

Spectroscopic and kinetic studies, experimental and theoretical, of relevance to Interstellar Chemistry!? Hydrogen Bonding?

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Outline of the talk

- INTRODUCTION Astrochemistry/Astrophysics.
- Our tools
 - Experiment: Pulsed Nozzle Fourier Transform Microwave Spectrometer (Bangalore)
 - Slit-jet FTIR spectrometer (Rennes, France)
 - Theory: Ab initio, DFT and AIM Theories
- Studies on '**Hydrogen bonded complexes**':
 - Phenylacetylene-H₂O (O-H \cdots π and C-H \cdots O)
 - Phenylacetylene-H₂S
- Conclusions.

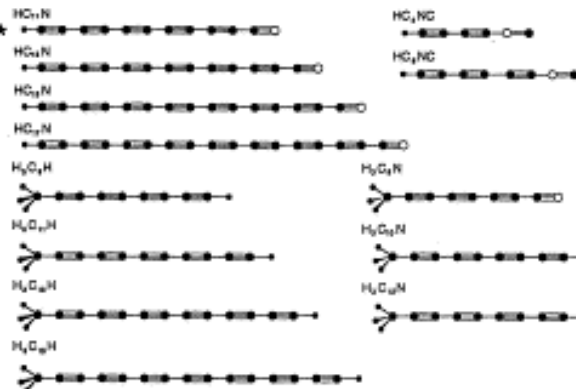
INTRODUCTION

“The laboratory astrophysics of radio molecules is complete in the sense that the lines of astronomical interest have either been measured directly or can be calculated with high precision”

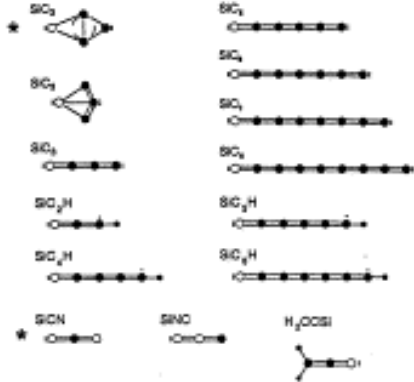
P. Thaddeus and M. C. McCarthy

Spectrochim. Acta Part A **57(4)** 757 (2001)

Polyynes



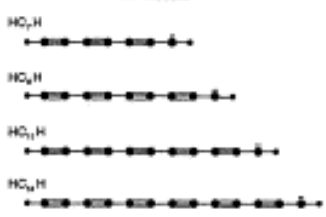
Silicon carbon chains and rings



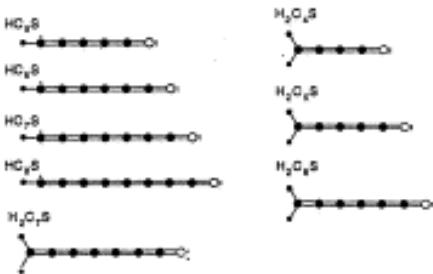
That was not an outlandish claim by the Authors but a claim made after detecting 77 reactive species in a 4 year period.

This was done with the addition of a pulsed discharge nozzle to the Fourier transform microwave spectrometer, which has high sensitivity AND high resolution simultaneously!

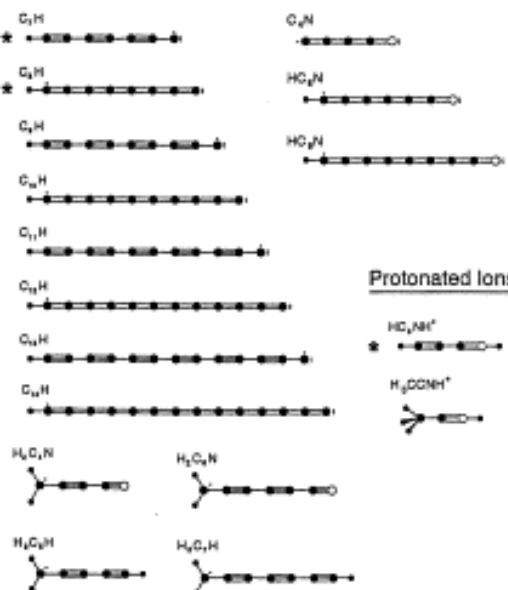
Symmetric carbon chain radicals



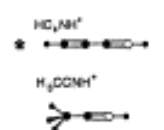
Sulfur carbon chains



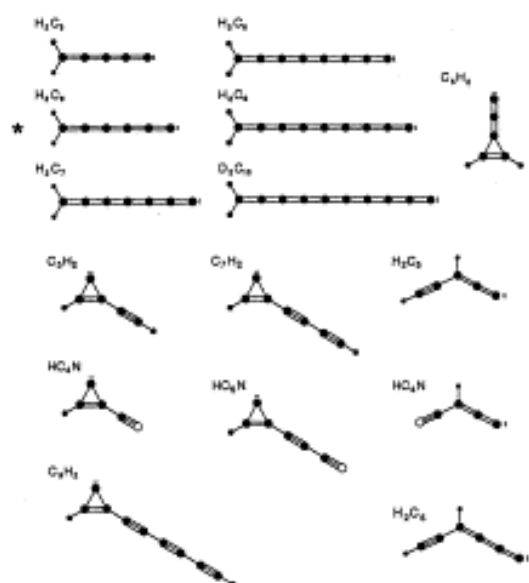
Carbon Chain Radicals



Protonated ions



Carbenes



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Is Microwave spectroscopy not relevant to Astrophysics anymore?

- No, it is very relevant!
- Unambiguous identification of molecules/radicals/ complexes in the gas phase is more possible with microwave spectroscopy than any other technique!

Complexes in the interstellar space?

- W. H. Klemperer and V. Vaida, PNAS 103, 10584 (2006)

“Molecular complexes play a large role in the chemistry of the interstellar medium, in particular in giant molecular clouds...Laboratory model compound studies in concert with direct astronomical observations are needed to elucidate the role of molecular complexes in “close in” planetary atmospheres and “far away” interstellar media”.

PAH (Kaiser, *Angew. Chem. Int. Ed.* 2007, 46, 6866 –6869)

- During the last decades, polycyclic aromatic hydrocarbons (PAHs) and other related aromatic compounds, such as ionized PAHs, have received considerable attention from astronomers, astrobiologists, environmentalists, and the combustion community. In the interstellar medium, PAH like species account for up to 10% of the cosmic carbon budget.
- Suspected carriers of UIR (unidentified infrared emission) and DIB (diffuse interstellar bands)
- Despite the crucial importance of PAHs, even the formation route of the very first building block of this type of compounds (namely, the **phenylacetylene** molecule, C_6H_5CCH) is unknown.

phenylacetylene

- Crucial intermediate for the formation of PAH
- Under the low temperature conditions in the interstellar medium phenylacetylene and it's complexes could be found!
- Experimental data on complexes of phenylacetylene complexes could prove useful.
- It is a multifunctional molecule that can form a variety of hydrogen bonds!

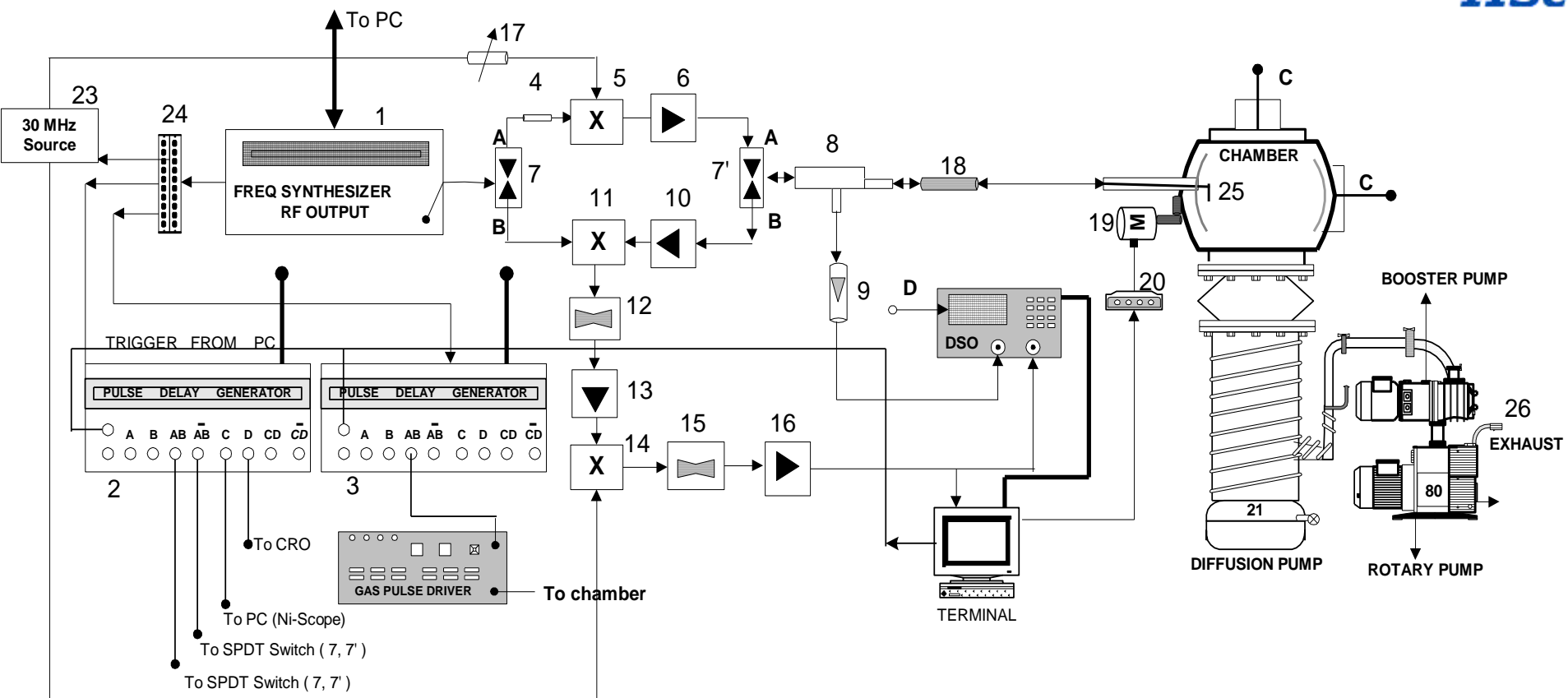
What can microwave spectroscopy tell us?

- Transition frequencies are needed to confirm the presence in interstellar medium.
- Rotational constants give us structural information!
- Nuclear quadrupole coupling constants can help in pinning down the orientation of the molecules
- Splitting due to tunneling/hindered-rotations can give us information about the barriers to such motion.
- A home-made pulsed nozzle Fourier transform microwave spectrometer is used in which a supersonic molecular beam is probed by a Fourier transform microwave spectrometer.



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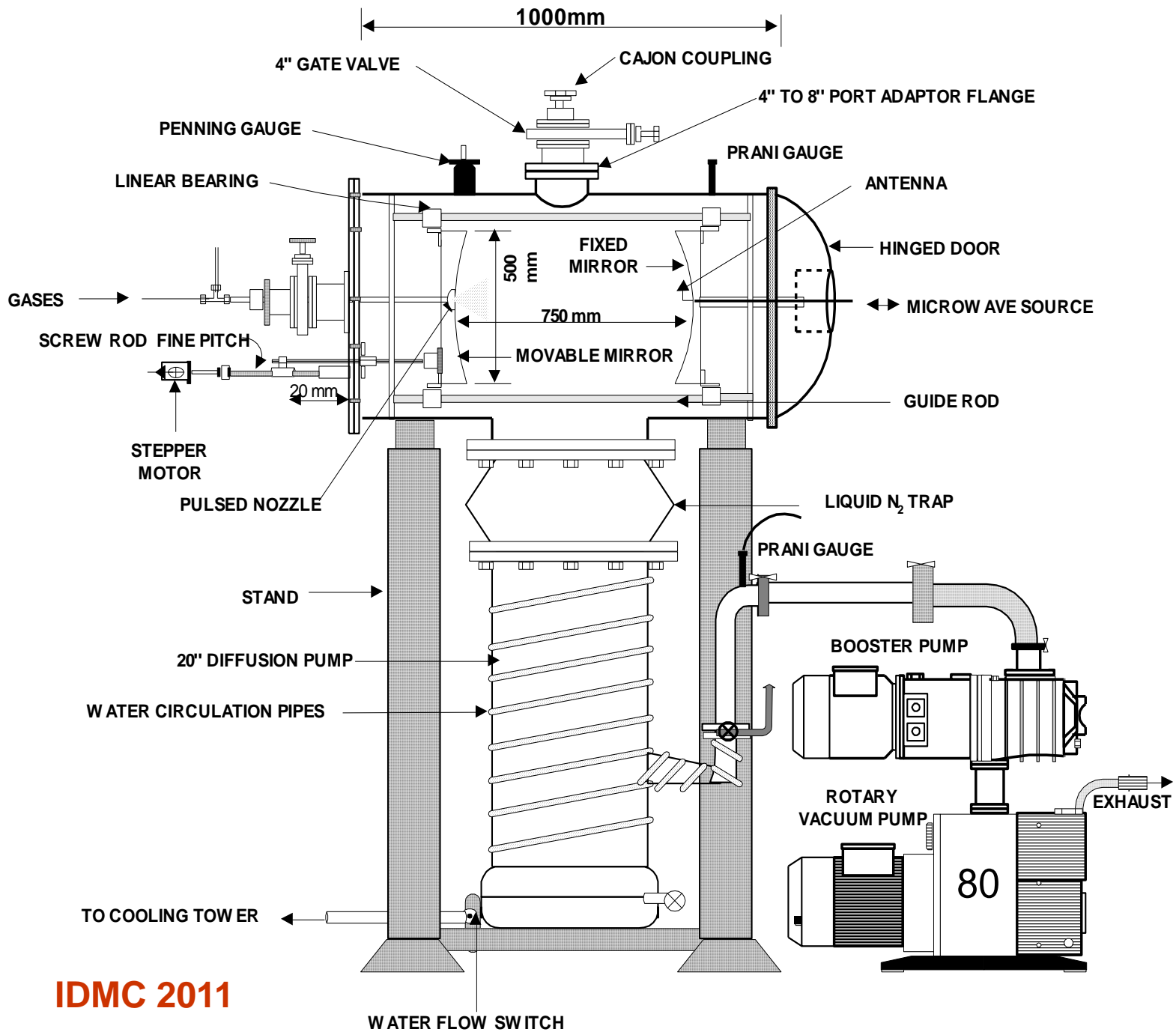
Pulsed Nozzle Fourier Transform Microwave Spectrometer



