

5. Laser Induced Fluorescence

General

- Introduction to LIF; Theory
- Species concentrations
- Temperature measurements
- Multi-dimensional imaging

Applications

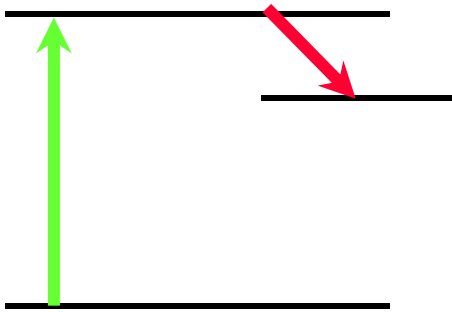
- Engines
- Gasturbines
- Furnaces/boilers-Biomass applications



Laser-induced fluorescence

LIF:

Measures e.g, NO, OH,
CH, CN, C₂, O₂, fuel-tracer



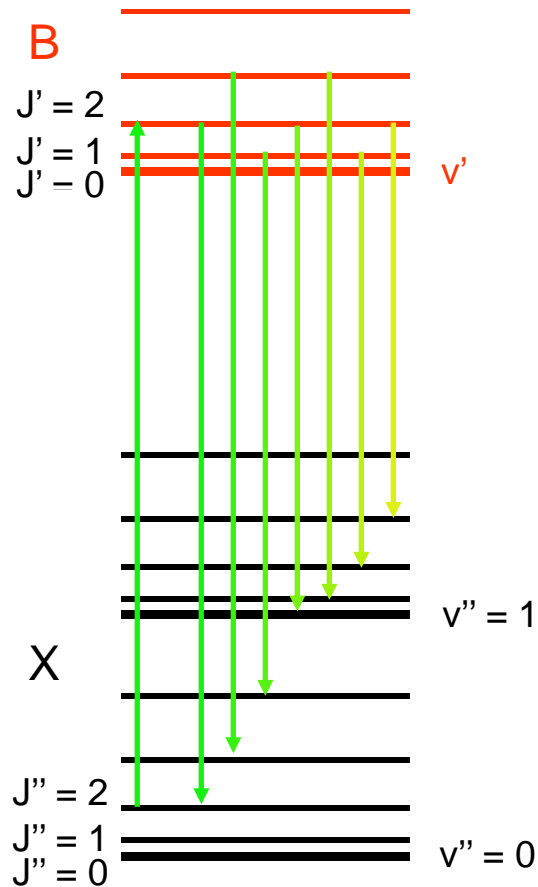
General features:

- High sensitivity
- 2D imaging capabilities
- Spontaneous technique
- Measures temp. and konc.
- Quantification problem



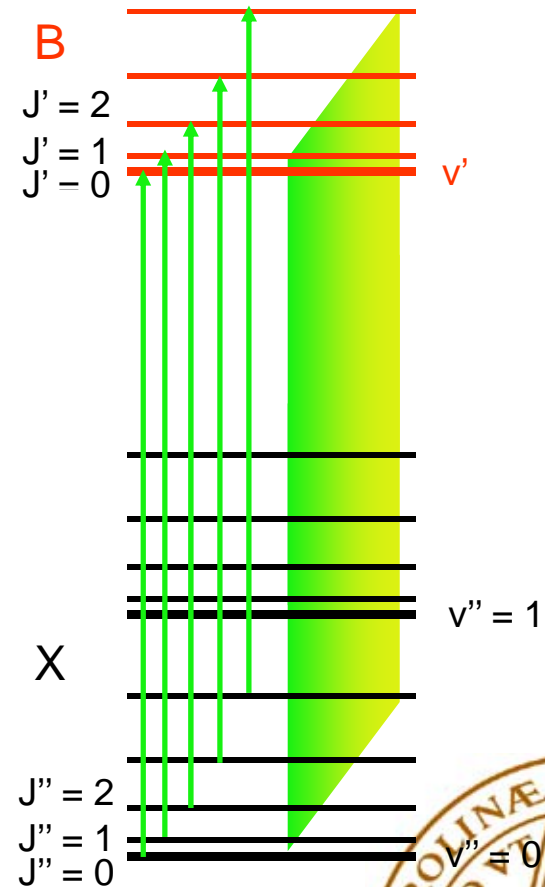
Different LIF approaches

Fluorescence spectrum



Laser tuned to a specific absorption line and the spectrometer is scanned

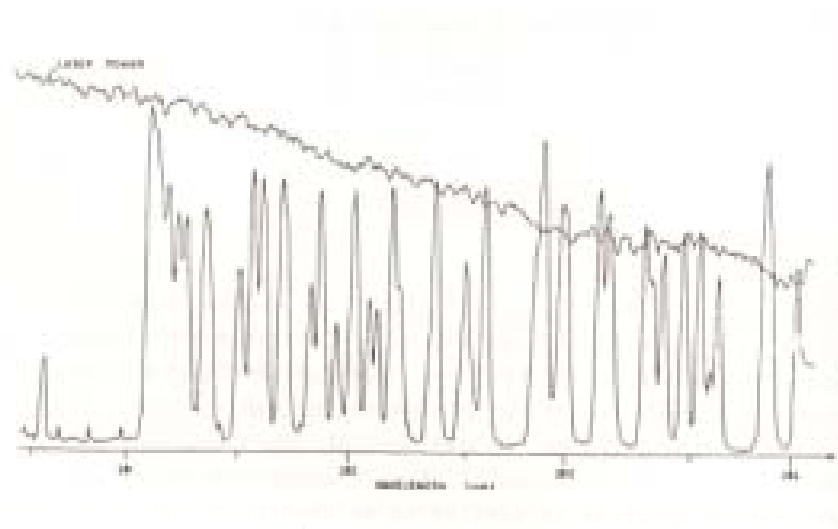
Excitation scan



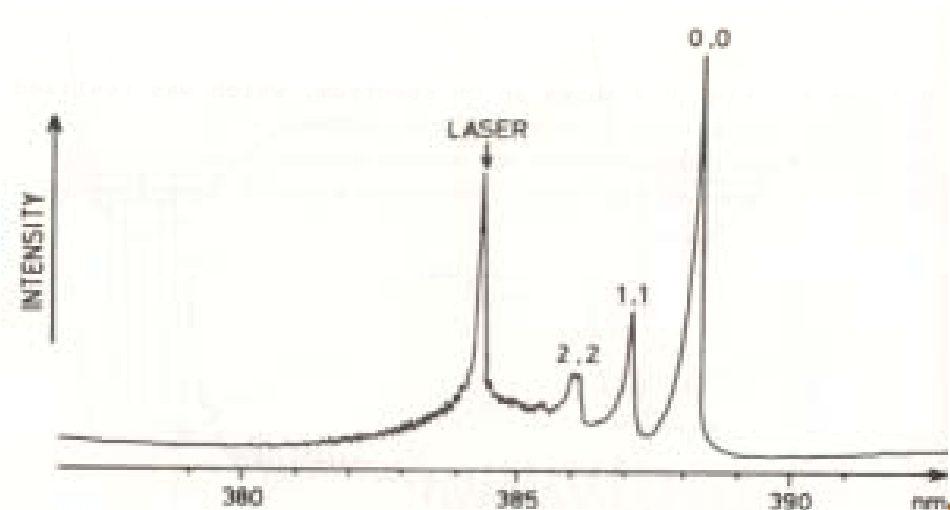
Laser is tuned across the various absorption lines and the total fluorescence is monitored



Excitation and fluorescence spectra



Excitation spectrum of OH



Fluorescence spectrum of CN



Important molecules detected by LIF

Table I

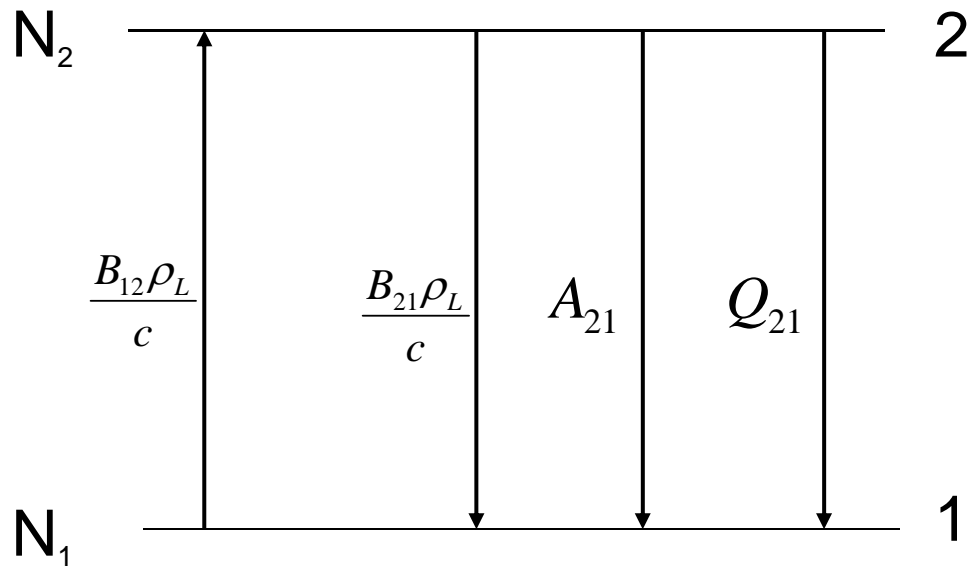
Molecule	Abs. wavelength (nm)
OH	~306
C ₂	~516
CH	~431
CN	~388
NH	~336
NO	~226
CH ₂ O	~320-360
NO ₂	450-470



LIF Theory

$$S \sim A_{21} N_2,$$

How is N_2 related to N_{tot} ?



Rate equation analysis

$$\frac{\partial N_1(t)}{\partial t} = -N_1(t) \frac{B_{12} \rho_L}{c} + N_2(t) \left(A_{21} + Q_{21} + \frac{B_{21} \rho_L}{c} \right)$$

$$\frac{\partial N_2(t)}{\partial t} = N_1(t) \frac{B_{12} \rho_L}{c} - N_2(t) \left(A_{21} + Q_{21} + \frac{B_{21} \rho_L}{c} \right)$$

$$N_{tot} = N_1 + N_2 \quad \text{and assume steady state; } dN/dt=0$$

$$b_{ij} = B_{ij}/c$$

$$A_{21}/B_{21} = 8\pi h/\lambda^3$$



Results

$$N_2 = \frac{N_{tot} b_{12} \rho_L}{A_{21} + Q_{21} + (b_{21} + b_{12}) \rho_L}$$

$$S = A_{21} \frac{N_{tot} b_{12} \rho_L}{A_{21} + Q_{21} + (b_{12} + b_{21}) \rho_L}$$

$$S = N_{tot} V F_p b_{12} \rho_L \underbrace{\frac{A_{21}}{A_{21} + Q_{21} + (b_{12} + b_{21}) \rho_L}}_{\text{Stern-Vollmer factor} = Y}$$



Evaluate

$$S = N_{tot} V F_p b_{12} \rho_L \frac{A_{21}}{A_{21} + Q_{21} + (b_{12} + b_{21}) \rho_L}$$

Low laser limit: $(b_{12} + b_{21}) \rho_L \ll (A_{21} + Q_{21})$

$$S = N_{tot} V F_p b_{12} \rho_L \frac{A_{21}}{A_{21} + Q_{21}}$$



LIF in the linear regime

$$S = N_{tot} V F_p b_{12} \rho_L \frac{A_{21}}{A_{21} + Q_{21}}$$

Fluorescence efficiency

- The fluorescence is linearly proportional to the input laser irradiance
- Since most often $A_{21} \ll Q_{21}$, the fluorescence efficiency is generally $\ll 1$, which diminishes the sensitivity
- For quantitative measurements usually Q_{21} has to be evaluated
- $Q_{21}(p, T, \text{composition}) \Rightarrow$ difficult to obtain quantitative data

For quantitative measurements it is critical to measure/estimate Q !!



