High-precision mid-IR molecular spectroscopy with frequency-stabilised Quantum Cascade Laser

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Outline

I. Motivation: high-precision experiments with molecules

II. QCL frequency stabilization and tuning

III. Application to high-resolution spectroscopy

With financial support from

- OFTEN project from European Metrology Research Programme EMPIR
- Agence Nationale de la Recherche with Labex First-TF and PVCM project
- Région Ile-de-France (DIM Nano-K)
- CNRS and Université Paris 13.

High precision experiments with molecules

- Molecules are complementary to atoms to study very tiny effects of fundamental physics
  - more complex structure, more richer physics
  - molecules may be more sensitive to certain effects
  - fundamental tests of physics
    - Electric Dipole Moment of the electron (ThO, De Mille,Gabrielse,Doyle)
    - Fundamental constants measurement (k_B, U. Napoli & LPL, $m_e/m_{p,}$ U. Dusseldorf & LKB) and time-space variation (LPL, VUA, LENS)
    - Test of the symetrization postulate ($O_{2,}$ CO_2, G. Tino)
    - Parity violation (due to weak interaction)(LPL)
- Most of these experiments are based on high resolution spectroscopy

High precision molecular spectroscopy

- Our objectives
  - Probe molecular absorption lines at low pressure, with a linewidth 10 kHz to 100 Hz
  - Achieve an absolute uncertainty of the frequency scale better than a few kHz, possibly < 0,3 Hz (10^{-14})

- Mid-IR Quantum Cascade Laser (QCL)
  - widely tunable, available in all the mid-IR, mW to W power levels, compact
  - But free-running linewidth ~1 MHz → frequency stabilisation needed
  - Challenging: frequency uncertainty (accuracy) down to 10^{-11}-10^{-15}
    - Uncertainty of a commercial spectrometer > 10 MHz / 3×10^{-7}

Probing molecules with Quantum Cascade Lasers

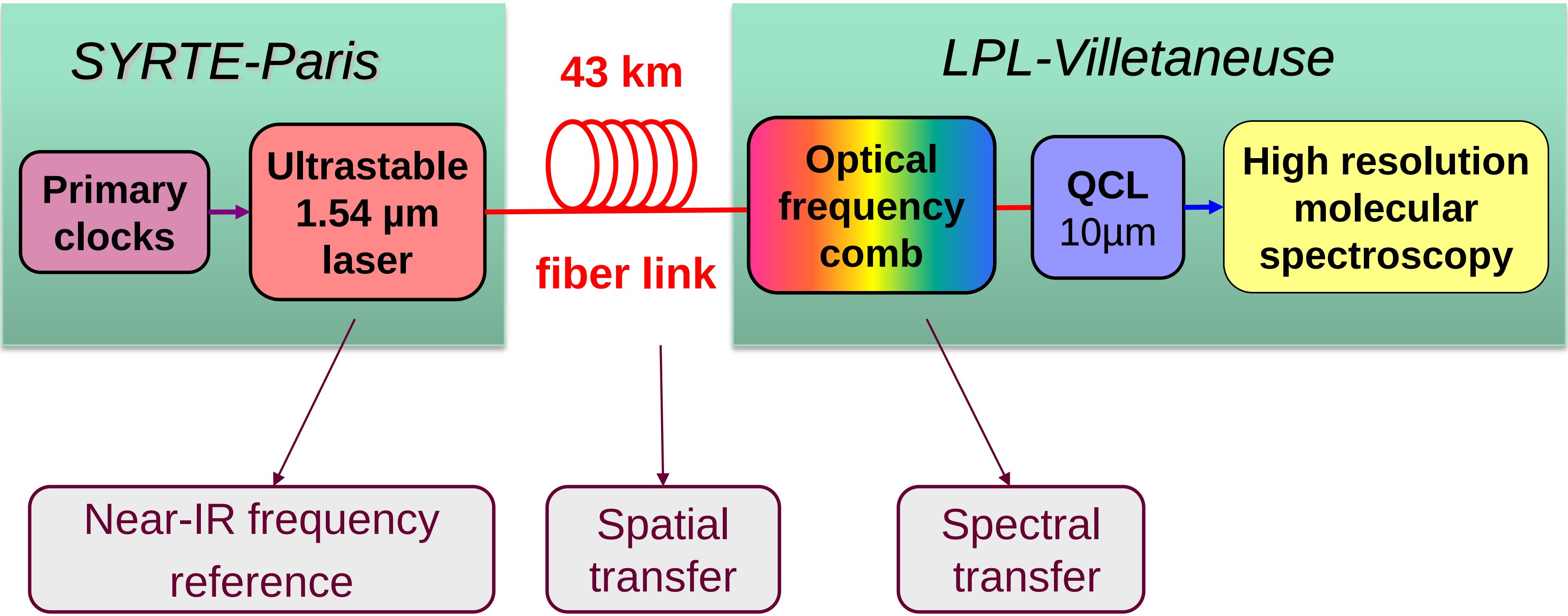
- Frequency stabilization techniques developed since 15 years
  - Fabry-Perot cavity, molecular line, injection, phase-locking to a frequency standard...

    → stability ≥ a few 10^{-14} , accuracy ≥ 10^{-12}

    → limited by mid-IR frequency reference
- To go further, near-IR frequency reference+primary standard !
  - Near-IR ultrastable lasers have record stability and can be monitored to primary standards in metroly institutes
  - Bridge the gap between NIR and MIR with an optical frequency comb

  → Stability and/or accuracy of the best frequency standards transferred to the mid-IR laser

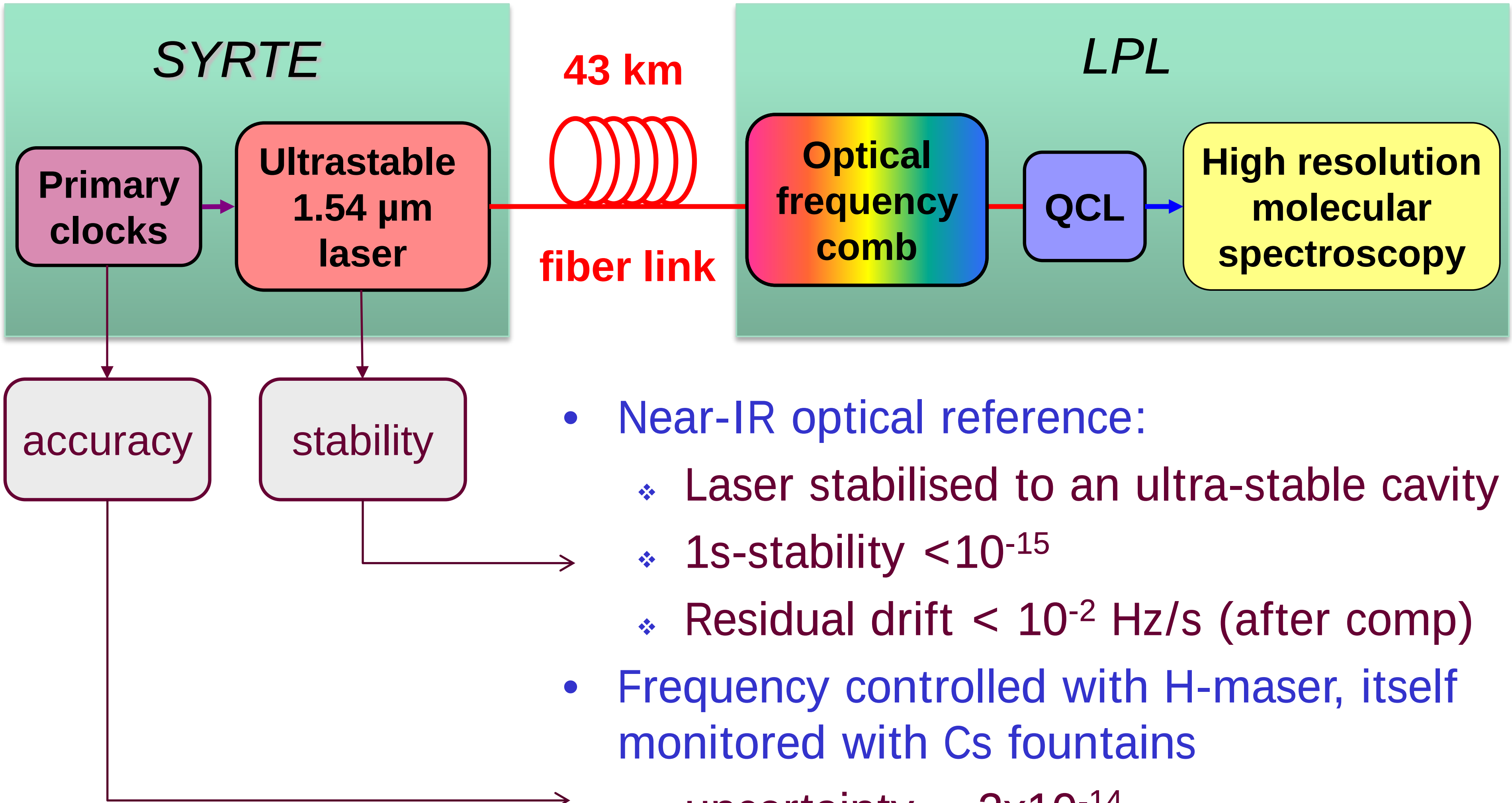
QCL stabilization onto a NIR frequency reference



Argence et al, Nat. Photon. 2015,

see also similar set-up around 6 µm with a 642-km optical link between Turin and Florence, G. Insero et al, Scientific Reports 2017

