Chapter 7: Gas-Phase Concentration measurement

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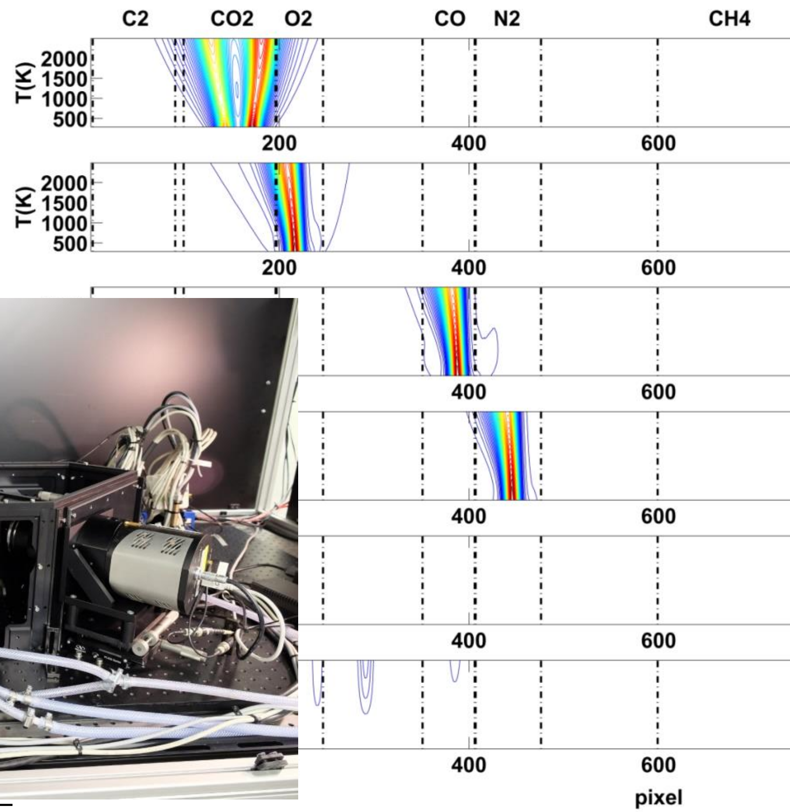

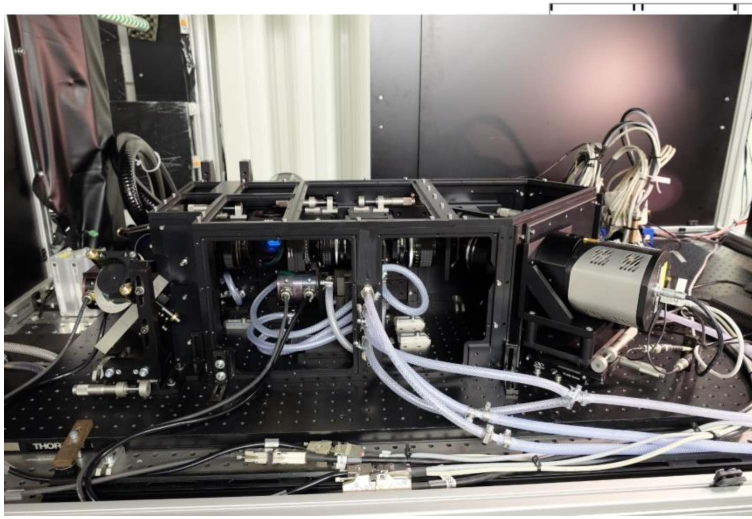

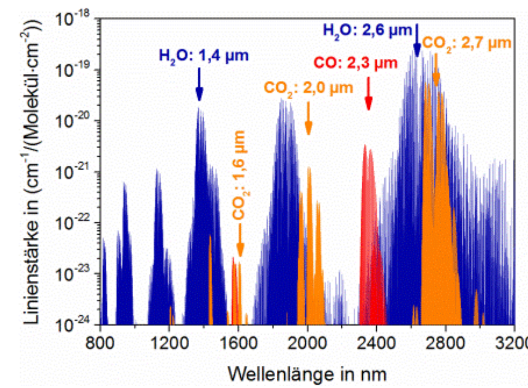

Spectroscopy

Motivation for quantitative species concentration measurement

- Quantitative concentration measurements are motivated by various scientific and technological issues
- Target species depends on the combustion process
  - Mixture fraction
  - Reaction progress and intermediate species concentration
  - Pollutants
  - …
- A quantitative species measurement in combustion application requires information of local gas temperature (density correction and method-related correction such as quenching correction in LIF)
  - Best option: measure simultaneously local temperature

Methods in the NIR/UV/VIS for temperature measurements via Boltzmann distribution

- Laser absorption spectroscopy (LAS)
- Laser-induced fluorescence (LIF)
- Raman spectroscopy (RS)

Laser absorption spectroscopy (1)

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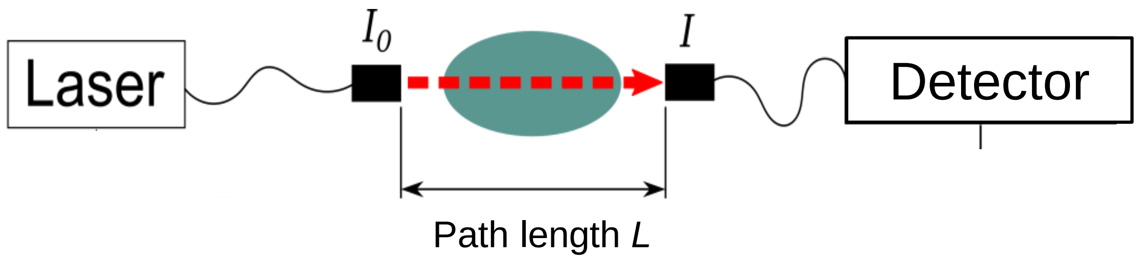
- Experimental setup



- Deduce number densities from Beer-Lambert's law
  (shown in its simplest form)

$$I(L) = I_0 \exp\left(-L \cdot N_J \cdot \sigma_{j \leftarrow i}\right) \Leftrightarrow N_J = \frac{\ln\left(I(L) / I_0\right)}{L \cdot \sigma_{j \leftarrow i}}$$

Calibration free (once the path length and absorption cross-section is known)

Line-of-sight: no resolution along laser beam path

→ restrictions for application in turbulent flames

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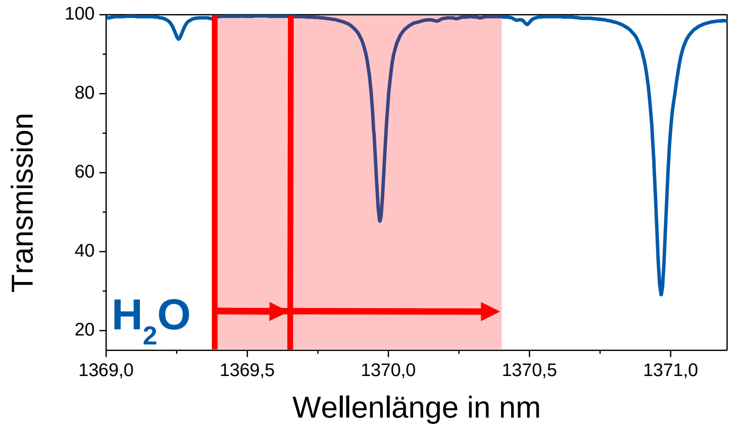
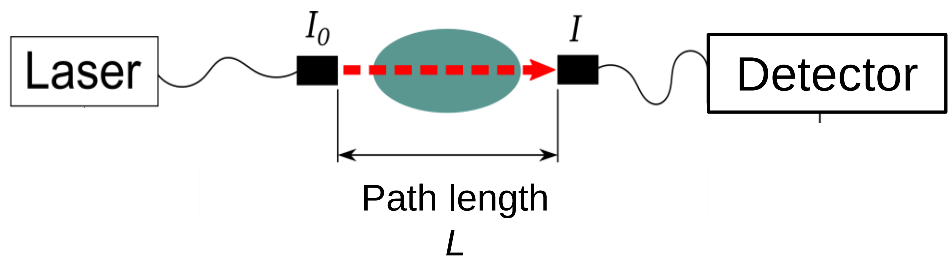
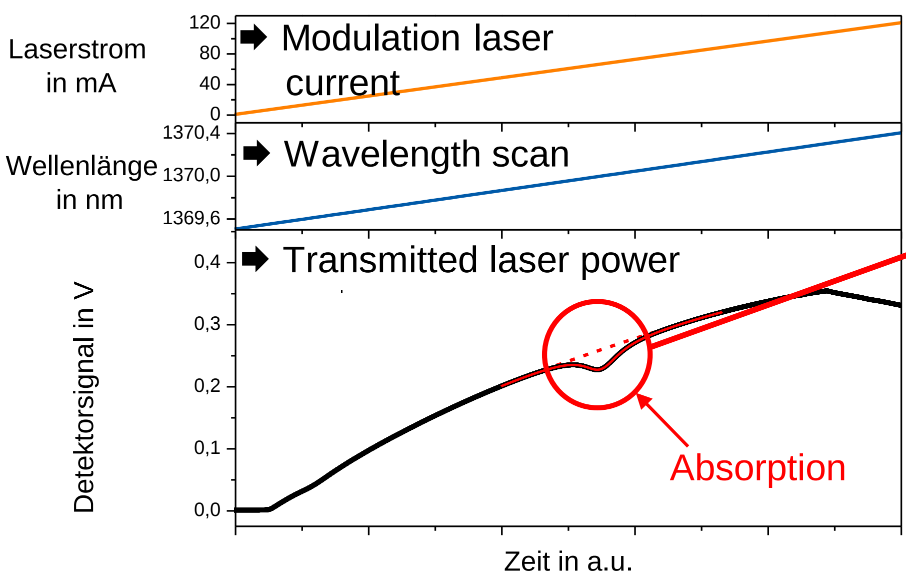
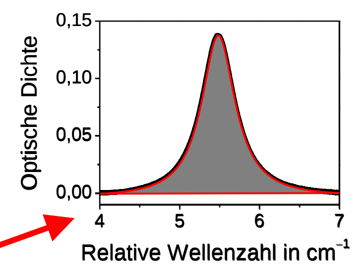
Tuneable diode laser absorption spectroscopy TDLAS





Lambert-Beer-law





Ideal gas law

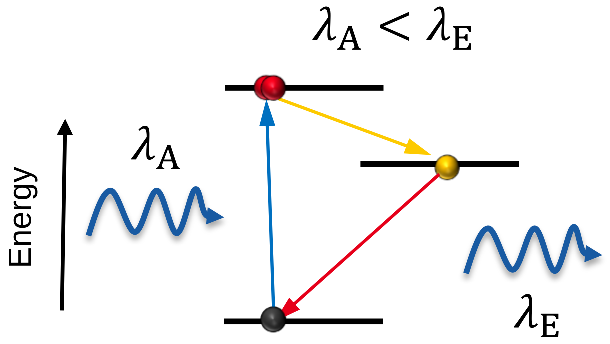
species concentration

$$c = \frac{k_B \cdot T}{S(T) \cdot L \cdot p} \int \ln\left(\frac{I_0(\nu)}{I(\nu)}\right) \frac{d\nu}{dt}\, dt$$

Laser Induced fluorescence: Principle

Step 1: Absorption

- Electronic excitation of molecules by laser radiation
- Wavelength λ_A



Step 2: Spontaneous emission (fluorescence)

- Spectrally red-shifted $\lambda_A < \lambda_E$
- Upper state lifetime few ns
- Measure of local number density

- Linear LIF regime

$$I_{LIF}(x) = N_1(x)\sigma\gamma(\nu)I_{laser}(x)\frac{\tau_{tot}}{\tau_{sp}}U\frac{\Omega}{4\pi}\varepsilon\eta$$

Laser Induced fluorescence: Experimental setup

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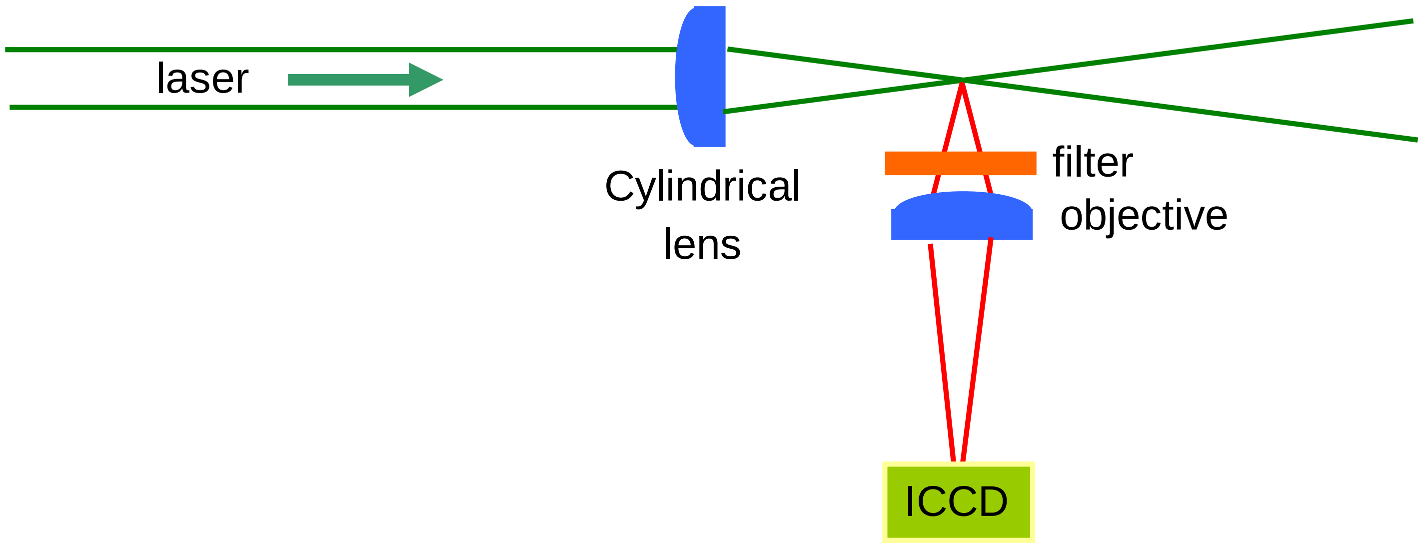
- Experimental setup



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Laser Induced fluorescence: pros and cons

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- Good spatial resolution (90° detection angle)
- Sensitive
- Calibration required to determine $U \frac{\Omega}{4\pi} \varepsilon\eta$

$$I_{LIF}(x) = N_1(x)\sigma\gamma(\nu)I_{laser}(x)\frac{\tau_{tot}}{\tau_{sp}}U\frac{\Omega}{4\pi}\varepsilon\eta$$

- Total lifetime τ_{tot} needed but often not known!

$$\tau_{tot} = \frac{1}{A + P + Q}$$

A: Einstein A-coefficient, molecular property, often known

P: Predissociation rate, molecular property, often known

Q: Quenching rate, depends on gas matrix, pressure, temperature $\rightarrow$ PROBLEM

Total lifetime τ_{tot} makes quantitative LIF challenging!

