Development of PAS- and WMS-based sensors , traceable to Optical Gas Standards

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Outline

PAS-based sensors

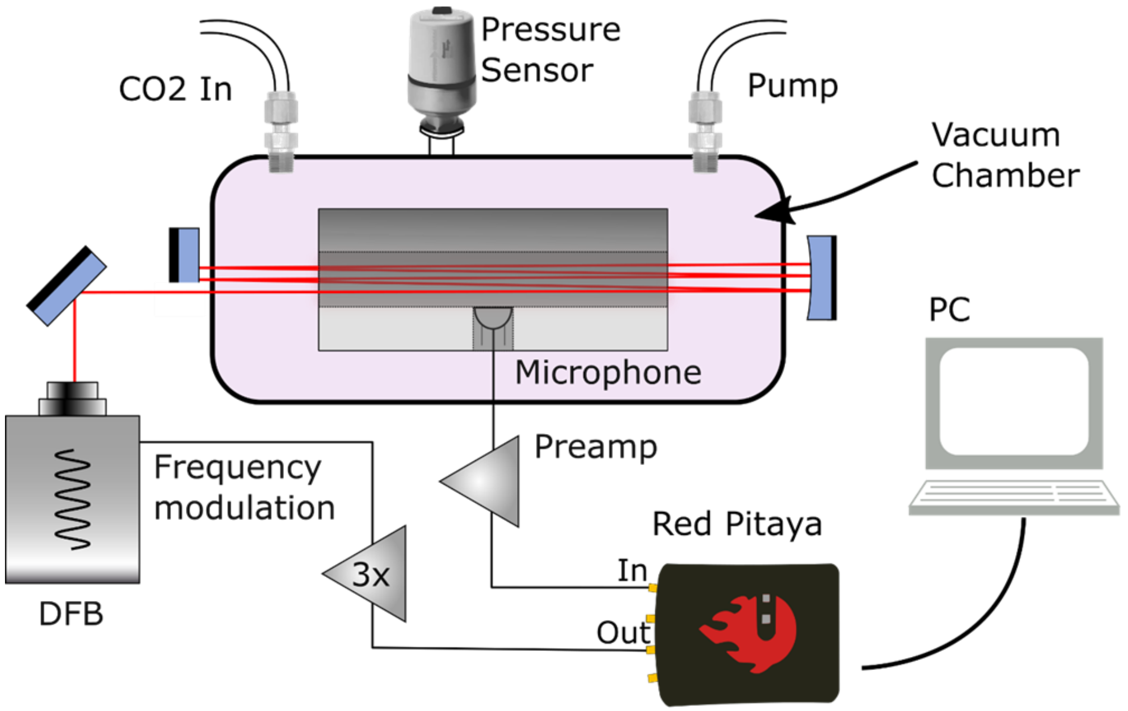
WMS-based sensor

Optical Gas Standards

Summary

Traceable emission measurements

A1.2.3 M30	DFM and INSTRUMATIC Marine will develop a new online method for emission monitoring based on a compact PAS. The sensor will be designed to address the molecular species CH_3OH, NH_3 and CO as in A1.1.3 and be calibrated using the optical methods developed in A1.1.3. The PAS sensor will be combined with a dilution probe sampling system to provide on-line dynamic emission measurements.	**DFM,** INSTRUMATIC

