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Nonlinear Optical Diagnostics of Diesel Spray

Final Report

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INTRODUCTION

The mechanisms of fuel spray development within engines, particularly processes including atomization, vaporization, and mixing of the fuel and air, are critical in the design and optimization of diesel engines. Whereas laser-based in-situ diagnostics have been developed and applied to spark ignition engines and flames, analogous advanced diagnostics on fuel droplets and sprays in diesel engines have not been developed. In order to optimize the diesel engine in terms of performance, fuel economy, and particulate (soot) and gaseous (NO_x) emissions, it is desirable to develop an advanced optical diagnostic technique specifically directed at diesel droplets which are not yet at their critical temperature and pressure, where the liquid-gas interface no longer exists.

This proposal involves the development of laser-based, in-situ, and nearly real-time diagnostic techniques which specifically provide information on the droplets which are NOT at their critical temperature and pressure. The proposed optical diagnostic approach has the potential of providing information on the droplet chemical composition, size, shape, surface tension, bulk viscosity, and evaporation rate when there is droplet-droplet collective interaction.

During the four years of DOE support, significant progress has been made toward furthering the understanding of nonlinear optical effects in fuel sprays and single liquid droplets with radius (a) much larger than the input laser wavelength (λ_{input}), i.e., droplets with large size parameters $x = 2\pi a/\lambda_{\text{input}}$. We have attempted to apply nonlinear optical spectroscopy to determine the chemical composition of the droplet, the droplet morphology (size, shape, and index of refraction), and the physical properties of the droplet (surface tension and bulk viscosity). Our research efforts can be divided into two parts: (1) understanding of nonlinear optical effects; and (2) application of nonlinear optical spectroscopy and imaging to fuel droplets and sprays.

A transparent droplet with a circumference larger than the wavelength acts as a thick lens to focus the input radiation just outside the droplet shadow face and to concentrate the input radiation mainly in a region just inside the droplet shadow face. Although the external intensity maximum is an order of magnitude larger than the internal intensity maximum, laser-induced breakdown (LIB) can be initiated within the shadow face of fuel droplets. LIB sets an upper limit on the input-laser intensity that can be used in any nonlinear optical spectroscopic diagnostics.

A micrometer-size transparent droplet also acts as an optical cavity to provide feedback (with high Q factor) for the internally generated nonlinear radiation. In addition, a droplet with a large size parameter gives rise to a quantum electrodynamic (QED) effect that causes the spontaneous emission coefficient (e.g., for the fluorescence and spontaneous Raman processes) to be enhanced. Consequently, at input laser intensities below the LIB threshold, several nonlinear optical processes can occur within the droplets. In particular, lasing, stimulated Raman scattering (SRS), and third-order sum frequency generation (TSFG) can be produced in sprays and single droplets.

The three unique properties of the droplets (acting as a lens and optical cavity as well as enhancing the spontaneous emission coefficient) are applied to provide chemical, morphological, and physical properties of the sprays and droplets. The lasing properties of dye-doped fuel droplets are used to distinguish large droplets from smaller droplets and liquid ligaments in a spray. The SRS spectra from pure fuel droplets are used to identify the chemical composition, size, and the relative evaporation rates. The laser-induced electrostrictive distortion of the droplet shape is used to determine the droplet surface tension and bulk viscosity. The hyper-Raman scattering from an optical cell and the TSFG from droplets are investigated in order to further our understanding of additional and competing nonlinear optical processes. Characterization of low-light-level two-dimensional

detectors (CCD and Mepsicron) are made because these two newly available detectors enable us to increase the detection sensitivity of the nonlinear optical signals from sprays and individual fuel droplets.

RESEARCH ACCOMPLISHMENTS

A brief summary is presented of our main findings related to the fundamentals of nonlinear optical effects in single droplets and to the application of nonlinear spectroscopy to chemical composition, droplet morphology, and physical properties of fuel sprays and droplets. Details of our accomplishments can be found in the publication resulting from the research (see page 23).

