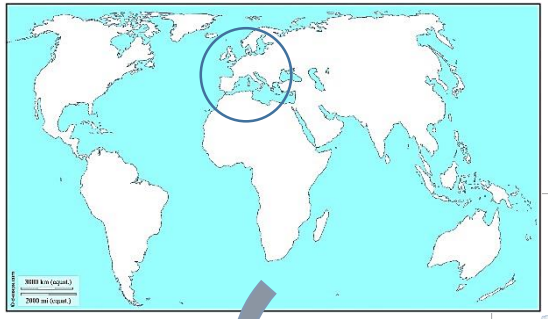
ISMS 2019 – CHAMPAIGN-URBANA, ILLINOIS

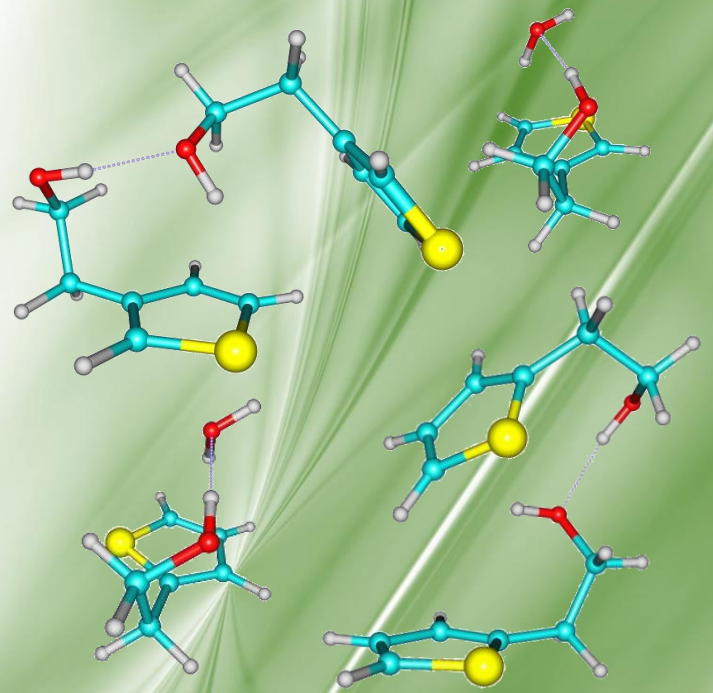
DIMERIZATION AND MICROSOLVATION OF 2- AND 3-THIOPHENEETHANOL

M. Juanes[1], R.T. Saragi[1], L. Enriquez[2], M. Jaraíz[2], A. Lesarri[1]

[1]Departamento de Química Física y Química Inorgánica, **UNIVERSIDAD DE VALLADOLID** (Spain)

[2]Departamento de Electrónica, ETSIT. **UNIVERSIDAD DE VALLADOLID** (Spain)





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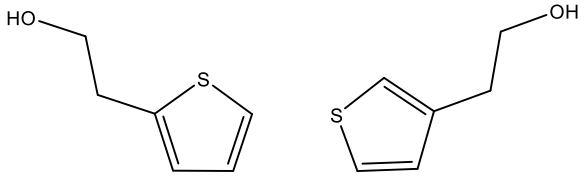
Outline

1. HYDROGEN BONDING MODELS:

- Hydrogen Bonding (HB): Sulfur vs. Oxygen
- *Dimerization* & *Microsolvation*:

2&3-Thiopheneethanol (2-TPE, 3-TPE)

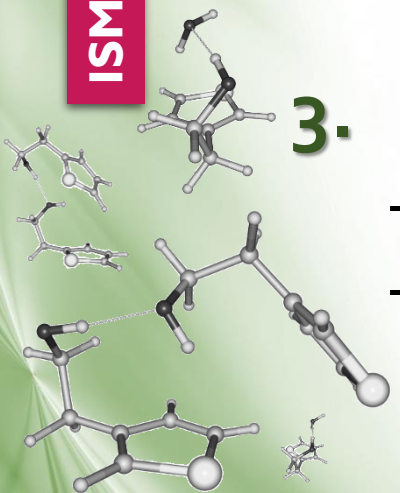


2. EXPERIMENT:

- The lab: Chirped-pulsed FT-Microwave Spectroscopy

3. RESULTS:

- (2-TPE)2, (3-TPE)2, 2-TPE···H_2O, 3-TPE···H2O
- Structural influence of Sulfur HB



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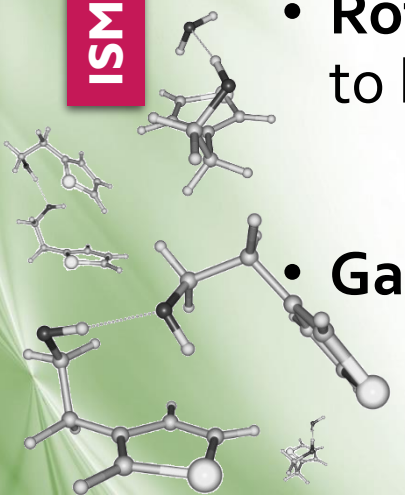
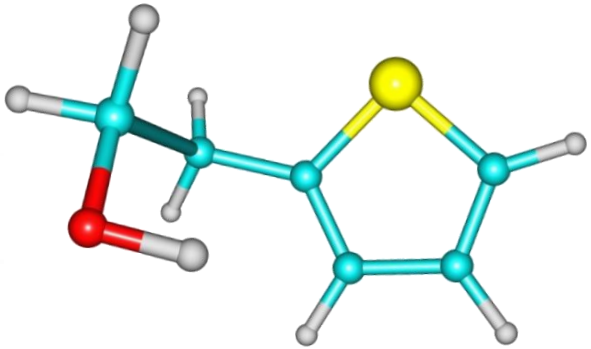
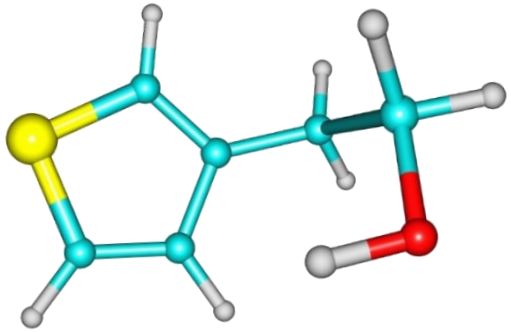
Sulfur and Oxygen HBs

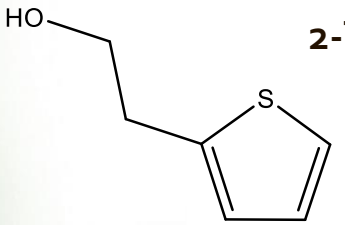
- **HB in Low-electronegativity** atoms
  - O-H···S, S-H···O, S-H···S, etc
- **Chalcogen Bonds**: **Sulfur** as *electrophilic* centers
  - R-S···B
- Different behavior of similar structures where **Oxygen** and/or **Sulfur** take the **main role**
- **Rotational analysis** of hydrogen-bonded clusters allows to have experimental results to compare
- **Gas phase vs. Crystals:**
  - **Isolated clusters in gas-phase:** *Molecular models*



