# Molecular Precision Spectroscopy for Probing Variability of Fundamental Constants: the SETI2COF project

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• Outline

1) Fundamental constants (FC) variation, dark matter, frequency references

2) Sensitivity to FC variability from precision measurements:
-Modelisation of sensitivity from $^{12}C_2H_2$ transitions at 1.5 μm
-Modelisation of sensitivity from $^{127}I_2$ transitions at 0.5 μm
-Constraints on FC variation from molecular spectroscopy and clocks

3) Instrumental developments and first spectroscopic measurements

4) Conclusion

# 1) Variation of fundamental constants from precision measurements with molecular frequency references

# • Fundamental Constants and Ultralight Dark Matter

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- The Standard Model (SM) and the General Relativity (GR) theories

=> fundamental constants (FC) are free parameters of the theory

Uzan, C. R. Physique 16, 576 (2015)

=> CODATA 2022 recommended values of fundamental constants

https://physics.nist.gov/cuu/Constants/index.html

=> Failure of SM&GR to explain observational data on mass distribution in the Universe

=> Introducing galactic DM : $\rho_{DM} = 0.4\ \mathrm{GeV/cm^{-3}}$ ; $v \cong 230\ \frac{\mathrm{km}}{\mathrm{s}}$; $\sigma_v \cong 10^{-3}c$; $\tau_c = 10^{-4}/\omega_\phi$

- BSM theories: DM is sub-eV bosonic field $\phi(t) = \phi_0 \cos(\omega_\phi t)$ ; $\omega_\phi \cong \frac{m_\phi c^2}{\hbar}$; $\phi_0 = \sqrt{\frac{4\pi G \rho_{DM}}{\omega_\phi^2 c^2}}$

Arvanitaki *et al*, PRD 91, 015015 (2015); Stadnik *et al*, PRL 115, 201301 (2015); Freese *et al*, RMP 85,1561 (2013)

- UDM-induced variation of fundamental constants

- fermion X=(e,u,d,s) masses : $m_X(\phi) = m_X\left(1 + d_{m_X} \cdot \phi/\sqrt{c\hbar/8\pi G}\right)$

- fine structure constant : $\alpha(\phi) = \alpha\left(1 + d_\alpha \cdot \phi/\sqrt{c\hbar/8\pi G}\right)$

- QCD scale parameter : $\Lambda_{QCD}(\phi) = \Lambda_{QCD}\left(1 + d_g \cdot \phi/\sqrt{c\hbar/8\pi G}\right)$

- $\mu(m_e, \Lambda_{QCD}, m_X) = m_p/m_e$ : $\mu(\phi) = \mu\left(1 - \left(d_{m_e} + d_g + 0.036 d_{\hat{m}}\right) \cdot \phi/\sqrt{c\hbar/8\pi G}\right)$

Damour and Donoghue, PRD 82, 084033 (2010)

**=> Atomic, molecular and optical cavity resonance frequencies depend on FC:**

- atomic optical transition $f_{A,opt} = C_{A,opt}\frac{\alpha^2 m_e c^2}{4\pi\hbar}\cdot F_{opt}\,(\alpha)$
- atomic hyperfine transition $f_{A,HF} = C_{A,HF}\frac{\alpha^2 m_e c^2}{4\pi\hbar}\left(g_i\left(m_q/\Lambda_{QCD}\right)\times m_e/m_p\right)\cdot F_{HF}(\alpha)$
- vibrational molecular transition : $f_{vib} = C_{vib}\frac{\alpha^2 m_e c^2}{4\pi\hbar}\sqrt{m_e/m_p}$
- rotational molecular transition : $f_{rot} = C_{rot}\frac{\alpha^2 m_e c^2}{4\pi\hbar} m_e/m_p$
- optical cavity resonance : $f_C = C_C\frac{\alpha m_e c^2}{\hbar}\cdot F_C\,(\alpha, m_X, \Lambda_{QCD}\,)$

**=> Parametrization in terms of $(\alpha, \mu, \hat{m}/\Lambda_{QCD})$ with appropriate sensitivity coefficients:**

$$\frac{\Delta f_{C,A,M}}{f_{C,A,M}} = Q_\alpha^{C,A,M}\frac{\Delta\alpha}{\alpha} + Q_\mu^{C,A,M}\frac{\Delta\mu}{\mu} + Q_q^{C,A,M}\frac{\Delta(\hat{m}/\Lambda_{QCD})}{\hat{m}/\Lambda_{QCD}}$$

- **Snowmass 2021 DM white paper**

Antypas *et al*, arXiv 2203.14915

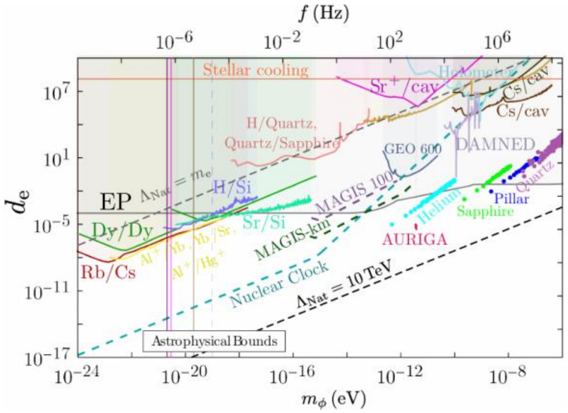
**=> Atomic clocks comparisons**

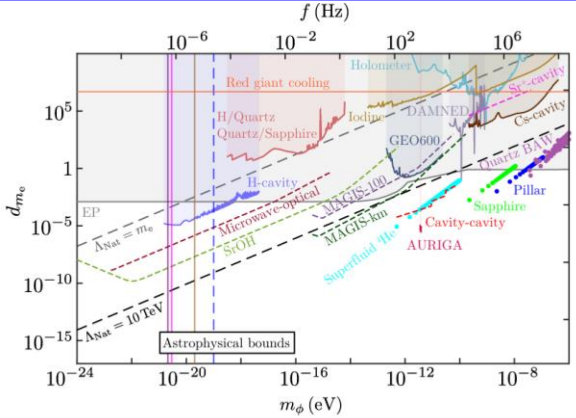
- Rb/Cs clock comparisons

Hees *et al*, Phys. Rev. Lett. 117, 061301 (2016)

**=> Atomic interferometry**

Abdalla *et al*, EPJQT 12, 42 (2025)

