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## Si Traceable High Precision Spectroscopy Of Ozone Using A Quantum Cascade Laser At 9.5 Micrometer

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# SI TRACEABLE HIGH PRECISION SPECTROSCOPY OF OZONE USING A QUANTUM CASCADE LASER AT 9.5 MICROMETER



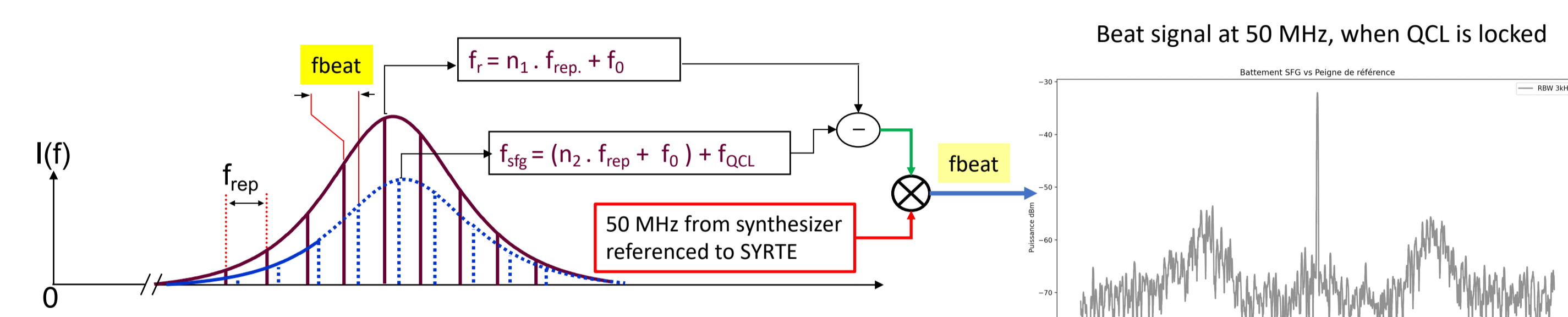
H. Elandaloussi<sup>1</sup>, N. Cahuzac<sup>1,2</sup>, M. Leuliet<sup>1</sup>, P. Marie-Jeanne<sup>1</sup>, C. Rouillé<sup>1</sup>, T. Zanon-Willette<sup>1</sup>, M. Manceau<sup>2</sup>, O. Lopez<sup>2</sup>, B. Darquié<sup>2</sup>, M. Abgrall<sup>3</sup>, C. Janssen<sup>1</sup>

1 LERMA, Sorbonne Université, Observatoire de Paris, PSL Université, CNRS  
 2 LPL, Université Sorbonne Paris Nord (Univ Paris 13), CNRS  
 3 LNE-SYRTE, Sorbonne Université, Observatoire de Paris, PSL Université, CNRS

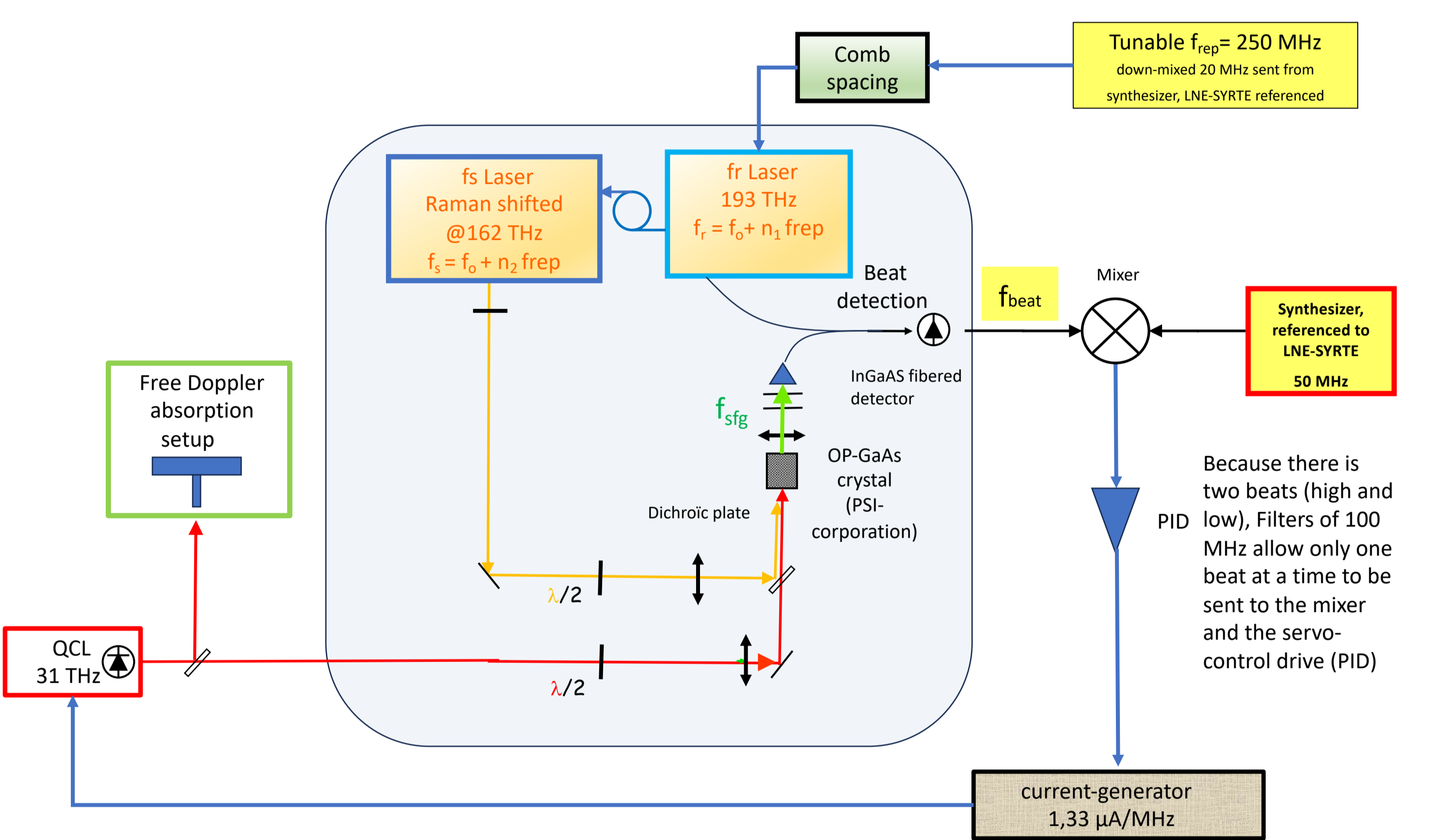
At Sorbonne-Université, we have developed a SI traceable mid-infrared QCL spectrometer for the investigation of ozone and other molecules of atmospheric and astrophysical interest. Ozone, in particular, has unresolved issues in the mid-IR spectral region at 9.5  $\mu\text{m}$ , where large uncertainties and inconsistencies in ozone broadening [1] and pressure shift [2] parameters exist. There is also the question of appropriately representing molecular line shapes [3]. Following previous work [4, 5], we have implemented a laser stabilisation scheme based on an optical frequency comb (OFC) referenced to the international system of units (SI) via an optical fiber which links to the REFIMEVE network [6]. To compare the QCL at 31 THz to a reference laser frequency comb at 193 THz (SI traceable), a sum frequency generation (SFG) scheme between the QCL and an OFC at 162 THz in an oriented patterned GaAs crystal is implemented.

