

MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

1983

**AFOSR/AFRPL**  
**CHEMICAL ROCKET**  
**RESEARCH MEETING**

**ABSTRACTS AND AGENDA**

**INCLUDES:**

**ABSTRACTS ON ADVANCED**  
**DIAGNOSTICS OF REACTING FLOW**

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**28 FEBRUARY TO 3 MARCH 1983**  
**LANCASTER, CALIFORNIA**

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<b>ENERGETIC MATERIALS</b>	<b>EXHAUST PLUMES</b>	
<b>PROPELLANTS</b>	<b>COMBUSTION STABILITY</b>	
<b>CHEMICAL KINETICS</b>	<b>ACOUSTICS</b>	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
This document contains expanded abstracts from the Air Force basic research program on chemical rocket propulsion. The document contains the agenda for the Chemical Rocket Research Meeting held at Lancaster, CA on 28 February to 3 March 1983. A special section focuses on combustion instability related internal flow and acoustic interactions. Major topics include: energetic material combustion, metal combustion, diagnostics of reacting flow, chemical kinetics, thermal properties, synthesis of new ingredients, combustion stability, acoustic interaction, and plumes.		

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Agenda

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Abstracts of Research

Section 2 - Chemical Rocket Research  
Abstracts of Research

Section 3 - Advanced Diagnostics of Reacting Flows  
Abstracts of Research

Appendix 1 Chemical Propulsion Research Goals

Appendix 2 Space Propulsion

Index to Abstracts and Investigators

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 MATTHEW J. KERRIN  
 Chief, Technical Information Division



PREFACE

This document serves dual purposes: (1) provides a status report on the Air Force's basic research program on chemical propulsion and (2) serves as the program for the contractors' meeting on Chemical Rocket Research. Two related topics will be the subjects of contractors meetings planned for March 1984: nonconventional propulsion for space and advanced diagnostics of reacting flows.

Most of the abstracts follow a specific format. The text begins with a short statement of relevant scientific questions addressed by the research, followed by an explanation of the approach. A statement of the uniqueness of each approach was solicited from the authors. The major portion of the text is devoted to a discussion of results obtained during the last twelve months. The abstracts should describe two figures: Figure 1 illustrates the main features of the approach and Figure 2 presents a primary accomplishment.

Hard copies of the vugraph material and collateral information are in file folders (one for each presentation) prepared for placement on a table at the rear of the meeting room.

One of the primary objectives of the meeting and this booklet is to encourage the attendees to interpret the technical barriers and to consider new research approaches. Since a 25 to 30 percent annual turn-over is built into the program, each year opportunities exist for new research approaches and for new principal investigators. Several of the presentations provide guidance on research directions to some of technological challenges. However, prospective principal investigators should not feel constrained by this guidance and are encouraged to look beyond the indentified goals. The location of the meeting promotes interchanges among the attendees by being held near organizations interested in the research. Questions can be directed to either:

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AFOSR/NA  
Bolling AFB  
Washington, DC 20332  
Phn: (202) 767-4937  
Autovon: 297-4737

or

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AFRPL/XXR  
Edwards AFB, CA 93534  
Phn: (805) 277-5206  
Autovon: 350-5206

AGENDA SUMMARY

WORKING SESSION ON  
COMBUSTION INSTABILITY RELATED INTERNAL FLOW AND ACOUSTIC INTERACTIONS

February 28 - Monday

0730 Registration  
0800 Discussion of issues and agenda  
0830 Internal flows and acoustics  
1130 Summary of research issues  
1200-1300 Lunch  
1300-1700 Internal flow couplings to burning surfaces  
1700-1730 Summary of research issues

1983 AFOSR/AFRPL CHEMICAL ROCKET PROPULSION RESEARCH MEETING

March 1 - Tuesday

0800 Registration  
0830 Announcements  
0835 WELCOME by Don A Hart, Director, AFRPL  
0845 Ram Rocket Processes  
0945 Special Topics  
1135-1200 AFOSR Interests in Rocket Propulsion, Leonard H Caveny, AFOSR  
1330-1625 Metalized Propellants  
  
1630-1655 Administrative Meeting for AFOSR Contractors

March 2 - Wednesday

0745 Late Registration  
0800-1200 Combustion  
1300 Air Force Rocket Propulsion Technology, Richard R Weiss, Chief  
Scientist, AFRPL  
1345-1445 Thermodynamics and Kinetics  
1500-1630 Rocket Exhaust Plumes  
1630 International Interactions in Rocket Combustion, Ronald L Derr,  
NWC, China Lake, CA  
  
1700 Social Hour (Cash Bar) - Antelope Valley Inn

March 3 - Thursday

0745 Late Registration  
0800-1200 Advanced Energetic Ingredients  
1300 AFRPL Research Interests in Propulsion, Robert A Biggers, AFRPL  
1315 Rocket Motor Materials  
1345 Structural Mechanics  
1520 Adjourn Meeting

AGENDA

AFOSR/AFRPL WORKING SESSION  
on  
COMBUSTION INSTABILITY RELATED INTERNAL FLOW AND ACOUSTIC INTERACTIONS  
(Non-metallized Propellants)

Antelope Valley Inn, Lancaster, CA

Monday (AM)  
28 February 1983

TIME NUM.

- 0730 Registration
- 0800 Discussion of agenda. Leonard H Caveny, AFOSR/NA  
and Jay Levine, AFRPL
- 0810 Summary of related 6.2 programs. Jay Levine

Topic Internal Flows and Acoustics

TIME NUM.

- 0830 1 COUPLING BETWEEN VELOCITY OSCILLATIONS AND SOLID PROPELLANT  
COMBUSTION. Robert S Brown, Paul G Willoughby, and R C Waugh,  
Chemical Systems Division, Sunnyvale, CA
- 2 COMBUSTION OSCILLATIONS IN HETEROGENEOUS SYSTEMS. Moshe BenReuven  
and Martin Summerfield, Princeton Combustion Research  
Laboratories, Inc, Princeton, NJ
- Comments by Gary Flandro, University of Utah, Salt Lake City, UT
- 3 APPLICABILITY OF CURRENT COMBUSTION INSTABILITY ANALYSIS  
APPROACHES. Ben T Zinn and Brady R Daniel, Georgia Institute of  
Technology, Atlanta, GA
- 4 ROCKET MOTOR AEROACOUSTICS. Warren C Strahle, Georgia Institute  
of Technology, Atlanta, GA
- 1130 Summary of research issues. Discussion leaders: Norman S Cohen  
and Ben T Zinn
- 1200-1300 Lunch

AFOSR/AFRPL WORKING SESSION  
on  
COMBUSTION INSTABILITY RELATED INTERNAL FLOW AND ACOUSTIC INTERACTIONS

Monday (PM)  
28 February 1983

Topic: Internal Flow Couplings to Burning Surfaces

TIME	NUM.	
1300	5	ASSUMED FLOW FIELD EFFECTS IN MODELLING VELOCITY COUPLED COMBUSTION RESPONSES. Leon D Strand and Norman S Cohen, Jet Propulsion Laboratory, Pasadena, CA
	6	NONSTEADY INTERNAL FLOW INTERACTIONS. Robert L Glick, Purdue University, West Lafayette, IN
		Comments by Joseph Baum and Jay Levine, AFRPL/PAC
		Comments by F E C Culick, California Institute of Technology
		Comments by H B Mathes and Klaus C Schadow, NWC, China Lake, CA
1700		Summary of research issues. Discussion leaders: Moshe BenReuven and Robert Brown
1730		Closing comments. Jay Levine and Leonard H Caveny

1983 AFOSR/AFRPL CHEMICAL ROCKET RESEARCH MEETING

Antelope Valley Inn, Lancaster, CA

TUESDAY (AM)

1 March 1983

TIME NUM.

0800 Registration

Session Chairman: Leonard H Caveny, AFOSR/NA

0830 Announcements

0835 WELCOME: Don A Hart, Director, AFRPL/CC

Topic: Ram Rocket Processes

TIME NUM.

0845 7 FUEL RICH SOLID PROPELLANT COMBUSTION BEHIND BLUFF BODY. Warren C Strahle, Jechiel (Jeff) I Jagoda, and James E Hubbartt, Georgia Institute of Technology, Atlanta, GA

0915 8 & 9 FUEL-RICH SOLID PROPELLANT BORON COMBUSTION: Analysis and Experiment. Merrill King, Ronald S Fry, and James Komar, Atlantic Research Corp, Alexandria, VA

Topic: Special

0945 10 OVERVIEW OF STANFORD PROGRAM ON ADVANCED DIAGNOSTICS FOR REACTING FLOWS. Ronald K Hanson, C Thomas Bowman, Sidney A Self, Robert L Byer, Donald Baganoff, Brian J Cantwell, and Lambertus Hesselink, Stanford University, Stanford, CA

1015 Break

1040 OVERVIEW: AIR FORCE Rocket Propulsion Technology, Richard R. Weiss, Chief Scientist, AFRPL

1135 11 OVERVIEW: AFOSR INTEREST IN ROCKET PROPULSION. Leonard H Caveny, AFOSR/NA.

1200 LUNCH (Reconvene at 1330)

TUESDAY (PM)

1 MARCH 1983

Session Chairman: Robert L Geisler, AFRPL/MKP

Topic: Metalized Propellants

TIME	NUM.	
1330	12	BEHAVIOR OF ALUMINUM IN COMBUSTION OF SOLID ROCKET COMBUSTION. Edward W Price and Robert K Sigman, Georgia Institute of Technology, Atlanta, GA.
1400	13	AERODYNAMIC BREAKUP - METAL DROPLETS. James E Craig, Spectron Development Laboratory, Costa Mesa, CA
1430	14	COMBUSTION KINETICS OF METAL OXIDES AND HALIDE RADICALS. Arthur Fontijn, Rensselaer Polytechnic Institute, Troy, NY
1500		Break
1515	15	COMBUSTION OF ALUMINIZED, FLUORINE-RICH PROPELLANTS. Dirk J Willard and Robert L Geisler, AFRPL/MKP
1545	16	DETERMINATION OF THE COMBUSTION MECHANISMS OF ALUMINIZED PROPELLANTS. John P Renie and John R Osborn and
	17	EFFECT OF ACCELERATION ON METALIZED COMPOSITE PROPELLANTS. Robert A Frederick, John C Matson, and John R Osborn, Purdue University, West Lafayette, IN
1625		ADJOURN SESSION
1630-1655		ADMINISTRATIVE MEETING FOR AFOSR CONTRACTORS ONLY

WEDNESDAY (AM)

2 MARCH 1983

0745 Late Registration

Session Chairman: Wayne E Roe, AFRPL/PAC

Topic: Combustion

TIME	NUM.	
0800	18	MECHANISMS FOR ACOUSTIC SUPPRESSION. Merrill W Beckstead, D L Gordon, and Richard L Ruan, Brigham Young University, Provo UT
0830	19	DIAGNOSTICS FOR HIGH PRESSURE COMBUSTION MECHANISMS. David P Weaver, AFRPL/PAP and David Campbell, University of Dayton Research Institute
0915	20	MODELING OF DEFLAGRATION TO SHOCK-TO-DETONATION TRANSITION (DSDT) in GRANULAR SOLID PROPELLANTS. Herman Krier, P Barry Butler, and Daniel W Coyne, University of Illinois at Urbana-Champaign, Champaign, IL
0945		SPRAY CHARACTERIZATION USING THE VISIBILITY AND INTENSITY OF A DOPPLER SIGNAL. Cecil F Hess, Spectron Development Laboratory, Costa Mesa, CA (New start)
1000		Break
1020	21	COHERENT OPTICAL SPECTROSCOPY IN FLAMES. John W Daily, University of California, Berkeley, CA (Brief status report)
1040	22	NON-STEADY COMBUSTION OF COMPOSITE PROPELLANTS. Leon D Strand and Norman S Cohen, Jet Propulsion Laboratory, Pasadena, CA
1100	23	THERMOPHYSICAL PROPERTY DETERMINATIONS USING TRANSIENT TECHNIQUES. Raymond E Taylor, Purdue University, West Lafayette, IN
1130		SUMMARY: WORKING SESSION ON COMBUSTION INSTABILITY RELATED INTERNAL FLOW AND ACOUSTIC INTERACTIONS. Robert S Brown, Chemical Systems Division and Moshe BenReuven, Princeton Combustion Research Laboratories, Inc
1200		LUNCH (Reconvene at 1300)

WEDNESDAY (PM)

2 MARCH 1983

Session Chairman: Wilbur C Andrepont, AFRPL/DYP

TIME NUM.  
1300 24 INVITED PRESENTATION: COMPOSITE PROPULSION FOR TRANSATMOSPHERIC  
LAUNCH SYSTEMS - A PERSPECTIVE ON RESEARCH CHALLENGES.  
Raymond Edleman, SAI, Inc, Chatsworth, CA

Topic: Thermodynamics and Kinetics

1330 25 EVALUATION AND COMPILATION OF THE THERMODYNAMIC PROPERTIES OF HIGH  
TEMPERATURE SPECIES. Malcom W Chase, The Dow Chemical Company,  
Midland, MI

1400 26 CRITICAL EVALUATION OF HIGH TEMPERATURE CHEMICAL KINETIC DATA.  
Norman Cohen, Karl Westberg, Aerospace Corporation, Los Angeles,  
CA and Lewis H Gevantman, National Bureau of Standards,  
Gaithersburg, MD

1430 Break

Topic: Rocket Exhaust Plumes

TIME NUM  
1445 27 RESONANT CARS DETECTION OF OH RADICALS. James F Verdick and Alan  
C Eckbreth, United Technology Research Center, East Hartford, CT  
(Brief status report)

1500 28 VAPOR PRESSURE OF SALT-HCl-H<sub>2</sub>O SOLUTIONS BELOW 0 C. Eugene  
Miller, University of Nevada, Reno, NV

1530 29 FLOW OF GAS-PARTICLE MIXTURES. Melvyn C Branch, University of  
Colorado, Boulder, CO

1600 30 ADVANCE COMBUSTION/PLUME DIAGNOSTICS. Jay D Eversole, University  
of Dayton Research Institute, Dayton, OH

Topic: Special

1630 INVITED PRESENTATION: INTERNATIONAL INTERACTIONS IN ROCKET  
COMBUSTION RESEARCH. Ronald L Derr, NWC, China Lake, CA

1700 ADJOURN SESSION

1700 SOCIAL HOUR (Cash Bar)

THURSDAY (AM)

3 MARCH 1983

0745 Late Registration

Session Chairman: Frank Roberto, AFRPL/MKP

Topic: Advanced Energetic Ingredients

TIME	NUM.	
0800	31	ELECTROLYTIC PREPARATION OF NOVEL AZIDODINITRO COMPOUNDS. Milton B Frankel, Rocketdyne Division, Rockwell International, Canoga Park, CA (New start)
0815	32	SYNTHESIS AND CHEMISTRY OF ENERGETIC METALLOTETRA-AZADIENES. William C Trogler, Northwestern Univ, Evanston, IL (New start)
0830	33	HMX COMBUSTION MODIFICATIONS. Joseph E Flanagan, Milton B Frankel and Dean O Woolery, Rocketdyne Division, Rockwell International, Canoga Park, CA
0900	34	ROLE OF SOLID PHASE PHENOMENA IN NITRAMINE PROPERTIES AND DECOMPOSITION. Thomas B Brill, Richard J Karpowicz, and Thomas M Haller, University of Delaware, Newark, DE
0930	35	SYNTHESIS OF DIFLUORAMINOXY-, DIFLUORAMINO- OR FLUORODIAZONIUM-CONTAINING MATERIALS. Jean'ne M Shreeve, Univ of Idaho, Moscow, ID (New start)
0945		Break
1000	36	INITIAL THERMOCHEMICAL DECOMPOSITION MECHANISMS OF ENERGETIC INGREDIENTS: DEUTERIUM ISOTOPE EFFECTS AND ISOTHERMAL DECOMPOSITION STUDIES. Berge B Goshgarian, Michael B Collidge, and Scott A Shackelford, AFRPL/LKLR
1025	37	POLYMERS CONTAINING AZIDE AND NITRATE ESTER GROUPS. Stan Morse, University of Dayton Research Institute, Dayton, OH
1055	38	MODIFICATION OF PROPELLANT BINDER NETWORK FOR IMPROVEMENT OF MECHANICAL PROPERTIES. C Sue Kim, California State University at Sacramento, Sacramento, CA (New Start)
1125	39	NEW SYNTHETIC TECHNIQUES FOR ADVANCED PROPELLANT INGREDIENTS: SELECTIVE CHEMICAL TRANSFORMATIONS AND NEW STRUCTURES. Scott A Shackelford, Stephen P Herrlinger, and Robert D Chapman, AFRPL/LKLR
1150	40	MECHANISTIC COMBUSTION INTERACTIONS OF ISOTOPICALLY LABELED PROPELLANT INGREDIENTS. Scott A Shackelford and Berge B Goshgarian, AFRPL/LKLR (New Start)
1200		Lunch (Reconvene 1300)

THURSDAY (PM)

3 MARCH 1982

Session Chairman: Lawrence P Quinn, AFRPL/MKBM

TIME NUM.

1300 OVERVIEW: AFRPL RESEARCH INTERESTS IN ROCKET PROPULSION. Robert A Biggers, AFRPL/XRX

Topic: Rocket Motor Materials

1320 41 CARBON-CARBON PROCESSING VARIABLES. Wesley P Hoffman, AFRPL/MKBN

Topic: Structural Mechanics

1350 42 STRUCTURAL NATURE OF CRACK GROWTH IN SOLID PROPELLANT. Chi T (Jimmie) Liu, AFRPL/MKPB

1420 43 PROPELLANT NONLINEAR CONSTITUTIVE THEORY EXTENSION. Gene Francis, Chemical Systems Division, United Technologies, Sunnyvale, CA

1450 44 THERMOMECHANICALLY COUPLED VIBRATIONS IN A CYLINDRICAL GEOMETRY LACKING SYMMETRY: A FINITE ELEMENT SOLUTION PROCEDURE. Richard W Young, University of Cincinnati, Cincinnati, OH

1520 ADJOURN SESSION AND MEETING

## COMBUSTION INSTABILITY RELATED INTERNAL FLOW AND ACOUSTIC INTERACTIONS

The realities of rocket motor combustion instability are clear in view of the recurring developmental problems. Combustion instability considerations always accompany propulsion system development. As performance and operational gains are pursued various forms of instability are a likely consequence.

A range of views exists on how to deal with combustion instability as part of the price (and risk) of propulsion system development. The occurrence of instability is not usually a consequence of bad design practices. Thus best efforts are applied to avoid combustion instability, but when it does occur, it is addressed by available methods. Recent assessments lead to the realization that the ability to anticipate the effects of configuration and propellant formulation changes on rocket motor stability is limited primarily by the inability to relate internal flows, acoustic interactions, and propellant combustion responses. Accordingly, several investigators directed their attention to the topic of this session.

The goals of this working session are to focus more sharply the research on the identified approaches and to promote additional collaboration among the investigators. The most important feature of the session is the emphasis on the narrowly defined topic, i.e., flow field effects on combustion instability. The session format includes:

- Presentation material made available to the participants one week prior to session.
- Formal part of each presentation limited to 10 minutes. (Speakers assumed that the audience reviewed the presentation material prior to the session.)
- Most of the time reserved for low key discussions on the specific topic being presented.
- No premium is to be placed on arriving at a consensus. (Diversity of approach is expected and is not necessarily a problem.)

Recent research results have defined several critical issues. The following are examples of items which relate to the research being pursued:

- Velocity coupled combustion responses are largely flow field (chamber) dependent.
- Turbulent flow fields in rocket chambers must be characterized.
- Computation of acoustic and flow processes suffer from the large uncertainties associated with flow entrained particulate intermediates (i.e., density and size distribution as function of position).
- Advancements in instrumentation that permit direct determinations of pressure and velocity response characteristics.
- Batch-to-batch as well as test-to-test variations of observed motor responses and stability limits point to difficulties in achieving deterministic models.
- Acoustic gain and loss terms are small and very difficult to isolate and to relate to any one particular source.

Each of the associated processes presents important research challenges. Attempts to make quantitative determinations on any one of them leads to large uncertainties. Indeed, in many situations the prediction of a trend is a significant accomplishment.

Coupling Between Velocity Oscillations and  
Solid Propellant Combustion

R. S. Brown, P. G. Willoughby, and R. Dunlap  
Chemical Systems Division/United Technologies

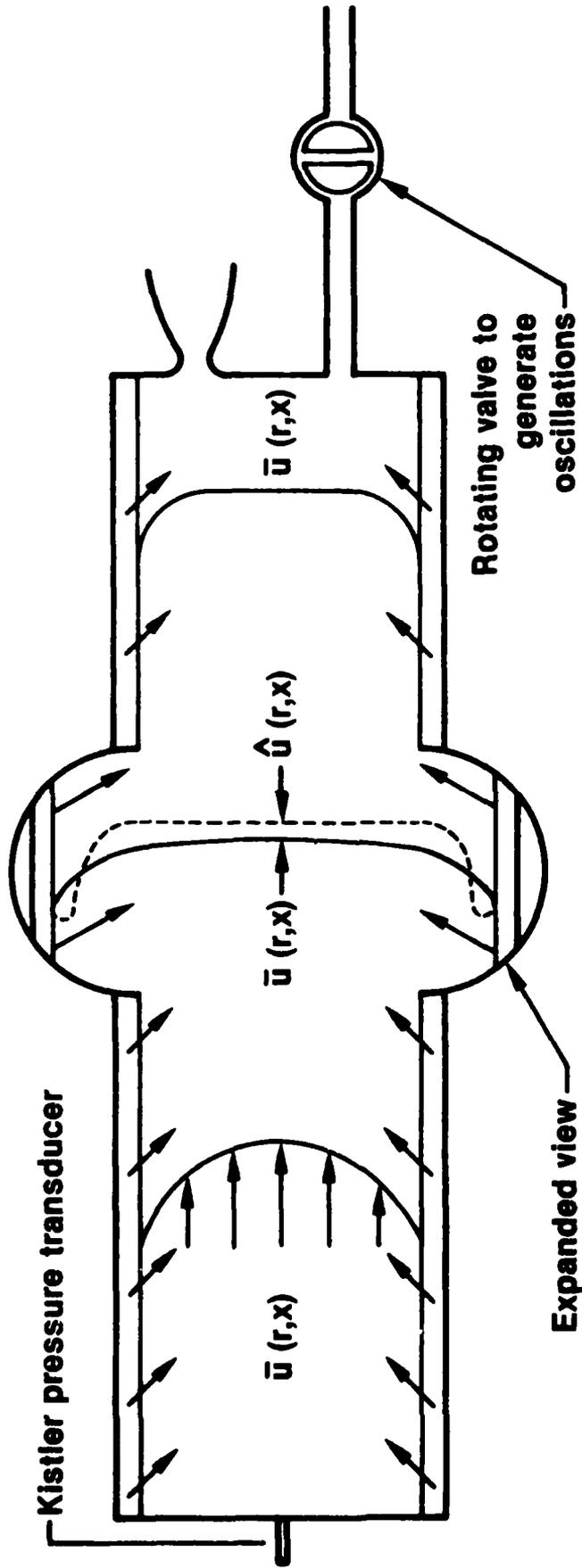
Abstract

The characteristics of the oscillatory flowfield associated with velocity coupling have never been investigated; yet heuristic models for this coupling have been seriously deficient in explaining motor and laboratory burner data. The fundamental issue is how the acoustic velocity oscillations in the core flow are transmitted to the propellant surface to generate burning rate oscillations. Resolution of this issue is the primary objective of experimental studies being conducted at CSD and analytical studies being conducted at Princeton Combustion Research Laboratories.

The experimental approach is to simulate the flow environment of a simple solid propellant rocket motor using cold flow techniques developed by CSD. Oscillatory flows are superimposed on the mean flow by combining a rotating valve with a steady-state nozzle as shown in Figure 1.

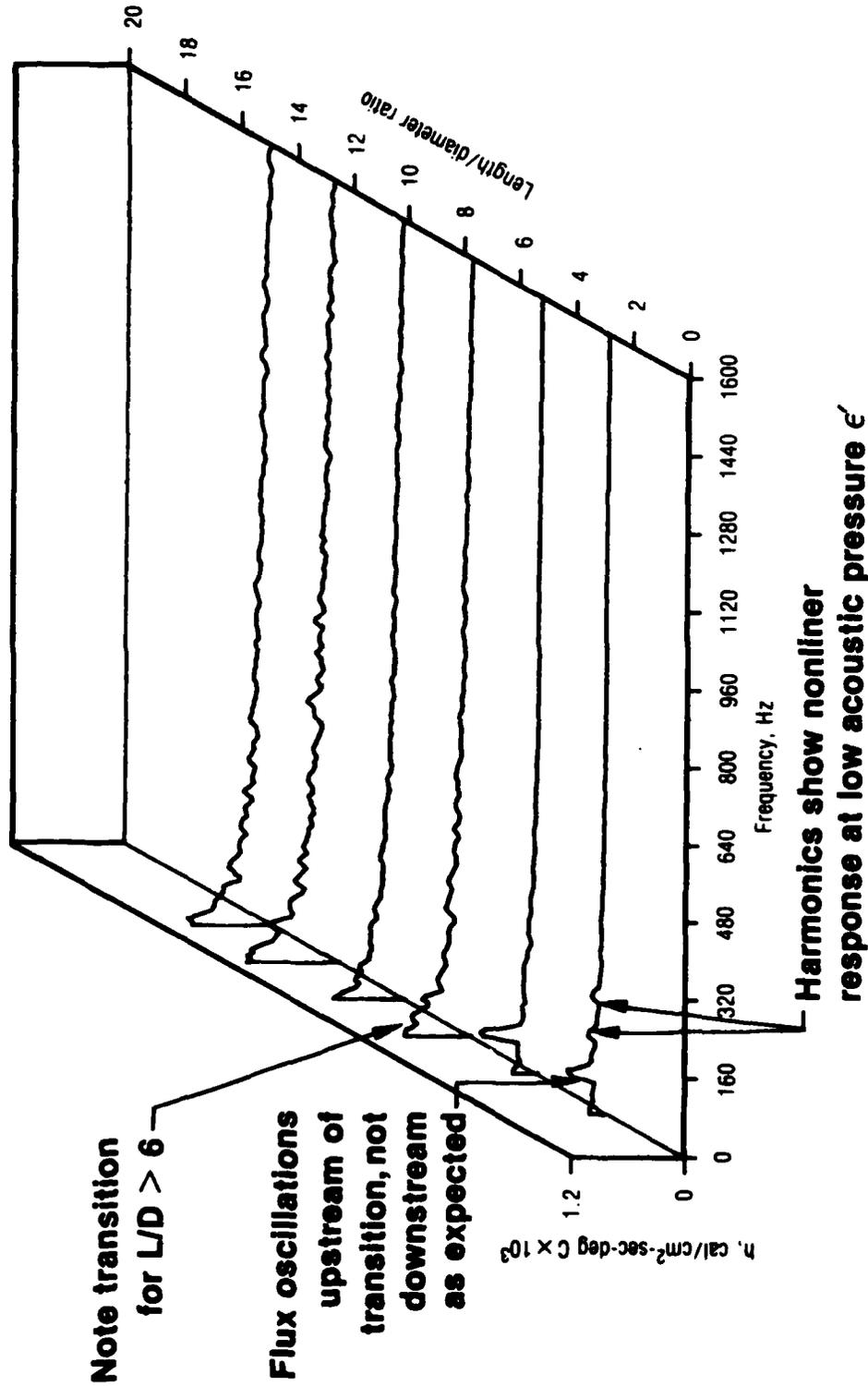
Cold flow data from this simulated solid propellant rocket motor have shown the flow towards the head-end follows a rotational-inviscid flow profile. For  $L/D > 7$  to 10, the velocity profile transitions towards a turbulent flow profile. Measurements with low amplitude pressure oscillations (0.05%) show heat transfer oscillations are generated upstream of the transition point, as shown in Figure 2. At higher pressure amplitudes (0.3%), significant harmonic content is generated upstream of the transition and linear response is produced downstream of the transition. The nonlinear behavior is consistent with the effects expected from acoustic streaming close to the simulated propellant surface. These results suggest that velocity coupling effects first appear towards the head-end of the motor. As the pressure amplitude increases, the effects spread towards the aft-end, an effect which contradicts the heuristic models. These results also suggest velocity coupling is highly nonlinear, especially at low chamber flow rates, which is consistent with velocity coupled T-burner and dual rotating valve data.

# VELOCITY COUPLING WITH SOLID PROPELLANT COMBUSTION



- Objective
  - Investigate heat transfer effects of:
    - Acoustic boundary layer
    - Turbulence generation
    - Vortex-boundary interaction
- Approach
  - Simulate motor flow with  $N_2$  through walls
  - Measure oscillatory heat flux
  - Measure oscillatory velocity

# OSCILLATORY HEAT FLUX RESPONSE TO PRESSURE WAVES (DRIVING AT 82 HZ ONLY, $\epsilon' = 0.054\%$ )



Conclusion: Results differ significantly from stability models

ANALYSIS OF COMBUSTION OSCILLATIONS IN  
HETEROGENEOUS SYSTEMS

MOSHE BEN-REUVEN AND MARTIN SUMMERFIELD  
PRINCETON COMBUSTION RESEARCH LABORATORIES, INC., PRINCETON, NJ

This study is aimed at elucidation of the physical mechanisms capable of driving acoustic instability in solid propellant motors, particularly of the type termed velocity-coupled instability. Previous studies on the coupling between velocity oscillations and the combustion process in solid propellant motors have demonstrated the complexity of the overall phenomenon, but have not yet defined the basic mechanisms nor how they operate under flow conditions prevailing in rocket chambers. The first and second tasks of this research, critical literature review and order of magnitude analyses of velocity coupling mechanisms, respectively, are virtually complete. The present part of the study is intended for analytical simulation of the interior flow field within a solid propellant grain. The focus is on the Stokes layer, with the objective of investigating the particular instability mechanism of visco-acoustic coupling. Preliminary analysis has indicated that this mechanism is both plausible and sufficiently powerful to drive nonlinear vibrations. A comprehensive analytical model of the flow field within the viscous wall layer region has been currently derived, for an axisymmetric, nonsteady flow field configuration. For simulation of the cold flow test results generated at UTC/CSD, four conservation equations are incorporated for continuity, momentum and energy. A semi-explicit finite difference numerical algorithm is being constructed, using a nonuniform fixed mesh. Effects of gas phase combustion, turbulence, and non-steady solid propellant regression will be modeled and incorporated in modular form (independent subprogram groups) in the final version of the numerical finite difference code.

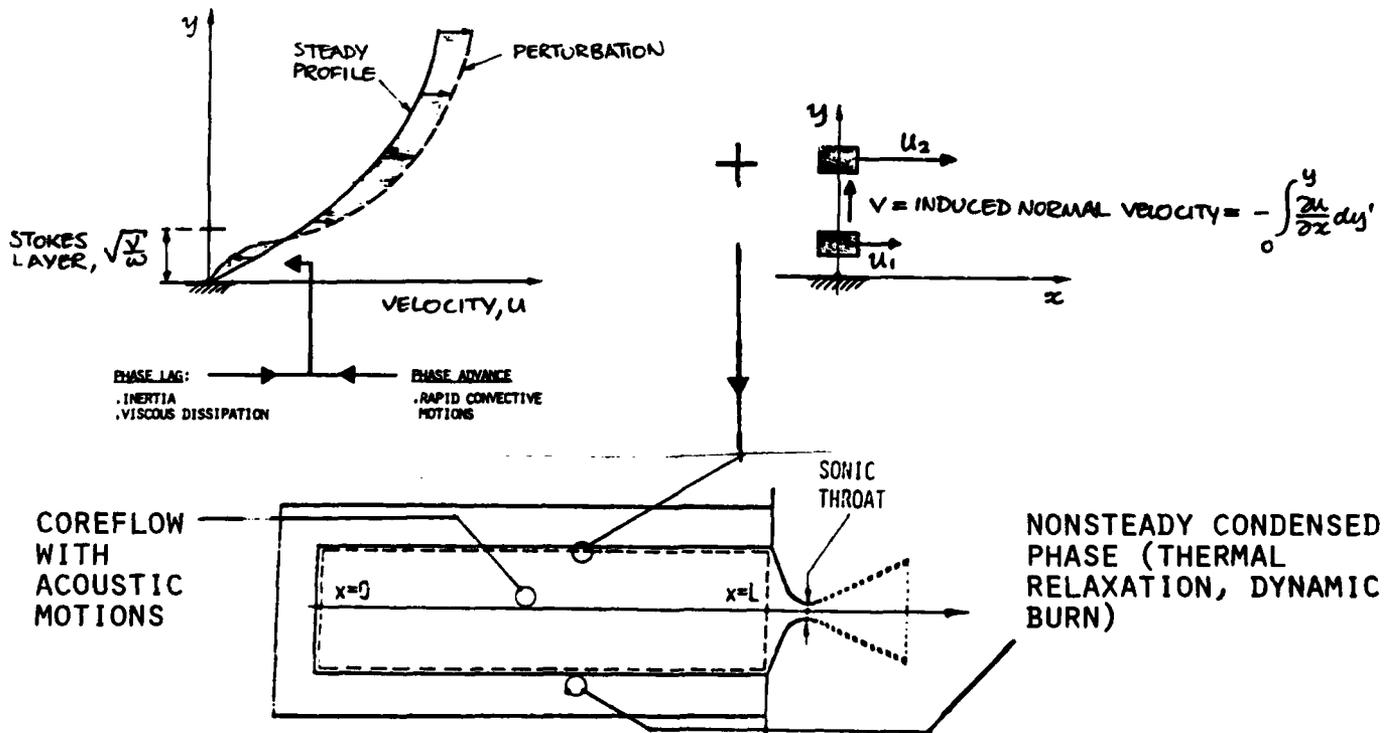
APPROACH:

ANALYSIS OF VELOCITY-COUPLED INSTABILITY MECHANISMS.  
 ONE DOMINANT MECHANISM IS VISCO-ACOUSTIC COUPLING:

WITHIN THE VISCOUS SUBLAYER (STOKES LAYER) WHERE PRIMARY COMBUSTION OCCURS:

FREQUENCY-DEPENDENT SURFACE  
 HEAT TRANSFER (FIRST ORDER),  
 WITH PHASE RELATIVE TO  
 ATTENDANT PERTURBATION.

DC-COMPONENT: ACOUSTIC STREAMING,  
 WHEN U, V NOT OUT OF PHASE, NET  
 X-MOMENTUM TRANSFER OCCURS.  
 (SECOND ORDER).

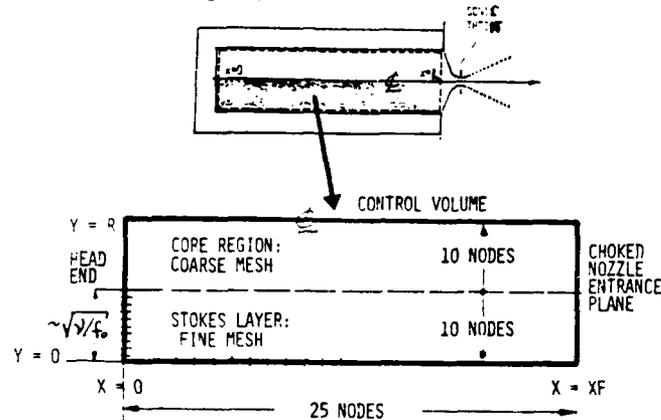


THE VISCO-ACOUSTIC MECHANISM IS FIRST ANALYSED  
 BY FULL NUMERICAL SIMULATION OF COLD FLOW TESTS  
 BEING CONDUCTED BY DR. BROWN, UTC/CSD.

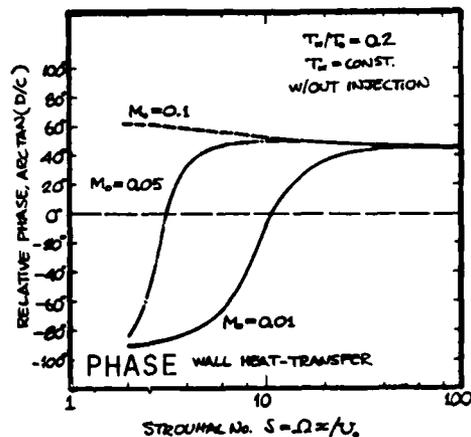
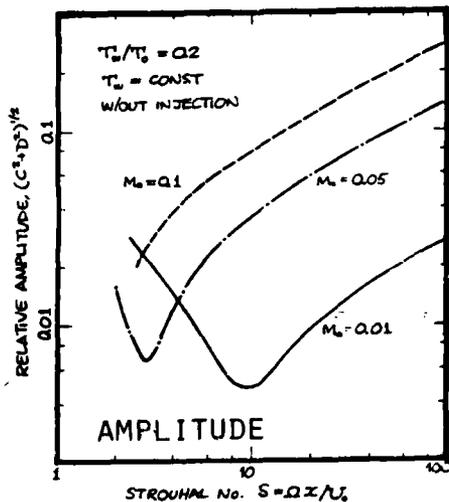
## ACCOMPLISHMENTS

MODELING-COMPLETE; FOR NONSTEADY, AXISYMMETRIC, COMPRESSIBLE, VISCOUS INTERNAL FLOW FIELD (EQUATIONS OF MOTION, BOUNDARY DATA), FOR SIMULATION OF COLD FLOW TESTS.

NUMERICAL CODE BEING DEVELOPED: FINITE DIFFERENCE, SEMI-EXPLICIT SCHEME (WITH FIXED MESH SHOWN), FOR SOLUTION OF THE COMPLETE NONLINEAR SYSTEM.



NONSTEADY PROPELLANT BURNING, TURBULENCE (2 ADDITIONAL DIFF. EQUATIONS OF  $K, \epsilon$  APPROACH) AND GAS PHASE COMBUSTION, WILL BE ADDED TO INITIAL CODE IN MODULAR FORM.



ORDER OF MAGNITUDE ANALYSIS INDICATES EXPECTED EFFECTS OF STROUHAL NO. AND MEAN FLOW MACH NO. ON SURFACE HEAT TRANSFER. THESE INCLUDE EFFECTS OF FREQUENCY,  $X/D$  AND (IMPLICITLY) PRESSURE.

**INVESTIGATION OF THE APPLICABILITY  
OF CURRENT COMBUSTION INSTABILITY  
ANALYSIS APPROACHES**

**BEN T. ZINN and BRADY R. DANIEL**

**AEROSPACE ENGINEERING  
GEORGIA TECH, ATLANTA, GA 30332**

This research program investigates the applicability of current analyses of combustion instability in solid propellant rocket motors. The program consists of a recently initiated theoretical investigation and an ongoing experimental study.

An outline of the theoretical efforts is provided in Figure 1. To date, the analysis of the stability of solid rockets involved two steps. In the first step the admittances of various interior surfaces of the combustor (e.g., the burning propellant surface, the nozzle entrance plane, etc.) are determined in separate theoretical and/or experimental investigations. These data were then utilized as inputs in a separate analysis that determines the stability of the rocket motor. Because of the complexity of the combustion instability problem, a quantitative verification of the results of such analyses has never been attained. However, considerations of the physics of the problem raise questions about the validity of the two step approach, the assumption that the effects of finite regions (e.g., the combustion zone) can be described by wall admittances, and the neglect of multi dimensional effects in the analysis of axial instabilities.

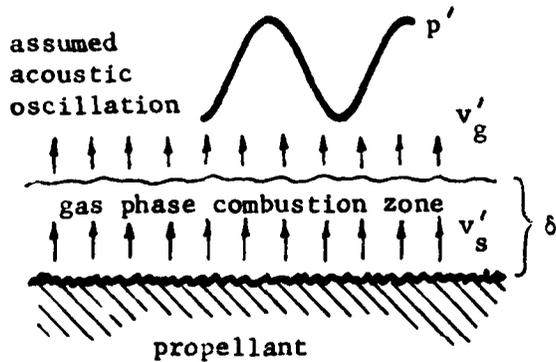
Additional indications of the possible inadequacy of the above mentioned approach are provided by thermoacoustic research into the cause of acoustic oscillations in tubes utilized in Helium liquefaction experiments, See Fig. 1. An attempt to analyze this problem by utilizing an approach similar to the one utilized in combustion instability analyses has failed to produce agreement with experiments. On the other hand, an approach (Rott, 1969) that analyzes the problem without separating the tube volume into separate regions produced stability limits that are in excellent agreement with experimental observations. The presentation will outline these approaches and discuss efforts to extend Rott's approach to rocket motors stability analyses.

The experimental efforts involved the utilization of the modified impedance tube setup in the determination of solid propellants velocity coupled response functions. The experimentally determined propellant response function is the one that results in the "best" fit between the predictions of a state of the art combustion instability model and measured impedance tube, pressure wave structure; see Fig. 2. To date, acceptable agreement between these sets of data has not been obtained and the results suggest that this lack of agreement is due to the inadequacy of the theoretical formulation of the problem.

SOLID PROPELLANT ROCKET MOTOR STABILITY ANALYSIS

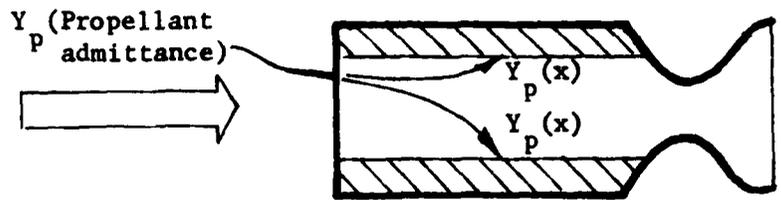
STEP A

Determination of the propellant response from a separate combustion zone analysis



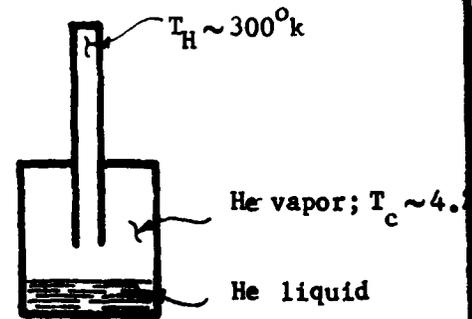
STEP B

Rocket Motor Stability Analysis



THERMOACOUSTICS STABILITY ANALYSES

- Helium Liquefaction Experiment
- $T_H/T_C \sim 70$
- Spontaneous oscillations occur in the tube.

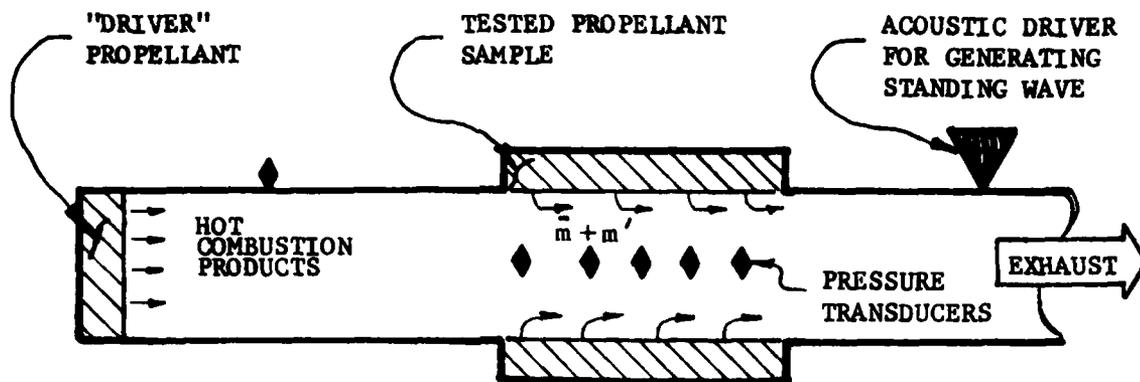


- A stability analysis (Kramer, 1949) similar to the one utilized in solid rockets (see above) could not predict the stability limits observed in the Helium experiments.
- A second stability analysis (Rott, 1969) that does not separate the tube's volume into separate regions (e.g., the core and the Stokes layer) provides excellent predictions of the observed stability limits.

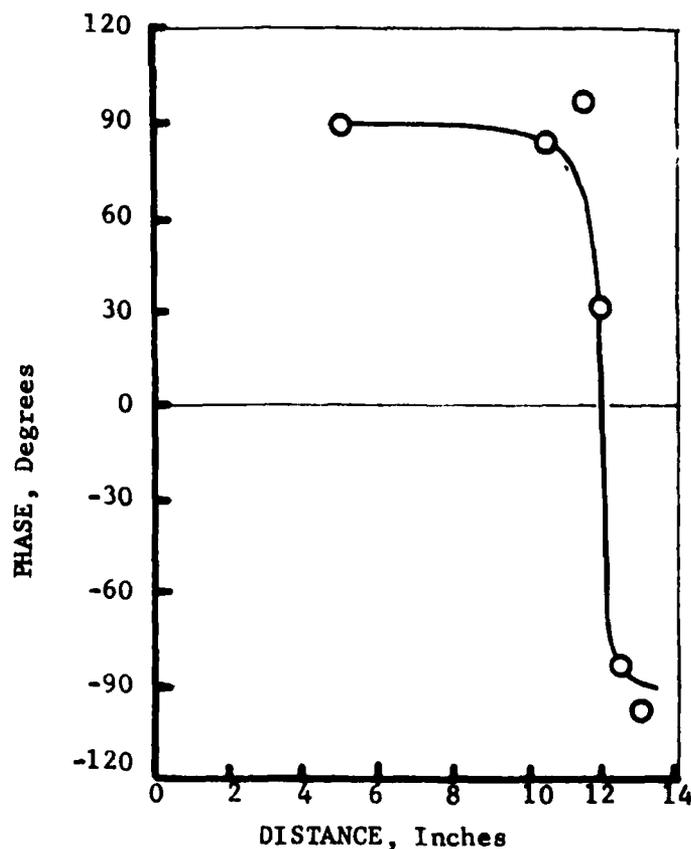
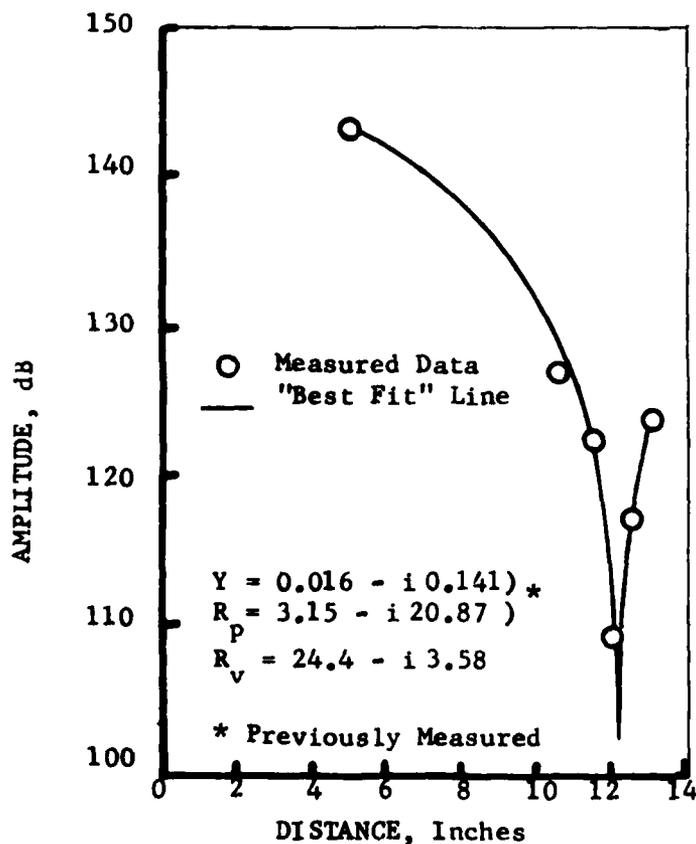
QUESTION Can Rott's approach be extended to solid propellant rocket motors stability analyses?

Figure 1. Considerations of Solid Propellant Rocket Motors and Thermoacoustic Stability Analyses.

FIGURE 2: "BEST VALUES" OF THE VELOCITY COUPLED RESPONSE FUNCTION  
 DETERMINED BY THE IMPEDANCE TUBE METHOD



Schematic of the Modified Impedance Tube Setup.



Comparison Between Predicted and Measured Amplitude and Phase  
 Distributions in the Modified Impedance Tube.

## ROCKET MOTOR AEROACOUSTICS

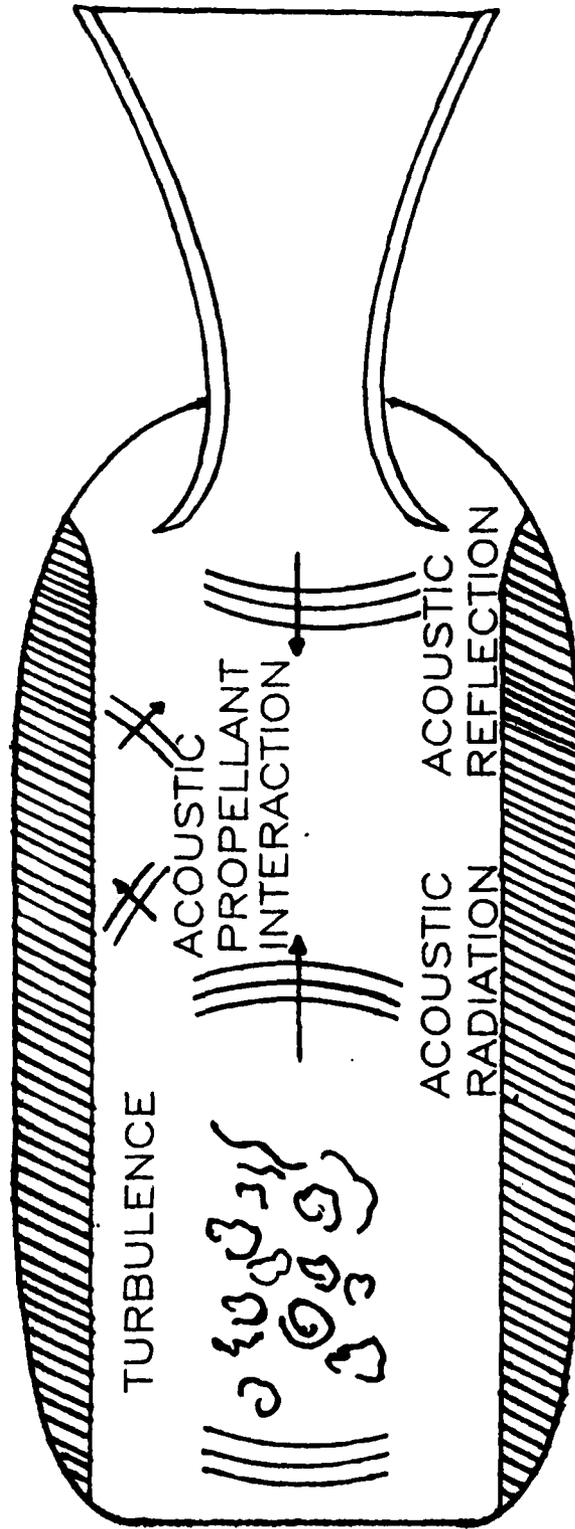
Warren C. Strahle  
Georgia Institute of Technology  
Atlanta, GA

Rocket motor combustion chamber pressure fluctuations are a source of rocket motor vibration that currently escapes predictability. The purpose of this program is to provide a theory, with experimental verification, that will enable prediction of the internal pressure and thrust fluctuation levels and spectra, given the turbulence structure and propellant impedance characteristics.

The physics involved are depicted in Figure 1. Turbulence acts as a source of propagational pressure waves which interact with the boundaries of the flow field, including the propellant. A stationary random oscillation will be set up with the dominant frequencies being near those of natural acoustic modes of the chamber gases. By measurement of turbulence characteristics in motor simulators and through use of an advanced aeroacoustics theory agreement is sought between acoustic predictions and measurements.

Figure 2 shows an interesting calculated result, which has been verified experimentally. the turbulence source is shown as a highly random fluctuating signal. The result for pressure, however, shows a rather regular oscillation at the fundamental longitudinal mode frequency. The magnitude of the pressure oscillation is critically dependent upon the propellant feedback characteristics; in Fig. 2 a particular feedback law was chosen.

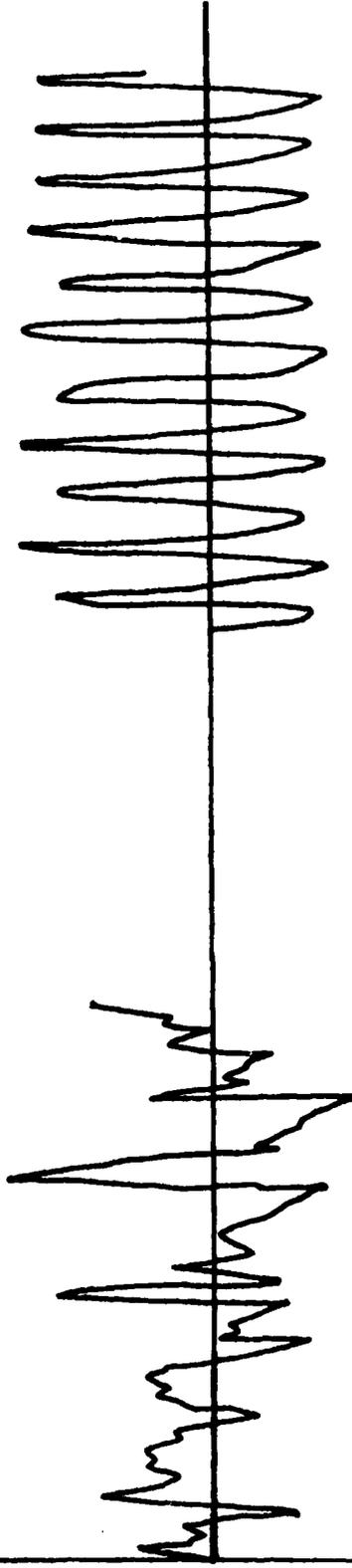
TURBULENCE GENERATED PRESSURE FLUCTUATIONS



RESULTANT STATIONARY  
OSCILLATION IN  $P'$

SOURCE STRENGTH

SOURCE  
BEHAVIOR  
OR 0  
 $P'$



TIME (SEC)

SOLID ROCKET AND SPACE PROPULSION STUDIES

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Nonsteady interactions in reacting, internal flows of propulsion systems with large volumetric energy release rates depend upon detailed phenomena of both flowfield and combustion process. However, for the linear descriptors most useful for stability and design, these interactions are related to average flowfield/combustion process variables by transfer functions. Consequently, two basic scientific questions of practical importance arise naturally:

(i) measurement of and scaling of these transfer functions and (ii) establishment of domains of validity. The approaches taken in this research to answering these basic questions are experimental because a base of reliable data does not exist while first order analyses do. The approach employs direct, insitu measurements of phenomena in subscale propulsion system hardware that can be forced into controlled, repeatable oscillations and supportive measurements in analog, cold flow systems. Two complimentary diagnostic techniques are being studied/employed: pressure, magnetic velocimetry for acoustic admittance and energetics related measurements and penetrative radiation for burning rate and burning rate response measurements. The direct nature of the diagnostics, the realism of the subscale system (required for similarity) and the control, repeatability, and relatively long observation time (important for S/N enhancement) afforded by forced oscillations contrasts markedly with other experimental approaches (T-burner, rotating valve burner, impedance tube) and demonstrate the uniqueness of this approach.

A basic question is the domain of validity of linear representations (current analytical models demand that the couplings traverse a path of quasi-steady states). Initial explorations of this question employed a hydraulic analog; flow phenomena were defined photographically. Figure 1 sketches results for the laminar portion of the flow (turbulent portion did not occur) and shows two important features: periodic near wall flow reversals out of phase with the core and periodic turbulization. Consequently, existing analytical models for these couplings may not have a large domain of validity. Since the near wall equations of motion for transpired and impermeable walls differ appreciably, these results also underscore a need for realism in devices employed to quantify these couplings. Figure 2 presents an X-ray intensity contour for a five pointed star obtained from a diametral scan and shows the existance of characteristic structures related to geometry that can be employed to deduce the internal contour. This suggests that insitu burning rate measurements may also be possible with cyclically symmetric grains.

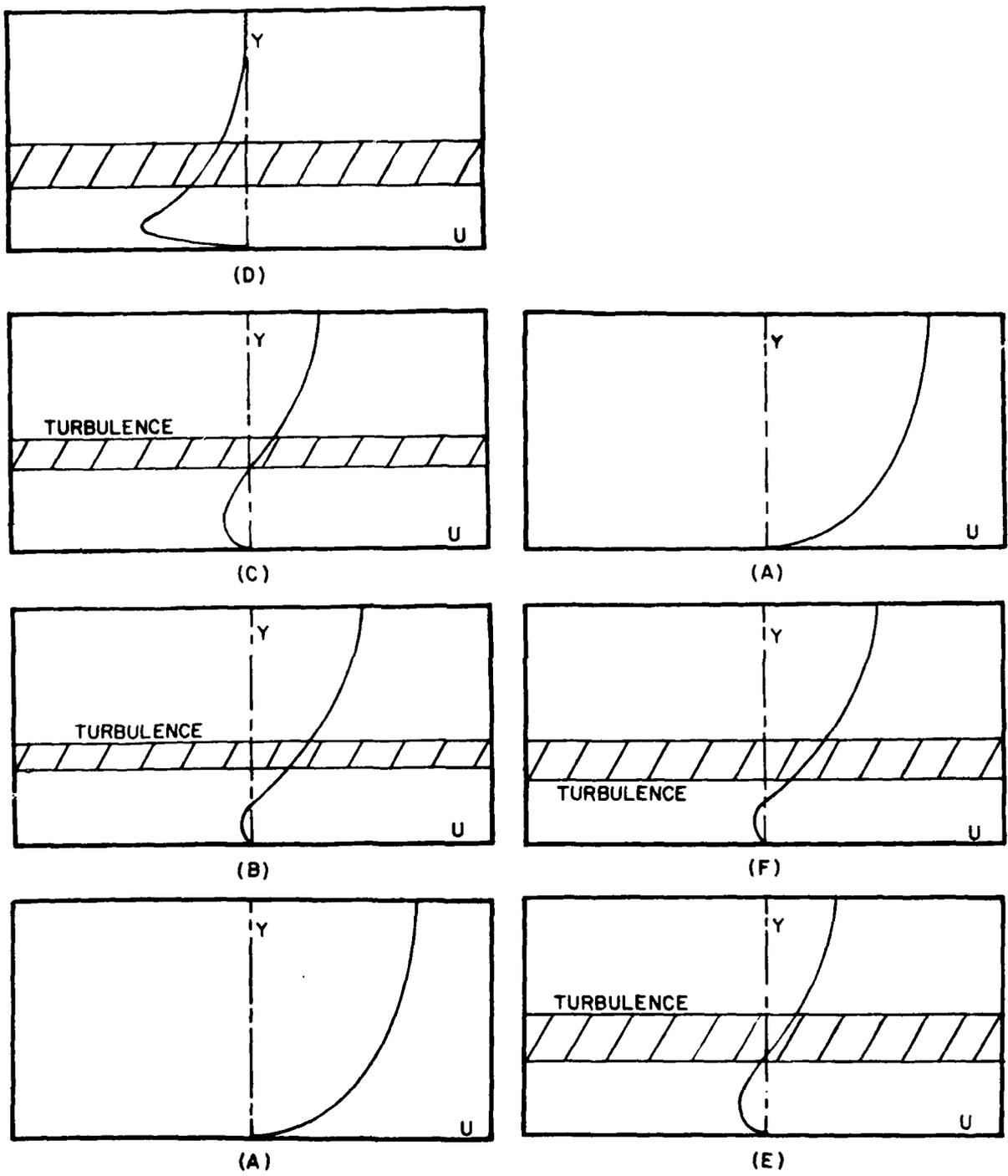


Fig. 1 Oscillatory flow cycle

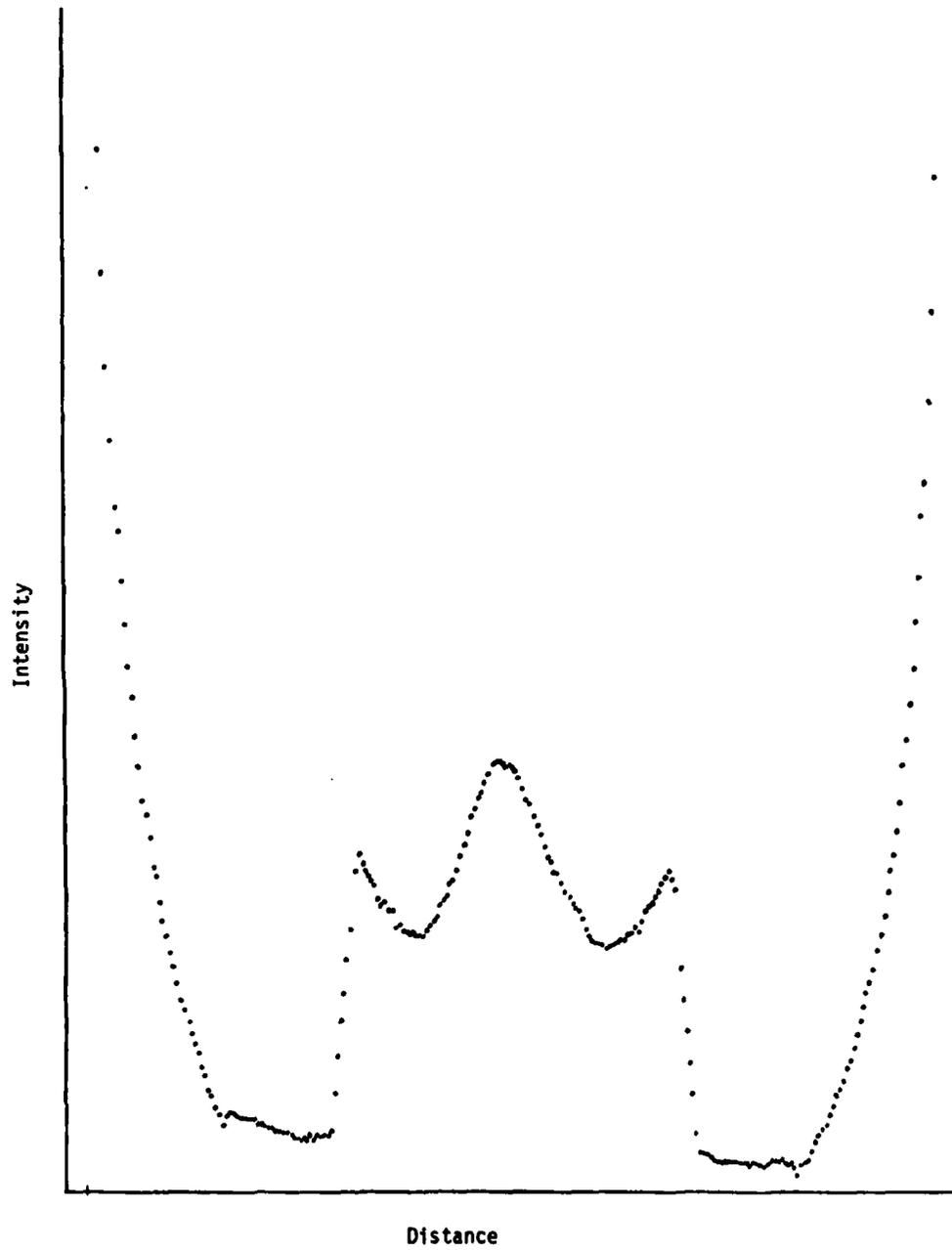


Fig. 2 Intensity/distance profile for 5-point star grain.

