Coherent anti-Stokes Raman Scattering

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HOW IT STARTED

The challenge: measure aerodynamic and reactive flows
- fast
- non-intrusively
- with good spatial resolution
The early days of molecular CO$_2$ & CO lasers: getting rate constants in homonuclear diatomics

Measuring H$_2$ vibrational relaxation

Audibert, Ducuing, Joffrin, Lukasik
First CARS setup at Onera

for point measurements

for visualisation

Régnier & Taran APL (1973)
CARS signal vs $\text{H}_2$ density in air
Visualisation of supersonic $\text{H}_2$ jet
H₂ distribution in horizontal Bunsen flame
The work in its context

• The pioneers
  • Maker & Terhune, Phys Rev. 137 (1965)
  • Shen & Bloembergen, Phys. Rev. 177 (1965)
  • Hauchecorne, Kerhervé & Mayer, J. Physique 32 (1971)
  • Lukasik & Ducuing, Phys Rev. Let. 28 (1972)
  • De Martini, Giuliani & Santamato, Optics Comm., 5 (1972)
Making CARS a practical tool
Coherent Raman Anti-Stokes Scattering: geometry

Assets:
- Signal strength
- Collimation
Spatial Resolution

- Phase-matching condition required for an efficient CARS signal production

\[ \vec{k}_{CARS} = \vec{k}_3 = \vec{k}_0 + \vec{k}_1 - \vec{k}_2 \]

**Collinear Phase-Matching**

**Planar Phase-Matching**

Eckbreth APL (1978)
Spatial Resolution

**Collinear Phase-Matching:**

The confocal parameter is $4$ for a $5$ mm diameter beam when using a $250$ mm focal length. Poor spatial resolution.

**Planar Phase-Matching:**

For diffraction-limited laser beams of $6$ mm diameter, separated by $8.5$ mm and focused with a $250$ mm focal length lens, $99$ % of the signal is created over less than $3$ mm.
Spectral analysis
Scanning CARS (only for stable media)

\[ |\chi_{CARS}(\omega_1 - \omega_2)|^2 \]

Dye laser or OPO is swept over resonance

Laser spectral bandwidths much smaller than Raman line width.

CARS signal strength mirrors resonance

\[ I_3(\omega_3) \]

\[ I_3'(\omega_3') \]
Stokes laser bandwidth larger than Raman line width, covering numerous Raman transitions.

\[ |\chi_{CARS}(\omega_1 - \omega_2)|^2 \]

\[ I_2(\omega_2) \]

\[ I_3(\omega_3') \]

Roh, Schreiber, Taran APL (1976)
Motivation

- Improvement of the design and the optimization of high performance combustion efficiency of rocket and aircraft propulsion combustors.

- Detailed investigation of elementary processes (fuel injection, atomization, droplet vaporization, turbulent mixing, combustion,...) required.

→ **Advanced Laser Diagnostics**

- Gaseous Combustion

- Two-phase Combustion
  
  Liquid: Kerosene/Air Combustion
  
  LOX/GH₂, LOX/CH₄ Cryogenic Combustion

  Solid: Solid Propellant Combustion

- Non-reactive flows

  Turbulence, mixing layer, ...
CARS Diagnostic (temperature and species concentration)

- CARS signal several orders of magnitude stronger than spontaneous Raman scattering.
- CARS produces a coherent signal beam that can be fully collected whereas a small fraction of the scattered light is collected for incoherent processes.
- Thermal background radiation can be eliminated because the CARS beam is collected within a small solid angle.
- Signal, shifted to shorter wavelengths than those of the laser beams, has little interference from laser-induced fluorescence.
- Using a broadband single-shot procedure, single-shot measurements are possible with good spatial resolution and good detectivity $\sim 10^{17}$ mol/cm$^3$. 
CARS process: theory

Four wave mixing process

**Step 1**: Coherent Excitation of the vibrational state in the fundamental electronic states.

Use two laser waves with a wavelength difference equal to the vibrational frequency of the probed molecule.

