High-precision mid-IR molecular spectroscopy with traceability to primary frequency standards using sub-Hz frequency comb-stabilized QCLs

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Precision measurements with molecules

- Complementary to measurements in atoms for precision tests of fundamental physics:

measure constants	m_e/m_p (Schiller, Ubachs, Hilico – $HD^{(+)}$, $H_2^{(+)}$) k_B (Gianfrani, H_2O - LPL, NH_3),…
measure their variations in time	α (J. Ye, OH) m_e/m_p (De Natale, Maddaloni, CF_3H - LPL, SF_6)
test parity & time-reversal symmetry (eEDM)	Hinds (YbF), DeMille/Doyle/Gabrielse (ThO),…
test parity symmetry	D. DeMille (BaF), LPL (chiral species),…
Test the symmetrization postulate	Tino, De Natale,… (O_3, CO_2, NH_3,…)

- Many are based on high-resolution spectroscopy, often in the mid-IR domain

- Increasing demand for precision spectroscopy of polyatomic molecules for physical chemistry studies:

  → modeling our atmosphere

  → interpreting astrophysical and planetary spectra

  → study collision physics

  → …

Precision measurements with molecules

- Need efficient mid-IR laser sources of well-controlled frequency
- Mid-IR quantum cascade lasers (QCLs) are promising
  - ✓ continuous-wave
  - ✓ available in the 3-25 µm range
  - ✓ tuneability over several 100 GHz or more
  - ✓ mW to W power levels
  - × free-running line width 10 kHz to few MHz ⟶ frequency stabilization needed
- Several frequency stabilization schemes developed in the last years

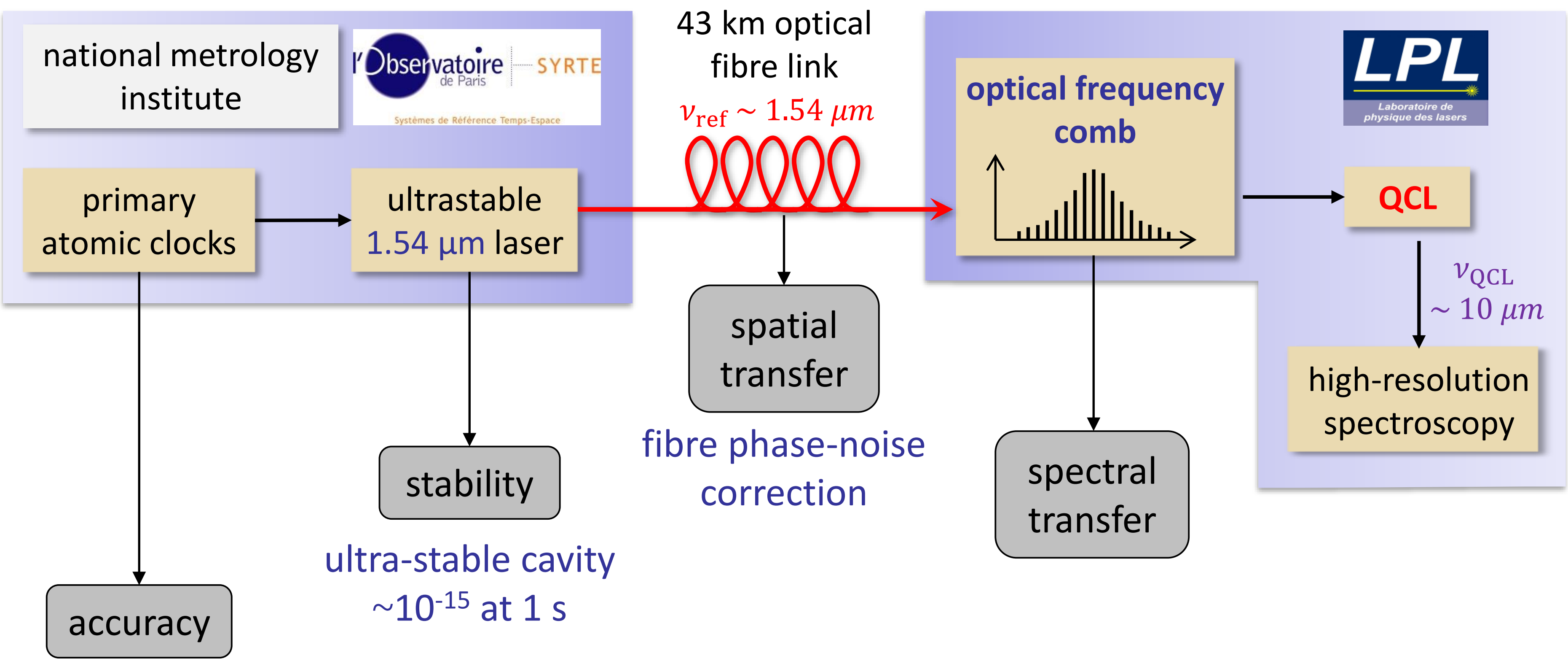
  ⟶ stable cavities, molecular lines, injection locking, optical frequency combs,…
- **Challenges:** achieve ultimate metrological frequency purity and accuracy
  traceability to *primary frequency standards*
  available *anywhere*

  ⟶ use the best near-IR ultra-stable lasers found in metrology institutes as reference

  ⟶ use ultra-stable optical fiber links

  ⟶ use an optical frequency comb (OFC) to bridge the gap between near-IR and mid-IR

