Spectroscopy of polyatomic molecules cooled by collisions with a buffer gas in a cryogenic cell

M Saffre, A. Bonifacio, A Cournol, SK Tokunaka, M Goncalves, A Kaladjian, JM Bieniewska, TE Wall, R Hendricks, BE Sauer, MR Tarbutt, **M Manceau**, B Darquié

Laboratoire de Physique des Lasers, Villetaneuse
Centre for Cold Matter, Blackett Laboratory, Imperial College, London

July 4, 2023

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 (Hinds/Tarbutt, CH - Inouye, KRb - **LPL**, **SF_6**)
test fundamental symmetries	parity & time-reversal symmetry (eEDM): Hinds/Tarbutt (YbF), Cornell/Ye (HfH^+), DeMille/Doyle/Gabrielse (ThO) parity symmetry: D. DeMille (BaF), Budker, Patterson & **LPL** (**chiral species**)
QED tests, 5^{th} force	Schiller, Hilico/Karr, Ubachs, Koelemeij – $HD^{(+)}$, $H_2^{(+)}$
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

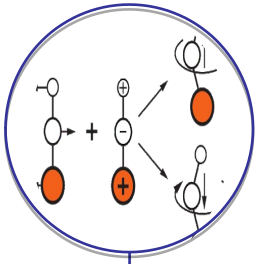
→ Require advanced manipulation techniques (already demonstrated in atomic physics):

control/cool internal & external degrees of freedom
individual internal **states addressability**
state-selective high **detection-sensitivity** and -rate
long **coherence times**
chemical stability…

Cold polyatomic molecules for fundamental physics…

Precision measurement of time-reversal symmetry violation with laser-cooled polyatomic molecules

Kozyryev & Hutzler, Phys Rev Lett (2017)



Electron EDM

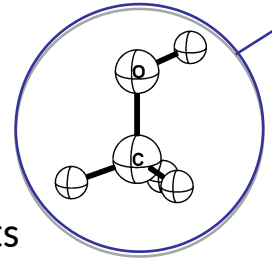
A new experiment to test the parity symmetry in cold chiral molecules using vibrational spectroscopy

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

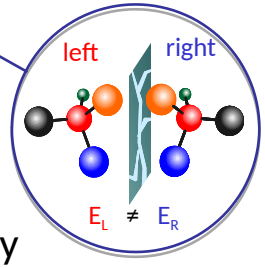
A stringent limit on a drifting proton-to-electron mass ratio from alcohol in the early universe

Bagdonaite *et al.*, Science (2013)

Tests of fundamental physics

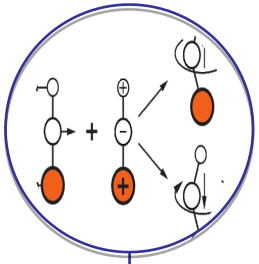


Drifting constants



Parity violation (PV)

Cold polyatomic molecules for fundamental physics…



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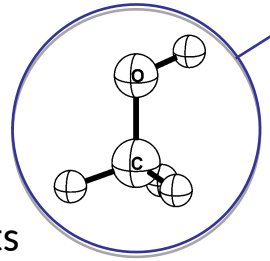

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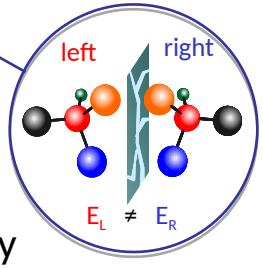

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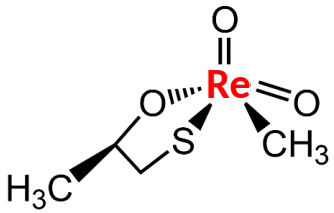
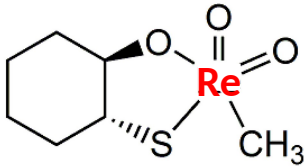
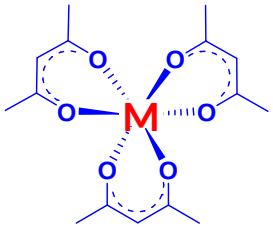
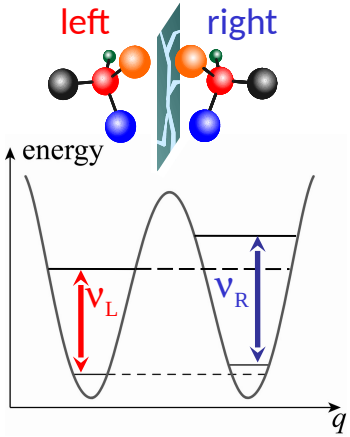




M: Ru, Ir, Os

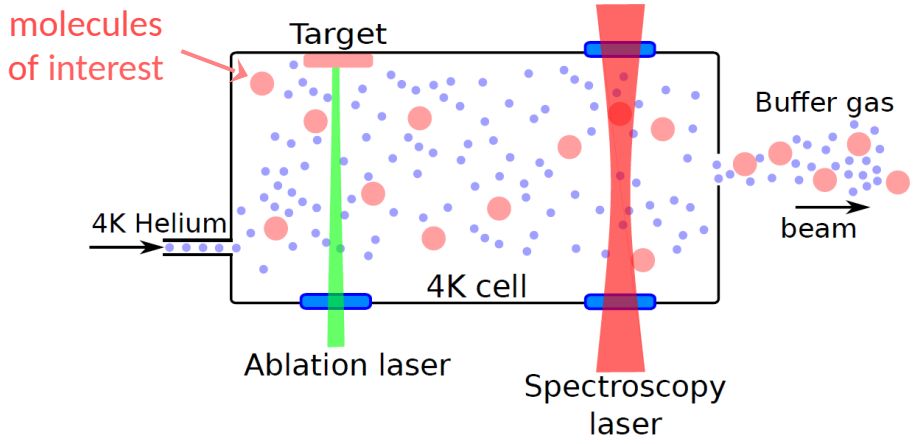


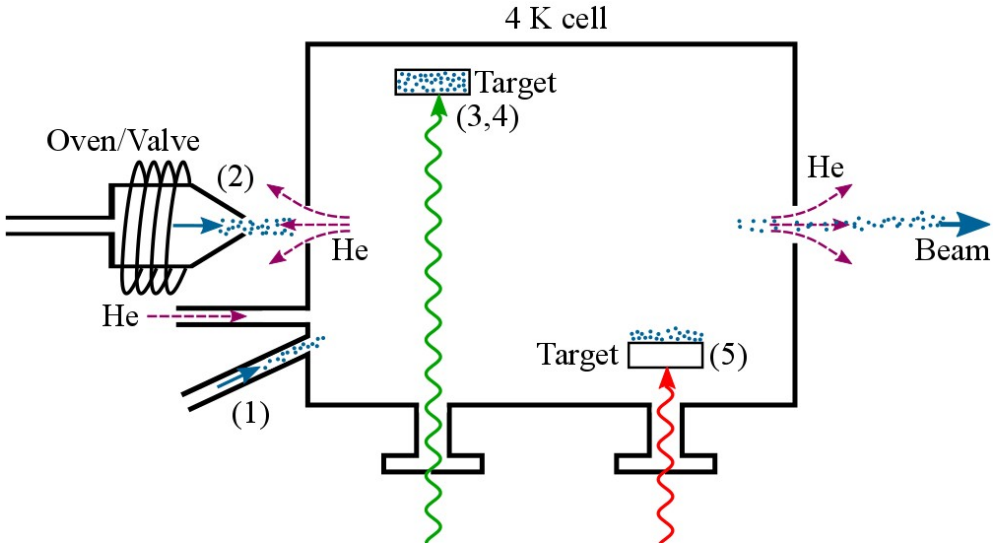


$\Delta\nu_{PV} = |\nu_L - \nu_R| \neq 0$

mHz to Hz

Buffer-gas cooling to ~K





1) Capillary loading
2) Beam loading
3) Laser ablation
4) Matrix-assisted desorption
5) Laser-induced acoustic desorption

well suited to solid state species

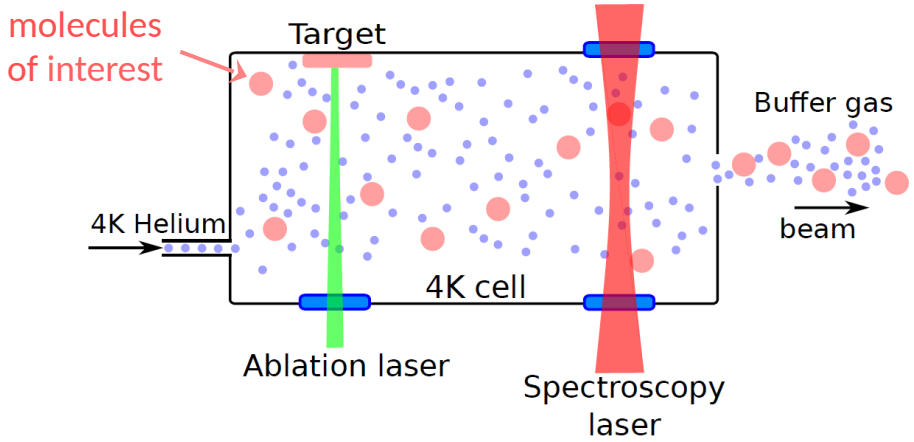
Buffer-gas cooling to ~K

Spectroscopy in the cell

narrower lines

stronger signals

simplified spectra



Buffer-gas-cooled molecular beams

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

collision-free

high flux (**supersonic x 10**) → more signal

low velocity (**supersonic / 10**) → better resolution

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

extend to new complex polyatomic species

Internationally advocated for precision measurements:
D. DeMille, De Natale, J. Doyle, M Tarbutt, D Patterson, G. Rempe, J. Ye,...
(crucial precursor step to **laser cooling** or trapping)

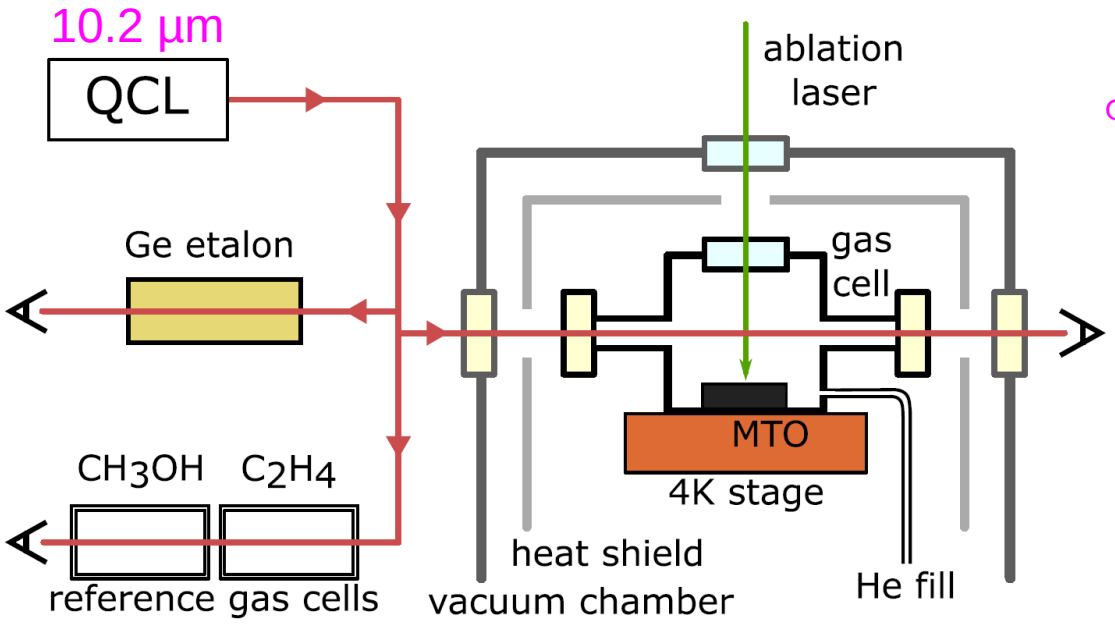
Buffer-gas cooling of MTO

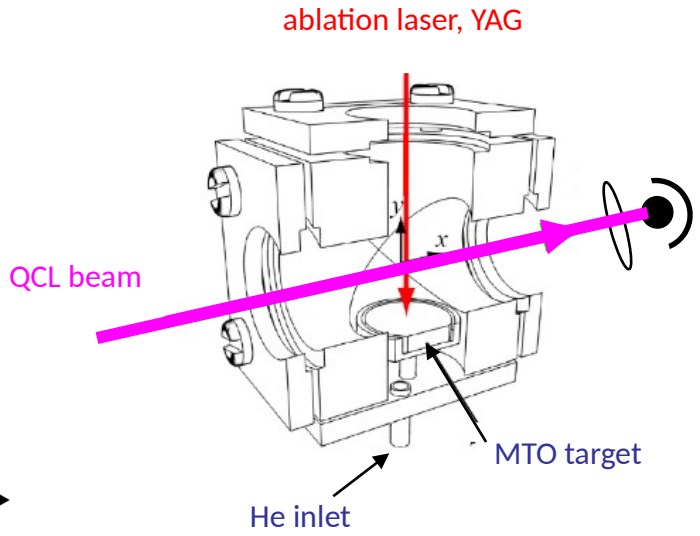
Imperial College London

Collaboration with Mike Tarbutt at Imperial College

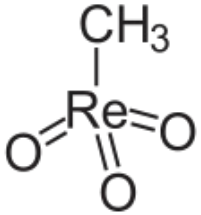
we've taken one of our QCL to London

tests in one of their cryogenic chamber





MTO:
methyltrioxorhenium



→ precursor of chiral candidate species for a **PV test**

→ ideal achiral test molecule

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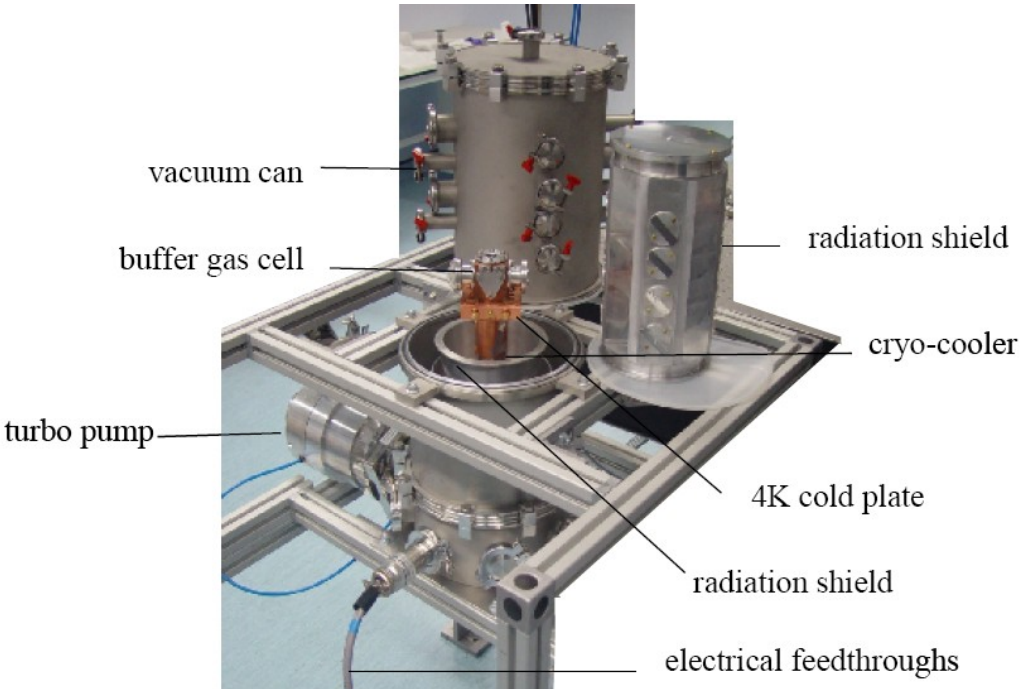

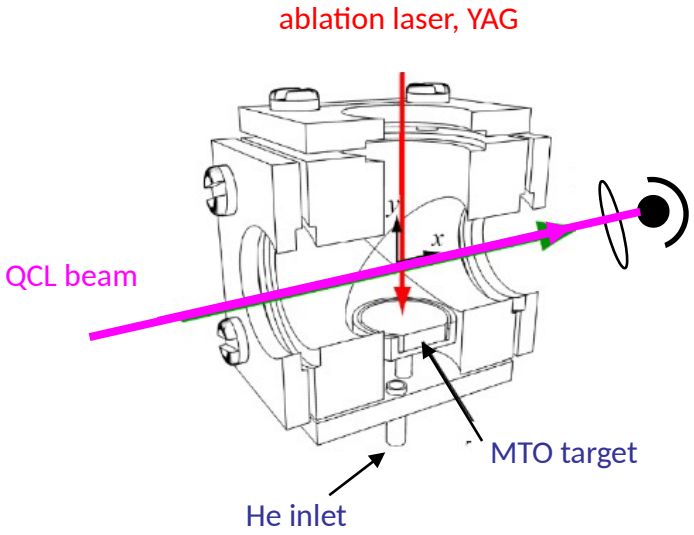

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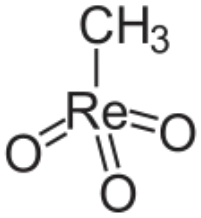

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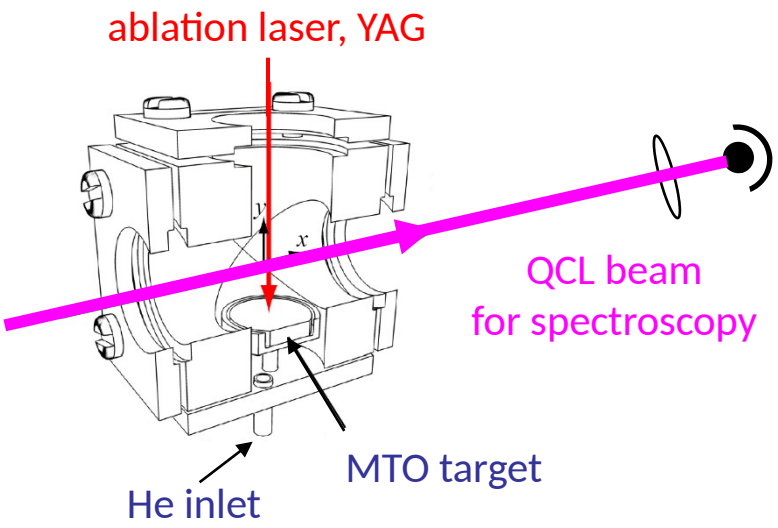
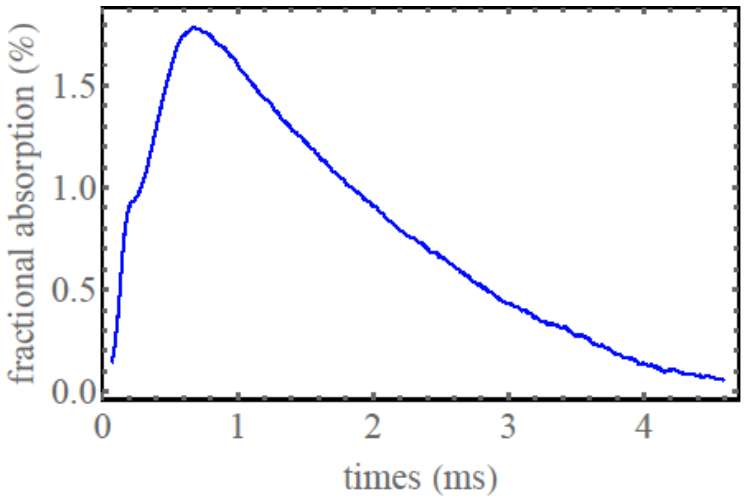
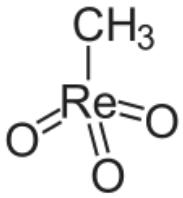
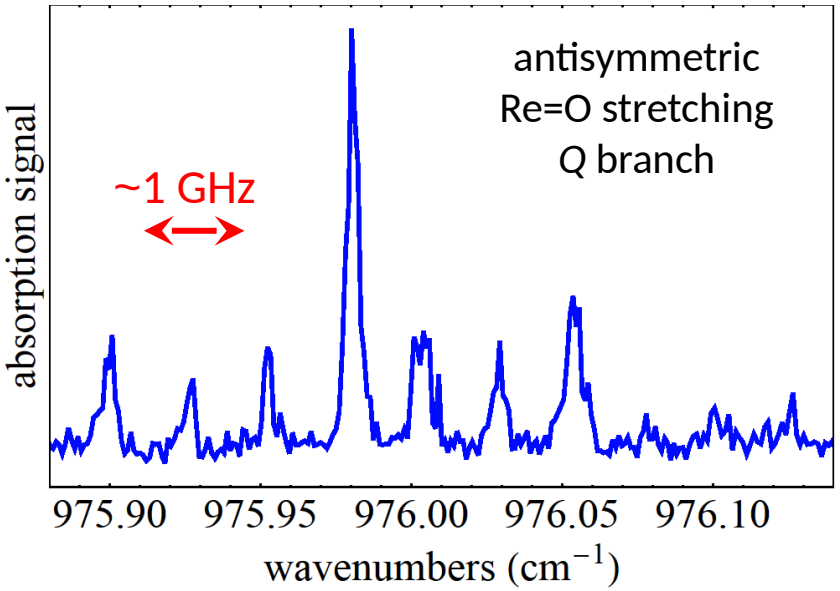


after one ablation pulse



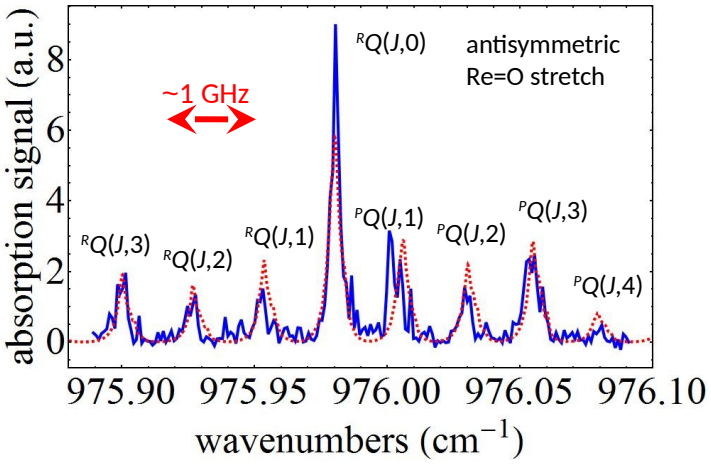


MTO spectrum

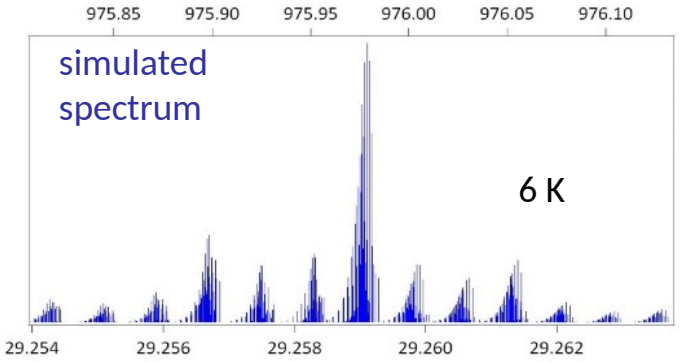


Tokunaga et al, *New J. Phys.* (2017)
Asselin et al, *Phys. Chem. Chem. Phys.* (2017)

Antisymmetric Re=O stretch of MTO



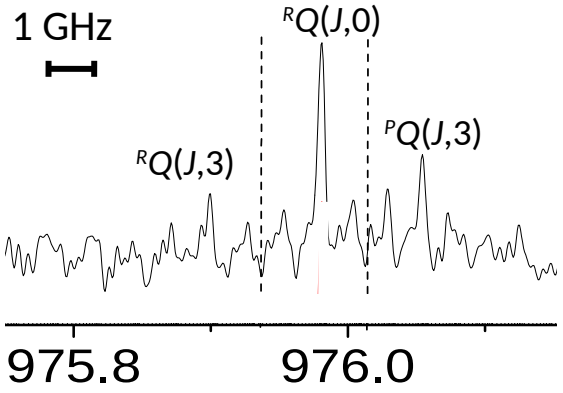
- 1st organo-metallic species buffer-gas-cooled
- survives laser ablation
- T_{rot} = 6 ± 3 K



8 MHz resolution (combination of frequency noise, Doppler and collisions)

A novel spectroscopic tool in itself

FTIR spectroscopy in a jet

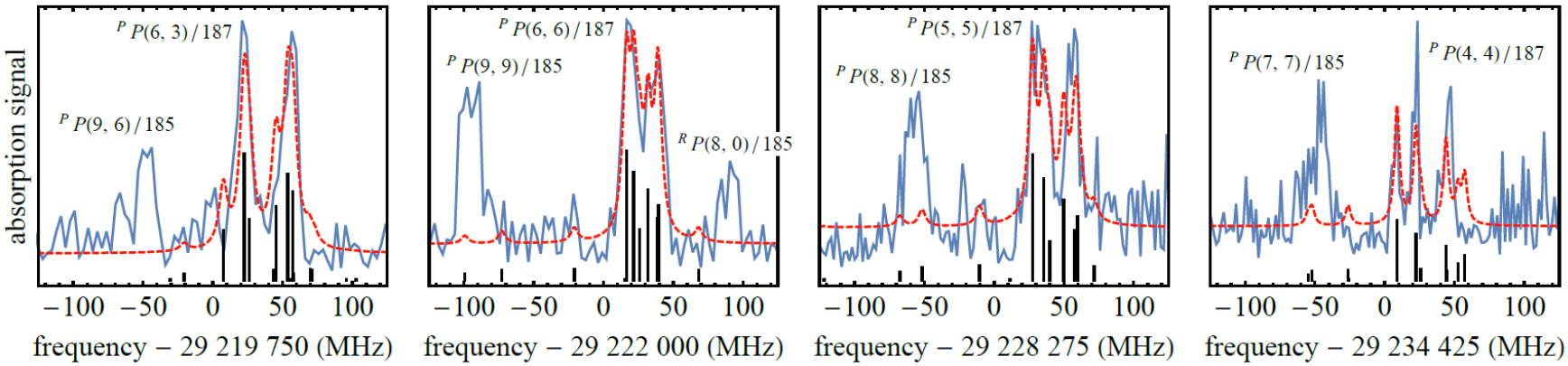


Tokunaga et al, *New J. Phys.* (2017)
Asselin et al, *Phys. Chem. Chem. Phys.* (2017)

Rotation and hyperfine-resolved spectroscopy

~8 MHz resolution, ~30 MHz accuracy → already allows for precision measurements:

Examples of $^{P}P(J,K)$ rovibrational transition of the ^{187}Re=O antisymetric stretching mode



experiment
fit
fitted hyperfine components

hyperfine structure partially resolved

→ fit to a symmetric top hyperfine hamiltonian

→ hyperfine parameters in the v = 1 excited state

quadrupole coupling constant: eQq^{exc} = 716 (3) MHz
ΔeQq << 1 → little variation with vibration

→ unprecedented for such a complex molecule

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

Buffer-gas cooling of trioxane

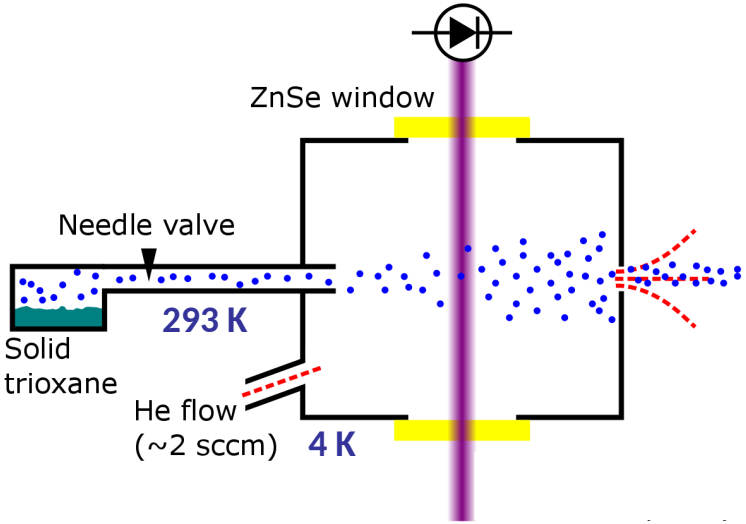
potential sources of formaldehyde in cometary comae
→ relevant prebiotic chemistry

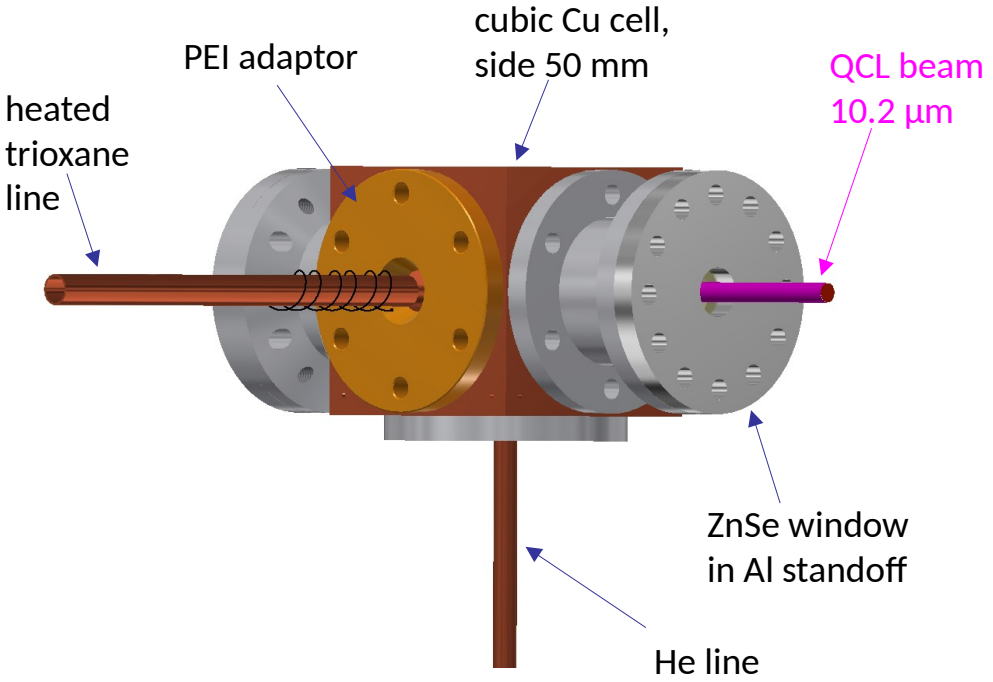
solid at room temperature, with high vapour pressure (4 mbar)
→ **can be loaded directly into the cell**

toward beam production

trioxane:

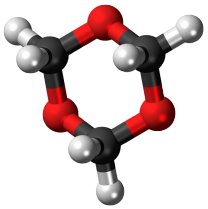
$(CH_2O)_3$ – 12 atoms

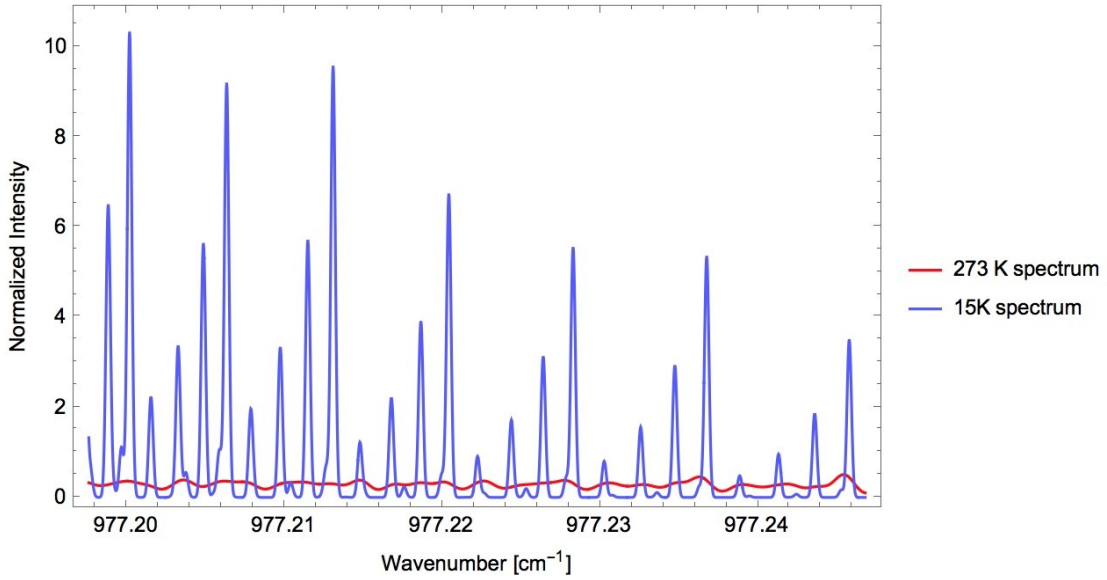




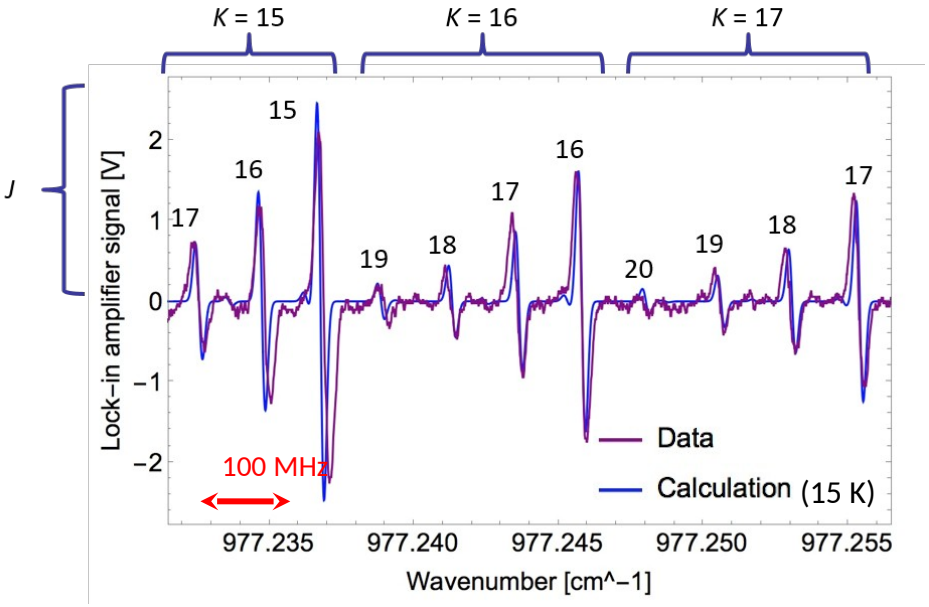
ν_5 vibrational mode around 977 cm^{-1} → probed using the QCL

1,3,5-trioxane: Q branch of the ν_5 band





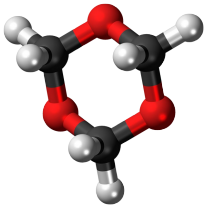
$\Delta J = 0$
$\Delta K = 0$

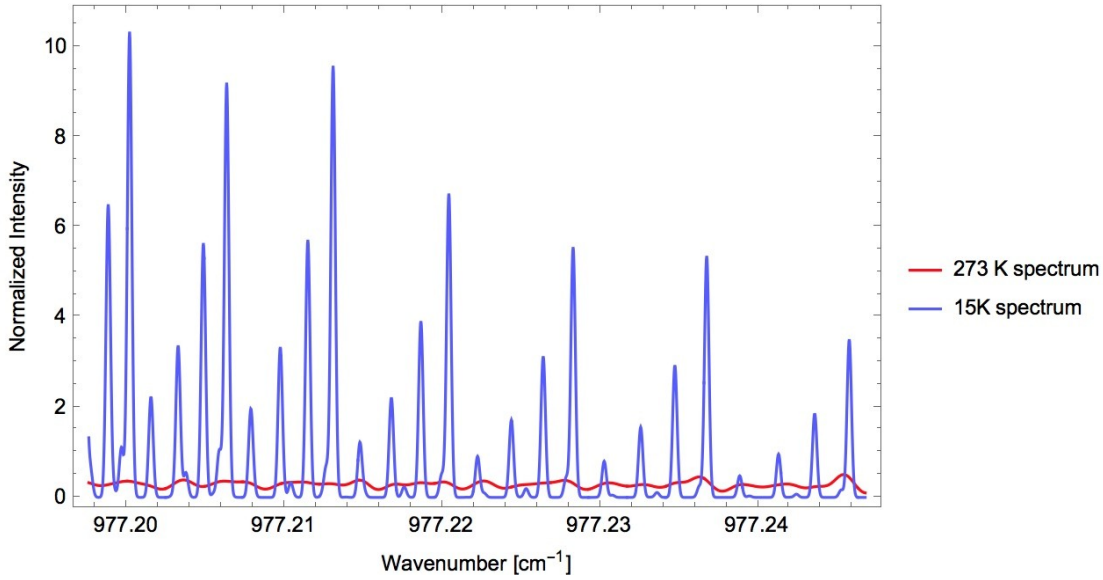


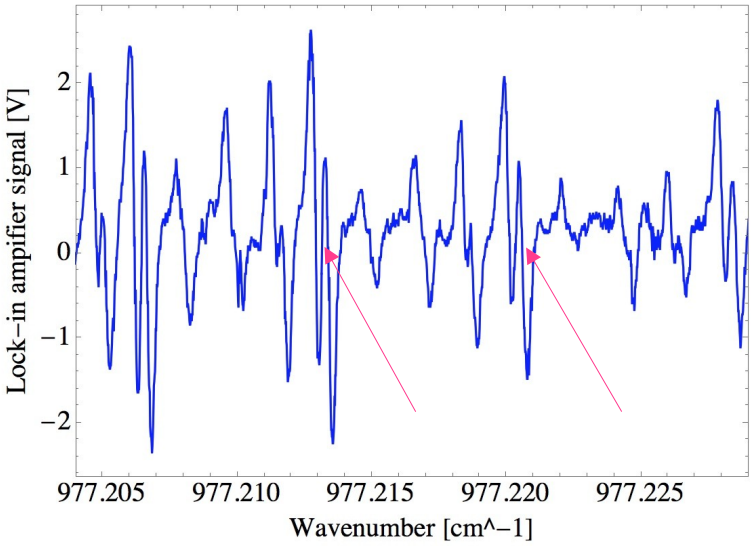
Linear absorption spectroscopy

- frequency modulation, harmonic 1
- T < 15 K
- 7.5 MHz resolution (combination of frequency noise, Doppler and collisions)

1,3,5-trioxane: Q branch of the ν_5 band





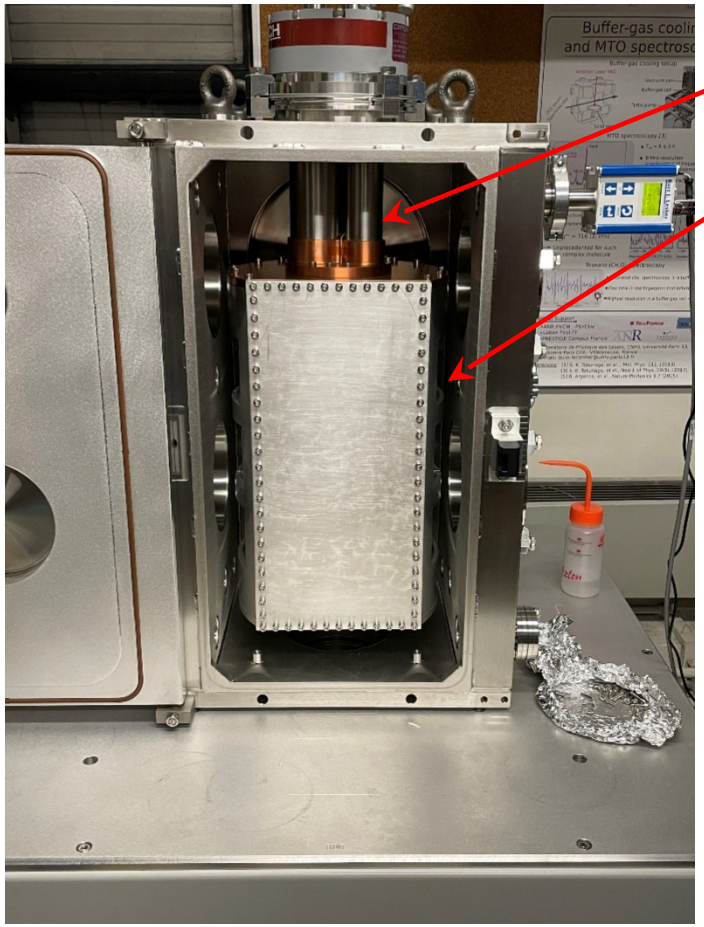


Saturated absorption spectroscopy

- first time in the **fingerprint** mid-infrared region
- Sub-Doppler resolution (<1MHz) in buffer-gas cell

largest species for which saturated abs. spectroscopy has been demonstrated

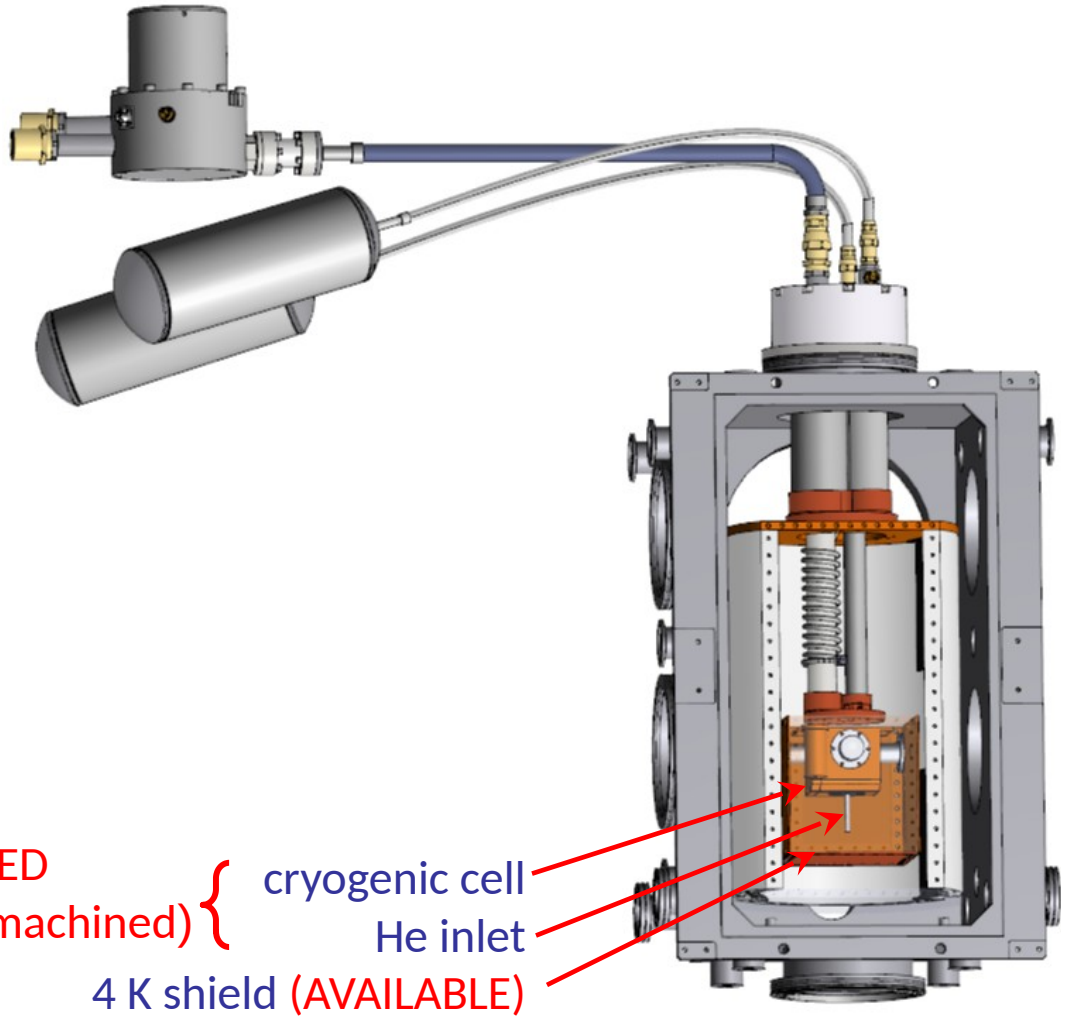
3rd generation setup under construction at LPL



cryocooler

40 K shield

IN PLACE



TO BE INTEGRATED
(already designed and machined)