Similar to FT-NMR. Instead of RF, a microwave pulse is applied. Double superheterodyne detection is used by which the signal in 2-26 GHz range is brought down to ≤ 1 MHz before digitization

Arunan, Tiwari, Mandal and Mathias Curr. Sci. 2002

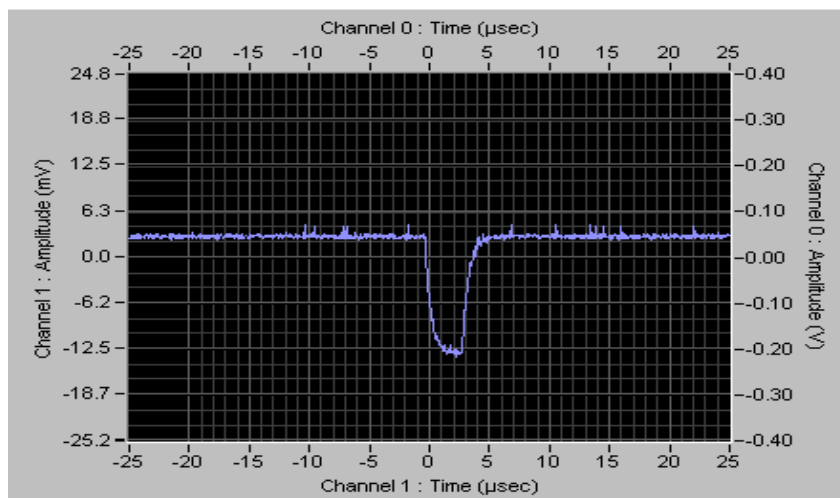




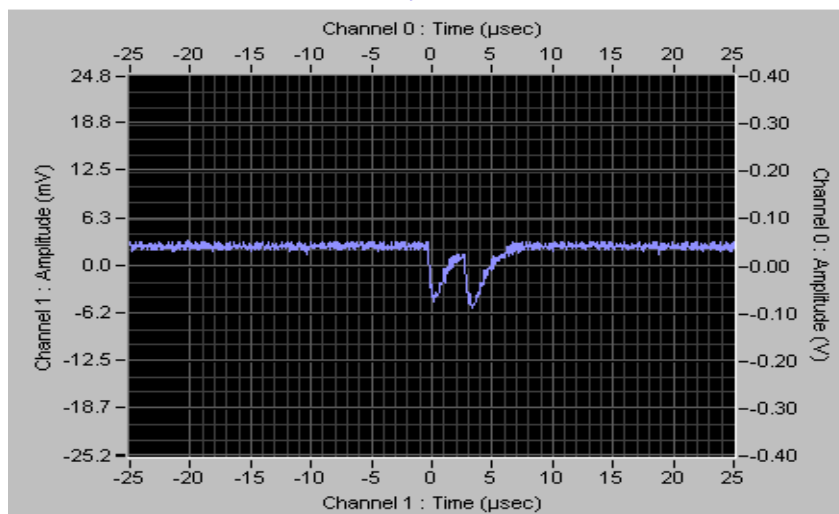
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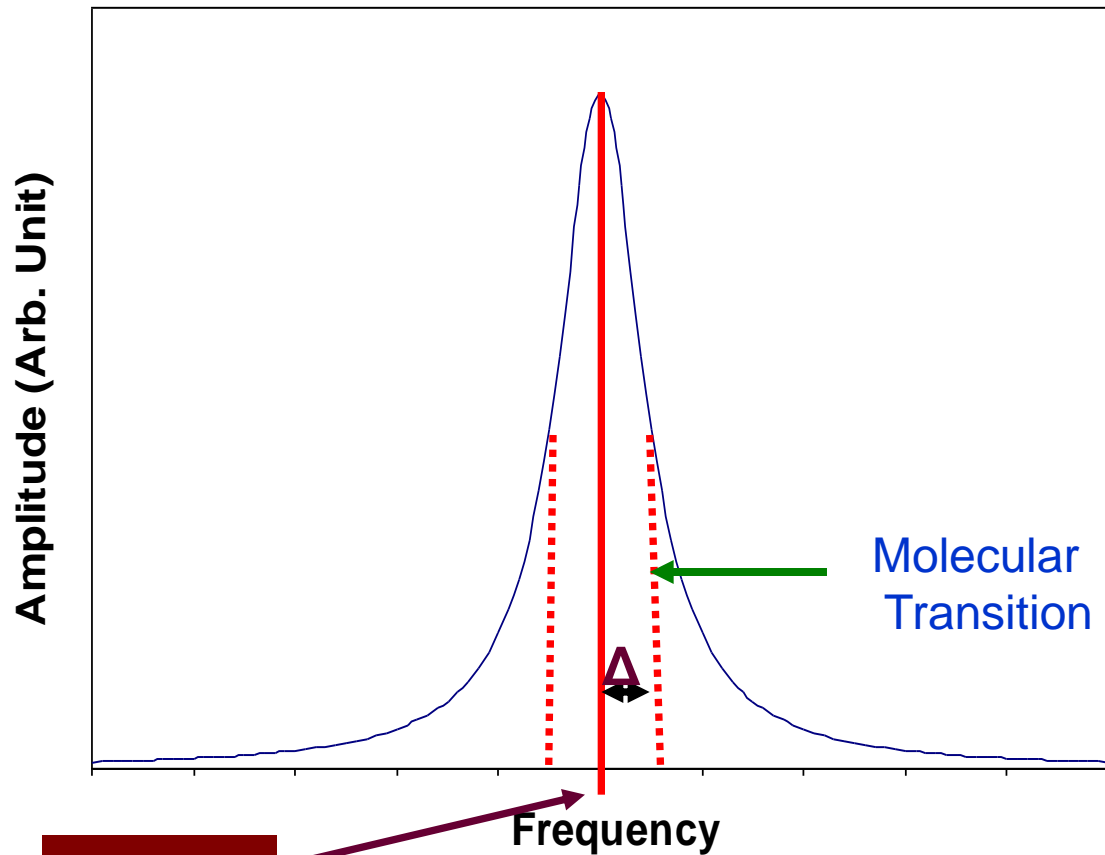
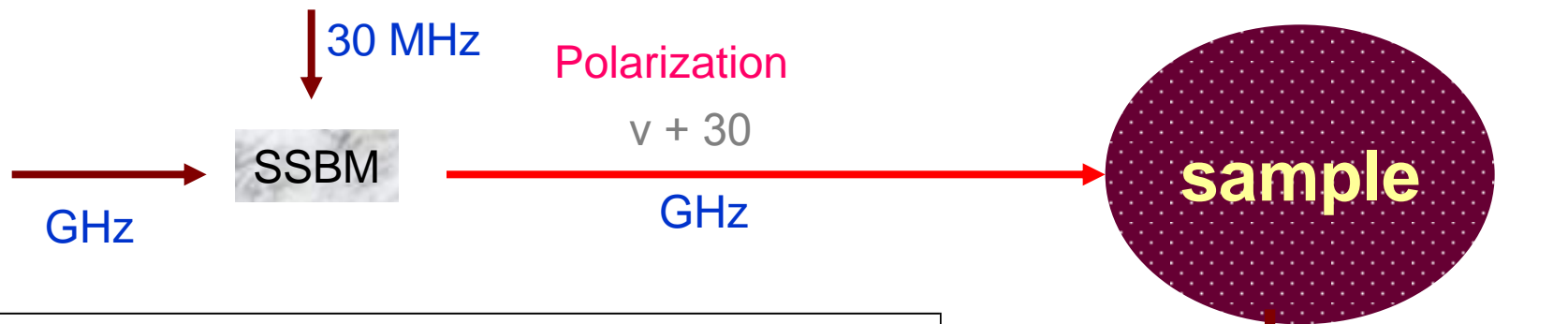
Tuning of the Fabry-Perot Cavity



When the cavity is not in tune



When the cavity is in tune



$\nu + 30$

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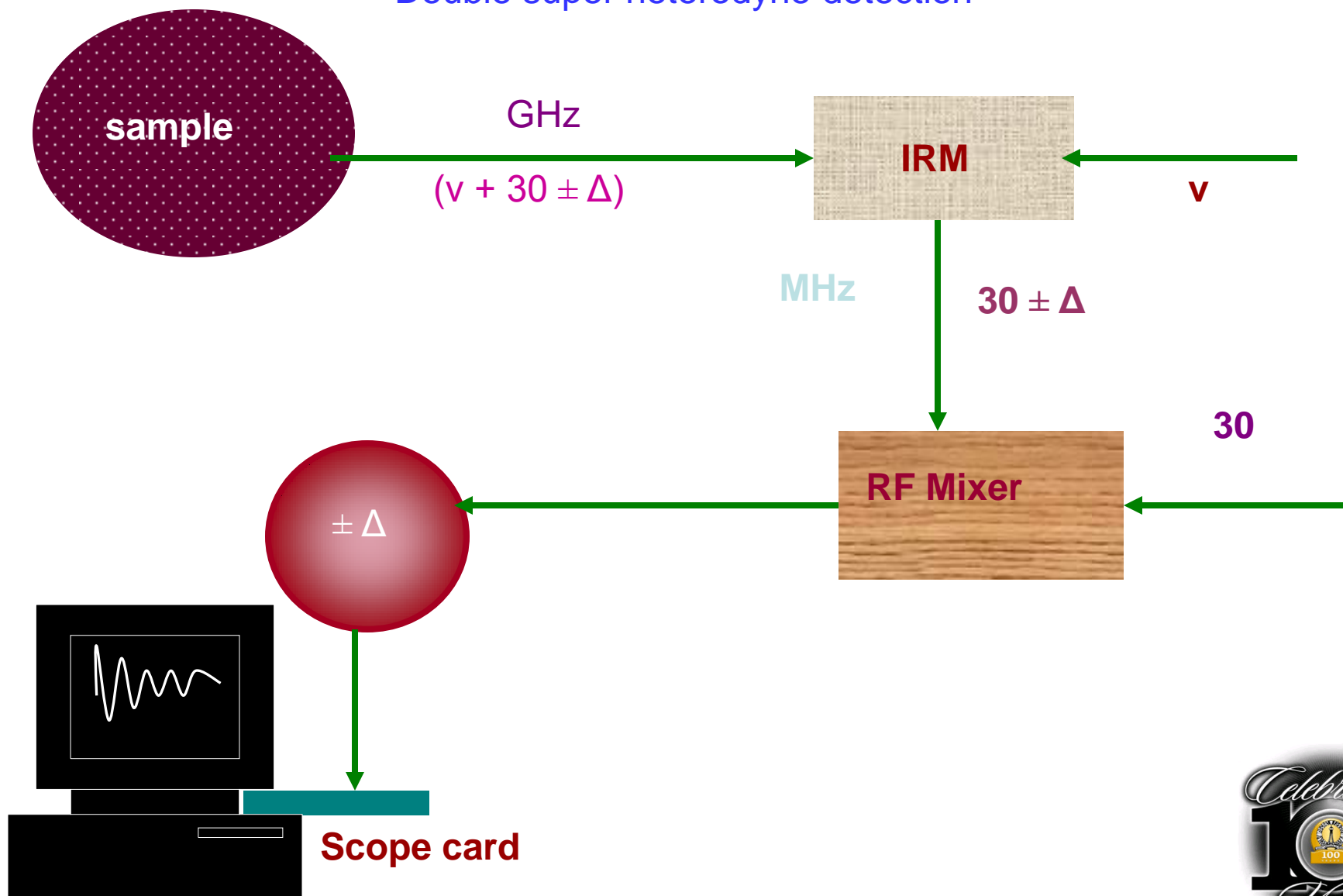
$(\nu + 30 \pm \Delta)$

