11. Non-linear optical techniques

- Introduction
- Degenerate four wave mixing, DFWM
- Polarization Spectroscopy, PS
- IR measurement (IRPS, IR-DWM)
- (Stimulated Emission, SE)

Diagnostic dilemma:

- **LIF**
  - High sensitivity,
  - 2D imaging,
  - Spontaneous technique (sensitive to strong background)
- **CARS**
  - Coherent technique
  - One-point measurements
  - Low sensitivity

Need: A coherent technique with high sensitivity and 2D imaging possibility

Candidates:DFWM, PS and SE (one point)

Nonlinear optics

Thus far, the induced polarization of molecules has 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:

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

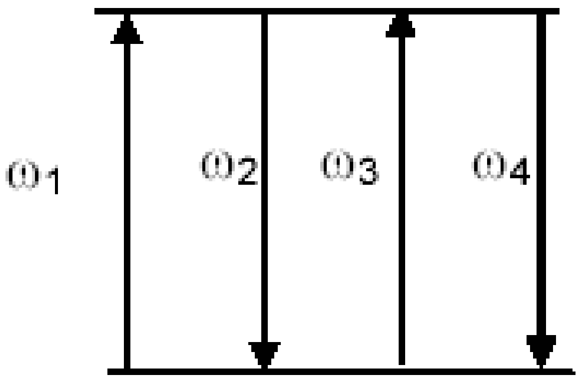
$$\vec{P} = \varepsilon_0 \left(\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \ldots.. \right)$$

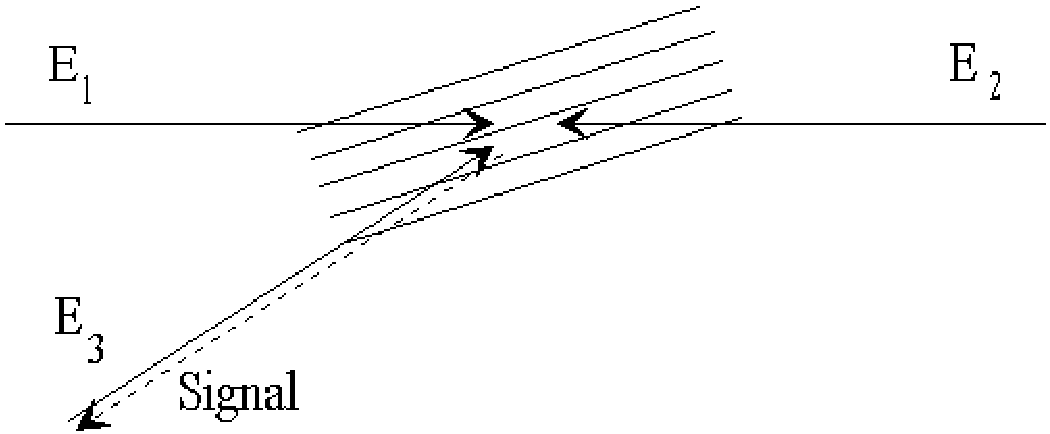
For gases, which are isotropic (inversion symmetry), the even order polarizations vanish

DFWM and PS are four-wave mixing processes based on the nonlinear response via the third-order susceptility ($\chi^{(3)}$), in the same way as CARS.

DFWM

Can be described in terms of a grating phenomena

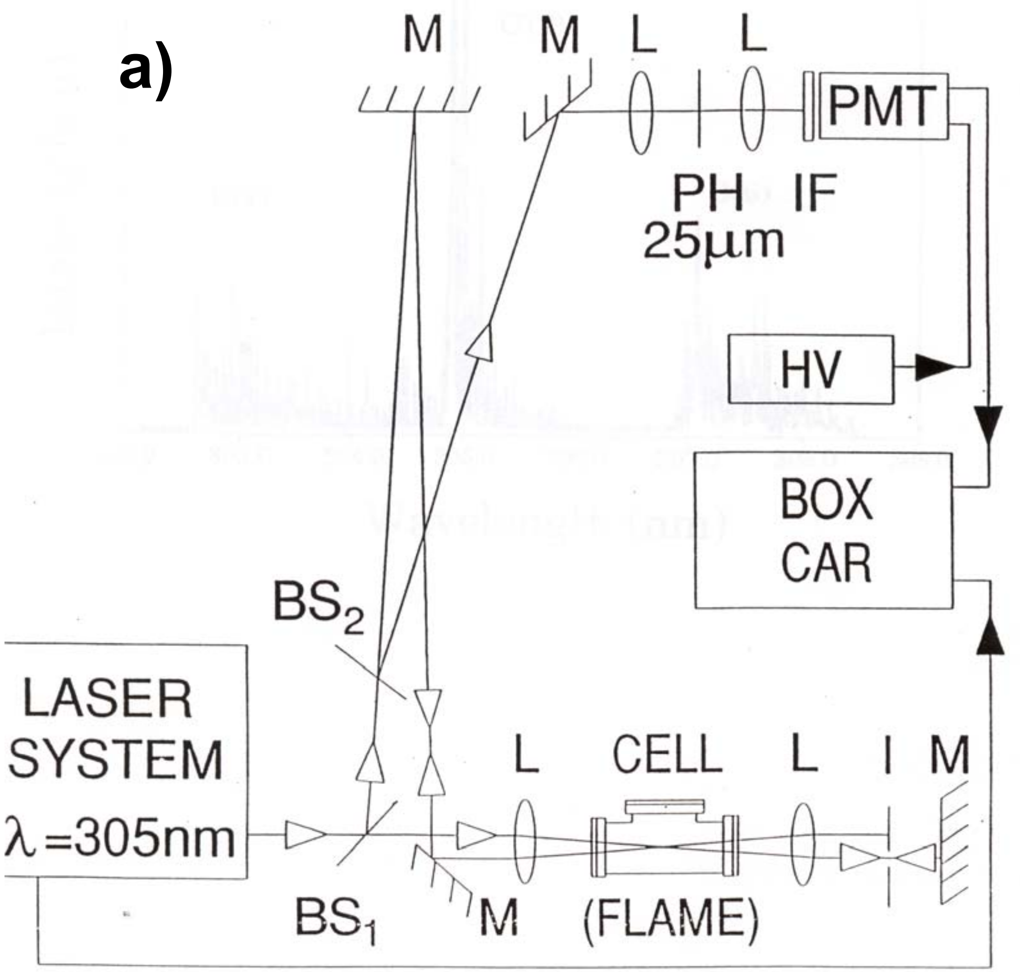


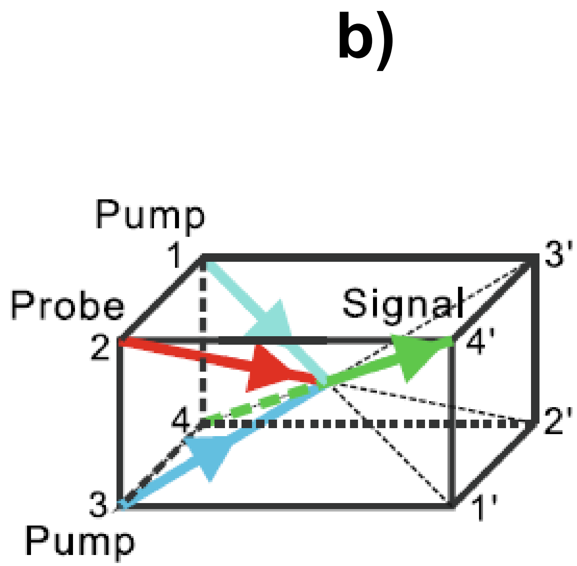


ω, laser frequency, tuned to an atomic/molecular resonance

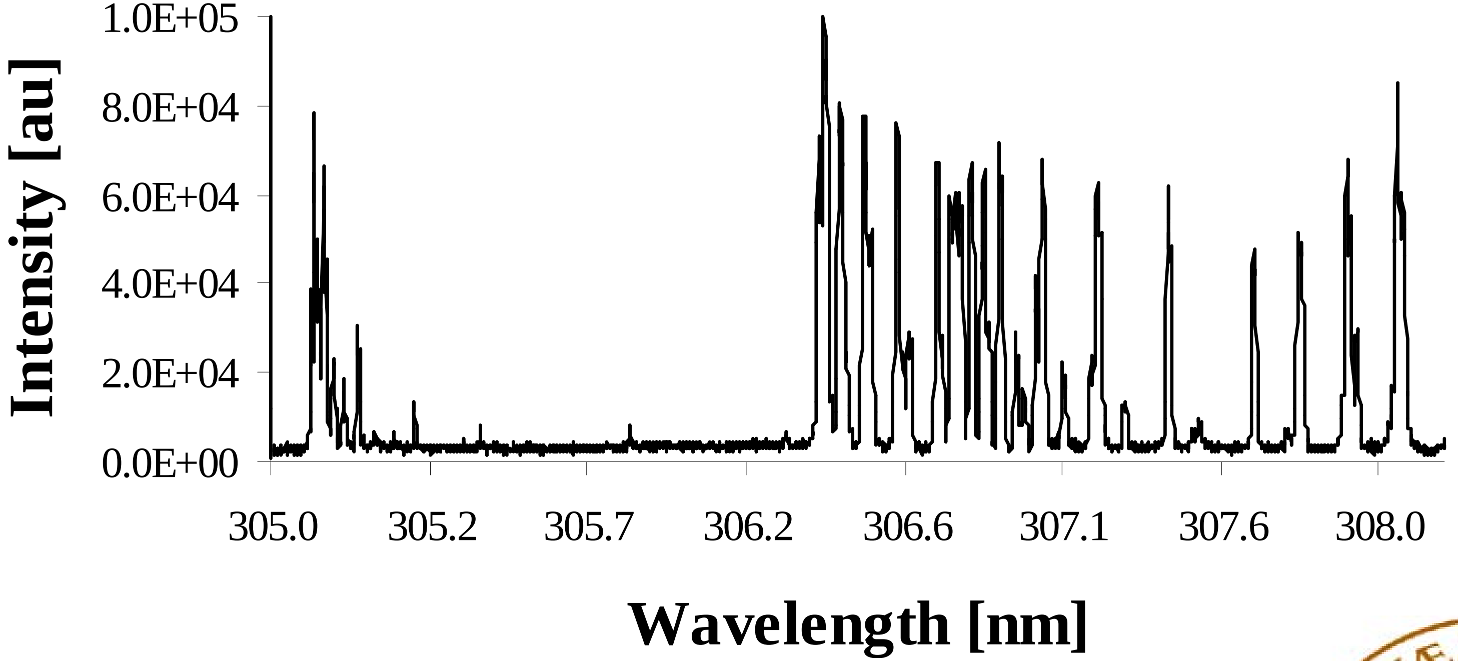
$$I_{DFWM} \propto I_P^2 I_{\mathrm{Pr}} N^2$$

Experimental set-up

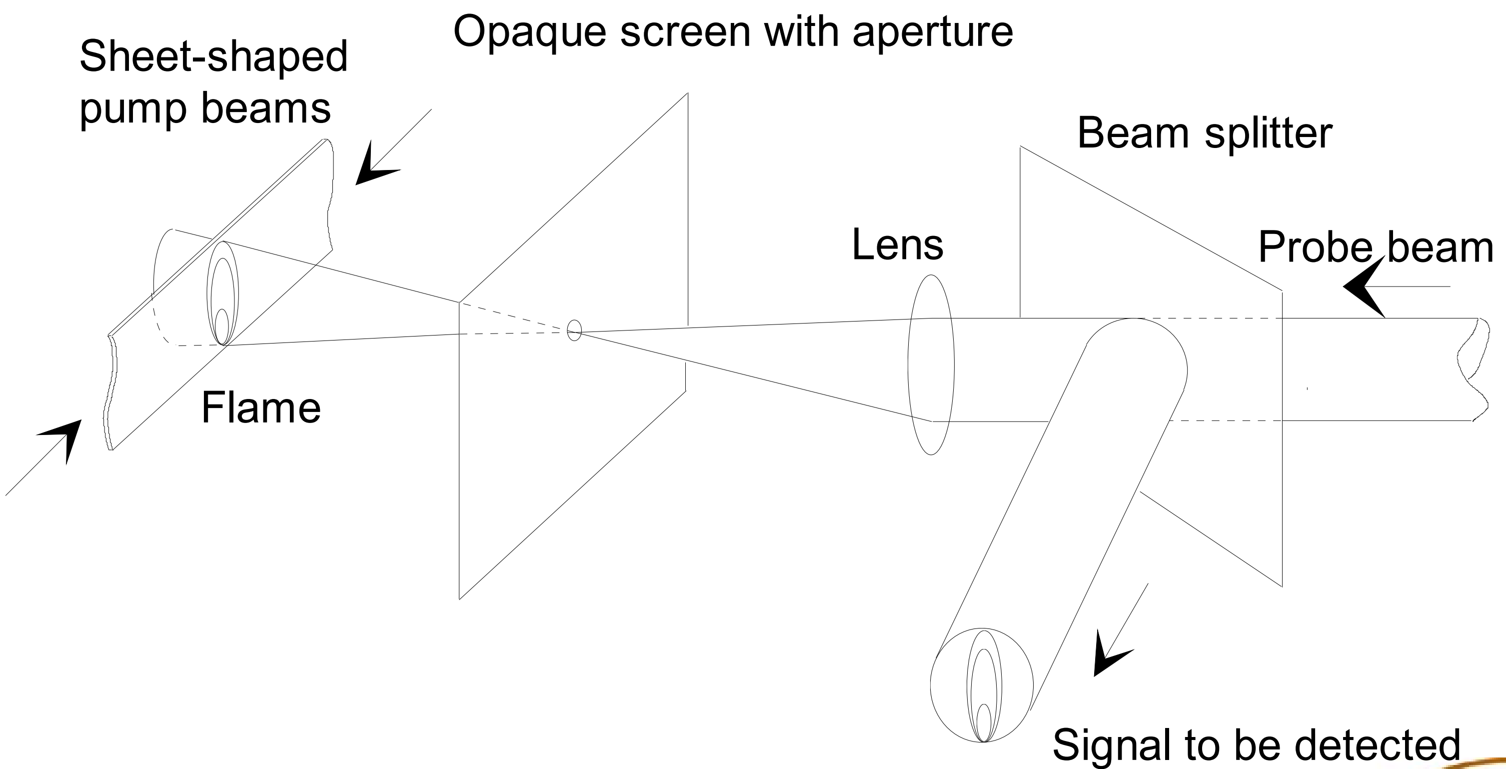




Detection of ammonia and OH

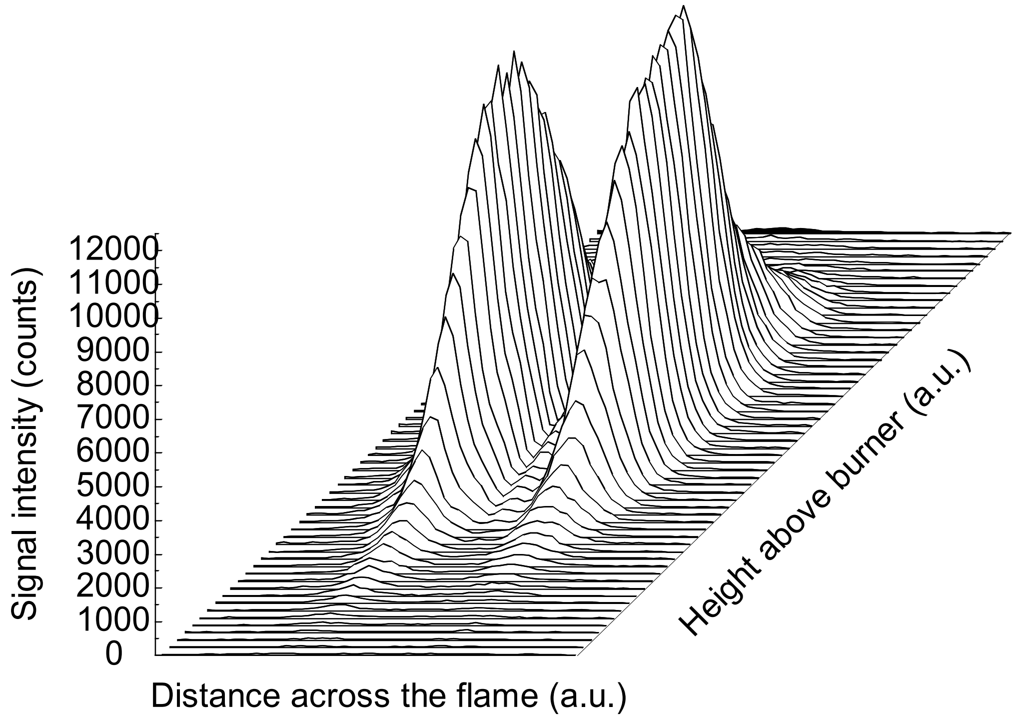


2D imaging



Sheet-shaped
pump beams
Opaque screen with aperture
Beam splitter
Lens
Probe beam
Flame
Signal to be detected

