

# HYDROGEN BONDING AND OTHER MOLECULAR INTERACTIONS: BACKGROUND AND INTRODUCTION



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IUPAC DISCUSSION MEETING

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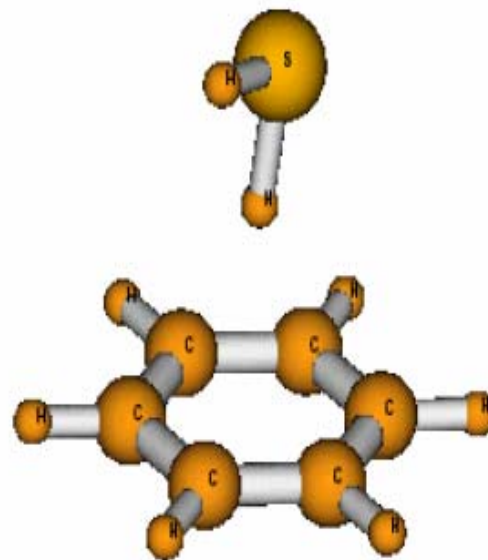
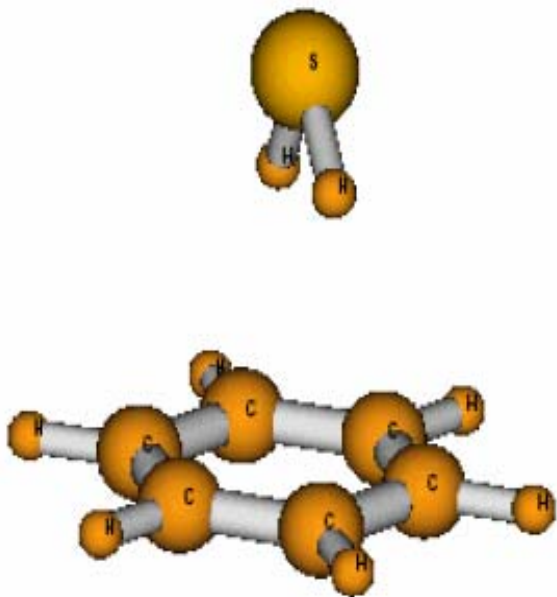
# Background and Introduction: personal view\*



- Rotational spectrum of two important “hydrogen bonded dimers” revealed accurate structural information (1993).



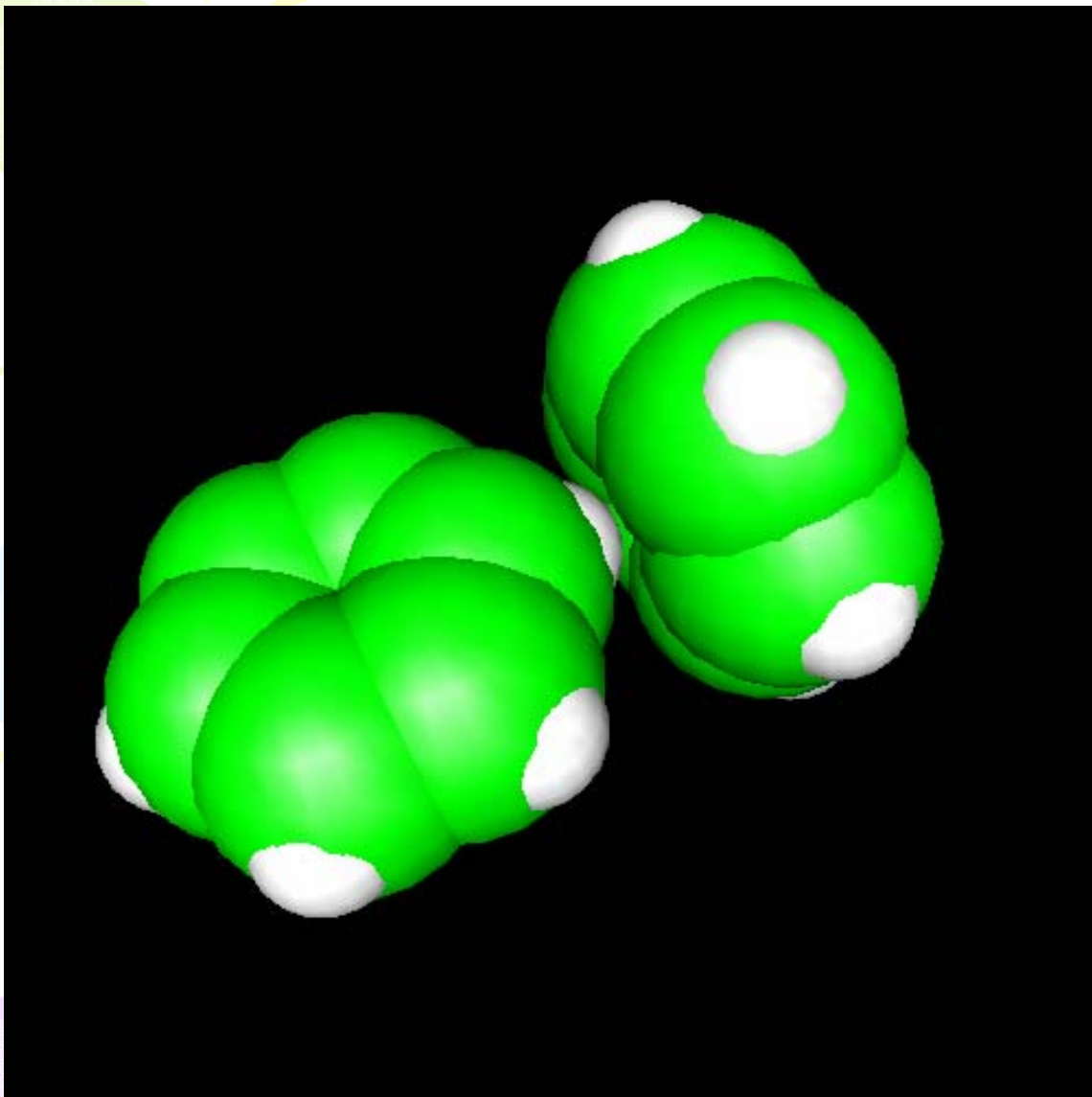
*\*Key word of ‘hydrogen bonding’ in SciFinder gave 346,465 references on 30 August 2005 and 370,275 references on 30 August 2006. Our work on these two dimers would not be among them*