QCL stabilization to a near-IR frequency reference



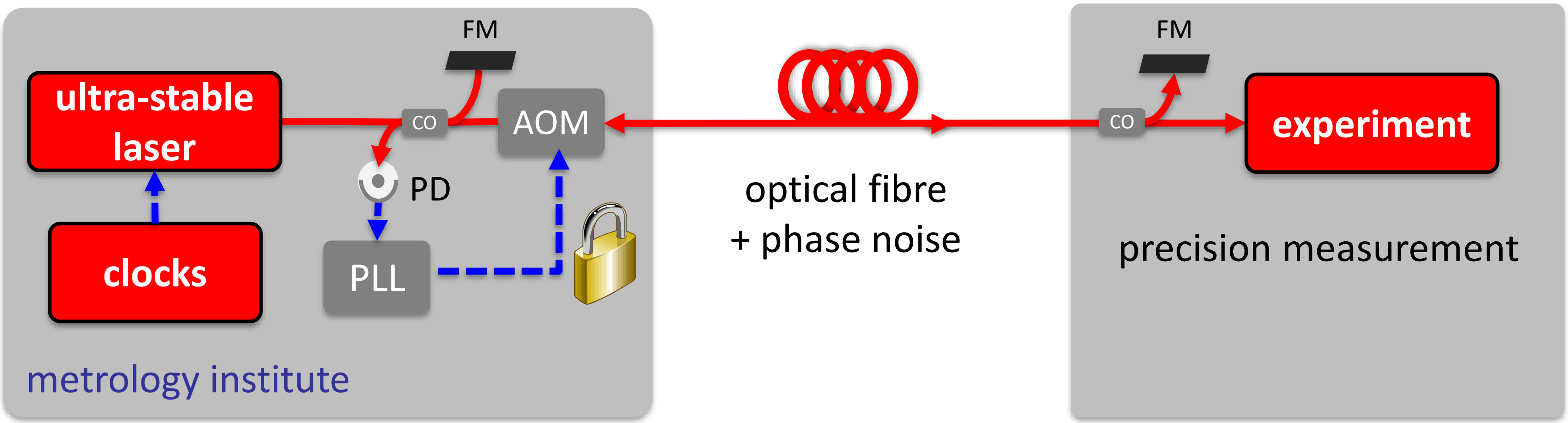
$\sim 10^{-14}$ (H-maser)
$\sim 10^{-16}$ potentially (Cs fountain)

$$\nu_{\mathrm{QCL}} = \frac{n}{N}(\nu_{\mathrm{ref}} + \Delta_1) + \Delta_2$$

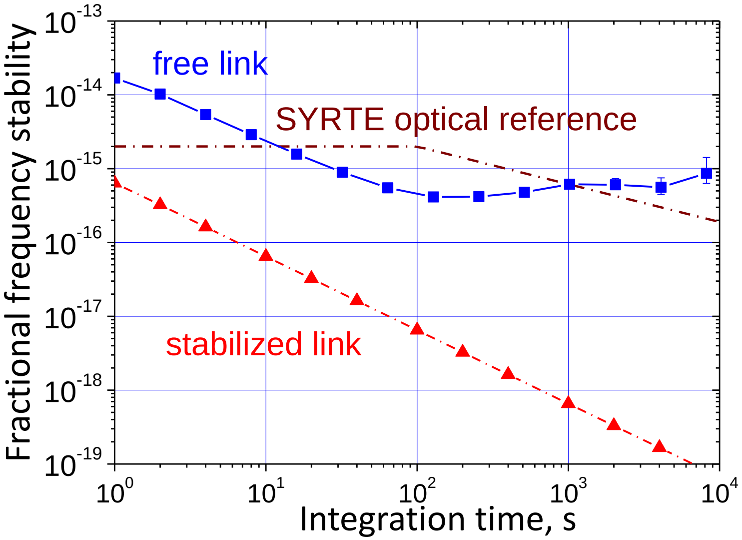
M Abgrall, Y Le Coq, R Le Targat,
W-K Lee, D Xu, P-E Pottie

Chanteau et al, *New J. Phys.* (2013)
Argence et al, *Nature Photon.* (2015)
see also: Insero et al., *Sci. Rep.* (2017)

Optical fibre link for ultra-stable frequency transfer

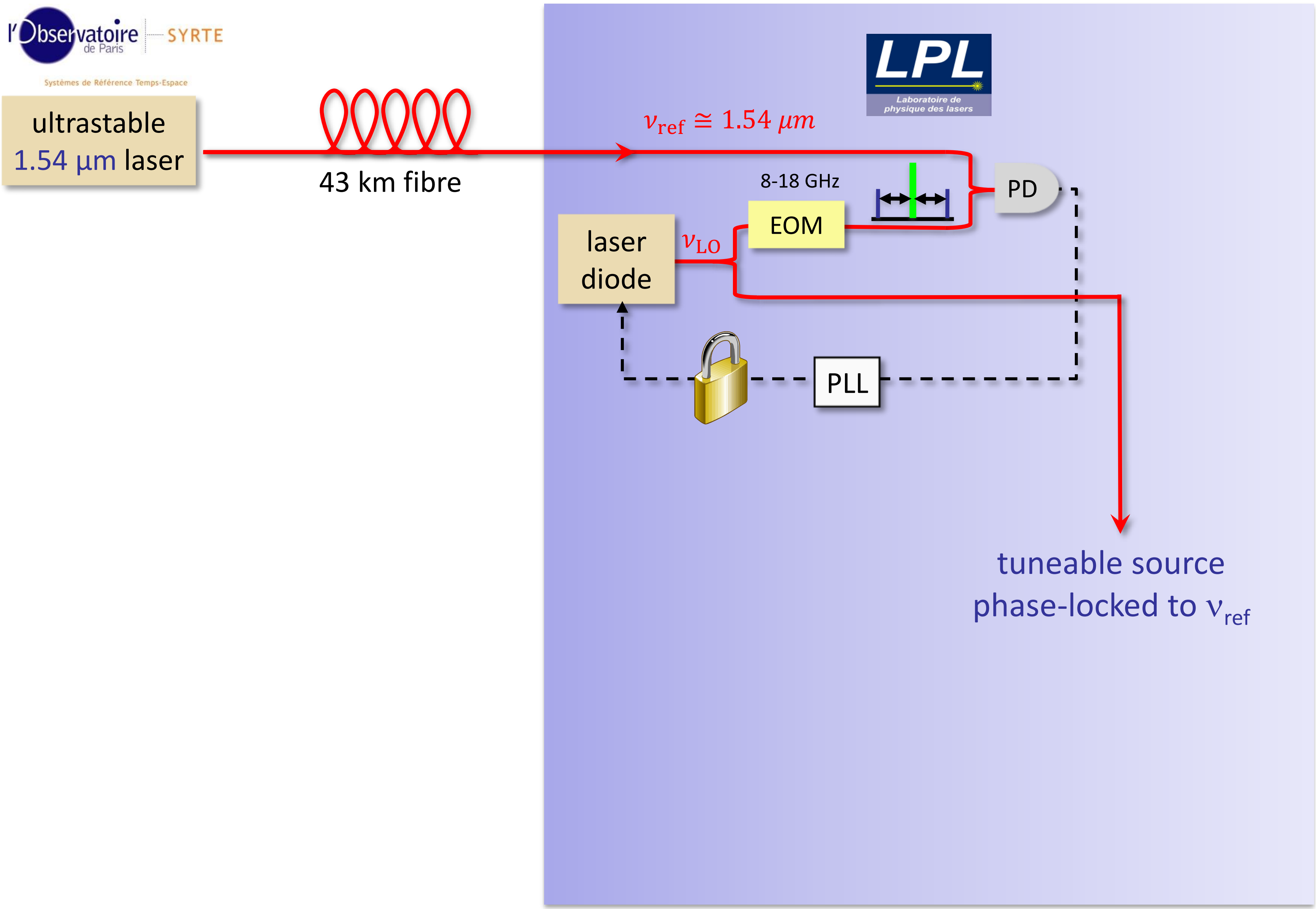


- correction of the propagation noise
- added noise (transfer instability)
  - a few 10^{-16} after 1 s
  - $\sim 10^{-19}$ after ~a day
- frequency inaccuracy $< 10^{-19}$

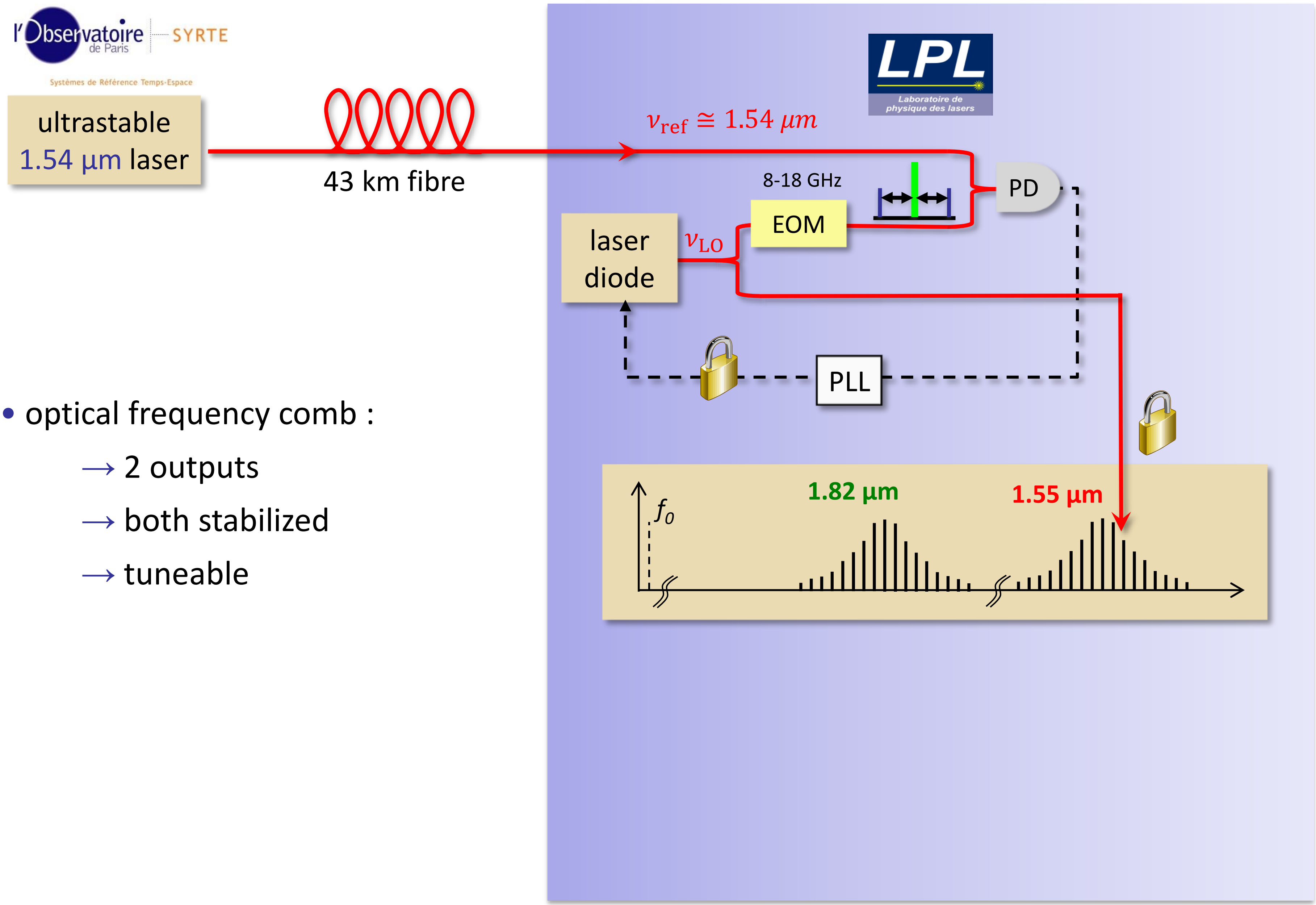


Lee et al., *Appl. Phys. B* (2017)

QCL stabilization to a near-IR frequency reference

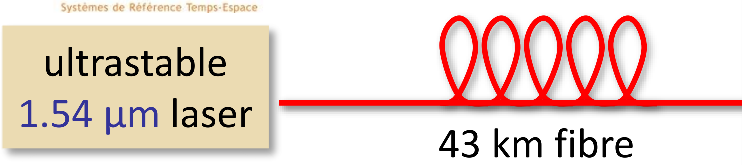


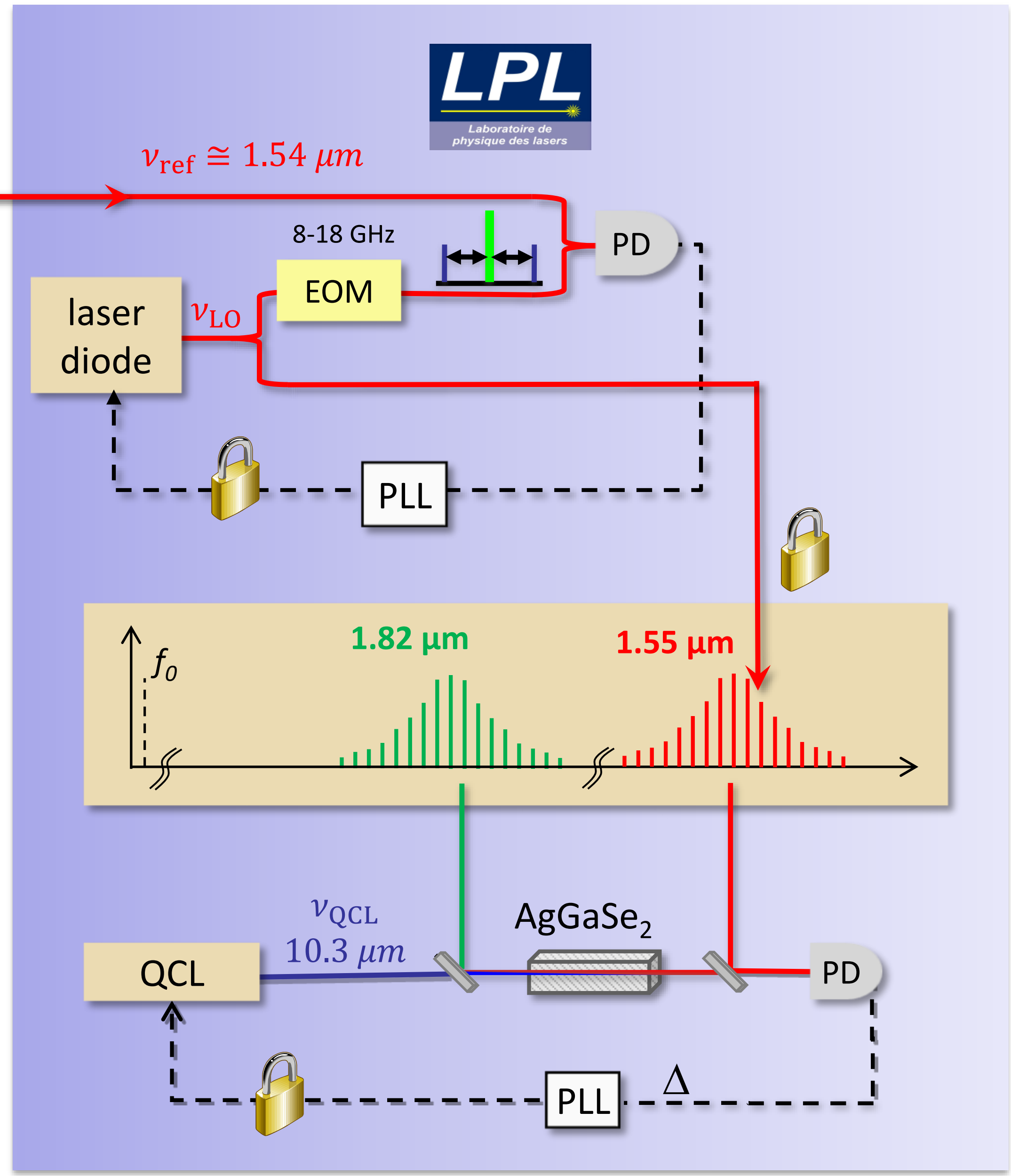
QCL stabilization to a near-IR frequency reference