## Frequency control of the Quantum Cascade Laser

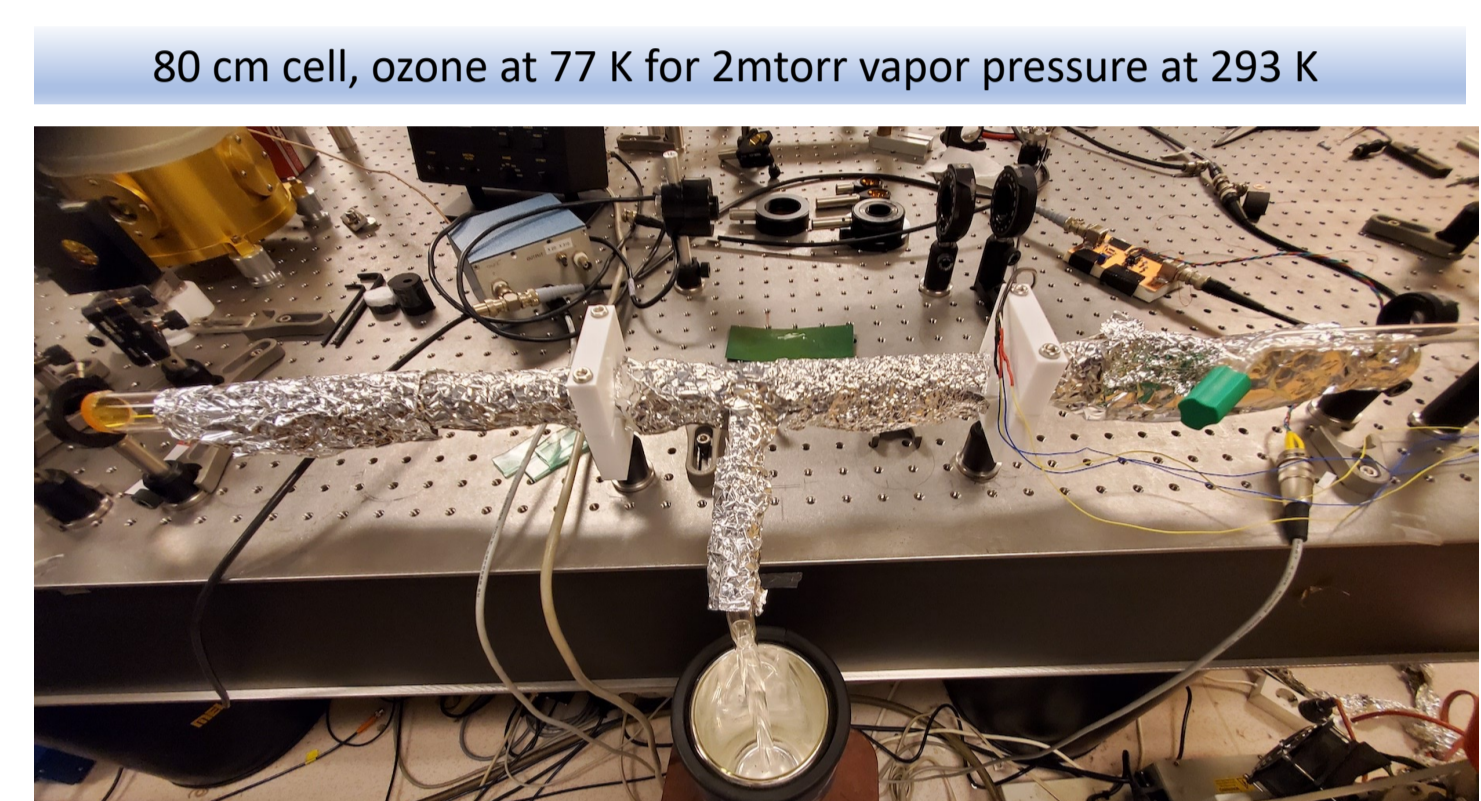
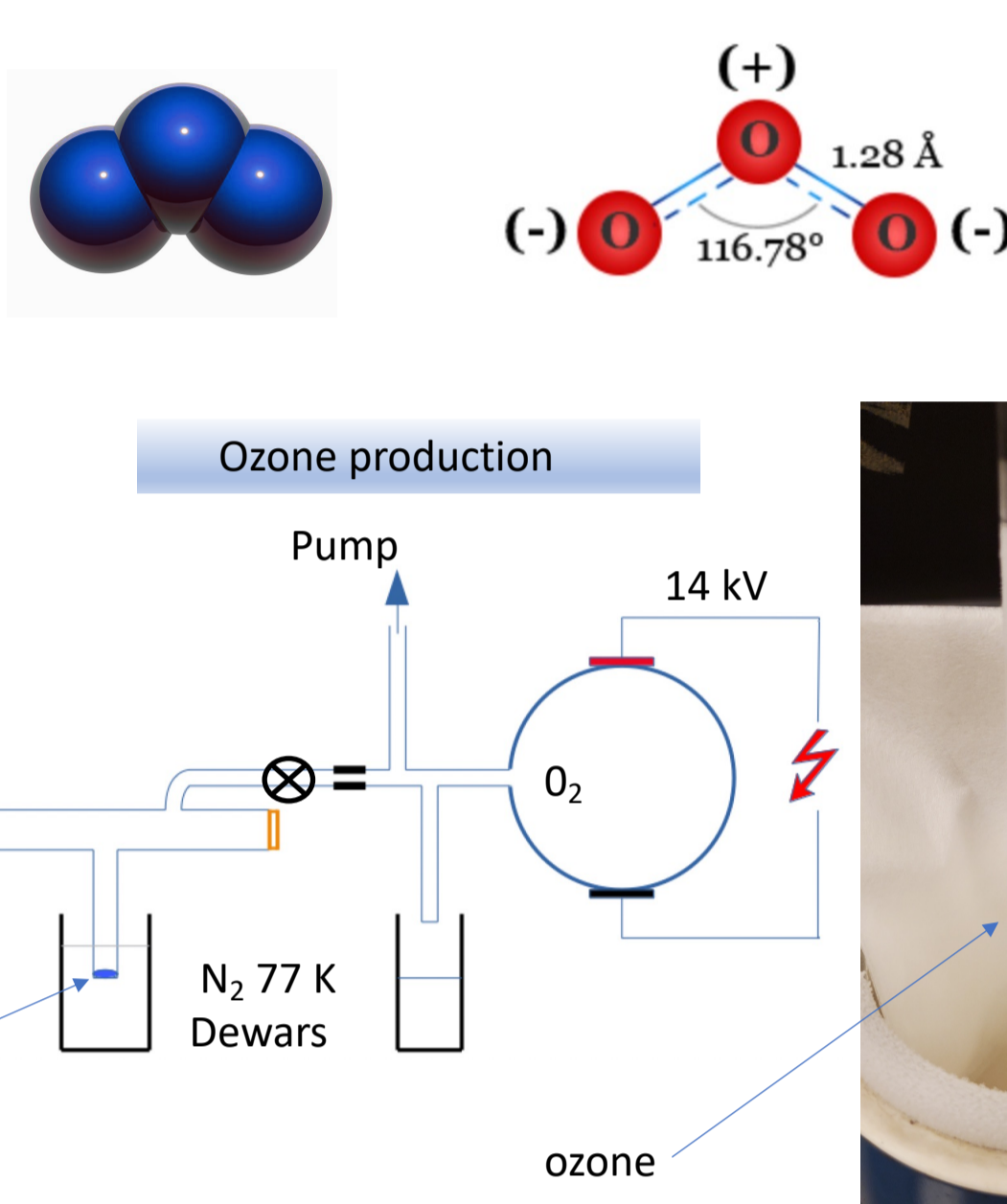
To control the QCL frequency emission around 31 THz, we sum its frequency with an optical-frequency-comb (OFC) at 162 THz to produce an optical frequency comb (OFC) at 194 THz. The sum frequency  $f_{\text{sig}}$  is compared to a SI traceable optical frequency comb at 193 THz, noted  $f_r$ . Frequencies are fixed by the controlled repetition rate frequency  $f_{\text{rep}}$  and the frequency offset  $f_0$ , both SI traceable.