S. Suzuki, P.G.Green, R.E.Bumgarner, S.Dasgupta, W. A. Goddard III and G.A. Blake\*, *Science*, **257**, 942 (1992) (> 20 GHz)

H. S. Gutwosky, T. Emilsson and E. Arunan, *J. Chem. Phys* **99**, 4883 (1993)  
(3-20 GHz.)

There was no mention of OH••• $\pi$  interactions or  
OH••• $\pi$  hydrogen bonding in our paper  
what's in a name?

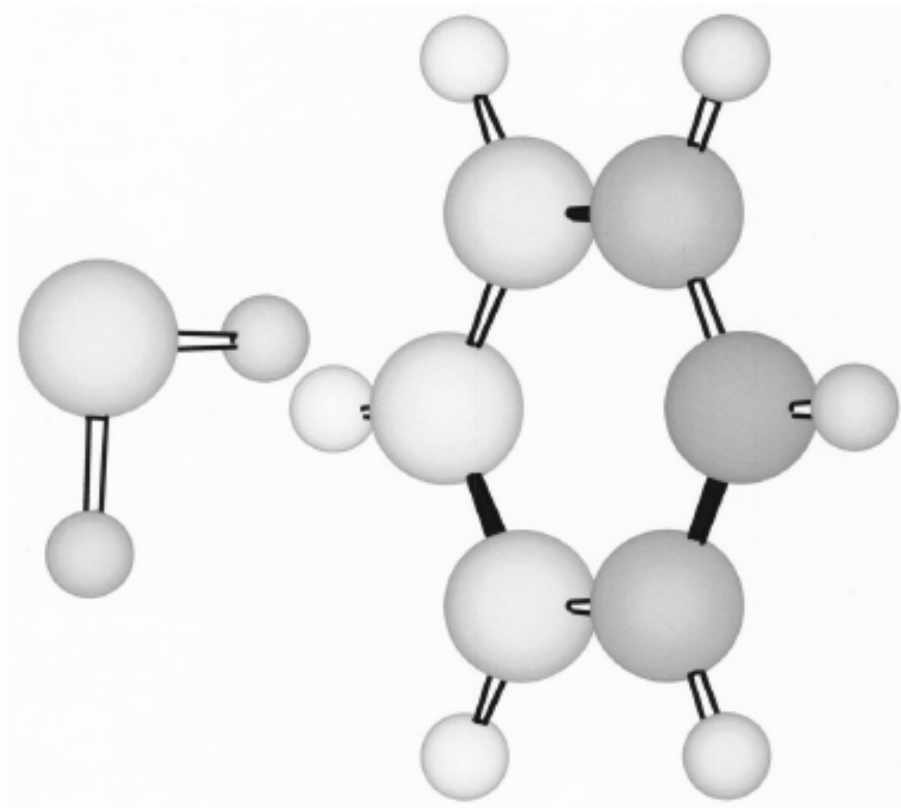


Arunan and Gutowsky J. Chem. Phys.  
98, 4294 (1993)

