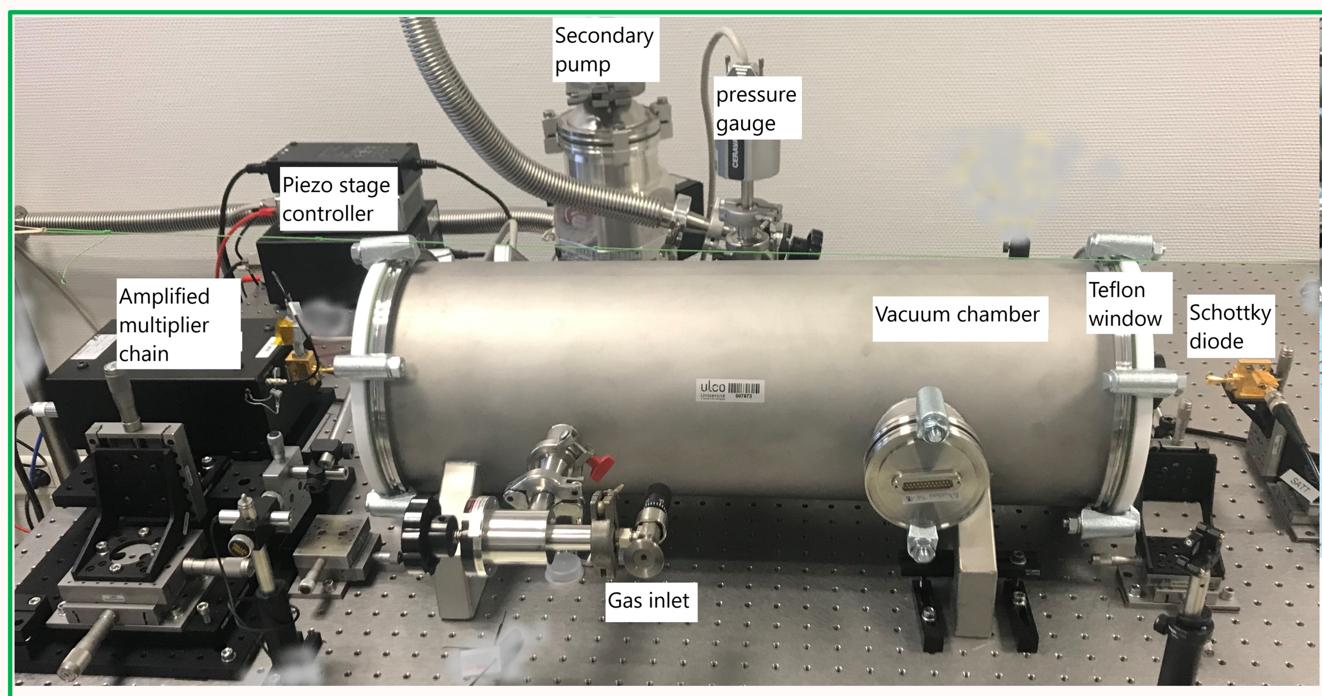
INTRA-CAVITY MILLIMETER SPECTROMETER FOR THE DETECTION OF SEMI-VOLATILE ORGANIC VAPORS

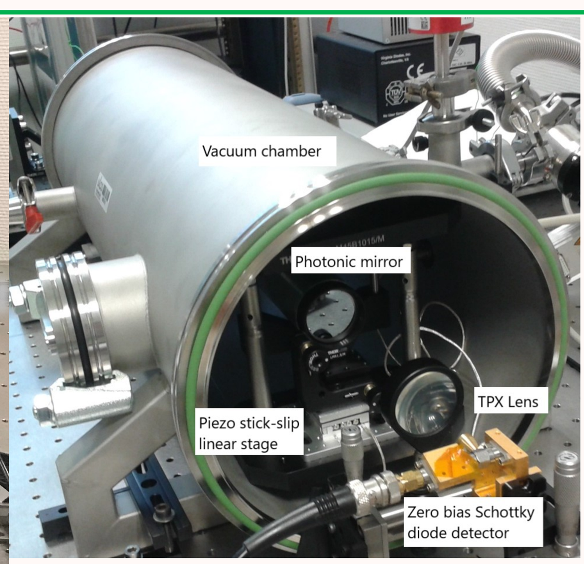
Fabien Simon, Mhamad Chrayteh, Coralie Elmaleh, Francis Hindle, Gaël Mouret, Arnaud Cuisset

Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France

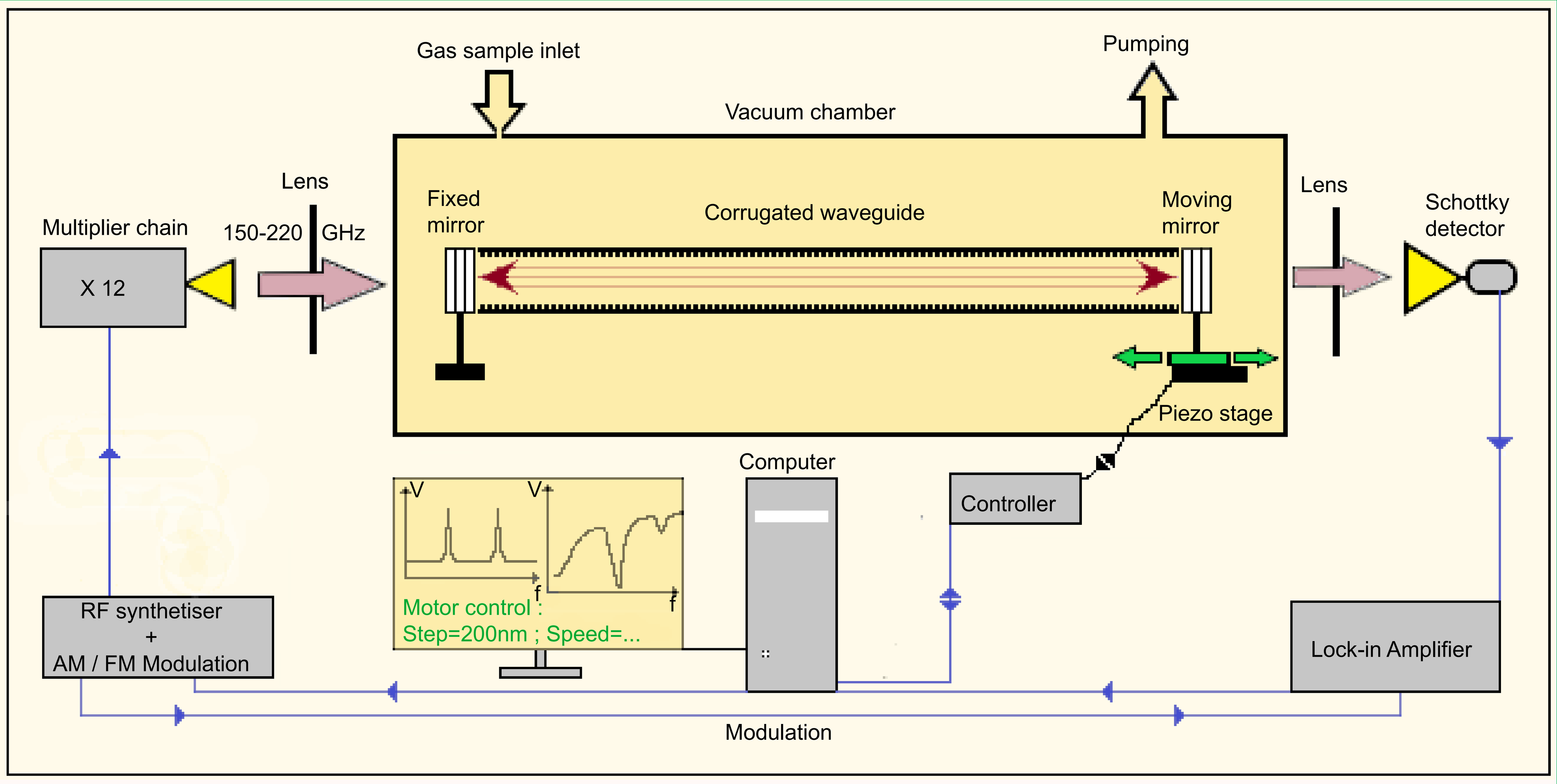
Corresponding author: fabien.simon@univ-littoral.fr

Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring-Down Spectroscopy (CRDS) are well established for sensitive infrared measurements of gas phase compounds at trace level using their rovibrational signatures [1,2]. The recent successful development of a THz Fabry-Perot spectrometer shows that such techniques may be employed at THz and submillimeter frequencies [3] to probe the rotational transitions of light polar compounds. Here we present the development of a new millimeter resonator based on a low-loss corrugated waveguide with highly reflective photonic mirrors obtaining a finesse above 3500 around 150 GHz. Cavity length is controlled thanks to one moving mirror mounted on a stick-slip piezo linear stage in the nanometer resolution range. With an effective path length of one kilometer, a significant sensitivity has been evaluated by the measurement of line intensities lower than 10^{-26}cm^{-1}/(molecule/cm^2). First spectroscopy measurements have been carried out with nitromethane, a degradation product of TNT. This spectrometer will be used to detect semi-volatile organic vapors at trace level which could not be envisaged with a conventional detection technique [4,5].



