INTERMOLECULAR BONDING

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Current Science Editorial Board Meeting
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- IUPAC Task group of 14 international experts

₹

DST, CSIR, IFCPAR, IUPAC, IISc

Outline of the talk

- INTRODUCTION
- Bonding/hydrogen bonding and….
- Pulsed Nozzle Fourier Transform Microwave Spectrometer.
  - H_2O/H_2S complexes, hydrogen bond definition!
  - Ar-propargyl alcohol complex, OH---Ar, Ar---C interations?
  - Carbon bond?
  - Dynamics of a bond (Faraday Discussions in Banaglore January 2015)
- CONCLUSIONS

My research proposal at KSU 13 November 1988

- Spectroscopic investigations of Lithium Bonded Complex FLi---NH_3
- Have built the pulsed nozzle Fourier transform microwave spectrometer that I had proposed and investigated a large number of weakly bound complexes.
- Have published a few (computation) papers on lithium bonding.
- I had written this statement in my proposal “Hydrogen bonding is as unique in intermolecular interactions as hydrogen is in the periodic table”
- 27 years since, I can say: Oh yes that is true.

Bonding within a molecule

- Coulson “Sometimes, it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination.”

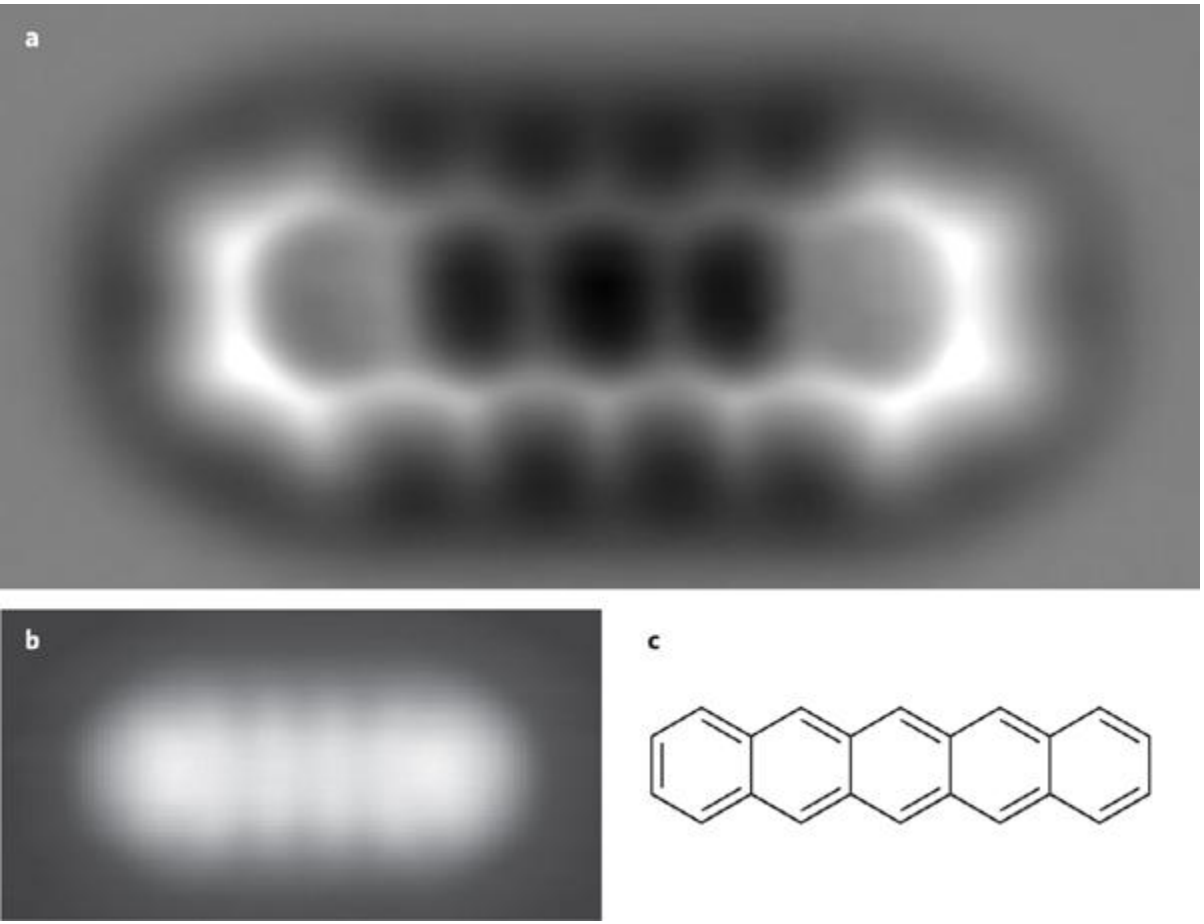
Van der Waals on molecules!

- "It will be perfectly clear that in all my studies I was quite convinced of the real existence of molecules, that I never regarded them as a fragment of imagination, nor even as mere centres of force effects." (studies from 1860s)
  - *From his Nobel address as quoted in A Ya Kipnis, B E Yavelov, and J S Rowlinson, Van der Waals and Molecular Science, Oxford University Press, Oxford, 1996.*

Bonding within a molecule

- Hoffman: “I think that any rigorous definition of a chemical bond is bound to be impoverishing, Push the concept to its limits. Be aware of the different experimental and theoretical measures out there. Accept that at the limits a bond will be a bond by some criteria, maybe not others. Respect chemical tradition, relax, and instead of wringing your hands about how terrible it is that this concept cannot be unambiguously defined, have fun with the fuzzy richness of the idea.”
- Arunan: “*Chemical bonds are made of electrons*

Pentacene imaged



a, AFM image of pentacene acquired with a CO-modified tip, note the identification of not only atomic positions but C–C and even C–H bonds.[1]
b, STM image of pentacene on Cu(111).
c, Molecular structure of pentacene. Figures reproduced with permission: **a**,**b**, © 2009 AAAS.

Science 28 August 2009: Vol. 325 no. 5944 pp. 1110-1114 DOI: 10.1126/science.1176210
The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

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Chemical and Engineering News turned 90 in 2013 and they picked 9

Thanks to Prof. R. N. Zare
And Prof. B. Shakashiri

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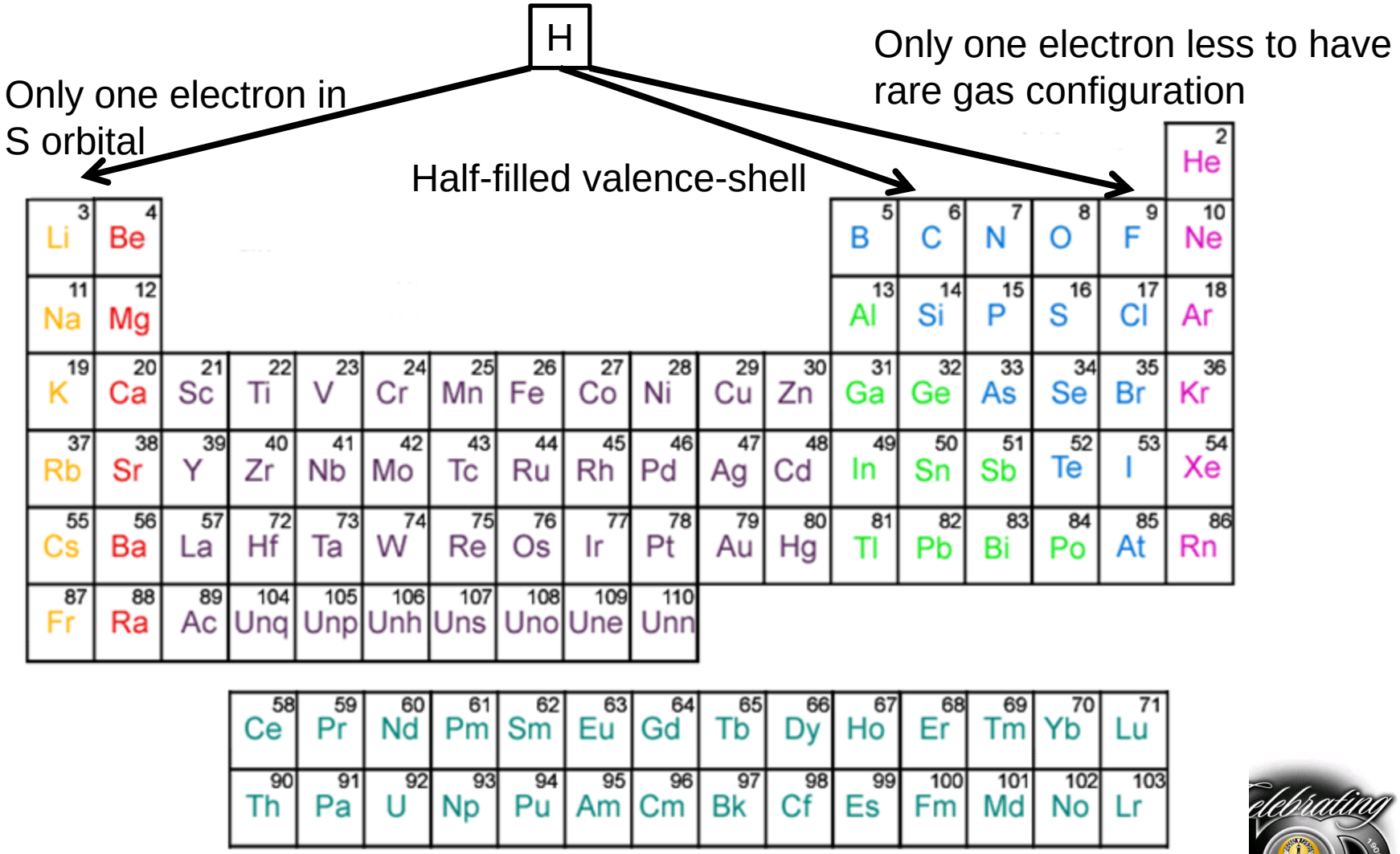
Hydrogen bond in Scifinder: The last few years!

- Every hour there is at least one paper containing the words ‘hydrogen bond’ published somewhere **and** entered in SciFinder (2005-2011) (I verified).DNA, Water, Life! Confirmed it on 26 November 2015
- Number 1 entry among the popular words in the title of papers (Noted from a talk by Prof. D. Kim, Seoul National University 2nd Asian Spectroscopy Conference).
- Could there be anything left about hydrogen bond that is not known?

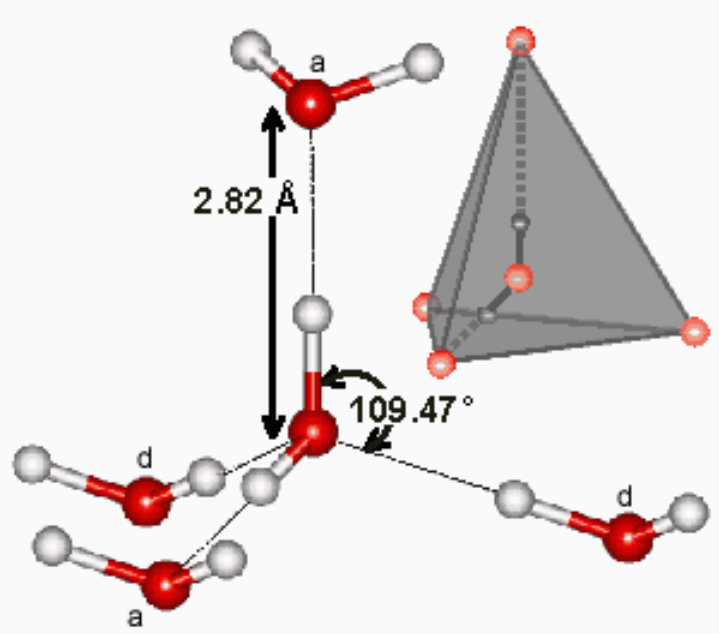
Only hydrogen bond?



Intermolecular interactions or intermolecular bonds?

- Van der Waals equation is the origin.
- Van der Waals forces, Van der Waals radius (when the atoms barely touch another one ‘without’ interacting or bonding and Van der Waals volumes were all commonly used.
- Van der Waals interactions was the term used to refer to all intermolecular interactions, until….

Water and hydrogen sulphide in condensed phase



H_2O at 0 °C 4 neighbours

http://www.lsbu.ac.uk/water/hbond.html

Hydrogen bonding

H_2S at – 60 °C 12 neighbours

Packing of spheres from Wikipedia

Van der Waals interaction

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What is a hydrogen bond?

- Precise definition of a hydrogen bond was still elusive in late 90s when I joined IPC[1] (IUPAC accepted our recommendation in 2011, more later)!
- Several criteria are listed usually for X-H•••Y[1]

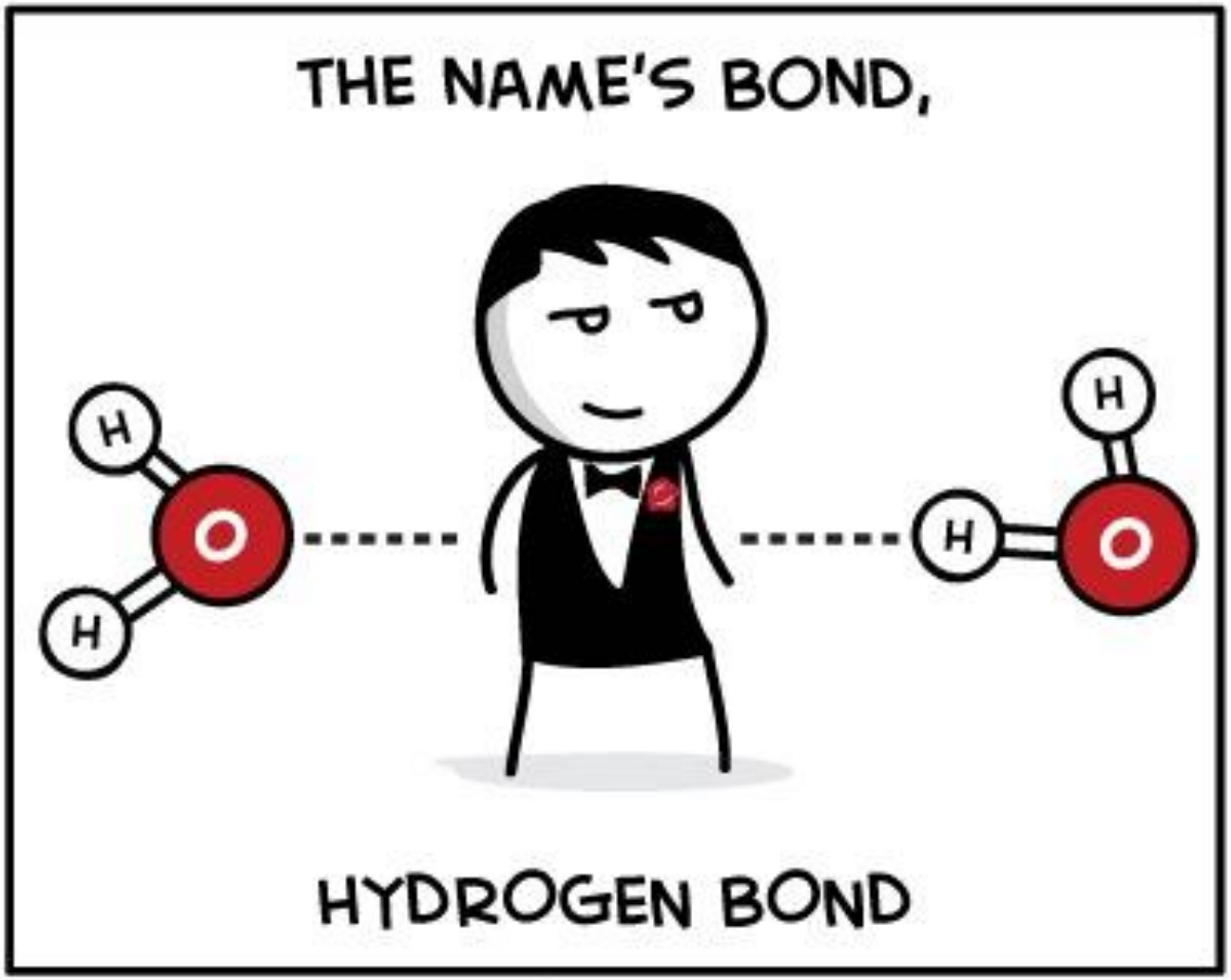
Structural:

- Earlier X---Y distance or recently H---B bond length is less than the sum of their van der Waals radii.
- X-H•••Y is linear

(Microwave Spectroscopy can help in verifying both and the results challenge both these conventional wisdom as a criteria for H bonding)

[1] S. Scheiner, Hydrogen Bonding, Oxford University Press 1997
G. Jeffrey, Introduction to hydrogen bonding, 1997
G. R. Desiraju and T. Steiner, Weak Hydrogen Bond, 1999

What is a hydrogen bond?



Dick Zare
Sent me
This cartoon
From the web

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What is a hydrogen bond?

- "Water … shows tendencies both to add and give up hydrogen, which are nearly balanced. Then … a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together… Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak bond"

  Latimer and Rodebush

  JACS **42**, 1419 (1920)

Lone pairs as hydrogen bond acceptor

M. L. Huggins

- "The bydrogen bond or hydrogen bridge concept has proved to be one of the most useful structural concepts in modern sciences --- I therefore take pride in the fact that I was the first to introduce the hydrogen bond concept"
- "It seemed reasonable to me that a non bonding electron pair – a "lone pair" as I called it – should have a considerable attraction for a positively charged proton, even if it is already bonded to another atom."

M.L.Huggins in **Angew. Chem. Int. Ed. Eng. 10, 147 (1971)**

(M. L. Huggins had an M.S. Organic Chemistry Thesis submitted to Berkeley in 1919. Not available now. Keep all reports safely!)

What is a hydrogen bond?

- Hydrogen bonding started with N, F, O lone pairs as acceptors, but the π bonded pairs as acceptors was recognized long ago!
- S.K.K.Jatkar, IPC Faculty member in 1943 gave a lecture in Department of Electrical Sciences, with this title.
- He has also published a paper 'Hydrogen bonding in benzene' in the Quarterly Journal of Indian Inst. Sci. (1943) with Nagamani Shama Rao.
- Do we really need two electrons to form a hydrogen bond?

CH as donors π electrons also as acceptors

Pimentel and McClellan (1960)

"A hydrogen bond is said to exist when:

1) there is evidence of a bond

2) there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom"

There is no restriction on hydrogen bond donors or acceptors. Is diborane hydrogen Bonded? Both A and B are less electronegative than H and in all other cases of A-H, A is more electronegative than H

IUPAC Definition 1997

- A form of *association* between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e. N, O or F. Hydrogen bonds may be intermolecular or intramolecular. With a few exceptions, usually involving fluorine, the associated energies are less than 20–25 kJ mol–1 (5–6 kcal mol–1).

Interestingly, there is no lower limit specified!

