AG FIRST-TF 2026

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SI-Traceable Precision Microwave Molecular Spectroscopy for Fundamental Physics

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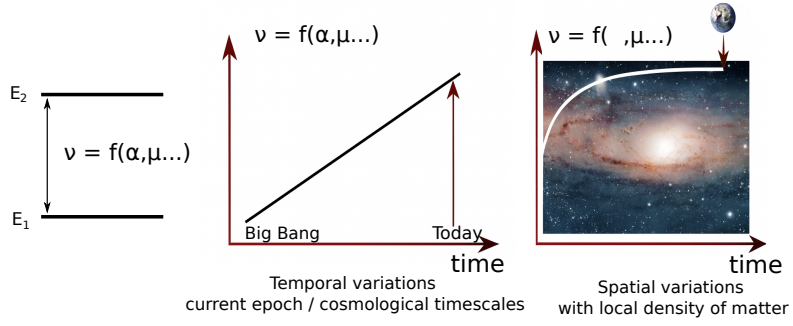
1. Molecular microwave (MW) spectroscopy for precision measurements
2. Measurements at LPL and UC Louvain
3. MW spectroscopy as a detection tool

1. **Molecular microwave (MW) spectroscopy for precision measurements**
2. Measurements at LPL and UC Louvain
3. MW spectroscopy as a detection tool

Molecular spectroscopy and μ variation

Probing variations of $\mu = m_e/m_p$

- **Molecular transition frequencies depend on $\mu = m_e/m_p$**
- **Measure frequency variations**
  - Clock comparisons: present-day drift
  - Laboratory vs. astrophysical spectra: cosmological timescales



Molecular spectroscopy and μ variation

- **Sensitivity coefficient K_μ : frequency response to $\Delta\mu$**

$$\frac{\Delta\nu}{\nu} = K_\mu \frac{\Delta\mu}{\mu},$$

Molecular spectroscopy and μ variation

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- **Scaling with μ:**

$K_\mu^{\mathrm{el}} \approx 0$ **(electronic energies weakly depend on μ),**

$K_\mu^{\mathrm{vib}} \approx -\frac{1}{2}$ **(since $\omega_{\mathrm{vib}} \propto \sqrt{1/\mu_{\mathbf{red}}}$),**

$K_\mu^{\mathrm{rot}} \approx -1$ **(since $\omega_{\mathrm{rot}} \propto \frac{\hbar^2}{2I}$, $I \propto \mu_{\mathbf{red}}$)**

Molecular spectroscopy and μ variation

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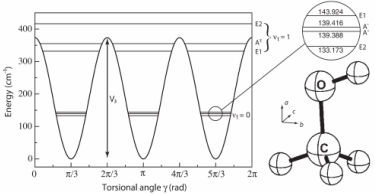
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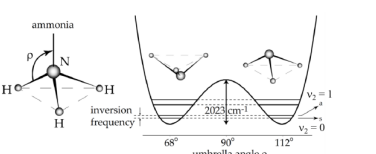
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- **Enhanced sensitivity: LAM modes : Tunneling / inversion modes $|K_\mu| \gg 1$ potential $\approx \exp(\sqrt{\mu})$.**



Jansen et al., Physical Review A 84, 062505 (2011).



Ground Frequency splitting : 24 GHz

Jansen et al., Chem. Phys. 140.1 (2014).

Molecular spectroscopy and μ variation

Methanol and constraints on $\Delta\mu$

- **Current constraints from high redshift molecular absorbers (methanol):**

$$|\Delta\mu/\mu| < 3 \times 10^{-7} \quad (3\sigma)$$

  implying $\dot{\mu}/\mu \sim 10^{-17}$ yr^{-1} if a linear change is assumed.