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How to make LIF quantitative – options

1. Quantification of τ_{tot} : Measure τ_{tot} = fct(T, species), once τ_{tot}(T, species) is known measure LIF simultaneously with T and species (via Raman/Rayleigh)
2. Calibration: determine $C = C(T)$ in $I_{LIF}(x) = C(T)\left[N_1(x)\right]$

   →Example CO-LIF in application example flame-wall interaction
3. Saturated LIF: does not really work, not detailed here
4. Combine 1D-LIF with absorption spectroscopy (see CST 158, 2000, Pixner et al.)

$$V(x) = \frac{\int_0^x F(x')dx'}{\int_0^L F(x')dx'} = \frac{\exp\left(-\sigma\int_0^x N_1(x')dx'\right)-1}{\exp\left(-\sigma\int_0^L N_1(x')dx'\right)-1}$$

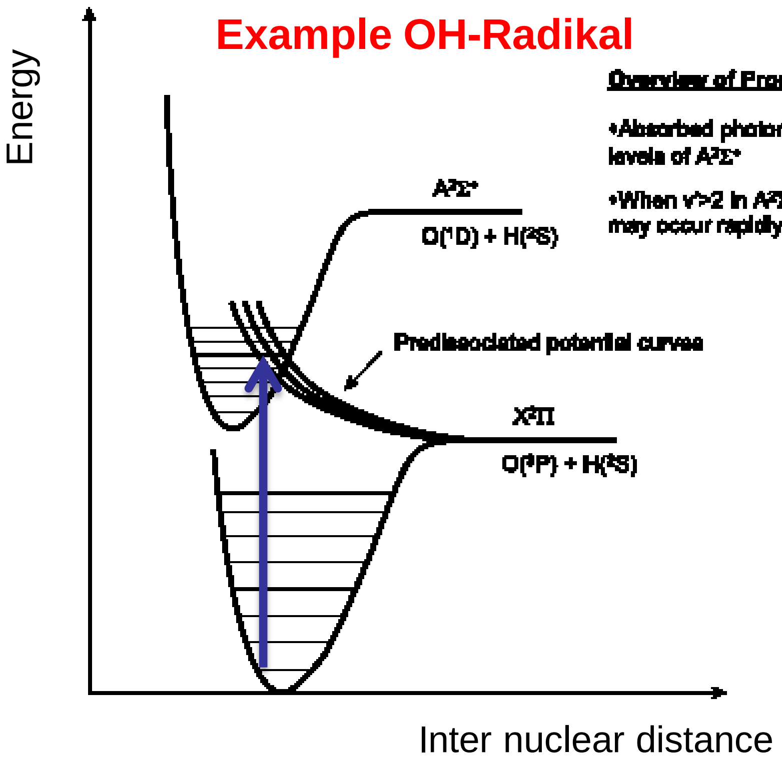
$$N_1(x) = -\frac{1}{\sigma}\cdot\frac{(T-1)\frac{dV(x)}{dx}}{(T-1)V(x)+1}$$

$$T = \frac{I(L)}{I(0)} = \exp\left(-\sigma\int_0^L N_1(x')dx'\right)$$

How to make LIF quantitative – options

5. Predissociative LIF: Independent of Q; low SNR, works for few molecules at low pressure

Example OH-Radikal

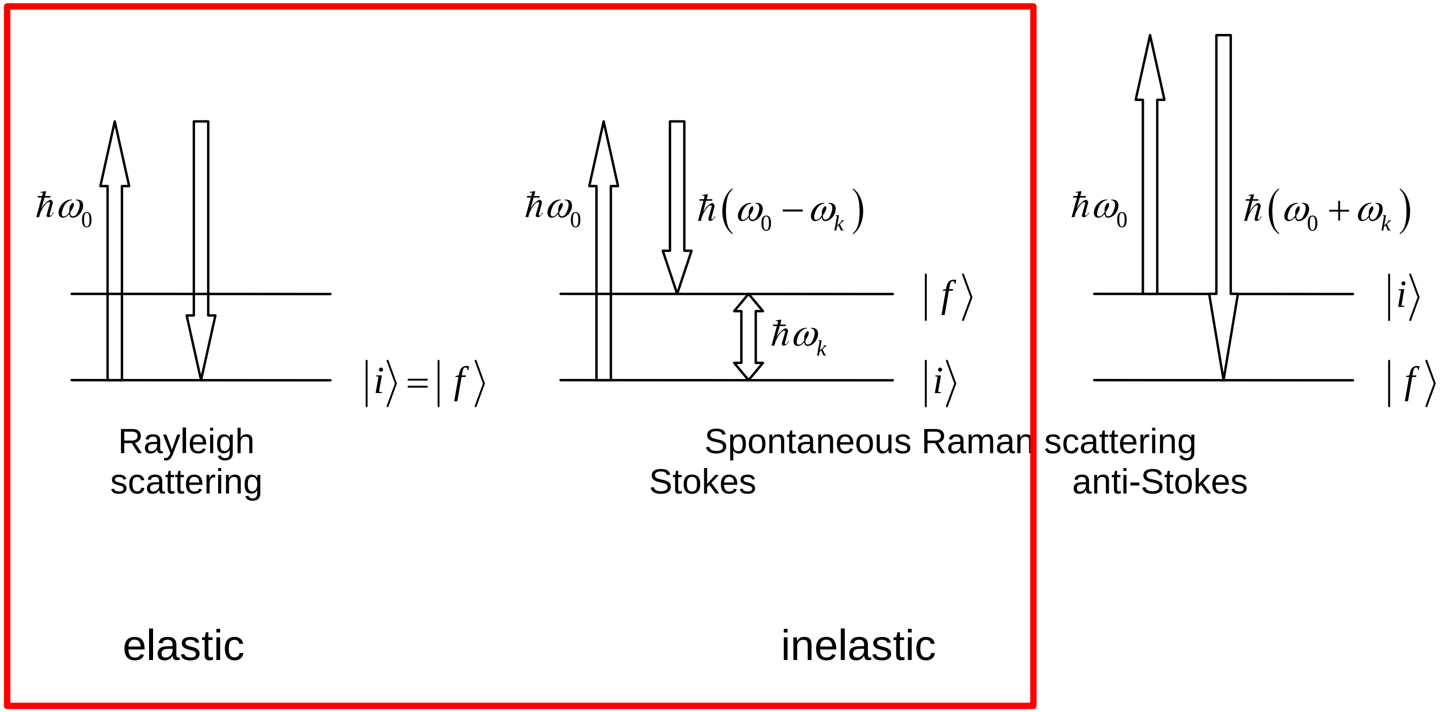


$$\tau_{tot} = \frac{1}{A+P+Q}, \text{ for } P >> Q : \tau_{tot} = \frac{1}{A+P}$$

Excitation at 248 nm by KrF-Excimer Laser
(A-X) (3-0)-band

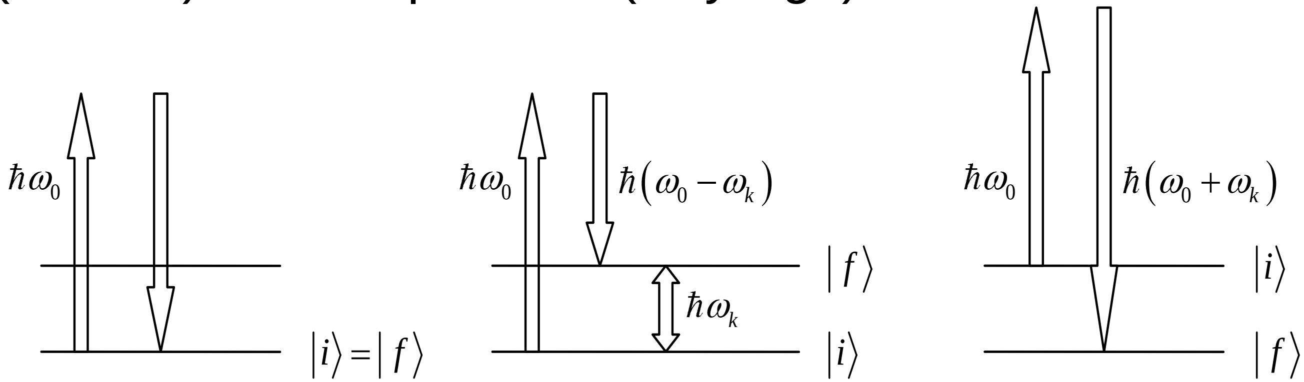
Raman spectroscopy

- Elastic and inelastic light scattering of photons off molecules



Combined Raman/Rayleigh spectroscopy

- Multi-scalar method: instantaneous measurement of main species (Raman) and temperature (Rayleigh)



Rayleigh scattering

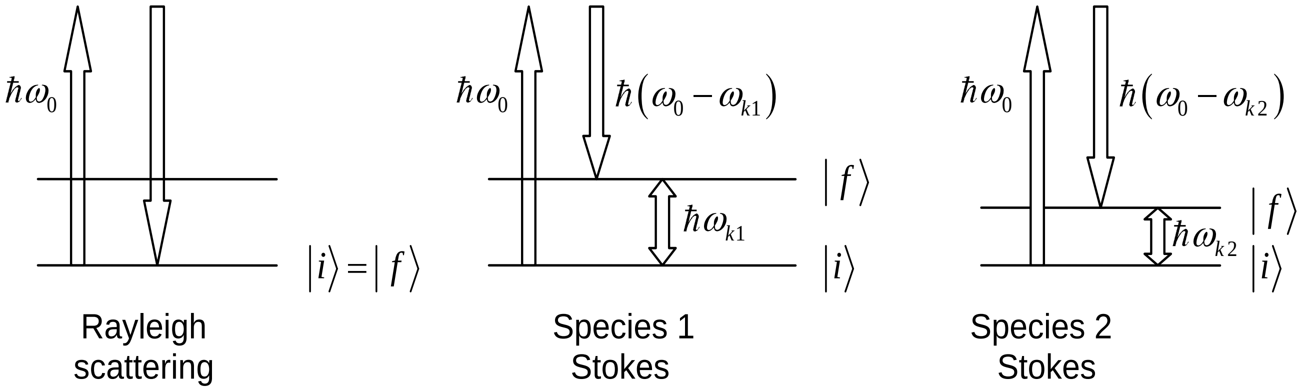
Spontaneous Raman scattering

Stokes

anti-Stokes

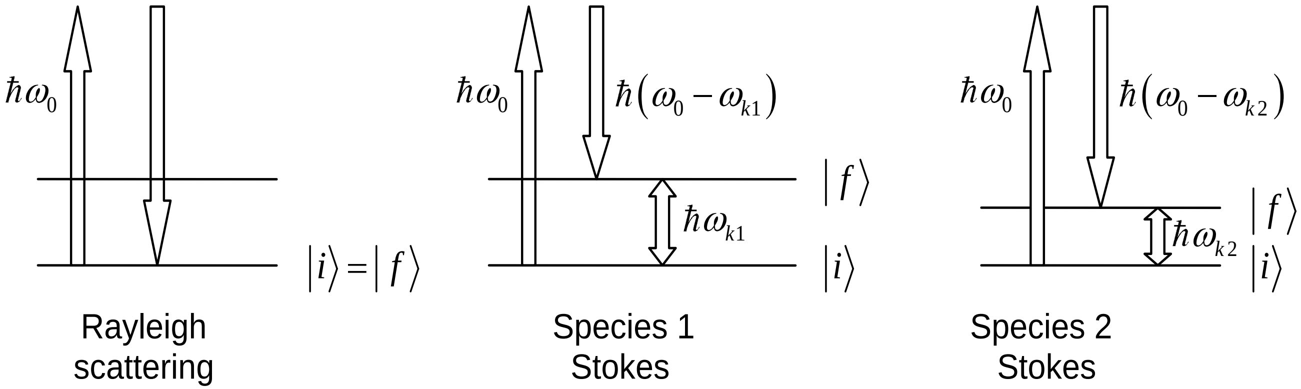
Combined Raman/Rayleigh spectroscopy

- Multi-scalar method: instantaneous measurement of main species (Raman) and temperature (Rayleigh)



Combined Raman/Rayleigh spectroscopy

- Multi-scalar method: instantaneous measurement of main species (Raman) and temperature (Rayleigh)



- Spectral dispersion and simultaneous meas. of: CO_2, O_2, CO, N_2, CH_4, H_2O, H_2, equivalence ratio (phi), Temp.
- **Challenges:**
  - Low Raman scattering cross-sections and single-shot requirement
  - Data evaluation of noisy data
  - 1D application, high spatial resolution

Raman spectroscopy: selection rules and spectra

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- Selection rules

$$\Delta J = 0, \pm 2$$

$$\Delta J = 0 \rightarrow \text{Q-branch}$$

$$\Delta J = +2 \rightarrow \text{O-branch}$$

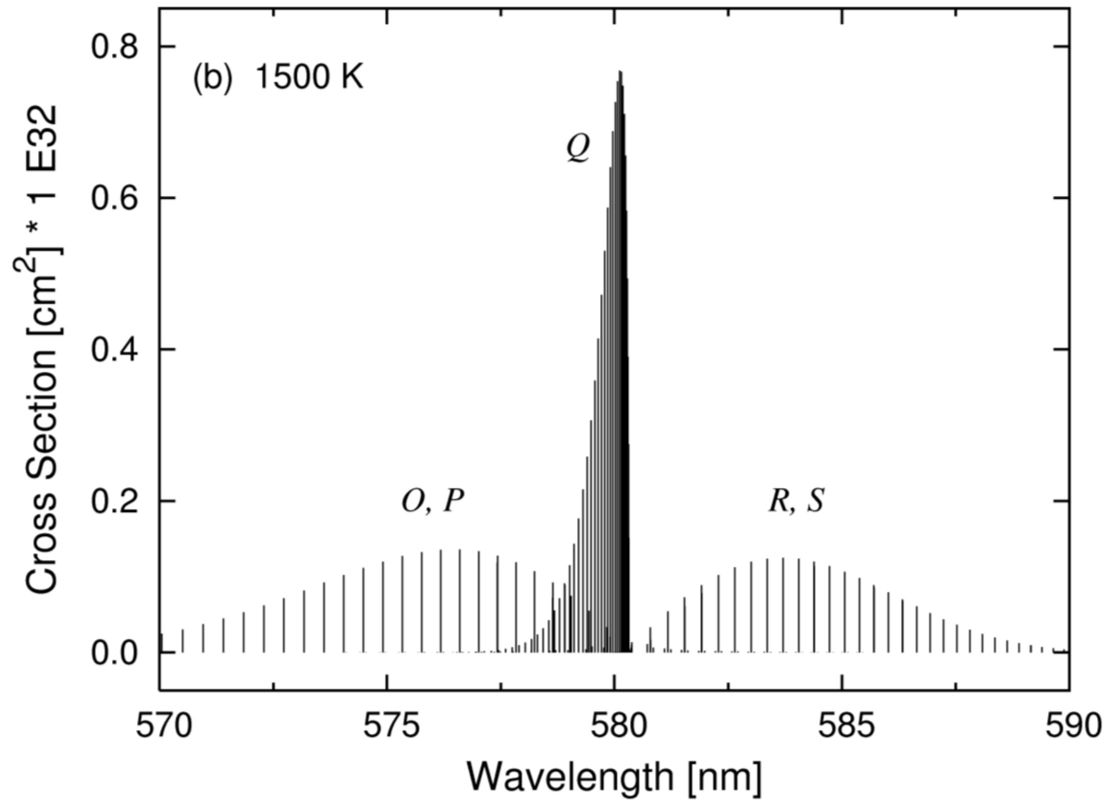
$$\Delta J = -2 \rightarrow S\text{-branch}$$

Oxygen molecule O_2, T = 1500 K

Simulated “stick spectrum” – infinite resolution

Ro-vibronic Stokes Raman

Exception: very weak R and P-lines



Raman spectroscopy: setup

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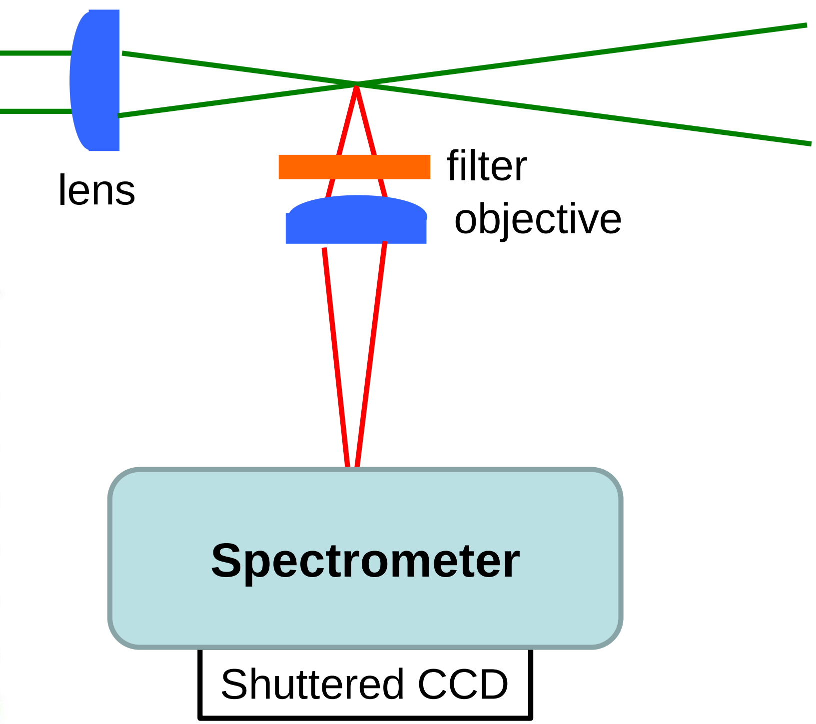
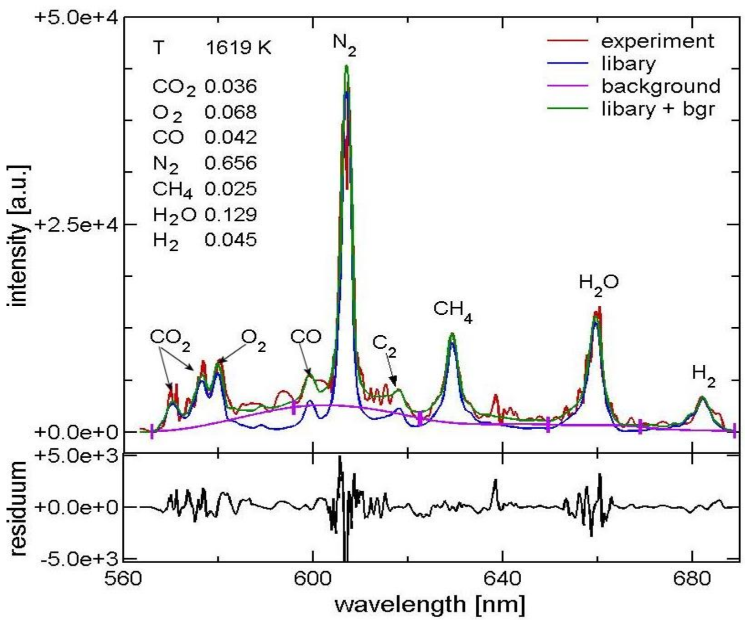
- Experimental setup