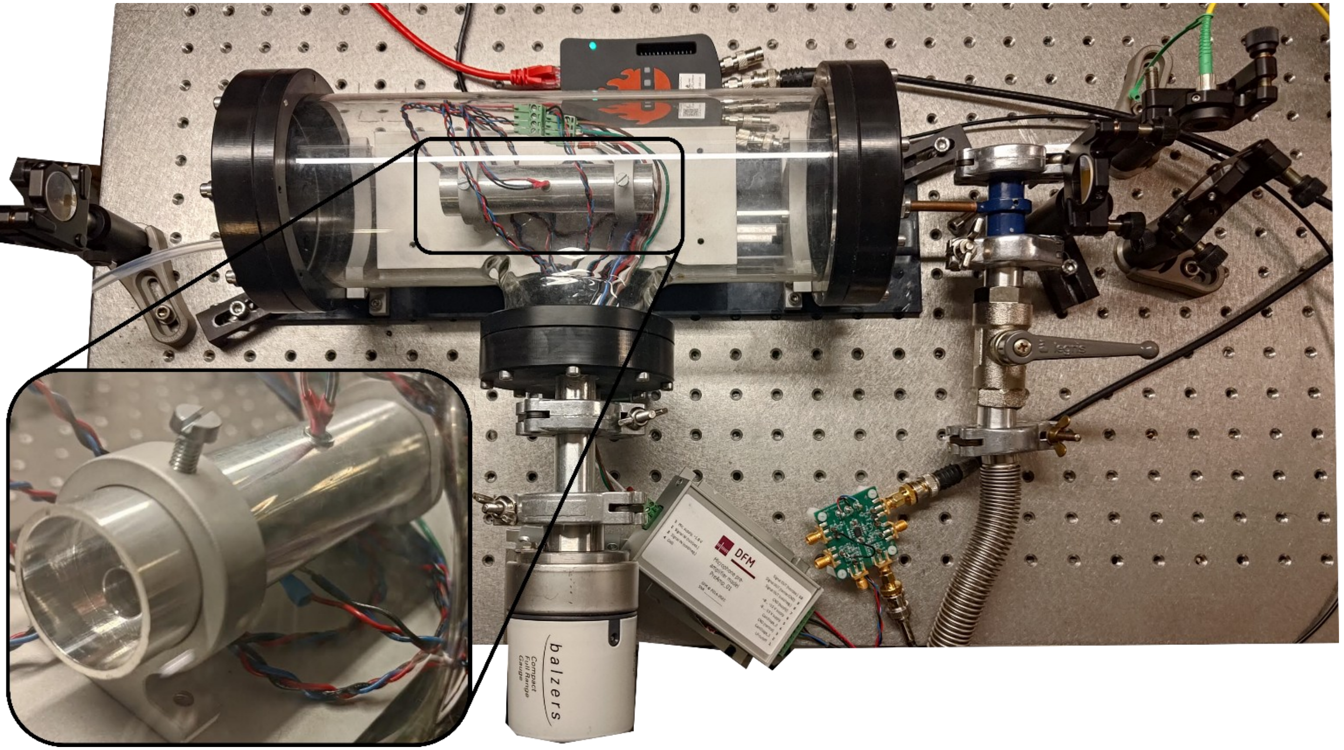


Schematic view of ver. 1 of the experimental PAS setup

Photoacoustic cell

Low-cost Red Pitaya for data acquisition

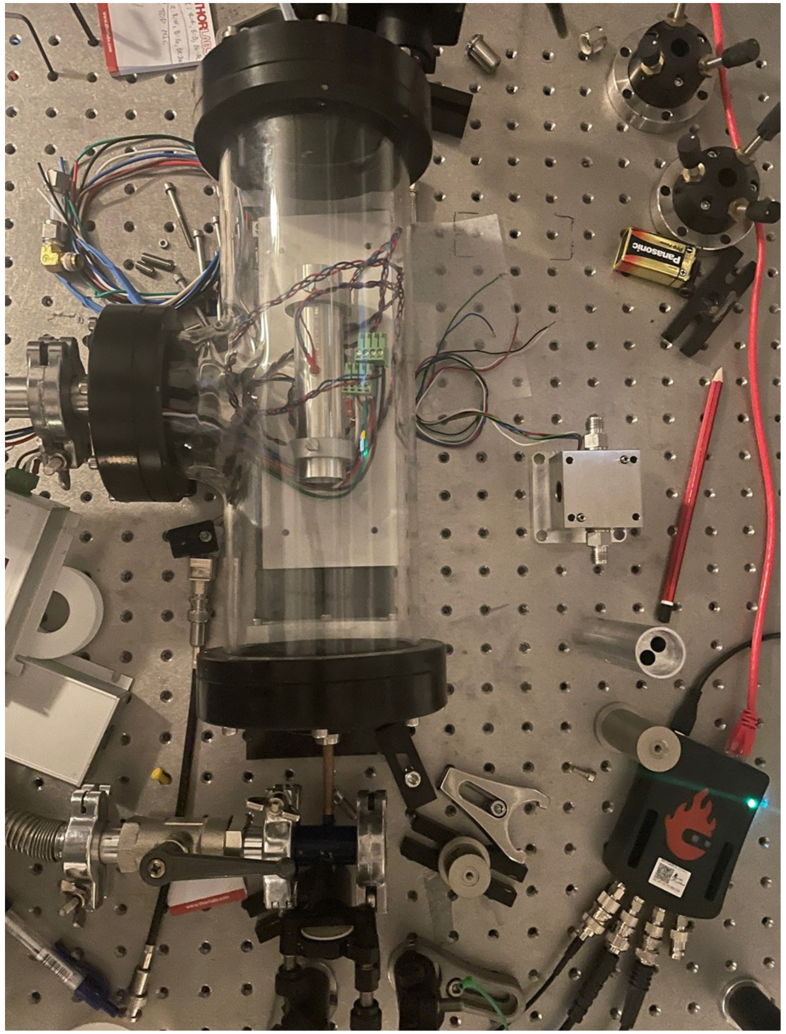
Laser beam from optical fibre

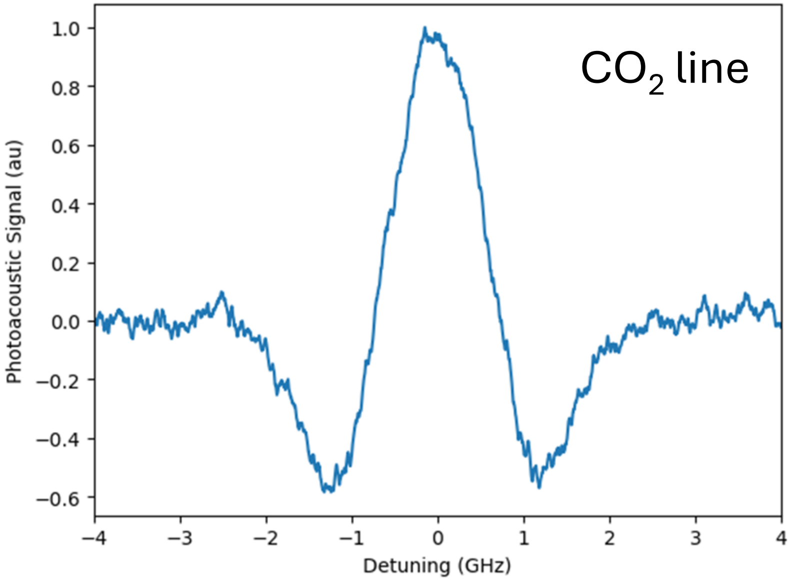


Acoustic resonator

Wide and fine tunable laser used for excitation and molecular transition identification (1550 – 1630 nm)

