New perspectives on the search for a parity non-conservation effect in chiral molecules

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October, 4th 2011

Introduction: parity, a broken symmetry

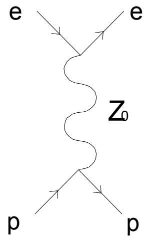
Parity operation: $(x, y, z) \xrightarrow{\mathbf{P}} (-x, -y, -z)$

1956 : **Lee and Yang** – Prediction of parity non-conservation by weak interaction in the K meson decay

1957 : **Wu et al.** – 1st experimental observation in β decay of the cobalt nucleus $^{60}\mathrm{Co} \longrightarrow {}^{60}\mathrm{Ni} + \bar{\nu} + e^-$

1967 : **Weinberg, Glashow and Salam** – electro-weak theory

1973 : **CERN** – observation of neutral currents



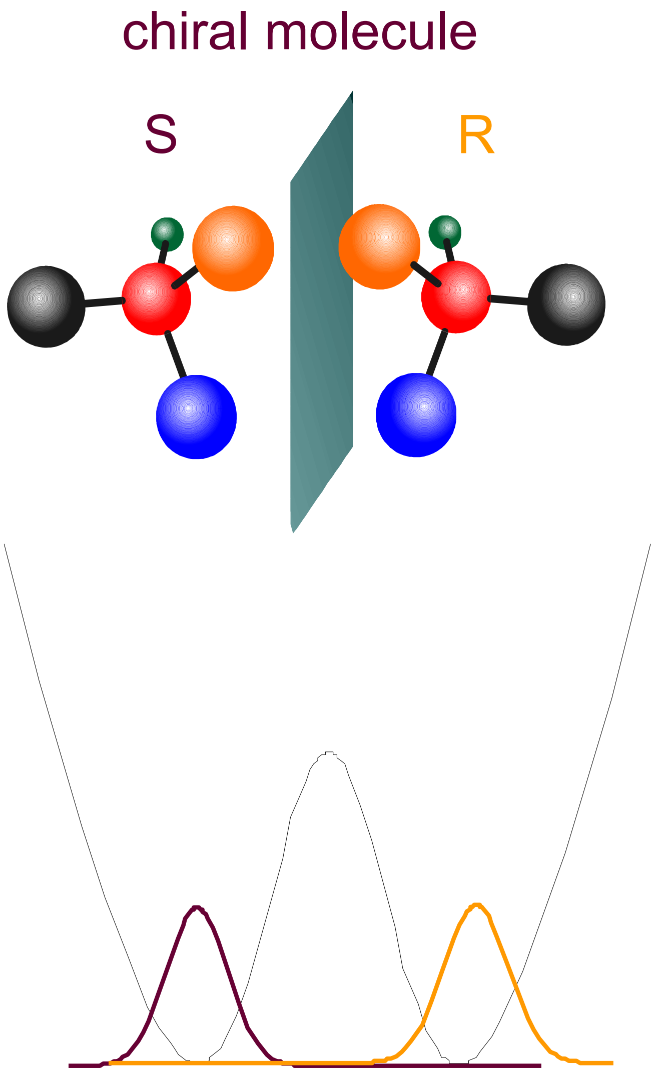
✓ major ingredient of the standard model of particle physics

✓ belongs to the high energy physics world?

Z^0 boson mass:

91 GeV or 10^{16} J mol^{-1} or 10^{25} Hz or 10^{15} cm^{-1}

Introduction: parity violation in chiral molecules

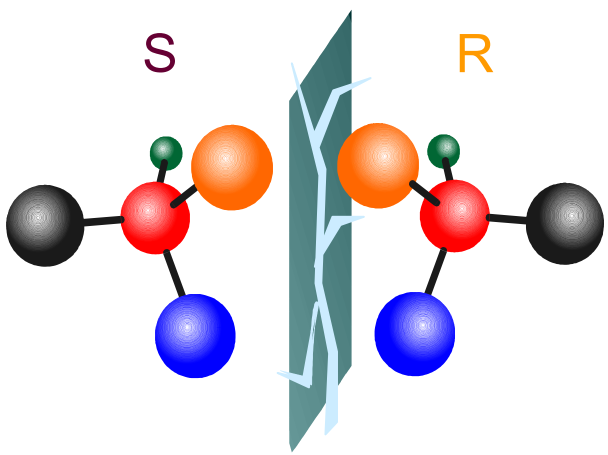


when parity is conserved

R ↔ S: $\Delta_r H_0 = 0$

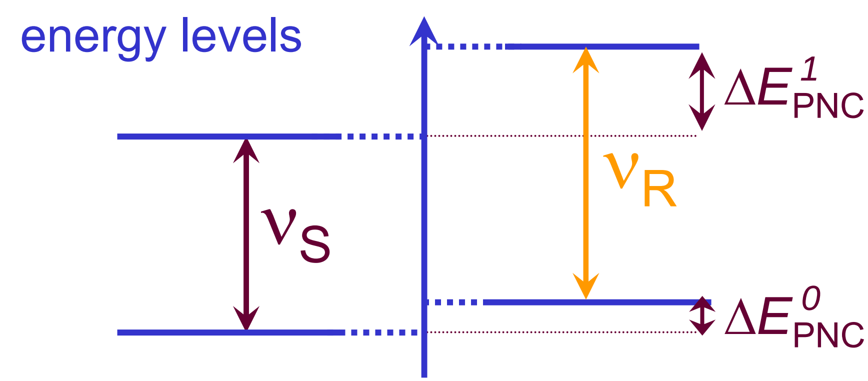
Introduction: parity violation in chiral molecules

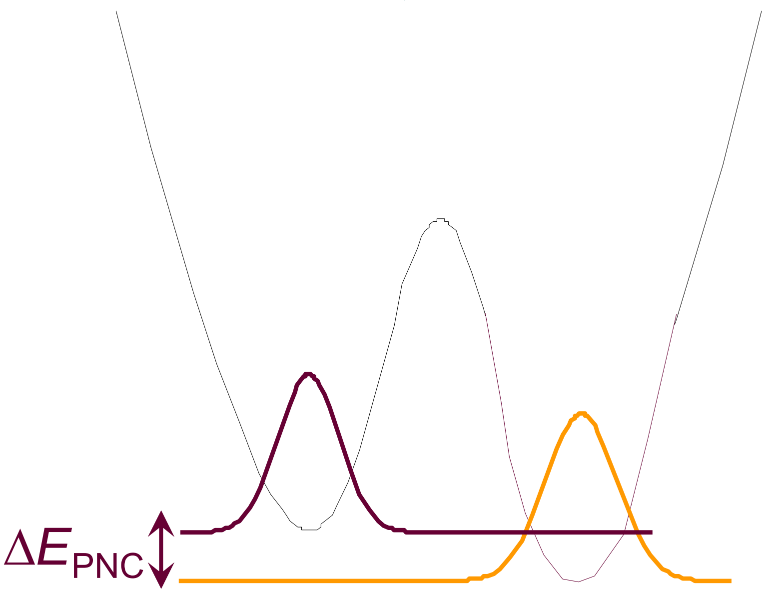
Rein, *J. Mol. Evol.* (1974); Letokhov, *Phys. Lett.* (1975)



weak interaction ⇒ parity not conserved

- R ↔ S: $\Delta_r H_0 = \Delta E_{PNC} \, N_A \neq 0$
- $\Delta_r H_0 \sim 10^{-11}$ J mol^{-1}
- $\Delta E_{PNC} \sim 100$ aeV ~ 100 mHz



