INVESTIGATION OF PURE ROTATION OF ETHYNYLBENZONITRILE ISOMERS USING CHIRPED-PULSE W-BAND SPECTROSCOPY
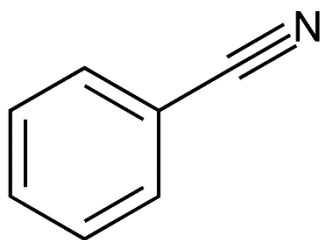
J-T. Spaniol[1], K.L. Kelvin Lee[2], O. Pirali[1], M-A. Martin-Drumel[1]

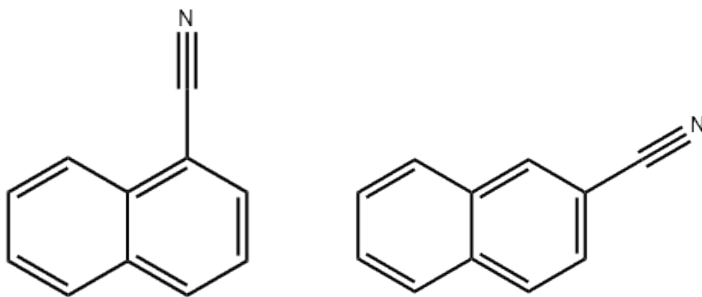[1]Université Paris Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay, France
[2]Department of Chemistry, MIT, Cambridge, MA, USA

Jean-Thibaut Spaniol │ *June 2021*

Cyano-substituted molecules: an interesting family

Some already detected in interstellar medium

Benzonitrile (PhCN) [1]

1-,2- cyanonaphthalene ($C_{11}H_7N$) [2]

Some already studied by our team:

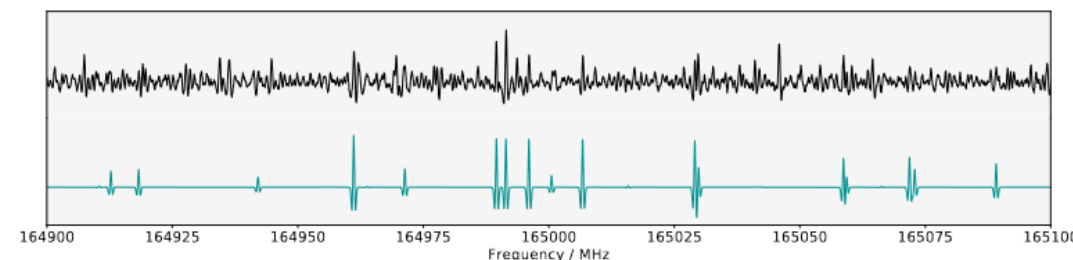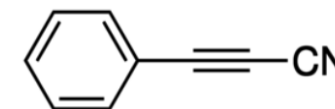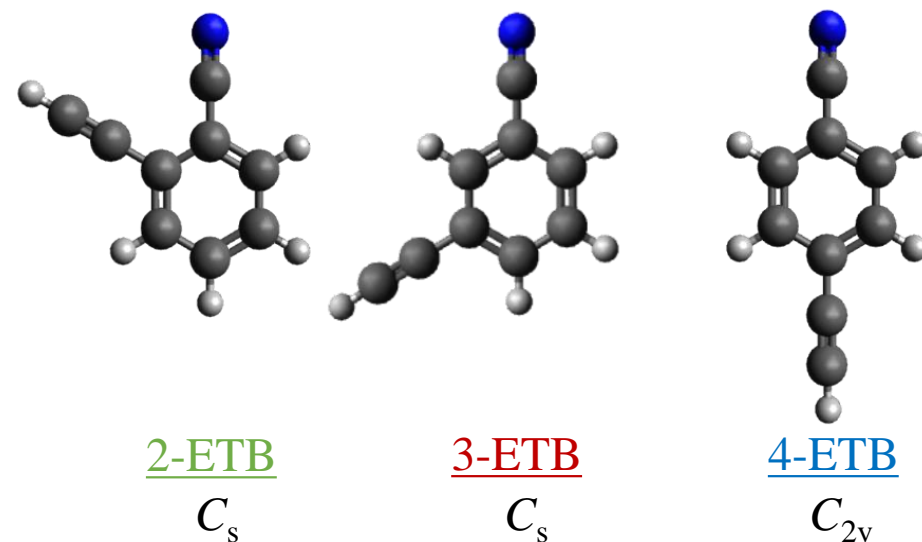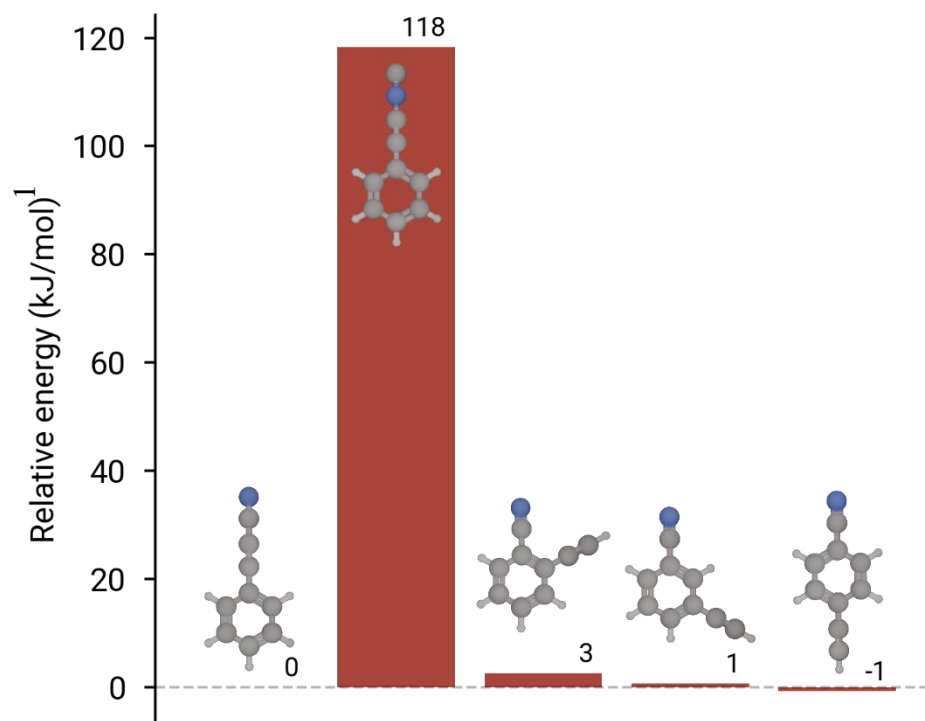Phenylpropiolonitrile (PhC_3N)

Figure 4: Portions of the millimeter-wave spectrum of PhC_3N in comparison with a simulation of the pure rotational transitions in the ground vibrational state using the best-fit set of spectroscopic constants (Table 3). The simulation has been performed using the PGOPHER software and the resulting trace was then post-processed with a second derivative to allow a more straightforward comparison with the experimental spectrum. The line density in the experimental trace is far greater than our simulation, very likely because of lines from vibrational satellites.