I. CHARACTERIZATION OF TWO NEW DETECTORS

In the past decade, advances in detectors capable of providing multiwavelength analysis have significantly lowered the detection limit in optical spectroscopy. The advantages of an optical multichannel analyzer (OMA) with one-dimensional multielement detectors to simultaneously monitor a range of wavelengths have been reported by us.¹ OMA's with two-dimensional detectors provide the extra advantage of spatial or temporal information along with spectral information. Two state-of-the art two-dimensional detectors, a high quantum efficiency charge-coupled device (CCD) and a position sensitive resistive anode detector (Mepsicron), have been recently introduced. We compared the CCD and Mepsicron with the conventional one-dimensional intensified linear photodiode array. Multiorder spontaneous Raman scattering from a silicon crystal is used as the "standard" weak source. The use of these three detectors by one group on the same Si

1. R.K. Chang and M.B. Long, "Optical Multichannel Detection," in *Light Scattering in Solids II, Topics in Applied Physics*, Vol. 50, M Cardona and Güntherodt, eds. (Springer-Verlag, Heidelberg, 1982), p. 179

sample provides a comparison of the operational details, the data correction techniques, and the relative sensitivity of each of the three detectors.

In order to introduce the CCD and Mepsicon to other spectroscopists, we briefly reviewed the construction and operation of the three detectors in our new publication (see DOE sponsored publication #1 on page 23). The various noise sources pertinent to each detector are enumerated in some detail as an understanding of the specific noise generation processes is essential to achieve the optimum signal-to-noise ratio attainable in each detector. Various data correction procedures applied to the raw input data have been presented, as well as the results of each correction procedure on the weak multiorder Raman spectrum from Si.

The CCD and Mepsicon detectors offer a substantial improvement in low-light-level sensitivity over the decade-old detectors, such as the intensified photodiode array, silicon intensified target (SIT) vidicon, and the intensified SIT (I-SIT) vidicon. Therefore, throughout this research on nonlinear optical diagnostics of fuel sprays and droplets, we made use of the increased sensitivity of the CCD and Mepsicon.

II. FUNDAMENTALS OF NONLINEAR OPTICAL EFFECTS

(a) Hyper-Raman Scattering of Organic Liquids

Hyper-Raman spectroscopy, first predicted in 1959 and observed in 1965, can provide molecular vibrational mode information complementary to the information obtained from Raman and IR spectroscopy of molecules with inversion symmetry (e.g., benzene or pentane). Because the hyper-Raman signal is frequency shifted from the second harmonic of the incident-laser radiation, hyper-Raman spectroscopy is potentially helpful in studying low-frequency rotational and vibrational modes which are difficult to measure in the IR and

are overwhelmed by the strong elastic scattering from the interior of the diesel engines. The hyper-Raman signal intensity increases as the square of the incident-laser intensity. However, the input intensity is constrained by the LIB threshold of the sample. Even near the LIB threshold, the hyper-Raman signal is typically five to seven orders of magnitude weaker than the spontaneous Raman scattering signal.

We initially thought that hyper-Raman scattering should be observable from benzene and pentane droplets for the following reasons: (1) the droplet morphology increases the input-laser intensity inside the droplet; (2) the QED effect enhances the hyper-Raman scattering coefficient; (3) the cw pumped acousto-optically Q-switched Nd:YAG laser (with 260 nsec duration and 5 kHz repetition rate) provides a train of high-intensity mode-locked laser pulses (with 100 psec duration and has one pulse every 12.5 nsec); and (4) the high sensitivity Mepsicron detector which can be synchronously gated with the mode-locked pulse train. After many attempts, we failed to detect hyper-Raman signals from benzene droplets and were forced to investigate the hyper-Raman scattering from liquids in an optical cell.

The hyper-Raman spectra of benzene (C_6H_6) and deuterated benzene (C_6D_6), which are centrosymmetric molecules, were observed from an optical cell. The purely hyper-Raman active vibrational modes (ν_{20} , ν_{10} , and ν_6) have been observed and identified for the first time. The hyper-Raman active and IR-active modes (ν_4 , ν_{14} , and ν_{13}) were also detected and identified. For non-centrosymmetric molecules, such as CCl_4 , the hyper-Raman and Raman-active modes were also detected. However, for such liquids, the effect of SRS in populating the vibrational levels and modifying the hyper-Raman Stokes and anti-Stokes spectra was observed. Further details of hyper-Raman scattering investigation of centrosymmetric and non-centrosymmetric molecules of organic liquids can be found in the DOE sponsored publication #2 on page 23.

(b) Third-Order Optical Sum Frequency Generation

Because the SRS intensity from droplets is used to determine the concentration of various species within the droplet, it is important to understand all nonlinear optical processes that can deplete the SRS intensity. We reported the first observation of optical third-harmonic generation (THG) and, more generally, third-order sum-frequency generation (TSFG) by the internal fields which can be of the input-laser frequency ω_{input} and of the various higher-order Stokes SRS frequencies $\omega_{\text{js}} = \omega_{\text{input}} - j\omega_{\text{vib}}$, where j denote the j th-order Stokes SRS. The conversion of the Raman radiation in the red to third-order sum frequency radiation in the blue and throughout the visible range depletes some of the SRS intensity.

