Instrumental developments for measuring parity violation in cold chiral molecules using vibrational spectroscopy

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Precision measurements with molecules

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

measure constants	m_e/m_p (Schiller, Hilico/Karr, Ubachs, Koelemeij – $HD^{(+)}$, $H_2^{(+)}$) k_B (Gianfrani, $H_2{}^{18}O$, CO_2, C_2H_2 - LPL, NH_3),…
measure their variations in time	α (J. Ye, OH) - m_e/m_p (De Natale, Maddaloni, CF_3H - 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: D. DeMille (BaF), LPL (chiral species),…
QED tests, 5^{th} force	W. Ubachs (H_2, HD^+),…
test the symmetrization postulate	Tino, De Natale,… (O_3, CO_2, NH_3,…)

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

Require advanced manipulation techniques already demonstrated in atomic physics:

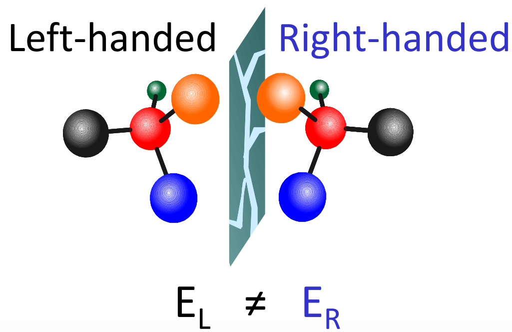
- o control and cooling of internal and external degrees of freedom
- o individual hyperfine states addressability
- o state-selective high detection-sensitivity and -rate
- o high-resolution spectroscopy
- o long coherence times
- o chemical stability

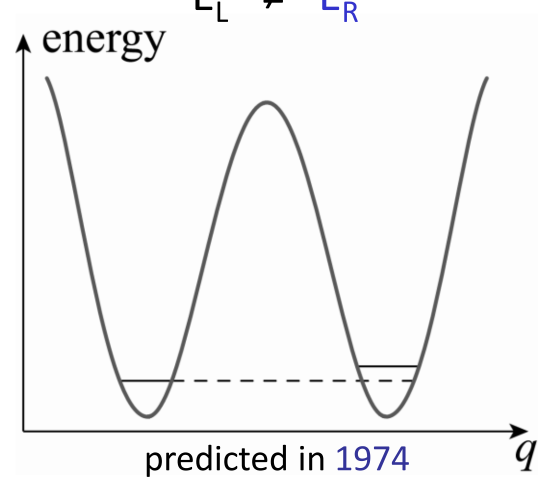
Parity, a broken symmetry

the weak nuclear force violates parity

- predicted by Lee and Yang (1956)
- observed in nuclear and high-energy physics
- observed in atoms (Bouchiat, 1982; Wieman, 1997) - effect $\propto Z^3$

never observed in chiral molecules





predicted in 1974
Rein, *J. Mol. Evol.* (1974)

- probe the Standard Model and physics beyond it in the low-energy regime

→ enhanced effects $\propto Z^5$
→ nuclear-spin dependent contributions, anapole moments, isotopic effects and neutron skin,…

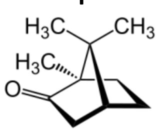
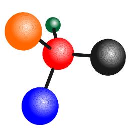
- link to biomolecular homochirality
- evaluate relativistic quantum chemistry
- advanced manipulation techniques for polyatomic species

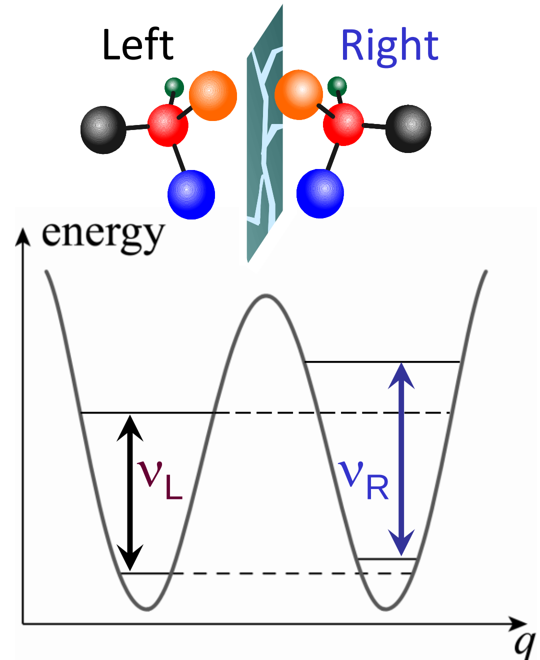
Parity violation in chiral molecules

several proposed experimental methods

- Lethokov's proposal (1975): vibrational spectroscopy (~30 THz)

The attempts so far

molecule	experimental sensitivity	$\Delta\nu_{PV}^{calc}/\nu$
camphor 	10^{-8} (Oka, 1977)	3×10^{-19} (Schwerdtfeger, 2004)
CHFClBr 	2.5×10^{-13} (Chardonnet, 2002)	8×10^{-17} (Schwerdtfeger, 2005)



$$\Delta\nu_{PV} = |\nu_L - \nu_R| \neq 0$$

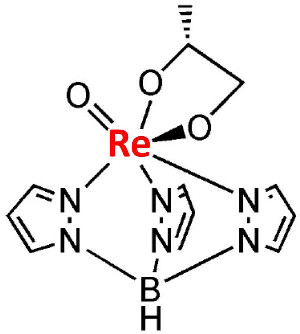
→ **produce samples of 'better' molecules**

