Application of Spatially Precise Laser Diagnostics to Fundamental and Applied Combustion Research

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Recent applications of spatially precise, spectroscopically based laser diagnostics for measurement of combustion temperature and species are reviewed. Four techniques are analyzed: Rayleigh scattering, spontaneous Raman scattering, laser-induced fluorescence spectroscopy (LIFS), and coherent anti-Stokes Raman spectroscopy (CARS). The impact of these techniques on both fundamental research and applied problems is considered.

Introduction

AFTER years of development, spatially precise laser diagnostics for combustion temperature and species are now entering the arsenal of the combustion researcher and are beginning to affect combustion science and engineering. In addition to the obvious attributes associated with their nonintrusive and in-situ character, laser-based techniques can possess concurrently high spatial and temporal resolution, which makes them far more preferable for use in turbulent combustion applications than traditionally employed techniques. In this paper, we will highlight some of the recent contributions made by light-scattering and wave-mixing techniques suitable for thermometry and chemical composition determinations. In addition, new developments and applications of the various approaches will be described which will also serve to assess their current status.

Four diagnostic techniques will be discussed, namely, Rayleigh scattering, spontaneous Raman scattering, laser-induced fluorescence spectroscopy (LIFS), and coherent anti-Stokes Raman spectroscopy (CARS). The first three may be loosely classified as light-scattering techniques in which the signal is incoherently distributed over 4π sr in accord with dipole radiation laws. CARS is an example of what physicists term wave mixing that results in the generation of a coherent, laser-like signal beam. Rayleigh scattering is not explicitly species specific, while the other three techniques are. The Raman-based approaches are commonly used for thermometry and are complementary to LIFS in regard to species applicability and sensitivity. Raman techniques typically possess only major species sensitivity, i.e., mole fractions $>10^{-3}$ and are applicable to all molecules in sufficient concentration. LIFS is applicable to molecular radicals, molecules, and atoms with spectrally accessible electronic absorptions and is sensitive on a 1 ppm or, occasionally, lower level.

By design, our focus here will be primarily on the utilization of these techniques for measurements at a single point. The employment of these approaches for measurements over a two-dimensional field is an important development and is the subject presently of intensive research attention.[1,2] Such techniques when developed will permit spatial correlations and expedite insight into fundamental phenomena. Much of the fundamental physics, early literature, and progress in these spectroscopically based approaches have been reviewed in previous papers[3-6] and will not be repeated here. The techniques will be addressed in the following order: Rayleigh, Raman, CARS, and LIFS and the treatment will encompass both recent fundamental contributions and practical applications.

Rayleigh Scattering

Rayleigh scattering is the elastic scattering of light quanta or photons from molecules. Elastic implies that there is no energy exchange between the photons and target molecules and, thus, the scattering is unshifted in frequency from the incident light. There is, consequently, no way to distinguish the scattering emanating from various constituents. Furthermore the scattering cannot be distinguished from other elastic scatterers such as particles or windows, walls, etc. Since particle scattering cross sections are 10–20 orders of magnitude higher than Rayleigh, the measurement environment must be virtually free of particles. Considerable care must also be exercised to trap the Rayleigh-inducing laser beam and to minimize spurious scattering. In an atmospheric pressure flame, the Rayleigh efficiency will be on the order of 10^{-11}, i.e., the ratio of collected Rayleigh scattered energy to incident laser energy. Spurious scattering must be suppressed so as to be two orders of magnitude or more lower.

Since the scattering from various constituents cannot be differentiated, the Rayleigh signal varies linearly with the total number density and will also be composition sensitive. In constant density mixing studies between two constituents with marked differences in their Rayleigh cross sections, the variation of the Rayleigh intensity can be employed to track the mixing.[7] In flame studies, it is a relatively simple matter to tailor the reactant mixture, in either premixed or diffusion flames, so that the total Rayleigh-scattering cross section varies by no more than a few percent as combustion proceeds. The total Rayleigh signal is then strictly proportional to the total number density and independent of composition. For the low-Mach-number combustion studies, where the constant-pressure assumption can be made, gas temperature is inversely proportional to the number density or, equivalently, the Rayleigh signal. In a similar manner, the mass-normalized total cross section can be held approximately constant so that the total Rayleigh signal will be strictly proportional to the mass density of the gaseous mixture.

Despite its lack of species specificity and restriction to nearly particle-free situations, Rayleigh scattering is a very powerful tool for fundamental combustion studies due to its signal strength and simplicity. At an overall efficiency of $\sim 10^{-11}$, a 1-W continuous, visible wavelength laser will

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yield 2500 signal photons every 100 μs. A photomultiplier tube with a 20% quantum efficiency will record this signal with a quantum noise-limited accuracy of about ±4%. Thus, one can perform density measurements or thermometry in atmospheric pressure turbulent flames at a several kilohertz sampling rate, which is essentially real time. In addition, calibration and data reduction are straightforward, requiring no sophisticated spectroscopic codes.

The laser required for Rayleigh scattering is essentially that required and provided in commercial laser anemometers. By adding a Rayleigh optical collection and detection system, it is relatively straightforward to provide a laser anemometer with a mass density or thermometry capability. If high-seed particle densities are used for the velocimetry, however, the Rayleigh channel will be saturated by particle scattering in each signal integration interval. By decreasing the seeding level, it is possible to perform velocity and density/temperature measurements nearly simultaneously. The Rayleigh signal is tracked in real time until a particle enters the sampling volume, which is quite evident by the sudden increase in signal magnitude. The velocity measurement can be tagged with the Rayleigh density or temperature just prior to particle arrival. The seeding rate generally needs to be reduced to a level where it is no longer possible to follow the flow in real time. Nevertheless, the medium can still be statistically analyzed.