2&3-Thiopheneethanol

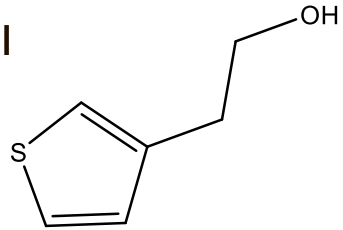




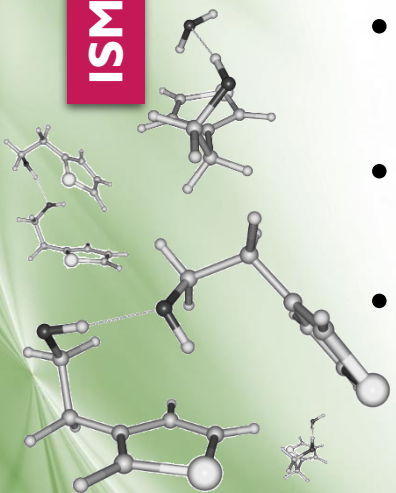


2-Thiopheneethanol
2-TPE

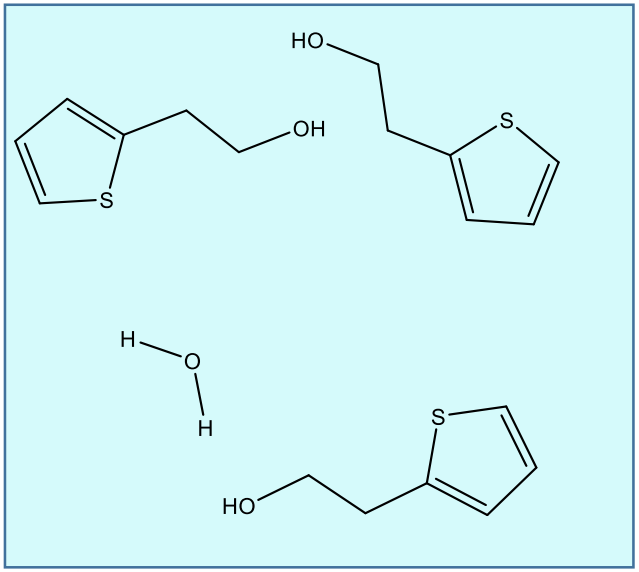
3-Thiopheneethanol
3-TPE

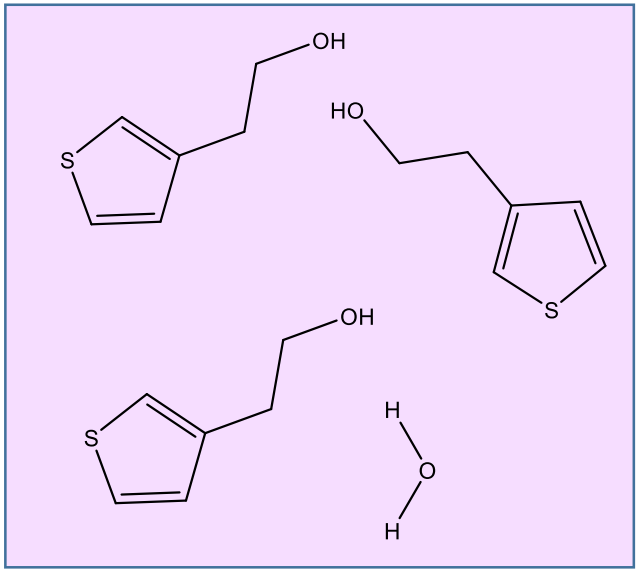


- **Structural isomerism**:
  - Same **molecular-composition** and similar structures
- Differences at the **Sulfur location** (-2 or -3)
- *Low-barrier* orientation of the **–alcohol** group



Dimerization & Microsolvation





- **Moderate Hydrogen bonds** involving **hydroxyl groups:**
  - **O-H···O, O-H···S**
- **Different orientations** of water in the **monohydrates**
- **Several binding sites** at the **dimer**
  - + other *plausible interactions*

Intermolecular Clusters

- Previous experimental data:

SULFUR HYDROGEN BONDING:

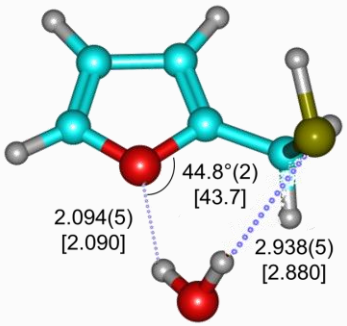
A COMPARISON OF THE DIMERS AND MONOHYDRATES OF THENYL AND FURFURYL ALCOHOLS AND MERCAPTANS

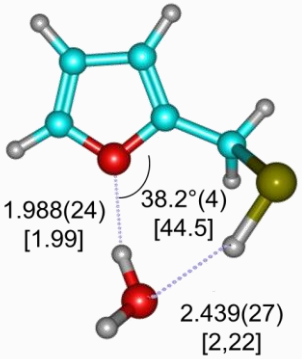
M. Juanes, A. Lesarri *et al.* (Presented at **ISMS 2018, TJ09**)

Sulfur Hydrogen Bonding in Isolated Monohydrates:

FURFURYL MERCAPTAN VERSUS FURFURYL ALCOHOL

M. Juanes, A. Lesarri *et al.*, **Chem. Eur. J. *2018,*** *24, 6564 – 6571*





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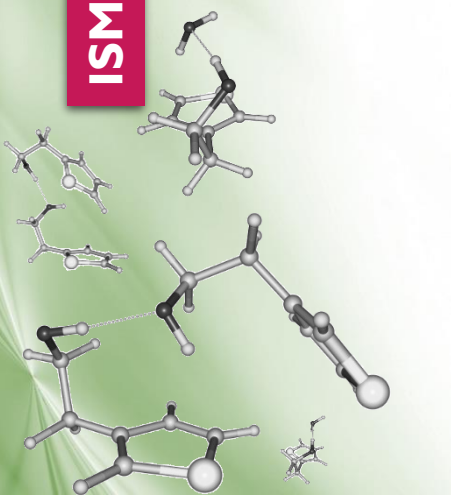
Experiment



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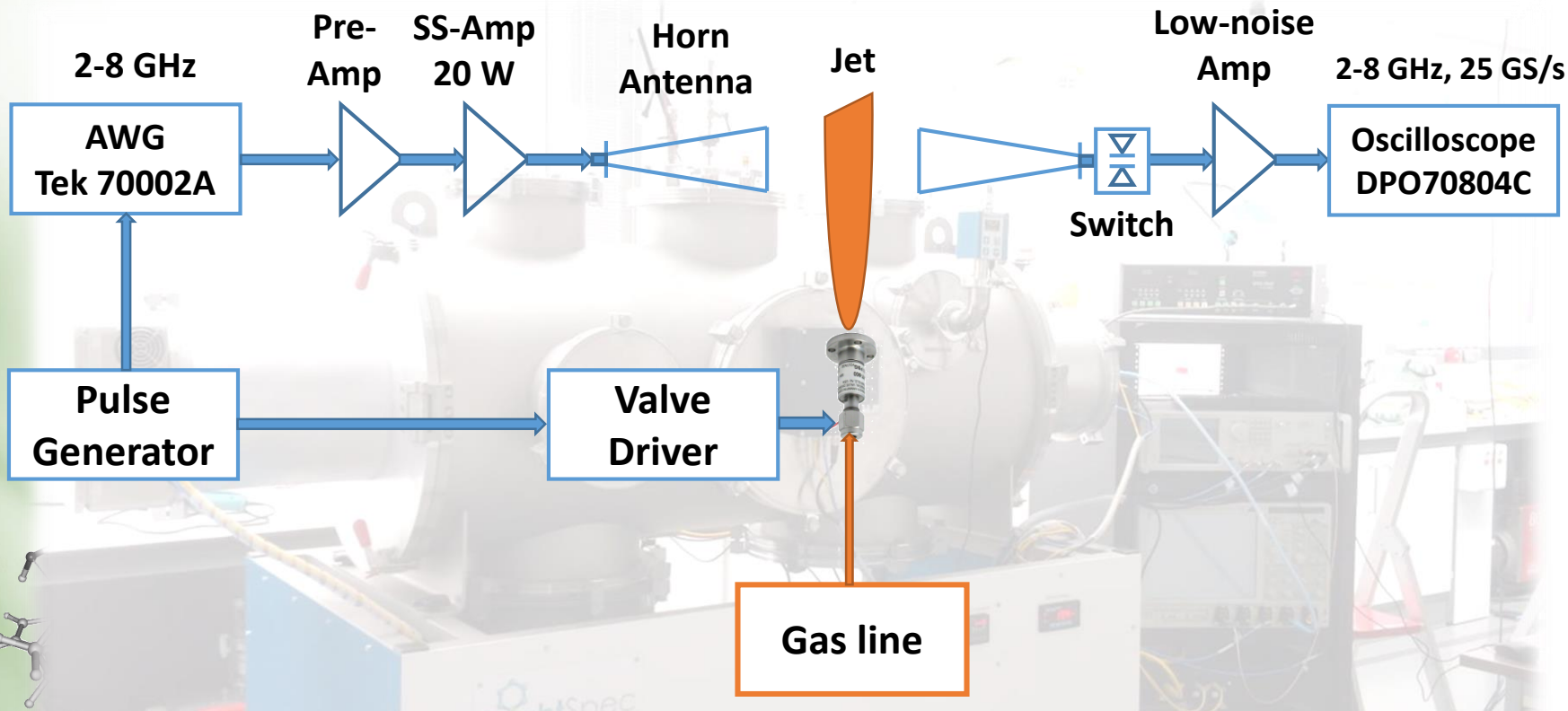
Chirped-pulsed FTMW @Valladolid



Brooks Pate "design"

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)

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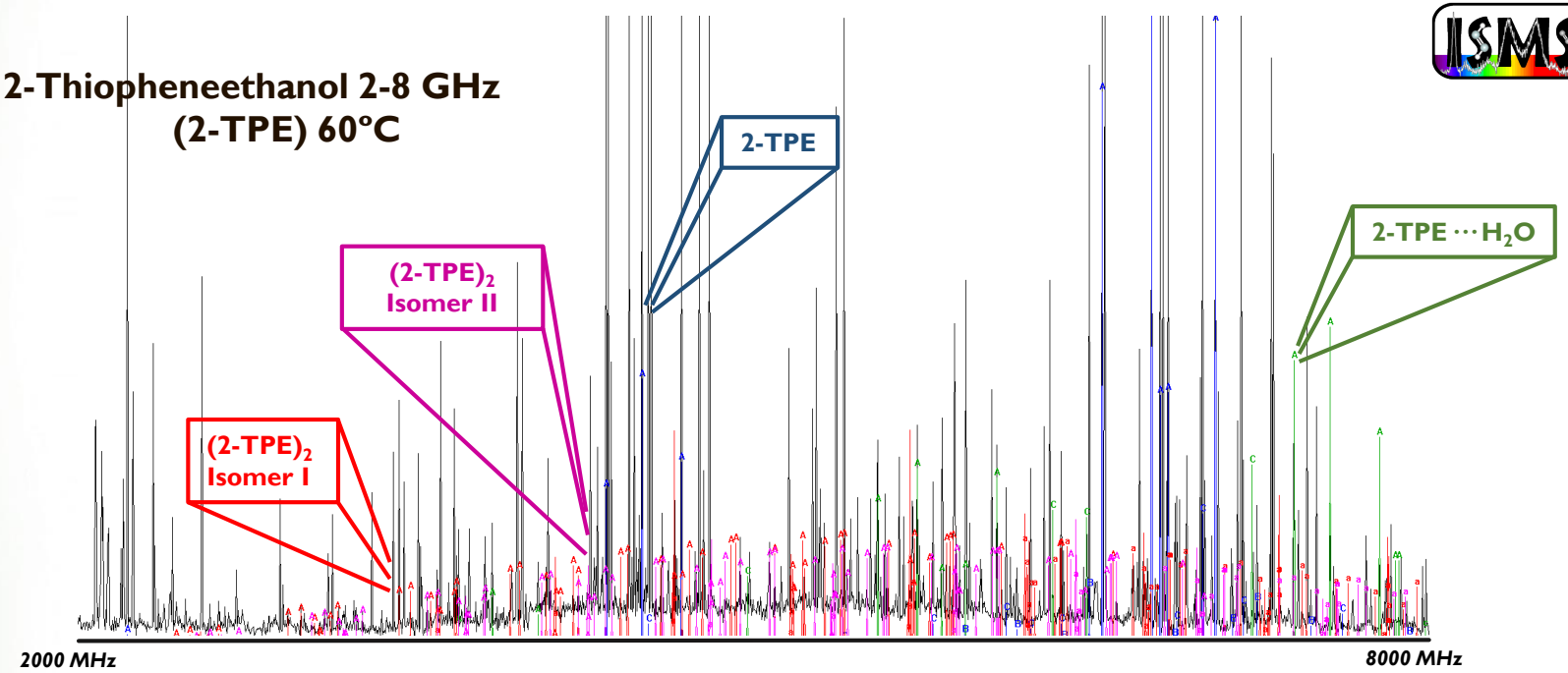
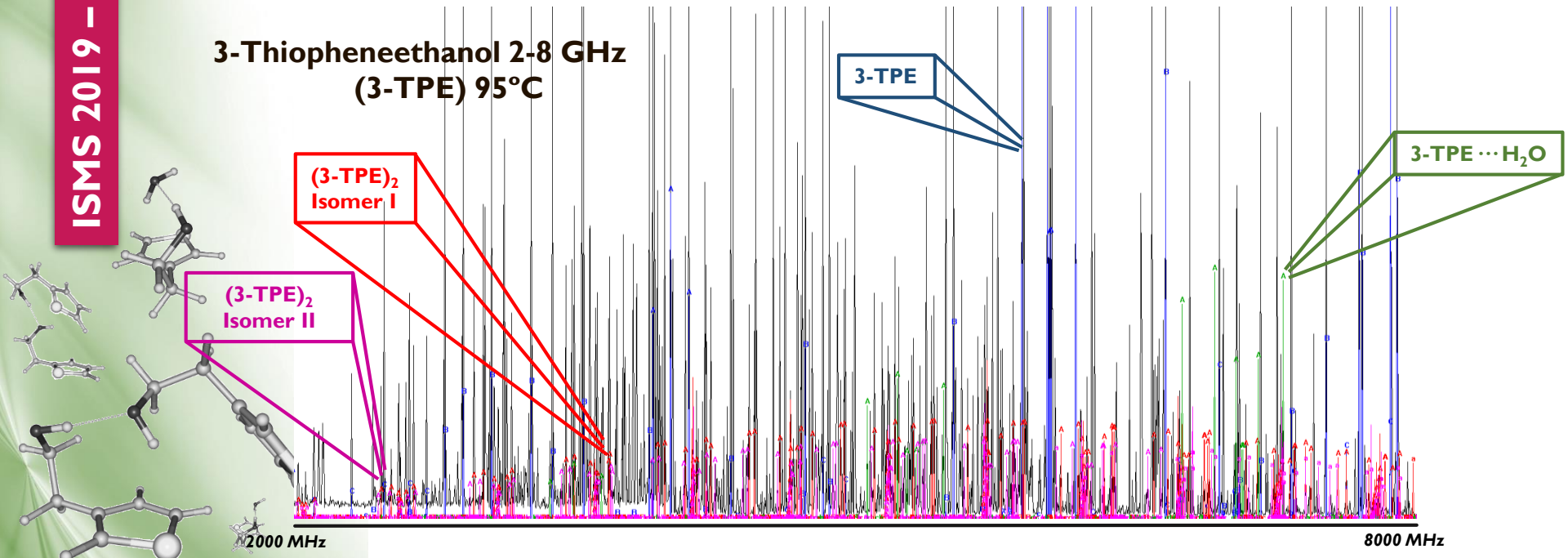
2-Thiopheneethanol 2-8 GHz (2-TPE) 60°C



