High-precision mid-infrared spectroscopy with a widely tuneable SI-traceable optical-frequency-comb-stabilised QCL

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Outline

- Motivation: precise spectroscopic measurements with molecules
- QCL stabilization allowing wide tuneability
- High-precision spectroscopic measurements
- Summary / Perspectives

Precision measurements with molecules

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

measure constants	m_e/m_p (Schiller, Hilico, Ubachs – $HD^{(+)}$, $H_2^{(+)}$) k_B (Gianfrani, $H_2{}^{18}O$, CO_2 - LPL, NH_3),…
measure their variations in time	α (Ye, OH) - m_e/m_p (Truppe/Hinds/Tarbutt, CH - Bethlem, NH_3 - LPL, SF_6)
test fundamental symmetries	parity & time-reversal symmetry (eEDM): Hinds (YbF), Cornell/Ye (HfH^+), DeMille/Doyle/Gabrielse (ThO) parity symmetry: DeMille (BaF), LPL (chiral species),…
QED tests, 5th force	W. Ubachs (H_2, HD^+),…
test the symmetrization postulate	Tino,… (O_3, CO_2, NH_3,…)

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

- Frequency references for frequency metrology

provide an almost continuous set of references throughout the MW, THz, IR, visible, UV

- precision spectroscopy of polyatomic molecules for physical chemistry studies:

atmospheric physics, astrophysics, collision physics, chemical dynamics and reaction, trace gas detection, breath analysis…

Precision measurements with molecules

- Need efficient mid-IR laser sources of well-controlled frequency
- Mid-IR quantum cascade lasers (QCLs) are promising
  - ✓ cw, mW to W power levels
  - ✓ 3-25 μm range
  - ✓ tuneability ~100 GHz or more
  - × 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, combs,…

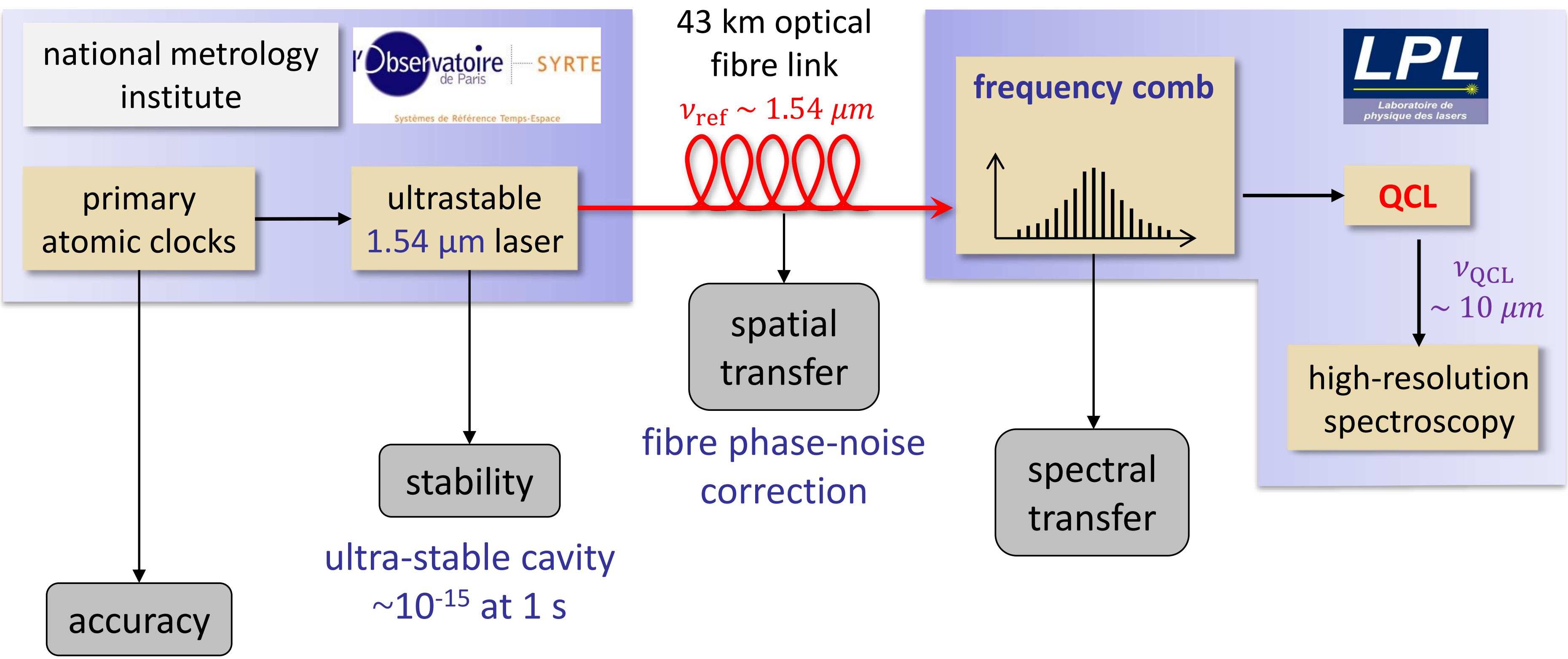
- **Challenges:**
  - most stable reference → near-IR ultra-stable lasers
  - traceability to a primary standard