$f_{\text{sig}} - f_r = f_{\text{beat}} = (n_2 - n_1) f_{\text{rep}} + f_{\text{QCL}}$ ;  $(n_2 - n_1)$  is an integer  $\sim 125\,847$ .  
 The  $f_{\text{rep}}$  around 250 MHz is controlled by a  $f_{\text{down}} = 20$  MHz synthesizer as:  $f_{\text{rep}} = 245\text{ MHz} + \frac{f_{\text{down}}}{4}$   
 Changing  $f_{\text{down}}$  by 0.1 Hz, alters  $f_{\text{rep}}$  and thus  $f_{\text{QCL}}$  by 3.1 kHz



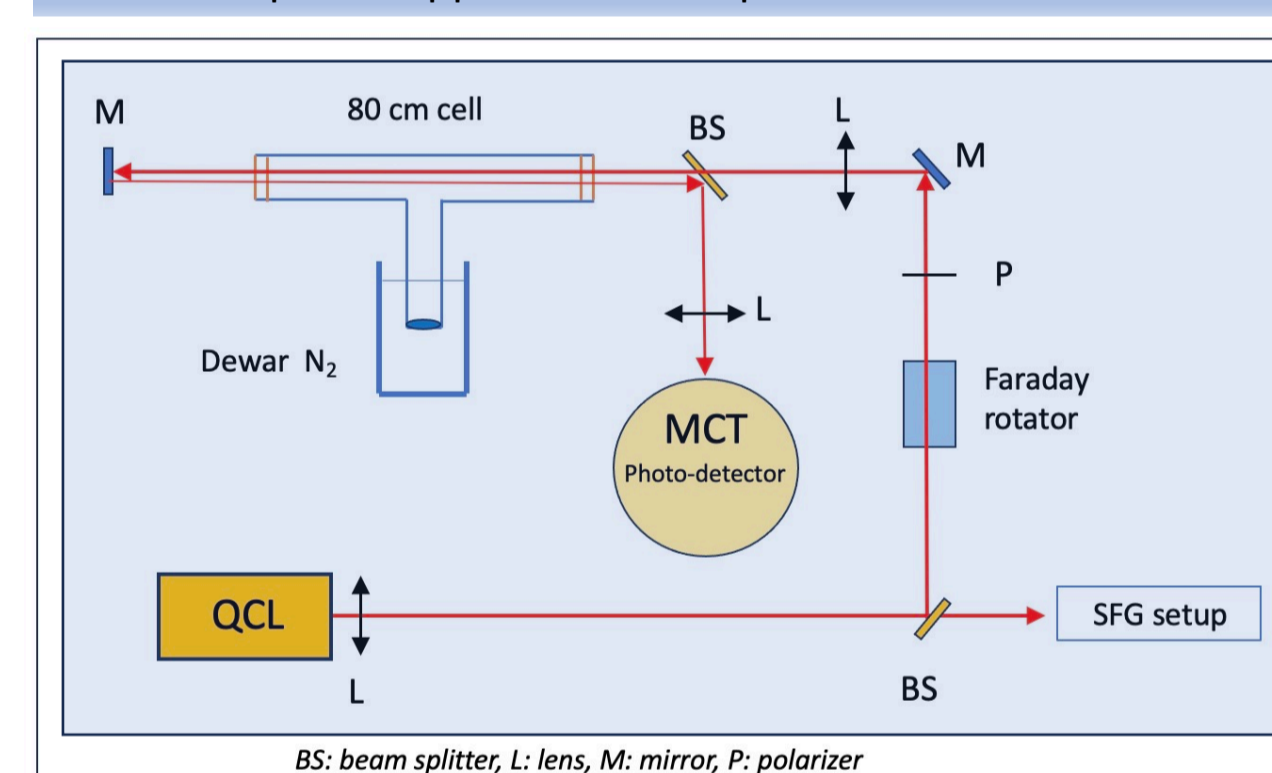
## Ozone, Doppler and Doppler-free spectroscopy setup



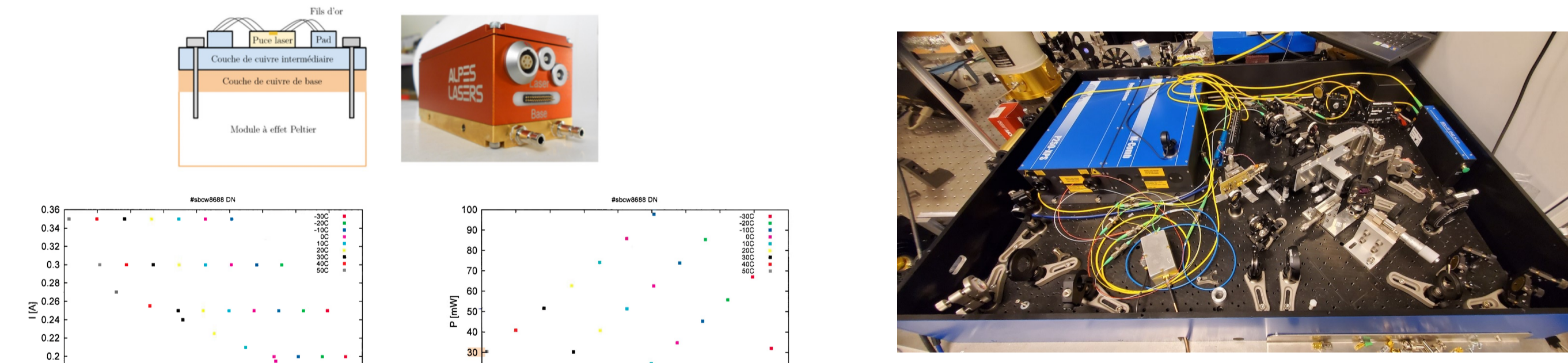
Sum frequency generation laser comb at 1.85  $\mu\text{m}$  + QCL-laser at 9.5  $\mu\text{m}$ . Beat detection using laser comb at 1.55  $\mu\text{m}$