A series of discrete emission peaks is detected from single micrometer-sized carbon tetrachloride, benzene, cyclohexane, and dodecane droplets. If monochromatic near-IR input-laser radiation is used, the detected spectrum throughout the visible range consists of a series of discrete peaks (see Fig. 1). The series starts at the blue third harmonic ($3\omega_{\text{input}}$) of the input laser and extends to the red ($\omega_{\text{TSFG}} = 3\omega_{\text{input}} - p\omega_{\text{vib}}$) as a result of four-wave mixing of the input radiation and the multiorder Stokes SRS. The integer p extends from $p = 0$ to $p = 3j_{\text{max}}$, where j_{max} is the highest order of the Stokes SRS, which for carbon tetrachloride $j_{\text{max}} = 9$, benzene $j_{\text{max}} = 3$, cyclohexane $j_{\text{max}} = 1$, and dodecane $j_{\text{max}} = 1$.

The THG at $3\omega_{\text{input}}$ from the droplets is at least two-orders-of-magnitude larger than that from an optical cell (4-cm long) containing the same liquid. However, several factors need to be considered before quantitative explanation can be given for the large increase in the THG intensity from CCl_4 droplets (collected at 90°) compared with that from CCl_4 in a 4-cm cell (collected collinearly). First, it is necessary to calculate the internal intensity enhancement for a droplet, which can be readily performed for the

incident-laser radiation but is difficult to estimate for the SRS radiation. Second, it is necessary to estimate the fraction of THG and/or TSFG that emerge from the droplet at 90° . Third, the phase-matching condition for the input-laser and SRS radiation confined in the droplet must be better understood and estimated. Fourth, the spatial overlap of the various internal waves (laser and various order Stokes SRS) must be calculated. Lastly, the frequency overlap of the THG or TSFG radiation with the morphology-dependent resonances (MDR's) must be calculated. Although it is not possible yet to quantify the newly observed THG and TSFG data, the observation of discrete peaks throughout the visible spectrum indicates the importance of four-wave mixing processes in single droplets. Besides THG and TSFG, other four-wave mixing processes that can occur within a droplet are coherent anti-Stokes Raman scattering (CARS) and degenerate four-wave mixing (DFWM) which can lead to optical phase conjugation (OPC).

Figure 1.

Detected third-order sum frequency signal from benzene, cyclohexane, and dodecane droplets. The horizontal axis is scaled in the wavelength (top axis) and in the shift from the third-harmonic generation peaks of the near-IR input laser (bottom axis). The satellite peaks of cyclohexane droplets with a δ shift from the m peaks are indicated.

(c) Heuristic Model for Nonlinear Processes in Droplets

The observation THG and TSFG spectra indicate the importance of four-wave mixing processes of the intense radiation (at ω_{input} and ω_{S}) confined in the droplet. In addition, the temporal characteristics of the SRS from droplets indicate that the growth and decay of the various order Stokes SRS (at frequencies $\omega_{\text{S}} = \omega_{\text{input}} - j\omega_{\text{vib}}$) are also governed by four-wave mixing processes.² With a multimode input laser, there is a delay time between the various order Stokes SRS and the input-laser pulses. Moreover, there is a correlated growth and decay of the j th- and the $(j+1)$ th-order Stokes SRS waves.² With a single-mode input laser, the SRS intensity has much less fluctuation (see DOE sponsored publication #5 on page 23) and, thereby, provides more accurate concentration information. However, with single-mode laser pumping, the SRS wave is not directly pumped by the input-laser radiation but is pumped by the stimulated Brillouin waves that are directly pumped by the input-laser radiation. Recent experiments have shown that there is a time delay between the stimulated Brillouin pulse and the input-laser pulse, as well as a correlated growth and decay of the Brillouin signal and the SRS.³

To our knowledge, there does not exist a set of nonlinear-wave equations that can describe the experimental observations of the delay times and correlated growths and decays among the Brillouin and the various-order Stokes SRS waves in single droplets. A heuristic model for the growth and coupling of nonlinear processes in droplets has recently been developed (see DOE sponsored publication #8 on page 23). The standard one-dimensional nonlinear-wave equations are modified. The propagation direction of the

2. W.-F. Hsieh, J.-B. Zheng, and R.K. Chang, "Time Dependence of Multi-order Stimulated Raman Scattering from Single Droplets," *Opt. Lett.* **13**, 497 (1988).