Low dispersion spectrum



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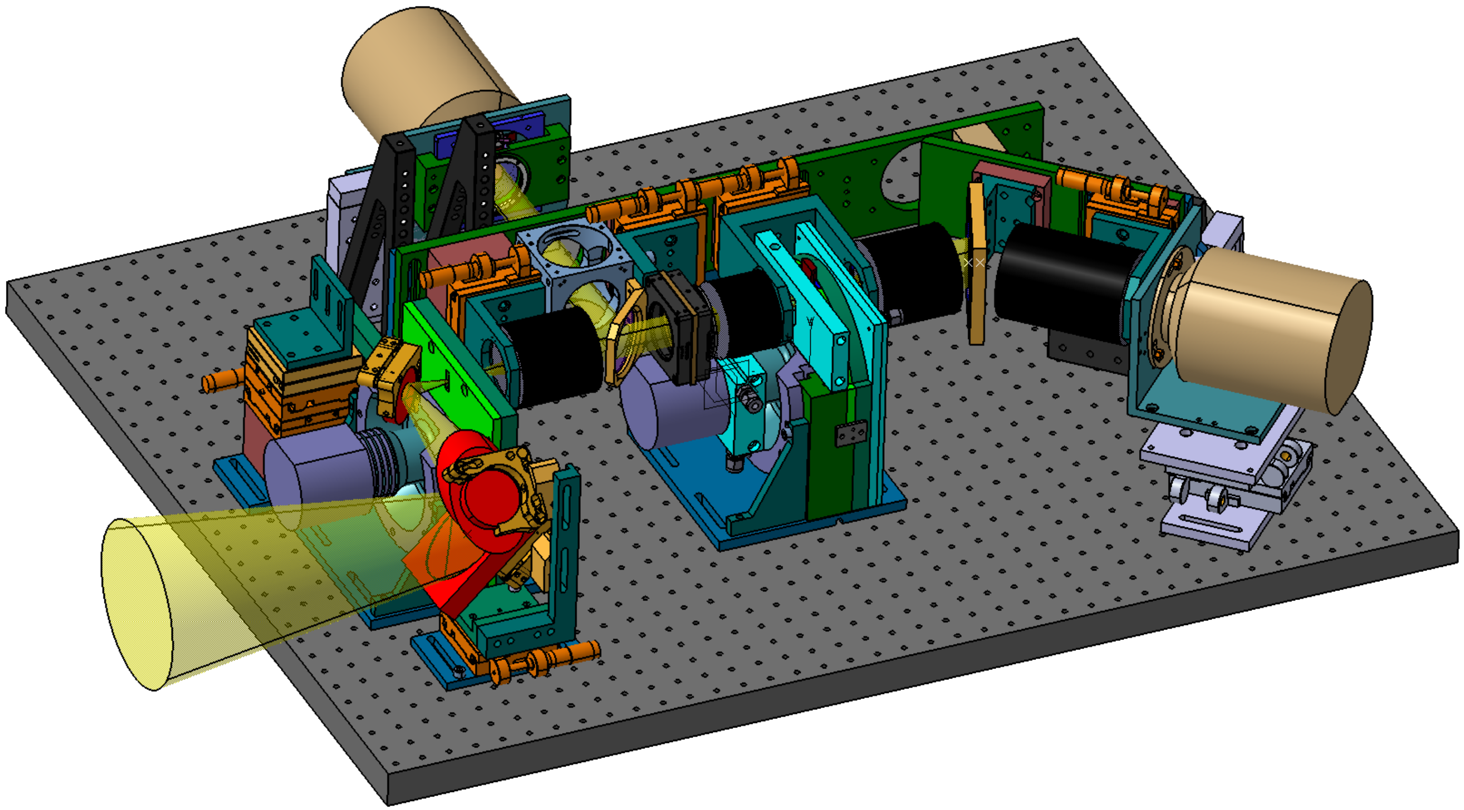
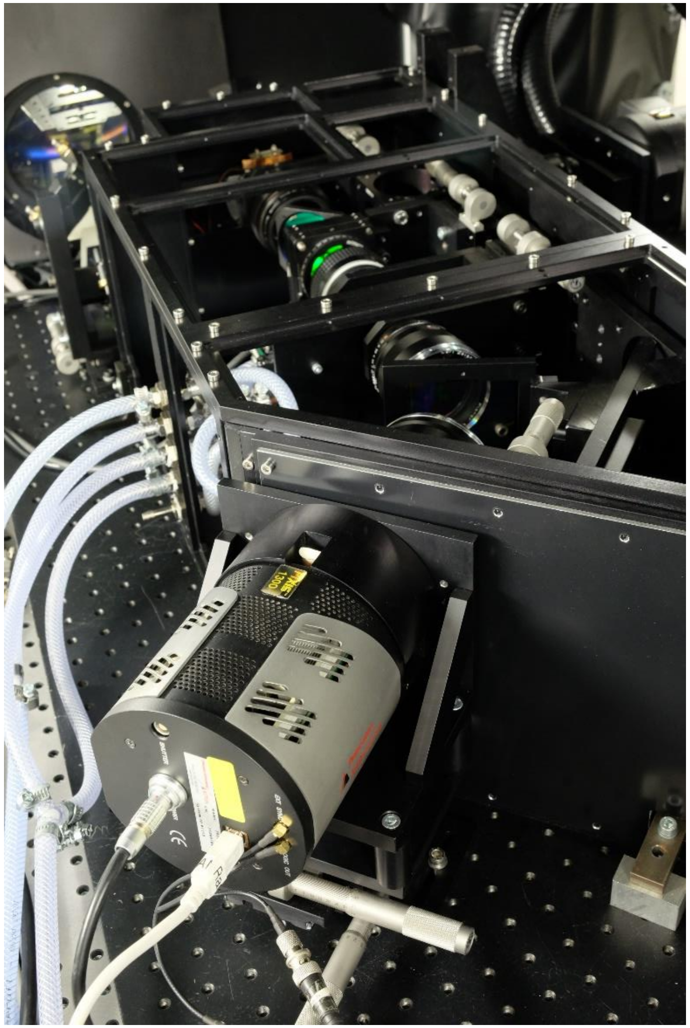
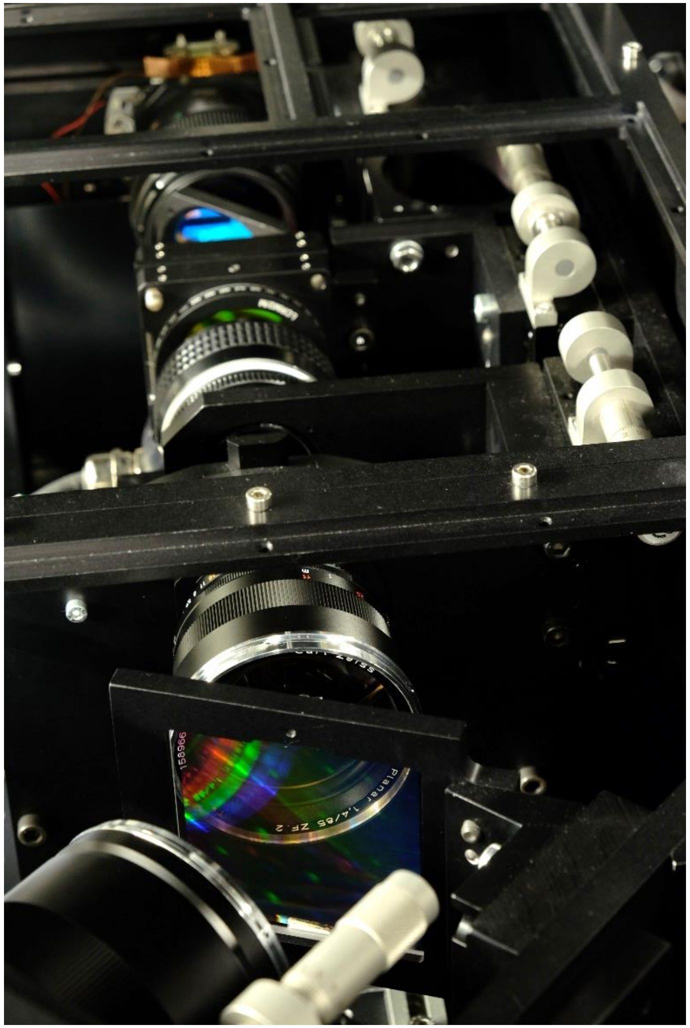
1D Raman/Rayleigh: spectrometer

- New TU Darmstadt design



1D Raman/Rayleigh: spectrometer





1D Raman/Rayleigh spectroscopy: iterative post-processing procedure

- **Raman (inelastic) scattering → concentrations $N_i(r)$**

$$S_{ram,i}(\vec{r}) \propto \sigma_{ram,i}\left(T(\vec{r})\right)\ I_{Laser}\ \ N_i(\vec{r})$$

- **Rayleigh (elastic) scattering → temperature $T(r)$**

$$S_{ray}(\vec{r}) \propto \sigma_{ray}\left(N_i(\vec{r})\right) I_{Laser} \sum N_i(\vec{r})$$

$$\sigma_{ray} = \sum_i \left(\frac{N_i(\vec{r})}{\sum_j N_j(\vec{r})} \right) \sigma_{ray,i} \xrightarrow{\text{Ideal gas law}} T(\vec{r}) \propto \frac{1}{\sum N_i(\vec{r})}$$

→ Determination of N_i, T by iterative procedure:
Need $\sigma_{ram,i}$ of each species *i*

Different options for data evaluation

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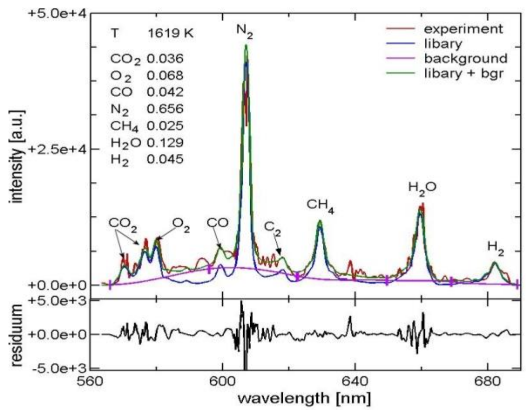
- Spectral fit



- Matrix inversion (MI) method

$$\vec{S} = \underline{\underline{M}} \cdot \vec{N}$$

$$\Rightarrow \vec{N} = \underline{\underline{M}}^{-1} \cdot \vec{S}$$

Combining the strength of both
→**The Hybrid MI-method**

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A Hybrid Method for Data Evaluation in 1D Raman Spectroscopy

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Motivation

- Spontaneous Raman scattering
  - important technique in combustion research
  - major species, scalar gradients, scalar dissipation
  - need best possible accuracy, precision, and spatial resolution
  - improvements in detection hardware and methods of analysis

- Two approaches to data analysis for hydrocarbon flames; both are complicated

- “Hybrid” method of Raman data analysis
  - combine strengths of methods used by Sandia and TU Darmstadt
  - reduce level of expertise needed to interpret Raman data

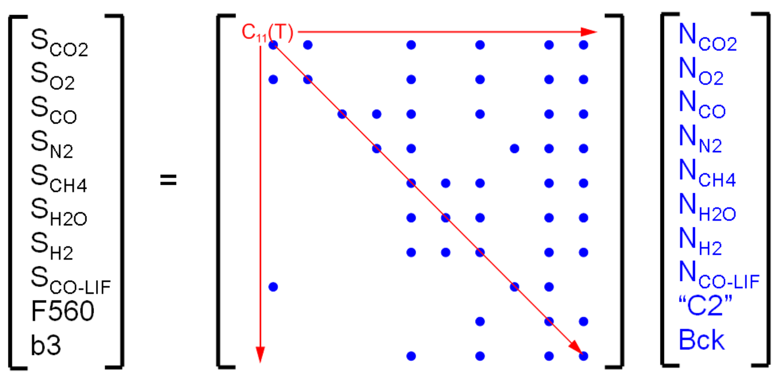
- Demonstrate using laminar flame measurements from Sandia system
  - Premixed CH_4/air flat flames
  - Laminar H_2 jet flame (no hc fluorescence interference)

Matrix Inversion (Sandia)

- On-chip binning of Raman bands to reduce camera readout noise
- Matrix equation relating signals and sources

$$S_{CO2} = C_{1,1}(T) x N_{CO2} + C_{1,2}(T) x N_{O2} + C_{1,5}(T) x N_{CH4} + C_{1,7}(T) x N_{H2} + C_{1,9}(T) x C2 + C_{1,10}(T) x Bck$$

Raman — Raman crosstalk — fluorescence — background



- Extensive calibrations to determine temperature dependence of matrix elements for Raman response and crosstalk (represented as polynomials)
- Solve inverse problem to get species concentrations and temperature
- Iterate on Rayleigh temperature (1K conversion, 3-4 iterations)

Spectral Fitting (TU Darmstadt)

- Individual rovibrational Raman transitions calculated for each species, based on Placzek´s theory of polarizability (TUD Ramses code)
- Each Raman transition convolved with experimentally determined apparatus function, then all convolved Raman transitions superposed
  - Rayleigh scattering image → apparatus function in this work
  - Raman bands broaden with increasing temperature due to the population of higher quantum states
  - Spectral library composed of temperature-dependent Raman bands
- The spectral library for each molecule is calibrated to an experimental spectrum measured in a gas sample with known mole fraction and temperature.
- Details of fitting procedure (Dirk Geyer thesis)

Pro's and Con's

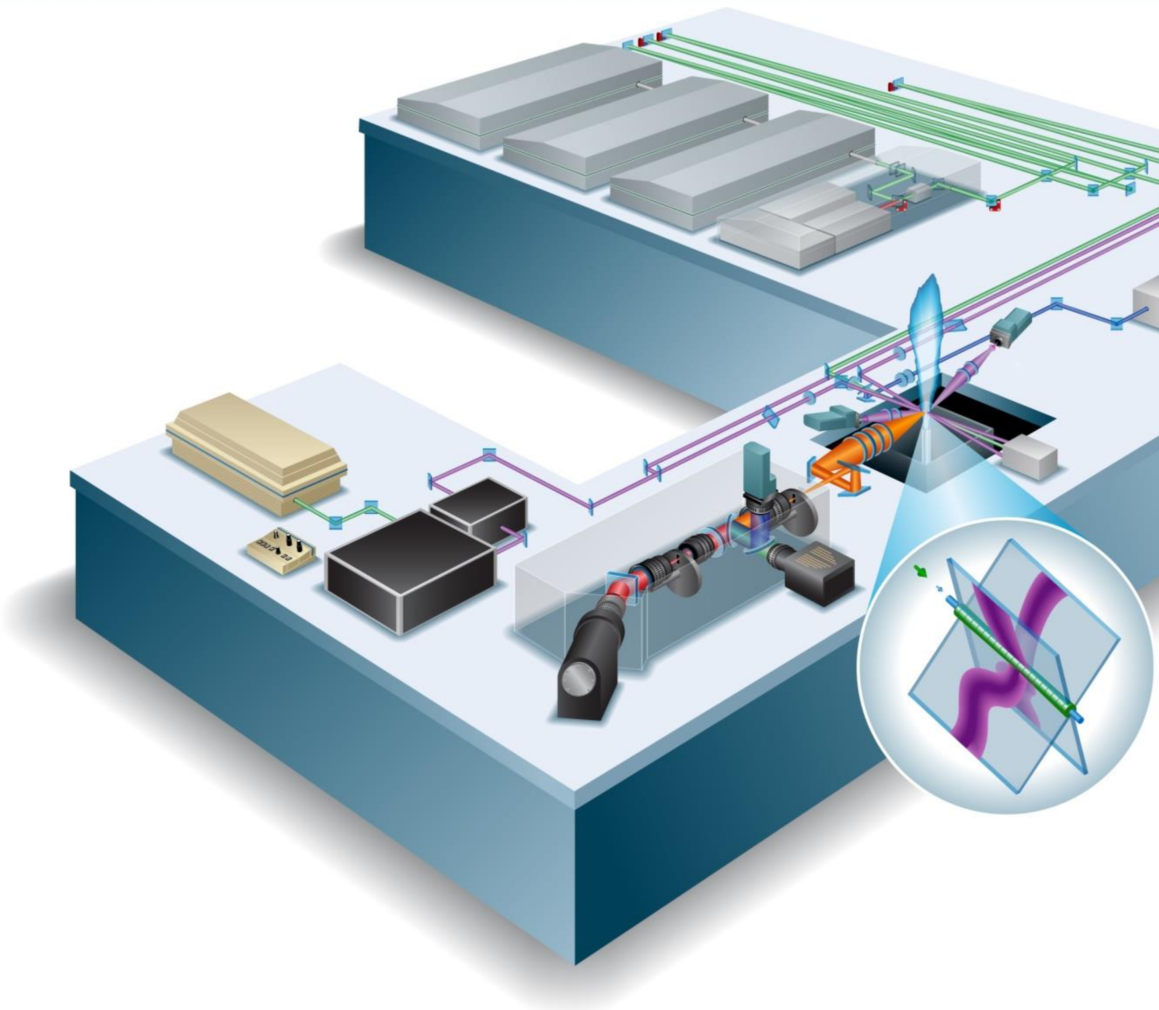
Matrix Inversion (old version)

