ISMS 2019 – CHAMPAIGN-URBANA, ILLINOIS

HYDROGEN BONDING IN THE MONOHYDRATES AND HOMODIMERS OF CYCLOHEXYLAMINE AND CYCLOHEXANETHIOL

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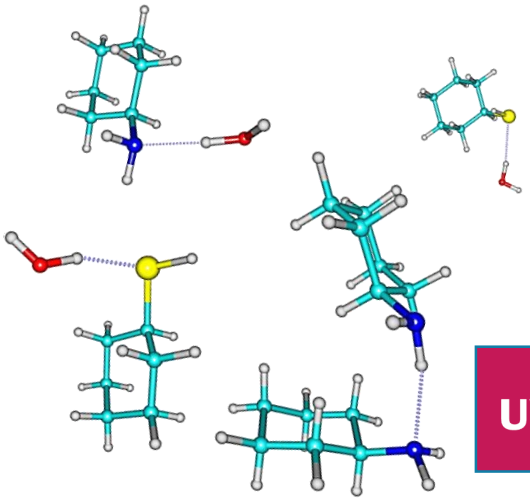
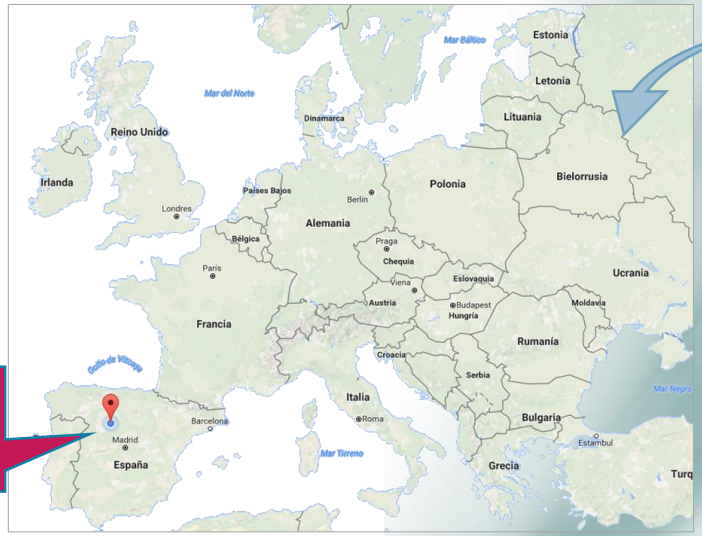


UVa

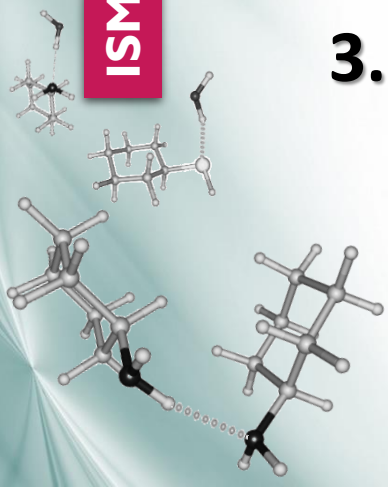


Outline

1. **MODEL**:
   - Cyclohexanethiol (CHT) & Cyclohexylamine (CHA)
   - **Conformation / LAMs**
   - **Hydrogen Bonding for N and S** interactions

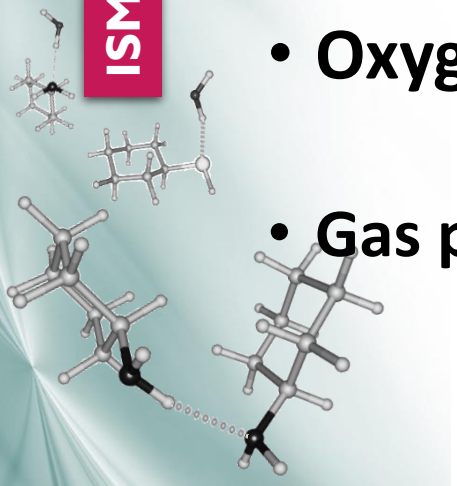
2. **EXPERIMENT**:
   - **Univ. Valladolid**: Chirped-pulsed FT-MW
   - **Univ. Hannover**: Ph.D. visit

3. **RESULTS**:
   - **Microsolvation**: CHA···H_2O, CHT···H_2O, $(Cyclohexylamine)_2$ experimental conformations
   - **Sulfur/Nitrogen HB** comparison & benchmarking



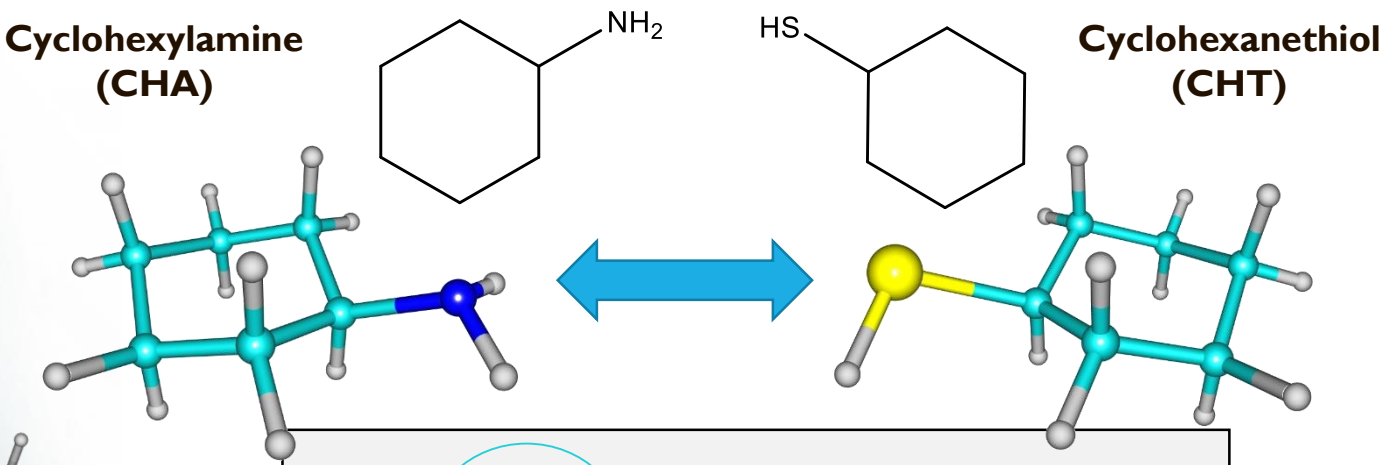
Hydrogen Bonding models

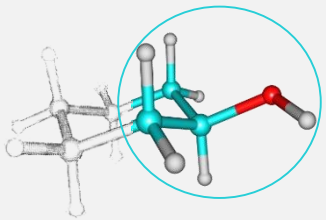
- **Water/Hydroxyl** groups form moderate O-H···B HBs
- **Hydrogen bonds** (HBs) to **sulfur** centers (O-H···S, S-H···O, etc) are weak interactions of dispersive character, with reduced structural influence compared to conventional first-row HBs
- **Rotational analysis** of HB clusters allows comparing the different behavior of oxygen, nitrogen and sulfur compounds
- **Oxygen HB is reference!**: Multiple crystal data
- **Gas phase vs. Crystals:**
  - **Isolated clusters in gas-phase:** *Molecular models*



Cyclohexylamine & -thiol

- **Cyclohexanol** dimer and microsolvation: *Published* PCCP
- **Six-membered ring** with a **–thiol** (CHT) or **–amine** (CHA)
- **Saturated aliphatic skeleton**: No π-ring interactions
- **LAMs***: Low-barrier* **–thiol** or **–amine** internal rotations
  - Tunnelling hyperfine effects





