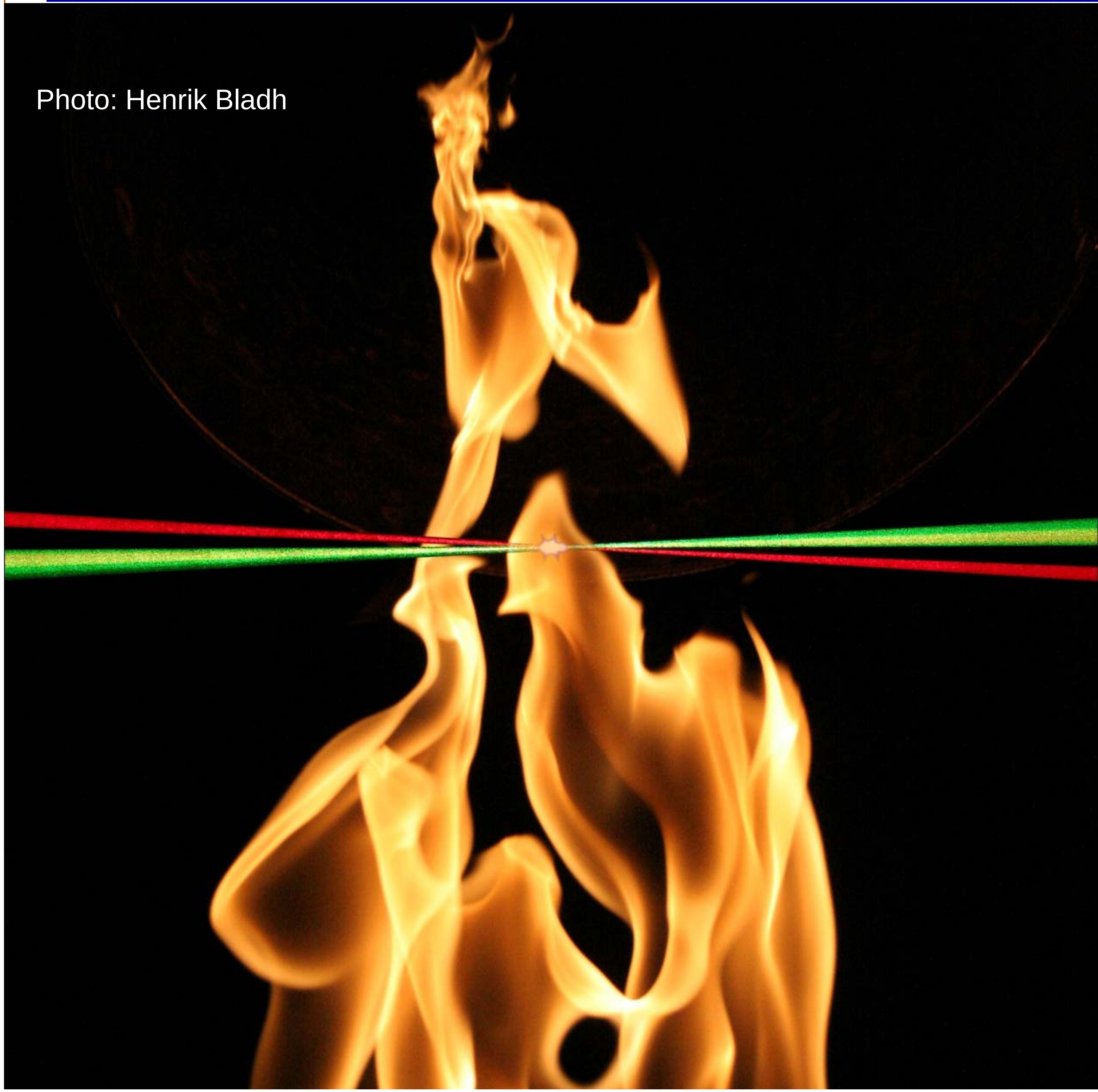
10. CARS

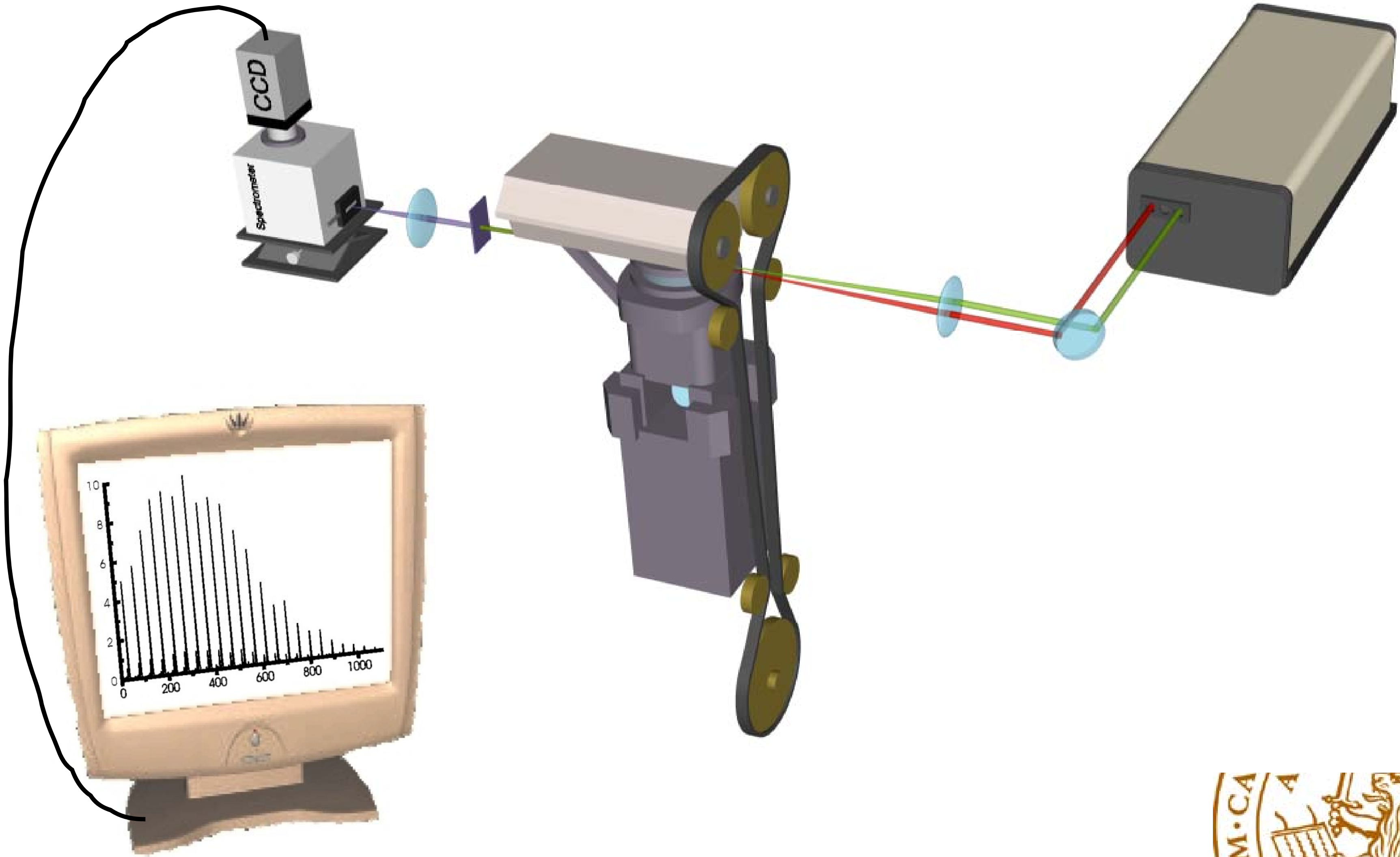


- Introduction
- Theory
- Rotational CARS/vibrational CARS
- Temp . & conc. measurements
- Applications

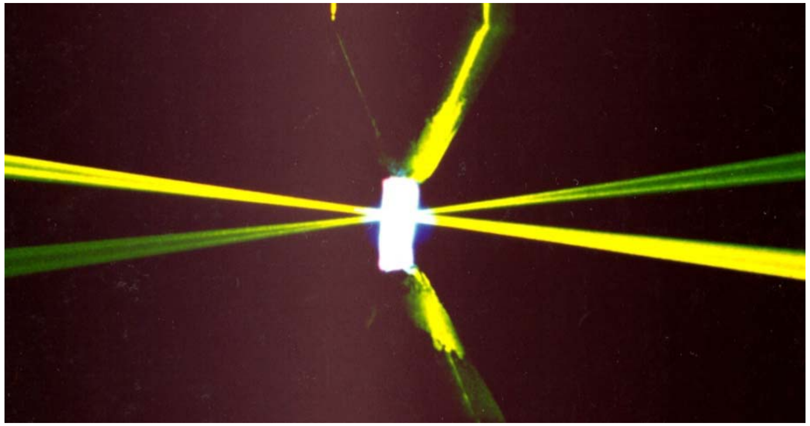
Classification of techniques

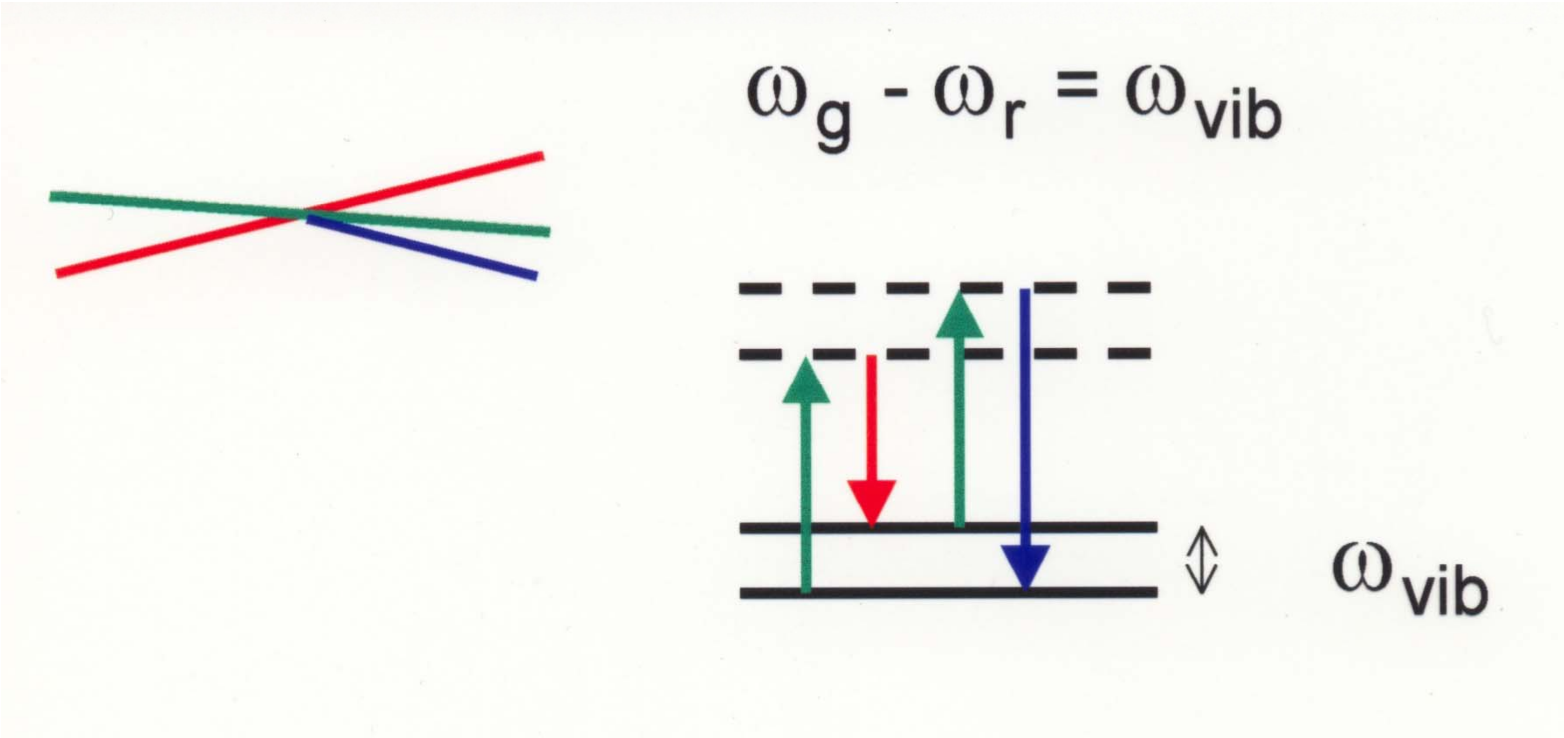
Approach / Level	Incoherent	Coherent
Major species	Raman Scattering	CARS
Minor constituents	LIF	PS/DFWM

CARS



CARS conceptual behaviour





Background - CARS

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 N_2, O_2, CO_2, H_2O, CO, H_2

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:

$$\vec{P} = \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + ...$$

$$\vec{P} = \varepsilon_0 \left(\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + ... \right)$$

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

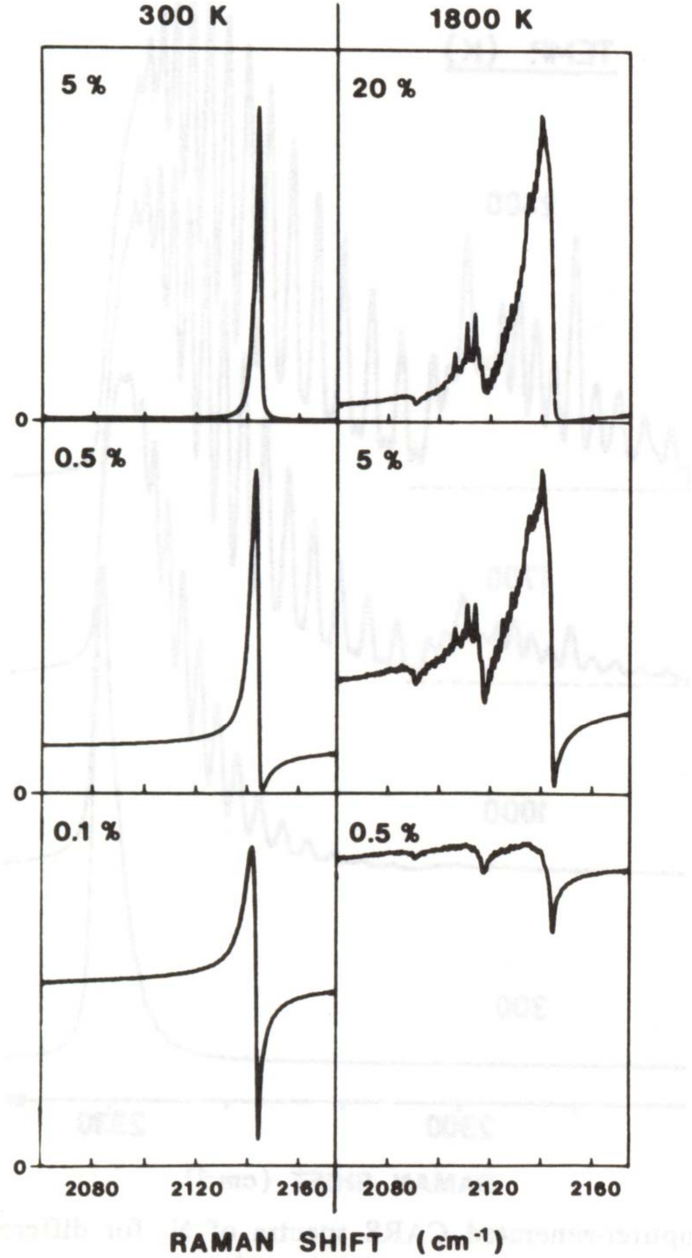
CARS is a four-wave mixing process based on the nonlinear response via the third-order susceptility ($\chi^{(3)}$)

CARS theory

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

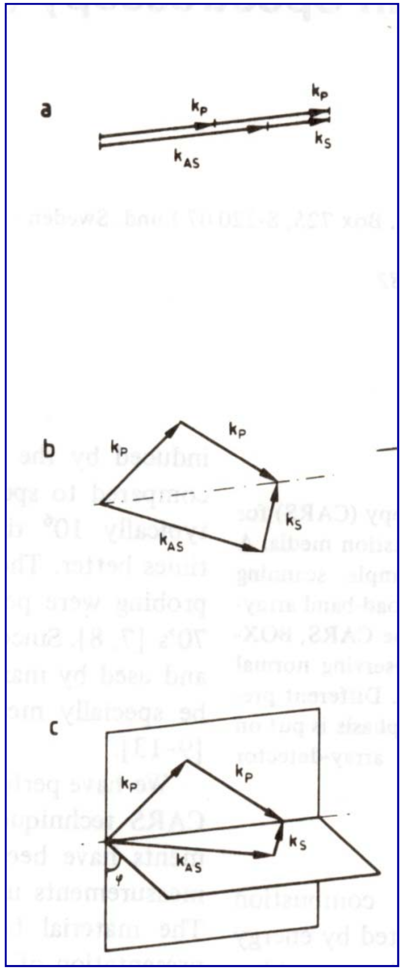
- ω_{CARS} is the CARS signal frequency ,
- I_i is the irradiance in laser beam *i*,
- χ_{CARS} is the CARS susceptibility,
- *l* is the interaction length,
- the last factor is the phase-matching condition, that takes the value 1 if perfect phase-matching is achieved.