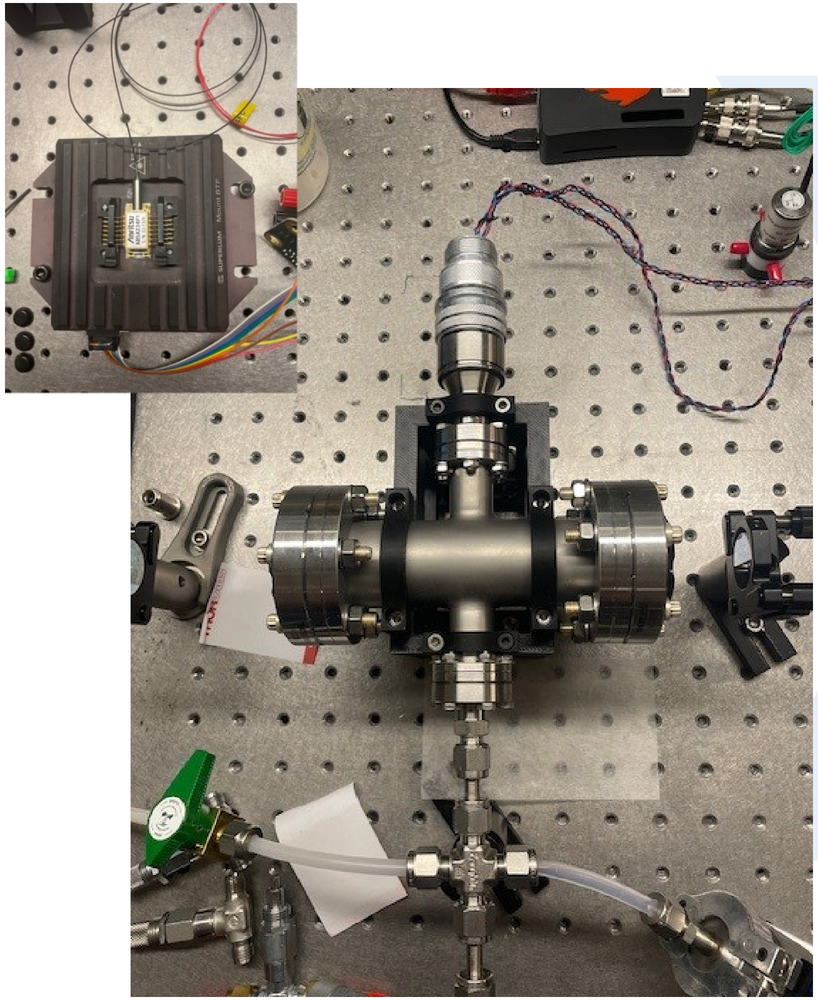
Multipath photoacoustic spectroscopy

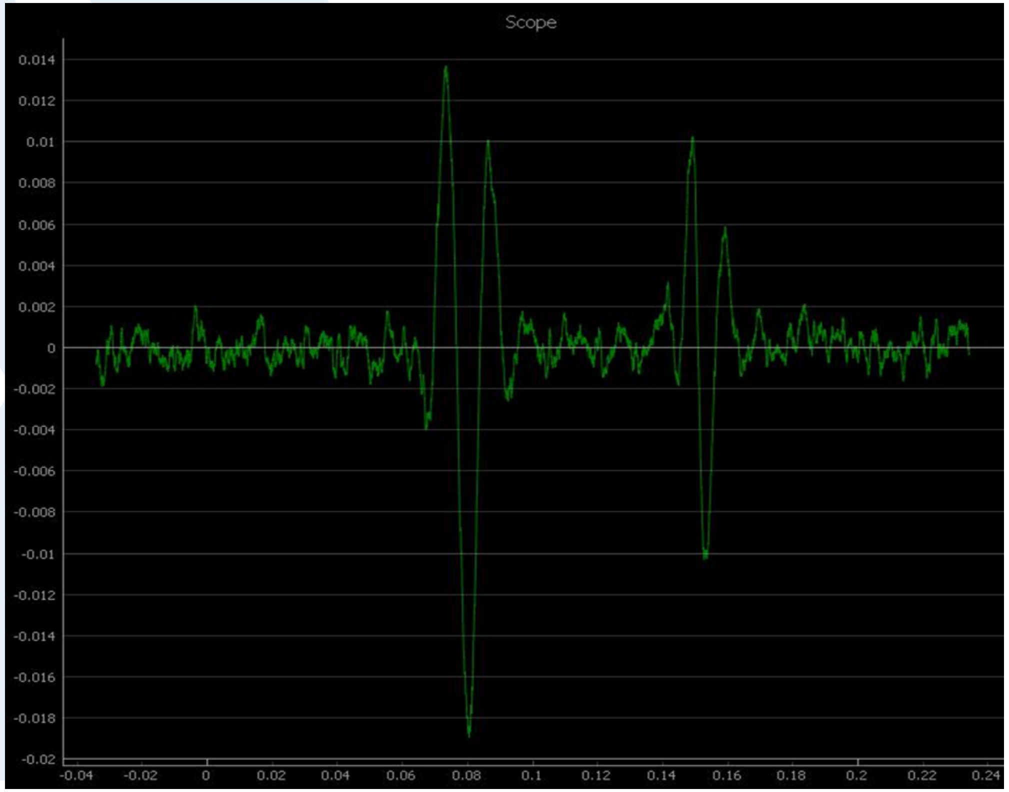




- Few mbar
- 15mW Optical Power
- Optical Pathlength 30 cm
- Laser Frequency modulated at 775 Hz
- Signal demodulated at 1550 Hz.
- Acquisition time ~ 3s
- Power SNR ~ 13

Compact photoacoustic cell





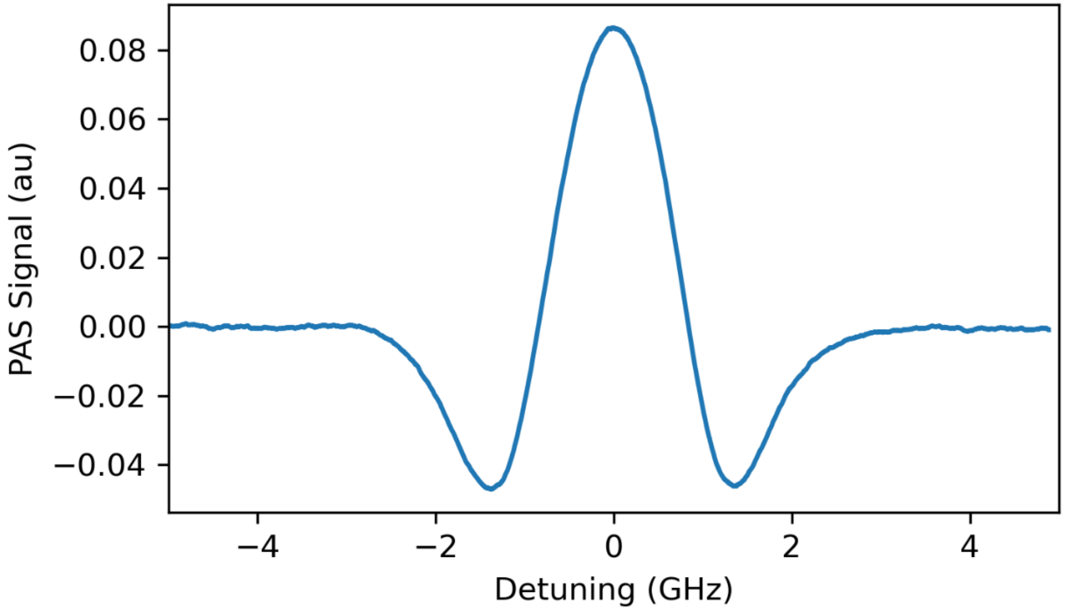
~ 25 ppm CO_2 in N_2

1573.925 nm and 1574.070 nm

$$S_{PA} = S_m P F \alpha$$

P radiation power
α absorption coefficient
S microphone sensitivity
F cell-specific constant,

