Spectroscopie rotationelle et vibrationnelle d'espèces d'intérêt astrophysique en laboratoire

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université PARIS-SACLAY

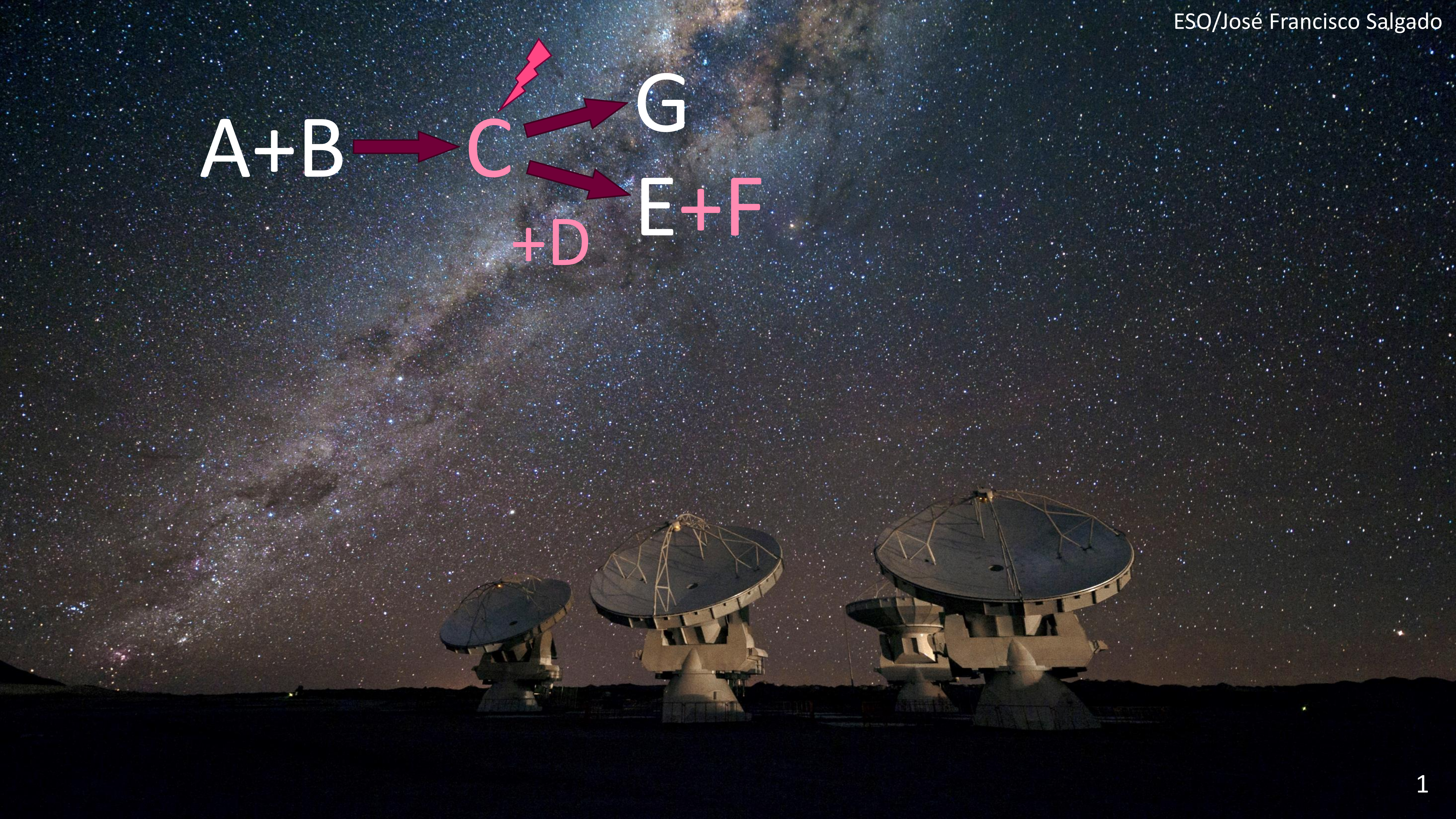
cnrs

SOLEIL SYNCHROTRON

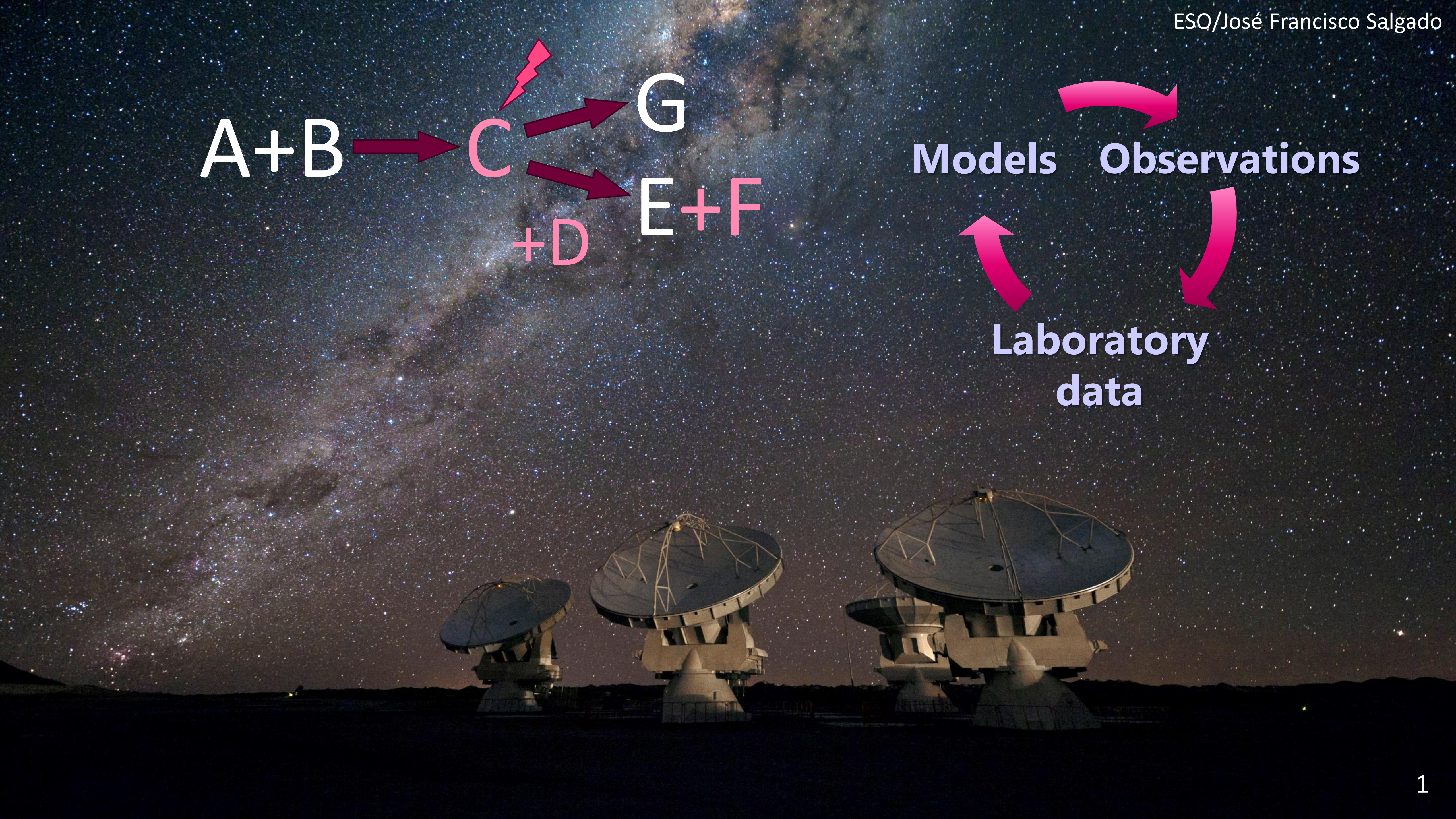
ISMO

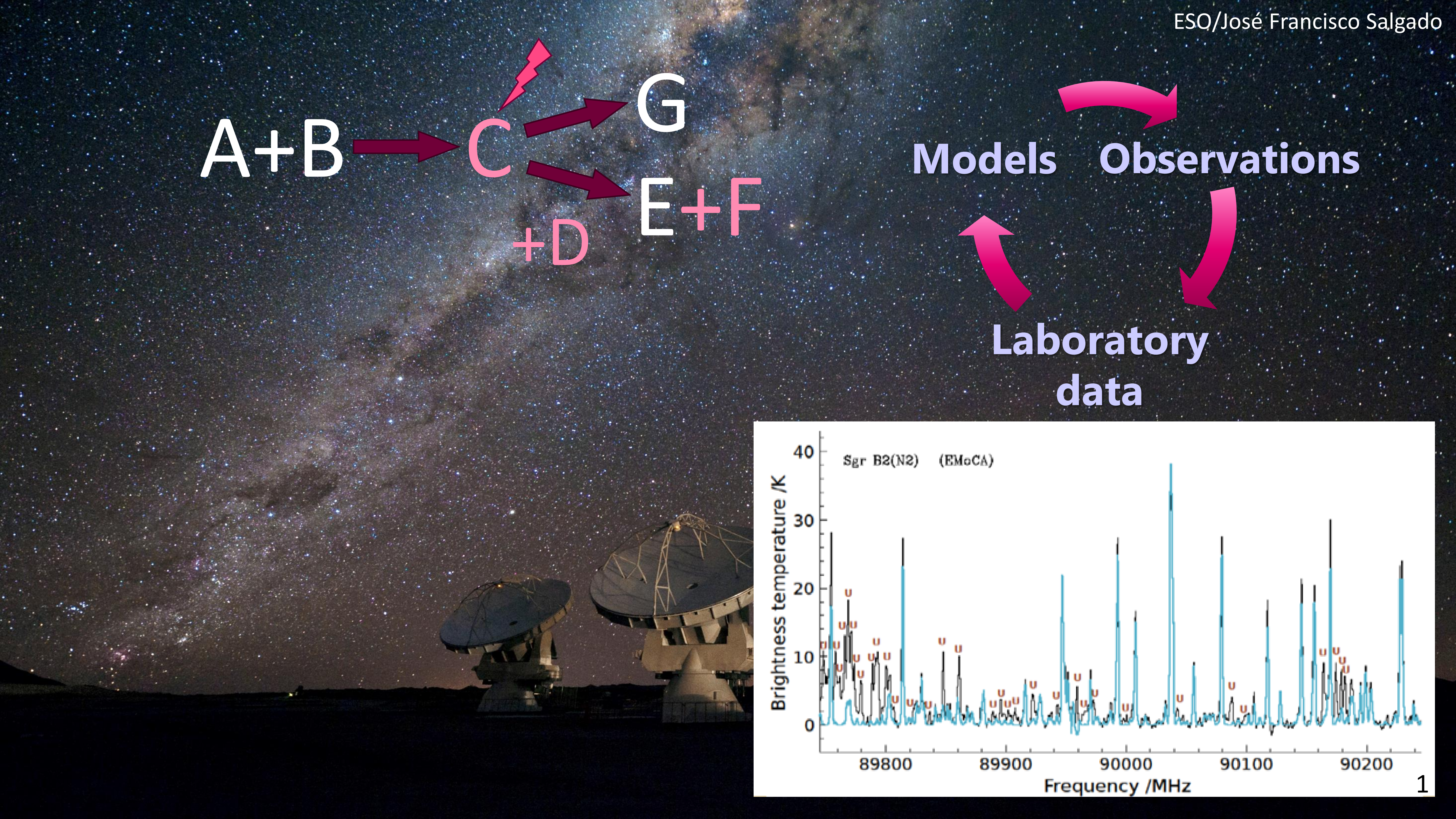
ÉCOLE DOCTORALE Ondes et Matière (EDOM)

Olivia Chitarra | ***November 16, 2021***



ESO/José Francisco Salgado


ESO/José Francisco Salgado
A+B
C
+D
G
E+F
Models
Observations
Laboratory
data


ESO/José Francisco Salgado
A+B
C
G
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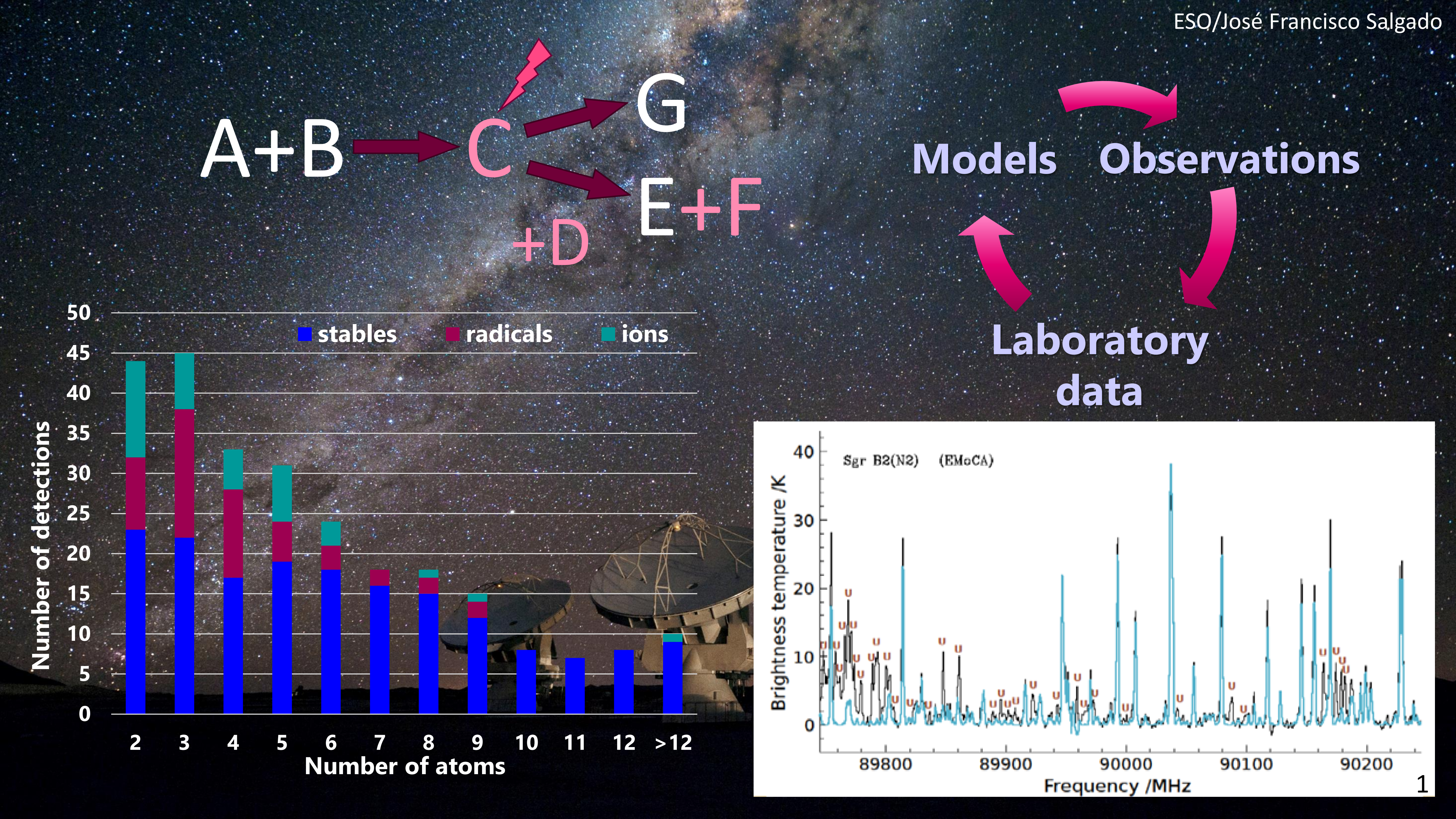
Models
Observations
Laboratory data
Sgr B2(N2) (EMoCA)
Brightness temperature /K
0
10
20
30
40
89800
89900
90000
90100
90200
Frequency /MHz
U


ESO/José Francisco Salgado
A+B → C → G
E+F
+D
Models
Observations
Laboratory data
stables
radicals
ions
Number of detections
Number of atoms
50
45
40
35
30
25
20
15
10
5
0
2
3
4
5
6
7
8
9
10
11
12
>12
Sgr B2(N2) (EMoCA)
Brightness temperature /K
Frequency /MHz
40
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89800
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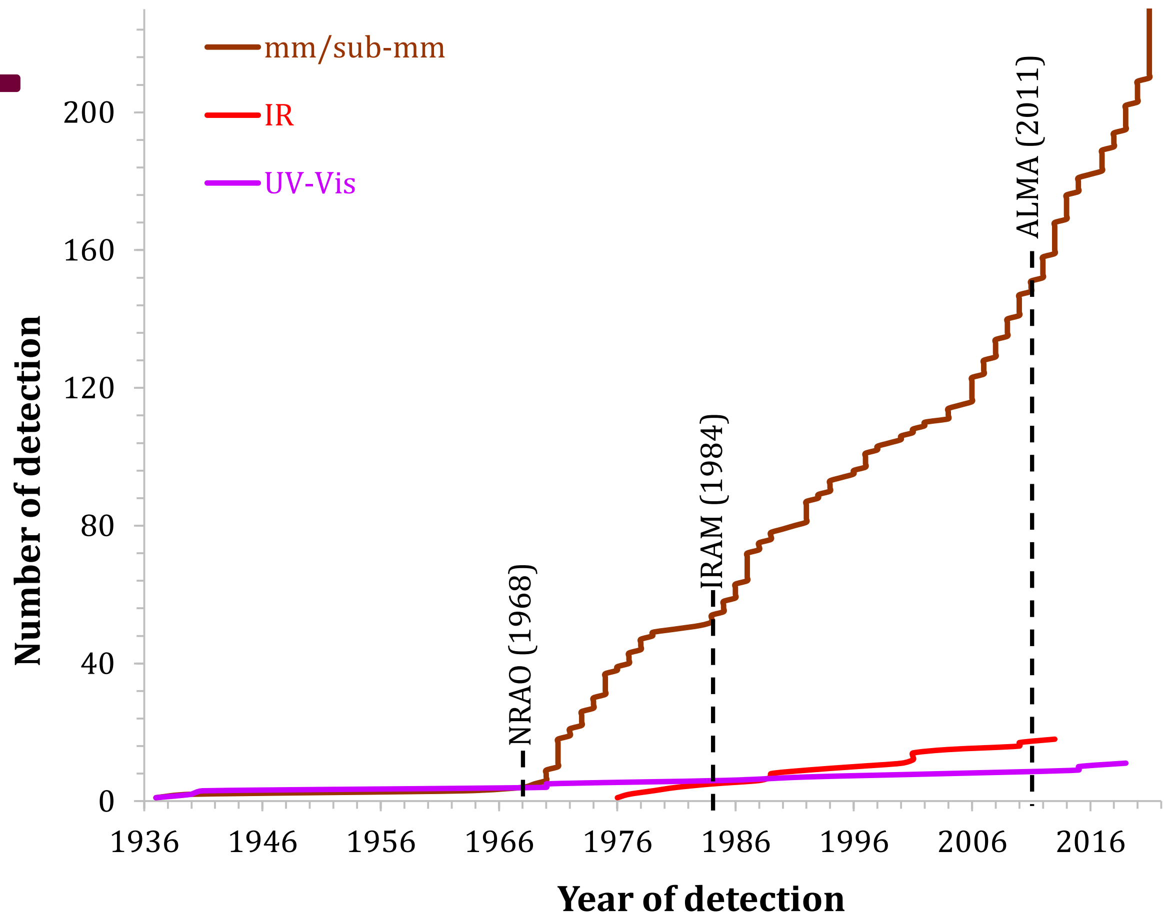
1

High Resolution Spectroscopy in the lab



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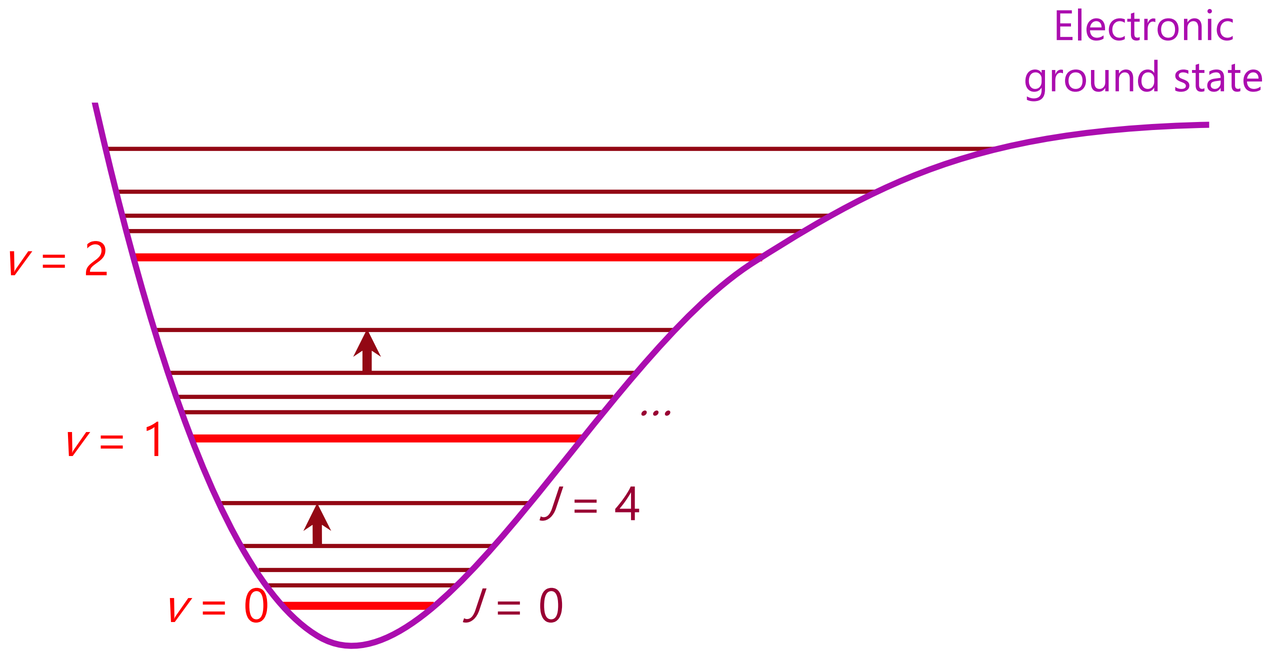