3. J.-Z. Zhang, G. Chen, and R.K. Chang, "Pumping of Stimulated Raman Scattering by Stimulated Brillouin Scattering within a Single Droplet: Input Laser Linewidth Effects," *J. Opt. Soc. Am. B* **7**, 108 (1990).

nonlinear waves along the length of an optical cell is changed to be along the droplet circumference. In the computer simulation, the spatial distribution of the internal input-laser intensity is calculated from the well known Lorenz-Mie theory and the time profile of the measured input-laser pulse is used. The model includes radiation losses because of non-zero absorption, leakage from the droplet rim, and depletion in generating other nonlinear waves via the FWM processes. For multimode input-laser radiation, the growth and decay of the 1st- through 4th-order Stokes SRS are calculated as a function of the Raman gain coefficient and phase matching of the FWM process. In the model with single-mode input-laser radiation, the generation of stimulated Brillouin scattering (SBS) is included. Because the SBS has a 3X lower threshold than the SRS, the SBS grows before the SRS and serves as a pump for the SRS.

Although the model is heuristic, good agreement between the calculated and the experimentally observed delay times as well as the correlated growth and decay of nonlinear pulses is found. The two adjustable parameters in the model are the gain coefficients for the SRS and SBS and the wave-vector mismatch among the four waves within the droplet. We believe that this heuristic model is useful to the main objective of this project which is to apply the SRS as a means to determine the chemical composition and concentration of species in the fuel droplet as well as to provide information on the droplet size, shape, surface tension, bulk viscosity, and evaporation rate.

III. APPLICATION OF NONLINEAR SPECTROSCOPY

(a) Laser-Induced Shape Distortions of Droplets

One of the objectives is in-situ determination of the surface tension and bulk viscosity of the fuel droplets. Previously we observed oscillation of the droplet-laser emission peaks as the droplet shape is slightly deformed because of the nonuniform heating

within the droplet by a second laser beam.⁴ The oscillation frequency about the laser emission wavelength is proportional to the square root of the surface tension and the decay of the oscillation amplitude is inversely proportional to the bulk viscosity. There are two main disadvantages to this diagnostic technique. First, a laser dye must be added to the fuel droplets and the intensity of the first-input laser must exceed the droplet lasing threshold. Second, there is a need for a second-input laser to create a nonuniform heating in the droplet.

A new technique of creating a shape distortion of fuel droplets does not require the addition of dyes in the fuel and a second laser. Laser-induced droplet shape distortion is achieved through the electrostrictive force created by an high-energy input-laser pulse. We reported on the observation of large amplitude bulging from the shadow face of a single droplet soon after the high-energy laser pulse is shut off (see Fig. 2a). At higher input-laser energies, the bulging from the droplet shadow face is in the form of a narrow liquid cylinder that is capable of expelling smaller droplets from one end (see Fig. 2b). After tens of microseconds, the droplet exhibits damped oscillations in its quadrupole mode (prolate spheroid to sphere to oblate spheroid to a sphere and back to a prolate spheroid). The oscillation period is again related to the square root of the surface tension and the damping rate is inversely related to the bulk viscosity. Although the initial experiments were performed on water droplets, we have observed similar laser-induced shape distortions in dodecane and pentane droplets. For more details see DOE sponsored publication #4 on page 23.

4. H.-M. Tzeng, M.B. Long, R.K. Chang, and P.W. Barber, "Laser-Induced Shape Distortions of Flowing Droplets Deduced from Morphology-Dependent Resonances in Fluorescence Spectra," *Opt. Lett.* **10**, 209 (1985).

Figure 2a.

Framing camera photographs of laser-irradiated water droplets ($a \approx 50 \mu\text{m}$) recorded at various time delays Δt after the dye-laser pulse (100 mJ, 400 nsec duration). The top photograph in the left-hand column is for $\Delta t = 0$, and the bottom photograph in the right-hand column is for $\Delta t = 22 \mu\text{sec}$. Successive photographs correspond to every $2 \mu\text{sec}$. The laser direction is from left to right.

Figure 2b.

Same as in Fig. 2a, except that the dye-laser pulse energy is increased to 200 mJ. The top photograph in the left-hand column is for $\Delta t = 1 \mu\text{sec}$, and the bottom photograph in the right-hand column is for $\Delta t = 15 \mu\text{sec}$.

