TECHNICAL ENHANCEMENTS OF A SUBMILLIMETER-WAVE SPECTROMETER: LABORATORY DETECTION OF NEW LINES OF METHANOL RADICAL DERIVATIVES

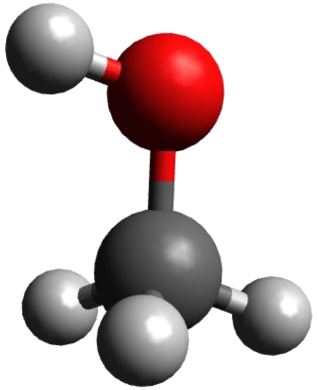
J-T.Spaniol[1], O.Chitarra[1], T.S.Hearne[1], M-A. Martin-Drumel[1], O.Pirali[1]

[1]Université Paris Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405, Orsay, France

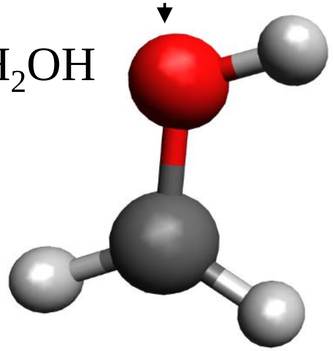
Jean-Thibaut Spaniol | *June 2021*

Methanol radical derivatives: an astrophysical interest

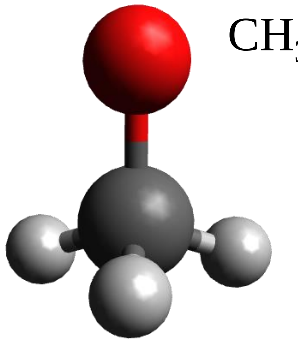
CH_3OH



CH_2OH



CH_3O



Many molecules in space are radicals:

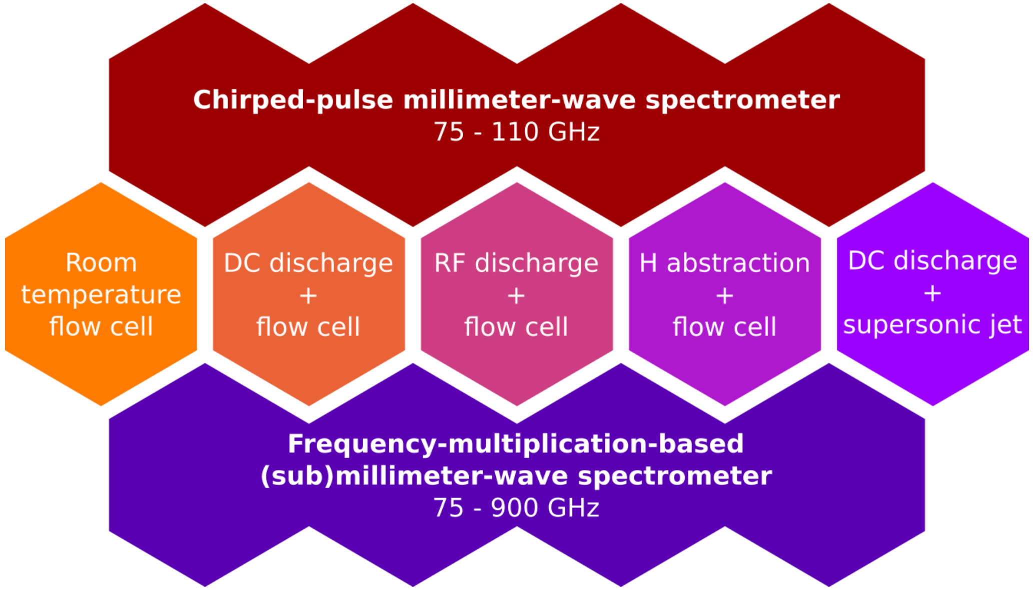
→ Major importance for astrochemistry!

Why should we investigate rotational spectrum of methanol radical derivatives?

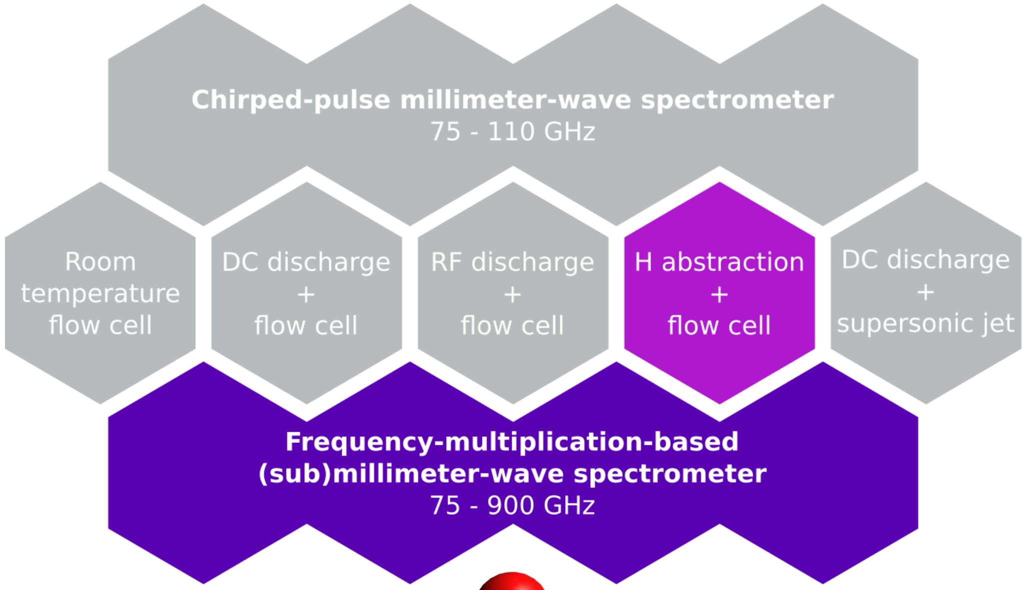
- C, O and H containing species
- CH_2OH potentially precursor of Complex Organic Molecules[1]
- CH_3O already detected in the Interstellar Medium [2]

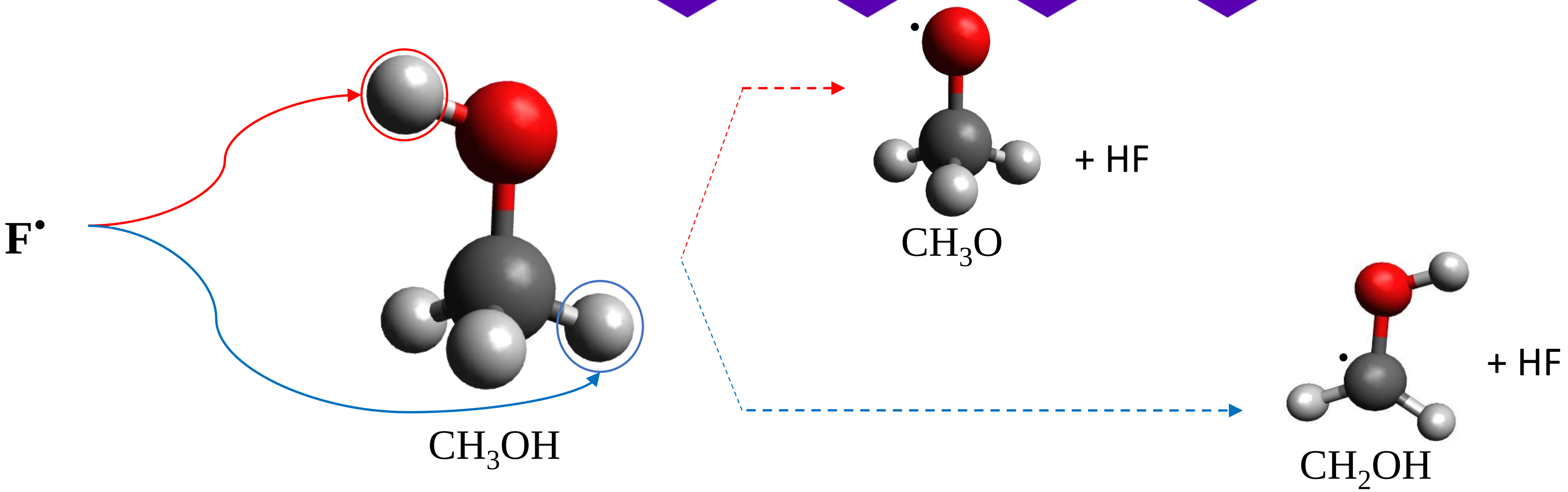
1. T. Butscher et al., MNRAS, 453, 1587, 2015
2. J. Cernicharo et al., ApJ, 759, pL43, 2012