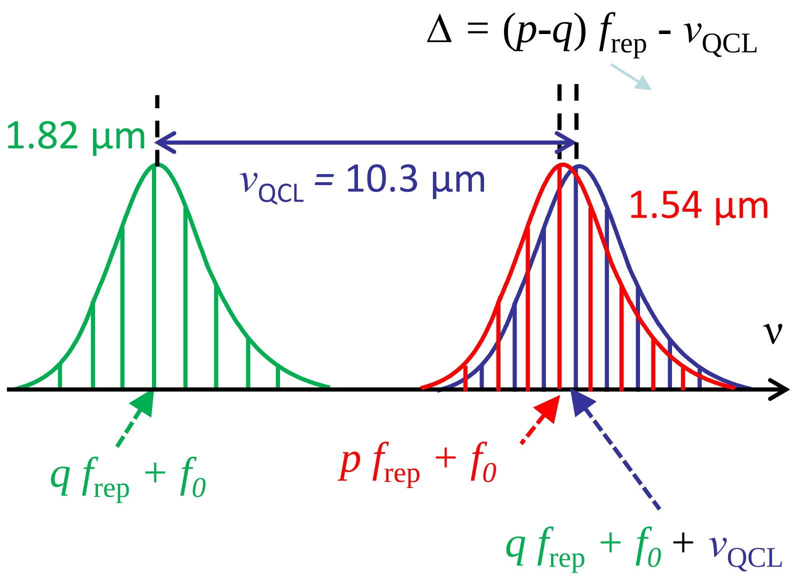
- optical frequency comb :
  - ⟶ 2 outputs
  - ⟶ both stabilized
  - ⟶ tuneable

QCL stabilization to a near-IR frequency reference





- sum frequency generation:

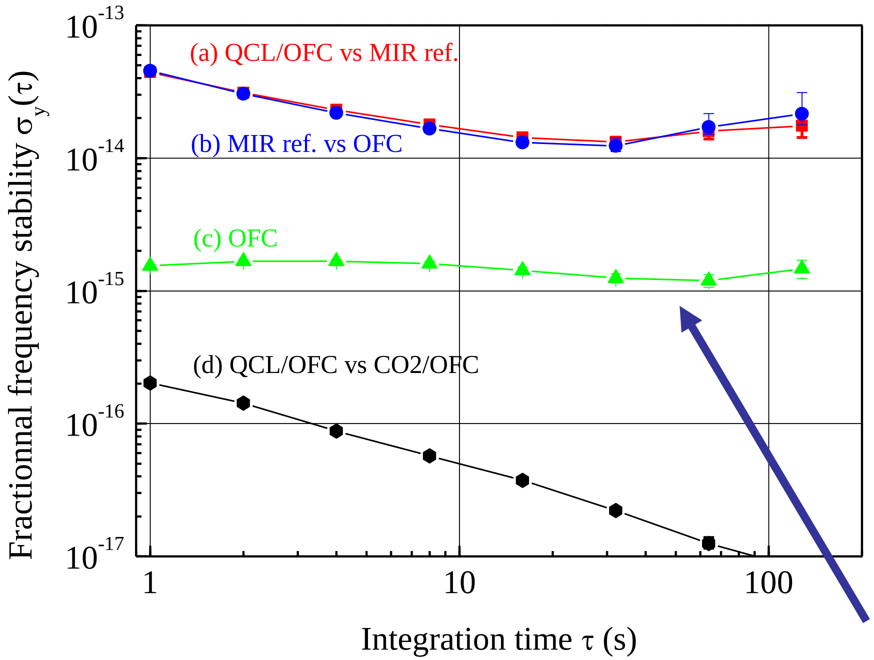


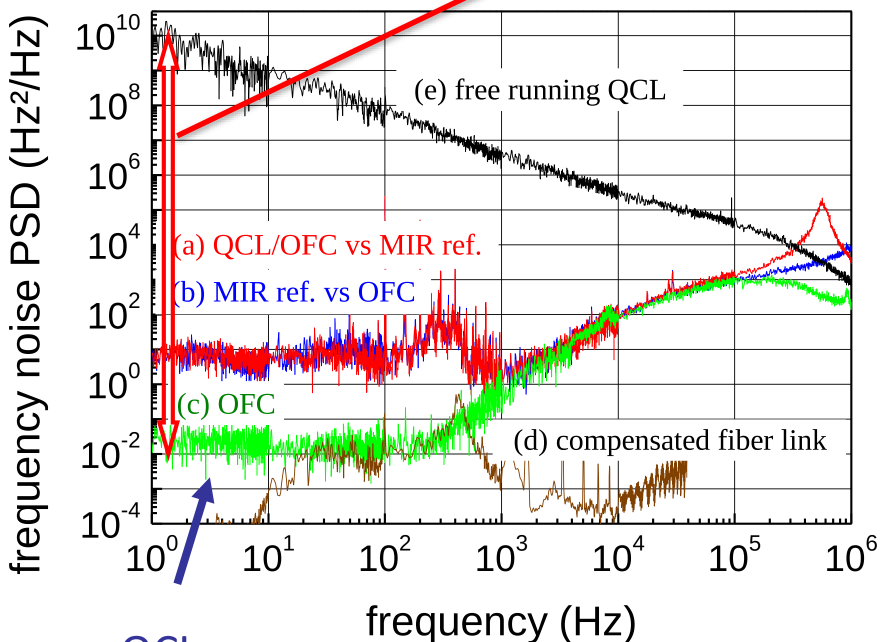
- direct link from near-IR and mid-IR
- QCL tuneable over ~1.5 GHz