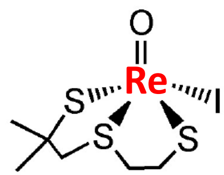
→ **build a more sensitive machine**

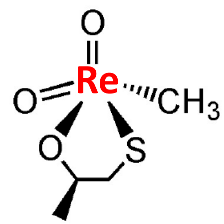
PV in chiral molecules: our strategy

Molecules with measurable PV:

rhenium, $Z_{Re} = 75$







- **100** to **1000 ×** bigger PV effect (10^{-14} - 10^{-13}) for rhenium complexes
- synthesized but in solid form

T. Saue

P. Schwerdtfeger

J. Crassous

L. Guy

Darquié et al, *Chirality* (2010)
Saleh et al, *Phys. Chem. Chem. Phys.* (2013)
Saleh et al, *Chirality* (2018)

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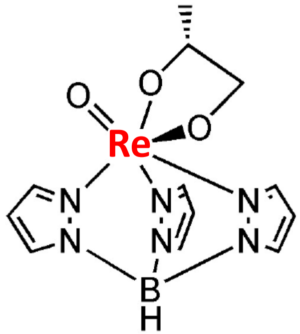

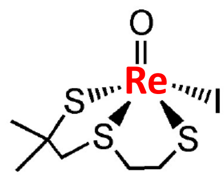

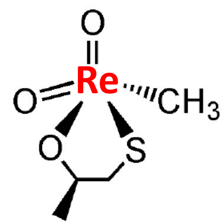

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CTCP Centre for Theoretical Chemistry and Physics — P. Schwerdtfeger

UNIVERSITÉ DE RENNES 1 — J. Crassous

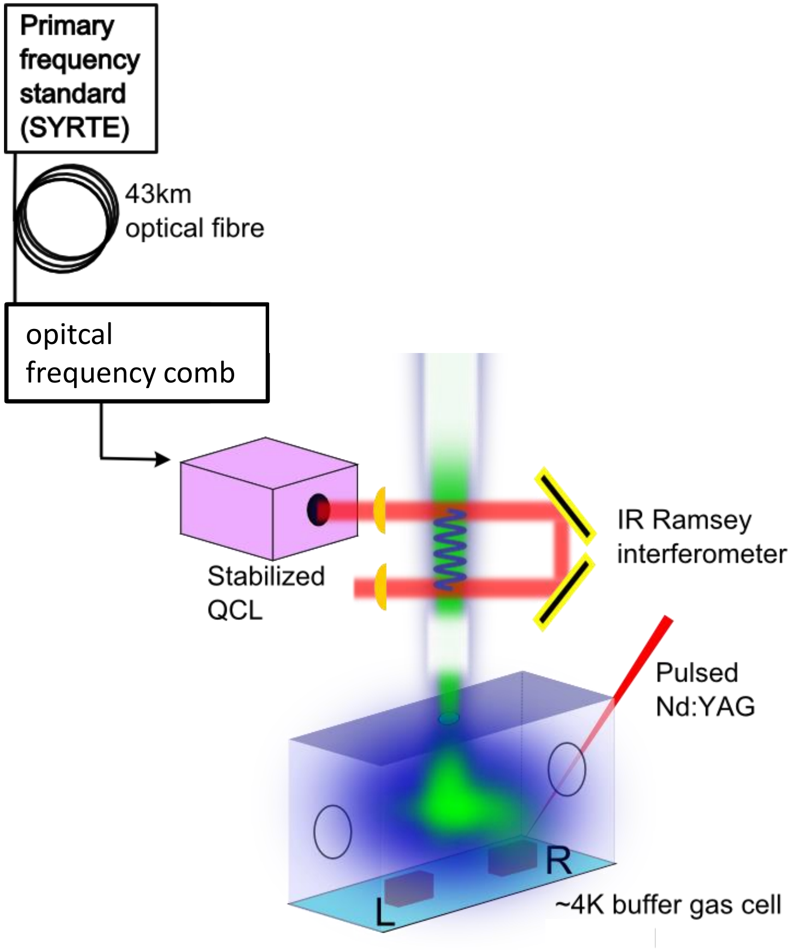
ENS DE LYON — L. Guy

Darquié et al, *Chirality* (2010)
Saleh et al, *Phys. Chem. Chem. Phys.* (2013)
Saleh et al, *Chirality* (2018)

Challenges when working with such complicated molecules:

1. solids ⟶ difficulty making intense sources in the gas phase (beams)
2. state-of-the-art CO_2 lasers typically used are not tuneable enough
3. direct detection of mid-IR laser absorption is not sensitive enough

A novel more sensitive machine



Develop an experiment comprising:

2:

quantum cascade laser (QCL) based Ramsey interferometer ⇔ primary frequency standards

remarkable tuneability and spectral purity

1:

buffer-gas-cooled molecular beam

cold, slow, intense

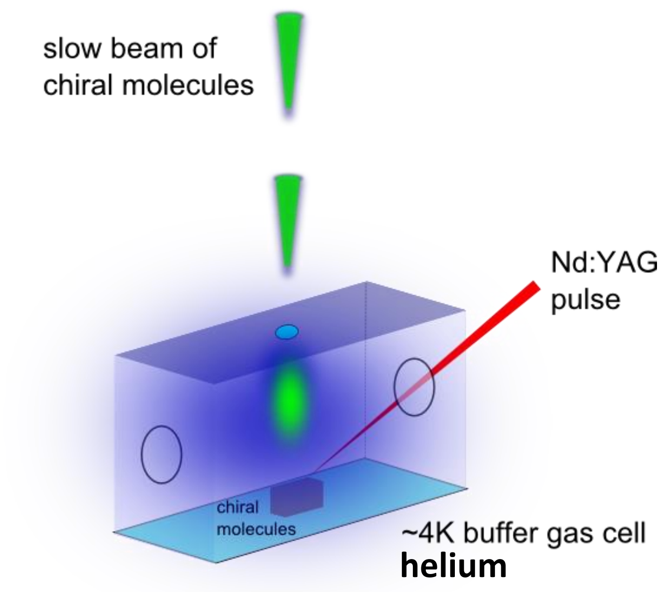
Frequency metrology approach:

- molecular beam Ramsey interferometry
- more than **100 × better** expected sensitivity: **$< 10^{-15}$**

Buffer-gas-cooled molecular beam

Hutzler, Lu, Doyle, *Chem. Rev.* **112**, 4803 (2012)

technique adapted to solid state species



for diatomics and light radicals, most intense cold molecular beam to date

- cold (4K)
- high flux (**supersonic x 10**)
- low velocity (**supersonic ÷ 10**)

