UNIVERSITÀ
DEGLI STUDI
DI PADOVA

Raman spectroscopy for inline analysis of combustion processes

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Third year admission - 13/09/2023

Institutions:

https://cisas.unipd.it/

Centre of studies and activities for space “G. Colombo”, throughout space studies and research, CISAS aims to contribute to an inter and multidisciplinary formation of a new profile of Graduates and Researchers with knowledge and competence in the different fields required by fundamental sciences, applied research and industrial activities

http://www.ifn.cnr.it/

The Institute of Photonics and Nanotechnology deals with innovative research in the fields of photonics and nanotechnology. Both on basic research aspects and applied to the development of Optical and optoelectronic devices.

https://www.pipe40-project.eu/

PiPe4.0 aims to establish a new measurement paradigm in the quality assessment of fuel gas distribution following the reconfiguration of gas flows through the grid, including hydrogen-enriched natural gas, biomethane and biogas.

Motivation:

Main Goal:

- Qualitative and quantitative inline realtime analysis of gasses related to combustion products.

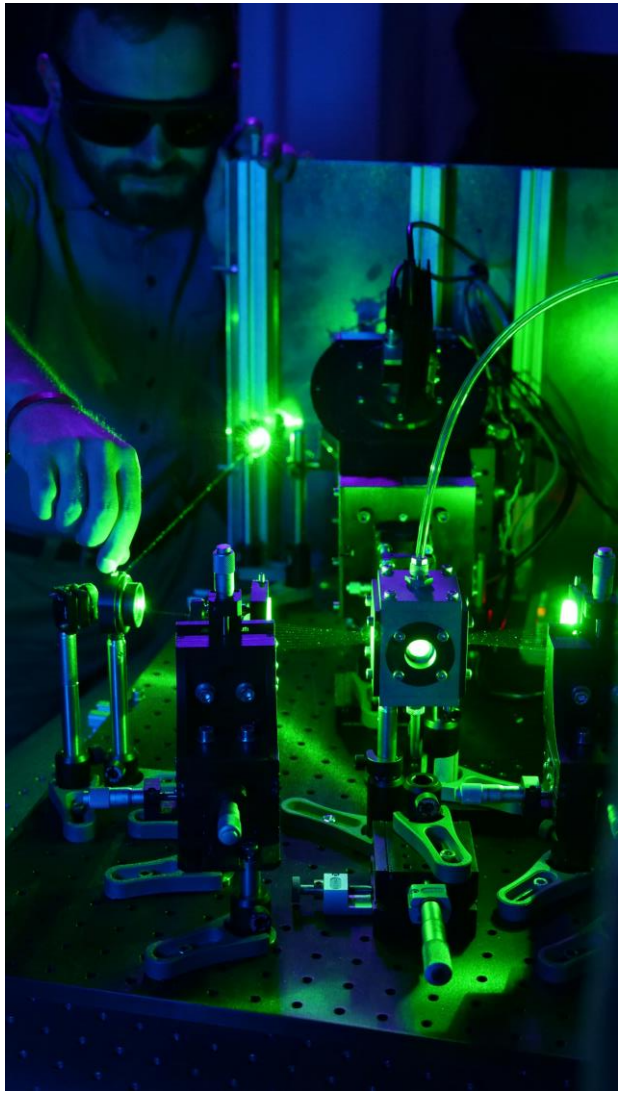
The requirements needed to perform this diagnostic analysis are:

a) Fast response

b) High sensitivity

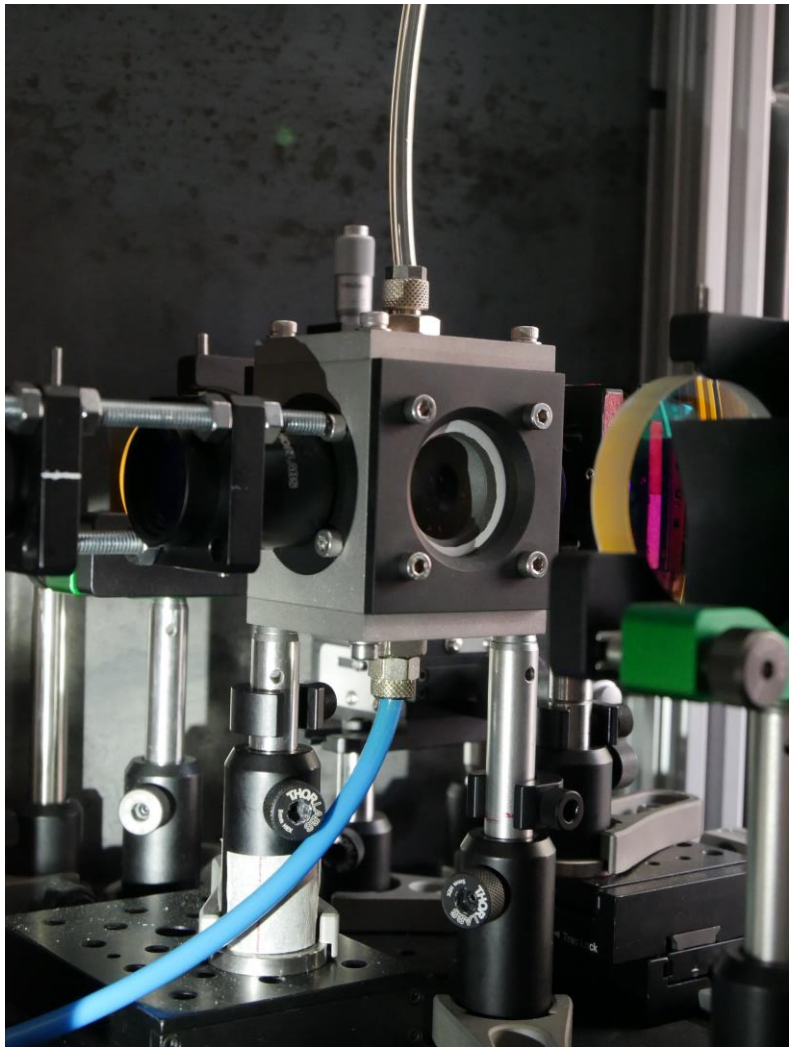
c) Ability to perform analysis in harsh environment

d) Multispecies gas detection



Raman spectroscopy, why?

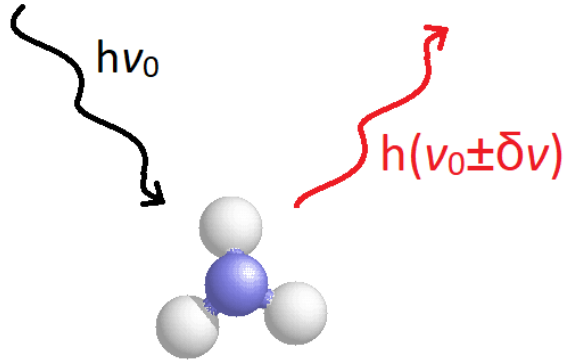
- ✓ Detection of gasses such as N_2 ed H_2
- ✓ Multi-species gas detection using a single channel
- ✓ Does not require IR technology (@532 nm)
- ✓ Non-destructive and non-invasive technique
- ✓ No sample preparation is needed
- ✓ Gives information about the process dynamic
- ✓ «Affordable»



We don't use instruments…
… we build our own instrument!

Introduction:

Raman emission is proportional to:



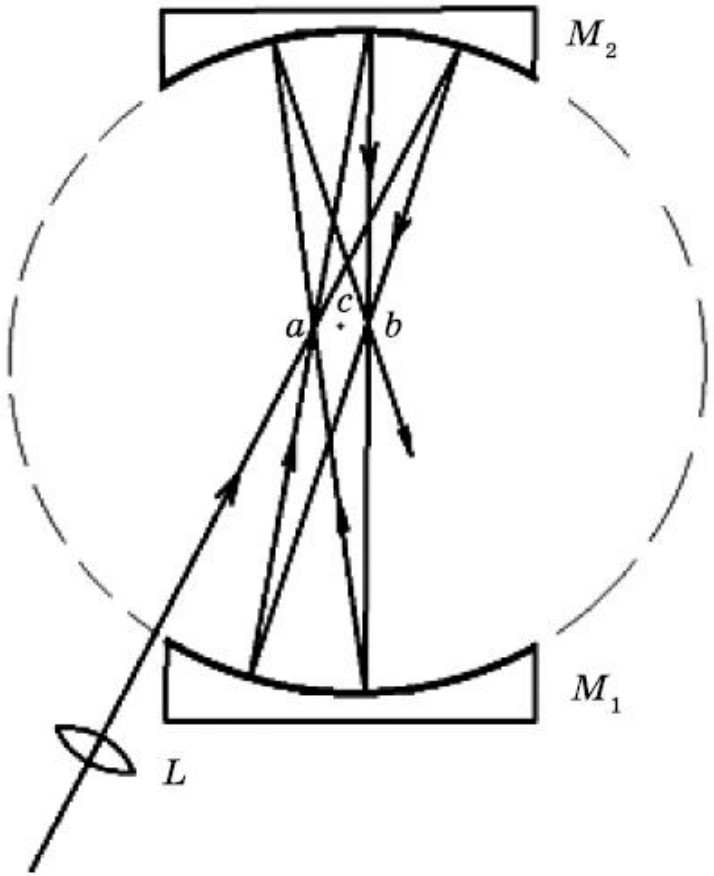
- Intensity of the incident radiation (laser pump power)
- $1/\lambda^4$ (wavelength of the laser pump)
- Intrinsic properties of the molecule (cross section)
- Concentration of molecules in the light-matter interaction region (density of the sample)

Where can we improve the generation and the detection of the Raman scattering?

