SULFUR HYDROGEN BONDING IN THE OLIGOMERS OF AROMATIC THIOLS

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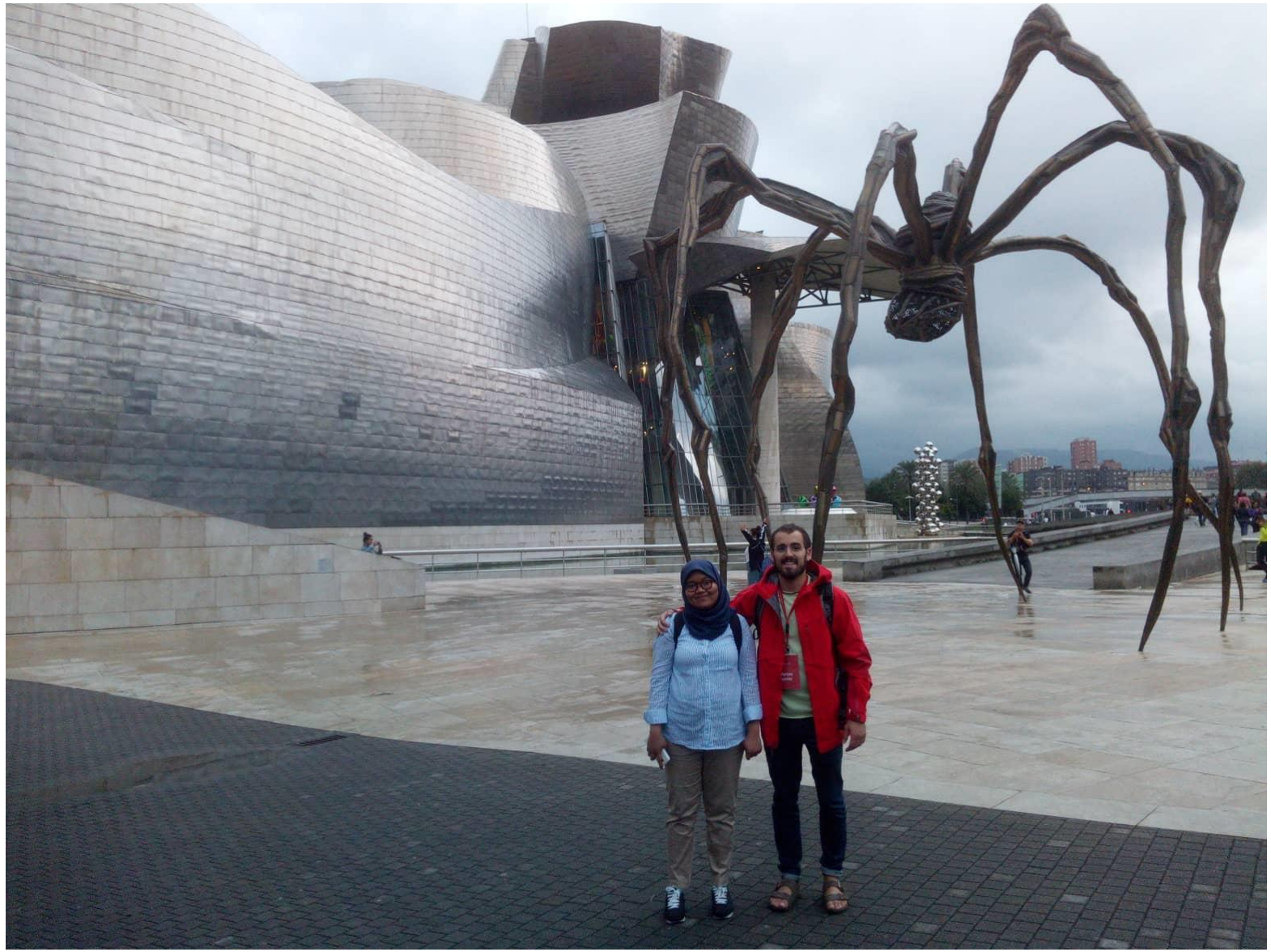
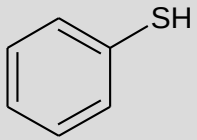
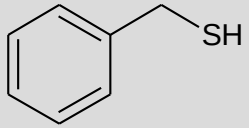


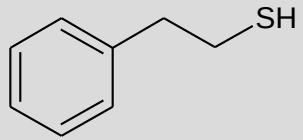
Rizalina & Marcos at HRMS2018, Bilbao (Spain)

Outline

- Molecular model
  - Intermolecular clusters
  - Sulfur hydrogen bonding
- Experiment
  - Chirped-Pulsed Microwave Spectroscopy
- Results
  - Homodimers: thiophenol, phenylmethanethiol, and 2-phenylethanethiol.



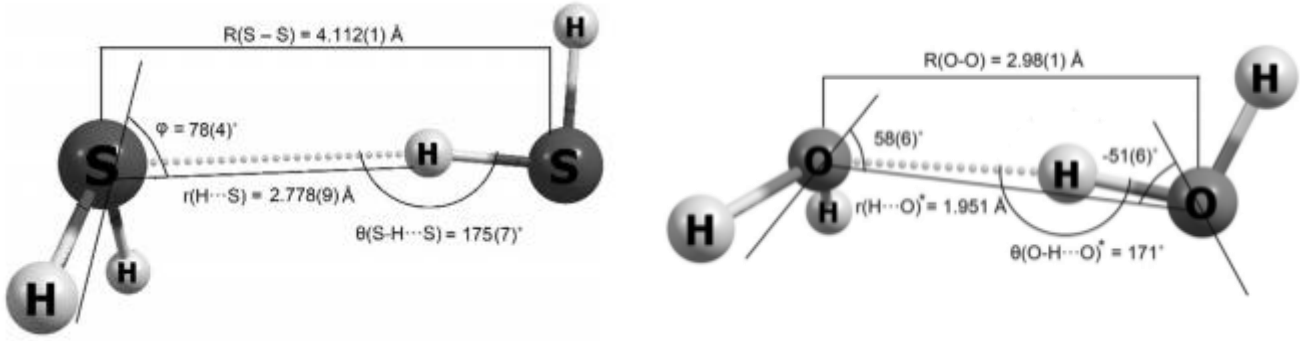




  - Trimer

Sulfur Hydrogen Bonding

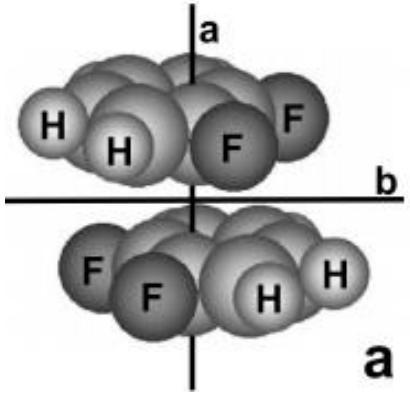
- Hydrogen bonds (HBs) to sulfur centers are weak interactions of dispersive character, with reduced structural influence compared to conventional first-row HBs like O–H···O, O–H···N or N–H···O.
- H–S···H vs. H–O···H

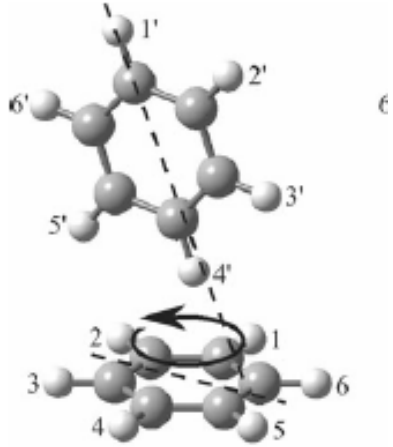


- Rotational analysis of hydrogen-bonded clusters comparing the different behaviour of oligomers of aromatic thiols.

