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Annual Report

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Sandia Combustion Research Program
Annual Report
1988

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COMBUSTION RESEARCH AT SANDIA

P. L. Mattern, Director

During the late 1970s, in response to a national energy crisis, Sandia proposed to the U.S. Department of Energy (DOE) a new, ambitious program in combustion research. Our strategy was to apply the rapidly increasing capabilities in lasers and computers to combustion science and technology. Shortly thereafter, the Combustion Research Facility (CRF) was established at Sandia's Livermore location. Designated a "user facility," the charter of the CRF was to develop and maintain special-purpose resources to support a nationwide initiative—involving U.S. universities, industry, and national laboratories—to improve our understanding and control of combustion.

Today, the Combustion Research Facility occupies a unique niche among DOE "user facilities." Our resources are diverse and include specialized lasers, computers, and more than two dozen laboratories optimized for the study of combustion-related processes. One of our strongest assets is our highly trained resident technical staff, with backgrounds and skills covering a broad spectrum of disciplines in the combustion sciences.

The Office of Basic Energy Sciences within the DOE provides support for the operation of the facility, for individual and collaborative visits by users, and for fundamental research by Sandia staff in combustion-related chemistry, reacting flows, and advanced diagnostic methods. These basic studies are complemented by applied research programs supported by DOE's Offices of Conservation and

Fossil Energy. Also, when the specialized resources of the CRF are required, we have taken on work for several offices of the Department of Defense, NASA, and the NRC.

Our mission emphasizes the meaningful involvement of industry and universities. The Visiting Scientist Program reflects our commitment to this goal. As is evident in Figure 1 of Section 11, more than 800 scientists came to the CRF in 1988 for short visits, typically to exchange ideas and information on combustion-related research and technology. Figure 2 shows the continued increase in long-term collaborative and independent research at the CRF: in 1988, 71 scientists were in residence for two weeks or more. The slight growth from 1987 to 1988 reflects the fact that there are only some 40 professional scientists associated with our Combustion Program. In addition, we continue to strengthen our ties with local universities and seek to expand a highly successful post-doctoral research program.

"Industrial competitiveness" and "technology transfer" have become increasingly familiar phrases in the national laboratory community. Working Groups (see Section 11), organized through CRF programs and comprising staff from industry, academia, and national laboratories, are a decade-old concept here at the CRF and continue to provide a valuable forum for the meaningful exchange of problems, ideas, and information. Based on the success of this form of interaction, we recently have extended this idea to pulse and spray combustion,

and we believe even more strongly that working groups represent an important model for meaningful and effective exchange of technology with industry. Several research projects described in this report were stimulated by working groups and involve the on-site participation of industry scientists. DOE's Industry Technology Fellowship program, supported through the Office of Energy Research, has been instrumental in the success of some of these joint efforts. The remainder of this report presents results of calendar year 1988, separated thematically into eleven categories. Refereed journal articles appearing in print during 1988 and selected other publications are included at the end of Section 11. Our "traditional" research activities—combustion chemistry, reacting flows, diagnostics, engine and coal combustion—have been supplemented by a new effort aimed at understanding combustion-related issues in the management of toxic and hazardous materials. We are proud to report continued progress in areas that affect directly U.S. economic competitiveness, including pulse combustion and high-temperature materials.

During the past year, we have continued to improve existing facilities and bring new ones on line. Facility laser systems, installed in the first years of operation of the facility, have been upgraded and improved. A preliminary version of a new laser system that probes ultrafast chemical events with femtosecond pulses is now operational. Implementation of a computer network that makes Cray-class supercomputers available to in-house researchers and Visiting Scientists is now complete. In addition, a new shock-tube facility that emphasizes laser-based diagnostics is now operational. These new capabilities significantly increase the breadth and depth of resources available at the CRF

for combustion-related science.

What does the future hold for the CRF? In FY 1987 and 1988, \$4.8 million was appropriated by the U.S. Congress to construct Phase II of the Combustion Research Facility. Providing opportunities for new combustion science, this project will double existing laboratory space, add next-generation laser and computer systems, and complete the office building. Present plans for new equipment—developed in concert with the CRF-user community—include a femtosecond laser source for chemistry studies, a pulse-burst laser for high-speed imaging and spectroscopy, and access to scientific supercomputing. We believe that these capabilities, when utilized by our visiting and in-house researchers, will help the U.S. to address its combustion-related challenges of the 1990s and beyond. To finish the project, an additional \$16.8 million will be required in coming fiscal years.

Our research will strive to take maximum advantage of the new capabilities coming on line and will seek to provide an overlap with the wide interests of new Visiting Scientists. Control of toxics, pollutants, and other by-products of energy use that despoil our environment will continue to motivate our mainstream program. We are broadening the charter of our energy conservation research into continuous combustion, and are seeking the establishment of a research program to develop the technology base still needed for the clean combustion of coal beyond the year 2000. As before, we will continue to invest a small fraction of our effort in new, forward-looking activities.

This report will, I hope, stimulate your curiosity about combustion science. I trust you will want to know more. Give me a call—I look forward to hearing from you.

Section 1

Combustion in a shock tube involves many transient chemical species whose concentrations may be probed with a tunable pulsed laser. This photograph shows one laser probe configuration in which a green-yellow laser sheet crosses a shock-heated gas flow that is reacting under idealized flame-like conditions. Our new Shock Tube Facility was designed to attack problems in the combustion of energetic materials.

The Sandia Shock Tube Facility consists mainly of a tunable pulsed-laser system, a pair of linear-array photodiode detectors, and a chemical shock tube with many windows. Transient chemical species, which are important in combustion, are generated as a shock wave passes through mixtures of reactive gases. A laser flash captures one-dimensional images of the shock-induced combustion. The resulting chemical species concentrations are used in direct comparisons with computer models of the

chemistry. The uniform temperature and pressure conditions during the brief shock experiments are well suited for combustion-chemistry modeling.

Timing in the brief shock experiments is achieved with optical triggers at several positions along the tube. A low-power laser is deflected onto baffled photodiodes when the shock passes through the laser path. Trigger signals are used to synchronize the pulsed probe laser and detector shutter with the shock wave, as well as to measure the shock wave speed.

Section 1

Facilities and Special Equipment

The Combustion Research Facility (CRF) is a 51,500 square-foot, four-building complex located on the east side of Sandia National Laboratories Livermore. The CRF, which includes an office building, laboratory, auditorium, and mechanical equipment building, provides a highly sophisticated research environment for the resident staff and visiting researchers. It is located outside the Sandia security area to permit easy access for visitors.

A number of unique features have been incorporated in the CRF: three central facility laser systems that provide state-of-the-art diagnostics, access to a broad range of computers ranging from minis and superminis to two-million-word Cray systems, and a sophisticated microprocessor-controlled laboratory safety system.

A high-temperature, multifuel flow reactor and a large spray flame facility, both fully optically accessible, provide specialized multiphase combustion environments.

The Facility Laser System

The Facility Laser System consists of three centrally located lasers and a facility beam distribution (periscope) system. Light from these lasers may be transmitted to any of the laboratories in the Combustion Research Facility using the facility periscope system.

R. L. Schmitt

The three facility lasers, Diana, Sirius, and Dye Blaster, have been in operation for several years. Each has different capabilities, as described here:

Diana

Diana is a flashlamp-pumped dye laser system designed for single-shot temperature and species concentration measurements in turbulent environments. This laser delivers the high pulse energy required for single-shot spontaneous Raman scattering measurements in a relatively long pulse ($\sim 2 \mu\text{s}$) that prevents dielectric breakdown in the focused beam. Diana consists of a prism-tuned oscillator followed by three amplifiers and produces 500-mJ- to 5-J-per-pulse depending on the dye used. Diana can be tuned from 400 nm to 600 nm using a variety of dyes.

This year we continued to make improvements in the performance and reliability of the laser system. We began testing new high-voltage modulators (the energy-storage capacitor, high-voltage switch, and triggering circuitry) of our own design. Our new design uses air to cool the hydrogen thyristors instead of flowing water, eliminating the problems we have had with water leakage and subsequent arcing inside the high-voltage section. The new modulators will also reduce RF electrical noise emitted from the laser and should be easier to service.

Bob Dibble, Rob Barlow, and Bob Lucht used Diana and a Nd:YAG-pumped dye laser to measure simultaneous spontaneous Raman scattering and OH fluorescence in an H_2/Ar flame and in a lifted H_2 flame. These measurements were the first simultaneous, spatially resolved measurements of major species concentrations, temperature, and hydroxyl radical concentration in nonpremixed turbulent flames. Quenching corrections based on the Raman-scattering data were applied to the LIF data for each laser shot, making the OH concentration measurements quantitative. For these meas-

urements, Diana was fired at 5 Hz and synchronized to the 10-Hz Nd:YAG laser system using a divide-by-two circuit provided by the Nd:YAG laser.

Bob Dibble, Rob Barlow, and Sten Stårner (a visiting scientist from University of Sydney) used the combined OH fluorescence and spontaneous Raman scattering apparatus to investigate departures from chemical equilibrium in a wide variety of turbulent hydrocarbon flames. As with the previous work, Diana was tuned to 532 nm and synchronized with the 10-Hz Nd:YAG laser.

Prof. Marshall Long, Brandon Yip, and Kevin Lyon (all from Yale University), Bob Dibble, and Rob Barlow used Diana for Rayleigh-scattering measurements on a nonreacting mixture of Freon 22 and H_2 . For this work, Diana was tuned to 532 nm using Coumarin 521 dye. The data were used to determine differential diffusion of H_2 with respect to Freon 22. The differential diffusion of light species (such as H_2 or H atoms) with respect to heavier molecules has important implications for turbulent combustion models.

Mehdi Namazian (Altex Technologies, Inc.) and Bob Schefer have continued to use Diana and their Raman-imaging system to measure methane concentration in nonpremixed jet and bluff-body flow and flames. For these experiments, Diana was tuned to 444 nm (using Coumarin 440), and two-dimensional images of Raman-scattered light were recorded using two cameras. This two-camera system allowed measuring methane concentration between 100% and 0.2% with good accuracy. Two bluff-body sizes and various flow conditions were tested to find similarity parameters which control mixing in bluff-body flows.

Bob Schefer and Mehdi Namazian also used Diana for simultaneous two-dimensional mapping of CH and CH_4 concentration in nonpremixed jet and bluff-body stabilized flames. For these experiments, Diana was modified to operate with two rear mirrors and thus produced two independently tunable wavelengths (431.5 and 444 nm). The shorter wavelength was used to excite fluorescence from

CH and the other was used for spontaneous Raman-scattering measurements of CH_4 . Two cameras were used to simultaneously record the CH and CH_4 signals. These two-dimensional images have played a key role in resolving the flame structure and have led to the important realization that the seemingly different jet and bluff-body flames have similar underlying structures.

Sirius

Sirius is a multipurpose laser system for nonlinear optical techniques such as CARS (coherent anti-Stokes Raman spectroscopy) and IRS (inverse Raman spectroscopy). The Sirius laser system consists of a Q-switched, frequency-doubled, Nd:YAG laser system, a narrow-band tunable dye laser, and a broadband dye laser. The Nd:YAG laser is a Molelectron MY-34 which has been modified for single-frequency operation. The laser is injection-seeded to ensure reliable single-frequency operation, and the laser cavity has been modified to a self-filtering unstable resonator (SFUR) to improve the spatial beam quality.

This year we improved Sirius in several ways. To compensate for the low energy inherent in the SFUR resonator design, we added an additional Nd:YAG amplifier to the system. In this configuration, the laser produces 10-ns-long pulses with pulse energies of up to 200 mJ at 532 nm, almost double the energy we achieved without the amplifier. Since the additional amplifier worsens the destabilizing effect of amplified stimulated emission into the oscillator, we installed a permanent-magnet Faraday isolator between the amplifiers and the oscillator. We also upgraded the master oscillator of the injection-seeding system with a Lightwave Electronics diode-laser-pumped Nd:YAG ring laser. This laser provides several milliwatts (CW) of single-frequency power for injection seeding and eliminates timing problems associated with the gain-switched laser we used previously.

This year, Roger Farrow and Greg Sitz used Sirius for high-resolution CARS measurements of vibrational transition linewidths in H_2 . For these measurements the single-frequency, 532-nm output from Sirius was used both as a pump beam for a pulse-amplified ring dye laser and as a Stokes beam for the CARS measurements.

These researchers also used Sirius and another single-frequency Nd:YAG laser to measure state-to-state energy transfer rates of N_2 . The 532-nm output of Sirius pumped a pulse-amplified, ring dye laser that was used to populate the $v = 1$ state of a single rotational level of N_2 via stimulated Raman pumping. Then, after a suitable delay to allow collision-induced population transfer, a frequency-doubled dye laser pumped by another single-frequency Nd:YAG laser was used to probe the $v = 1$ population via multiphoton ionization. The data were used to determine the rotational relaxation rates for the $v = 1$ state of N_2 .

Dye Blaster

The Dye Blaster is a Q-switched, frequency-doubled, Nd:YAG laser that provides additional capability to pump dye lasers located in remote user laboratories. This laser has been useful both for users who lack a Nd:YAG laser and for users with experiments that require several lasers. The Dye Blaster is a Quanta-Ray DCR-2 that produces up to 350 mJ at 532 nm in ~7-ns-long pulses. It can be synchronized with other lasers or experimental apparatus as required.

Bob Schefer used Dye Blaster to perform time and spatially resolved measurements of the OH concentration in turbulent, nonpremixed flames. For these experiments, the 532-nm beam from the Dye Blaster was used to pump a tunable dye laser. The output of the tunable dye laser was frequency-doubled to 284 nm and used for fluorescence excitation of the OH molecule. In addition to single-point measurements, a cylindrical lens was used to form the laser into a sheet for two-dimensional imaging of the OH concentration distribution.

Bill Flower used Dye Blaster to determine the instantaneous spatial structure of the sooting regions of nonpremixed, turbulent, jet flames. These measurements were made by forming the 532-nm beam from Dye Blaster into a sheet using cylindrical lenses and recording Mie scattering from soot particles using a two-dimensional CCD camera. These images clarify the instantaneous structure of the sooting regions, complementing Bill's previous quantitative measurements of the time-averaged soot-volume-fraction field in high-pressure, nonpremixed, turbulent, jet flames.

The Facility Computers

Computing hardware available to users at the CRF has not changed greatly this year. However, our network has continued to grow, our software has been improved, and there are plans for significant hardware changes in the months ahead.

D. E. Benthussen

In last year's report, we mentioned that with a Cray-1S, a VAX 8650, and three VAX 11/780s, we had enough computer power in place to meet our general-purpose, time-sharing needs through the middle of 1989. Therefore, we have turned our attention this year to other aspects of computing. For example, several upgrades have been made to the operating system software for the Cray and VAX computers. We also upgraded at least once during the year virtually all of the software systems running on our machines, including the compilers, database managers, graphics, word processors, spreadsheets, etc. Our usage statistics indicate that the Cray is usually used to capacity, as is the VAX 8650. Usage of the VAX 11/780s has leveled off and is even decreasing, since users are moving their scientific jobs to the much faster VAX 8650, and personal computers have replaced the VAXes for word processing.

All Combustion Research Facility (CRF) computers are attached to an Ethernet network known as the Restricted-Access Network (RAN). Although this network is a Sandia-wide unclassified network, a large number of users are doing combustion-related work; much of the growth of the RAN is due to the growth of combustion-related computing capability. We have added nine additional VAX nodes to the network for a total of 27. Most of these are used for experiment control or modeling, but two of them are workstations for software development. Another significant change to the network this year has been the large increase in terminal access. This was accomplished by nearly doubling the number of terminal servers (highly versatile devices for connecting terminals to computers via Ethernet) and by making the RAN terminal connections available through a newly installed AT&T Private Branch Exchange (PBX) at Sandia. Using the telephone system to establish terminal connections provides a way to send data over existing telephone wires, and by using terminal servers to connect the PBX to our computers, we can realize the best features of both systems.

We have also been working on the implementation plan for the next major upgrade to the RAN.

These plans call for the two existing VAX clusters on the RAN—one at the CRF and the other at Sandia's Central Computing Facility—to be consolidated to make more efficient use of disk storage, which is now divided between the two clusters. We also plan to replace the three VAX 11/780s with a single computer that has 14 times the power of a VAX 780 (i.e., 14 "VAX units of performance," or VUPs). That, in conjunction with the VAX 8650, will bring the total central processing unit (CPU) capacity in the RAN cluster to 20 VUPs, more than twice what it is today. We will continue to use DEC's proprietary VMS operating system in the VAX cluster. The Cray-1S, which is accessible via the RAN, will be replaced with a Cray XMP-24 running the UNICOS operating system, Cray's version of UNIX. This machine will have two CPUs, four million words of memory, and a large auxiliary memory used as a high-performance solid-state disk. The new VAX cluster, resulting from the consolidation of the two present RAN clusters, will be located in the Central Computing Facility. We will install a Remote Data Processing Station (RDPS), consisting of a MicroVAX III located in the CRF computer room, to provide printing services and allow CRF users to read and write magnetic tapes and removable disks. We also plan to add a UNIX-based file server to our network to serve files to a new generation of high-performance workstations now appearing on the market.

In the future, most workstations will run the UNIX operating system. When our Cray computers are converted to UNICOS, the workstations will be able to communicate with, control jobs on, and even log into the Cray computers using standard networking protocol utilities. We also expect to add a new software product called the VMSBRIDGE to the VAXes. This product will allow UNIX workstations to mount file systems residing on the VMS-based VAX cluster, thereby providing in the UNIX environment some of the attractive features of VMS, such as volume shadowing and controller failover. Also, we have been participating in the testing of the DEC implementation of X-windows software, a widespread protocol for working with many windows, or jobs, simultaneously on a workstation. The prod-

uct DECWINDOWS is now available and will be useful in both the VMS and UNIX environments. The workstations mentioned earlier were used to support the testing of DECWINDOWS and are now being used to convert CRF computer codes to the UNIX operating system in preparation for the more distributed computing environment being implemented on the RAN.

Some of the upgrades described here have been accomplished in the past year, some will occur in the next few months, and it is still several months before the new Cray computer will be in place, but we are making steady progress toward the realization of a powerful, distributed computing network of the kind described in last year's annual report.

Figure 1. The Restricted-Access Network (RAN) is an Ethernet network that interconnects Sandia Livermore's unclassified computing, including combustion-related computing at the Combustion Research Facility. The RAN provides access to two VAX clusters and a Cray-1S, plus workstations, laboratory computers, and printers. A gateway to ARPAnet and a dial-back modem system allow communication to computer networks outside Sandia.

The Combustion Research Shock Tube Facility

A new shock tube has been developed with emphasis on pulsed laser-based diagnostic. Initially, the device will be applied to problems in the combustion chemistry of energetic materials.

J. A. Gray

Chemical reactions at elevated temperatures are a central theme in many combustion studies. While laboratory flames are the most common means of producing realistic combustion environments, such flames retain the full complexity of fluid mixing. Many flames also exhibit large temperature and concentration gradients that make basic chemical studies almost prohibitive. Using computer modeling in combustion, we are not yet able to describe the chemical kinetics together with fluid motion in all three spatial dimensions in a real flame. Modeling of chemical species is best done under idealized conditions of uniform pressure and temperature. Shock tubes are well-proven laboratory tools for chemical studies in which reactions are driven by pure gas-dynamic heating at well-defined, yet variable temperatures and pressures. A new shock tube has recently been designed at the Combustion Research Facility (CRF) with special emphasis on optical diagnostics of energetic materials chemistry. Testing is now underway.

The figure on page 1-iii of this section shows how a pulsed, Nd:YAG-pumped, dye-laser system is coupled to the CRF shock tube. The tube has an internal diameter of 3.81 cm and an overall length of 4.25 m. Seventeen fused-silica windows allow us to perform a variety of laser-based combustion diagnostics near one end of the device. The tunable dye laser beam is expanded using a cylindrical telescope and passes through large oval windows (12.7 cm by 1.27 cm) to monitor direct absorption. Laser-induced fluorescence (LIF) is also collected perpendicular to the laser beam axis through a 4:1 imaging system to monitor chemical species profiles behind incident shocks. Linear array detectors, each having 1,000 channels, sample the reduced images from the 10-cm-wide laser excitation region. Since the shock tube may only be fired at a repetition rate of typically 1 mHz, it is essential that we use more than one array detector.

For typical incident shocks in which the combustion chemistry occurs diluted in an argon bath at 2000 K, the 10-cm-sample region contains 100 microseconds of kinetic information acquired on each 5-ns laser pulse. Since the gas flow is essentially frozen during a laser pulse, the 0.1-mm spatial resolution effectively limits the fastest reactions that

we can study to approximately 100 ns. Operating conditions may be varied such that combustion mixtures are shock heated to temperatures of 1200 to 2500 K and total pressures of 200 to 2000 mb. With the range of temperatures and partial pressures of reactants that are available, we can adjust the combustion rates of many systems to fall within the diagnostic time scales of the device in its present configuration with the laser apparatus.

Shock wave velocity is measured optically in the new device. A helium-neon laser is divided into four parts that cross the tube at various distances along the wave travel direction. Photodiodes detect the arrival of the shock front as the abrupt density change deflects the laser beam onto the photodiodes for about 1 microsecond. The amplified signals from the photodiodes trigger time measurements and also synchronize the fast laser pulse with the chemistry occurring in the viewing region. Wave speed data is processed on a laboratory computer with known gas dynamic relations to calculate final temperatures and pressures from measured initial values.

In addition to high-temperature gas-phase chemistry, we plan to study ignition of solid thin films of energetic materials with the shock tube facility. Figure 1 shows the special reentrant end-plate design that allows us to use optical diagnostics at the end wall of the shock tube. LIF is produced in the reaction zone just above the film surface following passage of the reflected shock that raises gas temperatures to 4000 K and pressures to 10 bar. The hot compressed gas remains undisturbed for approximately 1 ms to initiate thermal decomposition and vaporization of the solid film. Products near the surface are spatially resolved to 0.01 mm using a 20X telescope with the linear array detectors.

With a dye laser that is readily tunable from 200 to 800 nm, we expect to observe concentration profiles for species such as OH, CN, NO, CO, C₂, CH, NH, H, and O. Previous laser studies in shock tubes have been limited to fewer species, but we must survey many chemical intermediates and products to validate complex computer models for chemistry of energetic materials. One model¹ contains 236 chemical reactions involving 49 separate

Figure 1. Schematic of the reentrant end plate on the Sandia Shock Tube Facility. Five window ports provide ample optical access to the reflected shock region where hot gases ignite solid thin-film samples. Short-pulse laser diagnostics are synchronized with ignition chemistry, and the resulting data are compared to detailed computer models.²

intermediate and product gases. In premixed combustion systems such as these, short-lived intermediates play a key role in converting energetic molecules into heat and stable products. Models that accurately predict the details of idealized laboratory experiments are expected to offer insight into the behavior of actual burning propellant and to guide the development of improved new propellants.

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Section 2

The photograph shows a 30-torr methane-oxygen-argon flame viewed through a window in the vacuum chamber. This flame is typical of those studied using multiphoton excitation.

Combustion Diagnostics

Two-photon-excited stimulated emission (SE) has been studied in a variety of atomic and molecular systems for over a decade; this process is also called amplified spontaneous emission. The effect that SE may have on diagnostic applications of multiphoton-excited fluorescence (FL) detection has received little attention until a recent report describing SE from atomic oxygen in flames (see page 2-4). We have made similar two-photon excitation measurements to study SE and FL from atomic hydrogen in flames.

As shown in Figure 1, two-photon 205-nm excitation is used to populate the 3S and 3D states of atomic hydrogen. We observe visibly (by eye), highly directional SE from the subsequent 656-nm transition down to the 2P state. Intensity dependences of the FL and SE signals provide an excellent means of confirming their different dependences on the density of excited atoms, as illustrated in Figure 2. In the lower-energy region of this plot, the data representing the FL measurements lie along the dashed line drawn with a slope of 2, consistent with the I^2 dependence of the two-photon process. The data representing the SE measurements have a stronger intensity dependence in the lower-energy region, becoming very similar to the FL measurement in the higher-energy region. The low-intensity behavior illustrates the exponential-gain regime of SE, followed by saturation and a linear-gain regime, where the SE and FL signals have similar intensity dependences. We are continuing to study two-photon-excited stimulated emission, both to determine its effect on fluorescence detection methods, and to investigate its use as a new diagnostic technique.

Figure 1: Energy levels of atomic hydrogen relevant to two-photon excitation studies.

Figure 2: Intensity dependences of the stimulated emission (SE) and fluorescence (FL) signals measured simultaneously in a 72-torr hydrogen-oxygen-argon flame.

Section 2

Combustion Diagnostics

One of the primary thrusts of the combustion research program at Sandia National Laboratories is the development of diagnostic techniques that take advantage of the latest advances in modern technology. This development effort has three objectives: innovative methods for measurements in combustion systems, a quantitative understanding of the usefulness and limitations of these methods, and the transfer of technology from research to application environments.

Because of their nonintrusive nature and great versatility, laser-based optical techniques—both point-resolved and two-dimensional imaging—receive the strongest emphasis. Laser-induced fluorescence, spontaneous and coherent Raman spectroscopy, laser Doppler velocimetry, and multiphoton optogalvanic spectroscopy are but a few of the diagnostic methods that are being developed to measure temperature, species concentrations, velocity flow fields, and other parameters of key importance to the understanding of combustion phenomena. The capabilities of such techniques depend directly on the availability of laser sources with unique spatial, temporal, and spectral properties; thus, an important feature of the combustion diagnostics program is the development of high-performance lasers that meet the requirements of specialized situations. In addition to laser-based optical probes, modern intrusive probes are also being developed and evaluated.

Sandia's efforts to develop advanced combustion diagnostics, especially advanced laser-based optical probes, are supported primarily by the Chemical Sciences Division of the Department of Energy's Office of Basic Energy Sciences. Work in this program is complemented by work in the applied research programs to develop diagnostic techniques for specific combustion applications.

Photochemical Effects in 243-nm Two-Photon Excitation of Atomic Hydrogen in Flames[†]

This paper describes photochemical production of H and OH observed during irradiation of flame gases with 243-nm laser radiation. Two mechanisms are proposed to explain the observed wavelength and intensity dependences of the photochemical process.

J. E. M. Goldsmith

Several species (e.g., H and O) that are of interest in combustion studies have dipole-allowed transitions only at wavelengths less than 200 nm. Because these wavelengths are strongly absorbed by flame gases, multiphoton excitation using near-UV wavelengths (200-400 nm) provides an important means for detecting such species in combustion environments. The high-intensity optical radiation required for multiphoton excitation has the potential for inducing a variety of photochemical effects in the environment being probed, and we have reported previously such effects in 205-nm excitation of atomic hydrogen¹ and 226-nm excitation of atomic oxygen.² This article describes different types of photochemical effects observed during 243-nm excitation of atomic hydrogen.

The longest wavelength (and therefore, in general, the least likely to cause significant photochemical perturbations) that can be used to provide two-photon excitation of atomic hydrogen is 243 nm. Such excitation can be used to detect H in flames either by observing the ion-electron pairs produced by subsequent photoionization, or by using a second laser beam at 656 nm to excite resonance fluorescence from the state excited by the two-photon absorption process. In using the latter scheme to measure a relative concentration profile of H in a premixed atmospheric-pressure hydrogen-oxygen flame, we observed an artificially high H concentration at heights well above the burner surface, where the natural concentration is very low. As in the case of 205-nm excitation, the behavior of the H signal indicated that photolysis of water was the source of H, but with a *nonlinear* dependence on 243-nm intensity, rather than the linear dependence observed in the 205-nm study.

Because photolysis of water produces H and OH, and OH is much easier to measure than H, we used the apparatus shown schematically in Figure 1 to investigate the photolysis process by monitoring the OH concentration in the flame. Immediately after photolysis by the 243-nm pulse from the first laser system, OH was detected using single-photon, laser-induced fluorescence (LIF) with a pulse from the second laser system. The top part of Figure 2 shows the resulting OH LIF signal recorded as the 243-nm wavelength was scanned across the atomic hydrogen 1S-2S two-photon transition. The dashed line indicates the level of the OH signal observed in the absence of 243-nm excitation. It is evident that the 243-nm radiation leads to some enhancement in the OH concentration when it is not resonant with the atomic hydrogen transition, but that the enhancement is much greater when it is resonant with the transition. The bottom part of the figure shows the OH emission observed with only the 243-nm radiation present.

Figure 1. Schematic diagram of apparatus used to monitor production of OH by irradiation of flame gases with 243-nm pulses.

[†]App. Opt. 28, 1206 (1988).

We measured the dependence of the OH LIF creation signal on the 243-nm pulse energy (i.e., the difference between the signal and the dashed line in the top of Figure 2). Measurements made with the 243-nm laser beam detuned from the atomic hydrogen 1S-2S resonance indicate an I^2 intensity dependence, consistent with two-photon excitation of H_2O followed by rapid predissociation. Measurements made with the laser beam tuned to the resonance indicate an apparent $I^{3.4}$ intensity dependence, suggesting that an additional photochemical mechanism has come into play. We believe that this mechanism is initiated by two-photon excitation to the 2S state of atomic hydrogen present in the flame. Water vapor has electronic transitions at the Lyman- α wavelength corresponding to this energy, so there is some probability that the electronically excited atoms will transfer their energy to water molecules when they collide in the flame. The electronically excited water molecules then would fall apart into H and OH fragments, with the OH fragments subsequently detected by the OH LIF probe, leading to the enhanced signal observed. Modeling of this process shows that over the range of pulse energies used, the true intensity dependence appears similar to a single $I^{3.4}$ dependence, consistent with our measurements.

We have used successfully both 243-nm and 205-nm two-photon excitation to measure atomic hydrogen profiles in a variety of low-pressure flames. Proper application of both techniques becomes more challenging at higher pressures, however. In a lean (equivalence ratio 0.8), atmospheric-pressure, hydrogen-oxygen flame, we were able to observe photochemical production of hydrogen atoms using 243-nm excitation, but reasonable measurement of a flame profile was possible by reducing the laser intensity, whereas this was not the case using 205-nm excitation. The photochemical creation mechanisms involved likely play an important role in this difference; as the laser intensity is decreased, the magnitude of the photochemical contribution to the total concentration of atomic hydrogen decreases much more rapidly for the multiphoton 243-nm processes than for the single-photon 205-nm process. Similarly, we were successful in measuring atomic hydrogen concentration profiles in rich atmospheric-pressure, ethylene-oxygen-argon flames using 243-nm excitation, but were unsuccessful using 205-nm excitation.

These studies support the contention that longer excitation wavelengths are generally preferable to shorter excitation wavelengths, simply because the likelihood that a photon will have sufficient energy to break a chemical bond increases

as its wavelength is decreased. Because the relative importance of a photochemical production mechanism depends strongly on the details of the flame environment being probed (such as natural concentration of the species being measured, concentrations of potential photochemical precursors present, temperature, pressure, etc.), it becomes necessary to determine almost on a case-by-case basis whether or not photochemical perturbations are likely to influence measurements made using these (and other) multiphoton excitation schemes.

Figure 2. OH fluorescence signal excited by the 281-nm probe beam (Figure 1) monitored as the 243-nm pump beam is scanned across the atomic hydrogen two-photon 1S-2S resonance. Top part of figure: increase in OH fluorescence signal observed away from the two-photon resonance (wings of curve) and much larger increase observed on resonance; the dashed line represents the nascent OH fluorescence signal observed with the 243-nm beam blocked. Bottom part of figure: OH emission observed with only the 243-nm beam present.

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Two-Photon-Excited Stimulated Emission from Atomic Oxygen in Flames and Cold Gases[†]

Two-photon-excited stimulated emission from atomic oxygen has been studied in flames and room-temperature flows of O₂ and N₂O.

M. Aldén,* U. Westblom,* and J. E. M. Goldsmith

Multiphoton excitation techniques, combined with fluorescence (FL) or ionization detection, have proven to be very powerful methods for detecting a variety of species in harsh environments, such as flames, where conventional single-photon techniques are often not applicable. Proper application of these techniques requires an understanding of the physical mechanisms that depopulate the laser-excited state, so that the fraction of excited atoms or molecules that are actually detected can be reliably calculated. This paper describes our observation of stimulated emission (SE) following two-photon excitation of atomic oxygen. This SE process is often termed amplified spontaneous emission (ASE); it is not the same as superradiance, although the distinction between the two is somewhat subtle.

Two-photon-excited SE has been observed before in a variety of media. Its potential influence on diagnostic techniques based on multiphoton excitation has received little attention, and to our knowledge it has not been detected in atomic oxygen, a very important species in a variety of environments. A partial energy-level diagram of atomic oxygen is shown in the inset in Figure 1 (not to scale). Two-photon 226-nm excitation of the 2³P - 3³P transition has been used to observe oxygen atoms in flames with both fluorescence and ionization detection. In this study, we compare 845-nm 3³P-3³S FL and SE signals induced by the two-photon excitation. (Throughout this paper, "fluorescence" or FL refers to the signal collected at right angles to the laser beam, and "stimulated emission" or SE refers to the signal collected in the direction of the laser beam.)

One of our first concerns was to prove that the signal observed along the laser beam was in fact SE, and not simply FL collected in the forward direction. In a 15-torr H₂/O₂ flame with equivalence ratio 0.8, we found that the forward-direction signal was more than 10⁴ times stronger than the right-angle FL. Performing a similar measurement using

single-photon laser-induced fluorescence of OH (for which lack of a population inversion prevented stimulated emission from being possible), we determined that the forward-direction FL signal was at least ten times weaker than the right-angle signal.

Because FL and SE have distinctly different dependences on the density of excited atoms or molecules responsible for their emission, their signals should behave differently as the excited-state density is varied through changes in excitation conditions. We first studied this difference by measuring intensity dependences of the FL and SE signals in three environments: a 15-torr H₂/O₂ flame with equivalence ratio 0.8, a 380-torr flow of room-temperature N₂O, and a 380-torr flow of room-temperature O₂. The studies performed in the N₂O and O₂ flows relied on photochemical production of oxygen atoms by photolysis of the parent gas by the 226-nm laser pulses. The atomic oxygen in the flame was produced primarily by combustion, although some photochemical production cannot be ruled out. The results of these measurements are presented in Figure 1. In all three cases, the low-intensity behavior of the SE is clearly different from the FL signal.

The solid lines passing through the points representing the FL measurements in Figure 1 are least-squares fits that indicate the low-pulse-energy behavior of these signals (the dashed lines are extrapolations to the higher-intensity region). The slopes of the lines for the flame, N₂O, and O₂ measurements are 1.59, 2.95, and 4.15, respectively. The latter two slopes are consistent with one- and two-photon photolysis of N₂O and O₂, respectively, followed by two-photon excitation to give the resulting slopes of 3 and 4. A slope of 2 might be expected for the flame measurement, but rapid single-photon photoionization and/or partial saturation of the two-photon transition can reduce the observed slope. The fall-off from the low-intensity behavior of these measurements of the higher-intensity points (i.e., the gap between the dashed lines and the data points) could be due to these effects, but could also be due to rapid depletion of the two-photon-excited state by the SE, a very different physical mechanism.

[†]Opt. Lett. 14, 305 (1988)

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Figure 1. Intensity dependences of fluorescence (open symbols) and stimulated emission signals (filled symbols) in a lean (equivalence ratio 0.8), 15-torr H_2/O_2 flame (circles), a 380-torr flow of room-temperature N_2O (triangles), and a 380-torr flow of room-temperature O_2 (squares). Each intensity dependence was recorded with an independent scale factor for the signal (the stimulated emission signals were actually much stronger than the fluorescence signals). Inset: Energy levels and transitions relevant to two-photon-excited fluorescence (FL) and stimulated emission (SE) in atomic oxygen (not to scale).

As mentioned previously, the SE signal was on the order of 10^4 times stronger than the FL signal for the geometries we used. A technique that takes advantage of this large signal could be a valuable addition to the selection of diagnostic methods available for environments such as flames. Several difficulties in its application are immediately apparent, however. SE is a line-of-sight method, integrating (though not necessarily in a linear fashion) a signal along the laser beam, and is much more difficult to model for diagnostic applications. One potential advantage it has over FL is the possibility of making the SE process faster than the collisional quenching rate, eliminating (or at least reducing) the influence of variations of quenching rates on the magnitude of the signal. Another potential advantage is provided by the bidirectionality of the SE signal. It is created in both directions along the laser beam, and collection of the SE signal in the back-scatter direction (opposite to the propagation direction of the laser beam) provides a diagnostic technique that requires optical access in only one direction and over a very small solid angle (defined by the dimensions of the laser beam).

To explore the use of SE as a diagnostic method, we measured vertical profiles in a flat flame. Because the physical properties in this flame vary only in the vertical direction, lack of spatial resolution along the horizontal laser beam is not a handicap. The resulting profiles measured in the equivalence-ratio 0.8, 15-torr H_2/O_2 flat flame by simultan-

eously recording the SE and FL signals as the height of the burner was varied are shown in Figure 2. The profiles are very similar, encouraging further studies.

Because of the relatively broad range of excitation conditions under which we observed SE in this study, we believe that it is present (although not observed) in most two-photon excitation studies of atomic oxygen. The 845-nm wavelength of the radiation precludes observation of the beam by eye, as was first used for detection of SE in a study of two-photon excitation of CO. Because laser-induced fluorescence measurements are generally not performed along a laser beam, SE is unlikely to have been observed electronically. Stimulated emission is, in fact, likely to be common during two-photon excitation, because parity considerations often prevent the excited atom or molecule from radiatively decaying directly to the ground state. However, there will generally be an unpopulated, lower-lying state of opposite parity to which it can decay, providing an ideal three-level configuration for SE.

Our discussion of stimulated emission here has been based on differences in its behavior from conventional laser-induced fluorescence measurements. One major concern arising from these observations is the impact SE might have on the FL measurement itself, because SE can deplete the excited atomic state at a rate faster than spontaneous emission, thus reducing the FL signal. We are currently investigating two-photon-excited SE in several species, both from the point of view of determining its impact on FL measurements, and to investigate applications of stimulated emission detection as a diagnostic technique.

Figure 2. Vertical profiles recorded in a 15-torr equivalence ratio 0.8 H_2/O_2 flame using fluorescence (open squares) and stimulated emission detection (filled circles) with the 26-nm laser beam attenuated to 0.4 mJ/pulse and averaging 10 laser shots per point.

Saturation Line Shapes and Intensities for Coherent Anti-Stokes Raman Scattering Spectra of Hydrogen[†]

Saturated CARS spectra of the Q(1) vibrational line of hydrogen at 100 and 3050 torr are measured using high resolution pump and Stokes lasers. Saturation spectra and intensities are calculated by numerically integrating the time-dependent density matrix equations for pressures from 1 to 100,000 torr.

R. P. Lucht and R. L. Farrow

At low laser powers, coherent anti-Stokes Raman scattering (CARS) line shapes and spectral profiles are independent of the intensities of the pump and Stokes laser beams. As laser intensities increase, however, CARS spectra are perturbed by Stark effects and by saturation of the Raman transition. Saturation effects become more important in perturbing line shapes as laser linewidths become smaller than Raman linewidths and/or the rate of relaxation processes decreases. For hydrogen, prediction of saturation intensities and line shapes is complicated by the importance of velocity-changing collisions, which do not dephase the Raman polarization but narrow the transition linewidth. The frequency of velocity-changing collisions is much faster than that of dephasing collisions; however, narrowing only occurs when the former exceeds the Doppler linewidth frequency. Consequently, the saturation behavior of hydrogen Q-branch lines is a complicated function of pressure.

We have performed experimental measurements of saturation line shapes and intensities for the CARS vibrational spectrum of the hydrogen Q(1) line using high-resolution, nearly Fourier-transform-limited pump and Stokes lasers.¹ The experimental system is shown in Figure 1. We employed high-resolution scanning techniques to ob-

tain spectra of the Q(1) transition of H₂ in a static cell. A single-frequency Nd:YAG laser produced a smooth, nearly Gaussian second-harmonic pulse with a duration of 18 ns and a full width at half maximum linewidth <45 MHz. A pulse-amplified ring dye laser was used for the Stokes beam. The output after pulse amplification was up to 10 mJ per pulse at 682 nm, with a 75-MHz linewidth and a pulse duration of 12 ns. All laser polarizations were parallel and vertically oriented. The relative beam angles were sufficiently small, <1.5°, that essentially forward-scattering Raman line shapes were measured.

The pump and Stokes lasers have electric fields that are well-characterized functions of time, and the density matrix equations for the hydrogen CARS interaction are numerically integrated using the measured pump and Stokes laser pulse shapes.² The interaction of the pump and Stokes beams with the Q(1) hydrogen resonance is shown schematically in Figure 2 for a particular velocity group. A system of differential equations is solved to determine the total population, excited state population, and Raman polarization $Q_k(t)$ for each velocity group during the laser pulses.

Doppler and motional narrowing effects are included in the calculations by summing CARS amplitudes from different velocity groups at each

Figure 1. Schematic of high-resolution CARS experiment.

Figure 2. Schematic illustration of the CARS interactions and collisional processes for a single velocity group of the hydrogen molecule.

[†]Journal of Optical Society America B, submitted (1988).

time step during the numerical integration. Depending on the gas pressure, the density matrix equations for the Raman polarization $Q_k(t)$ are solved for up to 101 velocity groups. It is necessary to treat these effects at this fundamental level, rather than by performing a frequency convolution, because of the complicated temporal nature of the CARS amplitude for a saturated resonance; the CARS pulse shape is very dependent on detuning and is different for each velocity group. Motional narrowing effects are included by allowing population transfer between velocity groups. A hard collision model is used, and it is assumed that the Raman polarization is not dephased by the velocity-changing collisions.

Comparison between theory and experiment is shown in Figure 3 for CARS spectra from pure hydrogen at 100 torr. For the higher intensity spectra, saturation is clearly indicated by the presence of the saturation dip and by the broadening of the line. Agreement between the theory and experiment is very good. For the most highly saturated hydrogen line, motional narrowing has a significant influence on the line shape; the wings of the line are much stronger than would be predicted in the absence of motional narrowing.

The pressure dependence of the saturation intensity, defined as the laser intensity product $I_p I_s$ at which the CARS intensity is reduced to half of its normalized unsaturated value, is shown in Figure 4.

Figure 3. Experimental and calculated line shapes for the Q(1) line of hydrogen at 100 torr.

Figure 4. Pressure dependence of the saturation intensity for the Q(1) line of hydrogen.

Experimentally, it was found that it was easier to saturate the Q(1) line at 3050 torr than at 100 torr; the theoretical calculations show the same trend and predict a minimum in saturation intensity at 2000 torr.

The experimental results are multiplied by a factor of 0.17 so that experimental and theoretical saturation intensities are equal at 100 torr. Experimental saturation intensities are higher because of the laser beam intensity profiles, which are approximately Gaussian; "top-hat" profiles are assumed for the theoretical calculations.

At pressures below 10 torr, the response of the molecule is transient and nearly independent of collision rates. Consequently, the saturation intensity approaches a limiting value. At pressures between 10 and a few hundred torr, the lasers couple effectively with only a few velocity groups and the saturation intensity increases as pressure and the rate of velocity-changing collisions increases. At higher pressures, population transfer among velocity groups is very rapid and all molecules couple effectively with the laser radiation. In the pressure range around 1000 torr, the effect of velocity-changing collisions is to decrease the saturation intensity, due to the narrowing of the Raman linewidth by these collisions. At pressures above a few thousand torr, dephasing collisions control the saturation process, and the saturation intensity increases strongly with pressure.

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Coherent Anti-Stokes Raman Spectroscopy Investigation of Reorientational Contributions to H₂ Raman Linewidths[†]

We report direct observations of the contributions of molecule-reorienting collisions to the linewidths of H₂ Q-branch transitions, measured at 296 K using high-resolution, coherent anti-Stokes Raman spectroscopy (CARS).

R. L. Farrow and G. O. Sitz*

Linewidths of anisotropic rotation-vibration transitions are subject to broadening by *J*-reorienting collisions. These contributions, if they can be distinguished from other broadening processes, provide information on the angle-dependent part of the molecular interaction potential. Van Kranendonk¹ and Gordon² have shown that the reorientational broadening in H₂ Raman Q-branch transitions may be obtained by subtracting the linewidths observed for the isotropic and anisotropic intensity components. We have measured anisotropic and isotropic Q-branch spectra of H₂ at 296 K, for densities between 0.12 and 5.0 Amagat, using high-resolution, coherent anti-Stokes Raman spectroscopy (CARS). Collisional broadening coefficients for the anisotropic spectra are found to be significantly larger than those for the isotropic components, due to the effects of *J*-reorienting collisions.

We used a high-resolution, scanning CARS system described in detail elsewhere.³ Measurements were obtained with a non-planar, crossed-beam geometry using a stabilized, single-frequency Nd:YAG laser and a pulse-amplified ring dye laser.

Gordon² has given a semiclassical description of processes that produce collisional broadening and frequency shifts in ro-vibrational spectral lines. Three physical effects are distinguished: (1) lifetime broadening due to rotationally inelastic collisions, (2) collision-induced dephasing of the radiation field due to phase shifts of the rotation (or of the vibration in a ro-vibrational transition), and (3) amplitude modulation of the field due to collisions that reorient the molecular angular momentum. The reorientation effect corresponds to collision-induced transitions among the *m*-sublevels; these transitions change the direction but preserve the magnitude of the angular momentum vector, *J*. Amplitude modulation of the scattered field results because the amplitude depends on the orientation of *J* with respect to the field direction.

Assuming the statistical independence of different types of collisions and small broadening cross sections, the line-broadening contributions from these processes are separable and additive. Thus, the total collision linewidth can be generally written as $\Gamma_{\text{total}} = \Gamma_{\text{rot-relax}} + \Gamma_{\text{pure-deph}} + \Gamma_{\text{reor}}$ where the terms on the right hand side arise from the effects (1) - (3) above. For H₂, these linewidths are relatively small and of comparable magnitudes.

To compare the isotropic and anisotropic Q-branch linewidths in H₂, we measured spectra using the following polarization geometries: laser and analyzer polarizations vertical (referred to as parallel), and pump beam polarizations vertical with Stokes and analyzer polarizations horizontal (referred to as perpendicular). The parallel geometry yields scattering via the $\chi_{1111}^{(0)}$ susceptibility tensor element, consisting of predominantly isotropic contributions. The perpendicular geometry yields scattering by $\chi_{1221}^{(0)}$, which is purely anisotropic.

We obtained collisional broadening coefficients by fitting experimental spectra to a soft-collision line shape model. The resulting coefficients were in good agreement with those for Q(0)-Q(4) measured by Hunt *et al.*⁴ using electric-field-induced absorption, and with those of Rahn and Rosasco,⁵ who used inverse Raman spectroscopy.

The broadening coefficients for the isotropic and anisotropic components are shown in Table I, and examples of spectra for Q(1) and Q(3) are shown in Figure 1. Due to smaller Raman cross sections and larger linewidths, anisotropic CARS intensities were up to 10⁴ times weaker than isotropic intensities for the same transitions and laser powers. The larger linewidths resulted from additional broadening by reorienting collisions, as discussed above. As seen in Table I, relative to the isotropic linewidth, the reorientation contribution was most important for Q(1) and less so for Q(2) and Q(3). (This contribution is, of course, absent in Q(0), which has no anisotropic component.) We find that the reorientation effect is more important than rotational relaxation in broadening the anisotropic component of Q(1).

[†]Journal of Optical Society of America B, accepted (1988)

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Table I

Collision-broadening coefficients (FWHM) for the isotropic and anisotropic components of the Q-branch of n-H₂ at 296 K, in units of 10⁻³ cm⁻¹/Amagat. Uncertainties in the last significant figures are shown in parentheses.

<i>J</i>	Γ_{aniso}^a	Γ_{iso}^a	$\Gamma_{\text{aniso}} - \Gamma_{\text{iso}}^a$	$\Gamma_{\text{aniso}} - \Gamma_{\text{iso}}^b$	Γ_{iso}^b	Γ_{quad}^c
0	-	2.67(15)	-	-	2.2	-
1	5.0(5)	1.80(10)	3.2(5)	3.4	0.6	4.8(8)
2	6.2(5)	3.02(15)	3.2(5)	3.0	2.6	5.6(6)
3	6.0(5)	4.23(20)	1.8(5)	1.6	3.6	6.0(2)
4		3.31(20)			3.0	
5		2.32(20)				

^aThis work.

^bCalculation by Van Kranendonk¹ for 273 K.

^cElectric-quadrupole absorption measurements for the $v = 0 \rightarrow 1$ Q-branch reported by Kelley and Bragg⁶ (for comparison with Γ_{aniso}).

To our knowledge the only theoretical calculation of linewidths for anisotropic Q-branch intensities was reported by Van Kranendonk.¹ This calculation is based on the quadrupole-quadrupole interaction, neglects the effects of elastic vibrational dephasing, assumes straight-line trajectories, and employs a single molecular velocity. Nevertheless, the theoretical predictions for the difference between

anisotropic and isotropic linewidths are in excellent agreement with our observations (see Table I).

The present Q-branch linewidths can also be compared to results from other experiments. The broadening of electric-quadrupole transitions is identical to that of anisotropic Raman transitions. Table I compares electric-quadrupole collisional linewidths for the $v = 0 \rightarrow 1$ H₂ Q-branch at room temperature measured by Kelley and Bragg⁶ to our (total) linewidths for the anisotropic component of the Raman Q-branch. The results agree within experimental uncertainties. Finally, the collisional linewidths observed in anisotropic Rayleigh scattering were shown by Gordon² to be determined solely by reorienting collisions. Hermans *et al.*⁷ recommend a value of $3.60(3) \times 10^{-3}$ cm⁻¹/Amagat for the Rayleigh linewidth, which is comparable to our result for the reorientation part of Q(1): $3.2(5) \times 10^{-3}$ cm⁻¹/Amagat. This comparison presumes no vibrational dependence in the reorientation cross section, since the Raman transition involves both $v = 0$ and $v = 1$ levels.

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Figure 1. CARS spectra of the isotropic ($I_{||}$) and anisotropic ($I_{\perp}$) components of the H₂ Q(1) and Q(3) transitions. The dots are data and the solid lines are fits using the Galatry soft-collision line shape model. The gas density and temperature were the same for both spectra. The difference in collisional linewidths between each symmetry component is a direct measure of broadening by elastic reorienting collisions.

Evidence for Speed-Dependent, Inhomogeneous Broadening in Collisional Line Profiles of Vibrational Raman Transitions

We report observations of asymmetries and other non-Lorentzian features in collisional line profiles of hydrogen vibrational Raman transitions broadened by rare gases.

R. L. Farrow, L. A. Rahn, and G. O. Sitz*

Although the vibrational Raman spectrum of molecular hydrogen has been studied widely at room temperature and below,¹ surprisingly little is known about its line broadening at high temperatures and with foreign-gas perturbers. It is precisely this knowledge, however, that is needed for modeling coherent anti-Stokes Raman (CARS) spectra of hydrogen in combustion experiments.

We have measured non-Lorentzian collisional line profiles in vibrational Raman transitions of hydrogen broadened by rare gases. (The latter are purely isotropic perturbers and are key to understanding more complex molecule-molecule interactions.) The profiles are asymmetric and exhibit other non-Lorentzian features at densities ranging from 0.2 to 50 Amagat. To our knowledge, these are the first such collisional profiles observed in vibrational spectra in the impact regime, i.e., at densities of a few Amagat.

The spectra were obtained using high-resolution inverse Raman spectroscopy (IRS) and high-resolution CARS. Both experiments employed frequency-stabilized, transform-limited, pulsed lasers obtained from pulse-amplified ring dye lasers and from injection-seeded, frequency-doubled Nd:YAG oscillators.

Departures from a Lorentzian profile were most evident when the rare-gas perturbers had masses much greater than the hydrogen radiator, at 2 atomic mass units (AMU). Figure 1 shows CARS spectra of the Q(1) transition of hydrogen broadened by krypton, argon, and helium, where the hydrogen mole fraction is 2% in each mixture and the total density is 7.3 Amagat. The spectrum perturbed by helium (4 AMU) is in excellent agreement with a Lorentzian profile; however, spectra perturbed by argon (40 AMU) and krypton (84 AMU) show significant deviations. The latter appear to result partially from Gaussian-like features in the data, in that the profiles are wider near their half-height and lower in the wings than a Lorentzian. We also

observed asymmetries, which are more pronounced for broadening by argon than by krypton. The sense of the asymmetries is such that the peak of a profile is displaced to lower Raman shift than the first moment. The asymmetries were observed at pressures as low as 150 torr for 10% hydrogen in argon at 295 K.

Figure 1. Background-free, experimental CARS spectra (data points) of the Q(1) transition of hydrogen broadened by various perturbers at 295 K. The hydrogen mole fraction is 2% and the total density is 7.3 Amagat in each gas mixture. The continuous lines are best-fit Lorentzian profiles (note the square-root of intensities is plotted) and fit residuals. The residuals show that lines broadened by the heavier perturbers, argon and krypton, exhibit asymmetries and non-Lorentzian features.

Figure 2 shows that the non-Lorentzian features are most pronounced for mixtures with low hydrogen concentrations and that they rapidly disappear as the hydrogen concentration is increased. The frequency of the transition changes for different mixtures because the density-shift of argon is more negative at room temperature than the self-density-shift of hydrogen.²

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Figure 2. Experimental IRS spectra (data points) of the $Q(1)$ transition of hydrogen broadened by argon at 295 K, for different mole fractions of hydrogen. The total density is 7.3 Amagat for each mixture. The continuous lines are best-fit Lorentzian profiles and fit residuals. Note that asymmetries are pronounced in the data for low hydrogen concentrations but diminish rapidly for higher concentrations. The observed change in line position is due to the argon density shift, which is negative.

We propose that these effects arise from speed dependences in the hydrogen density shifts by argon: the frequencies of radiators traveling at different speeds within the Boltzmann distribution are shifted by collisions with argon by different amounts, resulting in inhomogeneous contributions to the collisional profile.³ This interpretation is supported by IRS measurements of the argon-shift coefficients at different temperatures that show significant dependences on collision speeds and by a line-profile model based on these data. The model also incorporates the effects of speed-changing collisions, which narrow the inhomogeneous part of the profile.

Figure 3 shows IRS spectra from mixtures of 2% hydrogen in argon at 295 K and 1000 K, at a total density of ~ 14 Amagat. The data are compared to Lorentzian profiles (upper panels) and to the speed-dependent model (lower panels). The model

describes these and other observations (not shown) to nearly within the experimental noise. By varying the frequency of speed-changing and dephasing collisions for best fit, we find that hydrogen speed tends to be conserved even after several velocity-changing collisions with argon. Remarkably, the best-fit dephasing frequency indicates that *most* of the linewidth observed at 1000 K is due to speed-dependent inhomogeneous broadening. Since current line-broadening theories generally do not consider these effects, we believe that further investigations of their significance are justified.

Figure 3. Experimental IRS spectra (data points) of the $Q(1)$ transition of hydrogen broadened by argon at 295 K and 1000 K. The data are compared to best-fit Lorentzian profiles and to the model profile described in the text. Note the significant increase in Lorentzian residuals in (c) as compared to (a); we propose that this is primarily due to an increase in inhomogeneous width arising from speed-dependent density shifts.

Use of a Charge-Coupled Device Camera for Broadband CARS Measurements[†]

We have demonstrated the use of an unintensified charge-coupled device (CCD) camera for the measurement of broadband coherent anti-Stokes Raman scattering (CARS) signals. The use of an unintensified CCD camera rather than an intensified linear photodiode array (PDA) for signal detection offers considerable advantages for CARS applications, including higher resolution and improved instrument function, larger dynamic range, and a two-dimensional format.

D. J. Rakestraw, R. P. Lucht, and T. Dreier*

In most present CARS experiments, signals are acquired with intensified PDAs.¹ Photodiode arrays have a large dynamic range and are very sensitive when used with a multichannel plate (MCP) intensifier to overcome the large dark current and read noise of the PDA. However, the MCP intensifier limits the resolution of the intensified PDA (IPDA) detector system because amplification smears the image over four to five pixels on the PDA.

To investigate the use of CCD cameras for CARS measurements, the linear IPDA was replaced with a Photometrics CCD camera system. The CCD camera provides a two-dimensional image of CARS intensity, as shown in Figure 1; the spectrum is dispersed along the horizontal dimension of the camera. CARS spectra were processed by summing the signals from pixels in the same column for all rows with a significant number of counts; this process cor-

responds to the generation of vertical superpixels. The advantage of having the CARS signal spread over many rows is that it is harder to saturate an individual pixel element. In most of our experiments² using the IPDA, it was necessary to attenuate the CARS beam to avoid saturation.

Room air nitrogen CARS spectra are shown in Figure 2 for the two detector systems. Rotational structure is barely evident in the spectrum recorded with the IPDA, whereas it is clearly evident in the CCD spectrum. Although the pixel size for the IPDA and CCD is similar (25 and 23 microns, respectively),

Figure 1. Three-dimensional plot of a broadband CARS spectrum of nitrogen obtained using a CCD camera. A conventional intensity vs wavelength plot of this spectrum is shown in Figure 3.

Figure 2. Room air nitrogen CARS spectra taken with (a) the IPDA and (b) the CCD camera. The experimental spectra are represented with solid lines and theoretical fits are shown using dotted lines. Both spectra were taken using laser energies of approximately 12 mJ (total) at 532 nm and 1 mJ at 607 nm and were the average of 200 laser shots.

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the resolution for the CCD system is better because it is not necessary to use an intensifier. The full width at half maximum of the instrument function used for fitting a theoretical spectrum to the experimental spectrum for the CCD is a factor of two smaller than for the IPDA. Determination of the temperature of unburned gases in the engine is difficult because the first hot band of nitrogen is very weak at temperatures below 1000 K, and the temperature is determined primarily from the shape of the fundamental band. Therefore, temperature measurement accuracy is related directly to spectral resolution.

Because of the low dark noise of the CCD camera, it is very useful for averaging numerous laser shots over long time periods. For the engine experiments, data is collected at a rate of 1.6 Hz; the engine speed is 600 rpm and there are two skip (non-fired) cycles for every fired cycle. The high-temperature spectrum shown in Figure 3 was obtained by integrating on the CCD for five minutes and is the average of 480 laser shots. The signal-to-noise ratio of the spectrum and the agreement between theory and experiment are very good. Because of the high spectral resolution, the even-odd rotational structure of the high- J lines in the fundamental band is clearly evident.

Nitrogen CARS spectra obtained from the engine must be normalized for the frequency spectrum of the dye laser.² In our experiment, a nonresonant spectrum is generated by filling the engine with approximately four atmospheres of pure oxygen; the resonant CARS susceptibility for pure oxygen is negligible near the nitrogen bandhead. Normalization of the engine CARS data is performed by

Figure 3. Nitrogen CARS spectrum acquired from the burned gas region of the Sandia research engine. The spectrum was integrated for five minutes (480 laser shots) on the CCD detector. The experimental data are represented by the solid line, and a theoretical fit using a temperature of 2310 K is shown using a dotted line. Laser energies of 10 mJ (total) at 532 nm and 1.0 mJ at 607 nm were used to obtain this spectrum.

dividing the summed nitrogen spectrum by the summed nonresonant spectrum (nitrogen superpixel/nonresonant superpixel).

Experimentally, it was found that the frequency spectrum of the nonresonant signal was different for different rows on the CCD, suggesting that the dye laser spectrum varies spatially over the beam profile; in some cases we found that the spectrum was substantially different in the upper and lower rows of the illuminated area. The dependence of the frequency spectrum in the vertical dimension at the exit slit of the spectrometer may be a significant problem for acquisition of CARS signals using a linear IPDA if the CARS beam is defocused or misaligned so that not all of the signal is collected by the 2.5-mm high intensifier. If the vertical positions of the nitrogen CARS and nonresonant signals on the intensifier are different, systematic errors may be introduced during the normalization process. Such systematic errors are easily avoided when a CCD detector is used.

The CCD array may increase the effectiveness of shot-by-shot nonresonant referencing schemes such as the one used by Pealat *et al.*³ where the resonant CARS spectrum is divided pixel by pixel (or superpixel by superpixel) by a nonresonant reference spectrum. One problem with past schemes has been that the Raman lines in the resonant CARS spectrum have been much narrower than the frequency widths of resolution elements (four to eight pixels) on vidicon or IPDA multichannel detectors. Thus, not all dye laser modes, which are within the frequency range of a resolution element, couple effectively with the Raman line(s) within the same resolution element. However, in the reference channel, all these modes couple effectively with the frequency-independent nonresonant susceptibility, and the nonresonant referencing will not be representative. If the Raman lines are resolved by the detector resolution elements, however, the same dye laser modes will contribute to the resonant CARS and nonresonant reference signals. Using the CCD array, we should be able to resolve nitrogen Raman lines at pressures above a few atmospheres, thus making shot-by-shot referencing feasible for engine CARS measurements.

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Nonlinear Gaussian Expansions of Stochastic Processes: Super-Gaussian Effects in Coherent Anti-Stokes Raman Spectroscopy[†]

We propose a new approach to the analysis of stochastic processes (such as fluctuating laser fields) with super-Gaussian statistics: the expansion of stochastic processes in terms of first and higher powers of Gaussian components, which are used as a basis set. This approach is applied to treat the super-Gaussian correlation effects observed in coherent anti-Stokes Raman scattering experiments using frequency-doubled, pump-laser fields. Our results give much better agreement with experimental data than do previous theories.

A. M. F. Lau and R. L. Farrow

Many nonlinear laser spectroscopic measurements are known to be sensitive to the fluctuations in the laser fields. To obtain the frequencies needed in many experiments, the laser fields are produced from a multimode, fundamental field by n-harmonic generation. At present, there is no reliable method of *a priori* predicting the fluctuation statistics of the resulting n-harmonic generated fields. The question addressed here is thus quite general: what are the field statistics of the resulting laser field after n-harmonic generation from a multimode fundamental field?

We propose a novel approach to the analysis of stochastic processes $E(t)$ containing super-Gaussian statistics (such as the n-harmonic fields generated from multimode fields) based on a flexible and systematic expansion in terms of first and higher powers of basis components $G_m(t)$,

$$E(t) = \sum_{m=1}^n [G_m(t)]^m, \quad (1)$$

where each $G_m(t)$ is statistically independent and obeys Gaussian statistics. Previous approaches^{1,2} neglect all other intermediate powers of G_m as well as either $G_1(t)$ or $[G_n(t)]^n$. A mathematical advantage of the above expansion is that because all the stochastic components are Gaussian, higher-order correlation functions of each component G_m can be decorrelated rigorously.³

We demonstrate this approach by analyzing the super-Gaussian effects observed in the measurements of coherent anti-Stokes Raman spectra (CARS) of the $O(18)$ transition of nitrogen.¹ In these

measurements, two pump beams, split from a dye laser pumped by a frequency-doubled, multimode Nd:YAG laser (1.0 cm^{-1} full width at half maximum linewidth at 532 nm), and an independent Stokes beam were focused into a gas cell containing pure nitrogen to generate the coherent anti-Stokes beam using a crossed-beam CARS geometry. The anti-Stokes intensity was monitored as a function of the variable relative delay (small compared with the temporal pulse width) between the two pump beams. Therefore, its magnitude depends on the statistics of the field fluctuations in the pump beams and their correlation. For example, in a set of measurements performed on the $O(18)$ transition at 500 torr and 296 K, the resonant and the nonresonant anti-Stokes intensity components versus delay were measured separately by splitting the anti-Stokes beam and using dual polarizers and detectors. Their ratio was found to vary by almost a factor of two when the delay changed from 0 to 2 cm (Figure 1). Since the ratio of the resonant to the nonresonant signal often is used to calibrate concentration measurements, this variation could cause considerable uncertainty in the analysis of CARS data.

Using only the first and second terms of Equation (1) in our CARS calculations, we fit the results to the nonresonant CARS data of nitrogen at 500 torr as shown in Figure 1, determining the only adjustable parameter, namely the relative intensity between the two terms. With no further adjustment of this parameter, our results give much better agreement with the data at 500 and 4500 torr, than the Gaussian¹ and the squared-Gaussian model,² as shown in Figures 1 and 2. The results at 4500 torr serve as an independent test of the theory and the small discrepancies may be due to uncertainties in the experimental measurements.

[†]Opt. Lett. 14, 367 (1988).

Figure 1. Comparison of experimental (solid dots) resonant and nonresonant CARS intensities and their ratios (measured on the $O(18)$ transition of nitrogen at 500 torr and 296 K) with theoretical results using the present theory (solid lines), Gaussian (dashed lines) and squared-Gaussian (dotted lines) statistics to model the fluctuations in the pump laser fields.

Figure 2. Comparison of experimental (solid dots) resonant and nonresonant CARS intensities and their ratios (measured on the $O(18)$ transition of nitrogen at 4500 torr and 296 K) with theoretical results using the present theory (solid lines) with the same field statistics determined from the 500-torr data. Results of the Gaussian (dashed lines) and the squared-Gaussian (dotted lines) models are also presented for comparison.

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High-Resolution Inverse Raman Spectroscopy of the CO Q-Branch[†]

High-resolution spectroscopic measurements of the pressure dependence of the Raman vibrational Q-branch spectrum of pure CO are reported. Measurements are made at room temperature over the pressure range 0.5 to 6 atm. Broadening coefficients and pressure-shift coefficients are reported.

A modified exponential-gap rate law model is used to predict the pressure-dependent spectra.

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For reliable diagnostic information on temperature and pressure to be obtained by the use of coherent Raman spectroscopic techniques, one requires accurate knowledge of the Raman spectral line shape and its variation with temperature, pressure, and species concentration. We present here the results of a study of the spectral line shape of the Raman vibrational Q-branch of pure CO at room temperature over the pressure range 0.5 to 6 atm.

The quasi-CW inverse Raman spectrometer system has been described previously.¹ A detailed study of the pressure dependence of the Q lines for $J = 18-24$ was performed and accurate values of the linear pressure-broadening coefficients for $J = 0-24$ were determined. These values are a refinement of earlier measurements^{1,2} for $J = 0-18$ and extend the available data up to $J = 24$. Representative experimental spectra are presented in Figure 1 with fits that are described below. Under the assumption that the dominant line-broadening mechanism for the CO Q-branch is rotationally inelastic collisions, we test the ability of a modified exponential gap (MEG) law model¹ to describe the J dependence of the line-broadening coefficients and the spectral shape of the collisionally narrowed Q-branch. Spectra of the bandhead spectral region measured at 2.9 and 6.0 atm are presented in Figure 2. The fits to these data and the resulting residuals, also plotted in Figure 2, are described below.