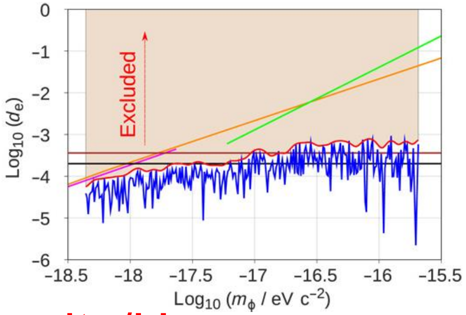



**=> Atomic clocks/cavity comparisons**

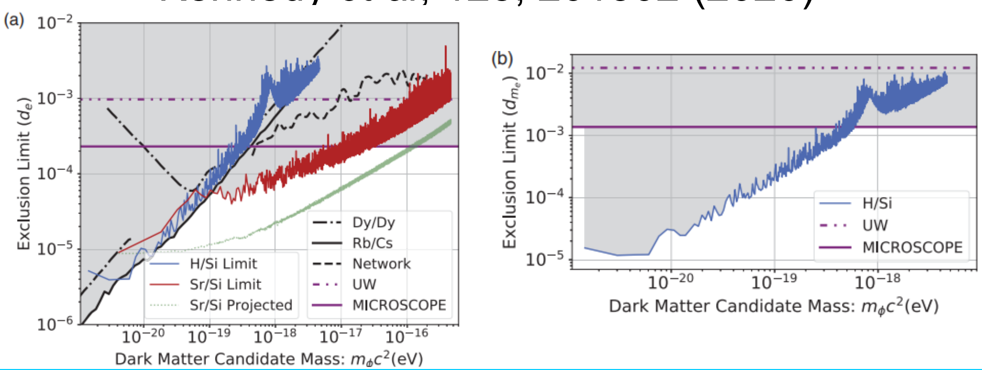
- Sr clock/cavity network comparison by GPS

Wcislo *et al*, Sci. Adv. 4, eaau4869 (2018)




- Sr clock/cavity/H maser comparisons

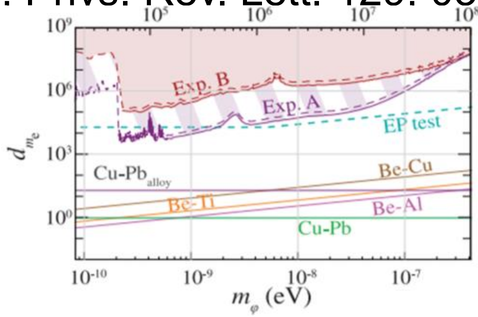
Kennedy *et al*, 125, 201302 (2020)




**=> Spectroscopy experiments**

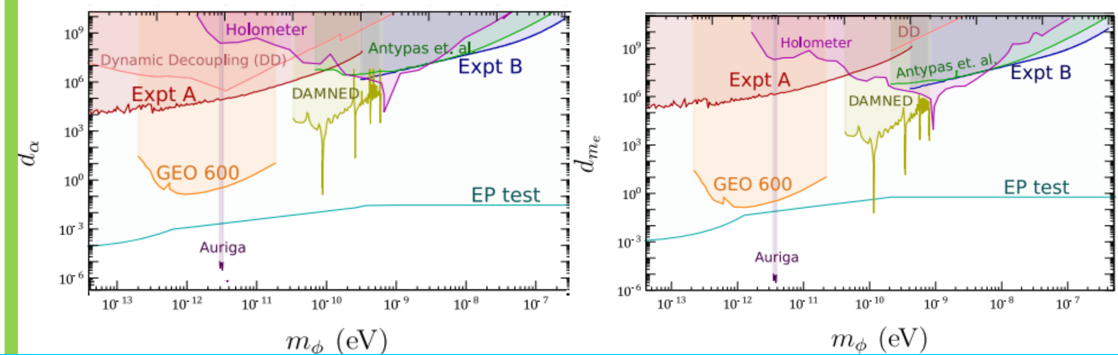
- Cs polarization spectroscopy

Tretiak *et al*. Phys. Rev. Lett. 129. 031301 (2022)




- $I_2$ linear & Doppler-free spectroscopy

Oswald *et al*, Phys. Rev. Lett. 129, 031302 (2022)



# 2) FC variations from precision measurements with acetylene and molecular iodine transitions

# • Sensitivity of the acetylene rovibrational transitions

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- Effective Hamiltonian models for rovibrational energy levels:

Vibrational energy:

$$E_V/hc = \sum_{i=1}^{5} \omega_i \left(v_i + \frac{d_i}{2}\right) + \sum_{i\le j=1}^{5} x_{ij} \left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right) + \sum_{i\le j=4}^{5} g_{ij} \left(l_i + \frac{d_i}{2}\right)\left(l_j + \frac{d_j}{2}\right) + \ldots$$

Rotational energy:

$$E_R/hc = B_{eff}[J(J+1) - k^2] + D_{eff}[J(J+1) - k^2]^2 + \cdots$$

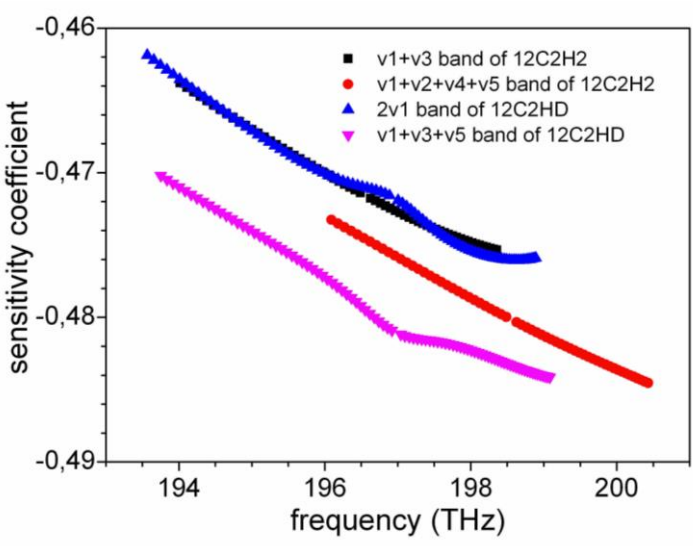
$$B_{eff} = B_0 - \sum_{i=1}^{5} \alpha_i \left(v_i + \frac{d_i}{2}\right) + \cdots; D_{eff} = D_0 + \sum_{i=1}^{5} \beta_i \left(v_i + \frac{d_i}{2}\right) + \cdots$$

