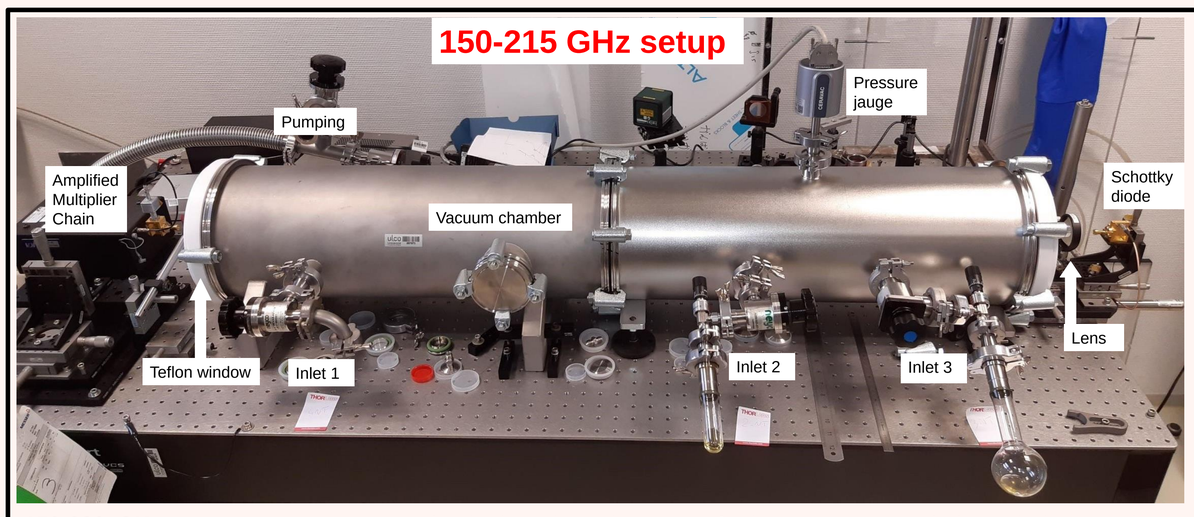
CEAS and CRDS at THz frequencies for trace level gas analysis

Fabien Simon, Coralie Elmaleh, Arnaud Cuisset, Francis Hindle and Gaël Mouret

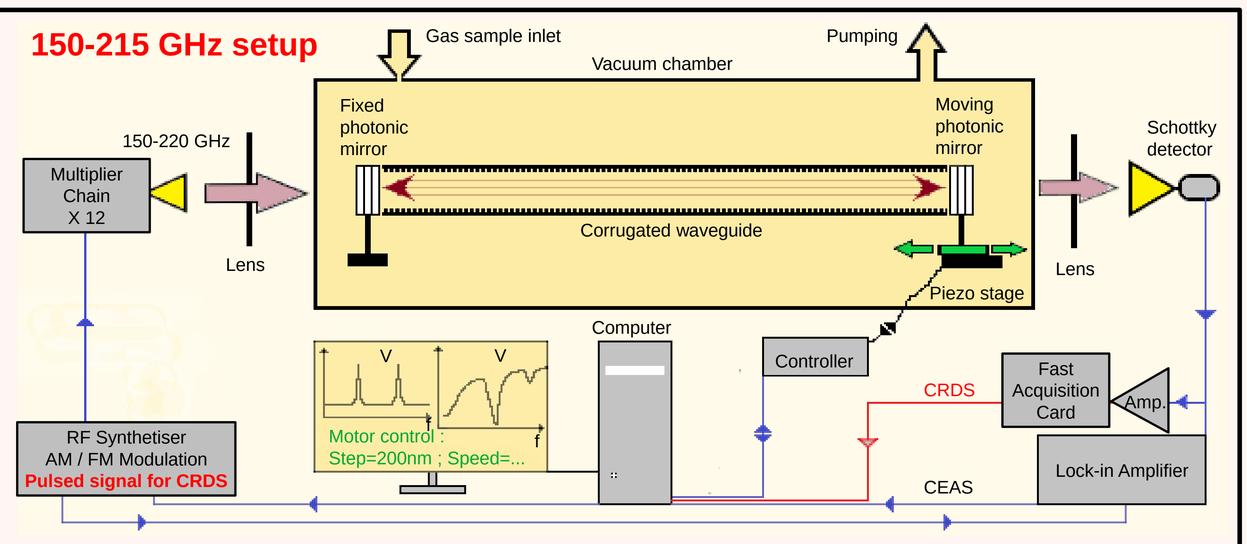
Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, 189 A Av. Maurice Schumann 59140 Dunkerque, France
Corresponding author: fabien.simon@univ-littoral.fr