In the pressure range of our interest, the effects of phase- and internal-state-changing collisions on the spectrum of the isotropic Q-branch of a simple diatomic such as CO can be described by a relaxation matrix equation. In this study, we follow two widely used approaches to fitting spectra which

depend, in general, on the "unknown" parameters to specify the relaxation matrix. The first is a perturbation theory² appropriate for weak mixing, i.e., for collisional mixing frequencies (the inverse of state-to-state rates) which are small compared to the frequency separation of the Q-branch transitions of interest. The second involves the specification of all the elements of the relaxation matrix by a rate law for state-to-state transitions¹ and the inversion of the complete, frequency-dependent matrix equation. The two approaches can easily be intercompared since the line-mixing coefficient of the perturbation theory can be calculated directly from the relaxation matrix rate law.

Figure 1. Inverse Raman spectra of the CO Q-branch for $J=18-24$ at 295 K for various values of pressure noted. The experimental spectra are compared with calculations based on perturbation theory.

[†]SPIE 912, 171 (1988).

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Figure 2. Inverse Raman spectra of the CO Q-branch at 295 K for the pressures noted. The experimental spectra ($J=0-18$) are compared with calculations based on the best MEG law (see text). The residuals (observed minus calculated) are also plotted and multiplied by a factor of three for visibility.

We have used both of the fitting approaches discussed above and the spectral data reported here and in References 1 and 2 to determine a set of line-broadening coefficients as a function of J . These results are determined in a manner that is insensitive to the details of either the spectral model or the rate law used to specify the relaxation matrix. The values of the line-broadening coefficients have been used to determine the parameters of the MEG law. This law is best fit to the observed J dependence by least-squares adjustment of the parameters α , β , and δ (identical to those defined in Reference 1). The parameters that give the best fit are $\alpha = 0.0126 \text{ cm}^{-1}/\text{atm}^{-1}$, $\delta = 1.322$, and $\beta = 1.346$. The overall goodness of fit, expressed by a root-mean-square (rms) deviation, is within 0.001 cm^{-1} (i.e., on average 2%) that is within the rms deviation of the data.

Since collisional collapse has the appearance of pulling all the Q-branch lines toward the most probable J in the spectrum, it is important that line mixing be small if one is interested in accurate values of line-shift coefficients. The spectra of the $J = 18-22$ transitions, shown in Figure 1, are of sufficiently high signal-to-noise and have sufficiently small line mixing that reasonably accurate values of pressure-shift coefficients can be determined. Pressure shifts have been determined from fitting each transition individually by use of the perturbation

theory. A careful assessment of the variation of the shift with J leads us to the conclusion that there is no significant J dependence of the shift. Pressure shifts have also been determined by fitting all of the transitions as a group using both perturbation theory and full matrix inversion. Weighted linear regressions to the frequency offsets versus pressure for each fitting approach yield slopes that are then averaged to give a pressure-shift coefficient, $-0.0032 \pm 0.0003 \text{ cm}^{-1}/\text{atm}$, for the Q-branch of self-broadened CO at room temperature.

Energy-gap rate law models provide simple, J -dependent parametrizations of the state-to-state rates for rotational energy transfer. This complete description of the state-to-state rates also allows specification of the entire relaxation matrix which describes the collisional narrowing (collapse) of the Q-branch of molecules such as CO. The MEG law description is compared to experimental spectra which show significant collapse at 2.9 and 6.0 atm in Figure 2. The Q-branch positions are calculated with the value of the pressure shift discussed above. The difference between the experimental data and the spectral model is shown, with a convenient offset, below the spectra. Similar plots that use the perturbation theory are shown in Figure 1. All these comparisons are based on the best linewidths and best MEG law results just described. We note that the two spectral models give essentially indistinguishable results for the spectra in Figure 1. All the other spectra, which show significant collapse, are best fit by the inversion of the complete relaxation matrix equation.

We see from Figure 2 that the agreement between experiment and theory is generally good and the basic physics of the collapse seems to be well described by the MEG law and the relaxation matrix theory. There are, however, systematic differences evident in the residuals shown below the spectra which we associate with a lack of accuracy in the MEG law. In particular, we speculate that the current MEG law, which accurately describes the line-broadening coefficients over the entire range of J for CO, underestimates the line interference at low J .

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Pump-Probe Measurements of State-to-State Rotational Energy Transfer Rates in N_2

We have measured state-to-state rotational energy transfer rates for N_2 ($v=1$) at 298 K. We use the technique of stimulated Raman pumping to prepare a selected rotational state of the N_2 . After allowing an appropriate time interval for collisions to occur, we use 2+2 resonance-enhanced multiphoton ionization to detect the population of the pumped level and the relative population of levels to which rotational energy transfer has occurred.

G. O. Sitz* and R. L. Farrow

State-to-state energy transfer rates often dominate the intermediate and high pressure Raman spectra of gases commonly found in combustion environments.¹ To interpret such spectra and to model accurately the corresponding physical system, these state-to-state rates must be known. A variety of phenomenological models have been devised to predict these rates, but actual state-resolved measurements are available for relatively few systems. Accordingly, we have undertaken a study to measure directly rotational energy transfer rates in N_2 .

The apparatus used for these studies is shown schematically in Figure 1. The two colors needed for the stimulated Raman pumping process are from a frequency-doubled, injection-seeded

Nd:YAG laser and a tunable pulse-amplified ring dye laser. In addition to providing the narrow bandwidths (2.0 and $3.0 \times 10^{-3} \text{ cm}^{-1}$, respectively) necessary for complete selection of the pumped state, these single-mode lasers have smooth, Gaussian-like temporal waveforms (full widths of 14 and 10 ns, respectively). Both properties yield very uniform excitation of population for each pulse, compared to the use of multimode lasers. The frequency difference of the two lasers is tuned to excite a chosen transition in the N_2 Raman Q branch. Subsequent detection of the N_2 is accomplished by 2+2 resonance-enhanced multiphoton ionization (REMPI) via the (2,1) band of the $a^1\Pi_g - X^1\Sigma_g^+$ two-photon transition. Tunable UV light needed to excite this transition (at a wavelength near 286 nm) is

Figure 1. Schematic drawing of the experimental apparatus used for N_2 energy transfer measurements. Stimulated Raman pumping is used to prepare a selected rotational level of N_2 , $v=1$. At a variable time later, REMPI is used to probe all the rotational-state populations in the $v=1$ level.

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generated by frequency doubling the output of a second Nd:YAG-pumped dye laser. The output from all three lasers (the two Raman-pumping lasers and the UV probe laser) are focused into a cell containing N_2 gas, typically at a pressure of 1 torr. Ions created by the UV probing process are detected with a biased parallel-plate arrangement.

Figure 2 shows an example of the data. Plotted is the total ion current measured as a function of the UV probe wavelength for several different delays between pump and probe at a fixed pressure. In this case, the $Q(4)$ Raman line is being pumped, and the pressure is 1 torr. Knowledge of the two-photon line strengths appropriate to the $a^1\Pi_g - X^1\Sigma_g^+$ transition allows us to determine time-dependent rotational state populations from spectra such as those shown in Figure 2. Note the absence of transitions corresponding to odd rotational levels in Figure 2. This absence is a result of the nonzero nuclear spin of the nitrogen nucleus, which couples to the nuclear rotation J to form ortho (even J) and para (odd J) rotational states. These states are not coupled by collisions, that is, ΔJ odd collisional transfer is not allowed.

Figure 2. 2 + 2 REMPI spectra of the (2,1) band of the N_2 $a^1\Pi_g - X^1\Sigma_g^+$ transition at three different pressure-time products following excitation of the $Q(4)$ Raman line. Total ion current is monitored as a function of UV probe wavelength.

A number of models exist in the literature for predicting rotational energy transfer rates.² One such model that has been successfully used to fit inverse Raman spectra of N_2 is the modified exponential gap or MEG model.¹ In Figure 3, we show a comparison between measured rotational-state populations and those predicted by the MEG model. In this case the $J = 14$ level is selected in the Raman pumping step and the delay between pump and probe is 50 ns. We see that the model predicts accurately the populations for the neighboring J levels (10, 12, and 16).

Figure 3. Comparison of measured rotational-state populations with those calculated from the modified exponential gap model. Experimentally, the $Q(14)$ line was selected in the Raman pumping step.

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Electronic Quenching and Vibrational Relaxation of NO ($A^2\Sigma$, $v'=1$) by H_2O from Laser-Induced Fluorescence[†]

Laser-induced fluorescence from nitric oxide doped into low-pressure $H_2/O_2/Ar$ flames was used to determine collisional deactivation rates for electronic quenching and vibrational relaxation in the $A^2\Sigma$ state of nitric oxide. Temporally resolved NO fluorescence from the $A^2\Sigma \rightarrow X^2\Pi$ transition originating from the $v'=1$ and $v'=0$ levels was analyzed with a three-level rate equation model to determine the quenching cross sections and vibrational relaxation cross section for H_2O at 1340 K.

R. J. Cattolica, T. A. Mataga,* and J. C. Cavolowsky*

The nitric oxide molecule has been investigated extensively with spectroscopic techniques. Energy levels, line positions, and line strengths are well known from spectroscopic measurements and associated theoretical modeling. For the $X^2\Pi$ electronic ground state of nitric oxide (NO), energy-transfer rates have been measured over a wide range of temperature (300 to 7000 K). For the $A^2\Sigma$ state, however, energy transfer rates have been available only for moderate temperatures (< 1000 K). For combustion applications of laser-induced fluorescence (LIF) from nitric oxide, additional information on energy transfer rates for the $A^2\Sigma$ state is needed at higher temperatures (> 1000 K) to estimate signal strengths, laser-saturation power, and detectability limits.

In this investigation, we have used pulsed, laser-induced fluorescence to examine collisional energy transfer (electronic and vibrational) in the $A^2\Sigma$ state of nitric oxide in a series of low-pressure (76, 38, and 19 torr) $H_2/O_2/Ar$ flames. The laser system for the experiments consisted of a frequency-doubled (532-nm, 220-mJ, 10-Hz) Nd:YAG laser (Quanta-Ray DCR-1A) pumping a dye laser (oscillator plus amplifier), followed by frequency doubling and Raman shifting in a hydrogen cell. For the fluorescence measurements, the NO (1,0) $Q_2(26) + R_{12}(26)$ transition was excited using the frequency-doubled output of Kiton Red, Raman shifted to the third anti-Stokes wavelength, 214.3 nm. The laser pulse shape was measured with a 500-ps vacuum diode (ITT F4018). The fluorescence signal from nitric oxide in the burned-gas region 40 mm above a 60-mm-diameter burner was collected and focused onto the entrance slit of a 0.25-m monochromator (3-nm bandwidth) with a single 150-mm focal-

length ultraviolet lens used at $f/4$. In the experiments, the spectrometer was positioned on either the NO ($v'=1$, $v''=4$) band at 252.2 nm or NO ($v'=0$, $v''=1$) band at 234.5 nm. The fluorescence signal from the monochromator was measured using a photomultiplier tube (Hamamatsu R955) with a nonuniform dynode-voltage distribution to obtain 2-ns temporal resolution. The photomultiplier output and the laser pulse shape from the vacuum diode were recorded simultaneously with a single Tektronix 7912AD transient digitizer at a 1-GHz sampling rate. Both the transient and integrated fluorescence signals were stored on a computer.

For a 76-torr $H_2/O_2/Ar$ flame, the temporally resolved measurements of the excitation, laser pulse, and the subsequent fluorescence emission from the directly excited NO ($v'=1$, $v''=4$) band and the collisionally populated NO ($v'=0$, $v''=1$) band are plotted in Figure 1. To analyze these data, we used a three-level, rate-equation model to describe the laser-excitation and fluorescence-emission process. This rate-equation model reduced to a pair of first-order, ordinary differential equations (ODE) that describe the rate of change of the number density in the $v'=1$ and $v'=0$ vibrational levels. These differential equations were integrated numerically to predict the time history of the number density in these vibrational levels and the associated fluorescence observed in the NO (1,4) and NO (0,1) bands. The only independent parameters in this model are the temporal shape of the laser pulse, the electronic quenching rates for $v'=0$ and $v'=1$, and the vibrational relaxation rate. The measured laser pulse shape was introduced into the differential equations by a functional representation through a simple linear interpolation subroutine. The quenching and vibrational relaxation rates were found from a least-squares fit of the measured and predicted transient fluorescence signals. In Figure 1, the three-level model prediction of the NO (1,4) and NO (0,1) fluorescence are also plotted. The

[†]Journal of Quantitative Spectroscopy and Radiation Transfer, accepted (1988).

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Figure 1. Laser-induced fluorescence signals from the $A^2\Sigma$ state of nitric oxide in a 76-torr $H_2/O_2/Ar$ flame. The $NO(1,4)_{fluor}$ and $NO(0,1)_{fluor}$ are measured fluorescence emission from the (1,4) and (0,1) bands of the $A^2\Sigma \rightarrow X^2\Pi$ transition. The $NO(1,4)_{model}$ and $NO(0,1)_{model}$ are calculated emissions from an integration of a three-level rate equation model.

agreement between experiment and model is excellent for collisional quenching rates of $1.22 \times 10^8 s^{-1}$ for $v'=1$ and $1.21 \times 10^8 s^{-1}$ for $v'=0$ and a vibrational relaxation rate of $6.1 \times 10^6 s^{-1}$. Since the primary collision partner for energy transfer in the burned-gas region of these low-pressure flames is H_2O , these measured electronic and vibrational energy-transfer rates can be converted to H_2O collision cross sections using the known water concentration and the measured gas temperature for this flame, 1340 K. The resulting electronic-quenching cross sections are $36 \pm 2 \text{ \AA}^2$ for $v'=1$ and $35 \pm 3 \text{ \AA}^2$ for $v'=0$. The vibrational relaxation cross section from $v'=1$ to $v'=0$ is $1.8 \pm 0.4 \text{ \AA}^2$. In Figure 2, we plot the variation of

quenching cross section for $v'=1$ and $v'=0$ for the experiments conducted at all three pressures (76, 38, and 19 torr) as a function of gas temperature. These quenching cross sections show a slight increase with decreasing temperature. A comparison in Figure 2 with the much higher measured¹ cross section for H_2O ($102 \text{ \AA}^2$) at ambient temperature is indicative of the importance of the role of the attractive part of the intermolecular potential in the electronic quenching of nitric oxide.

Figure 2. Variation of the electronic quenching cross section of nitric oxide for $v'=1$ and $v'=0$ by H_2O as function of temperature.

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Theory of Molecular Transition Moment Determination by Autler-Townes Spectroscopy: $D^1\Pi_u - E,F^1\Sigma_g^+$ Bands of H_2^+

Vibronic transition moments between two electronic states of a molecule by the Autler-Townes effect (also known as ac, optical or dynamical Stark splitting) is investigated. For representative bands of $H_2(D^1\Pi_u - E,F^1\Sigma_g^+)$, we calculate their Autler-Townes spectra and examine their dependences on laser detuning, intensity, bandwidth, and the Doppler effect. With moderate laser requirement, the Autler-Townes splitting of a large number of D - E,F vibronic transitions in H_2 should be observable so that their transition moments may be deduced.

A. M. F. Lau and W. M. Huo*

Recently, Quesada *et al.*¹ have observed the Autler-Townes effect in the two-color, four-photon ionization of H_2 via the double resonant levels $E,F^1\Sigma_g^+$ ($v=6, J=1$) and $D^1\Pi_u$ ($v'=2, J'=2$). By fitting the calculated spectra with the observed spectra, they deduced the vibronic transition moment between these two states. They noted that pairwise state-selectivity, insensitivity to other molecular parameters (such as relaxation rates) in the *strong saturation* regime of the effect, and the need to measure only external laser parameters (such as intensity and frequency detuning), but not absolute state population, are some of the advantages of the Autler-Townes measurement of transition moments over other methods. Coupled with multiphoton excitation to high-lying levels and multiphoton ionization or fluorescence monitoring techniques, this method seems particularly well suited for measuring absolute values of transition moments between excited electronic states.¹

To deduce the *electronic* transition moment by various known methods (including the r-centroid approximation),² it is necessary to measure a number of vibronic transition moments between the same pair of electronic states. The vibronic transition moment measured in Reference 1 is probably the strongest among the D - E,F band system.

Here, we investigate which other D - E,F vibronic transition moments should also be observable by this method and what would be the requirements on the laser parameters.

Ab initio results³ of vibronic transition moments between the (E,F) state, $v=6$ and the D state, $v'=1-14$ are shown in Table I. The $v'=2 - v=6$ transition for which Autler-Townes splitting was observed in Reference 1 is clearly among the strongest transitions. By far the majority of the vibronic transition moments are not as strong. Therefore, in addition to the $v'=2 - v=6$ transition, we choose a few representative bands of lesser strengths and investigate the dependencies of their Autler-Townes spectra on laser detuning, intensity, bandwidth, and the Doppler effect. The ionization spectra as functions of the two-photon resonance detuning Δ_a of the UV probe laser are calculated using density-matrix equations of motion for the molecule coupled to the laser field. We use the same experimental and theoretical parameters as those given in Reference 1, except where stated otherwise.

One set of our results shows that by reducing the probe laser bandwidth in the experiment in Reference 1, the resolution of the Autler-Townes doublet is improved dramatically, enabling the observation of weaker transitions with moderate laser power. The experimental UV (probe) laser bandwidth in Reference 1 was 0.7 cm^{-1} . For the two-photon (E,F)-X transition, this becomes effectively a 1.4-cm^{-1} bandwidth and is the dominant contribution in the transverse relaxation rates Γ'_{21} and Γ'_{31} . It is feasible experimentally, to reduce the UV laser bandwidth by a factor of 5 and still maintain enough signal. In Figure 1, we present our results showing the major improvement of spectral resolution of the Autler-Townes doublets for the narrow-band case (solid lines) over the previous broadband case (dotted lines). For the ($v'=2,4 - v=6$) transitions,

¹Chem. Phys. Lett. **157**, 108 (1988).

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Table I
Franck-Condon factors, r-centroids, and
transition-matrix elements between
H₂ (E,F) state, v=6 and D state, v'=1 - 14

v'	Franck-Condon factor	r-centroid (au) ^b	transition moment (au) ^b
0	0.1169 (-3) ^a	1.7270	-0.04156
1	0.1732 (-1)	4.3545	0.3600
2	0.7878	2.3520	1.9700
3	0.6823 (-3)	19.1136	0.007036
4	0.3569 (-1)	2.4922	0.1883
5	0.3049 (-2)	4.7549	0.01148
6	0.1250 (-2)	4.6346	-0.04034
7	0.1205 (-1)	3.5842	-0.02696
8	0.3857 (-3)	3.8802	0.006737
9	0.1003 (-1)	4.0355	0.01182
10	0.3303 (-3)	3.4731	-0.003019
11	0.7270 (-2)	3.5485	0.01396
12	0.2718 (-1)	5.7412	0.06901
13	0.7607 (-1)	5.5254	0.08645
14	0.6747 (-2)	4.2914	0.004418

^a(n) denotes powers of ten.

^b(au) denotes atomic unit.

even the *Doppler-averaged, narrow-band* spectra (dashed lines) are better resolved than the *Doppler-free, broadband* spectra. On the other hand, comparison among the narrow-band spectra shows that the elimination of the Doppler effect dramatically improves the spectral resolution of the doublet. Figure 1(c) shows a previously unresolved doublet (in the broadband case) can be resolved in the narrow-band case.

The above results show that with moderate pump laser intensity ($\leq 1 \text{ GW/cm}^2$) and narrow probe laser bandwidth ($\leq 0.14 \text{ cm}^{-1}$), Doppler-free Autler-Townes spectra of H₂ (D - E,F) can be resolved for those bands with vibronic transition moment greater than 0.05 atomic units (au). The experimental conditions assumed in these calculations are not very stringent.¹ Clearly, Autler-Townes spectroscopy of weaker transitions can be achieved with even narrower laser bandwidths and weaker probe (ionization) laser intensity.

Figure 1. Probe-laser, narrow-bandwidth effect on the multiphoton ionization spectra of H₂ with several D-E,F (v' - v) bands at different pump-laser intensities. The Doppler-free, narrow band (solid line) and the Doppler-averaged, narrow-band spectra (dashed line) have better resolution in each case than the Doppler-free, broadband spectrum (dotted line).

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Theory of Higher-Order Collision-Enhanced Wave Mixing

Wave-mixing experiments on sodium in a flame reveal higher-order, collision-enhanced resonances in the form of subharmonics. Higher-order diagrammatic perturbation theory predicts these features and additional novel higher-order phenomena as well.

R. Trebino and L. A. Rahn

Collision-enhanced resonances represent an interesting class of nonlinear-optical processes, which have potential application to collision diagnostics and excited-state spectroscopy. They occur because collisional dephasing can rephase quantum-mechanical amplitudes that ordinarily cancel out exactly, thereby allowing otherwise unobservable wave-mixing resonances to be seen. This is an especially interesting phenomenon because these resonances are coherent effects that are induced by an incoherent process (collisional dephasing). First predicted¹ in the late 1970s and eventually observed² in 1981, these novel effects have now been seen in a wide variety of four-wave-mixing experiments, ranging from self-focusing to coherent anti-Stokes Raman spectroscopy. Recently, we have extended these observations to higher order, where we have shown both experimentally³ and theoretically⁴ that higher-order, collision-enhanced effects exist in nonlinear optics, appearing as subharmonics of two-photon resonances. Indeed, we have found that collision-enhanced processes are ideal systems for studying higher-order, nonlinear-optical effects because very high orders can be made to contribute with little or no saturation broadening. Recently, we have performed experiments on sodium in a flame using six- and eight-wave-mixing geometries, where even higher-order effects appear. In addition, we have developed a computer model of these effects that computes orders of the nonlinear-optical susceptibility as high as $\chi^{(11)}$. It uses diagrammatic perturbation theory⁵ and includes all eight hyperfine and Zeeman levels of the sodium ground electronic state. This model yields good agreement with experimental spectra from six- and eight-wave-mixing geometries and also predicts several novel features of higher-order wave mixing that have not previously been considered. For example, deep holes occur in resonance lines of many higher-order contributions in the absence of saturation.

While perturbation theory clearly cannot hope to explain all features of collision-enhanced phenomena (e.g., power-broadening and saturation

effects), it is better able to handle the large number of states (nine) in this problem than other high-intensity methods, such as dressed-state or continued-fraction techniques.⁴ We have determined the most important perturbation-theory diagrams for collision-enhanced, ground-state resonances in all orders and have derived analytical expressions for $\chi^{(N)}$ (see Figure 1). Our computer program sums these expressions over all combinations and permutations of the eight Zeeman and hyperfine ground-electronic-state levels and all laser frequencies and polarizations. As a result, the program generates theoretical spectra within the framework of perturbation theory with few additional assumptions.

Figure 1. The four most important Feynman-like diagrams describing collision-enhanced, ground-state resonances in six-wave mixing. The states, S, S', and S'', are ground electronic levels, while P, P', and P'' are electronically excited states. The numbers, 1 and 2, represent the laser frequencies ω_1 and ω_2 . The number of such diagrams for collision-enhanced N-wave mixing is $2^{(N/2-1)}$. When state, frequency, and polarization combinations and permutations are included, the number of terms that must be summed is much larger.

Figures 2 and 3 show experimental and theoretical spectra for the six- and eight-wave-mixing geometry experiments. Agreement between these spectra is good. Slight discrepancies occur because we have not convolved the theoretical spectra with the laser line shape (a much more difficult problem in higher order). In addition, the Zeeman line in the experimental eight-wave spectrum is a factor of five stronger than in the theoretical spectrum, due probably to ten- and twelve-wave-mixing contributions, where we have found that it is stronger.

We have also found that higher-order theoretical spectra display some unexpected effects. For example, contributions due to processes at least four orders higher than that of the beam geometry (e.g., $2\omega_1 - \omega_2 + (\omega_1 - \omega_1) + (\omega_2 - \omega_2)$ in a $2\omega_1 - \omega_2$ geometry) show strong holes in spectral lines. This is due to cancellations between singly and triply resonant terms, the latter yielding narrower lines and having opposite sign. Computed spectra also predict new high-order selection rules that have not been derived analytically.

Figure 2. Experimental (a) and theoretical (b) spectra for experiments on sodium in a flame using a six-wave-mixing $3\omega_1 - 2\omega_2$ geometry. The theoretical spectrum has been calculated by adding all six- and eight-wave-mixing processes that satisfy the phase-matching condition for the $3\omega_1 - 2\omega_2$ beam geometry. Resonances at 0 cm^{-1} and 0.06 cm^{-1} correspond to two-photon Zeeman and hyperfine resonances, respectively, and are seen in low-intensity four-wave-mixing experiments. Higher-order features are the subharmonics—resonances at $\pm 1/2$ of the hyperfine resonance frequency—that are due to four-photon resonances.

Figure 3. Experimental (a) and theoretical (b) spectra for experiments on sodium in a flame using an eight-wave-mixing $4\omega_1 - 3\omega_2$ geometry. This spectrum contains only the eight-wave-mixing processes that satisfy the phase-matching condition for the $4\omega_1 - 3\omega_2$ beam geometry. Resonances at 0 cm^{-1} and 0.06 cm^{-1} correspond to two-photon Zeeman and hyperfine resonances, respectively, and are seen in low-intensity four-wave-mixing experiments. Higher-order features are the subharmonics—resonances at $\pm 1/2$ and $\pm 1/3$ of the hyperfine resonance frequency—which are due to four- and six-photon resonances, respectively.

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Rise-Fall Ambiguities and Their Removal From Frequency-Domain Nonlinear-Optical Diagnostics[†]

Many frequency-domain diagnostic techniques measure only the magnitude of the Fourier transform of a temporal response and, hence, do not uniquely determine the response. We show, for a commonly used response, that the spectral line shape is equally well described by two different values of one parameter. Finally, we show how to eliminate this ambiguity.

R. Trebino, C. E. Barker,* and A. G. Kostenbauder**

In principle, each function of a Fourier transform pair uniquely determines the other. In practice, however, combustion diagnostics, such as coherent anti-Stokes Raman spectroscopy (CARS) and fluorescence that operate in the frequency domain, often yield only the magnitude, and not the phase, of the frequency response. As a result, the corresponding medium temporal response is not uniquely determined. Obvious (and trivial) ambiguities include constant phase factors, displacement of the origin, and simultaneous inversion and complex conjugation. Less obvious, and far less trivial, ambiguities also exist, even if the class of possible temporal responses is restricted. The study of such ambiguities is known as the phase retrieval problem and has received much attention.

We have considered techniques that measure the magnitude of the frequency response and study a specific, commonly used temporal response, the sum of two exponentials:

$$h(t) = \theta(t) \{ A \exp(-t/\tau_f) + B \exp(-t/\tau_s) \} \quad (1)$$

where $\theta(t)$ is the unit step function, τ_f and τ_s are fast and slow time scales, $A \equiv \alpha/\tau_f$, $B \equiv (1-\alpha)/\tau_s$, and α is the relative weight. We have shown that knowledge of the magnitude of the frequency response of this decay does not uniquely specify the parameter α . Specifically, for every measurable line shape, there are always two possible values of α . We refer to this ambiguity as a rise-fall ambiguity because it often results in a temporal response involving a rapid fall and then a slower fall having an identical line shape to that of a very different temporal response, one involving a rapid rise and then a slower fall. This type of ambiguity could be particularly troublesome, especially when each of the above

responses corresponds to a different physical phenomenon or when rises and falls both potentially occur.

We have demonstrated this ambiguity (see Figure 1) in experiments on the optical-Kerr effect in carbon disulfide using a nonlinear-optical, frequency-domain technique that involves measuring the strength of an induced grating as a function of the frequency difference between the two writing beams, $\omega_1 - \omega_2$. A third beam, at frequency ω_3 , probes the grating, producing a signal beam at the

Figure 1. Experimental results for the optical-Kerr effect in carbon disulfide with negligible quadrature-phase coherent background. (a) Diffraction efficiency vs frequency difference, $\omega = \omega_1 - \omega_2$. The solid line indicates the best fit, obtained for two different values of α : -0.91 and $+0.31$. (b) Plot of $\chi^2(\alpha)$ vs α for the data in Figure 1a. Observe the presence of two minima with about the same minimum value, indicating ambiguity in the fit for the parameter α .

[†]Opt. Lett. 13, 865 (1988).

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frequency $\omega_0 = (\omega_1 - \omega_2) + \omega_3$. Measuring the diffraction efficiency as ω_1 is scanned yields the squared magnitude of the Fourier transform of the medium temporal response. This technique is one of a class of optical frequency-domain methods, which generally measure the squared magnitude of the Fourier transform of the temporal response of a medium and that have been used to study a wide range of effects. Despite their wide use, however, potential ambiguities have not, to our knowledge, been recognized.

We have demonstrated a simple, single-scan method for removing ambiguities in sum-of-exponentials problems (see Figure 2), that involves the introduction of a constant, coherent background. In this method, the background must necessarily contain some quadrature (imaginary) phase. It requires tuning the probe frequency to a value $\sim \pm 1/\tau$ from that of the fixed-frequency excitation beam,

Figure 2. Experimental results for the optical-Kerr effect in carbon disulfide with substantial quadrature-phase coherent background. (a) Diffraction efficiency versus frequency difference, $\omega = \omega_1 - \omega_2$. The solid line indicates the best fit, obtained for a single value of α of $+0.26$. The dashed line indicates a fit using $\alpha = -0.91$. (b) Plot of $\chi^2(\alpha)$ vs α for the data in Figure 2(a). Observe the presence of only one absolute minimum, indicating that ambiguity in the fit for the parameter α has been removed.

where τ is an effective time scale of the medium response, which introduces into the signal beam significant contributions from a new process: $(\omega_3 - \omega_2) + \omega_1$. In this process, the beams at frequencies ω_3 and ω_2 write the grating and the (variable-frequency) beam at ω_1 probes it. Because the frequency difference between the two writing beams is constant, the strength of this contribution is approximately constant throughout a scan. This process has the same phase-matching and coherence properties and strength as does the $(\omega_1 - \omega_2) + \omega_3$ process. Finally, the coherent background contributed by the $(\omega_3 - \omega_2) + \omega_1$ process has a strong component of quadrature phase.

To see that ambiguities exist in sum-of-exponentials line shapes, note that the Fourier transform (with respect to $\omega \equiv \omega_1 - \omega_2$) of Equation (1), can be written:

$$\Gamma_{\alpha\beta\gamma}(\omega) = (1 + i\omega\tau_\alpha) / [(1 + i\omega\tau_\ell)(1 + i\omega\tau_s)] + \beta + i\gamma \quad (2)$$

where $\tau_\alpha \equiv \alpha\tau_s + (1-\alpha)\tau_\ell$, and coherent background, $\beta + i\gamma$, has been added. We ask whether there exists α' , β' , and γ' , such that $|\Gamma_{\alpha'\beta'\gamma'}(\omega)|^2 = |\Gamma_{\alpha\beta\gamma}(\omega)|^2$ for all ω . We find that this is the case, and we obtain two solutions: a trivial one, $\alpha' = \alpha$, $\beta' = \beta$, and $\gamma' = \gamma$, and a nontrivial one:

$$\alpha' = -2\tau_\ell/(\tau_s - \tau_\ell) - 2(\beta - i\gamma)(\tau_s + \tau_\ell)/(\tau_s - \tau_\ell) - \alpha \quad (3)$$

with $\beta' = \beta$, and $\gamma' = -\gamma$. The nontrivial solution represents the troublesome ambiguity and the expression for it in Equation (3) is exact.

The introduction of quadrature-phase coherent background removes the ambiguity because it yields a complex value for α' . Since a complex relative weight violates the assumption of a real decay, it is, therefore, not an ambiguity. Even if complex weights are allowed, quadrature phase may remove the ambiguity because the alternative solution for α is necessarily accompanied by ambiguity in γ : $\gamma' = -\gamma$. Thus, if only the sign of γ is known, the presence of coherent, quadrature-phase background removes complex ambiguities. Note that, whether the ambiguity is real or complex, any nonzero amount of quadrature-phase background is sufficient to remove the ambiguity, although in practice, the presence of experimental noise implies that a minimum value will be necessary.

Exalite 392E: A New Laser Dye for Efficient CW Operation Between 373 and 408 nm[†]

We have demonstrated efficient, CW dye-laser operation between 373 and 408 nm using Exalite 392E, a new laser dye. Dye-laser output powers in excess of 250 mW are obtained at 392 nm.

F. P. Tully and J. L. Durant, Jr.

Continuous-wave dye lasers operating from the near ultraviolet through the blue spectral region have been developed during the past fifteen years. However, excluding frequency-doubling techniques, continuous-wave (CW) dye-laser operation below 392 nm has been achieved only using the dye polyphenyl 1. Continuous-wave operation of this dye has been reported in the range 362 - 412 nm with a maximum output power of 70 mW at 383 nm. Polyphenyl 1, however, is very expensive, only reluctantly soluble in hot (160°C) ethylene glycol, and absorbs the 351- and 363-nm Ar⁺-laser lines inefficiently.

Recently, we began to study CN-radical chemical kinetics in pulsed-laser photolysis/CW laser-induced fluorescence (LP/LIF) experiments. Our initial studies utilized polyphenyl 1 tuned near 387 nm. While LIF signal levels were sufficient to perform kinetic studies, we found the polyphenyl 1 dye laser difficult to maintain over an extended period. Shortly after our experiments began, Exciton Chemical Corporation announced their new Exalite series of dyes for ultraviolet, pulsed-laser operation. In subsequent discussions with Exciton Chemical Corporation, we learned of an experimental dye, Exalite 392E, that might be suitable for ultraviolet, CW-laser operation. We report here successful tests of this new dye.

We determined the absorption coefficient, ϵ , for Exalite 392E as a function of wavelength. There are two absorption bands of comparable strength ($\epsilon_{\text{max}} \approx 4 \times 10^4$ liter/mol·cm) centered at 214 and 336 nm. Figure 1 displays those results that are relevant to an all-lines-UV Ar⁺-laser pump source. All ultraviolet Ar⁺-laser pump wavelengths are strongly absorbed by the Exalite 392E dye. Between 365 and 380 nm, ϵ decreases precipitously (by a factor of ~30) to a value of 130 liter/mol·cm. Above 380 nm, ϵ diminishes gradually to a value of 6 liter/mol·cm at 450 nm. Exalite 392E does not absorb significantly throughout the remainder of the visible and the near-infrared spectral regions.

Figure 1. Decadic, molar absorption coefficient ϵ versus wavelength for laser dye Exalite 392E dissolved in ethylene glycol. The ultraviolet Ar⁺-laser pump wavelengths are indicated.

[†]Appl. Opt. 27, 2096 (1988).

We utilized commercially available equipment in all of our laser experiments. The UV output (333-364 nm) of an Ar⁺ laser pumped a linear dye laser containing a three-plate birefringent filter as the only tuning element. Exalite 392E dissolved in ethylene glycol in a few minutes at room temperature to produce a 1.6-mM dye solution.

Figure 2 displays the dye-laser tuning curve for Exalite 392E. In this experiment, we pumped the Exalite 392E dye laser with 3.5 W all-lines-UV from the Ar⁺ laser. We utilized an output coupler that is 7% transmitting at 387 nm. The laser output is greater than 250 mW at 392 nm, and it significantly exceeds that from a polyphenyl 1 dye laser throughout the 373-408-nm tuning range. While we have not performed quantitative dye-lifetime studies, the dye-laser output power did decrease by about 10% after 20-watt-hours Ar⁺-laser irradiation.

In Figure 3 we plot dye-laser output power versus Ar⁺-laser pump power, utilizing the 7%-transmitting output coupler in the Exalite 392E dye laser. The lasing threshold appears at 850-mW Ar⁺-laser pump power. We found this threshold to be reduced to 750-mW pump power when a 2%-transmitting output coupler is used. Based on the data plotted in Figure 3, we compute a slope efficiency equal to 10%.

Figure 2. Dye-laser output spectrum using laser dye Exalite 392E.

We have performed only a few tests aimed at optimizing Exalite 392E dye-laser performance. We measured the fractional absorption of the pump-beam radiation in the dye jet to be 0.45. Presumably, one could obtain higher dye-laser output powers by increasing the dye concentration above 1.6 mM. However, given the steep dependence of ϵ on a wave-length between 365 and 380 nm, we would expect such an increase to be accompanied by a red-shift of the dye-laser tuning curve. We tested a variety of output couplers in the dye laser and found optimum performance at 392 nm for those transmitting 4-7% of the intracavity power. Finally, we found that the dye-laser output power is quite sensitive to the dye-nozzle pressure, increasing by 30% as the pressure is raised from 75 to 110 psi. Closed-cycle refrigerated cooling combined with higher dye-nozzle pressures appears to be a potentially promising improvement.

Exalite 392E renders polyphenyl 1 obsolete in our chemical kinetics studies. It combines higher dye-laser output powers with a significant improvement in the dye-solution preparation process.

Figure 3. Dye-laser output power at 392 nm versus Ar⁺-laser pump power.

Permanent-Magnet Faraday Isolators for Q-Switched Nd:YAG Laser Applications[†]

We describe the design of high-performance, single-pass, permanent-magnet Faraday isolators that are simple to construct and use. These isolators are designed for use with Q-switched Nd:YAG laser systems used for spectroscopy and combustion diagnostics.

R. L. Schmitt and L. A. Rahn

Optical isolators based on the Faraday effect have long been used in laser systems to prevent destabilizing feedback and, in multiple amplifier systems, to prevent parasitic oscillations and optical damage due to amplification of back-scattered light. Laser system designers have, however, often avoided using Faraday isolators because large, water-cooled electromagnets driven by pulsed power supplies were required to produce magnetic fields of sufficient strength for Faraday rotation in glass. Recent advances in rare-earth, permanent-magnet technology allow the construction of permanent-magnet Faraday isolators which, in contrast to previous designs, operate continuously, are compact, consume no power, and do not require cooling.

We have designed high-performance, single-pass, permanent-magnet Faraday isolators that are simple to construct and use. Special emphasis is placed on isolators designed for use with Q-switched Nd:YAG laser systems operating at 1.06 μm , where the radial variation of the magnetic field must be taken into account to ensure that the isolation provided by the design is adequate.

A Faraday isolator is the optical equivalent of a diode; linearly polarized light is permitted to pass in one direction only. The device relies on Faraday rotation, the rotation of the plane of polarization of light propagating through a material parallel to an applied magnetic field, to provide nonreciprocal optical rotation. The operation of a Faraday isolator is illustrated in Figure 1. Linearly polarized light passing through the device in the forward direction passes through the first polarizer, is rotated 45 degrees by the Faraday rotator, and finally passes unattenuated through the second polarizer. If any of this light is reflected back toward the source, it experiences an additional 45 degrees of rotation traveling through the Faraday rotator and is completely rejected by the polarizer. Thus, the Faraday isolator acts as an optical diode, permitting light to flow in one direction only.

The rotation of the plane of polarization of light in passing through a Faraday rotator is given by

$$\theta = V \int B_z dz$$

where V is the Verdet constant of the material and B_z is the component of the magnetic induction parallel to the propagation direction of the light. The integral is carried out over the length of the glass in the rotator. Note that the rotation depends on the orientation of the magnetic field.

Using a simple model for permanent magnets, we have developed a computer code that calculates the net magnetic induction due to an arrangement of permanent magnets. We have used

Figure 1. A Faraday isolator depends on polarized light and nonreciprocal (Faraday) polarization rotation. Linearly polarized light passing through the device in the forward direction passes through the first polarizer, is rotated 45 degrees by the Faraday rotator, and finally passes through the second polarizer (virtually unattenuated). If any of this light is reflected back toward the source, it experiences an additional 45 degrees of rotation traveling through the Faraday rotator and is completely rejected by the polarizer. Thus, the Faraday isolator acts as an optical diode, permitting light to flow in one direction only.

[†]SPIE 912, 206 (1988).

this code to predict the performance of our Faraday rotator designs. The predictions of this code agree well with our measurements and we find that the code is valid for a variety of magnetic materials and geometrical arrangements.

The basic permanent-magnet Faraday isolator design considered here consists of a series of axially magnetized, cylindrical, permanent magnets arranged with alternating polarities (i.e., adjacent magnets repel one another). This arrangement, illustrated in Figure 2(a), produces a magnetic field inside the hole with the majority of its field strength parallel to the direction of light propagation. The principal advantage of this design is the nearly factor-of-two enhancement of the magnetic field near the interface between opposed magnets. By placing paramagnetic Faraday rotator glass (Hoya FR-5) inside every other magnet, the regions of highest magnetic field can be used to produce the maximum Faraday rotation. Note that glass cannot be placed inside every magnet or the net rotation of the device would be nearly zero since adjacent magnets have fields of the opposite sign. It is possible, however, to use the reversed field of the empty magnets by incorporating wave plates or by using diamagnetic glass. The excessive cost of the former and the small Verdet constants of the latter may make these options impractical unless space or weight is severely restricted by the application.

We have constructed a Faraday isolator with a clear aperture of 6 mm using Nd-Fe-B permanent magnets (with a surface magnetic field strength of $B_s = 12,200$ Gauss). This design, illustrated in Figure 2, uses 5 magnets, each 2 cm in length and 5 cm by 5 cm on a side. Faraday rotator glass is placed in the second and fourth magnet to achieve a net rotation of 41.3 degrees at $1.064 \mu\text{m}$.

The theoretical magnetic induction, normalized to magnetization for the above configuration, was calculated and the results are shown in Figure 2(b). The solid line represents the value of the magnetic induction on the axis of the cylinder ($r = 0$) while the dashed line shows the value near the edge of the hole in the cylinder. This figure illustrates how the opposed magnet configuration enhances the magnetic field strength near the interface, since the field at the surface of one magnet is $\mu_0 M/2$.

We have also designed and constructed a Faraday isolator with a clear aperture of 13 mm. This larger aperture is suitable for use in isolating a laser oscillator from its amplifiers or in isolating amplifiers in multi-amplifier systems. This isolator uses a total of 10 cm of Hoya FR-5 glass to achieve 40 degrees of rotation at $1.06 \mu\text{m}$. Although the optimum

rotation is 45 degrees, this design still provides excellent rejection of back-scattered light with acceptable attenuation in the forward direction.

We have modeled permanent-magnet Faraday isolators and we have used the resulting calculations to design high-performance isolators. We have developed design curves and formulas that simplify the task of designing permanent-magnet Faraday isolators for a variety of different requirements including operating wavelength, aperture, and acceptable leakage. Measurements using a variety of commercially available magnetic materials agree well with calculations and scaling factors for these materials have been tabulated.

We have used these isolators in our injection-seeded Nd:YAG laser systems to isolate the master oscillator from the slave laser and also in Doppler-free spectroscopy using counter-propagating laser beams.

We have transferred this technology to both private industry and other laboratories. As a result, several small companies now design and build Faraday isolators based on our designs. It is expected that the high performance and ease of implementation of devices like these will make them useful in many applications.

Figure 2. (a) Typical arrangement for a permanent-magnet Faraday rotator. A stack of 5 magnets arranged with alternating polarities contains Faraday glass inside every other magnet. The calculated magnetic induction for a 6-mm-diameter rotator is shown in (b). The solid line indicates the on-axis value, and the dashed line indicates the value near the edge of the inner hole.

Section 3

It is now becoming possible to study motions that occur in molecules on their natural, femtosecond time scales. The ultrashort optical pulses required for these studies are generated in a continuously pumped, ring dye laser by introducing this saturable-absorber dye jet into the laser cavity. The resulting 40-femtosecond-long pulses make it possible to investigate the details of many intramolecular dynamical processes.

Combustion Chemistry

The colliding-pulse, mode-locked dye laser is a powerful tool for generating optical signals to study ultrafast processes in molecules. The laser is set up in the form of a ring and is pumped by a continuous-wave, argon-ion laser. The saturable-absorber dye jet produces mode-locked operation of the laser with optical pulses propagating in both directions around the ring and colliding in the thin jet. The resulting temporally short pulses contain a correspondingly broad range of frequencies. Prisms P_1 - P_4 are adjusted to equalize transit times around the ring for all important frequencies, thus minimizing the pulse length.

After a pulse leaves the laser through the partially reflecting output mirror, its duration is measured by autocorrelation, a process in which the pulse is split into two parts that interact in a frequency-doubling crystal. Before these two pulses enter the crystal, a precise variable delay is introduced in the form of a slightly extended path for one of them. Measuring the intensity of frequency-doubled light as a function of delay allows determination of pulse length. Typical values are about 40 fs for the laser used at the CRF.

The pulses obtained from the laser are appropriate for investigating a variety of dynamical processes in molecules. Initial research has involved the dye malachite green dissolved in water and has probed quantum beats and perturbed free-induction decay. Future work will explore the rates of elementary reactions and of energy flow in molecules in both condensed- and gas-phases.

Section 3

Combustion Chemistry

Under the sponsorship of the Department of Energy's Office of Basic Energy Sciences, Sandia National Laboratories undertakes fundamental experimental and computational research in combustion chemistry. This work provides information needed to understand the complex chemical processes involved when fuels are burned. The program emphasizes determining the rates of elementary processes using state-of-the-art diagnostics and stresses the close coupling of experiment, theory, and modeling.

Staff and visitors investigate elementary reactions important to the burning of fuels or the production of pollutants. Typical experiments utilize slow-flow reactors together with such techniques as laser photolysis and laser-induced fluorescence (LIF) to generate and detect, respectively, reactive species. Using mass spectrometry and LIF as diagnostic tools for experiments conducted in low-pressure flames, researchers study the kinetic mechanisms involved in prototypical combustion systems. Other experiments and related theoretical efforts address fundamental questions of molecular dynamics—questions that must be answered to develop complete models of kinetic processes.

Theoretical calculations of potential energy surfaces enable predictions of the product distributions that result when reactive species interact. These calculations are useful in extrapolating measured reaction rates. Computer modeling of the complete kinetics for combusting systems defines the dominant reaction pathways.

The experimental, theoretical, and modeling programs are focused on topics of importance to energy-producing technology. Themes of current emphasis include the formation and destruction of nitrogen-containing pollutants and the oxidation of hydrocarbons.

Femtosecond Transient Absorption of Malachite Green

The induced absorption decay measured for malachite green in water exhibits oscillations corresponding to vibrational motions of the molecule. Femtosecond transient-absorption experiments of this type should allow us to study ultrafast intramolecular dynamics as they are occurring.

C. C. Hayden and R. Trebino

Many of the chemical reactions of polyatomic molecules involve unstable, highly-energetic, intermediate species. Knowledge of the dynamical processes occurring in such highly excited molecules is, therefore, important for understanding the rates and pathways of many chemical reactions. These intramolecular energy-redistribution processes are usually extremely fast, frequently having subpicosecond time scales. The recent development of methods for producing femtosecond laser pulses now provides the time resolution needed to directly observe these short-lived events. We are currently developing experimental techniques for applying femtosecond lasers to the study of the dynamics of highly excited molecules. In addition, we have initiated theoretical studies of the interaction of molecules with intense optical fields on very short time scales to obtain the understanding necessary for interpreting the experimental results.

To generate femtosecond pulses, we have assembled a colliding-pulse, mode-locked dye laser operating at 625 nm. This laser now routinely produces a stable train of pulses at a repetition rate of about 90 MHz with pulse widths of less than 40 femtoseconds and an average output power of about 30 mW. With this laser system, we are studying transient absorption changes induced by intense excitation pulses. The output of the dye laser is split into two separate pulse trains; one, with about 90% of the intensity, excites the sample while the weaker one probes the absorption. By precisely controlling the optical path lengths, with 0.1 micron resolution, we vary the delay between the excitation and the probe pulses and thus measure absorption as a function of time relative to the excitation pulse. The details of our experimental setup are shown in

Figure 1. To measure very small changes induced in the absorption, we modulate the excitation pulse train and detect the modulation of the probe beam transmission with a lock-in amplifier. A laboratory computer records and displays the signal while controlling the delay time between the pulses.

The initial sample material we have chosen for transient-absorption measurements is malachite green in liquid solution. Its induced-absorption decay has been studied previously but has not been

Figure 1. Experimental setup for transient-absorption measurements. The incoming pulse is split into probe and excitation pulses. The excitation pulse is delayed by a precisely variable amount, and the two pulses are focused into the sample. The transmitted probe-pulse intensity is measured by a photodiode.

fully explained. Figure 2 shows the absorption change we observe in a solution of malachite green in water as a function of delay time following excitation by 40-femtosecond laser pulses. The excitation pulse changes the transmission of the probe pulse by only about 1 part in 10^4 . The oscillatory behavior superimposed on the decay of the induced transmission is similar to that recently observed elsewhere by related techniques.^{1,2} These oscillations

Figure 2. Change in the probe absorption of malachite green in water as a function of time delay following an excitation pulse. Oscillatory behavior is observed with a period of approximately 150 femtoseconds.

can be modeled as coherent excitations of molecular motions, so the experiment actually reveals the vibration of a molecule in real time. This motion modulates the absorption probability, but it is not yet understood with which states of the molecule it is associated. It is surprising to see a simple oscillatory pattern in the decay of an excitation in such a large molecule, where a large number of states could potentially be involved. We plan measurements with different excitation wavelengths to see whether these oscillations are sensitive to the states within the electronically excited manifold that are accessed in the experiment.

The observation of time-dependent molecular motions is a first step toward studying the dynamics of intramolecular processes in real time. The transient-absorption technique is particularly well suited for this because it directly measures the evolution of a molecular system away from an initially excited configuration. After some further development to increase the sensitivity, we plan to extend this technique to gas-phase samples, so that effects of the solvent on the short-time dynamics can be eliminated.

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Unimolecular Decomposition and IVR in Highly Excited Methyl Hydroperoxide[†]

Quasiclassical trajectory calculations show that intramolecular vibrational redistribution (IVR) occurs more quickly in CH₃OOH when a C-H bond is excited than it does when the O-H bond is excited to a similar energy. The opposite is true for the rate at which unimolecular rupture of the O-O bond occurs.

G. A. Fisk, H. Gai,* and D. L. Thompson*

Recent advances in experimental capabilities make it possible to study the details of dynamical processes in molecules on the time scales at which atoms move. There is now an opportunity to couple theory and experiment to understand at the most fundamental level how, for instance, intramolecular forces redistribute throughout a molecule energy initially localized in one of its parts. We undertook this quasiclassical trajectory study to determine the nature of intramolecular vibrational redistribution (IVR) in methyl hydroperoxide, CH₃OOH and how energy flow influences the rate of unimolecular decomposition. Other work reported in this volume describes the experimental capabilities being developed at the Combustion Research Facility for studying ultrafast processes.

The potential energy surface we constructed for our calculations is an empirical, anharmonic valence force field calibrated using available information for CH₃OOH and for other molecules that contain similar functional groups. The analytical form of the potential is

$$V_{\text{total}} = V_{\text{stretch}} + V_{\text{bend}} + V_{\text{torsion}}$$

where

$$V_{\text{stretch}} = \sum D_i [1 - \exp(-\alpha_i(r_i - r_i^0))]^2,$$

$$V_{\text{bend}} = 0.5 \sum K_i (\theta_i - \theta_i^0)^2, \text{ and}$$

$$V_{\text{torsion}} = \sum a_i [1 - \cos(ip)].$$

The equilibrium geometry is that given by Bair and Goddard.¹ Table I displays the bond-dissociation energies D_i , equilibrium bond lengths r_i^0 , and stretching parameters α_i of the Morse potentials used in the calculations. We took bending force constants for

the HCH, HCO, and COO angles, θ_i , from dimethyl peroxide, and the OOH force constant is from hydrogen peroxide. The torsion potential for the dihedral twisting motion around the O-O bond, ϕ , is a truncated Fourier series with $a_1 = -7.53$, $a_2 = -2.94$, and $a_3 = -0.37$ in kcal/mol. The CH₃ group undergoes free rotation about the C-O bond. We account for the fact that the COO and OOH bending force constants decrease to zero as the O-O separation increases to large values through multiplication of the appropriate terms in V_{bend} by a switching function varying smoothly from one to zero.² A normal-mode analysis of our potential performed using analytical second derivatives gave good agreement with the vibrational frequencies suggested by Vedenyev *et al.*³

Our primary interest is in the dynamics of CH₃OOH molecules that initially contain more energy in either a C-H bond or the O-H bond than is required to break the O-O bond. We determined the behavior of such molecules by integrating the classical equations of motion using a fourth-order Runge-Kutta-Gill routine with a fixed step size of 2.446×10^{-16} s. Initial conditions were assigned as described by Bintz, Thompson, and Brady.² For each set of initial conditions, we computed ensembles of 20 trajectories. Trajectories were integrated up to 1 ps for studying IVR and up to 5 ps (or until dissociation occurred) for determining dissociation rates.

Table I
Morse-Potential Parameters of the Bonds in CH₃OOH

Bond	D_i (kcal/mol)	r_i^0 (Å)	α_i (Å ⁻¹)
C-H	94	1.111	2.079
O-H	88	0.967	2.478
O-O	47	1.452	2.512
C-O	69	1.446	1.820

[†]Journal of Chemical Physics, submitted (1988).

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Figure 1 presents results for CH_3OOH in which either a C-H bond was initially excited to $v_{\text{CH}} = 12$ at a total energy, including zero-point energy, of 105.1 kcal/mol or the O-H bond was excited to $v_{\text{OH}} = 10$ at 102.5 kcal/mol. Separability of the energies in the internal coordinates was assumed in generating the data for the ensemble averages shown in the figure. The top left frame (for CH excitation) or the top right frame (for OH excitation) shows the energy in the initially excited mode as a function of time. The other frames illustrate the excitation of the modes into which the energy flows as time progresses. Although the total energy is nearly the same for the two cases shown, its flow is quite different. CH excitation decays within about 0.2 ps, and most of the energy flows into the bends of the CH_3 group. OH excitation requires about twice as long to decay, and little of it reaches the CH_3 group on the

Figure 1. Plots of the time evolution of the average vibrational energy in the modes of methyl hydroperoxide for initial excitation to $v_{\text{CH}} = 12$ (curves without arrows, left ordinate) and $v_{\text{OH}} = 10$ (curves with arrows, right ordinate). The modes are CH stretch, OH stretch, CH stretch, OOH bend, CH stretch, COO bend, total CH_3 bending, OO stretch, COOH torsion, CO stretch.

time scale of the calculation. Extensive calculations at several initial excitations show that, for our surface, energy flows directly from the excited mode only to nearby modes. The rate at which it does so depends on whether there exists a mechanical resonance between the donor and acceptor modes. Energy transfer is rapid when the ratio of the instantaneous vibrational frequencies of the donor and acceptor modes is approximately equal to the quotient of two small integers.

To determine whether the initial location of vibrational excitation influences the rate of unimolecular decomposition, we calculated the rate of O-O bond rupture for $v_{\text{CH}} = 12$ and for $v_{\text{OH}} = 10$, states at about 104 kcal/mol total energy. Dissociation was assumed to have occurred when the O-O bond length exceeded 5 Å. The rate constant k was taken to be the best-fit slope of a plot of $\ln(N_i/N_0)$ versus time, where N_0 and N_i are the number of trajectories not exhibiting dissociation initially and at time t , respectively. For $v_{\text{CH}} = 12$, $k = 0.18 \text{ ps}^{-1}$, and for $v_{\text{OH}} = 10$, $k = 0.35 \text{ ps}^{-1}$. Even though the rate constant for dissociation is much smaller than the rate constant for decay of initial excitation, it is almost twice as great when the excitation initially resides in the O-H bond. This suggests that statistical theories are not adequate for predicting rates of unimolecular reactions in selectively excited molecules like CH_3OOH and that we need a better understanding of the dynamics of ultrafast processes.

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Photofragment Imaging: The 266-nm Photodissociation of $\text{CD}_3\text{I}^\dagger$

We have used photofragment imaging techniques to study the internal-state and velocity distributions as well as the angular momentum alignment of methyl fragments following photodissociation of CD_3I molecules by 266-nm radiation.

D. W. Chandler, J. W. Thoman, Jr.,* M. H. M. Janssen,** S. Stolte,** and D. H. Parker***

Photofragment imaging is used to study the internal-state and velocity distributions of methyl fragments following photodissociation of CD_3I molecules by 266-nm radiation. The methyl fragments are state-selectively ionized via 2 + 1 resonance-enhanced multiphoton ionization (REMPI) through the $3p_z$ Rydberg state. The photofragment imaging technique,^{1,2} which records the entire velocity distribution for the state-selectively ionized fragment, allows us to record the velocity distribution of the ionized photofragments with a single pulse. Because the methyl fragment is state-selectively ionized by the REMPI process and the parent methyl iodide molecule is cooled in a molecular beam, the velocity of the ion mirrors the internal state distribution of the iodine atom born in coincidence with the selected state of the methyl. For a selected state of the methyl radical, two velocities are seen. The faster fragments are born in coincidence with ground-state iodine, $\text{I}(^2\text{P}_{3/2})$, and the slower fragments are born in coincidence with excited-state iodine, $\text{I}(^2\text{P}_{1/2})$. The intensity ratio of fast to slow methyl fragments is then unique to each internal state of the methyl fragment and is used to help assign the methyl REMPI spectrum.

By scanning the frequency of the ionization laser while detecting ions of all velocities, the rotationally resolved 0_0^0 band of the CD_3 spectrum shown in Figure 1 is recorded. From analysis of this spectrum, we find that the K quantum number is nearly conserved (i.e., spinning around the top axis) upon dissociation and that, on average, 3 units of tumbling angular momentum are found in the fragment after the dissociation.

Setting the ionization laser's wavelength resonant with a transition in CD_3 results in an image on the ion-detector screen. By recording images for various transitions, we determine the $\text{I}(^2\text{P}_{1/2})$ to

$\text{I}(^2\text{P}_{3/2})$ ratio for each ionized state of the methyl fragment. This is illustrated with the images shown in Figure 1, which displays images from two different band systems. The spectrum is of CD_3 in the region of the 0_0^0 band. This origin band overlaps the 1_1^1 band system. The Q-branch bandhead of the band 1_1^1 is designated in Figure 1. Images taken at the Q-branch bandhead of the two transitions show distinctly different branching ratios between the $\text{I}(^2\text{P}_{1/2})$ and $\text{I}(^2\text{P}_{3/2})$ exit channels.

Figure 1. Experimental and calculated 2+1 resonance-enhanced multiphoton ionization spectra of CD_3 in the region of the 0_0^0 band (left image) of the $^3p_z(^4\text{A}''_1) \leftarrow \bar{X}(^2\text{A}''_1)$ electronic transition following photolysis of CD_3I with 266-nm radiation while recording both slow and fast methyl radicals. The images at the top of the figure are taken with the ionization laser tuned to the indicated features. The image at the right, showing the two pronounced rings, is taken while resonant with a transition, the 1_1^1 band, originating from the first excited vibrational level of the C-D stretching mode of the CD_3 .

[†]Chem. Phys. Lett. **156**,151 (1988).

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By determining the dependence of the intensity of the REMPI signal on the polarization of the ionization-laser beam relative to that of the dissociation-laser beam, we can learn about the alignment of the angular momentum vector of the fragment. The top two images in Figure 2 show the intensity of the spatial distribution of ions detected with different polarizations of the REMPI-laser beam relative to the photolysis beam's polarization. The top of Figure 2 shows the image taken with both laser beams polarized parallel to the ordinate of the image. The middle image shows the image taken when the photolysis-laser beam is polarized as in the top image but the ionization-laser beam is polarized perpendicular to the plane of the image. The bottom image is the difference between the upper two images. The top two images are not identical because the photolysis event produces fragments whose angular momentum vectors, J , are aligned in the laboratory reference frame and are therefore sensitive to the polarization of the ionization-laser beam.

The J alignment is typically defined in terms of a Legendre expansion where the coefficients of the expansion, A_k , are the moments of the distribution. The sharper the distribution, the higher number of moments required to define it. The photodissociation results from absorption of a single photon by the parent molecule (leading to a $\cos^2\theta$ velocity distribution), the total integrated REMPI signal gives information about only the lowest two moments: the A_0 (monopole) and the A_2 (quadrupole) terms. Because the imaging technique allows us to monitor individual velocity groups, we are able to eliminate the averaging of the REMPI signal induced by the original $\cos^2\theta$ absorption of the photodissociation-laser beam.

This ability to observe a single velocity group allows us to determine higher-order moments of the product angular-momentum distribution from the angular and polarization dependence of the REMPI signal than would otherwise be possible. Because we use a two-photon transition in the REMPI process in addition to the two previously mentioned moments, we can also determine the A_4 (hexadecapole) moment of the angular-momentum distribution. To determine experimentally the distribution of J , we analyze the dependence of the intensity at the peak of the image on the angle between the polarization vectors of the laser beams.

By modeling CD_3I as a pseudotriatomic (I-C-D_3), which is fragmented in a sudden photodissociation event, the laboratory frame measurements of the alignment moments can be related to the I-C-D_3 bend angle at the moment of dissociation. These measurements will be compared to the expected bend angle given by the zero-point bend for the appropriate mode in the parent CD_3I molecule.

Figure 2. CD_3 images following the 266-nm photolysis of CD_3I . The top two images are taken while the frequency of the ionization laser is fixed at 333.2 nm, the $0(5)$ transition of the 0_0^0 band of the 3P_1 ($^2A''_1$) $\leftarrow$ x ($^2A''_2$) electronic transition of CD_3 . For the top two images, the polarization of the photolysis laser is held fixed with polarization parallel to the ordinate of the image and the ionization laser polarization is rotated from parallel to the ordinate (top image, Fig. 2a) to perpendicular to the plane of the image (middle image, Fig. 2b). The difference in the pictures is shown in the bottom panel (Fig. 2c); note the scale change between the images. The intensity profile taken vertically through the center of the image is shown superimposed on each image. If there were no correlation between the velocity of the fragments and the alignment of the molecule's angular-momentum vector, the images would subtract to zero.

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Atomic, Molecular, and Particulate Emission from Laser-Vaporized Carbon[†]

We have performed optical emission studies on the species generated by the laser vaporization of graphite into a pulsed helium flow. The spectra are comprised of structured emission from atomic and diatomic carbon and continua due to the incandescence of hot carbon particles.

E. A. Rohlfling

In recent years, there has been a great deal of interest in the physical and chemical properties of gas-phase atomic clusters in the size range of one to hundreds of atoms. On a basic level, there is a desire to understand the unique size-dependent properties of these species and the trend from atomic to bulk properties as size increases. The practical impetus for cluster research stems from the development of new experimental techniques for the generation of clusters. The most powerful of these techniques is one in which a laser is used to vaporize the element of interest in the throat of a supersonic nozzle expansion. Cluster formation occurs as the laser-induced plasma plume is cooled and the vapor condenses; subsequent free-jet expansion into vacuum creates cold, isolated clusters that can be probed using a variety of techniques, such as laser-induced fluorescence, resonantly enhanced multiphoton ionization, and time-of-flight mass spectrometry.

Of all the elements for which gas-phase clusters have been produced, perhaps none has evoked more interest than carbon. However, despite the growing number of researchers that have used laser vaporization of graphite in the throat of a nozzle expansion to produce carbon clusters,^{1,2} we still lack a detailed knowledge of how these species are formed in such a source. As part of a program to investigate the spectroscopy of small carbon clusters and to assess the relation of larger carbon clusters to the formation of soot in combustion, we have performed two types of studies on the laser-vaporization source: (1) direct, vaporization-laser-induced emission with short flow channels (i.e., the channel from the vaporization point to the free-jet expansion) and (2) laser-induced emission on species that are formed using a long flow channel; these conditions are similar to those typically used to produce carbon-cluster beams.

With short flow channels, the emission at short downstream distances is dominated by atomic carbon lines and three band systems of C_2 : $d^3\Pi_g-a^3\Pi_u$ (Swan), $C^1\Pi_u-A^1\Pi_u$ (Deslandres-d'Azambuja), and $D^1\Sigma_u^+-X^1\Sigma_g^+$ (Mulliken). A survey spectrum of these bands is shown in Figure 1. Partially rotationally resolved spectra of the $\Delta v=-1$ Swan bands are analyzed using a band contour approach to obtain rotational temperatures ($T_{rot} \sim 1000$ K) and rough vibrational distributions for C_2 $d^3\Pi_g$. The high nascent vibrational temperature ($T_{vib} \sim 10,000$ K) is consistent with a dissociative mechanism for the formation of C_2 . Since all the structured emission can be accounted for by C and C_2 , our data shows no evidence of transitions attributable to larger carbon clusters.

The direct emission spectrum from the short-channel source becomes a weaker, structureless continuum when viewed at long downstream distances. Similar, more intense long-lived continua are induced by a low-fluence laser at 266, 355, or 532 nm when it crosses the expansion emanating from a source with a long flow channel. When excited close

Figure 1. Low-resolution (0.88 nm FWHM) survey spectrum of the emission observed 0.4 cm downstream of the carbon-cluster source operated with a short-flow channel. Atomic and diatomic carbon transitions are indicated.

[†]J. Chem. Phys. **89**, 6103 (1988).

to the nozzle, the laser-induced emission is readily visible to the naked eye and illuminates the free-jet expansion for 4-5 cm. Two examples of laser-induced continua are shown in Figure 2. We attribute these continua to the incandescence of hot carbon particles and fit them to a model in which the Planck blackbody function is modified by the particle emissivity. Size-dependence enters through the Mie calculation of particle emissivity as a function of particle size and emission wavelength. We find that the emission continua give accurate measures of the

Figure 2. Continuum emission from carbon particles produced by the long-channel source and heated by a 266-nm laser ($\sim 40 \text{ mJ/cm}^2$). Top panel: Heated and observed at 8.6 cm downstream, $T=3800\text{--}4000 \text{ K}$. Lower panel: Heated at 0.4 cm downstream and observed $42 \mu\text{s}$ later at 8.6 cm downstream, $T=2500\text{--}2900 \text{ K}$. The smooth curves are fits to the data using the particle blackbody emission model; the spectra are normalized to the fitted maxima.

particle temperatures and reveal that in the laser-induced emission experiments the particles are readily heated to the vaporization point of carbon, $T=3800\text{--}4000 \text{ K}$ (Figure 2, top panel). When particle excitation is performed at the nozzle orifice and the emission is detected 8.6 cm downstream, the particle temperature is found to be $T=2500\text{--}2900 \text{ K}$ (Figure 2, lower panel). This provides a measure of the radiative cooling that occurs in the first $42 \mu\text{s}$ after the laser pulse.