1. B. A. McGuire et al. Science, 359, p202–205, 2018.
2. B. A. McGuire et al. Science, 371, p1265–1269, 2021.

Z. Buchanan et al. Journal of Molecular Spectroscopy, 377, p111425, 2021.

Investigation of 3 isomers of PhC$_3$N: 2-, 3-, 4-ethynylbenzonitrile (ETB)

2-ETB
C_s

3-ETB
C_s

4-ETB
C_{2v}

DFT Geometry Optimization
(ωB97XD/cc-pVQZ, harmonic + scaled[2])

Molecules	A (MHz)	B (MHz)	C (MHz)	μ (Debye)		
				a	b	c
2-ETB	2002	1329	799	3.9	-2.3	0
3-ETB	2697	903	677	3.6	2.5	0
4-ETB	5647	705	627	-4.3	0	0

1. Z. Buchanan et al. Journal of Molecular Spectroscopy, 377, p111425, 2021.
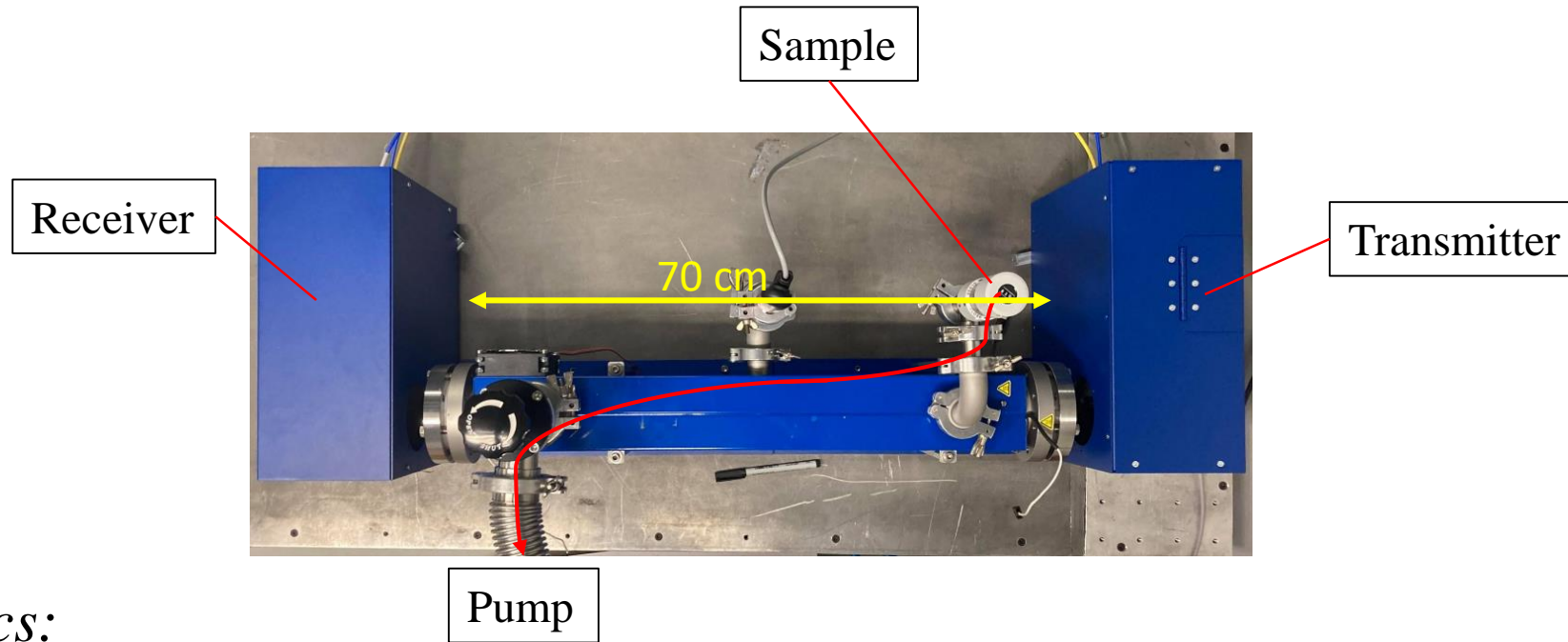2. 2. K. L. K. Lee et al. Journal of Physical Chemistry A, 124(5) p898–910, 2020