**Step 2**: Probe the coherent excitation via a third laser beam (usually, $\omega_0 = \omega_1$).

**Step 3**: Produce an anti-Stokes beam characteristic of the thermodynamic properties of the molecule

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

Energy level diagram
Fundamental aspects of CARS

The wave equation which governs the propagation of optical wave $E(r)$ in a medium is

$$\nabla^2 \tilde{E}(\omega_j, \vec{r}) + \frac{\omega_j^2}{c^2} \tilde{E}(\omega_j, \vec{r}) = -\mu_0 \omega_j^2 \tilde{P}(\omega_j, \vec{r})$$

In an isotropic medium, the polarization at $\omega_3$ is given by

$$\tilde{P}(\omega_3, \vec{r}) = \tilde{P}^{(1)}(\omega_3, \vec{r}) + \tilde{P}^{(3)}(\omega_3, \vec{r}) = \varepsilon_0 \chi^{(1)} \tilde{E}(\omega_3, \vec{r}) + \tilde{P}^{(3)}(\omega_3, \vec{r})$$

(Summation of linear and nonlinear terms)

This expression can also expressed as

$$P_i^{(3)}(\omega_3, \vec{r}) = \varepsilon_0 \chi^{(3)}_{ijk\ell} (-\omega_3, \omega_0, \omega_1, \omega_2) E_j(\omega_0, \vec{r}) E_k(\omega_1, \vec{r}) E_\ell(\omega_2, \vec{r})$$

$$\omega_0 + \omega_1 + \omega_2 - \omega_3 = 0$$
The Third-Order Susceptibility

\[ P_{x}^{(3)}(\omega_{3}, \vec{r}) = \varepsilon_{0} 3 \chi_{xxxx}^{(3)}( - \omega_{3}, \omega_{1}, \omega_{1}, - \omega_{2}) E_{x}^{2}(\omega_{1}, \vec{r}) E_{x}( - \omega_{2}, \vec{r}) \]

\[ P^{(3)}(\omega_{3}, \vec{r}) = \varepsilon_{0} \chi_{CARS} E^{2}(\omega_{1}, \vec{r}) E( - \omega_{2}, \vec{r}) \]

The wave equation for a CARS signal beam propagating along the z-axis is given by

\[ ik_{3} \frac{\partial E(\omega_{3})}{\partial z} \exp(i k_{3} z) = - \frac{\omega_{3}^{2}}{c^{2}} \chi_{CARS} E^{2}(\omega_{1}) E^{*}(\omega_{2}) \exp\left[ i \left( 2\vec{k}_{1} - \vec{k}_{2} \right) \cdot \vec{r} \right] \]
When the phase-matching condition is satisfied then

\[ \exp(i k_3 z) = \exp\left[i\left(2\vec{k}_1 - \vec{k}_2\right) \cdot \vec{r}\right] \]

and

\[ E(\omega_3) = i k_3 \frac{\omega_3^2}{c^2} \chi_{CARS} E^2(\omega_1) E^*(\omega_2) \int_0^\ell dz \]

\[ = i \frac{\omega_3}{c} \chi_{CARS} E^2(\omega_1) E^*(\omega_2) \ell \]

The intensity of the CARS signal is then given by

\[ I_3 = \frac{1}{2} c \varepsilon_0 |E(\omega_3)|^2 = \frac{\omega_3^2}{c^4 \varepsilon_0^2} I_1^2 I_2 |\chi_{CARS}|^2 \ell^2 \]
CARS Susceptibility

\[ I_{CARS} = I_3 \propto \left| \chi_{CARS}(\omega_1, \omega_2) \right|^2 I_1^2 I_2 \ell^2 \]

\[ \chi^{(3)}(\omega) = \chi_R^{(3)}(\omega) + \chi_{NR}^{(3)}(\omega) \]