CHEMICAL ROCKET PROPULSION

- Abstracts of Research -

FUEL RICH SOLID PROPELLANT COMBUSTION  
BEHIND A BLUFF BODY

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Georgia Institute of Technology  
Atlanta, Georgia

The predictability for recirculatory turbulent reacting flows with mass addition is currently unknown. In the solid fueled ramjet (SFRJ), however, it is precisely such a flow field which is responsible for flame retention and local fuel regression rates. Through a combination of theory and experiment, with appropriate model adjustments, predictability of such a flow field is desired.

Figure 1 shows the experimental/theoretical configuration. In order that predictability may be attained, turbulence mass, heat and vorticity transport models must be verified and/or postulated. Current modeling in the case of reacting flows with high exothermicity is judged inadequate. With the techniques of LDV, Rayleigh scattering and RAMAN spectroscopy, detailed maps of the appropriate turbulence quantities will be attained and theoretical models will be developed.

Figure 2 shows a result of LDV measurements in the current facility under cold flow, no mass addition conditions. The theoretical calculations are based upon  $k-\epsilon$  modeling. Shown are the mean flow velocity and axial intensity at two different locations, for clarity. Also shown is the reattachment point. It is clear that even in this highly simplified flow current calculation procedures have some deficiencies.

**Deficiencies**

Predictability of recirculatory  
 turbulent reacting flows  
 with mass addition  
 Tailoring of flow field  
 e.g. concentration of hot O<sub>2</sub>  
 Understanding of Mach No. and  
 altitude flame retention limits  
 Understanding of competition of  
 kinetics, heat and mass  
 transfer at grain-gas interface

RAYLEIGH  
 RAMAN  
 RAMAN-LDV  
 RAYLEIGH-LDV

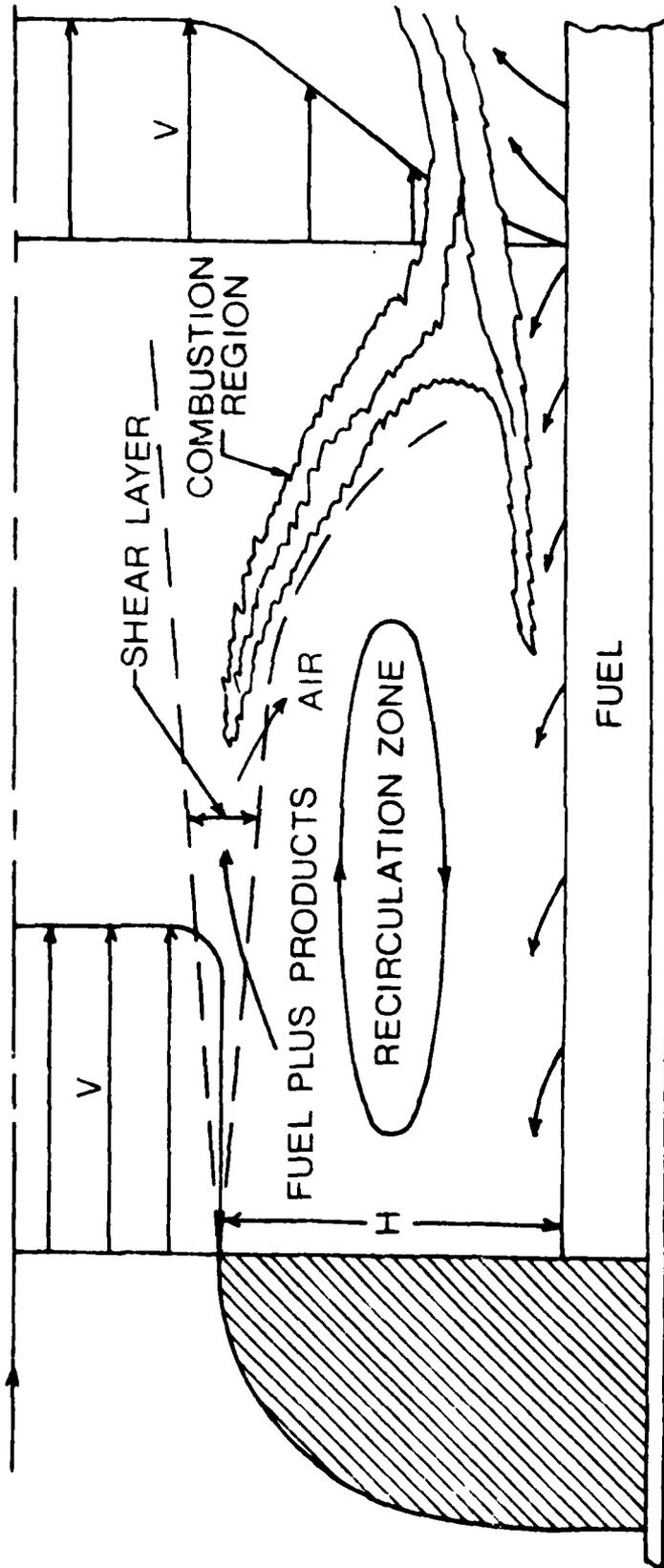
**Measurements**

$\bar{T}$   
 $\bar{Y}_{O_2}$   
 $\bar{Y}_{CO}$   
 $\dots$   
 $\bar{u}'T'$

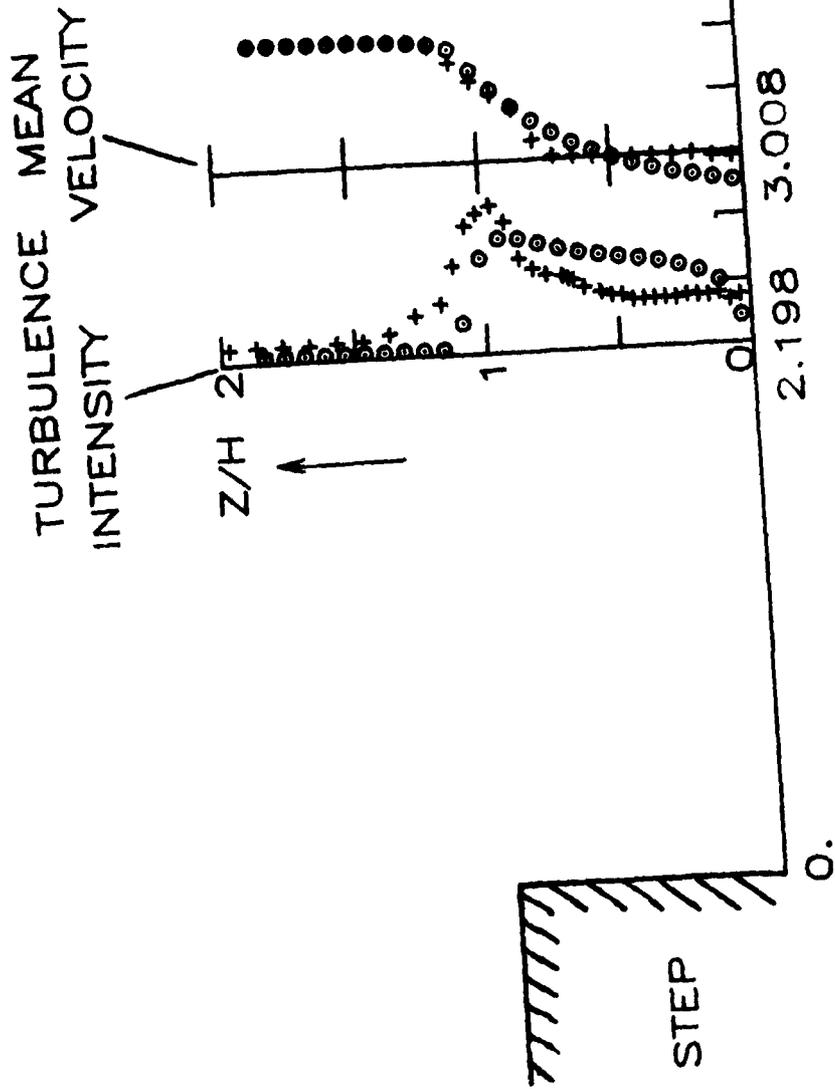
$\frac{\bar{u}'Y'_{O_2}}{\bar{u}'Y'_{CO}}$   
 $\dots$

Modeling  
 and  
 Comparison  
 with  
 Experiment

MECHANISTIC  
 UNDERSTANDING



+ Experiment-LDV  
o Theory



REATTACHMENT POINT  
Experimental value lies between  $X/H=7$  and 8

FUEL-RICH SOLID PROPELLANT BORON COMBUSTION (ANALYSIS)

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Atlantic Research Corporation  
Alexandria, VA

The aims of the analytical modeling phases of this program are evaluation of hypotheses regarding mechanisms of ignition/combustion of boron particles, agglomerates, clouds, and compacted grains in laboratory and airbreathing combustor environments, and provision for interpolation and extrapolation of data in analysis of potential combustor designs. A general outline of the approach appears in Figure 1. The uniqueness of this effort lies in the attempt to develop proper mathematical description of the unit processes with subsequent combination via a building-block approach for definition of approaches for maximizing use of boron's heating value in practical combustors-emphasis is placed on the fact that boron presents unique ignition/combustion problems that require careful attention to staging of the temperature/composition environment.

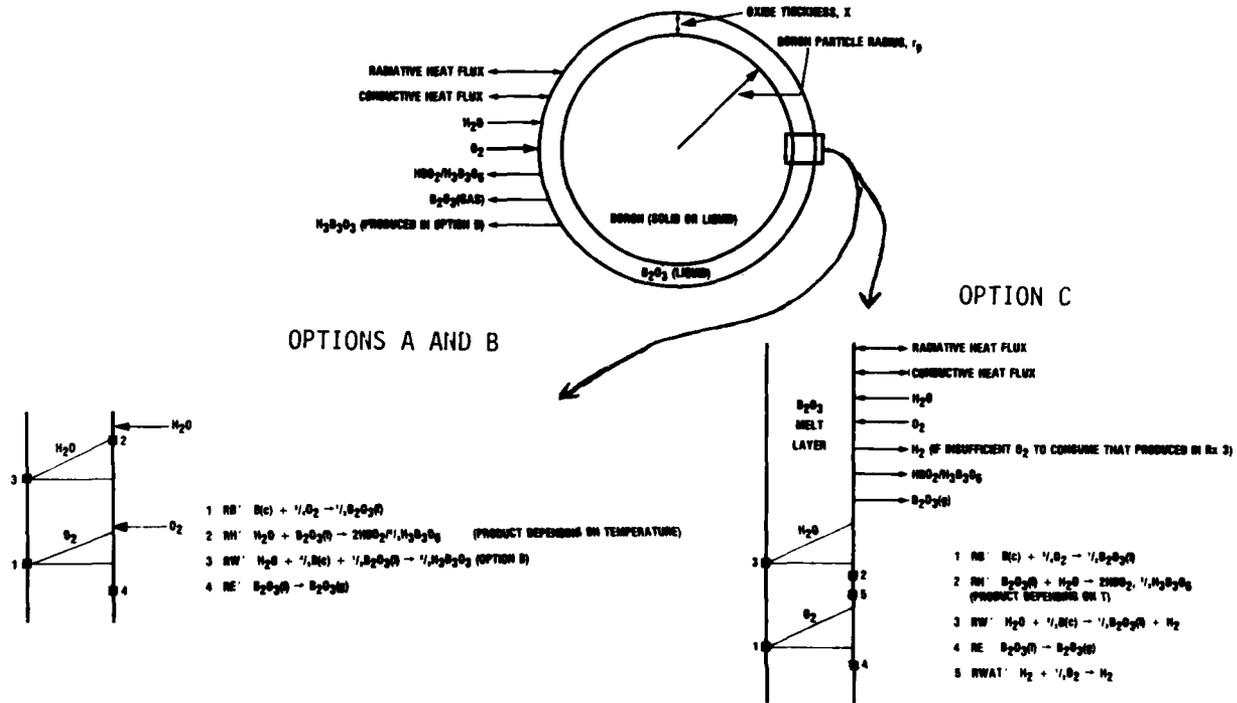
A model of ignition of initially oxide-coated boron particles has been developed. Several optional scenarios are considered for the effects of water gas, as depicted in the first figure. In this model, differential equations describing the rate of change of particle temperature, particle velocity, oxide thickness, and particle size are numerically integrated until thermal runaway occurs (after removal of the oxide coating and boron melting) or until it becomes obvious that such runaway will not occur. The time at which runaway occurs is defined as the ignition time. Preliminary comparisons of model predictions with Macek data for single-particle ignition in wet and dry environments are quite encouraging, as shown in Panel I of Figure 2. Exercise of the model for several ambient gas composition versus time profiles suggests a possible staging procedure for minimization of boron ignition times. (Panel II, Fig. 2).

Several quasi-steady-state models of clean boron particle combustion in  $O_2/N_2$  atmospheres under diffusion-limited conditions have been examined. A very simplified closed-form expression yields burn rates nearly identical to the most rigorous model examined. This rigorous model, however, is required for calculation of extinguishment condition boundaries (defined by  $P_{B_2O_3, s} > VP_{B_2O_3}$ ). (Figure 2, Panel III). Modeling has been extended to allow for finite-rate surface kinetics. Calculations of burn times with these models indicate a shift from  $d^2$ -law behavior to  $d^1$ -law behavior for small particles. The most complete model has been extended to treat B-H-O-N-C systems. Macek burn-time data for small particles, obtained in atmospheres containing  $H_2O$  and  $CO_2$  as well as  $O_2$ , are fit well with the final model (BCOMBKIN). (Panels IV and V of Figure 2). Allowance for finite-rate gas kinetics has little additional effect on predicted burning rate. BCOMBKIN is currently being extended to include radiative heat transfer and transient effects. Ultimately this model will be attached to the ignition model (at completion of oxide removal) for a unified ignition/combustion model.

A preliminary model of a boron slurry ramjet combustor as a well-stirred ignition zone followed by sequential plug-flow zones with staged air addition has been developed to aid in design of such combustors. In this model, the single particle boron ignition model (modified to allow for cloud effects) has been coupled with mass and enthalpy balances for the various zones and the simplified burning rate expression. Modifications to allow for kinetics limitations as calculated with BCOMBKIN are currently being added.

FIGURE 1

I. PROCESSES INCLUDED IN MODELING OF SINGLE BORON PARTICLE IGNITION



II. BORON COMBUSTION MODELS STUDIED

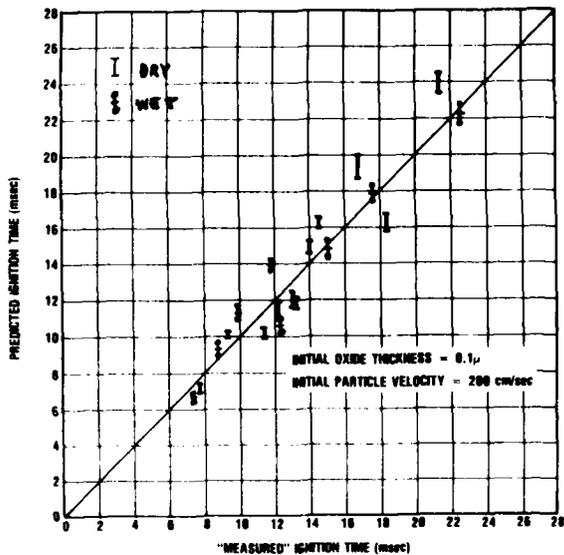
- I. DIFFUSION-LIMITED COMBUSTION, B-O-N SYSTEMS
  - A. SINGLE ONE-STAGE REACTION OF BORON TO  $B_2O_3$  GAS AT SURFACE
  - B. SURFACE REACTION OF  $B_2O_3(g) + B(c) \rightarrow B_2O_2(g)$  AT SURFACE
  - C. SURFACE REACTION OF  $B_2O_3(g) + B(c) \rightarrow BO(g)$  AT SURFACE
  - D. SURFACE REACTION OF  $B_2O_3(g) + B(c) \rightarrow BO, B_2O_2$  AT SURFACE
  - E. SHIFTING EQUILIBRIUM THROUGHOUT GAS PHASE AND AT SURFACE
- II. ALLOWANCE FOR FINITE-RATE SURFACE KINETICS, B-O-N SYSTEMS
  - A. SINGLE ONE-STAGE REACTION OF BORON TO  $B_2O_3$  GAS AT SURFACE
  - B. KINETICS VARIANT OF ID.
  - C. KINETICS VARIANT OF IE.
- III. DIFFUSION-LIMITED COMBUSTION, B-H-O-N-C SYSTEMS
- IV. ALLOWANCE FOR FINITE-RATE SURFACE KINETICS, B-H-O-N-C SYSTEMS (BCOMCON CODE)
- V. EXAMINATION OF FINITE-RATE GAS-PHASE KINETICS EFFECTS.

III. MODEL FOR CALCULATION OF BORON CONVERSION IN A SLURRY RAMJET COMBUSTOR

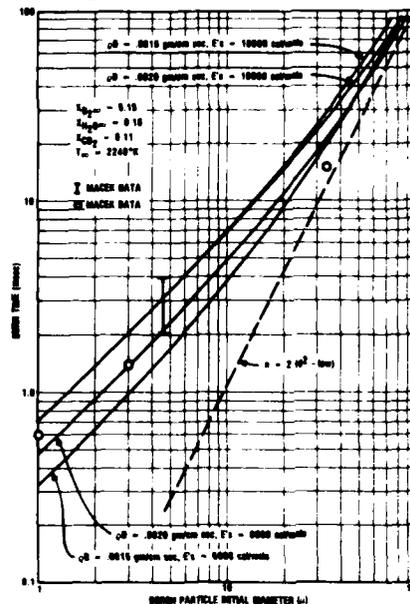
- PERFECTLY STIRRED REACTOR ZONE FOLLOWED BY INCREMENTAL PLUS FLOW DOWNSTREAM ZONES**
1. DEFINE INPUT FLOW RATES, BORON PARTICLE SIZES, GEOMETRY, ETC.
  2. ASSUME ALL HC AND  $M_0$  BURNED; GUESS FRACTION OF BORON BURNED
  3. DO MASS AND ENERGY BALANCES TO CALCULATE PBR COMPOSITION, TEMPERATURE, MEAN RESIDENCE TIME
  4. CALCULATE RESIDENCE TIME DISTRIBUTION USING  $P(\tau) > 0 = \exp(-\theta/\tau)$
  5. SET UP  $i \times j$  "BINS" OF PARTICLE SIZE-RESIDENCE TIME COMBINATIONS
  6. USE IGNITION MODEL TO CALCULATE  $\tau_{IGN}$  FOR EACH "BIN"
  7. USE BURN-RATE LAW AND  $\tau_{RES} - \tau_{IGN}$  TO CALCULATE FRACTION OF BORON IN EACH BIN BURNED IN PBR.
  8. SUM AND RECYCLE TO STEP 2
1. USE OUTPUT FROM LAST ZONE AS ONE FEED AND SPECIFIED AMOUNT OF BYPASS AIR AS SECOND FEED.
  2. USE MASS AND ENERGY BALANCES TO CALCULATE BIN TEMPERATURE AND COMPOSITION, AND RESIDENCE TIME DELTA IN THIS INCREMENTAL ZONE.
  3. FOR "BINS" IN WHICH BORON ENTERS THIS ZONE ALREADY IGNITED, USE BR LAW TO CALCULATE FRACTION BURNED IN THIS ZONE AND CUMULATIVE VALUE.
  4. USE RESTART IGNITION MODEL FOR "BINS" NOT PREVIOUSLY IGNITED TO CALCULATE PROGRESS TOWARD IGNITION. IF IGNITION OCCURS IN THIS INCREMENT USE BR LAW WITH CUMULATIVE RESIDENCE TIME MINUS IGNITION TIME TO CALCULATE FRACTION BURNED.
  5. SUM UP CUMULATIVE FRACTION BURNED OVER ALL "BINS" TO GET OVERALL AMOUNT BURNED BY THE END OF THIS ZONE.
  6. USE ENERGY AND MASS BALANCE TO CALCULATE COMPOSITION, TEMPERATURE, ETC. LEAVING THIS INCREMENT.

FIGURE 2

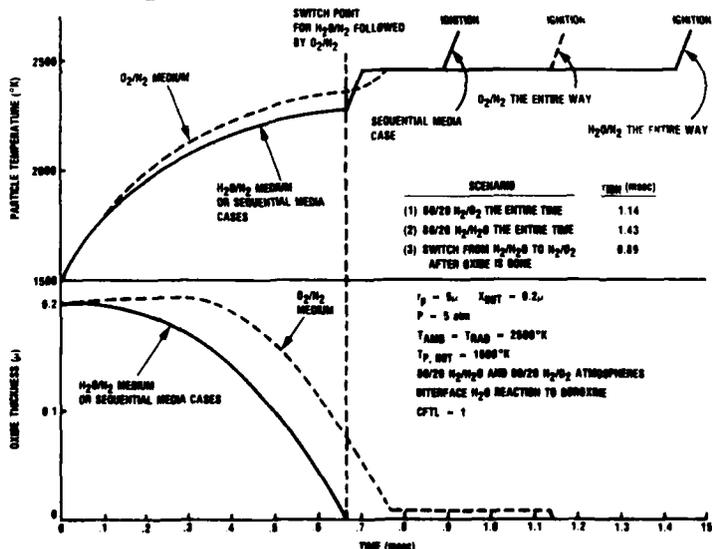
I. COMPARISON OF IGNITION MODEL PREDICTIONS WITH DATA



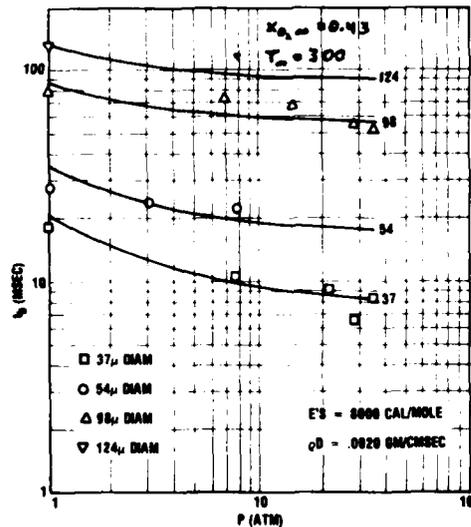
III. COMPARISON OF COMBUSTION MODEL PREDICTIONS WITH FFB DATA



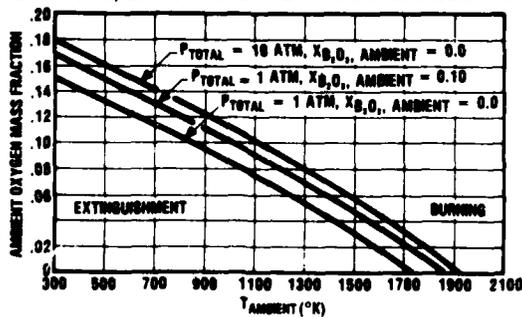
II. POSSIBLE EFFECTS OF STAGED ENVIRONMENTAL CONDITIONS ON BORON IGNITION



IV. COMPARISON OF COMBUSTION MODEL PREDICTIONS WITH MACEK LASER-IGNITED BORON DATA



V. PREDICTED BURNING/EXTINGUISHMENT BOUNDARIES FOR BORON PARTICLES



FUEL-RICH SOLID PROPELLANT  
BORON COMBUSTION (Experimental)

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Atlantic Research Corporation  
Alexandria, Virginia 22314

This experimental study is aimed at understanding the relative influence of the mechanisms involved in boron particle ignition and combustion. Experimental data are acquired on the ignition and combustion of boron particles, agglomerates and clouds, and combustion and ignition phenomena in slurry ramjet combustors and consolidated fuel grains in high temperature air crossflow. This information is vital to identifying means of using the full potential of boron fuels.

Combustion of a consolidated boron fuel grain in a high temperature air crossflow involves stabilizing a flame within the turbulent boundary layer above the ablating grain surface. Important factors include radiation feed-back to the surface from particles in the main stream and turbulence characteristics of the main stream and boundary layer regions. Investigations of these mechanisms are conducted in a two-dimensional windowed combustor under conditions closely simulating flow characteristics of full-scale systems. Flame structure dynamics are studied with high speed photography. Particle size interferometry and isokinetic particle sampling are used to characterize particle size distributions above the grain surface. Radiation effects are studied by optical pyrometry in conjunction with heat flux gages embedded in the grain. Two component laser anemometry is used to measure mean velocity and to determine turbulence characteristics. Raman techniques will be used to characterize the temperature field above the grain. The grain ablation behavior is studied with embedded fiber optic probes and thermocouples. During this period, the apparatus and diagnostics were assembled.

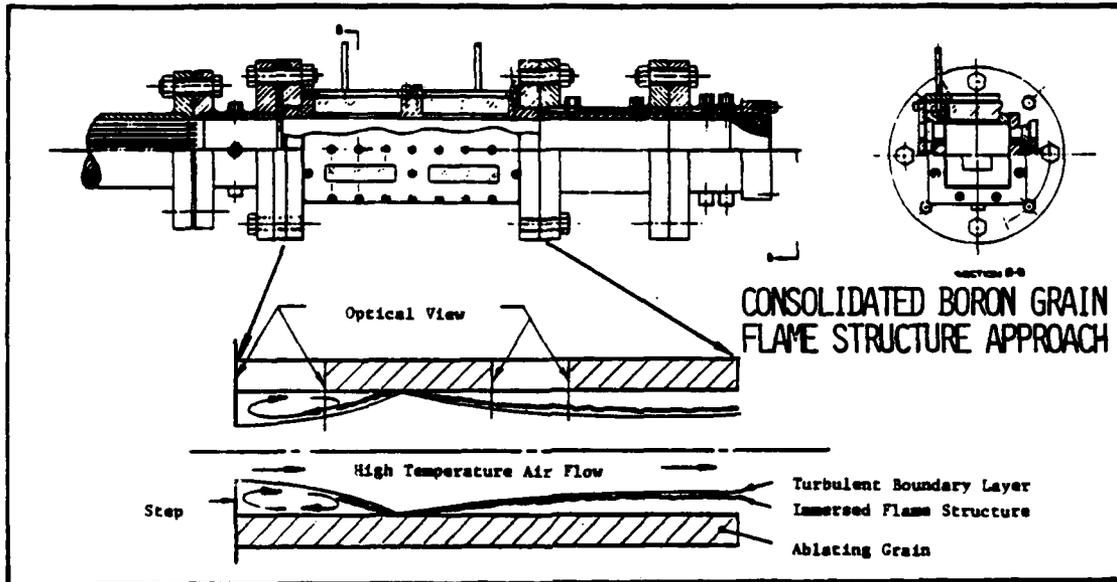
Combustion of boron dust or slurry in a ramjet combustor includes as a critical element partial conversion of boron clouds of given size distributions in a well-stirred ignition zone. Analysis of reactor blow-off stability and fractional conversion was evaluated for design of an experimental study of these phenomena. The apparatus designed will be capable of variable fuel flow rates, particle size distributions, air flow rates, swirl and combustor volume. Necessary diagnostics will include high speed photography, combustor pressure and temperature, and exhaust particulate and gas sampling. Boron particle size distributions in injected fuel dust or slurry are to be characterized via S.E.M. and in-situ by laser-scattering measurements in a cold flow dynamic injection environment.

The single particle results of this research are derived from boron combustion in a flat flame burner. Size ranges vary from approximately 10 to 70 microns. Propane and carbon monoxide fuels have been used to generate flames with varying water vapor concentrations. Data to substantiate the size range and the techniques utilized to effect the narrow size distributions of particles have been collected. These data are correlated with those from a visibility processor, which provides particle size changes and velocity in the combustion zone. Single particle events were also captured on a unique electro-optic camera, coupled with a laboratory data system. Storage of electronic images permitted repeated analysis of the data, and application of signal enhancement techniques. These results, compared with photographic analysis, provide substantiated measurements of the ignition time, oxide-removal periods and total combustion time.

# BORON COMBUSTOR DYNAMICS

## PROBLEM

- COMBUSTION EFFICIENCY RESIDENCE TIME DEPENDENT
- COMPLEX FLOW GEOMETRIES
- NON-INTRUSIVE DIAGNOSTICS REQUIRED
- LIMITED MODELING WITHOUT EXPANDED DATA BASE

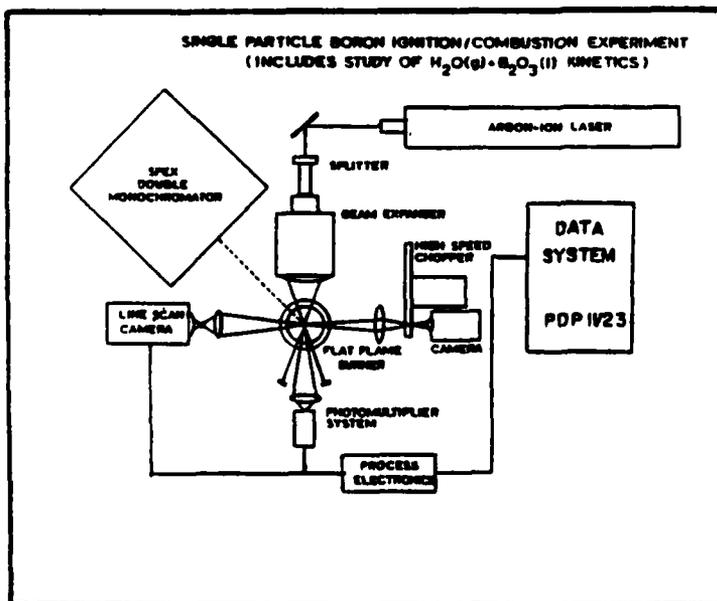


## NEEDS

- FLOW FIELD DEFINITION
- DETERMINE EFFECTS OF RADIATION
- EXPANDED DATA BASE
- METHODS FOR IMPROVING COMBUSTION EFFICIENCY

## APPROACH

- MEAN AND FLUCTUATING PROPERTIES
- OPTICAL DIAGNOSTICS
- SPATIALLY AND TEMPORALLY RESOLVED PROBES
- LABORATORY SCALE COMBUSTOR



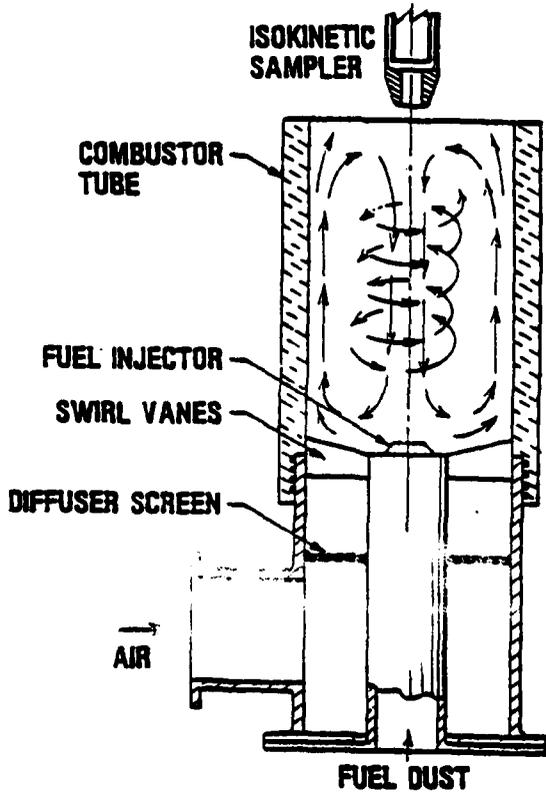
## SINGLE PARTICLE COMBUSTION

### OBJECTIVES

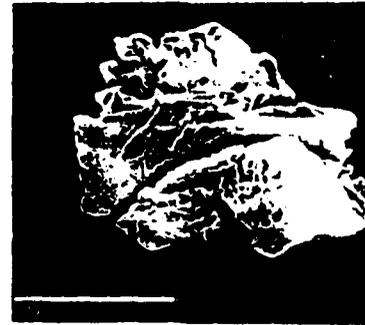
- IGNITION TEMPERATURE
- BURNING RATE
- PARTICLE SIZE
- FLAME TEMPERATURE
- PARTICLE TEMPERATURE
- SPECIES IDENTIFICATION
- IGNITION TIME
- $B_2O_3 - H_2O$  KINETICS

SUMMARY ACCOMPLISHMENTS

● STIRRED REACTOR DESIGN



● PARTICLE MORPHOLOGY



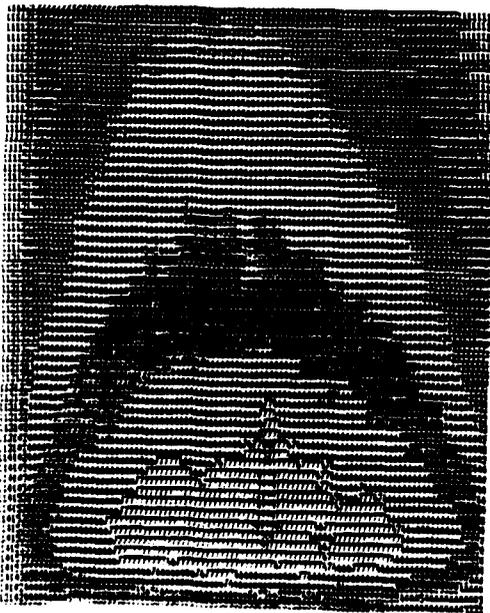
Boron after Oxide Removal



B<sub>2</sub>O<sub>3</sub> Surface Topology

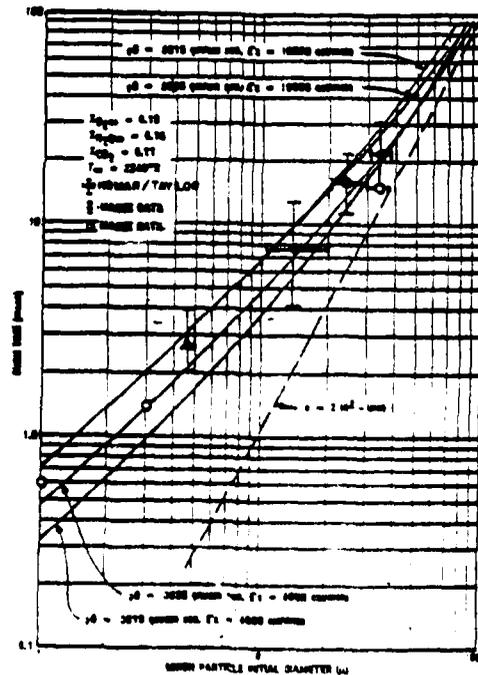
● NON-INTRUSIVE DIAGNOSTICS

Electronic Array Camera



Single Particle Event in Flat Flame Burner

● COMPARISON OF BURN TIME DATA FOR SMALL PARTICLES WITH CALCULATIONS MADE USING SCOMBKON CODE



OVERVIEW OF STANFORD PROGRAM ON  
ADVANCED DIAGNOSTICS FOR REACTING FLOWS

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Donald Baganoff†, Brian J. Cantwell†, and Lambertus Hesselink†

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ABSTRACT

Increasing demands on Air Force combustion systems and rapid advances in instrumentation technology have combined to stimulate considerable interest in the development of modern, primarily laser-based diagnostics for combustion research. This presentation will provide an overview of AFOSR-sponsored work at Stanford to establish promising new diagnostic techniques for measurements in reacting flows.

The Stanford program is a relatively large, interdisciplinary effort involving seven faculty in three departments. The various research topics have been selected to provide a spectrum of activities, ranging from fundamental to applied research. Generally, the objective is to provide improved measurement capabilities for quantitative visualization of flows and for determining quantities such as species concentration, temperature, particle size, particle number density and velocity, preferably with high spatial and temporal resolution. Projects to develop techniques for measuring and displaying flow parameters in a plane or throughout an extended volume are included, as are projects to apply newly developed techniques to selected flows of fundamental interest.

Current research topics are listed in Figure 1 (see following page) together with a statement indicating the quantities to be determined. Major accomplishments during the past year include (see other abstracts in this volume for additional details): (1) first instantaneous, multiple-point species measurements (OH, NO, Na) in a flame, accomplished using planar laser-induced fluorescence (PLIF) and an intensified photodiode array (100 × 100) detector; (2) first multiple-point velocity measurements in a gaseous flow without particle seeding, accomplished using Doppler-modulated absorption of tunable narrow-linewidth laser radiation with PLIF detection; (3) first application of optical Stark modulation of tunable diode laser radiation for spatially resolved absorption measurements of species concentration (CO) in a flame; (4) first application of a tunable ring dye laser for species (OH) measurements in a shock tube; and (5) successful development of a method for scanning a single mode cw dye laser over ranges > 75 GHz at repetition rates in excess of 4 kHz, at visible and UV (by intracavity frequency doubling) wavelengths.

Abstract 10 pg 2

- TUNABLE LASER ABSORPTION/FLUORESCENCE PROBES (Hanson) - Development of absorption and fluorescence techniques for spatially and temporally resolved species or temperature measurements using tunable (IR, visible and UV) laser sources and either intrusive optical fiber probes or fast-sampling probes with miniature in-line measurement cells.
- CROSSED-BEAM CONCEPTS (Hanson) - Development of techniques for spatially resolved species measurements by modulated absorption of a weak tunable UV or IR laser probe beam crossed with a strong tunable laser pump beam operating resonant (saturated absorption) or non-resonant (ac-Stark effect) with the probe beam.
- COMPUTED ABSORPTION TOMOGRAPHY (Byer) - Development of techniques for measuring species concentration, density or temperature in a plane using multiple observations and computer deconvolution methods.
- COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (Byer) - Development of techniques and measurements of species concentration, temperature, velocity and fundamental spectroscopic parameters using various novel CARS configurations.
- PARTICLE SIZING (Self) - Development of particle size measurement techniques using two-color transmissometry and a wire-filter sampling probe.
- PACKAGED FIBER OPTIC TEMPERATURE PROBE (Self) - Development of a compact, portable instrument, based on the line reversal concept, for fast response temperature measurements in seeded combustion flows.
- QUANTITATIVE FLOW VISUALIZATION (Hanson) - Development of techniques for spatially and temporally resolved measurements of species, temperature and velocity in a plane using novel variations of laser-induced fluorescence.
- THREE-DIMENSIONAL FLOW VISUALIZATION (Hesselink) - Development of a novel holographic technique for the 3-d display of species, temperature or velocity data obtained from a family of cross-sectional (planar) data sets or observations.
- MEASUREMENTS IN A TURBULENT REACTING FLOW (Bowman) - Development and characterization of a 2-d turbulent reacting shear flow facility, and the development and application of diagnostics for studying turbulent flowfield structures.
- EVAPORATING FLOW STUDIES (Baganoff and Cantwell) - Assembly and characterization of a new facility for studies of droplet evaporation in laminar and turbulent flows, and the development of techniques, based on laser fluorescence and anemometry concepts, for monitoring the liquid and gas phases in a droplet-laden flow.
- RAPID TUNING RING DYE LASER (Hanson) - Development of a technique for rapidly scanning a single mode laser to enable fast recording of fully resolved absorption and fluorescence spectra, and exploratory studies of wavelength modulation concepts for species and temperature measurements in two-phase flows and in transient systems.

Figure 1. Current Research Topics

OVERVIEW: AFOSR RESEARCH INTERESTS IN ROCKET PROPULSION

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Propulsion requirements for planned systems continue to present critical challenges that are not satisfiable using present technologies. It is the nature of propulsion systems that continued improvements in propulsive efficiency are essential to maintaining the winning edge. For many classes of rocket motors, approaches have matured to the point that obvious advancements have been implemented. Thus, most new systems specify another round of performance gains which often leads to difficult research challenges. Also, broad classes of problems (e.g., combustion instability, service life, signature, low temperature structural integrity) are never solved entirely and reoccur often as as important considerations (and compromises) prior to propulsion system qualification.

Powerful motivations continue for basic research on topics such as energetic materials, reacting flows, and propulsive processes. Many phenomena which are accommodated by specific designs are not explained adequately in terms of physical processes. Periodically, this lack of understanding produces major setbacks. In this sense, rocket motor processes present scientific challenges suggesting that the right research will lead to higher performance, reduced risk, reduced development costs, longer service life, etc.

Hopefully the presentations will stimulate thinking on the more challenging and relevant goals. During the next year, opportunities exists for new approaches and for new principal investigators. Several of the presentations will introduce recent plans and goals.

During the last year, the propulsion research program was broadened in anticipation of the space propulsion needs of the 1990's. New research is beginning on non-conventional propulsion for space maneuvering and orbit raising. Formidable technical barriers accompany the promises of major performance gains being attributed to electrical thrusters and beamed energy thrusters. As indicated in Appendix 2 the primary emphases are on topics relating to electrode life time, power limits, beamed (laser) energy absorption, and plasma flow processes. Since orbiting propulsion systems place an extraordinary premium on performance, additional research on the synthesis of ingredients was initiated (i.e., note Thursday morning session). Even though space missions can justify the use of relatively expensive propellants, unanticipated problems limit the introduction of major new rocket propellant ingredients to a once in a decade occurrence. Possibly improved research approaches can prevent the sequential discovery of disqualifying properties and characteristics.

The real challenge in chemical propulsion is to provide the basis for increasing rocket motor energy-density without unsatisfactory stability, physical properties, signatures, etc. Toward these goals, we have a healthy investment in combustion of conventional propellants, stability mechanisms, and synthesis of new ingredients. We are striving to provide additional research opportunities in combustion (including burning rate control) of new and advanced propellant ingredients, active suppression in instability, and nonconventional propulsion. Re-thinking the research approaches to the more persistent energy conversion challenges is particularly timely in view of the recent advancements in quantitative 2D visualization of reacting flows.

BEHAVIOR OF ALUMINUM  
IN SOLID PROPELLANT COMBUSTION

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Aluminum and other nonvolatile particulate ingredients in solid propellants exhibit very complex behavior on the burning surface and in the solid propellant flame. The details of such behavior are largely undetermined because the microscopic and hostile nature of the combustion zone limits experimental observation. The objective of the present work is to clarify the behavior of nonvolatile ingredients, clarify the processes that control the behavior, and hence provide the means to control behavior in ways that improve propellant combustion. The approach is to 1) assemble all available information about conditions in the combustion zone, about the nonvolatile ingredient, and about behavior or effect of the ingredient during propellant combustion; 2) assemble a scenario (hypothesis) for details of the behavior and controlling processes; 3) devise experiments to test the validity of components of the scenario; 4) iterate on, and test the scenario until it is fully tested and validated; and 5) use the resulting theory to predict combustion behavior, and test the predictive capability by combustion experiments. Uniqueness of the approach is in the development of an array of experimental methods and test strategies designed to unravel a complex process that is very difficult to observe directly (Fig. 1). Relatively heavy emphasis is placed on establishing the mechanistic processes responsible for behavior of nonvolatile particles, particularly aluminum.

The effort during the last year has been on consolidation of the work on behavior of aluminum into a qualitative theory for AP-hydrocarbon binder propellants. An evaluation of key elements of the theory was made by predicting and measuring certain critical agglomeration trends in propellants with bimodal AP distribution (Fig. 2). Effort is presently shifting to:

- a) aluminum behavior in other propellant systems;
- b) response of aluminum behavior to transient flow disturbances;
- c) behavior of other nonvolatile particles (ZrC, BC,  $Al_2O_3$ ,  $Cr_2O_3$ ,  $Fe_2O_3$ , W).

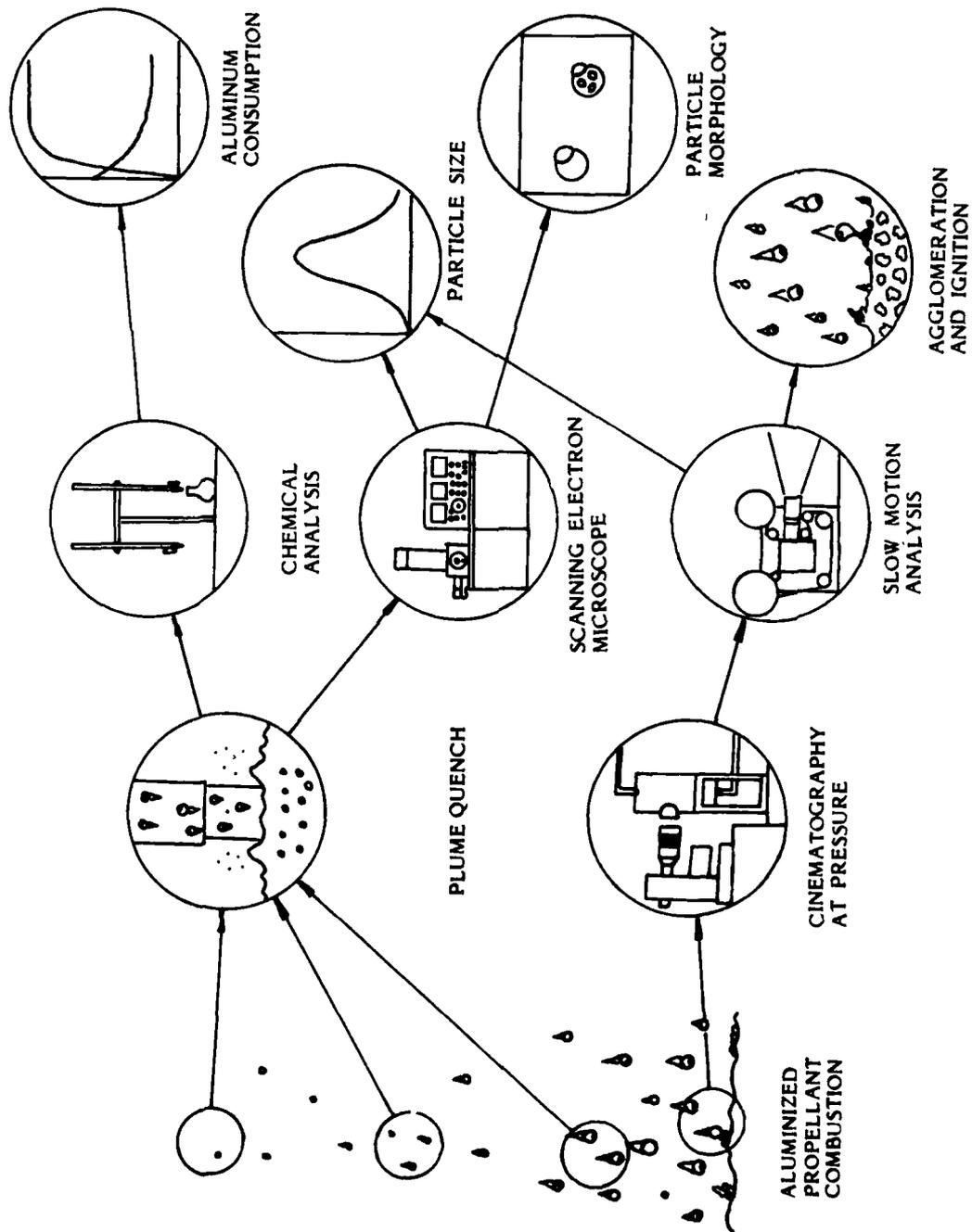


Fig. 1. Description of combination of methods to study aluminum behavior in combustion of propellants.

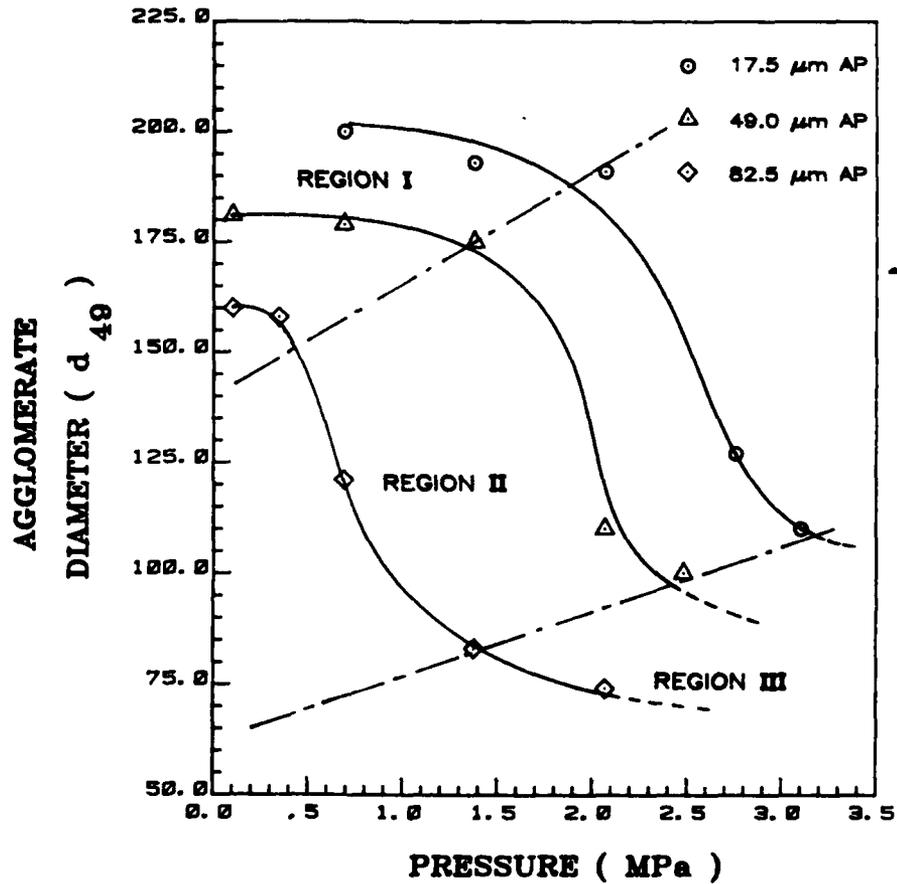


Fig. 2 Experimental verification of aluminum accumulation-ignition-agglomeration theory using propellants with bimodal oxidizer particle size and three different sizes for fine component.

Region I: Aluminum concentration continues until ignited by AP-binder flamelets of coarse oxidizer.

Region II: Transition region.

Region III: Aluminum concentration is limited by presence of AP-binder flamelets on all AP particles.

AERODYNAMIC BREAKUP - METAL DROPLETS

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The breakup of AL/AL<sub>2</sub>O<sub>3</sub> agglomerates in solid propellant rocket nozzles is a critical process effecting combustion efficiency and two-phase flow losses. While direct observation of agglomerate breakup has been made in subscale nozzles, the dynamics and mechanisms of breakup remain to be characterized. These phenomena for high surface tension metal droplets may differ significantly from those associated with conventional liquid droplets. Proper scientific scaling techniques must be developed to extrapolate subscale laboratory data to full scale rocket motor pressures, temperatures, and sizes. The principle goal of this investigation is to provide increased understanding of the fundamental breakup mechanisms of high surface tension AL/AL<sub>2</sub>O<sub>3</sub> agglomerates in aerodynamic nozzles.

Droplet breakup experiments in aerodynamic nozzle contractions have been conducted in which conventional liquids and higher surface tension liquids (Mercury) were examined. A key element of the experiment is the use of laser diagnostics. Pulsed laser holography has provided droplet and fragment observations with resolutions not previously possible. Laser velocimetry has provided droplet dynamics data revealing dramatic accelerations prior to breakup.

A primary result of the LDV droplet trajectory measurements is the Weber number/breakup time correlation of Figure 1. A two-dimensional nozzle was designed to subject injected droplets to an aerodynamic load sufficient that droplet breakup would occur in the nozzle. The droplet Weber number along its trajectory was calculated for various droplet sizes, liquids and gas velocities. Experiments revealed that rigid droplet trajectory calculations underestimated droplet accelerations prior to breakup. The mechanism for enhanced acceleration was presumed to be droplet flattening, and the result was that droplet Weber numbers were much lower than predicted. Experiment conditions (gas velocity) were adjusted so that droplet breakup occurred, and Weber number histories were determined along the nozzle. The position of maximum Weber number coincided with droplet breakup. This critical Weber number and the associated breakup time are plotted in Figure 1. A breakup zone is identified in which droplet failure occurs for various size droplets, liquid types, and gas velocities. Droplet trajectories were calculated without benefit of the breakup correlation for the final experimental conditions and two are shown in Figure 1. In each case, the peak Weber number is overestimated by about (3X), suggesting that a model for droplet flattening in the drag calculation is appropriate.

The nozzle as modified for high velocity Hg experiments and the breakup of Hg droplets are illustrated in Figure 2. Breakup occurs in the subsonic (M = 0.5) portion of the nozzle. The series of photographs displays (1) the initial droplet ( $\phi = 200 \mu\text{m}$ ), (2) a flattened droplet, (3) the breakup mechanism in a double pulse image ( $\Delta t = 10 \mu\text{s}$ ), and (4) fragments.

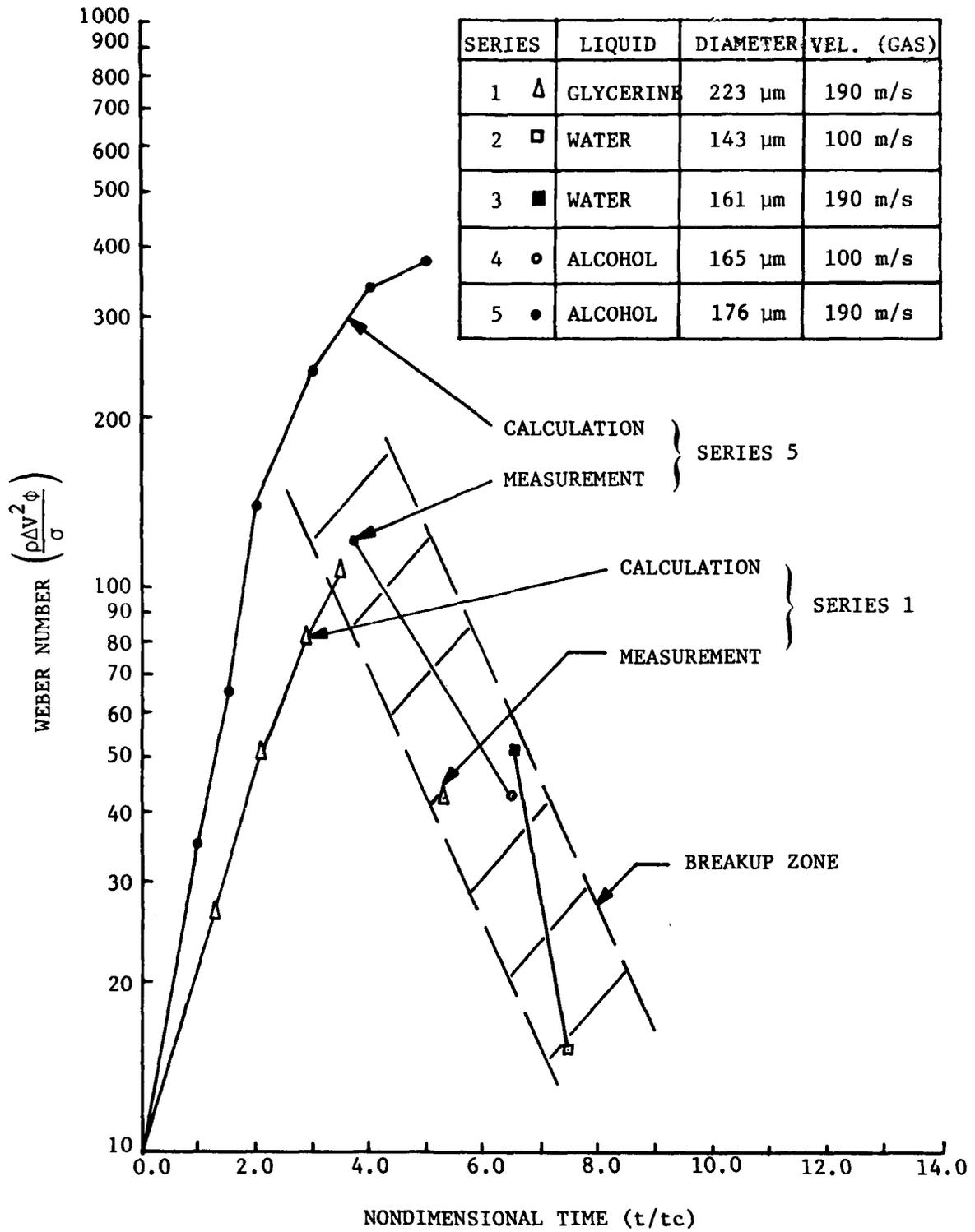


FIGURE 1. COMPARISON OF CALCULATED WEBER NUMBER HISTORIES WITH VALUES MEASURED AT DROPLET BREAKUP,  
 $\left(t_c = \left(\frac{\rho \phi^3}{\sigma}\right)^{\frac{1}{2}}\right)$

## Aerodynamic Breakup - Mercury Droplets



FIGURE 2. AERODYNAMIC NOZZLE FACILITY FOR DROPLET BREAKUP EXPERIMENTS, AND HOLOGRAPHIC RECONSTRUCTION OF Hg DROPLET BREAKUP ( $\phi = 200 \mu\text{m}$ ,  $We = 9, 17, 36$ , NA, Top to Bottom).

COMBUSTION KINETICS OF METAL OXIDE AND HALIDE RADICALS

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Kinetic data, over wide temperature ranges, on oxidation reactions of metal atoms, Me, and metal monoxide and monohalide radicals, MeY, are essential input information for several aspects of Air Force Rocket Propulsion development. These include: air breathing propulsion, retarding or prevention of submicron metal oxide particle formation and advanced solid propellant formulations. To provide a means for establishing mechanisms and measuring rate coefficients and their temperature dependences,  $k(T)$ , the HTFFR (high-temperature fast-flow reactor) technique was developed.<sup>1</sup> This unique tool provides measurements on isolated elementary reactions in a heat bath. With traditional high temperature techniques such isolation is usually impossible to achieve; as a result, data on any given reaction depend on the knowledge of other reactions occurring simultaneously, leading to large uncertainties. HTFFR has primarily been used for the study of Me-oxidation reactions. It is the goal of the present program to similarly provide data on MeY-oxidation reactions.