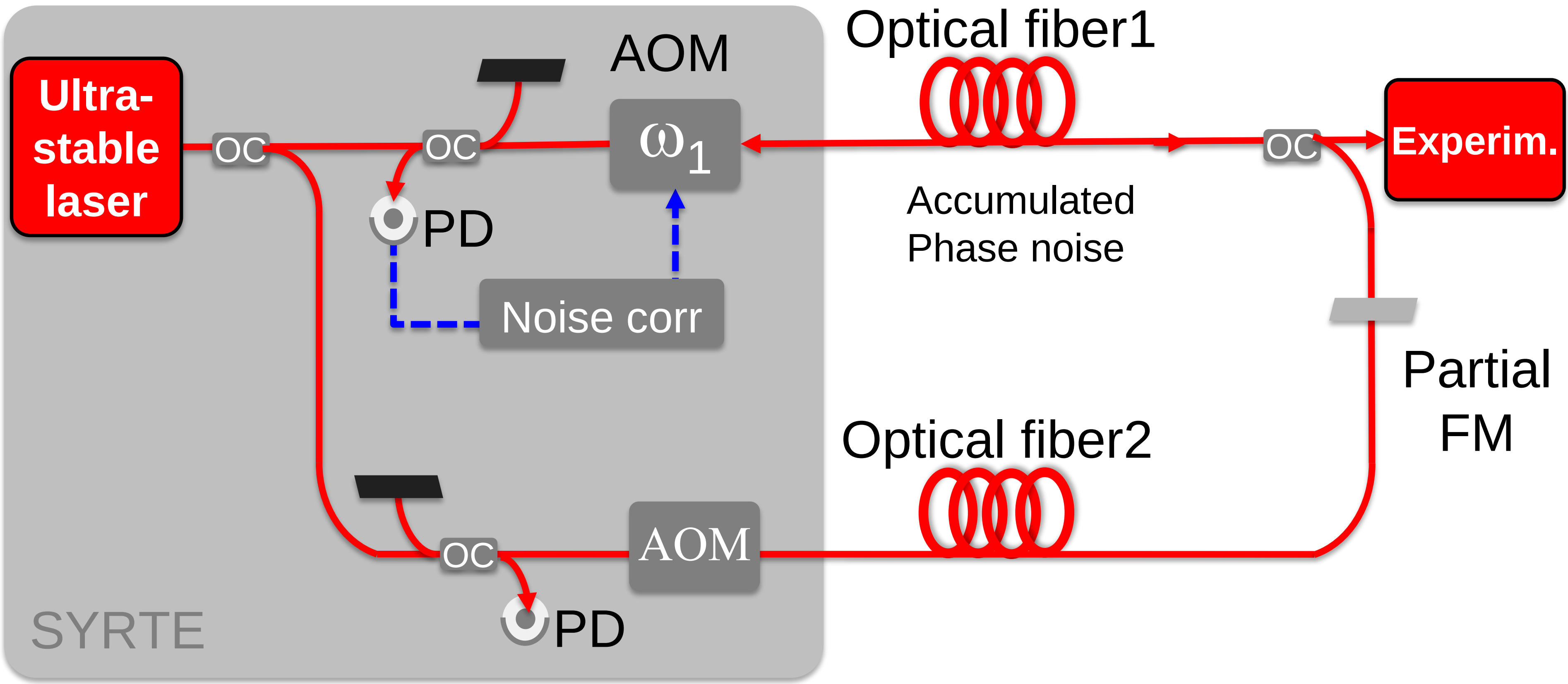
The remote frequency reference



- Near-IR optical reference:
  - Laser stabilised to an ultra-stable cavity
  - 1s-stability $<10^{-15}$
  - Residual drift $< 10^{-2}$ Hz/s (after comp)
- Frequency controlled with H-maser, itself monitored with Cs fountains
  - uncertainty ~ $2\text{x}10^{-14}$

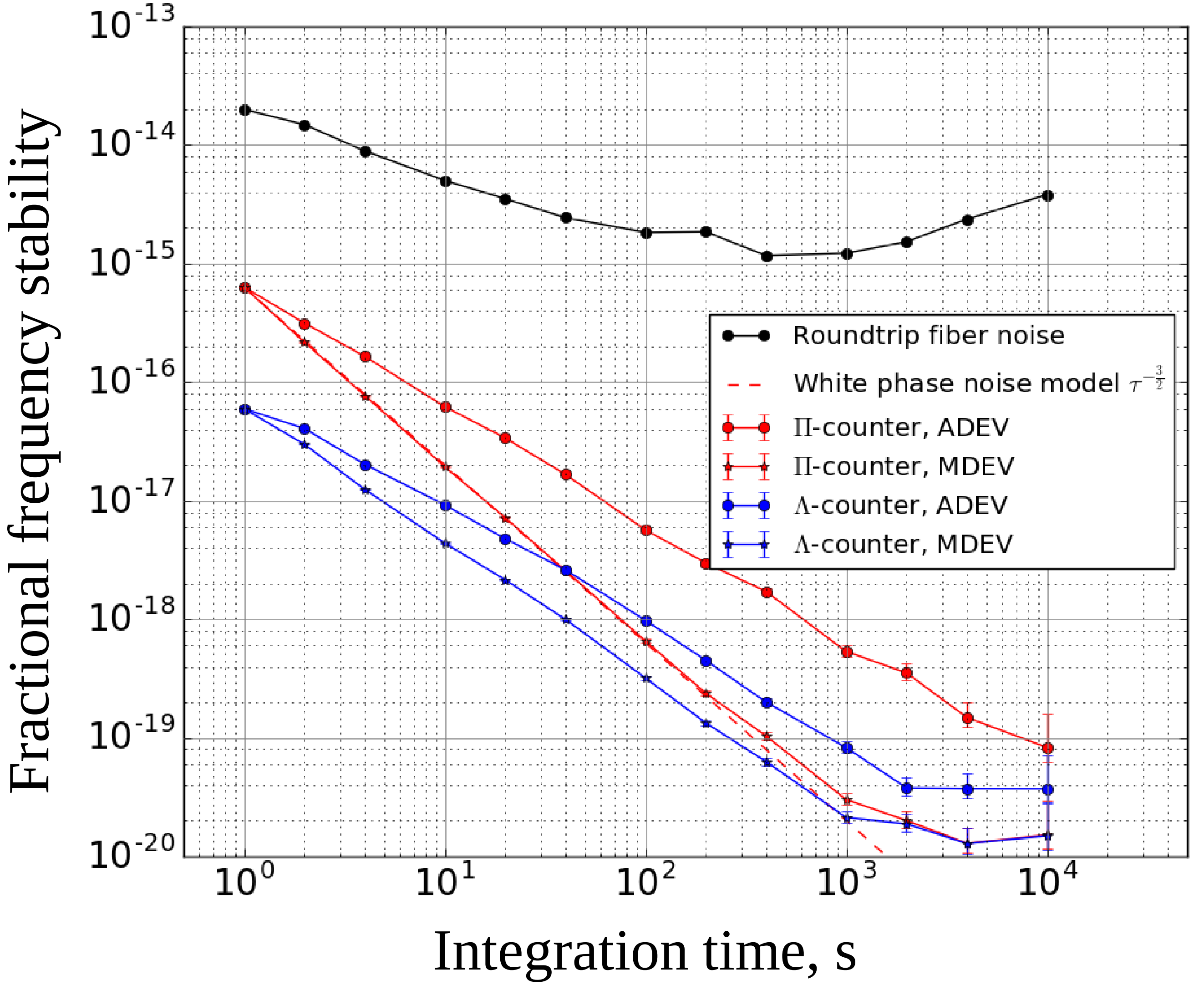
43-km optical link between SYRTE and LPL

2 parallel dark fibers: fiber1 with active noise compensation
fiber2 assessment of the link performance by two-way frequency comparison



W K Lee et al, APB 2017, D. Xu et al, OE 2018

Frequency stability of the 43-km fiber link



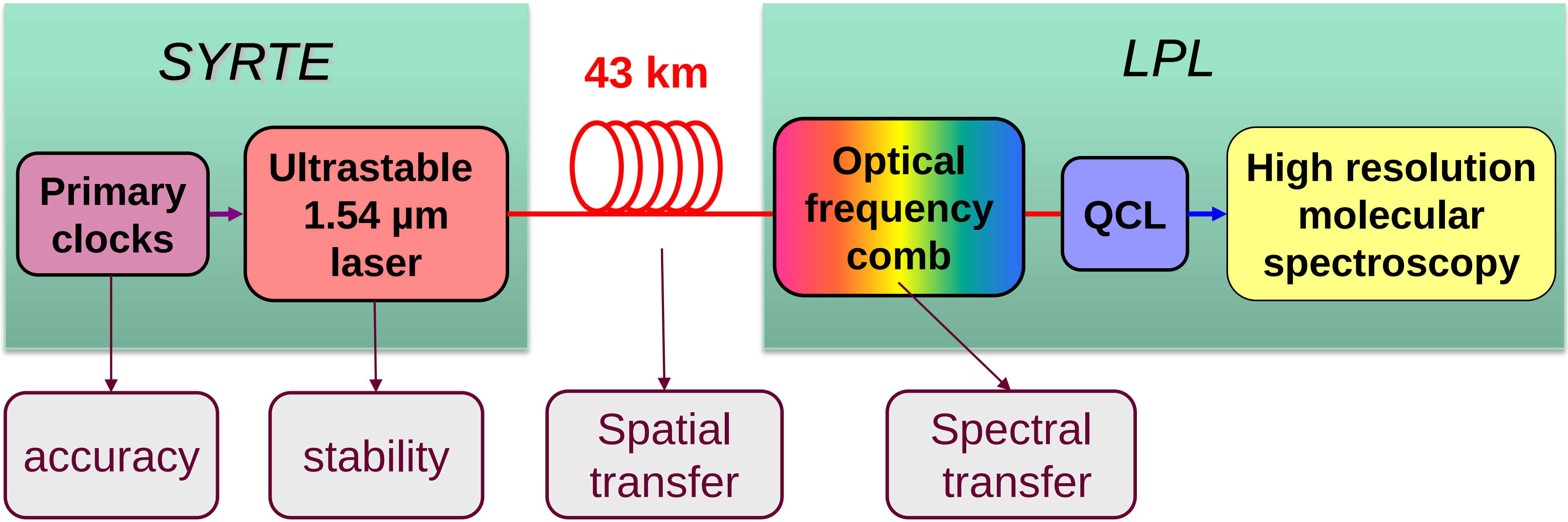
Π-type counter

Overlapping Allan deviation
$<10^{-15}$ at 1s
$<10^{-19}$ at 10^4 s

Accuracy: 4×10^{-20}

For longer link (a few hundreds of km), residual noise is higher and only long-term stability and accuracy are preserved