Resonant term
Non-resonant term

\[ \chi_R^{(3)}(\omega) = \frac{iN}{\hbar} \sum_j \alpha_j \sum_k \alpha_k \Delta \rho_k^{(0)} G_{jk}^{-1} \]

\[ G_{jk} = i(\omega_P - \omega_S - \omega_R)\delta_{jk} + (\frac{\Gamma_j}{2} - i\Delta_j)\delta_{jk} + W_{jk}(1 - \delta_{jk}) \]

\[ \chi_{nr} \text{ depends on the effects of remote vibrational resonances and those associated with the nonlinear distortion of the electron cloud of the molecules caused by the intense laser fields.} \]
Polarization Arrangement

Goal: Cancelling the non-resonant contribution

\[
\tilde{E}(\omega_3) = 3i \frac{\omega_3}{2c} \left[ \chi_{1122}^{(3)} \hat{e}_0 \cdot (\hat{e}_1 \cdot \hat{e}_2) + \chi_{1212}^{(3)} \hat{e}_1 \cdot (\hat{e}_0 \cdot \hat{e}_2) + \chi_{1221}^{(3)} \hat{e}_2 \cdot (\hat{e}_0 \cdot \hat{e}_1) \right] \\
\times E(\omega_0) E(\omega_1) E^*(\omega_2) \ell
\]

- The two pump beams are propagating separately and with different polarizations, the angles between the x axis and the incident field polarizations are \(\theta_i\).
- Analysing of the two fields using a polarizer rotated by angle \(\Phi\) with respect to the x axis.

\[
P_3 = 1.3 \times 10^{-46} \omega_3^4 P_1 P_1' P_2 \left| \chi_{1111R}^{(3)} \cos \theta_1' \cos \theta_1 \cos \Phi + \chi_{1221R}^{(3)} \sin \theta_1' \sin \theta_1 \cos \Phi + \chi_{1122R}^{(3)} \sin (\theta_1' + \theta_1) \sin \Phi \\
+ \chi_{1111NR}^{(3)} (\cos \theta_1' \cos \theta_1 \cos \Phi + \frac{1}{3} \sin \theta_1' \sin \theta_1 \cos \Phi + \frac{1}{3} \sin (\theta_1' + \theta_1)) \sin \Phi \right|^2
\]

Complete rejection of the non resonant contribution
But reduction of the signal by a factor of 16

\[
\theta_1' = \theta_1 = 120^\circ \\
\Phi = 60^\circ
\]
**Experimental Setup**

**Pump Laser:** seeded Nd:YAG laser operating in the green.

**Stokes laser:** Broadband dye laser or OPO

**Reference channel: flow of Argon**

Nonresonant CARS signal created to monitor the shot to shot fluctuations of direction and of pulse energy of the lasers beams and of the spectral shape of the Stokes laser.
Coherent Anti-Stokes Raman Scattering Measurements of Temperature and Concentration
Nitrogen CARS is widely used for temperature measurements in flames, sophisticated models of the nitrogen CARS spectrum have been developed.
CARS Temperature Measurements

T = 1500 K

T = 2000 K
Raman linewidths $\Gamma_j = 2\gamma_j$ are needed for modeling of the $N_2$ CARS spectrum.

L. Rahn and R. Farrow
Collisional Narrowing of the CARS Spectrum

Collisional narrowing causes a collapse of the nitrogen Q-branch spectrum at high pressures. Effect must be modeled accurately because a pressure increase and a temperature decrease have approximately the same effect on the spectrum.
Collisional Narrowing of the CARS Spectrum

- P = 1.0 MPa
- T = 300 K

- P = 5.0 MPa
- T = 300 K
Data processing is performed by comparing the experimental spectra to the theoretical ones using a least-square fitting routine.

\[(\log I_i^{\text{exp}} - \log I_i^{\text{theo}})I_i^{\text{theo}}\]
Applications
Buoyant diffusion $\text{H}_2/\text{air}$ flame

- Cooperation with M. Roquemore and V. Katta (Wright Patterson Air Force Base, Dayton, USA)