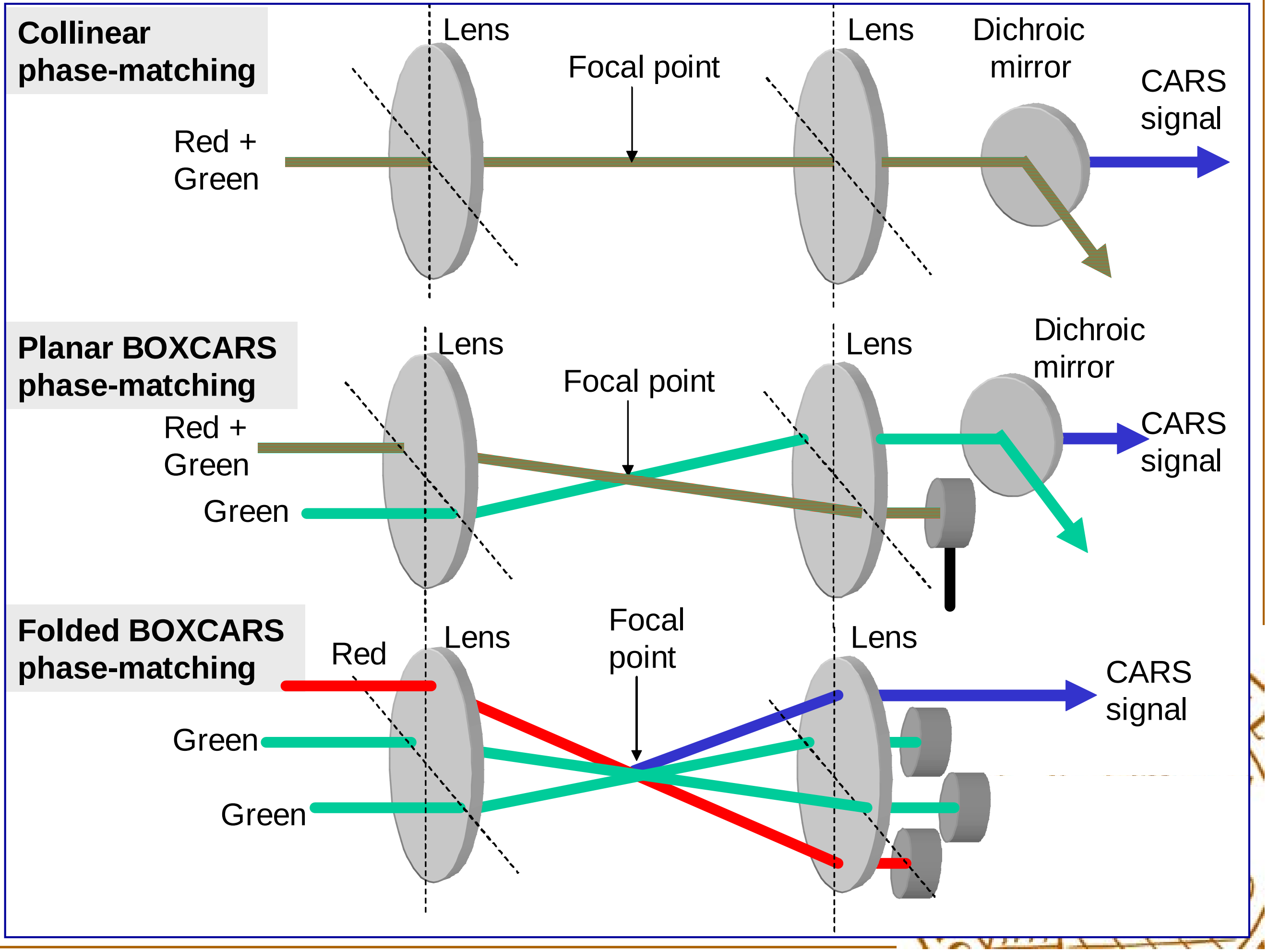
Calculated CARS spectra of CO



Phase matching implication on the CARS set-up

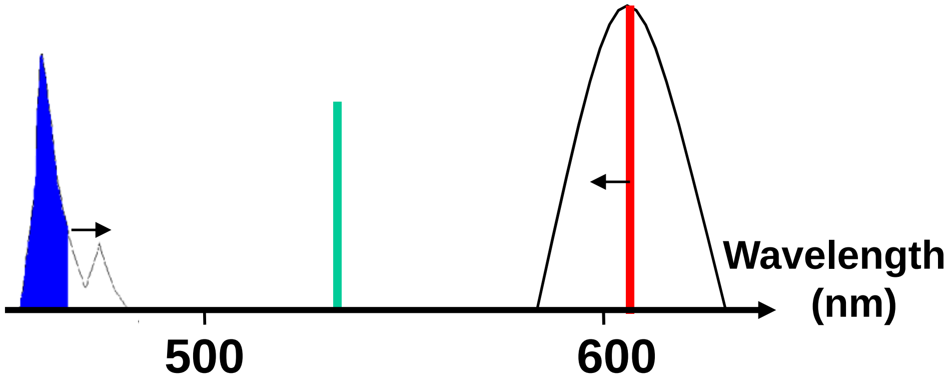
$$\vec{k}_{CARS} = 2\vec{k}_1 - \vec{k}_2 \qquad \left|\vec{k}_i\right| = \frac{2\pi n_i}{\lambda}$$





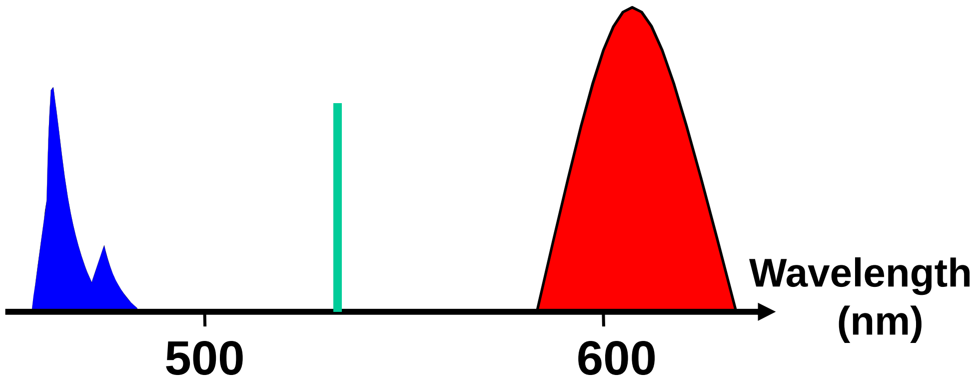
Generation of CARS spectra

Scanning CARS



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

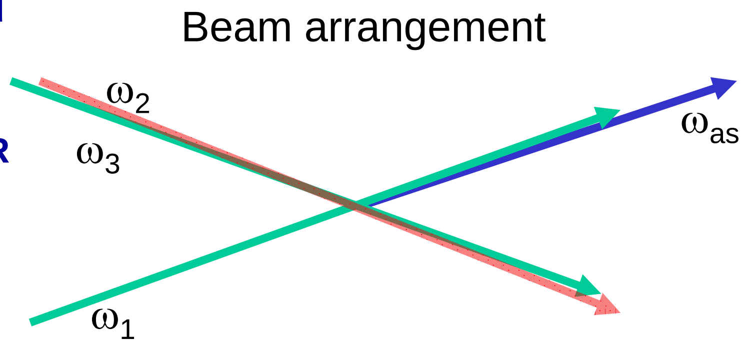
Broadband CARS

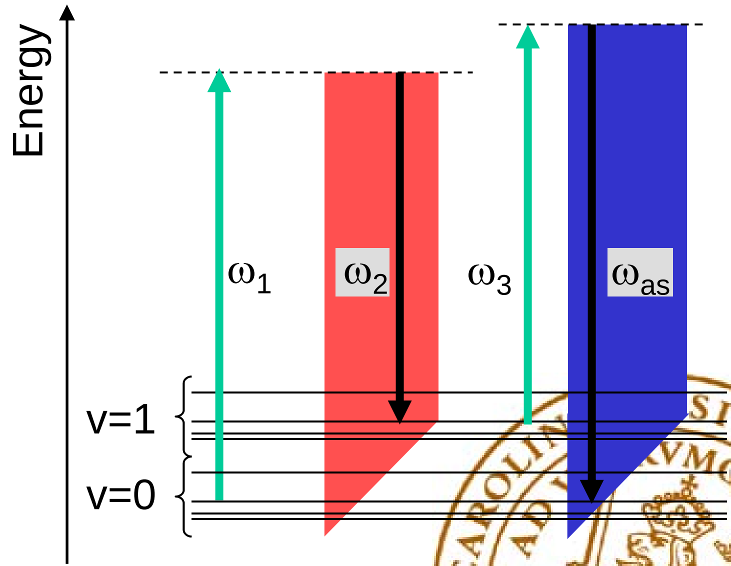


Advantage:
Spectra is obtained within 10 ns ⇒
can be used in turbulent flames

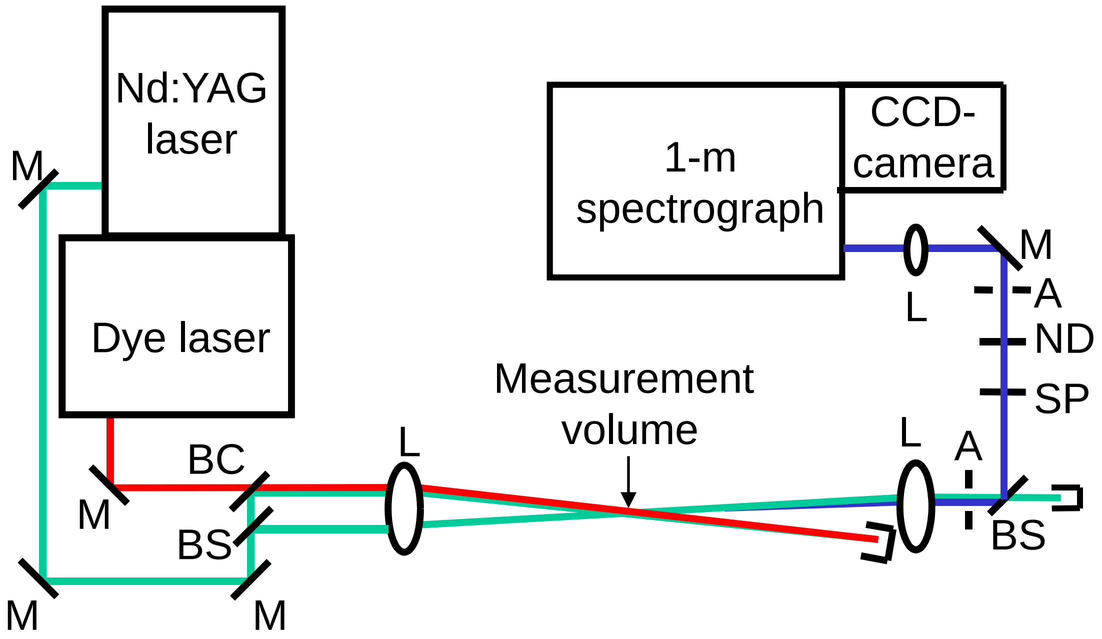
The selection of wavelengths

- **The energy difference between ω_1 and ω_2 must match a vibrational Raman resonance in the molecule. $\omega_1 - \omega_2 = \omega_R$**
- **For nitrogen, with $\omega_R = 2331\ \mathrm{cm}^{-1}$, 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: $\omega_{CARS} = \omega_1 - \omega_2 + \omega_3$, 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)



M = Mirror
BS = Beam splitter
BC = Beam combiner
A = Aperture
ND = Neutral density filter
CCD = Charge-coupled device
L = Lens
SP = Short-pass filter

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.

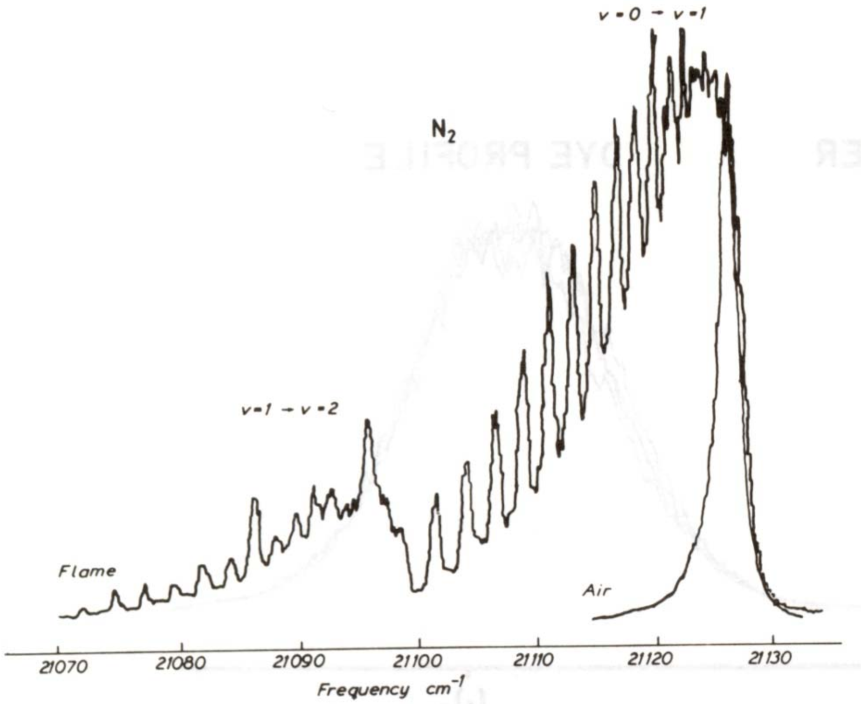
Optical components

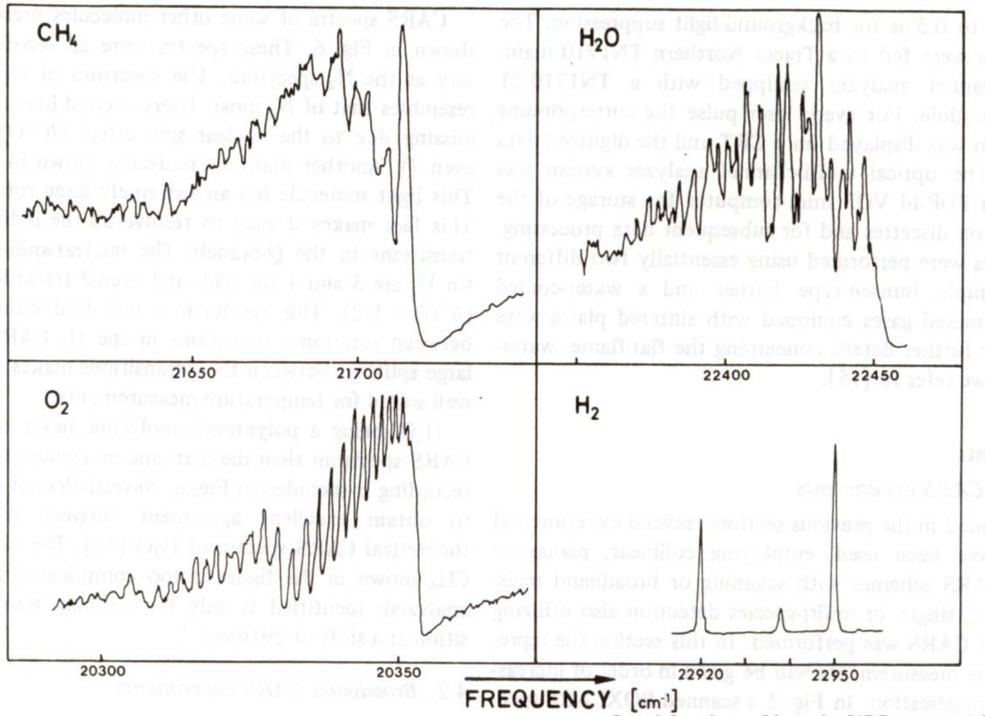
Special optics that can stand high pulse energies are needed.