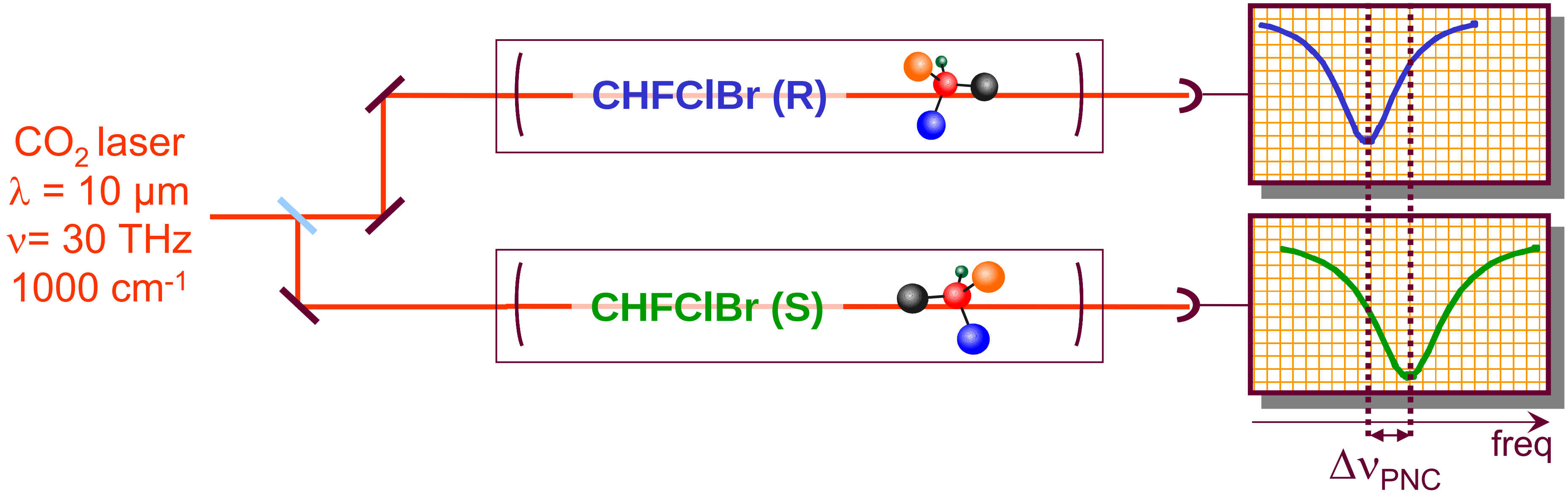


$\Delta\nu_{PNC} = | \nu_S - \nu_R | \neq 0$

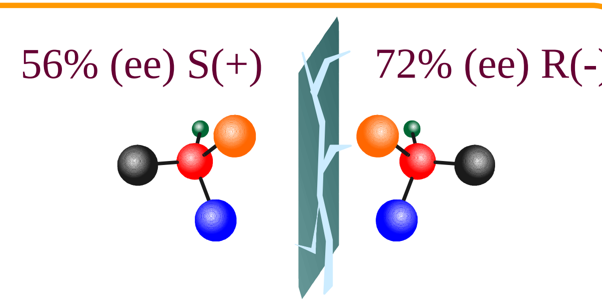
- from ~ mHz to ~ Hz
- from ~ aeV to ~ feV (10^{-18} à 10^{-15} eV)
- from ~ 10^{-13} to ~ 10^{-10} J mol^{-1}

A first attempt on CHFClBr

Daussy et al, *Phys. Rev. Lett.* (1999); Ziskind et al, *Euro. Phys. J. D* (2002)



A. Collet et J. Crassous (1998-2000)



Costante et al, *Angew Chem Int Ed Engl* (1997)
Costante-Crassous et al, *J. Am. Chem. Soc.* (1997)

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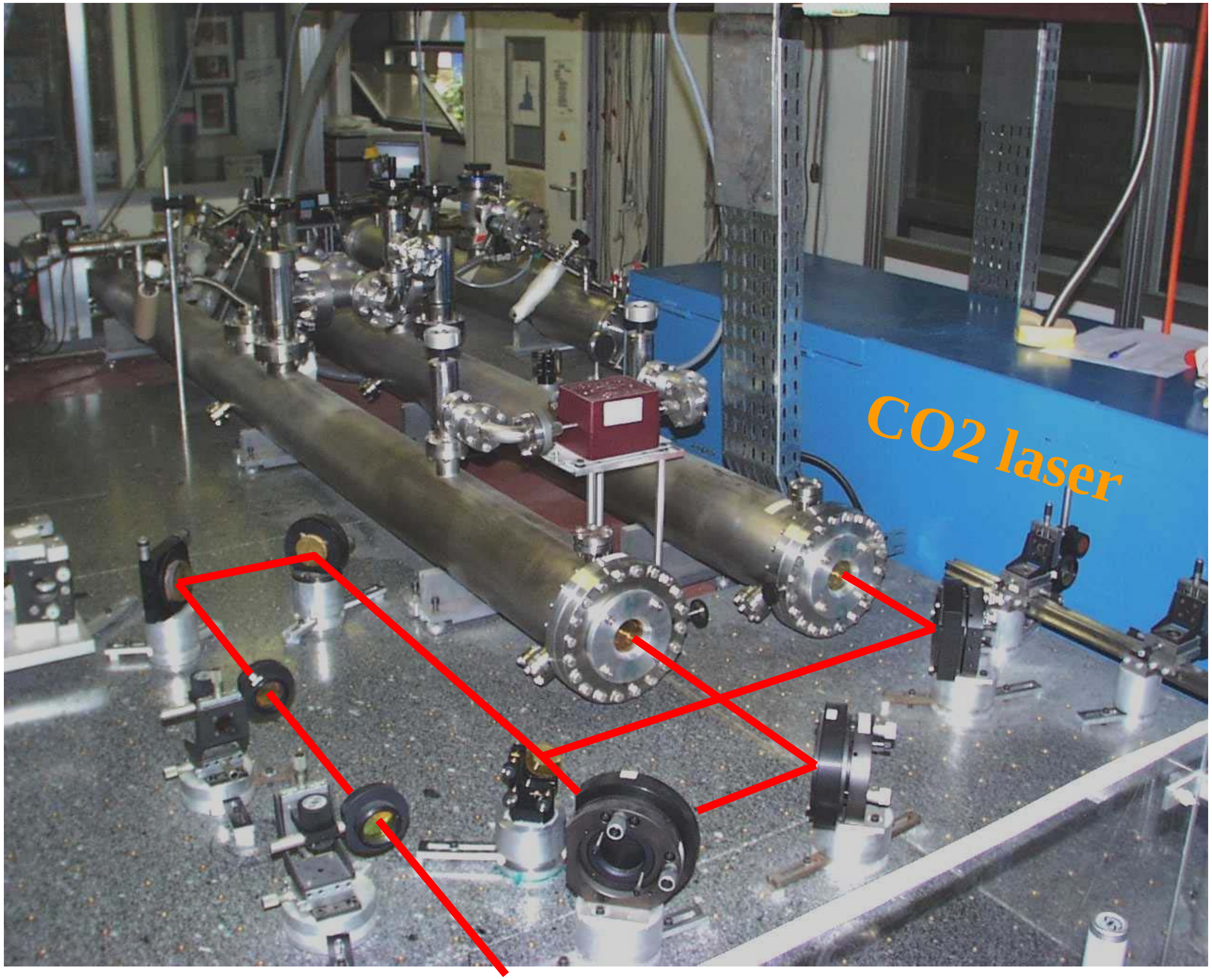

A first attempt on CHFClBr

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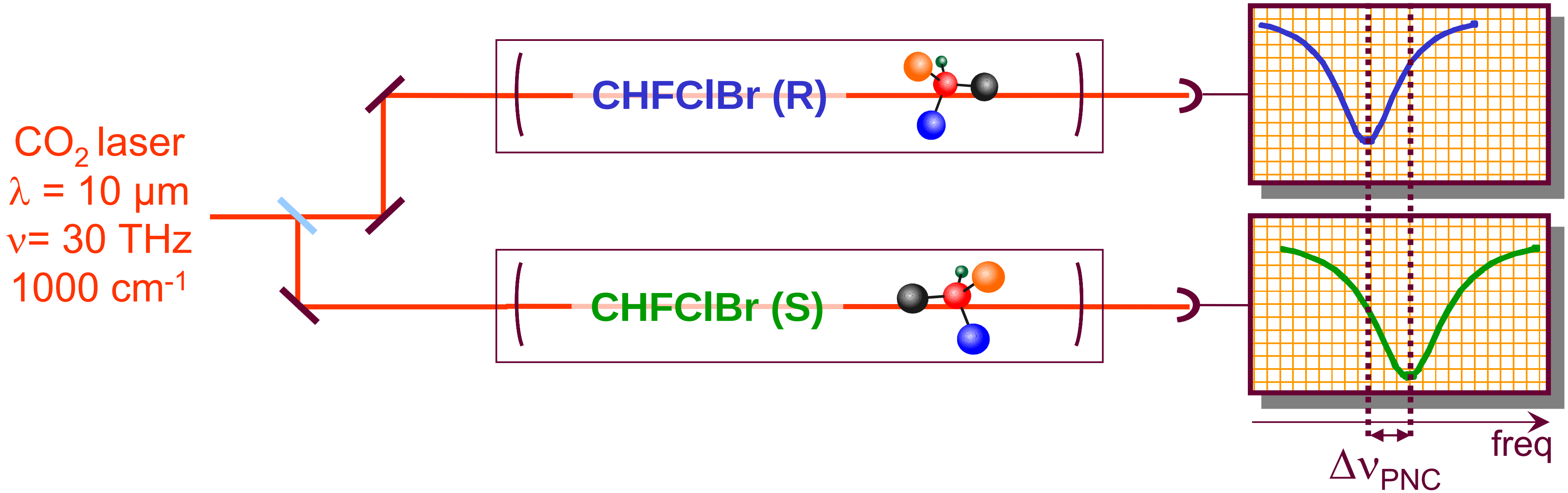


- ✓ saturated absorption spectra – line width ~ 60 kHz
- ✓ measure the frequency difference between the 2 line centers
- ✓ sensitivity: ~ 8 Hz or $2{,}5\times10^{-13}$ in fractional value

result $\Rightarrow$

$$\Delta\nu_{PNC} \leq 8 \text{ Hz}$$

$$\Delta\nu_{PNC}/\nu \leq 2{,}5\times10^{-13}$$

What to do next ?

Limits of the previous test

✓ sensitivity limited by collisions

✓ line width ~ 60 kHz (2×10^{-6} cm^{-1})

✓ calculated shift for CHFClBr:

$\Delta\nu_{NCP}$ = 2.4 mHz (8×10^{-17})

(exp sensitivity 8 Hz)

Schwerdtfeger et al, *Phys. Rev. A* (2002)
Schwerdtfeger et al, *Phys. Rev. A* (2005)

Possible improvements

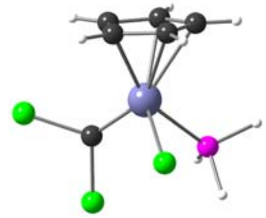
✓ supersonic jet spectroscopy: no collisions (+ cold molecules)

✓ Ramsey fringes spectroscopy (matter-wave interferometer): line width ~ 100Hz (3×10^{-9} cm^{-1})

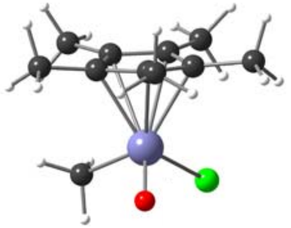
✓ more favorable new molecules: organo-metallic complexes

$\Delta\nu_{NCP}$ ~ 1 Hz (5×10^{-14})

$Os(\eta_5\text{-}C_5H_5)(=CCl_2)Cl(PH_3)$

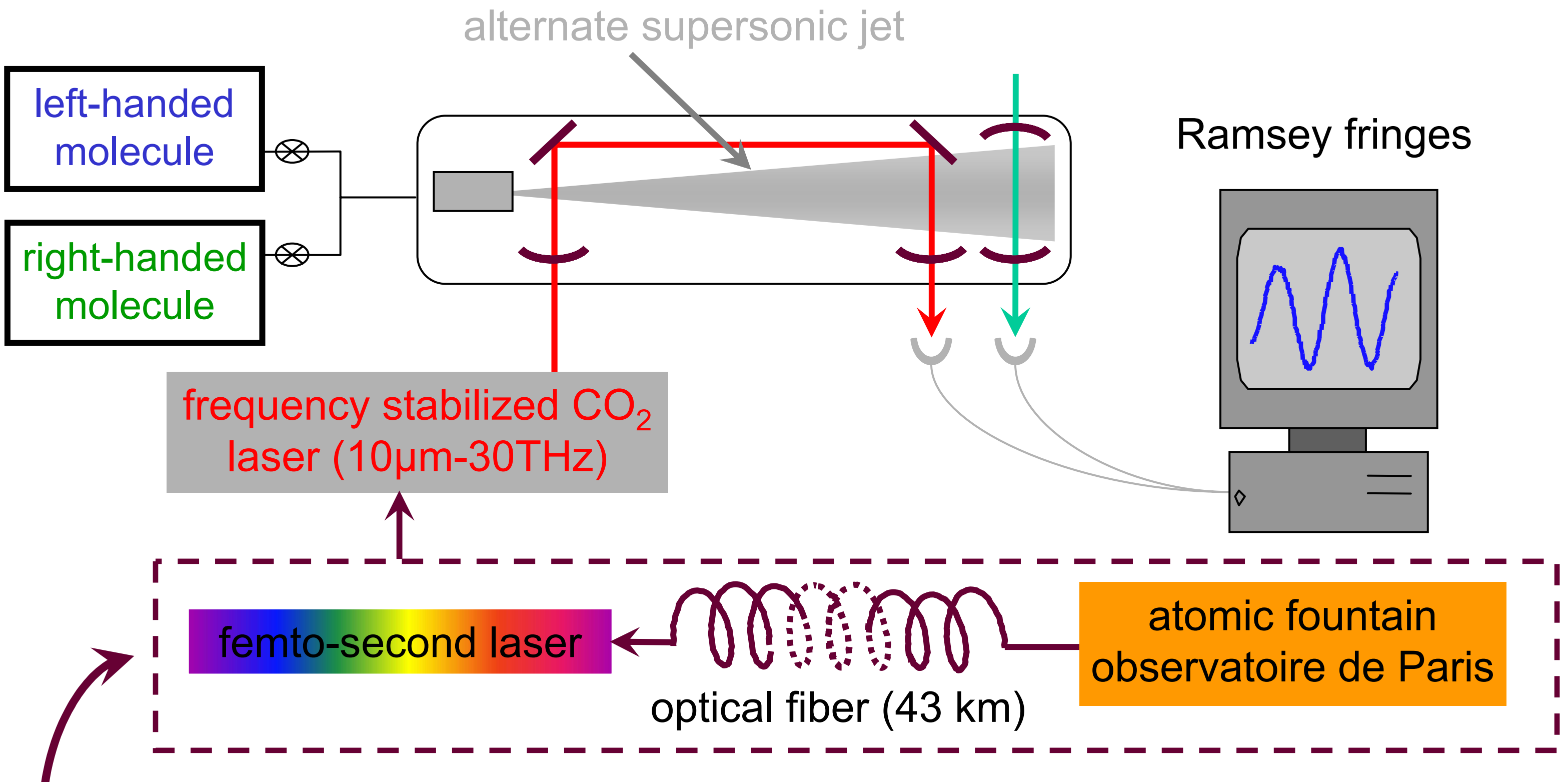


$Re(\eta_5\text{-}Cp^*)(=O)(CH_3)Cl$



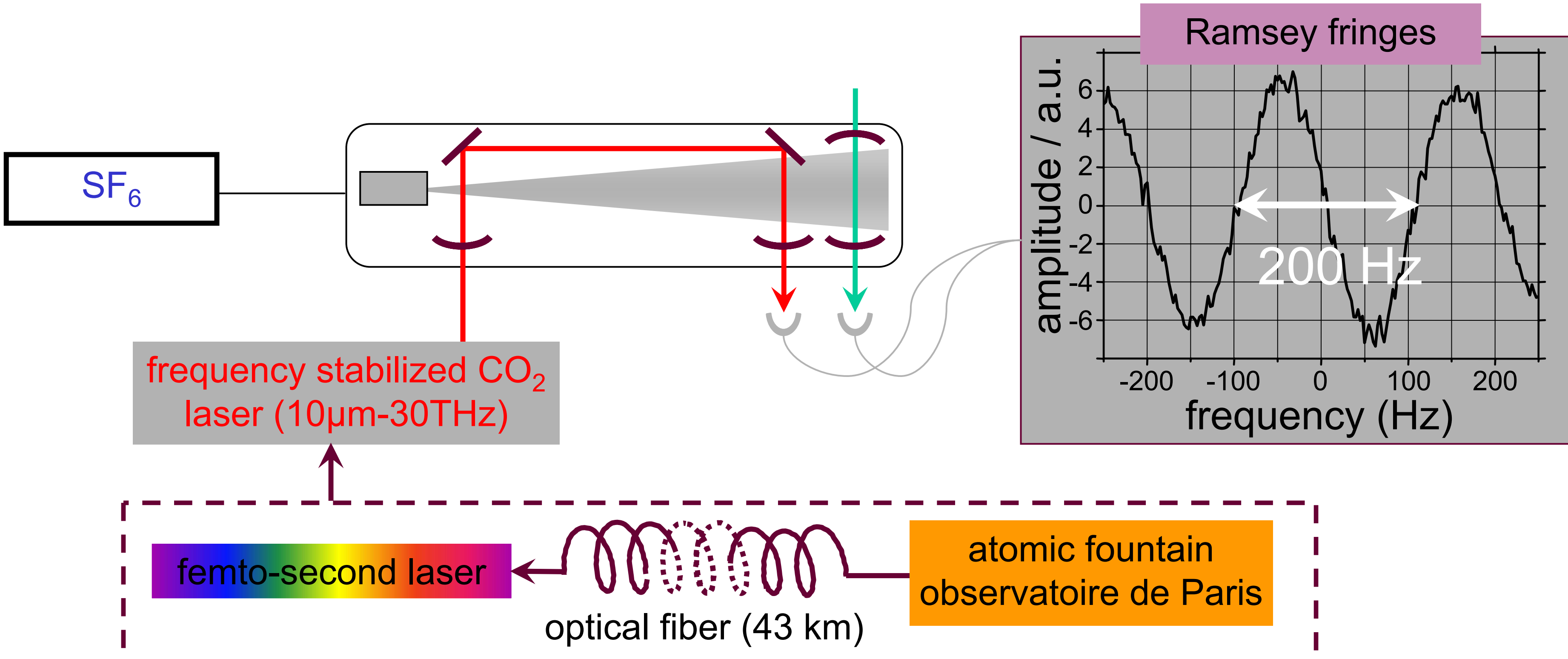
Schwerdtfeger and Bast, *J. Am. Chem. Soc.* (2004)
De Montigny, *Phys. Chem. Chem. Phys.* (2010)

New experimental set-up



- ✓ alternate (right/left) supersonic jet ⇒ cancel out systematics
- ✓ control of the absolute CO_2 laser frequency

“New” experimental set-up



Works with SF_6 already!

sensitivity on the line center pointing: ~ 0,6 Hz soit 2×10^{-14}

$\Rightarrow$ expected sensitivity for a differential measurement: < 0.1 Hz soit ~ 10^{-15}

Shelkovnikov et al, *Phys. Rev. Lett.* (2008)

Requirements for the candidate molecule ?

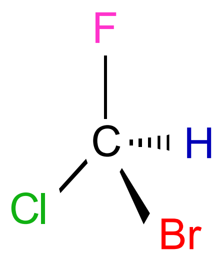
- ✓ show a large PNC shift $\Delta\nu_{PNC}$;
- ✓ be available in large ee, ideally in enantiopure form;
- ✓ allow the production of a supersonic expansion;
- ✓ be available at gram-scale;
- ✓ as "simple" as possible (experimental sensitivity depends on the partition function);
- ✓ avoid nuclei with a quadrupole moment to avoid large hyperfine structure;
- ✓ have an intense band within the CO_2 laser operating range (850–1120 cm^{-1})
- ✓ have a suitable 2-photon transition (joining a v = 0 and a v = 2 level).

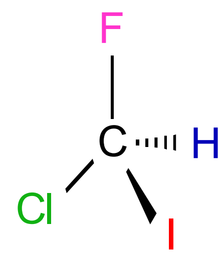
Molecules considered for a new PV test

J. Crassous, L. Guy, T. Saue, R. Bast, P. Schwerdtfeger

<u>methane chiral derivatives :</u> liquid phase

$\Delta\nu_{NCP}$ = 2.4 mHz
C-F stretching





$\Delta\nu_{NCP}$ = 24 mHz
C-F stretching

⇒ too weak PNC shift!

⇒ low stability (iodinated compounds)

⇒ synthesis in enantiopure form and gram quantity is difficult

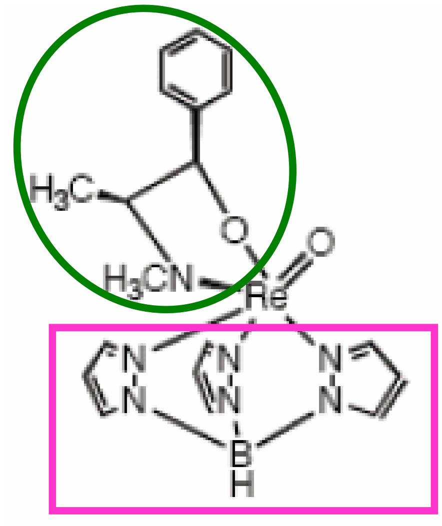
Crassous et al, *J. Phys. Chem. A* (2003)
Jiang et al, *Chirality* (2005)
Soulard et al, *Phys. Chem. Chem. Phys*. (2006)

Schwerdtfeger et al, *Phys. Rev. A* (2002)
Schwerdtfeger et al, *Phys. Rev. A* (2005)

Molecules considered for a new PV test

J. Crassous, L. Guy, T. Saue, R. Bast, P. Schwerdtfeger

Tp ligand-based oxorhenium complexes: solid phase



Tp(Re=O)Ephe

⇒ calculation of the PNC shift complicated

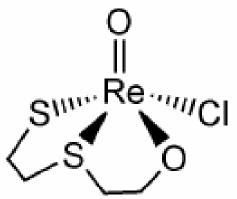
⇒ not suitable for molecular beam experiment (too high sublimation temperature, >250°C)

Lassen et al, *Inorg. Chem.* (2006)

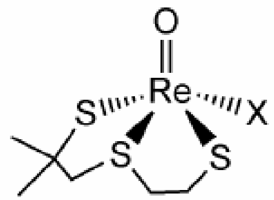
Molecules considered for a new PV test

J. Crassous, L. Guy, T. Saue, R. Bast, P. Schwerdtfeger

<u>Sulfur ligand-based oxorhenium complexes:</u> solid phase

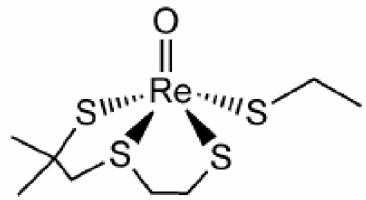


SPY-5-42-*C*-**2**

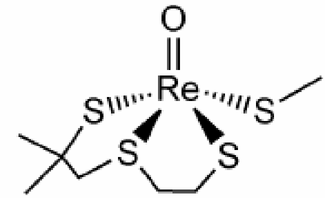


X = Cl : SPY-5-52-*C*-**3**

X = I : SPY-5-52-*C*-**4**



SPY-5-54-*C*-**5**



SPY-5-54-*C*-**5b**

	PNC shift (Hz)	
Compound	HF	B3LYP
2	−2.056	−0.206
3	+0.168	+0.064
4	+0.157	+0.069
5	−1.585	−0.102
5b	−1.021	−0.084

compounds **4** and **5** synthesized and separated

$\Delta\nu_{NCP}$ = ~ 0.1 to 1 Hz

Re=0 stretching

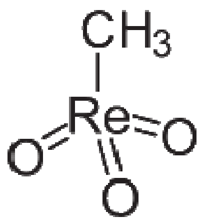
$\Rightarrow$ not suitable for molecular beam experiment, decompose upon heating

De Montigny et al, *Chem. Comm.* 4841 (2009); De Montigny, *Phys. Chem. Chem. Phys.* (2010)

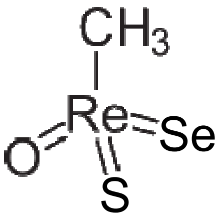
New approach

J. Crassous, L. Guy, T. Saue, R. Bast, P. Schwerdtfeger

methyltrioxorhenium (MTO)



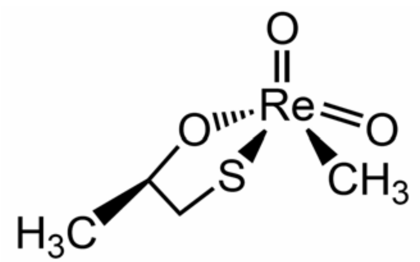
- ✓ sufficiently low sublimation temperature (< 100°C)
- ✓ calculated PNC shift large enough for some chiral derivatives:



$\Delta\nu_{PNC}$ ~ 400 mHz

Re=0 stretching

⇒ synthesis and separation of chiral derivatives under progress



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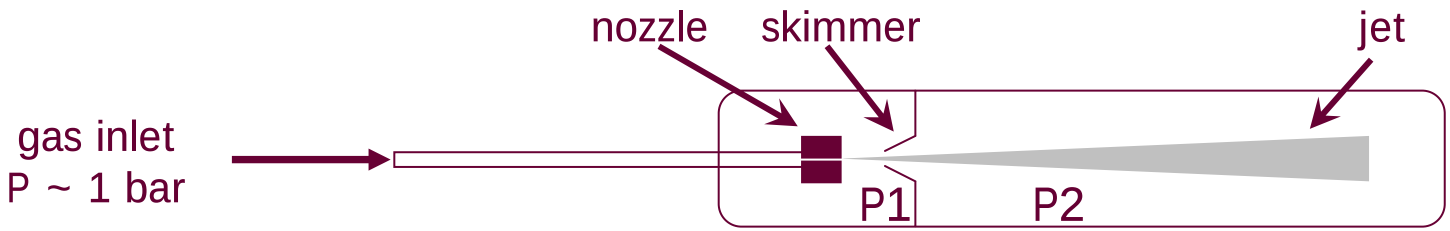
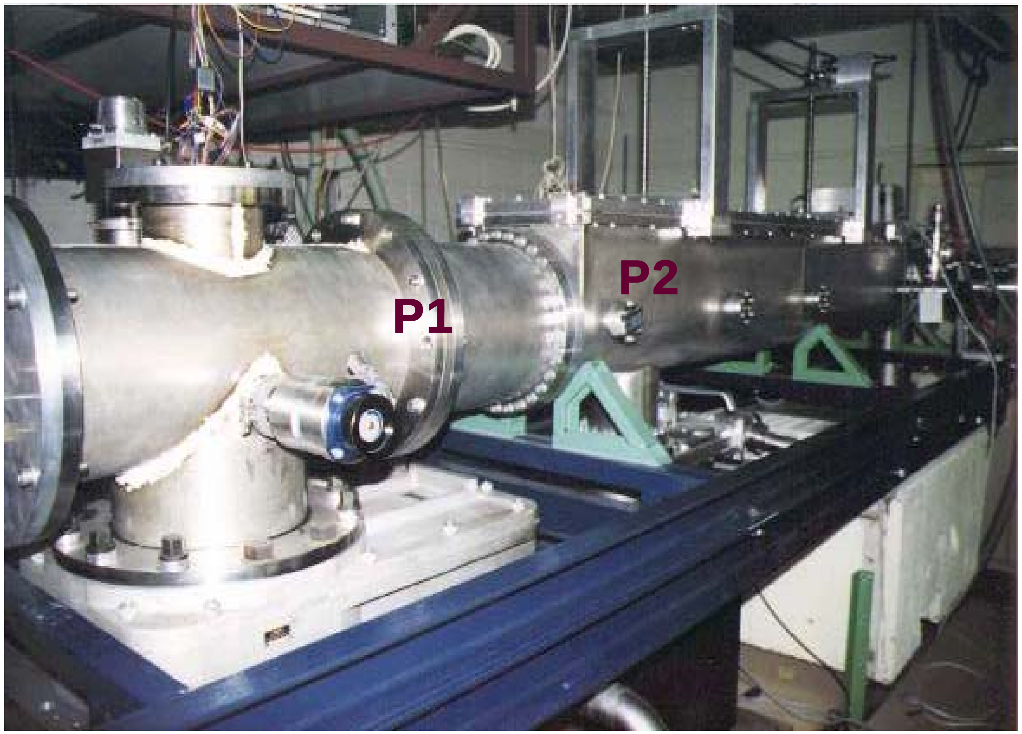
Darquié et al, *Chirality* (2010)

Experimental set-up

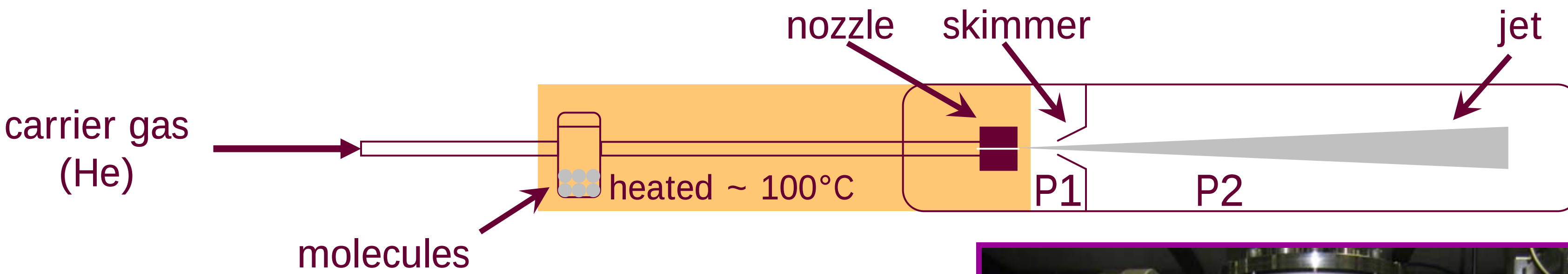


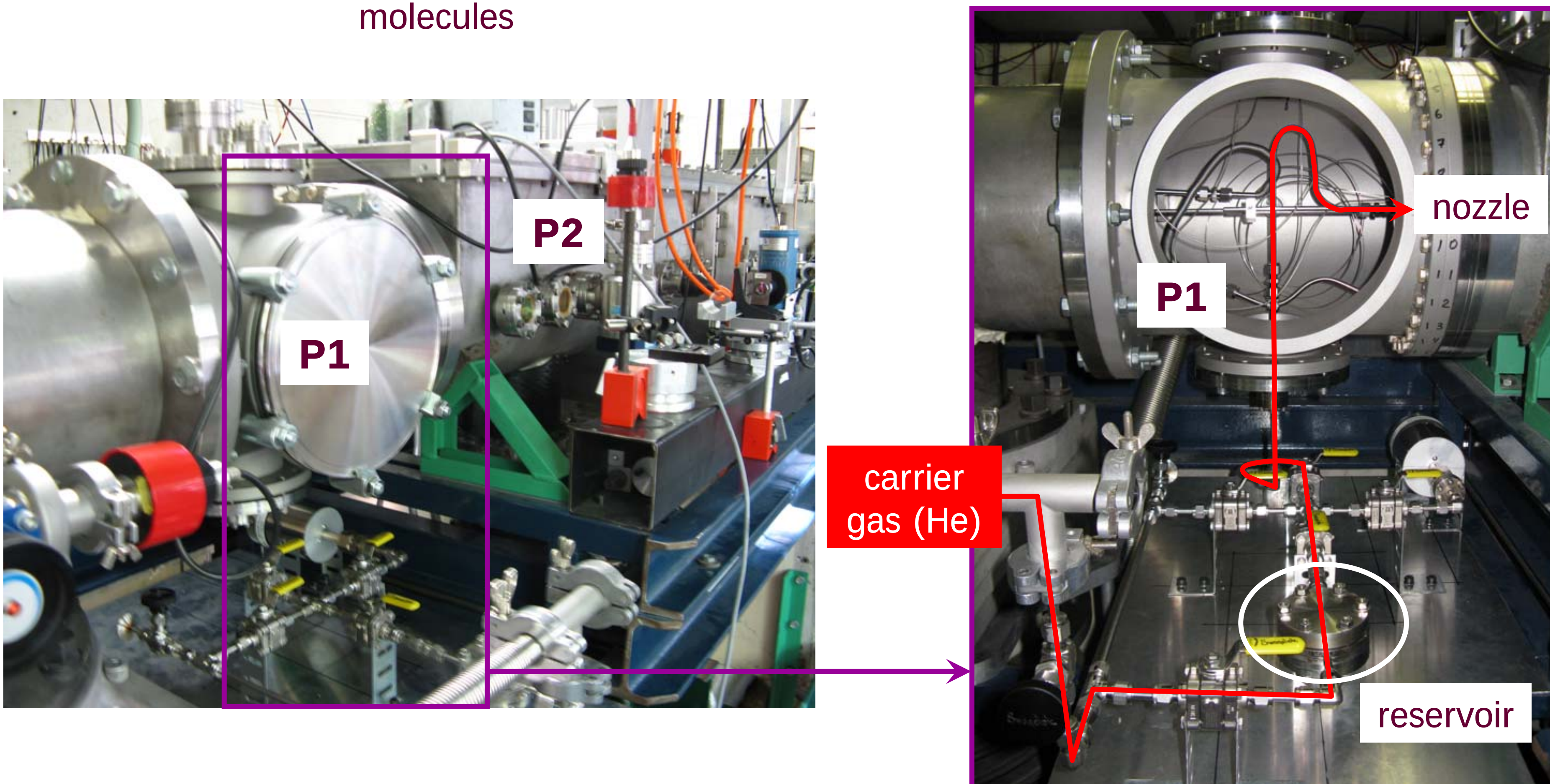


translational and rotational cooling ~ 10K

jet velocity ~ 400 to 2000 m/s

Experimental set-up

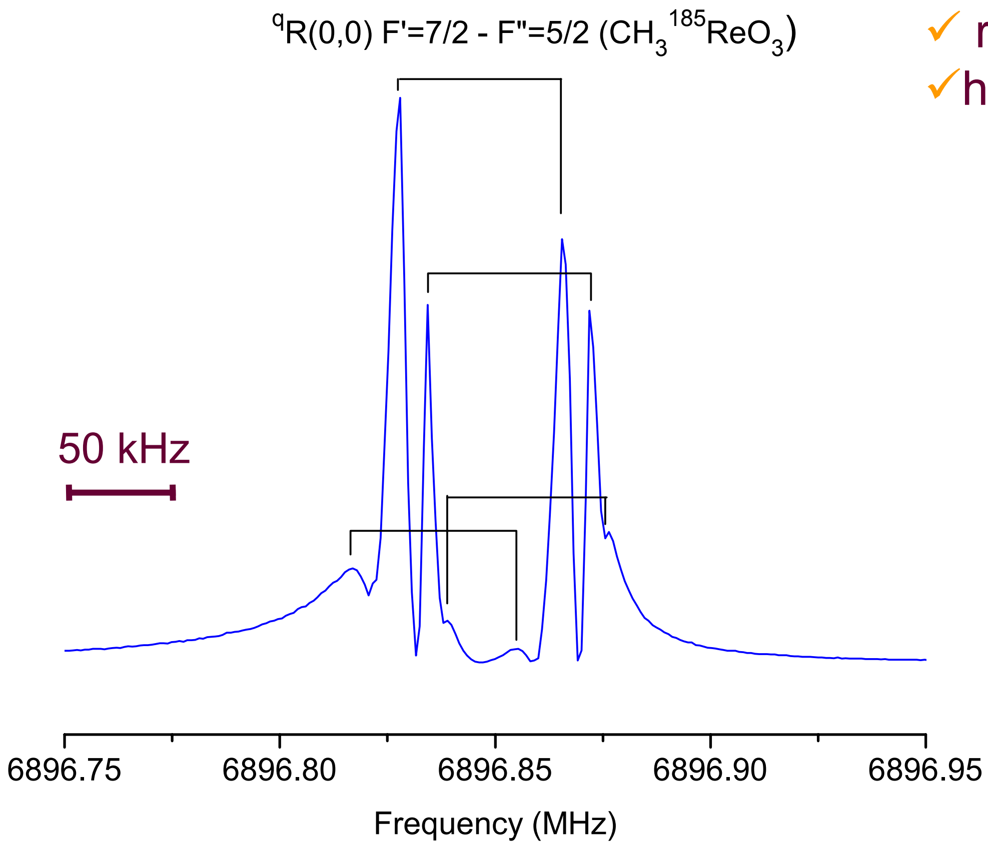




Jet-spectroscopy of MTO

- ✓ ideal achiral test molecule, parent molecule of candidates for the PNC test
- ✓ gas phase rovibrational spectrum never observed yet

Fourier-Transform MicroWave spectroscopy
(by T. Huet, PhLAM, Lille)