Figure 1 illustrates the novel apparatus which has been constructed this year for the study of the  $BCl + O_2$  reaction. It can, with but minor modifications, also be used for work on other MeY species ( $AlF$ ,  $BO$ ,  $AlO$  etc.). Basically the apparatus consists of two vertical high temperature reactors in series. In the upstream (lower) reactor  $BCl_3$  reacts with solid boron at about 1500 K to produce  $BCl$  radicals. In the downstream reactor the relative concentration of these radicals is measured as a function of  $[O_2]$ ,  $P$ ,  $T$  and  $t$  to determine  $k(T)$ . The frequency doubled radiation of a dye laser, pumped by an excimer laser, is used for these measurements. The sensitivity of this fluorescence technique allows observations on very low concentrations of  $BCl$ , which prevents interference from nucleation reactions. Both  $OBCl + O$  and  $BO_2 + Cl$  are possible product combinations; to distinguish between these separate laser spectroscopic observations will be made.

Figure 2 shows the type of 300-1900 K results obtained in HTFFR studies of metal atom reactions. It demonstrates the necessity to experimentally determine rate coefficients over wide temperature ranges, as clearly neither reaction obeys the simple Arrhenius law  $k(T) = AT^{1/2} \exp(-E_A/RT)$ , often assumed when extrapolating rate data obtained over narrow temperature ranges. The figure illustrates merely two types of non-Arrhenius behaviour; an extensive discussion of  $k(T)$  vs.  $T$  behaviour of combustion reactions, and our current understanding of it, has recently been prepared.<sup>2</sup>

Experimental work with the HTFFR facility described above is in the early stages.

1. A. Fontijn, S.C. Kurzius and J.J. Houghton, Fourteenth Symposium (International) on Combustion, p. 167, (1973).
2. A. Fontijn and R. Zellner in "Reactions of Small Transient Species: Kinetics and Energetics", A. Fontijn and M.A.A. Clyne, Eds., Academic Press, to be published fall 1983, Chap. 1.

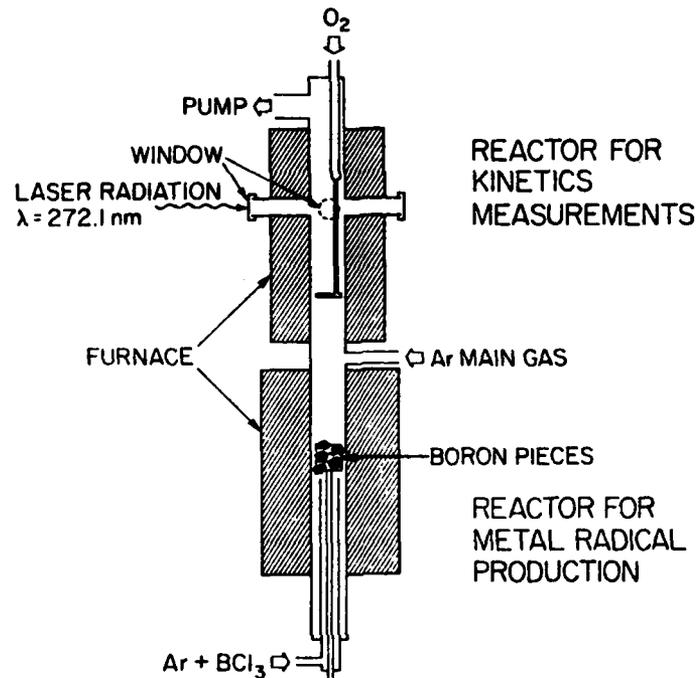


FIGURE 1: SCHEMATIC OF HTFFR APPARATUS FOR MEASUREMENT OF METAL RADICAL OXIDATION REACTION RATE COEFFICIENTS OVER LARGE TEMPERATURE RANGES, APPARATUS IS SHOWN AS USED FOR STUDY OF THE  $BCl + O_2$  REACTION.

- Reactant concentrations, pressure, temperature and average gas velocity are independently variable.
- Distance movable  $O_2$  inlet to window plane is proportional to time.
- Measurements of  $BCl$  concentrations are made at the window plane using laser induced fluorescence.

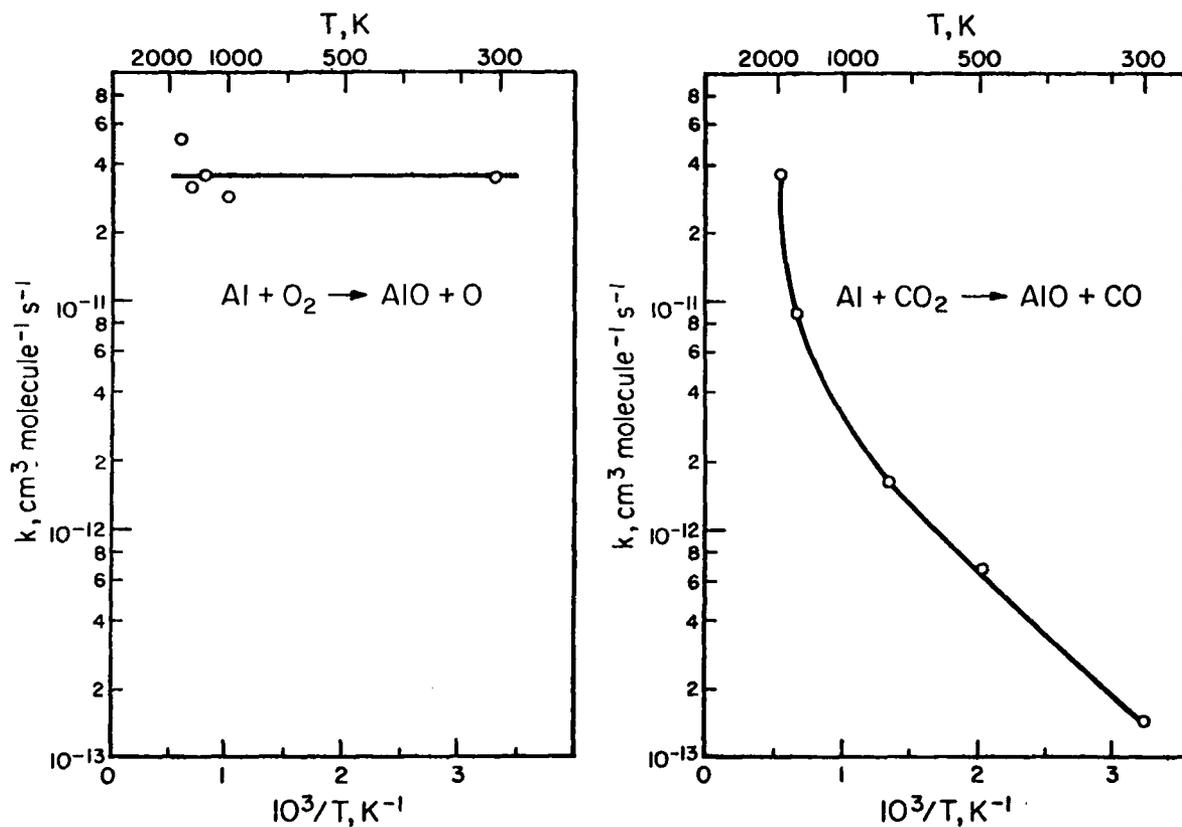


FIGURE 2: SOME HTFFR RESULTS ON ATOM REACTIONS

Each open circle represents approximately a dozen measurements covering about an order of magnitude variation in each of pressure, average gas velocity and initial metal atom and oxidizer concentrations.

DETERMINATION OF THE COMBUSTION MECHANISMS  
OF ALUMINIZED PROPELLANTS

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Composite solid propellants containing powdered metals are of interest due to their highly energetic and stable combustion characteristics. However, prediction of the performance of a solid rocket motor is difficult if it burns metalized solid propellants. This is primarily due to the unknown factors associated with metal particle/agglomerate two-phase flow behavior within the motor combustion chamber and nozzle. A thorough investigation is being conducted for determining important mechanisms associated with metal combustion including those controlling surface/near surface agglomeration, metal particle/agglomerate combustion characteristics in a motor environment, and particle breakup and two-phase flow behavior in a nozzle flow field.

This experimental research program involves measuring the aluminum/aluminum oxide particle size and size distribution under carefully controlled conditions simulating the combustion chamber and nozzle entrance region of a solid propellant rocket motor. A servo-positioning strand window bomb has been demonstrated capable of burning strands of solid propellant under high pressure conditions while holding the burning surface fixed in space to an accuracy of approximately plus or minus 100 microns, or close to the scale of the surface roughness. While the propellant strands are burning within the bomb, a computer controlled data acquisition system extracts instantaneous burning rate and environmental condition data for analysis.

With the servo-positioning strand window bomb holding the burning propellant surface stationary in space, aluminum/aluminum oxide particle size and size distribution data is extracted via an imaging-type particle size analyzer. This device consists of a pulsed light source, a Motorola closed circuit television camera as an imaging receiver, the Purdue/Parker Hannifin electronic package to decipher and analyze the data, and a PDP 11V03 computer to process the data. Such an imaging-type particle size analyzer is unique in that it should prove to be an accurate, non-intrusive diagnostic tool for particle size and size distribution measurements within simulated motor chamber/nozzle flowfields.

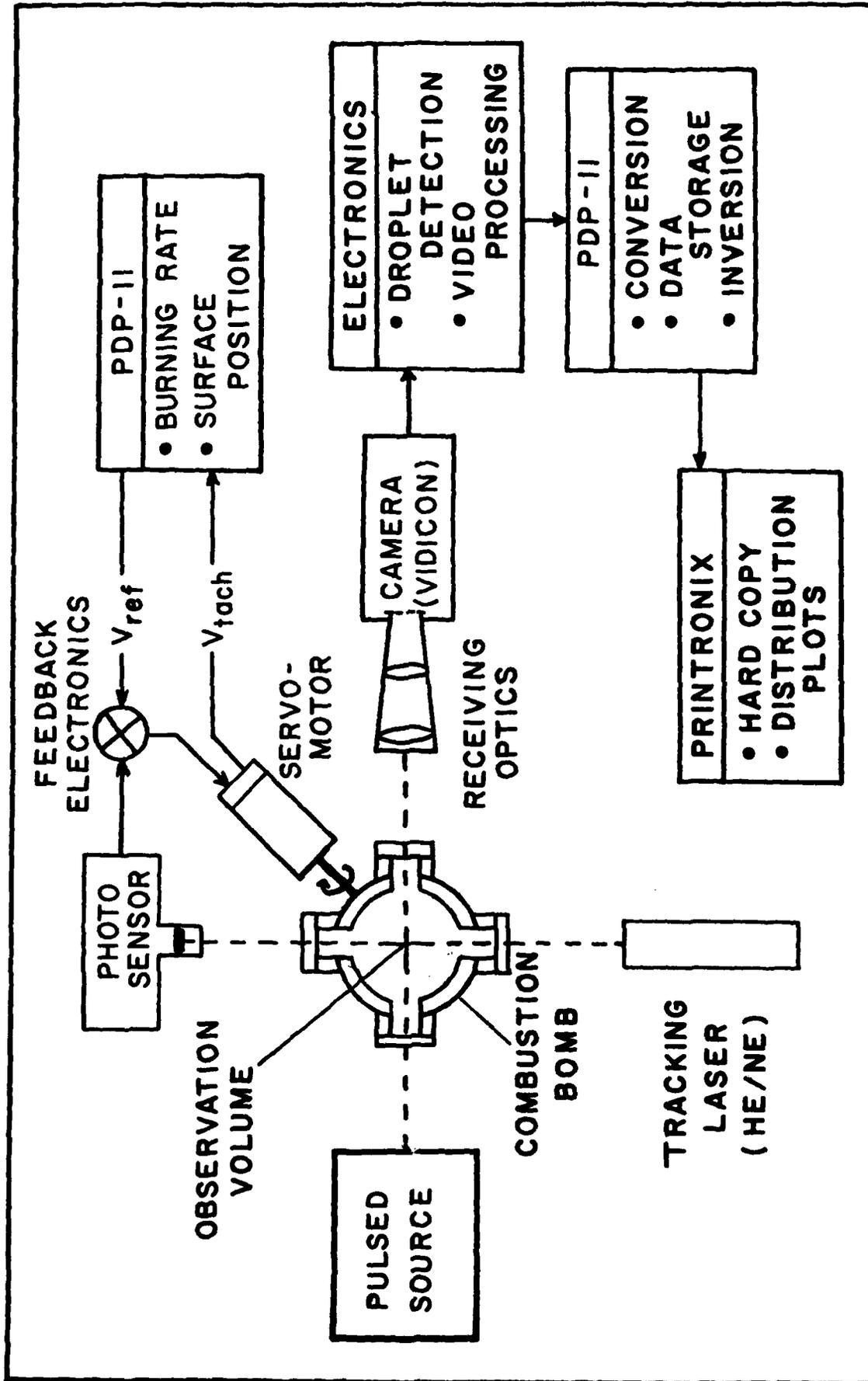
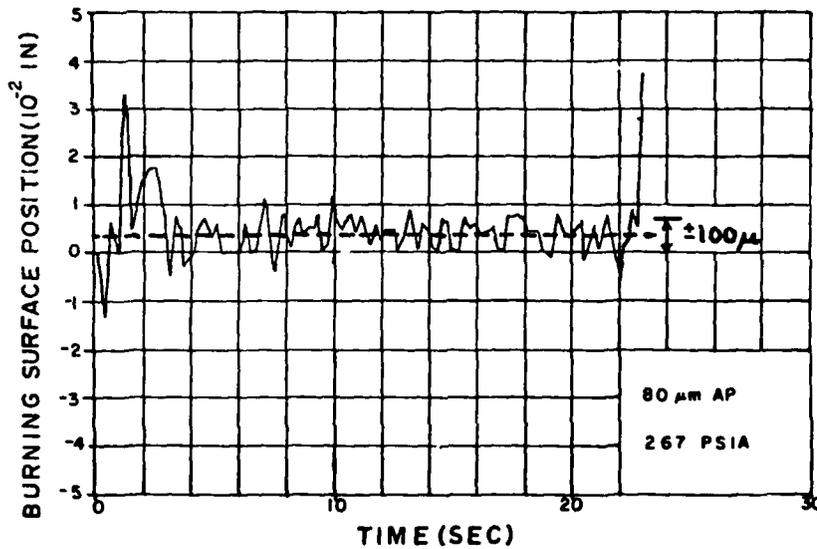


DIAGRAM OF EXPERIMENTAL APPARATUS

**EXPERIMENTAL RESULTS**

- **SERVO-POSITIONING STRAND WINDOW BOMB**
  - **INSTANTANEOUS SURFACE POSITION**
  - **INSTANTANEOUS BURNING RATE**



- **PURDUE/PARKER HANNIFIN PARTICLE SIZE ANALYZER**
  - **ALUMINUM/ALUMINUM OXIDE PARTICLE SIZE DISTRIBUTION SPATIAL DEPENDENCY**
  - **ALUMINUM/ALUMINUM OXIDE PARTICLE/GAS PHASE FLOW DYNAMICS**
  - **ALUMINUM PARTICLE BURNING RATE BEHAVIOR**
  - **ALUMINUM PARTICLE AGGLOMERATION BEHAVIOR**

EFFECT OF ACCELERATION ON METALIZED  
COMPOSITE PROPELLANTS

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W. Lafayette, Indiana 47907

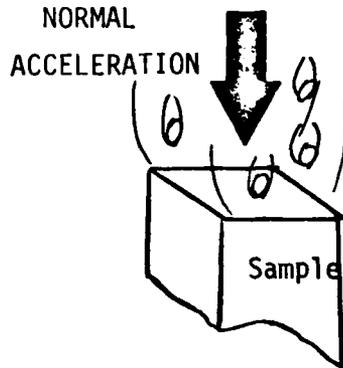
This research is concerned with describing solid propellant combustion augmentations and possible motor performance losses caused by low level accelerations (0-25 g's). An important aspect of this problem is to develop a mechanistic understanding of Al/Al<sub>2</sub>O<sub>3</sub> agglomerate formation and a description of agglomerate behavior in the gas flow. By determining the agglomerate's size and trajectory, a description of their effect on propellant burning rate and their potential for motor case impingement is possible.

Several experimental approaches have been employed to determine the propellant burning rate, Al/Al<sub>2</sub>O<sub>3</sub> agglomerate sizes, and the agglomerate trajectories. The spin window bomb has been used to impose acceleration fields on small sized propellant strands. Two basic configurations have been employed. (1) Acceleration directed normal and into the burning surface and (2) acceleration directed laterally across the burning surface. In the later configuration, the larger agglomerates are drawn from the gas flow by the acceleration field and collected on a mylar sheet. Microscopic size analysis is then possible on the collected agglomerates. High-speed photography provides burn rate, agglomerate size and agglomerate trajectory information for both configurations. Also, other standard methods have been employed to determine particle sizes.

During the past year all spin window bomb movies have been re-analyzed to determine propellant burn rates. Further, agglomerate sizes and trajectories above the propellant surface have been determined. Three supporting agglomerate size approaches have been completed with one propellant. All results indicated that significant agglomeration of the original aluminum is taking place (up to 30x original size) and this could cause significant amounts of slag in a low-acceleration rocket motor. These experimental results and burning rate results from another AFRPL program are currently being used to evaluate and improve the ALPEM combustion model.

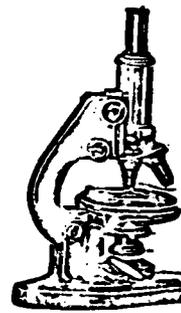
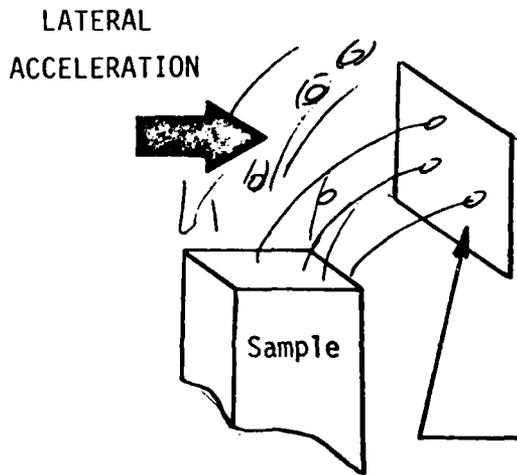
# FEATURES OF APPROACH

## EXPERIMENTAL TECHNIQUES



### FILM ANALYSIS

- BURN RATE
- AGGLOMERATE VEL.
- AGGLOMERATE SIZES

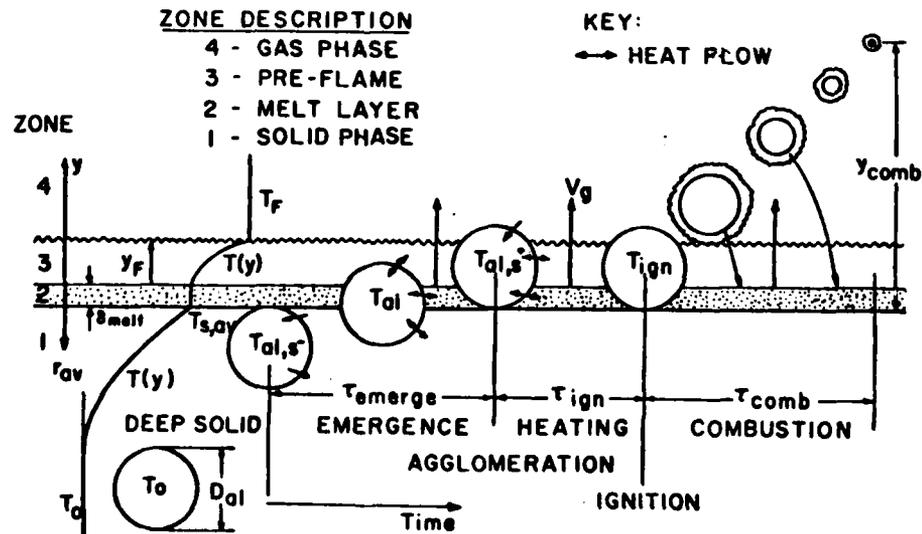


### MICROSCOPIC ANALYSIS

- PARTICLE SIZE
- SIZE DISTRIBUTION
- AUTOMATED

AGGLOMERATES STICK  
TO CLEAR MYLAR

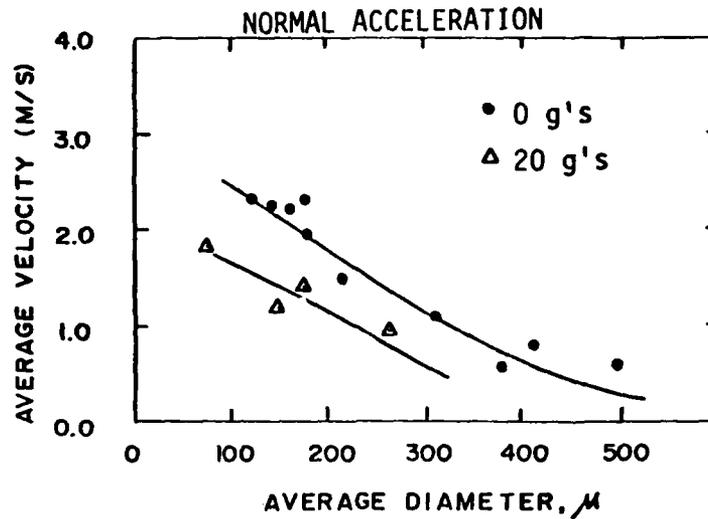
## COMBUSTION MODEL (ALPEM)



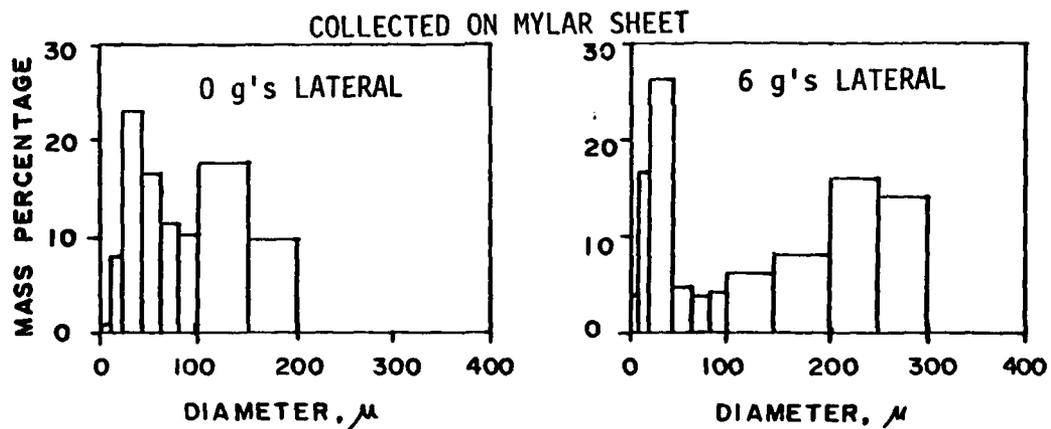
Aluminum Particle Surface/Near Surface Scenario

# RESULTS

## AGGLOMERATE VELOCITIES



## AGGLOMERATE SIZE DISTRIBUTION



## BURN RATE MODELING (ANTICIPATED)

- COMPARE ALPEM PREDICTIONS TO BURN RATE DATA
- MODIFY ALUMINUM PARTICLE SIZES TO MATCH EXPERIMENTAL RESULTS
- DEVELOP AGGLOMERATION DESCRIPTION

**MECHANISMS FOR ACOUSTIC SUPPRESSION**

**Principal Investigator: Merrill W. Beckstead**  
**Co-investigators: D. L. Gordon and R. L. Raun**  
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Acoustic suppressants are commonly added to low smoke and smokeless propellants to avoid the problem of combustion instability. However, the basis for selecting the type, size and concentration of suppressant particle for optimum performance is not well founded. These suppressants apparently work by one or more of three mechanisms:

- (1) energy loss due to viscous dissipation of drag forces,
- (2) modification of the propellant combustion response function, or
- (3) energy interchange due to distributed combustion.

Figure 1 illustrates the approach, some of the technical advantages, the data to be collected and the data analysis to be performed. The principle purpose of this work is to determine the effects that distributed combustion of acoustic suppressants has on combustion instability.

The experimental basis for the technical approach is the Rijke tube, a gas burner with an attendant paddle to control (stop and start) the oscillations (see Figure 2). This burner has been built, tested, modified and thoroughly characterized both at steady conditions as well as at various oscillatory conditions, with frequencies ranging from 500 to 1500 Hz.

Advantages of this approach include allowing a separation of the first and third mechanisms mentioned above by testing an additive independent of the propellant burning surface, avoiding the use of expensive solid propellants, and allowing for careful monitoring and control of frequency, O/F ratio, temperature and particle addition.

It is expected that several mechanisms will be shown to act together to dampen acoustic oscillations, with one mechanism perhaps dominating under certain conditions and another mechanism dominating at other times.

## **MECHANISMS FOR ACOUSTIC SUPPRESSION**

### **PROGRAM APPROACH**

Use a modified Rijke tube gas burner and a paddle for oscillation control to simulate a rocket motor environment with the purpose of studying the mechanisms by which acoustic suppressants work.

Study three types of particles (very reactive, slightly reactive, and inert) to determine the effect of heat release on the acoustic wave and separate the effects of distributed combustion from the viscous damping effects.

### **TECHNICAL ADVANTAGES**

(1) An additive can be tested independent of the propellant burning surface, allowing a separation of mechanisms between the modification of the burning surface response and distributed combustion effects.

(2) The system can readily be tested with and without particles, thus evaluating the system effects.

(3) Various types of particles (reactive or inert) can be tested under identical conditions to better identify actual mechanistic action.

(4) Solid propellants do not need to be mixed, cured, etc., thus reducing costs tremendously.

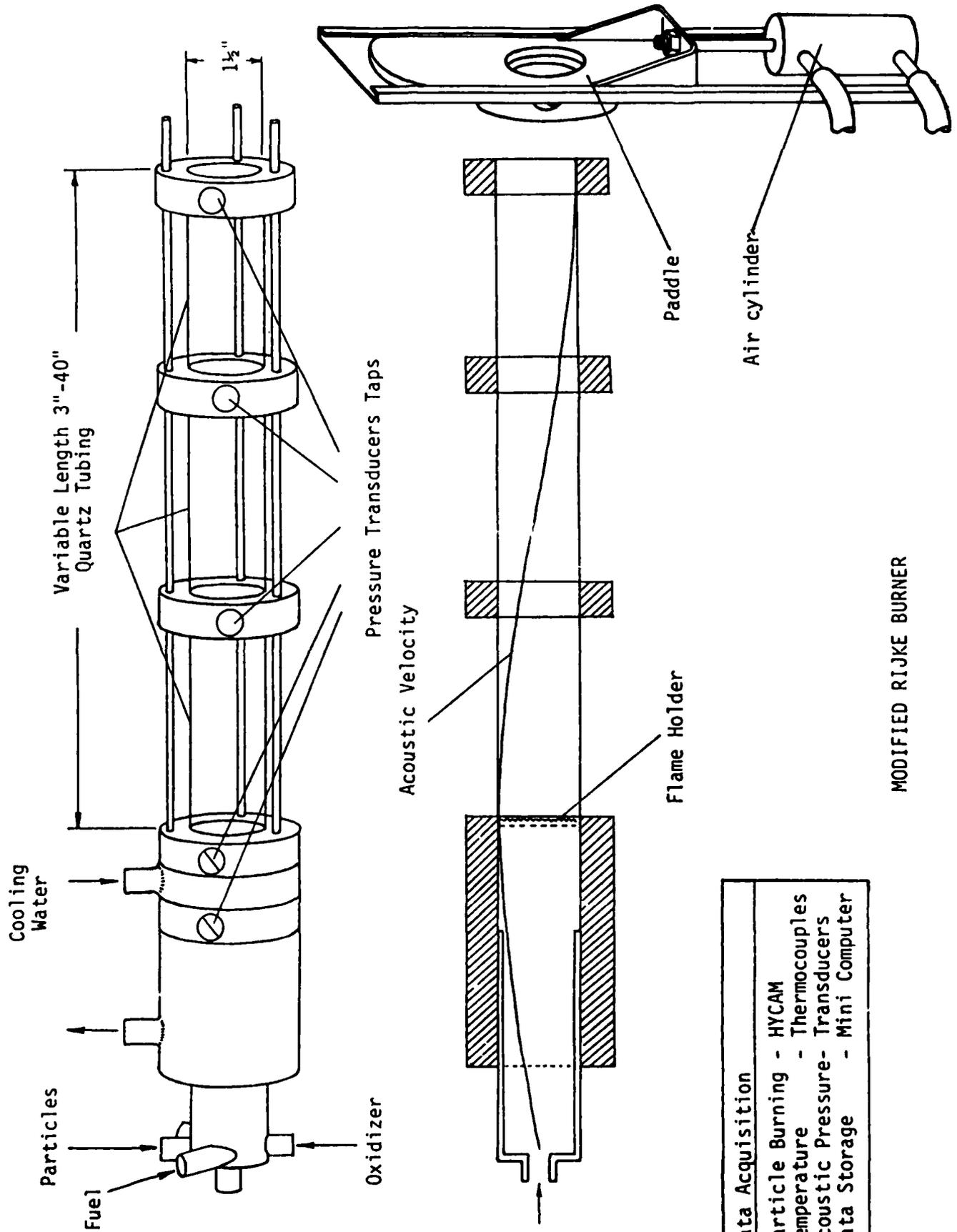
(5) Particle addition can be carefully monitored and controlled.

### **DATA COLLECTION**

- (1) pre-combustion particle size distributions
- (2) gas flow rates
- (3) particle flow rates
- (4) acoustic pressure amplitudes (at 2 or more locations)
- (5) particle combustion tracking (high speed movies)
- (6) post combustion particle collection and examination
- (7) selected wall temperatures

### **DATA ANALYSIS**

- (1) acoustic growth rate measurements
- (2) acoustic mode shape reconstruction
- (3) particle combustion times
- (4) viscous particle damping calculations



Data Acquisition	
Particle Burning	- HYCAM
Temperature	- Thermocouples
Acoustic Pressure	- Transducers
Data Storage	- Mini Computer

MODIFIED RIJKE BURNER

MODELING OF DEFLAGRATION-TO-SHOCK-TO-DETONATION  
TRANSITION (DSDT) IN POROUS SOLID PROPELLANTS \*

Herman Krier, Principal Investigator  
University of Illinois at Urbana-Champaign

SUMMARY

Advanced formulations for solid propellants continue to be more energetic and the possibility of deflagration to detonation transition (DDT) is real, especially if the propellant motor grain becomes porous due to damage by accidental stimuli. In our previous AFOSR funded work on transient analysis for DDT in a porous propellant bed, it was shown that steady detonation characteristics (CJ pressure, CJ temperature, detonation velocity) were predicted without requiring the precursor shock common to most detonations in homogeneous materials[1]. This was referred to by some as the "convective burn" model. In Ref. 1 it was shown that the high surface-to-volume ratio of very small (1/10mm diameter) propellant particles, high burning rate-pressure indices (0.9 to 1.0), and confinement of product gases (due to the tight packing and enclosing walls) all combined to cause a rapid enough gas generation rate to build and sustain pressures equivalent to those observed in granular bed experiments reported in Refs. 2, 3. However, as stated above, the model analysed in Ref. 1 did not attempt to treat the stress waves propagating into the unburned porous material. It is the purpose of this paper to analyse the propagation and shock formation of these compression waves generated at the products-reactants interface.

In confined DDT experiments, A.W. Campbell [3] has shown by using a similar test arrangement to that used in [2], but with segmented granulated compressed HMX explosive, that detonation may be a result of shock initiation. To explain Campbell's results, a new mechanism describing the detonation of porous propellants was given. Compression waves originating at the burning front propagate ahead causing compaction of the unreacted porous mixture resulting in the formation of a solid plug thereby eliminating further convective flame propagation. The compression waves continually generated at the burning front propagate through the solid plug. Coalescence of these compression waves form a shock wave which initiates the explosive resulting in a detonation.

Our current research therefore is focused on shock initiation mechanisms stemming from compression waves in confined burning porous propellant.

RESEARCH OVERVIEW

Shown in Figure 1 is a schematic representation of what we envision as the six part DSDT process. Superimposed on each section of the figure is a line representing the gas porosity (gas volume/total volume) as a function of bed location. A value of  $\phi$  equal to unity represents a zone of all gas while  $\phi$  equal to zero indicates a homogeneous solid.

Portion A represents the initial blast caused by the ignitor used to initiate DSDT in the bed. In the second portion, the convectively burning porous bed is shown to be pressurizing the region behind the ignition front. This is a result of the product gases being confined by the walls. The porosity variation for this time indicates an all gas makeup in this particular zone. Actually, there is a finite reaction zone where the propellant is decomposing into the product gases. Our work, presented in Reference 1, showed that if the reactive material consisted of mm size particles, this reaction zone may be very large. This results

\* Work supported by AFOSR, under Grant No. 81-0145; Dr. Michael Stroschio is Program Manager. Graduate students P. Barry Butler and Daniel W. Coyne are assigned to this research.

in a slower pressurization rate of the gas cavity. Illustrated in the last four parts of Figure 1 is what we refer to as the second possible branch of DSDT, the shock compression branch. Parts C-E, pore collapse, plug formation and shock formation are concepts which are currently being studied.

Reference 4 represents our latest published research on shock development from compression waves due to confined burning.

### RESULTS

The early compression of a packed bed of porous propellant due to confined deflagration can be approximated by a linear pressure-time loading, causing complete pore collapse and shock formation [4]. Figure 2 is a shock hydrodynamics calculation which compares the pressure buildup into a shock for both a porous propellant and a non porous, solid propellant, for the same ramp-type pressure loading. Here the porous material has developed into a 3 GPa (30 kbar) shock within a 10 cm distance. Such a shock would likely cause initiation to a detonation.

The effect of increasing porosity on the distance and time of shock formation is shown in Table 1. Increasing porosity causes the shock to form in less time and in a shorter distance. Also shown in Table 1 are the shock velocities and particle velocity behind the shock as determined from the finite difference computer calculation and the theoretical shock velocity as determined from the jump conditions (conservation of mass and momentum across a shock).

TABLE 1  
Shock Parameters for HMX at Different Initial Porosities

Shock Formation	$\alpha_o = 1.0$	1.2	1.4
distance* (cm)	32.0	11.5	9.0
time* ( $\mu$ sec)	105	60	54
Shock* velocity (cm/ $\mu$ sec)	0.37	0.27	0.24
Particle* velocity (cm/ $\mu$ sec)	0.042	0.069	0.088
Theoretical shock velocity (cm/ $\mu$ sec)	0.367	0.273	0.250
Shock strength (GPa)	3.0	3.0	3.0

\*results from finite difference calculations with  $P(0,t) = (0.075 \text{ GPa}/\mu\text{sec})t$

### CONCLUSIONS

The results support the intuitive conclusion that a shock will run-up in a much shorter distance in a porous material than in a homogeneous solid, an important result for determining whether or not a particular explosive will transit to detonation. Another point emphasized was the necessity to utilize a thermodynamically correct state equation and to forgo simplifying assumptions even though they provide for expedient solutions.

Also shown was that when applied to most propellants the pore collapse model indicates complete pore closure at very low pressures relative to the enormously high stress levels generated by the evolving reactant gases.

The next step in our DSMT model will be to couple the reactive chemistry of HMX to the governing equations. Since the temperature of the porous solid plays a key role in determining the reaction rate of the explosive, it is important to have a method for accurate temperature calculations in porous materials. Included in this effort will be the recognition of possible localized hot spot temperatures which can be significantly greater than the temperature rise in the

bulk material.

It will be this work in reactive chemistry, combined with the shock development work of this paper that will complete an overall DSDT model.

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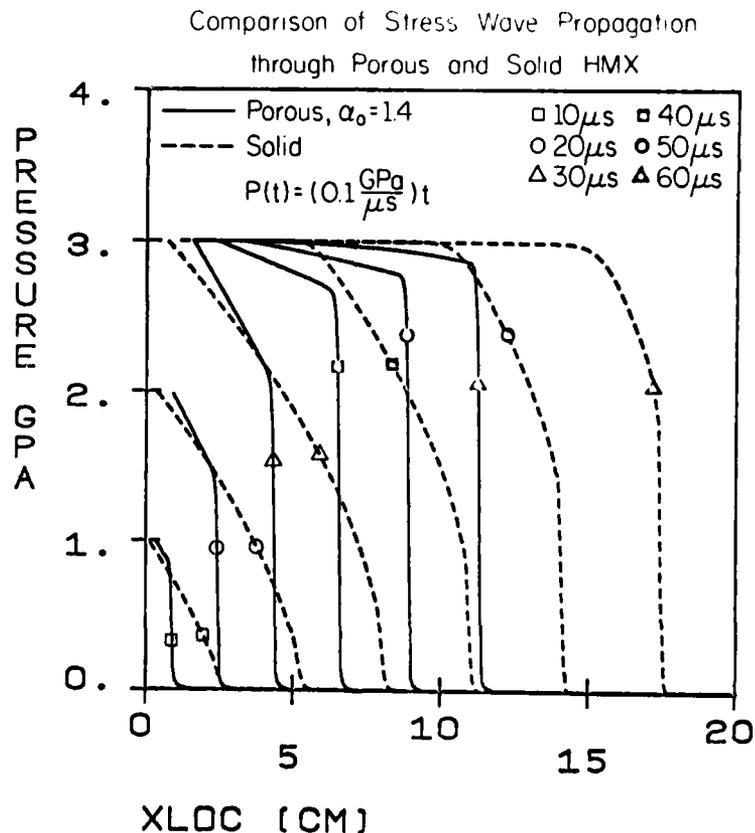
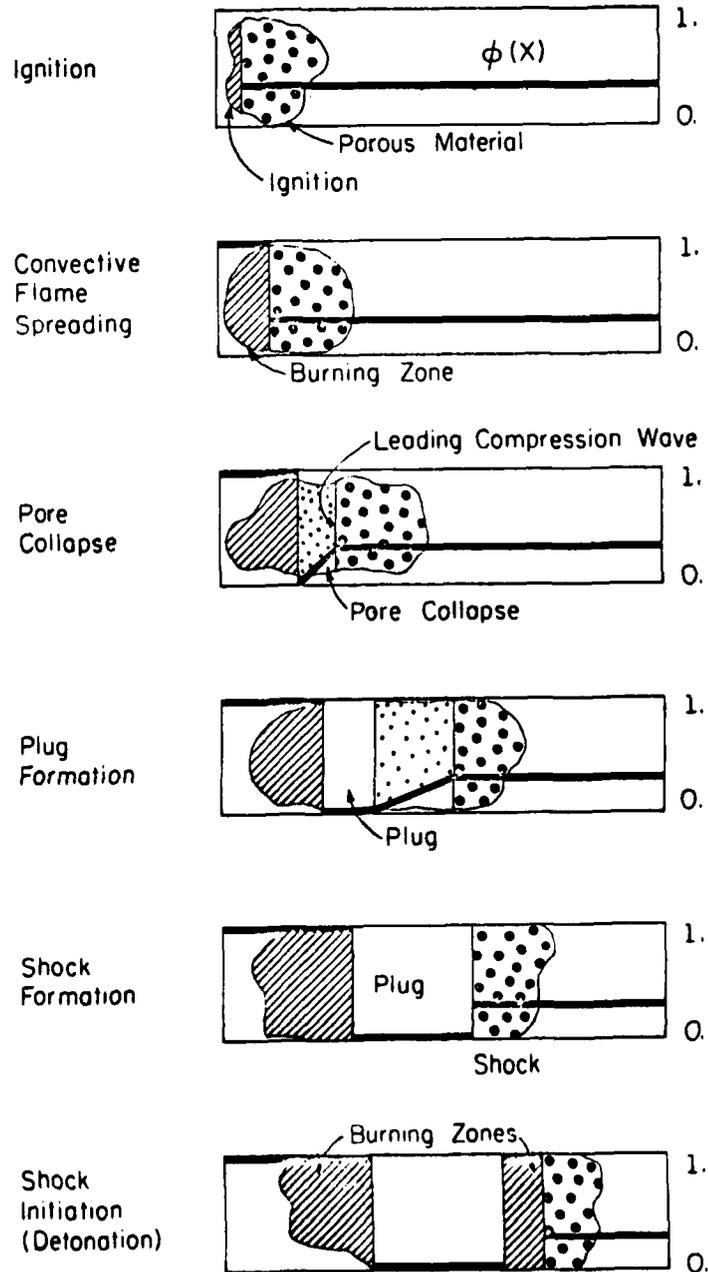


FIGURE 2 Comparison of the pressure front to final shock development in a porous material and a nonporous solid, clearly showing that a porous material will develop a shock much sooner.

FIGURE 1 Six part representation of DSDT  
(A) Ignition of porous material  
(B) Convective Flame Spreading with pressure rise  
(C) Pore Collapse; (D) Plug formation  
(E) Shock Formation; (F) Shock Initiation to Detonation



COHERENT OPTICAL TRANSIENT SPECTROSCOPY IN FLAME

John W. Daily

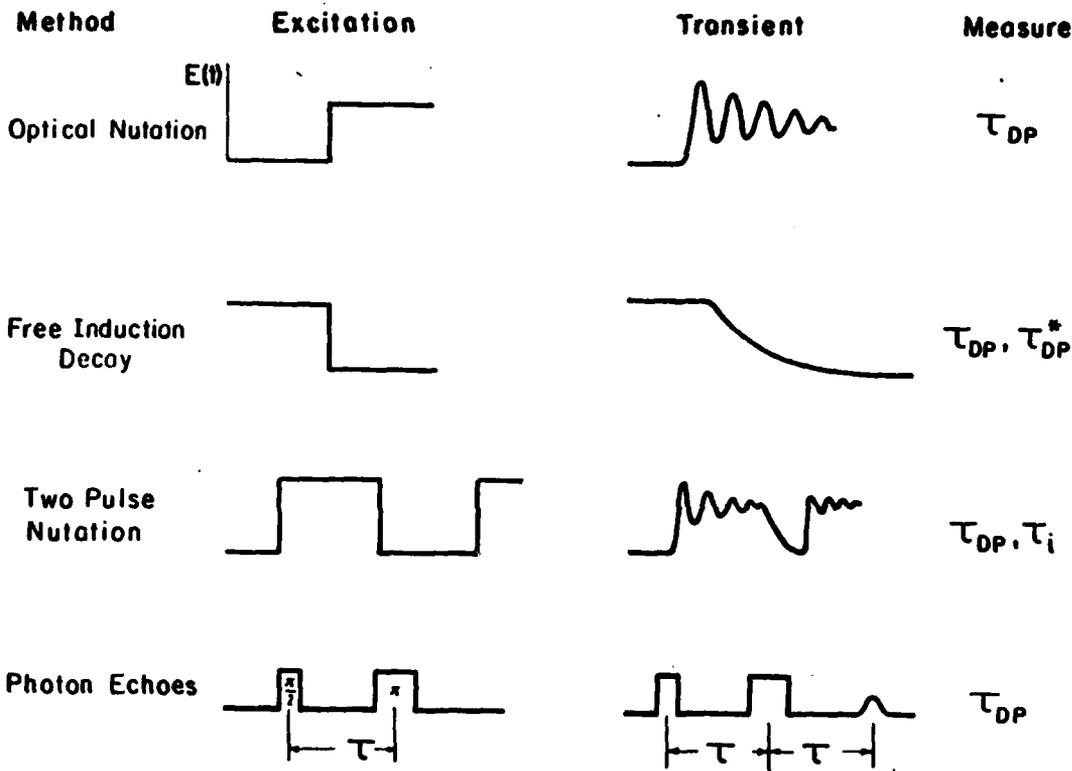
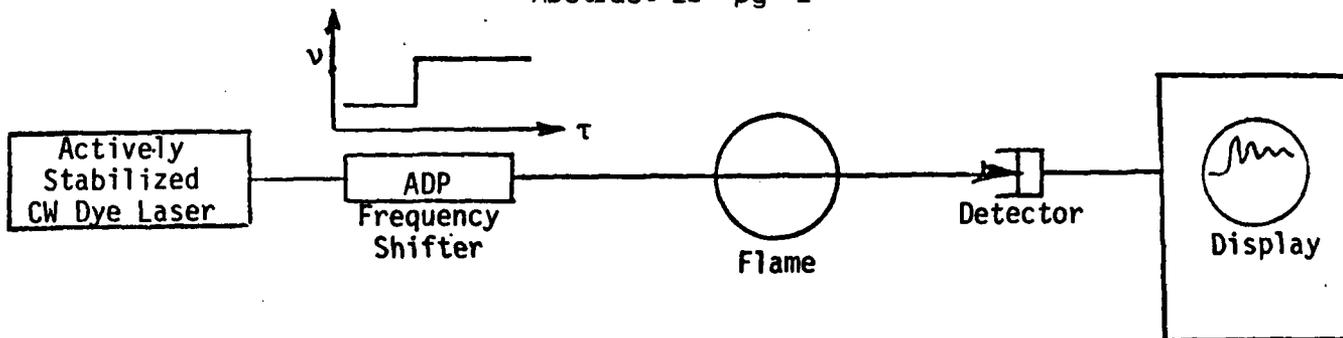
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Coherent optical transient spectroscopy is a technique in which the transient response of a group of molecules to laser excitation is observed. The uniqueness of the method lies in the fact that when transient experiments are conducted on a time scale short compared to collisional relaxation times, coherent phenomena occur which enable one to directly observe the rates of a variety of collisional processes. Furthermore, the coherent phenomena can be quite strong, resulting in large signals and thus high data rates. Processes such as state-to-state energy transfer, optical dephasing and velocity redistribution can be studied.

An example experiment is shown in Figure 1. An actively stabilized CW dye laser is used as a source. By passing the beam through a traveling wave modulator to which a high voltage pulse has been applied, the frequency may be shifted up to 15 GHz within 50 psec for periods of several nanoseconds. Thus, one may shift into or out of resonance with an absorption line of interest and observe the transient behavior that results. One type of transient is optical nutation in which the laser beam is suddenly shifted into resonance with an absorption line and the absorption signal observed. The decay rate of the transient signal is the collisional dephasing rate for that transition and thus a direct measure of the line width. Also illustrated in Figure 1 are several types of excitation, the transient they produce and the quantities one can obtain.

Over the last year, our work has focused on developing the theoretical capability for predicting various coherent phenomena that arise due to optical excitation of diatomic radical species of interest in flames. For example, shown in Figure 2 is the expected response to a two pulse nutation experiment in which the rotational relaxation rate for a molecule like OH or CH is determined by measuring the nutation signal strength as a function of pulse delay. Continuing the experiment to longer time delays one may also trace out chemical decay which gives a measure of state to state chemistry. By systematically varying flame composition and stoichiometry, one can study the kinetics of such processes over a wide range of in situ conditions.

We have assembled and are currently testing the apparatus for performing coherent transient experiments in the visible region and will soon have preliminary results for CH.



Measure

Learn

Why Important

$\tau_{DP}$   
 Optical Dephasing

Line Widths

Nonlinear Raman spectra require linewidth information for interpretation

$\tau_{DP}$   
 Doppler Dephasing

Velocity  
 Redistribution Rates

Give handle on collision integral for use in evaluating transport properties

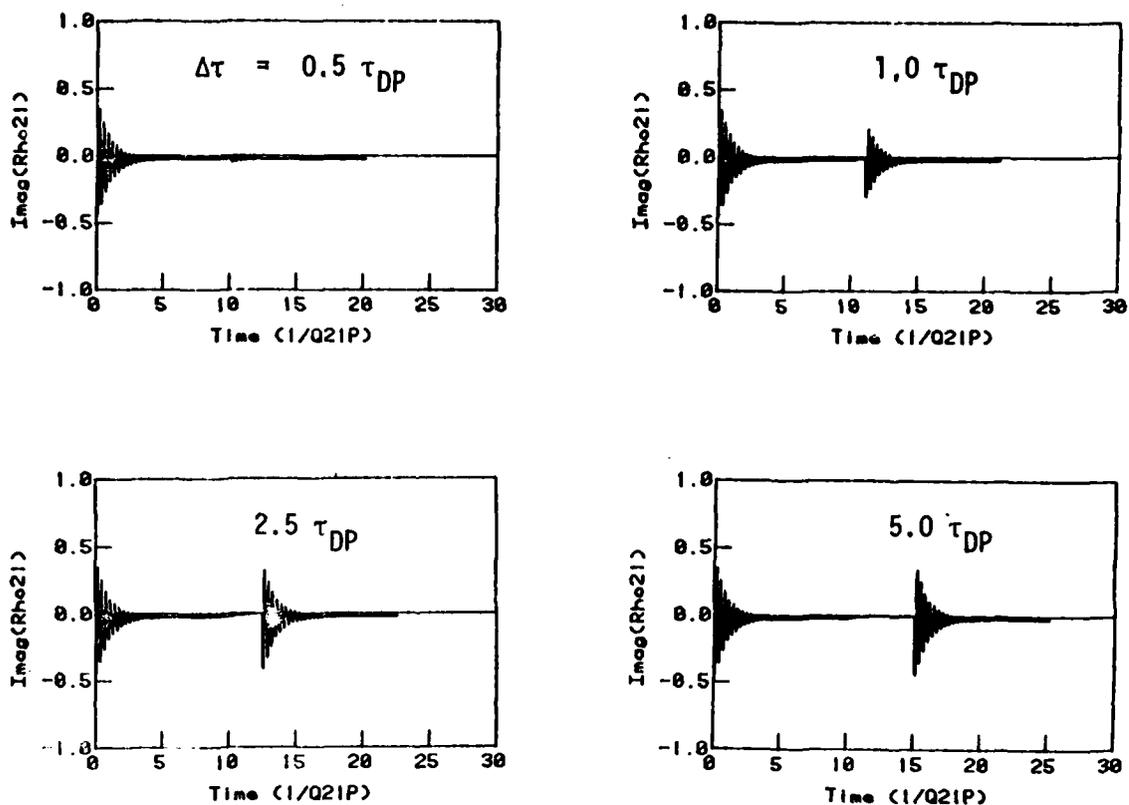
$\tau_i$   
 State Decay Rates

State to State  
 Energy Transfer Rates

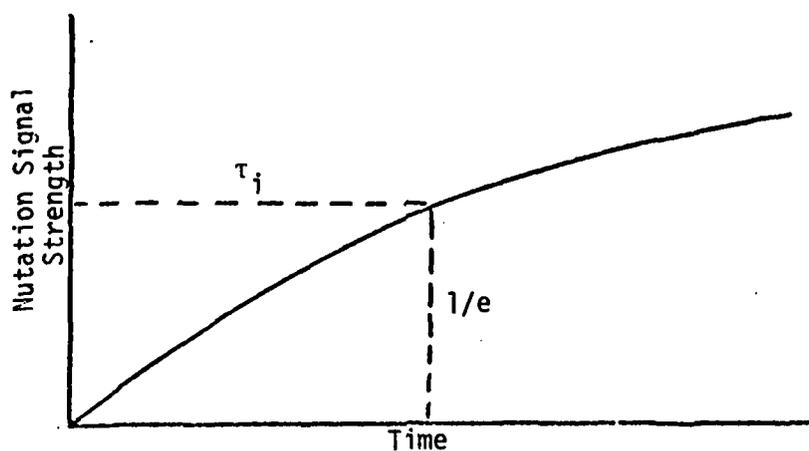
Required for accurate correction of quenching effects in fluorescence spectroscopy

Chemical  
 Relaxation Rates

Direct measure of state to state chemical rates give important insight into combustion kinetics



- a) An example of the effect of delay time on the two pulse nutation signal. At small delays the population in the excited state is unchanged. As the delay increases, more ground state molecules are available for the transient response.



- b) The integral of the transient response is proportional to the ground state population. Plotting the integral against time traces out the decay of population from the excited state and gives a direct measure of the energy decay rate.

Figure 2 Two Pulse Nutation

NON-STEADY COMBUSTION OF COMPOSITE PROPELLANTS

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This research is aimed at developing an understanding of the nature of the fine structures or heterogeneity of composite propellants and its effect on their combustion instability characteristics. Is it a macroscopic or merely microscopic feature? Is it random or ordered? What dimensions characterize the frequency components, if any? Are there particular preferred frequencies, those which exhibit a greater fluctuation strength, or is it merely white noise? Does it show up in the combustion process at constant pressure? Does it couple with pressure and velocity perturbations?

The approach being followed consists of (1) refining and determining the feasibility of experimental techniques, Fig. 1, developed in previous AFOSR-funded programs to determine any periodicities in propellant make-up, and (2) extend the modeling effort to describe the combustion contributions to non-linear velocity-coupled instability, accounting for composite propellant heterogeneity. The research therefore seeks to understand the nature and properties of the effect of particle size on non-linear instability, something no other investigation is doing.

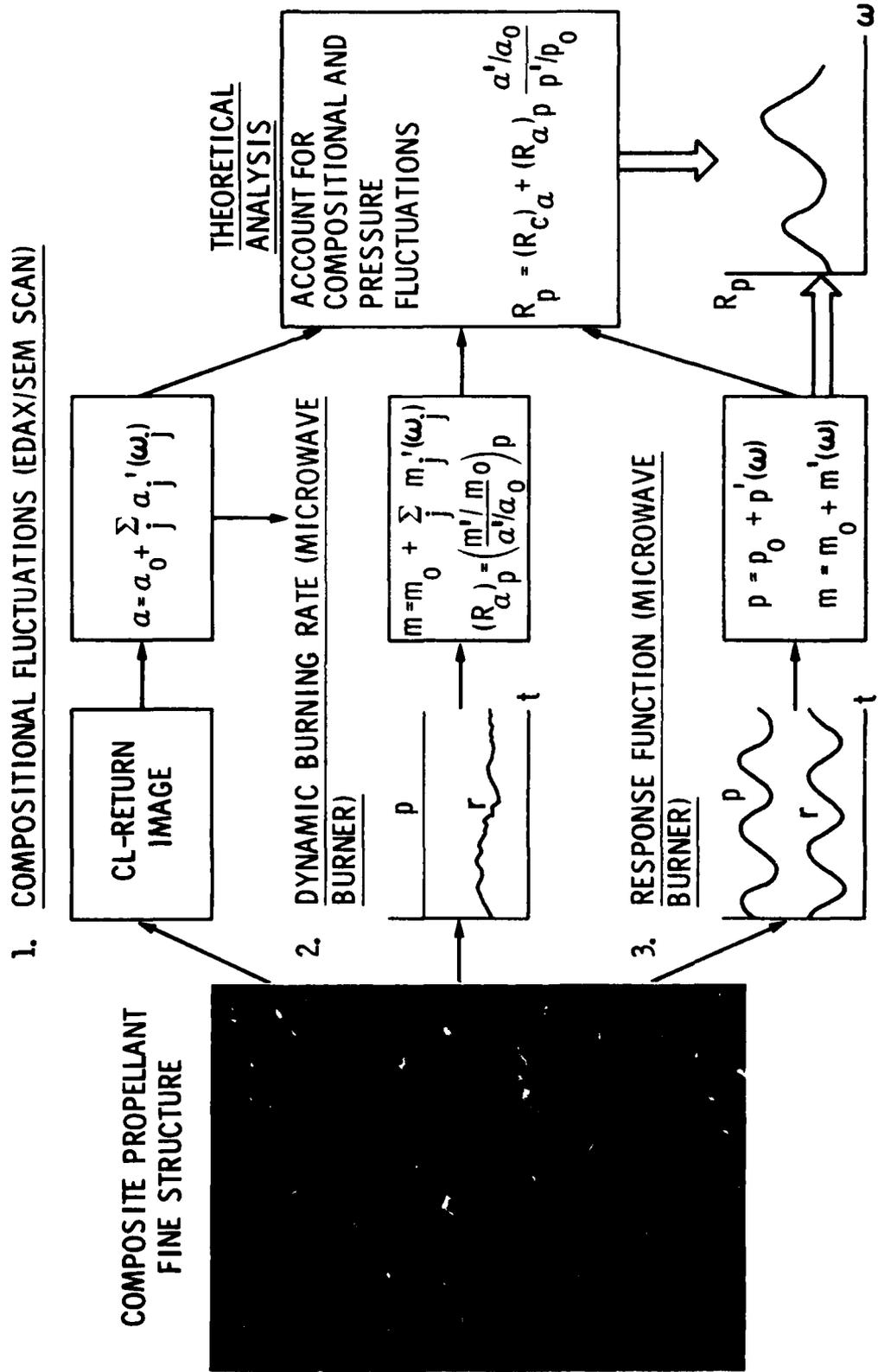
Three screened-oxidizer propellants, formulated to highlight particle size effects, are being utilized in the experiments. Dynamic burning rate data with improved signal-to-noise characteristics were obtained. They will be Fourier-analyzed to determine their frequency spectral density. Pressure-coupled response function data were obtained over the frequency range 40-1500 Hz. The dynamic burning rate frequency spectra will be compared to the combustion response vs. frequency characteristics to see if some dominant frequency or frequencies appear in the combustion response. The relationships will be determined between these and any preferred frequencies resulting from the Fourier analysis of energy dispersive analysis (EDAX) scans of the propellant surfaces.

As a first step in the analysis of non-linear instability, a working model for the linearized velocity-coupled combustion response function was developed. It does not address the modeling of the flow field and boundary layer phenomena, which are subjects of work in progress elsewhere -- it is purely a combustion response model, and therefore makes an assumption about the influence of the fluid mechanics merely to be able to state a boundary condition for the combustion analysis. The model combines elements of response to velocity perturbations, pressure perturbations, and compositional perturbations due to the heterogeneity of composite propellants. Properties of the response function have been calculated over a range of the governing variables. Fig. 2-a shows the effects of AP particle size and pressure upon the phase-leading peak values of the imaginary part of the velocity response -- Fig. 2-b the effects of AP particle size and mean crossflow velocity.

Progress has also been made toward formulating a high frequency combustion response model applicable to nitramine/minimum smoke propellants.

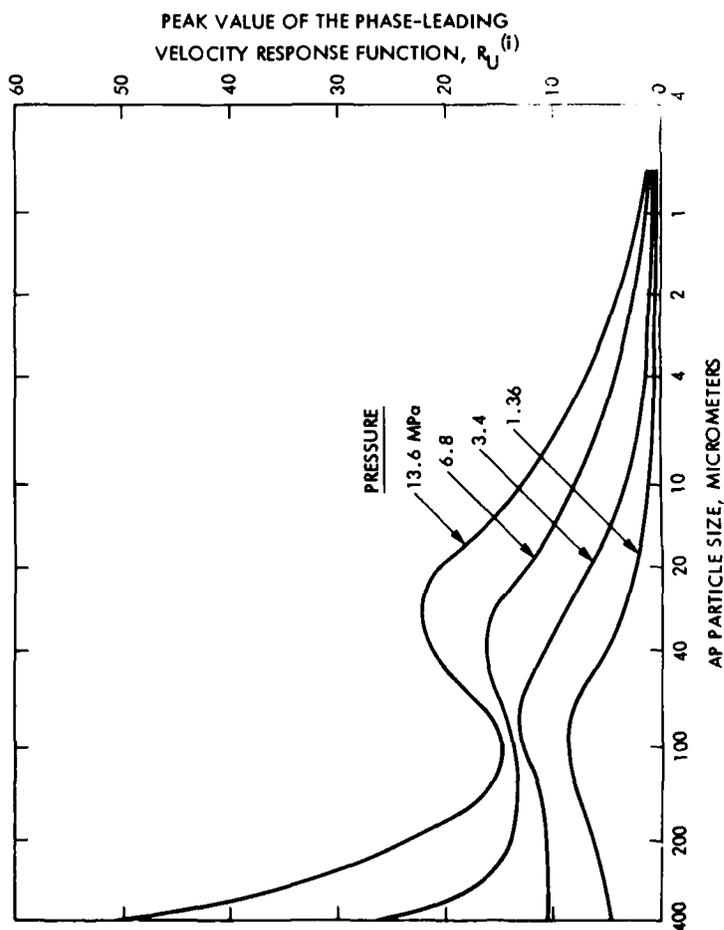
# HOW DOES AP SIZE DISTRIBUTION AFFECT COMBUSTION INSTABILITY?