An illustration of the power of the combined Rayleigh/laser Doppler velocimeter (LDV) approach is evident in the work of Driscoll et al.[8] By measuring instantaneous mass densities and velocities in a turbulent H_2/air simple jet diffusion flame (Reynolds number ~24,000), it was possible to evaluate the turbulent axial and radial mass fluxes, $\overline{\rho' u'}$ and $\overline{\rho' v'}$, where the bar denotes the ensemble average, the prime the fluctuation magnitude (e.g., $\rho - \bar{\rho}$), and the axial and radial velocity components u, v. From the measured probability distribution functions, mean quantities were also obtainable. From the results, it was found that the gradient diffusion assumption in the axial flow direction, i.e.,

$$\overline{\rho' u'} = -D_T \frac{\partial \bar{\rho}}{\partial x}$$

commonly employed to model $\overline{\rho' u'}$ in first-order closure was seldom obeyed. In the above equation, D_T is the turbulent diffusivity. Thus, the turbulent axial mass flux was predominantly countergradient. Radial turbulent mass fluxes did exhibit a gradient diffusion behavior throughout.

Thus, Rayleigh scattering, despite its limitations, is a very powerful technique, when intelligently employed, for fundamental turbulent combustion research. The technique is highly developed and is fairly easily implemented.

Spontaneous Raman Scattering

Raman scattering is the phenomenon of inelastic scattering between the incident photons of light and the target molecules. Inelastic implies that there is energy exchange between the light quanta and the internal energy modes of the molecules. Typically, one examines scattering associated with vibrational mode exchange. Since the vibrational energies of the various molecules of combustion interest are quite different, the Raman signatures from the various constituents are well separated spectrally, making it possible to monitor many species simultaneously with a single laser. The laser can operate at any wavelength without the necessity of being tuned to specific molecular resonances. Visible wavelengths are favored since the strength of the scattering, i.e., the Raman cross section, scales as the fourth power of the scattered frequency. Unfortunately, despite these advantages, Raman scattering is very weak. For a major constituent in an atmosphere pressure flame, the Raman efficiency is typically on the order of 10^{-15}–10^{-14}. Use of a continuous laser of a few Watts is restricted to temporally steady laminar flames because of the low signal rates. Furthermore, flame luminosities must be quite low so as not to compete with the Raman signal. Real-time turbulence measurements are possible in cold jets of gases with large Raman cross sections, e.g., CH_4.

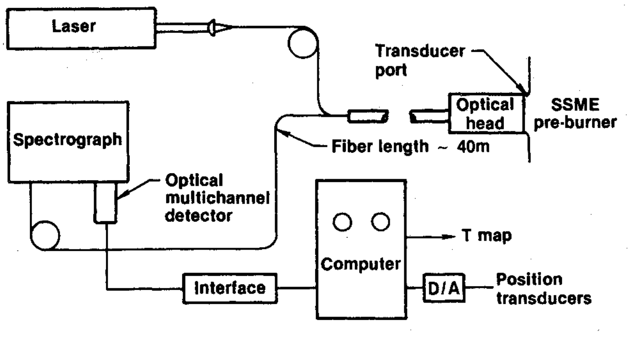


Fig. 1 Overall schematic of fiber-optic Raman thermometer for Space Shuttle Main Engine (SSME) preburner temperature profiling.

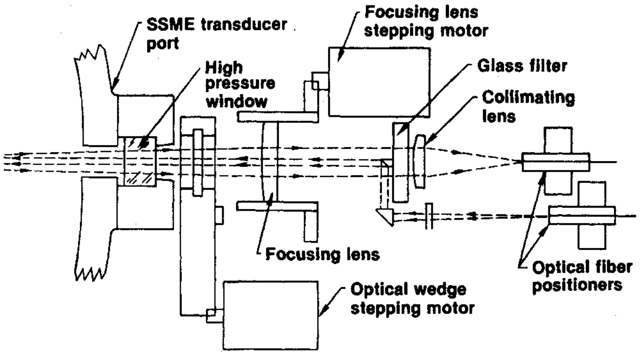


Fig. 2 Interior design of fiber-optic Raman thermometer optical instrument head.

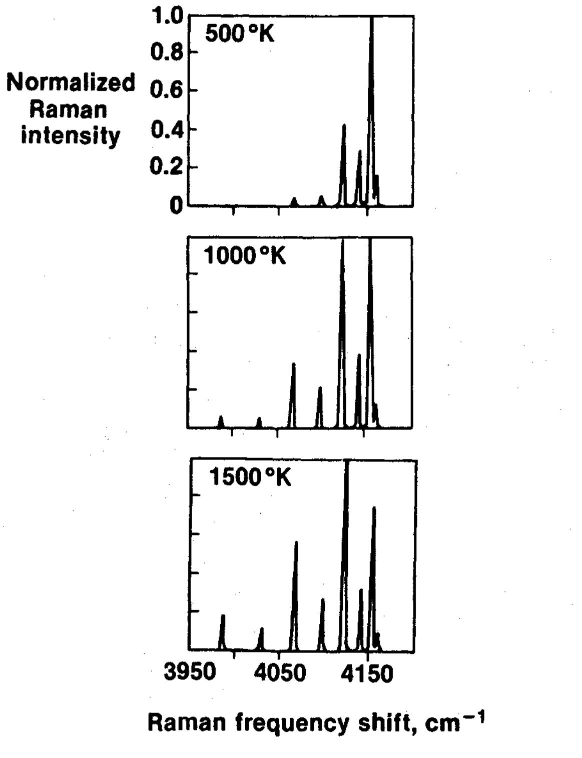


Fig. 3 Temperature variation of the vibration-rotation Stokes Raman spectrum of hydrogen (calculations were performed for 380 atm pressure and a 2 cm^{-1} slit width).