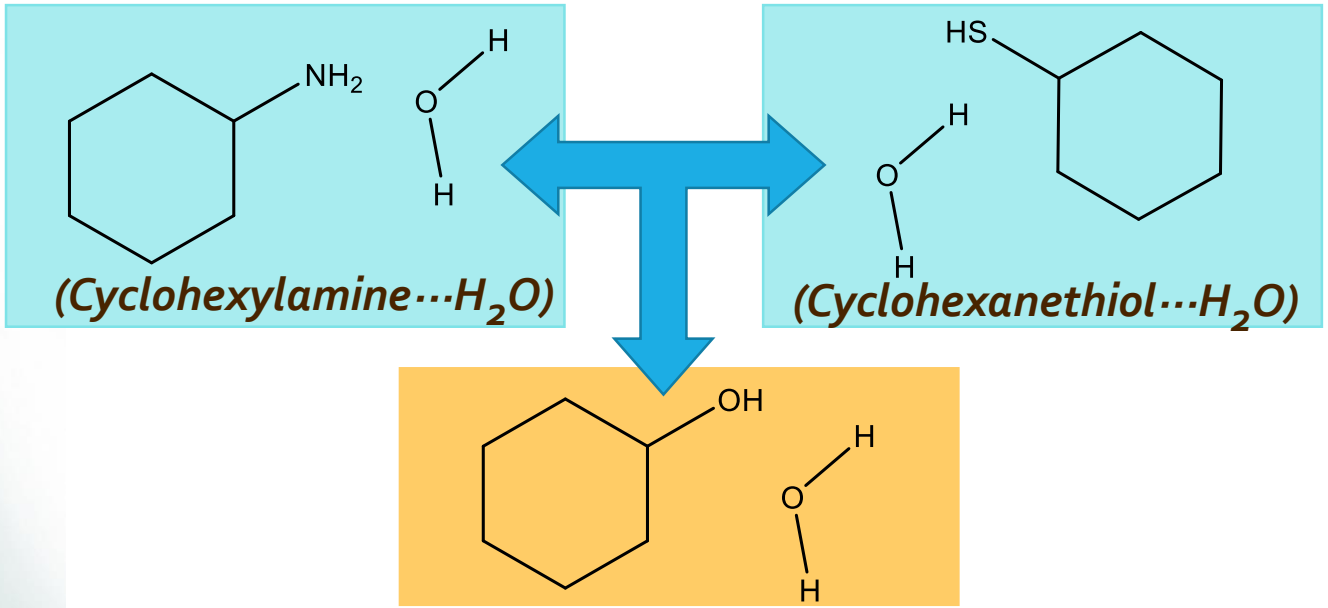
Previous studies: Six-membered ring

Cyclohexanol

M. Juanes, A. Lesarri, *et al.*, ***PCCP,*** **2019**, 21, 3676

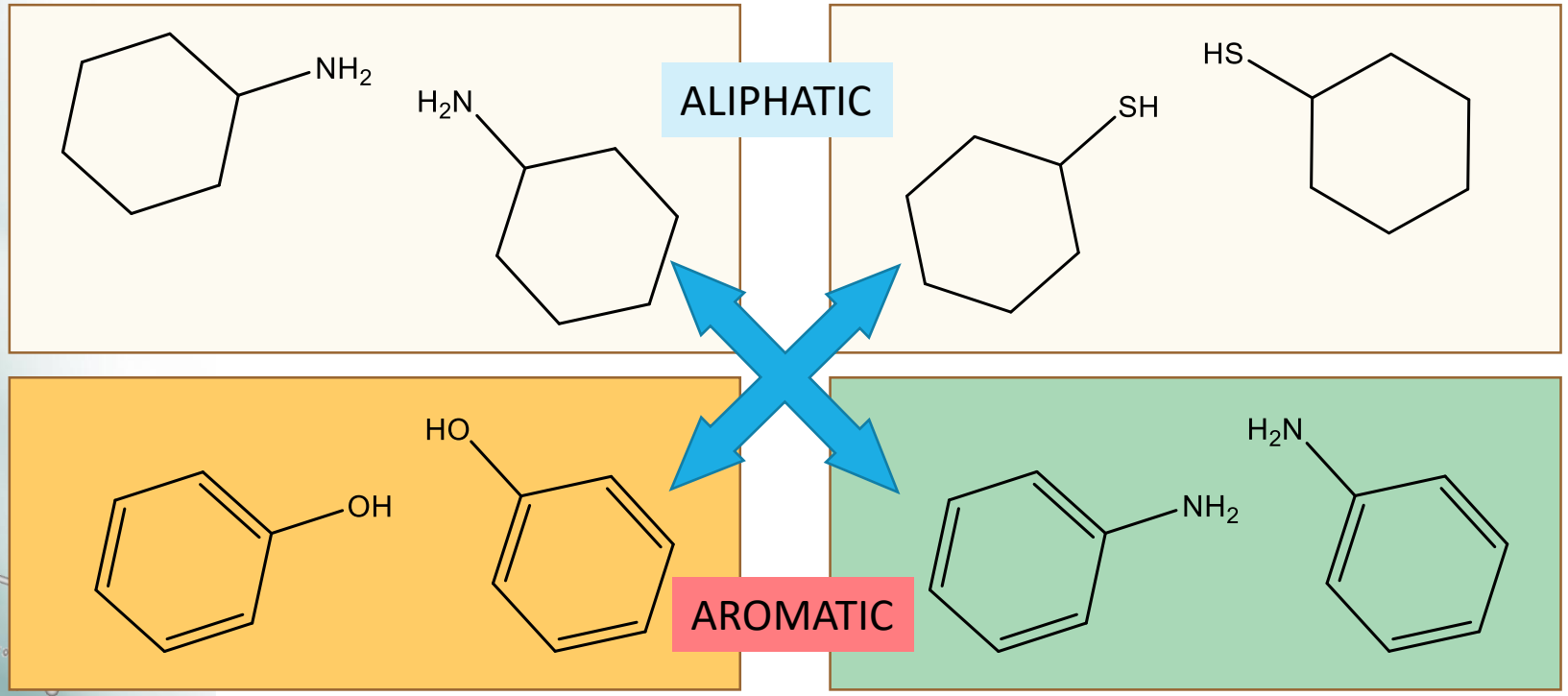
Monohydrated dimers

- Different **binding sites** / **HB strengh** / **LAM**s
  - Different amine/thiol group orientations
  - O-H···N? vs N-H···O? and O-H···S? vs S-H···O?
- The **orientation**, **conformation** and **structure** of water strongly depends on the attached monomer
- Ring influence?



(Homo)dimers

- **Hydrogen Bond: N-H···N** (2 donors, 1 acceptor)
- Previous studies to **compare** and **quantify** different HB interactions
- Better understanding of the complex generation