Benzene dimer, c.m.-  
c.m distance  $4.96\text{\AA}$   
Structure proven to  
be T-shaped  
Distance very close  
to what is found in  
crystal! As of today,  
the most direct  
evidence for the  
structure in the gas  
phase.

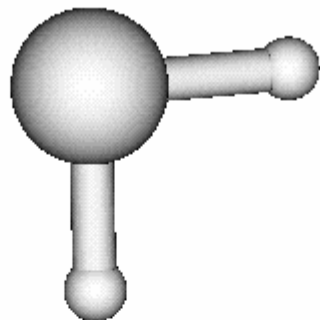
No mention of C-  
H $\cdots\pi$  interactions/  
H Bond

# $C_6H_6-H_2S$ dimer

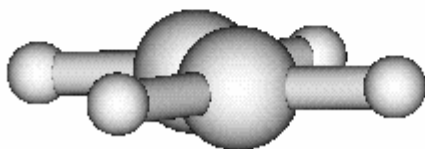


Structurally very similar to  $C_6H_6-H_2O$ .  
Binding energy is a little less.  
Rotational spectrum reveals evidence for large amplitude motions in both dimers.  
MMC calculations (Dykstra) predicted the geometry and dynamics reasonably well.

# $C_2H_4-H_2S$ 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

# $C_6H_6-H_2S$ dimer



- Tauer, Derrick and Sherril, *J. Phys. Chem. A.* **109**, 191 (2005) reported ab initio calculations on this dimer as a model for **sulfur- $\pi$**  interaction.
- High level **restricted** ab initio calculations resulted in 'H bonded' geometry, as the global minimum.
- S down geometry is lower in energy than the sum of two monomers.
- No frequency calculations to characterize the stationary point.
- Raghavendra found it to be a saddle point of order 2.

# Ab initio results

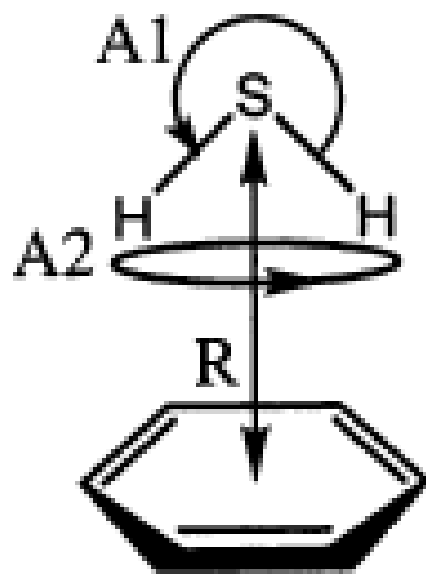


Figure 1. Geometry specification for H<sub>2</sub>S–benzene dimer. The “swing” angle A1 is in the  $C_{2v}$  plane of the complex, the “twist” angle A2 is centered on the  $C_{2v}$  axis, and the intermonomer distance  $R$  is measured from the center of the benzene ring to the sulfur atom. Experimental bond lengths and angles were used as described in the text.



# Ab initio conclusion

Analysis of the interaction using symmetry-adapted perturbation theory, together with the potential energy curve for rotation of the H<sub>2</sub>S unit relative to the benzene ring, suggests that the sulfur- $\pi$  interaction here is primarily an electrostatic attraction between the partial positive hydrogens in H<sub>2</sub>S and the negatively charged  $\pi$  electrons of benzene.

Where is sulfur- $\pi$  interaction here? Why not SH- $\pi$  interaction? or S-H $\cdots\pi$  hydrogen bond?