Acquisition set-ups available at ISMO
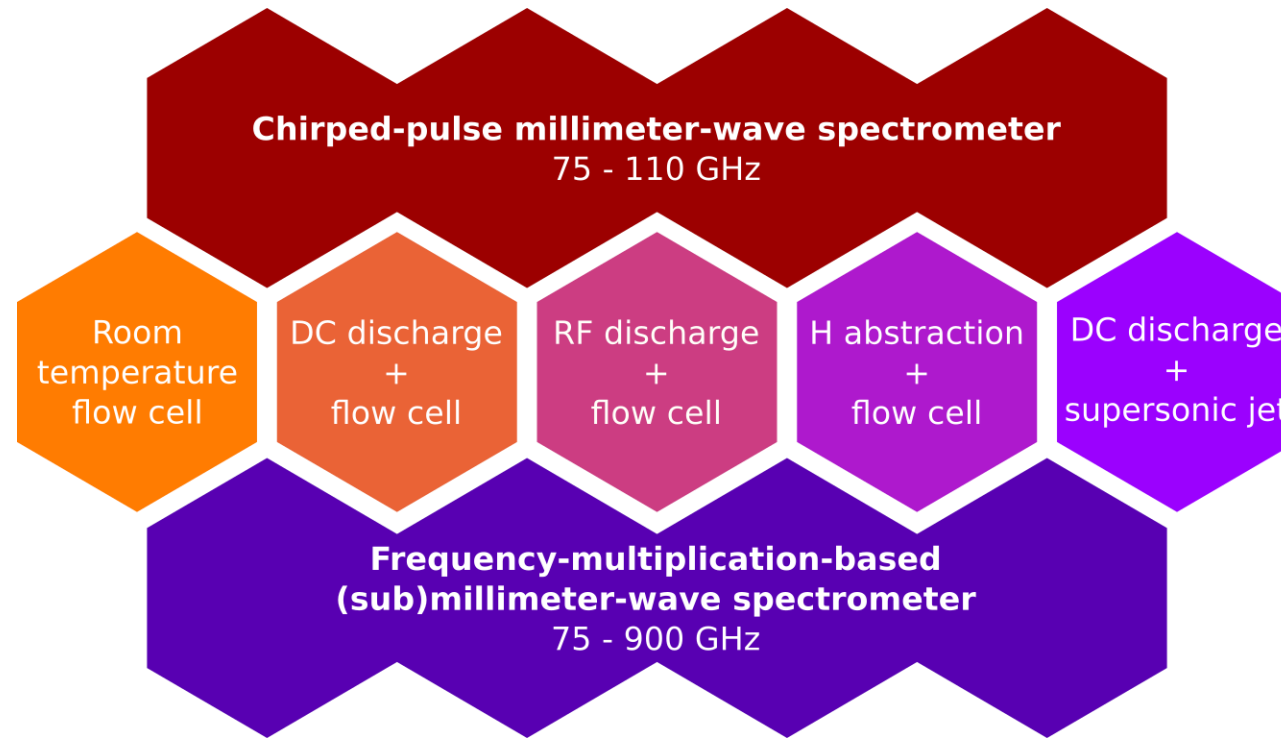
Acquisition set-ups available at ISMO
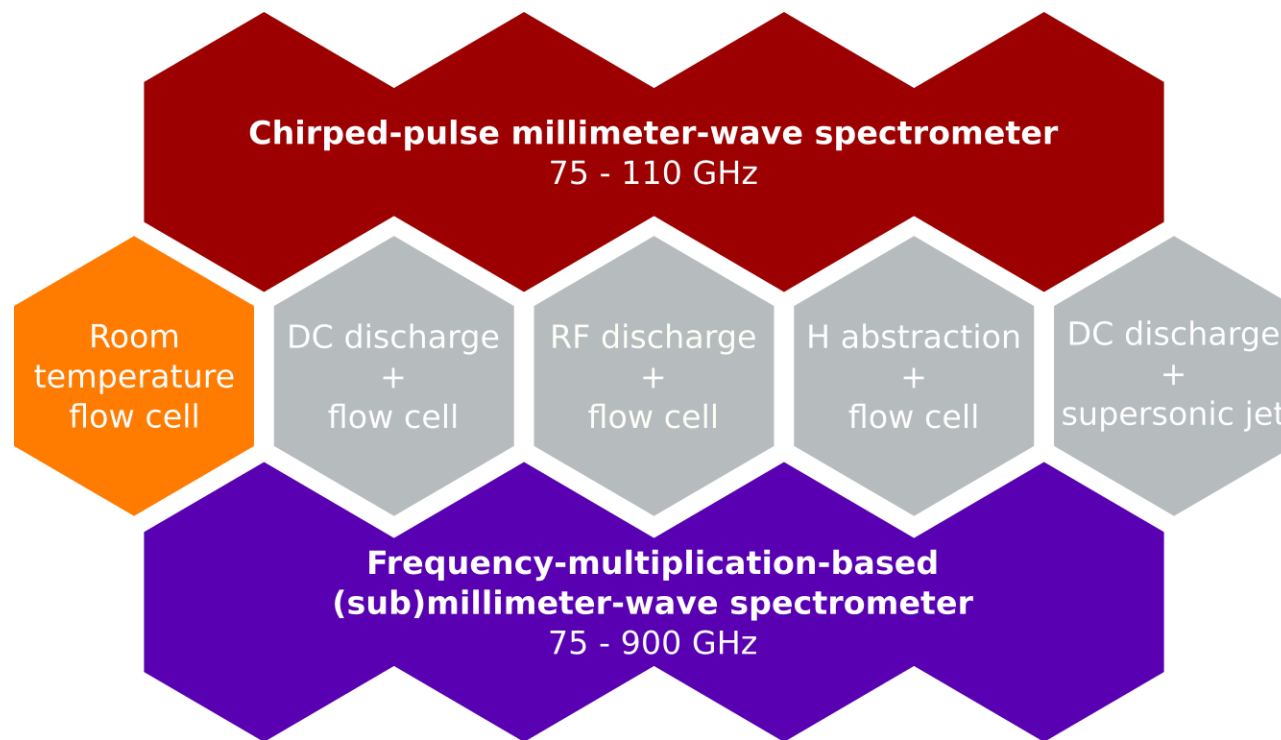
W-band Chirped-Pulse Spectroscopy

Characteristics:
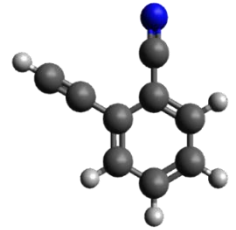
Frequency range: 75-110 GHz

Commercial (BrightSpec)

Sequential chirp, 30 MHz segments (HDR mode)

1 million averages within 2h

Pulse length: from 0.1 to 0.5 µs

FID length: up to 4 µs

G. G. Brown et al. Review of Scientific Instruments, 79(5) p053103, 2008.
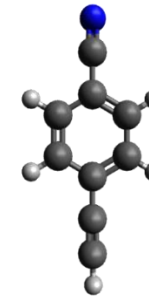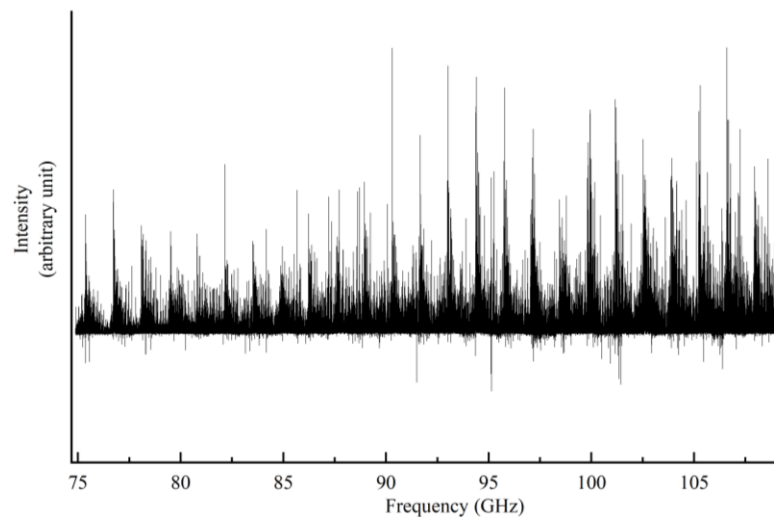
Laboratory acquisition

2-ETB

Settings:
- 1 million averages
- Pressure: $1.4 \, 10^{-3}$ mbar
- $SNR_{max} \sim 140$
- Pulse Length: 0.5 µs

3-ETB

Settings:
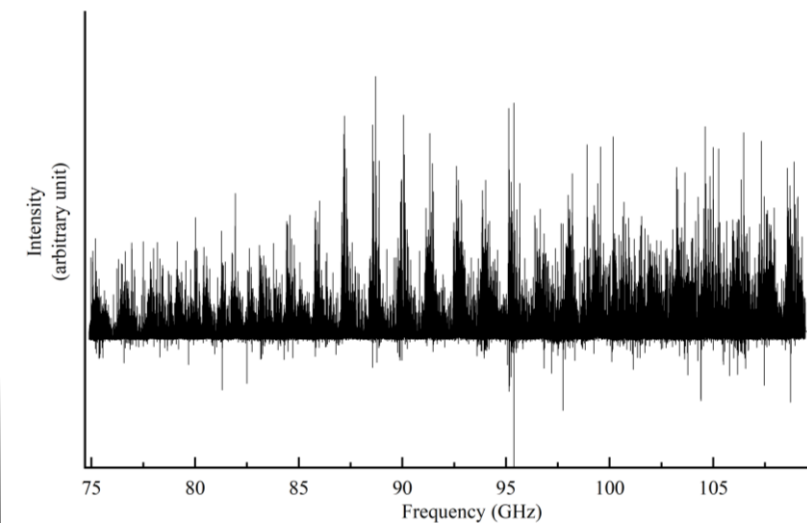- 1 million averages
- Pressure: $1.2 \, 10^{-3}$ mbar
- $SNR_{max} \sim 90$
- Pulse Length: 0.25 µs

4-ETB

Settings:
- 1 million averages
- Pressure: $2.2 \, 10^{-3}$ mbar
- $SNR_{max} \sim 130$
- Pulse Length: 0.5 µs

2-ETB

Settings:
- 1 million averages
- Pressure: $1.4 \; 10^{-3}$ mbar
- $SNR_{max} \sim 140$
- Pulse Length: $0.5 \; \mu s$
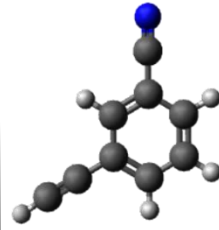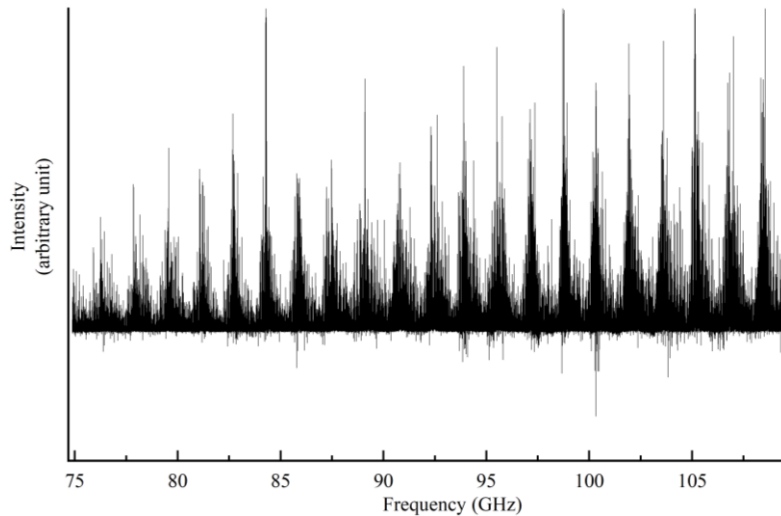
3-ETB

Settings:
- 1 million averages
- Pressure: $1.2 \; 10^{-3}$ mbar
- $SNR_{max} \sim 90$
- Pulse Length: $0.25 \mu s$

4-ETB

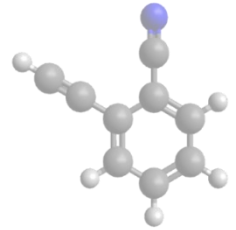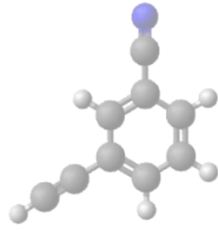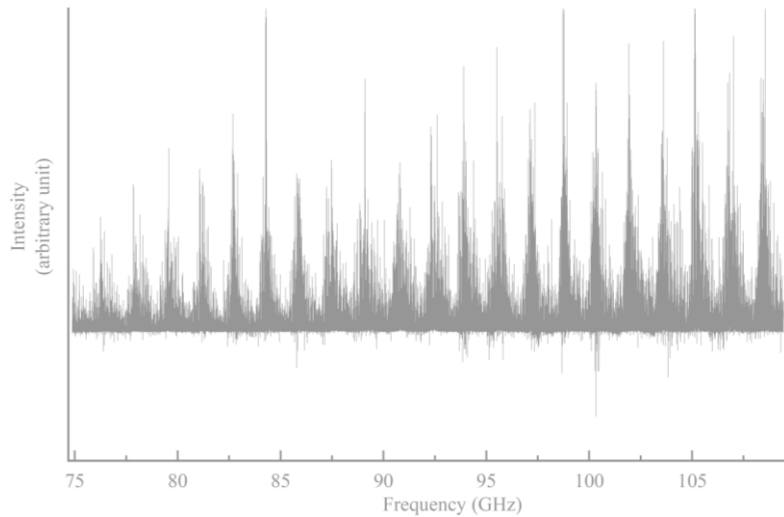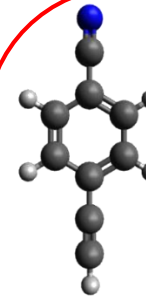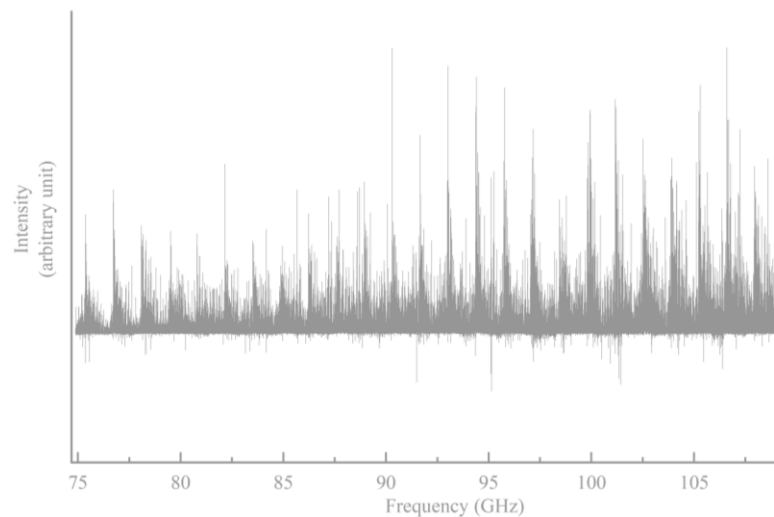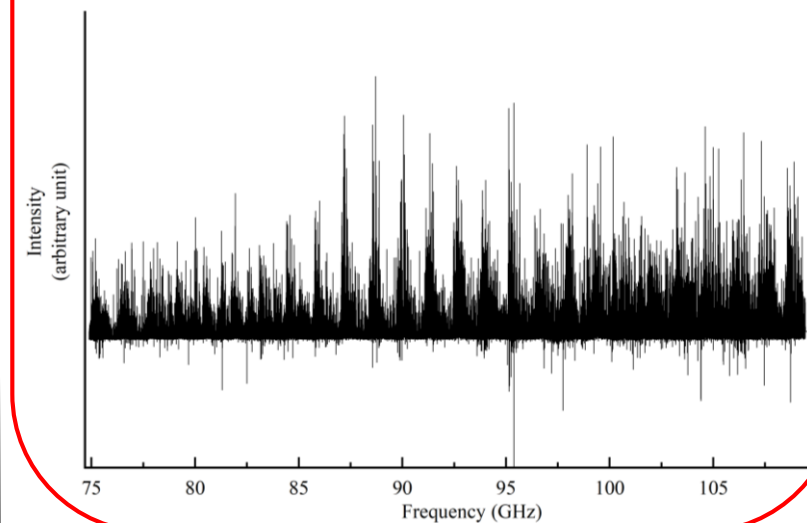
Settings:
- 1 million averages
- Pressure: $2.2 \; 10^{-3}$ mbar
- $SNR_{max} \sim 130$
- Pulse Length: $0.5 \; \mu s$

Graphical exploitation of the spectra: principle

PGOPHER[1]:
Modelize and fit spectra using a set of constants

Loomis-Wood for Windows, Asymmetric top (LWWa)[2]:
Graphical assignment of transitions

1.C.M.Western, Journal of Quantitative Spectroscopy and Radiative Transfer, 186, p221-242, 2017
2.W. Lodyga et al. Journal of Molecular Spectroscopy. 243, p182-188, 2007