Molecular transition

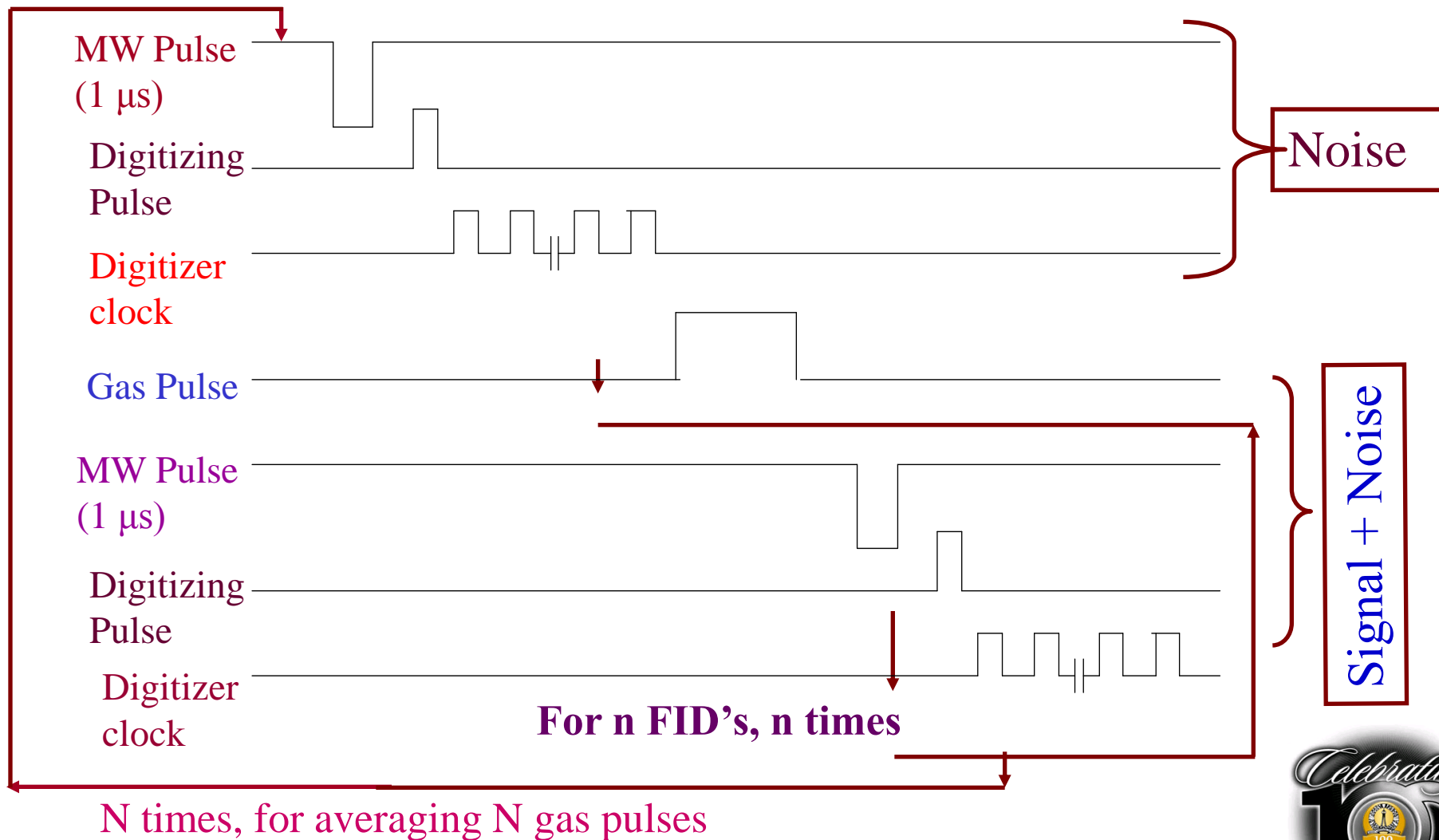


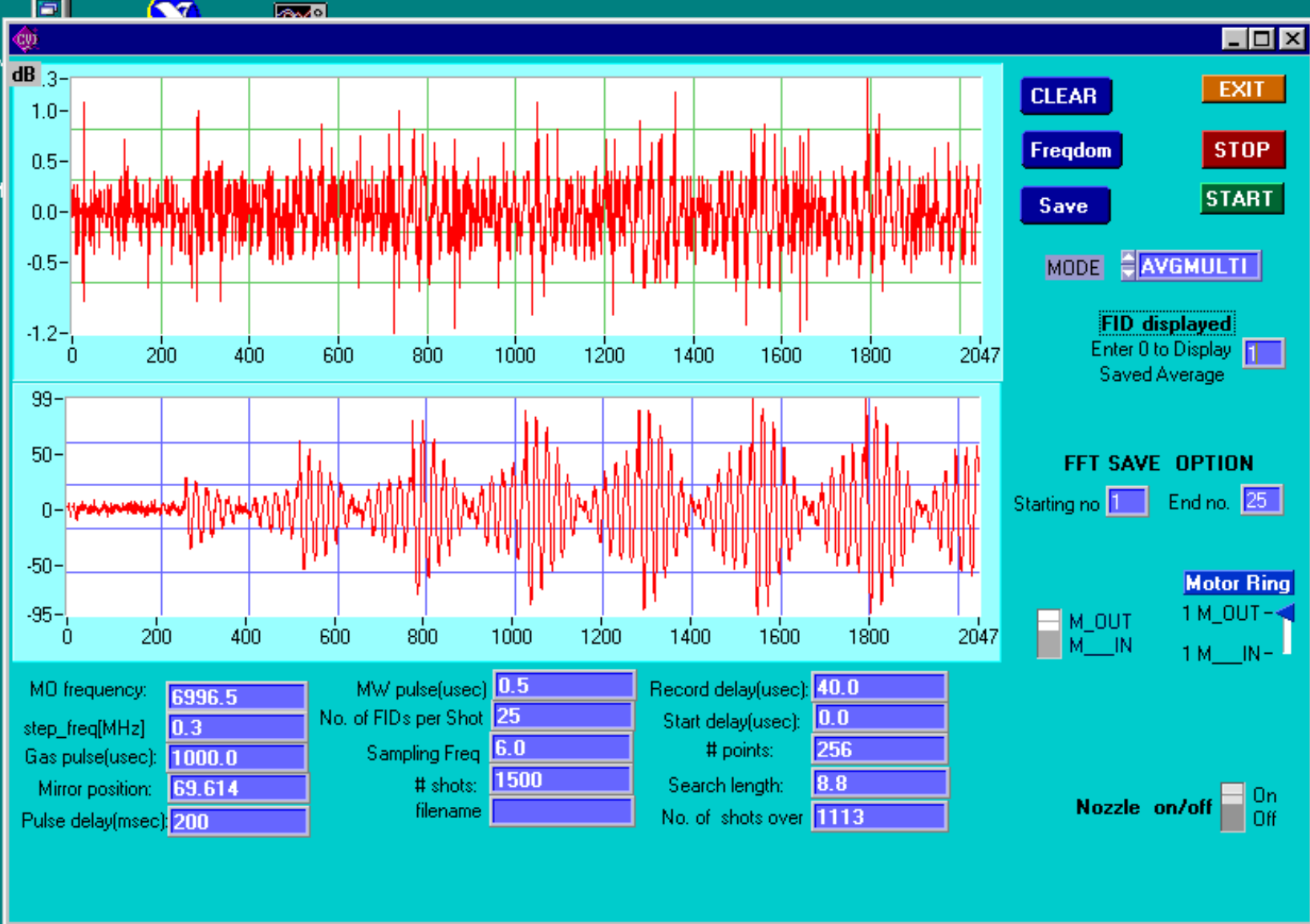
Detection and Downconversion

Double super heterodyne detection

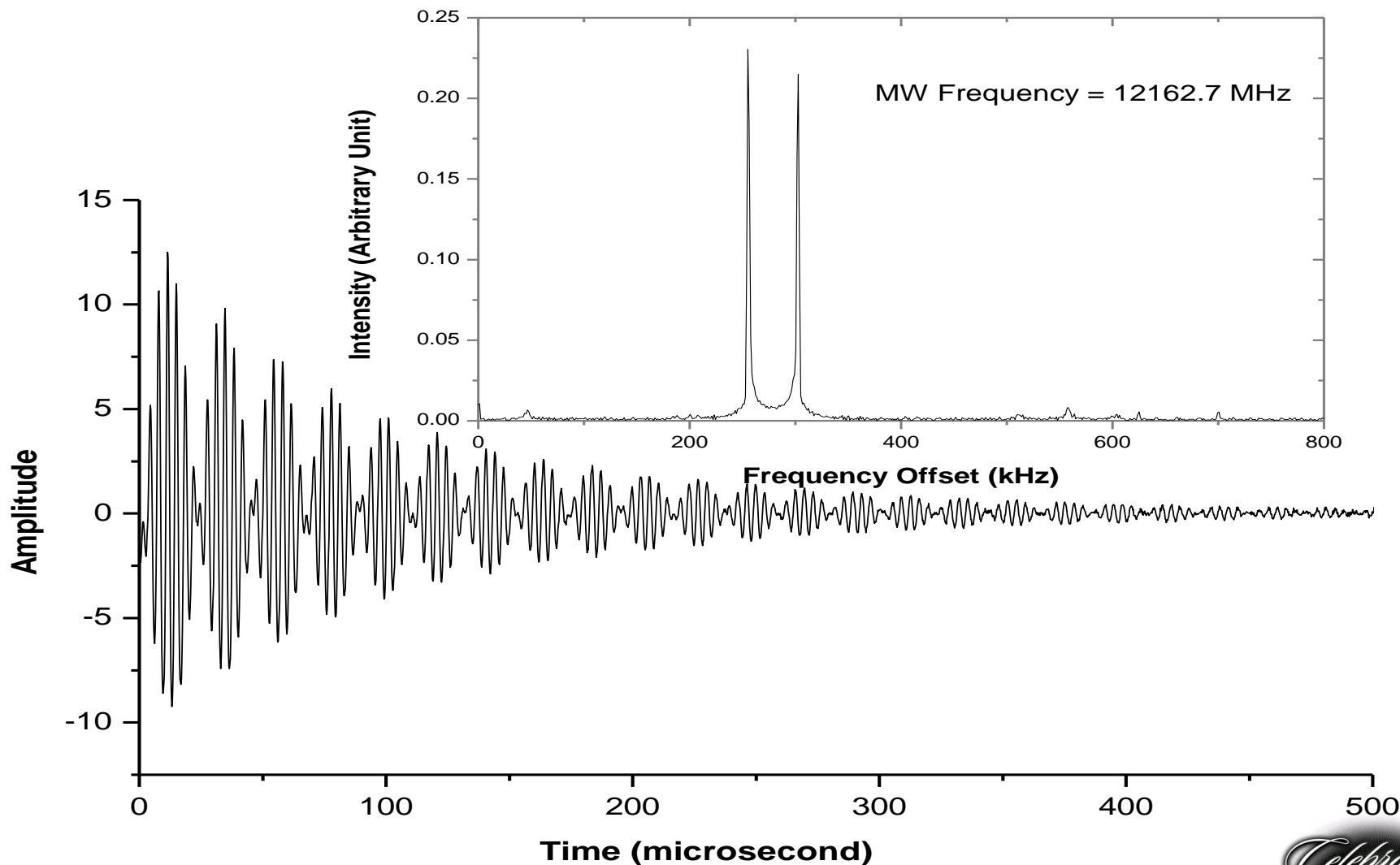


Pulse sequence of the experiment





Time domain and corresponding frequency domain signal

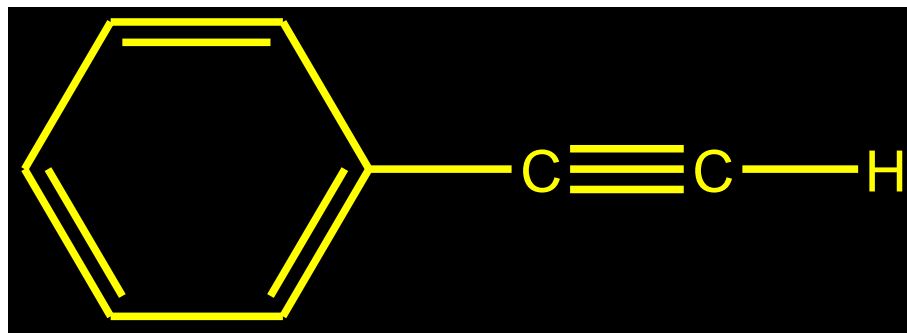


Phenylacetylene-H₂O complex

Microwave spectrum of phenylacetylene monomer is known

H. Dreizler, H.D. Rudolph, B. Hertke, J. Mol. Struct. 698 (2004) 1.

Where will H₂O bind?