Make Q small: High laser intensity

$$Y = \frac{A_{ij}}{A_{ij} + (b_{ij} + b_{ji})\rho_L + Q_{ij}}$$

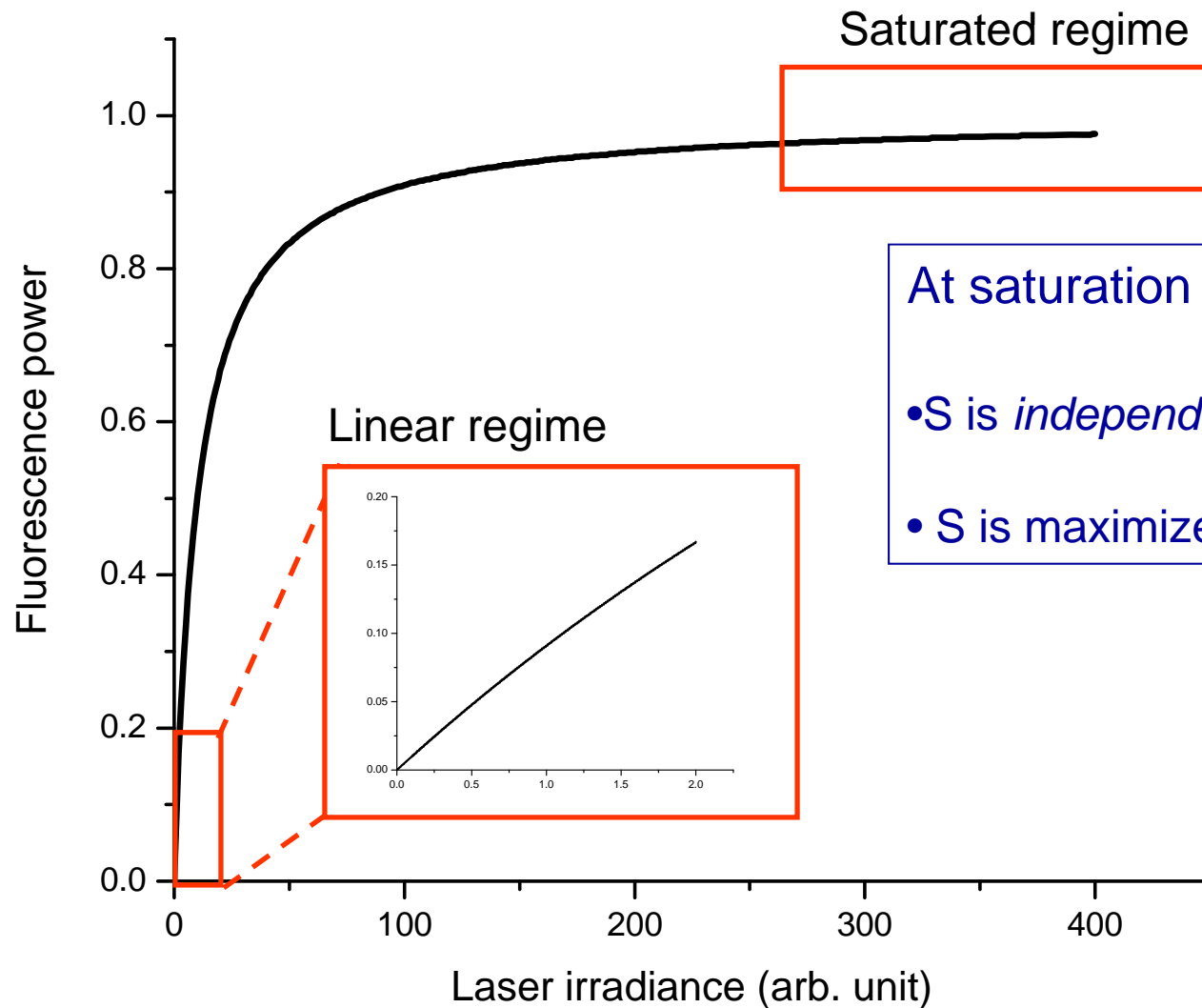
$$(b_{12} + b_{21})\rho_L \gg (A_{21} + Q_{21})$$

$$S = A_{21} V N_{tot} \frac{b_{12}}{b_{12} + b_{21}}$$

Saturation



Fluorescence power versus laser irradiance



At saturation

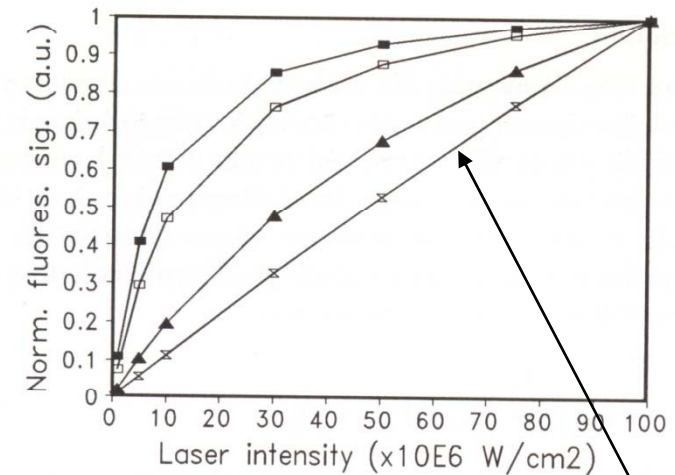
- S is *independent* of both ρ and Q_{21}
- S is maximized \Rightarrow sensitivity maximized

Power dependence



Saturation

- Saturation depends on Q
- Saturation depends on spatial, temporal and frequency laser wing effects



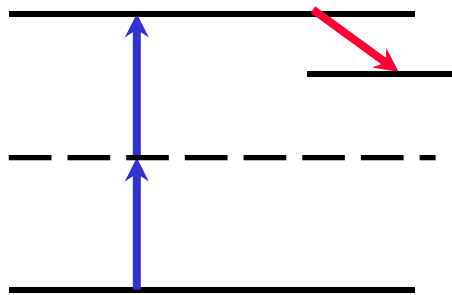
High Q

$$\rho_L(t, z, r, \nu) = \rho_L^\circ \text{Exp}\left(-\left(\frac{t}{T}\right)^2\right) \text{Exp}\left(-\left(\frac{r}{R(z)}\right)^2\right) F(z) \frac{K}{(\nu - \nu_0^2) + K}$$



Two-photon LIF

Differences between one- and two-photon LIF:



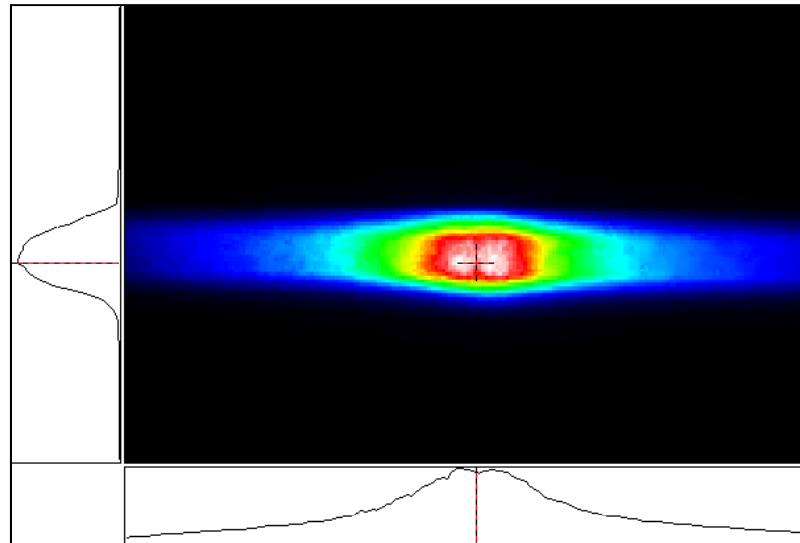
- Different selection rules
- Doppler-free measurements possible
- Temporal behaviour of laser pulse important
- LIF signal proportional to the laser-intensity squared

Species	Exc. λ (nm)	Em. λ (nm)
H	2x205	656
O	2x226	845 (777)
N	2x211	870 (822,744)
C	2x280	910
CO	2x230	400-725
H ₂	2x193	830
H ₂ O	2x248	400-500
NH ₃	2x305	550-575 (720)



Difference between one and two-photon LIF

- $I_{\text{one-photon}} \sim I/A \times A = I$, independent on focusing
- $I_{\text{two-photon}} \sim (I/A)^2 \times A = I^2 / A$



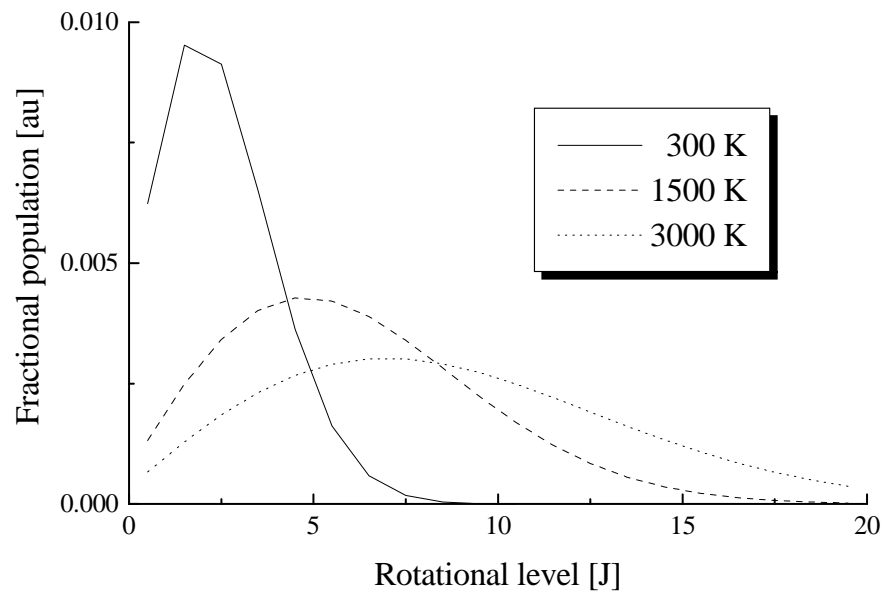
LIF thermometry

- Any method that reflects the distribution of population over two or more individual vibrational rotational states can in principle be used for temperature measurement. LIF is such a method.
- LIF thermometry restricted to high temperatures if molecular radicals are employed. For OH temperatures above ~ 1500 K are needed.
- If atomic species, such as metal atoms, are used, these have to be seeded into the flame or flow.
- If LIF was used for concentration measurements it is definitely convenient to apply it for thermometry too.



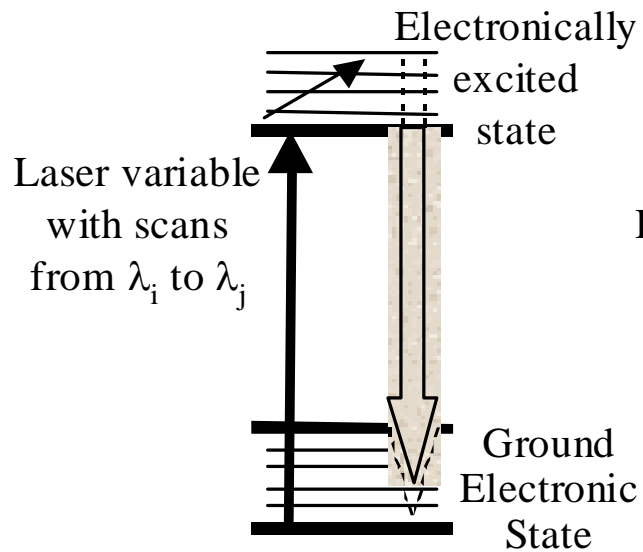
Temperature measurements

$$n_j = \frac{(2J + 1)N_{tot} \text{Exp}\left(-\frac{E_j}{kT}\right)}{Q_{vib}Q_{rot}}$$