Setup for Doppler free absorption measurements



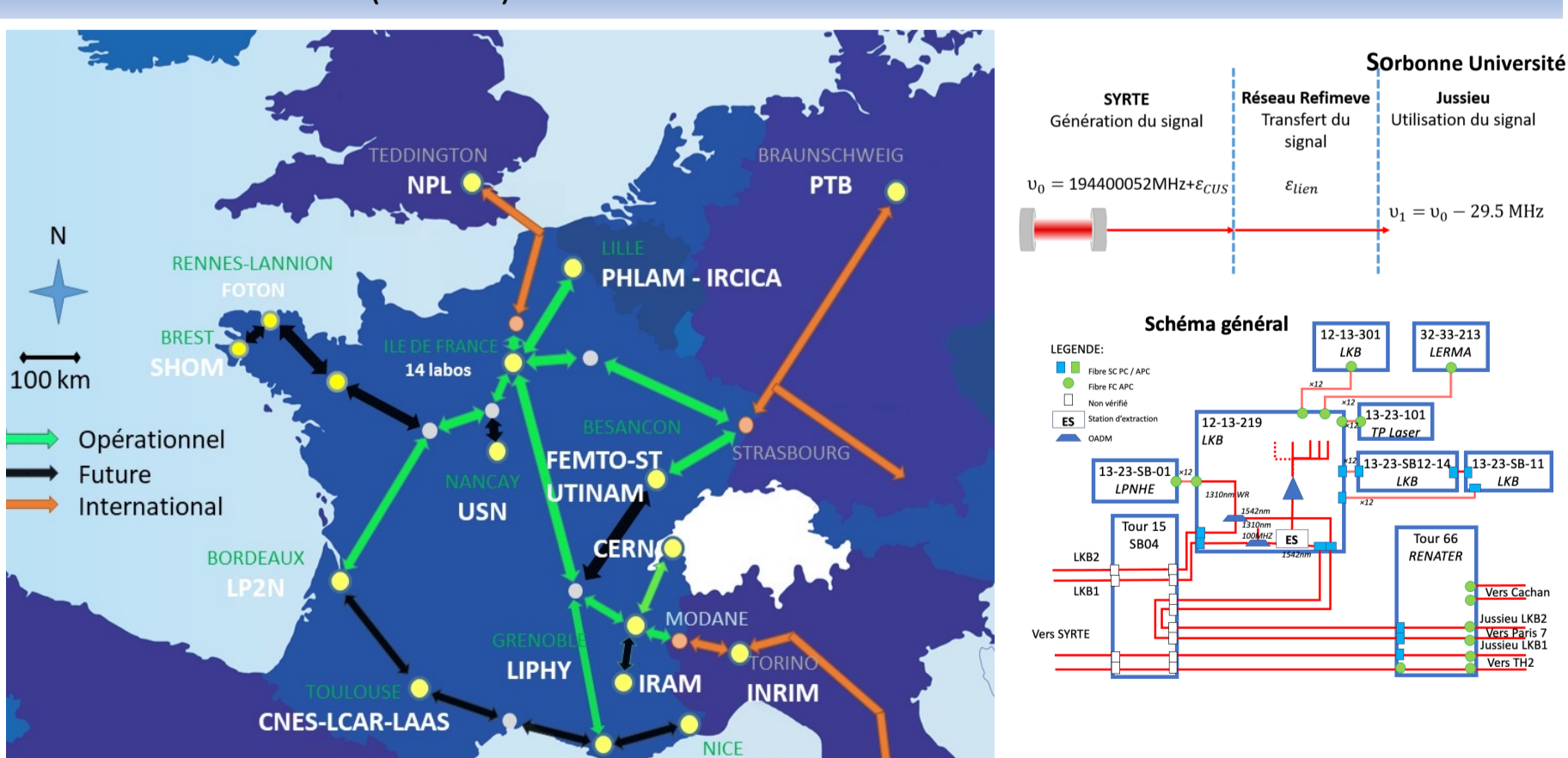
## Spectrometer instrumentation



Input current as a function of the single mode emission frequencies and temperature

Output power as a function of the single mode emission frequencies and temperature

Refimeve+ Link from LNE-Syrte-Observatoire de Paris to LERMA-Observatoire de Paris at Sorbonne Université (Jussieu) and other labs



Determination of QCL emission frequency

$$f_{\text{sig}} = n_2 \cdot f_{\text{rep}} + f_0 + f_{\text{QCL}}$$

$$f_r = n_1 \cdot f_{\text{rep}} + f_0$$

$$f_{\text{beat}} = f_{\text{sig}} - f_r$$

The QCL frequency can be written as :