CO_2 PAS spectrum at 1572.33 nm

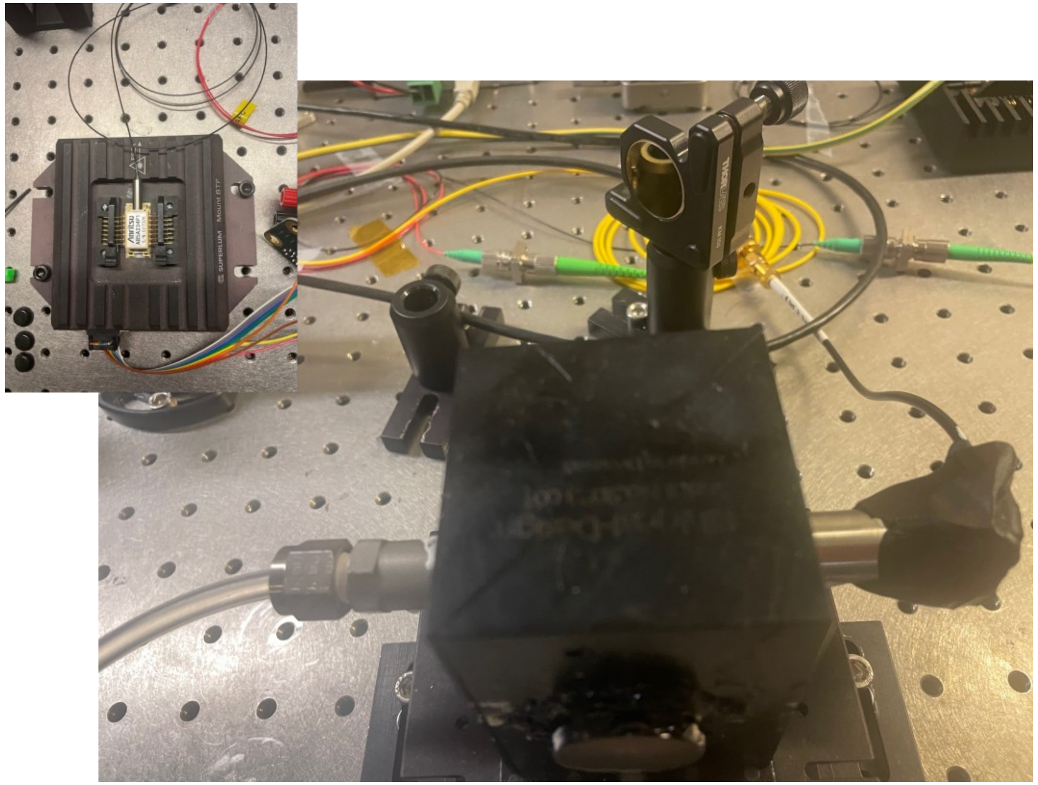


Laser wavelength scanned across the molecular transition at a frequency f_{scan} = 10 Hz.

The optical frequency is modulated at 685 Hz and demodulated at 1370 Hz

PAS based on Integrating Sphere

Ver. 2 of the experimental PAS setup



An integrating sphere-based system can be made very compact, provide multiple beam passes and better sustain a rugged environment

PAS sensitivity

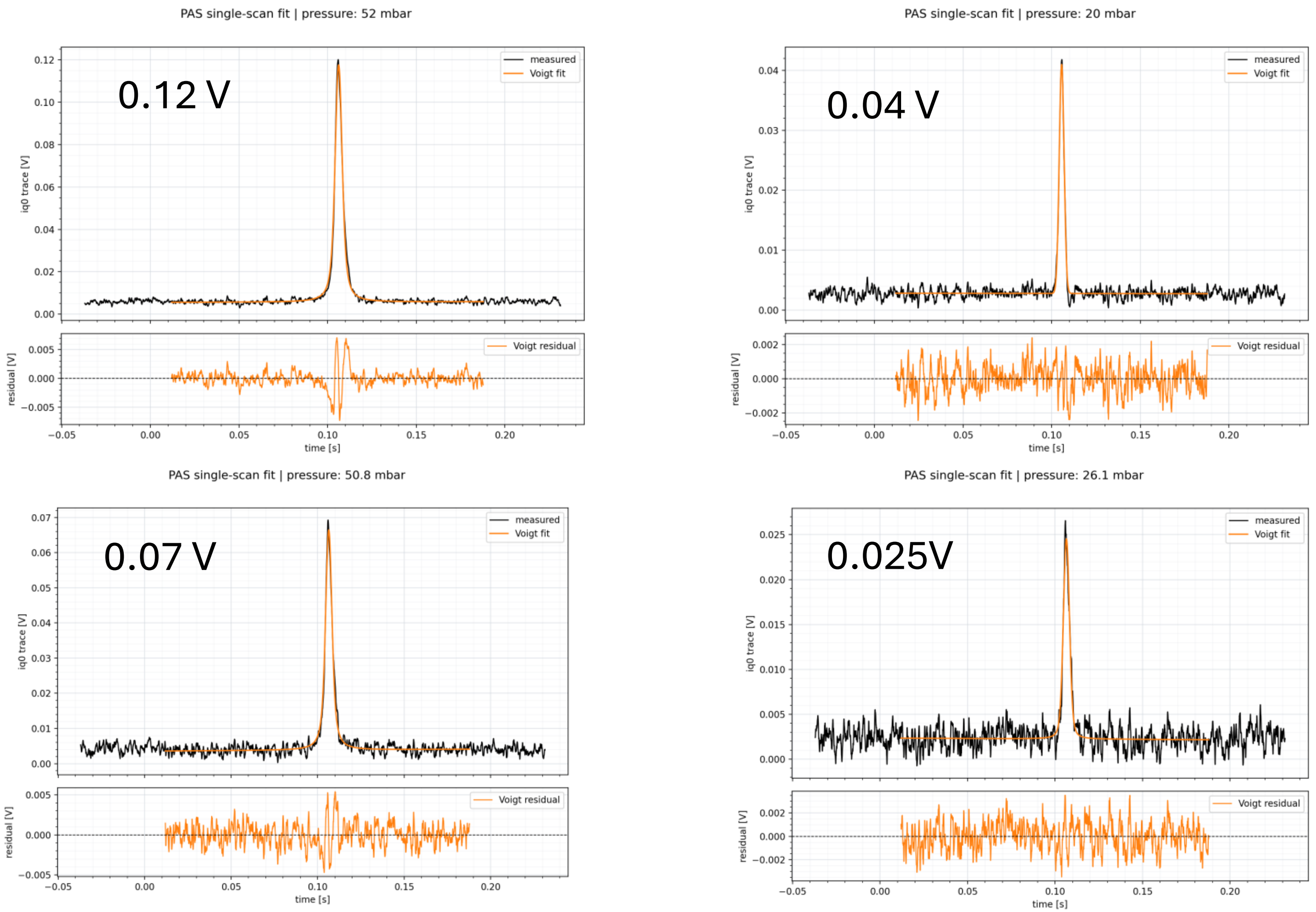
PAS sensitivity is strongly dependent on operating pressure. The pressure affects:

- the microphone's response
- the cell's acoustic resonance (Q-factor)
- the gas relaxation processes