Experimental set-ups available at ISMO



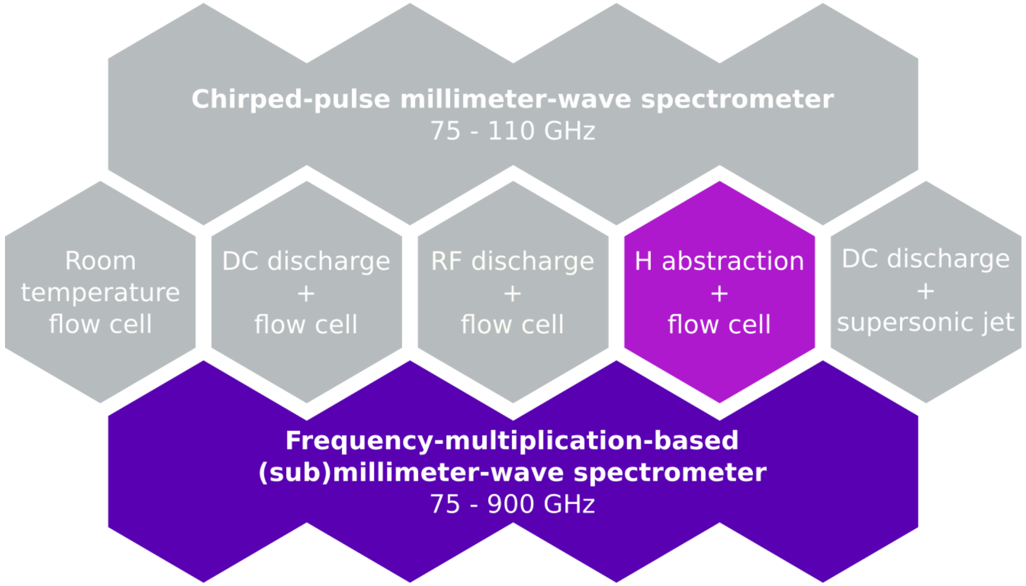
Experimental set-ups available at ISMO





Y.Endo et al., J. Chem. Phys. 81, p122, 1984

Experimental set-ups available at ISMO



Challenges

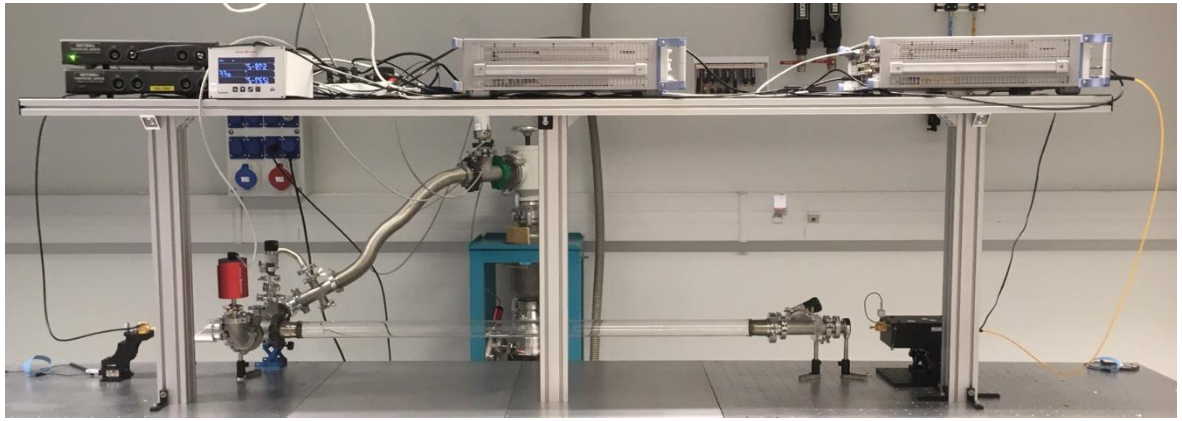
Low SNR for radicals → Need to improve our sensitivity ($A=\varepsilon * l * c$)

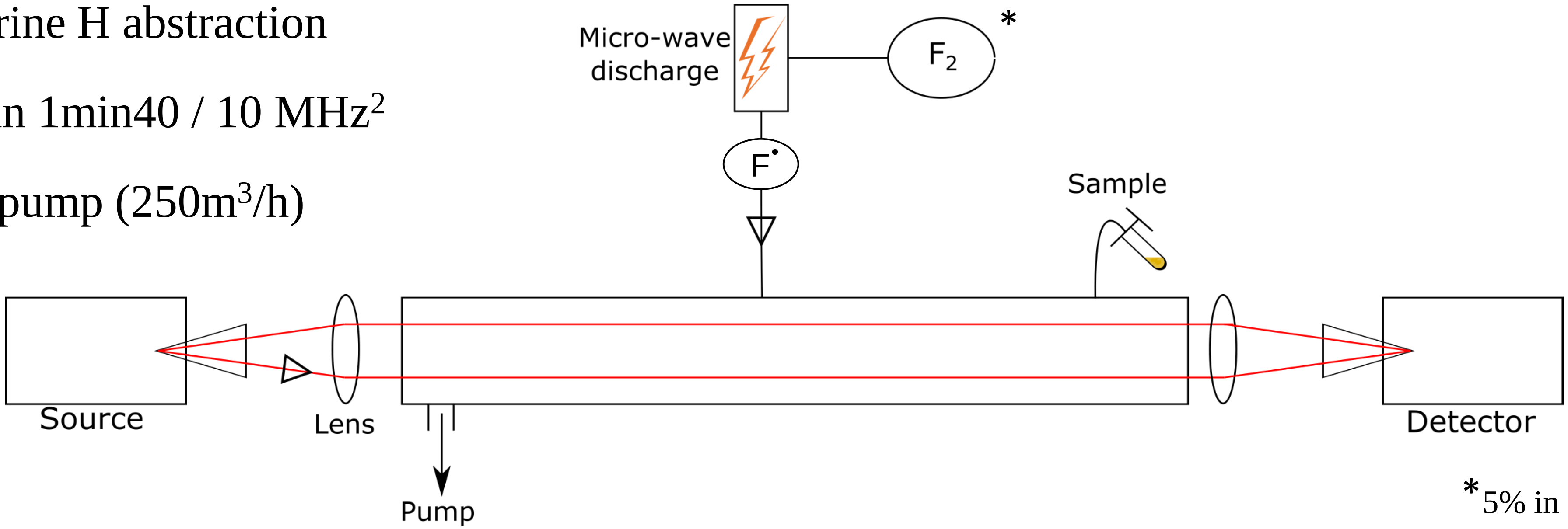
Sometimes hidden in precursors lines → Need to improve our discrimination power

Initial experimental set-up[1]

Characteristics:

- Synthetizer (2-20 GHz) + frequency multiplier (VDI)
- Detector: Shottky diode or bolometer
- FM modulation + 2F detection
- 150 cm cell
- Radical produced by fluorine H abstraction
- Typical spectra recorded in 1min40 / 10 MHz[2]
- Roots + primary vacuum pump (250m^3/h)