# Badger and Bauer, *J. Chem. Phys.* **5**, 839 (1937)

- First paper to talk about the lengthening of X-H bond and red-shift in X-H frequencies\*
- “Recently, there has been considerable interest shown in a peculiar form of linkage sometimes known as the “hydrogen **bond**” in which as hydrogen atom, usually belonging to an hydroxyl or amino group, appears to serve as a connecting **bridge** between two electronegative atoms.”

\* Blue shifting H bonds are well established now

# Badger and Bauer (1937)contd.



- “In order to establish such criteria one must of course decide what is meant by a hydrogen bond. Shall the term be reserved for certain cases in which O-O or other inter-nuclear distance concerned and energy required to break the bond lie within rather narrow limits, or shall it be extended to include a great variety of weaker interactions such as are responsible for the low frequency of vibration of the O-H group in single molecules of the acids and in ortho-chlorophenol, and for a part of the heats of vaporization of HCN and HCl? **These latter, of course, merge into the group of interactions known as van der Waals forces.**”
- Today these are accepted as genuine intra- and inter-molecular hydrogen bonds

S. J. Grabowski, W. A. Sokalski, and J. Leszczynski,  
*J. Phys. Chem.A.* **108**, 5823 (2004)



- Nature of X-H•••H-Y dihydrogen bonds\* and X-H••• $\sigma$  interactions

*"A complete analysis (AIM, energy decomposition, CBS limit...) of the different parameters of the complexes shows that the stronger complexes may be classified as H bonded and the weaker complexes may be classified as van der Waals"*

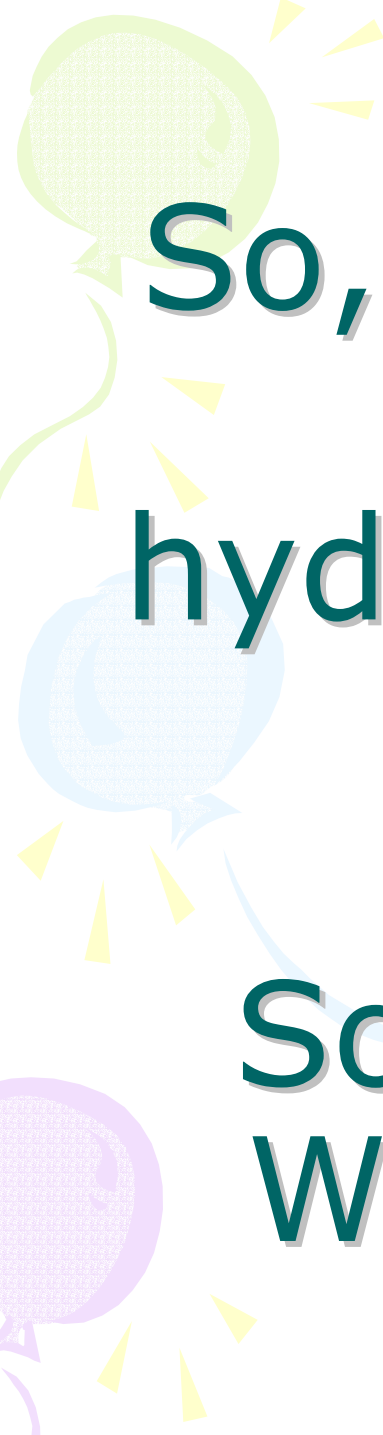
\* Naresh Patwari will be talking about dihydrogen bonds

P. Munshi and T. N. Guru Row, *J. Phys. Chem. A.* **109**, 659 (2005)

- Analysis of weak C-H $\cdots$ O and C-H $\cdots$  $\pi$  interactions in substituted coumarins by charge density analysis

*“Based on the set of criteria (Koch and Popelier) defined using the AIM theory it has become possible to distinguish between a hydrogen bond (C-H $\cdots$ O) and **van der Waals interaction (C-H $\cdots$  $\pi$ )”***

*(key criterion being the mutual penetration of H and the acceptor; it depends on the van der Waals radii of atoms used, which is somewhat arbitrary)*

On the left side of the slide, there are three decorative balloons: a green one at the top, a blue one in the middle, and a purple one at the bottom. Each balloon has a string of yellow triangular streamers hanging from it.

So, every one agrees  
that we have  
hydrogen bonding and  
van der Waals  
interactions.

So what is van der  
Waals interaction?