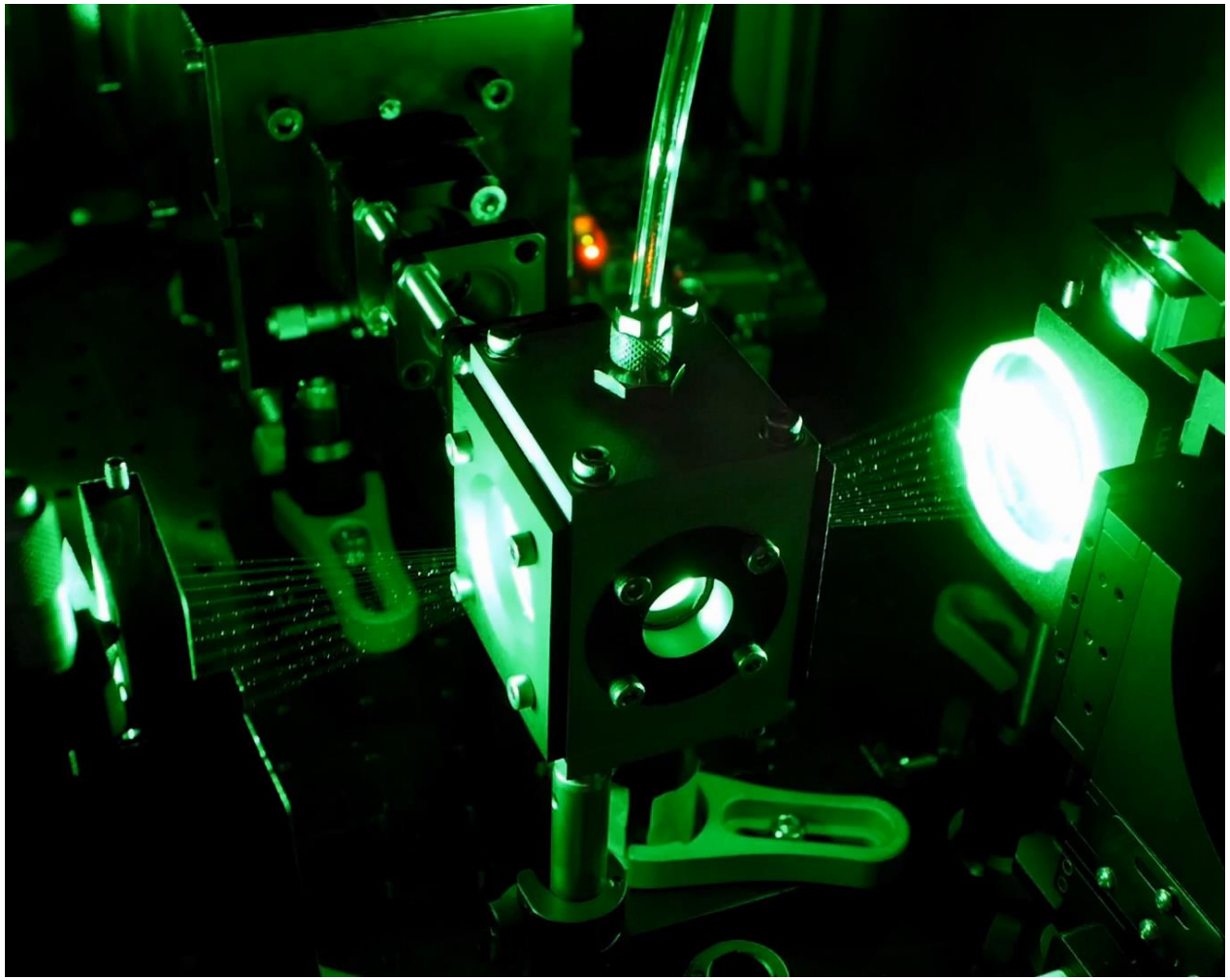
Scattering generation → Incident radiation → λ / Incident power

Scattering detection → Detector / Spectrometer

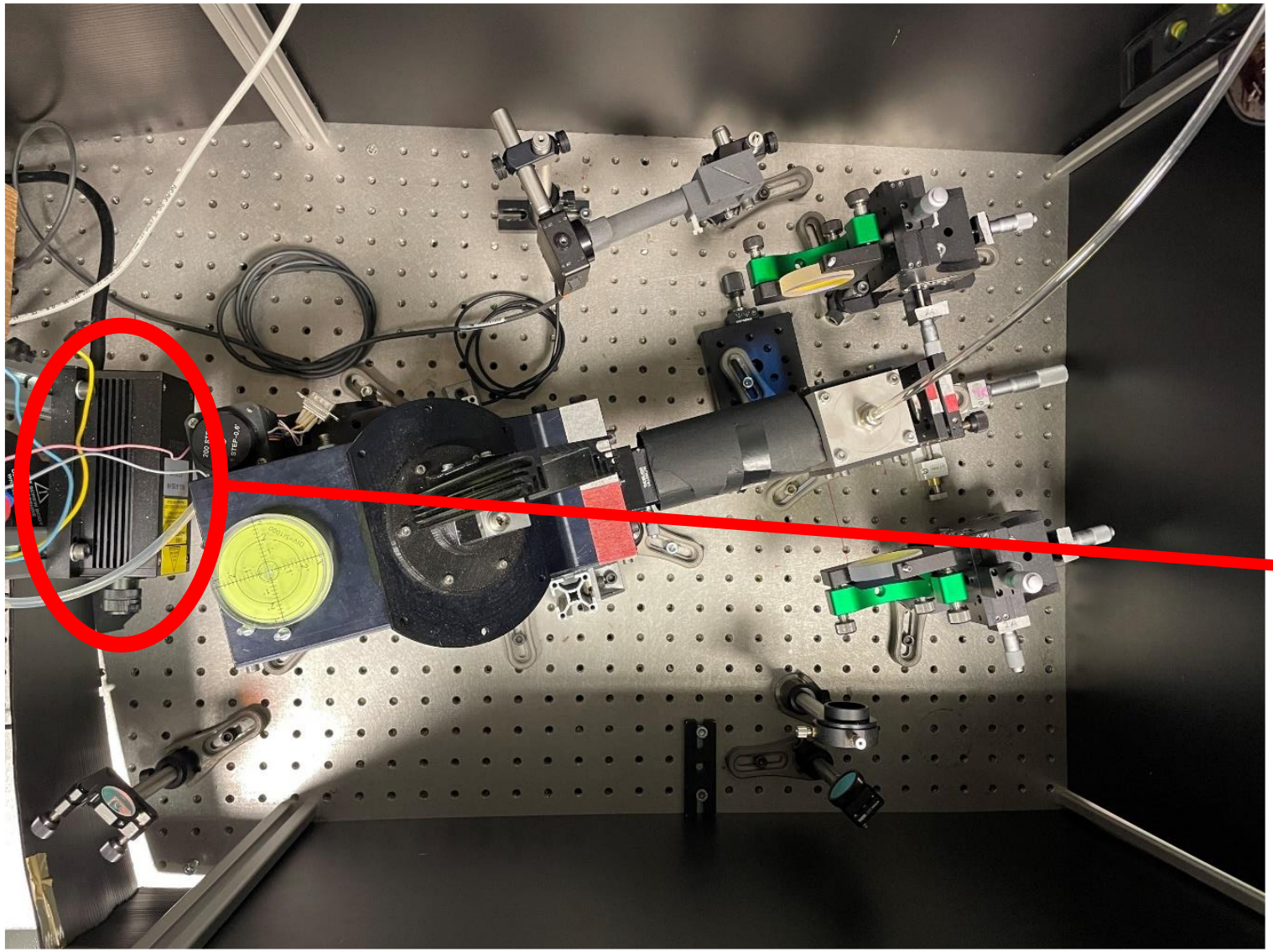
Multi-pass Setup:



Dmitry V. Petrov, "Multipass optical system for a Raman gas spectrometer," Appl. Opt. 55, 9521-9525 (2016)

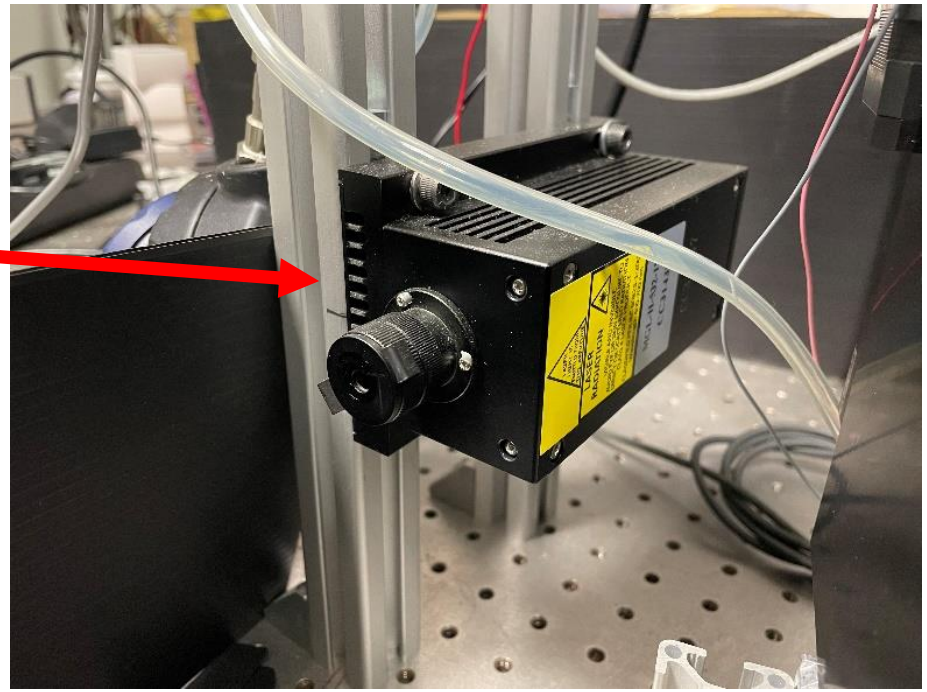


Multi-pass Setup:

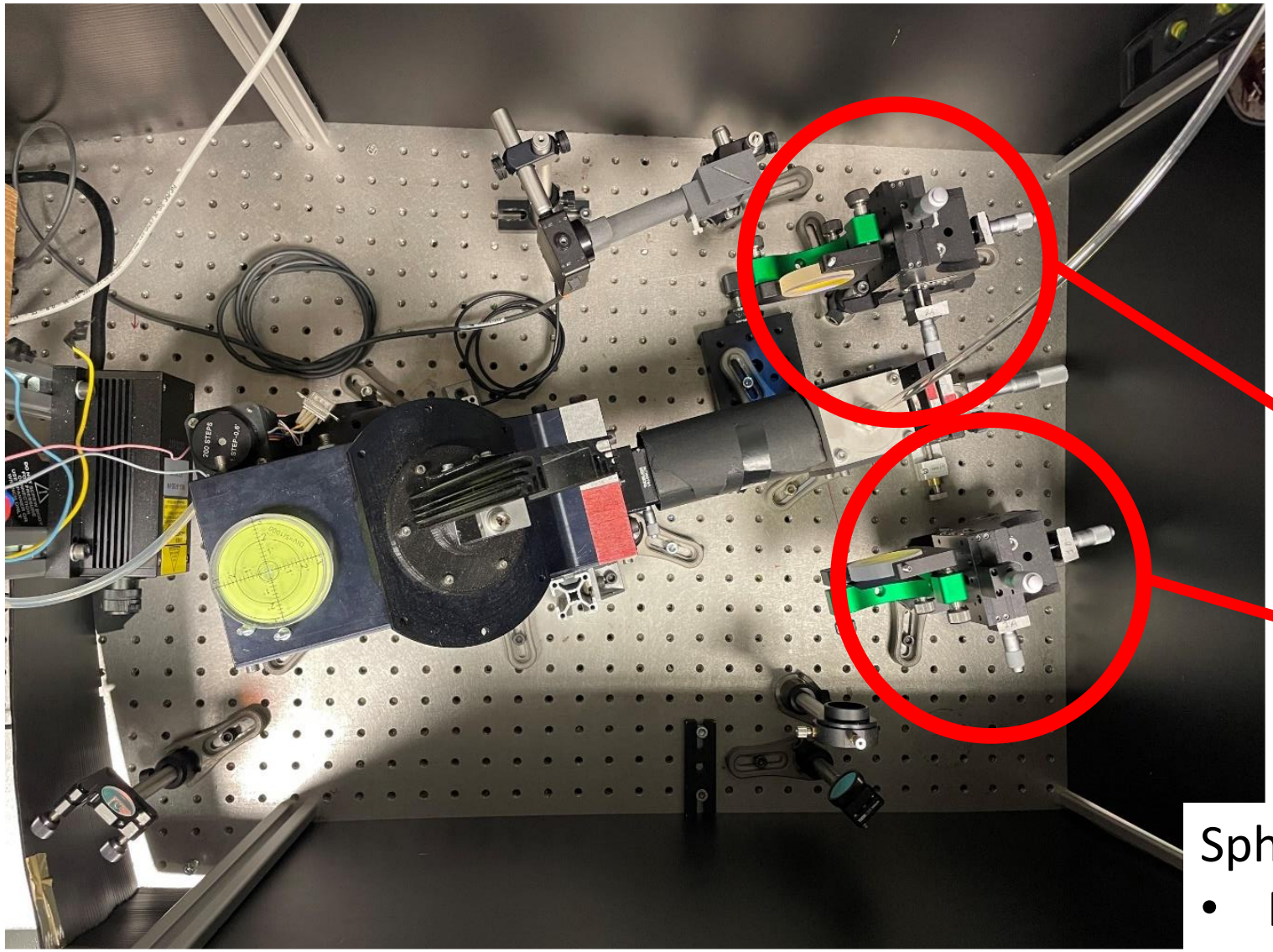


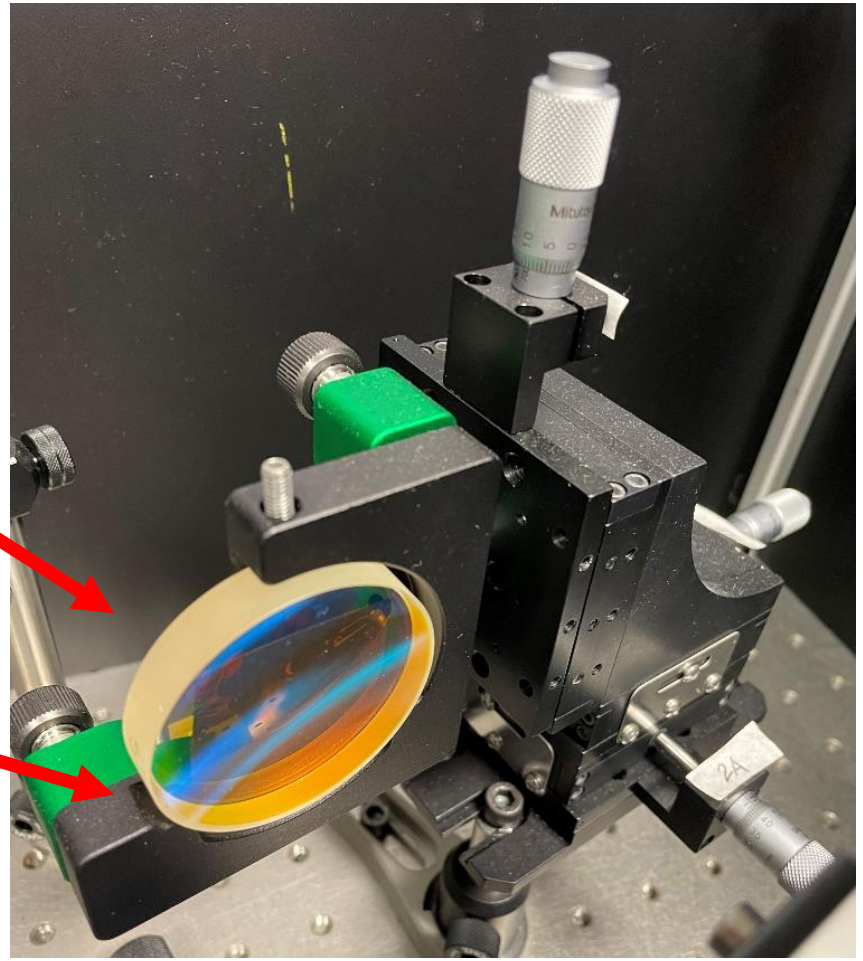
Laser source:

- Nd:YAG CW 532 nm
- 1.163 W
- Spectral width <0.2 nm



Multi-pass Setup:

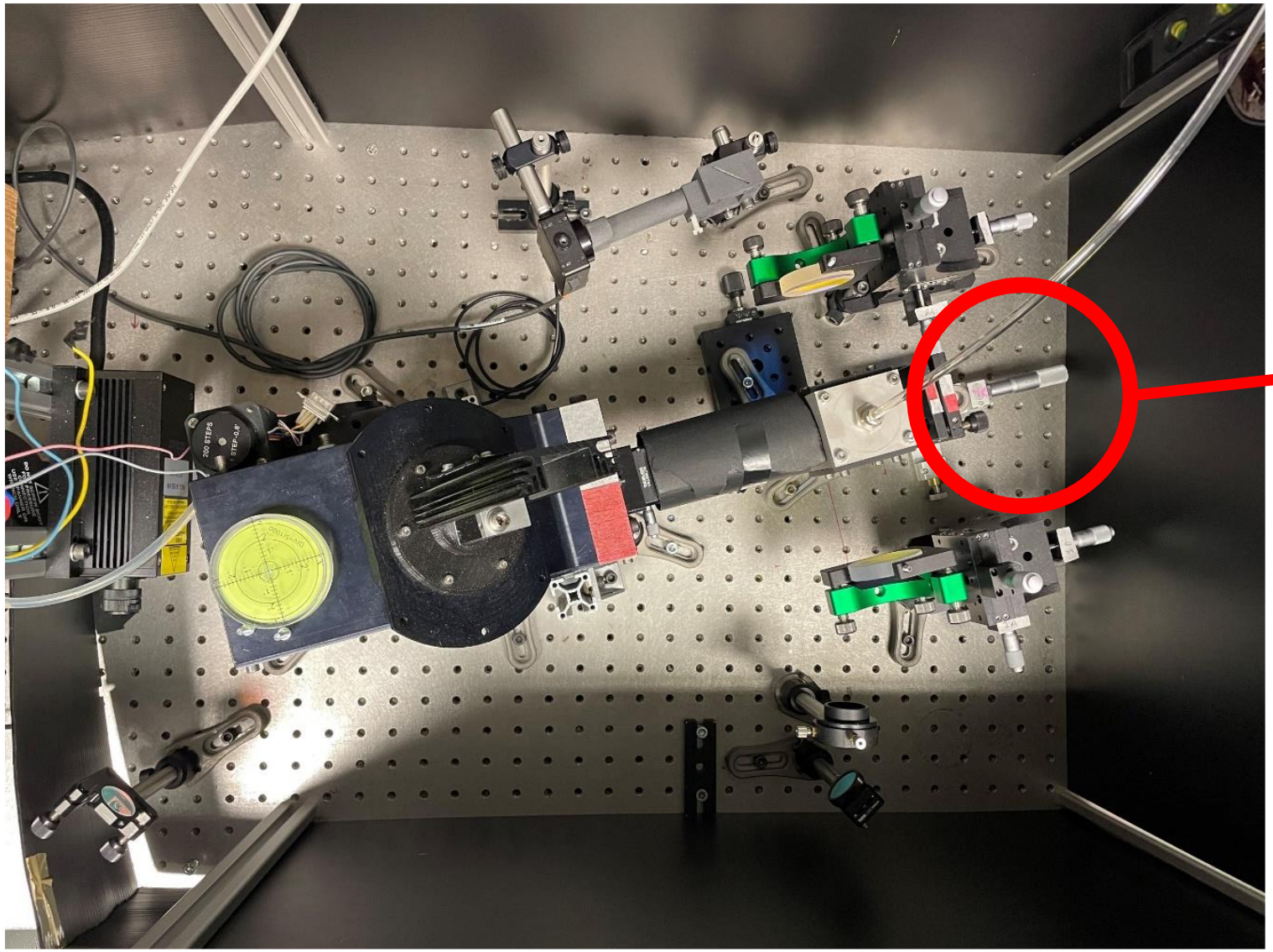


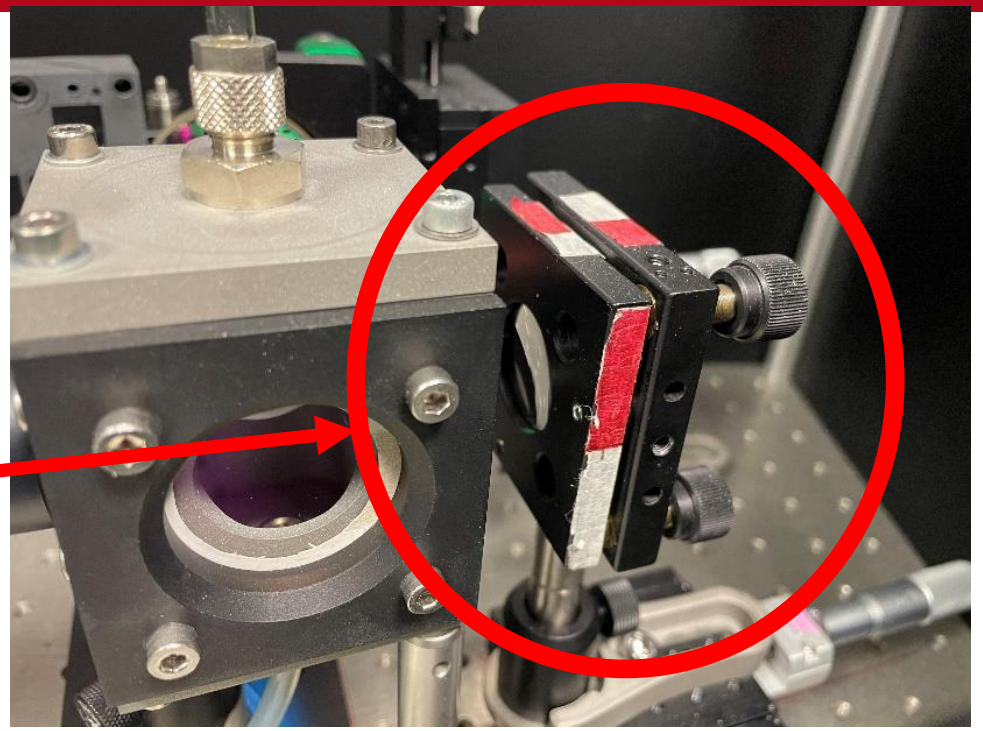


Spherical mirrors for the beam reflection:

- Focal distance 100 mm

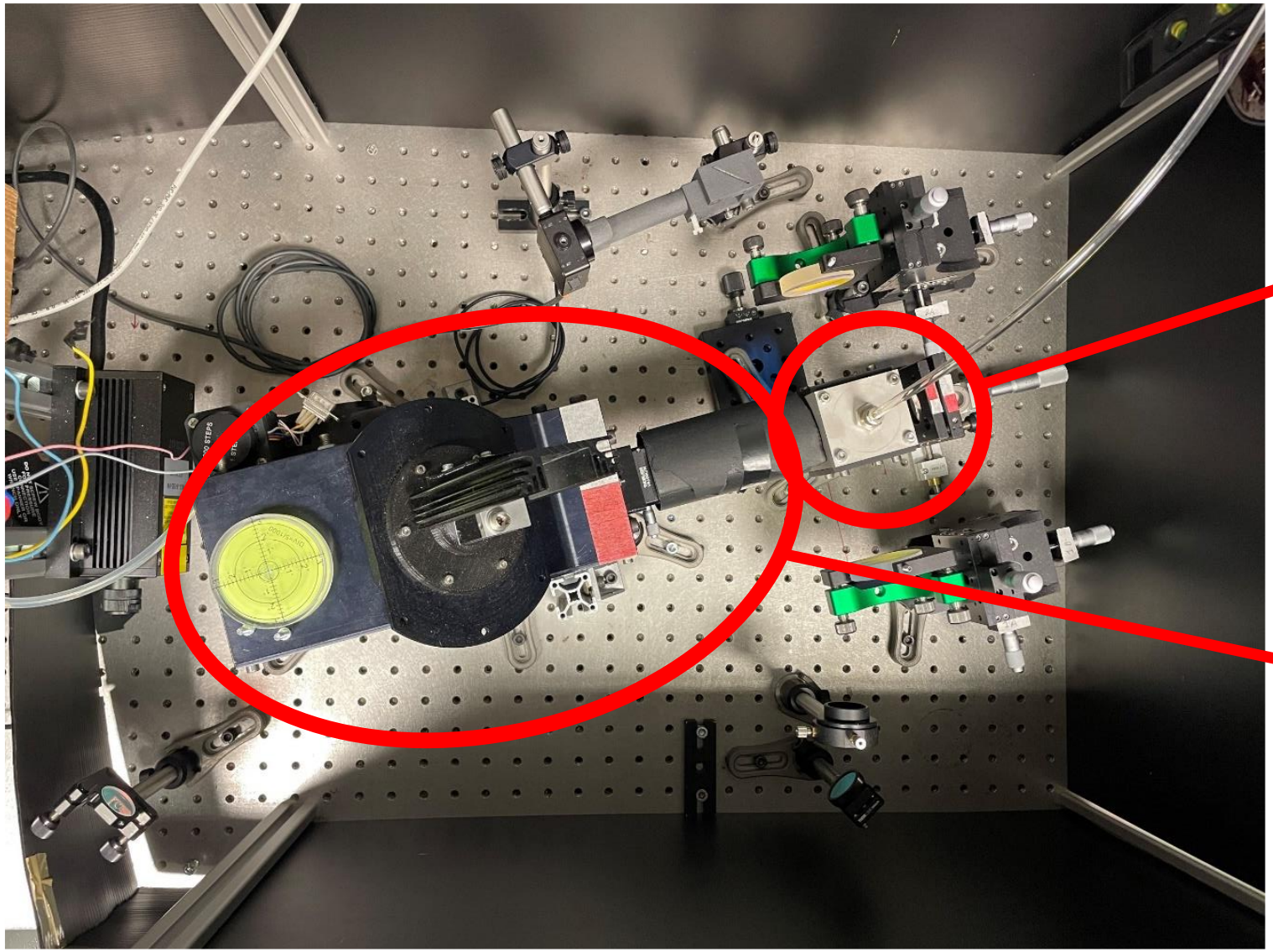
Multi-pass Setup:





Spherical mirror to reflect Raman scattering in the spectrometer

Multi-pass Setup:



Gas analysis cell:

- Equipped with windows for the passage of the laser beam and Raman scattering

Dispersion grating spectrometer

- 90 deg configuration
- Equipped with a collimation and filtering system of incoming radiation
- Coupled with a CMOS detector
- Dispersion 10 nm/mm

Spectral range:

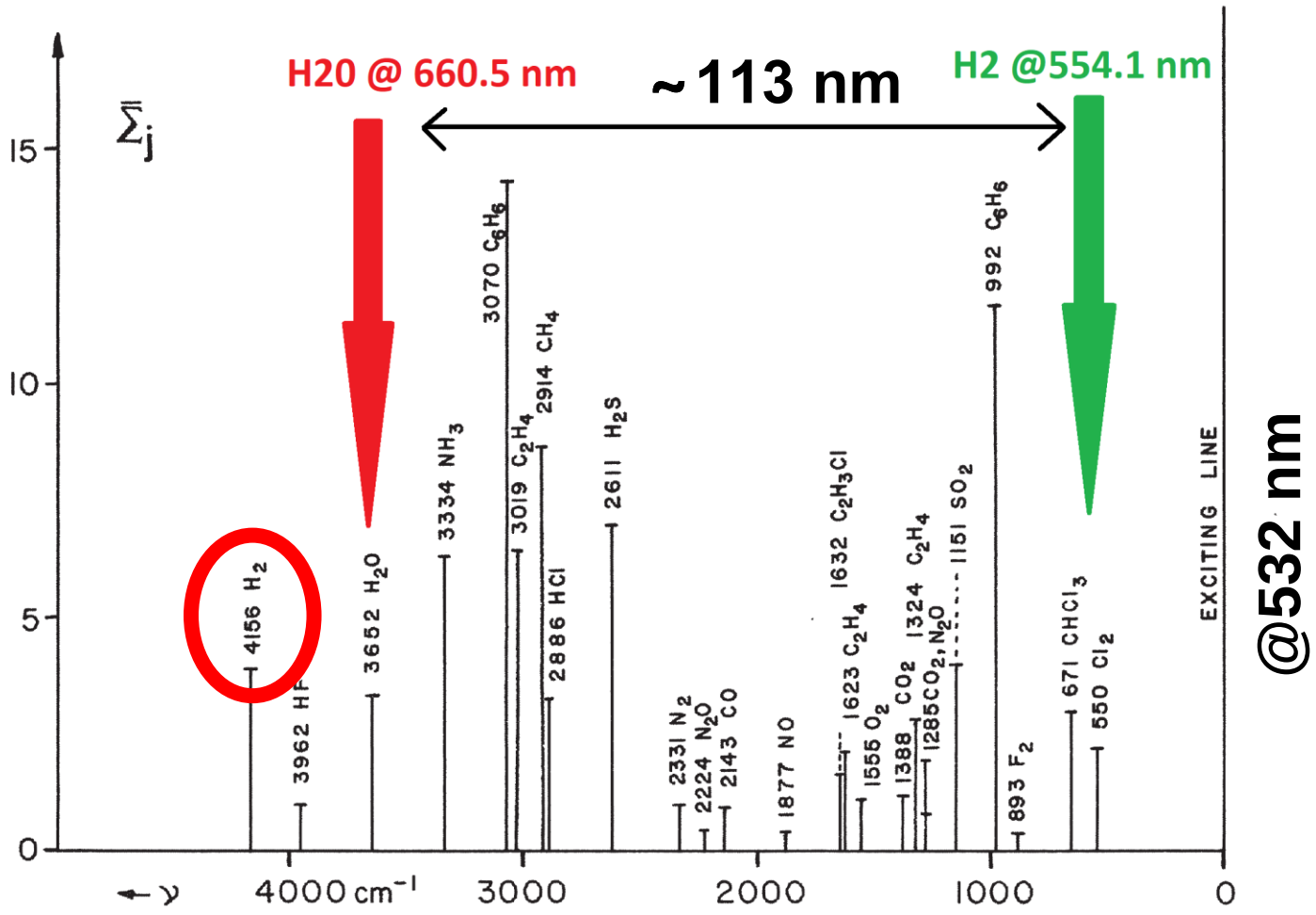
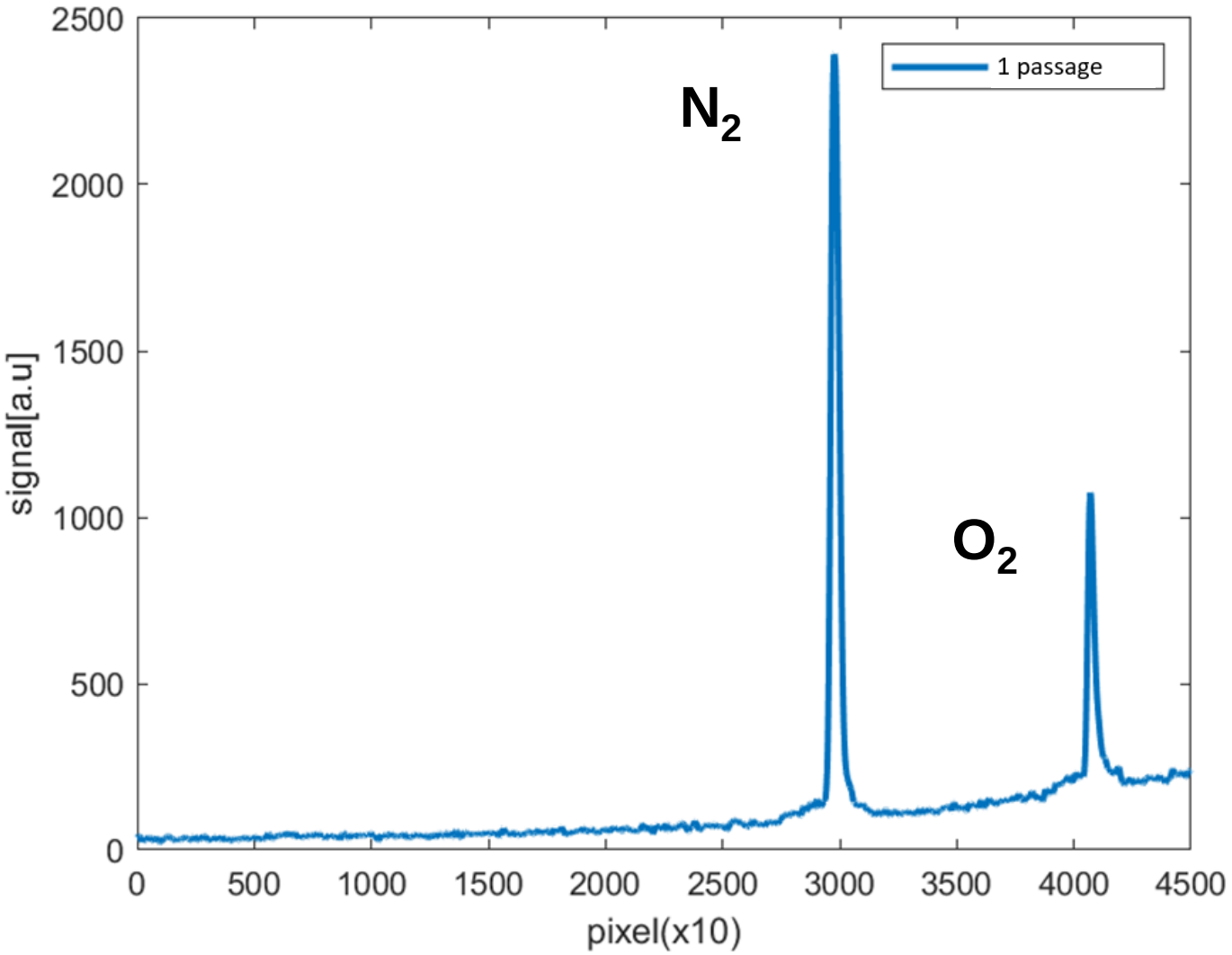


Fig. 4.11. Averaged relative normalized differential Raman scattering cross sections for important gases as function of Raman wavenumber shift. Dotted lines indicate resonance increase in the near UV

Gas	Raman shift cm-1	Cross section relative to N2 (532 nm)
Methane	1535	0,1
	2917	8,6
Ethane	993	1,2
	2914	15
Propane	870	1,6
	2908	19,6
n-Butane	827	1,9
	2890	15,6
iso-Butane	794	2,8
	2880	8,4
N2	2331	1
O2	1555	1
CO	2143	0,9
CO2	1285	0,8
	1388	1,1
H2	587	1,6
	4156	3,9
H2O	3657	2,5

Raman Spectroscopy of Gases and Liquids
Edited by A. Weber

Results: signal intensity



Ambient air spectrum

- Atmospheric pressure
- Integration time: 2.5 s
- Gain Camera: 0 dB

No presence of the analisys cell:

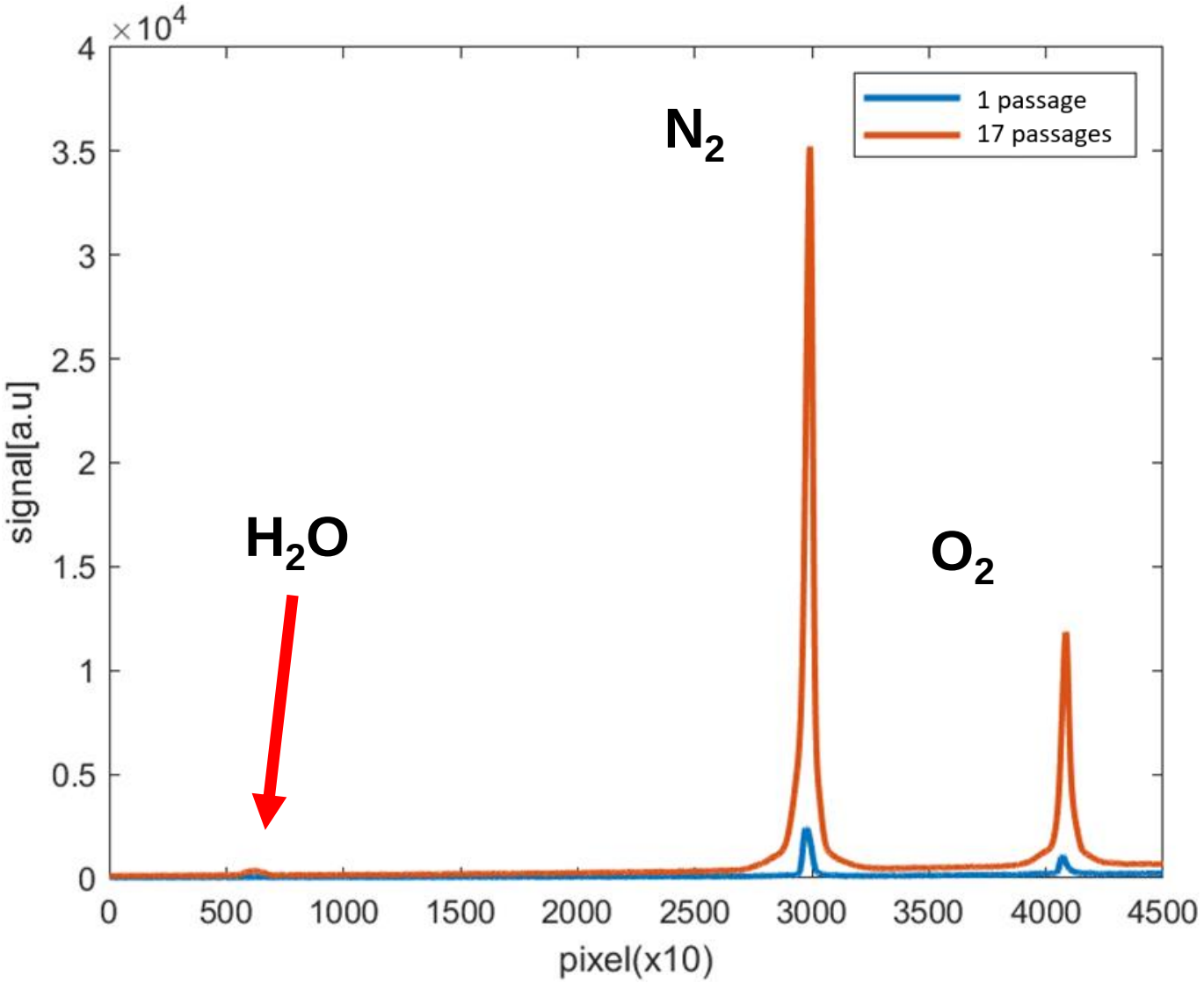
- There are no attenuations of the beam power given by the presence of the windows

Comparison in conditions:

- Single passage

1

Results: signal intensity



Ambient air spectrum

- Atmospheric pressure
- Integration time: 2.5 s
- Gain Camera: 0 dB

No presence of the analisys cell:

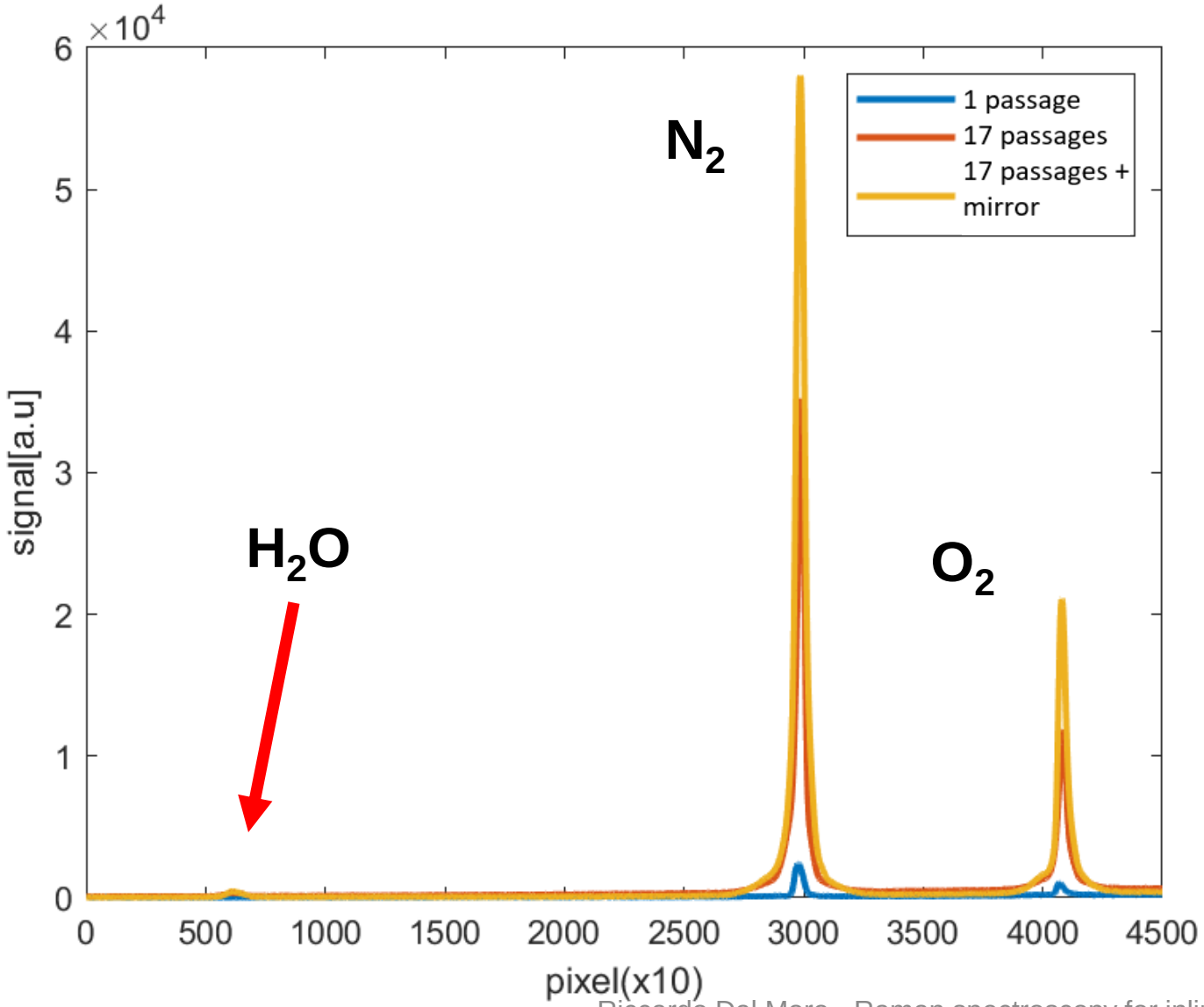
- There are no attenuations of the beam power given by the presence of the windows

Comparison in conditions:

- Single passage
- 17 passages

1
16.10

Results: signal intensity



Ambient air spectrum

- Atmospheric pressure
- Integration time: 2.5 s
- Gain Camera: 0 dB

No presence of the analisys cell:

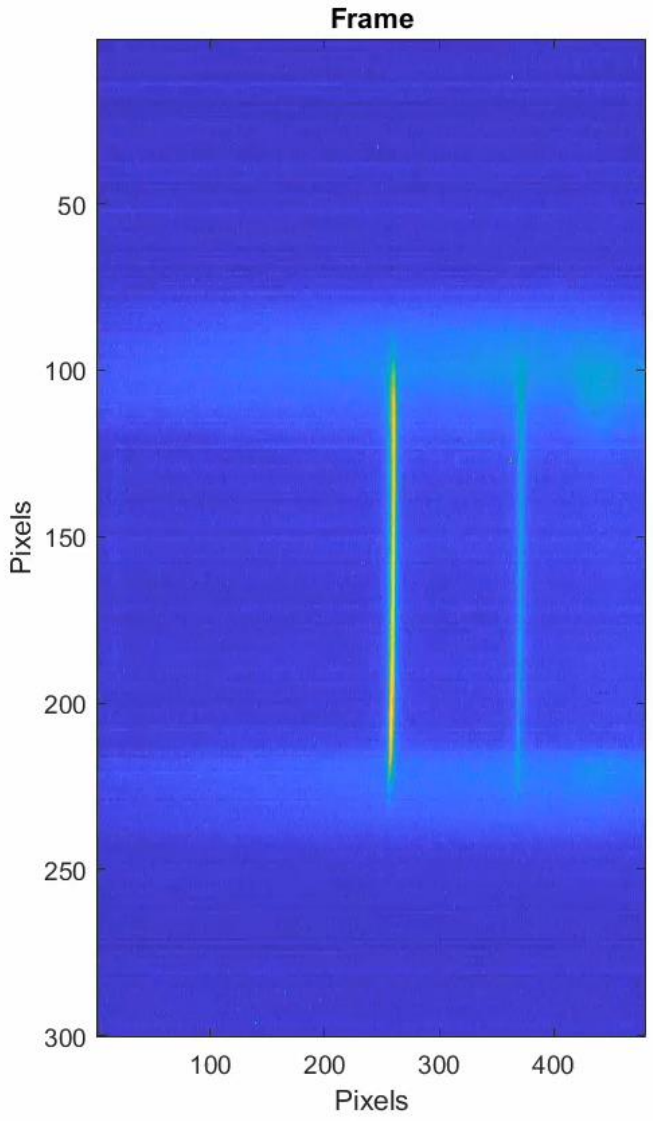
- There are no attenuations of the beam power given by the presence of the windows