## APPROACH

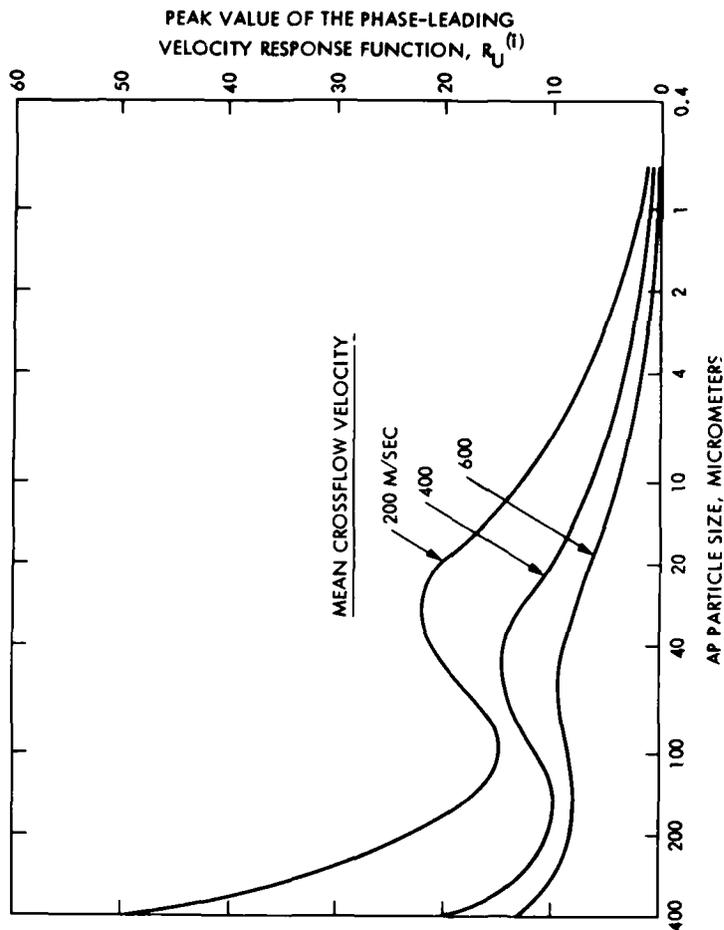


# PRIMARY ACCOMPLISHMENTS

**FIG. 2-a**  
 CALCULATED EFFECTS OF AP PARTICLE SIZE AND  
 PRESSURE ON A PEAK VALUE OF THE VELOCITY  
 RESPONSE, 88% AP AND 200 m/sec MEAN  
 CROSSFLOW VELOCITY



**FIG. 2-b**  
 CALCULATED EFFECTS OF AP PARTICLE SIZE AND  
 MEAN CROSSFLOW VELOCITY ON A PEAK VALUE  
 OF THE VELOCITY RESPONSE, 88% AP AND 13.6 MPa  
 PRESSURE



THERMOPHYSICAL PROPERTY DETERMINATIONS USING TRANSIENT TECHNIQUES

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Knowledge of the thermophysical properties of rocket propellants, especially at higher temperatures where significant decomposition occurs, is necessary for understanding various physical processes which take place in the combustion of these propellants. In this program, determinations of the thermophysical properties of HMX, RDX, and AP are being made.

Shown in Figure 1 is the general approach for making the thermophysical property determinations of a material when the thermal conductivity is difficult to measure directly. Two thermal properties are being measured: (1) specific heat using a Perkin-Elmer model DSC-2 Differential Scanning Calorimeter, and (2) thermal diffusivity using a laser flash apparatus. All measurements are made under digital computer control for data acquisition and analysis. The product of these results and the densities of the propellants, yields the thermal conductivity of the material.

Specific heat results have been obtained in both the  $\beta$  and  $\delta$  phases of HMX. In addition, studies have been made on the thermophysical properties behavior of partially decomposed HMX, since the material present at combustion consists of HMX plus decomposition products.

Specific heat as a function of temperature for single crystals of HMX in both their  $\beta$  and  $\delta$  phases are shown in Figure 2. Delta phase results were obtained using two techniques: (1) short range results from 477-486°K just after the phase transition ( $\beta \rightarrow \delta$ ), and (2) extended range results from 415-485°K. The second technique was possible due to hysteresis in the conversion of  $\delta$ -HMX back to  $\beta$ -HMX following cooling from above the phase transition temperature. As seen in Figure 2, the  $\delta$  phase results are in very close agreement to those in the  $\beta$  phase. In addition, the results for a powdered blend of HMX were obtained and yielded good agreement to that of the single crystals. Also, the specific heat of HMX inter-mixed with decomposition products was found to be slightly larger than for pure HMX.

Studies to determine the thermal diffusivity of HMX are currently underway. The three sample configurations which have been studied are: (1) HMX powder pressed into a stainless steel cup, (2) HMX powder pressed into a teflon cup with a stainless steel disk with a stainless steel bottom, and (3) a HMX powder pellet attached to a stainless steel disk with graphite paste. The first configuration was found to give erroneous results due to heat leakage from the side walls into the sample, but the second two arrangements gave much better results when tested with standard materials. Pressed HMX has been tested for transparency in the IR region and it was found that there was no difficulty in measuring the rear face temperature rise with an IR detector.

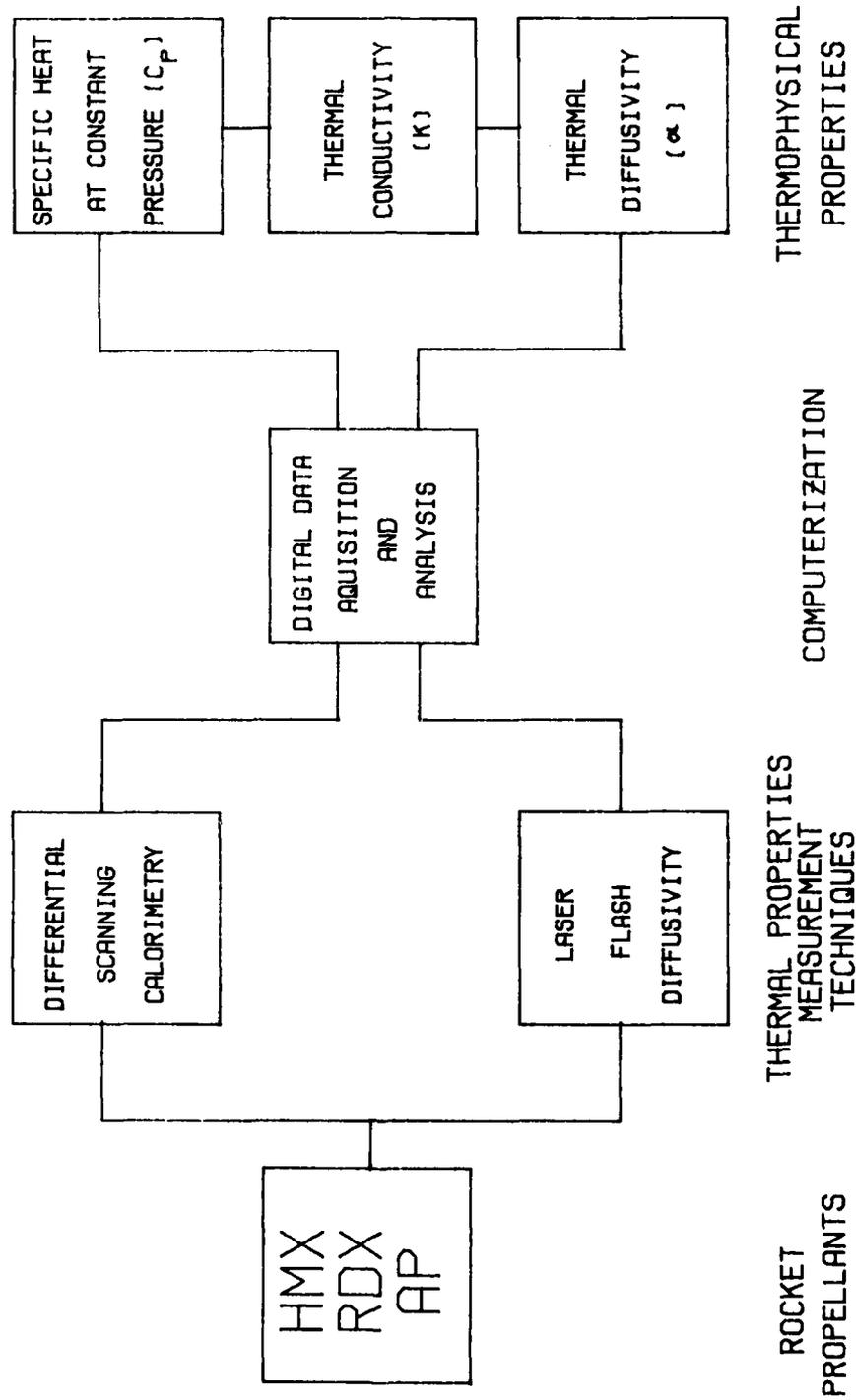


Figure 1. Thermophysical Property Determination.

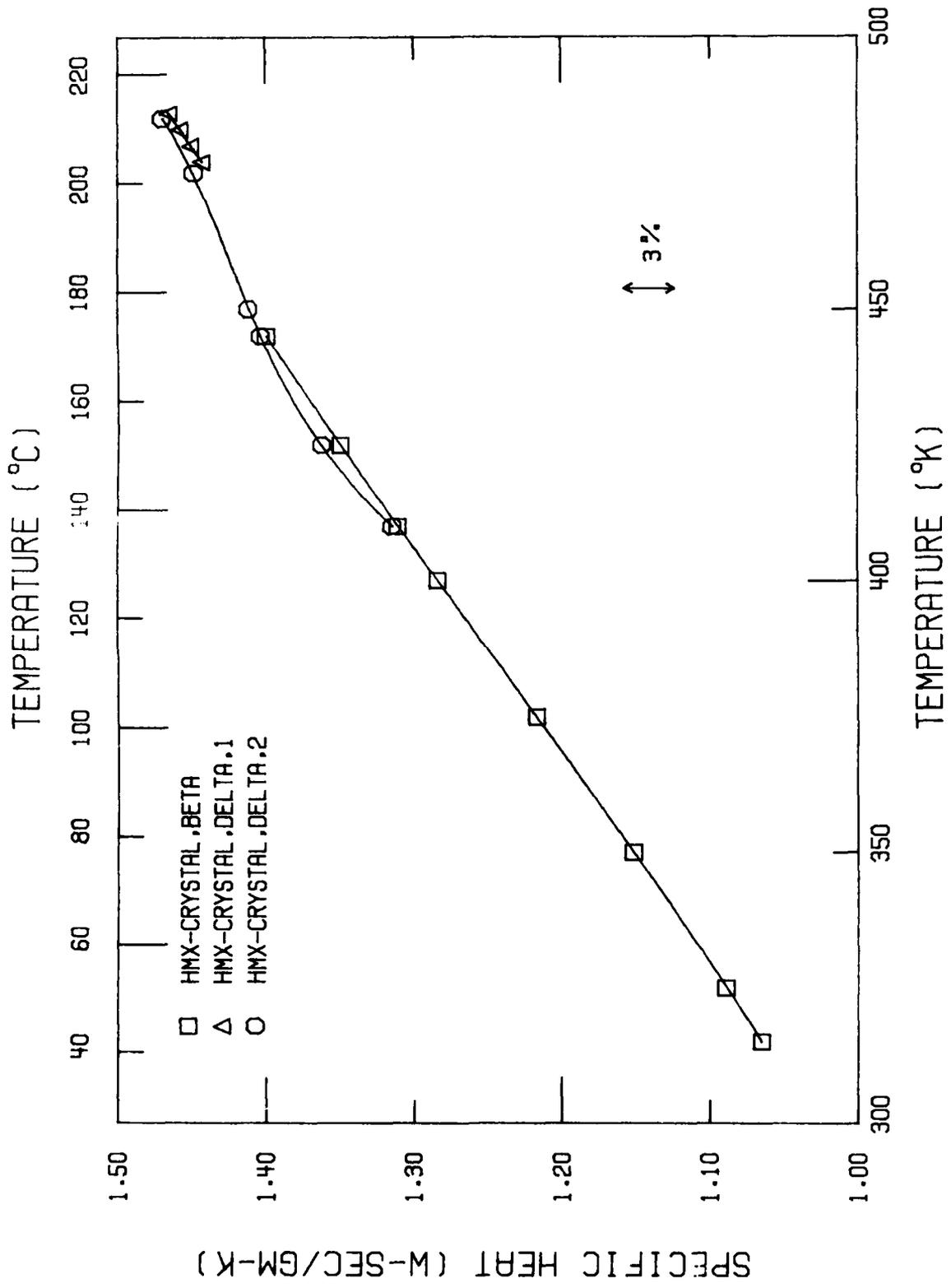


Figure 2. Specific heat of HMX in the  $\beta$  and  $\delta$  phases.

COMPOSITE PROPULSION FOR TRANSATMOSPHERIC LAUNCH SYSTEMS:  
A PERSPECTIVE ON RESEARCH CHALLENGES

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ABSTRACT

Space systems are providing increasingly critical support to both our strategic and tactical forces. This fact was emphasized by the recent decision to establish an operational space command in the Air Force. Continued improvements to space programs require extensive and innovative developments from a technology base which is narrower than we need. Propulsion is one of the key areas requiring a broader range of systems to accommodate the need for significant improvements in performance, including higher payload-to-gross lift-off weight. Airbreathing engines offer about 6 to 20 times higher fuel specific impulse (or proportionately lower fuel consumption) than rockets, so that their use parallel to the booster rockets can save a substantial portion of the large first-stage fuel mass, even though the airbreathing engines are currently heavier than rockets. Recent in-depth engine-vehicle-trajectory optimization studies indicate that composite engines (integrated airbreathing/rocket systems) can increase the payload fraction by a factor of five (5). To bring this potential to fruition, inputs to the technology base are required.

The presentation will cover the potential of composite engines for transatmospheric launch and will address the technology base requirements in the context of research needs in combustion. Subsonic and supersonic combustion will be discussed in relation to developments required in various areas such as fuels, combustion modification techniques, flame stabilization, and combustion instabilities.

EVALUATION AND COMPILATION OF THE THERMODYNAMIC  
PROPERTIES OF HIGH TEMPERATURE SPECIES

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The JANAF Thermochemical Tables are a set of continually updated self-consistent thermodynamic data currently available in a well-established format which can be quickly and easily used. These tables result from reviewing all literature sources, evaluating the accuracy of the experimental data/-theoretical calculations, calculating temperature-dependent thermodynamic functions, and publishing thermochemical tables for use in the Air Force community. Considerable effort is directed to discussing both the uncertainties in the data and the experimental data necessary to reduce this uncertainty.

The selection of species to be studied depends on current and future Air Force interests. In generating the obvious products of this project, there are three main concerns currently of interest. First and foremost, the upcoming publication of a "third edition" is necessitating an updating of all the elemental reference states. Second, the aluminum- and boron-containing species are being refined for inclusion in the third edition. The emphasis is not only to provide current reliable tables in this area but also to highlight and prioritize the missing/weak experimental data. Third, cooperative ventures are playing an important role in reducing duplicative efforts.

**JANAF THERMOCHEMICAL TABLES**

DOW CHEMICAL U.S.A.  
Physicochemical Studies  
1707 Building  
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**Date Established** 1959.

**Sponsoring Organizations** U.S. Air Force, Office of Scientific Research (AFOSR).  
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Robert L. Vance

**Description of System or Service** JOINT ARMY-NAVY-AIR FORCE THERMOCHEMICAL TABLES (JANAF) are compilations of thermochemical data for species of interest at high temperatures and of thermodynamic properties as a function of temperature. JANAF THERMOCHEMICAL TABLES are obtained by a careful search, critical evaluation, and selection of the literature or by the estimation of certain data, and published with a complete discussion of the data treatment and selection as well as the inclusion of all pertinent references.

**Scope of Subject Coverage** Heat capacity, enthalpy, entropy, free energy functions, heats, and free energies of formation for compounds of the elements H, D, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Br, Kr, Sr, Zr, Nb, Mo, I, Xe, Cs, Ba, Hf, Ta, W, Hg, and Pb.

**Input Sources** Published and unpublished chemical literature.

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**Magnetic Tape Services** Supplements 1-current, with numerical values only (no writeup or references) are available on tape with individual supplements extra.

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JANAF THERMOCHEMICAL TABLES

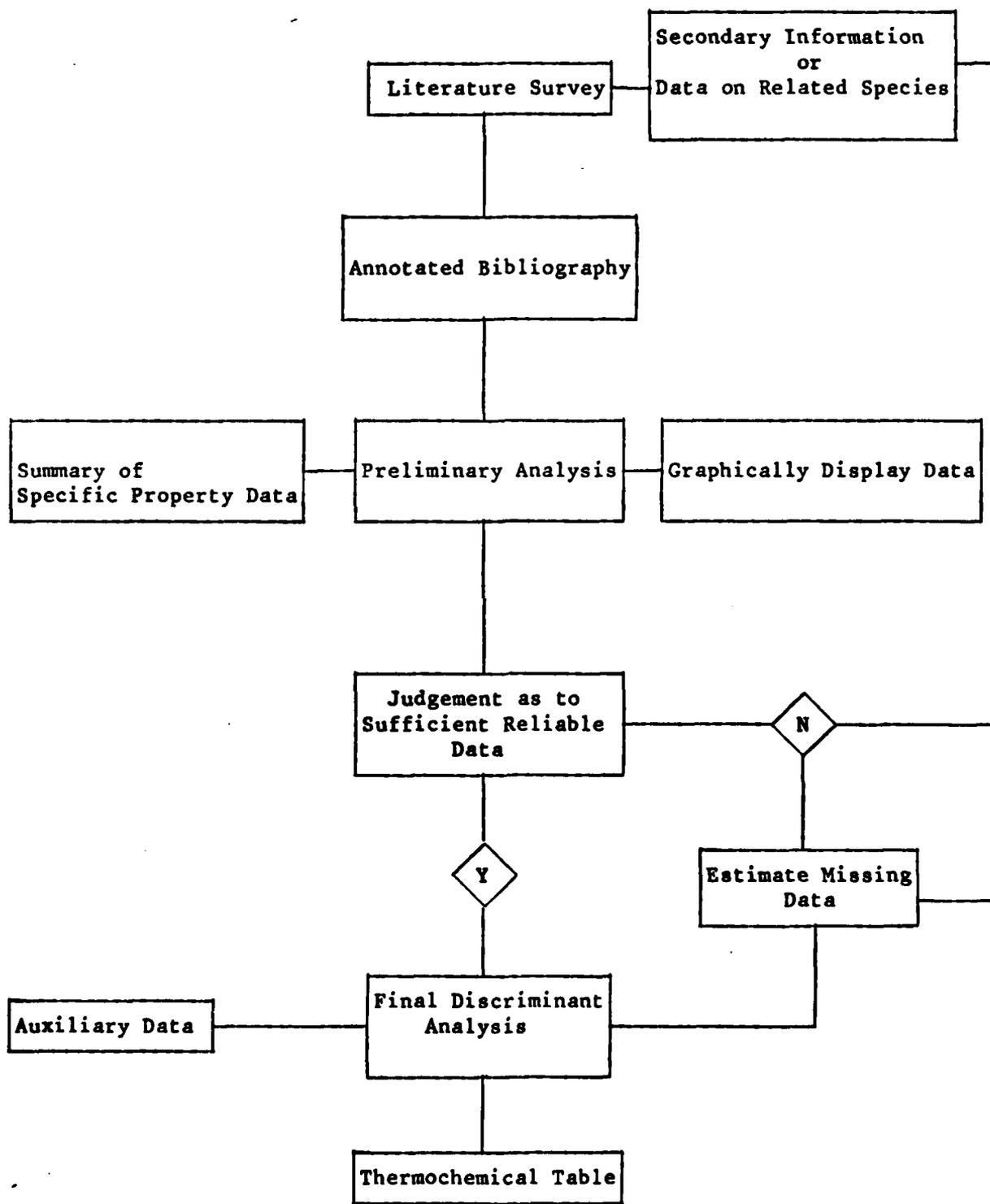


FIGURE 1

CRITICAL EVALUATION OF HIGH TEMPERATURE CHEMICAL KINETIC DATA

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and

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The rapid growth in chemical kinetic data, and simultaneously in the number of nonspecialists who require such data in DOD-related work, has created a need for a reliable, easy-to-use compilation of evaluated rate data and recommended rate coefficients. To answer this need, a program for the evaluation of kinetic data and for the preparation of consistently formatted data sheets patterned after the JANAF Thermochemical Tables was undertaken with the joint support of the Air Force Office of Scientific Research and the National Bureau of Standards. One such data sheet is shown in Figs. 1 and 2.

The first task of this program was to examine other approaches to data evaluation and compilation and to develop a compact format of broad utility. Succeeding tasks were to develop the methods for using theory to assess the reasonableness of the experimental measurements and to extrapolate them to higher temperatures. High-temperature data are of special interest to the Air Force, and this is the first data-evaluation program that routinely extrapolates rate coefficients for bimolecular reactions using methods more sophisticated than the familiar Arrhenius expression. Theory is also used to predict rate coefficients for important reactions for which there are no experimental data. The steps involved in preparing a data sheet will be discussed. Periodic revisions are made as new experimental data or better theoretical methods become available.

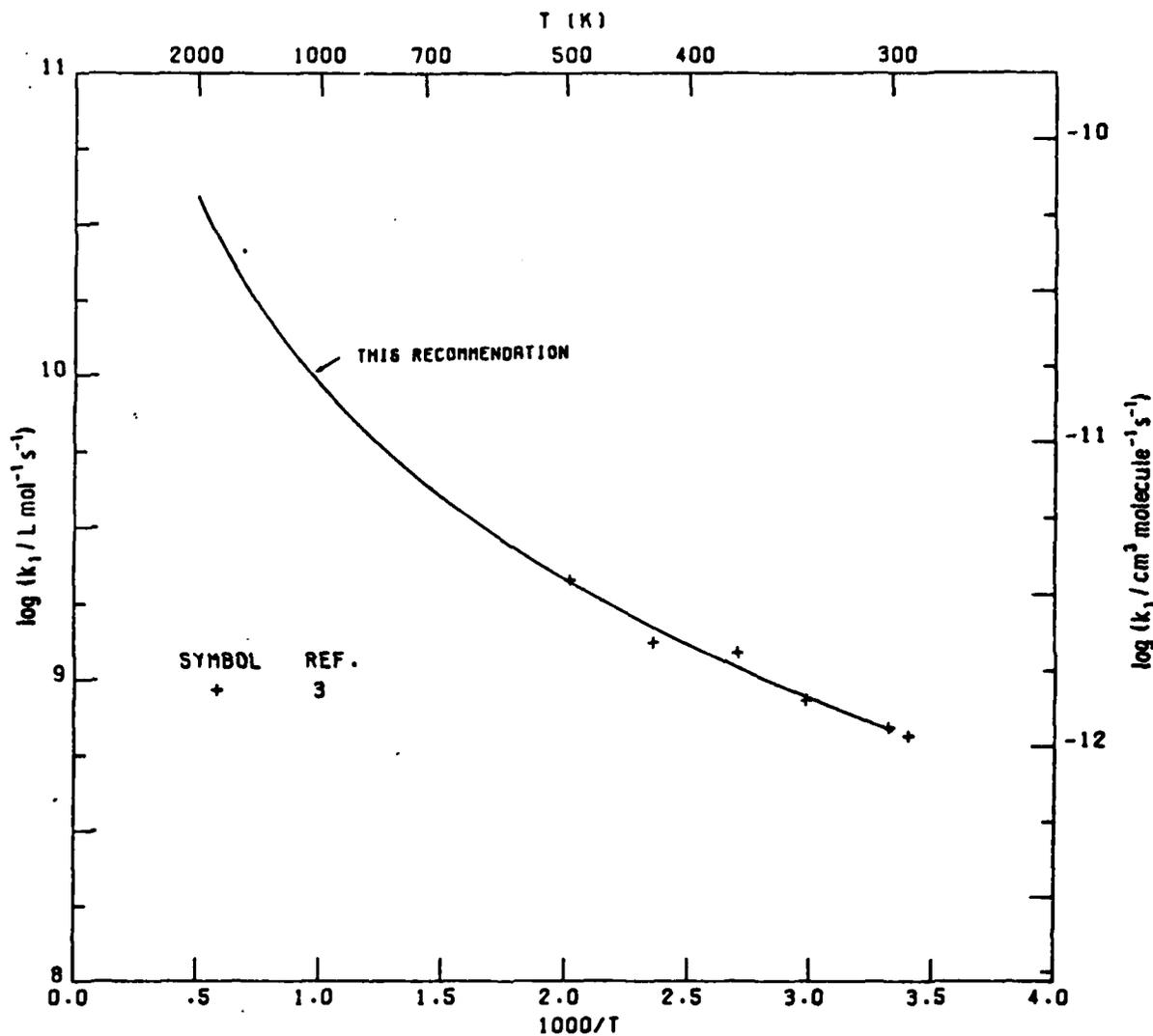
To date 35 sheets have been prepared for reactions of interest of various Air Force programs and published in a technical report. These include six reactions important in hydrogen-oxygen combustion ( $H + O_2$ ,  $O + H_2$ ,  $OH + H_2$ ,  $OH + OH$ ,  $H + H + M$  [2 sheets]); 7 in hydrogen halide chemical lasers ( $H/D + F_2$ ,  $F + H_2/D_2$ ,  $H + Cl_2$ ,  $Cl + H_2$ ); 15 in hydrocarbon oxidation ( $OH +$  methane, ethane, propane, butane, isobutane, cyclobutane, cyclopentane, pentane, isopentane, neopentane, cyclohexane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, octane, neo-octane), five in aluminum or boron propellant systems ( $Al + O_2$ ,  $AlO + H_2$ ,  $AlO + OH$ ,  $AlOH + OH$ ,  $B + O_2$ ); and two in the oxygen-iodine chemical laser ( $O_2(^1\Delta) + O_2(^1\Delta)$  and  $O_2(^1\Delta) + I(^2P_{1/2})$ ). Ten more involving other reactions of  $OH$  and  $O$  atom attack on hydrocarbons, halogenated methanes, and  $NH_3$  are in progress. These reactions range from those for which experimental data are plentiful to those for which no data are available.

The preparation of the series of data sheets for  $OH +$  alkane reactions was accompanied by theoretical efforts to develop a method for using transition state theory to extrapolate experimental data to higher temperatures. The theoretical approach for reactions with such large molecules is quite different from what can be done with simple reactions, such as  $F + H_2$ , for which reliable a priori potential energy surfaces are available. The  $OH +$  halogenated methane reactions provide a good test for the extension of this approach to a broader class of  $H$  abstraction reactions.



$$\Delta H_{298}^{\circ} = -90.8 \pm 4 \text{ kJ mol}^{-1} \text{ (-21.7 kcal mol}^{-1}\text{)}$$

$$\Delta S_{298}^{\circ} = 26.0 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (6.2 cal mol}^{-1} \text{ K}^{-1}\text{)}$$



RECOMMENDED RATE COEFFICIENTS

<u>k</u>	<u>k(T)</u>	<u>Range</u>	<u>k(298)</u>	<u>Units</u>
$k_1$	$1.0 \times 10^4 T^{2.0} \exp(-90/T)$	300-2000 K	$6.9 \times 10^8$	$\text{L mol}^{-1} \text{s}^{-1}$
	$1.7 \times 10^{-17} T^{2.0} \exp(-90/T)$		$1.1 \times 10^{-12}$	$\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$

Uncertainty in  $\log k_1$ :  $\pm 0.2$  for 300-750 K, increasing to  $\pm 0.4$  at 2000 K. Because the reverse reaction will be unimportant at any temperature, values for  $K(T)$  and  $k_{-1}$  are not recommended.



#### THERMOCHEMISTRY

Thermochemical data for  $\text{H}_2\text{O}$  are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for  $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3$  (2,2,3,3-tetramethylbutane, or neo-octane) are taken from Stull et al.<sup>1</sup> Data for the neo-octyl radical are taken from Kerr and Parsonage.<sup>2</sup> An analytic expression for  $K(T)$  has not been calculated because the reverse reaction will never be important: at low temperatures it is too endothermic to occur, and at high temperatures the neo-octyl radicals are unstable.

#### MEASUREMENTS

Only one experimental study of this reaction has been reported. Greiner<sup>3</sup> measured  $k_1$  over the temperature range of 294-495 K using flash photolysis of  $\text{H}_2\text{O}$  as an OH source, monitoring OH disappearance by kinetic absorption spectroscopy. His results for other alkanes, obtained by the same technique, are in good agreement with those reported by other workers.

#### CALCULATIONS

Transition state theory (TST) calculations were carried out for  $k_1$  in order to extrapolate the rate coefficient beyond the temperature range of the experimental data.  $S^\ddagger(300)$  was estimated to be  $475.7 \text{ J mol}^{-1}\text{K}^{-1}$  by group additivity methods, using neo-octane as a model compound.<sup>4</sup> Vibrational frequencies were taken to be the same as for neo-octane except for the removal of a C-H stretch ( $3100 \text{ cm}^{-1}$ ) an HCH bend ( $1400$ ) and a CCH bend ( $1100$ ); and the addition of the following frequencies:  $3700$  (OH stretch),  $2200$  (C-H stretch);  $1000$ ,  $800$ ,  $600$ , and  $600$  (deformations). The two new internal rotors were assumed to have partition functions  $Q_r(300) = 8.8$  and  $6.2$ , and barriers to rotation  $V = 8.4$  and  $4.2 \text{ kJ mol}^{-1}$ , respectively. The electronic degeneracy of the activated complex,  $g_a^\ddagger$  was assumed to be 2. The resulting values of  $k_1(T)$  are well-fitted by the expression,  $k_1 = 1.0 \times 10^4 T^{2.0} \exp(-90/T) \text{ L mol}^{-1}\text{s}^{-1}$ , in good agreement with the other data of Ref. 3.

#### DISCUSSION

Neo-octane, like neopentane, is of theoretical interest because it contains only primary H atoms, so there is only one product of the OH attack. Using the "universal" rate coefficient of Baldwin and Walker<sup>5</sup> (adjusted with our own recommended value for  $k_{\text{H}_2+\text{OH}}$ ) we calculate  $k_1 = 4.2 \times 10^6 T^{1.3} \exp(-765/T)$ , which agrees, within 50% for 300-2000 K, with the TST result described in the above section. We therefore recommend the expression  $k_1 = 1.0 \times 10^4 T^{2.0} \exp(-90/T) \text{ L mol}^{-1}\text{s}^{-1}$  over the temperature range of 300 - 2000 K, with an uncertainty in  $\log k_1$  of  $\pm 0.2$  up to 750 K, increasing to  $\pm 0.4$  at 2000 K.

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RESONANT CARS DETECTION OF OH RADICALS

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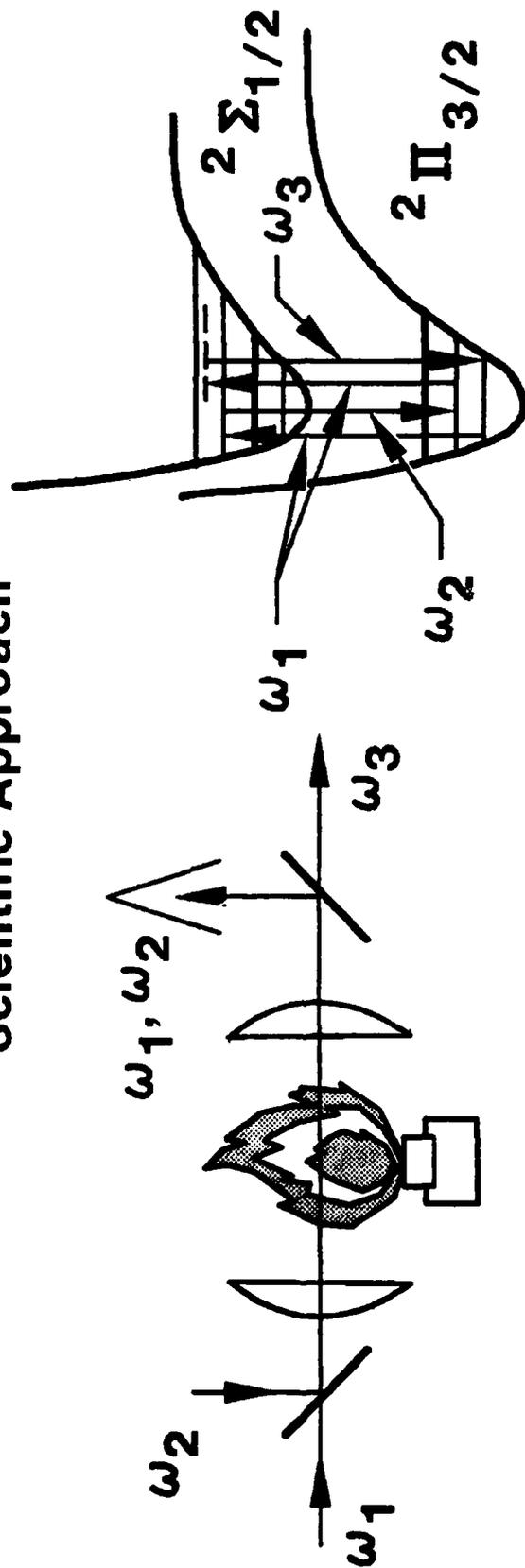
Coherent anti-Stokes Raman spectroscopy (CARS) is an important spectroscopic technique which fulfills several requirements (good spatial and temporal resolution, remote, non-perturbing, good accuracy and high pressure capability) for probing hostile environments that are of primary interest to the Air Force. Demonstrated examples include CARS measurements of temperature and concentration of burning rocket propellants and gas turbine engines. CARS is a coherent, nonlinear-optical process in which beams of different frequencies,  $\omega_1$  and  $\omega_2$ , mix together in a material medium to generate a new frequency,  $\omega_3$ , which appears as a laser-like beam. At atmospheric pressure, normal CARS methods are limited to species whose concentration is about 1 percent or greater. The scientific question which this program addresses is, can CARS diagnostics be extended to minority species, e.g., OH, by means of electronically resonant CARS?

The hydroxyl radical was chosen as a candidate molecule because of its extreme importance in combustion and atmospheric chemistry. The overall goal is to observe resonant CARS in OH, and then to explore the improvement in minor species detectivity attainable with electronic resonance enhancement. Achievement of this goal requires an understanding of the physics of electronic resonant CARS spectroscopy which includes the effect of tuning through the resonance, laser linewidth dependence, choice of electronic transition, and saturation considerations. Additionally, the subject of multiple electronic resonances, e.g., combinations of  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  electronically resonant, must be investigated and compared with the singly electronically resonant case. Finally, a quantitative assessment of the CARS detectivity limit for OH must be made.

At UTRC, late in 1982, the first observation of resonance CARS in OH was made. The amplitude of the OH CARS spectrum was very sensitive to the precise tuning of  $\omega_1$  to the OH electronic resonance. The shape of the OH CARS spectrum remained essentially the same, apart from the expected shift, when  $\omega_1$  was tuned to resonance with  $Q_1(14)$  of  $2\Pi_{3/2}(V=0)-2\Sigma_{1/2}(V=1)$  rather than  $P_1(9)$ . The most striking feature of the OH resonant CARS spectrum is its much greater amplitude than the adjacent conventional CARS  $H_2O$  spectrum. This is especially impressive when it is noted that in the  $CH_4/O_2$  flame the  $H_2O$  concentration may be four to five times that of OH, and that the CARS signal scales as the square of the concentration. For these reasons, the  $H_2O$  CARS spectrum should completely dominate the OH CARS spectrum. That the reverse situation is observed strongly indicates that electronically resonant CARS will improve the detectivity of minority species, such as OH, in combustion environments.

# RESONANT CARS DETECTION OF OH RADICALS

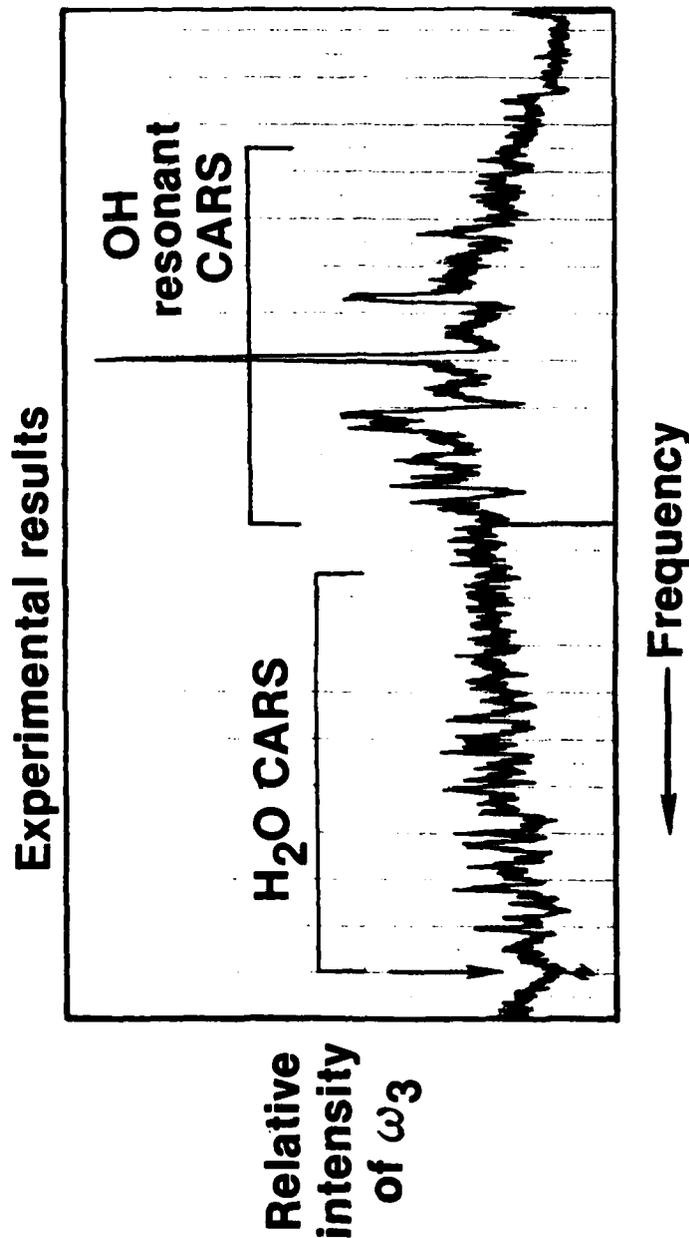
## Scientific Approach



## GOALS

- Improve CARS species detectivity via electronic enhancement
- Study the physics of resonant CARS spectroscopy
- Investigate multiple electronic resonances
- Determine the CARS detectivity limit for OH

# RESONANT CARS DETECTION OF OH RADICALS



- First observation of resonant CARS in OH
- OH CARS spectrum stronger than that of H<sub>2</sub>O
- CARS signal for OH sensitive to  $\omega_1$  tuning
- OH CARS spectra similar for different  $\omega_1$  resonances

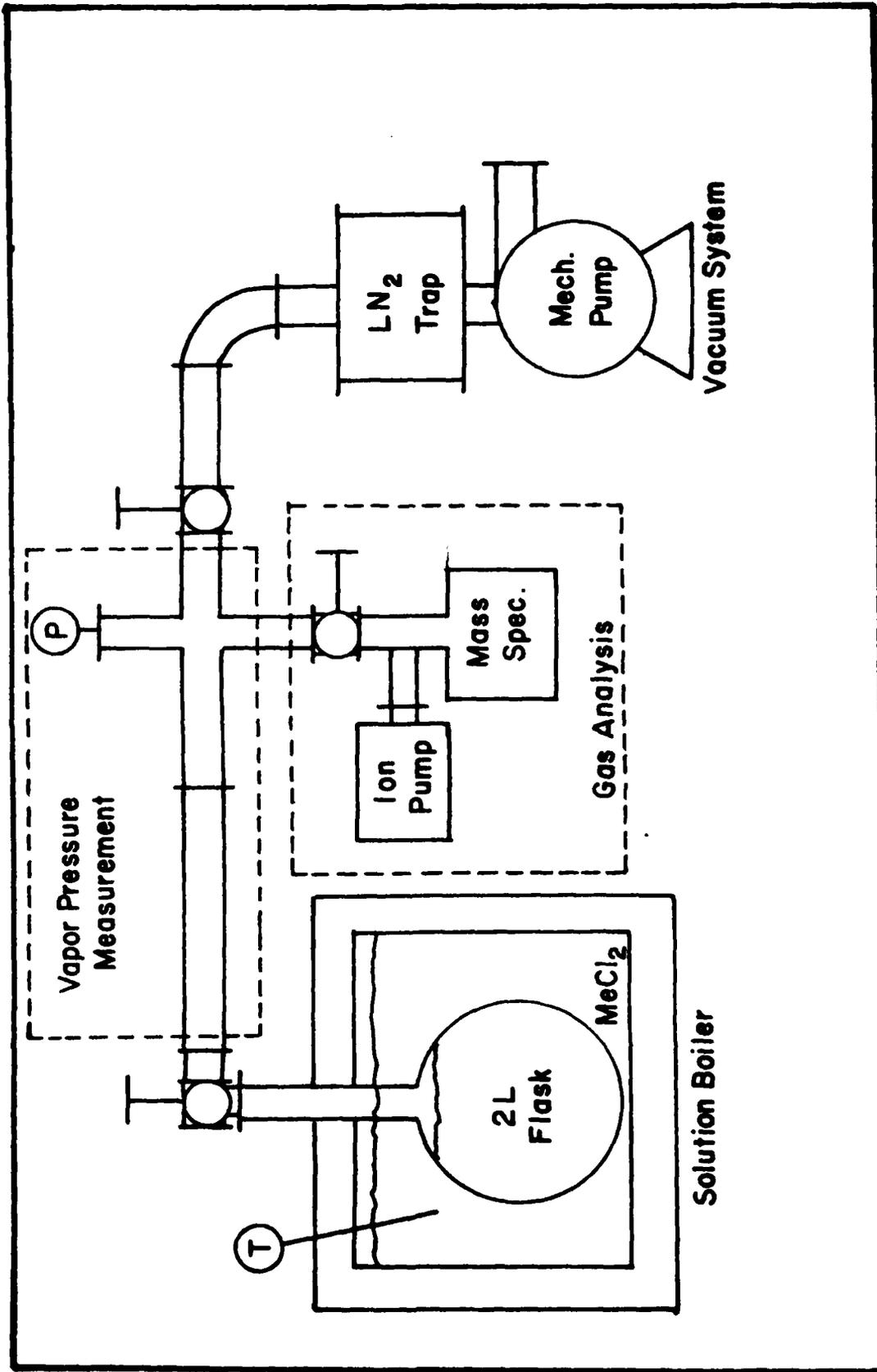
THE VAPOR PRESSURE OF SALT-HCl-WATER  
SOLUTIONS BELOW 0C

Eugene Miller  
University of Nevada  
Mackay School of Mines  
Reno, Nevada

Secondary smoke which forms in the plumes of reduced smoke solid rockets is comprised of hydrochloric acid droplets. The equilibrium vapor pressures of hydrochloric acid solutions are fundamental to the development of this smoke. Inorganic salts introduced into the propellant formulation as processing aids, burn rate modifiers or contaminants nucleate the condensation of droplets, dissolve in the acid significantly modifying its vapor pressure and hence the incidence and density of the smoke. No vapor pressure data existed for temperatures below 0C before the present AFOSR sponsored work for either pure or salted hydrochloric acid solutions. In addition, extrapolations of existing data from temperatures above 0C were unsatisfactory.

Sodium and calcium chloride salts were selected for the study since they are the major salts present in the plume which impact on the vapor pressure of the hydrochloric acid smoke droplets. As shown in Figure 1, the total equilibrium pressures for selected solutions were measured by means of sensitive capacitance gauges. The solutions were contained in a 2-liter pyrex flask immersed in a methylene chloride bath cooled by a two-stage mechanical refrigeration system. Removal of air from the flask and ducts was accomplished by means of a mechanical vacuum pump in series with a liquid nitrogen trap. Vapor compositions were determined using a quadrupole mass filter spectrometer (VGA). Liquid sample compositions were measured with an electroconductometric bridge using appropriate standards.

During the last year, the full range of acid compositions with intermediate concentrations of sodium chloride was completed supplementing the previous measurements for saturated solutions. A trend chart showing the effect of dissolved NaCl on the vapor pressures of H<sub>2</sub>O and HCl for the range of salt molalities and acid concentrations covered in the study is given in Figure 2. In general for saturated solutions, the effect of dissolved NaCl is to decrease the vapor pressure of H<sub>2</sub>O (except for 12N acid) and to increase that of HCl. This would mean a possible increase in secondary smoke for all smoking conditions for reduced smoke propellants except at very low ambient temperatures where the droplet acid concentrations would be the highest. For lower acid concentrations and intermediate NaCl molalities, the vapor pressure and smoke characteristics are the same as for the saturated solutions, but for higher acid concentrations the vapor pressures of both the water and HCl are greater than those of the unsalted solutions suggesting less smoke formation at the onset. Additional measurements for acid containing calcium chloride have been initiated.



**FIGURE 1**  
**Schematic of Experimental Apparatus**

SOLUTION VAPOR PRESSURE & SECONDARY SMOKE TRENDS  
FROM 0 TO -40C:REDUCED SMOKE PROPELLANTS

<u>Nominal Acid Normality (calc. @ room temp.)</u>	<u>Decreasing NaCl Molality @ Saturation</u>	Partial Pressure Ratio, NaCl Sol'n: Pure HCl Sol'n $\frac{H_2O \text{ \& \; } HCl}{m_{NaCl}}$ , intermediate/saturated
2	↓	-    /.LT.1 & .GT.1 /(More Smoke)
4		.LT.1 & .GT.1/.LT.1 & .GT.1 (More Smoke) / (More Smoke)
6		.EQ.1 & .LT.1 / .LT.1 & .GT.1 (Same Smoke) / (More Smoke)
8		.GT.1 & .GT.1 / .LT.1 & .GT.1 (Less Smoke) / (More Smoke)
10		.GT.1 & .GT.1 / .LT.1 & .GT.1 (Less Smoke) / (More Smoke)
12		-    /.GT.1 & .GT.1 /(Less Smoke)

Figure 2

FLOW OF GAS PARTICLE MIXTURES

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Department of Mechanical Engineering  
University of Colorado  
Boulder, Colorado

Abstract

This report summarizes studies being conducted to characterize the flow of a gas-particle mixture in an axisymmetric jet (Figure 1). Previous studies have included development of a flexible two-phase flow experimental facility and development and utilization of an optical technique for measurement of particle concentration profiles. Other diagnostic methods were used to measure gas velocity and temperature profiles and particle size distribution. More recently, experimental data and interpretation of those results have been completed for heat and mass transfer in an axisymmetric gas-solid two phase jet. The average values of turbulent gas Prandtl number and turbulent particle Schmidt number were derived from the measurements and used in interpretation of results. These dimensionless numbers are expressed as a function of the density ratio between the particle flow and the gas and as a function of Reynolds number. An important result is the finding that heavier particles disperse faster than lighter particles in the two-phase jet flows. A simplified treatment of the interaction between solid particles and turbulent eddies gave results which supported the conclusions of the experimental study.

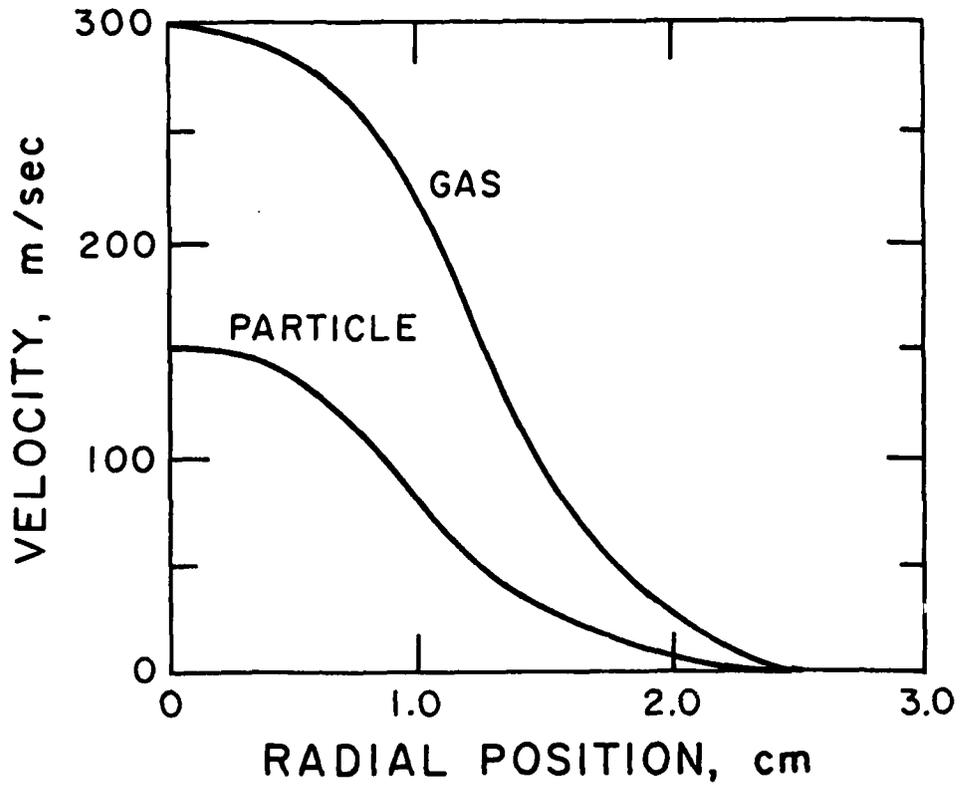
A dual beam, self-aligning LDV system is under development to measure the particle velocities. The system which is used in our experiments has a commercially available TSI counter-type signal processor. This signal processor serves as a high frequency filter which identifies and validates individual particle doppler bursts and calculates the frequency and hence corresponding particle velocity of the bursts. The data rate from the signal processor is very rapid and these data must be averaged externally to the signal processor. The electronics which is under development provides this data logging, averaging and statistical analysis.

The principal challenges presented by these investigations are the very high (~300 MHz) doppler signals characteristic of the optical arrangement used and the tradeoff between doppler frequency and spatial resolution. Heavily particle laden jets have additional problems of overlapping doppler bursts which must be separated from single particle bursts for accurate data interpretation. It is also clear from our earlier investigations that the particle velocities and trajectories are significantly different than the gas velocity for large (greater than 10  $\mu\text{m}$ ) particles (Figure 2).

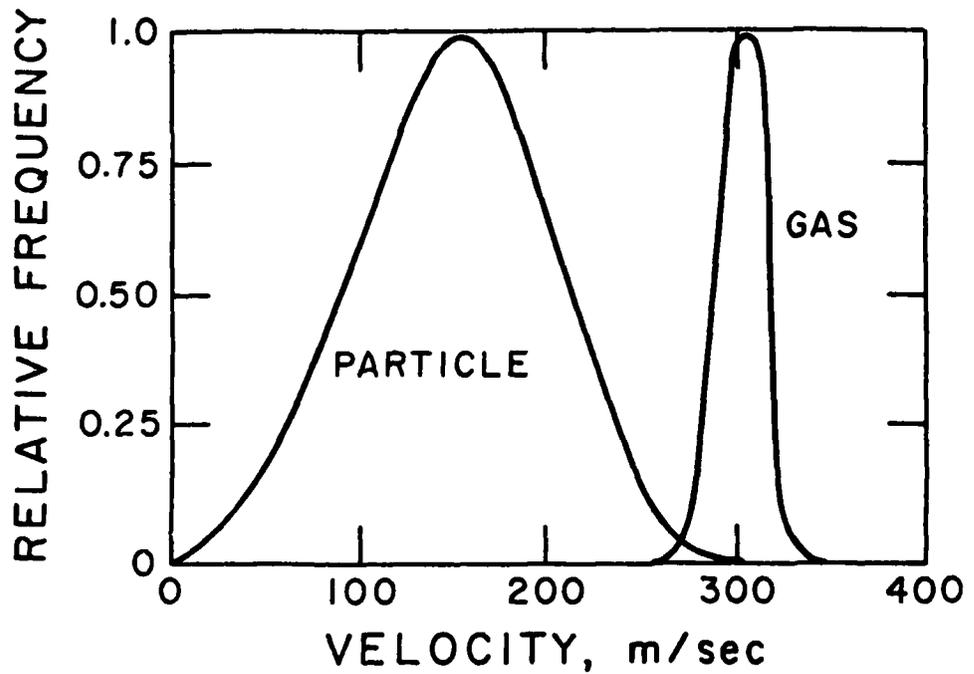
Figure 1

OUTLINE OF SCIENTIFIC APPROACH

- Program Goals: Improved understanding of two-dimensional mixing of solid-gas two-phase flows at shear flow interfaces
- Scientific Method:
- (a) Detailed experimental characterization of shear layer under well characterized laboratory conditions
  - (b) Comparison of experimental data to advanced computational techniques to evaluate computational accuracy
  - (c) Extension of computational methods to rocket nozzle and plume flows for which experimental data are not available
- Areas of Importance of Research Results:
- (a) Nozzle flow of rocket engines with metallized propellants
  - (b) Exhaust plumes of metallized rocket propellants
  - (c) Fluid dynamic mixing processes which might influence metal oxide condensation or agglomerate formation



(a)



(b)

Figure 2. Gas and particle velocity in jet.  
(a) Radial profiles, (b) Velocity distribution. Expected results of measurements.

ELECTROLYTIC PREPARATION OF NOVEL AZIDODINITRO COMPOUNDS\*

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Improved performance still remains the top priority for the Air Force's tactical and space propellants. More energetic ingredients in terms of oxidizers, plasticizers, and polymers, which have acceptable physical properties, are necessary to fulfill this requirement.

Polynitro compounds have proven to be very useful ingredients for all types of propellant and explosive applications. Compounds of the 1,1-dinitro-methyl class  $[RC(NO_2)_2X, X = NO_2, CN, CH_3, F]$  have been of particular interest for these applications. In the continued search for energetic compounds with high oxygen content, the 1,1,1-azidodinitro compounds ( $X = N_3$ ) appears to be particularly attractive since the azido moiety contributes a positive 80 kcal of energy without detracting from the overall oxygen content. A basic research program will be conducted on the electrolytic synthesis of 1,1,1-azidodinitro compounds by the reaction of 1,1-dinitro compounds with azide ion. This technique is considered to be the most feasible one for obtaining the desired type of reactions.

\* Start Date of February 1983

SCIENTIFIC APPROACH

BACKGROUND

- 1,1,1-AZIDODINITROALKANES PREPARED ELECTROLYTICALLY\*



COMPOUNDS POSSESS REASONABLE PHYSICAL PROPERTIES  
(IMPACT SENSITIVITY AND THERMAL STABILITY)

- PREPARATION OF 1,1,1-AZIDODINITROETHANE VERIFIED
- THEORETICAL PERFORMANCE CALCULATIONS CONFIRMED SIGNIFICANT PERFORMANCE GAIN WITH POSTULATED AZIDODINITRO COMPOUNDS

\* C. M. WRIGHT, U.S. PATENT 3,883,377, 13 May 1975

ANTICIPATED PROGRAM RESULTS

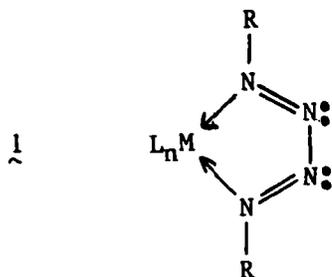
- SYNTHESIS OF PARENT 1,1-DINITRO COMPOUNDS
- BASIC STUDIES ON ELECTROLYTIC AZIDE SUBSTITUTION OF 1,1-DINITROETHANE
  - SOLVENT SYSTEM
  - ANODE REACTION OF AZIDE ION
  - ANODE REACTION OF 1,1-DINITROETHANE ANION
  - ANODE REACTION OF COMBINED 1,1-DINITROETHANE AND AZIDE ANIONS
- BASIC ELECTROCHEMICAL STUDIES ON AZIDE SUBSTITUTION OF OTHER MODEL COMPOUNDS
  - ETHERS, NITRAMINES
- ELECTROLYTIC SYNTHESIS OF TARGET COMPOUNDS
  - $\text{CH}_2 - [\text{OCH}_2\text{C}(\text{NO}_2)_2\text{N}_3]_2$
  - $\text{O}_2\text{NN}-[\text{CH}_2\text{C}(\text{NO}_2)_2\text{N}_3]_2$
  - $\text{N}_3(\text{NO}_2)_2\text{CC}(\text{NO}_2)_2\text{N}_3$
  - $\text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{N}_3$   


SYNTHESIS AND CHEMISTRY OF ENERGETIC METALLOTETRAAZADIENES

William C. Trogler

Chemistry Department, Northwestern University  
Evanston, Illinois 60201

Metallotetraazadienes, 1, contain an unsaturated transition metal-nitrogen ring and an usually high M/N ratio for a low valent organometallic complex



L = a ligand; e.g. CO

M = a transition metal; e.g. Fe, Co, Ti

R = alkyl, aryl, or SiR<sub>3</sub>

Until we began a systematic study of the synthesis, structure, photochemistry and electronic structure of metallotetraazadienes, there was little known about the chemistry and physical properties of these unusual molecules. Our interest was prompted by the expected high-energy content of these compounds; the metal free R-N=N=N-R moiety is unknown. Tetraazadiene complexes have often been prepared by the reaction between an organic azide, such as CH<sub>3</sub>N<sub>3</sub>, and a metal carbonyl. Therefore, we expected much of the energy content of the parent azide to be retained in the metal complex.

Metallotetraazadienes may find obvious application as propellents themselves or as binders for unstable organic azides. Less obvious applications include their use as burn modifiers for nitrogen-based fuels, and as a source of new nitride composites and films. Their chemistry also provides information about the metal catalyzed decomposition of unsaturated nitrogen compounds.

Three strategies for the synthesis of new metallotetraazadienes and related ring systems are proposed (Figure 1): 1) the reaction of organic azides with dinitrogen complexes, and labile hydride or phosphite compounds; 2) the reaction of 1,4-dilithio(bis(trimethylsilyl)tetrazene) with metal dihalide complexes; 3) 1,3-dipolar cycloaddition of organic azides to metal-nitrene, metal-alkylidene, and metal-alkylidyne moieties. Our synthetic targets include early transition metal tetraazadiene complexes, which are expected (on theoretical grounds) to be less stable and more reactive than the presently known late transition metal complexes. After preparing and characterizing these compounds, their photochemical and thermal decomposition reactions will be explored (Figure 2) with the goal of generating exceptionally reactive intermediates. An attempt will be made to correlate the electronic structure (from spectroscopic studies and X<sub>α</sub> calculations) of metallotetraazadienes with their reactivity. High temperature pyrolysis reactions will be studied and the solid metal-nitride products characterized. These latter materials could be conducting ceramics. In the presentation I will summarize our preliminary results.