For turbulent flame studies, multijoule-pulsed lasers are employed to perform measurements in a single-laser pulse. Such lasers are typically restricted to pulse rates in the 1-10 Hz range and thus one is forced to sample statistically the turbulent combustion event. These measurements are typically constrained to hydrogen-fueled diffusion flames or premixed hydrocarbon-fueled flames. In the presence of soot particles, the pulsed laser heats the carbonaceous particles into the 4000-6000 K range. This laser-modulated soot incandescence, temporally in phase with the Raman signature, represents a serious interference and restricts the applicability of Raman scattering to relatively clean flames.[3] Aside from the low data rate, the technique is thus quite applicable to fundamental turbulent flame studies where one desires major species concentration information in addition to temperature.

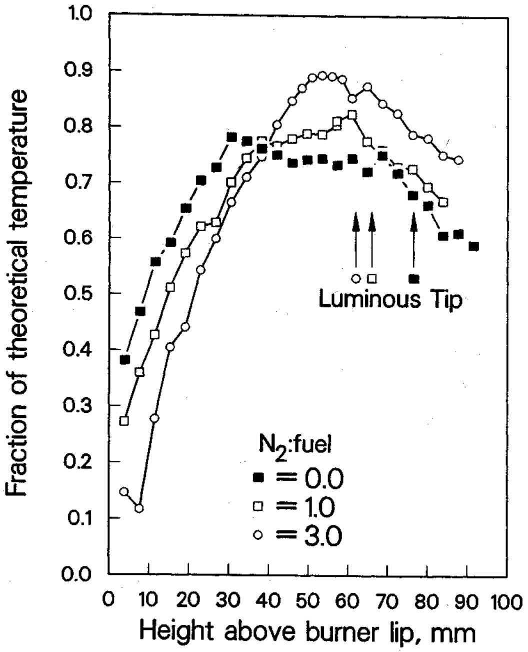


Fig. 4 CARS axial temperature profiles with N_2 fuel jet dilution in an axisymmetric, overventilated, laminar ethylene diffusion flame (measured temperatures are normalized to the anticipated adiabatic flame temperature).

Pulsed Raman scattering has been applied to turbulent hydrogen/air diffusion flames to compare temperature and density fluctuations with turbulent flame models.[9] In that work, the importance of including the effect of differential diffusion of lighter species was identified as necessary for model agreement with the experimental data. A multispecies Raman approach (temperature, N_2,O_2,H_2,H_2O) has been combined with LDV measurements of instantaneous velocity to measure conserved scalar fluxes in turbulent nonpremixed H_2/air flames.[10] Of particular importance in modeling turbulent diffusion flames is the correlation of velocity and conserved scalar. Using such correlations, measurements such as these will permit direct evaluation of the turbulence submodels employed for closure. In general, such submodels are evaluated indirectly on the basis of comparisons between overall model predictions and measured mean values.

In the area of practical application, the utilization of spontaneous Raman scattering for temperature measurements in the preburner of the Space Shuttle Main Engine (SSME) will be highlighted here.[11] In the fuel preburner, hydrogen is reacted with oxygen under very fuel-rich conditions to create a hot gas stream to drive the propellant turbopumps. Temperature profiles are desired in the preburner exhaust stream to evaluate designs aimed at minimizing thermal stressing of the fuel pump turbine blades. Nonuniform temperature profiles entering the fuel turbopump are hypothesized to be a potential factor in the limited lifetime of this component. Preburner pressures are on the order of 5000 psi with temperatures in the 1000 K range. Equilibrium calculations indicate H_2 to constitute about 90% of the burned gases with the balance being H_2O. Concentrations of atomic hydrogen and hydroxyl (OH) are estimated to be less than 1 ppb.

An optical diagnostic technique was sought that could perform temperature measurements every 10^{-2} s with a spatial resolution better than 1 cm. In the current hardware, there is only one optical port. There are two additional transducer ports so disposed that no diametral line-of-sight optical access exists between any combination of two ports. Other instrumental challenges during stand testing include engine movement during operation due to gimbaling, the surrounding condensation cloud from the cyrogenic propellant lines,

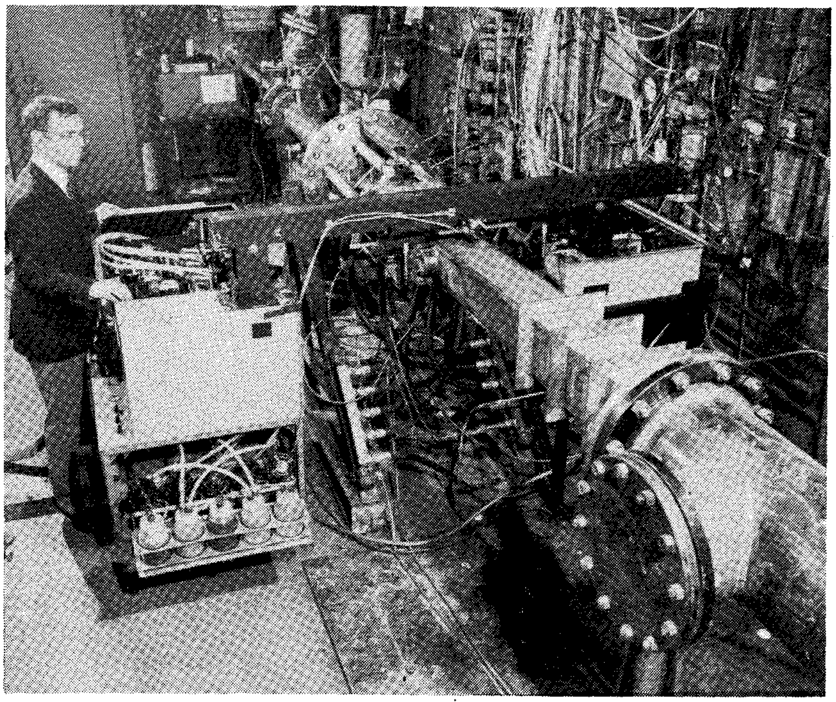


Fig. 5 Installation of mobile CARS instrument about the UTRC supersonic combustion facility.