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Experiment

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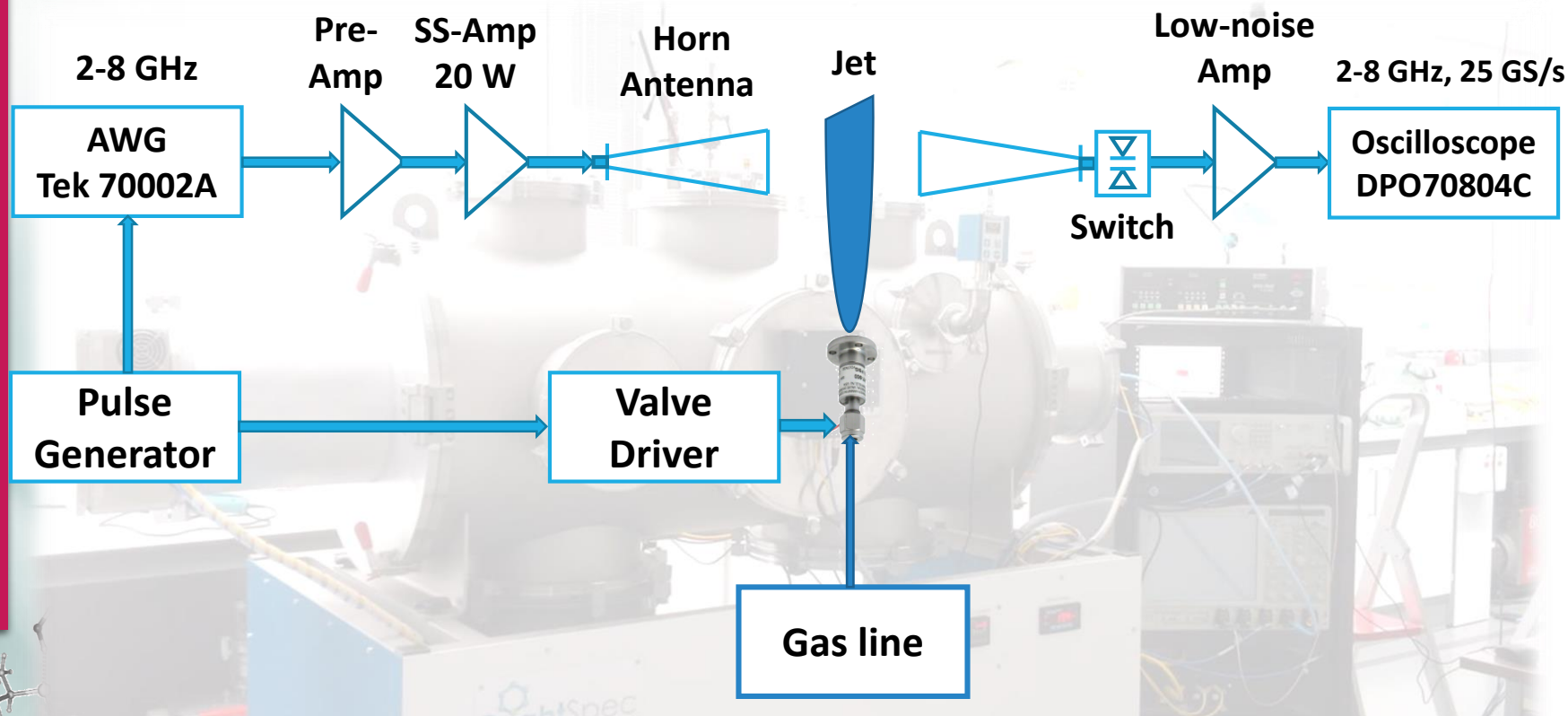
Chirped-pulsed FTMW @ Valladolid



Brooks Pate's design
BrightSpec

Chirped-Pulsed FT-MW spectrometer

Facultad de Ciencias, Univ. Valladolid (Spain)

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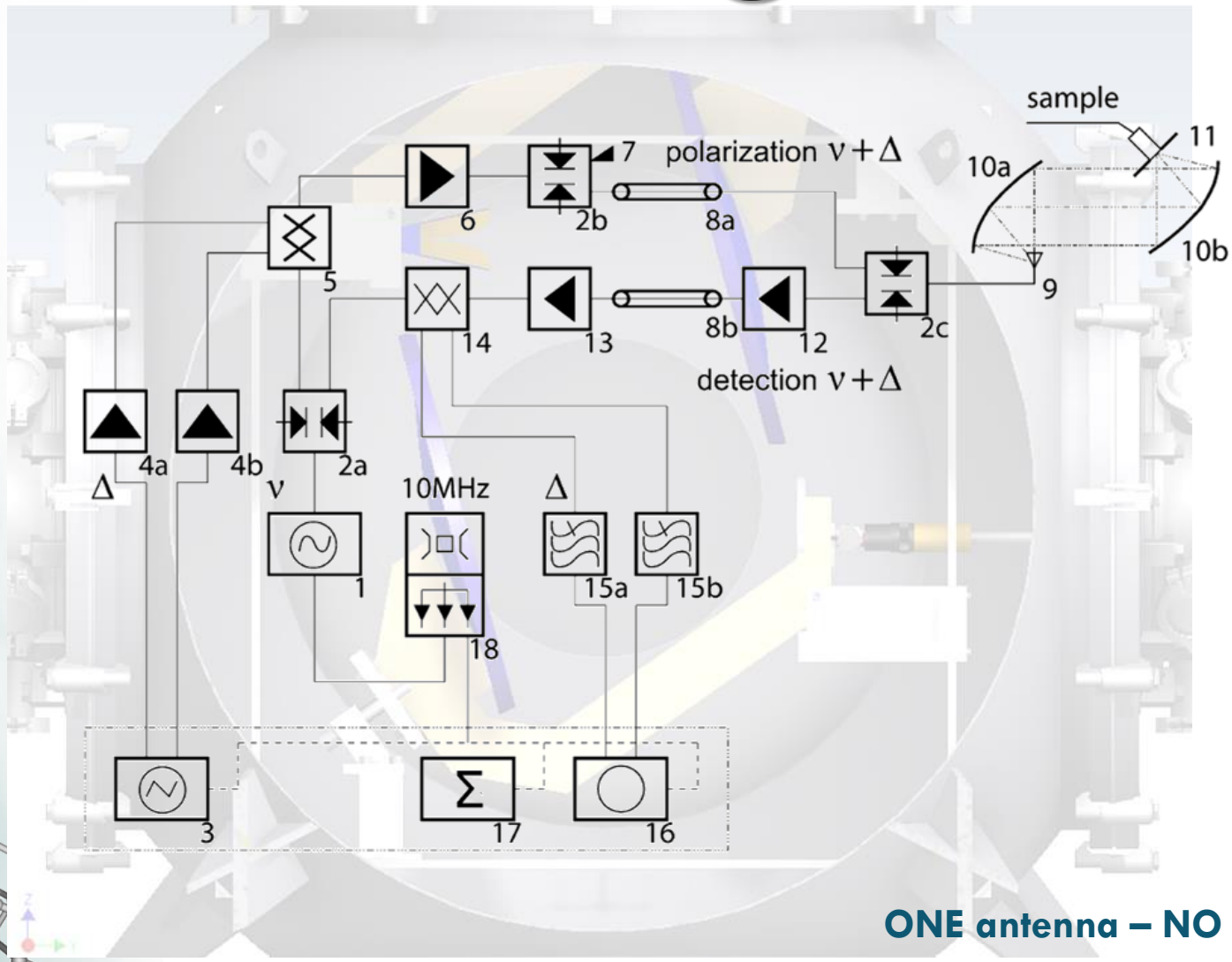
Chirped-pulsed FTMW @ Valladolid

Chirped-Pulsed FT-MW spectrometer

Facultad de Ciencias, Univ. Valladolid (Spain)

IMPACT FTMW @ Hannover



ONE antenna – NO switches!