2D OH image using DFWM



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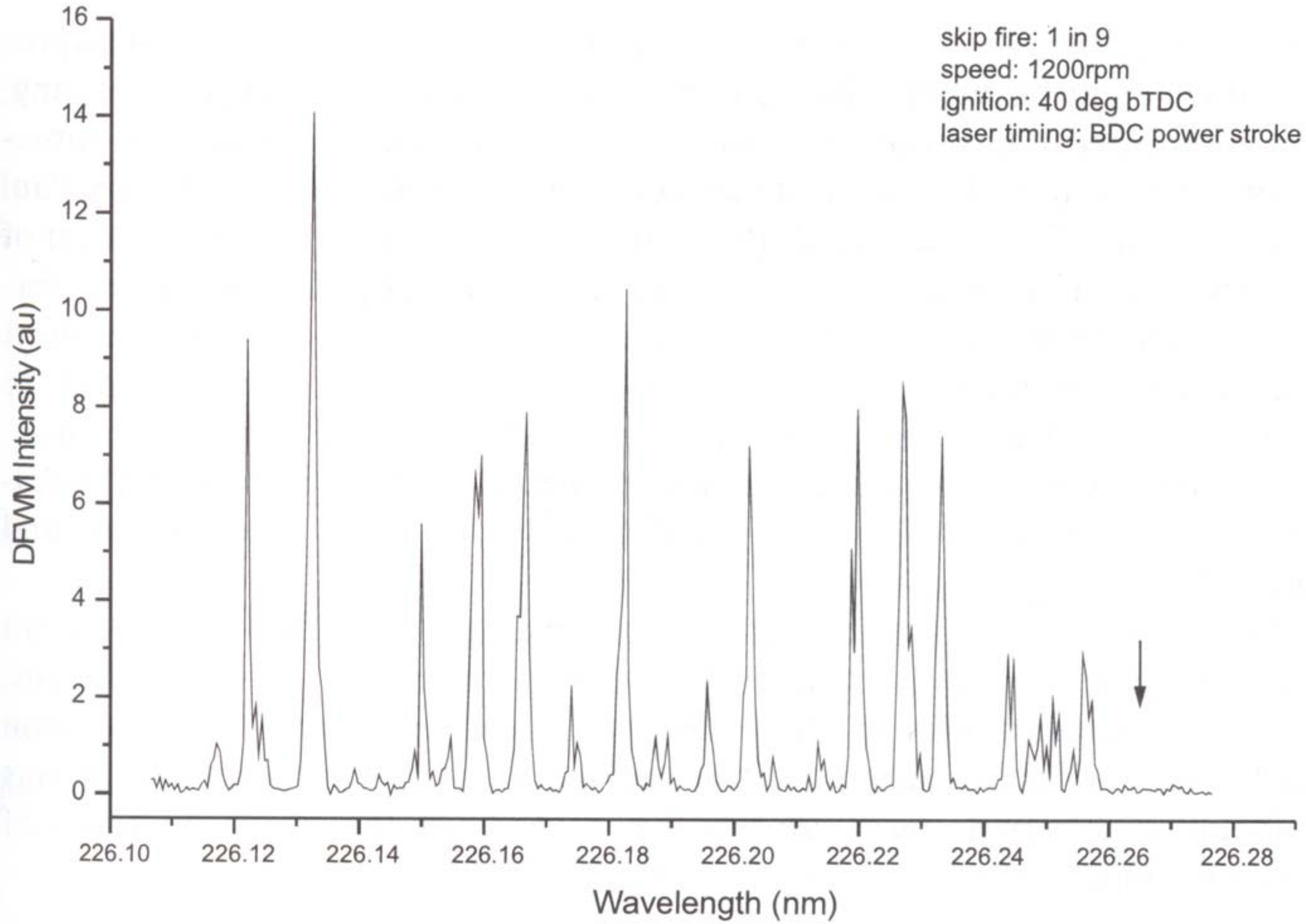
DFWM application



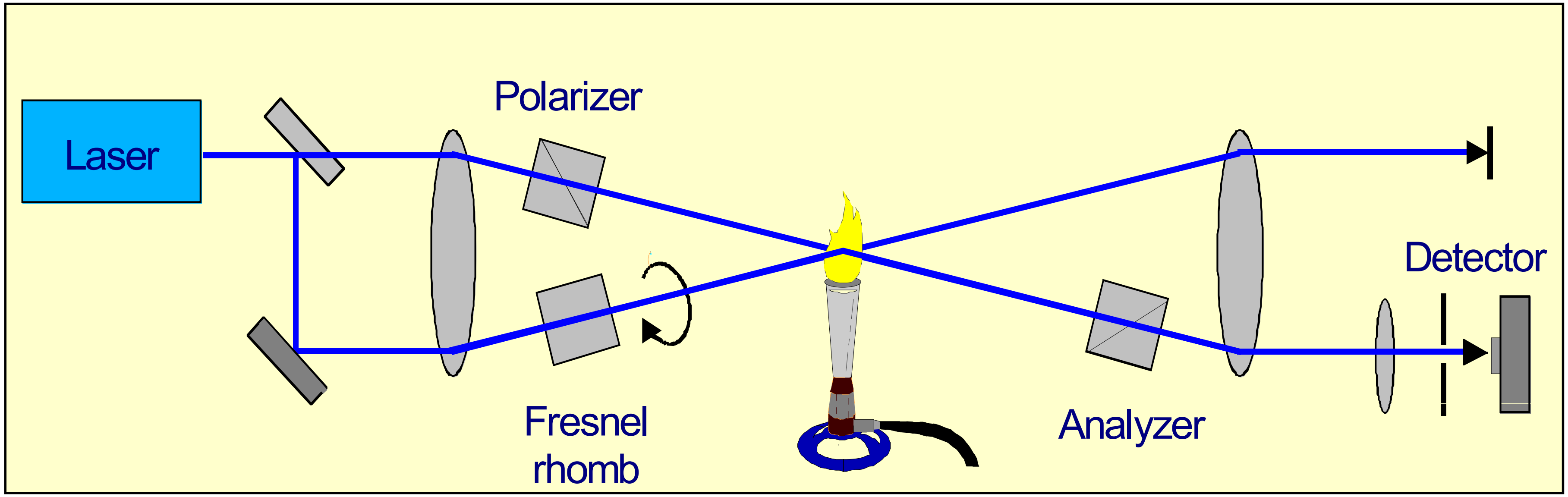
P. Ewart et al.

DFWM summary

- Coherent technique with high sensitivity (ppm)
- 2D imaging possible
- Complex theory
- Advanced procedures for laser beam alignement
- Problem with background scattering

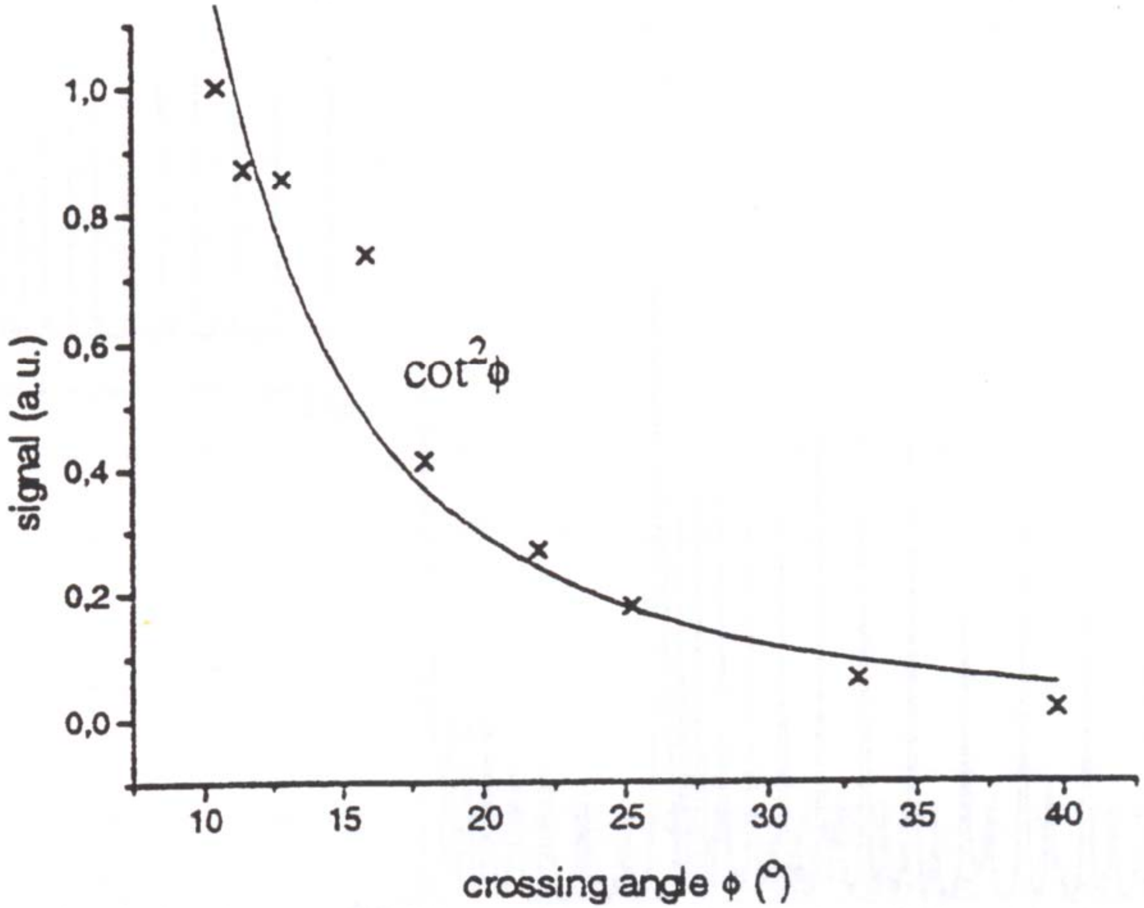
Polarization spectroscopy

A pump beam induces an optical anisotropy (Birefringence and Dicroism), which is measured as a change in the polarization of the probe beam

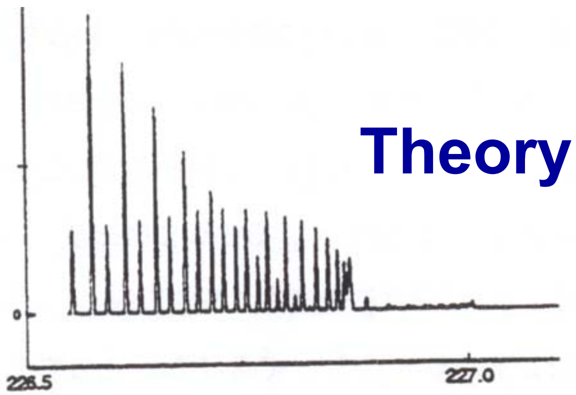


$$I_t \propto (N^0 B_{J''J'} \zeta_{J''J'})^2 I_p^{\,2} I_{pr}$$

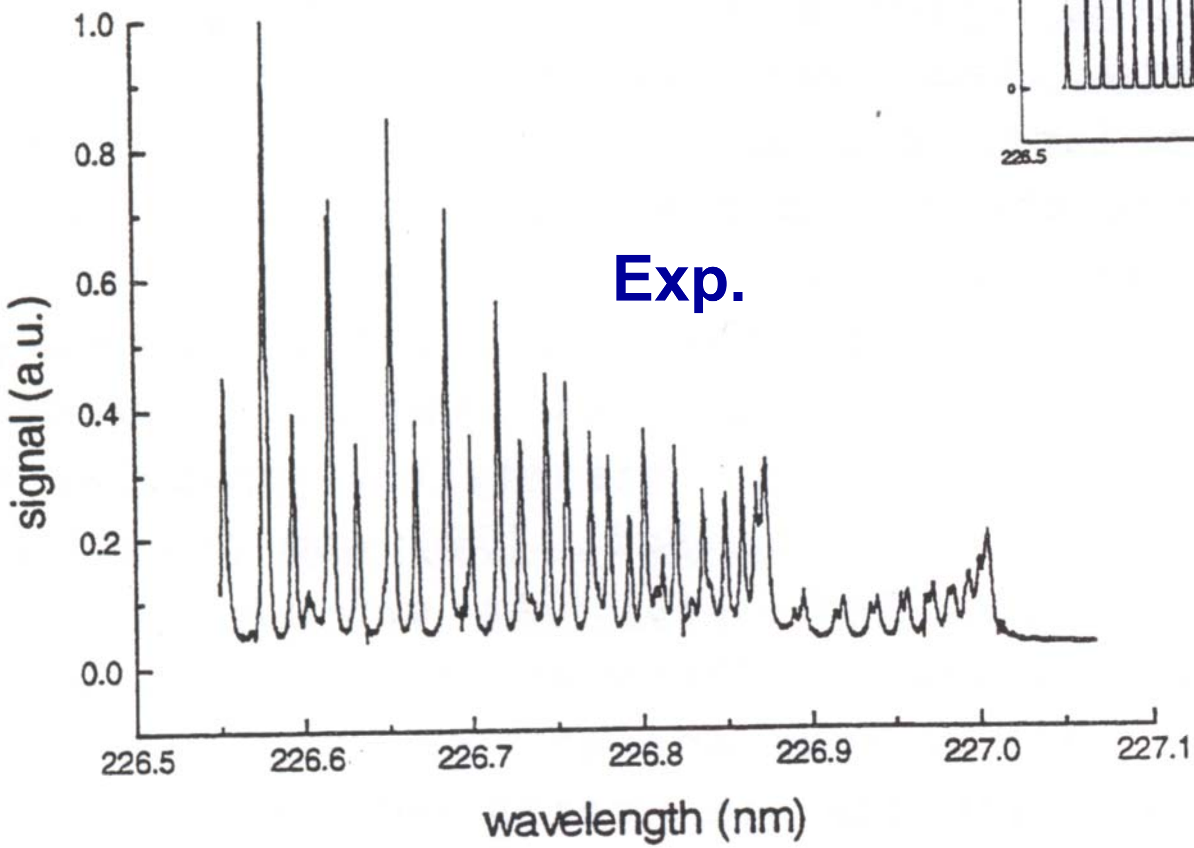
PS signal dependence on crossing angle



Scanning experiments (NO)