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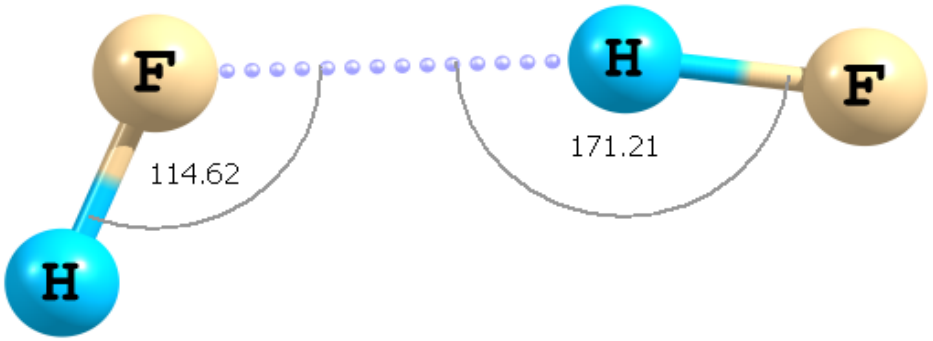
Penguin Dictionary, London

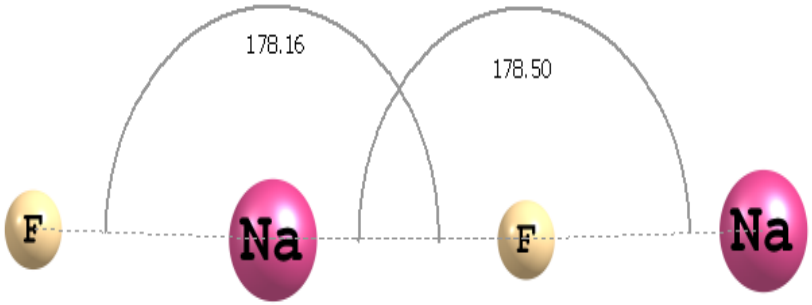
- A weak **electrostatic chemical bond** which forms between covalently bonded hydrogen atoms and a strongly electronegative atom with a lone pair of electrons. The hydrogen bond is of enormous importance in biochemical processes, especially the N-H•••N bond which enables complex proteins to be built up. Life would be impossible without this type of bond.

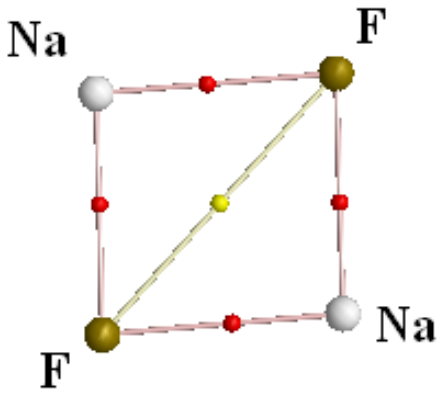
Nature of the forces

- Pauling: It has to be electrostatic as it can not be chemical (covalent).
- Israelachvilli: No more than a particularly strong type of directional dipole-dipole interaction.
- IR shift and intensity enhancement can not be explained by ‘simple electrostatics’.
- Electrostatic, inductive, and dispersive forces, charge-transfer/covalency, and exchange repulsion all play varying roles depending on the donor and acceptor (Dispersion dominated hydrogen bonds: Wategaonkar).
- **There is no single physical force that can be attributed to hydrogen bonding!**

HF dimer vs NaF dimer







Dipole-dipole interactions predict linear or anti-parallel,
Both observed for alkali halide dimer, Neither for HF dimer

R. Parajuli and E. Arunan, *Chem. Phys. Lett.* **568**, 63 (2013)

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Energy criteria

1. Pauling: between 8 – 42 kJ mol^{-1} (1939) $(FHF)^-$ does not fall in this limit
2. IUPAC: upper limit of 20-25 kJ mol^{-1} and no lower limit (1995).
3. Emsley, Jeffrey and Saenger and Desiraju and Steiner:

   strong 63-167 kJ mol^{-1},

   medium 17-63 kJ mol^{-1}

   weak < 17 kJ mol^{-1}.

Binding energy is not a useful criterion and it is arbitrary. Is there a better criterion?

Spectroscopic criteria

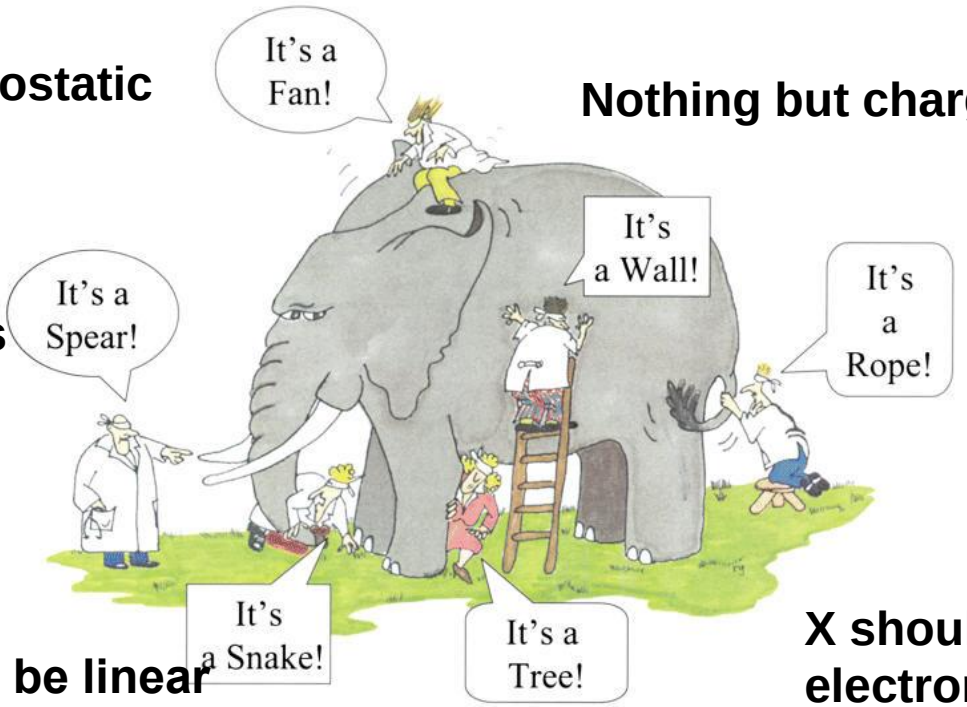
- Red-shift of A-H stretching frequency and an increase in its intensity were observed in most cases (some blue-shifting hydrogen bonds have been seen, Hobza and no-shift H bond speculated: Jemmis).
- The H in A-H is strongly de-shielded resulting in downfield shift of the NMR peak (remains true largely).
- Microwave spectroscopy can give us structure but it can not directly tell us whether there is a ‘hydrogen bond’.

Elephant and six blind men (Hydrogen bonding and six scientists)

Simple electrostatic

Nothing but charge-transfer, covalency

X---Y distance less than van der Waals radii sum



Should have red-shift in X-H

X-H•••Y should be linear

X should be highly electronegative F, O, N

X-H•••Y Hydrogen bond

Can someone talk to all the six blind men and put the pieces together and find out what the elephant really is?

http://www.proprofs.com/quiz-school/story.php?title=blind-men--elephant

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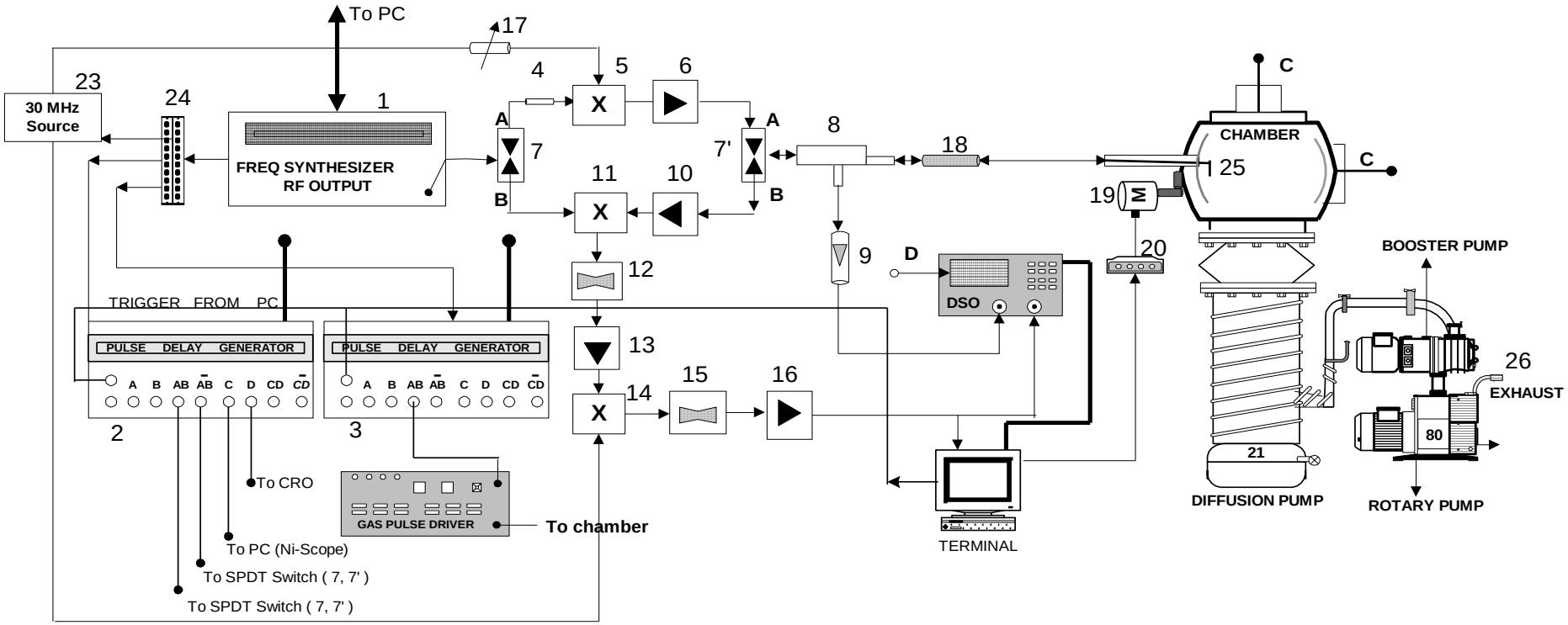
What is in a name?

- "What's in a name? That which we call a rose by any other name would smell as sweet."
  - *Romeo and Juliet (II, ii, 1-2)*
- You can know the name of a bird in all the languages of the world, but when you're finished, you'll know absolutely nothing whatever about the bird... So let's look at the bird and see what it's doing — that's what counts. **I learned very early the difference between knowing the name of something and knowing something.**
  - Richard Feynman
- Naming things is important, an extreme: ‘How to tell the carrot from the cat – which to grate and which to pet?’.
  - Carol K. Yoon, NY Times column as quoted by P. Balaram in Current Science Editorial 97, 465 (2009)
- Taxonomy: It is important to classify/categorize

Pulsed Nozzle Fourier Transform Microwave Spectrometer



Arunan, Dev and Mandal, *Appl. Spectrosc. Rev*. **39**, 131 (2004)

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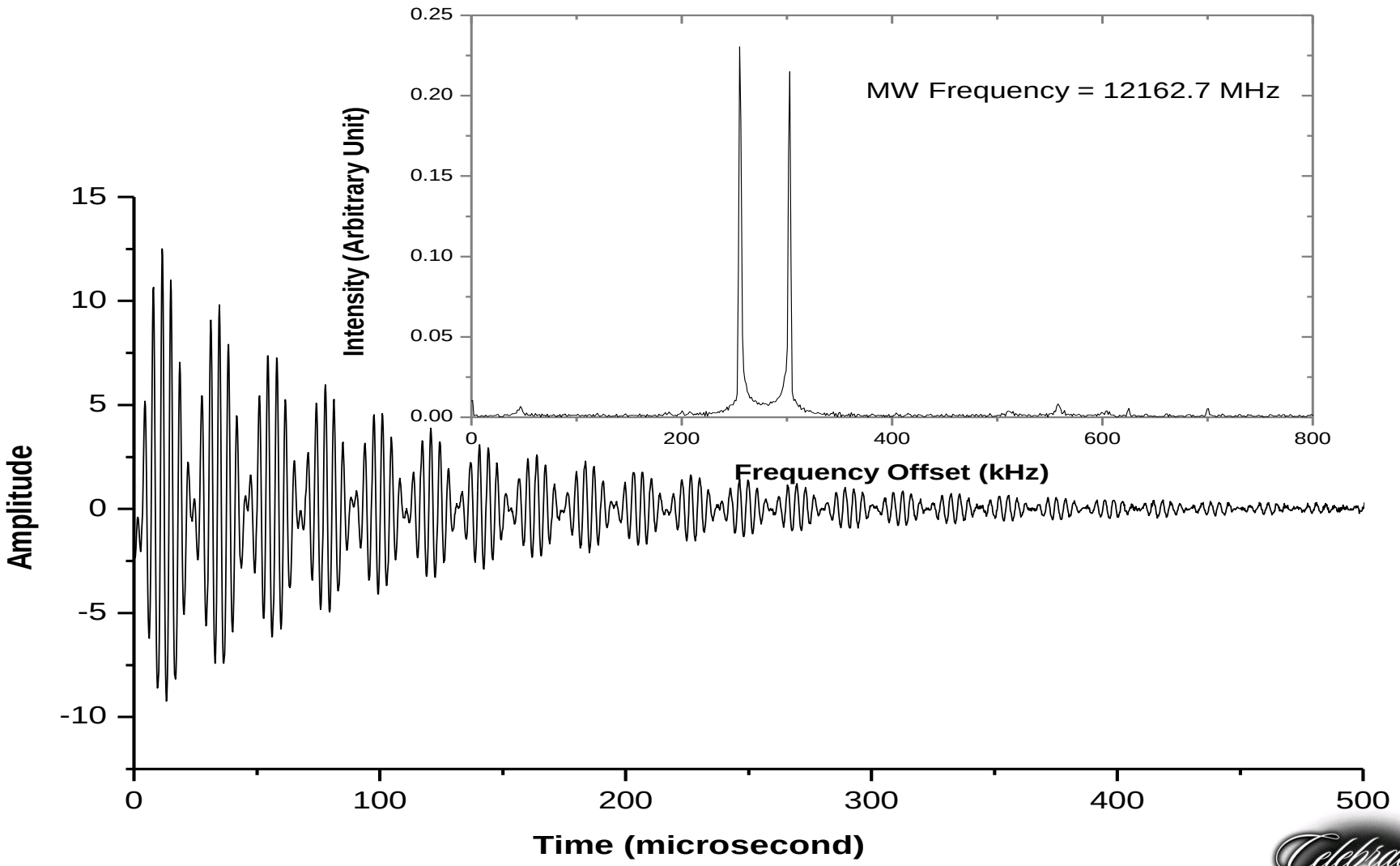
Time domain and corresponding frequency domain signal



J = 0 → 1 transition of OCS at 12162.979 MHz.

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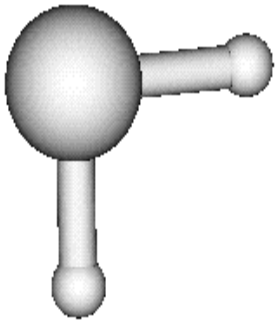
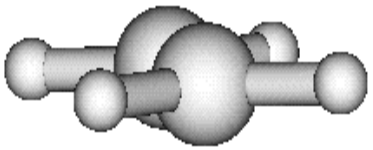
C_2H_4-H_2S

- C_2H_4-HX (X = F, Cl, and OH) all have π-hydrogen bonded structures.
- Is H_2S strong enough as a π -hydrogen bond donor?
- Compare H_2O/H_2S complexes.
- Where to look for C_2H_4-H_2S transitions?
- Microwave spectrum can give the structure accurately!

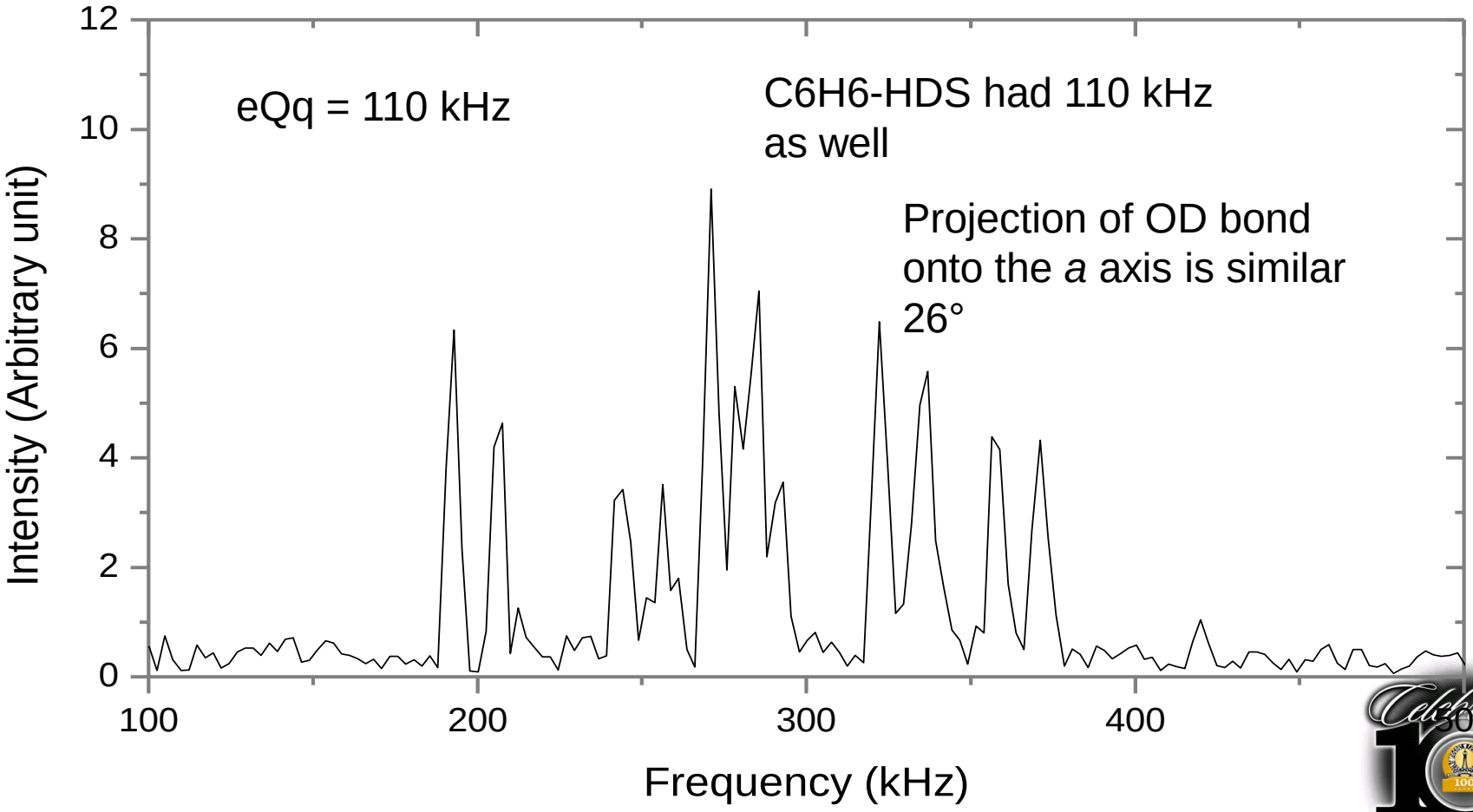
Theoretical calculations (MP2 level)



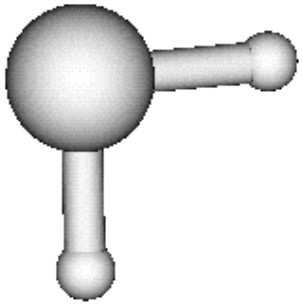


constant	6-31 G*	6-311 ++G**
A	22884	22945
B	1967	2000
C	1858	1917

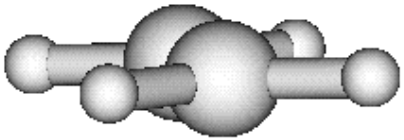
J=0→1 spectrum of C_2H_4-HDS showing D quadrupole coupling and C_2H_4 tunneling splitting



C_2H_4-H_2S dimer



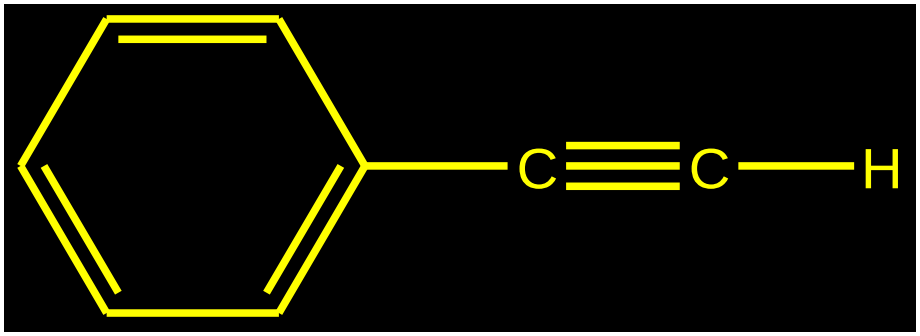
Structurally very similar to C_2H_4-H_2O
Binding energy is less
Rotational spectrum reveals evidence for large amplitude motions.