J.-U. Grabow et al., *J. Mol. Spectrosc.* **280** (2012) 54–60

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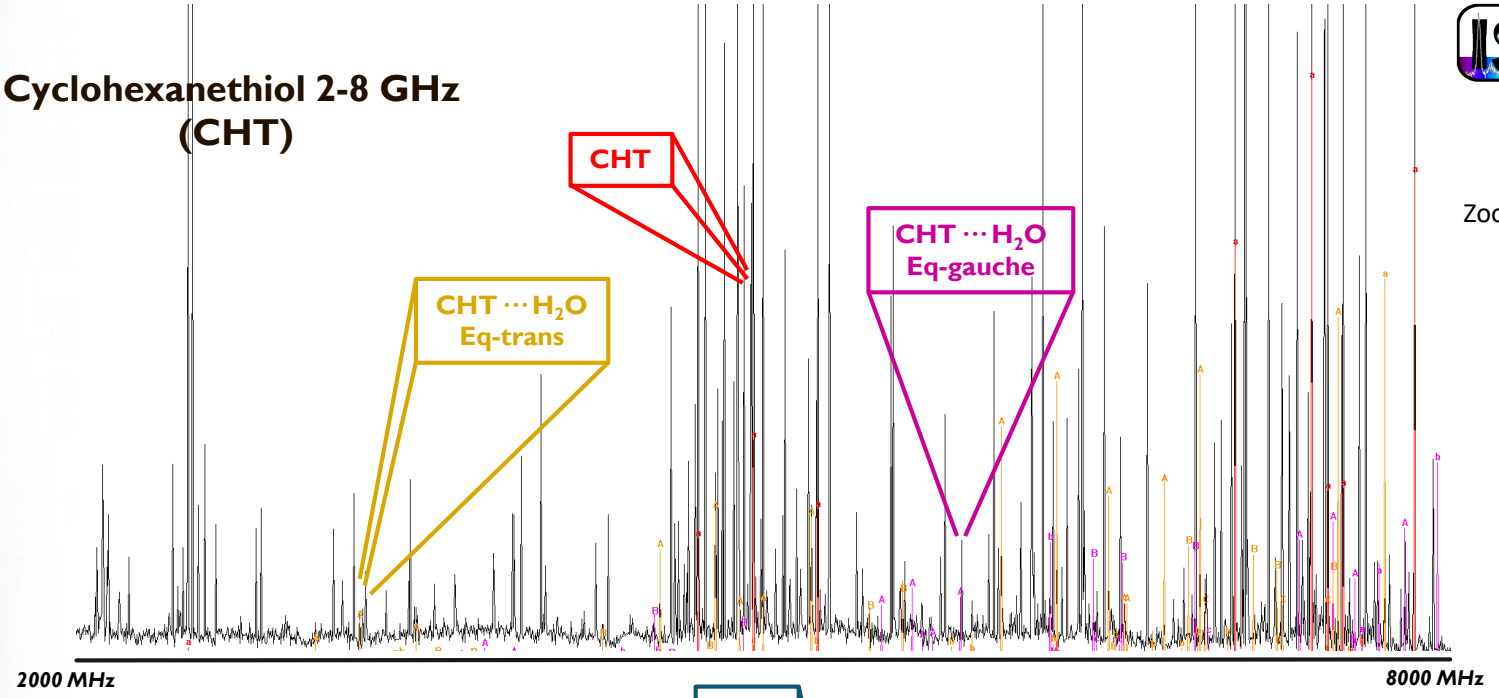
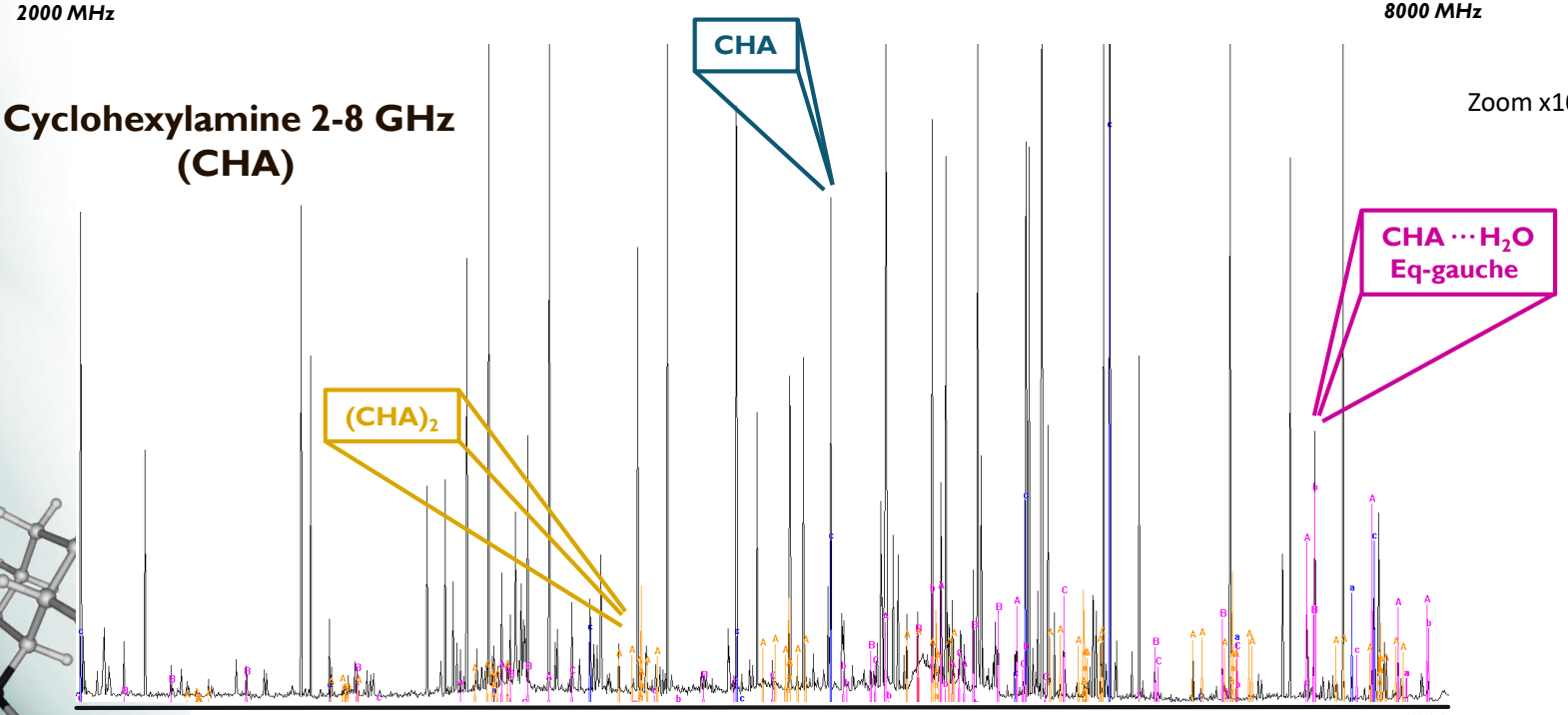
Cyclohexanethiol 2-8 GHz (CHT)



Cyclohexylamine 2-8 GHz (CHA)



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Results

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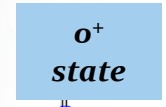
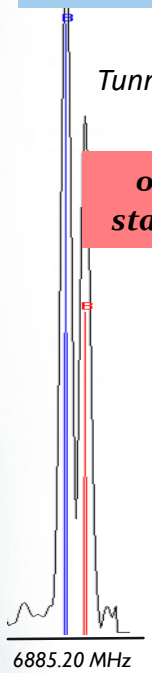
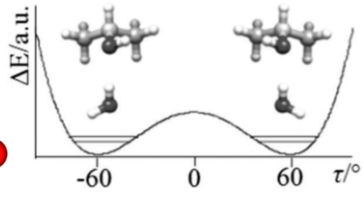
Cyclohexanethiol ···H_2O