3-Thiopheneethanol 2-8 GHz (3-TPE) 95°C



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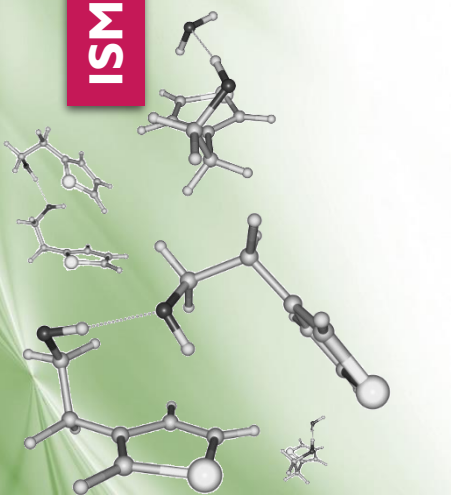
Results



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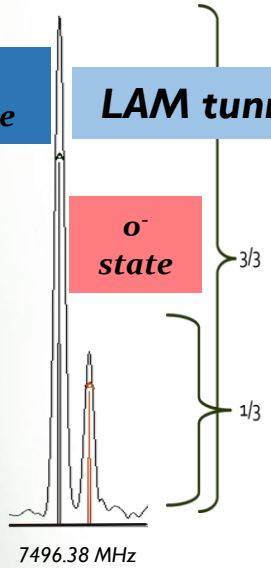
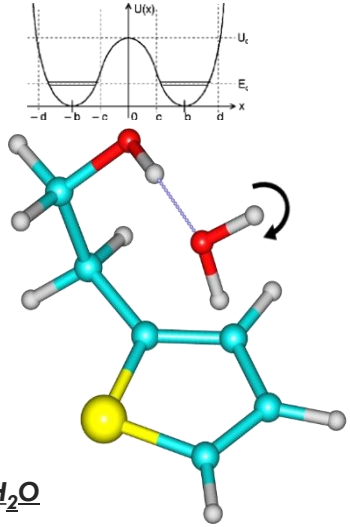
2&3-Thiopheneethanol···H_2O

$4_{04} \leftarrow 3_{03}$

Tunnelling splitting



Relative intensity rate 1:3, exchange of equivalent pair of hydrogens atoms, agree with the statistical weight 1:3 associated to the internal rotation of water



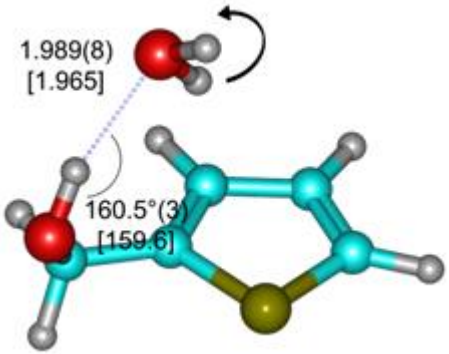
2-TPE ··· H_2O

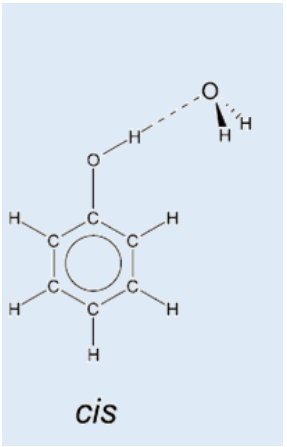
2-TPE···H_2O

	Experimental o+	Experimental o-	Theory
A / MHz	1793.2651(16)	1793.5589(46)	1778.23
B / MHz	1053.7033(10)	1053.6940(22)	1076.40
C / MHz	880.0628(12)	880.1024(18)	892.98
D_J / kHz	0.231(40)		0.2228
D_{JK} / kHz	0.59(11)		0.6050
D_K / kHz	[0.]		0.1220
d_1 / kHz	[0.]		-0.0162
d_2 / kHz	[0.]		-0.0026
$\lvert\mu_a\rvert$ / D			2.36
$\lvert\mu_b\rvert$ / D			0.63
$\lvert\mu_c\rvert$ / D			0.66
σ / kHz	6.1	8.4	
N	35		