FIGURE 1

Synthesis of New Metal-Tetraazadiene Compounds-A Three Pronged Approach:

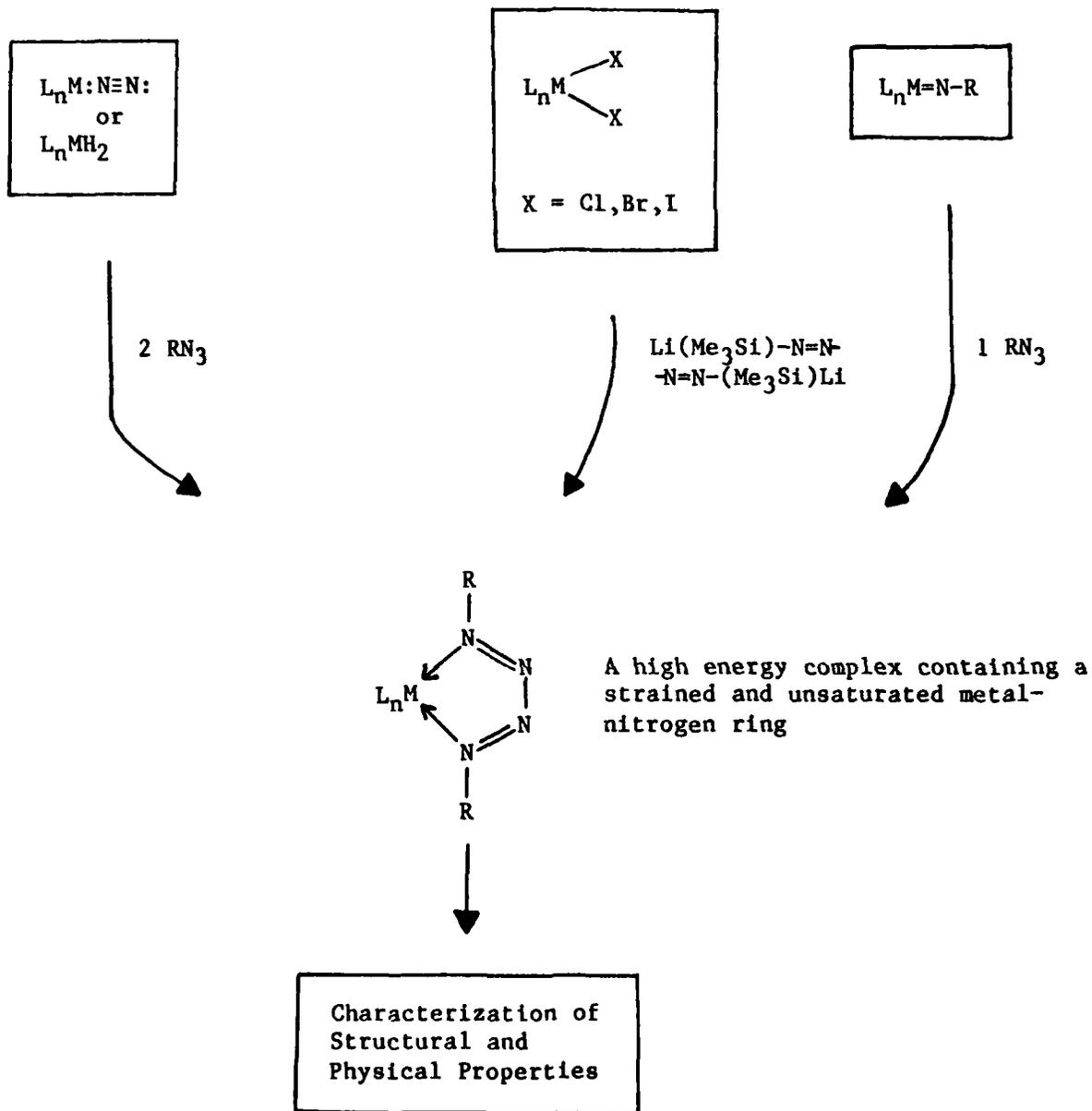
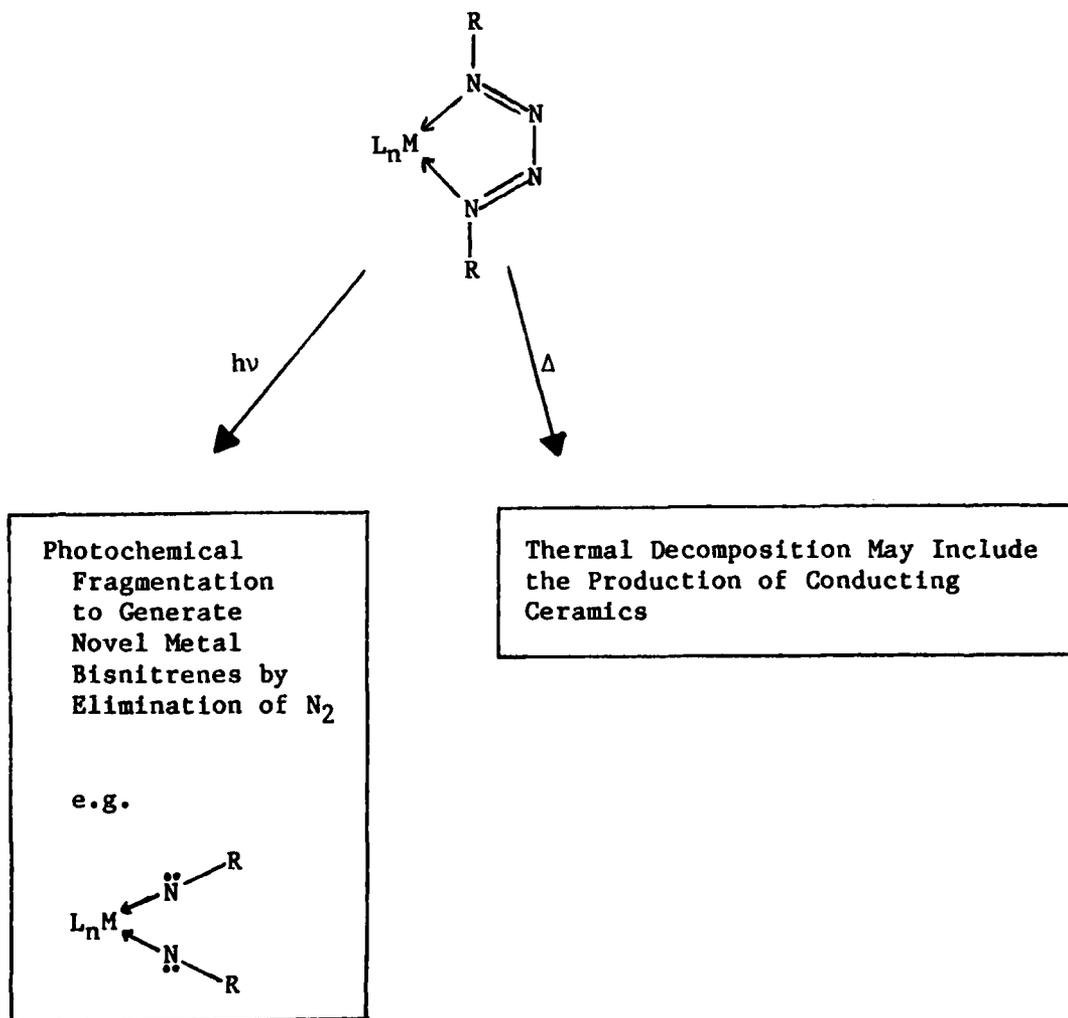


FIGURE 2

Reactivity of Metal-Tetraazadiene Complexes:



### HMX COMBUSTION MODIFICATIONS

Joseph E. Flanagan, Milton B. Frankel, Dean O. Woolery

Rocketdyne Division  
Rockwell International  
Canoga Park, CA 91304

The increasing utilization of HMX and RDX in a wide spectrum of propellant applications has resulted in a more critical need to solve the low burning rate problems associated with these cyclic nitramines.

An understanding of the decomposition mechanisms at heating rates and temperatures similar to those experienced in actual propellants is required so that the flame chemistry can be properly altered via: 1) modification of the ingredient's molecular structure; or 2) incorporation of additives which will yield decomposition products that interact with the cyclic nitramines decomposition products.

The current effort has focused upon modifying the structure of HMX to replace a nitro group with an energetic side group, such as azidomethyl, and the incorporation of energetic additives that yield reactive amidogen radicals.

1-Azidomethyl-3,5,7-trinitraza-1,3,5,7-tetrazacyclooctane (AZMTTC) was successfully prepared via the utilization of the unique reagent acetyl azide. However, incorporation of AZMTTC into a standard HMX propellant did not result in a large increase in burning rate. Pyrolysis studies on pure AZMTTC indicated that large quantities of  $N_2O$  and  $CH_2O$  were produced in the region 300 to 800°C.

Utilization of the di-TAG salt of azobistetrazole (TAGZT) has yielded the best increases in burning rate. TAGZT produces high quantities of  $NH_3$  molecules upon decomposition.

Salient features of TAGZT incorporation are:

- 1.) At 1000 psi the acceleration in burn rate is constant despite binder type ( $H_{ex} = -1500 \rightarrow +700$  cal/gm).
- 2.) HMX particle size does not affect the acceleration rate.
- 3.) At 250 psi, RDX is accelerated twice as much as HMX which may be due to the closer matching of decomposition temperatures and longer flame zones.

Utilization of TAG-5AT yielded very little acceleration of HMX, but a 50-percent increase in RDX. This again is thought to be related to a mismatch of decomposition temperatures.

Pyrolysis experiments with two alkali azides (Na & Li) indicated a drastic shift in HMX decomposition products. However, only a 20-percent increase in burning rate was observed.

Several other ingredients yielded decomposition products which should be highly reactive with the nitramine decomposition products, but none were nearly as effective as TAGZT.

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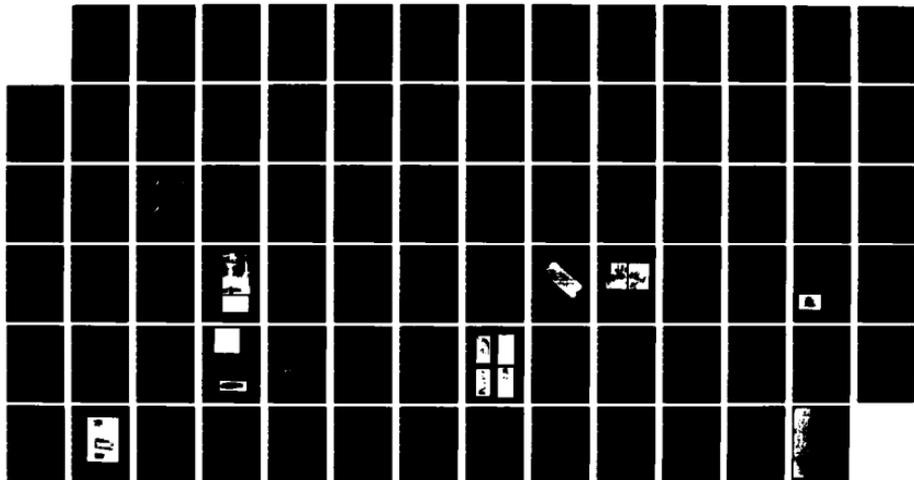
1983 AFOSR/AFRPL CHEMICAL ROCKET RESEARCH MEETING  
ABSTRACTS AND AGENDA IN. (U) AIR FORCE OFFICE OF  
SCIENTIFIC RESEARCH BOLLING AFB DC L H CAVENY ET AL.  
FEB 83 AFOSR-TR-83-0351

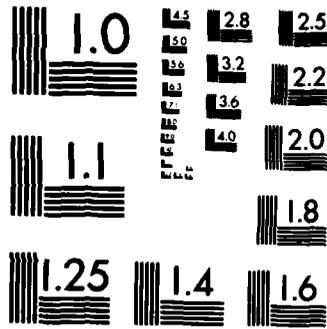
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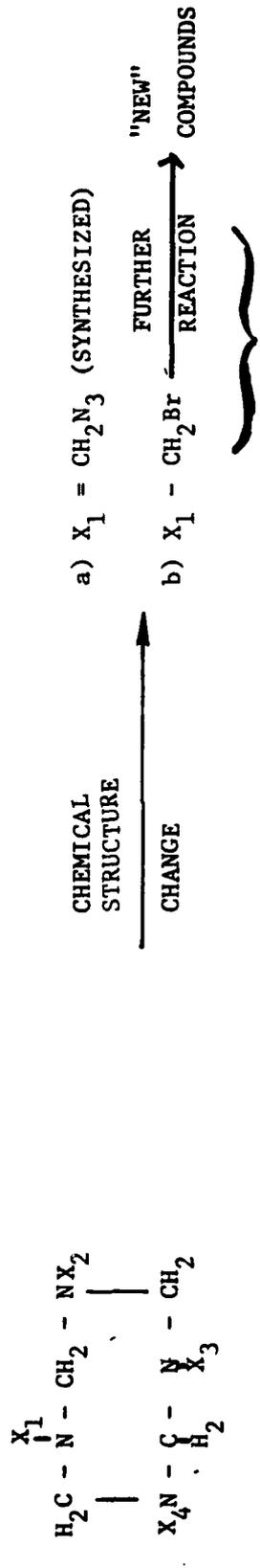
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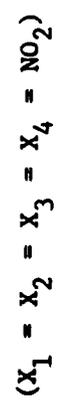


MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

SCIENTIFIC APPROACH



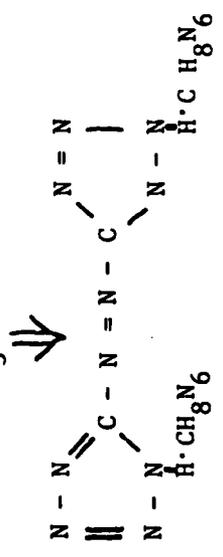
RESULT IN MODIFICATION OF CYCLIC NITRAMINE RUPTURE



HMX  
 ↓  
 DECOMPOSITION

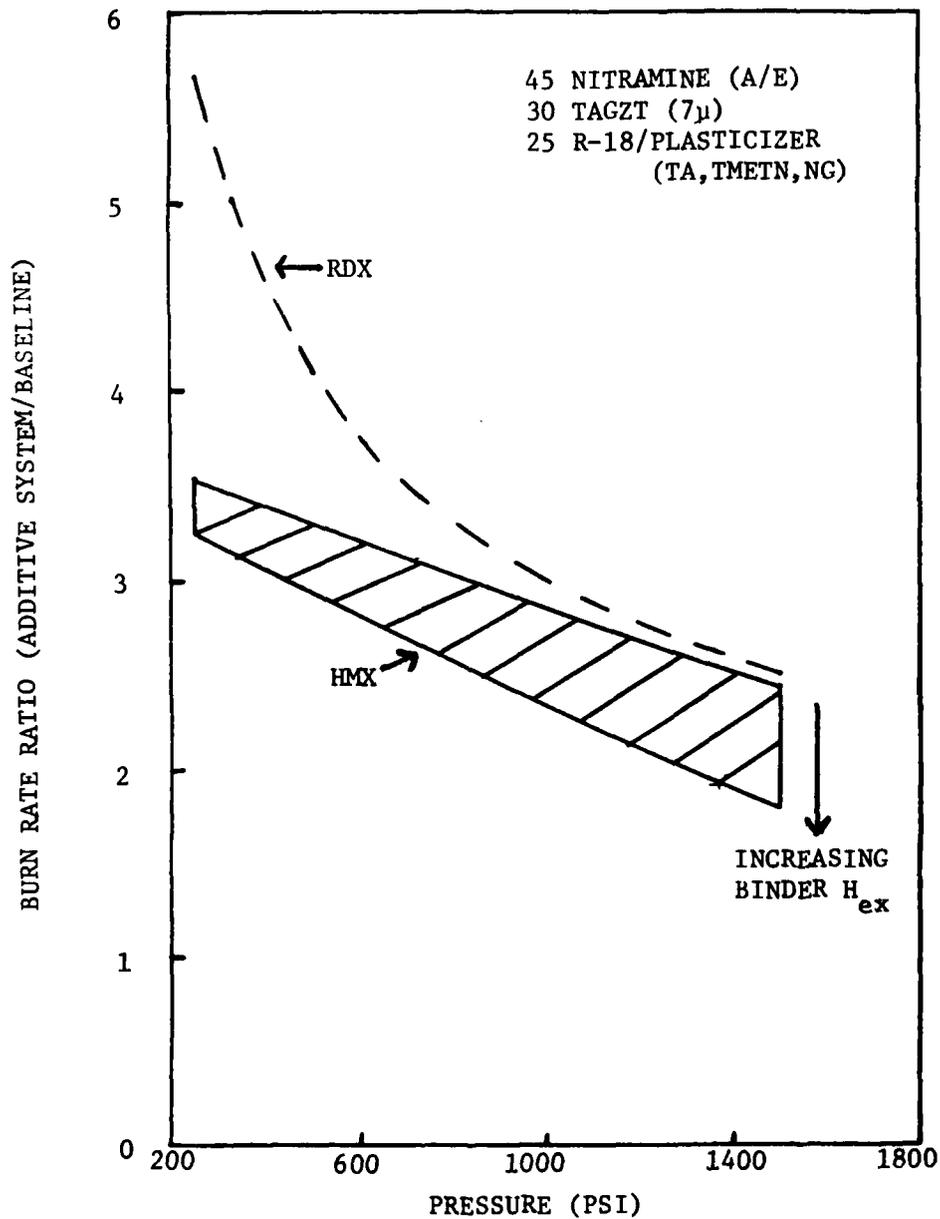
MAIN REACTIVE SPECIES  
 (NO, HCN, N<sub>2</sub>O)

REACTIVE ADDITIVE WHICH YIELDS NH<sub>2</sub> RADICAL SOURCES VIA NH<sub>3</sub> @ PROPER CONCENTRATION AND T



TAGZT

PRIMARY ACCOMPLISHMENT



THE ROLE OF SOLID PHASE PHENOMENA IN NITRAMINE PROPERTIES AND DECOMPOSITION

Thomas B. Brill, Richard J. Karpowicz and Thomas M. Haller  
Department of Chemistry  
University of Delaware  
Newark, Delaware 19711

The objective of our research has been to elucidate the molecular processes that control the important condensed phase phenomena in energetic nitramines. These processes include the rate controlling steps in the thermal decomposition, the changes in density which may produce fracturing of the particles, and the intermolecular forces that might allow incorporation of homogeneous dopants.

A number of separate approaches have been used to solve these problems. We have made extensive use of the solid phase transitions of HMX as a probe of the intermolecular forces in the crystal lattice. The kinetics of the thermally induced phase transitions have been studied by Fourier transform infrared (FT-IR) spectroscopy. The similarity between the Arrhenius parameter ( $E_a$  and  $A$ ) for the phase transitions and the values measured for decomposition suggests that the rate of phase transitions and the rate of condensed phase thermal decomposition are controlled by the same molecular process. This process is the rate at which the HMX molecules and their decomposition products can be separated from one another.

$^{14}\text{N}$  nuclear quadrupole resonance (NQR) spectroscopy has been used to learn about the relative amount of molecular motion in solid RDX compared to HMX. The temperature dependence of the  $^{14}\text{N}$  NQR frequencies is related to the torsional oscillations in the solid. The results show that more molecular motion exists in RDX than occurs in HMX. We conclude from this that the decomposition of RDX in the condensed phase is less subject to the lattice phenomena than is HMX.

Single crystal X-ray diffraction of HMX solvates is being conducted to learn how the HMX lattice is able to accommodate dopants. A new polymorph of the complex between HMX and DMF (N,N-dimethylformamide) has been discovered. In keeping with the extensive polymorphism for HMX, the solvates of HMX appear to exhibit the same tendency.

Using FT-IR spectroscopy we have been able to observe spectroscopically for the first time the elusive  $\beta$  polymorph of RDX. We do not believe that  $\beta$ -RDX is important in the thermal decomposition of the nitramine because we have not been able to generate it in the absence of thymol. However, the IR spectrum suggests that the material is a true polymorph and not an RDX-thymol solvate.

A recent new major research direction has been the use of rapid scan FT-IR in an attempt to identify some of the transient species in the condensed phase during high rate heating. A  $\text{CO}_2$  laser is being used to generate high heating rates. IR spectra acquisition rate of up to 50 scans  $\text{sec}^{-1}$  is being achieved.

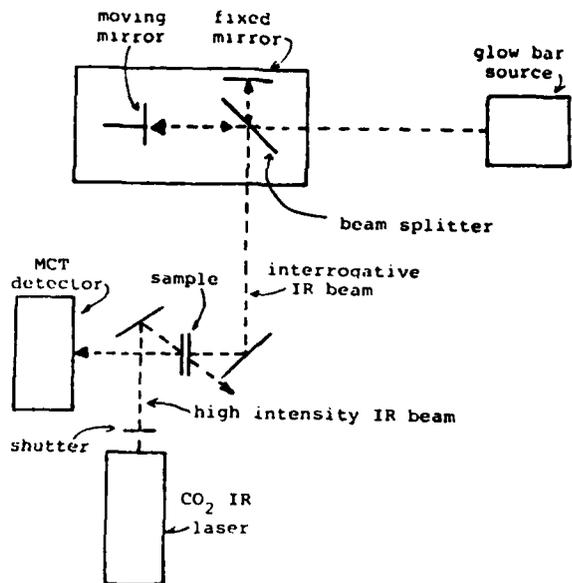
### TECHNICAL APPROACHES

UNIVERSITY OF DELAWARE

P.I.: THOMAS B. BRILL

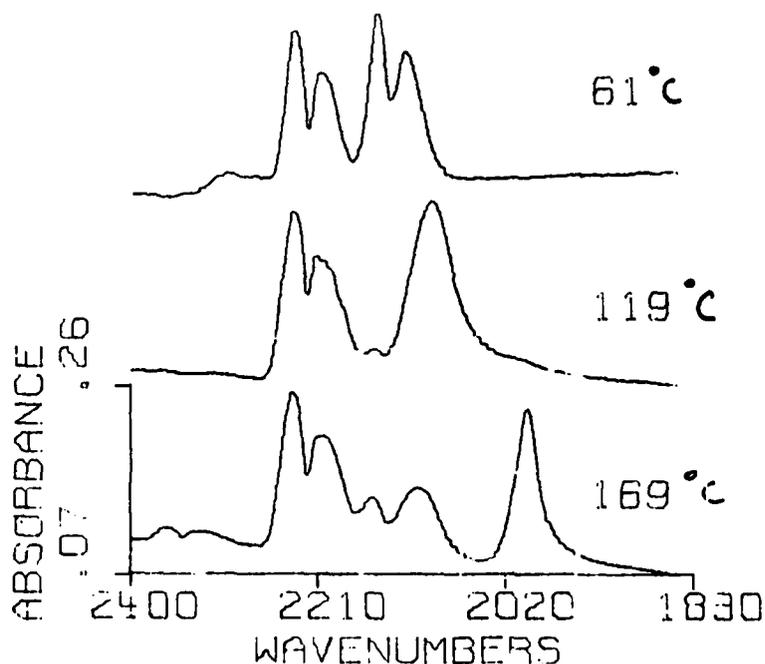
### HIGH RATE THERMAL DECOMPOSITION STUDIES BY FOURIER TRANSFORM INFERARED

#### METHODS



By bringing together two infrared beams -- a CW beam for high rate heating and a modulated beam for interrogation -- the change in molecular vibrations as a function of a rapid temperature rise can be measured. Rapid scan capabilities using an HgCdTe detector and a very high moving mirror velocity yield dynamic molecular information during fast temperature rises.

#### RESULTS (PRELIMINARY)



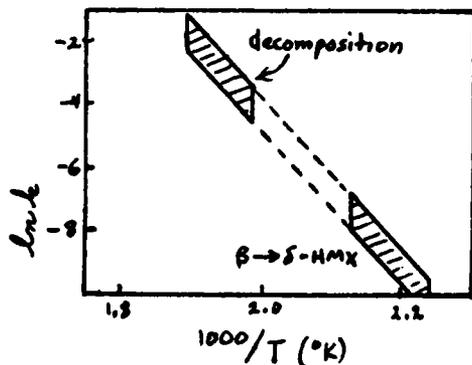
Dramatic spectral changes with temperature are being observed with some nitramine complexes. N-methylazido-3,5,7-trinitrotetrazocyclooctane recently synthesized at Rocketdyne shows substantial differences as the temperature increases. We are in the process of identifying the condensed phase chemical species. Polymorph transitions and chemical reactions are being observed in situ.

TECHNICAL ACCOMPLISHMENTS (1982)

UNIVERSITY OF DELAWARE

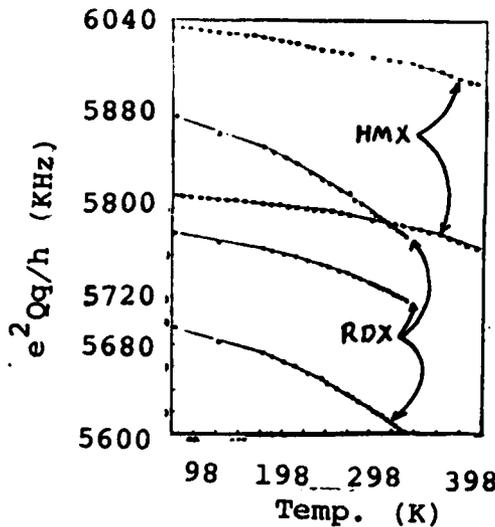
P.I.: THOMAS B. BRILL

SOLID PHASE TRANSITION KINETICS IN HMX



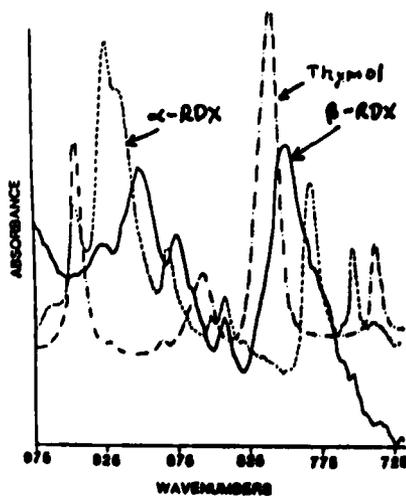
The β→δ-HMX phase transition has the same Arrhenius parameters as the condensed phase thermal decomposition. Therefore, decomposition in the condensed phase is largely controlled by the intermolecular forces.

COMPARISON OF MOLECULAR MOTION IN RDX AND HMX



The temperature coefficients for the <sup>14</sup>N nuclear quadrupole coupling constants are about twice as large for RDX as they are for HMX. This indicates that the intermolecular forces in RDX are overall less than those in HMX. Therefore, intermolecular forces play a less important role in RDX as they do in HMX.

A SECOND POLYMORPH OF RDX



Spectral evidence of the second polymorph of RDX (= β-RDX) was obtained from FT-IR studies. However, we do not feel that it is of concern in the decomposition of RDX.

SYNTHESIS OF DIFLUORAMINOXY-, DIFLUORAMINO- OR  
FLUORODIAZONIUM-CONTAINING MATERIALS

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University of Idaho  
Moscow, Idaho 83843

Future rocket propulsion advances require stable high energy propellant oxidizers. The research is concerned with the synthesis of stable, highly oxidizing compounds which contain nitrogen-fluorine bonds, such as difluoraminoxy, difluoramino, or fluorodiazonium groups and the subsequent investigation of their physical and chemical properties.

Several routes to these compound types are currently under investigation or will be attempted during the next several months.

(a) The Lewis acid catalyzed introduction of  $-ONF_2$  into F-olefins and functionalized F-olefins via reactions of  $NF_3O$ .

(b) Photolysis or thermolysis of  $N_2F_4$  with hypofluorites and/or hypochlorites to form mono or bis  $-ONF_2$  compounds,  $R_fONF_2$  or  $R_fCF(ONF_2)_2$ .

(c) Mixed  $-ONF_2$  and  $-NF_2$  compounds via F-acyl fluorides and  $HNF_2$ .

(d) Deoxygenation of N-fluoroazoxy compounds to fluorodiazonium compounds,  $R_fN=NF$ .

(e) Synthesis of  $R_fN=NR$  compounds where R is a good leaving group which can be displaced by fluorine.

(f) Metathetical reactions of difluorodiazine-Lewis acid salts with salts containing large stabilizing cations and anions of the form  $[CY_3]^-$ , where Y =  $NO_2$ ,  $NF_2$ , etc.

STABLE HIGH ENERGY PROPELLANT OXIDIZERS

NEW NITROGEN-FLUORINE-CONTAINING COMPOUNDS

PROPERTIES

STABLE

HIGHLY OXIDIZING

LARGE PERCENTAGE OF ACTIVE FLUORINE

LOW SHOCK SENSITIVITY

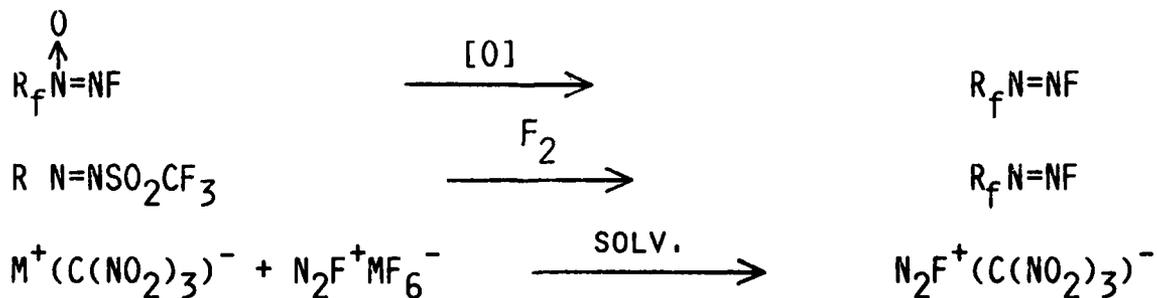
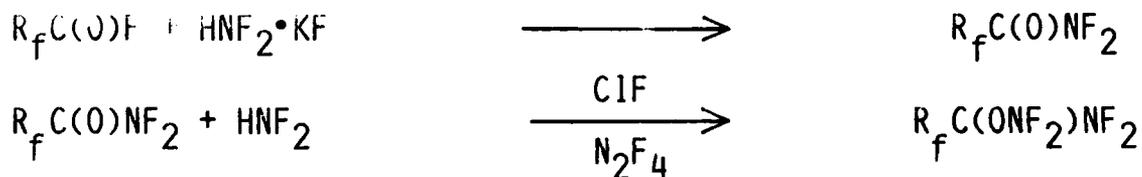
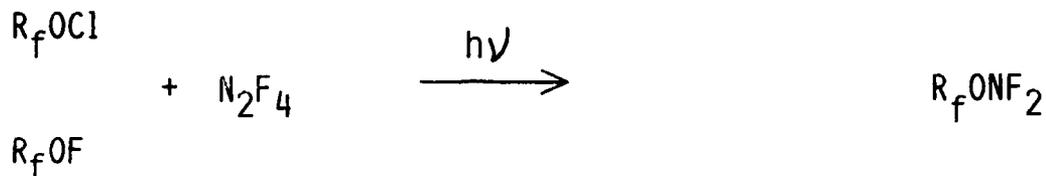
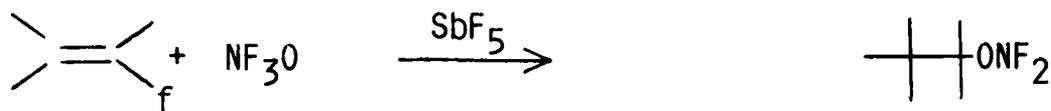
HIGH TEMPERATURE COMPATIBILITY

ROUTES

VOLATILE SIMPLE N-F MOLECULES → COMPLEX N-F SPECIES

METATHETICAL REACTIONS

OXIDIZERS



INITIAL THERMOCHEMICAL DECOMPOSITION MECHANISMS  
OF ENERGETIC INGREDIENTS: DEUTERIUM ISOTOPE EFFECTS AND  
ISOTHERMAL REACTION STUDIES

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The thermochemical decomposition mechanism and associated kinetics of selected energetic ingredients are being investigated. Special attention is being given to the very early stages of the thermochemical decomposition reactions since earlier investigations revealed that key chemical steps can occur prior to detectable exothermic activity or autocatalytic response. Deuterium isotope effects are being used in conjunction with isothermal thermochemical analysis techniques to isolate, identify and elucidate in-situ the key bond ruptures and steady-state component reactions that control the complex thermochemical decomposition process. Three tasks comprise this effort.

Task 1 The thermochemical decomposition mechanism and kinetics of deuterated and unlabeled HMX were investigated collaboratively with R.N. Rogers, J.L. Janney, and M.H. Ebinger of the Los Alamos National Laboratory. Isothermal DSC (IDSC) investigations were conducted 2-7°C below the melting point of HMX (553-548°C), and three distinct physical states resulted during the overall decomposition: a solid, a mixed melt, and a liquid phase. Three different deuterium isotope effects (DIE) were found depending upon which physical state predominated during decomposition. The solid phase produced a primary DIE indicating that C-H bond rupture was the rate-limiting step; the mixed melt phase produced an apparent inverse isotope effect; and, the liquified stage afforded a value consistent with a secondary DIE caused by ring rupture. While slow thermochemical decomposition in a lightly confined IDSC cell produced three DIE results, a more highly confined isothermal pyroprobe deflagration at similar temperatures produced only a primary DIE; but, very highly confined time to explosion (Henkin) tests provided evidence that an inverse DIE operates. Preliminary evidence suggests that the rate-determining reactions in thermochemical HMX responses may depend upon the predominant physical state that results from a given type of thermochemical event (i.e., slow decomposition, deflagration, explosive deflagration). Similar investigations are planned with RDX and DNNC.

Task 2 Isothermal DSC (IDSC) investigations of deuterated liquid TNT, HNBB, and HNS will be investigated to study systematic relationships between ingredient chemical structure and thermochemical decomposition mechanisms. Earlier IDSC/deuterium isotope effect investigations at another AF laboratory (FJSRL) revealed the thermochemical decomposition of TNT and its "dimeric" analogue (HNBB) both are controlled by C-H bond rupture. HNS is an unsaturated analogue of HNBB and is significantly more thermally stable; but, its decomposition mechanism is unknown. A mechanistic elucidation with HNS should reveal how its vinyl C-H bond structure improves thermochemical stability.

Task 3 Investigations to use elucidated thermochemical decomposition mechanisms in the modification of thermochemical rate processes is scheduled for a later start.

These three tasks address the problem of systematic thermochemical properties control via initial molecular structural design and/or chemical additive modification of inherent thermochemical decomposition mechanisms.

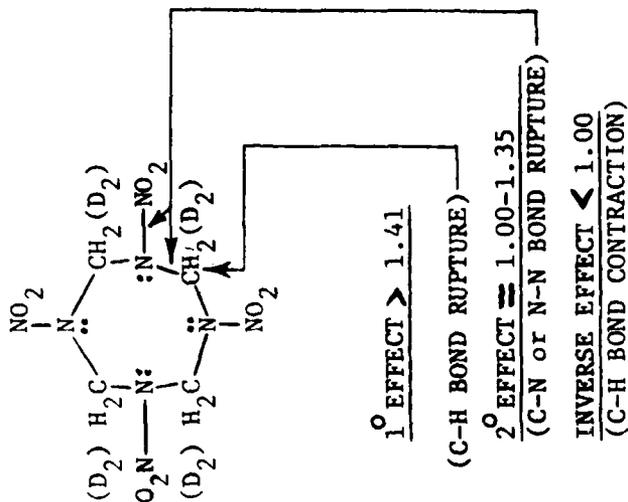
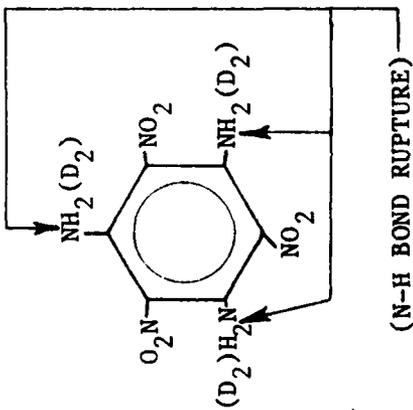
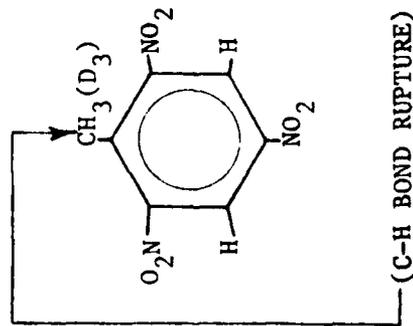
APPROACH

INITIAL THERMOCHEMICAL DECOMPOSITION MECHANISM/KINETICS ELUCIDATION → RATE-CONTROLLING STEP

- STRUCTURE/MECHANISM RELATIONSHIPS
- RATE/MECHANISM MODIFICATION

DEUTERIUM ISOTOPE EFFECTS (DIE) IN ISOTHERMAL DECOMPOSITION REACTIONS

- DIE is ratio between unlabeled (H) and deuterated (D) compounds
- (1) Reaction Rates  $k_H/k_D$  (2) Induction Times  $t_D/t_H$
- DIE Types (confirmed and possible)



TNT  
 S.A. SHACKELFORD, J.W. BECKMANN  
 AND J.S. WILKES, J. ORG. CHEM.,  
 42, 4201 (1977)

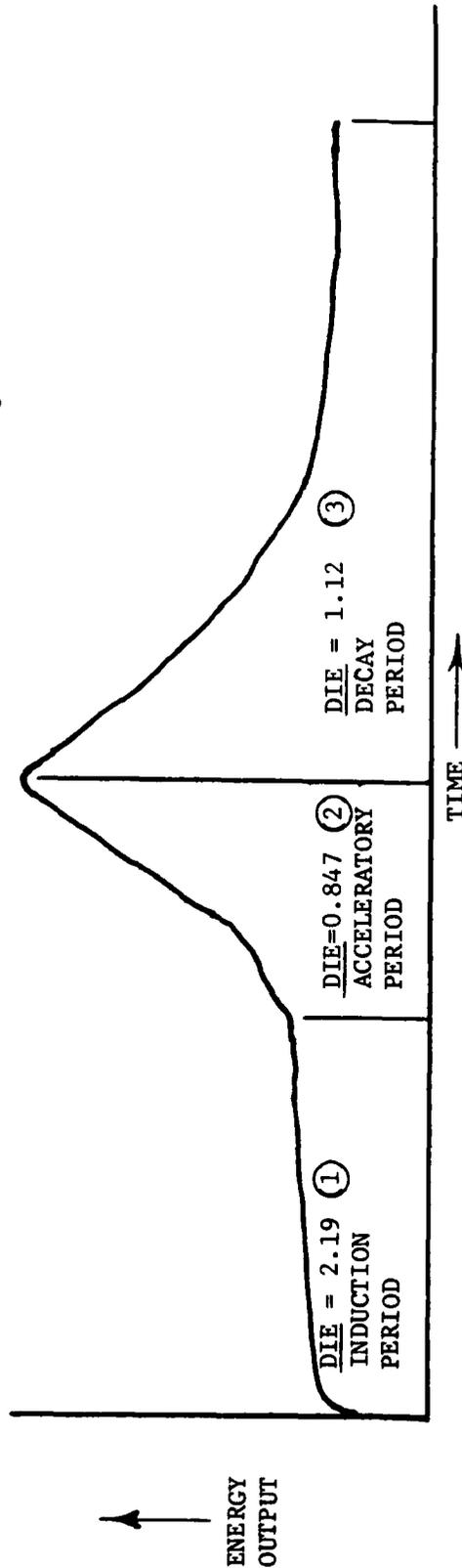
TATB  
 R.N. ROGERS, J.L. JANNEY,  
 AND M.H. EBINGER  
THERMOCHEM. ACTA. (IN PRESS)

HMX  
 ~ IN PROGRESS ~  
 (AFRPL & LANL)

RESULTS

**TASK 1: MECHANISM/KINETICS ELUCIDATION**

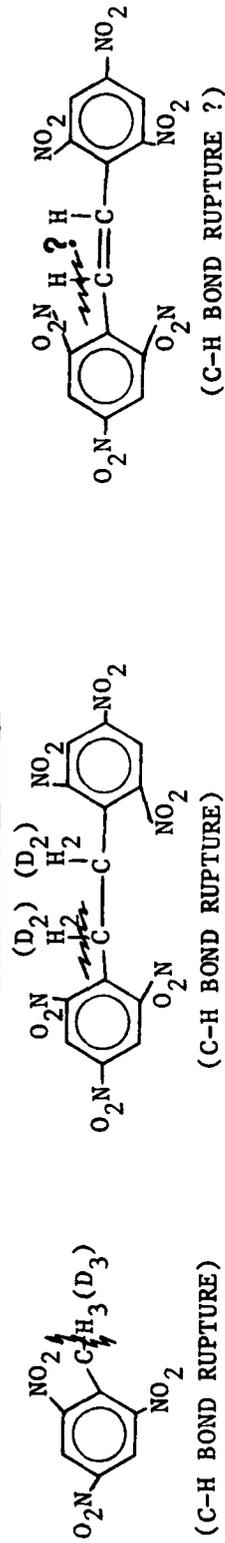
- DEUTERIUM ISOTOPE EFFECTS (DIE) IN THE ISOTHERMAL DSC SPECTRA OF HMX & d<sub>8</sub>-HMX



- CONCLUSIONS:**
- ①: C-H bond rupture, rate-controlling process
  - ②: C-H bond contraction during rate-controlling process
  - ③: C-N ring cleavage, probable rate-controlling process

- Rate-controlling process could be determined by predominant physical state
- Given thermochemical events may be driven by different physical states and, therefore, different rate-controlling mechanisms

**TASK 2: MOLECULAR STRUCTURE/DECOMPOSITION MECHANISM RELATIONSHIPS (CURRENT START)**



Examination of Polymers Containing Azide  
and Nitrate Ester Groups

Stan Morse

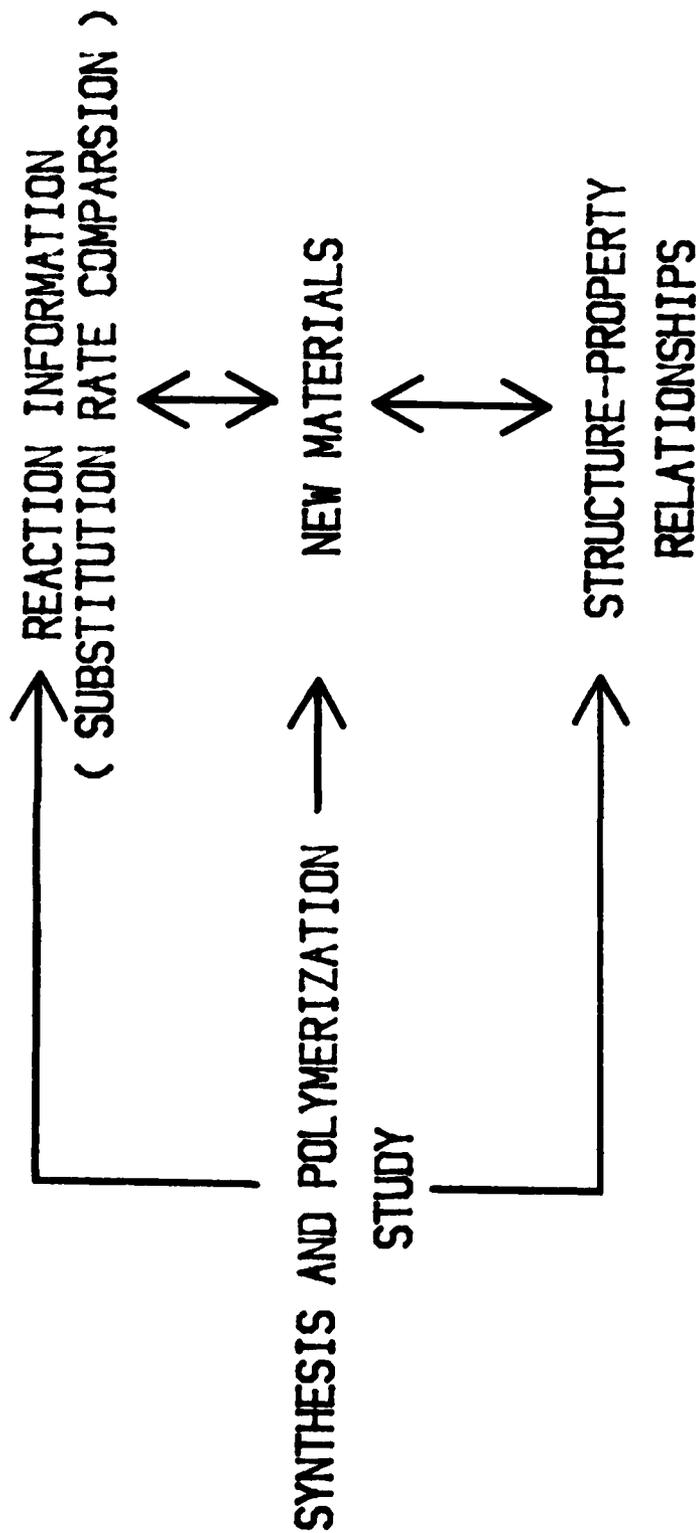
University of Dayton Research Institute

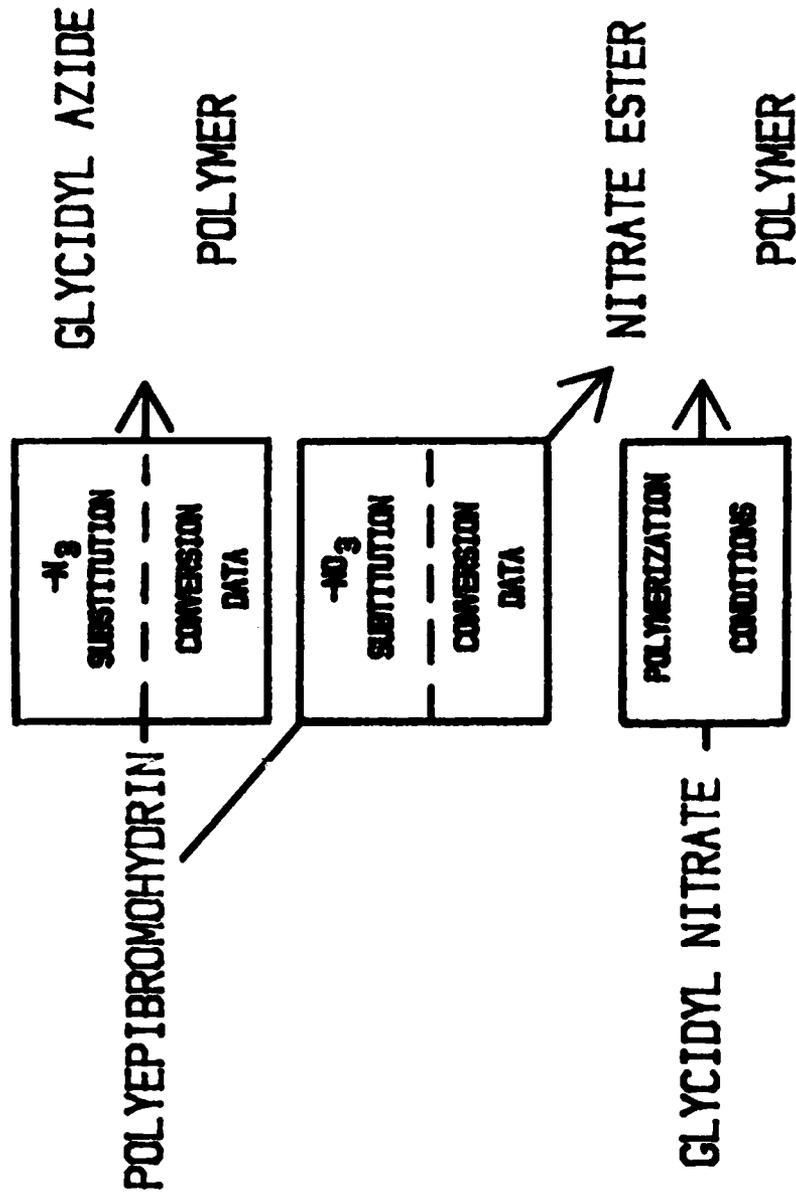
Many properties of polymers effect the ultimate use of the material and because the molecular structure of polymeric chains determine the overall properties of a specific polymer, a study of structural property correlations and synthetic modification of properties has been undertaken. New synthetic methods and polymerization procedures have been investigated, and questions concerning correlations of structure with changes in the physical properties of the polymers have been addressed.

The approach centers on synthesis efforts to produce new energetic polymers by cationic polymerization procedures or by modification of known polymers. Synthetic approaches have also been investigated to obtain structurally controlled materials for a systematic correlation study of structure and properties. Because of the resistance of polyepichlorohydrin to nucleophilic substitution of some anionic groups and because of the benefits offered by polyethers, other polyethers with the capacity for nucleophilic substitution were sought. The polymerization of epibromohydrin was carried out and the substitution chemistry of the polymer was studied. To compare this polymer with polyepichlorohydrin, substitution with azide in dimethylformamide was studied. Comparison reactions were also run with  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ . The polymerization of glycidyl nitrate was also studied as a route to an energetic polymer. Varying the catalysis and initiation of the monomer provided changes in molecular weight and functionality.

Information on synthetic techniques for producing energetic polyethers is limited and kinetic information on substitutions of energetic groups on polyethers is even more scarce. Systematic structure-property relationships are of interest to many in polymer chemistry, but data on energetic polymers is lacking.

Data from this research demonstrates that an azide polymer from polyepibromohydrin can easily be formed. Kinetic data comparisons of similar reactions with polyepichlorohydrin show a much faster rate of substitution at the same conditions. The polyepibromohydrin also shows a much faster rate with the reaction of  $\text{AgNO}_3$  in acetonitrile. However, similarities are apparent in the lack of reactivity with other materials. Preliminary data indicates that polyglycidyl nitrate can be produced easily from the acid catalyzed polymerization of the monomer. Molecular weights in the 2000-3000 range are obtained with hydroxyl equivalent weights between 1000 and 1600.





MODIFICATION OF PROPELLANT BINDER NETWORK FOR  
IMPROVEMENT OF MECHANICAL PROPERTIES (NEW EFFORT)

C. Sue Kim

California State University, Sacramento  
Sacramento, California

Availability of hydroxy-terminated prepolymers is limited, and formulation chemists are usually confined to selecting one of the available polymers, and resort to optimization of mechanical properties of solid propellant by:

- (1) Selection of plasticizers and oxidizers as dictated by the required impulse and burning rate and slope;
- (2) Optimization of crosslinker, curative and catalyst;
- (3) Optimization of solid particle sizes and their distributions; and
- (4) Selection of bonding agents for propellants of higher solid content.

Recent publications by Mark<sup>(1)</sup> indicate that it may also be possible to improve mechanical properties of solid propellants by creating a bimodal elastomeric network of long and short polymeric chains for the binder systems.

The objective of this project is to determine the possibility of improving mechanical properties of energetic propellants, based on the bimodal network concept developed by Mark. Mark's findings, however, are based on the stress-strain plots of elastomeric bimodal networks of polydimethylsiloxanes (PDMS) at near equilibrium conditions. Contrary to PDMS, the prepolymers for energetic propellants have high inter- and intramolecular attractions and higher rotational energy barriers. Furthermore, the solid propellants are highly filled systems. Hence, they are strongly rate and temperature dependent, and these viscoelastic behaviors have to be examined to determine if the advantages of the bimodal network still exist under high strain rates and low temperatures.

Two energetic prepolymers, glycidylazidopolymers (GAP) and polydinitropropyl acrylate (PDNPA) will be selected as short chain polymers, and one from polyethylene glycols (PEG), polycaprolactones (PCP), polytetramethylene glycols (Teracol), and 50/50-ethylene oxide/tetrahydrofuran copolymers (EO/THF polymer) will be selected as a long chain polymer for this study. The approach and the expected results are depicted in Figures I and II, respectively.

(1) M.A. Uorente, A.L. Andrady, and J.E. Mark, J. Poly. Sci., Poly. Phys. Ed., 19, 621 (1981).

FIGURE I: APPROACH

A. Selection of Prepolymers and Plasticizers

Bimodal combinations of selected prepolymers of long and short chains will be examined for good compatibility and low melting point. Selections will be made from:

(1) Plasticizers:

- (a) Nitroplasticizer (BDNPF/A)
- (b) Triethyleneglycoltrinitrate (TEGTN)
- (c) Diethyleneglycoldinitrate (DEGDN)
- (d) Butanetrioltrinitrate (BTTN)

(2) "Long-Chain" Prepolymers:

- (a) PEG
- (b) PCP
- (c) Teracol
- (d) EO/THF Polymer

(3) "Short-Chain" Energetic Prepolymers:

- (a) GAP (Rocketdyne and Aerojet)
- (b) PDNPA (To be synthesized)

B. Synthesis of PDNPA

- (1) Various molecular weight,
- (2) Various functionality ( $f = 2.0-4.0$ ), and
- (3) OH groups at the end of the chains are primary, and those along the chains are secondary.

C. Curatives (Each or combination of)

- (1) N-100 (will create bimodal network)
- (2) HDI (will create multimodal network)

D. Stress-Strain Properties

Selected bimodal binder network will be evaluated at  $-65^{\circ}\text{F}$ ,  $77^{\circ}\text{F}$ , and  $150^{\circ}\text{F}$ .

E. Effect of Filler

Selected networks from above will be examined to see if the favorable properties of the binders are retained in the filled system.

FIGURE II: EXPECTED RESULTS

- A. Combinations of Plasticizers such as BTTN/DEGDN and BTTN/TEGDN will give lower melting point.
- B. Preliminary study indicates that PEG is most favorable as the "Long-Chain" prepolymer, with the exception of its tendency to crystallize at low temperatures. This may be remedied through modification of PEG.
- C. Two favorable bimodal (multimodal) systems will be possible.
  - (1) GAP/PEG
  - (2) PDNPA/PEG

NEW SYNTHETIC TECHNIQUES  
FOR ADVANCED PROPELLANT INGREDIENTS:  
SELECTIVE CHEMICAL TRANSFORMATIONS AND NEW STRUCTURES

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Edwards AFB, CA 93523

New chemical transformations and methods are being investigated which potentially lead to energetic target compounds with new or novel molecular structures, or which improve synthetic routes to known compounds that are currently expensive propellant luxuries. Three of four scheduled research tasks have been initiated.

Task 1 Nucleophilic substitution of alkyl bromides with silver triflate were conducted to form precursor triflate ester compounds for conversion into key energetic ingredients. Syntheses of specific triflate ester intermediates provide a facile and selective pathway to energetic compounds not available by direct synthetic routes. The scope and limitations of triflate ester syntheses using alkyl halide and triflate salt reactions have not been investigated systematically; this is especially true with dihaloalkanes. Monobromoalkanes react much more slowly with silver triflate than analogous  $\alpha$ ,  $\omega$ -dibromoalkanes. Certain solvents induce monobromoalkanes to isomerize and provide rearranged triflate products; however, the simpler dibromoalkanes fail to exhibit this behavior. There is a greater tendency to form the ditriflate product as chain length increases in the simple  $\alpha$ ,  $\omega$ -dibromoalkanes up to 1, 4-dibromobutane. At this point, reaction products become more sensitive to the reaction conditions and undergo decomposition.

Task 2 Electrophilic additions between carbonyl and alkene compounds with energetic triflate esters were attempted. These addition reactions could provide a selective method for the direct introduction of energetic substituents into unsaturated organic compounds wherein overall anti-Markownikoff addition results with a concomitant regeneration of the double bond. Preliminary results in reactions between ketones and the fluorodinitroethyl triflate reagent imply that energetic  $\alpha$ ,  $\beta$ -unsaturated ethers are probably formed.

Task 3 Collaborative mechanistic studies were initiated with D.F. Shellhamer in alkene methoxyfluoro additions with methanolic xenon difluoride solutions. Elucidation of this boron trifluoride catalyzed alkoxyfluorination mechanism could permit a regioselective control which produces an anti-Markownikoff adduct. The substitution of fluorodinitroethanol for methanol offers a potentially attractive method for introducing the energetic fluorodinitroethoxy moiety to terminal olefinic carbon atoms. Except for specific Michael additions, this synthetic transformation is unknown in polynitroaliphatic chemistry. Preliminary investigations of this alkoxyfluorination mechanism were begun by reacting norbornene with xenon difluoride in 10-14% boron trifluoride/methanol solution. Isomeric products were isolated and are being identified. The structure of these isomers should provide definitive evidence for the detailed chemical mechanism.

Task 4 The potential synthesis and characterization of energetic borazine compounds are scheduled for a later start.

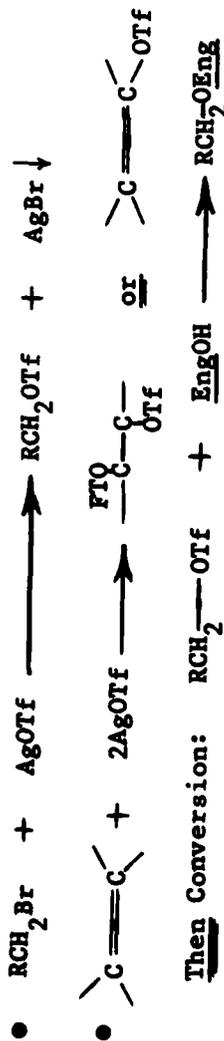
These tasks address the necessary elements of an effective synthesis effort: (a) novel transformations, (b) improved synthetic routes, and (c) new target structures or compounds.

APPROACH

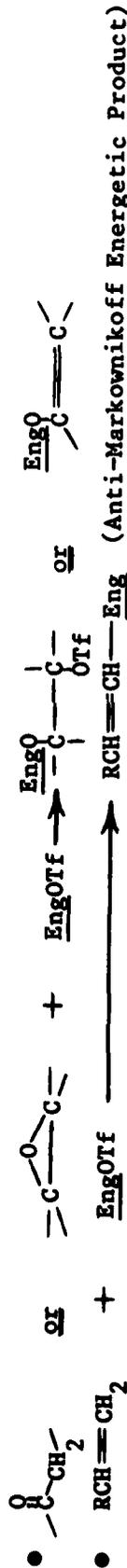
SELECTIVE SYNTHETIC TRANSFORMATIONS → NOVEL STRUCTURES

- IMPROVED SYNTHETIC ROUTES
- NEW TARGET COMPOUNDS

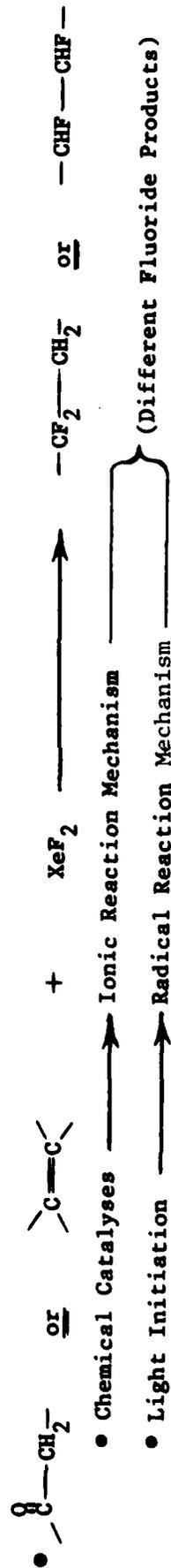
**TASK 1: TRIFLATE SALTS (Selective Intermediate Syntheses)**



**TASK 2: ENERGETIC TRIFLATE ESTERS (Direct Energetic Compound Syntheses)**



**TASK 3: XENON DIFLUORIDE FLUORINATION (Selective Fluorination)**

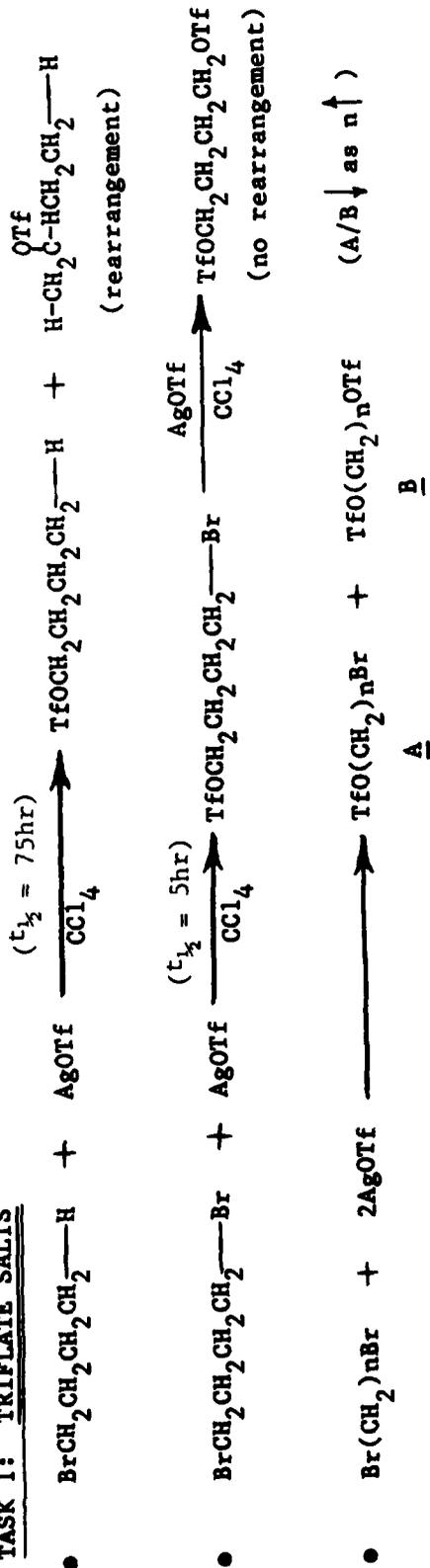


OTf = Triflate Group

Eng = Energetic Chemical Structure (i.e., polynitroalkyl or NO<sub>2</sub> moieties)

RESULTS

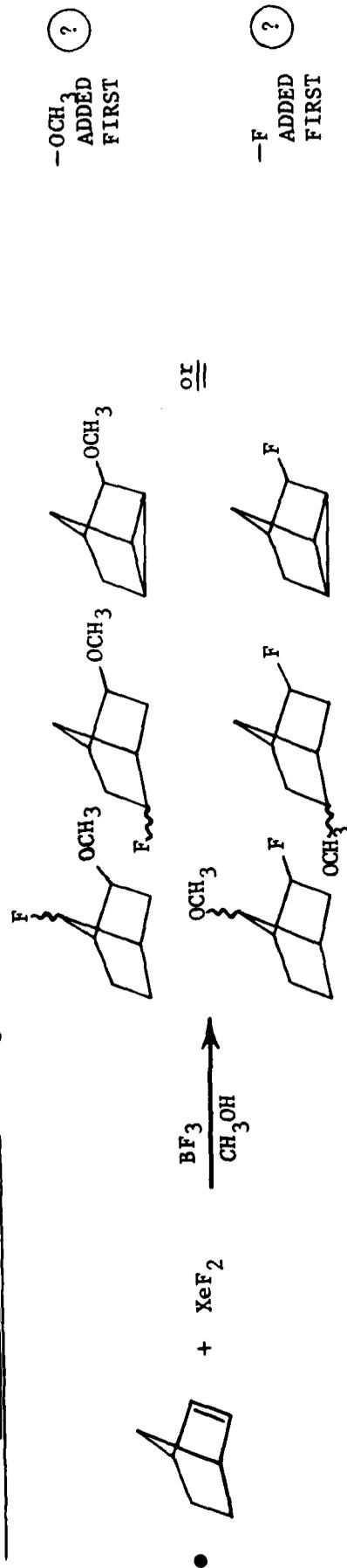
TASK 1: TRIFLATE SALTS



TASK 2: TRIFLATE ESTERS



TASK 3: SELECTIVE FLUORINATION (OCH<sub>3</sub> OR F ADDITION FIRST ?)