$\text{H}_2/\text{air}$ Flame

- Large domain of temperature and species concentration investigated
N₂ - CARS Thermometry

Data processing

![Graph showing data processing](image)

Temperature

![Temperature profile](image)

Temporal profile

![Temporal profile graph](image)

Temperature accuracy: 2%
**H₂ - CARS Thermometry and Concentration**

### Data processing

![Graph showing rotational energy distribution and calibration procedure](image)

**Calibration procedure**

![Graph showing signal DRASC H₂ vs concentration H₂](image)

**Laminar H₂-Air**

At room temperature

### Temporal profile

![Graph showing temperature and concentration profiles](image)

**Temporal profile**

- **r = 5 mm**
- **r = 10 mm**

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**Concentration (%)**

- **Température (K)**
  - 0
  - 5
  - 10
  - 15
  - 20
  - 25
  - 30
  - 35
  - 40
  - 45
  - 50

**Time (ms)**

- 0
- 5
- 10
- 15
- 20
- 25
- 30
- 40
- 50
- 60
- 70
- 80
- 90
- 100
**H₂ - CARS Thermometry and concentration**

Comparison Temperature N₂ - H₂

![Graphs showing temperature comparison](image)

**H₂ Concentration**

![Graph showing H₂ concentration](image)

*Temperature accuracy ≈ 2 %*
Comparison between Experiment and Theory

Temperature

Measured

Computed

2250 K

[H₂]

Measured

Computed

Simulation performed by V. Katta & M. Roquemore (Wright-Patterson Air Force Base, Dayton, USA)
Cryogenic Propellant Combustion

- Investigation focused on Liquid Oxygen and gaseous Hydrogen reactants
- Propellant used in many performance engines like Vulcain (Ariane 5)

Flame Vizualisation at 3.0 MPa using Shadowgraphy

Mascotte facility (Onera)

→ Temperature and Species concentration measurements

⇒ Probing of H₂ and H₂O

Cooperation with DLR and GPI
Experimental Setup

- Optical fiber
- Reference channel
- Combustion chamber
- Spectrograph
- Spectrograph reference H2
- Spectrograph signal H2
- Laser
- Laser beam arrangement:
  - H2: Planar BOXCARS
  - H2O: USED CARS
- Jitter ≤ 200 ns
- Probe volume dimensions:
  - H2: 0.8 mm × 100 µm
  - H2O: 2 mm × 150 µm
High Pressure H₂ CARS Spectra

- Single-shot measurements

Subcritical (for O) Pressure

Supercritical Pressure

P = 3.0 MPa  
T = 1900 K  
5% H₂, 95% H₂O

P = 6.5 MPa  
T = 1620 K  
81% H₂, 19% H₂O
Cryogenic Combustion at 3.0 MPa

\[ m_{H_2} = 25 \text{ g/s} \]

\[ m_{H_2O} = 50 \text{ g/s} \]
Supercritical Condition (P=6.5 MPa)

- Series of 300 single-shot measurements with a validation rate exceeding 80 %

\[
\begin{align*}
\dot{m}_{H_2} &= 45 \text{ g/s} \\
\dot{m}_{H_2O} &= 100 \text{ g/s}
\end{align*}
\]
Cryogenic Combustion LOX/CH₄

- CARS Thermometry on CH₄

P = 0.1MPa, T= 1200 K

Pressure effect
Figure 4. Axial temperature profile in the quench region of the kerosene-fueled RQL combustor at atmospheric pressure. The data points were taken in a plane below a row of secondary air holes.

