10. CARS

- Introduction
- Theory
- Rotational CARS/vibrational CARS
- Temp. & conc. measurements
- Applications
# Classification of techniques

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CARS conceptual behaviour

\[ \omega_g - \omega_r = \omega_{\text{vib}} \]
Coherent anti-Stokes Raman scattering/spectroscopy (CARS) is a technique that is used for:

- temperature measurements
- concentration measurements

Species with high concentrations (> ~1%) are probed N₂, O₂, CO₂, H₂O, CO, H₂

The first demonstration of CARS in flames was made in 1973 by Taran et al. and in an IC engine by Stenhouse et al. (1979)
Characteristics of CARS

- Signal generated as a new laser beam
- Pointwise thermometry with high accuracy
- Signal blue shifted relative to the primary lasers
- Complex theory
- Relatively complicated experiments
- Operator skill is needed
- Two approaches: - Vibrational CARS
  - Rotational CARS
Nonlinear optics

Thus far in the course, the induced polarization of molecules has almost always (except for frequency doubling/mixing) been assumed to depend linearly on the applied electromagnetic field. This is, however, only valid for incident radiation of low intensity.

Generally, the induced polarization is a nonlinear function of the applied electromagnetic field:

\[ \vec{P} = \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \ldots \]

For gases, which are isotropic (inversion symmetry), the even order polarizations vanish.

CARS is a four-wave mixing process based on the nonlinear response via the third-order susceptibility (\(\chi^{(3)}\))
CARS theory

\[ S \propto \omega_{CARS}^2 I_1 I_2 I_3 |\chi_{CARS}|^2 l^2 \left( \frac{\sin(\Delta k l/2)}{\Delta k l/2} \right)^2, \quad \chi_{CARS} = \chi_R + \chi_{NR} \]

- \( \omega_{CARS} \) is the CARS signal frequency,
- \( I_i \) is the irradiance in laser beam \( i \),
- \( \chi_{CARS} \) is the CARS susceptibility,
- \( l \) is the interaction length,
- the last factor is the phase-matching condition, that takes the value 1 if perfect phase-matching is achieved.
Calculated CARS spectra of CO
Phase matching implication on the CARS set-up

\[ \vec{k}_{\text{CARS}} = 2\vec{k}_1 - \vec{k}_2 \quad \left| \vec{k}_i \right| = \frac{2\pi n_i}{\lambda} \]

Collinear phase-matching

Planar BOXCARS phase-matching

Folded BOXCARS phase-matching

Focal point

Lens

Dichroic mirror

CARS signal

Red + Green

Red + Green

Red

Green

Green

Green

Red
Generation of CARS spectra

Drawback:
It takes time to scan a spectrum ⇒ can be used in stationary flames only

Advantage:
Spectra is obtained within 10 ns ⇒ can be used in turbulent flames
The selection of wavelengths

• The energy difference between $\omega_1$ and $\omega_2$ must match a vibrational Raman resonance in the molecule. $\omega_1 - \omega_2 = \omega_R$

• For nitrogen, with $\omega_R = 2331 \text{ cm}^{-1}$, it means a Nd:YAG laser wavelength of 532 nm and a dye laser spectral profile centred around 607 nm.

• The CARS signal is at frequency: $\omega_{\text{CARS}} = \omega_1 - \omega_2 + \omega_3$, which for nitrogen is at a wavelength of 473 nm. ($\omega_1 = \omega_3$)

• By operating the dye laser in broadband mode all transitions can be monitored simultaneously.
Experimental setup (vibrational CARS)

Laser source
The most common laser system for CARS is a Nd:YAG + dye laser system with repetition rate 10 Hz and pulse duration of ~10 ns.

Optical components
Special optics that can stand high pulse energies are needed.

Detection system
High-resolution spectrometer + CCD-camera
Experimental CARS spectra (scanned)
Temperature measurements

- The temperature is normally measured from the CARS spectrum of nitrogen, since nitrogen often is present at high concentration before as well as after combustion.

- The temperature is evaluated from the spectral shape and not the total intensity.

- The temperature is evaluated by fitting the experimental spectra using a library of theoretical spectra.
Broadband CARS ($N_2$)

\[ \omega_{AS} = 2 \omega_p - \omega_S \]

$T = 1900$ K
CARS on SO$_2$
What does thermal equilibrium mean?

Flame: $T_{\text{vib}} = T_{\text{rot}}$

Discharge: $T_{\text{vib}} \neq T_{\text{rot}}$
Concentration measurements

• Concentration measurements are normally made from the spectral shape.

• The figure shows an experimental spectrum with contributions from H₂, CO, and N₂.

• The lower figure shows the same experimental data together with a fitted curve. The evaluation gave all three concentrations together with the temperature.

Figures are from Stufflebeam and Eckbreth, Combust. Sci. and Tech. 66, 163-169 (1989)
Rotational CARS

Conventional rotational CARS (C-RCARS)

Dual-broadband rotational CARS (DB-RCARS)
Experimental set-up for rotational CARS

An experimental setup for dual-broadband rotational CARS is using basically the same experimental parts as for vibrational CARS.

Some optical components such as mirrors and filters are replaced.

**M** = Mirror  **ND** = Neutral density filter
**BS** = Beam splitter  **CCD** = Charge-coupled device camera
**BC** = Beam combiner  **L** = Lens
**A** = Aperture  **SP** = Short-pass filter
**CL** = Cylindrical lens
Temperature measurements

- The spectral shape of a rotational CARS spectrum varies strongly as a function of temperature.
Concentration measurements

- Rotational CARS spectra from many species ($\text{N}_2$, $\text{O}_2$, $\text{CO}$, $\text{CO}_2$) appear in the same spectral region.

- Concentration evaluation is made from the relative intensities of the lines.
Rotational CARS spectra for different molecules

- Linear molecules give clear distinct spectra.
- Smaller molecules have higher B-constants and result in wider spectra.
Advantages with CARS for practical applications

- Signal as a new laser beam
- Strong signal
- CARS signal on the anti-Stokes side
- Measurements on nitrogen molecules (max signal)

Special issue: High pressure effects

Ref: Eckbreth et al.
Applications to engines
Vibrational CARS applications

CARS spectra:

In a burning spray of JET-A

Burning of solid propellants

A.C. Eckbret et al.
Limitations with conventional CARS

- Low spatial resolution - In order to keep a sufficient signal strength it has been important to keep the crossing angle between the laser beams small ⇒ rather low spatial resolution (≈ 1-3 mm)

- Limited signal strength in an environment with low transmission - The CARS signal scales as (laser intensity)$^3$ ⇒ at strong laser attenuation, the signal strength is too low
Probe volume considerations

Reaction zone

- Thickness: ~100 μm

Probe volume diam.: ~100 μm
Probe volume length: ~1-3 mm

CARS probe volume

Unburned gas
~300 K

Burned gas
~2000 K

The result will be a “mixed spectrum” with a strong low-temperature part.
Comparison between collinear CARS and BOXCARS
Limitations with conventional CARS

- Low spatial resolution - In order to keep a sufficient signal strength it has been important to keep the crossing angle between the laser beams small ⇒ rather low spatial resolution (~ >1-3 mm)

- Limited signal strength in an environment with low transmission - The CARS signal scales as \( (\text{laser intensity})^3 \) ⇒ at strong laser attenuation, the signal strength is too low

Potential solution: 2-\( \lambda \) CARS
One measuring situation where $2-\lambda$ CARS has to be used.
Concept of $2\lambda$ CARS:
Use a two colour dye laser instead of a broad-band dye laser $\Rightarrow$ higher spectral intensity

Broadband CARS

2 $\lambda$ CARS
Experimental approach to produce a two colour dye laser
Wavelength selection in $2\lambda$ CARS
Features of $2-\lambda$ CARS

Advantages:
• ~30 times higher signal intensity $\Rightarrow$
  Higher spatial resolution, experiments in
  very applied areas possible

Disadvantages:
• More complex experimental set-up
• Somewhat lower temperature precision
  (~5 % comp to ~3% with broadband CARS)
Application: High spatially resolved temperature measurement in model of an after-burner

(VOLVO Aero Corporation, Trollhättan)
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Temperature pdf:s at a distance 150 mm from the bluff body at different radial distances
Practical diagnostics - CARS
Practical diagnostics - CARS

CARS, Single shot (10ns)
constant thermal load 72 MW
4.5 m from focusing lens

mean value 1352 K
std. deviation 187K

temperature (K)

Suction Pyrometer
constant thermal load 72 MW

4 m from focusing lens

temperature (K)

4.5 m from focusing lens

mean value 1352 K
std. deviation 187K
Pressure dependence for rotational CARS

If pressure increases

- the signal increases
- the linewidths will be broader
Rotational CARS spectra from an engine

- Single-shot spectra in the compression phase of engine burning natural gas.
- Both nitrogen and oxygen lines are observed.
- Below each experimental spectrum the difference between the experimental spectrum and the best-fit theoretical spectrum is shown, illustrating good spectral fits.

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c: 32 CAD ATDC, 32 bar, 2550 K
d: 56 CAD ATDC, 15.5 bar, 2435 K
Sooty flame diagnostics: Vib CARS

- Sooty flame
- "Clean" flame

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
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<tbody>
<tr>
<td>N₂ flame</td>
<td>Ar flame</td>
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<tr>
<td>C₂ emission</td>
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a) fitted \( \chi_{NR} \) and T
b) Only fit T with estimated \( \chi \)
Sooty flame diagnostics: Rot. CARS

![Graphs showing Raman shift vs. intensity and temperature vs. height above burner.](image)
Summary: CARS

- strong coherent signal
- point measurement technique
- complex theory
- double-ended technique
- can be applied to harsh environments, since background radiation is easily discriminated, anti-Stokes signal (low fluorescence interferences)
- mainly for temperature measurements, where temperature is measured from spectral profile
- high accuracy for temperature measurements
- can sometimes be used for concentration measurements, but for major species only.
Summary:
Rotational CARS vs Vibrational CARS

- Same experimental complexity
- Both methods are very accurate thermometers: Uncertainty 1-2% of T
- Rotational CARS: better at high P, low T
  Vibrational CARS: better at low P, high T
- Rotational CARS: many species simultaneously
  Vibrational CARS: often one species only with a setup
- Rotational CARS: Problems may arise with rejection of light at 532 nm because of spectral closeness.