# van der Waals interactions?



- A van der Waals complex is a collection of two or more atoms or molecules held together by **van der Waals or dispersion forces**.
    - **E. R. Bernstein**, *Ann. Rev. Phys. Chem.* **46**, 205 (1995)
- (There is some circuitous reasoning here, and may be that is the best one can do)

# van der Waals interactions?



- The isotropic terms are **exchange repulsion and dispersion**, the sum of which is often called 'van der Waals interaction'
    - **G. R. Desiraju and T. Steiner** p 17 of their book *The Weak Hydrogen Bond* (1997)
- (neither of these forces are really isotropic)



# van der Waals interactions?



- The standard picture – **size repulsion and induction plus dispersion attraction** – is commonly referred as the van der Waals interaction.
  - **V. Aquilanti, E. Cornicchi, M. M. Teixidor, N. Saendig, F. Pirani, and D. Capelletti** *Angew. Chemie. Int. Ed.* **44**, 2356 (2005)

# van der Waals interactions?



- van der Waals binding relies on the long-range weak attraction between permanent and induced electric dipole (and higher) moments as well as instantaneous asymmetric charge distributions in atoms and molecules (dispersion interaction)

– Koperski *van der Waals complexes in supersonic beams*, Wiley-VCH 2003

- The forces of attraction and repulsion between molecules are called van der Waals forces.
  - **A. J. Stone** *The Theory of Intermolecular Forces*, Clarendon Press, Oxford 1996
- If one considers van der Waals equations as the origin for van der Waals interactions, it appears obvious that all intermolecular interactions, including hydrogen bonding, should be classified as van der Waals interactions. van der Waals interactions could be further classified as hydrogen bonding, halogen bonding etc...
  - **E. Arunan**, written for ISRAPs Bulletin (2005)
- But, what about directionality?

# H bond vs van der Waals! C-H•••O interaction



- Directionality, isotropic vs anisotropic potentials!
- H<sub>2</sub>O-CH<sub>4</sub> complex. Early ab initio studies<sup>1</sup> predicted C-H•••O 'hydrogen bonds' (V-O)
- PNFTMW spectroscopic studies<sup>2</sup> showed the structure to be O-H•••Δ, one of the tetrahedral planes in CH<sub>4</sub> (F-H)
- Advanced ab initio studies<sup>3</sup> found this geometry to be the global minimum.

<sup>1</sup> Novoa et al. *J. Chem. Phys.* **95**, 5179 (1991)

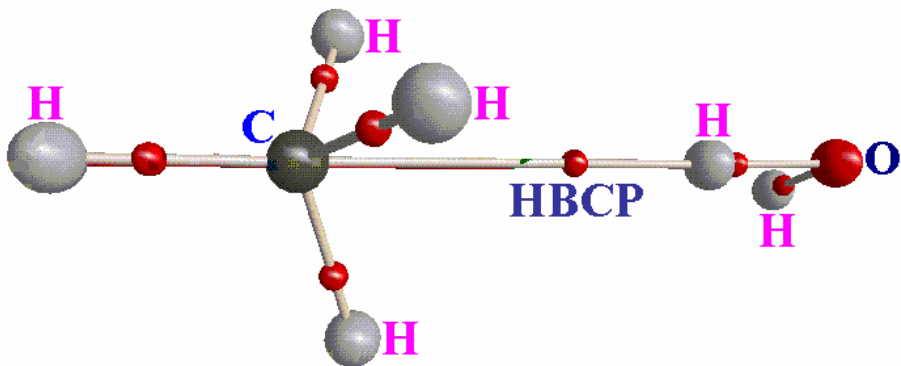
<sup>2</sup> Suenram et al. *J. Chem. Phys.*, **101**, 7230 (1994)

<sup>3</sup> Szczesniak et al. *J. Chem. Phys.*, **98**, 3078 (1993)

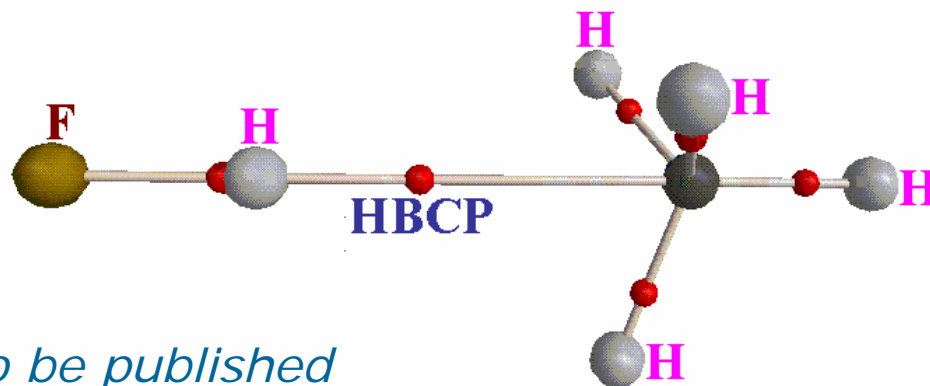
# CH<sub>4</sub>-HX geometry



MP2(FULL)/aug-cc-pVTZ.