The extraction of particle size from the wavelength-resolved emission spectra is difficult because the wavelength dependence of the particle emissivity is not a strong function of particle size in the visible and infrared (i.e., near the Rayleigh limit) where most of the emission is observed. Particulate emission is sensitive to size in the ultraviolet, but in this region there is a large uncertainty in the complex index of refraction for carbon particles, data that is necessary for the Mie calculations. Assuming a single particle size and using the best values available for the complex index of refraction for soot particles gives particle radii of $\sim 100 \text{ nm}$ and $\sim 60 \text{ nm}$ for the long and short flow channels, respectively. Despite the systematic uncertainty in particle size, these data provide the first direct evidence that large carbon particles are produced in a laser-vaporization cluster source. A reasonable mechanism for the growth of such particles is simply the condensation of the laser-induced vaporization plume in the flow channel.

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Laser-Induced Fluorescence Spectroscopy of Jet-Cooled C_3

We have obtained laser-induced fluorescence spectra of a new band system of C_3 under jet-cooled conditions. Dispersed fluorescence spectra map the vibrational energy levels of the ground state.

E. A. Rohlfiing

Carbon clusters have been the subject of intense research activity in recent years because of their unique properties and because of their potential importance in combustion and astrophysical phenomena. Nonetheless, spectroscopic data for carbon clusters is largely lacking; no gas-phase spectra have been reported for any cluster larger than C_3 . Interestingly enough, C_3 was one of the few species that was detected in space before it was observed in the laboratory. The 405-nm band group was observed by Huggins¹ in 1881 in one of the first spectroscopic studies of comets. A complete laboratory study of this system was made by Gausset *et al.*,² they assigned the 405-nm transition as $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ in which both ground and excited states are linear. Very recently, Morse *et al.*³ have found a new band system of C_3 in the 266-302 nm region using mass-selective resonant, two-photon ionization. The vibronic structure in this spectrum is exceedingly complex and has not been assigned; rotationally resolved spectra show that most bands have Σ_g^+ vibronic symmetry. In this article, we describe our preliminary work on this new band system of C_3 using laser-induced fluorescence (LIF).

We produce C_3 by laser vaporization of a graphite target rod inside the throat of a nozzle during a pulsed supersonic expansion of helium carrier gas. The 532-nm laser conditions are mild (<0.5 J/cm² in a 6-7 ns pulse) and produce C_3 via thermal vaporization without extensive plasma formation. The C_3 /helium free-jet expansion is crossed at a distance of 8-15 nozzle diameters downstream by a frequency-doubled dye laser that excites the C_3 fluorescence. For excitation scans, the fluorescence is imaged through a bandpass or solar-blind filter onto a photomultiplier tube. For dispersed fluorescence studies, the excitation laser excites a specific ro-vibrational line and the fluorescence is imaged onto the entrance slit of a 0.75-m spectrometer. The dispersed spectrum is detected at the spectrometer exit with 0.07-nm resolution by an optical multichannel analyzer.

The rotationally resolved LIF excitation scan of the 33,147-cm⁻¹ band of C_3 is shown in Figure 1. The absence of a Q branch immediately leads to the assignment of this band as one of $\Sigma_u^+ - \Sigma_g^+$ vibronic symmetry. Only even-numbered P and R lines are seen for the $^{12}C_3$ molecule because ^{12}C has a nuclear spin of zero and thus only even rotational levels are allowed in the $^1\Sigma_g^+$ ground state. By performing combination differences on the observed R and P lines, we determine the upper and lower rotational constants as: $B' = 0.3923 \pm 0.0033$ and $B'' = 0.4306 \pm 0.0013$. The B'' value is in excellent agreement with the known value ($B'' = 0.4305$) for the lowest vibrational state in the ground state.² Similar analyses have been performed for ten other vibronic bands and, with one exception, all these bands arise from cold C_3 . As discussed by Morse *et al.*,³ C_3 has no electronic states in this spectral region that have dipole-allowed transitions from the ground state. However, several states can borrow oscillator strength from dipole-allowed states ($^1\Sigma_u^+$ or $^1\Pi_u$) through vibronic coupling.

The dispersed fluorescence spectrum obtained by exciting the P(2) line of the 33,595-cm⁻¹

Figure 1. Rotationally resolved LIF excitation spectrum of the 33147-cm⁻¹ band of jet-cooled C_3 . R and P branch assignments are labeled.

band is shown in Figure 2. This and the ten other spectra that we have obtained are remarkable in that they extend to energies as high as $17,000\text{ cm}^{-1}$. These data provide the first glimpses of the vibrational structure of C_3 at high energies and should allow a greatly improved determination of the ground-state potential-energy surface. In this regard, C_3 is unique because of its extreme floppiness; the frequency of the bending fundamental, ν_2 , is $\sim 63\text{ cm}^{-1}$. At energies below 5000 cm^{-1} , our spectra can be assigned in the usual normal mode notation (ν_1, ν_2, ν_3) where the three quantum numbers label the symmetric stretch, bend, and antisymmetric stretch motions, respectively. Such assignments are made for the $(0, \nu_2, 0)$ and $(0, \nu_2, 1)$ progressions in Figure 2. This type of structure is typical; for each combination of ν_1 and ν_3 , there is a progression in the low-frequency-bending mode. Since the excited state has Σ_u vibronic symmetry, transitions are allowed to ground-state vibrational levels of Σ_g or Π_g symmetry. The former occur only for even values

Figure 2. The low-energy region of the dispersed fluorescence spectrum obtained from excitation of the $P(2)$ line of the $33,595\text{-cm}^{-1}$ band of jet-cooled C_3 . Ground-state vibrational assignments for the pure bending progression $(0, \nu_2, 0)$ and the antisymmetric stretch-bend progression $(0, \nu_2, 1)$ are shown.

of ν_2 and ν_3 ; the latter occur only when ν_2 and ν_3 are both odd. The intensity of the $(0, \nu_2, 1)$ progression identifies the nature of the vibronic coupling for this transition. One of the electronic states in the ultraviolet region is a ${}^1\Pi_g$ state that can couple to the strongly allowed ${}^1\Pi_u$ state of the 405-nm band group through ν_3 (Σ_u symmetry).

We are just beginning to analyze the dispersed fluorescence spectra. At low energies, the conventional normal-mode formula for the vibrational term energy can be applied. However, the anharmonic terms that couple the bend to the stretches are very large. We find that symmetric stretching dramatically increases the effective bending frequency, while antisymmetric stretching greatly reduces it. This is manifested in Figure 2; the spacing between adjacent members of the $(0, \nu_2, 0)$ progression is clearly larger than that in the $(0, \nu_2, 1)$ progression. An extrapolation of this strong coupling to higher energies produces meaningless results. The high-energy regions are very rich because of the high density of vibrational states that result from the low bending frequency. A more sophisticated analysis, making use of a high-level *ab initio* potential energy surface and semiclassical dynamics, may be required to understand the vibrational structure of this most interesting molecule.

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Semiclassical Calculation of Vibrational Spectra Using *Ab Initio* Quantum Chemical Energies: H₂O and NCO

The vibrational spectra of several important molecules have been investigated by a recently developed theoretical method and the implications of this method to dynamics, scattering theory, and chaos are discussed. An extension of the method to the treatment of the dynamics for much larger systems using accurate quantum chemical methods is proposed.

M. L. Koszykowski and C. M. Rohlfing

The semiclassical calculation of vibrational energy levels has been a topic of considerable research interest for the past decade. These studies have ranged from the development of methods for predicting accurate vibrational spectra to fundamental questions about energy redistribution, chaos, and reaction-rate theory. All dynamical methods begin by choosing a potential energy surface, which is often only a simple model or a semi-empirical fit with parameters obtained from limited spectroscopic data. This has reduced the predictive value of such studies, especially at higher energies where classical chaos becomes important. In particular, chaos has been demonstrated to be extremely sensitive to high-order derivatives in the potential surface, with physically similar surfaces exhibiting vastly different regions of chaotic motion.

These limitations have motivated the development of a new method where potential points are used directly without the intermediate step of fitting to an analytic function. This approach uses a spline under tension to locally develop an analytic representation of the surface which is smooth and has continuous derivatives. The initial testing of the method on O₃ has been reported previously. Two additional molecules have since been considered and the method extended to highly excited vibrational states. The results for H₂O and NCO, a linear radical (Renner-Teller) species, are presented here.

H₂O is a major combustion product as well as a species which has been studied theoretically using spectroscopically derived potentials. NCO is an important prototype since spectroscopic detection of intermediate radicals in model flames is essential for validating fundamental chemical reaction models. That is, identification of radicals such as NCO can help elucidate the reaction mechanisms of nitramine decomposition and combustion. Theoretical techniques can provide the spectroscopic information necessary for the detection of postulated radicals when no experimental data currently exist.

The quantum chemical calculations of the potential energy surfaces for H₂O and NCO near the bottom of the well were performed as follows: for H₂O, a grid of points corresponding to bond lengths from 0.66 - 1.50 Å and bond angles from 98 - 108° was chosen. For NCO, a grid of points corresponding to bond lengths from 1.13 - 1.26 Å and bond angles from 150 - 180° was chosen. Electron correlation was included by first computing a full-valence, complete-active-space (CAS) self-consistent-field wave function and then performing a contracted configuration-interaction calculation from selected CAS references. An atomic natural orbital basis set was employed to calculate total energies for each geometry in C_s symmetry.

Classical trajectories were run on the grid of computed potential energy points. The transition frequencies are obtained by calculating the relevant correlation function; from linear response theory, the Fourier transform of the time correlation function is the spectrum. The splitting between the vibrational levels of the Renner-Teller states of NCO, 49 cm⁻¹, was derived using the standard primitive semiclassical treatment. The fundamental frequencies and relative intensities for H₂O and NCO are listed in Tables I and II.

For highly excited vibrational states of H₂O, an extensive survey of points in four-dimensional phase space was run to seek regions of classical chaos. For energies up to 60% of the bond strength, no chaos was observed. This result is very encouraging since experimentally no indication of intra-

Table I
Vibrational Frequencies for H₂O

Transition	Theor. Harmonic Frequency	Theor. Frequency	Expt. Frequency
ν_1	3733	3704	3657
ν_2	3809	3789	3756

molecular relaxation in the water molecule at these energies is observed. Previous studies of water on empirical surfaces show classical chaos for energies well below 50% of the bond energy, even though the potentials mimic the vibrational spectroscopy of the lower states extremely well and lead to the correct energetics for reactions.

The applicability of this method to molecular dynamics is being investigated. Incorporating gradients into these calculations will enable the direct following of a trajectory, and therefore the need for a complete grid of points will be eliminated. This will allow the treatment of much larger molecules than otherwise could be afforded computationally.

Table II
Vibrational Frequencies and Relative Intensities for NCO

Transition	Theor. Relative Intensity	Theor. Harmonic Frequency	Theor. Frequency	Expt. Frequency
ν_1	0.9	1387	1306	1270
ν_2	0.4	581	509	535

Infrared Spectroscopy of Combustion Intermediates

We have obtained a high-resolution infrared spectrum of HNCO, an important combustion intermediate and pollution-control additive.

L. R. Thorne and F. P. Tully

We are presently focusing our efforts on determining combustion mechanisms for energetic nitramines by characterizing and modeling the flame structure of related low-pressure flames. Since the parent nitramine molecule fragments very early in the combustion process, the overall combustion mechanism of a particular nitramine may be divided into "submechanisms" for the individual fragments. We are currently investigating the combustion of HCN with NO_2 and the closely related system, $\text{C}_2\text{N}_2 - \text{NO}_2$, which is simpler than the $\text{HCN} - \text{NO}_2$ system because of the absence of hydrogen.

An important part of determining combustion mechanisms involves detecting chemically reactive intermediate species. Isocyanate radical, NCO , is an important intermediate in our current model for low-pressure $\text{C}_2\text{N}_2 - \text{NO}_2$ flames and we anticipate that isocyanic acid, HNCO , will prove to be an important intermediate in $\text{HCN} - \text{NO}_2$ flames. Furthermore, HNCO occurs in C. F. Melius' model for nitramine steady-state flames, i.e., HNCO is important in Region B of the secondary flame zone of an RDX (a six-membered ring nitramine) flame. Thus, detecting HNCO in flames will aid in establishing the combustion mechanism in $\text{HCN} - \text{NO}_2$ and RDX flames. In addition, HNCO is the active ingredient in the RAPRENOx² process for the reduction of NO emission from combustion systems.

The newest of our combustion diagnostic tools for low-pressure flames is an infrared absorption spectrometer (BOMEM, DA3.002) fitted with a low-pressure burner in the sample compartment. Infrared absorption spectra are obtained as a function of height above the burner surface in order to develop a concentration profile for various species of interest. The BOMEM spectrometer provides exceptional resolution which is an invaluable aid in avoiding the confusion associated with overlapping absorption lines from the complex mixture of gases characterizing most combustion processes. A necessary prerequisite to the flame studies is to obtain reference spectra of species whose profiles are to be measured. In this regard, we have obtained the infrared spectrum of the ν_1 band (N-H stretching mode) of HNCO , which is shown in Figure 1.

HNCO was synthesized by vaporizing, then pyrolyzing, cyanuric acid $(\text{HOCN})_3$ in a two-stage vacuum furnace. Solid cyanuric acid was vaporized in the first stage held at 325°C and then pyrolyzed to produce HNCO in the second stage, which was held at 450°C . The effluent from the furnace was trapped at 77 K in a liquid nitrogen trap. The product HNCO was purified with flowing argon while holding the product at -70°C using a dry ice-acetone bath. This reduced the HCN and CO_2 concentrations in the final product.

The first detailed study of the infrared spectrum of HNCO was reported by Herzberg and Reid.³ Figure 1 shows the ν_1 band of HNCO at 0.8 cm^{-1} resolution. This is a hybrid band having the characteristics of a parallel ($\parallel$) band and a perpendicular ($\perp$) band superimposed on one another. In this case, the $\perp$ -component (characterized by a series of sharp, line-like Q-branch transitions) is stronger than the $\parallel$ -component (characterized by a broad double maximum, i.e., P- and R-branches). The $^1\text{Q}_1$ -, $^1\text{Q}_3$ -, $^1\text{Q}_5$ -, $^3\text{Q}_2$ -, $^3\text{Q}_4$ -branches are split by a perturbation of the $K = 2$ and $K = 4$ in levels in the upper vibra-

tional state. The perturbation extends over a considerable range of J values and follows the selection rule $\Delta K = 0$.²

We have also obtained the spectra of the ν_1 band at high resolution. Prior to this study, the highest resolution spectrum reported in the literature is that of Carlotti *et al.*⁴ with a resolution of 0.25 cm^{-1} . Figure 2 shows only a small portion of the spectrum, the pQ_2 -branch, which was obtained at a resolution of 0.004 cm^{-1} , the spectrometer's highest resolution. At this resolution, the width of the observed lines is not

Figure 2. Transmission spectrum of pQ_2 branch of the ν_1 band of HNCO at high resolution (0.004 cm^{-1}). The branch is partially overlapped by transitions of the pP_2 -branch (indicated with arrows).

limited by the resolution of the spectrometer, but is dominated by Doppler and pressure broadening. The observed width (full width at half height) is 0.018 cm^{-1} , consistent with the experimental conditions (pressure = 5 torr, temperature = 298 K).

We are presently assigning the high resolution spectra of the ν_1 band to determine the spectroscopic constants, and in the near future we will use the reference spectra obtained at 0.1 cm^{-1} resolution to help determine the flame structure of the HCN - NO_2 low-pressure flame.

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Kinetic Study of the Reaction Between CN and O₂ from 295 to 710 K[†]

We have extended the highly precise laser photolysis/CW laser-induced fluorescence technique to the study of the reaction of CN with O₂. NCO forms as a direct product of the reaction.

J. L. Durant, Jr. and F. P. Tully

The laser photolysis/CW laser-induced fluorescence (LP/CW LIF) technique has proven to be a powerful tool for the precise measurement of absolute rate coefficients in OH-radical reactions. With the development of Exalite 392E, a new CW laser dye operating throughout the wavelength region 373 - 408 nm, the variety of free-radical reactions that may be studied using this technique has increased. This advance promotes investigation of reactions of the CN radical, a species important in both NO_x formation and destruction and in the combustion of energetic materials.

One CN-radical reaction of particular importance in combustion processes is that with molecular oxygen. Studies published prior to 1978 were well represented by the Arrhenius expression $k = 4.0 \times 10^{-11} \exp(-3.7 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. However, between 1983 and 1987, four laboratories reported room-temperature kinetic studies that favored rate coefficients up to a factor of three faster than an average of the older data.¹ During this same period, two shock-tube investigations determined high-temperature rate coefficients that are even smaller than the older low-temperature results.¹ These results suggest that both the reaction-rate coefficient and its temperature dependence are in doubt. We initiated this study to clarify the kinetics of the CN + O₂ → products reaction, which has three exothermic channels,

Channel (a) is expected to be the predominate channel, while channel (c) is considered highly unlikely.

Experiments were carried out in a low-pressure quartz cell, which could be heated resistively. Excimer-laser photolysis data of C₂N₂, which formed CN radicals, were obtained. The time dependence

of the CN concentration was then followed using CW laser-induced fluorescence.

Figure 1 displays a typical [CN] decay and demonstrates the extremely high signal-to-background ratio obtainable with this apparatus. The ability of the experiment to monitor precisely even small CN concentrations greatly enhances the range of initial conditions amenable to study. This freedom to vary the initial parameters serves as a diagnostic that makes potential kinetic interferences readily apparent. We varied the CN-precursor concentration, the photolysis-pulse energy and repetition rate, the probe dye-laser power, and the total reactor pressure over wide ranges and observed no significant effects on the measured rate coefficients.

Figure 1. Typical CN decay profile. [C₂N₂] = 2.5×10^{14} molecules/cm³, [O₂] = 9.1×10^{12} molecules/cm³, excimer flux = 0.45 mJ/cm². The line is a single-exponential fit to the data and includes a background contribution from scattered light.

[†]Chem. Phys. Lett. **154**, 568 (1988).

Our measured pseudo-first-order decay constants range from less than 100 s^{-1} to nearly 4000 s^{-1} . In the absence of added O_2 , CN disappears from the probed volume both by diffusion and by reaction with background impurities. Figure 2 shows a typical plot of the measured pseudo-first-order rate coefficient, k' , versus $[\text{O}_2]$ at one fixed temperature. The desired bimolecular reaction-rate coefficient, k , equals the slope of the least-squares straight line through the $([\text{O}_2], k')$ data points.

We collected data at seven temperatures over the range 295 - 710 K, and the resulting rate coefficients are plotted, as $\log k$ versus $1000/T$, in Figure 3. The assigned error limits principally reflect our estimate of systematic uncertainties, which we believe to be $\sim 5\%$ at the 95%-confidence level. The combination of extraordinarily precise [CN] profiles and careful calibration of mass-flow meters produces statistical uncertainties that are less than 1%. We compute a best-fit, two-parameter Arrhenius expression of $k(T) = (1.24 \pm 0.04) \times 10^{-11} \exp[(1630 \pm 100) \text{ J mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in which the stated error limits are 2σ values. While our results differ from older work, we are in extremely good agreement with three other studies that were carried out simultaneously with ours.

Figure 2. Plot of k' vs $[\text{O}_2]$ for $\text{CN} + \text{O}_2$ at 400 torr and 341 K. The line is the least-squares fit to the points.

We quantified the temporal evolution of NCO at room temperature. For these experiments, we first obtained the [CN]-decay profile, then scanned the dye laser to an NCO transition and switched the bandpass filter, finally measuring the [NCO]-growth profile. For each O_2 concentration, the [NCO]-growth rate is consistent with the [CN]-decay rate, proving that NCO forms directly in the $\text{CN} + \text{O}_2 \rightarrow$ products reaction. It should be noted that the NCO concentrations measured are not absolute, and cannot be easily related to CN concentrations. As a result, these observations are mute concerning the size of the $\text{NCO} + \text{O}$ product channel.

Our measurement of the reaction rate coefficient for the $\text{CN} + \text{O}_2 \rightarrow$ products is consistent with a picture of a radical-radical association reaction, with NCO being formed as a direct product of the reaction.

Figure 3: Arrhenius plot of our kinetic data for the $\text{CN} + \text{O}_2$ reaction (filled circles). Also plotted is an average of the pre-1978 data (dotted line) and the results of subsequent studies¹ (open symbols).

Reference:

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Kinetic Study of the Reactions of CN with Ethane and Propane

Absolute rate coefficients for the reactions of CN with ethane, propane, and five of their deuterated isotopes are determined over the temperature range 294 - 736 K. We derive site-specific rate coefficients for abstraction and characterize the primary- and secondary-site isotope effects for CN + alkane reactions.

W. P. Hess,* J. L. Durant, Jr., and F. P. Tully

The reactions of CN radicals are important in a variety of environments, ranging from astrophysics to NO_x formation and destruction in combustion. The CN radical reacts very rapidly with many compounds, and nearly gas-kinetic rate coefficients have been measured for its reactions with unsaturated hydrocarbons and some large alkanes at room temperature. Unfortunately, a better understanding of CN-radical reactivity is hampered by sparse experimental data.

Recently, we extended the laser photolysis/CW laser-induced-fluorescence technique to probe CN kinetics. We use this technique to determine rate coefficients for the reactions of CN with C_2H_6 (k_1), C_2D_6 (k_2), CH_3CD_3 (k_3), C_3H_8 (k_4), C_3D_8 (k_5), $\text{CH}_3\text{CD}_2\text{CH}_3$ (k_6), and $\text{CD}_3\text{CH}_2\text{CD}_3$ (k_7) from 294 to 736 K. The detailed kinetic measurements allow us to determine temperature-dependent, site-specific rate coefficients for the CN + propane reaction and to characterize the temperature dependence of the kinetic isotope effect for both primary- and secondary-site H-atom abstraction.

The experimental technique is a modification of the laser photolysis/CW laser-induced-fluorescence (LP/CWLIF) method developed for OH-radical reaction kinetics. CN radicals form following 193-nm, excimer-laser photolysis of C_2N_2 in a heatable quartz flow cell. The CN radical concentration is then probed by exciting the P(7) or the P(11) line in the (0,0) band of the CN ($\text{B} \leftarrow \text{X}$) transition with a CW dye laser operating near 388 nm.

The absolute rate coefficients for the reactions of CN with C_2H_6 (k_1), C_2D_6 (k_2), and CH_3CD_3 (k_3) at six temperatures between 294 and 725.5 K are plotted, as $\log k_i(T)$ versus $1000/T$, in Figure 1. All Arrhenius plots show smooth curvature that cannot be described with a simple two-parameter expression. The CN + ethane data may be fit to the modified Arrhenius expression $k_i(T) = AT^n \exp(-E/RT)$. The optimized best-fit representations

(displayed as the solid lines in Figure 1) are in the units $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_1(T) = 7.40 \times 10^{-15} T^{1.29} \exp(+512 \text{ cal mol}^{-1}/RT)$, $k_2(T) = 8.32 \times 10^{-16} T^{1.57} \exp(+460 \text{ cal mol}^{-1}/RT)$, and $k_3(T) = 1/2 (k_1(T) + k_2(T))$. The expression for $k_3(T)$ emphasizes the result that the reactivity of an abstraction site is not affected by the isotopic content of a neighboring site. The curved, upward sloping Arrhenius plots for the CN + ethane reactions imply that at least a small reaction barrier exists for these reactions. The kinetic isotope effect for CN + ethane, k_1/k_2 , is plotted, as $\log(k_1/k_2)$ versus $1000/T$, in Figure 2. The solid line, through the circle points, depicts the optimized fit of the data to the expression $k_1/k_2 = (1.30 \pm 0.03) \exp(1+277 \pm 18 \text{ cal mol}^{-1}/RT)$. A significant isotope effect exists over the entire temperature range investigated, with the value of k_1/k_2 falling from 2.07 at 294 K to 1.54 at 725.5 K.

Figure 1. Arrhenius plot of the kinetic data for the reactions $\text{CN} + \text{C}_2\text{H}_6$, $\bullet$; $\text{CN} + \text{C}_2\text{D}_6$, $\square$; $\text{CN} + \text{CH}_3\text{CD}_3$, $\blacktriangle$; $\text{CN} + \text{C}_3\text{H}_8$, $\circ$; $\text{CN} + \text{C}_3\text{D}_8$, $\diamond$; $\text{CN} + \text{CH}_3\text{CD}_2\text{CH}_3$, $\blacksquare$; and $\text{CN} + \text{CD}_3\text{CH}_2\text{CD}_3$, $\blacktriangle$. The dotted lines are fits to the data derived from the individual abstraction-site rate coefficients. The total experimental uncertainty is approximately 5%.

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Figure 2. Arrhenius plot of the kinetic isotope effect for primary site, $\circ$ —; and secondary site, $\square$ — abstraction by CN. The dotted and dashed lines correspond to primary- and secondary-site abstraction from alkanes by OH.

The absolute rate coefficients for the reactions of CN with the various isotopic propanes are depicted by the open data points and dotted lines in Figure 1. Although the CN + propane rate coefficients fit on a smooth curve, the data cannot be represented accurately even by a three-parameter expression. The rate coefficients for all four CN + propane reactions show little temperature dependence between 294 and 475 K, but increase discernibly above 500 K.

We may determine site-specific rate coefficients from the CN + propane rate data, $k_4 - k_7$, and the primary-site kinetic isotope effect, k_1/k_2 . The results are described by the three-parameter expressions, $k_{11}^p(T) = 3.58 \times 10^{-15} T^{1.14} \exp(+566 \text{ cal mol}^{-1}/RT)$, $k_{11}^p(T) = 2.63 \times 10^{-16} T^{1.47} \exp(+568 \text{ cal mol}^{-1}/RT)$, $k_{11}^s(T) = 3.30 \times 10^{-13} T^{0.56} \exp(+649 \text{ cal mol}^{-1}/RT)$, and $k_{11}^s(T) = 2.96 \times 10^{-13} T^{0.52} \exp(+656 \text{ cal mol}^{-1}/RT)$, and are displayed in Figure 3. Here, $k_{11}^p(k_{11}^s)$ and $k_{11}^p(k_{11}^s)$ represent the rate coefficients per H- or D-atom for abstraction from individual primary- and secondary-sites in propane. We find that the rate coefficient for CN + secondary-site H-atoms decreases with increasing temperature, but that the rate coefficient for CN + primary-site H-atoms increases with increasing temperature.

Linear combinations of the site-specific rate coefficients produce six parameter expressions for each rate coefficient, k_4 , k_5 , k_6 , and k_7 . The dotted lines in Figure 1 represent these expressions. Near

room temperature, abstraction from secondary sites in propane is slightly favored; approximately 57% of the reaction proceeds through this channel. As the temperature is increased, the primary-site channel becomes favored, and this channel accounts for roughly 58% of the overall reactivity at 736 K.

It is useful to compare the kinetic isotope effect of CN + alkane reactions with the analogous OH + alkane reactions. In Figure 2, we plot the kinetic isotope effect for OH + primary C-H ($\Delta H_{\text{rxn}} = -20 \text{ kcal/mol}$) and OH + secondary C-H ($\Delta H_{\text{rxn}} = -23 \text{ kcal/mol}$). If we assume that the predominant product of the CN + alkane reactions is HCN, we find that this trend is continued for CN + primary C-H ($\Delta H_{\text{rxn}} = -26 \text{ kcal/mol}$) and CN + secondary C-H ($\Delta H_{\text{rxn}} = -29 \text{ kcal/mol}$). The magnitude and temperature dependence of the kinetic isotope effect, for the reactions of CN with primary- and secondary-site H-atoms, are consistent with an H-atom abstraction mechanism. The strength of this trend and the reaction thermochemistry argues strongly against a significant HNC product channel.

We have determined accurate rate coefficients for reactions of CN with ethane, propane, and five deuterated isotopes. The reactivity of each abstraction site is independent of the isotopic content of the neighboring site, and we extract site-specific reaction rate coefficients for CN + primary and secondary H- and D-atoms. The kinetic isotope effect for the reactions of CN with ethane and propane are consistent with an H-atom abstraction mechanism.

Figure 3. Arrhenius plot of the individual rate coefficients for primary- and secondary-site H- and D-atom abstraction by CN: k_{11}^p , $\square$ —; k_{11}^p , $\circ$ —; k_{11}^s , $\blacksquare$ —; and k_{11}^s , $\bullet$ —.

Hydrogen-Atom Abstraction from Methanol by OH[†]

Absolute rate coefficients for the reactions of OH with CH₃OH and CD₃OH are reported. The measured kinetic isotope effect yields insight into the branching ratio for H-atom abstraction from the methyl versus the hydroxyl site in methanol.

W. P. Hess* and E. P. Tully

Hydroxyl-radical reactions are extremely important in both atmospheric and combustion chemistries because OH is a dominant reactive species in hydrocarbon oxidation. Methanol reactivity impacts these chemistries because of the increasing use of clean-burning oxygenated fuels. This reaction is also of fundamental interest since two separate H-atom abstraction channels may contribute to the overall reactivity and the branching ratio for abstraction from the methyl versus the hydroxyl group will probably be strongly temperature dependent. In this report, we present determinations of the absolute rate coefficients for the reactions

and

The rate constants k_1 and k_2 are measured over the temperature range $293 \leq T \leq 866$ K at a pressure of 700 torr of helium buffer gas.

We perform all experiments using the laser photolysis/laser-induced fluorescence technique. OH is produced by the reaction of O(¹D₂) with H₂O following pulsed, 193-nm laser photolysis of N₂O. The subsequent OH kinetics are then probed, in real time, by laser-induced fluorescence. Because $[\text{OH}] \ll [\text{methanol}]$ in all reactive experiments, pseudo-first-order kinetic conditions exist and we obtain exponential "reaction-only" $[\text{OH}]$ dependences.

The absolute rate coefficients measured for reactions (1) and (2) are plotted, as $\log k_i(T)$ versus $1000/T$, in Figure 1. These Arrhenius plots of k_1 and k_2 show smooth upward curvature that is distinctly stronger for the reaction of OH with CD₃OH.

Because these measurements cannot be described adequately by a two-parameter Arrhenius equation, the data are fit to the three-parameter expression $k_i(T) = AT^n \exp(-E/RT)$ by a nonlinear least-squares analysis. The resultant best-fit representations, displayed as the solid lines in Figure 1, are, in the units $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_1(T) = 5.89 \times 10^{-20} T^{2.65} \exp(+883 \text{ cal mol}^{-1}/RT)$, and $k_2(T) = 1.28 \times 10^{-22} T^{3.48} \exp(+1275 \text{ cal mol}^{-1}/RT)$. At 294 K, our value of $k_1 = (9.34 \pm 0.41) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in good agreement with the majority of the literature values. However, the temperature dependence of k_1 measured here is quite different from that of the previous studies, and it provides a smooth transition from the low-temperature data to the high-temperature results.

Figure 1. Arrhenius plot of the OH + methanol reaction rate coefficients $\circ$, CH₃OH; Δ , CD₃OH. The solid lines plot the best fit of the data to the expression $k(T) = AT^n \exp(-E/RT)$.

[†]J. Phys. Chem. **93**, 1944 (1988).

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OH reacts with CD_3OH significantly more slowly than with CH_3OH over the entire 293-866 K temperature range investigated. At 293 K, we determine a rate constant of $4.35 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (2). Large primary kinetic isotope effects, which result from deuterium substitution at H-atom abstraction sites, are well known in $\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}$ reactions. The kinetic isotope effect for methanol, k_1/k_2 , displays an unusual temperature dependence that is plotted as $\log(k_1/k_2)$ versus $1000/T$ in Figure 2. The data break naturally into two regions at approximately $T = 625 \text{ K}$. Kinetic isotope effect, k_1/k_2 , varies exponentially with $1/T$ for $T \leq 625 \text{ K}$; a best-fit expression, $k_1/k_2(T) = (1.42 \pm 0.05) \exp[(+243 \pm 14) \text{ cal mol}^{-1}/RT]$, results from fitting the data using nonlinear least-squares analysis. At temperatures above 625 K, however, k_1/k_2 falls sharply below the extrapolation of this best-fit expression (Figure 2).

In earlier studies of the effects of deuterium substitution on $\text{OH} + \text{C}_2\text{H}_6$, C_3H_8 , and C_4H_{10} alkane reactivity, we show conclusively that the isotopic species in an "uninvolved" reactive site does not affect the reaction kinetics at a neighboring site. If we assume that this separation of reactivity may be extended to methanol, then

$$k_1 = k_{\text{H}} + k_{\text{OH}} \text{ and } k_2 = k_{\text{H}} + k_{\text{OD}} \quad (3).$$

Figure 2. The kinetic isotope effect, k_1/k_2 , as a function of $1000/T$ (K). The solid line is an exponential fit to the six low-temperature points.

At low temperatures, we would expect reactions (1) and (2) to be dominated by abstraction from the methyl group rather than the hydroxyl group, since the C-H bond strength (94 kcal mole⁻¹) is much smaller than the O-H bond strength (104 kcal mole⁻¹) in methanol. The sharp decrease in k_1/k_2 for temperatures above ~625 K may be interpreted as an increase in the relative importance of H-atom abstraction from the hydroxyl hydrogen in CH_3OH . While the branching ratio for reaction (1), $f = k_{\text{OH}} / (k_{\text{OH}} + k_{\text{CH}_3})$, cannot be quantitatively extracted from the limited isotopic data, we estimate that nearly half the reactivity proceeds through the $\text{H}_2\text{O} + \text{CH}_3\text{O}$ channel at our highest measurement temperature. Abstraction of the hydroxyl hydrogen in CH_3OH (and CD_3OH) by OH is likely to be a relatively high activation-energy process because of the large O-H bond energy. The onset of this reaction channel, above 625 K, is consistent with this conclusion and with the steep high-temperature dependence observed in this work for $k_1(T)$ and $k_2(T)$. The measured kinetic isotope effect supports a model in which H-atom abstraction from the methyl group dominates reactivity at low temperatures and H-atom abstraction from the hydroxyl hydrogen becomes important as $T \rightarrow 1000 \text{ K}$.

Catalytic Conversion of Alcohols to Alkenes by OH[†]

Kinetic and mechanistic studies of the gas-phase reactions between hydroxyl radicals and $\geq C_2$ -alcohols are described. Hydrogen-atom abstraction by OH from β -sites in alcohols produces HO-alkene intermediates that rapidly dissociate to OH + alkene at elevated temperatures. This reactive sequence constitutes a catalytic mechanism for the net transformation $C_nH_{2n+1}OH \rightarrow H_2O + C_nH_{2n}$.

W. P. Hess* and F. P. Tully

The reactions of OH with $\geq C_2$ -alcohols are critical steps in the combustion of alcohol fuels and additives. We report here our initial results on the reaction kinetics of OH with C_2 -, C_3 -, and C_4 -alcohols, and prove the existence of an efficient catalytic pathway for the gas-phase chemical conversion of alcohols to alkenes, $C_nH_{2n+1}OH \rightarrow H_2O + C_nH_{2n}$.

We performed all experiments using the laser photolysis/laser-induced fluorescence technique. OH formed following pulsed, 193-nm laser photolysis of alcohol/ N_2O / H_2O /helium gas mixtures. After reaction initiation, we measured time-resolved OH concentration profiles as functions of alcohol number density using continuous-wave, laser-induced fluorescence. Bimolecular rate coefficients, $k_i(T)$, were derived from the slope of the least-squares straight line through the ($[alcohol]$, decay constant) data points.

For each OH-alcohol reaction, the obtained Arrhenius plot was structured. This structure related directly to the temperature-dependent mechanistic of the reaction. In the OH-ethanol reaction, for example, H-atom abstraction by OH from the CH_3 -group produced CH_2CH_2OH , the same intermediate that formed in the OH + ethene addition reaction. In ongoing work on OH-ethene kinetics, we have shown that CH_2CH_2OH rapidly dissociated to form $C_2H_4 + OH$ at elevated temperatures. From the standpoint of the OH-ethanol reaction, CH_2CH_2OH dissociation forms C_2H_4 , regenerates OH, and slows the (monitored) OH disappearance rate due to H-atom abstraction from the methyl group in ethanol.

Figure 1 displays Arrhenius plots of our data for the related reactions $OH + C_2H_4 \rightarrow$ products

and $OH + CH_3CH_2OH \rightarrow$ products. The link between these reactions is their common intermediate, CH_2CH_2OH . OH reacts with ethanol by three channels:

Hydrogen-atom abstraction by OH from the CH_3 -group, channel (A), produces CH_2CH_2OH that, at elevated temperatures, eliminates OH to form C_2H_4 . This reactive sequence constitutes an OH-catalyzed mechanism for the gas-phase conversion $C_2H_5OH \rightarrow H_2O + C_2H_4$. Conversely, reaction via channels (B) and (C) produces radical isomers that would require an intramolecular H-atom migration prior to any decomposition into $C_2H_4 + OH$.

The branching ratio for reaction among channels (A), (B), and (C) will vary strongly with temperature. On the basis of bond strengths, one would expect $k(B) > k(A) > k(C)$ at low temperatures, with $k(A)$ and $k(C)$ growing in relative importance as the temperature increases. Figure 1(b) shows that the measured rate coefficients for the OH-ethanol reaction increase monotonically above $T = 650$ K. Above this temperature, CH_2CH_2OH dissociation is fast relative to the experimental time scale. Thus, to a first approximation, $k(A)$ describes the kinetics of ethene formation, and channel (A) produces no net OH removal. Since we monitor the OH disappearance rate, the measured $[OH]$ profiles above $T = 650$ K principally reflect the sum of reaction through channels (B) and (C). Experiments involving $^{18}OH + CH_3CH_2^{16}OH$ confirm this mechanistic interpretation.

The influence of HO-alkene decomposition on OH + alcohol kinetics is not limited to the radical species CH_2CH_2OH . OH-catalyzed conversion of

[†]Chem. Phys. Lett. **152**, 183 (1988).

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$\geq C_2$ -alcohols to alkenes is a general mechanism for all alcohols that have β -site hydrogen atoms available for abstraction. Figure 2 displays ^{16}OH and ^{18}OH concentration profiles measured for the reactions $^{16}\text{OH} + (\text{H}_3\text{C})_2\text{CH}^{16}\text{OH} \rightarrow \text{products}$ and $^{18}\text{OH} + (\text{H}_3\text{C})_2\text{CH}^{18}\text{OH} \rightarrow \text{products}$. The shapes of the decays are markedly different. In both cases, the initial

Figure 1. (a) Arrhenius plot for the reaction $\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{products}$. Low-temperature data points and solid line represent the kinetics of the high-pressure-limit addition reaction. The high-temperature data points and solid line describe the kinetics of the H-atom abstraction reaction. The dotted curve depicts the phenomenological OH disappearance rate as the recombination/dissociation reactions approach chemical equilibrium during the 1-50 millisecond of the experiment. Vertical dashed lines indicate the range of temperatures over which biexponential [OH] profiles are observed. (b) Arrhenius plot for the reaction between hydroxyl radical and ethanol: $\circ$, kinetic data for the reaction $^{16}\text{OH} + \text{C}_2\text{H}_5^{16}\text{OH} \rightarrow \text{products}$; ∇ , kinetic data for the reaction $^{18}\text{OH} + \text{C}_2\text{H}_5^{18}\text{OH} \rightarrow \text{products}$. The solid line is a smooth curve drawn through the circle points; the dotted line is the extrapolation to higher temperatures of the $k(T) = AT^n \exp(-E/RT)$ fit to the five lowest-temperature circle points. Vertical dashed lines indicate the temperature range over which $\text{CH}_3\text{CH}_2\text{OH}$ dissociates to $\text{OH} + \text{C}_2\text{H}_4$ during the observation period of the experiment. Error bars represent $\pm 2\sigma$ estimates of the total experimental uncertainty.

(fast) portion of the [OH] profile is determined by the total rate of reaction of hydroxyl radical with $(\text{H}_3\text{C})_2\text{CH}^{16}\text{OH}$. β -site hydrogen-atom abstraction forms the HO-alkene intermediate $\text{H}_3\text{CCH}^{(16)}\text{OHCH}_2$, that, at elevated temperatures, decomposes to ^{16}OH + propene. This catalytic conversion reactive sequence is responsible for the difference between the measured (biexponential) $[^{16}\text{OH}]$ and (single-exponential) $[^{18}\text{OH}]$ profiles. The fraction of OH-alcohol reactivity that proceeds through the catalytic (β -site) channel depends on the detailed molecular structure of the alcohol. Our results definitively show that OH-catalyzed conversion of $\geq C_2$ -alcohols to alkenes is an efficient reaction mechanism at elevated temperatures.

Figure 2. $[^{16}\text{OH}]$ and $[^{18}\text{OH}]$ profiles obtained in studies of hydroxyl-radical reactions with 2-propanol. Every third data point is plotted: $\square$, $^{16}\text{OH} + (\text{H}_3\text{C})_2\text{CH}^{16}\text{OH} \rightarrow \text{products}$, $T = 535 \text{ K}$, $P = 700 \text{ torr helium}$, $[\text{2-propanol}] = 4.064 \times 10^{13} \text{ molecule cm}^{-3}$; $\circ$, $^{18}\text{OH} + (\text{H}_3\text{C})_2\text{CH}^{18}\text{OH} \rightarrow \text{products}$, $T = 544 \text{ K}$, $P = 700 \text{ torr helium}$, $[\text{2-propanol}] = 3.952 \times 10^{13} \text{ molecule cm}^{-3}$. The solid line fits to the data are obtained using the reaction model described in .

Rich Flame Chemistry

Recent experiments and modeling show that we understand the chemical mechanism that governs stoichiometric acetylene/oxygen flames. We must refine our mechanism before we can understand how aromatic species are formed in rich flames burning aliphatic fuels.

J. V. Volponi, L. Durant, Jr., G. A. Fisk, R. J. Kee, and J. A. Miller

The mechanisms by which polycyclic aromatic hydrocarbons (PAH) and soot are formed in flames are not yet well understood, although some progress is being made. Particularly interesting from a chemical point of view is how aromatic compounds, leading to PAH, are formed in flames of aliphatic fuels. In order to understand this process better, we have begun to study the structure of low-pressure, rich ($1.0 < \phi < 2.0$) acetylene/oxygen flames. Using conventional probe-sampling techniques, we have measured the concentrations of the stable reactants and products (C_2H_2 , O_2 , CO , CO_2 , H_2 , H_2O), as well as that of diacetylene, a species commonly mentioned as a possible precursor to PAH and soot formation. These data are supplemented by spectroscopic measurements of temperature and of CH and OH concentrations. The comparison of this data with our model predictions leads to insight of the underlying reaction mechanism.

The concentrations of the stable- and radical-gas species formed in these flames are determined experimentally using a low-pressure flame apparatus. This system consists of a 9.7-cm-diameter, sintered, premixed, flat-flame burner housed in a vacuum chamber maintained at 25 torr. Stable flame-gas species are sampled through a quartz microprobe attached to a differentially pumped, quadrupole mass spectrometer operating in a chopped molecular beam mode. The OH and CH radical species are measured by laser-excitation spectroscopy (LES) using a frequency-doubled, excimer-pumped dye laser. Laser-excitation spectroscopy is also used to determine flame temperatures. Concentration and temperature profiles are obtained by translating the burner vertically relative to the microprobe or laser beam.

Figures 1 through 4 show comparisons of our experimental results with the predictions of the kinetic model developed in our laboratory. These comparisons, as well as others, indicate that the present kinetic model is extremely reliable up to an equivalence ratio of approximately 1.5. Under these conditions, the chemistry is dominated by the $O + C_2H_2$ reaction

and subsequent reactions of HCCO and CH_2 . Beginning at $\phi \approx 1.5$ and for richer flames, the model becomes increasingly unreliable. This corresponds to the increasing influence of the C_3 - and C_4 -hydrocarbon chemistry in the mechanism, even affecting the major species profiles. C_3 and C_4 species arise in the mechanism from reactions, such as

and the sequence

The latter comes into play when the flames become so rich that the $O + C_2H_2$ reaction begins to lose influence. The oxidation of the C_3 and C_4 species is the part of our mechanism that requires more attention.

Figure 1. Comparisons of model predictions with experiment for major species (C_2H_2 , O_2 , CO , H_2O) in the stoichiometric flame.

Figure 2. Comparison of model predictions with experiment for CO₂ in the stoichiometric flame.

Figure 4. Comparison of model predictions with experiment for C₄H₂ and CO₂ in the φ = 1.67 flame.

Figure 3. Comparison of model predictions with experiment for major species (C₂H₂, O₂, CO, H₂O) in the φ = 1.67 flame.

Pressure Effects in the Reaction of OH with CO

We have measured absolute rate coefficients for the reaction between OH and CO at 293 K over the pressure range 25-865 torr of helium. In contrast to previous studies, we find that the reaction rate coefficient depends weakly on helium pressure. This result removes a conceptual ambiguity concerning the mechanism of this critical reaction.

F. P. Tully

The reaction $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ is a critical process both in atmospheric and combustion chemistry. It is thought to proceed through formation of an energized $\text{HOCO}^\ddagger$ complex, and, for buffer gases N_2 , O_2 , CF_4 , and SF_6 , experimental OH-loss rates are found to increase as the buffer-gas pressure is raised. For helium and argon buffer gas, however, several authors have found the reaction to be independent of pressure. If collisional deactivation of $\text{HOCO}^\ddagger$ explains the pressure dependence of the reaction for the strong colliders, a similar, but perhaps weaker, dependence should exist for helium and argon buffer gases.

Using the laser photolysis/CW laser-induced fluorescence technique, we measured absolute rate coefficients for the reaction between OH and CO at 293 K as a function of helium buffer-gas pressure. Pseudofirst-order rate constants k' , corrected for the effects of OH diffusion, were determined as functions of $[\text{CO}]$ and $[\text{He}]$. Figure 1 plots $([\text{CO}], k')$ data at several helium buffer-gas pressures. Effective second-order rate coefficients, k , are computed as the slope of the least-squares straight line through the $([\text{CO}], k')$ data points.

Figure 1. Diffusion-corrected, pseudo-first-order rate constants, k' , as functions of CO concentration at selected helium buffer-gas pressures: $\square$ —, 25 torr; $\diamond$ —, 138 torr; $\triangle$ —, 400 torr; $\circ$ —, 750 torr. Lines through the data are least-squares best fits.

We find that k varies smoothly from 1.54×10^{-13} to $2.02 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the pressure range 25-865 torr of helium. Our data are listed in Table I and plotted in Figure 2. Clearly, the OH + CO reaction rate coefficient does depend on helium buffer-gas pressure. Not surprisingly, this dependence is weak, as $\text{HOCO}^\ddagger$ loses little energy per collision with helium. These precise kinetic measurements refute the earlier pressure-independent studies and remove a major conceptual ambiguity for this critical reaction. Attempts to model the obtained pressure dependence theoretically are underway.

Figure 2. Rate coefficient versus helium buffer gas pressure for the reaction between OH and CO at 293 K. Error limits indicate $\pm 2\sigma$ estimates of the total experimental uncertainty.

Section 4

This color-enhanced, high-resolution image of laser Rayleigh scattering from a plane through the centerline of an underexpanded jet reveals the complex structure of turbulent mixing layers.

1944-1945 lows

High resolution, planar laser imaging provides a wealth of information on the structure of turbulent mixing and reacting flows, where wide ranges of spatial scales exist. The color-enhanced image on the preceding page shows the structure of a supersonic, underexpanded jet. The apparatus used to obtain this image is diagrammed (above). The beam from a pulsed, doubled Nd:YAG laser is expanded into a narrow sheet to illuminate a plane through the centerline of a supersonic jet. Elastically scattered light from air molecules and from extremely fine nucleated water droplets is collected perpendicular to the laser sheet and imaged by a camera lens onto a solid-state CCD array. The CCD array is comprised of 384×576 pixels, with each pixel corresponding to 40×40 microns in the object plane. Spatial resolution in the third dimension is determined by the thickness of the laser sheet, which is 100 microns. The resulting high resolution image shows the shock pattern of the underexpanded jet and reveals the presence of vortical structures imbedded within the turbulent mixing layers. The growth of these vortical structures, which are similar

to those observed in subsonic turbulent mixing layers, is the primary mechanism for entrainment of reactants into turbulent flames. In supersonic combustion, the total time available for mixing and reaction is extremely short, on the order of 1 ms. Because molecular mixing is a prerequisite to chemical reaction, rapid mixing of reactants in turbulent shear layers is a critical process in supersonic combustion. Imaging experiments such as this are providing data on the structure of supersonic mixing layers and on the effects of compressibility and heat release on the spreading rate of supersonic flames.

Planar laser imaging techniques have also been applied to subsonic flames. A two-camera system was used to obtain simultaneous planar images of CH_4 Raman scattering and CH laser-induced fluorescence in turbulent, nonpremixed, and bluff-body-stabilized flames. The instantaneous structure of sooting regions of turbulent nonpremixed jet flames at pressures from 1 to 8 atmospheres was visualized using planar Mie scattering. Articles on each of these experiments are included in this section on Reacting Flows.

Section 4

Reacting Flows

A multidisciplinary program in reacting flows establishes an important link between fundamental studies of combustion chemistry and the real world of practical combustion. The objective of the program, which is sponsored by the Division of Chemical Sciences in the Department of Energy's Office of Basic Energy Sciences, is to use experimentation and computer modeling to increase our understanding of the fundamental interactions between chemistry and fluid dynamics in chemically reacting flows. Research results will be used to improve predictive capabilities for turbulent combustion of hydrocarbon fuels. Experimental studies include flows involving complex fluid mechanics but simplified chemistry; these flows are used to probe primary turbulent transport mechanisms. Studies of flows with complex chemistry but simplified fluid mechanics help identify combustion mechanisms responsible for the formation and growth of soot. Concomitant modeling studies employ stochastic approaches to predict turbulent flow quantities and deterministic approaches to predict unsteady flame structure and effects of flow fields on soot growth and transport.

An important element of the experimental program is the development of new laser diagnostic techniques capable of imaging portions of the flow field in a temporally resolved manner. These diagnostics make it possible to obtain two-dimensional measurements of major and minor chemical species and velocity during time scales that are short compared with the characteristic chemical or fluid dynamical time scales involved in combustion. Obtaining such measurements at high frequency makes it possible to follow the temporal development of unsteady reacting flows.

Regular workshops are held with scientists from universities and industry who are involved with the fundamental aspects of reacting flow research. These meetings provide a forum for information discussion of new developments and research opportunities in the field.

Effect of Damköhler Number on Superequilibrium OH Concentration in Turbulent, Nonpremixed Jet Flames[†]

Time-resolved point measurements of mixture fraction, temperature, and hydroxyl radical concentration are obtained for the first time in nonpremixed, turbulent, hydrogen-air flames. This is accomplished by combining spontaneous Raman scattering with linear, laser-induced fluorescence (LIF). This technique is used to quantify departures from equilibrium in low Damköhler number flames, where the time scales of turbulent mixing are competitive with the time scales of chemical reactions.

R. S. Barlow, R. W. Dibble, J.-Y. Chen, and R. P. Lucht

Previous Raman-scattering experiments¹ have shown that significant departures from chemical equilibrium can occur in turbulent hydrogen flames. Such departures from chemical equilibrium result when the time scale of turbulent transport becomes competitive with the time scales of chemical reactions. Knowledge of the behavior of the radical pool under these conditions represents an important step in understanding the effects of turbulence on flame chemistry. Accurate prediction of radical concentrations in highly strained turbulent flames is a critical test for combustion models.

In these experiments, spontaneous Raman scattering and laser-induced fluorescence (LIF) are combined to perform the first simultaneous measurements of major species concentrations, temperature, and hydroxyl concentration.² The experimental apparatus is shown in Figure 1. The jet flame is centered in a vertical, forced-draft wind tunnel. Laser beams for Raman scattering and LIF pass through the test section collinearly. The Raman scattering system uses DIANA, the facility flashlamp-

pumped dye laser (532 nm, 2 μs, 1 J/pulse). For LIF measurements, the beam from a Nd:YAG-pumped, frequency-doubled dye laser is combined onto the axis of the beam for Raman scattering using a dichroic mirror. These data define the instantaneous, local collisional-quenching environment of the OH molecules in the laser probe volume, allowing us to use linear LIF and apply quenching corrections for every laser shot, making the OH measurements quantitative.

Measurements were made in two flames of 22% argon in hydrogen with Reynolds numbers of 8500 (Case A) and 17,000 (Case B). Figure 2 includes results for an ensemble of 1000 individual measurements at $x/D = 30$, $y/D = 2$ in the Case B flame. (D is the nozzle diameter.) The solid curves are calculated adiabatic equilibrium conditions. These data are typical of regions of high reaction rates. Temperature depressions below equilibrium are evident. Hydroxyl concentration is almost always in superequilibrium, and the range of mixture fraction over which high OH concentrations occur is much broader than for the equilibrium curve.

Interactions between fluid dynamics and chemistry in turbulent flames can be characterized in terms of the Damköhler number, the ratio of a characteristic time scale of the flow to a characteristic time scale of chemical reactions $Da = \tau_{\text{flow}}/\tau_{\text{chem}}$. For $Da \gg 1$, chemical reaction rates are rapid compared to rates of turbulent mixing and chemical equilibrium is approached everywhere in the system. Conversely, for $Da \ll 1$, mixing rates are rapid compared to reaction rates and the system approaches the limit of a homogeneous, reacting mixture. When the Damköhler number is of order unity, mixing rates and reaction rates are competitive and departures from chemical equilibrium are expected to be sensitive to changes in either τ_{flow} or τ_{chem} .

A characteristic time scale for turbulent mixing is the large-eddy-turnover time

$$\tau_{\text{flow}} = \frac{\delta l/2}{U_c - U_\infty}$$

Figure 1. Schematic of experimental apparatus for simultaneous measurement of Raman scattering and OH LIF.

[†]Combustion and Flame, accepted (1988).

where $\delta_{1/2}$ is the width (full width, half maximum) of the jet velocity profile, U_c is the mean centerline velocity, and U_w is the coflow velocity. Two chemical time scales characterize hydrogen flames at atmospheric pressure, one for the rapid two-body reactions ($\tau_{\text{chem, 2-body}} = 20 \mu\text{s}$) and another for the slower three-body, radical-recombination reactions. In atmospheric-pressure flames, the characteristic time for three-body reactions is approximately 3 ms.

Damköhler numbers based on these time scales are given in Table I for three-flame conditions. $Da_{2\text{-body}}$ is greater than unity by at least a factor of ten for the flame conditions studied here. These high Damköhler numbers indicate that the two-body reaction rates are relatively rapid compared to the turbulent mixing rates. However, for the Case A and Case B flames, and for many nonpremixed, turbulent flames of practical importance, the Damköhler numbers formed using the three-body chemical time ($Da_{3\text{-body}}$) are less than unity. Such low Damköhler numbers indicate that radical concentrations and the process of reducing the total number of moles via the recombination reactions will be affected by fluid mechanics.

Figure 2. Ensemble of simultaneous measurements of (a) major species mole fractions and temperature and (b) hydroxyl radical mole fraction at $x/D = 30$, $y/D = 2$ in the Case B flame. The solid curves show adiabatic equilibrium conditions.

As shown in Figure 3, conditional averages of OH mole fraction increase and temperatures decrease as Damköhler numbers decrease because of competition between the time scales of turbulent transport and the time scale of the three-body radical recombination reactions.

Table I
Damköhler Numbers for the Turbulent Flames

	x/D	τ_{flow} (ms)	$Da_{2\text{-body}}$	$Da_{3\text{-body}}$
Case A	30	1.0	26	0.18
	50	2.3	50	0.33
Case B	30	0.53	13	0.09

Figure 3. Conditional averages of (a) hydroxyl mole fraction and (b) temperature for three flame conditions show that departures from equilibrium increase as Damköhler numbers decrease.

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Pdf Modeling of Chemical Nonequilibrium Effects in Turbulent, Nonpremixed, Hydrocarbon Flames[†]

An approach for modeling nonequilibrium chemistry in turbulent, hydrocarbon, nonpremixed flames with a four-scalar, constrained-equilibrium chemistry submodel is developed. Results of Monte Carlo simulations demonstrate that the model is capable of predicting a significant departure from chemical equilibrium.

J.-Y. Chen and W. Kollman*

Departures from chemical equilibrium appear in reacting flows at conditions where the characteristic time of the hydrodynamics becomes comparable with the characteristic time of the chemical reaction. Significant departures from chemical equilibrium can occur in turbulent flows by intense mixing. Modeling the turbulent combustion of propane with a coflowing stream of air in a round jet configuration is considered as an example for developing a general approach to deal with chemical nonequilibrium effects in turbulent flows.

Due to the complexity of chemical kinetics in hydrocarbon-air combustion, it is necessary to restrict the number of scalar variables to a minimum to keep the numerical computations treatable. To meet this demand, the notion of constrained equilibrium¹ is adopted here to develop a chemical kinetics model. This method treats the progress of reactions in complex systems as a series of equilibrium states subject to a set of appropriate constraints, which are controlled by the rate-limiting steps. One major advantage of this approach is the significant simplification of numerical computation, especially for complex systems. Moreover, the resulting kinetics model can be improved systematically by including additional constraints. The only obvious disadvantage of the method is that the set of appropriate constraints must be identified; they, of course, are problem-dependent.

The constraints chosen for the propane jet flame are: (1) the total number of moles per unit mass n , (2) the number of moles of C_3H_8 per unit mass $n_{C_3H_8}$ and (3) the number of moles of CO per unit mass n_{CO} . For a given mixture fraction f , this reaction scheme consists of four scalars. The evolution of the three constraints is assumed to be determined by the following rate-controlled steps. First,

the consumption of fuel is described by a global break-up model²

which allows only forward reaction. Second, the oxidation of CO is governed mainly by

and the radical pool is controlled by the slow three-body recombination reactions

The forward rates of reactions (ii) to (vi) are those recommended by Warnatz³ and the reverse rates are determined from their respective equilibrium constants. Accordingly, the changing rates for the three constraints are:

$$\begin{aligned} \frac{d}{dt}(n) &= 9/2R_i - R_{iii} - R_{iv} - R_v - R_{vi} \\ \frac{d}{dt}(n_{C_3H_8}) &= -R_i \\ \frac{d}{dt}(n_{CO}) &= 3R_i - R_{ii} \end{aligned}$$

where R_k are the net forward reaction rates. For a given mixture fraction, integration of these three rate equations, together with the thermochemical properties calculated by minimizing the Gibbs free-energy subject to the three constraints, determines the whole chemical processes.

Turbulent combustion is modeled by using a combination of a stochastic simulation technique for the joint scalar probability-density function (pdf) equation⁴ and a finite-difference procedure for a

[†] Twenty-Second Symposium (International) on Combustion (The Combustion Institute, 1989), p. 645.

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second-order closure scheme⁵ for the velocity field. Monte Carlo simulations of the joint scalar pdf have been performed for a propane-air, turbulent, nonpremixed jet flame with an exit velocity of 32 m/s and a Reynolds number of 40,000. From these simulations, any joint statistics among the scalars are readily available. A typical scatter plot for the joint statistics between temperature T and the mixture fraction f is shown in Figure 1. At a fixed f , the mixture temperature is bounded by the room temperature and the completely burned temperature. Points lower than the maximum temperature are an indication of departure from chemical equilibrium. As can be seen from this plot, a large number of points are below the maximum temperature limits indicating a significant departure from chemical equilibrium.

Figure 1. Predicted instantaneous relationship between temperature T and the mixture fraction f for a propane-air, turbulent, nonpremixed jet flame. Shown are an ensemble of 10,000 Monte Carlo statistics at 10 diameters downstream and radial location 1.24 diameters from the jet centerline.

In addition to the T - f plots, the joint pdfs are useful in providing insights into the turbulent combustion process. For example, Figures 2 and 3 present the predicted joint pdf between f and CO concentration in a three-dimensional and a contour plot, respectively. The spike near the origin in Figure 2 indicates the existence of cold air entrained from the coflowing stream. The shape of the joint pdf in the combusting fluids is rather complex and far different from any analytic shapes usually assumed in conventional moment closure schemes. Similar to the T - f plots, at chemical equilibrium, the CO concentration should be a single function of f . However, the contour plot in Figure 3 shows that at a given f , a range of CO concentrations is possible, indicating again the nonequilibrium nature of this flow.

Figure 2. Predicted joint pdf between CO and the mixture fraction f for a propane-air, turbulent, nonpremixed jet flame. Joint statistics are obtained at 10 diameters downstream and radial location 1.24 diameters from the jet centerline showing 3-D patterns.

Figure 3. Predicted joint pdf between CO and the mixture fraction f for a propane-air, turbulent, nonpremixed jet flame. Joint statistics are obtained at 10 diameters downstream and radial location 1.24 diameters from the jet centerline showing constant contour curves.

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Soot Formation in Nonpremixed Turbulent-Jet Flames at Elevated Pressure[†]

We have determined local, time-averaged, soot-volume fractions in nonpremixed, turbulent-jet flames at pressures up to 0.8 MPa. Such measurements provide information that is important for the development of soot-formation models for high-pressure systems.

W. L. Flower

For atmospheric-pressure, nonpremixed, turbulent-jet flames, considerable data are available for the time-averaged and fluctuating values of soot concentrations, temperature, and radiation properties. However, no measurements of local soot concentrations previously have been available for well controlled, high-pressure, turbulent flames. Such detailed measurements of the soot field in high-pressure, turbulent flames are important for developing soot-formation models that will be useful for the many real combustion systems that operate at high pressures. This study provides the first such measurements in simple, high-pressure, turbulent-jet flames.

Nonpremixed, turbulent-jet flames of ethylene in air were supported on a small (< 0.15 -cm diameter), vertical, circular tube surrounded by a small pilot flame and a coflowing air stream. The burner was enclosed in the pressure vessel used for previous laminar-flame studies.¹ Mean unburned-gas jet velocities for the various flames ranged from 700 to 5700 cm/s, much greater than the coflow air velocity (8-50 cm/s). Flames at pressures from 0.1 to 0.8 MPa (1-8 standard atmospheres) were investigated.

The flames appeared nearly laminar immediately above the burner port, undergoing a transition to turbulence several centimeters above the burner. At the lowest pressures, the flames appeared blue in the region closest to the burner, no yellow luminosity from soot being evident until several centimeters above the burner. At higher pressures, luminosity from soot was visible starting at the burner port. For all pressures and flow conditions, the intensity of soot emission increased visibly with axial height above the burner, at least up to the location of the maximum soot concentration. The diameter of the yellow luminous region increased with height above the burner until near the flame tip, where the final luminosity consisted of wandering yellow streamers of soot. While no soot was visible

after the luminous region for some experiments, many of the flames did emit soot in the form of a dark gray plume. Luminous flame lengths were predicted well by the correlations of Becker and Liang.²

Soot-particle measurements were made using standard laser-light-scattering techniques. The beam from an argon-ion laser (0.5 W at 514.5 nm) was chopped mechanically before passing horizontally through the flame. A silicon photodiode was used to measure the intensity of light transmitted through the flame, from which the integrated soot-volume fraction along the beam path was determined. A lock-in amplifier referenced to the laser-chopping frequency measured the photodiode output. The time-averaged transmitted signal was determined by averaging 200 measurements of the photodiode output over a 1-s period.

The fraction of the initial laser intensity propagated through the flame, I/I_0 , is related to the integral of the soot-volume fraction f_v along the beam path through the flame by $\int_{-\infty}^{+\infty} f_v dy = -C(\lambda, m) \int_{-\infty}^{+\infty} \ln(I/I_0)$, where y is the coordinate along the laser beam ($y=0$ on the flame centerline). The proportionality factor $C(\lambda, m)$ contains the dependence of the extinction coefficient on wavelength λ and on the particle complex refractive index m . The procedure followed here was to measure the transmission of laser light through the flame on a chord parallel to the y axis to determine the integral of the soot-volume fraction along the chord. At a fixed axial location, the burner was traversed in the horizontal direction orthogonal to the laser beam (z -direction) to determine the horizontal profile of light-attenuation. This procedure was repeated at 3-10 axial locations in each flame. The measured light-attenuation profiles, which were normalized by baseline profiles measured with no flame, provide sufficient information to determine the full radial variation of the time-averaged, soot-volume fraction. Integration of the light-attenuation profiles over all values of the lateral coordinate z at a given axial position yields the total soot-volume fraction in the flame cross section.

Shown in Figure 1a is the integrated soot-volume fraction $\int_{-\infty}^{+\infty} f_v(x, y, z) dy$, determined from

[†] Twenty-Second Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, PA, 1989) p. 425.

Figure 1. (a) Measurements of the chord-integral through the flame of the soot-volume fraction (O) as a function of horizontal displacement from the flame centerline. Measurements for a flame at 0.5 MPa are shown at an axial position equal to about half of the luminous flame length. The solid lines represent the Gaussian profile that best fits the data. (b) Radial soot-volume-fraction profile determined by inversion of the best fit to the integrated soot volume fraction of (a).

the measured light-attenuation profile at an axial position near half of the luminous flame length. This profile represents the projection of the function $f_v(x,y,z)$ onto the z -axis. Since the flame is axisymmetric, the measured projection provides sufficient information to determine $f_v(x,y,z)$ on a finite grid using numerical inversion techniques. Here, instead, a fast and simple inversion was accomplished analytically by noting that the projection of Figure 1a is approximated quite well by a Gaussian function $P(x,z) = P_0 \exp[-(z/\sigma)^2]$, where the amplitude P_0 and width σ depend on the axial position x . The curve in Figure 1a is the Gaussian that best fits the measurements. Projections for other flames and axial positions were also closely approximated by Gaussians. The axisymmetric function that has a Gaussian projection is defined uniquely by a Gaussian function of $r = (y^2 + z^2)^{1/2}$ with the same width σ . Hence, since the projections of f_v are Gaussian, the radial distributions of f_v are also Gaussian and may be determined from the projections. Figure 1b shows the radial distribution of soot-volume fraction determined from the fit to the data of Figure 1a.

