

# Towards Probing Ultralight Dark Matter Couplings with Acetylene Spectroscopy

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- 1) From UDM couplings to SM to frequency variations of AMO resonances
- 2) Potential from infrared precision measurements with  $^{12}\text{C}_2\text{H}_2$ 
  - Modelisation and measurement of a  $^{12}\text{C}_2\text{H}_2$  transition at  $1.55 \mu\text{m}$
  - Constraints on UDM couplings to SM
- 3) Potential from frequency measurements of a MW acetylene clock
  - Acetylene MW transitions with enhanced sensitivity to  $\mu$ -variation
  - Molecular theory and metrological performances of a MW clock
  - Constraints from frequency measurements of a MW acetylene clock
- 4) Conclusion

# 1) Variation of fundamental constants from precision measurements

## • Why Acetylene?

## • Objectives

### - State-of-the-art molecular theory and precision measurements

Global Hamiltonian models : Herman and Perry, PCCP 15, 9970 (2013); Lyulin and Perevalov, JQSRT 177, 59 (2016)

Ab-initio theory : Chubb *et al*, JQSRT 204, 42 (2018)

Instrumentations for high-resolution spectroscopy; spectroscopic data; molecular databases HITRAN, GEISA, ...

Cold molecules research : Aiello *et al*, Nat. Commun. 13, 7016 (2022)

### - Search for variability of fundamental constants; understand nature of dark matter

Uzan, Living Rev. Relativity 14, 2 (2011)

Safronova *et al*, Rev. Mod. Phys. 90, 025008 (2018)

## • Applications of the acetylene molecular theory and spectroscopy

### - Atmospheric science

Whitby and Altwicker, Atmos. Environ. 12, 1289 (1978)

### - Astrophysics

Didriche and Herman, Chem. Phys. Lett. 496, 1 (2010)

### - Frequency metrology

Recommandation Comité Consultatif des Longueurs 1, 2009; Riehle *et al*, Metrologia 55, 188 (2018)

### - Probe variations of fundamental constants

Constantin, Vibrational Spectroscopy 85, 228 (2016)

### - Photonic-molecular integration

Tharpa *et al*, Opt. Lett. 31, 2489 (2006); Takiguchi *et al*, Opt. Lett. 36, 1254 (2011)

Zektzer *et al*, Laser Photonics Rev. 14, 1900414 (2020)

- The Standard Model and the General Relativity : FC are free parameters of the theory

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

- CODATA 2018 recommended values of fundamental constants

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

- Variability from couplings to cosmology and to local fields

- UDM: sub-eV scalar field  $\phi(t) = \phi_0 \cos(\omega_\phi t)$ ; pulsation  $\omega_\phi \cong \frac{m_\phi c^2}{\hbar}$ ; amplitude  $\phi_0 = \sqrt{\frac{4\pi G \rho_{DM}}{\omega_\phi^2 c^2}}$

- Galactic halo model :  $\rho_{DM} = 0.4 \text{ GeV/cm}^{-3}$ ;  $v \cong 230 \frac{\text{km}}{\text{s}}$ ;  $\sigma_v \cong 10^{-3}c$ ;  $\tau_c = 10^{-4}/\omega_\phi$

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

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

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

Damour and Donoghue, PRD 82, 084033 (2010)

=> Sensitivity of atomic, molecular and optical cavity resonance frequency:

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

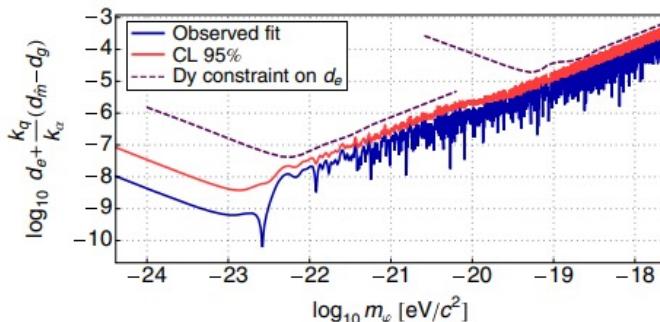
- atomic optical transition  $f_{A,opt} = C_{A,opt} \frac{\alpha^2 m_e c^2}{4\pi\hbar} \cdot F_{opt}(\alpha)$
- atomic hyperfine transition  $f_{A,HF} = C_{A,HF} \frac{\alpha^2 m_e c^2}{4\pi\hbar} (g_i(m_q/\Lambda_{QCD}) \times m_e/m_p) \cdot F_{HF}(\alpha)$
- vibrational molecular transition :  $f_{vib}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

# • Searches for UDM with atoms and molecules

## => Atomic clocks comparisons

- oscillations from scalar fields of Rb/Cs clocks

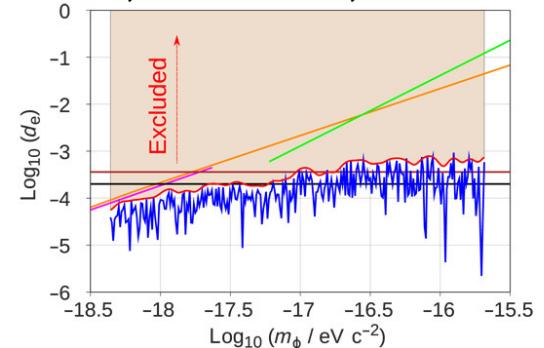
Hees *et al*, Phys. Rev. Lett. 117, 061301 (2016)



## => Atomic clocks/cavity comparisons

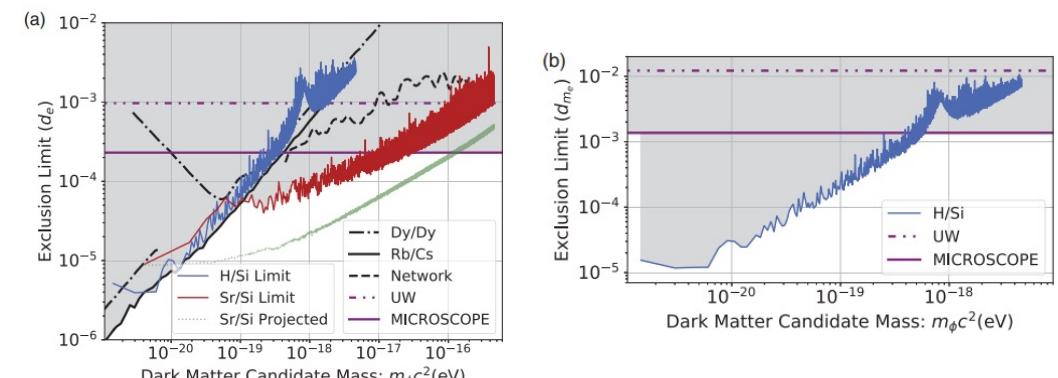
- Sr clock/cavity network comparison by GPS

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



## => Sr clock/cavity/H maser comparisons

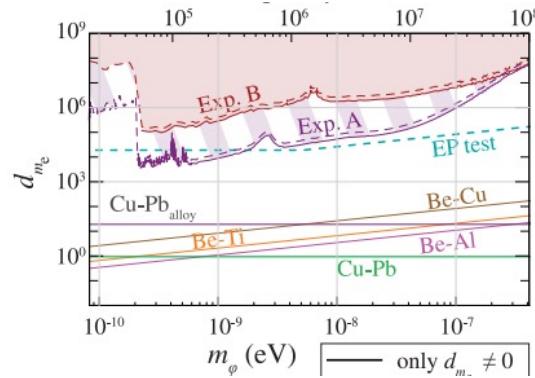
Kennedy *et al*, 125, 201302 (2020)