and the attendent high noise and vibration levels associated with a high-thrust rocket engine. This situation, of course, makes it highly desirable to locate remotely all laser, spectrographic detection, and computational equipment and use fiber-optic links.

Various optical approaches to thermometry were evaluated during a conceptual design phase. Coherent optical techniques such as coherent anti-Stokes Raman (CARS)[12] and stimulated Raman gain, although spatially precise, require line-of-sight optical access which is not available in the preburner. Laser-induced fluorescence spectroscopy (LIFS)[13,14] of OH is a demonstrated thermometric technique but, at the low temperatures prevailing in the preburner, there is insufficient OH concentration for practical signal levels. Also, transmission of the ultraviolet wavelengths (~300 nm) required for OH excitation through fiber-optic links would be difficult. At the pressures prevailing in the preburner together with the strong Raman cross section of H_2, spontaneous Raman scattering is sufficiently strong to meet the instrument design goals if several watts of continuous laser power can be delivered to the measurement location. Furthermore, the interferences usually of concern in applying Raman techniques to combustion, associated with high luminosity levels and particulate loadings, are absent in fuel-rich H_2/O_2 combustion.

The overall instrument concept is schematically illustrated in Fig. 1. A continuous-wave argon ion laser with a power on the order of 10 W is focussed into a fiber-optic link and transmitted to the optical head whose design is illustrated in Fig. 2. In the head, the laser power emanating from the "transmitter" fiber is recollimated and passes through a Newtonian telescope whose separation is adjustable. The telescope focusses the laser irradiation to a point in the preburner. The Raman scattering is collected along the same axis in the backward direction, is collimated by the intermediate lens, and is focussed, after filtering, into the "receiver" fiber where it is transported, as seen in Fig. 1, to the remotely located spectrographic instrumentation for analysis. Obscuration of the low-angle paraxial Raman rays is purposely provided to enhance the axial spatial resolution of the measurement. A custom-designed spectrograph is employed in which the expanding output from the fiber optic, inserted directly into the spectrograph, is dispersed and focussed by a concave holographic grating onto an intensified, one-dimensional photodetector array. The H_2 Raman signature impinging on the optical multichannel detector is digitized and sent to a minicomputer for analysis. As seen in Fig. 3, the H_2 vibrational-rotational Raman spectrum appears as a sequence of distinct transitions whose relative intensity distribution is quite temperature sensitive.

Employment of the optical fiber approach is not as straightforward as one might initially suspect. To attain the requisite spatial and spectral resolution, fibers on the order of 50-100 μm in diameter need to be employed. At low-laser energies, the dominant transmission loss mechanism in the optical fiber is due to Rayleigh scattering of the light by the glass. At an input power level of 10 W into a 100-μm-diam fiber, the intensity in the fiber is on the order of 100 kW/cm^2. Nonlinear conversion effects, i.e., stimulated Brillouin or stimulated Raman, can become important and cause the fraction of power transmitted to decrease with increasing laser input power. These effects depend upon both fiber length and quality. With selected fibers in lengths of 40 m, laser outputs in excess of 4 W input have been attained.[11] Development of this concept into a prototype instrument is in progress.

Coherent Anti-Stokes Raman Spectroscopy (CARS)

CARS[12] evolved during the 1970s in response to the limited practical applicability of spontaneous Raman scattering. As mentioned earlier, due to the weakness of spontaneous Raman scattering and its incoherent character, it typically suffers serious interferences from flame luminosity and laser-induced soot heating and polycyclic aromatic fluorescences for near uv excitation wavelengths. Since the late 1970s, CARS has been demonstrated in many practical devices such as gas turbine combustor simulations, jet engines, internal combustion engines including diesels, coal gasifier exhausts, simulated MHD exhaust streams, and propellant flames. CARS has nominally the same atmospheric pressure detection capabilities as spontaneous Raman, namely temperature and major species. Another advantage of CARS is that these detection sensitivities are realized at laser energies typically an order of magnitude below those required for spontaneous Raman scattering. Correspondingly, these lower energy/pulse lasers operate at an order of magnitude or higher repetition rate, greatly reducing the time required to gather a statistically significant data set.

In CARS, laser beams at two different frequencies are "wave mixed" by crossing and focussing the beams at the measurement point. Key to the process is the frequency difference between the two beams, which is adjusted to access Raman-active vibrational-rotational modes of the species of interest. Since the higher-frequency "pump" laser is typically at a fixed wavelength, the lower-frequency "Stokes" laser is generally a wavelength-adjustable dye laser. For diagnostic work, the dye laser is made spectrally broadband to access simultaneously all of the Raman resonances in a given band region; such an approach permits single-pulse, instantaneous (10^{-8} s) measurements of medium properties. In general, thermometry derives from spectral analysis of the temperature-dependent signatures and concentration from the strength of the signal. CARS is a rather unique spectroscopy in that the signatures also become concentration sensitive in the 0.5-20% range typical of many of the important reactant and product species in combustion, e.g., CO, O_2, H_2O, and CO_2. This permits concentration measurements from spectral shapes rather than signal intensity levels that can be adversely affected by turbulent refractive effects and soot/fuel droplet attenuation. One disadvantage of CARS relative to Raman scattering, aside from both experimental and spectral complexity, is that one can nominally measure only one constituent at a time as CARS is usually implemented. One recent development we will describe shortly is an approach that removes this limitation.