Figure 2 shows the integrated soot-volume fraction on the flame cross section as a function of flame-length-normalized axial position for four flames with fixed characteristic time τ_f (the ratio of the jet velocity to the luminous flame length L) and fixed flame-tip Reynolds number Re_L . Integrated soot-volume fractions were obtained by numerical integration of the actual measurements; integrals of the Gaussian curve fits differed from these values by less than 1-3%. The trends apparent in Figure 3, as well as for the other flames studied here, are similar to those observed in laminar flames;³ i.e., an early-time region of soot formation is followed by a region of soot removal due to oxidation. The position of the peak of the axial soot-volume profile remains fixed at $x/L = 0.55$ for the flames of Figure 2, although the luminous flame length L varies by a

factor of 2. For these flames, the peak integrated soot-volume fraction increases as $p^{1.4}$, close to the $p^{1.2}$ dependence determined previously for laminar diffusion flames.³ If soot concentrations are sufficiently high, the oxidation region may be effectively terminated due to the drop in temperature resulting from radiative losses, as observed previously for laminar flames and atmospheric-pressure, turbulent flames.

Previous measurements in atmospheric-pressure, turbulent-jet, diffusion flames indicate that more soot is formed in flames with longer characteristic residence times τ_f , and that, for sufficiently long residence time, the quantity of soot formed approaches a limiting value that is independent of τ_f . Fuel-flowrate-normalized peak soot fluxes determined here for flames at 0.1 and 0.2 MPa display a dependence on residence time that is consistent with these previous observations. However, results for flames at 0.3, 0.5, and 0.8 MPa indicate that, at fixed pressure, the peak normalized-soot flux is lower for flames with longer residence times. The inverse dependence of peak soot fluxes on residence time at elevated pressures may result from the greater radiative heat transfer from the highly luminous, optically thick, high-pressure flames. For flames with longer residence times, there is a greater net radiative-energy loss before the location of the peak soot-volume fraction, causing a decrease in temperature and a reduction of soot-formation rates in the region of overall soot production.

Figure 2. Axial profiles of the integral of the soot-volume fraction over the flame cross section, $\int_{-\infty}^{+\infty} f_v(x,y,z) dy dz$, determined from light-attenuation measurements. Shown are results for flames at 0.11 MPa (∇), 0.22 MPa (Δ), 0.37 MPa ($\diamond$), and 0.47 MPa (O) with fixed τ_f and Re_L .

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Visualization of Sooting Regions in Turbulent Nonpremixed Flames: Measurement of Planar Mie Scattering Using a Charge-Coupled-Device Camera

The instantaneous structure of the sooting regions of turbulent nonpremixed flames is visualized using planar Mie scattering.

W. L. Flower

In a previous paper,¹ we presented detailed measurements of the time-averaged structure of the sooting regions of nonpremixed turbulent-jet flames of ethylene in air at pressures from 0.1 to 0.8 MPa (1 to 8 standard atmospheres). The peak of the time-averaged, soot-volume fraction for such flames was on the flame centerline at all axial positions for which the soot-volume fraction was measurable. Here, we examine the instantaneous spatial structure of the sooting regions of these same flames. We visualize this structure using planar Mie scattering by soot particles. Such visualizations allow us to identify the zones in the flames where soot is found at an instant in time and to determine the instantaneous structure or topology of these zones. This information is important not just for the insight it provides into the soot formation process, but also for the picture it provides of other turbulent structures in nonpremixed-jet flames.

Measurements were made in sooting nonpremixed, turbulent-jet flames of ethylene in air. These flames, as well as the burner and flow channel, have been described in detail previously.¹ Basically, the burner consisted of a 0.097-cm-inside-diameter tube delivering ethylene, surrounded by a second, concentric, outer tube (0.3-cm outside diameter). A small premixed, ethylene-air pilot flame was supported on the gap between the two tubes to prevent the central turbulent-jet flame from lifting off the burner port. Coflowing air surrounded the burner assembly, which was enclosed within a flow channel designed to withstand internal pressures up to 1.0 MPa. Flames at pressures of 0.1, 0.2, 0.3, 0.5, and 0.8 MPa were examined. At the lowest pressures (0.1 and 0.2 MPa), flames were operated at an ethylene flowrate of 4.25 standard liters per minute (2.86 g/min); flames at fuel flowrates of both 4.25 and 10.0 standard liters per minute (2.86 and 6.72 g/min) were examined at the higher pressures.

The laser source for these experiments is a Q-switched, frequency-doubled, Nd:YAG laser, located in a remote facility approximately 20 m from the flame laboratory. The laser was externally triggered with a pulse duration of 10 ns. The frequency-

doubled green output (532 nm) from the Nd:YAG laser was directed through a periscope system to the flame laboratory, where the beam was down-collimated using a telescope consisting of a 50-cm-focal-length biconvex, spherical lens followed by a -16.9-cm-focal-length biconcave, spherical lens. Two cylindrical lenses then expanded the circular beam in the vertical direction, while maintaining collimation. A 30-cm-focal-length plano-convex, cylindrical lens focused the vertically expanded beam into a thin vertical sheet with an observed thickness less than 0.1 cm for 2.5 cm to either side of the burner centerline (the approximate maximum lateral extent of the turbulent flame). Light scattered by soot particles located in the laser sheet was collected at $f/16$ by a camera lens that imaged the flame to an unintensified charge-coupled-device array (Thomson CSF, 384 x 576 pixel) mounted in a Photometrics CH220 camera head.

To maximize the visibility of the images of the sooting regions, it is necessary to minimize exposure of the camera to intense broadband incandescence from soot particles, while still detecting Mie-scattered light resulting from the narrowband, pulsed, probe laser. This is accomplished using a combination of spectral filtering and temporal shuttering of the collected radiation. A 10-nm-band-pass interference filter centered at 532 nm minimized the broadband soot incandescence reaching the camera. Mechanical shuttering of the collected radiation was accomplished using a variable-speed chopper placed in the collection path. All but one window of the chopper wheel was masked so that when the chopper operated at 130 revolutions per second, the chopper window passed collected radiation for 0.12 ms every 7.5 ms. Every fifteenth reference pulse was used to trigger the probe laser, for a net laser pulse repetition rate of 9 Hz. An adjustable electronic delay in the trigger line was set so that the chopper window opened at the same time that the probe laser illuminated the particles in the flame. A second, single-shot, electromechanical shutter was triggered by the laser to expose the detector for a single chopper window coinciding with illumin-

ation of the flame by a laser pulse. Following data acquisition, the image of the sooting regions provided by Mie scattering was displayed on a monitor and stored subsequently in an IBM PC/AT computer for analysis and display.

Images of the flames obtained with the laser blocked displayed peak signals on the order of a few percent of the peak Mie-scattering signals obtained with laser illumination, confirming that the broadband flame radiation was rejected adequately. Examination of the images obtained with the laser unblocked also show that the signals in the regions above or below the laser sheet are small relative to the Mie-scattering measurements in the region illuminated by the laser.

To account for variations in the beam intensity across the laser sheet, each two-dimensional image was normalized by a reference image that characterizes the beam intensity profile. The reference images were obtained by using the same optics and camera system to record the Rayleigh-scattering intensity profile when the vessel was filled with Freon 22 to a pressure of 0.85 MPa.

Visualizations of the sooting regions are largely qualitative since the intensity of Mie-scattered light is a function of both particle size and particle number density, in addition to the complex refractive index of the particles. It is not possible to determine independent information on either the size or number density, even in the simple case of Rayleigh scattering by monodispersed particles with known optical properties. Quantitative analysis of the measurements is further hindered by the attenuation of both the incident and scattered light. Measured time-averaged attenuations through the complete flame are close to 99% at 0.8 MPa.¹ Hence, it is not possible to know the actual incident laser intensity at any point, nor the fraction of the scattered light from that point that will reach the camera. Nevertheless, the images are useful to show the location and topology of the sooting regions of the flames.

An image of the sooting regions of a 0.2-MPa flame is shown in Figure 1a. The flame-tip Reynolds number for this flame is $Re_L = 6900$ and the characteristic flow time $\tau_f = L/u_o$ (where L is the flame length and u_o is the jet velocity) is $\tau_f = 8.2$ ms. The region shown in Figure 1a is centered at an axial position near half of the luminous flame length, about 12 cm above the tip of the burner. Bright regions in the photograph represent regions of high light scattering from soot, indicating locally high soot concentrations. Figure 1a illustrates that, at the mid-flame-height position, the soot is found in relatively narrow, intertwined layers. At lower positions in the flame, similar images show that the soot is found in two essentially separate thin sheets

that appear to be rolling up. Little scattering from soot is observed in the region between the two sheets. Above the mid-flame-height position, the soot-laden regions become still more convoluted.

Previous measurements¹ show that, on a time-averaged basis, the peak soot-volume fraction is found on the flame centerline (Figure 1b). Since the images of the sooting regions (Figure 1a) show no large central core of high soot loading at an instant in time, the fact that the maximum time-averaged soot-volume fraction appears on the flame centerline must result from the time-varying motion of the localized regions of high soot loading.

Figure 1. (a) Planar image of Mie scattering from soot particles in a 0.2-MPa turbulent-jet, nonpremixed flame of ethylene in air for an axial position near half of the luminous flame length. Bright regions indicate zones of locally high scattering of light by soot particles located in a thin 4-cm-high region containing the flame axis. (b) At the same axial location, the time-averaged soot-volume fraction peaks on the flame centerline.

Reference:

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Visualization of Supersonic Flows with Planar Laser Imaging

High-resolution, planar-laser imaging has been used to visualize the structure of turbulent shear layers in an underexpanded sonic jet. The effect of compressibility on the entrainment rate of reactants into turbulent mixing layers is an important consideration in supersonic combustion.

R. W. Dibble, R. S. Barlow, M. G. Mungal,* M. B. Long,** and D. C. Fourquette***

Supersonic flows and supersonic combustion have received recently renewed interest because of the current program to develop the National AeroSpace Plane (NASP). This vehicle will rely upon air-breathing engines rather than rocket propulsion to achieve hypersonic flight. Consequently, its engines must be designed to allow fuel and air to mix and react efficiently at supersonic speeds. The effect of compressibility on the growth rate of turbulent mixing layers is a critical issue in supersonic combustion. While much work has been done on the study of supersonic flow (including shock waves, shock-wave boundary-layer interactions, shock reflections and expansions, and detonations waves), our understanding of compressible, turbulent mixing layers is limited. This article describes the use of planar-laser imaging to visualize the structure of supersonic flows containing turbulent mixing layers. Planar-laser imaging provides spatially resolved information unavailable from traditional visualization techniques, such as shadow-graph or schlieren photography.

The system used to obtain the images is shown schematically in the introduction to this section of the Annual Report. The beam from a pulsed, frequency-doubled Nd:YAG laser (300 mJ/pulse at 532 nm) is formed into a narrow sheet by a combination of cylindrical and spherical lenses, and this laser sheet passes through the flow of interest. A camera lens images the Rayleigh-scattered light from the laser sheet onto an unintensified CCD array. The array has 384×576 pixels, with each pixel width corresponding to 40 microns in the object plane. Spatial resolution in the third dimension is determined by the thickness of the laser sheet, which is 100 microns. The pulse duration of the Nd:YAG laser is 10 ns, short enough to freeze the flow.

We have used this system to explore the structure of an underexpanded jet. For these experiments, compressed air at 7 atmospheres was discharged through a converging nozzle into ambient air. This flow adjusts to the ambient pressure through a series of expansion waves, compression waves, and shocks as shown in Figure 1. The central portion of the jet overexpands initially to supersonic speeds, and is then decelerated and compressed by a normal shock, often called a Mach disk. The incident

Figure 1. Sketch of the structure of an underexpanded jet, showing the region imaged in Figure 2.

Mach number at the disk is 3.5. A reflected shock is formed at the intersection of the barrel shock and the Mach disk. From this intersection (the triple point), a slip line separates the supersonic fluid that has passed through the oblique reflected shock from the subsonic fluid downstream of the normal shock.

Figure 2 shows three instantaneous, false color, laser-Rayleigh-scattering images from a plane through the centerline of the underexpanded jet; the fourth frame (lower right) is an average of 30 instantaneous images. The images show the intensity of Rayleigh-scattered light from air molecules and from fine nucleated water droplets, formed from the water vapor present in the compressed air supply.

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Figure 2. Three color-enhanced, instantaneous, laser-Rayleigh-scattering images from a plane through the centerline of an underexpanded air jet reveal the structure of two turbulent shear layers, one along the jet boundary and another along the slip line downstream of the triple point. The fourth frame (lower right) is the result of averaging 30 instantaneous images. The location of the image frame with respect to the nozzle is shown in Figure 1.

The image frame, which is outlined in Figure 1, includes the barrel shock, Mach disk, and reflected shock. The three instantaneous images also resolve the structure of the turbulent shear layers in this supersonic flow. There are two turbulent shear layers visible: one along the jet boundary and the other along the slipline, downstream of the triple point. In both shear layers, there is evidence of large-scale vortical structures similar to those observed in subsonic turbulent mixing layers. These roll-up structures result from the Kelvin-Helmholtz instability, and their growth constitutes the primary mechanism for entrainment of fluid into the mixing layer. The 30-frame average masks the structural features of the turbulent mixing layers, and illustrates the value of instantaneous images in understanding the physics of the turbulent mixing process.

To quantify the effects of compressibility on a shear layer, Papamoschou and Roshko¹ and Bogdanoff² have introduced the concept of the convective Mach number, which is the Mach number seen by an observer moving at the speed of the local

organized structure. When the convective Mach number is below 0.3, the effects of compressibility are small, and the shear layer will have the same growth rate (overall entrainment rate) as an incompressible layer. However, as convective Mach number increases, growth rate of the shear layer decreases because the effect of compressibility is to dampen the amplification of the Kelvin-Helmholtz instability. Just downstream of the triple point, the shear layer exists between supersonic and subsonic streams. Here, the convective Mach number is high enough for compressibility effects to be significant. Consequently, the initial growth rate of the turbulent shear layer is slow. Further downstream, as the central core fluid accelerates, the convective Mach number decreases, and the growth rate of the shear layer increases.

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Instantaneous Flame Zone Structure in Turbulent, Nonpremixed Flames[†]

A two-camera imaging system was used to obtain instantaneous planar images of CH₄ Raman scattering and CH laser-induced fluorescence in turbulent, nonpremixed-jet and bluff-body, stabilized flames. The images were used to study flame-stabilization mechanisms and the relationship between turbulence and flame structure in the flame initiation regions of these flows.

M. Namazian,* R. W. Schefer, and J. T. Kelly*

Simultaneous, multispecies imaging data¹ are important for understanding turbulent combustion processes and for developing and validating combustion models. In this study, planar imaging of CH₄ Raman scattering and laser-induced CH fluorescence are used to study the initial region of jet and bluff-body flames. CH is an intermediate species that marks the region where CH₄ is consumed rapidly. The jet flow has a dominant flow direction and the mean properties vary more rapidly in the radial direction. The bluff-body flow has substantial recirculation and the mean properties vary significantly in the streamwise as well as cross-stream directions. Both bluff-body and jet flames are studied to define the similarities and differences between flame structures under widely different flow and mixing conditions.

For the measurements, the facility flash-lamp-pumped dye laser, Diana, was modified to produce beams at both 431.5 and 444 nm. The beam was formed into a 0.2-mm-thick sheet of light by a multipass cell consisting of two cylindrical reflectors. The 431.5-nm light was used to excite the (0,0) band of the A²Δ - X²Π system of CH, fluorescence of the resulting (0,1) transition was observed at 489 nm. Coincidentally, spontaneous Raman scattering from CH₄ occurred near 489 nm for a 431.5-nm excitation. To separate the CH₄ and CH contributions, the 444-nm light was used to produce a spontaneous Raman signal from CH₄ at 510 nm. The signals were recorded with two separate, intensified, vidicon detectors. Subtraction of the detected signals generated by the 431.5-nm- and 444-nm-wavelength beams yielded separate measurements of CH₄ and CH concentrations.

The burner consisted of an axisymmetric bluff-body (50-mm diameter) with methane fuel supplied through a centrally located 5.4-mm-diameter tube. The fuel-jet velocity for all measurements

was 21 m/s, corresponding to a Reynolds number of 7,000. For the bluff-body flow, air was supplied through a coaxial jet surrounding the bluff-body at a velocity of 25 m/s. Measurements in the nonpremixed jet were made in the same burner with no coaxial air flow.

Figures 1a and 1b show contour plots of two instantaneous images of CH₄ and CH concentrations for jet and bluff-body flames. In both cases, the burner is situated at an axial distance $x=0$ mm, which is located below the imaged field. Both the CH and CH₄ data are normalized by the Raman signal for pure methane at room temperature. In both flows, the instantaneous reaction zone, as defined by CH, consists of a narrow envelope that follows the fuel structures. The jet flame is lifted, which results in a CH-free zone up to approximately $x \sim 20$ mm in Figure 1a. At and beyond the lift-off height, the reaction zone is aligned with the 0.1-CH₄ contour level. The reaction zone of the bluff-body flame, shown in Figure 1b, is also aligned with the 0.1 contour that lies in the vicinity of the stagnation zone.

The CH₄ profiles through the flame, conditional on CH, can be made similar by normalizing the distance coordinate by the flame thickness and the concentration by values at the boundaries of the flame. Figure 2 shows the mean normalized-methane concentration defined by:

$$Y = \frac{C - C_f}{C_f - C_a} \quad (1)$$

versus the normalized coordinate:

$$\Lambda = \frac{l - l_a}{l_f - l_a} \quad (2)$$

where C is the instantaneous CH₄ concentration within the reaction zone, l is the coordinate normal to the reaction zone, and f and a designate fuel and air sides of the reaction zone, respectively. In figure 2, the mean CH concentration normalized by its peak value is also plotted. In both flames, the CH and CH₄ distributions are similar. The mean value

[†] Twenty-Second Symposium (International) on Combustion (The Combustion Institute, 1989), p. 627.

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Figure 1. Instantaneous concentration contours for CH_4 (0.1 dashed, 0.2 dotted, and 0.3 solid) and CH (0.4 light shaded and 0.8 dark shaded) for a) jet and b) bluff-body flames. Fuel-jet velocity in both cases is 21 m/s. Air-flow velocity in the bluff-body flow is 25 m/s.

of the CH_4 concentration at the air side, and at the fuel side, are 0.05 and 0.16 for the jet flame and 0.05 and 0.12 for the bluff-body flame. At $\Lambda=0.5$ (the flame center), the variance, v , is 0.2 for both flames. In both cases, the normalized CH_4 concentration could be approximated by $v=(1-\Lambda)^2$. The relationship between CH and CH_4 and the similarity between the jet and the bluff-body flames suggest that the reaction zones of these flames are governed by similar mechanisms and could be described by a common model.

Just before the point of flame initiation, fuel concentrations are 0.1, the level at which the premixed CH_4 reaction rate peaks. The CH_4 data, combined with mixing time estimates for eddies smaller than the experimental resolution, support the concept that fuel and air are premixed at the flame initiation point. Therefore, premixed flame concepts are appropriate for analyzing lifted jet flames. The reaction zone, as indicated by Cr-I, spans the range of fuel concentrations from 0.05 to 0.16. This range is consistent with the flammability limits of cold, premixed CH_4 and air. The high CH_4 concentrations within the CH envelopes indicate that only a fraction of the fuel is consumed in the reaction zone. The consistency of CH_4 concentrations prior to and within the flame supports the presence of reaction occurring within small structures that occupy only a limited volume, and is consistent with a dissipative eddy model for turbulent, nonpremixed flames.²

Figure 2. Conditional mean values of normalized CH_4 and CH concentration versus the normalized reaction zone distance in jet (solid line) and bluff-body (dashed line) flames.

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1. B. F. Magnussen and B. H. Hjertager, *Sixteenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, PA, 1976), p. 719.
2. M. Namazian, J. T. Kelly, and R. W. Schefer, *Twenty-Second (International) Symposium on Combustion* (The Combustion Institute, Pittsburgh, PA, 1989), p. 627.

OH Imaging in Nonpremixed, Turbulent-Jet Flames

Planar, laser-induced fluorescence was used to image the instantaneous OH concentration field in turbulent, lifted-jet flames. The images were used to study flame-stabilization mechanisms and the relationship between turbulence and flame structure in the flame initiation regions of these flows.

R. W. Schefer, M. Namazian,* and J. T. Kelly*

Knowledge of the instantaneous flame-zone structure is important to our understanding of the mechanisms controlling turbulent combustion and the interaction between turbulence and flame-zone chemistry. Previous studies in turbulent-jet and bluff-body stabilized flames used planar imaging of CH_4 Raman scattering and CH laser-induced fluorescence to define the instantaneous flame-zone structure and its relationship to the large-scale turbulence and mixing.^{1,2} In the present experiment, the instantaneous OH concentration distribution is measured in a turbulent, lifted-jet flame using planar, laser-induced fluorescence. OH is an important species in flame chemistry, and an understanding of its formation characteristics is necessary to our understanding of flame-zone chemistry and the development of physically realistic chemistry sub-models for turbulent combustion modeling.

The UV laser radiation for the fluorescence excitation of the OH molecule was provided by a Nd:YAG-pumped, dye-laser system (Rhodamine 590 dye) with subsequent frequency doubling using a KDP crystal. A 5-ns laser pulse, with 10 mJ of energy, was used to pump the $Q_1(8)$ transition ($v''=0 \rightarrow v'=1$) of the OH $A^2\Sigma \rightarrow X^2\Pi$ electronic band at 283.55 nm. The laser beam was formed into a sheet of laser light with the multipass cell system used previously in CH_4 - and CH -imaging measurements.¹ The fluorescence signal was collected perpendicular to the laser sheet and focused onto an intensified vidicon camera. A narrow-band filter located in front of the camera allowed only the light from the (1,1) vibrational band (312 nm) of the OH molecule to be detected. With this optical system, the 100 x 100 pixel format of the camera provided a spatial resolution of 400 x 400 microns. An advantage of using the multipass cell over the more conventional technique of passing the laser beam through a cylindrical lens is that the laser-sheet intensity is nearly 30 times greater. This increased intensity makes it possible to approach conditions necessary for the

use of saturated fluorescence and thus reduces collisional quenching effects as a source of error in quantifying the OH concentration.

The burner consisted of a 5.4-mm-diameter fuel jet located in the center of a 50-mm-diameter circular disk. Methane was injected through the central fuel tube at a velocity of 21 m/s, corresponding to a fuel-jet Reynolds number of 7,000. At this flow condition, the visible flame is initiated at an axial position, x , approximately 30 mm downstream of the burner face and at a radial distance, y , consistent with the fuel-jet radius. The lower part of the flame is blue and is connected to an irregular yellow flame that begins at about 50 mm downstream.

Figure 1 shows the contour plot of an instantaneous image of the OH concentration. The OH concentration (molecules/volume) is presented in arbitrary units, with relative concentration contour levels of 0.2, 0.3, and 0.4 indicated by the dotted, dashed, and solid lines, respectively.

Figure 1. Instantaneous contour plots of OH concentration in a lifted, CH_4 -jet flame. Contour lines correspond to OH concentration levels of 0.2 (dotted line), 0.3 (dashed line), and 0.4 (solid line).

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dashed, and solid lines, respectively. The initial reaction zone consists of a narrow envelope located in the mixing region adjacent to the central fuel jet. The jet flame is lifted, which results in an OH-free zone up to approximately $x=35$ mm. A comparison of several images shows that both the instantaneous lift-off height and the radial location of the reaction zone varies with time.

The radial variation in the flame location results in the bimodal probability distribution of the OH concentration shown in Figure 2. The distribution corresponds to the radial location where the time-averaged OH is maximum and is calculated from 200 instantaneous images. The distribution is bimodal, with a spike corresponding to zero OH and a second peak associated with finite OH concentrations. This bimodality is consistent with a relatively thin flame zone that moves radially about its mean location. The zero peak thus corresponds to those times in which the instantaneous flame zone is outside the measurement volume, while the broader peak corresponds to those times when part of the flame zone is located within the measurement volume.

Time-averaged radial profiles of the OH concentration were obtained by statistically averaging 400 instantaneous images. Shown in Figure 3 is the time-averaged radial profile at an axial distance of 35 mm. The maximum OH concentration occurs approximately 9 mm from the jet centerline.

Figure 2. Probability density distributions of normalized OH concentration in lifted, CH_4 -jet flame. Distribution corresponds to an axial location of 35 mm downstream and a radial location 9 mm from centerline.

The maximum concentration of 3.9×10^{15} molecules/ cm^3 is nearly 2.5 times greater than the equilibrium value of $\phi=1.0$.

The relative locations of the OH, CH, and CH_4 distributions can be seen from comparison with the time-averaged CH and CH_4 profiles, also included in Figure 3. The close correspondence between the maximum OH and CH can be seen clearly. For both OH and CH, the maximum concentrations occur in the mixing region adjacent to the central fuel jet where the CH_4 concentration is within the flammability limits and reaction is most intense. The CH peak is shifted slightly toward the centerline where conditions are more fuel rich, consistent with the role of CH as an intermediate hydrocarbon species that is produced during fuel breakdown. The OH distribution is somewhat broader than the CH distribution, since disappearance of OH outside the primary flame zone is controlled by relatively slow three-body recombination reactions.

Figure 3. Radial profiles of the time-averaged OH, CH, and CH_4 concentrations in a lifted, CH_4 -jet flame. Profiles are for an axial distance of 35 mm downstream.

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1. M. Namazian, J. T. Kelly, and R. W. Schefer, *Twenty-Second (International) Symposium on Combustion* (The Combustion Institute, Pittsburgh, PA, 1989), p. 627.
2. R. W. Schefer, M. Namazian, and J. T. Kelly, *Twenty-Second (International) Symposium on Combustion* (The Combustion Institute, Pittsburgh, PA, 1989), p. 833.

Simulation of Unsteady Flame Propagation[†]

Constant-density flame propagation in a flow with a single wavelength and a single frequency reveals the flame shape dependence on the flow frequency. Cusps in the flame front occur only at low frequency.

W. T. Ashurst, G. I. Sivashinsky,* and V. Yakhot*

We have investigated the effect of velocity fluctuations on premixed flame propagation in a synthetic flow that has only one spatial component and one temporal frequency. We have selected this simple flow because the propagation of a flame in a turbulent flow is one of the most fundamental and challenging problems of combustion theory. The direct numerical calculation of turbulent flame propagation involves the simultaneous solution of the chemical kinetics coupled with the hydrodynamic equations. The stiffness of the chemical reaction terms combined with nonlinear flow makes this task very difficult. For many practical applications, it is known that the flame thickness, which is determined by a reaction-diffusion process, is much smaller than the smallest turbulent length scale, which is determined by the large-scale flow geometry. Turbulence, therefore, affects the flame by strain rates that are slowly varying when measured in terms of the flame thickness. If we assume that changes in the reaction-diffusion structure due to strain are small, then it is reasonable to consider the reaction zone to be asymptotically thin.

However, in this work we consider the flame thickness to be zero and only solve for the geometry of the flame during its propagation. A spatially nonuniform flow will wrinkle the flame and greatly increase the flame surface and it is this wrinkling that primarily increases the combustion rate in a turbulent flow in comparison to reaction in laminar flow. We also neglect thermal expansion and investigate the effect of the flow on flame propagation, but not the effect of heat release on the flow. We find that the nonlinear properties of this constant-density flame are rich enough so that we do gain important insights that are relevant to the more realistic flame propagation process.

It is convenient to formulate this passive-front propagation problem as an equation for a

scalar field $G(x,t)$ whose zero-level surface $G = 0$ represents a flame-front configuration

$$\frac{\partial G}{\partial t} + \mathbf{v} \cdot \nabla G = u_L |\nabla G|,$$

where $\mathbf{v}$ is the convective velocity ($\nabla \cdot \mathbf{v} = 0$) and u_L is the flame propagation speed, which may be a function of $G, \mathbf{v}$ and their derivatives. We define a new scalar g that describes the perturbations from a flat flame that propagates in the negative x direction as $G = g(x,y,t) - x$.

As a simple model of turbulent eddies with finite lifetimes, we consider flame propagation in a flow with one spatial wavelength that is modulated at frequency ω . In this two-dimensional flow, the x component of velocity is $u_{RMS} \sin ky \cos \omega t$ and the y component is zero. Here, we present the zero-frequency limit and, in this case, our monochromatic flow will create a flame with bulges that are connected by a cusp and the total combustion rate will be much larger than that given by a flat flame. The x component of velocity is proportional to $\sin ky$, and so we assume a steady flame shape with spatial dependence only upon the y coordinate: $g(y,t) = u_T t + F(y)$, giving the equation of motion as

$$u_T - \sqrt{2} u_{RMS} \sin ky = u_L (1 + g_y^2)^{1/2},$$

where the amplitude is set so that the spatial root-mean-square velocity is u_{RMS} . Solving for the slope we get

$$g_y = \pm ([u_T/u_L - \sqrt{2}(u_{RMS}/u_L) \sin ky]^2 - 1)^{1/2}.$$

Only one value of u_T gives a flame shape that is consistent with bulges connected by cusps and that is

$$u_T = u_L + \sqrt{2} u_{RMS},$$

because for larger u_T values, the slope will be greater than zero at the velocity extreme associated with the bulge locations. For smaller values, the slope will be undefined at some locations. Figure 1 shows how this flame shape depends on the ratio of u_{RMS} to u_L .

[†]Combust. Sci. and Tech. **62**, 273 (1988).

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Figure 1. At zero frequency, the flame shape is composed of bulges connected by cusps when the flow has a single velocity component that is aligned with the flame propagation direction, $u \propto \sin ky$. One wavelength of the velocity is shown (at left) along with three flames for turbulent intensities (referenced to the laminar flame speed) of 0.1, 1.0 and 2.0.

We have shown analytically that at high frequency, the flame surface perturbations will vanish but for finite, nonzero frequencies, we have used numerical simulations in order to determine the total amount of flame surface. In Figure 2, we give the flame speed u_f dependence upon frequency for three different RMS values in a traveling flow: $u = u_{RMS} \sin(ky + \omega t)$. The other velocity component is zero. For $\omega > ku_L$ the results again indicate that any cusp nature in the flame shape disappears as the u_f value approaches u_L at large frequency. What is surprising is the rapid transition from cusp to smooth flame shape with increasing frequency and the concomitant decrease in flame speed. At zero frequency, we see very good agreement with the predicted value of $u_L + \sqrt{2}u_{RMS}$ shown by the horizontal dash. We see that the larger RMS velocity results also have a larger frequency band in which one will observe flame cusps (more of a plateau for the large RMS in comparison to the other profiles).

We have shown asymptotically and numerically that a constant-density flame will exhibit different geometrical shapes, which depend on the flow time scales. In particular, a frozen flow may yield a flame surface composed of bulges connected by cusps, whereas a pulsating flow may dampen the flame motion to the extent that only a flat, laminar flame surface will be possible. The cusp nature disappears when the eddy frequency becomes comparable to $u_L k$, where u_L is the laminar flame speed

and k is a characteristic wave number of the flow. Flame shapes obtained with a sheet of laser light¹ within a spark-ignited engine show a cusp nature only at low engine RPM, in agreement with the frequency criterion given above.

We also note that our frequency criterion for the disappearance of flame cusps gives the Gibson scale discussed by Peters.² The turbulent eddy frequency is $\omega \approx \epsilon^{1/3} \lambda^{-2/3}$, where ϵ is the turbulent kinetic-energy decay rate and λ is the eddy size. There should be no flame cusps when $\omega \lambda \geq u_L$, which gives a minimum eddy size of $\lambda \approx u_L^3 / \epsilon$. Eddies that are smaller have larger frequencies and result in a smooth flame surface, whereas eddies that are larger than this Gibson scale u_L^3 / ϵ will corrugate and wrinkle the flame.

Figure 2. Flame speed dependence on frequency in the traveling wave flow, u_{RMS} values are: $u_L/2$ ($\diamond$), u_L ($\circ$) and $3 u_L$ ($\square$); where u_L is the constant laminar flame speed. The predicted $\sqrt{2}$ zero-frequency value is indicated by a horizontal dash.

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1. A. O. zur Loye and F. V. Bracco, "Two-Dimensional Visualization of Premixed-Charge Flame Structure in an IC Engine," (SAE, New York, NY, 1987) Paper No. 870454.
2. N. Peters, *Twenty-First Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, PA, 1989), p. 1231.

Concentration Modification Through Preferential Diffusion in Sooting Diffusion Flames[†]

Inert gases with widely varying mobilities were added to the fuel side of a counterflow diffusion flame. The results suggest that soot formation is affected by concentration modification of the fuel and soot precursors due to the different diffusivities of the inert additives.

R. L. Axelbaum,* C. K. Law,* and W. L. Flower

Flame phenomena are influenced strongly by diffusion of the reactants. The diffusivities of the various species in a flame are not equal, in general, and the local reactant concentrations will depend on the extent to which the diffusivities differ. This study examines the effect on soot formation when inerts of different diffusivities are added to either reactant stream.

The counterflow diffusion flame established in the forward stagnation region of a porous cylinder is used in this study. The cylinder is mounted horizontally in a vertical wind tunnel. The oxidizer is supplied by the wind tunnel while the fuel gas (ethylene or propane) is ejected from the porous cylinder. The upstream oxidizer velocity is maintained at 38 cm/s for all studies, and the fuel ejection parameter is held constant at $f_w = -3.0$. Inert gases added to the fuel are krypton, argon, neon, and helium.

Temperature measurements are obtained with silica-coated Pt/Pt-13% Rh thermocouples. Soot measurements are obtained using standard light-scattering techniques and velocities by laser-Doppler velocimetry (LDV). All measurements are taken along the forward stagnation streamline.

Gas sampling of the stable species is performed with an uncooled, quartz microprobe. The probe has an internal plunger that allows soot build-up at the probe orifice to be removed periodically. Gas samples are obtained by batch sampling into evacuated vessels, and the gas analysis is performed by quantitative mass spectrometry.

The fuel reaches the flame zone in a counterflow diffusion flame by diffusing across the stagnation plane into the oxidizer side. Lighter species, which can diffuse more easily across the streamlines, accumulate preferentially in the region of the stagnation streamline, while heavier species are swept away preferentially. Consequently, when helium is added to the fuel, preferential diffusion reduces the fuel concentration and, hence, the soot

loading as compared to the addition of krypton to the fuel.

Soot volume fractions along the stagnation streamline are plotted in Figure 1 for flames using propane as the fuel. The curves show a strong relationship between the mobility of the inert added to the propane and the maximum soot loading for the flame. Krypton, the least mobile inert, yields the greatest soot loading while helium, the most mobile, yields the lowest.

To determine whether the cause for the change in the soot loading is modification of the fuel concentration, we also measured temperature, velocity, and species concentration profiles for these flames. Maximum flame temperatures decrease slightly with increases in mobility of the inert, krypton, yielding the highest temperature (1911 K), and helium, the lowest (1879 K). The influence of this difference was investigated by varying the flame temperature in such a way that the reactive species concentrations are not affected. The results show that even with a 43-K increase in the maximum measured temperature the soot loading increases by

Figure 1. Soot volume fraction as a function of distance from burner surface for propane/enriched air (25% O₂) counterflow diffusion flames with inert addition on the fuel side.

[†]Twenty-Second Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, PA, 1989), p. 379.

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measured temperature the soot loading increases by only 13%. Therefore, temperature effects appear to have only a small role in explaining how the inerts influence the soot-volume fractions. The measured velocity fields are essentially unchanged as the inert is varied.

The insensitivity of the velocity and temperature fields to additive mobility, implies that the local concentrations of the reactive species have been modified. Figure 2 compares measured mole-fraction profiles of helium and argon for the helium- and argon-diluted flames, respectively. The concentration of the inert diluent in the flame region is higher in the helium-diluted flame than in the argon-diluted flame.

Since the local concentrations of the additives differ, the local fuel concentrations could be

Figure 2. Mole-fraction profiles of inert additives in a 20% He/80% C_3H_8 and 20% Ar/80% C_3H_8 flame in air.

affected. Near the flame, the concentration gradients are found to be greater for the helium-diluted flame, which implies that the mole fraction of the fuel will be locally less; measured mole fraction profiles for the parent fuel support this. However, the concentration gradients are so steep near the flame that spatial measurement errors of just 0.1 mm could influence the conclusions. Fortunately, there is an alternative means of demonstrating the effects of preferential diffusion that is not sensitive to spatial accuracy.

Concentration modification of the fuel will lead to changes in the concentrations of the species deriving from the fuel. The maximum concentration these species attain in the flame is insensitive to location and is a good indicator of the relative availability of soot precursors. Table I lists the maximum mole fractions for all measured species except for ethane and 1,3-propadiene (allene), which did not display obvious maxima. The mole fractions are all higher in the argon-diluted flame and, in the case of potentially important soot-particle precursors (butadiyne, butadiene and benzene), the mole fractions are 15-25% higher. Hence, the local mixture composition is indeed modified by preferential diffusion.

The effect of inert mobility on the oxidizer side of a propane flame was also considered. Contrary to when the inerts were added to the fuel side, the maximum soot-volume fractions were found to be almost identical. Transport of fuel from the stagnation point to the flame is totally dependent on diffusion while transport of oxidizer to the flame is assisted by convection. Therefore, it is reasonable that the mobility of the inert added to the fuel would have a strong influence on fuel concentrations while adding the same inert to the oxidizer side would have little effect on fuel concentrations.

Table I
Maximum Mole Fraction of Stable Species

Species	Maximum Mole Fraction		% Diff.
	20% He / 80% C_3H_8	20% Ar / 80% C_3H_8	
Hydrogen (H_2)	0.038	0.042	+10
Carbon Monoxide (CO)	0.052	0.057	+9
Carbon Dioxide (CO_2)	0.086	0.091	+6
Methane (CH_4)	0.017	0.018	+6
Acetylene (C_2H_2)	0.018	0.020	+10
Ethylene (C_2H_4)	0.030	0.032	+6
Propene (C_3H_6)	0.0066	0.0070	+6
1,3-Butadiyne (C_4H_2)	0.00042	0.0004	+14
1,3-Butadiene (C_4H_6)	0.00066	0.00089	+26
2-Butene (C_4H_8)	0.00063	0.00068	+7
Cyclopentadiene (C_5H_6)	0.00021	0.00024	+12

A Linear-Eddy Model of Turbulent, Shear-Layer Mixing[†]

A novel method for simulating turbulent mixing is applied to turbulent shear layers. The distinctive features of mixing measured in liquid and in gaseous shear layers are reproduced.

A. R. Kerstein

Recent experimental studies of turbulent, planar, shear-layer mixing indicate that the mixing rate, suitably normalized, is a decreasing function of Reynolds and Schmidt numbers, possibly depending only on the Peclet number $Pe = Sc Re$ over a wide range of Sc values.¹ Also, the concentration at which the concentration-field probability distribution function (pdf) peaks is found to be independent of spatial location.

In the present work, a simple stochastic mixing model has been found to reproduce both the measured parameter dependences of the mixing rate and the qualitative features of the concentration pdf. Furthermore, the model reconciles the observed differences between planar shear-layer mixing and the thermal mixing layer in grid turbulence without postulating any fundamental differences between the respective mixing processes.

The computational model is based on the linear-eddy approach, which the author recently introduced as a means of modeling scalar transport in configurations for which a broad range of length scales must be resolved. The computational domain is limited to one spatial dimension to facilitate the resolution of all relevant length scales for Reynolds numbers of practical interest. The present application involves computations for Re of order 10,000, comparable to experimental conditions.

The computational domain represents a transverse coordinate of the flow field. Simulated time evolution corresponds to the streamwise evolution of a spatially developing flow. During a simulated realization, the scalar field evolves by Fickian diffusion, representing molecular processes (i.e., Schmidt number effects), and by randomly occurring rearrangements of the scalar field along the line, representing turbulent convection. In the formulation adopted here (denoted the block-inversion model), each rearrangement event involves spatial inversion of the scalar field along a randomly

selected segment of the line. The event frequency and segment size distribution are scaled in accordance with the usual Kolmogorov cascade picture. For instance, the ratio L/L_k of largest to smallest allowed segment size determines the Reynolds number scaling according to $Re \sim (L/L_k)^{4/3}$. The diffusivity of a marker particle induced by the succession of rearrangements, interpreted as the turbulent diffusivity, depends on L (integral scale), L_k (Kolmogorov scale), and an event-rate parameter. The ratio of turbulent to molecular diffusivity determines the Peclet number, and thus Sc according to $Pe = Sc Re$. The time evolution of L , L_k , and the transverse span of the shear layer (which determines the range in which block inversions are allowed) is assigned based on the observed spatial development of shear layers. In particular, Re is assumed to increase linearly with downstream distance.

Figure 1 shows computed results for the product thickness δ_p as a function of Re . Product

Figure 1. Product thickness δ_p (a normalized measure of mixing) versus $\log_{10} Re$, predicted by linear-eddy simulations for liquid (•) and gaseous (x) shear layers. The dashed horizontal line corresponds to the mean predicted value 0.32 for liquids. Also shown are the gas results (+) expressed as $-\log_{10} (\delta_p - 0.32)$ for comparison to a straight line whose slope corresponds to the Broadwell-Breidenthal³ prediction, $\delta_p - 0.32 \sim Re^{-1/2}$.

[†]Combustion and Flame, accepted (1988).

thickness is defined as the ratio of the molar concentration of product to the molar concentration of a deficient reactant in one of the free streams forming the shear layer. For $Sc=600$ (low molecular diffusivity, corresponding to liquid), δ_p is independent of Re , while for $Sc=0.7$ (high molecular diffusivity, corresponding to gas), δ_p decreases with Re until it reaches the liquid value. Both of these trends are consistent with experiments. In particular, the predicted linear dependence of δ_p on $\log_{10} Re$ is observed in gaseous shear layers.² At high Re , the results for gas phase match the slope of a solid line corresponding to $\delta_p \sim 0.32 \sim Re^{-1/2}$, where 0.32 is the mean predicted value for liquid (dashed horizontal line). This functional dependence is predicted by the Broadwell-Breidenthal model of shear-flow mixing, based on a simple picture of slow entrainment by large (size-L) eddies followed by rapid

homogenization by small (size- L_k) eddies.³ The linear-eddy model reconciles the Broadwell-Breidenthal model with the experimental data by showing that the $Re^{-1/2}$ dependence may occur only at values of Re higher than those at which measurements were performed.

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Section 5

Two-dimensional, time-dependent computations of flame-vortex interactions provide new insight into the microstructure of reacting turbulent flows. We have shown that flame generation of vorticity in the swirling flow about a vortex is a result of unequal acceleration in the hot gases. In the computed diffusion flame shown here, the rotation direction of the new vorticity is antisymmetric with respect to the reaction zone (the extreme values of clockwise vorticity are red; dark blue indicates the extreme values of counter-clockwise vorticity). The initial vortex, not shown, had only counter-clockwise rotation.

Combustion Modeling

Flame distortion by turbulent flow causes changes in chemical reactions and intense turbulence may even quench all reaction. Turbulent flow can change the flame structure by straining or bending the flame surface or by changing the boundary conditions of temperature, fuel, and oxidizer outside the reaction zone. Chemistry, via the release of heat, can change the flow through the baroclinic production of new vorticity, as shown on the previous page. Turbulence is used to enhance mixing of fuel and oxidizer and thus the understanding and control of turbulent reacting flow has been an active area of research.

We treat an isolated vortex and find that the wrapping, folding, or wrinkling of a nonpremixed flame in a swirling flow is controlled by the ratio of vortex circulation Γ to the binary diffusion coefficient D , as shown in these examples of a flame sheet near a vortex. In these three simulations, we have fixed the value of Γ and varied the diffusion by a factor of eight and display the results after one turnover time of the vortex. The flame sheet model assumes infinite chemical reaction rate, so fuel and oxidizer cannot coexist, and thus the amount of reaction is equal to the diffusive flux of fuel and oxidizer at the flame sheet. This diffusive flux decreases with increasing time unless the strain-rate of the swirling flow counteracts the broadening of the diffusion zone.

The flame tip is produced by the maximum swirl velocity, which is at the edge of the vortical region, and in these pictures enough time has elapsed from the initially straight flame for a nondiffusive interface ($D = 0$) to be wrapped once around the vortex core; that is, one turnover time. The length of this flame tip is governed by a balance between convection and diffusion and we illustrate this by using a three-sided control volume: two sides along the flame and the third in the oxidizer region. Along the flame-sheet sides, the arrows denote the diffusive flux of the oxidizer. This oxidizer combines with the flux of fuel to produce the product and along the third side the arrows denote the convection of oxidizer. To show the diffusion at small D , the scaling of diffusion arrows is twice that of the convection scaling. The diffusive flux is dependent on strain rate and diffusion coefficient. In these three examples, the velocity and strain fields are essentially the same, so the convection of oxidizer is the same. Hence, we see that the length of the flame tip increases as D decreases, since smaller D requires more flame surface to consume the oxidizer that has been convected into this control volume.

The amount of flame tip rotation around the vortex depends on diffusion because an oxidizer that is convected to the tip region is consumed at the flame by a rate proportional to the diffusive flux. In these three simultaneous flows, the convective velocities are similar but the diffusion differs by factors of two and four. The arrows denote the fluxes. For visibility, the scaling of the diffusive flux is twice that of the convective flux of oxidizer.

Section 5

Combustion Modeling

Combustion modeling at Sandia National Laboratories emphasizes the application of innovative mathematical and numerical approaches to predict the mutual influences of reactions and fluid transport mechanisms. Most combustion applications include, in addition to chemical kinetics, complex fluid dynamics associated with a combination of multidimensional geometries, unsteady conditions, moving boundaries, and two-phase transport. Our current modeling research programs attempt to provide a fundamental understanding of these subprocesses so that future simulations will contain more realistic chemical and physical descriptions of combustion phenomena. The areas selected for study are strongly influenced by ongoing experimental research activities in which direct comparison with data from well-characterized experiments verify and extend our combustion models.

Kinetic Modeling of the RAPRENOx Process

The chemical kinetics underlying RAPRENOx are analyzed and discussed. The kinetic model developed predicts accurately the experimental results of Siebers and Caton.

J. A. Miller and C. T. Bowman*

An important class of methods for controlling NOx emissions from practical combustors is abatement, or aftertreatment. Such methods include SCR (selective catalytic reduction), Thermal De-NOx (ammonia injection), urea injection, and RAPRENOx (cyanuric acid injection). RAPRENOx is a particularly promising process whose underlying chemistry is not yet fully understood. It is our purpose to provide such an understanding.

In early experiments, Perry and Siebers¹ reported large amounts of NOx removal on short time scales both in flow reactor experiments and from diesel exhaust. Although it was clear even then that the short time scales were due at least partially to surface initiation, they proposed the following homogeneous, gas-phase mechanism following sublimation and decomposition of the cyanuric acid to isocyanic acid:

Following initiation, the sequence (a), (b), (c), (e) results in a net gain of one hydrogen atom per cycle. Consequently, as long as $k_c > k_d$, the process is a branched, hydrogen-atom chain and will be self-sustaining.

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Siebers and Caton,² in experiments subsequent to those of Perry and Siebers, found that, in the absence of surfaces, NO removal did not occur rapidly enough to be of practical interest (gas-phase decomposition of HNCO does not occur rapidly enough). To accelerate the process, they added various quantities of CO, O₂, and H₂O and measured the gas composition at a reaction time of approximately 0.8 s. Our kinetic model accounts for all their observations, quantitatively in most instances. Important features of the model are shown diagrammatically in Figure 1.

Under the conditions of Siebers and Caton, the process is initiated through the "wet CO" oxidation mechanism,

Figure 1. Reaction path diagram for RAPRENOx.

This sequence of reactions serves as a source of hydroxyl, which allows the conversion of HNCO to NCO,

Nitric oxide removal occurs through the reaction,

studied by Perry several years ago, resulting in the formation of N_2O , an undesirable. Thus, because of the excess of O_2 over HNCO, reaction (i) dominates reaction (a) in the competition for hydrogen atoms, and N_2O is produced as a by-product of the reaction. Figures 2 and 3 show, respectively, the experimental product distributions for the standard conditions

Figure 2. Measured species concentrations at the exit of a quartz flow reactor as a function of reactor temperature for fixed initial mole fractions of NO (330 ppm), CO (1260 ppm), O_2 (12.3 %), H_2O (4.5 %), and cyanuric acid (470 ppm, corresponding to 1410 ppm HNCO at complete conversion), with the balance N_2 . The residence time in the reactor is approximately 0.8 s. The data are from Siebers and Caton.

given by Siebers and Caton and our model predictions for the same cases. The agreement is very good except for a slight temperature shift in the results. This shift is probably a consequence of the model assumption that the conversion of cyanuric acid to HNCO is instantaneous, an assumption that may not be valid at the lower temperatures.

Figure 3. Model predictions for the conditions of Figure 2.

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Nitric-Oxide-Doped $H_2/O_2/Ar$ Flames: Experimental and Modeling Results[†]

The predicted behavior of nitric oxide added to $H_2/O_2/Ar$ flames using a one-dimensional flame code has been compared to flame experiments covering a range of pressure and temperature. The pressure dependence of the removal of NO through the sensitivity of the recombination reaction forming HNO was observed in both the model calculations and experiment. It was found that NO removal depends on the competition between radical attack on HNO that either recycles NO or forms NH.

R. J. Cattolica, J. A. Cavolowsky,* and T. G. Mataga*

Understanding the behavior of nitric oxide in $H_2/O_2/Ar$ flames is important because it is the basis for the subsequent study of the interaction of NO with additional chemical additives. Furthermore, such understanding is needed for the interpretation of H_2/O_2 -fueled scramjet experiments in hypersonic flow facilities that are contaminated with NO.

Nitric-oxide-doped flame experiments^{1,2,3,4} have covered a range of pressure (760 to 35 torr) and temperature (1750 to 1050 K), and have varied in the observed behavior of nitric oxide and other species. We have modeled the behavior of NO in these flame experiments using the Sandia Premixed Flame Code. This computational simulation is based on a steady, isobaric, one-dimensional model of the flame with boundary conditions specifying the gas flow rates and temperature at the cold boundary and zero gradients at the hot boundary. Although the temperature distribution in the flame can be calculated, effects of heat transfer are incorporated better into the model by specifying a measured temperature profile. The reaction set (19 species, 58 reactions) and rate constants used in the model were taken from Thorne *et al.*⁵

The interaction of NO with the chemical kinetic mechanism of an H_2/O_2 flame begins with its catalytic effect on the ignition process occurring on the reactant side of the flame. Successful flame propagation is determined by the competition between the chain branching (1) and three-body recombination reaction (2):

NO reacts with HO_2 to form NO_2 , which then reacts with H atoms to reproduce the NO and OH:

The enhancement of the H_2/O_2 ignition processes by

NO becomes more significant as the rate of (2) is increased at higher pressures (> 0.5 atm). Nitric oxide removal in the H_2/O_2 system begins with the formation of HNO by recombination:

The removal of NO is dependent on the competition between radical attack of HNO that either produces NH or recycles the nitric oxide:

The NH produced by this process reacts to molecular nitrogen by the following nitrogen-atom-controlled reaction sequence:

Because of the pressure sensitivity of the recombination process forming HNO (5), the NO removal mechanism is expected to be enhanced as the pressure is increased.

The behavior of the measured NO concentration in 76 torr, fuel-lean and fuel-rich flames¹ is shown in Figures 1a-1b along with the measured temperature profiles. In the lean flame, NO is reduced initially by 30%, but recovers to 90% of the original doping level. In the rich flame, a 45% reduction in NO from its initial level is observed. The modeling results are also plotted in Figures 1a-1b and indicate only an 8% and 20% removal respectively, for the lean and rich flames using this reaction set. The model result for the lean flame shows no recovery in the nitric oxide concentration. Increasing the rate constant for HNO formation (5) by a factor of ten results in an increase in NO removal to 15% for the lean flame and 40% for the rich flame, but no recovery of NO concentration in the lean flame is predicted.

The NO concentration and temperature profiles in a fuel-rich, atmospheric-pressure flame ($\Phi=1.6$) have also been reported.² The 35% removal of NO in this flame is confined to the first 1 mm above its sintered-bronze burner. Our model predicts 25%

[†] Twenty-Second Symposium, (International) on Combustion (The Combustion Institute, 1989) p. 1165.

*University of California, Berkeley, CA.

Figure 1. Measured and predicted nitric oxide concentration profiles in $H_2/O_2/Ar$ flames: (a) 76 torr $\Phi=0.88$ (Reference 1) and (b) 76 torr $\Phi=1.22$ (Reference 1). Reaction 5 is the kinetic rate constant for the recombination reaction forming HNO.

removal of nitric oxide in the first 2 mm above the burner surface, with an additional 40% reduction further downstream, resulting in nearly twice the overall removal as observed in the experiment. Increasing the rate constant for HNO formation (5) by a factor of ten increases the NO removal, in further disagreement with the measurements. The NO profile recalculated with (5) lowered by a factor of three is in better agreement with the overall removal of NO, but disagrees with the observed rapid removal near the burner surface. Similar variation in the predicted NO concentration profile can be obtained by varying the rates for either (6) or (7) by a factor of three. The possibility of burner surface reactions in the experiment removing NO, which are not accounted for in the flame model, makes a definitive comparison with the model difficult.

In lean and stoichiometric, low-pressure (35 torr) flame experiments,³ relative concentration profiles show no significant removal. The modeling results for these flames indicate no loss of NO, in agreement with the experiments. However, agreement with OH concentration is not good. In the stoichiometric flame, the measured OH concentration increased by a factor of three with the addition of NO. Our model for this flame shows no effect on OH concentration with the addition of NO. It has been suggested that the increase in OH results from the enhancement of HO_2 formation by (2) with NO as significant collision partner and the subsequent production of OH through reactions (3) and (4). We have enhanced the third body efficiency of NO in (2) by a factor of fifty and find no significant effect on the predicted OH concentration. We have also made LIF measurements of OH in a similar flame at 35 torr and find that NO has no effect on the OH concentration profiles, in agreement with model predictions.

Low-pressure flame gas temperatures, based on LIF measurements of OH rotational temperature, were lower substantially than in Reference 1. Within the uncertainty limits of our LIF measurements ($\pm 10\%$ NO), no significant removal of nitric oxide was observed. While the measurements indicate some NO removal for the lean and near-stoichiometric flames, the modeling results are qualitatively different, indicating maximum NO loss in the rich flames. The modeling indicates that removal of NO is dependent on the competition between radical attack reactions (6-8). Uncertainty in the rate constants for these reactions makes it difficult to predict quantitative NO reduction comparable to the experimental accuracy. To investigate further the competition between reactions (6-8), we have examined the effect of NO addition on the OH concentration in these flames, we found, however, no change in either the measured or predicted OH profiles.

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Model for Solid-Solid Combustion

We have developed a model of combustion in condensed phases. Asymptotic analysis gives analytic results for three example geometries. Numerical results are presented for one case including both "burn out" and quenching.

R. C. Armstrong and M.L. Koszykowski

Modeling of solid-solid combustion is relatively undeveloped compared to gas-phase flame theory. We have developed a simple model for the former, based on an arrangement of two materials that form a continuous phase at all compositions and on heat release by interdiffusion. We assume that the lowest enthalpy (greatest heat release) results when the final burned state is a 50/50 mixture. In this picture, the two materials form a continuous solid-solid or liquid solution throughout all accessible compositions. Although some systems of interest may not conform to a model of this simplicity, a number of them do (e.g., nickel/aluminum). Further, this model has the virtue of containing all of the essential physical differences between solid-solid flames and gas-phase flames.

In both solid-solid and gas-phase flames, the combustion wave propagates by thermal-diffusive transport of heat from a heat-releasing, inner-flame region to colder, unreacted regions ahead of the flame. In the case of gas-phase flames, the heat release is due to a locally homogeneous molecular reaction. In the case of solid-solid combustion, release is due to a nonhomogeneous, diffusive process between two materials. It is the nonhomogeneous nature of diffusion that yields new features in the flame dynamics. Our approach is to focus on the geometry of this nonhomogeneity and how it affects the flame dynamics, using two methods: a numerical model that probes areas not amenable to closed-form theory and an analytic, asymptotic theory that probes limits that occur over lengths too widely differentiated to be realized on a computer.

The asymptotic theory assumes that the activation energy for diffusion is large and uses this energy as a scaling parameter, similar to activation energy asymptotics for gas flames. The difference introduced in the solid-solid flames is the geometry of arrangement and orientation of the two substances undergoing combustion. The heat release zone should be thin (thinness measured by the inverse of the activation energy) compared to the thermal conduction zone. This, in turn, defines another distance corresponding to the size of the differ-

entiated domains of the two substances undergoing combustion and can be assumed to be much smaller than the reaction zone thickness. What remains is to select a specific geometry for the binary system. We have selected three possibilities: slabs of labile (plastic) material "A" and material "B" alternating (1) perpendicular to the flame, (2) parallel to the flame, or (3) a randomly distributed medium. The asymptotic flame speeds for each were calculated. The speeds for the first two cases are identical, since the thickness of the heat-release zone is large compared to the thickness of the slabs: thus, individual slabs are out of touch with slabs that are far enough away for the temperature to vary appreciably. The physics for all three cases is essentially the same, and their resulting flame speeds differ only by a numerical factor (if the length statistic for the random medium is considered to be the same as a quarter of the lamina thickness). Thus, the simple, nonrandom models are preferable for predicting the behavior of practical systems.

The numerical model allows us to look at more complicated cases, such as a condition similar to the parallel case above, but with slab thicknesses that vary over an order of magnitude. A numerical simulation was performed for the parallel case. The spatial domain was taken to be 30 units long with each layer being 0.15 units wide (units are normalized by the thermal diffusivity and time and are, therefore, arbitrary). The far boundary was held at room temperature; thus, when the flame runs into the far wall, it hits an infinite heat sink and is extinguished. In a departure from the analytic theory, one pair of slabs (4 times the width of the rest of the slabs) was put 1/3 of the way down the reactor. The results of this simulation are shown in a series of time slices in Figure 1. This is clearly a situation that is not amenable to the analytic theory and may illustrate the so-called "burn-out" phenomenon. The small slabs form the initial deflagration wave, and the larger slabs burn long after the wave passes. A reactor made up of only the wide slabs will not sustain a self-propagating wave.

(a)

(b)

(c)

(d)

Figure 1. Gives the results of a numerical simulation for the parallel case in four time slices. The spatial dimension is arbitrary because it is normalized by the thermal diffusivity and the absolute time. The reactor is filled with slabs 0.15 units thick and a pair of slabs four times thicker than this are placed a third of the way down the reactor. (a) Shows the deflagration wave ignited and propagating down the reactor; (b) shows the wave passing through the thick slabs without those slabs being consumed; (c) shows the deflagration wave after passing through the thick slabs, while the thick slabs themselves are slowly being consumed; (d) is taken after the deflagration wave has been extinguished on the cold boundary.

Downward Flame Propagation in Vertical Channels: Interaction of Steady Nonaxisymmetric Modes and Spinning Propagation of Cellular Flames[†]

A nonlinear stability analysis is used to describe the interaction of steady, nonaxisymmetric modes of cellular flame propagation in a long vertical channel. It is shown that certain classes of mode interactions give rise to orbitally stable, spinning flames.

S. B. Margolis and G. I. Sivashinsky*

In a recent study¹ of downward flame propagation in vertical channels, a nonlinear evolution problem was derived in the limit of weak buoyancy to describe the spatial and temporal motion of the flame front near the cellular stability threshold (*i.e.*, for Lewis numbers slightly less than the critical value below which steady, planar burning is unstable to steady, but nonplanar, disturbances). Thus, in a cylindrical geometry (Figure 1), the basic state corresponds to a steady, planar flame propagating downward (in the $-x_3$ direction), and the equation for the scaled perturbation in the location of the flame front $\Phi(r, \theta, t)$ as a function of the scaled transverse coordinates and time is given by

$$\frac{\partial \Phi}{\partial t} + \frac{1}{2}(\nabla \Phi)^2 + \nabla^2 \Phi + 4\nabla^4 \Phi + G(\Phi - \bar{\Phi}) = 0, \quad (1)$$

where G is a scaled buoyancy parameter ($G > 0$ for downward propagation) and $\bar{\Phi}$ denotes the average of Φ over the cross-sectional area of the channel. In addition, it was shown¹ that for thermally insulating walls, Φ must satisfy the additional condition

$$\mathbf{n} \cdot \nabla \Phi = \mathbf{n} \cdot \nabla (\nabla^2 \Phi) = 0 \quad (2)$$

on the walls of the channel ($\mathbf{n}$ denotes the unit normal to the channel wall). Here, we summarize the results of a recent study which shows that this model is capable of describing the spinning cellular structures that are sometimes observed in downward-propagating flames in vertical channels.²

The basic solution of the problem (1) - (2) corresponding to steady, planar burning is $\Phi = 0$, a solution that exists for all values of the buoyancy parameter G and the channel radius R . A linear stability analysis then shows that perturbations of the

form $\Phi = e^{\pm i\nu\theta} J_\nu(\lambda r)$, where λ and ν denote the radial and angular wave numbers of the disturbance, will either grow or decay in time depending on the value of G . The neutral stability boundary $G(\lambda)$, on which these perturbations neither grow nor decay, is shown in Figure 2.

For $R < \infty$, the wall conditions (2) admit only discrete radial wave numbers $\lambda_{\nu,\mu} = c_{\nu,\mu}/R$, $\nu = 0, 1, 2, \dots$, $\mu = 1, 2, 3, \dots$, where $c_{\nu,\mu}$ is the μ th root of $J'_\nu(\lambda R) = 0$. Thus, as G decreases, the basic solution first loses stability, for a given R , to disturbances of the form $\Phi \sim e^{\pm i\nu\theta} J_\nu(\lambda_{\nu,\mu} r)$, at the simple eigenvalue $G = G_s = c_{\nu,\mu}^2/R^2 - 4c_{\nu,\mu}^4/R^4$, where the values of the mode numbers ν and μ are such that they maximize G_s . However, as Figure 2 indicates, there are special values $R = R_c$ such that there are two adjacent pairs of mode numbers, (ν_1, μ_1) and (ν_2, μ_2) , $c_{\nu_1,\mu_1} < R_c/\sqrt{8} < c_{\nu_2,\mu_2}$ which simultaneously give the same value $G = G_c$ at which the basic solution first loses stability. Here, the values R_c and G_c are given by

$$R_c^2 = 4(c_{\nu_1,\mu_1}^2 + c_{\nu_2,\mu_2}^2), \quad G_c = \frac{1}{16} \left[1 - \frac{(c_{\nu_1,\mu_1}^2 - c_{\nu_2,\mu_2}^2)^2}{c_{\nu_2,\mu_2}^2 + c_{\nu_2,\mu_2}^2} \right] \quad (3)$$

In the neighborhood of such a double eigenvalue, there exist solutions of Equations (1) - (2) of the form

$$\Phi_0 = A(\tau_1, \tau_2) e^{i\nu_1\theta} J_{\nu_1}(c_{\nu_1,\mu_1} r/R_c) + \text{c.c.} + B(\tau_1, \tau_2) e^{i\nu_2\theta} J_{\nu_2}(c_{\nu_2,\mu_2} r/R_c) + \text{c.c.} + C(\tau_1, \tau_2), \quad (4)$$

where "c.c." denotes the complex conjugate of the preceding term. A nonlinear analysis then determines evolution equations for the complex amplitudes A , B , and C , the last of which determines the deviation in the mean propagation speed from that of steady, planar burning.

When one angular wave number is twice the other (*i.e.*, when $\nu_2 = 2\nu_1$ or $\nu_1 = 2\nu_2$), the equations for A and B admit time-periodic solutions of the form $A \sim |A|e^{i\phi_A\tau_1}$ and $B \sim |B|e^{i\phi_B\tau_1}$, where the slow time $\tau_1 = \epsilon\tau$, $\epsilon = |R - R_c|^{1/2}$. When these expressions for A and B are substituted into Equation

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(4), it is seen readily that the solution (4) corresponds to a spinning, nonplanar flame. Furthermore, this solution is only one member of a whole class of time-periodic modes of burning for which the magnitudes $|A|$ and $|B|$ are also periodic in τ_1 , for it corresponds to the center of the phase-plane portrait shown in Figure 3. This figure also indicates that these spinning, cellular flames are stable in the orbital sense, for a small perturbation of a limit cycle in Figure 3 at most perturbs the solution onto a neighboring limit cycle. Figure 3 was obtained for the mode interaction corresponding to $(\nu_1, \mu_1) = (1, 1)$ and $(\nu_2, \mu_2) = (2, 1)$, which satisfies the necessary condition that $\max(\nu_1, \nu_2) = 2 \min(\nu_1, \nu_2)$ for spinning propagation of cellular flames.

Figure 1. Downward flame propagation in a long vertical channel.

Figure 2. The neutral stability boundary. The set of discrete modes denoted by solid markers is for a case ($R=R_c$) in which $G=G_c$ is a double eigenvalue of the linear stability problem. When the channel radius R is perturbed from R_c , the double eigenvalue G_c splits into two simple, but closely spaced, eigenvalues, as indicated by the circular markers. The particular placement of the markers in the figure corresponds to the $(1, 1) + (2, 1)$ interaction.

Figure 3. Phase-plane trajectories for the magnitude $|A|$ of the complex amplitude A .

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A Computer Model for the Transport and Chemical Reaction of Debris in Direct Containment Heating Experiments[†]

Numerical simulations of experiments pertinent to the direct heating of nuclear reactor containments have been performed. The calculations demonstrate the effect of unusual debris-transport scenarios on the resulting pressure histories.

K. D. Marx

Considerable experimental and theoretical work has been addressed recently to the investigation of the direct heating of the atmosphere in nuclear reactor containment buildings.¹ Such direct containment heating (DCH) could occur in reactor accidents in which molten debris is expelled from the reactor core into the containment volume. The heat content of the debris would be increased by exothermic chemical reactions with the oxygen in the atmosphere, and heat exchange from the debris to the atmosphere would result in an increase in containment pressure. Interest in these processes stems from the question as to whether the pressure could exceed the design limits of the reactor.

Recent experiments in the Surtsey facility at Sandia National Laboratories in Albuquerque, New Mexico, have demonstrated some interesting phenomena associated with debris dispersal.² We have completed a series of numerical simulations which aid in the interpretation of these experiments. The computer code that is used as a basis for the calculations is the KIVA code developed at Los Alamos National Laboratory.³ This code has been extensively modified to describe DCH phenomena.

The Surtsey facility consists of a container 10 m high by 3.6 m in diameter. Debris formed by igniting a thermite powder is ejected from a chute at the bottom of the container with a predominantly upward velocity. The facility is equipped with pressure and temperature transducers and various instruments for gas and debris analysis.