Pressure dependance of PAS signals

Modulation frequency and phase optimization

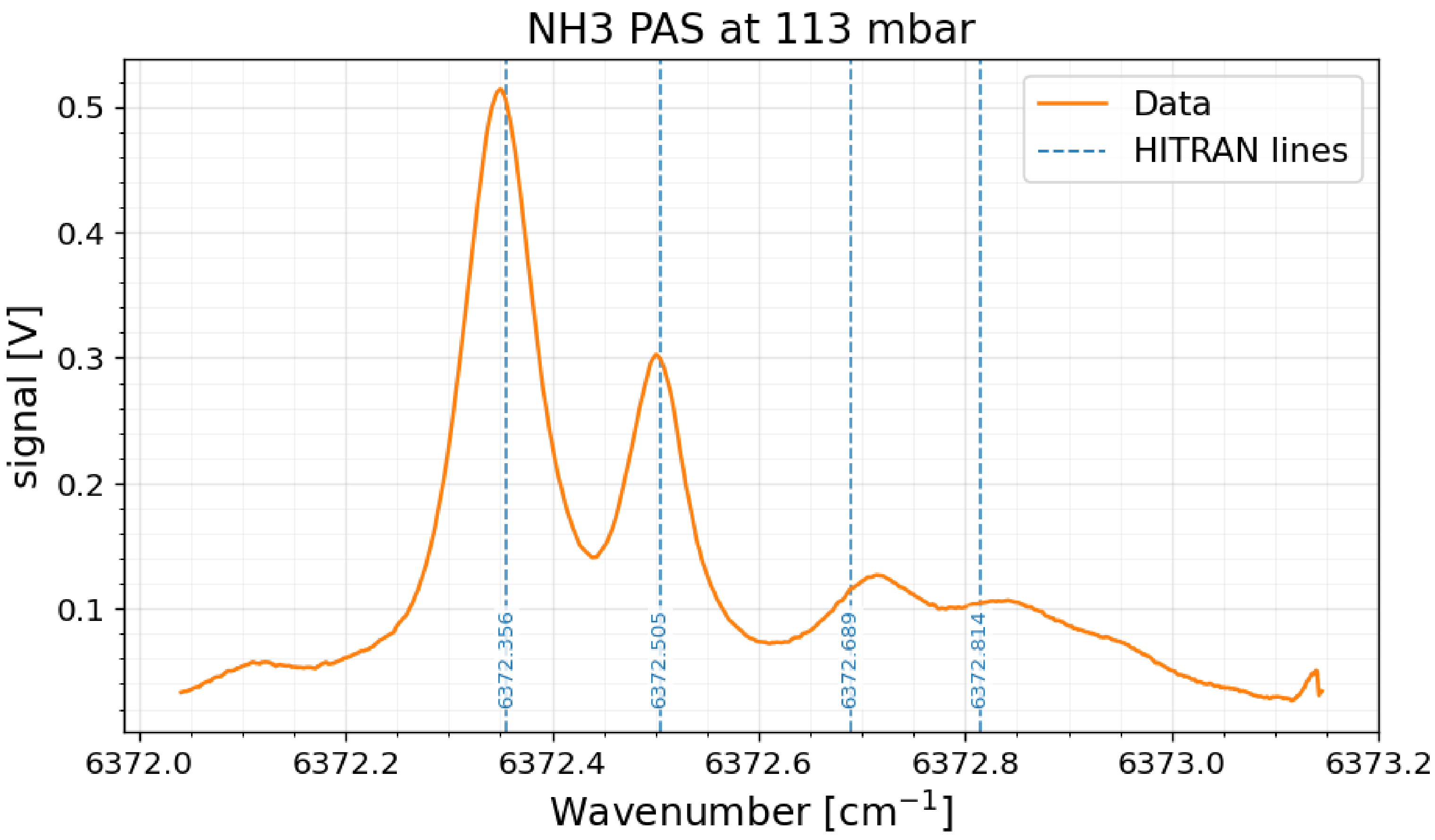
No optimization



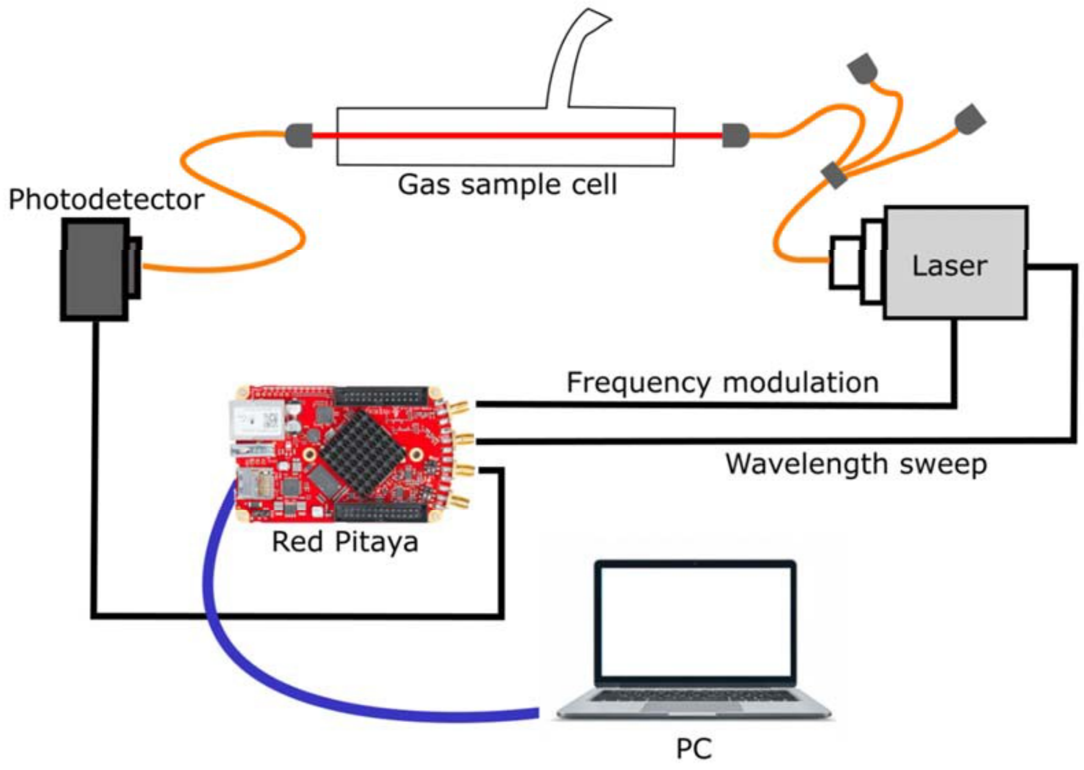
NH_3 PAS spectrum at 1569.278 nm

Pressure: 113 mbar
Target species: ammonia (NH3)
Target line center [cm^-1]: 6372.356
Pulse modulation frequency [Hz]: 8719
Demodulation phase [deg]: 186