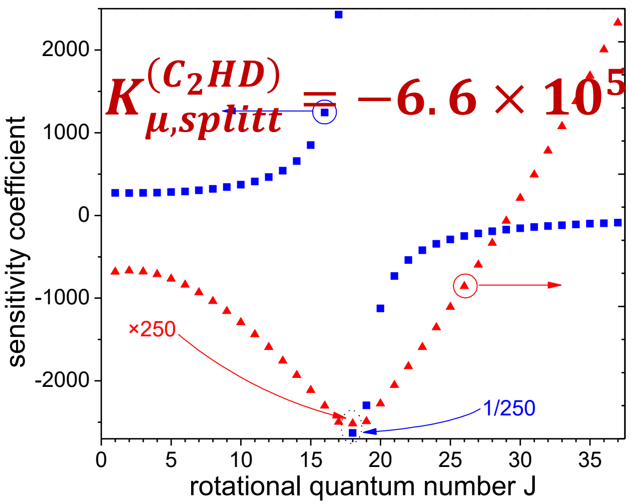
Rovibrational energy levels couplings (l-type, Coriolis, Fermi,…)

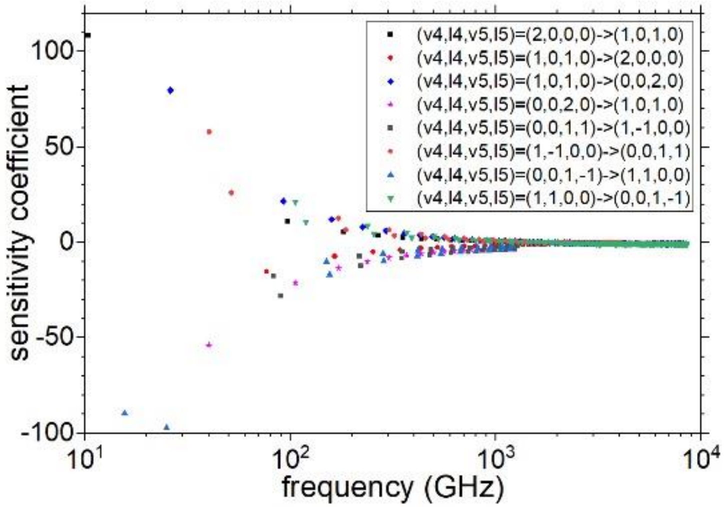
$$W_{l-type}/hc = (\sqrt{2}\, q_4/2)\sqrt{(J(J+1) - k^2)((J(J+1) - k^2) - 2)}$$

µ-dependence of the Hamiltonian constants:

$$\omega_i \sim 1/\sqrt{\mu}, x_{ij} \sim 1/\mu, g_{ij} \sim 1/\mu, \ldots;\ B \sim 1/\mu, D \sim 1/\mu^2, \alpha \sim 1/\mu^{3/2}, \beta \sim 1/\mu^{5/2}, \ldots; q \sim 1/\mu^{3/2}, \ldots$$

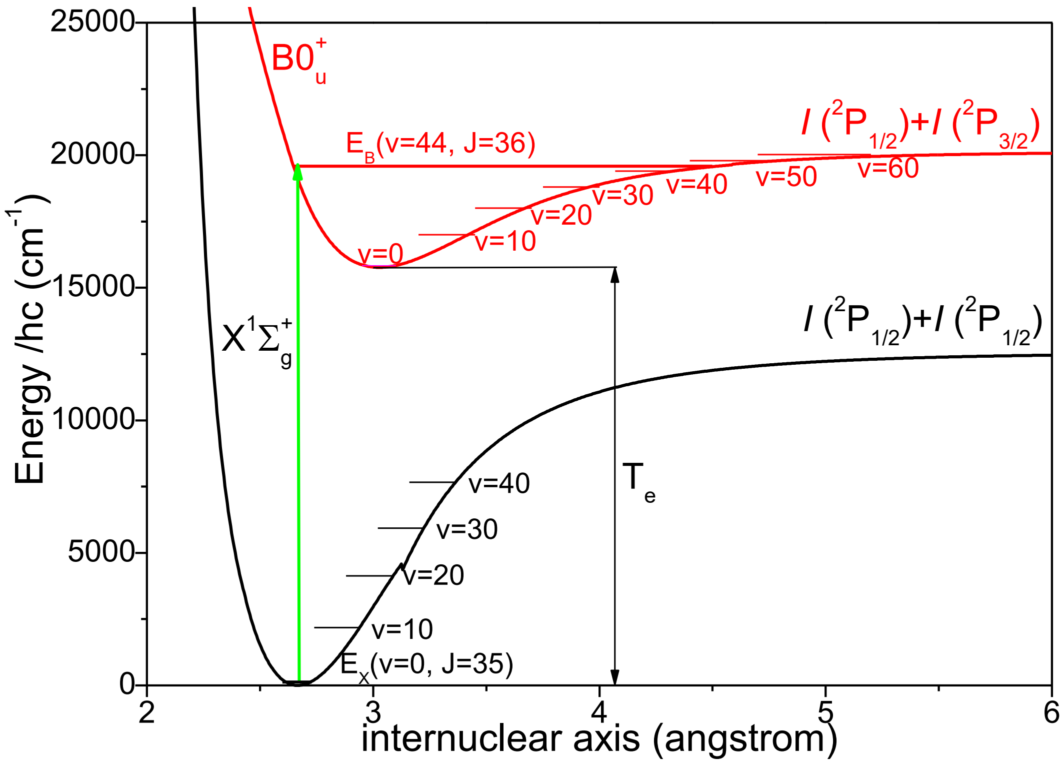



Constantin, Vibrational Spectr. 85, 228 (2016); Proc. EFTF 2015, Proc. CLEO Europe 2023

# • Sensitivity of the molecular iodine rovibronic transitions




-rovibronic energies from the Schrödinger equation

=> Dunham parameters

$$E_X(v'',J'') = G_X(v'') + B_X(v'') \times (J''(J''+1)) - D_X(v'') \times (J''(J''+1))^2 + H_X(v'') \times (J''(J''+1))^3$$

$$E_B(v',J') = T_e + G_B(v') + B_B(v') \times (J'(J'+1)) - D_B(v') \times (J'(J'+1))^2 + H_B(v') \times (J'(J'+1))^3 + L_B(v') \times (J'(J'+1))^4 + M_B(v') \times (J'(J'+1))^5$$