Sulfur Hydrogen Bonding

- Structural shape of homodimers of aromatic rings: Parallel, T-shaped.
  - Difluorobenzene dimer (Goly et al. 2002), benzene dimer (Schnell et al., 2013)

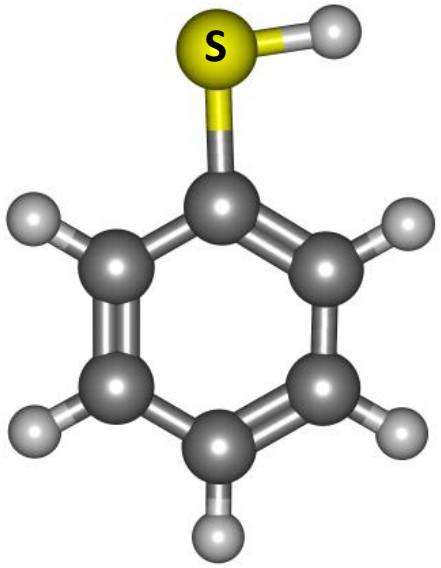




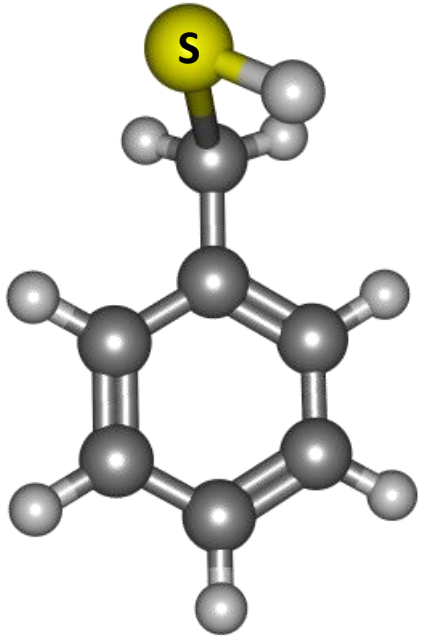
- Experimental and theoretical comparison.
- Isolated clusters in gas-phase: molecular models.

Thiophenol, phenylmethanethiol, and 2-phenylethanethiol

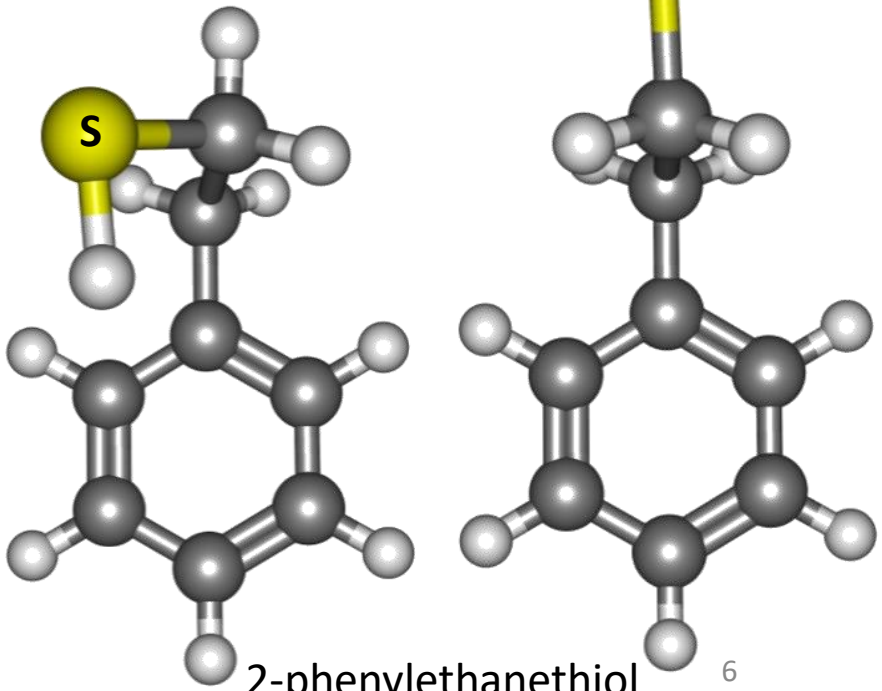
- Organosulfur compound with different alkyl group.
- Each conformer has tunnelling splittings due to thiol group torsions
- 2-phenylethanethiol has two stable conformers: gauche and trans.



Thiophenol



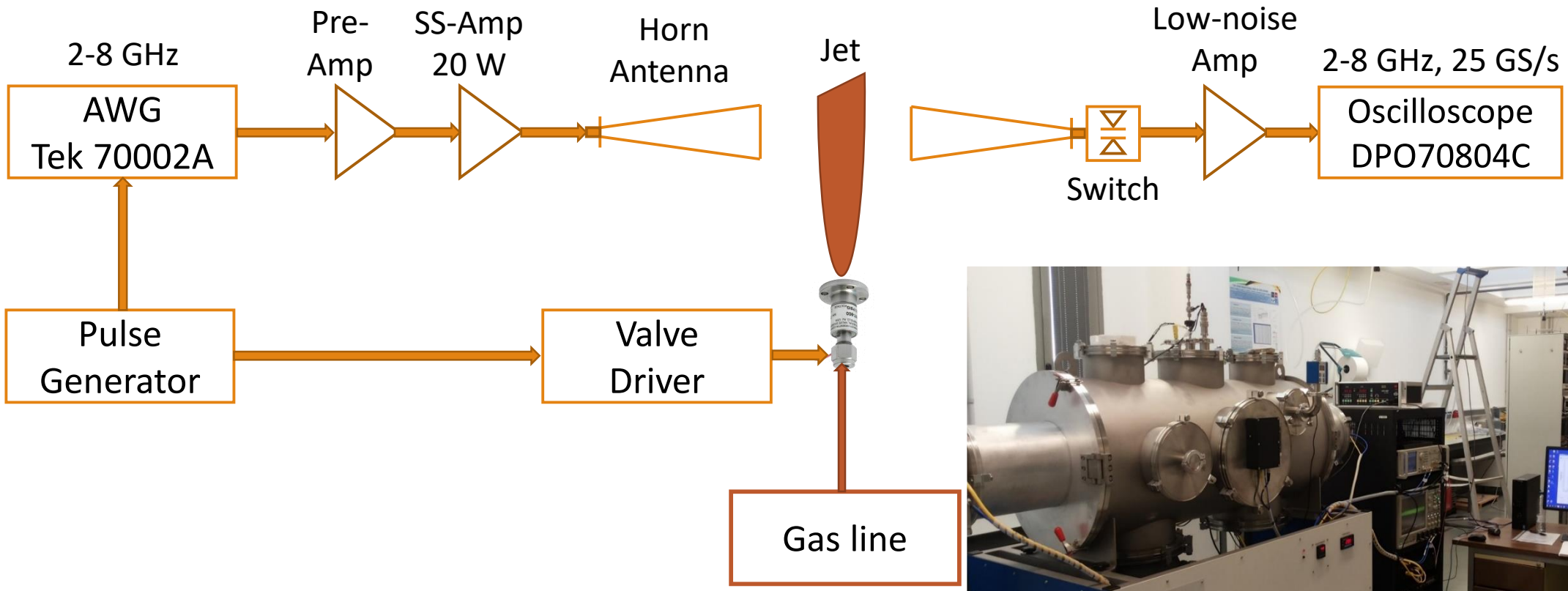
Phenylmethanethiol



2-phenylethanethiol

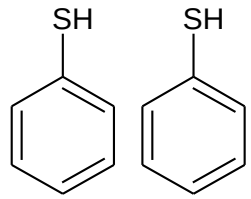
Experimental Method

Chirped-pulse FT-Microwave Spectrometer (Rotational spectrum 2-8 GHz)



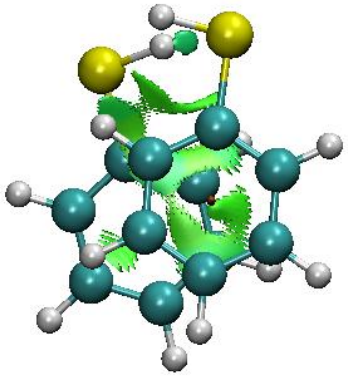
Results and Discussion

Thiophenol

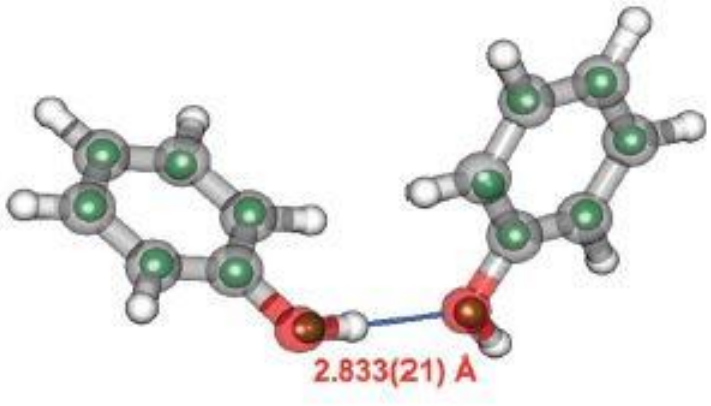


Thiophenol Dimer

- The interactions in the dimer are stabilized by weak interaction of S–H···S.
- Two phenyl rings are stacked, displaying a π–π interaction.
- Phenol dimer has hinge-like structure. (Seifert 2013)