- **Local (Milky Way) studies compare terrestrial vs. interstellar environments:**

$$|\Delta\mu/\mu| < 2 \times 10^{-8}\ (\mathrm{NH_3}), \quad < 6 \times 10^{-8}\ (\mathrm{CH_3OH}).$$

- **Constraints are limited by laboratory accuracy on microwave transitions ($\sim$ 10 kHz).**

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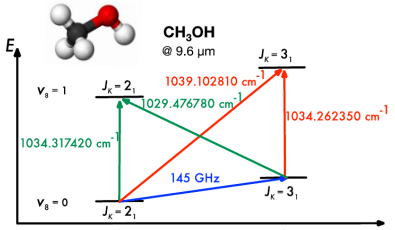
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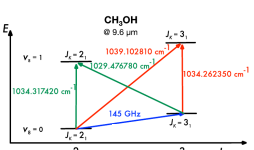
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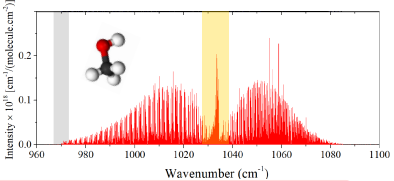


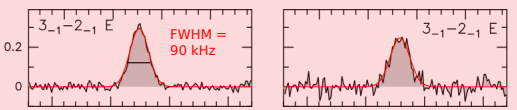
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Molecular spectroscopy and μ variation

Methanol and constraints on $\Delta\mu$







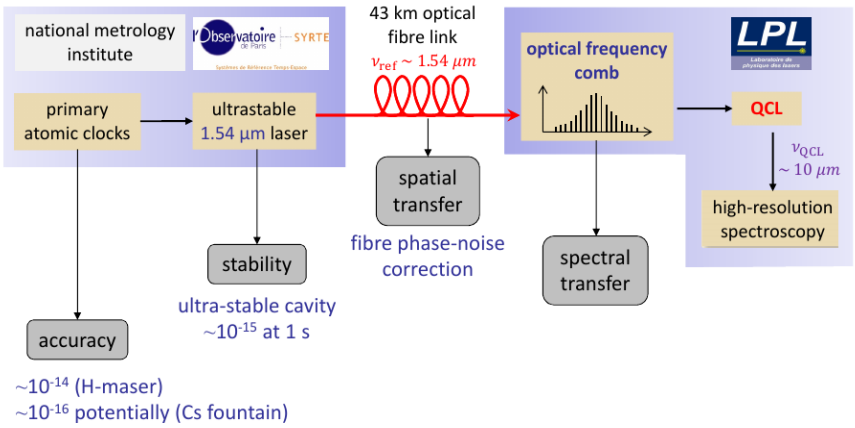
Source	Transition	Observed frequencies[a] [MHz]	FWHM [MHz]	T_{mb} [mK]	T_{RADEX} [mK]	τ_ν	E_{up} [K]	E_{low} [K]	Sensitivity coefficients	Band
L1498-1	$2_{-1} \rightarrow 1_{-1}$ E	96739.376 ± 0.001	0.046 ± 0.003	556 ± 15	524	0.23	12.2	7.7	-1.0	E090
α = 04 : 10 : 56.6	$2_0 \rightarrow 1_0$ A+	96741.388 ± 0.001	0.049 ± 0.003	716 ± 15	620	0.27	6.8	2.3	-1.0	
δ = +25 : 09 : 08.0	$2_0 \rightarrow 1_0$ E	96744.560 ± 0.007	0.055 ± 0.003	32 ± 17	60	0.03	19.5	15.0	-1.0	
	$3_{-1} \rightarrow 2_{-1}$ E	145097.464 ± 0.001	0.085 ± 0.001	374 ± 14	412	0.23	19.0	12.2	-1.0	E150
	$3_0 \rightarrow 2_0$ A+	145103.212 ± 0.001	0.077 ± 0.001	426 ± 12	423	0.23	13.6	6.8	-1.0	
	$1_0 \rightarrow 1_{-1}$ E	157270.877 ± 0.003	0.079 ± 0.005	137 ± 19	94	0.44	15.0	7.7	-3.5	
	$2_0 \rightarrow 2_{-1}$ E	Not detected			52	0.32	19.5	12.2	-3.5	
L1498-2	$2_{-1} \rightarrow 1_{-1}$ E	96739.365 ± 0.002	0.048 ± 0.003	508 ± 75	545	0.37	12.2	7.7	-1.0	E090
α = 04 : 10 : 47.0	$2_0 \rightarrow 1_0$ A+	96741.380 ± 0.001	0.054 ± 0.003	608 ± 69	619	0.42	6.8	2.3	-1.0	
δ = +25 : 10 : 18.0	$2_0 \rightarrow 1_0$ E	Not detected			60	0.04	19.5	15.0	-1.0	
	$3_{-1} \rightarrow 2_{-1}$ E	145097.440 ± 0.001	0.097 ± 0.005	325 ± 29	360	0.36	19.0	12.2	-1.0	E150
	$3_0 \rightarrow 2_0$ A+	145103.191 ± 0.002	0.091 ± 0.003	372 ± 26	357	0.30	13.6	6.8	-1.0	
	$1_0 \rightarrow 1_{-1}$ E	157270.858 ± 0.010	0.100 ± 0.013	115 ± 38	88	0.66	15.0	7.7	-3.5	
	$2_0 \rightarrow 2_{-1}$ E	Not detected			41	0.41	19.5	12.2	-3.5	