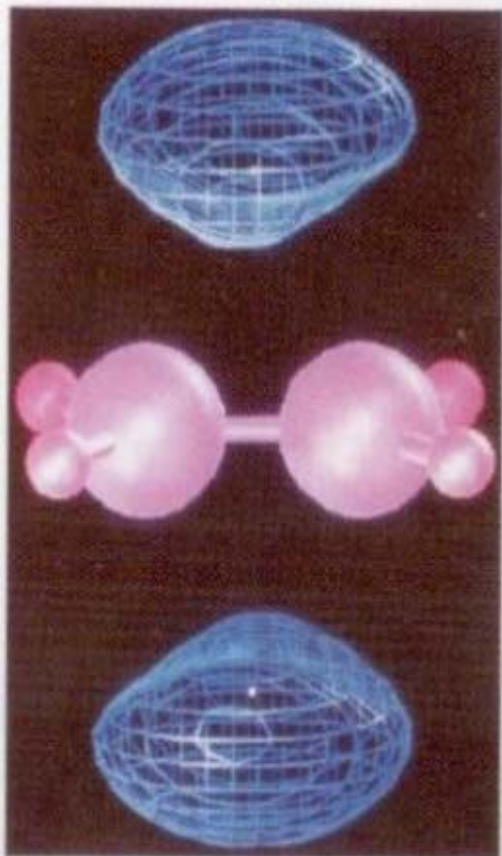
Systems	$\rho$	$\nabla^2\rho$
H <sub>4</sub> C---HF	0.0113	-0.0099
H <sub>4</sub> C---H <sub>2</sub> O	0.0078	-0.0076



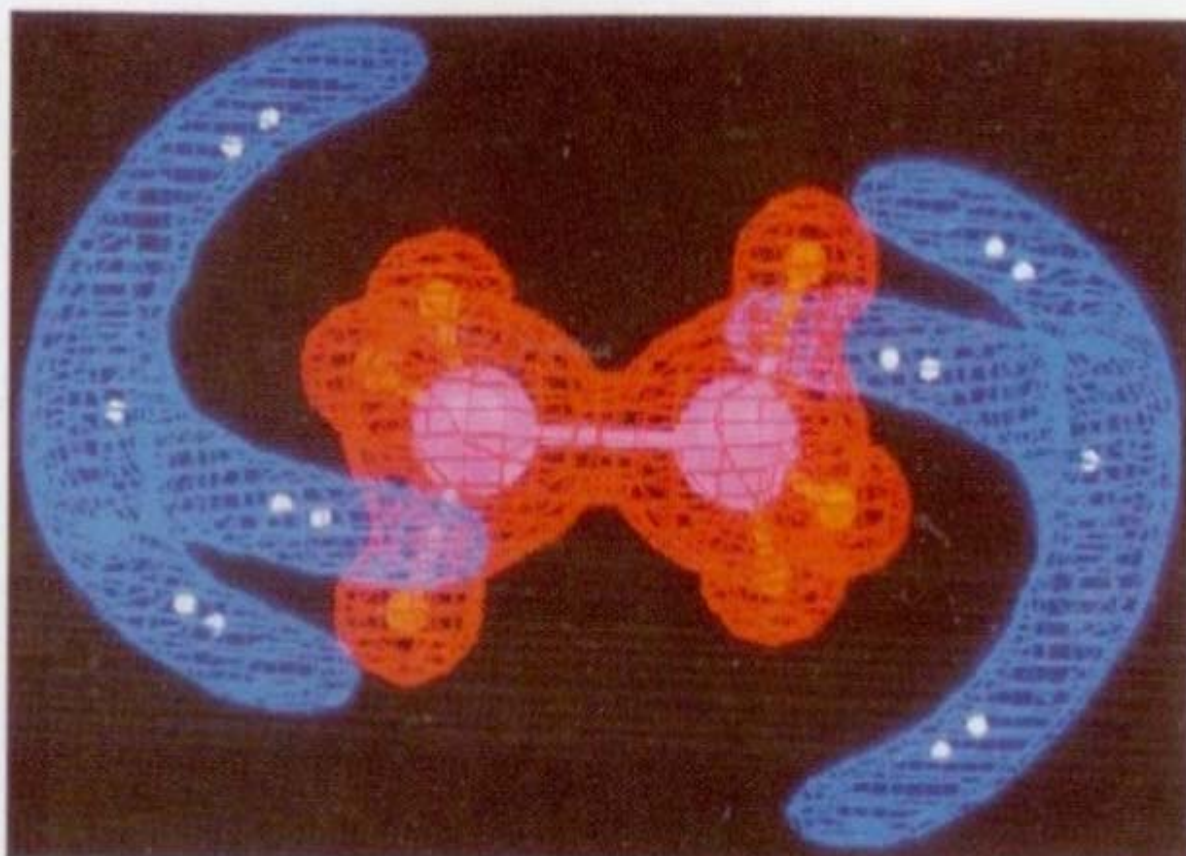
*Raghavendra and Arunan, to be published*