Blue lines indicate wavenumbers from the HITRAN database



Basic optical fiber-based WMS design

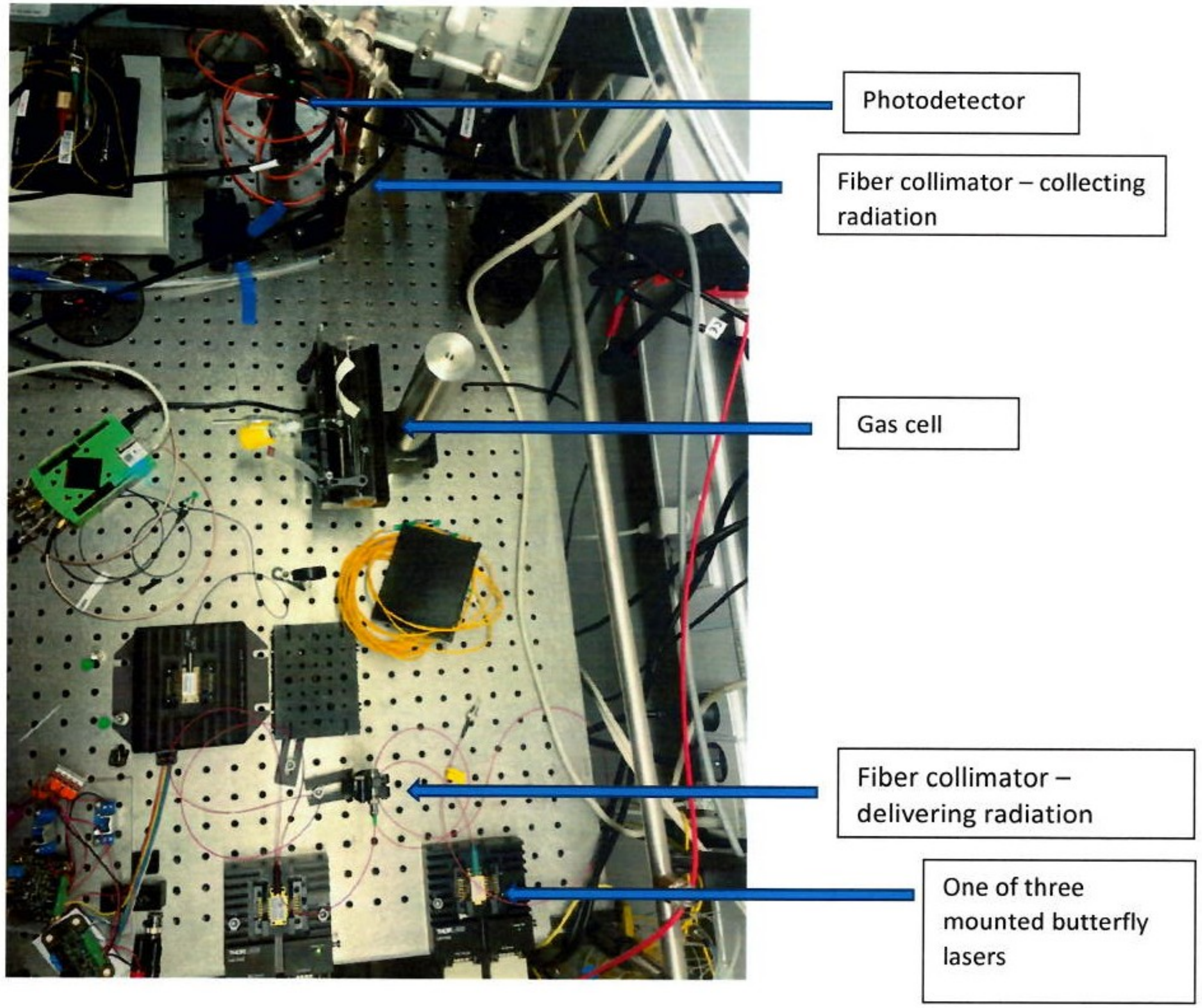


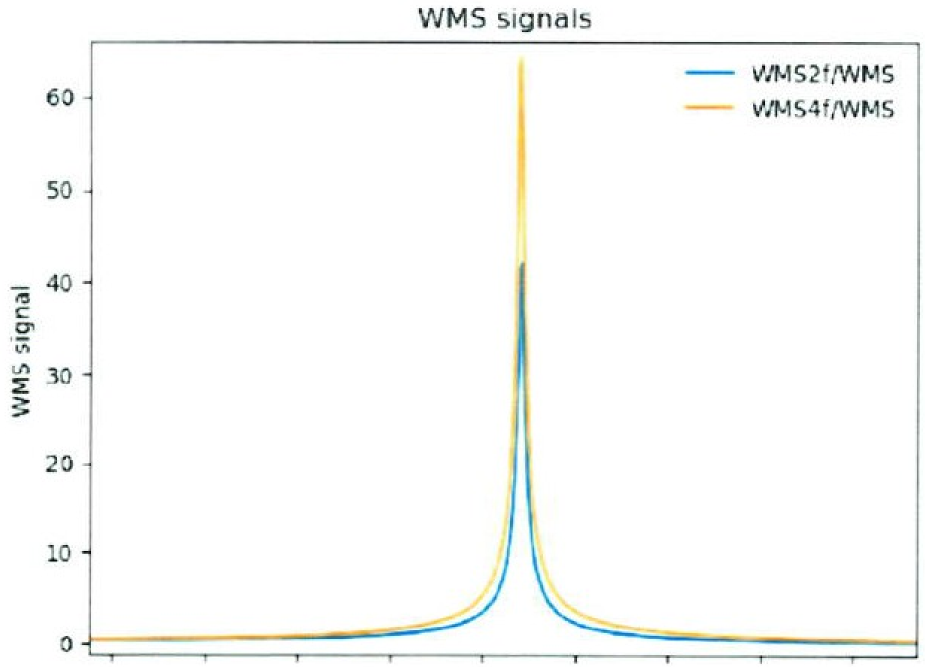
WMS is an alternative method to PAS

WMS is a direct absorption method allowing for a simpler calibration method

WMS is less sensitive to environmental perturbations and external noise

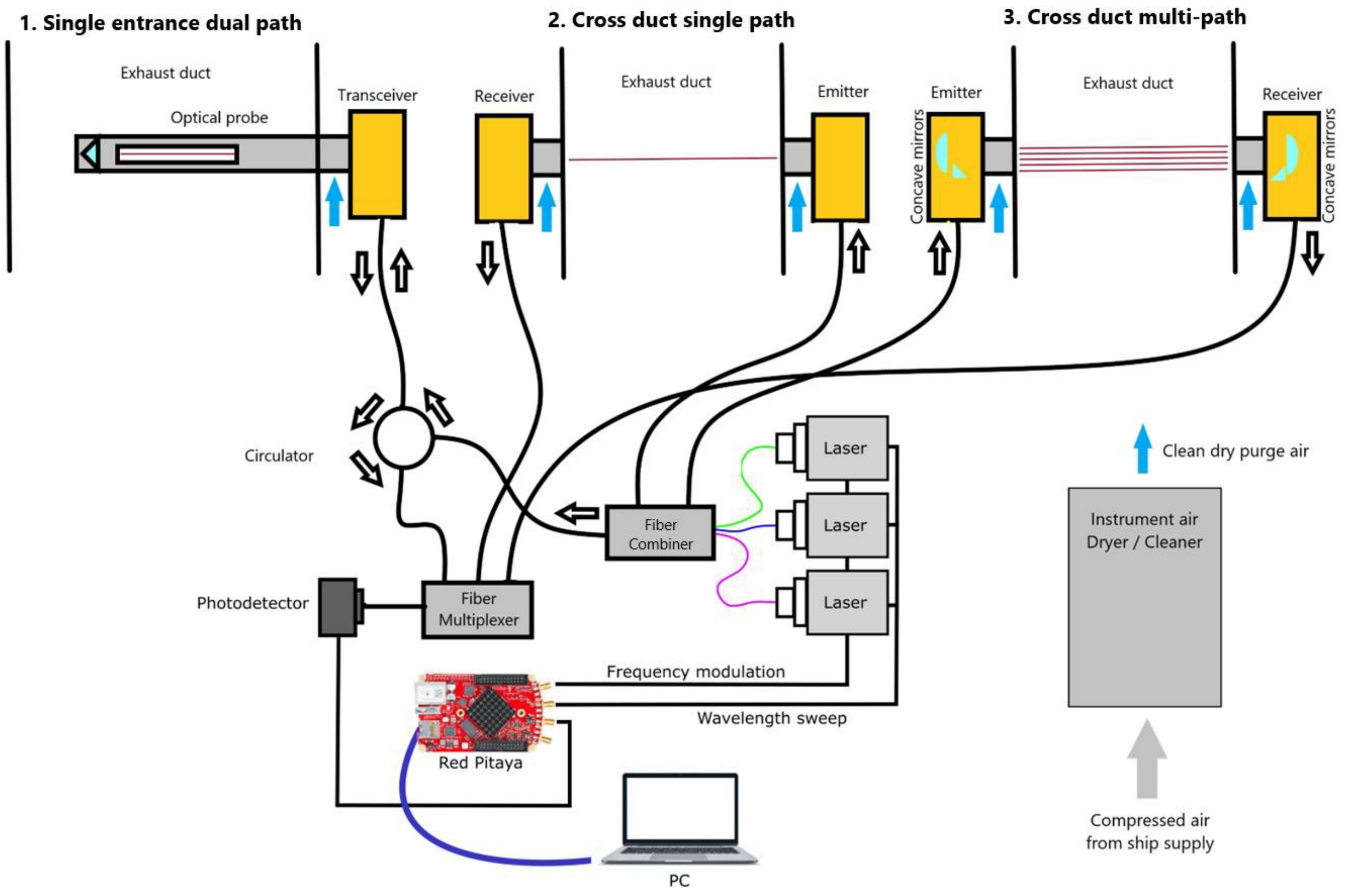
WMS laboratory setup





Single NH_3 line at 1537 nm

Proposed designs of the WMS onsite system



The most stable and accurate setup of the three will be chosen for onsite measurements.

Optical Gas Standards

DFM and PTB will develop traceable optical spectroscopy-based methods and facilities for absolute concentration measurements of gaseous species.