  } available in metrology institutes only

  → ultra-stable optical fiber links

  → frequency comb to bridge the gap between near-IR and mid-IR

SI-traceable frequency-comb-stabilised QCL



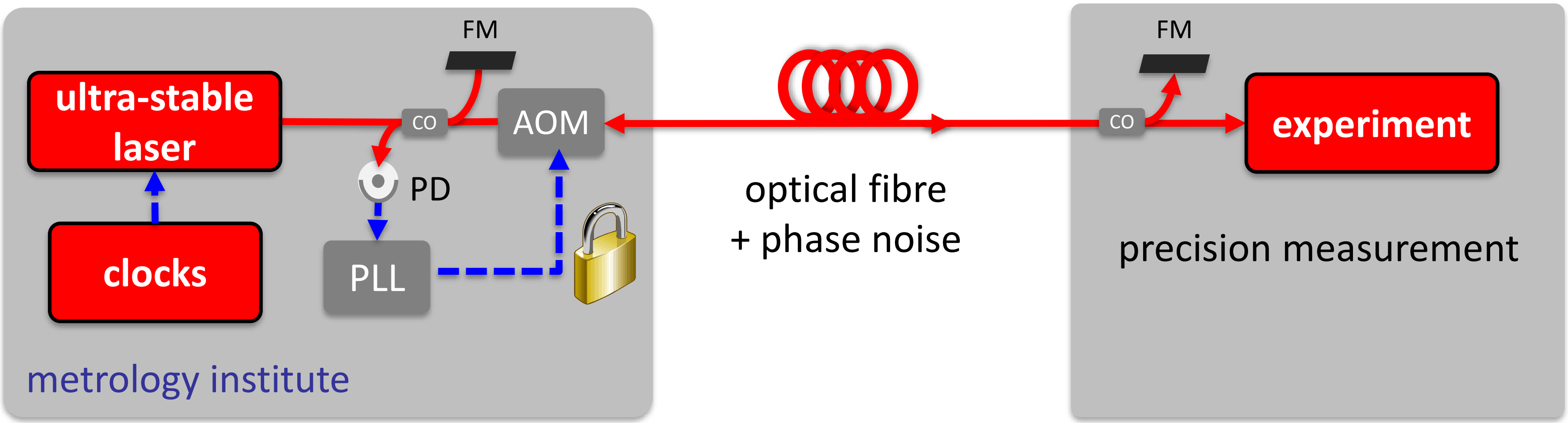
~10^{-14} (H-maser)
~10^{-16} potentially (Cs fountain)

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

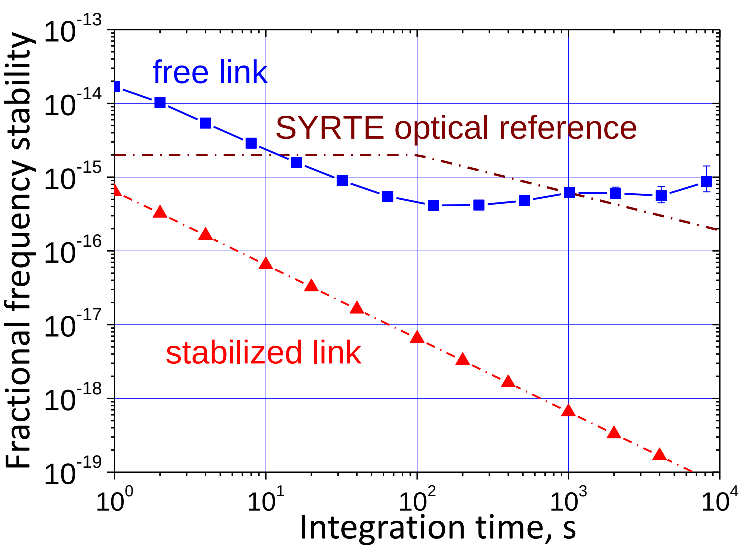
M Abgrall, Y Le Coq, R Le Targat, H Álvarez Martinez, W-K Lee, D Xu, P-E Pottie

Chanteau et al, *New J. Phys.* (2013)
Argence et al, *Nature Photon.* (2015)
Santagata et al, *Optica* (2019)
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
  - ~10^{-19} after ~a day
- frequency inaccuracy < 10^{-19}

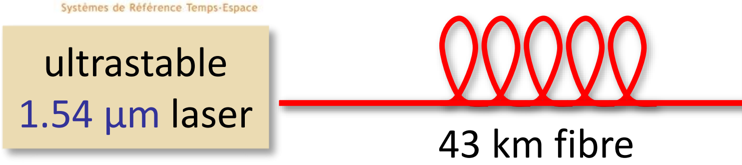


Lee et al., *Appl. Phys. B* (2017)

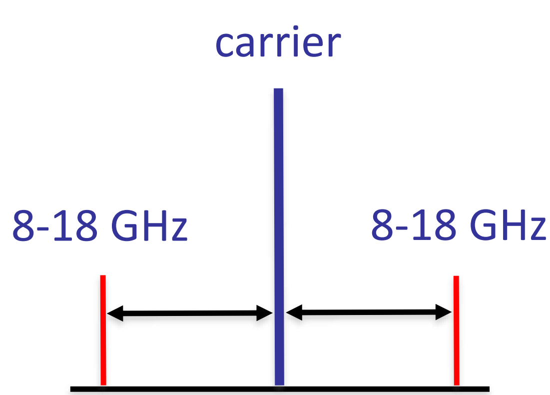
l'Observatoire de Paris — SYRTE
Systèmes de Référence Temps-Espace