Stability transfer using an optical frequency comb



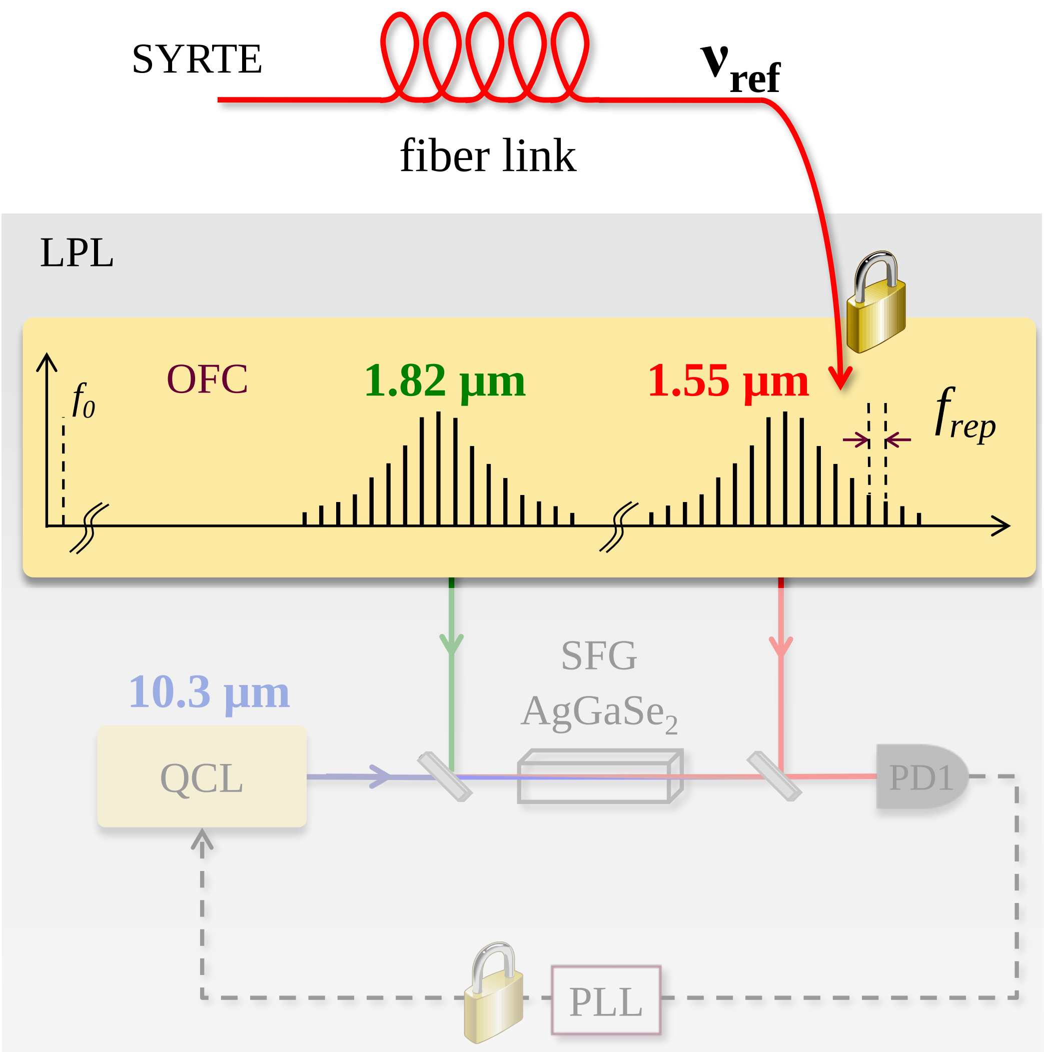
Near-IR frequency reference

- 1s-stability ~10^{-15}
- Uncertainty ~2×10^{-14}

Optical fiber link

- Transfer without any degradation of the stability and uncertainty
- Residual noise: $10^{-15}\ \tau^{-1}$ from 1 to 10^4 s

QCL frequency stabilization (1)



Comb locked to optical reference

a) Beatnote between a comb mode ($N f_{rep} + f_0$) and the frequency reference

$$\Delta = \nu_{ref} - (N f_{rep} + f_0)$$

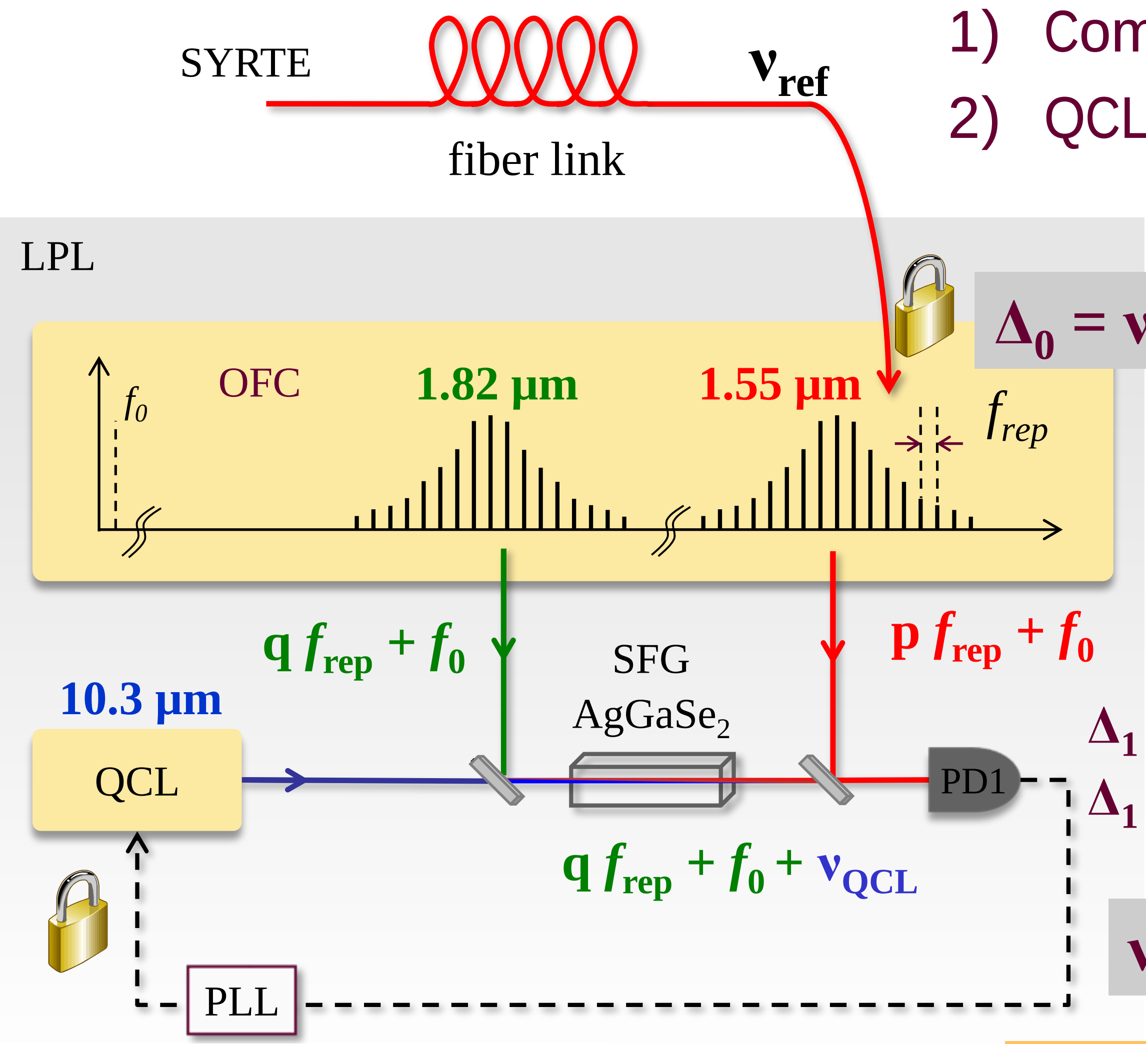
b) Remove comb offset f_0 (by mixing with f_0 beatnote)

$$\Delta_0 = \nu_{ref} - N f_{rep}$$

c) Process this phase-error signal with a phase-lock loop to lock comb repetition rate to the SYRTE remote reference

QCL frequency stabilization (2)

