Femtosecond Coherent Anti-Stokes Raman Scattering: Recent Applications and the Surprisingly Beneficial Effects of Moderate Pump and Stokes Chirp

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18 Jan 2018
Acknowledgments

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- Funding for this research was provided by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Geoscience and Biosciences, Gas Phase Chemical Physics Program, Grant No. DE-FG02-03ER15391, and by the King Abdullah University of Science and Technology in Thuwal, Saudi Arabia under the Center Competitive Funding Program, Subaward No. ORS 1975-01.
Outline of the Presentation

• Introduction and Motivation

• Raman Scattering and Coherent Anti-Stokes Raman Scattering (CARS) Spectroscopy

• Chirped-Probe-Pulse (CPP) Fs CARS
  Measurements of Temperature in Flames: Frequency Spread Dephasing

• CPP FS CARS Measurements in Spray and Sooting Flames

• Effects of Moderate Pump/Stokes Chirp

• Conclusions and Future Work
Raman effect:

\[ \omega_{pr} \rightarrow \omega_{pr} \rightarrow \omega_{pr} \]

Chandrasekhara Venkata Raman (1888-1970)
1930 Nobel Prize in Physics

Leonid Isaakovich Mandelshtam (1879-1944)
He called it “combination light scattering”.

Stokes scattering  anti-Stokes scattering

Slides courtesy of Alexei Sokolov
Raman Scattering

Species-specific, spatially resolved, quantitative, weak signal, applicable only for clean flames
Fig. 2 Schematic of high-performance Raman scattering apparatus. There are four main components to the system: frequency-doubled Nd: YAG pulsed laser, pulse stretcher, high-speed electromechanical shutter, and spectrograph/backside-illuminated CCD camera. Legend—RC: rotary chopper motor/blade combination; LS: leaf shutter; PC: personal computer.
Fig. 3 Typical single-shot Raman spectra (532 nm excitation) measured in the turbulent methane–air flame. Eleven shots are shown out of a total 400 shots obtained by the measurement at \((r, x) = (10, 9)\).
Interesting facts:

- The CARS phenomenon was first reported in 1965 by P. D. Maker and R. W. Terhune, two researchers of the Scientific Laboratory at the Ford Motor Company.
- The name coherent anti-Stokes Raman spectroscopy was assigned almost ten years later, by Begley et al. at Stanford University in 1974.
Ns CARS for Gas-Phase Diagnostics

\[ \omega_{as} = \omega_{p2} - \omega_s + \omega_{p1} \]

\[ v = 1, J \]

\[ v = 0, J \]

\[ \omega_{p1}, \omega_s, \omega_{p2} \]

2330 cm\(^{-1}\)
Nonresonant Background for CARS

\[ \omega_{CARS} = \omega_3 = \omega_0 + \omega_1 - \omega_2 \]

Nonresonant Four-Wave Mixing

\[ \omega_{NR} = \omega_3 = \omega_{CARS} \]
Ns CARS for Gas-Phase Diagnostics

Broadband Dye Laser Spectrum

Frequency

Single-Shot Multiplex CARS Spectrum

\( v^x = 0, v^z = 1, v^y = 2 \)

Frequency

(CARS Intensity)\(^{1/2}\)

Temperature: T = 500 K

Temperature: T = 2000 K

Raman Shift (cm\(^{-1}\))
Ns CARS for Gas-Phase Diagnostics

• Nanosecond CARS using (typically) a Q-switched Nd:YAG laser and broadband dye laser is a well-established technique for combustion and plasma diagnostics

• Actively developed in 1980’s for combustion after Alan Eckbreth at UTRC tried to make Raman scattering measurements in combustor primary zone, discovered massive interference due to laser heating of soot particles to 10,000K – now called laser-induced incandescence
Ns CARS in Gas Turbine Combustor
Ns CARS for Gas-Phase Diagnostics

- Nonintrusive
- Coherent Laser-Like Signal
- Spatially and Temporally Resolved
- Excellent Gas-Temperature Measurement Technique
- Nonresonant Background
- Collisional/Linewidth Effects
- Data-Acquisition Rates: No Correlation Between Laser Shots at 10 Hz
- Broadband Dye Laser Mode Noise

Good  Bad  Both
Fsec CARS for Gas-Phase Diagnostics

- Fs lasers have much higher repetition rates than ns Q-switched Nd:YAG lasers: > 1 kHz versus ~10 Hz, plus can eliminate many of the other drawbacks – no need to measure collisional linewidths.

- For application as a diagnostic probe for turbulent flames, signal levels must be high enough to extract data on a single laser shot from a probe volume with maximum dimension ~ 1mm.

- How effectively can Raman transitions with line width ~ 0.1 cm\(^{-1}\) line width be excited by the fs pump and Stokes beams (200 cm\(^{-1}\) bandwidth)? Answer: very effectively.