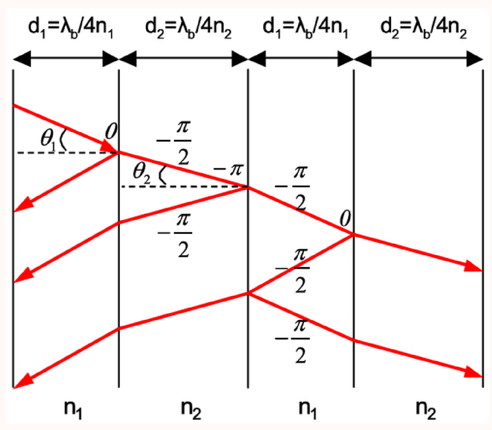


The setup



Photonic mirrors

Schematic diagram of a distributed Bragg reflector structure



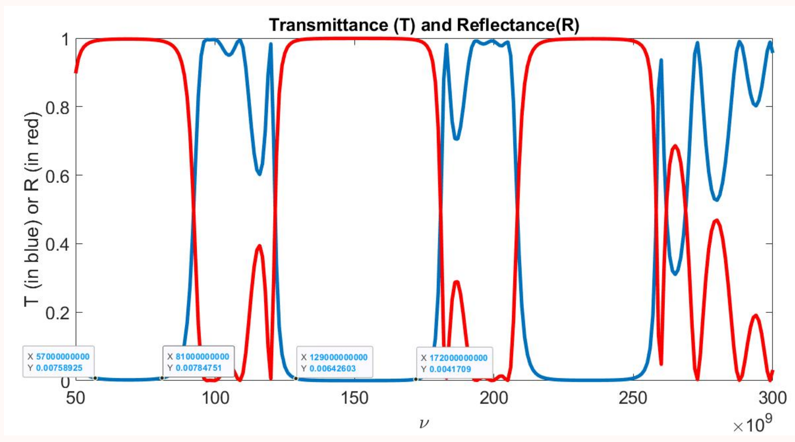
n_1 high indice
n_2 low indice
λ_0 resonant wavelength of the Bragg mirror in vacuum

Multiple reflections, constructive interferences

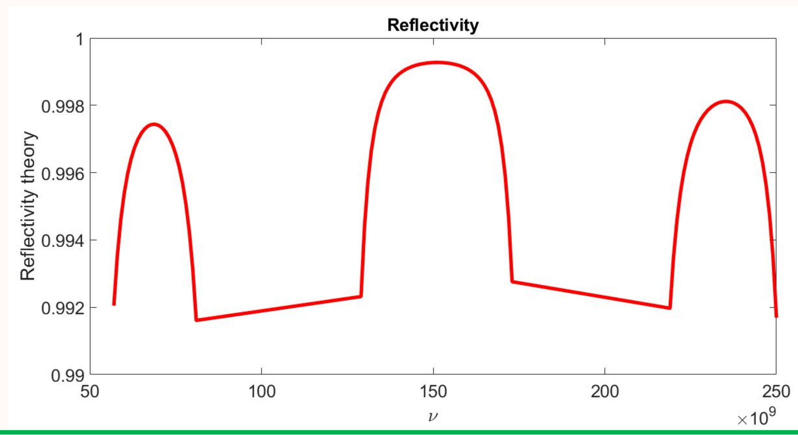
Multiple transmissions, constructive Interferences

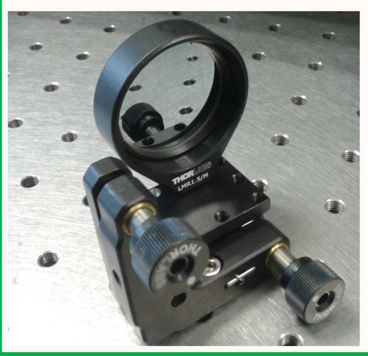
In the case of **normal incidence**, the reflectance at an interface is given by the relation : **R = [(n1 – n2) / (n1 + n2)]²**

Figure and text extracted and translated from [6].