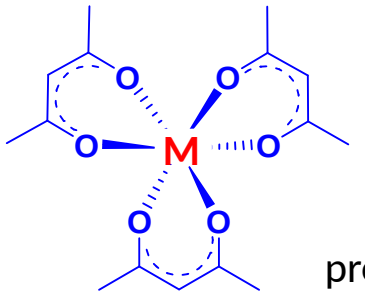
cryogenic cell

He inlet

4 K shield (AVAILABLE)

Outlook

Buffer-gas cooling of **chiral species** of interest for a **PV test**:



Δ- **M**(acac)$_3$

M: Ru, Ir, Os,...

propeller-like topology

Ru: $\Delta\nu_{PV}$ ~ 100 mHz (10^{-15})

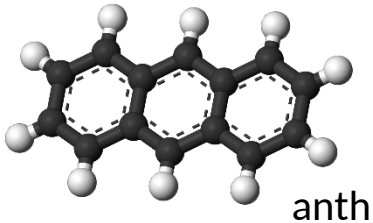
Os: $\Delta\nu_{PV}$ ~ 1 Hz (10^{-14})

intense C-O stretch @ 6.5 µm

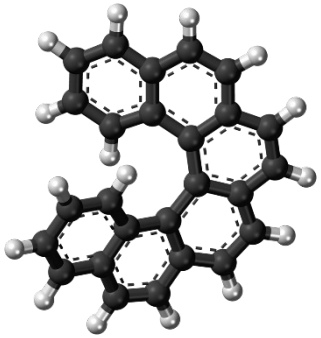
Fiechter et al, *arXiv* (2021)

Buffer-gas cooling of new polyatomic species of **atmospheric/astrophysical interest**:

Polyaromatic hydrocarbons (PAHs) and related species



anthracene



helicene

Demonstration of **buffer-gas-cooled molecular beams**

Doppler spectroscopy with free-running QCLs

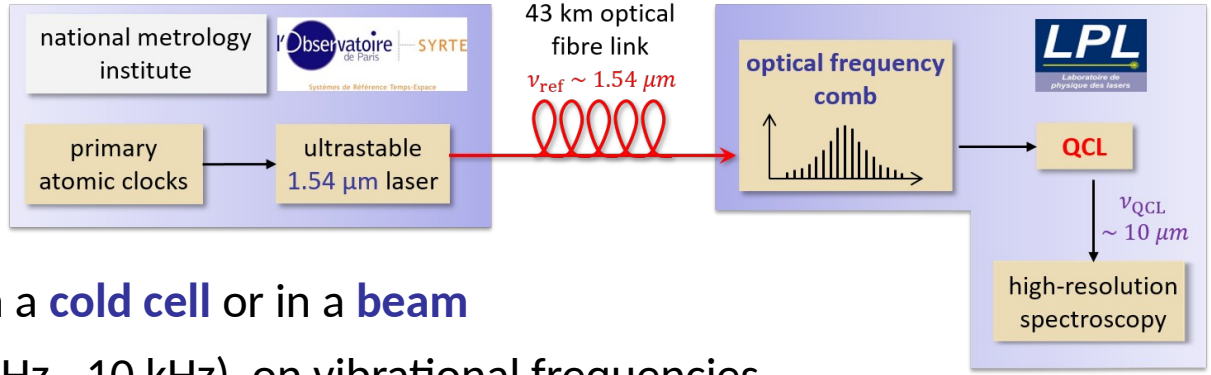
Outlook

Precise spectroscopic measurements:

⇒ using the **sub-Hz metrology-grade QCLs** available in the lab

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

10 µm, 6.4 µm, 17 µm…

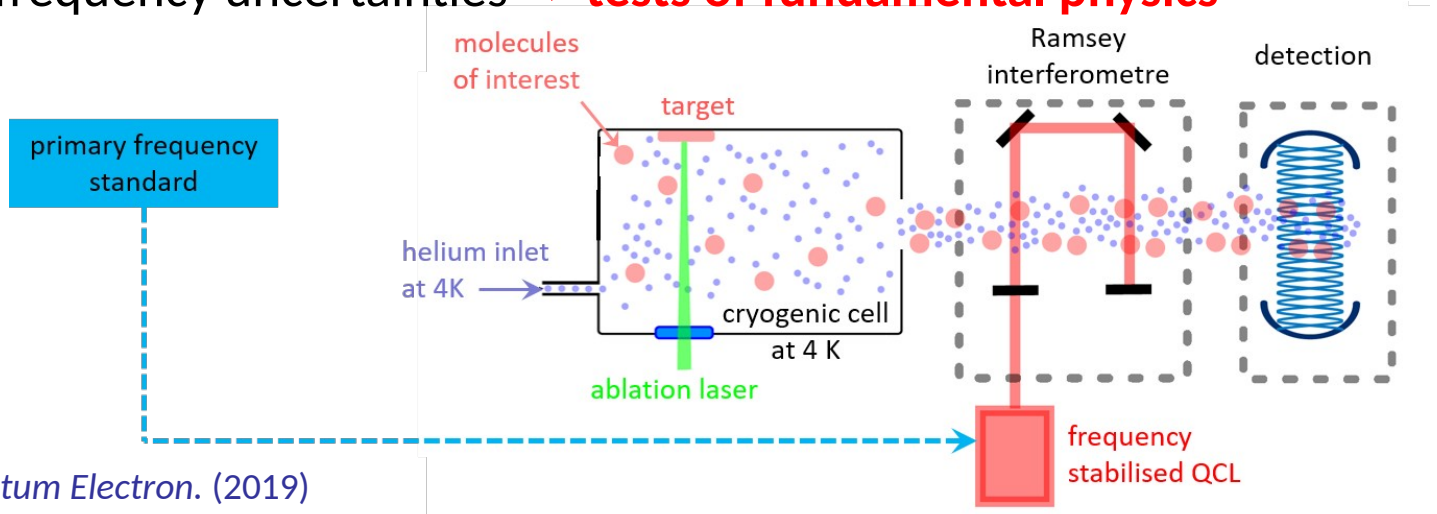


⇒ **sub-Doppler** spectroscopy in a **cold cell** or in a **beam**

⇒ **10^{-10} - 10^{-12} uncertainty** (100 Hz - 10 kHz) on vibrational frequencies

⇒ enriching **molecular databases**

- Build **Ramsey interferometry** machine for reaching record **10^{-15} (sub-Hz)** vibrational frequency uncertainties **=> tests of fundamental physics**



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

People involved

@LPL
M. Saffre (PhD student)
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former membres
A. Cournol (postdoc)
S.K. Tokunaga

Imperial College London
B. Sauer
M.R. Tarbutt

former membres
J. Bieniewska (PhD student)
R. Hendricks (postdoc)
T. Wall (postdoc)

Sponsors