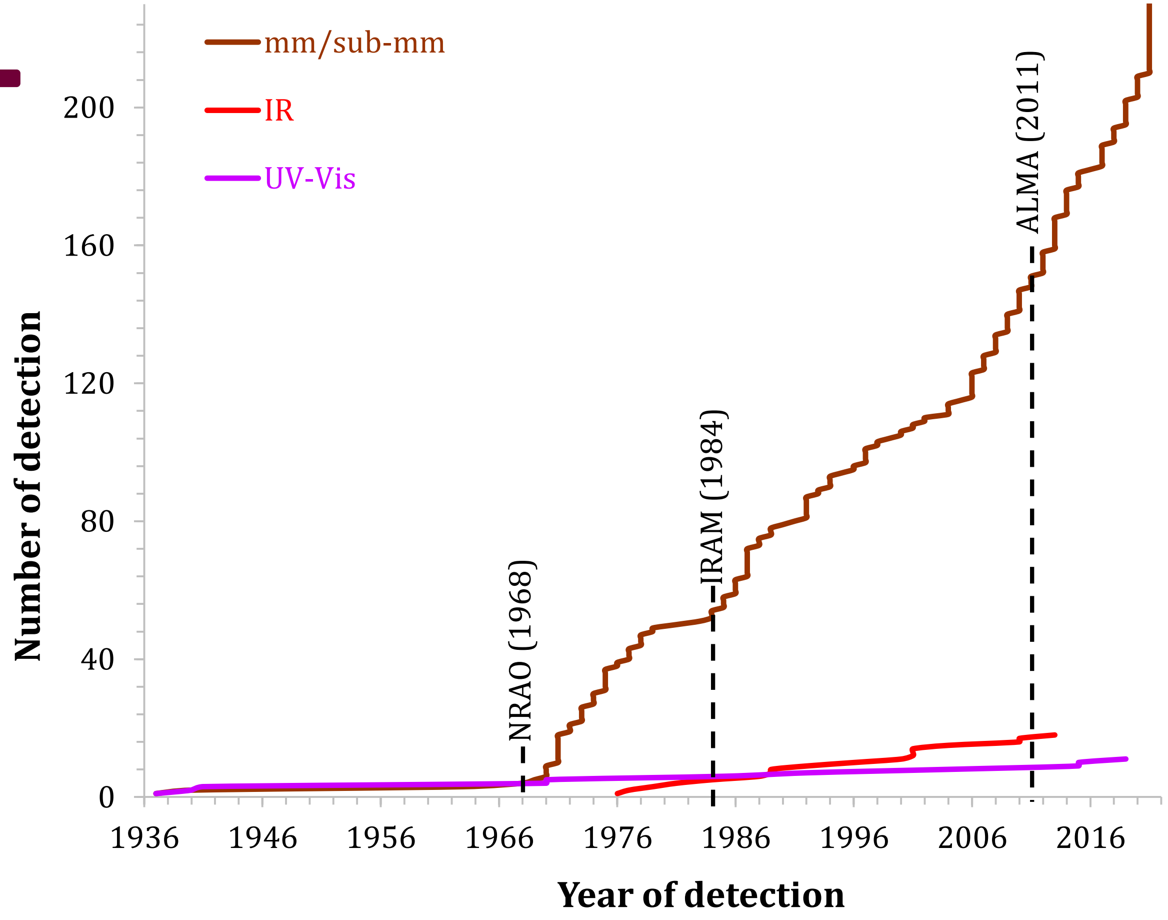

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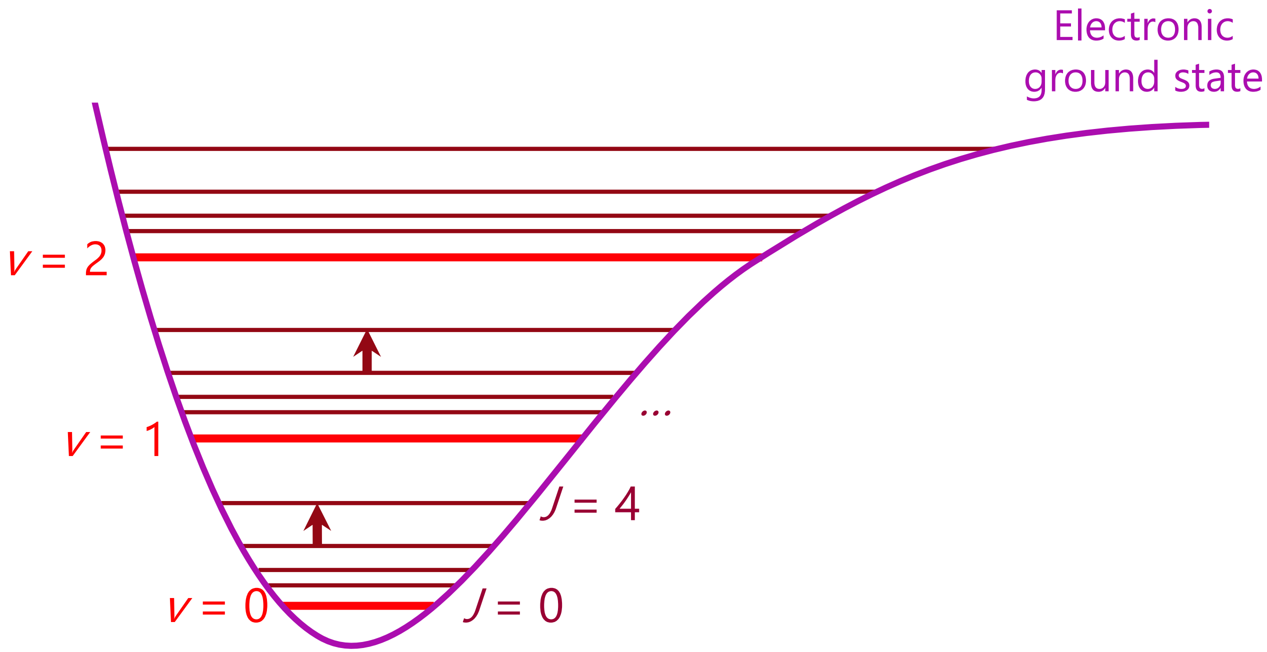
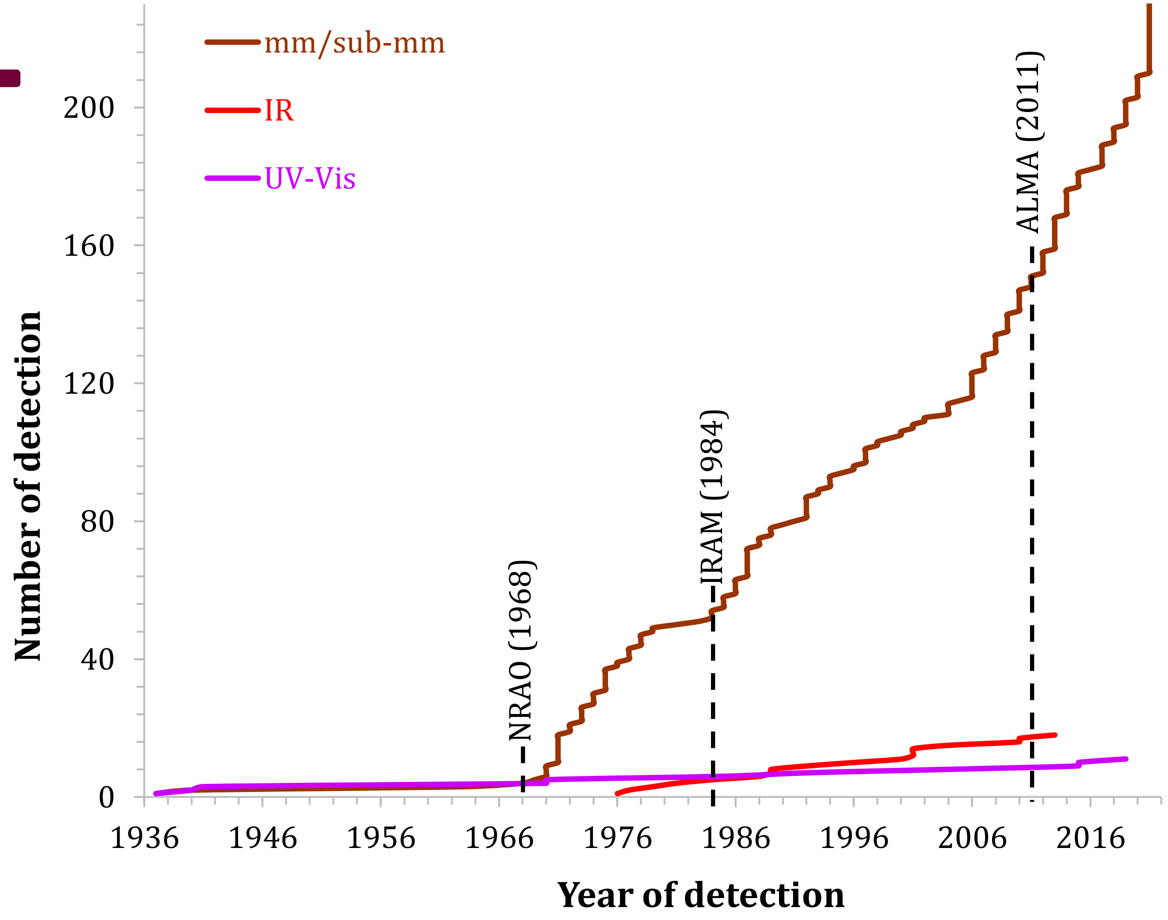




centimeter wave | millimeter wave | far infrared | infrared | visible | UV

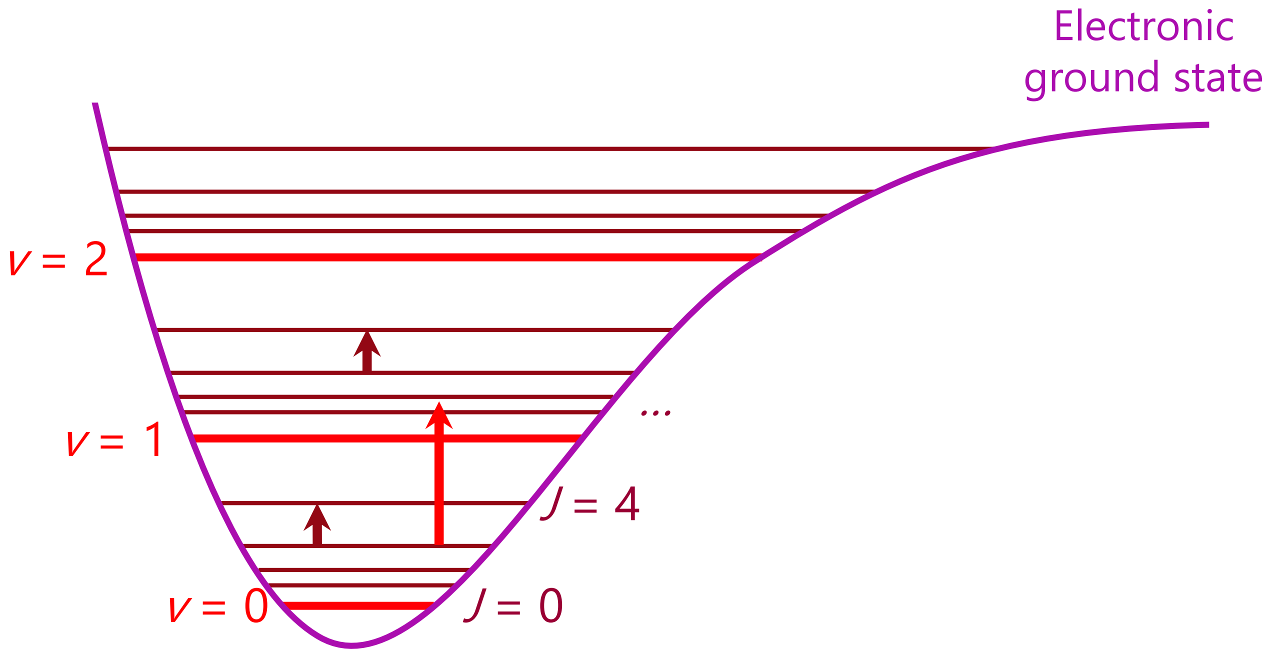
75 – 900 GHz

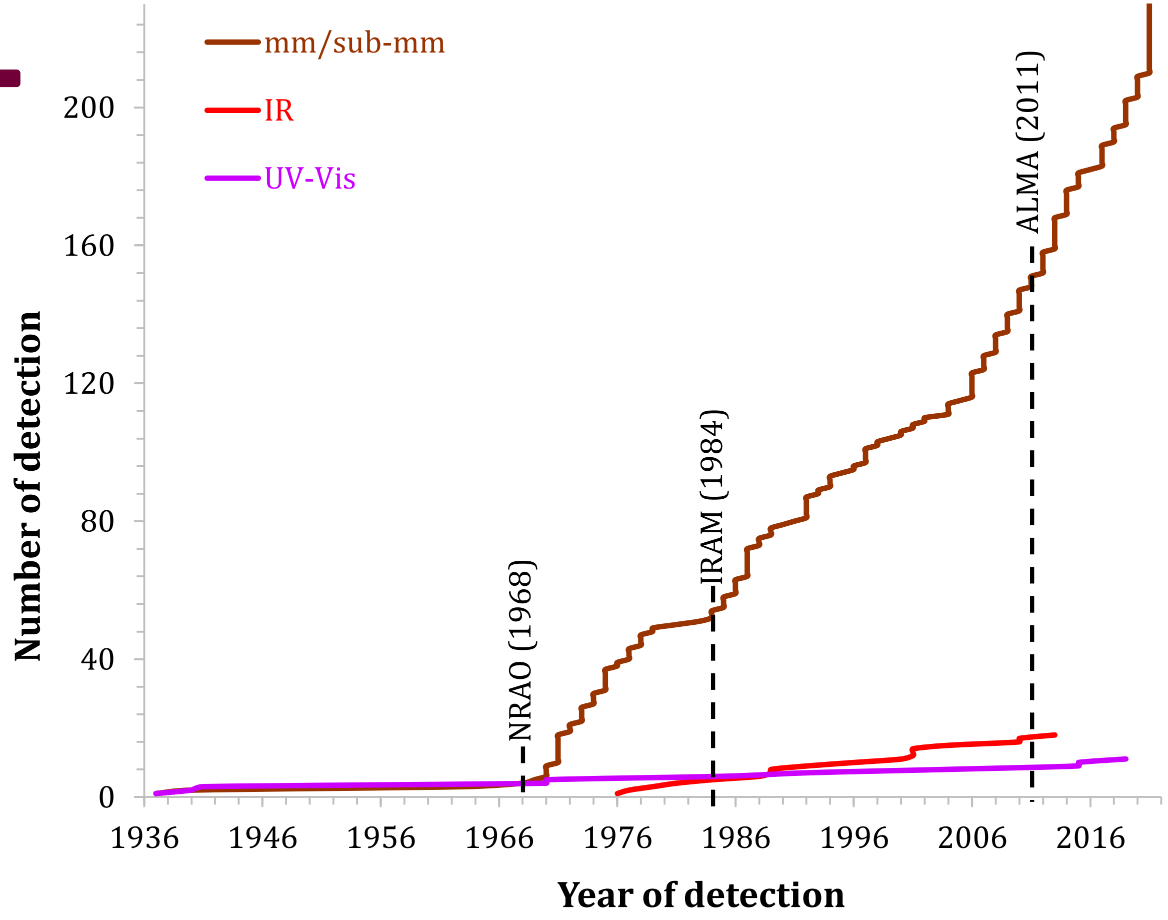
0.3 – 4 mm

2.7 – 31.7 cm^{-1}

$3.3e^{-4}$ – $3.9e^{-3}$ eV

High Resolution Spectroscopy in the lab





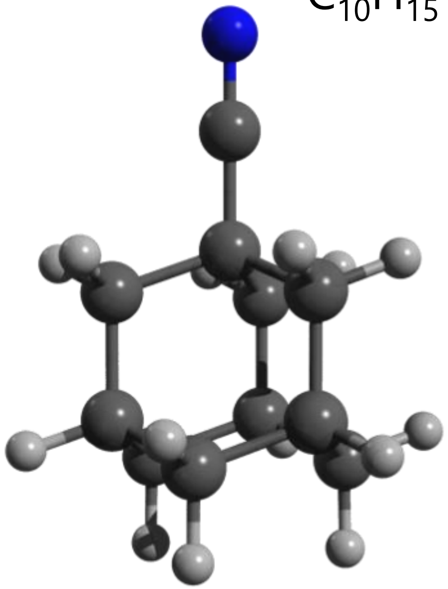
centimeter wave | millimeter wave | far infrared | infrared | visible | UV

75 – 900 GHz
0.3 – 4 mm
2.7 – 31.7 cm^{-1}
3.3e^{-4} – 3.9e^{-3} eV

5 – 1500 cm^{-1}
2,94e^{-3} – 0,2 mm
1500 – 101 930 GHz
6,2e^{-3} – 4,2e^{-1} eV

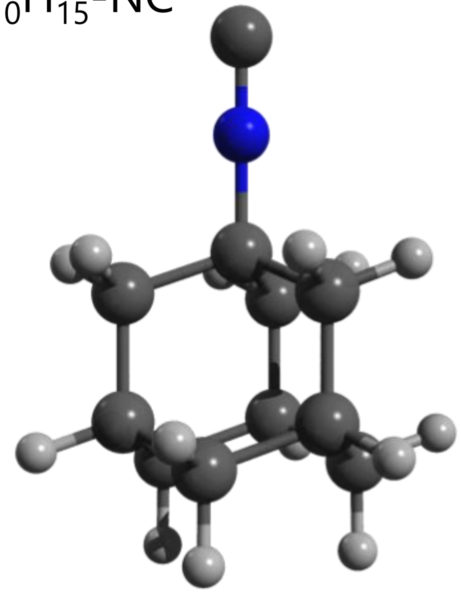
High Resolution Spectroscopy in the lab

$C_{10}H_{15}$-CN



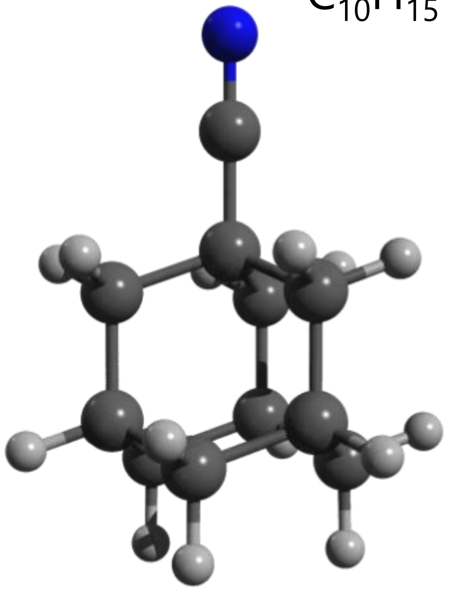
CyanoAdamantane

$C_{10}H_{15}$-NC



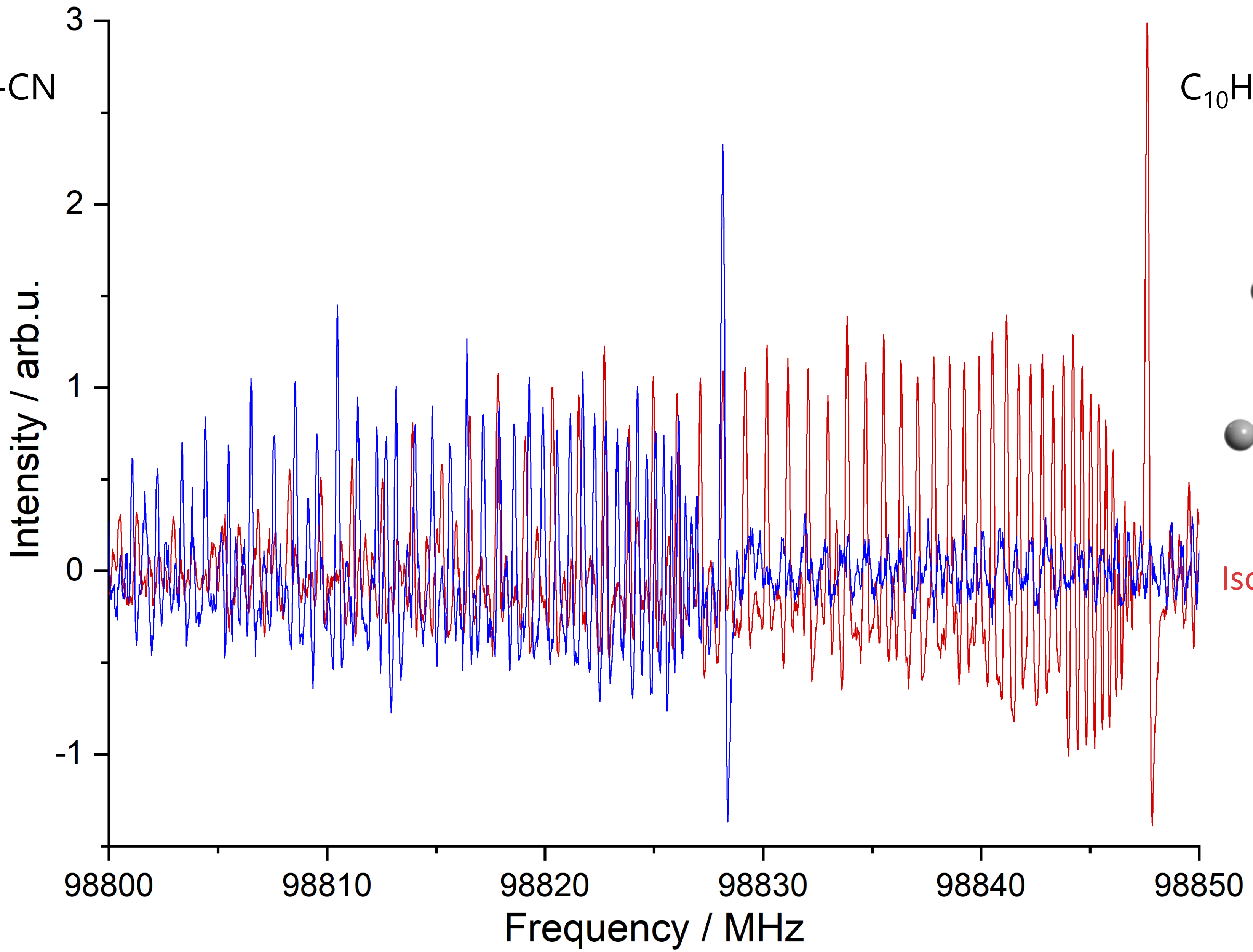
IsocyanoAdamantane

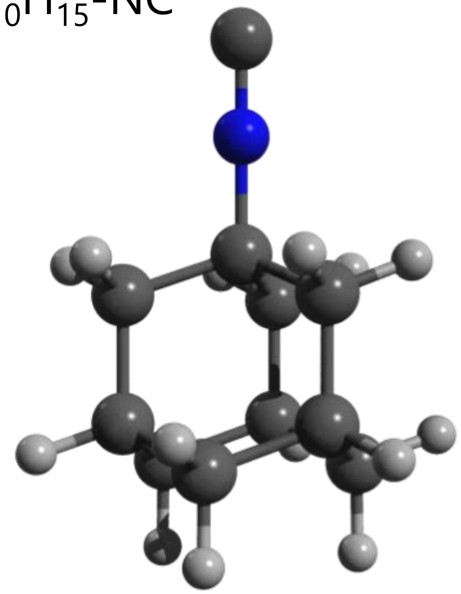
High Resolution Spectroscopy in the lab



$C_{10}H_{15}$-CN

CyanoAdamantane





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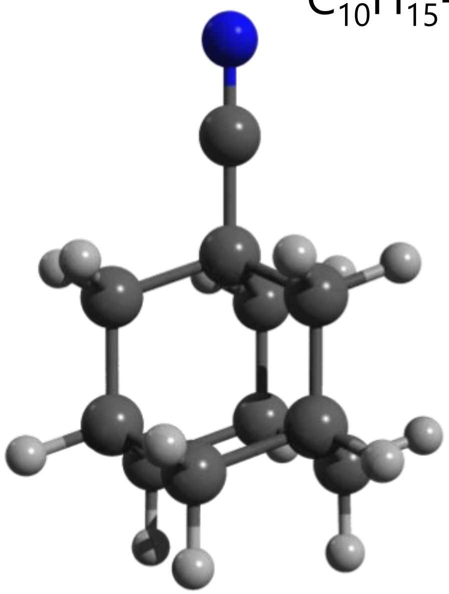

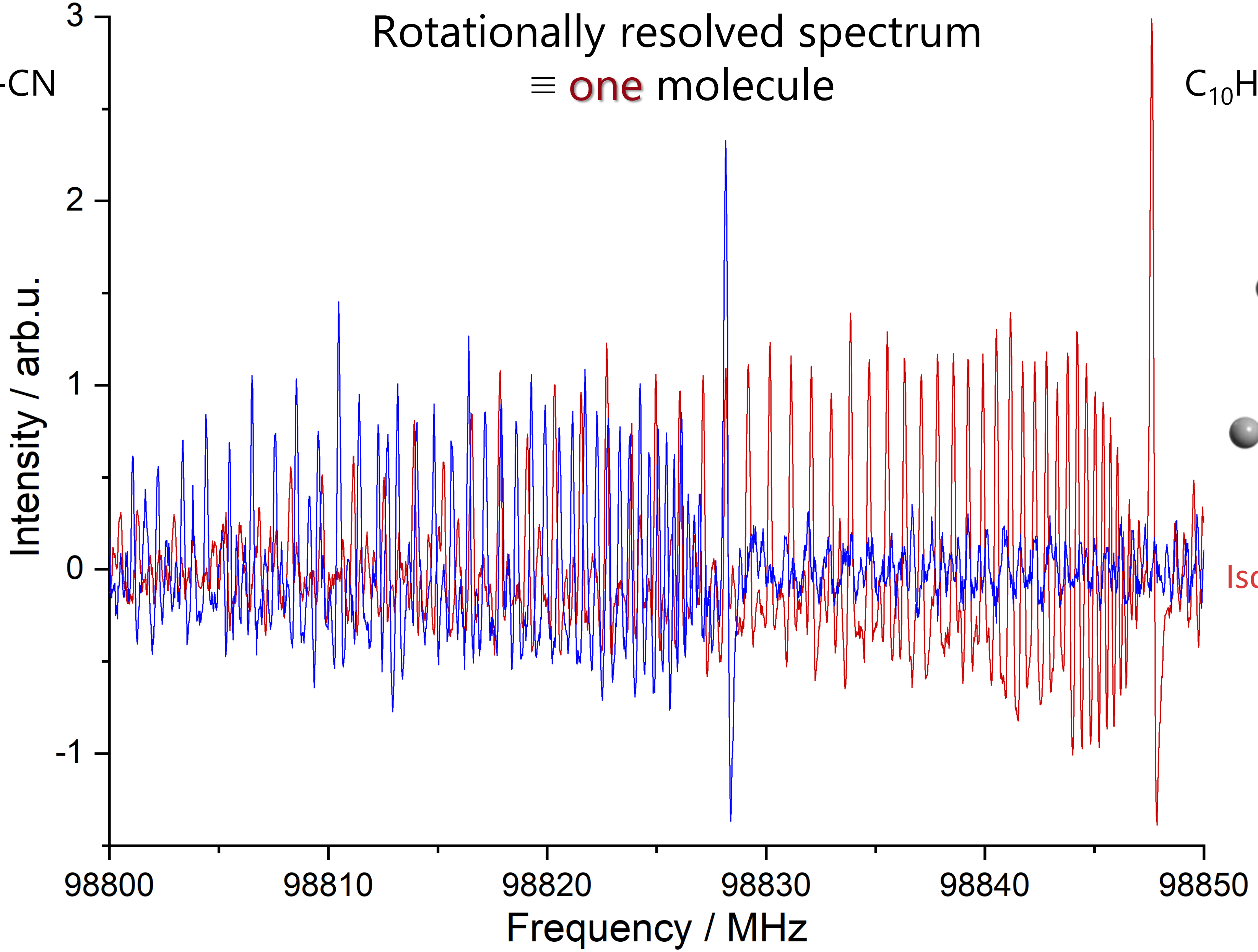

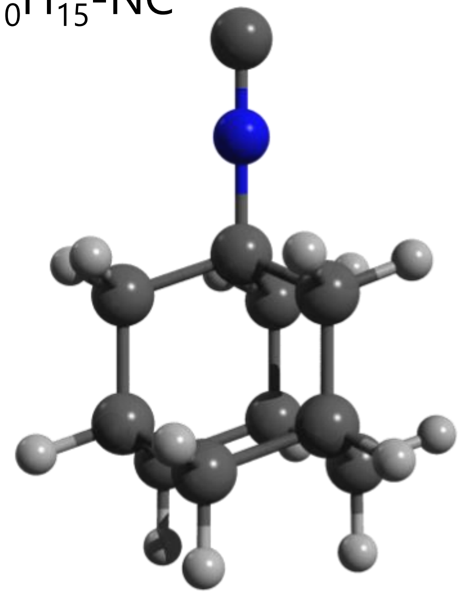

ISMO

ESO/José Francisco Salgado

Chirped-pulse millimeter-wave spectrometer
75 - 110 GHz

+ Broadband
+ Fast
+ High sensitivity
- Limited spectral range
- Limited resolution

Frequency-multiplication-based (sub)millimeter-wave spectrometer
75 - 900 GHz

+ High spectral range
+ High resolution
- Monofrequency
- Slow

ESO/José Francisco Salgado

Chirped-pulse millimeter-wave spectrometer
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Room temperature flow cell

DC discharge + flow cell

RF discharge + flow cell

H abstraction + flow cell

DC discharge + supersonic jet

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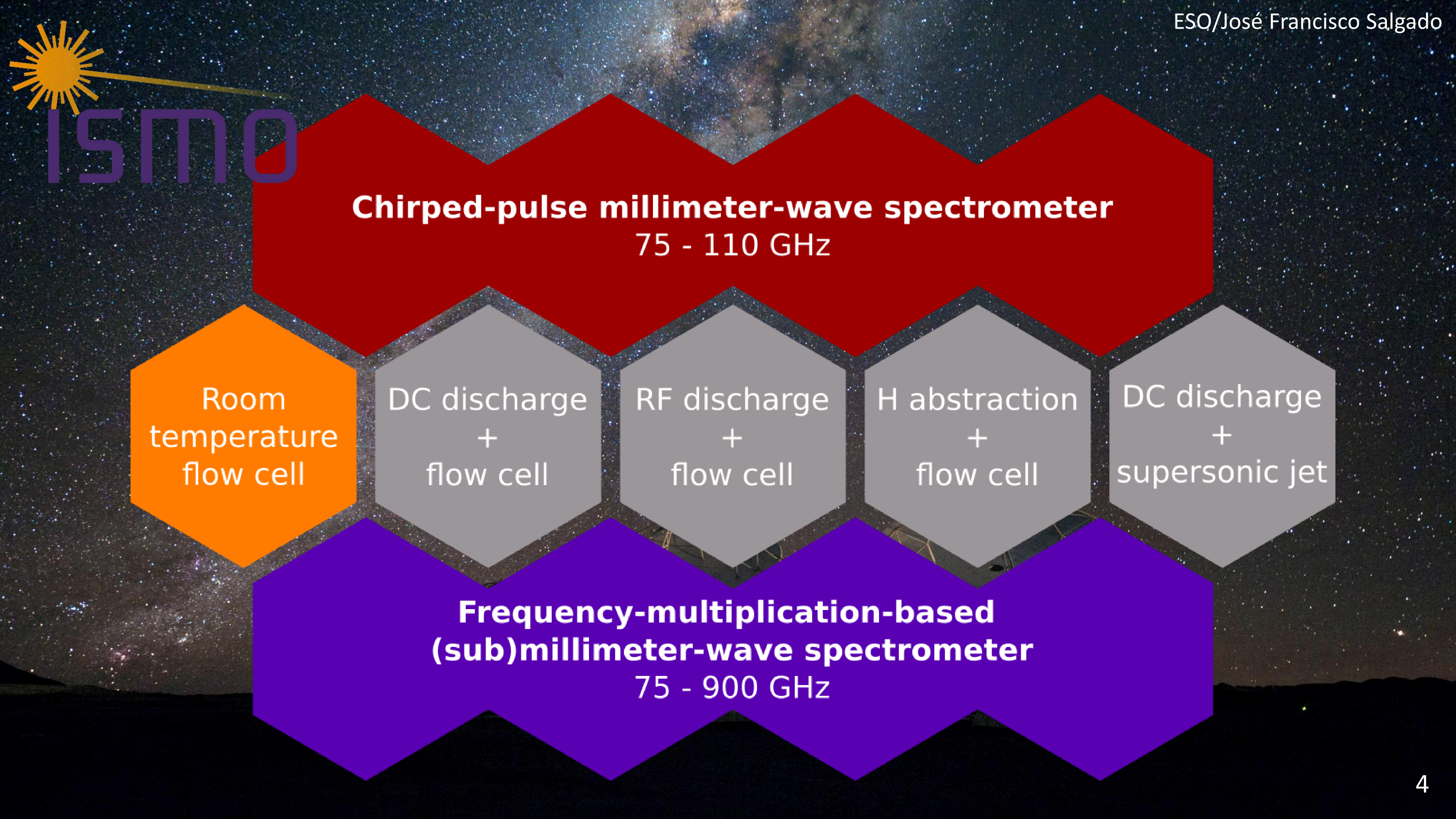

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Study of stable molecules

- Quantum chemical calculation
- Experimental measurement of spectra
- Spectral analysis
- Fit of rotational parameters
- Search for the molecule in the ISM

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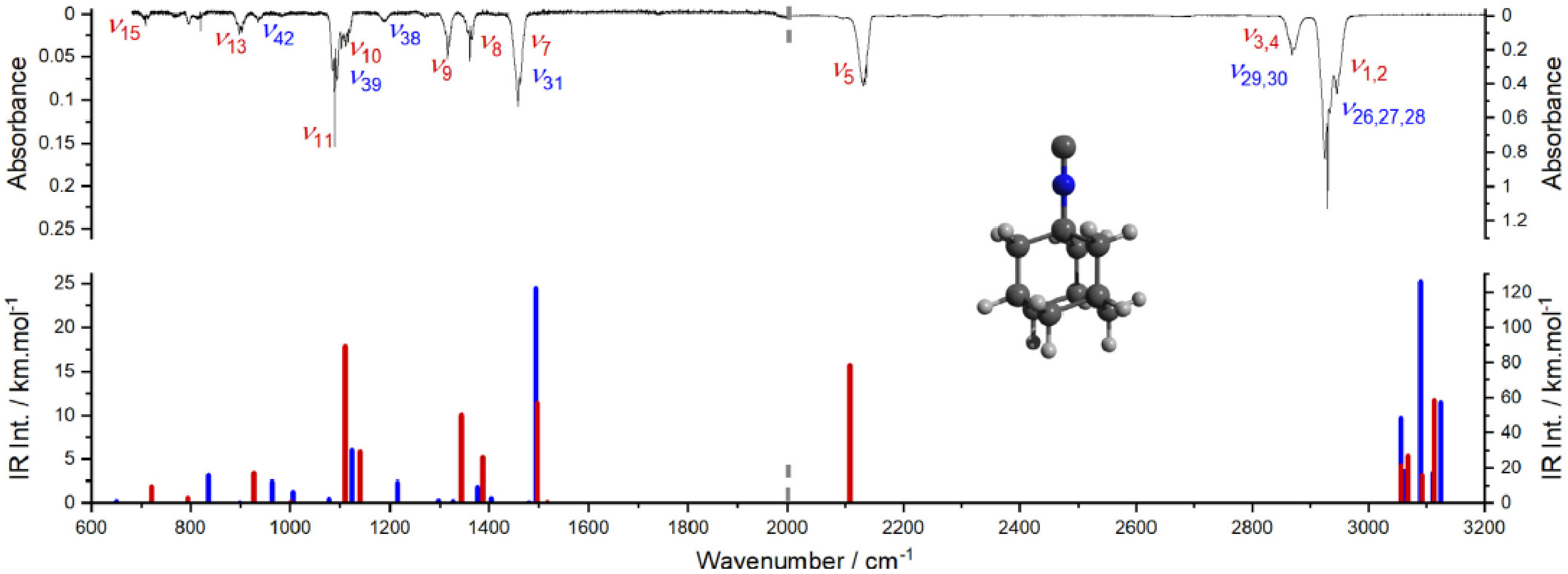

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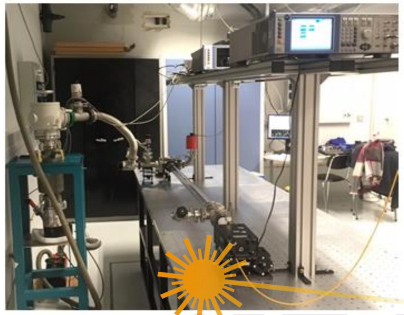
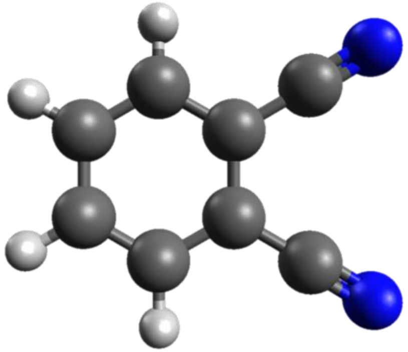
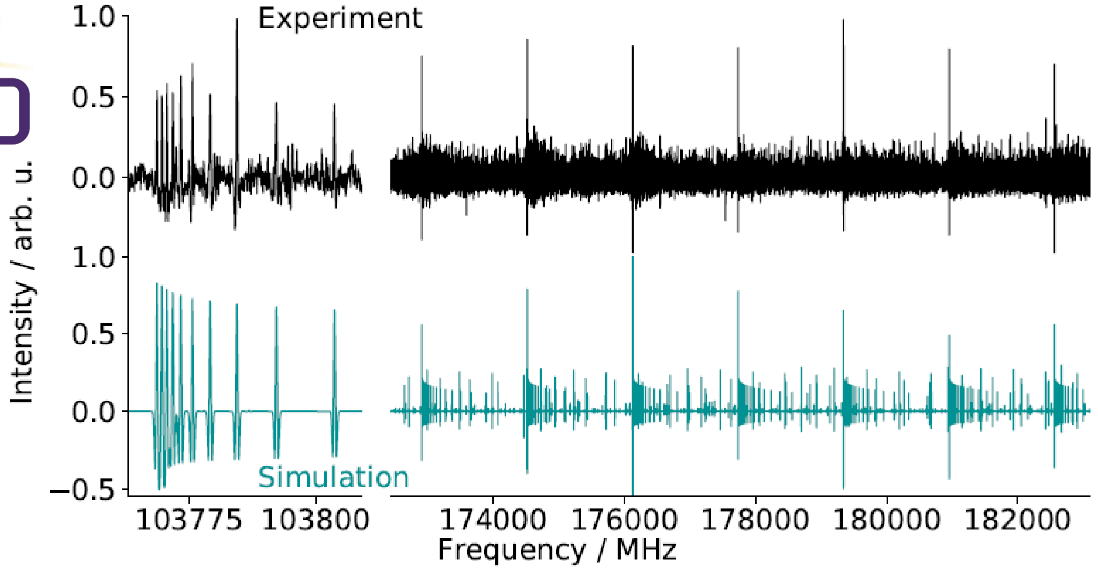
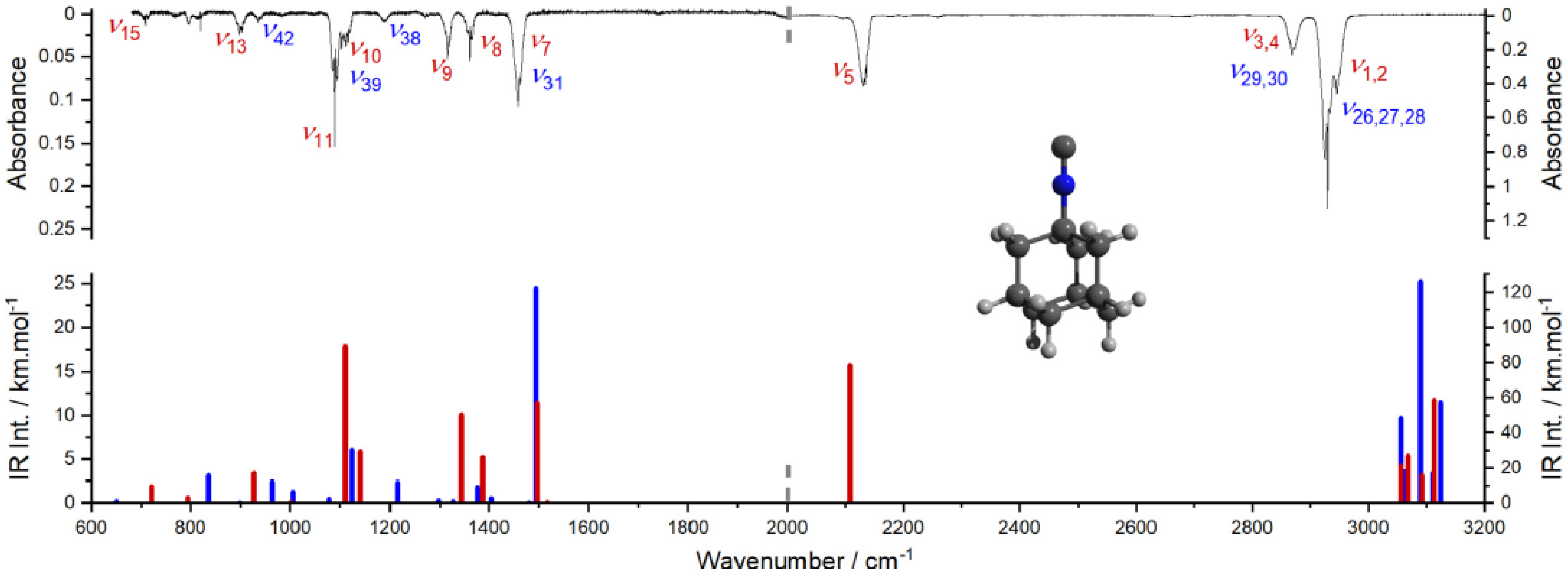


ISMO





SOLEIL SYNCHROTRON



Study of stable molecules

O. Chitarra et al., *J. mol. Spec.*, 378, 111468, 2021
O. Chitarra et al., *A&A.*, 652, A163, 2021

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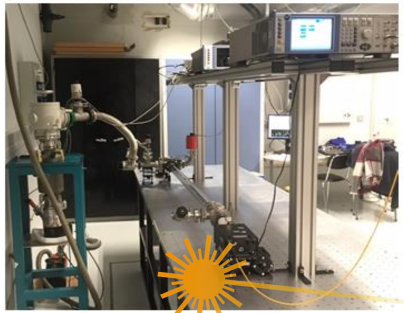

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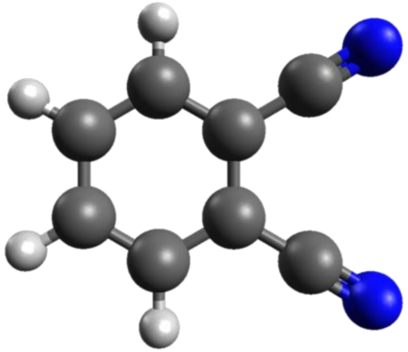

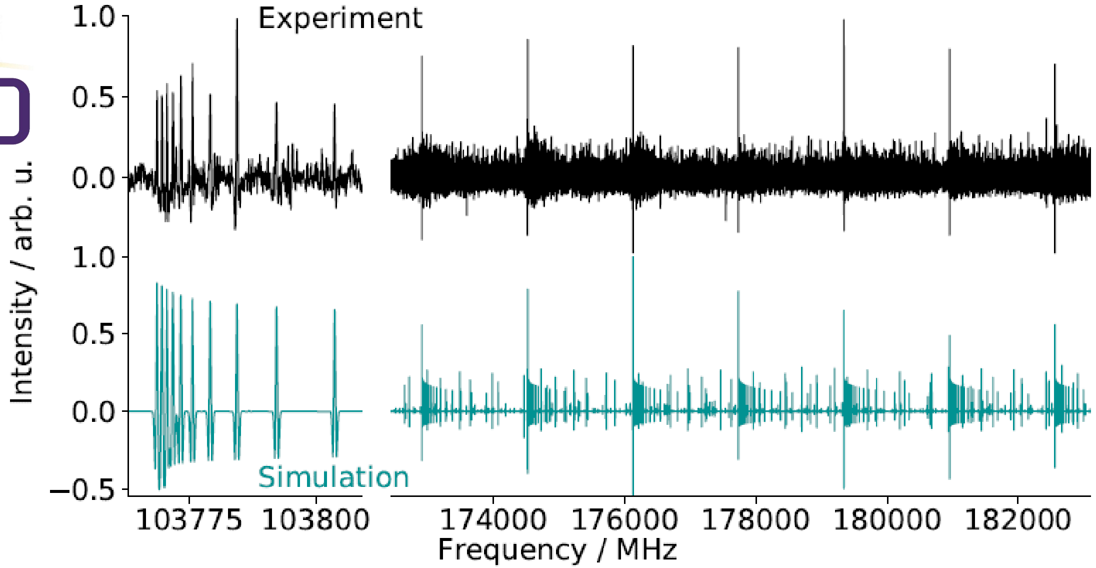

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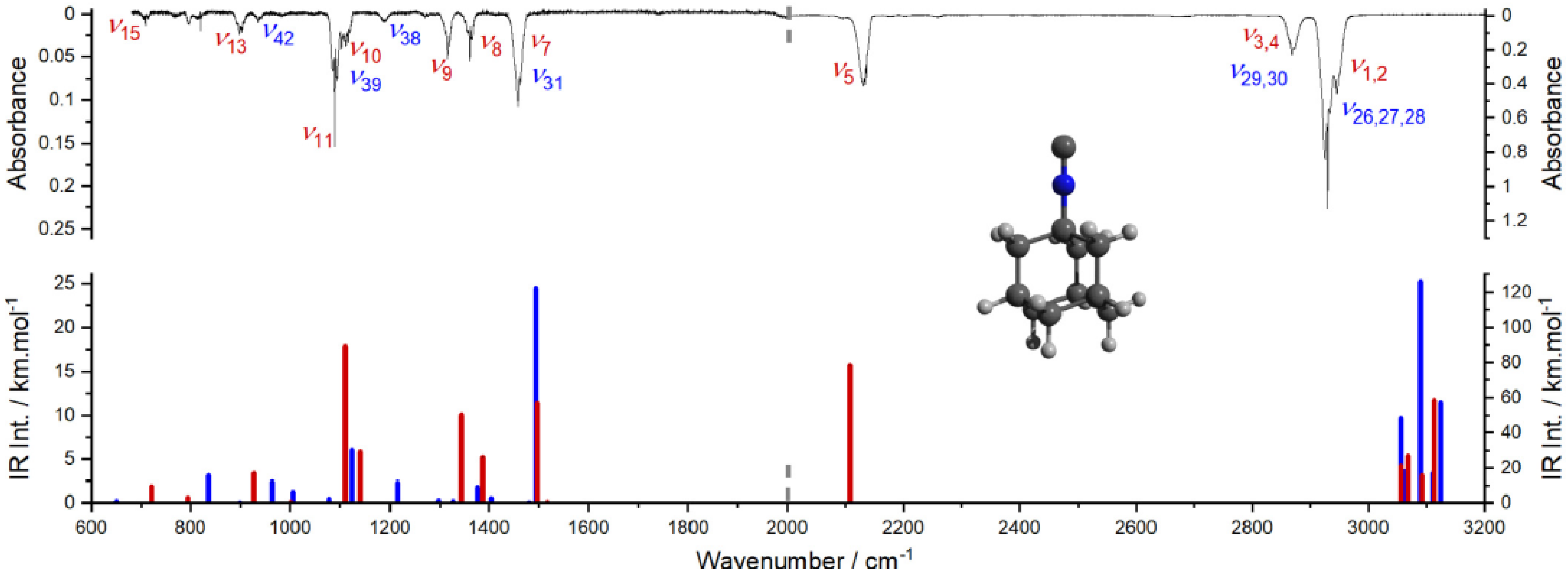

ESO/José Francisco Salgado

Chirped-pulse millimeter-wave spectrometer
75 - 110 GHz

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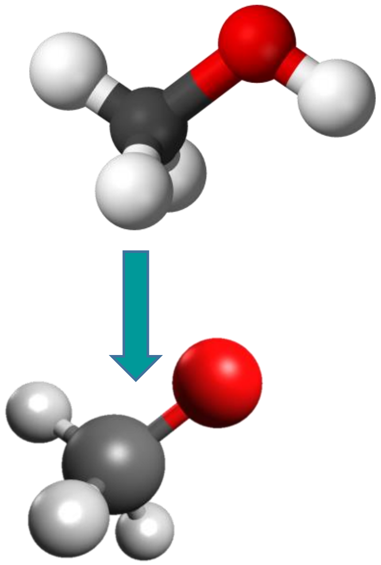
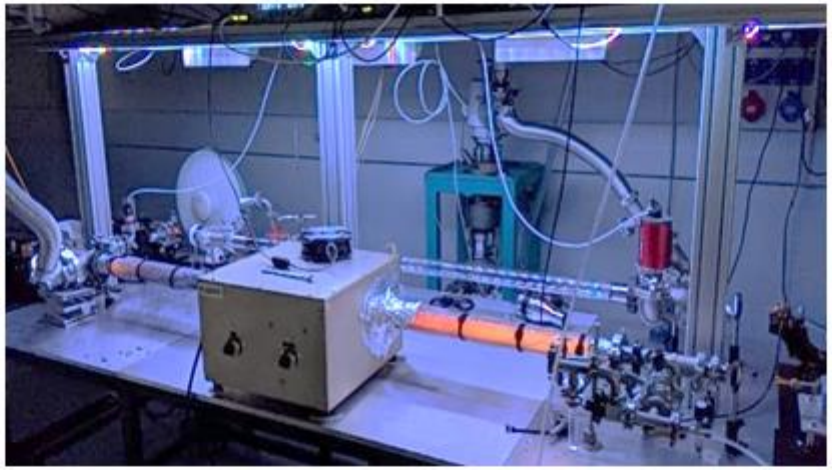
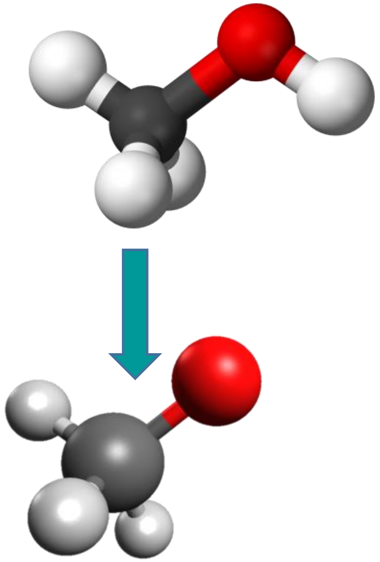
Study of reactive species



Study of reactive species

RF discharge

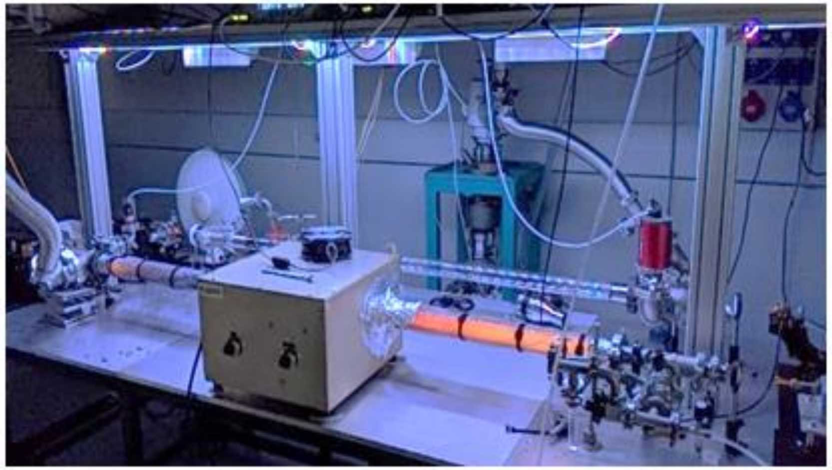




- Non specific method
- (Very) weak signal of radicals

Study of reactive species

RF discharge



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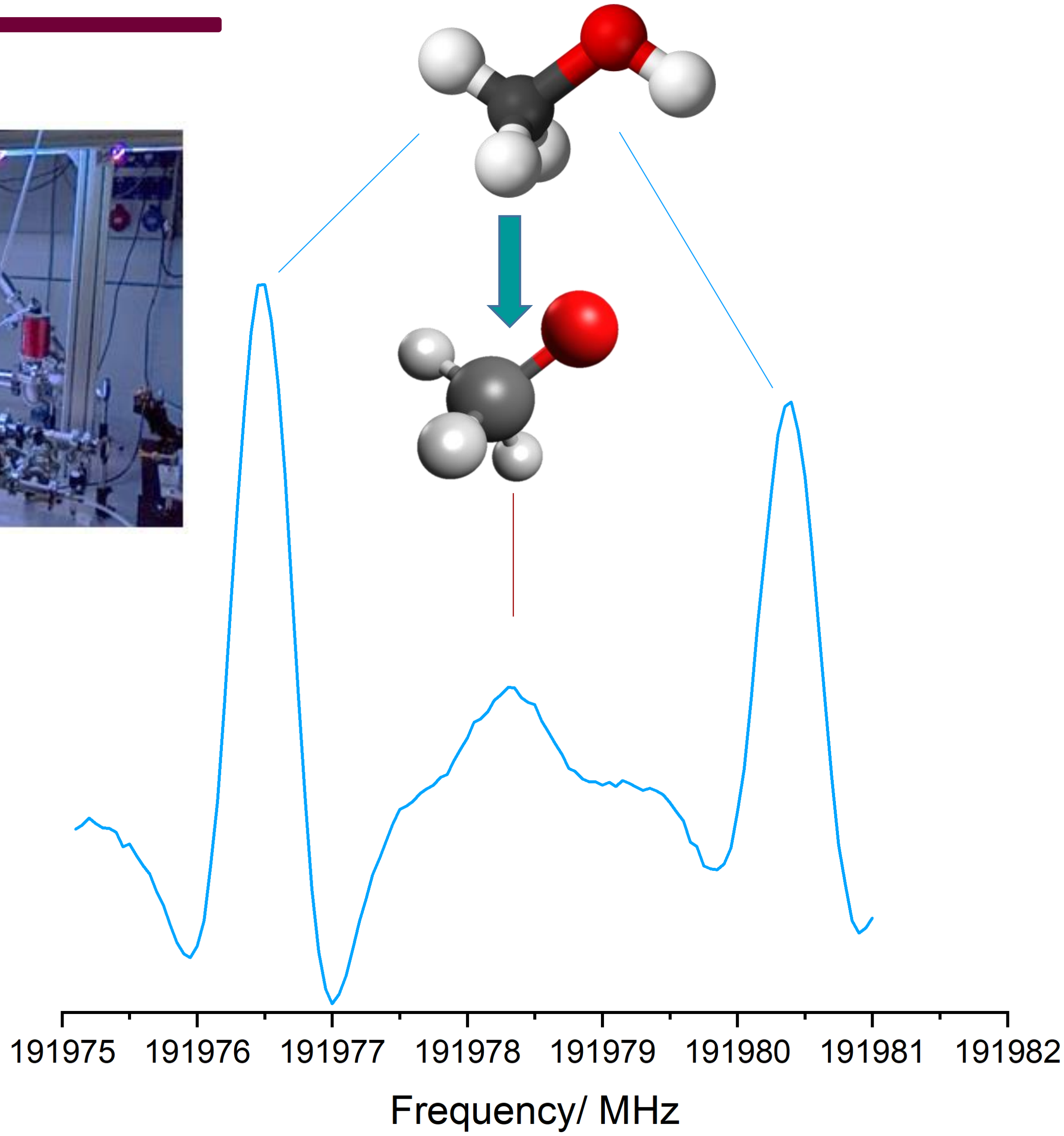

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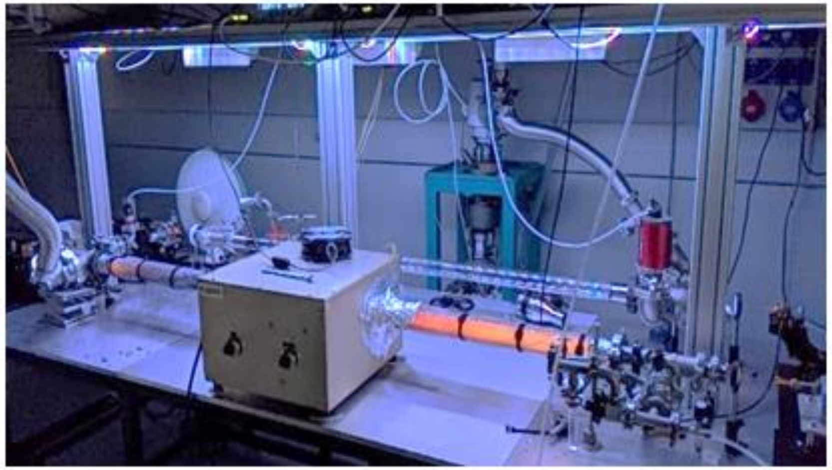

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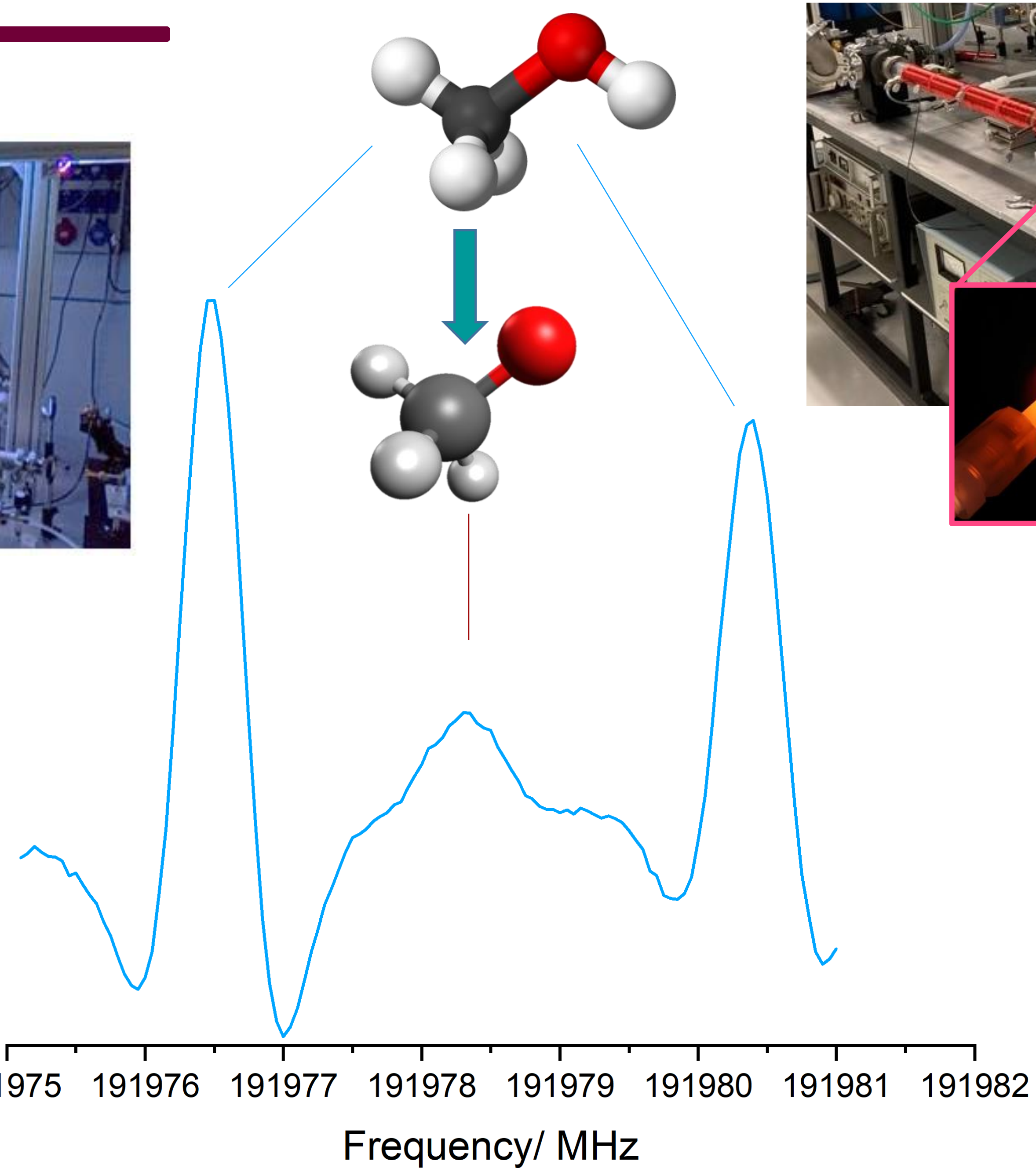
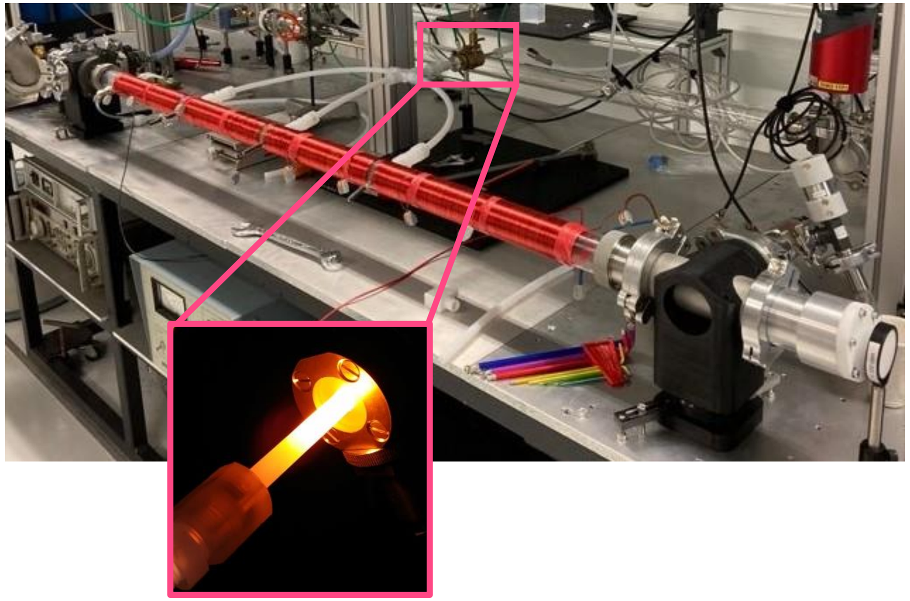


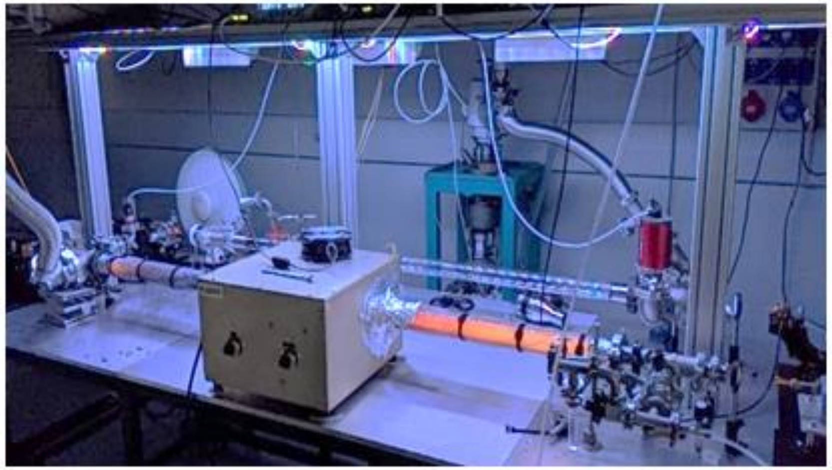
H abstraction



- Selective method
- Limited SNR
- More dangerous

Study of reactive species

RF discharge



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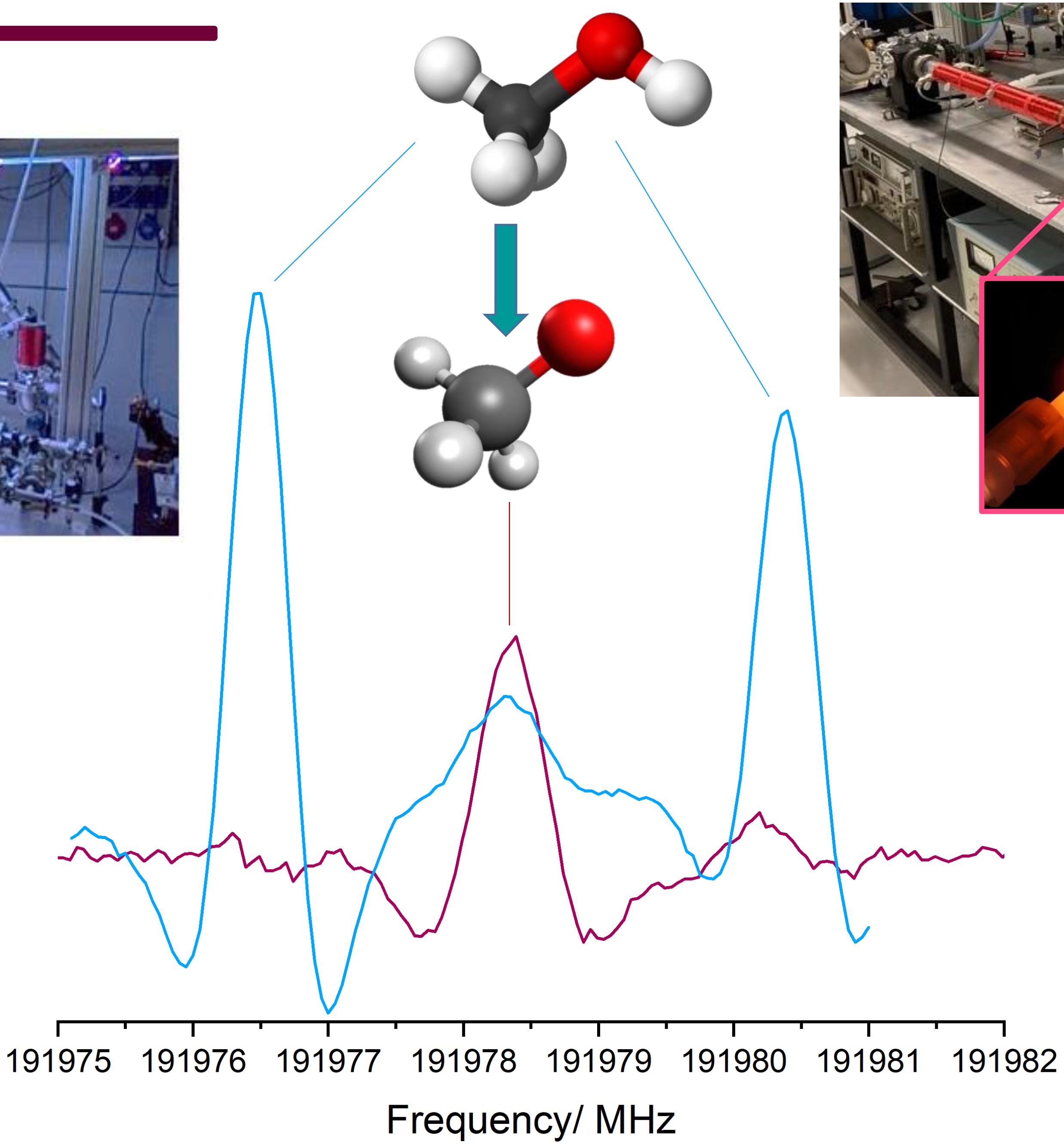

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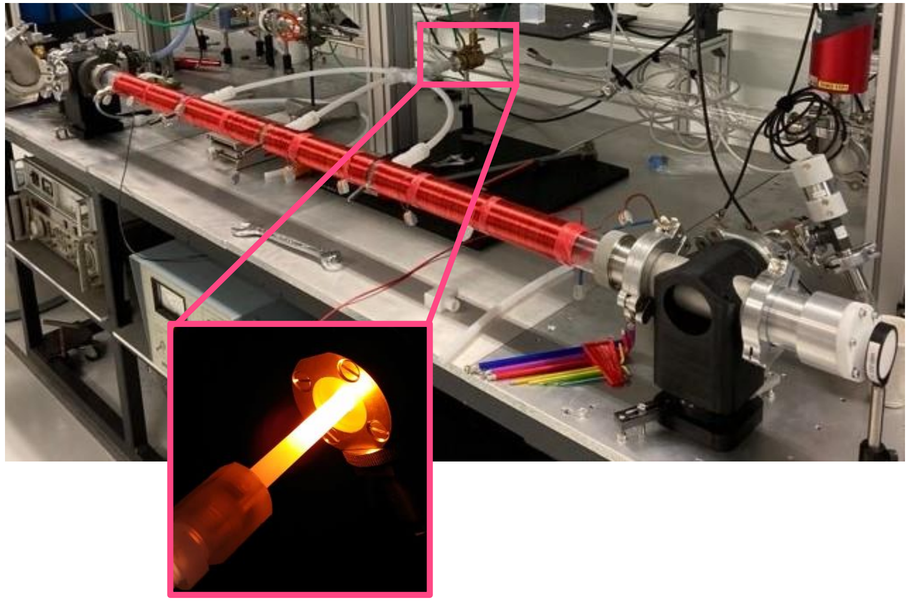

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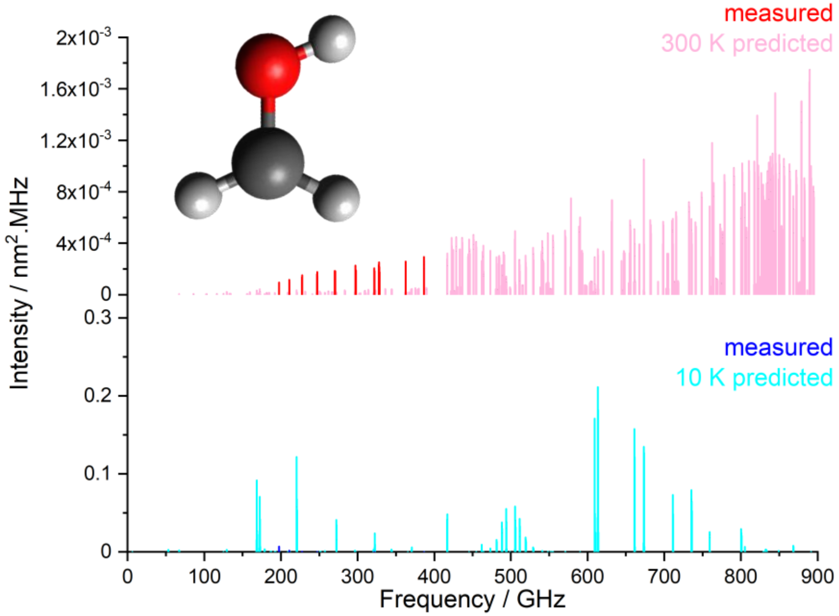
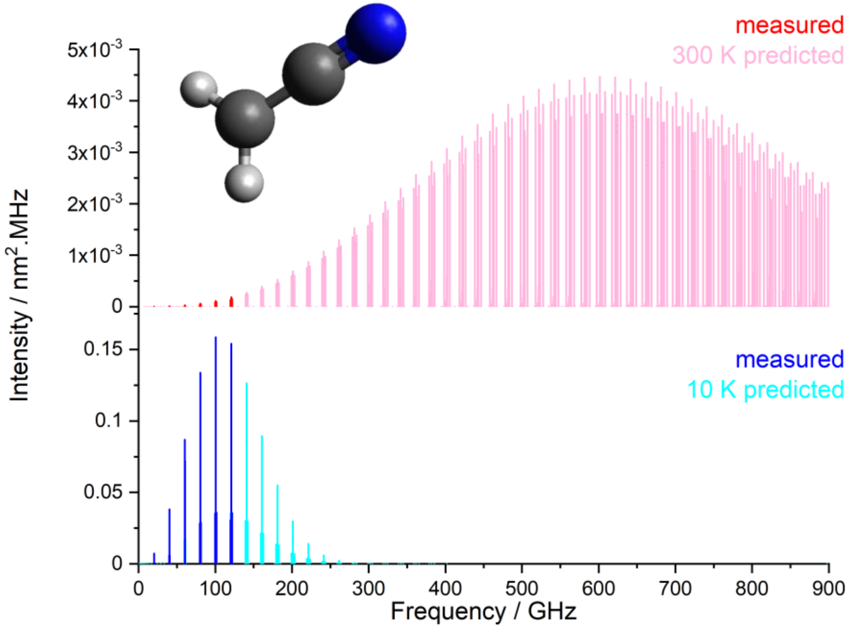
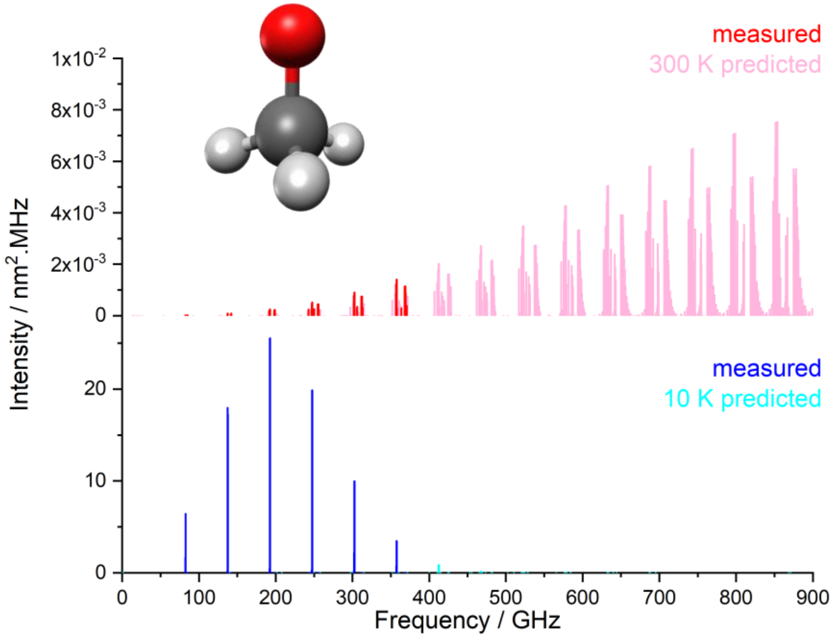


Bermudez, C., et al., 2017



Saito, S., et al., 1997
Ozeki, H., et al., 2004



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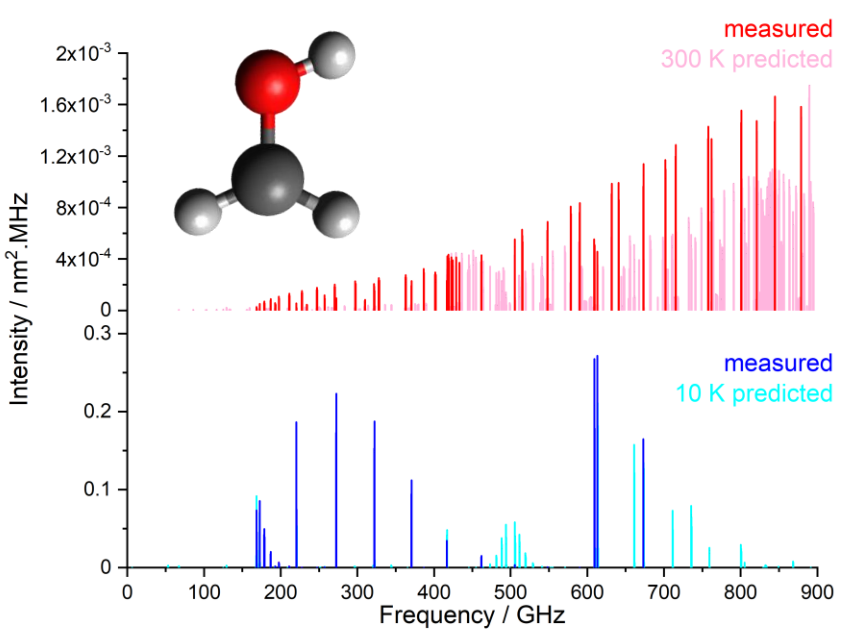

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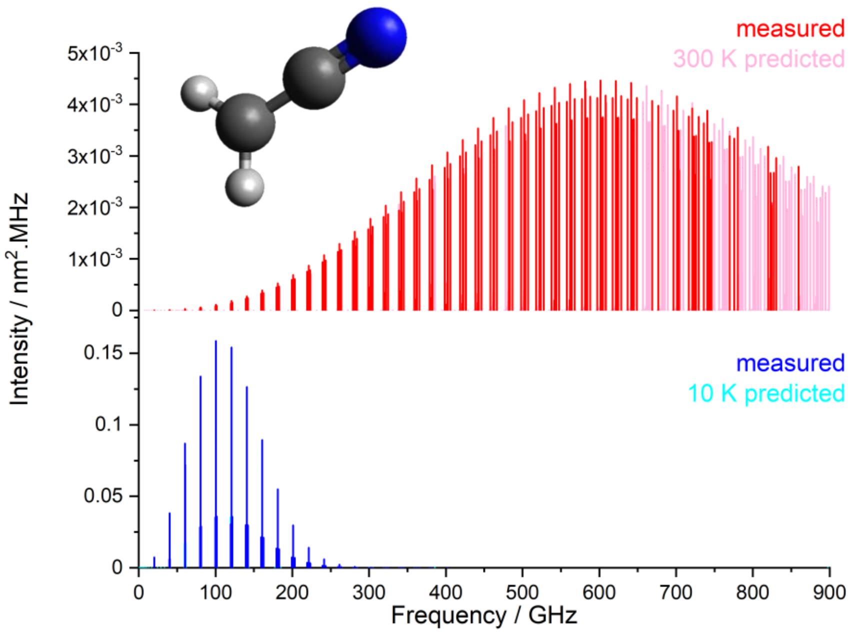

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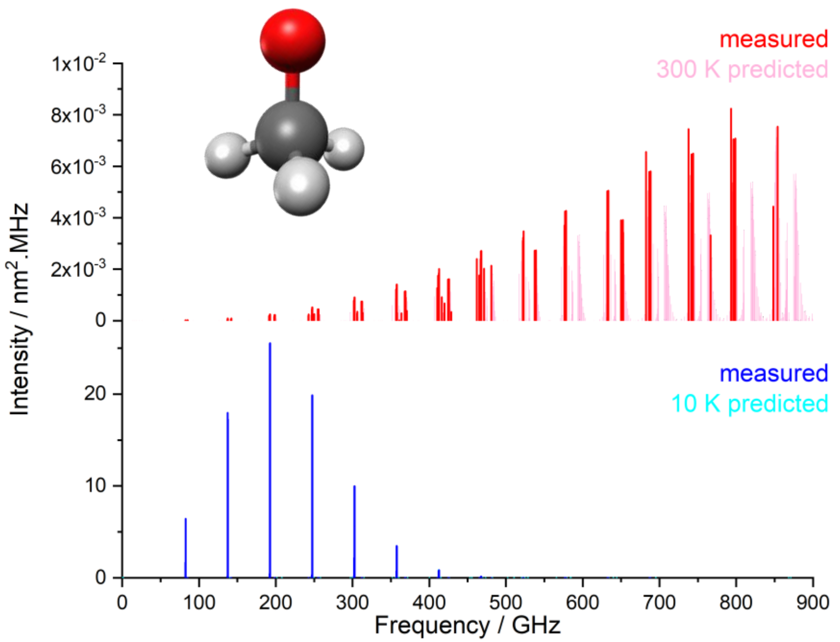

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❑ Advantages

- Selective method of production of radicals
- Measurement up to 900 GHz
- High spectral resolution

❑ Limitations

- Room temperature measurement
- Line by line measurement
- Limited sensitivity

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Chirped-pulse millimeter-wave spectrometer
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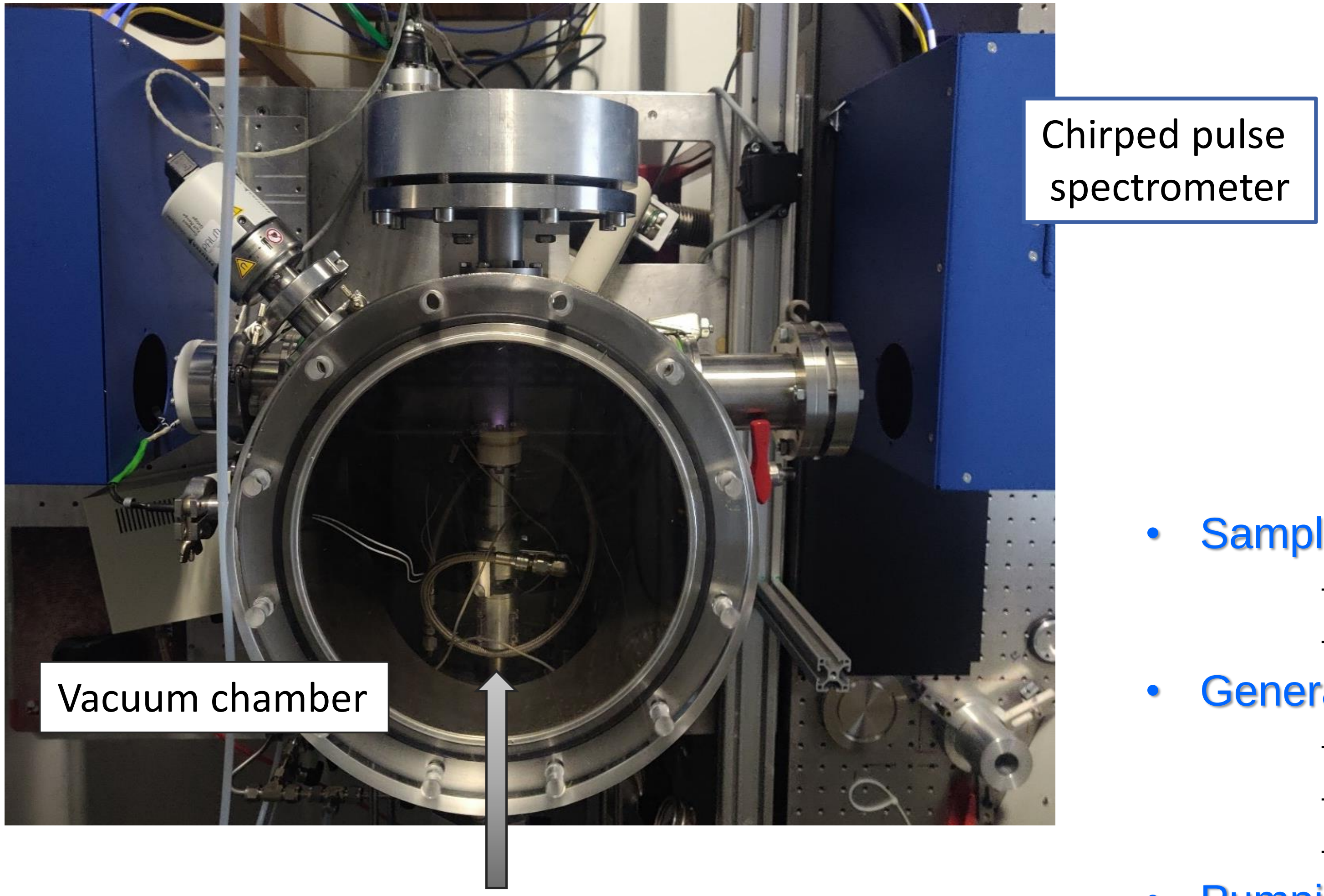
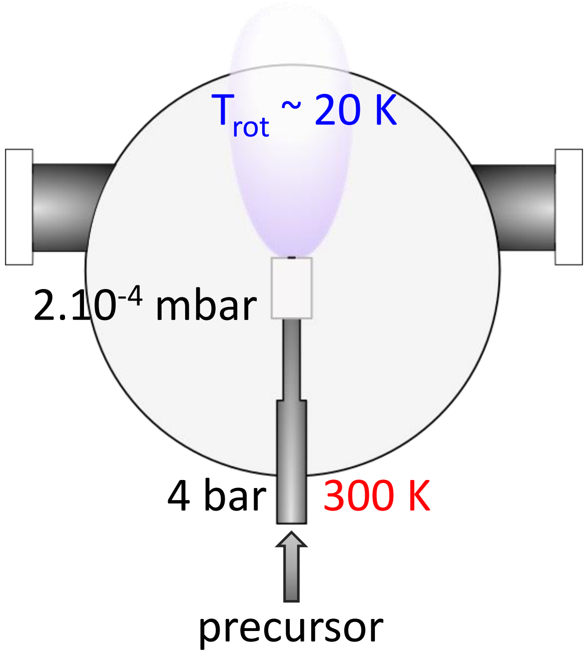
Pulsed jet discharge experiment

Injection Discharge Detection



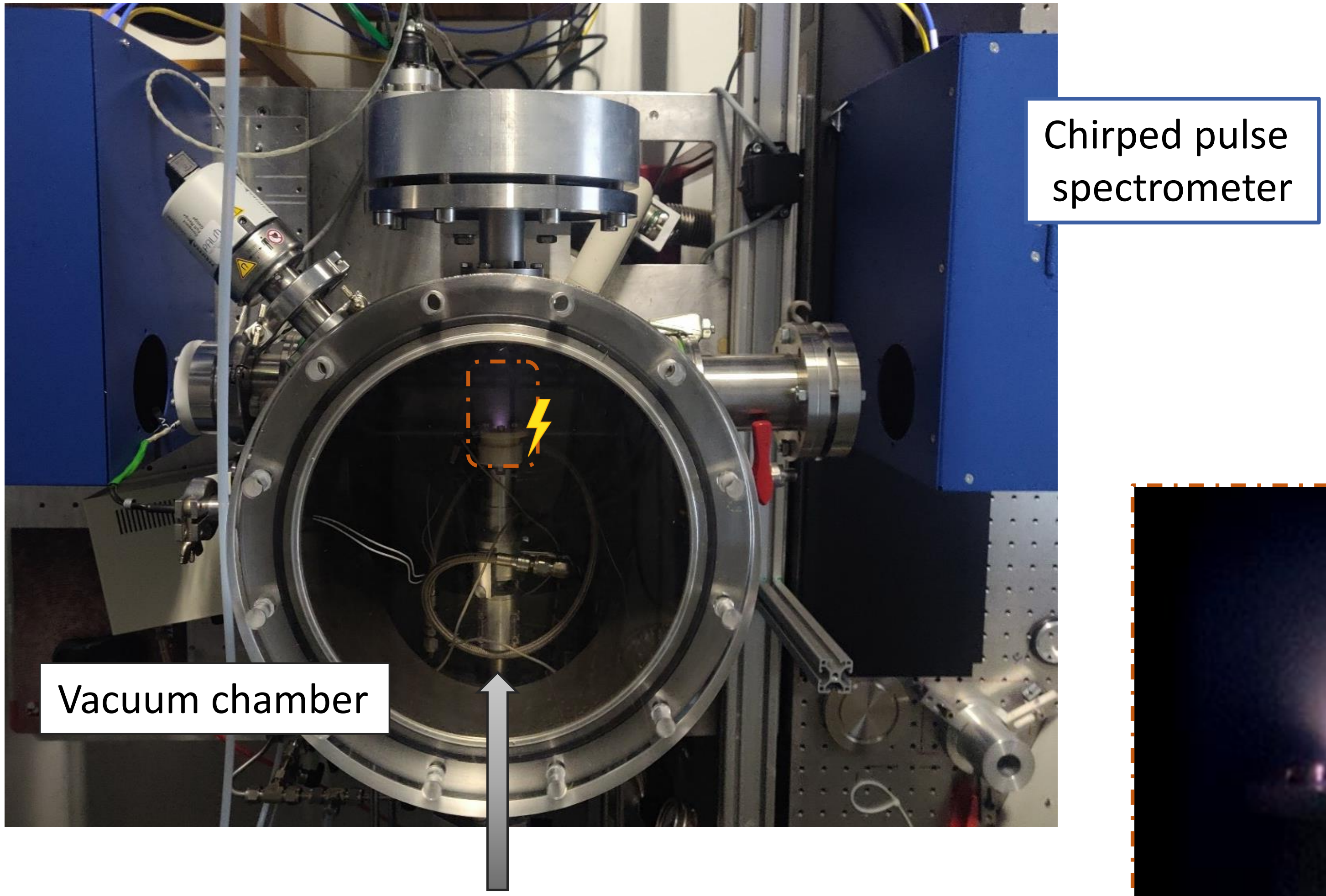
Precursor seeded in buffer gas



- Sample:
  - → Precursor seeded in He or Ar
  - → Typical dilution: ~ 0.5 %
- General valve:
  - → Pulse valve series 9 by Parker Hannifin
  - → Repetition rate: 5-25 Hz
  - → Gas pulse duration: ~ 400 μs
- Pumping system:
  - → diffusion pump (7200 m^3/h)
  - → primary pump (30 m^3/h)

Pulsed jet discharge experiment

Injection **Discharge** Detection



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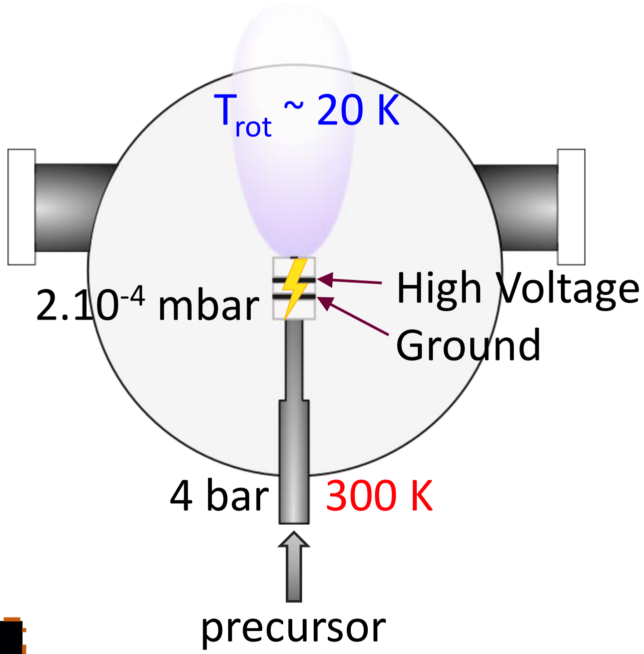
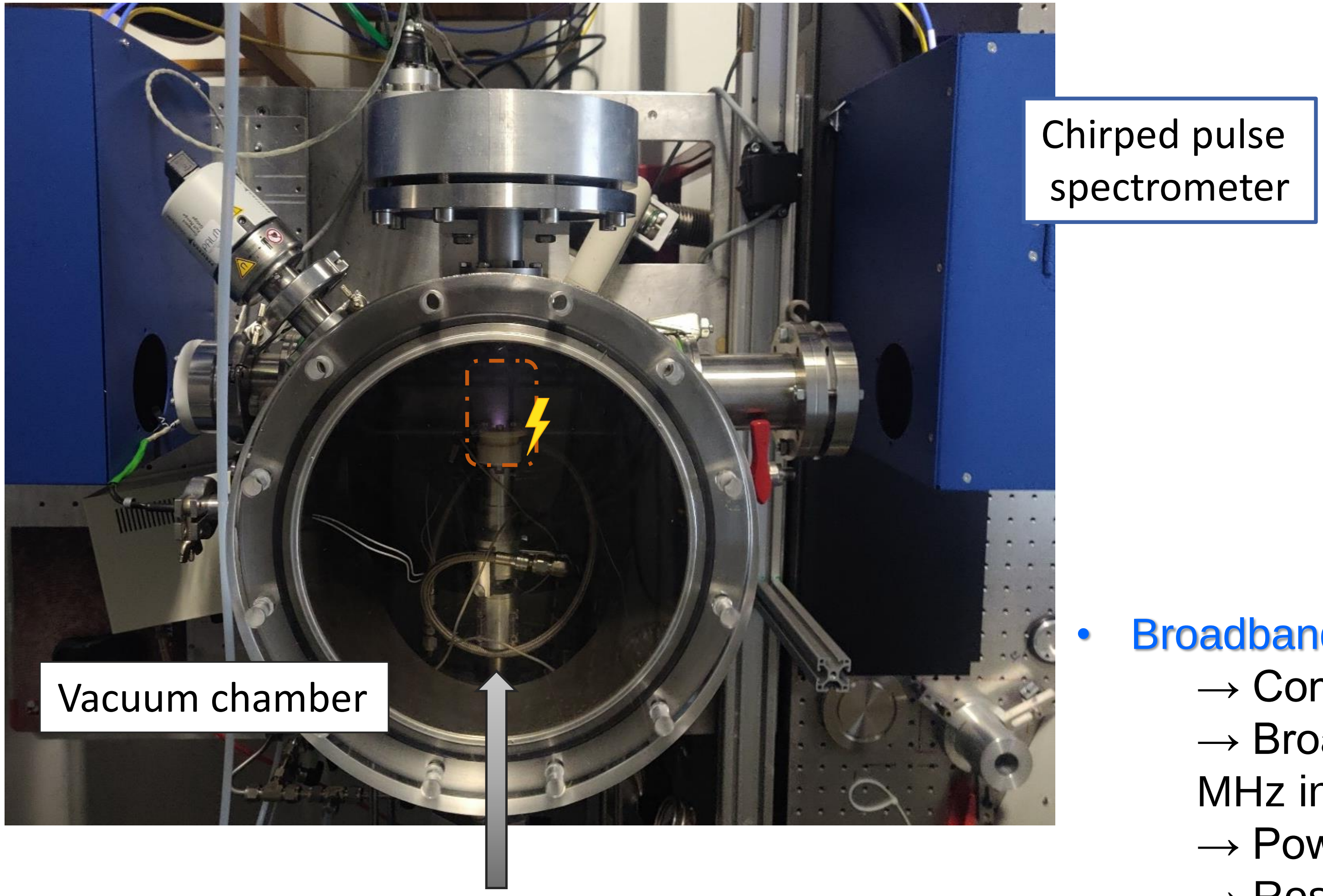
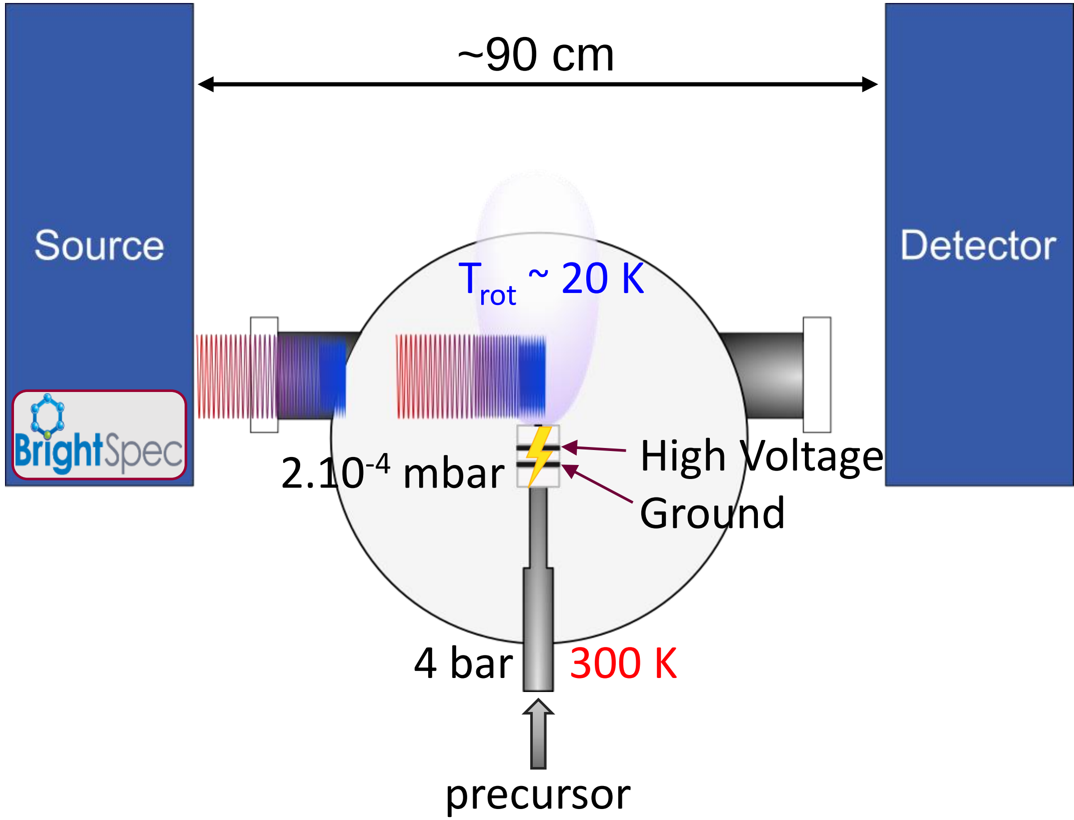


- **Electric discharge:**
  → Stainless steel electrodes (2.5mm and 5 mm wide slit)
  → Voltage: 1000-3000 V
  → Resistance: 10-50 kOhm

Pulsed jet discharge experiment

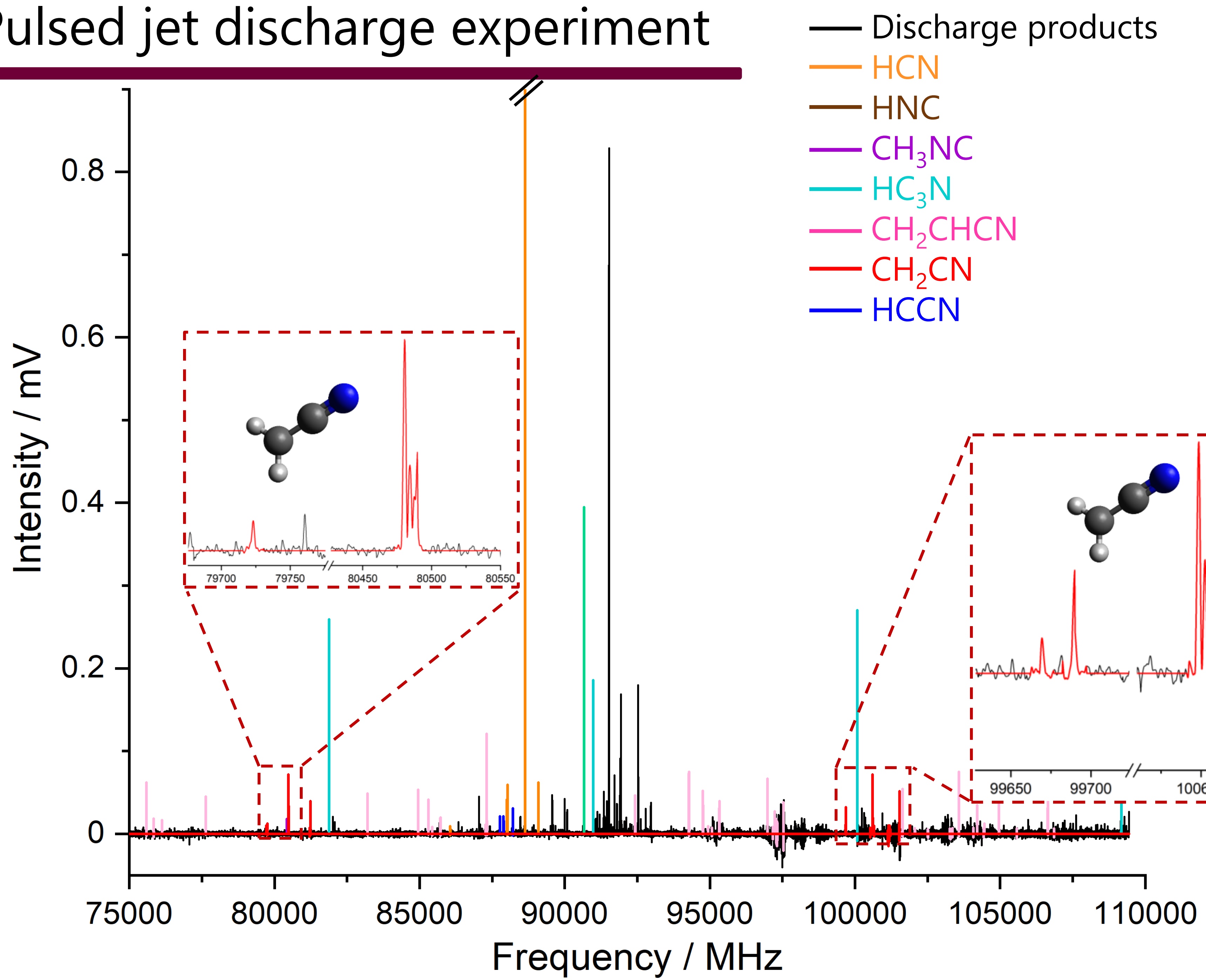
Injection Discharge **Detection**

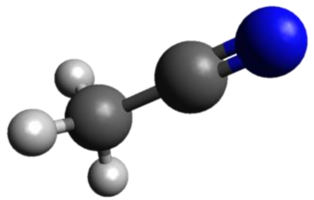




- Broadband chirped pulse Fourier transform spectrometer:
  → Commercial
  → Broadband bandwidth: 75-110 GHz (sequential: 30 MHz in HDR mode)
  → Power: ~30 mW
  → Resolution: ~100 kHz

Pulsed jet discharge experiment





- → Electric discharge: +1000 V, 50 kOhm
- → 0.6 % CH_3CN in Ar
- → Frequency rate: 25 Hz
- → Averages: 5000 (~2h)
- → SNR: ~ 10–450

Conclusions and Perspectives

ESO/José Francisco Salgado

Frequency multiplication based spectrometer

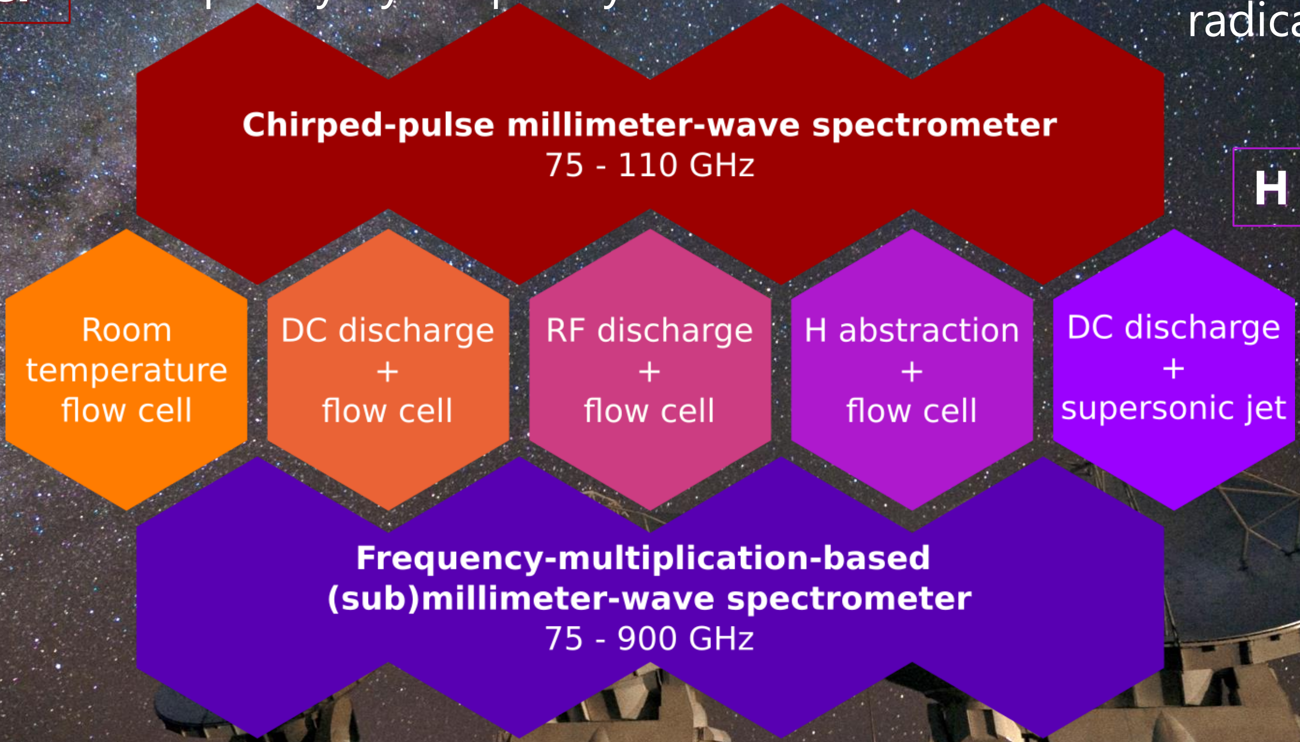
- 75 – 900 GHz spectral covering
- High resolution but limited sensitivity
- frequency by frequency

Pulsed jet discharge set-up

- Supersonic expansion: $T_{rot} \sim 10$ K
- Rich discharges: non selective to radicals

Chirped pulse spectrometer

- 75 – 110 GHz spectral covering
- High sensitivity but limited resolution
- Broadband



H abstraction by F atom

- Room temperature set-up
- Selective method of production

Conclusions and Perspectives

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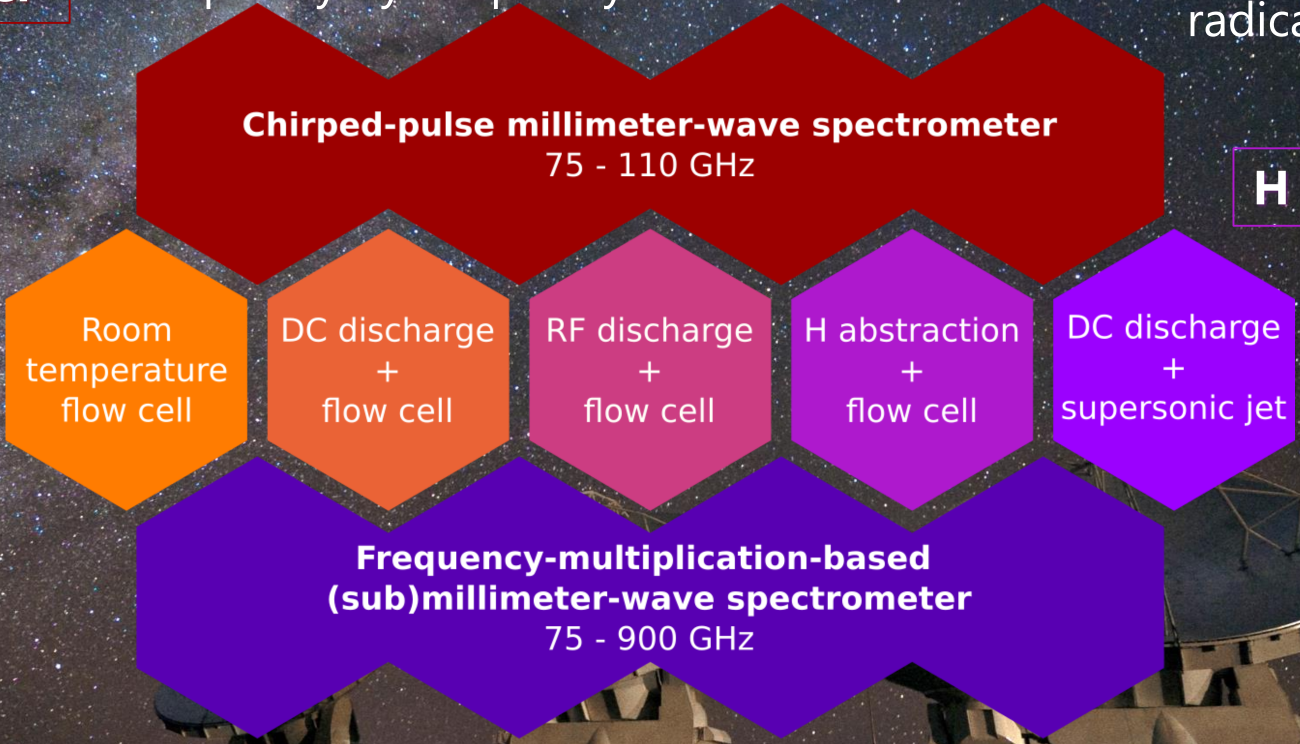


Pulsed jet discharge set-up

- Supersonic expansion: $T_{rot} \sim 10$ K
- Rich discharges: non selective to radicals

H abstraction by F atom

- Room temperature set-up
- Selective method of production

Radicals already observed

$CH_3OH \rightarrow CH_3O$, CH_2OH
$CH_3CN \rightarrow CH_2CN$, HCCN
$CH_2CHCN \rightarrow \alpha\text{-}CH_2CCN$
$CH_3CHO \rightarrow CH_3CO$, CH_2CHO, HCO
$C_2H_4 \rightarrow C_3H$ (l- and c-) and C_3H_2 (l-and c-)

Conclusions and Perspectives

ESO/José Francisco Salgado

Frequency multiplication based spectrometer

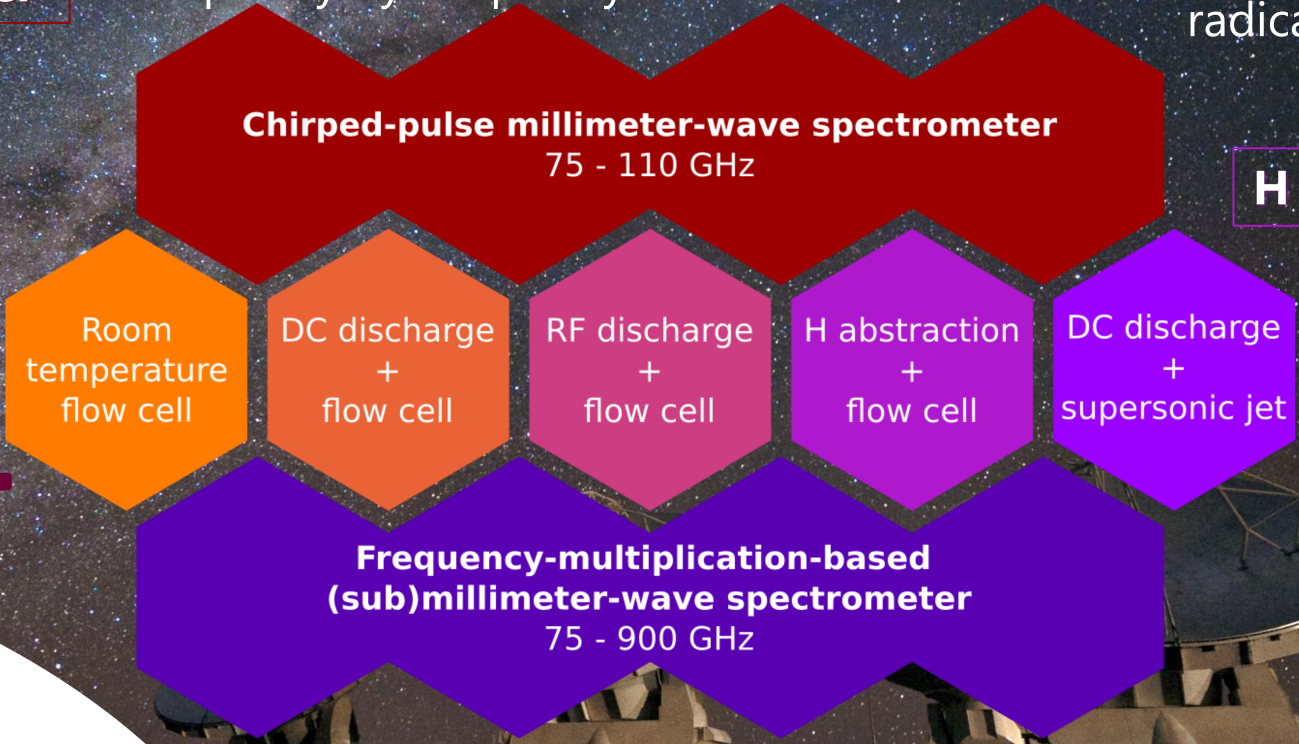
- 75 – 900 GHz spectral covering
- High resolution but limited sensitivity
- frequency by frequency

Pulsed jet discharge set-up

- Supersonic expansion: T_{rot} ~10 K
- Rich discharges: non selective to radicals

Chirped pulse spectrometer

- 75 – 110 GHz spectral covering
- High sensitivity but limited resolution
- Broadband



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Acknowledgments

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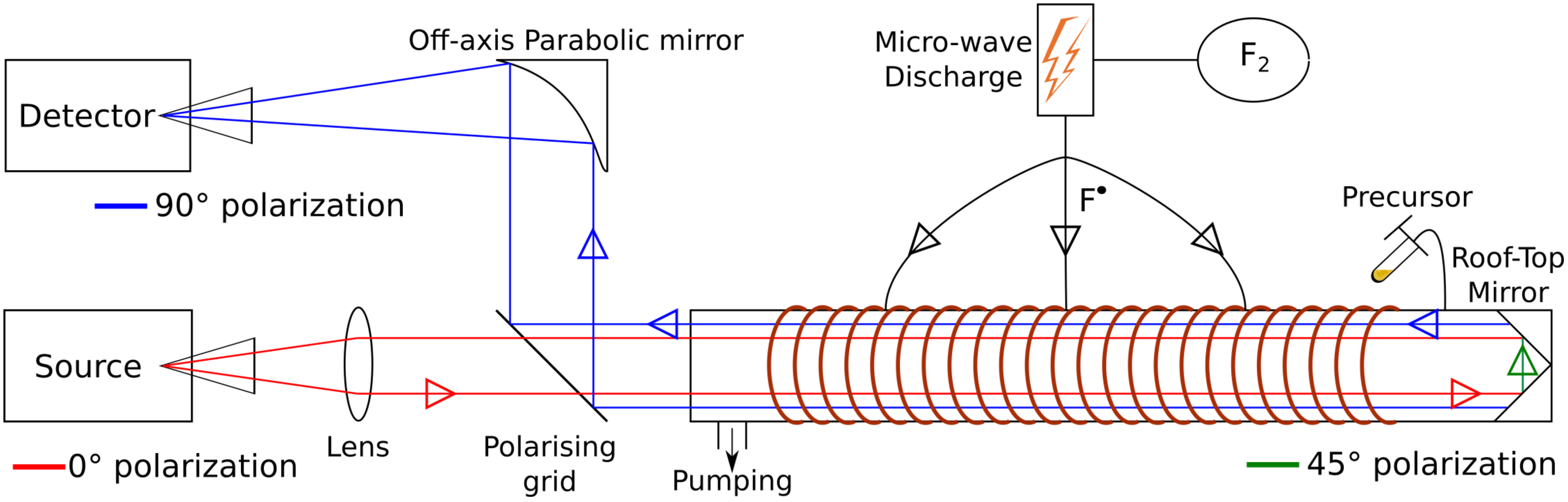
ACAV+
îledeFrance
pcmi
cnrs

Experimental method

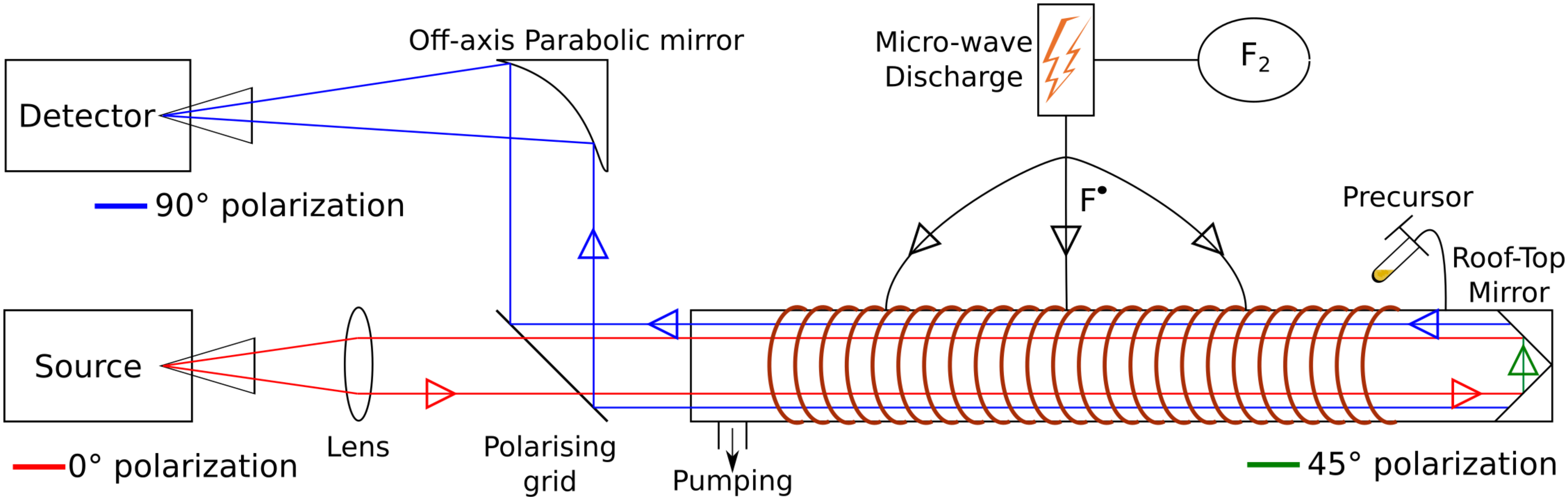
O. Chitarra et al., A&A, 644, A123, 2020



Experimental method

$F_2 \rightarrow 2F^{\bullet}$

O. Chitarra et al., A&A, 644, A123, 2020



Production

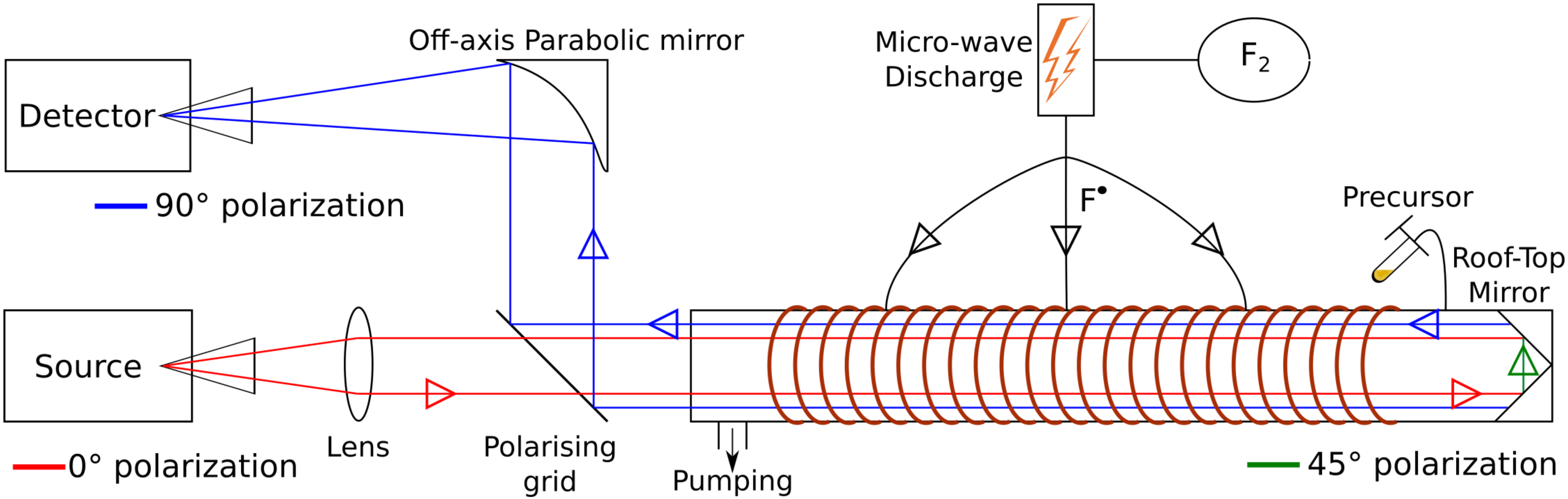
Hydrogen abstraction from precursor by fluorine atom

$$R\text{-}H + F^{\bullet} \rightarrow HF + {}^{\bullet}R$$

$$\boxed{CH_3CN + F^{\bullet} \rightarrow HF + {}^{\bullet}CH_2CN}$$

Experimental method

O. Chitarra et al., A&A, 644, A123, 2020



Production

Hydrogen abstraction from precursor by fluorine atom

Acquisition

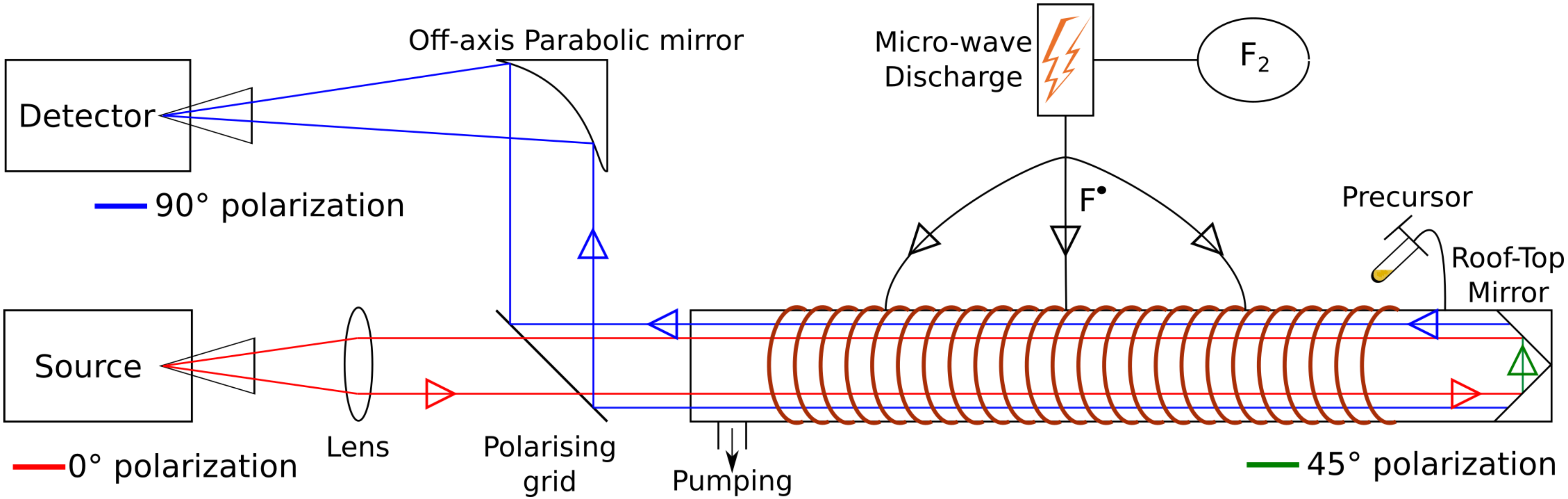
f_m = 48.2 kHz

Frequency multiplication chain spectrometer:

75-900 GHz

Experimental method

O. Chitarra et al., A&A, 644, A123, 2020



Production

Hydrogen abstraction from precursor by fluorine atom

Acquisition

f_m = 48.2 kHz

Frequency multiplication chain spectrometer:

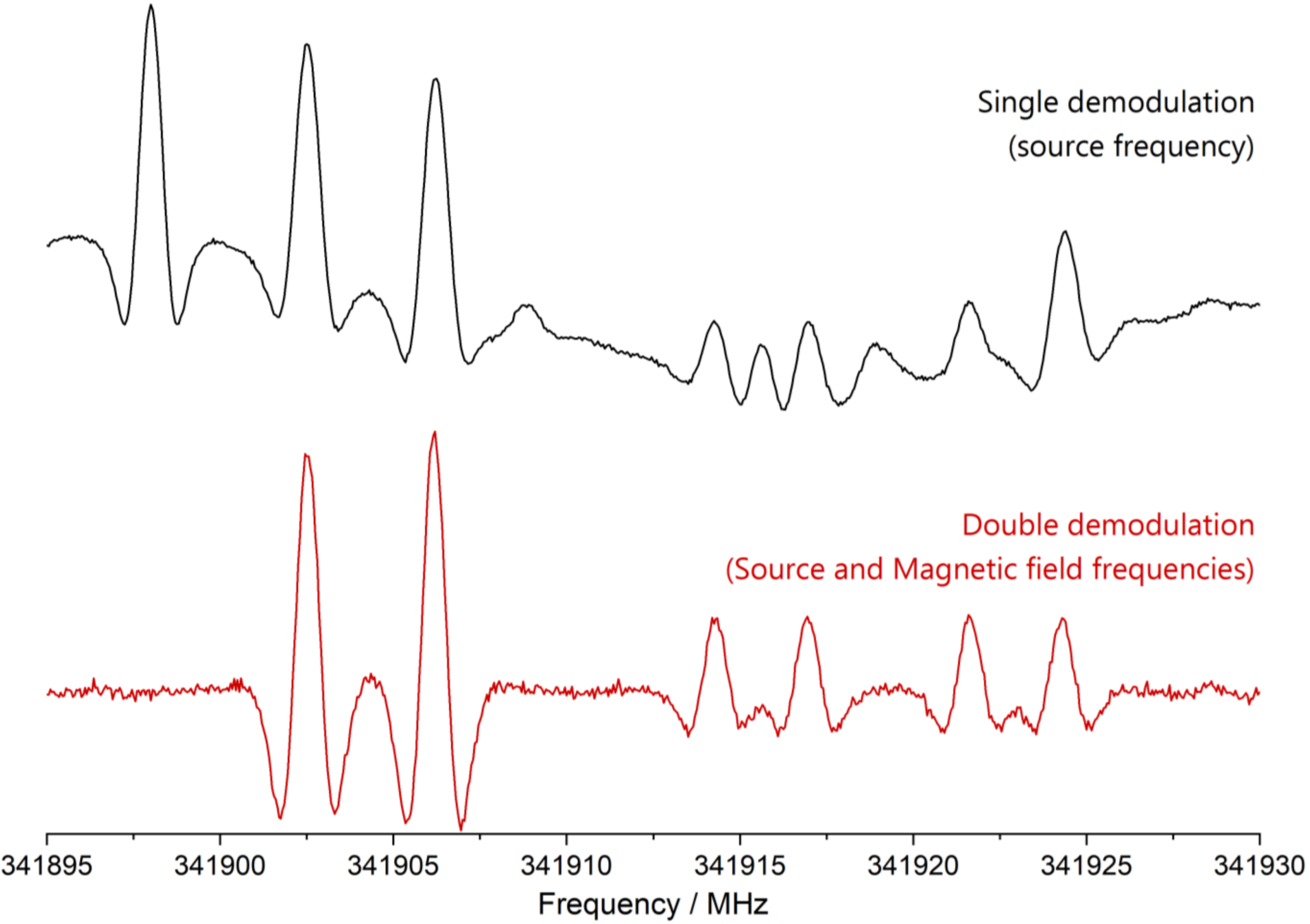
75-900 GHz

f_m = 70 Hz

Magnetic Field Modulation to distinguish paramagnetic lines

Advantages of the double modulation

Scan duration: 12 min
SNR : 20-500



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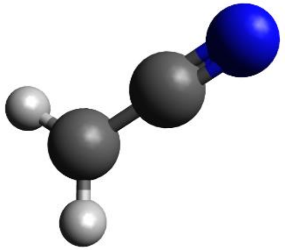
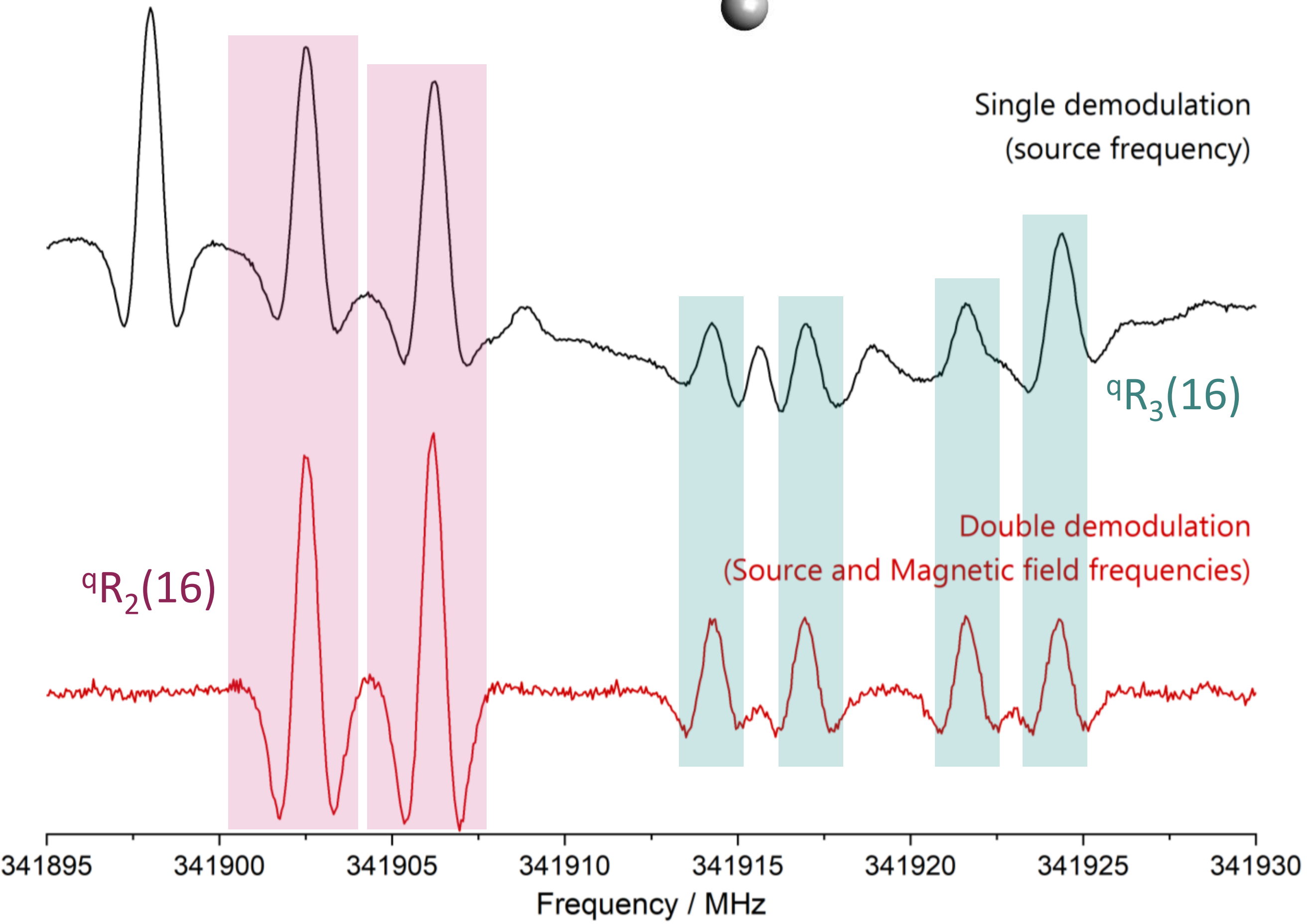
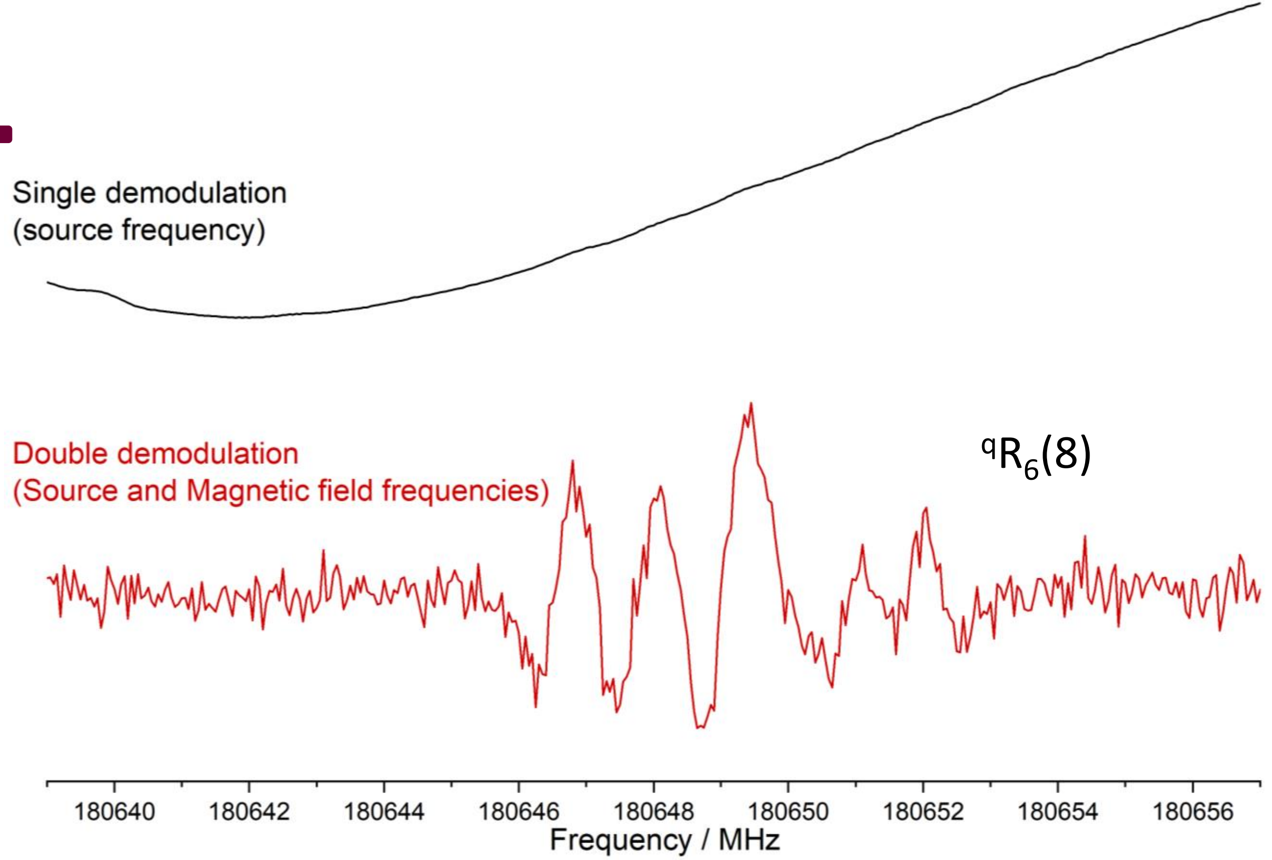




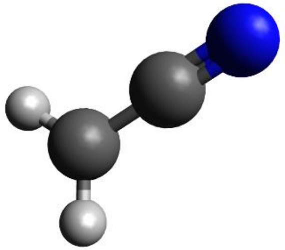
❖ Transitions arising from open-shell species **only**

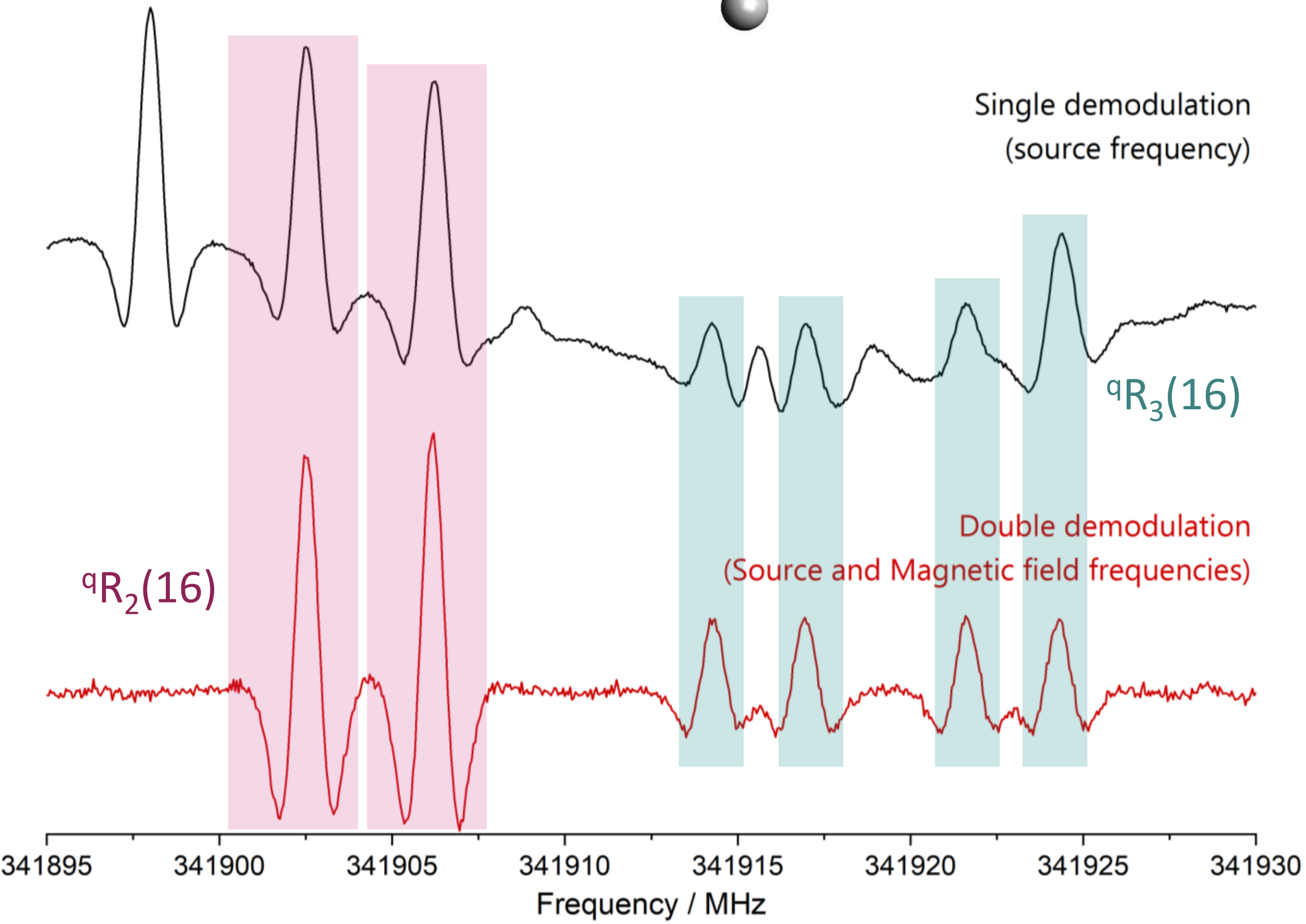
Advantages of the double modulation



Scan duration: 24 min
SNR : 5-10

Scan duration: 12 min
SNR : 20-500



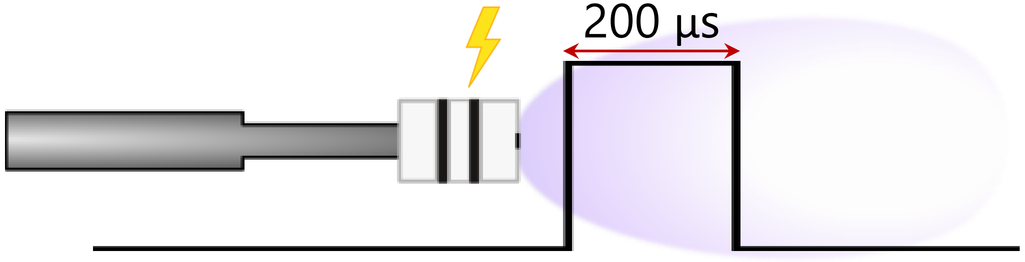


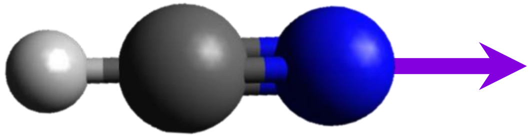
❖ Transitions arising from open-shell species **only**