Theory

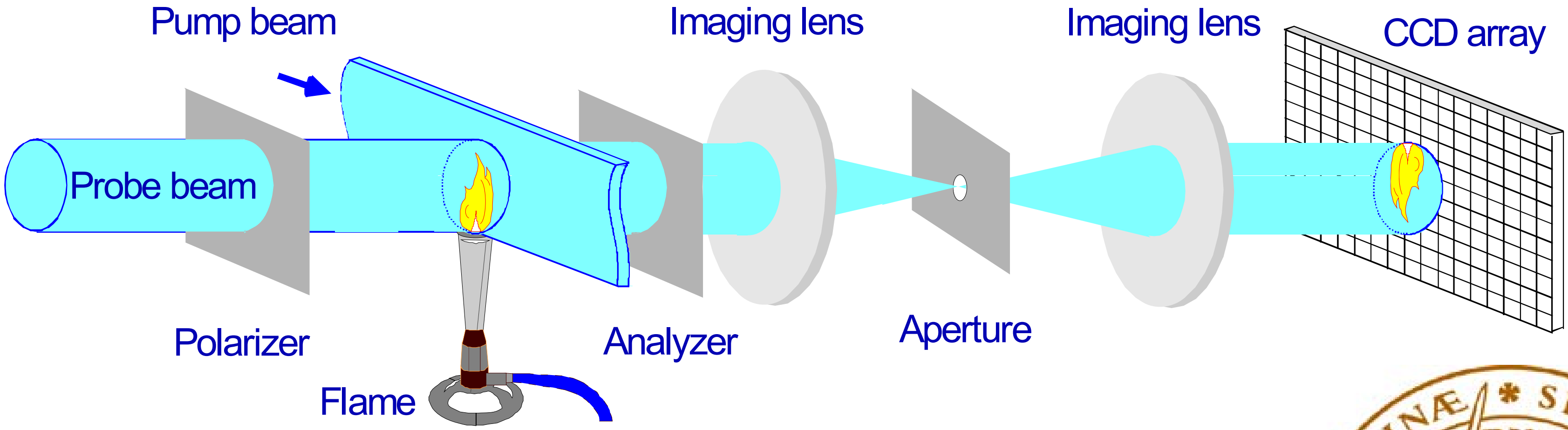


Exp.

Two dimensional imaging

- A strong linearly polarized pump beam formed to a narrow sheet of light crosses an unfocussed weaker probe beam in the flame