*Electron rich region is hydrogen bond acceptor*

# $C_2H_4$ and $C_2H_6$



$\pi$  acceptor



Generic Molecular orbital acceptor  
Electron rich region

From Shirsat and Gadre, *Electrostatics of Atoms and Molecules*

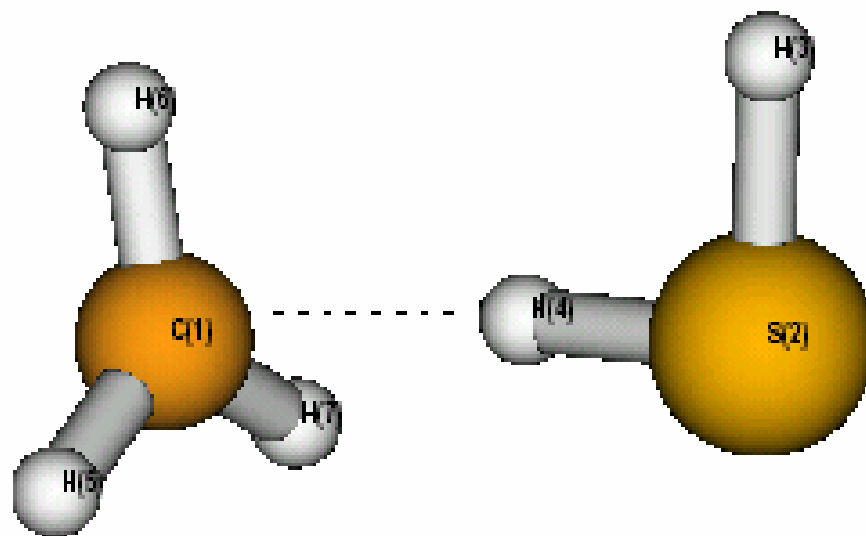


# Some points to ponder about!



- The  $\text{OH}\cdots\Delta$  interaction is like a typical hydrogen bond as the electron density in  $\text{CH}_4$  is maximum in that region.
- The dispersion energy is responsible for the overall anisotropy of the potential energy surface (*in  $\text{CH}_4\text{-H}_2\text{O}$  complex*) and obtaining the right global minimum. Without dispersion V-O is more stable than F-H.
- Authors note that F-H minimum becomes deeper because of the smaller steric hindrance!
- Desiraju and Steiner have shown that  $\text{C-H}\cdots\text{O}$  contacts are predominantly linear i.e. H bonds
- Legon showed that a weaker secondary interaction can make the H bond non-linear

# One electron H bonds CH<sub>3</sub> with acceptor with HF, HCl, H<sub>2</sub>O and H<sub>2</sub>S



*Raghavendra and  
Arunan to be  
published*

Methyl radical with an unpaired electron can act as a hydrogen bond acceptor with H<sub>2</sub>S

Alkorta et al. reported theoretical work on CH<sub>3</sub>---HF  
*Ber. Bunsenges. Phys. Chem.* **102**, (1998) 429