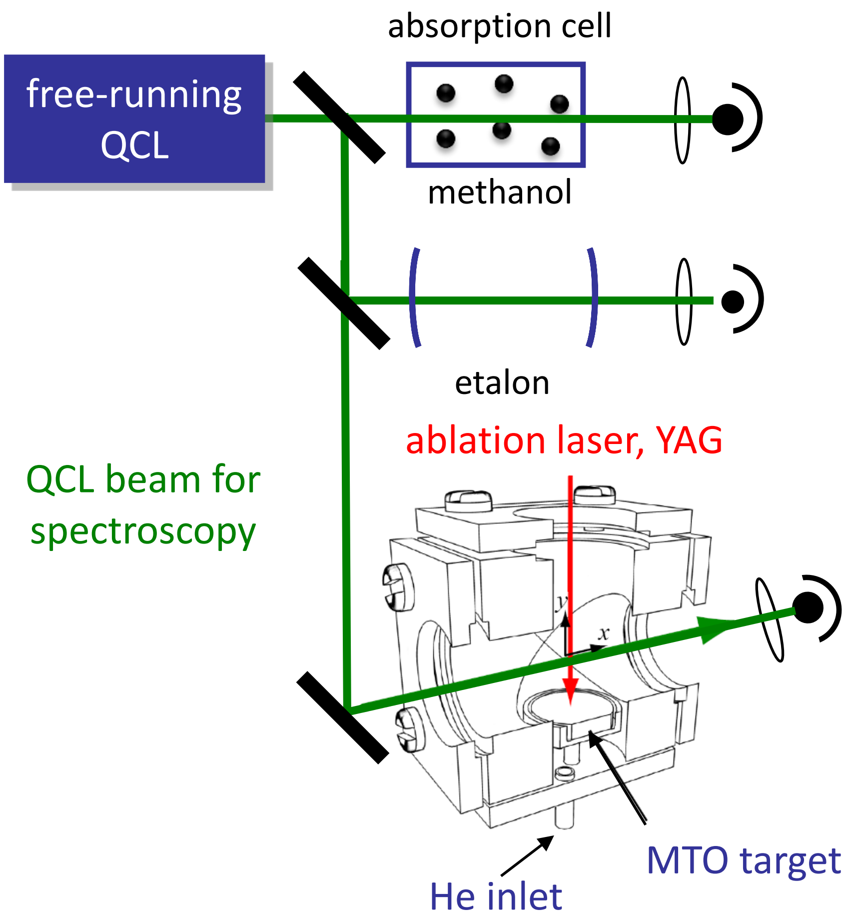
  → increase in resolution

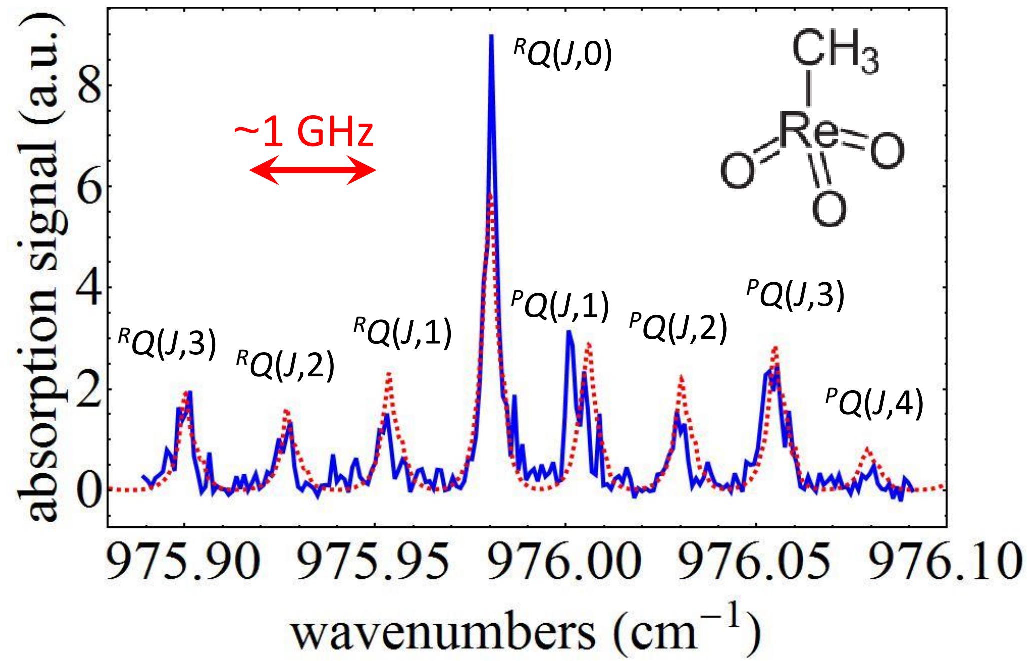
…extend to new complex chiral species

Internationally advocated for precision measurements: J. Doyle (Harvard), D. DeMille (Yale), Ed Hinds (Imperial College), De Natale (LENS), G. Rempe (MPQ), J. Ye (JILA),…

Buffer-gas cooling of MTO

- collaboration with M. Tarbutt and Ed Hinds at Imperial College
- we've taken a QCL to London
- tests in one of their cryogenic chamber



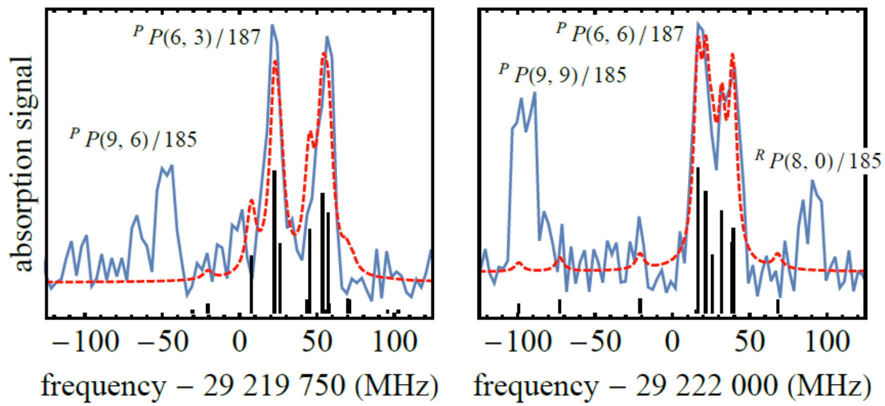


- **MTO**: methyltrioxorhenium achiral parent of chiral candidate species
- 1st organo-metallic species buffer-gas-cooled
- survives laser ablation!
- T_{rot} = 6 ± 3 K
- very promising for buffer-gas beams production

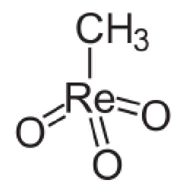
Tokunaga et al, *New J. Phys.* (2017)
Asselin et al, *Phys. Chem. Chem. Phys.* (2017)

Buffer-gas cooling polyatomic species

<u>Precise spectroscopic measurements already possible</u>



<u>MTO</u>



experiment
fit
fitted hyperfine components

hyperfine structure partially resolved in isolated rovibrational transitions

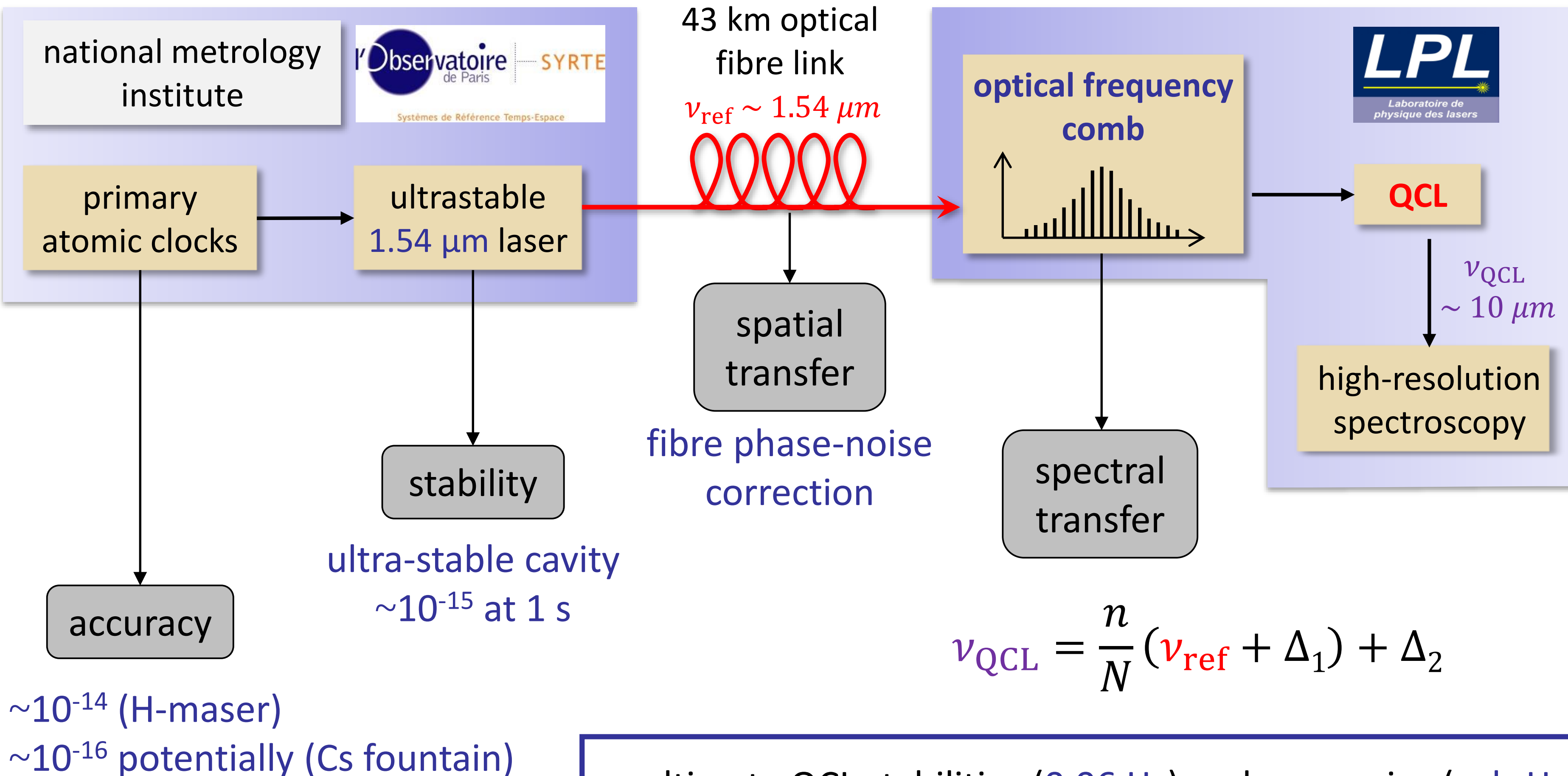
⟶ hyperfine parameters in the v=1 excited state