## => Spectroscopy experiments

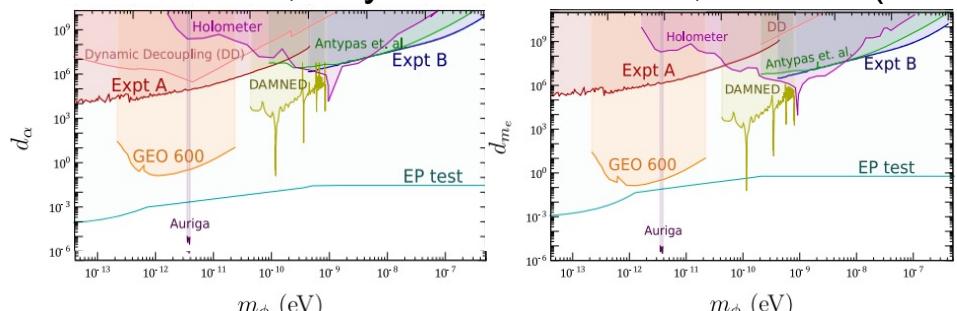
- Cs polarization spectroscopy

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



## - I<sub>2</sub> Doppler/Doppler-free spectroscopy

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



## 2) Potential from infrared precision measurements with $^{12}\text{C}_2\text{H}_2$

# • Acetylene molecular theory

## Fundamental vibrational modes

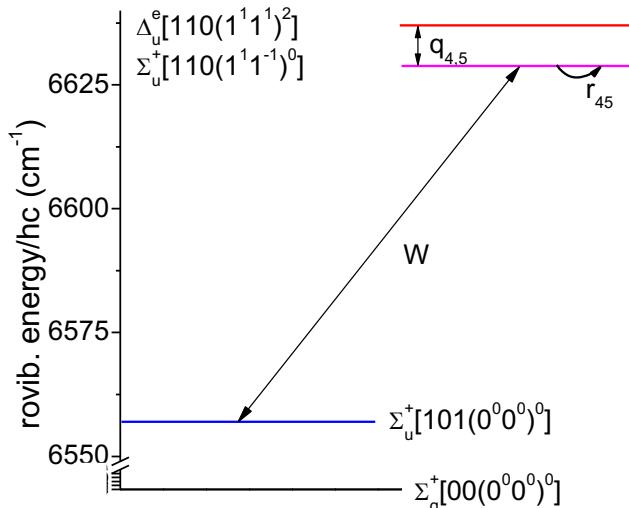
|  |                |                          |                             |
|--|----------------|--------------------------|-----------------------------|
|  | v <sub>1</sub> | 3401.15 cm <sup>-1</sup> | Symmetric CH stretching     |
|  | v <sub>2</sub> | 1982.68 cm <sup>-1</sup> | Symmetric CC stretching     |
|  | v <sub>3</sub> | 3313.20 cm <sup>-1</sup> | Antisymmetric CH stretching |
|  | v <sub>4</sub> | 608.99 cm <sup>-1</sup>  | Trans-bending               |
|  | v <sub>5</sub> | 729.21 cm <sup>-1</sup>  | Cis-bending                 |

Hermann, Mol. Phys. 105, 2217 (2007)

## Polyads

$$(v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5}) \\ k = l_4 + l_5; J \\ N_s = v_1 + v_2 + v_3 \\ N_r = 5v_1 + 3v_2 + 5v_3 + v_4 + v_5$$

## Energy levels ~196 THz



## Effective Hamiltonian

Vibrational term:  $G_v[v] = \sum_s \omega_s (v_s + g_s/2) + \sum_{s \leq s'} (v_s + g_s/2)(v_{s'} + g_{s'}/2) + \sum_{k \leq k'} g_{kk'} l_k l_{k'}$

Rotational term:  $F_r(J, k) = B[v](J(J+1)-k^2) - D[v](J(J+1)-k^2)^2 + H[v](J(J+1)-k^2)^3$

Hamiltonian matrix :

$$\begin{pmatrix} E[110(I^I I^I)^2, JJ + \frac{\rho_{45}}{4} J(J+1)(J(J+1)-2)] & \frac{q_4 + q_5}{2} \sqrt{J(J+1)(J(J+1)-2)} & 0 \\ \frac{q_4 + q_5}{2} \sqrt{J(J+1)(J(J+1)-2)} & E[110(I^I I^I)^0, JJ + r_{45}] & W \\ 0 & W & E[101(0^0 0^0)^0, J] \end{pmatrix}$$

Unperturbed energy levels:

$$E[110(1¹¹¹)², JJ] = (v_2 + g_{45}) + (B_2 + \gamma^{45})(J(J+1)-4) - (D_2 + \delta^{45})(J(J+1)-4)^2 + (H_2 + h^{45})(J(J+1)-4)^3$$

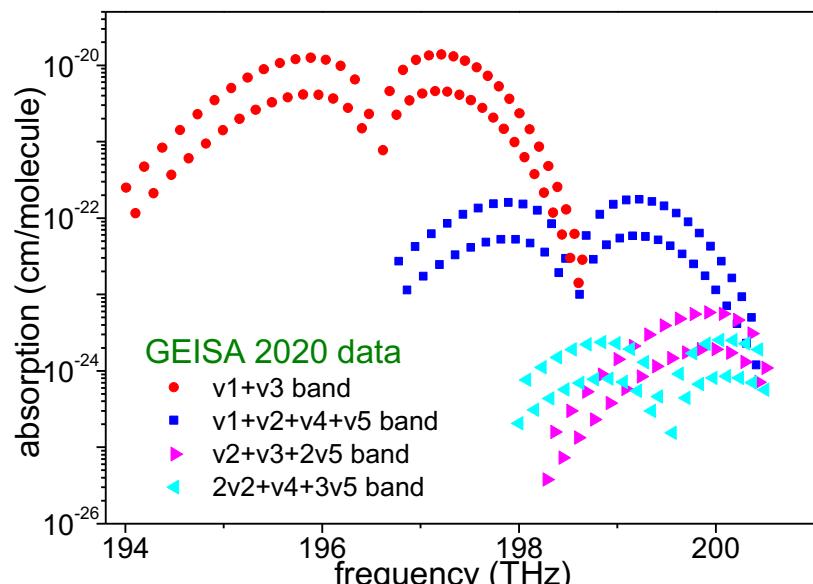
$$E[110(1¹¹¹)⁰, JJ] = (v_2 - g_{45}) + (B_2 - \gamma^{45})J(J+1) - (D_2 - \delta^{45})(J(J+1))^2 + (H_2 - h^{45})(J(J+1))^3$$

$$E[101(0⁰⁰⁰)⁰, JJ] = v_1 + B_1 J(J+1) - D_1 (J(J+1))^2 + H_1 (J(J+1))^3$$

$$E[000(0⁰⁰⁰)⁰, JJ] = B_0 J(J+1) - D_0 (J(J+1))^2 + H_0 (J(J+1))^3$$

Keppler et al, JMS 175, 411 (1996)

## High-resolution spectroscopy



=> GEISA 2015 <sup>12</sup>C<sub>2</sub>H<sub>2</sub> linelist

Jacquinet-Husson et al, JMS 327, 31 (2016)

# • Sensitivity of the parameters to a variation of $\mu$

| Constant                       | Value (GHz)      | $K_A$         | Constant                | Value (GHz)    | $K_A$ | sensitivity coefficient     |
|--------------------------------|------------------|---------------|-------------------------|----------------|-------|-----------------------------|
| $B_0$                          | 35.274974565(42) | -0.9974937(4) | $x_{14}$                | -416.1(42)     | -1    | $K_A = d \ln A / d \ln \mu$ |
| $D_0 (\times 10^6)$            | 48.77824(39)     | - 2.01457(5)  | $x_{15}$                | -315.4(48)     | -1    |                             |
| $H_0 (\times 10^{12})$         | 57(18)           | - 3           | $x_{22}$                | -223.4(21)     | -1    |                             |
| $\alpha_1 (\times 10^3)$       | 206.986(33)      | - 1.5         | $x_{23}$                | -184.7(33)     | -1    |                             |
| $\alpha_2 (\times 10^3)$       | 185.308(39)      | - 1.5         | $x_{24}$                | -381.6(30)     | -1    |                             |
| $\alpha_3 (\times 10^3)$       | 176.332(33)      | - 1.5         | $x_{25}$                | -45.9(22)      | -1    |                             |
| $\alpha_4 (\times 10^3)$       | -40.5780(26)     | - 1.5         | $x_{33}$                | -828.3(36)     | -1    |                             |
| $\alpha_5 (\times 10^3)$       | -66.9159(12)     | - 1.5         | $x_{34}$                | -300.4(42)     | -1    |                             |
| $\gamma^{44} (\times 10^4)$    | -19.720(33)      | - 2           | $x_{35}$                | -280.0(48)     | -1    |                             |
| $\gamma^{55} (\times 10^4)$    | -32.954(15)      | - 2           | $x_{44}$                | 103.7(16)      | -1    |                             |
| $\gamma^{45} (\times 10^4)$    | -67.641(12)      | - 2           | $x_{45}$                | -66.9(30)      | -1    |                             |
| $\beta_1 (\times 10^8)$        | -42.45(27)       | - 2.5         | $x_{55}$                | -71.2(16)      | -1    |                             |
| $\beta_2 (\times 10^8)$        | 5.93(44)         | - 2.5         | $g_{44}$                | 23.42939(27)   | -1    |                             |
| $\beta_3 (\times 10^8)$        | -40.99(40)       | - 2.5         | $g_{45}$                | 198.00315(24)  | -1    |                             |
| $\beta_4 (\times 10^8)$        | 103.13(23)       | - 2.5         | $g_{55}$                | 104.21008(19)  | -1    |                             |
| $\beta_5 (\times 10^8)$        | 77.76(18)        | - 2.5         | $r_{45}$                | -187.03212(33) | -1    |                             |
| $\delta^{44} (\times 10^{10})$ | -517(18)         | - 3           | $r_{J45} (\times 10^4)$ | 58.565(19)     | -2    |                             |
| $\delta^{45} (\times 10^{10})$ | -1184(22)        | - 3           | $p_{45} (\times 10^8)$  | -52.79(90)     | -2    |                             |
| $\delta^{55} (\times 10^{10})$ | -446(17)         | - 3           | $q_{04} (\times 10^3)$  | -157.3485(36)  | -1.5  |                             |
| $B_1$                          | 34.8877668(57)   | -0.991972(1)  | $q_{05} (\times 10^3)$  | -139.7165(36)  | -1.5  |                             |
| $D_1 (\times 10^6)$            | 47.8852(39)      | - 2.0061(2)   | $q_{44} (\times 10^5)$  | 53.45(33)      | -2    |                             |
| $B_2$                          | 35.002840(20)    | -0.993256(1)  | $q_{45} (\times 10^5)$  | -237.3(1.3)    | -2    |                             |
| $D_2 (\times 10^6)$            | 48.107(60)       | - 2.0277(36)  | $q_{54} (\times 10^5)$  | -330.1(1.4)    | -2    |                             |
| $v_1$                          | 196576.8494(18)  | - 0.47159(9)  | $q_{55} (\times 10^5)$  | -113.86(36)    | -2    |                             |
| $v_2$                          | 198922.7020(21)  | - 0.48114(7)  | $q_{J4} (\times 10^8)$  | 117.82(19)     | -2.5  |                             |
| $x_{11}$                       | -743.8(66)       | - 1           | $q_{J5} (\times 10^8)$  | 115.351(69)    | -2.5  |                             |
| $x_{12}$                       | -350.2(39)       | - 1           | $W$                     | 193.87198(96)  | -1    |                             |
| $x_{13}$                       | -3223(16)        | - 1           | $W_J (\times 10^5)$     | -101.93(60)    | -2    |                             |