PGOPHER

LWWa

Quantum Chemical Calculations

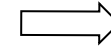Set of rotational constants

PGOPHER

LWWa

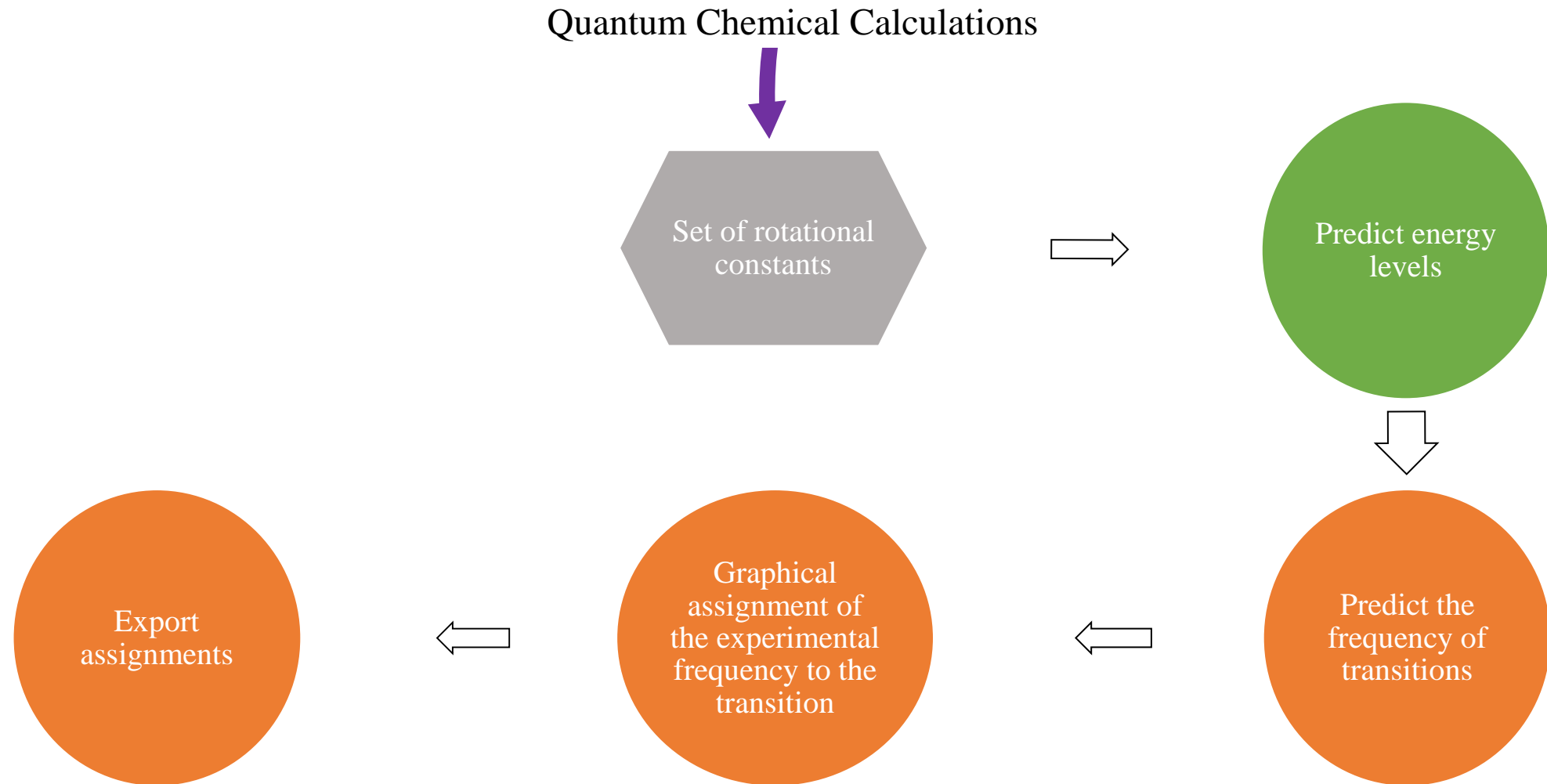Quantum Chemical Calculations

Set of rotational constants

Predict energy levels

Graphical exploitation of the spectra: principle

PGOPHER

LWWa

Quantum Chemical Calculations
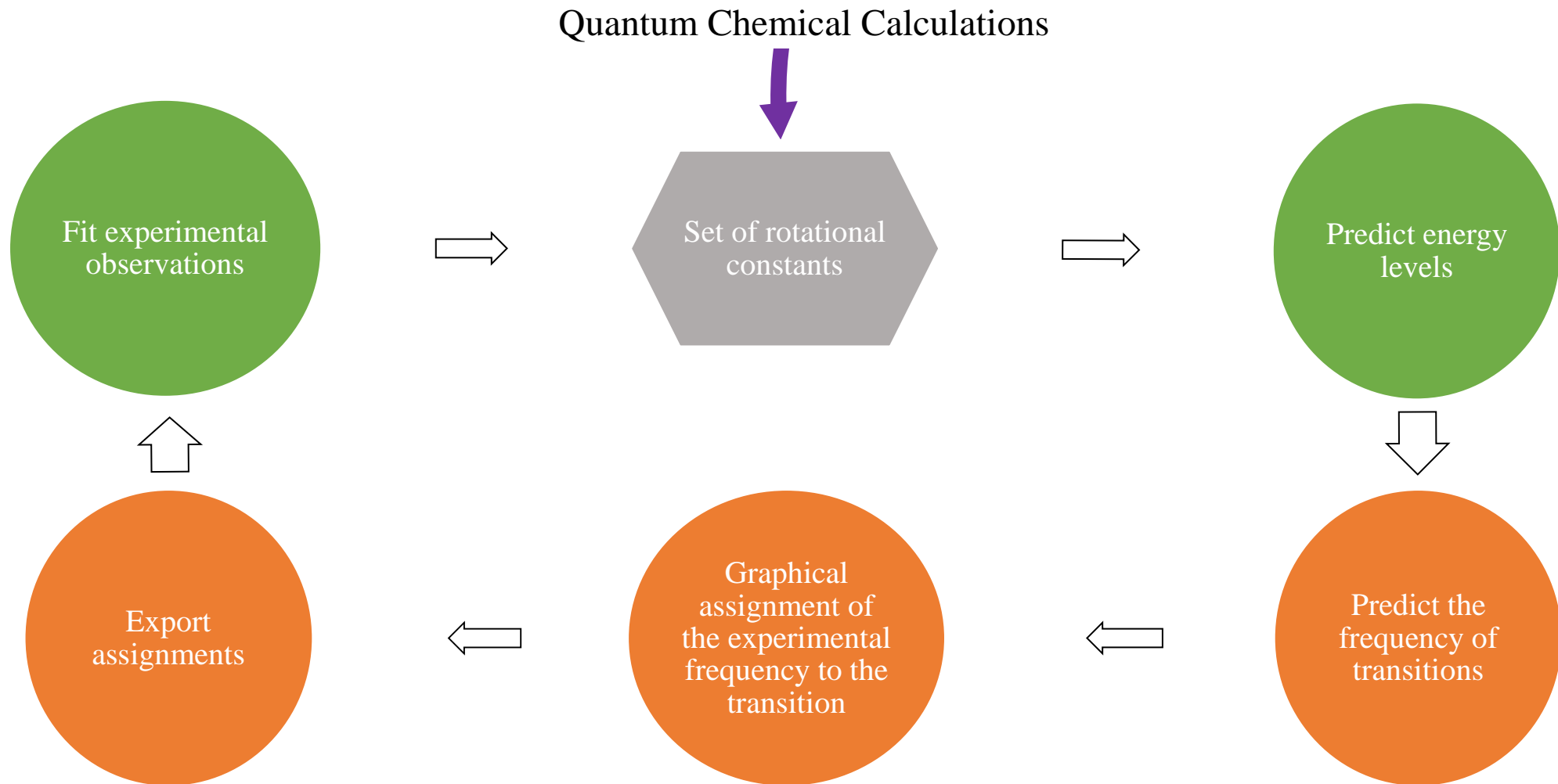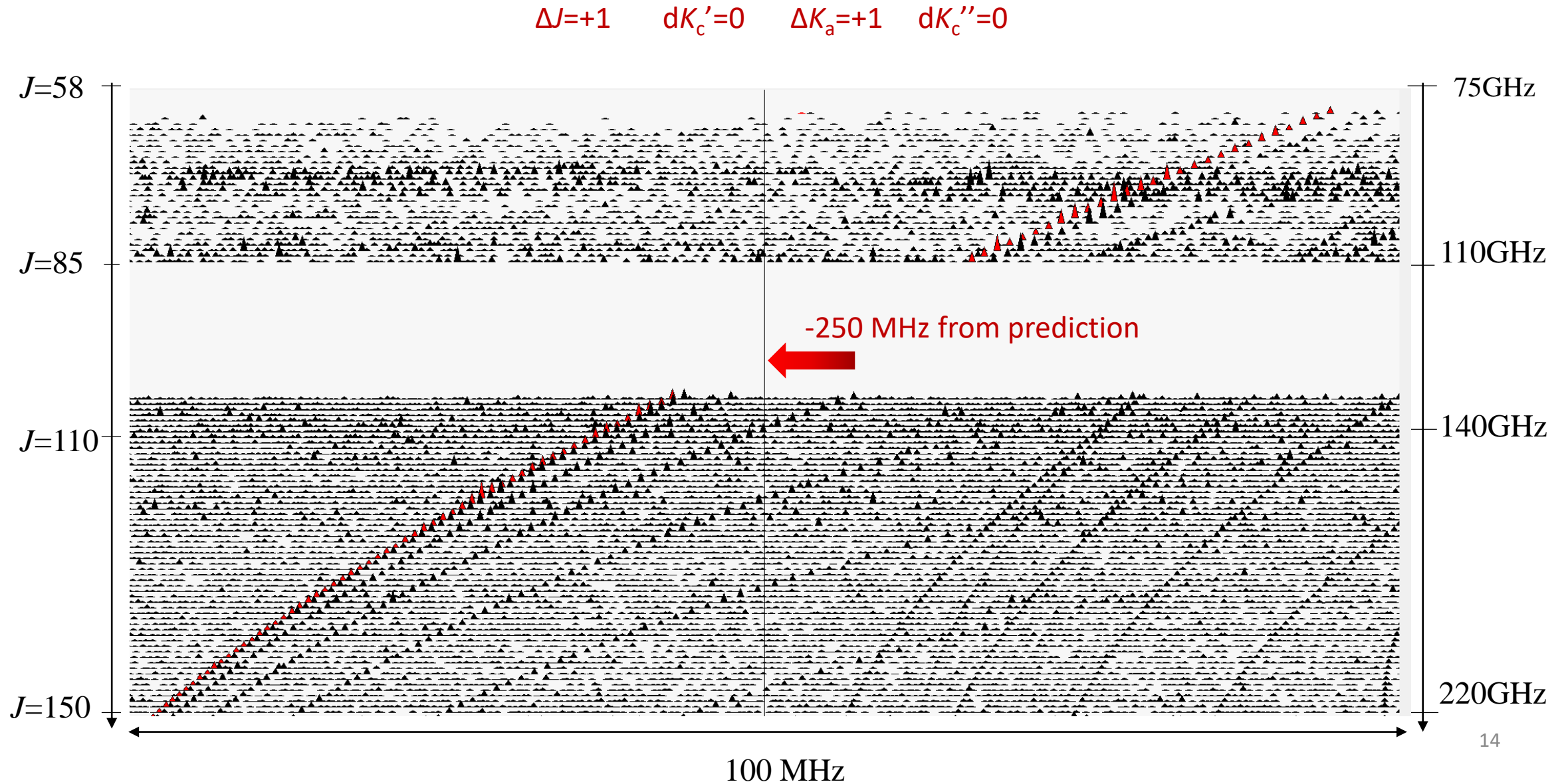
Set of rotational constants

Predict energy levels

Predict the frequency of transitions

Graphical assignment of the experimental frequency to the transition

Export assignments

Graphical exploitation of the spectra: principle

PGOPHER

LWWa

Quantum Chemical Calculations

Fit experimental observations

Set of rotational constants

Predict energy levels

Export assignments

Graphical assignment of the experimental frequency to the transition

Predict the frequency of transitions

$\Delta J=+1 \qquad dK_c'=0 \qquad \Delta K_a=+1 \qquad dK_c''=0$

-250 MHz from prediction

100 MHz

14

Experiment

Simulation

Frequency (GHz)

First vibrational excited states:

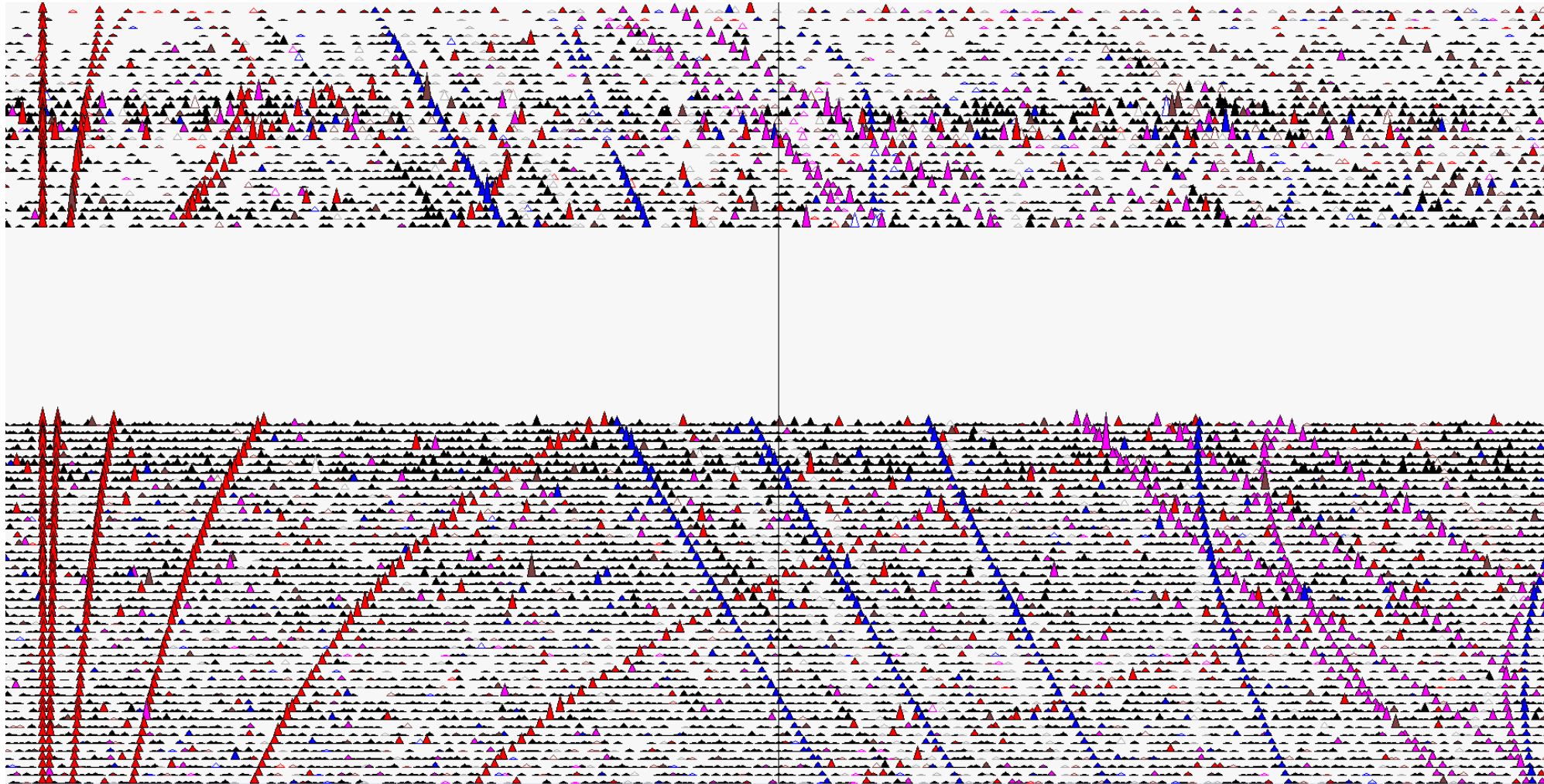ν_{26} = 1 @ 74 cm^{-1}
(oop bending)

ν_{39} = 1 @ 117 cm^{-1}
(ip bending / wagging)

ν_{26} = 2 @ 148 cm^{-1}

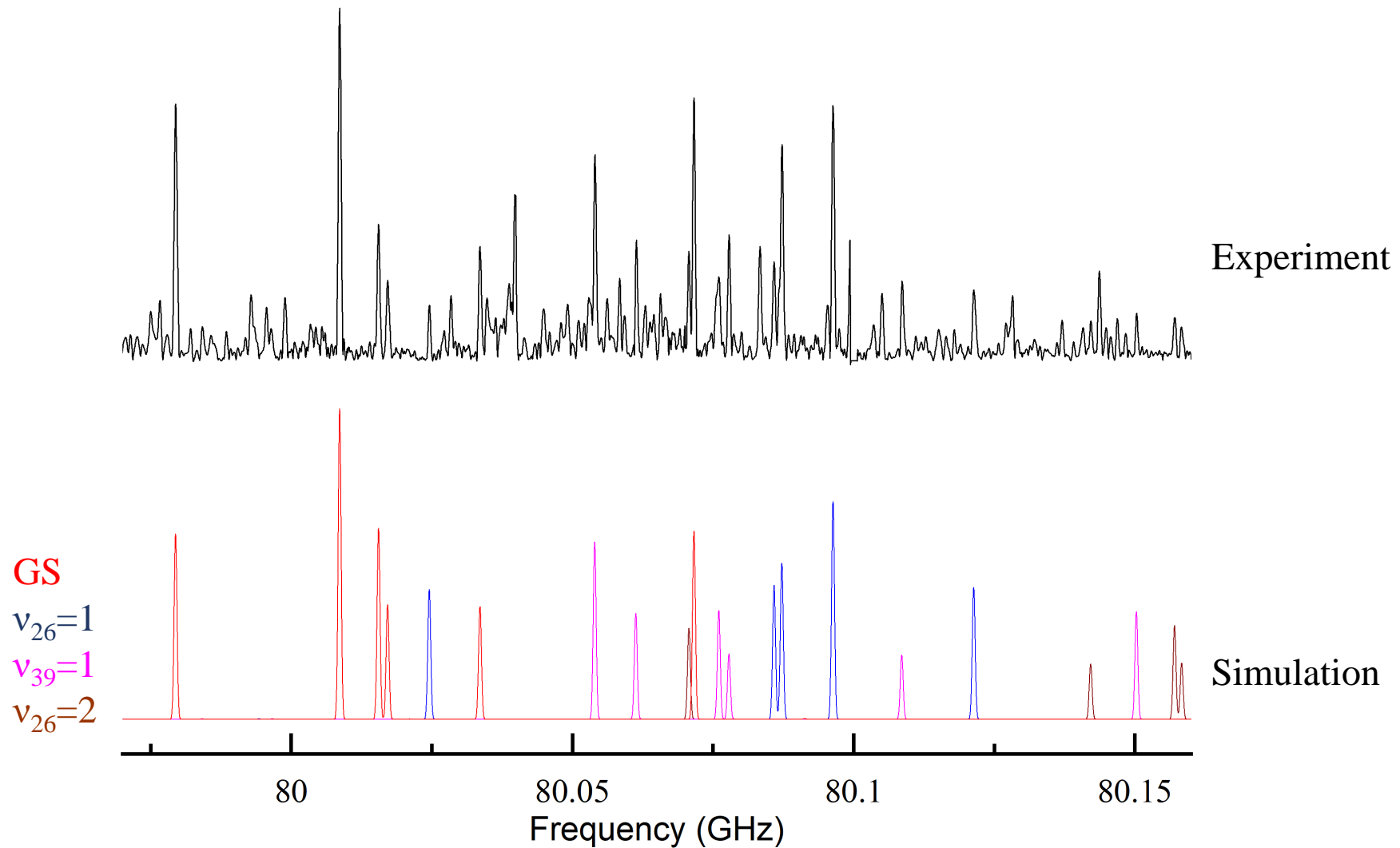DFT Frequency calculation (ωB97XD/cc-pVQZ, anharmonic)

First vibrational excited states:

$\nu_{26} = 1$

$\nu_{39} = 1$

$\nu_{26} = 2$

Exploitation of 4-ETB spectrum: What's left?
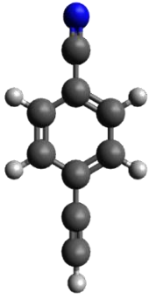
Experiment

GS
$\nu_{26}=1$
$\nu_{39}=1$
$\nu_{26}=2$

Simulation

Frequency (GHz)

80   80.05   80.1   80.15

4-ETB

- 20 743 lines assigned
- 4 states investigated
- Error ~ 0.046 MHz

	A		B		C	
	DFT	EXP	DFT	EXP	DFT	EXP
GS	5647	5646	705	709	627	630
$v_{26}=1$	5529	5542	708	710	628	630
$v_{29}=1$	5732	5747	708	710	630	630
$v_{26}=2$	5425	5443	708	710	631	632