[a] corrected for the radial velocity of L1498

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Molecular spectroscopy and μ variation

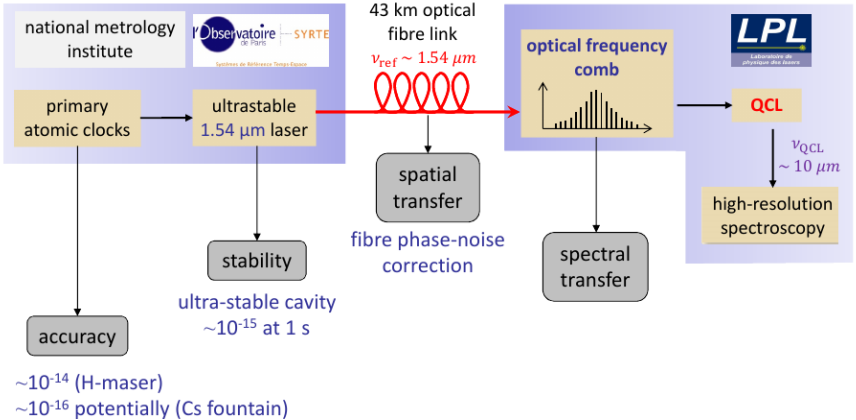
widely tunable SI-traceable mid-infrared QCL at 10 μm



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

Molecular spectroscopy and μ variation

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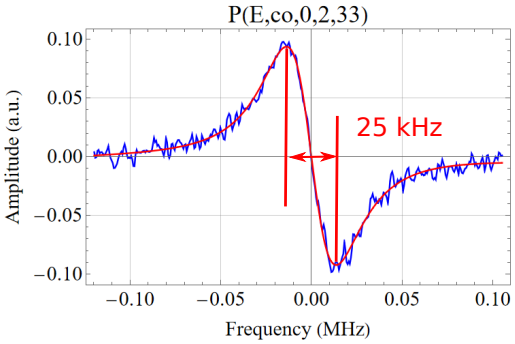


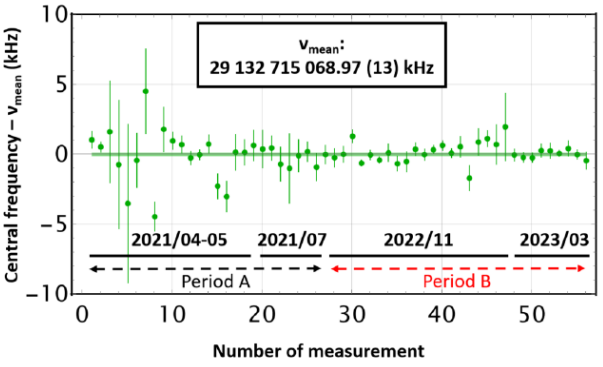
- **ultimate stabilities (0.06 Hz) and accuracies (sub-Hz)**
- **narrowest QCL so far (0.1 Hz)**

