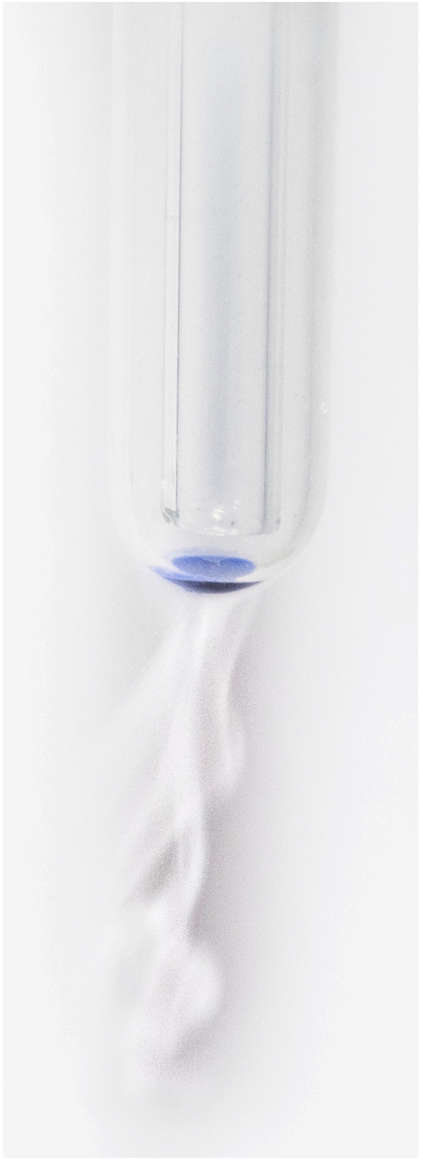
AG FIRST-TF 2023

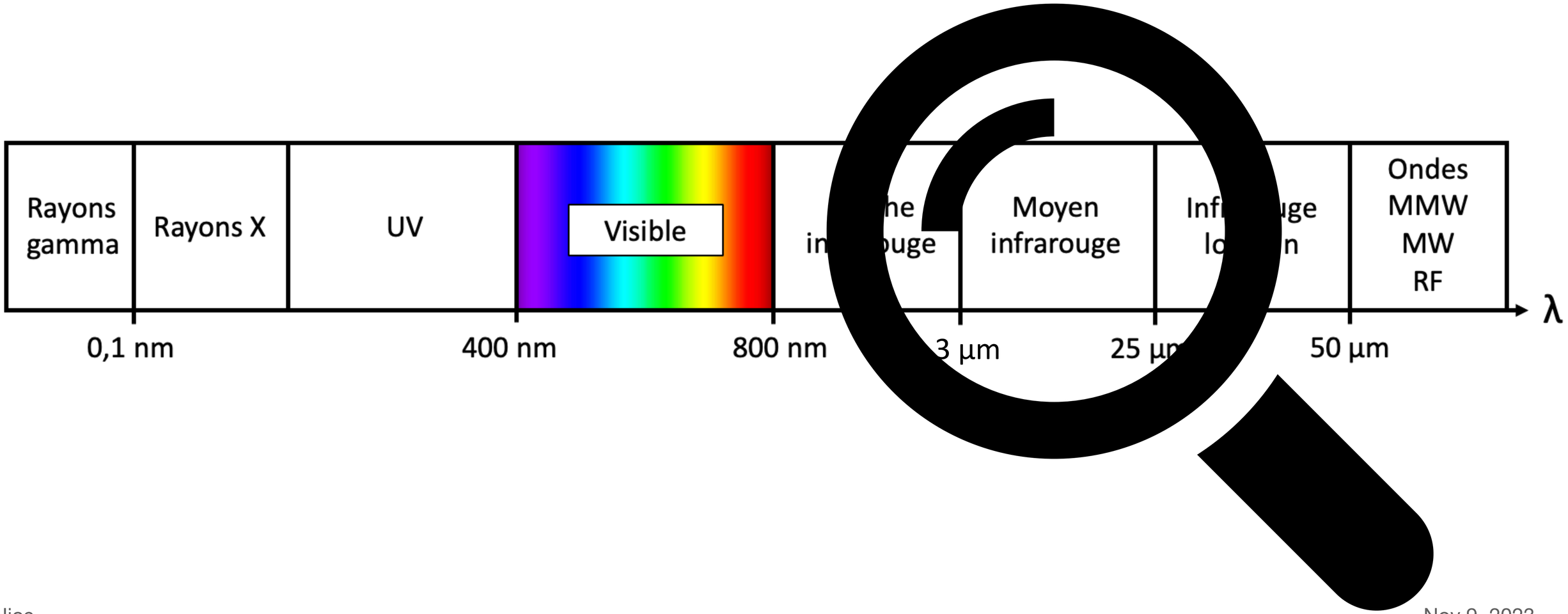
Vers une spectroscopie moléculaire ultra-résolue et traçable au système international d'unités (SI) dans l'infrarouge moyen

C. Janssen, *M. Abgrall, H. Alvarez-Martinez, A. Amy-Klein, B. Argence, N. Cahuzac, E. Cantin, B. Darquié, H. Elandaloussi, L. Hilico, J.-P. Karr, R. Le Targat, M. Leuliet, Y. Liu, L. Lorini, O. Lopez, M. Manceau, P. Marie-Jeanne, M. Mazouth, A. Mbardi, B. Pointard, P.-E. Pottie, C. Rouillé, M. Saffre, M. Tønnes, T. Zanon-Willette*

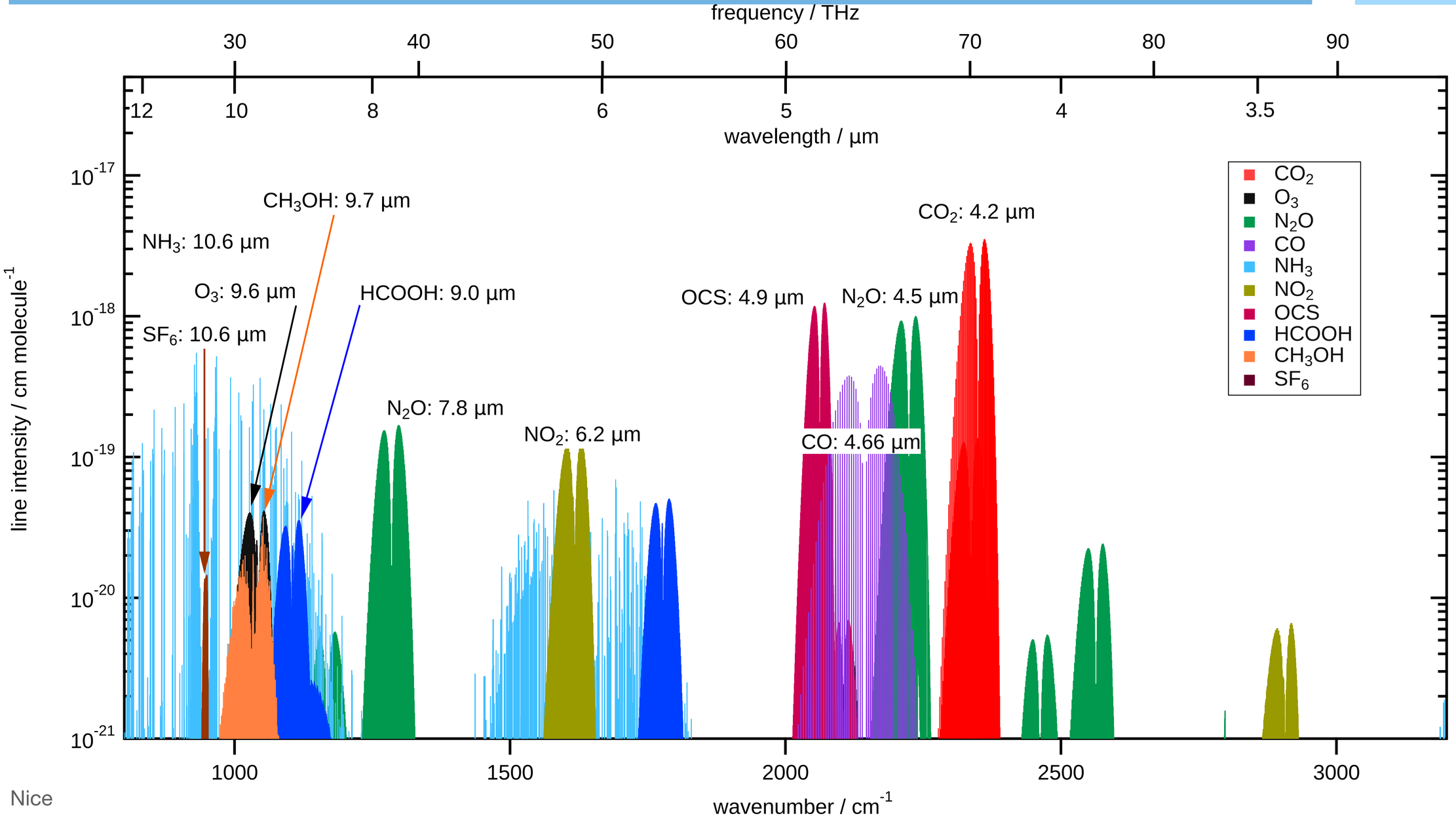
***LERMA**, Paris, France*
***LKB**, Paris, France*
***LPL**, Villetaneuse, France*
***LNE-SYRTE**, Paris, France*