(**) B3LYP-GD3BJ/def2_TZVP

Water as proton aceptor
In thenyl and phenol derivatives





UVa

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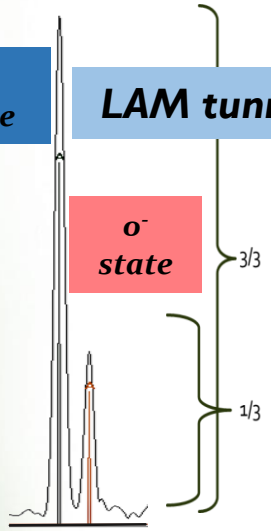
2&3-Thiopheneethanol···H_2O

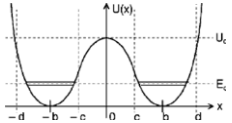
$4_{04} \leftarrow 3_{03}$

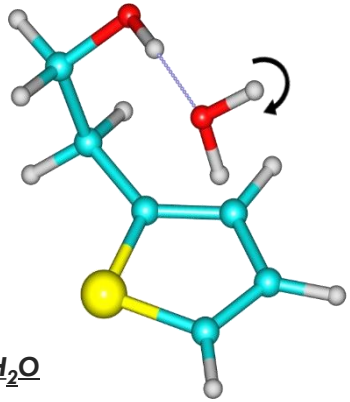
Tunnelling splitting



LAM tunnelling

Relative intensity rate 1:3, exchange of equivalent pair of hydrogens atoms, agree with the statistical weight 1:3 associated to the internal rotation of water





2-TPE ··· H_2O

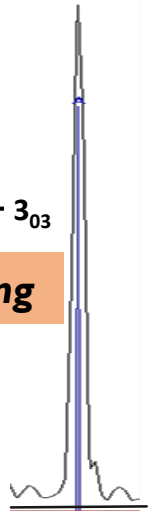
2-TPE···H_2O

	Experimental o+	Experimental o-	Theory
A / MHz	1793.2651(16)	1793.5589(46)	1778.23
B / MHz	1053.7033(10)	1053.6940(22)	1076.40
C / MHz	880.0628(12)	880.1024(18)	892.98
D_J / kHz	0.231(40)		0.2228
D_{JK} / kHz	0.59(11)		0.6050
D_K / kHz	[0.]		0.1220
d_1 / kHz	[0.]		-0.0162
d_2 / kHz	[0.]		-0.0026
$\lvert\mu_a\rvert$ / D			2.36
$\lvert\mu_b\rvert$ / D			0.63
$\lvert\mu_c\rvert$ / D			0.66
σ / kHz	6.1	8.4	
N	35		

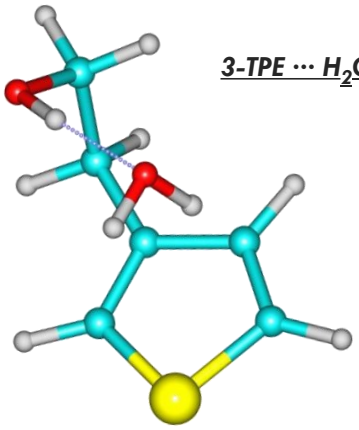
(**) B3LYP-GD3BJ/def2_TZVP

No LAM tunnelling

$4_{04} \leftarrow 3_{03}$



3-TPE ··· H_2O



3-TPE···H_2O

	Experimental	Theory**
A / MHz	1955.3241(27)	1988.97
B / MHz	943.1887(17)	950.85
C / MHz	808.1594(20)	818.50
D_J / kHz	0.147(61)	0.1663
D_{JK} / kHz	0.47(16)	0.2542
D_K / kHz	[0.]	0.7205
d_1 / kHz	[0.]	-0.0150
d_2 / kHz	[0.]	0.0042
$\lvert\mu_a\rvert$ / D		2.42
$\lvert\mu_b\rvert$ / D		0.82
$\lvert\mu_c\rvert$ / D		0.89
σ / kHz	10.2	
N	21	

(**) B3LYP-GD3BJ/def2_TZVP

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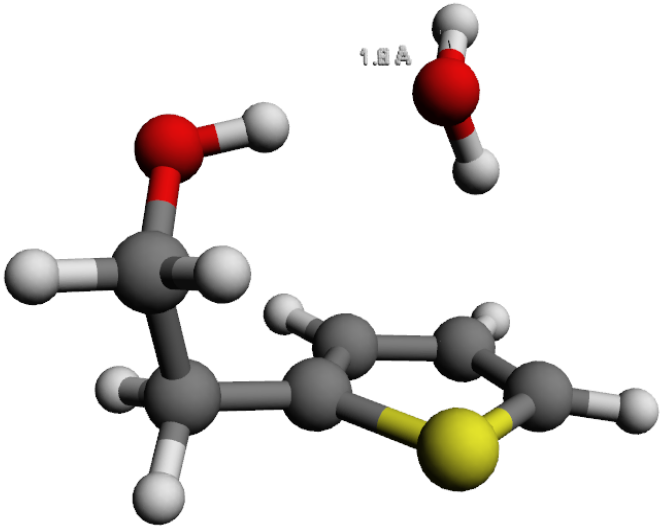
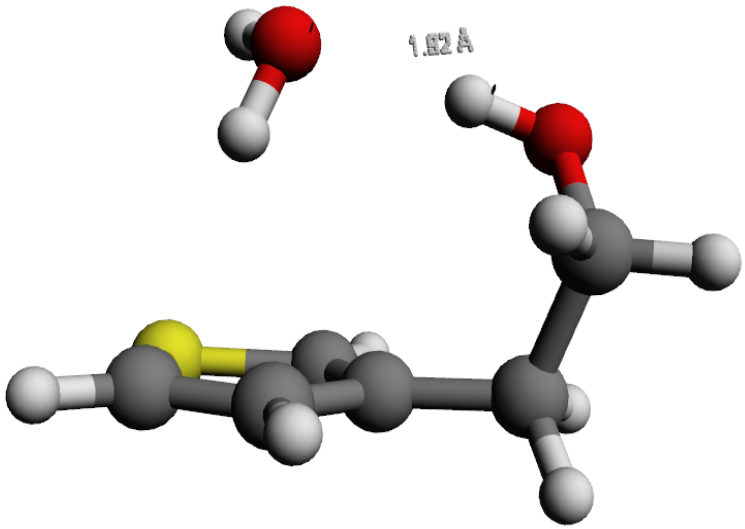
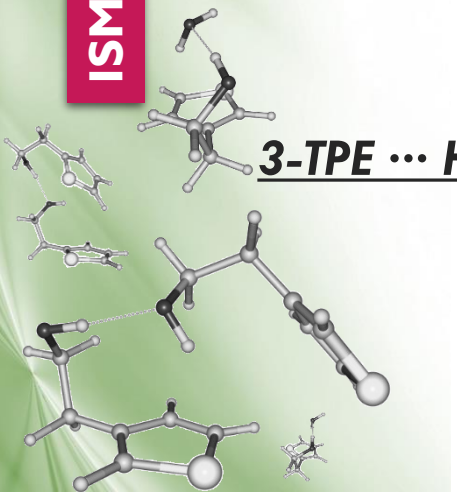
2&3-Thiopheneethanol···H_2O