The electrostriction force density is $f = \nabla[(n^2 - 1)I/2c]$, where ∇ is the spatial gradient, n is the index of refraction of the liquid, and c is the speed of light in air. We were only able to make a crude estimate of the bulge amplitude based on a pseudomomentum model of the input-laser radiation at the internal focal spot which is located along the principal diameter and just within the droplet shadow face. Since our publication appeared in print, the group in the Chinese University of Hong Kong has made a detailed calculation of the droplet bulge amplitude as a function of time by using the Navier-Stokes equation for the fluid and the Lorenz-Mie theory for the internal intensity distribution of the input-laser radiation.⁵ The temporal behavior of the experimentally observed bulge and that of the calculated (with the full hydrodynamic and electrodynamic model) were in excellent agreement. With this model, more accurate values of the surface tension and bulk viscosity can be extracted from the temporal behavior of the bulge than from the droplet shape undergoing quadrupole oscillations.

(b) SRS from Fuel Droplets

Based on our knowledge of nonlinear optical interactions in liquids and droplets, considerable amount of research effort was directed toward SRS of fuel droplets. Throughout our investigation, we were aware of the research and development underway at the Shell Research at Thornton, England. SRS has been used to study diesel related hydrocarbons such as pentane, hexane, and toluene in droplet form.⁶ The Shell work indicated that a major limitation of the SRS technique is the opacity of the fuel, such as

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5. H.M. Lai, P.T. Leung, K.L. Poon, and K. Young, "Electrostrictive Distortion of a Micrometer-Sized Droplet by a Laser Pulse," *J. Opt. Soc. Am. B* **6**, 2430 (1989).
 6. M. Golombok and D.B. Pye, "Multimode Stimulated Raman Scattering in Fuel Droplets", *Chem. Phys. Lett.* **151**, 161 (1988); "Stimulated Raman Scattering in Diesel Injected Fuel Sprays," *J. Phys. D: Appl. Phys.* **22**, 851 (1989).

standard D-2 diesel fuel, which exhibits significant absorption for the wavelengths less than 560 nm. In our laboratory, SRS spectra were readily observed when we used a dye laser (with 565 nm output) to minimize absorption of Mobil D-2 diesel fuel droplets (see DOE sponsored publication #5 on page 23).

To demonstrate that SRS can be achieved in a polydispersed spray of organic liquid, we used a standard oil burner nozzle. An ethanol spray emerging from the vertically directed nozzle was photographed through a green filter to transmit the elastic scattering (see Fig. 3a) and through a red filter to transmit the wavelength-shifted SRS radiation (see Fig. 3b). The elastic scattering (both primary and secondary) is caused by fuel vapor, droplets of all sizes, and liquid ligaments, whereas the SRS radiation is emitted by only the few larger size droplets. The preferential selection of larger droplets by the SRS process is substantiated by using the Lorenz-Mie formalism to calculate as a function of fuel droplet radius, the Q-factor, and the number density of modes.

Figures 3a and 3b.

Photographs of an ethanol spray emerging from a vertically directed nozzle and illuminated by a horizontal laser beam. (a) Shows the elastic scattering image taken through a green filter. (b) Shows the SRS image taken through a red filter.

Figure 4a shows the complete SRS spectra from single monodispersed droplets (produced with the Berglund-Liu vibrating orifice generator) of toluene, pentane, Exxon Aromatic-150, and Mobil D-2 diesel fuel. For aromatic fuel droplets, the SRS exhibits a strong carbon-ring breathing mode ν_2 near 1000 cm^{-1} Raman shift. The SRS peaks labeled $2\nu_2$ is the 2nd-order Stokes SRS which is prevalent at high input-laser intensity or when the concentration of the aromatic component is large in a fuel mixture. In fact, through the cascade first-order SRS processes, SRS peaks associated with the 3rd-order and 4th-order Stokes SRS have been detected. For the alkane fuel droplets (such as pentane and dodecane), the SRS exhibits a strong C-H stretching mode in the 2900 cm^{-1} range. The Exxon Aromatic 150 consists of 98% aromatics, which exhibit SRS peaks at 1420 cm^{-1} for the carbon-ring breathing mode and at 2970 cm^{-1} for the C-H stretching mode. The Mobile D-2 droplets had one weak SRS peak in the 1140 cm^{-1} range for the carbon-ring breathing mode and two strong peaks at 2900 cm^{-1} and 2950 cm^{-1} for the C-H stretching modes.

Figures 4a and 4b.

(a) Multishot averaged SRS spectra (low spectral resolution) from droplets of toluene, pentane, Exxon Aromatic-150, and Mobil D-2 diesel fuel. The ordinate is I_{SRS} in arbitrary units, and the abscissa is the Raman shift from the incident laser frequency.