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

Molecular spectroscopy and μ variation

Methanol spectroscopy with a QCL: FP cavity

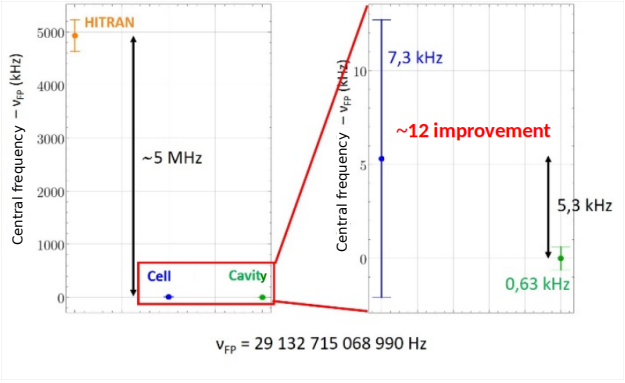




Molecular spectroscopy and μ variation

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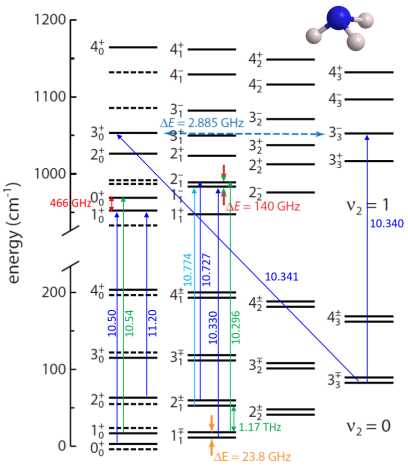
Systematics	Correction (Hz)	Uncertainty (Hz)
QCL frequency calibration	0	5
Pressure shift	$-\alpha_{\text{pressure}}p$	110
Power shift	/	/
Gas-lens effect	0	0
Fitting model	0	500
Second-order Doppler effect	0	18
Other effects (Black-body radiation shift, Zeeman effect, Recoil doublet, Wave-front curvature)	0	< 1
Total systematic	$\boldsymbol{-\alpha_{\text{pressure}}p}$	**510**
Statistics	/	**130**
Total	$\boldsymbol{-\alpha_{\text{pressure}}p}$	**530**



- 25 kHz linewidth
- 600 Hz line centre uncertainty

Molecular spectroscopy and μ variation

Towards laboratory–astrophysics comparisons



- **Target astrophysical molecules**
  - NH_3 and CH_3OH
- **Improve MIR molecular spectroscopy**
  - Sub-100-Hz line-centre uncertainties
- **Identify the most relevant schemes**
  - Astrophysically observed MW transitions
  - Large K_μ sensitivity
  - Accessible MIR combination differences
- **Build robust laboratory frequencies**
  - Identify limiting systematics

Molecular spectroscopy and μ variation

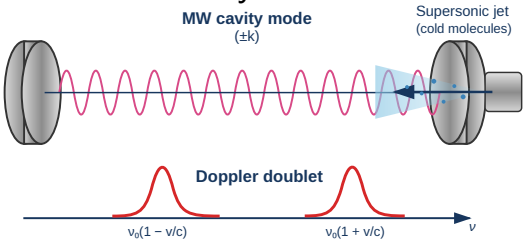
Cross-validation by direct MW measurements

- **MIR route**
  - Ultra-precise rovibrational frequencies
  - MW intervals from combination differences
- **MW route**
  - Direct measurement of the same rotational intervals
  - Independent instrumentation chain
- **Different systematic effects**
  - Independent uncertainty budgets

- Measuring molecular MW transition frequencies at the **10-100 Hz level** ?