- Pro's
  - Lower noise
  - Faster acquisition & processing
- Con's
  - Extensive calibrations required
  - Cannot calibrate accurately at some conditions
  - Spectral information lost
  - Impractical to account for beam steering or spatial dependence of response function

Spectral Fitting

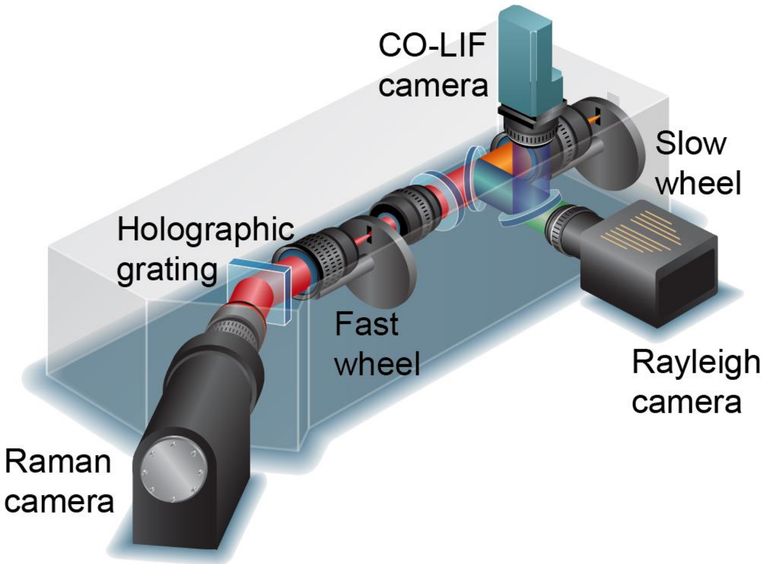
- Pro's
  - Based on quantum mechanical theory
  - One calibration per species
  - Beam steering handle automatically
  - Background corrected more rigorous
- Con's
  - Higher readout noise
  - Slower data acquisition rate
  - Significant time/effort in fitting

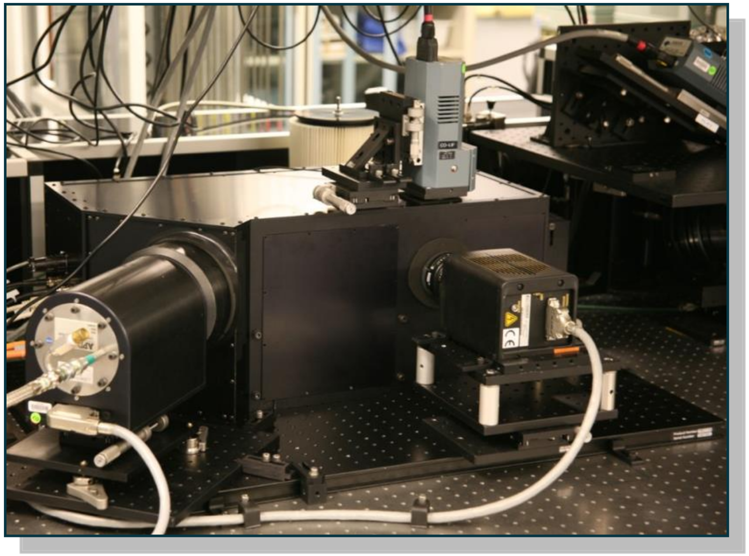
Turbulent Combustion Laboratory: Raman/Rayleigh/CO-LIF & Crossed OH PLIF

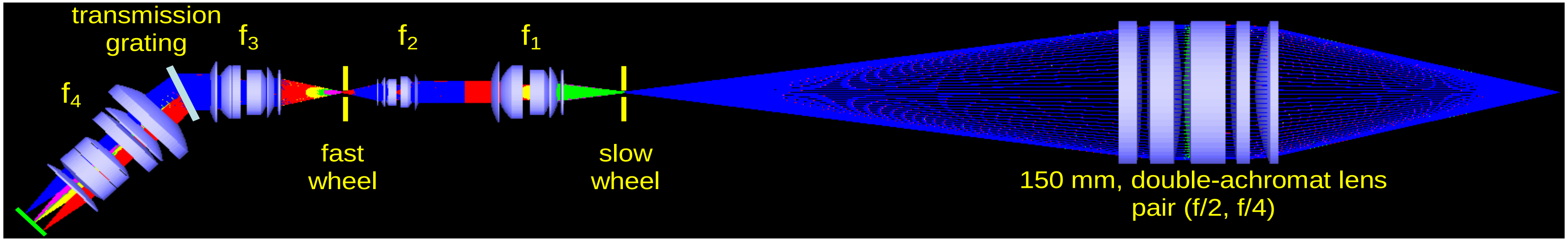


- T, N_2, O_2, CH_4, CO_2, H_2O, H_2, CO
- 6-mm segment
- Mixture fraction, reaction progress
- 3D flame orientation
- 1D, 3D scalar gradients, dissipation

Detection System

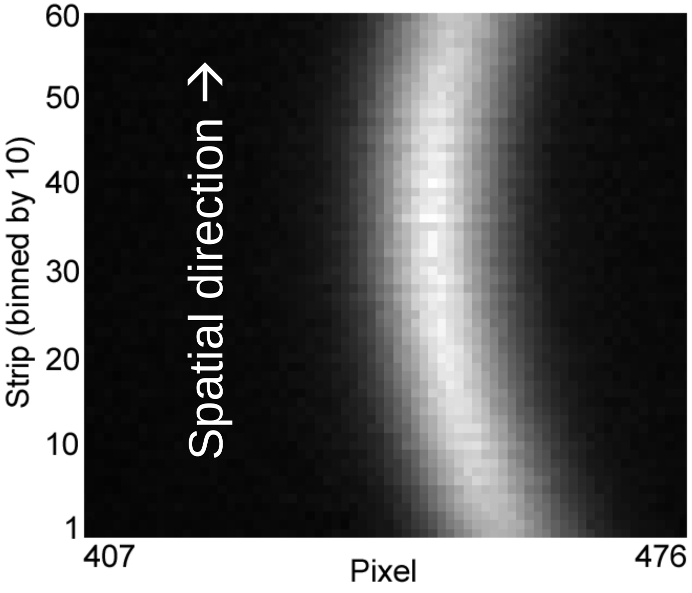






- LSF 40-60 μm
- Transmission grating
- Mechanical gate: 3.9 μs gate (FWHM)
- 103 μm data spacing

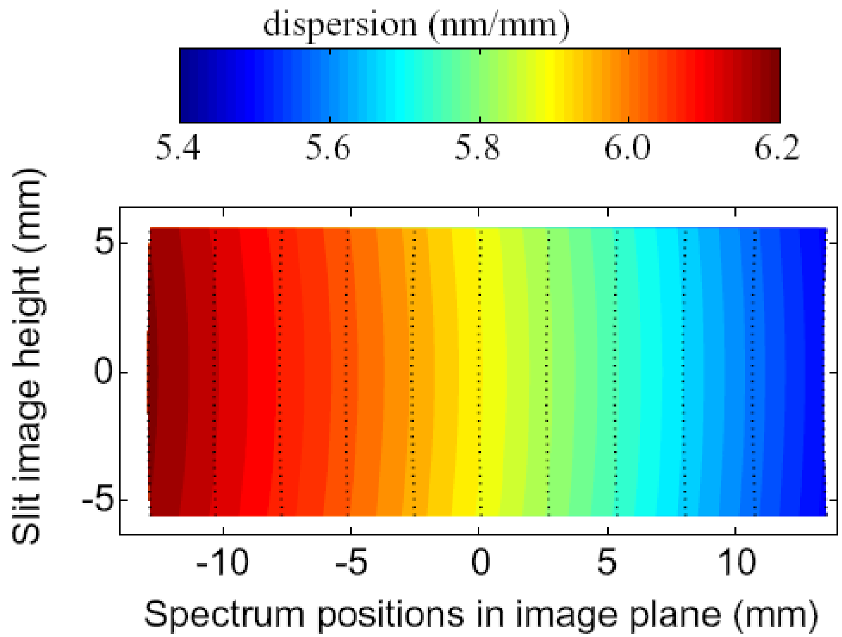
Optical Bowing Effect

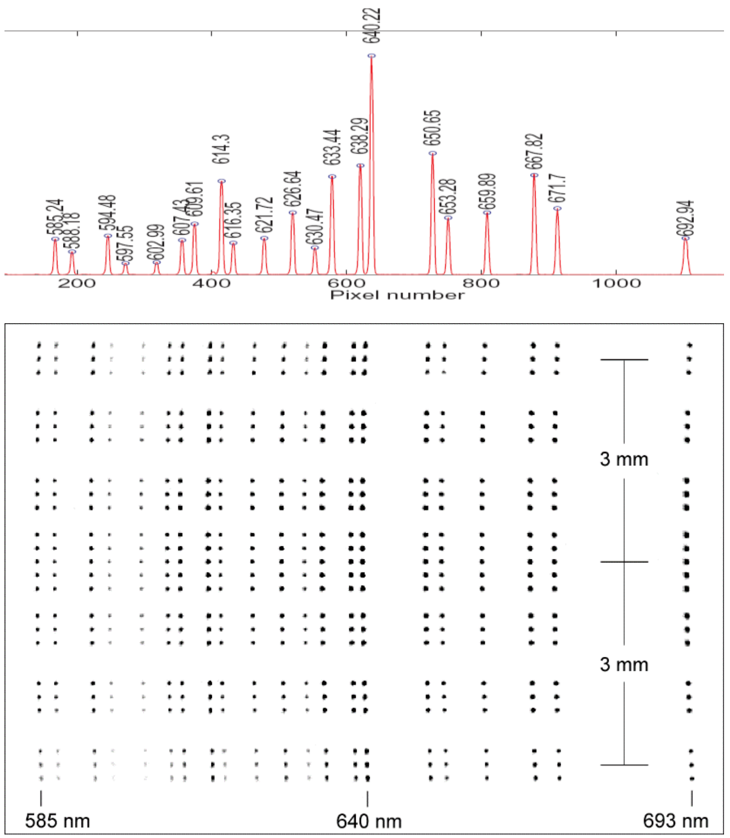


Wavelength →

- Image of N_2 Raman scattering in air
- Low f-number spectrograph
  - bowed image of slit
  - Jun Zhao, Appl. Spectr. 57, 11 (2003) 1368-1375
- Calculated (Zemax) and measured
  - Map CCD for wavelength at each pixel
- Must account for this optical effect