Referee: Please do not call it a Hydrogen bond!
Bridging hydrogen bonding van der Waals (dispersion?) interactions

M. Goswami, P. K. Mandal, D. J. Ramdass, and E. Arunan, *Chem. Phys. Lett.* **393**, 22 , (2004)

Phenylacetylene: Where will H_2O bind?



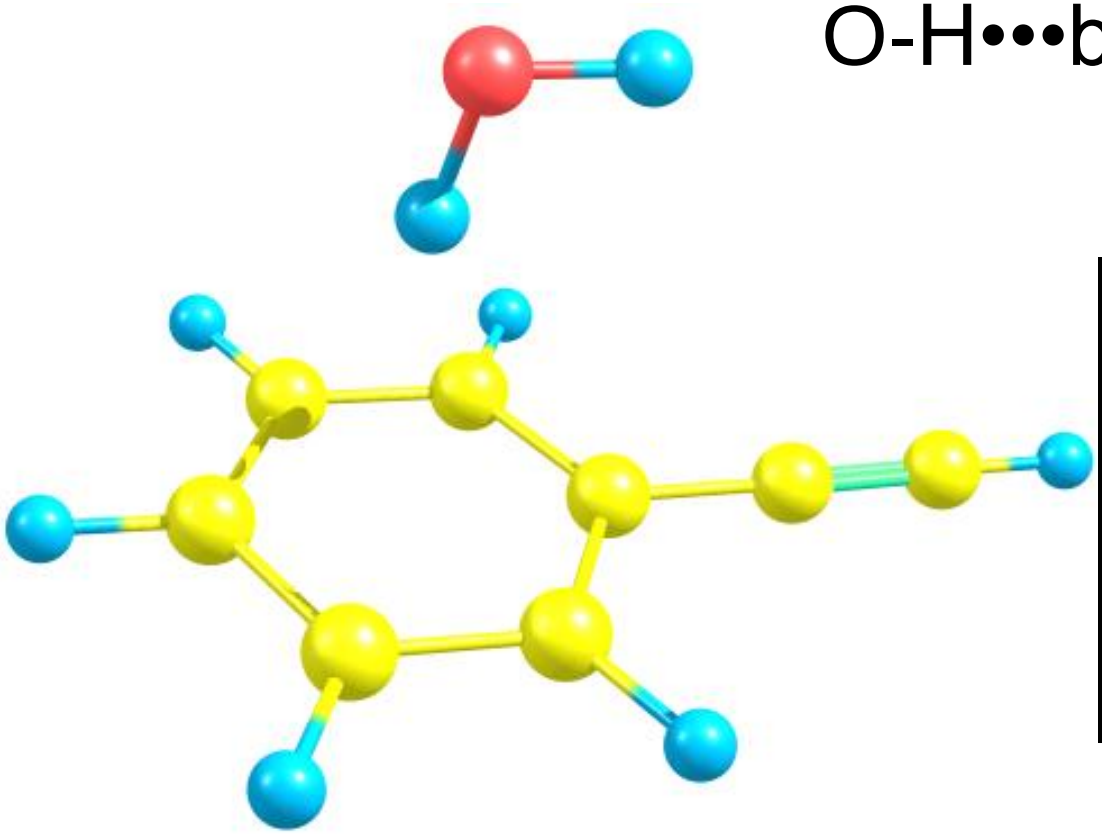
Phenyl ring π-cloud: could be hydrogen-bond acceptor

Acetylenic π-cloud: could be hydrogen-bond acceptor

Acetylenic C-H: could be hydrogen-bond donor

Naresh Patwari's IR-UV double resonance experiments suggested that the structure is none of the above!

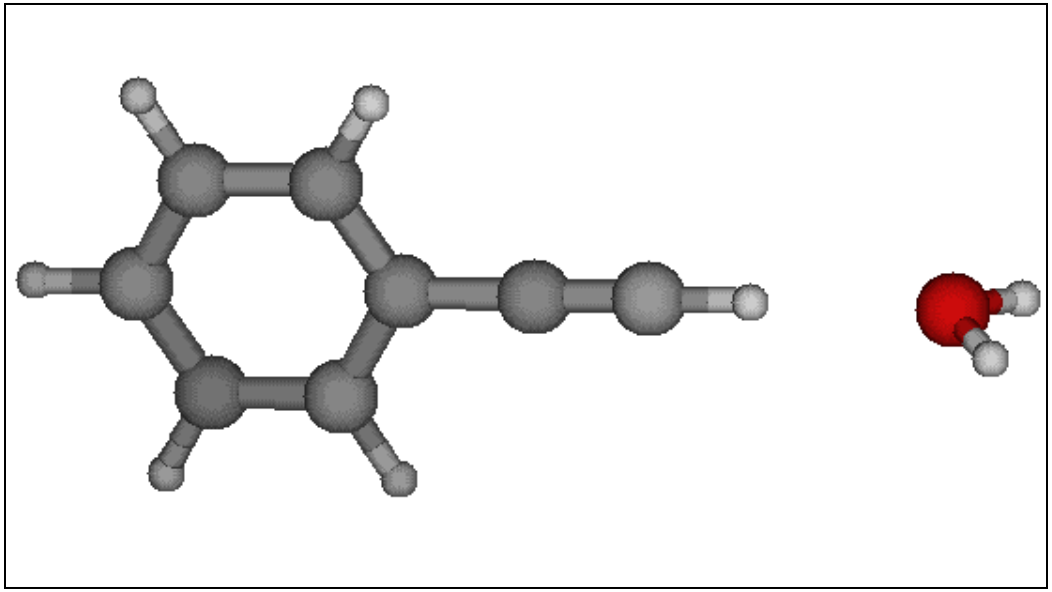
Phenylacetylene-water



O-H•••benzene π interaction

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

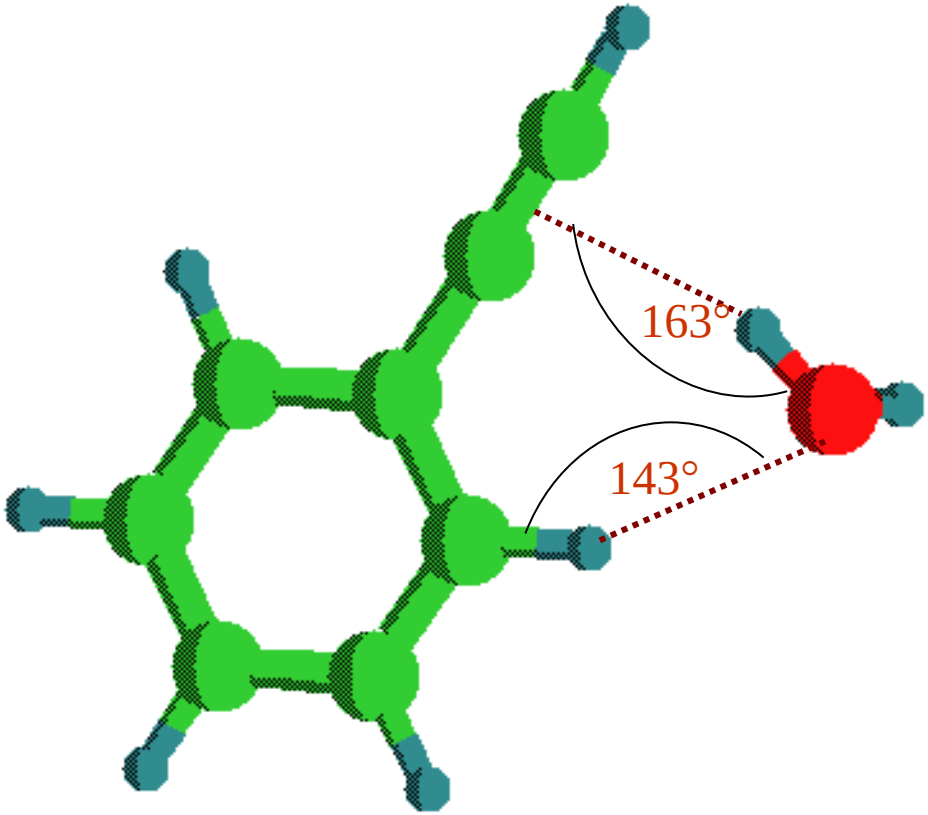
Phenylacetylene-water



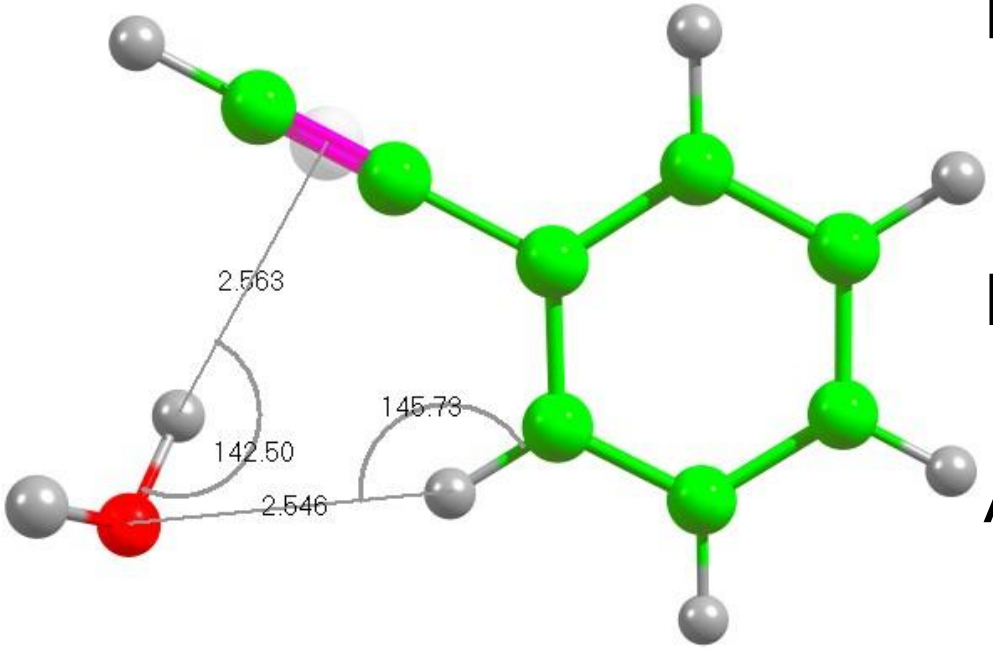
C-H•••O interaction

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

Phenylacetylene-water



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



But, what interactions are present in this structure?

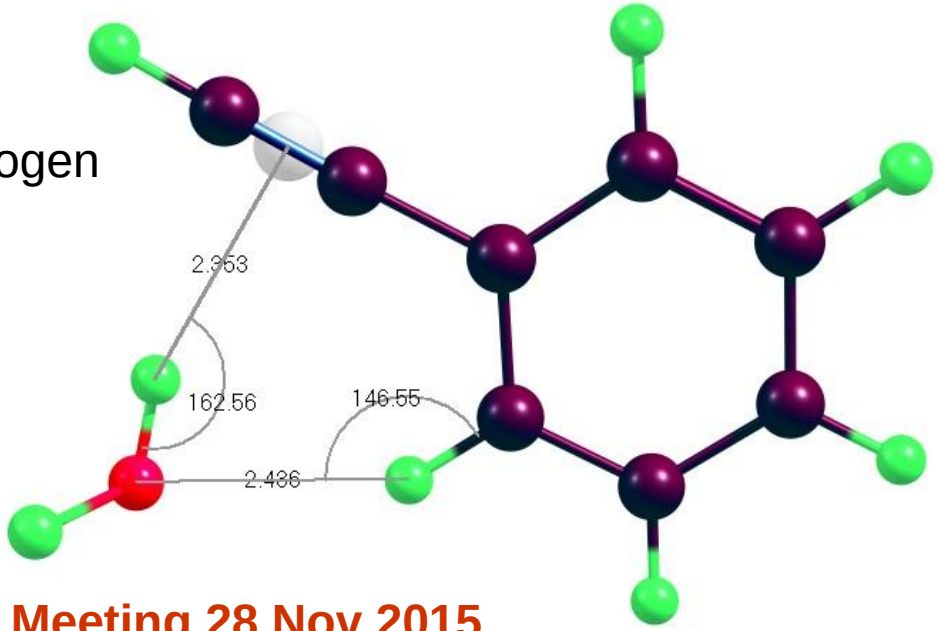
Microwave spectrum does not tell us!

Atoms in Molecules Theory does.

Experiment

M. Goswami and E. Arunan
PCCP **13**, 14153 (2011)
special issue on Weak Hydrogen Bonds, Strong Effect

Theory



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Quantum Theory of Atoms in Molecules

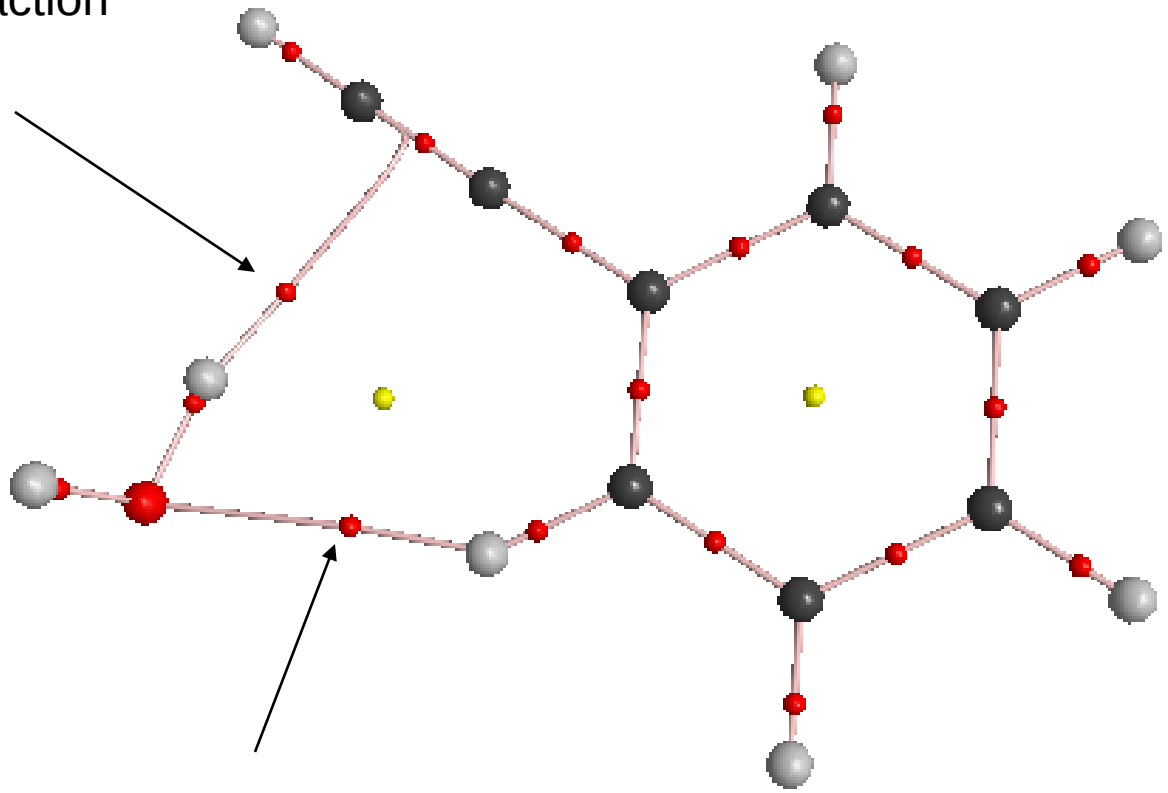
- Explores the total electron density in a molecule which leads to drawing boundaries of atoms within a molecule. The critical points in the electron density help in identifying which of the atoms are directly bonded.
- X-ray diffraction provides experimental picture (deformation density is used)
- Bader introduced the name, though electron density topology have been used by many earlier, Politzer, Gadre, Klein…
- Has been extensively used, abused and criticized

Atoms in Molecules Theory

- A conversation between three theoretical chemists (Roald Hoffman, Sason Shaik and Henry Rzepa, *Angew Chemie. Int Ed. Engl 2013) about bonding in* C_2
- **Roald:…and got widely different results. I like to show these to people who claim there is a good way to define a bond. Of course they'll tell me that I should do a QTAIM analysis.**
- **Sason: Better define that.**
- **Henry: Quantum Theory of Atoms and Molecules, QTAIM, a method based on the topology of the electron density ρ,[14] has its uses.**
- **Roald: I was saying that tongue-in-cheek, Henry. I am no great fan of QTAIM – in the hundreds of QTAIM papers that crowd the literature, I have yet to see one that makes a chemical prediction, or suggests an experiment.**
  - **(The same issue has an essay 'Chemistry in India' written by four of us)**