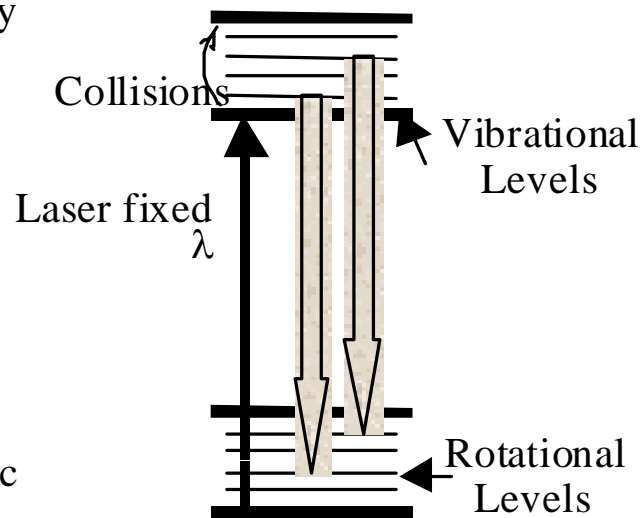


Various techniques

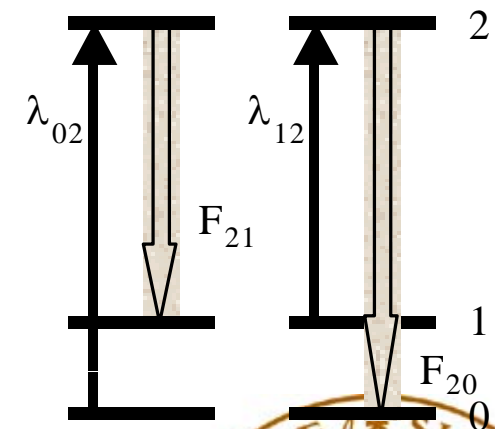
Excitation Scans



Thermally-Assisted



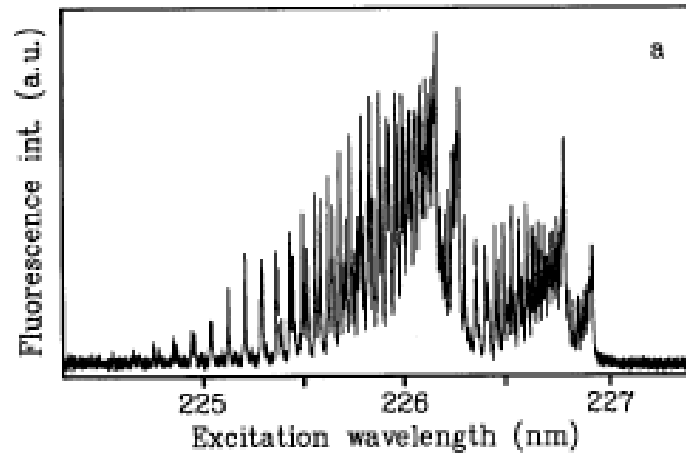
Two-Line



Excitation spectra

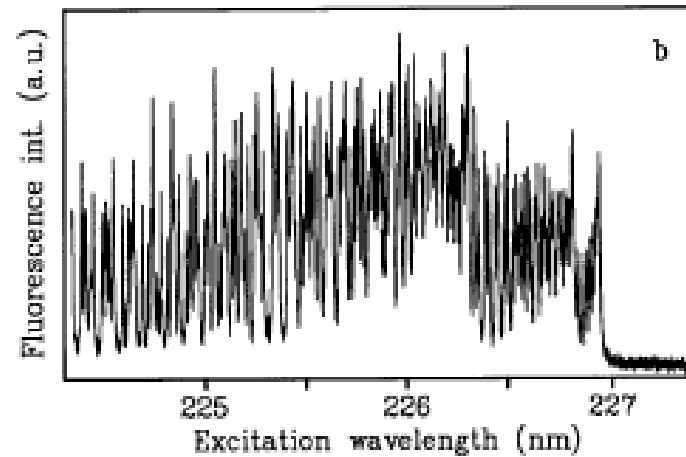
NO room

T~ 300 K

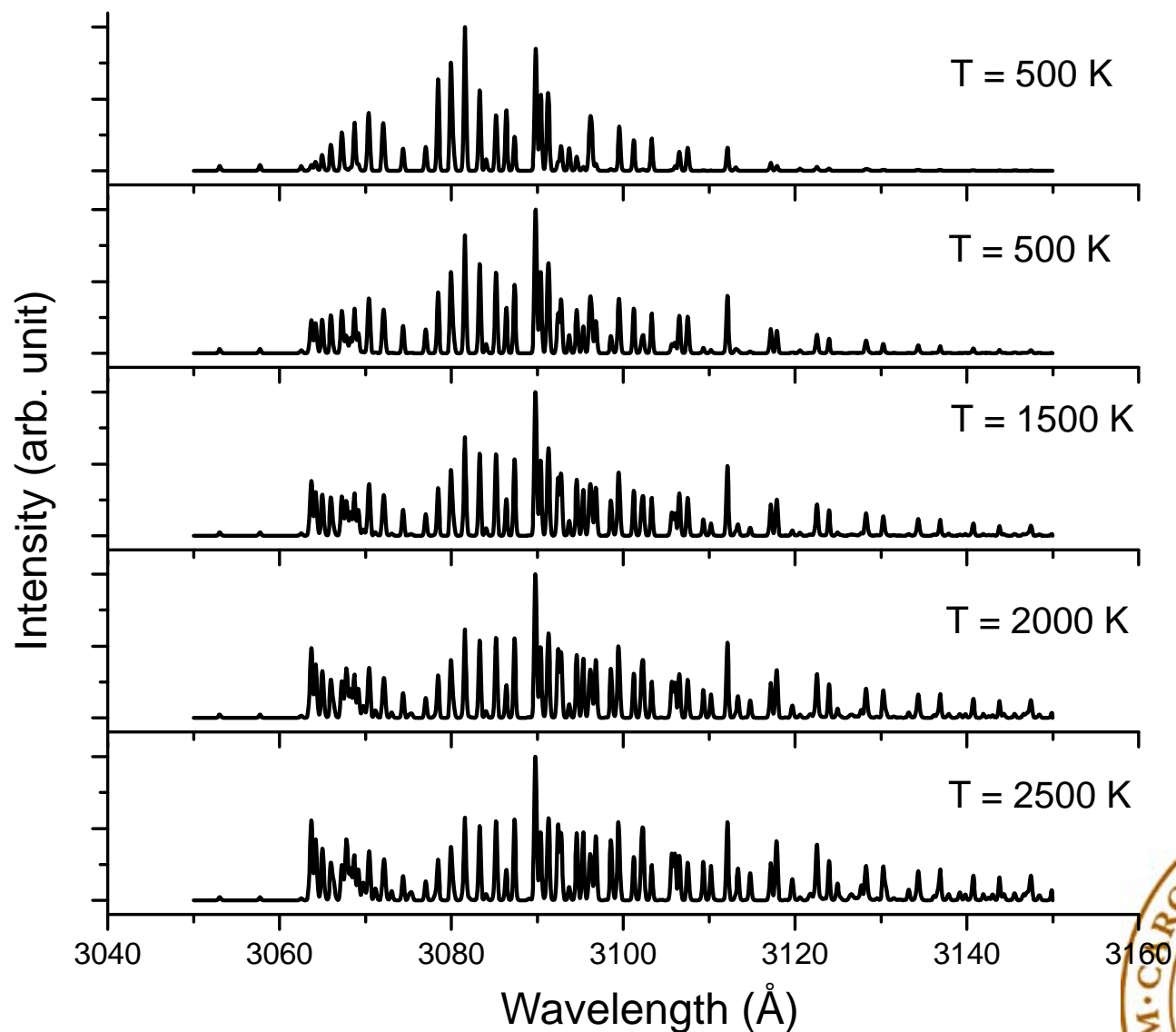


NO flame

T~ 2000 K

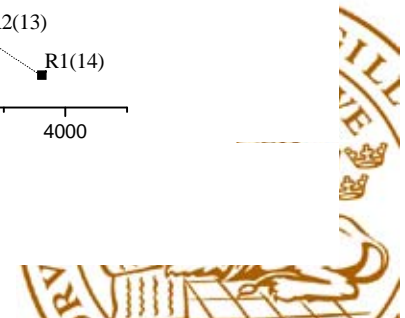
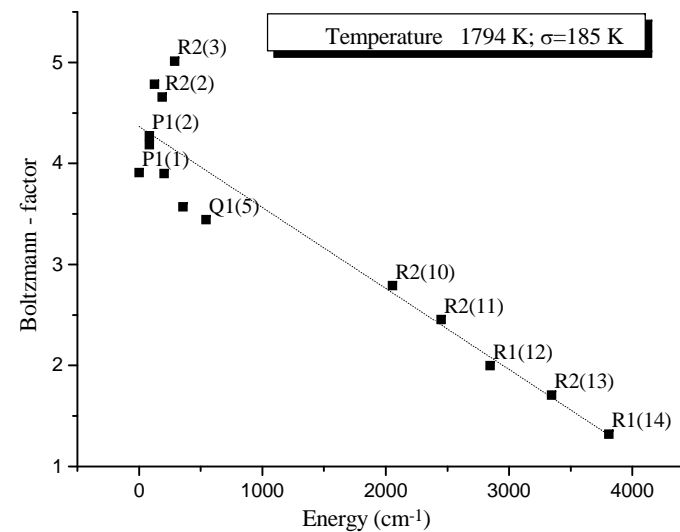
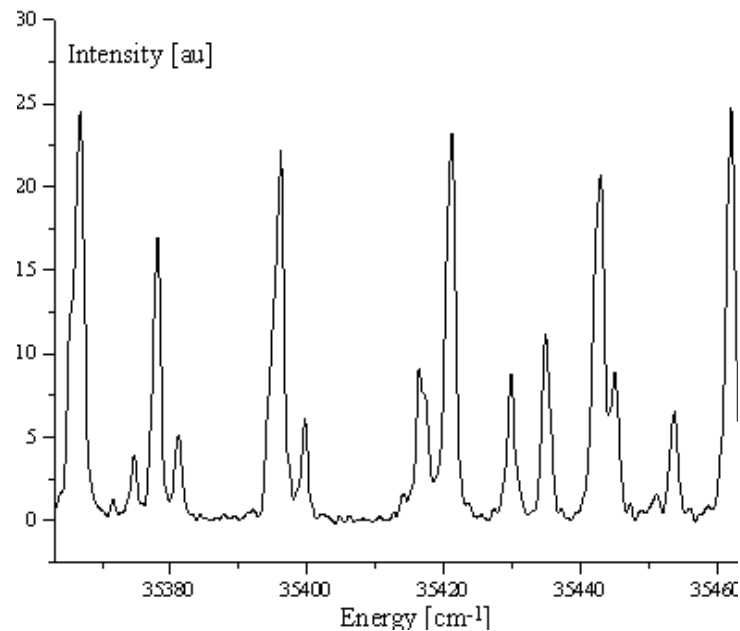


Excitation scans of OH A-X (0,0)



Plotting approach for yielding T

$$\ln(n_i) \sim -E_i/kT$$



Single shot 2D LIF flame thermometry strategies: Two-line excitation

Two-line molecular fluorescence: e.g OH, NO, ketones

Problems:

- **Applicable only in areas where the species is located; high T (OH) , low T (ketones)**
- **Excitation in UV, may cause background emission, trapping etc,**
- **Require relatively high laser intensities**
- **Problems in fuel rich environments**
- **Complex set up (NO)**



Two-Line Atomic Fluorescence (TLAF)

- Atoms usually possess much higher transition probabilities than molecules \Rightarrow Very low laser power can be used for excitation
- Excitation can be made in the visible region
- Measurements in sooty flames can be made
- Usually metal atoms are seeded into the flame
- The tracer species should be selected based on:
 - temperature sensitivity
 - complexity of the emission spectrum
 - minimum intrusion on the combustion process



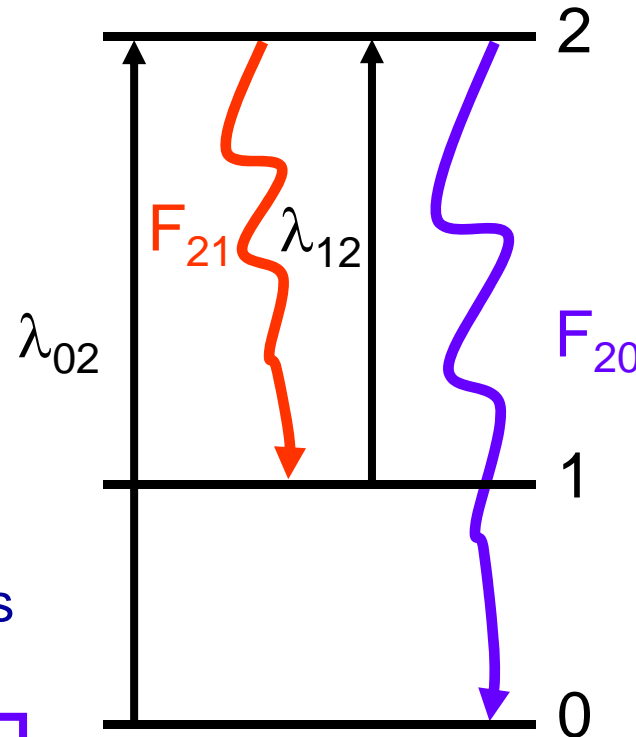
Two-line LIF thermometry

Basic idea:

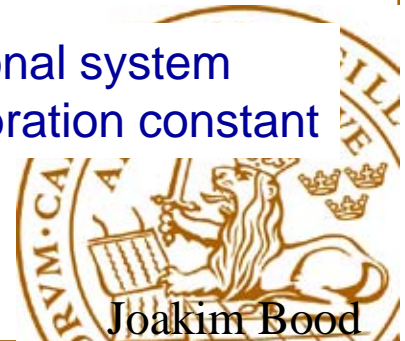
To measure the relative population of two states \Rightarrow T from Boltzmann expression

Excitation to the same upper state \Rightarrow F_{21} and F_{20} are equally affected by quenching and energy transfer processes

$$T = \frac{(E_1 - E_0)/k}{\ln \frac{F_{21}}{F_{20}} + \ln \frac{I_{12}}{I_{02}} + 4 \ln \frac{\lambda_{21}}{\lambda_{20}} + \ln C}$$