- The intersection volume imaged onto an image intensified CCD camera

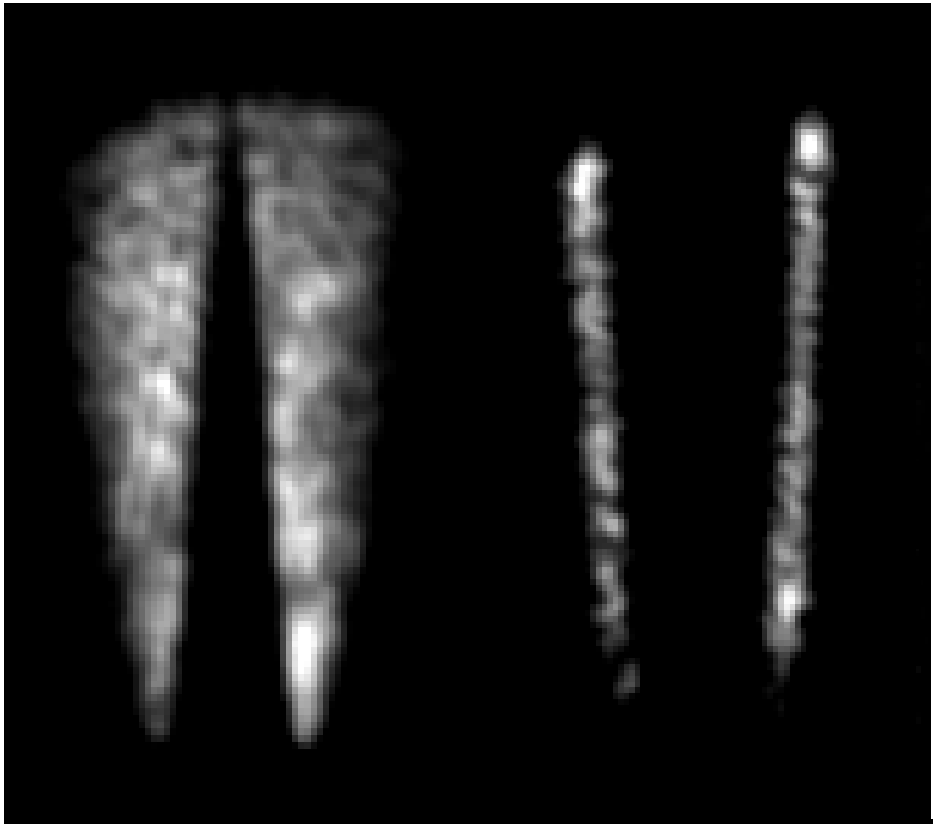


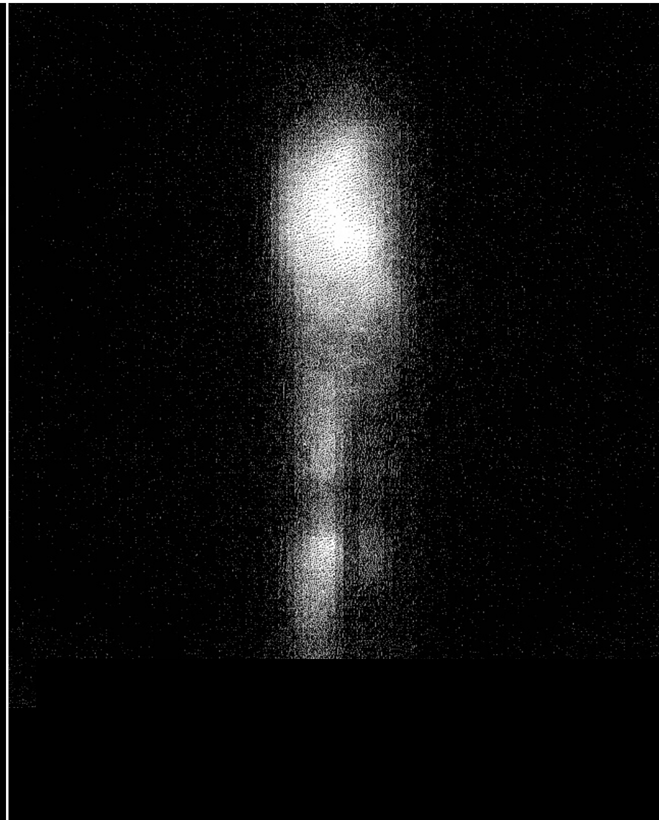
⇨ SIGNAL DISTRIBUTION IN ONE PLANE IN THE FLAME RECORDED

Imaging of OH and NO in flames

Images of OH signal distributions recorded in a CH_4/O_2 flame

NO PS in a H_2/N_2O flame



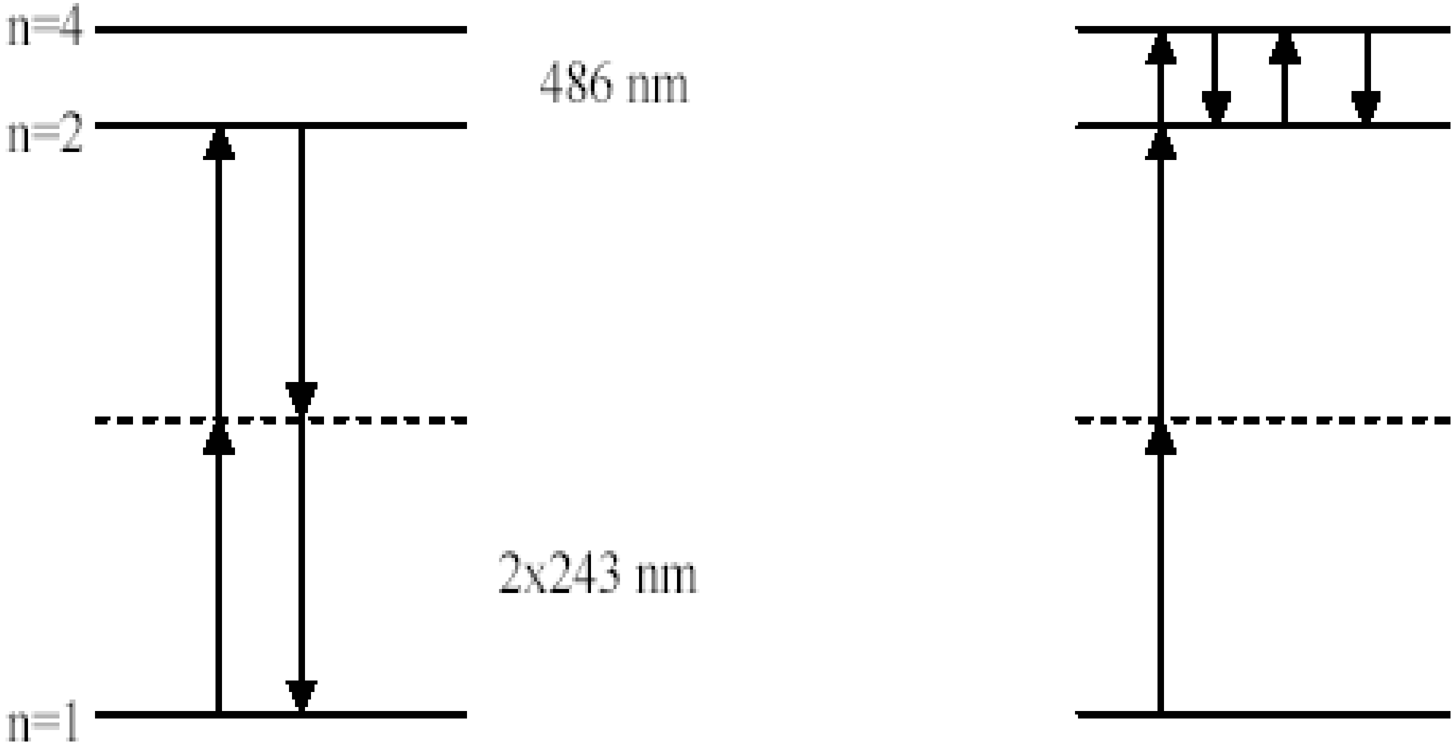


Two-photon PS

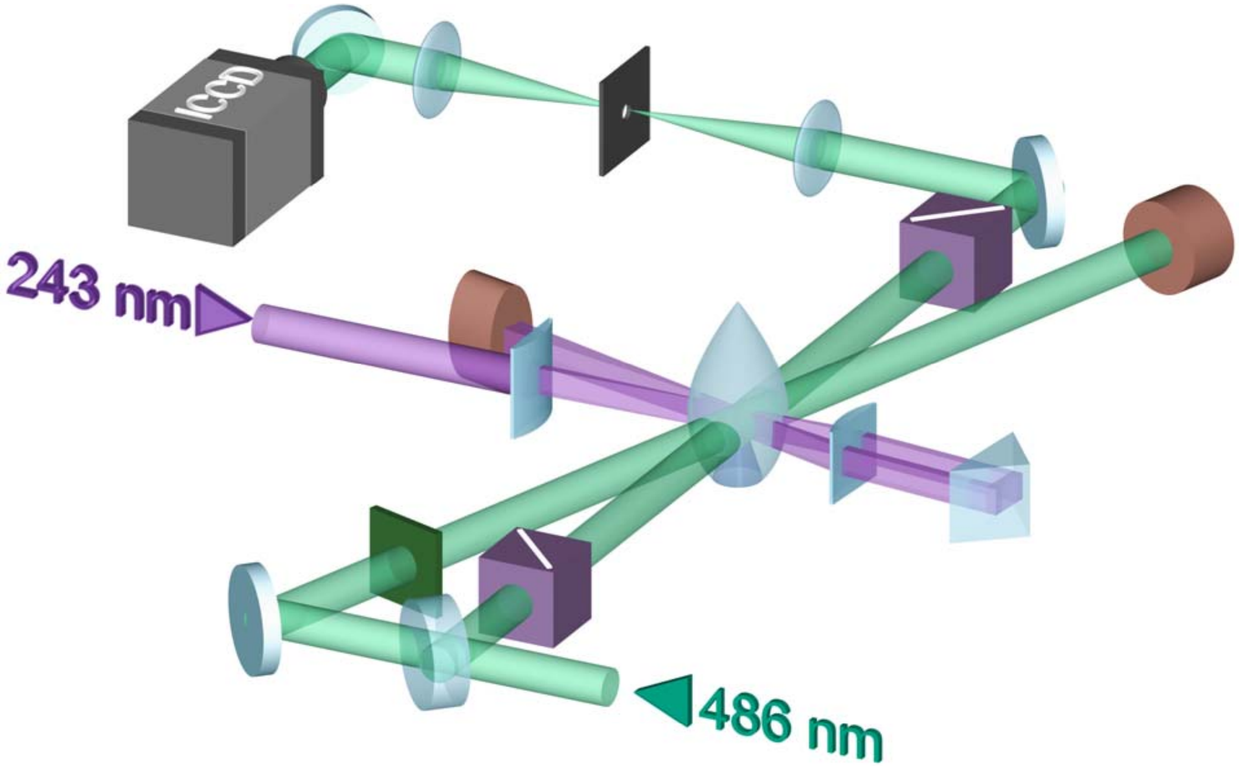
examplified by H atom detection

Conventional approach

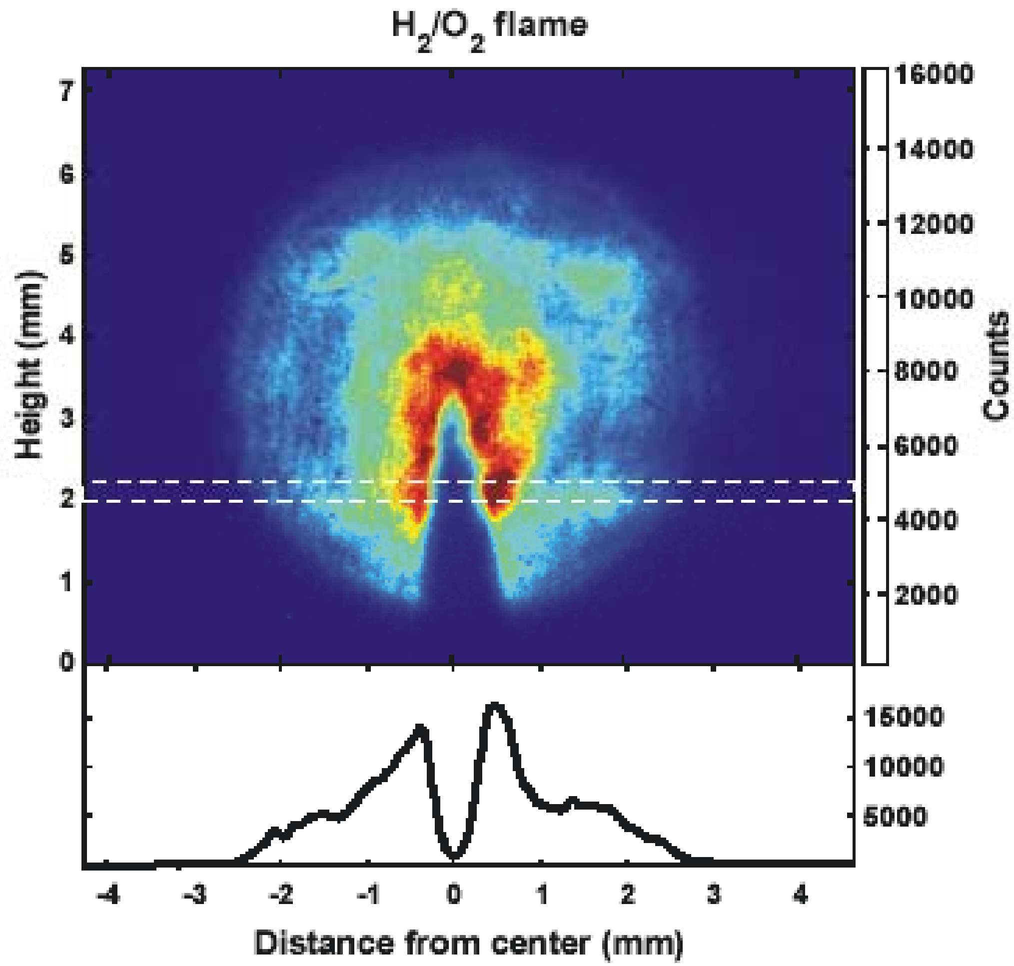
New approach



Experimental set-up



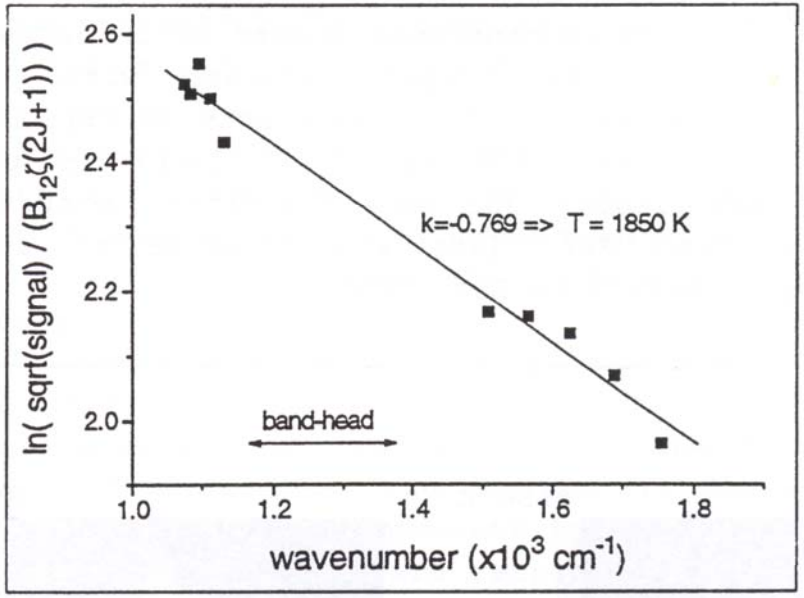
Single shot 2D visualization of H



Temperature measurements

$$N^0 \propto (2J+1)\exp(-E_r(J'')hc/kT)\ ,$$

$$I_t \propto (N^0 B_{J''J'}\zeta_{J''J'})^2 I_p{}^2 I_{pr}\ ,\quad \ln\left(\frac{\sqrt{I_t}}{(2J+1)B_{J''J'}\zeta_{J''J'}}\right) \propto \frac{E_r(J'')hc}{kT}$$



Temperature measurements

- Need for single shot, if possible, 2D T visualization

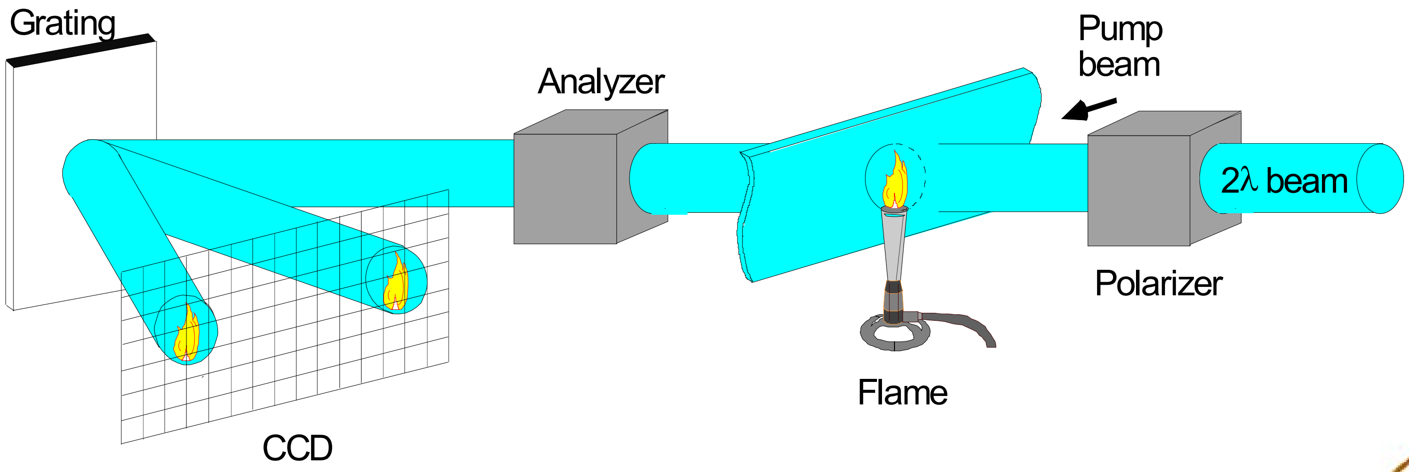
- Two-line excitation where T is given by;

$$T(x,y) = \frac{2(\mathrm{E}_1 - \mathrm{E}_2)/k}{2\ln\left[B_1\zeta_1(2J_1+1)/B_2\zeta_2(2J_2+1)\right] - \ln\left[I_1(x,y)/I_2(x,y)\right]}$$

2D temperature imaging

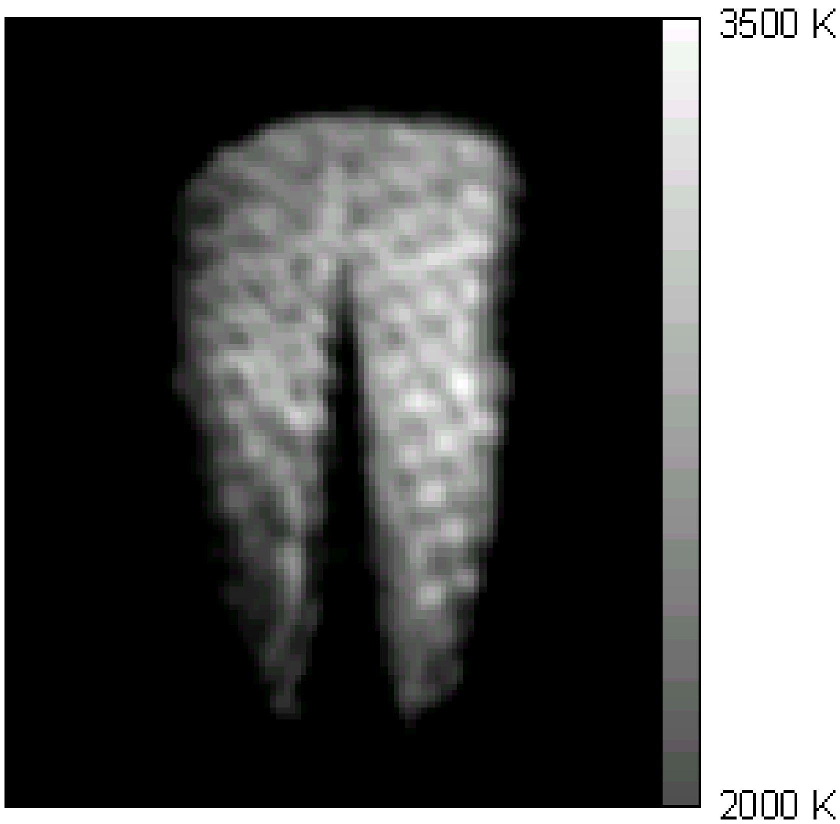
2D temperature maps can be extracted from signal distribution images, which are recorded with the laser wavelength tuned to resonance with two different rotational lines

Single pulse two-dimensional temperature visualization



- dual-wavelength dye laser for excitation
- diffraction grating for spatial separation of the two images
- image-intensified CCD camera for image recording

2D temperature imaging



Challenges to achieve high single shot precision:

• Stable dye laser beamprofiles, or proper referencing

Polarization spectroscopy: Summary

- High sensitivity, (ppm)
- Good spatial resolution by crossed laser beams
- 2D imaging possibilities
- Two-photon (2D) experiments demonstrated
- Rather complex theory
- Possible problems with pressure induced birefringences (e.g. from windows in an engine)
- Sensitivity limited by extinction ratio of polarizers

Why measurements in the IR spectral region?

- **In the UV/vis, only a limited number of species (OH, CH, NH, C_2, NO, CH_2O, ..) can be probed with resonant LIF, DFWM, PS.**

- **Many combustion important species CO_2, CO, H_2O, N_2O, C_2H_2, CH_4 and other HC molecules or radicals, pose no accessible single-photon electronic transition in the UV/visible, but have strong absorption in the mid-infrared (2-5µm) via ro-vibrational transition.**

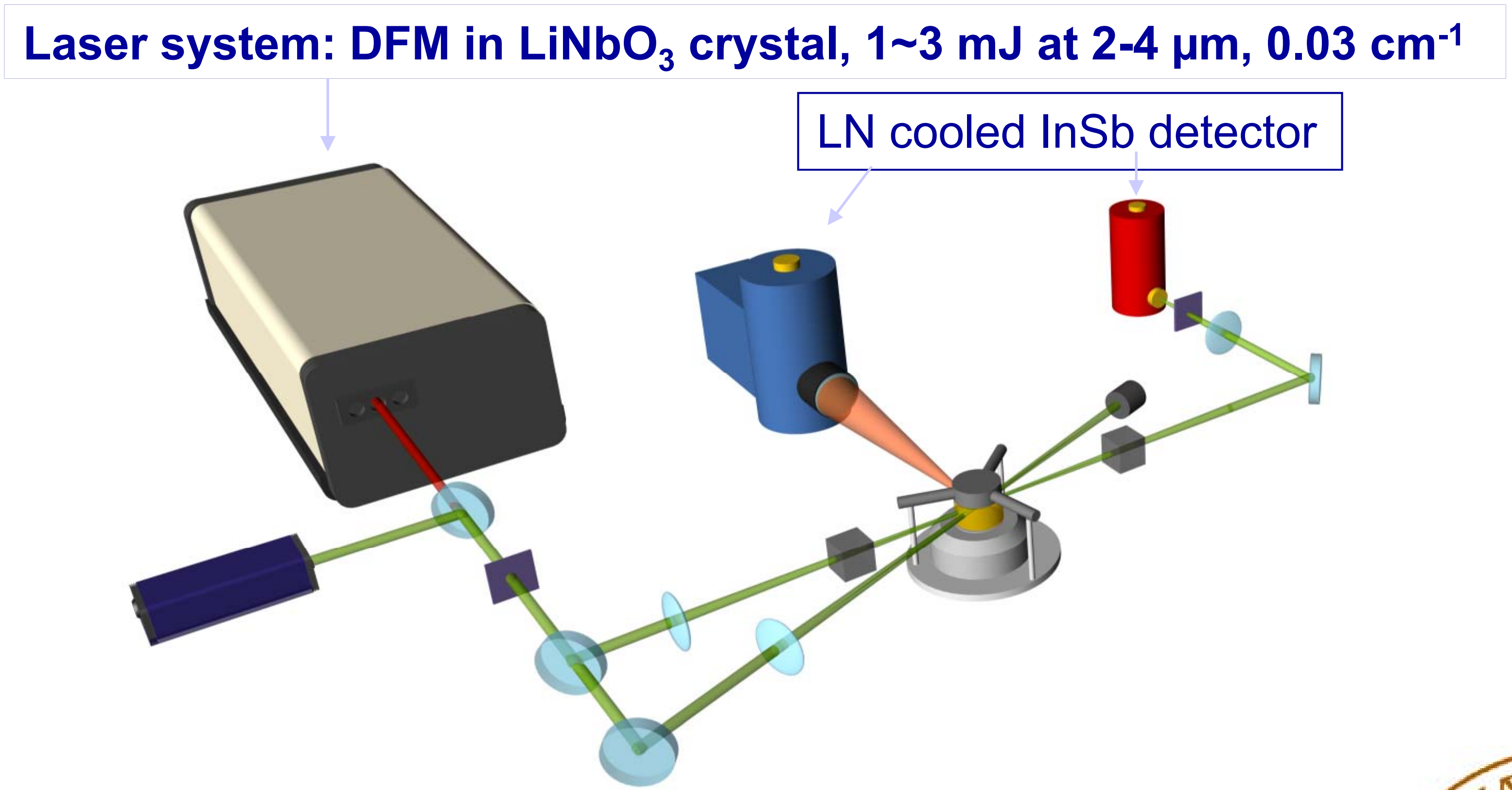
- **Spatially and temporally resolved measurements needed**