The first Surtsey experiment (referred to as DCH-1) employed a debris mass of 9.5 kg. This is a relatively small amount of debris relative to concentrations in potential reactor configurations. Our numerical simulation of this experiment resulted in a peak pressure of 0.116 MPa gauge, within 22% of

the experimental result of 0.095 MPa. In a later experiment (DCH-3), 80 kg of debris was injected. The experimental pressure data is shown as the solid line in Figure 1. The peak pressure is 0.204 MPa. The results of a numerical simulation using the same model as for DCH-1 are given by the chain-dashed line. The peak pressure is 0.355 MPa.

Two important points are evident in these results. First, the scaling of peak pressure with debris mass is far from linear in both the experiment and the computation. (This was anticipated.) When the injected debris mass is increased, the gas in the container reaches a high temperature more quickly, and the heat transfer from the debris to the gas via convection and radiation thereby proceeds more slowly. This means that the debris has time to stick to the wall or ceiling or to fall out to the floor and transfer its heat to the container, rather than to the gas. This explains the basic nonlinearity observed.

The second significant aspect is that the relative disagreement between computation and experiment has become greater. The computational peak pressure is now 74% greater than that obtained from experiment. Furthermore, the experimental

Figure 1. Computer simulations of the DCH-3 experiment compared to the experimental pressure history.

[†]Trans. Am. Nucl. Soc. 57, 363 (1988).

pressure history exhibits two peaks, which do not appear in the computation. The possible explanation for these results that we have pursued computationally is as follows: Because of the slower cooling of the debris, it remains molten for a longer period of time. This means that it can stick to the walls more easily; hence the potential heat source is diminished more rapidly than anticipated in the earlier computational model. Furthermore, the double peak in the pressure data can be caused by the sticking of molten debris on the ceiling of the container and its subsequent dripping off the surface. It would then fall back down through the atmosphere and provide a delayed heat release resulting in the second peak. An alternative explanation is that the debris is trapped in a swirling cloud

near the ceiling for some time; the heat can be confined in the cloud due to the thermal saturation effect described above. When the cloud disperses, the heat will be released. There is experimental evidence for the fall of hot debris down through the container at the time of the second pressure peak, consistent with either of these scenarios.

A computer simulation was performed in which the trapping probability was increased and an appropriate delayed fall of debris from the ceiling was introduced. The sequence of events depicted in Figure 2 illustrates the processes occurring in the simulation. The pressure history is plotted as the dashed line in Figure 1. It shows that the behavior of the computed pressure history is now brought into much closer alignment with experiment.

Figure 2. Sequence of particle plots and isotherms showing the injection of debris into the Surtsey container and subsequent dripping of hot debris from the ceiling.

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The Effect of Shear on Particle Lift, Drag, and Heat Transfer[†]

Three-dimensional calculations have been performed to study the dependence of force and heat transfer on shear. Knowledge of the stress distributions on particles will aid understanding of droplet breakup processes, while surface heat flux distributions provide insight into drop heat up.

D. S. Dandy and H. A. Dwyer*

The transport of particle-laden flows plays an important role in many combustion processes and, as a consequence, a great deal of experimental work has been done to study the effects of the coupling between fluid flow, heat and mass transfer and drop shape.¹ All theoretical work done thus far on drops and particles at finite Reynolds numbers has been limited to the case where the outer flow field is assumed to be axisymmetric, thereby reducing the computational domain to two dimensions. Approximate solutions have been obtained for drops in the limit of very small deformation for either high or low Reynolds number. Numerical solutions for drops and particles at finite Reynolds numbers have either required that the body remain spherical in shape, or allowed to deform in a finite manner, but all have assumed that the flow is uniform and the domain is infinite in extent.

A more realistic situation is for the particle or drop to be moving in the presence of an obstacle such as a wall, and this additional surface will influence the flow field around the particle. For flow past a planar surface, the flow near the wall is a simple shear flow, and thus any particle present in this region would experience a linear flow field, with the fluid velocity going to zero at the wall. The nonuniformity of this flow results in a force imbalance on the particle surface in the direction normal to the wall, causing the particle to drift away from the wall. The drag (that is, the force on the particle in the direction of the bulk fluid motion) would also be affected by the nonuniform velocity distribution in the outer fluid. Approximate solutions in the limit of low Reynolds number R have been obtained² using analytical techniques to study the effects of walls on the motion of single particles. No analysis for particles or drops in shear flows at finite Reynolds number have been published, primarily due to the three-dimensional nature of the system. This flow problem is important and is the first step in the study of

the motion and breakup of droplets in shear flows near walls.

We assume that a spherical particle is suspended in a shear flow whose undisturbed velocity is given by $U_\infty + \omega x$, where U_∞ is the undisturbed velocity at the centerline of the particle, x is the distance measured from the particle center, and ω is the shear rate. The particle temperature is held fixed at a value one-tenth that of the temperature in the fluid far from the particle, and although the flow is not isothermal, we assume that it is incompressible, and that the fluid properties do not vary with temperature.

The goals of this work are to study the coupling between flow types (the Reynolds number R and the dimensionless shear rate a), the resulting velocity and pressure fields, and heat transfer characteristics in order to quantify the relationship between the computed values of the lift coefficient C_L , the drag coefficient C_D , the Nusselt number N , and the characteristics of the outer flow R and a . Solutions have been computed at a range of Reynolds numbers spanning three orders of magnitude, $0.1 \leq R \leq 100$, and shear rates spanning two orders of magnitude, $0.005 \leq a \leq 0.4$. For a 100- μm particle, these dimensionless quantities correspond to particle centerline velocities ranging from approximately 1.5 cm/s up to 1,700 cm/s and shear rates ranging from 0.5 s^{-1} to $67,000 \text{ s}^{-1}$.

For this problem, a spherical-type, boundary-fitted, coordinate grid is used in the discretization of the flow domain. The grid-generation technique was developed for construction of general, three-dimensional, boundary-fitted, nonorthogonal grids for use in free-surface problems; in the present study, the grid reduces to an orthogonal, spherical-type grid. The full Navier-Stokes equations and the thermal energy equation are solved on this grid using a recently developed finite-volume formulation that is capable of accurately computing time-dependent, three-dimensional flows.

Plotted in Figure 1 is the dimensionless lift on the sphere as a function of the Reynolds number, for a fixed shear rate $a = 0.1$. This graph can be

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separated into two regions: In the first, for $R < 40$, the lift coefficient decreases sharply with increasing R , and in the second, for $R > 40$, the lift coefficient is essentially independent of the Reynolds number. The invariance of C_L with R demonstrates the relative efficiency of lift forces at finite Reynolds numbers. In other words, increases in the inertia of the flow (ρU_∞) are accompanied by a linear increase in the amount of lift imparted to the particle, whereas at lower values of R , where viscous effects dominate, the lift coefficient is proportional roughly to the velocity U_∞ .

At values of the Reynolds number below unity, where an analytical solution for the lift force exists,³ we can obtain a simple relationship between the dimensionless lift and the dimensionless shear

Figure 1. The dimensionless lift on a spherical particle as a function of Reynolds number for a dimensionless shear rate of 0.1.

Figure 2. The relationship between lift and shear rate at a Reynolds number of 0.1. The symbols denote results from the present work, while the dashed line is from the exact solution of Saffman.

rate. This relationship is displayed in Figure 2 for $R = 0.1$. The symbols represent the results from this work, while the dashed line is the analytical solution.

For values of the shear rate studied here, it was found that, while the rate of heat transfer to the particle surface increased monotonically with increasing Reynolds number, the heat transfer rate was insensitive to the value of α at fixed R , as demonstrated in Figure 3. The dimensionless rate of heat transfer N is independent of α . Thus, although the surface distribution of heat flux changes with the shear rate, in an integral sense the average temperature gradient at the particle surface depends only on the Reynolds number—that is, on the value of the centerline velocity.

We have found also in this work that the drag force on the particle increases with both R and α , but that the drag coefficient decreases monotonically with increasing Reynolds number for fixed shear rate. Further, for fixed α , the drag coefficient, normalized by the drag coefficient for uniform flow, is constant for Reynolds numbers in the range $40 \leq R \leq 100$. Therefore, the drag on a particle at specified values of ω and U_∞ is a constant fraction of the drag on a particle in uniform flow at the same centerline velocity.

Figure 3. The dimensionless rate of heat transfer as a function of the dimensionless shear rate for two different values of the Reynolds number.

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The Effect of Particle Shape on Energy and Momentum Transport[†]

Numerical studies of flow past nonspherical bodies have been performed to examine the relationships between an external three-dimensional flow field and forces, torques, and heat-transfer rates to particles and drops.

D. S. Dandy and H. A. Dwyer*

The study of the transport behavior of nonspherical particles in uniform flows has been of interest to experimentalists for many years. Particle-laden flows are a common situation in many processes, particularly in those involving combustion. Both coal particles and liquid drops are introduced commonly into oxidizing atmospheres in the form of sprays. The distortion and breakup of burning drops, and the devolatilization and combustion of coal particles, are fundamentally important processes, yet they are both little understood, except on gross, macroscopic scales. Until recently, numerical studies of drops or particles were limited to two-dimensional or axisymmetric cases, due to the complex, nonlinear phenomena being modeled and to the lack of computational power necessary to successfully investigate these problems.

We assume that a cold particle of temperature T_p is suspended in a steady, uniform flow whose freestream velocity is U_∞ and temperature is T_∞ . The particles studied in the investigation are ellipsoids with aspect ratios varying from 1:1 (spherical) to 4.1:1. The coordinate system has been generated by revolving a planar, elliptical, coordinate system about the major axis of the ellipse. Angle of attack of the particle was varied from zero degrees (parallel to the major axis) to 90 degrees (normal to the major axis). The Reynolds number has been defined using a characteristic length scale based on the minor axis radius, and it has been studied parametrically over the range $10 \leq R \leq 100$. The particle is assumed to be rigid and to have a no-slip surface. It is also assumed that the outer flow is incompressible and that the fluid properties are independent of temperature, allowing the outer fluid to be characterized by the constant parameters density ρ , viscosity μ , and thermal diffusivity κ .

The equations governing fluid motion and heat transfer are the continuity equation, the Navier-Stokes equations, and the thermal energy equation, written in integral form, and stated with respect to a frame of reference fixed at the center of the particle. The full three-dimensional form of the governing equations is solved to obtain velocity, pressure, and temperature at every point in the domain.

For the case where a particle is oriented so the major axis is parallel to the bulk velocity, the flow field is axisymmetric. The results for all particle aspect ratios in this orientation show that maxima in surface pressure and heat flux occur at the front stagnation point. The pressure field changes rapidly over the forward portion of the surface (that is, pressure gradients are large near the front of the particle) and then remains relatively uniform over the rear portion. In contrast, the heat flux is distributed more uniformly over the entire surface of the particle and does not exhibit an increase at the rear stagnation point as does the pressure field. Instead, the heat flux decreases monotonically from the forward stagnation point to the rear stagnation point.

When the particle is oriented to the flow at any angle greater than zero degrees, the flow field is fully three-dimensional. An interesting aspect of the three-dimensional flows is that the point on the surface where the maximum heat flux occurs does not correspond to the point where the maximum in pressure occurs. This can be seen clearly in Figure 1, where the flow is parallel to the xy -plane and impinges on the particle at an angle of 45° , and in Figure 2, where the flow is parallel to the same plane, but impacts the particle at an angle of 90° (that is, parallel to the y -axis). The maximum in the heat flux contours is shifted away from the forward stagnation point. This is particularly noticeable in Figure 2, since not only are there two points of maxima heat flux (as opposed to one point for all orientations less than 90°), but these points lie very close to the tips of the particle. In all cases the maximum heat flux is

[†]Physics of Fluids, submitted (1988).

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shifted towards the tips of the ellipse (ends of the major axis) where the acceleration of the fluid is the greatest. The ratio of the pressure drag to the total drag of a sphere at the same Reynolds number seems to be a function of shape and orientation, and all geometries yield different values. The primary trend is that the ratio of pressure drag decreases with streamlining the body shape. Detailed observations of the friction drag, however, show a much different trend, and a definite correlation with body surface area can be seen. This result is confirmed when the Nusselt number of the flows is compared to the Nusselt number of the sphere at the same Reynolds number, Figure 3. The Nusselt number for these flows, with a Prandtl number of unity, is related closely to the skin friction, and the results display similar trends (a sort of Prandtl's analogy for blunt, three-dimensional bodies).

Figure 1. Surface contours for (a) pressure and (b) heat flux for a 2.2:1 ellipse oriented at an angle of 45° to the oncoming flow. Maximum pressure occurs at the flow stagnation point, but maximum heat flux occurs near the tip of the ellipse.

Figure 2. Surface contours for (a) pressure and (b) heat flux for a 2.2:1 ellipse oriented at an angle of 90° to the oncoming flow (the flow is parallel to the y -axis). Maximum pressure occurs at the stagnation point, but there are two points of maximum heat flux, occurring near the tips of the ellipse.

Figure 3. The dimensionless rate of heat transfer, normalized by values for flow past a sphere, as a function of Reynolds number.

Flame Generation of Vorticity[†]

*Premixed flame propagation is simulated in the velocity field of an isolated vortex.
Density gradients in the flame combine with pressure gradients to form
new vorticity in the burnt gas indicating a flame generation of turbulence.*

W. T. Ashurst and P. A. McMurtry*

The structure of turbulent flow can be described by its vorticity and, from available computer simulations, it is a useful concept to describe the intense vorticity as "rod-like" in that one dimension is much greater than the other two. These rods are not necessarily straight nor are they always aligned with their neighbors. Because of this geometrical nature of the intense vorticity, a possible feature of turbulent, premixed combustion is the encounter between a flame and a vortex. In our numerical simulations, we consider an isolated vortex in two dimensions and solve for the flame structure during its propagation around and through the vortex. We include the creation of new vorticity caused by misalignment between the density and pressure gradients.

Discrete vorticity in a Lagrangian reference frame is used but the baroclinic production, or destruction, of vorticity given by $(1/\rho^2) \nabla \rho \times \nabla P$ is defined on an Eulerian grid. The density gradient $\nabla \rho$ is obtained from the calculated reaction rate in our single-scalar flame. In terms of the progress variable c that varies from zero to unity, the temperature is $T = T_0 + c \tau T_0$, and with the assumption that reaction occurs at constant thermodynamic pressure, the density is $\rho = P_0 / T$. The heat release parameter τ has the value of four in these simulations. The local, time-dependent reaction rate defines the volume expansion term in the velocity field. While the thermodynamic pressure is assumed constant, the dynamic pressure is calculated from the time-dependent velocity field on the grid used to convect the reacting scalar. Thus, $\nabla P = -\rho (D\vec{u}/Dt)$. The vorticity production is converted into Lagrangian vortices by determining the vortex circulation as the triple product of baroclinic production rate, time-step, and grid-cell area.

In our simulations, as the initially flat flame approaches the vortex, a flame tip region is created by the maximum swirl velocity; i.e., a small region of flame begins to wrap around the vortex, (see sketch in Figure 1). In this tip region, the density gradient across the flame thickness combines with the vortex-induced, radial-pressure gradient to create vorticity within the flame tip, which has the opposite rotation of the initial vortex. After observing some of the initial simulation results, it was possible to construct a simple model of this production of opposite rotation. Ignoring the contribution of the new vorticity (i.e., using only the initial radial-pressure gradient), the model estimates that a negative twin vortex is

Figure 1. Sketch of initial conditions for premixed flame propagation in the presence of an isolated vortex. The laminar flame speed is V_f and the vortex produces a maximum swirl speed of U_m at radius R_m . In the flame-tip region, the flame-density gradient combines with the radial-pressure gradient to produce vorticity with rotation opposite to that of the initial vortex.

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produced after the tip region has been wrapped once around the vortex. Hence we would obtain a dipole-like structure from the initial monopole of vorticity. However, further nonlinear development of this tip region leads to the production of vorticity with both signs of rotation.

For our selected parameters, the initial vortex circulation Γ_0 is the ratio of flame-passage to vortex turnover time. The flame-passage time is the time required for flame propagation across a distance equal to the vortex diameter ($= 2R_m$ in Figure 1) and the turnover time is $2\pi R_m / U_m$. Figure 2 presents the instantaneous creation of circulation for five different rotation rates. In all cases, we see that the creation of negative circulation has a period with slope ≈ -2 , which is related to the generation of vorticity in the tip region.

Figure 3 presents the flame shape, discrete-vorticity velocity vectors, and contours of the vorticity at two times for the case of flame-passage time twice that of the vortex turnover time. The flame motion is from right to left and the initial circulation is positive, counterclockwise rotation. At the

Figure 2. Time development of the baroclinic production of circulation in cases with slow, medium, and fast rotation rates. The ratio of flame-passage time to the vortex turnover time is Γ_0 , the initial vortex circulation. Note that in each case, there is a period with negative creation rate with slope -2. This creation occurs in the flame-tip region.

first time shown, the negative vorticity is in the flame-tip region but at later times, the negative vorticity is spread around the initial vortex core. Area integration of the vorticity indicates a 70% loss from the initial value but integration of only the positive vorticity shows very little reduction. It is the creation of the negative vorticity that gives the appearance of circulation loss. The effect on the far-field velocity would be a weakening one but in the neighborhood of the vortex, the velocity fluctuations would become stronger.

We conjecture that flame generation of turbulence occurs for those three-dimensional vortex structures that encounter the flame "side-on" and have rotation times comparable to the flame-passage time.

Figure 3. Computed flame geometry, shown by contours of the progress variable, and discrete-vorticity velocity vectors (on the left) and contours of vorticity (on the right) at two times. The flame passage time is twice the vortex turnover time. At early times the negative vorticity (dotted contour lines) is in the flame-tip region but at later times the negative vorticity surrounds the initial positive vorticity.

Section 6

Flame processes are used to manufacture a wide variety of materials, including optical fiber. The photograph shows a methane/oxygen flame produced by a Vapor Axial Deposition burner employed in optical fiber synthesis; the bright white streaks result from the decomposition of silica precursors to form silica particles. Spontaneous Raman spectroscopy (SRS) has yielded spatially resolved temperature profiles of this flame. Scattering by silica particles of a frequency-doubled Nd:YAG laser used in the SRS experiments produces the two green spots.

The figure shows a schematic of a Vapor Axial Deposition (VAD) burner and flame used in optical fiber manufacturing. In the VAD process, silica is formed by injecting silicon tetrachloride (SiCl_4) vapor, mixed with oxygen, through Tube 1 into a methane/oxygen flame. Methane enters the flame through Tubes 3, 5, and 7, while oxygen flows through Tubes 2, 4, 6, and 8. The submicron particles that are formed deposit thermophoretically on a rotating mandrel and are processed further to produce optical fiber.

The lean methane/oxygen flame produces temperatures as high as 3000 K, generating considerable amounts of bright blue radiation. Decomposition of SiCl_4 generates the white light in the flame. Since oxidation of SiCl_4 requires oxygen at temperatures above 1350 K and hydrolysis requires hot water vapor, particles do not form until diffusing SiCl_4 contacts hot gas from the flame. SRS temperature profiles determined by spontaneous Raman spectroscopy in the radial and axial directions confirm this. As a result, a cylinder of particles forms around the centerline, seen in the photograph as two streaks of white light; the scattering of laser light (shown by the two green dots in the photograph) reveals the presence of silica particles. When hot combustion products reach the centerline (4.5 - 5.0 cm above the burner), the cylinder merges into a single bright flame.

This burner was developed to create high temperatures along the flame centerline and to confine the silica particles formed to a narrow stream. Optimization of such a complex manufacturing process requires knowledge of the flame characteristics that affect particle deposition and, in particular, flame temperatures. Sandia researchers have obtained temperature measurements in this VAD flame using spontaneous Raman spectroscopy with high spatial resolution. The results have yielded new insight into the structure of VAD flames and will assist in the development of computational models designed to predict particle deposition rates.

Section 6

High-Temperature Materials

Research in high-temperature materials at Sandia National Laboratories is sponsored primarily by the Materials Sciences Division of the Department of Energy's Office of Basic Energy Sciences. Emphasis is on the use of laser-based techniques—primarily Raman scattering, nonlinear optical spectroscopies, and other supporting analytical methods—to study systems *in situ* and in real time. This effort focuses on the interface between the material surface and its gaseous environment and includes research in the formation of thin films or particles; adsorption and segregation studies; flame-generated species, including deposition onto immersed materials, with concomitant gas/surface and deposit/substrate reactions; and the development of advanced diagnostic methods for application to these and other multiphase studies. The work is interdisciplinary in character, involving the chemistry, physics, and fluid mechanics of the systems studied using nonperturbing probes and modern computational techniques.

Work described here utilizes Raman scattering to understand material reactions in systems ranging from alloy and ceramic surfaces under high-temperature conditions to flames used for material synthesis, including silica-laden flames used in optical fiber manufacturing. The development of Raman diagnostics for flames containing high concentrations of silica particles has resulted in the first nonintrusive temperature measurements in an optical fiber synthesis flame.

In the area of metal and ceramic interfaces, we discuss recent work that elucidates the light-scattering mechanisms that are found for alloys and high-temperature superconductor ceramics at temperatures characteristic of processing conditions. Continued exploration of new optical second-harmonic generation techniques—capable of providing real time, *in situ* interface information at the atomistic level from ultra-high vacuum to ambient pressure conditions—has yielded fundamental data for metal surfaces on the modification of their properties by adsorbates and on the effect of polycrystalline structure on diagnostic probe applications.

Spontaneous Raman Measurements of Temperature in an Optical Fiber Preform Flame[†]

Dramatic changes in flame structure are observed when a silica precursor is added to flames used by the optical fiber industry.

M. D. Allendorf, J. R. Bautista,* and E. Potkay*

The manufacture of communications-grade optical fiber employs high-temperature, gas-phase synthesis techniques to provide impurity-free materials, thus minimizing optical losses over long distances. In one of these techniques, Vapor Axial Deposition (VAD),¹ a methane/oxygen flame is used to decompose silicon tetrachloride (SiCl_4) in the presence of excess oxygen to form silica. The submicron particles formed are deposited by thermophoretic forces onto a preform, which is further processed to make optical fiber. Complex burner geometries have been developed to increase flame temperatures, promote reaction of the silicon tetrachloride, and confine particulates to a well-defined volume for efficient deposition. To assist in the difficult process of flame optimization, computational models are being developed to predict deposition rates; such models require spatially resolved experimental measurements of key flame characteristics for verification.² Temperatures within the flame are particularly important, since they provide a monitor of the extent of combustion, as well as insight into the deposition process (particle growth is affected strongly by the temperature-dependent viscosity of silica).

In this work, we have characterized a methane/oxygen VAD flame in the absence of silica particles, using spontaneous Raman scattering (SRS) from oxygen present in the flame. These are the first spatially resolved temperature measurements in a flame of this type. In addition, we have made limited measurements of temperature in the presence of silica particles, formed by the addition of silicon tetrachloride vapor to the flame. These measurements provide insight into particle formation in VAD flames and indicate that further experiments using spatially resolved optical techniques (such as SRS) will be of considerable value in optimizing this complex manufacturing process.

All measurements were made in diffusion flames produced by a VAD burner consisting of eight concentric quartz tubes, the largest having an outer diameter of 32 mm. Mass flow controllers (MFC) were used to determine the flow of fuel and oxidizer to the burner. Tubes 3, 5, and 7 were connected to a single MFC feeding methane to the flame. Oxygen entered the burner through Tubes 4, 6, and 8; these were also controlled by a single MFC. Tubes 1 and 2 were controlled by separate MFCs. Oxygen, with or without silicon tetrachloride vapor, entered the flame through the central tube (Tube 1); nitrogen was also substituted for oxygen (without silicon tetrachloride vapor). Tube 2 provided additional oxygen. Gas flow rates were as follows: Tube 1, 3.0 slpm; Tube 2, 3.0 slpm; Tubes 3, 5, and 7, 15.5 slpm total flow; Tubes 4, 6, and 8, 35 slpm total flow. Silicon tetrachloride vapor was obtained by bubbling oxygen through liquid silicon tetrachloride at room temperature. Approximately 1.6 grams SiCl_4 /min (~ 1.0 ml/min of liquid SiCl_4) was deposited in the flame.

In the absence of silica particles, flames approximately two feet high and extremely luminous were produced by the VAD burner. Addition of SiCl_4 to the flame produced a bright streak of radiation along the flame centerline, doubling the radiation-energy density. Raman spectra could be obtained only under these conditions by using pulsed lasers combined with gated detection techniques. In our experiments, we used a frequency-doubled, 20-Hz Nd:YAG laser; as much as 450 mJ/pulse could be focused into the flame in the absence of silica particles without optical breakdown. When silica particles were present, breakdown thresholds decreased by a factor of 5-10, depending upon location within the flame. Raman measurements were still possible in the presence of particles, however, as no laser-modulated incandescence was observed.

Figure 1 shows temperature profiles (determined by fitting theoretical oxygen Raman spectra to flame data) measured on the flame centerline and in the radial direction at several locations above the

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burner surface. The sharp increase in temperature along the centerline, peaking near the adiabatic flame temperature (3036 K) indicates the presence of a flame front. The low temperatures along the centerline up to ~ 3.0 cm above the burner are due to the high, cold-gas velocity through Tube 1 (> 8 m/s) and explain the absence of silica particles in this region (SiCl_4 requires temperatures above 1375 K to achieve substantial reaction rates with oxygen). Steep temperature gradients are observed also in the radial direction, but could not be followed further than 2.0 mm from the centerline due to low oxygen concentrations and spectral interference from CO_2 .

Figure 1. Centerline (a) and radial (b) temperature profiles in a VAD flame obtained by fitting theoretical spectra to oxygen Raman spectra measured in the flame. Error bars without data points are shown at locations at which spatial inhomogeneity is apparently large. For the radial profile, data are shown at 0.51 cm (circles), 1.27 cm (squares), 2.54 cm (triangles), and 3.81 cm (diamonds) above the burner.

The addition of SiCl_4 causes dramatic changes in flame structure. Figure 2 shows axial temperature profiles obtained with and without SiCl_4 . These data indicate that the flame front has moved to a location higher on the centerline, probably 5.0 - 5.5 cm above the burner, when SiCl_4 is added to the flame. Evidence of CO_2 in spectra taken above 4.0 cm also disappears. This is due, presumably, to the increase in momentum of the gases in Tube 1 when SiCl_4 is added to the flame. Preliminary results of a computational model support this hypothesis.

We conclude from these studies that substantial changes in flame structure occur when SiCl_4 is added to VAD flames. The shift of the axial thermal front is clearly of importance to process engineers attempting to optimize the position of the deposition surface to promote higher deposition efficiency. It is thus essential to account for the thermodynamic properties and chemical reactions of silicon tetrachloride in computational models of silica formation in VAD flames. We are now attempting to understand the effects of SiCl_4 , using computational models of flame chemistry and fluid mechanics.

Figure 2. Effect of silicon tetrachloride addition on axial oxygen vibrational temperatures. Data indicated by triangles are for the flame in the absence of SiCl_4 , and data shown by squares are for 7.2 mole-percent SiCl_4 added to the flame through Tube 1.

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Spontaneous Raman Spectroscopy in Flames Containing High Concentrations of Silica Particles[†]

In contrast with carbon soot particles, large numbers of submicron silica particles in flames do not inhibit spontaneous Raman measurements.

M. D. Allendorf and R. E. Palmer

Combustion processes are used currently by industry to produce large quantities of refractory oxides such as fused silica, titanium dioxide, and uranium oxide. In addition to these bulk materials, communications-grade optical fiber is manufactured by the vapor axial deposition (VAD) process, which uses a flame to decompose silicon and germanium chlorides and co-deposit the resulting oxides on a preform. Gas-phase, combustion-synthesis techniques offer high purity and control over powder-particle size, level of agglomeration, and other powder characteristics. Increasingly, optimization and control of complex manufacturing processes (such as flame synthesis) are being approached through the development of computational models that predict production rates and materials properties as a function of key process variables. Verification of these models, as well as insight into the physical and chemical phenomena controlling synthesis, requires detailed knowledge of temperature, since measurements of gas-phase species concentrations, particle size, and particle-number density are all functions of temperature.

We have applied spontaneous Raman spectroscopy (SRS) to hydrogen/methane/oxygen/nitrogen flames containing high concentrations ($> 10^9/\text{cm}^3$) of small ($< 0.2 \mu\text{m}$ diameter) silica particles. The data reported here are the first spatially resolved, time-averaged SRS measurements obtained in the submicron, high-number-density regime, conditions that approach those typical of flame synthesis processes. The results show that, in contrast with carbon soot particles, which emit large quantities of broadband visible radiation at high temperatures, the addition of large numbers of silica particles has little or no effect upon the SRS measurements. Spontaneous Raman spectroscopy thus appears to be a promising technique for measurement of flame temperatures and concentrations in VAD flames¹ containing higher densities of silica particles than observed in these experiments.

All measurements were made in the post-flame gases of $\text{CH}_4/\text{H}_2/\text{O}_2/\text{N}_2$ flames stabilized by a stainless steel honeycomb burner with dimensions $25 \text{ mm} \times 100 \text{ mm}$. Nitrogen and oxygen were fed through the honeycomb, while fuel gases (with nitrogen added to match fuel/oxidizer, cold-gas velocities) flowed through tubes inserted into the honeycomb. A lean gas mixture was used, resulting in excess oxygen (mole fraction 0.06) and substantial nitrogen (mole fraction 0.63) in the post flame gases. Silica particles were formed by the decomposition of hexamethyldisiloxane (HMDS) vapor, fed to the flame by bubbling nitrogen through liquid HMDS at room temperature. The HMDS-saturated nitrogen gas was premixed with the flame oxygen and entered the flame through the burner honeycomb. A CW argon-ion laser operating at 514.5 nm was used to generate the Raman signal, combined with a retroreflecting, multipass cell to increase the average laser power to 60 - 75 watts. Scattered Raman light was collected at 90° to the laser beams and focused onto the slits of a double monochromator. The signal was detected by a 1024-element, intensified-diode array. Typical integration times required to record both spectrum and baseline were about two minutes. Flame temperatures were obtained by fitting theoretical library spectra to the nitrogen Raman data.

The flame produces small amounts of background radiation in the absence of particles, but there is no visible increase in flame radiation upon introduction of HMDS to the flame, although it was necessary to record the Raman baseline in the presence of particles to achieve an accurate subtraction. For purposes of comparison with other experiments performed in flames containing silica particles, profiles of particle size (Figure 1a) and number density (Figure 1b) as a function of height above the burner were measured, using dynamic light scattering to determine particle diameter and absolute scattering measurements to obtain particle-number densities. Comparison of the number densities with other silica-producing systems reported indicates that conditions produced by this

[†]High Temperature Science, accepted (1988).

burner are similar to other experimental flames that have been studied but contain ~ 100 times fewer particles per unit volume than have been found in burners used in the optical fiber manufacturing industry.

Figure 1. Flame profiles of silica particle diameter (a) and number density (b).

A typical background-corrected, nitrogen Raman spectrum obtained in the silica-laden flame and its associated theoretical fit is shown in Figure 2. It is clear from the data in Figure 2 that the presence of as many as 10^9 silica particles/cm³ does not affect seriously our ability to obtain high-quality Raman spectra. Data obtained in the presence of particles are only slightly noisier than data obtained in the clean flame. No broadband radiation from fluorescence, particle Mie- or Raman-scattering, or laser heating of the particles was evident. These results are in contrast to SRS measurements in hydrocarbon flames containing similar concentrations of sub-micron soot particles, in which Raman data could not be obtained due to intense background radiation from particles and laser-modulated incandescence.

We have calculated the amount of thermal background radiation produced by $\sim 10^8$ cm⁻³ 100-nm-diameter silica particles at 2000 K and com-

pared it with the radiation energy density calculated for the same number of carbon soot particles of comparable size.^{2,3} Silica particles produce about 1300 times less thermal radiation than carbon soot particles, emitting only ~ 0.2 mW/cm³ nm sr. It is likely that this is an upper limit, since we could not distinguish between radiation produced by particles and any chemiluminescence that could result from the combustion of HMDS. This demonstrates that the injection of up to 10^9 /cm³ of transparent particles into a flame or other hot environment should not prevent the use of time-averaged SRS to measure flame temperatures or concentrations. Thus, even though particle loadings in methane/oxygen flames employed in optical fiber manufacturing are estimated to be as much as 100 times higher than those obtained here, thermal background radiation is not expected to cause significant interference with SRS measurements.

Figure 2. A theoretical fit to a nitrogen Raman spectra obtained 12.5 cm above the burner. The difference between theory and data is shown on the horizontal line below the spectra. The temperature obtained from this fit was 1933 K.

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Inelastic Light Scattering in $\alpha\text{-Fe}_2\text{O}_3$: Phonon versus Magnon Scattering[†]

Raman-scattering measurements of $\alpha\text{-Fe}_2\text{O}_3$ at temperatures between 300 and 1175 K and of $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ mixed oxides at 300 K have been performed. The temperature dependence of the frequency, width, and intensity of the 1320 cm^{-1} peak near and above the Néel temperature (960 K) of $\alpha\text{-Fe}_2\text{O}_3$ establishes that this peak arises from phonon scattering and not from two-magnon scattering as previously reported in the literature. The 1320 cm^{-1} peak is shown to be an overtone of a phonon that is forbidden and unobserved in $\alpha\text{-Fe}_2\text{O}_3$ but is observed in $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions.

K. F. McCarty and D. R. Boehme

Raman scattering from $\alpha\text{-Fe}_2\text{O}_3$ has been the subject of several investigations.¹ Given the magnetic structure of $\alpha\text{-Fe}_2\text{O}_3$, magnon scattering must be considered in addition to phonon scattering. Below the Néel temperature (T_N) of 960 K, $\alpha\text{-Fe}_2\text{O}_3$ is antiferromagnetic. Single-crystal studies have identified the seven Raman-active, zone-center phonons allowed in the corundum-type structure of $\alpha\text{-Fe}_2\text{O}_3$.¹ These allowed one-phonon bands all occur below $\sim 620\text{ cm}^{-1}$. However, there is an additional band at approximately 1320 cm^{-1} of considerable intensity. This band has been shown to be resonantly enhanced over much of the visible spectrum.¹

On the basis of calculations and the temperature dependence of the intensity,¹ the 1320 cm^{-1} band has been interpreted as arising from two-magnon scattering. Martin *et al.*¹ measured the temperature dependence of the 1320 cm^{-1} band up to approximately 670 K, nearly 300 K below T_N . The decrease in normalized Raman intensity on approaching 670 K was taken as supporting the assignment of the 1320 cm^{-1} band as two-magnon scattering.

Here, the intensity of the 1320 cm^{-1} band has been examined at temperatures up to 1175 K, over 200 K above the Néel point of $\alpha\text{-Fe}_2\text{O}_3$. The temperature dependence of the frequency, width, and intensity establishes that it arises from phonon scattering and not from magnon scattering. Data are presented showing that the 1320 cm^{-1} band is an overtone (second order) of a first-order phonon band which is forbidden and unobserved in $\alpha\text{-Fe}_2\text{O}_3$ but is observed in $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions.

An $\alpha\text{-Fe}_2\text{O}_3$ pellet of sintered powder (Puratron grade) in a flow of oxygen was used to obtain the Raman spectra as a function of temperature. The

510.6-nm laser line of a copper-vapor laser ($\sim 30\text{-ns}$ pulse length) and a diode array detector gated in synchronization with the 6-kHz pulse train of the laser allowed efficient rejection of the blackbody radiation imaged from the sample and furnace.

As a function of temperature, Figure 1 illustrates the normalized intensity of the 1320 cm^{-1} band obtained by dividing by the sum of the peak areas of the fundamental phonons at ~ 300 and $\sim 415\text{ cm}^{-1}$. While this normalized intensity decreases by a factor of about 2.2 from room temperature to 1175 K, there is no indication that the intensity extrapolates to zero at temperatures above 1175 K. Instead, the normalized intensity decreases smoothly with temperature. Increasing the temperature from 300 to 1175 K caused the peak to shift downward in frequency by 42 cm^{-1} . The full width at half maximum (FWHM) of the peak increased from about 65 cm^{-1} at 300 K to about 120 cm^{-1} at 1125 K.

Figure 1. Normalized intensity of the 1320 cm^{-1} band of $\alpha\text{-Fe}_2\text{O}_3$ as a function of temperature. The values, normalized to the sum of the peak areas of the ~ 300 - and $\sim 415\text{-cm}^{-1}$ phonons, show that no significant changes occur near the Néel temperature of 960 K.

[†]Solid State Commun. 68, 799 (1988).

The two-magnon scattering of other anti-ferromagnets strongly shifts with temperature and the peaks become extremely broad on approaching T_N . In addition, the intensity of two-magnon scattering decreases significantly with increasing temperature. These results are to be contrasted with the present findings. First, the 1320 cm^{-1} peak shifted by only 42 cm^{-1} over an 875 K difference in temperature. This represents $\sim 3\%$ shift in frequency relative to the frequency of the peak. Second, the FWHM approximately doubled over an 825 K difference in temperature and showed no anomalous behavior near T_N . Third, there was little change in the normalized intensity of the 1320 cm^{-1} peak between 300 and 1175 K .

While the observed behavior of the 1320 cm^{-1} peak is not consistent with two-magnon scattering, it is consistent with phonon scattering. Both the small changes in frequency and the slight broadening found at higher temperatures are accounted for by the anharmonicity of the $\alpha\text{-Fe}_2\text{O}_3$ lattice. For example, the 3% relative change in frequency of the peak is in good agreement with the 3 to 7% changes measured for four of the fundamental phonon peaks from 300 to 1175 K .

The 1320 cm^{-1} peak can be assigned as a phonon overtone on the basis of light-scattering results from solid solutions of Fe_2O_3 and Cr_2O_3 . These materials exhibit a new, strong Raman-scattering feature that varies nearly linearly as a function of composition from 664 cm^{-1} for $\text{Fe}_{1.73}\text{Cr}_{0.27}\text{O}_3$ to 685 cm^{-1} for $\text{Fe}_{0.40}\text{Cr}_{1.60}\text{O}_3$. Besides $\alpha\text{-Fe}_2\text{O}_3$, all the mixed-metal solid solutions and Cr_2O_3 exhibit a Raman band in the region of 1350 cm^{-1} that is also nearly a linear function of composition. The room temperature data of Figure 2 show that the $\sim 1350\text{ cm}^{-1}$ peaks of the mixed-metal materials occur at almost exactly twice the frequency of the $\sim 675\text{ cm}^{-1}$ peaks, clearly establishing that the $\sim 1350\text{ cm}^{-1}$ peaks are overtones of the $\sim 675\text{ cm}^{-1}$ peaks. Extrapolation of the frequency-composition relationship of the solid solutions to pure $\alpha\text{-Fe}_2\text{O}_3$ predicts a value of approximately 661 cm^{-1} for this feature. The overtone of this unobserved band would be expected at approximately $2 \times 661 = 1322\text{ cm}^{-1}$, in excellent agreement with the experimental value of 1319 cm^{-1} .

The phonon nature of the $\sim 675\text{-cm}^{-1}$ band of $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions has been confirmed by measurements of its temperature dependence. All the solid solutions prepared exhibit significant scattering intensity at room temperature for the $\sim 675\text{ cm}^{-1}$ band. However, the Néel temperatures of the chromium-rich solid solutions are considerably below room temperature. For example, the Néel temperature of $\text{Fe}_{0.4}\text{Cr}_{1.6}\text{O}_3$ is approximately 150 K . Further, the 685-cm^{-1} band of $\text{Fe}_{0.4}\text{Cr}_{1.6}\text{O}_3$

has significant intensity at temperatures exceeding 675 K , more than 525 degrees over its Néel temperature. Thus, the temperature dependence of the $\sim 675\text{-cm}^{-1}$ band establishes that it is phonon in origin. Based upon the relatively narrow width of the band (with FWHM values comparable to the known fundamental phonon bands), it is reasonable to assume that the $\sim 675\text{-cm}^{-1}$ band is one-phonon in origin.

Figure 2. Comparison establishing that the $\sim 1350\text{ cm}^{-1}$ bands of the solid solution $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ are overtones (second-order phonons) of the $\sim 675\text{ cm}^{-1}$ phonons. The $\sim 675\text{ cm}^{-1}$ phonons are observed only in the mixed-cation materials and are not Raman allowed in pure $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 .

It is likely that for $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 , these phonons are symmetry- or selection-rule forbidden but become allowed in the mixed-metal solid solutions as a result of symmetry-breaking processes. Based on the IR spectra of $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 , it is tempting to assign the $\sim 675\text{-cm}^{-1}$ peak to a phonon, normally only IR-active, that becomes Raman-active due to the breaking of symmetry centers in the structure. For example, $\alpha\text{-Fe}_2\text{O}_3$ has an E_u phonon at $\sim 593\text{ cm}^{-1}$ and an A_{2u} phonon at $\sim 594\text{ cm}^{-1}$. Similarly, Cr_2O_3 has an E_u phonon at $\sim 672\text{ cm}^{-1}$ and an A_{2u} phonon at $\sim 630\text{ cm}^{-1}$. These values are in reasonable agreement with the values of 661 cm^{-1} and 694 cm^{-1} extrapolated from Figure 2 for the unobserved modes of $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 , respectively. Overall, the $\sim 1350\text{-cm}^{-1}$ peak, observed for the entire $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution, is an overtone of a fundamental phonon observed only for the mixed-metal solid solutions.

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High-Temperature Raman Measurements of Single-Crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [†]

We report *in situ* Raman spectra from single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at temperatures from 20 to 770°C. As $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ is heated above ~100°C, a three-dimensional reorganization (disordering) of the oxygen in the structure results in the formation of oxygen vacancies at the O(4) sites.

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The electrical properties of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ depend critically upon the oxygen content and thermal history of the material. The Raman-active phonon modes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ are highly sensitive to oxygen content and are dominated by Cu-O vibrations and, therefore, probe the structure responsible for superconductivity. We report here Raman spectra from single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at temperatures from 20 to 770°C in oxygen and from $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ at temperatures from 20 to 545°C in argon.

Copper has two distinct sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: planar sites, Cu(2), and linear chain sites, Cu(1). The planar sites are actually distorted square pyramids with strong bonding to the planar oxygens (O(2) and O(3) sites) and weaker bonding to the out-of-plane oxygen (O(4) site). The coordination of the other copper site, Cu(1), depends upon whether the structure is orthorhombic (superconducting) or tetragonal. In the basal plane (*i.e.*, $z=0$) of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$, Cu(1) and O(1) form linear O-Cu-O chains along the *b*-axis. Additional oxygen atoms, O(4), connect to the chains, making Cu(1) planar and four-coordinate. In the tetragonal phase, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the O(1) and O(5) sites are either partially and equally occupied in a random manner ($\sim 0.6 < x < 1.0$) or are both totally vacant in the ordered phase, $\text{YBa}_2\text{Cu}_3\text{O}_{6.0}$.

The Raman measurements were made at elevated temperatures in a microprobe equipped with a hot stage through which gas could be flowed. The thin, platelet-shaped crystal was heated from room temperature (RT) to 770°C in pure oxygen and slowly cooled. An oxygen-deficient material was prepared by heating the crystal in purified argon at 545°C, resulting in a composition of $\text{YBa}_2\text{Cu}_3\text{O}_{6.24 \pm 0.1}$.

Figure 1 shows the Raman spectra obtained during cooling from 770°C to RT in a flow of pure oxygen. Between RT and 315°C, only small changes occur in the intensity and position of the Raman peaks at 435 cm^{-1} and 500 cm^{-1} . Above ~500°C, the

500 cm^{-1} phonon band shifts sharply downward in frequency, a new broad peak develops at ~570 cm^{-1} , and the 435 cm^{-1} phonon band remains practically unchanged in intensity and frequency. At 770°C, a single broad peak is observed centered around 440 cm^{-1} .

In situ neutron diffraction measurements in oxygen environments have established that

Figure 1: Raman spectra of single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ during cooling from 770°C to RT in O_2 . The estimated oxygen content is ~6.5 at 770°C and rises to ~7 at 450°C. Below 450°C, a constant oxygen content of ~7 exists. A defect-induced phonon at ~570 cm^{-1} appears above ~500°C and increases in intensity with increasing temperature and loss of oxygen.

[†]Phys. Rev. B **38**, 2914 (1988).

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$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ loses oxygen above $\sim 450^\circ\text{C}$ by forming vacancies on the O(1) and O(4) sites and that oxygen atoms then begin to occupy the O(5) sites at a slower rate.¹ The growth of the $\sim 570\text{ cm}^{-1}$ peak is clearly associated with increasing loss of oxygen and establishes that the peak results from oxygen vacancies. Based upon the observed IR spectrum and calculations of the lattice dynamics, the $\sim 570\text{ cm}^{-1}$ Raman peak can be assigned to the IR mode observed at $\sim 575\text{ cm}^{-1}$, becoming Raman active through the loss of local inversion symmetry associated with the formation of oxygen vacancies (defects).

Figure 2 shows the spectra obtained upon heating the $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ crystal from RT to 170°C in argon. Over a temperature range of $\sim 50^\circ\text{C}$ (from 90 to 140°C), the peak at 475 cm^{-1} decreases dramatically in intensity while the $\sim 570\text{ cm}^{-1}$ peak increases in intensity. The peaks at 330 and 445 cm^{-1} are largely unchanged in intensity and frequency over this temperature range.

The 475-cm^{-1} mode (A_{1g} symmetry in the tetragonal phase) consists of the symmetric stretch of the O(4) oxygen atoms along the c -axis about Cu(1). The 445-cm^{-1} mode (A_{1g}) consists of the in-phase bend of oxygen in the CuO_2 planes (O(2) and O(3)) along the c -axis. The 330-cm^{-1} mode (B_{1g}) consists of the out-of-phase motion of O(2) and O(3) along the c -axis. The dramatic changes in the phonon structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ near 100°C are interpreted as follows: With increasing temperature, a portion of the O(4) atoms move from their normal positions at the apex of the square pyramid into vacant sites at O(1) and O(5) positions on the Cu-O basal plane. The occupancy of the basal plane at the expense of the O(4) sites accounts for the loss of intensity of the 475 cm^{-1} peak and the increase in intensity of the normally forbidden peak at $\sim 570\text{ cm}^{-1}$. This rearrangement does not alter the geometry or occupancy of the CuO_2 planes. Therefore, the 330- and 445-cm^{-1} modes, involving only the motion of the oxygen atoms within the planes, are not affected. *In situ* neutron diffraction has recently established that vacancies at O(4) exist at elevated temperatures.¹ The O(4) vacancy concentration was found to be about 0.1 atoms per unit cell at 490°C for a composition of approximately $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$. The present results suggest that the O(4) vacancy concentration is significantly greater for material with a larger oxygen deficiency and that the O(4) vacancies form at relatively low temperatures ($\sim 100^\circ\text{C}$).

On the basis of thermodynamic considerations and 2-D models of the bonding interactions on the Cu-O basal plane, phase diagrams for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ have been predicted.² Model calculations have considered only order/disorder transformations within the Cu-O basal plane.² As shown here, as $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ is heated above $\sim 100^\circ\text{C}$, the

structure disorders by breaking the Cu(2)-O(4) chains along the c -axis. This is a 3-D rearrangement of oxygen atoms, not just a 2-D rearrangement of the oxygens in the basal plane. This study suggests that more attention be placed in investigating vacancies at the O(4) sites, particularly in oxygen-deficient and quenched materials.

Figure 2: Raman spectra of single crystal $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ during heating from RT to 170°C in Ar after cooling from 545°C in Ar. As $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ is heated above $\sim 100^\circ\text{C}$, dramatic changes occur in the phonon bands, resulting from a 3-D reorganization (disordering) of the oxygen in the structure involving the formation of oxygen vacancies at the O(4) sites.

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Optical Second-Harmonic Generation from Ni(110) with Adsorbed CO[†]

Optical second-harmonic generation from Ni(110) was measured and compared with that from Ni(111). Such measurements are critical to applying this diagnostic technique to polycrystalline

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Optical second-harmonic generation (SHG) is an interface-sensitive technique that provides real-time monitoring of surface geometry and chemistry. Since optical excitation and detection are employed, the technique can be used at ambient pressure. Applications to surfaces in high-temperature environments will generally involve polycrystalline surfaces. The crystalline grains have a variety of orientations and thus expose a variety of crystal planes. In order to probe chemical changes on these surfaces using SHG, it is critical to understand the different nonlinear optical response of various crystal planes. Here we present observations for Ni(110) and contrast them with observations for Ni(111) presented in the following paper (see p. 6-12 this issue).

Several researchers have observed optical second-harmonic generation from Ni(111) with adsorbed CO using excitation wavelengths of 532,¹ 700,² and 1064 nm.³ The coverage dependence of the second-harmonic intensity is similar at these three wavelengths. These data for CO adsorption on Ni(111) have been fit by assuming Langmuir adsorption of CO to a single site and linear dependence of the second-order, nonlinear susceptibility on CO coverage. In this simplified model, the derivative of coverage with respect to exposure is:

$$d\theta/d\varepsilon = S_0 (1-\theta/\theta_s) \quad (1)$$

where ε is the exposure, θ is the surface coverage, S_0 is the initial sticking probability, and θ_s is the saturation coverage. The second-harmonic intensity is given by

$$I(2\omega) = A^2 |1 + B\theta/\theta_s|^2 \quad (2)$$

Here A and B are constants and B is generally complex.

Our experiments examined the effect of CO adsorption, excitation wavelength, and temperature on the intensity of second-harmonic radiation generated at the Ni(110) surface. The surface was mounted in an ultrahigh vacuum system using ion- and cryopumping to attain a 2×10^{-10} torr base pressure.

Experiments were performed using the 1064-nm beam and the doubled 532-nm beam from a Nd:YAG laser, and the 700-nm beam from a dye laser pumped by the Nd:YAG laser. In all these experiments, p-polarized excitation was used and the p-polarized component of the second-harmonic intensity was measured. We were unable to compare directly the absolute second-harmonic intensities from clean Ni(110) with our previous work on Ni(111), since only one crystal could be mounted at a time and since the optical system was completely realigned between experiments. Nonetheless, it was clear that the signal level for SHG from clean Ni(110) was very much smaller than from clean Ni(111). We estimate the ratio was two orders of magnitude.

The effect of adsorbed CO on the second-harmonic intensity generated from Ni(110) is compared with the effect for Ni(111) in Figure 1. The signals from the clean surfaces using 700-nm excitation have been normalized to an initial value of one. The second-harmonic intensity from clean Ni(110) drops by a factor of about two upon saturation adsorption of CO, whereas the signal level from clean Ni(111) drops by a factor of about *two hundred* upon similar CO adsorption. Thermal desorption measurements have demonstrated substantial adsorption of CO on Ni(110); thus, this major difference for the two surfaces must be attributed to differences in electronic structure. The data of Figure 1 were fit using Equations 1 and 2 and varying A, B, and S_0 to obtain an optimum least-squares fit to each of the intensity versus exposure measurements.

Experiments were also conducted at 532- and 1064-nm excitation wavelengths for CO on Ni(110) to determine whether resonant or near-resonant conditions might be present at these wavelengths. The coverage dependence using 532-nm excitation was very similar to that shown for Ni(110) at 700 nm in Figure 1. Changing to 1064-nm excitation produced a considerably greater fall off in the second-harmonic intensity upon adsorption of CO as shown in Figure 2. The optical setup used does not allow absolute measurement of SHG efficiencies as a function of wavelength, and thus the curves were normalized to a value of one for the clean surface.

[†] *Proceedings of Topical Meeting on Microphysics of Surfaces, Beams, and Adsorbates* (Optical Society of America, 1989), in press.

Figure 1. Second-harmonic intensity generated at Ni(110) and Ni(111) surfaces as a function of CO exposure. Data were normalized to a value of one for the clean surfaces. For Ni(110) the intensity was independent of azimuthal orientation. For Ni(111) the azimuthal orientation was $\psi=0^\circ$, where ψ is the angle between the scattering plane and the 211 direction. The excitation wavelength was 700 nm.

Using 1064-nm excitation, the second-harmonic intensity was observed to decrease by a factor of about seven upon saturation adsorption of CO on Ni(110). These data were also fit using Equations 1 and 2.

These observations of the second-harmonic intensity from Ni(110) can be understood, at least in part, by considering the surface electronic structure of this surface. Inverse photoemission experiments on this surface show an unoccupied surface state at

Figure 2. Second-harmonic intensity generated at Ni(110) surface as a function of CO exposure at excitation wavelengths of 700 and 1064 nm. Data were normalized to a value of one for the clean surfaces.

about 2.7 eV above the Fermi level at the γ point.⁴ This state, labeled S_1 by Goldman *et al.*, disperses upward in energy upon approaching the center of the surface Brillouin zone. The largest photon energy used in our experiments is 2.34 eV. Resonant excitation would require excitation from occupied electronic states below the Fermi level to unoccupied

states such as this surface state. For the S_1 surface state on Ni(110), resonance at excitation frequencies used in these experiments is thus impossible. This is in direct contrast to the situation for Ni(111) where an unoccupied surface state exists as low as 0.5 eV above the Fermi level and exhibits dispersion allowing resonance at a wide range of ω .⁴ We believe that this different electronic structure explains the dramatic difference in second-harmonic generation efficiency at these two surfaces.

The wavelength dependence of the effect of CO on second-harmonic intensity from the Ni(110) surface is more difficult to explain. Our experiments show the greatest effect of CO on the second-harmonic intensity for 1064-nm excitation. Inverse photoemission experiments show a state which disperses from the Fermi level at the Y point to about 2 eV above the Fermi level at a point intermediate between G and Y.⁴ This state is "a composite structure incorporating a surface resonance near Y."⁵ This implies that the state has significant electron density both at the surface and in the bulk and that the ratio of surface-to-bulk density increases near Y. Resonant excitation from electronic states below the Fermi level to this state could account for a portion of the SHG from Ni(110). For excitation at 1064 nm, resonance could excite this state relatively close to the Y point where its surface character would be the greatest. This might account for the greater sensitivity of second-harmonic generation to CO adsorption on Ni(110) at 1064 nm than at 700 or 532 nm (see Figure 2).

Experiments of this type are critical for interpretation of SHG data from polycrystalline surfaces. They emphasize the important role that electronic structure plays in determining the second-harmonic response of various metallic surfaces with and without adsorbates.

In summary, second-harmonic generation from Ni(110) was much weaker than from Ni(111); there was little or no azimuthal dependence of the second-harmonic intensity, and the effect of adsorbates on the second-harmonic intensity was much less than for Ni(111).

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The Effect of Adsorbed CO on Azimuthally Resolved Optical Second-Harmonic Generation from Ni(111)[†]

A nonlinear optical probe is sensitive to surface symmetry and to the energetics and dynamics of adsorption and desorption.

R. J. M. Anderson and J. C. Hamilton

Optical second-harmonic generation (SHG) has become an important probe of interface structure and composition. A particularly useful application is the use of the second-harmonic (SH) intensity change to monitor the modification of a surface by adsorbates. Since the material property responsible for SHG at an interface is the second-order susceptibility (a third-rank tensor), the SH intensity is dependent on the symmetry of the surface electronic structure as well as the energies of surface electronic states. At an ordered surface, an adsorbate could therefore alter the SH intensity by changing the energies and/or the symmetries of surface electronic states.

In this paper, we report SHG intensity as a function of CO coverage and azimuthal sample orientation for Ni(111). The adsorption system CO on Ni(111) is one of considerable complexity involving three distinct adsorption sites for molecularly adsorbed CO. The clean surface has C_{3v} symmetry, which results in a three-fold, symmetric, SH intensity as a function of azimuthal rotation about the surface normal. The symmetry of the CO overlayer alone at saturation coverage is C_{4v} . Since the adsorbate changes the overall point-group symmetry of the surface region responsible for second-harmonic generation, this is a particularly interesting test case.

For p-polarized incident and detected light at a surface of C_{3v} symmetry, the second-harmonic intensity is

$$I_{\text{SHG}} \propto |\chi|^2 = |A + B \cos(3\psi)|^2. \quad (1)$$

Here χ is the second-order susceptibility, and A and B are linear combinations of the isotropic and anisotropic tensor elements, respectively. The symmetry components of the susceptibility depend linearly on fractional CO coverage, giving

$$\chi \propto A(1 - C_A \theta/\theta_s) + B \cos(3\psi)(1 - C_B \theta/\theta_s), \quad (2)$$

where C_A and C_B are constants.

Although adsorption of CO on Ni(111) is complex, we shall treat the data using a one-site Langmuirian adsorption model. That is, the coverage, θ , as a function of exposure, ϵ , is

$$d\theta/d\epsilon = S_0(1 - \theta/\theta_s). \quad (3)$$

The adsorption data were fit by Equations 2 and 3 using a least-squares fitting routine to vary S_0 , A, B, C_A , and C_B . Best fit of the data, assuming Langmuirian adsorption, gives $C_A = 1.05 \times \exp(i11^\circ)$, $C_B = 0.87 \times \exp(-i2^\circ)$, and $A/B = 3.57$ with an initial sticking probability on the order of unity, in agreement with thermal desorption measurements made using quadrupole mass spectroscopy. Figure 1 shows a polar graph of Equation 2 plotted using the constants derived from the least-squares fit. Individual points are taken from the adsorption data. Also included are data taken at intermediate azimuthal orientations for the clean surface. For saturation coverage, the SH intensity is almost independent of azimuthal sample orientation.

It is not possible generally to separate surface and bulk contributions to the susceptibility for a clean surface. However, it is possible to study relative contributions from surface and bulk by chemical means since the bulk contribution will not be affected by adsorption of gases or other surface chemical changes. For $\psi = 0^\circ$, the ratio of the second-

Figure 1. Calculated square root of the SHG intensity as a function of azimuthal angle, ψ , for carbon monoxide coverages, $t=0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5 . The square root of SHG is proportional to the magnitude of the second-order nonlinear susceptibility, χ . The anisotropy is continuously reduced as carbon monoxide is adsorbed on the surface.

[†]Chem. Phys. Lett. **51**, 455 (1988).

harmonic intensity from the clean surface to that from the carbon-monoxide-saturated surface is approximately 40. It is clear that for 700-nm excitation, the major contribution to the nonlinear second-order susceptibility can be attributed to the surface, since very little SHG is observed from Ni(111) with a saturation coverage of carbon monoxide. Furthermore, it appears that the changes in the nonlinear susceptibility are virtually independent of the site occupied by the carbon monoxide molecules, since the susceptibility varies linearly with coverage, independent of adsorption-site distribution.

Perhaps the most surprising aspect of this data is the persistence of three-fold symmetry in the SH intensity over the whole range of CO coverages. This is true even though IR data shows occupation of two-fold sites lacking C_{3v} symmetry. There are two possible explanations for the persistence of three-fold intensity: (1) the three-fold symmetry is broken for individual domains, but coherent optical interference between the three domains on the surface results in a three-fold symmetric pattern, or (2) the electronic states that give rise to the second-order nonlinear susceptibility retain their three-fold symmetry even after CO adsorption. This would be plausible if the initial states for resonant SHG were the somewhat localized d-band-derived states at the surface. If CO adsorption binds some of this electron density, it is possible that sites remaining free of CO would retain their three-fold symmetry, giving rise to the observed SH intensity pattern. This is consistent with the resonant excitation that we have proposed as a source of the large SH intensity from clean Ni(111).¹ We tend to prefer the second explanation based upon the excellent fit to the data using Equations 2 and 3; however, the first explanation cannot be ruled out for the experimental data presented here.

Isosteric heats of adsorption for CO adsorption on Ni(111) are strongly dependent on coverage, with a marked decrease at $\theta \sim 0.25$. This coverage dependence of the heat of adsorption must be included to model the thermally activated desorption of CO from Ni(111). The rate of desorption is written

$$d\theta/dt = -\nu \theta^n \exp(-E(\theta)/RT), \quad (4)$$

where ν is a frequency factor, n is the reaction order for desorption, and $E(\theta)$ is the coverage-dependent activation energy. For CO on Ni(111), we assumed first-order desorption kinetics. The coverage dependence of the activation energy was approximated by discrete values $E(\theta_i)$ for $\theta_i = 0.0, 0.05, 0.10, \dots, 0.40$ with a linear dependence between these values. Equations 2 and 4 were used with the values of A , B , C_A , and C_B from the adsorption fit to calculate the SH intensity. A least-squares fit to the data was used to determine ν and $E(\theta)$. The best fit was obtained with $\nu = 2.2 \times 10^{12}$. The best-fit values for $E(\theta)$ are plotted

in Figure 2. The activation energy for desorption is large at low coverages (~ 26 kcal/mole) and decreases with increasing coverage above ~ 0.25 monolayer. These desorption-activation energies agree reasonably well for $0.1 < \theta < 0.4$, with the isosteric heat of adsorption for CO previously reported in the literature.²

Figure 2. Activation energy for desorption of carbon monoxide from Ni(111) as a function of coverage. These values were derived from a least-squares fit of Equation 4 to the thermal desorption data using Equation 3 with coefficients, A/B , C_A , and C_B derived from the adsorption data.

The results presented here show the azimuthal and CO coverage dependence of SH intensity generated at the Ni(111) surface using 700-nm excitation. We find that three-fold azimuthal symmetry of the SH intensity persists over a wide range of coverages, even though IR experiments show that CO is located predominantly in the two-fold sites. We suggest that most of the SH intensity is derived from resonance with a transition involving at least one electronic state localized in the vicinity of unoccupied sites. These states apparently retain three-fold symmetry even upon CO adsorption in nearby sites. Thus, the SH intensity can be described by the C_{3v} symmetry of these states. These results emphasize the critical importance of an understanding of the symmetry of the surface and adsorbate electronic-wave functions which give rise to the second-order nonlinear susceptibility.

References:

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Section 7

A two-component, forward-scatter laser Doppler velocimetry (LDV) system is used to measure gas velocities as a premixed-charge flame propagates diametrically across the combustion chamber along a path normal to the optical axis. Shown at the left is one of the spent LDV beams being used to detect when the flame arrives at the probe volume. Refractive-index gradients deflect the beam off a photodetector as the flame passes. The sidewall location of the valves is visible through the large window in the head of the Sandia research engine.

Combustion in Engines and Furnaces

Laser Doppler velocimetry (LDV) is one of several diagnostics routinely used in our studies of premixed-charge combustion in spark ignition engines. The two-component, forward-scatter configuration shown is used most often, but the design of the Sandia research engine also permits the incident laser beams to enter the engine through the large window in the head for either backscatter or 90-degree detection of the signal.

Because of cycle-to-cycle variations in the combustion rate and the large velocity gradient across premixed-charge flames, it is essential to make conditional velocity measurements based on the location of the flame surface. The figure shows one of the spent LDV beams in the vertical plane being used to detect when the flame surface passes the LDV probe volume. The beam is focused onto an aperture in

front of a photodetector, and refractive-index gradients in the passing flame deflect the beam off the detector, creating a flame-arrival signal.

The near real-time position of the flame as it propagates along a diameter of the combustion chamber can be measured by collecting the natural light emitted by the flame through the large window and imaging it onto a linear array of optical fibers terminated by photodetectors. The time history of the flame's passage yields the propagation speed as it crosses the LDV probe volume. The simultaneous measurement of the flame propagation speed and the unburned gas velocity immediately ahead of the flame gives a direct measure of the turbulent burning velocity on a cycle-resolved basis, which is therefore free from bias from cyclic variations in the combustion rate.

Section 7

Combustion in Engines and Furnaces

Under the sponsorship of the Department of Energy's Office of Energy Conversion and Utilization Technologies (ECUT), Sandia National Laboratories is pursuing a broad program of research on the combustion processes in internal combustion engines. The program focuses on the application of advanced laser diagnostics to provide insight into critical problems impeding the development of improved engine concepts. The problem areas under investigation include the interaction between precombustion fluid mechanics and combustion, end-gas autoignition leading to engine knock, and the autoignition and combustion properties of alternative fuels for diesel applications. Research involves the development of nonperturbing, laser-based methods that provide time- and space-resolved measurements inside combustion engines. A continuing focus this year is the application of these diagnostics toward more practical engine configurations.

A complementary activity that focuses broadly on continuous combustion systems for furnace and boiler applications has begun to produce interesting new results. The program focuses on the application of advanced laser diagnostics to provide insight into critical problems impeding the development of improved furnace concepts. The initial emphasis of this program is to perform an experimental investigation of the pulse combustion process and to incorporate this new understanding into a physically based computer model. The model that has evolved is being used by industry to speed the design of compact, high efficiency, multifuel pulse combustors.

We have completed a new Spray Combustion Facility recently to study the critical processes of group combustion in steady spray flames. Laser imaging techniques may provide new insight into the controlling processes to enable combustor designers to meet future needs for increased fuel flexibility and efficiency, increased industrial productivity, and control of emissions.

Fiber-Optic Instrumented Spark Plug for Measuring Early Flame Development in Spark Ignition Engines[†]

A standard spark plug with eight optical fibers installed in a ring at the base of the threaded region is used to measure the motion and rate of growth of the early flame kernel.

P. O. Witze, M. J. Hall,* and J. S. Wallace**

Keck *et al.*¹ have used the analysis of high-speed schlieren movies of early flame development to conclude that a major cause of cyclic variations in cylinder pressure measurements is the growth rate and location of the early flame kernel. To perform this analysis, optical access to the engine combustion chamber is required, which excludes investigation in unmodified production engines. Also, because the quantification of photographic images is a laborious task, the technique is often impractical for the investigation of the statistical aspects of early flame behavior, since this requires the processing of hundreds of images.

Spicher and Velji² solved the optical access problem by installing as many as 240 optical fibers in the walls of the combustion chamber. The flame luminosity detected by each fiber is monitored with a high-speed transient recorder and this information is subsequently used to reconstruct the three-dimensional evolution of the burned-gas volume. We have adapted their technique to the immediate region of the spark plug, but use just eight fibers so that simple, digital data acquisition can be used. We achieve access to the engine by using a modified spark plug in a manner similar to Douaud *et al.*,³ who installed three ionization probes in the base of the threaded region of a standard spark plug. This allowed them to monitor the direction and rate of growth of the flame kernel in three directions in real time. Because these point measurements were made in the plane at the base of the spark plug, there is some difficulty in relating them to the actual size of the three-dimensional flame. Because our probe responds to the passage of the flame across the line-of-sight of the optical fibers, the two-dimensional perimeter of the burned gas volume is sensed.