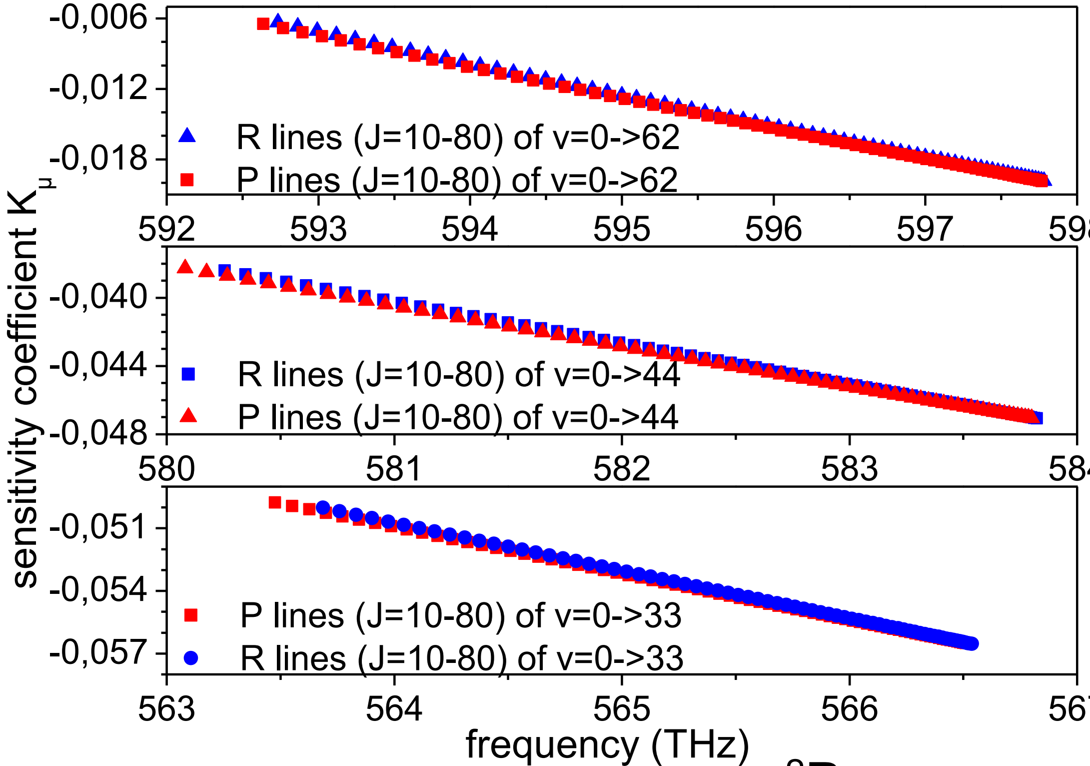
=> Adjustment of tens of thousands FTS lines

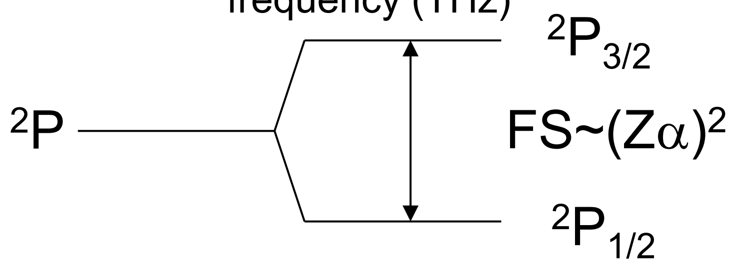
Gerstenkom and Luc, J. Phys. France 46, 867 (1985)

=>sensitivity coefficients to variations of μ, α

Constantin, Proc. IFCS, 9234878 (2020)

$$K_\mu = \frac{d\ln f_{(v'',J'')\to(v',J')}}{d\ln\mu}, \quad K_\alpha = \frac{d\ln f_{(v'',J'')\to(v',J')}}{d\ln\alpha}$$