C non-dimensional system dependent calibration constant

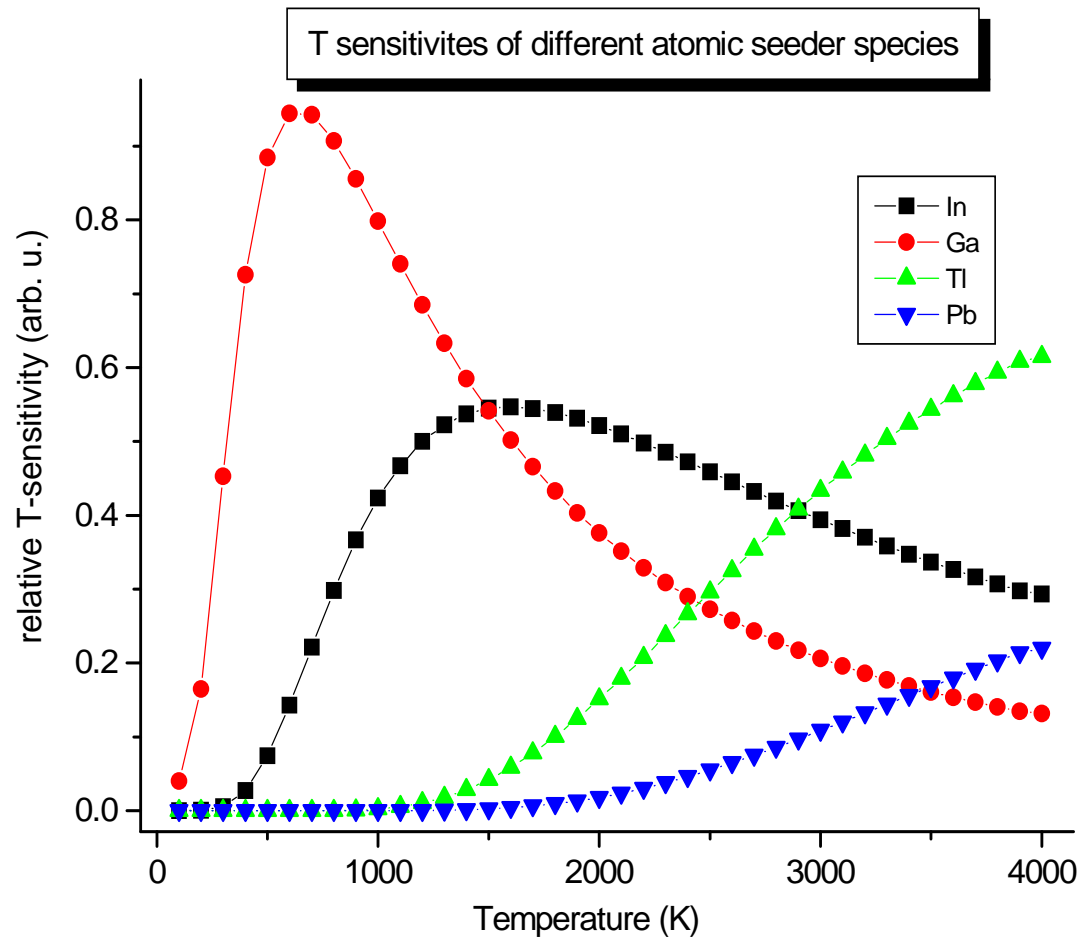


Two-line fluorescence

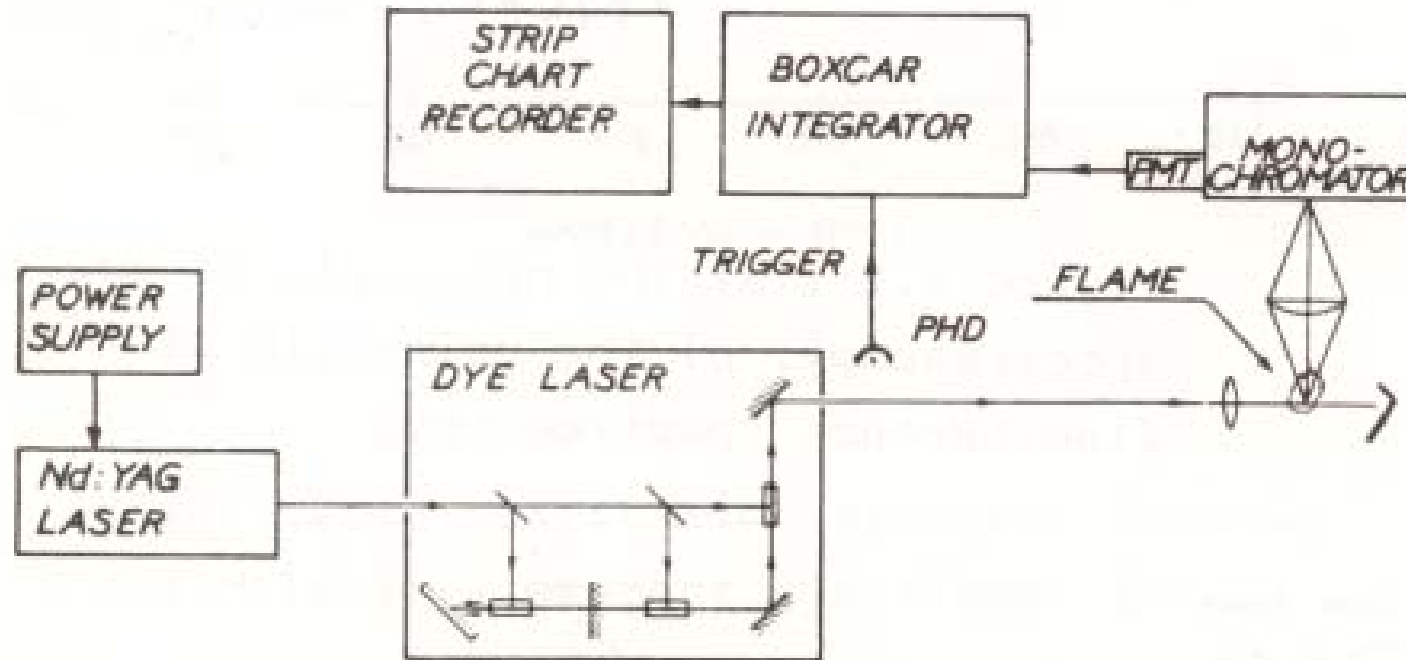
Species	λ_1 (nm)	λ_2 (nm)	ΔE (eV)
Gallium	403.4	417.3	0.109
Indium	410.3	451.3	0.274
Thallium	377.6	535.0	0.966
Lead	339.4	461.9	1.320



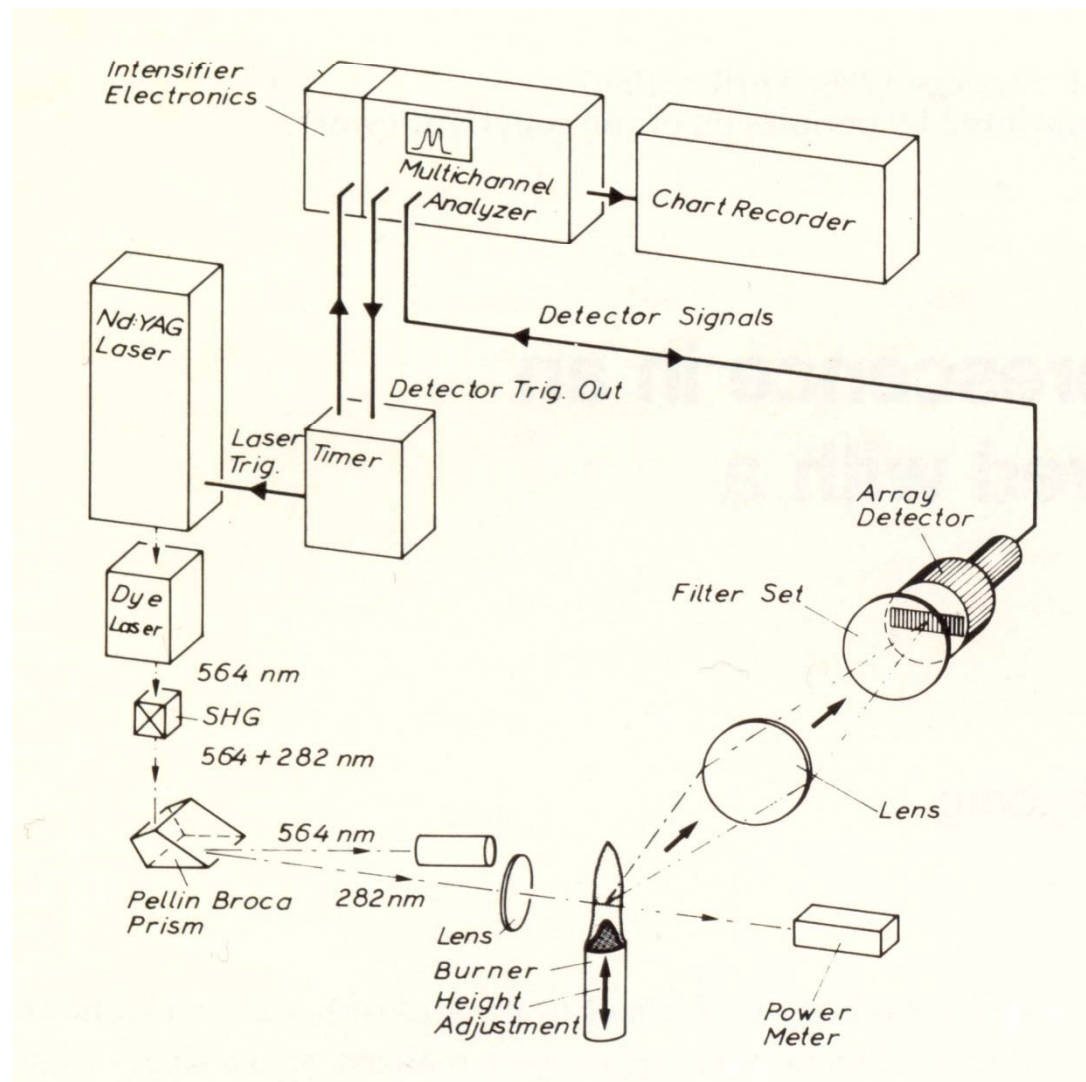
Temperature sensitivities



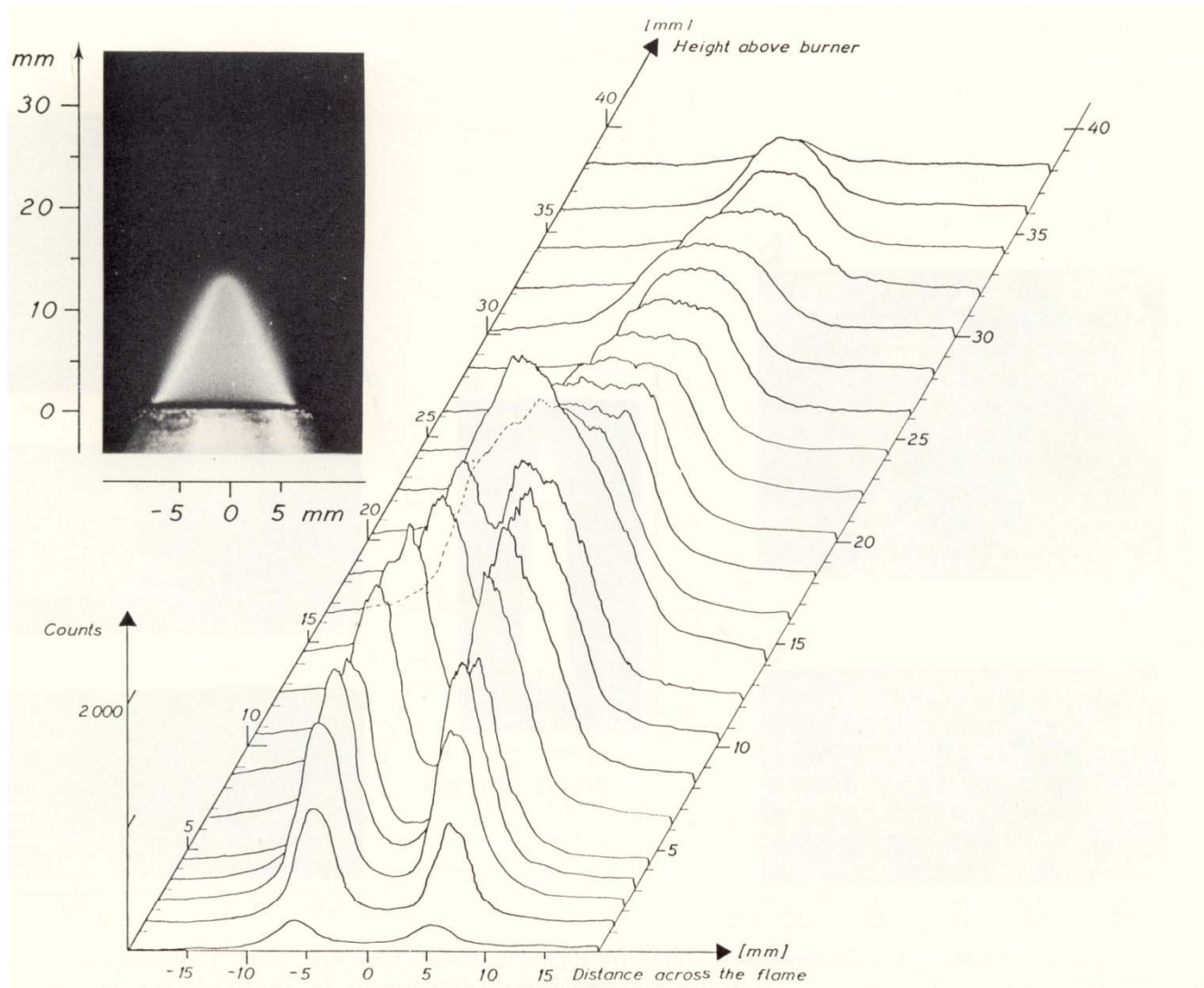
LIF set-up: 0D



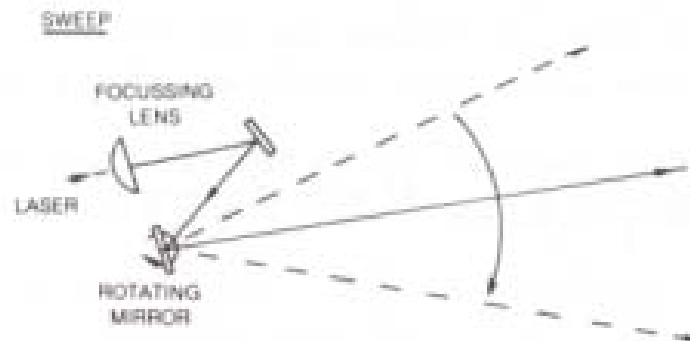
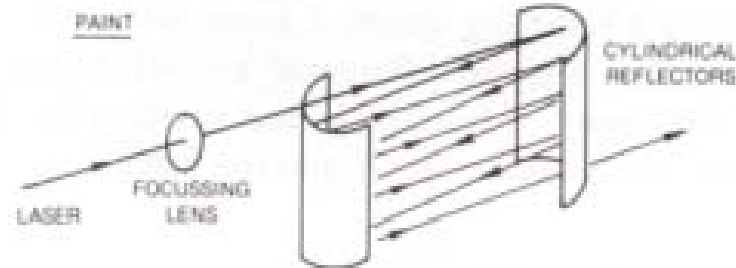
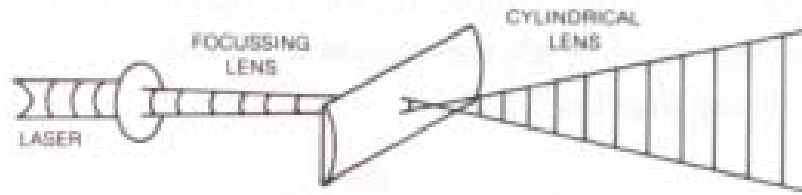
Multi-point visualization: 1D