After years of development and feasibility demonstrations, CARS is being increasingly applied to both laminar and turbulent flame studies. Time-resolved CARS and LDV measurements have been performed in turbulent premixed reacting flows stabilized by a bluff body.[15] Measurements were performed in a 50-mm i.d. quartz combustion tunnel with a central 24-mm-diam conical plug. Single-shot CARS thermometry was employed at a 25-Hz rate and correlated with velocity measurements. If a velocity measurement occurred within 20 ms of a temperature determination, it was assumed that the measurements were simultaneous. Under these conditions, no correlation was found between the velocity and temperature fluctuations. Furthermore, in certain regions of the flow, countergradient fluxes were inferred. In a similar vein, but in a different experiment, CARS and LDV have been employed for measurements in the near wake of an axisymmetric bluff body stabilized propane diffusion flame.[16] These experiments were performed in a 25.4-cm-diam tunnel with a 14-cm-diam centerbody. Fuel injection was via a nozzle located in the centerbody axis. The near-wake temperature field was mapped from CARS temperature probability distribution functions consisting of 1500 temperature measurements at each location. Velocity and temperature field measurements were compared with TEACH code predictions. Strong similarity was found between the measured CARS and predicted TEACH temperatures, indicative that the code was predicting the major qualitative

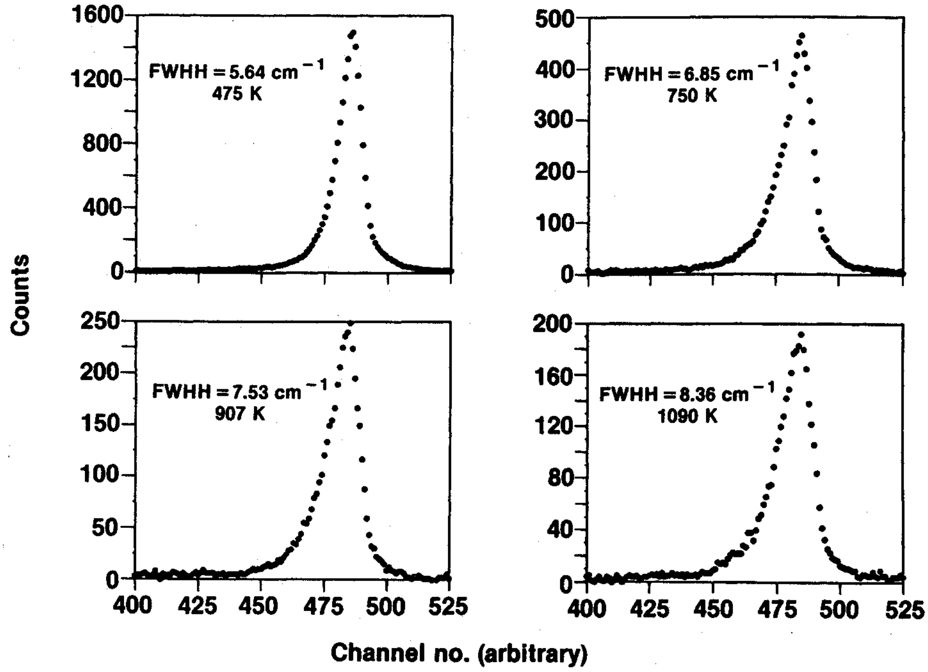


Fig. 6 Single-pulse (10^{-8} s) N_2 CARS spectra from $M = 3$ supersonic combusting stream. The abcissa is an optical frequency scale with each detector channel representing 0.53 cm^{-1} (cm^{-1} is a frequency unit given by inverse wavelength, e.g., 473.3 nm is 21,128 cm^{-1}).

features of the process. The bimodal shapes of the temperature probability distribution functions suggest the major transport mechanism in the shear layer is due to large-scale vortices shed from the bluff body. It was also found that physical thermocouple probes perturbed the near-wake flowfield to a degree that such measurements were not reliable.

In our laboratory, CARS has been extensively employed for temperature profiling in laminar, sooting diffusion flames.[17] Due to the key role played by temperature vis-a-vis soot formation, many of these studies have been performed with dilution of the central fuel jet to control the temperature in the fuel pyrolysis zones. In addition, angular dissymmetry Mie scattering measurements have been performed to ascertain the corresponding soot size and number density distributions. Measurements have been performed on overventilated diffusion flames stabilized on a 1.27-cm-diam stainless steel tube. CARS measurements were made in a 100-μm-diam by 700 μm long cylindrical sampling volume. One interesting example of this work is displayed in Fig. 4 where centerline axial temperature profiles are shown for ethylene flames at various dilution levels. As diluent (N_2) is added to the central fuel jet, depression of the temperature in the pyrolysis region is evident. There is also marked reduction in the total amount of soot formed in these flames with increasing dilution. Interestingly, in the upper portions of these flames, the diluted flames actually reach a higher fraction of the adiabatic flame temperature (and higher absolute temperature) than the undiluted flames. This is attributed to the reduction in soot radiation heat loss accompanying the reduction in the total amount of soot formed.