Rk: scaled harmonic constants for GS, anharmonic constants for ES (scaled on GS)

Results
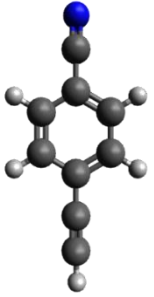
4-ETB

- 20 743 lines assigned
- 4 states investigated
- Error ~ 0.046 MHz

	A		B		C	
	DFT	EXP	DFT	EXP	DFT	EXP
GS	5647	5646	705	709	627	630
$v_{26}=1$	5529	5542	708	710	628	630
$v_{29}=1$	5732	5747	708	710	630	630
$v_{26}=2$	5425	5443	708	710	631	632

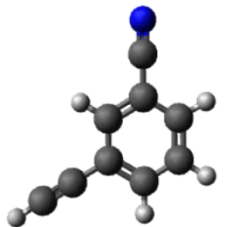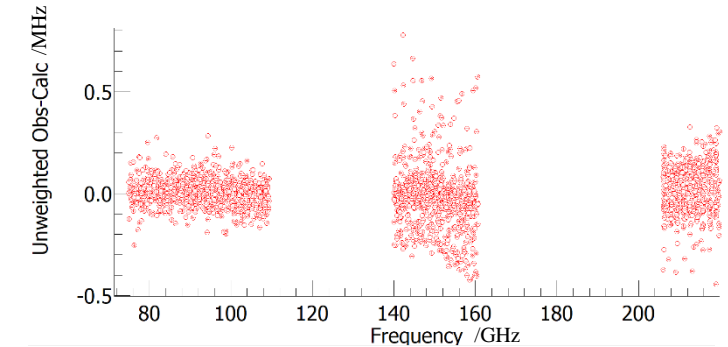*Rk: scaled harmonic constants for GS, anharmonic constants for ES (scaled on GS)*
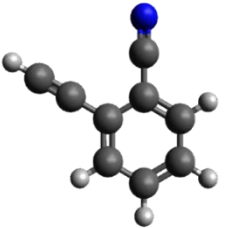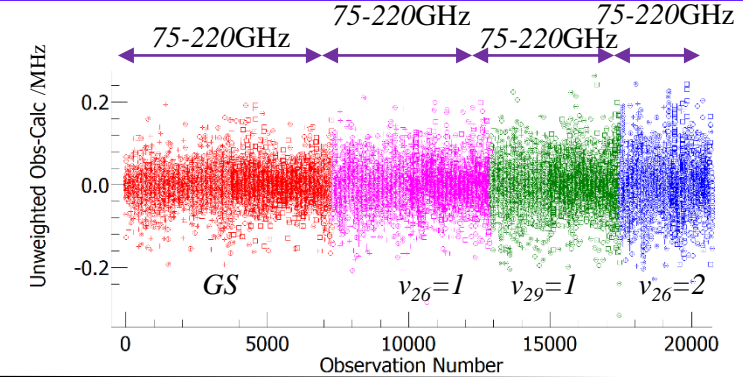
2-ETB

- 5 000 lines assigned
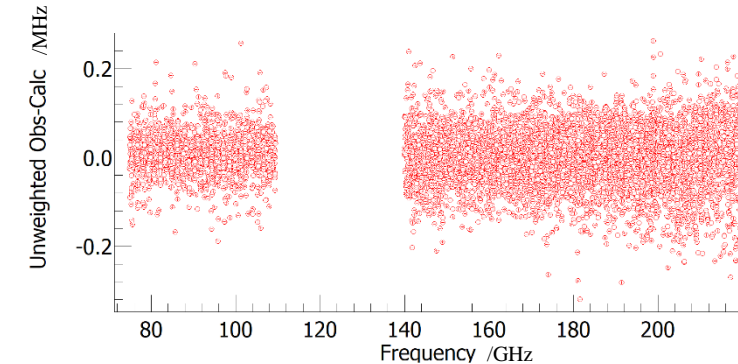- Only ground state investigated
- Work in progress

	A		B		C	
	DFT	EXP	DFT	EXP	DFT	EXP
GS	2002	2027	1329	1329	799	802

3-ETB

- 14 036 lines assigned
- Only ground state investigated
- Work in progress

	A		B		C	
	DFT	EXP	DFT	EXP	DFT	EXP
GS	2697	2705	903	907	677	679

Perspectives

- Assignment of lines to vibrational excited states of 2 and 3-ETB
- Interstellar searches
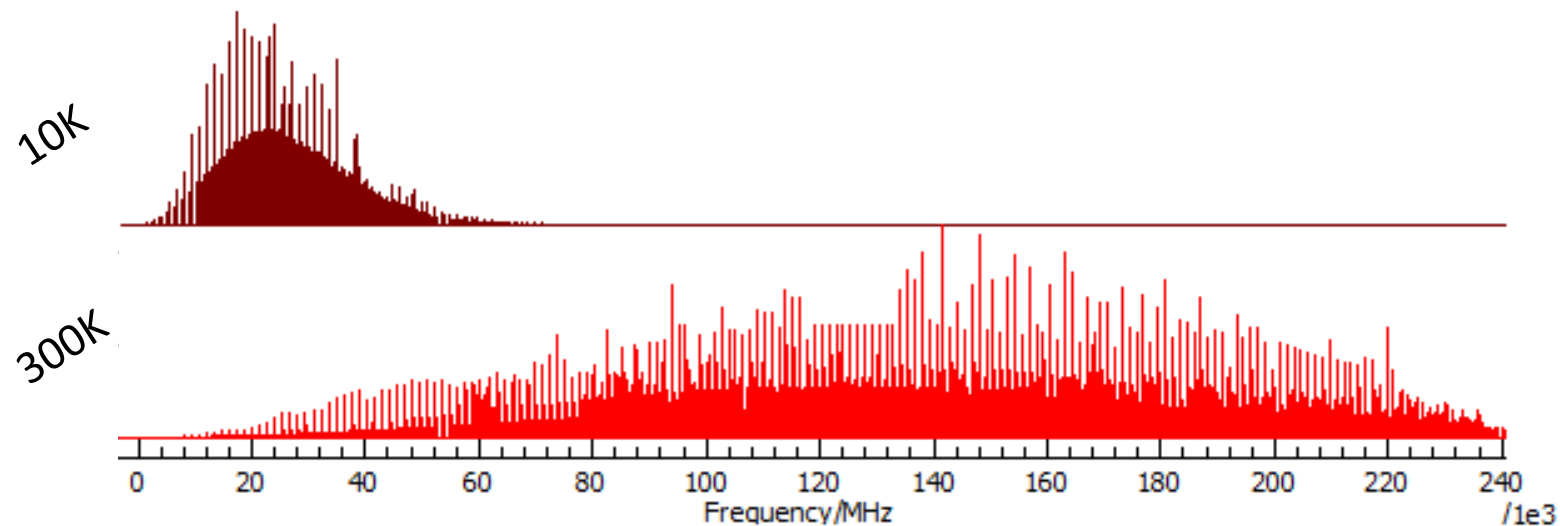
Acknowledgements

Collaborators:

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Department of Chemistry, MIT, Cambridge, USA

Kelvin Lee

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