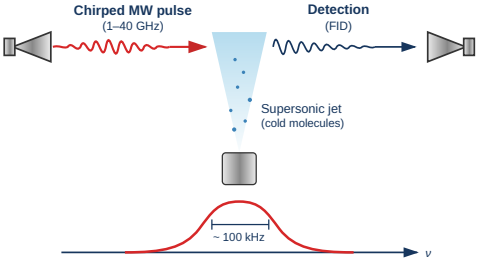
Molecular spectroscopy and μ variation

Cavity FTMW



- **High sensitivity**
- **Doppler doublet / Residual shifts : molecular-beam dynamics**

Chirped-pulse FTMW



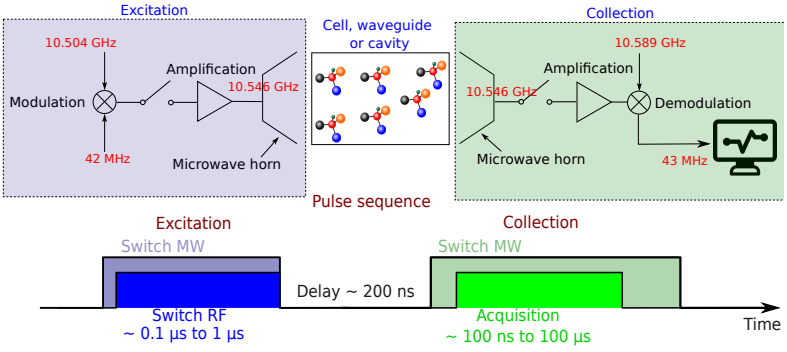
- **Broadband excitation : 10's of GHz covered**

- Optimized for spectroscopy : sensitivity / Rotational transitions resolution
  - MW frequency uncertainties: **typically at the kHz level**

1. Molecular microwave (MW) spectroscopy for precision measurements
2. **Measurements at LPL and UC Louvain**
3. MW spectroscopy as a detection tool

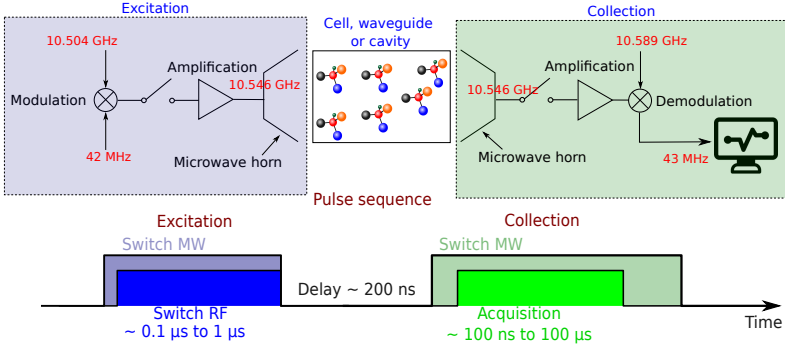
MW measurements at LPL and Louvain

Microwave spectroscopy setups

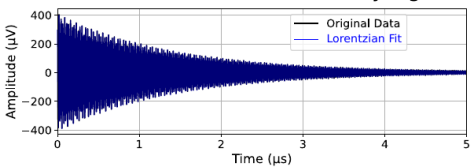


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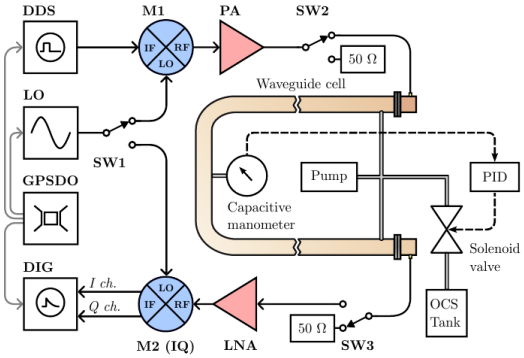