NCI plot



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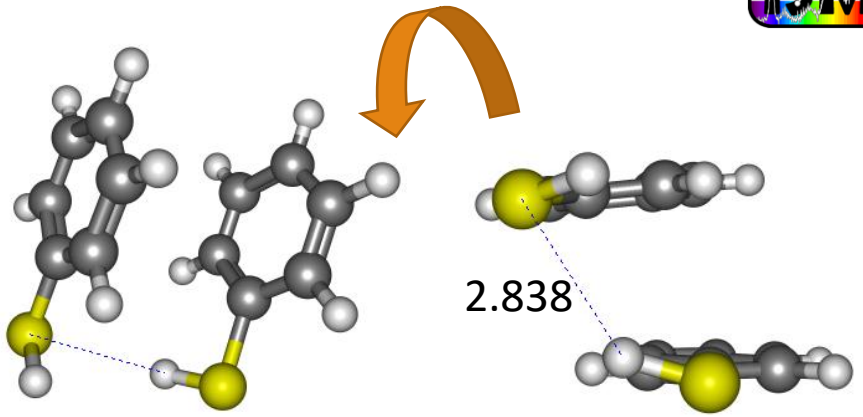
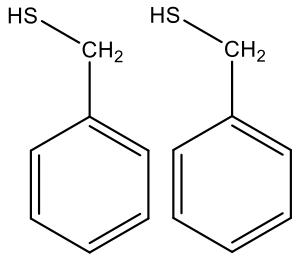
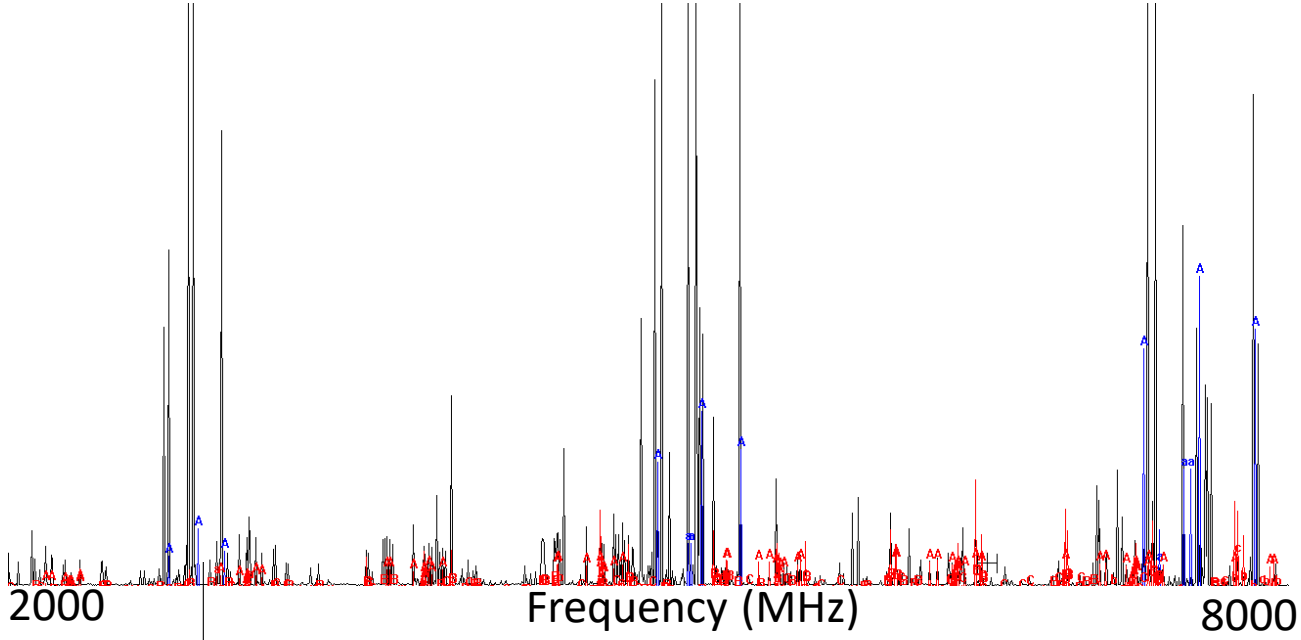


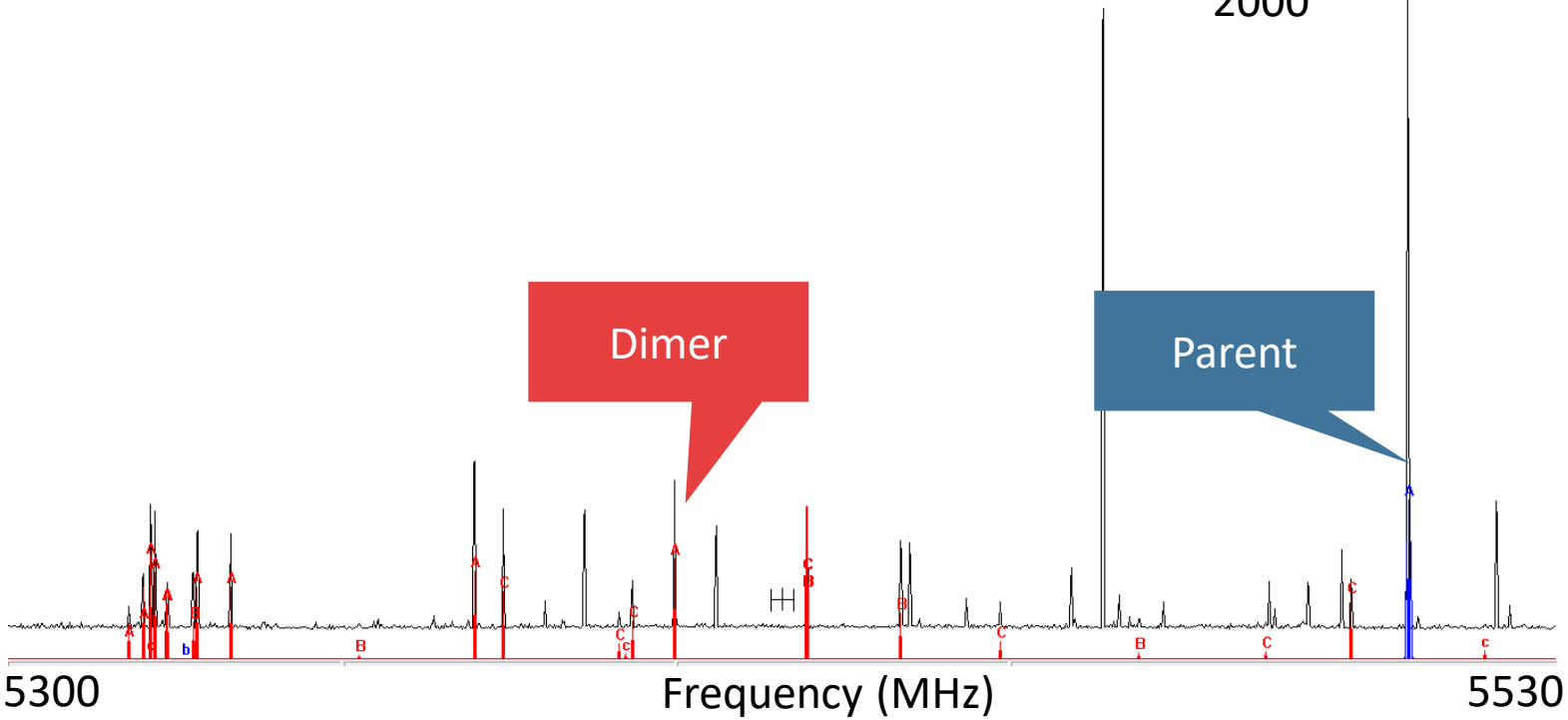
	EXP.	THEORY
A / MHz[a]	662.75808(55)	690.74
B / MHz	499.46373(41)	498.55
C / MHz	338.61929(36)	346.52
D_J / kHz	-2.1513(29)	0.3583
D_{JK} / kHz	42.737(11)	-0.5804
D_K / kHz	-40.4876(97)	0.2690
d_1 / kHz	-0.08678(76)	-0.0326
d_2 / kHz	-1.17981(28)	0.0104
$\|\mu_a\|$ / D	-	0.1
$\|\mu_b\|$ / D	Y	1.5
$\|\mu_c\|$ / D	-	0.3
N[b]	130	
s / kHz	14.5	