$5_{33} \leftarrow 5_{24}$
Tunnelling splitting

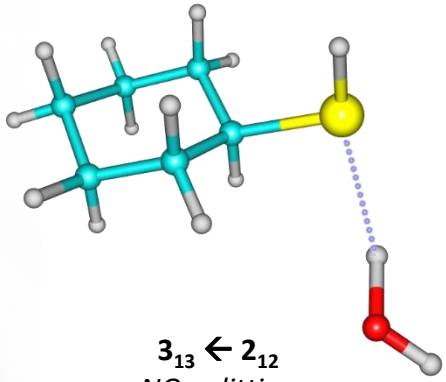
Concerted LAM



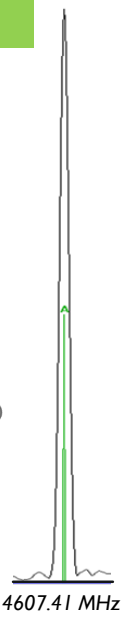
EQUATORIAL GAUCHE

	EQUATORIAL GAUCHE		Theory**
	o+	o-	
A / MHz	1873.8204(96)	1873.8534(94)	1919.72
B / MHz	1019.5331(29)	1019.5292(29)	1033.88
C / MHz	902.7858(15)	902.7888(15)	929.40
D_J / kHz	0.368(31)	0.414(33)	0.2012
D_{JK} / kHz	1.85(22)	0.33(18)	0.9760
D_K / kHz	0.55(65)	3.44(70)	-0.1907
d_1 / Hz	[0.]	[0.]	-0.0085
d_2 / Hz	0.016(10)	0.030(16)	0.0124
$\|\mu_a\|$ / D			0.13
$\|\mu_b\|$ / D			0.60
$\|\mu_c\|$ / D			0.64
ΔE_{ZPE} / kJ mol^{-1}			0.0
ΔG / kJ mol^{-1}			2.7
σ / kHz	15.2		
N	58		

EQUATORIAL TRANS



$3_{13} \leftarrow 2_{12}$
NO-splitting



	EQUATORIAL TRANS	Theory**
A / MHz	2206.3913(88)	2198.70
B / MHz	937.9093(19)	951.20
C / MHz	714.7963(18)	717.60
D_J / kHz	1.284(52)	0.4172
D_{JK} / kHz	-3.43(20)	-0.7203
D_K / kHz	10.3(18)	3.3669
d_1 / Hz	[0.]	-0.0548
d_2 / Hz	-0.060(22)	-0.0167
$\|\mu_a\|$ / D		0.89
$\|\mu_b\|$ / D		0.73
$\|\mu_c\|$ / D		0.69
ΔE_{ZPE} / kJ mol^{-1}		0.18
ΔG / kJ mol^{-1}		0.00
σ / kHz	15.9	
N	34	

(**) *B3LYP-GD3BJ/def2_TZVP*

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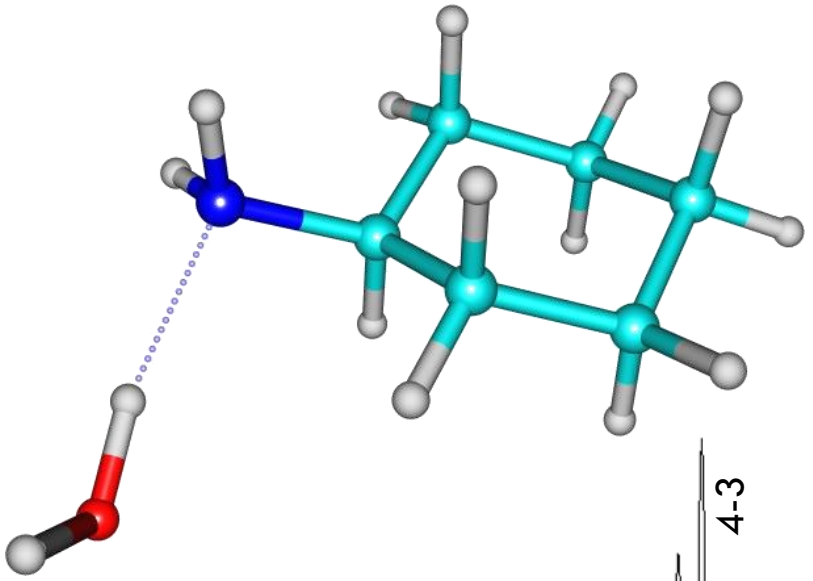
Cyclohexylamine ··· H_2O

EQUATORIAL GAUCHE-TRANS

	Experimental	Theory**
A / MHz	3100.6238(26)	3150.64
B / MHz	1063.22662(65)	1053.62
C / MHz	873.11113(81)	869.08
D_J / kHz	0.683(15)	0.7103
D_{JK} / kHz	-3.108(92)	-3.6594
D_K / kHz	9.91(57)	9.0788
d_1 / Hz	-0.0784(75)	-0.1009
d_2 / Hz	[0.]	-0.0094
$\lvert\mu_a\rvert$/ D		2.10
$\lvert\mu_b\rvert$/ D		1.41
$\lvert\mu_c\rvert$/ D		2.12
χ_{aa} / MHz	-2.0102(65)	-2.05
χ_{bb} / MHz	0.8159(84)	0.82
χ_{cc} / MHz	1.1944(84)	1.23
σ / kHz	12.3	
N	103	

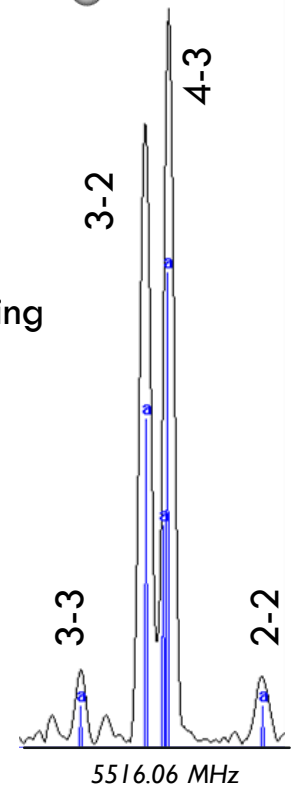
(**) *B3LYP-GD3BJ/def2_TZVP*



No LAM tunnelling

^{14}N Nuclear Quadrupole Coupling

$3_{13} \leftarrow 2_{12}$



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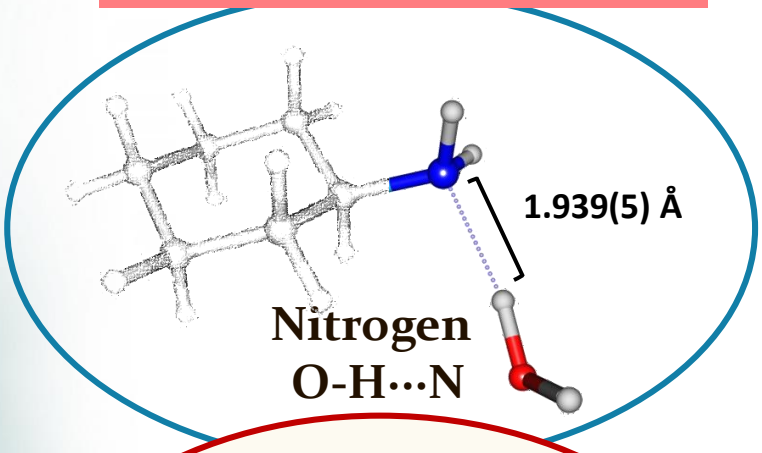
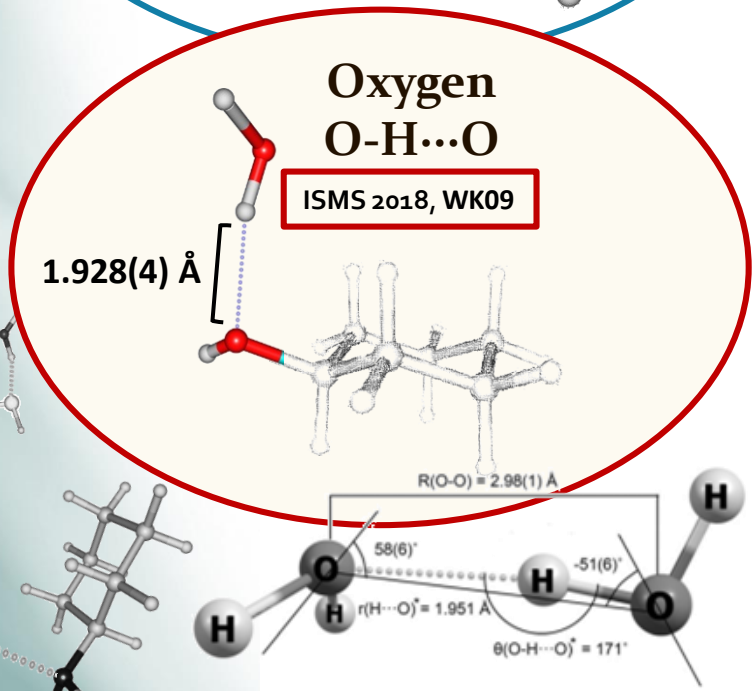
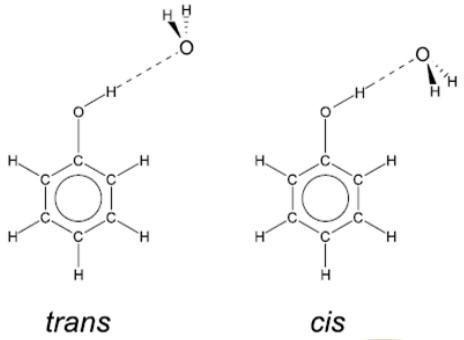
Sulfur vs. Nitrogen vs. Oxygen HB