- OTf = Triflate Group =  $-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{CF}_3$   
 - FDNE = Fluorodinitroethyl Group =  $-\text{CH}_2\overset{\text{NO}_2}{\underset{\text{NO}_2}{\text{C}}}\text{F}$

MECHANISTIC COMBUSTION INTERACTIONS  
OF  
ISOTOPICALLY LABELED PROPELLANT INGREDIENTS

Scott A. Shackelford and Berge B. Goshgarian

Air Force Rocket Propulsion Laboratory  
Edwards AFB, CA 93523

The fundamental chemical reaction mechanisms which produce and release the energy necessary for chemical propulsion have to be elucidated under the ballistic, pressure, and temperature conditions encountered in a rocket combustor. This must be done to address the current technological barriers responsible for nitramine burn rate limitations, unpredictable propellant performance tailorability, and expensive empirical evaluation procedures. This investigation is designed to elucidate in-situ the key rate-limiting chemical mechanisms and ingredient interactions which control the global combustion process. Isotopically labeled propellant ingredients will be used to detect potential deuterium isotope effects and to determine the randomness of isotopic scrambling in the combustion products. Three tasks will comprise this work unit.

Task 1 involves the combustion of individual deuterated and unlabeled ingredients to determine if C-H bond rupture is the rate-controlling step in the overall combustion process. Potential deuterium isotope effects should reflect themselves as a change in burn rates between the unlabeled and deuterated ingredient. Initially HMX will be studied using pressurized packed powder and pressed pellet glass tube combustion experiments in a collaborative venture with R.N. Rogers and D.A. Flanigan. Micromotor firings with HMX and  $d_8$ -HMX will follow. RDX and DNNC will also be investigated.

Task 2 addresses the question of molecular diffusion in a rocket combustor. Individual propellant ingredients appropriately labeled with  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and/or  $^{18}\text{O}$  will be fired in a rocket micromotor, and the kinetically frozen products will be collected for analysis. The degree of randomness found in the scrambled isotopic product labels compared to that expected if complete thermodynamic equilibrium were achieved prior to nozzle kinetic freeze out will demonstrate the amount of intramolecular diffusion or thermodynamic versus kinetic control exhibited by a given ingredient. HMX, RDX, and DNNC will be studied initially.

Task 3 is concerned with ingredient-ingredient interaction and diffusion control in a formulated propellant. Altered ingredient combustion reaction mechanisms could result from intermolecular interactions. Micromotor firings initially will be conducted with formulations containing one labeled ingredient and one unlabeled; the products will be collected for analysis. The degree of random isotopic scrambling and exchange in the combustion products will be determined and compared to that expected if a complete ingredient-ingredient equilibration were established prior to nozzle kinetic freeze-out. Initially, labeled HMX, RDX, or DNNC oxidizer will be combined with an unlabeled binder ingredient. This bi-ingredient system will be built one ingredient at a time until a complete propellant formulation is studied. Eventually, the chemical mechanism or diffusion process responsible for overall combustion performance in different types of propellant can be compared.

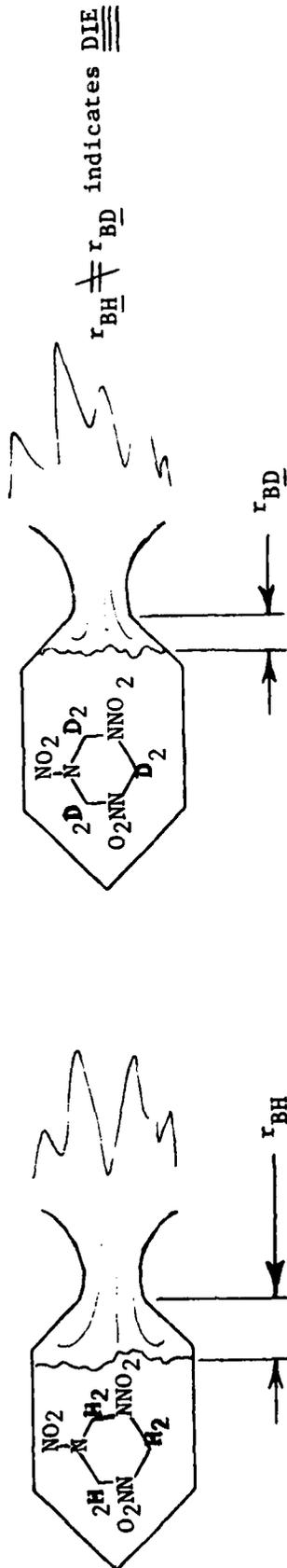
These three tasks address the need for elucidating the fundamental chemical reaction mechanisms (a) to potentially identify rate-limiting bond ruptures, (b) to determine the degree of molecular kinetic versus thermodynamic control, and (c) to measure the amount of ingredient-ingredient diffusion encountered in a rocket motor combustor.

APPROACH

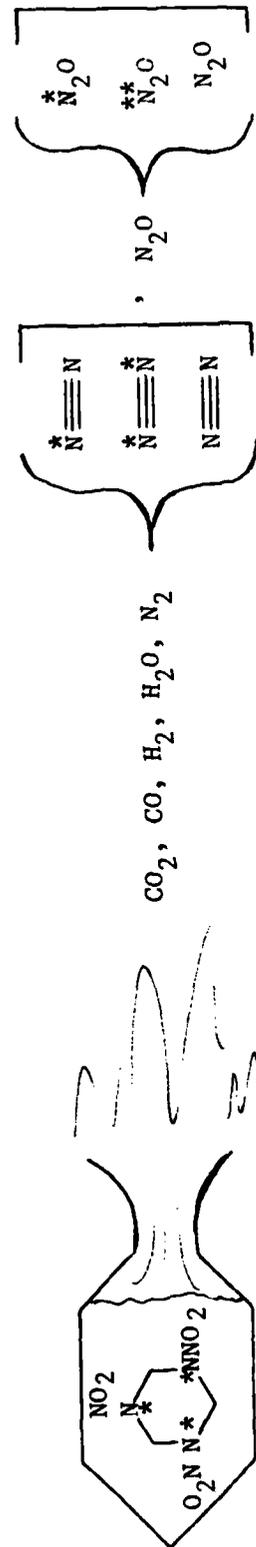
CHEMICAL MECHANISM ELUCIDATION IN GLOBAL COMBUSTION PROCESSES →

- IDENTIFICATION OF RATE-LIMITING BOND RUPTURE
- DETERMINATION OF MOLECULAR KINETIC VS THERMODYNAMIC CONTROL
- MEASUREMENT OF INGREDIENT DIFFUSION CONTROL

○ DEUTERIUM ISOTOPE EFFECTS (DIE) IN CHEMICAL COMBUSTION MECHANISMS

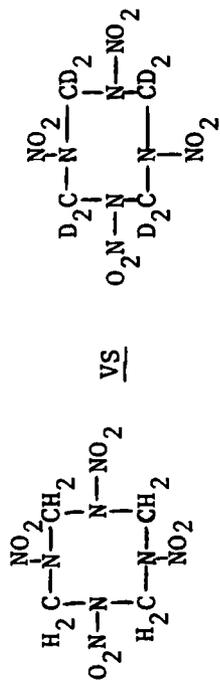


○ ISOTOPIC SCRAMBLING RANDOMNESS IN CHEMICAL COMBUSTION MECHANISMS



POTENTIAL RESULTS

• DEUTERIUM ISOTOPE EFFECT (DIE) TO IDENTIFY RATE-LIMITING BOND RUPTURE/REACTION STEP



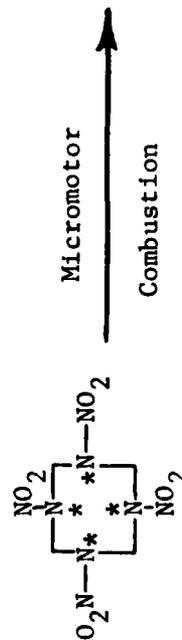
Burn Rate  $r_{\text{BH}}$

Burn Rate  $r_{\text{BD}}$

$$\begin{array}{l}
 r_{\text{BH}}/r_{\text{BD}} > 1.41 \\
 = 1.00-1.35 \\
 < 1.00
 \end{array}$$

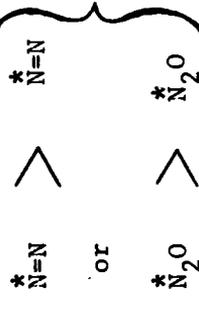
$1^{\circ}$  DIE (C-H Bond Rupture)  
 $2^{\circ}$  DIE (N-N or C-N Bond Rupture)  
Inverse DIE

• ISOTOPIC SCRAMBLING RANDOMNESS TO DETERMINE INTRA- & INTERMOLECULAR DIFFUSION



		<u>Products</u>	
CO <sub>2</sub>	*N <sub>2</sub> O	*N <sub>2</sub> O	*N <sub>2</sub> O
CO	*N <sub>2</sub> O	*N <sub>2</sub> O	*N <sub>2</sub> O
H <sub>2</sub>	N <sub>2</sub> O	N <sub>2</sub> O	N <sub>2</sub> O
H <sub>2</sub> O	N <sub>2</sub> O	N <sub>2</sub> O	N <sub>2</sub> O

If



Actual Isolated Amount  
 Random Calculated Amount

CARBON-CARBON PROCESSING VARIABLES INVESTIGATION

W. P. HOFFMAN

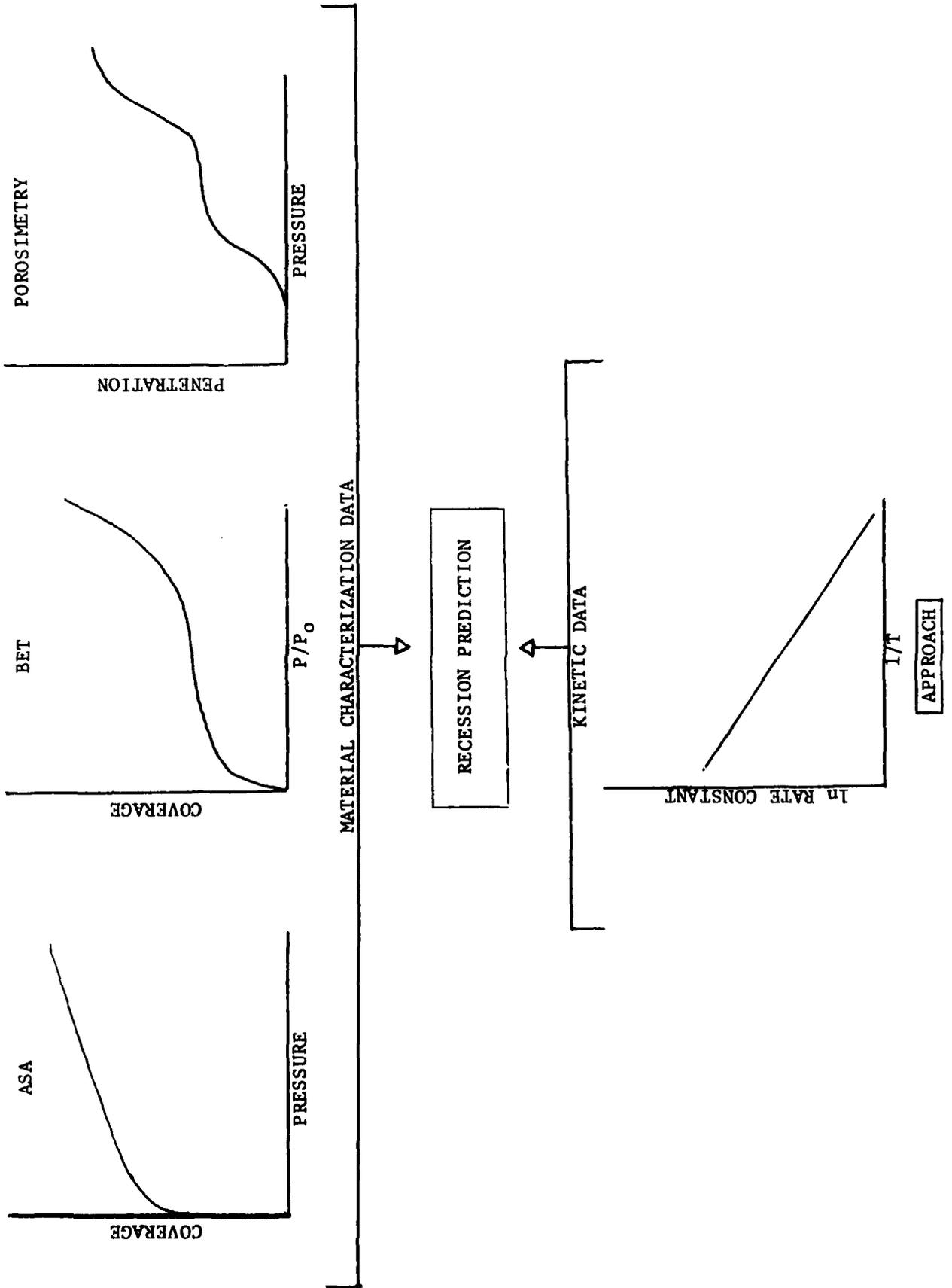
AIR FORCE ROCKET PROPULSION LABORATORY

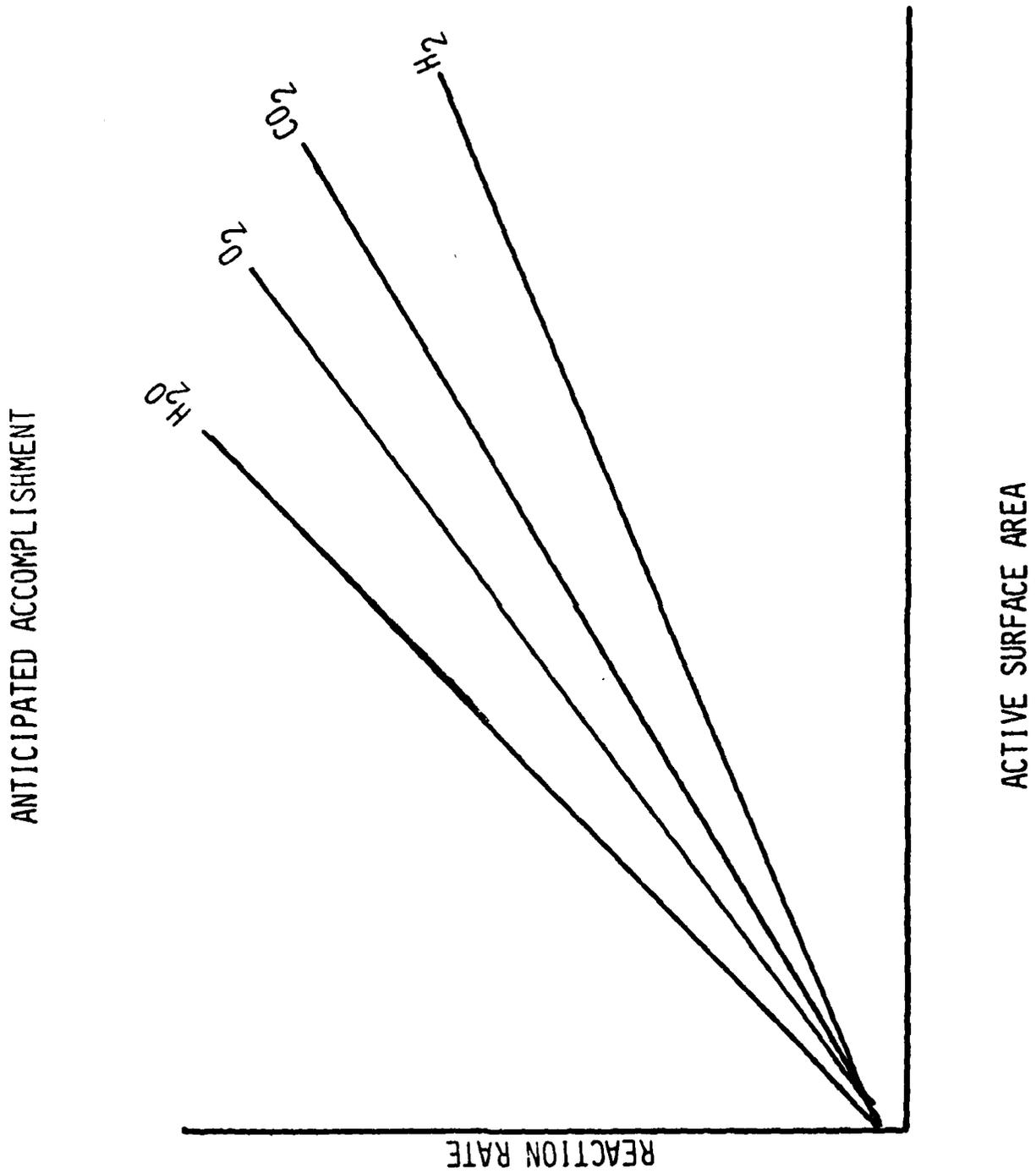
AFRPL/MKBN EDWARDS AFB, CA 93523

The chemistry and physics of carbon-carbon composites is not well understood even though they are being evaluated as nozzle materials in a number of Air Force programs. This lack of understanding includes the surface ablation kinetics of these materials. There is conjecture about the specie (s) principally responsible for recession. However, there is no definitive data available either pertaining to the principle specie (s), or to the kinetics of the heterogeneous reactions with carbon under rocket nozzle conditions. Therefore, the nozzle designer has no firm theoretical basis on which to predict the performance of his nozzle design. He is forced to make predictions based on data from actual motor firings. The nozzle and conditions used in these firings may or may not represent the composite material and operating conditions that the designer has chosen. The objective of this program is to fill this gap in our knowledge of surface reaction kinetics and their relation to carbon-carbon material construction and processing. This is being accomplished by (1) extensive surface characterization of the carbon-carbon materials and (2) by measuring the kinetics of the heterogeneous reactions between carbon-carbon materials and the various species present in the rocket motor exhaust. This will give the designer a firm basis on which to predict the performance of his nozzle.

During this past year, work continued on the build-up of the new ablation system, which will use a heliostat in conjunction with a solar concentrator to heat the carbon sample. Extensions for the heliostat petals were designed, manufactured and installed. Design of the modified concentrator facets was completed and the manufacture of the facets is almost complete. Upon installation of these facets the ablation system will be functional. While this build-up has progressed, work in the Materials Characterization Laboratory has continued. An automated data acquisition system has been installed. This system digitizes all data which can then be analyzed, recalled, and plotted. In addition, linear temperature programmers were installed as furnace controllers for desorption studies.

Initial characterization work has centered on Pitch (VSB-32) and PAN (T-300) carbon fibers used in contemporary nozzle construction. Although these fibers have been found to have similar total surface areas, they have been found to have significantly different pore structures and active surface areas. The differences in active surface areas have been found to track differences in recession properties.





STATISTICAL NATURE OF CRACK GROWTH IN SOLID PROPELLANT

C.T. LIU

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The main objective of the Structural Mechanics Research program is to advance current understanding of crack growth behavior in solid propellants. The specific objective of this present research program is to investigate the statistical nature of crack growth.

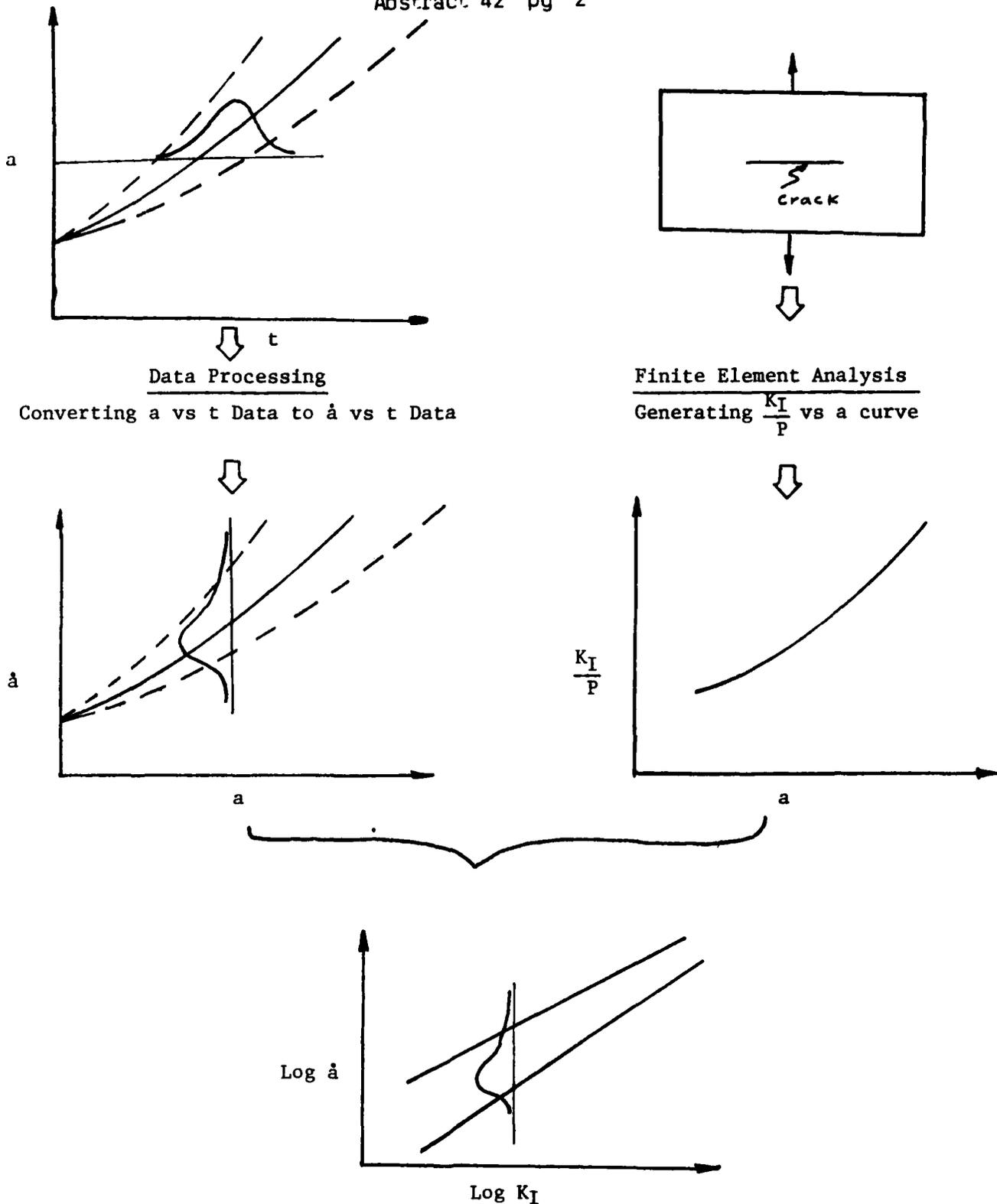
During the past few years, a considerable amount of work has been done studying crack growth behavior in solid propellants based on linear viscoelastic fracture mechanics. There are many papers that have been published concerning the relationships between the crack growth rate,  $\dot{a}$ , and the stress intensity factor,  $K_I$ . These papers published information that was based on data obtained from testing a relatively small number of specimens. The usefulness of this relationship depends on how accurately this relationship describes the crack growth behavior in the material. Due to the non-homogeneity of material properties (on the microscopic scale) of a highly filled solid propellant, the crack growth behavior in the material does not necessarily show a definite growth characteristic under the same loading conditions. Therefore, a large scatter in the test data is expected, and a precise statement on crack growth behavior cannot be made. Therefore, it is essential to examine the characterization of the statistical feature of the crack growth behavior.

The determination of the functional relationship between the crack growth rate and the stress intensity factor requires the analysis of the discrete data relating the instantaneous time,  $t$ , to the corresponding crack length,  $a$ , and to determine the instantaneous stress intensity factor for a given crack length. A description of data processing and theoretical analysis is shown in the following paragraphs. A schematic representation of the basic approach is shown in Figure 1.

In order to determine the stress intensity factor at the crack tip, it is necessary to relate load on the specimen to crack and specimen dimensions. A three-dimensional finite element computer code, TEXGAP-3D, was used to determine the stress intensity factor and the load on the specimen as a function of crack length. The results of the finite element analysis were used to determine the functional relationship between the ratio of the stress intensity factor to the load and the crack length. This relationship is independent of the Young's modulus and the applied constant displacement, and was utilized in the reduction of experimental data to calculate the stress intensity factor for a given instantaneous crack length and the associated load.

The raw data, obtained from the crack propagation test, are the half crack length,  $a$ , and the time required to obtain each length. The crack length  $a$  is measured from the center of the specimen. The rate of crack propagation  $\frac{da}{dt}$  was determined by using four different methods: (1) the secant method, (2) the modified secant method, (3) the spline fitting method, and (4) the total polynomial method. The crack propagation data were analyzed statistically to determine the functional relationship between the stress intensity factor and the crack growth rate. The statistical distribution of  $\frac{da}{dt}$  as a function of  $K_I$ , and the coefficient of variation as a function of  $K_I$ , were also determined, using a modified Virkler's statistical computer program. The statistical distribution considered was (1) normal, (2) 2-parameter log-normal, (3) 3-parameter log-normal, (4) 3-parameter Weibull, and (5) 3-parameter gamma. Three goodness of fit tests, a regression analysis, the chi-square test, and the Kolmogorov-Smirnov test, were used to determine how well the data fit a certain distribution.

At the time of this writing, statistical analysis has not been completed, but the effect of methods of  $\frac{da}{dt}$  calculation on the variability of crack growth data is clearly shown in Figure 2.



Statistical Analysis

- Statistical distribution of  $\dot{a}$  as a function of  $a$  and  $K_I$
- Statistical model of crack growth
- Variability and statistical distribution of the parameters in the crack

Figure 1. Schematic Representation of Basic Approach

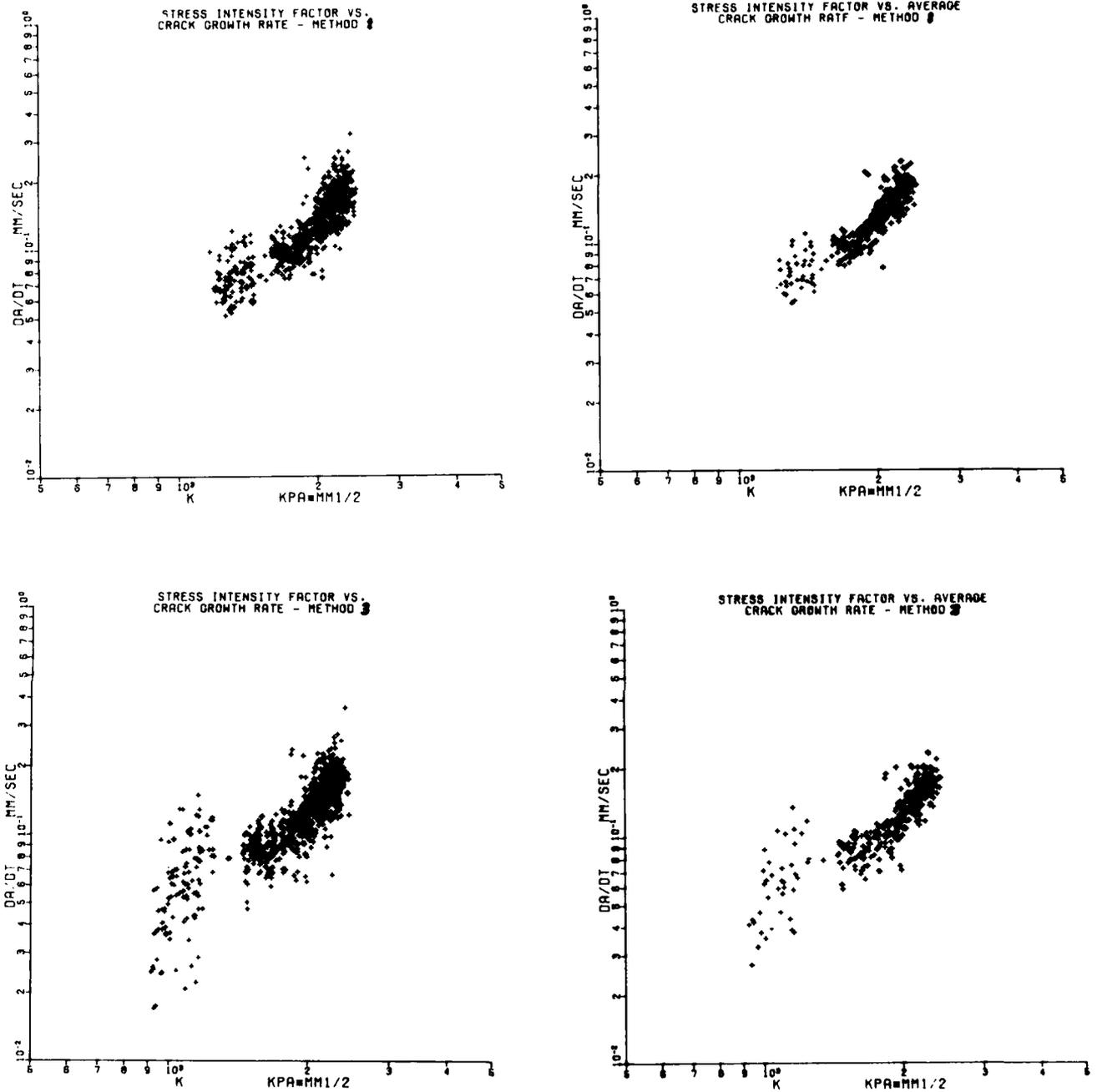


Figure 2. Log  $\dot{a}$  vs Log  $K_I$  data calculated by the Secant Method and the Spline fitting Method.

THERMOMECHANICALLY COUPLED VIBRATIONS IN A CYLINDRICAL GEOMETRY  
LACKING SYMMETRY; A FINITE ELEMENT SOLUTION PROCEDURE

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Cincinnati, OH 45221

The purposes of this project are to develop a general algorithm for the solution of steady state thermomechanically coupled viscoelastic boundary value problems in polar coordinates and to illustrate use of the algorithm on a specific problem.

The materials to be considered are linear viscoelastic solids whose volumetric response is assumed to be elastic. The constitutive relations, however, have a nonlinear thermal dependence and enough mechanical energy is dissipated into heat during vibration that the elevation of temperature cannot be neglected. The equations of thermal and dynamic equilibrium are therefore coupled nonlinearly.

The dynamic equations are linear in displacements and their derivatives while the thermal equation is quadratic in the same terms. Given the nature of the constitutive laws, all the field equations contain a nonlinear function of temperature and spatial derivatives of that function. The thermal equation can be linearized in the temperature, however, by using the dynamic equations to express these thermal nonlinearities in terms of displacements. The equations have then been partially linearized. Results of this analysis are presented in general terms.

The modified equations are solved iteratively. An initial guess for the temperature field is made and the displacement field calculated based upon this guess. Temperatures are then recalculated from the displacements and the process is repeated until convergence is achieved.

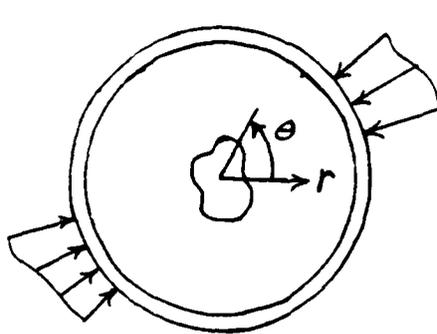
In the iterative algorithm it will be necessary to express the field variables as collections of point values at a finite number of locations and interpolations between those point values. This is best accomplished through use of isoparametric finite elements, which offer geometric flexibility and the necessary continuity of the field variables.

It is to be expected that the solution of any specific boundary value problem will contain numerical difficulties such as troublesome convergence or dependence of the solution upon the mesh configuration. Additionally, solutions of thermomechanically coupled problems are known often to depend discontinuously upon the amplitude and the frequency of the forcing functions. A specific boundary value problem will be solved as a means of illustrating ways of dealing with these numerical difficulties.

This project is designed to set up a framework for the solution of a class of design problems of interest to AFRPL and to illustrate the practical application of the solution procedure. The results of the research should also provide AFRPL with an enhanced capability numerically to investigate the effect of various constitutive assumptions.

This project is a logical extension of research done by the principal investigator and others on the use of finite differences in solving one-dimensional problems in thermoviscoelasticity and the principal investigator is unaware of any previous extension of that work to two-dimensional problems.

THE PROBLEM AND FEATURES OF ITS MODELING



$$L(\theta) e^{i\omega t}$$

CYLINDRICAL BODY WITH ASYMMETRIC LOADINGS AND CENTRAL VOID

STEADY-STATE SINUSOIDAL LOADING

STATE OF PLANE STRAIN

STEADY-STATE SINUSOIDAL RESPONSE TO LOADING

$$c(r, t) = c_3(r) + [c_1(r) + i c_2(r)] e^{i\omega t}$$

$c$  = COMPONENT OF DISPLACEMENT, STRAIN OR STRESS

CONSTITUTIVE RELATIONSHIPS:

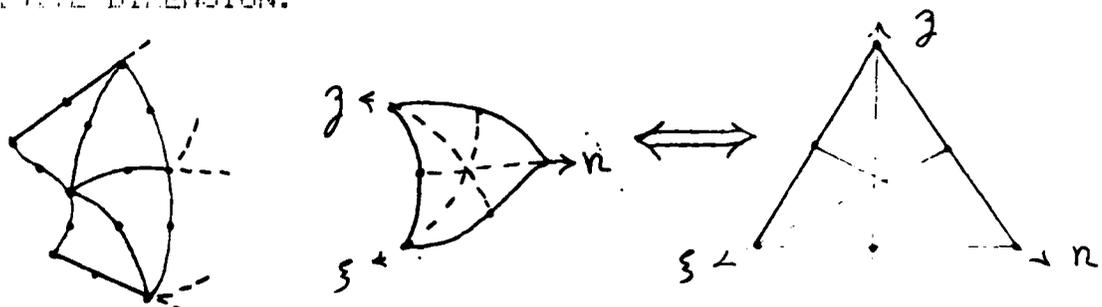
LINEAR THERMOVISCOELASTIC DEVIATORIC COMPLEX MODULUS

$$(S_{ab1} + i S_{ab2}) = [G_1(T, \omega) + i G_2(T, \omega)] (e_{ab1} + i e_{ab2})$$

RELAXATION MODULUS (QUASI-ELASTIC)  $S_{ab3} = G_0 e_{ab3}$

BULK MODULUS (ELASTIC)  $\sigma_{VOL} = E_K (\epsilon_{VOL} - 3\alpha(T - T_0))$

USE OF THE SIX-NODE QUADRATIC, ISOPARAMETRIC FINITE ELEMENT TO DISCRETIZE THE DOMAIN AND REDUCE THE FIELD PROBLEM TO FINITE DIMENSION.



MANIPULATION OF THE DISCRETIZED FIELD EQUATIONS INTO PARTIALLY LINEARIZED FORM.

$$[K] \underline{u} = \underline{b}(\underline{T}; \omega) \quad , \quad [D] \underline{T} = \underline{g}(\underline{u}; \omega)$$

SOLUTION BY SUCCESSIVE ALTERNATIVE CALCULATION OF TEMPERATURE AND COMPONENTS OF DISPLACEMENT.

FIGURE 1

PRIMARY GOALS OF THE RESEARCH

1. DERIVATION OF THE EQUATIONS OF DYNAMIC AND THERMAL EQUILIBRIUM, IN POLAR COORDINATES, FOR A GENERAL THERMAL DEPENDENCY IN THE COMPLEX MODULUS.
2. PARTIAL LINEARIZATION OF THE FIELD EQUATIONS

$$\alpha E_K \left\{ \begin{matrix} T, r \\ T, \theta \end{matrix} \right\} = \underline{f} \left( r, E_K, G_0, u_m, \frac{\partial u_m}{\partial r}, \dots, \frac{\partial^2 u_m}{\partial \theta^2} \right), \quad m = 5, 6$$

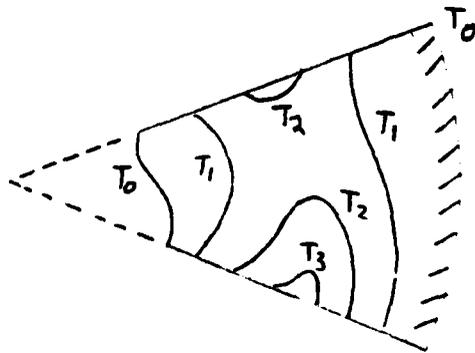
$$\rho \omega^2 r^2 u_m = g_m \left( r, E_K, G_p, \frac{\partial G_p}{\partial r}, \frac{\partial G_p}{\partial \theta}, u_m, \frac{\partial u_m}{\partial r}, \dots, \frac{\partial^2 u_m}{\partial \theta^2} \right) \quad \begin{matrix} m = 1, 4 \\ m = 1, 4 \\ p = 1, 2 \end{matrix}$$

$$\frac{K}{w} \nabla^2 T = G_2(T, w) h \left( r, u_m, \frac{\partial u_m}{\partial r}, \frac{\partial u_m}{\partial \theta} \right) \quad m = 1, 2, 3, 4$$

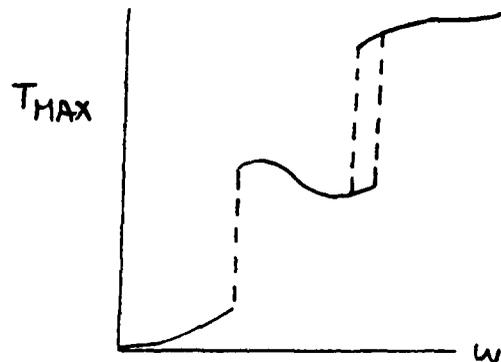
WHERE  $\underline{f}$  AND  $g_m$  ARE LINEAR IN DISPLACEMENTS AND DERIVATIVES AND  $h$  IS QUADRATIC IN DISPLACEMENTS.  $G_2$  IS SOLVED FOR FROM

$$\left[ A \left( r, \alpha, E_K, G_0, u_m, \dots, \frac{\partial^2 u_m}{\partial \theta^2} \right) \right] \left\{ \begin{matrix} G_1 \\ G_{1,T} \\ G_2 \\ G_{2,T} \end{matrix} \right\} = \underline{b} \left( \rho, w, r, E_K, u_m, \dots, \frac{\partial^2 u_m}{\partial \theta^2} \right)$$

3. DEVELOPMENT OF A CONVERGENT, EFFICIENT ITERATIVE ALGORITHM FOR THE SUCCESSIVE ALTERNATING CALCULATIONS OF TEMPERATURE AND COMPONENTS OF DISPLACEMENT.
4. ILLUSTRATIVE SOLUTION OF A BOUNDARY VALUE PROBLEM FOR A SPECIFIC MATERIAL, GEOMETRY AND LOADING.



CONTOURS OF FIELD VARIABLES



PARAMETRIC STUDIES

FIGURE 2

ADVANCED DIAGNOSTICS IN REACTING MEDIA

A multidisciplinary research task is underway to provide new diagnostic techniques which are needed for the advancement and understanding of combustion systems, air-breathing and rocket engines, efficient fuel utilization, plume signatures, and signal attenuation. This task is parallel to the present tasks on rocket propulsion and air-breathing propulsion. The research is helping to overcome deficiencies in obtaining reliable measurements of important parameters in the reacting flows of practical, hostile combustion environments and the inability to reliably validate combustion models. The research objectives include: to originate more sensitive, selective, precise, reliable, and rapid diagnostic methods for measuring important parameters in air-breathing and rocket engine reacting flows; to investigate, validate and apply the instrumentation concepts; and to measure fundamental parameters required to implement the approaches. The results are accelerating the reduction to practice of new nondisturbing techniques for accurately measuring reacting flows. While many of the physical principles have been anticipated, this endeavor is enabling combustion researchers to confront the realities of obtaining useful measurements. Investigation, verification and application of advanced instrumentation and diagnostics for reacting flows is being conducted as an integrated, multidisciplinary program. For example, combustion scientists have identified measurement needs and interacted with physicists, chemists, et al to incorporate advances in areas such as optics, molecular dynamics, and sensors. Physical phenomena which have promise for new diagnostic techniques are being explored. Where necessary, fundamental physical parameters needed to implement the techniques are being determined. Techniques are being validated through intercomparisons with standard techniques and laboratory scale reacting flows.

Rapid improvements and lower costs of data acquisition components, sensors, lasers, and digital electronic components are presenting several series of 'first ever' research opportunities. Particularly significant are the researches which are leading to 2D, rapid sequence quantitative images revealing temperature, species concentration, and (even) velocity in turbulent flames. Since the quantitative images can be captured in nanosecond time, the first comprehensive data on the turbulent structures of flames is forthcoming. The point source diagnostic techniques of the late 1970's are rapidly becoming the key elements in the 2D and 3D quantitative techniques of the 1980's. The resulting rapid advances in instrumentation will revolutionize the research approaches to many energy conversion processes.

A contractor's meeting on this topic is being planned for March 1984. As an interim report, the abstracts on AFOSR managed research are included.

ABSTRACTS OF RESEARCH

ADVANCED DIAGNOSTICS OF REACTING FLOWS

NUM.

- 10 +OVERVIEW OF STANFORD PROGRAM ON ADVANCED DIAGNOSTICS FOR REACTING FLOWS. Ronald K Hanson, C Thomas Bowman, Sidney A Self, Robert L Byer, Donald Baganoff, Brian J Cantwell, and Lambertus Hesselink, Stanford University, Stanford, CA
- 21 +COHERENT OPTICAL SPECTROSCOPY IN FLAMES. John W Daily, University of California, Berkeley, CA
- 27 +RESONANT CARS DETECTION OF OH RADICALS. James F Verdick and Alan C Eckbreth, United Technology Research Center, East Hartford, CT
- 45 \*SPECIES MEASUREMENTS BY TUNABLE LASER ABSORPTION TECHNIQUES. Ronald K Hanson, Stanford University, Stanford, CA
- 46 \*COMBUSTION RELATED CARS SPECTROSCOPY. E Gustafson and Robert L Byer, Stanford University, Stanford, CA
- 47 \*NOISE THERMOMETRY IN COMBUSTION PROCESSES. Stephen P Gill and John D Watson, Artec Associates, Haywood, CA
- 48 \*STUDY OF EVAPORATING FLOW USING LASER-INDUCED FLUORESCENCE. Donald Baganoff and Brian Cantwell, Stanford University, Stanford, CA
- 49 \*DETERMINATION OF LIQUID DROPLET EVAPORATION RATES IN A SPRAY BY INELASTIC LIGHT SCATTERING. Richard K Chang, Marshall B Long, and Boa-Teh Che, Yale University, New Haven, CT
- 50 \*MAGNETICALLY COUPLED VELOCIMETERS. Carl Spight ,AMAF, Inc, Columbia, MD
- 51 \*PICOSECOND LIDAR. Robert Goulard, George Washington University, Washington, DC
- 52 \*COMPUTED LASER TOMOGRAPHY FLOW DIAGNOSTICS. K E Bennett, G W Faris, and Robert L Beyer, Stanford University, Stanford, CA
- 53 \*QUANTITATIVE FLOW VISUALIZATION. Ronald K Hanson, Stanford University, Stanford, CA
- 54 \*QUANTITATIVE THREE DIMENSIONAL FLOW VISUALIZATION. Lambertus Hesselink, Stanford University, Stanford, CA
- 55 \*MEASUREMENTS IN TURBULENT REACTING FLOWS. Craig T Bowman, Stanford University, Stanford, CA
- 56 \*MULTIDIMENSIONAL VELOCITY MEASUREMENTS IN REACTING FLOWS. Holger T Sommer, Carnegie Mellon University, Pittsburg, PA
- 57 \*PACKAGED, FIBEROPTIC SPECTRORADIOMETER. Sidney Self, Stanford University, Stanford, CA
- 58 \*PARTICLE SIZING FOR ROCKET EXHAUSTS. Sidney Self, Stanford University, Stanford, CA

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+Presentation is part of contractors meeting.

\*Presentations will not be made.

SPECIES MEASUREMENTS BY TUNABLE LASER ABSORPTION TECHNIQUES

Ronald K. Hanson

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Stanford University  
Stanford, California 94305

This research seeks to provide sensitive, species specific techniques for monitoring gaseous concentrations in reacting flows. The development of such techniques has the potential for significant impact on various scientific and engineering aspects of combustion and propulsion. One promising approach, which has been pursued particularly at Stanford, utilizes absorption spectroscopy as the sensing process and seeks to combine recently developed tunable laser sources with a variety of novel absorption probes, including configurations yielding high spatial resolution. The resulting diagnostics appear well suited to meet a variety of practical and fundamental measurement requirements.

The program includes several related research projects, ranging from work to provide improved laser sources, to exploration of new sensing phenomena or probe configurations, to demonstration of promising techniques in laboratory combustion flows. A summary of current projects is given below. Figures 1-3 provide highlights of work on: (1) an intrusive absorption probe using a tunable IR diode laser; (2) remote measurements in a shock tube using a fiber-optic link; and (3) an intrusive absorption/fluorescence probe using a pulsed tunable UV/visible dye laser.

Tunable UV/Visible Techniques (cw ring dye laser)

- development of a fiberoptic absorption/fluorescence probe
- development of fast-scanning ring dye laser for measurements in transient and two-phase flows
- development of fiberoptic links for remote absorption measurements in a shock tube and a combustion tunnel
- investigation of off-resonance laser fluorescence for reduced sensitivity to quenching

Tunable IR Techniques (cw diode laser)

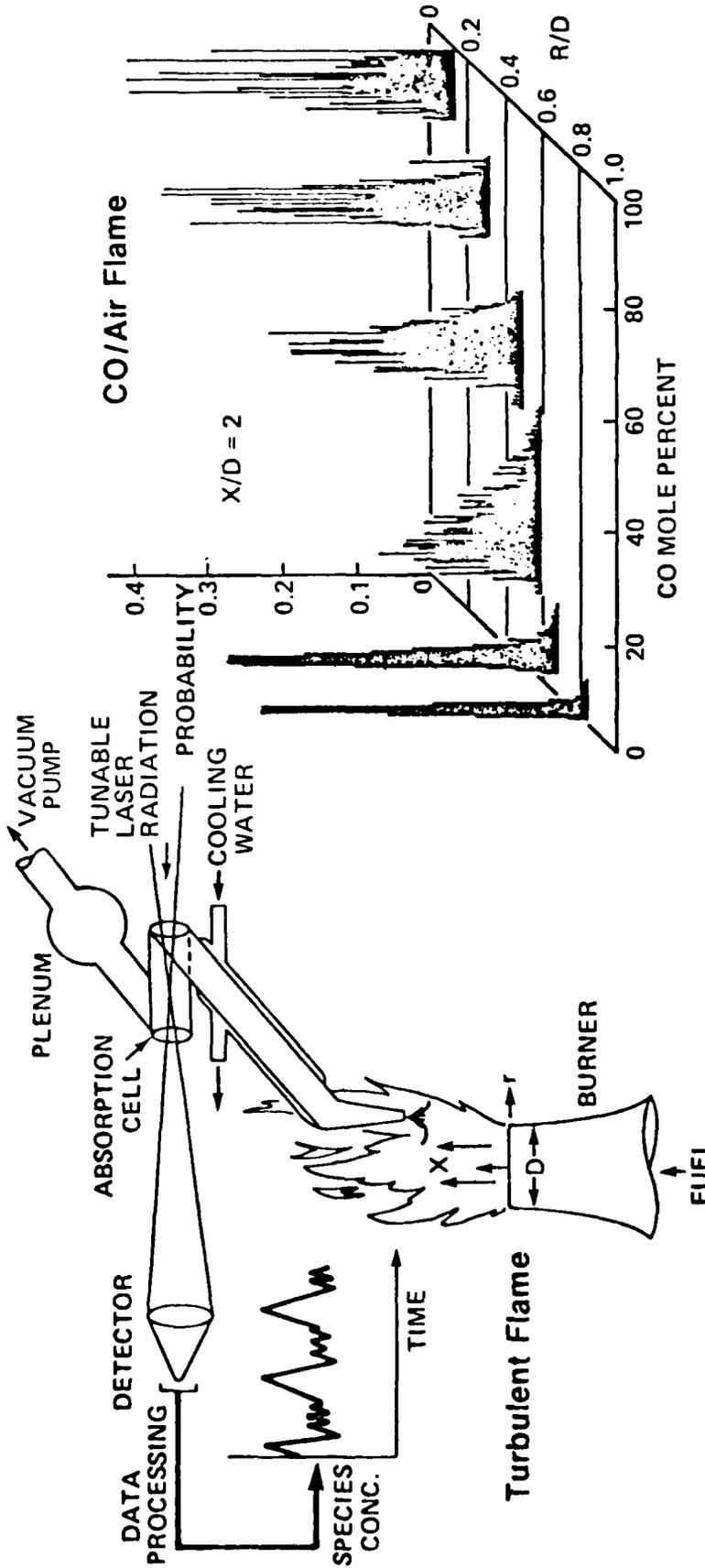
- development and validation of a variable pathlength (Light Guide) probe for continuous, real-time species measurements
- development and validation of a fast-sampling probe with an in-line absorption cell for continuous, real-time species measurements

Crossed-Beam, Modulated Absorption Techniques (cw ring dye laser, cw diode laser, pulsed YAG/dye laser)

- studies of beam interactions using resonant (saturated absorption) and non-resonant (ac-Stark effect) pump and probe laser sources.

## SPECIES DETERMINATION

### TUNABLE-LASER ABSORPTION SAMPLING PROVIDES CONTINUOUS (REAL-TIME) SPATIALLY RESOLVED SPECIES MEASUREMENTS

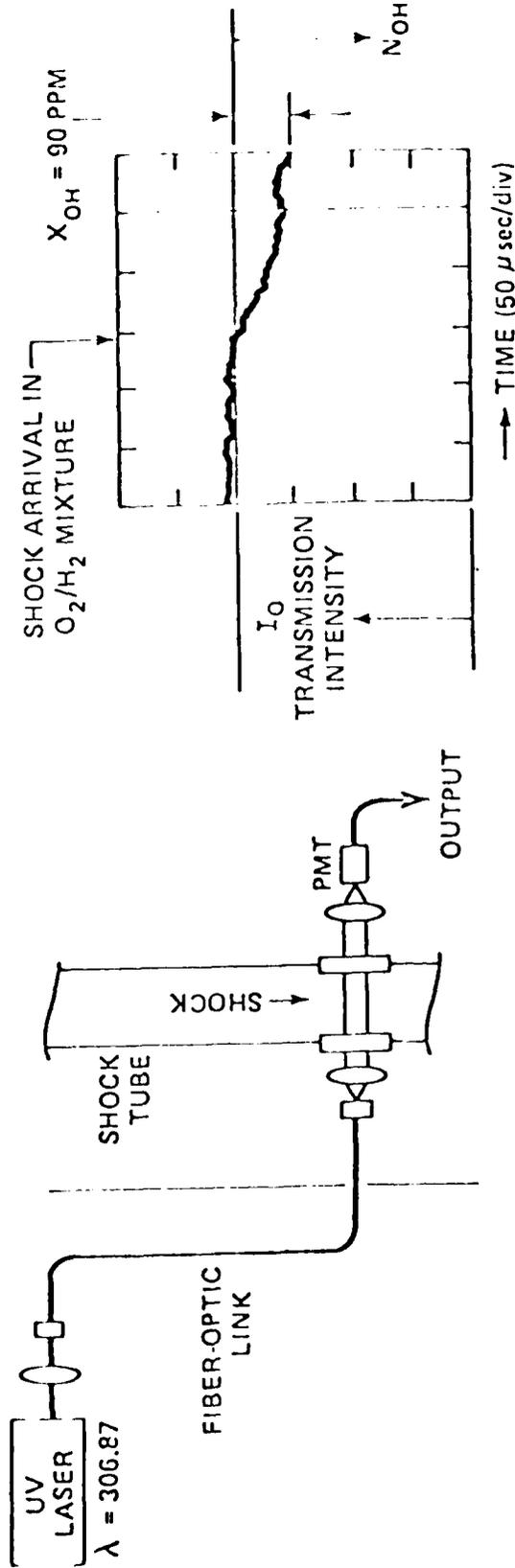


- First Continuous-Time Species Measurements in Flame  
Yield Critical Data for Turbulence Flames.

Hanson/Stanford Univ

Figure 1. Laser absorption sampling probe for temporally and spatially resolved combustion measurements using a tunable IR diode laser.

# REMOTE OPTICAL ACCESS/SPECIES DETERMINATION



Rate of OH Increase used to  
Establish Kinetic Relationship

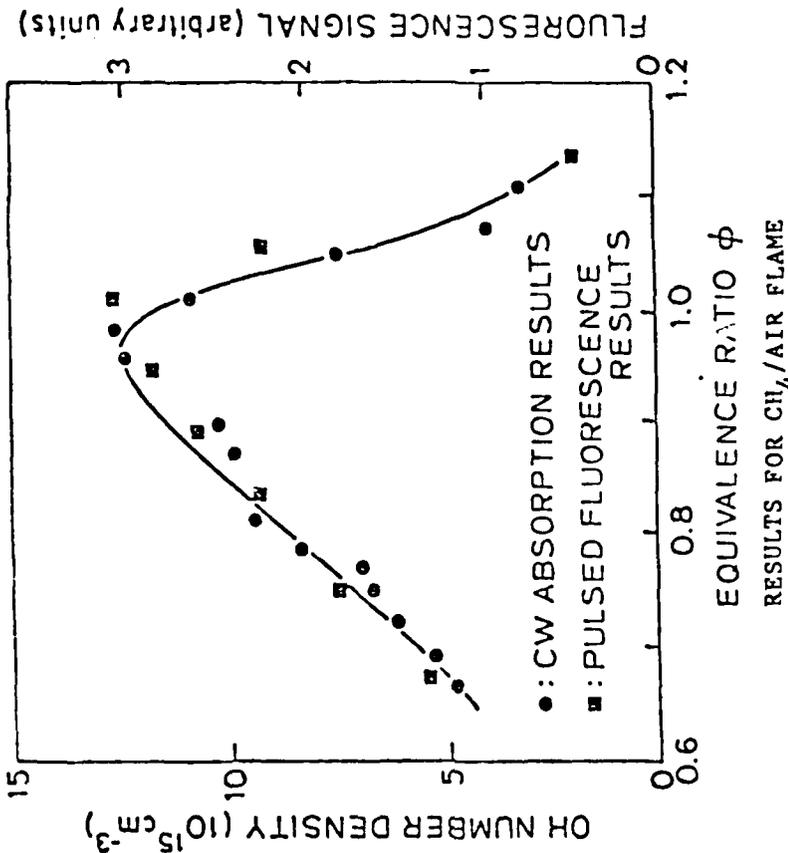
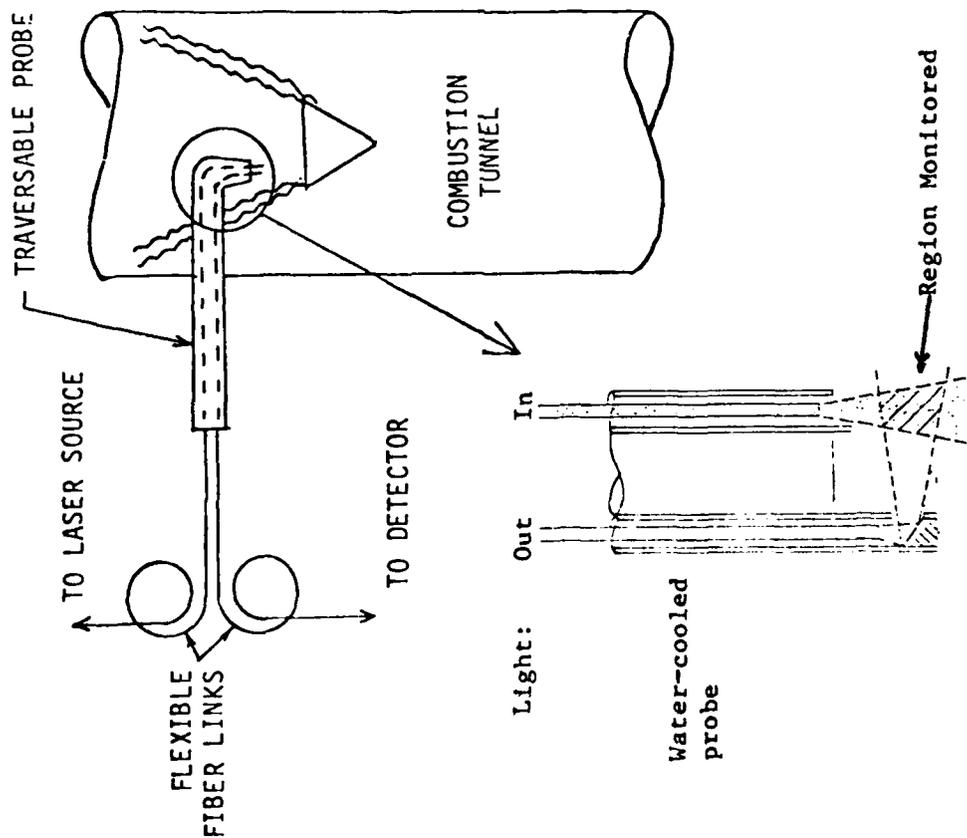
Fiber-Optic Link to  
Shock Tube Experiment

- FIBER OPTICS ESTABLISHED AS A SOLUTION FOR REMOTE MEASUREMENTS  
IN HOSTILE ENVIRONMENTS
- CAPABILITY ESTABLISHED TO ACCURATELY DETERMINE SPECTROSCOPIC  
PARAMETERS AND SPECIES CONCENTRATIONS UNDER HOSTILE CONDITIONS

Hanson/Stanford Univ

Figure 2. Schematic of system used to monitor OH in a shock tube using a remotely located, frequency-doubled cw ring dye laser.

REMOTE DETECTION OF SPECIES  
 USE OF FIBER-OPTIC PROBE WITH LASER-EXCITED FLUORESCENCE  
 ENABLES REMOTE MEASUREMENTS IN ENCLOSED COMBUSTOR SYSTEMS



- FIBER OPTIC LINKS ALLOW REMOTE PLACEMENT OF LASER/DETECTION/ANALYSIS SYSTEMS
- TRAVERSABLE PROBE SUITED FOR USE IN SYSTEMS WITH LIMITED OPTICAL ACCESS
- LASER-EXCITED FLUORESCENCE GIVES SENSITIVE (PPM) DETECTION OF REACTIVE SPECIES ( E.G., OH, CH, CN)
- TECHNIQUE SUCCESSFULLY DEMONSTRATED FOR OH
- FIRST SOLUTION TO PROBLEM OF RADICAL SPECIES MEASUREMENTS IN COMBUSTORS WITHOUT OPTICAL ACCESS

Figure 3. Fiber optic fluorescence probe for use with tunable pulsed lasers and enclosed combustors.

COMBUSTION RELATED CARS SPECTROSCOPY  
AT STANFORD UNIVERSITY

E. Gustafson and R.L. Byer

Over the past three years we have carried out work in high resolution CARS spectroscopy that has culminated in the highest resolution CARS spectra ever measured. At a resolution of 205 MHz the dominant broadening mechanism is transit time broadening. We have developed a lineshape theory that includes the transit time broadening effect and produces excellent agreement with the experimental results. Transit time broadening, however, is not the only unusual broadening mechanism in the supersonic jet.

The molecular motions in the jet, parallel to the laser beam propagation direction, produce a geometric Doppler broadening due to the distribution of transverse velocities with radial position in the jet. To calculate this effect we needed to know the velocity flow field of the supersonic jet. Using the method of characteristics, we have performed the numerical calculation and have prepared tables and plots of the isentropic expansion zone of the under expanded supersonic jet for ratios of specific heats =  $(n + 5)/(n + 3)$  and  $n = 1, 2, \dots, 20$ . With these results and the isentropic flow relations, the jet flow field is completely determined.