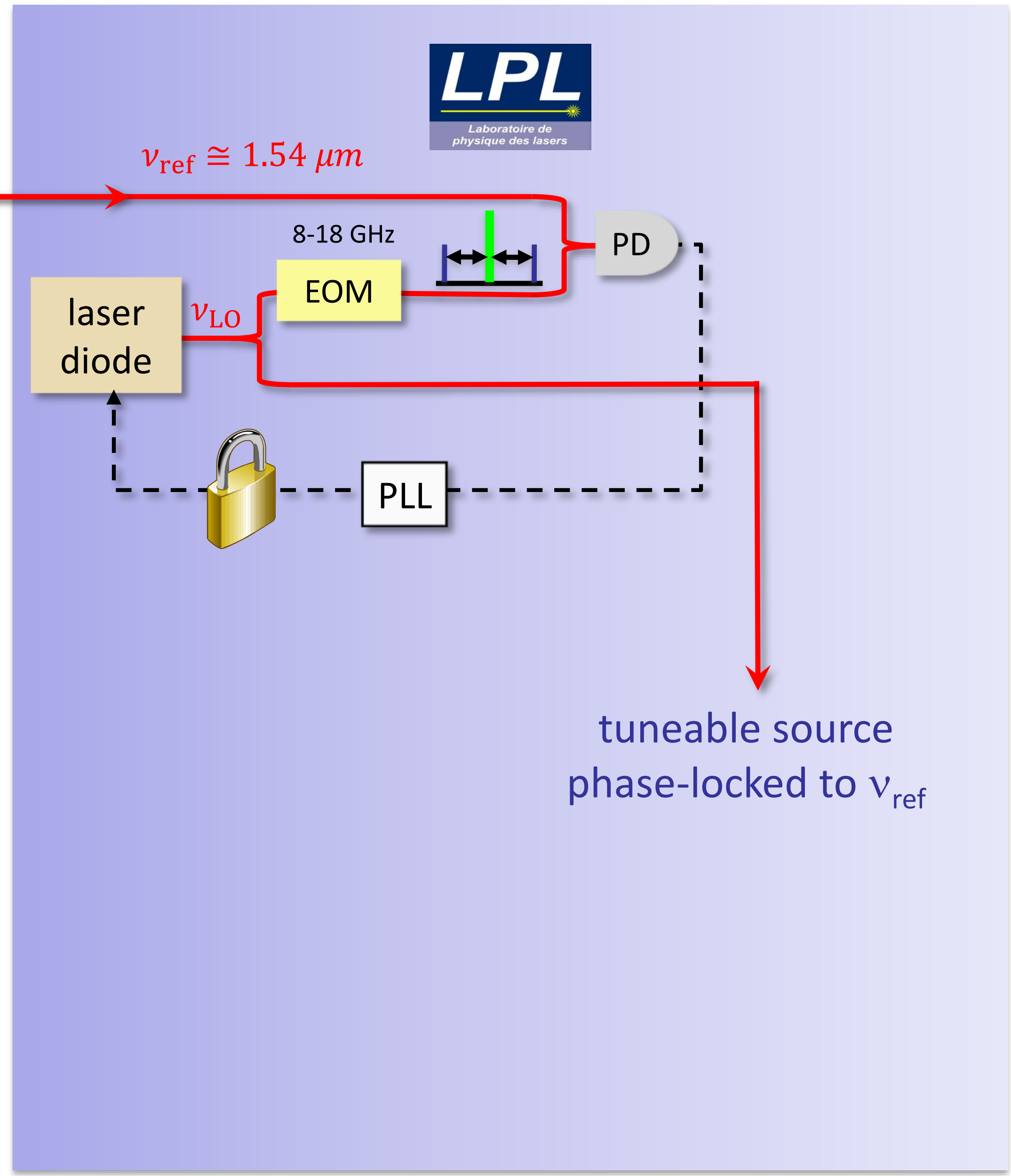
M Abgrall, Y Le Coq, R Le Targat, H Álvarez Martinez, W-K Lee, D Xu, P-E Pottie

QCL stabilization to a near-IR frequency reference



- microwave electro-optic modulator tuneable from 8 to 18 GHz
- home-made 8-18 GHz synthesizer:
  - ⟶ YIG oscillator
  - ⟶ phase-jump free
  - ⟶ phase-locked to a DDS





QCL stabilization to a near-IR frequency reference

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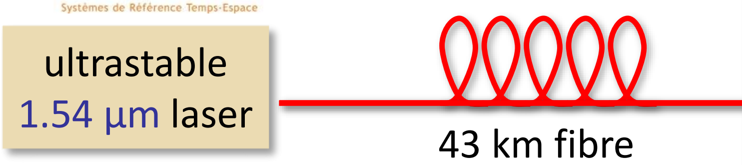
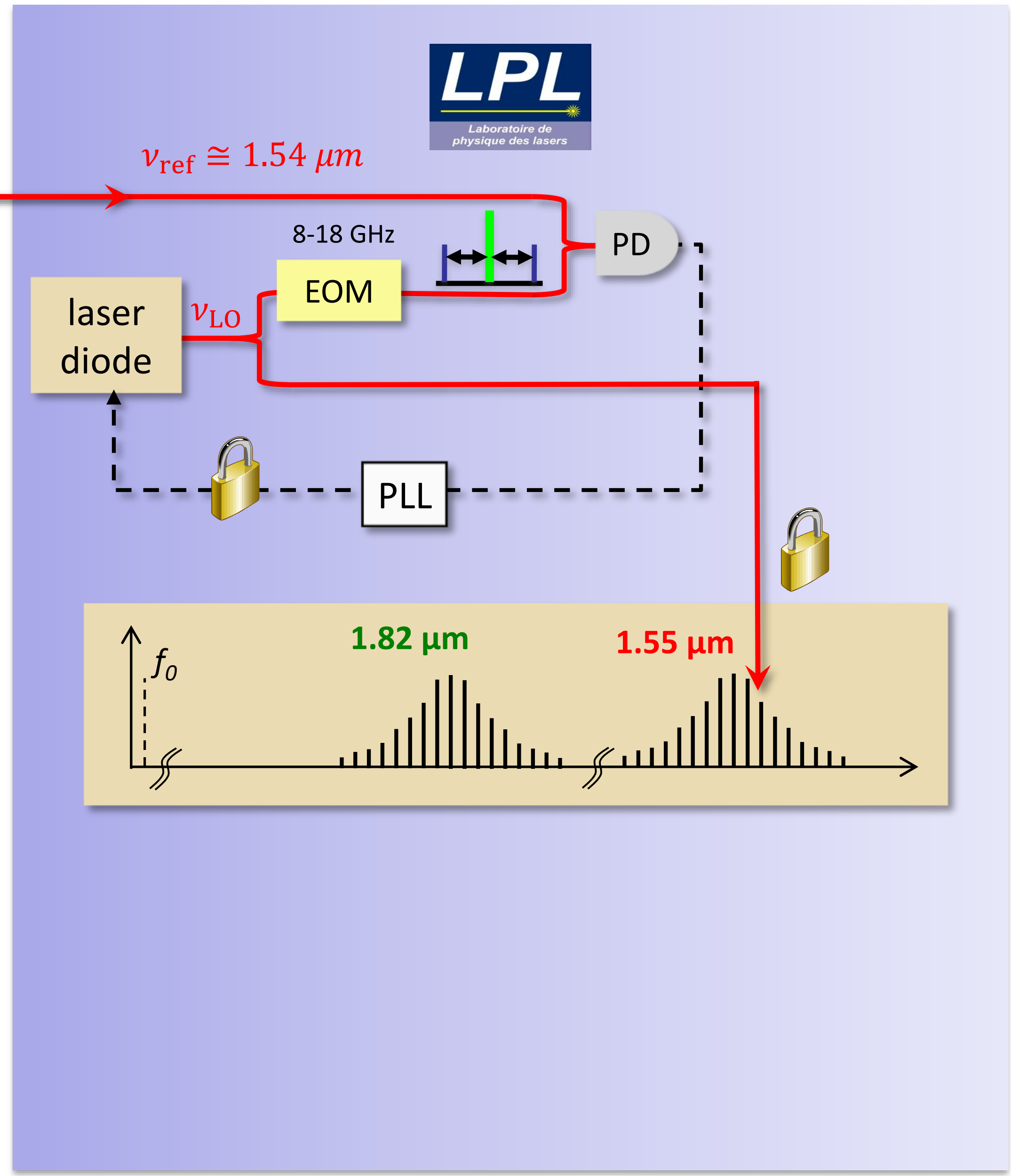
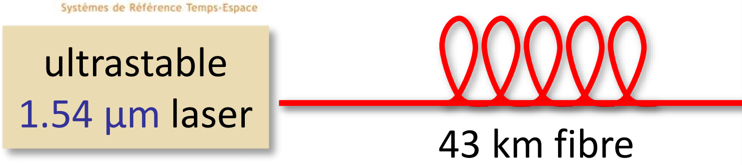