Water always proton donor

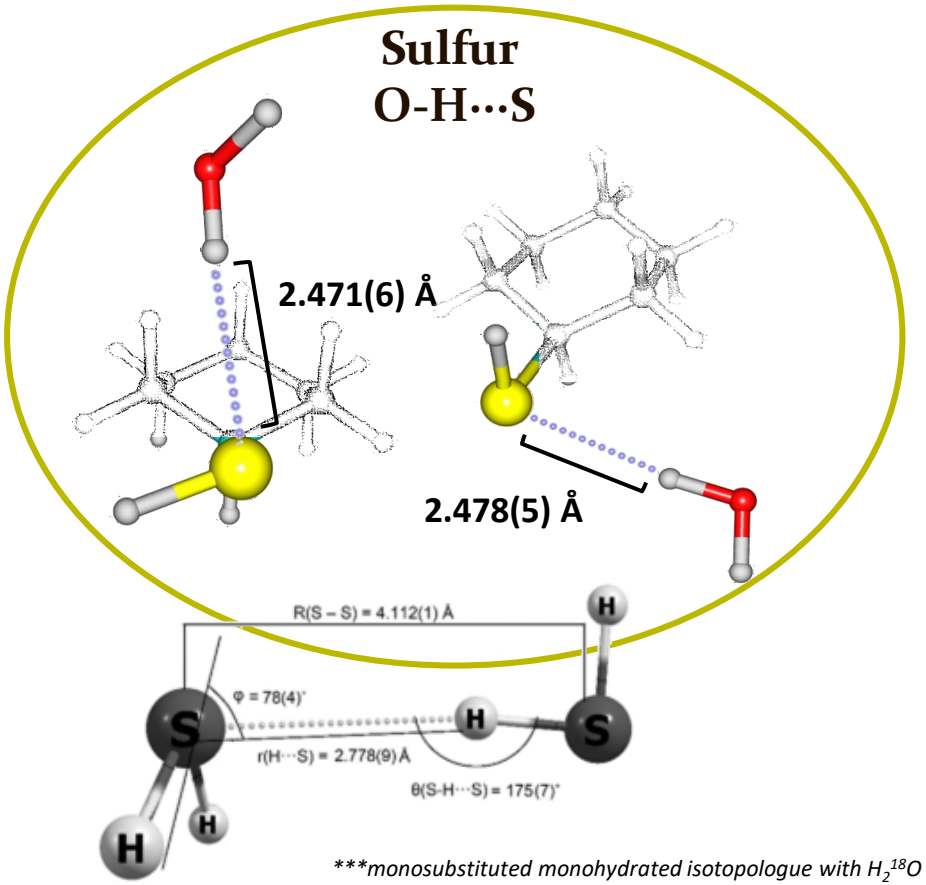






Water proton aceptor in PhOH

ChemPhys, 283 (2002), 185



****monosubstituted monohydrated isotopologue with $H_2{}^{18}O$ was used to calculate the effective structure (r_0)****

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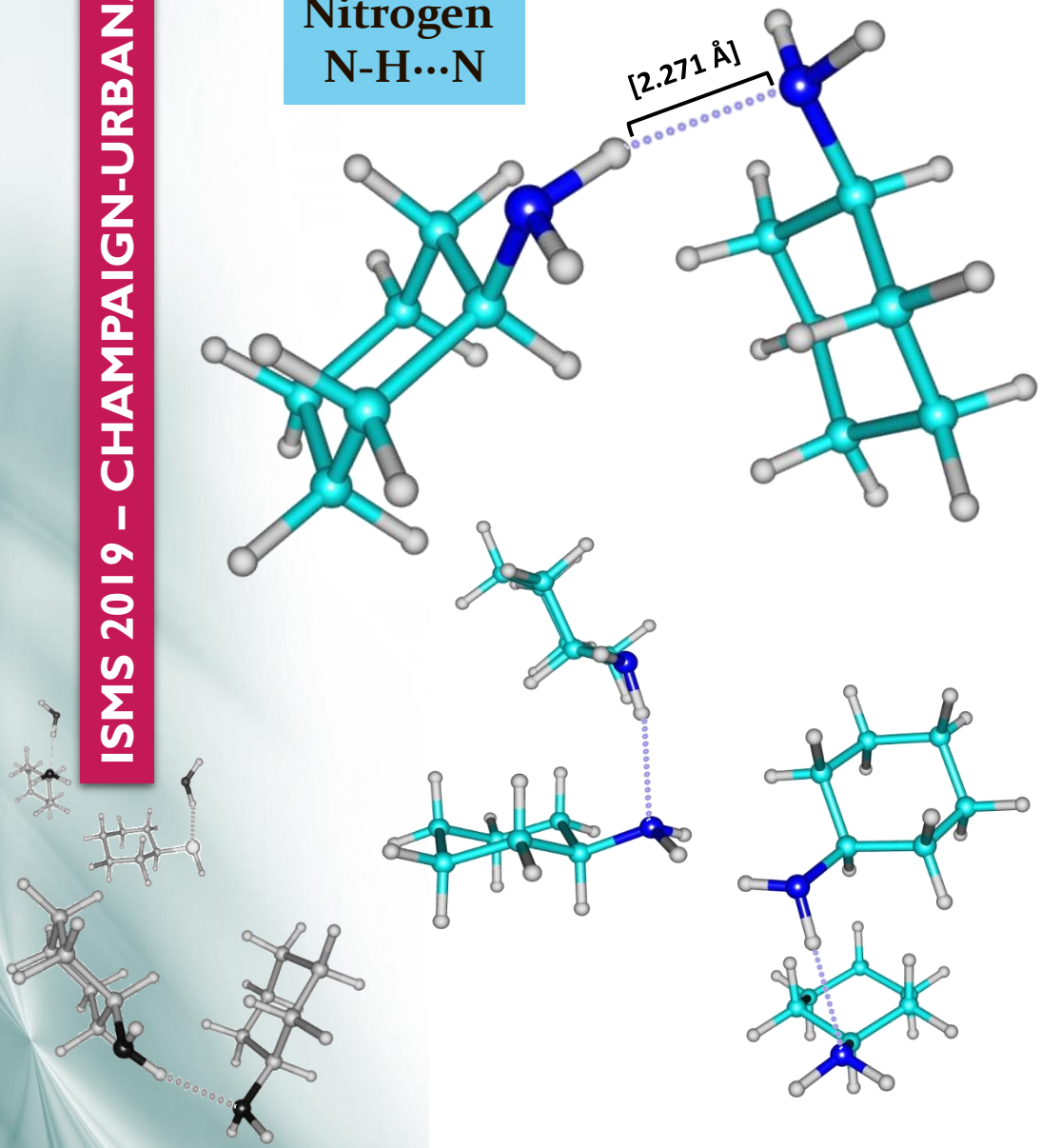
(Cyclohexylamine)$_2$

Nitrogen N-H···N

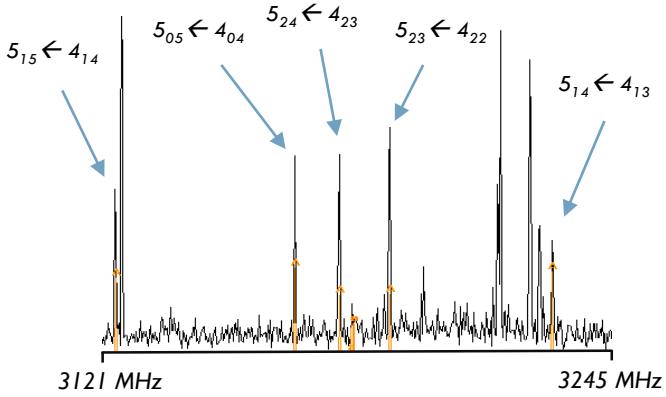


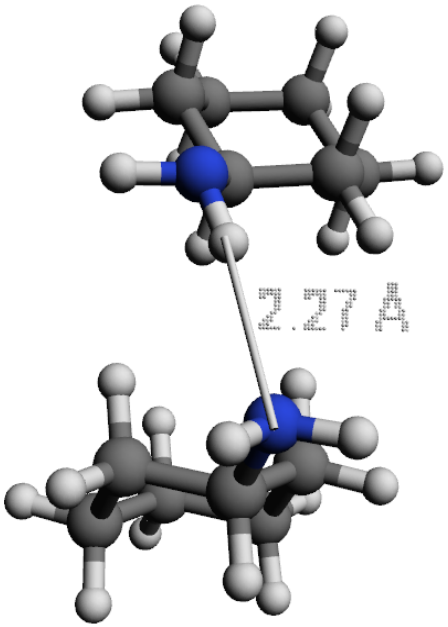
(EQUATORIAL GAUCHE-GAUCHE)$_2$

	Experimental	Theory**
A / MHz	929.17(10)	929.17
B / MHz	330.2589(17)	341.12
C / MHz	306.7403(16)	316.63
D_J / kHz	0.1693(27)	0.1525
D_{JK} / kHz	-0.453(31)	-0.3019
D_K / kHz	[0.]	0.5039
d_1 / kHz	-0.0221(37)	-0.0220
d_2 / kHz	[0.]	-0.0010
$\lvert\mu_a\rvert$/ D		2.58
$\lvert\mu_b\rvert$/ D		0.64
$\lvert\mu_c\rvert$/ D		0.20
σ / kHz	24.4	
N	69	

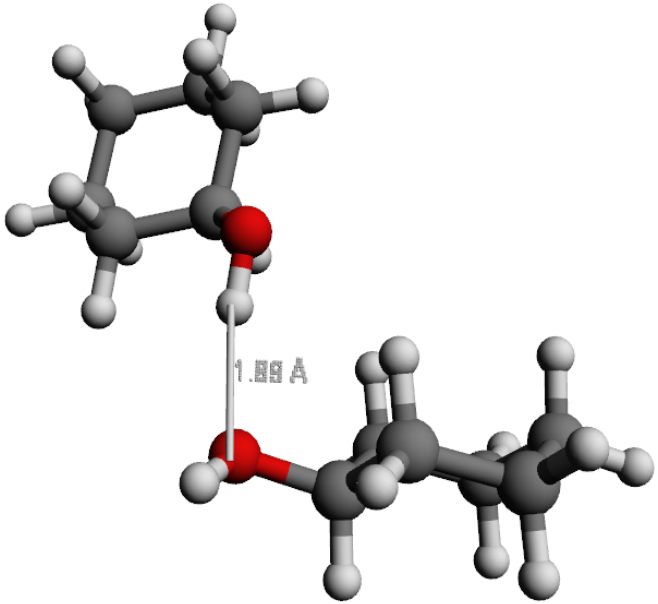
(**) B3LYP-GD3BJ/def2_TZVP

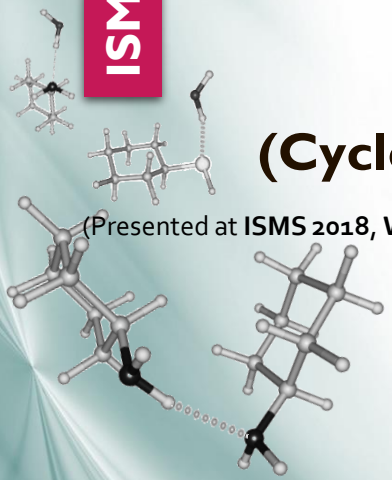
Illustration of some μ_a - type rotational transitions of J ≡ 5 ← 4





(Cyclohexylamine)$_2$





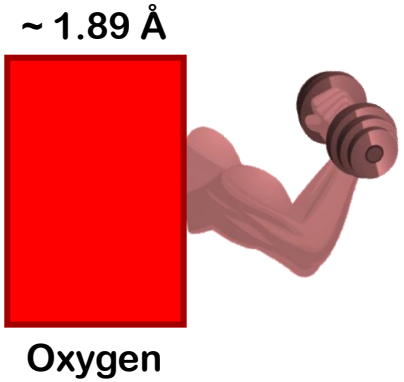
(Cyclohexanol)$_2$

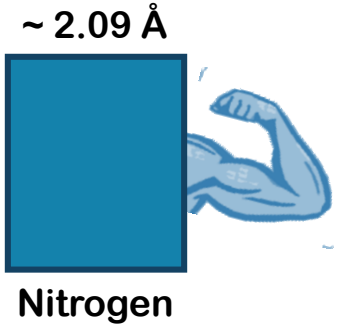
(Presented at **ISMS 2018, WK09**. M. Juanes, A. Lesarri, *et al.*)

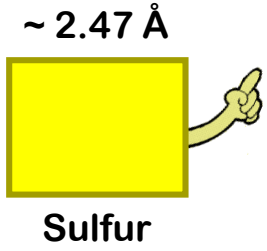
Conclusions – Structural Data

Type	HB	Distance (Å)	
Monohydrated	O-H ⋯ **O**	**1.928(4)**	Cyclohexanol ⋯ H_2O
	O-H ⋯ **S**	**2.471(6)**	Cyclohexanethiol ⋯ H_2O
		2.478(5)	
	O-H ⋯ **N**	**1.939(5)**	Cyclohexylamine ⋯ H_2O
Homodimer	O-H ⋯ **O**	**[1.891]**	$(Cyclohexanol)_2$
	O-H ⋯ **N**	**[2.271]**	$(Cyclohexylamine)_2$

B3LYP-GD3BJ/def2TZVP







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Conclusions – Energy Decomposition

Type	*HB*	$\Delta E_{Electrostatic}$	$\Delta E_{induction}$	$\Delta E_{Dispersion}$	$\Delta E_{Exchange}$	ΔE_{Total}	
Monohydrated	O-H ⋯ **O**	-46.05	-12.47	-11.62	42.74	-27.40	Cyclohexanol ⋯ H_2O
	O-H ⋯ **S**	-35.15	-10.61	-12.50	39.09	-19.17	Cyclohexanethiol ⋯ H_2O
		-32.02	-9.78	-10.29	34.49	-17.60	
	O-H ⋯ **N**	-61.60	-19.68	-13.25	62.34	-32.18	Cyclohexylamine ⋯ H_2O
Homodimer	O-H ⋯ **O**	-46.90	-13.69	-18.56	49.08	-30.06	$(Cyclohexanol)_2$
	O-H ⋯ **N**	-28.54	-7.94	-24.06	41.03	-19.51	$(Cyclohexylamine)_2$