B3LYP-GD3BJ/def2TZVP

Phenylmethanethiol dimer

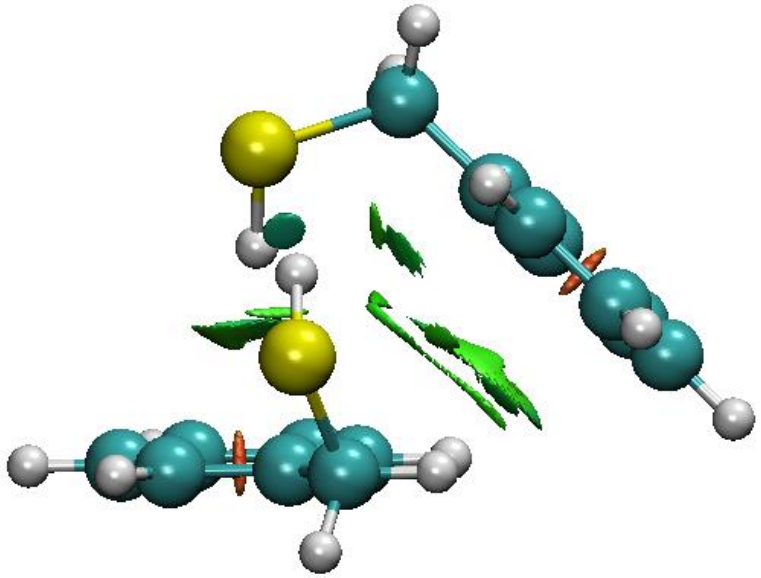




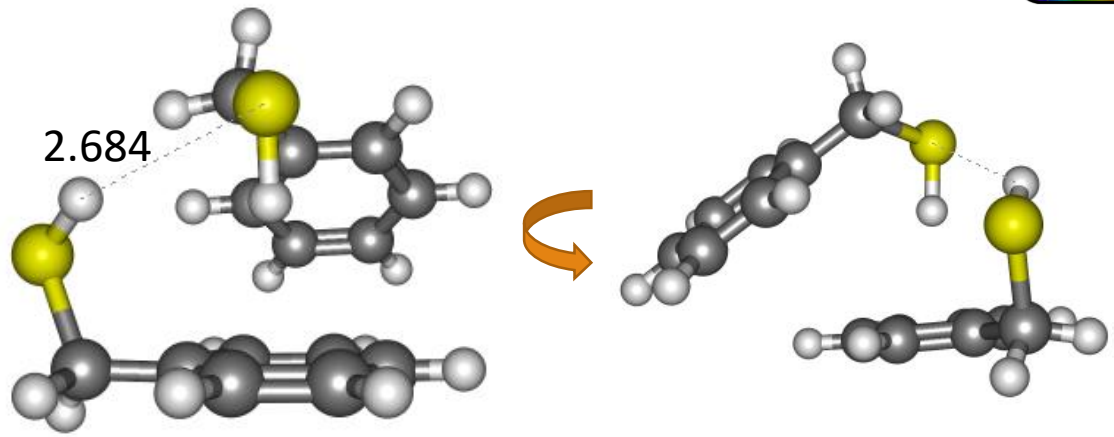


Phenylmethanethiol dimer

- The interactions in the dimer are stabilized by weak interaction of S–H···S.
- Interaction to the aromatic ring:
  - S–H···π
  - C–H···π