assumed : $K_\alpha = 2$

# • DM direct detection by laser spectroscopy of acetylene

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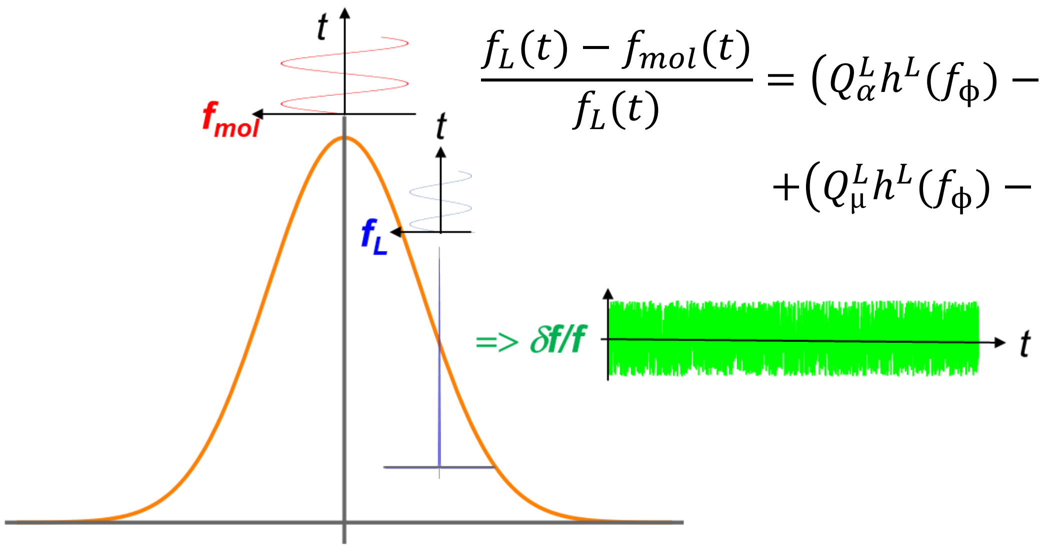
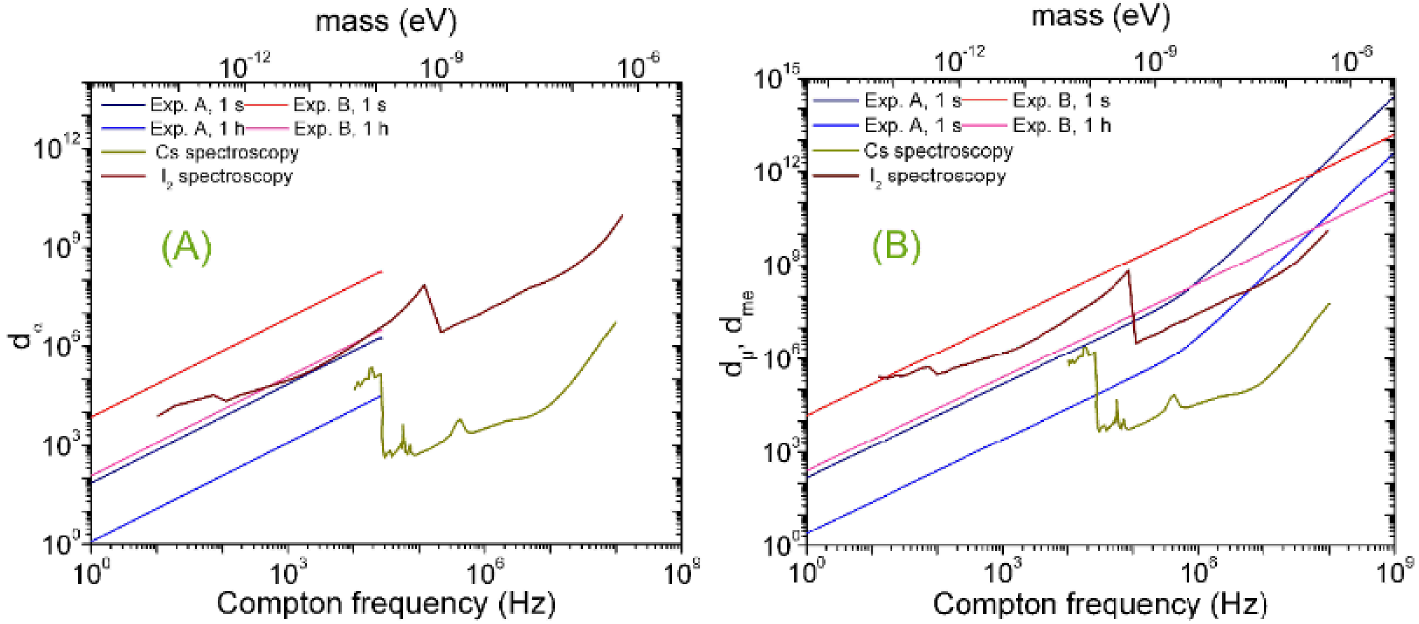



$$\frac{f_L(t)-f_{mol}(t)}{f_L(t)} = \left(Q_\alpha^L h^L(f_\phi) - Q_\alpha^{mol} h^{mol}(f_\phi)\right)\frac{\Delta\alpha(t)}{\alpha}$$
$$+\left(Q_\mu^L h^L(f_\phi) - Q_\mu^{mol} h^{mol}(f_\phi)\right)\frac{\Delta\mu(t)}{\mu}$$

REFIMEVE network
- 1542 nm cavity-locked laser
- fractional stability ~$10^{-15}$ @1s
- fractional uncertainty ~$10^{-14}$
- phase-stabilized optical link

Exp. A : Doppler-free acetylene spectroscopy with $\delta f/f=10^{-14}\,(\tau/1\mathrm{s})^{-1/2}$

Exp. B : Doppler-broadened acetylene spectroscopy with $\delta f/f=10^{-12}\,(\tau/1\mathrm{s})^{-1/2}$




=> Improved constraints in the kHz range, sensitive to DM couplings to the nuclear interaction

Constantin, Proc. EFTF 2023

# • DM search by frequency comparisons of $^{127}I_2$ optical clocks

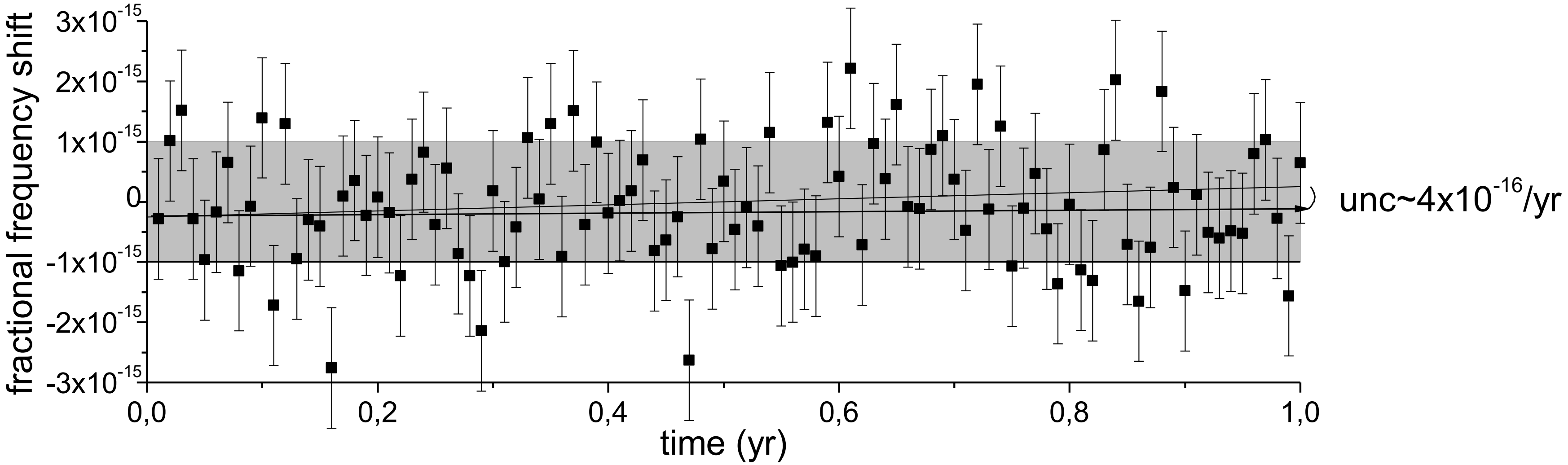


-Relative time variation of clock frequency ratio: $$\frac{d\,ln\left(f_{I_2}/f_{Clock}\right)}{dt} = \left(K_\mu^{I_2} - K_\mu^{Clock}\right)\frac{d\,ln\,\mu}{dt} + \left(K_\alpha^{I_2} - K_\alpha^{Clock}\right)\frac{d\,ln\,\alpha}{dt}$$