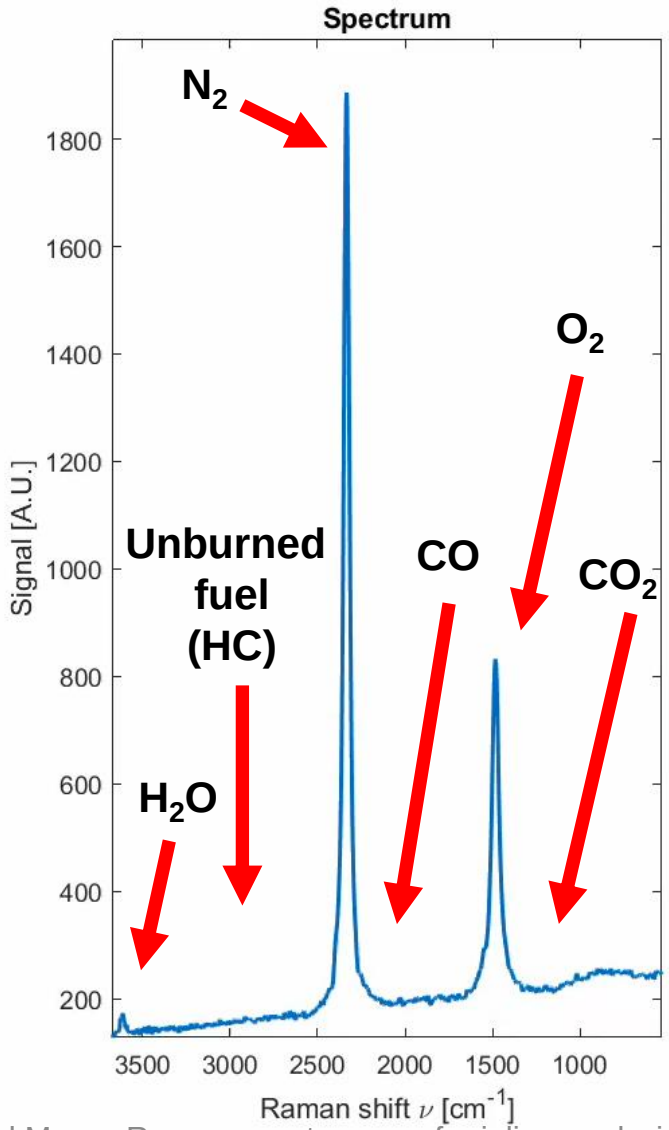
Comparison in conditions:

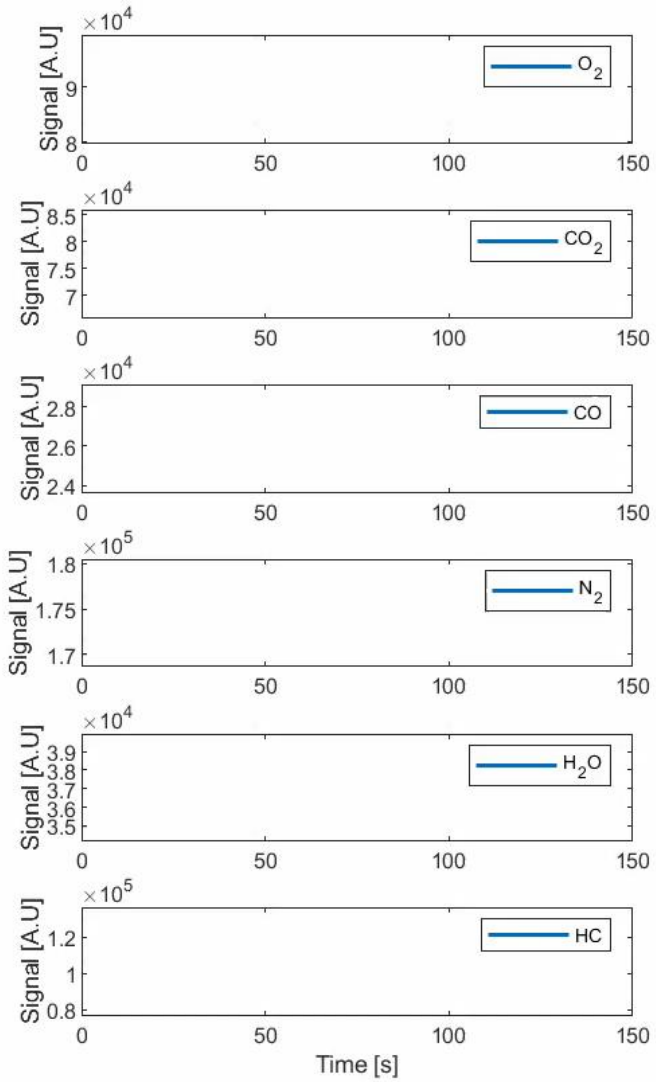
- Single passage
- 17 passages
- 17 passages + mirror

1
16.10
29.86

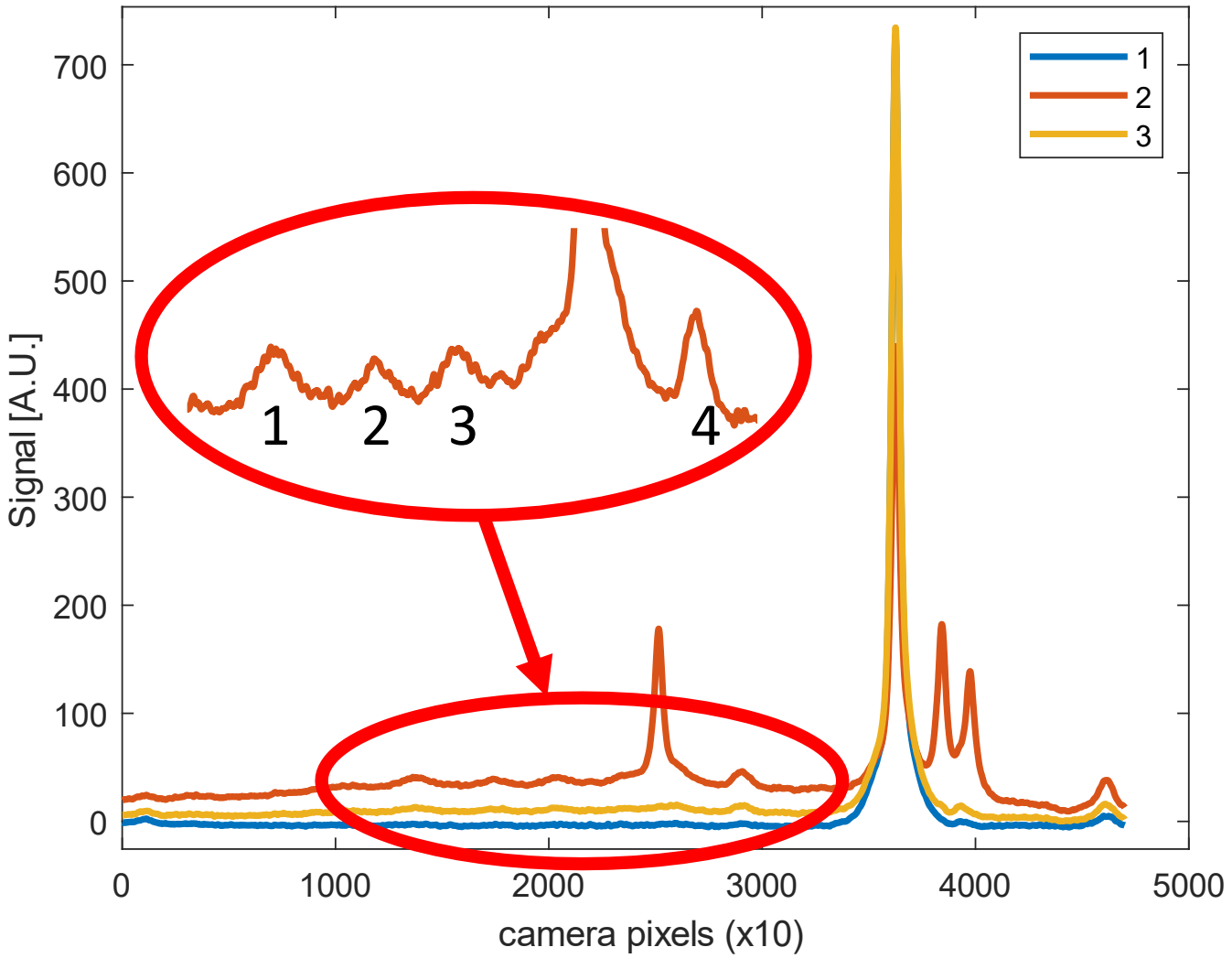
Results: qualitative analysis @150 ms, ≈ 0.7 bar







Results: qualitative analisys: NO_x detection



Acquisition parameters:

- Integration time: 0.5 s
- Gain camera: 0 dB
- Test on a Dumas method analyzer

Dumas method is a method of elemental analysis for the quantitative determination of nitrogen in chemical substances.

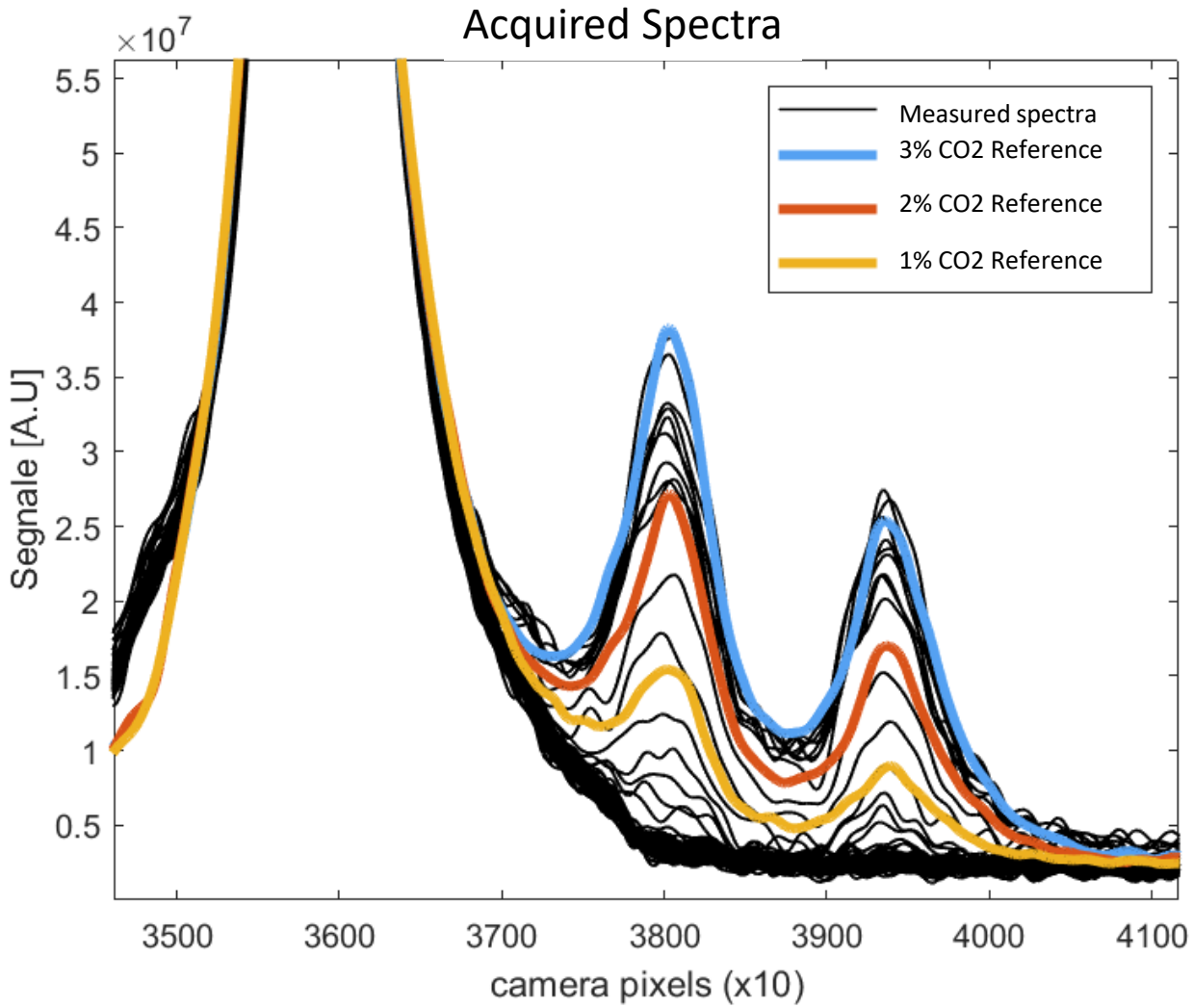
Results: qualitative analisys DeepU project

DeepU project tests, collaboration between:

- Department of Geosciences, UniPD
- Fraunhofer IAPT, Hamburg, Germany

The Deep U-tube heat exchanger combines laser and cryogenics gas for the development of a breaktrought drilling technology for geothermal plants.

Results: qualitative analisys DeepU project

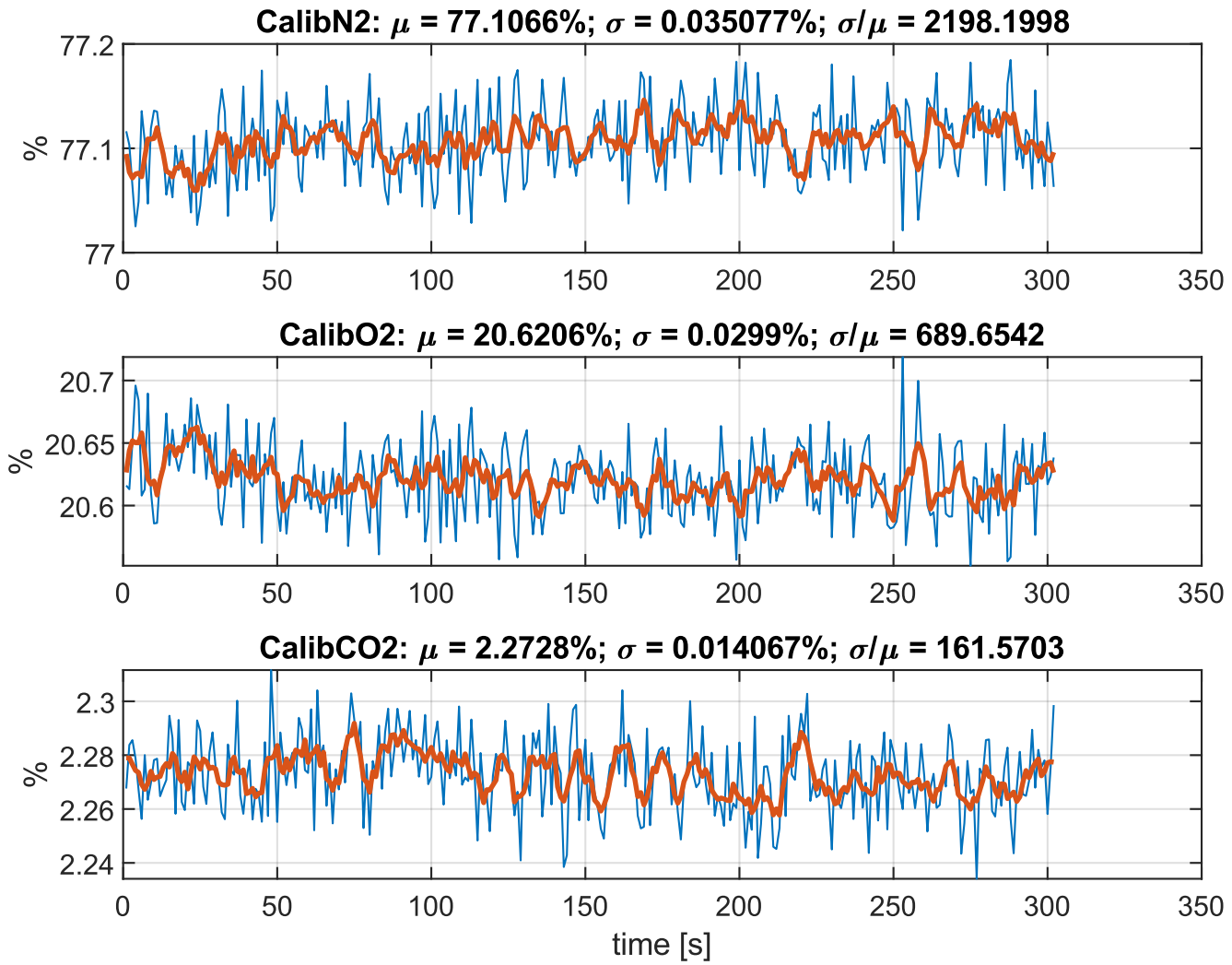


DeepU project tests, collaboration between:

- Department of Geosciences, UniPD
- Fraunhofer IAPT, Hamburg, Germany

Different kind of lithologies were tested: Only in the case of limestone drilling was measured the presence of gasses different from the atmospheric composition.

Results: quantitative analisys (work in progress!)



Acquisition parameters:

- Integration time: 1 s
- Pressure: 1.18 Bar
- 300 spectra
- Gain camera: 0 dB

Example:

Air with 2% of CO_2:

- N_2 77.107% (σ = 0.035%)
- O_2 20.621% (σ = 0.029%)
- CO_2 2.272% (σ = 0.014%)

On a mixture with 2% of H_2:

- H_2 1.753% (σ = 0.017%)

Conclusion

- The multipass prototype is fully trasportable and reached the TRL6
- Qualitative analysis performed up to 6.7 Hz (150 ms)
- Quantitative measures on a bunch of different calibrated gasses

This study has demonstrated that Raman spectroscopy can be a useful tool for combustion diagnostics, as it can be made fast enough to follow the time scale of combustion transients. The system can perform analyses with an acquisition time of 0.15 seconds (at operating pressure of 0.7 Bar), which is a significant achievement in Raman spectroscopy on gaseous samples.

There is room for improvement:

Test with spectrometers with different dispersion

Optimization of the fitting algorithm for the quantitative analysis

Increase the reliability of the alignment and the miniaturization of the system

Thanks for the attention!

Nice video of the instrument!

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