Although CARS has been demonstrated in a variety of practical combustion devices,[12] we will focus on its recent successful demonstration in a supersonic combusting flow.[18] The demonstrations were performed in a combustion facility at United Technologies Research Center (UTRC) designed to examine flame propagation in a Mach 3 propane/air mixture. The supersonic flow was generated by a blowdown facility that flowed 4.5 kg/s through a water-cooled two-dimensional nozzle into a gradually expanding, rectangular cross-section combustion tunnel. Ignition was accomplished by injection of high-temperature exhaust gases from a H_2/air burner through a pilot located about 20 cm downstream of the nozzle throat. The flow cross section at that point was approximately 7.6 cm high by 15.2 cm wide with the unburned propane/air mixture at 0.6 atm static pressure and 420 K static temperature. The CARS demonstrations were performed approximately 65 cm downstream of the pilot.

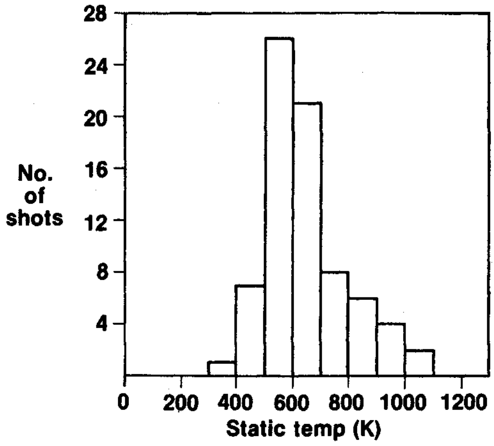


Fig. 7 CARS temperature histogram during mean steady supersonic combustion operation.

A mobile CARS instrument, designed by UTRC for such field applications, was employed for these demonstrations. It consists of three basic components, essentially the second generation of a CARS instrument developed earlier for jet engine exhaust measurements.[19] A cart-mounted transmitter with power supply contains a Nd:YAG laser and the associated optics necessary to align the system and generate the laser beams necessary to produce CARS. A receiver separates the CARS signal from unwanted radiation, uses the residual beams to generate a reference CARS signal for concentration measurements, and focusses the CARS signal into an optical fiber for transmission to the third subsystem, the data acquisition and control console. This subsystem contains a spectrograph and optical multichannel detector to digitize the CARS spectral signature and a data acquisition computer for magnetic tape data storage. Remote controls are also provided to operate the laser and to adjust the optical alignment of various components in the transmitter and receiver to optimize the CARS signal level. A separate computer (VAX 11/750) is presently used to perform the spectral data reduction. In the near future, a single Microvax computer mounted in the control rack will perform all functions.

A photograph of the mobile CARS instrument installed about the supersonic combustion test facility is shown in Fig. 5. The beam directing and translating system was anchored to the transmitter and receiver and bridged the combustion tunnel. It supported a pair of field lenses for beam focussing to the measurement point and subsequent recollimation. These lenses could be translated to move the measurement point laterally, a feature not exploited in the initial demonstrations. In the tests conducted, instantaneous single-shot thermometry was performed at a 20-Hz repetition rate during the approximately 20-s duration combustion runs. Samples of four single-shot N_2 CARS spectra are displayed in Fig. 6. The temperature was deduced from the full width at half height of these signatures for simplicity. During the transient operation of the tunnel, there is a 5-s period of fairly steady (in a mean sense) operation. A temperature histogram obtained during this period is displayed in Fig. 7. The temperature spread is not surprising, as the CARS measurements were made near the tunnel centerline, not far downstream of the floor-mounted pilot, and are probably near the outer edge of the combustion region at that location. As fluctuations cause this region to wander, a wide distribution of temperatures is sampled. The temperature rises seen are modest, but nevertheless in the range anticipated based on proximity to the pilot and the flow speed. Nonintrusive laser diagnostics are clearly desirable for the evaluation of supersonic combustion and advanced propulsion concepts and these initial experiments demonstrated the feasibility of such promising diagnostics.

One of the limitations of CARS, as normally implemented, is the inability to interrogate more than one constituent at a time. Except for a few fortuitous instances of closely spaced Raman resonances, one requires a separate Stokes dye laser source for each constituent to be measured. Using two separate Stokes lasers, N_2 and O_2 have been simultaneously measured.[20] In reality, employing more than two Stokes sources becomes quite cumbersome and complex. We have recently developed a dual broadband Stokes approach to CARS that permits several species, i.e., more than two, to be measured simultaneously.[21,22]

The basic concept, and the one demonstrated to date, is illustrated in Fig. 8. Assuming the laser beams are oriented appropriately, the pump beam at ω_1 wave mixes separately with each Stokes source at ω_2 and ω_2' in normal two-color CARS processes. In addition, there is a three-color CARS process, again assuming proper beam orientation, in which CARS is produced for Raman resonances corresponding to the frequency differences $\omega_2 - \omega_2'$. Since both ω_2 and ω_2' are broad, their frequency differences span a wide frequency region, permitting a multiplicity of constituents to be addressed. Particularly serendipitous in hydrocarbon-fueled combustion is the fact, as illustrated in Fig. 8, that when the Stokes sources are positioned to coincide with the major products of the combustion, namely CO_2 and H_2O, the moderately heavy diatomics of interest (N_2, CO, and NO) are covered by the frequency differences of the two and can be observed via the three-color process. In fact, the CARS spectra of these constituents occur at the same wavelengths they would if generated by a two-color process. Despite the employment of two broadband sources in the three-color mixing, spectral resolution is determined by the pump laser linewidth and/or spectrometer resolution just as in two-color mixing. This arises from the fact that the resonant Raman excitation frequencies are well defined by the constituent molecules and not by the manner in which the coherent excitation of these modes is created. The narrow-band pump laser then "scatters" off of this coherent Raman excitation with the resultant spectral resolution determined by the pump laser and/or spectrometer employed.