Detection system

High-resolution spectrometer + CCD-camera

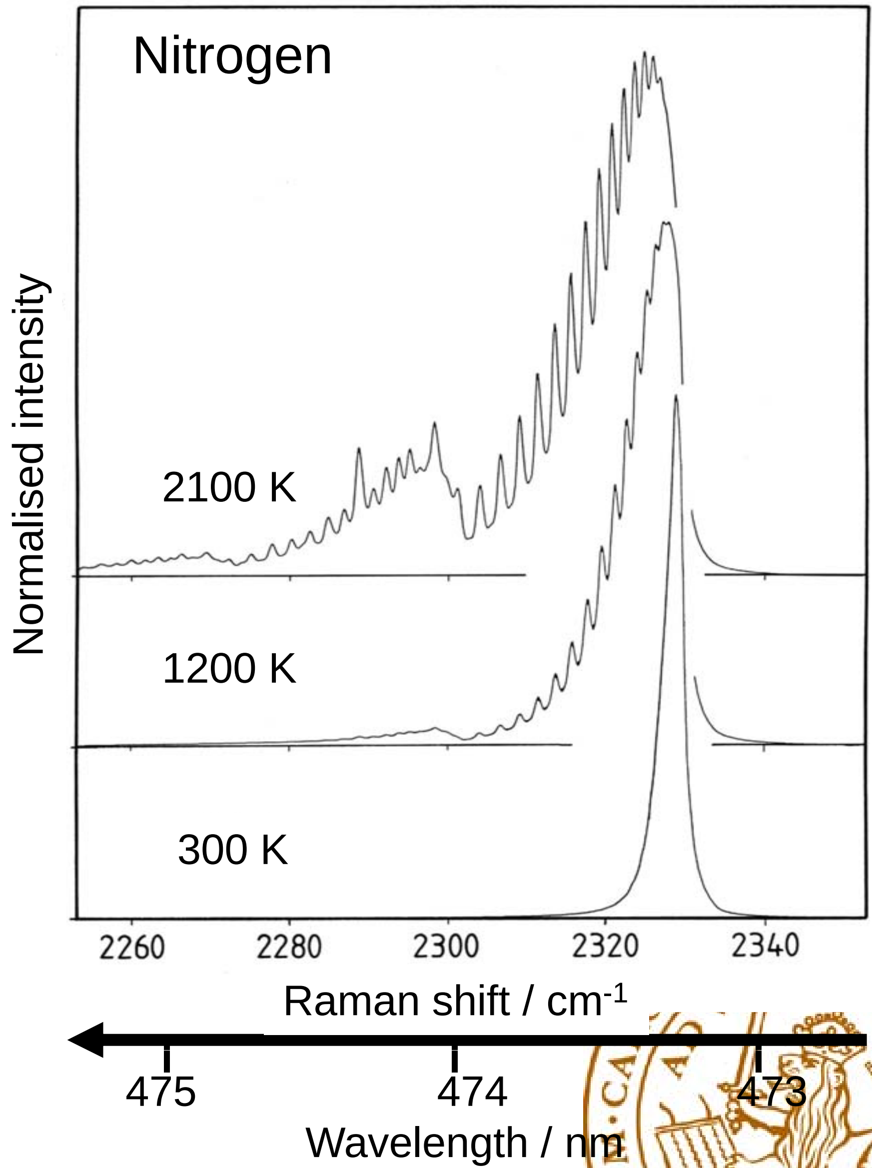
Experimental CARS spectra (scanned)



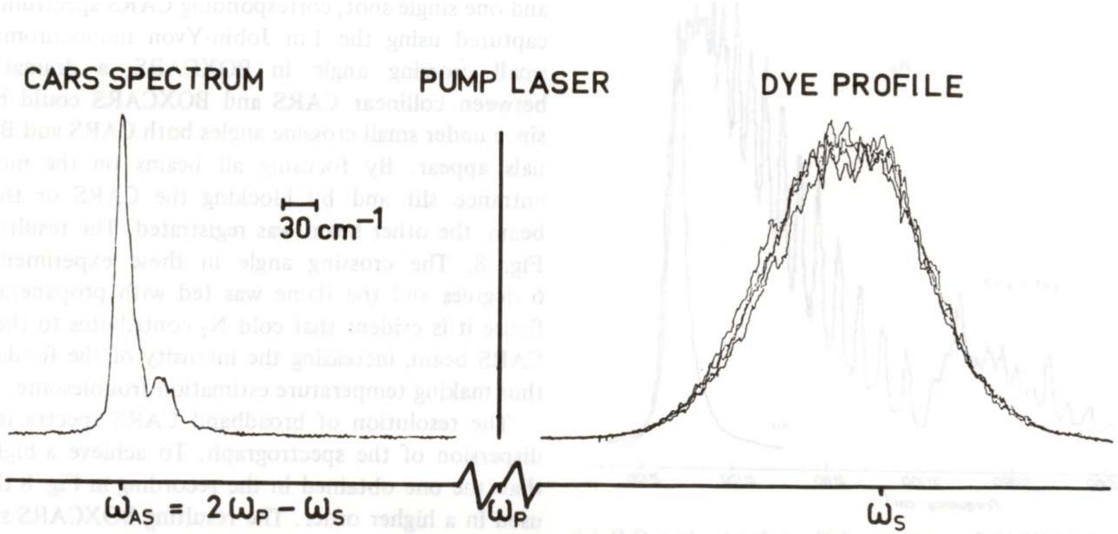


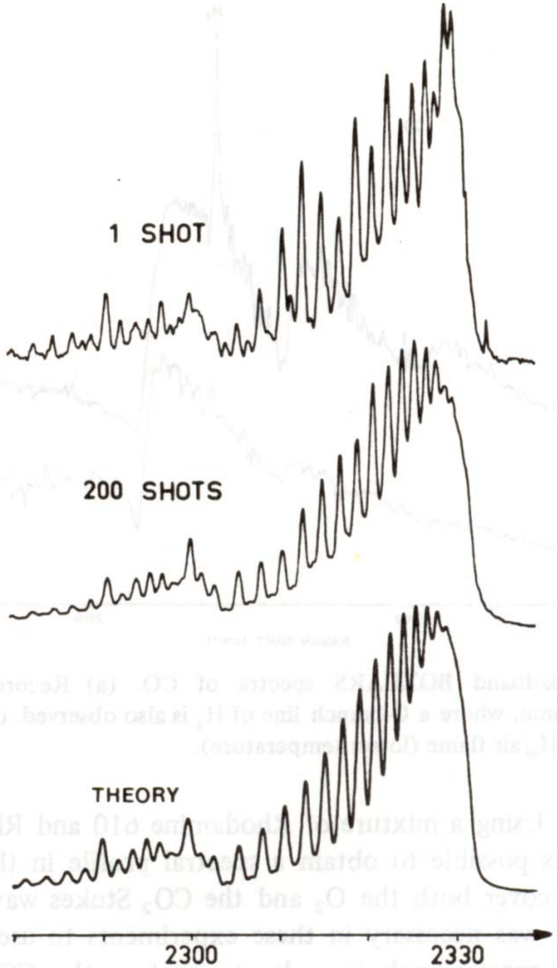
Temperature measurements

- 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.



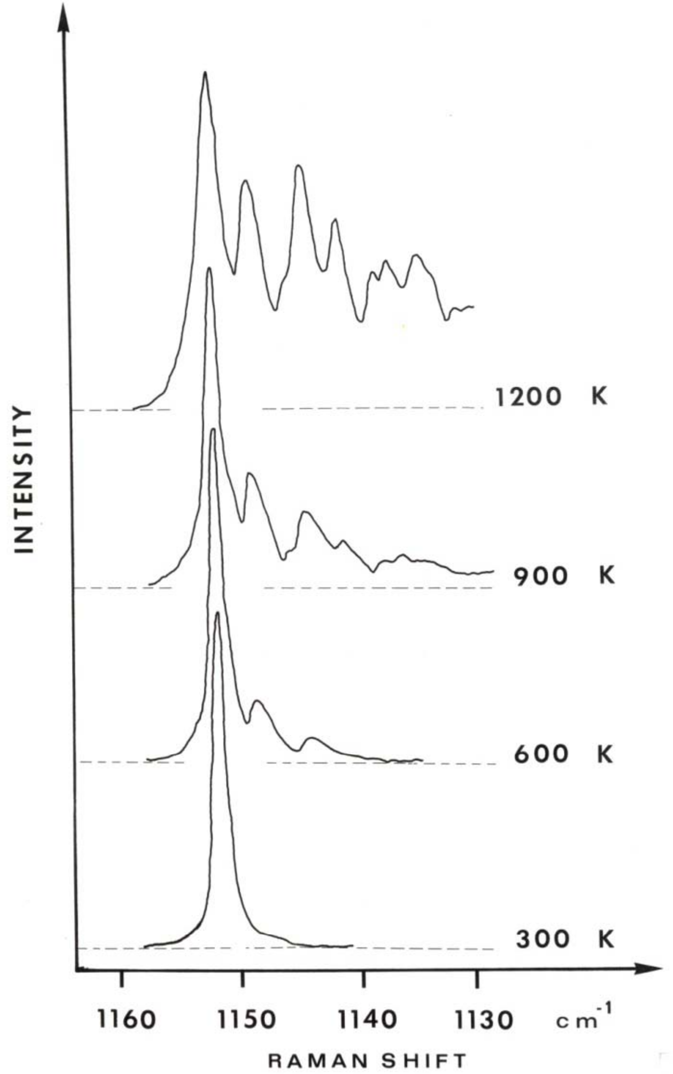
Broadband CARS (N_2)

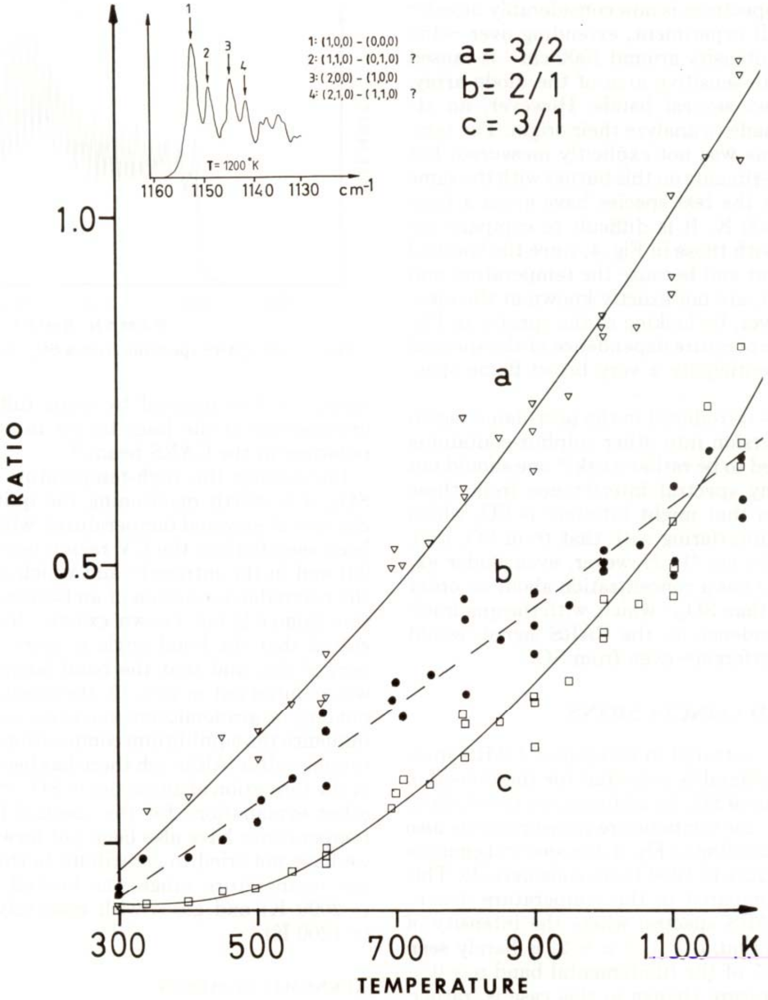




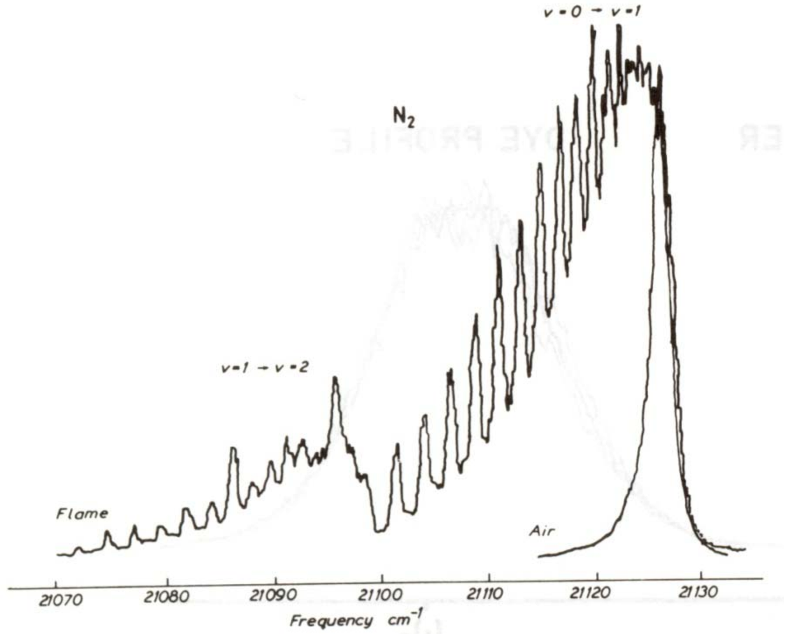
T = 1900 K

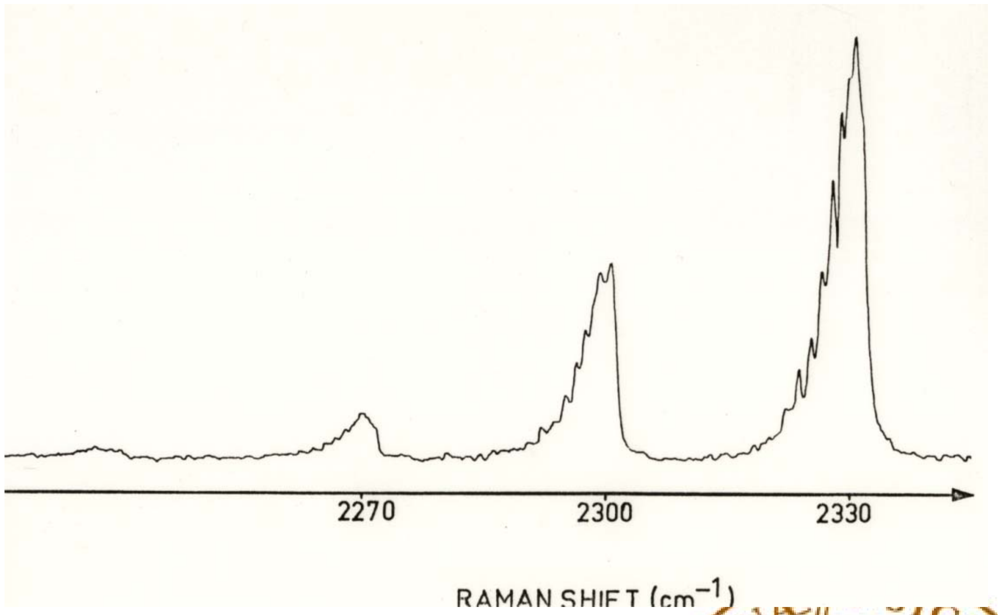
CARS on SO_2


INTENSITY
1200 K
900 K
600 K
300 K
1160
1150
1140
1130
cm-1
RAMAN SHIFT


1: (1,0,0) - (0,0,0)
2: (1,1,0) - (0,1,0) ?
3: (2,0,0) - (1,0,0)
4: (2,1,0) - (1,1,0) ?
T= 1200 °K
1160 1150 1140 1130 cm-1
a = 3/2
b = 2/1
c = 3/1
RATIO
1.0
0.5
a
b
c
300
500
700
900
1100 K
TEMPERATURE

What does thermal equilibrium mean?



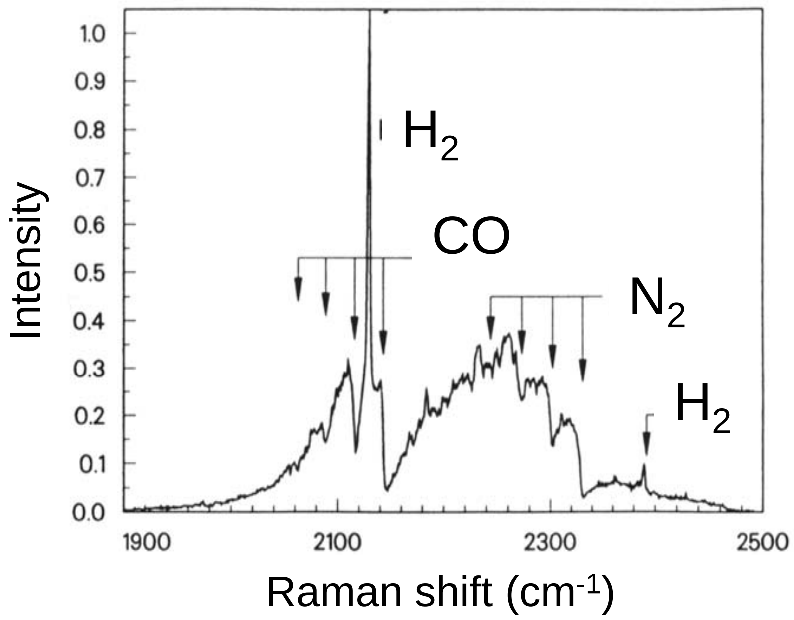


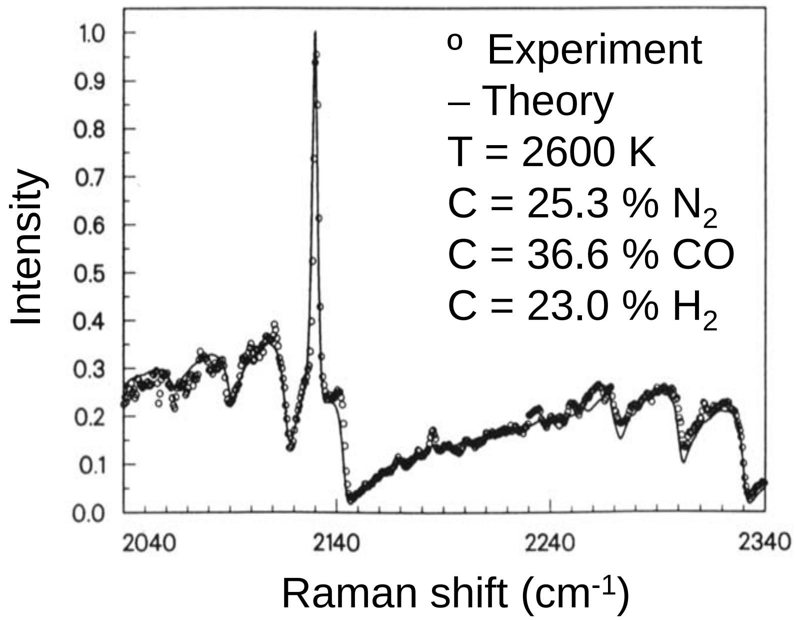
Flame: $T_{vib}=T_{rot}$

Discharge: $T_{vib}\neq T_{rot}$

Concentration measurements

- Concentration measurements are normally made from the spectral shape.
- The figure shows an experimental spectrum with contributions from H_2, CO, and N_2.
- The lower figure shows the same experimental data together with a fitted curve. The evaluation gave all three concentrations together with the temperature.