- How do we extract temperature and concentration from the measured single-shot fs CARS signals?
Optical System for Fs CARS with Mechanically Scanned Probe

Probe Beam - $\omega_3$
675 nm, 70 fsec

Stokes Beam - $\omega_2$
800 nm, 70 fsec

Pump Beam - $\omega_1$
675 nm, 70 fsec

CARS Signal $\omega_4$ at Probe Time Delay:

Translation Stage

Delay Line for Probe

Raman Coherence

Probe Time Delay $\tau$

Beam Dumps for Probe, Pump, Stokes
Calculated Time Dependence of CARS Intensity with Time-Delayed Probe Beam

At $t = 0$ psec, all Raman transitions oscillate in phase = giant coherence

At $t > 20$ psec, Raman transitions oscillate with essentially random phases
Calculated Time Dependence of CARS Intensity with Time-Delayed Probe Beam

(a) CARS Intensity (arb. units) vs. Time (psec)

(b) CARS Intensity (arb. units) vs. Raman Shift (cm\(^{-1}\))

Different curves represent different temperatures: 300 K, 500 K, 1000 K, and 2000 K.
Temperature can be determined from the decay of the initial Raman coherence due to frequency-spread dephasing – Raman transitions oscillate with different frequencies.
Raman Excitation for Fs Pump and Stokes Pulses

• There is a drastic difference in laser bandwidth (150-200 cm\(^{-1}\)) and Raman line width (0.05 cm\(^{-1}\)) for 100-fs pump and Stokes laser pulses.

• How effectively do the laser couple with the narrow Raman transitions?

• Can single-laser-shot fs CARS signals be obtained from flames? (The answer is yes)
Coupling of 70-Fs Pump and Stokes Pulses with the Raman Coherence

Pump Beam
675 nm, 200 cm$^{-1}$

Stokes Beam
800 nm, 200 cm$^{-1}$

Optical Frequency
Optical System for Single-Pulse fs CARS with Chirped Probe Pulse

Probe Beam - $\omega_3$
660 nm, 70 fsec

Stokes Beam - $\omega_2$
780 nm, 70 fsec

Pump Beam - $\omega_1$
660 nm, 70 fsec

CARS Signal Beam - $\omega_4$

Dispersive Rod
60 cm SF11

Chirped Probe Pulse
2-3 psec

Delay Line for Probe

Turbulent Flame or Gas Cell

Raman Coherence

To Spectrometer and EMCCD

20 Single-Shots with Chirped Probe Pulse

\[ t_{0,pr} = 1.0 \text{ ps} \]
\[ \Phi = 0.5 \]
Ultrafast CARS
- Independent from collisional effects
- Stable, high PRF
- Good mode quality

Single-Shot Temperature Measurements at 5 kHz: DLR Swirl-Stabilized Burner
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OPA: Optical Parametric Amplifier
BS: Beam Splitter
CR: Chirping Rod
WP: Zero Order Wave Plate
A: Aperture
TP: Thin Film Polarizer
L: Lens
LS: Linear Translation Stage
EMCCD: Electron Multiplying Charge-Coupled Device

PURDUE UNIVERSITY
Single-Shot Temperature Measurements at 5 kHz: DLR Swirl-Stabilized Burner
Frequency content of 5 kHz temperature measurements provides insight into the dynamics of large scale structures in the flow.
Frequency content of 5 kHz temperature measurements provides insight into the dynamics of large scale structures in the flow.
Spectral Fitting: Temperature Calibration

Single Shot # 6000, \( \phi = 0.7 \) (\( T_{ad} = 2012 K \))

Single-Laser-Shot Temperature Measurement
- **Floating:**
  - Temperature
  - Horizontal and vertical shift
  - Ratio of resonant to non-resonant response

\[ A(\omega') = |A(\omega')| \exp[jY(\omega' - \omega_0)] \]

<table>
<thead>
<tr>
<th>Laser Shot Number</th>
<th>Adiab.Temp.</th>
<th>SS.Temp.</th>
<th>Fit.Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>1989 K</td>
<td>1931 K</td>
<td>1.4E-3</td>
</tr>
<tr>
<td>1900</td>
<td>1989 K</td>
<td>2009 K</td>
<td>0.2E-3</td>
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<tr>
<td>2000</td>
<td>1989 K</td>
<td>2059 K</td>
<td>0.7E-3</td>
</tr>
<tr>
<td>2100</td>
<td>1989 K</td>
<td>1854 K</td>
<td>2.0E-3</td>
</tr>
</tbody>
</table>

\( T_{avg} = 1989 \, K; \)
Accuracy = 1.17%;
Precision = \( \pm 1.19\% \)
CPP fs-CARS LASER System – Overview

Probe Volume:
- Pump: 100 μJ, 60 fs, λ₀ 800
- Stokes: 50 μJ, 60 fs, λ₀ 982

- Probe: 200 μJ, 3.5 ps, λ₀ 800
- Spatial resolution ~ 60 μm x 800 μm
Univ. Sydney Needle Spray Burner (SYNSBURN™) for Premixed, Diffusion, and Spray Flames

In addition to liquid-fuel spray flames:

• Premixed flame of methane-air
• Diffusion flame of ethylene-nitrogen
SYNSBURN™ Offers Full Control Over Spray Flame Conditions

**Acetone Flames Measured**

- **Fuel and Air Loadings**

<table>
<thead>
<tr>
<th>Flame Case</th>
<th>nAF2</th>
<th>nAF6</th>
<th>nAF7</th>
<th>nAF8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Fuel Flow</td>
<td>75</td>
<td>45</td>
<td>75</td>
<td><strong>45</strong> (g/min)</td>
</tr>
<tr>
<td>Airblast velocity</td>
<td>36</td>
<td>36</td>
<td>60</td>
<td><strong>48</strong> (m/s)</td>
</tr>
<tr>
<td>Air-to-Fuel ratio</td>
<td>0.36</td>
<td>0.22</td>
<td>0.22</td>
<td><strong>0.16</strong> (by mass)</td>
</tr>
</tbody>
</table>

**Experimental Variables**
- Fuel Loading
- Spray Density

**Liquid Fuel Type**
- Acetone, \( \text{C}_3\text{H}_6\text{O} \)
- Ethanol, \( \text{C}_2\text{H}_6\text{O} \)
Hypothesis:
Heat release driven by droplet evaporation

Test:
Acetone significantly more volatile than ethanol

Observation:
Increased acetone temperature profile at x/D = 20
N-EF8-25 -- (C$_2$H$_6$O)

Temperature Spectrum at x/D = 5.0

Tight distribution over pilot flame: r/D = 0.8

Wider spread at inner and outer pilot flame interface regions: r/D = 0.6 & r/D > 1.0
Purdue Gas Turbine Combustion Facility: Advanced Optically Accessible Test Rigs
Fs CARS: High-Pressure Aviation Gas Turbine Test Rig
Potential Advantages of fs CARS

- Data rate of 1-100 kHz would allow true time resolution, study of turbulent fluctuations and of transient combustion events.

- Data rate of 1-100 kHz as opposed to 10 Hz would decrease test time considerably in practical applications.

- Fs CARS, unlike ns CARS, is insensitive to collision rates even up to pressure > 10 bars (fs CARS signal increases with square of pressure).

- Fs laser pulses are near-Fourier-transform limited, noise may be decreased significantly for single-shot measurements.
Chirped Probe Pulse (CPP) fs CARS in Argon

Probe Delay Time (ps)

-3 -2 -1 0 1 2 3 4 5

$[E_{Pu}(t) E_{St}(t)]^2$
Temperature Measurements in Flames

Chirped Probe Delay Time = 2 ps

Signal Frequency (cm⁻¹)

S(ω) (arb. units)

500 K
1000 K
1500 K
2000 K

Signal Frequency (cm⁻¹)
Temperature Measurements in Flames

Chirped Probe Delay Time = 2 ps

Signal Frequency (cm\(^{-1}\))

S(\(\omega\)) (arb. units)

- **500 K**
- **1000 K**
- **1500 K**
- **2000 K**
Numerical Model of fs CARS in N₂

• A model of the CARS process in nitrogen based on direct numerical integration of the time-dependent density matrix equations has been developed [Lucht et al., Journal of Chemical Physics, 127, 044316 (2007)].

• Model is nonperturbative and is based on direct numerical integration of the time-dependent density matrix equations.
• Most significant difference for fs CARS compared to ns CARS is the potential for data rates of 1-100 kHz as compared to 10-30 Hz for ns CARS.
Numerical Model of N₂ CARS

\[ k^{1}\Sigma^{+}_u \quad \underline{\underline{\begin{array}{c} v_k \ \ J_k \ \ M_k \\ 0 \quad 9 \quad -9,+,9 \\ 0 \quad 8 \quad -8,+,8 \\ 0 \quad 7 \quad -7,+,7 \\ \end{array}}} \]

\( k^{1}\Sigma^{+}_u - X^{1}\Sigma^{+}_g \) transition strength
varied to match N₂ Raman cross section

Collisional Bath Levels

\( \omega_1 \omega_2 \omega_3 \omega_4 \)

\[ v_e \quad J_e \quad M_e \quad v_g \quad J_g \quad M_g \]
\[ 1 \quad 8 \quad -8,+,8 \quad 0 \quad 8 \quad -8,+,8 \]

\( X^{1}\Sigma^{+}_g \)