Our resulting design is shown in the upper portion of Figure 1; the lower half of the cross-sectioned drawing shows the production spark plug design. Eight 1.0-mm-diameter holes were bored

through the threaded portion of the plug using electro-discharge machining (EDM). Because the end of each fiber is flush with the surface of the spark plug, the transmitted light is collected from within a 23° included-angle acceptance cone. The light collected by the fibers in the spark plug is transmitted through fiber-optic cords to individual photomultiplier tubes, where the response signals are amplified and used to trigger transistor-transistor logic (TTL) signals using voltage comparators. That is, when the amount of light detected by each fiber exceeds a predetermined level, an initially low, digital signal is set high. The signals from the eight fibers form a one-byte digital word that is monitored by an on-line computer. Whenever a bit in the word changes, the computer records the new word and the engine crank angle position of the word changes. The shaft encoder on our engine has 0.2 crank angle degree (CAD) resolution, which corresponds to 11 ms at 300 rev/min.

Figure 1. The lower half of the sectioned drawing shows the production spark-plug design and the upper half shows the modifications made to install eight optical fibers.

The measurements obtained with the spark plug probe are presented as the flame velocity $\vec{V}_i$, which we define as the time-averaged velocity of the flame as it moves from the spark gap to fiber i . That is,

$$\vec{V}_i = \frac{\vec{R}_i}{t_{R_i} - t_{ign}} \quad (1)$$

where $\vec{R}_i$ is the vector distance from the spark gap to the center of the i th fiber, t_{R_i} is the time when the flame is detected at the i th fiber, and t_{ign} is the time of ignition.

[†]SAE (1988), Paper No. 881638.

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While $\vec{v}_i$ is the fundamental measurement obtained with the spark plug probe, for practical reasons it is necessary to define statistical quantities that characterize the average flame velocity for continuous operation of the engine at constant conditions. The ensemble-averaged flame velocity $\langle \vec{v}_i \rangle$ is defined as

$$\langle \vec{v}_i \rangle = \frac{1}{N} \sum_{i=1}^N \vec{v}_{i,j} \quad (2)$$

where N is the number of engine cycles used in the average. Similarly, the standard deviation of the flame velocity σ_i is

$$\sigma_i = \left[\frac{1}{N} \sum_{i=1}^N (\vec{v}_{i,j} - \langle \vec{v}_i \rangle)^2 \right]^{1/2} \quad (3)$$

As a demonstration of the utility of this spark-plug probe, we chose to compare two cases of markedly different fluid mechanics. By putting a shroud on the sidewall-located intake valve of our engine, a high level of swirl is produced without the usual corresponding increase in turbulence; in fact, the turbulence is actually less than with the shroudless intake valve, because in the latter case, the sidewall location of the intake valve produces a tumbling vortex motion that generates additional turbulence during compression. The spark plug probe was installed in the flat engine head at the radial position $r = 0.4 R$, where R is the bore radius.

Ensemble-averaged, flame-velocity measurements for these two flow conditions are given in Figure 2. For the case with swirl, the flame-velocity pattern clearly shows the effects of convection in the swirl direction. Note also the large asymmetry in the standard deviation; the very low variation in the upwind direction we believe is indicative of the greater combustion stability normally associated with swirling flows. The results for the measured maximum pressures reveal that the combustion duration for

the high swirl case is considerably longer than for the case with little swirl. We interpret this to be a reflection of the large differences in turbulence levels.

Figure 2. Ensemble-averaged polar diagrams of the flame velocity for different flow-field conditions. The shaded regions indicate one standard deviation boundary. The engine speed was 600 rev/min, with ignition at 350 CAD.

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1. J. C. Keck, J. B. Heywood, and G. Noske, "Early Flame Development and Burning Rates in Spark Ignition Engines and Their Cyclic Variability," (SAE, New York, NY, 1987), Paper No. 870164.
2. U. Spicher and A. Velji, *Twentieth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, PA, 1984), p. 19.
3. A. Douaud, G. de Soete, and C. Henault, "Experimental Analysis of the Initiation and Development of Part-Load Combustion in Spark-Ignition Engines," (SAE, New York, NY, 1983), Paper No. 830338.

Linear Fiber-Optic Array for Measuring the Transient Propagation of a Premixed-Charge Flame[†]

A linear array of 16 optical fibers is used to collect and transmit visible emissions from a freely propagating flame to individual detectors, enabling real-time measurement of flame motion along a line.

P. O. Witze, D. E. Foster,* and H. Kroeger**

The most widely used technique for studying flame development is high-speed cinematography, using either visible luminosity, schlieren/shadowgraph techniques, or two-dimensional imaging. While there is no doubt that cinematography provides the most comprehensive information about the evolution of the flame shape, it is not a very practical source of quantitative data for statistical analysis of the combustion process. Thus, there is a need for high-speed, flame-measurement techniques that utilize more limited information than a complete two-dimensional description of the evolution of the flame surface.

We have been pursuing the concept of using a continuous light field imaged onto a one-dimensional array detector,¹ such as simulated in Figure 1. A laser-schlieren image of the propagating flame is imaged onto a linear photodiode array aligned with the diameter of the combustion chamber coincident with the spark plug. The laser-light intensity detected by the photodiodes is measured by scanning the array at a fixed frequency, which produces an analog signal like the one simulated in Figure 1(b). By high-pass filtering this signal, it can be made to look like Doppler "bursts" that can be processed at high speeds by a conventional laser-Doppler velocimeter (LDV) burst-counter-type signal processor; the number of cycles in the first Doppler burst of each scan of the array is simply proportional to the distance of the flame from the end wall. We have also applied this detection technique by using the real image of the visible luminosity from the flame, as illustrated in Figure 1(c). This approach is easier to implement because there is only one Doppler burst for each scan of the array, and because the source of the image is created naturally.

In principle, this flame-position measuring technique is simple to implement; in practice, we have not been able to find a commercially available photodetector that meets our requirements. The linear photodiode array that we selected has 256 elements, but because the array is only 6.3 mm long, it is difficult to focus the flame image onto the detector. More limiting, however, has been our inability to scan the array at a rate fast enough to resolve the flame motion. This constraint occurs because the scanning process also performs the task of re-initializing the capacitive-charge associated with each photodiode; when the scan rate is too fast, the device response is variant until a saturation condition is reached. The highest scan rate that we have successfully achieved is 2 MHz per photodiode, or 7.6 kHz per scan of the array. For a typical flame propagation period in an engine of eight crank angle degrees (CAD), this scan rate results in 33 flame-position measurements at an engine speed of 300 rev/min, which is more than adequate; in contrast, at 2400 rev/min, only four

Figure 1. Detection of flame motion of optical imaging: (a) laser schlieren photographs of a premixed-charge flame propagating across a disk-shaped combustion chamber; (b) simulated response of a linear photodetector array to the schlieren image; (c) simulated response to the visible luminosity image.

[†] Twenty-Second Symposium (International) on Combustion (The Combustion Institute, 1989), p. 1897.

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measurements are obtained. Although we believe that modifications can be made to the photodiode-array electronics to improve these scan rates, it is still evident that the basic concept is inefficient, in that very high spatial resolution is being achieved by using a large number of closely spaced detectors, but at the expense of poor temporal resolution. A more efficient approach would be to use a smaller number of widely spaced detectors that can be monitored in real time for a wide range of engine speeds. It was this realization that led to the development of the detector to be described here.

Because our goal is to maximize temporal resolution, we chose to build a flame-position detector having just 16 measurement points, corresponding to a single two-byte computer word. The physical size of the receiver head was selected to be practical, since both the light sensitivity and spatial resolution of the device depend on the area ratio of each of the 16 individual sensors to the area of the flame image and not on the actual size of the receiver itself. Figure 2 shows a diagram of the device we built. One-millimeter-diameter plastic optical fibers collect the light; this selection was based on the low cost and ease of working with plastic, as well as the large size relative to typical glass fibers. The diameter of the head holding the fibers is 51 mm, so that each fiber collects 0.038 percent of the average light intensity striking the head. The spacing between the fiber centers is 3.0 mm, but we increase the spatial resolution by placing a mask on the head that has slit apertures 0.42-mm wide.

The light collected by each fiber is directed onto individual end-window photomultiplier tubes. The photomultiplier signals are amplified prior to processing by voltage comparators, which generate transistor-transistor-logic (TTL)-compatible signals

Figure 2. Linear fiber-optic array detector. The sixteen 1.0-mm-diameter plastic fibers are spaced on 3.0-mm centers; improved spatial resolution is provided by the mask with 0.42-mm-wide slit apertures.

when the voltage exceeds the threshold setting. Thus, the final output signal from the device is a 16-bit word interfaced to a computer through a digital I/O board. The computer is programmed to look for changes in this word, which correspond to the passage of the flame across successive fibers. Whenever a change in the word is detected, the computer records either the engine crank angle or the clock time of the change; because the fibers detect the presence of the flame sequentially along the array, it is not necessary to record the 16-bit word itself. This polling operation by the computer is performed at a 90-kHz rate, which corresponds to 0.2 CAD resolution at 3000 rev/min, which is sufficient temporal resolution for any engine application of interest.

To demonstrate the performance of this device, real-time measurements of flame position for three different engine cycles are shown in Figure 3. The actual data are indicated by the symbols, and the lines represent cubic-spline fits to the flame-position data and the resulting flame-speed calculations. These results clearly demonstrate the degree of cyclic variability that can occur in engine combustion rates.

Figure 3. Single-cycle, real-time measurements of flame position and flame speed.

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1. P. O. Witze, *Exp. Fluids* **3**, 174 (1985).

Observation of Turbulent Flame Structure in an Internal Combustion Engine Using Laser-Induced Fluorescence[†]

Laser-induced fluorescence from OH radicals has been used to provide two-dimensional images of a turbulent, propagating flame front in an operating engine.

R. M. Green

One of the problems currently faced by engine designers is the lack of an adequate understanding of the flame-propagation process. This difficulty has been compounded by the development of the lean-burn engine, in which slow burn and bulk flame quench are major concerns. A considerable research effort is now underway in an attempt to improve our understanding of the turbulent flame-propagation process.

Recent work in our laboratory has been directed toward understanding the correlation between the turbulent, in-cylinder fluid motion and the shape (or structure) of the flame front. In a prior study,¹ we used a Mie-scattering technique to mark the flame-front position within a thin sheet of laser light. While that work provided some interesting insight into the highly wrinkled and convoluted structure of the turbulent flame, the technique proved to be difficult to implement because of the rapid fouling of the windows by the particles seeded in the intake flow. To overcome this difficulty, we turned to a technique that uses the OH radical to mark the location of the flame front,² since OH occurs naturally in both the reaction zone and the postflame gases and does not have to be seeded into the intake flow; furthermore, it will not foul the windows.

The experiments were performed in the Sandia optical research engine. For the current work, the engine was operated with an unshrouded intake valve that resulted in a very weak mean motion at top dead center (TDC); however, the strong, tumbling intake flow results in a high turbulence intensity at TDC—0.8 m/s at 300 rpm and 2.0 m/s at 600 rpm. Operating the engine using a skip-fire strategy resulted in low cyclic variability, making it easier for us to fire the laser repeatably when the flame front was located in the region observed. The engine was run unthrottled on a stoichiometric mixture of propane and air and was fired every third cycle.

A pair of small windows, diametrically opposed in the sidewalls, allowed us to pass a 9-mm-wide sheet of laser light horizontally through the combustion chamber. A large window above the piston permitted us to image a portion of the laser sheet on a two-dimensional detector. Frequency-doubled output from a dye laser was converted to a thin, colimated sheet using a long focal-length, spherical lens and a pair of cylindrical lenses. In the region where the light sheet intersected the imaging optics, the thickness of the light sheet was about 0.12 to 0.14 mm. The detector was an SIT-vidicon camera that included a second stage of intensification. Both image intensifiers were gated for a time interval of 5 to 10 μ s (that included the laser pulse) so that we collected the fluorescence emission while reducing the flame emission background to a negligible level.

A 9-mm by 13-mm region of the sheet of laser light was imaged on the face of the detector with a magnification of about 1.5. The output of the vidicon was digitized in a 100 x 100 pixel format so that the inter-pixel spacing was approximately 100 μ m. The dye laser pumped a transition in the (0-1) vibrational band near 281 nm, fluorescence emitted by transitions in the (1-1) vibrational band near 312 nm was observed.

Figures 1a and 1b are representative of the many flame images obtained. The present data appear consistent with the results obtained using the Mie-scattering technique. A qualitative comparison reveals that the geometric scale of the wrinkling of the flame front as a function of engine speed is quite similar between the two measurement techniques. The image in Figure 1a illustrates the flame shape characterized by the lower turbulence level at 300 rpm, while Figure 1b represents the case of a higher turbulence level obtained at 600 rpm. These figures demonstrate the effect of flow-field turbulence on the structure of the propagating flame front. The greater degree of wrinkling of the flame at 600 rpm results in a much larger area of the reaction zone and thus, a faster rate of propagation of the flame.

We plan to incorporate results such as these in models for the quantitative prediction of the rate of

[†]SAE (1988), Paper No. 881631.

Figure 1. Two-dimensional images of the laser-induced fluorescence from OH radicals behind the propagating flame front in an engine. (a) 300 rpm: turbulence intensity of 0.8 m/s, (b) 600 rpm: turbulence intensity of 2.0 m/s.

flame propagation in production-engine designs. In summary, this work has shown that the technique of laser-induced fluorescence can be an effective tool in the study of the important combustion processes in an internal combustion engine.

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1. T. A. Baritaud and R. M. Green, International Congress and Exposition (SAE, New York, NY, 1986), Paper No. 860025.
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Are Gas Velocities in a Motored Piston Engine Representative of the Pre-Ignition Fluid Motion in a Fired Engine?[†]

Laser-Doppler velocimetry measurements show that the mixture motion in a motored engine can be significantly different from the pre-ignition flow when the engine is fired.

P. O. Witze, M. J. Hall,* and M. J. Bennett**

It is assumed routinely that pre-ignition gas velocities in a fired engine are similar to those measured in a motored engine. However, four features of fired-engine behavior suggest that differences from motored operation might be expected. First, because the intake valve typically opens before the exhaust stroke is complete, hot exhaust gases temporarily flow into the intake port, raising wall temperatures in this region. Second, these hot gases in the intake system combine with the unscavenged gases in the clearance volume, to both dilute and raise the temperature of the fresh fuel-air charge inducted into the engine cylinder; this natural dilution is often in addition to the exhaust gas recirculation (EGR) used for pollution control in today's automobiles. Third, because the blowdown process following combustion is considerably different from the exhausting of a motored air-fuel charge, differences in the residual fluid motion in the cylinder can be expected to influence the ensuing intake process. Fourth, gas property effects can be expected from differences in density and viscosity.

We made our measurements in the engine combustion chamber shown in Figure 1. Both the intake and exhaust valves are located in the side-wall of the clearance volume and move in the radial direction. Two intake-valve configurations were used: one with a shroud that directed the intake flow along the cylinder circumference, producing strong swirl, and the other without a shroud, which gave a less-organized tumbling motion because of the sidewall location of the valve.

The engine was operated in a skip-fired mode, with combustion occurring every fifth engine cycle. The engine block, head, and intake air were all maintained at a temperature of 353 K. A stoichiometric propane-air mixture was ignited at 350 crank angle degrees (CAD), where top dead center (TDC) of the compression-expansion strokes

is defined as 360 CAD. The engine was run at speeds of 300 and 1200 rev/min, and the laser-Doppler velocimetry (LDV) measurements were made from 270 to 350 CAD for each fully scavenged fired cycle and the unscavenged cycle that followed. Measurements were made for the two spark-plug locations shown in Figure 1, such that the LDV probe volume was either centered within the spark gap or located at a considerable distance from flow disturbances created by the plug. Only the velocity component in the swirl direction, parallel to the piston surface, was measured. The LDV measurements were ensemble-averaged over a large number of engine cycles, using four CAD-wide windows within which a time average is also made.

Figure 1. Schematic of the engine combustion chamber, showing the position of the LDV probe volume and the two locations used for the spark plug.

[†]Experiments in Fluids, accepted (1988).

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Shown in Figure 2 are our measurements for the tumbling-motion condition produced by the shroudless valve. The open symbols represent data obtained from the cold, scavenged cycles, and the solid symbols are for the hotter, unscavenged cycles.

The results presented show very large differences between the scavenged and unscavenged cycles for both the mean velocity and the turbulence intensity when the measurements were obtained with the spark plug located away from the LDV probe volume (see Figure 1). Particularly surprising to us is the higher turbulence level for the hotter unscavenged cycles; we expected the turbulence to be lower because there is less mean motion available for turbulence production, and because the dissipation rates were expected to increase with the higher gas temperatures. Instead, the turbulence data suggest a large production in turbulence that peaks at 340 CAD.

In contrast, when the spark plug is moved to put the probe volume in the center of the spark gap, only small differences are seen between the scavenged and unscavenged cycle measurements. It is also interesting to note that the unscavenged cycle data are far more sensitive to the spark-plug location than are the scavenged-cycle data.

The results using the shrouded intake valve that produced high swirl showed that the differences between the scavenged- and unscavenged-cycle measurements are insignificant everywhere. Swirl that persists up to the time of ignition adds order and energy to the flow field, which reduces the likelihood for velocity differences between motored and fired engines; if the swirl motion is destroyed prior to ignition, to produce turbulence, the statement is far less likely to be valid.

Figure 2. Comparisons between scavenged (open symbols) and unscavenged (closed symbols) cycle LDV measurements of the mean velocity and turbulence intensity within and away from the spark-plug gap, for a no-swirl flow field produced by a shroudless valve. The data have been normalized by the mean piston-speed, $\bar{U}_p$, which was 3.3 m/s at 1200 rev/min.

Velocity Measurements in a 5.8 Liter Stratified-Charge Rotary Engine[†]

Laser-Doppler velocimetry has been used to investigate the flow field in a prototype 5.8 liter stratified-charge rotary engine. One rotor of the two-rotor engine was fired to drive the second "motored" rotor in which the velocity measurements were made.

P. M. Dimplefeld* and P. O. Witze

The Stratified-Charge Omnivorous Rotary Engine (SCORE[™]) is a patented engine concept that offers exceptional power density with a multifuel capability. The 580 Series engine used for this study is being developed for applications in large military vehicles and stationary power plants. Because stratified-charge rotary engines are both complex and relatively new when compared to piston engines, the experience base that is important for efficient engine design is limited in the rotary-engine field. The need to take advantage of contemporary technology was recognized early in the development stages of this engine. Parallel to the "cut and try" method, which is still the most reliable path to a new engine design, a computer simulation approach is also being pursued.^{1,2} The experimental data presented in this paper were obtained to support this modeling activity.

The particular engine we used had two rotors; one rotor was fired and acted as the dynamometer to drive the second motored rotor. A cross-sectioned schematic of the engine is shown in Figure 1. The rotor turns at one-third the engine crank speed such that there is one power impulse during each crank revolution. The three faces of the rotor are equivalent to individual pistons in a reciprocating engine. Note the combustion bowl cutouts in the faces of the rotor, analogous to the bowls used in stratified-charge piston engines. A unique feature of the engine is its tolerance to a broad range of fuels, which is achieved by the combination of low compression ratio (8.5), spark-assisted ignition, and fuel-air mixture stratification by direct injection. Shown in the upper right-hand region of Figure 1 are the spark plug, the adjacent pilot fuel injector, and the main fuel injector used to create the stratified burn. A fixed, small amount of fuel is injected by the pilot injector across the spark gap, producing a pilot flame

that then ignites the larger amount of fuel injected by the main injector, where the latter is varied to match the engine load; the engine is not throttled.

In order to perform laser-Doppler velocimetry (LDV) measurements, four windows were installed in the perimeter surface of the engine (called the trochoid), as shown in Figure 1. Window A provides access to the compression zone, B to the expansion zone, C to the exhaust zone, and D to the intake zone. An additional Window E was installed in the outer face of the intake manifold; this window was needed to gain access to Window D and also enabled measurements to be made in the intake manifold itself. To prevent damage to the windows from the apex seals of the rotor, the windows were set back from the trochoid surface by 0.8 mm. This setback resulted in leakage past the apex each time a seal crossed a window.

An unusual feature of rotary engines, in contrast to reciprocating engines, is that the individual engine events occur in different locations in the

Figure 1. Cutaway schematic of the SCORE[™] rotary engine, showing the locations of the windows installed for optical access to the motored rotor of the two-rotor engine.

[†]Proceedings of Fourth International Symposium on Applications of Laser Anemometry to Fluid Mechanics (Lisbon, Portugal 1988), p. 1.13.

*DOE Industrial Technology Program participant.

engine. This makes it necessary to move the LDV optics about the perimeter of the engine as different zones of the engine cycle are investigated. We chose to do this by cantilevering the optics off of a vertical table located at one end of the engine. Three heavy-duty posts supported a sliding base that could be positioned at variable distances from the table. The base itself could be rotated about the axis of the support posts, which allowed the incident LDV optical axis to be aligned normal to the window surface. Finally, the beam splitter, focusing lens, and backscatter-receiving optics were mounted on a traversing mechanism that allowed the measurement volume to be moved along a path normal to the window surface.

Because the rotor surface periodically passed through the LDV probe volume causing momentary saturation of the photomultiplier tube, it was necessary to place an acousto-optic modulator (AOM) in the path of the output beam from the laser. The power signal driving the AOM was gated synchronously with the engine cycle such that whenever the rotor surface intersected the incident LDV beam path, the laser output was diverted into a beam stop.

Mean velocity and turbulence intensity measurements made in this rotary engine show that the flow field is far more complex than one might expect for a flow driven at constant speed. A principal source of this complexity is the continual change of the rotor-face orientation relative to a fixed reference frame, as seen in the diagrams in the bottom of Figure 2. The data presented in this figure were obtained through Window A in the compression zone, as indicated by the arrow in the diagrams. The mean velocity is seen to decrease, remain constant for varying periods of time depending on the distance from the window, and then increase during the period shown. This retarding of the flow well below the mean rotor speed is believed to be due to a "squish" flow produced as the leading flank of the rotor crosses the minor axis of the trochoid. As the rotor continues to turn, this squish effect reverses in direction at about -60 crank angle degrees, causing an acceleration of the flow.

The turbulence intensities shown in Figure 2 do not behave in the expected manner, since it is believed generally that squish flows are accompanied by increased turbulence. This suggests that the squish motion is not characterized by the jet-like shear action found in reciprocating engines, but rather is a bulk-flow motion governed by a more gradual rate of volume change. Note also that the relative turbulence intensity is approximately 50 percent in the central region of this figure and that the turbulence field is spatially uniform.

Measurements made in the compression zone (Window A) at different engine speeds are

Figure 2. Velocity measurements within the compression zone at five locations 73.7 mm from the sidewall of the rotor housing. The dashed line indicates the mean rotor-apex speed of 19.3 m/s for an engine speed of 2400 RPM.

shown in Figure 3, normalized by the mean apex speed. Both the mean velocity and turbulence intensity data collapse to a single curve, although the range of engine speeds is too small to justify any extensive conclusions.

Figure 3. Variation of velocity and turbulence intensity with engine speed. These data have been normalized by the mean apex speed of the rotor.

References:

1. F. Grasso, M.-J. Wey, J. Abraham, and F. V. Bracco, "Three-Dimensional Computations of Flows in a Stratified-Charge Rotary Engine," (SAE, New York, NY, 1987), Paper No. 870409.
2. J. Abraham, M.-J. Wey, and F. V. Bracco, "Pressure Non-Uniformity and Mixing Characteristics in Stratified-Charge Rotary-Engine Combustion," (SAE, New York, NY, 1987), Paper No. 880624.

Cycle-Resolved LDV Measurements in a Motored Diesel Engine[†]

Cycle-resolved, laser-Doppler velocimetry measurements of tangential mean velocities and turbulence intensities were made in a motored, single-cylinder Cummins diesel engine. The measured turbulence intensities were compared to values computed using an in-cylinder fluid dynamics code that incorporates a k-ε turbulence model.

A. O. zur Loye,* D. L. Siebers, T. L. McKinley,* H. K. Ng,* and R. J. Primus*

The flow field in a diesel engine can affect its emissions drastically. Differences in mean and turbulent fluid motions at the start of injection can cause significant changes in the formation of emissions products, such as hydrocarbons, NO_x, and soot, during the premixed and the diffusion phases of combustion in a diesel. As a result, information about the in-cylinder flow field are useful to engine designers.

Numerous measurements of in-cylinder flow fields in diesel engines and devices simulating diesel engines have been made using both hot-wire and laser-Doppler velocimetry (LDV). However, most of these measurements have been made in engines employing high swirl and/or "squish" to enhance mixing. The objective of this work was to measure the in-cylinder flow field in a motored diesel engine that, by design, has low squish and low swirl. The engine used was a single cylinder Cummins NH-series diesel engine modeled after a production four-stroke, inline, six-cylinder, direct-injection engine.

Four major modifications were made to the engine to gain optical access: (1) a 3.81-cm-thick steel spacing ring (having four 3.02-cm-diameter quartz windows) was inserted between the head and the block, (2) one of the two exhaust valves was replaced by a 3.34-cm-diameter quartz window, (3) the compression ratio was lowered from 14.5:1 to 10:1, and (4) an axisymmetric piston with self-lubricating, bronze-impregnated TFE piston rings was used. The special rings allowed operation of the engine with minimal cylinder lubrication.

The overall layout of the experimental set-up is shown schematically in Figure 1. The crankshaft position was monitored with two shaft encoders with 1° and 0.2° resolution. A standard, forward-scatter LDV system was used. The LDV optics were

mounted to allow relocation of the probe volume without affecting the alignment of the optics.

Crankshaft position from the shaft encoder and velocity information from the counter were acquired through a digital I/O board by an IBM PC/AT microcomputer and later processed on the same

Figure 1. Schematic of the laser-optic-instrumented Cummins engine and the laser-Doppler velocimetry layout.

machine. A cycle-resolved analysis of the data was performed following the basic analysis of Liou *et al.*¹

Velocity measurements were made 0.9 cm below the head along a cylinder diameter at two engine speeds: 300 rpm and 600 rpm. Figure 2 shows profiles of the ensemble-averaged, tangential velocity at each speed for three different crank angles. The profiles in Figure 2 indicate that before top dead center (TDC) compression, the flow deviates significantly from solid-body rotation and is three-dimensional in nature, a characteristic that we attribute to an intake-induced tumbling motion. At TDC and after, the profiles indicate that the tumbling motion has broken up, leaving a weak solid-body rotation for the rest of the cycle. Figure 2 also shows that the mean flow scales well with engine speed over the rpm range examined.

Profiles of the tangential turbulence intensities are shown in Figure 3 for the same conditions as in Figure 2. The figure shows that the turbulence intensity is relatively homogeneous at the measure-

[†]SAE (1988), Paper No. 890618.

*Cummins Engine Company, Columbus, IN.

Figure 2. Normalized velocity profiles of the ensemble-averaged, tangential velocity component at three crank angles. Circles indicate location of the cylinder liner. (The mean piston speed at 300 rpm is 1.5 m/s.)

scales well with engine speed. At TDC compression, the turbulence intensity is about 1/6 the mean piston speed. This intensity is lower than the value of about 1/2 the mean piston speed that is often observed by researchers.

The measured turbulence intensity as a function of crank angle at a radius of 4.45 cm is shown in Figure 4, along with the turbulence intensity computed for the conditions of our experiment with a two-dimensional version of KIVA.² (KIVA is an in-cylinder fluid dynamics code with a k- ϵ turbulence model.) The purpose of comparing the measured and the computed turbulence intensities was to evaluate the ability of this version of KIVA to predict turbulence intensities in our quiescent, low-squish, low-swirl engine.

In general, the measured and computed turbulence intensities agree within 25%. However, prior to TDC, the model predicts a decay in turbulence intensity not noted in the measurements. We attribute this lack of agreement to the production of turbulence resulting from the breakup of the large-scale, three-dimensional tumbling motion noted prior to TDC in the ensemble-averaged velocity profiles. This breakup is a process that cannot be predicted by the two-dimensional model. After TDC, when the ensemble averaged velocity profiles indicate that the flow is nearly two-dimensional, the trends and the values of the measured and the predicted turbulence intensities agree very well.

Figure 3. Normalized tangential component of the turbulence intensity at three crank angles. Circles indicate location of the cylinder liner. (The mean piston speed at 300 rpm is 1.5 m/s.)

Figure 4. Comparison between measured and computed turbulence intensities at $r = 4.45$ cm. (The mean piston speed at 600 rpm is 3.0 m/s.)

References:

1. T. M. Liou and D. A. Santavirta, Trans. SAE **92**, 131 (1983).
2. A. O. zur Loye, D. L. Slebers, T. L. McKinley, H. K. Ng, and R. J. Primus, "Cycle-Resolved LDV Measurements in a Motored Diesel Engine and Comparison to k- ϵ Model Predictions," (SAE, New York, NY, 1988), Paper No. 890618.

Removal of Nitrogen Oxide from Exhaust Gas with Cyanuric Acid[†]

The effects of exhaust-gas composition and surfaces on nitric oxide (NO) reduction with isocyanic acid formed from cyanuric acid have been investigated in a quartz flow reactor. We have found that exhaust-gas composition and surface composition have significant effects on the cyanuric acid-NO reduction process.

D. L. Siebers and J. A. Caton*

Isocyanic acid (HNCO), formed by sublimation and decomposition of cyanuric acid (CA), will selectively reduce nitric oxide (NO) in the exhaust of combustion systems.¹ However, the conditions for which NO reduction occurs and the details of the chemical mechanism of NO reduction are not understood completely. In this work, we examine the effects of exhaust-gas composition and the composition of surfaces on this NO reduction process.

Experiments were conducted in an electrically heated, quartz flow reactor using both exhaust from a diesel engine and mixtures of N₂, O₂, H₂O, CO, and NO that simulated exhaust gas. The temperature range of the experiment was 700 K to 1350 K. The NO concentrations were measured with a chemiluminescent NO_x analyzer. Infrared-absorbing species were identified and measured with a Fourier transform, infrared spectrometer.

Figure 1 demonstrates some of the effects of exhaust-gas species on the cyanuric acid-NO reduction process using simulated exhaust gas. The figure is a plot of the outlet-to-inlet NO ratio as a function of reactor temperature for four combinations of O₂, H₂O, and CO in the exhaust. The results in Figure 1 clearly show that the exhaust-gas composition has a strong effect on the cyanuric acid-NO reduction process. The O₂, H₂O, and CO concentrations in the exhaust determine the temperature at which NO reduction occurs and the magnitude of the NO reduction for the overall temperature range examined.

The major effects of CO, O₂, and H₂O occur through the wet CO oxidation mechanism. Oxidation of CO in the presence of H₂O, which occurs whether or not CA has been added to the exhaust, increases the supply of free radicals through the following reactions in the wet CO oxidation mechanism:

Radical species in these reactions, in particular OH and H-atoms, are also important in the proposed cyanuric acid-NO reduction mechanism.² As a result, anything that enhances or diminishes the wet CO oxidation mechanism and, therefore, the supply of free radicals, will enhance or diminish the gas-phase cyanuric acid-NO reduction process, as demonstrated in Figure 1.

Figure 1. The effect of O₂, H₂O, and CO on the NO concentration in simulated exhaust gas as a function of the reactor temperature. The exhaust preheater, cyanuric acid vaporizer, reactor flow rates are 1.0 slpm, 0.2 slpm, and 1.2 slpm, respectively, and the reactor inlet species are O₂ = 12.3%, H₂O = 4.5%, CO = 1260 ppm, NO = 330 ppm, and CA = 470 ppm.

Figure 2 shows the concentrations of HNCO, CO, NO, and N₂O as a function of the reactor temperature in treated diesel engine exhaust. Low HNCO concentration at a reactor temperature of 700 K indicates that the CA does not decompose and form HNCO in the CA vaporizer. Decomposition occurs at much higher temperatures in the reactor with the peak HNCO concentration, 1350 ppm, occurring at 1000 K. Peak HNCO concentration accounts for all but 4% of the 470 ppm of CA at the reactor inlet and indicates that the decomposition is approximately 100% efficient.

[†]Combustion and Flame, accepted (1988).

*Sandia Faculty Program participant.

The results in Figure 2 also show that N_2O can be produced by the cyanuric acid-NO reduction process. For the conditions in the figure, formation of N_2O starts at 1000 K, when the HNCO concentration begins to decrease. N_2O production reaches a maximum at 1190 K, the temperature corresponding to maximum NO reduction, and then decreases with further increases in temperature. The amount of N_2O produced below a temperature of 1190 K is comparable to the amount of NO removed.

Because of the growing concern over N_2O emission by combustion processes, more information is needed concerning the production of N_2O by the cyanuric acid-NO reduction process, in particular the amount produced during actual application of the process. The most likely mechanism for the formation of N_2O is given by combining the mechanism for oxidation of HNCO by OH with the NCO + NO mechanism proposed for N_2O formation:¹⁴

The decrease in N_2O above 1190 K in the quartz reactor experiments is the result of thermal decomposition of the N_2O .

Figure 2. The concentration of species in treated diesel exhaust as a function of the reactor temperature. The exhaust preheater, cyanuric acid vaporizer, reactor flow rates are 1.0 slpm, 0.2 slpm, and 1.2 slpm, respectively. The reactor inlet species are $O_2 = 12.3\%$, $CO_2 = 5.8\%$, $H_2O = 5.2\%$, $CO = 260$ ppm, $NO = 330$ ppm, cyanuric acid = 470 ppm, plus hydrocarbons, particulates, etc.

The effect of a hematite (Fe_2O_3) surface on NO reduction by CA in diesel exhaust is shown in Figure 3. Powdered Fe_2O_3 was suspended on a quartz wool matrix and placed in the quartz reactor. The shaded region in Figure 3 represents the range of the NO data for the conditions of Figure 3 with no Fe_2O_3 in the reactor. The significantly lower temperature at which NO reduction occurs with a surface of Fe_2O_3 in the reactor is apparent. The temperature range where NO reduction occurs, 700 K to 800 K, is approximately 200 K lower than the lowest temperature at which gas phase NO reduction was noted.

Figure 3: Comparison of the NO reduction in diesel exhaust with a surface of Fe_2O_3 (symbols) and without a surface of Fe_2O_3 (shaded region) in the reactor as a function of reactor temperature. (All conditions with and without Fe_2O_3 correspond to those in Figure 2.)

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1. R. A. Perry, "NO Reduction Using Sublimation of Cyanuric Acid," U. S. Patent No. 4,731,231 (1988).
2. J. A. Miller and C. T. Bowman, "Mechanism and Modeling of Nitrogen Chemistry in Combustion," *Progress in Energy and Combustion Science*, accepted (1988).
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4. R. A. Perry, *J. Chem. Phys.* **82**, 5485 (1985).

Comparison of Exhaust Gas Additives for Nitric Oxide Removal[†]

A comparison is made between the nitric oxide (NO) reduction obtained with the cyanuric acid and the ammonia NO reduction processes. In addition, the decomposition of dry urea is explored.

Our findings indicate that the chemical mechanisms of the cyanuric acid and the ammonia processes are significantly different and that the urea process is a hybrid of those two processes.

J. A. Caton* and D. L. Siebers

Selective, noncatalytic techniques for removing nitric oxide (NO) from exhaust gases include the addition of ammonia (NH₃), urea, or cyanuric acid (CA) to the hot exhaust. We have compared CA and NH₃ as nitric oxide reducing agents and have examined the decomposition of dry urea. The experiments were conducted in an electrically heated quartz flow reactor using mixtures of N₂, O₂, H₂O, CO, and NO that simulated exhaust gases. The temperature range of the experiment was 700 K to 1350 K. (For details on the CA process, see article on p. 7-14 this issue.)

The NO reduction obtained as a function of temperature with NH₃ and with CA for exhaust gas containing three combinations of H₂O and CO is shown in Figures 1 and 2. The exhaust O₂ concentration is 1.9% in Figure 1 and 12.3% in Figure 2. The figures show reactor outlet NO concentrations normalized by the inlet NO concentrations (in percent) versus the reactor temperature. The two O₂ levels are representative of the range of O₂ concentrations in the exhaust gases of many combustion systems and correspond to overall equivalence ratios of 0.9 and 0.5 (or about 10 and 100% excess air) for most hydrocarbon-fueled combustion processes.

Figure 1 shows that NO reduction greater than 95% was obtained between temperatures of 1150 K and 1250 K with the NH₃ process for exhaust with 1.9% O₂ and no H₂O or CO. When H₂O was added, only a slight change was noted in the NH₃ process. Adding both the H₂O and 1260 ppm of CO to the exhaust (a) decreased the maximum NO reduction to 90%, (b) lowered the temperature at which the maximum NO reduction occurred to 1060 K, and (c) narrowed the temperature range for high NO reduction. Adding more NH₃ did not alter the above results.¹

[†]Combustion Science and Technology, submitted (1988).

*Sandia Faculty Program participant.

Starting with the 1.9% O₂ and no H₂O or CO, Figure 1 shows that NO reduction was considerably less for the CA process than for the NH₃ process in the temperature range examined. For the CA process, maximum NO reduction occurred at 1350 K and net production of NO occurred between temperatures of 1150 and 1260 K. When 4.5% H₂O was added to the exhaust, the NO reduction increased and shifted to lower temperatures. When both H₂O and 1260 ppm of CO were added to the exhaust, further increases in the NO reduction and decreases in the temperature at which the reduction occurred were observed. For the latter case, the NO reduction was greater than 80% for reactor temperatures between 1230 K and 1350 K. This level of NO reduction is approximately equal to the NO reduction obtained by the NH₃ process under the same conditions.

Behavior of the NH₃ process with 12.3% O₂ in the exhaust, shown in Figure 2, is similar qualitatively to that observed in Figure 1 for 1.9% O₂. However, the maximum NO reduction is significantly less and shifted to a temperature 50 K lower for each combination of H₂O and CO at the higher O₂ concentration. The behavior of the CA process with 12.3% O₂ in the exhaust is also similar qualitatively

Figure 1. NO reduction using either NH₃ or cyanuric acid as a function of reactor temperature for O₂=1.9% and NO=330 ppm.

Figure 2. NO reduction using either NH_3 or cyanuric acid as a function of reactor temperature for $\text{O}_2=12.3\%$ and $\text{NO}=330$ ppm.

to the low O_2 case in Figure 1. Quantitatively, the NO reduction for each exhaust composition is greater and shifted to lower temperatures.

By comparing the trends for the CA and the NH_3 processes in Figures 1 and 2, two general observations can be made. First, adding more O_2 , adding H_2O (except for the NH_3 process), or adding both H_2O and CO lowered the temperature at which NO reduction first occurred for both processes. For the NH_3 process, adding H_2O without CO had little effect on the NO reduction temperature. Second, although adding O_2 , H_2O , and CO lowered the temperature at which NO reduction occurred for each process, addition of these species affected the amount of NO removed by each process differently. Adding more O_2 , adding H_2O , or adding both H_2O and CO in general decreased the NO reduction obtained by the NH_3 process and increased NO reduction obtained by the CA process. For example, the maximum NO reduction for the NH_3 process for the 1.9% O_2 case with no H_2O and CO decreased from 99% to 75% when the O_2 concentration was increased to 12.3% and H_2O and CO were added. Just the opposite happened for the CA process; the maximum NO reduction increased from 40% to 95% for the same changes.

The differences discussed above coupled with other differences noted between the two processes, such as a factor of ten higher production of N_2O by the CA process, suggest that the detailed chemical mechanisms of the CA and the NH_3 processes are very different. One major difference is in the primary NO removal path for each process. The primary NO removal path for the CA process involves the conversion of isocyanic acid (HNCO) to NCO and the reaction of NCO with NO based on a

recent kinetics model of the CA process.² Based on a well-developed model of the NH_3 process, the primary NO removal path for the NH_3 process involves the conversion of NH_3 to NH_2 and the subsequent reaction of NH_2 with NO.^{2,3}

Based on these trends, potential applications for the CA process may include hydrocarbon combustion systems that have relatively high CO and O_2 concentrations or systems that can be modified to produce locally high CO and O_2 concentrations at the point of CA injection, such as staged combustors. On the other hand, the NH_3 process may be better suited for systems with low CO and O_2 concentrations at the point of NH_3 injection.

Finally, in our work using urea as an NO reducing agent, we found that dry urea decomposes into equal amounts of HNCO and NH_3 and that the decomposition is complete at a temperature of 700 K in the residence time of our experiment, as shown in Figure 3. Since HNCO is the decomposition product of CA, this observation suggests that the urea-NO reduction process is a hybrid of the CA and the NH_3 processes with both synergistic and antagonistic effects possible between the HNCO and the NH_3 .

Figure 3. HNCO and NH_3 concentrations resulting from the decomposition of dry urea in nitrogen as a function of the vaporizer temperature.

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3. R. K. Lyon and J. E. Hardy, *Industrial Engineering and Chemical Fundamentals* **25**, 19 (1986).

Investigation of Spray-Flame Structure in a Near-Axisymmetric, Optical-Access Research Furnace[†]

Four distinct types of macrostructure are found to exist for a steady, confined spray flame. Analysis of each structure provides insight into the flame stabilization mechanism of typical furnace spray flames.

C. F. Edwards

Of the 5.8 billion barrels of crude oil consumed in the United States in calendar year 1986, more than 2.3 billion were used in spray combustion devices—furnaces, boilers, gas turbines, diesels—making spray combustion the largest mode of petroleum consumption in this country.¹ However, little is known about the combustion zone structure of these flames due to the highly complex, multiphase, turbulent nature of spray combustion.

Studies are being performed in the Sandia Optical-Access Research Furnace to elucidate the structure of steady spray flames. Figure 1 shows a schematic of the significant features of the apparatus. The furnace is octagonal in cross section with walls made entirely of fused silica—permitting maximum optical access. Fuel and atomizing air are carried to the flame through the nozzle support tube while main combustion air is supplied as a swirling stream through the concentric annular passage.

Flame macrostructure has been evaluated as a function of swirl number, excess air ratio, and atomizing-air/fuel ratio using kerosene fuel. Conventional photography of the luminous flame zone has revealed four types of structure that may be assumed over the operating domain, while gated digital photography and image processing have provided an ability to quantify mean flame position and extent of fluctuations in the flame.

Figure 2 illustrates the flame structure in a particularly interesting operating region. In this region, either of two distinctly different stabilization mechanisms can be observed, each with a high degree of stability. Figure 2a shows an externally stabilized flame structure characterized by a lack of visible internal flame zone and the presence of flamelets along the outer edge of the spray sheath. Figure 2b shows a probability density map of the luminous flame position obtained by imaging 512,

1-ms digital exposures. The central contour indicates the mean flame boundary for this mode of stabilization.

In Figures 2c and 2d, the second mode of stabilization is shown. This mode is characterized by a luminous, internal-flame zone and the absence of flamelets external to the flame sheath. Since either of these two structures can be assumed by the flame under identical operating conditions, it is only the path of approach to this condition that determines which of the structures will prevail. Approach from an operating condition that favors external stabilization will result in that mode's retaining control of the flame while approach from a region of internal stabilization results in the latter mode's retaining control.

Figure 1. Schematic of significant features of the Sandia Optical-Access Research Furnace

[†]Heat Transfer Vol. II (ASME, New York, NY, 1988), p. 99.

Figure 2a-d. Flame structures observed using kerosene fuel in the Sandia Optical-Access Research Furnace.

Reference:

1. *Annual Energy Review* (U.S. Department of Energy, 1986), Publication No. DOE/EIA-0384(86).

Novel Injection System Demonstrated in a Prototype Commercial Pulse Combustor

To sustain stable oscillations in a pulse combustor, Rayleigh's criterion requires that energy release must be in phase with, and at the peak of, the resonant pressure wave. A new reactant injection system has been developed to control dynamically this required phasing.

J. O. Keller, T. T. Bramlette, L. Evens,* and R. Marchand*

Significant progress has been made in recent years toward the understanding of the fundamental parameters governing pulse combustion operation. Rayleigh's criterion requires that to sustain the pulsations, energy release must be in phase with, and at the peak of, the resonant pressure wave. It is well demonstrated that this condition must be met or pulsations will cease. Keller *et al.*^{1,2} identified four characteristic times that determine the phase relationship between energy release and the resonant pressure wave. These characteristic times are the time required to mix the fuel and air (a species-mixing time), the time required to mix the reactants with the residual products to an appropriate ignition temperature (a fluid dynamic mixing time), the time required for chemical ignition to occur (a chemical kinetics ignition delay time), and the cycle time (the reciprocal of the system resonance frequency). They demonstrated and quantified the importance of these characteristic times in a laboratory-scale test combustor and established that, for their laboratory combustor, the characteristic fluid dynamic mixing time contributed to over 80% of the total ignition delay time. This is fortunate since the fluid dynamic mixing time can be modified readily by changing the reactant injection characteristics of the combustor.

A novel method of controlling fluid dynamic mixing in a prototype commercial pulse combustor was demonstrated recently.³ The valve system used in this study was constructed with a centerbody located at the entrance to the combustion chamber, as shown in Figure 1. This centerbody created an annular jet-injection profile for the reactants. The location of this centerbody was adjustable, allowing the characteristic dimension of the annular jet to be varied monotonically and continuously. Such a variation was desirable, since Bramlette⁴ showed that the characteristic mixing time scales (at least to first order) as $\tau_{\text{mixing}} \sim R/U$,

where R is a characteristic dimension of the jet and U is its mean velocity. Although this annular jet is different geometrically from the circular geometry discussed by Bramlette, it was found that these results were still applicable: as the annular dimension decreased, the characteristic mixing time decreased, and as the velocity of the jet increased, the mixing time decreased.

Figure 1. Injection system for variable fluid dynamic mixing times. Moving the centerbody closer to the upstream end of the combustion chamber increases the rate of mixing by decreasing the characteristic dimension of the annular jet and, for a constant firing rate, increasing the mean injection velocity of the reactants.

Shown in Figure 2 is the response of the combustor's operating frequency to changes in the characteristic mixing time, obtained by varying the valve centerbody position. Decreasing the centerbody spacing, thereby increasing the rate of mixing, results in a higher operational frequency, consistent with Rayleigh's criterion. For very short mixing times (small centerbody distances, or a narrow annular space), the results presented in Figure 2 show a sudden jump in frequency. This discontinuity is caused by a change in flame stabilization modes. These results demonstrate that wide dynamic ranges in frequency are possible by simply modifying the fluid dynamic mixing time.

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In summary, control of the fluid dynamic mixing provides a means for the compensation of variable fuel properties, different combustor firing rates, variations in heat transfer, or manufacturing tolerances—factors that can influence the timing of energy release in a given pulse combustor. Frequency control may also be desirable because, in general, it is easier to attenuate higher frequency sound, and higher frequencies tend to increase heat transfer.⁵

Figure 2. Pulse combustor resonant frequency for various centerbody spacings. The present injection system allows this pulse combustor to operate over a range of frequencies from approximately 90 to 120 Hz. For fast mixing, the combustor operates at its second harmonic.

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5. J. E. Dec and J. O. Keller, *Combust. Flame*, accepted (1988).

Pulse Combustor Dynamics: A Numerical Study[†]

A numerical model has been developed to explain the complex interactions that occur in a Helmholtz-type pulse combustor. The model can also be used to assist in the design of commercial systems.

P. K. Barr and H. A. Dwyer*

Heating devices employing steady pulsating combustion have proved to be both energy efficient and low emitters of pollutants, but the coupling between fluid dynamic oscillations and fuel combustion to produce these desirable effects is not well understood.¹ To develop new products for home heating and commercial use, one must be able to scale the units by logical changes in geometry and operating conditions. A numerical model of a pulse combustor has been developed to simulate the nonlinear wave motion resulting from the periodic combustion process. The wave pattern is followed in time by integrating the unsteady, one-dimensional equations of continuity, momentum, and energy for variable-area geometry, including losses due to friction and heat transfer. The resulting periodic wave pattern is governed by the pulse combustor geometry, the fuel mixture, and the combustion and injection processes. The method of determining the optimal design frequency of the pulse combustor is based on Rayleigh's criterion, which states that for stable combustion-driven flow oscillations, the energy release must be in phase with the resonant pressure wave. The phase relation between the heat release and the combustion chamber pressure, called the Rayleigh efficiency η , is used to compare the magnitudes obtained at different forcing frequencies. Since the Rayleigh efficiency reaches a maximum when the combustion process provides the strongest reinforcement of the pressure waves, the optimal operating frequency occurs when η is a maximum. By considering various system parameters, the Rayleigh efficiency can be displayed as a multidimensional surface whose shape characterizes the sensitivity of the combustor performance to those parameters.

Figure 1 shows the variation of η with frequency for simulation of a typical pulse combustor. Also shown in this figure are plots of the combustion chamber pressure versus the nondimensional cycle

time, obtained at different frequencies. The figure shows that the frequency producing the maximum

Figure 1. The Rayleigh efficiency η as a function of frequency (top), overlaid with the pressure waves produced at the indicated frequencies versus normalized cycle time. In the bottom, the mean flow rate as a function of frequency, overlaid with plots of the injection profiles obtained at the indicated frequencies versus normalized cycle time. The optimal operating frequency is identified from the maximum of η , which also produces the most sinusoidal pressure wave and a large flow rate.

[†]Numerical Approaches to Combustion Modeling, E. Oran and J. Boris, eds. (American Institute of Aeronautics and Astronautics, Washington, DC, 1988), in press.

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value of the Rayleigh efficiency also produces the strongest pulsations, as indicated by the peak-to-peak amplitudes. Because the flow through the inlet valve is controlled by the combustion chamber pressure, the optimal design frequency also produces large flow rates through the valve, as indicated in the bottom figure.

The model can also be used to show the effect of the shape of the time-varying combustion process. A sinusoidal energy release $\dot{Q}$ profile produces a sinusoidal pressure wave, as was shown in Figure 1. Figure 2 shows that to produce strong oscillations, significant combustion should take place

over a short time period, rather than occurring over the entire cycle. If large magnitude oscillations are desired, the energy release should be adjusted to resemble more closely a delta function. This can be done by modifying the fluid mixing and changing the chemical kinetics of the reactants.

The figures demonstrate the ability of the model to identify operating conditions that will improve the performance of pulse combustors. A family of such simulations provides design guidance to manufacturers who otherwise would have to perform a very expensive and time consuming set of laboratory experiments.

Figure 2. Comparison of the wave dynamics obtained from four different energy release profiles $\dot{Q}$ shown in the top row.

Reference:

1. A. A. Putnam, F. E. Belles, and J. A. C. Kentfield, Prog. Energy Combust. Sci. 12, 43 (1986).

Section 8

This photograph shows the experimental test section located beneath the last of seven flow-reactor modules in the Multifuel Combustor. As described on the overleaf, this new facility allows simulation of the combustion conditions within an industrial, coal-fired boiler. A key feature of the facility is the open test section that allows complete access for the CRF's laser diagnostics to the ash-laden combustion stream. The residence time of reacting coal particles within the vertical, down-flow reactor is varied easily using the flexible feed lines. The temperature history to which these particles are exposed is controlled by electrical heaters within each flow-reactor module and by use of dilution gases. A 15-centimeter-wide flow of combustion products is delivered to the open, bench-top test section. Available diagnostics include the dual-beam, particle-counter-sizer laser velocimeter shown in the photograph.

The Multifuel Combustor (MFC) is the newest of a suite of high-temperature facilities available for coal combustion research at the CRF. The combustor occupies a large high-bay laboratory and simulates the environment experienced by a coal particle as it travels through a commercial-scale boiler, but with sufficient control and access to the reacting stream to permit detailed scientific measurements. Researchers can use the CRF's central facility lasers or the complement of optical diagnostics and physical sampling probes associated with the MFC to monitor the combustion flow.

As shown in the figure, the MFC is oriented vertically with combustion gases flowing from top to bottom. A methane-fired flame is stabilized in the cylindrical gas burner (shown at the top) to preheat the airstream and to supply a clean, vitiated airflow to a series of seven modules, at peak temperatures of 700 K to 1800 K and velocities of 0.5 to 3 m/s. The nominal firing rate of the main combustor is 0.5×10^6 Btu/hr. The first six modules contain silicon carbide heating elements between refractory layers to control heat loss from the vitiated flow; the last module contains no heating elements. Each of these modules provides access ports for the addition of test fuels, dilution air, or combustion additives, or for the insertion of thermocouples. Test fuels, such as pulverized coal or coal-water slurries, are introduced through any of these ports by special lances that direct the coal particles downward into the vitiated airstream. Coal, air, and natural gas feed rates are adjustable to allow control over gas composition and temperature, as well as particle loading and residence time. The combustion residence time of the test fuel increases as the fuel insertion point is moved upward, away from the test section. By adjusting (a) the total flow rates of methane and air to the gas burner, (b) the insertion location of the test fuel, (c) the location and magnitude of the flow rate of dilution air, and (d) the guard heater currents, the Multifuel Combustor can:

- Simulate the entire time-temperature profile of an industrial combustor,
- Permit access in the open test section to any point along the time-temperature profile, or,
- Operate in an isothermal, turbulent-flow-reactor mode.

By way of comparison, the other bench-scale, laminar-flow reactors currently used in the Char Combustion and Coal Devolatilization Laboratories at the CRF simulate the devolatilization and char oxidation regimes of pulverized coal combustion. The MFC extends the range of residence times from a few hundred milliseconds up to four seconds. Access to the "burnout" phase of pulverized coal combustion, without resorting to high excess oxy-

gen concentrations, is fabricated.

A unique feature of the Combustor is the open test section located at bench-top height on the ground floor. The absence of walls in the test section, together with the excellent control and flexibility of the operating parameters, makes the MFC particularly useful for conducting coal mineral-matter-related research. Deposition—fouling or slagging—on temperature-controlled steam tubes or surfaces that are suspended in the 15-cm-wide flow of combustion products can be monitored using *in situ* optical techniques. Surface properties can be determined as a function of the measured properties of the particle-laden Combustor flow. Optical diagnostics that are available for these kinds of experiments include a laser/particle-counter-size velocimeter, a Fourier transform infrared spectrometer, a laser/surface Raman scattering system, and a high-speed video imaging system.

Figure 1. Schematic of the Multifuel Combustor showing controls on the first floor and the cylindrical gas combustor and flexible test-fuel feed lines on the second floor. Also shown is a typical experimental arrangement on the optical table.

Section 8

Coal Combustion

Under the sponsorship of the Department of Energy's Office of Fossil Energy, a broad program of fundamental research on the combustion of pulverized coals has been developed at Sandia National Laboratories. These studies are aimed at predicting and measuring the rates and mechanisms of the devolatilization of coals and coal-water slurries and the subsequent oxidation of the residual chars. Special emphasis is given to determining the high temperature transformations and evolution of mineral species imbedded in the original coal. Experimental studies use well-controlled laboratory flow reactors to obtain spatially and temporally resolved information during the combustion of size-classified samples of well-characterized coals. The reactors are instrumented with advanced optical detection systems, including a Sandia-patented, particle-sizing pyrometer for *in situ* observation of particle size, temperature, and velocity.

The newest of the facilities, the Multifuel Combustor (see opposite) allows realistic simulation of combustion conditions in a full-scale industrial boiler. The combustor is being used to determine the importance of fragmentation during char combustion and to conduct *in situ* measurements of the transformation and deposition of mineral species on simulated boiler steam tubes during the combustion of pulverized coal and coal-water slurries. In addition, work continues on the development and validation of new laser diagnostics for application to particle-laden flows. One of these new techniques, laser spark spectroscopy, has proved useful for direct, *in situ* measurement of the elemental chemical constituents of coal particles in a reacting flow.

These experimental efforts are complemented by theoretical and computational modeling aimed at describing the devolatilization and oxidation of individual coal particles, as well as at predicting the behavior of industrial coal combustors.

Time-Resolved Particle Temperature and Mass Loss Measurements of a Bituminous Coal During Devolatilization[†]

An in-situ method is used for measuring simultaneously the size, temperature, and velocity of individual coal particles during pyrolysis at rapid heating conditions. The measured particle temperature history is combined with mass loss determinations from solid sampling experiments to determine overall coal devolatilization rates.

T. H. Fletcher

The rate of release of coal pyrolysis products is dependent on the particle temperature and reaction history. During rapid particle heating (10^3 - 10^5 K/s typical of pulverized combustion applications), published rates of volatiles released for similar coals and similar heating conditions differ by up to 5 orders of magnitude at any given temperature between 800 and 1400 K. The differences in reported pyrolysis rates are most likely attributable to insufficient characterization of particle temperature during heat up, where most devolatilization reactions occur.

Coal pyrolysis studies were performed in 100% nitrogen in a laminar flow reactor. Coal introduced into the reactor through a water-cooled injection tube flowed along the reactor centerline with little radial particle dispersion. Electric heaters control gas temperatures in the flow reactor. The transparent flow reactor walls allow radiant emission from the coal particles to be monitored and analyzed at any axial location. Two gas temperature conditions were used in this study, with maximum centerline gas temperatures of 1250 and 1050 K. Particle heating rates in this reactor were approximately 10^4 K/s.

An infrared, sizing pyrometer was used to measure the size, temperature, and velocity of individual particles in the flow reactor at different axial locations.¹ The emission from a particle was imaged onto a particle-sizing mask similar to that used by Tichenor *et al.*,² and split into two wavelengths using bandpass filters centered at 1.3 and 2.2 μm . The pyrometer system allowed measurement of single-particle temperatures as low as 850 K for 100- μm -diameter particles. The tar cloud did not influence the pyrometry measurements at the wavelengths and gas temperatures employed in this

study, as evidenced by the facts that measured coal particle diameters (100 - 180 μm) were smaller than would be expected from a tar cloud (0.5 - 2 mm) and emission intensities for coal particles were similar to those obtained from the calibration studies involving pure carbon particles.

Measured particle temperatures as a function of residence time in the flow reactor are shown in Figure 1 for a high-volatile, Pittsburgh #8 coal (106 - 125 μm diameter). Multiple points represent the range of measured coal particle temperatures. Calculations of particle temperature were performed to interpolate between measurement points and to extrapolate the initial heating conditions. The particle energy equation was solved numerically, using measured gas temperatures, particle velocities, and particle densities. Variations in particle properties as a function of temperature and extent of reaction are also considered. The solid line in Figure 1 represents the best fit to the particle temperature data, as explained by Fletcher.¹

Figure 1. Comparison of measured (discrete points) and calculated (curves) particle temperatures as a function of residence time in the flow reactor for a highly volatile Pittsburgh #8 coal (106 - 125 μm diameter). Maximum gas temperatures for the two gas conditions are (a) 1250 K and (b) 1050 K.

[†]Combustion and Flame, submitted (1988).

A water-cooled, helium-quench probe was used to collect solid samples isokinetically. The inner wall of the probe was made from porous tubing, allowing helium to transpire through the wall to reduce tar deposition. The sample collection system featured on-line, aerodynamic separation of tars and aerosols from char particles using a virtual impactor and cyclone system to prevent redeposition of tar onto char particles.

Elemental analysis of solid samples collected at different residence times was performed using inductively coupled plasma (ICP) spectroscopy. The inherent concentration of titanium, silicon, and aluminum in the coal, as well as total ash, were all used as tracers in this study to determine mass loss due to devolatilization. The use of four independent tracers allows statistical analysis for the average mass loss as well as the associated confidence limits. The scatter indicates 90 of a 5-sample collection and with the measurement of the chemical composition of the char particles. Figure 2 shows the measured mass release using the average of the four different tracers for reactor conditions of 1250 K for a Pittsburgh #8 high-volatile, bituminous coal (106 - 125 μm size fraction).

Measured mass-release rates of devolatilization and corresponding particle temperatures must be correlated using some type of kinetic rate model. Proposed rate models range from simple one-step Arrhenius expressions to detailed multi-species reaction systems with distributed activation energies and Monte Carlo lattice statistics. Measured rates of volatiles released in this experiment can be compared only with other measured rates using the proposed rate expressions. The continuous lines indicated in Figure 2 show a comparison of this mass release data with three commonly used correlations developed from other reported data where particle temperatures were not measured. These three correlations represent extremes in reported devolatilization rates. The devolatilization rates indicated by the data are well represented by the most rapid rate expression³ shown in Figure 2. The other two rate correlations do not predict correctly the time (and hence temperature) at which devolatilization begins during particle heating.

Rate coefficients developed from these data can be applied realistically to pulverized-coal combustion calculations, since the particle temperatures used to obtain the rate coefficients are characterized well experimentally.

Figure 2. Measured and predicted rates of mass loss as a function of residence time for 115- μm -diameter coal particles using different reported kinetic-rate expressions at the 1250 K gas condition. Data points represent the fraction of coal released as volatile matter as determined from the average of four tracers. Continuous lines represent kinetic rate correlations by (a) Ubhayakar *et al.*,³ (b) Niksa *et al.*,⁴ and (c) Kobayashi *et al.*,⁵

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A Chemical Model of Coal Devolatilization Using Percolation Lattice Statistics[†]

A chemical kinetic model of coal devolatilization has been developed that describes product evolution rates and yields at rapid heating conditions. Products are grouped into the broad categories of gas, tar, and char based on molecular weight and reaction history. The behavior of different coal types is related to differences in the chemical structure of the parent coal.

T. H. Fletcher, A. R. Kerstein, D. M. Grant,* and R. J. Pugmire*

Previous modeling efforts at Sandia described the coal molecule as a linear chain of nuclei connected by bridges.¹ A more detailed model of devolatilization, emphasizing the chemical content of pyrolysis gases, has been developed recently² and has been combined with a Monte Carlo description of the coal molecule to treat tar formation and release. Our new model is an attempt to describe the effect of coal type on pyrolysis behavior without the computational burden of Monte Carlo calculations.

The chemical percolation devolatilization (CPD) model treats coal as a macromolecular array of clusters representing the interconnections of aromatic ring structures of various sizes and types. These clusters are connected by a variety of chemical bridges of different bond strengths. Percolation analysis, applied to a Bethe lattice (a loopless tree structure), allows a probabilistic description of the bridge-breaking process in closed form, providing an efficient alternative to Monte Carlo techniques.

Inputs to the CPD model include structural parameters based on solid-state ¹³C NMR (nuclear magnetic resonance) analyses of the parent coal pertaining to the relative sizes and populations of aromatic clusters, peripheral groups, and stabilized char bridges.² Estimates of the degree of branching of the interconnections among aromatic clusters are also inferred from the NMR data. Kinetic parameters are assumed to be identical for coals of all types; differences in tar and gas yields for different coal types are explained by differences in the initial chemical structure. A global model for gas release is used, rather than models for individual species. The mean activation energy for the gas release was chosen to be an average of the 20 species treated in the gas release model of Solomon *et al.*³ Activation energies are distributed in a manner corresponding to sequential release of gases as a function of

molecular weight; the apparent activation energy is changed according to a Gaussian distribution based on the fractional yield. Mass transfer effects on release of gas and tar are not yet treated in this model.

The reaction sequence proposed in this model is pictured below. A labile bridge L breaks to form a highly reactive intermediate L^* that is consumed by two competitive processes: (1) release of the bridge remnants as light gas g_2 , with a rapid relinking of the two sites within the reaction cage to give a char bridge c and (2) temporary stabilization of the remnants into side chains δ , with the bridge remaining broken. The side chains are converted eventually into light gas fragments g_1 through a slower reaction step.

The initial coal matrix consists of a near-infinite array of aromatic clusters connected by labile bridges. As bridges between aromatic clusters break, the probability increases that a group of clusters no longer contains connecting bridges to the infinite coal lattice. These finite clusters are condensable at room temperature and are defined in the model as coal tar. The percolation statistics provide a mathematically convenient representation of the rate of generation of finite clusters (tar precursors) from the infinite coal lattice. The generation of finite clusters from the infinite coal lattice is highly nonlinear and critically dependent on the number of cross-connecting bridges per aromatic cluster (the coordination number). The nonlinear relationship between the number of broken bridges and the fraction of clusters detached from the infinite coal lattice is illustrated in Figure 1 for different values of the coordination number $\sigma + 1$.

[†]Energy and Fuels, accepted (1988).

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Figure 1. The dependence of the fraction of finite clusters generated from an infinite lattice with coordination number $\sigma+1$ as a function of the fraction of unbroken bridges p .

A comparison of CPD model calculations with devolatilization data for an Illinois #6 coal obtained in an entrained flow reactor by Serio *et al.*⁴ is shown in Figure 2. Kinetic parameters used here are similar to those reported by Solomon for this set of data. The good agreement in both the time of gas and tar release and in the rates of release indicates the applicability of lattice statistics to the treatment of coal devolatilization. Good agreement has been achieved also with devolatilization data for a Montana Rosebud subbituminous coal and a North Dakota Zap lignite in the same flow reactor without changing the kinetic parameters in the model.

The model is being modified currently to account for effects of heating rate and pressure on pyrolysis products as a function of coal type. Experiments are underway to investigate changes in the chemical structure of partially devolatilized coals using ¹³C NMR spectroscopy.

Figure 2. CPD model calculations compared with Serio⁴ data for Illinois #6 coal particles heated to 1040 K in an entrained flow reactor.

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Burning Rates of Baseline Coals and Their Physically Cleaned Products

Combustion tests of baseline and physically cleaned coals indicate that their char particles burn at similar rates in gaseous environments characteristic of practical pulverized coal combustors.

R. E. Mitchell

An experimental program was undertaken to assess the combustion characteristics of cleaned coals. The program involved comparing the burning rates of baseline coals with the burning rates of their cleaned products. In one case, raw Kentucky #9 coal and its medium-cleaned and deep-cleaned products were compared, and in another, run-of-mine (ROM) Pittsburgh #8 coal and its Powhatten-cleaned* and CQDC-cleaned* products were compared. On a dry basis (db), the raw Kentucky #9 coal, a high-volatile-B bituminous coal, contains 15% ash and its medium- and deep-cleaned products contain 10.3% and 6.4% ash (db), respectively. The ROM Pittsburgh #8 coal, a high-volatile-A bituminous coal, contains 33.7% ash (db) and its Powhatten- and CQDC-cleaned products contain 11.3% and 8.6% ash (db), respectively. The baseline and cleaned coals were obtained from the Electric Power Research Institute's Clean Coal Test Facilities.

In the experimental program, the size, temperature, and velocity of individual particles of the raw coals and of their cleaned products were measured at selected residence times in a laminar flow reactor.¹ Samples of partially reacted chars were extracted from the reactor at the selected residence times. Each sample was analyzed to determine the extent of burnoff, the apparent density, and the elemental composition of the material collected. The data obtained were used to determine parameters that describe the burning rates of the char particles of the raw coals and of their cleaned products.^{2,3}

Figure 1 shows the apparent chemical reaction rate coefficients determined for the char particles of the raw Kentucky #9 coal when all the carbonaceous particle material is assumed to be converted to CO at the particle surface. An apparent reaction order of 0.35 provided the best correlation between apparent rate coefficients and the particle temperatures. The value determined for the activation energy (36.5 kcal/mole) is in the range expected

for the burning of impure carbon particles whose burning rates are limited by the combined effects of pore diffusion and the intrinsic chemical reactivity of the particle material.