Dependence on molecular structure parameters => sensitivity to  $\mu$ -variation

Constantin, Vibrational Spectr. 85, 228 (2016)

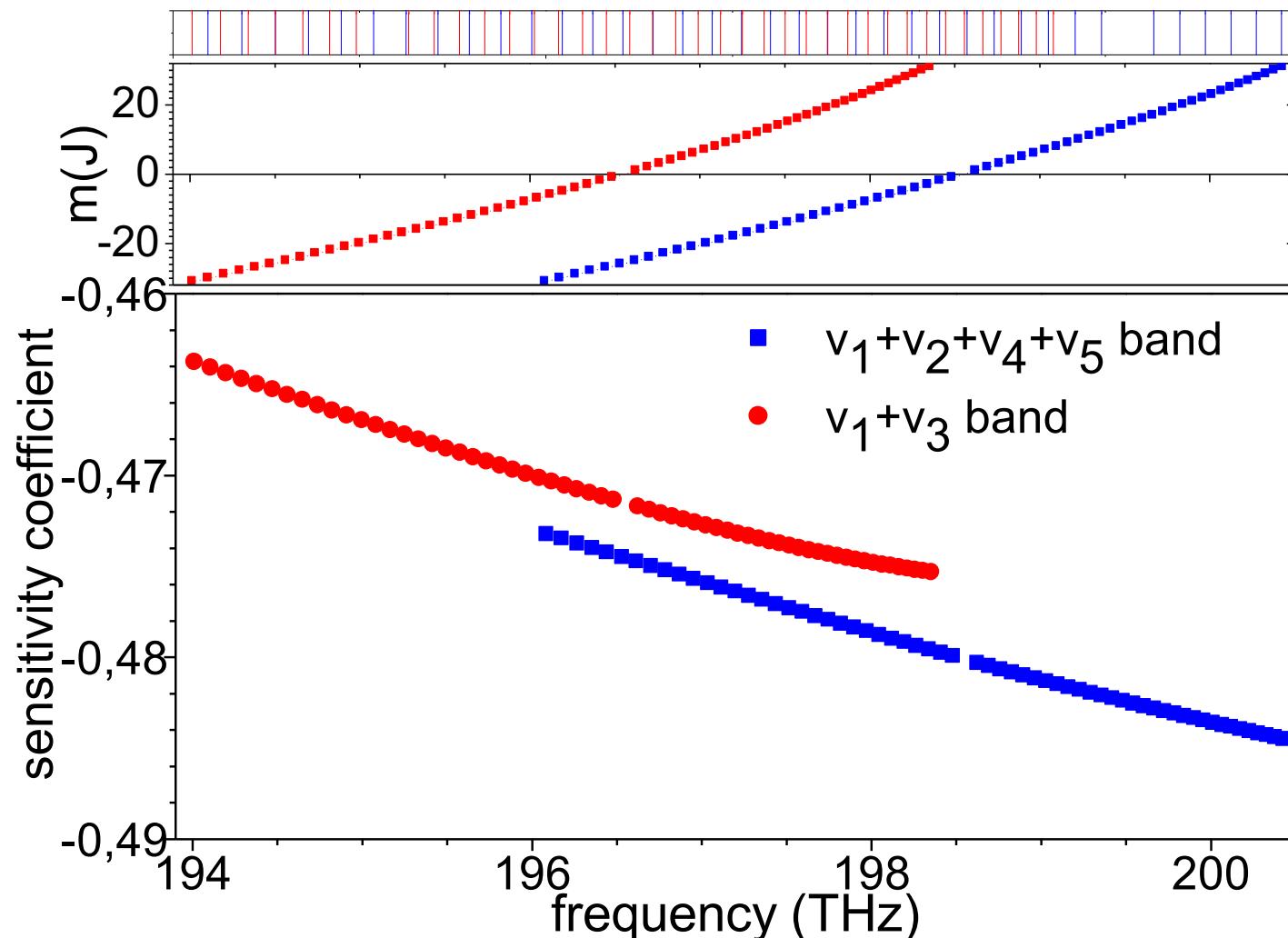
- Sensitivity of the transitions to a variation of  $\mu$

-Hamiltonian approach to calculate sensitivity to  $\mu$ -variation of  $^{12}\text{C}_2\text{H}_2$  reference transitions

Constantin, Vibrational Spectr. 85, 228 (2016)

Prediction of acetylene frequency in function of  $\mu$  & derivative of simulated data

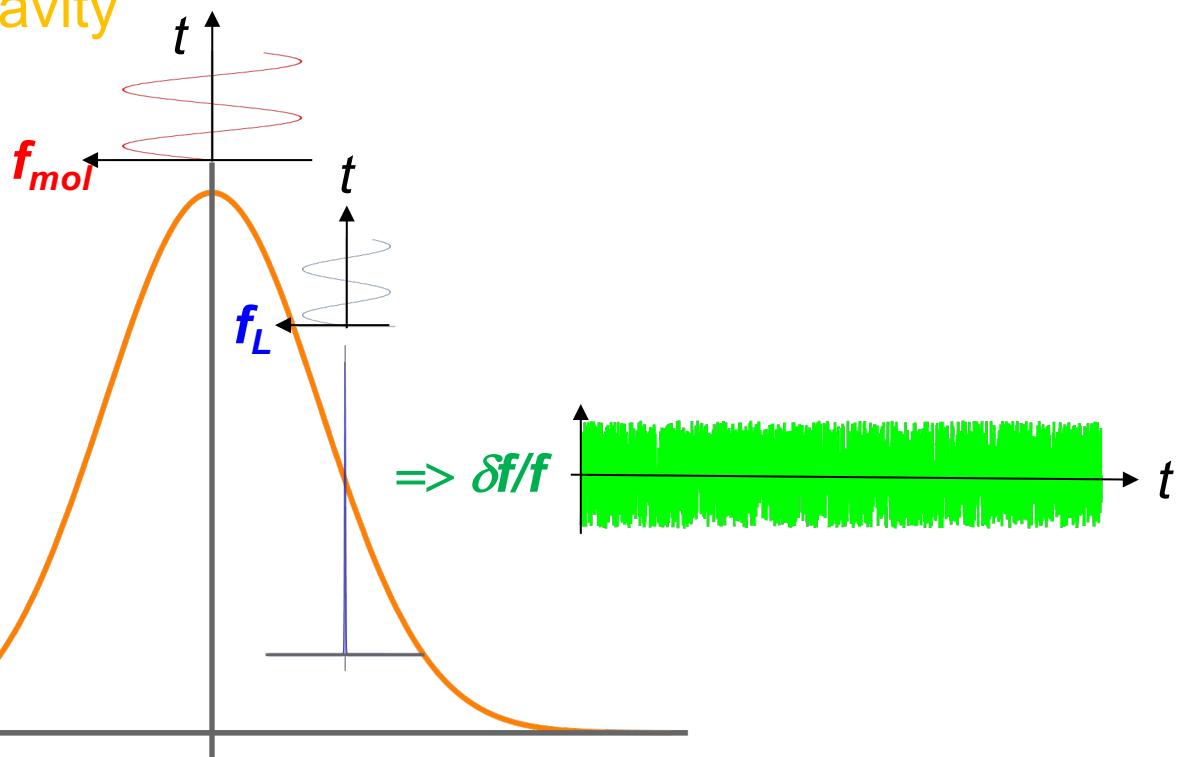
=>Sensitivity of reference transition P(16) of the  $v_1+v_3$  band of  $^{12}\text{C}_2\text{H}_2$  :  $K_\mu = -0.468$



- Principle of the experiment

- Laser stabilized on a FP cavity

- Molecular resonance



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

- Sensitivity coefficients :  $Q_\alpha^L \cong 1$ ;  $Q_\mu^L \cong 0$ ;  $Q_\alpha^{mol} = 2$ ;  $Q_\mu^{mol} = -0.47$

Pašteka et al, PRL 122, 160801 (2019); Constantin, Vibrational Spectr. 85, 228 (2016)

- Response functions  $h^L$ ,  $h^{mol}$  with high-frequency cutoffs

-frequency cutoffs : linewidth of the molecular line, delay in propagation of sound in the ULE spacer, ...

