Gas Analysis with High-Resolution Fabry-Perot Spectrometry in the 550-650 GHz Range

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***Abstract*—The development of a high finesse THz cavity has enabled the construction of a Fabry-Perot spectrometer. This approach can be applied to the THz and submillimeter wavelength allowing the rotational transitions to be probed. The intra-cavity power levels have permitted the sub-Doppler Lamb-dip profiles of ethanol to be observed. The quantification of a trace of H2S is demonstrated with a detection limit around 60 ppb.**

Keywords—TeraHertz, Rotational Spectroscopy, CRDS, CEAS, Fabry-Perot, Lamb-dip.

I. INTRODUCTION

Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring-Down Spectroscopy (CRDS) are well established as very sensitive methods for the measurements in the infrared domain of gas phase compounds at trace level from their rovibrational signatures [1,2]. The recent successful development of a THz Fabry-Perot spectrometer shows that such techniques can be applied to the THz and submillimeter wavelength to measure rotational transitions. A high-finesse Fabry-Perot cavity working between 550 and 650 GHz has been built [3]. This 48 cm long terahertz resonator is composed of flat photonic mirrors with estimated reflectivity of 99,95% and a corrugated waveguide. Finesse values as high as 4000 have been obtained around 620 GHz. On the full spectral range, typical values are between 1600 and 4000 (Fig. 1).

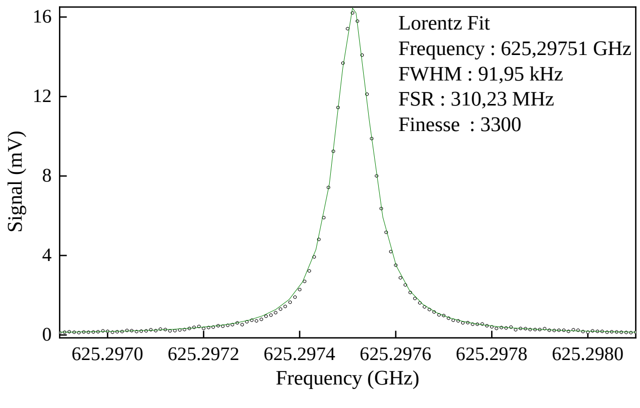

Fig. 1. Typical resonance mode of the THz cavity with a finesse of 3300 at 625.2975 GHz. (*Corresponding THz path L_{eff} ~1.03 km*)

To obtain high-resolution spectra, the position of the cavity mode and emission frequency of the source must be simultaneously scanned. This is achieved by varying the cavity length by adjusting the position of photonics mirrors using piezo actuators. A PID control loop is established to lock the resonance of the cavity to the emission frequency. Then, two experimental protocols can be undertaken with this cavity assisted spectrometer, CEAS or CRDS mode as shown in the experimental setup (Fig. 2).

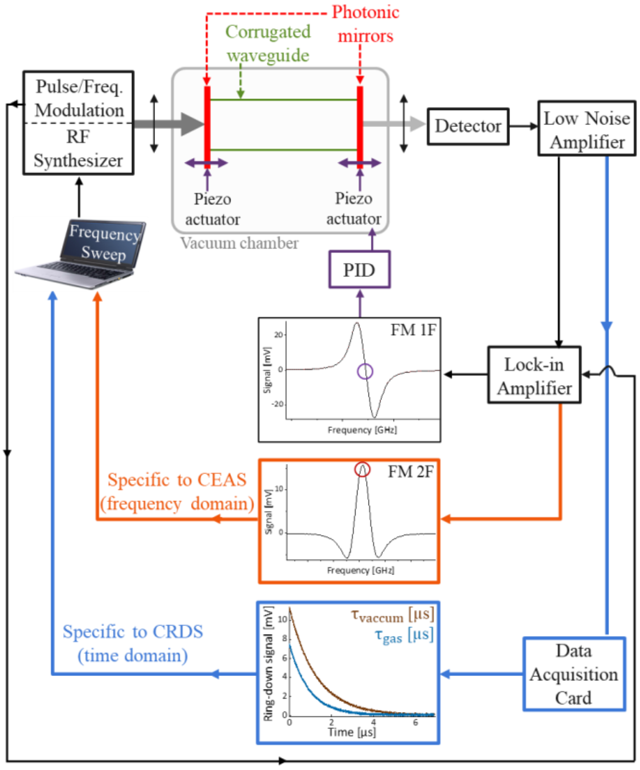

Fig. 2. Experimental setup (*in orange: setup specific to CEAS ; in blue: setup specific to CRDS*)

II. CEAS RESULTS

With this setup, we scan the source frequency to measure the molecular absorption. The CEAS signal for a rotational transition of ethanol centered at 618.160 GHz is shown in Fig 3 (red line). This is confirmed by successive measurements of the cavity mode (black lines) that reduce in amplitude and broaden while passing the molecular absorption line. There is a strong correlation between the maximum of each resonance and the molecular signal obtained using a frequency modulation and detection at the second harmonic (FM-2F). We can also see that the finesse decreases once the absorption is observed. The finesse is representative of intracavity absorption.