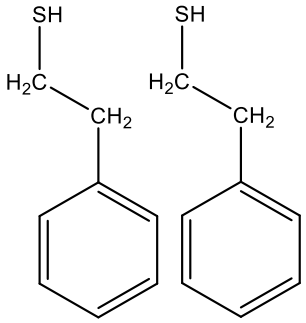
NCI plot

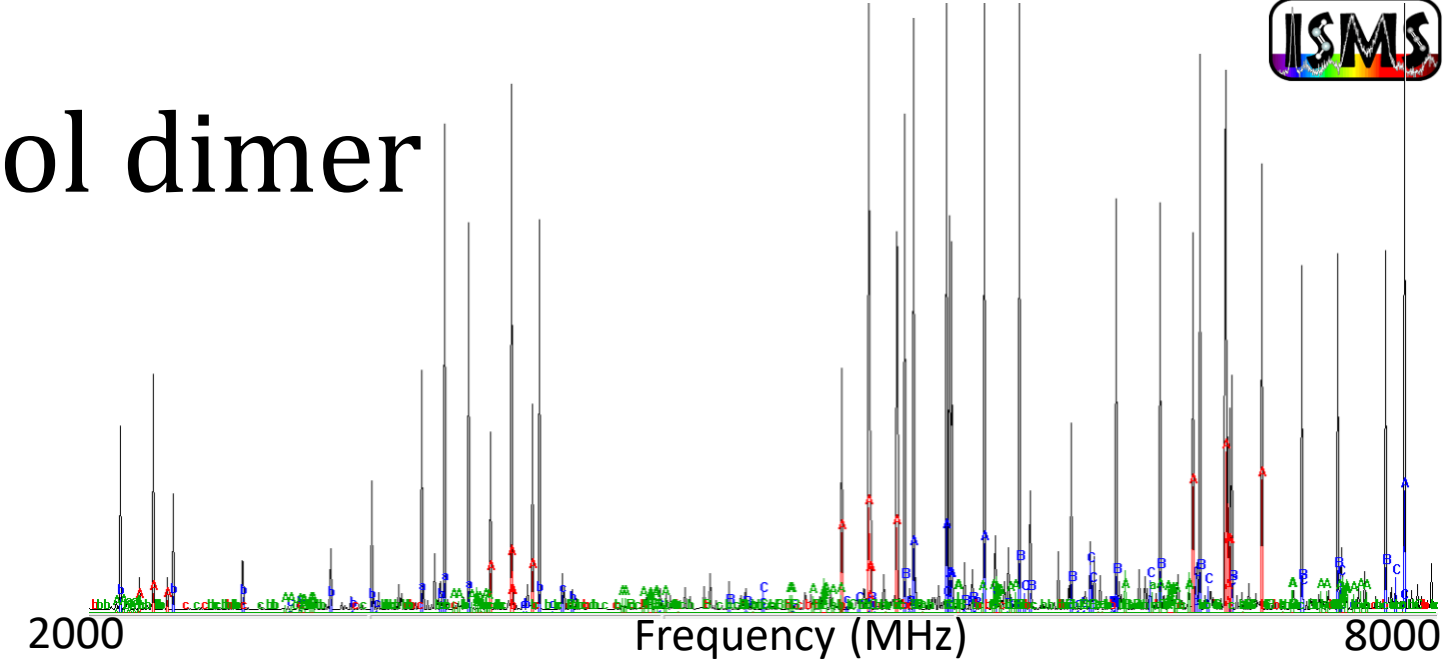


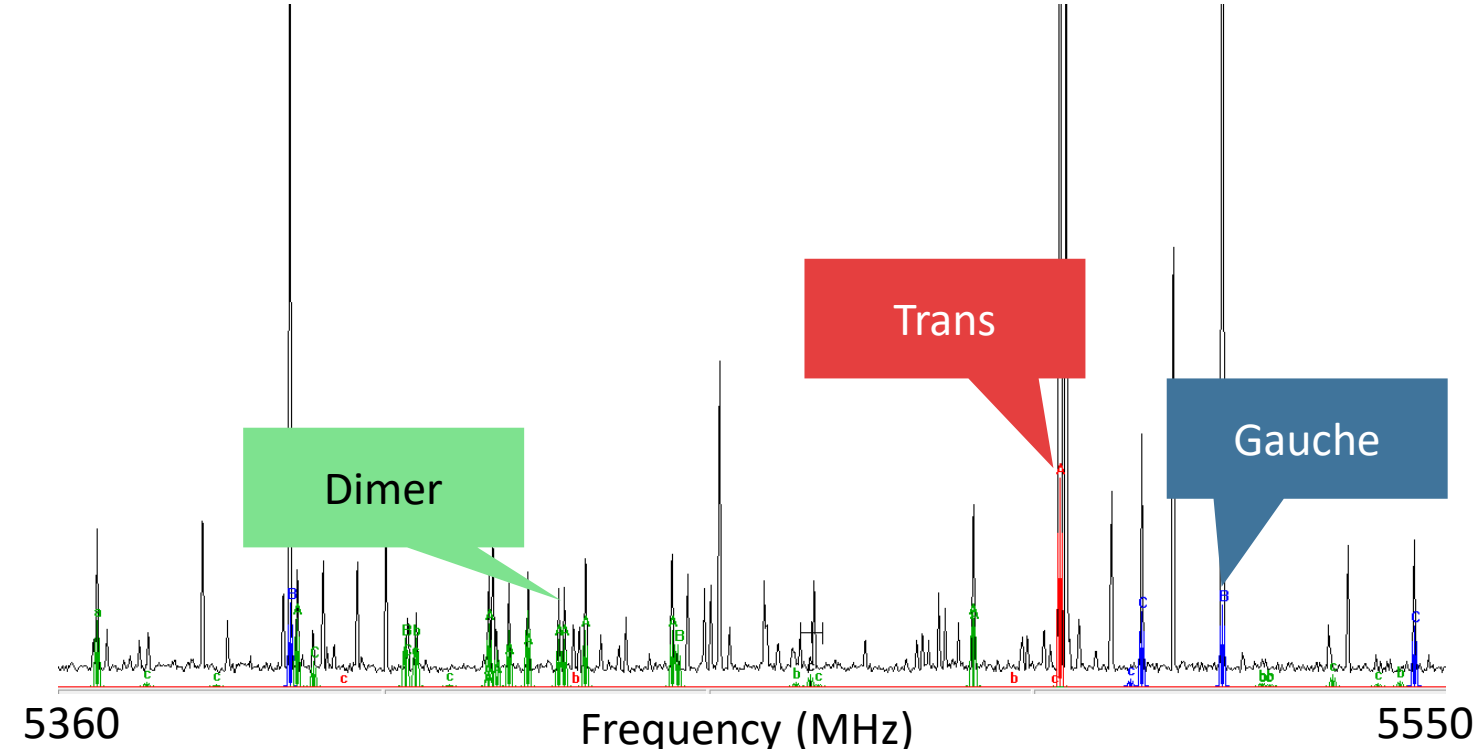
	EXP.	THEORY
A / MHz[a]	490.79216(17)	498.41
B / MHz	344.12732(12)	352.92
C / MHz	317.21115(11)	325.95
D_J / kHz	0.03861(51)	0.03232
D_{JK} / kHz	0.0642(18)	0.05835
D_K / kHz	-0.0718(20)	-0.06618
d_1 / kHz	-0.00375(33)	-0.00259
d_2 / kHz	0.00089(13)	0.00068
$\|\mu_a\|$ / D	Y	1.5
$\|\mu_b\|$ / D	Y	1.7
$\|\mu_c\|$ / D	Y	1.3
N[b]	337	
s / kHz	8.5	

B3LYP-GD3BJ/def2TZVP

2-phenylethanethiol dimer

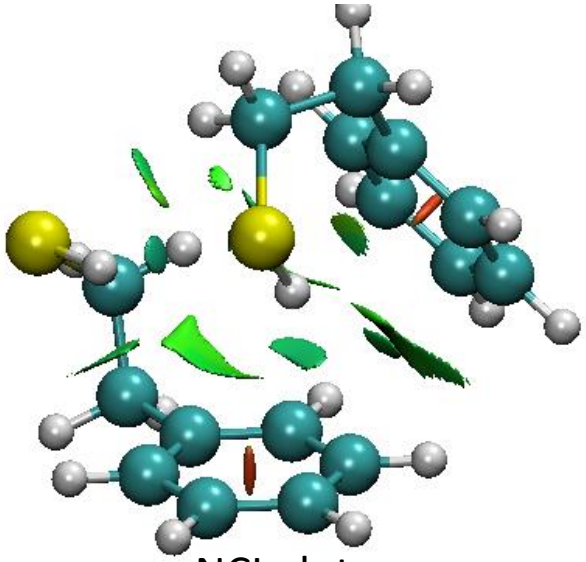




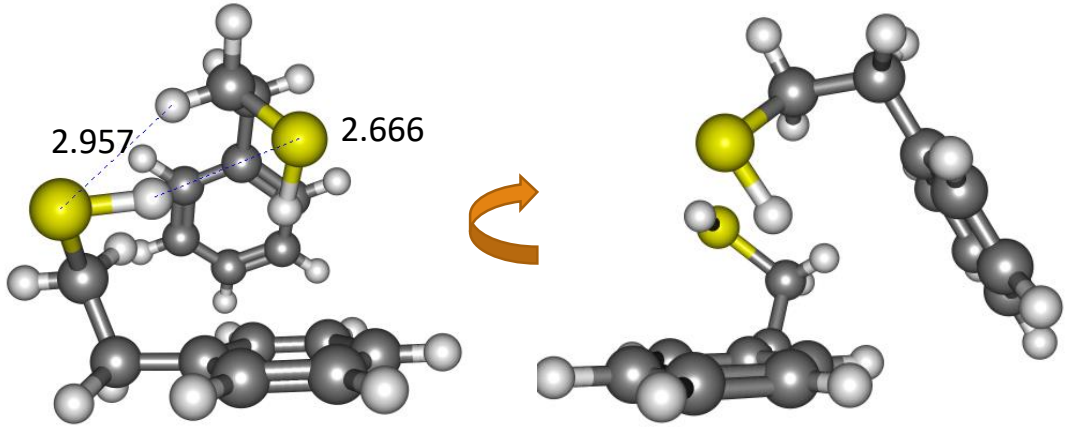


2-phenylethanethiol dimer

- The configuration is g+g- meaning both of PEM molecules have gauche arrangement.
- The interactions in the dimer are stabilized by weak interaction: S–H···S, C–H···S.
- Also by S–H···π and C–H···π interactions to the aromatic ring.



NCI plot

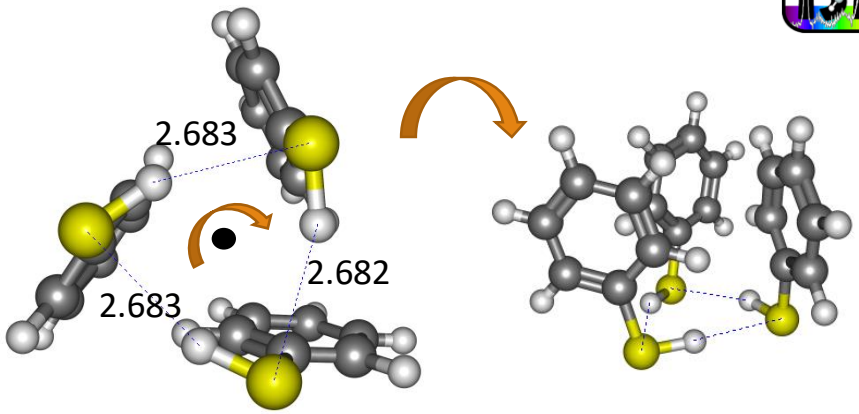


	EXP.	THEORY
A / MHz[a]	390.90036(69)	395.074
B / MHz	279.72940(25)	288.233
C / MHz	262.05386(26)	266.919
D_J / kHz	0.02523(92)	0.01417
D_{JK} / kHz	0.1021(33)	0.0142
D_K / kHz	1.339(11)	0.1051
d_1 / kHz	[0.]	-0.1018
d_2 / kHz	-0.00468(40)	0.0004
$\|\mu_a\|$ / D	Y	1.8
$\|\mu_b\|$ / D	Y	0.9
$\|\mu_c\|$ / D	Y	1.1
N[b]	229	
s / kHz	19.6	

B3LYP-GD3BJ/def2TZVP

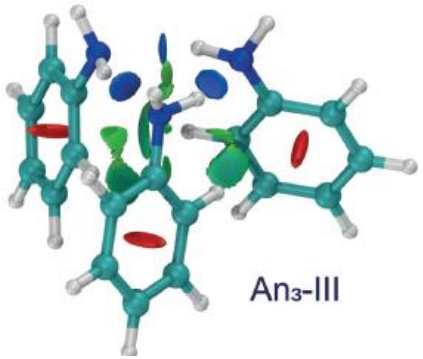
Thiophenol Trimer

- Thiophenol trimer is a symmetric top, has a C_3 symmetry.
- Water trimer-like hydrogen bonding, with C–H ⋯ π interaction.
- The trimer exhibits similar feature as in the phenol trimer and one of conformer of aniline trimer.