Measured Free induction decay signal



MW measurements at LPL and Louvain

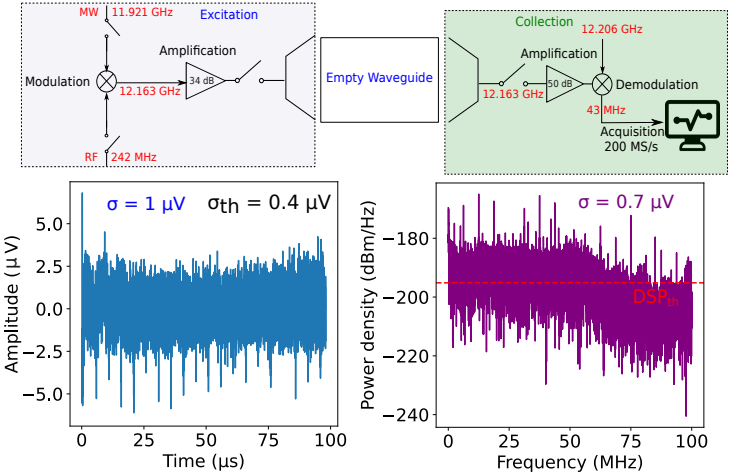
Microwave spectroscopy setups



- **Coherent excitation followed by FID detection**
- **Signal averaging : up to $\sim 10^7$ FIDs traces**
- **OCS R(0) transition @ 12 GHz as a test (Large dipole moment / well-studied)**

MW measurements at LPL and Louvain

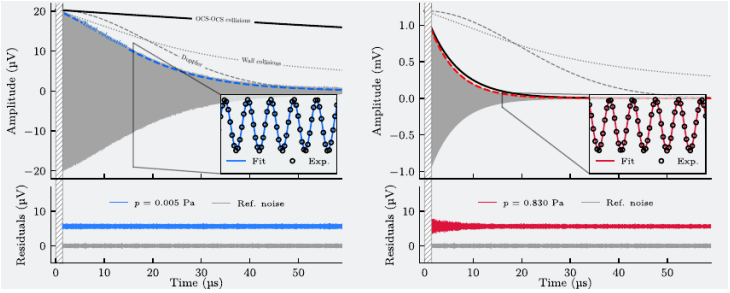
Background noises



- Timing-sequence optimization + amplification $\longrightarrow \sim$ **thermal-noise floor**

MW measurements at LPL and Louvain

OCS: line shape and frequency determination



Time-domain FID model

$$f(t) = A\, s(t) \cos(2\pi\nu t + \phi)$$

qSDV + wall relaxation

$$s(t) = \underbrace{W(t)}_{\text{wall collisions}} \underbrace{\frac{e^{-(\Gamma_0 - \frac{3}{2}\Gamma_2)t}}{(1+\Gamma_2 t)^{3/2}}}_{\text{collisional broadening + speed dependence}} \underbrace{e^{-\frac{(k v_0 t)^2}{4(1+\Gamma_2 t)}}}_{\text{Doppler}}$$

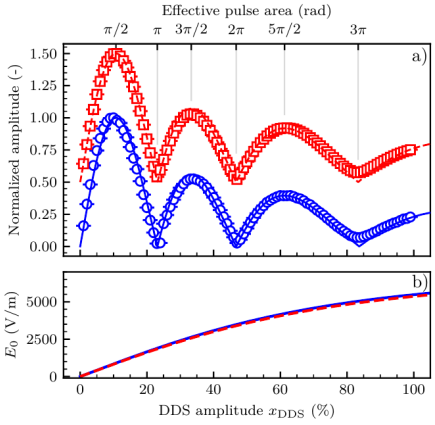
- **Fit directly in the time domain**
- **Line centre ν as a fit parameter**

- $\nu_0 = 12\,162\,978\,559$ Hz $\sigma_{\text{stat}} \sim 10$ Hz $\sigma_{\text{sys}} \sim 500$ Hz ? (Lineshape, pulse area, pressure ...)

FID curves from UC Louvain.

MW measurements at LPL and Louvain

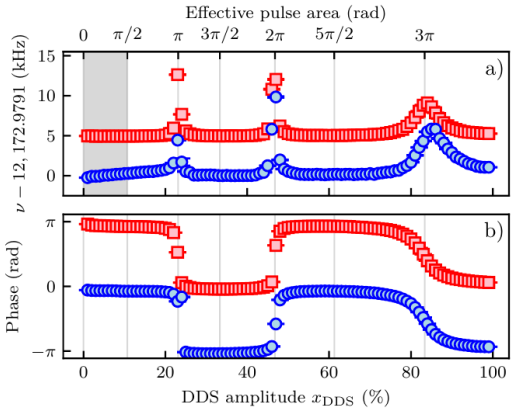
Outlook



- **Understand and reduce systematics**
  - Pulse-area dependent frequency shifts
  - MW switching transients / residual fields
  - Pressure dependence and line-shape model
- **Target μ-sensitive transitions**
  - CH_3OH: 6.668519 GHz $\quad K_\mu \simeq -42$
  - CH_3OH: 12.178597 GHz $\quad K_\mu \simeq -33$
  - NH_3: 23.694495 GHz $\quad K_\mu \simeq +4.46$
- **Extend the spectrometer**
  - Current range: 2–20 GHz
  - Towards > 20 GHz for NH_3