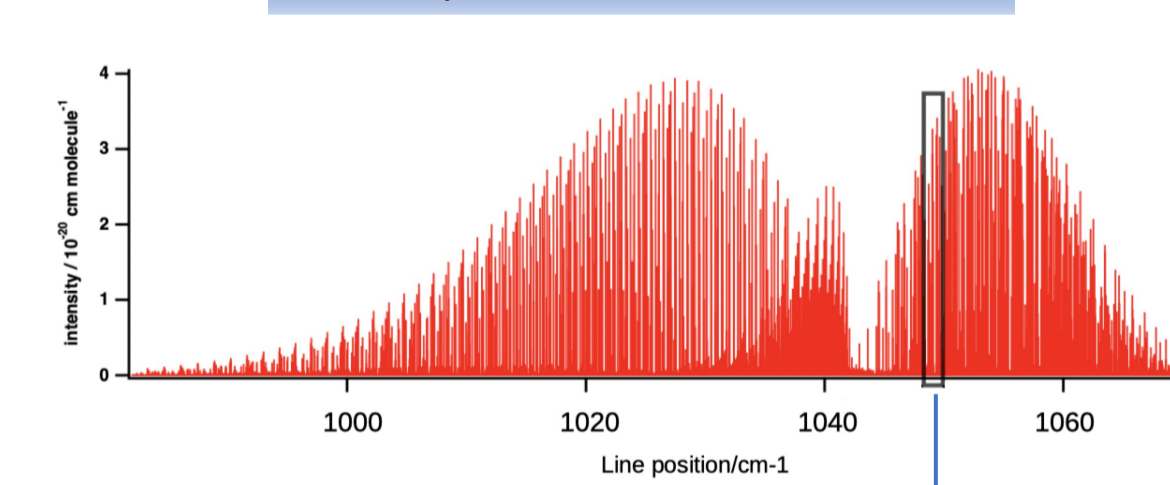
$$f_{\text{QCL}} = (n_1 - n_2) f_{\text{rep}} + f_{\text{beat}}$$

The OFC is controlled by a DDS referenced to the 100 MHz RF (H-maser) signal from LNE-SYRTE, that is distributed via optical fibre to SU-Jussieu for instruments synchronization.

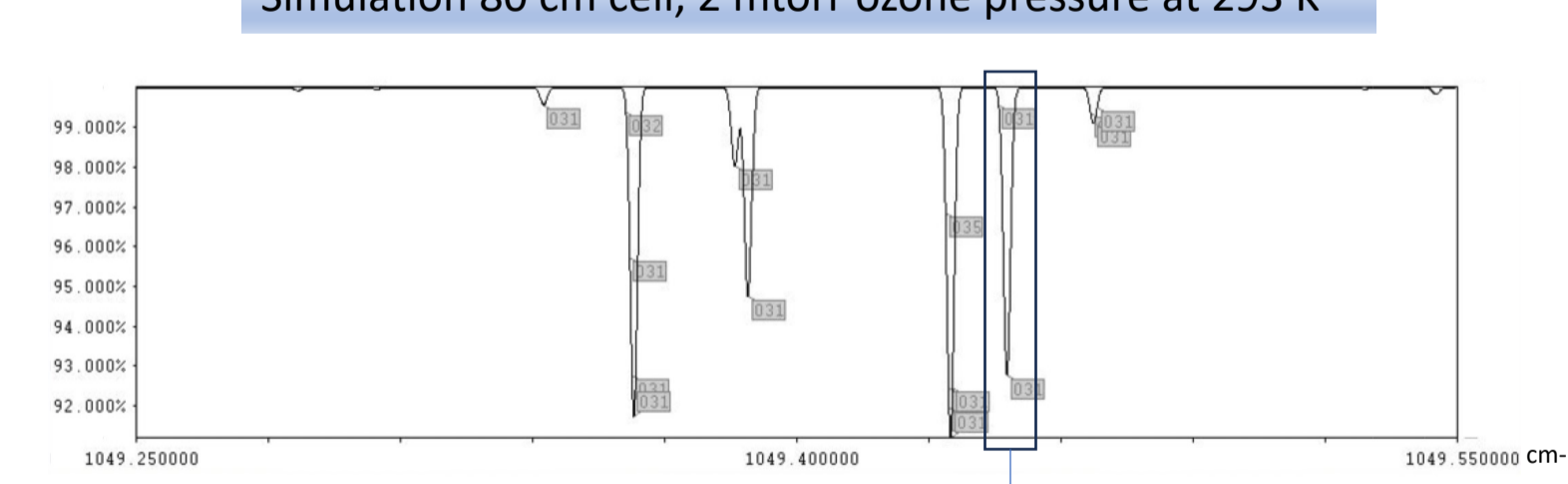
## Ozone spectrum and lines measurement

As a first demonstration of the spectrometer performances, we report on ozone line positions in the  $\nu_3$  R-branch from saturated absorption spectroscopy with line center determinations at the 50 kHz level. This is almost three orders of magnitude more accurate than the current uncertainty index ( $< 10^{-3}$  cm $^{-1}$ ) given in the HITRAN 2020 database.