(b) Single laser shot SRS spectra (high spectral resolution) spanning the C-H stretching region of Exxon Aromatic-150 and Mobil D-2 diesel fuel droplets.

Figure 4b shows the expanded SRS spectra from Exxon Aromatic-150 and Mobil D-2 in the C-H stretching range. The series of SRS peaks is associated with MDR's which are within the broad spontaneous Raman profile of the C-H stretching modes. The MDR's provide sufficient optical feedback for SRS even on the wings of the spontaneous Raman profile. The frequency or wavelength separation of the series of SRS peaks can provide a highly accurate value of the droplet radius.

Before we can extract relative species concentration information from the SRS intensity of a multicomponent fuel droplet, we had to investigate the fluctuations of the SRS signal. Both single-mode and multimode Q-switched Nd:YAG lasers were used. The fluctuations of the SRS intensity in the single-mode case are much smaller than the multimode case. In the multimode operation, the temporal profile of the incident laser pulse exhibits numerous high intensity spikes of picosecond duration. Thus, the stochastic nature of the multimode intensity profile is expected to lead to larger SRS intensity fluctuations, because the SRS intensity is exponentially dependent on the input-laser intensity. In all the data with fuel droplets, we used an injection-seeded single-mode laser.

In order to extract relative species concentration information from the SRS intensity I_{SRS} of a multicomponent liquid droplet, the input-laser intensity I_{input} must be constrained so that the I_{SRS} is in the exponential growth region. Figure 5a shows that the I_{SRS} versus I_{input} is in the exponential region so long as I_{input} is kept below 0.2 GW/cm^2 for the carbon-ring mode of toluene and 0.45 GW/cm^2 for the C-H mode of pentane. So long as the I_{SRS} of all the species are kept in the exponential region, the natural logarithms of I_{SRS} of each species is proportional to the concentration of each species. With $I_{\text{input}} = 0.1 \text{ GW/cm}^2$, Fig. 5b shows that the ratio of the natural logarithms of the I_{SRS} from toluene and pentane droplets (with radius $\approx 45 \text{ }\mu\text{m}$) is a linear function of the ratio of their

concentration. When the aromatic and alkane concentration ratio exceeds 0.3, it is not clear why there is a deviation from linearity.

Figures 5a and 5b.

(a) ISRS from single monodispersed toluene and pentane droplets ($a \approx 45 \mu\text{m}$) as a function of I_{input} . Each data point represents the average of 72 laser shots. The error bars are the standard deviation of the ISRS.

(b) The ratio of the natural logarithms of ISRS from the toluene v_2 mode and the pentane C-H stretching region as a function of their concentration ratio at $I_{\text{input}} \approx 0.1 \text{ GW/cm}^2$.

(c) SRS from Water Droplets Containing Ions

The topic of extracting concentration ratios of species from the natural logarithm ratios of ISRS was investigated further with water droplets containing nitrate and sulfate ions (see DOE sponsored publications #6 on page 23). Although our experimental study is confined mainly to nitrate salt, our conclusions are applicable to other salts such as sulfates and multicomponent fuel such as D-2 diesel.

As I_{input} is increased, the observed I_{SRS} can be separated into four distinct regions shown in Fig. 6. Spontaneous Raman scattering is expected to occur in Region I when I_{input} is below the threshold necessary for SRS. SRS is expected to increase exponentially in Region II when I_{input} exceeds the threshold necessary for SRS. Saturation in the SRS is expected to occur in Region III when the 1st-order Stokes SRS is depleted partially because of generation of 2nd-order Stokes SRS, which in turn is depleted partially in generating 3rd-order Stokes SRS. Once the laser-induced breakdown threshold (LIB) occurs in Region IV, the SRS is expected to fluctuate because the internally produced plasma absorbs and scatters the SRS radiation and quenches the SRS.

Figure 6.

The output Raman intensity as a function of I_{input} can be separated into the following four regions: (I) the spontaneous Raman scattering output is linearly dependent on I_{input} ; (II) the SRS output is exponentially dependent on I_{input} ; (III) saturated SRS results from competing nonlinear optical processes and the SRS output is dependent on I_{input} ; and (IV) Laser-induced breakdown results in large fluctuations in I_{SRS} and quenching of the SRS.