Atoms in Molecules Analysis

OH•••π interaction



C-H•••O interaction

Two ring critical points

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

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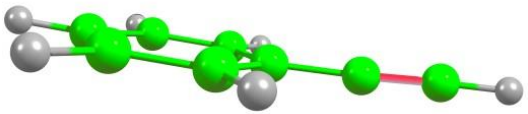
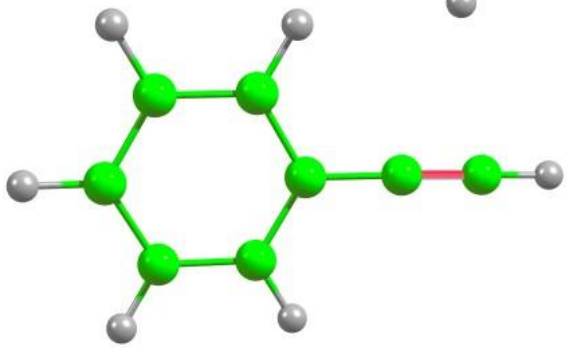
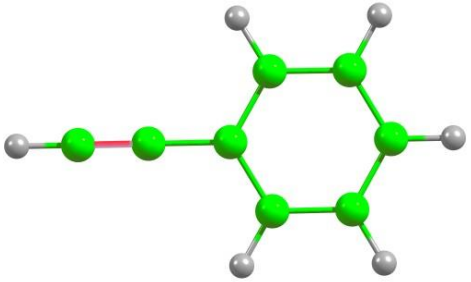
Phenylacetylene•••H_2S



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

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





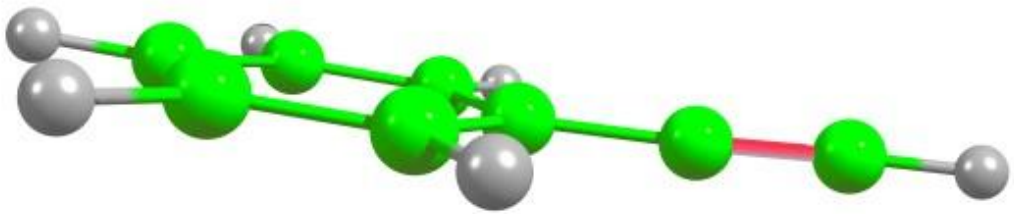
A=5374 MHz
B=313 MHz
C=296 MHz

Rotational Spectroscopy can distinguish

Structure of Phenylacetylene•••H_2S

Experiments

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



Theory

A=1207 MHz
B=1134MHz
C=732 MHZ

M. Goswami and E. Arunan J. Mol. Spectrosc. 268, 147-156 (2011)

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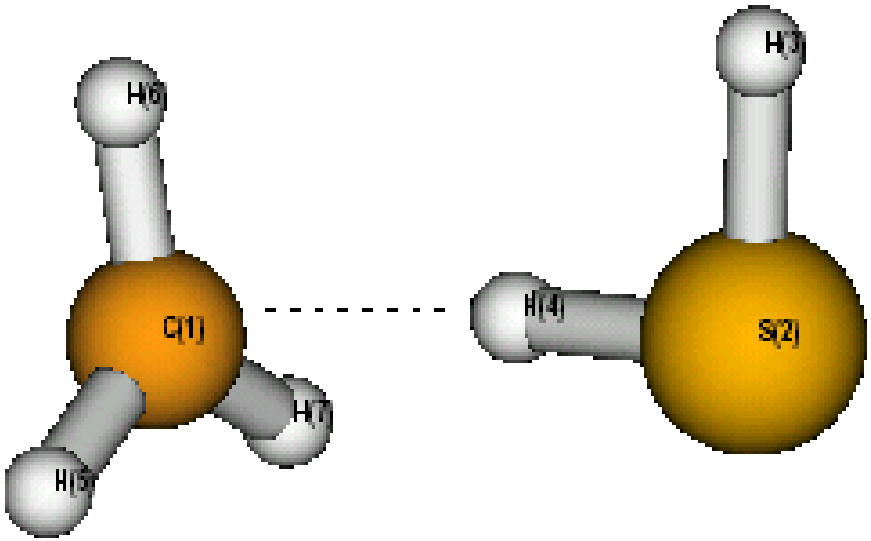
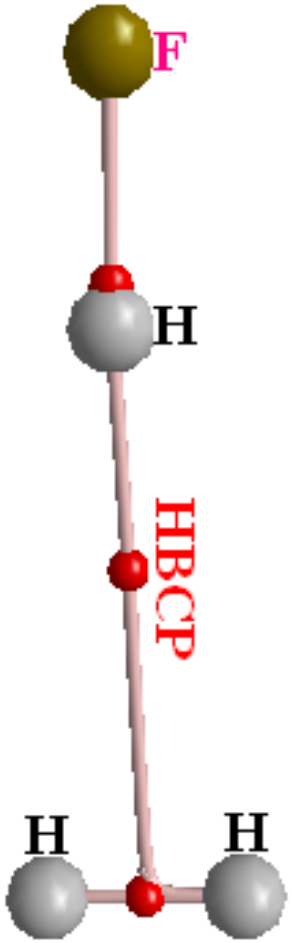
Methyl radical



Methyl radical with an unpaired electron can act as a hydrogen bond acceptor with H_2S

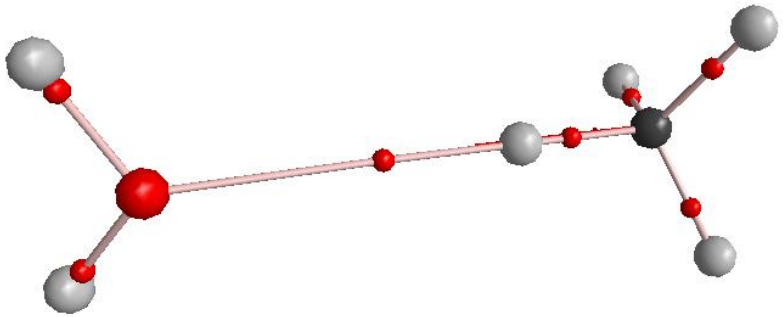
B. Raghavendra and E. Arunan, *J. Phys. Chem. A* **2007**, *111*, 9697

H_2 molecule as H bond acceptor



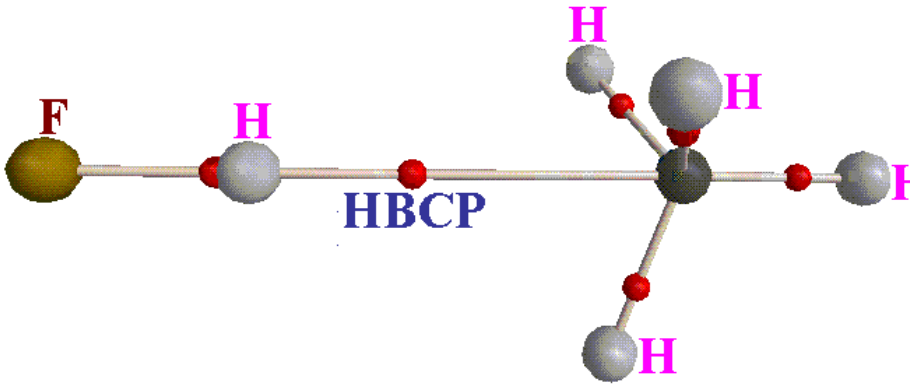
Experiment and theory confirm that the Electron deficient H from HF is interacting With the sigma bond electrons of hydrogen Molecule.

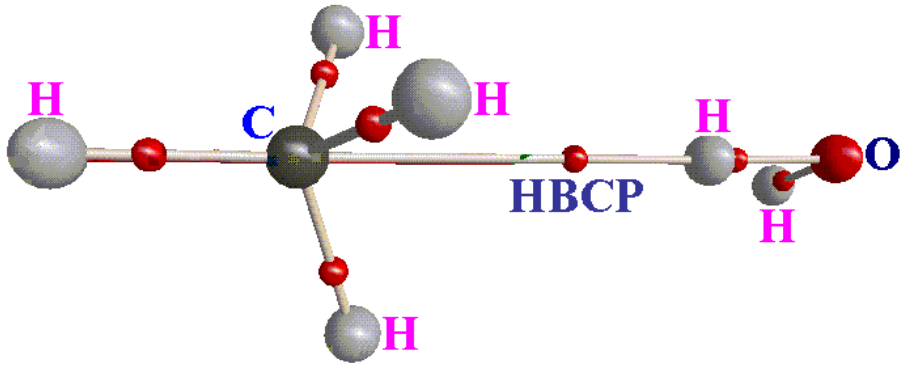
CH_4-H_2O complex, C-H---O H bond?



- This structure is a minimum in the potential surface.
- It has a (3,-1) bond critical point.
- Most of the theoretical work deal with this C-H•••O H bond.
- However, this is not the global minimum and not found in the experiment

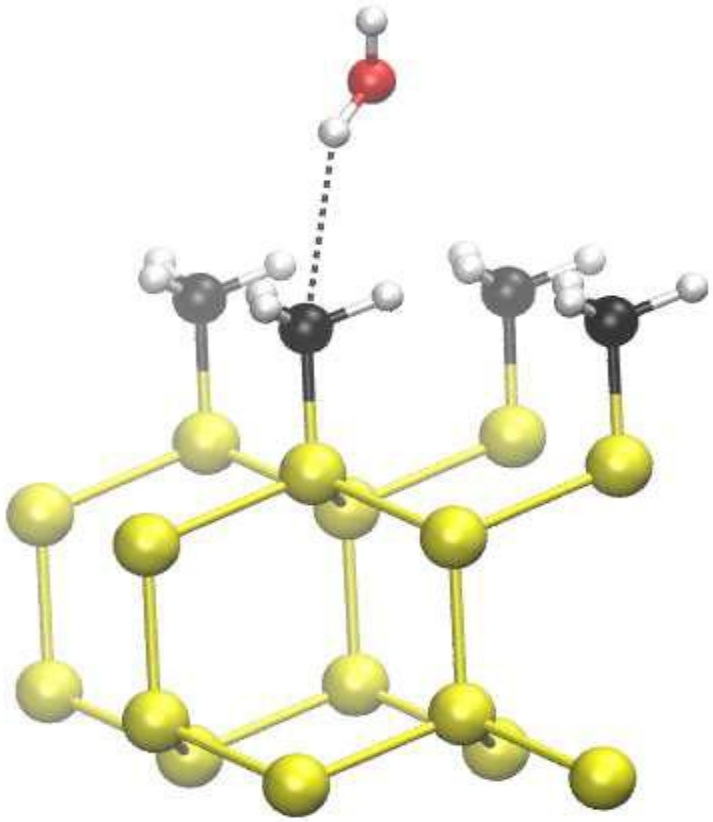
CH_4-HX global minimum geometry
It is CH_5^+





Raghavendra and Arunan, Chem. Phys. Lett **467**, 37 (2008)
(submitted earlier to Phys.Chem.Chem.Phys. One referee was very pleased and another one suggested that it should be rejected ""As this complex has already proven to be bound by dispersive forces"
Oka, Nesbitt found CH5+ spectrum, which is CH_3^+---H_2 complex!
CPL editor sent a personal note thanking us for submitting it to CPL (has improved the 5 yr impact factor of CPL ☺)

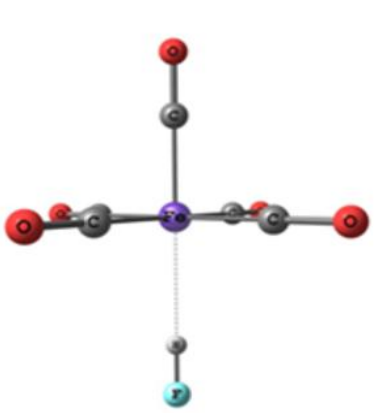
Water on Si-CH_3 surface



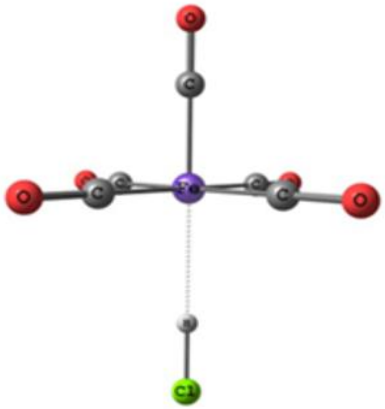
A. Ambrosetti*, F. Costanzo, and P. L. Silvestrelli

J. Phys. Chem. C, 2011, 115 (24), pp 12121–12127
DOI: 10.1021/jp202704c
Publication Date (Web): May 13, 2011

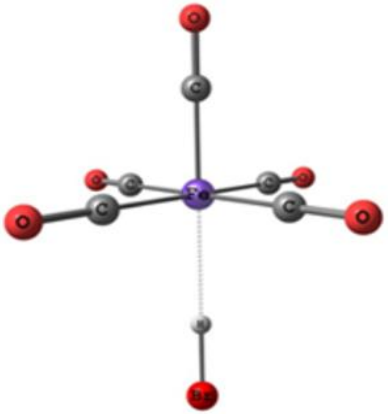
Iron pentacarbonyl accepts H bond!



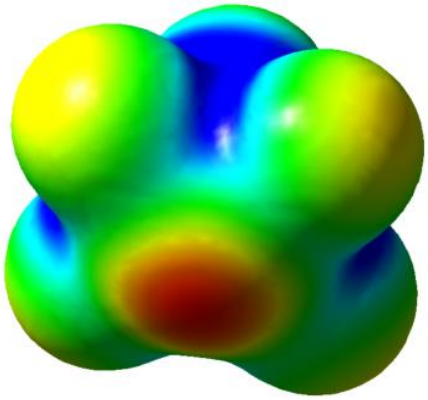
$Fe(CO)_5\cdots HF$



$Fe(CO)_5\cdots HCl$



$Fe(CO)_5\cdots HBr$



These complexes show red-shift of 300 cm-1 and have binding energies of the order of 3-5 kcal/mole. They can stabilize the square pyramidal geometry!

P. Aiswaryalakshmi, D. Mani and E. Arunan
Inorg. Chem. 52, *9153* **2013**.

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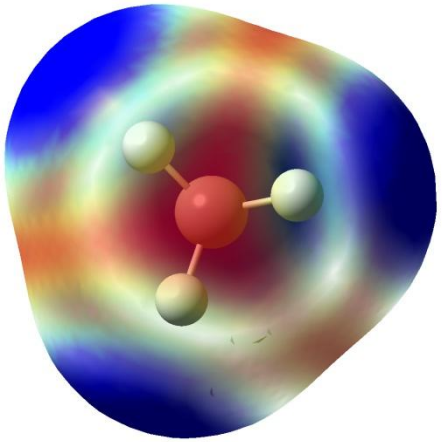
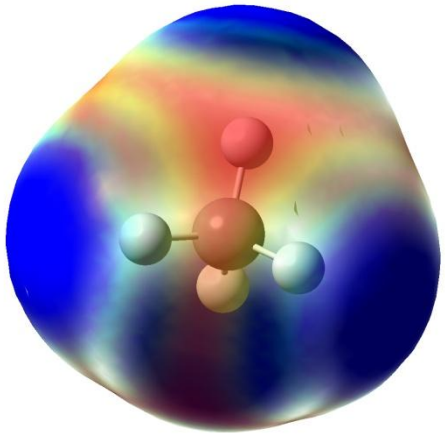
Where are the electrons in CH_4

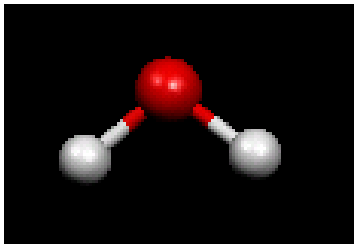


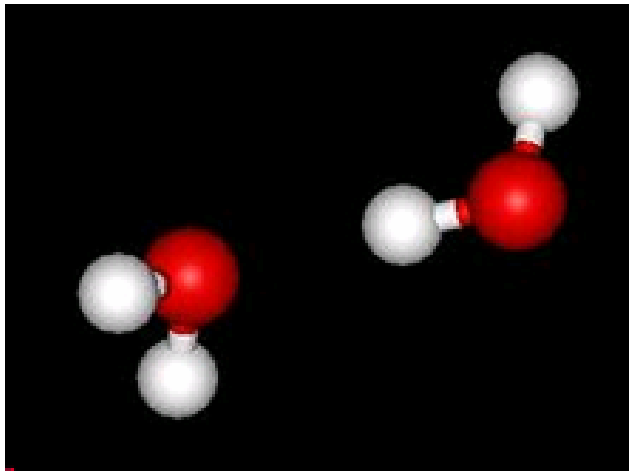
Water forms H bonds with its lone pair of electrons
Ethylene forms H bonds with its π pair of electrons
CH_3 radical can form H bonds with its unpaired electron
H_2 can form H bonds with its σ electrons
CH_4 forms H bonds with the face center rich in electons
Kr (with an electronegativity of 3) forms with all its electrons



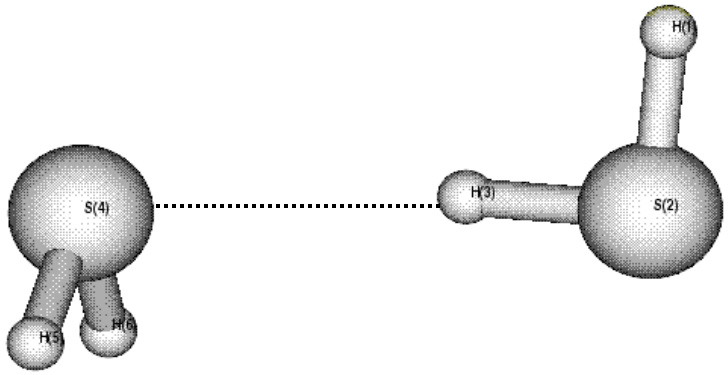
Hydrogen bond is the bond between an electron deficient Hydrogen in XH and some electron rich region in another Molecule!

Gas phase: $(H_2O)_2$ and $(H_2S)_2$



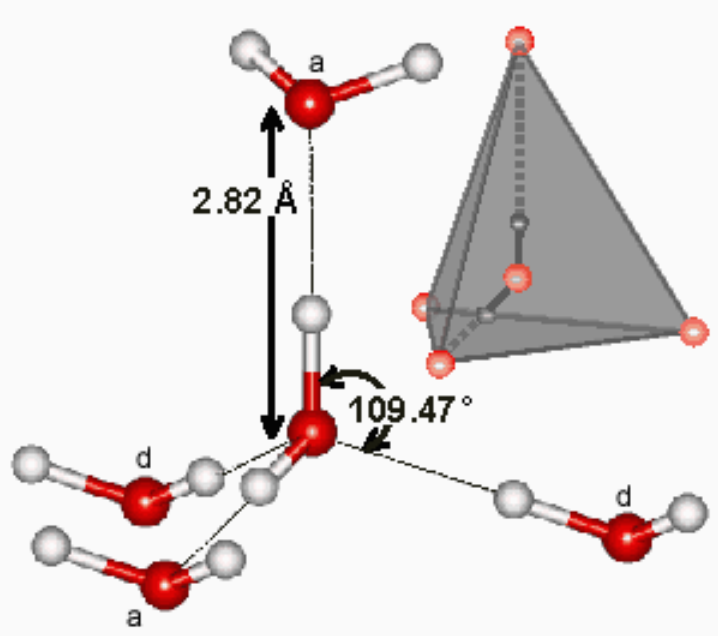


	R (Å)	θ°
H_2O	0.97	104.5
H_2S	1.34	92



P. K. Mandal, F. J. Lovas, E. Arunan, unpublished

Water and hydrogen sulphide in condensed phase



H_2O at 0 °C 4 neighbours

H_2S at – 60 °C 12 neighbours

http://www.lsbu.ac.uk/water/hbond.html

Packing of spheres from Wikipedia

Aren,t these different?

Isn't there a border between these two?

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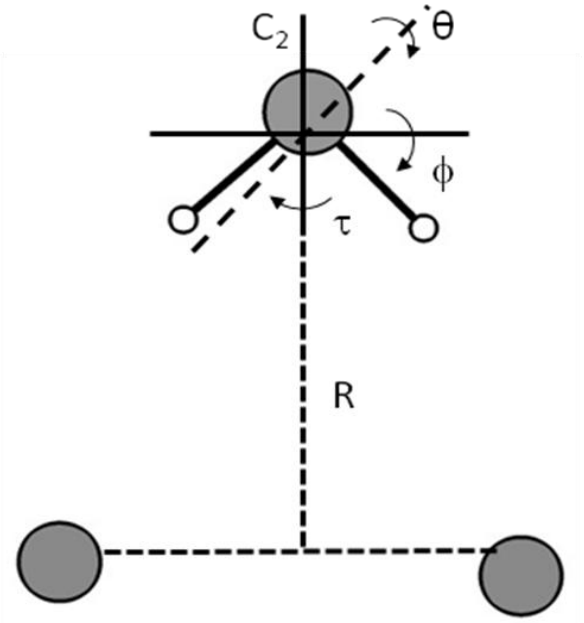
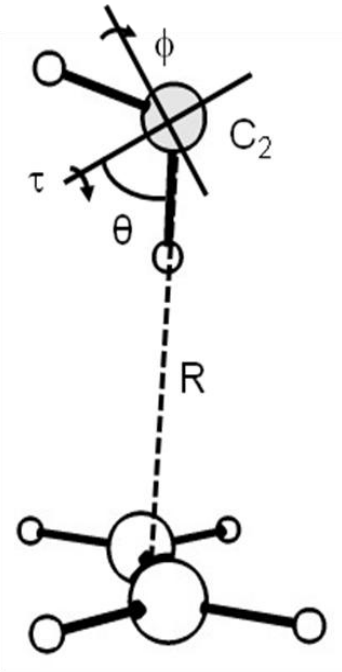
When does a complex or molecule reveal the effect of Hydrogen bond?

- For a ‘hydrogen bonded complex’, the zero point energy along any large amplitude vibrational coordinate that destroys the orientational preference for the hydrogen bond should be significantly below the barrier along that coordinate so that there is atleast one bound level.
  - Goswami and Arunan PCCP **11**, 8974 (2009) perspective article

Computational methodolgy

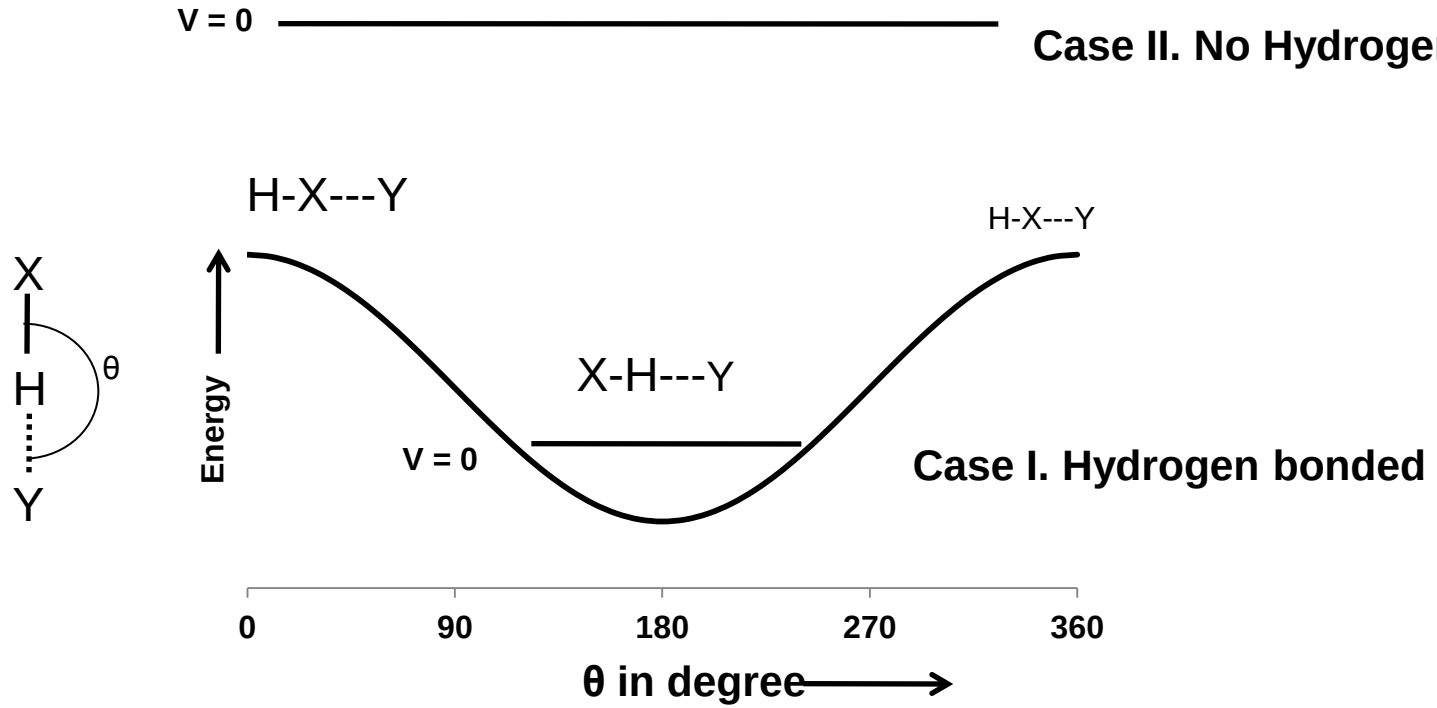
All the calculations were done at MP2/aug-cc-pVTZ level



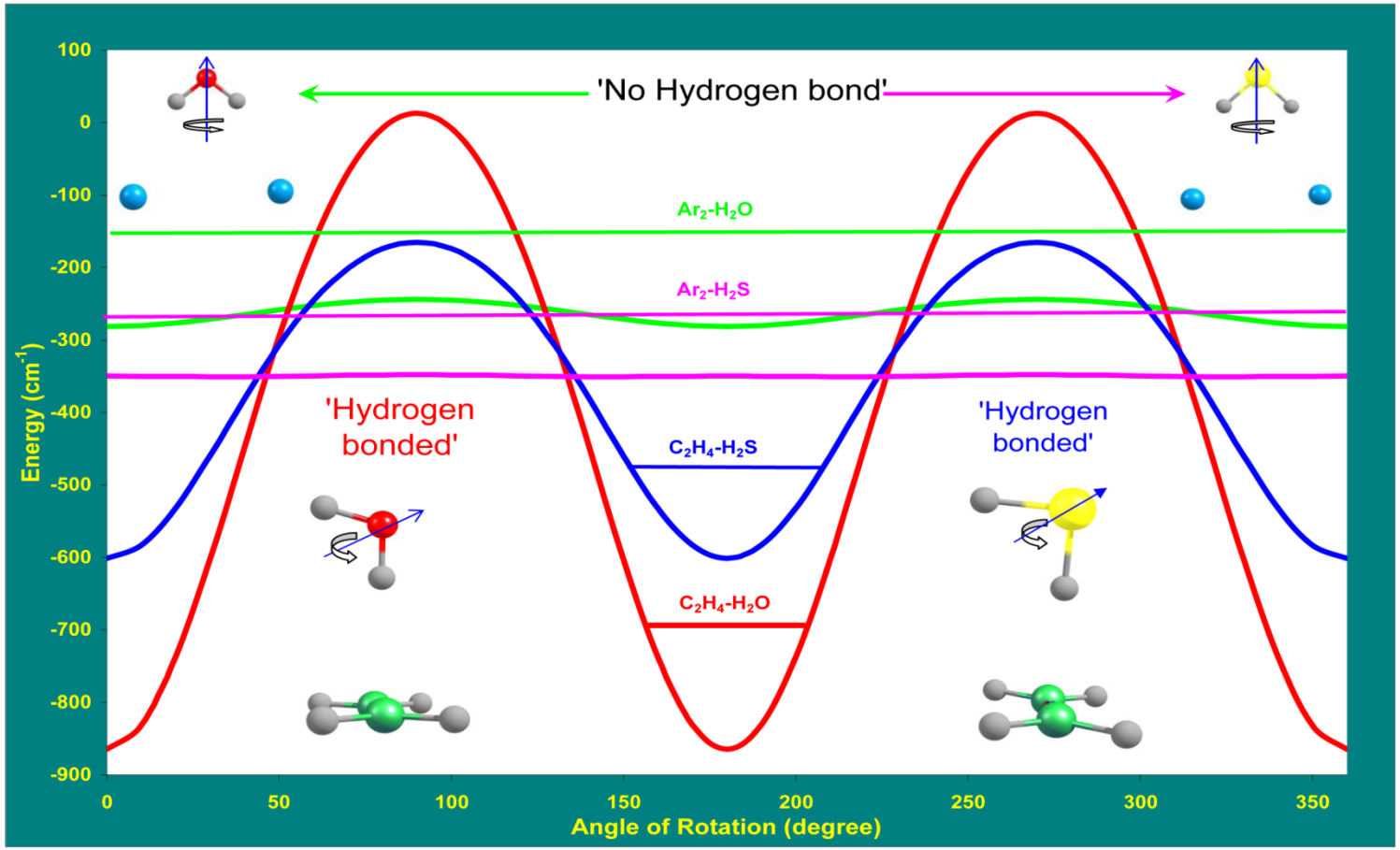


	R (Å)
$Ar_2\cdots H_2O$	3.4
$Ar_2\cdots H_2S$	3.8
$C_2H_4\cdots H_2O$	3.4
$C_2H_4\cdots H_2S$	4.0

What is the best criterion of calling a system as hydrogen-bonded?

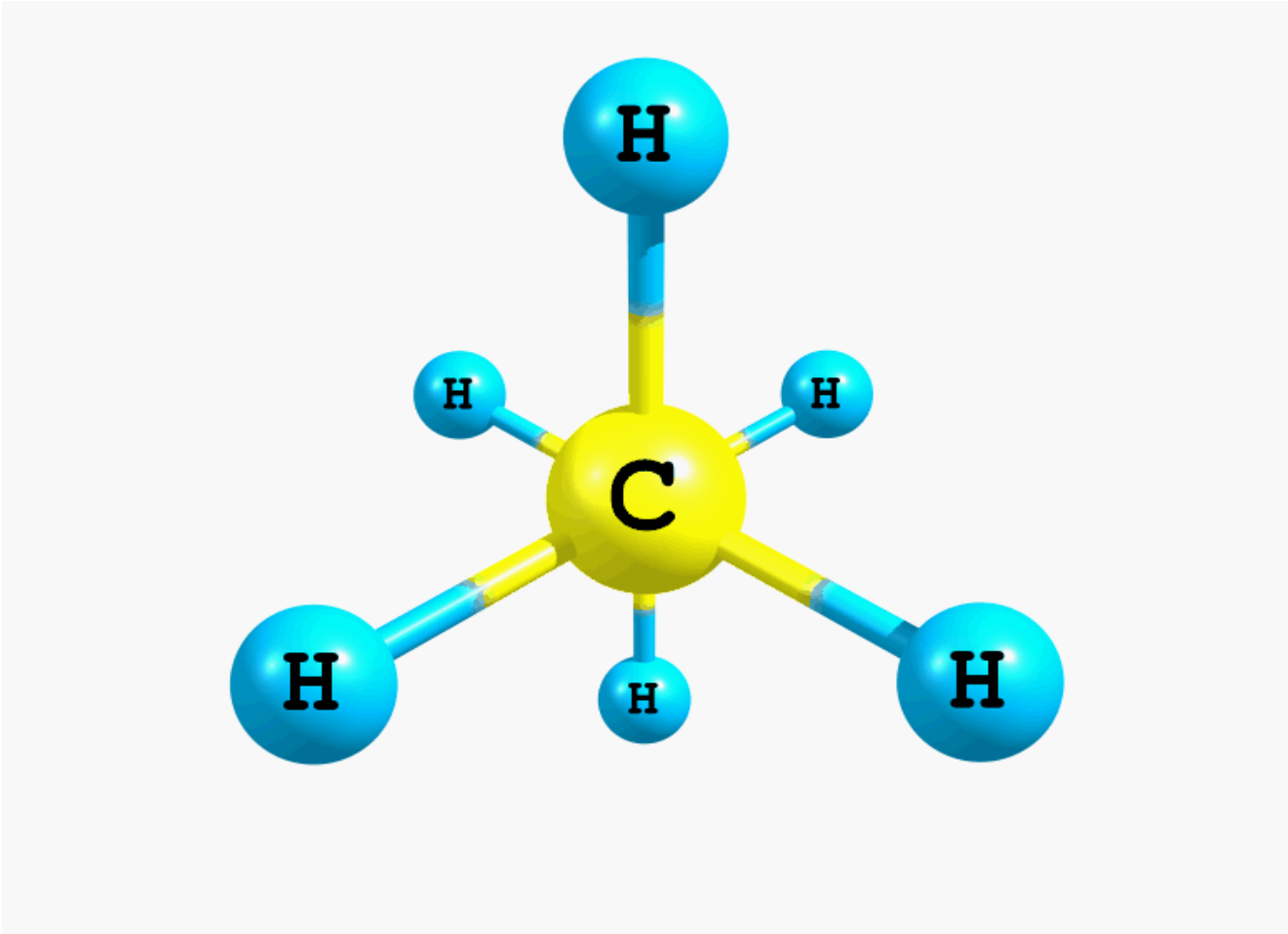


Model system: $Ar_2\cdots H_2O/H_2S$ and $C_2H_4\cdots H_2O/H_2S$

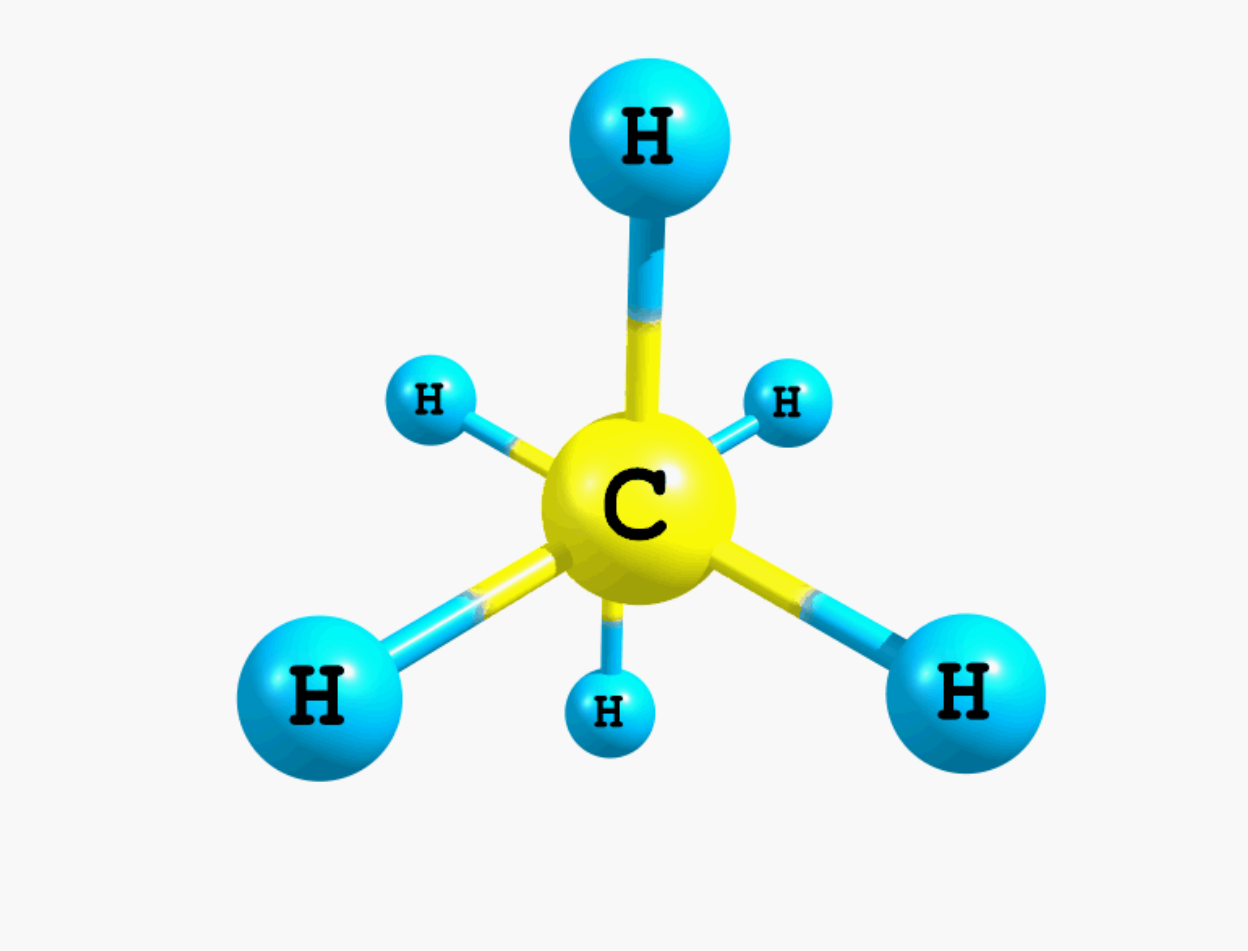


–Goswami and Arunan PCCP (2009) perspective article

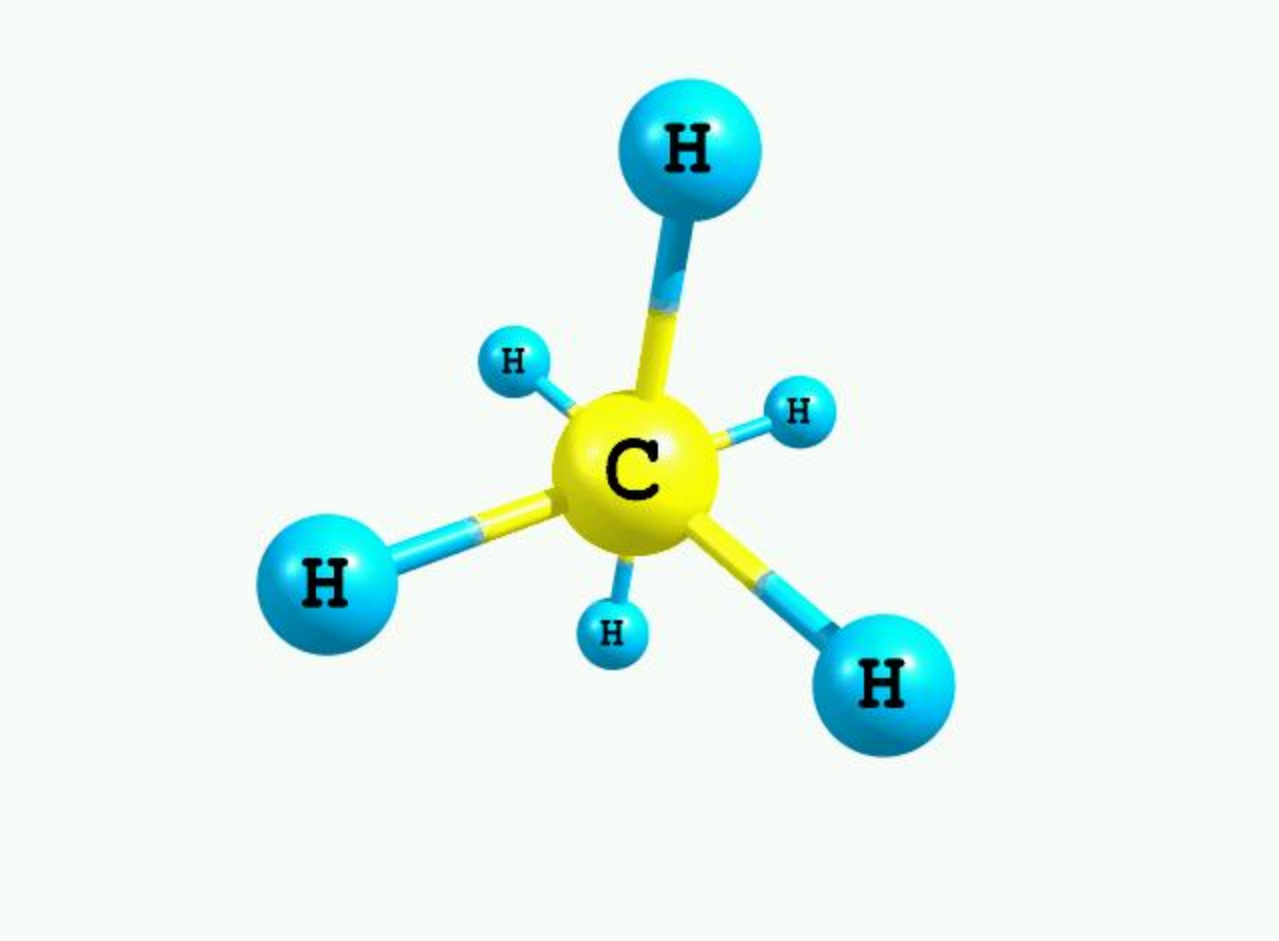
Torsion in ethane, staggered



Towards hindered rotation



Free rotation, no more eclipsed or staggered



We predicted hydrogen sulphide solid to have hydrogen bonding at lower temperature in 2008. Could someone confirm?