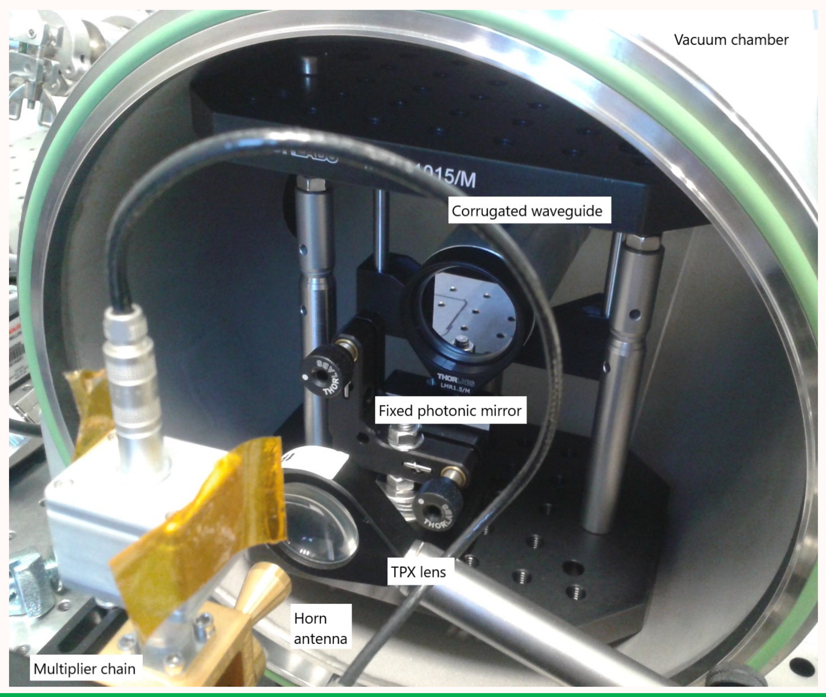
Matlab code simulations for Transmittance, Reflectance and Reflectivity [7].





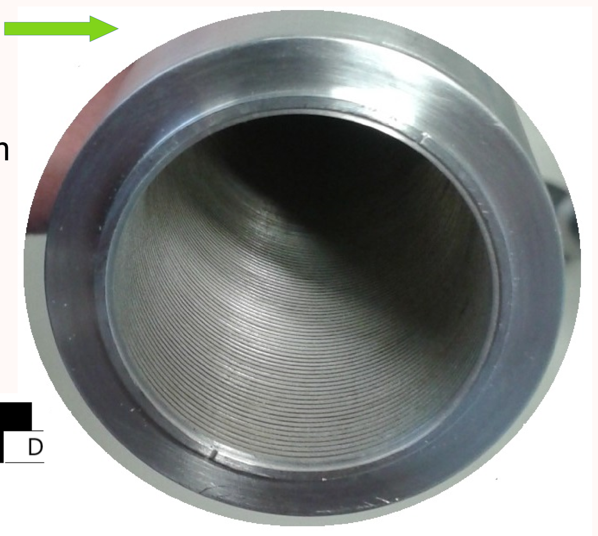
Photonic mirror with 4 silicon wafers of 441 µm thickness, and 4 spacer washers of 469 µm thickness.
Silicon indice ~ 3,48
Air indice ~ 1

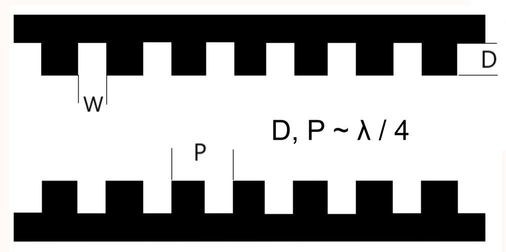
Forbidden band ~ 130-170 GHz
Resistivity > 20.000 Ω.cm
Reflectivity > 99,95 %



General Atomics low loss corrugated waveguide.

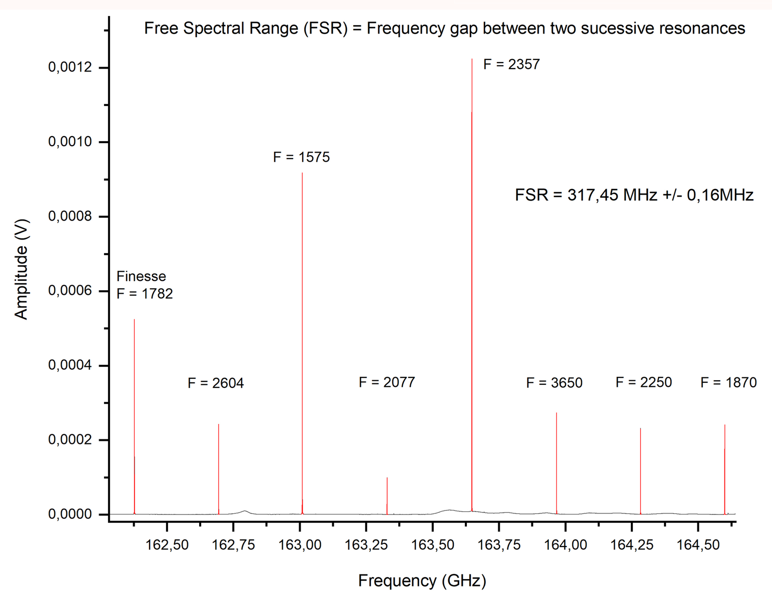
Internal diameter 31,75 mm
Length 467 mm

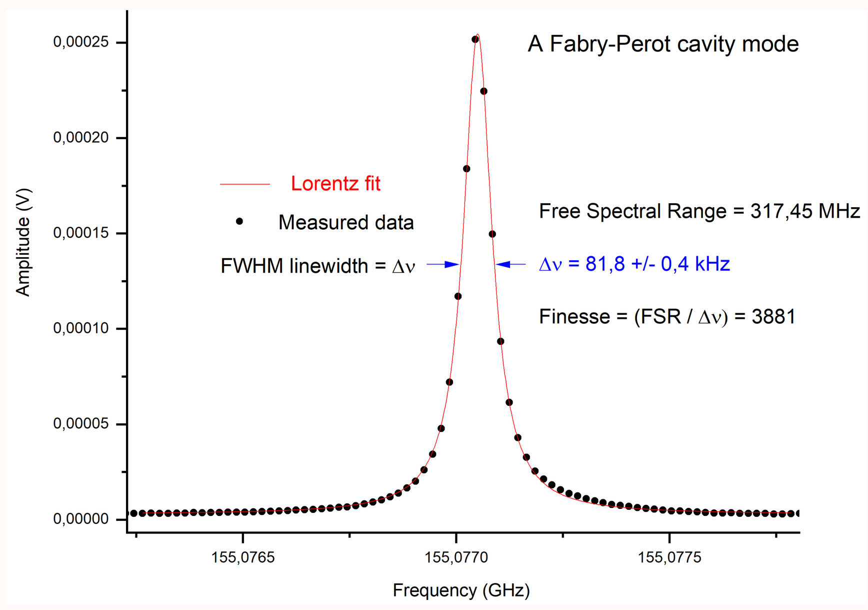




Corrugated Waveguide

Fabry-Perot resonator, cavity modes

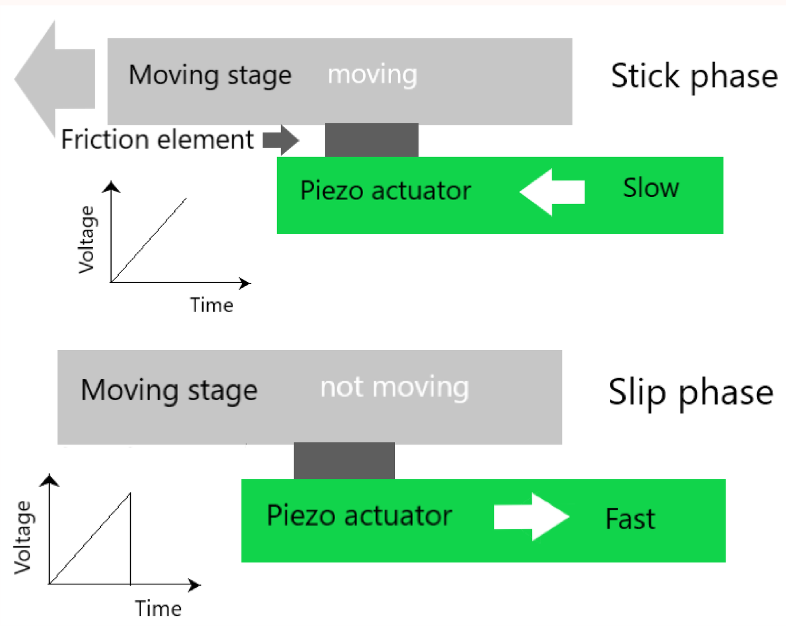




Free Spectral Range : FSR (Hz) = c / (2.L)
Finesse : F = FSR / Δν = π.√(R.e$^{-\alpha L}$) / (1 – R.e$^{-\alpha L}$)
Equivalent interaction pathlength (m) : Leq = 2.F.L / π
Mirrors losses = 1 – R Total losses = R.e$^{-\alpha L}$

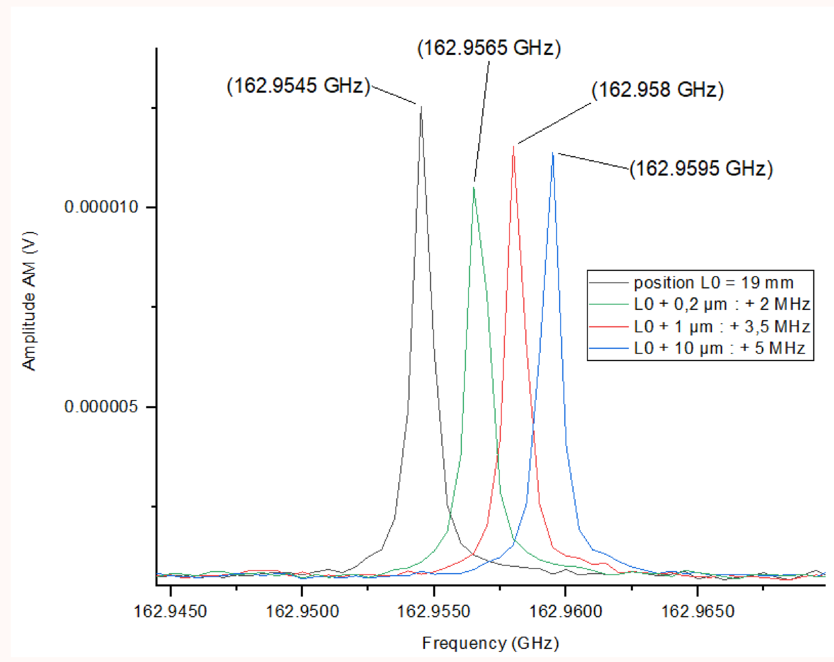
c = speed of light (m.s^{-1})
L = Fabry-Perot cavity length (m)
R = Mirrors reflectivity
α = Waveguide losses per unit of length (m^{-1})

Piezo « stick-slip » linear stage vacuum compatible



Closed-Loop optical sensor resolution : 1 nm

Cavity mode displacement with cavity length changes



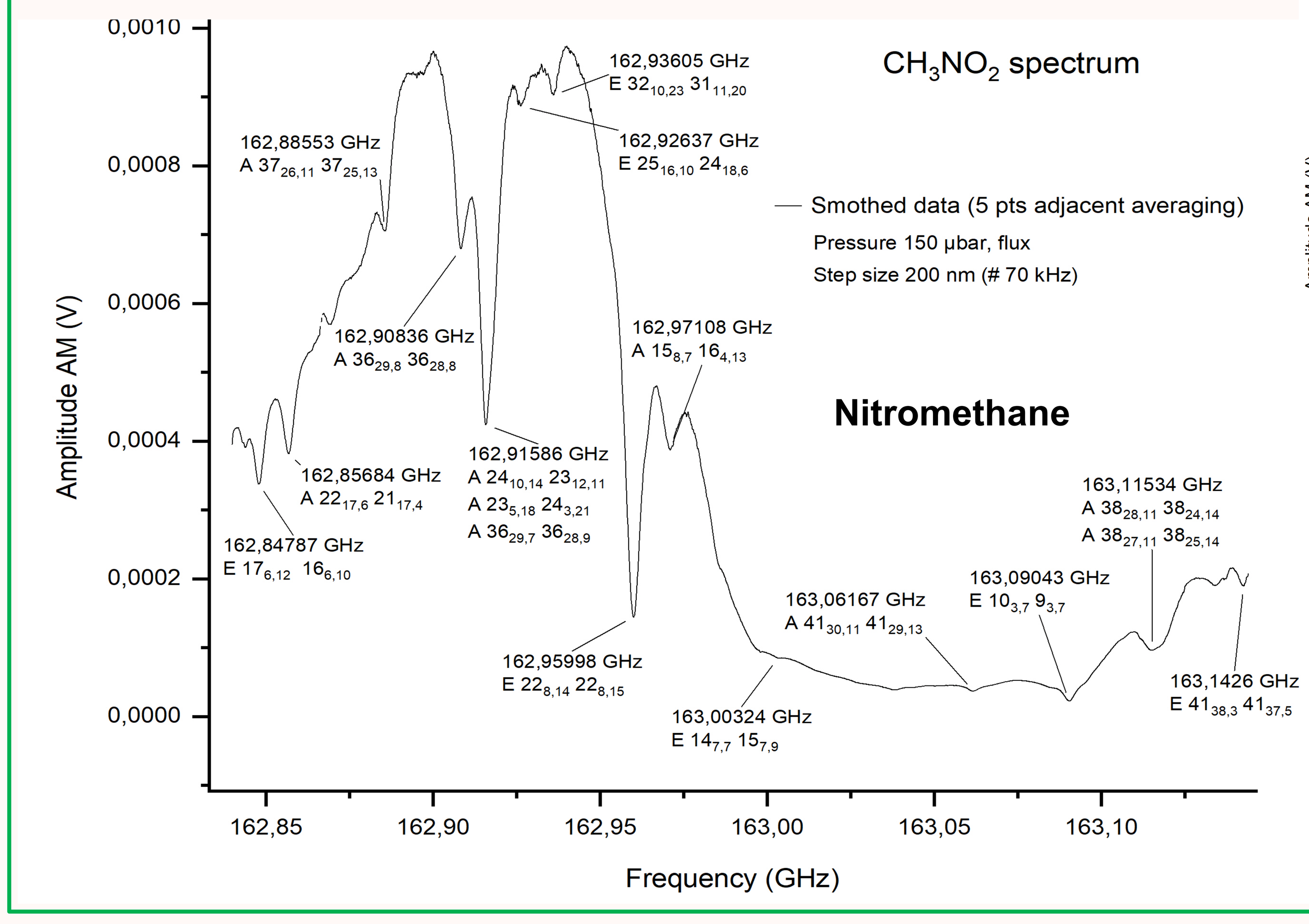
Expression of variation of frequency over cavity length :

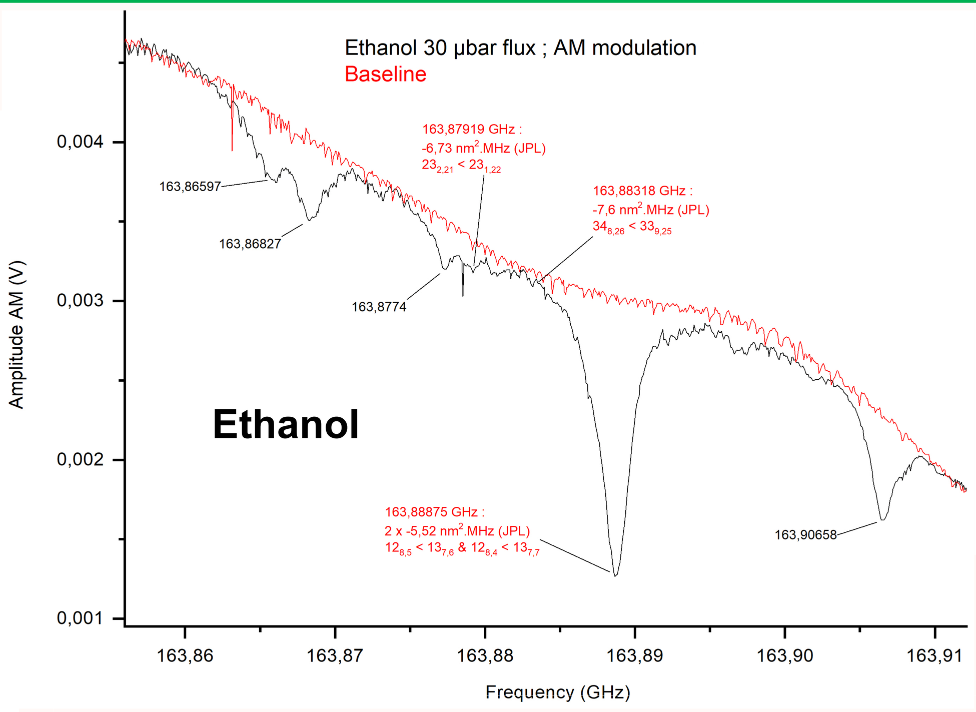
$$\Delta\nu = \frac{C}{2}\,q\,\left(\frac{1}{l_0-\delta}-\frac{1}{l_0}\right)$$

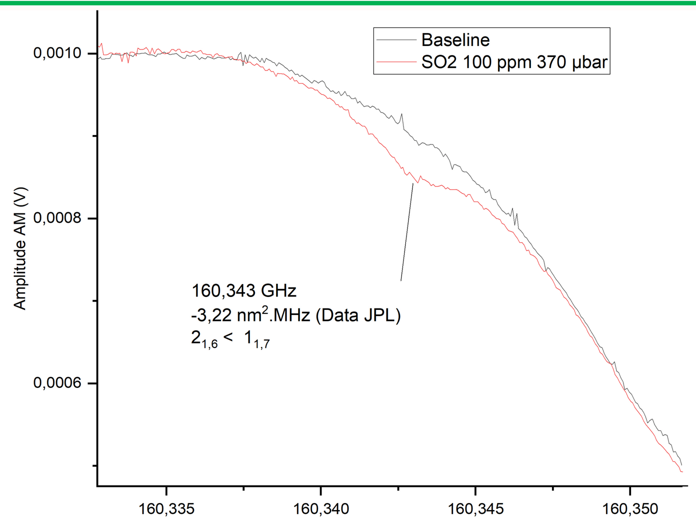
q = Frequency / FSR
ν = Frequency (Hz)
L = l_0 = cavity length (m)
ΔL = δ (m)

Ex : for ΔL = 200 nm,
Δν ~68,5 kHz at 160 GHz

Here we present the first experimental results of our setup

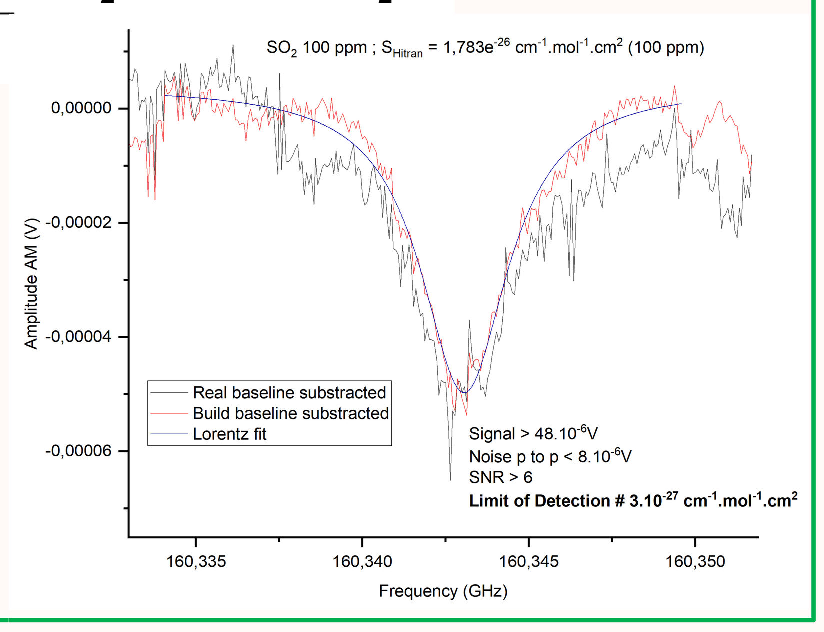






First evaluation of the actual Limit of Detection (LoD) has been carried out with SO_2 (100 ppm, modulation of amplitude).
LoD (AM) :
S_{min} ~ 3.10^{-27} cm^{-1}.mol^{-1}.cm^{-2} (Hitran unit)
Equivalent to ~ 1.10^{-8} nm².MHz (JPL unit)

SO_2 100 ppm in N_2



For traces in air, the maximum of the molecular absorption coefficient α (cm^{-1}) is given by :

$$\alpha_0[\text{trace}] = S.\chi / (k_B.T_0.\pi.\gamma_{air})$$

S = line intensity (cm^{-1}.mol^{-1}.cm^{-2}) k_B = Boltzman constant (cm^3.atm.K^{-1})
T_0 = temperature (K) χ = (trace partial pressure) / (air partial pressure)
γ_{air} = air broadening coefficient (cm^{-1}.atm^{-1})
$\alpha_0[SO_2\ 2_{1,6} \leftarrow 1_{1,7}$ 100 ppm] ~ 1,38.10^{-6} cm^{-1} **α_{min} = α_0[trace] / SNR[p to p] ~ 2,3.10^{-7} cm^{-1}**

Perspectives

- Motor control adjustments (software) for Signal to Noise improvement
- Trace level detection of semi-volatile organic vapors
- CRDS implementation for traces quantification
- New set of photonic mirrors for higher finesse
- Testing of other waveguides (longer one, coated ones...)

References

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[3] F. Hindle et al. Optica, 6, 1449-1454, (2019).
[4] G. Mouret et al. IEEE Sensors, 11, 133-138, (2013).
[5] A. Roucou et al., ChemPhysChem, 19, 1056-1067, (2018).
[6] C. Levallois, « Étude et réalisation de lasers à cavité verticale mono et multi-longueurs d'onde émettant à 1,55 µm »
[7] H.V. Baghdasaryan et al. Opto-Electronics Review 18(4), 438–445

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