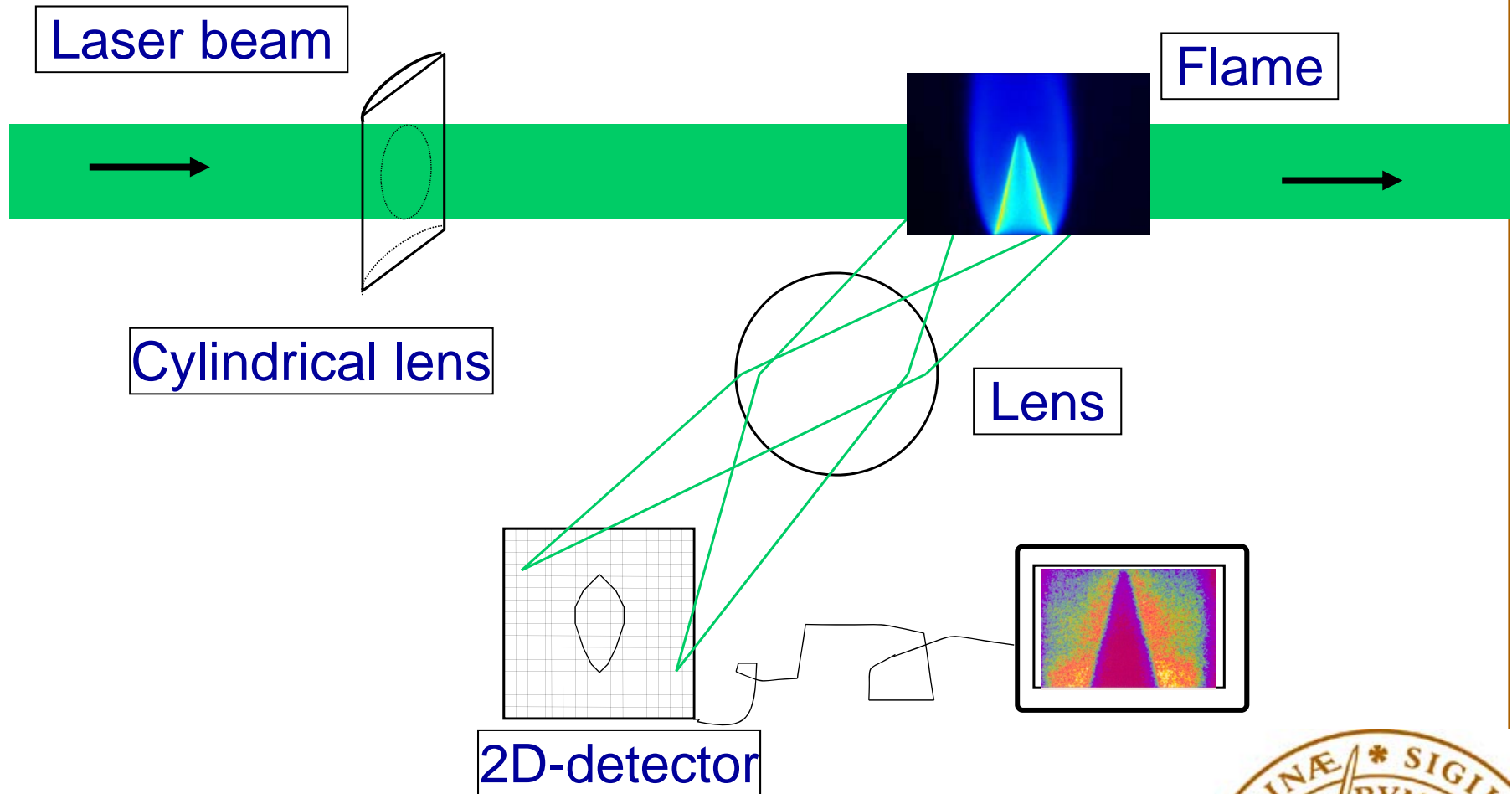
Multi-point visualization: 1D

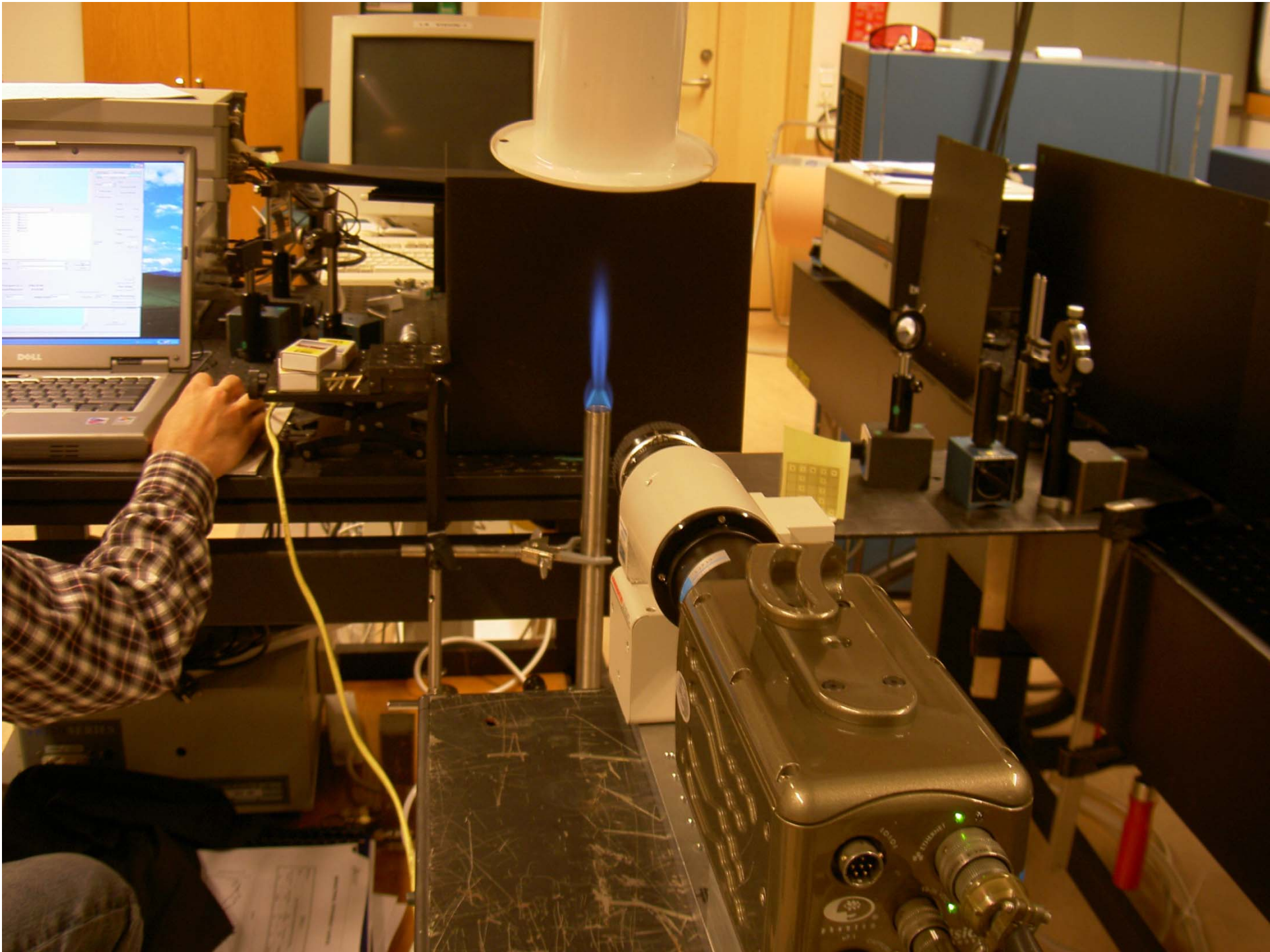


Two-dimensional visualization: 2D



Two-dimensional measurements





CH visualization

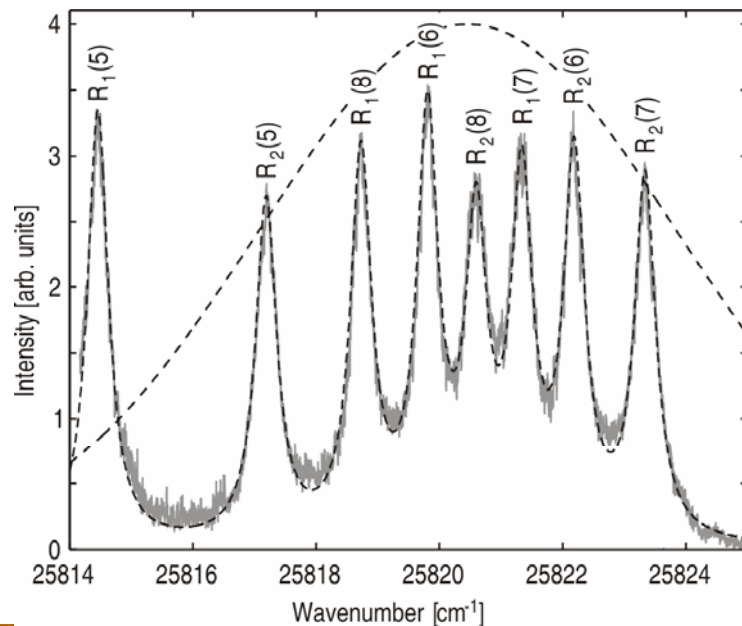
Motivation: Intermediate in NO_x formation

Flame front marker

Approach: Excitation X-B at ~ 387 nm

Emission B-X, A-X; ~ 430 nm

Broadband excitation

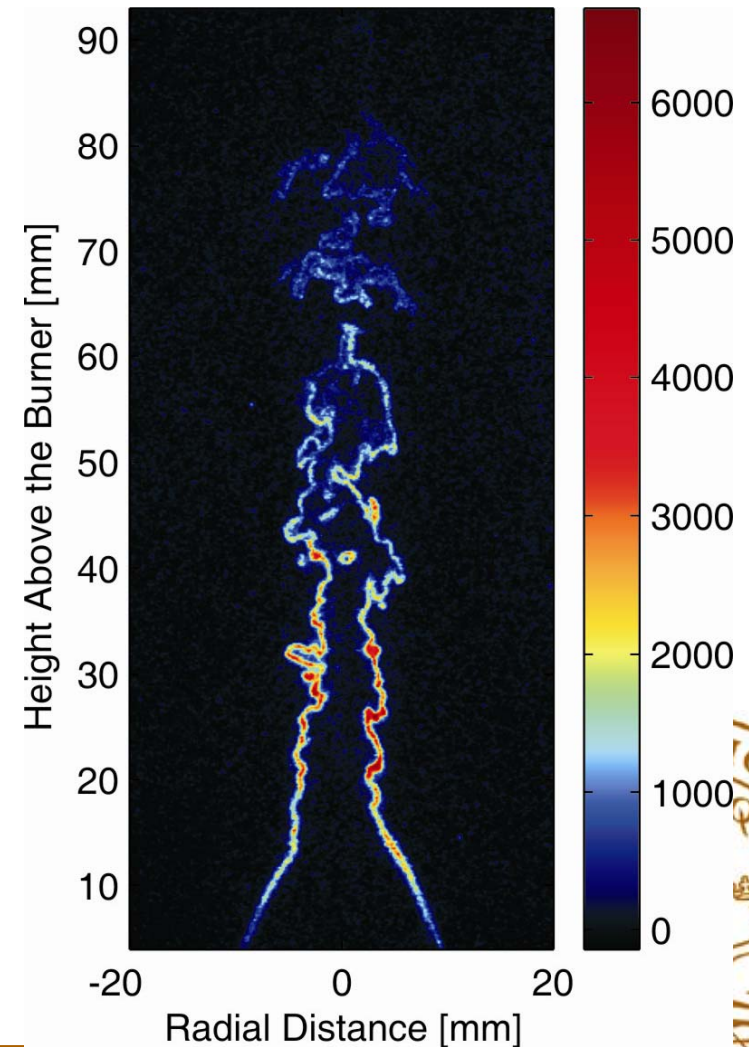
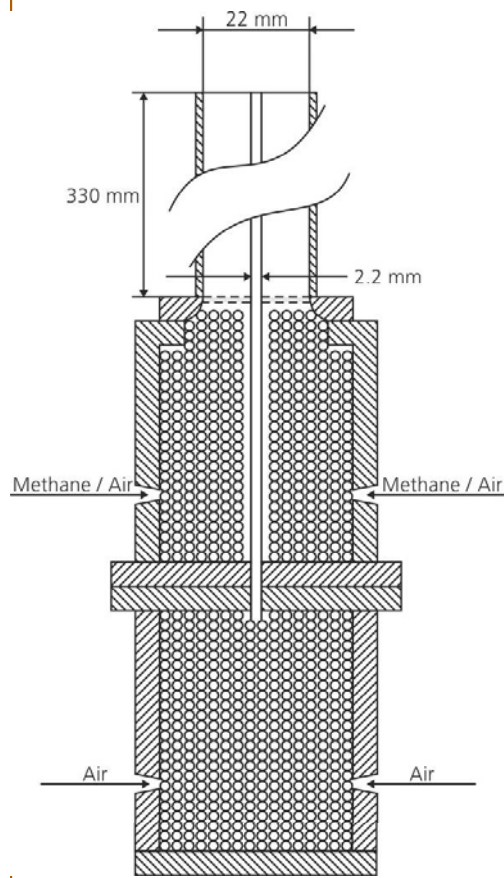