eQq^{exc} = 716 (3) MHz

⟶ unprecedented for such a complex species

Tokunaga et al, *New J. Phys.* (2017)
Asselin et al, *Phys. Chem. Chem. Phys.* (2017)

QCL stabilization to a near-IR frequency reference



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

- ultimate QCL stabilities (0.06 Hz) and accuracies (sub-Hz)
- narrowest QCLs laser so far (0.2 Hz)

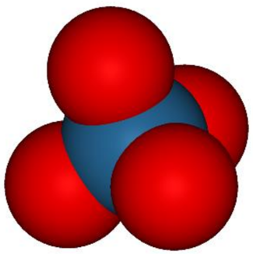
l'Observatoire de Paris SYRTE — Systèmes de Référence Temps-Espace

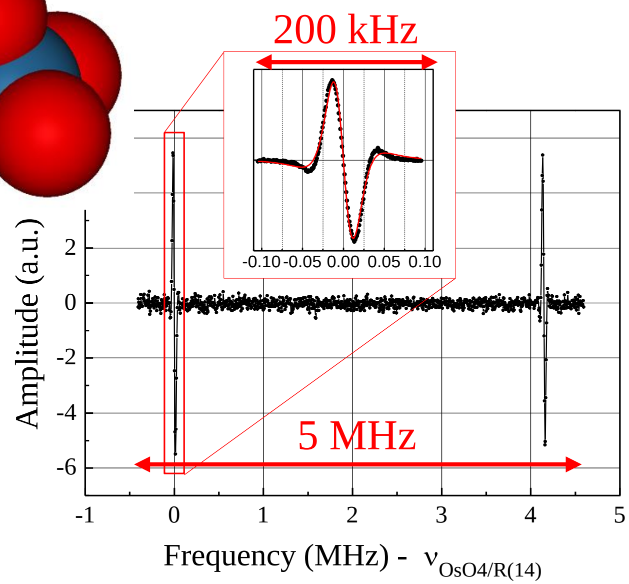
M Abgrall, Y Le Coq, R Le Targat, H Álvarez Martinez, W-K Lee, D Xu, P-E Pottie

Chanteau et al, *New J. Phys.* (2013)
Argence et al, *Nature Photon.* (2015)
see also: Insero et al., *Sci. Rep.* (2017)