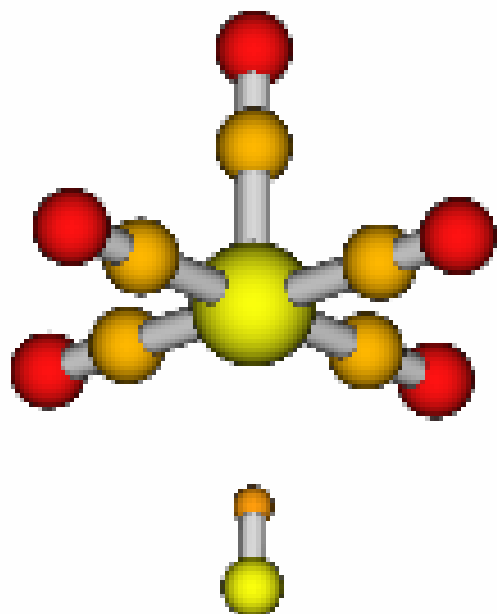


# Comparison of one electron hydrogen bond and conventional hydrogen bond

B3LYP/6-311++G\*\*

Dimer	Binding energy without bsse correction	Binding energy with bsse correction	Hydrogen bond length in Å	Bond angle of the hydrogen bond	Freq. shift in $\text{cm}^{-1}$
$\text{H}_3\text{C}\text{---}\text{HCl}$	-2.40	-2.62	2.112	179.9	+330.3
$\text{H}_2\text{O}\text{---}\text{HCl}$	-6.54	-5.826	1.855	179.0	+262.7

# $\text{Fe}(\text{CO})_5$ (IPC) as an acceptor



$\text{Fe}(\text{CO})_5\text{-HX}$  X = F/Cl  
F shows  $458\text{ cm}^{-1}$  red-shift  
Cl shows  $440\text{ cm}^{-1}$  red-shift  
At B3LYP/6-311++G\*\* level  
MW Experiments to be done

*Aiswaryalakshmi and Arunan to be published*

*Naresh Patwari*

*Rose-Petruck's group looked at solvated  $\text{Fe}(\text{CO})_5$  in benzene*

*And postulated  $\text{C}_6\text{H}_6$  coordinated in the 6<sup>th</sup> position*

# What is a hydrogen bond?

- Hydrogen bond acceptors could be lone pair,  $\pi$  pair, unpaired electrons, Rg atoms? Any electron rich region.
- Hydrogen bond donors could be H covalently bound to any atom with more electronegativity than H.
- Most of the existing definitions, including that of IUPAC do not reflect this.
- Analogous experimental and theoretical results on Li and Cl bonding\* are abundant.

*\*Guru Row will be talking about halogen bonding*

# IUPAC Task Group



- Ibon Alkorta (Madrid, Spain)
- Elangannan Arunan (Bangalore, India, Co-Chairman)
- David C. Clary (Oxford, UK)
- Robert H. Crabtree (Yale, USA)
- Joseph J. Dannenberg (CUNY, USA)
- Gautam R. Desiraju (Hyderabad, India)
- Henrik G. Kjaergaard (Otago, New Zealand)
- Pavel Hobza, (Prague, Czech republic)
- Roger A. Klein (Bonn, Germany)
- Karl Kleinermanns (Düsseldorf, Germany)
- Anthony C. Legon (Exeter, UK)
- Benedetta Mennucci (Pisa, Italy)
- David J. Nesbitt, (Colorado, USA)
- Joanna Sadlej (Warsaw, Poland)
- Steve Scheiner (Utah, USA, Co-Chairman)  
(Web conferencing planned )

# Aim of the project

- This project aims 1) to take a comprehensive look at intermolecular interactions and classify them and 2) to give a modern definition of the hydrogen bond, taking in to account all current experimental and theoretical information, and including hydrogen bonded systems both in gaseous and condensed phases as well as in chemical and biological systems.

# IUPAC Pisa Workshop September 2005



- 22 talks in 3 days
- 12 Task group members
- 10 Contributed speakers
- 17 participants

# IUPAC Bangalore Meeting 18 September 2006



- 4 Core members from task group + Scheiner - videoconferencing
- 5 External experts
- Core group to finalize the recommendations this week.
- All comments welcome

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# Acknowledgements

## IUPAC

- Bryan Henry, President
  - Fabienne Meyers, Publishing
  - Enid Weatherwax, Administrative
  - Linda Yapp, Accounting
  - Prof. S. Chandrasekaran, IISc.
- 
- IPC Department and IISc



A green balloon with a white grid pattern and a white string is positioned in the top left corner.

Thank you all for  
being here!

A blue balloon with a white grid pattern and a white string is positioned in the middle left area.

We will begin