SAPT(0)/jun-cc-pVDZ results in **kJmol^{-1}**

	HB	$\Delta E_{Electrostatic}$	$\Delta E_{Dispersion}$
Monohydrated	O-H ⋯ **O**	++	+
	O-H ⋯ **S**	++	++
	O-H ⋯ **N**	+++	+
Homodimer	O-H ⋯ **O**	++	++
	O-H ⋯ **N**	+	+++

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Conclusions

- **Isolated clusters in gas-phase provide structural and energetic information on** hydrogen bonding
- Comparison between oxygen, sulfur and nitrogen compounds illustrate HB ***patterns***
- **Chirped-pulse MW spectroscopy** is a powerful tool for intermolecular interactions
- **Benchmark for theory:** DFT+Dispersion
  - Good theorical models crucial
  - Starting point for other clusters

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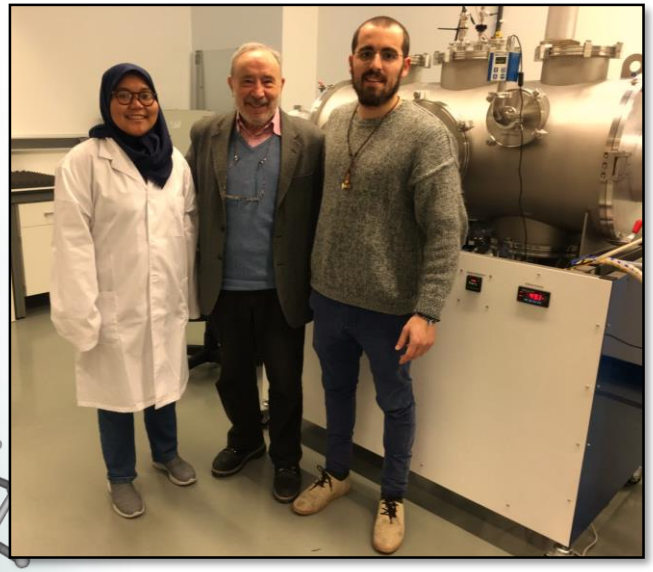
Team

D. Obenchain J. Grabow

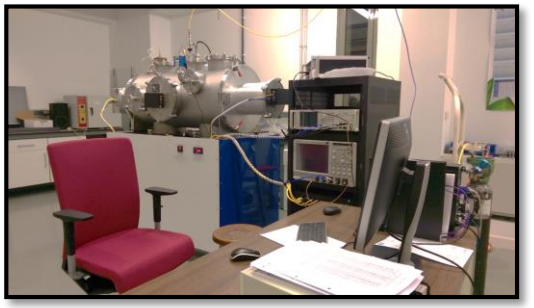
Alberto Lesarri

Project-head
PhD Supervisor

L. Evangelisti



R.T. Saragi W. Caminati M. Juanes



Chirped-Pulsed FT-MW spectrometer
Facultad de Ciencias, Univ. Valladolid (Spain)

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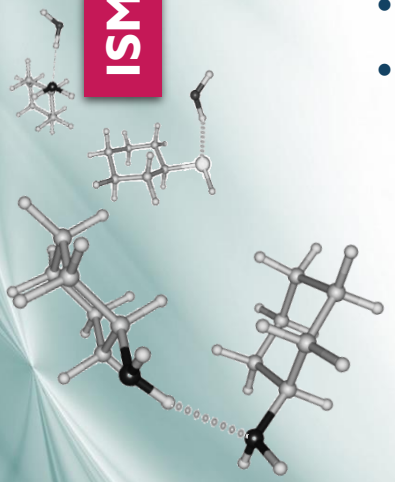
Thank you very much!

Acknowledgements

- **FPI Grant:** BES-2016-077736
- **MICINN-FEDER Project** PGC2018-098561-B-C22



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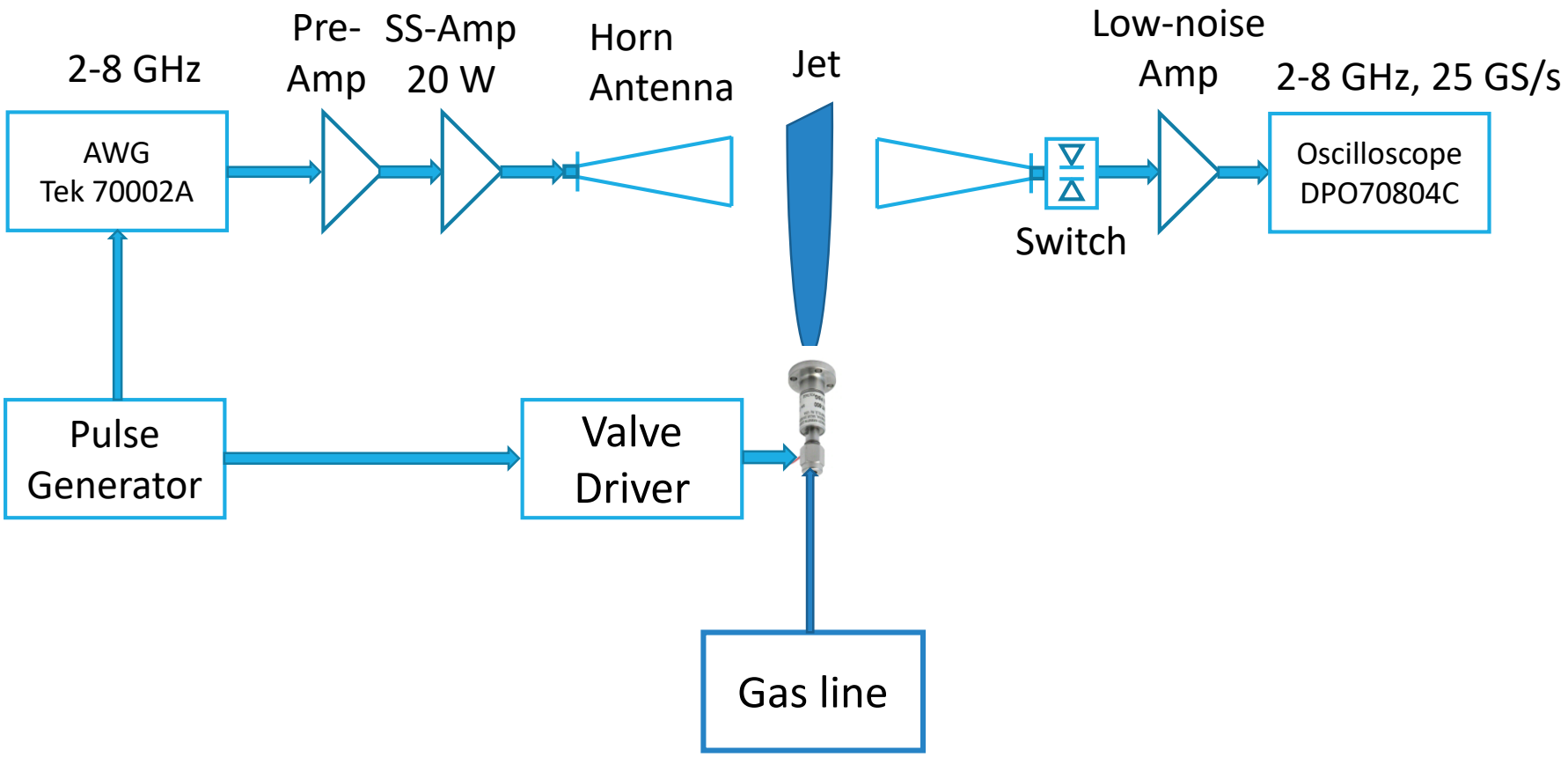

The detection is made of a power limiter (omitted in the drawing), a PIN-diode switch and the low-noise amplifier. Both the AWG and the scope (Tektronix) are 25 MSamples/s, but the bandwidth of the scope is 8 GHz. The chirp is usually 4 microseg. The limiting factor is the solid state power amplifier for excitation, which is 20W