Ultra-precise spectroscopy with QCLs: record frequency uncertainties

OsO_4 saturated absorption spectrum
around 29 THz

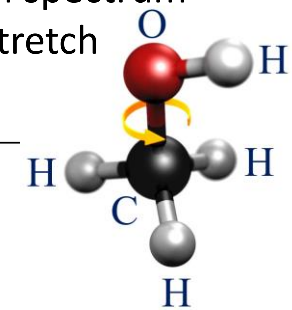


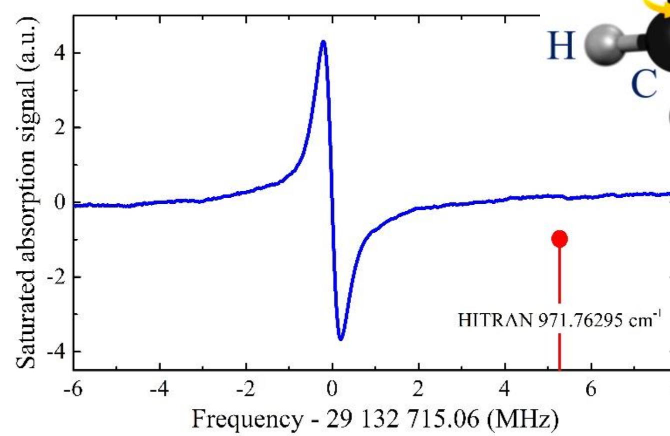


~200 finesse 1.5-m long Fabry-Perot cavity

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

Methanol saturated absorption spectrum
P(E_1,co,0,2,32) line, C-O stretch



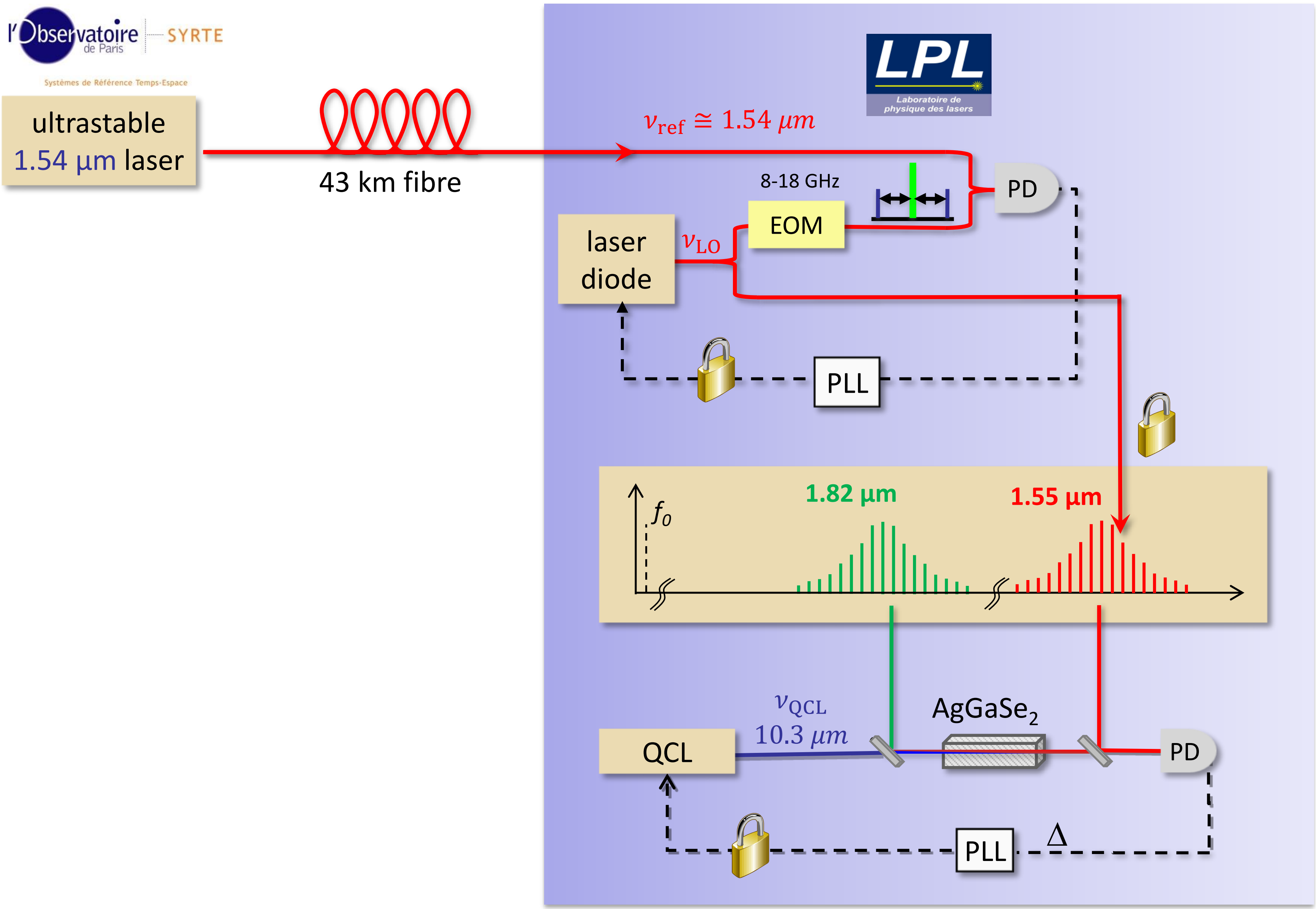


in a multipass cell

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

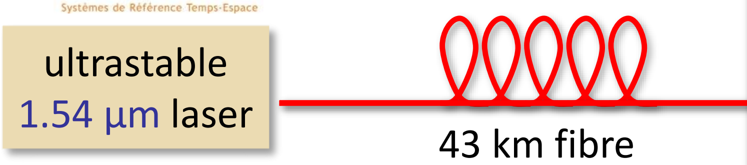
near-IR metrological level transferred to the mid-IR ⇒ ‘atomic physics’ types of precise measurements on molecules