Due to the spectral energy partitioning inherent in the use of two broadband sources, the dual broadband signals are somewhat weaker than would normally pertain in two-color wave mixing. For dynamic measurements, dual broadband CARS might be restricted to elevated-pressure combustion applications, e.g., gas turbines, diesels, or propellant burning. At elevated pressure, the signal decrease accompanying dual broadband CARS would be compensated by the nominal quadratic scaling of the CARS signal with density. With engineering development, dual broadband CARS looks promising for removing one of the major drawbacks to CARS diagnostics.

Laser-Induced Fluorescence Spectroscopy (LIFS)

The aforementioned scattering and wave-mixing techniques are incapable of measuring species in low concentration, i.e., ppm levels, due to the lack of sensitivity. The pool of radical species, so important in combustion and pollutant chemistry, resides at these concentrations and is thus inaccessible to the techniques previously discussed. Fortunately, most radicals possess electronic transitions in the ultraviolet and can be measured with laser-induced fluorescence spectroscopy (LIFS). Conversely, most of the major species have absorptions far in the vacuum ultraviolet and are currently detected via Raman-based approaches. For those that can be accessed via one or two photon absorptions (e.g., O_2 and CO, respectively), LIFS may provide increased sensitivity. For the most part, however, Raman approaches and LIFS are complementary to one another in regard to species sensitivity and applicability.

Fluorescence is the spontaneous emission of radiation from an upper state excited in a variety of ways; here, our attention will be on excitation created by laser absorption, which today is the most convenient and spatially precise approach. Of course, for the fluorescence to occur, the molecule cannot photodissociate upon absorption of the photons. Besides spontaneously emitting, the molecule may

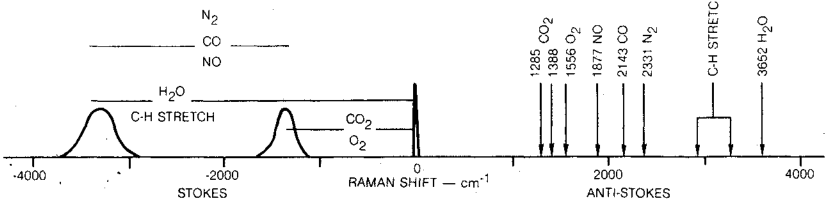


Fig. 8 Dual broadband Stokes approach to simultaneous, multiple-species CARS measurements.

be collisionally deactivated, a process known as quenching. For radicals in flames, quenching typically exceeds the spontaneous emission by three to four orders of magnitude. Despite this inefficiency, fluorescence is still a very sensitive way to monitor a localized absorption. Nevertheless, the quenching rate enters directly into determination of the species number density from the strength of the fluorescence and quenching "corrections" need to be applied.[3-6,13] There are a number of ways of doing this successfully and LIFS is routinely applied to flame chemistry investigations. In many such studies, it is the relative concentration profile that is really of interest. As long as the quenching rate does not vary markedly, the raw fluorescence intensity profiles can be used directly.

In turbulent or time-varying flame applications, the quenching rates may vary markedly with the extent of reaction and quantitative evaluation of the quenching corrections may be quite imprecise. In these applications, it is desirable to saturate the fluorescence, i.e., saturate the absorption. In this approach, the laser intensity is increased to such a level that the absorption and stimulated emission rates dominate the state population rate equations. In the ideal case, the fluorescence becomes independent of both the quenching and the input laser intensity. In reality, rotational/vibrational energy transfer often needs to be modeled in the data reduction process.[23] Furthermore, the saturation laser intensity is a function of the quenching and rotational energy transfer rate and saturation can be difficult to achieve.

In the case of hydroxyl (OH), this has all been worked out quite successfully and saturated LIFS has been applied to single-shot OH determinations in turbulent, H_2/air diffusion flames.[24] In these flames, probability distribution functions of OH number density were assembled at various spatial locations from 2048 individual single-shot measurements. The measurements confirmed the existence of super-equilibrium levels of OH in the various flames studied. The highest average number densities (calculated from the probability distribution functions) in a laminar diffusion flame were a factor of two higher than calculated for a stoichiometric flame under equilibrium. In the turbulent flames, peak single-pulse OH concentrations were factors of three to four higher than equilibrium predictions. Data such as these should prove useful in the detailed evaluation of turbulent combustion chemistry models that also predict super-equilibrium radical concentrations.

An interesting and potentially important application of LIFS is the use of "exiplex"-forming additives to liquid fuels to permit the separate detection of fuel in the liquid and vapor phases.[25] Coupled with two-dimensional digital imaging, quantitative visualization of evaporating fuel sprays appears very promising and may have major impact on understanding the fundamentals of fuel spray behavior. "Exciplex" is a shorthand term for excited state complex and the basic photophysics of the technique is illustrated in Fig. 9. An organic additive *M*, which is typically unsaturated and either olefinic or aromatic, is doped into the fuel at low concentration together with another additive known as the quencher. The quencher may be a component of the fuel in certain instances. The organic additive is selected to be coevaporative with the fuel. With electronic excitation of the additive, generally by ultraviolet laser absorption, the additive will fluoresce in the vapor phase slightly shifted to longer wavelengths than the incident radiation. In the liquid phase, however, the excited additive will bind together with the quencher to form an excited state molecule or exciplex, which displays a fluorescence spectrum well red-shifted from the vapor-phase spectrum of the additive. By binding with the additive, the nomenclature "quencher" becomes ap-