1) Comb locked to optical reference
2) QCL locked to comb



$$\Delta_0 = \nu_{ref} - N f_{rep}$$

$$\Delta_1 = (q f_{rep} + f_0 + \nu_{QCL}) - (p f_{rep} + f_0)$$

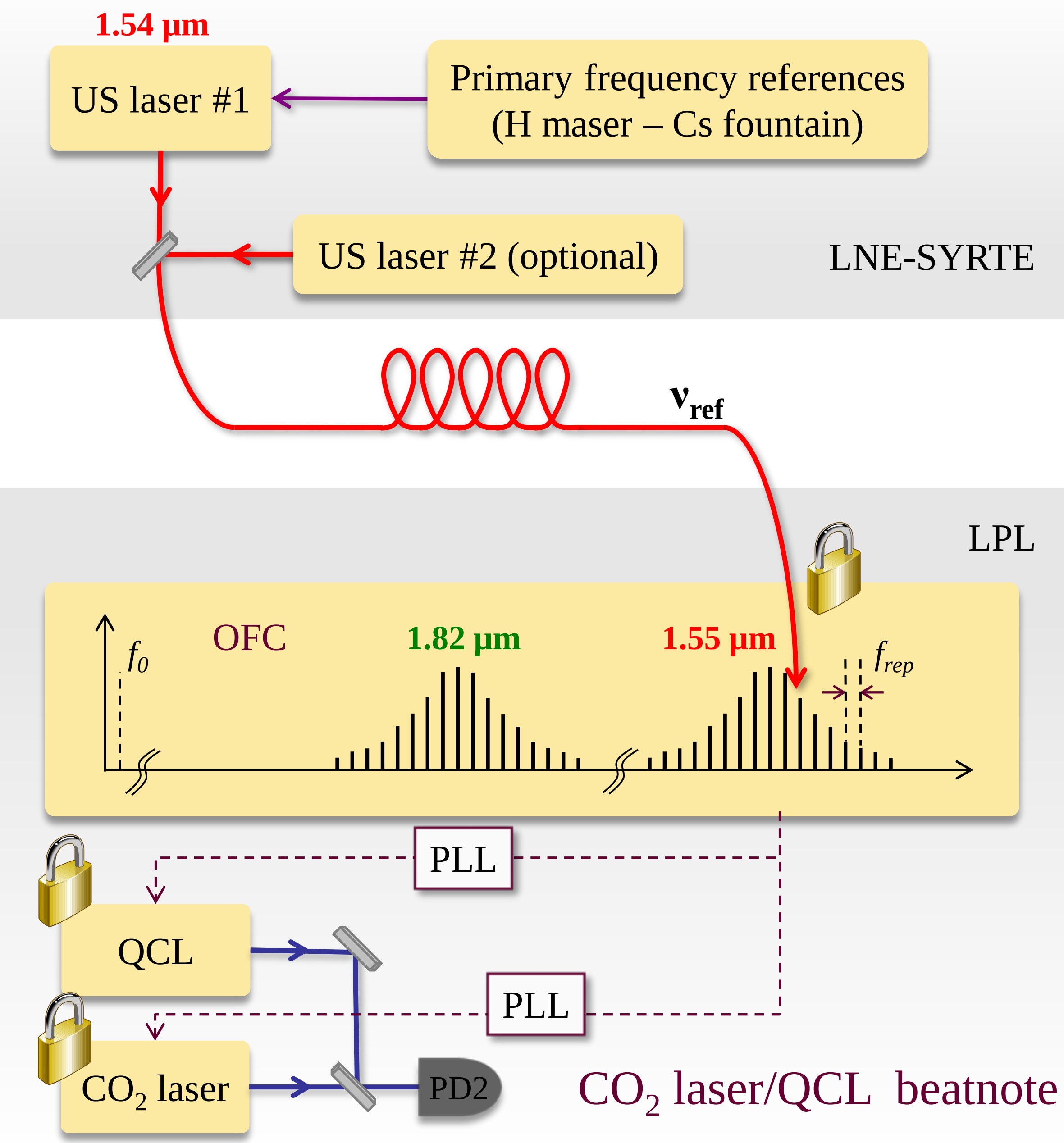
$$\Delta_1 = \nu_{QCL} - (p-q) f_{rep}$$

$$\nu_{QCL} = n f_{rep} + \Delta_1$$

$$\nu_{QCL} = \frac{n}{N}(\nu_{ref} - \Delta_0) + \Delta_1 \sim \frac{n}{N}\nu_{ref}$$

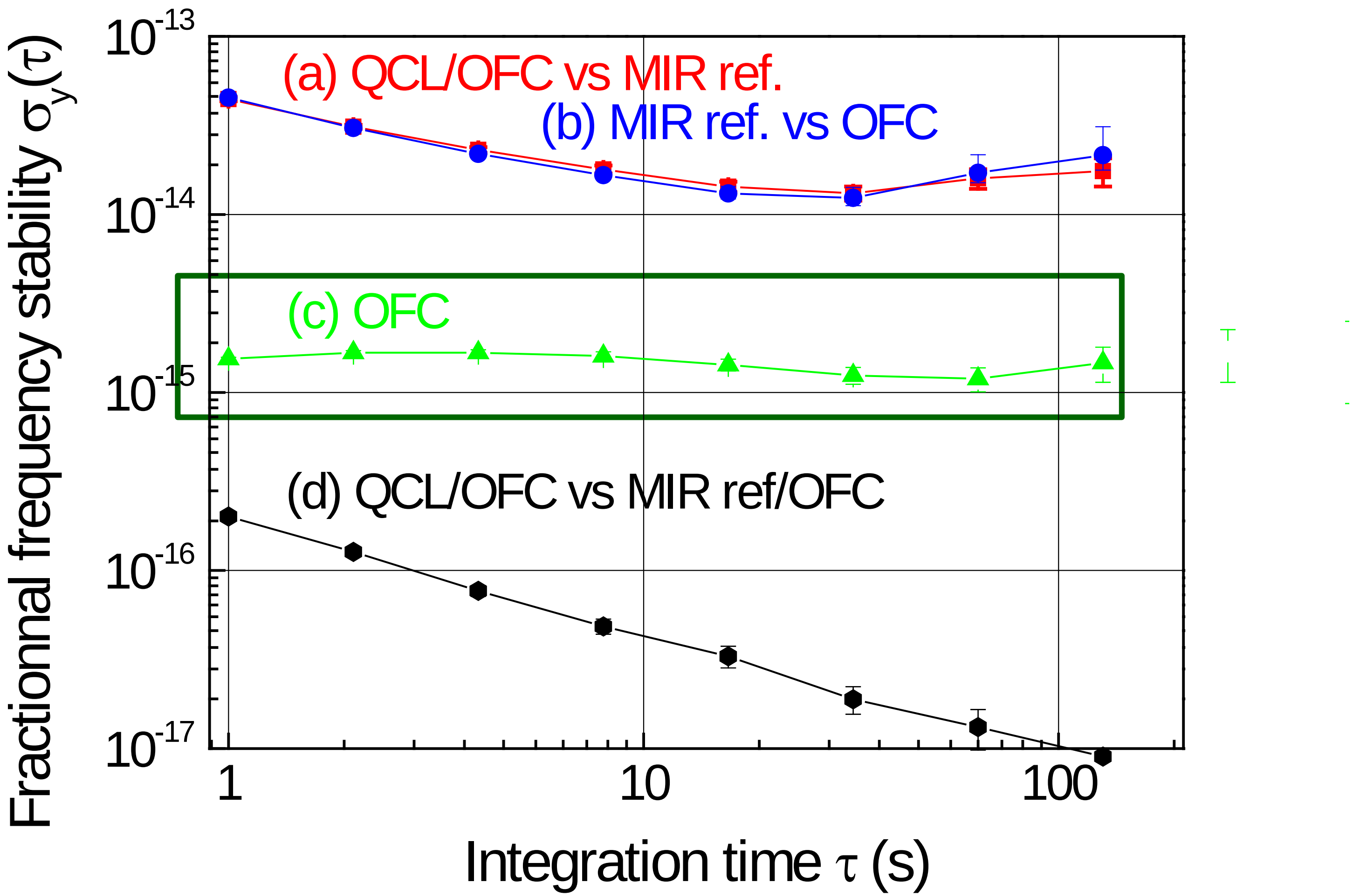
Sum-frequency generation
with 9-11 µm tunability

Measurement of the QCL stability



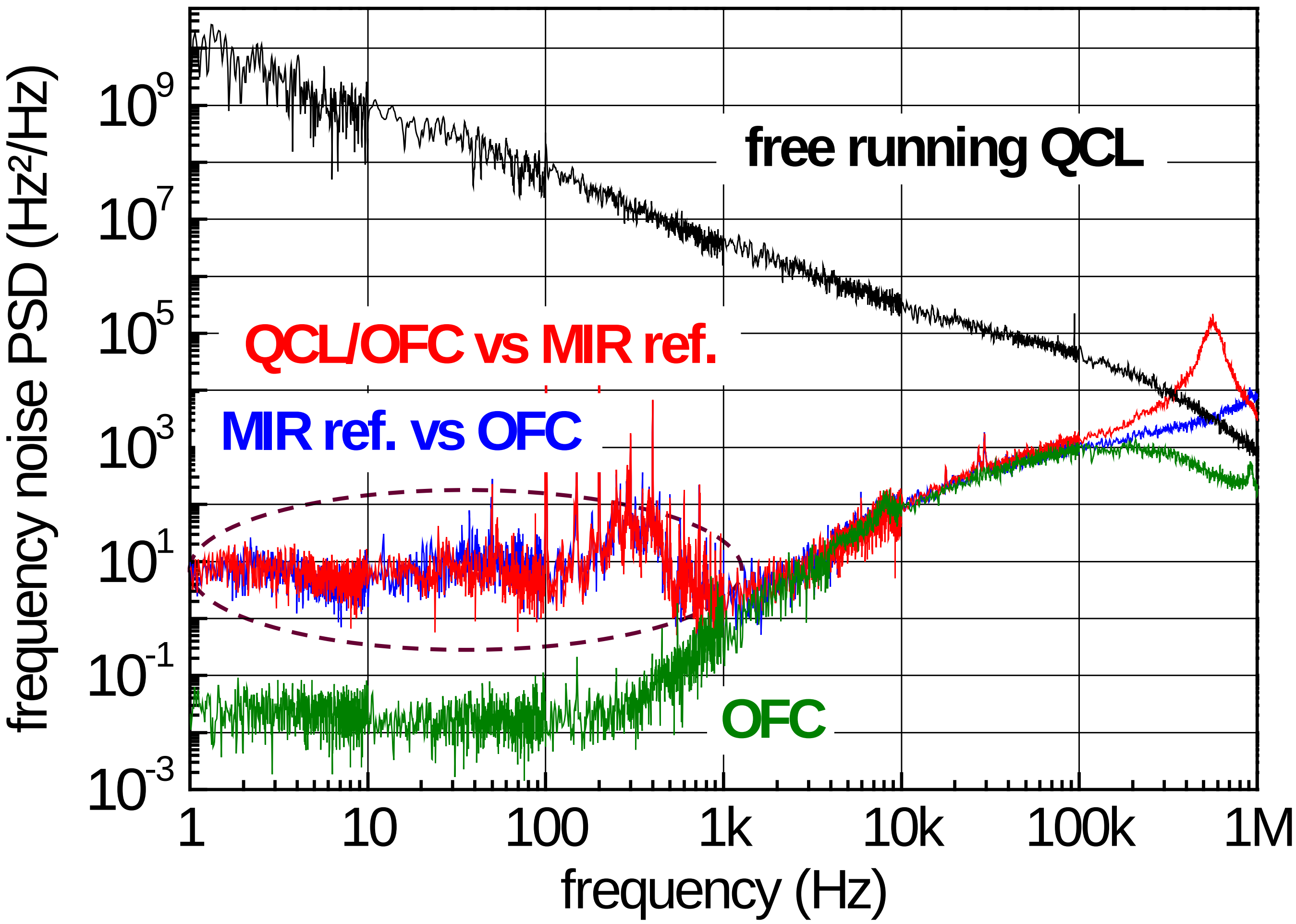
- Assessment of the comb stability with a second ultrastable laser
- Assessment of the PLL performance by locking simultaneously the QCL and a CO_2 laser to the OFC

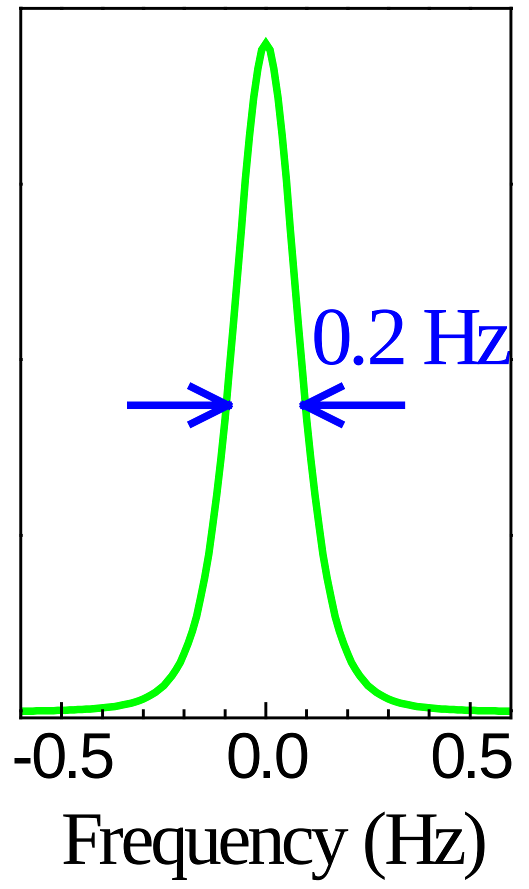
QCL frequency stability



⇒ QCL stability ~ 1,5x10^{-15} (0,05 Hz) from 1s to 100 s

QCL frequency noise & linewidth

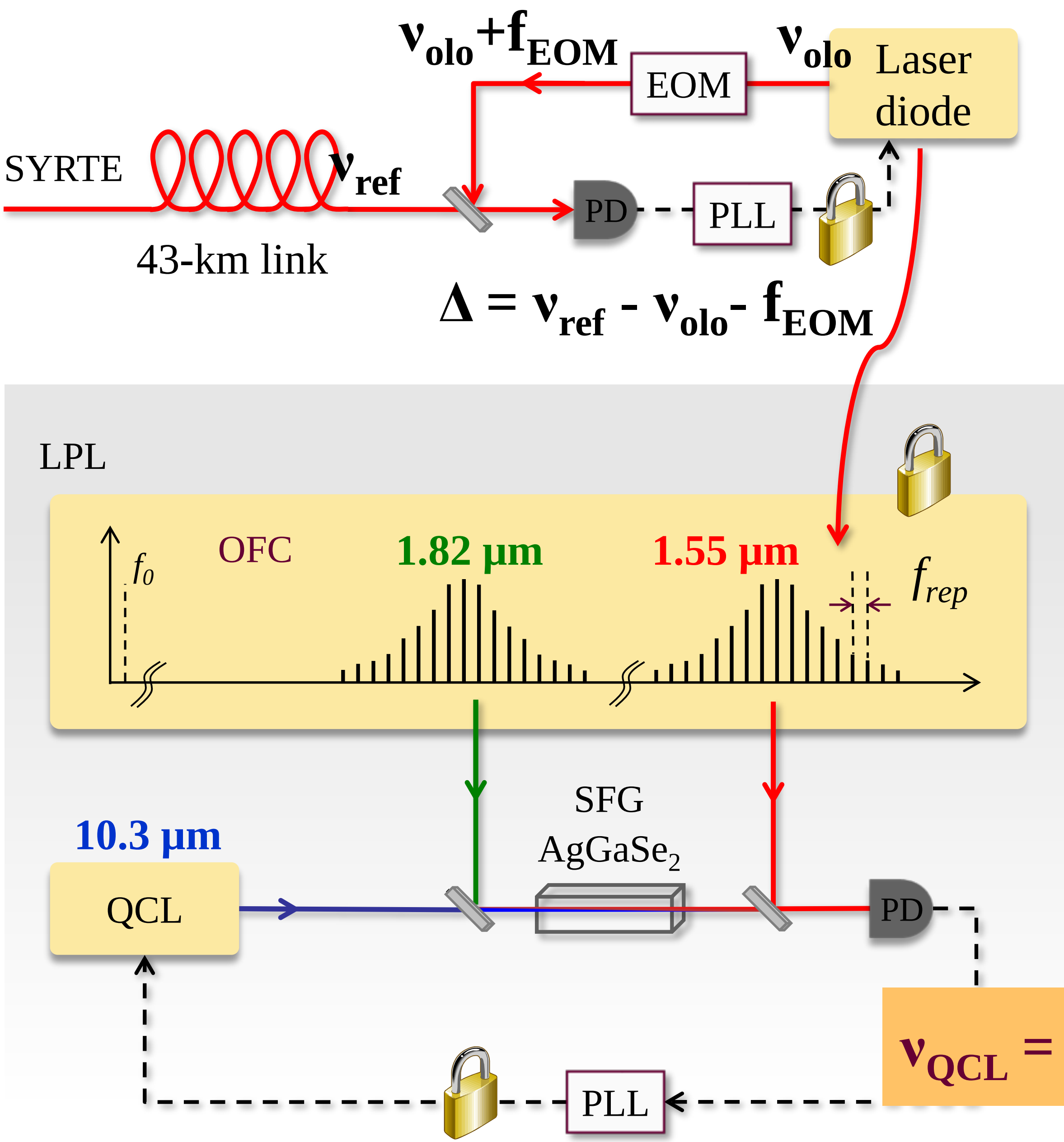




⇒ QCL frequency noise ~10^{-2} Hz^2/Hz between 1 and 100 Hz

⇒ QCL linewidth ~ 0,2 Hz ($7x10^{-15}$)

QCL frequency tuning



Laser diode sideband locked to the SYRTE reference

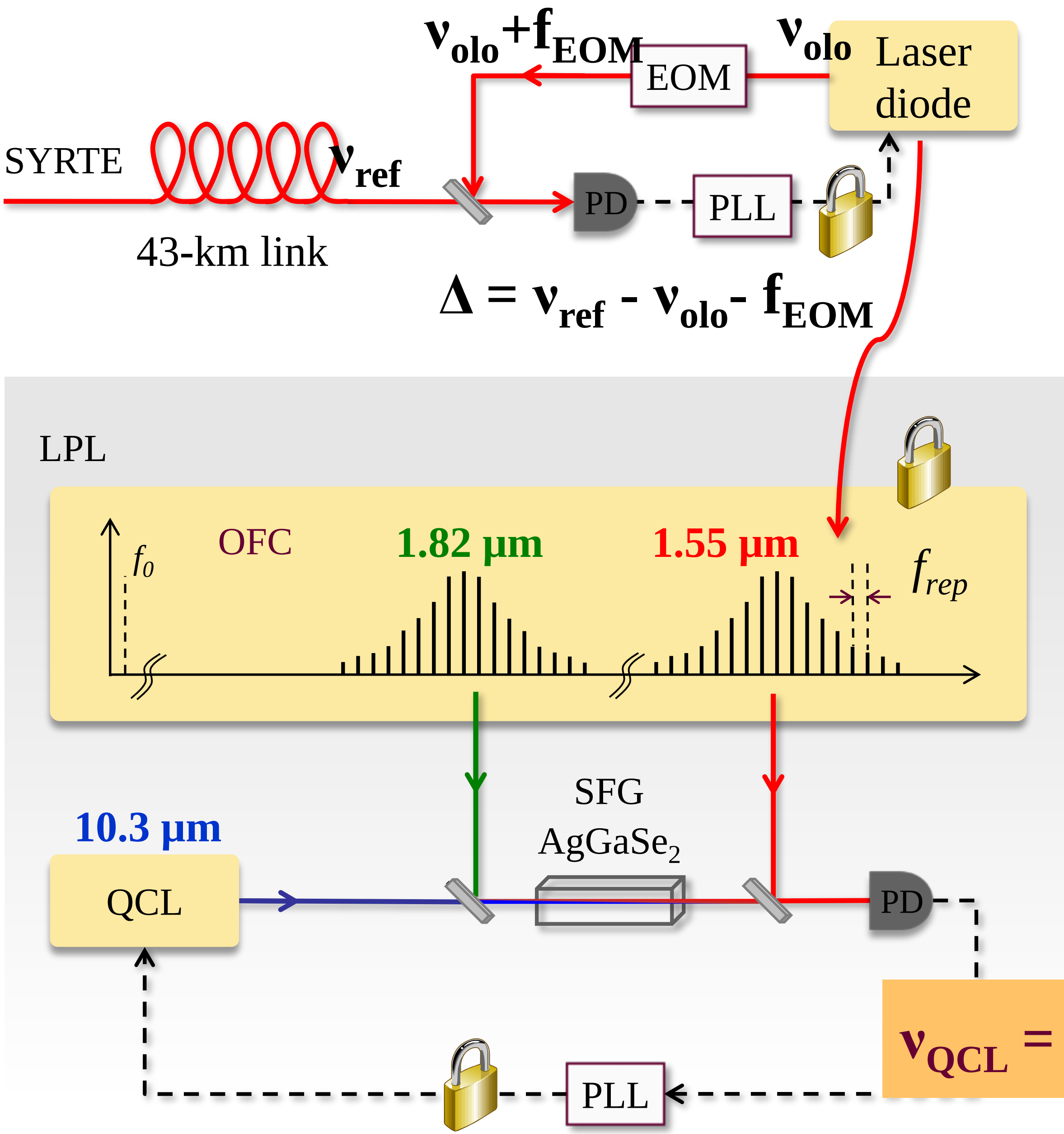
EOM tuned on 8,5 GHz

- ✓ Laser diode tuned on 8,5 GHz
- ✓ f_{rep} tuned on 10 kHz
- ✓ QCL tuned on 1,2 GHz

$$\nu_{QCL} = \frac{n}{N}(\nu_{olo} - \Delta_0) + \Delta_1$$

$$\nu_{QCL} = \frac{n}{N}(\nu_{ref} + f_{EOM} - \Delta - \Delta_0) + \Delta_1$$

QCL frequency tuning



Laser diode sideband locked to the SYRTE reference

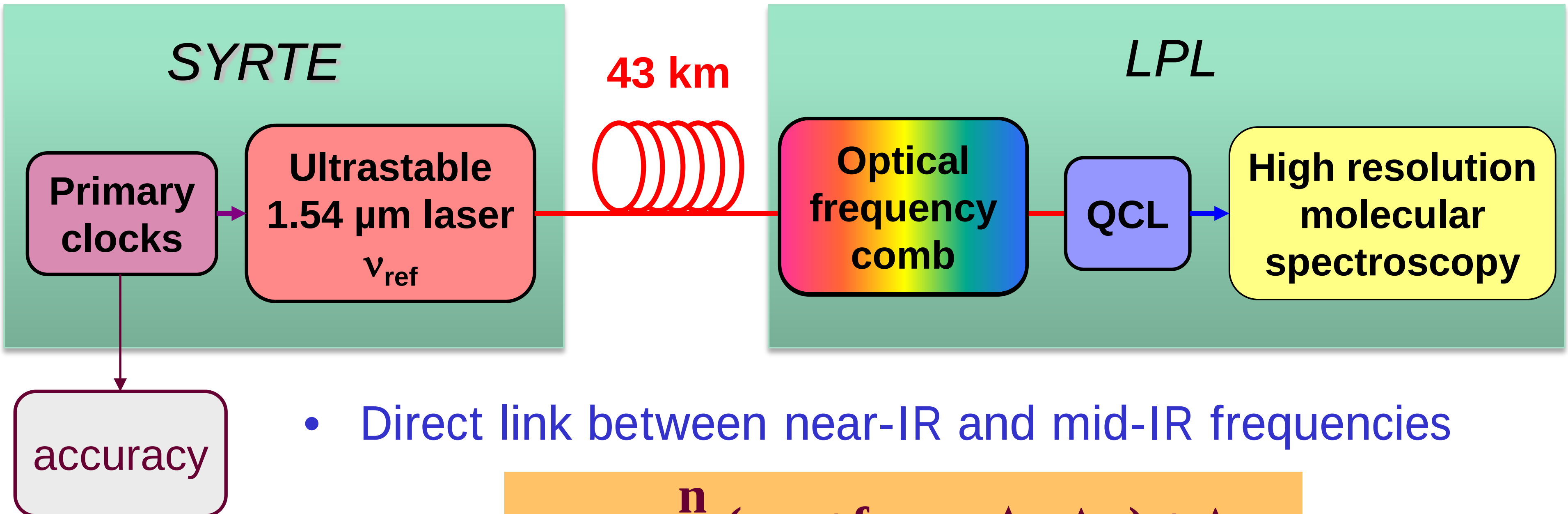
EOM tuned on 8,5 GHz

- ✓ Laser diode tuned on 8,5 GHz
- ✓ f_{rep} tuned on 10 kHz limited to 3 kHz
- ✓ QCL tuned on 1,2 GHz – limited to 400 MHz

$$\nu_{QCL} = \frac{n}{N}(\nu_{olo} - \Delta_0) + \Delta_1$$

$$\nu_{QCL} = \frac{n}{N}(\nu_{ref} + f_{EOM} - \Delta - \Delta_0) + \Delta_1$$

QCL frequency traceability to primary standards



- Direct link between near-IR and mid-IR frequencies

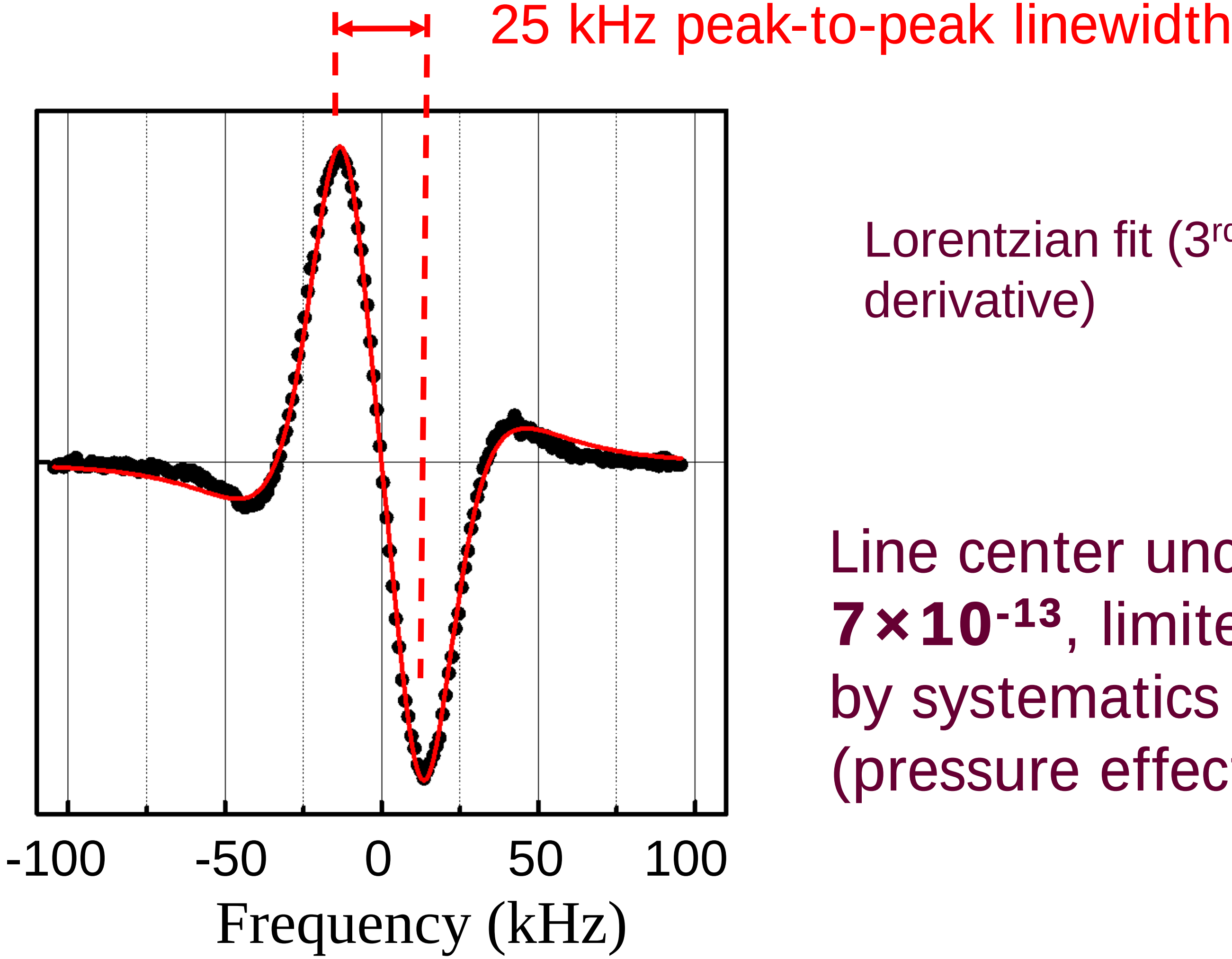
$$\nu_{QCL} = \frac{n}{N}\left(\nu_{ref} + f_{EOM} - \Delta - \Delta_0\right) + \Delta_1$$