An exponential dependence of I_{SRS} as a function of increasing I_{input} was indeed observed for nitrate and sulfate ions in water droplets (with radii $\approx 45 \mu\text{m}$). Beyond the exponential region, the saturation region was also verified experimentally. In the saturation region, I_{SRS} had a sublinear dependence on I_{input} . Beyond the saturation region, LIB did

cause the SRS to be quenched.^{7,8} Consequently, in order to extract species concentration information from I_{SRS} , the laser intensity must be kept below the LIB region and preferably below the saturation region.

The I_{SRS} dependence on the nitrate concentration was investigated while keeping I_{input} fixed at 0.15 GW/cm^2 , which is well within the exponential growth region. Figure 7 shows that the ratio of the natural logarithms of I_{SRS} from nitrate and water is plotted as a function of the concentration ratio of the nitrate and water. The measurement was not extended beyond 4 molar NH_4NO_3 at $I_{\text{input}} = 0.15 \text{ GW/cm}^2$, because the strong SRS signal of the nitrate depleted the input intensity and the SRS threshold of H_2O became unreachable. The linear dependence of the ratio of the natural logarithms of I_{SRS} as the nitrate and water concentration ratio is increased reconfirms the similar data shown in Fig. 5b for toluene and pentane.

Figure 7.

The ratio of $\log_e(I_{\text{SRS}})_{\text{nitrate}}$ and $\log_e(I_{\text{SRS}})_{\text{water}}$ is noted to be linearly dependent on the ratio of the nitrate concentration and the water concentration. The aqueous droplets ($a \approx 45 \mu\text{m}$) contain different NH_4NO_3 concentrations, and the single-mode I_{input} is fixed at 0.15 GW/cm^2 .

7. R.K. Chang, J.H. Eickmans, W.-F. Hsieh, C.F. Wood, J.-Z. Zhang, and J.-B. Zheng, "Laser-Induced Breakdown in Large Transparent Water Droplets," *Appl. Opt.* **27**, 2377 (1988).
8. W.-F. Hsieh, J.-B. Zheng, and R.K. Chang, "Transmission through Plasma Created by Laser-Induced Breakdown of Water Droplets," *Opt. Lett.* **14**, 1014 (1989).

(d) Two-Dimensional Imaging of Fuel Sprays

Sprays are essential in the operation of diesel engines. The spray diverges as it leaves the nozzle and forms liquid ligaments. These ligaments subsequently break-up into droplets which evaporate as the air entrainment into the diverging spray increases. The constituents of a spray emerging from a hollow-cone nozzle are either in the vapor or liquid phase. The liquid phase consists of three components: ligaments, small droplets and large droplets.

In the elastic scattering images of the spray, which is green when the second harmonic of a Nd:YAG laser is used, it is not possible to distinguish the vapor and liquid phases or the three components of the liquid phase (see Fig. 3a). The elastic scattering from the vapor is much weaker than that from the liquid phase. However, it is possible to use inelastic light scattering techniques such as SRS to distinguish the large droplets because these droplets preferentially provide large optical feedback for the internally generated SRS (see Fig. 3b).

Another inelastic light scattering technique to distinguish the different constituents of the spray in the two-dimensional images is based on the fluorescence and laser emission of the liquid phase of the spray. Fluorescence images from the vapor can be eliminated by selecting a dye which has a low concentration and poor quantum efficiency in the vapor phase. Rhodamine 6G, being an ionic dye molecule, has a low vapor pressure and poor quantum efficiency in air. Consequently, when Rhodamine 6G is added to the liquid emerging from the nozzle, the orange fluorescence image is mainly from the liquid ligaments and droplets of all sizes in the spray. Only the larger droplets achieve the lasing threshold, analogous to the SRS process which require large amounts of optical feedback (i.e., with high Q factor) preferentially provided by larger droplets. The lasing emission from larger droplets is red shifted relative to the fluorescence emission peak, because the

lasing threshold is lowered by avoiding the dye absorption that increases toward the blue side of the fluorescence peak.

Figure 8 shows the orange-fluorescence and red-lasing images of the nozzle spray. The incident green pump beam is propagating from right to left. The orange-fluorescence emission is from the smaller droplets and liquid ligaments. The red-lasing image from a few large droplets can be distinguished from the orange-fluorescence image of the liquid ligaments and numerous small droplets. With this technique, it is possible to determine within a spray the existence of large droplets, which are more effective in penetrating the combustion chamber.