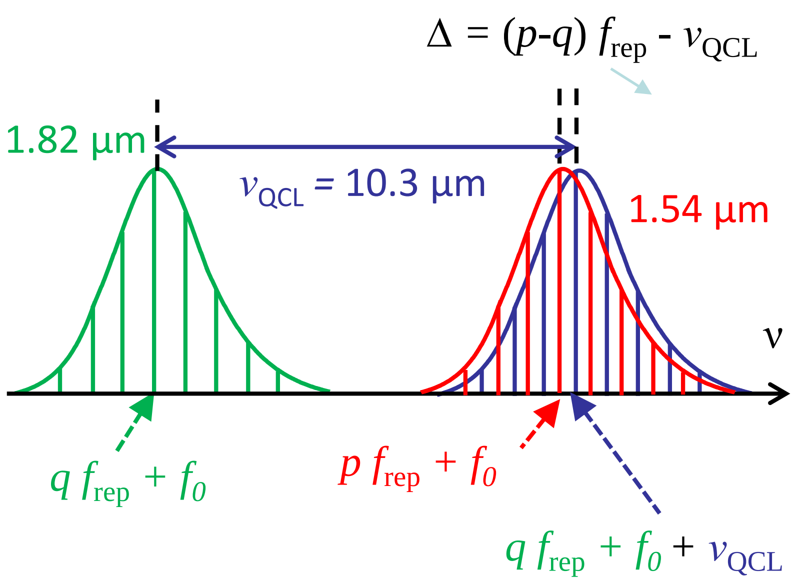


- optical frequency comb :
  - ⟶ 2 outputs
  - ⟶ both stabilized
  - ⟶ tuneable

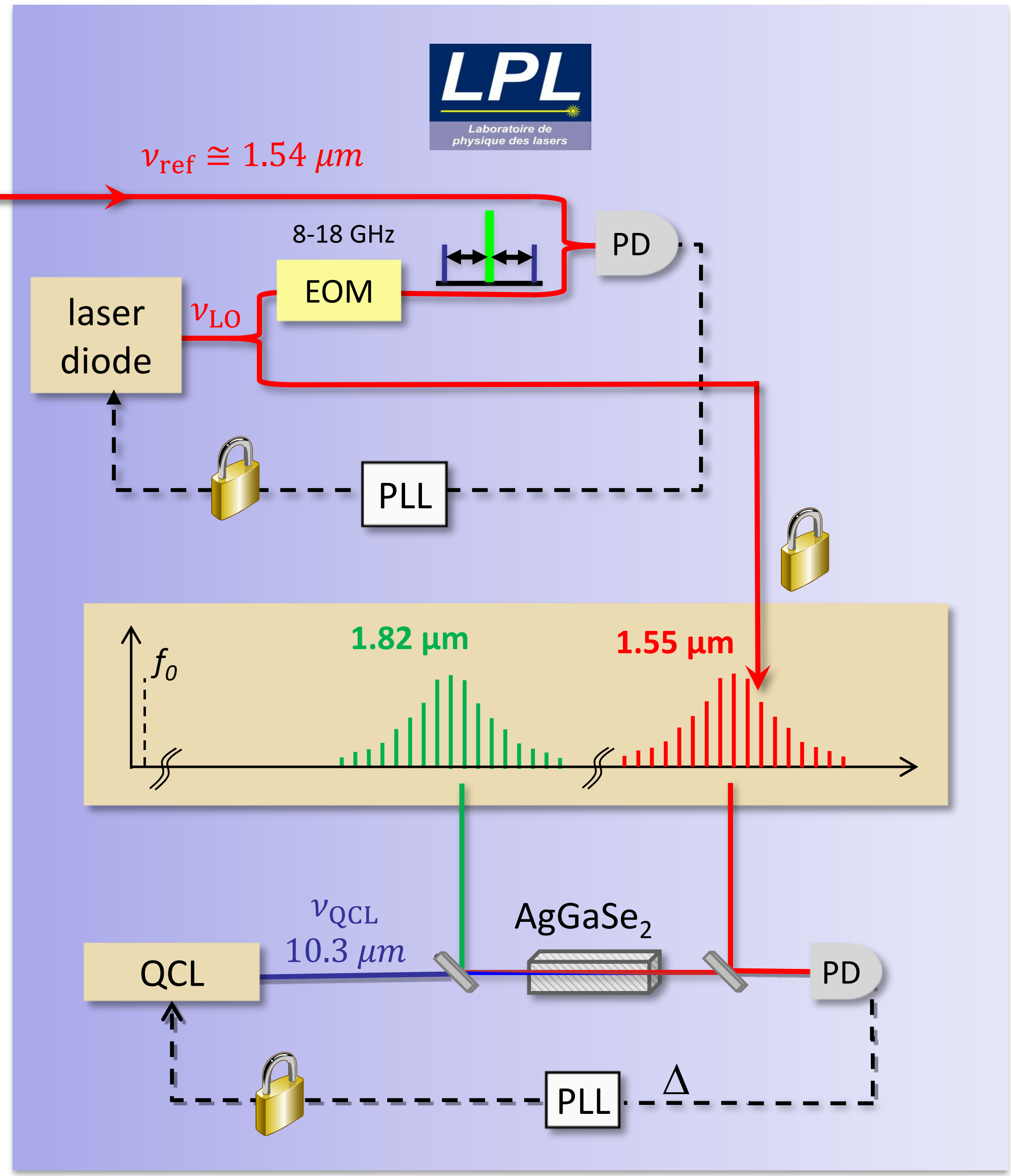
QCL stabilization to a near-IR frequency reference