Uncertainty ~ 4×10^{-14} (1 Hz) limited by the near-IR 1-s frequency measurement

Referenced to RF local oscillator disciplined to GPS + monitored to RF reference from SYRTE
Contribution to QCL unc: 10^{-15}

Saturated absorption spectroscopy of OsO_4

Absorption lines in the vicinity of the R(14) CO_2 line center

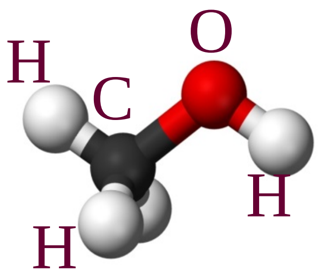


Lorentzian fit (3rd + 5th derivative)

Line center uncertainty **7×10^{-13}**, limited by systematics effects (pressure effects)

B. Argence et al, Nature Photonics 2015

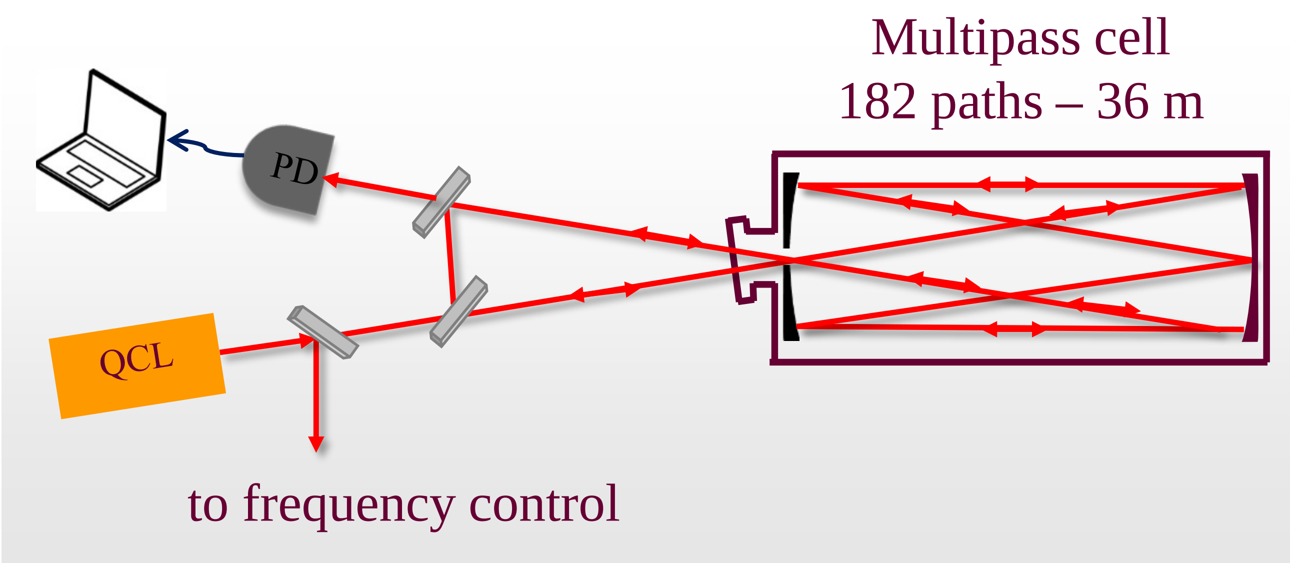
High-resolution spectroscopy of methanol



- One of the most abundant interstellar and protostellar molecules
  - Probe of interstellar clouds
  - Contribute to the “grass” of any radio astronomy spectrum
- Second most abundant organic molecule in earth’s atmosphere
  - Impact on air quality
- One of the simplest asymmetric-top molecule with hindered internal rotor
  - Fundamental spectroscopy

- Previous measurements of rovibrational lines
  - HITRAN data base – uncertainty $5x10^{-7}$ = 15 MHz
  - One measurement at a few kHz

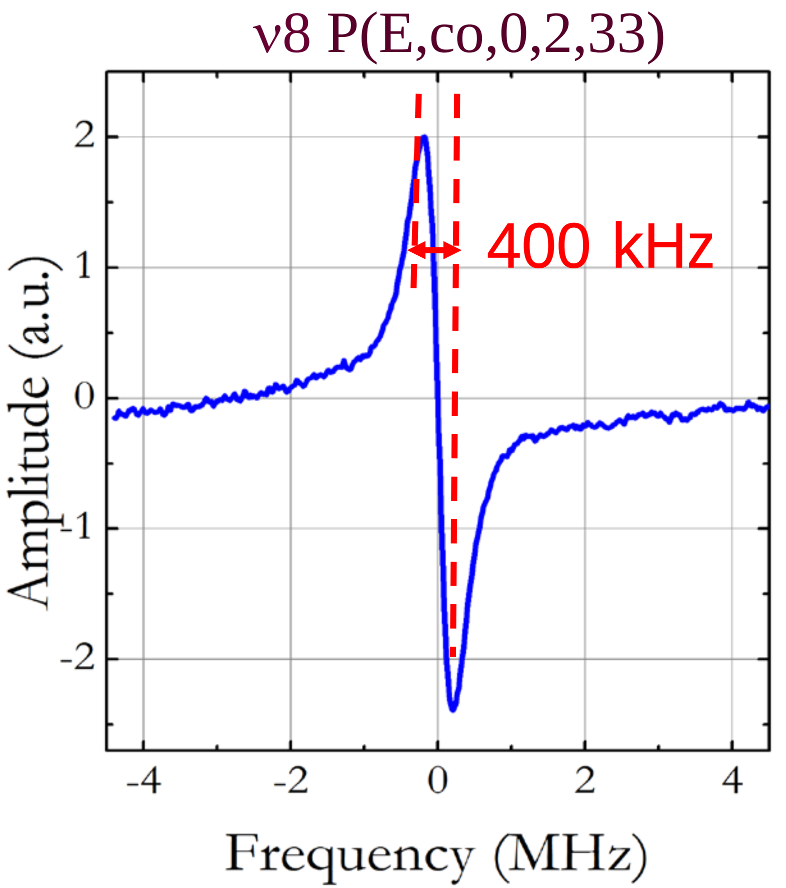
High-resolution spectroscopy of methanol



Saturated absorption in a multipass cell

- Spectroscopy at ~971.9443 cm^{-1} (29,133 THz or 10,3 μm)
- Frequency modulation, 1-f detection
- Pressure 7 μbar, power ~1-2 mW

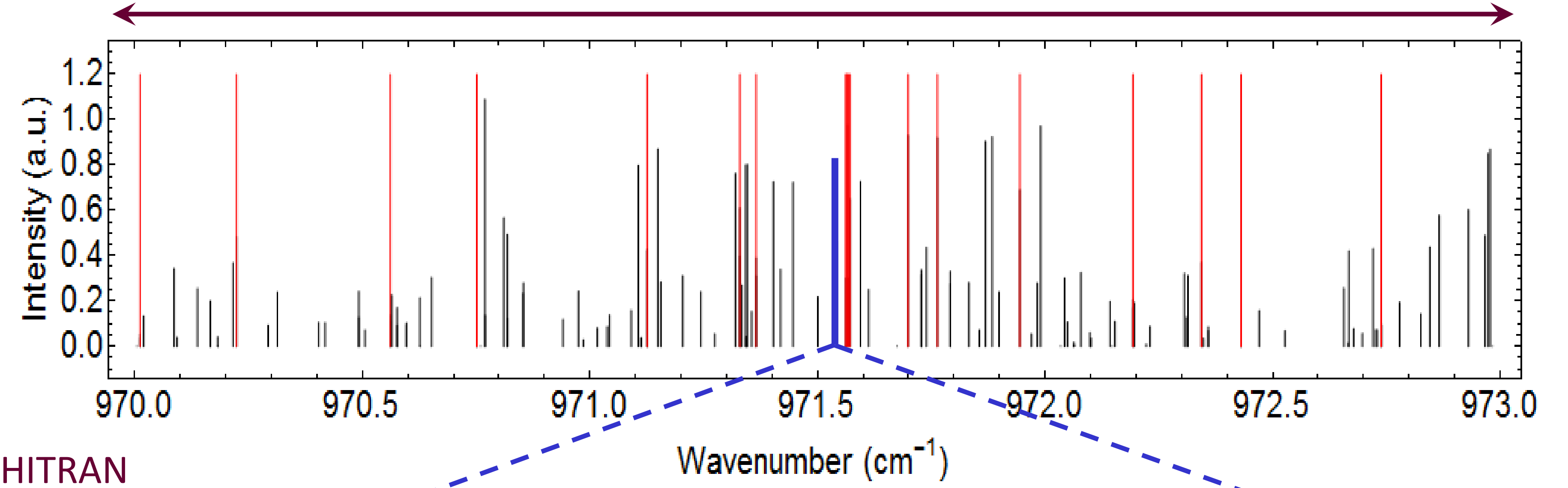
High-resolution spectroscopy of methanol



- Average of 5 up and down spectra, time constant of 2 s/point, frequency step: 15 kHz