Hydrogen sulphide at low T and high P

- The structure becomes gradually ordered with the signature of hydrogen bond formation.
- H_2S is a good model system where we can tune the hydrogen bond strength from “absent or very weak to structurally significant”.
  - J. S. Loveday, R. J. Nelmes, S. Klotz, J. M. Besson, and G. Hamel, *Phys. Rev. Lett.* 2000, **85**, 1024.

IUPAC TASK GROUP

- E. Arunan , Bangalore (Chairman)
- Steve Scheiner, Utah (Co-chairman)
- G. R. Desiraju, Bangalore, (core-group, was in Hyderabad)
- R. A. Klein, Bonn (core-group)
- J. Salej Warsaw (core-group)
- I. Alkorta, Spain
- David Clary, Oxford
- Robert Crabtree, Yale
- J. J. Dannenberg, New York
- Pavel Hobza, Prague
- Henrik Kjaergaard, Otago (now in Copenhagen)
- A. C. Legon, Bristol
- Benedetta Mennucci, Pisa
- David Nesbitt, Colarado.

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New IUPAC Definition

- **The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.**

E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, "Definition of the hydrogen bond", **Pure Appl. Chem.** 83, 1619 and 1637 (2011)

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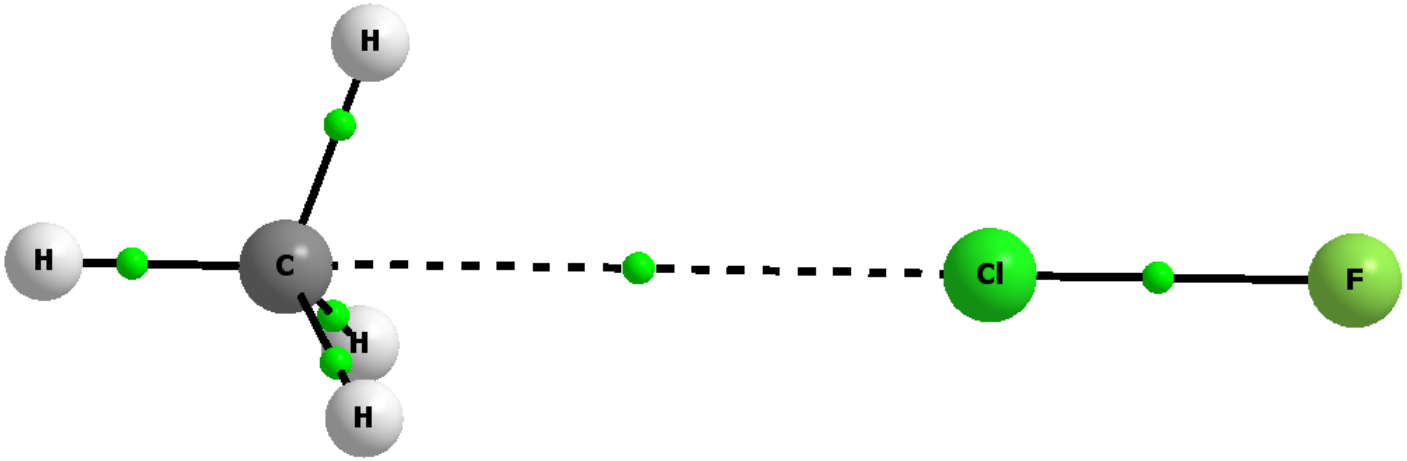
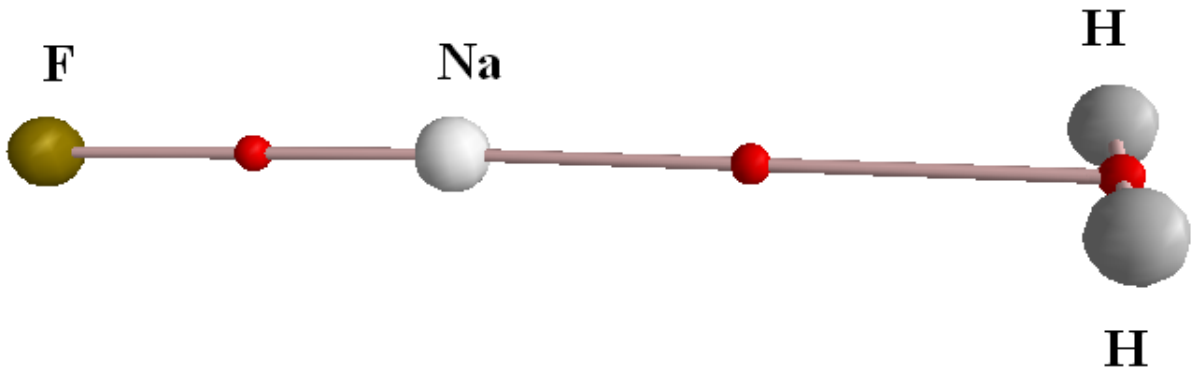
CH_4 can accept a halogen bond too! FCl---CH_4 complex



Legon and coworkers microwave spectrum
Devendra Mani AIM and ab initio theory, to be published
IUPAC has setup another task group to define halogen bonding
Following the successful completion of the hydrogen bond project.
Legon, Desiraju are both common members. Metrangolo and Resnati chairs

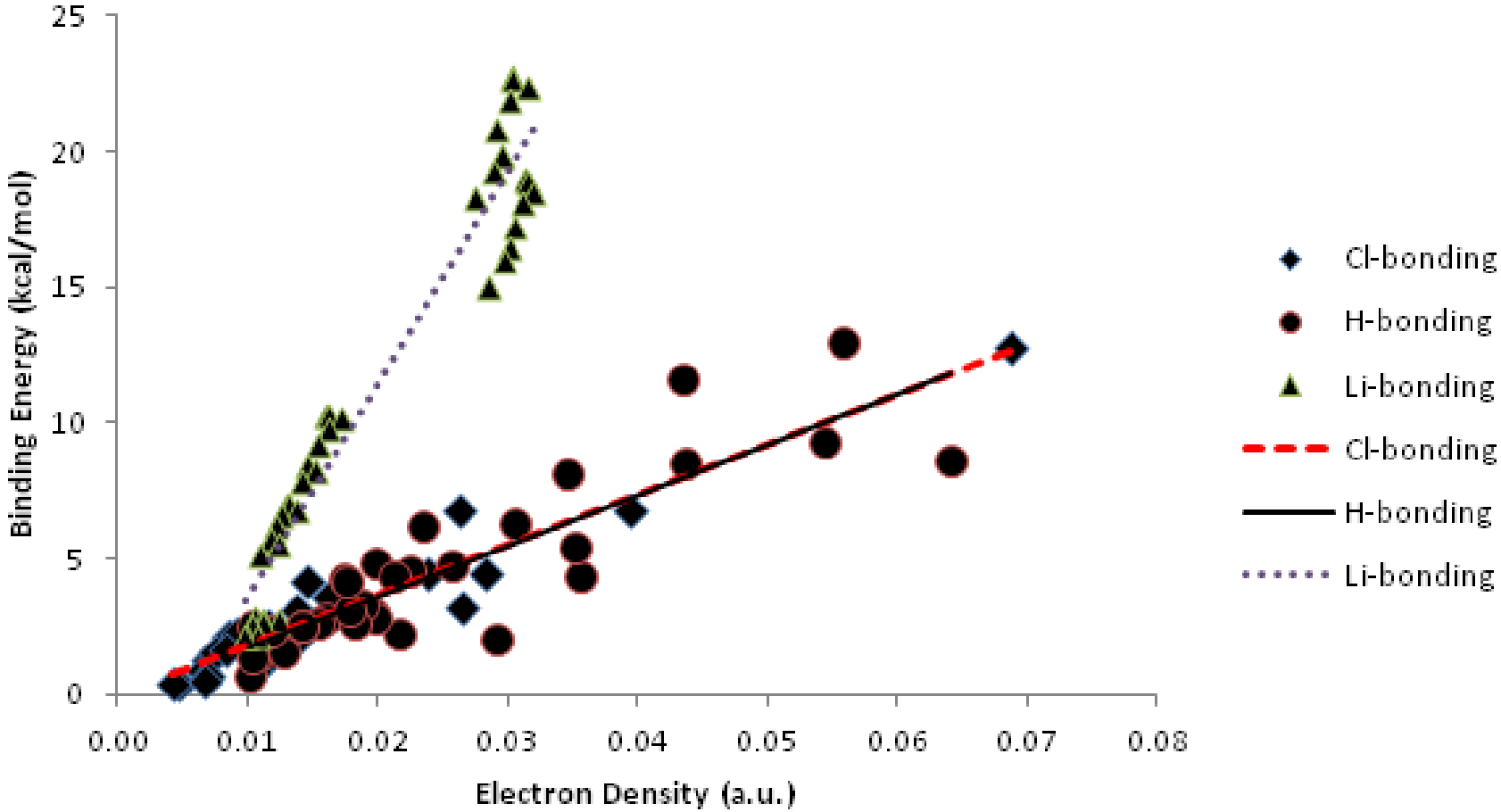
Sodium bond in FNa---H2 complex



Electron densities at the BCP are a good measure of the binding energy

R. Parajuli and E. Arunan, *Chem. Phys. Lett.* **568**, 63 (2013)

H/Cl/Li bonding



Abhishek Shahi and E. Arunan, PCCP 2014

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Review of Annu. Rev. Phys. Chem.

- Review on beryllium clusters by Heaven, Merrit and Bondybey.

dimer	Distance Å	Energy cm^{-1}	van der Waal"s radii sum	Nature of bonding
Li	2.67	8517	3.64	covalent
Be	2.54	930	3.06	?
Mg	3.40	430	3.46	Van der Waals
Ne	3.10	29	3.08	Van der Waals

- **Of course, chemists do not worry much about metal clusters and if not a 'beryllium bond' may have been defined to highlight the uniqueness in its interaction in comparison to magnesium (van der Waals) and lithium (covalent). The internuclear distance in Ne2 and Mg2 are closer to the sum of their van der Waals radii."**

– E. Arunan, *Curr. Sci.* **102**, 501 (2012)

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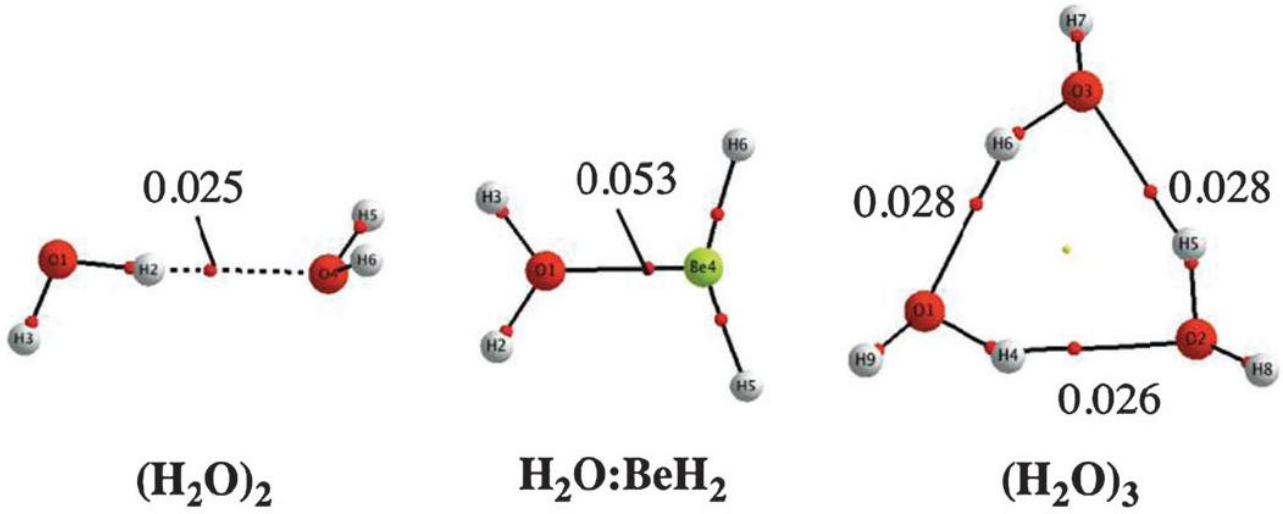
Beryllium bond

- **Laura Albrecht** [a], **Russell J. Boyd** *[a], **Otilia Mó** [b] **and Manuel Yáñez** "Cooperativity between hydrogen bonds and beryllium bonds in (H2O)nBeX2 (n = 1–3, X = H, F) complexes. A new perspective"

Phys. Chem. Chem. Phys., 2012, **14**, 14540-14547



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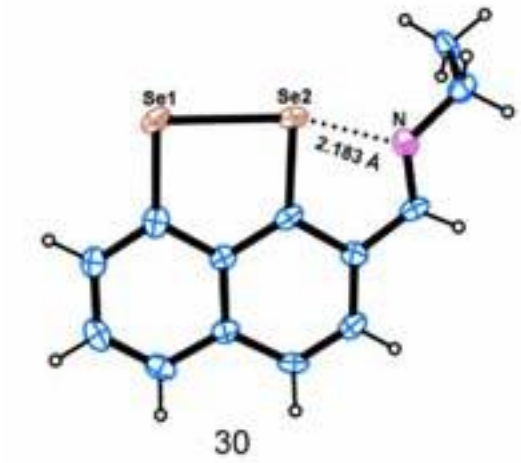
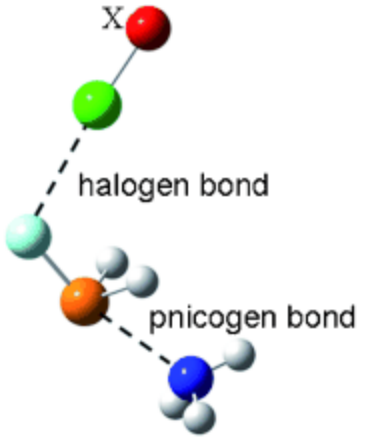
Chalcogen and pnicogen bonding

Manna, D.; Mugesh, G. "Regioselective Deiodination of Thyroxine by Iodothyronine Deiodinase Mimics: An Unusual Mechanistic Pathway Involving Cooperative Chalcogen and Halogen Bonding",
J. Am. Chem. Soc. *134*, 4269 - 4279 (2012).
Se---N interactions



Qing-Zhong Li et al.
ChemPhysChem
Volume 13, Issue 5,
pages 1205–1212, April 10, 2012



$XCl\text{-}FH_2P\text{-}NH_3$

(X = F, OH, CN, NC, FCC)

Steve Scheiner proposed pnicogen bond in 2011

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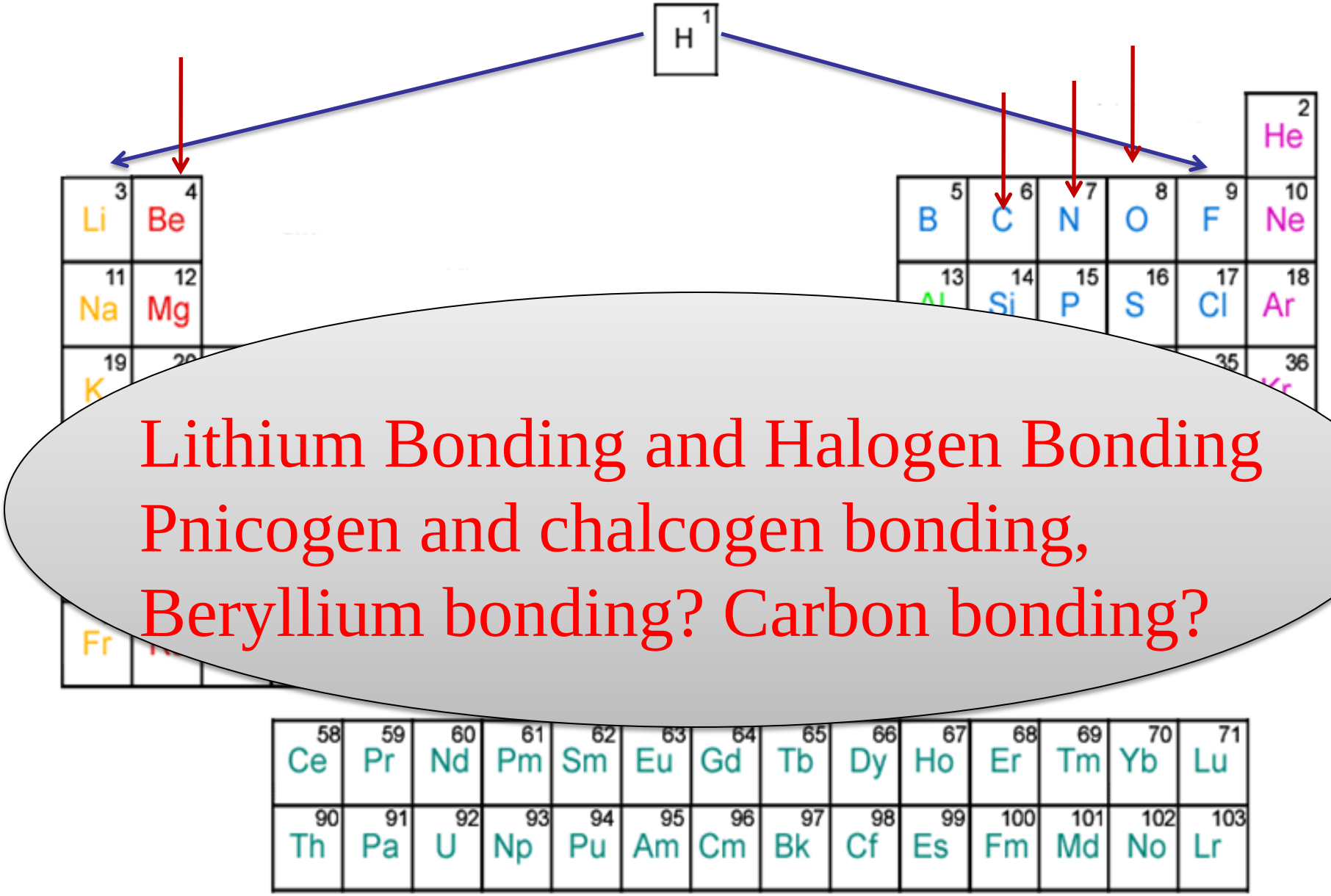

Lithium Bonding and Halogen Bonding Pnicogen and chalcogen bonding, Beryllium bonding? Carbon bonding?