T_{jet} ~ 4K

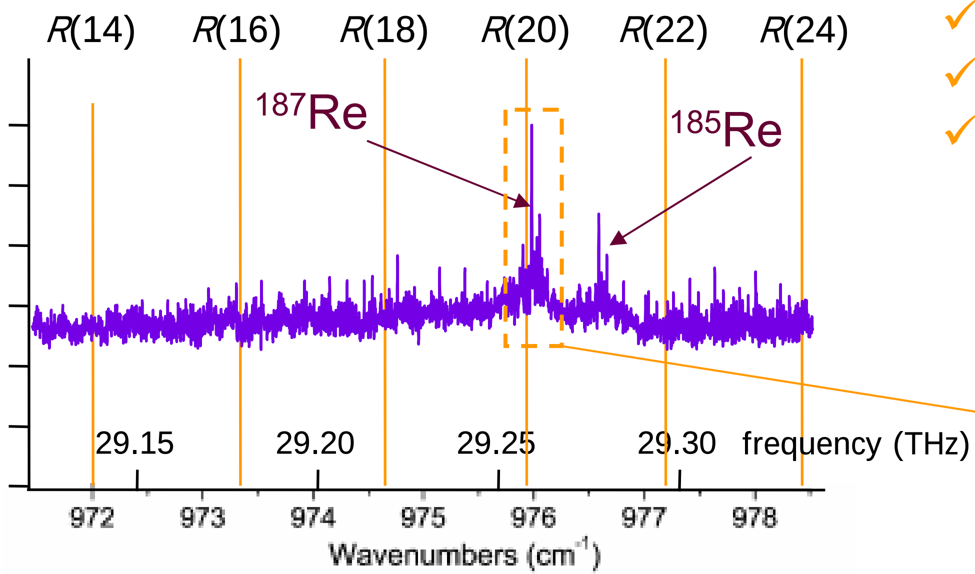
- ✓ rotational spectroscopy
- ✓ hyperfine structure partially resolved

Stoeffler et al, *Phys. Chem. Chem. Phys.* (2011)

Jet-spectroscopy of MTO

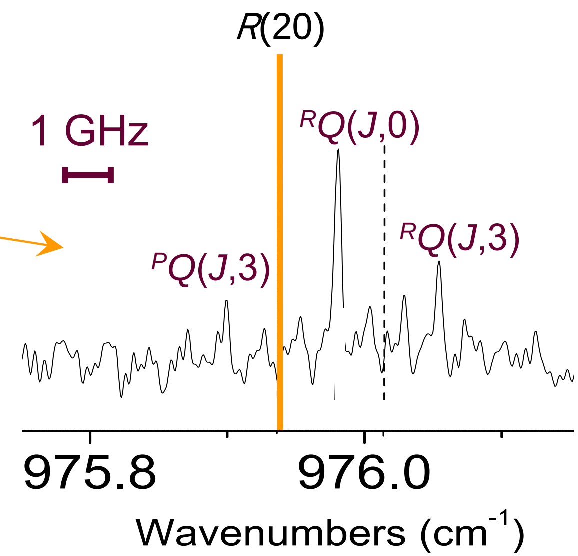
- ✓ ideal achiral test molecule, parent molecule of candidates for the PNC test
- ✓ gas phase rovibrational spectrum never observed yet

<u>Fourier-Transform InfraRed spectroscopy</u>
(by P. Asselin and P. Soulard, LADIR, Paris)



$T_{jet} \sim 10K$

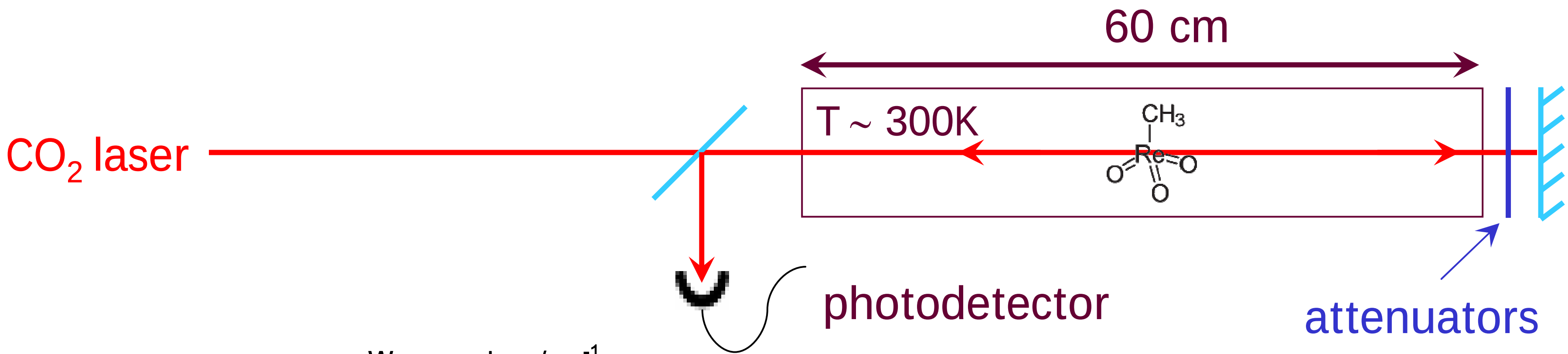
- ✓ rovibrational spectroscopy
- ✓ antisymmetric Re=0 stretching
- ✓ hyperfine structure not resolved

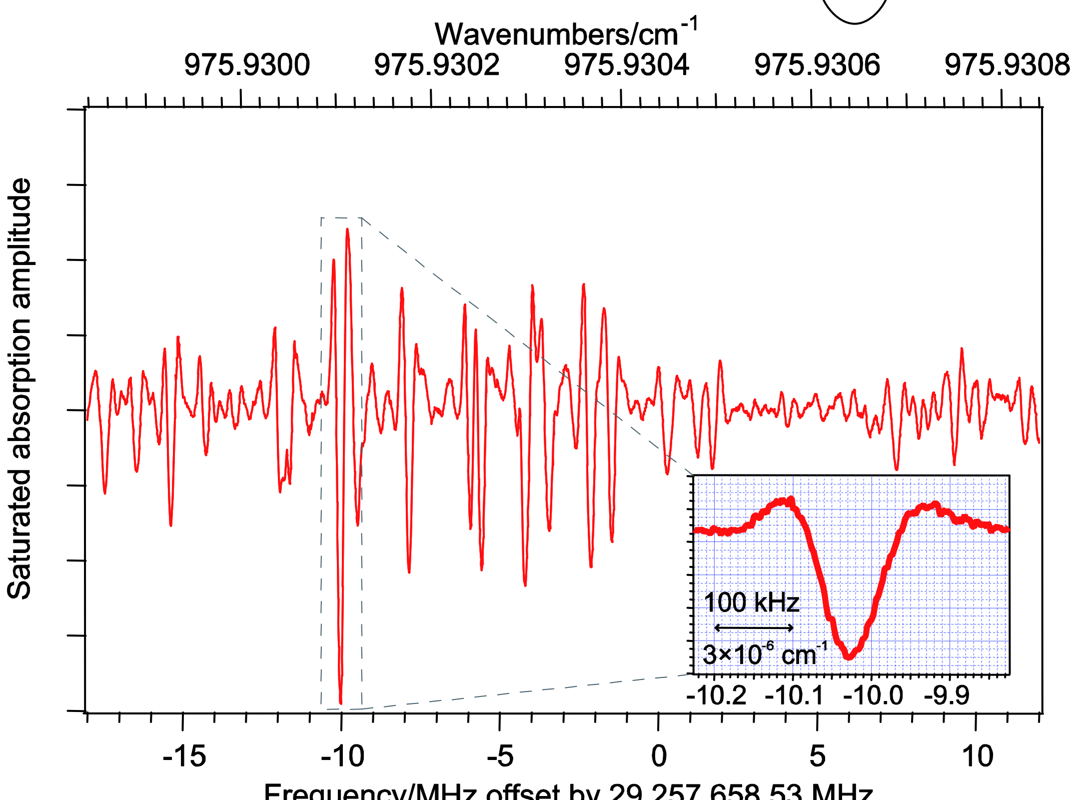


- ✓ demonstration of supersonic jet-spectroscopy of organometallic molecules
- ✓ signal accessible to the CO_2 laser

Stoeffler et al, *Phys. Chem. Chem. Phys.* (2011)