CARS in Practical kerosene/air Combustors

- Same experiments performed at ONERA on a multi-point injection system at pressure up to 19 bar (TLC European Research Program)

HYPERSOONICS STUDIES
LBK wind tunnel
Experimental set-up

CARS bench

Testing chamber

Disk

Nozzle

Flow

Reference cell

Signal detection

Reference detection

Probe volume: 20 mm-long x 100 μm in diameter
## LBK wind tunnel

- **Stagnation conditions**

<table>
<thead>
<tr>
<th>Air</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate</td>
<td>49 g/s</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.3 bar</td>
</tr>
<tr>
<td>Total enthalpy</td>
<td>7.3 MJ/kg</td>
</tr>
<tr>
<td>Temperature</td>
<td>3910 K</td>
</tr>
</tbody>
</table>

- **Conical Nozzle**

| Throat diameter      | 29 mm            |
| Exit diameter        | 200 mm           |
| Length               | 405 mm           |

- **Conditions at the probe volume (995 mm from the throat)**

| Mach number          | 7.5              |
| Static pressure      | 14 Pa            |
Shock layer on disk at LBK

50 mm
Temperature measurement with CARS

**N₂ CARS Spectrum**

- Signal (arb. units)
- Raman shift (cm⁻¹)
- V=0 → V=1
- V=1 → V=2

**Boltzmann Diagram**

- \( N_j / g_j (2J+1) \)
- Rotational energy (cm⁻¹)
- \( T = 330 ± 9 \text{ K} \)
  - \( V=0 \rightarrow V=1 \)
- \( T = 334 ± 9 \text{ K} \)
  - \( V=1 \rightarrow V=2 \)
- \( T_{\text{vib}} = 2510 ± 130 \text{ K} \)
Nitrogen CARS spectra

Free stream

Ortho-lines (J even)

Para-lines (J odd)

V = 0 → V = 1

V = 1 → V = 2

Raman shift (cm⁻¹)

Signal (arb. units)

2330 2340 2350 2290

Shock layer

Ortho-lines (J even)

Para-lines (J odd)

V = 0 → V = 1

V = 1 → V = 2

Raman shift (cm⁻¹)

Signal (arb. units)

2330 2340 2350 2360 2290
Temperature Distributions in the Shock Layer

Temperature Distributions

Temperature versus Distance from the model (mm)

- $T_{\text{rot}}$
- $T_{\text{vib}}$
- $T_{\text{vib}}(N_2)$
- Theory

Temperature (K)

Distance from the model (mm)
Density Profile in the Shock Layer

Density (kg/m$^3$)

Distance from the model (mm)

- **CARS measurement**
- **Theory**
Coherent anti-Stokes Raman Scattering in the time domain
Velocity measurements by time-domain CARS

Excitation step + Read-out step
Coherence grating

Fringe spacing ~ 10 µm

Ribet I., Scherrer B., Bouchardy P., Pot T., Taran J.-P., Lefebvre M.
Supersonic flow diagnostics by single-shot time-domain CARS
Experimental set-up

Long pulse production

Nd:YAG oscillator

Ampli

1064nm

x2

532nm

AO

λ/4

λ/2

ω₁+ωₐ

ω₁

532nm

Short pulse production

FS

Ampli

532nm

x2

534-540nm

OPO

OPA

SFG

ω₂
Velocity measurements (free stream)

Heater ON

Heater OFF

R5 wind tunnel (Mach 10)

![Graph showing velocity measurements](image)
Velocity, temperature and density in bow shock
Molecular degrees of freedom through the shock

Boltzmann diagram

Static temperature and velocity

- Shock
- High J
- Small J
- High J

Energy (cm$^{-1}$)

Temperature (K)

Velocity (ms$^{-1}$)

X(mm)

Static temperature and velocity
Velocity measurements above a flat plate

100 mm downstream the leading edge
OTHER NON-EQUILIBRIUM MEDIA

- Low-pressure discharges
  - H2, N2, O2, etc.
- Photochemistry
  - H2CO (Moore)
- Explosives
  - Lead azide (Rosenwaks)
RESONANCE-ENHANCED CARS

• Druet, Attal-Trétout, with
  • Gustafson,
  • Bordé,
  • Dumont,
  • Kelley,
  • etc.
CONCLUSION

• I – with CARS, we have witnessed a remarkably productive cross fertilisation between laser optics and molecular physics

• II – hypersonics is, really, a problem in quantum mechanics