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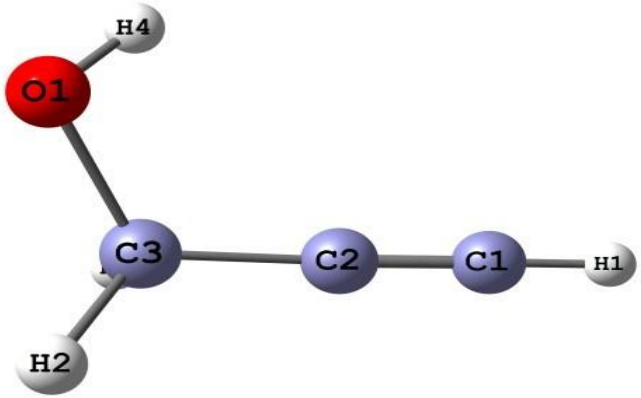
Ar-propargyl alcohol dimer
Towards carbon bonding



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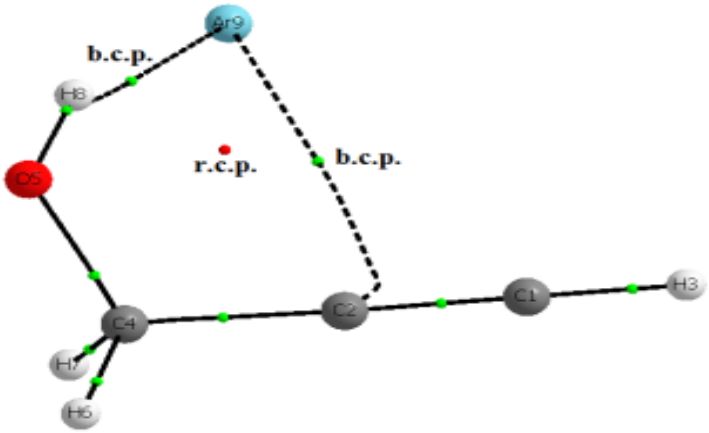
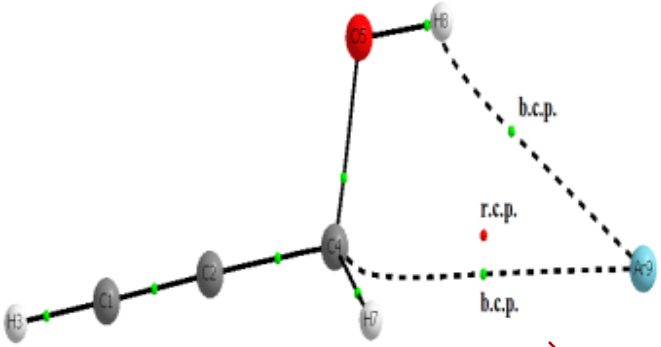
Nature of interactions: AIM analysis

Microwave spectrum proves this structure

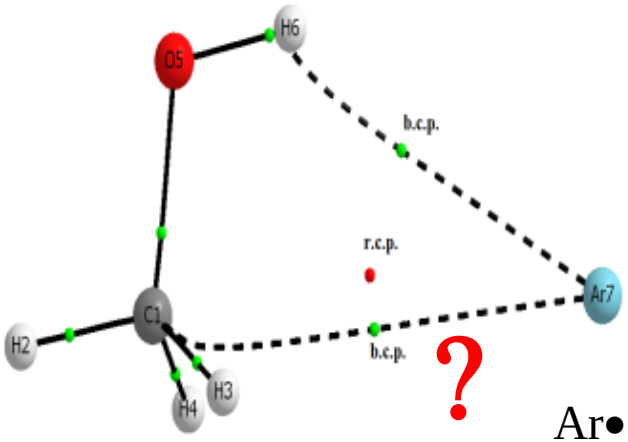


Ar••• g-PA



Ar••• t-PA

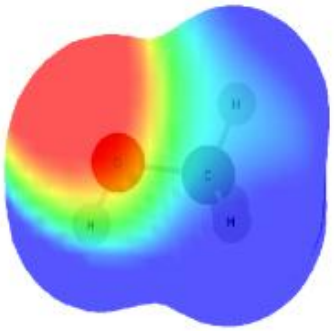
?

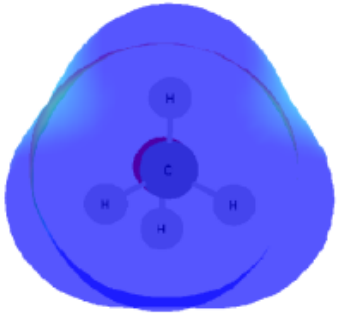


?

Ar••• methanol

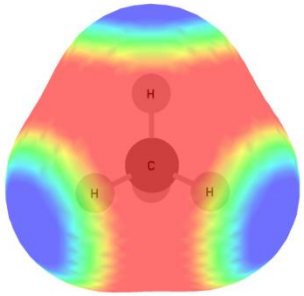
Methanol ESP surface

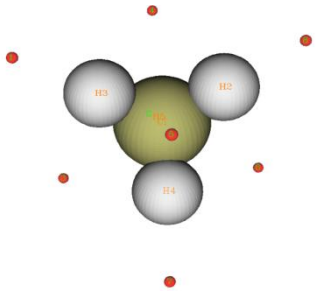




ESP value at face centre +50.2 kJ.mol^{-1}

- **Tetrahedral face of methane has a –ve centre!**

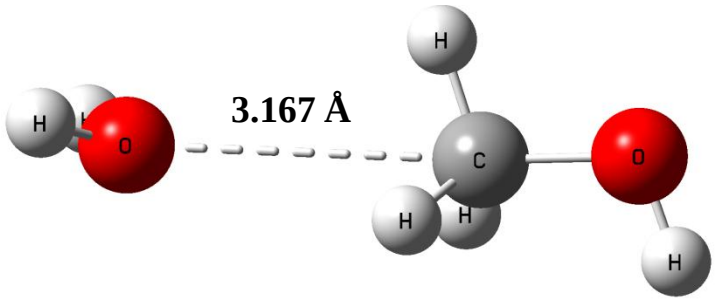


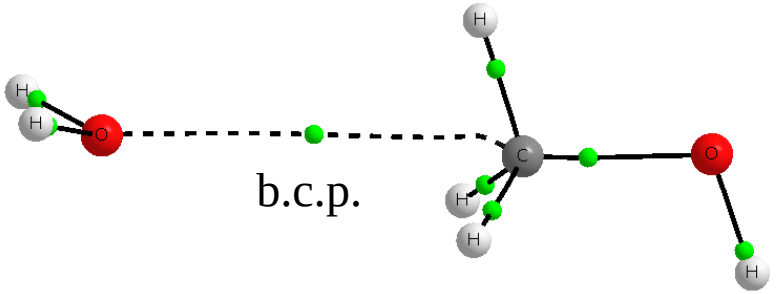


ESP value at face centre = -7.5 kJ.mol^{-1}

$H_2O\bullet\bullet\bullet CH_3OH$ complex

$H_2O\bullet\bullet\bullet CH_3OH$ complex was optimized taking initial geometry in which oxygen of water points towards the CH_3 face of methanol.





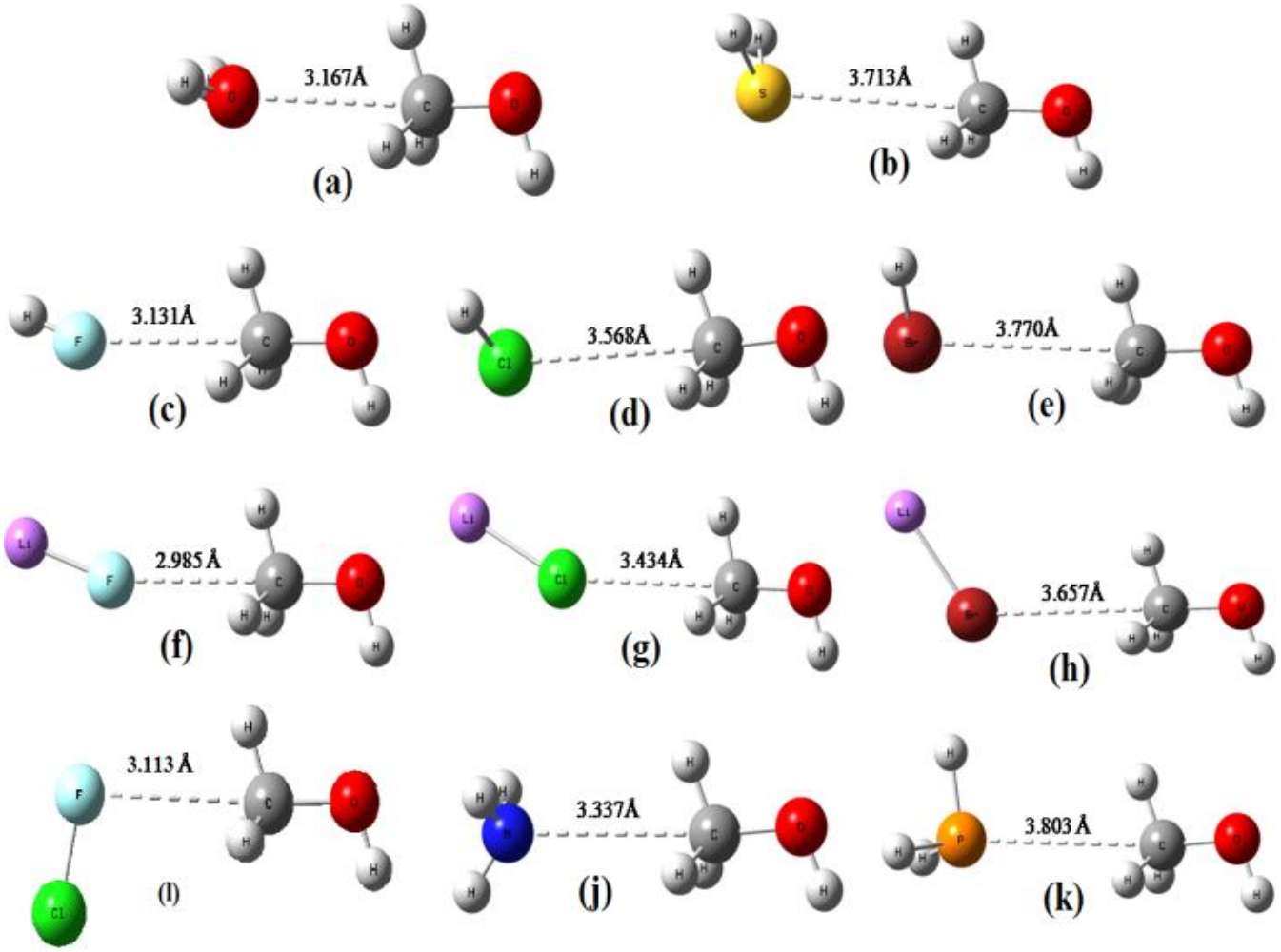
BSSE corrected interaction energy = 4.2 kJ mol^{-1}

Electron density ρ(r), at intermolecular b.c.p. = 0.0050 a.u.

Laplacian of electron density $\nabla^2\rho(r)$ at intermolecular b.c.p. = 0.0248 a.u.

Is this a general interaction ?

Similar interaction with other molecules



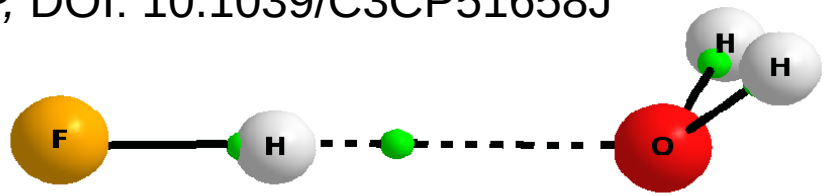
Optimized geometries for (a) H_2O•••CH_3OH, (b) H_2S•••CH_3OH, (c) HF•••CH_3OH, (d) HCl•••CH_3OH, (e)HBr•••CH_3OH, (f) LiF•••CH_3OH, (g) LiCl•••CH_3OH, (h) LiBr•••CH_3OH, (i) ClF•••CH_3OH, (j) H_3N•••CH_3OH and (k) H_3P•••CH_3OH complexes.

D.Mani, E. Arunan, PCCP, DOI: 10.1039/C3CP51658J

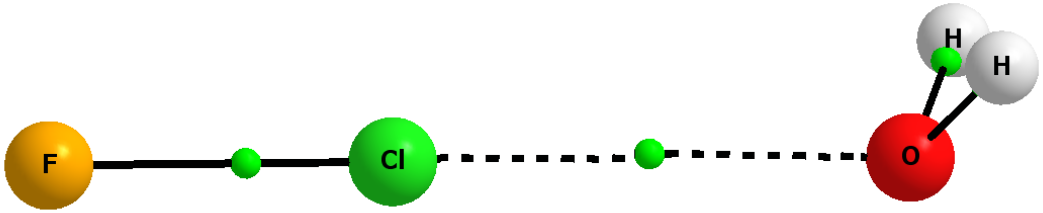
Current Science Meeting 28 Nov 2015

Nomenclature ?

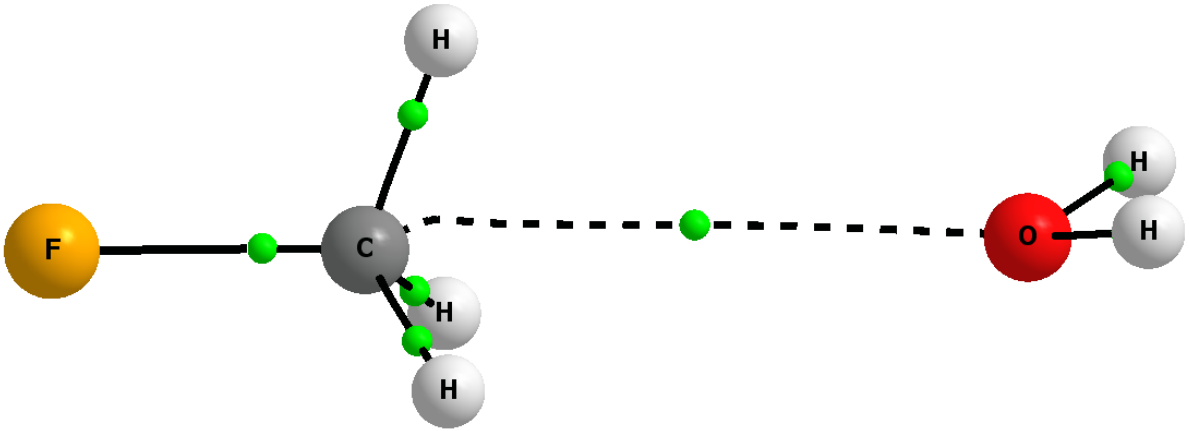
D.Mani, E. Arunan, PCCP, DOI: 10.1039/C3CP51658J



F-H ••• O "Hydrogen bond"



F-Cl ••• O "Halogen bond"

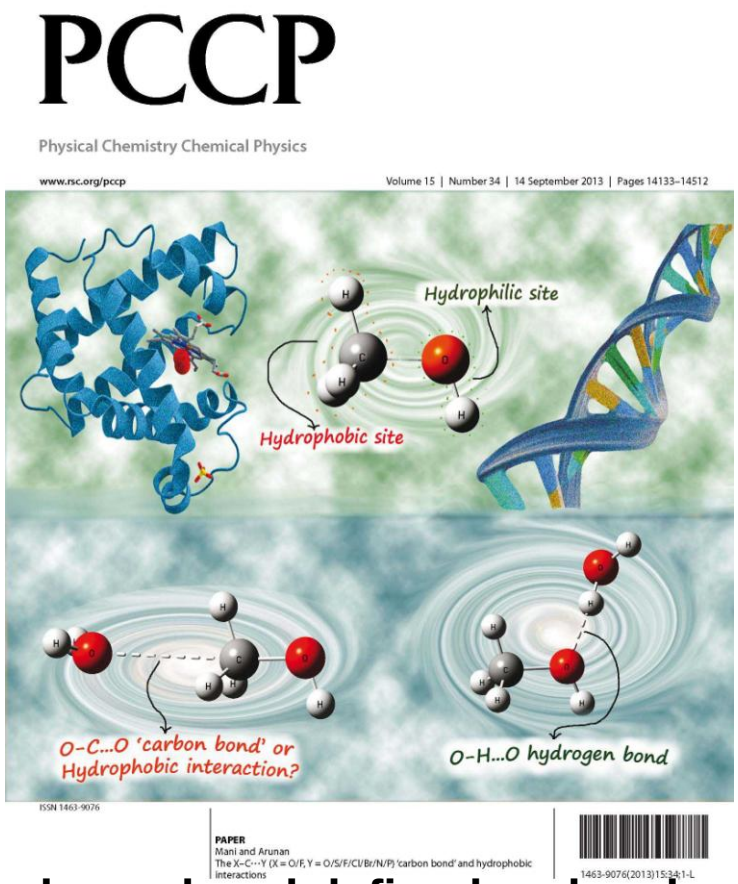


F-C ••• O "Carbon bond"

X-C---Y Carbon bonding shows

- Red-shift in C-X stretching frequency
- Linear X-C---Y
- Distance between C and Y less than the sum of van der Waals radii.
- Bond critical point between C and Y
- Hyper-conjugation n-σ^* overlap between Y lone pairs and C-X anti-bonding orbitals
- Finally, referees, editors all agreed and there was a blog. Became the number 1 paper downloaded in that period (not read?)

Carbon bond covered



Hydrogen bond seen, halogen bond defined and carbon bond proposed: intermolecular bonding, a field that is maturing!