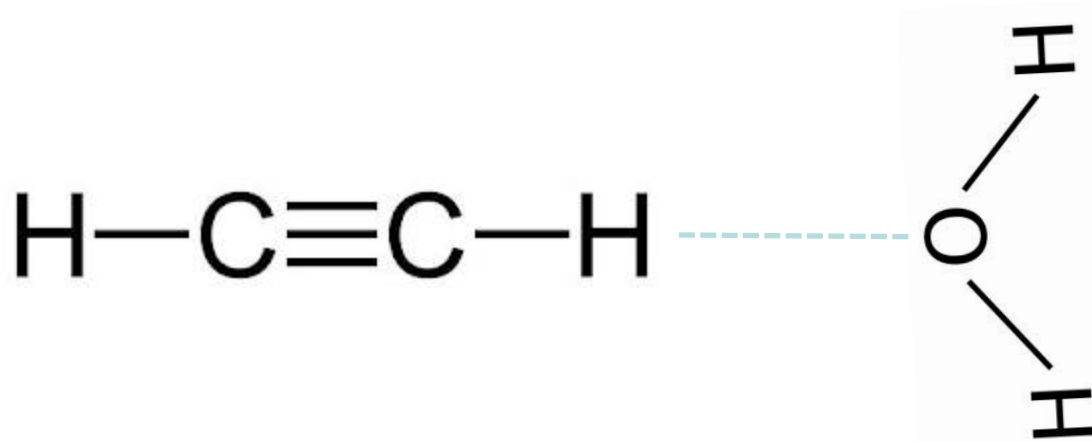
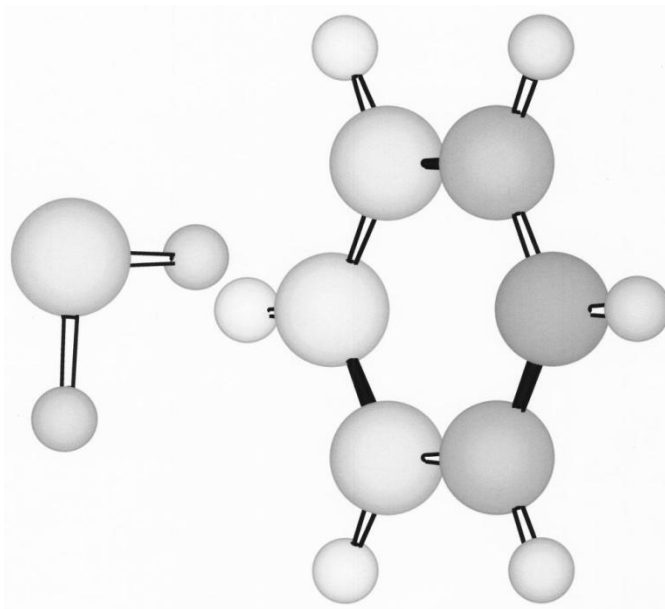


Phenyl ring π -cloud: could be hydrogen-bond acceptor

Acetylenic π -cloud: could be hydrogen-bond acceptor

Acetylenic C-H: could be hydrogen-bond donor

Benzene-H₂O
OH---pi interaction



CH---O interaction

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Legon-Millen's rules

Geometry of B---HX, hydrogen bonded complexes

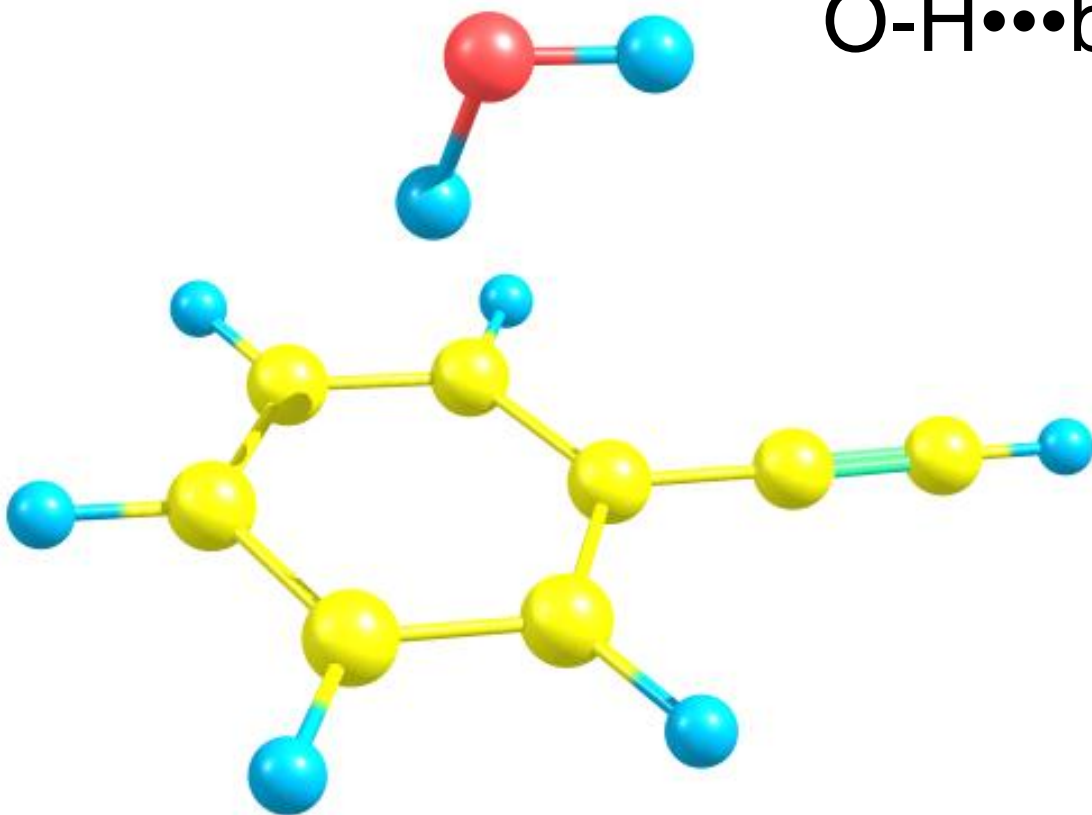
- ✓ Rule 1 says "if 'B' has lone-pair, the axis of H-X molecule coincides with that of lone-pair"
- ✓ Rule 2 says "if 'B' has no non-bonding electron pair but has π -bonding electron pairs, the axis of the H-X molecule intersects the internuclear axis of the atoms forming the π -bond and is perpendicular to the plane of symmetry of the π -bond"
- ✓ Rule 3: "Rule 1 is definitive when 'B' has both non-bonding and π -bonding pairs."

These rules were derived from a large set of experimental data where X=F, Cl, CN and 'B' is having either lone-pair or π -electrons or both.

Reference: Legon and Millen, Chem. Soc. Rev., 16, 1987, 467

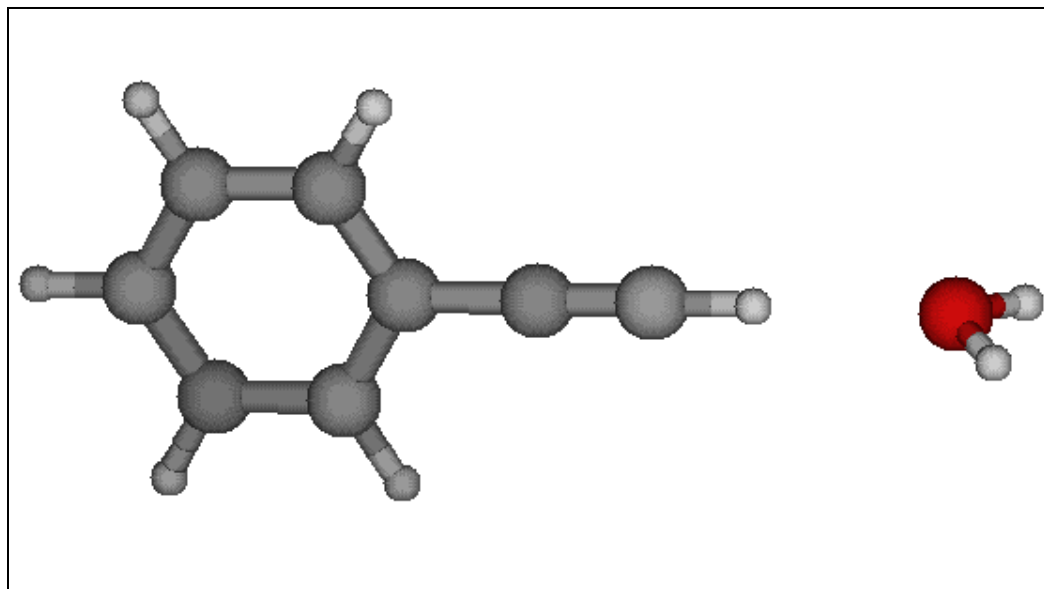
Phenylacetylene-water

O-H...benzene π interaction



A (MHz)	2083
B (MHz)	1132
C (MHz)	995

Phenylacetylene-water



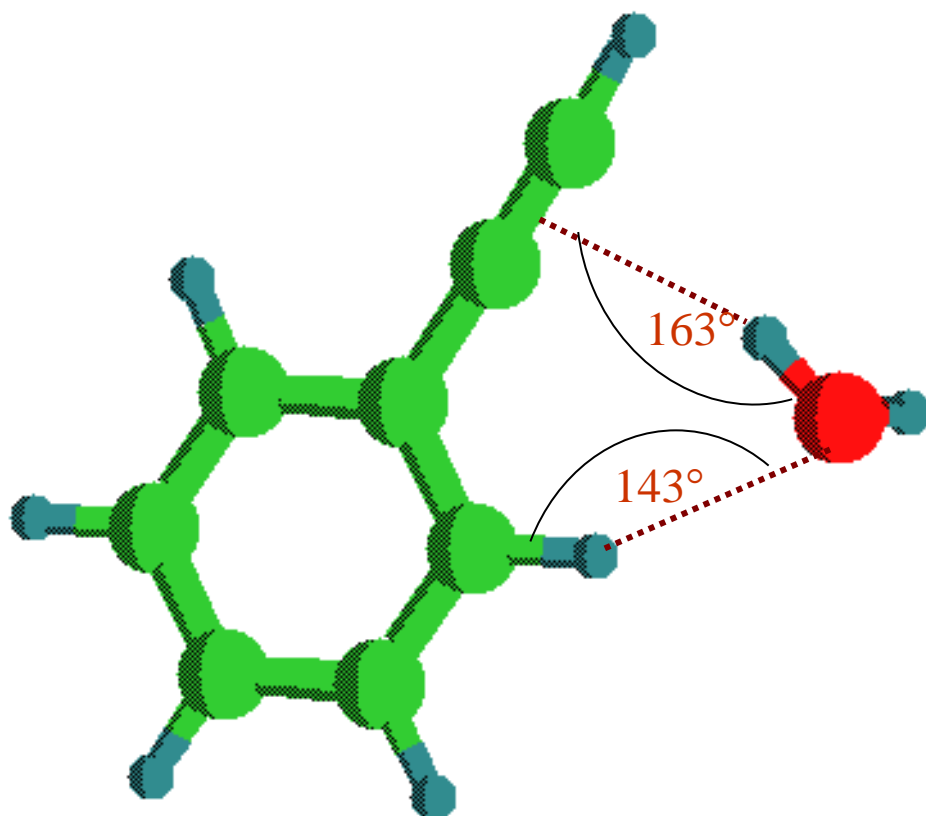
A (MHz)	5518
B (MHz)	506
C (MHz)	464

C-H...O interaction

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Phenylacetylene-water



A (MHz)	2678
B (MHz)	998.0
C (MHz)	729

Initial search in Argon from 7-9.2 GHz

$3_{31}-4_{32}$	7144.3570	} → Argon-phenylacetylene lines
$3_{12}-4_{13}$	7150.5070	
$3_{12}-4_{23}$	7446.5318	
$3_{21}-4_{22}$	7582.1946	
$4_{32}-5_{23}$	8001.6611	
	8143.0807	(within 17 MHz of the predicted 4(0,4)-5(0,5) transition for the ab initio predicted structure!)
$4_{23}-5_{14}$	8288.3467	} → Argon-phenylacetylene lines
$4_{13}-5_{14}$	8584.3707	
$4_{13}-5_{24}$	8696.6241	
$3_{21}-4_{32}$	8959.1046	

One weak signal depending on phenylacetylene and water could be seen after averaging for 1000-1500 gas pulses in Argon. The signal appears in 100 shots in Helium.