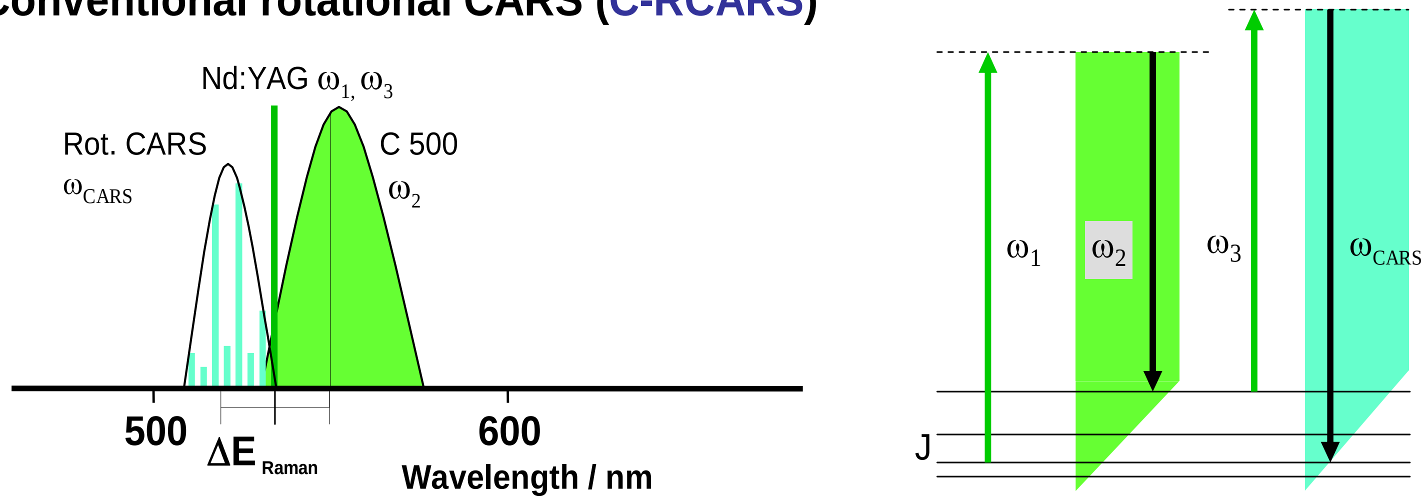




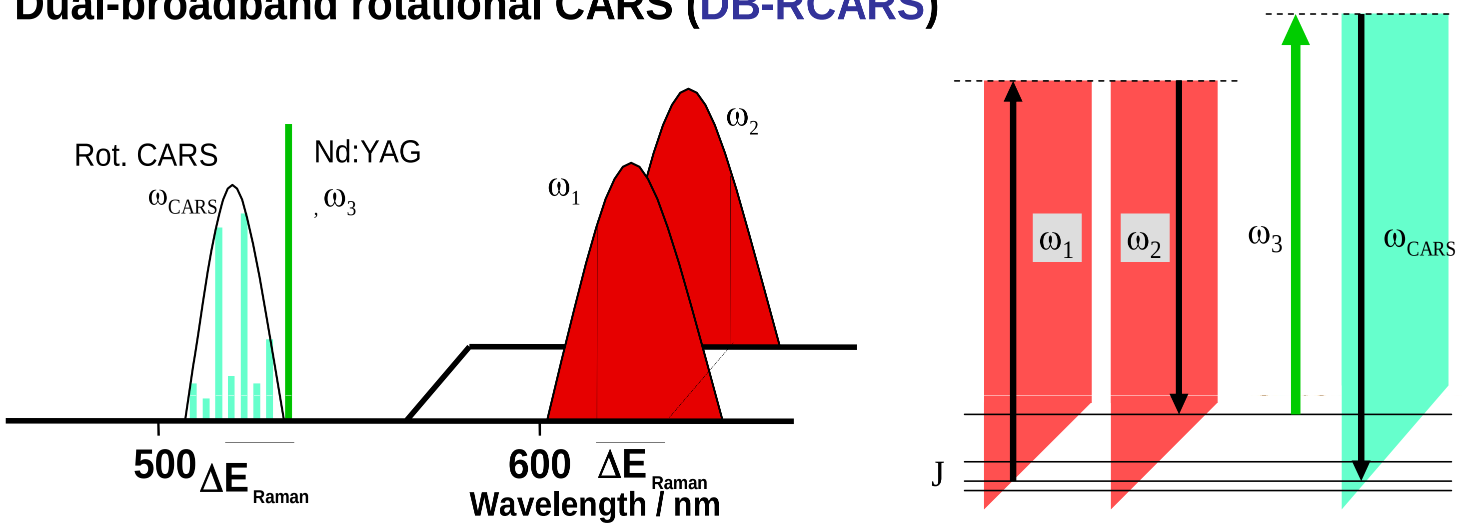
Figures are from Stufflebeam and Eckbreth, Combust. Sci. and Tech. 66, 163-169 (1989)

Rotational CARS

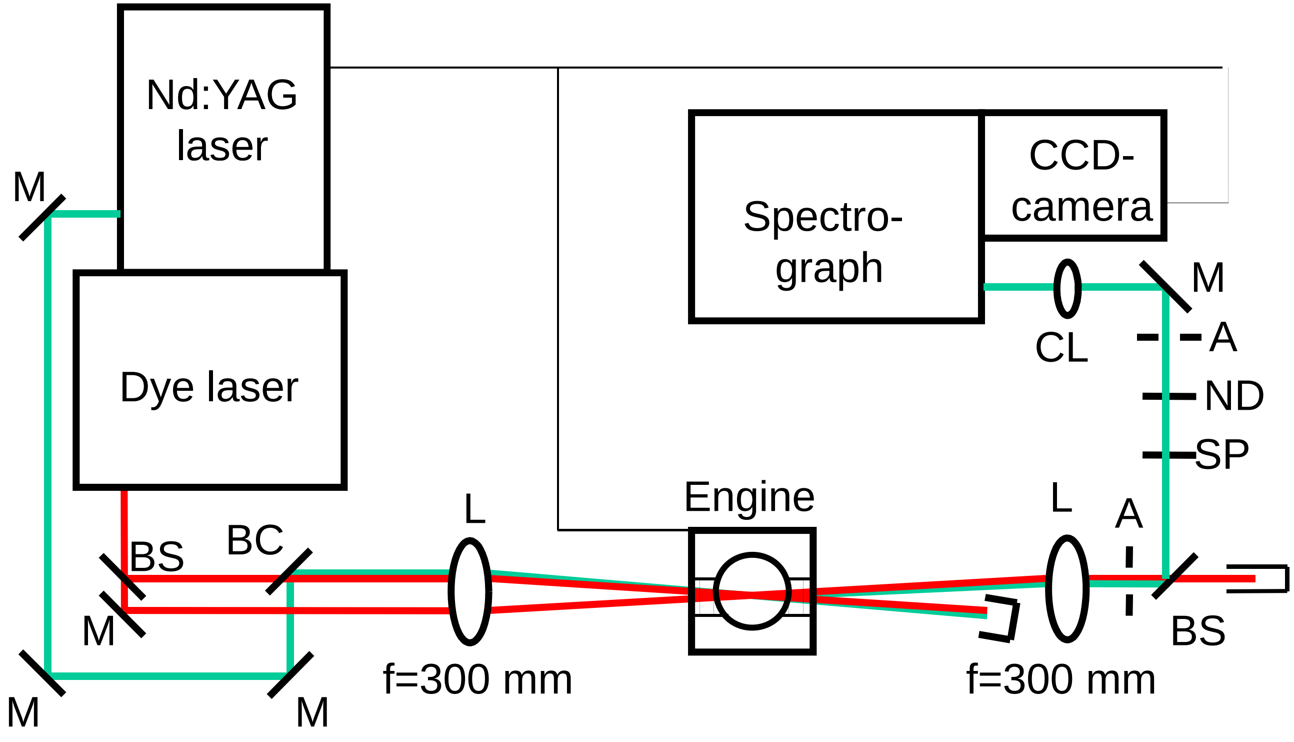
Conventional rotational CARS (C-RCARS)



Dual-broadband rotational CARS (DB-RCARS)



Experimental set-up for rotational CARS



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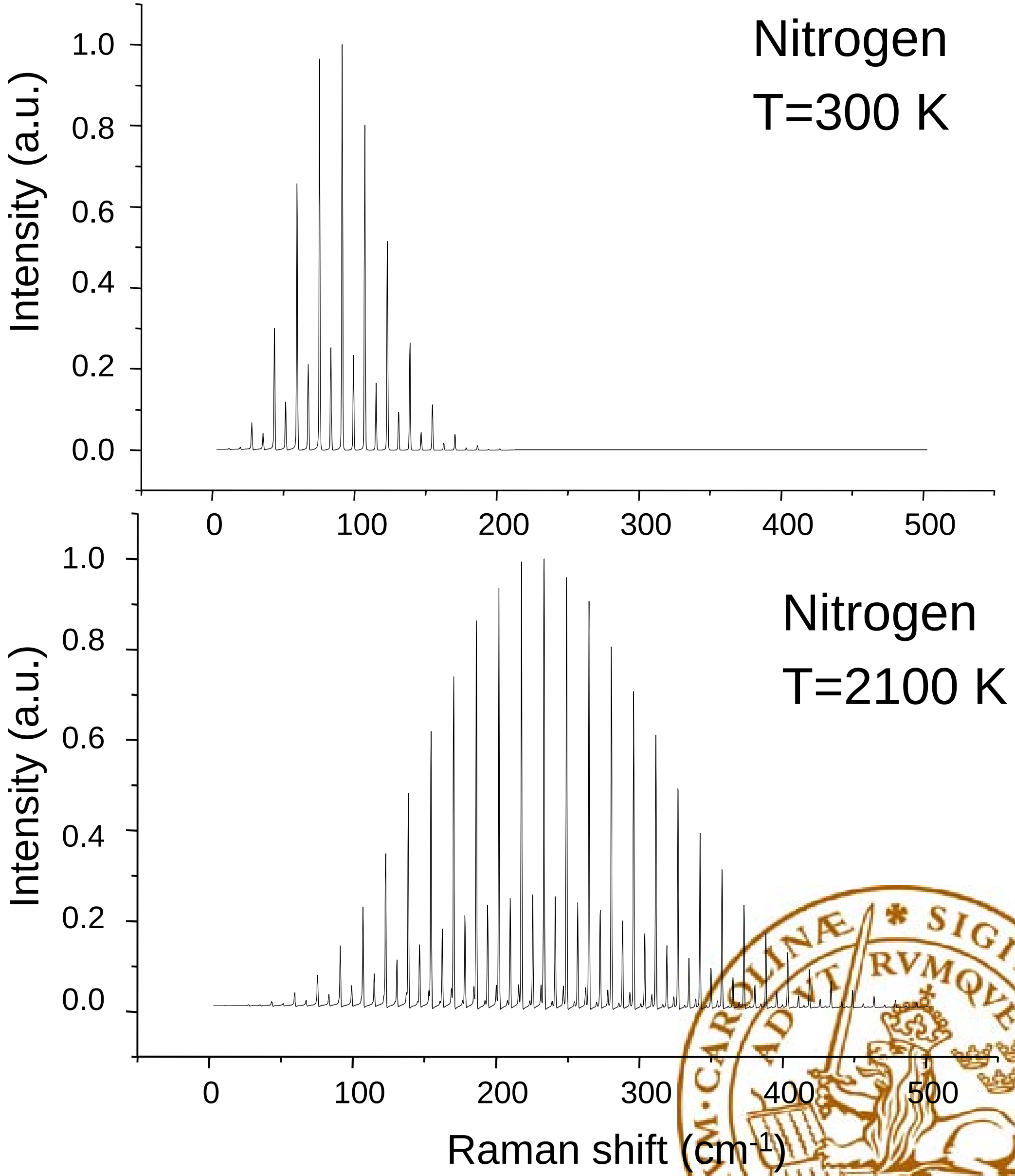
CL = Cylindrical lens
ND = Neutral density filter
CCD = Charge-coupled device camera
L = Lens
SP = Short-pass filter

- **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.**

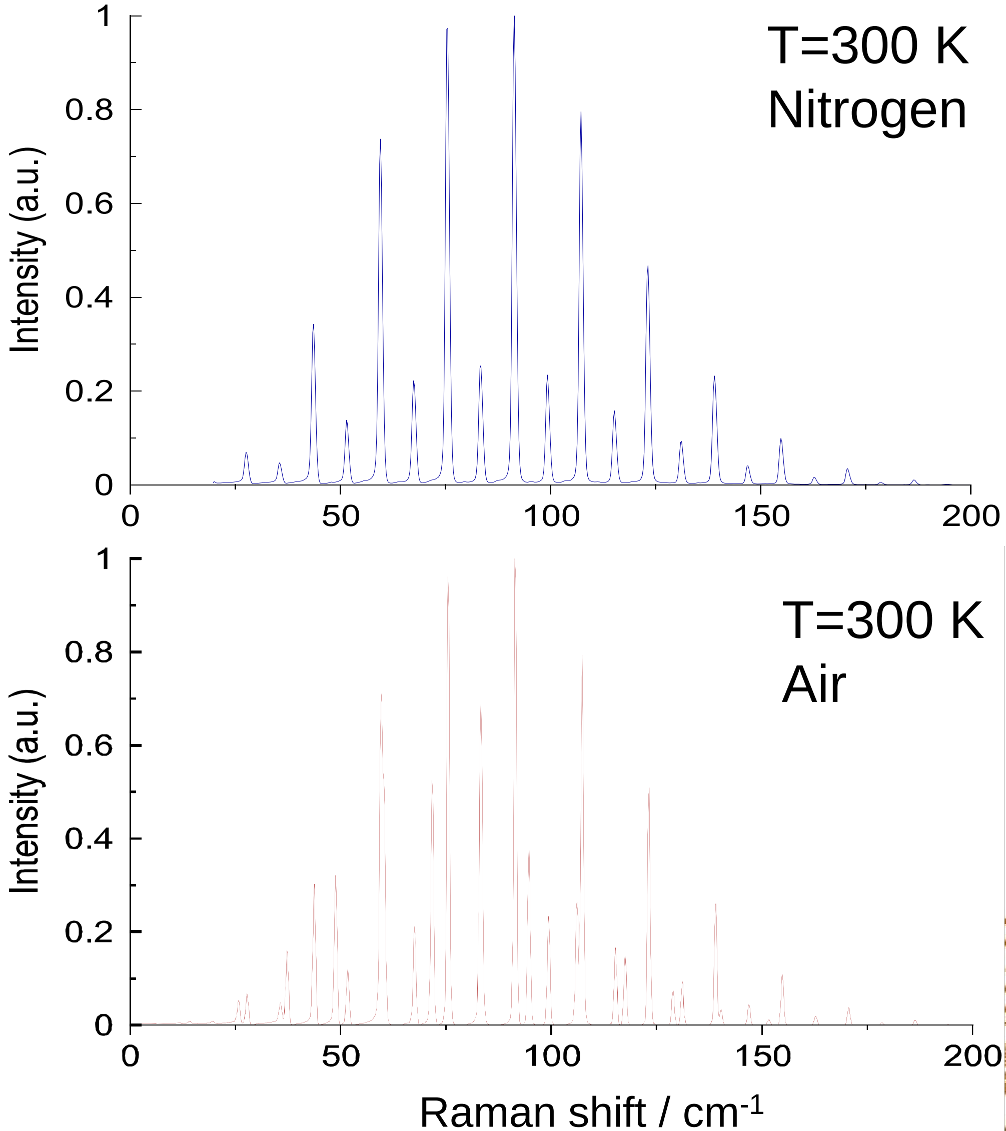
Temperature measurements

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



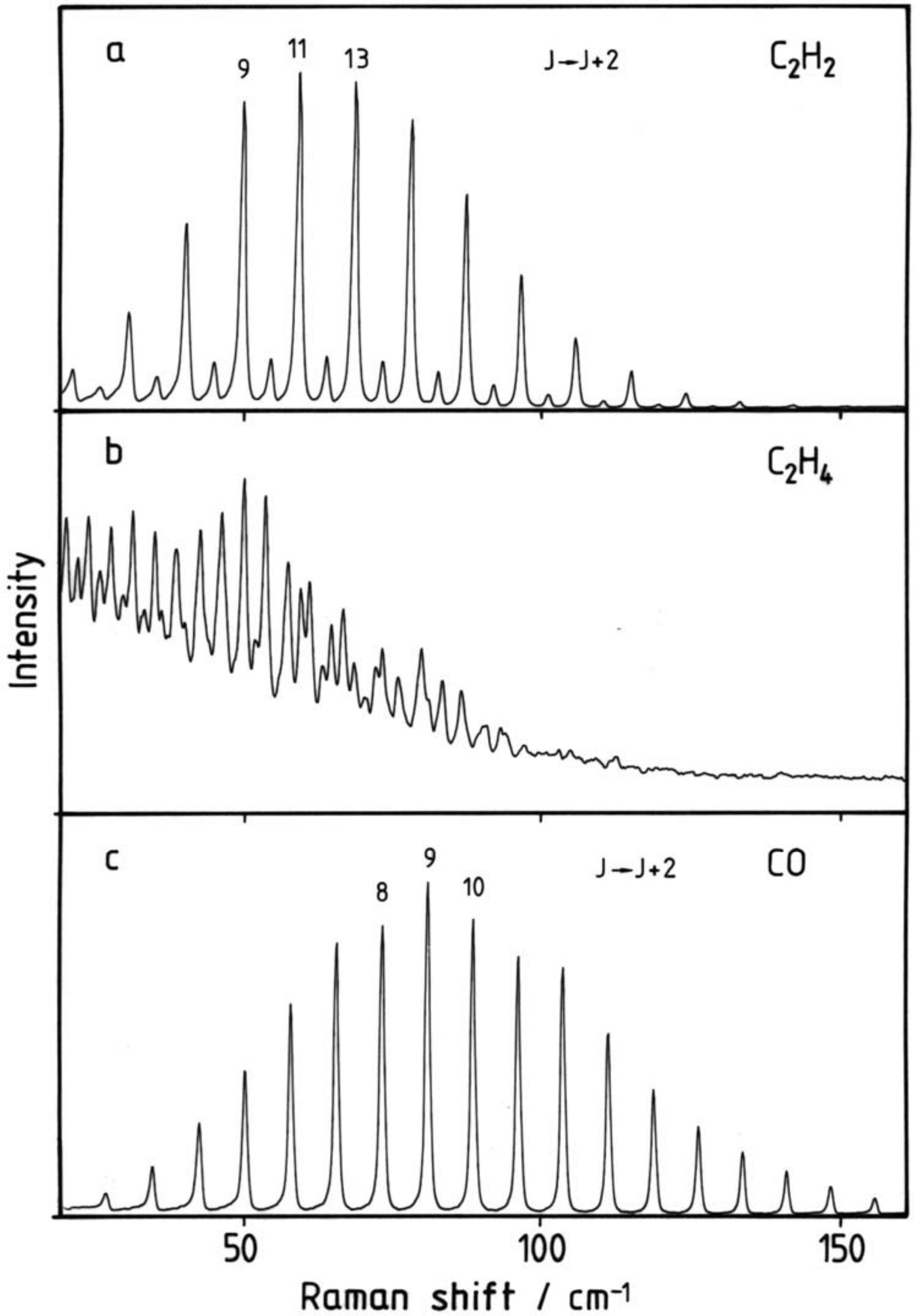
Concentration measurements

- Rotational CARS spectra from many species (N_2, O_2, CO, 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