MW measurements at LPL and Louvain

Outlook

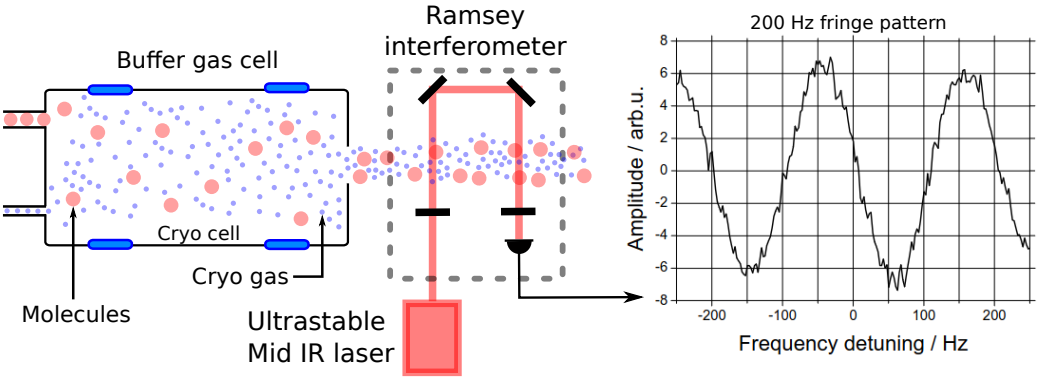


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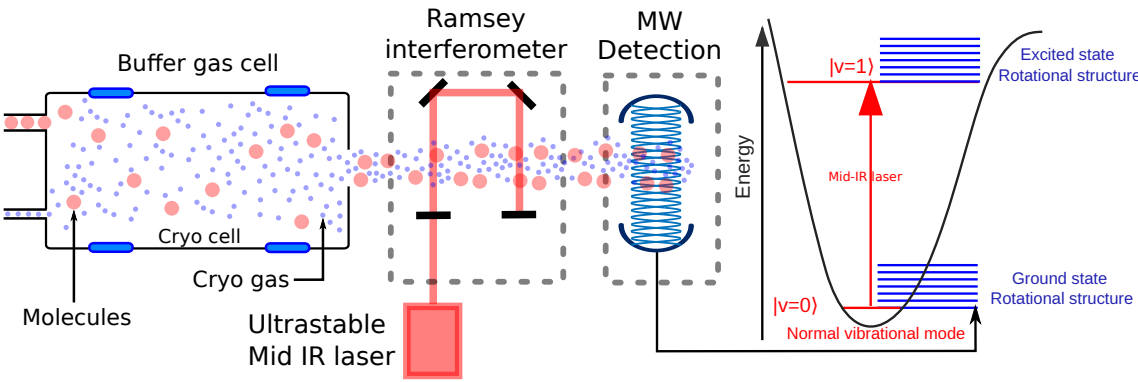
Rovibrational frequency determination at $\delta\nu/\nu \sim 10^{-14}$



- **Slow buffer-gas molecular beam + Ramsey interrogation**
  - Slow beam (~ 100 m/s): long interaction time
  - < 100 Hz frequency resolution

MW spectroscopy as a detection tool

Rovibrational frequency determination at $\delta\nu/\nu \sim 10^{-14}$



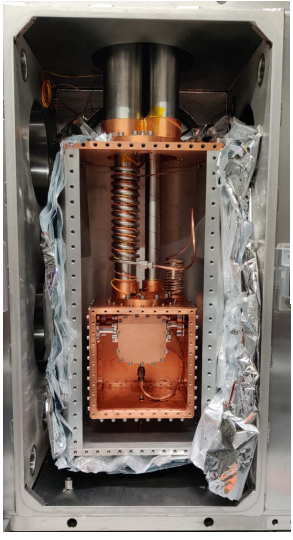
- **Double resonance scheme**
  - MIR Ramsey interrogation
  - MW detection with high sensitivity