Argon-phenylacetylene (Dreizler and co-workers, *J. Mol. Str.*, 825, 2010)

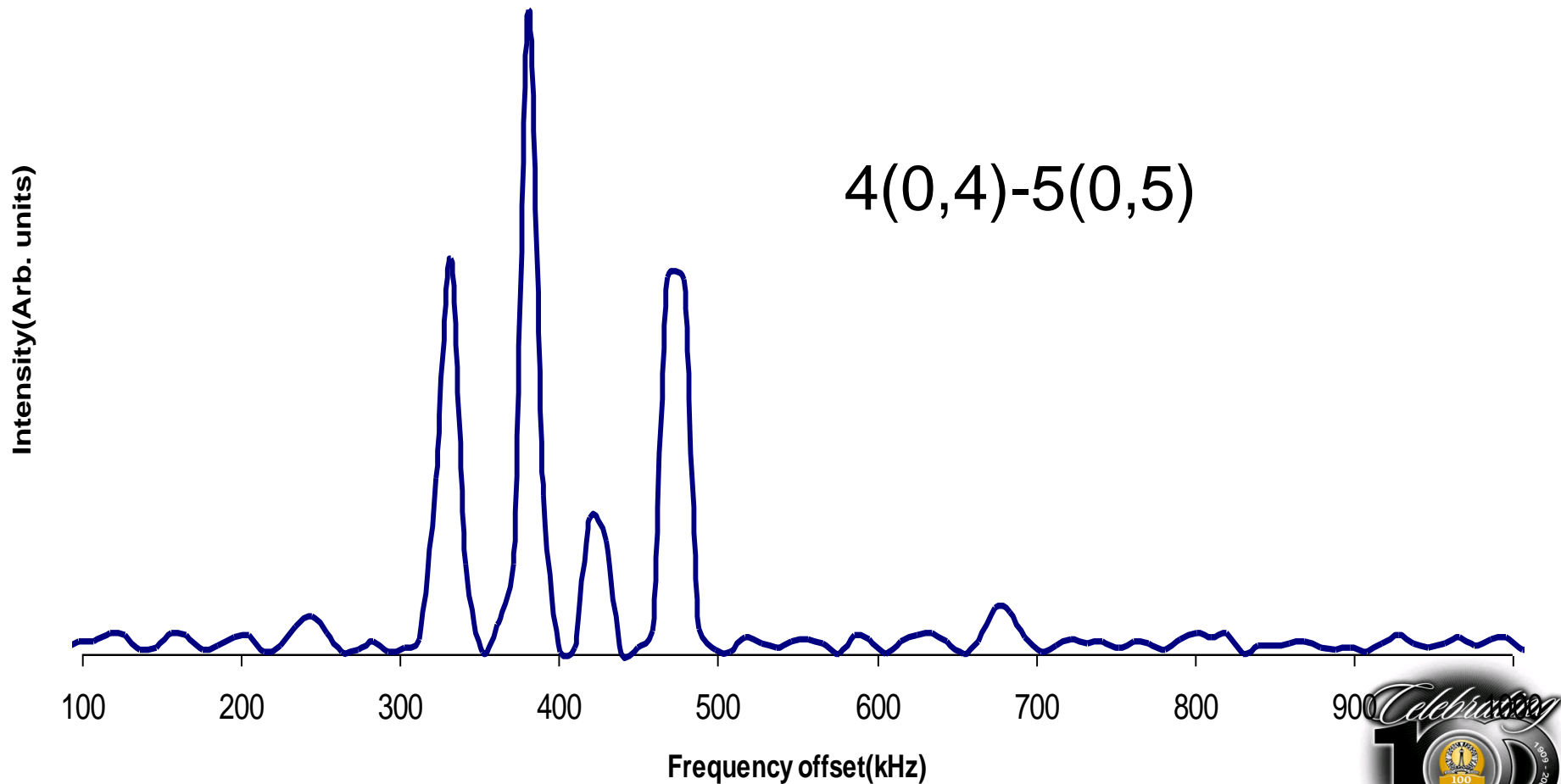
Some transitions were newly measured, but could be fit with the same

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Hamiltonian as reported by Dreizler

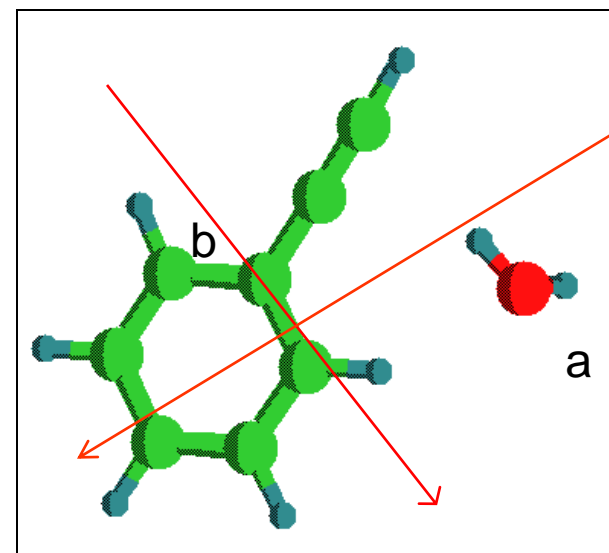


Search using Helium shows a doubling of the transitions



Transitions	Series1	Res. (kHz)	Series2	Res. (kHz)
	-	-	7313.3681	-0.3
4 ₁₃ -3 ₁₂	7377.2239	-0.8	7377.1167	-1.5
4 ₁₄ -3 ₀₃	7469.9099	-3.1		
5 ₁₅ -4 ₁₄	7871.0364	-0.2	7870.0680	0.2
5 ₀₅ -4 ₀₄	8143.0807	1.0	8142.2742	0.8
5 ₂₄ -4 ₂₃	8575.9471	5.3	8575.4126	1.2
5 ₁₅ -4 ₀₄	8699.4556	2.5	8698.9750	2.2
2 ₂₁ -1 ₁₀	8747.9047	-2.8	8750.8803	-0.1
2 ₂₀ -1 ₁₁	9041.4890	-1.8	9041.1213	1.2
6 ₀₆ -5 ₁₅	9042.5188	-1.1	9044.6475	0.2
5 ₂₃ -4 ₂₂	9072.0932	0.3	9071.8680	-0.6
5 ₁₄ -4 ₁₃	9153.4035	-0.1	9153.2243	0.8
6 ₁₆ -5 ₁₅	9391.9782	-2.6	9390.7862	1.1
7 ₁₆ -6 ₂₅	9574.4927	1.4	9572.3070	-0.1
6 ₀₆ -5 ₀₅	9598.8931	-0.3	9597.8176	-1.9
6 ₁₆ -5 ₀₅	9948.3535	-0.8	9947.4832	-1.3
3 ₂₂ -2 ₁₁	10211.3150	5.9	10214.0197	-0.2
6 ₂₅ -5 ₂₄	10239.0055	-2.9		
6 ₃₄ -5 ₃₃	10477.6610	-0.001		
7 ₀₇ -6 ₁₆	10687.3803	0.2	10685.8271	1.6
6 ₁₅ -5 ₁₄	10874.3312	-0.2	10874.0427	1.0
7 ₁₇ -6 ₁₆	10895.7674	1.6	10894.3327	-0.4
6 ₂₄ -5 ₂₃	11004.1483	-1.8		
7 ₀₇ -6 ₀₆	11036.8388	-2.2	11035.4849	-5.6
7 ₁₇ -6 ₀₆	11245.2288	2.1	11243.9982	0.1
7 ₂₆ -6 ₂₅	11875.5196	-0.5	11874.6923	-0.7
8 ₀₈ -7 ₁₇	12266.3368	1.9	12264.5854	-1.5
8 ₁₈ -7 ₁₇	12385.8729	-1.3		
8 ₀₈ -7 ₀₇			12473.0986	4.0

Lines in red were not found in the initial searches with Ar. Search in He led to the observation of these lines



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Fitted parameters for Phenylacetylene-H₂O

Parameters	Series1 (Stronger)	Series2 (Weaker)
A (MHz)	2672.092(3)	2673.135(3)
B (MHz)	996.3581(8)	996.3929(9)
C (MHz)	731.7055(4)	731.5733(4)
d ₁ (kHz)	0.077(3)	0.091(4)
d ₂ (kHz)	1.1(1)	1.5(1)
D _J	0.366(6)	0.392(8)
D _{JK}	-0.58(2)	-0.69(2)
D _k	5.1(6)	6.9(5)
Sd(kHz)	2.2	1.7
# ¹	27	24

Fitted parameters for the isotopomers of Phenylacetylene...H₂O

Parameters	C ₈ H ₆ ...D ₂ O		C ₈ H ₆ ...H ₂ ¹⁸ O		C ₈ H ₅ D...H ₂ O		C ₈ H ₆ ...HOD
	Strong	weak					
A (MHz)	2625.266(7)	2625.044(6)	2616.32(1)	2615.382(3)	2602.00(2)	2602.99(3)	2672.744(4)
B(MHz)	951.432(2)	951.414(2)	956.6621(6)	956.6468(4)	976.61(2)	976.645(4)	979.0377(1)
C(MHz)	707.623(8)	707.636(8)	705.8253(6)	705.9508(1)	716.020(8)	715.891(1)	722.5126(7)
d₁(kHz)	0.056(5)	0.070(6)	0.077	0.091	0.34(5)	0.34	0.092(5)
d ₂ (kHz)	2.7(1)	1.1(2)	1.1	1.5	6(3)	6	1.5(2)
D _J	0.39(1)	0.40(1)	0.366	0.392	0.9(1)	0.9	0.38(1)
D _{JK}	0.17(1)	-0.6(1)	-0.58	-0.69	-4.4(4)	-4.4	-0.7(1)
D _k	44(1)	4.8(1)	5.1	6.9	-130(4)	-130	5.4(8)
SD(kHz)	3.1	2.6	2.2	1.7	1.9	3.1	3.9

Structure of phenylacetylene...H₂O

Theory

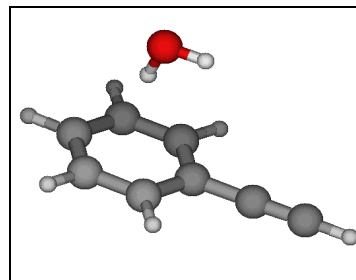
A (MHz)	2678
B (MHz)	998.0
C (MHz)	729

Experiment

A (MHz)	2672
B (MHz)	996
C (MHz)	731

Re-optimisation of phenylacetylene...H₂O starting from the monomer optimized geometries gave a still closer value for MP2/aug-cc-pVDZ level!

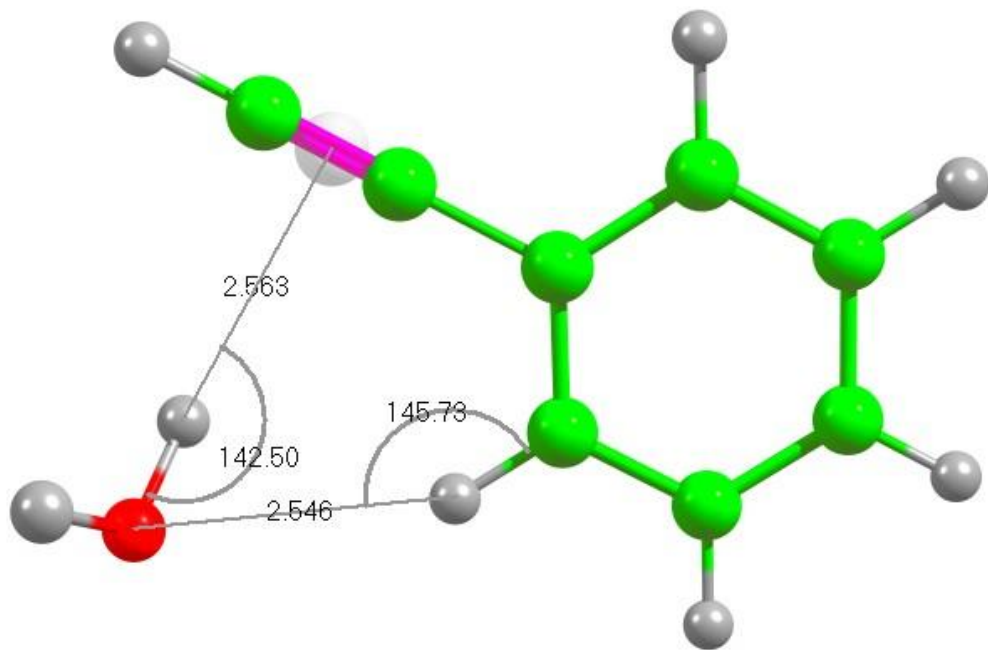
A (MHz)	2673
B (MHz)	999.0
C (MHz)	729



$$\Delta = -181 \text{ amu}\text{\AA}$$

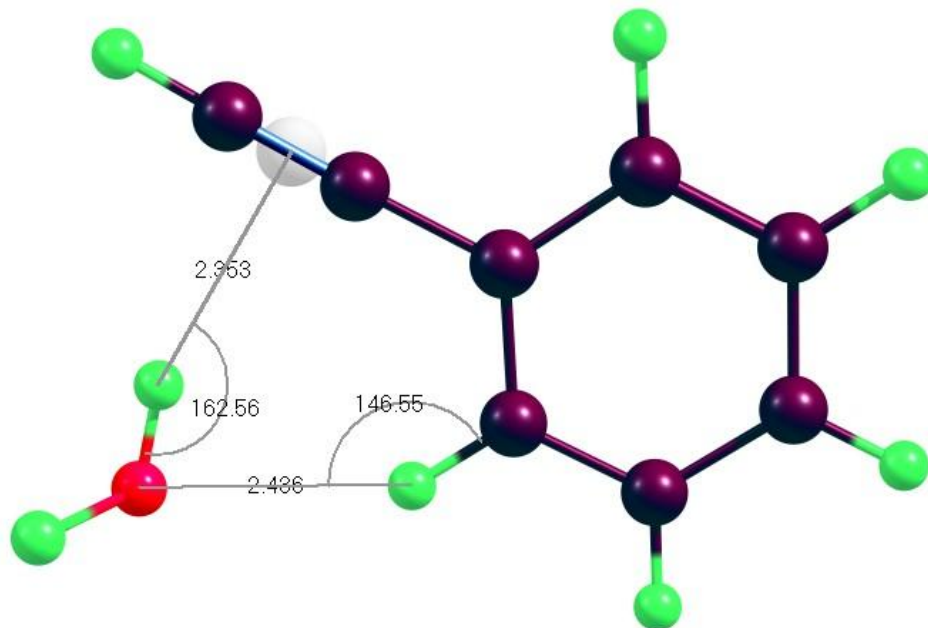
Experimental inertial defect, $I_c - I_a - I_b = -5.67 \text{ amu}\text{\AA}$

The H₂O oxygen is lying in the plane of phenylacetylene



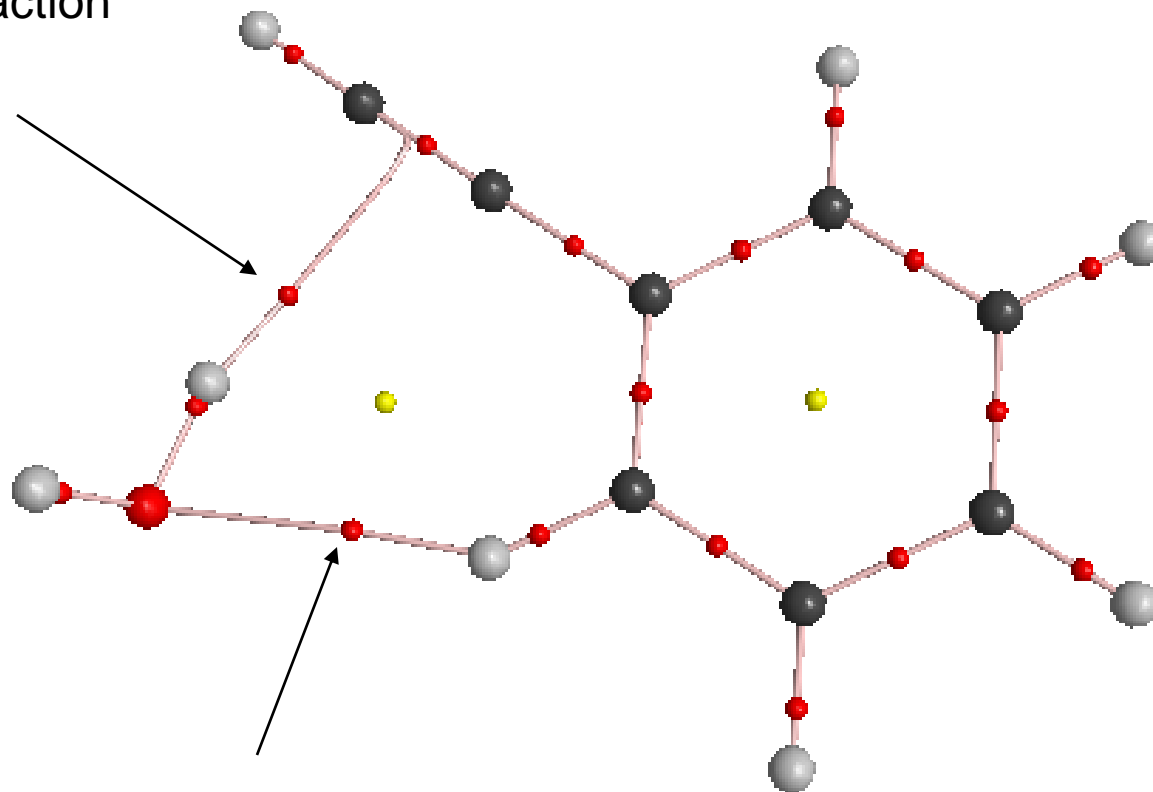
Experiment

Theory



Atoms in Molecules Analysis

OH... π interaction

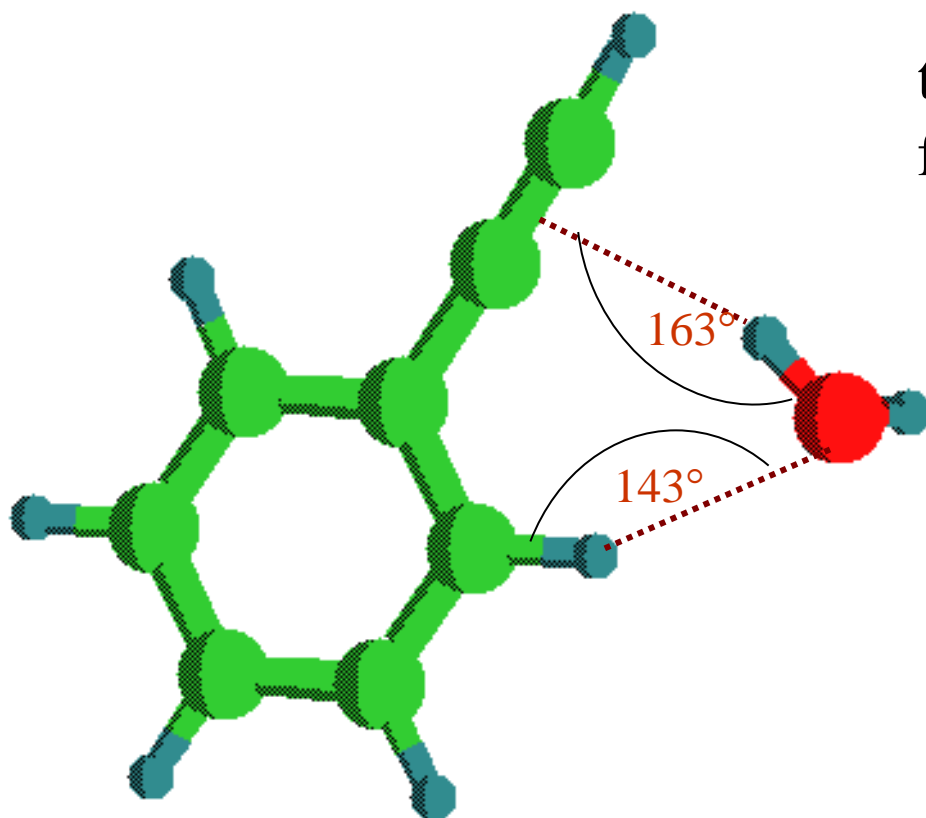


C-H...O interaction

Two ring critical points

Electron density at BCP for O-H... π is 0.013 a.u.
at BCP for C-H...O is 0.011 a.u.

Phenylacetylene-water complex



Y-H---X (X is the midpoint of the tripple bond) angle(A) in degrees for YH-HCCH complexes:

Y(donor atom)	A
F	180° ^{1,2}
Cl	180° ^{4,5}
Br	180° ⁵
O	179° ³

The secondary C-H...O interaction makes the O-H... π non linear
M. Goswami and E.Arunan, *Phys. Chem. Chem. Phys.*

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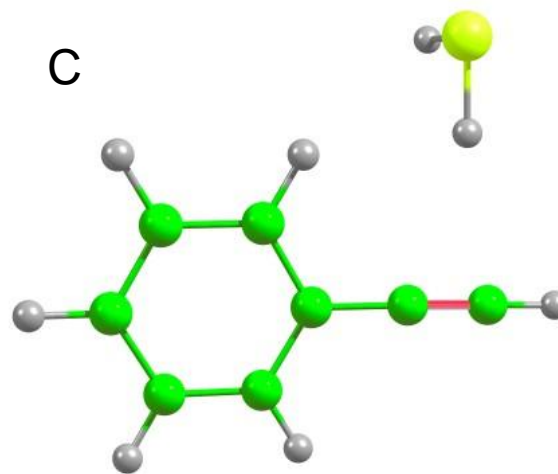
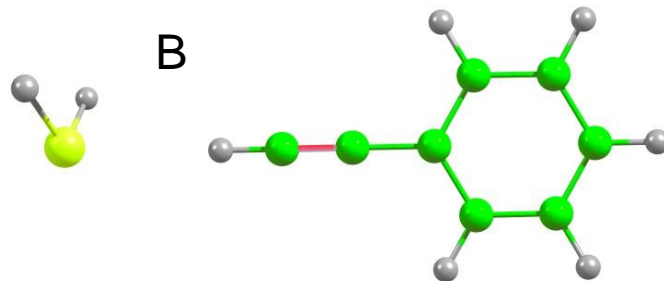
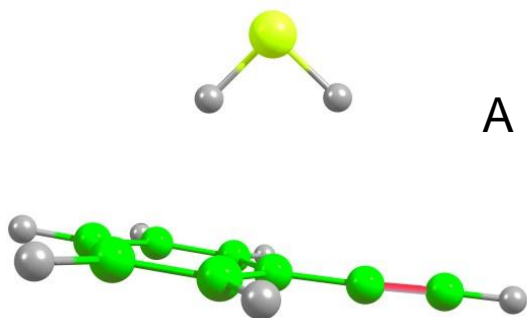


Summary on H₂O complex

- Microwave spectrum of phenylacetylene-H₂O unambiguously confirms the nearly planar structure involving both O-H... π and C-H...O interactions.
- Each transition is a doublet for all the H₂O complexes whereas it is a singlet for HOD
- Both the interactions seem to be equally strong

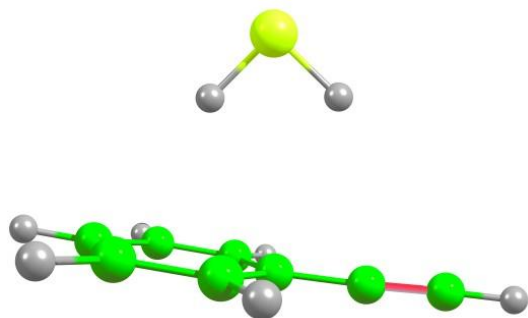
Microwave Spectroscopic studies of phenylacetylene...H₂S complex

Optimised geometries of phenylacetylene...H₂S at MP2(full)/aug-cc-pVDZ level

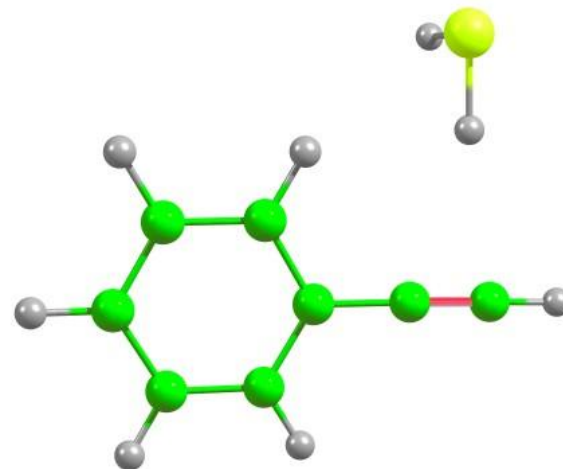


	Binding energies(kcals/mol)
A	-6.0
B	-2.7
C	-4.2

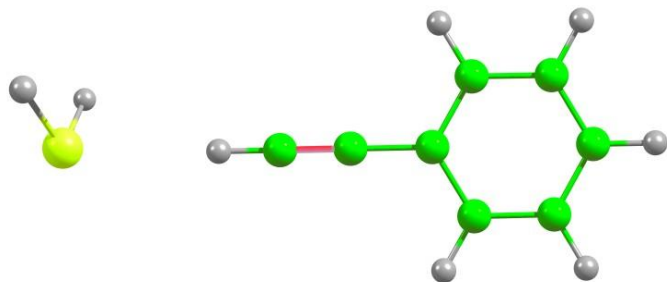
Rotational constants from *ab initio*



A=1279 MHz
B=1176 MHz
C=782 MHz



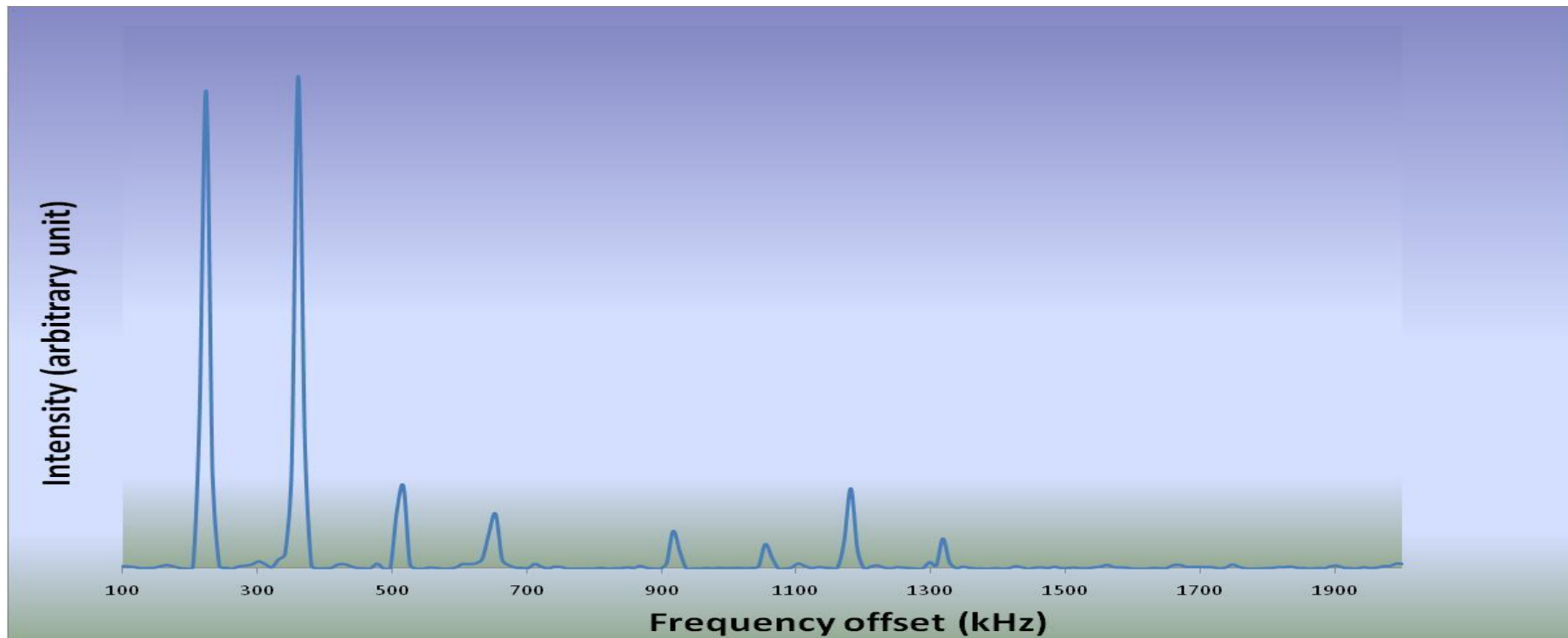
A=2209 MHz
B=652 MHz
C=506 MHz



A=5374 MHz
B=313 MHz
C=296 MHz

Rotational Spectroscopy can distinguish

$6_{34}-7_{25}$, $7_{35}-6_{24}$ transitions of phenylacetylene---H₂S collected using Helium as carrier gas



2	0	2	-	1	0	1	3394.286100	-.005730	.
2	1	2	-	1	1	1	3330.657000	-.002542	.
2	1	2	-	1	0	1	3403.074000	.005904	.
2	1	1	-	1	1	0	4134.435600	.003205	.
3	1	3	-	2	1	2	4826.099600	-.003005	.
3	0	3	-	2	0	2	4834.232500	.000405	.
3	1	3	-	2	0	2	4834.881200	.002329	.
4	1	4	-	3	0	3	6294.615500	-.036011	.
4	0	4	-	3	0	3	6294.615500	.001136	.
4	1	4	-	3	1	3	6294.000800	-.003934	.
4	0	4	-	3	1	3	6294.000800	.033213	.
4	2	3	-	3	1	2	7193.609100	.003360	.
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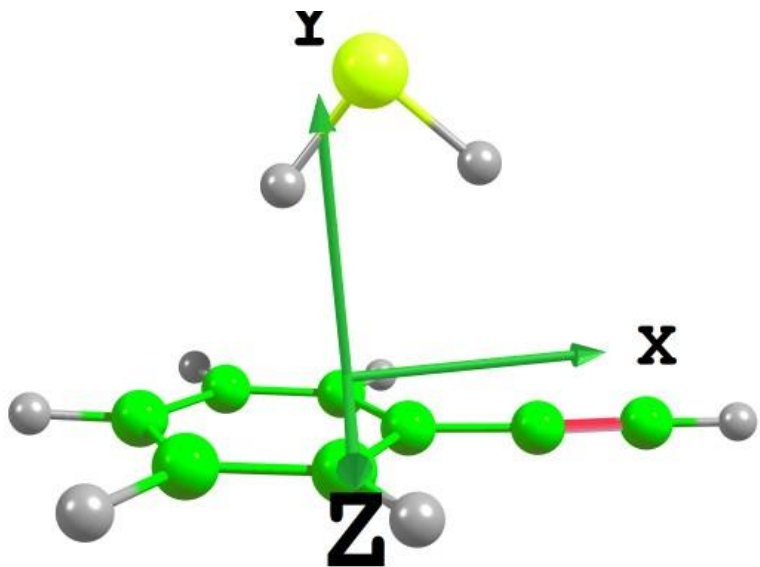
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11	2	9	-10	3	8	18285.948500	-.005647



Both a and b-dipole transitions

Two series!



Fitted parameters for the Phenylacetylene- \cdots H₂S and its isotopomers

	H ₂ S		H ₂ ³⁴ S	C ₈ H ₅ D		HSD	D ₂ S
	I(strong)	II(Weak)		I(Strong)	II(Weak)		
A(MHz)	1206.551(7)	1206.732(7)	1203.4(1)	1159.94(2)	1160.18(2)	1224.093(7)	1219.193(4)
B(MHz)	1134.152(6)	1134.056(6)	1097.6(3)	1129.11(1)	1128.93(2)	1111.107(7)	1108.204(4)
C(MHz)	732.192(6)	732.141(8)	715.652(7)	716.020(8)	712.6391(7)	728.6674(5)	725.914(3)
d1(kHz)	0.7(2)	2.0(2)	-	1.6(6)	-0.9(7)	1.72(9)	1.41(5)
d2 (kHz)	13.1(2)	14.4(3)	-	2.1(4)	-0.6(4)	2.8(2)	3.41(9)
D _J (kHz)	1.6(5)	4.2(4)	-	3(1)	-2(1)	3.7(2)	3.1(1)
D _{JK} (kHz)	23(1)	17(1)	-	-4(3)	0.6(4)	-5.4(6)	-1.9(2)
D _k (kHz)	-27.0(3)	-32(1)	-	11(1)	20(1)	12.3(7)	7.6(4)
SD(kHz)	6.8	10.6	7.5	3.2	3.2	5.9	

Experiment shows H₂S is lying close to 'a' principal axis!

Structure of phenylacetylene...H₂S

Experiments

A=1207 MHz

B=1134MHz

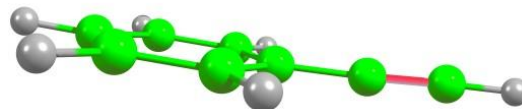
C=732 MHz

Theory

A=1279 MHz

B=1176 MHz

C=782 MHz



Summary on H₂S complex

- Phenylacetylene •••H₂S shows a π bonded perpendicular geometry
- Each transition is observed as a doublet for H₂S and a singlet for HDS
- Presence of other large amplitude motion in addition to the exchange of two hydrogens

Conclusions

- Microwave spectrum of phenylacetylene-H₂O/H₂S complexes have been recorded.
- Microwave spectrum of phenylacetylene-H₂O unambiguously confirms the nearly planar structure involving both O-H... π and C-H...O interactions.
- Both interaction seems to be equally strong
- In contrast, phenylacetylene ...H₂S shows a π bonded perpendicular geometry
- Legon-Millan rules need to be refined for molecules with multiple possibilities.

IR-UV double resonance studies (*G. N. Patwari and co-workers*)

✓ Phenylacetylene monomer: Fermi resonance between acetylenic C-H stretch and a combination of one quantum of C≡C stretch and two quanta of C≡C-H bend.¹

✓ Phenylacetylene-water acetylenic C-H stretch region

disappearance of the Fermi resonance in the acetylenic C-H stretch region (shift of -3 cm⁻¹. Rules out the structure A)

✓ Phenylacetylene-water O-H stretch region:

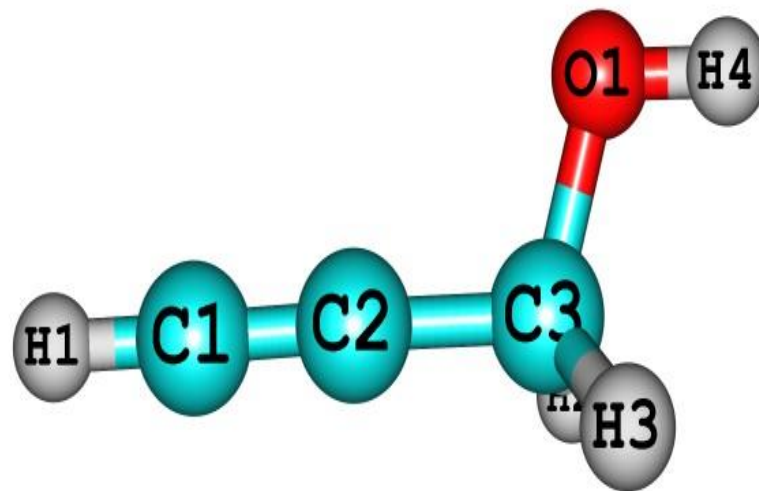
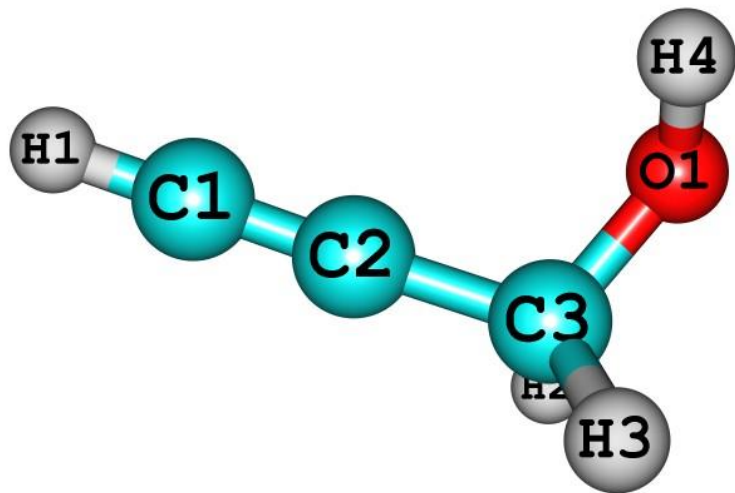
3724 cm⁻¹ (free O-H stretch)

3629cm⁻¹(H-bonded O-H stretch)

