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

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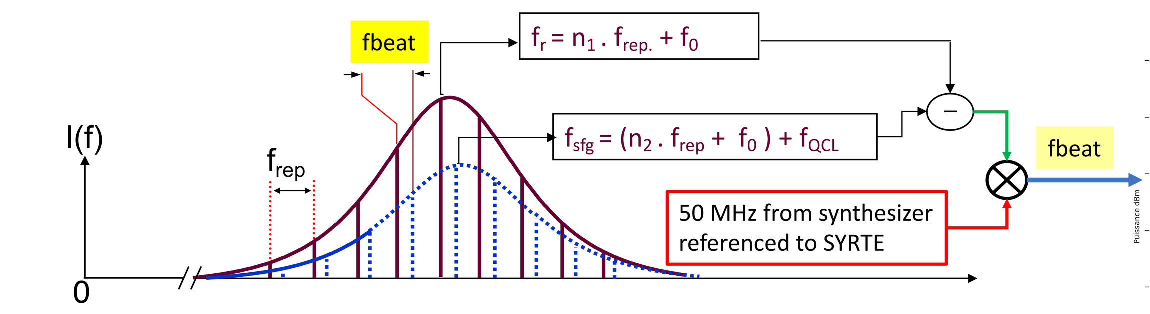
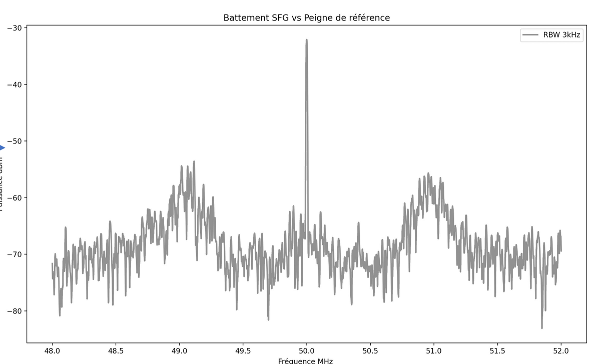
At Sorbonne-Université, we have developed a SI traceable mid-infrared QCL spectrometer for the investigation of ozone and other molecules of atmospheric and astrophysical interest. Ozone, in particular, has unresolved issues in the mid-IR spectral region at 9.5 µm, where large uncertainties and inconsistencies 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 fequency f_{sfg} 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_{rep} and the frequency offset f_0 , both SI traceable.



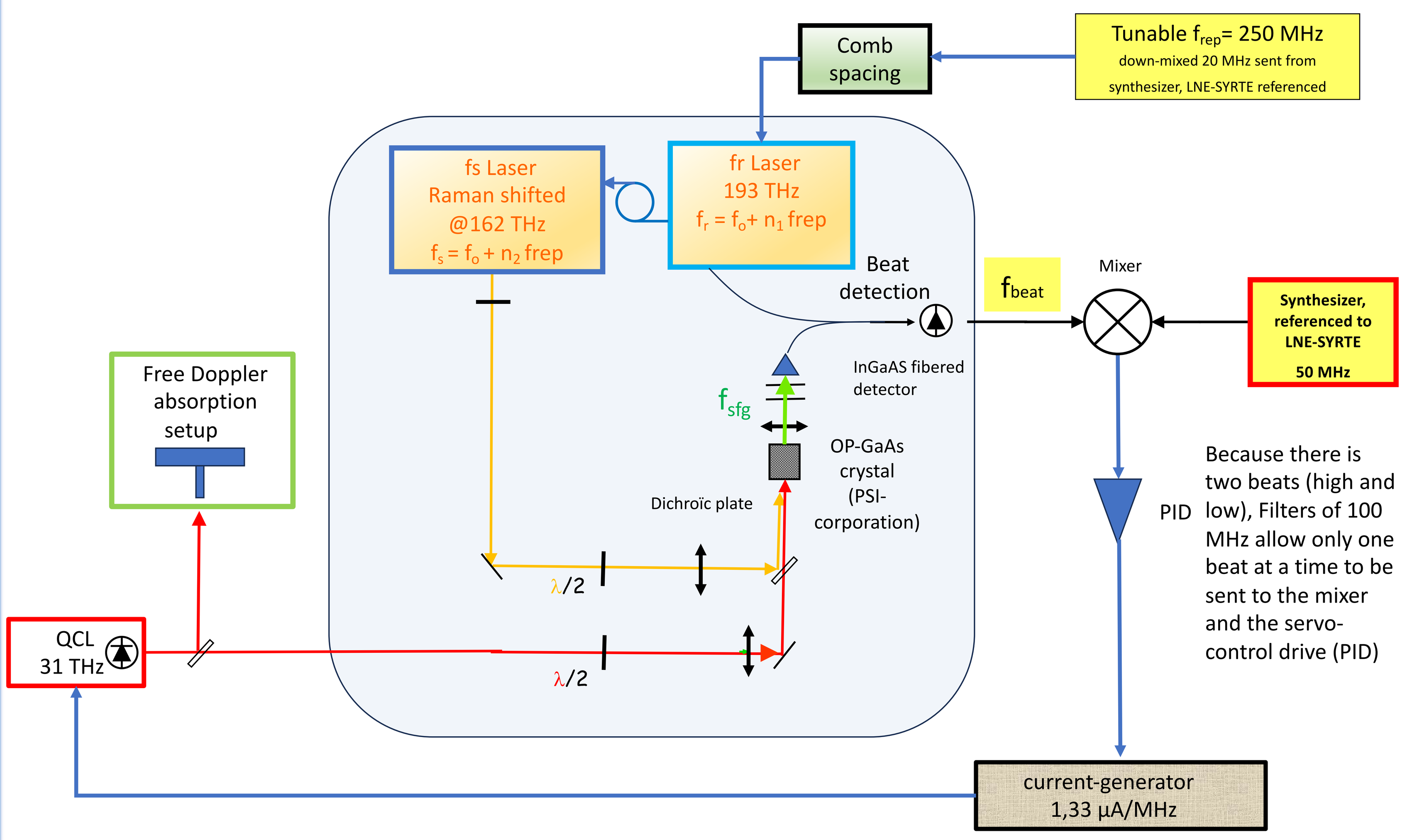
Beat signal at 50 MHz, when QCL is locked



f_{sfg}- f_r = f_{beat} = $(n_2 – n_1) f_{rep} + f_{QCL}$; $(n_1 – n_2)$ is an integer ~ 125 847.

The f_{rep} around 250 MHz is controlled by a f_{down} = 20 MHz synthesizer as : $f_{rep} = 245 \text{ MHz} + \frac{f_{down}}{4}$

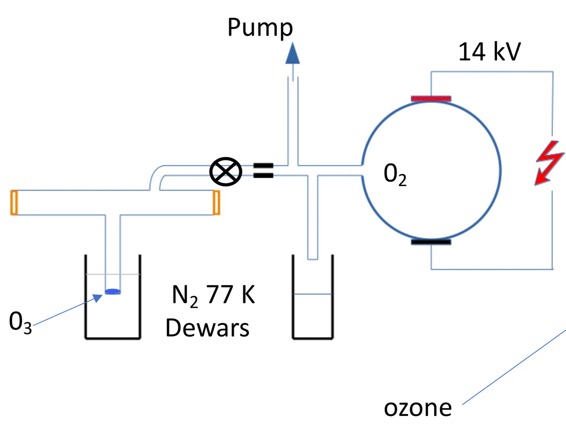
Changing fdown by 0.1 Hz, alters f_{rep} and thus f_{qcl} by 3.1 kHz

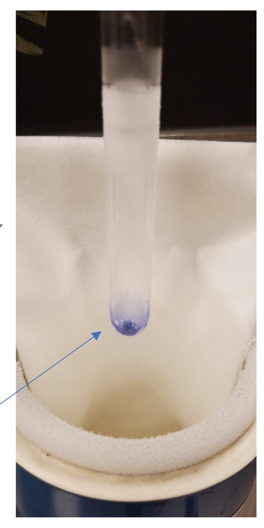


Because there is two beats (high and low), Filters of 100 MHz allow only one beat at a time to be sent to the mixer and the servo-control drive (PID)

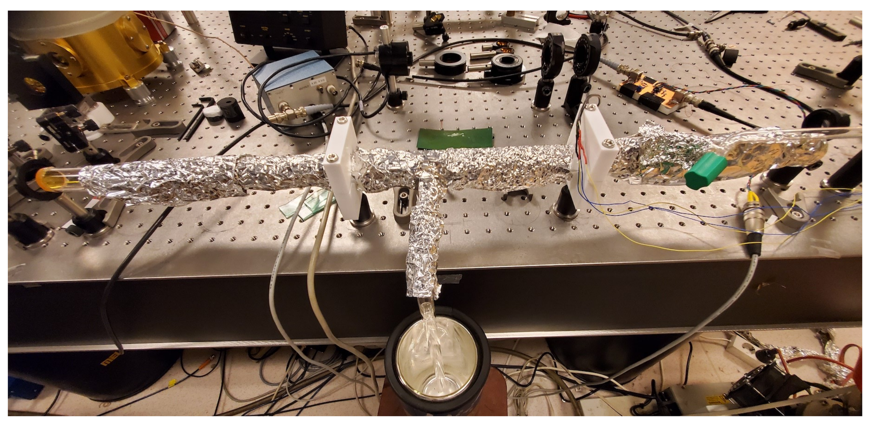
Ozone, Doppler and Doppler-free spectroscopy setup

Ozone production

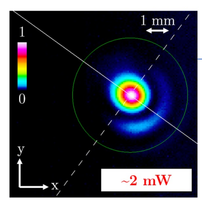


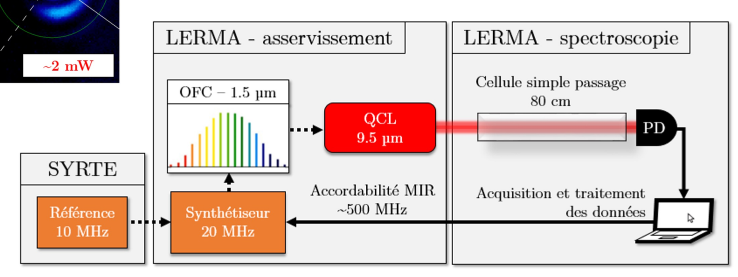


80 cm cell, ozone at 77 K for 2mtorr vapor pressure at 293 K

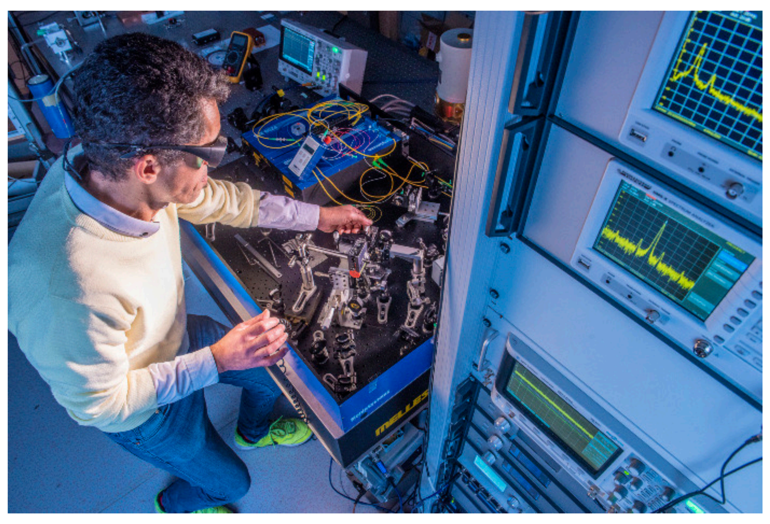


Beam profile at the entrance of the cell

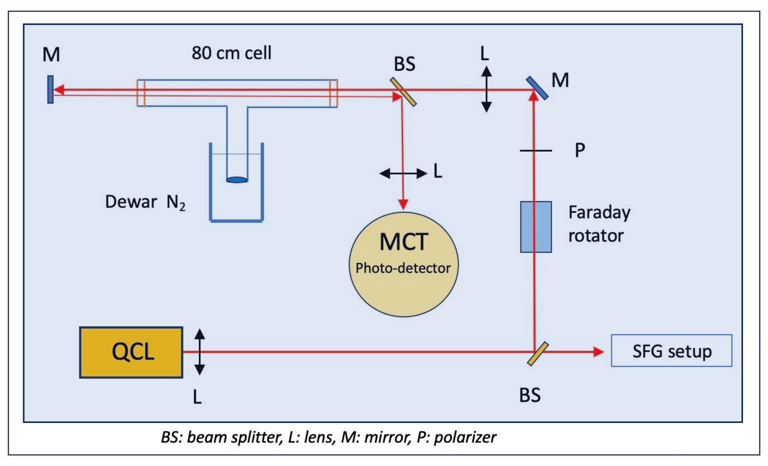




Sum frequency generation laser comb at 1,85 µm + QCL-laser at 9.5 µm. Beat detection using laser comb at 1.55 µm

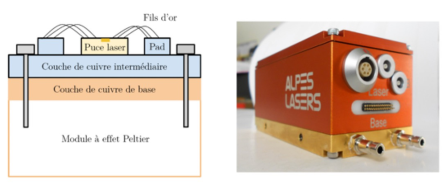


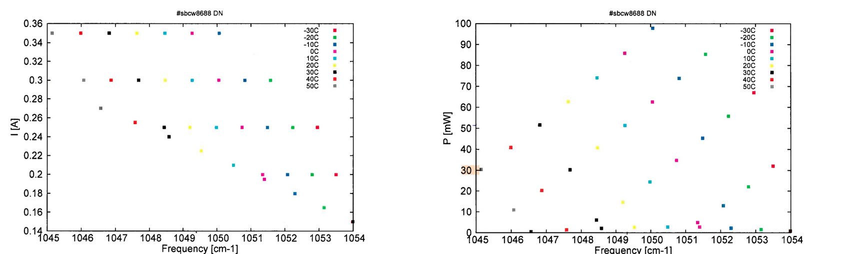
Setup for Doppler free absorption measurements



BS: beam splitter, L: lens, M: mirror, P: polarizer

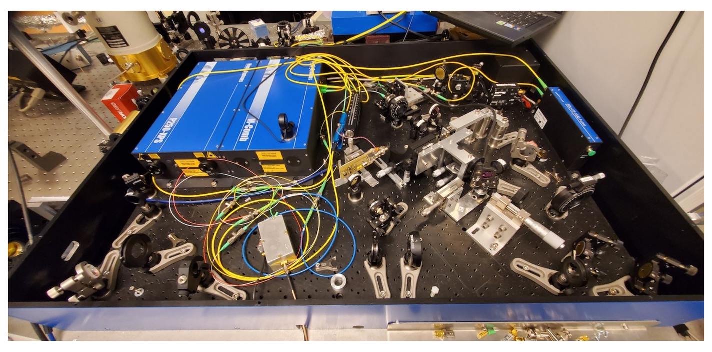
Spectrometer instrumentation



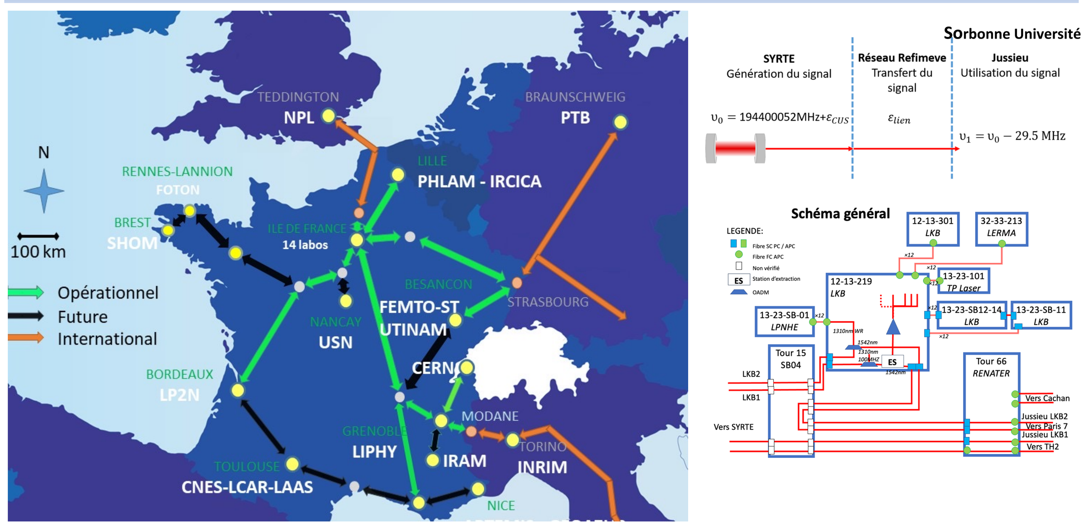


Input current as a function of the single mode emission frequencies and temperature

Ouput 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

$f_{sfg} = n_2 . f_{rep} + f_0 + f_{QCL}$

$f_r = n_1 . f_{rep.} + f_0$

$f_{(beat)} = f_{sfg} – f_r$

The QCL frequency can be written as :

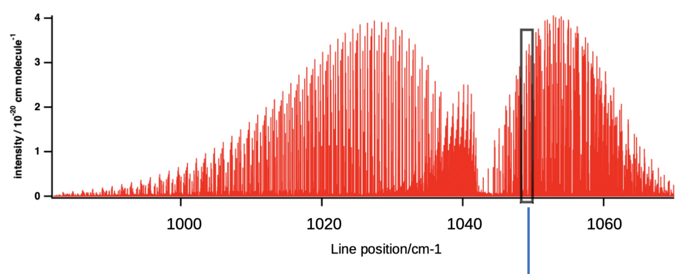
$f_{QCL} = (n_1 – n_2)\, frep + f_{beat}$

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.

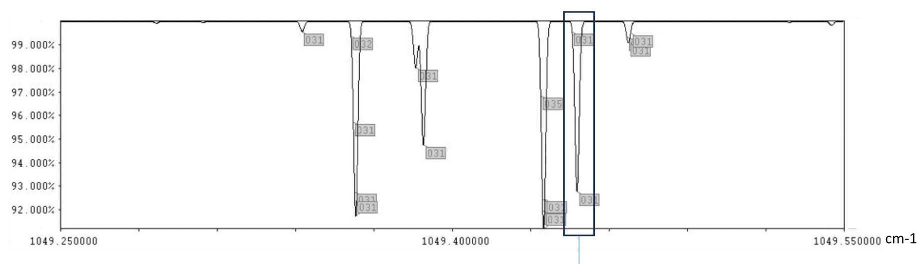
Ozone spectrum and lines measurement

As a first demonstration of the spectrometer perfomances, we report on ozone line positions in the v_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.

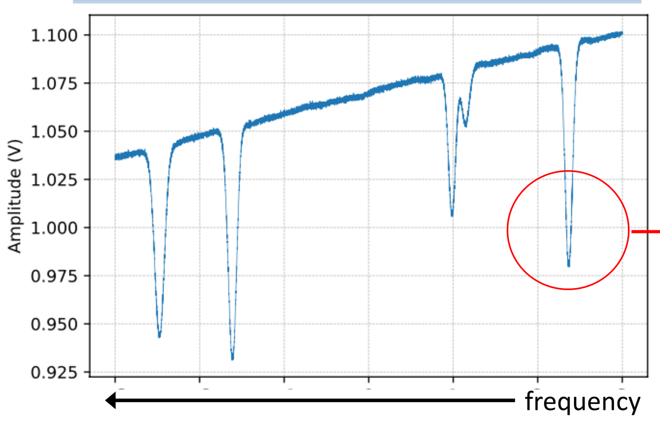
Ozone spectrum Hitran-database



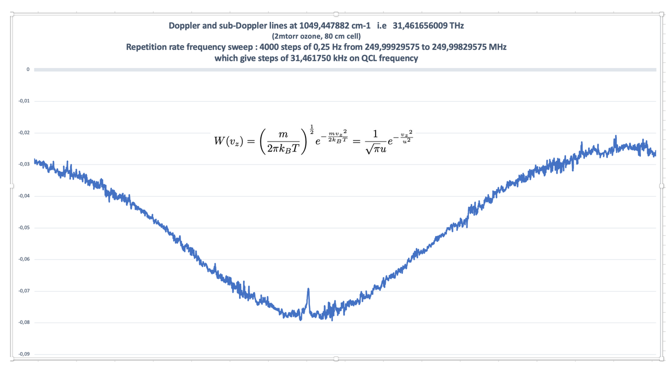
Simulation 80 cm cell, 2 mtorr ozone pressure at 293 K



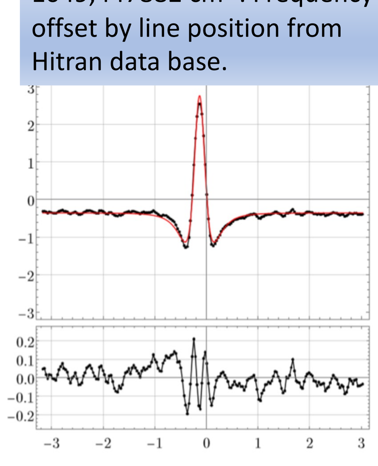
QCL down frequency sweep by current ramp



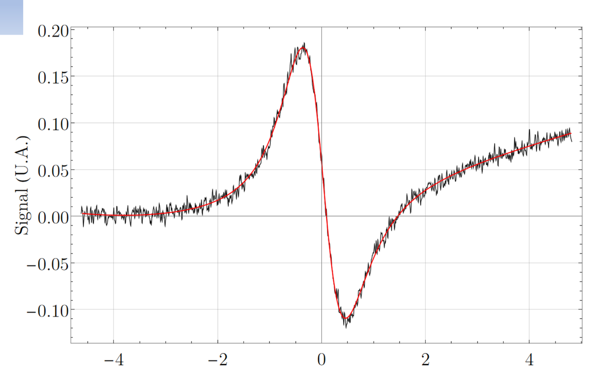
QCL frequency tuning by sweeping OFC repetition rate while locking QCL on OFC



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 $^{16}O_3$ using sub-Doppler spectroscopy.
- Improvement towards <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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