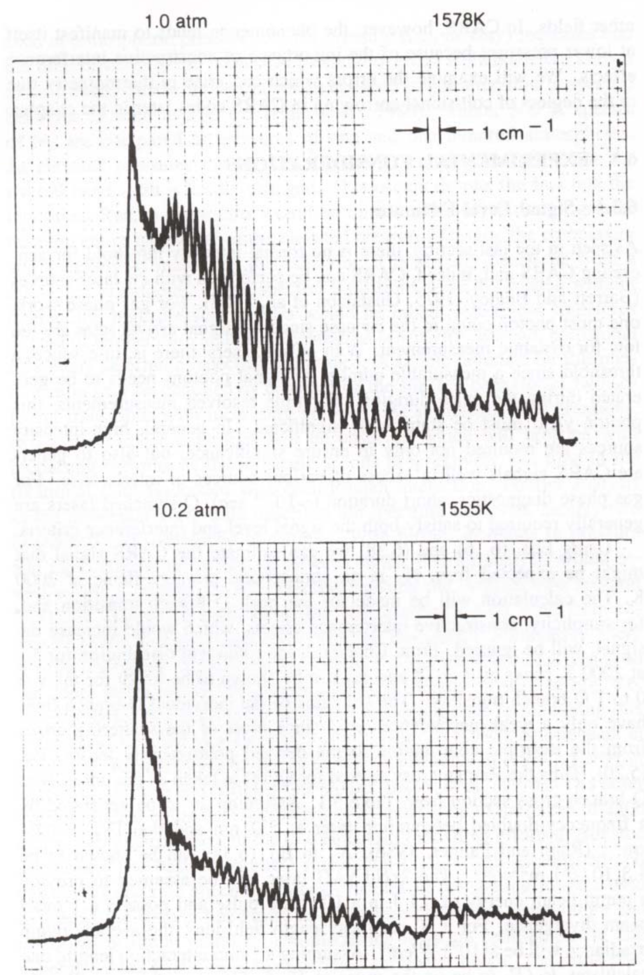
- Linear molecules give clear distinct spectra.
- Smaller molecules have higher B-constants and result in wider spectra.



Advantages with CARS for practical applications

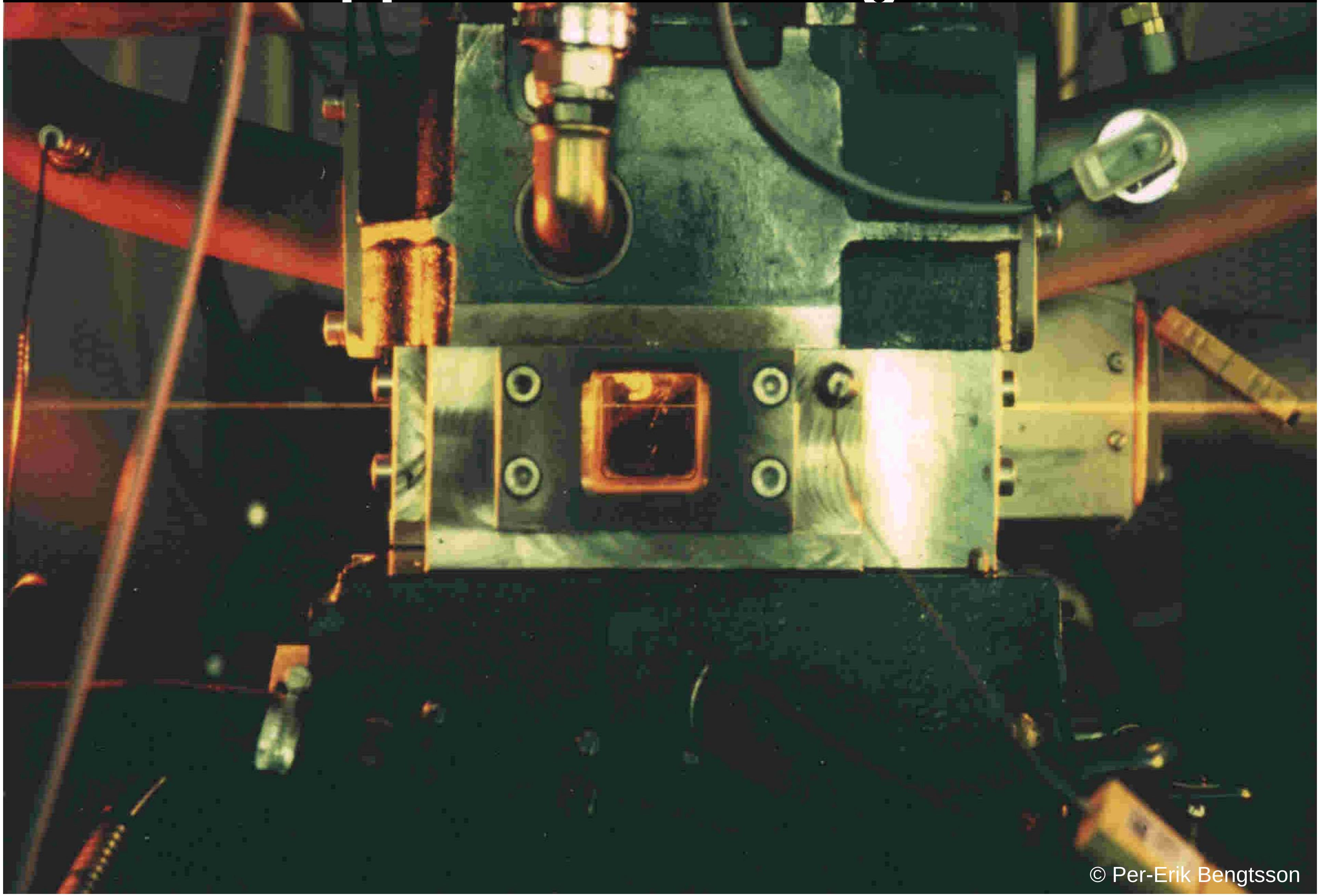
- **Signal as a new laser beam**
- **Strong signal**
- **CARS signal on the anti-Stokes side**
- **Measurements on nitrogen molecules (max signal)**

Special issue: High pressure effects

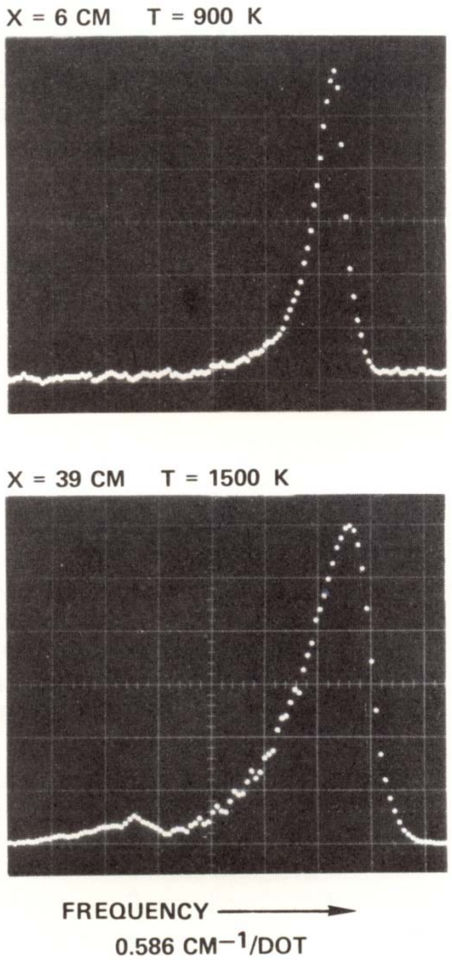


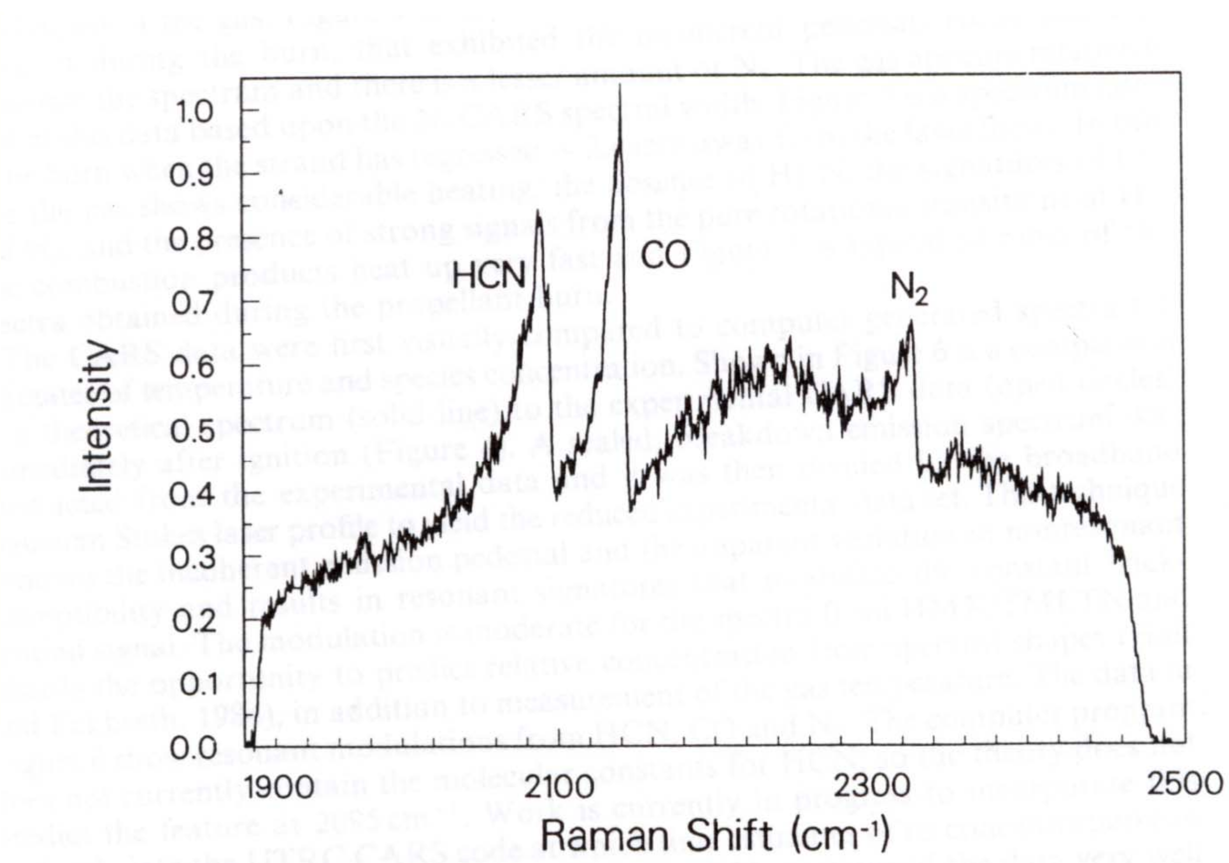
Ref: Eckbreth et al.

Applications to engines



Vibrational CARS applications





CARS spectra:

In a burning spray of JET-A

Burning of solid propellants

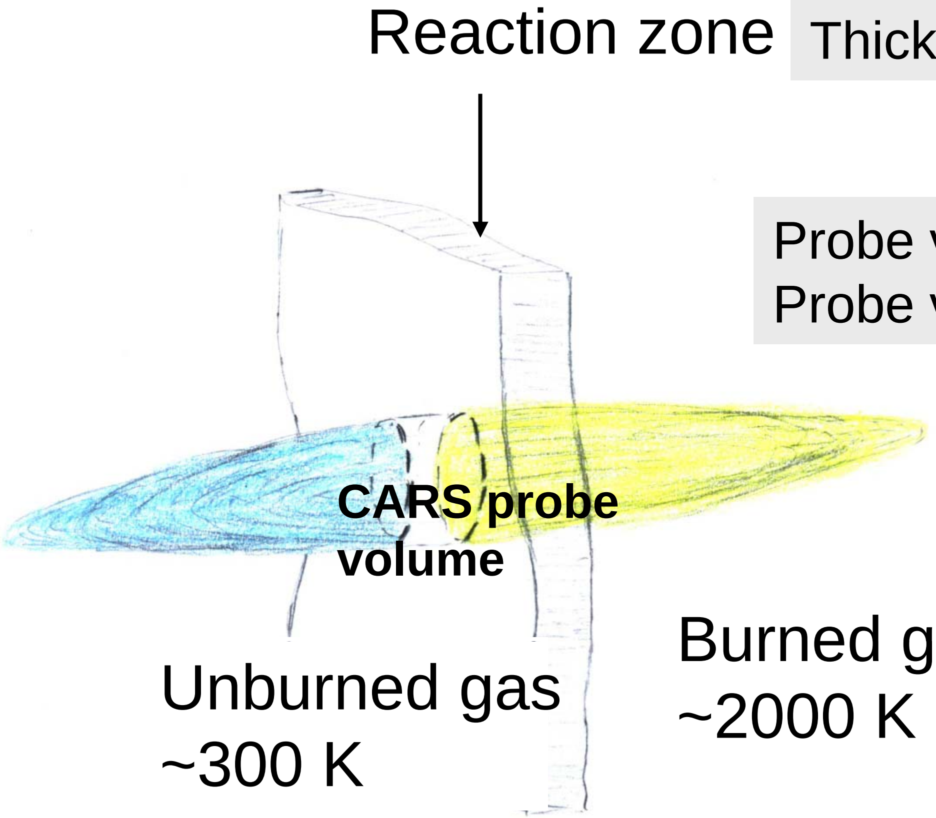
A.C Eckbret et al.

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

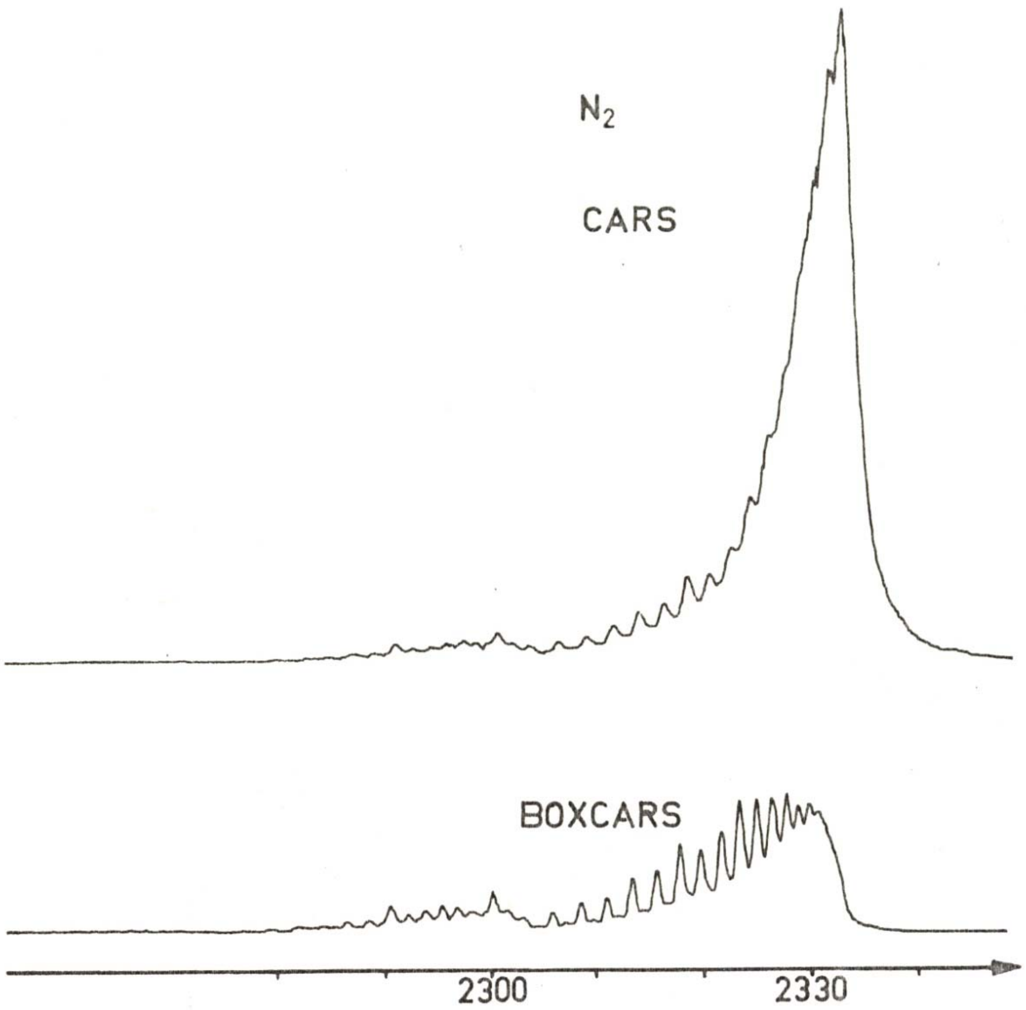
Thickness: ~100 μm



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

The result will be a "mixed spectrum" with a strong low-temperature part

Comparison between collinear CARS and BOXCARS



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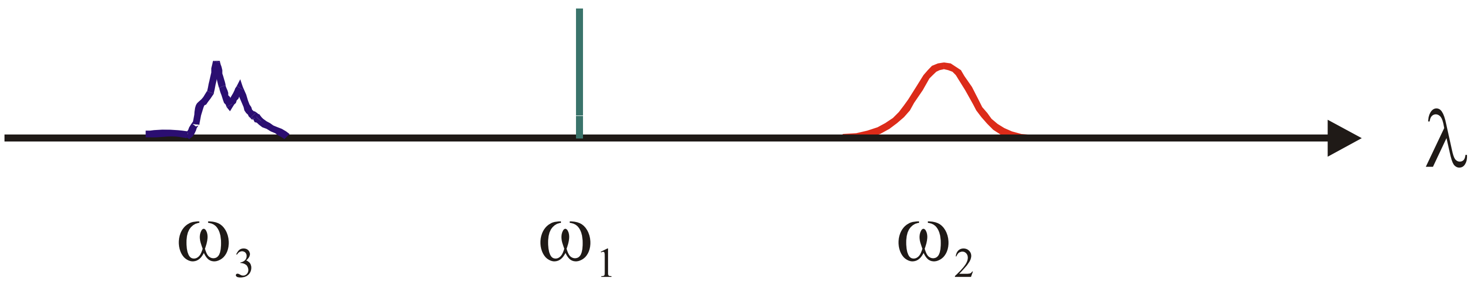
Potential solution: 2-λ CARS