IRPS/IRDFWM

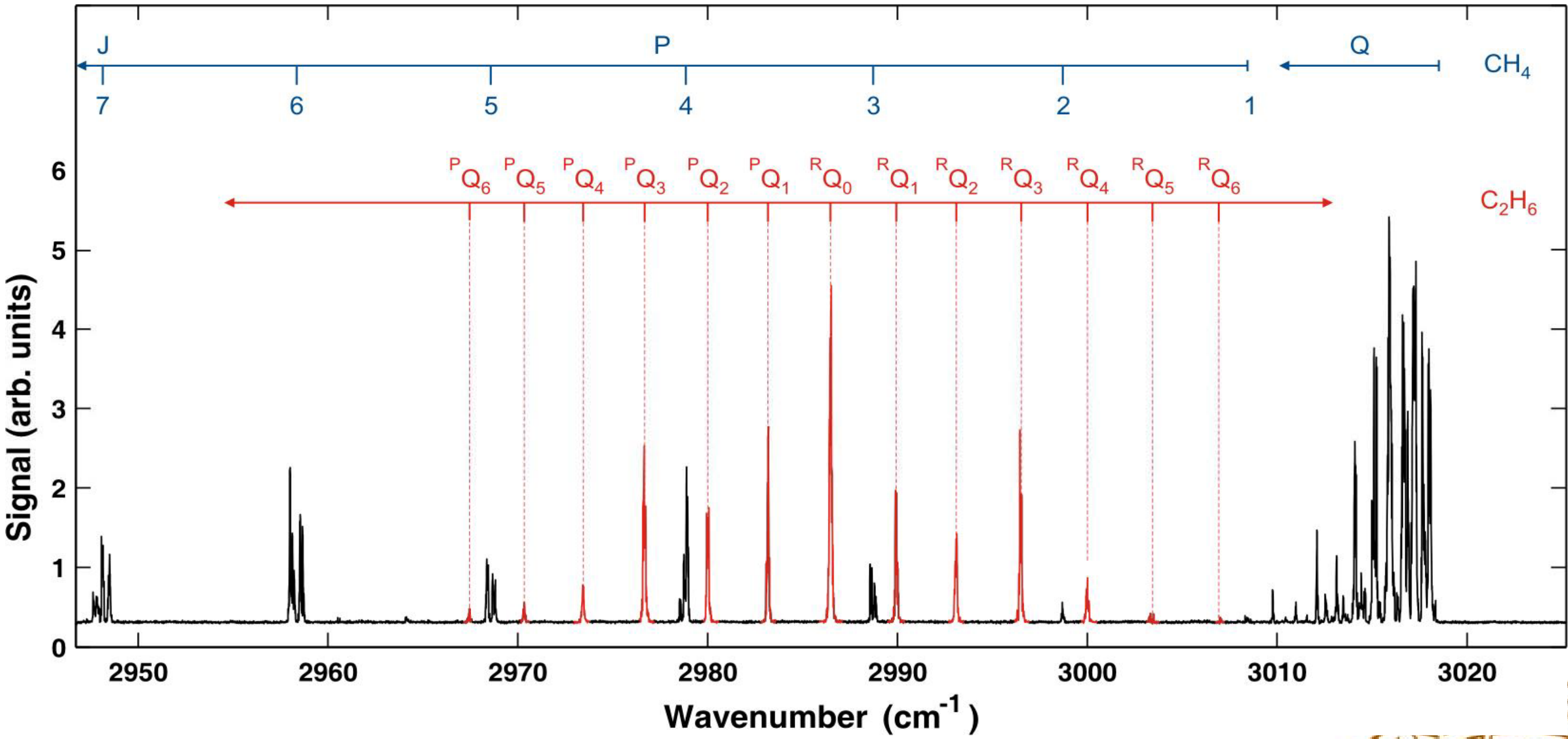
- Challenges
  - **Spectral interferences, especially in combustion environments where many species exist in a narrow spectral range**
  - **Doing non-linear experiments with invisible laserbeams**

- Opportunity
  - **Probing sensitively many important combustion intermediate species which otherwise are inaccessible with non-intrusive spatially resolved methods**

Typical IRPS experimental setup

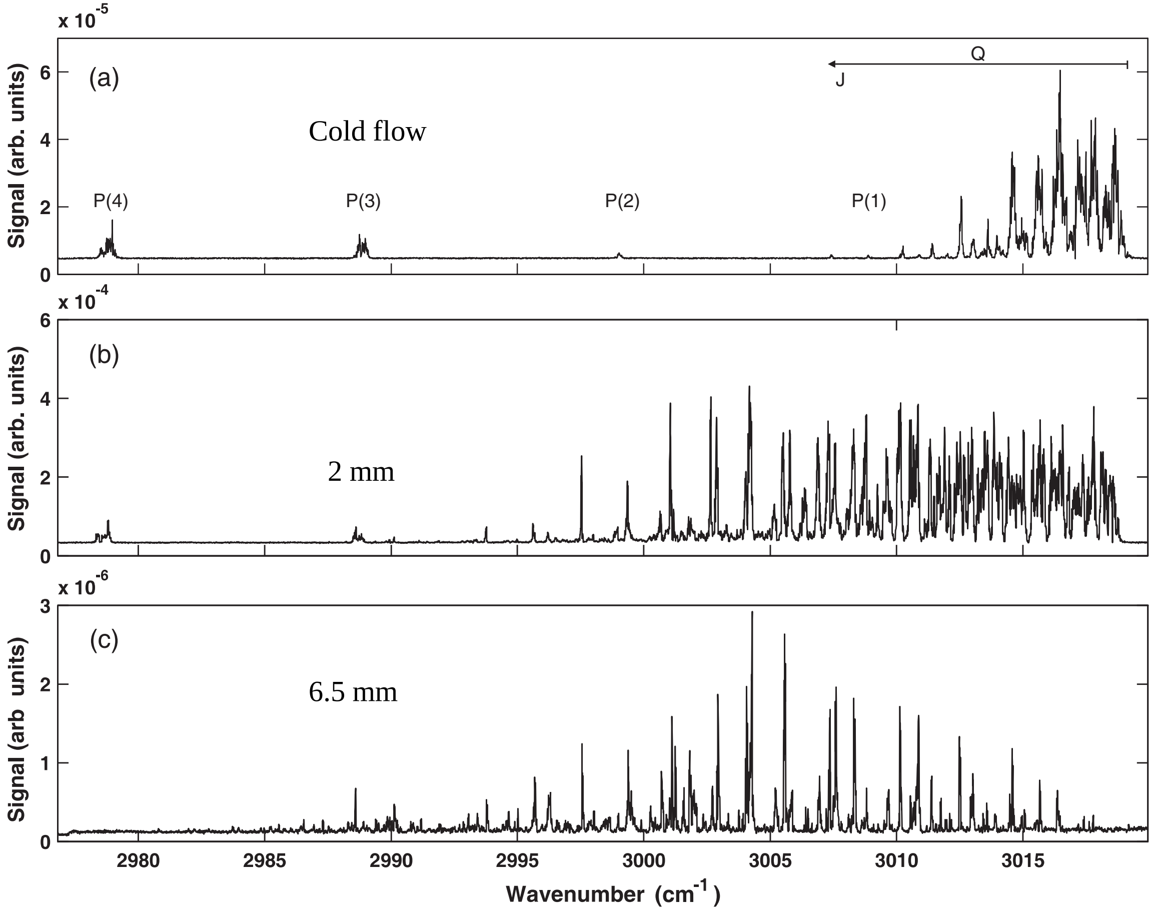


IRPS spectra of CH_4 and C_2H_6



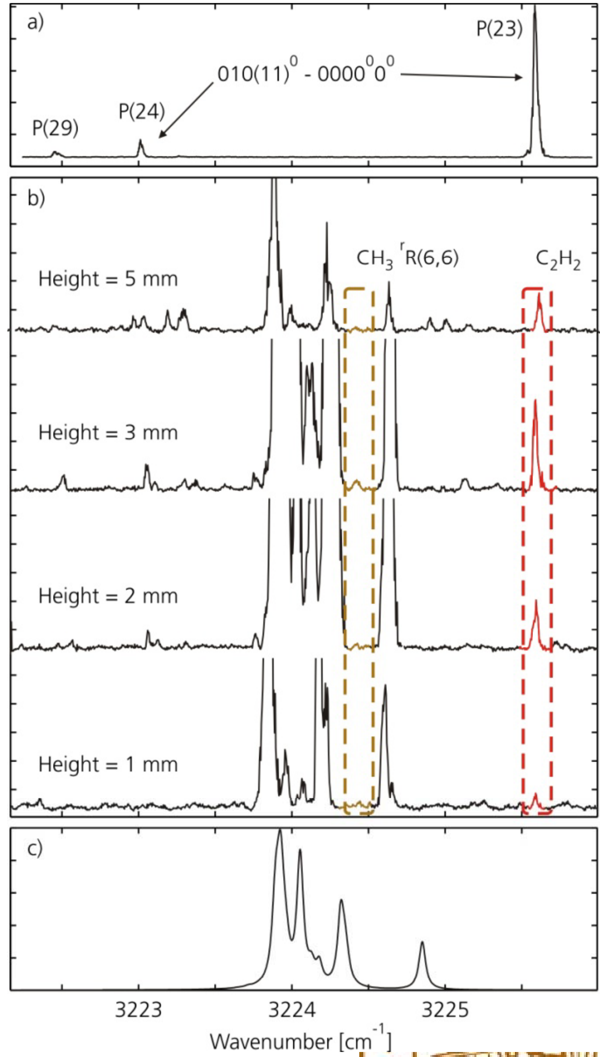
1.93% of CH_4 and 0.57% of C_2H_6 mixed with Ar at 1 atm pressure.

Methane flame detection



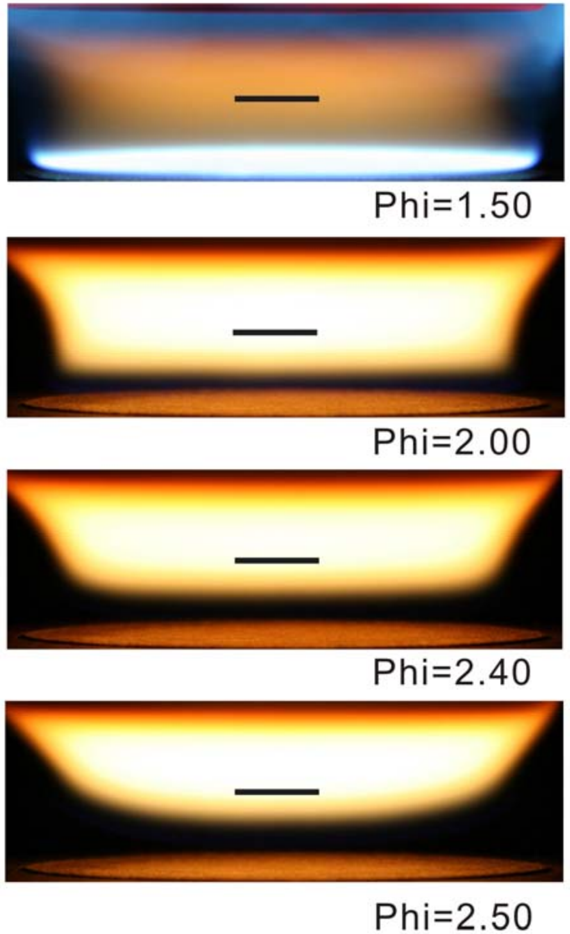
Detection of acetylene and methyl with IRPS in a CH_4/O_2 (50 mbar, Φ=1.5) flame

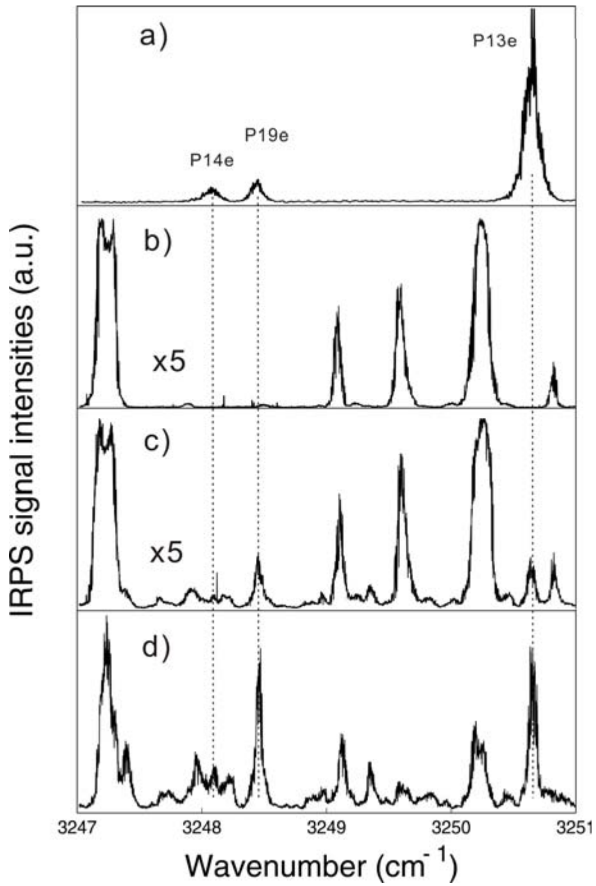
- **Excitation scan of P(24) and P(23) C_2H_2 lines in a gas flow**
- **Calculated IRPS spectra of hot methane**
- **Excitation scan above the burner**
  - at 1 mm abover the burner
  - at 2 mm abover the burner
  - at 3 mm abover the burner
  - at 5 mm abover the burner
- **Acetylene, C_2H_2, detected**
- **Methyl, CH_3, detected**



Li et al. 31st Comb Symp.

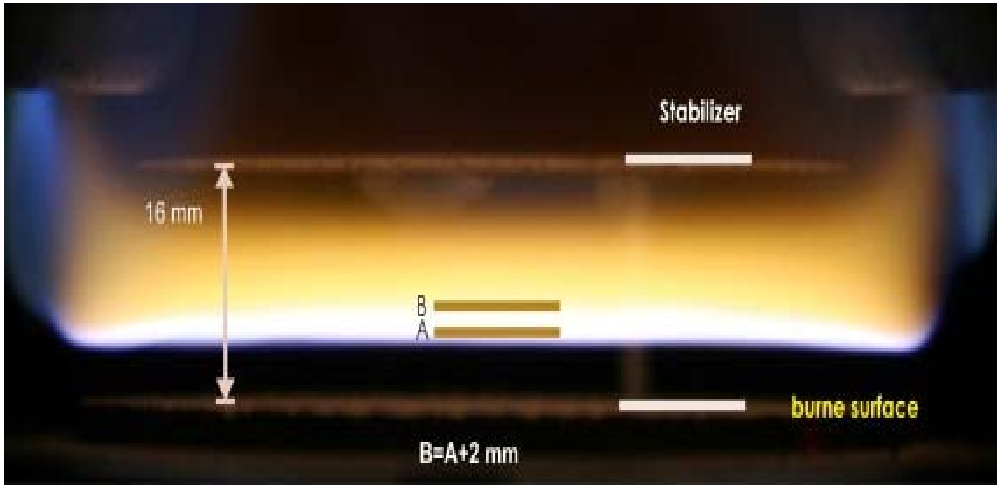
IRPS detection if C_2H_2 in sooty flames

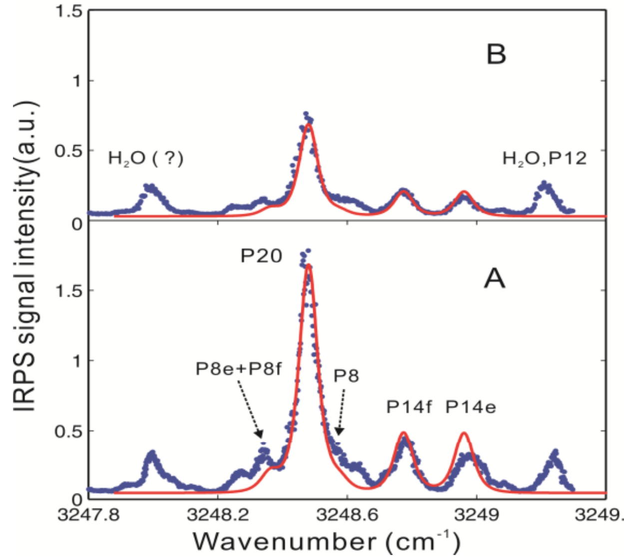


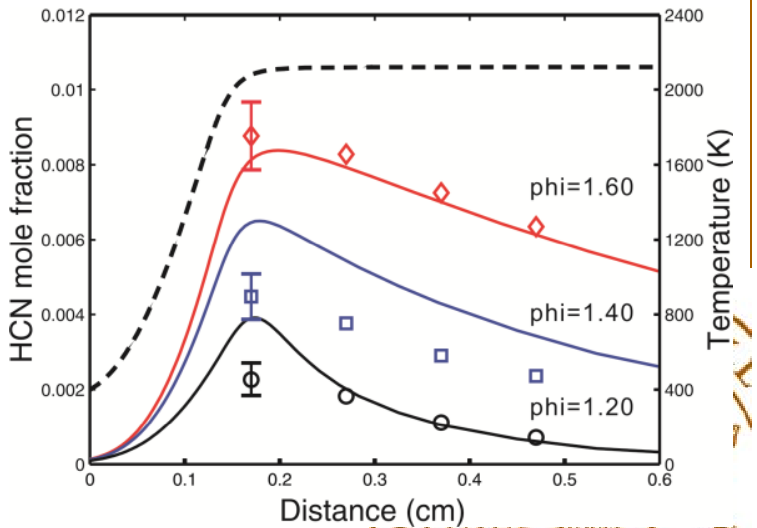


IRPS excitation spectra in calibration gas: a) and flames: b) Φ = 1.00, c) Φ = 1.50 and d) Φ = 2.50.