MIR spectral region



MIR : molecular fingerprint region

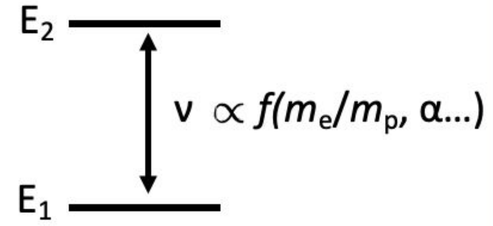


Source :
HITRAN 2022

Different motivations

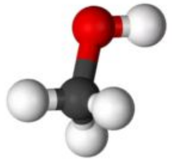
Study of fundamental constants

$\frac{m_e}{m_p}$ Electron - proton mass ratio



Value : *Hilico , Ubachs Schiller – $HD^{(+)}$, $H_2^{(+)}$*

Tempo-spatial variability : *Ubachs – methanol* ***LPL*** *– SF_6*

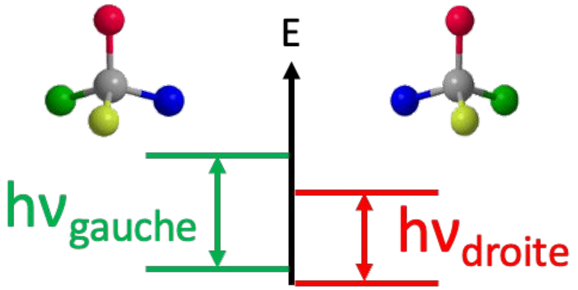


methanol

Objectif <1 kHz (qq 10^{-11})

Tests of fundamental symmetries

chiral molecules

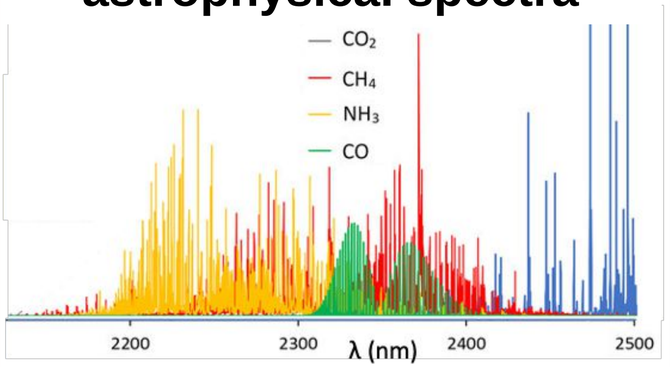


$\nu_{gauche} \neq \nu_{droite}$

weak force

$|\nu_{gauche} - \nu_{droite}|$ **~ 0,1 Hz - 1 Hz (qq 10^{-15})**

Measurement and interpretation of atmospheric & astrophysical spectra



V. Avetisov et al., Sensors (2019)

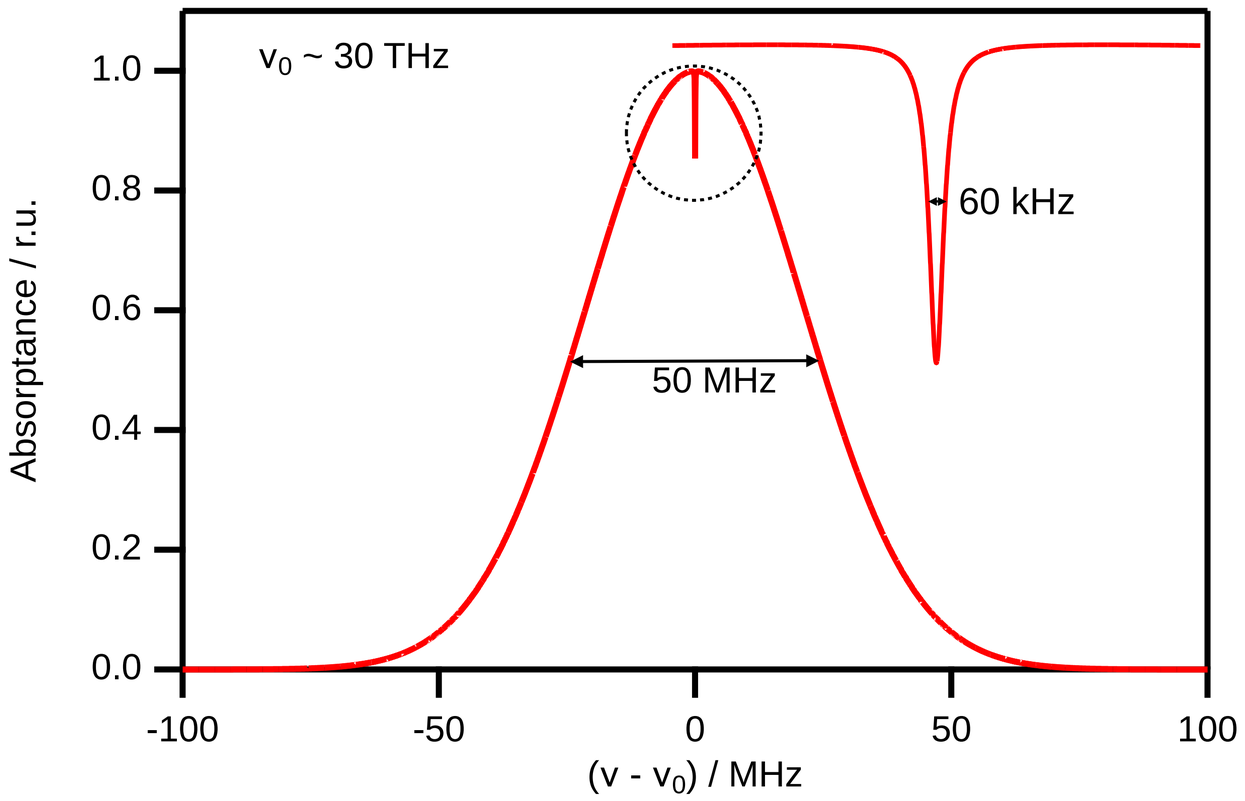
Improve molecular data bases

→ Detect and uniquely identify molecules in remote environments

→ Improve measurement accuracy, and assure SI traceability for critical species (GHG, polluants)

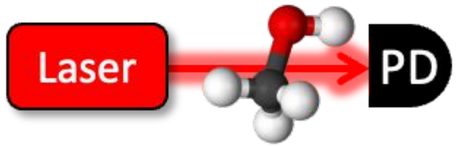
Saturated Absorption Spectroscopy

High resolution for high precision



Physical limitations

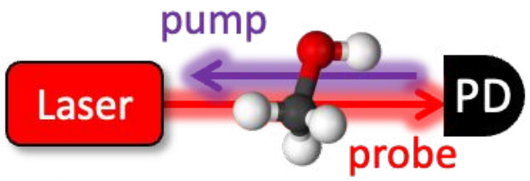
Direct absorption



Thermal broadening (Gaussian)

- Doppler effect Δν ~ 100 MHz

Saturated absorption



Coll./transit broadening (Lorentzian)

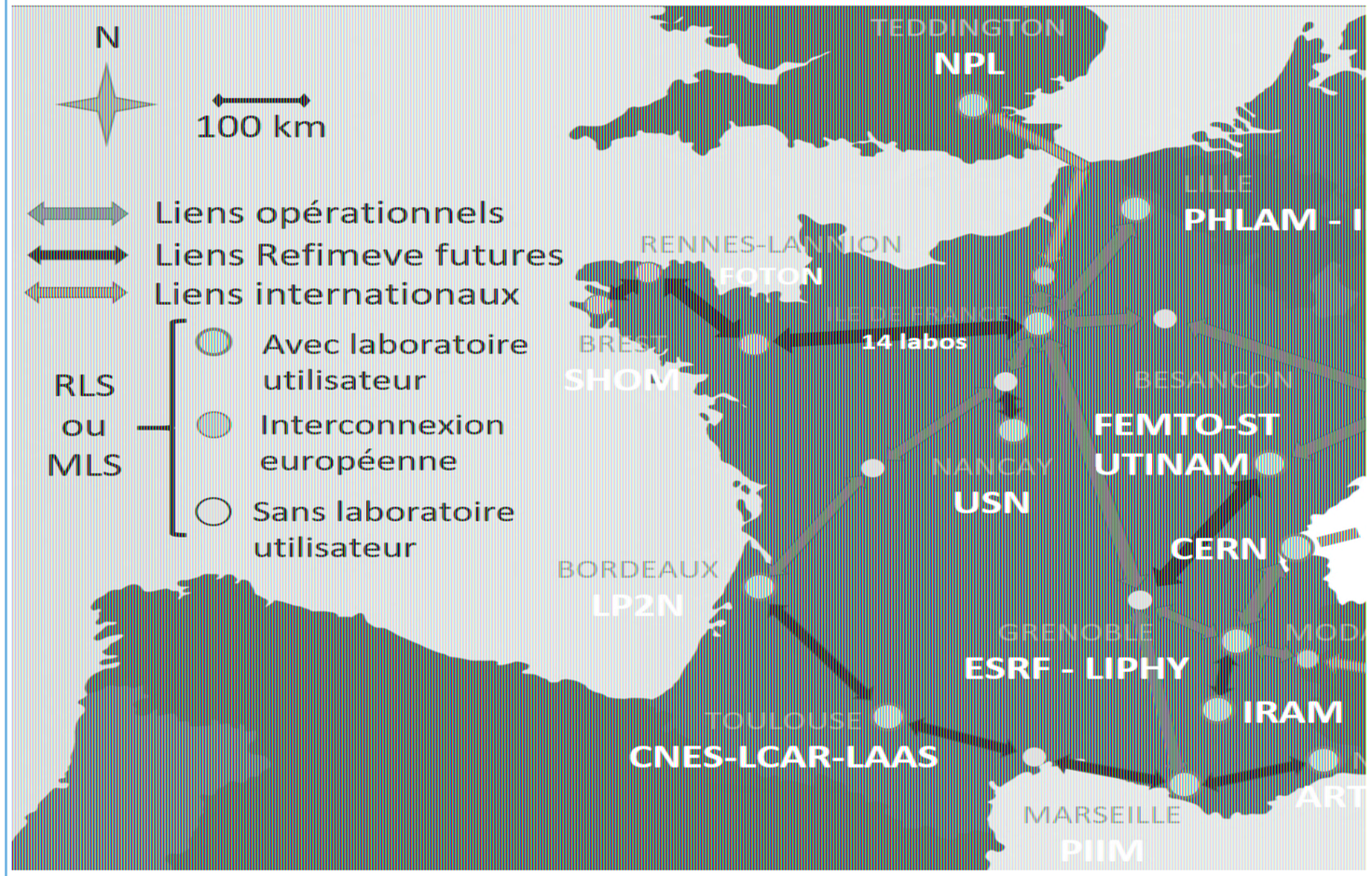
- Pressure effect Δν ~ 100 kHz (1 Pa)
- Transit broadening Δν ~ 100 kHz (1 mm)
  Δν ~ 10 kHz (1 cm)
- Power broadening $\Delta\nu = \Delta\nu_0\sqrt{1+S} \simeq \sqrt{2}\Delta\nu_0$

Technical limitations

- Laser width and stability → Ultrastable laser source

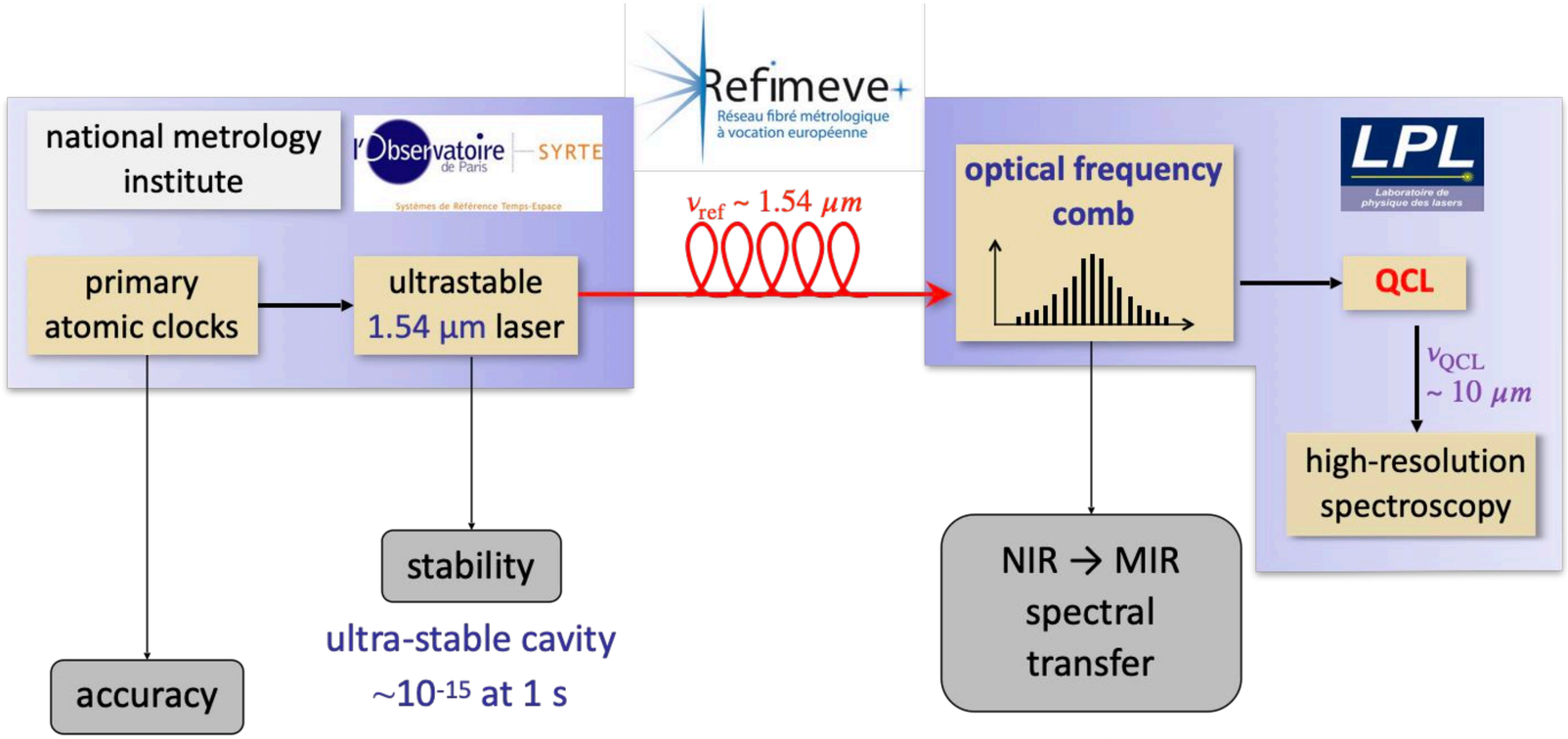
REFIMEVE: SI traceable frequency reference

Dissemination of ultrastable frequency reference via fibre network

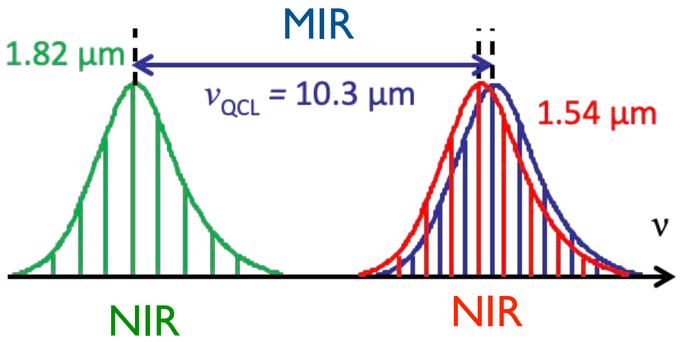


- Piloting institutions: LNE-SYRTE & LPL
- Link to nat. frequency standard (LNE-SYRTE)
- Users: Research Institutions
- Distribution by French academic research network RENATER using dedicated repeater stations
- Link to NML of neighbouring countries
- 2 signals:
  - Optical (main) signal: 1.55 µm (< 10^{-15} @ 1s)
  - RF signal (Paris area): 100 MHz (10^{-14} @ 1s)

SI traceable MIR QCLs linked to atomic clocks



$\nu_{QCL} \sim \nu_{NIR} - \nu_{NIR}$

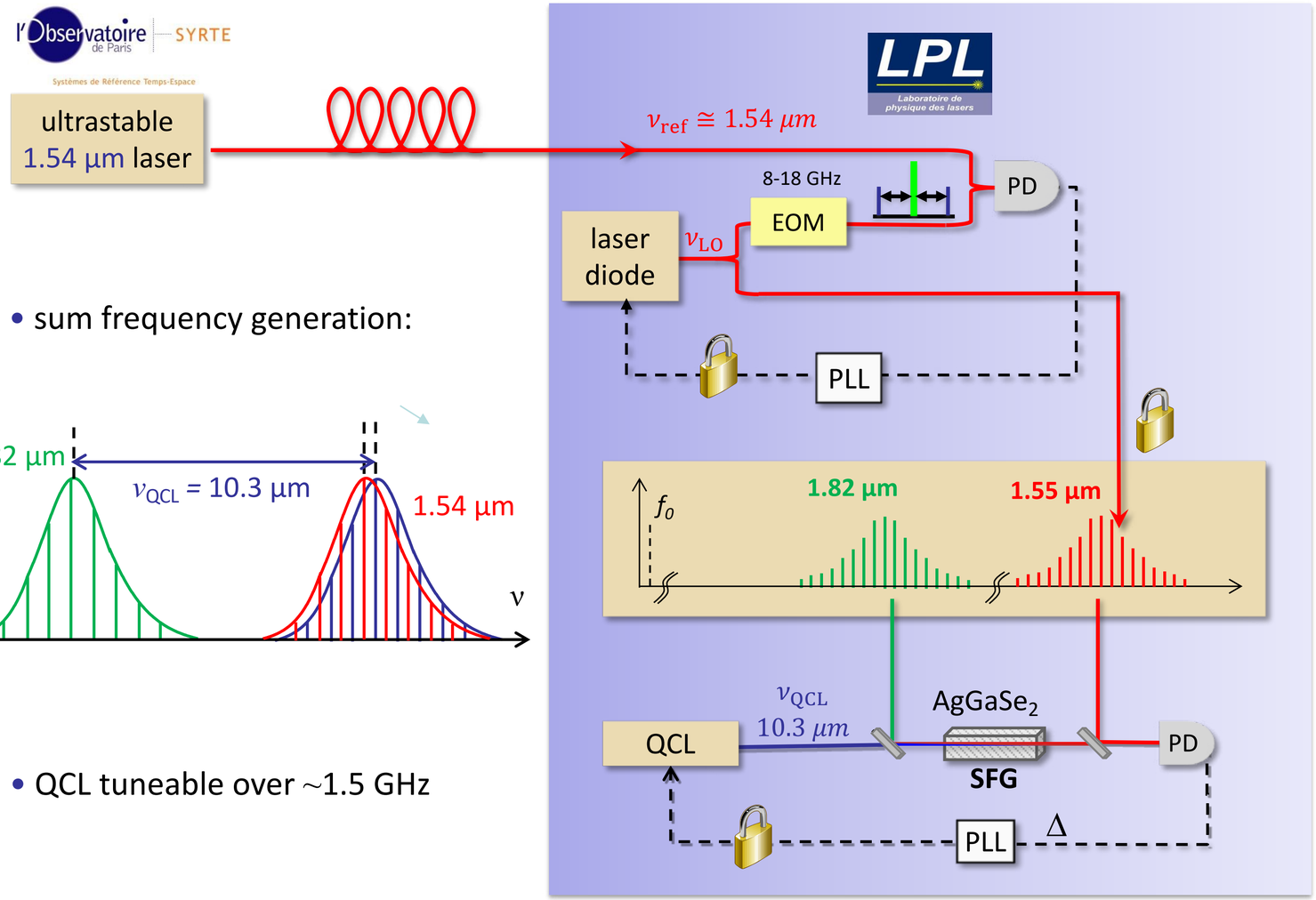


l'Observatoire de Paris SYRTE
Systèmes de Référence Temps-Espace

M Abgrall, Y Le Coq, P-E Pottie, R Le Targat

Chanteau et al, *New J. Phys.* (2013)
Argence et al, *Nature Photon.* (2015)
Santagata et al, *Optica* (2019)

SI traceable MIR QCLs locked to OFC



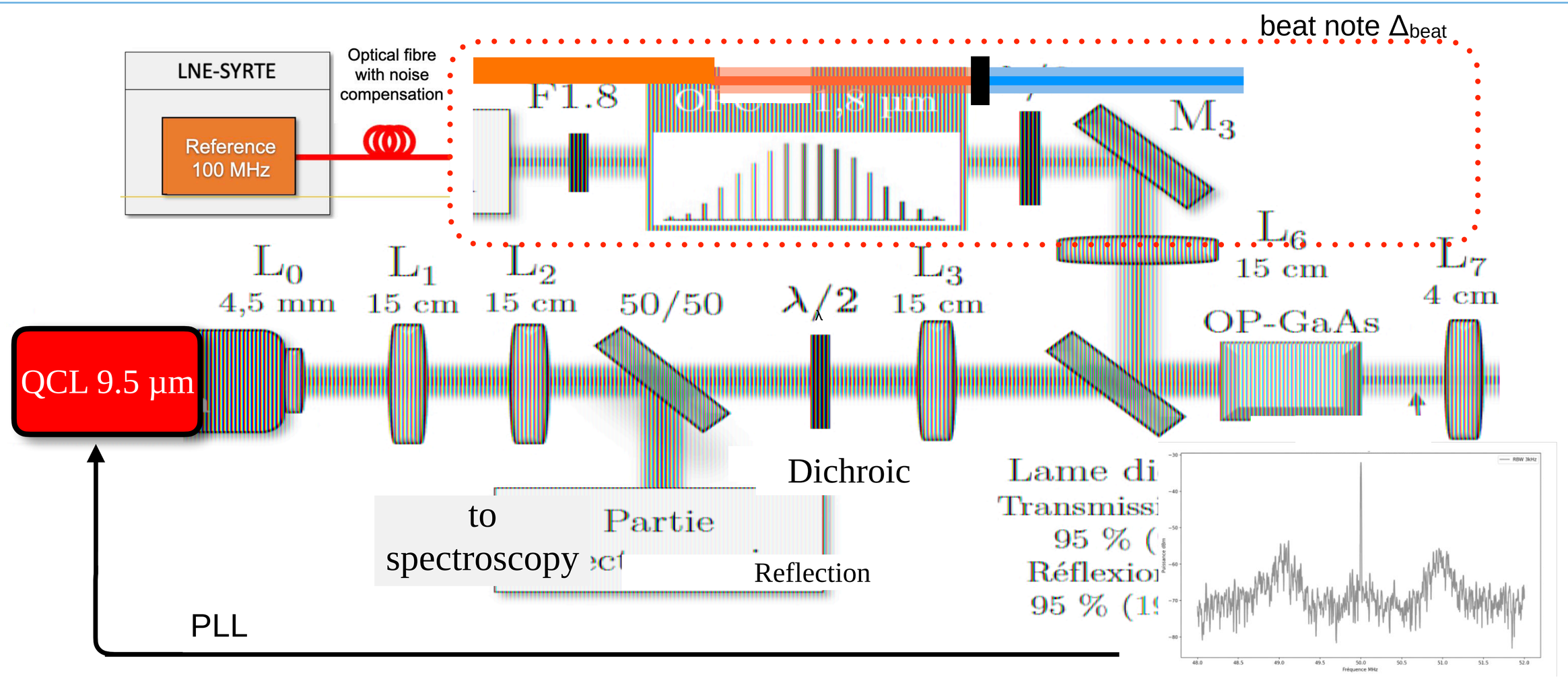
- sum frequency generation:

- QCL tuneable over ~1.5 GHz

Stabilisation scheme allows

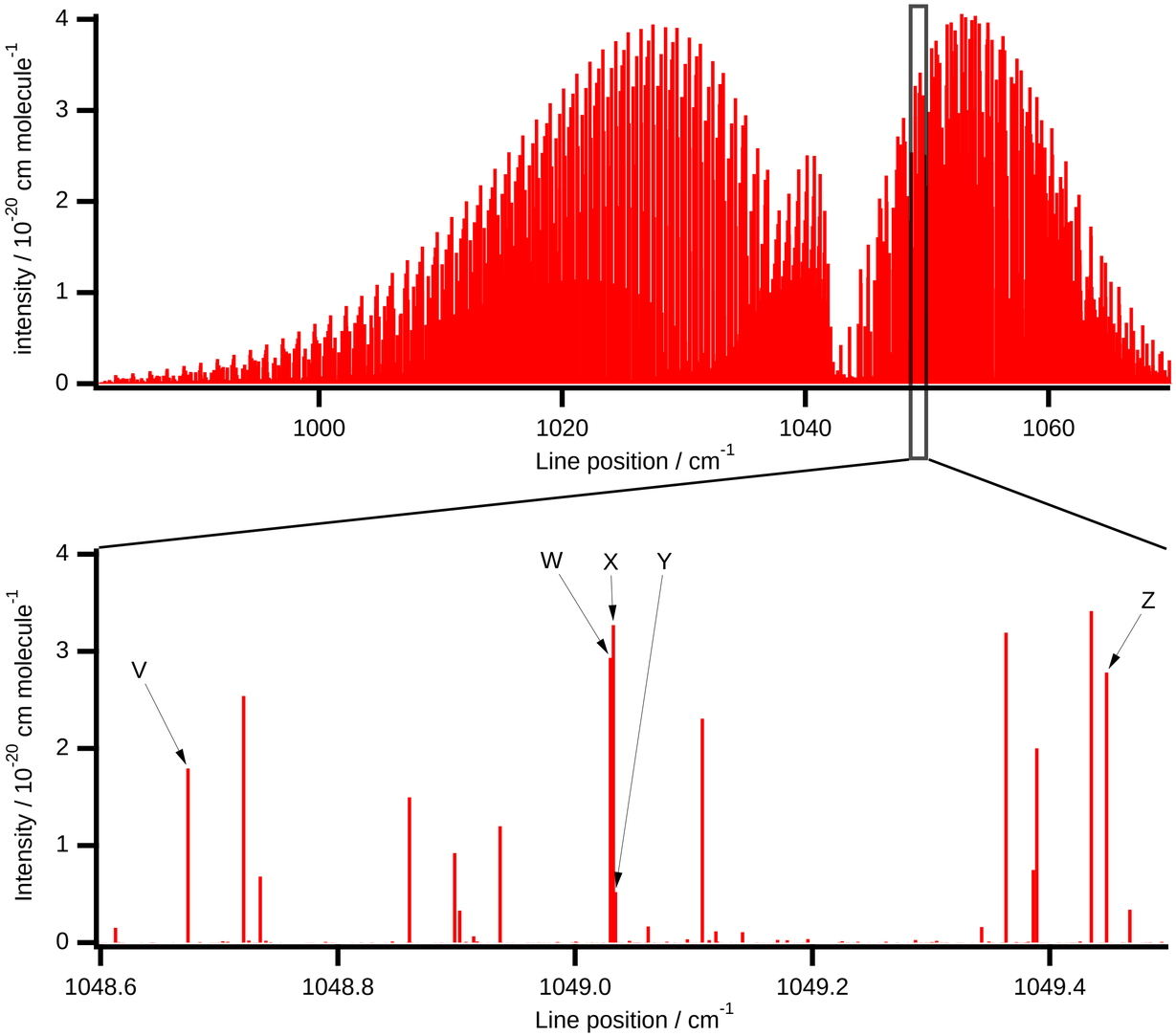
- < 10^{-15} rel. frequency stability (0.1-10 s)
- SI traceable *f* uncertainty < 10^{-14} (1s)

Setup @ LERMA



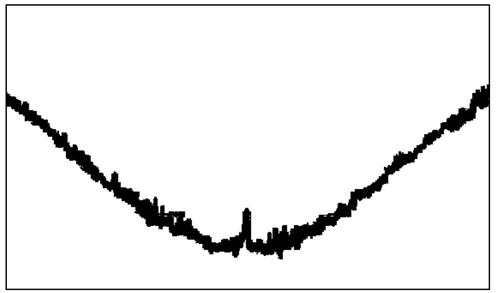
$$\nu_{\mathrm{QCL}} = (n_1 - n_2) f_r + \Delta_{\mathrm{beat}} \ , \ f_r \simeq 250\,\mathrm{MHz}$$

Study of selected O_3 lines @ LERMA



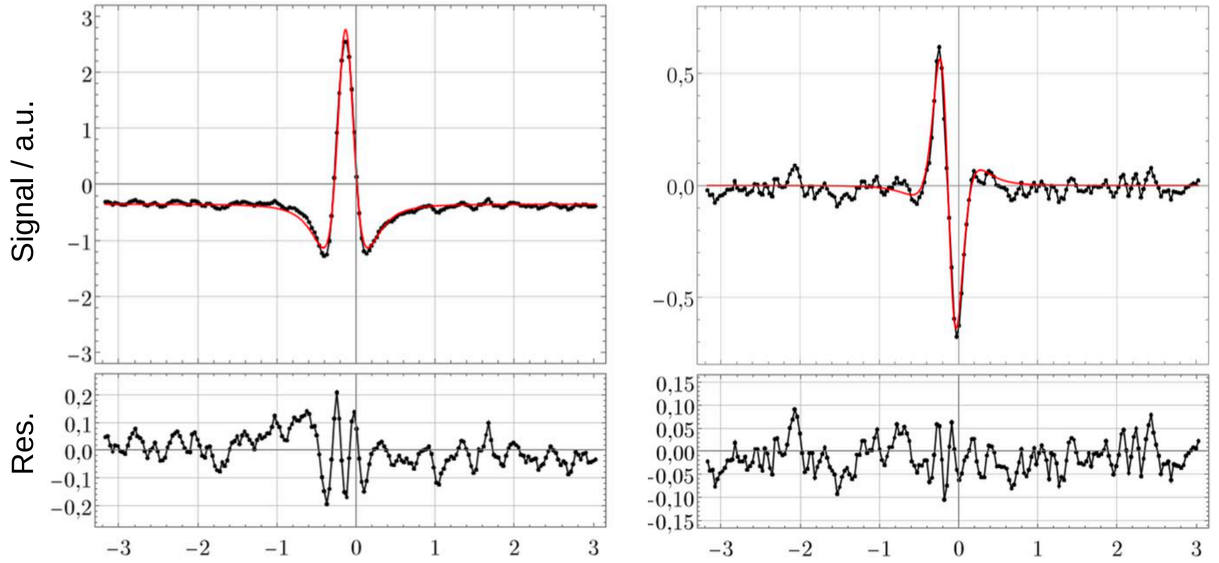
Line Z

Direct absorption



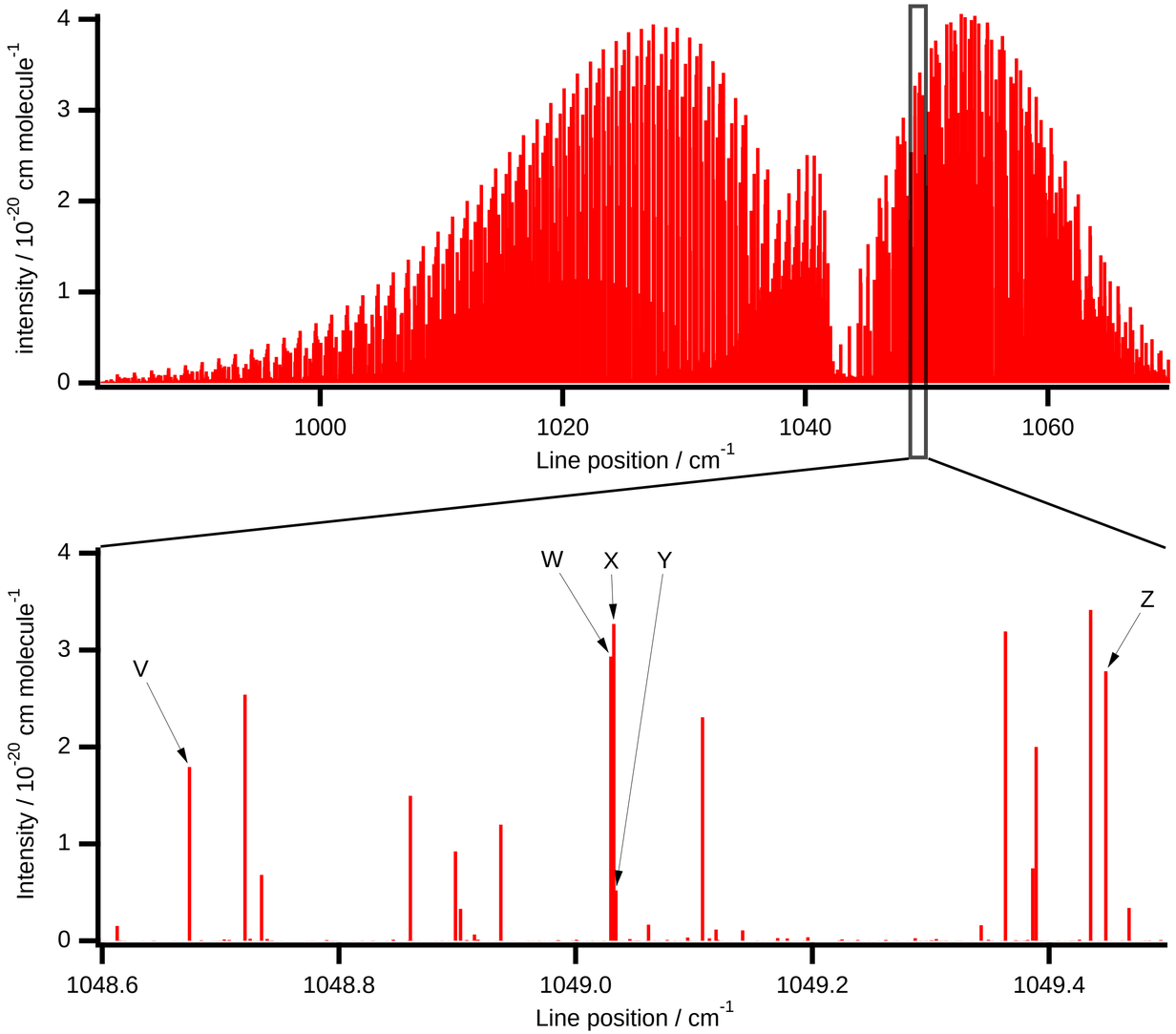
Second harmonics

Third harmonics



(*f* - 31461656.01) / MHz

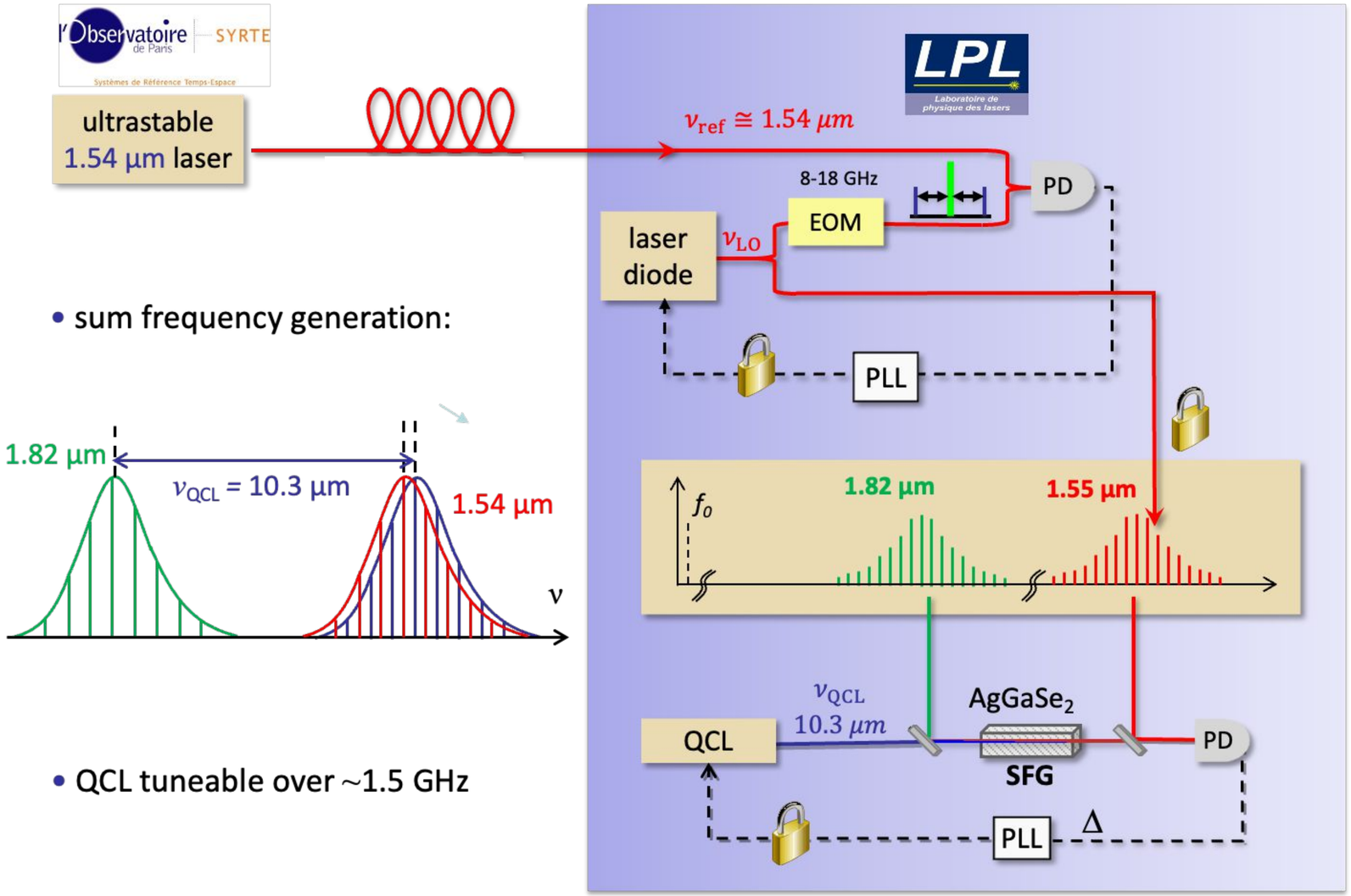
Study of selected O_3 lines @ LERMA



Line ($J_{Ka,Kc} \leftarrow J_{Ka,Kc}$)	Pos / cm^{-1} (HITRAN)	Pos / MHz (TW) u = 0.05 MHz	Pos / MHz (HITRAN) u = 3-30 MHz	Diff. / kHz (HITRAN-TW)
V ($19_{13,6} \leftarrow 18_{13,5}$)	1048.673642	31 438 444.717	31 438 444.9	**180**
W ($9_{2,7} \leftarrow 8_{2,6}$)	1049.029700	31 449 119.145	31 449 119.2	**60**
X ($9_{9,9} \leftarrow 8_{9,8}$)	1049.032171	31 449 193.254	31 449 193.3	**50**
Y ($16_{10,7} \leftarrow 15_{10,6}$)	1049.033936	31 449 246.076	31 449 246.2	**120**
Z ($10_{3,8} \leftarrow 9_{3,7}$)	1049.447882	31 461 655.885	31 461 656.0	**120**

- If significant (slight blue-shift in HITRAN) of about 0.1 MHz
- Line positions (strong lines of v_3 fundamental band) seem much more reliable than 3-30 MHz uncertainty range
- Uncertainty (50 kHz ~ **2 10^{-9}**) due to unexplained variability in line position determinations.

SI traceable MIR QCLs locked to OFC



- sum frequency generation:

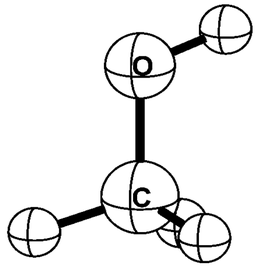
- QCL tuneable over ~1.5 GHz

Stabilisation scheme allows

- < 10^{-15} rel. frequency stability (0.1-10 s)
- SI traceable *f* uncertainty < 10^{-14} (1s)

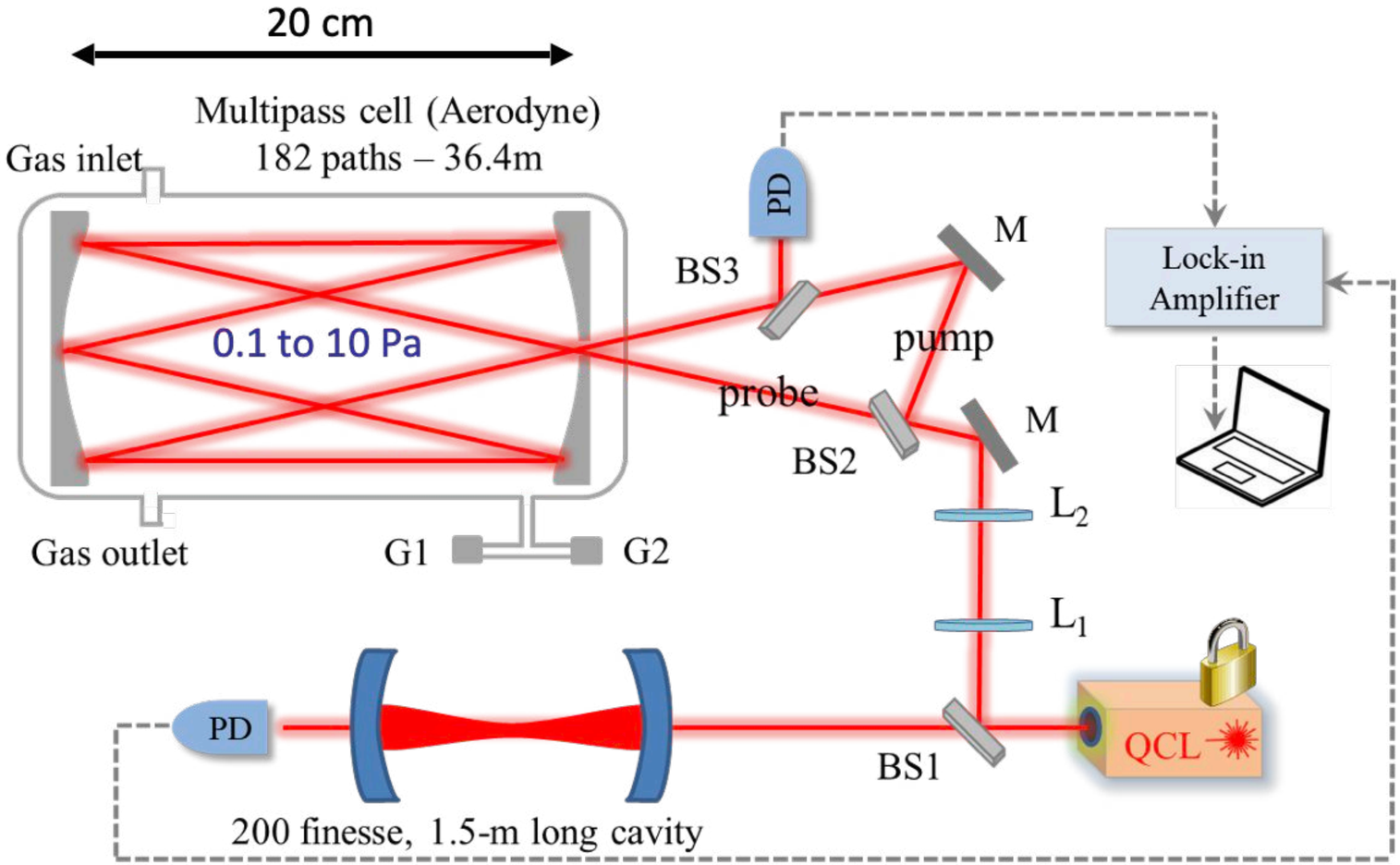
Ultra-precise QCL-based MIR spectroscopy at LPL

Saturated absorption spectroscopy of CH_3OH

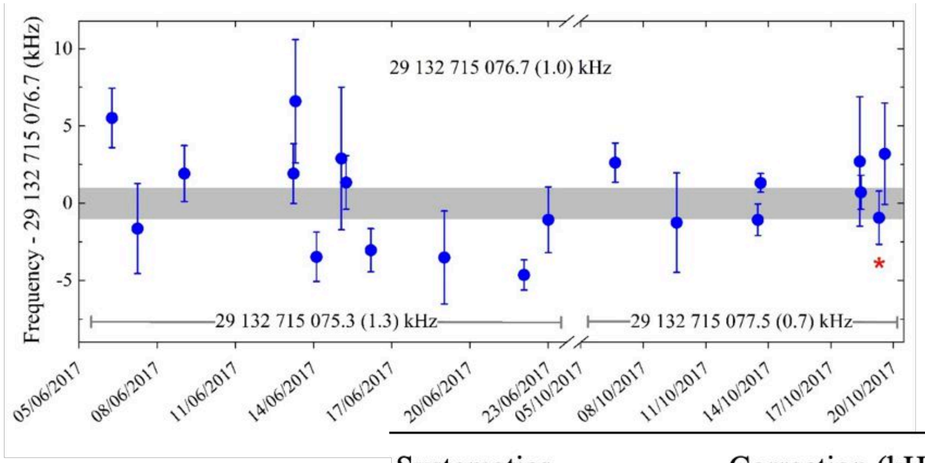


- abundant interstellar and protostellar molecule
- abundant organic molecule in atmosphere (leads to production of ozone)
- sensitive to variations of m_e/m_p

Spectroscopy Setup



Record uncertainties @ LPL



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

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

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**

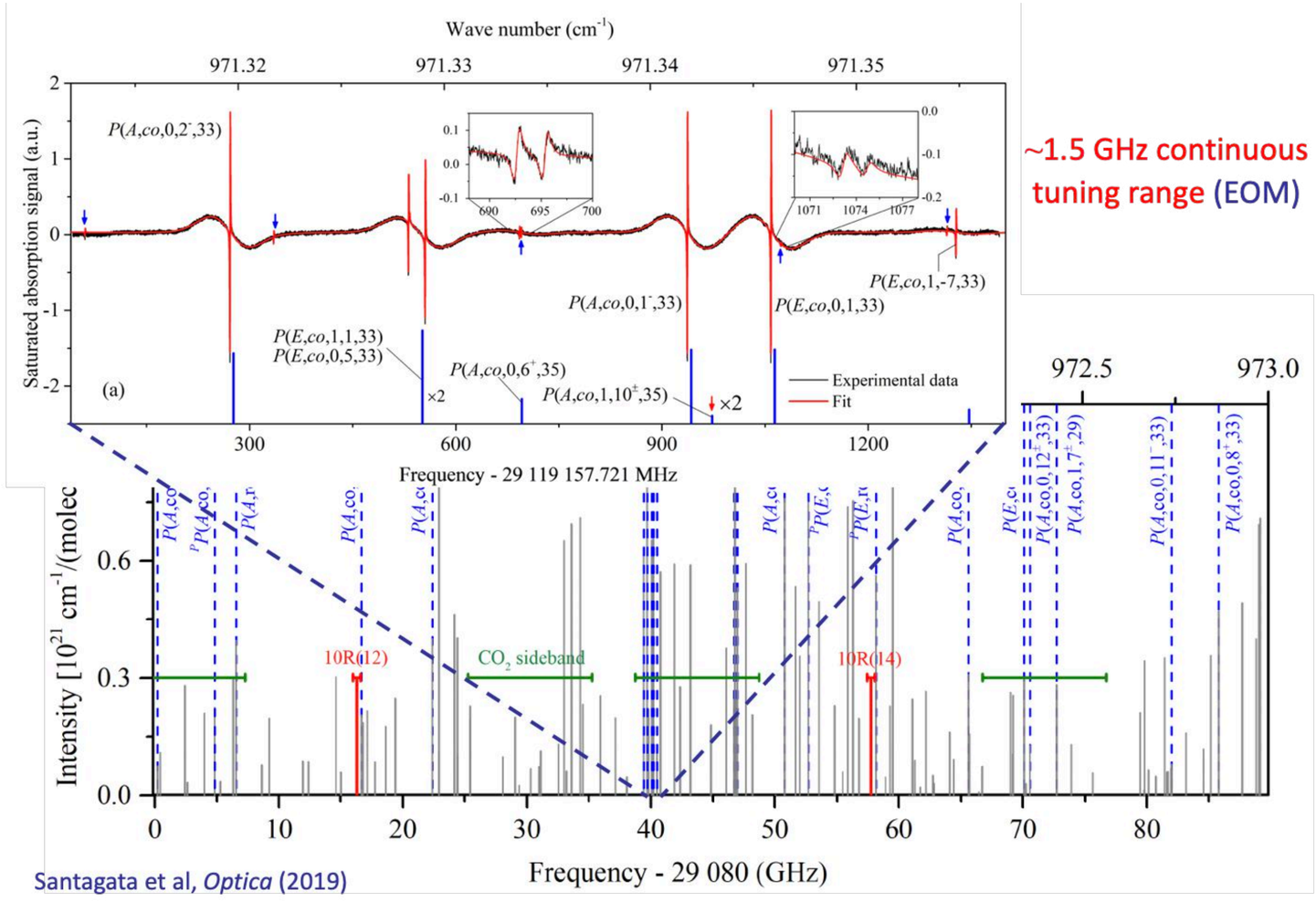
→ 7.4 kHz global uncertainty

~2000 improvement over previous measurements

Santagata et al, *Optica* (2019)

- Record uncertainty on methanol line positions
- Rel frequency stability : 3.8 10^{-11} (stat)
- Total relative uncertainty : 2.5 10^{-10}
- *FPC leads to ~10 times reduced systematic uncertainty*

Spectral coverage and tuneability @ LPL



~1.5 GHz continuous tuning range (EOM)

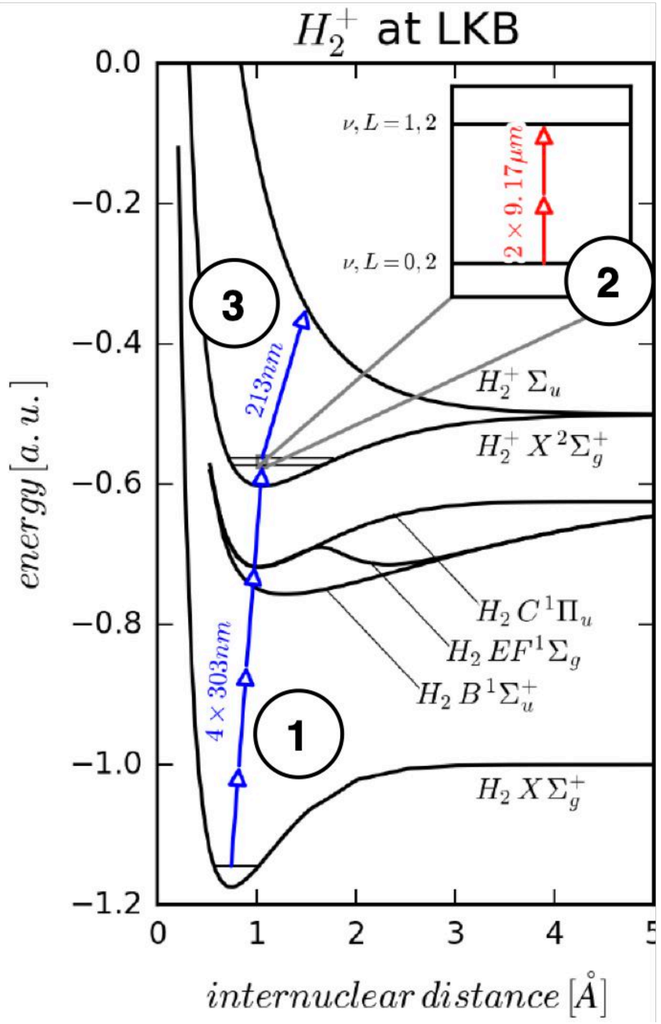
~ 100 GHz full tuning range of QCL

- Longest continuous single scan tuning (1.5 GHz)
- Shift wrt to HITRAN database (blue sticks) is evident
- Database incomplete
- Fine structure can be revealed

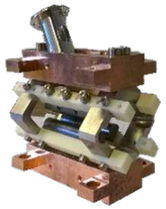
Resonance Enhanced Multiphoton Dissociation spectroscopy of H_2^+ @ LKB

m_e/m_p from H_2^+ spectroscopy

- $\nu \propto \sqrt{m_e/m_p} \rightarrow \frac{\Delta(m_e/m_p)}{m_e/m_p} = 2\frac{\Delta\nu}{\nu}$
- 3 body : $p^+ + p^+ + e^-$
- (1,2) ← (0,2) transition can be calculated at the $7 \cdot 10^{-12}$ accuracy level



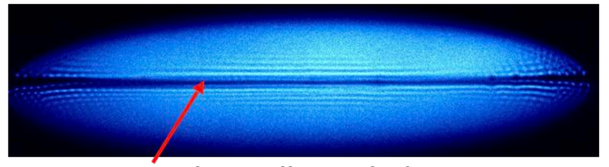
Experiment overview


Ion trap

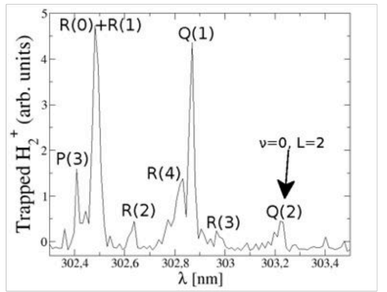
+


Be+ cooling laser

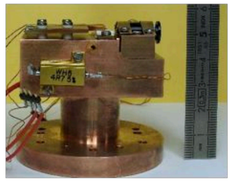
=


Sympathetically cooled H_2^+ ions in a Be+ crystal

1. State selected H_2^+ production by 3+1 REMPI at 303 nm in v=0, L=2

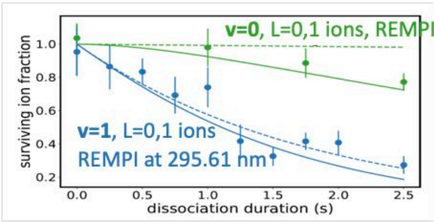


2. Two-photon excitation at 9.17 µm



S.I.-referenced QCL source

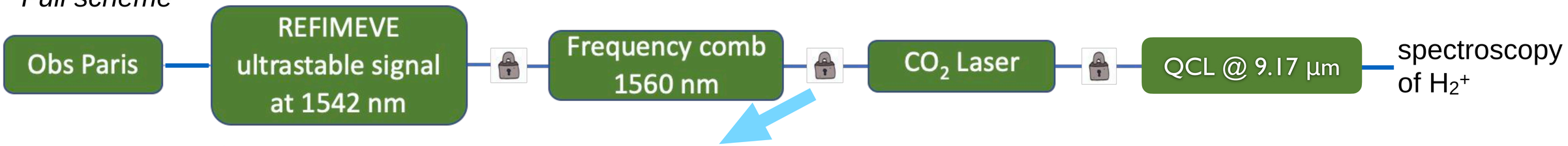
3. Selective photodissociation at 213 nm



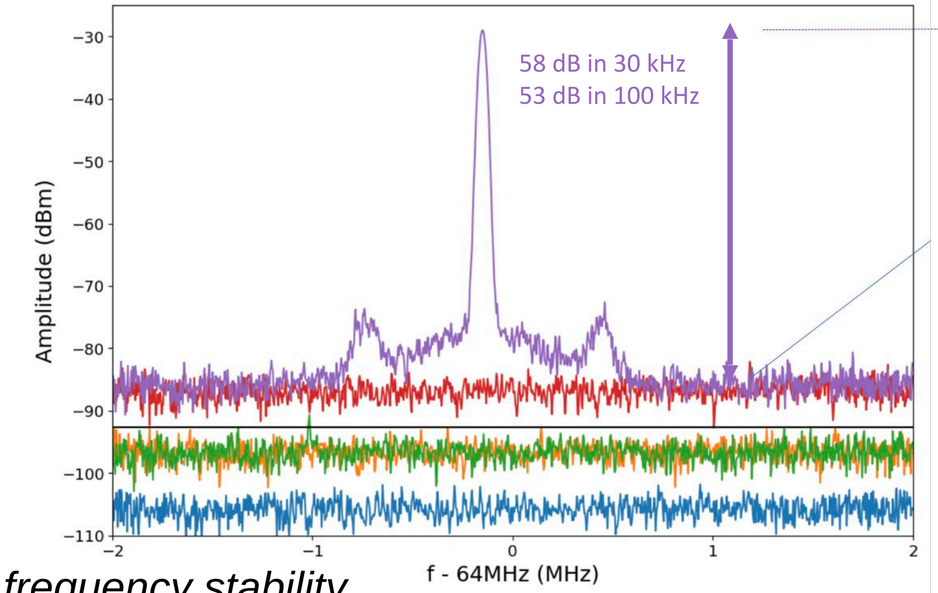
Schmidt & al, 2020

Resonance Enhanced Multiphoton Dissociation spectroscopy of H_2^+ @ LKB

Full scheme



Beatnote SFG comb/original comb (RBW = 30 kHz)



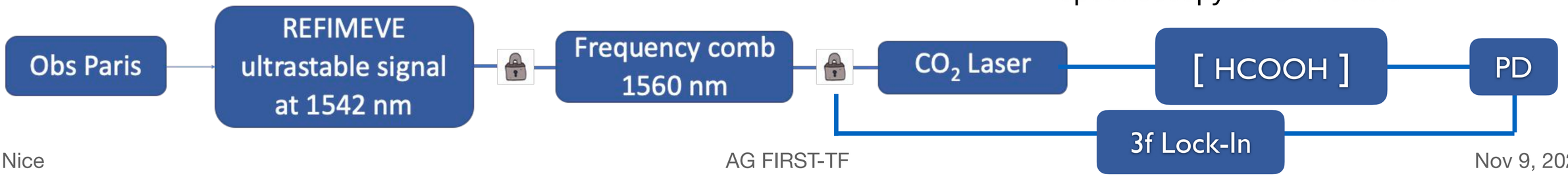
Max beat signal 10 dB less than ideal theory