❖ Baseline free

Rotational Spectroscopy in supersonic expansion

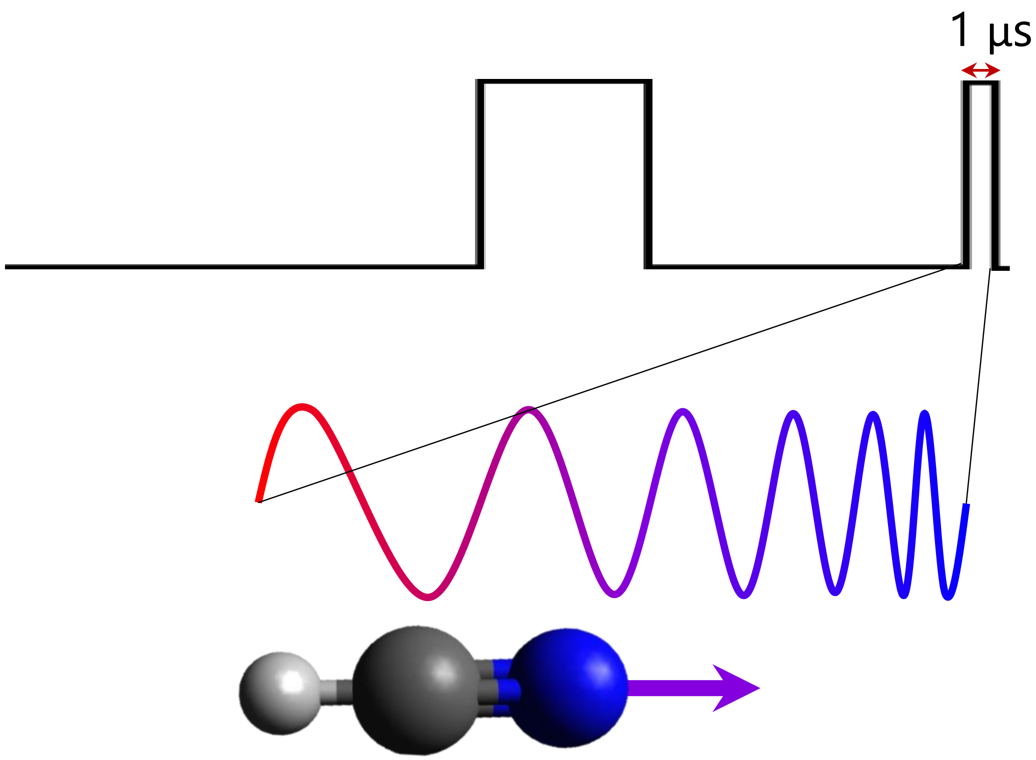
Pulsed molecular beam





Rotational Spectroscopy in supersonic expansion

Short radiation pulse: f_0 (75 GHz) to f_n (110 GHz), Power : ~30 mW



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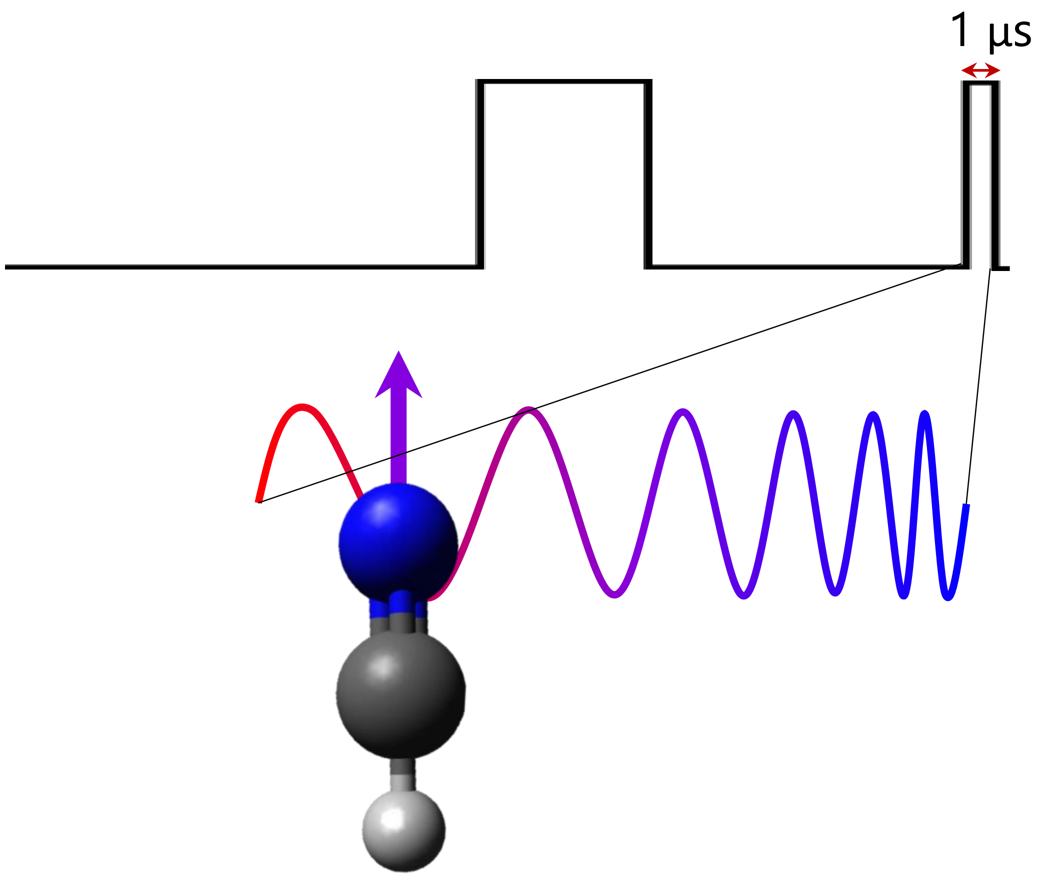
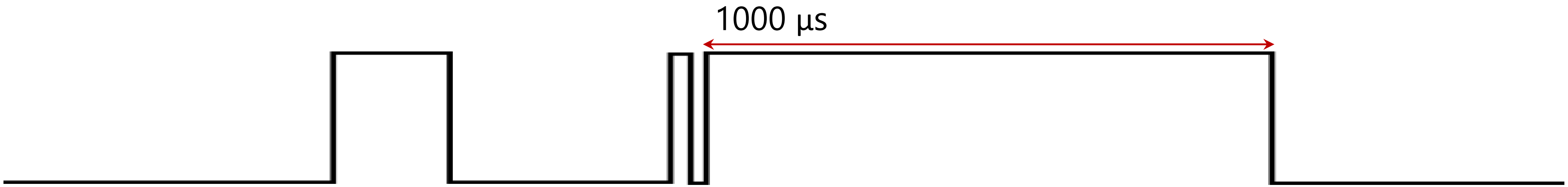
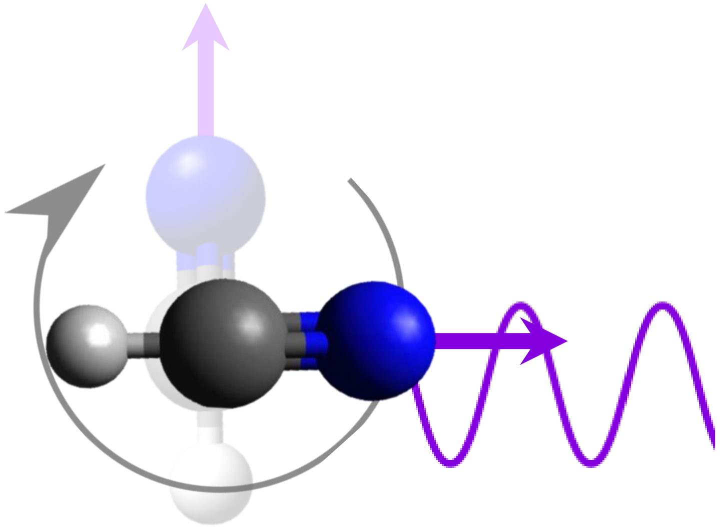


Rotational Spectroscopy in supersonic expansion

Detection of the FID emission signal





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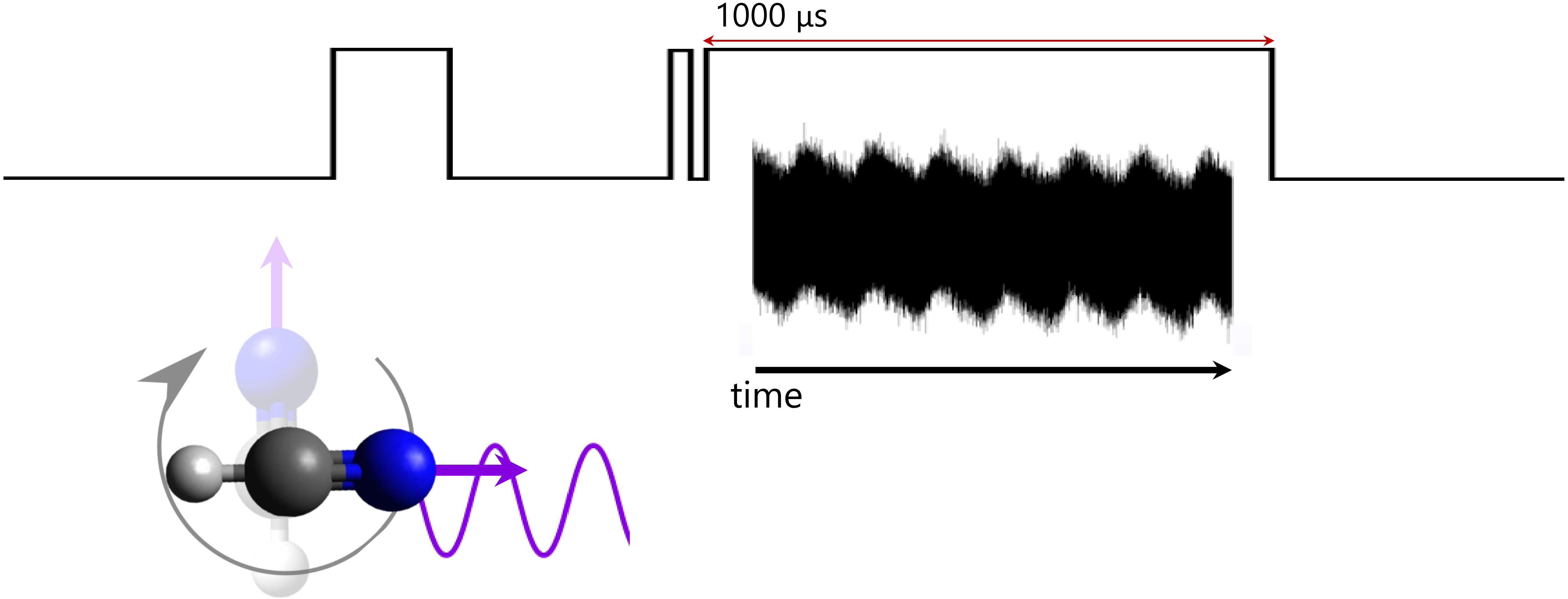

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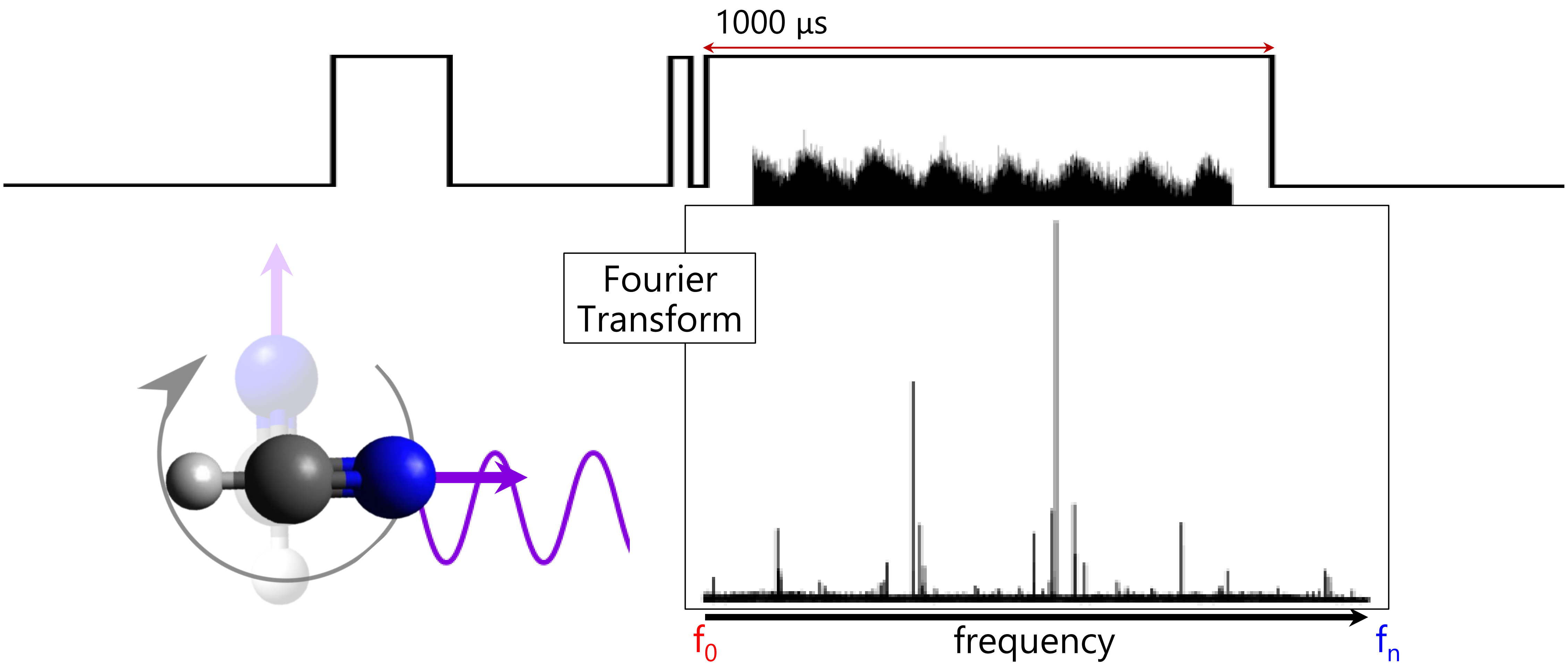
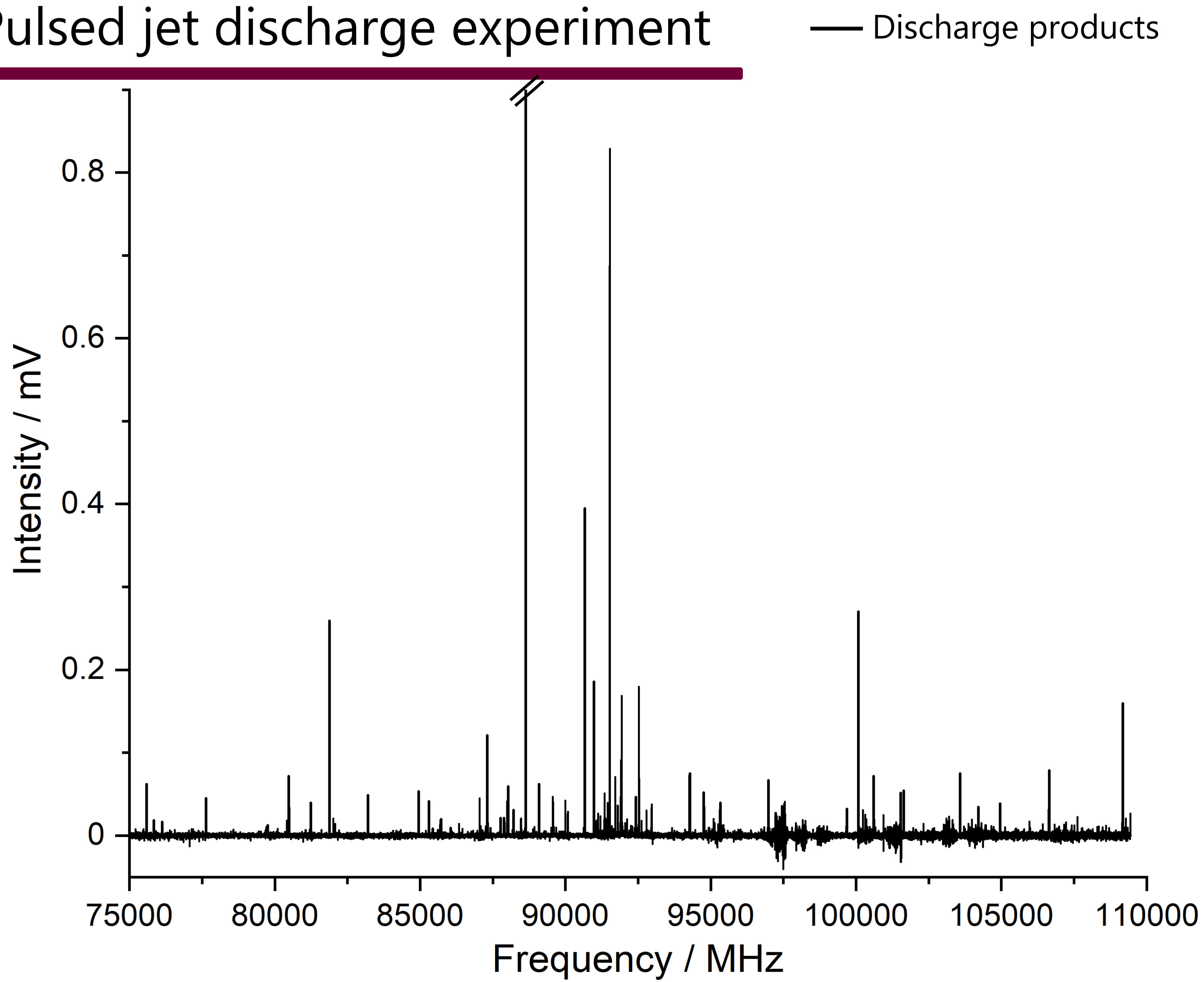
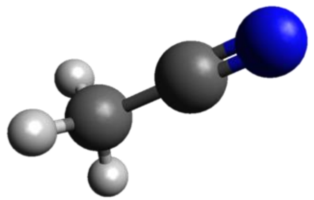


Pulsed jet discharge experiment





→ Electric discharge:
+1000 V, 50 kOhm
→ 0.6 % CH_3CN in Ar
→ Frequency rate: 25 Hz
→ Averages: 5000 (~2h)
→ SNR: ~ 10–450

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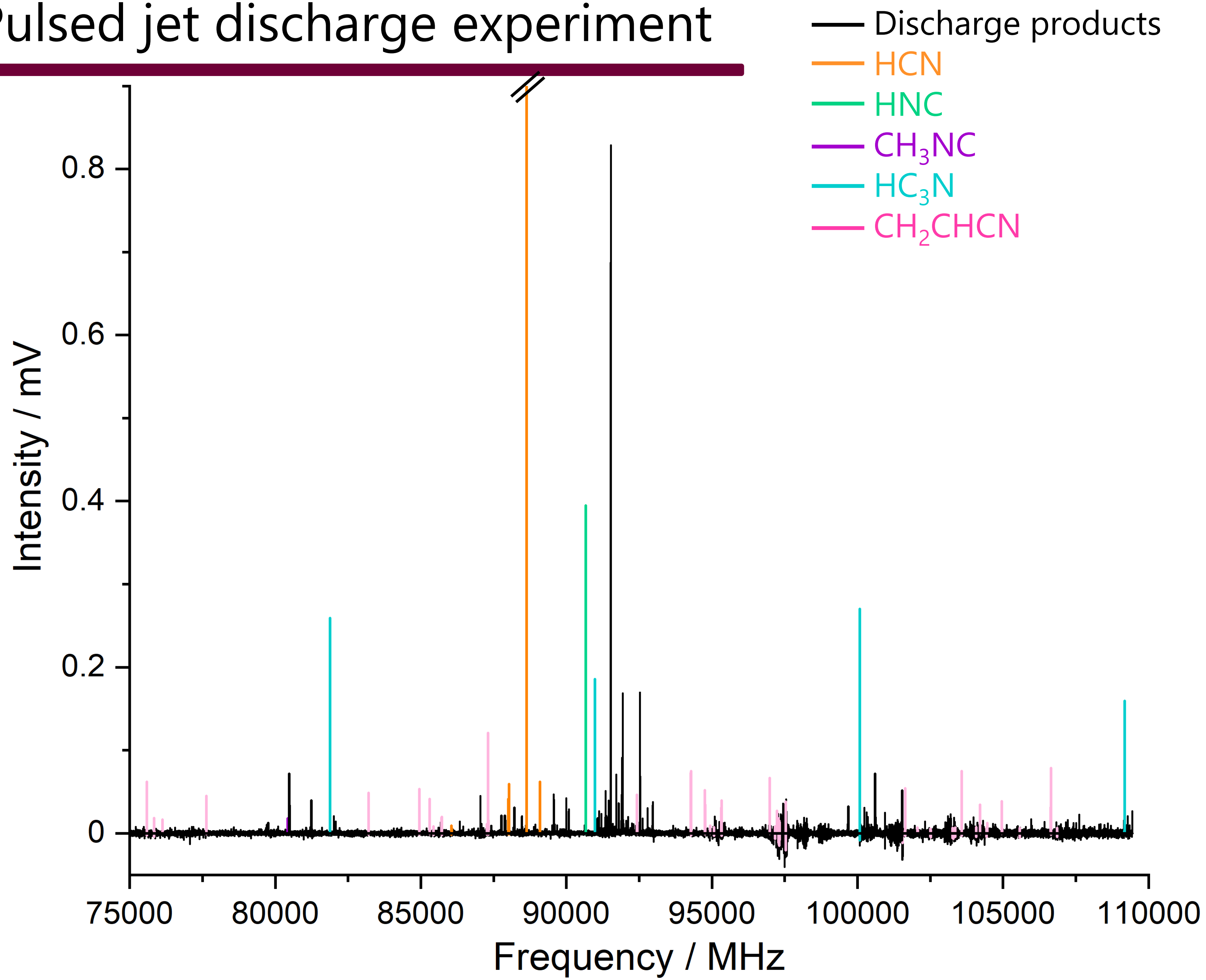

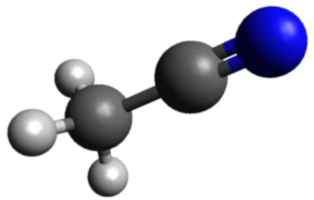

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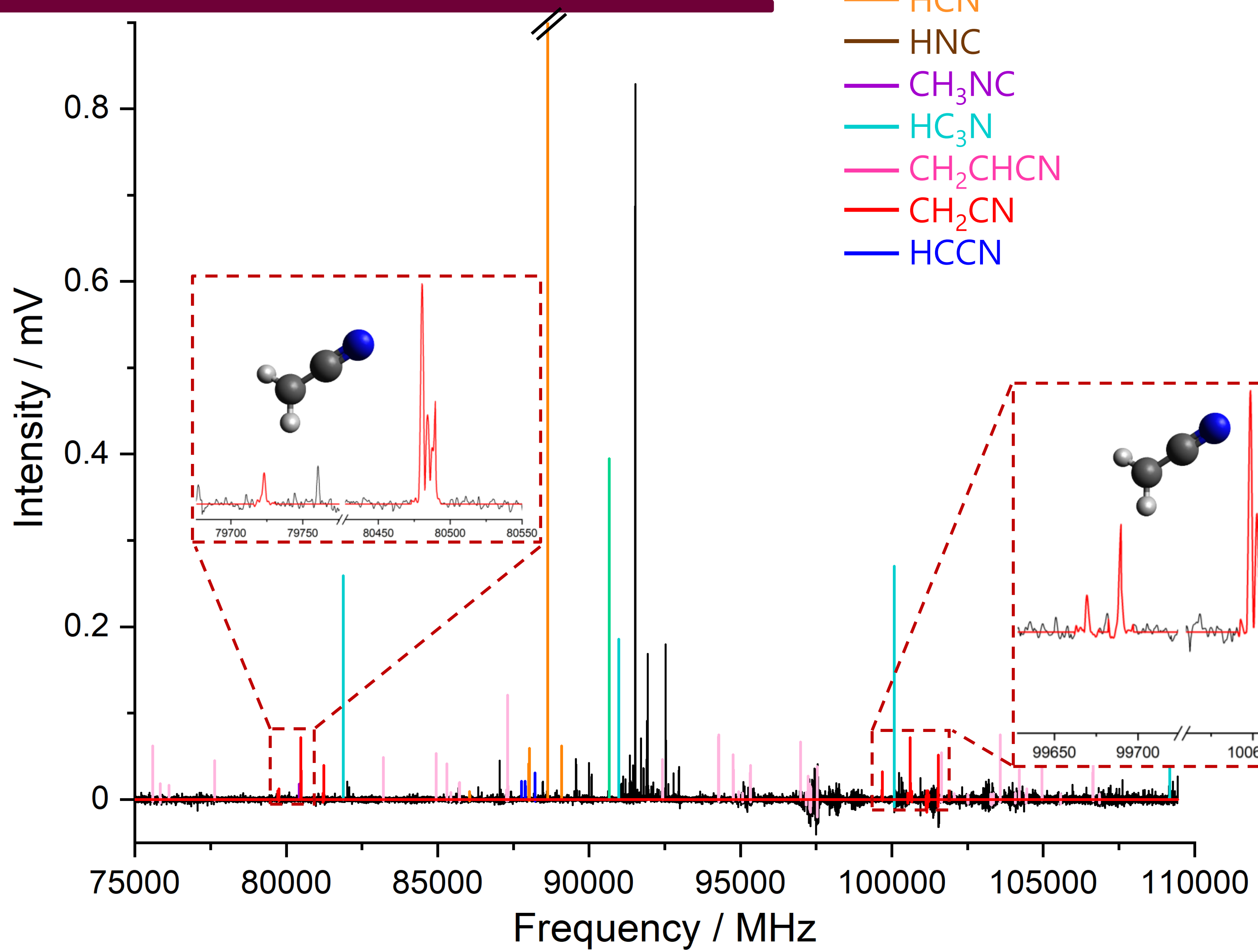

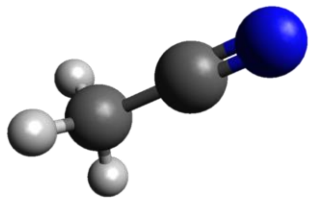

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