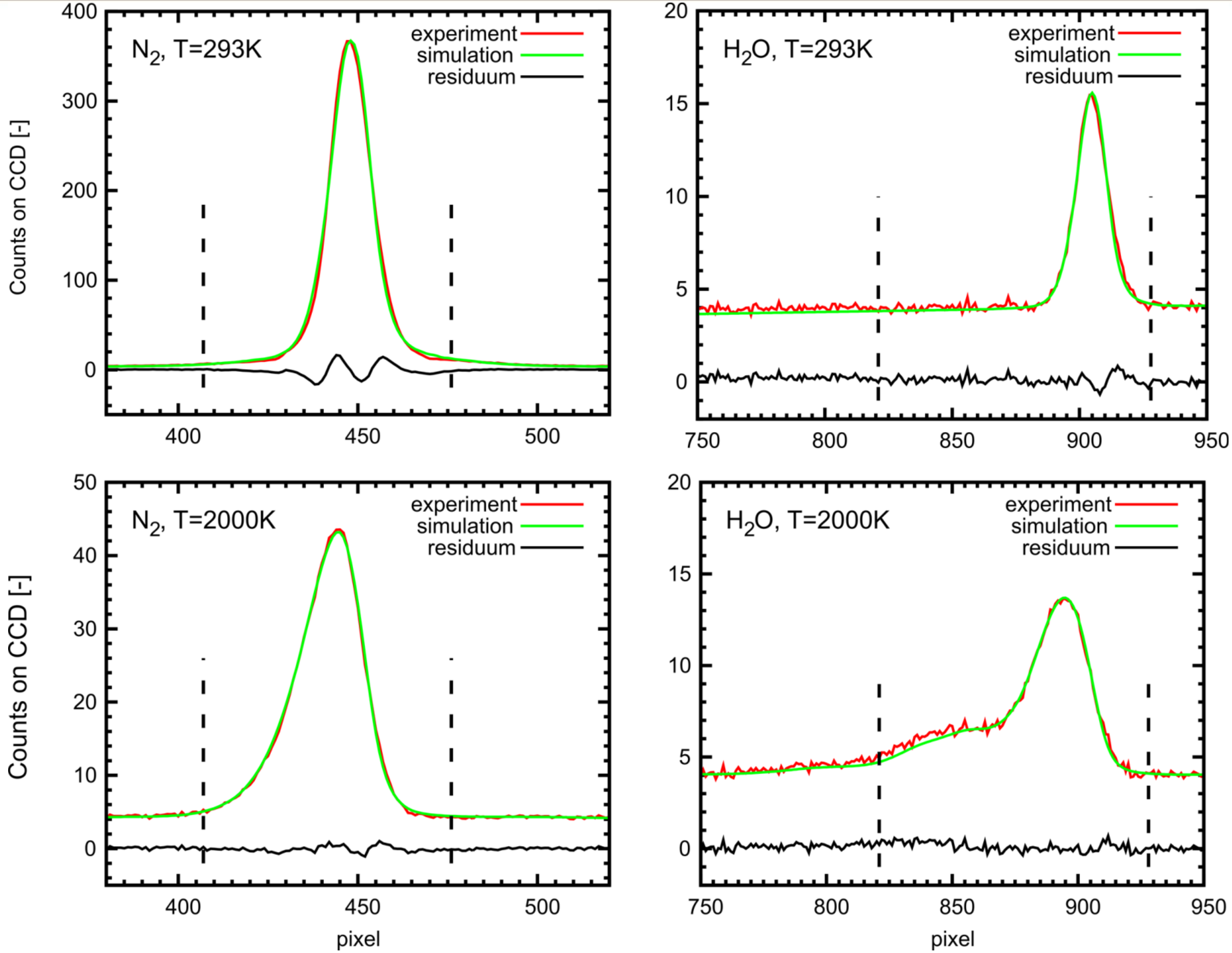
Spectrometer Characteristics



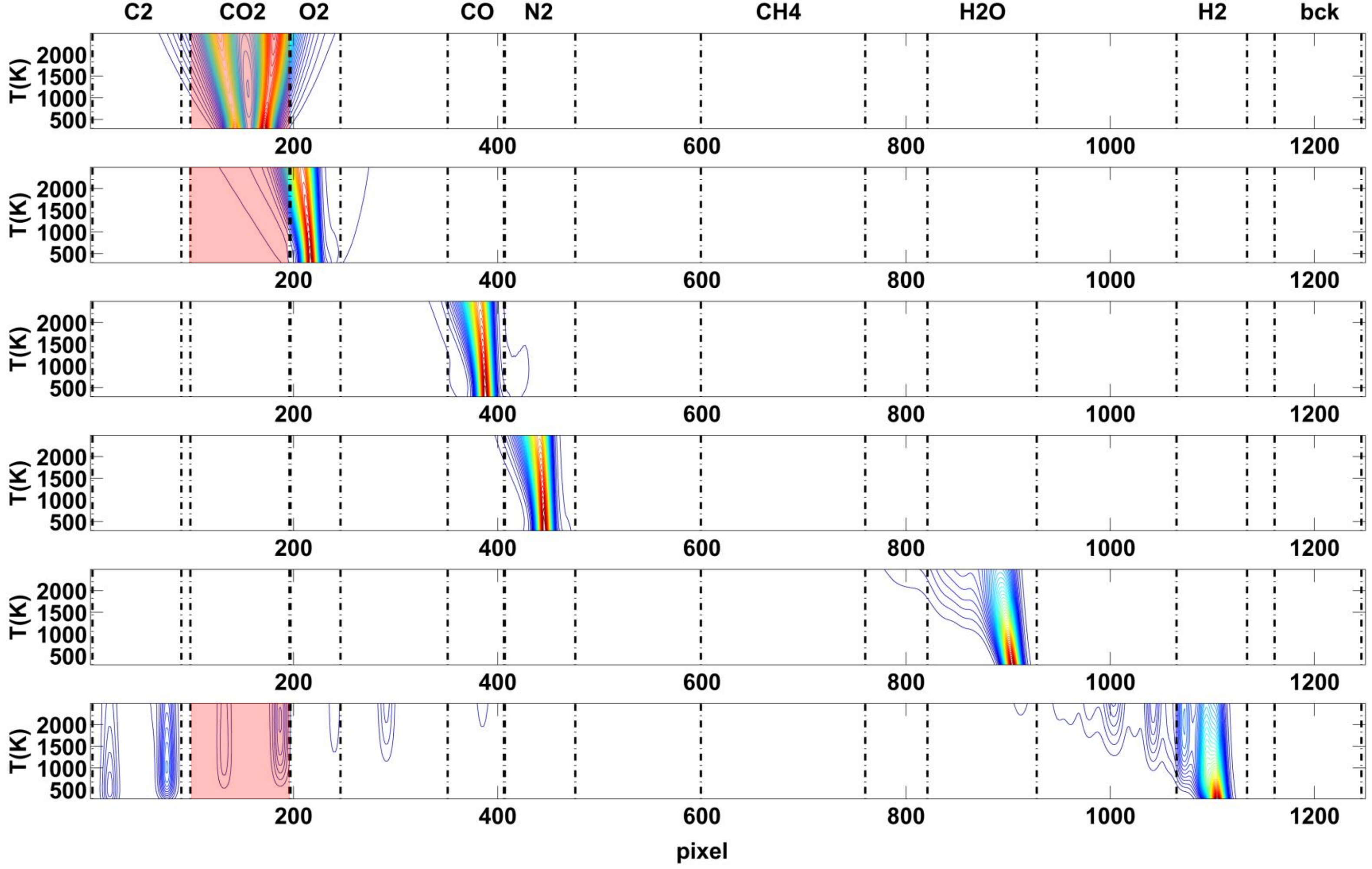


- Calculated (Zemax) dispersion is not linear across the image plane
- Spectral/spatial calibration using neon lamp and target with 50-μm holes on 200-μm centers

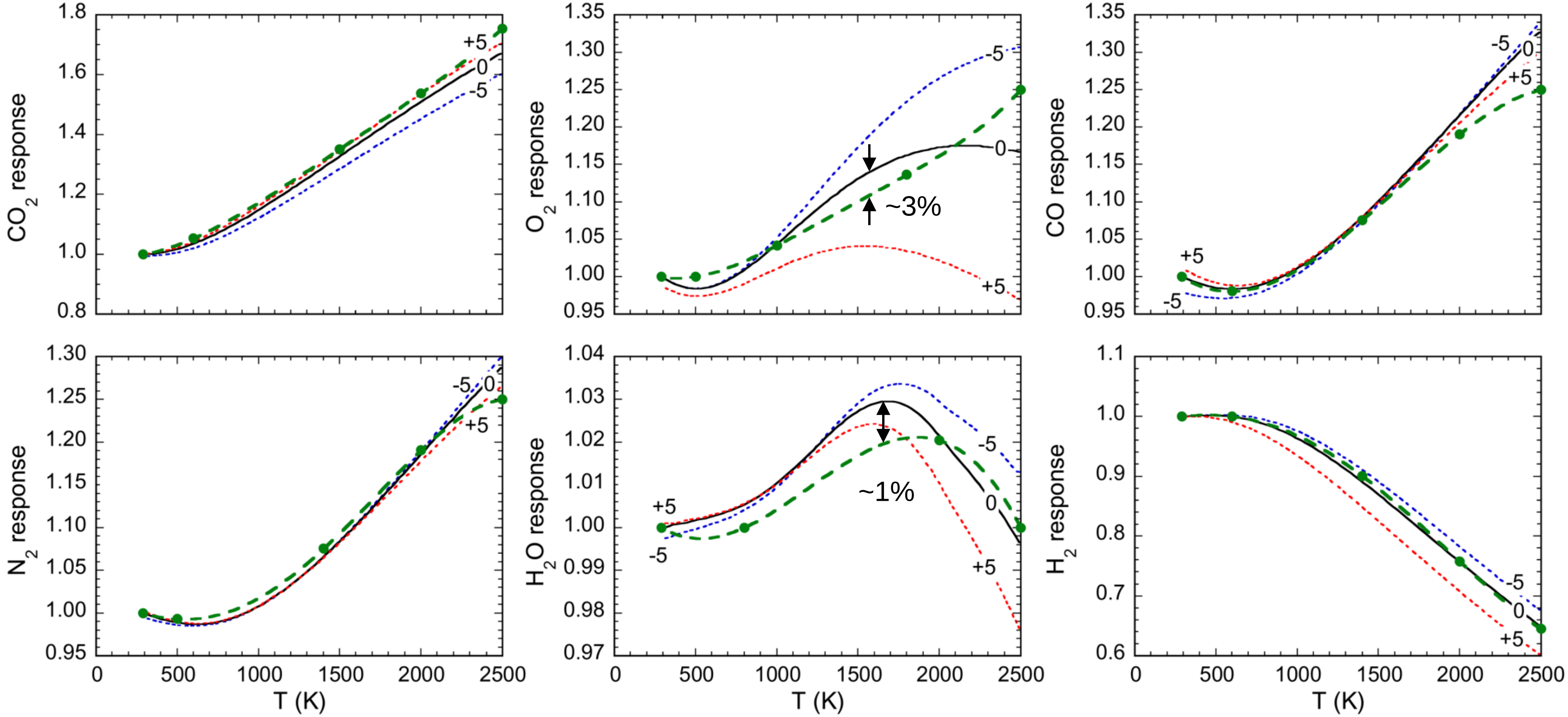
Spectral Library vs. Measurement



Calculated Spectral Libraries (Ramses code)

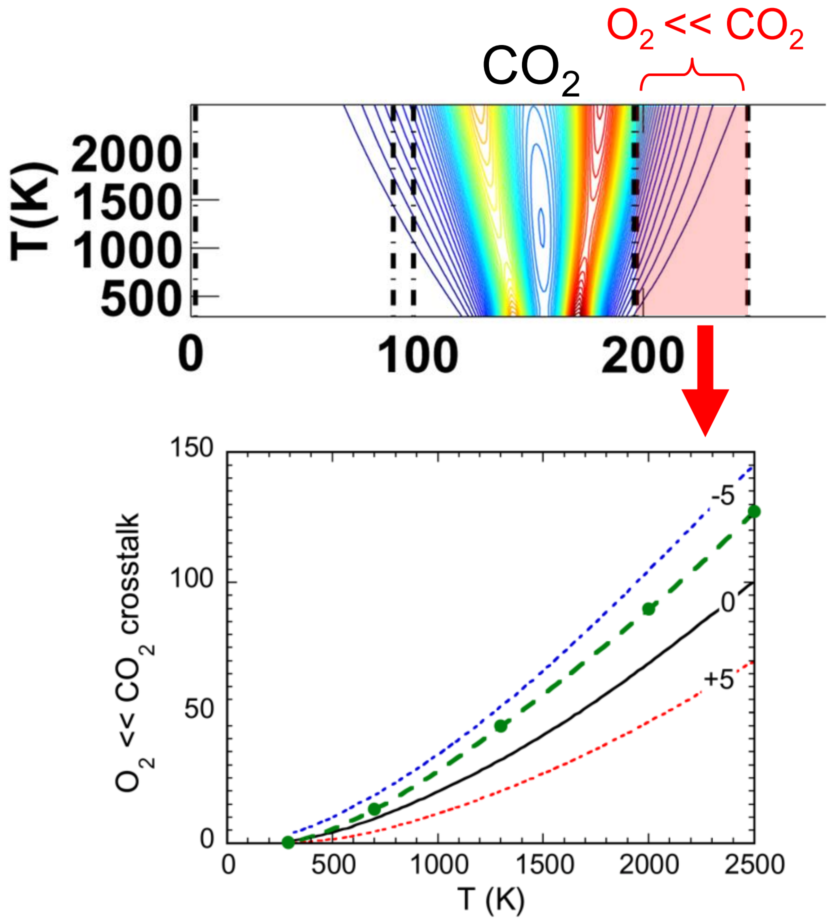


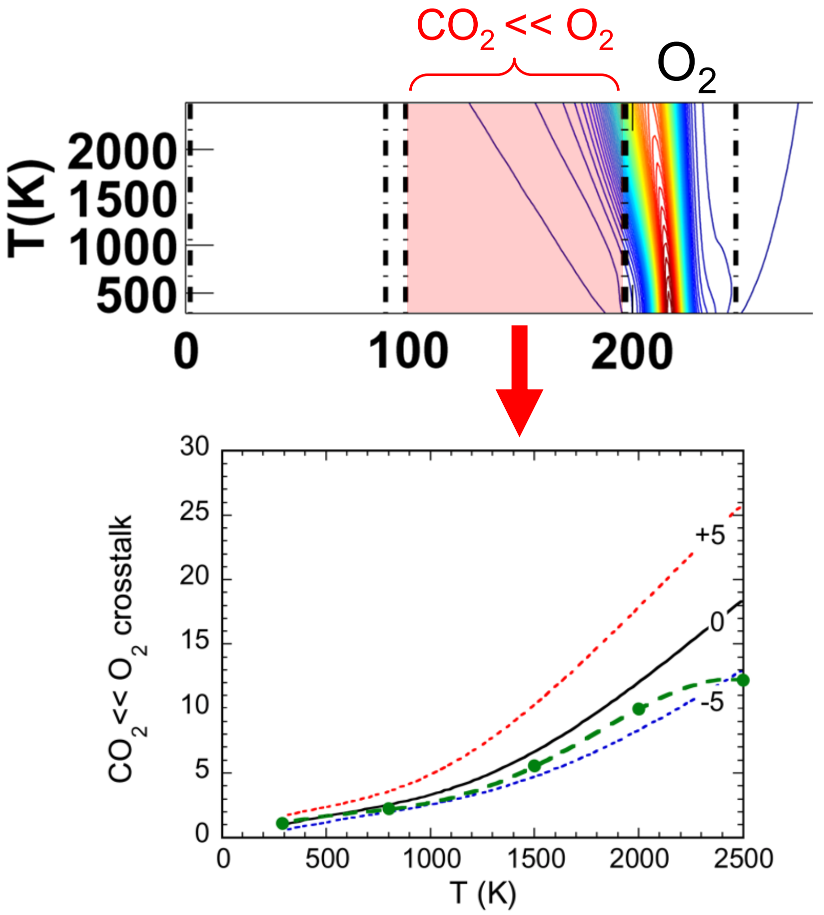
Major Species Response Curves



- Good agreement, except for O_2 curve shape at high T
- O_2 response sensitive to bowing effect and beam steering

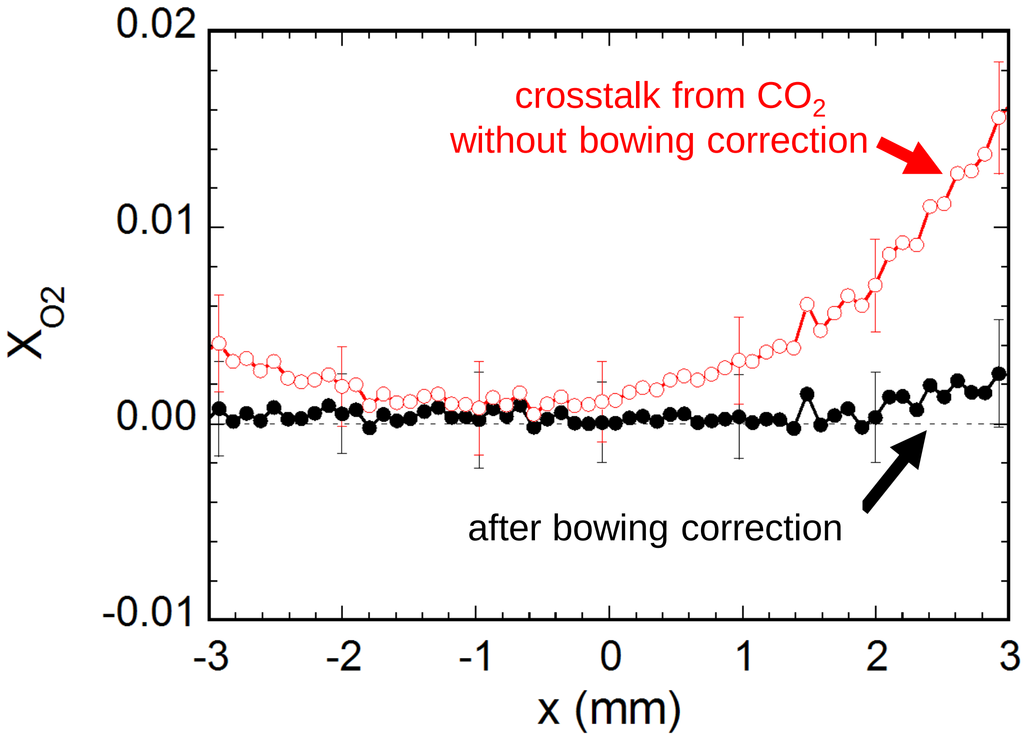
Crosstalk between CO_2 and O_2





- Greater uncertainty in calibration polynomials
- Sensitive to bowing effect and beam steering

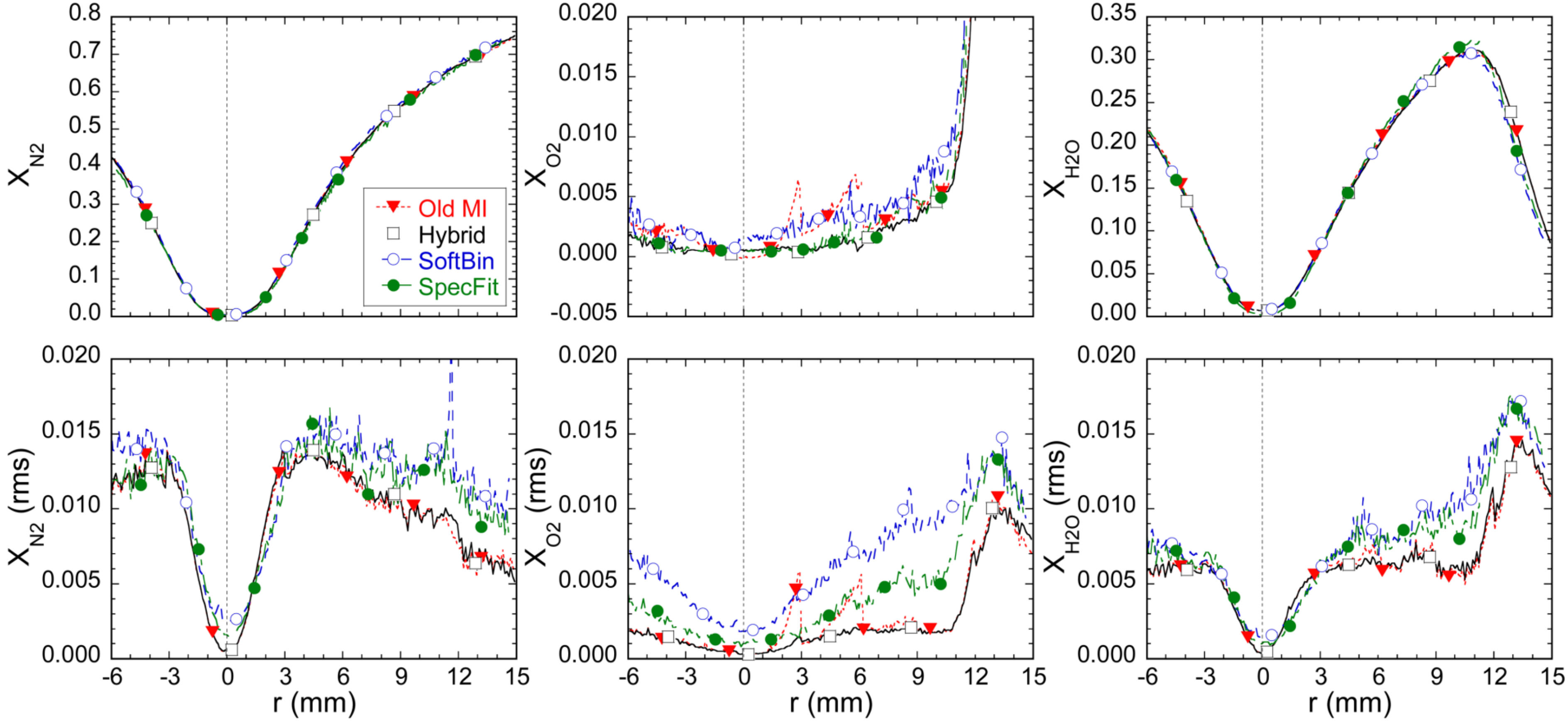
Effects of Image Bowing on O_2 Errors



premixed CH_4/air
"flat" calibration flame

- O_2 mole fraction should be zero in the rich flame products (ϕ=1.3)
- Bowing effect leads to error of X_{O2} ~ 1.6% due to uncorrected CO_2 crosstalk