- sum frequency generation:



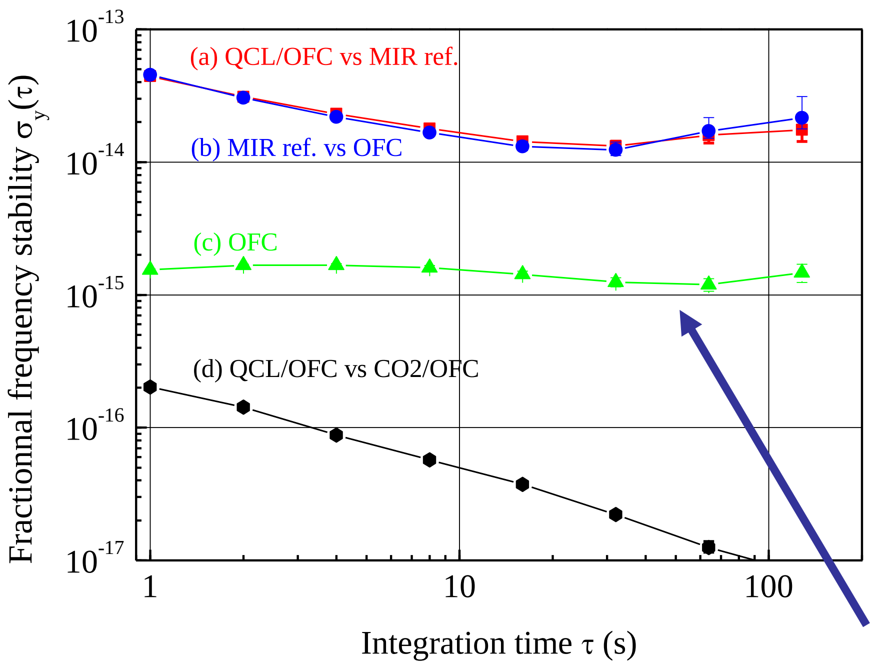
- direct link from near-IR and mid-IR
- QCL tuneable over ~1.5 GHz

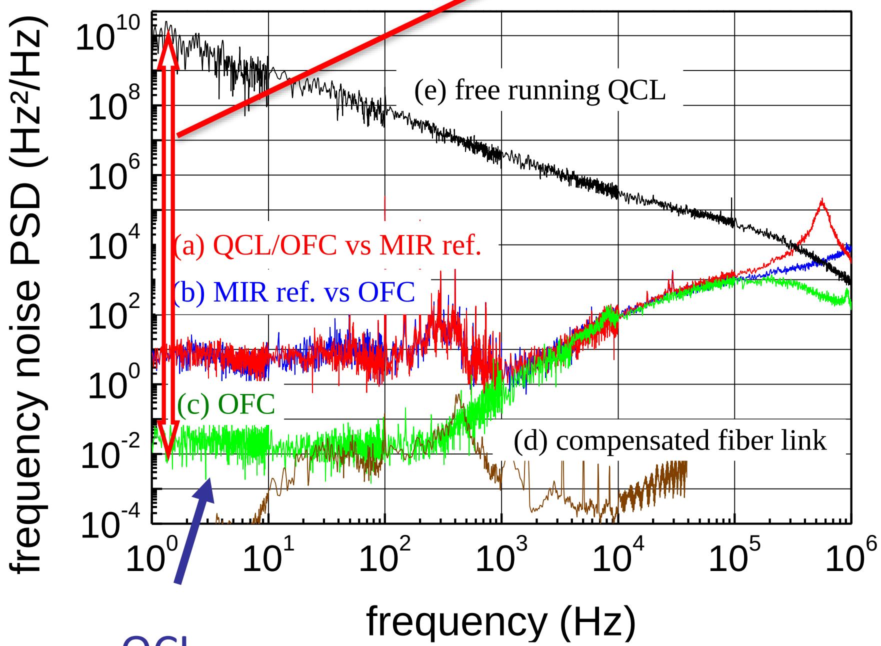


Performances of the stabilized QCL

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

12 orders of magnitude noise reduction!