	EXP.	THEORY
A / MHz[a]	-	234.31
B / MHz	233.07124(18)	234.26
C / MHz	-	202.17
D_J / kHz	-0.01226(45)	0.01194
D_{JK} / kHz	-	-0.11129
D_K / kHz	-	0.10550
d_1 / kHz	-	0.00003
d_2 / kHz	-	-0.00007
$\lvert\mu_a\rvert$ / D	-	0.0
$\lvert\mu_b\rvert$ / D	-	0.0
$\lvert\mu_c\rvert$ / D	y	3.0
N[b]	13	
s / kHz	5.8	

B3LYP-GD3BJ/def2TZVP



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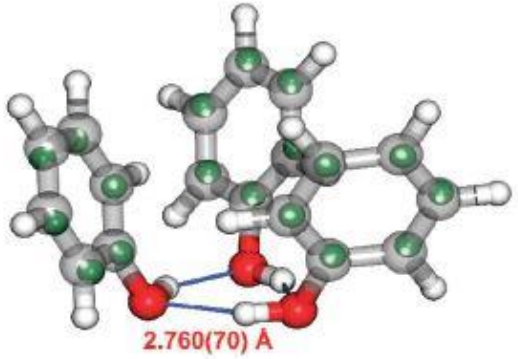

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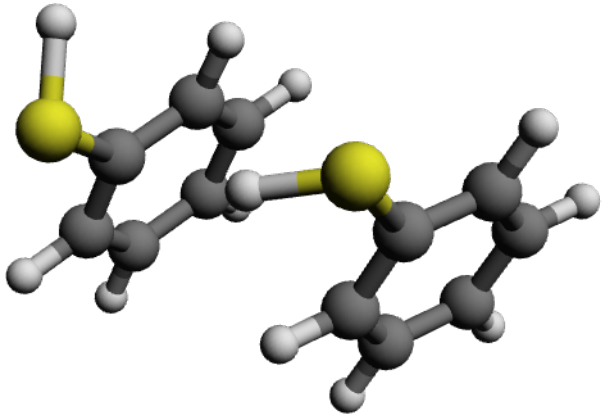
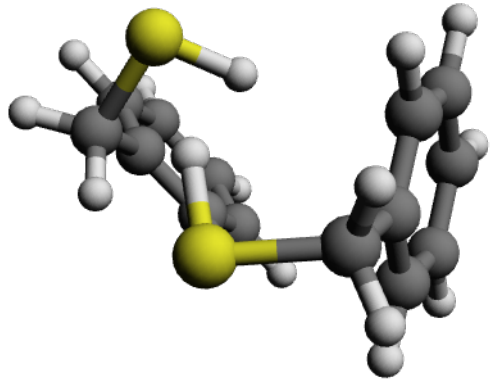
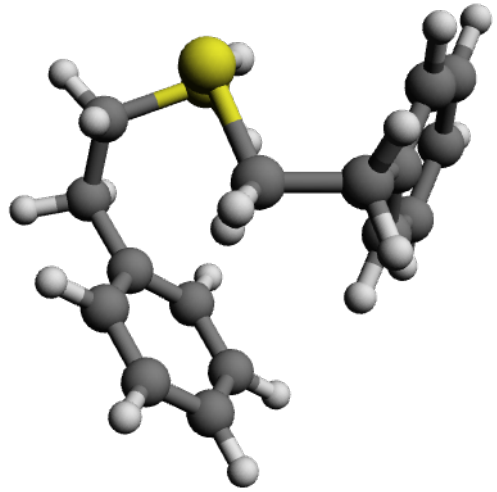
Thiophenol dimer



Phenylmethanethiol dimer



2-phenylethanethiol dimer



Structural Data

r(S-H···S)	B3LYP-GD3BJ/def2TZVP (Å)
Thiophenol dimer	2.84
Phenylmethanethiol dimer	2.68
2-Phenylethanethiol dimer	2.67
Thiophenol trimer	2.68

Energy Decomposition

r(S-H···S)	$\Delta E_{Electrostatic}$	$\Delta E_{induction}$	$\Delta E_{Dispersion}$	$\Delta E_{Exchange}$	ΔE_{Total}
Thiophenol dimer	-5.98	-1.70	-10.82	12.02	**-6.42**
Phenylmethanethiol dimer	-9.66	-2.98	-13.30	17.00	**-8.81**
2-Phenylethanethiol dimer	-9.49	-3.05	-13.97	18.22	**-8.22**

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

Conclusions

- Isolated clusters in gas-phase provide structural and energetic information on hydrogen bonding.
- Comparison between the oligomers provide interaction involving sulfur and aromatic ring.
- MW spectroscopy + supersonic expansions is able to characterize the intermolecular interactions.
- Benchmark for ab initio and DFT calculations.

… See more at:

RH. MINI-SYMPOSIUM: **NON-COVALENT INTERACTIONS**

- **RH04:** HYDROGEN BONDING IN THE MONOHYDRATES AND HOMODIMERS OF CYCLOHEXYLAMINE AND CYCLOHEXANETHIOL

- **RH08:** DIMERIZATION AND MICROSOLVATION OF 2- AND 3-THIOPHENEETHANOL

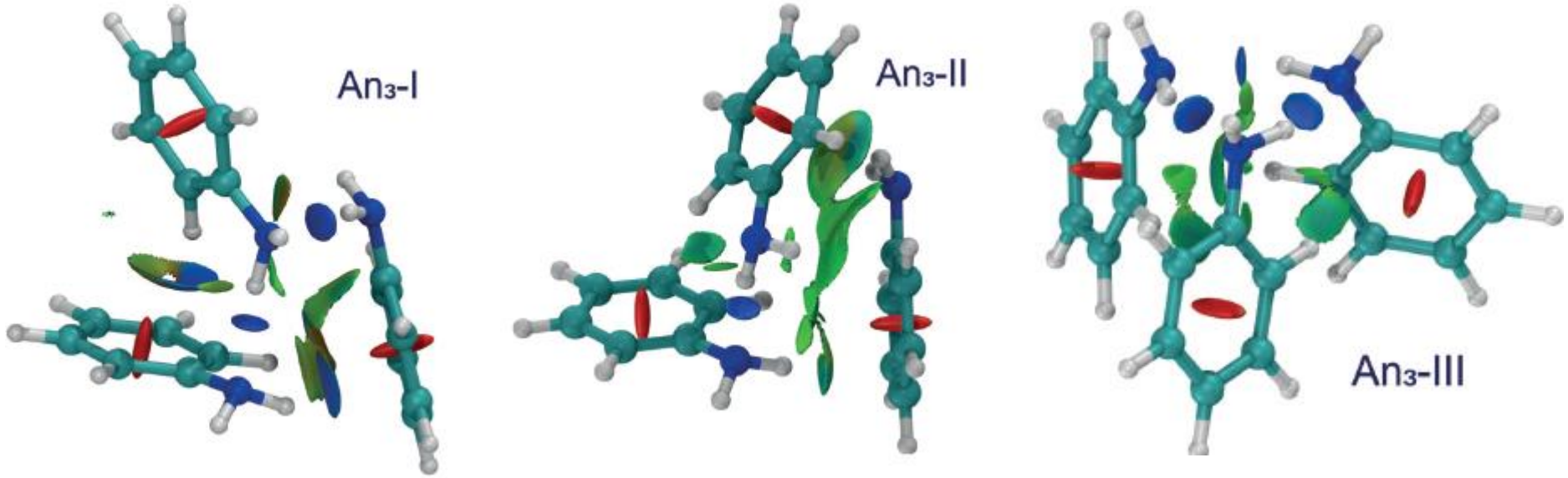
Thursday, 2019-06-20, 01:45 PM
Noyes Laboratory 100

Thank you!