Performances of the stabilized QCL

Argence et al, *Nature Photon.* (2015)
see also: Insero et al., *Sci. Rep.* (2017)

12 orders of magnitude noise reduction!





QCL stability

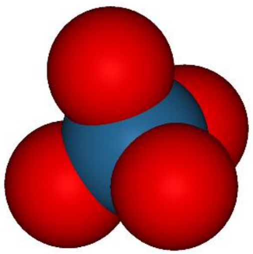
QCL noise

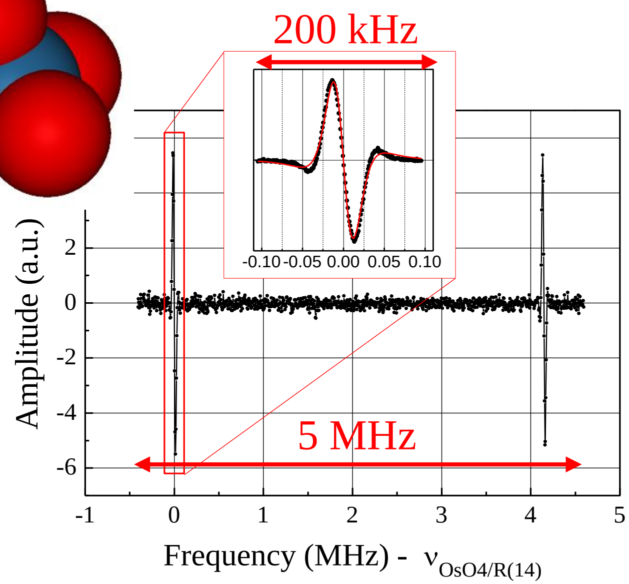
- ultimate QCL stabilities (0.06 Hz @ 1s) and accuracies (sub-Hz, 10 mHz potentially)
- narrowest QCL so far (0.1 Hz)

Allows the level of near-IR ultra-stable lasers to be transferred to the mid-IR
⇒ ‘atomic physics’ types of precision measurements on molecules

Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

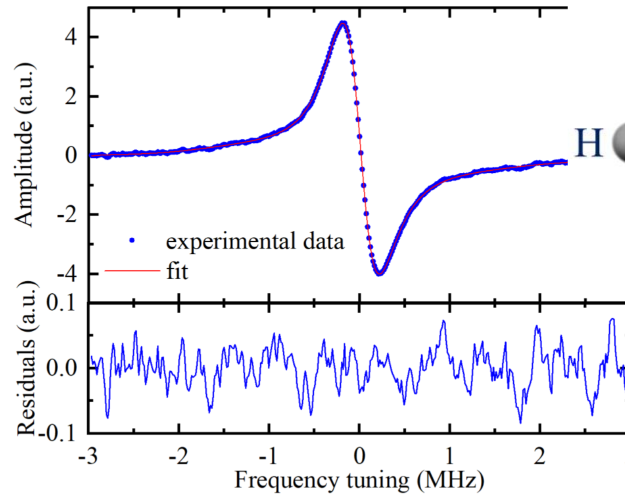
OsO_4 saturated absorption spectrum around 29 THz

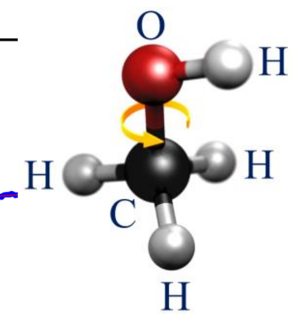




- ~25 kHz linewidth
- a few 10 Hz uncertainty
- state-of-the-art

Methanol saturated absorption spectrum P(E_1,co,0,2,32) line, C-O stretch





- ~400 kHz linewidth
- a few kHz uncertainty
- 10^2-10^4 improvement compared to literature / HITRAN database

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- in a ~100 finesse 1.5-m long Fabry-Perot cavity
- frequency modulation 9.5 kHz, deviation 36 kHz
- 3rd harmonic detection, time constant: 5 ms

- in a multipass cell
- frequency modulation 20 kHz, deviation 50 kHz
- 1st harmonic detection, time constant: 100 ms

Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

OsO_4 saturated absorption spectrum
around 29 THz

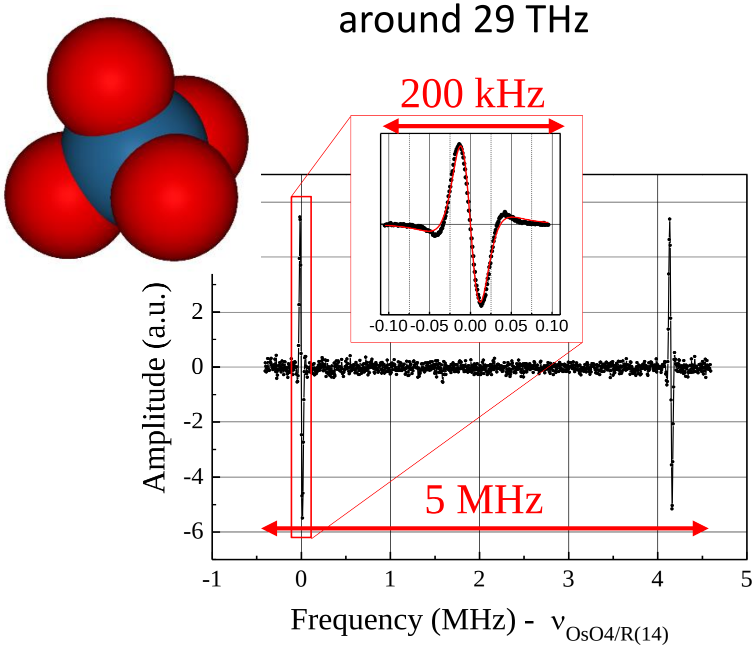

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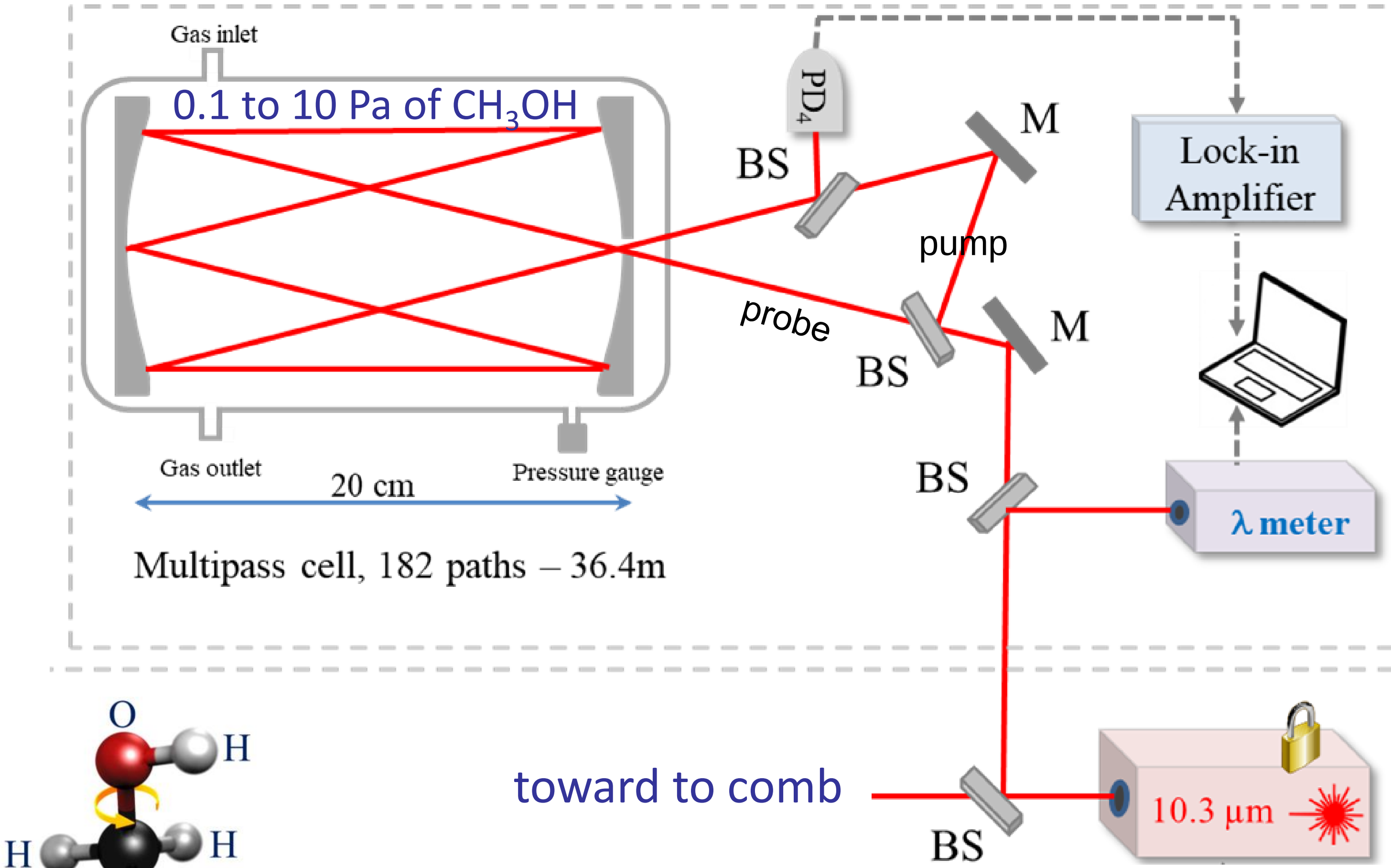
Table 1 | Absolute frequencies of five OsO_4 absorption lines in the vicinity of the R(14) CO_2 laser line.