QCL stability

QCL noise

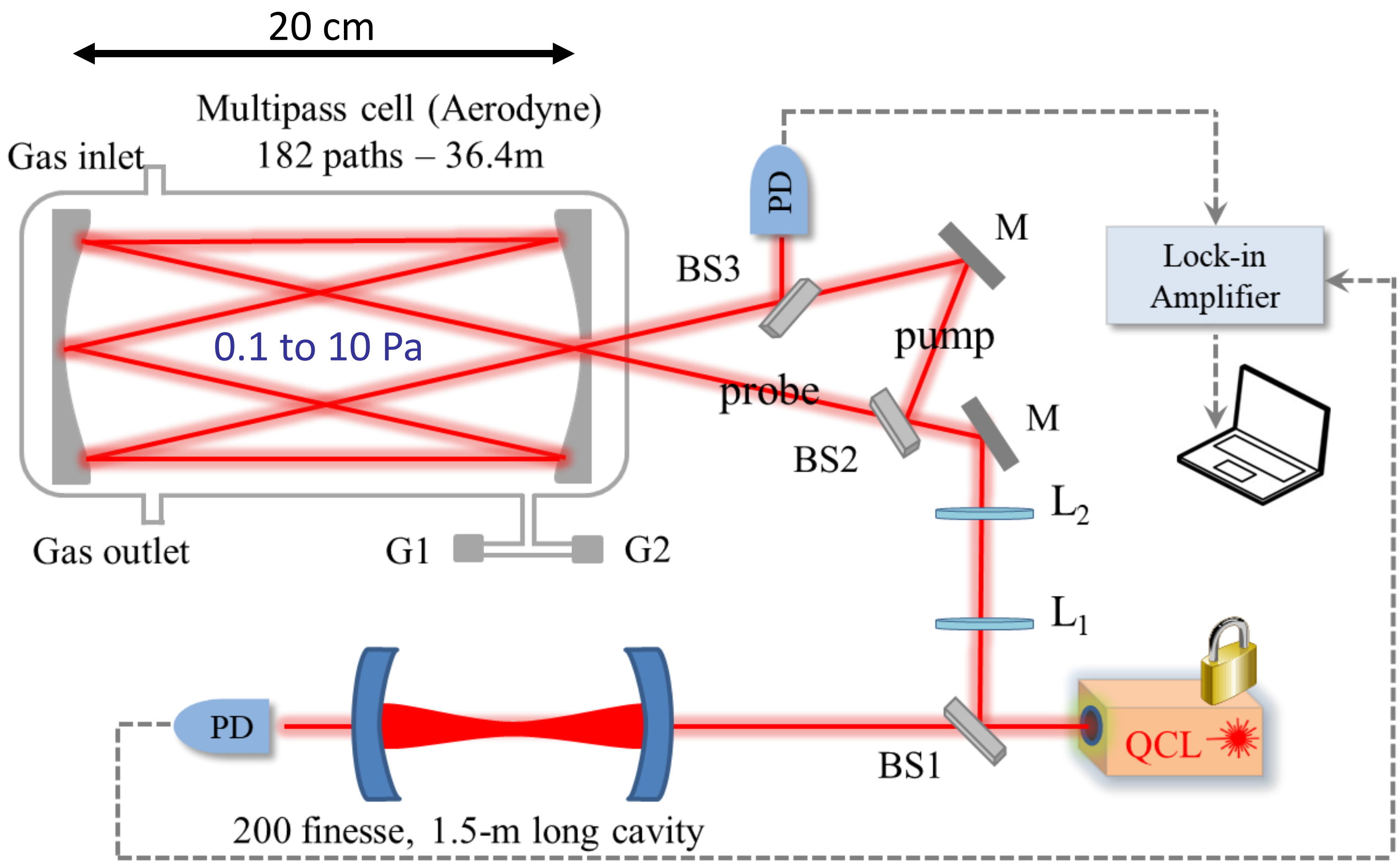
- ultimate QCL stabilities (0.06 Hz @ 1s) and accuracies (sub-Hz, 10 mHz potentially)
- narrowest QCL so far (0.1 Hz)

⇒ **'atomic physics' types of precision measurements on molecules**

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

saturated absorption spectroscopy

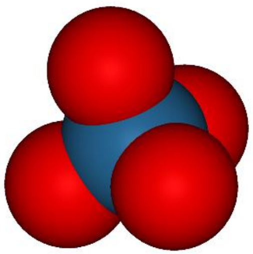
in a multi-pass cell or a Fabry-Perot cavity