2-TPE ··· H_2O





3-TPE ··· H_2O

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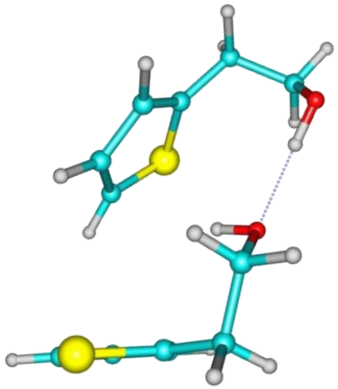
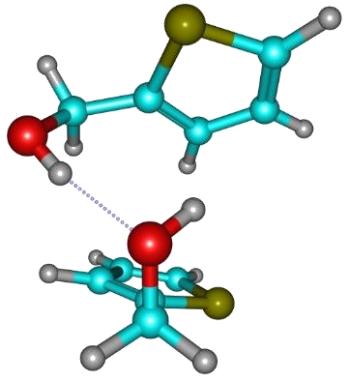
(2&3-Thiopheneethanol)$_2$

	Experimental	Theory**
A / MHz	716.0309(14)	715.76
B / MHz	284.14186(43)	291.08
C / MHz	246.44652(35)	252.87
D_J / kHz	0.02883(95)	0.0253
D_{JK} / kHz	-0.062(11)	-0.0587
D_K / kHz	0.164(49)	0.1558
d_1 / Hz	-0.00417(85)	-0.0033
d_2 / Hz	[0.]	0.0000
$\lvert\mu_a\rvert$/ D		-2.32
$\lvert\mu_b\rvert$/ D		1.15
$\lvert\mu_c\rvert$/ D		-0.59
ΔE_{ZPE} / kJ mol^{-1}		0.00
ΔG / kJ mol^{-1}		0.00
σ / kHz	11.2	
N	95	

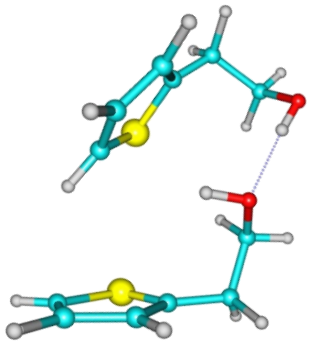
(2-TPE)$_2$ - *Isomer I*

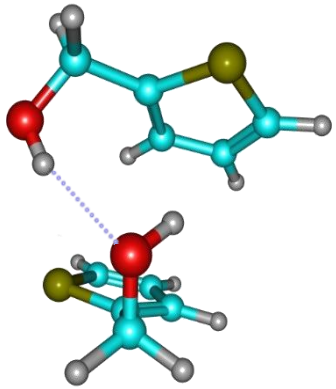




OH···O HBs in thenyl and TPE derivatives

	Experimental	Theory**
A / MHz	725.065(18)	732.72
B / MHz	274.85657(31)	277.67
C / MHz	237.92831(40)	240.59
D_J / kHz	0.0148(11)	0.0127
D_{JK} / kHz	[0.]	0.0188
D_K / kHz	[0.]	0.0600
d_1 / kHz	[0.]	-0.0012
d_2 / kHz	[0.]	-0.0002
$\lvert\mu_a\rvert$/ D		2.18
$\lvert\mu_b\rvert$/ D		1.22
$\lvert\mu_c\rvert$/ D		0.11
ΔE_{ZPE} / kJ mol^{-1}		2.43
ΔG / kJ mol^{-1}		1.65
σ / kHz	11.4	
N	58	





(2-TPE)$_2$ - *Isomer II*

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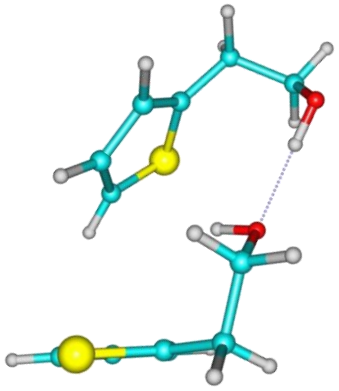
(2&3-Thiopheneethanol)$_2$

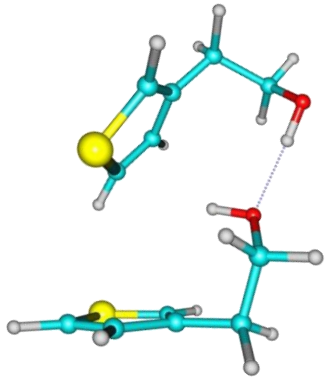
ISMS

	Experimental	Theory**
A / MHz	716.0309(14)	715.76
B / MHz	284.14186(43)	291.08
C / MHz	246.44652(35)	252.87
D_J / kHz	0.02883(95)	0.0253
D_{JK} / kHz	-0.062(11)	-0.0587
D_K / kHz	0.164(49)	0.1558
d_1 / Hz	-0.00417(85)	-0.0033
d_2 / Hz	[0.]	0.0000
$\lvert\mu_a\rvert$/ D		-2.32
$\lvert\mu_b\rvert$/ D		1.15
$\lvert\mu_c\rvert$/ D		-0.59
ΔE_{ZPE} / kJ mol^{-1}		0.00
ΔG / kJ mol^{-1}		0.00
σ / kHz	11.2	
N	95	