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 [1,2]. Such resonant techniques may be employed at submillimeter [3] and millimeter wavelengths, **and ultra-sensitive high-resolution THz spectrometers may be designed**. Here we report about two THz Fabry-Perot spectrometers based on low-loss waveguides and highly reflective photonic mirrors, both achieving an effective path length of more than one kilometer.
The first set-up operating in the frequency range 550-650 GHz targets light species at trace concentration, such important industrial pollutants as SO_2, NOx, NH_3, HCl, HCN, CO, H_2S…
The second set-up operates between 150 and 215 GHz. It is designed to detect heavier molecules also at trace level, such as explosive taggants, which cannot be envisaged with a conventional detection technique [4, 5].



150-220 GHz resonant spectrometer is designed to detect explosive taggants and degradation products vapors, at trace concentrations. Mono and dinitrotoluenes, 2,3 Dimethyl 2,3 Dinitrobutane (DMNB), are some of the target molecules, with low saturation vapor pressure. Spectra **over** several GHz can be recorded.

The 550-650 GHz setup of similar design, is dedicated to trace level detection of light polar compounds. A molecular absorption coefficient as low as 2.10^{-8} cm^{-1} is accessible to detection.



150-220 GHz setup : cavity length is controlled with one moving mirror mounted on a stick-slip piezo linear stage. There is no feedback loop. Cavity's tuning is ensured by calculation of the required displacement and periodic control of the mode position.

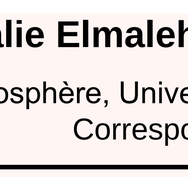
550-650 GHz setup : cavity length is controlled with a PID regulator locked on the maximum of a cavity mode, thanks to piezo actuators.

CEAS technique at THz frequencies

To extend the limited sensitivity of direct absorption techniques in this band, CEAS has been adapted to millimeter and sub-millimeter wavelengths. The idea is to increase the interaction length between gas sample and light, to increase sensitivity.
At a resonant frequency of a L length cavity, the equivalent interaction path length is **Leq = 2.F.L / π**

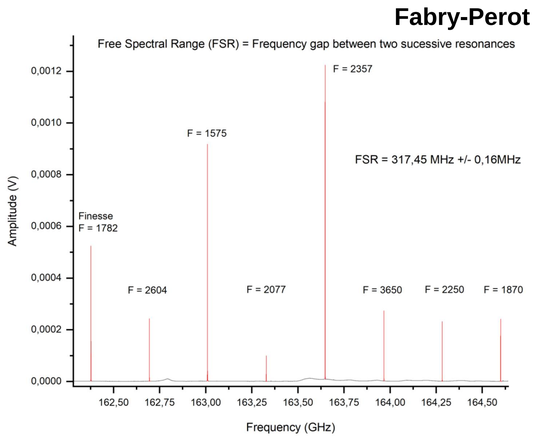
The Finesse F is a measure of the total losses of an optical cavity.

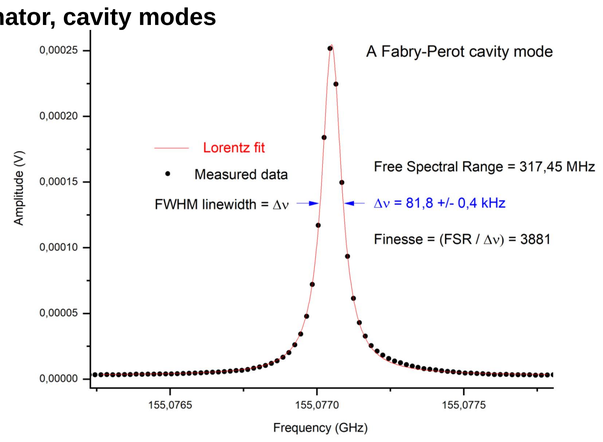
The absence of spherical mirrors at THz frequencies and the highly divergent beam **make it necessary to use a waveguide.**



General Atomics low loss corrugated waveguide.

Fabry-Perot resonator, cavity modes



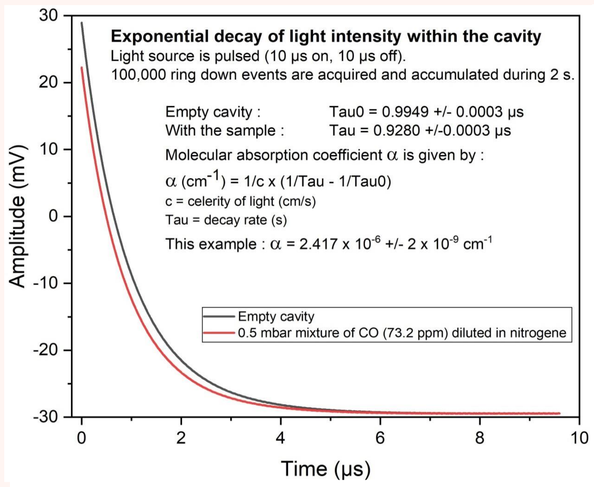


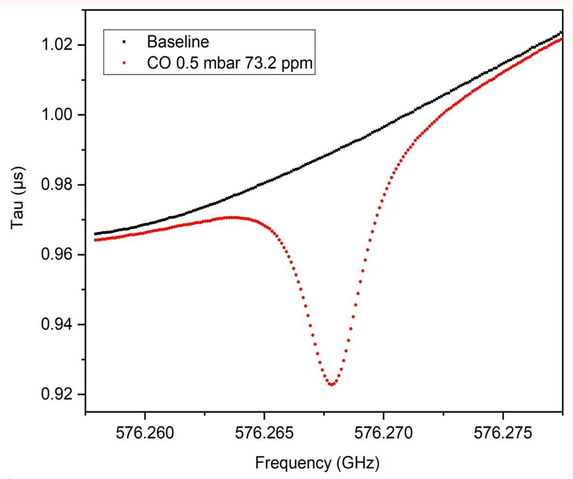
o Free Spectral Range : FSR (Hz) = c/(2.L)
o Finesse : F = FSR / Δν = π.√(R.$e^{-α.L}$)/(1 – R.$e^{-α.L}$)
o Mirrors losses = 1 – R o Total losses = (1-R).$e^{-α.L}$

c = speed of light ($m.s^{-1}$)
L = cavity length (m)
α = Waveguide losses per unit of length (m^{-1})

CRDS technique at THz frequencies

CRDS consists in measuring the exponential decay rate of the light intensity within the cavity, as a function of time, when light source is off. This require a pulsed light source.
The **Ring-Down Times Tau & Tau0**, which are the exponential decay time constants, are measured with and without the sample, when light source is off.





Measurement at the J = 5 ← 4 transition frequency of $^{12}C^{16}O$, 576.2679 GHz

α (cm^{-1}) = 1/c x (1/Tau – 1/Tau0)
Alpha's area give access to direct quantification [6].
∫ α(v) dv = S x C

α (cm^{-1}) : molecular absorption coefficient
v (cm^{-1}) : wave number

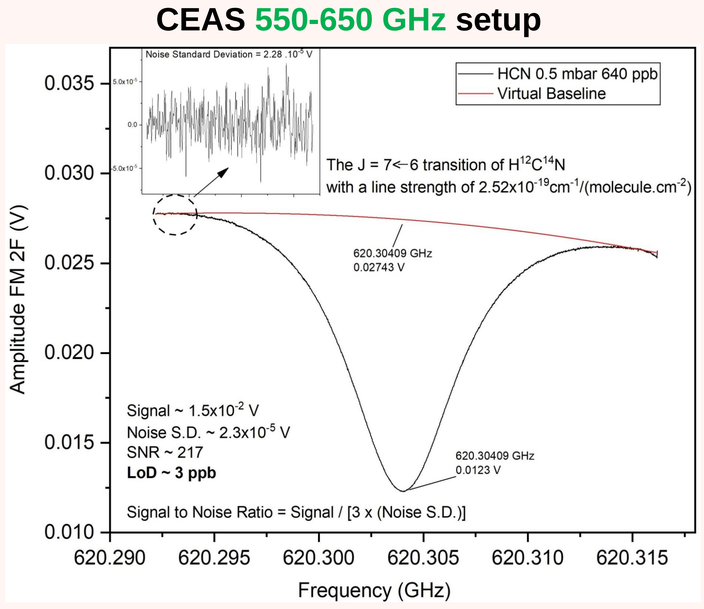
Each point of this CRDS spectrum represents the measured decay rate with or without the sample.

Tau is related to the Finesse F of the cavity :

F = 2.π.FSR.Tau **Tau = 1/(2.π. Δv)**
FSR (Hz), Tau (s), Δv (Hz)

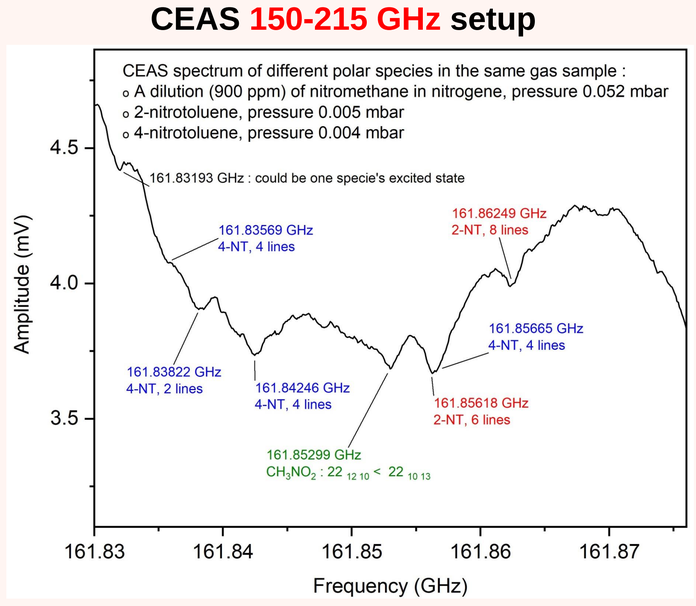
S (cm^{-1} / (molecule.cm^{-2})) : line strength
C (molecule / cm^3) : sample's concentration

CEAS 550-650 GHz setup



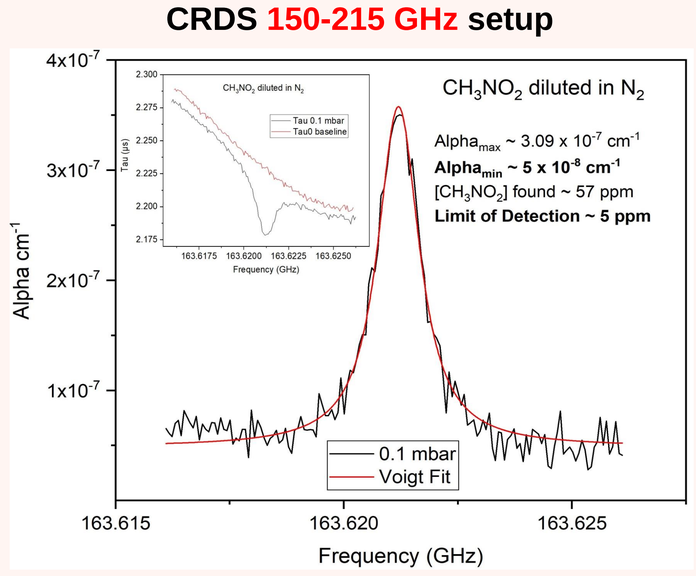
The gas trace contained **640 ppb** of HCN diluted in nitrogen.
The Signal to Noise Ratio (SNR) can be evaluated at **SNR ~ 220**
This lead to a **Limit Of Detection (LOD) of 3 ppb** for HCN.
The minimum line strength detectable is **S_{lim} ~ 7.5 x 10^{-28} cm^{-1}/(molecule.cm^{-2})**

CEAS 150-215 GHz setup



THz spectroscopy can discriminate each compound of a gas mixture.
2-NT and 4-NT, weakly volatile species with very « congested » spectra, are diluted in a dilution of CH_3NO_2 in N_2. The challenge is to detect individually each specie at trace level, in a « continuum » of absorptions.

CRDS 150-215 GHz setup



The J = 9 $_{6\,4}$ ← 8 $_{6\,3}$ transition of nitromethane, an intermediate product in the TNT synthesis. The trace is supposed to contain **67 ppm, but** our method of dilution and injection was not perfect (leaks…)

A concentration of **57 ppm of CH_3NO_2 is deducted from alpha's area.**
Limit of Quantification : less than 5 ppm. **$Alpha_{min}$ ~ 5 x 10^{-8} cm^{-1}**

Perspectives

- Room temperature detection of DMNB, a major explosive taggant
- Detection of dinitrotoluenes, compounds with a very low saturated vapor pressure
- Trace level detection of mononitrotoluenes
- CRDS technical improvements, to have access to individual quantification of semi-volatile species diluted in the same gas matrix.

References

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