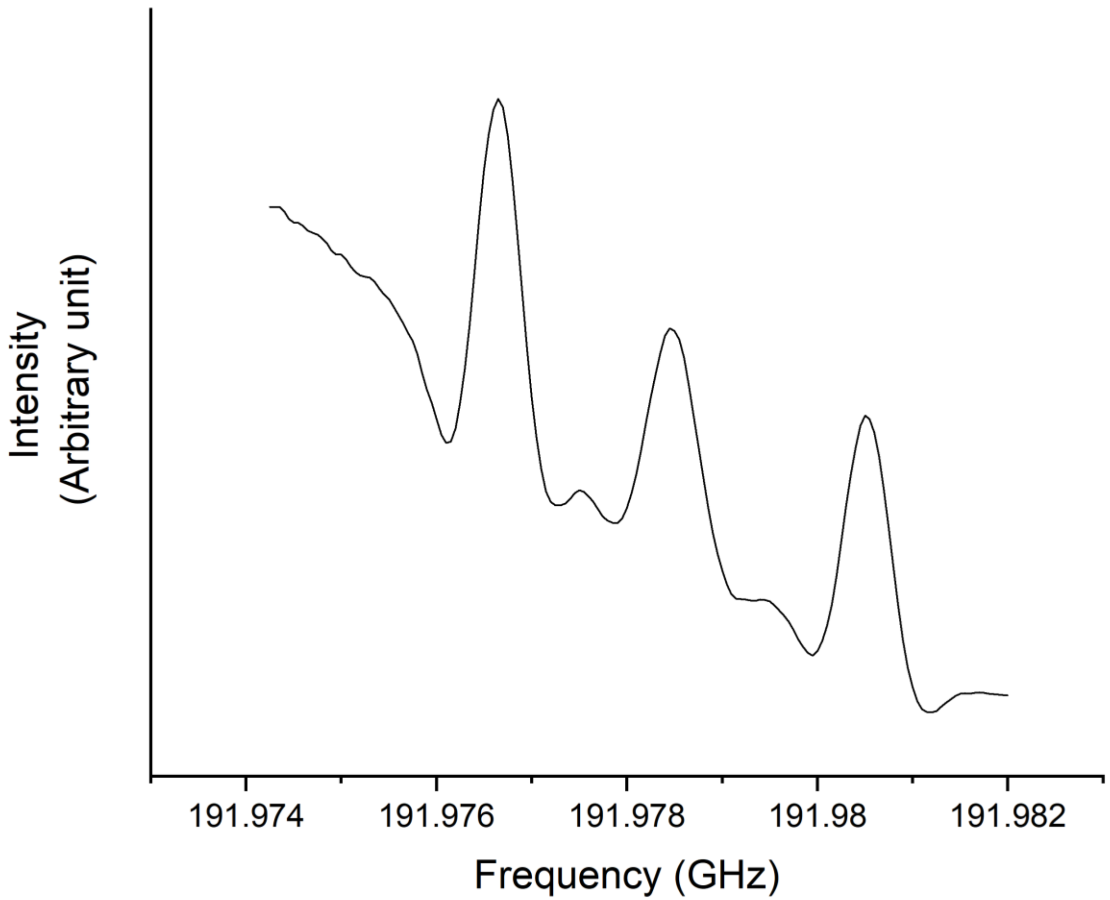


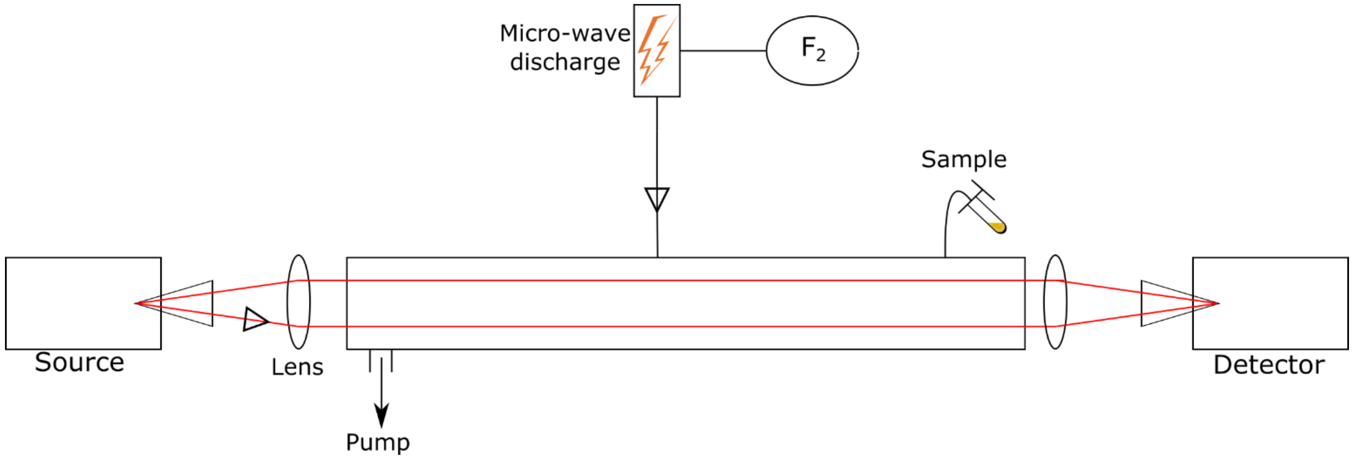
1. O.Chitarra et al. A&A. 644. 2020
2. Step of 50kHz,
   Time constant of frequency modulation 500ms

*5% in He

Initial experimental set-up

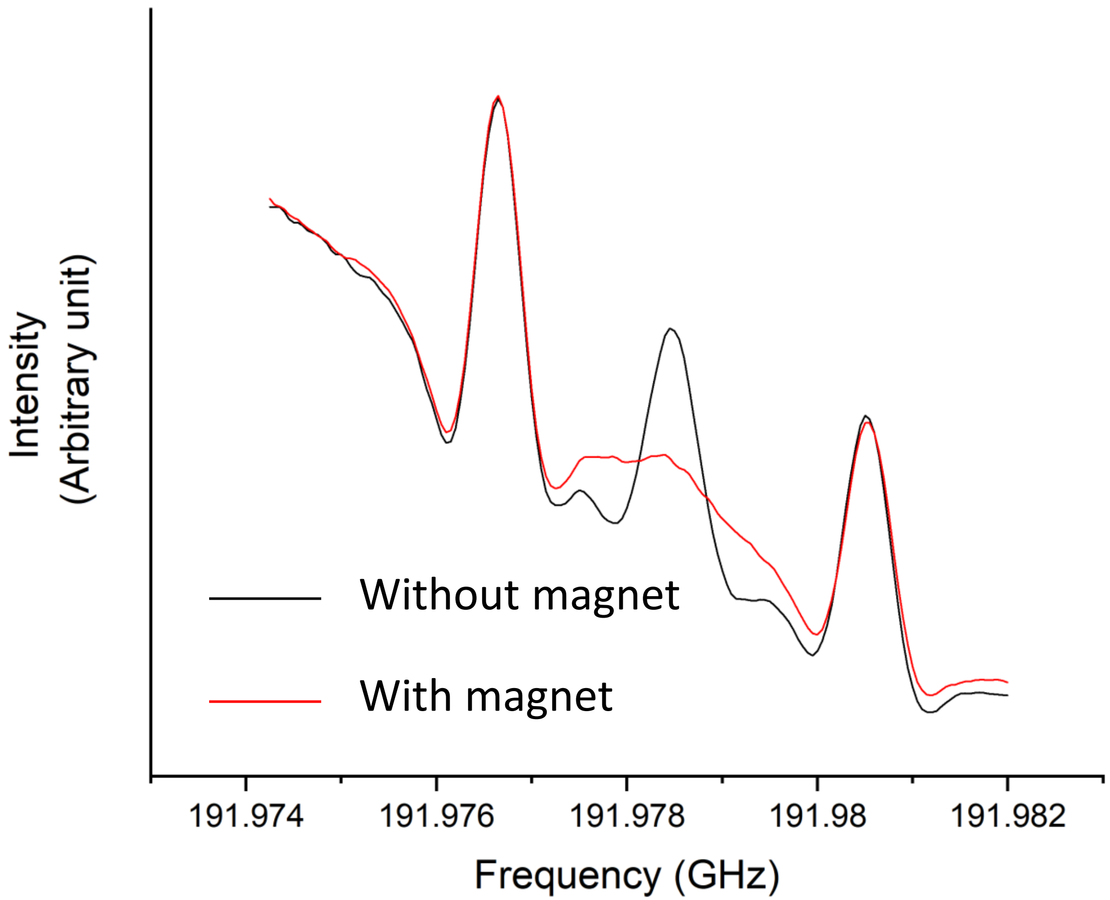
$CH_3OH + F^{\bullet} = CH_3O^{\bullet} + HF$

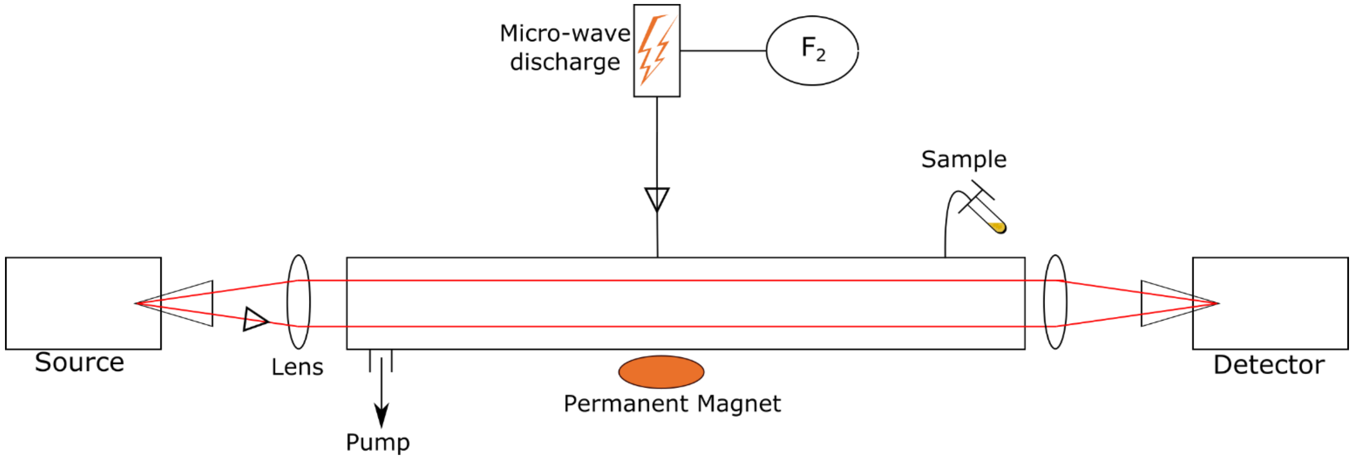




Initial experimental set-up

$CH_3OH + F^{\bullet} = CH_3O^{\bullet} + HF$





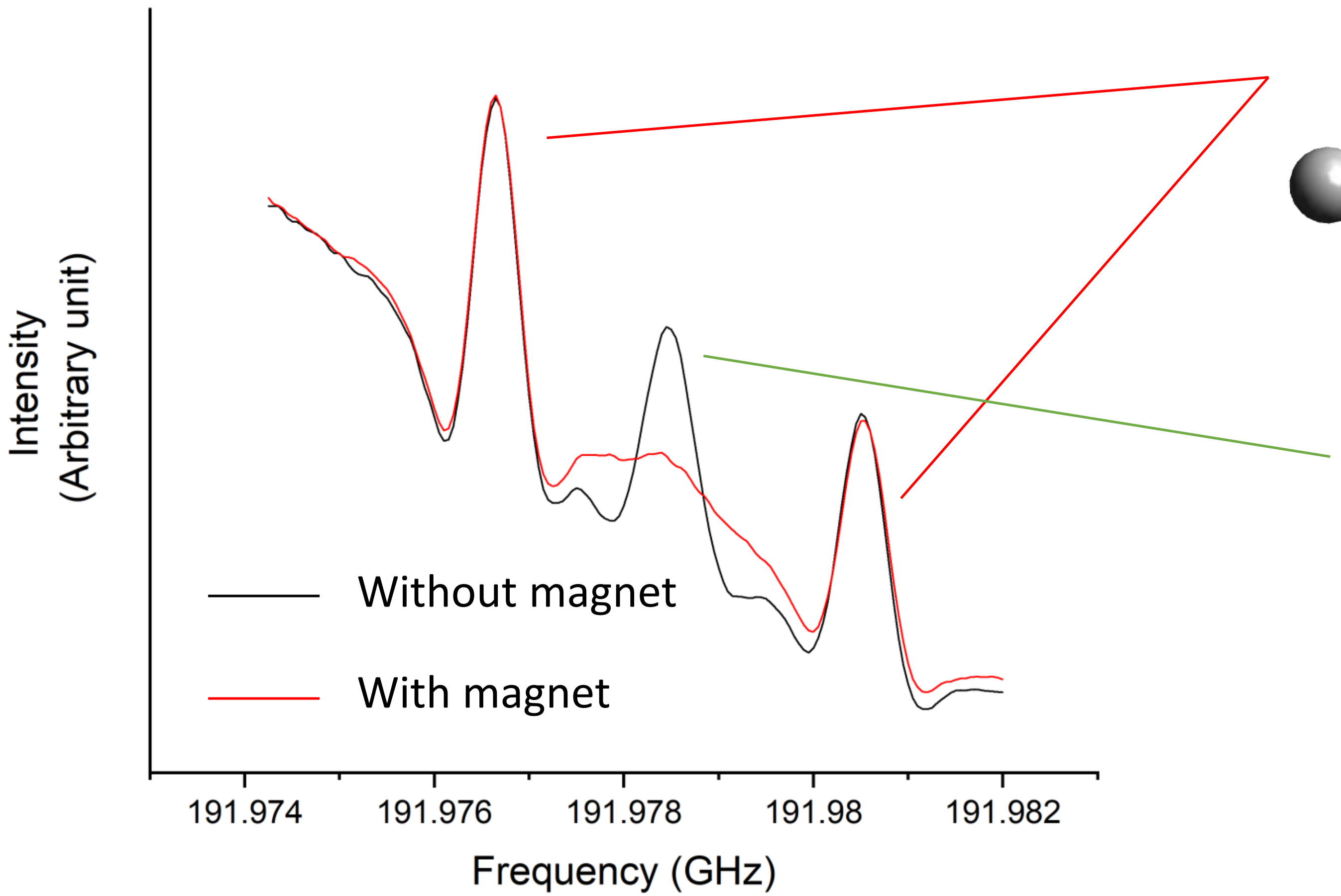
Effect of the magnetic field on an open-shell species[1]:

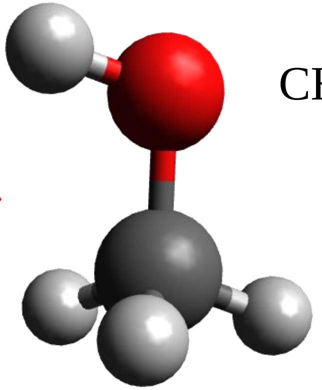
Zeeman Interaction

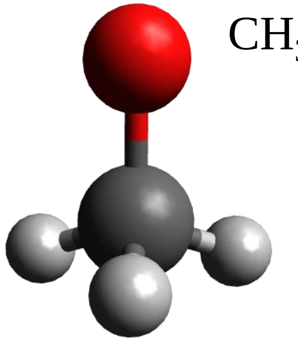
1. C.K. Jen et al. Physical Review, 74(10), p1396–1406, 1948

Initial experimental set-up

$CH_3OH + F^{\bullet} = CH_3O^{\bullet} + HF$



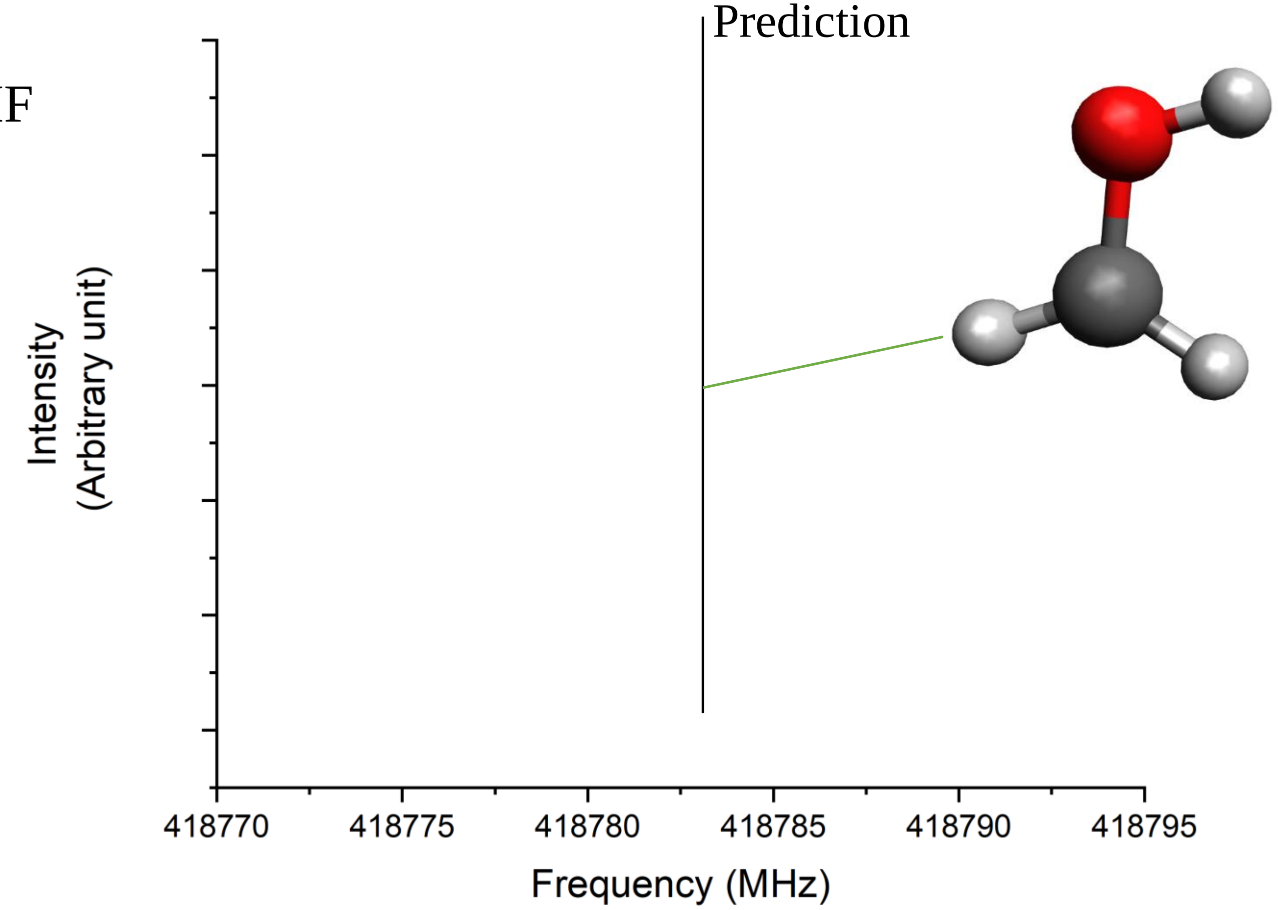




Initial experimental set-up

Effect of the magnetic field on an open-shell species[1]:

$CH_3OH + F^{\bullet} = {}^{\bullet}CH_2OH + HF$



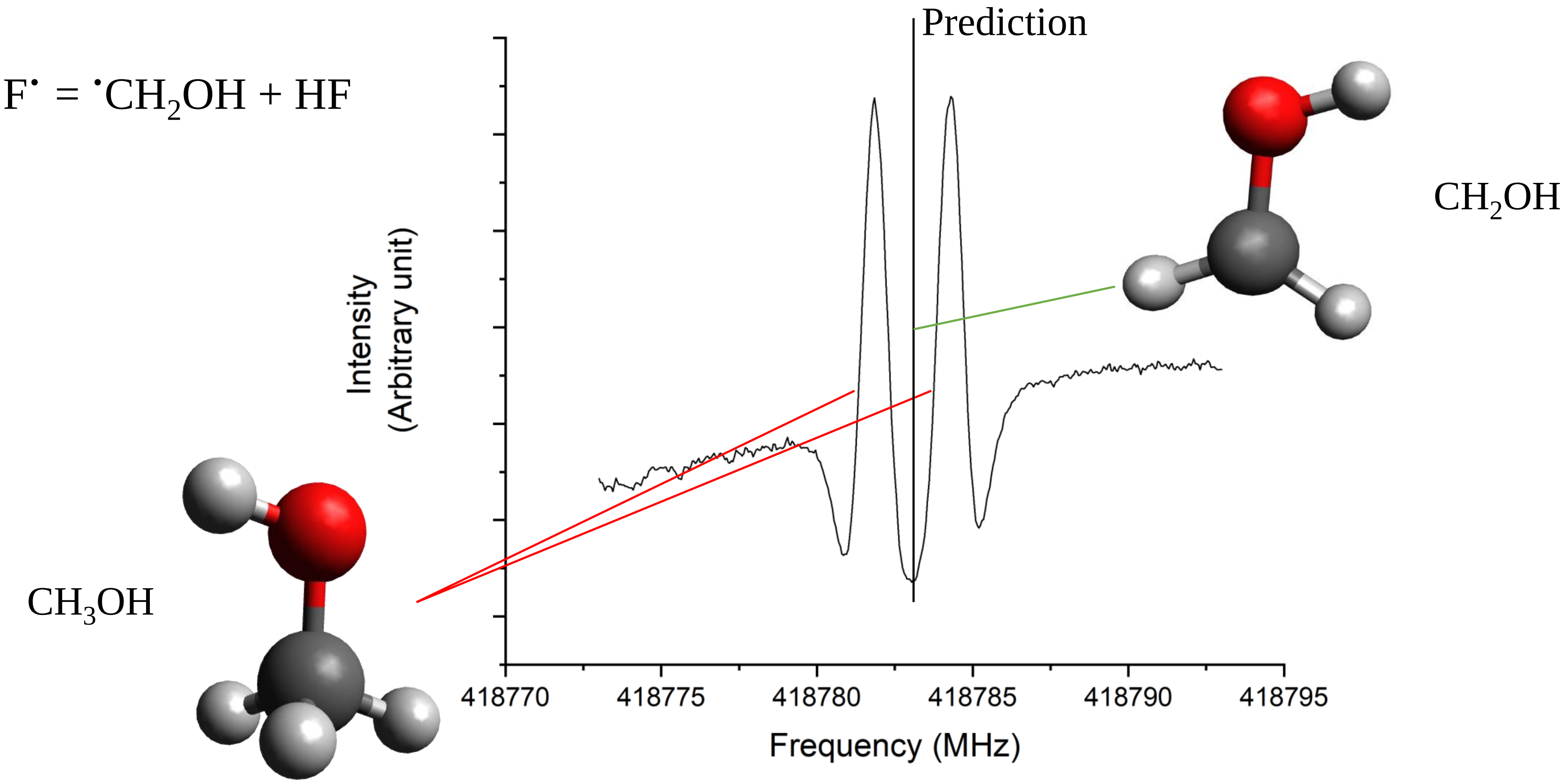
CH_2OH

1. C.K. Jen et al. Physical Review, 74(10), p1396–1406, 1948

Initial experimental set-up

Effect of the magnetic field on an open-shell species[1]:

$CH_3OH + F^{\bullet} = {}^{\bullet}CH_2OH + HF$

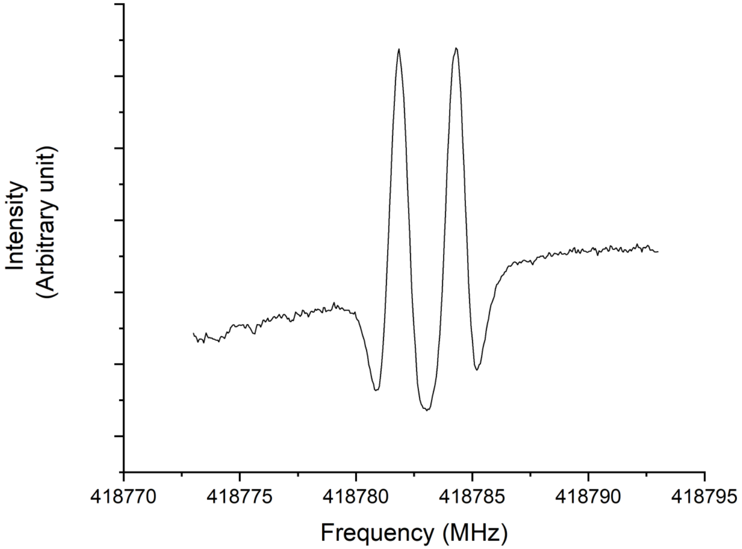


1. C.K. Jen et al. Physical Review, 74(10), p1396–1406, 1948

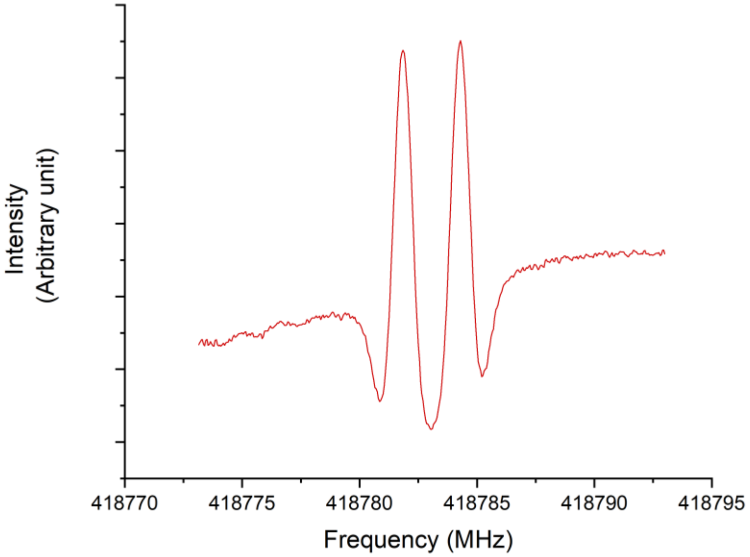
Initial experimental set-up

Effect of the magnetic field on an open-shell species[1]:

Zeeman Interaction



Without magnet

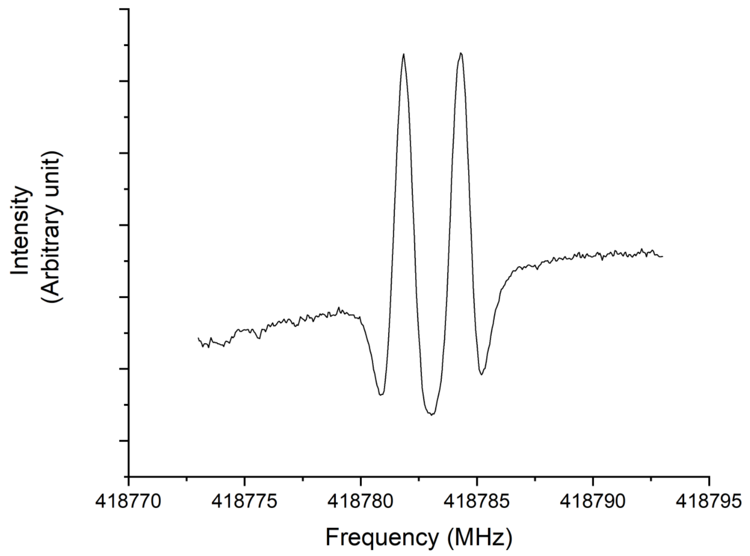


With magnet

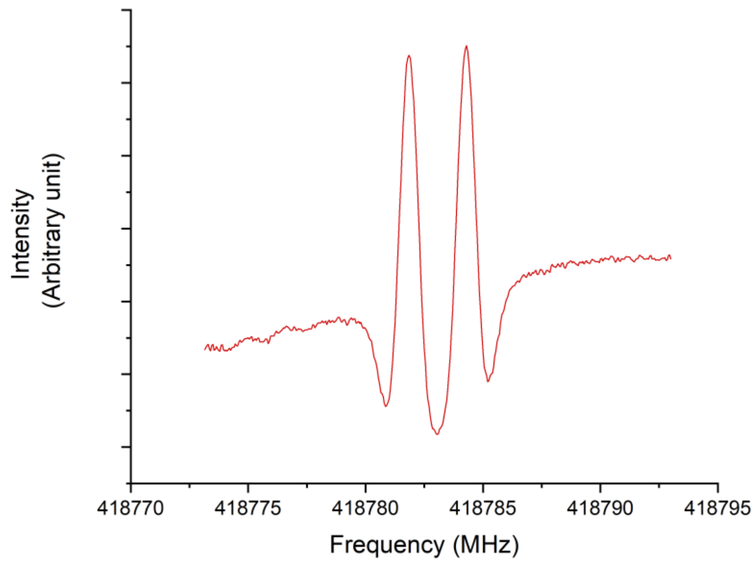
1. C.K. Jen et al. Physical Review, 74(10), p1396–1406, 1948

Initial experimental set-up

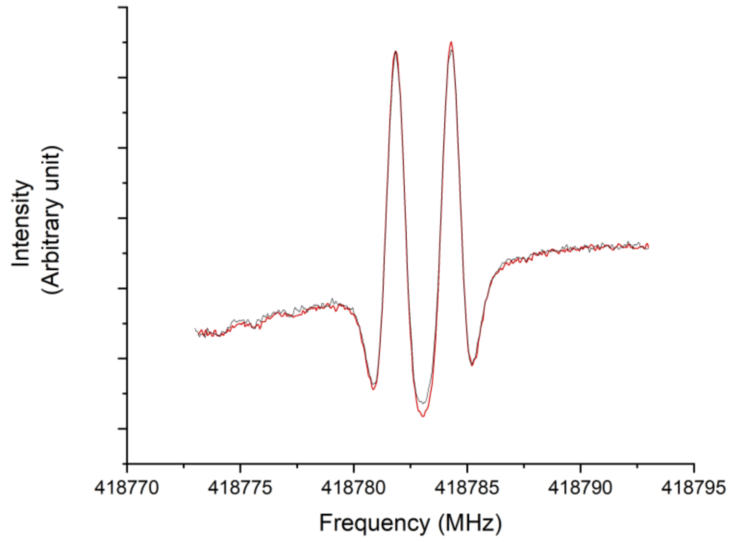
Effect of the magnetic field on an open-shell species[1]:



Without magnet



With magnet

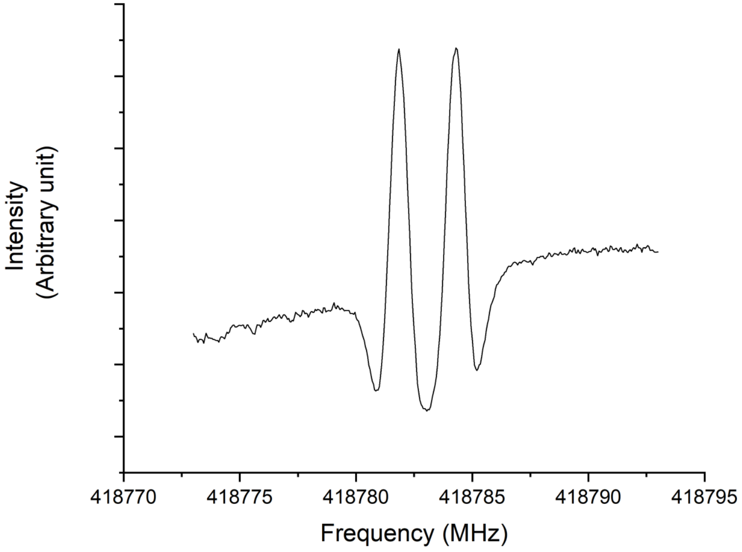


Comparison

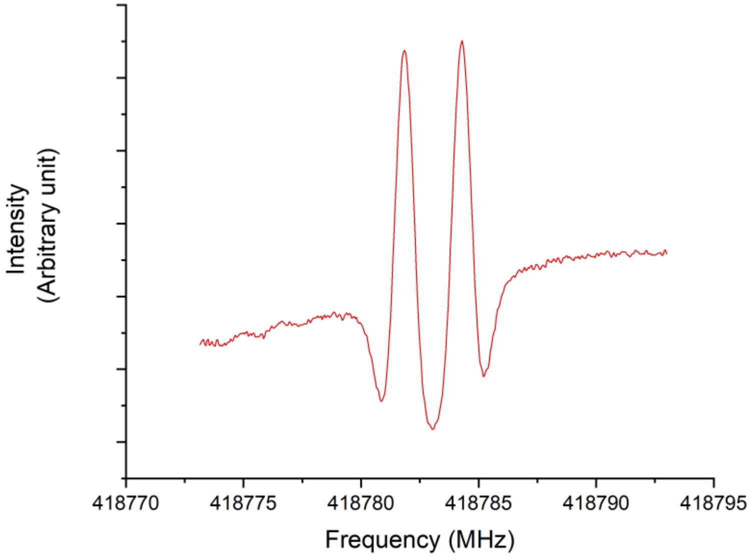
1. C.K. Jen et al. Physical Review, 74(10), p1396–1406, 1948

Initial experimental set-up

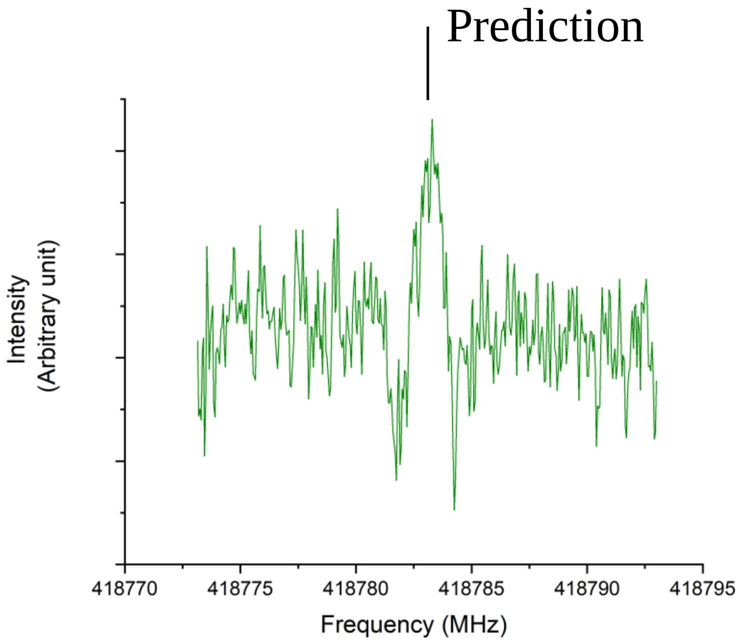
Effect of the magnetic field on an open-shell species[1]:



Without magnet



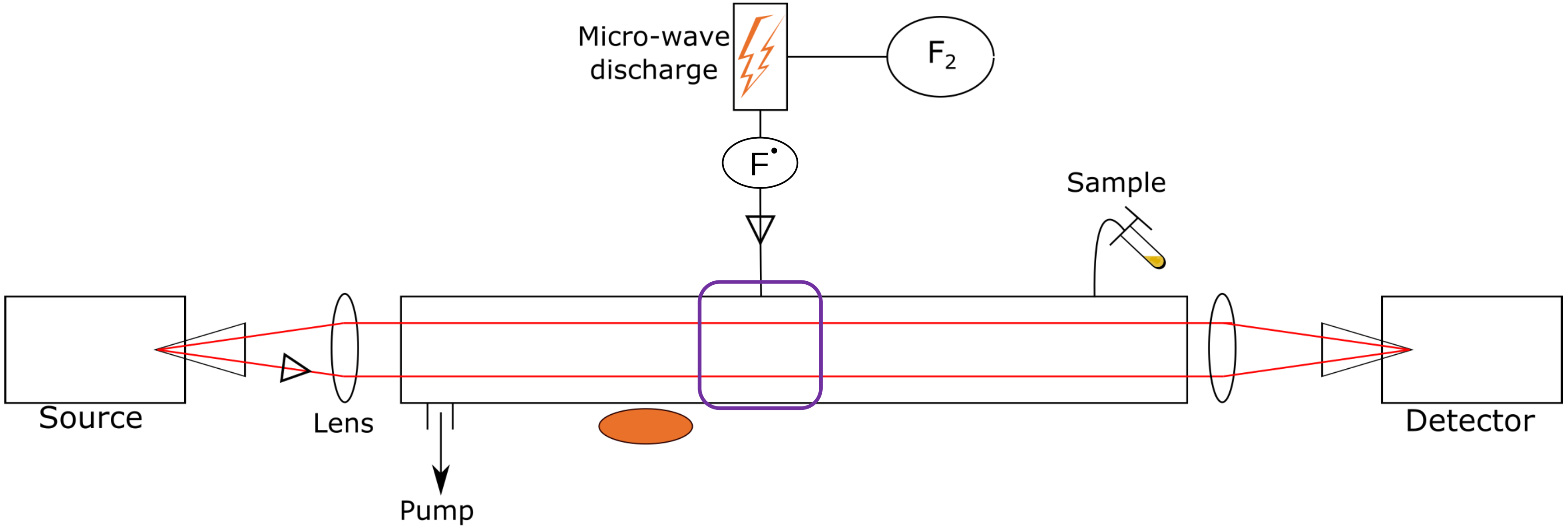
With magnet



Difference spectrum

1. C.K. Jen et al. Physical Review, 74(10), p1396–1406, 1948

Initial experimental set-up

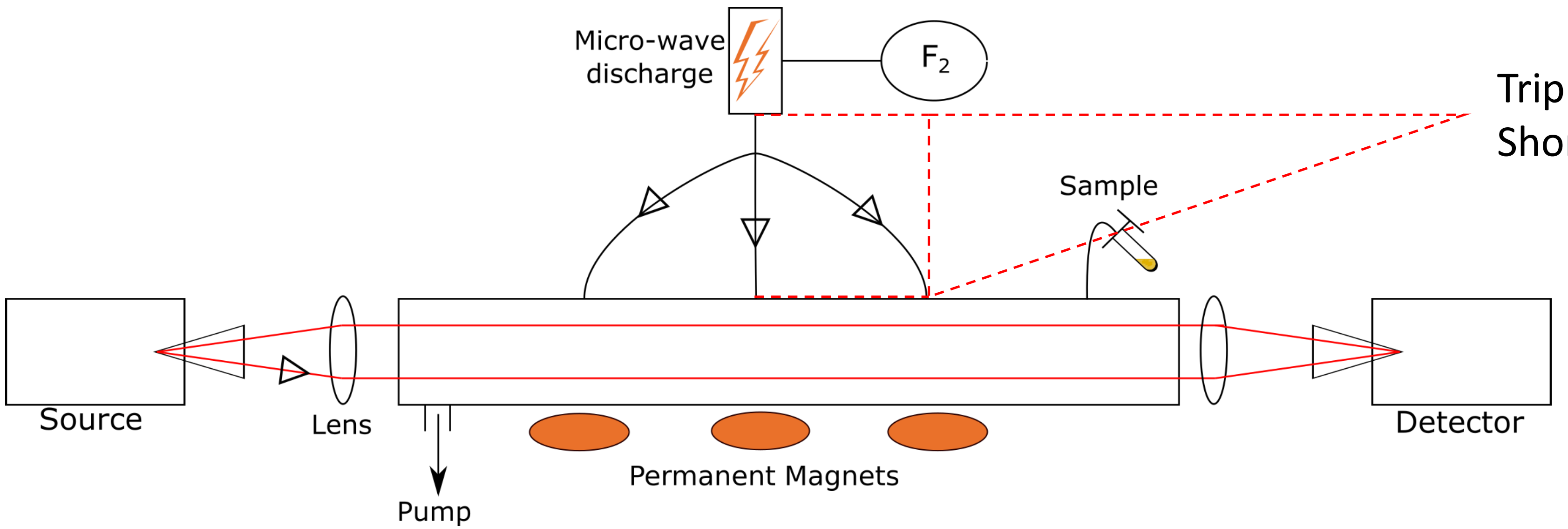


➡ No signal of CH_2OH !

➡ Very short area of radical production!