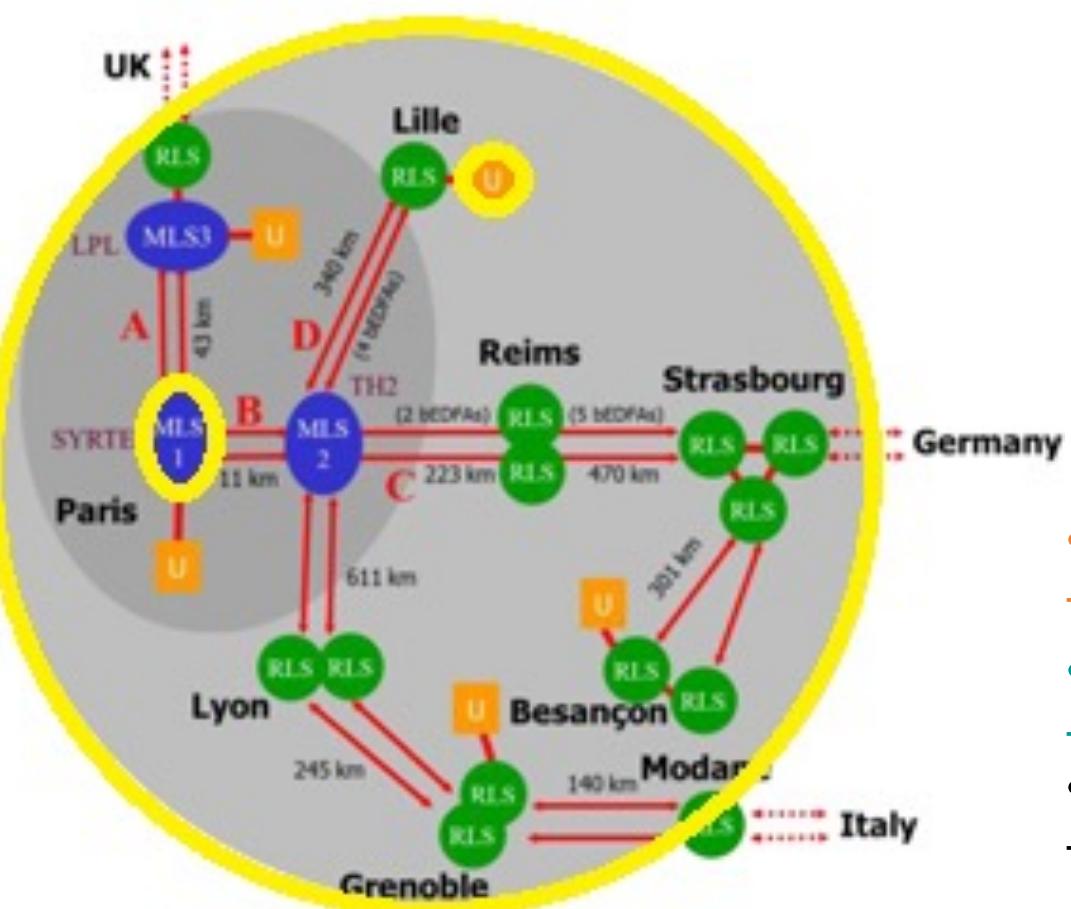
## • Towards a network spectrometer

### - REFIMEVE network :

- 1542 nm laser locked to ULE cavity/H maser

- phase-stabilized fiber link

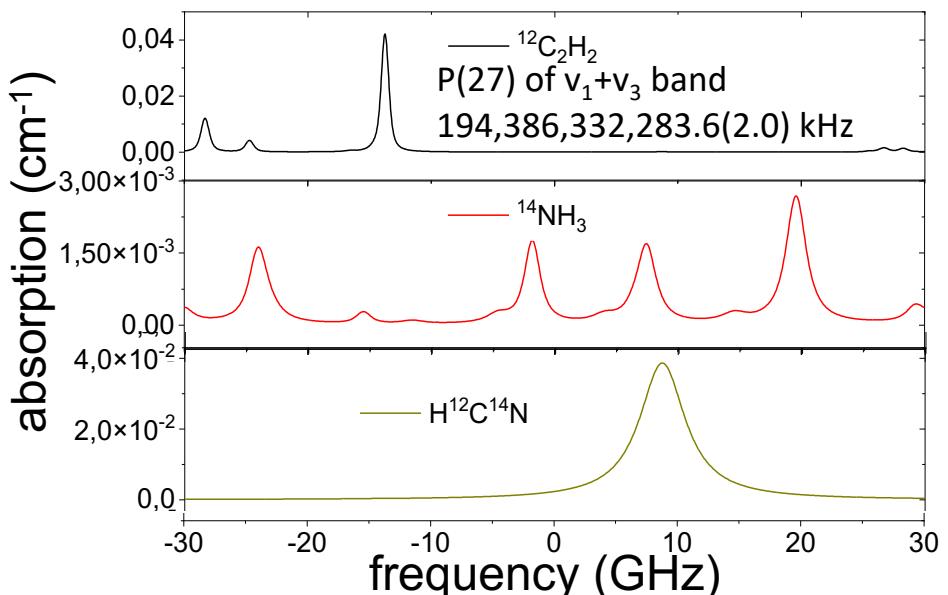
Cantin *et al*, New J. Phys. 23, 053027 (2021)



=> fractional stability  $<10^{-15} (\tau/1\text{s})^{-1/2}$

=> fractional uncertainty  $<10^{-14}$

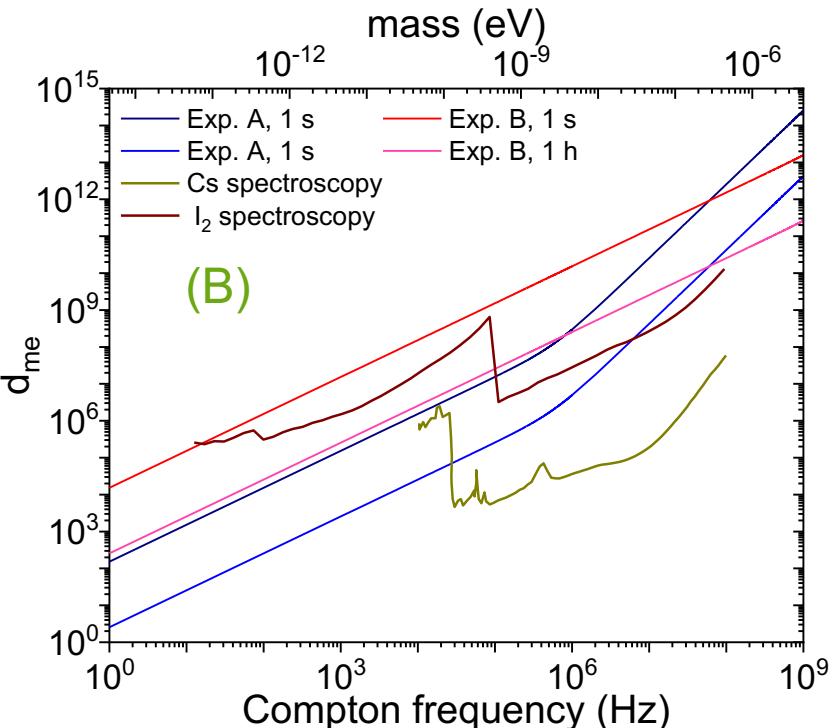
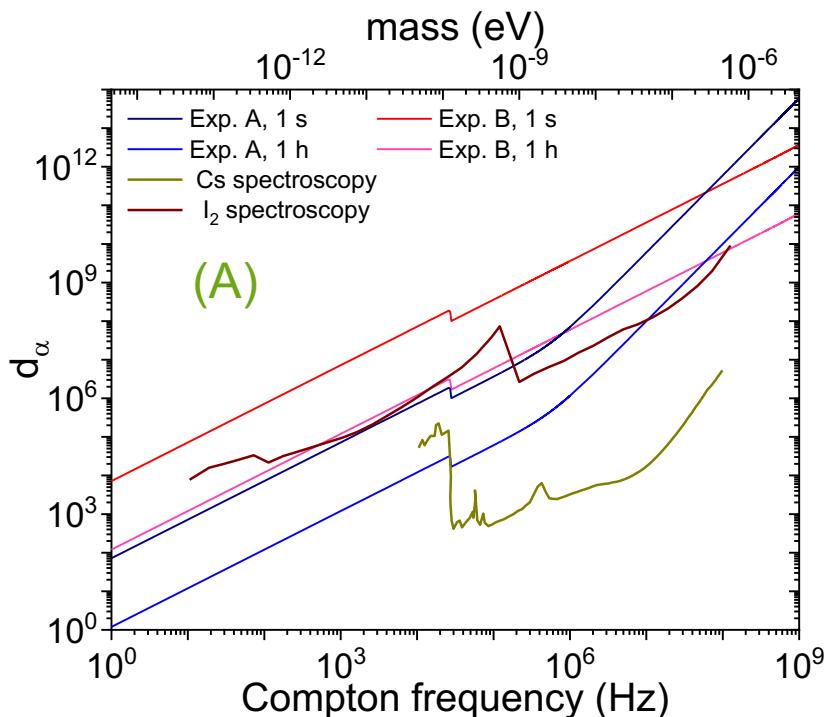
=> Signal to PhLAM almost continuously at  
194,400,084,500.000(25) kHz



- Broadband tuning with optical modulators  
-LiNbO<sub>3</sub> photonic platform
- Fast data acquisition at 1 Gsa/s level  
-fast DAQ and data storage
- Low-noise absorption detection  
-differential detection, noise-eater implementation,...

=> compact/robust molecular spectrometer  
=> integration into the optical fiber network  
Constantin, Proc. IFCS-EFTF 2023 Paper Id 7354

- Exp. A : recording a Doppler-free molecular line with  $\delta f/f = 10^{-14} (\tau/1\text{s})^{-1/2}$
- Exp. B : recording a linear absorption molecular line with  $\delta f/f = 10^{-12} (\tau/1\text{s})^{-1/2}$
- High-frequency cutoffs in the response of the experimental setup
  - Sound propagation in ULE spacer  $f_{c1} = 27 \text{ kHz}$
  - Molecular transition sub-Doppler  $f_{c2A} = 100 \text{ kHz}$  and linear absorption  $f_{c2B} = 4 \text{ GHz}$  linewidths



=>improved limits on Compton frequencies domain by one order of magnitude

=>potential to improve the state-of-the-art constraints at low frequencies by averaging

## 2) Potential from frequency measurements of a MW acetylene clock

# • Principle of the proposed experiment

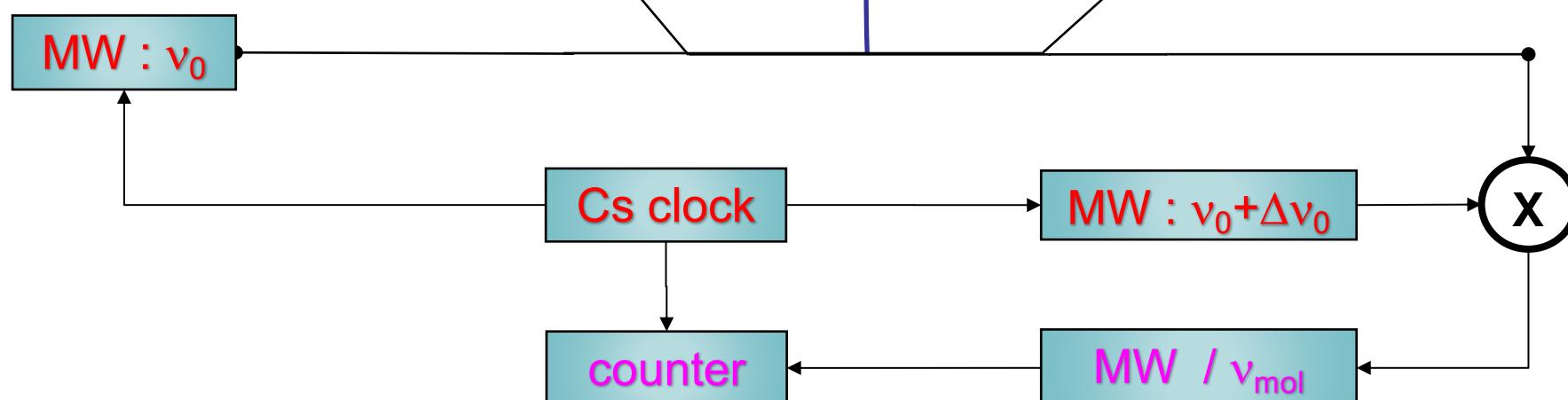
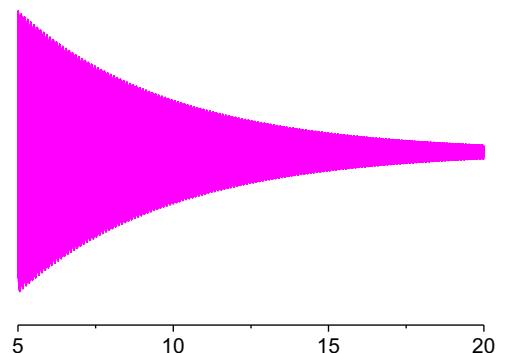
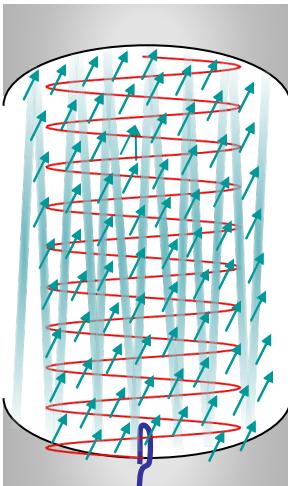
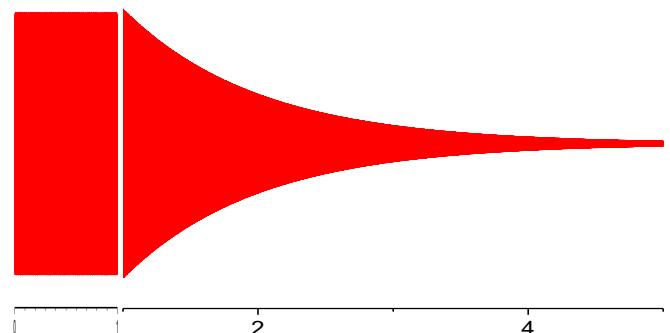
## Measurement of a MW transition with enhanced sensitivity coefficient to $\mu$ -variation

Constantin, Proc. CLEO-Europe/EQEC paper ED-1.4 (2023)

$$E_{cav} = E_0 \cdot \cos(2\pi\nu_0 t) \text{ for } 0 < t < \tau_p;$$

$$E_0 \cdot e^{-(t-\tau_p)/\tau_{cav}} \cos(2\pi\nu_0(t - \tau_p)) \text{ for } t \geq \tau_p$$

$$E_{FID} = \exp\left(-2\pi\Delta\nu_{HWHM}^{press}t - (\pi\Delta\nu_{HWHM}^{Doppler}t)^2/\ln(2)\right) \times E_{mol} \cdot \cos(2\pi\nu_{mol}(t - \tau_p - 4\tau_{cav}) + \theta)$$



State preparation

- heating
- optical pumping
- MW  $\pi/2$  pulse

Cavity ringdown  
Molecular FID

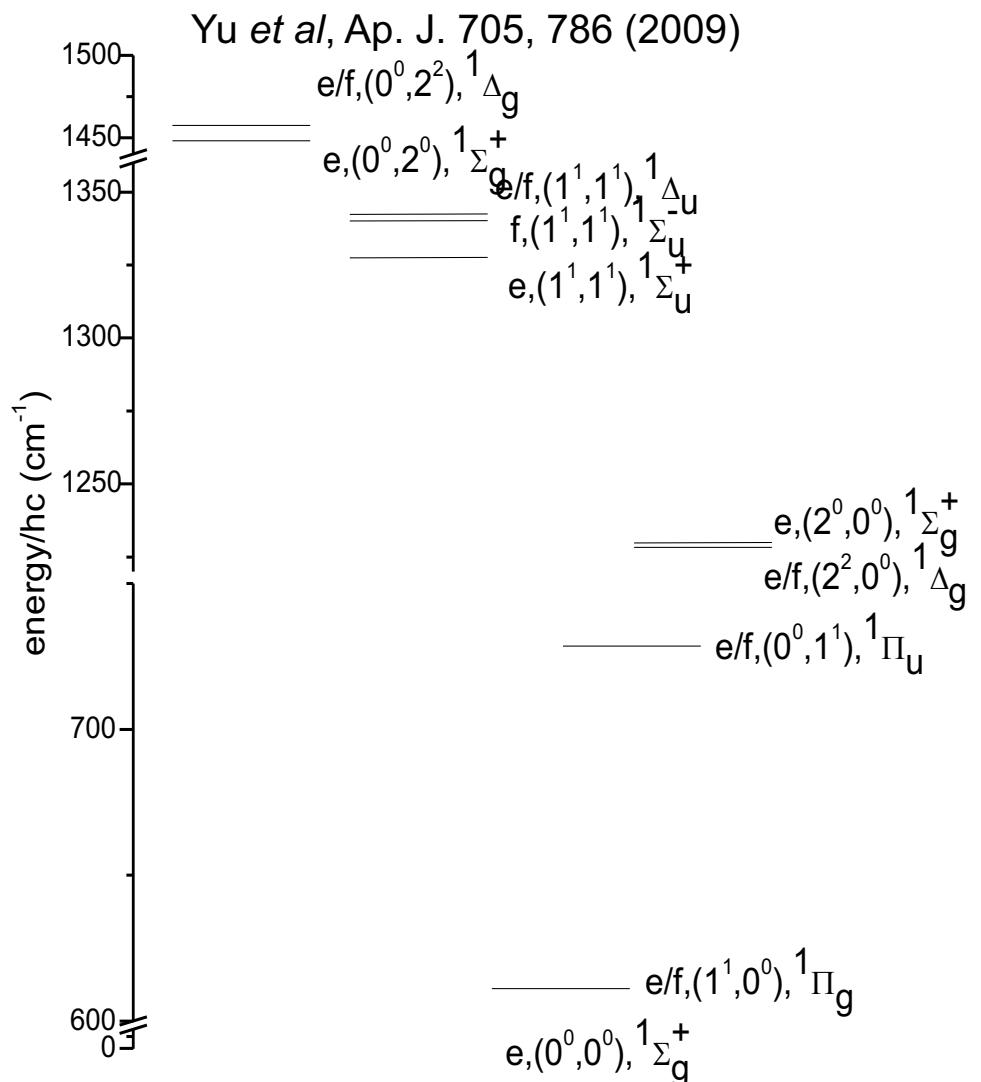
Heterodyne mixing  
FFT+MW osc. locking

$\text{C}_2\text{H}_2/\text{Cs}$  frequency measurement

Vibrational energy:  $v_4^{14}$ ,  $v_5^{15}$

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

$$\omega_i \sim 1/\sqrt{\mu}; x_{ij} \sim 1/\mu; g_{ij} \sim 1/\mu, \dots$$



Vibrational energy:  $v_4^{14}$ ,  $v_5^{15}$

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

$$\omega_i \sim 1/\sqrt{\mu}; x_{ij} \sim 1/\mu; g_{ij} \sim 1/\mu, \dots$$

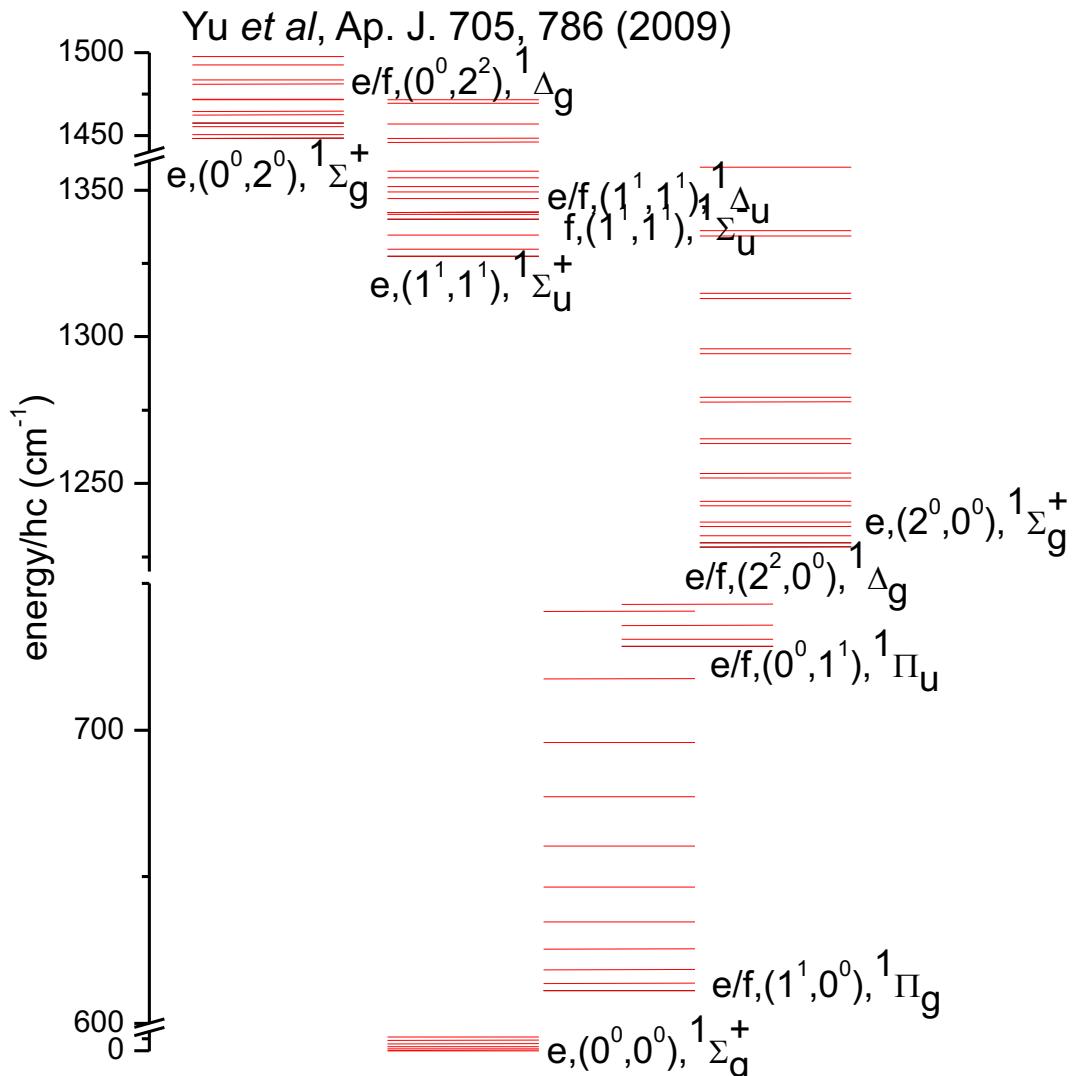
Rotational energy:  $J$ ,  $k=l_4+l_5$

$$E_R/hc = B(v_4^{l_4}, v_5^{l_5})[J(J+1) - k^2] + D(v_4^{l_4}, v_5^{l_5})[J(J+1) - k^2]^2 + \dots$$

$$B(v_4^{l_4}, v_5^{l_5}) = B_0 - \sum_{i=4}^5 \alpha_i \left( v_i + \frac{d_i}{2} \right) + \dots$$

$$D(v_4^{l_4}, v_5^{l_5}) = D_0 + \sum_{i=4}^5 \beta_i \left( v_i + \frac{d_i}{2} \right) + \dots$$

$$B \sim 1/\mu; D \sim 1/\mu^2; \alpha \sim 1/\mu^{3/2}; \beta \sim 1/\mu^{5/2}$$



Rotational & vibrational I-type interactions and doublings

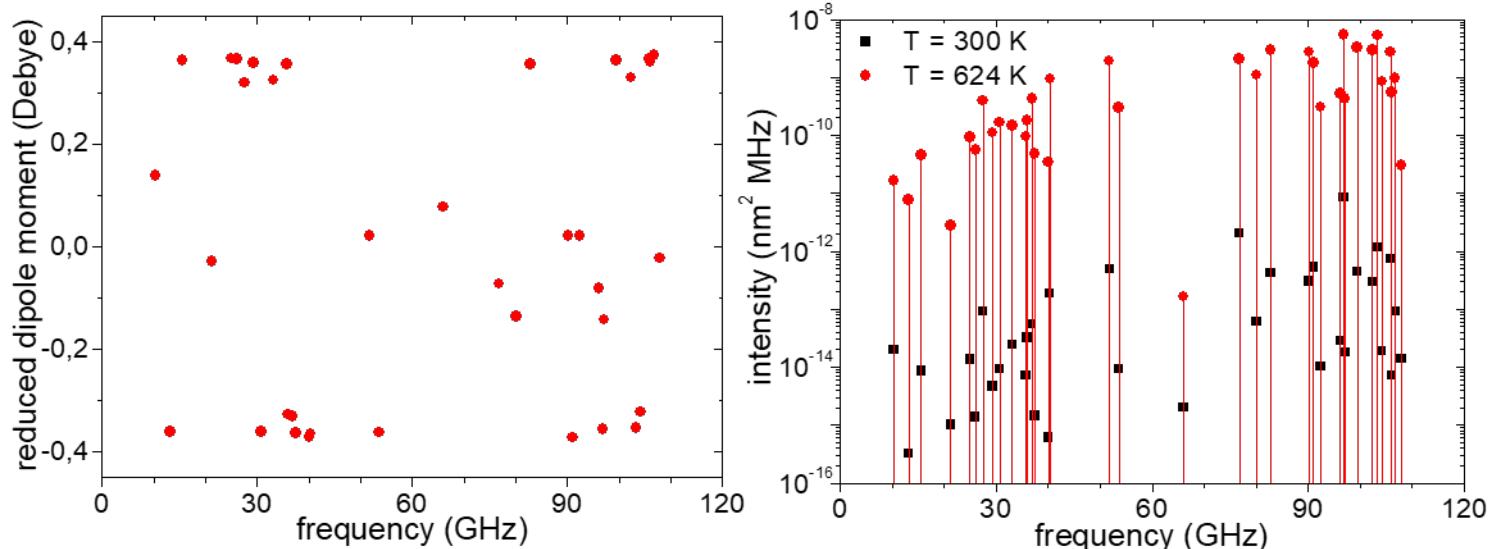
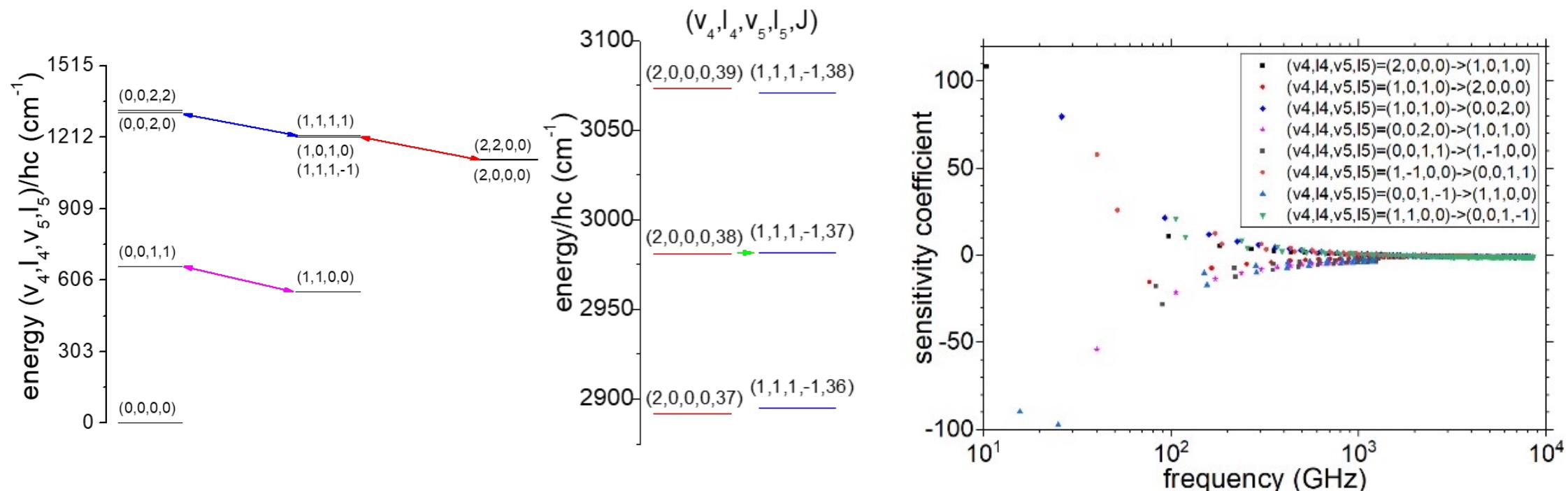
$$For example \quad M = J(J+1) - k^2 : \begin{pmatrix} E_R(J, 0) + E_V(2^{0,\pm 2}, 0^0) & (\sqrt{2} hcq_4(2,0)/2)\sqrt{M(M-2)} \\ 0 & E_R(J, 0) + E_V(2^{0,\pm 2}, 0^0) \pm (hcp_4/2)M(M-2) \end{pmatrix}$$

$$(\sqrt{2} hcq_4(2,0)/2)\sqrt{M(M-2)}$$

$$E_R(J, 0) + E_V(2^{0,\pm 2}, 0^0) \pm (hcp_4/2)M(M-2)$$

=> Energy level prediction with  $10^3$ - $10^7$  Hz accuracy ; estimation of the  $\mu$ -sensitivity

# MW transitions with enhanced sensitivity to $\mu$ -variation



# • Frequency stability from a $^{12}\text{C}_2\text{H}_2$ microwave line

Transition  $(v_4^{l_4}, v_5^{l_5}, J, \text{sym}) = (2^0, 0^0, 38, e^1 \Sigma_g^+) \rightarrow (1^1, 1^{-1}, 37, e^1 \Sigma_u^+)$

Exp. param. :  $\nu_{\text{mol}} = 10363 \text{ MHz}$ ,  $L = 1 \text{ m}$ ,  $w_0 = 0.1 \text{ m}$ ,  $Q_0 = 10^5$

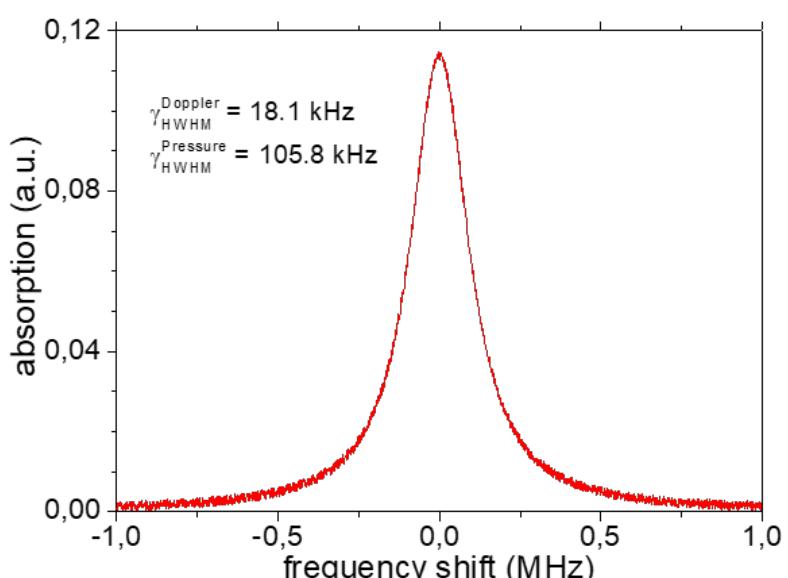
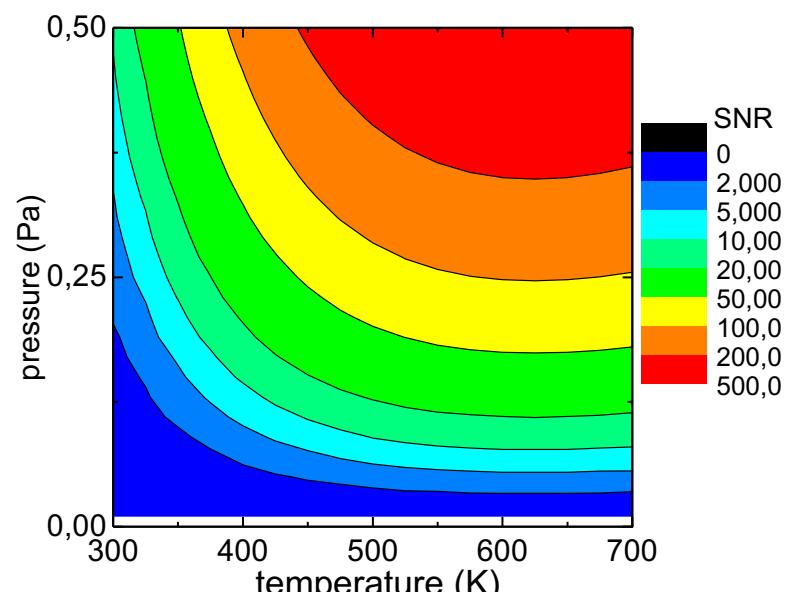
$\pi/2$  MW pulse; full population transfer from  $|g\rangle$  to  $|b\rangle$

$$\text{FID power} : P_{\text{FID}} = \frac{16}{9} \pi^2 Q_0 \nu_0 (\mu_{ab} \Delta N_0)^2 \pi w_0^2 L \left( \frac{\int_0^{\kappa E_0 \tau_p} J_1(u) du}{\kappa E_0 \tau_p} \right)^2$$

Campbell *et al*, J. Chem. Phys. 74, 813 (1980)

$$\text{Noise power} : P_{\text{noise}} = kT_{\text{noise}} B \approx kT_{\text{exp}} / \tau_{\text{cav}}$$

Optimization with constraint  $B = \gamma_{\text{cav}} \sim \gamma_{\text{mol}} \Rightarrow T_{\text{exp}} = 624 \text{ K}$ ;  $P_{\text{exp}} = 0.24 \text{ Pa}$ ;  $\text{SNR} = 94$



$$\Rightarrow \text{Allan fractional instability} : \sigma_{\delta f_{\text{mol}}/f_{\text{mol}}}(\tau) \approx \frac{P_{\text{FID}}/P_{\text{noise}}}{Q_{\text{mol}}} \sqrt{\frac{T_c}{\tau}} \cong \frac{2.1 \times 10^{-10}}{\sqrt{\tau/1\text{s}}}$$