The sub-Doppler Lamb-dip is visible close to the center of the frequency predicted at 618.160625 GHz by the Jet Propulsion Laboratory (JPL) for the $19_{06\text{-}14} \leftarrow 18_{05\text{-}13}$ rotational transition belonging to the transition state [4,5] (zoomed in Fig. 4). Instead of one individual rotational transition which is listed in the JPL database, a doublet of sub-Doppler lines is observed. The rotational-torsional

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spectrum of ethanol is complicated with large amplitude motions involving -OH torsion [5] and -CH_3 internal rotation [6]. Such molecular motions produce tunneling splitting of rotational energy levels with different order of magnitude. Larger splittings are observed for -OH torsion with a barrier height of 400 cm^{-1}, leading to *gauche-*, *gauche+* and *trans* states. SubMHz line splittings are obtained for the torsion of -CH_3 with a barrier height of 1173.76 cm^{-1} for the *trans* state and 1331 cm^{-1} for the *gauche* states. As presented in Fig 3, subMHz line splittings associated to the methyl torsion were revealed by Lamb-dip measurements, completing the previous data obtained for -CH_3 internal rotation in *trans* state up to 600 GHz by J. C. Pearson *et al.*. These splittings have also been newly observed for the *gauche* states.

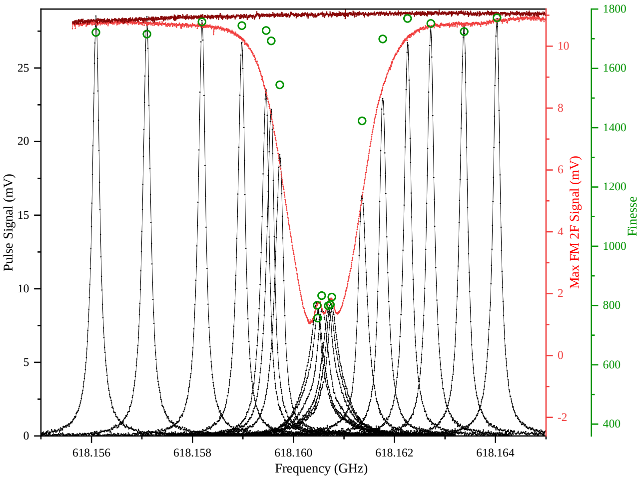

Fig. 3. CEAS of Ethanol (C_2H_5OH) P=3µbar, T=300K (red: molecular signal FM-2F; dark red: baseline; black: superposition of several resonances registered by moving the piezo actuators of the cavity; green: finesse of each resonance).

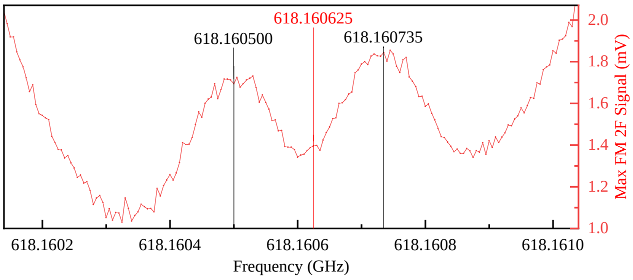

Fig. 4. Zoom on the absorption of the fig. 3. Predicted line frequency in the JPL spectroscopic database: f_{JPL}= 618 160 625 ± 5,3 kHz (transition 19_{06-14} <- 18_{05-13}, in red). F_{CEAS}: 618 160 500 kHz & 618 160 735 kHz (indicated in black)

III. CRDS RESULTS

By recording the ring down time with and without gas sample, we can calculate the frequency-dependent absorption coefficient directly proportional to the absorbent concentrations. The Fig. 5 shows an example of an absorption profile for the $5_{05-00} \leftarrow 5_{04-01}$ rotational transition of trace of H_2S diluted in nitrogen. The H_2S concentration was determined to be 0.489 ± 0.059 ppm (2σ), and the gas input was 0.504 ± 0.010 ppm (2σ). It demonstrates that strongly polar compounds may be measured with a ppb level of concentration [7].

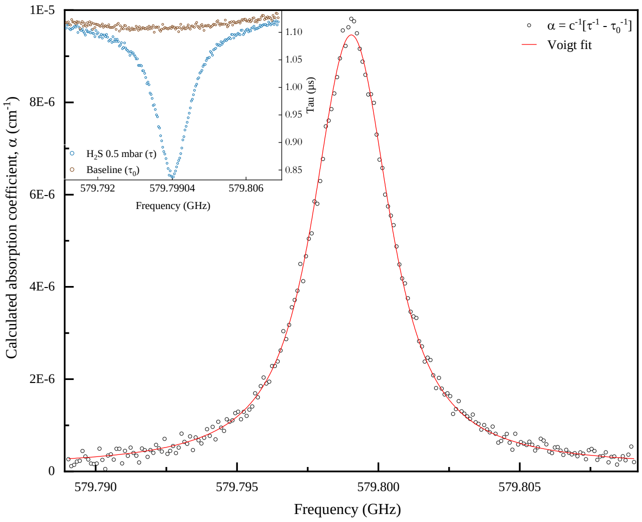

Fig. 5. Calculated absorption coefficient. Top-left: CRDS on the $5_{05-00} \leftarrow 5_{04-01}$ rotational transition of H_2S centered at 579,799042 GHz, measured in flux at a pressure of 504 microbars (and T=294K).

IV. CONCLUSION

We demonstrated the possibility to resolve hyperfine structures of rotational transitions using CEAS. High-resolution sub-Doppler saturated-absorption Lamb dips were measured at pressures of no more than 6µbar on rovibrational lines of C_2H_5OH from 550 to 620 GHz. With this technique, it is possible to completely resolve rotational lines with sub-MHz splitting. We also report the first THz-CRDS measurements above 600 GHz. A sub-ppm of calibrated H_2S mixture was easily detected.

With our setup we are able to quantify traces of gas at a level that can reach ppb, while being able to perform sub doppler measurements.

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