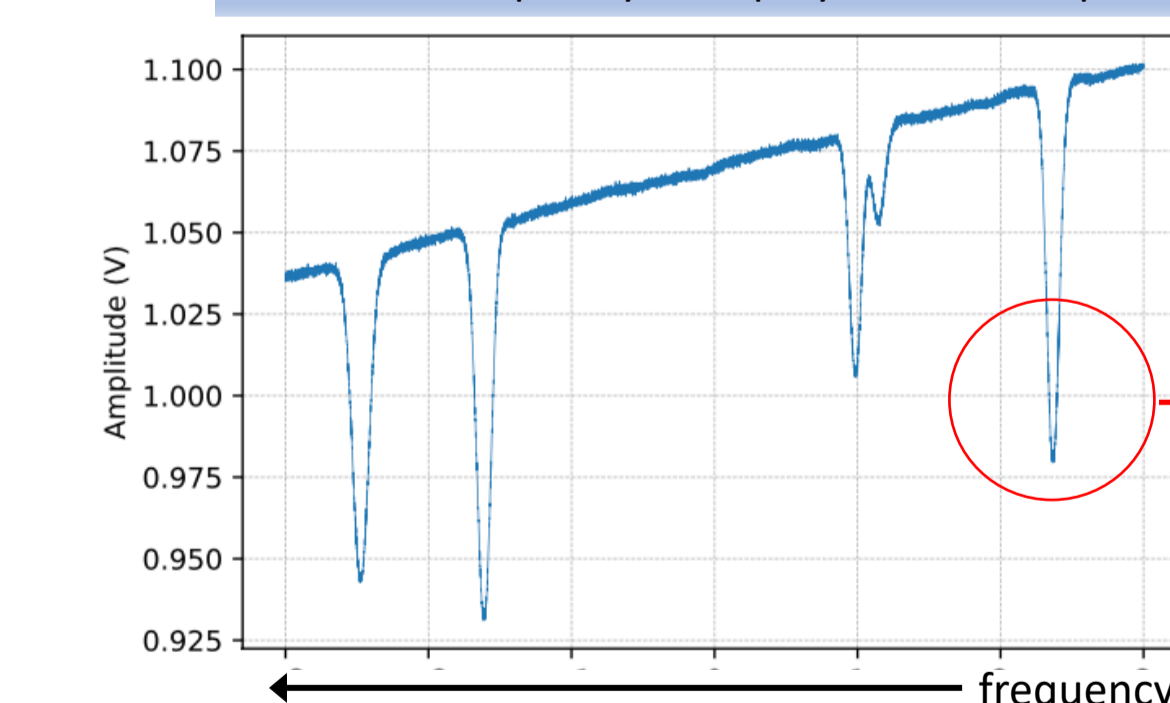
Ozone spectrum Hitran-database



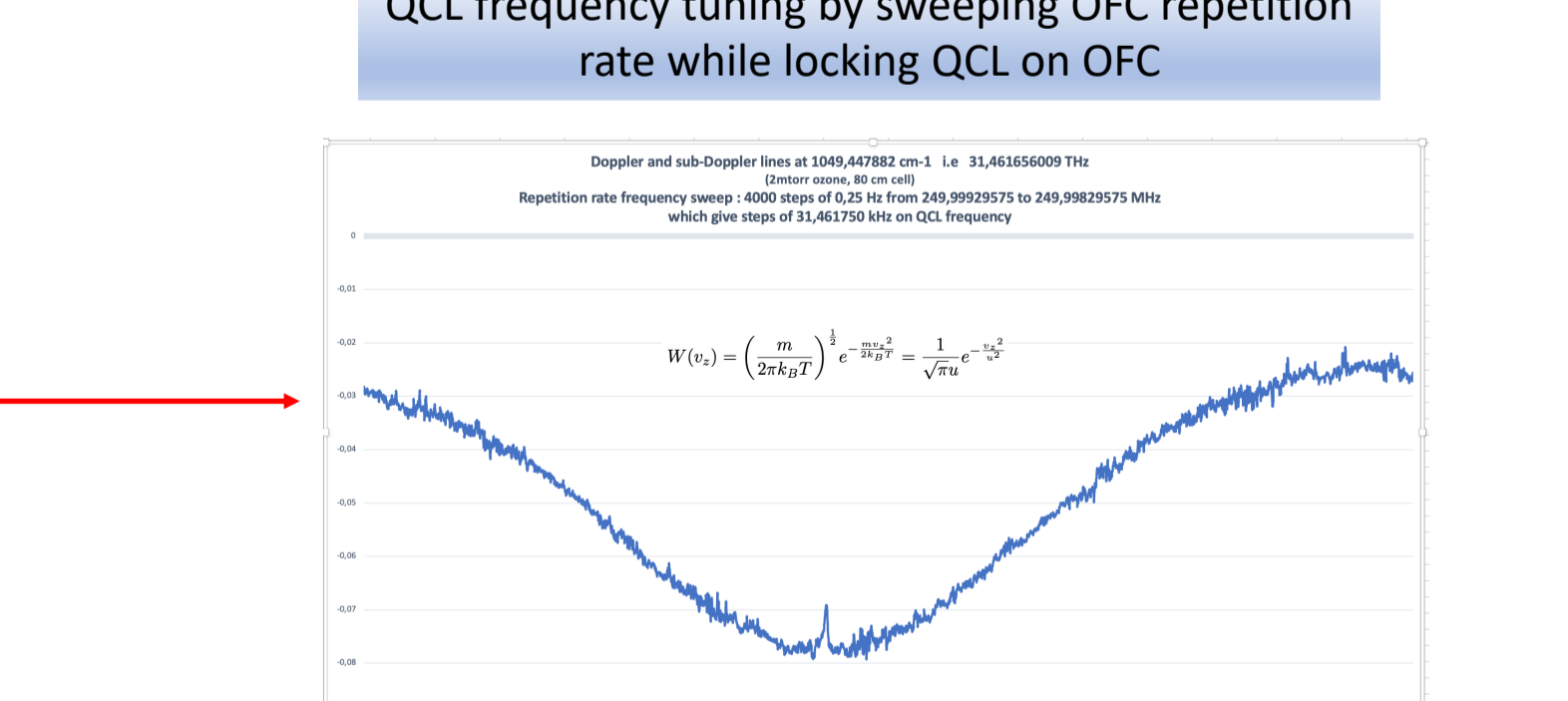
Simulation 80 cm cell, 2 mtorr ozone pressure at 293 K