Figure 1 shows the cw CARS apparatus spectrum of the  $\nu_1$  Q-branch of methane taken in a supersonic expansion. The effective temperature is 31.50K. The spectrum fully resolves the  $J = 0, 1$  & 2 rotational components of methane. The theoretical fit is in excellent agreement with the experimental data if transit time broadening is included.

The continued improvement of CARS spectroscopy will result in the increased quantitative understanding of the quantum structure of every major and minor combustion species. We have continued to develop CARS as a high resolution spectroscopic tool both experimentally and theoretically. Theoretically we have built on the lineshape theory of Henesian by including the new supersonic jet CARS broadening mechanisms of transit time broadening and geometric Doppler broadening. In addition we have carried out numerical calculations of the supersonic jet that will make it a more convenient spectroscopic tool.

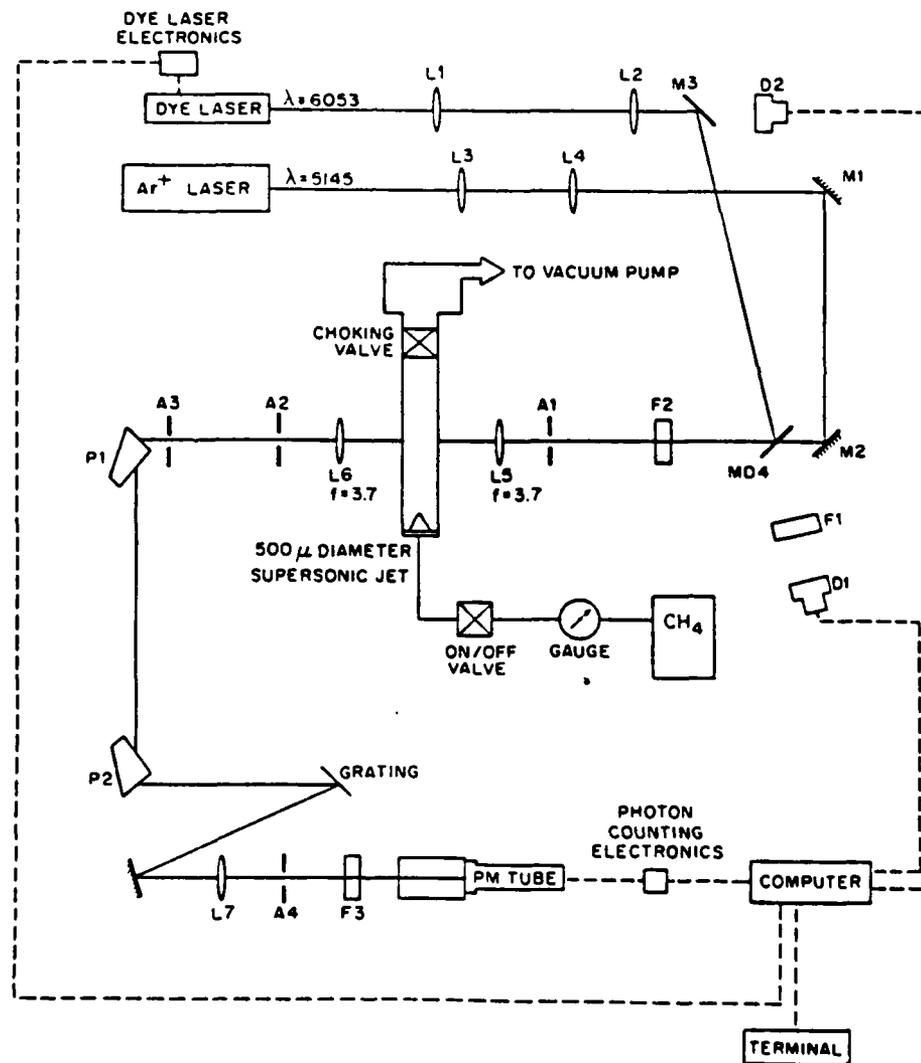


FIGURE 1

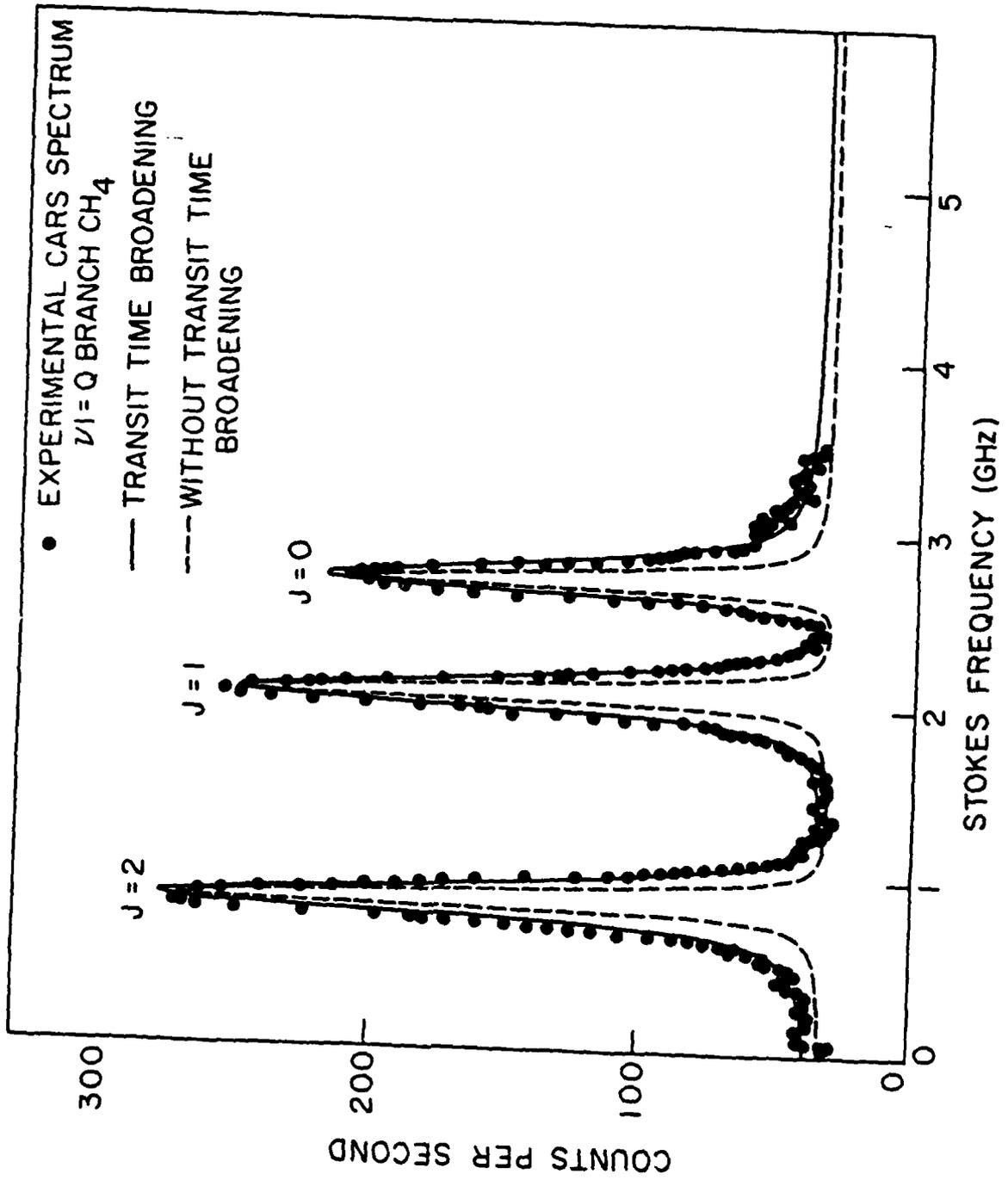


FIGURE 2

STUDY OF EVAPORATING FLOW USING  
LASER-INDUCED FLUORESCENCE

Donald Baganoff and Brian Cantwell  
Stanford University  
Stanford, California

Time scales for droplet evaporation often exceed time scales for chemical reaction or turbulent mixing in spray combustion. In such cases droplet evaporation is the physical process which limits the overall reaction rate. An improved understanding of the development and evolution of the vapor field in droplet laden flows is an essential step toward an improved understanding of spray combustion.

The aim of the research is to develop a spatially and temporally resolved technique based on laser induced fluorescence for measuring the concentration field around evaporating drops in an unsteady flow.

Our initial approach is to suspend the droplets in a vertically rising, diverging flow, where the weight of a droplet is approximately balanced by its drag. Because larger droplets have larger terminal velocities, the streamwise velocity gradient will cause separation of the droplets by size and allow quasi-steady suspension at different streamwise stations. See Figure 1. A unique variable pressure facility with a vertically oriented test section has recently been completed and preliminary experiments have begun. See Figure 2(a). Some of the work done as part of the initial check-out of the facility has already provided data for the three-dimensional flow imaging technique being developed by Professor Hesselink.

The use of iodine as a trace substance in studying droplet evaporation depends on the availability of a carrier liquid which has vapor pressure and diffusion characteristics which match those of iodine. A number of substances have been investigated and a close match has been found with Octanol which has the property of a light fuel oil.

Studies have been completed which show that for broadband excitation of the iodine molecule by the 514.5 nm output of the argon ion laser, attenuation of the laser beam is modest over the distances planned for the experiments. However, for line-center, narrow-band excitation, beam attenuation will require corrections in data analysis. The wavelength dependent variable-absorption path length adds an interesting dimension to the study in that detuned excitation would make both the droplet and the iodine vapor visible, while line-center excitation would only show the low density outer vapor field. For broadband excitation we have shown that the fluorescence intensity is proportional to iodine number density for the conditions of the experiment.

A crossed-beam saturation technique is presently being explored for the tuned condition which holds the promise of a stronger signal than fluorescence. Two coherent primary beams produce a spatial variation of absorption which acts as a diffraction grating to a probe beam which is detected. Figure 2(b) shows the transmitted signal of beam 1 (upper trace) as it is being modulated by the interaction with a chopped beam 2 (lower trace). We believe the oscillations are a result of the fringe-pattern movement of the crossed coherent beams in the supersonic jet in which the test was conducted.

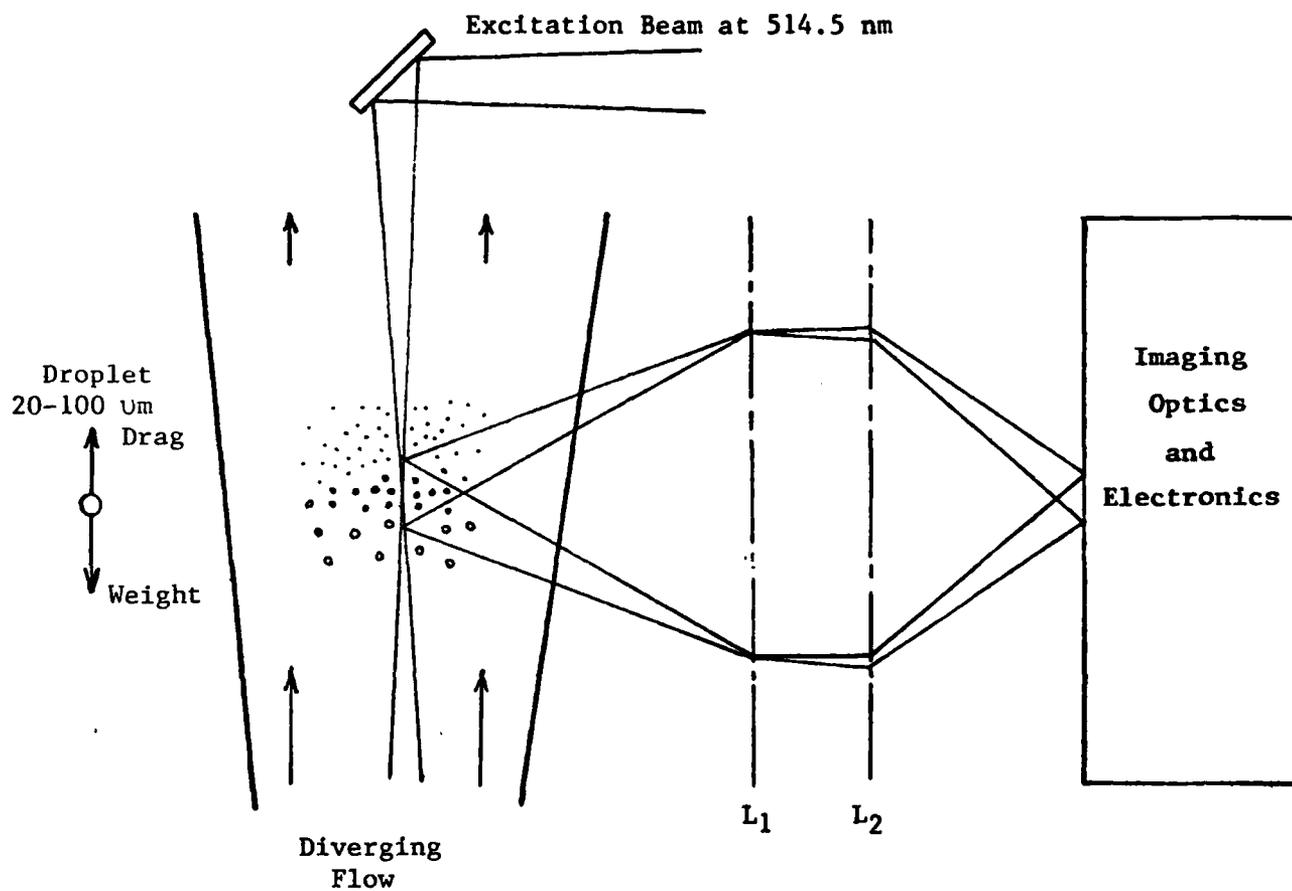


Figure 1. Multipoint Concentration Measurements about Evaporating Drops

(a)

Vertical test  
section →



(b)

Transmitted beam  
Writing beam

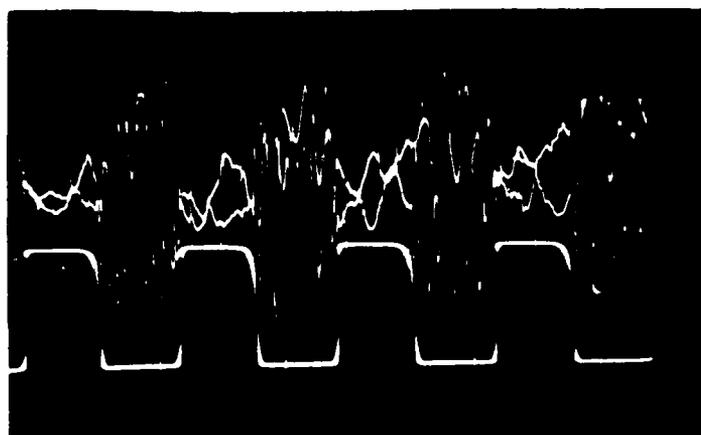


Fig. 2 Completed and calibrated test facility for producing and supporting droplets for study (a), and preliminary results on mixing of crossed coherent laser beams in iodine (b).

DETERMINATION OF LIQUID DROPLET EVAPORATION RATES IN A SPRAY  
BY INELASTIC LIGHT SCATTERING

Richard K. Chang, Marshall B. Long, and Boa-Teh Chu  
Yale University  
Center for Laser Diagnostics  
New Haven, Connecticut 06520

An understanding of the process of spray evaporation and combustion is important for the design of liquid fuel combustion devices. The evaporation process is influenced by many interacting physical processes, including the incident heat flux, conduction, and convection, as well as the surrounding vapor environment. Therefore, a need exists to measure the size, shape and evaporation rates of droplets in the presence of other droplets in the spray.

A new optical technique for measuring particle size and evaporation rates has been developed which will make it possible to measure important physical quantities and thereby lead to a more complete understanding of the evaporation process. The method is based on the morphology-dependent resonances in the fluorescence spectra from droplets containing a fluorescent dye. The fluorescence intensities are measured as a function of wavelength at a fixed angle. This technique differs from the standard optical method for particle size determination which infers the particle size from the angular pattern of monochromatic radiation elastically scattered by an ensemble of droplets. The current technique, in addition to being much more sensitive for droplet size measurement, makes it possible to monitor the size and evaporation rate of a single "tagged" particle in a spray of other droplets containing no fluorescent dye.

The configuration of the experiment is shown schematically in Fig. 1. A pulsed  $N_2$  laser is used to excite a fluorescent dye dissolved in the droplets in a spray. The fluorescence emission is collected and dispersed spectrally with a spectrograph, giving the intensity of fluorescence radiation along one axis in the focal plane of the spectrograph. The other axis contains spatial information and thus, if a two-dimensional detector is used, the fluorescence emission from a number of different particles in the spray can be collected and recorded simultaneously.

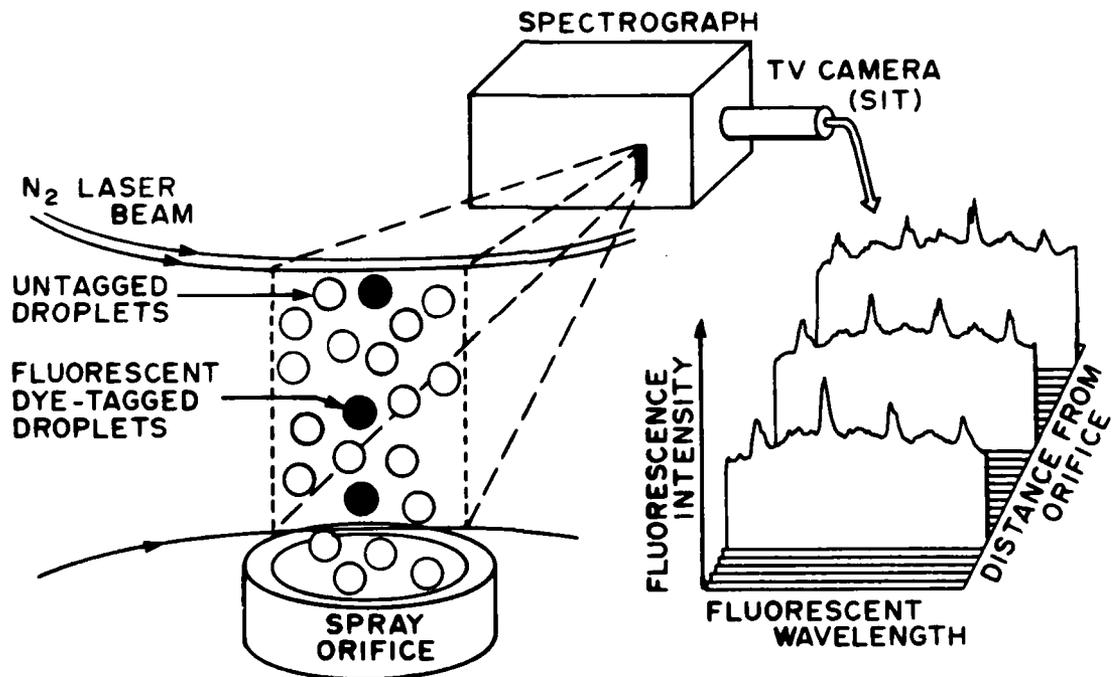
Figure 2 shows the fluorescence emission spectra from five different droplets in a spray obtained in a single laser pulse (5 ns). The intensity peaks in the fluorescence spectra correspond to the wavelengths that are resonant with the natural modes of the particles. The size of each particle can be determined to a high degree of accuracy ( $\sim 100$  Å in a  $10 \mu\text{m}$  droplet) by comparing the spectra with the calculated spectra for different sized particles. The particle size is determined solely by the position of the peaks in the spectra and not by the absolute fluorescent intensity. The technique is therefore insensitive to fluctuations in the laser intensity and changes in the dye concentration as the liquid evaporates. If a few tagged particles are introduced into a spray of untagged particles, the sizes of only the tagged particles will be determined, thus making it possible to measure the effect of different spray environments on the droplet evaporation.

We gratefully acknowledge the support of this work by the Air Force Office of Scientific Research (Grant No. F49620-82-K-0005).

## Air Force Basic Research Achievement

### DROPLET SIZE & SHAPE DETERMINATION

SHARP PEAKS IN FLUORESCENCE SPECTRA DETERMINE DYE-TAGGED DROPLET'S SIZE, SHAPE AND EVAPORATION RATE IN A SPRAY OF UNTAGGED DROPLETS



- FIRST INSTANTANEOUS ACCURATE DETERMINATION OF DYE-TAGGED DROPLET SIZE
- DOWNSTREAM EVOLUTION YIELDS EVAPORATION RATE OF SINGLE DYE-TAGGED DROPLET IN SPRAY
- SIZE AND SHAPE FROM MULTIPLE DYE-TAGGED AND UNTAGGED DROPLETS CAN BE DETERMINED FROM BROADBAND ELASTIC SCATTERING

TZENG, CHANG, LONG / YALE UNIV

FIGURE 1

## SINGLE-SHOT FLUORESCENCE EMISSION FROM FIVE DROPLETS

LASER PULSE - 5nsec

DROPLET DIAMETER -  $33\mu\text{m}$

DROPLET VELOCITY - 16 m/sec

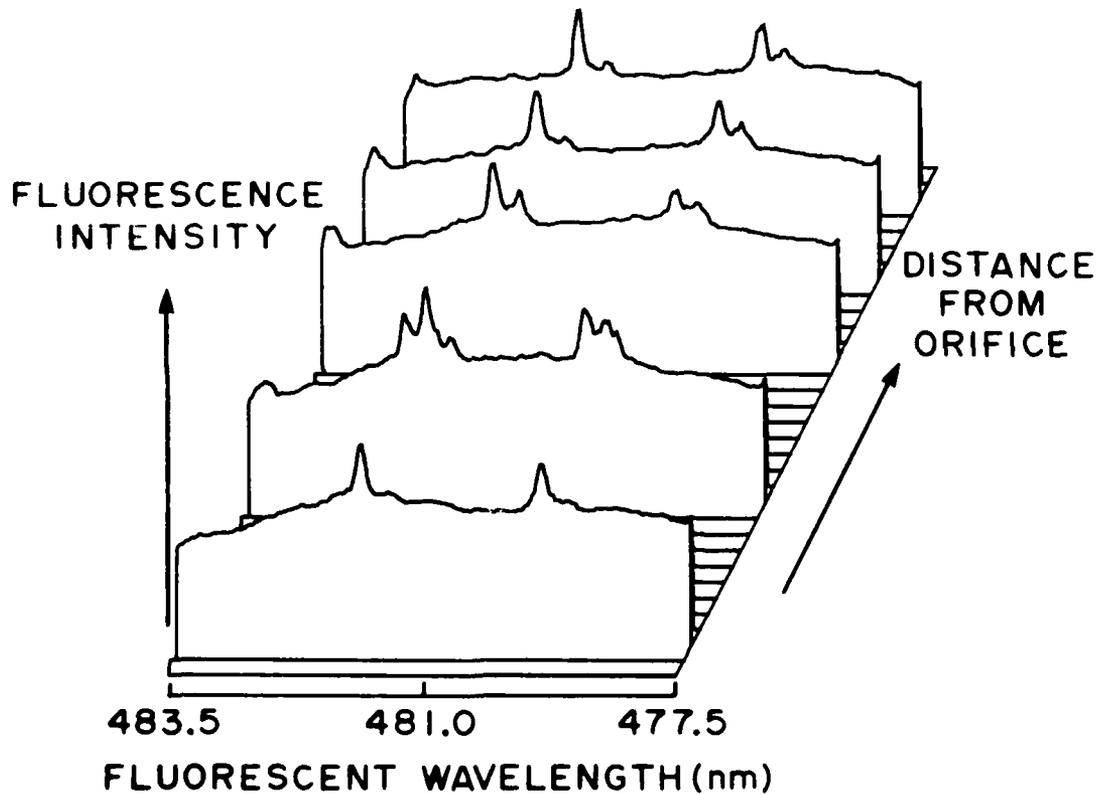


FIGURE 2

EXPERIMENTAL DEMONSTRATION OF MAGNETICALLY  
COUPLED VELOCIMETERS

Dr. Carl Spight  
AMAF Industries, Inc.  
Columbia, Maryland

A program of experimental verification is underway which will demonstrate the feasibility of a totally non-intrusive flow-field diagnostic for weakly turbulent, high temperature chemically reacting flows. This effort follows a phase of theoretical analysis and computer simulation to demonstrate the approach conceptually. This effort will result in viable designs for AC magnetic field-coupled velocimeters capable of measuring the mean and the turbulent velocity structure of flow-fields typical of rocket combustion chambers and exhaust nozzles.

Approach

An array of AC magnetic field generating coils exposes a combustion flow-field to a field structure which, as an applied field, can be modified at will. Induced perturbations in that field due to eddy effects (due to flow conductivity) and motional effects (due to across field motion of the flow) are picked up by an array of probe coils. Both arrays are external to the flow. The voltage measured by the probe array has been previously shown through theoretical analysis to be relateable to weighted moments (i.e., integral moments) over the spatial structure of the velocity flow-field. The applied field structure is controlled in such a way as to yield a finite and unique number of moments from which the velocity structure can be inferred. Previous efforts by other researchers to develop inductive flowmeters based on magnetic coupling have either not sought to unfold the velocity structure from their data or have had no way to uniquely and explicitly design the moments being measured. The use, however, in this effort of lead field theoretic analysis as a design basis has made that possible.

The experimental phase of the effort has three major components:

1. Design and testing of a data acquisition/processor system
2. Construction of propane combustor test station
3. Assembly of the probe and drive arrays

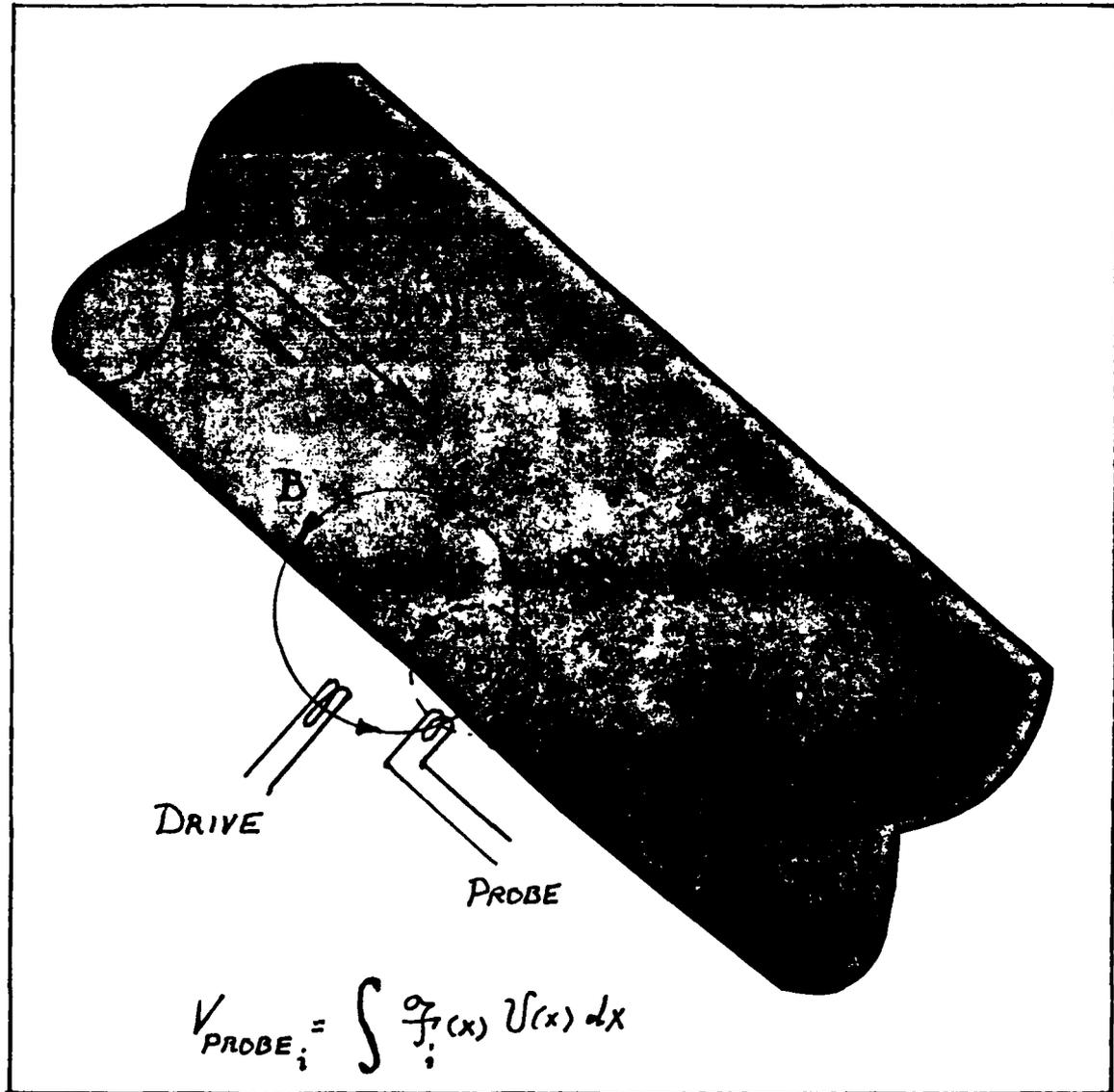


FIG 1

Span of Research Program: Dec 1980-Dec 1983

Accomplishments of Year Two (Dec 1981-Dec 1982):

- a. Design and construction of propane combustion test stand
- b. Design and construction of data acquisition/processor (DA/DP) system

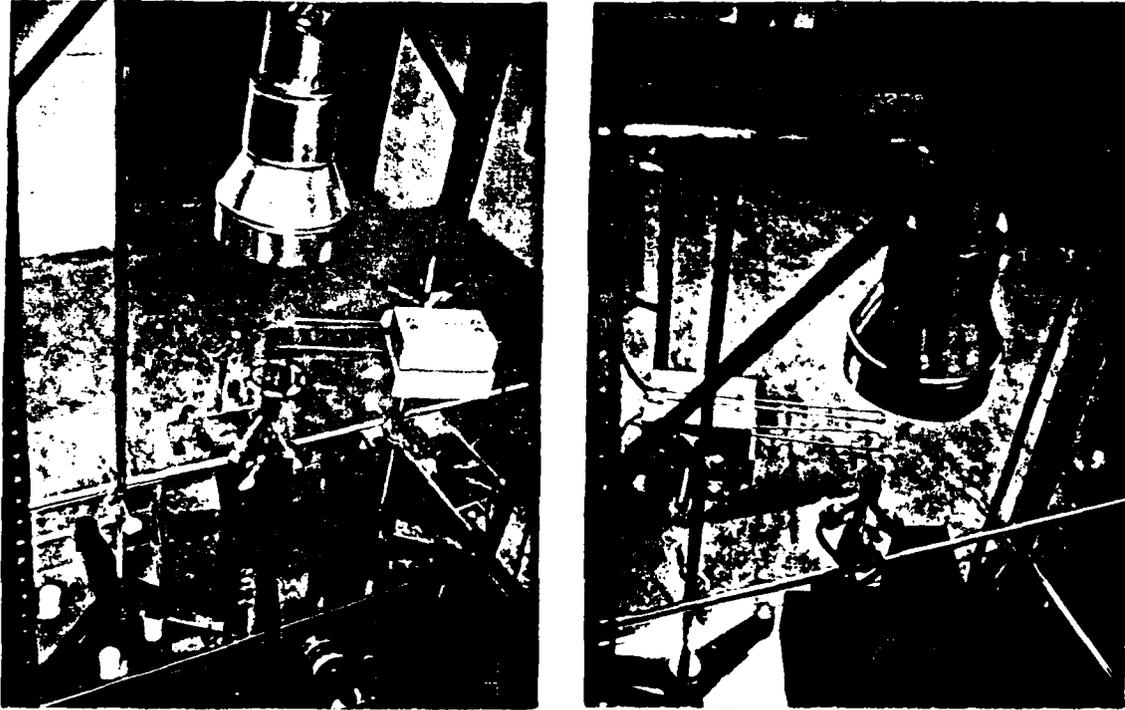


FIG 2 a.

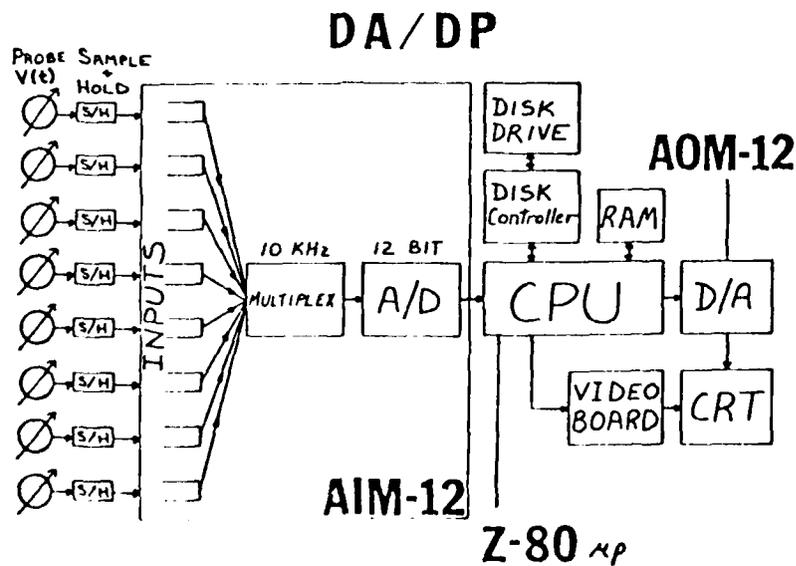


FIG 2 b.

PICOSECOND LIDAR TECHNIQUES IN  
LABORATORY AND FIELD DIAGNOSTICS

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The growing availability of very short laser pulses in the range of picoseconds ( $10^{-12}$  sec), opens a new potential in the field of diagnostics. It is now possible to observe chemical events over time intervals as short as  $10^{-9}$  sec (e.g., fluorescence, bond-selective chemistry,...) without overlap with the much shorter triggering signal. Also, very fast interactions (scattering, absorption) are neatly separated in time from slower sources.

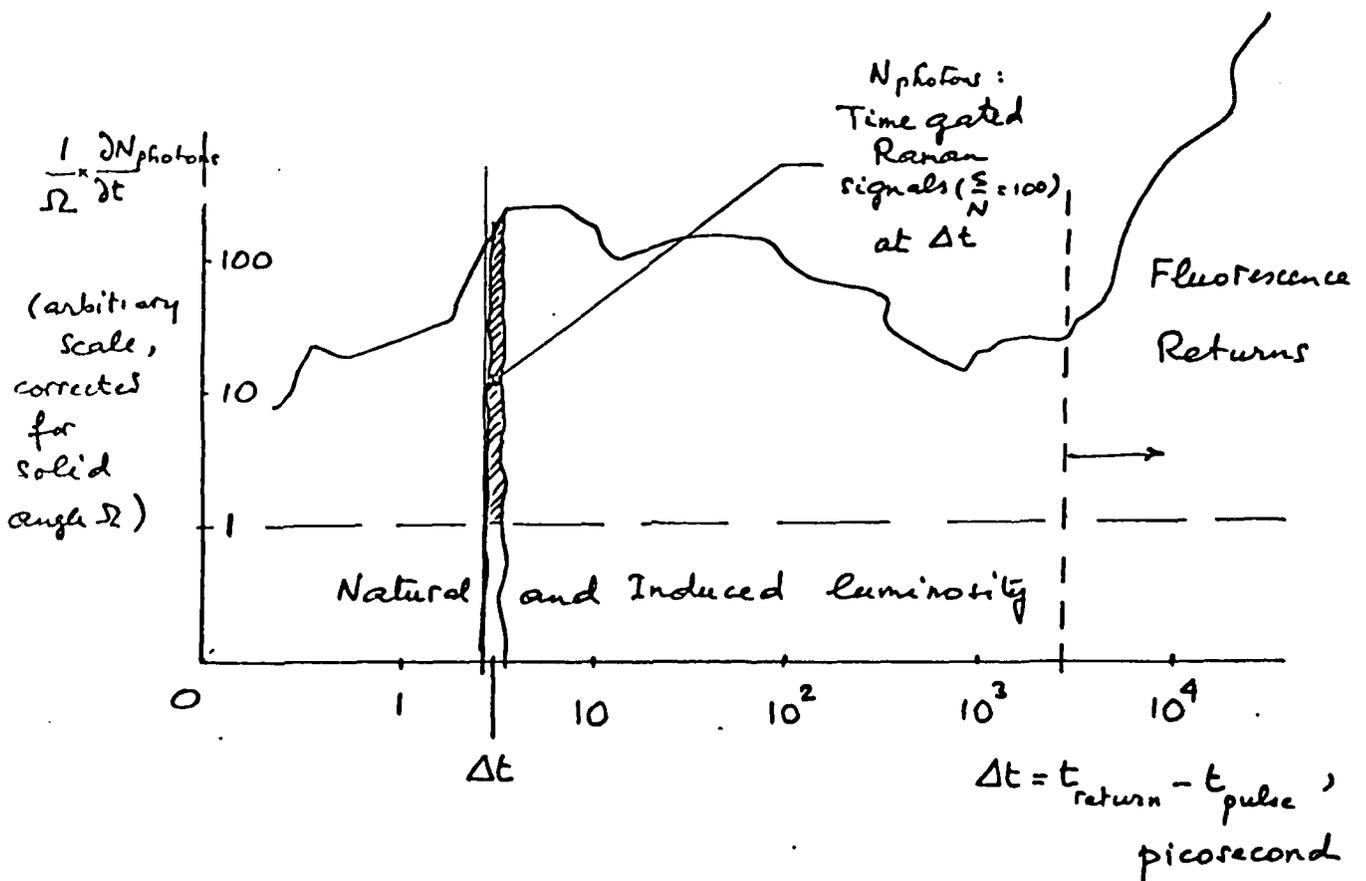
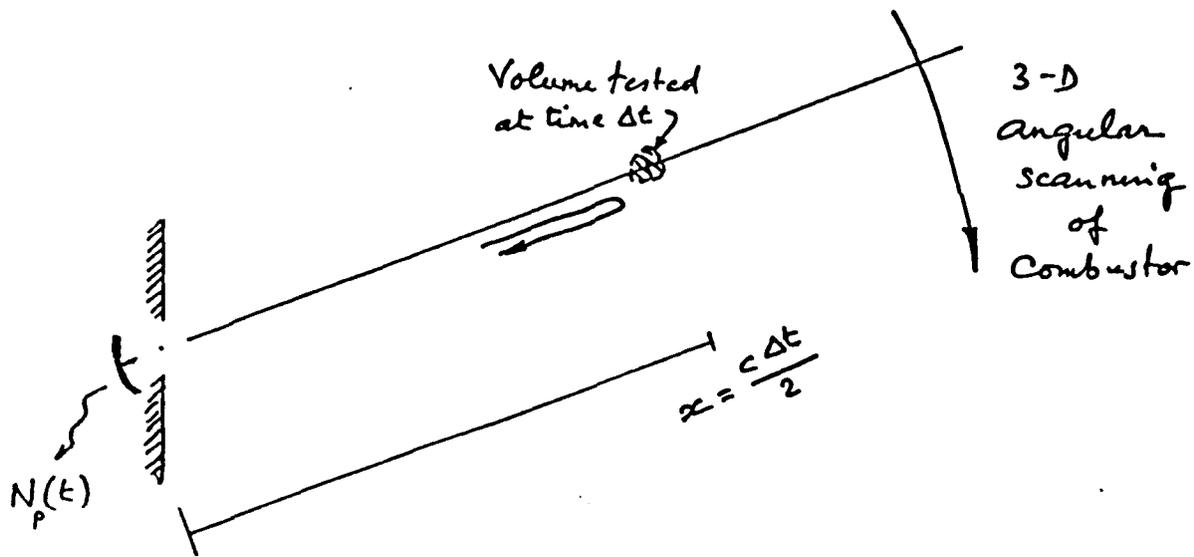
Two specific effects are of special interest to industrial flame diagnostics and propulsion exhaust remote sensing. One is the elimination of background noise, since the picosecond time-gating of the detector will collect the whole signal of interest but only a tiny fraction of the time-spread noise background (e.g., soot, walls,...). The other is related to the very short length of these pulses ( $\sim$  cm): it is the possibility to use the lidar/radar principle to convert the time history of the measured back scattered signals into a centimeter-resolved space distribution along the beam. In this fashion, Raman and other techniques can yield a detailed map of concentrations and temperatures in three-dimensional space, even in sooty combustors background, with the need of only one single porthole.

The current effort was initiated in November 1982. Its experimental phase is carried out in the laboratories of the UC Berkeley (Prof. John Daily, ME). An initial lidar lay out has been tested and the necessary mode-locking system will be available again later this Spring to pursue the experiment. The special challenge of this part of the work lies with the need to process relatively few Raman photons, through a high repetition mode photon counter (82 MHz).

On the review side, inquiries have given us the benefit of the experience of several groups interested in several distinct aspects of our problem:

- a) earlier experiments in background noise elimination - with nanosecond lasers - show the need to analyze more precisely the heating process of small soot particles [Flower (Sandia)]. This is being pursued currently.
- b) two recent conferences (NBS and the Optical Society of America) have illustrated the many applications where the lidar concept has proved dependable and successful (Raman, DIAL, Rayleigh and fluorescence). Thus, the possible picolidar applicability to stronger optical interactions should be considered.
- c) among these applications, two make use of picosecond lasers to resolve the detailed structure of ocean waves ( $\sim$  10cm) [Abshire, NASA] and the multiple scattering process in dense liquids ( $\sim$  2mm) [Elliott, Oregon Grad. Center).

There seems to be a consensus among experimenters, that streak cameras are appreciably more reliable than wave digitizers, even at a fairly high photon rate. This need coincides with a sizable reduction in the cost of sensing equipment: The new Hamamatsu cameras are now in the \$27,000 range.



Picosecond Response in time-space

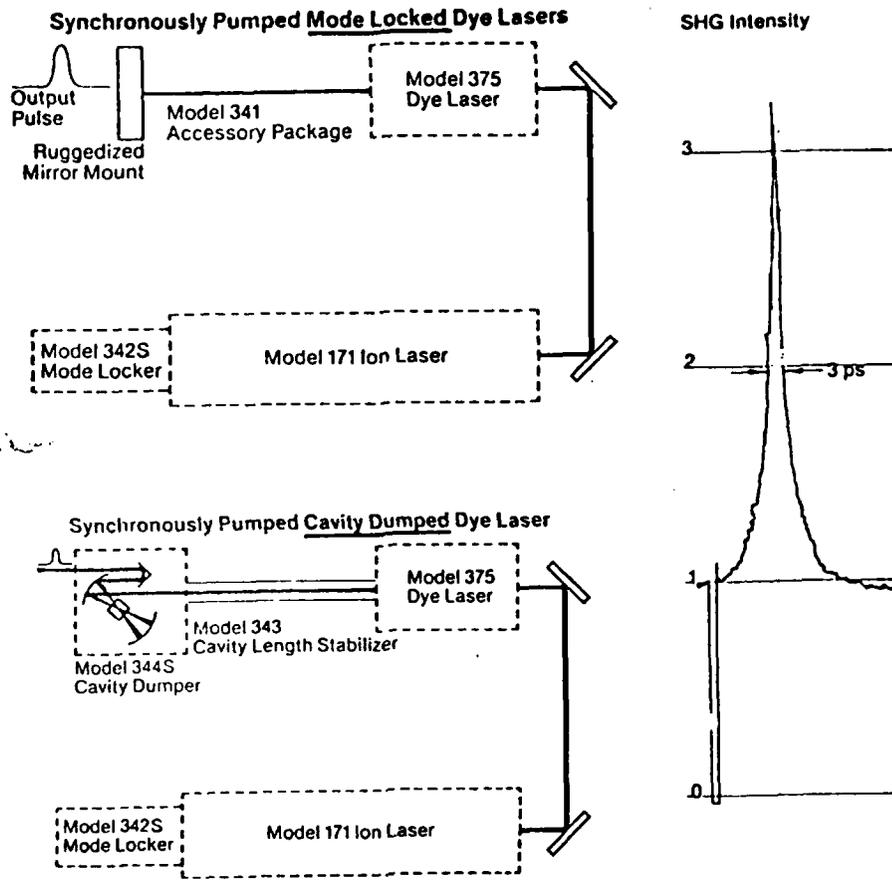
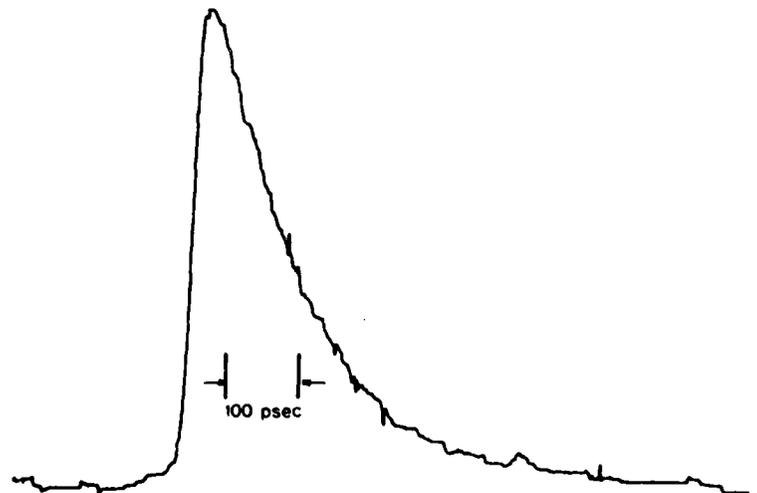
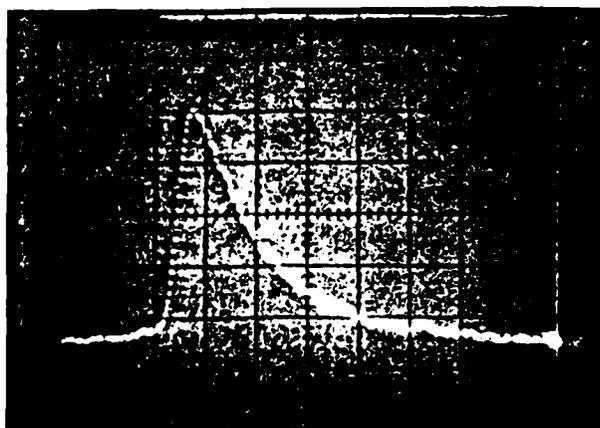


Fig. 1 - The two types of synchronously pumped laser systems (Spectra Physics). The figure on the right corresponds to the first type.



FLUORESCENCE DECAY OF DSCI\* IN METHANOL

Fig. 2 - An Imacon-Syncroscan Tube image (10 psec resolution)

COMPUTED LASER TOMOGRAPHY FLOW DIAGNOSTICS

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Computed tomography is a method of reconstructing images from its line integrals along a large number of intersecting rays in a plane. Simulations have shown that reconstructive tomography can provide good spatial resolution of the density of a species in gases.<sup>1</sup> Laser probed computed tomography provides a non-intrusive method of measuring physical quantities in a plane rapidly, in contrast with point measurement techniques. Furthermore, tomography does not require the ability to have access outside the plane of interest. This feature makes tomography a very interesting diagnostic technique whenever three dimensional access is not possible as is the case in opaque or very large systems. Owing to the fact that absorption measurements are made, tomography data is easier to interpret than fluorescence data whenever large pressure differences affect the fluorescence rate through quenching, as in supersonic flow.

We have built a 24 inch diameter detector ring with 90 photodiode detectors to measure the iodine vapor concentration in a laminar flow by measuring the absorption of the 5145 Å argon laser scattering from the perimeter of the ring. Our scanning geometry, shown in Fig. 1, allows a spatial resolution of 2-5 mm, and data acquisition times under 0.1 second. We have a system capable of investigating the sensitivity, signal and sampling requirements for optical tomographic measurements of physical systems.

One feature of the convolution back projection method of tomographic reconstruction is that it automatically interpolates the density for regions where there is insufficient information from the sampling processes. Figure 2 shows the first laser absorption tomographic reconstruction of an iodine vapor cloud. The spokes result from the high spatial frequencies inherent in the hard edges. Our apparatus, and theoretical calculations allow us to make theoretical and experimental comparisons of laser tomography for combustion and flow diagnostics.

References:

1. D.C. Wolfe and R.L. Byer, "Model Studies of Laser Absorption Computed Tomography for Remote Air Pollution Measurement", Appl. Optics, vol. 21, p.1165 (April 1982).

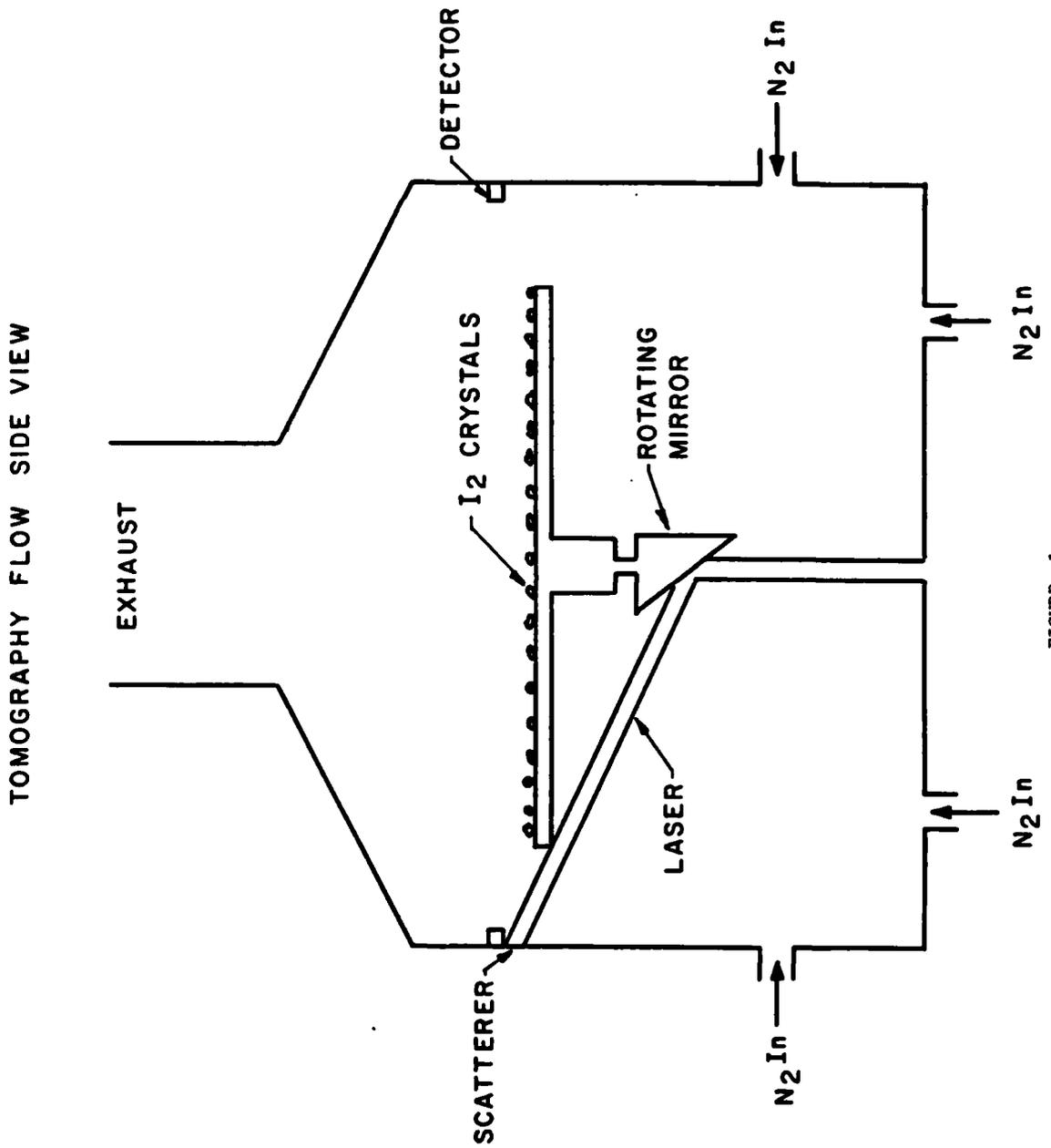
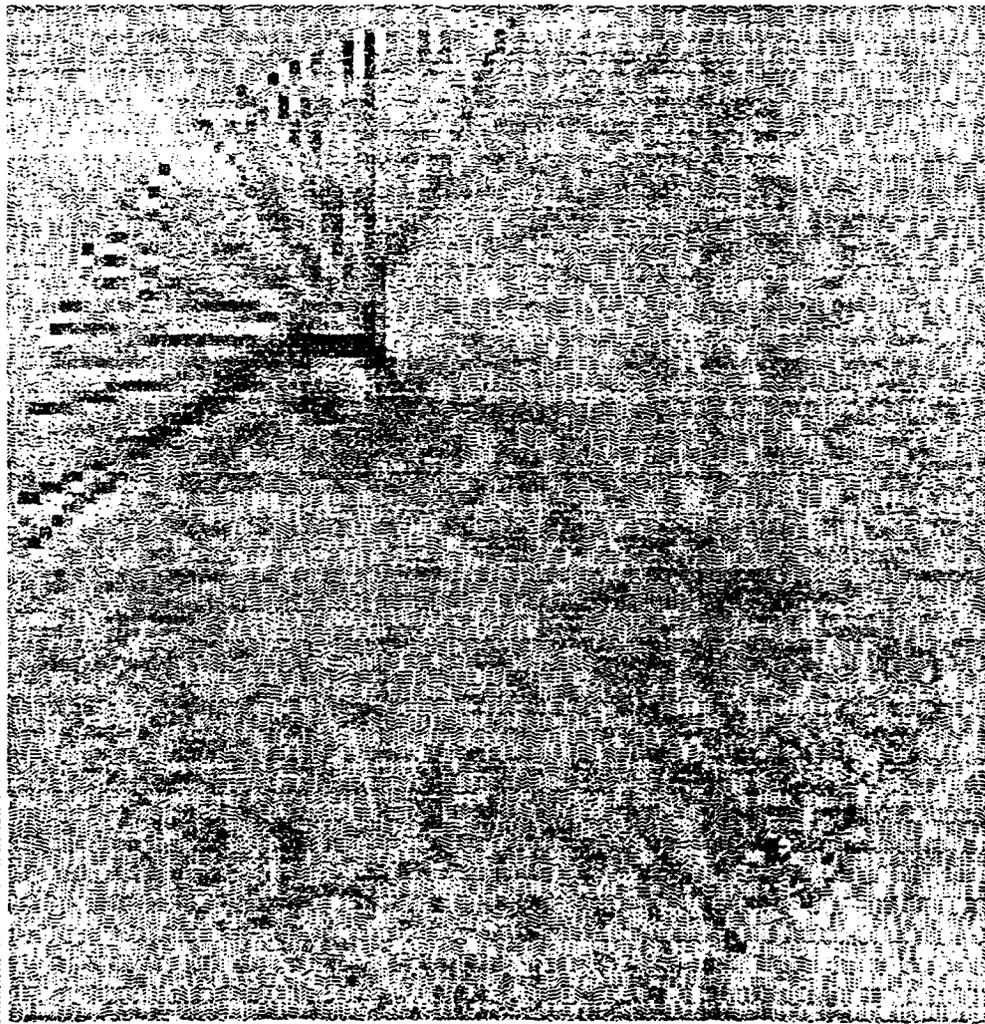


FIGURE 1



FILE:sep15                    COLOR MAP, BINS 1- 16==>>  
DATA MAX. = 3.221726E+00    DATA MIN. = -1.287896E+00

FIG. 2 --Reconstruction of a rectangular cloud of iodine vapor.

QUANTITATIVE FLOW VISUALIZATION

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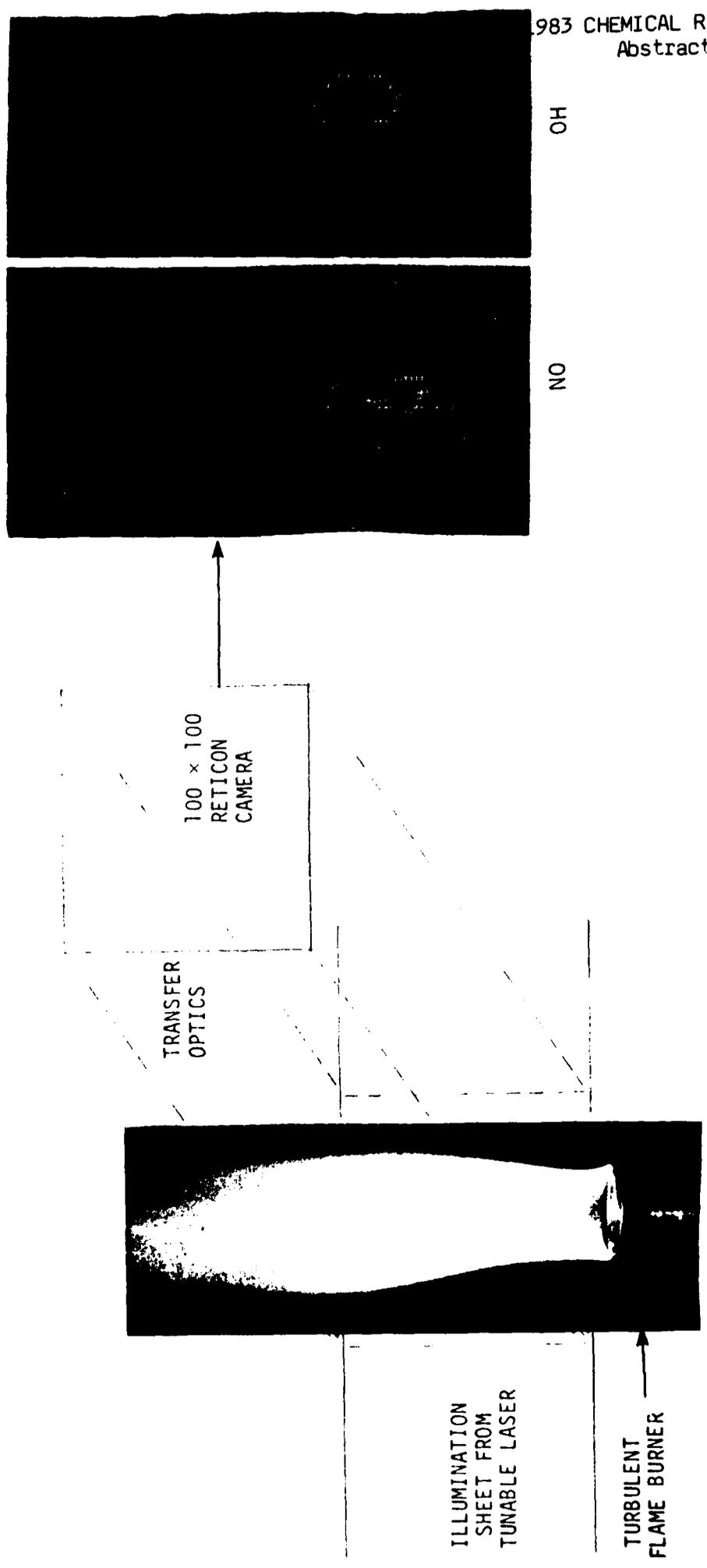
The utility of flow visualization in fluid mechanics is well established. At present, most visualization techniques are qualitative and are based on line-of-sight approaches poorly suited for flows with three-dimensional characteristics. With the development of laser-based light scattering techniques, it should be possible to obtain temporally resolved, quantitative records of flow properties throughout a plane (and ultimately throughout a volume) using sheet illumination and techniques such as Raman, fluorescence or Mie scattering. Pioneering work in this direction using Mie scattering from seeded particles was initiated at Yale a few years ago, and during this past year significant progress has been made at Stanford, Yale and SRI using fluorescence- and Raman-based methods.

Distinguishing features of the Stanford project are: (1) use of fluorescence rather than Raman or Mie scattering; (2) emphasis on recording at high repetition rates, thereby allowing studies of the real-time evolution of fluid mechanical structures; (3) use of an intensified photodiode array rather than a vidicon detector; and (4) the goal of establishing measurement capabilities for multiple quantities, including species concentrations, temperature and velocity.

The advantages of fluorescence are that the gas can be tagged at a molecular level, thereby avoiding lag, and the signal is species specific. The major disadvantage of fluorescence has been that of properly accounting for quenching. We believe this can be handled through calibration or by using a variation of the process, known as off-resonance fluorescence, which is weaker but serves to minimize the dependence of signal level on variable quenching parameters.