1°: Increase synthesis yield

$$A=\varepsilon * l * \underline{c}$$



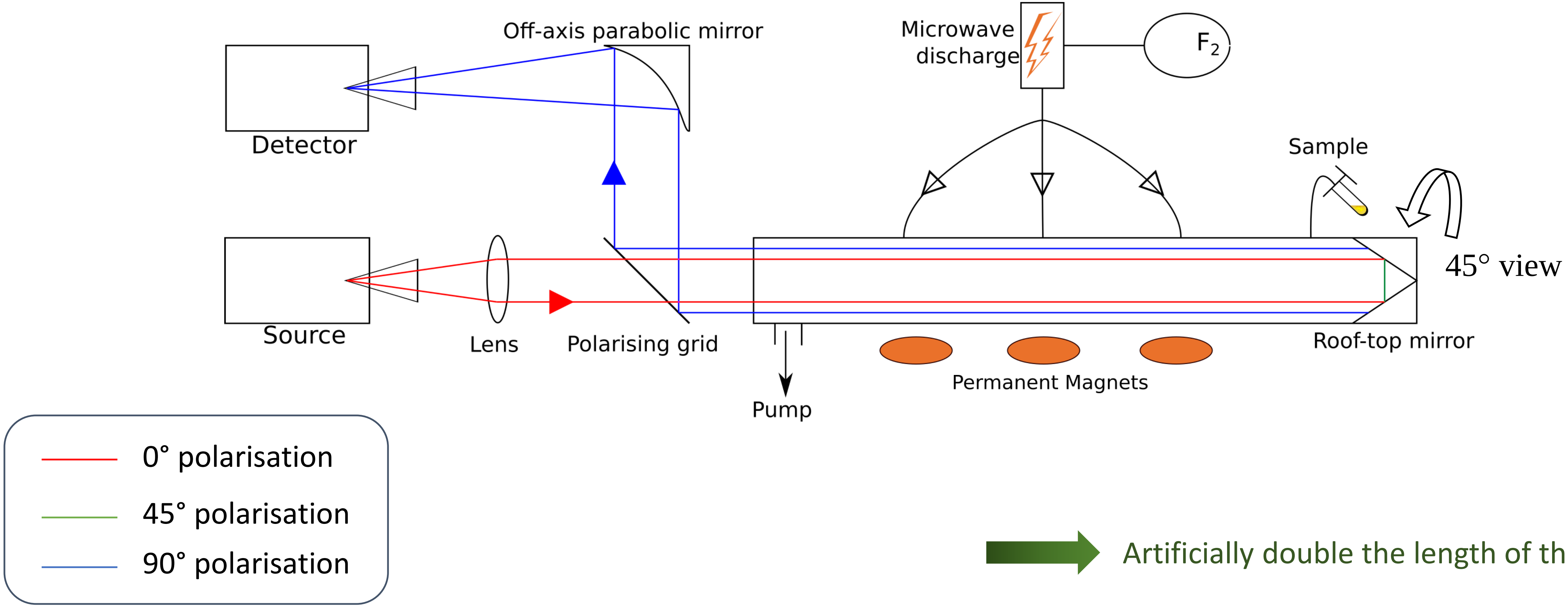
Triple areas of radicals production
Shortened injection tube from 1m25 to 40cm

Decrease recombination of atomic fluorine

Increase synthesis yield of radicals

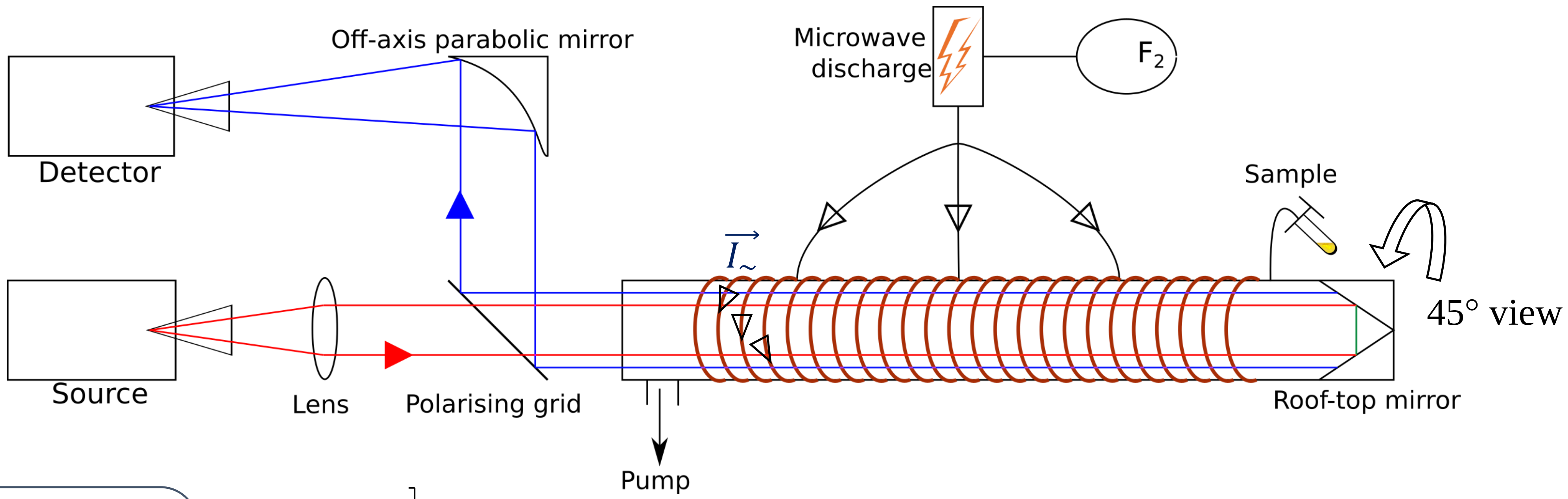
2°: Increase absorption length

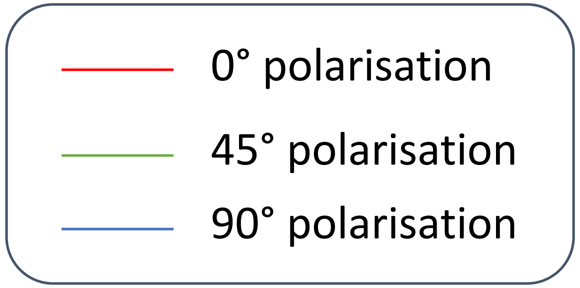
$$A=\varepsilon * l * c$$

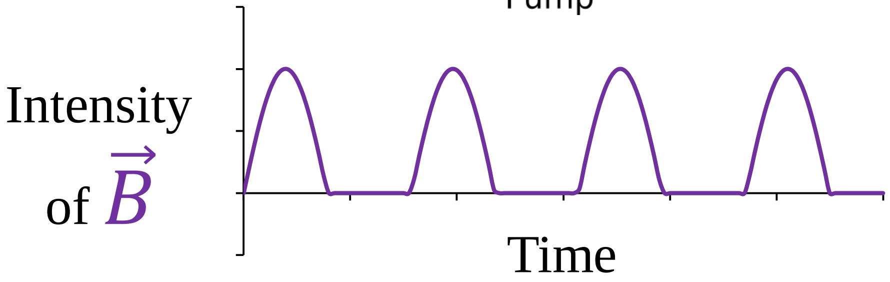


Artificially double the length of the cell

3°: Improve discrimination



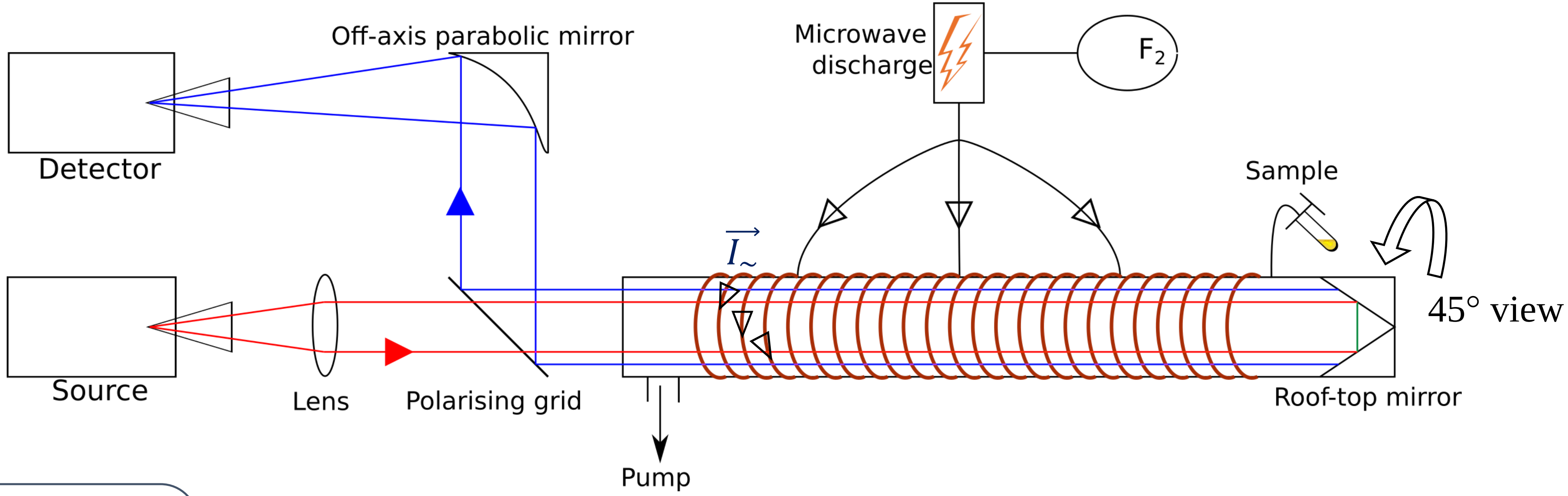




800 coils for 1m30 cell

AC of 2 A produced by audio amplifier + diode for 16 G magnetic field

3°: Improve discrimination



0° polarisation
45° polarisation
90° polarisation

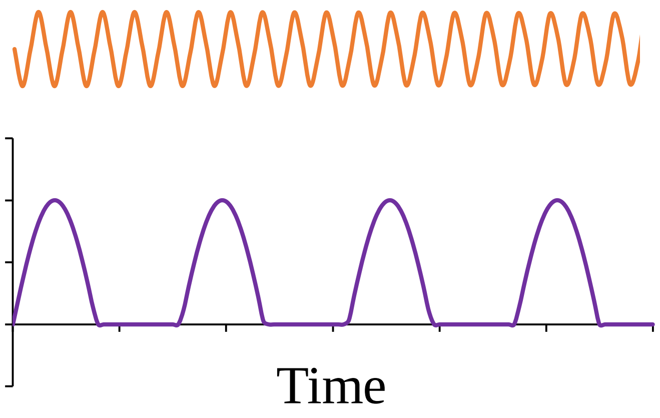
→ Modulated magnetic field all along the cell