- Doctoral contract UVa
- MINECO/FEDER Project PGC2018-098561-B-C22

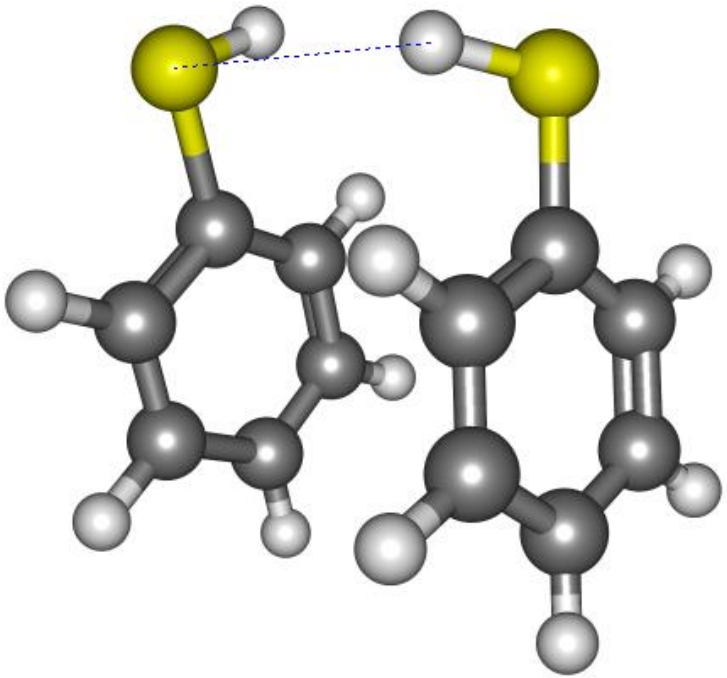
Universidad de Valladolid

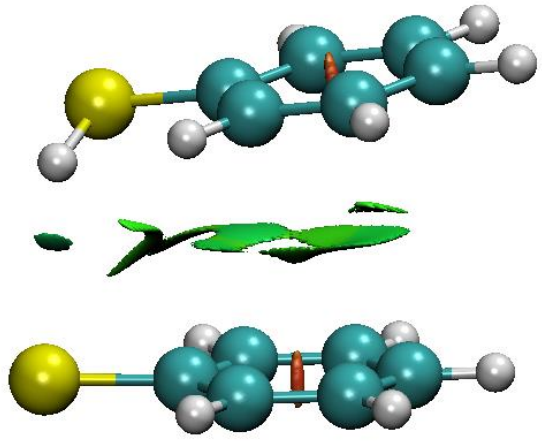
Aniline Trimer (Pérez et al. / Angew. Chem. Int. Ed. 2018, 57)

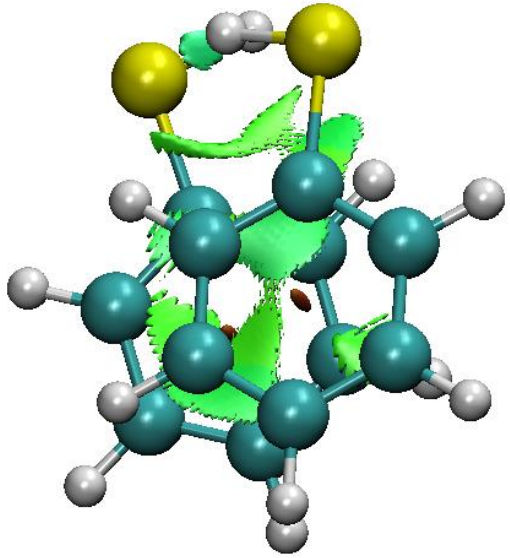


Thiophenol dimer

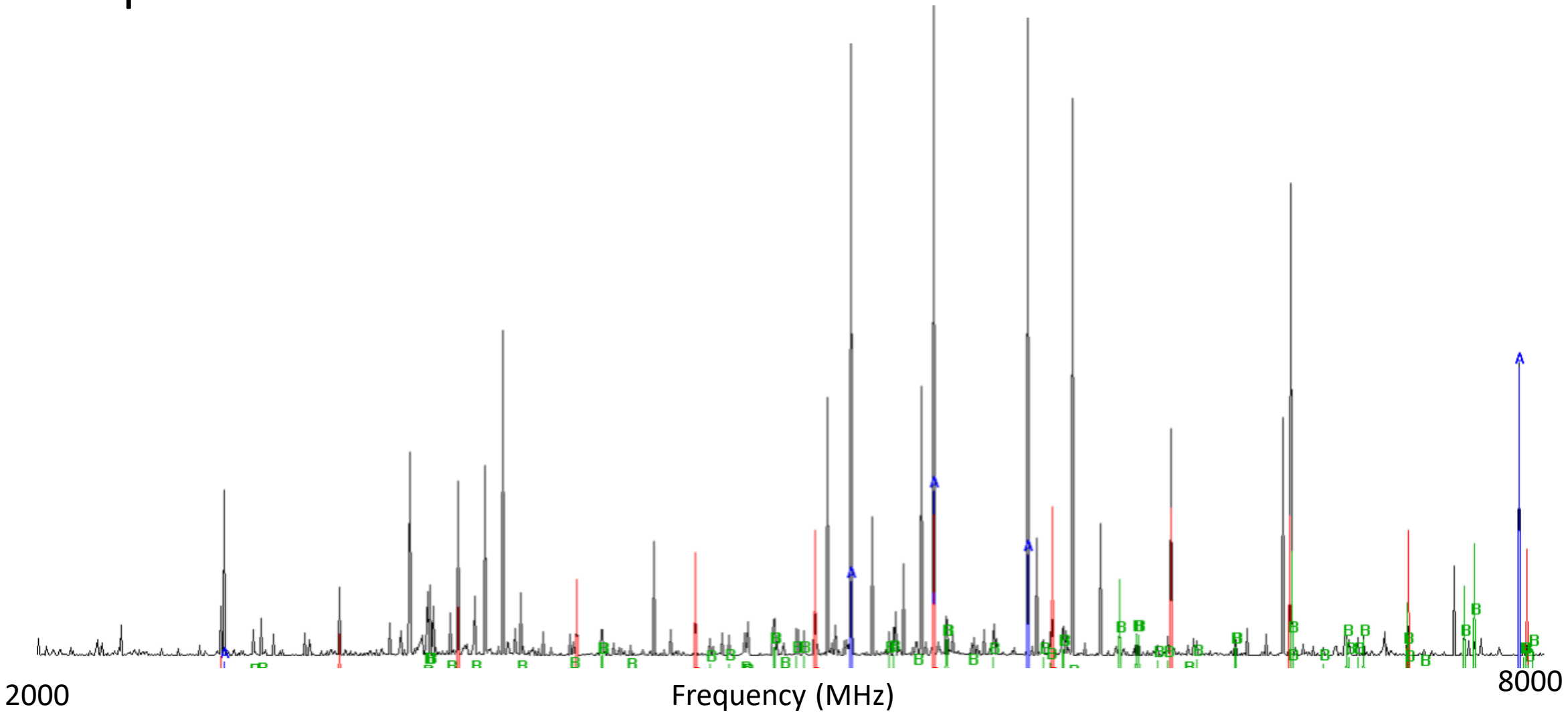
	EXPERIMENTAL	B3LYP-D3/DEF2TZVP		
	CS7	CS6	CS8	CS7
A / MHz[a]	662.75808(55)	630.01	633.88	690.74
B / MHz	499.46373(41)	527.33	525.89	498.55
C / MHz	338.61929(36)	433.55	434.54	346.52
D_J / kHz	-2.1513(29)	0.1617	0.1703	0.3583
D_{JK} / kHz	42.737(11)	-0.2190	-0.2235	-0.5804
D_K / kHz	-40.4876(97)	0.1170	0.1195	0.2690
d_1 / kHz	-0.08678(76)	0.0216	0.0212	-0.0326
d_2 / kHz	-1.17981(28)	0.0385	0.0241	0.0104
$\|\mu_a\|$ / D	-	0.0	-0.7	-0.1
$\|\mu_b\|$ / D	y	1.6	1.1	-1.5
$\|\mu_c\|$ / D	-	-1.1	-0.2	0.3
N[b]	130			
s / kHz	14.5			
ΔE/kJ mol^{-1}[c]		0.0	0.40	0.57
ΔG / kJ mol^{-1}		0.0	0.28	-2.18