An activation energy of 36.5 kcal/mole accurately characterizes the temperature dependence of the apparent chemical reaction rate coefficients of the raw Kentucky #9 coal char particles at each measurement height. The extent of burnoff at the measurement heights ranged from 65% to 85% on a dry, ash-free basis (daf). The fact that the rate coefficients of particles at varying extent of burnoff exhibit the same temperature dependence may imply that during burnoff, there is no change in the chemical reactivity of the char.

Figure 1. Apparent chemical reaction rate coefficients of the char particles of raw Kentucky #9 coal burning in the 12-mole-% oxygen environment. CO is assumed to be the sole reaction product.

*Powhatten and Coal Quality Development Center (CQDC) are two of EPRI's clean coal test facilities.

Figure 2 shows the close agreement in the fits to the apparent reaction rate coefficients determined for the char particles of the raw Kentucky #9 coal and for its cleaned products. Within the scatter observed in the data, the same Arrhenius parameters can be used to describe the rate coefficients of each of the coals. The combustion tests performed suggest that the chemical reactivity of the char particles of the raw Kentucky #9 coal and the chemical reactivities of the char particles of its cleaned products are the same.

The chemical reactivity of the char particles of the ROM Pittsburgh #8 coal and the chemical reactivities of its Powhattan-cleaned and CQDC-cleaned products were also found to be similar. The char particles of each of the coals were found to burn at rates limited by the combined effects of pore diffusion and the intrinsic chemical reactivity of the particle material. An activation energy near 22 kcal/mole was found to depict accurately the temperature dependence of the rate coefficients of the chars of the Pittsburgh #8 coals. For the ROM coal, no significant differences were observed in the rates of carbon oxidation during the early, middle, or late stages of burnoff. The apparent reaction rate coefficients exhibited the same temperature dependence for extent of burnoff ranging from 60% to essentially 100% (daf).

Analyses of the data obtained with the parent, uncleaned Kentucky #9 and Pittsburgh #8 coals and their cleaned products indicate that the various cleaning processes did not alter the overall particle burning rates of the coal chars. Results of other tests⁴ concerned with the combustion behavior of the Kentucky #9 coals indicate that the lower ash loadings of the cleaned coals have beneficial effects on utility boiler operation. The reduction in ash quantity due to cleaning was observed to (1) improve pulverization in terms of grinding energy requirements and reduction in fuel abrasion/mill wear, (2) decrease fly ash erosion, (3) decrease slagging and fouling characteristics, and (4) reduce sulfur dioxide emissions (because of the lower sulfur content of the cleaned coals). The tests performed in this study indicate that the cleaned coals should not result in increases in particle burnout times with concomitant increases in the carbon content of the fly ash.

Figure 2. A comparison between the fits to the apparent reaction rate coefficients determined for the char particles of raw Kentucky #9 coal and of its cleaned products.

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The Thermal Influences of Ash on the Temperatures Attained by Burning Coal Char Particles[†]

The size, temperature, and velocity of individual coal char particles burning in a flow reactor were measured. Variations observed in the temperatures of particles of the same size were found to be largely a consequence of the variation in the ash content of the particles.

R. E. Mitchell

Variations in the burning times of coal char particles have been observed by many investigators. These variations have been attributed to several effects: (a) a distribution in the size and shape of particles, (b) a distribution in the availability of the internal particle surfaces, (c) burnout of the most reactive coal constituents, (d) utilization (or loss) of active sites, (e) variation in catalysis by mineral matter, and (f) particle fragmentation. In recent experiments, we used our particle-sizing pyrometer¹ to measure the size and temperature of individual coal char particles as they burned in a laminar flow reactor and found that at similar residence times, particles of the same size differed in temperature. The temperature differences were generally less than 100 K during the early-to-middle stages of burnoff, but became as large as 300 to 500 K (depending upon the gaseous conditions in the reactor) in the late-to-final stages.

By testing coals having different ash content, we noted that the temperature range of particles of the same size decreased as the ash loading of the coal decreased. This suggests that some of the variations in the temperature of particles of the same size may be due to the variation in the ash content of the particles. To test whether variation in the ash content of particles could account for the differences observed in the temperature of particles of the same size, we solved the differential equations describing a particle's mass, momentum, and energy as it burns in the flow reactor.^{2,3} The effective heat capacity and emissivity of the particle were determined by weight-fraction averaging the respective properties of the ash and carbon in the particle. During the numerical integrations, the measured gas temperature, velocity, and oxygen concentration profiles in the reactor were imposed.

Figure 1 shows results of calculations made employing the overall particle burning rates determined for the char particles of Lower Wilcox coal,

a lignite from Texas that contains 20% ash, on a dry basis (db). The broken lines represent temperature profiles of 125 μm particles having different ash contents and the solid line represents the gas temperature profile. At a height of about 10 cm in the reactor, calculated particle temperatures span only 40 K, a range that agrees with the measurements. By the time particles reach the 20-cm height, those having ash contents greater than about 20% have either burned out (temperatures represented by the lower branches of the curves) or are cooling to their non-burning states (temperatures represented by the steep transition portions of the curves). Particles having ash content less than about 15% are burning actively (temperatures represented by the upper branches of the curves). Thus, particle temperatures at the 20-cm height in the reactor span more than 300 K and reflect burning particles having ash content less than about 15% and extinguished particles having ash content greater than about 20%. At the 25-cm height in the reactor, the situation is similar, but now only particles having ash content less than 5% are burning actively, the rest having either reached burnout or their final stages of burn-off. Although the Lower Wilcox coal contains only about 20% ash (db, a bulk measurement), it is not

Figure 1. Particle temperature profiles in the flow reactor calculated using the burning rates determined for the Lower Wilcox coal char particles.

[†]Twenty-Second Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, PA, 1988), p. 69.

unreasonable to expect individual char particles to have ash content that differs from this. In fact, some particles may be pure ash and some relatively ash-free.

Figure 2 shows similar results obtained when the overall particle burning rates determined for Blue #1 coal, a subbituminous coal from New Mexico that contains 4% ash (db), are used in the calculations. Due to the low values employed for the ash content of the particles, the range in the calculated temperatures of particles of the same size is low, being less than 40 K at heights in the reactor less than about 22 cm. Such low variations are in accord with the variation in the measured particle temperatures at these heights. At the 25-cm height in the reactor, particles having ash content greater than 10% have reached burnout, and the span in the particle temperatures increases to about 500 K, reflecting actively burning particles and particles that have burned out.

Figure 2. Particle temperature profiles in the flow reactor calculated using the burning rates determined for the Blue #1 coal char particles.

The calculations indicate an increase in the temperature range of particles of the same size with burnoff, an effect observed from experiment. This is a consequence of using a particle emissivity that approaches the emissivity of ash as burnoff progresses. The calculations show that the higher the ash-loading of the coal, the earlier in burnoff the properties of the ash affect the burning characteristics of the char.

The calculations support the conclusion that the differences in the temperature of particles of the same size are largely a consequence of the particle-to-particle variations in ash content. The temperature differences lead to differences in the burning rate and burning time of particles of the same size. Of course, variations in the availability of internal particle surfaces, differences in the reactivity of the coal constituents, loss of active sites, and catalytic effects may also lead to differences in particle burning rates and burnout times, but the dominant effect appears to be due to variations in the ash content of particles.

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Population-Balance Model of Physical Transformations of Ash During Char Oxidation[†]

A population-balance model, involving a set of coupled rate equations, is formulated to represent the agglomeration of fused ash droplets on the surface of an oxidizing char particle. The model predicts novel features and trends, including bimodal droplet distributions observed in related experiments on vapor condensation.

A. R. Kerstein

Experimental observations of the evolution of surface ash during char oxidation suggest the following scenario governing the physical transformations of ash during char oxidation. Oxidation-induced surface recession exposes mineral matter in the particle interior. This mineral matter melts at combustion temperatures, forming droplets on the particle surface. These droplets may coalesce immediately with previously formed droplets, causing those droplets to grow. Droplets that are not immediately subsumed in this manner may agglomerate upon subsequent contact with neighboring droplets due to droplet growth.

Other relevant mechanisms are agglomeration due to droplet motion and droplet removal due to particle fragmentation. Though included in the model, these mechanisms are omitted from the present discussion.

A population-balance model is formulated based on the two-dimensional schematic picture shown in Figure 1. The horizontal line represents a portion of the perimeter of a partially reacted char particle, the bisected circles tangent to it represent ash droplets adhering to the perimeter, and the filled circles represent incipient droplets, *i.e.*, ash in the particle interior that will nucleate into droplets upon contact with the receding particle perimeter. The incipient droplets are distributed randomly, but without overlap, within the particle interior. They are all assigned identical diameter and mass, both normalized to unity.

Surface droplets grow by subsuming incipient droplets as those droplets reach the surface, and by agglomeration. Agglomeration is deemed to occur when the shadows of two surface droplets overlap due to droplet growth. Figure 1 represents a portion of the perimeter of a notional char particle

of infinite radius. The occurrence of agglomeration is denoted by an asterisk at the point of contact of the shadows of two neighboring droplets. Incipient droplets not shadowed by other droplets are themselves depicted with shadows. This indicates that they will evolve as surface droplets subsequent to their exposure.

Under these assumptions, all droplets have integer mass. Analysis of the scenario outlined above yields the following equation for the rate of change of the number N_s of mass- s surface droplets per unit perimeter length

$$\frac{dN_s}{dR} = (s-1)^{1/2} N_{s-1} - s^{1/2} N_s + \frac{1}{2(1-C)} \sum_{i=1}^{s-1} N_i N_{s-i} - \frac{TN_s}{1-C} + (1-C) \delta_{s1} \quad (1)$$

Here, $T = \sum_{s=1}^{\infty} s N_s$, $C = \sum_{s=1}^{\infty} s^{1/2} N_s$, and R is the normalized spatial coordinate directed normally inward from the particle perimeter.

Figure 1. Two-dimensional schematic representation of ash phenomenology on the perimeter of an oxidizing char particle. Bisected circles represent surface droplets and filled circles represent incipient droplets in the particle interior. Dashed curves demarcate the evolving "shadows" of the surface droplets, *i.e.*, the zones whose incipient droplets are assumed to coalesce with the respective surface droplets. Shadows are also shown on those incipient droplets that later emerge as distinct surface droplets, rather than coalescing with existing surface droplets. The asterisk at the intersection of two shadows signals an agglomeration event.

[†]Combustion and Flame, accepted (1988).

Figure 2 shows numerical solutions for the number fraction N_i/T , grouped in bins of geometrically increasing size, for several values of the perimeter recession distance R . It is interesting to note that the transient distributions are bimodal. The location of the transient peak increases in proportion to $R^{2/3}$. In contrast, the curve corresponding to the notional limit $R \rightarrow \infty$ is monotonic.

The bimodality is in qualitative agreement with a mass distribution obtained by Monte Carlo simulation of ash agglomeration during surface recession.¹ (That unexpected result was the original motivation for this study.) Analysis of Equation (1) indicates that the distribution N_i can be separated into two weakly coupled parts, namely a steady-state distribution at small s reflecting the balance between agglomeration and the source at $s=1$ and a transient distribution at large s that resembles the classical similarity solution for agglomeration with no source. Thus, the analysis provides a mathematical basis for the observed features. Analogous features have been reported in published measurements and Monte Carlo simulations of droplet nucleation and growth-induced agglomeration during vapor condensation on surfaces.² The present analysis likewise explains these observations.

Figure 2. Predicted surface-droplet mass distributions for a notional char particle of infinite radius. (Successive mass bins double in width.) Solid curves correspond to scaled perimeter recession distance $R=1.0$ (O), 2.0 (Δ), 4.0 (+), 8.0 ($\times$), and 16.0 ($\diamond$). The dashed curve is the limit curve corresponding to infinite recession.

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The Release of Iron During the Combustion of Illinois #6 Coal[†]

The formation of an iron fume during the combustion of coal particles has been observed. Experiments have identified a mechanism for the formation of this fume that is different from previously reported mechanisms for release of inorganic material from coal. This mechanism attributes the release to the thermal decomposition and subsequent chemical reactivity of pyrite, the major iron-containing mineral in the coal.

L. L. Baxter and R. E. Mitchell

Mineral impurities in coal are the source of many of the most severe practical problems in the operation of utility and industrial coal combustors. These impurities typically account for about 15% of the mass of the coal and are the source of such problems as particulate loadings in combustor stack gases and decreased thermal efficiency of combustors due to deposition on heat transfer surfaces. The mineral grains in the coal can undergo both chemical and physical transformations as the coal combusts. The inorganic materials responsible for the formation of fly ash and wall deposits are related to the original coal minerals through these transformations. Such transformations sometimes involve the escape or evolution of inorganic material from the coal particle. The focus of this research effort is on one such transformation involving iron.

Iron is one of the prevalent elements in coal mineral matter. Iron has a pronounced influence on the physical and thermal properties of both combustor deposits and fly ash. For example, the emissivity of fly ash generally increases with increased iron content and the temperature at which deposits sinter on surfaces (making them more difficult to remove) decreases with increased iron content. Combustor efficiency and particulate emissions may both be improved by an increased understanding of the rates and mechanisms of iron release from coal particles.

Data collected in a laminar flow reactor indicate a rapid loss of iron from coal/char particles as they reach the incipient stages of heterogeneous oxidation. Figure 1 illustrates a typical measurement of the amount of iron in the coal particles as a function of residence time in the reactor, normalized by the original amount of iron in the coal. As much as half of the iron in an Illinois #6 coal is released over a 2-ms period during this early stage of combustion.

The results are repeatable for different levels of bulk oxygen concentration (6 and 12%) and for different particle sizes (80 and 115 μm).

Iron leaves the coal char particles too rapidly to be explained satisfactorily with vaporization processes. Vaporization processes are the traditional explanation for evolution of inorganic material from char particles. An additional suggestion that vaporization is not the mechanism of iron release is the observation that the extent of iron loss increases with decreasing particle size; this trend is opposite that expected for vaporization of inorganic species under these conditions. These, and other, experiments suggest that the loss of iron from the particles occurs only if the iron appears in the form of pyrite in the original coal and if there is oxygen available to the particle surface during combustion.

A mechanism for iron evolution is postulated that explains the observed data and correctly predicts sensitivities to variables such as particle

Figure 1. The normalized iron content of an Illinois #6 coal as a function of residence time. In this experiment, the particles ranged in size from 106 - 115 μm , the gas contained 6-mole-% oxygen, and the gas temperature varied from ≈ 1850 to 1600 K over the particle residence time shown.

[†]Combustion and Flame, submitted (1988).

size. This mechanism is illustrated conceptually in Figure 2. Pyrite thermally decomposes to form pyrrhotite at a temperature of approximately 820 K. Pyrrhotite has an approximate chemical formula of Fe_7S_8 and no definite crystalline structure. About half of the coal mass is volatilized simultaneously, with the volatiles consuming the oxygen in the immediate vicinity of the particle. The pyrrhotite grains are reactive to oxygen and highly porous. The char particles and pyrrhotite are exposed to oxygen at the end of coal devolatilization as the cloud of coal volatiles convectively separates from the particle. The porous pyrrhotite grains disintegrate as they react

Figure 2. A conceptual illustration of the major features of the mechanism of iron-fume formation during coal/char combustion.

with oxygen to form iron and sulfur oxides. The iron-containing nodules of the pyrrhotite, which are about $0.1 \mu\text{m}$ in diameter, form an iron-containing fume, part of which escapes to the surrounding gas phase.

Analyses of collected samples of char particles from combustion environments by a scanning electron microscope (SEM) verify many aspects of this mechanism. Figure 3 illustrates two of the most important aspects. Part (a) of the figure illustrates the detailed structure of a representative pyrrhotite grain immediately before the release of iron from the coal particle. This SEM was taken from one of the solid samples on which the data at 47-ms residence

time in Figure 1 are based. Note the porous structure of the pyrrhotite grain. Part (b) of the figure is representative of the iron-containing residue on char particle surfaces immediately after the evolution of the iron to the gas phase. Most of the small particles littering the surface of the char particle are iron oxide grains of about $0.1 \mu\text{m}$ diameter. The original residue of the pyrrhotite grains can also be seen as disintegrated pockets of inorganic material over several regions of the particle surface.

This mechanism identifies some of the practical variables that can be used to control the fate of pyrite and its decomposition products during coal combustion. The typical gas temperature and composition to which a particle is exposed in a full scale combustor is controlled by a variety of means to reduce pollutant production and maintain high carbon conversion. These methods include forming regions of fuel-rich stoichiometry in the reactor and altering heating rates and gas temperatures to which the particles are subjected. The same controls will impact the extent of iron-fume formation of pyrite-bearing coals and will impact the amount, chemical composition, and size distribution of coal fly ash.

Figure 3. Scanning electron micrographs illustrating (a) the detailed structure of the porous pyrrhotite grains, and (b) disintegrated pyrrhotite grains on char particle surfaces in the midst of iron oxide particulate.

Laser-Spark Spectroscopy for *In Situ* Analysis of Particles in Combustion Flows

Laser-spark spectroscopy and near-forward Mie scattering are being used as optical techniques for in-situ measurements on particles in combustion environments. These two laser-based methods give information about the elemental composition, size, and velocity of pulverized coal particles in an entrained flow reactor.

D. K. Ottesen

The object of this research program is the *in-situ* determination of particle characteristics for coal, char, and mineral matter in the combustion zone of an entrained flow reactor. Laser-spark spectroscopy¹ is being used to determine the elemental composition of individual coal particles, while particle size and velocity are measured using a two-color, light-scattering technique.²

The two laser beams that are used to make sizing measurements are also used to trigger a high-power, Nd:YAG laser when a particle is centered in the confocal volume of the CW laser beams. The laser energy deposited in the particle rapidly heats the material, forming a plasma. The hot elemental species contained in this "spark" produce a series of intense emission lines that are detected using a grating spectrometer with a diode-array detector.

Time-resolved spectroscopy is used to maximize the observed emission from neutral or singly ionized atoms. This simplifies considerably the number of observed emission lines and their interpretation. Species detected in coal by this method thus far include: C, H, O, N, Li, Na, K, Mg, Ca, Ba, Sr, Al, Si, Ti, Mg, and Fe. The detection limit is apparently < 100 ppm for most metals in a single particle.

Measurements on particles in a combustion environment this past year have demonstrated that the signal/noise ratio of the observed emission spectrum is not degraded by the combustion process.³ These data were acquired over the wavelength range of 240 - 780 nm and illustrate the technique's applicability for *in-situ* measurements in combustion flows.

There are several critical issues that complicate the application of emission spectra to the quantitative elemental analysis of particles. Major concerns are: (1) variations in plasma temperature during the measurement time, across the spectrometer field-of-view, and from particle to particle;

(2) possible self-absorption of emitted radiation for very strong transitions; (3) matrix effects that would cause the composition of the plasma not to be representative of the particle composition; and (4) insufficient sampling during analysis because only a portion of the total particle was converted to a plasma.

Effective plasma temperatures have been calculated using several Mg and Fe transitions with the assumption of local thermal equilibrium. Very good relative agreement was obtained for the two groups of lines, and an average temperature of 10,500 K was calculated for our time delay of 2 μ s following plasma initiation. These temperatures were then applied to Boltzmann and Saha analyses of the integrated line intensities. This allowed us to extract the elemental composition of the individual particles relative to a reference line. For times early in the combustion process, a logical choice was the carbon neutral transition at 247.9 nm that is easily observed and not prone to self-absorption.

Figure 1. Fitting coefficients for Si I and C I emission intensities in laser-spark spectra for 41 individual coal particles.

An example of this is shown in Figure 1 for fitting coefficients relating silicon to carbon emission intensity in 41 coal particles. The large scatter of the points clearly illustrates the heterogeneity of the coal particles in silicon-containing minerals. On the other hand, a plot of silicon-versus aluminum-fitting coefficients in Figure 2 shows a linear correlation that would be expected for clay minerals containing aluminosilicates. The scatter in these data is probably due to the presence of silicon in quartz, which would be completely uncorrelated with the silicon present in clays.

Problems with self-absorption of radiation for more intense transitions are generally avoided due to the availability of many observed lines for each of the several elements present in coal. Self-checking to avoid this difficulty was incorporated into our analytical computer code.

Our primary effort is now focused on the statistical analysis of large sets of spark emission data for several well-characterized coals in order to assess the magnitude of matrix effects. These effects cause the enrichment of the more volatile constituents in the plasma relative to the parent solid particle, and can bias significantly the spectroscopic analysis.

Comparison of a preliminary spectroscopic analysis to bulk chemical analyses and studies using scanning electron microscopy indicate that matrix effects are important for this measurement technique. Careful calibration through these statistical analyses, along with measurements on homogeneous samples such as impregnated char particles, will define ultimately the accuracy of particle composition determinations. When these results are combined with the simultaneous particle size and velocity measurements, the resulting comprehensive statistical picture should be most helpful in understanding the evolution, and eventual fate, of inorganic species such as ash and pollutants in pulverized coal combustion.

Figure 2. Fitting coefficients for Si I and Al I emission intensities in laser-spark spectra for 68 individual coal particles.

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Rates of Mineral-Matter Deposition in Coal-Fired Boilers: Coal Type and Particle Residence-Time Dependencies[†]

Mineral-matter deposition in coal-fired furnaces was studied in the Multifuel Combustor. Both coal type and particle residence time strongly influenced the deposition rates and physical characteristics of the deposits.

L. L. Baxter, K. R. Hencken, and N. S. Harding*

The structure of deposits in full-scale, coal-fired boilers and the rates at which they form depend on both their location and the type of coal being fired. In this study, the Multifuel Combustor (MFC) was used to investigate the effect of these variables systematically in an environment representative of full-scale boilers.

A sectional view of a typical pulverized-coal-fired boiler is shown in Figure 1. The flame in the boiler is located in the bottom one-third of the radiant section. In the type of boiler illustrated here, the coal is transported pneumatically into the radiant section through burners in the side wall. There are other types of pulverized-coal-fired boilers, but essentially all generate a coal flame in the bottom one-third of the radiant section. The hot gases emitted from the flame flow upward through the radiant section, turn around the nose, and flow through the convection section. From the convection section, the gases flow through particulate- and gas-cleanup systems and are vented to a smokestack. Deposition of inorganic material from the coal is most prevalent in the radiant and convection sections. The boilers are quite large, typically 50-meters-high and 20-meters-across in both directions. They consume coal at rates as high as several hundred tons/hr. Typical U.S. coals contain 10 - 15% mineral matter, yielding a mineral feed rate to the boiler of several tens-of-tons per hour.

Experiments conducted in the MFC examined the structure and rate-of-deposit formation under conditions representative of three different locations in the boiler, as indicated in Figure 1. The first is in the radiant section where there are strong influences from the coal flame. The walls in this section of the boiler are composed of alternating

tubes and membranes, with the tubes carrying water/steam. Deposition of inorganic material on these walls decreases the heat-transfer rate to the tubes and, therefore, the overall boiler efficiency. Particle residence time at this location in the boiler is approximately 0.5 s.

The second location simulated in the MFC is representative of conditions near the inlet of the convection section. In this section of the boiler, bundles of steam-bearing tubes are inserted in the flowing particle-laden stream to superheat the steam. Deposits in this section can plug the air passages between the tubes, causing an unscheduled shut-down and repair of the boiler. These deposits also decrease the heat-transfer efficiency to the tube. Particle residence times in this section of the boiler are approximately 1.0 - 1.5 s.

The final location simulated in the MFC is representative of conditions near the back end of the convection section of the boiler. This section also contains bundles of tubes in the particle-laden stream. The mechanisms of deposition are similar to those in the previous location, but particle residence time is in the range of 1.5 - 2.5 s.

Figure 1. A conceptual diagram of a full-scale, pulverized-coal-fired boiler. The three locations in the boiler that were simulated by the Multifuels Combustor are indicated.

[†]ASME Journal, submitted (1988).

*Consolidation Coal Company, Library, PA.

Five fuels were used in the experiment: they included a lignite from North Dakota (Beulah Zap), three high-volatile bituminous coals, one each from Kentucky, Illinois, and western Pennsylvania, and a blend of Pittsburgh and Upper Freeport (both high-volatile bituminous) coals. Coal blends are sometimes used in commercial boilers as one approach to managing deposition problems. (The deposition behavior of a coal blend may vary significantly from the deposition behavior of the individual coals of the blend.)

The mineral properties of these coals vary substantially except for the Kentucky and Illinois coals. For example, the fouling factor ($(\sum X_{\text{bases}} / \sum X_{\text{acids}}) X_{\text{Na}_2\text{O}}$) varies from 6.7 to 0.4, which covers a large range of fouling behavior. The initial deformation temperature of the ash in a reducing environment varies from 1390 to 1511 K.

The results of the experiment are graphically represented in Figure 2. The figure illustrates how the average rate of deposition varies monotonically with position in the boiler for a given type of coal: the highest rates being those nearest the flame where the gas and particle temperatures are highest. The rates of deposition noted in the figure are normalized to the highest rates observed; i.e., those for the Pittsburgh #8 coal near the burner.

Figure 2 also illustrates the dependence of deposition rate on coal type for each simulated location in the boiler. Some of the data for the lignite are not conclusive due to uncertainties in the coal feed rate and particle sizes. The largest rates of deposition are observed for the Pittsburgh #8 bituminous coal, which contains the highest percentages of sulfur and pyrite. Coals containing less sulfur or pyrite show less propensity to deposit. Coals with similar mineral forms, such as the Kentucky and Illinois samples, behaved similarly.

In addition to the strong coal type and boiler-position dependencies, the deposit structures and composition differ. The initial deposits generated from the iron-bearing coals (Pittsburgh #8, Illinois #6, and Kentucky #9) form columns of ash on the probe oriented in the direction of the approaching gas. The structure of the columns becomes less pronounced as the deposit ages, but it never entirely disappears. Furthermore, the deposit forms over a fairly narrow region of the probe. The deposits from the lignite do not tend to form column structures but rather cover the entire probe surface.

Future work in the MFC will focus on the *in situ* determination of surface composition, temperature, and thickness in an attempt to understand and control the chemistry and physics involved in deposition of inorganic material during coal combustion.

Figure 2. The variation of deposition rate with coal type and simulated location in the boiler.

The Dynamic Variation of Particle-Sticking Coefficients During Mineral-Matter Deposition in Coal-Fired Combustors[†]

Growth of mineral deposits has been studied in the Multifuel Combustor using high-speed video cameras and temperature-controlled deposition probes. The fraction of fly ash particles that adhere to the probe upon collision was found to vary substantially during deposit formation, taking on both positive and negative values.

L. L. Baxter, K. R. Hencken, and N. S. Harding*

Deposition of inorganic material on surfaces of coal-fired boilers is influenced by both vapor and particulate entrained in the gas phase. This study focuses on the particulate behavior. High-speed video images of particle-laden flow around a tube were obtained to determine the propensity of particles to stick when they collide with surfaces. This study focuses on the magnitude and time variation of a particle-sticking coefficient in an environment representative of coal combustion.

The rate of deposition of inorganic material on surfaces is known to depend on the type of coal used as fuel, the residence time of the particles in the combustor, the deposition tube surface temperature, the flue-gas composition and temperature, and the firing rate. In this study, the firing rate is defined as the rate of heat release per unit cross-sectional area of the combustor. The Multifuel Combustor (MFC) and associated experimental equipment were used to generate an environment in which each of these variables was controlled within a range representative of full-scale equipment. Five coals were used, varying in rank from lignites to a high-volatile bituminous blend. The particle residence times varied from 0.5 to 3.0 s. A carbon-steel tube was inserted in the particle-laden, hot gas flow and the surface temperature of the tube was maintained at about 500°C to simulate surface conditions in commercial-scale boilers. The gas composition included about 3% oxygen and the gas temperature was about 1200 K. The firing rate of the combustor was similar to that of typical full-scale boilers (10 kW/m²).

The particle-sticking coefficient, γ , typically is used to characterize the propensity of particles to stick on a surface upon collision. The total mass of deposit accumulated on a surface can be expressed in terms of this coefficient as follows:

$$m_d(t) = \int_0^t \gamma(t') \dot{q} dt' + O$$

where m_d is the total mass of the deposit per unit surface area and $\dot{q}$ is the mass flux of particles colliding with the surface. The term O accounts for other influences on the mass of the accumulated deposit, such as soot blowing. No influence, other than that of particle impaction, was studied during these experiments; therefore, the term O will be neglected.

The sticking coefficient, γ , is often regarded as a constant for a given set of operating conditions. The MFC provides optical access to the deposits as they grow which allows the complex nature of γ to be monitored. The complexity of γ is illustrated most clearly in the data for a Pittsburgh #8 coal under conditions that represent the near-flame region of a commercial boiler. Representative results of the experiment are shown in Figure 1, with approximate mass of deposit collected per unit area of the surface shown in Figure 2. The qualitative variation of γ with time for the other coals and operating conditions was similarly complex. However, the details of the behavior of γ were unique for each coal and each particle residence time. The factor γ will be treated as a function rather than a coefficient in the remaining discussion.

The initial values of the sticking function are very low for all of these coals at all particle-residence times studied. The high-speed video images capture the dynamic motion of the particles

[†]ASME Journal, submitted (1988).

*Consolidation Coal Company, Library, PA.

Figure 1. Representative variation of the sticking function with time (Pittsburgh #8 with particle residence time of about 0.5 s).

as they collide with the surface and indicate particle-sticking functions in the 0 - 0.005 range. In essentially all cases, the collisions are nonelastic, with large decreases in particle speed after collision. Both particles and accumulated deposit on the tube surface suffer deformation upon collision to account for the difference in kinetic energy.

The value of the sticking function initially increased for all coals at all residence times, eventually attaining values as high as 0.5 - 1.0 in some cases. The time required to reach the high values depends on coal type and residence time, varying from a few minutes to hours. The maximum value of the sticking function depends most strongly on coal type and less strongly on particle residence time. Experiments also indicate that the maximum value depends on firing rate.

As the deposit grows, it sometimes becomes unstable and collapses under its own weight. This collapse is caused by the additional stress of new particles added to the surface. This behavior implies a negative value for the sticking function. In the case of the data illustrated in Figures 1 and

Figure 2. Representative variation of deposit mass per unit area with time (Pittsburgh #8 with particle residence time of about 0.5 s).

2, the effective particle-sticking function attained negative values with very large magnitudes (too large to be represented conveniently in Figure 1). The deposit mass on the probe decreased significantly, but it did not become zero. That is, some residual deposit remained on the tube (see Figure 2).

The sticking function then became positive, again attaining values on the order of 0.5 - 1.0. The deposit thickness began to increase for the second time. This second growth resulted in a more dense deposit than the first. In all cases where the experiments were sustained during this second growth, the deposit thickness exceeded that of the first growth. After significant growth, deposit erosion again decreased the deposit thickness.

The sticking function never stabilized to a single value during these tests. These tests indicate the complexity of the particle-surface interactions during deposition of inorganic material. Future experiments in the MFC are planned that will attempt to resolve this complexity by detailed *in situ* studies of the temperature, thickness, chemical composition, and phase of the deposits.

The Effect of Slurry Surfactants on the Disaggregation of Coal-Water Slurry Particles During Combustion[†]

The presence of a surfactant in coal-water slurries tends to prevent disaggregation of coal aggregates during combustion. Disaggregation of coal particles has a potentially large positive influence on flame stability, burnout, and pollutant levels from flames.

L. L. Baxter and Z. G. Habib*

Coal-water slurries are among the most near-term alternatives to heavy fuel oils and diesel for electrical power generation and some applications in heat engines. On a mass basis, these slurries typically contain 45-70% coal, 1% total additive, and the remainder, water. The most common additives are stabilizers and dispersants. Stabilizers act to prevent the slurry particles from settling out of the water. The most common dispersants are surfactants, and in all cases, they are added to improve the rheological properties of the slurry. With proper engineering, slurries can be produced that flow through pipelines into combustors in a manner similar to heavy fuel oils.

Typical combustion behavior of the slurries is diagrammed schematically in Figure 1. Slurry droplets are atomized to produce a fine mist with average droplet diameters on the order of 55 μm . The average diameter of coal in the slurry is usually much smaller than that of the droplets produced during atomization. Therefore, typical droplets contain many coal particles. As these droplets dry, the individual coal particles aggregate together but the diameter of the cluster does not appreciably change. The coal particles soften as they heat up, fusing the individual particles in the aggregate. The aggregates then combust through a typically sequential process of devolatilization and oxidation, much the same as pulverized coal particles.

Experiments conducted in this study suggest that surfactants are promoting the formation of

slurry by promoting the formation of a fused surface around the slurry droplet. The dispersing action of the surfactant is responsible for this fused surface. Coal particles in the interior of the droplet repel one another. Therefore, particles tend to migrate to the droplet surface. The constraints of the droplet size and particle loading indicate that the smaller, more mobile particles will be deposited preferentially on the droplet surface. Slurry droplets form a thin surface layer of surfactant/coal particles.

Our experiments indicate that this thin surface layer inhibits slurry particle disaggregation. Figure 2 shows the results of a series of experiments in which slurry particle size was measured by an *in situ* particle size diagnostic, largely developed at Sandia. Results are shown for two slurries, one prepared with and the second without a surfactant. Other than the surfactant, preparation techniques for the slurries are identical. The figure shows the relative number of particles of a given size contained in each slurry as a function of time. At early times, (i.e., immediately after atomization), the particle size distribution of both slurries is identical. The figure shows the relative number of particles of a given size contained in each slurry as a function of time. At later times, the slurry containing no surfactant pro-

Figure 1. Schematic illustration of the behavior of slurry particles during coal combustion.

Figure 2. Number of particles detected in a spray generated from a slurry with no surfactant relative to a slurry with surfactant. Both time and size dependence are shown.

[†]Combustion and Flame, submitted (1989).

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duces significantly greater numbers of small particles than that containing surfactant. This increase in small particles is attributed to disaggregation of the largest particles. (Particles larger than about 50 μm were not detected by the instrument at all residence times.)

Further experimentation indicates that disaggregation of slurry particles occurs at the final stages of water vaporization but before coal softening or devolatilization. Disaggregation reduces the average particle size in the combustor by a factor of about 1.8. This reduction occurs after water vaporizes from the slurries, i.e., after the droplets are in the reacting flow. Disaggregation can be thought of as a secondary atomization process in this respect.

A computer code that predicts the fluid dynamics, heat transfer and particle combustion characteristics of axisymmetric combustors was modified to treat slurry droplet disaggregation and predict the impact it has on combustion characteristics. The data collected in these experiments were entered in the code and three calculations were performed. The first assumed that no secondary atomization occurs. A three-dimensional view of the temperature field for this case is shown in Figure 3. The height of the field represents temperature while the bases of the figure represent axial and radial locations, as labeled. Flow generally is in the axial direction, although the details of the flow field are complex. The atomizer is located at the origin of the axial and radial coordinates. The rapid rise in temperature (about a third of the distance into the combustor) represents an effective ignition point. The flame is lifted a substantial distance from the burner/atomizer.

The second calculation uses the same initial particle size distribution for the atomized spray but allows the particles to disaggregate. The extent

of disaggregation, or secondary atomization, was derived from the data collected in the previous experiments. A predicted gas-temperature field is shown in Figure 4, in the same format as Figure 3. Note that the flame is closer to the burner and has a more slender shape than in the case with no secondary atomization.

A final calculation was performed to determine the relative effectiveness of primary versus secondary atomization. In this case, the primary atomized droplet sizes were equated to the sizes of the previous case *after secondary atomization*. That is, the droplets began with smaller sizes but did not disaggregate. In this case, the flame is predicted to be strongly attached to the burner and to have a slender shape.

The trends shown in these predictions have several positive implications for commercial-scale equipment. Carbon burnout increases and NO_x levels decrease as the flame becomes more attached. Attached flames are more stable and controllable than detached flames. Finally, particles that react rapidly (due to their small size) may allow the dimensions of the combustor to be smaller compared to larger, less rapidly reacting particles.

Our experiments indicate that disaggregation of slurry droplets is enhanced if surfactants are not used in the slurries. Computer models predict the effect of these laboratory results on commercial-scale equipment. Particle disaggregation, or secondary atomization, of the extent seen in these experiments expands the operating window of commercial-scale equipment. However, changes in primary atomization have a more significant impact than disaggregation. Therefore, commercial-scale equipment would be expected to benefit from secondary atomization if it can be attained without compromising primary atomization.

Figure 3. Predicted temperature field in an axisymmetric slurry combustor with no particle disaggregation.

Figure 4. Predicted temperature field in an axisymmetric slurry combustor with particle disaggregation.

Coal Combustor Performance Calculations of the Combustion Engineering Fireside Performance Test Facility

A two-dimensional, axisymmetric coal combustor model was used to describe the combustion performance of the Fireside Performance Test Facility at Combustion Engineering's Kreisinger Development Laboratory. Numerical experiments show the importance of the secondary inlet swirl on combustion performance.

T. H. Fletcher

Effects of physical cleaning on coal combustor performance was recently studied in a series of experiments at the Fireside Performance Test Facility (FPTF) at Combustion Engineering's Kreisinger Development Laboratory in Windsor, CT. Physical cleaning processes attempt to reduce the noncombustible inorganic content (ash) in pulverized coal used for electric power generation. Three stages of cleaning were studied for a Pittsburgh #8 high-volatile A bituminous coal: (1) run-of-mine (ROM) coal (34% ash), (2) medium-cleaned C1 coal (11% ash), and (3) deep-cleaned C2 coal (9% ash). Pilot scale tests in the FPTF showed the presence of unacceptable levels of unburned carbon in the fly ash for the cleaned coals (12% carbon for the C1 coal and 8% carbon for the C2 coal). The presence of unburned carbon in the fly ash affects electrostatic precipitator performance and renders the fly ash unacceptable as a byproduct for commercial use.

In a recent collaborative study sponsored by EPRI, the same three coals (Pittsburgh #8 ROM, C1 and C2) studied in the FPTF were characterized in our Coal Devolatilization Laboratory and in our Char Combustion Laboratory using techniques described by Fletcher¹ and Mitchell.² Char oxidation coefficients were generated for each coal from two-color, sizing-pyrometer measurements of individual particles. The burning rates of the three coals were essentially identical when normalized on a dry, ash-free (daf) basis. The volatiles release rates and daf yields determined for these coals were also identical, within the scatter of the experimental data.

The devolatilization and char oxidation data obtained for these coals were used in a comprehensive, two-dimensional, axisymmetric coal combustor model³ to describe the performance of the FPTF for the Pittsburgh #8 C1 coal. Fluid mechanics were modeled using steady-state, finite-difference

techniques and the k- ϵ turbulence model for closure. Particle mechanics were modeled along Lagrangian trajectories using the PSI-CELL technique.⁴ Gas-phase turbulence was adjusted for the presence of particles, and the effect of turbulence on particle motion was modeled semi-empirically. Gas-phase chemistry is treated assuming reactions are micro-mixing-limited, with transport equations for the mixture fractions of inlet gas and coal off-gas, as well as their mean-square fluctuations. Instantaneous gas properties, such as temperature and species concentrations, were calculated from local elemental composition as a function of the two mixture fractions. Time-mean gas properties were calculated by convoluting the instantaneous properties over a Gaussian probability density function (PDF) based on the turbulence statistics of the mixture fractions. Gas and particle radiation were solved using a six-flux model that includes anisotropic and multiple scattering. Gas-phase emissivities were calculated for emitting species (H_2O and CO_2).

The main combustor section of the FPTF is 3.3 m long and 0.9 m in diameter. The primary air is used to entrain the pulverized coal. The secondary air enters through an annulus surrounding the primary air tube. Adjustable swirl vanes are located in the secondary annulus, and the swirl vanes are adjusted to produce reasonably flat radial gas temperature gradients. Tertiary combustion air is added through four tangentially oriented nozzles in a ring near the walls at an axial distance of 0.7 m. At the top of the combustion chamber, the flow is directed into a channel designed to simulate the superheater section, including four banks of air-cooled tubes.

The main combustion chamber of the FPTF is two-dimensional and axisymmetric, except for the four tertiary air jets. Tertiary jets are modeled as inlets along the entire circumference of the reac-

tor. Numerical experiments were performed using the combustor model to examine the effect of swirl number, reactor heat loss, and char reactivity on predicted combustor performance for the CE FPTF tests on the Pittsburgh #8 C1 coal.

The numerical experiments show that the degree of swirl in the secondary inlet stream significantly affects combustion performance. As the secondary swirl increases, a central recirculation zone develops which brings hot combustion gases into contact with unburned coal. Predicted flow patterns in the FPTF for a case with secondary swirl number of 1.5 are shown in Figure 1. Inlet velocities are 30-60 m/s, but the main flow pattern is along

the wall next to the burner. Centerline recirculation is indicated by the flow direction at an axial distance of 1.0-1.5 m.

The calculated coal-burnout profiles for different degrees of secondary swirl are shown in Figure 2. Burnout occurs earliest in the case with a secondary swirl number of 1.5, since gas temperatures are higher near the burner inlet due to increased recirculation of hot combustion products. It is possible that differences in combustion characteristics of different coal types examined in the FPTF may actually be caused by furnace operating conditions, rather than by differences in chemical reactivity of the parent coal.

Figure 1. Gas velocity patterns predicted in the FPTF when the secondary swirl number is 1.5. Length of each vector is proportional to the magnitude of the predicted gas velocity.

Figure 2. Effect of secondary swirl number on cumulative, radially integrated coal burnout in the FPTF. Reactor exit is located at $z = 3.3$ m.

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Section 9

Ignition and combustion characteristics of liquid propellant at high pressure are studied in a windowed pressure vessel. This photograph shows the propellant, contained in an open top quartz cuvet, just prior to ignition. Propellant ignition is accomplished by irradiating the top of the propellant sample with a pulsed carbon dioxide laser (the carbon dioxide laser beam is collinear with the red helium neon beam). Ignition and combustion are then studied using high-speed photography and spectroscopy.

Energetic Materials

Characterization of the ignition of propellants is important for both safety and design considerations. For safety, the sensitivity of the propellant should be known so that ignition occurs only when it is required. For design, it is useful to know the amount of heat necessary to ignite and sustain combustion. Controlling the heat input to a propellant sample in a well-defined experiment provides a method for determining propellant sensitivity and ignition characteristics.

This schematic shows the setup of a laser ignition experiment. The propellant, contained in the pressure vessel, is ignited by a carbon dioxide laser and is studied by high-speed photography and

emission spectroscopy. The infrared carbon dioxide laser beam can be controlled externally to provide a pulse of energy of the required energy and pulse duration. This beam, which is invisible, is then combined with a visible helium-neon laser beam to aid in controlling its direction. The combined beams enter through the top of the pressure vessel and impinge on a container of liquid propellant. High speed photographs, using an argon-ion laser as a light source, provide a record of gas generation in the liquid propellant. Emission spectroscopy of the ignition event provides a means of identifying chemical species.

Section 9

Energetic Materials

Our Research program in energetic materials emphasizes fundamental studies directed to further the understanding of the combustion chemistry and physics of energetic solids and liquids. The objective is to improve propellant performance through studies using advanced laser diagnostics and computer models. An ultimate goal is to develop the technology base leading to new propellants and explosives. Program sponsorship is derived primarily through a Memorandum of Understanding between the Department of Energy and Department of the Army

The experimental effort consists of solid propellant, thermal decomposition and deflagration studies as well as liquid monopropellant ignition and combustion studies. Related gas-phase flame experiments at reduced pressure are designed to investigate the two-stage flame character exhibited by many solid propellants, including chain-branching chemistry and thermal diffusion. Thermal decomposition studies of solid propellants using a modulated molecular-beam mass spectrometer are carried out to determine quantitatively the molecular fragments and reaction products that result from the decomposition.

A strong modeling program accompanies the experimental effort. Quantum chemistry calculations provide information about thermochemical heats of formation and possible reaction pathways for the decomposition of energetic molecules. Solid- and liquid-propellant deflagrations are being modeled analytically through the use of multi-dimensional thermochemical codes. These studies include liquid monopropellant droplet combustion calculations using a new code capability derived from hydrocarbon combustion work.

Concentration Effects on the Decomposition Rate of Hydroxylammonium Nitrate-Based Liquid Propellants[†]

Experiments on a range of liquid propellant formulations yield insight into the physical processes important in liquid propellant combustion.

S. R. Vosen

Measurements of the burning speed of hydroxylammonium nitrate-based (HAN-based) liquid propellants by conventional strand-burning techniques produce results which are very unusual and have not been explained adequately.¹ Specifically, the overall burning rate in a strand burner decreases with an increase of pressure. This trend has also been observed for HAN-water mixtures,² confirming that HAN decomposition is the rate-limiting step in the combustion of HAN-based liquid propellants.³ To further understand the reason for the pressure dependence of the burning rate of HAN-based propellants, the effect of hydroxylammonium nitrate concentration on the decomposition rate has been measured over a factor of 3 in concentration (from 5 to 13 M in water) and a factor of 6 in pressure (from 6 to 34 MPa). The results provide new insight into the importance of both chemical and physical effects governing the combustion of HAN-based liquid propellants.

The apparent decomposition rate as a function of pressure for 5.20, 7.02, and 9.10 M HAN mixtures

Figure 1. Mass decomposition rates for 5.20, 7.02, and 9.10 M HAN.

follows similar trends (see Figure 1). The decomposition rate decreases rapidly with an increase in pressure up to 13 MPa. At pressures greater than 13 MPa, it is pressure independent. High-speed cineradiography reveals a correlation between the shape of the decomposition interface and the change in the apparent decomposition rate with pressure. At low pressures, the interface is meniscus-shaped with small corrugations superimposed. The interface shape changes little as the decomposition propagates (on the time scale of tens or hundreds of ms), while the smaller scale instabilities change more rapidly (on the time scale of ms). Stated differently, small-scale instabilities have a higher oscillatory frequency than do the larger instabilities. As the pressure is increased, the meniscus becomes less pronounced. At pressures above 13 MPa, the interface is highly corrugated and changes rapidly with time, but has no large-scale meniscus. In both cases, the small-scale instabilities are on the order of 50 - 80 μ m in size. Thus, portions of the burning rate curve that are independent of pressure ($P > 13$ MPa for 5.2, 7.02, and 9.1 M HAN) correspond to a flat, corrugated decomposition front. Below 13 MPa, the burning rate versus pressure curve has a negative slope, corresponding to a pronounced meniscus-shaped decomposition front. At pressures less than, but closer to, 13 MPa, the decomposition front becomes flatter, resulting in a decrease in the apparent decomposition rate.

The decomposition rate of 11.05 and 13.00 M HAN mixtures, as a function of pressure from 7 MPa to 34 MPa, follows a slightly different trend from those of the less concentrated mixtures. For these mixtures, the decomposition rate decreases with increased pressure up to 34 MPa, the highest pressure at which experiments were done. The interface shape is similar to that seen for 5.20 to 9.10 M HAN mixtures at a pressure of less than 13 MPa. In other words, the interface has a large-scale meniscus that becomes less pronounced with increasing pressure, with smaller-scale instabilities superimposed. Presumably, the decomposition interface will become corrugated with no mean curvature at some higher pressure.

[†]Twenty-Second Symposium (International) on Combustion (The Combustion Institute, 1989), p. 1817.

To examine the effects of hydrodynamic instabilities on the apparent decomposition rate of HAN/water mixtures, the data were analyzed in terms of a driving force for hydrodynamic instabilities (that is, wave motion). Specifically, the ratio of the density of the decomposition products to unreacted liquid, ρ_d/ρ_u , was considered to be the main driving force for hydrodynamic instabilities. For each set of experimental conditions, a chemical equilibrium calculation was performed to determine ρ_d/ρ_u across the decomposition interface. The density ratio increases with pressure and decreases with increased HAN concentration.

The effect of density ratio on the apparent decomposition rate is shown in Figure 2, in which all data shown are a function of the density ratio. The correlation of the data is obviously much stronger than when one considers the decomposition rate as a function of pressure (see Figures 1 and 2). A close examination of the data in Figure 2 reveals a dependence of the decomposition rate with HAN concentration, but the dominant trend is the increase of the decomposition rate with density ratio (and hence pressure), indicating the importance of hydrodynamics at low pressure. The role of hydrodynamic instabilities is to deform the liquid interface into a pronounced meniscus, resulting in a larger interface area and hence a larger decomposition rate. At higher density ratios (corresponding to higher pressures), the liquid interface is distorted less and the apparent decomposition rate decreases. Eventually a density ratio is reached (≈ 0.15) where other forces (such as surface tension, viscosity and gravity) are dominant and the decomposition rate becomes independent of density ratio.

Figure 2. Apparent mass decomposition rate as a function of density ratio: 5.20, 7.02, and 9.10 M HAN.

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Hydrodynamic and Reactive/Diffusive Instabilities in a Dynamic Model of Liquid Propellant Combustion[†]

A dynamic model of liquid propellant combustion is introduced that couples the pyrolysis burning rate to the temperature and pressure fields. The model predicts both a stable parameter regime for steady, planar deflagration, and a new hydrodynamic and reactive/diffusive instability phenomena.

R. C. Armstrong and S. B. Margolis

The dynamic model of liquid propellant combustion that we introduce,¹ as with the classical models of Landau² and Levich,³ is applicable to those cases in which combustion can be approximated by an overall reaction at the liquid/gas interface (Figure 1). Appropriate limits, for which such an assumption is justified, include (1) those in which the gas flame occurs under near-break-away conditions or intrudes upon the liquid/gas interface and (2) that in which the liquid propellant simply undergoes exothermic decomposition at the surface without any significant distributed combustion. The latter, for example, appears to occur in some types of hydroxylammonium nitrate (HAN)-based liquid propellants at low pressure.⁴ If the liquid/gas interface is assumed simply to propagate normal to itself with a constant normal velocity, then steady, planar burning is intrinsically unstable unless other effects are present. Thus, Landau² showed that if the product of the gravitational acceleration (Fr^{-1}) normal to the interface and the coefficient of surface tension (γ) was sufficiently large relative to the mass burning rate, then this particular type of instability, referred to as hydrodynamic (or

Landau) instability, was suppressed. Later, Levich³ showed that the combined effects of gravity and (liquid) viscosity could produce a similar effect.

In the present work, we have adopted a more general, and more realistic, burning-rate law.

In particular, a temperature and pressure dependence on the normal propagation velocity is introduced, such as occurs, for example, when the mass burning rate is modeled by a condensed-phase pyrolysis law. In the absence of gravity, surface tension, and reaction-rate pressure sensitivity, a sufficiently large value of the reaction-rate temperature sensitivity is, at least for nonzero viscosities, capable of suppressing the hydrodynamic instability that results in a steady, but nonplanar (cellular), mode of burning. In addition, even larger values of this parameter result in a pulsating instability similar to the types of reactive/diffusive instabilities that are known to occur in other premixed combustion systems, such as solid propellants and combustion synthesis. The size of the stable region was found to depend on the values of both the gas- and liquid-phase Prandtl numbers; a decrease in these parameters was found to be generally destabilizing with respect to both types of instability. Nonplanar pulsating instabilities of the type predicted here have been reported recently in combustion experiments with HAN-based liquid propellants, such as mixtures of HAN and triethanolammonium nitrate (TEAN) with water.⁴

In the present work, we completely analyze the dispersion relation governing the stability of steady, planar burning in the limit of zero viscosity, allowing for nonzero values of not only the temperature sensitivity, but also the pressure sensitivity, gravity, and surface tension. When necessary, the analysis employs the ratio of gas-to-liquid density ρ as a small expansion parameter. In addition to providing a more complete description of the instabilities revealed in Reference 1, the results obtained here show that the effects due to the coupling of the burning rate with the pressure field lead to still more instability phenomena. These new results include the prediction of a pulsating, hydrodynamic,

Figure 1. Model geometry. The interface separates the unburned liquid propellant from the burned gaseous products.

[†]Combust. Flame 77, 123 (1989).

neutral-stability boundary and a reactive/diffusive cellular instability. The parameters Ξ and A_p , which measure, respectively, the temperature and pressure sensitivity of the pyrolysis reaction, will be regarded as critical parameters governing the stability of steady, planar burning, and the neutral-stability boundaries will be shown to be strong functions of both gravity and surface tension.

The results show that there are several types of instabilities that can render the steady, planar burning of liquid propellants unstable when the mass burning rate depends on both temperature and pressure. Sufficiently large and sufficiently small values of the pressure sensitivity parameter A_p , $A_p < 0$ are associated with hydrodynamic instability, which may be of two types, as illustrated in Figure 2, for $\Xi = 0$. The first of these is a cellular instability and the critical value of A_p (as a function of the disturbance wave number k for which it occurs) depends on gravity and surface tension. When $A_p = 0$, the resulting stability criterion for the gravity and surface tension is that obtained by Landau.² In addition, however, sufficiently small values of A_p result in a pulsating, hydrodynamic instability. This latter type of hydrodynamic instability, which is a new prediction for liquid propellants, is suppressed by nonzero values of the temperature sensitivity parameter Ξ . In contrast, the cellular (Landau) instability is essentially unaffected by the temperature dependence of the burning rate, at least in the limit of zero viscosity. However, the combined effect of viscosity and temperature sensitivity can suppress this type of hydrodynamic instability as well.²

Figure 2. Hydrodynamic, neutral stability boundaries for $\Xi=0$. The curves denoted by $\omega \neq 0$ and $\omega=0$ are pulsating and cellular stability boundaries, respectively.

In addition to these hydrodynamic instabilities, sufficiently large values of Ξ result in additional new instabilities of a reactive/diffusive nature, as illustrated in Figure 3. These may also be either pulsating or cellular types of instabilities, although for a given disturbance wave number k , the nature of the instability, if it occurs, will be of either one type or the other. Indeed, the pulsating boundary always terminates, since the pulsation frequency ω approaches zero, at the value of k for which the two boundaries intersect. The location of these stability boundaries depends on the values of the scaled hydrodynamic parameters $Fr^{-1} = \rho F^{-1}$, $\gamma^* = \rho \gamma$ and $A_p^* = A_p/\rho$, which represent effects due to buoyancy, surface tension, and pressure sensitivity, respectively. A decreasing value of A_p^* is stabilizing with respect to reactive/diffusive instability, but increasing either Fr^{-1} or γ^* produces the opposite effect. The latter trend apparently arises because gravity and surface tension, though stabilizing in a hydrodynamic sense, nonetheless inhibit the fluid motion that can counteract the perturbations which are otherwise reinforced through reactive/diffusive instability. The onset of a nonacoustic, pulsating instability is a new theoretical prediction in liquid propellant combustion and is observable experimentally in the deflagration of HAN-based liquid propellants at low pressures.⁴ Such low-frequency oscillations are also observable in many types of liquid-propellant rocket motors.⁵

Figure 3. Reactive/diffusive neutral stability boundaries for $\gamma^*Fr^{-1} > 9/4$ and $A_p^* \leq 0$ (figure drawn using the values $Fr^{-1} = 0.1$, $\gamma^* = 100$, $A_p^* = 0$).

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A One-Dimensional Model of the Thermal Decomposition of Hydroxylammonium Nitrate

A one-dimensional model of hydroxylammonium nitrate decomposition has been developed and compared with experiments performed in a high-pressure, strand-burner. Results indicate that quantities such as decomposition, temperature, and propagation speed are described well by one-step chemical kinetics.

D. S. Dandy

The thermal decomposition of a hydroxylammonium nitrate (HAN)-water system has been studied numerically for both planar and spherical geometries. Quantities such as decomposition temperature, species distributions, and propagation speed of the decomposition wave have been computed for six mixtures, ranging from 3.12 M to 13.00 M HAN. The HAN decomposition has been modeled successfully as a one-step, exothermic reaction and experimental results over the entire range of HAN molarities have been corroborated using only a single value for each of the constants present in the Arrhenius rate expression.

The motivation for studying the HAN-water system arises from experimental observations. It is believed that the initial reaction occurring in HAN-based, liquid propellant systems is thermal decomposition of HAN, followed by subsequent reactions to produce N_2O and NO_x compounds. Klein¹ has proposed that the first intermediates to be produced by HAN decomposition are H_2NOH and HNO_3 , and that it is this reaction that controls the liquid propellant burning process. The importance of HAN decomposition led to performing strand burner experiments to study the effects of varying HAN concentrations in water. The ability to use a simple, one-step model of the chemistry is of importance as it allows ready incorporation into existing gun codes.

The results presented here are based on the assumption that only one reaction occurs:

where the reaction can proceed only in the forward direction. Through trial and error, it was found that the kinetic properties of the HAN-water mixtures were represented accurately through use of the

Arrhenius form of the rate constant, with the rate constant k given by

$$k = 3 \times 10^{11} \exp[-20,000 / RT].$$

It is also assumed that the reactants and products are all a single phase; therefore, phase transition effects are ignored in this work. The thermodynamic and kinetic properties of the four chemical species present (HAN , H_2NOH , HNO_3 , H_2O) were all computed through use of the CHEMKIN computer code. The temperature- and pressure-dependent thermodynamic data for HAN are unknown, and were constructed using known data for several amine compounds. Data for H_2NOH , HNO_3 , and H_2O are known. The transport properties of the four compounds were approximated using best guesses for aqueous solutions and molten salts.

One-dimensional forms of the equations governing conservation of mass, momentum, and energy were solved, employing a dynamic, adaptive gridding scheme for accurate resolution of regions of high temperature and concentration gradients. The initial condition used in all calculations was a step-jump in temperature from the cold HAN-water mixture at 300 K to an equilibrium-products temperature and corresponding step-jumps in species mass fraction from the unreacted monopropellant to the equilibrium products. The results compared favorably with strand burner results.

Figure 1 displays the steady temperature profiles in the computational domain at various times for HAN concentrations in the range 3.12–13.00 M. The distance between curves, divided by the time $\Delta \tau$, represents the propagation rate of the reaction front into the cold monopropellant. A steady decomposition wave could not be sustained for the

3.12 M mixture; the decomposition reaction is not sufficiently exothermic to sustain reaction at this low HAN concentration.

The temperature profiles in Figure 1 reveal that the temperature gradient (that is, the steepness of a profile) increases with increasing HAN molarity. Thus, at higher molarities, propagation of the decomposition wave occurs on a time scale faster than the diffusion of energy through the medium, while at lower molarities diffusion is important and the decomposition front spreads out.

The species profiles in the domain for the six mixtures are shown in Figure 2. The profiles for the 3.12-M mixture (which are plotted on a different scale than the other five mixtures) indicate the presence of the product species H_2NOH and HNO_3 in the unreacted region. Although the decomposition

Figure 1. Temperature profiles arising from the decomposition of hydroxylammonium nitrate in a planar strand burner. The decomposition wave is propagating left-to-right; to the right of each decomposition wave is unreacted monopropellant and water at 300 K. The time between each curve is constant for each mixture.

reaction cannot sustain itself at this molarity, the products were introduced into the system and both diffuse to the right into the cold monopropellant as time increases. It is interesting that, for HAN molarities greater than 9.1, the H_2O mole fraction in the reaction zone dips below the equilibrium value it attains downstream in the products region. This dip is due to the rapid production of H_2NOH and HNO_3 in a very thin region, coupled with the slight increase of HAN in this same area.

It has been shown with this one-step kinetic model that the Sandia strand-burner results can be explained, and further, that quantities such as temperature and species profiles can be predicted, although these quantities cannot yet be verified experimentally.

Figure 2. Steady-state species profiles in the computational domain of the planar strand burner. Note that the ordinate for the 3.12 M case is a different scale than that for the other five cases.

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Thermal Decomposition of HMX and RDX in the Condensed Phase

The identification and determination of the temporal behavior of the rates of formation of the gaseous products from the pyrolysis of HMX at a constant temperature, 30 to 80 degrees below its melting point, in conjunction with transmission electron micrographs of the polymeric residue remaining after the decomposition, suggest that the products are formed in bubbles within the solid particles. The pressures within the bubbles may range up to 2000 psi.

R. Behrens, Jr.

Pyrolysis products from the thermal decomposition of HMX and RDX have been identified, and their rates of formation have been determined by making simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS)¹ and time-of-flight (TOF) velocity-spectra measurements on decomposing samples of HMX and RDX and their deuterium- and ¹⁵N-labeled analogues.

The rates of formation of the pyrolysis products from the isothermal decompositions of HMX that has a median particle diameter of 150 μm and is 30 C to 80 C below its melting point show an autocatalytic-like feature as reported previously.² The products from the decomposition are H_2O , HCN, CO, CH_2O , NO, N_2O , CH_3NHCHO , $\text{C}_2\text{H}_6\text{N}_2\text{O}$, octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA), and a nonvolatile residue (NVR). The rates of gas formation of each of the products vary by factors of up to forty during the isothermal decomposition. The molar ratio of N_2O to CH_2O formed during the entire decomposition is approximately 3:2. However, examination of the temporal behavior of the rates of formation of these two products shows a much wider variation during decomposition. The most interesting features are:

- during the acceleratory period, the rates of formation of H_2O and N_2O are approximately equal;
- the ratio of the rates of formation of N_2O to CH_2O varies from a maximum of 3 during the acceleratory phase to a minimum of 0.8 during the decay phase of the decomposition;
- the gas formation rates of the minor products, methylformamide, $\text{C}_2\text{H}_6\text{N}_2\text{O}$, and ONTNTA, increase slowly during the acceleratory phase and more rapidly when the rate of formation of gaseous formaldehyde increases; and
- the stoichiometry of the sample remaining in the reaction cell increases in carbon content as the sample decomposes. This is due to the more rapid evolution of N_2O and H_2O than carbon-containing products during the acceleratory phase of the decomposition.

Transmission electron micrographs of the NVR indicate that the residue consists of broken, hollow, elliptical shells that appear to be remnants of bubbles formed within the particles during the decomposition. Diameters of the shells range in size from 0.2 μm to 5 μm . The stoichiometry of the NVR is $\text{C}_{3.3}\text{H}_{2.7}\text{N}_{1.8}\text{O}_2$, based on elemental analysis. Further decomposition of the NVR at temperatures from 230 C to 750 C produce typically HCN, HNCO, CH_3NHCHO , $(\text{CH}_3)_2\text{NHCHO}$, and other products that include a long-chain hydrocarbon.

In contrast to the HMX results, RDX decomposition, at temperatures from 20 C below the melting point up to the melting point, show additional products to those observed in HMX decomposition. These are NO_2 and hydroxy-s-triazine, indicating that the RDX ring remains intact. No NVR is observed in the RDX decomposition experiments.

The results from the condensed phase decomposition of HMX and RDX suggest that the process that controls the identity and rate of release of gaseous products from these materials is complex and involves the coupling of physical processes and chemical decomposition mechanisms. The main aspects of a mechanism explaining the production of the products observed in these experiments is illustrated in Figure 1. The main physical processes appear to be vaporization of the HMX from the particle surface, nucleation of bubbles within the solid, followed by growth and coalescence of the bubbles. The products observed probably result from solid-, liquid-, and gas-phase reactions occurring within the bubbles that are released as the bubbles intersect the particle surface. For example, the formation of N_2O and H_2O at equal rates during the acceleratory stage of the isothermal decomposition of HMX may be due to the release of products from the very small gas bubbles that are formed within the HMX particles. Using the heat of sublimation to approximate the surface free energy of solid HMX, the estimated gas pressures in the smaller

Figure 1. A schematic representation of the processes that may be controlling the release of gaseous pyrolysis products during the thermal decomposition of HMX and RDX.

bubbles ($\sim 0.2 \mu m$) can be as high as 1000 psi to 2000 psi. Reactions at these high pressures may lead to the formation of the polymeric NVR during the decomposition. At the other extreme in our experiments are the results from the decomposition of RDX. The results from these experiments indicate that the gaseous products are released from the sample when it is in a molten state. Under these conditions, the pressure in the bubbles within the molten material would be much lower than in the experiments where HMX remains a solid. Under these conditions, we observe the products associated with N-N bond breaking, NO_2 and hydroxy-s-triazine. These are not observed in our HMX experiments in which the sample remains a solid. This may be due to the lower pressure of the gas within the bubbles in the RDX sample or the shorter containment time of the gas within the RDX. This may decrease the number of secondary reactions that may occur before observing the decomposition products.

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Modeling of Nitramine Propellant Flames

Nitramine combustion chemistry has been described by using a detailed flame model incorporating chemical kinetics.

C. F. Melius

The gas-phase flame chemistry of an RDX flame has been studied theoretically using a steady, laminar, one-dimensional, premixed flame model that incorporates detailed chemical reaction mechanisms. Over 60 species and 300 reactions were used to describe the RDX flame chemistry. The model was used to determine the flame speed and pressure dependence as well as the reaction pathways occurring in each of the reaction zones of the nitramine flame. The results provided a new description of the chemistry of a nitramine flame.

The results of the steady-state RDX flame at 1.7 MPa (250 psi) are given in Figures 1 and 2. In Figure 1, we present the temperature profile and species concentrations as functions of distance along

inuous) flame zone (corresponding to the final removal of HCN), there are two interdispersed combustion regions, ranging from 20 - 70 μm and 30 - 100 μm , which differ primarily in their reaction pathways. The mechanism changes, due to the higher temperature available later in the secondary flame, producing more O and N atoms. The results of the temperature profile (Figure 1) indicate that the RDX flame burns as a single flame, i.e., the secondary (or luminous) stage flame does not stand off the surface, as in a nitramine composite or double-base propellant. Furthermore, the results show that while the primary and secondary flames touch, they have not interpenetrated. The production and destruction rates for each chemical species (as shown for

Figure 1. Temperature and species concentration (mole fraction) profiles as a function of distance (μm) for the RDX flame at 1.7 MPa (250 psi). The origin corresponds to a temperature of 600 K.

the flame. In Figure 2, we present the formation and destruction rates for HCN. The oscillatory behavior demonstrates the complexity of the various reaction zones occurring in the flame. The results indicate the existence of a two-stage flame. In the primary flame zone, there is a decomposition or pyrolysis region (corresponding to the formation of HCN) which ranges from 2 to 7 μm and a combustion region (corresponding to the conversion of HCN to C_2N_2) which ranges from 6 to 20 μm . In the secondary (or lum-

Figure 2. Chemical production and removal rates as a function of distance (μm) for HCN in the RDX flame at 1.7 MPa, indicating the various reaction zones of the flame. The numbers on the curves refer to the specific elementary reaction given in the figure. The total rate for production or removal is also plotted.