HCN measurements in flames using IRPS

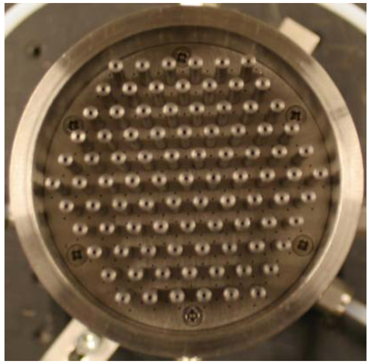


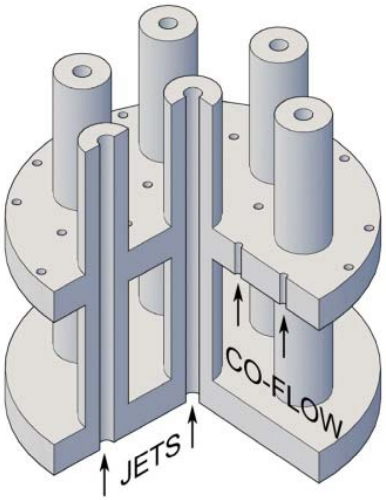




Sun et al. 2010

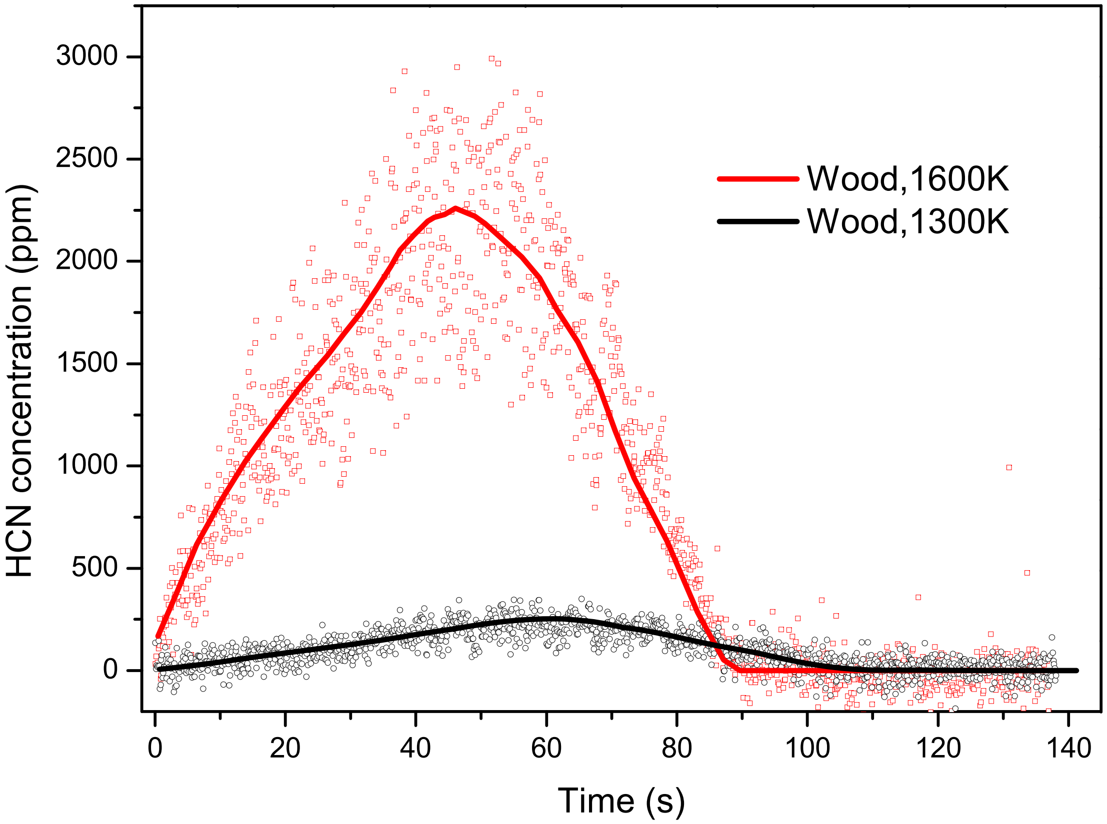
IRPS measurements: HCN release history of solid fuel combustion/gasification





Sun et al. 2011

IRPS measurements: HCN release history of solid fuel combustion/gasification

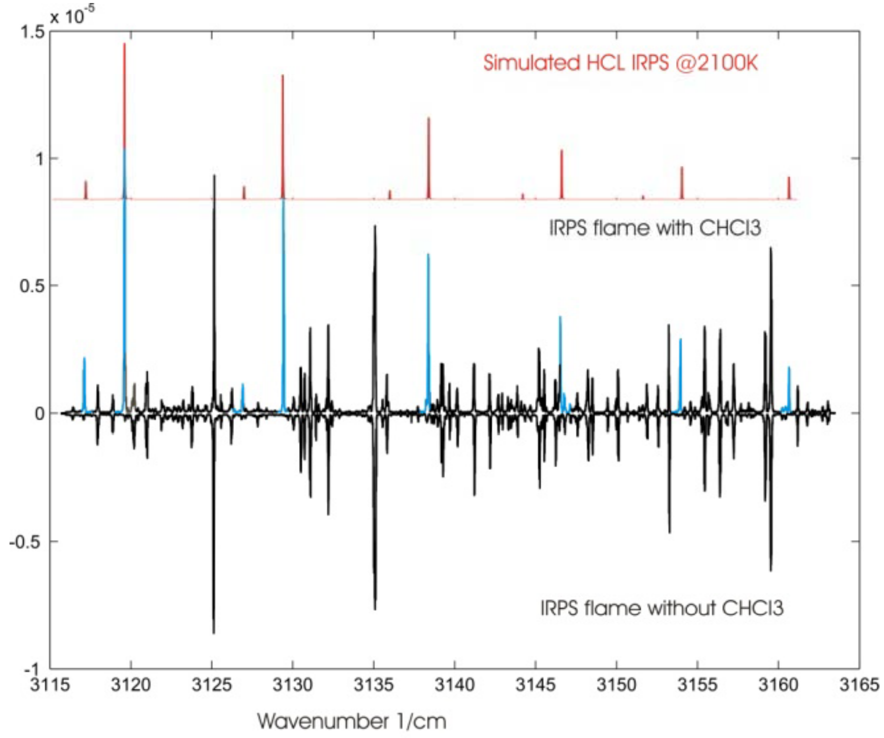


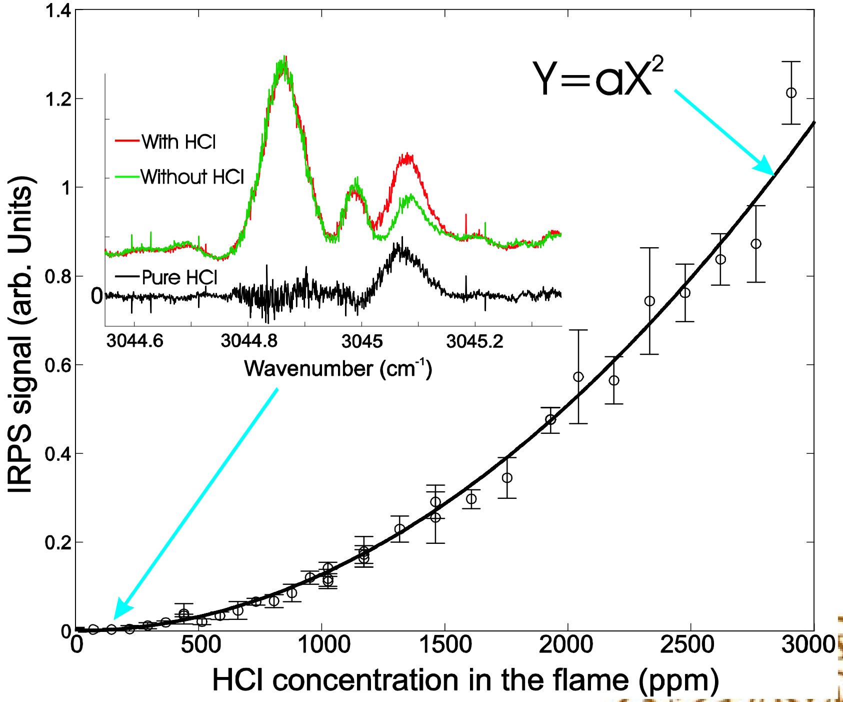
Comparison of HCN release at different temperatures for wood gasification.