The approach and initial results for measurements of species concentration and velocity are shown in Figs. 1 and 2 respectively. In both cases the flow is illuminated with a sheet of light from a tunable laser and the laser-induced fluorescence is recorded with an intensified Reticon array (100 × 100) coupled to a dedicated laboratory computer. In Fig. 1, instantaneous, single-frame results for NO and OH are shown obtained in a turbulent premixed flame. Sensitivity of below 100 ppm has been achieved with submillimeter spatial resolution. In Fig. 2, velocities in a steady, supersonic jet are inferred by scanning an absorption line of I<sub>2</sub> and measuring (via the broad-band fluorescence signal) the Doppler-shift in the peak wavelength. Sensitivity of a few m/sec and a recording time of 0.01 seconds is anticipated in the next generation of this experiment.

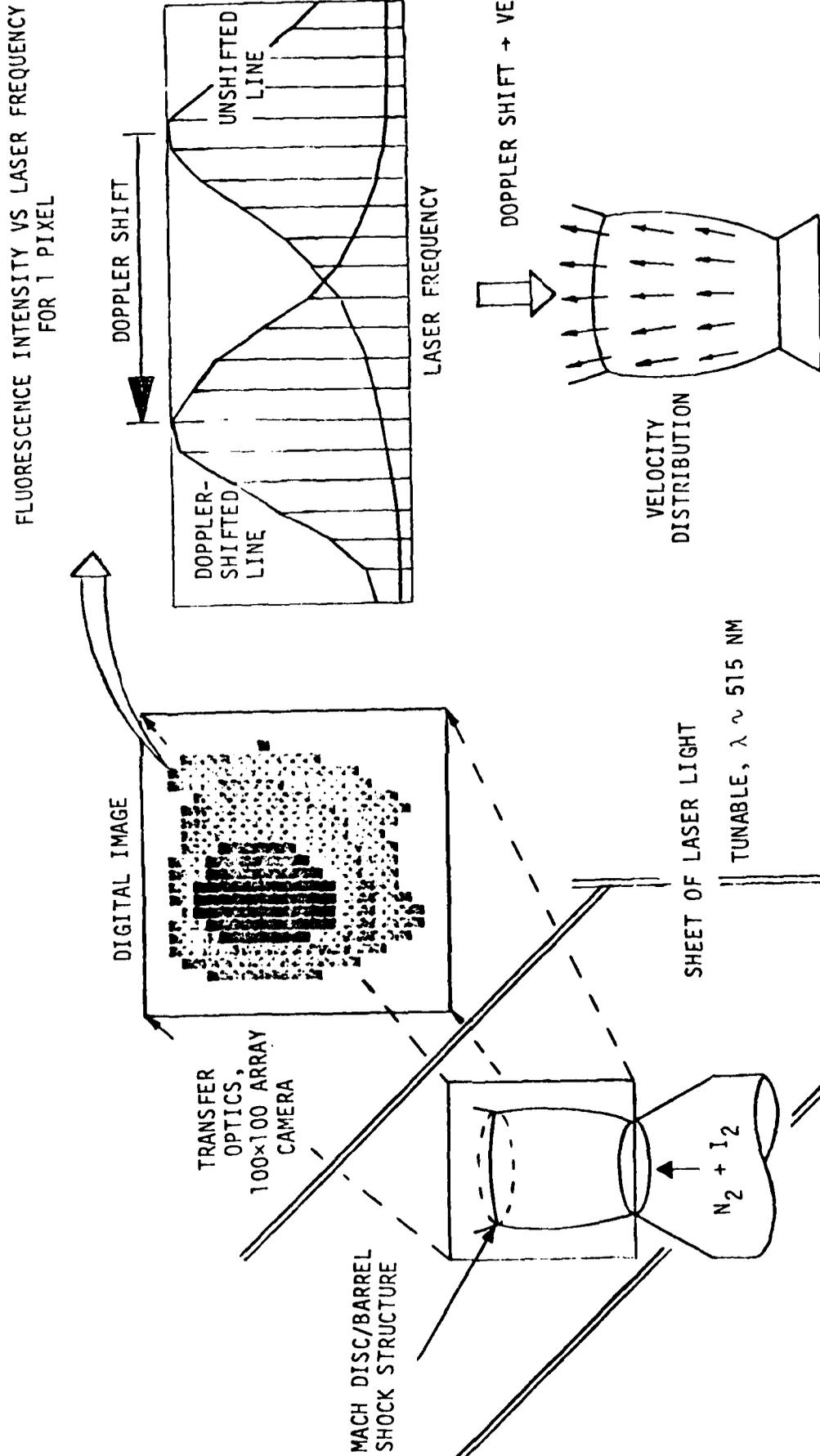
QUANTITATIVE FLOW VISUALIZATION  
PLANAR LASER-INDUCED FLUORESCENCE (PLIF) YIELDS  
2-D CONCENTRATIONS IN TURBULENT FLAMES  
DIGITAL SPECIES IMAGES



- FIRST INSTANTANEOUS MULTIPLE-POINT SPECIES MEASUREMENTS IN A FLAME ( $10^4$  POINTS)
- HIGH SPATIAL ( $0.4 \times 0.4 \times 0.2$  MM) AND TEMPORAL (5 NSEC) RESOLUTION
- POTENTIAL MAJOR IMPACT ON COMBUSTION MODELLING

FIG. 1. HIGHLIGHTS OF QUANTITATIVE FLOW VISUALIZATION PROJECT.

SIMULTANEOUS MULTIPLE-POINT VELOCITY MEASUREMENTS BY SENSING  
 DOPPLER-MODULATED LASER ABSORPTION WITH A DETECTOR ARRAY



- FIRST QUANTITATIVE MULTIPLE-POINT VELOCITY MEASUREMENTS IN A GAS FLOW
- NO PARTICLE SEEDING REQUIRED
- NO TEMPERATURE PERTURBATION (AS WITH SODIUM SEEDING)
- VERY GOOD AGREEMENT WITH THEORY
- GOOD PROSPECTS FOR EXTENSION TO SUBSONIC FLOWS WITH TEMPORAL RESOLUTION

Fig. 2 Highlights of Velocity Visualization Project.

## QUANTITATIVE THREE-DIMENSIONAL FLOW VISUALIZATION

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**Research Objective:** Turbulent combustion requires molecular mixing, a complicated three-dimensional process. Improved knowledge about the topology of the fluid elements which are fully mixed will greatly enhance our understanding of combusting flows. Presently no satisfactory three-dimensional spatially and temporally resolved technique exists for making such measurements. The objective of the research is to devise such a method. The focus of the effort is directed towards new approaches in data processing and data display with full 3-D parallax.

**Explanation of the approach:** The approach involves acquiring quantitative flow data in cross sectional planes at regular intervals throughout the three-dimensional flow field. The volumetric data are processed in a digital computer for feature extraction and image enhancement. The processed data associated with the stack of planes are synthesized into a continuous volumetric object using interpolation techniques and a multiplexed hologram of the flow field is computed. The flow field is reconstructed and displayed with true depth perception by illuminating the hologram with white light or laser radiation.

**Uniqueness of the approach:** i) Any quantitative data obtained in a stack of planes can be analyzed and displayed with the new technique, including velocity, temperature, pressure, density and species concentration. ii) Either coherent (laser) or incoherent (eg. fluorescence) radiation can be used to probe the flowfield, in contrast to holography which requires coherent light for data acquisition. iii) Digital data processing provides a solution for the cloud-within-a-cloud problem; opaque elements at the perimeter of the volume can be digitally removed or artificially made transparent to expose details in the interior.

**RESULTS: I. Data Acquisition** - The wake flow behind a circular cylinder has been studied in Professor Cantwell's droplet evaporation facility. A stationary sheet of laser light oriented perpendicular to the mean flow direction is used to illuminate a particle laden flow. Smoke is injected into the flow from two slots parallel to the cylinder axis and located at 45 degrees with respect to the front stagnation line, as indicated in Figure 1. The scattered radiation is simultaneously recorded on film with a high speed motion camera. Sequential frames in the movie thus represent planar cross sections of the three-dimensional streak line pattern made visible by smoke tracers. In a similar fashion species concentration has been measured in a laminar premixed methane-air flame seeded with sodium. The laser light is tuned to the sodium-D line and high resolution images of the fluorescent radiation are stored on motion picture film. The intensity on the film represents the number density of the tracer gas, and provides information about the topology of the combusting process.

**II. Data Processing** - An interface driver has been built to link our digital image processing facility to our VAX 11-780 and two edge detection software programs have been written, one based on the Sobel operator and the other on a Gaussian convolution method. A general purpose filtering and image enhancement program has been coded, and examples of the processed flow data are shown in Figure 2. Furthermore, software has been developed to generate multiplexed holograms, and a computer generated volumetric test pattern has been displayed for the purpose of evaluating errors in the hologram display process.

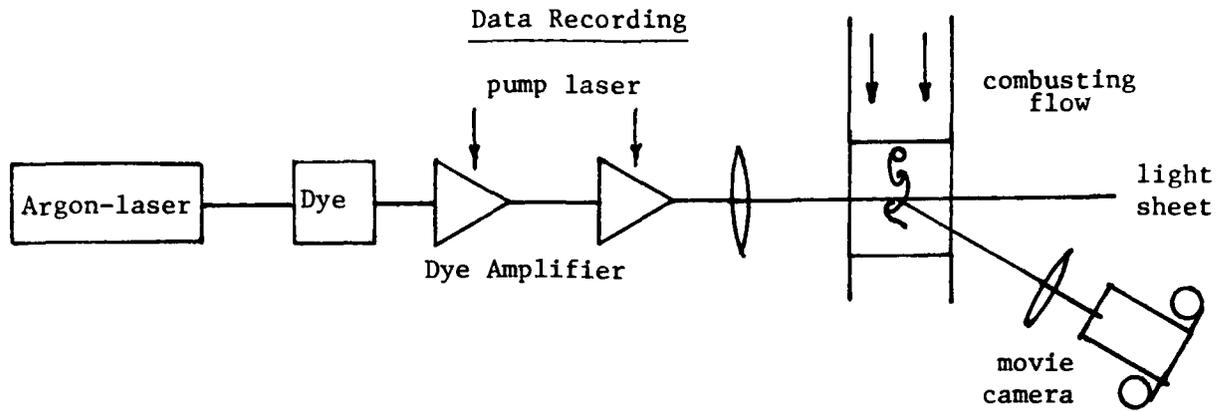
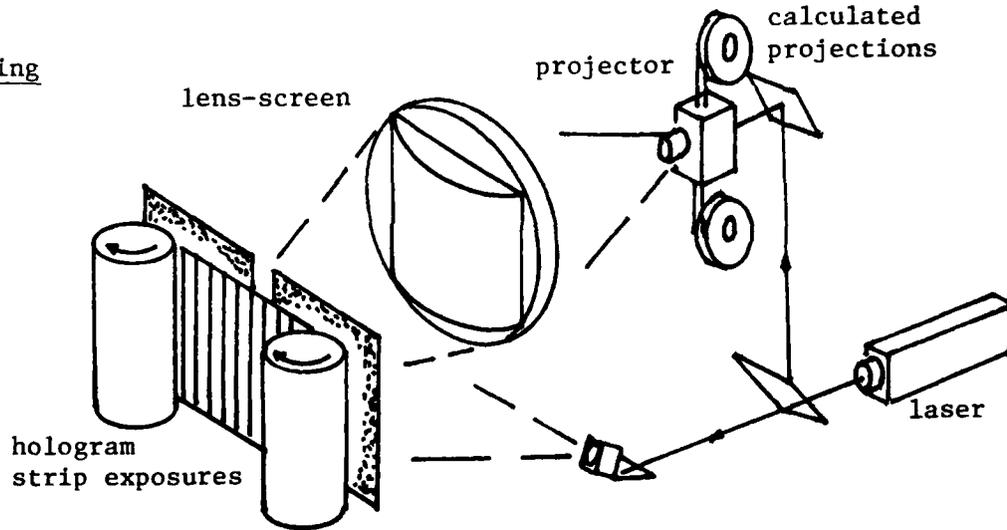


Image frames are digitized and processed for feature extraction, such as edge detection and a three-dimensional computer representation of the flow field is synthesized. Subsequently, stereo projections of the object onto a cylinder surrounding the object (as seen by an imaginary human observer) are calculated. These projections are used to synthesize a multiplexed hologram.

Synthesizing



Viewing

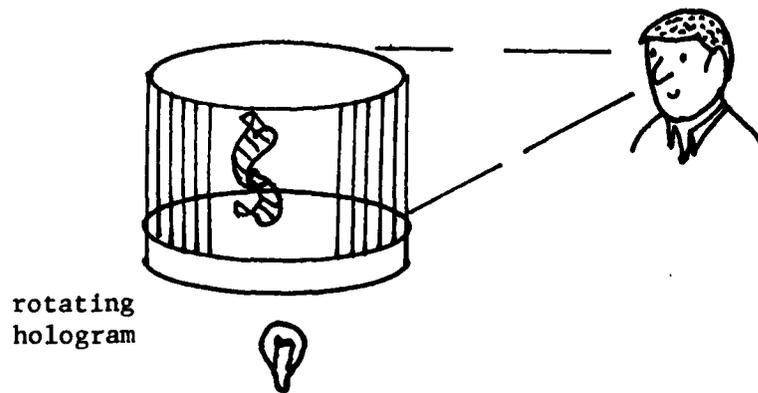
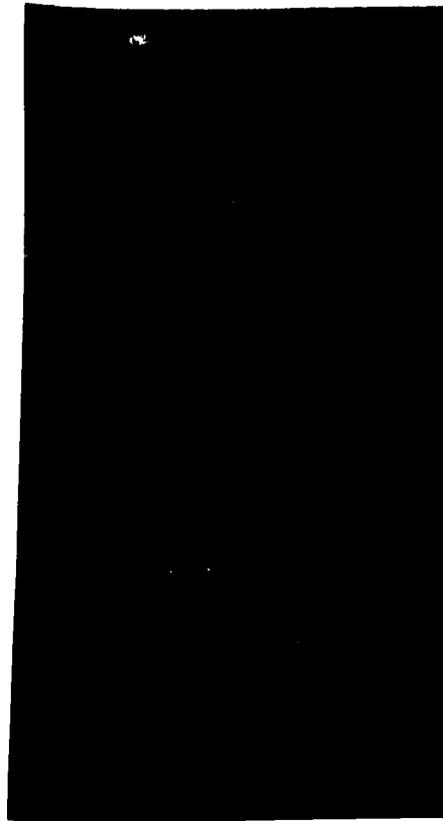


Fig. 1. Principle of the Approach



Particle streak pattern of a cylinder wake flow

(a) cross section perpendicular to mean flow



Pseudo color pictures of edge patterns obtained by processing the images with the Sobel operator. (not to scale)

Figure 2. Results

MEASUREMENTS IN TURBULENT REACTING FLOWS

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A principal motivation for the development of advanced diagnostic techniques for reactive flows is the need to characterize flow fields in practical combustion geometries. Flow field measurements are useful not only in understanding combustor performance but also in providing information for validating combustor models. The three principal objectives of the present research effort are: (1) to develop and characterize a laboratory-scale reacting flow which simulates essential features of practical combustor flow fields, (2) to apply various diagnostic techniques in order to evaluate these techniques and (3) to obtain data on turbulent reacting flow field structure in order to guide further development of new diagnostic techniques and to provide input to reacting flow models.

The flow configuration employed in this investigation is shown in Figure 1, along with a schematic diagram of a fiber optic absorption probe system which was developed for species concentration measurements. This unique plane, reacting shear flow facility provides a means of simulating fuel-air mixing regions in air-breathing engines. A variety of probe and optical diagnostic techniques have been employed to characterize the turbulent reaction field. Time-resolved velocity measurements have been made using hot wire anemometry. The fiber optic absorption system provides simultaneous, temporally and spatially resolved concentration measurements of both a reactant and product species ( $O_3$  and  $NO_2$ ).

Time-resolved velocity and species concentration measurements, Figure 2, provide a complete characterization of the reacting flow, which is available for evaluation and validation of newly-developed advanced diagnostic techniques. In addition, these data provide useful new fundamental information on turbulent reaction phenomena and may be applied toward the development of appropriate methods for including the coupling of fluid dynamics and chemistry in reacting flow field models.

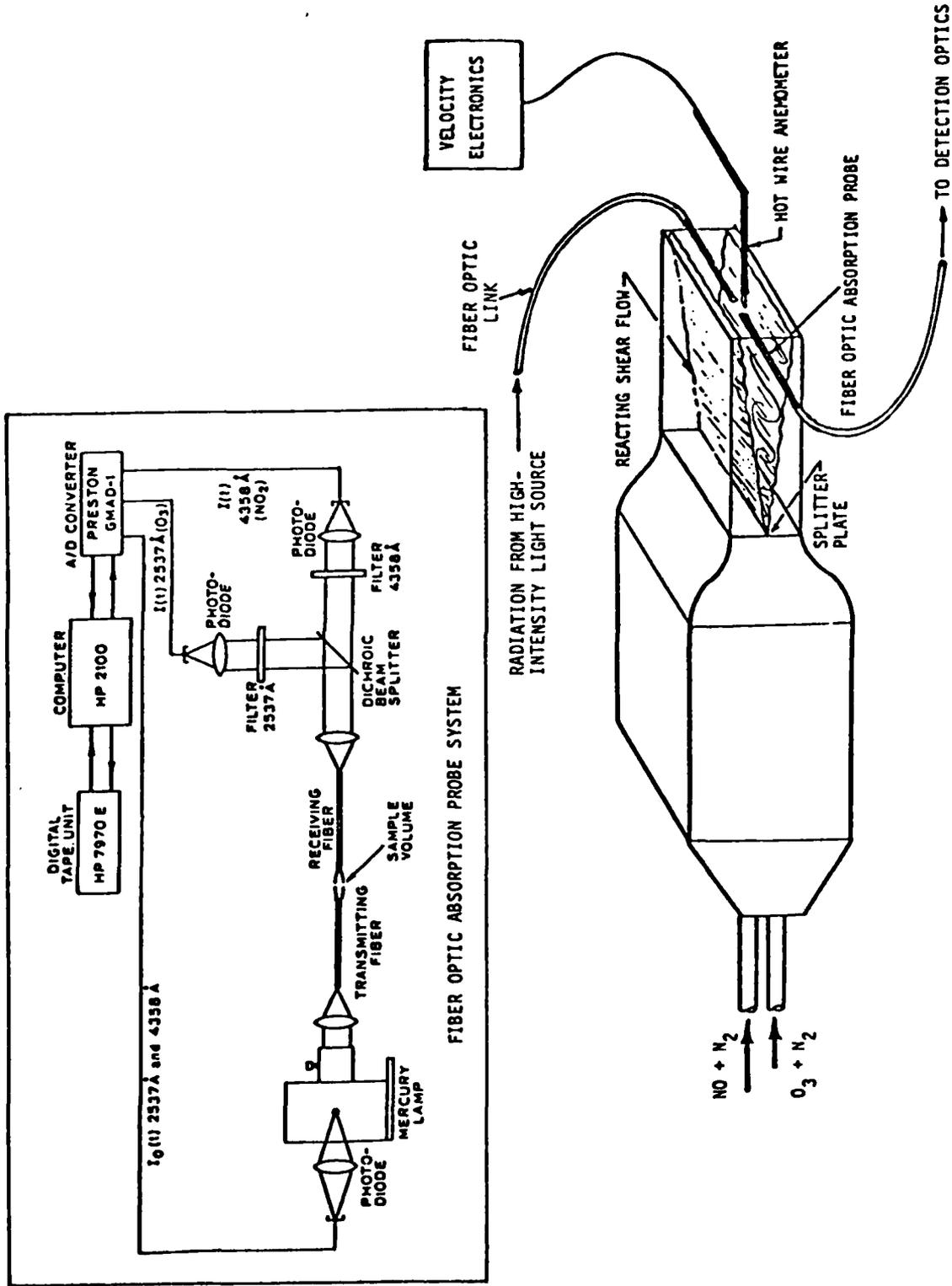


FIG. 1 REACTING MIXING LAYER FACILITY

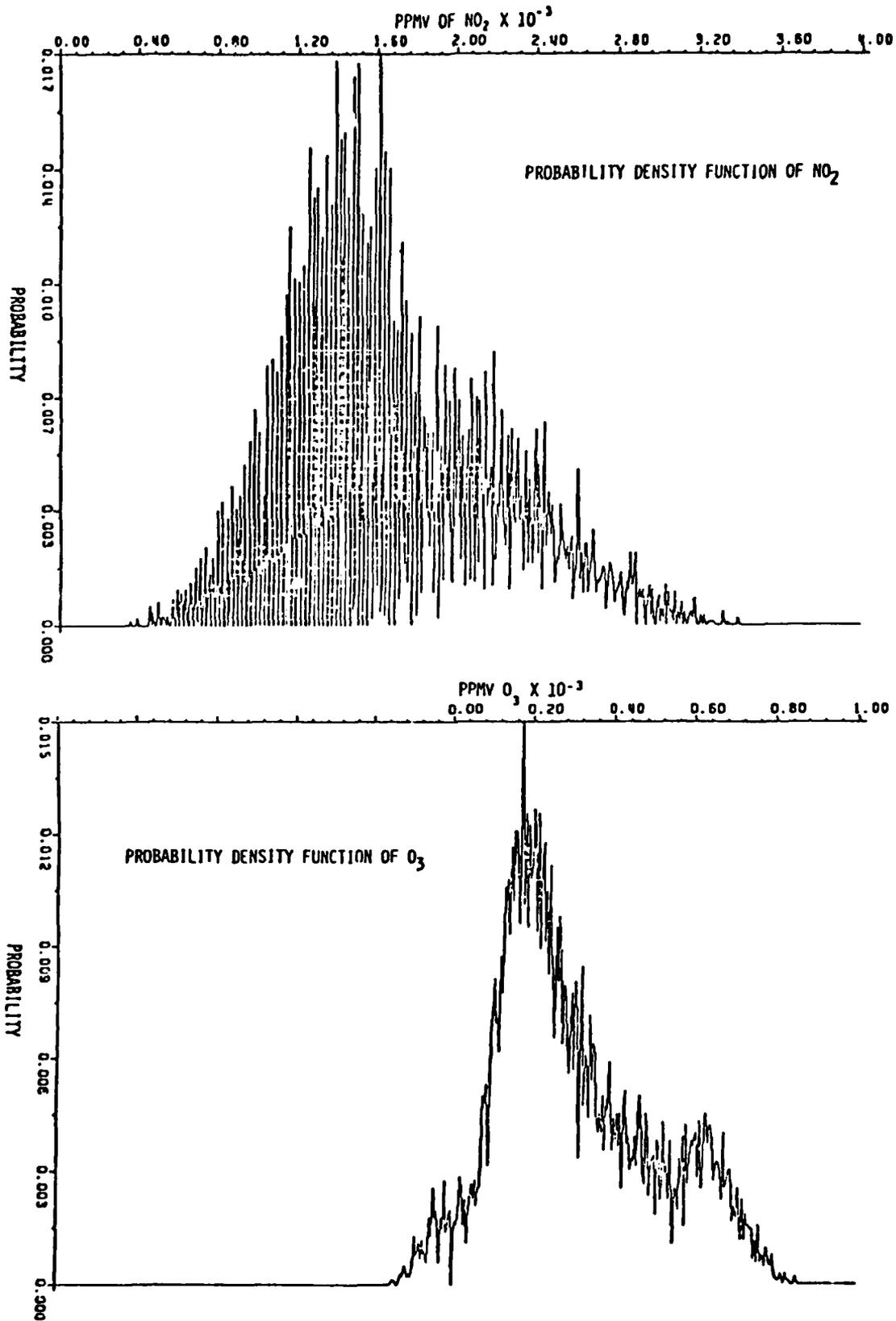


FIG. 2 PDFs of NO<sub>2</sub> and O<sub>3</sub> AT A LOCATION IN THE REACTING MIXING LAYER

TIME AND SPACE RESOLVED INSTANTANEOUS  
MEASUREMENT OF VELOCITY VALUES

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GRANT AFOSR 82-0266

ABSTRACT:

A wide range of flows of interest in science and engineering can be investigated by applying laser-doppler velocimetry (LDV). In its current configuration the LDV method is used to measure flow velocities and velocity distributions by recording the doppler shift of light scattered by particles in the flow of interest. However, some flows of interest exist, where the LDV-method does not produce satisfactory results in connection with existing signal analyzing systems. (Internal combustion engine, high turbulent flow). Current electronic data acquisition systems such as counter, tracker and digital correlator fail to analyze and process LDV signals generated by high turbulent flows and flows with fast changing velocity directions. Because wide band LDV acquisition systems are restricted to certain types of signals, their application in difficult flow situations is questionable. In order to overcome this problem associated with processing noisy LDV signals from instationary high turbulent flows, an optical spectrum analyzing method will be applied.

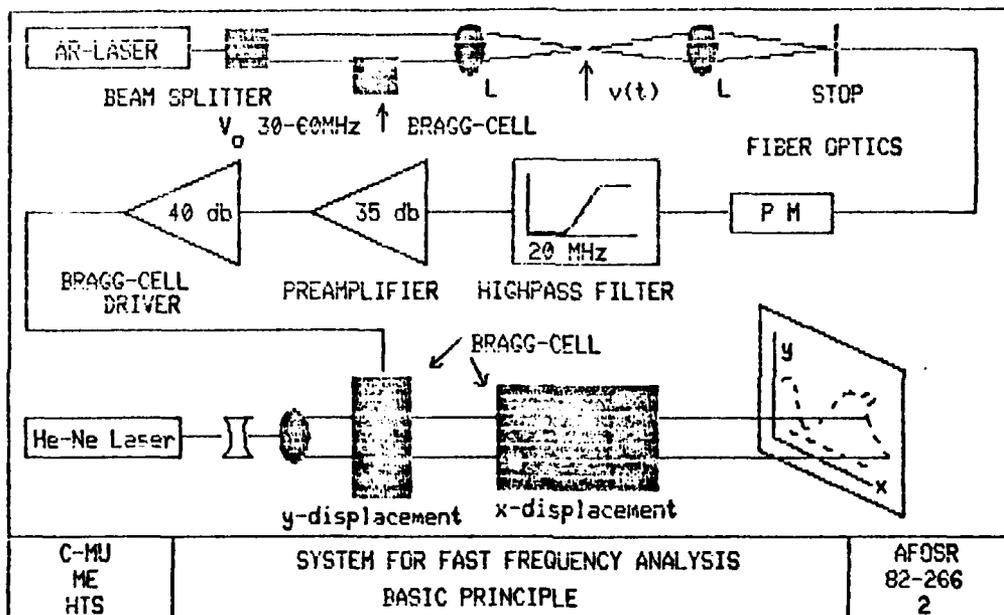
In addition to these requirements, the decoupling of the signal processing procedure from the form of the signal and the seeding density is of interest to extract the useful information related to the physics of the observed flow. The optimal solution of the above mentioned problems is produced by fast fourier-transform-techniques of the signals of interest. Using electronic frequency analyzers, the time necessary to process the signal is too long compared with the overall "LDV-Burst" time. Using optoelectronic fourier-transform by applying the optoacoustic effect of a bragg-cell it will be possible to produce real time spectra of about 30 MHz bandwidth at a mean-frequency of about 40 MHz. A schematic of the optoelectronic signal-processing system is given in the Figure.

The LDV-Burst received by the photomultiplier is high-pass filtered and amplified up to a power level of about 1-2 watt. This signal is used to generate an ultrasonic burst in the optical part of a bragg-cell. Laser light is defracted at the generated sonic wave-pattern and the angle of defraction is a function of the frequency feed into the bragg-cell. The intensity of the defracted laser beam (1. order of defraction) is a maximum if the laser beam is entering the cell under bragg-conditions. The displacement of the first order of defraction of the laser beam is directly proportional to the frequency, and can be stored photographically.

PROJECT STATUS:

The project was started with a detailed familiarization and literature review of design criteria for optoacoustic and electronic instrumentation. Bragg-cells of different vendors have been evaluated and components to build an optical spectrum analyzer are on order. Since the project is in its early state, measurements and a performance demonstration cannot be given at present.

SYSTEM FOR VELOCITY MEASUREMENT AND  
 INSTANTANEOUS FREQUENCY ANALYSIS.



PACKAGED, FIBER-OPTIC SPECTRORADIOMETER

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ABSTRACT

This research is aimed at satisfying the need for a standard, versatile instrument for temperature measurements in flames and combustion flows at temperatures where thermocouples or other probes are inapplicable.

A compact, packaged, automated spectroradiometer has been developed, based on the emission-absorption (line-reversal) technique using a resonance line of Sodium or Potassium seed. The optical system (Fig. 1a) employs fibers to transmit radiation from a standard lamp to the gas, and from the gas to a photodetector. Miniture choppers are used to generate a repetitive sequence of three signals:  $S_L$  from the lamp,  $S_G$  from the gas and  $S_{L+G}$  transmitted from the lamp through the gas. Following electronic demodulation (Fig. 1b) the three signals are used to calculate the gas temperature  $T_G$  from a simple algorithm in a mini-computer which outputs  $T_G$  with a time resolution of 1 msec. Spectral selection in the wing of the resonance line is achieved with an interference filter. A second detection channel, detuned from the resonance line, allows corrections to be made for particle laden flows. The whole instrument is packaged and mounted remotely from the combustion test rig to which it is coupled by fibers which may be of considerable length.

In the past year, three main advances have been achieved:

- (i) A versatile, benchscale, flat flame, diffusion burner (Fig. 2) has been constructed and tested as a vehicle for testing the instrument. Using CO or H<sub>2</sub> with oxygen it achieves flame temperatures exceeding 3000 K and can be seeded with K or Na vapor. It also has provision for feeding particulates such as Al<sub>2</sub>O<sub>3</sub> to simulate rocket exhausts.
- (ii) For measuring temperatures to 3000 K it has been demonstrated that quartz-tungsten-halogen lamps may be used in place of the conventional tungsten ribbon lamp as a reference source.
- (iii) An analysis based on the equation of radiation transfer has been completed which rigorously takes account of particle scattering and allows the instrument's output to be interpreted for measurements in particle laden flows.

Publication

S. A. Self, P. H. Paul and P. Young, "A Packaged, Fiber-Optic Spectroradiometer for High Temperature Gases with Automatic Readout", Sixth Symposium on Temperature: Its Measurement and Control in Science and Industry, N.B.S. March 1982.

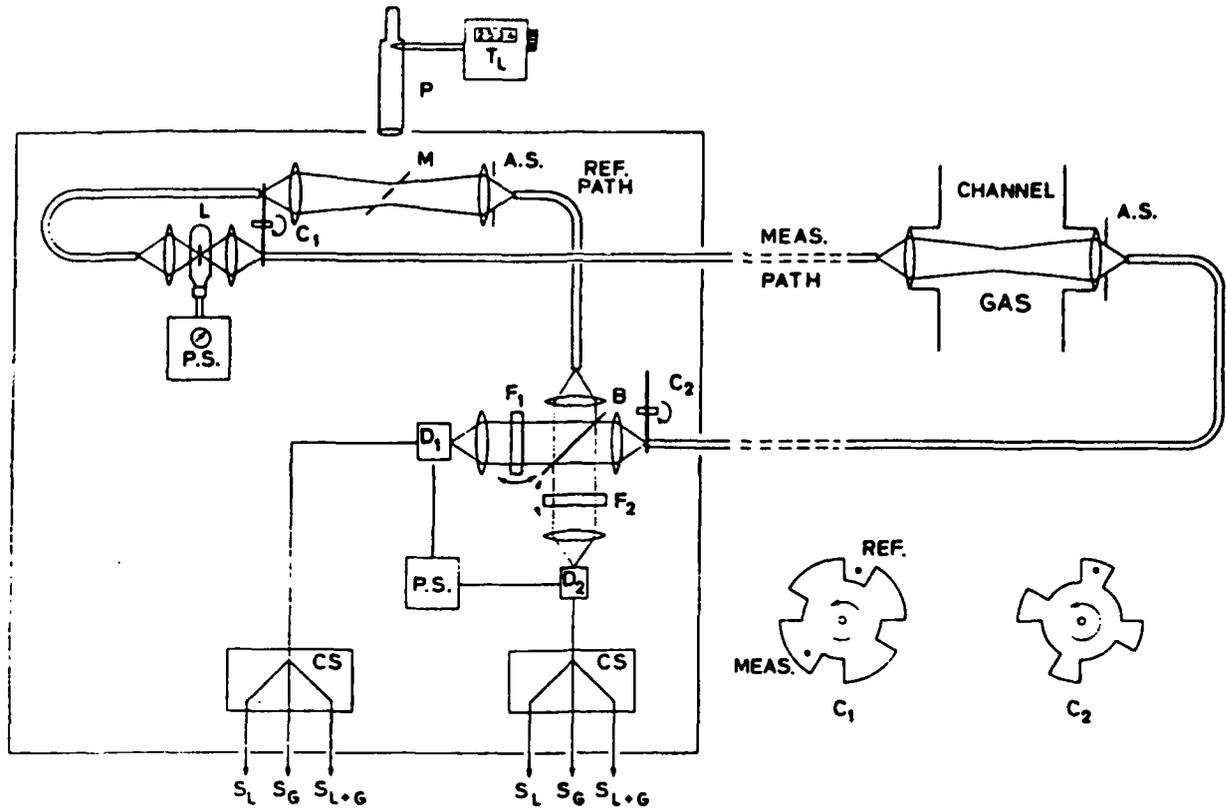


Figure 1(a). Optical Configuration: All components in boxed area are packaged and mounted remotely.

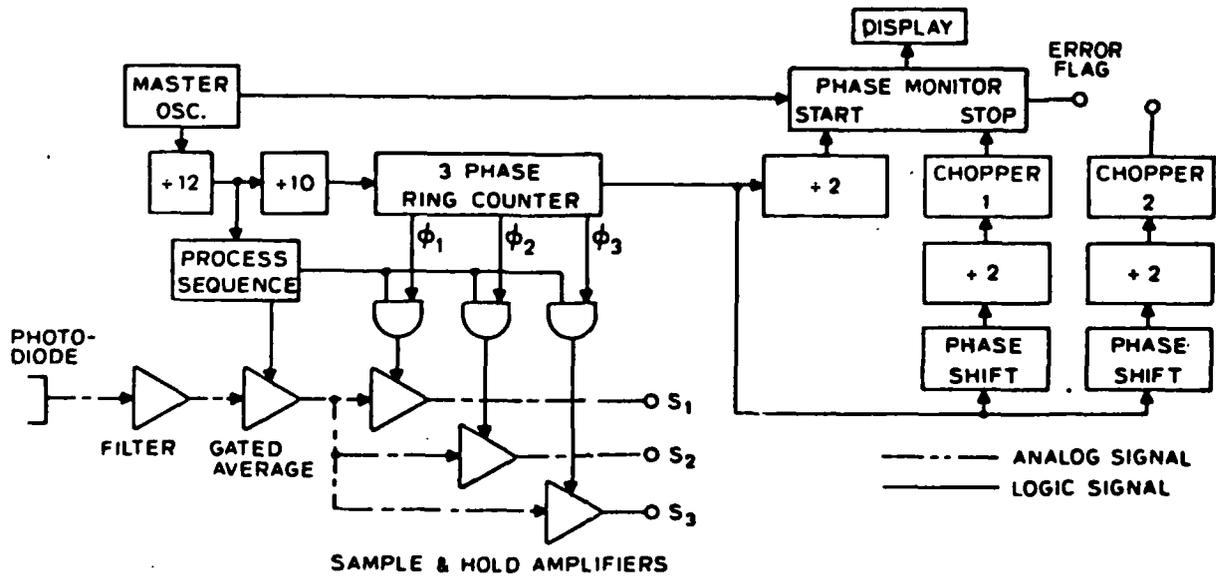


Figure 1(b). Channel Separating Electronics to Demultiplex the Chopped Signal Sequence.

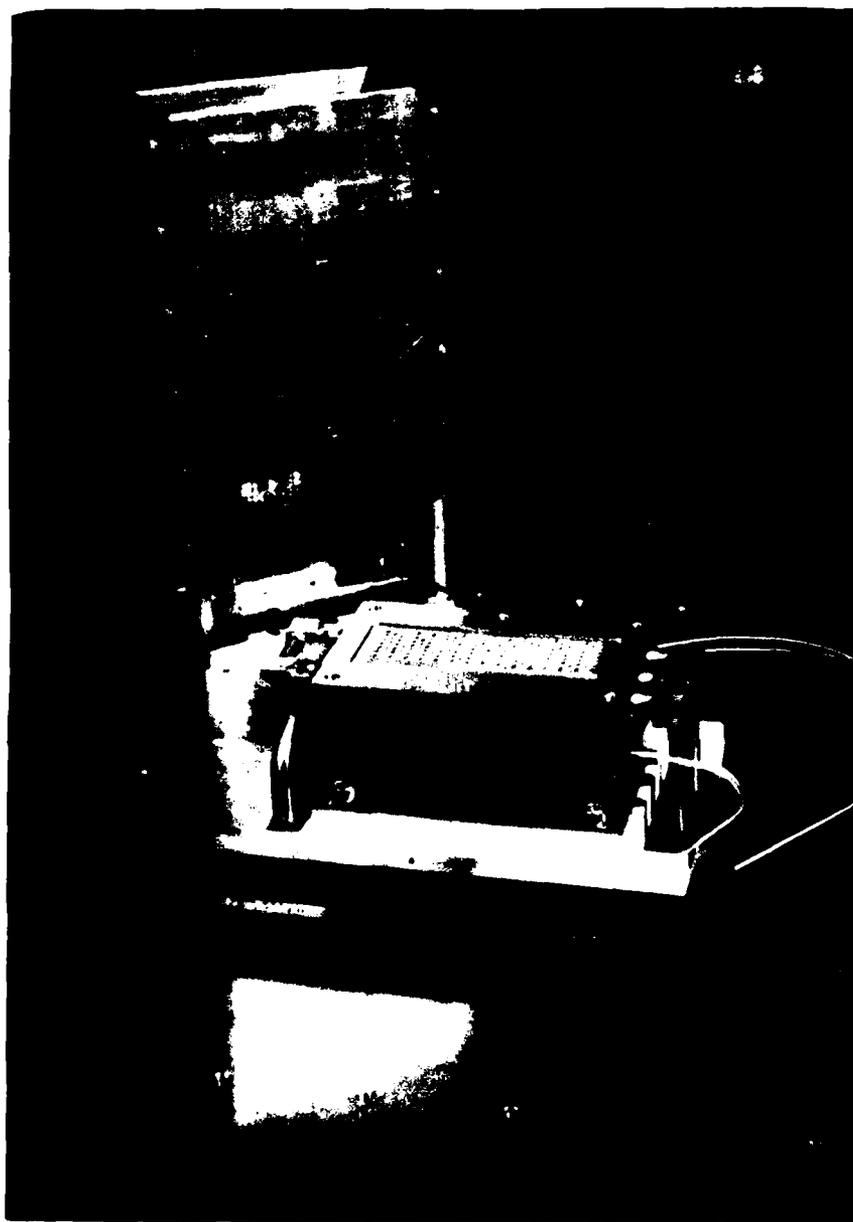


Figure 2. Versatile, high temperature burner (to 3000 K) with provision for alkali metal seed and particle injection; ceramic-lined chimney shown separately.

PARTICLE SIZING FOR ROCKET EXHAUSTS

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ABSTRACT

This work is aimed at developing instrumentation for measuring the size and concentration of macroscopic particles in solid fuel rocket exhausts. Two approaches are being used: a two-wavelength laser transmissometer (Fig. 1) and an in-situ sampling wire filter (Fig. 2), both of which have been successfully used previously in coal-fired combustion MHD flows[1,2].

Preliminary tests have been made at UTC on 2x4 solid propellant motors containing 3% Aluminum by mass.

With the transmissometer, the UV laser signal increased by about 5% while the IR signal decreased by  $\lesssim$  1% when the motor was fired. We conclude that the increase of the UV signal is due to strong emission at  $\lambda = 325$  nm which was inadequately rejected by the laser line filter ( $\Delta\lambda \sim 3$  nm). The small decrease in the IR signal at  $\lambda = 3.39$   $\mu\text{m}$  indicates that the mean particle size is submicron. Electron micrographs of the particles (identified as  $\text{Al}_2\text{O}_3$  by electron microprobe) also showed a preponderance of particles in the 0.1-0.3  $\mu\text{m}$  range.

It is concluded that in order to obtain reliable size measurements in rocket exhausts using the transmissometer, it will be necessary to use narrower band laser line filters. It is also clear that the technique would work better on rockets of higher metal loading and greater diameter, so that larger extinctions would be obtained.

References

- [1] P.C. Ariessohn, S.A. Self and R.H. Eustis, "Two-Wavelength Laser Transmissometer for Measurement of the Mean Size and Concentration of Coal Ash Droplets in Combustion Flows," Applied Optics 19, 3775-3781 (1980).
- [2] S.A. Self and R.L. Keating, "In-Situ Particle Sampling Filter for High Temperature, High Velocity Flows," HTGL Report #117, (May 1980).

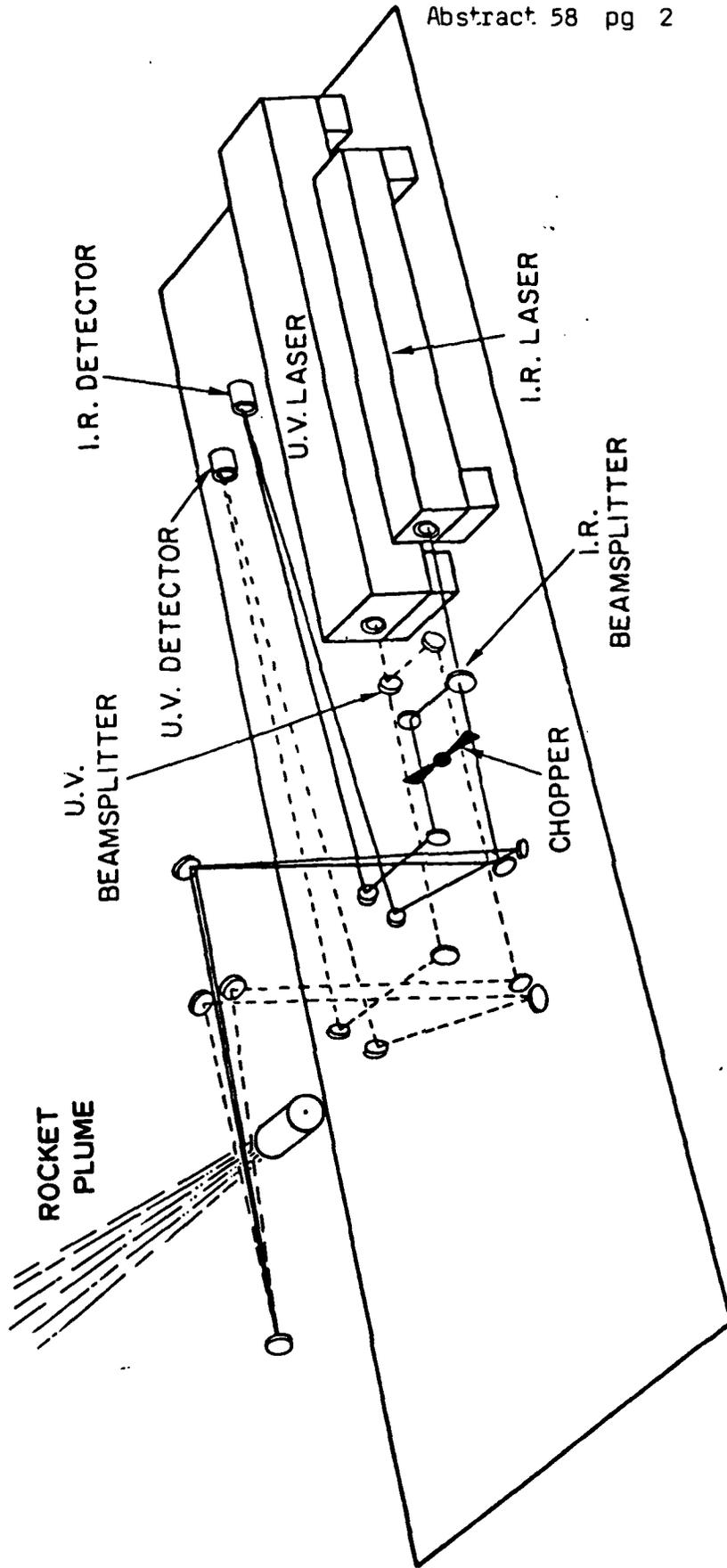


Figure 1. Schematic of two-wavelength laser transmissometer for measuring particle size in rocket plumes.

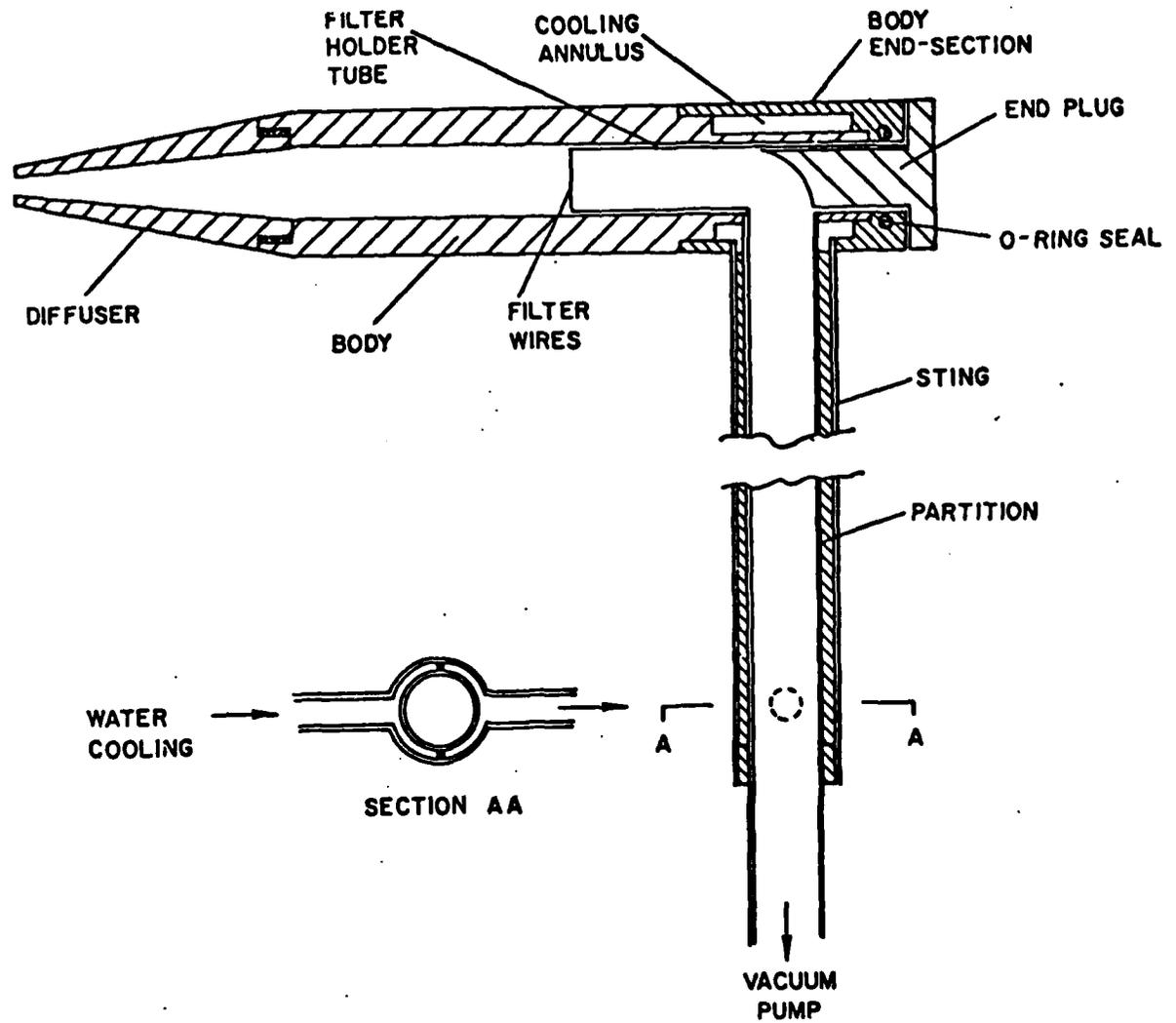


Figure 2. Particle sampling probe--construction details.

CHEMICAL PROPULSION RESEARCH GOALS

Research in support of rocket propulsion is directed at improving performance and toward developing a scientific understanding of phenomena associated with the generation of propulsive power. Research is being conducted from molecular to macroscopic scales in areas which include the dynamics of rocket combustion, the behavior and synthesis of propellant and insulation materials, the characteristics of exhaust plume formation and radiation, and the dynamics of advanced propulsion concepts. Further knowledge is needed in these areas to meet mid-term and long-term Air Force technology goals related to improving performance, reliability, penetrability, and durability for Air Force mission applications involving ballistic missiles, air launched missiles and propulsion in space. However, specific provisions are also included for research directed toward scientific opportunities which cannot be related to particular mission areas at this time.

Future Air Force space missions for communications, surveillance, and weapons systems will require substantially higher power and more efficient propulsion for orbit raising. Research is expected to lead to improvements of 10 to 20% in propulsion efficiency with improved liquid and solid propellants and 100 to 300% with non-conventional systems such as energy beaming, magnetoplasma-dynamics and nuclear power.

SPECIFIC GOALS

The following topics summarize many of the current goals which are being addressed by the ongoing research programs.

Solid Mechanics To improve understanding of damage tolerant design for new materials through extensive empirical and analytical approaches. To investigate fatigue, damage propagation and detection, fracture, and effects of spectrum loading and sequencing. To extend the existing theories to three dimensions, including the interaction between viscoelastic behavior and damage, the micromechanics of propellant structure, and the effects of temperature to obtain a theory that will predict propellant stress-strain behavior from simple tests. To establish an age-life model based on chemical reactions.

Noninterfering Diagnostic Techniques To achieve improved diagnostic techniques for measuring the gas and gas-particle flow properties representative of rocket systems including plumes. To improve understanding of the factors involved in sensing and detecting the chemical and physical properties related to rocket flow systems. To devise and improve diagnostic techniques to obtain rapid and quantitative spatially and temporally resolved measurements of temperature, pressure, velocity, species concentrations and densities, and particle/droplet size and distribution in optically dense, high-temperature reacting, unsteady, turbulent flowing media.

Nozzle and Plume Flows To achieve methods of performing screening measurements for gas/particle systems so that the influence of composition and

flow environment on particle formation and growth characteristics and range of particle sizes can be investigated. To characterize and obtain data on the condensation processes occurring in pure and mixed flows. To verify and improve predictive models for nucleation and condensation in multi-component, multiphase systems. To determine reaction pathways and to obtain chemical rate data for combustion chamber, nozzle, and exhaust plume flows. To improve and devise methodology for determining the spatial and temporal distribution of important species so that rate processes can be measured. To determine the mechanism of exhaust plume flame suppression in the presence of flame suppression additives.

Synthesis of Propulsion Materials To synthesize energetic ingredients leading to tough, high energy binders having low glass-transition temperatures and high thermochemical stability temperatures. To improve techniques to determine polymer properties. To conduct original synthesis of new, high energetic oxidizers.

Combustion To determine the behavior of energetic materials during combustion. To establish relationships between molecular structure, decomposition and combustion processes. To place emphasis on combustion, decomposition, and stability of advanced ingredients. To understand important heat release mechanisms so that research to modify burning rate and combustion efficiency can be directed at specific reaction sites. To explore methods for obtaining reactions rate data for solid and liquid energetic materials being heated at rates in excess of  $10^4$ K/s. To determine the effects of acceleration-fields on propellant ballistics. To characterize the mechanisms leading to changes in solid propellant properties and burning modes that produce transition from normal deflagration to detonation of rocket motor grains.

Combustion Instability To improve analytical methods for predicting the stability behavior of solid motors through development of theories to treat mechanisms such as nozzle damping, acoustic erosivity, pressure coupling, vortex streaming, vortex shedding, distributed combustion, particle and structural damping, and high velocity effects. To include effects of realistic 2-D and 3-D geometries. To examine more direct means of measuring acoustic admittance. To extend the use of laser Doppler velocimetry as a means of measuring steady and unsteady combustion characteristics of solid propellants. To investigate methodologies for measuring the unsteady velocity, pressure, and temperature components in multi-dimensional unsteady reacting flows. To visualize nonsteady, multi-phase flow and condensed-phase breakup for the purpose of understanding the role of transient processes on acoustic energy gains or losses. To determine and characterize acoustic energy gains and losses in terms of flow field parameters. To conduct verification of new combustion response measurement techniques. To investigate approaches to controlling instability through additives and chamber design. To achieve techniques for investing propellant responses at very high frequencies.

Metal Combustion To characterize the basic mechanisms and chemistry involved in the formation of metal oxide particulates. To experimentally determine the physical and chemical processes of metal droplet combustion. To explore methods of greatly reducing the size of metal oxide agglomerates entering

nozzle convergent sections. To improve methods for simultaneously measuring temperature and concentration of turbulent flame zones of multi-phase media so that conditions leading to metal combustion under ram-rocket conditions (particularly high altitude) can be characterized. To assess the role of fluorine in the combustion of fluorinated metallic propellants and to determine mechanisms that affect oxide particle size. To understand and to analytically describe the basic phenomena of metal particle combustion in solid and ramrockets. To quantify processes leading to formation of micrometer size oxide particles.

Surface Reaction Kinetics of Carbon/Carbon Composites To establish the relationship between carbon/carbon material processing variables and the kinetics of reaction of these materials with gases representative of rocket exhausts.

Performance Prediction To increase the scope, usefulness and reliability of the JANAF Thermochemical Tables; to obtain needed measurements of thermodynamic properties of combustion products of metallized propellants; and to measure fundamental vibrational frequencies and other molecular constants for accurate calculation of ideal gas properties of high temperature species. To improve techniques for modifying, controlling, and predicting the burning rates of composite propellants.

Electrical Propulsion To produce stable magnetoplasmadynamic flows for sustained high energy density operation and to project upper limits of energy density. To quantify conditions that tend to isolate cathodes from ion heating. To extend operational time of electrode and contact surfaces.

Beamed Energy Propulsion To quantify radiation mechanisms of energy transfer to working fluids, to assess the barriers to optical access for energy transmission, and to establish approaches for laser sustained plasma confinement. To enable consideration of candidate short wavelength energy beams with hydrogen; to determine if other working fluids and fuels offer promise. To produce conditions that vaporize and disperse metallic fuels being considered for use in low Earth orbits. To overcome cooling limitations on electrical propulsion systems operating continuously at tens of megawatts (electrical). To realize more weight efficient and less vulnerable heat rejection concepts for electrodes, chambers, and nozzles.

SPACE PROPULSION RESEARCH

Basic research leading to advanced concepts for space propulsion periodically receives high level attention but very little sustained, follow-up activity. The Space Shuttle capability plus the inevitability of the dominate Air Force role in space are prompting definitions of new propulsion and power requirements. The Air Force projections for the 1990's describe missions which can not be accomplished unless major propulsion advances are achieved.

During the last three decades, a number of novel and promising propulsion concepts have been considered. Prior to the present considerations, the concepts could have been placed in several categories, e. g.,

1. Sufficient onboard power did not exist.
2. Air Force requirements did not justify further research.
3. Solutions to fatal flaws could not be foreseen.
4. Potential for space contamination was too great.
5. An important technology was lacking.
6. Knowledge of the concept was narrowly held, thus it escaped attention.
7. Performance penalties were too great.

But probably the dominate consideration in previous years was that the Air Force could perform the required missions with conventional propulsion. Consequently, initiatives to provide technology and to overcome specific barriers were not sustained.

Important advancements in conventional propulsion systems for space can be achieved. The use of more energetic liquid propellants (e g, fluorine, lithium, and tri-propellant combinations) requires elimination of component degradation by corrosive oxidizers, establishing conditions for efficient combustion, understanding of toxicity limitations, etc. Advanced solid systems (offering the advantages of long term storage and compactness) require research to increase energy density, to achieve efficient combustion, and to reduce hazards sensitivity. The higher risk nonconventional propulsion systems are expected to yield performance improvement of between factors of 2 to 3, but in thrust ranges lower than the advanced chemical systems. Generic classifications of the candidate nonconventional propulsion concepts include: laser or solar driven, magnetoplasmadynamic, free radical and free atomic, nuclear, electromagnetic mass accelerators, and intermittent combustion. Several research barriers are common to most concepts: achieving accurate models to predict the coupling of external energy sources with the propulsive media, establishing efficient small scale experiments that can be related to full size configurations, overcoming component heating from plasmas, stability of high energy plasmas, life limits on chambers and electrodes.

In anticipation of increasing developmental activity the research on the following topics is being initiated:

FY83 WORK UNITS SPACE PROPULSION

REACTIVE FLOWS

- |  |                            |
|--|----------------------------|
| 0 ABSORPTION OF LASER ENERGY IN FLOWING MEDIA<br>- CONTINUOUS ABSORPTION MECHANISMS, BLEACHING<br>- PULSED ENERGY WAVE DYNAMICS              | PHYSICAL SCI<br>ROSEN/KEMP |
| 0 BEAMED ENERGY PROCESSES<br>- DYNAMIC GAS COUPLING RESULTING FROM LASER PULSE<br>- TRANSMISSION LOSS MECHANISMS                             | BDM<br>MYRABO              |
| 0 ENERGY CONVERSION VIA ELECTRO-MAGNETIC COUPLING<br>- UNIFY IR, UV, EM, THERMAL AND CHEMICAL STIMULI<br>- ACCELERATION USING DIPOLE MOMENTS | PENN STATE<br>MERKEL/MICCI |
| 0 INTERMITTENT COMBUSTION<br>- COUPLING OF IMPULSES FROM EXPLOSIONS<br>- MULTIDIMENSIONAL EFFECTS  | PCRL<br>BENREUVEN          |
| 0 LASER SUSTAINED PLASMAS<br>- CRITERIA FOR STEADY LOW REYNOLDS NUMBER FLOWS<br>- VELOCITY DEDUCED FROM EMISSIONS & INTERFEROGRAMS           | UT SPACE INSTI<br>KEEFER   |
| 0 RADIATION ABSORPTION<br>- PLASMA IGNITION MECHANISMS<br>- ABSORPTION IN SEEDED GASES   | ILLINOIS UNIV<br>KRIER     |

PLASMA FLOWS

- |   |                            |
|---|----------------------------|
| 0 PARTIALLY IONIZED PLASMAS<br>- ELECTRON DENSITIES IN NONEQUILIBRIUM FLOWS<br>- DISCHARGE INTERACTIONS WITH FLOW FIELD                         | STANFORD UNIV<br>KRUGER    |
| 0 SECONDARY STAGE ACCELERATION OF IONIZED GASES<br>- PLASMA-SURFACE COUPLING MECHANISMS<br>- STAGE OPTIMIZATION CHARACTERIZATION                | R&D ASSOC<br>TURCHI        |
| 0 DISCHARGE PLASMADYNAMICS FLOW REGIMES<br>- ACCOUNTING FOR MOMENTUM IN STABILITY ANALYSES<br>- ESTABLISH REGIMES INFLUENCING ELECTRODE EROSION | STUTTGART UNIV<br>SCHRADER |
| 0 MAGNETOPLASMADYNAMIC PERFORMANCE-LIMITS<br>- FLUID DYNAMICS AND PLASMA COUPLINGS<br>- CRITERIA FOR ANODE REGION INSTABILITIES                 | MIT<br>MARTINEZ            |

FY83 WORK UNITS SPACE PROPULSION (Continued)

MATERIAL INTERACTIONS

- |  |                 |
|--|-----------------|
| 0 PLASMA ACCELERATION EFFICIENCIES                 | JPL             |
| - ELECTRODE HEAT LOSS MECHANISMS                   | GABRIEL         |
| - ANODE SPUTTERED ION HEATING OF CATHODE           |                 |
| 0 PLASMA SHEATH WALL INTERACTIONS                  | CARNEGIE-MELLON |
| - HEATING TO WALLS FROM LOW PRESSURE PLASMA FLOWS  | LAWLESS         |
| - MECHANISMS OF ELECTRODE HOT SPOTS AND SPUTTERING |                 |

ENERGETIC MATERIALS

- |                                      |                 |
|--------------------------------------|-----------------|
| 0 AZIDONITRIDES                      | ROCKWELL        |
| - ELECTRO-SUBSTITUTION OF AZIDO-IONS | FRANKEL         |
| - STABILITY CHARACTERIZATION         |                 |
| 0 ENERGETIC FLUORINATED BINDERS      | SRI INTERNATION |
| - NITRATION PROCESSES                | BEDFORD         |
| -                                    |                 |
| 0 METALLOTETRAAZIDES                 | NORTHWESTERN U  |
| - SYNTHESIS OF RING STRUCTURES       | TROGLER         |
| - STABILITY CHARACTERIZATION         |                 |

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