Noise 5-6 dB above shot noise

Comb/comb beat note
1560 nm comb noise (~ 200 µW)
Expected shot noise
Electronic noise SFG comb noise (~ 200 nW)
Analyzer noise floor

Test frequency stability

spectroscopy of formic acid

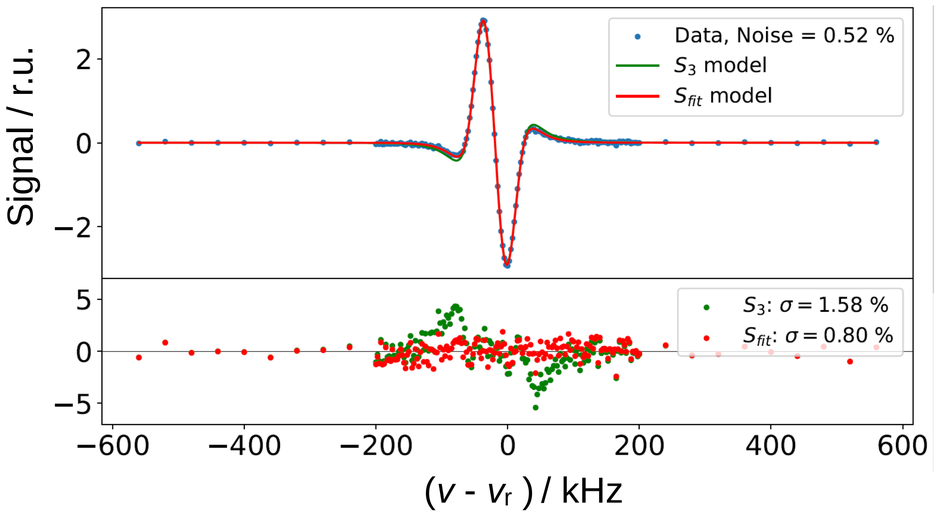


HCOOH at 9.17 µm as accuracy test @ LKB

Measurement campaign

4 optical powers	0.72, 1.44, 2.16 and 2.88 mW
4 pressures	0.5, 1, 1.5 and 2 µb
3 modulation depths	17.7, 26.6 and 33.4 kHz HWHM

10 scans up and 10 scans down 480 spectra



Central frequency analysis

$$\nu_c = 32\,708\,391\,980\,966\,(18)\ \text{Hz}$$

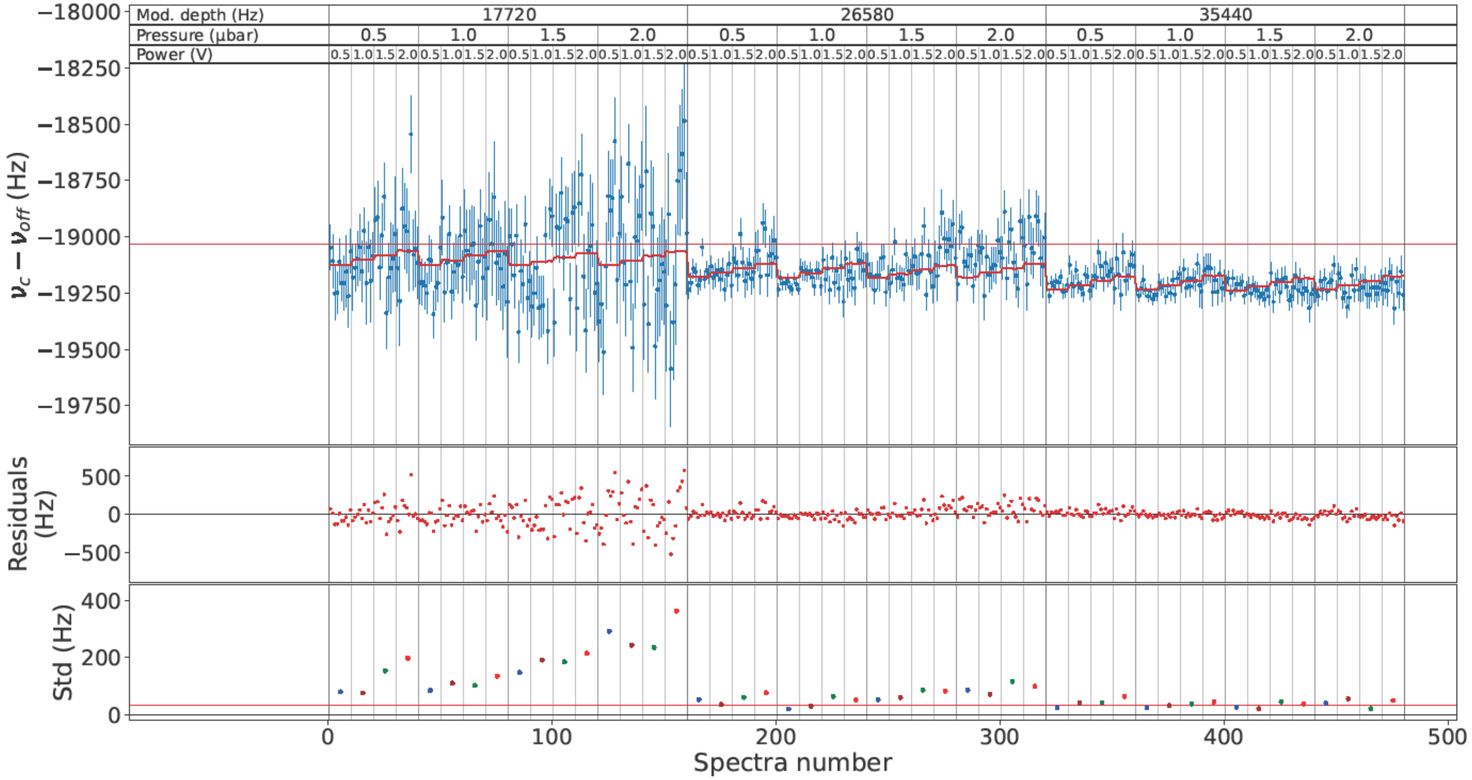
Stat **5.5 10^{-13}**

Frequency adjustment

$$\nu_c = \nu_0 + \alpha\, P + \beta\, I + \gamma\, M$$

Trends

- Very weak pressure shift
- Light shift ↗
- Slight modulation shift ↘



Conclusions

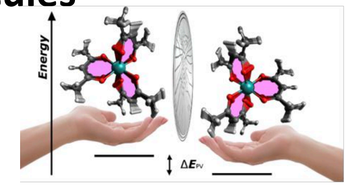
- Development and setup of ultrastable SI-traceable MIR spectrometers for ultra-high resolution molecular spectroscopy
- New and original measurements of ozone, methanol and formic acid line positions around 10 µm have been presented
- Achieved line centre uncertainties are in the 10^{-9} to $< 10^{-12}$ range
- Data can serve as unique benchmarks for molecular calculations
- and further development/measurements will constrain fundamental constants

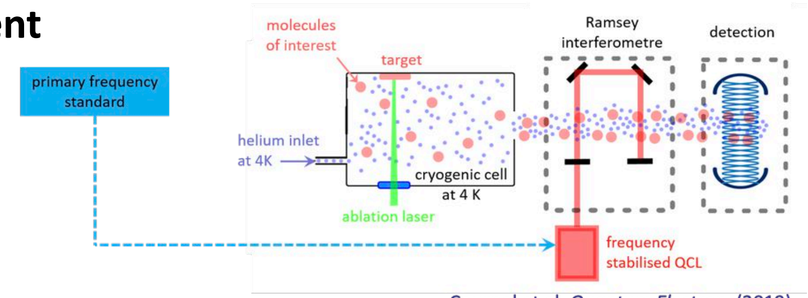
Perspectives

@ LPL

using a newly developed spectrometer

- **m_e/m_p time variation in the present epoch** using **CH_3OH**, NH_3, …
- test **fundamental symmetries** in **chiral molecules**





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

sub-Hz (10^{-14}-10^{-15}) target uncertainty

@ LKB

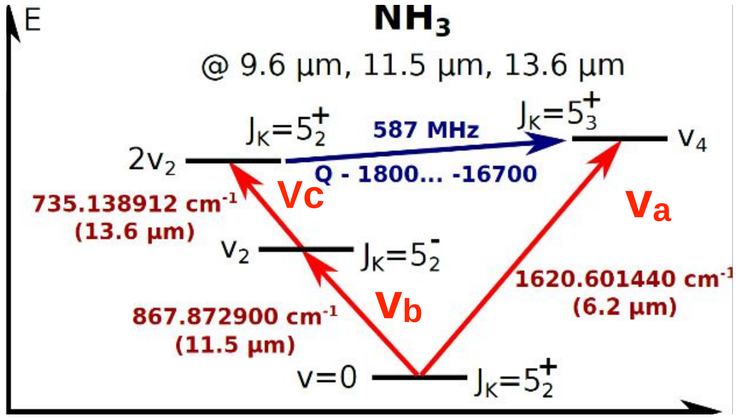
- **Fundamental constant measurement (m_e/m_p)** using MIR (9.17 µm) spectroscopy of H_2^+

sub-100 Hz (10^{-12}-10^{-13}) target uncertainty

@ LPL, LKB, LERMA

- **m_e/m_p variation (spatial & temporal)** in lab/space comparisons using CH_3OH, NH_3…

sub-kHz (10^{-11}) target uncertainty



$\nu_{RF} = \nu_a - \nu_b - \nu_c$

@ LERMA

Fundamental ozone molecular line shape and parameter measurements **(ν_0, γ, δ, S, …)** in the MIR for

- **unifying spectroscopic data between UV and IR**
- investigating **isotope dependencies**
- **extending spectral coverage**

sub-kHz (10^{-11}) target uncertainty

FIN

Thank you for your attention