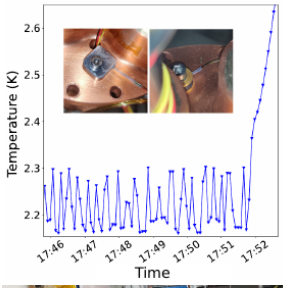
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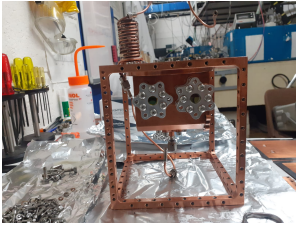
Towards sensitive cryogenic MW detection

- **Cryogenic platform @ LPL**
  - $T \simeq 2.2$ K
  - Buffer-gas cooling of complex molecules

- Cold complex molecules already demonstrated.





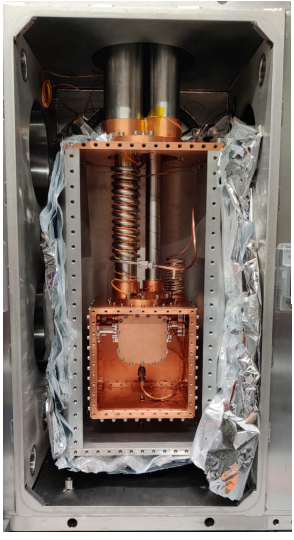


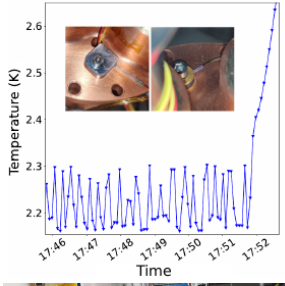
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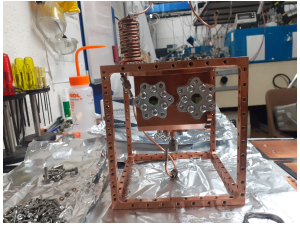
Towards sensitive cryogenic MW detection

- **Cryogenic platform @ LPL**
  - $T \simeq 2.2$ K
  - Buffer-gas cooling of complex molecules
- **Enhance MW detection**
  - High-Q superconducting cavity
  - Cryogenic low-noise electronics

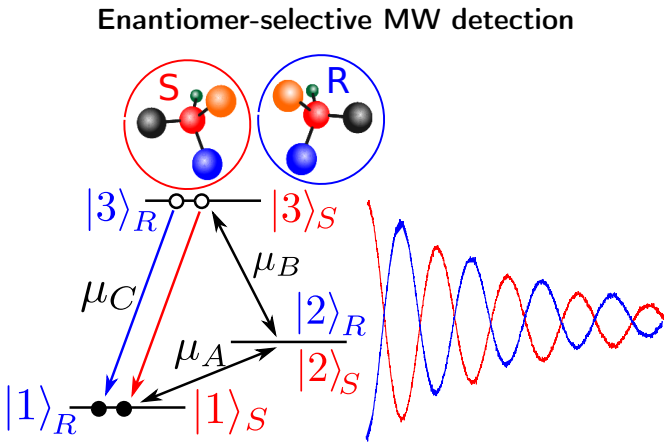
▸ Combine cold molecules and low-noise MW detection.







MW spectroscopy as a detection tool



- **Chiral molecules**
  - Three orthogonal electric-dipole components
- **Phase-sensitive response**
  - FID phase ⇒ molecular handedness
- **Sensitive and state-selective**
  - Species and enantiomer discrimination
  - All transitions are electric-dipole allowed

- Simultaneous measurement of both enantiomers: ↘ **systematics for parity-violation searches**.

Patterson & Doyle, PRL 111, 023008 (2013); Patterson, Schnell & Doyle, Nature 497, 475 (2013)

Thank you for your attention

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