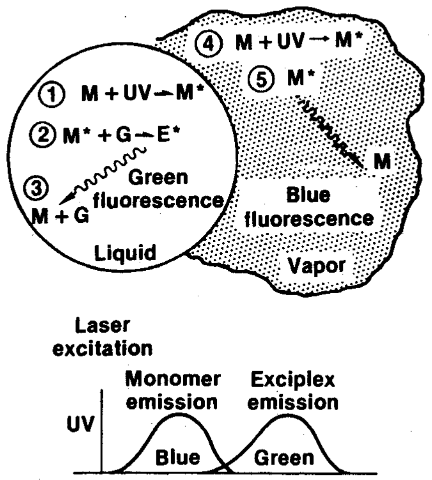
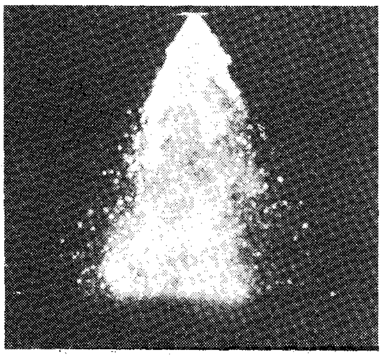
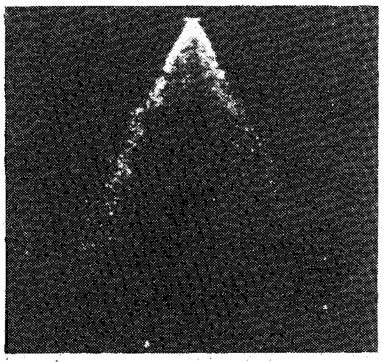


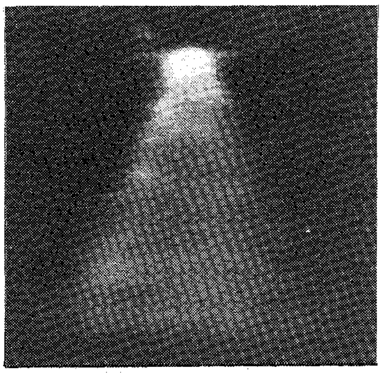
Fig. 9 Photophysical sequence for exciplex fluorescence fuel liquid/vapor visualization. In the diagram, *M* represents the selected additive and *G* the quencher, which together form the exciplex.



Liquid and vapor



Liquid only



Vapor only

Fig. 10 Single-pulse (10^{-8} s) photographs of an exciplex-doped, hollow-cone fuel spray. With the green filter, only the fuel liquid is observed; with the ultraviolet filter, the vapor distribution is visualized.

parent. The quencher, by forming the excited state complex with the additive, in essence quenches the additive's fluorescence by preventing its occurrence. Upon fluorescent emission, the additive-quencher complex dissociates in the ground electronic state. Formation of the exciplex is a reversible equilibrium process. However, at the densities prevailing in the liquid phase, the equilibrium is shifted so that exciplex formation is favored; in the gas phase, the equilibrium shifts in the other direction so that little exciplex formation occurs. In reality, there is generally some spectral overlap, but, with proper filtering, these can be avoided and the fuel liquid and vapor can be separately visualized.

The technique has been qualitatively demonstrated in simple hollow cone sprays as seen in Fig. 10. A thin sheet of ultraviolet laser light at 266 nm (the fourth harmonic of a neodymium: YAG laser) cut through the spray in a plane intersecting the central axis of the spray. Cetane was used as the fuel, TMPD (tetramethyl-p-phenylene diamine) as the additive, and naphthalene as the quencher. Black-and-white film was used to record the fluorescence from a single 10^{-8}-s pulse. The spray was photographed directly, then through a green filter where fuel in the liquid phase is visualized, and finally through an ultraviolet filter to visualize the vapor-phase fuel. In the liquid-phase photograph, one can see the liquid sheet formed by the nozzle, sheet breakup, and droplet formation. Investigations in progress are directed toward ascertaining the quantitative accuracy of the technique and formulating new additives suitable for fuels with different boiling points. When integrated with rapid, two-dimensional intensified array detectors, real-time studies of evaporating fuel sprays may become possible. Furthermore, by altering the molecular architecture of the additive, the exciplex spectrum can be made highly temperature sensitive permitting fuel droplet thermometry from spectral signature determinations.[26]

An exciting development of the last few years has been the use of multiphoton absorption techniques to permit the fluorescence detection of atomic radicals such as O, H, and N atoms.[27-29] Single-photon absorption excitation of these species is not possible, since their first electronic resonances reside in the deep vacuum-ultraviolet and are not transmitted by the combustion gases. With multiphoton absorption of wavelengths above 200 nm, these constituents can be spectrally accessed. Combined with OH LIFS measurements, O and H atom measurements should prove quite valuable to the kineticist attempting to unravel fundamental reaction mechanisms.

Conclusion

In an earlier review,[4,5] we concentrated on the diagnostic developments of the 1970s and forecasted that "In the next decade, combustion research should benefit greatly from the past decade of diagnostic development." It was the goal of this paper to illustrate some of the recent contributions laser diagnostic techniques have made to fundamental combustion science. Aside from the contributions to chemcial kinetics, which we did not cover, laser techniques have uncovered or confirmed theoretical predictions of countergradient diffusion, the effects of differential species diffusion, and super-equilibrium radical concentration levels, to name a few of the noteworthy findings. In addition, new and exciting applications are emerging that will hopefully affect combustion technology in a significant fashion. Furthermore, the laser diagnostics field is quite dynamic, with new refinements and developments occurring steadily, enhancing the measurement capabilities of these already powerful approaches.

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