The droplet radius can be determined for the few larger droplets that have exceeded the lasing threshold. Only a portion of the red lasing radiation from droplets needs to enter the entrance slit of a spectrograph equipped with a two-dimensional CCD detector at its exit plane. The entire red-lasing spectra from several individual large droplets (located at different heights along the spectrograph entrance slit) can be spectrally analyzed for each laser shot. The wavelength spacings of the lasing peaks can be matched to those of the droplet MDR's and, thus, the droplet size can be accurately determined. A size histogram of larger droplets can then be constructed after numerous laser shots. For more details of the fluorescence, lasing, and SRS imaging results, see DOE sponsored publication #7 on page 23.

SUMMARY

Progress has been made toward furthering the understanding of nonlinear optical effects in fuel sprays and single liquid droplets with radius greater than 10 μm . We have applied the nonlinear optical spectroscopic techniques to determine the following properties of droplets and sprays: (1) the relative concentration of aromatic and alkane components in simulated diesel fuel droplets from the ratio of the SRS intensity at the two frequencies

unique to the aromatic and alkane molecules; (2) the droplet radius from the series of SRS peaks which are related to the MDR's of the droplet acting as an optical cavity; (3) the droplet surface tension from the oscillation frequency of the droplet shape, which was distorted by the laser-induced electrostrictive forces; (4) the droplet bulk viscosity from the damping rate of the shape distortion amplitude, after droplet shape was distorted by the laser-induced electrostrictive forces; and (5) in a hollow-cone nozzle, distinguished the larger droplets (with radius above 10-20 μm) from the smaller droplets and liquid ligaments by noting the red-color shift of the large droplets that have achieved either the lasing threshold or the SRS threshold. We believe some of the diagnostic techniques developed during this DOE grant interval can be applied to investigations underway in other laboratories on optical access diesel engines.

Figure 8.

Wavelength shifted fluorescence and lasing image of a hollow-cone burner nozzle spray. An ionic fluorescent dye is added to the fuel. Fluorescence from the vapor is undetectable because of the low vapor pressure of the dye and the poor quantum efficiency. The yellow-fluorescence image is from the liquid ligament and small droplets. The red-lasing image is from the larger droplets that preferentially have higher optical feedback provided by the MDR's.

PUBLICATIONS RESULTING FROM THE RESEARCH

1. W.P. Acker, B. Yip, D.H. Leach, and R.K. Chang, "The Use of a Charge-Coupled Device and Position Sensitive Resistive Anode Detector for Multiorder Spontaneous Raman Spectroscopy from Silicon," *J. Appl. Phys.* 64, 2263 (1988).
2. W.P. Acker, D.H. Leach, and R.K. Chang, "Stokes and Anti-Stokes Hyper-Raman Scattering from Benzene, Deuterated Benzene, and Carbon Tetrachloride," *Chem. Phys. Lett.* 155, 491 (1989).
3. W.P. Acker, D.H. Leach, and R.K. Chang, "Third-Order Optical Sum Frequency Generation in Micrometer-Size Liquid Droplets," *Opt. Lett.* 14, 402 (1989).
4. J.-Z. Zhang and R.K. Chang, "Shape Distortion of a Single Water Droplet by Laser-Induced Electrostriction," *Opt. Lett.* 13, 916 (1988).
5. W.P. Acker, A. Serpengüzel, R.K. Chang, and S.C. Hill, "Stimulated Raman Scattering of Fuel Droplets: Chemical Concentration and Size Determination," *Appl. Phys. B* 51, 9 (1990).
6. A. Serpengüzel, G. Chen, and R.K. Chang, "Stimulated Raman Scattering of Aqueous Droplets Containing Ions: Concentration and Size Determination," *Particulate Science and Technology* (in press).
7. A. Serpengüzel, J.C. Swindal, R.K. Chang, and W.P. Acker, "Two-Dimensional Imaging of Sprays with Fluorescence, Lasing, and Stimulated Raman Scattering," submitted to *Appl. Opt.*.
8. A. Serpengüzel, G. Chen, R.K. Chang, and W.-F. Hsieh, "Heuristic Model for the Growth and Coupling of Nonlinear Processes in Droplets," submitted to *JOSA B*.

SCIENTIFIC COLLABORATORS

In addition to the principal investigator, the following people have participated in the project:

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October 4, 1991

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RE: DOE Final Report, Contract No: DE-AS04-87AL42879

Dear Mr. Sowa:

Enclosed please find a copy of the Final Report for the DOE grant. Again, please accept my apologies for being late in submitting the final report.

Sincerely yours,

Richard K. Chang

Richard K. Chang
Professor of Applied Physics,
Electrical Engineering, and Physics

RKC: ksa

Enc: final report

DATE

FILMED

8/4/94

END