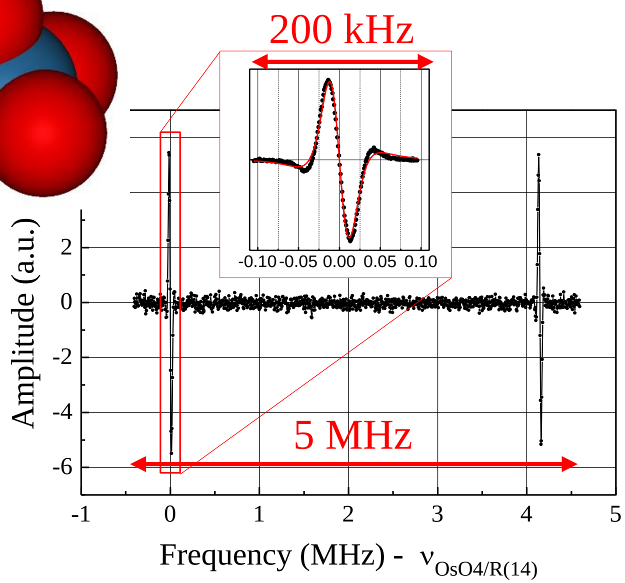


Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

saturated absorption spectroscopy

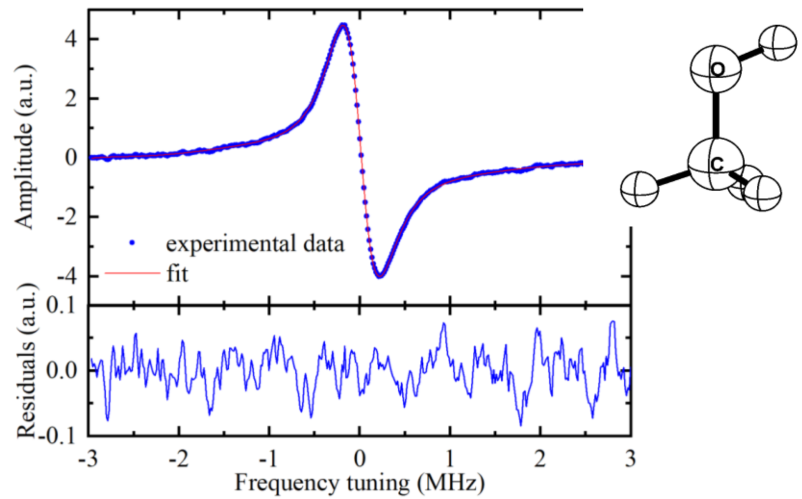
OsO_4 around 29 THz





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

Methanol, P(E,co,0,2,32) line, C-O stretch

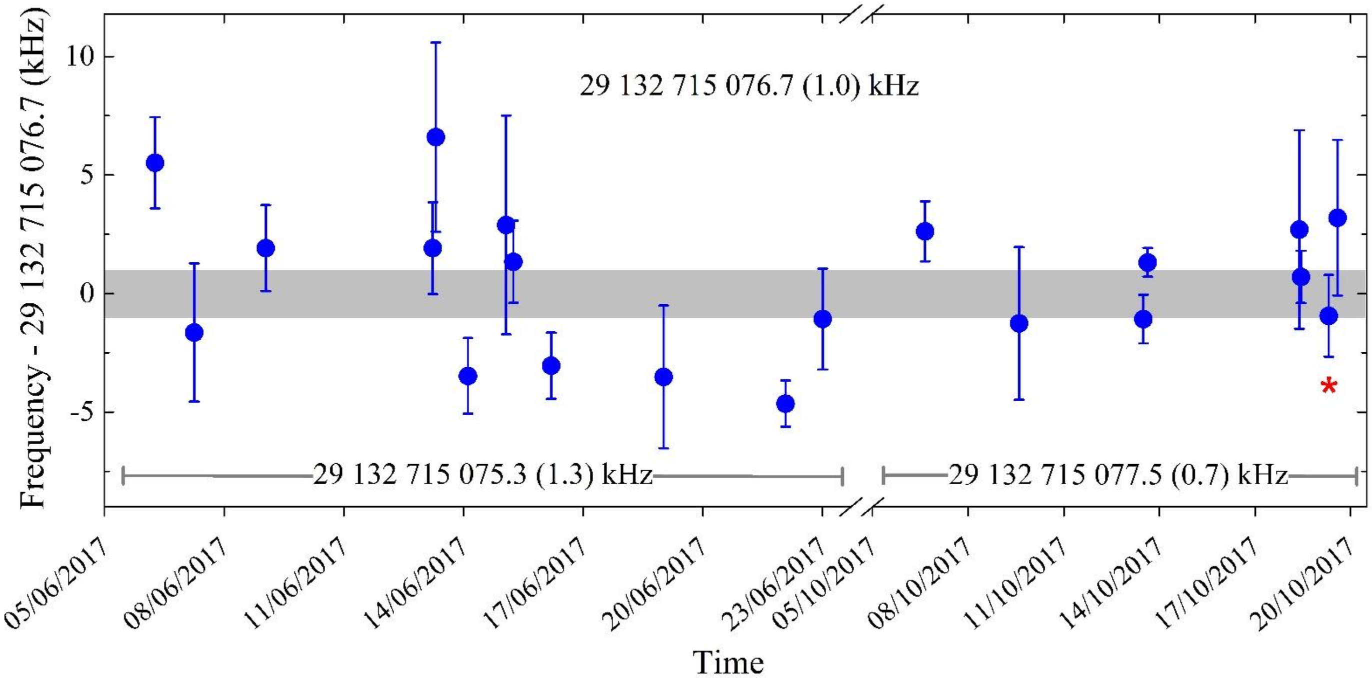


- ~400 kHz linewidth
- a few kHz uncertainty
- 10^2-10^4 improvement compared to literature / HITRAN database

- in a 1.5-m long Fabry-Perot cavity
- frequency modulation, 3^{rd} harmonic

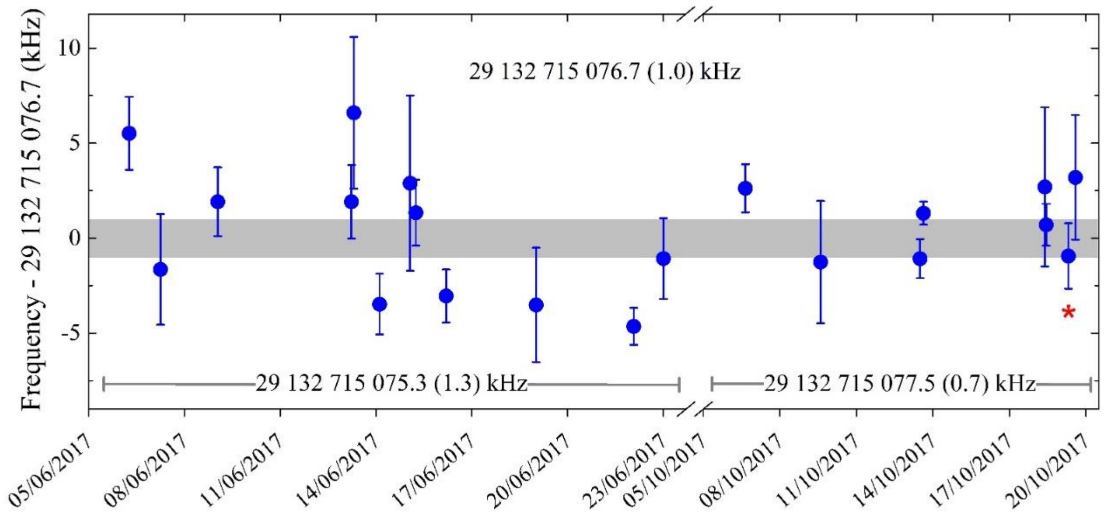
- in a multipass cell
- frequency modulation, 1^{st} harmonic

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



pressure broadening:
100.8 (0.2) kHz/Pa

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



P(E,co,0,2,33) line

29 132 715 074.3 (7.4) kHz
@ zero-power, zero pressure

→ 7.4 kHz global uncertainty

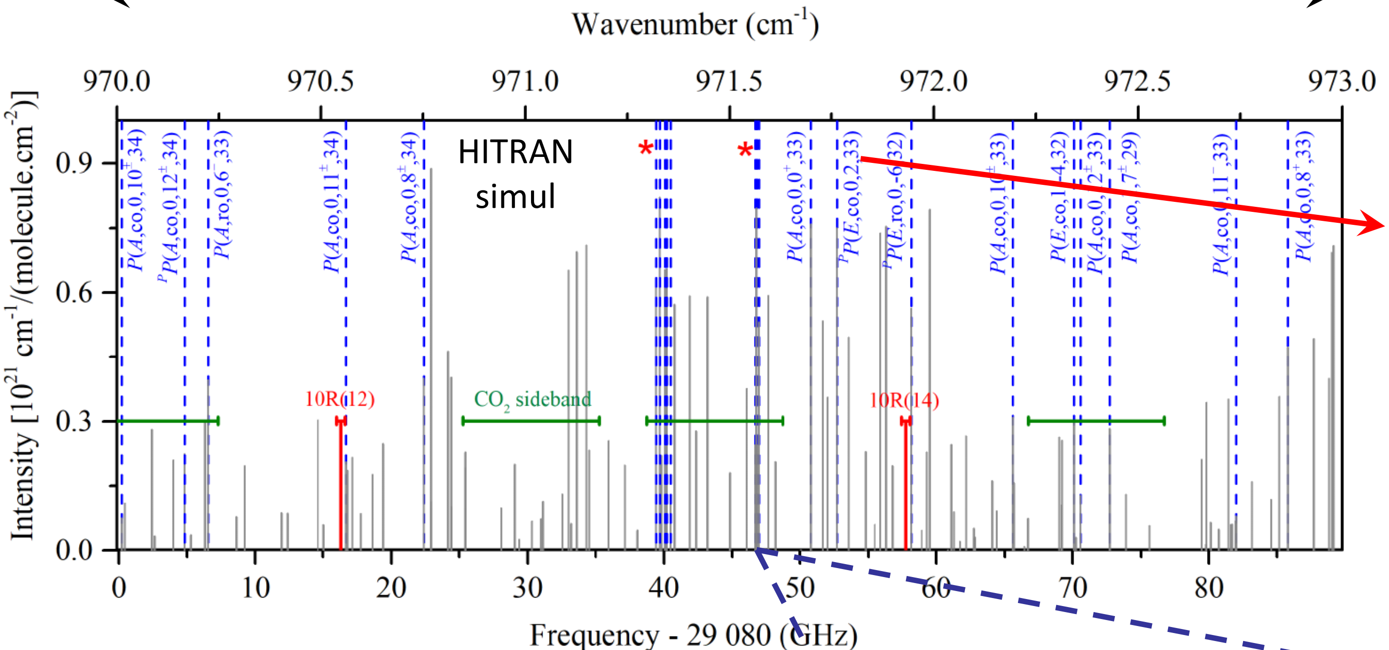
~2000 improvement over previous measurements

Systematics	Correction (kHz)	Uncertainty (kHz)
frequency calibration	0	< 0.0003
power shift	+16.94 kHz (June 2017) +12.32 kHz (October 2017)	1.4
pressure shift	-2.4	1
other spectroscopic effects	not measured, estimated <5 kHz	5
line fitting	0	5
Total systematics	+14.54 (June 2017) +9.92 (October 2017)	7.3
Statistics	0	1.1
Total	+14.54 (June 2017) +9.92 (October 2017)	**7.4**

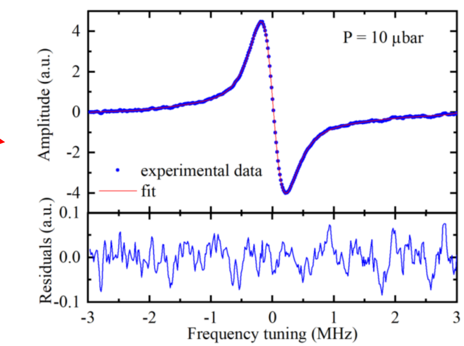
Santagata et al, *Optica* (2019)

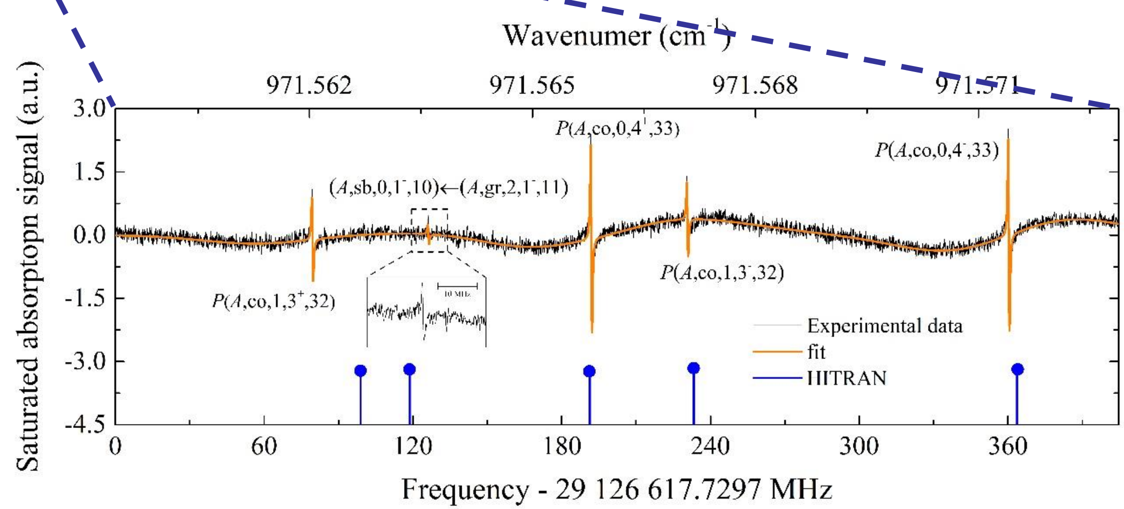
Ultra-precise spectroscopy with QCLs: spectral coverage/tuneability

~100 GHz covered, ~full QCL's tuneability



P(*E*,co,0,2,33)





Santagata et al, *Optica* (2019)

~400 MHz, continuous tuning range (EOM)

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, 1.5 GHz continuous tuning
- Saturated absorption spectroscopy of OsO_4, CH_3OH
  - → uncertainty on central frequency from a few 10 Hz to a few kHz
  - → unprecedented resolution: new lines and subtle patterns unreported so far

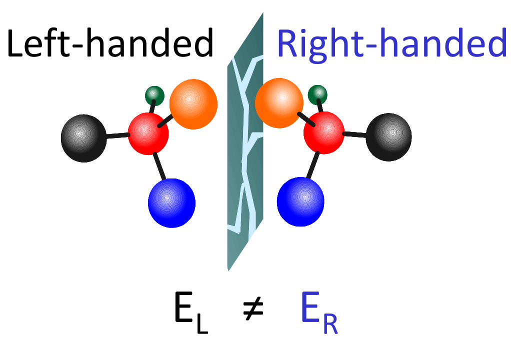
Allows the level of near-IR ultra-stable lasers to be transferred to the mid-IR
⇒ 'atomic physics' types of precision measurements on molecules

no longer constrained by CO_2 laser or any molecular reference
⇒ study of any species showing absorption between 3 and 25 µm

Summary / Perspectives

- Precise spectroscopic measurements of a variety of species
- Integration in a new generation molecular clock under construction

- Study of hyperfine structure of methanol
- me/mp time variation using CH_3OH or NH_3
- Measure the energy difference between the two enantiomers of a chiral molecule induced by the parity violation inherent in the weak interaction



Cournol et al, *Quantum Electron.* (2019)

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