(2-TPE)$_2$ - *Isomer I*



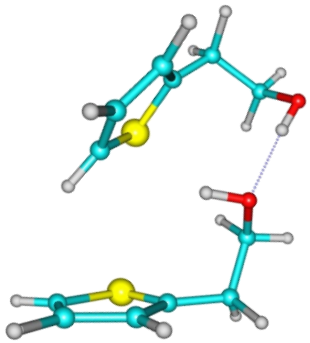
(3-TPE)$_2$ - *Isomer I*



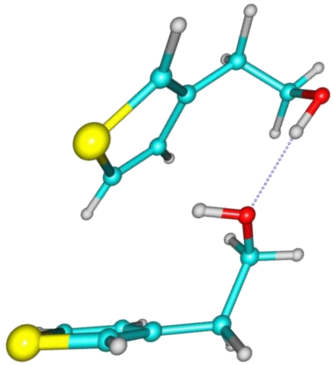
	Experimental	Theory**
A / MHz	674.55992(78)	687.63
B / MHz	273.90678(15)	276.64
C / MHz	239.49519(15)	241.97
D_J / kHz	0.01286(40)	0.0115
D_{JK} / kHz	0.0158(22)	0.0119
D_K / kHz	0.152(24)	0.1216
d_1 / Hz	[0.]	-0.0008
d_2 / Hz	[0.]	-0.0002
$\lvert\mu_a\rvert$/ D		2.15
$\lvert\mu_b\rvert$/ D		0.97
$\lvert\mu_c\rvert$/ D		0.17
ΔE_{ZPE} / kJ mol^{-1}		0.00
ΔG / kJ mol^{-1}		0.00
σ / kHz	12.5	
N	216	

	Experimental	Theory**
A / MHz	725.065(18)	732.72
B / MHz	274.85657(31)	277.67
C / MHz	237.92831(40)	240.59
D_J / kHz	0.0148(11)	0.0127
D_{JK} / kHz	[0.]	0.0188
D_K / kHz	[0.]	0.0600
d_1 / kHz	[0.]	-0.0012
d_2 / kHz	[0.]	-0.0002
$\lvert\mu_a\rvert$/ D		2.18
$\lvert\mu_b\rvert$/ D		1.22
$\lvert\mu_c\rvert$/ D		0.11
ΔE_{ZPE} / kJ mol^{-1}		2.43
ΔG / kJ mol^{-1}		1.65
σ / kHz	11.4	
N	58	

(2-TPE)$_2$ - *Isomer II*



(3-TPE)$_2$ - *Isomer II*



	Experimental	Theory**
A / MHz	674.29608(64)	684.44
B / MHz	290.11878(25)	292.91
C / MHz	236.48612(24)	239.74
D_J / kHz	0.01519(80)	0.0124
D_{JK} / kHz	[0.]	0.0117
D_K / kHz	0.130(15)	0.1270
d_1 / Hz	-0.00301(45)	-0.0023
d_2 / Hz	[0.]	-0.0002
$\lvert\mu_a\rvert$/ D		2.14
$\lvert\mu_b\rvert$/ D		0.00
$\lvert\mu_c\rvert$/ D		2.44
ΔE_{ZPE} / kJ mol^{-1}		0.36
ΔG / kJ mol^{-1}		0.07
σ / kHz	16.2	
N	188	

B3LYP-GD3BJ/def2_TZVP

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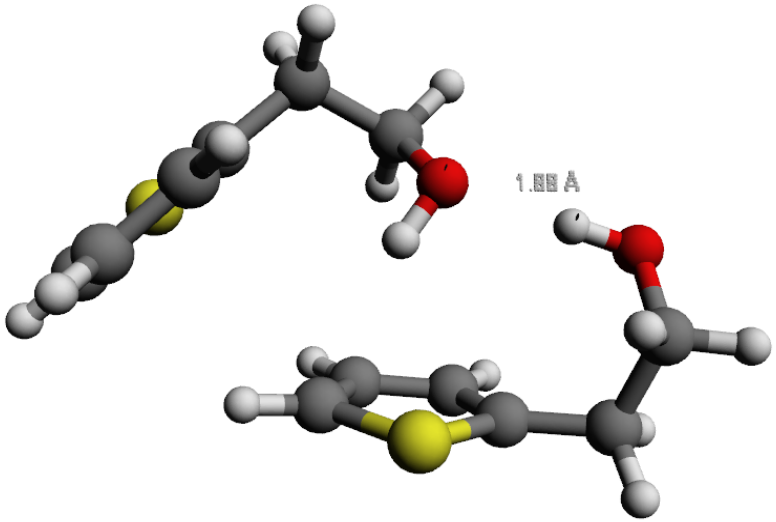
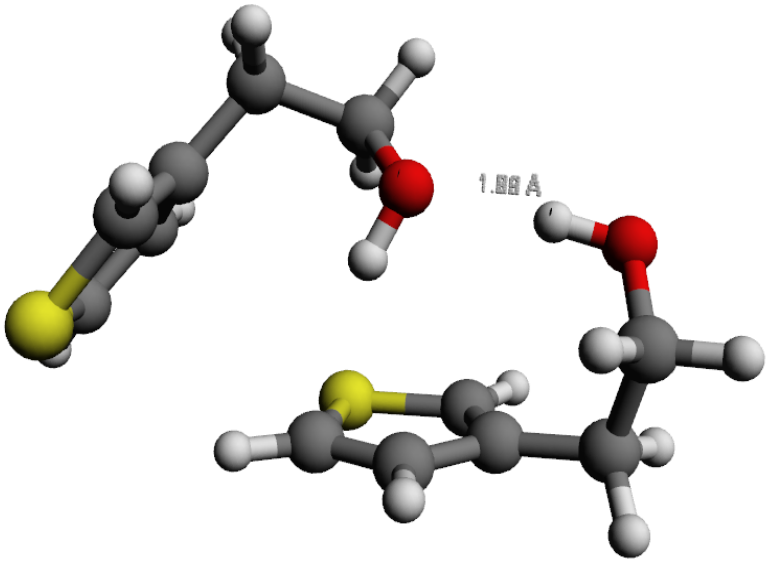
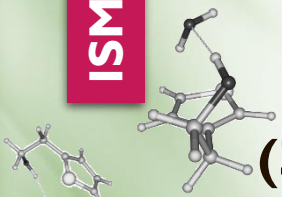
$(2\&3\text{-Thiopheneethanol})_2$

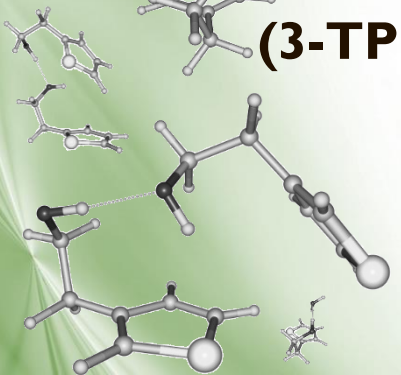


$(2\text{-TPE})_2$ - Isomer I





$(3\text{-TPE})_2$ - Isomer I



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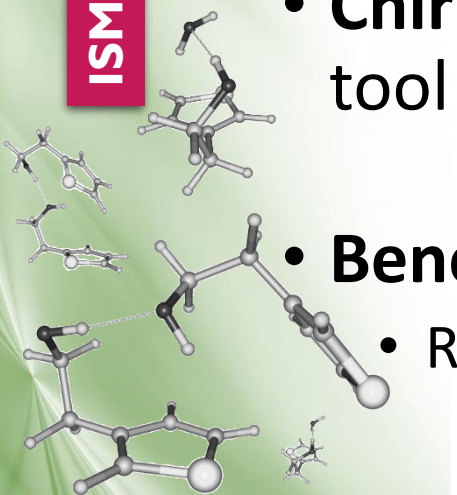
Conclusions