The methods will be validated by selected reference gas mixtures supplied by partners.

The methods will provide traceability of the sensors to be used for on-line measurements.

- DFM will develop a laser-based spectroscopic method for the determination of the absolute amount of **CH_3OH, NH_3 and CO**. The method will be based on tuneable diode lasers (NIR) and a Quantum Cascade Laser (QCL) (MIR). Associated measurement uncertainties will be evaluated.

Optical Gas Standards

Amount of fraction:

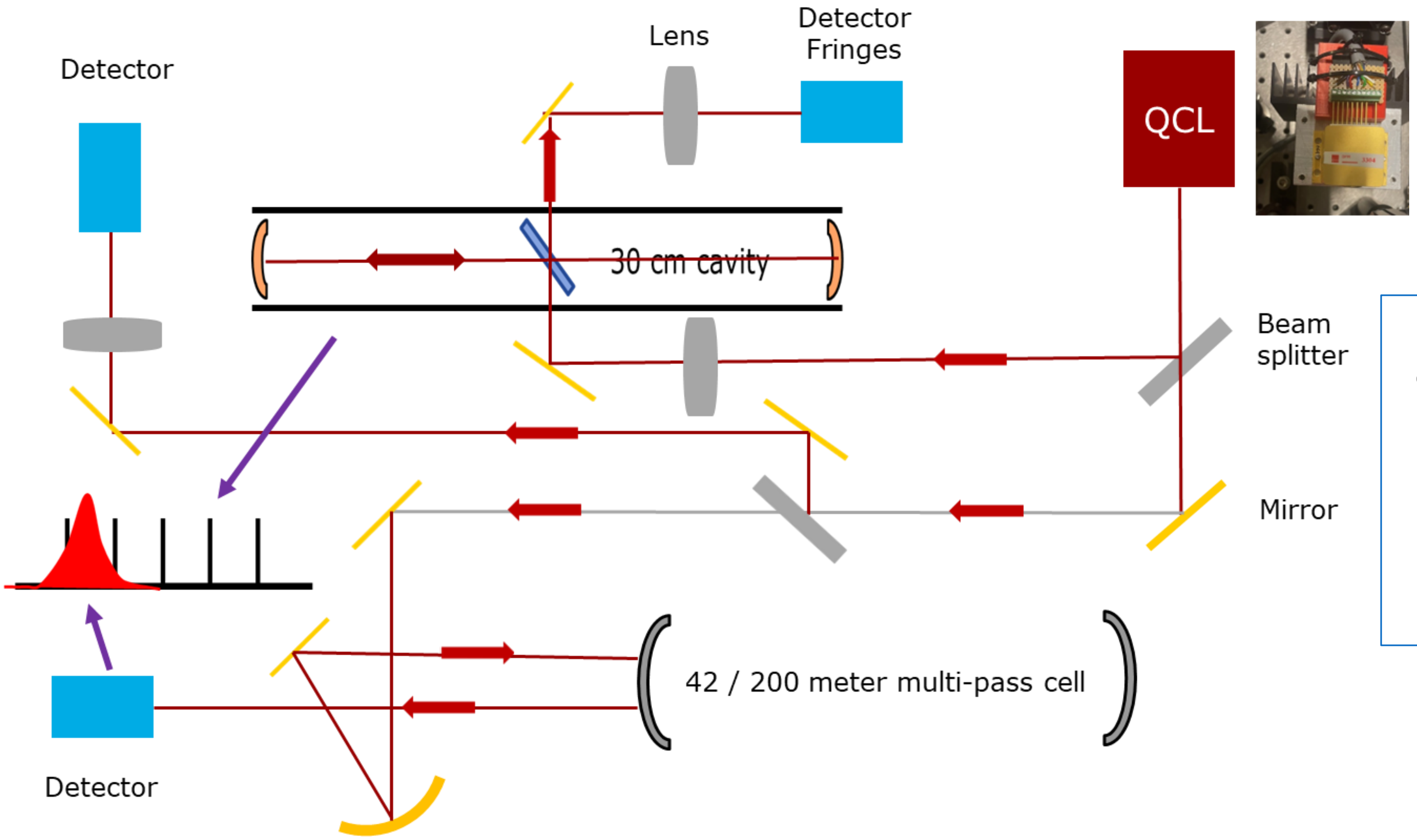
$$x_{\mathrm{molecule}} = \frac{k_B \cdot T}{S_T \cdot p \cdot L} \cdot A_{\mathrm{line}}$$

Where:
k_B Boltzmann's constant
T Gas temperature
S_T Molecular line strength for T
P Total gas pressure
L Optical pathlength
A_{line} Integrated absorption line area

The amount fraction result can be derived from the line area, the interaction length and the measured gas parameters T and p, simply by applying the equation to a given absorption transition with a known line strength S.

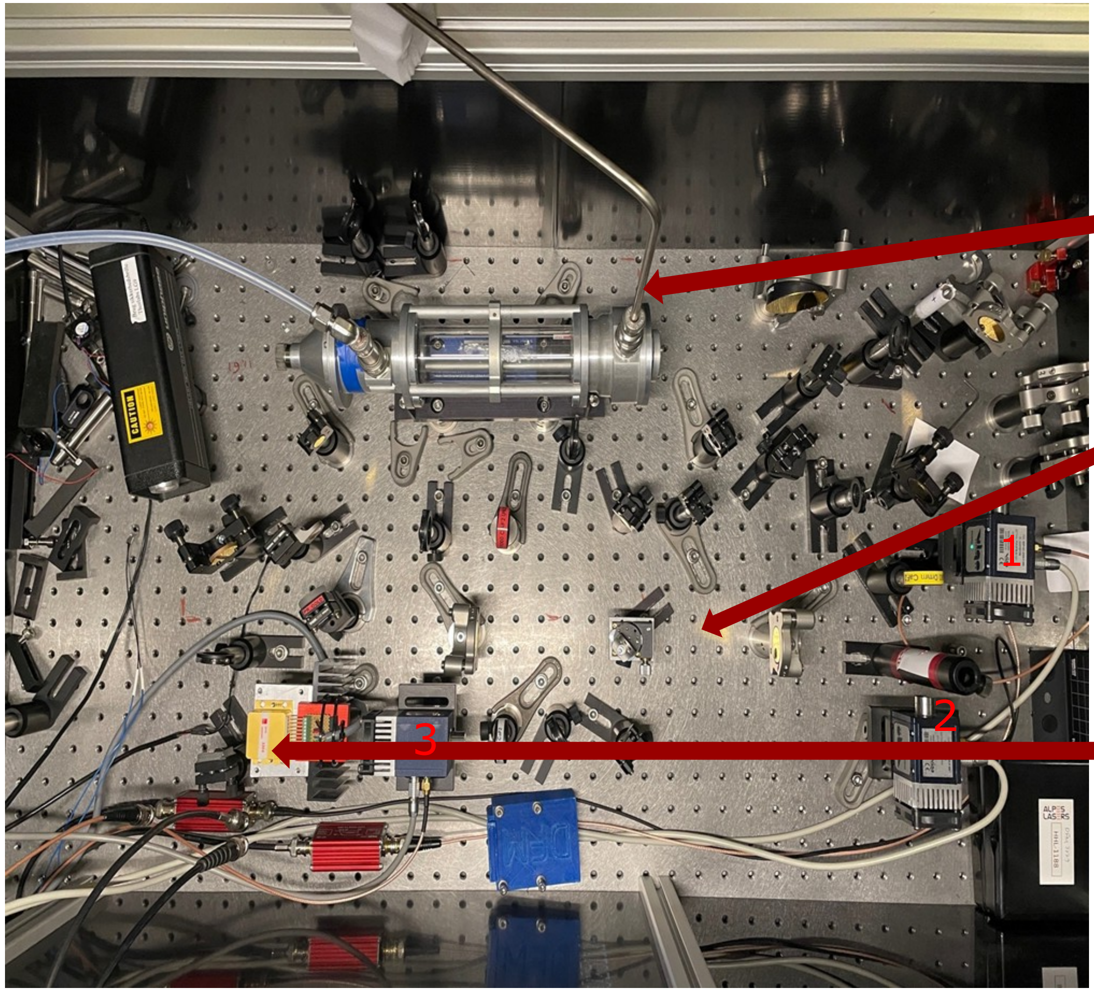
The uncertainty of the resulting amount fraction value depends on different influence quantities.

Schematics of the Optical Gas Standard



Amount of fraction calibration free method. Accurate knowledge of molecular line strength, temperature, pressure and absorption path length required.

Experimental OGS setup



Multipass gas cell
42 m

Frequency
reference cavity

Detectors 1, 2 and 3 monitor absorption, power and reference fringes, respectively.

QCL laser for monitoring ammonia.
Tunable diode laser for monitoring in the NIR region available

Conclusions

The PAS technique is highly sensitive; however, the optimization of the signal is time consuming in relation to continuous measurements.

The work will continue with focus on improving the sensitivity.

If the required sensitivity for NH_3 cannot be reached in the NIR region a MIR QCL laser will be used. (At 6.25 μm the absorption line intensity is 500 times stronger than at 1.57 μm).

The WMS system is less complicated to calibrate and therefore expected to be the most accurate

The proposed WMS sensor measures emissions directly (sniffer not required)

With respect to reliability and uncertainty of the OGS measurement results, a validation against gravimetrically prepared standards is recommended

Thank you for your attention!

Questions?