\sim two orders of magnitude
increased detectability

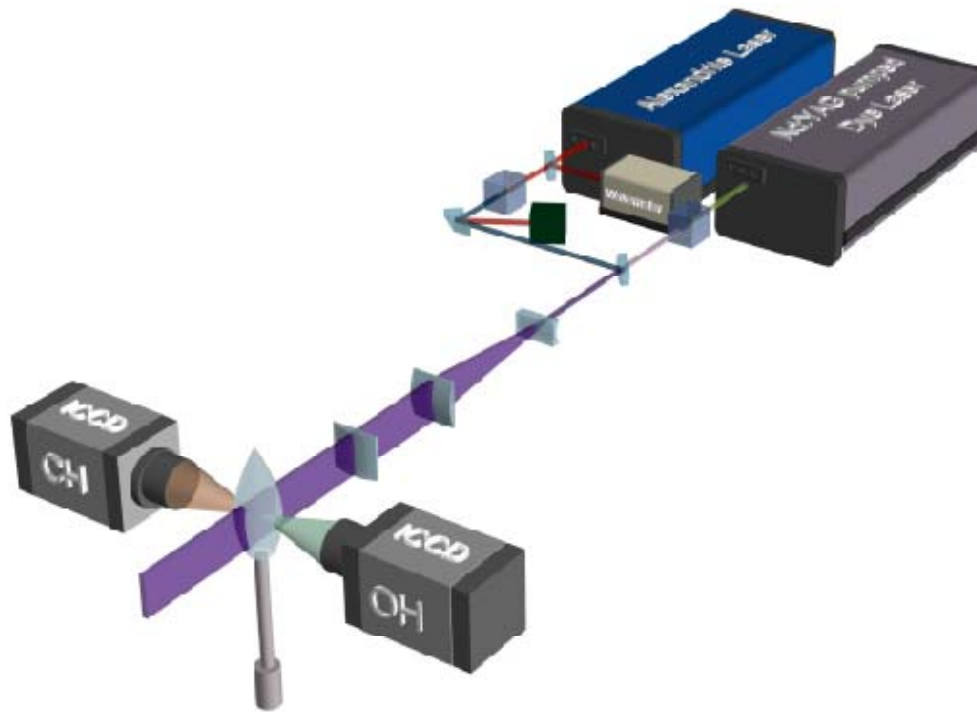
Kiefer et al, 31st Comb. Symp



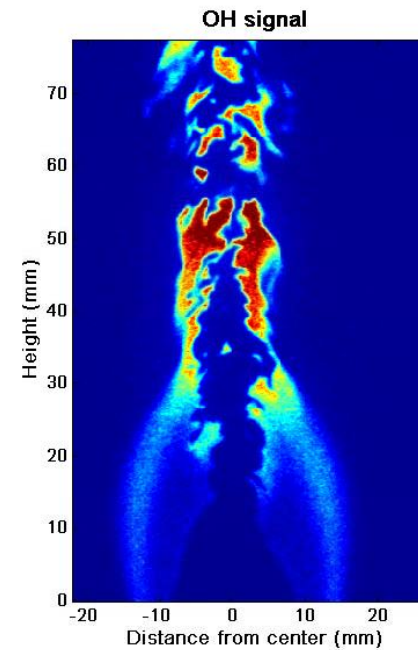
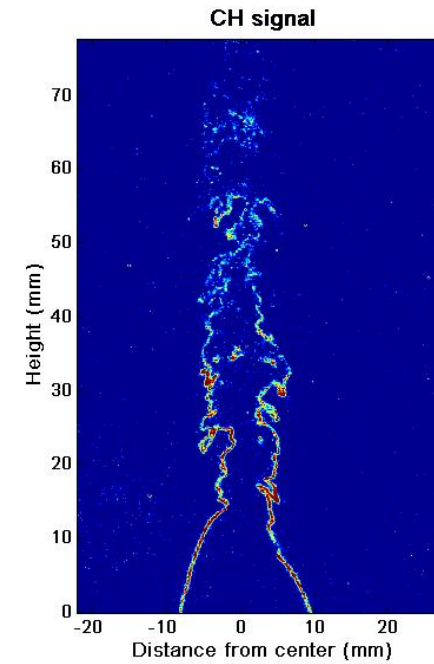
CH visualization in a turbulent flame



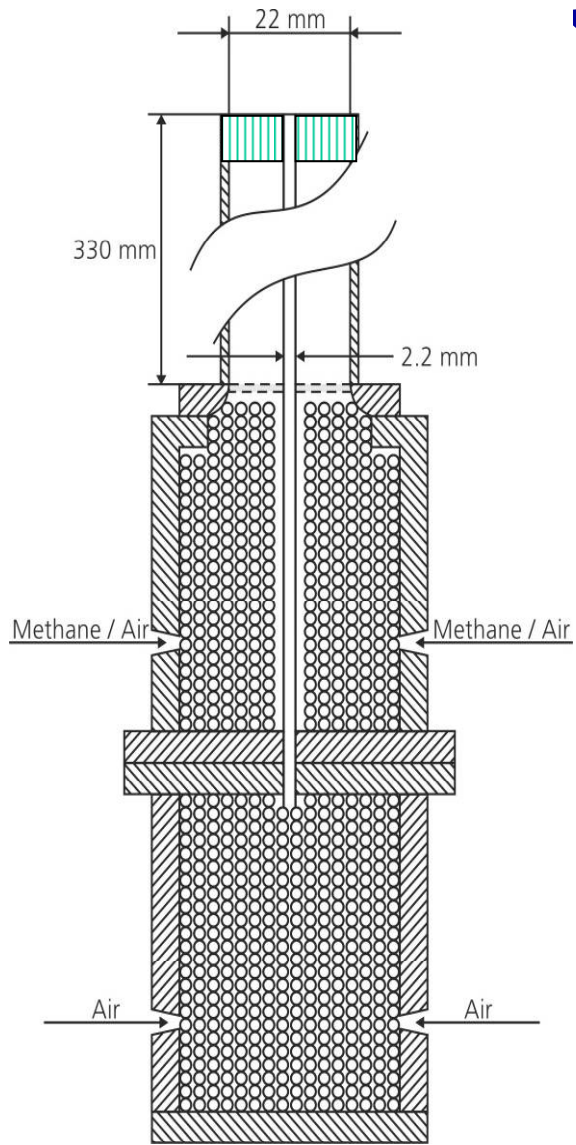
Multi species visualization CH, OH



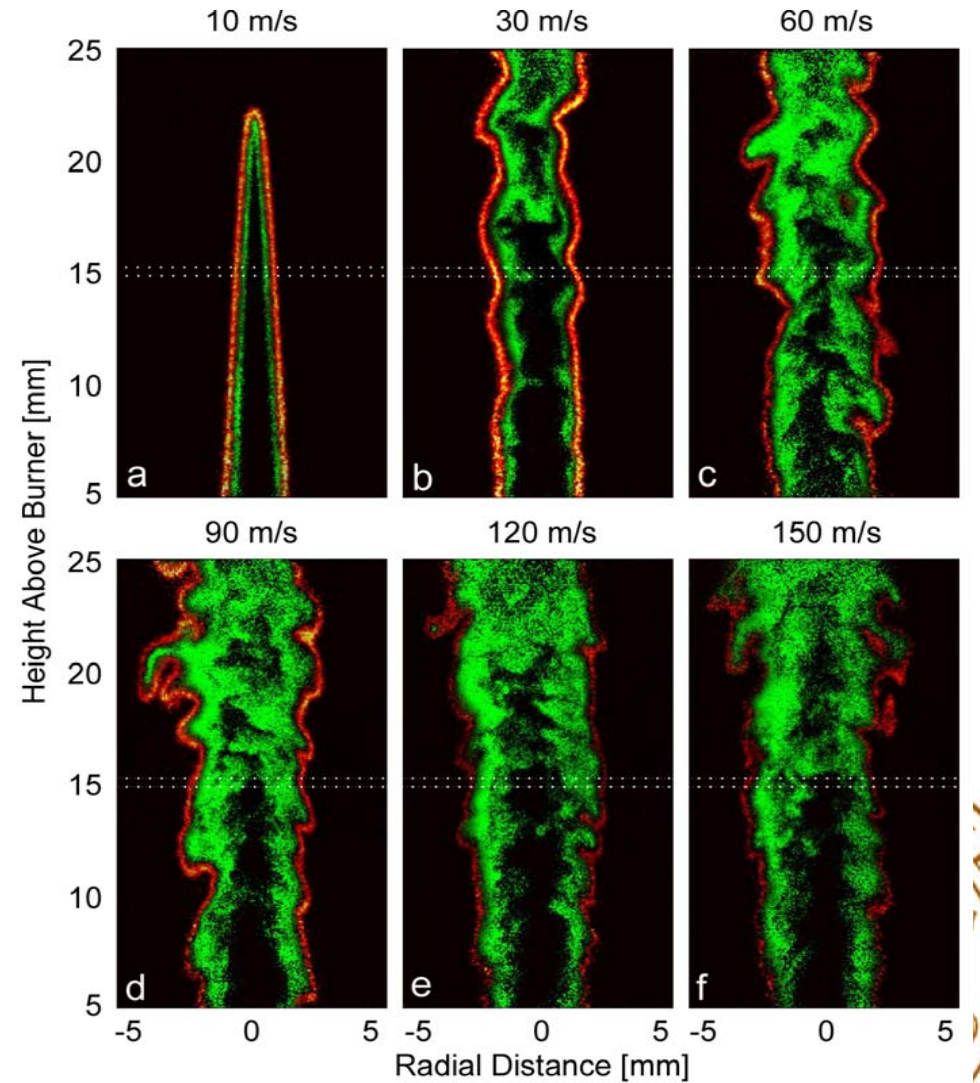
Kiefer et al, Comb.Flame 2008



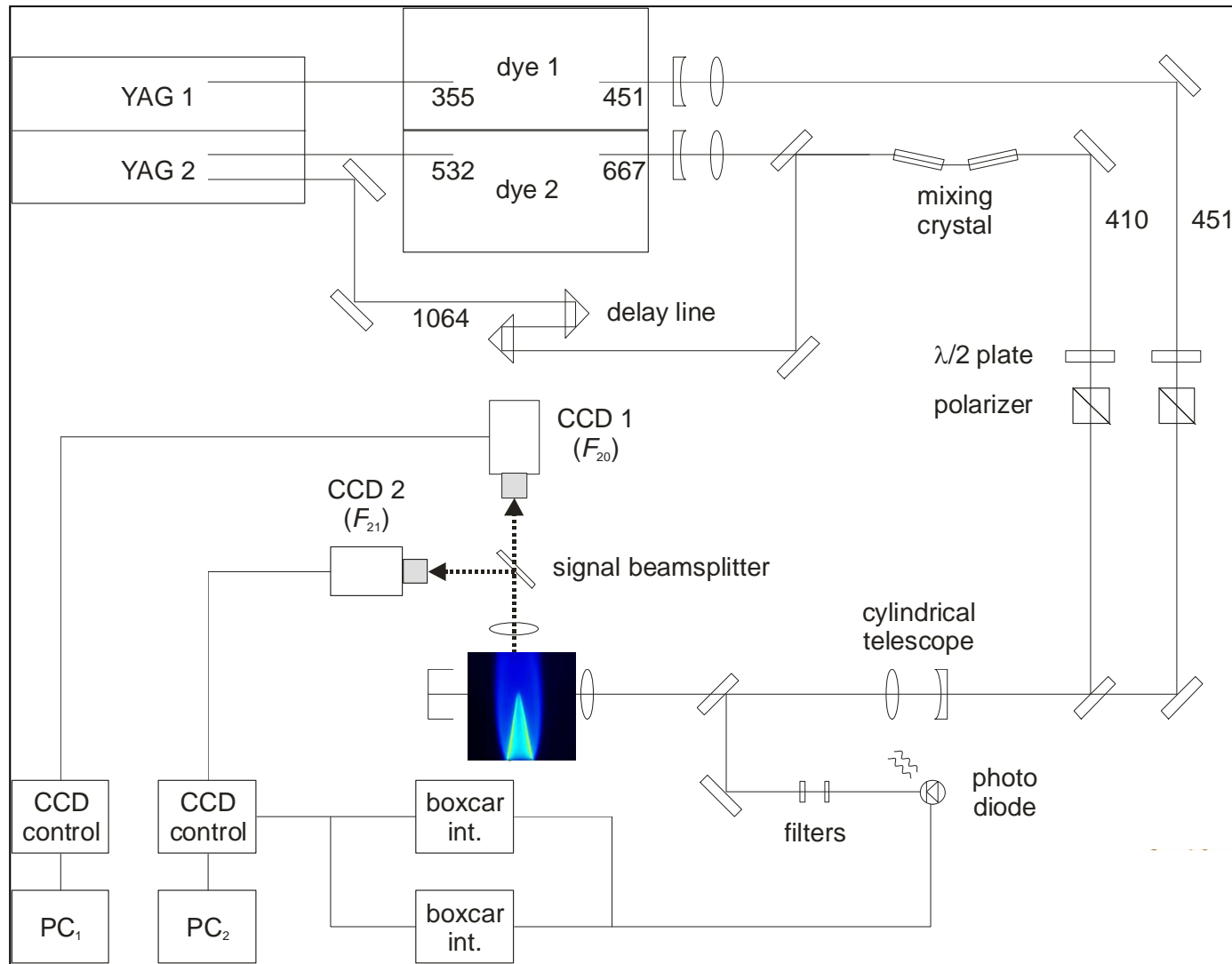
Simultaneously multi-species visualization CH , CH_2O