One measuring situation where 2-λ CARS has to be used

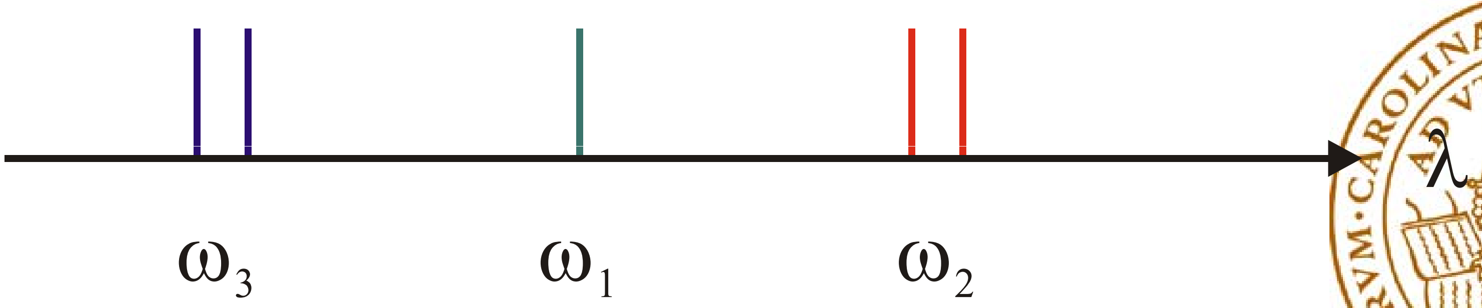
Concept of 2-λ CARS:

Use a two colour dye laser instead of a broad-band dye laser ⇒ higher spectral intensity

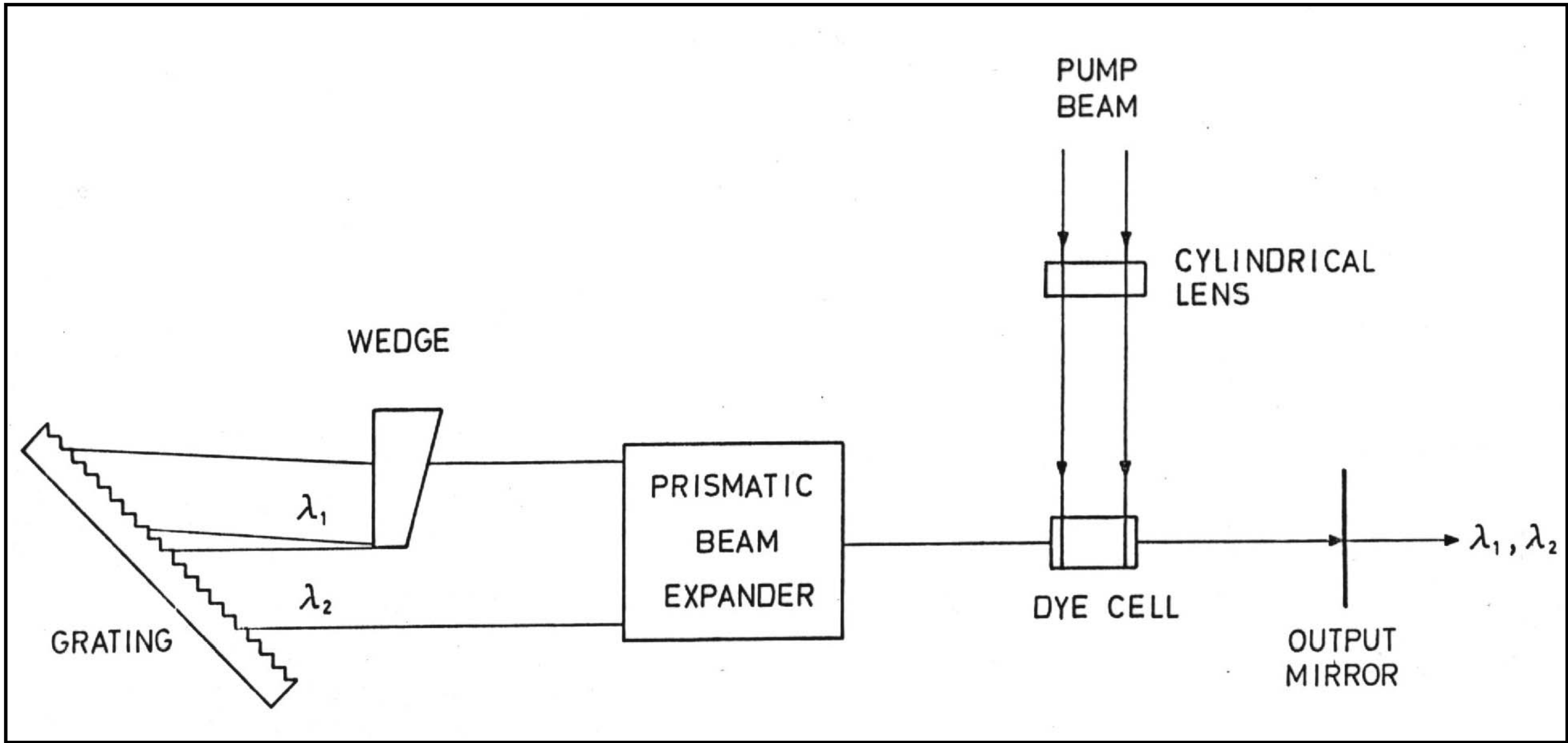
Broadband CARS



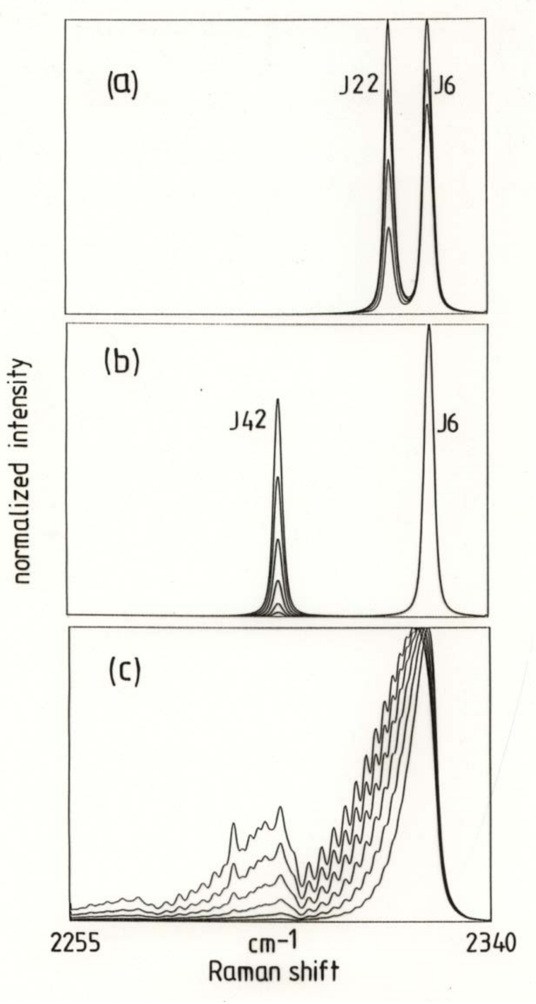
2 λ CARS

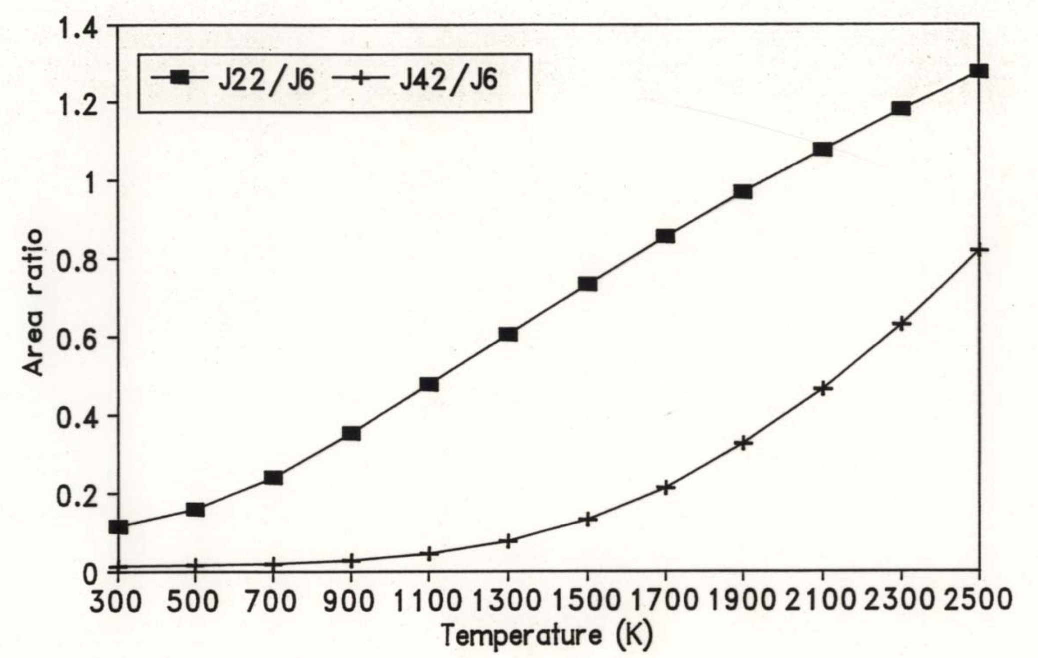


Experimental approach to produce a two colour dye laser



Wavelength selection in 2-λ CARS





Features of 2-λ CARS

Advantages:

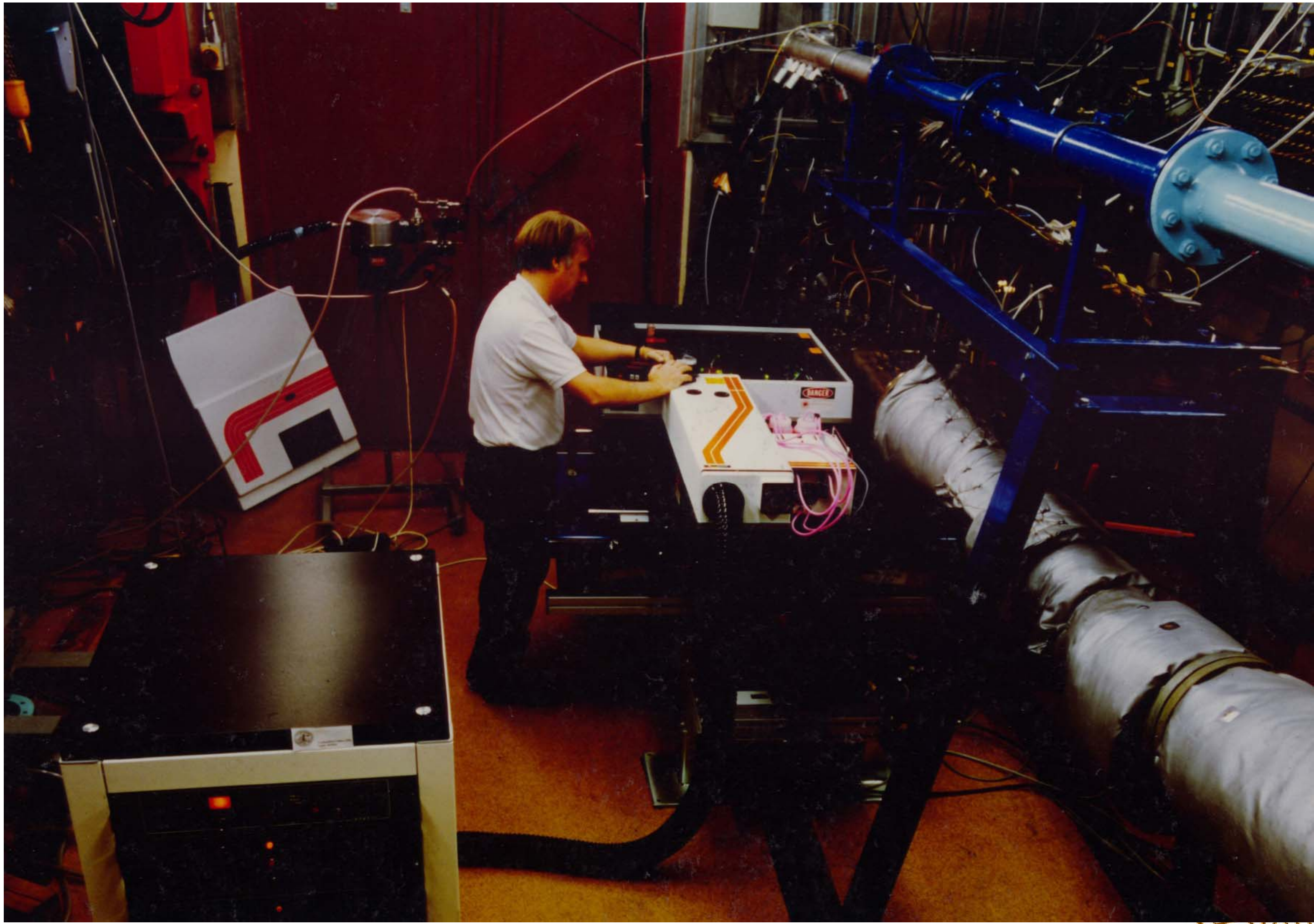
- **~ 30 times higher signal intensity ⇒ Higher spatial resolution, experiments in very applied areas possible**

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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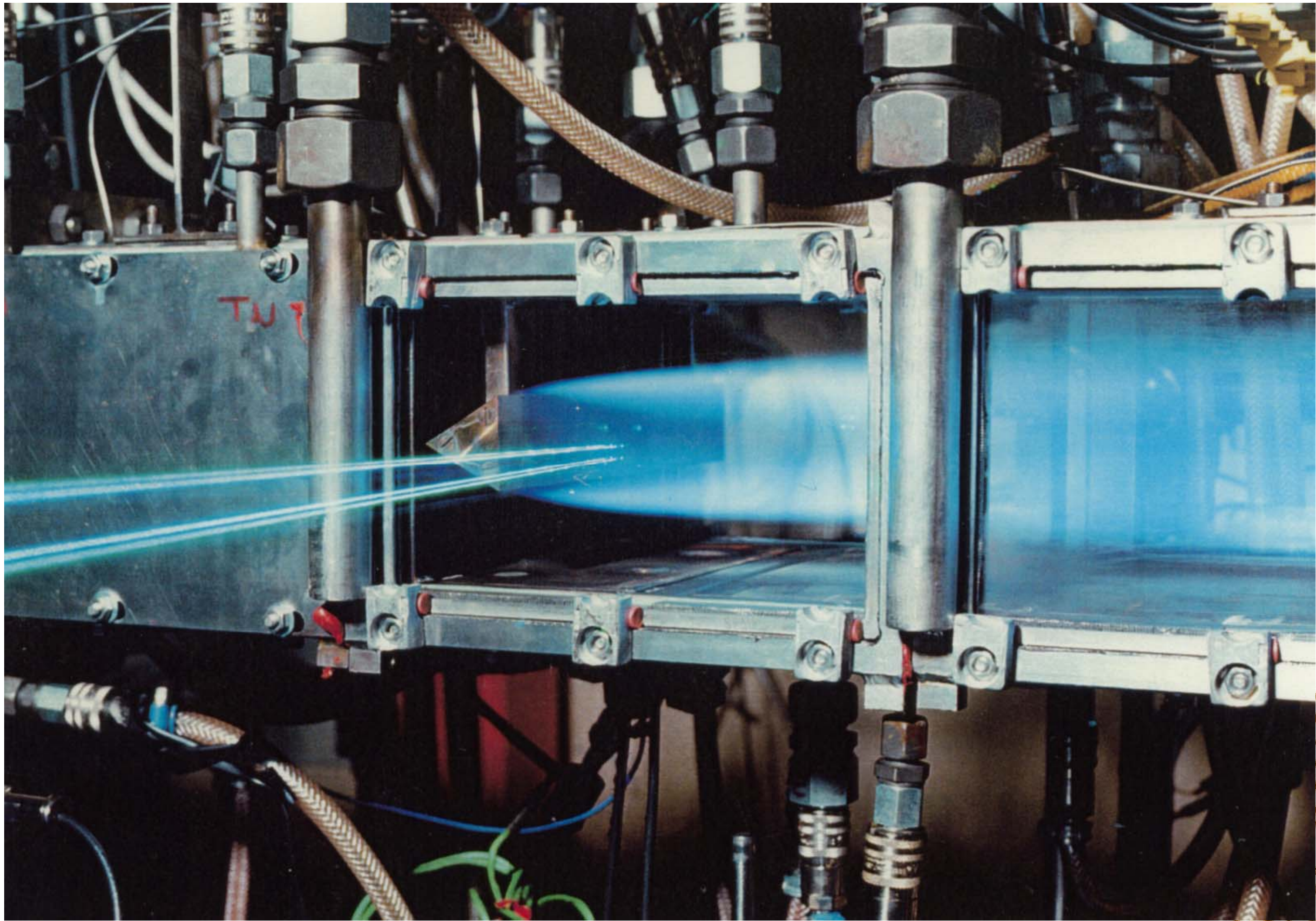