Saturated absorption spectroscopy of MTO in a cell at LPL





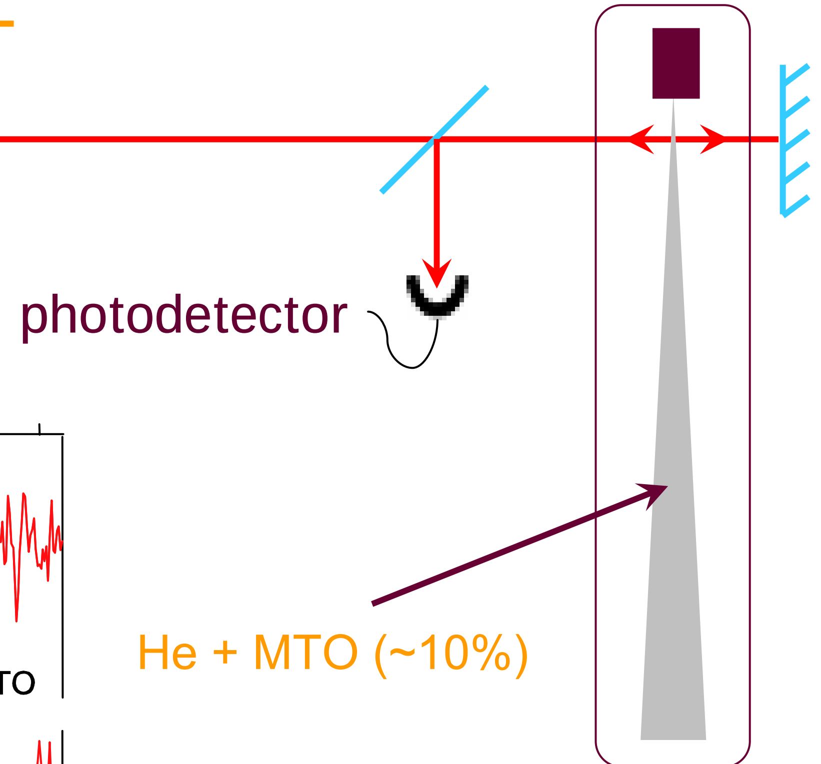
✓ working pressure ~ 10^{-3} mbar, < 100 mg of MTO needed

✓ rovibrational spectroscopy

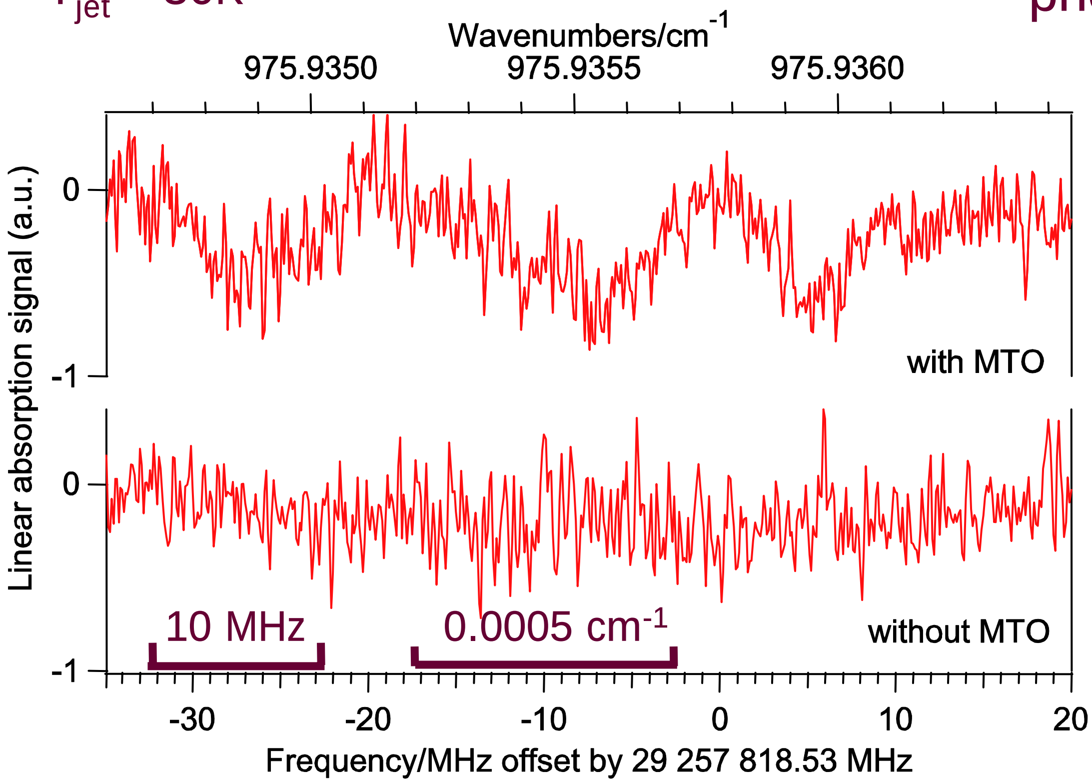
✓hyperfine structure partially resolved

Stoeffler et al, *Phys. Chem. Chem. Phys.* (2011)

Linear absorption jet-spectroscopy of MTO at LPL



T_{jet} ~ 30K



- ✓ rovibrational spectroscopy
- ✓ hyperfine structure not resolved
- ✓ major step

integration time: 40 min (2g/h^{-1})

Stoeffler et al, *Phys. Chem. Chem. Phys.* (2011)

Spectra analysis, fitting and simulations

Combined analysis of microwave (from PhLAM) and infrared spectra (from both LADIR and LPL) and global fit (using SPFIT program of H. Pickett)

	Set 1	Set 2
A/MHz	3849.81[a]	3854.01(1.27)
B/MHz	3466.96481(39)	3466.96481(39)
D_J/kHz	0.705(50)[b]	0.705(50)[b]
D_{JK}/kHz	2.208(118)[b]	2.208(118)[b]
eQq/MHz	716.54005(192)	716.54005(192)
C_{aa}/kHz	−52.22(37)[b]	−52.22(37)[b]
C_{bb}/kHz	−51.464(92)	−51.464(92)
ν_{as}/cm^{-1}	975.9665(3)	975.9667(3)
A'/MHz	3847.14(34)	3851.35(1.12)
B'/MHz	3463.4362(224)	3463.4362(224)
ξ	−0.0011(4)	0.0[a]
D'_J/kHz	0.705(50)[b]	0.705(50)[b]
D'_{JK}/kHz	2.208(118)[b]	2.208(118)[b]
eQq'/MHz	694.779(44)	694.779(44)
C_{aa}'/kHz	−52.22(37)[b]	−52.22(37)[b]
C_{bb}'/kHz	−53.005(149)	−53.005(149)

[a] Fixed value. [b] Fitted and constrained to the corresponding ground state/excited state value.

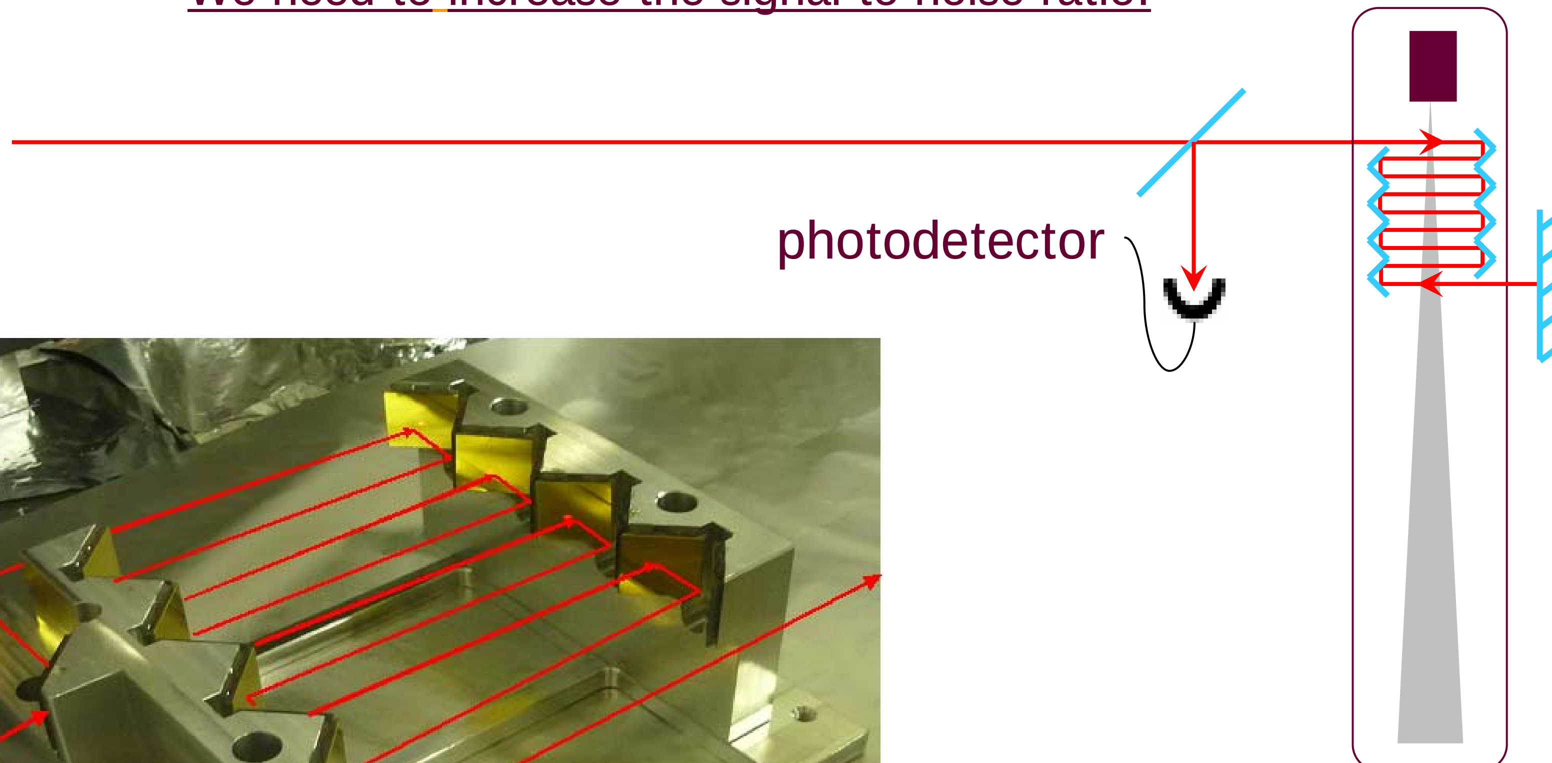
- ✓ a set of accurate spectroscopic parameters
- ✓ simulated spectrum ⇒ identify the most intense lines
- ✓ validate the approach chosen by our consortium
- ✓ procedure to reiterate with chiral candidates for PNC experiment