-Remote comparisons enabled with fiber links

| Clock transition | freq. (Hz) | $K_\mu$ | $K_\alpha$ | rel. unc. | rel. freq. drift (yr$^{-1}$) | ref. |
|---|---|---|---|---|---|---|
| $^{127}I_2$ R(26) 62-0 | $597.291\times10^{12}$ | -0.019 | 2 | $1\times10^{-15}$ | $4\times10^{-16}$ | Proc. IFCS, 9234878 (2020) |
| $^{127}I_2$ R(35) 44-0 | $583.119\times10^{12}$ | -0.045 | 2 | $1\times10^{-15}$ | $4\times10^{-16}$ | Proc. IFCS, 9234878 (2020) |
| $^{127}I_2$ R(56) 32-0 | $563.110\times10^{12}$ | -0.054 | 2 | $1\times10^{-15}$ | $4\times10^{-16}$ | Proc. IFCS, 9234878 (2020) |
| $^{133}$Cs clock | 9192631770 | -1 | 2.83 | 0 | 0 | Metrologia 55, 188 (2018) |
| $^{87}$Sr clock | 429228004229873.0 | 0 | 0.062 | $4\times10^{-16}$ | $(-3.3\pm3.0)\times10^{-16}$ | Nat. Commun. 4, 2109 (2013) |

• Estimation of performances of 100 frequency measurements performed during 1 year:




| Clock comparison | unc. $(1/\mu)(d\mu/dt)$ | unc. $(1/\alpha)(d\alpha/dt)$ |
|---|---|---|
| $^{127}I_2$(1)/Cs, $^{127}I_2$(2)/Cs, $^{127}I_2$(3)/Cs | $1.5\times10^{-14}$/yr | $1.8\times10^{-14}$/yr |
| $^{127}I_2$(1)/Cs, Sr/Cs | $6.0\times10^{-16}$/yr | $2.6\times10^{-16}$/yr |

=>Joint constraints for time variations of α, μ needed for benchmarking new BSM theories

Constantin, Proc. IFCS 2020

# 3) Experimental developments and preliminary results

# • Probing $C_2H_2$ absorption by optical network spectroscopy

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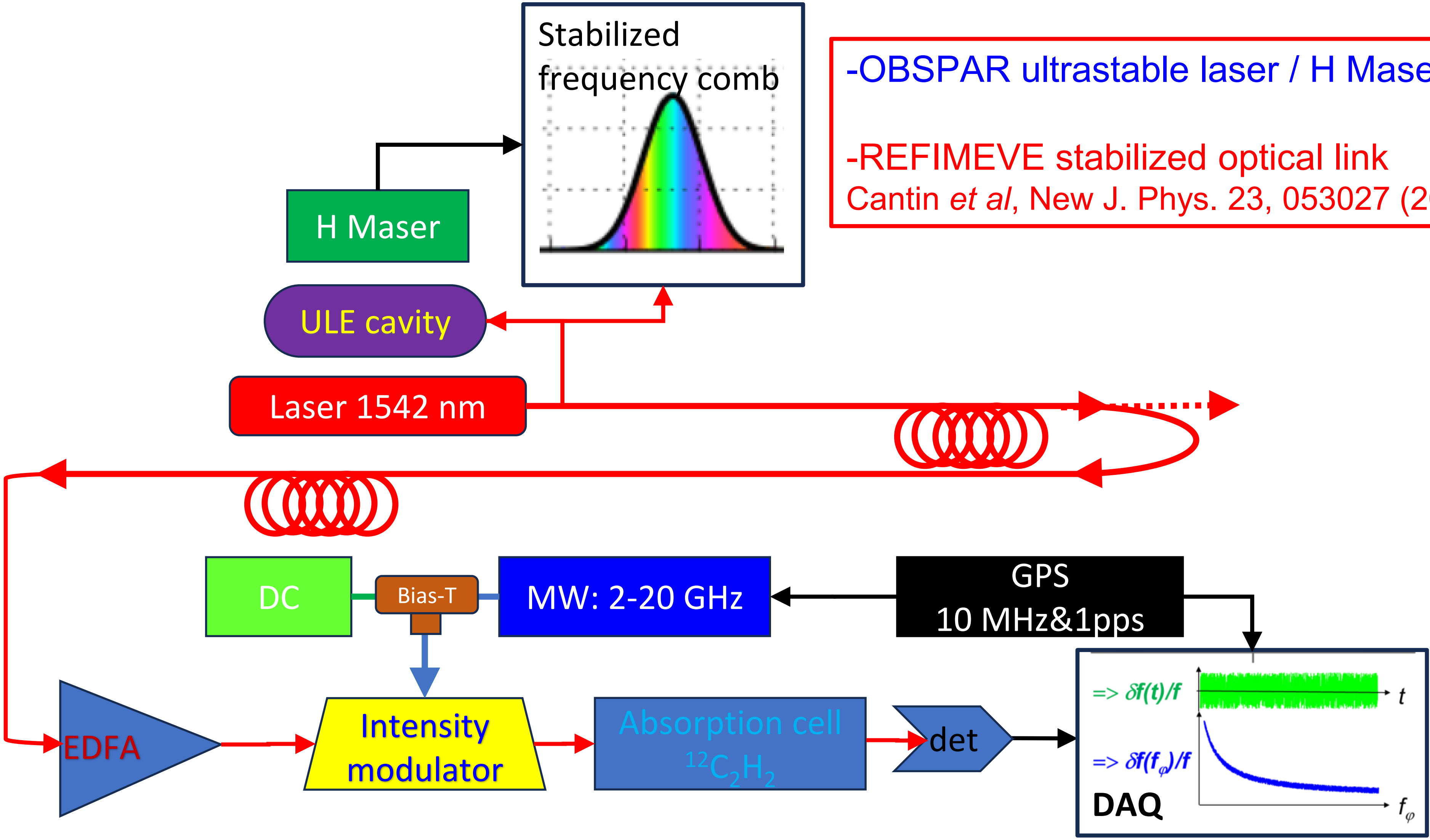



-OBSPAR ultrastable laser / H Maser

-REFIMEVE stabilized optical link
Cantin *et al*, New J. Phys. 23, 053027 (2021)