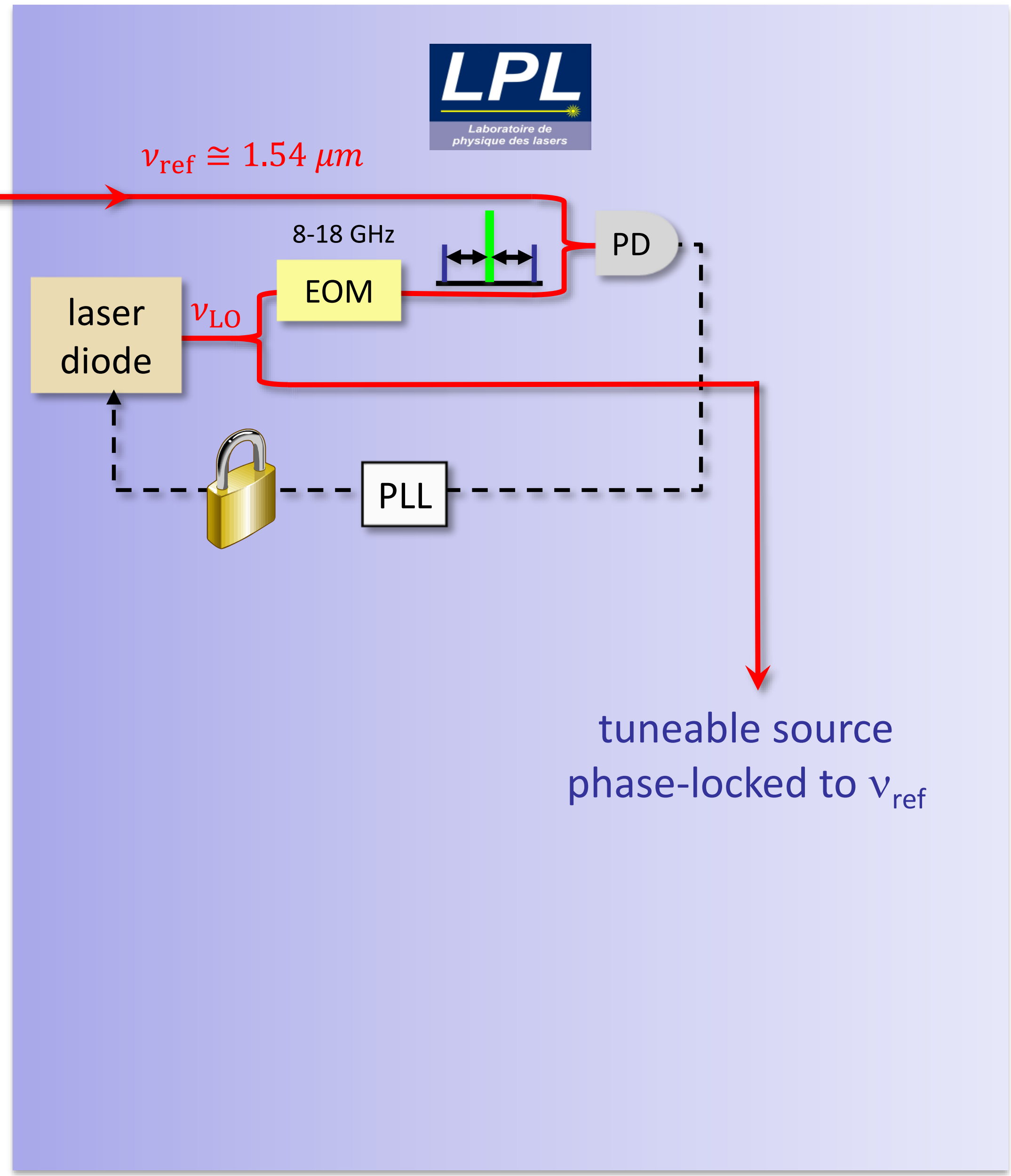
QCL stabilization to a near-IR frequency reference



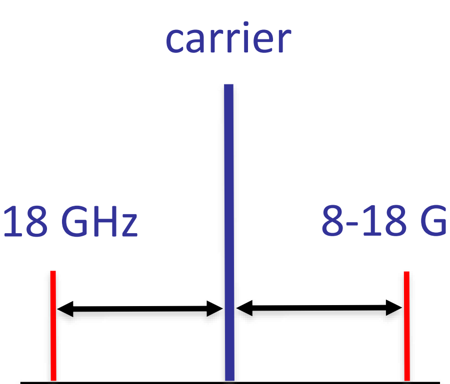
QCL stabilization to a near-IR frequency reference