E. Arunan, Current Science 10 October 2013 issue 892-894

Current Science Meeting 28 Nov 2015

Experimental verification by Prof. Guru Row of IISc in a few months

ChemComm

ChemComm

Dynamic Article Links►
View Article Online
DOI: 10.1039/C3CC47226D

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Experimental evidence for 'carbon bonding' in the solid state from charge density analysis

Sajesh P. Thomas, Mysore S. Pavan and T.N. Guru Row*

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Tetrel bond – σ-hole bond being a preliminary stage of S_N2 reaction

Sławomir J. Grabowski*[a,b]

Current Science Meeting 28 Nov 2015

Published online 25 October 2013

Chemical and Engineering News
January 6, 2014

VOLUME 92, NUMBER 1
JANUARY 6, 2014

C&EN
CHEMICAL & ENGINEERING NEWS

Serving the chemical, life sciences, and laboratory worlds

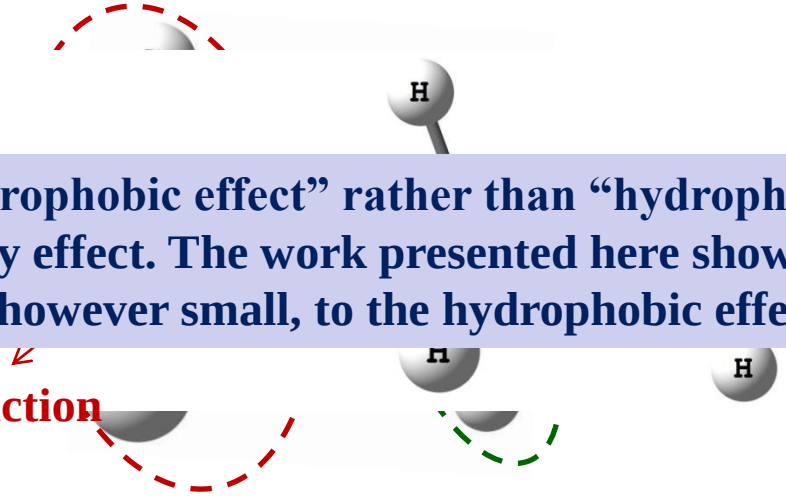
DEFINING A NEW CARBON BOND

Electronic effects that produce halogen bonds yield **NONCOVALENT INTERACTIONS** in other elements

JYLLIAN KEMSLEY, C&EN WEST COAST NEWS BUREAU

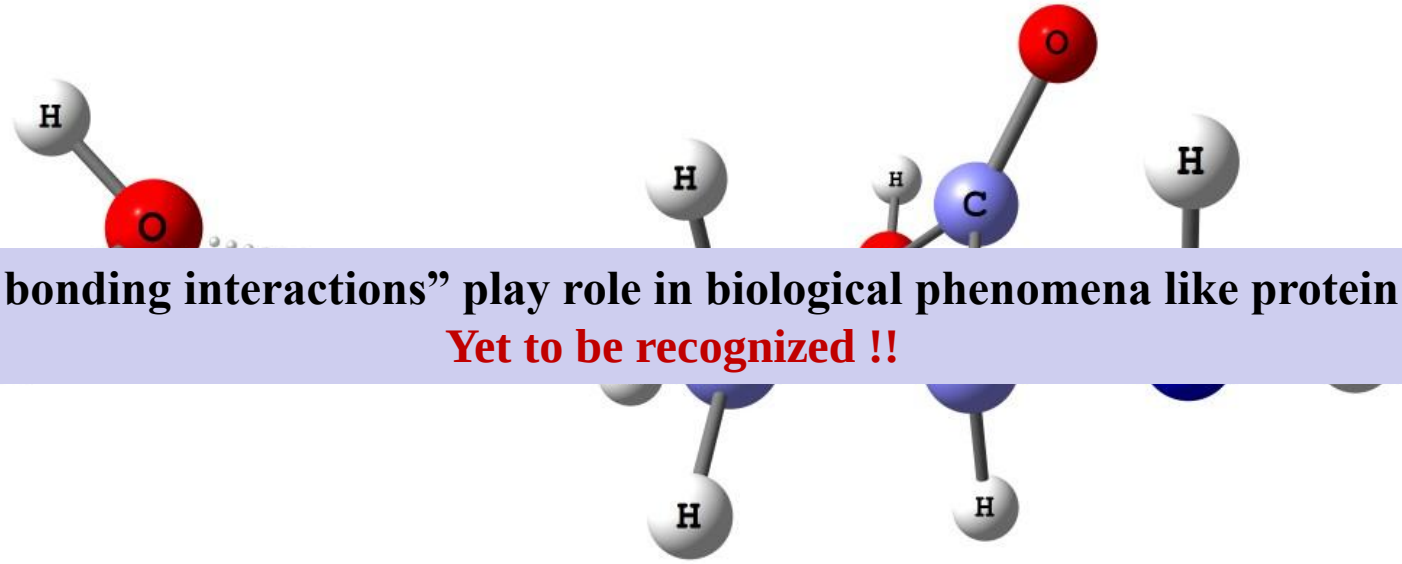
Current Science Meeting 28 Nov 2015

Carbon bonding and hydrophobic effect (interaction)



Experts prefer to call it "hydrophobic effect" rather than "hydrophobic interaction" because it is mainly an entropy effect. The work presented here shows there is enthalpy contribution , however small, to the hydrophobic effect.

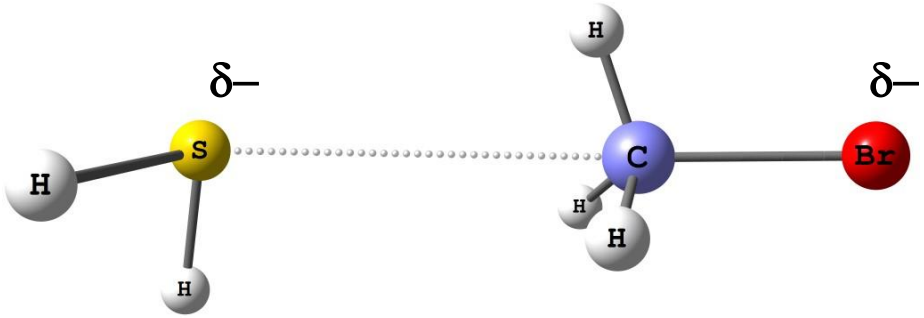
Carbon bonding with amino acids [$NH_2CH(R)COOH$]



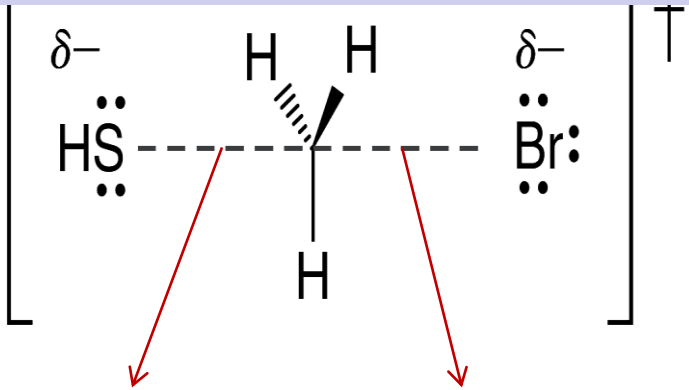
Do "carbon bonding interactions" play role in biological phenomena like protein folding ?
Yet to be recognized !!

Alanine•••water complex showing "carbon bonding" interaction

Carbon bonding and S_N2 reactions



"Carbon bonding interactions" may be responsible for the stabilization of S_N2 reaction intermediate !



Carbon bonds

More on hydrogen bonding Nov 2014

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Positively Charged Phosphorus as a Hydrogen Bond Acceptor

Anne S. Hansen, Lin Du, and Henrik G. Kjaergaard*

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Angewandte Communications

Bond Theory

DOI: 10.1002/anie.201405812

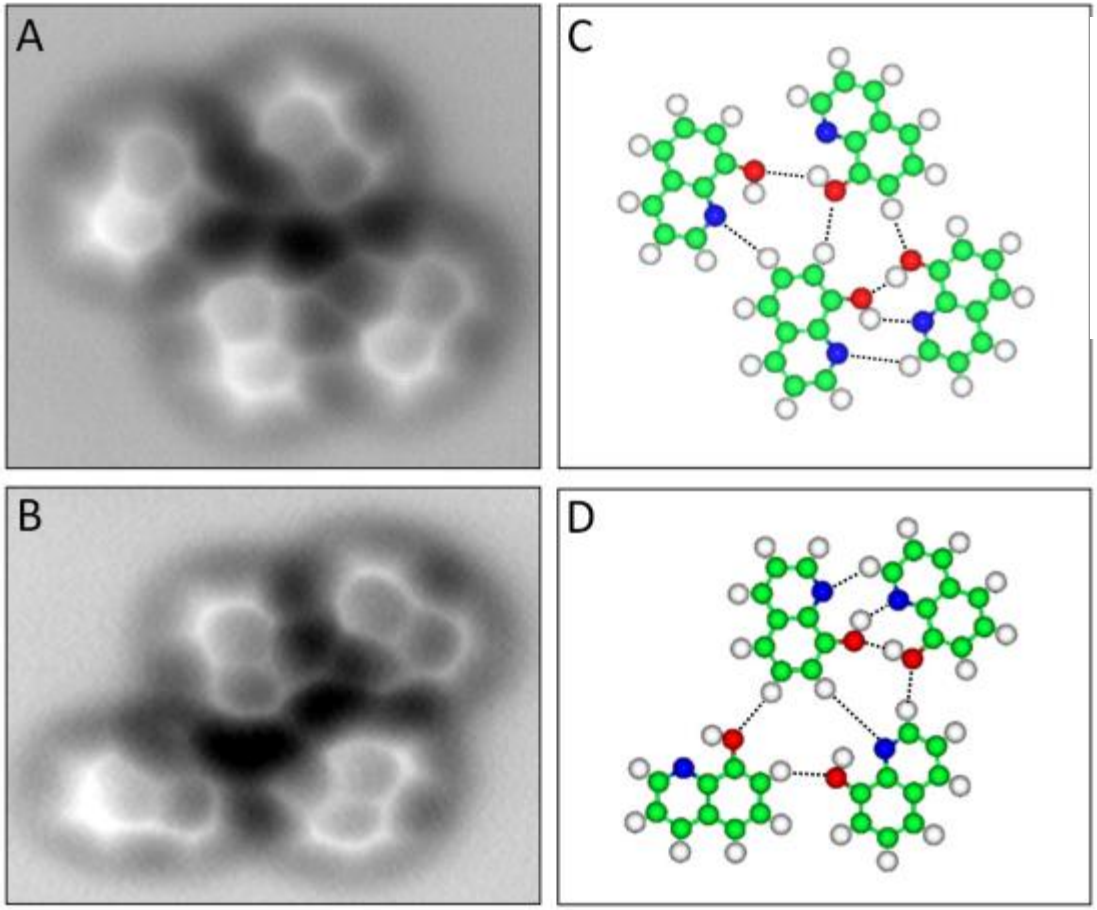
Anti-Electrostatic Hydrogen Bonds

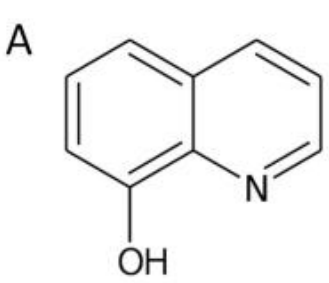
Frank Weinhold and Roger A. Klein*

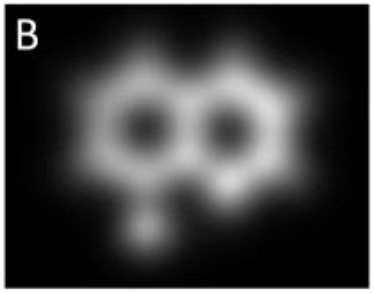
Current Science Meeting 28 Nov 2015

AFM image of hydrogen bonds

26 September 2013 / Page 1 / 10.1126/science.1242603







The first AFM image of hydrogen Bonding shows O-H---N and C-H---N hydrogen bonds! Science, Zhang et al. published Online Sep 2013

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NMR Evidence for ‘carbon bond’

THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

NMR Investigations of Non-Covalent Carbon Tetrel Bonds. Computational Assessment and Initial Experimental Observation

Scott A. Southern, and David L. Bryce

J. Phys. Chem. A, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpca.5b10848 • Publication Date (Web): 12 Nov 2015

Abstract. Group IV tetrel elements may act as tetrel bond donors, whereby a region of positive electrostatic potential (σ-hole) interacts with a Lewis base. The results of calculations of NMR parameters are reported for a series of model compounds exhibiting tetrel bonding from a methyl carbon to the oxygen or nitrogen atoms in various functional groups. The ^{13}C chemical shift (δ_{iso}) and the $^{1c}J(^{13}C,Y)$ coupling (Y = ^{17}O, ^{15}N) across the tetrel bond are recorded as a function of geometry. The sensitivity of the NMR parameters to the non-covalent interaction is demonstrated via an increase in δ_{iso} and in $|^{1c}J(^{13}C,Y)|$ as the tetrel bond shortens. Gauge-

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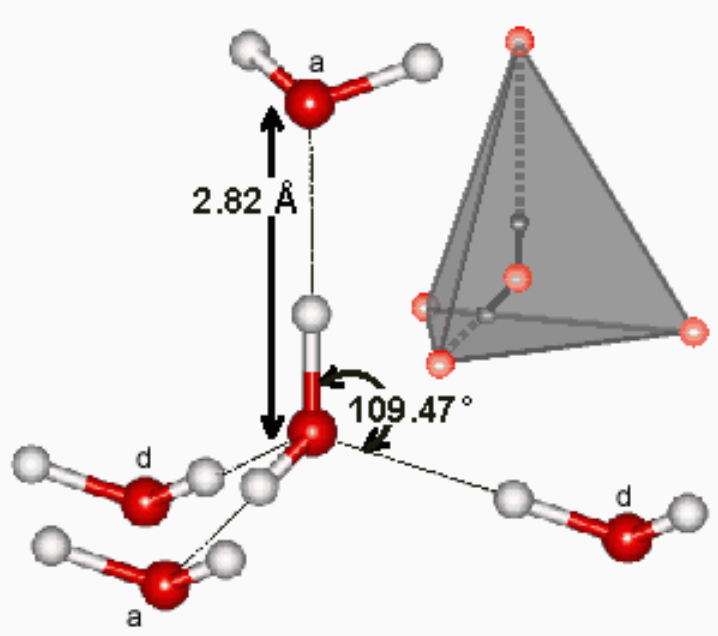
Water and hydrogen sulphide in condensed phase



H_2O at 0 °C 4 neighbours

H_2S at – 60 °C 12 neighbours

http://www.lsbu.ac.uk/water/hbond.html

Packing of spheres from Wikipedia

Aren,t these different?

Isn't there a border between these two?

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Apples and Oranges – A Comparison[1]

Scott A. Sandford
NASA Ames Research Center, Mountain View, California

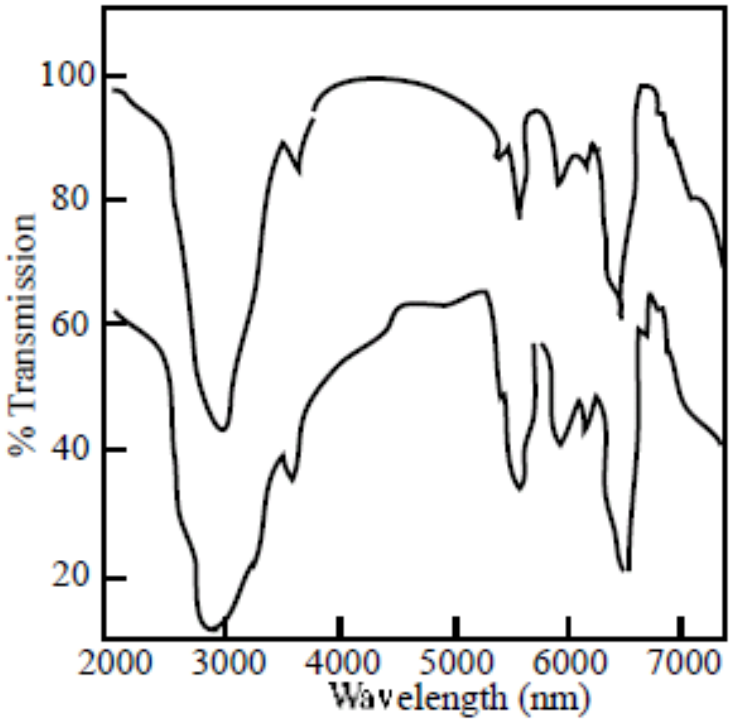

FIG. 2: FTIR spectra for apple (upper curve) and orange (lower curve). Curves have been offset for clarity.

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Thanks Dr. Ludovic Binnier

Conclusions

- Microwave spectroscopic investigations on weakly bound complexes have helped us in understanding hydrogen bonding from a fundamental view and also discover carbon bonding.
- It has also helped in a unified view of intermolecular interactions involving all elements and their molecules.
- Atoms in molecules theory has helped us in looking at the bonds!

Current Science articles

- **E. Arunan (1999) "Research News: Hydrogen bonding: A fascination forever!", Curr. Sci. 77, 1233**
- E. Arunan (2000) "Review of Chemistry of the Atmosphere by P. S. Sindhu" Curr. Sci. 78, 202
- E. Arunan (2000) "Herbert Sander Gutowsky: An obituary" Curr. Sci. 78, 749.
- E. Arunan (2000) "Review of Introduction to Atmospheric Chemistry by D. J. Jacob" Curr. Sci. 79, 1392.
- **E. Arunan (2007) "Meeting Report: Hydrogen bonding and other molecular interactions" Curr. Sci. 92, 17.**
- E. Arunan (2010) "Opinion: Scientometrics, Wisden, Science, Cricket and Leadership in India, Curr. Sci. 98, 993.
- **E. Arunan (2010) "Research News: Defining hydrogen bond through IUPAC" Curr. Sci. 99, 1493.**
- E. Arunan (2011) "Opinion: Indian Science: Catch up with India, then worry about China" Curr. Sci. 100, 21.
- **E. Arunan (2011) "Meeting report: Molecular interactions" Curr. Sci. 100, 284.**
- **E. Arunan (2011) " Review of the Annual Reviews of Physical Chemistry" Curr. Sci. 102, 501.**
- E. Arunan (2013) "Opinion: Is Indian science too theoretical?" Curr. Sci. 105, 15.
- **E. Arunan (2013) "Research news: Hydrogen bond seen, halogen bond defined and carbon bond proposed: Intermolecular bonding, a field that is maturing" Curr. Sci. 105, 895.**
- E. Arunan (2014) "The myth of falling standards: A life-long counter experience" 107, 555-556
- E. Arunan (2015) "What can scientists, science administrators do for 'Make in India'" 109, 1519-1520

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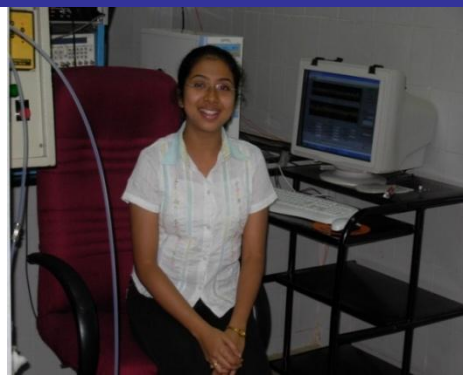
Thanks for listening



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