Comparison for Laminar H_2 Jet Flame



- Close agreement on mean values from hybrid-MI and spectral fitting
- Hybrid method yields better precision (on chip binning)
- Spectral fitting yields lower noise than MI with software binning

Conclusions

- Hybrid method of Raman data analysis has been developed
  - Calculated Raman libraries are integrated to determine temperature-dependent terms for matrix inversion
  - Response and cross talk for N_2, O_2, H_2, CO, CO_2, H_2O
- Combines advantages from both previous methods
  - Low noise from on-chip binning
  - Fast data acquisition and processing
  - Temperature dependence based on QM theory
  - Automatic correction for image bowing and beam steering
- Relatively easy to adapt to other Raman/Rayleigh systems

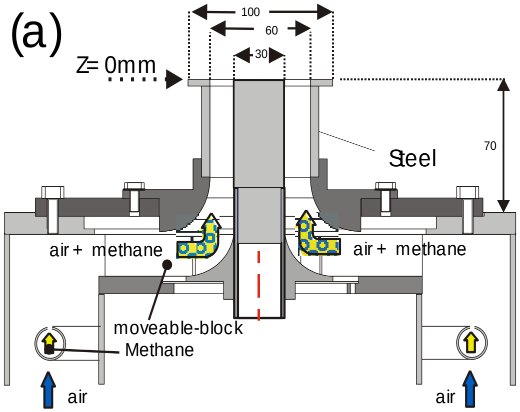
Application example

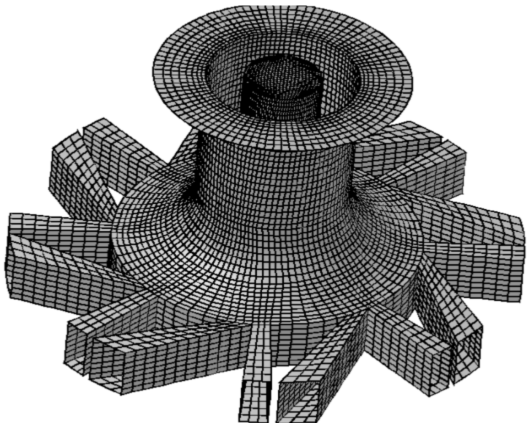
- Thermo-chemical state in swirling premixed flame:

  Gregor et int. Dreizler. Proc. Combust. Inst. 32, 1739 – 1746 (2009)

Thermo-chemical state in swirling premixed flame

- Burner



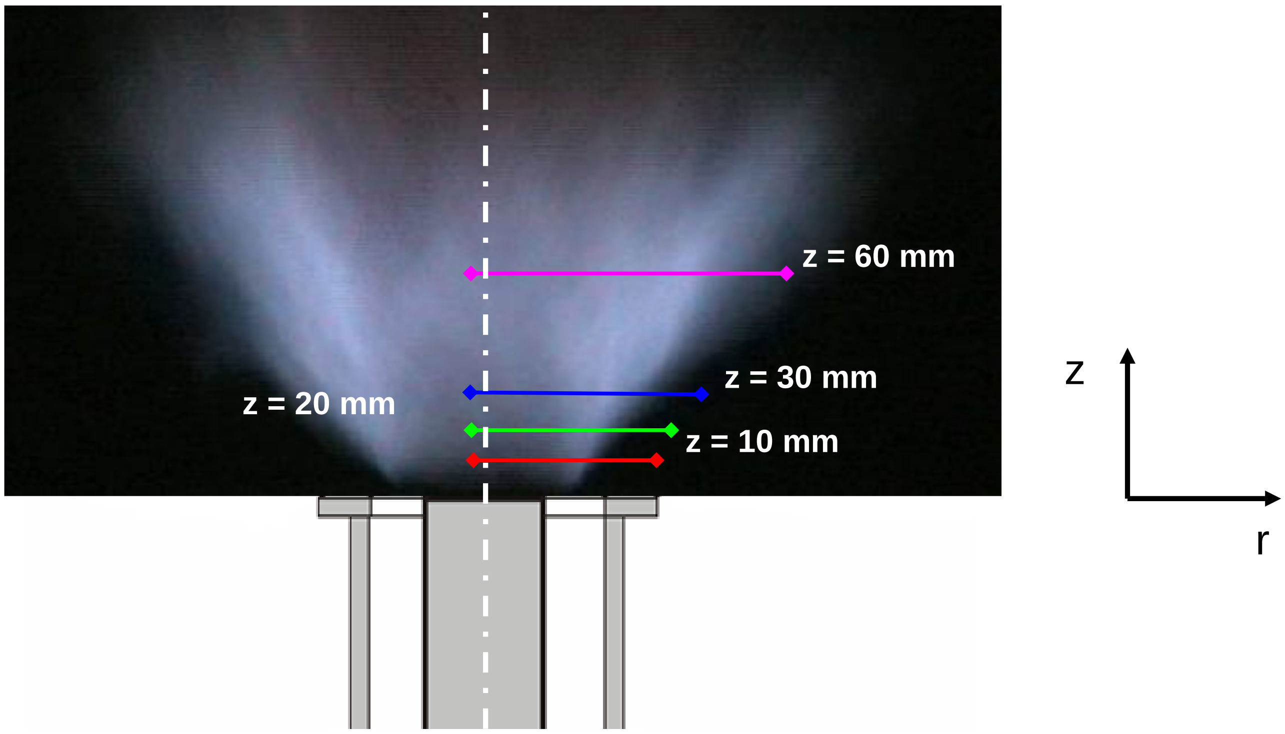


- Operational conditions

		PSF-30	*PSF-90*	*PSF-150*
$S_{0,th}$	[-]	0.75	0.75	0.75
P	[kW]	30	90	150
ϕ	[-]	0.833	0.833	1.0
$Re_{tot.}$	[-]	10000	29900	42300

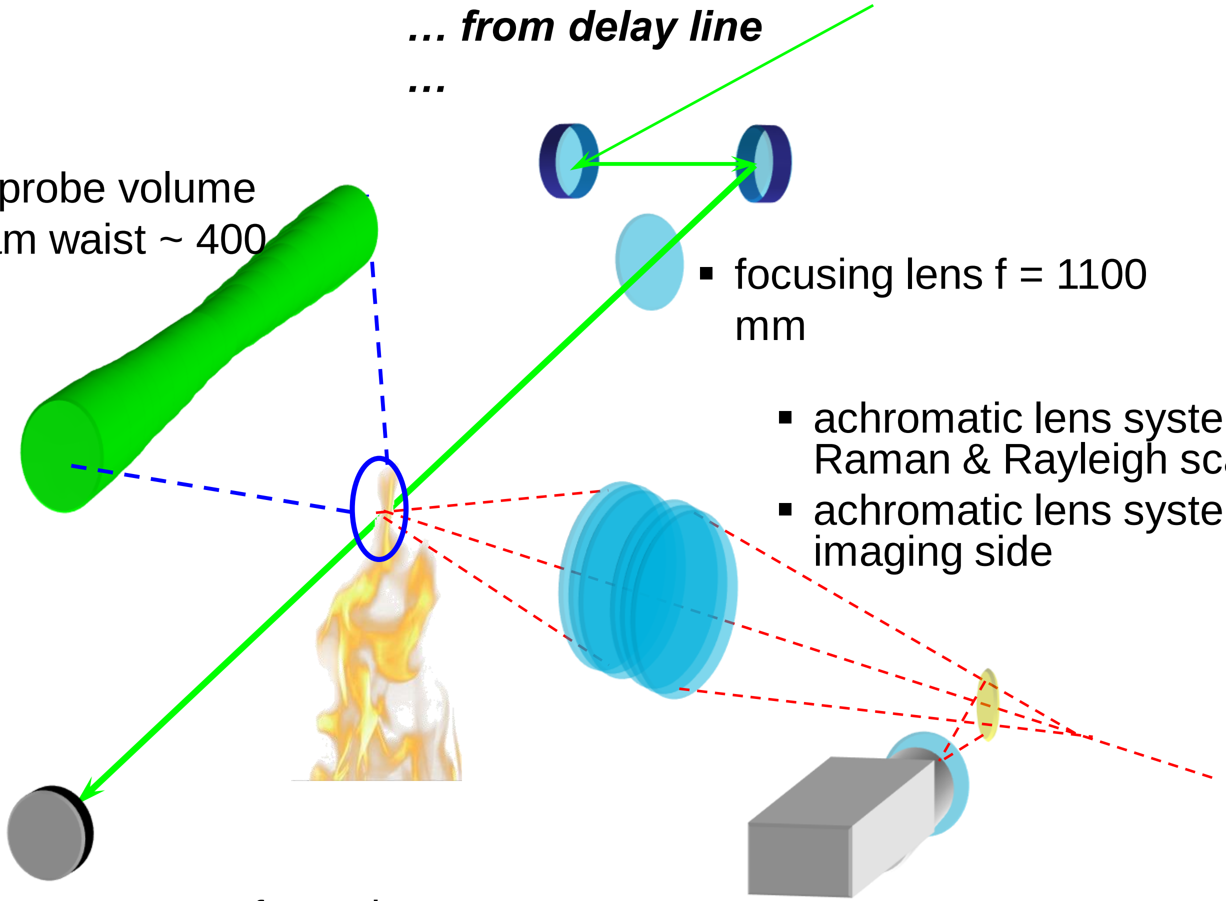
Measurement locations

- Radial profiles at 4 axial heights



Raman scattering – exp. setup

... from delay line ...



- 1D probe volume beam waist ~ 400 µm
- focusing lens f = 1100 mm
- achromatic lens system (f/# = 2) collecting Raman & Rayleigh scattered photons
- achromatic lens system (f/# = 4) focusing onto imaging side
- energy referencing
- ***Rayleigh:*** electron-multiplied thermo-electrically cooled CCD

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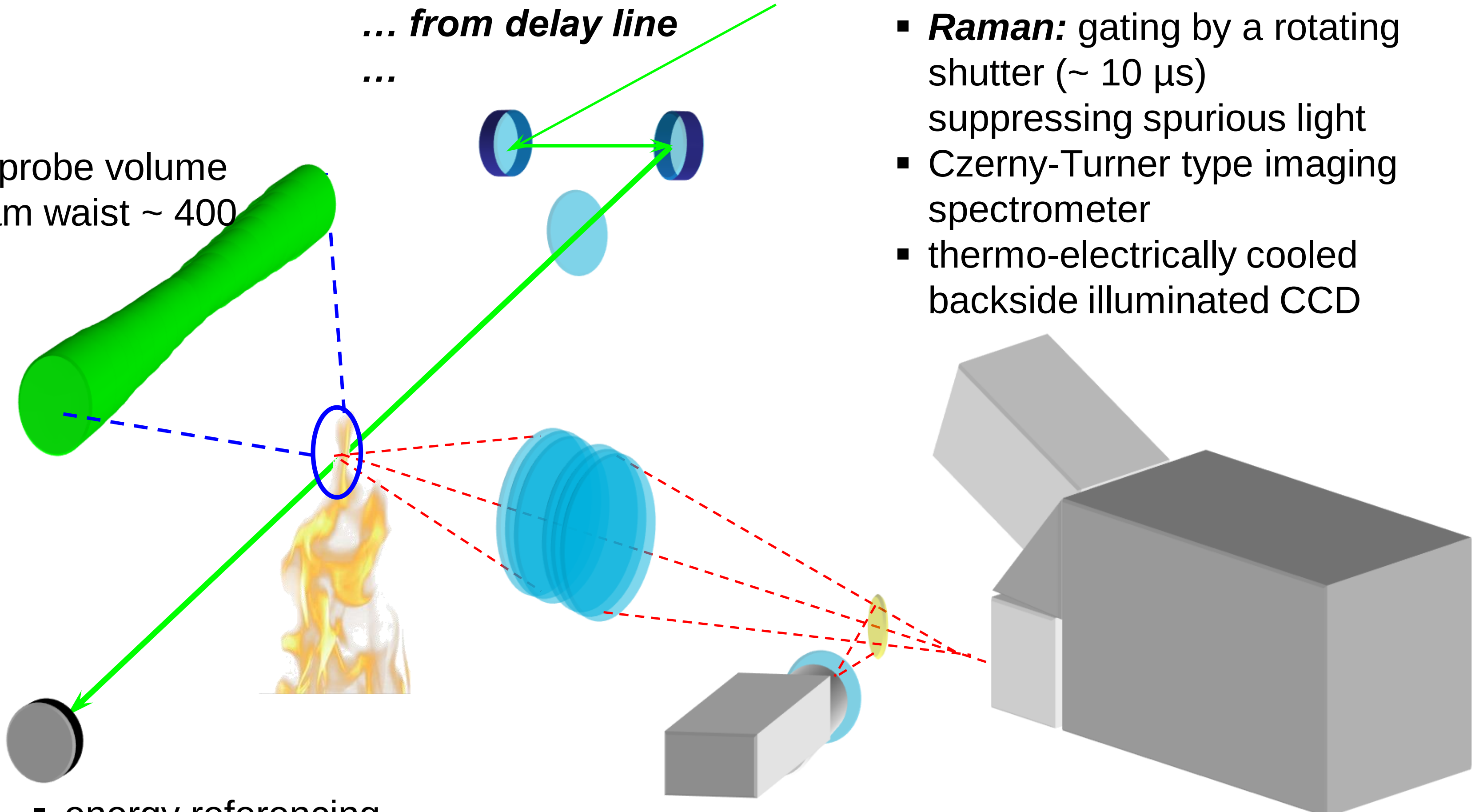
Raman scattering – exp. setup

- 1D probe volume beam waist ~ 400 µm

… from delay line …



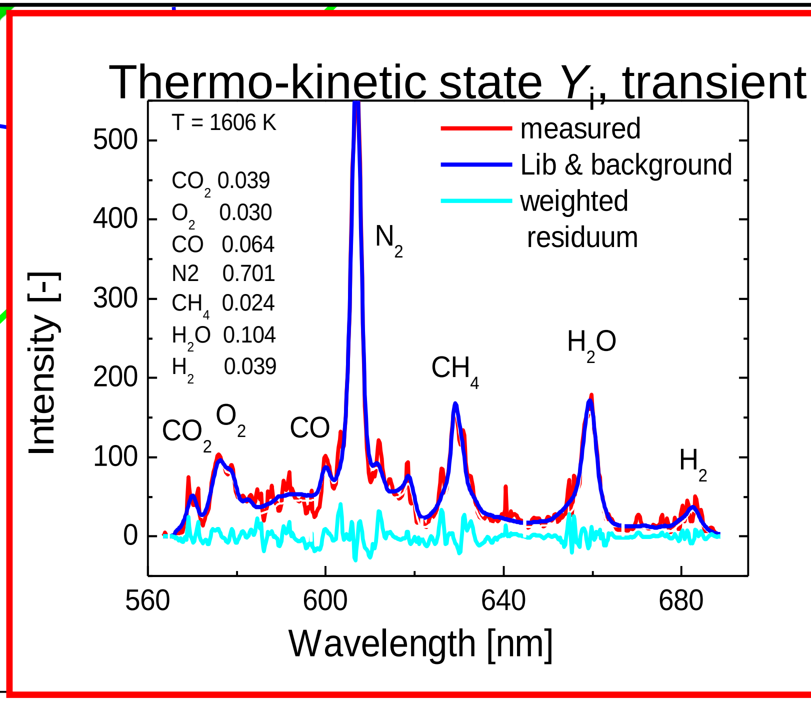
- energy referencing

- ***Raman:*** gating by a rotating shutter (~ 10 µs) suppressing spurious light
- Czerny-Turner type imaging spectrometer
- thermo-electrically cooled backside illuminated CCD

- steep cutoff long pass filter reflecting Rayleigh scattered light / transmitting Raman scattered light