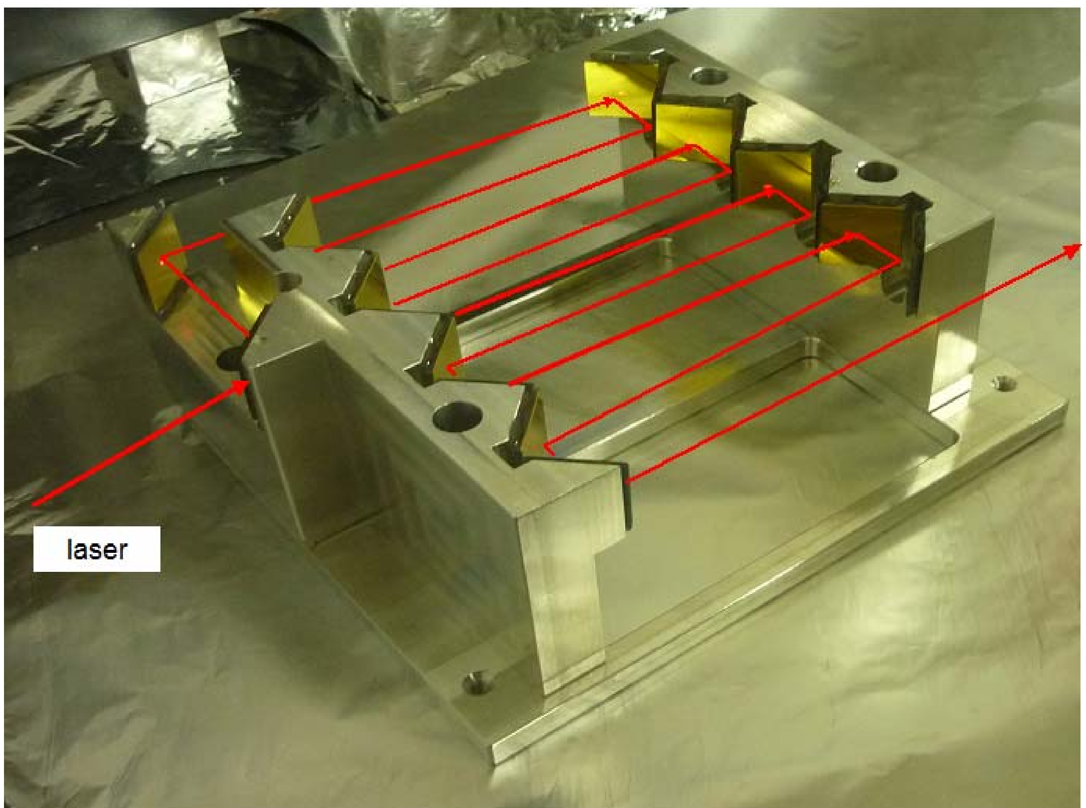
Stoeffler et al, *Phys. Chem. Chem. Phys.* (2011)

Towards higher resolution jet-spectroscopy

<u>We need to increase the signal to noise ratio!</u>

CO_2 laser

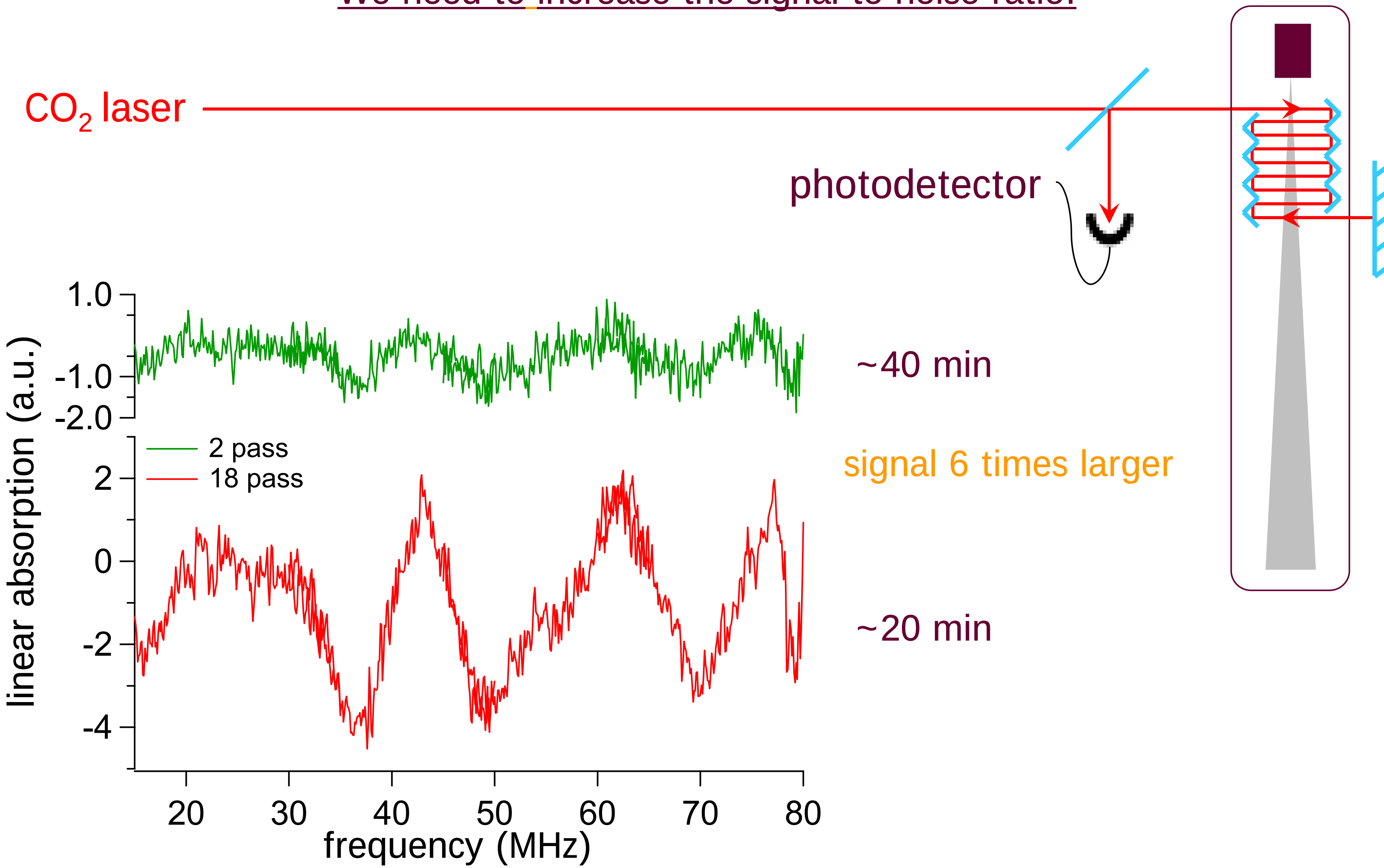




18 passes back and forth

Towards higher resolution jet-spectroscopy

We need to increase the signal to noise ratio!



Perspectives

- ✓ Further increase the linear absorption S/N $\Rightarrow$ line centre pointing
  - increase the number of passes
  - Fabry-Perot cavity
- ✓ Demonstrate ultra-high resolution spectroscopy of MTO in a jet $\Rightarrow$ saturated absorption
- ✓ 2-photon spectroscopy of MTO
- ✓ Ramsey fringes on MTO
- ✓ Reiterate the same whole study on chiral derivatives of MTO

Issues

- ✓ synthesis of large quantities of new chiral molecules with large ee
- ✓ confrontation with relativistic quantum chemistry calculations
- ✓ development of ultra-high resolution spectroscopy techniques for complex molecules
- ✓ confrontation with the electro-weak theory and the standard model, especially at low energy
- ✓ link with bio-homochiralité

Contributors

LPL Laboratoire de physique des lasers

Clara Stoeffler, Frédéric Auguste, Alexandre Shelkovnikov, Christophe Daussy, Olivier Lopez, Anne Amy-Klein, Christian Chardonnet

?





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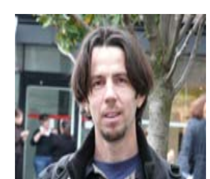
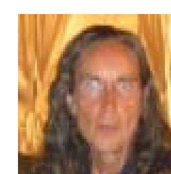

PhLAM

Thérèse Huet

Thank you for your attention

Work supported by:

Contracts NCPMol (2006-2010) and NCPChem (2011-2014)