- **Isolated clusters in gas-phase provide structural and energetic information on hydrogen bonding**
- **Comparison between oxygen and sulfur** compounds illustrate HBs interactions involving sulfur
- **Chirped-pulse MW spectroscopy** is a powerful tool for intermolecular interactions
- **Benchmark for ab initio and DFT** calculations
  - Role of empirical dispersion-corrected DFT



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Team

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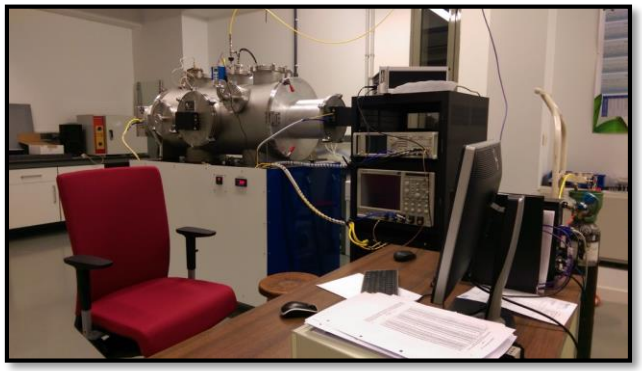
Alberto Lesarri

Project-head
PhD Supervisor

Lab team



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

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… Thank you very much!

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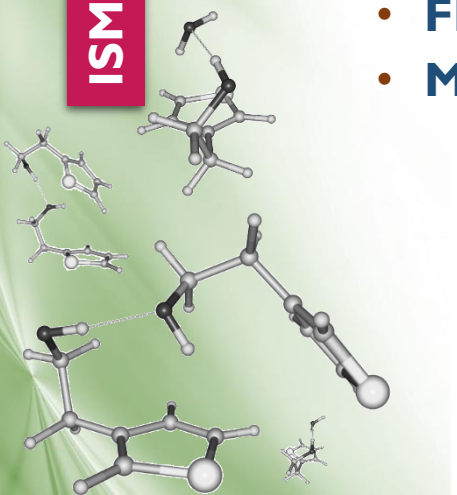

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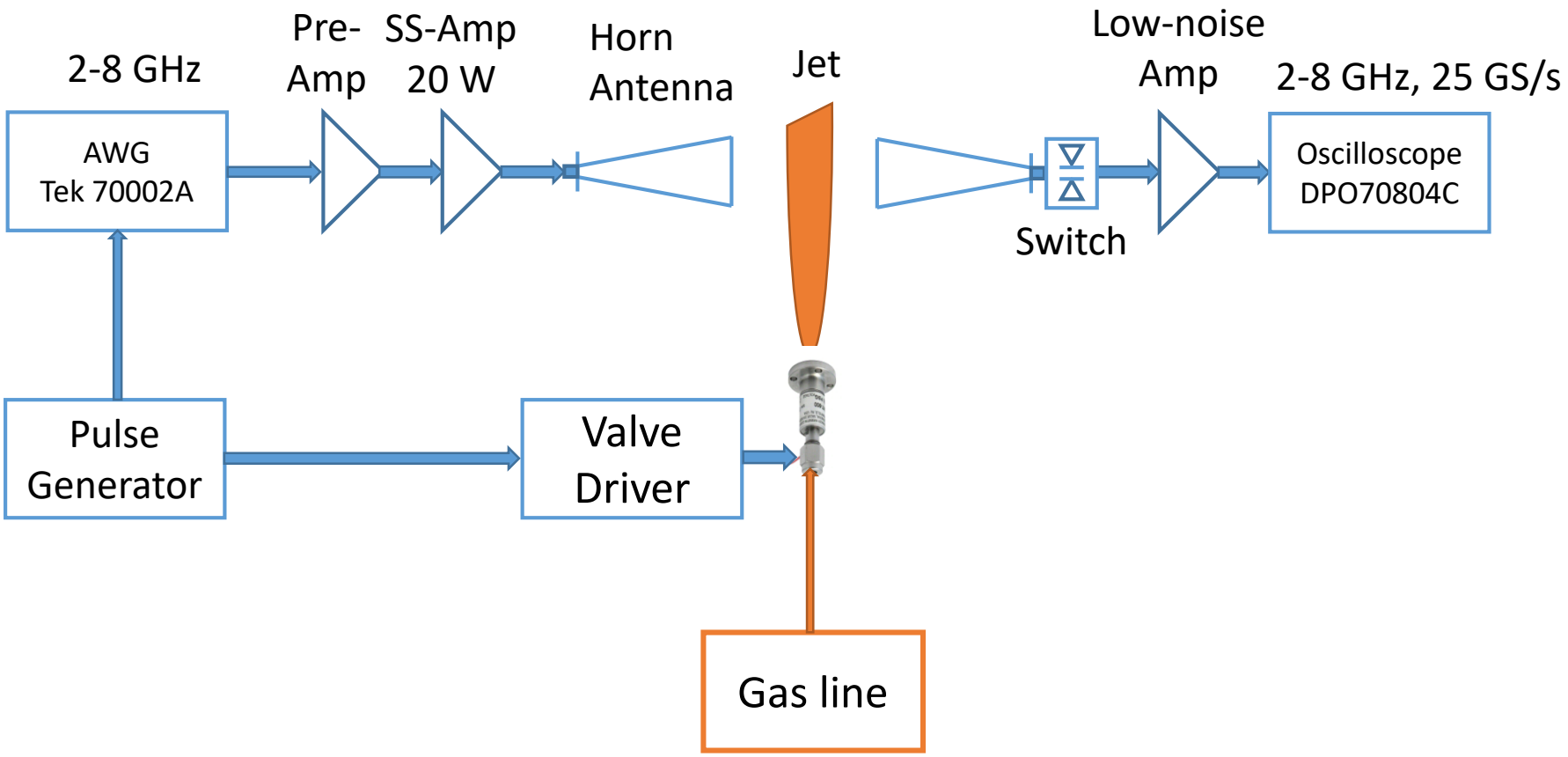

The detection is made of a power limiter (omitted in the drawing), a PIN-diode switch and the low-noise amplifier. Both the AWG and the scope (Tektronix) are 25 MSamples/s, but the bandwidth of the scope is 8 GHz. The chirp is usually 4 microseg. The limiting factor is the solid state power amplifier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