OsO_4 lines in the vicinity of the CO_2 R(14) laser line at 10.3 μm	Frequency shift from $\nu_{OsO4/R(14)}$ calculated from refs 39 and 41 (kHz)	Frequency shift from $\nu_{OsO4/R(14)}$ measured in this work (kHz)
$^{190}OsO_4$ reference line (unassigned)	0.000 (40)	−0.009 (22)
Unreported line	-	+4,147.399 (23)
$^{190}OsO_4$, $R(46)A_1^3(-)$	+101,726.83 (5)	+101,726.821 (32)
Unreported line	-	+123,467.401 (32)
Unreported line	-	+204,269.162 (33)

Argence et al, *Nature Photon.* (2015)

High-resolution spectroscopy of methanol

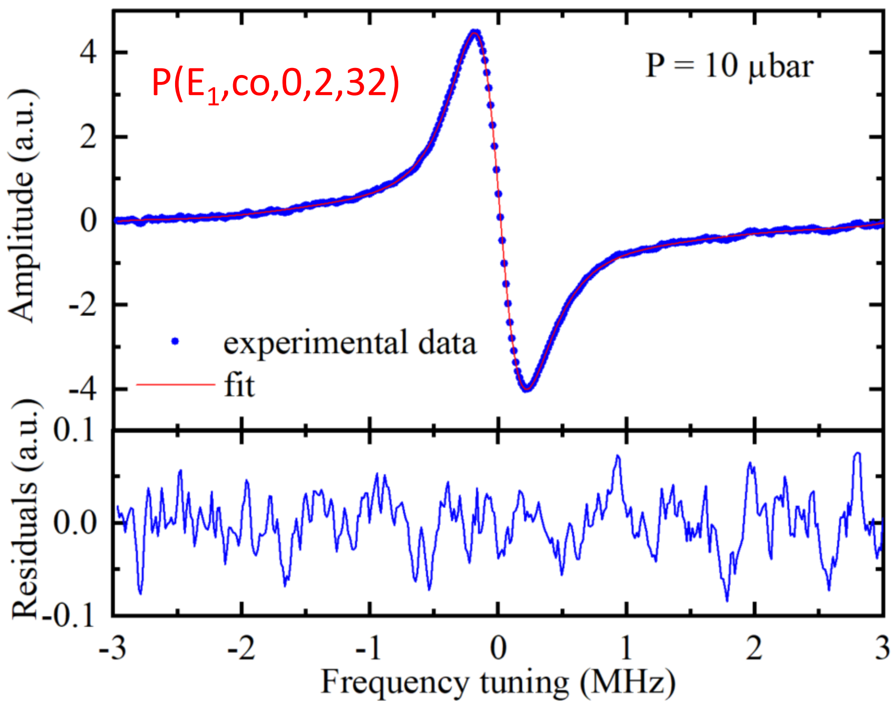
saturated absorption spectroscopy in a multi-pass cell

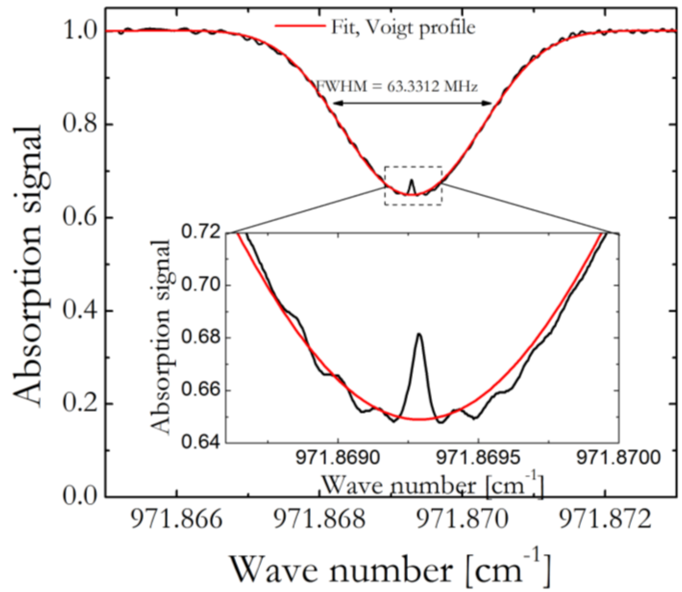


cw Alpes Laser QCL
243-273 K
967-973 cm^{-1} (180 GHz)

High-resolution spectroscopy of methanol

P(32, 2) E_1 line, C-O strectch





- FM @ 20 kHz, deviation 50 kHz
- 1st harmonic detection
- 100 ms lock-in amplifier time constant

Summary / Perspectives

- Precise and tuneable frequency control of a mid-IR QCL referenced to a comb
  - → stability and accuracy transfer from 1.54 µm to 10 µm
  - → direct link to primary frequency standards
  - → record stabilities/accuracies:
    - 0.05 Hz (2×10^{-15}) satbility @ 1 s
    - 0.1 Hz line width
    - 0.3 Hz (10^{-14}) accuracy, potentially 0.01 Hz (3×10^{-16})
  - → anywhere in 5-20 µm region potentially, ~1 GHz continuous tuning
- Saturated absorption spectroscopy of OsO_4/methanol
  - → ~10 Hz/~1 kHz uncertainty on the absolute frequency
  - → new lines and patterns unreported so far
- Precision spectroscopic measurement with polyatomic molecules
  - → tests of fundamental physics → measuring parity violation in chiral molecules talk by A. Cournol on Friday (FD04)
  - → metrology → Doppler broadening thermometry talk on Friday (FD03)
  - → atmospheric physics, astrophysics, collisions,…

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