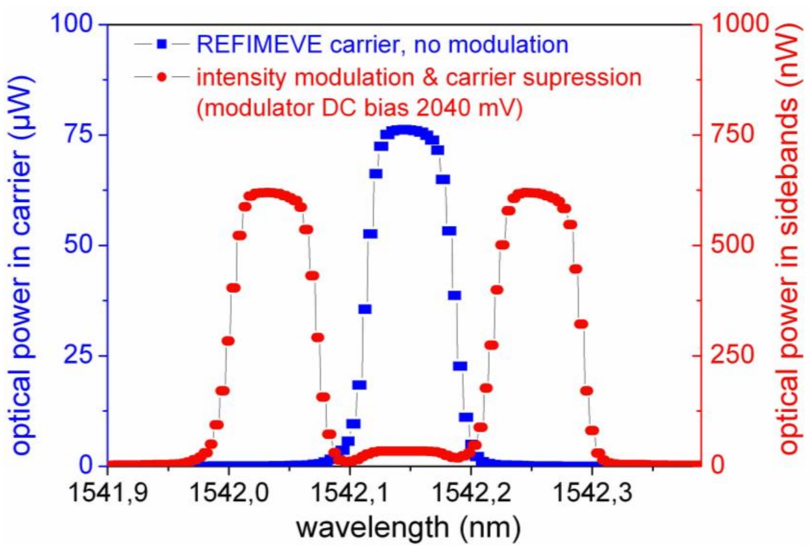
- EDFA amplification; frequency tuning with fiber-coupled LN intensity modulator (MW+DC)
- One-pass absorption path in a 5 cm-length cell filled with 12C2H2 at 50 Torr
- Photodetection with 1 GHz BW, 14 bits DAQ system sampling up to GSPS
- GPS time and MW frequency reference

=> Signal to PhLAM almost continuously at 194,400,084,500.000(25) kHz
=> Optical amplification to suitable power levels
=> Frequency tuning by sideband generation with LN intensity modulator

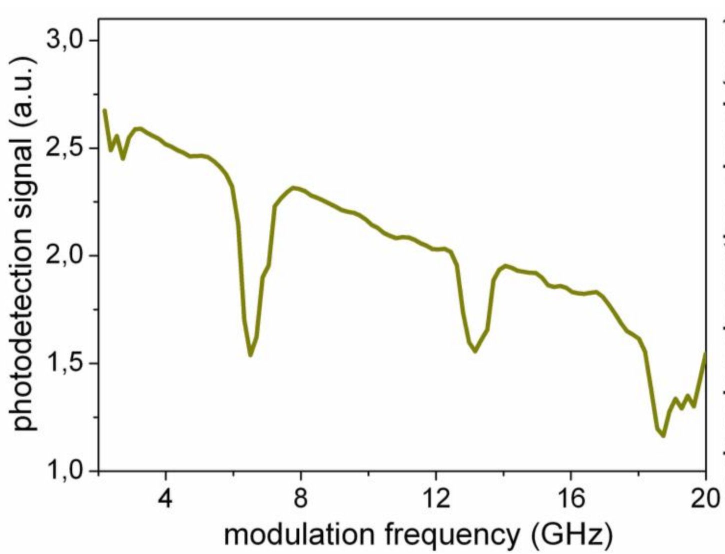
=> Frequency tuning up to 20 GHz but significant microwave frequency response

=> Spectroscopy by scanning of an auxiliary tunable laser across an acetylene line

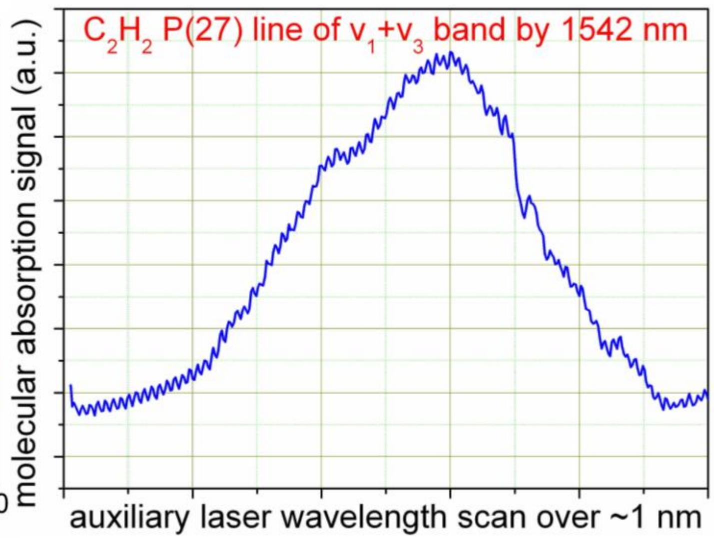
=> Need for optical intensity stabilization during frequency scanning