Sun et al. 2011

HCl measurements using IRPS

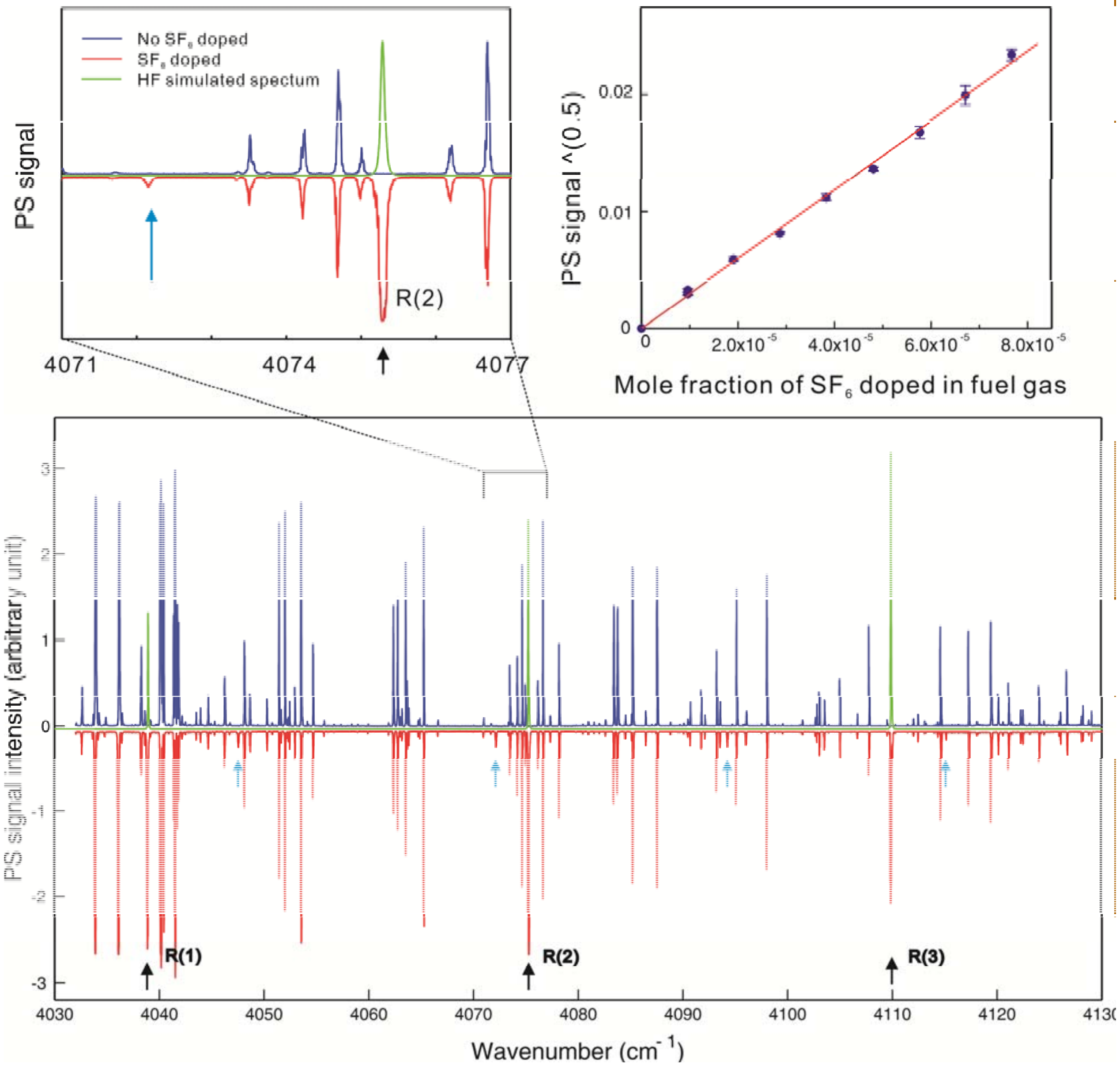
CH4 /O2 flame seeded with chloroform





Li et al. Opt. Lett 2008

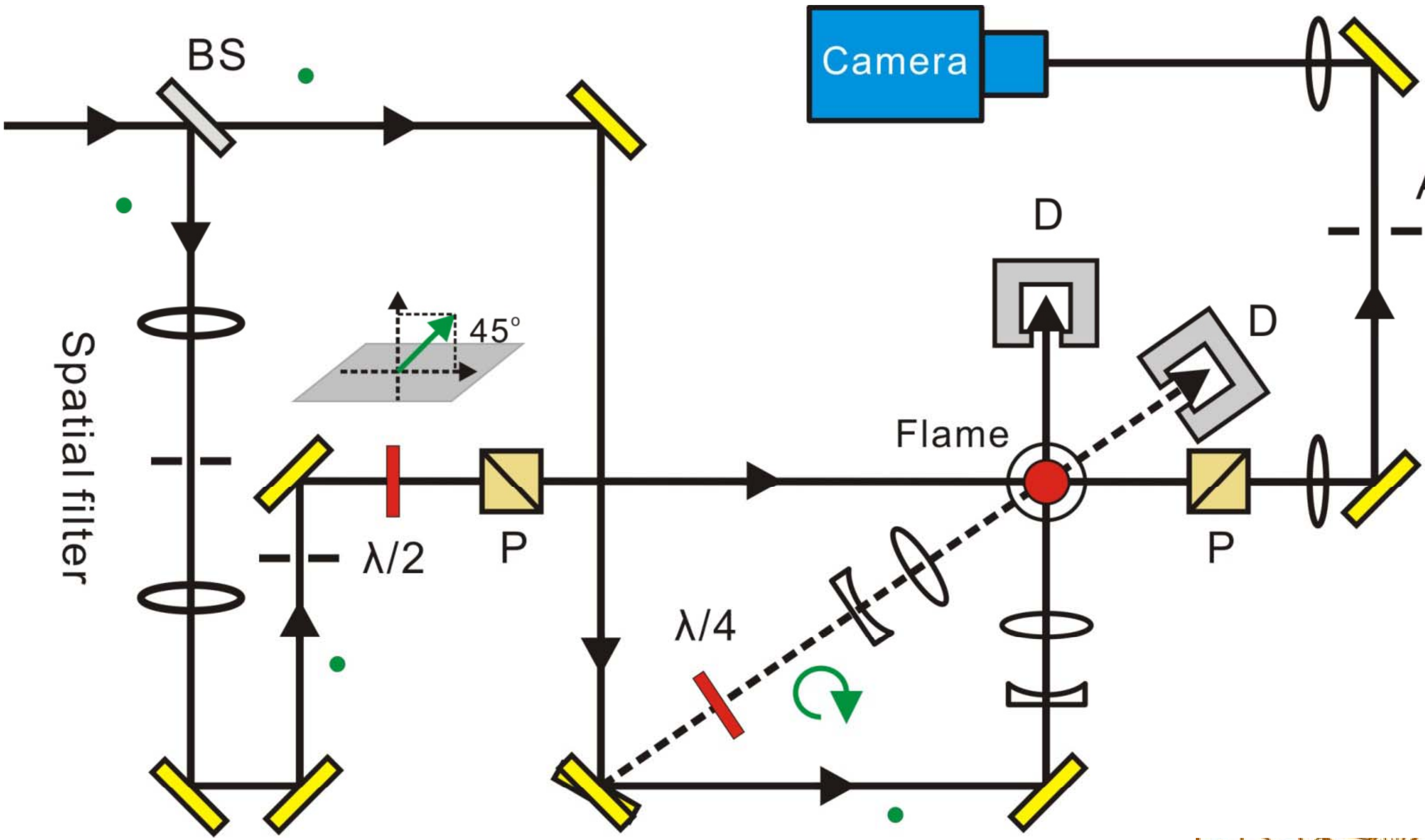
2D-IRPS measurements of HF in flames



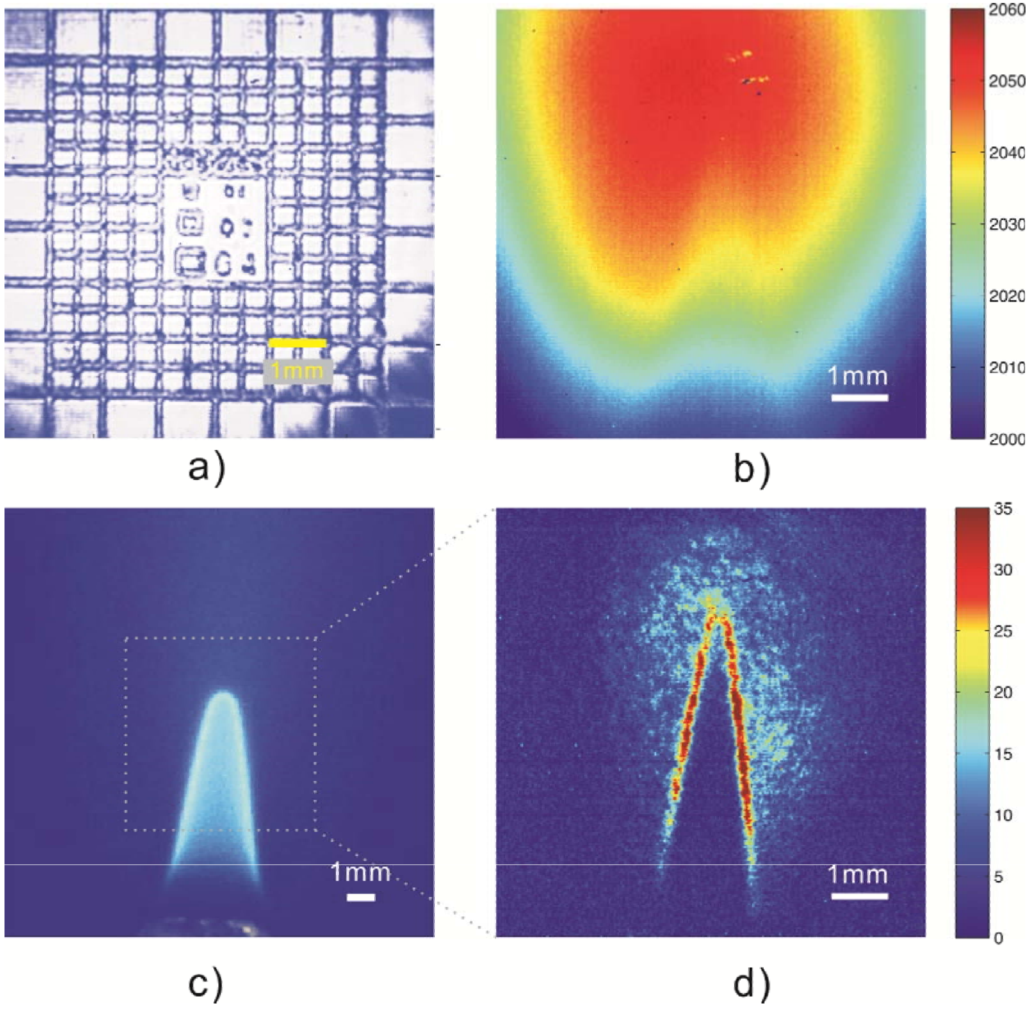
Spectra recorded in SF6 doped CH4/air flames, E.r.= 1.1, Mckenna type burner.
The blue arrows show HF hot lines.

Sun et al. : In preparation

Experimental set-up: 2D-IRPS

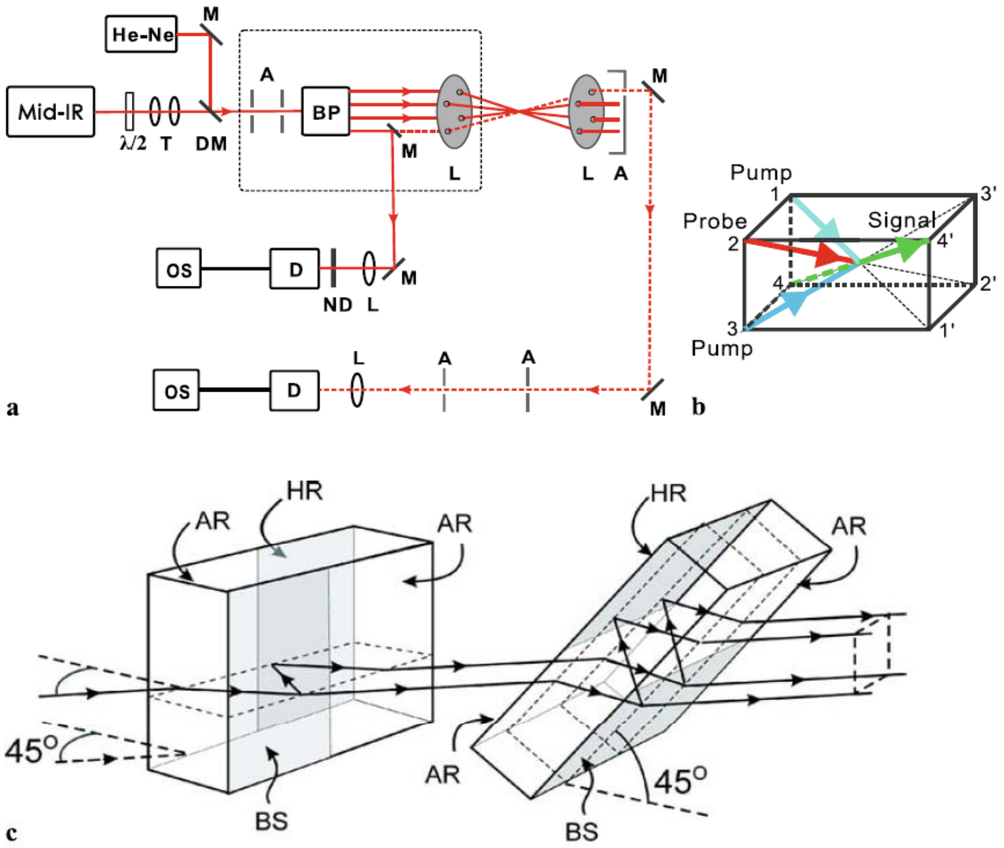


2D imaging of HF



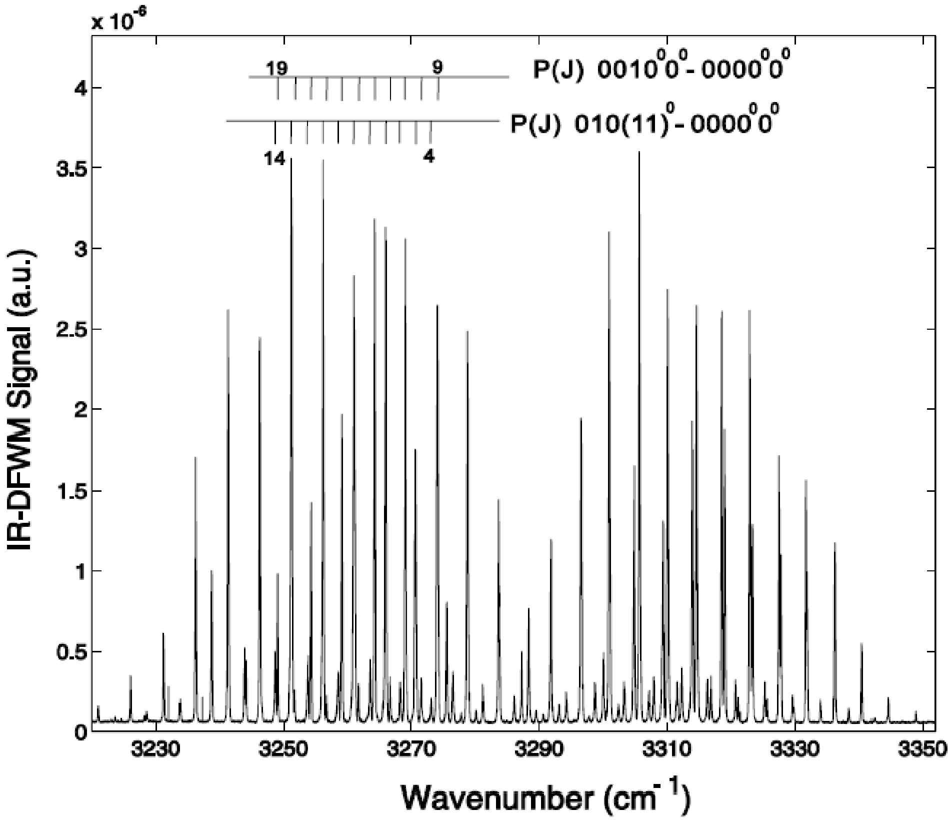
(a) Investigations of the spatial resolution of the imaging system
(b) Thermal radiation from the flame without spectral filter
(c) Photograph of the welding torch flame burning with CH_4/O_2 (Φ=2) doped with 2% SF_6
(d) 2-D IRPS imaging of HF. The wavelength of laser focused on R(3) line of HF

New experimental scheme for IR DFWM experiments

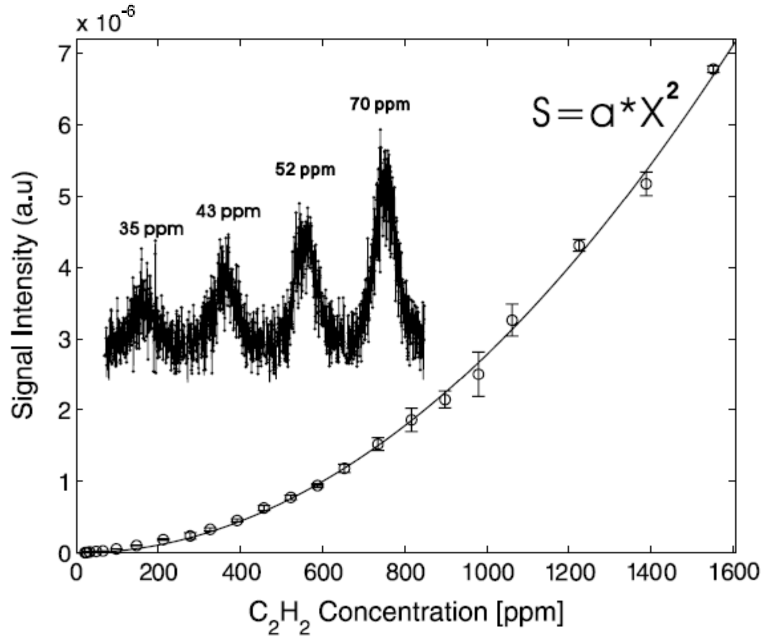


Z.W. Sun, Z. S. Li, B. Li, M. Aldén and P. Ewart, 'Detection of C2H2 and HCl with mid-infrared degenerate four-wave mixing with stable beam alignment: towards practical in situ sensing of trace molecular species', Appl. Phys. B 98, 593-600 (2010)