HCN in Figure 2) illustrate that they are still separated. Figure 2 indicates the remnants of a post-primary-flame dark zone or "preparation" zone near 20 μm (corresponding to the conversion of C_2N_2 back to HCN).

In a previous study¹ on RDX ignition, we found that well-stirred ignition took place in three stages, involving decomposition and two ignition

steps. A comparison of the ignition chemistry and the flame chemistry for production and destruction rates for each of the species indicates that the flame chemistry is similar to the ignition chemistry. In the decomposition or pyrolysis region, the HCN pathway dominates due to the high temperatures near the surface (700 - 900 K). Thus, the overall flame chemistry is similar to the chemistry of ignition at a high starting temperature (> 900 K). The majority of the decomposition occurs in the temperature range from 800 K to 1000 K, considerably above the melting point of RDX (478 K). The HONO and HNO formed in the pyrolysis zone provide some temporary heat, making up for the extremely endothermic decomposition reaction. HONO and HNO are then returned to NO_2 and NO in the primary flame zone. In the primary flame zone, we have the conversion of NO_2 to NO and the conversion of hydrogen-containing compounds to form water. Since the C-H bond in HCN is very strong, the majority of HCN remains until the second-stage flame zone. NO_2 acts as an inhibitor to the second-stage chemistry. In the secondary flame zone, HCN and NO are converted to CO, CO_2 , and N_2 . In addition, N_2O (which has remained relatively inert until this stage) is converted to N_2 .

The propellant burn rate, r , and its pressure dependence, v , can be given by $r = Bp^v$, where p is the pressure and B is a constant. For the 1.7 MPa RDX flame, we find a burn rate, r , of $0.5 \text{ gm/cm}^2/\text{s}$ with a pressure dependence (in this region), v , of 0.88, which is in good agreement with experimental values² of $0.7 \text{ gm/cm}^2/\text{s}$ and 0.835 for r and v , respectively. The secondary flame, rather than standing off, has abutted the primary flame due to the inhibiting effect of the NO_2 on the secondary flame. The dominance of the secondary flame on the flame

speed could explain why catalysts have little effect on nitramine flames, since catalysts may only affect the primary flame chemistry. This could also explain why catalysts do not affect many other propellants at high pressures, where the secondary flame approaches the primary flame and may control the overall flame speed. These results also should be valid for HMX flames, since the initial decomposition and subsequent reaction chemistry are similar. The major difference is that the higher boiling point for HMX can allow the formation of more N_2O and HC_2O . RDX and HMX have similar burning characteristics, consistent with the flame speed not being dominated by surface reactions.

The results of this study (using detailed chemical kinetics) provide a new description of nitramine flames. The flame is dominated by the secondary flame rather than the pyrolysis zone at the flame surface. Excellent agreement was obtained for species-concentration profiles and for burn velocities, including the pressure dependence. By including the appropriate elementary chemical reactions, one should be able to model composite nitramine propellants. The ability to simulate propellant flames accurately on a computer will also allow us to understand what is occurring in the flame of a propellant at high pressures, where it is difficult to do experiments due to the thinness of the reaction zone.

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Theoretical Characterization of the Minimum Energy Path for Hydrogen Atom Addition to N_2 : Implications for the Unimolecular Lifetime of HN_2 [†]

The minimum energy path for the reaction $H + N_2$ is characterized using accurate ab initio quantum chemical techniques. One-dimensional quantum mechanical tunneling results indicate that the HN_2 lifetime is very short, greatly limiting its role in both termolecular recombination reactions and combustion processes.

C. M. Rohlffing, S. P. Walch,* and R. J. Duchovic*

The reaction $NH_2 + NO$ constitutes one possible step in the complicated mechanism describing the fundamental chemistry of nitric oxide in combustion processes. Experimental studies provide indirect evidence on the existence of HN_2 species as a reaction product, although it has not been detected directly. A reliable estimate of the lifetime of HN_2 was thus needed since current combustion models assume it was sufficiently long-lived to participate in further critical reaction steps.

In this study, *ab initio* quantum chemical techniques were applied to the dissociation reaction $HN_2 \rightarrow H + N_2$ to accurately predict the minimum energy path, zero-point corrected barrier, and HN_2 lifetime. Atomic natural orbital (ANO) basis sets were employed since they flexibly describe electron correlation in both molecular and reaction path calculations. The N and H basis sets used were (13s8p6d4f)/[4s3p2d1f] and (8s6p4d)/[3s2p1d], respectively. To describe quantitatively the reaction surface, electron correlation beyond the traditional single-reference or self-consistent-field (SCF) wave function was required. That is, in a localized orbital description, more than one reference was needed to describe adequately the reactant, transition state, and products. A multiconfigurational approach,

known as complete-active-space (CAS) SCF, can describe smoothly such orbital changes over the course of a reaction. The final wave function consists of a contracted configuration interaction calculation of dynamic electron correlation from selected references of a valence CAS wave function.

Table I lists the stationary point properties of the HN_2 potential energy surface. The calculated zero-point corrected dissociation energy and barrier are 7.4 and 8.5 kcal/mol, respectively. The energetics were refined using slightly larger ANO basis sets, (13s8p6d4f)/[5s4p3d2f] on N and (8s6p4d)/[4s3p2d] on H, but the final results differed by less than one kcal/mol at the stationary points. The long range ($H + N_2$) features of the minimum energy path were similar to those found in a previous study of $H + O_2$. Combining these calculations with JANNAF thermodynamic data yields an endoergicity of 1.3 kcal/mol for the reaction $NH_2 + NO \rightarrow HN_2 + OH$.

The lifetime of the HN_2 species was estimated from both conventional transition state theory and a method that utilizes an Eckart barrier to compute one-dimensional quantum mechanical tunneling effects. Both methods give lifetimes on the order of 10^{-7} to 10^{-9} seconds, respectively, at 298.15 K. These short unimolecular lifetime estimates imply that the role of HN_2 in further chemistry was limited and the observation of this species experimentally will be very difficult.

[†]J. Chem. Phys. **90**, 3230 (1988).

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Table I
Stationary Points on the H + N₂ Surface^a

Property	H+N ₂ minimum	H—N ₂ saddlepoint	HN ₂ minimum
r _{NH}	20.00	2.753	2.007
r _{NN}	2.095	2.146	2.262
θ		118.6	116.3
ω ₁		1662i	2744
ω ₂	2303	2072	1583
ω ₃		771	1070
ΔE	-3.01	12.15	0.00
ZPE	3.29	4.06	7.72
ΔE _{ZPE}	-7.44	8.49	0.00

^aEnergies in kcal/mol, bond lengths in atomic units (1au = 0.529177 × 10⁻⁸ cm), angles in degrees, and frequencies in cm⁻¹.

Diffusional and Thermal Instabilities of a Solid Propellant Flame[†]

Even for large standoff distances, solid propellant flames exhibit intrinsic instability phenomena that differ significantly from those associated with freely propagating premixed flames.

S. B. Margolis and F. A. Williams*

The stability of a gas flame attached to a deflagrating solid propellant has been investigated through an asymptotic analysis in the limit of a large gas-phase activation energy. Since the diffusional/thermal model for solid propellant combustion that we employ relaxes the usual assumptions of gas-phase, quasi-steadiness and quasi-planarity, the overall stability of the deflagration is determined by both the stability of condensed-phase pyrolysis and the stability of the gas flame. The results show how the neutral stability boundaries for a freely propagating flame, which is obtained in an appropriate limit, are modified for a solid propellant flame. In particular, the cellular instability is suppressed by the proximity of the solid/gas interface for sufficiently small disturbance wave numbers, but the pulsating instability is usually enhanced by the proximity of the interface. In addition, the neutral stability boundaries possess features, such as relative maxima and multiple branches, that are not present in the corresponding stability boundaries for the freely propagating flame.

The present work is a continuation of series of studies^{1,2} of intrinsic instability in solid propellant combustion. These studies are distinguished from previous investigations of this phenomena in that the usual assumptions of gas-phase, quasi-steadiness and gas-phase, quasi-planarity have been relaxed, leading to predictions of new instability phenomena associated with the intrinsic instability of the gas flame. The relaxation of these assumptions for the gas phase has revealed the existence of both pulsating and cellular instabilities that are associated with diffusional/thermal flame instability. Consequently, the overall intrinsic stability of a deflagrating solid propellant incorporates features of both condensed-phase and gas-flame instability. In particular, this work has provided the first theoretical explanation of intrinsic cellular instability for solid propellants.³

The present study is devoted to the intrinsic stability of a flame attached to a deflagrating solid for relatively large values of the flame standoff distance. In the limit of infinite flame standoff, the stability boundaries associated with the diffusional/

thermal instability of a freely propagating gas flame are recovered. We thus follow the evolution of these stability boundaries as the flame standoff distance decreases from infinity. The particular scalings employed in this study, which permit a rigorous asymptotic derivation of a dispersion relation in the limit of large, overall, gas-phase activation energy Δ , assume that the gas-phase Lewis number is near unity ($Le = 1 + 1/\Delta$), that the (endothermic) heat of sublimation is small compared with the overall heat of reaction, and that the fraction of solid propellant that sublimates and burns in the gas phase (instead of being pyrolyzed directly to gaseous products) is near unity. These parameter regimes imply that the flame standoff distance $z_0 \propto -\ln(\zeta_0/\Delta)$, where ζ_0 is now regarded as a scaled measure of the flame standoff distance, the value of which can be related to other parameters in the problem. Thus, $\zeta_0 = 0$ corresponds to an infinite flame standoff distance, and small, positive values correspond to relatively large, but finite, values of this quantity.

The dispersion relation that we obtain from a linear stability analysis yields the neutral stability boundaries across which the basic solution for steady, planar burning loses stability to either pulsating or cellular (steady, but nonplanar) disturbances. Some of these results are illustrated (in Figures 1 and 2), in which we plot the neutral stability boundaries in the plane of the Lewis number parameter $l = \Delta(Le - 1)$ versus the transverse disturbance wave number k . In Figure 1, we set $\Delta = 50$, a moderately large value, and plot the stability boundaries for various values of ζ_0 . As ζ_0 increases from zero, the pulsating boundary executes small oscillations about the boundary for infinite flame standoff distance ($\zeta_0 = 0$). As ζ_0 continues to increase, however, the pulsating boundary shifts downward, indicating that the general effect of the solid on this stability boundary is destabilizing. For each value of ζ_0 , there is a characteristic wave number at which the pulsating stability boundary begins to deviate significantly from the boundary for freely propagating flames, corresponding to a disturbance wavelength that is comparable to the flame standoff distance. This characteristic wave number thus increases as the flame standoff distance decreases (i.e., as ζ_0 increases). For sufficiently large ζ_0 , the pulsating boundary dips below the $l = 0$ axis, indicating

[†]SIAM Journal of Applied Mathematics, accepted (1988).

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Figure 1. Pulsating stability boundaries for various values of the standoff distance parameter ζ_0 , with overall gas-phase activation energy $\Delta=50$, gas-to-solid density ratio $\rho=0.2$, gas-to-solid thermal diffusivity ratio $\lambda=1$, and gas-to-solid heat capacity ratio $c=1$.

that pulsating instability can also occur for Lewis numbers less than unity.

Figure 2 shows the pulsating stability boundaries for a larger value of the gas-phase activation energy, $\Delta = 150$. The same trends as those exhibited in Figure 1 are repeated for this case as well. In addition, for sufficiently large values of ζ_0 , the pulsating stability boundary dips below the level of the relative maximum in the cellular stability boundary (dotted curves), and for even larger values of Δ , these two boundaries can intersect. For these cases, steady, planar burning is absolutely unstable if all wave number disturbances are admissible. Of course, if sufficiently small wave number disturbances are inadmissible because of the finite transverse dimensions of the system, then steady, planar burning may still be stable for an appropriate range of l . Another feature that is present in this case of relatively large Δ is the multiplicity of solution branches, which occurs in the range $0.62 < \zeta_0 < 0.73$. This is shown clearly in the expanded Figure 2b. As ζ_0 increases toward and past the lower value in this range, the pulsating stability boundary first develops a local maximum, and then an isolated solution branch appears for small wave numbers. At a value less than 0.62724, the two branches connect at $\hat{k} = 0$, and as ζ_0 continues to increase, a single, multivalued boundary is formed. The pulsating boundary again becomes single-valued as ζ_0 increases past 0.73.

Figure 2. Pulsating stability boundaries for various values of the standoff distance parameter ζ_0 , with $\Delta=150$, $\rho=0.2$, and $\lambda=c=1$. The dotted curves in (a) denote some of the cellular stability boundaries.

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Stability of Homogeneous-Solid Deflagration with Two-Phase Flow in the Reaction Zone[†]

Many propellants, such as the nitramines, exhibit extensive bubbling in a foam layer during deflagration. Effects due to two-phase flow and interphase heat transfer are shown to play an important role in determining the stability of steady, planar burning.

S. B. Margolis and F. A. Williams*

Regions of two-phase flow in which significant exothermic chemical activity occurs are commonly observed during combustion of many homogeneous solid propellants. The two-phase region typically begins through nucleation in a softened "melt" to form a foam and results later in dispersion of condensed material as a fizz. The present study is applicable primarily to those propellants, such as nitramines, that show relatively little fizz, but that exhibit extensive bubbling in the foam layer. In particular, our analysis is concerned specifically with the stability of the deflagration when there is two-phase flow in an exothermic liquid layer containing bubbles, as illustrated in Figure 1.

Previous deflagration studies that have included distributed, two-phase effects have considered only the steady, one-dimensional problem, and most have required velocities to be the same in each phase.^{1,2} In a recent study, however, this assumption has been relaxed, allowing for the possibility of different velocities in different phases, with mechanisms identified that support the velocity differences.³ The present analysis extends that study by further exploiting the largeness of the overall activation energy to derive a nonsteady, multidimensional model of propellant deflagration with two-phase flow. This model is then used to identify a basic solution corresponding to steady, planar burning and to examine its linear stability. A neutral stability boundary is obtained in the space of parameters, across which the basic solution loses stability to infinitesimal pulsating disturbances. The rate of interphase heat transfer is shown to play a significant role in this phenomenon.

In the limit of large overall activation energy, the two-phase reaction zone collapses to a sheet, across which the temperature obeys certain continuity and jump relations that depend on local conditions. This model facilitates the description, including an analytical formula for the burning rate, of the basic solution that corresponds to steady, planar deflagration. However, this solution is not always stable to small perturbations. In particular, for sufficiently large values of an activation energy parameter β , steady, planar burning loses stability to nonsteady, nonplanar disturbances that correspond to oscillatory deflagration waves. These disturbances are of the same general type encountered previously as intrinsic pulsating instabilities in the separate-phase deflagration of solid propellants⁴ and the combustion synthesis of refractory materials.⁵

The results of the analysis presented here show the influences on the stability boundary produced by changes in nondimensional parameters that represent the ratios of the gas-phase density, thermal conductivity, and heat capacity to those of the condensed phase (r , l , and b , respectively), the ratio (s) of the liquid velocity perturbation (toward the solid) caused by Marangoni effects (lessened by two-phase, viscous effects) to the deflagration velocity, and the ratio (K) of the rate of interphase heat transfer to an appropriately scaled rate of streamwise convection of thermal enthalpy. In the limit of perfect interphase heat transfer ($K = \infty$), the onset of instability is enhanced for all disturbance wave numbers k by decreasing the density ratio r and/or the thermal conductivity ratio l , or by increasing the Marangoni parameter s , as illustrated in Figure 2. The first two of these effects are the same as those

Figure 1. Model geometry. The two-phase region is confined to the thin reaction zone, where shaded areas denote condensed unburned propellant, and the clear areas denote gaseous burned products.

[†]Combustion and Flame, accepted (1988).

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Figure 2. Neutral stability boundaries in the limit $K=\infty$ with $s \geq 0$. For fixed values of the remaining parameters, positive values of s are destabilizing.

encountered in separate-phase, solid-propellant deflagration with an intrusive gas flame,⁴ the neutral stability boundaries that are obtained formally from the present analysis by considering the limit in which K approaches infinity and s approaches zero.

The stabilizing influences of increasing r and l arise through enhanced coupling between the gas and condensed phases, thereby increasing the damping effect of the gas on the condensed-phase pulsating instability. A similar physical mechanism explains the newly calculated influence of the heat-transfer parameter K indicated in Figure 3. For $K = \infty$, the thermal contact between the liquid and gas in the two-phase reaction zone is maximum, so that the strong thermal coupling between the two phases dampens the intrinsic condensed-phase pulsating instability to the greatest extent possible. Consequently, as K is decreased, this interphase contact is lessened, thereby decreasing attenuation of the disturbance and generating an increased tendency toward oscillation. Increasing the Marangoni parameter s may be expected to increase the magnitude of liquid-phase velocity changes as well as decreasing interaction with the gas (by increasing the liquid

velocity towards the solid, away from the gas). Both of these influences, which enhance discrepancies between the gas- and condensed-phase velocities in the two-phase reaction zone, would be expected to increase the tendency towards instability, as found from the analysis. Therefore, in all respects, the results obtained here are qualitatively consistent with physical expectations. It seems particularly noteworthy that Marangoni flow can help to produce oscillatory instability in the deflagration of nitramines.

Figure 3. Neutral stability boundaries for $K=\infty$ and $1 < K < \infty$, showing that finite values of K are destabilizing. Both curves were drawn for the parameter values $r=0.5$, $s=0$, $l=b=1$, and the value $K=10$ was used to illustrate the $1 < K < \infty$ case.

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Section 10

Development of new and improved technologies for the detoxification of hazardous waste is an imperative our nation faces today. One promising new process we are pursuing at Sandia is supercritical water oxidation. The reactor shown on the right is designed to allow us to apply laser and other combustion diagnostics to study the oxidation of aqueous wastes in solution with supercritical water.

Toxics Conversion Technology

Supercritical water oxidation, described on pages 10-1 and 10-2, holds promise as an environmentally safe and fuel efficient process for the detoxification of hazardous waste. Sketched above is a new experimental facility we are using for initial studies of this new technology. The combustor is made of an Inconel alloy chosen to resist high pressure and temperature, chlorine attack, and super-

critical water corrosion. Optical access permits interrogation by Raman spectroscopy using the laser, monochromator, and optical multichannel analyzer shown. The control panel directs fluid flow into and out of the combustor including the extraction of samples that are analyzed subsequently in the gas chromatograph.

Section 10

Toxics Conversion Technology

Our program in toxics is directed toward the research, development, and demonstration of new and improved thermochemical processes for the detoxification of hazardous waste. Through technology exchange to the industrial sector, our program will lead ultimately to waste destruction technologies that offer cost-competitive and environmentally safe methods of toxic waste disposal. Contributions made at Sandia National Laboratories are in the application of advanced laser diagnostics and computer modeling and in carrying a process from the laboratory research stage to the demonstration stage, where waste streams of practical interest are used.

We are developing an experimental program that includes research projects in supercritical water oxidation, plasma processing, waste oxidation using molten nitrate salts, development of continuous monitors for fugative toxic emissions, and chlorinated hydrocarbon oxidation. In the supercritical water project, our interest is in using this emerging technology to purify waste water streams containing toxic chemicals. An optically accessible plasma reactor is being designed for use in the development of the technology required to detoxify concentrated hazardous liquids or solid slurries using a high-temperature plasma. Based on the considerable expertise we have developed (as part of Sandia's solar energy program) in engineering large molten salt systems and in understanding the chemical and physical properties of molten nitrates, we are pursuing the basic research necessary for the development of a chemical oxidation reactor using molten nitrate salts. The purpose of our trace species detection work is to develop on-line, real-time continuous emissions monitors to measure trace species concentrations of toxic, gas-phase effluents from waste incinerators and to detect and identify metal aerosols emitted from such incinerators.

A concomitant modeling effort includes the use of quantum chemistry to investigate reaction pathways in supercritical water oxidation and to address the thermochemistry of chlorine compounds, for which an experimental data base is lacking. We are working to develop an understanding of transport and chemical processes in supercritical reacting flows and in plasma flows. An important aspect of our modeling program is the use of detailed chemical kinetics to describe reacting flow systems.

Supercritical Water Oxidation of Toxic Wastes

We have constructed a facility designed for the experimental investigation of supercritical water oxidation of hazardous aqueous wastes. The high-temperature, high-pressure reactor is equipped with sapphire windows for optical access as well as sampling ports for fluid extraction and chromatographic analysis.

R. R. Steeper, M. S. Brown,* and S. C. Johnston

As part of Sandia's Toxics Conversion Technology program, we have launched an experimental study of supercritical water oxidation (SCWO) of hazardous wastes. United States industry treats and disposes of several hundred million tons of hazardous wastes each year, and the preponderance of this waste is in the form of contaminated water.¹ Federal facilities are faced with the same situation: at a recent DOE meeting,² groundwater treatment was singled out as the top priority for cleanup of government operations. Supercritical water oxidation appears to be ideally suited to address this problem—the technology has potential as an efficient, economical, and environmentally safe method to treat aqueous wastes.

Supercritical water oxidation occurs in a homogeneous-phase mixture of water plus combustibles at temperatures and pressures above the mixture critical point. For pure water, the critical point is 374°C and 220 atm—above these conditions, water is a fluid with unique properties. Figure 1 illustrates³ four properties of water at a constant pressure of 250 atm. As the temperature rises through the critical point, density drops sharply to a value of approximately one-tenth that of liquid water. The dielectric constant shows a similar, but less abrupt, change. The change in solvating power is dramatic: at supercritical conditions, water becomes an excellent solvent of organics as well as gases. In the same way, inorganic solubility abruptly changes at the critical point so that inorganics fall out of solution above the critical point.

Supercritical water oxidation takes advantage of these unique properties of supercritical water. Foremost is the opportunity to operate in a homogeneous regime. Phase changes that occur in conventional waste combustors demand energy

and retard mixing. In contrast, organics and oxidizers are both in solution in the SCWO process, facilitating complete and rapid reaction. The density range is such that liquid-like solvation occurs, coupled with gas-like, enhanced diffusivities. The fact that inorganics precipitate out of solution in the supercritical regime is potentially useful for separating metals from reaction products. These inherent advantages have been demonstrated elsewhere in preliminary experiments: published results^{3,4} show 99.99% complete destruction of halogenated, organic compounds in four minutes at 500°C, with indications of faster and more complete conversion at 600°C. Supercritical water oxidation might also prove useful in treating mixed wastes, where the toxic component could be removed by oxidation, and the radiological component (typically, a metal oxide or halide) could be removed in concentrated form by precipitation.

Figure 1. Properties of water at a constant pressure of 250 atm (see Reference 3).

*Sandia Postdoctoral Program participant

During the past year, a facility to investigate supercritical water oxidation of toxic wastes has been constructed. The facility has been designed to address several issues. First of all, it will be used to study a phenomenon recently demonstrated at the University of Karlsruhe, West Germany:⁵ diffusion flames in supercritical water. As depicted in Figure 2, these flames have been produced by injecting an oxidizer into a supercritical water/hydrocarbon solution. Industrial SCWO reactors will initially be designed to operate with low-temperature (600°C), distributed reactions. But with the possibility of transition to a high-temperature flame, it is important to learn to predict and control such combustion phenomena. Furthermore, it might be possible to utilize such "hydrothermal flames" to oxidize more rapidly aqueous wastes in compact reactors.

The second area of inquiry for our facility is SCW mixing processes. Uniform mixing is essential for complete destruction of wastes but very little is known about fluid dynamics in this regime.

Figure 2. Supercritical water combustor indicating a diffusion flame.

Application of Raman spectroscopy for species concentrations (and possibly measurement of temperatures) in SCWO systems is a third aspect of our research. Successful use of this diagnostic tool for aqueous solutions at supercritical conditions has been reported,⁶ but the presence of a diffusion flame imposes additional challenges. Figure 2 illustrates the configuration of the Raman system adapted to our reactor. Also shown are the fluid sampling and thermocouple probes that will provide comparison data for the Raman system. Because of the potential for increased species detection (due to the increased number density in SCWO systems), Raman measurements could provide important information regarding the extent of chemical reactions in SCW reacting flows.

The final aspect of our experimental program is the study of materials used to construct supercritical reactors. We are collaborating with Sandia's Material Sciences Department to characterize the performance of metallic and window components in our combustor. "Witness" samples have been prepared to gauge the extent of chlorine attack, hydrogen embrittlement, and supercritical water corrosion.

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Reaction Mechanism Modifications for Supercritical Water Oxidation: High-Pressure Hydrolysis Effects

We have used the BAC-MP4 theoretical method to show a marked effect of water clusters on reaction rates. These calculations show that significant populations of large water polymers exist, impacting present models of supercritical water oxidation.

C. F. Melius and N. E. Bergan

Understanding the reaction pathways and chemical kinetics in supercritical oxidizing flows is an important part of our modeling effort in supercritical reacting flows. Chemical kinetics in supercritical fluids have been studied by several researchers. Helling and Tester¹ measured global reaction parameters of carbon monoxide oxidation in supercritical water at temperatures and pressures similar to those in our region of interest. They fit their experimental data to both global and elementary Arrhenius rate expressions and separated the effects of a direct oxidation pathway (carbon monoxide oxidizing directly into carbon dioxide) and the water-gas shift reaction (carbon monoxide oxidizing with water to form carbon dioxide and hydrogen). Several gas-phase reaction models were compared to the data, but all models overpredicted the rate of carbon monoxide oxidation and underpredicted the rate of hydrogen production. Rofer *et al.*² have measured supercritical methane oxidation under similar conditions. Gas-phase reaction models also underpredict oxidation rates for their data.

Based on the large discrepancies between measured and predicted oxidation rates, we have investigated modifications to elementary reaction mechanisms and kinetics due to the presence of water. Formaldehyde (CH_2O), an important intermediate in the oxidation of gaseous hydrocarbons at atmospheric pressure, is easily hydrated to methanediol ($\text{CH}_2(\text{OH})_2$) in liquid water. This has a pronounced effect on overall reactivity, because the C-H bond strengths are stronger in methanediol than in formaldehyde, making formaldehyde a highly reactive molecule, whereas methanediol is fairly stable. Considering the importance of this reaction in liquid water, we chose to study formaldehyde hydration in supercritical water. Activation energies of transition-state structures were calculated for $(n+1)$ moles of additional water molecules, i.e.,

Rather than a trimolecular- or tetramolecular-reaction mechanism, one can also consider these reactions as bimolecular reactions with water dimers, trimers, e.g.,

Figure 1. Equilibrium concentration of water polymers at 350 atm.

In the supercritical region of water, these multiple clustered water species are numerous. Figure 1 shows the concentration of water clusters as a function of temperature at 350 atm calculated using ideal-gas equilibrium thermodynamics. Real gas effects are currently being studied by means of fugacity coefficients for each species. Activation energies, calculated using the BAC-MP4 method, are shown in Figure 2, indicating a dramatic lowering of the barrier height when additional water molecules are present. This effect is not due to hydrogen bonding stabilization of the activated complex, but rather to the chemical change in the transition-state structure due to ringed complexes, where all the water molecules participate in bond breaking and formation.

We have also considered the water shift

Figure 2. Calculated BAC-MP4 barrier heights for the hydration of formaldehyde to form methanediol, $\text{CH}_2\text{O} + (n+1)\text{H}_2\text{O} \rightarrow \text{CH}_2(\text{OH})_2 + n\text{H}_2\text{O}$, where n represents the number of additional water molecules involved in the transition state structure. The activation energies, ΔE , and enthalpy of reaction, ΔH , are given in kcal/mole.

reaction occurring through the formic acid intermediate (HCOOH) and assisted by additional water molecules, i.e.,

The calculated activation energies shown in Figure 3 indicate a similar dramatic effect of lowering the barrier height by additional water molecules. The presence of even more water molecules could further lower the barrier height. This reaction mechanism for the water-gas shift reaction is not considered in normal gas-phase combustion mechanisms, which treat the reaction by a radical pathway, i.e.,

followed by

We thus find that water molecules may play an important role in catalyzing reaction mechanisms in the gas phase in the region of supercritical water. Additional solvent effects of water due to hydrogen bonding as well as diffusion rate modifications can also play a role in supercritical oxidation. These effects will be incorporated in future chemical kinetics modeling efforts based on the CHEMKIN³ computer code.

Figure 3. Calculated BAC-MP4 barrier heights for the water shift reaction, $\text{CO} + (n+1)\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 + n\text{H}_2\text{O}$ via the formic acid intermediate. The number, n , indicates the number of additional water molecules involved in the transition state structure. The activation energies, ΔE , and enthalpy at reaction, ΔH , are given in kcal/mole.

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Multiplicity and Stability of Supercritical Combustion in a Nonadiabatic Tubular Reactor[†]

Combustible aqueous mixtures under supercritical pressures and temperatures are capable of supporting a self-propagating flame under certain conditions. We consider the multiplicity and stability of such flames in a nonadiabatic tubular reactor as a function of inflow velocity, inlet and volumetric heat loss parameters, reactor length, and overall activation energy.

S. B. Margolis and S. C. Johnston

The combustion of high-pressure supercritical fluids has important application in the chemical conversion of toxic wastes. Under these extreme conditions, organic compounds are completely miscible in water, and combustion can proceed without prior vaporization of the mixture. Properties of such mixtures have been surveyed¹ recently and supercritical $\text{H}_2\text{O}/\text{CH}_4 - \text{O}_2$ diffusion flames, with ambient supercritical temperatures in the 400 - 500 K range and reaction-zone temperatures in the neighborhood of 3000 K, have been observed at pressures of up to 2000 bar.² These studies imply that supercritical combustible mixtures are capable of supporting a self-propagating flame and, consequently, suggest the possibility of burning aqueous organic wastes in a supercritical tubular reactor (Figure 1). However, a reasonable model of this system differs in several significant respects from models that typically are used in chemical reactor theory. In particular, it is appropriate in the present problem to neglect mass diffusion relative to thermal diffusion due to the high density of supercritical mixtures and to model the cooled inlet as a flameholder to account for the heat losses that occur there. Our model also accounts for both transverse and axial diffusion (dispersion).

In our analysis, we exploit the largeness of the overall activation energy to derive an asymptotic model in which chemical reaction is confined to a thin reactive/diffusive zone whose location as a function of space and time is to be determined. In particular, we obtain the location of the steady, planar state as a function of inlet and volumetric heat loss coefficients (K and H , respectively), reactor length (L), flow velocity (μ), and activation energy (Δ). We find that a given flame location can correspond to more than one flow velocity, corresponding to a multiplicity of flame speeds. In addition, we analyze the stability of the high-speed branch to show that for sufficiently large values of

the activation energy, stability of steady, planar burning is lost to nonsteady, nonplanar disturbances which, for a cylindrical reactor, correspond to spinning and/or pulsating modes of supercritical combustion.

Thus, assuming that the nondimensional activation energy Δ is large but finite, we consider the case in which the inlet and volumetric heat loss coefficients are sufficiently small so that they can be scaled as $K \sim \kappa/\Delta$ and $H \sim h/\Delta$. In this regime, the location $x_3 = \Phi$ of a steady planar flame is given as

$$\Phi \sim \Phi_{\pm}^0 = L + \frac{1}{\mu} \ln \left[1 + \frac{\mu^2}{h} \ln \mu + \sqrt{\left(1 + \frac{\mu^2}{h} \ln \mu \right)^2 + \frac{\mu \kappa}{h} e^{-\mu L}} \right].$$

Typical plots of $\Phi_{\pm}^0$ as a function of the flow velocity μ are shown in Figure 2. For a finite reactor length ($L < \infty$), a steady flame can exist only for sufficiently small values of the heat loss parameters κ and h , the latter being restricted to $h < 1/e$ since the asymptotes $\mu_3(h)$ and $\mu_4(h)$ approach each other as $h \rightarrow 1/e$. It is seen readily that two flow velocities correspond to a given flame location, dividing the steady flame response into a high-speed, high-temperature branch and a low-speed, low-temperature branch. Values of $\Phi_{\pm}^0 < 0$ correspond to a flashback of the flame behind the inlet/flameholder. We anticipate that much, if not all, of the low-temperature branch is unstable and that the flame will either become unsteady or extinguish as μ decreases below a certain value.

In the limit of small κ , the high-speed branch is stable with respect to steady, nonplanar disturbances, but its stability with respect to time-dependent perturbations depends on the value of the activation energy parameter Δ . This is illustrated in Figure 3, which shows plots of the neutral stability boundary $\Delta(\kappa)$, where κ is the wave number of a pulsating disturbance. Thus, for sufficiently large values of this parameter, steady, planar burning is always unstable, but for more modest values of Δ , this solution branch is stable for an appropriate range of flow velocities μ for which the flame lies well within the interior of the reactor. However, as

[†]Combustion Science and Technology, accepted (1988).

Figure 1. Supercritical combustion in a tubular reactor. The figure depicts a possible laboratory configuration.

μ decreases so that the flame approaches the inlet (Figure 3), the stability boundary shifts downward, and the basic solution loses stability to disturbances that correspond to nonplanar, oscillatory modes of combustion. The same phenomenon occurs as μ increases so that the flame approaches the end of the reactor at $x_3 = L$. Thus, referring to the high-speed branch in Figure 2, there are, for modest values of Δ and small κ , two values μ_c and μ_{cc} , where $\mu_c < \mu_{cc}$, such that the basic solution is stable for $\mu_c < \mu < \mu_{cc}$. The neutrally stable points μ_c and μ_{cc} are thus possible bifurcation points at which time-dependent solution branches emanate from the high-speed

steady branch. As indicated in Figure 3, the maximum value of Δ for which some part of the basic solution branch is stable is generally found to decrease with increasing volumetric and inlet/flameholder heat losses.

Figure 2. Leading-order flame location Φ_0^0 as a function of flow velocity μ for $L=5$ and $h=0.4/e$.

Figure 3. Pulsating stability boundary $\Delta(k; \kappa, \mu, h, L)$ for the high-temperature, basic-solution branch with $L=5$ and $h=0.2/e$.

References:

1. E. U. Franck, J. Chem. Thermodynamics **19**, 225 (1987).
2. W. Schilling and E. U. Franck, Ber. Bunsenges. Phys. Chem. **92**, 631 (1988).

Computer Modeling of Transport and Chemical Processes in Supercritical Reacting Flows

We are extending our expertise in modeling atmospheric reacting flows to encompass supercritical fluids. Our objective is to develop fully coupled one- and two-dimensional models of the transport and chemical processes governing supercritical reacting flows.

N. E. Bergan, C. F. Melius, B. Butler,* J. Shephard,** F. M. Rupley, and R. J. Kee

In a closely coordinated experimental and theoretical research program, we are working to develop an understanding of transport and chemical processes in supercritical reacting flows. Central to this program, tying together theoretical and experimental results, is the development of a supercritical reacting-flow model with detailed chemical kinetics. This model uses the same type of approach as has been used in the Combustion Research Facility for the past ten years to study atmospheric, pressure-reacting flows.¹

We have two objectives for this model: first, to understand the mechanisms governing supercritical oxidizing flows and second, to develop a predictive capability to evaluate reactor designs. Given the challenging environment of high pressures, short reaction times, and small diffusion lengths, our experiments are limited in their ability to explore all physical regimes and separate nonlinear, coupled effects. In the laboratory, laser diagnostics will be used to identify temperature and species profiles. Our model will be used to further resolve these profiles and to identify rate-limiting steps (e.g., heat and mass transport and chemical reactions).

Modeling supercritical reacting flows presents several unique challenges, due mainly to the fluid's less-than-ideal behavior. The majority of combustion modeling is based on ideal gas assumptions. In the pressure and temperature regime of interest, fluids differ from ideal gases in several ways.

First, the gases are physically compressed, having a density on the order of 0.1 gm/cc, compared to 0.001 gm/cc for water vapor at atmospheric pressure. This affects the thermodynamic and transport properties through Van Der Waals-type molecular interactions. We are evaluating several real-gas equations of state and mixture rules, comparing their predictions to experimental data to determine the best correlations for supercritical fluids.

Supercritical transport properties such as species diffusion, viscosity, and thermal conductivity, will be evaluated using kinetic and hydrodynamic theories and experimental data.

The second important effect of nonidealities is in the chemistry of the reactions. Since supercritical fluids have properties of both gases and liquids, the reaction mechanisms could exhibit features of both gas-phase (radical species) and liquid-phase (ionic species) chemistry. Besides introducing new reaction mechanisms (see the article by Melius and Bergan, p. 10-4 this issue), we are also modifying the chemical kinetics to address rate changes due to 1) shifts in equilibrium constants of products and reactants (affecting forward and reverse reaction rates), 2) shifts in equilibrium constants of the transition state, and 3) diffusion limited behavior.

Figure 1 shows the structure and research focus of our modeling effort. An important element in this effort is modification of the CHEMKIN and TRANSPORT computer codes to account for nonideal fluid behavior. In a way that leaves the ideal-gas version of these codes untouched, we are writing a new "core" program to modify 1) the equation of state (defining thermodynamic and equilibrium properties), 2) the transport properties governing heat and mass transport, 3) mixture rules for thermodynamic and transport properties, and 4) the reaction rate constants and reaction mechanisms. This modification is based on experience gleaned from real-gas modifications of CHEMKIN for high-explosive detonations. We are working cooperatively with Sandia National Laboratories, Albuquerque, and Lawrence Livermore National Laboratory to make a flexible modification that can accommodate a wide variety of applications.

The first model that we are developing is for a plug-flow reactor, where conservation equations reduce to a set of nonlinear, ordinary differential equations. This allows us to develop reaction mechanisms, chemical kinetics, and real gas considerations on a mathematically simple problem.

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Figure 1. Computer model structure showing research focus for supercritical fluids modeling.

We are beginning by simulating experimental data from Helling *et al.*¹ and Rofer *et al.*² for supercritical oxidation of dilute mixtures of carbon monoxide and methane in water. Important results from this model include species and temperature profiles describing the reaction zone in supercritical reactors.

We will work closely with experiments to verify our model results. As we develop confidence in our reaction mechanisms and real gas, high pressure properties, we will extend our model to one- and two-dimensional, unsteady, diffusion flames.

References:

1. See e.g., R. J. Kee *et al.*, *Twenty-Second Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, PA, 1988), p. 1479; and N. E. Bergan *et al.*, "Hazardous Waste Droplet Studies," p. 10-12 this issue.
2. R. K. Helling and J. W. Tester, *Energy & Fuels* **1**, 417 (1987).
3. C. K. Rofer and G. E. Streit, "Kinetics and Mechanism of Methane Oxidation in Supercritical Water," LA-11439-MS, DOE/HWP-64, UC-721, (October, 1988).

Thermochemistry of Chlorinated Hydrocarbons Occurring in Oxidative Removal of Toxic Wastes

The thermochemistry of various chlorinated hydrocarbon molecules has been determined theoretically using the BAC-MP4 method.

C. F. Melius

Toxic wastes consisting of chlorinated hydrocarbons (CHC) can be removed using a variety of thermochemical means, such as incineration, supercritical fluid oxidation, or plasma processing. Research in this country and abroad is being conducted to model the combustion processes by means of detailed chemical kinetics.¹ However, the thermochemistry of many of the chemical species occurring in these models is not known experimentally. Furthermore, under supercritical oxidation or plasma waste processing, other radical and unstable molecular species can occur that would not be of significance under atmospheric combustion conditions.

The BAC-MP4 theoretical method has proved to be a useful approach to determine the thermochemical properties of unstable species occurring in hydrocarbon oxidation and NO_x pollutant formation. We have, therefore, applied this method to determine the thermochemistry of various chlorinated hydrocarbon molecules including those containing oxygen. Calculated heats of formation of various molecular species involving C₁ and C₂ compounds are given in Table I. Also listed for each molecule is a theoretically determined BAC-MP4

error estimate. Differences between the theoretical and reported experimental values are also given where available. As can be seen, very few experimental values are known for radical species or for species containing oxygen. One observes from the table that the isomers of a given chlorinated ethane have similar heats of formation while the isomers of a given chlorinated-ethyl radical favor the chlorines on the radical center (e.g., CH₃CCl₂ is more stable than CH₂ClCHCl, which is more stable than CHCl₂CH₂). Also of importance is the observation that methyl peroxy radicals become less stable with respect to dissociation (CH_nCl_{3-n}O₂ → CH_nCl_{3-n} + O₂). The stability of peroxy intermediates is of significance to cool flame oxidation as well as to supercritical conditions.

The BAC-MP4 thermochemical data for chlorinated molecules are being incorporated into the CHEMKIN data base for use in chemical-kinetics modeling. The BAC-MP4 method is also being applied to investigate the reaction mechanisms involved in the oxidation of chlorinated hydrocarbons.

Table I

BAC-MP4 heats of formation at 298 K (ΔH_f^0) for various chloro-hydrocarbons along with the BAC error estimate. Also given, when available, are differences between theory and experiment. Energies are in kcal/mole.

Molecule	(ΔH_f^0)	Error Est.	Theor. -Exp.	Molecule	(ΔH_f^0)	Error Est.	Theor. -Exp.
CCl ₂ CHClOH	-32.0	1.9	—	CH ₂ CClO	-11.5	3.3	—
CHClCCl ₂ OH	-31.7	1.3	—	CHClCHO	-6.0	4.2	—
CH ₃ CClO	-56.9	1.1	1.5	CHClCClO	-20.3	3.4	—
CH ₂ ClCHO	-41.0	1.1	—	CCl ₂ CHO	-12.5	4.5	—
CHClCHOH	-38.6	2.6	—	CCl ₂ CClO	-24.3	3.7	—
CH ₂ CClOH	-37.0	3.4	—	ClC ₂ O	42.2	3.6	—

Molecule	(ΔH_{f298}^0)	Error Est.	Theor. -Exp.	Molecule	(ΔH_{f298}^0)	Error Est.	Theor. -Exp.
CH ₃ Cl	-20.1	1.0	-0.5	C ₂ H ₃ Cl	4.7	1.8	-3.9
CH ₂ Cl ₂	-22.6	1.0	0.2	c-CHClCHCl	-1.1	3.0	-2.1
CHCl ₃	-23.3	1.2	1.3	t-CHClCHCl	-0.8	3.0	-1.8
CCl ₄	-20.2	2.6	2.7	CH ₂ CCl ₂	0.8	3.0	0.1
CH ₂ Cl	27.1	1.5	-2.8	C ₂ HCl ₃	-4.0	3.9	-2.1
CHCl ₂	20.4	2.1	-3.8	C ₂ Cl ₄	-5.7	4.1	-2.7
CCl ₃	16.6	2.6	-2.4	CH ₂ CCl	61.4	4.2	—
CHCl	75.5	3.9	—	CHClCH	64.8	4.1	—
CCl ₂	53.0	4.4	-3.9	CHClCCl	56.0	5.1	—
				CCl ₂ CH	62.3	5.4	—
CH ₃ CH ₂ Cl	-27.2	1.0	-1.1	C ₂ Cl ₃	54.4	6.3	—
CH ₂ ClCH ₂ Cl	-32.4	1.1	-1.7	HC ₂ Cl	55.0	5.1	—
CH ₃ CHCl ₂	-32.1	1.1	-1.4	C ₂ Cl ₂	56.2	9.4	—
CH ₂ ClCHCl ₂	-35.2	1.3	0.3	C ₂ Cl	134.2	7.9	—
CH ₃ CCl ₃	-33.6	2.0	0.5				
CHCl ₂ CHCl ₂	-36.0	2.3	-0.1	C ₆ H ₅ Cl	8.3	2.7	-3.9
CCl ₃ CH ₂ Cl	-35.3	2.7	—				
C ₂ Cl ₆	-32.4	7.7	2.1	CH ₂ ClOH	-55.5	1.1	—
CH ₃ CHCl	18.2	1.7	—	CH ₃ OCi	-14.1	1.2	—
CH ₂ ClCH ₂	23.0	1.2	—	CHCl ₂ OH	-66.6	1.0	—
CH ₂ CCl ₂	10.3	2.1	—	CCl ₃ OH	-66.3	1.3	—
CH ₃ ClCHCl	13.1	1.4	—	CHClOH	-16.7	1.4	—
CHCl ₂ CH ₂	20.2	1.2	—	CH ₂ ClO	-2.4	1.2	—
CH ₂ ClCCl ₂	6.0	1.9	—	CCl ₂ OH	-22.8	2.3	—
CHCl ₂ CHCl	10.3	1.3	—	CHCl ₂ O	-4.1	1.4	—
CCl ₃ CH ₂	18.8	1.5	—	CCl ₃ O	-4.4	1.5	—
CHCl ₂ CCl ₂	8.5	1.4	—	CHClO	-44.3	1.0	—
CCl ₃ CHCl	11.1	1.9	—	CCl ₂ O	-52.7	1.4	-0.1
C ₂ Cl ₅	7.4	2.7	—	CiCO	-6.5	2.8	-2.4
CH ₂ ClOO	1.2	1.8	—				
CHCl ₂ OO	-1.4	2.1	—				
CCl ₃ OO	-0.7	3.3	—				

Reference:

1. See, for example, S. B. Karra, D. Gutman, and S. M. Senkan, Comb. Sci. Tech. **60**, 45 (1988), or G. P. Miller, T. W. Lester, and V. A. Cundy, Western States Section/The Combustion Institute, Salt Lake City, UT (1988).

Hazardous Waste Droplet Studies

We have studied blending strategies and combustion characteristics of single droplets of hazardous waste. Experimental data are compared to computer model predictions and results show that steady burning of equal volatility fuel and waste can be modeled very well.

N. E. Bergan, R. R. Steeper, and H. A. Dwyer*

In spray-fired incinerators, liquid wastes are chemically destroyed by exposing them to high-temperature, oxidizing environments for a sufficient time. Typical spray-combustion models treat the spray as a fraction of a continuous flow, thereby describing the global or "averaged" combustion process. However, since regulations governing hazardous waste disposal require destruction efficiencies (ratio of hazardous waste destroyed to hazardous waste injected) as high as 99.9999%, we must understand the non-average, or individual droplet behavior to assure destruction. Individually burning droplets at the edge of sprays and oversize droplets that penetrate the flame zone may degrade the destruction efficiency if they escape undestroyed. Through our research, we are developing the tools to predict individual droplet combustion, thereby improving our understanding of how to destroy wastes in spray-fired incinerators.

In conjunction with researchers from U.C. Davis,¹ we conducted single-droplet experiments to study combustion characteristics of a chlorinated hydrocarbon, tetrachloroethane (TECA), blended with various hydrocarbon fuels. Chlorinated hydrocarbons are used heavily in industry as cleaning fluids and solvents. Many of these wastes have high enough heating values for incineration, yet they are difficult to burn since chlorine consumes the hydrogen radicals needed for chain-branching reactions. By blending these wastes with fuel, we attempt to promote ignition, increase the burning rate, and delay extinction of the droplets, enhancing the destruction efficiency.

In our computational study, we have developed a one-dimensional, numerical model to simulate combustion of multicomponent droplets. Figure 1 shows a schematic of the processes occurring during droplet vaporization and combustion. Our

model, based on one-dimensional, fully coupled, conservation equations for mass, momentum, and energy transfer,² is unique compared to other droplet models in its ability to simulate more than one component in the liquid phase.

Hydrocarbon oxidation chemistry is straightforward to simulate using a reduced reaction mechanism developed by Westbrook and Dryer.³ This two-step mechanism contains finite-rate kinetics for hydrocarbons, first oxidizing to carbon monoxide and water and then carbon monoxide oxidizing to carbon dioxide. However, chlorinated hydrocarbon chemistry is more difficult to simulate. No global reaction mechanisms are available. As a first approximation for the oxidation of TECA blended with a pure hydrocarbon, we duplicated the structure of Westbrook and Dryer's hydrocarbon mechanisms, adding HCl and Cl₂ formation in the first step. This simplified mechanism does not simulate competition for hydrogen radicals between the hydrocarbon fuel and TECA, nor any pyrolysis of TECA that may occur.

Figure 2 presents a comparison of numerical and experimental results for TECA blended with equally volatile nonane. In the experiment, droplets are injected into a heated, oxidizing environment, and size and concentration are measured as a function of time. The size histories (plotted as *symbols* in Figure 2) show a prolonged, straight-line behavior that defines the constant gasification rate predicted by the classical d²-law. This straight-line portion of the graph is usually preceded by a short, curved, pre-ignition region and often followed by a flatter, post-extinction region seen at the end of the droplet lifetime. The experimental data shown in Figure 2 are shifted in time to aid comparison with numerical data.

The numerical results presented in Figure 2 (plotted as *lines*) agree well with the experimental data in the constant gasification region, but not as well in the initial and final phases of the droplet

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Figure 1. Schematic of processes occurring during droplet combustion.

lifetime. This result is not surprising since global-reaction mechanisms used to simulate chemical reactions are not developed with the intent to simulate ignition and extinction phenomena. Elementary reaction steps, modeled using the CHEMKIN data base or an equivalent, are required to simulate the chemistry in unsteady burning regions. The model successfully captures the experimental trend of a markedly increased burning rate (increased slope) in a TECA droplet blended with only 25% (by volume) nonane.

With their similar volatilities, blending TECA and nonane allowed us to study multicomponent burning without the effects of preferential vaporization. Experiments were also conducted for unequal volatility mixtures. Results showed that blending TECA with a fuel having a *lower* volatility, such as dodecane, promotes a faster burning rate. Our model was not as successful in predicting this trend, most likely because the simplified reaction mechanisms do not capture kinetic effects of changing chlorine concentration in the droplet.

Figure 2. Droplet gasification behavior for pure and blended droplets.

References:

1. N. W. Sorbo, R. R. Steeper, C. K. Law, and D. P. Y. Chang, *Twenty-Second Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, PA, 1989), p. 2019.
2. N. E. Bergan, E. K. Flatbush, and H. A. Dwyer, "Combustion of Multicomponent Hazardous Waste Droplets," Spring Meeting of the Western States Section/The Combustion Institute, Salt Lake City, UT (1988).
3. C. K. Westbrook and F. L. Dryer, *Combust. Sci. and Tech.* **21**, 31 (1981).

Section 11

An in-cylinder optical probe is a recent addition to the ensemble of nonintrusive, diagnostic tools developed at the CRF.

Technology Exchange

Barrack Technology Corporation recently announced the commercial introduction of the CRF-developed, fiber-optic instrumented spark plug. The in-cylinder, combustion diagnostics product package, which also includes data acquisition electronics and data analysis software, measures the motion and rate of growth of the early flame kernel in a spark ignition engine.

The heart of the package consists of a standard spark plug with eight optical fibers installed in the ring of the base of the threaded region of the plug. The fibers collect the light emitted by the flame front as it crosses the field of view of each fiber. Data collected from the spark plug are processed using a data analysis package. Further details may be found in the article on page 7-1.

Section 11

Technology Exchange

For more than a decade, researchers at the CRF have sought aggressively to foster the exchange of combustion-related technology with U.S. industries and universities. Our cornerstone activity in this endeavor is the Visiting Scientist Program, bringing representatives from industries and universities to work side-by-side with the in-house research staff. Through 1988, approximately 7000 visitors have come to the facility. Many have stayed for extended periods of up to a year or more, bringing a diverse set of backgrounds, problems, and goals, and taking away CRF-generated technology, research techniques, computer codes, and expertise.

Another important means of fostering technology exchange is through Cooperative Working Groups that bring together industry, university, and national laboratory researchers to address common problems. Traditionally, groups organized by the CRF have focused on automotive industry issues such as combustion in direct-injection, stratified-charge and dilute homogeneous charge engines, emission control in diesel engines, and engine knock. Success has, in turn, led to the formation of three new groups, focusing on turbulent aerothermochemistry, spray, and pulse combustion.

Perhaps the most direct means of technology exchange is through the formation of new companies and the development of new products. CRF-generated inventions and processes have led to the formation of new companies. Examples are Insitac to commercialize particle sizing technology, and Technor to commercialize the RAPRENOx process for eliminating NOx from combustion emissions. In other instances, CRF technology has been incorporated into new products by existing companies. Examples include laser injection seeding technology, developed in our diagnostics research effort, now commercially available through Lightwave Electronics, Inc., and permanent-magnet Faraday isolators, available from Electro-Optics Technologies, Inc.

In the final analysis, technology exchange at the CRF is a complex, subtle, and dynamic process that depends critically on individual interactions between in-house researchers and their university and industry counterparts. This section describes some of the activities that have taken place in the past year.

Technology Exchange

The technology developed at the Combustion Research Facility is shared with industry, universities, and other government laboratories through the Visiting Scientist Program and through formal working groups that facilitate technology exchange for more applied uses, including commercialization.

G. B. Drummond

An important aspect of the Combustion Research Facility (CRF) program is technology exchange, the movement of research results to the combustion community. Exchange is effected through the Visiting Scientist Program, through Sandia's Postdoctoral Program, through the DOE's Industry Technology Program, and by participation in interactive working groups with U.S. industry, universities, other national laboratories, and through international collaborations.

Working Groups. Seven joint working groups are now active:

Topic: Direct-Injection, Stratified-Charge Combustion

Participants: General Motors, Princeton University, Los Alamos National Laboratory, Sandia National Laboratories.

Topic: Dilute Homogeneous-Charge Combustion

Participants: Ford, Science Applications, Inc., S-Cubed, Massachusetts Institute of Technology, University of California/Berkeley, Imperial College, University of Wisconsin, Integral Technologies, Inc., Pennsylvania State University, Sandia National Laboratories.

Topic: Diesel Combustion

Participants: Cummins, Exxon, Navistar, Physical Sciences, Southwest Research Institute, UTRC, Purdue University, Pennsylvania State University, Yale University, Los Alamos National Laboratory, Sandia National Laboratories.

Topic: Engine Knock

Participants: General Motors, UNOCAL, Princeton University, Drexel University, Lawrence Livermore National Laboratory, Sandia National Laboratories.

Topic: Aerothermochemistry of Turbulent Combustion

Participants: General Electric Company, California Institute of Technology, Cornell University, University of California/San Diego, University of Sydney (Australia), Sandia National Laboratories.

Topic: Spray Combustion

Participants: National Bureau of Standards, Jet Propulsion Laboratories, Los Alamos National Laboratory, Sandia National Laboratories.

Topic: Pulse Combustion

Participants: Lennox Corporation, Ford Energy Engineering, Gas Research Institute, Toshiba Corporation, Battelle Columbus, University of Michigan, Georgia Institute of Technology, University of California/Davis, Sandia National Laboratories.

Industrial Interactions. The Industry Technology Fellowship Program is funded by the DOE's Office of Basic Energy Sciences, Division of University and Industry Programs. It provides financial support, on a cost-sharing basis, for visits of industrial researchers to the CRF.

Interaction with industrial partners has resulted in close collaboration using CRF facilities. A fiber-optic-instrumented spark plug, developed at the Facility, has been commercialized by Barrack Technology. Measurements have been made in cooperation with automotive fuels companies on end-gas temperature history. Modeling and experimental work in in-cylinder diesel fluid motion, in collaboration with Cummins Engine, has provided a new level of insight into the complex three-dimensional flows in realistic heavy-duty diesel engines.

International Programs. On the global scale, the CRF is active in two programs of the International Energy Agency. In the internal combustion engine and furnace program, the CRF participates with representatives from Canada, France, Italy, Japan, Norway, Sweden, Switzerland, the United Kingdom, and West Germany to exchange research results in the areas of advanced piston-engine technology and in fundamental combustion studies. Some fifty research tasks are under way in this program.

The second program, in coal-combustion sciences, involves the CRF and other U.S. Researchers with representatives from Australia, Canada, and the Netherlands. Both of the programs are conducted at some of the most outstanding research institutions of the world.

Visiting Scientist Program

An extensive visiting scientist program encourages researchers to work side-by-side with the Combustion Research Facility staff and to take advantage of the Facility's unique resources.

G. B. Drummond

As a DOE major user facility, the Combustion Research Facility (CRF) is a national center for studying fundamental problems in energy-related combustion. An important element of the CRF charter provides for promoting the development and application of new combustion research tools (laser diagnostics, computational tools, etc.) with the active involvement of the combustion research community at large. The Visiting Scientist Program enables scientists from universities, industry, and other national laboratories to become involved in research at the CRF and to take advantage of the specially designed equipment and resources here. Research support provided to visiting scientists includes technicians and engineering staff dedicated to the project, computer time, shop work and other purchases necessary to support the project. Visitors generally provide their own salary, travel and living expenses, and agree that the results of their research be made available in the open literature. The facility can accommodate proprietary research only on a full cost-recovery basis.

Many visitors elect to work primarily on collaborative projects or to use established experimental setups to do their own research. However, they are free to execute their own research projects.

In the eight years since the Facility opened, we have had more than 6,000 technical visitors. (See Figure 1.) Many of the visits are brief, typically

lasting for one or two days. Visitors come to learn about the technical scope of the CRF program or to discuss specific combustion research problems of their own with the Facility staff.

Other visits are of a longer duration. The number of scientists who have spent two weeks or more at the CRF has reached more than 330, as shown in Figure 2. Those visiting in CY 88 (listed in Table I) have engaged in a wide variety of research projects and include representatives from universities, industry, other national laboratories, and governmental facilities. Thirteen of those came from foreign institutions.

Included in the numbers in Figure 2 are the Sandia Postdoctoral Program participants. Each year, Sandia Laboratories accepts a small, but growing, number of postdoctoral candidates for a one-year (renewable to two-year) appointment. The Facility draws physicists, chemists, mathematicians, and engineers who wish to work in the field of combustion research. Candidates are expected to move to industry and universities when their term of appointment ends; this provides another way to transfer CRF technology to the combustion community. Graduate students with an interest in combustion science are also in residence at the CRF—many working on theses under the guidance of a faculty advisor or a mentor assigned from the Sandia Staff.

Figure 1. Total visitor statistics since 1981.

Figure 2. Long-term visiting scientist statistics for the period 1981 to 1989.

CRF Visiting Researchers
October 1, 1987 - December 31, 1988

Name	Affiliation	Term of Stay	Collaborative Project
University			
Abrams, Martin	J. F. Kennedy H. S.	June 20, 88 - Aug 19, 88	Laser synchronization programming
Allen, Wesley ¹	UC Berkeley	Oct 1, 87 - Dec 31, 88	Theoretical chemistry
Arpaci, Vedat	Univ. of Michigan	Oct 1, 87 - May 31, 88	Heat transfer studies
Axelbaum, Richard	UC Davis	Oct 1, 87 - June 30, 88	Sooting flames
Bechtold, John ¹	Univ. of Michigan	Sept 1, 88 - Dec 31, 88	Propellant modeling
Bennett, Matthew	Co. entry Polytech.	Jan 4, 88 - Mar 31, 88	Engine optical diagnostics
Biernacki, Terry ¹	Yale Univ.	Jan 4, 88 - July 15, 88	Multiphoton spectroscopy
Caton, Jerry ³	Univ. of Texas	Oct 1, 87 - June 15, 88	RAPRENOx studies
Cavolowsky, John	UC Berkeley	Oct 1, 87 - Dec 31, 88	Hypersonic diagnostics
Dec, John	Univ. of Michigan	Oct 1, 87 - June 10, 88	Pulse combustion studies
Dreier, Thomas	Univ. of Heidelberg	Sept 1, 88 - Dec 31, 88	CARS studies
Dunn-Rankin, Derek	UC Irvine	Oct 1, 87 - Feb 28, 88	Coal-water slurries
Dwyer, Harry	UC Davis	Oct 1, 87 - Dec 31, 88	Combustion modeling
Eibeck, Pamela	UC Berkeley	July 5, 88 - Dec 31, 88	Pulse combustion studies
Fornaciari, Neal ²	Chabot College	Oct 1, 87 - Sept 15, 88	Spray combustion lab development
Fourquette, Dominique	Wellesley College	Sept 1, 88 - Dec 31, 88	Reacting flow research
Frasier, Roydon	Princeton Univ.	Nov 7, 88 - Dec 31, 88	Natural gas-fueled engines
Gai, HuaDong	Oklahoma State	Jan 11, 88 - Jan 22, 88	Chemical dynamics modeling
Gemmen, Randall	Univ. of Michigan	Oct 1, 87 - Dec 31, 88	Unsteady droplet dynamics
Glarborg, Peter	Tech. Univ. of Denmark	Nov 1, 88 - Nov 27, 88	Boundary layer modeling
Grant, David	Univ. of Utah	June 13, 88 - July 15, 88	Pulverized coal studies
Hall, Matthew ¹	Princeton Univ.	Oct 1, 87 - Dec 31, 88	Engine optical diagnostics
Hess, Wayne ¹	Univ. of Colorado	Feb 15, 88 - Dec 31, 88	Chemical kinetics research
Janssen, Maurice	Univ. of Nijmegen	July 18, 88 - Aug 12, 88	Photodissociation studies
Kang, Shin-Gyoo	MIT	May 16, 88 - May 27, 88	Combustion modeling
Kennedy, Ian	UC Davis	Oct 1, 87 - Dec 31, 88	Counterflow diffusion flames
Kollmann, Wolfgang	UC Davis	Oct 1, 87 - Dec 31, 88	Turbulence modeling
Komyathy, David ²	Chabot College	Oct 1, 87 - Sept 15, 88	Facility laser software development
Kumar, Arvind ³	Univ. of Missouri	May 9, 88 - Aug 19, 88	Energetic materials studies
Leung, Liu-Wang	UC Berkeley	Oct 1, 87 - May 30, 88	Turbulent flame research
Long, Marshall	Yale Univ.	July 18, 88 - Aug 12, 88	3D Imaging experiments
Loui, Dell	UC Davis	Oct 1, 87 - Nov 15, 87	Counterflow diffusion flames
Lyon, Kevin	Yale Univ.	July 18, 88 - Aug 12, 88	3D Imaging experiments
Mataga, Thomas	UC Berkeley	Oct 1, 87 - Dec 31, 88	Hypersonic diagnostics
McMurtry, Patrick ¹	Univ. of Washington	Oct 1, 87 - July 15, 88	Turbulence modeling
Mungal, Godfrey	Stanford Univ.	July 1, 88 - Sept 15, 88	Supersonic combustion research
Ng, Wilson ²	Granada H. S.	July 1, 88 - Aug 30, 88	Coal char combustion studies
Parker, David	UC Santa Cruz	Oct 1, 87 - Dec 31, 88	Molecular beam experiments
Pitz, Bob	Vanderbilt Univ.	July 11, 88 - July 22, 88	Supersonic combustion modeling
Pugmire, Ron	Univ. of Utah	June 13, 88 - July 15, 88	Pulverized coal combustion study
Radziemski, Leon	New Mexico State Univ.	July 1, 88 - Aug 15, 88	Spark spectroscopy
Repl'ogle, Bill ²	Chabot College	June 27, 88 - Sept 15, 88	Coal devolatilization
Sailor, Dave	UC Berkeley	Oct 6, 88 - Dec 31, 88	Pulse combustion studies

Name	Affiliation	Term of Stay	Collaborative Project
Sawyer, Bob	UC Berkeley	Sept 1, 88 - Dec 31, 88	2D imaging techniques
Silk, Robert	New Mexico State Univ.	May 31, 88 - Aug 19, 88	Laser spark spectroscopy
Sitz, Greg ¹	Stanford Univ.	Nov 16, 87 - Dec 31, 88	Laser diagnostic research
Stärner, Sten	Univ. of Sydney	Aug 22, 88 - Aug 12, 88	Turbulent flame studies
Stolte, Steven	Univ. of Nijmegen	July 6, 88 - July 29, 88	Photodissociation experiments
Thoman, John ¹	MIT	Oct 1, 87 - June 30, 88	Ion imaging
Wall, Terry	Univ. of Newcastle	Oct 31, 88 - Dec 31, 88	Coal char reactivity
Warnatz, Jürgen	Univ. of Heidelberg	Aug 22, 88 - Sept 1, 88	Combustion chemistry
Williams, Forman	Princeton Univ.	Mar 14, 88 - Mar 18, 88 and Aug 8, 88 - Aug 12, 88	Combustion modeling
Yakhot, Victor	Princeton Univ.	July 5, 88 - July 15, 88	Turbulence modeling
Yip, Brandon	Yale Univ.	July 18, 88 - Sept 16, 88	Imaging experiments

Industry

Evens, Lance	Lennox	June 27, 88 - Dec 31, 88	Pulse combustion studies
Hongo, Ichiro	Toshiba	Oct 1, 87 - Feb 28, 88	Pulse combustion studies
Hoskin, Dennis	Mobil Research	July 25, 88 - Nov 4, 88	Spray combustion measurements
Kelly, John	Altex	Oct 1, 87 - Dec 31, 88	2D shear layer studies
Marchand, Rob	Lennox Corp.	June 27, 88 - Dec 31, 88	Pulse combustion studies
Namazian, Mehdi	Altex	Oct 1, 87 - Dec 31, 88	2D shear layer studies
Ng, Henry ⁴	Cummins	Jan 29, 88 - Mar 31, 88	Engine particulate measurements
Perrin, Marc	Gaz de France	Oct 14, 88 - Dec 31, 88	Turbulent flame optical diagnostics
Perry, Bob	Technor	Oct 1, 87 - Dec 31, 88	RAPRENOx studies
Tack, Les	UNOCAL	Jan 25, 88 - Feb 5, 88 and May 23, 88 - June 3, 88	CARS/engine knock studies
zur Loye, Axel ⁴	Cummins	Oct 1, 87 - Dec 31, 88	Engine particulate studies

Government

Rosasco, Greg	NBS	July 11, 88 - July 22, 88	IRS of combustion species
Steele, Pat	U.S. Navy	Aug 15, 88 - Oct 15, 88	Hydrogen igniter studies
Young, Ron	NASA/Dryden	June 1, 88 - Aug 30, 88	Hypersonic studies

National Laboratories

Habib, Ziad	CNRS, Rouen	Apr 4, 88 - Dec 16, 88	Coal mineral matter behavior
Souché, Isabelle	CNRS, Poitiers	Oct 1, 87 - Sept 1, 88	Pyrogenic materials studies

- ¹ = Sandia Postdoctoral Program participant
² = Sandia Student Program participant
³ = Sandia Faculty Program participant
⁴ = DOE Industrial Technology Program participant

Publications 1988-89

Refereed Journal Articles

M. Aldén, U. Westblom, and J. E. M. Goldsmith, "Two-Photon-Excited Stimulated Emission from Atomic Oxygen in Flames and Cold Gases," *Opt. Lett.* **14**, 305 (1989).

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R. S. Barlow and J. P. Johnston, "Structure of a Turbulent Boundary Layer on a Concave Surface," *J. Fluid Mech.* **191**, 137 (1988).

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