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



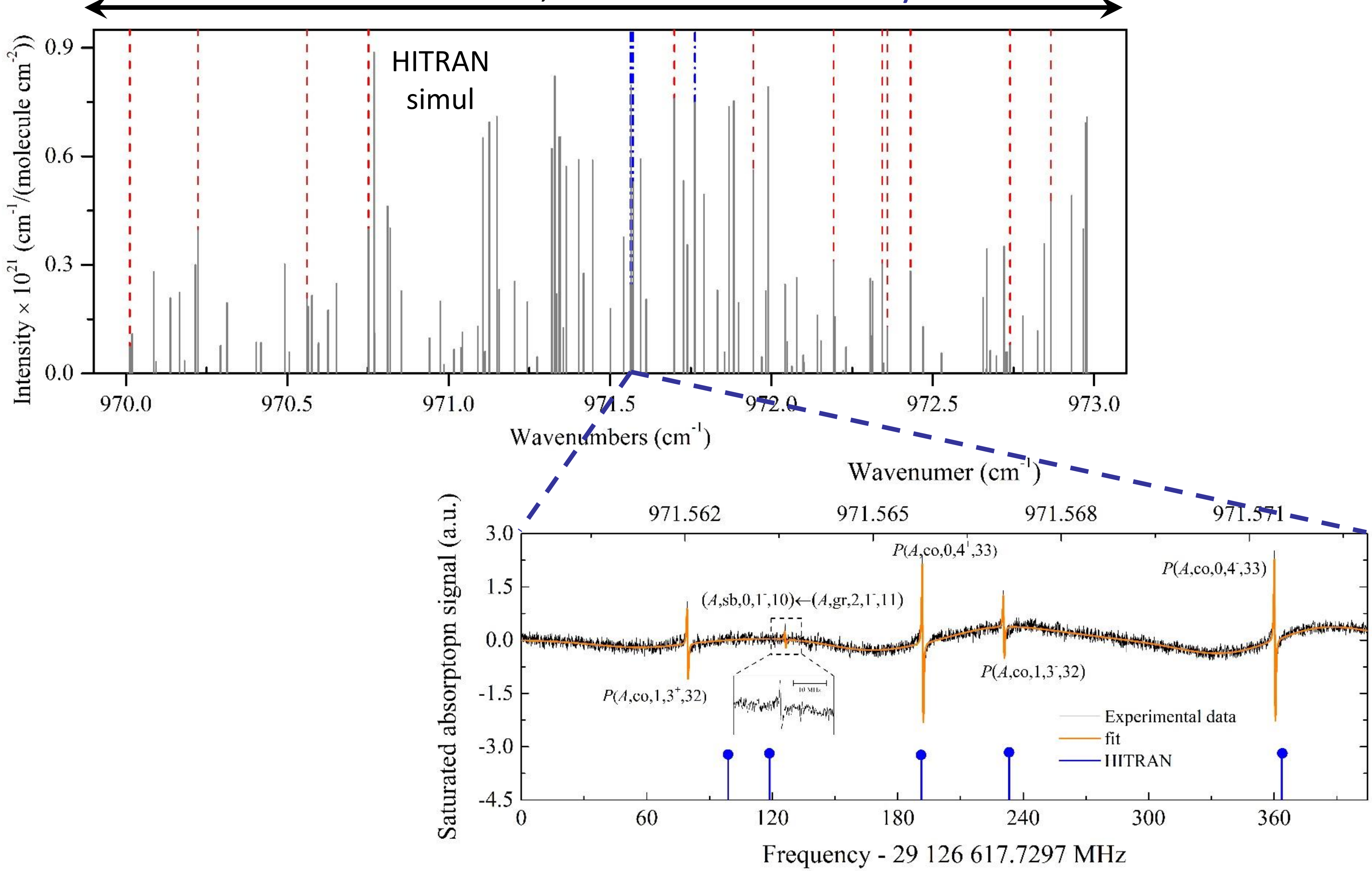


- microwave electro-optic modulator tuneable from 8 to 18 GHz
- home-made 8-18 GHz synthesizer:
  - ⟶ YIG oscillator
  - ⟶ phase-jump free
  - ⟶ phase-locked to a DDS



Ultra-precise spect. with QCLs: spectral coverage/tuneability/resolution

~100 GHz covered, ~full QCL's tuneability



~400 MHz, continuous tuning range (EOM)

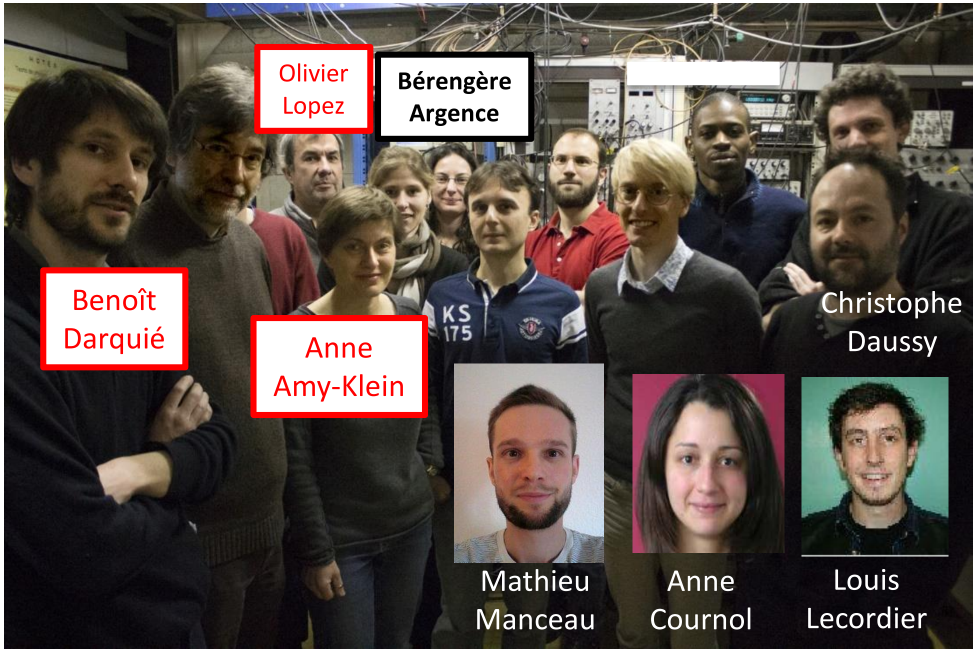
Summary / Perspectives

- Development of a molecular beam setup for Ramsey interferometry of chiral species
- Molecule considered: organo-metallic species in the solid phase
- Buffer-gas-cooling of MTO/trioxane
- QCL based spectrometers with record stabilities and accuracies

- new techniques for measuring and controlling complex molecules
- of interest to a wide community → testing physics with cold molecules, low temperature chemistry, spectroscopy, gas mixture analysis,…

- Perspectives: **build the Ramsey interferometry machine**,

⇒ buffer-gas-cooled beam, improve detection sensitivity using microwave detection (under progress), spectroscopy of chiral derivatives of MTO, the increase wavelength coverage, spectroscopy of other candidates, enantiomer-selective detection…

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