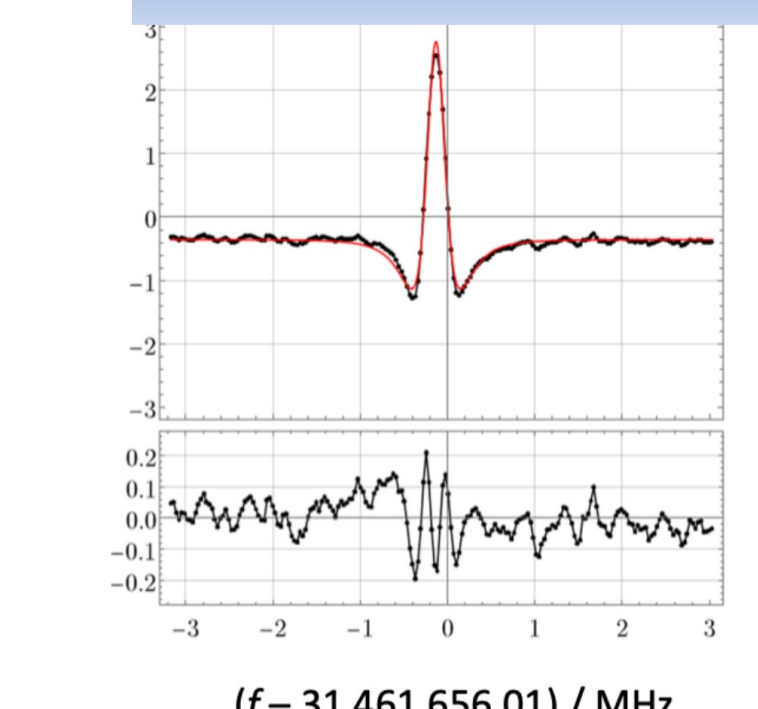
QCL down frequency sweep by current ramp



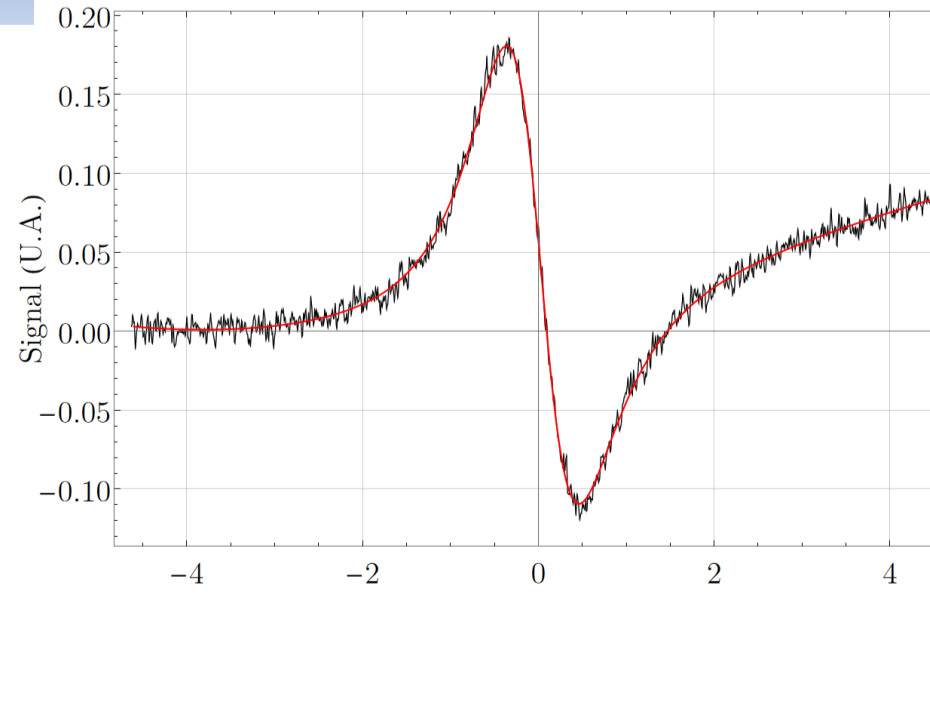
QCL frequency tuning by sweeping OFC repetition rate while locking QCL on OFC



Second harmonic of the ozone Doppler free absorption line at 1049.447882 cm $^{-1}$ . Frequency offset by line position from Hitran data base.



Doppler-free first harmonic modulation @ 10 kHz, 50 kHz deviation applied on the 50 MHz synthesizer



Conclusions

- Uncertainty (50 kHz) mainly limited by systematic effects
- Uncertainty almost three orders of magnitude smaller than in HITRAN (30 MHz).
- HITRAN2020 systematically shifted towards higher frequency, but very well within stated uncertainty.
- First absolute line position determination of the ozone main isotopologue  $^{16}\text{O}_2$  using sub-Doppler spectroscopy.
- Improvement towards  $< 4$  kHz uncertainty level is planned
- More systematic precision studies of line parameters (shape, position, pressure broadening and shift) are envisaged in the near future.

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 REGION ILE DE FRANCE



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