Raman scattering – exp. setup

Data evaluation is conducted with a spectral fitting method using theoretical Raman spectra



- energy

Raman scattering – spatial resolution

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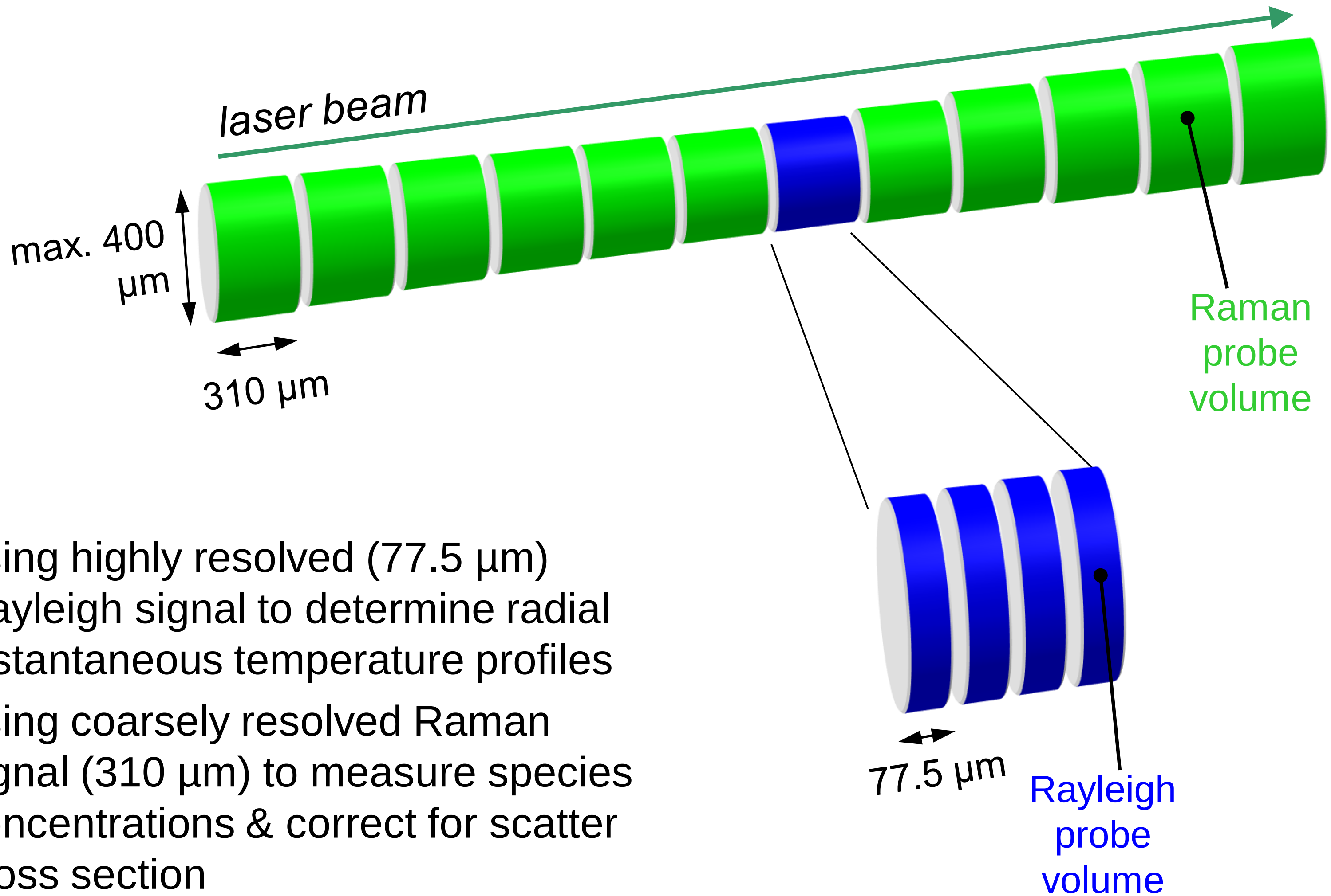
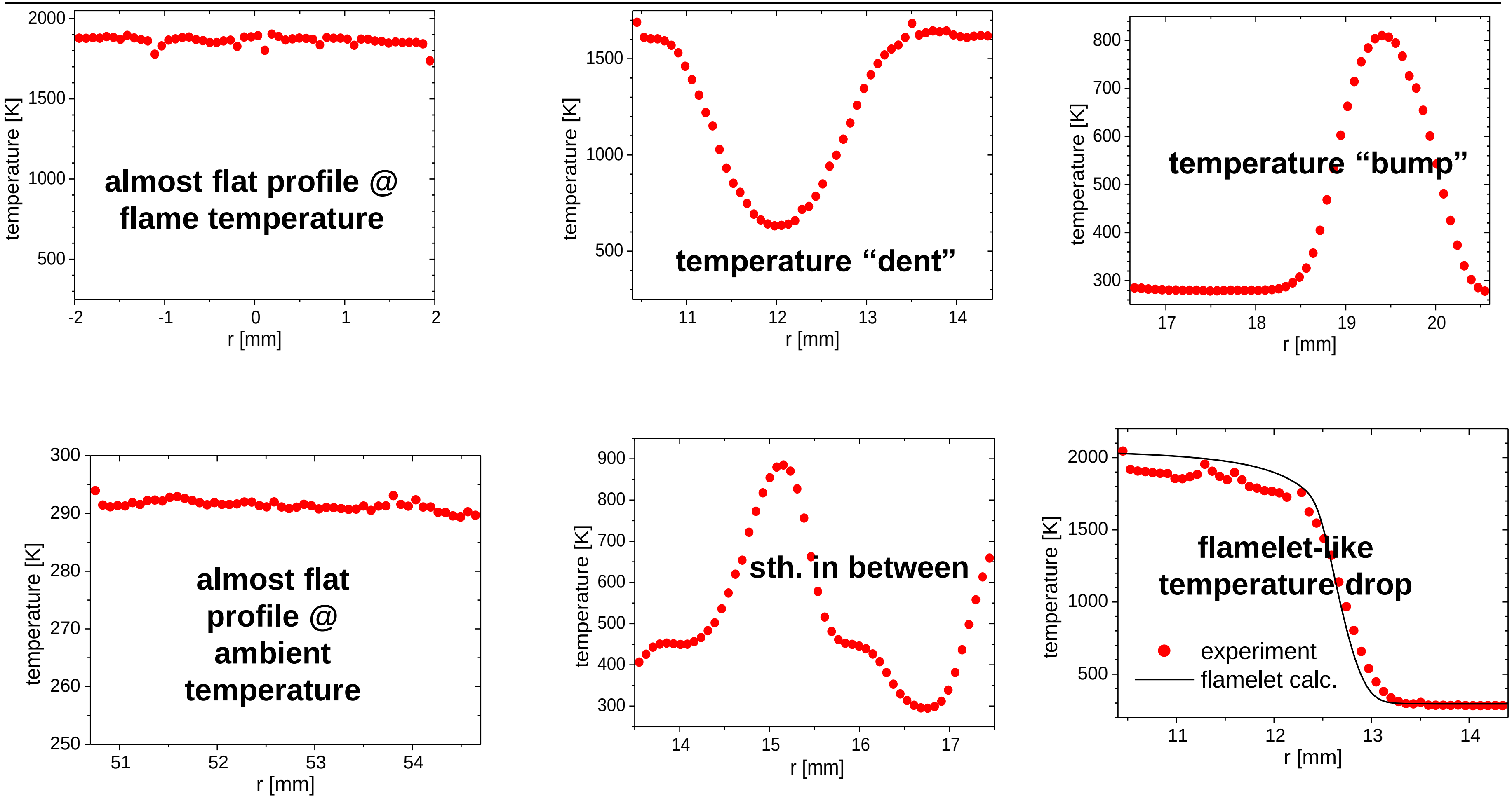


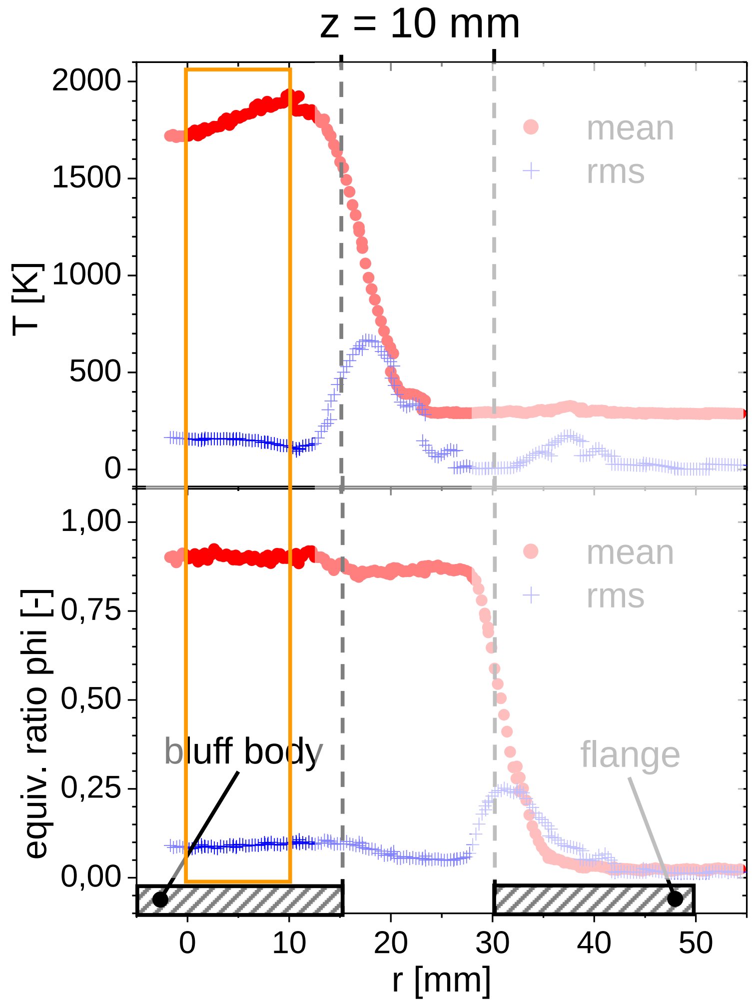
- using highly resolved (77.5 µm) Rayleigh signal to determine radial instantaneous temperature profiles
- using coarsely resolved Raman signal (310 µm) to measure species concentrations & correct for scatter cross section

RSM Reaktive Strömungen + Messtechnik

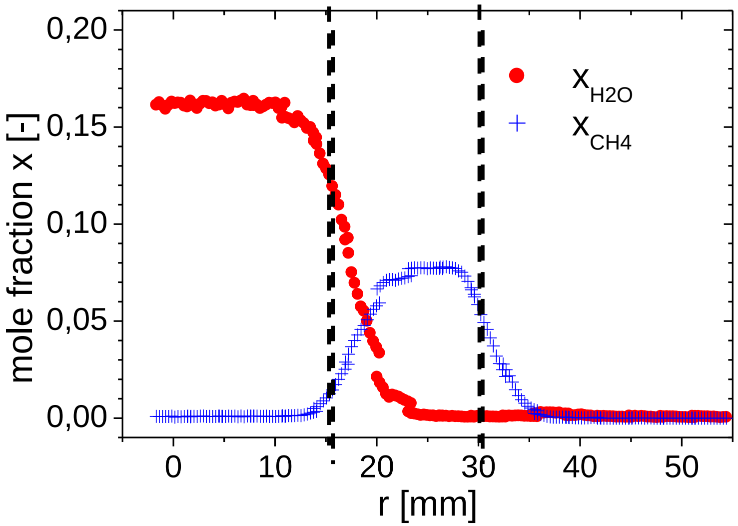
Raman scattering – spatial resolution



Radial Profiles (mean and rms)



- inner recirculation zone (~0-10mm):
  - fully burnt exhaust
  - heat loss to bluff body



Radial Profiles (mean and rms)

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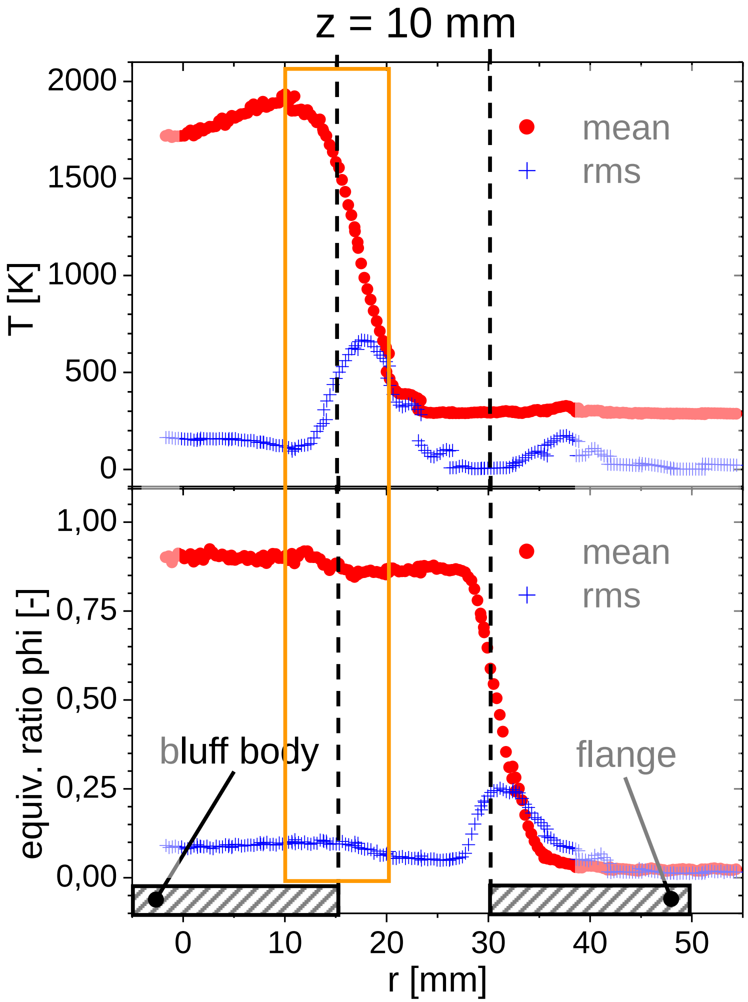
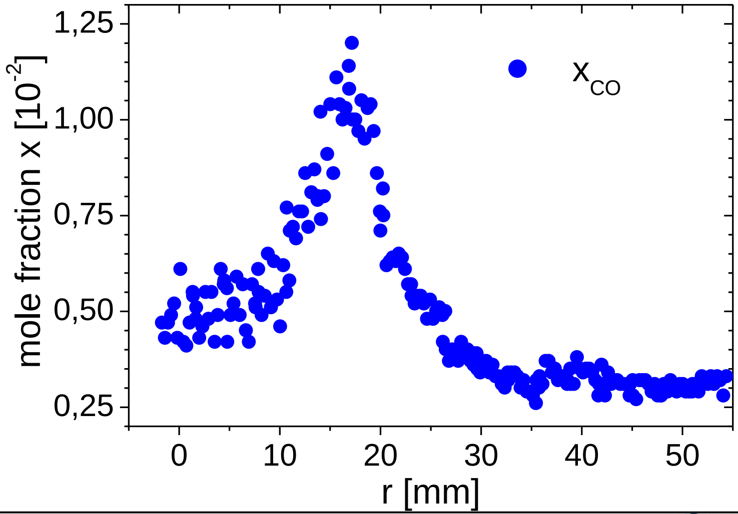