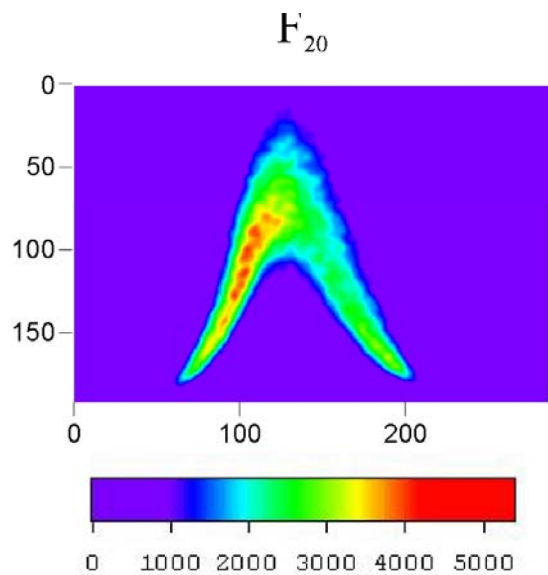
Li et al. ECM 2009, poster 259



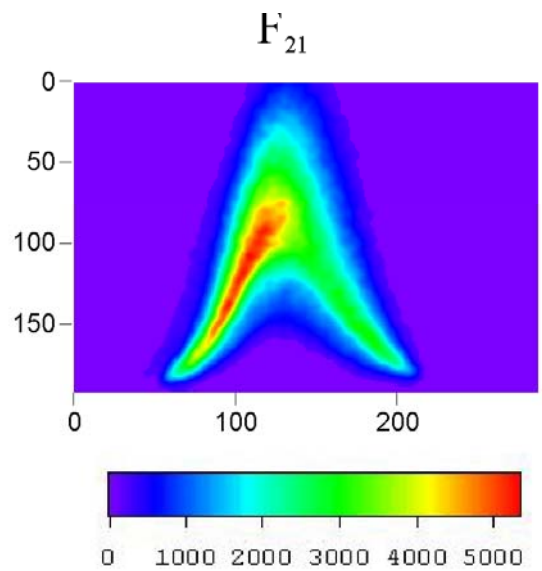
Exp set-up for 2D temperature measurements using TLAF



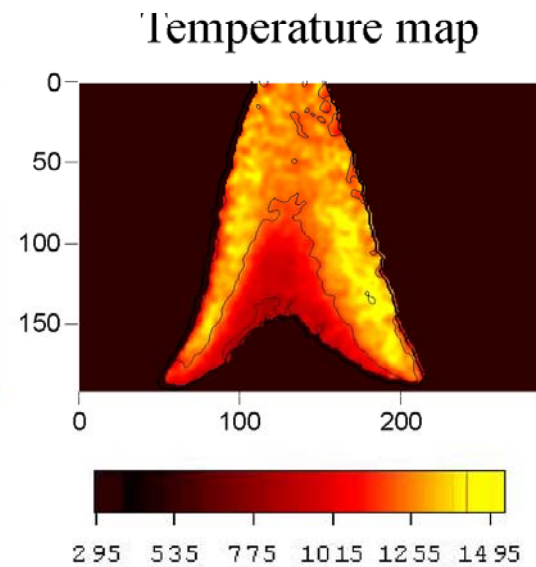
2D TLAF



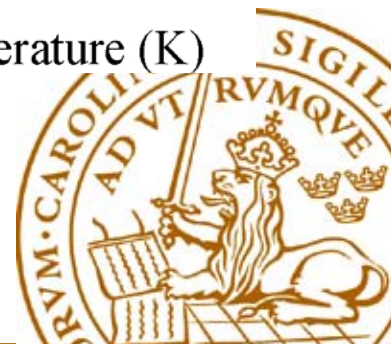
CCD counts



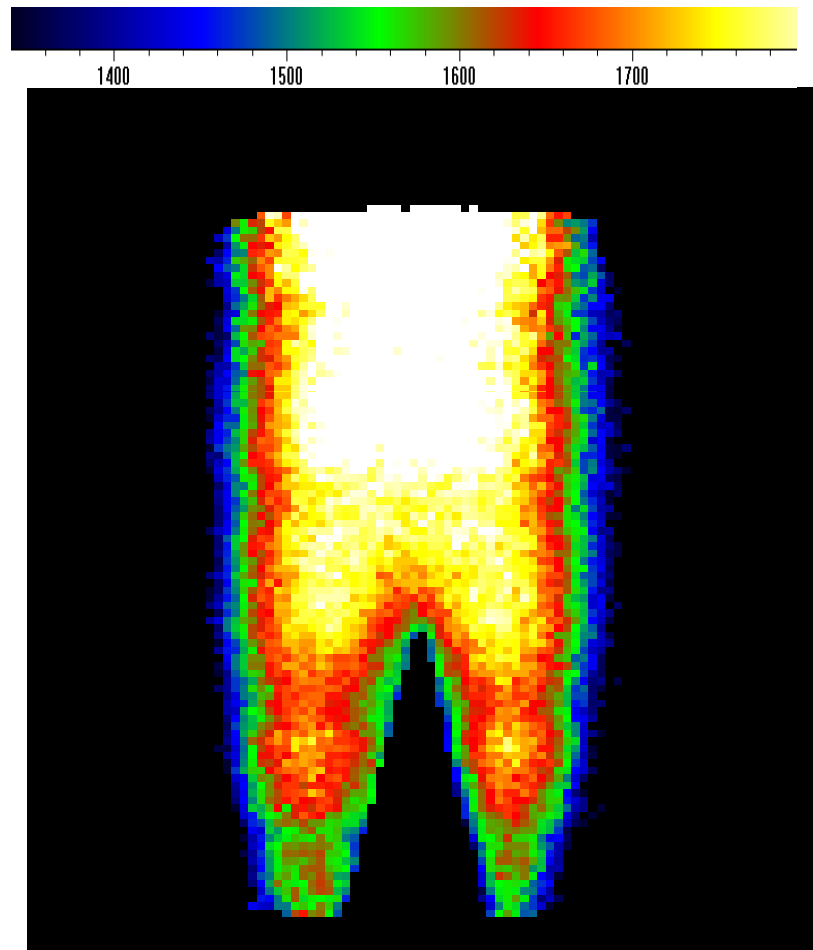
CCD counts



Temperature (K)

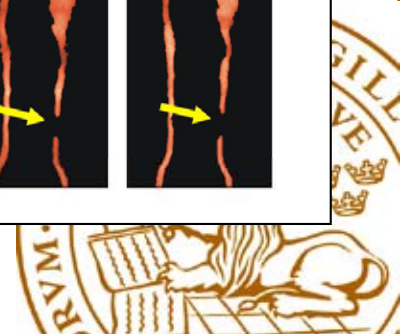
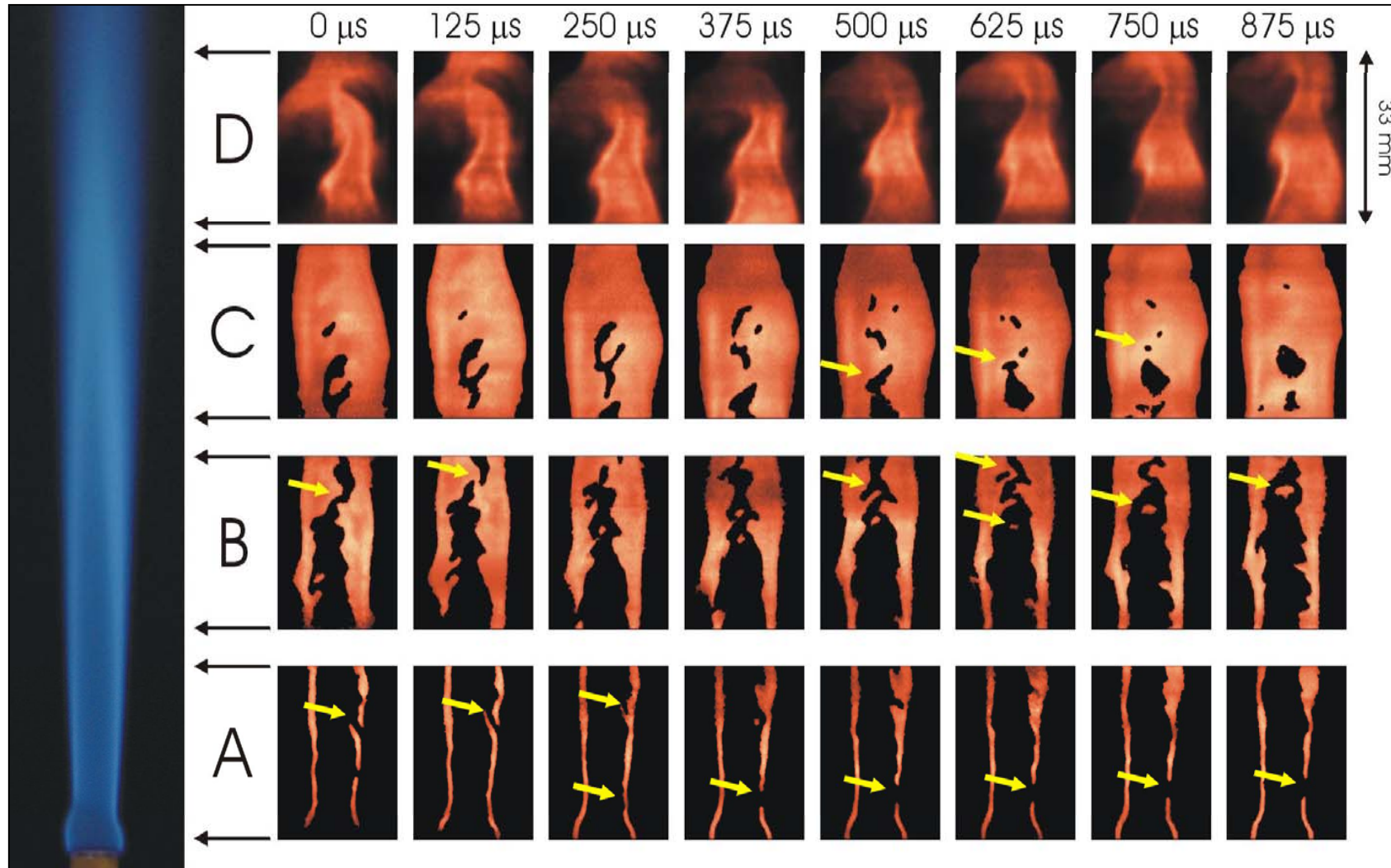
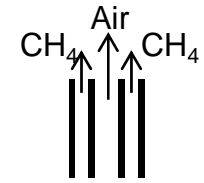


Temperature field in a Bunsen burner



High speed visualization I:

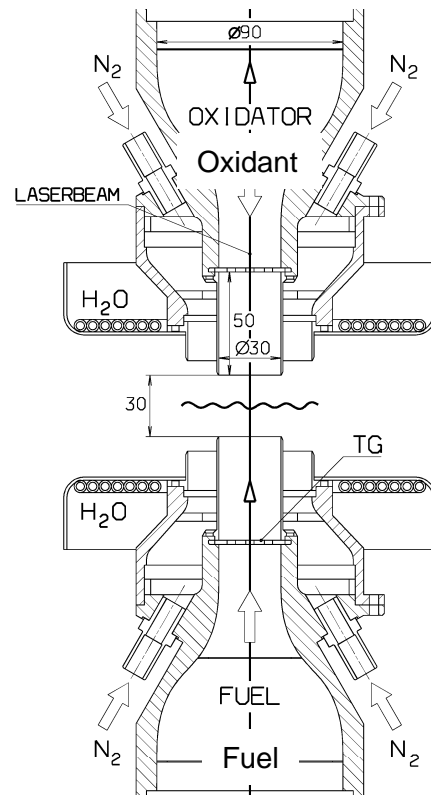
Turbulent non-premixed CH_4 /air flame, $\text{Re}=5500$



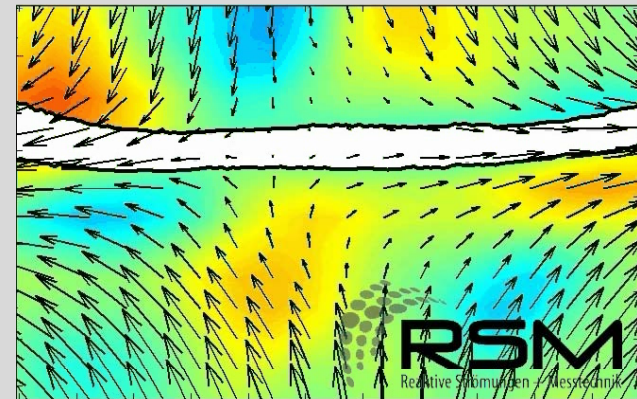
High speed visualization II.