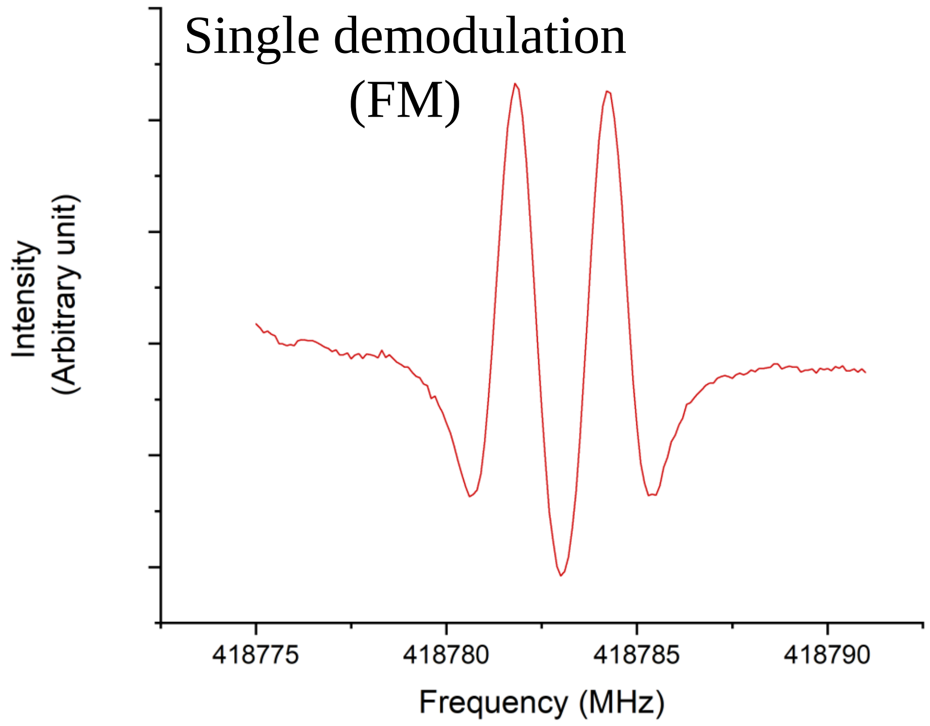
→ Larger magnetic field than previously → Larger Zeeman splitting

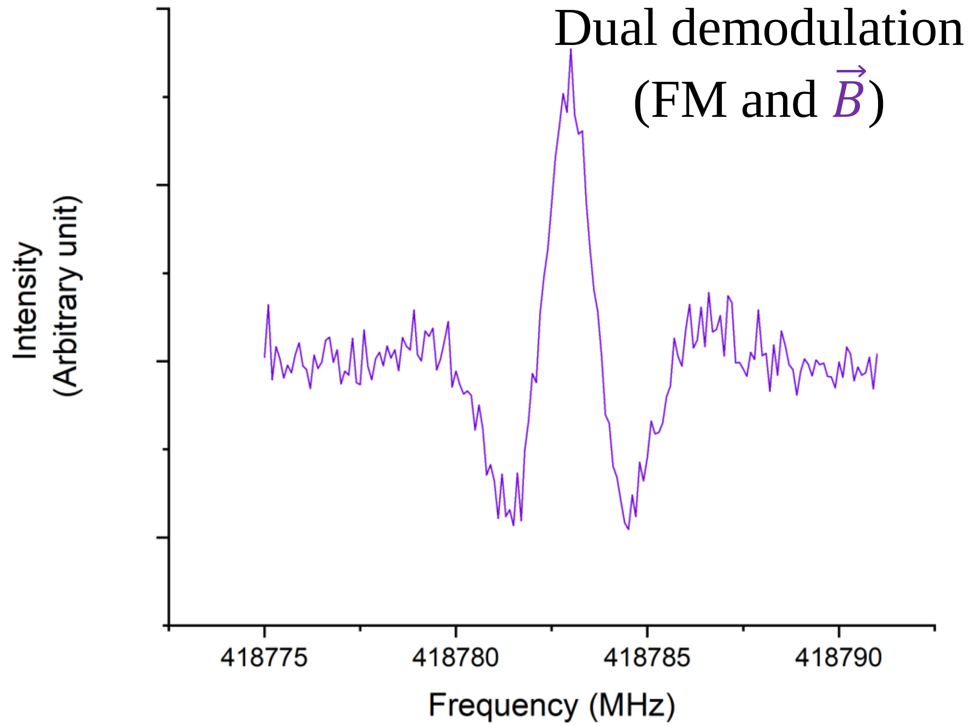
3°: Improve discrimination

Frequency modulation
(First lock-in)

Modulation of $\vec{B}$
(Second lock-in)







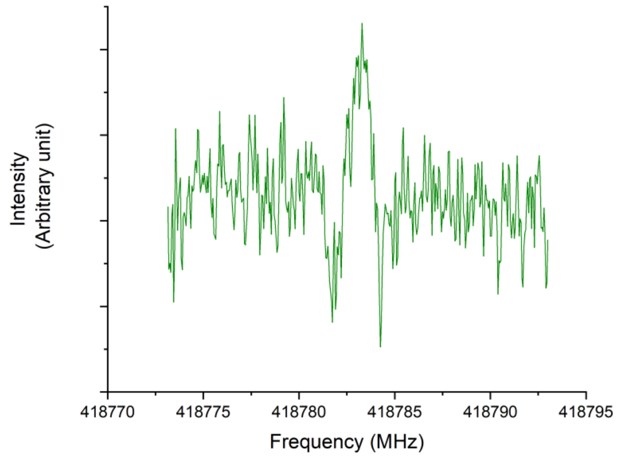
Results

<u>**Initial Set-Up**</u>

One area of production
Single passage
Single modulation (FM)

2 Spectra for each lines needed (total of 3min12 in usual conditions)

SNR~2 on weakest lines



<u>**Final Set-Up**</u>

Triple area of production
Double passage
Double modulation (FM+Magnetic field)

1 Spectrum for each lines needed (3min25 in usual conditions)

SNR~10 for the same line

<u>Initial Set-Up</u>

One area of production
Single passage
Single modulation (FM)

2 Spectra for each lines needed (total of 3min12 in usual cond

SNR~2 on weakest lines

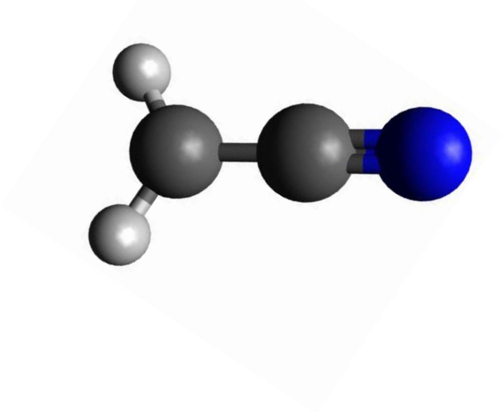
<u>**5 TIMES BETTER !!**</u>
in the same condition
for the same time

500 new lines of CH_2OH
and 476 new lines of CH_3O
measured up to 900 GHz

See O.Chitarra's talk (**WJ03**)

Conclusion and Perspectives

- New study on other interesting radicals: CH_2CN

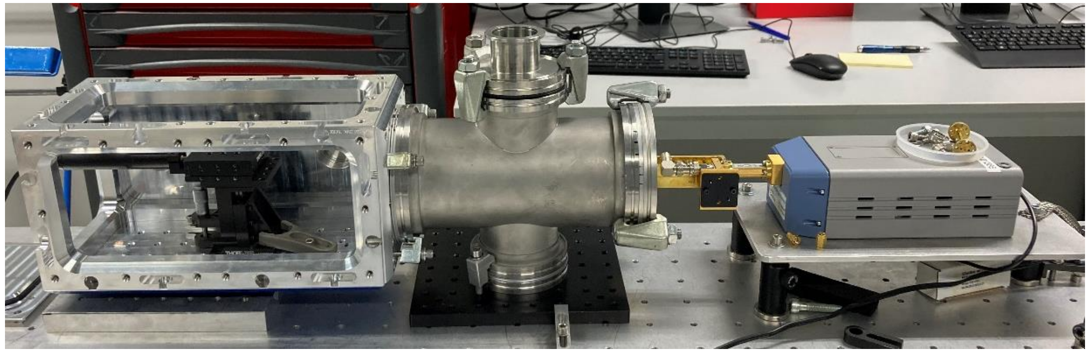


- Apply a larger current

  larger magnetic field means a better modulation

- Fabry-Perot Cavity

  => absorption will be increased by several orders of magnitude



Acknowledgement

Collaborators:

Institut des Sciences Moléculaires d'Orsay, France

Olivia Chitarra

Thomas Sandow Hearne

Marie-Aline Martin-Drumel

Olivier Pirali

Fabio Beccucci

Funding agencies: