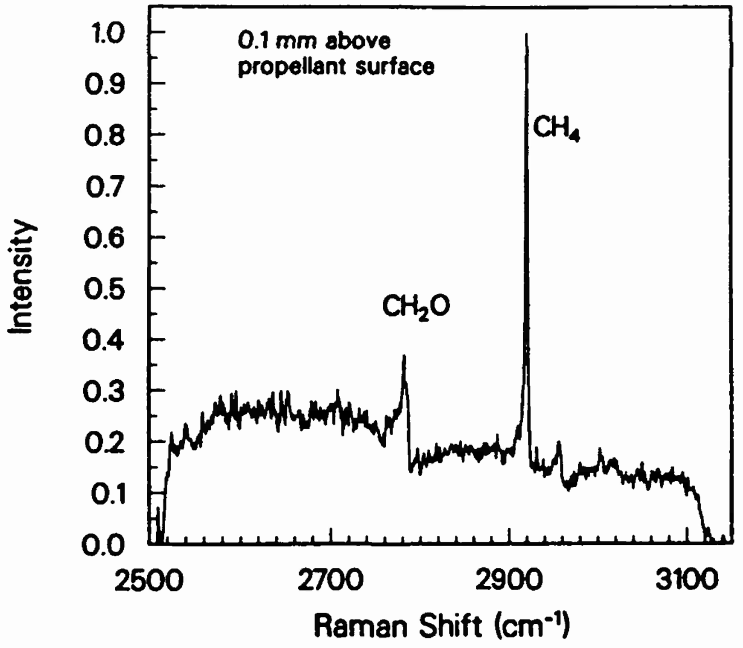


Figure 2. CARS spectrum from solid propellant combustion in the servo-controlled burner. This single shot spectrum was acquired approximately 100μ from the surface. The pressure was 12.8 atm, with a helium background purge. The signature of H_2CO and CH_4 are clearly evident.

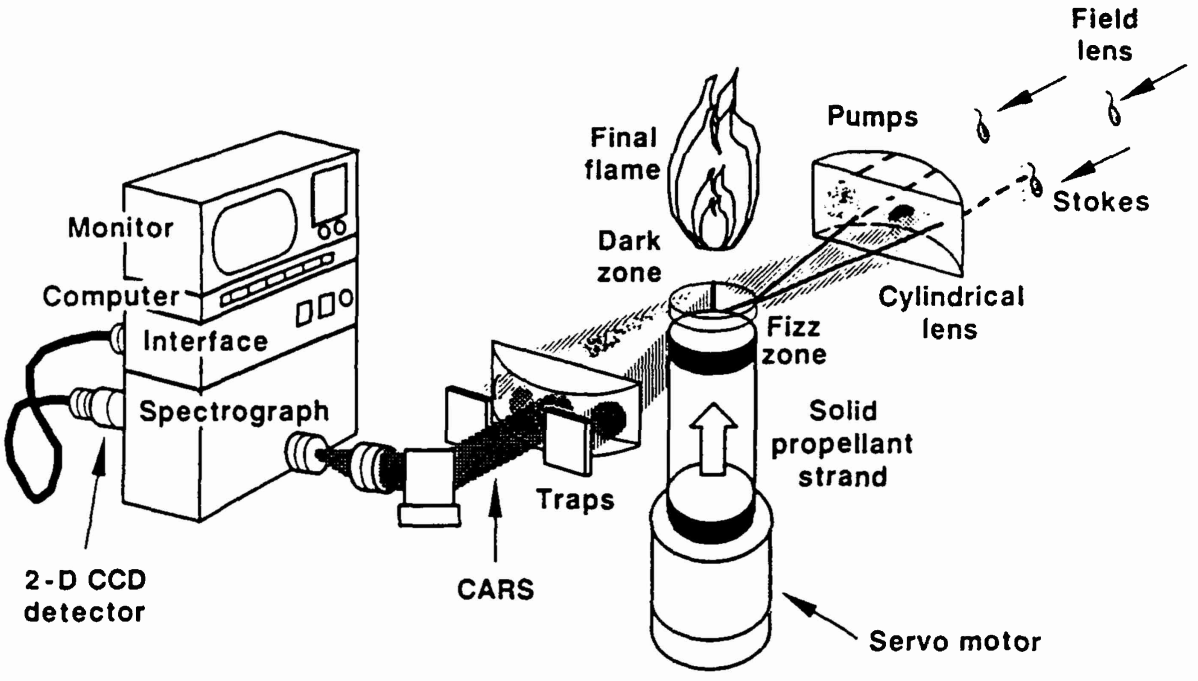
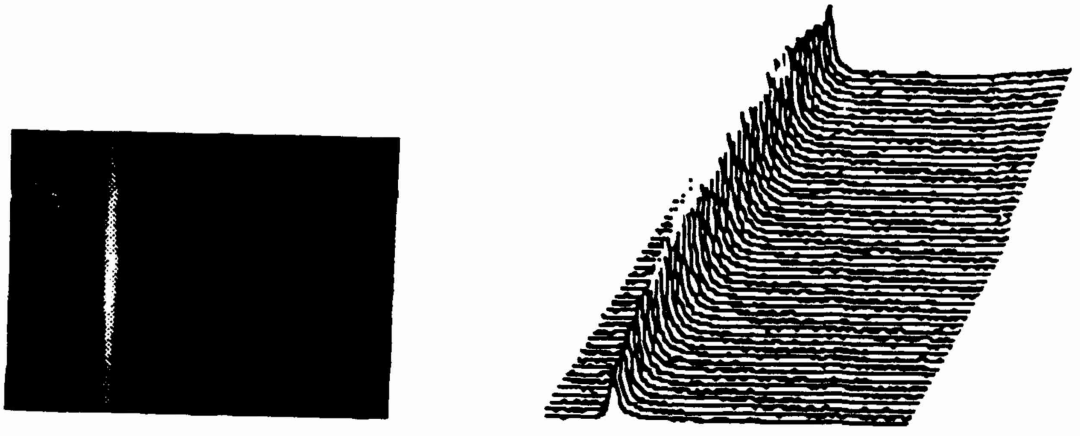


Figure 3. Linear CARS imaging geometry for gradient measurements near the propellant surface.



a. b.

Figure 4. Linear CARS image of N_2 from room air, 100 shot average.

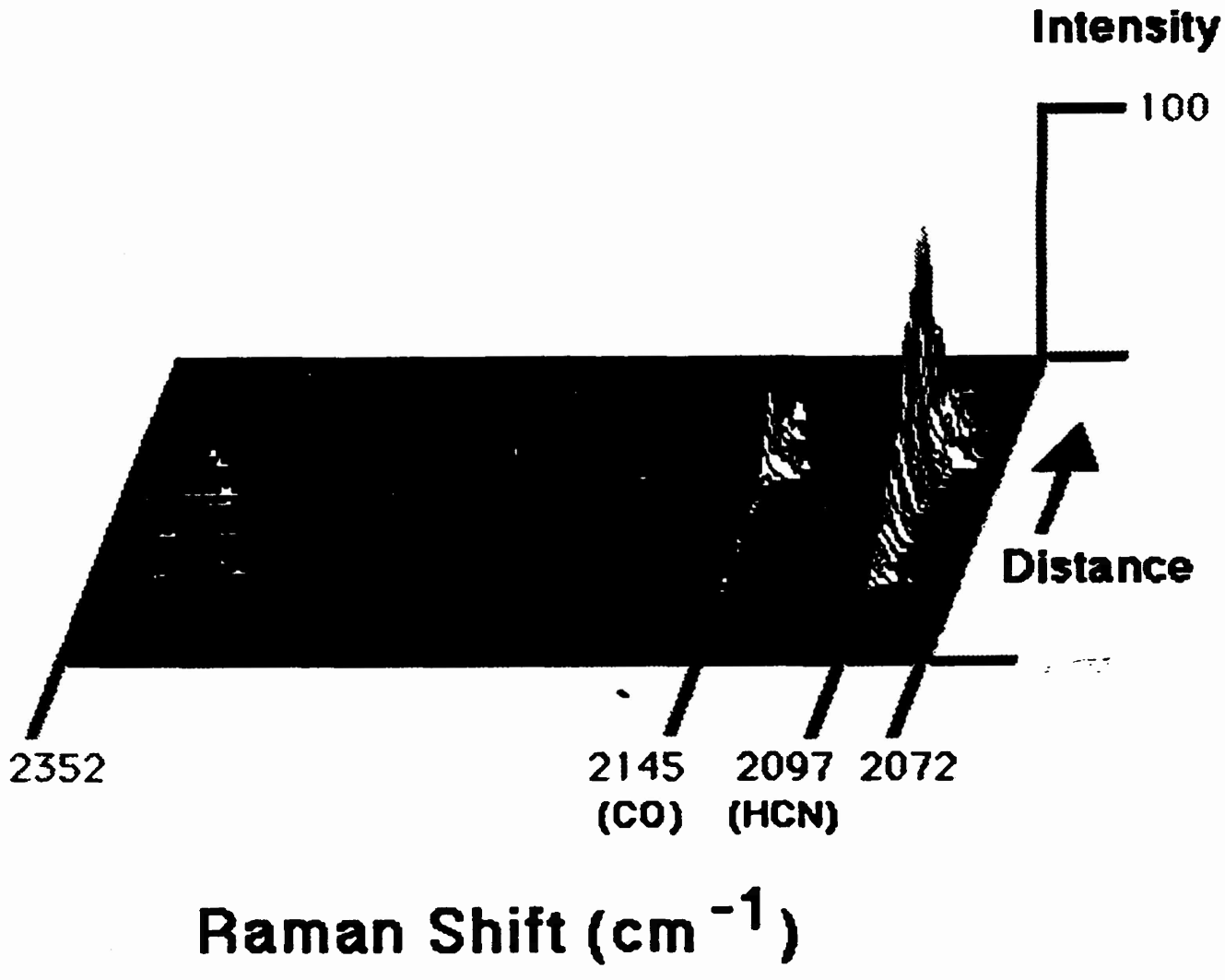


Figure 5. Single shot, linear CARS image from HMX/TMETN propellant combustion at 21.4 atm.

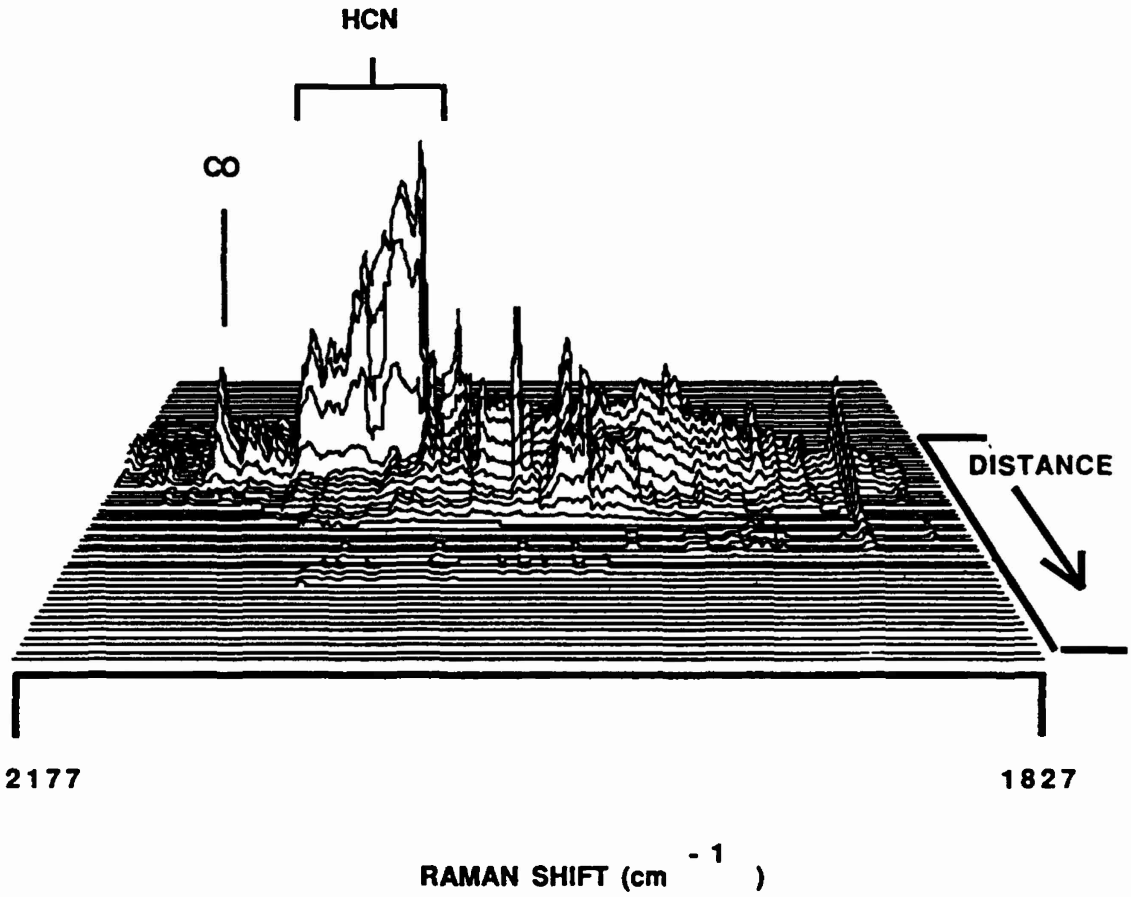


Figure 6. Single shot, linear CARS image from XM39 (LOVA) propellant combustion at 18 atm.