IR-DFWM experiments on C_2H_2

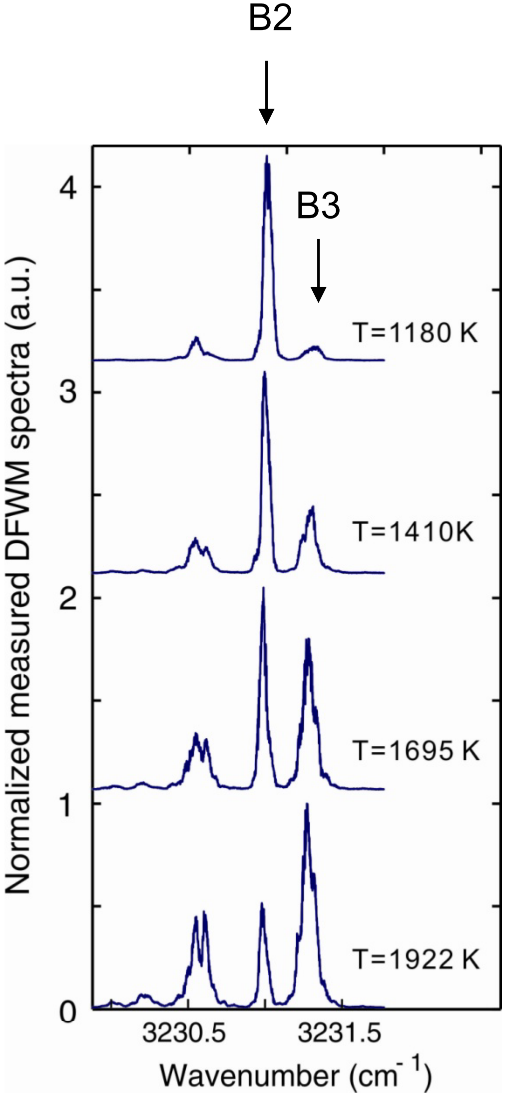


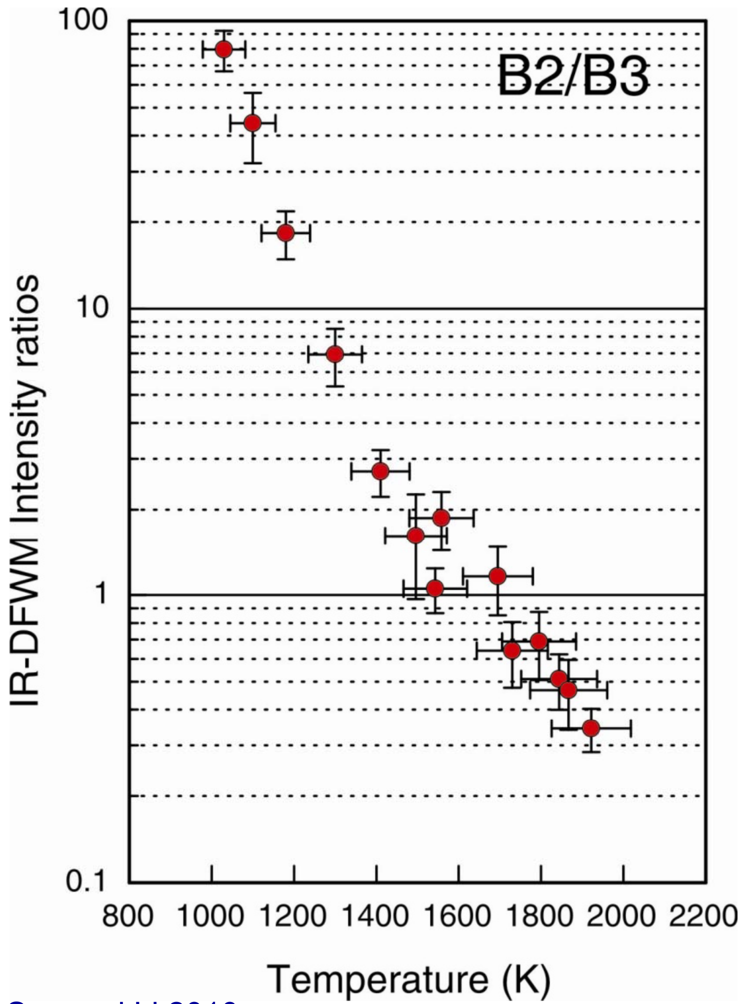
IR-DFWM spectrum of 510 ppm C2H2 in a nitrogen gas flow. Partial assignments of the spectral lines have been made



Investigation of detection limits

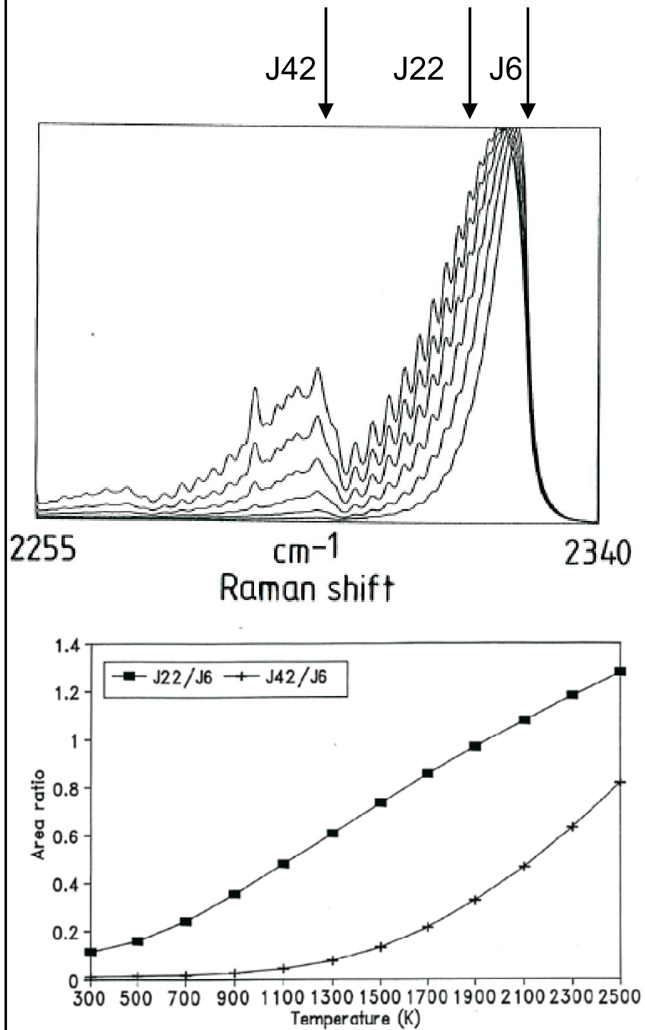
Thermometry using IR H_2O lines using IR-DFWM





Courtesy: Sun and Li 2010

Comparison-CARS

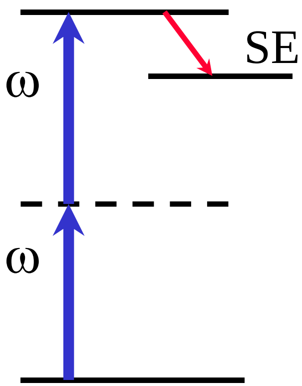


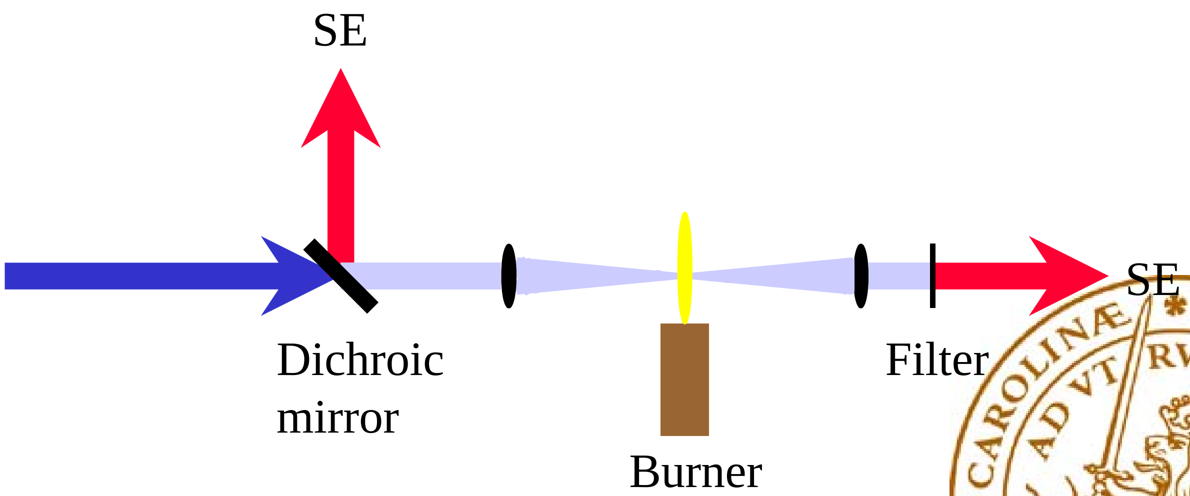
Löfström, Kröll and Aldén, Proc. Comb. Symp. **24,** 1637 (1992).

Stimulated Emission (SE)

Conceptual behaviour:

Two-photon UV excitation followed by laserlike emission in the visible/IR region





Stimulated Emission

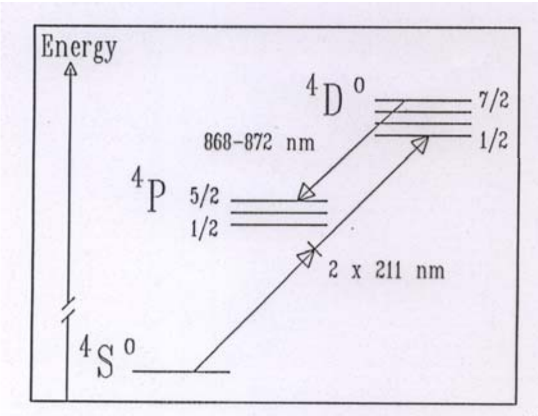
Advantages:

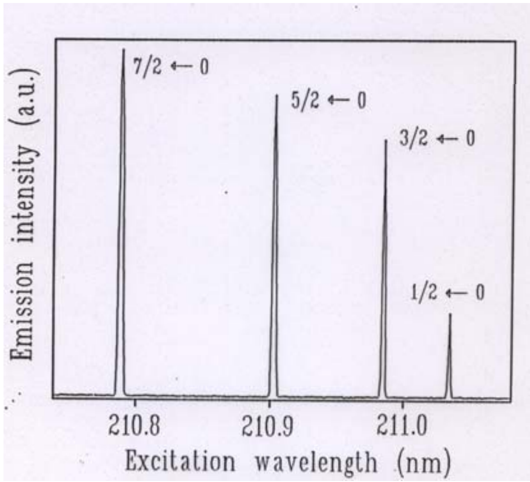
- Signal generated as a new beam
- Bidirectional signal
- Very strong signal
- Simple set-up
- Minor species detection (N,C)

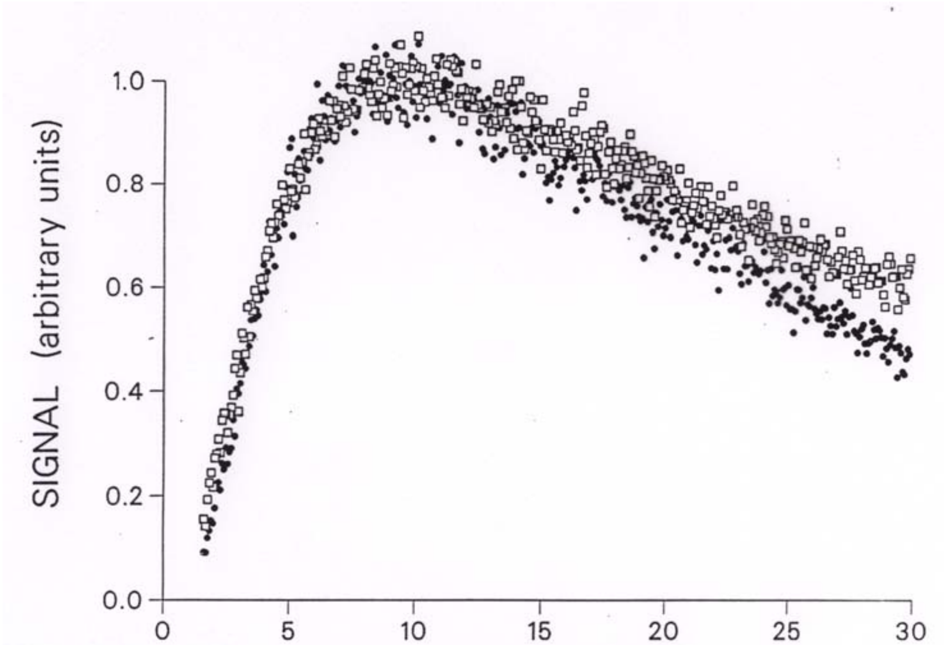
Disadvantages

- Difficult to model
- May interfere with LIF
- Low spatial resolution (?!)

Flame application of SE



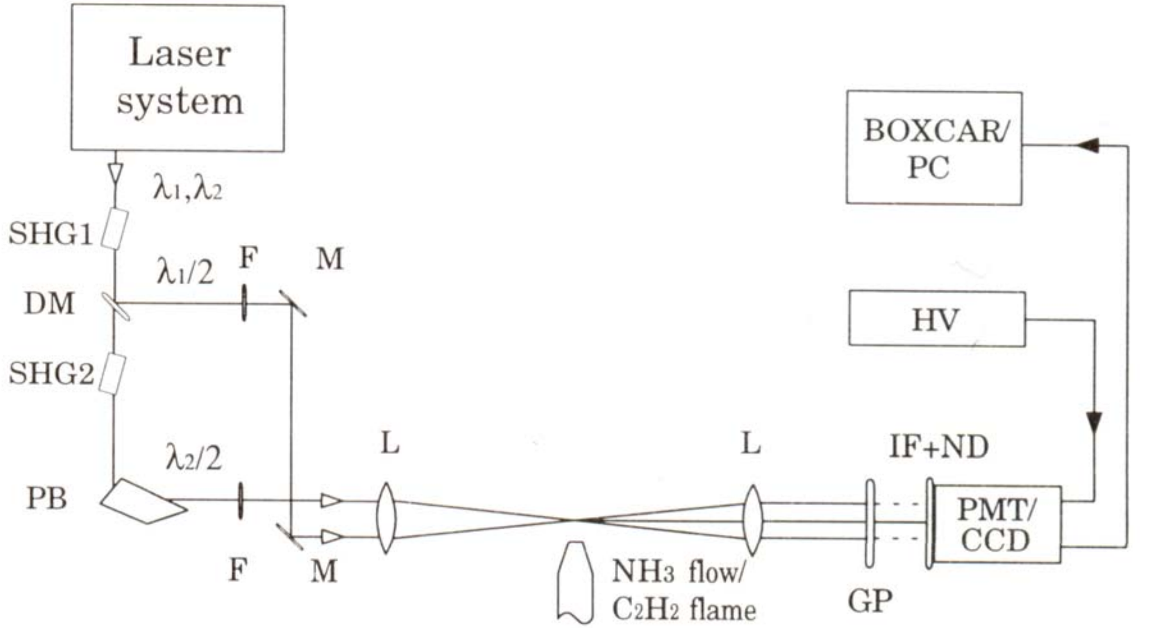


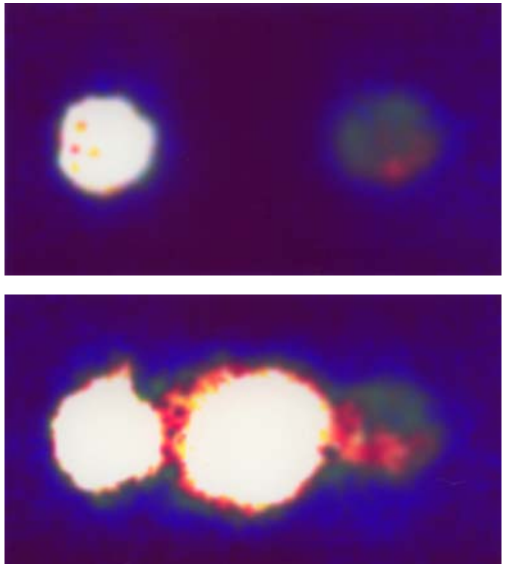


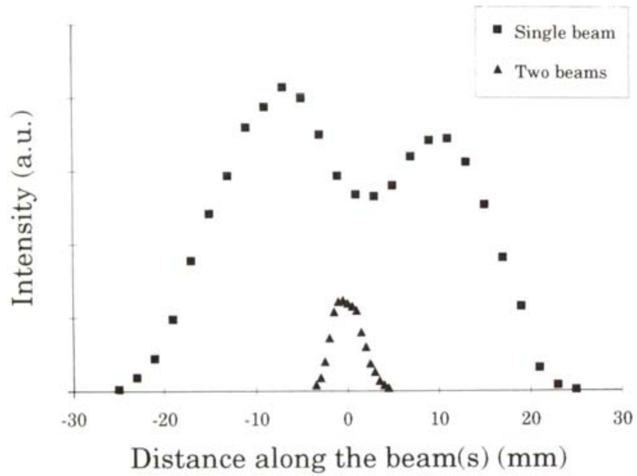
O atom detection

N atom detection

Increased spatial resolution using SE







Photochemical effects?