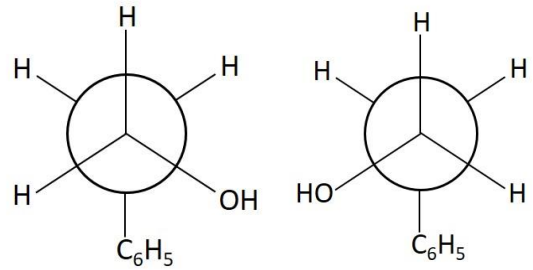




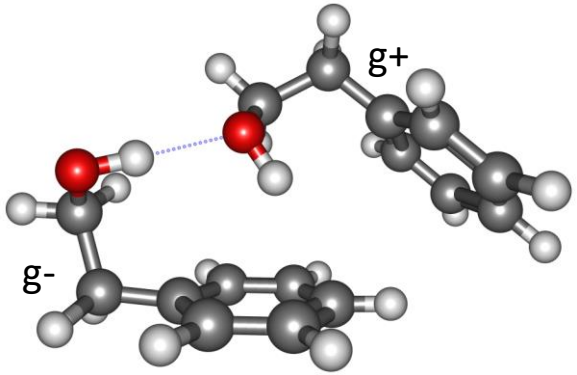
Thiophenol



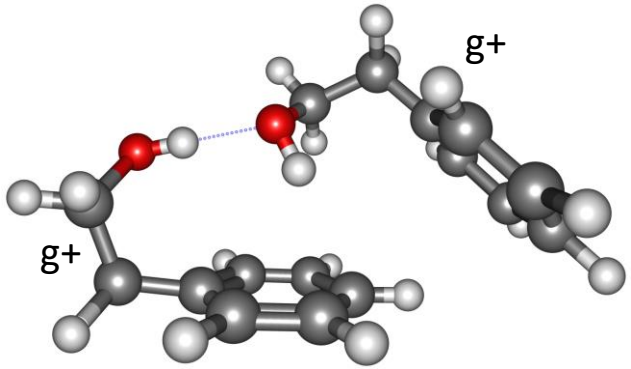
2-phenylethanol dimer



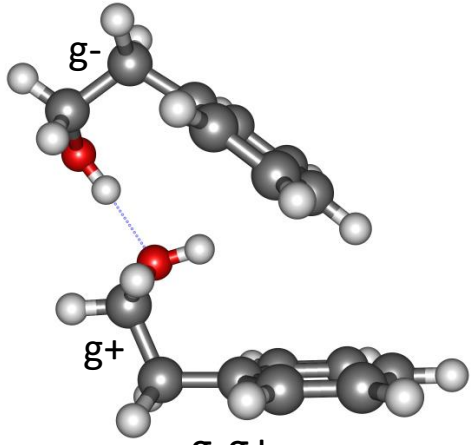
- Two isomers are stabilized by a combination of OH···O, OH···π and C-H···π interactions.



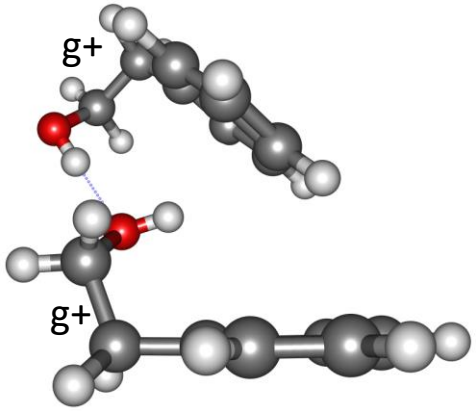
g-g+



g+g+



g-g+



g+g+

Difluorobenzene dimer (T. Goly et al. / *Chemical Physics* 283 (2002) 289–296)

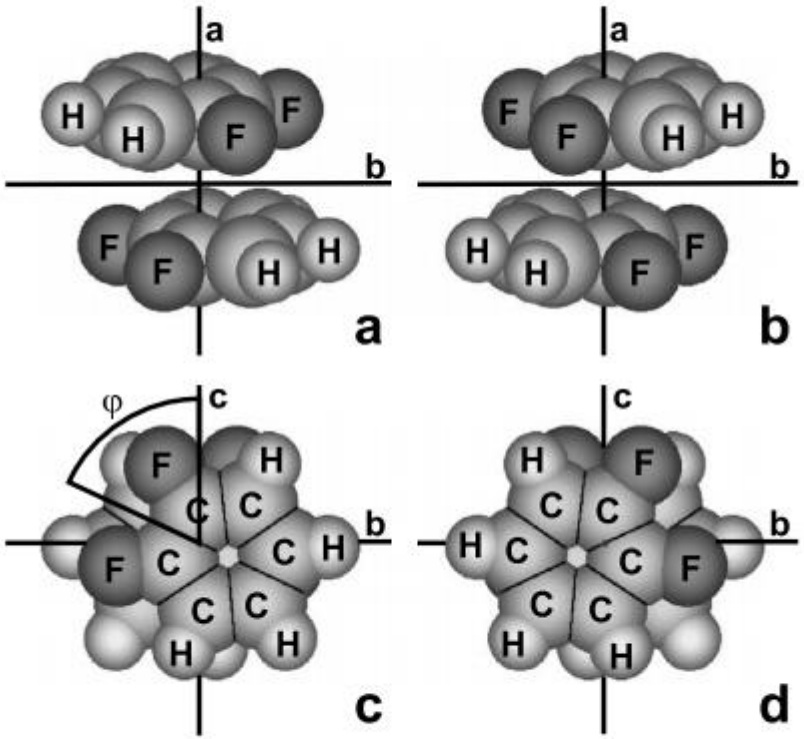
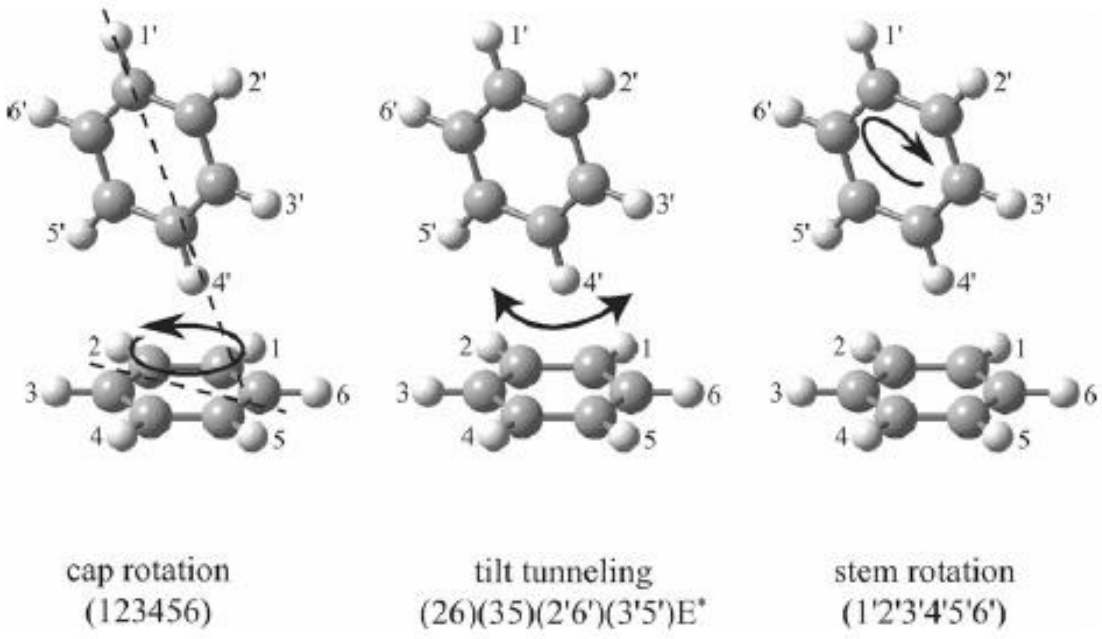


Fig. 1. Geometry of the *o*-DFB dimer. 1a and 1c show a proposed structure of one enantiomer, in a perspective view (a) and a projection on the *bc*-plane (c), respectively. Angle φ is the rotation of one monomer unit around the monomer *c*-axis. 1b and 1d show the other enantiomer.

- A stacked structure of diflurobenzene
- Since it is symmetric, there lines split (in total, some 180 doublet, all split by 105–115 kHz)

Benzene dimer (Schnell et al. / *Angew. Chem. Int. Ed. 2013, 52, 5180 – 5183*)



- Quartet splittings is observed, due to the tunneling process of a concerted motion involving hindered rotation of the stem.
- There is an internal rotation of the benzene ring located in the cap.