OSA resolution 70 pm




Pulse modulation at 250 Hz, lock-in $T_c$=100 ms, 10 scans




Pulse modulation at 250 Hz, lock-in $T_c$=100 ms, 1 manual scan

# • First experimental data recording and exploitation

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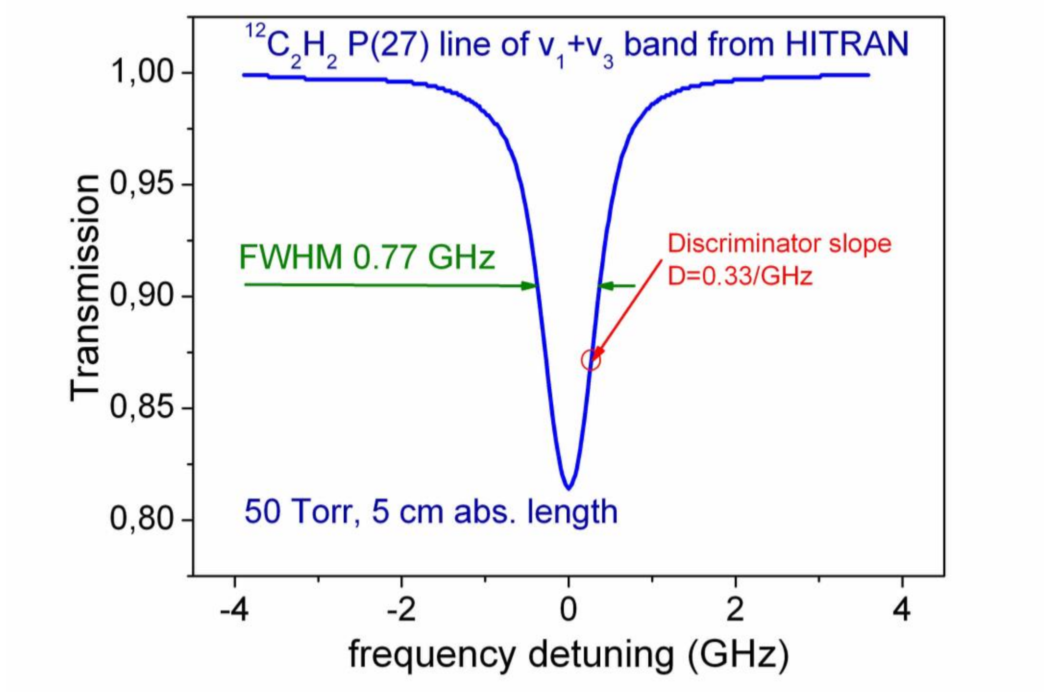
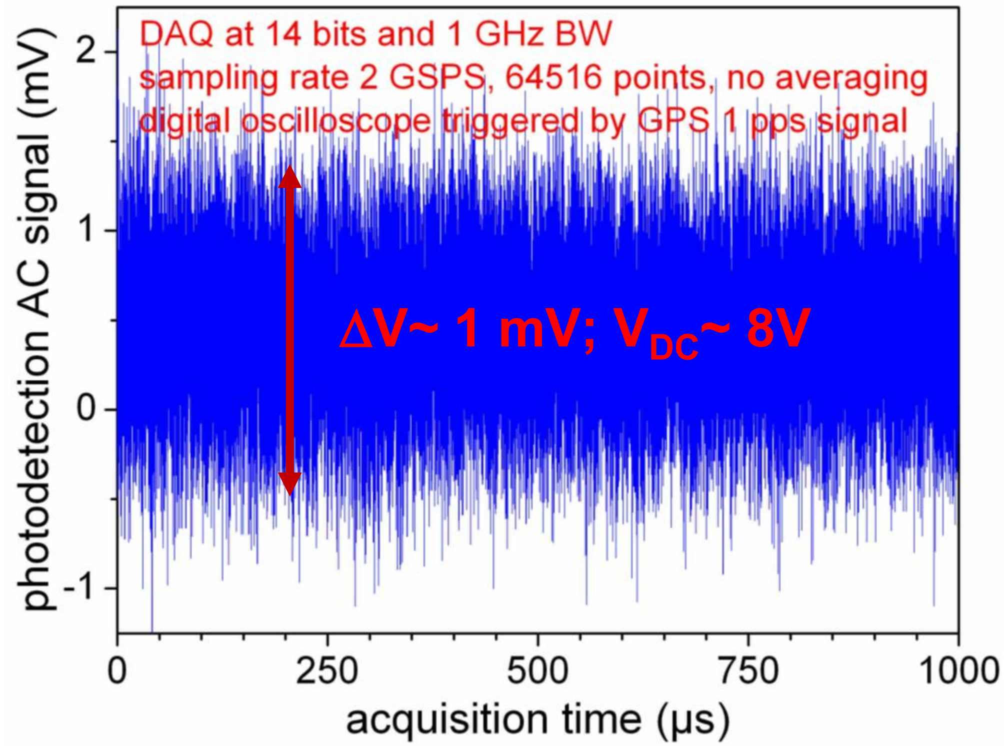



- Simulated experimental transfer function

-conversion of fluctuations $\Delta f$ <-> $\Delta V$ via slope

- Fast data acquisition

-sampling oscilloscope at 2 GSPS

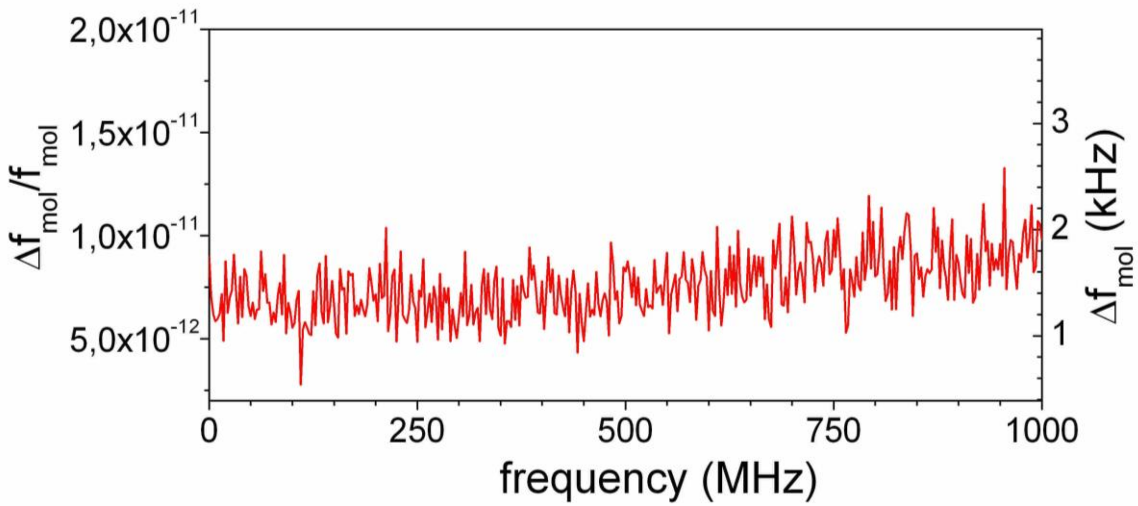
-MW spectrum analyser with BW>1 GHz

- Conversion of the photodetection signal in kHz-level frequency excursions

=> Spectroscopy with $10^{-12}$ precision, in line with previous estimations

=> Improvement by differential detection

Constantin, Proc. IFCS-EFTF 2023




10 kHz RBW, 400 points, 0.6 s averaging time/point

# • Conclusion

- Accurate determination of sensitivity coefficients to μ-variation for $C_2H_2$ and $I_2$ reference transitions
- Enhanced sensitivity from MW transitions and frequency splittings
- Evaluation of constraints from expected performances in precision measurements

- Laser spectroscopy experimental setup at 194 THz with precision at $10^{-12}$ level that exploits the REFIMEVE network signal

- Compact and robust molecular spectrometer
- Fiber-coupled components enabling easy integration into optical fiber networks

Thank you for your attention !

Acknowledgements

FIRST TF

GRAM Gravitation Références Astronomie Métrologie

Refimeve+ Réseau fibré métrologique à vocation européenne