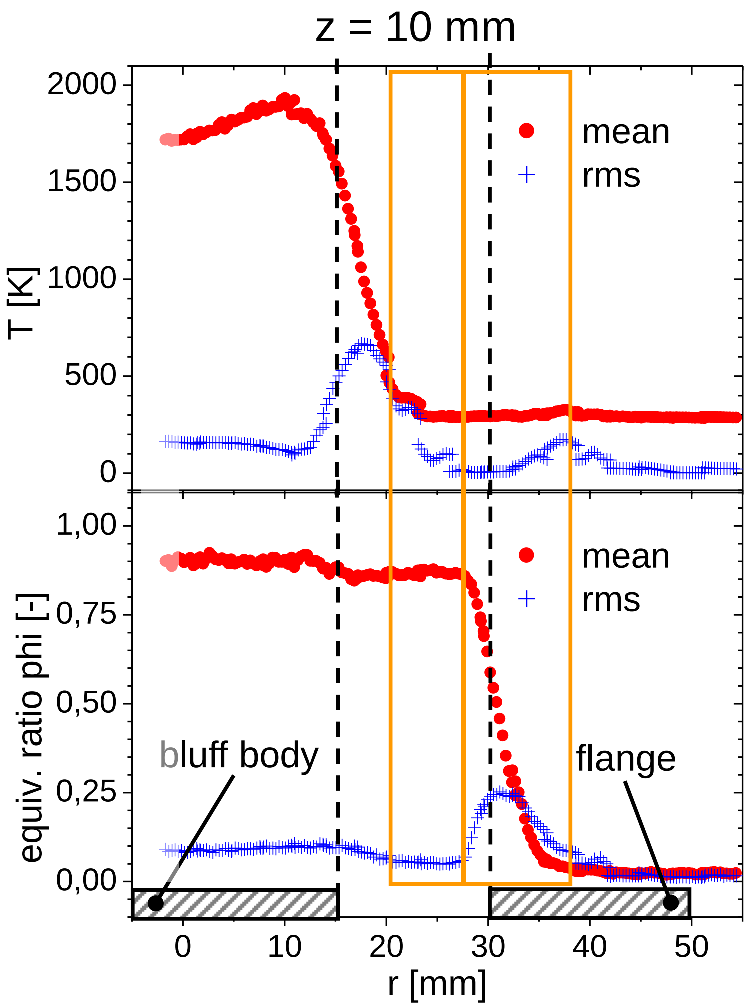
- inner recirculation zone (~0-10mm):
  - fully burnt exhaust
  - heat loss to bluff body
- inner mixing layer (~10-20mm):
  - strong intermittency hence high fluctuation levels
  - r ~ 17 mm: mean premixed flame front position as deduced from max. T & c gradients / max. CO concentration



RSM Reaktive Strömungen + Messtechnik

Radial Profiles (mean and rms)

TECHNISCHE UNIVERSITÄT DARMSTADT



- inner recirculation zone (~0-10mm):
  - fully burnt exhaust
  - heat loss to bluff body
- inner mixing layer (~10-20mm):
  - strong intermittency hence high fluctuation levels
  - r ~ 17 mm: mean premixed flame front position as deduced from max. T & c gradients / max. CO concentration
- central annular jet (~20-27mm):
  - almost unreacted fuel without dilution
- outer mixing layer (~27-38mm):
  - steep phi gradient towards surrounding air (phi = 0
  - second temperature maximum due to outer recirculation zone

Mean Radial Profiles - z Dependency

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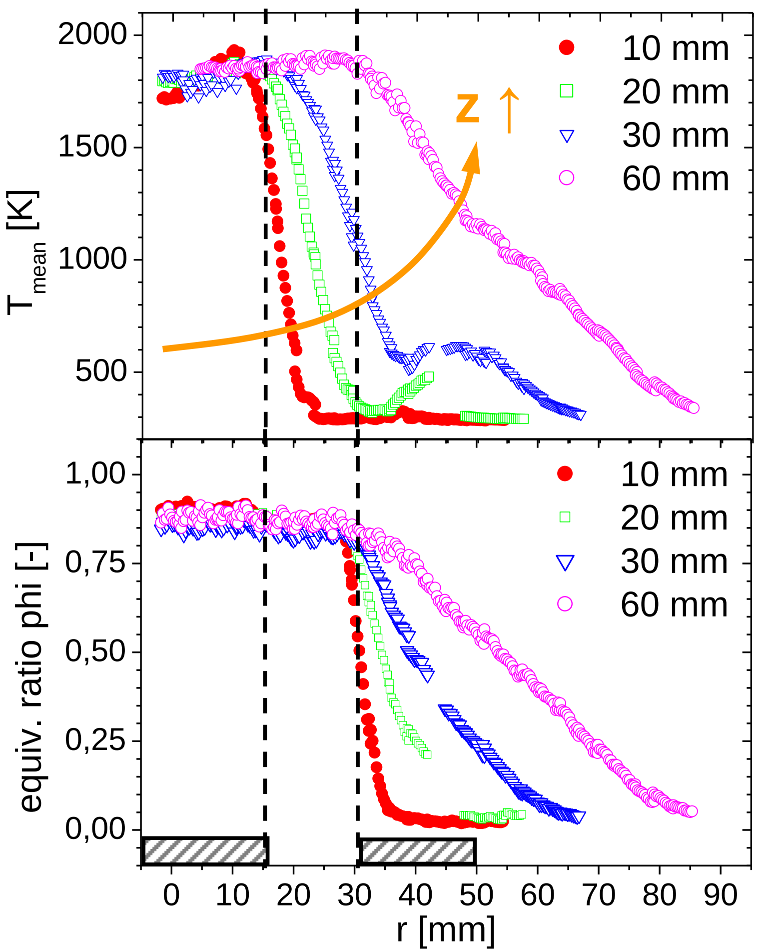
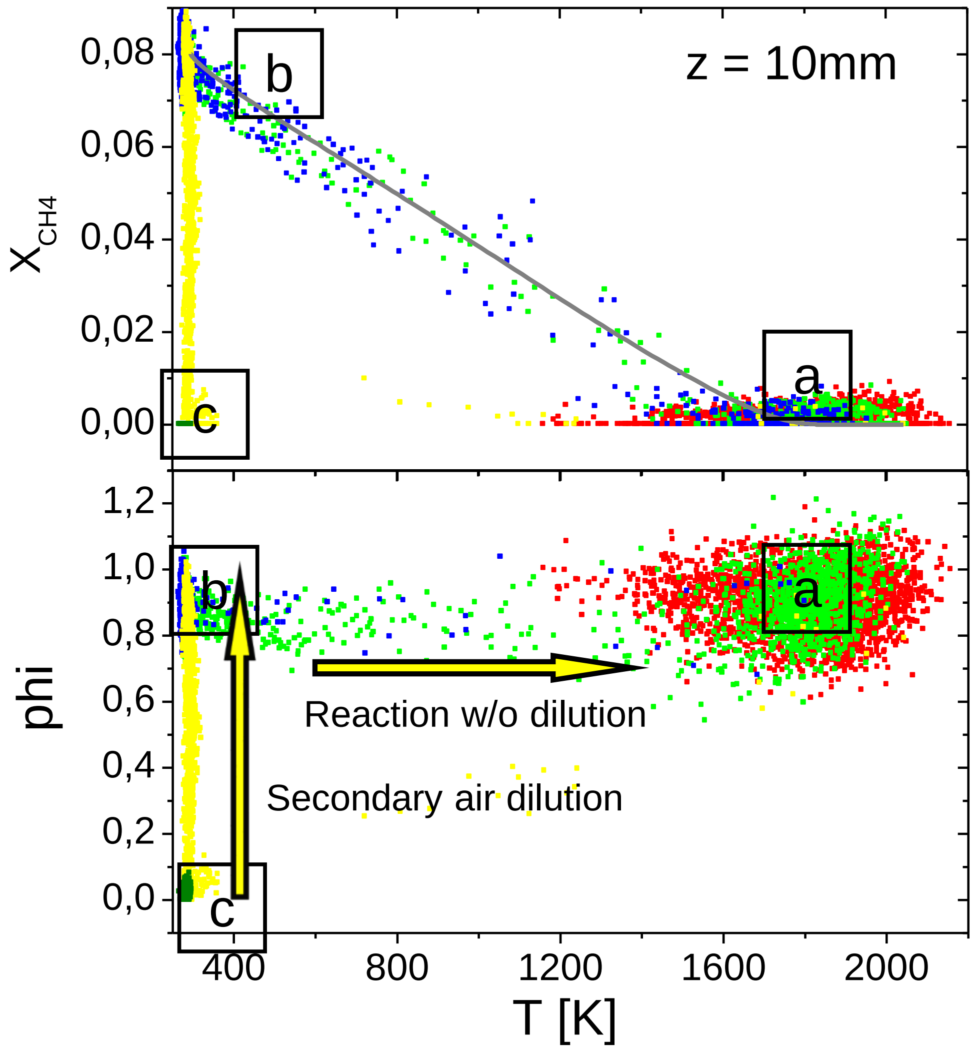


- for increasing height z:

- mean flame front position at larger radii
- wider flame brush & broader mixing layer hence flatter radial T & phi profiles
- distinct 2nd T maximum (up to z = 30mm) due to outer recirculation of exhaust
- premixed flame front is located in regions with very low stratification of nearly constant phi (up to z = 30mm)

Single Shot Correlations - Scatter Plots

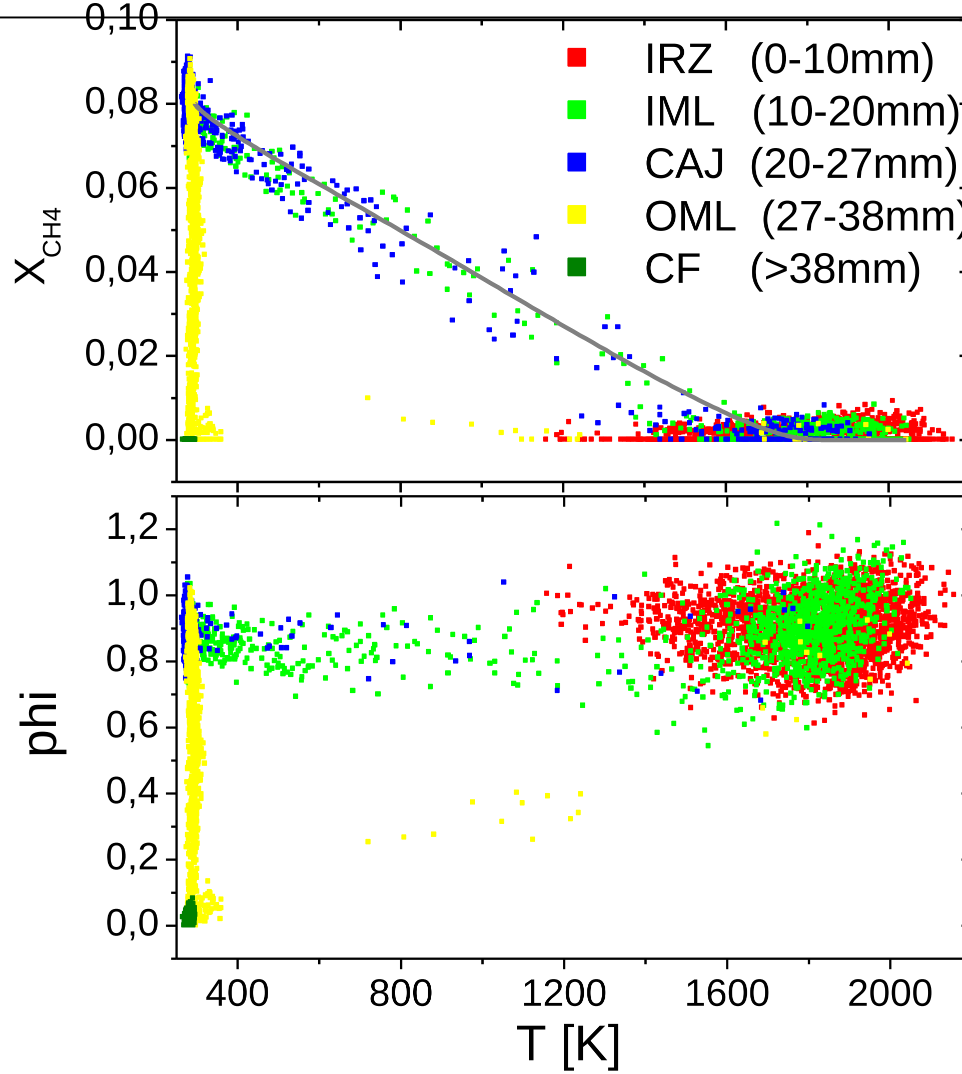
- single shot correlation between 2 or more scalars (e.g. T & CH4)
- each scatter corresponds to one single shot
- samples spanned between 3 thermo-kinetic states:
  - a) hot burnt exhaust
  - b) cold unburnt fuel
  - c) cold secondary air



Single Shot Correlations - Scatter Plots

- **samples can be assigned to flame regions:**
  - inner recirculation zone (0-10mm): fully burnt samples @ max T, no secondary air
  - inner mixing layer & central annular jet (10-27mm): burnt, unburnt or mixed samples, no secondary air
  - outer mixing layer (27 - 38 mm): mostly unburnt fuel and / or secondary air

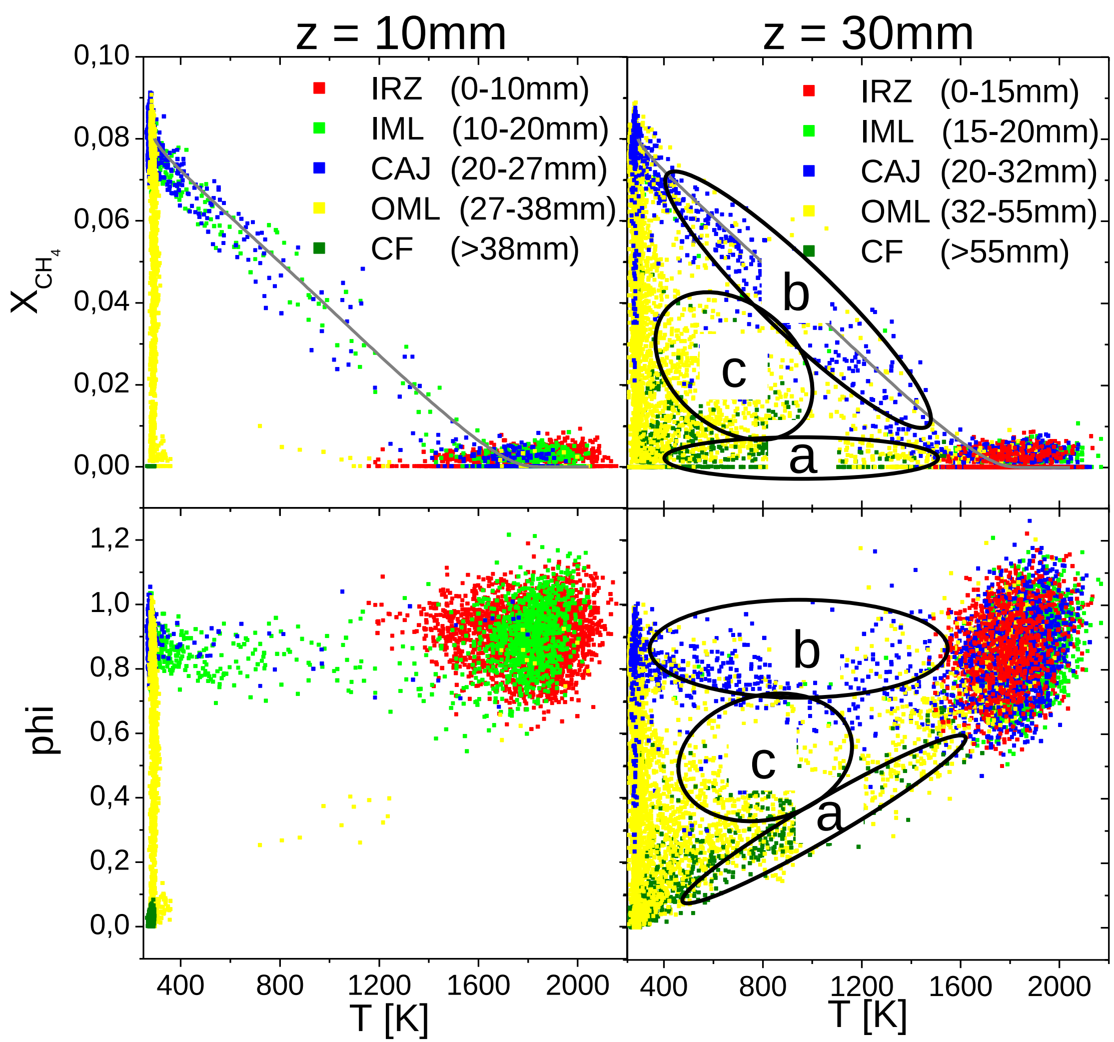
    rarely mixing between burnt samples and secondary air
  - coflow / flange (>38 mm): exclusively ambient air



Scatter Plots - z Dependency

- *at z = 30 mm:*
- significantly increased probability to measure intermediate samples due to:
  - a) secondary air entrainment into burnt exhaust (OML, CF)
  - b) mixing between burnt / unburnt fuel (CAJ) and reaction without dilution
  - c) mixing of air with reacted AND unreacted fuel

    or
  - slowed or extinguished reactions (CAJ, OML, CF)



Conclusions Raman/Rayleigh scattering in swirling premixed flame

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- Temperature is key-quantity (reaction progress)
- Thermo-kinetic state precisely measured
- Thermo-kinetic state is a prerequisite for understanding pollutant formation and finite rate chemistry effects
- Main findings are
  - In region of flame stabilization ($z < 30$ mm) premixed flame front is not located in areas of stratification but in areas of almost constant phi
  - typical reaction and / or mixing behavior can be assigned to different flame regions
  - intermediate reaction states are promoted by dilution with air
  - distinction between pure mixing and local flame quenching needs additional diagnostics monitoring intermediate species