G. N. Patwari and co-workers, J. Phys. Chem. A, 112, 2008, 3360

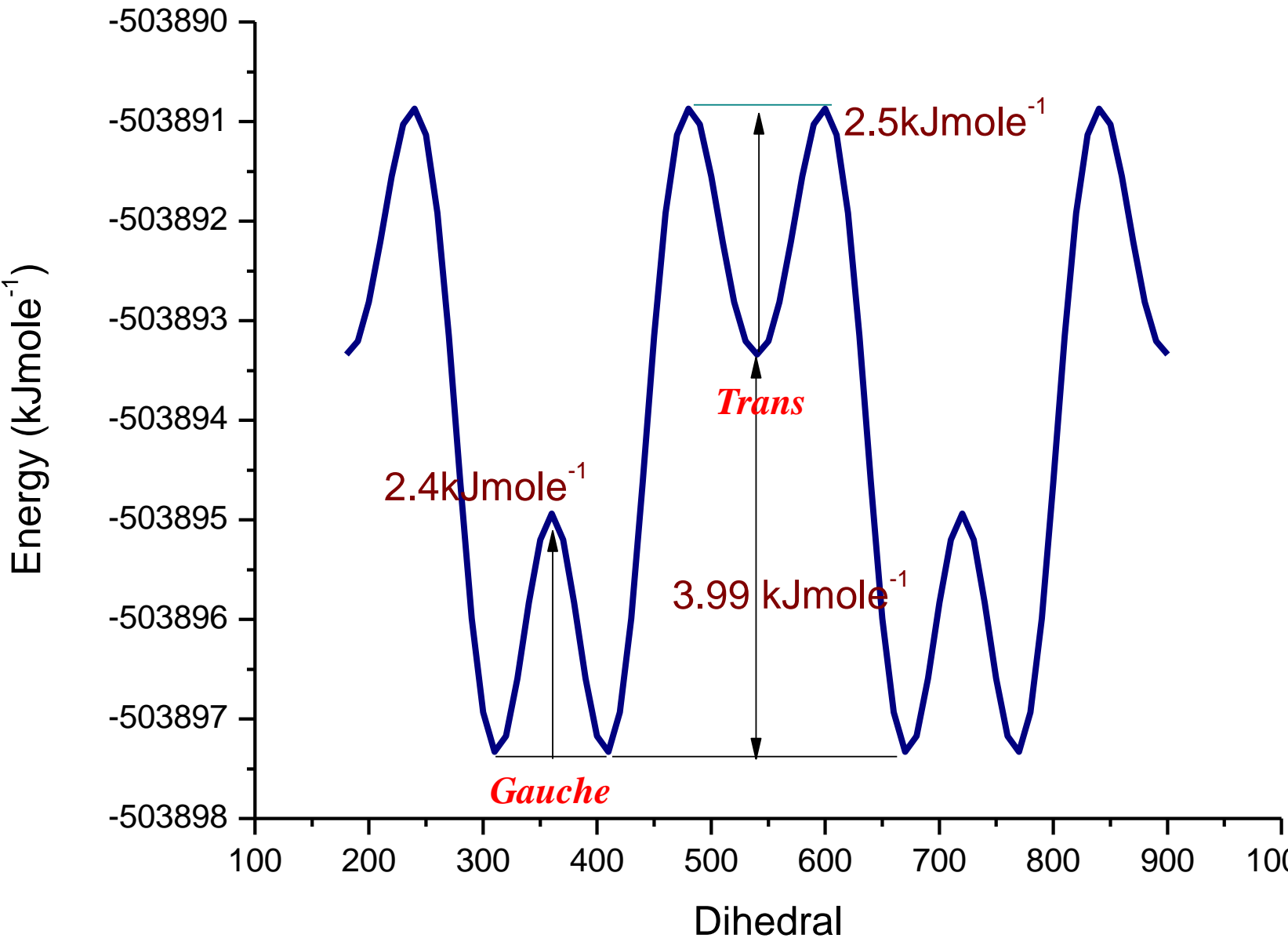
Propargyl alcohol

- Gauche form has been observed experimentally but there is no experimental evidence for trans form.^{1,2}*



1. Eizi Hirota, *Journal of Molecular Spectroscopy* 26, 335-350 (1968)
2. J.C. Pearson, B.J. Drouin, *Journal of Molecular Spectroscopy* 234 (2005)

— Energy



At b3lyp/6-311++G(d,p)



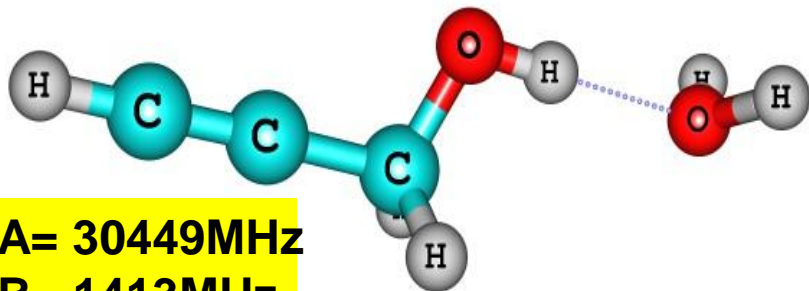
- **Can we stabilize the trans form by varying the experimental conditions ?**

- **What happens when complex of propargyl alcohol e.g. with water is formed ?**

- **Can we get the signature of presence of trans form by complex formation?**



Complex with water



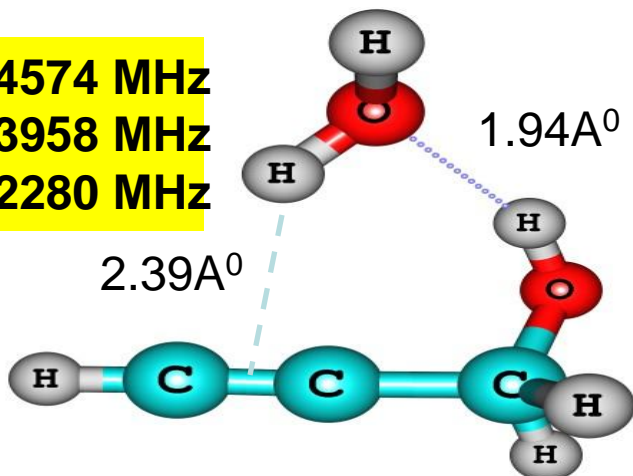
A= 30449MHz
B= 1413MHz
C= 1370MHz

Interaction energy= -5.4kcalmol^{-1}

Water as acceptor

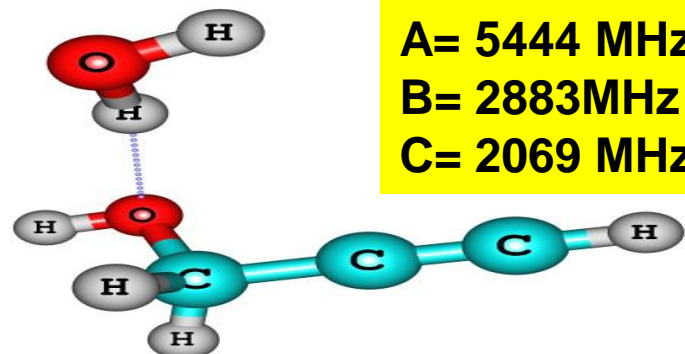
At mp2/6-311+G(d,p)

A= 4574 MHz
B= 3958 MHz
C= 2280 MHz



Water as acceptor

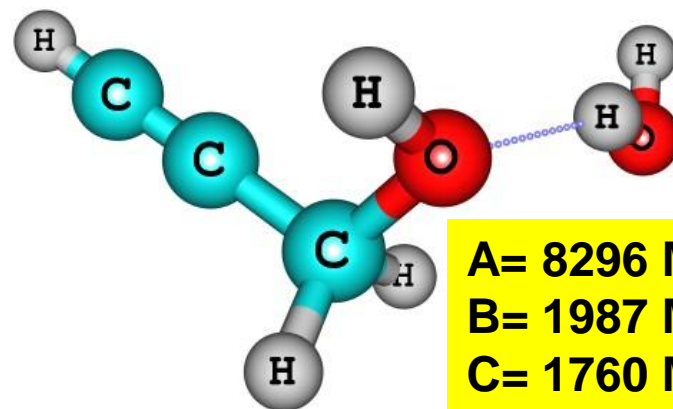
Interaction energy= -6.4kcalmol^{-1}



A= 5444 MHz
B= 2883MHz
C= 2069 MHz

Interaction energy= -5.0kcalmol^{-1}

Water as donor



A= 8296 MHz
B= 1987 MHz
C= 1760 MHz

Water as donor

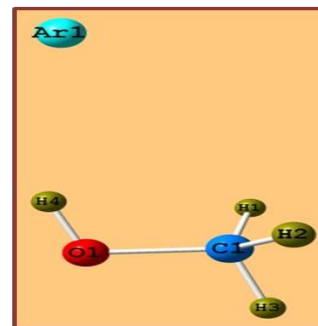
Interaction energy= -6.3kcalmol^{-1}



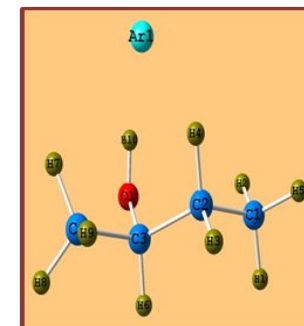
Ar----Propargyl alcohol complex

Ar-methanol complex⁴ :-

- hydrogen-Argon separation = 2.87 \AA^0
- oxygen-hydrogen-Argon angle = 151.6°
- COHAr dihedral angle ~ 0



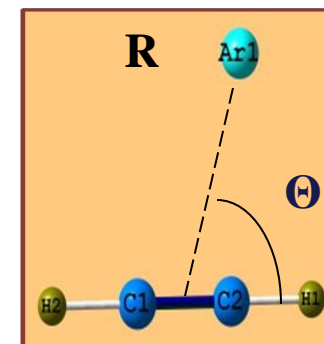
Ar- Methanol complex



Ar- Butan-2-ol complex

Ar-butan-2-ol complex⁵ :-

- hydrogen-Argon separation = 2.97 \AA^0
- oxygen-hydrogen-Argon angle = 134.4°
- COHAr dihedral angle = 49°

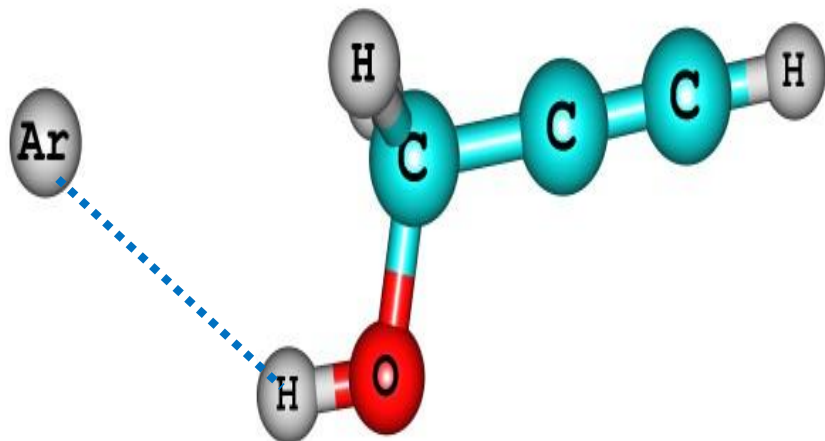


Ar- Acetylene complex

Ar- acetylene complex⁶:-

$$R = 4.04 \text{ \AA}^0$$
$$\Theta = 72^\circ$$

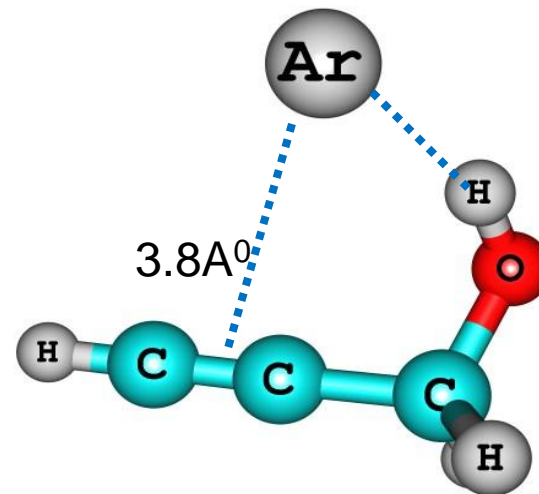
Ar - - propargyl alcohol complex:-



Interaction energy = $-1.82 \text{ kcalmole}^{-1}$

- hydrogen-Argon separation = 2.86 \AA
- oxygen-hydrogen-Argon angle = 138.8°
- COHAr dihedral angle $\sim 0^\circ$

A = 13563 MHz
B = 932 MHz
C = 877 MHz



Interaction energy = $-2.1 \text{ kcalmole}^{-1}$

- hydrogen-Argon separation = 2.81 \AA
- oxygen-hydrogen-Argon angle = 145.2°
- COHAr dihedral angle = 25.9°

A = 4312 MHz
B = 1684 MHz
C = 1281 MHz

At MP2/6-311+G(3df,2p)

Propargyl alcohol-Ar transitions?

- Several transitions have been observed and assignment is in progress.
- It appears that the trans form complex has been seen.
- Transitions do show some doubling possibly arising from C-O internal rotation.

Propargyl alcohol

- Vinyl alcohol (C₂H₄O) was found in 2001.
- Propanal (C₃H₆O) was found in 2006.
- Will propargyl alcohol (C₃H₄O) be found?
- This is again a multifunctional molecule that can form a variety of hydrogen bonded complexes.
- Will these complexes be found?

benzene

- Formation of benzene is still debated! A new pathway
 $C_2H + H_2CCHCH_2 \rightarrow C_6H_6 + H$ has been proposed (*PNAS January 11, 2011 vol. 108 no. 2 452-457*).
- Earlier proposals had propargyl radical as a key intermediate to benzene.