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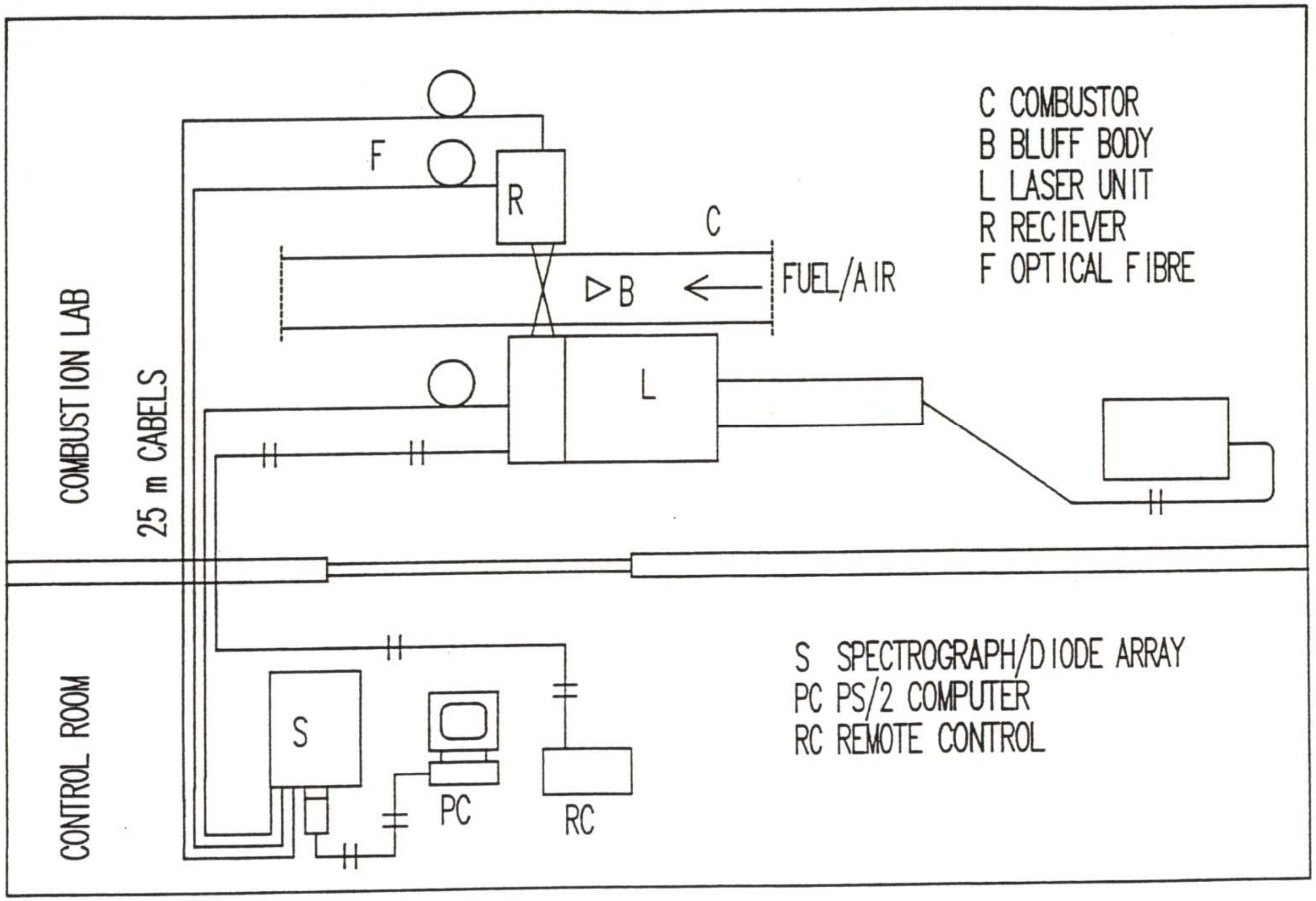
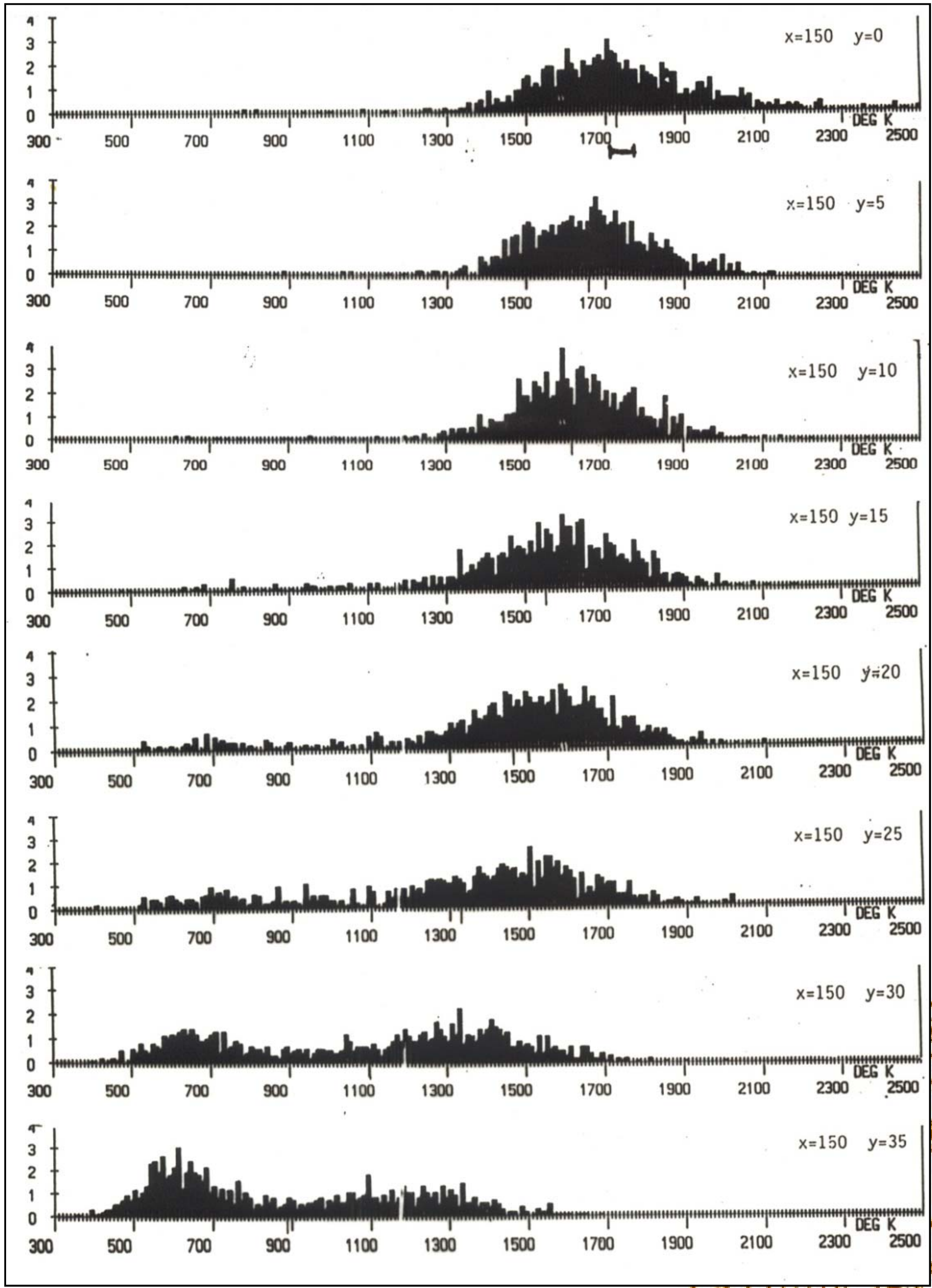
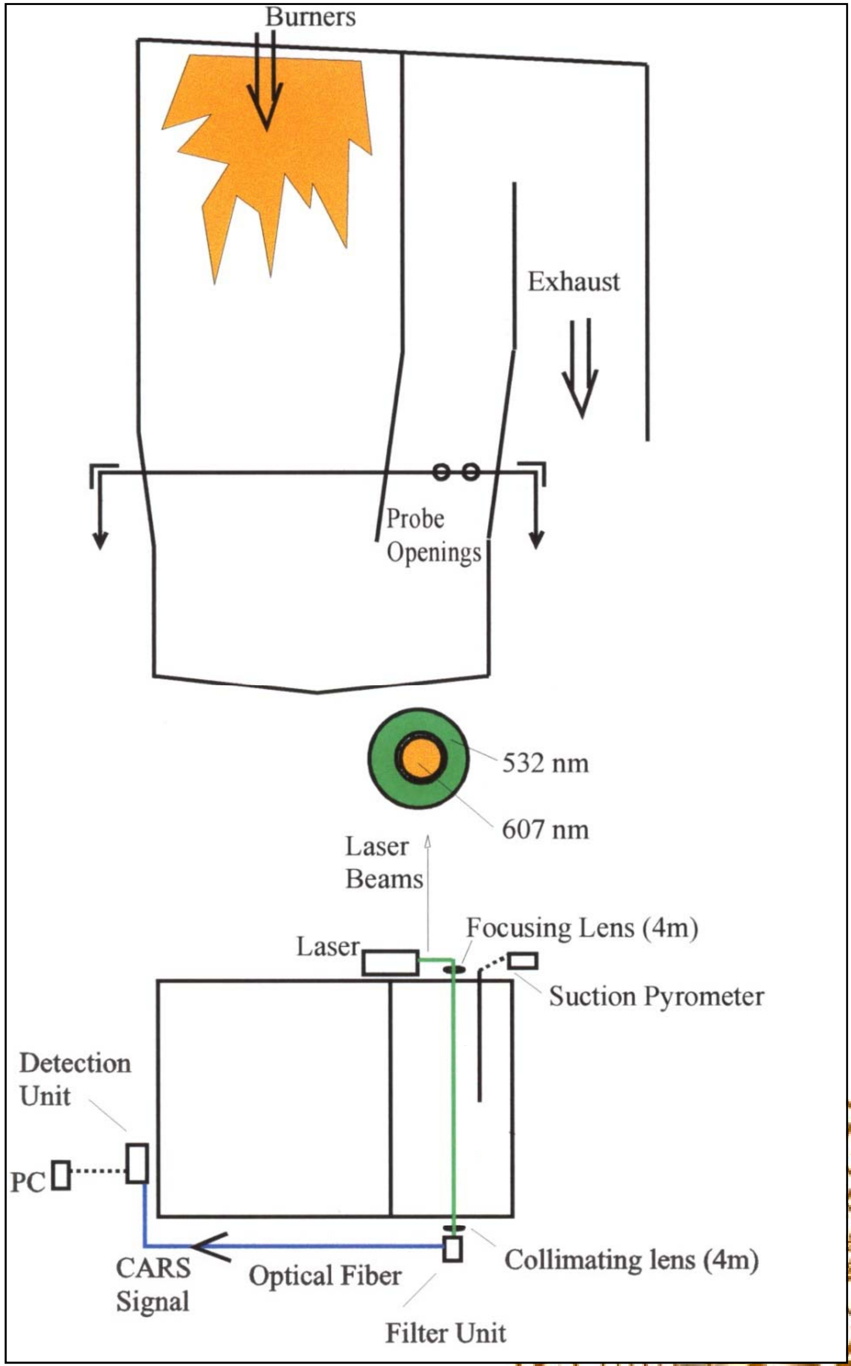


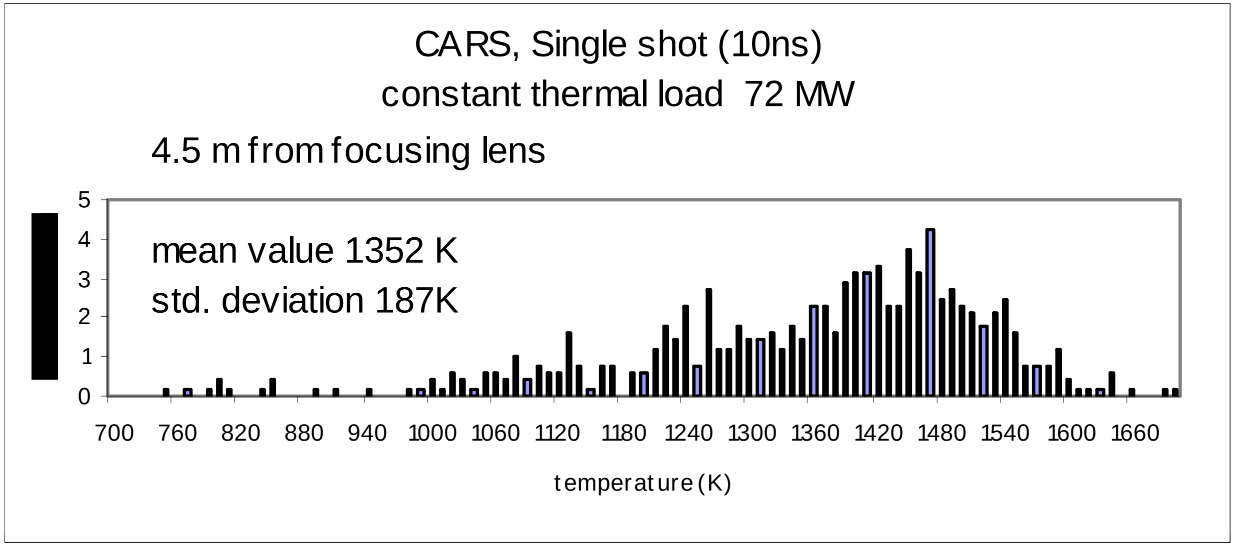
Temperature pdf:s at a distance 150 mm from the bluff body at different radial distances

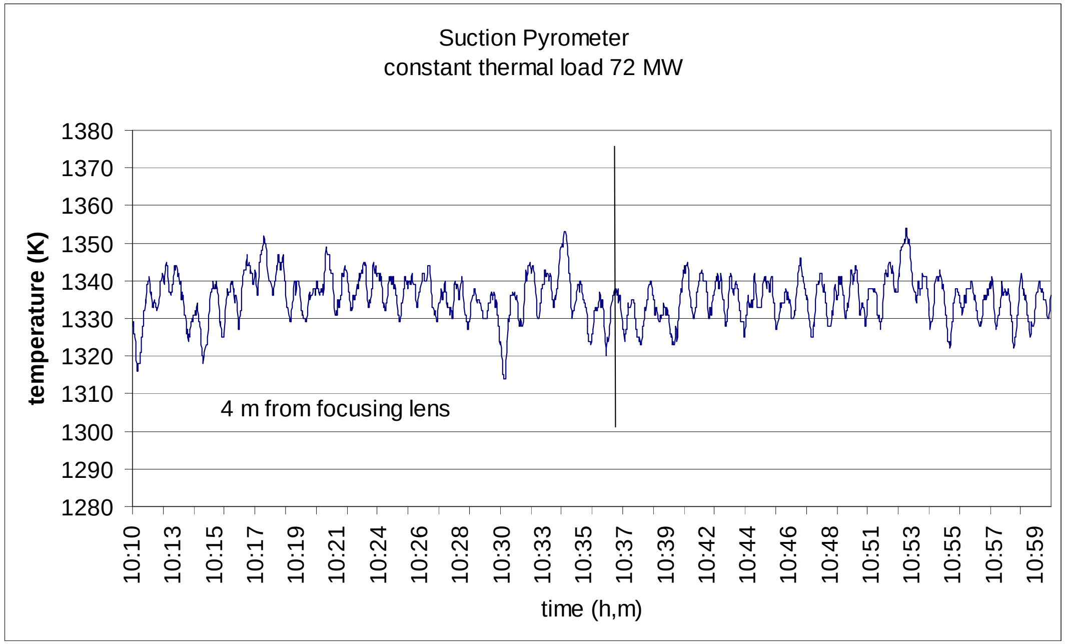


Practical diagnostics - CARS



Practical diagnostics - CARS

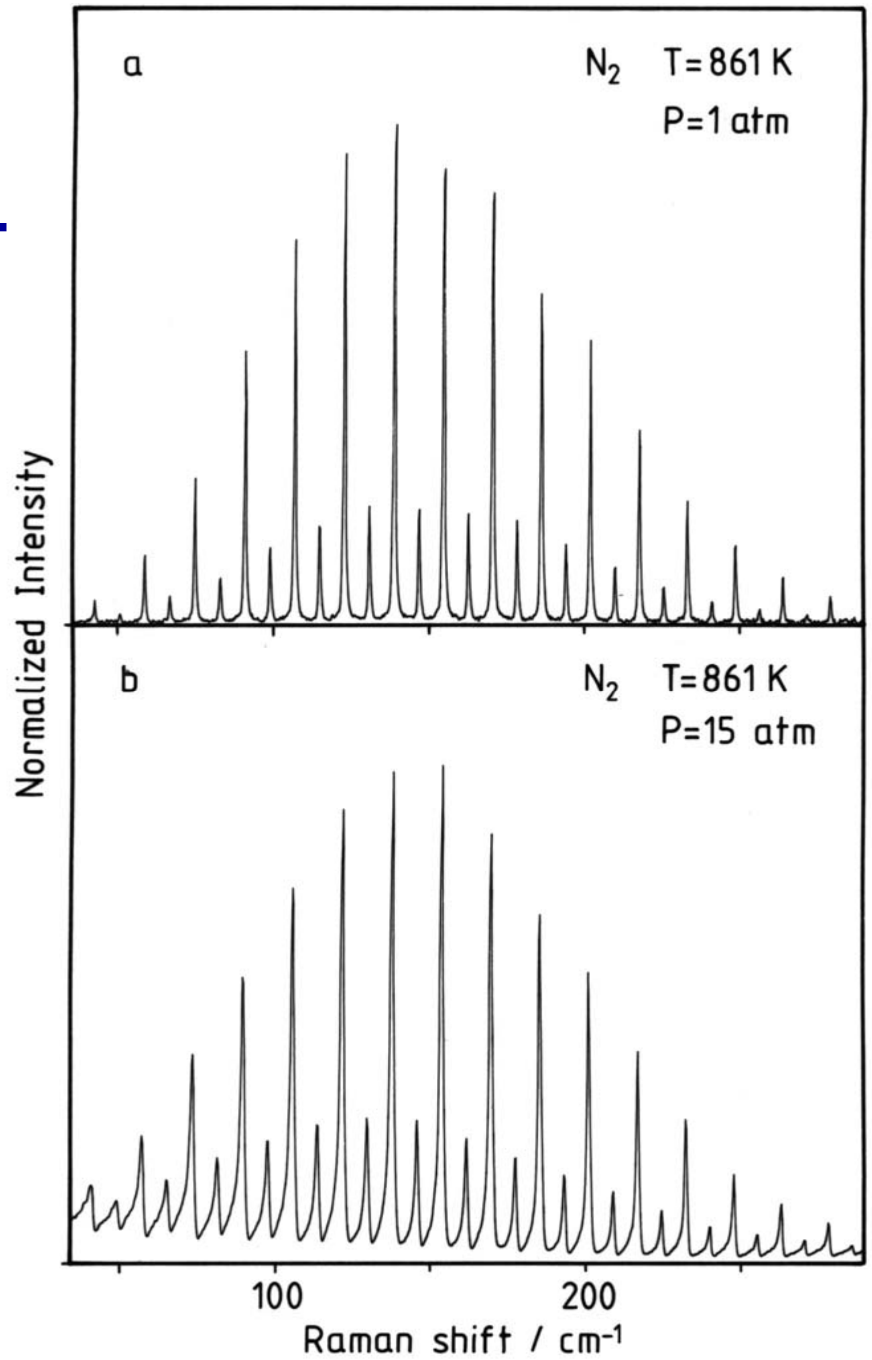




Pressure dependence for rotational CARS

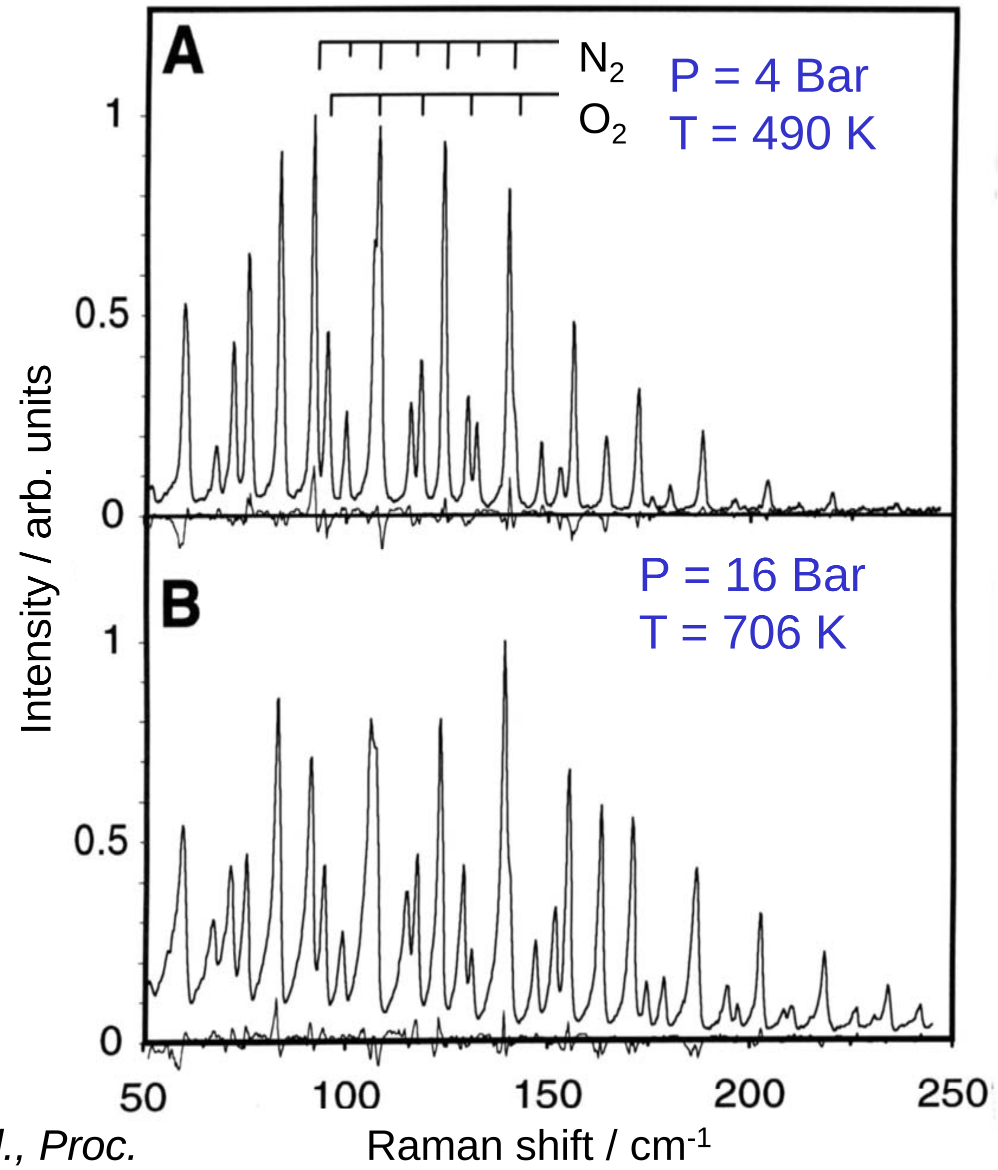
If pressure increases

- 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.



*Figures are from Bengtsson et al., Proc. Combust. Inst. **25**,: 1735-1742 (1994)*

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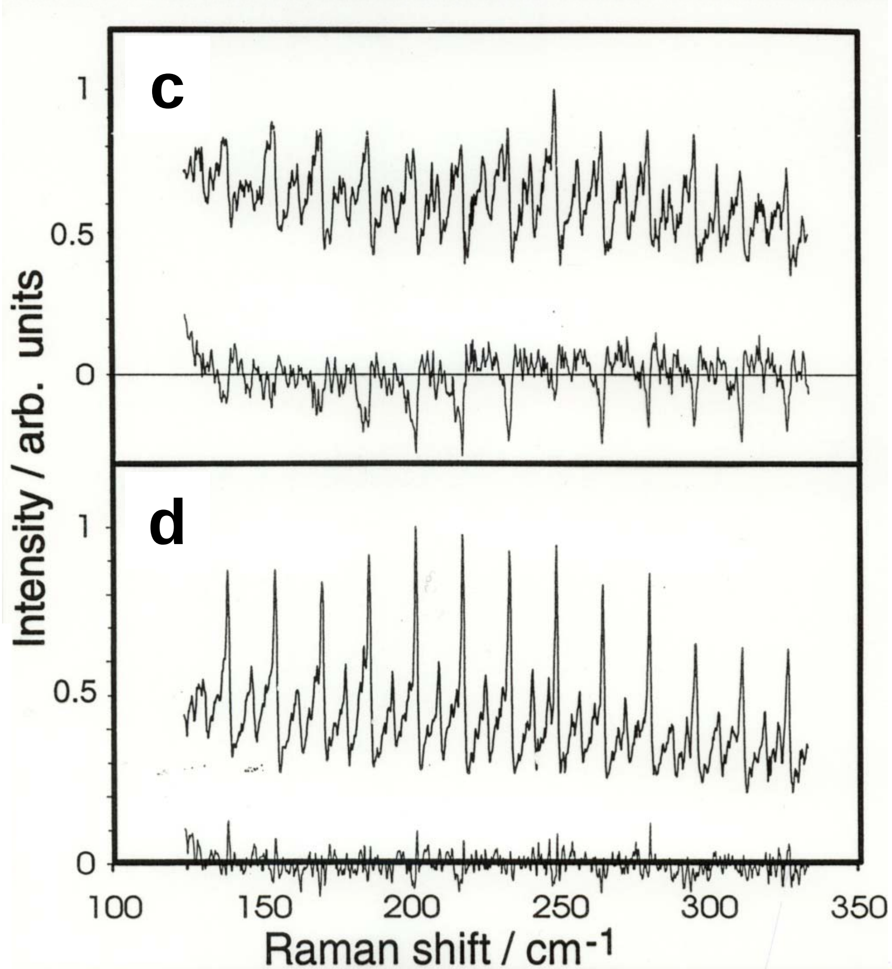
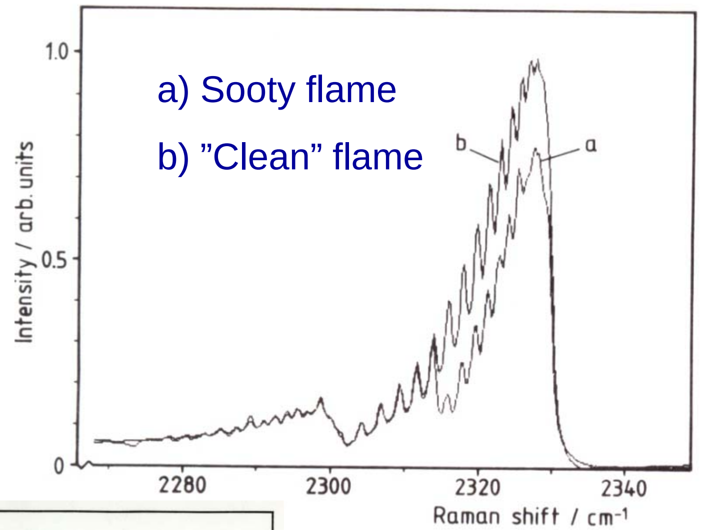


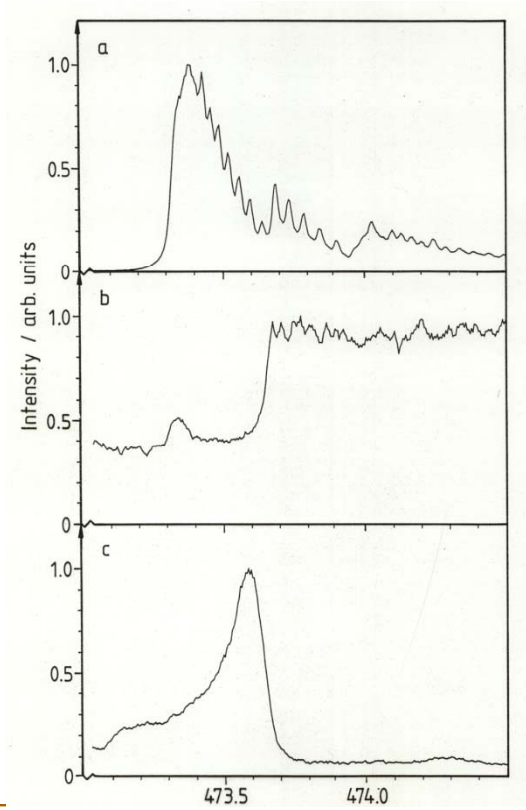
c: 32 CAD ATDC, 32 bar, 2550 K

d: 56 CAD ATDC, 15.5 bar, 2435 K

Figures are from Bengtsson et al., Proc. Combust. Inst. ***25****,: 1735-1742 (1994)*

Sooty flame diagnostics: Vib CARS

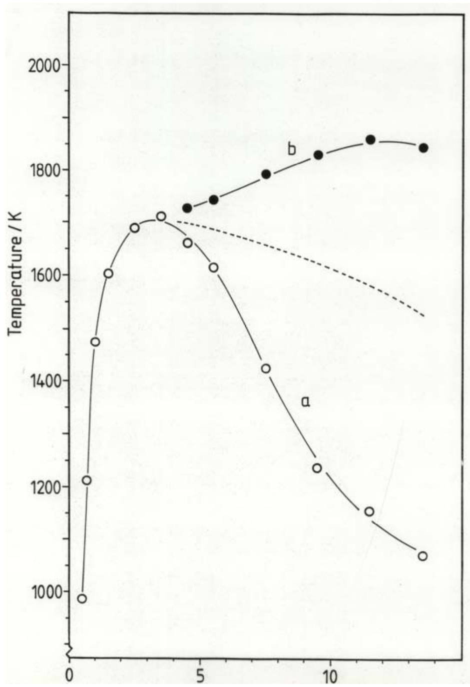




a) N_2 flame

b) Ar flame

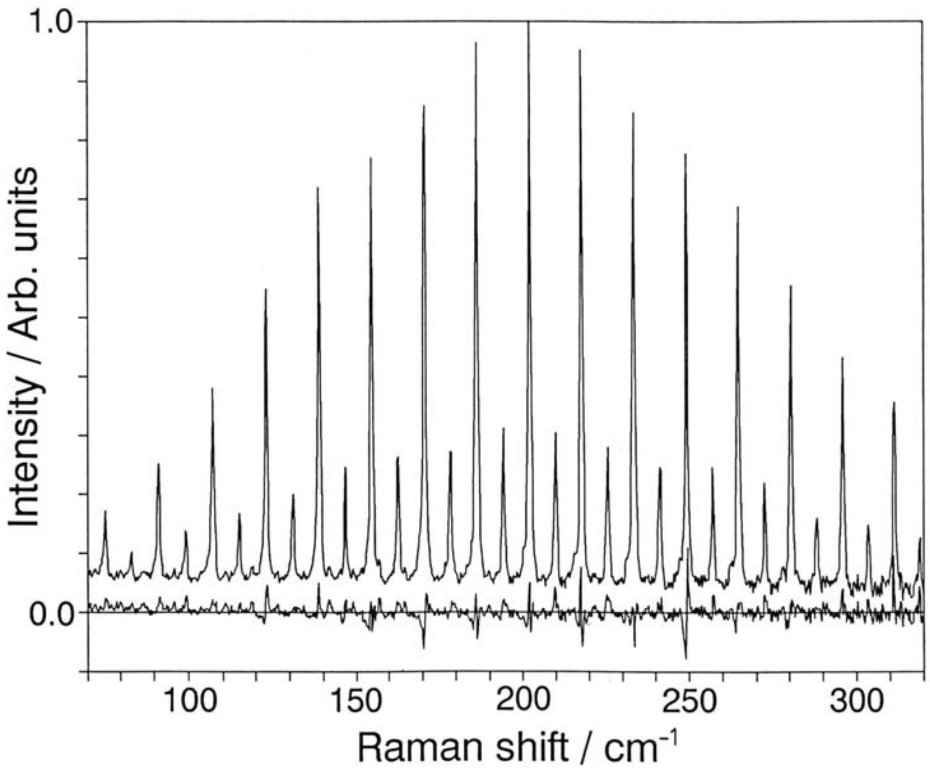
c) C_2 emission

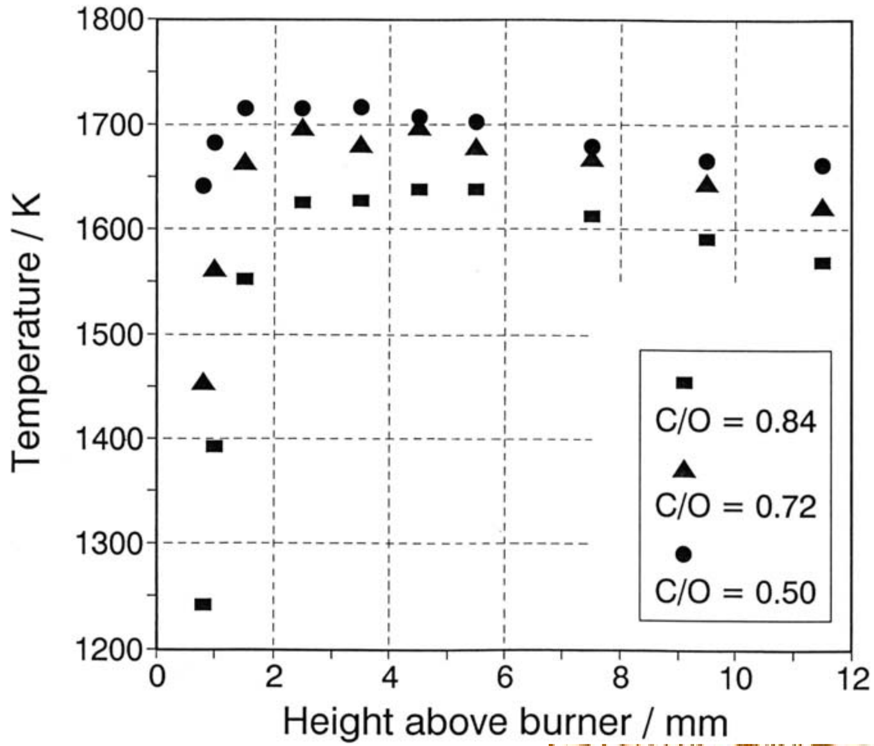


a) fitted χ_{NR} and T

b) Only fit T with estimated χ

Sooty flame diagnostics: Rot. CARS





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.