Flame extinction – simultaneous scalar/flow measurements

- Turbulent opposed jet flames as model-systems for aerodynamically induced extinction

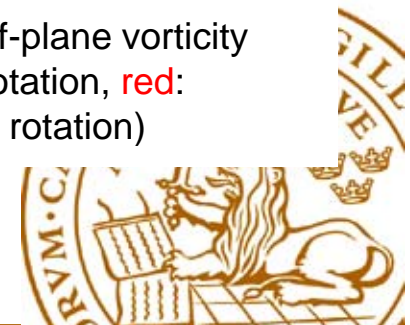


Simultaneous PIV and OH PLIF at 5 kHz repetition rate

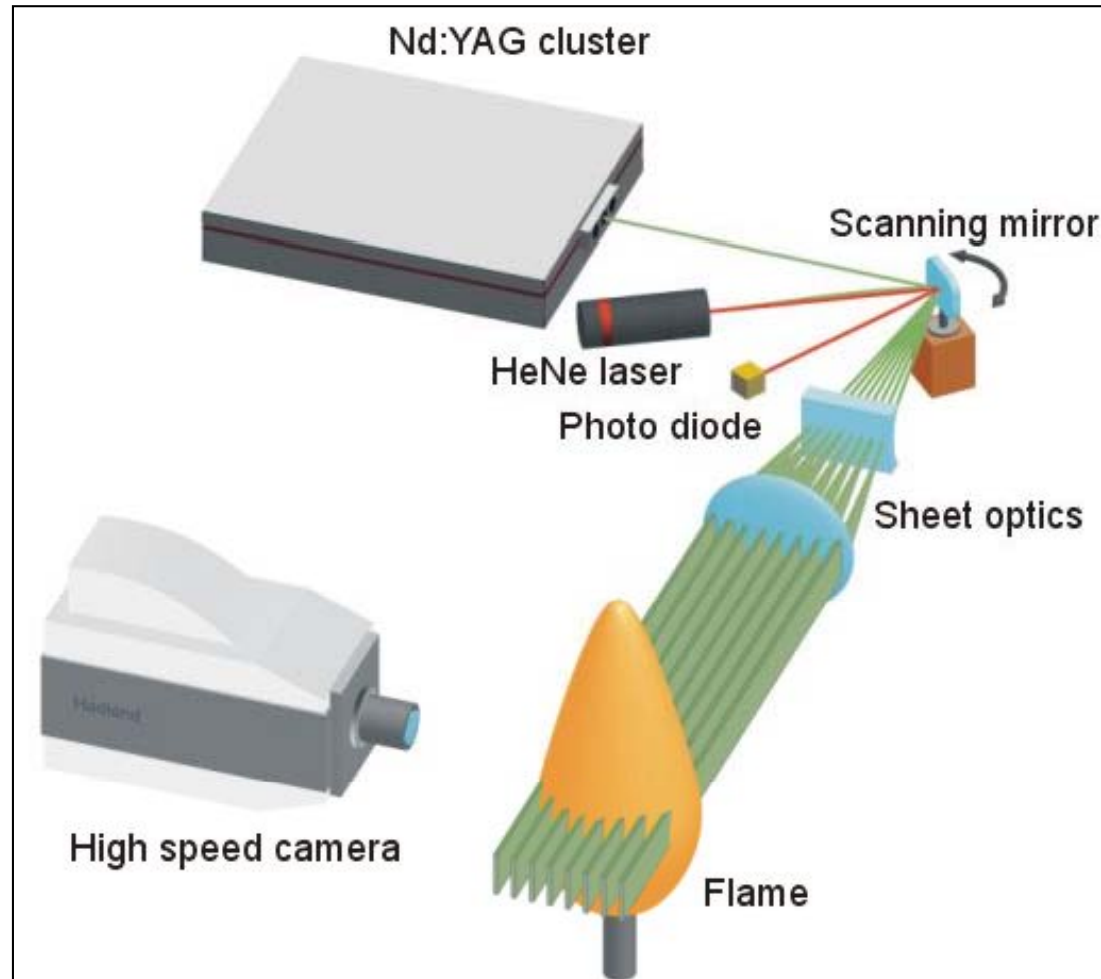


- *White area*: Instantaneous flame position from OH PLIF
- *Arrows*: Velocity vectors from PIV
- *Color-code*: Out-of-plane vorticity (blue: clockwise rotation, red: counter-clockwise rotation)

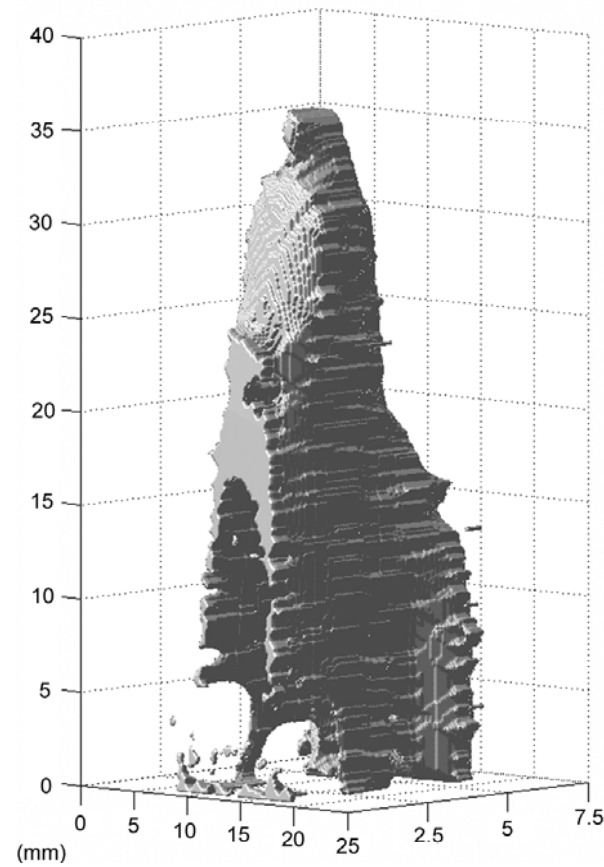
Courtesy: Andreas Dreizler (Böhm, Heeger, Boxx, Meier and Dreizler. Proc. of the Comb Inst 32 (2009) 1647)



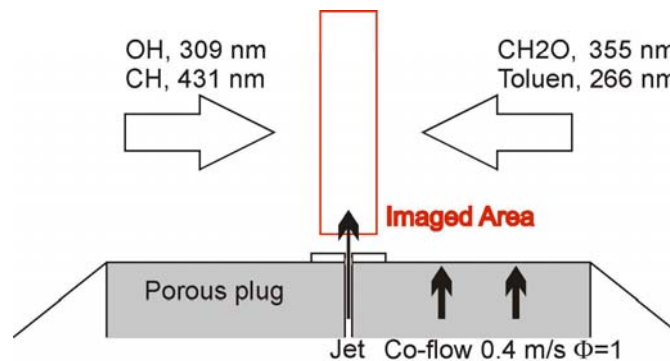
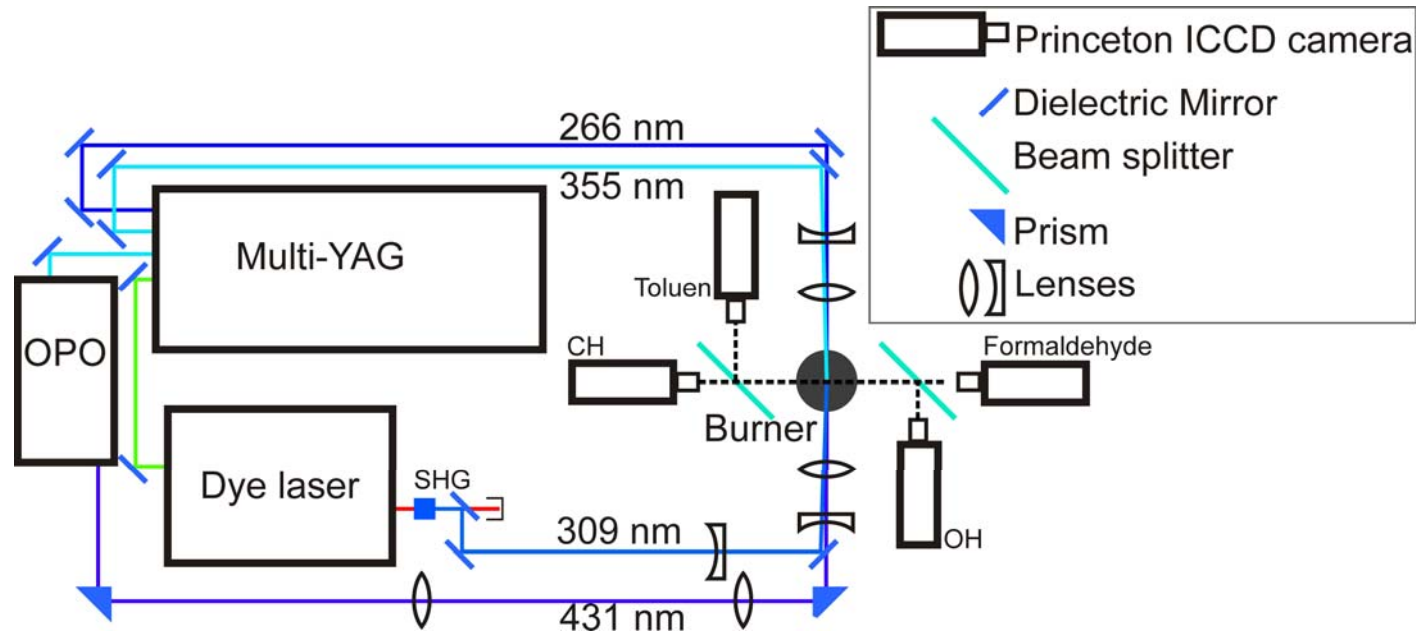
3D measurements



Formaldehyde visualization

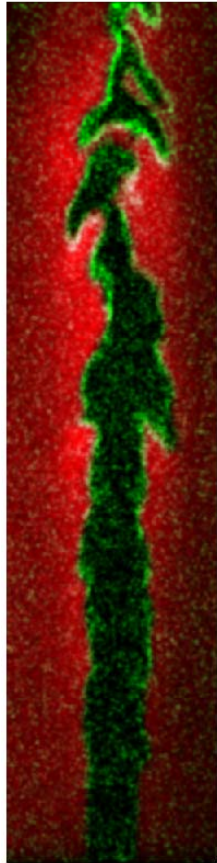


Multi-Species Measurements

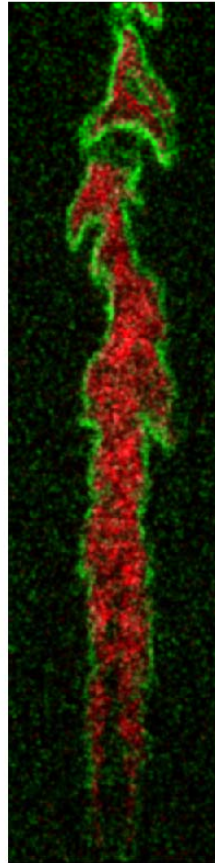


Multi-Species Measurements

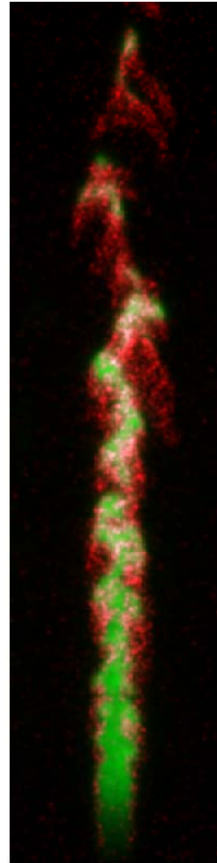
Jet speed 60m/s



OH
CH

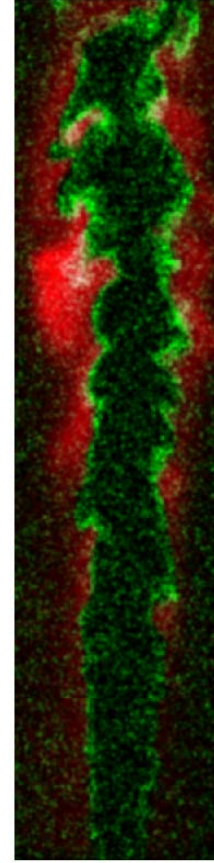


CH₂O
CH

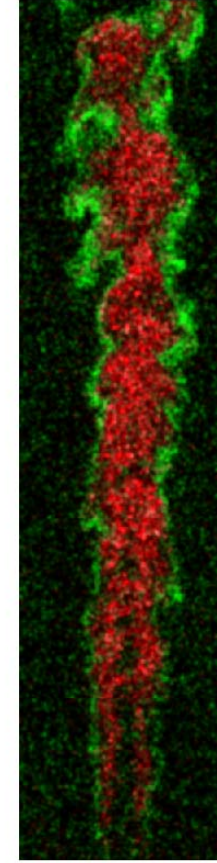


CH₂O
Toluen

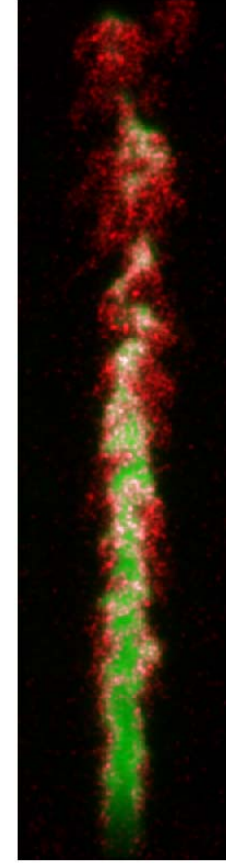
Jet speed 120m/s



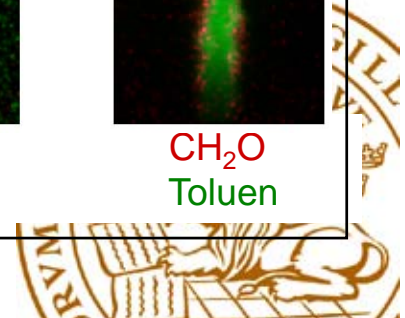
OH
CH



CH₂O
CH



CH₂O
Toluen



Summary: LIF

- Can measure 2D temperatures and species distributions
- Measure preferably atoms (O, H, N, C) and diatomic molecules (NO, OH, CH, CN, C₂, O₂, CO, H₂). Some polyatomic species (NH₃, H₂O, HCO, CH₂O)
- High sensitivity (ppm)
- Mainly used for one species detection
- Accuracy; concentration:
 - ~10% (stationary flame, all quenching parameters known)
 - ~30% (turbulent flame, no quenching corrections)
- temperature:
 - ~2% (point measurement)
 - ~8 % (2D measurement)
- Resonant excitation ⇒ Tunable laser needed
- Incoherent non-elastic scattering ⇒ Signal emitted in all directions
- Suffers from quenching, i.e. collisional deexcitation ⇒ quantitative species concentration measurements not trivial
- Problem with separation of multi-atomic species, e.g. PAH's
- Outlook: Further 3D visualization, high speed imaging (>kHz), velocity visualization without molecule seeding