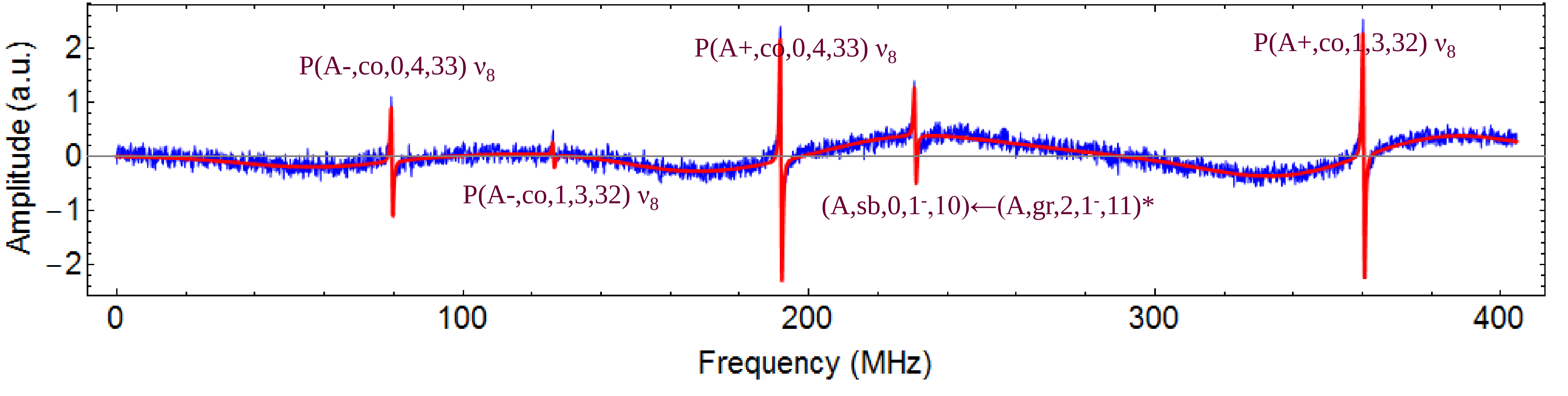
Spectroscopy of methanol: wide tunability

~100 GHz covered - 15 lines recorded

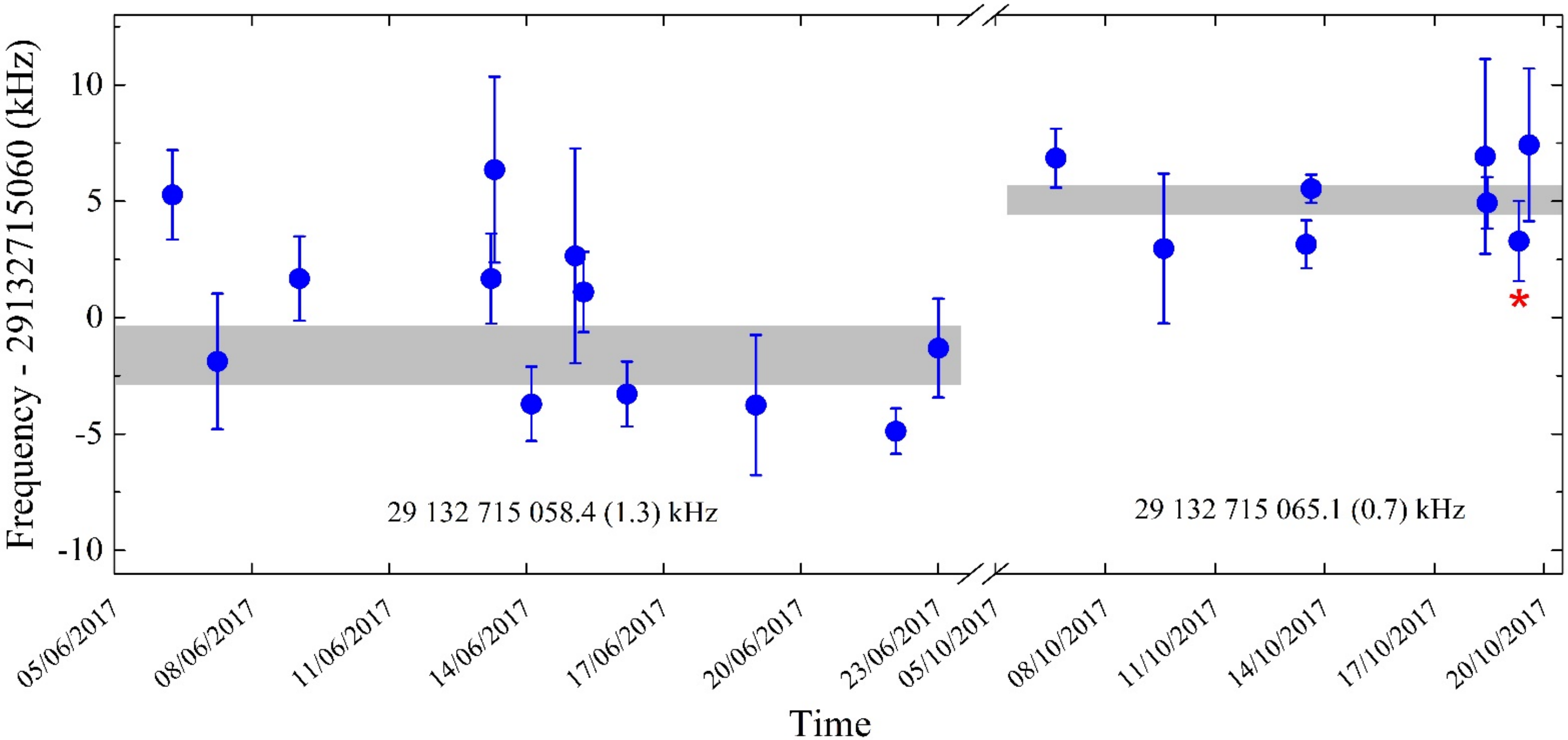


HITRAN simulation

~400 MHz, continuous tuning range (EOM)



High-precision frequency measurement



Frequency measurement of line ν8 P(E,co,0,2,33)

- 2 measurement campaigns
- Shift between two campaigns =power shift
- Improvment of statistical uncertainty with time

High-precision frequency measurement

Frequency measurement of line ν8 P(E,co,0,2,33)

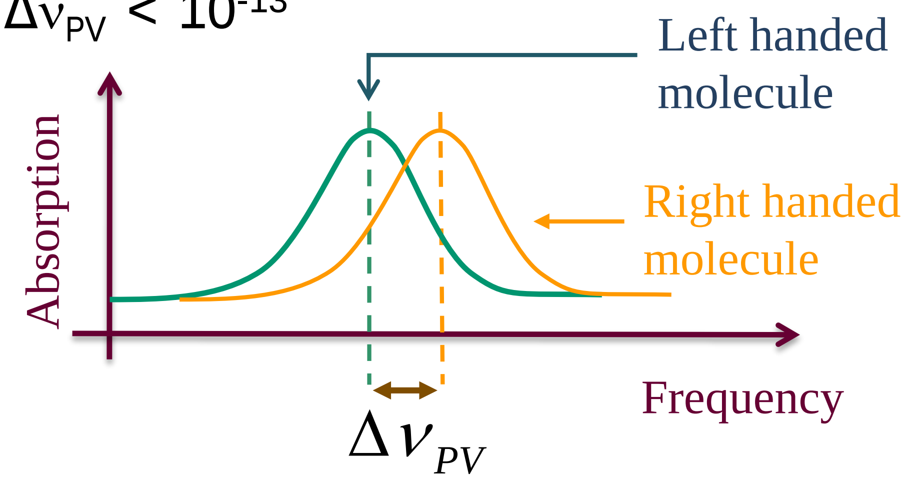
- Shifted from Hitran data base ~ - 5 MHz

	Correction (kHz)	**Uncertainty (kHz)**
frequency calibration	0	0.001
power shift	-16.94 kHz for June measurements -12.32 for October measurements	1,4
pressure shift	2.4	1
other spectroscopic effects	not measured estimated to be <5 kHz	5
line fitting	0	5
Total systematics	-14.74 for June measurements -9.92 for October measurements	**7.3**
Statistics		**1.1**
Total		**7.4**

Long-term objective: parity violation in molecules

- Context
  - Parity violation is expected due to weak interaction
  - Observed in nuclear physics and atoms
  - Never seen in molecules because it's too weak

- Test principle
  - Ultra high resolution spectroscopy of a chiral molecule
  - Relative frequency difference $\Delta\nu_{PV} < 10^{-13}$



- Required laser performance
  - Stability < a few 10^{-14}
  - Reproducibility ~ 10^{-14}

Project developed by Benoît Darquié

See for instance Darquié et al, *Chirality* (2010) + Tokunaga et al, NJP (2017)

Conclusion

- Transfer of frequency stability and accuracy from 1.54 µm to 10 µm
  - 5-20 µm spectral region can be reach with appropriate crystal
- QCL stabilisation with unprecedented spectral purity & accuracy
  - Linewidth < 0,2 Hz (7×10^{-15})
  - Stability < 0,05 Hz (2×10^{-15})
  - Accuracy ~ 1 Hz (4×10^{-14})
- Tunability
  - Demonstrated over 400 MHz
  - Could be increased to 1 GHz with a thermal tuning of the comb
- Perfect tool for ultra high sensitivity experiments with molecules
  - Study of methanol doublets
  - Spectroscopy of trioxane $(CH_2O)_3$ and ammonia NH_3 in progress

MMTF group

Benoît Darquié, Olivier Lopez, An Tran (Rosa Santagata missing)