# • Systematic frequency shifts of a $^{12}\text{C}_2\text{H}_2$ microwave line

Transition  $(v_4^{l_4}, v_5^{l_5}, J, \text{sym}) = (2^0, 0^0, 38, e^1 \Sigma_g^+) \rightarrow (1^1, 1^{-1}, 37, e^1 \Sigma_u^+)$  at 10363 MHz

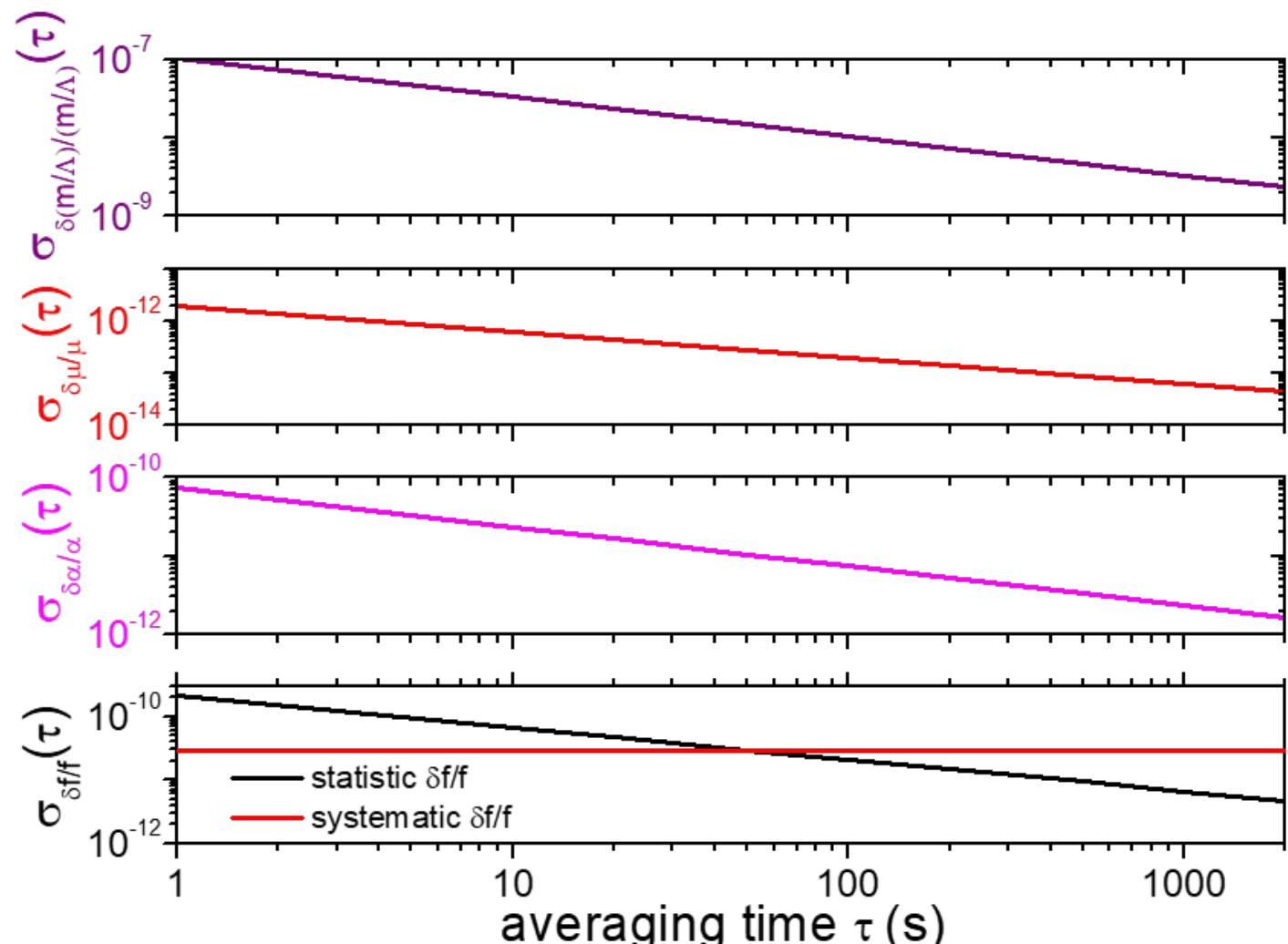
| <i>Systematic effect</i>   | <i>value</i> | <i>unc.</i> |
|--|--------------|-------------|
| Cavity pulling   | 44 kHz       | 0.22 Hz     |
| $f_{mol} - f_{mol,0} = (f_{cav} - f_{mol}) \times (Q_{cav}/Q_{mol})^2$         |              |             |
| param.: $\alpha_T = 5 \times 10^{-6}/^\circ\text{C}$                           |              |             |
| uncertainty: $\Delta T = 1^\circ\text{C}$ $(f_{cav} - f_{mol}) = \Delta\nu/10$ |              |             |
| Viennet <i>et al</i> , IEEE TIM 21, 204 (1972)                                 |              |             |
| Pressure shift   | 246 Hz       | 0.19 Hz     |
| extrapolation meas. v4+v5 band at high T and low p                             |              |             |
| param.: T=624 K; p=0.24 Pa; no J-dependence                                    |              |             |
| uncertainty: $\Delta T = 1\text{ K}$   |              |             |
| Dhyne <i>et al</i> , JQSRT 112, 969 (2011)                                     |              |             |
| Zeeman shift   | 28 Hz        | 86 mHz      |
| extrapolation meas. MVCD v4&v5 band; eval. M=J states                          |              |             |
| param.: B=48 $\mu\text{T}$   |              |             |
| uncertainty: $\Delta B = 0.15 \mu\text{T}$                                     |              |             |
| Tam <i>et al</i> , J. Chem. Phys. 104, 1813 (1996)                             |              |             |

| <i>Systematic effect</i>                                | <i>value</i>       | <i>unc.</i>        |
|---|--------------------|--------------------|
| DC Stark shift  | 6.4 $\mu\text{Hz}$ | 1.3 $\mu\text{Hz}$ |
| 1st order perturbation theory, eval. for M=0 states     |                    |                    |
| param.: E=1 V/m   |                    |                    |
| uncertainty: $\Delta\mu/\mu = 20\%$                     |                    |                    |
| Barnes <i>et al</i> , Chem. Phys. Lett. 237, 437 (1995) |                    |                    |
| BBR shift   | 1.4 mHz            | 9 $\mu\text{Hz}$   |
| ab-initio scalar polarizabilities, eval. for M=J states |                    |                    |
| param.: T=624 K   |                    |                    |
| uncertainty: $\Delta T = 1\text{ K}$                    |                    |                    |
| Russell and Spackman, Mol. Phys. 88, 1109 (1996)        |                    |                    |
| SODE shift  | -34.3 mHz          | 55 $\mu\text{Hz}$  |
| param.: T=624 K   |                    |                    |
| uncertainty: $\Delta T = 1\text{ K}$                    |                    |                    |
| Recoil doubling   |                    | negligible         |
| Autler-Townes doubling                                  |                    | negligible         |

# • Sensitivity to variations of fundamental constants

$$\frac{\Delta(f_{MW/mol}/f_{Cs})}{f_{MW/mol}/f_{Cs}} = (Q_\alpha^{mol} - Q_\alpha^{Cs}) \frac{\Delta\alpha}{\alpha} + (Q_\mu^{mol} - Q_\mu^{Cs}) \frac{\Delta\mu}{\mu} + (Q_q^{mol} - Q_q^{Cs}) \frac{\Delta(\hat{m}/\Lambda)}{\hat{m}/\Lambda}$$

- Sensitivity coefficients :  $Q_\alpha^{Cs} = 2.83$ ;  $Q_\mu^{Cs} = -1$ ;  $Q_q^{Cs} = 0.002$ ;  $Q_\alpha^{mol} = 0$ ;  $Q_\mu^{mol} = 109$ ;  $Q_q^{mol} = 0$



- Accurate theory for modeling frequency & frequency shifts of  $^{12}\text{C}_2\text{H}_2$  transitions
- Accurate determination of sensitivity coefficients to  $\mu$ -variation
- Enhanced sensitivity coefficients for MW transitions between near-resonant levels
  
- Development of spectrometers at 194 THz using the REFIMEVE network with precision at levels of  $(\delta f/f)^{\text{Doppler-free}} = 10^{-14} (\tau/1\text{s})^{-1/2}$  and  $(\delta f/f)^{\text{Doppler}} = 10^{-12} (\tau/1\text{s})^{-1/2}$
- Microwave molecular clock with  $(\delta f/f)^A = 2.1 \times 10^{-10} (\tau/1\text{s})^{-1/2}$  and  $(\delta f/f)^B = 2.9 \times 10^{-11}$
  
- Potential to improve constraints on UDM couplings to SM particles

Thank you for your attention !

### Acknowledgements

