



HYDROGEN BOND RADII: FROM MICROWAVE SPECTROSCOPIC, AB INITIO AND AIM STUDIES

E. Arunan

Inorganic and Physical Chemistry Department
Indian Institute of Science
Bangalore. 560 012 INDIA

IUPAC DISCUSSION MEETING

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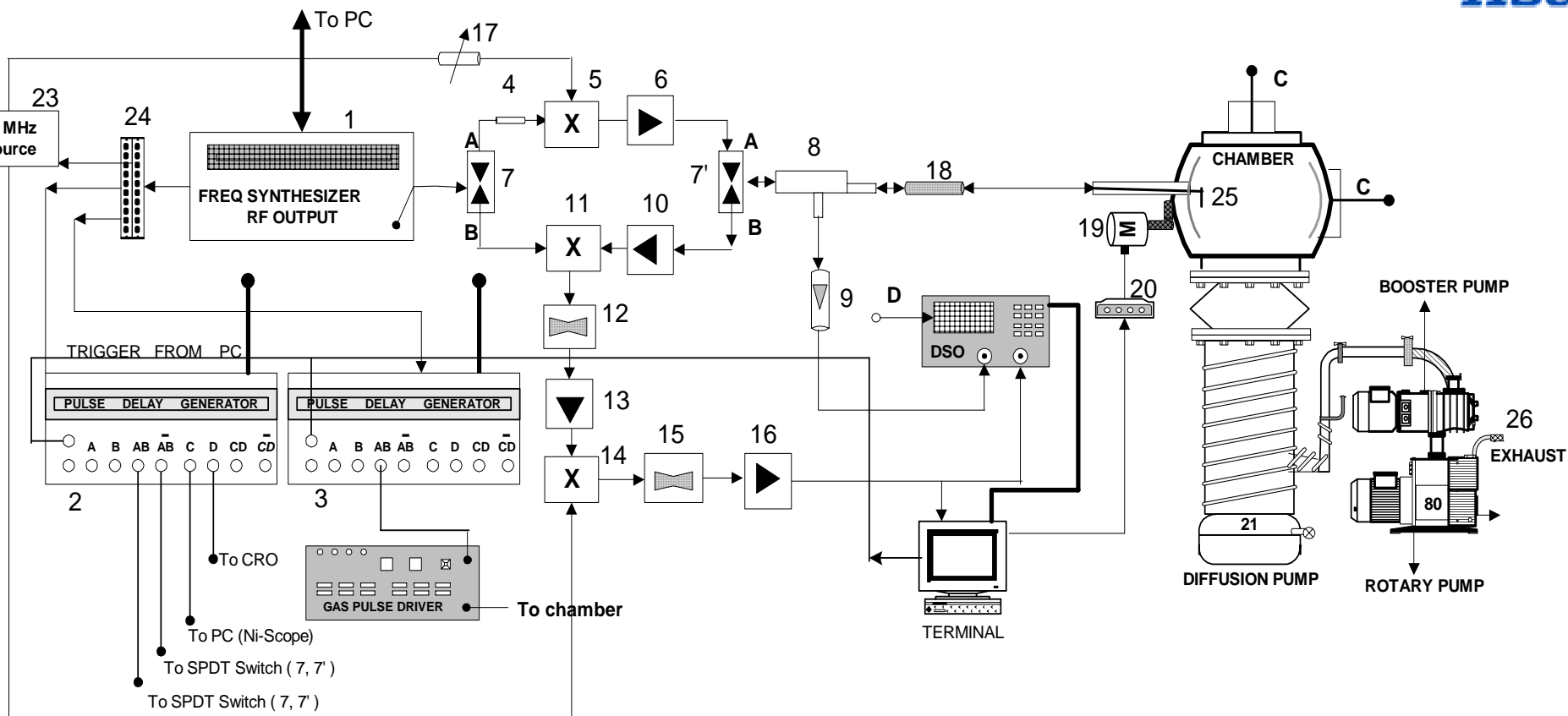
Acknowledgements

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Outline

- Pulsed Nozzle Fourier Transform Microwave Spectrometer.
- 'Hydrogen bonded complexes':
 - $C_2H_4-H_2S$ (S-H••• π)
 - Ar_2-H_2S (H bond?)
- Definition of a Hydrogen bond radius for several HX donors and acceptors:
 - Empirical, ab initio and AIM studies
- Recommended radii for H, C, F, N, O, S for strong, medium and weak hydrogen bonds
- Conclusions

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 $\leq 1\text{MHz}$ before digitization



Pankaj Mandal

$C_2H_4-H_2S$

- 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?

Rotational constants (MHz) for similar complexes



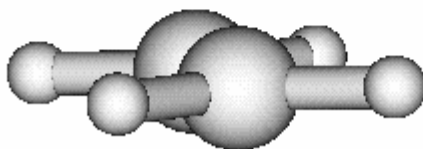
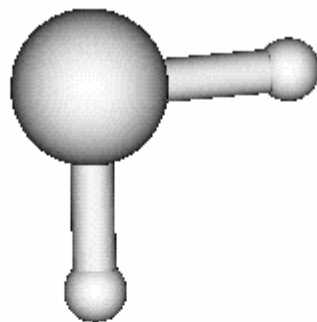
B	HF	H ₂ O	HCl	H ₂ S
Ar	3065.7	2988.2	1678.5	1681.4
Ar ₂	3576.5	3457.2	1733.9	1733.1
	1739.1	1731.8	1667.9	1617.7
	1161.0	1144.6	844.5	830.3
Ar ₃	1188.2	1172.1	843.9	819.0
C ₆ H ₆	2048.5	1994.8	1237.7	1168.5
C ₂ H ₄	24122	25960	25457	?
	4368.0	3823.6	2308.1	?
	3898.7	3452.1	2168.0	?

Weak acceptors

Strong acceptor

Moderate acceptor

MP2 level predictions



Constant (MHz)	6-31 G*	6-311 ++G**
A	22884	22945
B	1967	2000
C	1858	1917

Search for $C_2H_4-H_2S$

- $1_{01} \rightarrow 2_{02}$ for C_2H_4-HCl is at 8951.4 MHz
- Mausumi started searching for the same transition for $C_2H_4-H_2S$ from 8950 MHz down. Ab initio predictions at 7650 and 7834 MHz
- After a long, long search, she observed it at 7685.3 MHz (closer to C_2H_4-Ar 7655.7 MHz reported last year).
- Other lines could be predicted and observed.
- Each line was split in to four (two doublets).

Observed transitions for C₂H₄-H₂S



	Freq (MHz)	Res. (kHz)	Freq (MHz)	Res. (kHz)	Freq (MHz)	Res. (kHz)	Freq (MHz)	Res. (kHz)
0 ₀₀ -1 ₀₁	3839.2887	6.6	3839.5289	3.3	3842.5789	9.1	3842.8441	3.9
1 ₁₁ -2 ₁₂	7567.9895	2.0	7568.2071	-5.6	7573.8046	-5.1	7574.0447	-4.7
1 ₀₁ -2 ₀₂	7677.8746	4.2	7678.3620	6.5	7684.4786	12.1	7685.0082	3.1
1 ₁₀ -2 ₁₁	7779.9832	-1.5	7780.7434	0.8	7788.0750	-5.5	7788.9219	-5.1
2 ₁₂ -3 ₁₃	11350.9490	-3.6	11351.2883	-1.5	11359.7351	-6.7	11360.0947	-5.6
2 ₂₁ -3 ₂₂	11491.0770	-7.6	11491.8364	-7.1	11503.1952	-6.8	11504.0171	-10.2
2 ₂₀ -3 ₂₁	11492.4402	-5.8	11493.2019	-8.2	11504.5662	-9.1	11505.4004	-8.0
2 ₀₂ -3 ₀₃	11515.0758	4.4	11515.8051	10.9	11525.0275	10.1	11525.8346	15.0
2 ₁₁ -3 ₁₂	11668.8501	-1.7	11669.9797	-6.2	11681.0539	-5.2	11682.3206	-4.6
3 ₁₃ -4 ₁₄	15132.6796	-4.8	15133.1301	-2.6	15144.5033	-4.3	15144.9772	-6.4
3 ₂₂ -4 ₂₃	15319.6033	7.2	15320.6143	7.9	15335.8775	8.9	15336.9759	10.9
3 ₂₁ -4 ₂₂	15323.0052	6.4	15324.0305	8.4	15339.3111	9.8	15340.4269	10.0
3 ₀₃ -4 ₀₄	15350.1954	3.5	15351.1487	1.8	15363.5568	6.8	15364.6246	15.6
3 ₁₂ -4 ₁₃	15556.3646	-3.1	15557.8716	-3.5	15572.7576	-5.4	15574.4373	-6.9
4 ₁₄ -5 ₁₅	18912.7730	-0.5	18913.3293	-2.5	18927.7185	-1.5	18928.3108	-1.1
4 ₀₄ -5 ₀₅	19182.5398	0.09	19183.7196	0.2	19199.3912	-1.7	19200.6394	-6.2
4 ₁₃ -5 ₁₄	19442.0792	-1.6	19443.9559	-1.4	19462.7645	-1.3	19464.8552	-1.2

Fitted parameters for C₂H₄-H₂S

Parameters	L1	L2	U1	U2
A (MHz)	25961(34)	25968(42)	26189(55)	26204(61)
B (MHz)	1972.682(2)	1972.937(2)	1974.891(3)	1975.178(3)
C (MHz)	1866.658(2)	1866.646(2)	1867.732(3)	1867.715(3)
d ₁ (kHz)	-0.80(2)	-0.82(2)	-0.74(3)	-0.76(4)
d ₂ (kHz)	-0.21(2)	-0.22(2)	-0.24(3)	-0.24(3)
D _J (kHz)	14.30(2)	14.31(2)	13.26(3)	13.28(3)
D _{JK} (MHz)	1.0587(2)	1.0575(3)	0.9691(4)	0.9684(4)
Sd (kHz)	4.4	5.6	7.1	8.1

C_2H_4 -HDS/ H_2S studies



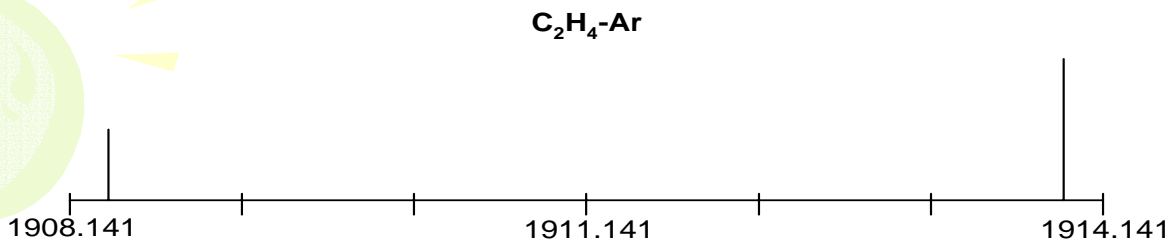
- D_2S showed both splitting, small became smaller and large became larger.
- HDS showed only the smaller splitting, comparable to D_2S .
- Obviously the smaller splitting is due to C_2H_4 tunneling.
- Larger splitting is due to internal rotation of H_2S . In general tunneling splitting decreases on deuteration.

Fitted Parameters for $C_2H_4-H_2^{34}S$, C_2H_4-HDS , $C_2H_4-D_2S$

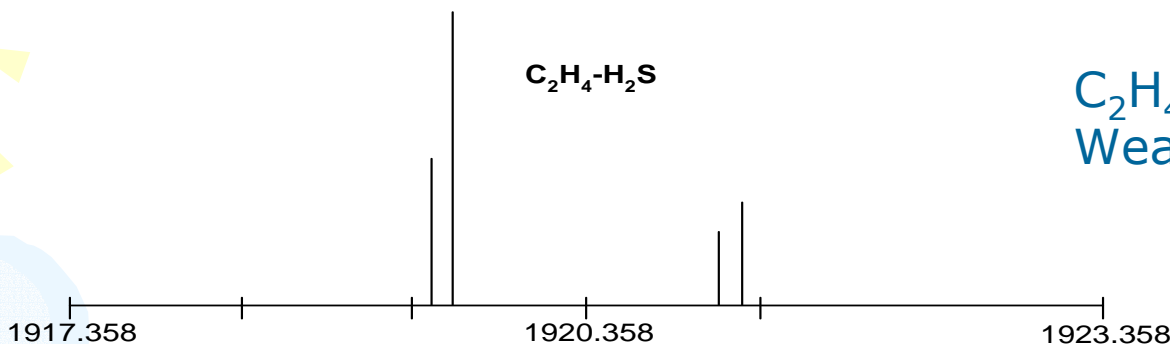


		A(GHz)	B(MHz)	C(MHz)	D_J (kHz)	D_{JK} (MHz)	Sd(kHz)
$C_2H_4-H_2^{34}S$	L1	25.9(16)	1922.87(1)	1822.06(1)	13.7(5)	1.011(17)	34.1
	L2	25.9(16)	1923.11(1)	1822.05(1)	13.8(5)	1.010(17)	35.0
	U1	25.9(14)	1924.73(1)	1822.85(1)	12.6(5)	0.928(15)	31.5
	U2	26.0(14)	1925.00(1)	1822.83(1)	12.7(5)	0.927(15)	30.9
$C_2H_4-D_2S$	L1	25.7(9)	1927.60(1)	1830.31(1)	11.9(2)	0.924(13)	45.5
	L2	25.6(9)	1927.67(1)	1830.30(1)	11.8(3)	0.925(13)	46.9
	U1	25.7(10)	1931.52(1)	1832.60(1)	12.0(3)	0.904(15)	53.4
	U2	25.7(10)	1931.60(1)	1832.60(1)	12.0(3)	0.904(16)	54.8
C_2H_4-HDS	L	25.9(10)	1964.60(1)	1859.51(1)	11.1(4)	0.882(18)	46.7
	U	25.9(10)	1964.68(1)	1859.50(1)	11.1(4)	0.882(18)	47.8

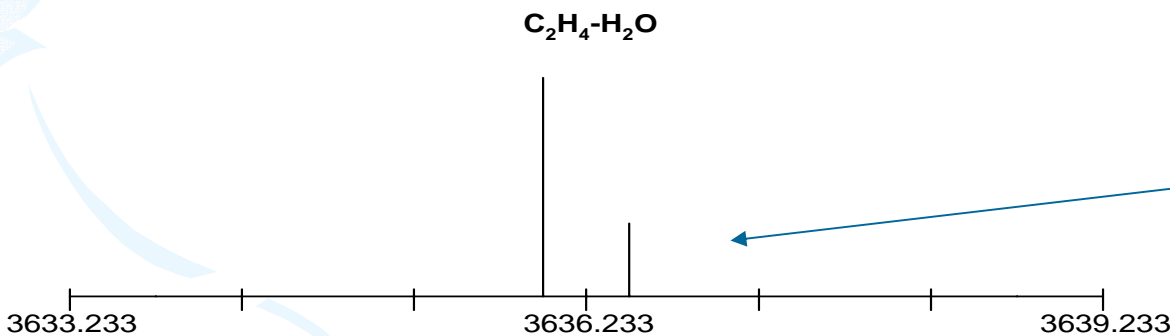
Intensity (Arbitrary unit)



C_2H_4 tunneling
Weak van der Waals bond



Both C_2H_4 and H_2S
Tunnel! Internal
Rotation!?



H_2O tunneling

Frequency (MHz)

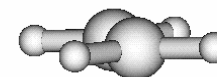
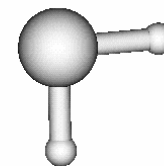
Other C_2H_4-HX ($X = F, Cl$) show no doubling of energy levels! Hydrogen bond is too strong. Larger the barrier smaller the splitting!

Splitting observed for H_2S , HDS and D_2S

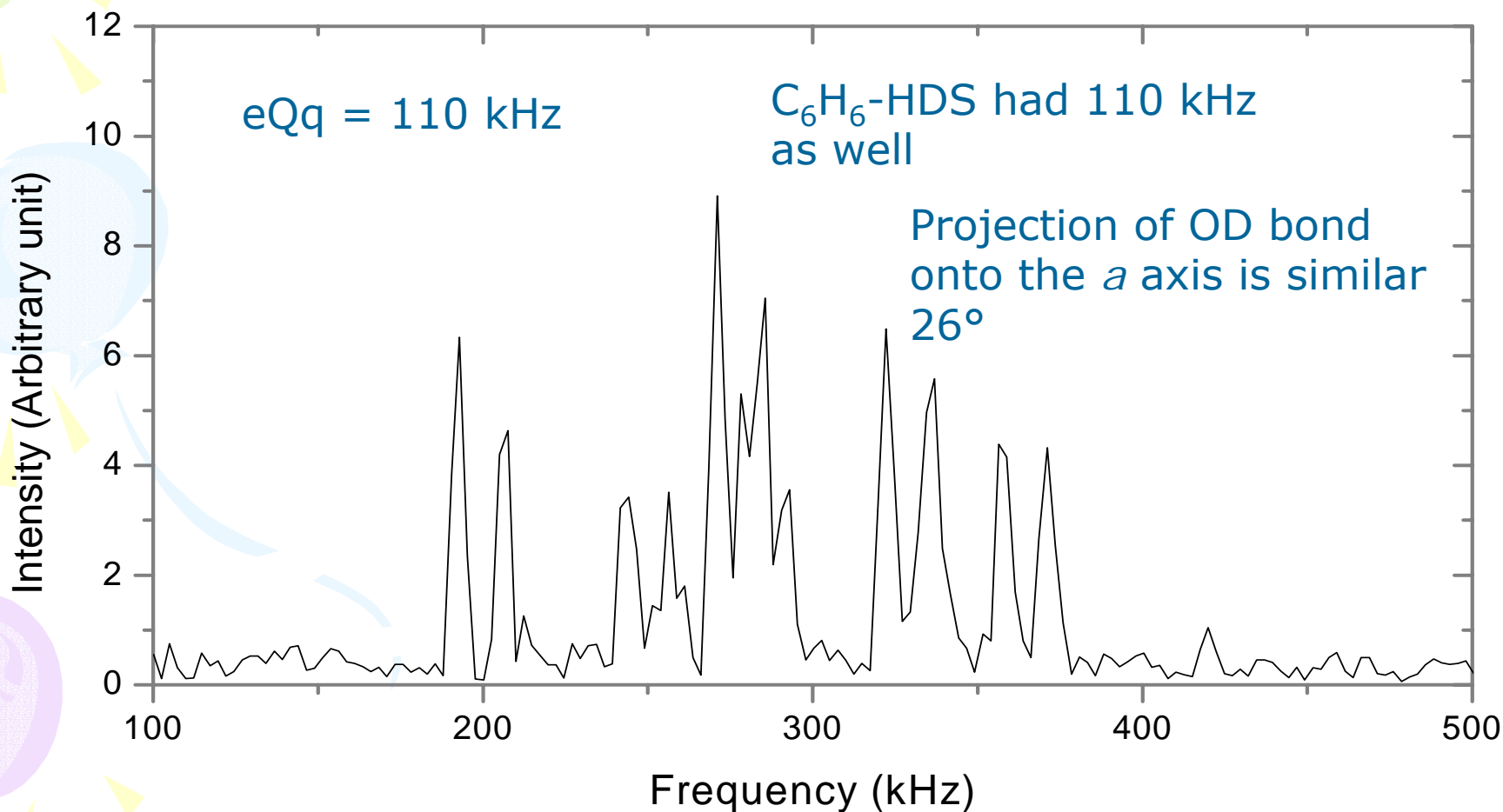
Isotop-Omer	Smaller MHz	Larger MHz
H_2S	0.14	1.67
H_2^{34}S	0.12	1.33
HDS	0.035	-
D_2S	0.035	3.11

SH bond in H_2S moves as C_2H_4 rotates

Deuterium bond is stronger than Hydrogen bond



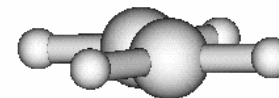
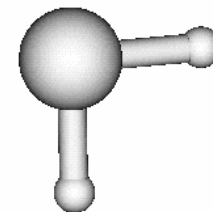
$J=0 \rightarrow 1$ spectrum of C_2H_4 -HDS showing D quadrupole coupling and C_2H_4 tunneling splitting



Substitution analysis

H₂S/HDS/D₂S/H₂³⁴S rotational constants can give substitution distances for both H and S from c.m.:

$$|r| = \left[\left(\frac{1}{2\mu} \right) (\Delta I_a + \Delta I_b + \Delta I_c) \right]^{\frac{1}{2}}$$



They are 1.034 Å, 1.852 Å, and 2.163 Å, respectively

Is $C_2H_4-H_2S$ a hydrogen bonded complex?



- Geometry is nearly the same as $C_2H_4-H_2O$
- Binding energy (kcal mol^{-1}) is less! MP2 results

	6-311++ G**	6-311++ G(3df,2p)	6-311++ G(3df,pd)	6-311++ G(3df,3pd)	Aug-cc- pVTZ
ΔE	-0.9	-1.53	-1.48	-1.43	-1.0
ΔE_{ZPE}	0.17	-0.75	-0.68	-0.63	-0.63
BSSE	1.26	0.59	0.61	0.81	1.21

S-H stretching frequency



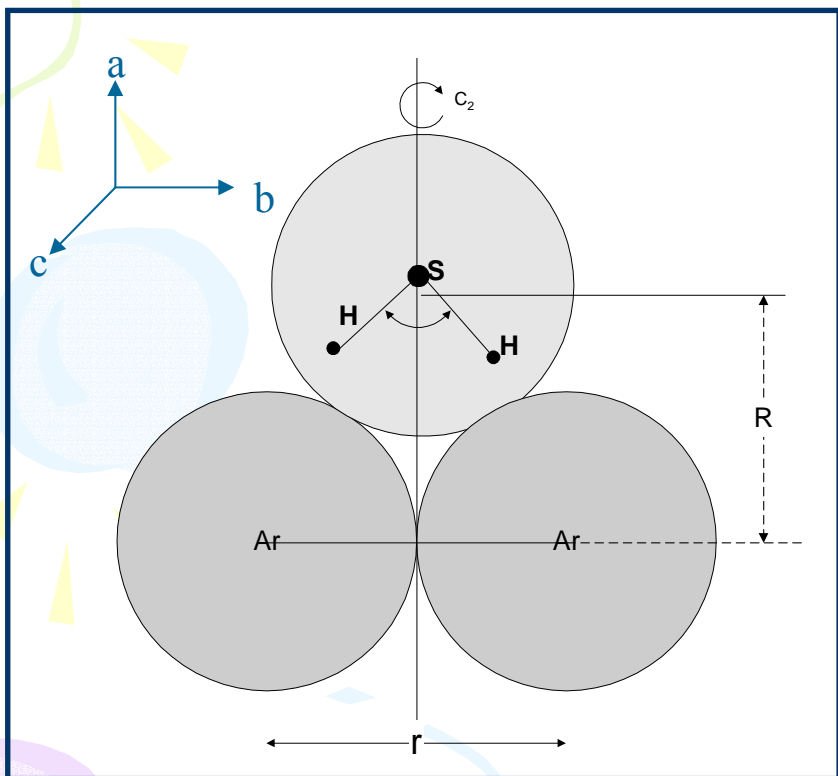
	S-H symmetric stretching	S-H asymmetric stretching
H ₂ S	2818	2838
Ar-H ₂ S	2817	2836
Ar ₂ -H ₂ S	2818	2837
H ₂ S-H ₂ S(a)	2817	2836
H ₂ S-H ₂ S(d)	2806	2830
C ₂ H ₄ -H ₂ S	2807	2829

Thiophenol in benzene solution shows a 16 cm⁻¹ red shift!

$\text{Ar}_2\text{-H}_2\text{S}$

- $\text{Ar}_m\text{-H}_2\text{O}$ complexes have been investigated in detail.
- Studies on analogous H_2S complexes would be useful for proper understanding
- Are these hydrogen bonded or van der Waals complexes?

Ar₂-H₂S asymmetric top

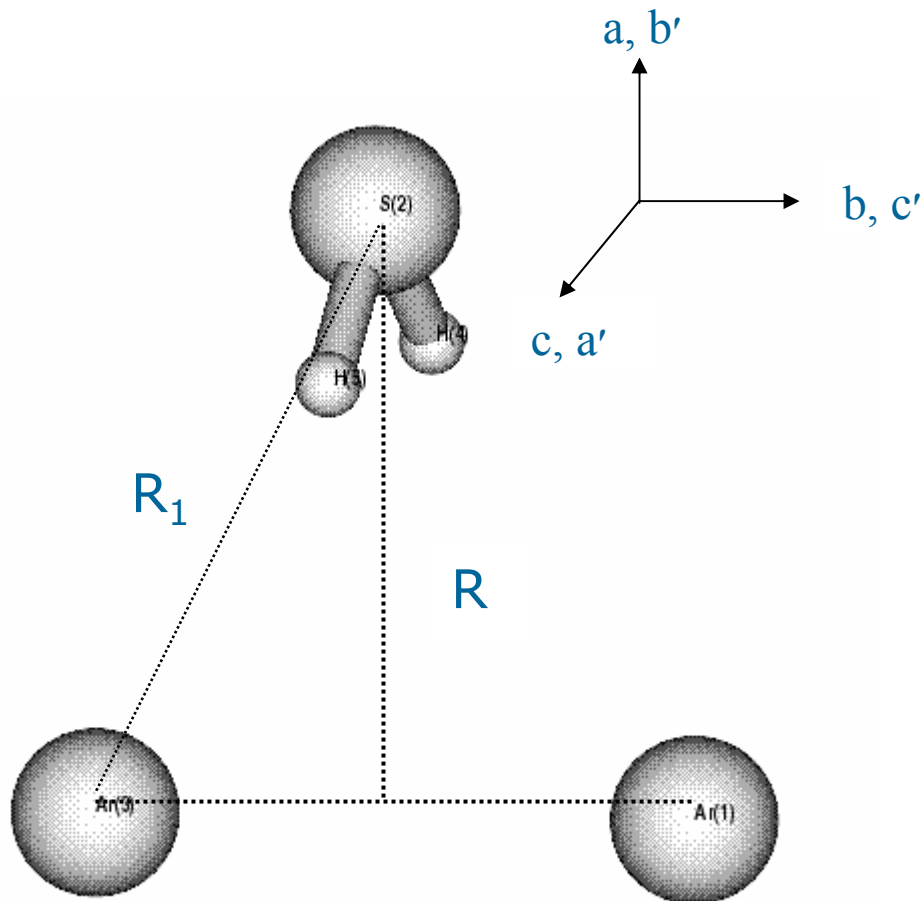


❖ Assuming H₂S to be effectively spherical, implies that only *a* dipole is present

$$ee \leftrightarrow eo \text{ and } oo \leftrightarrow oe$$

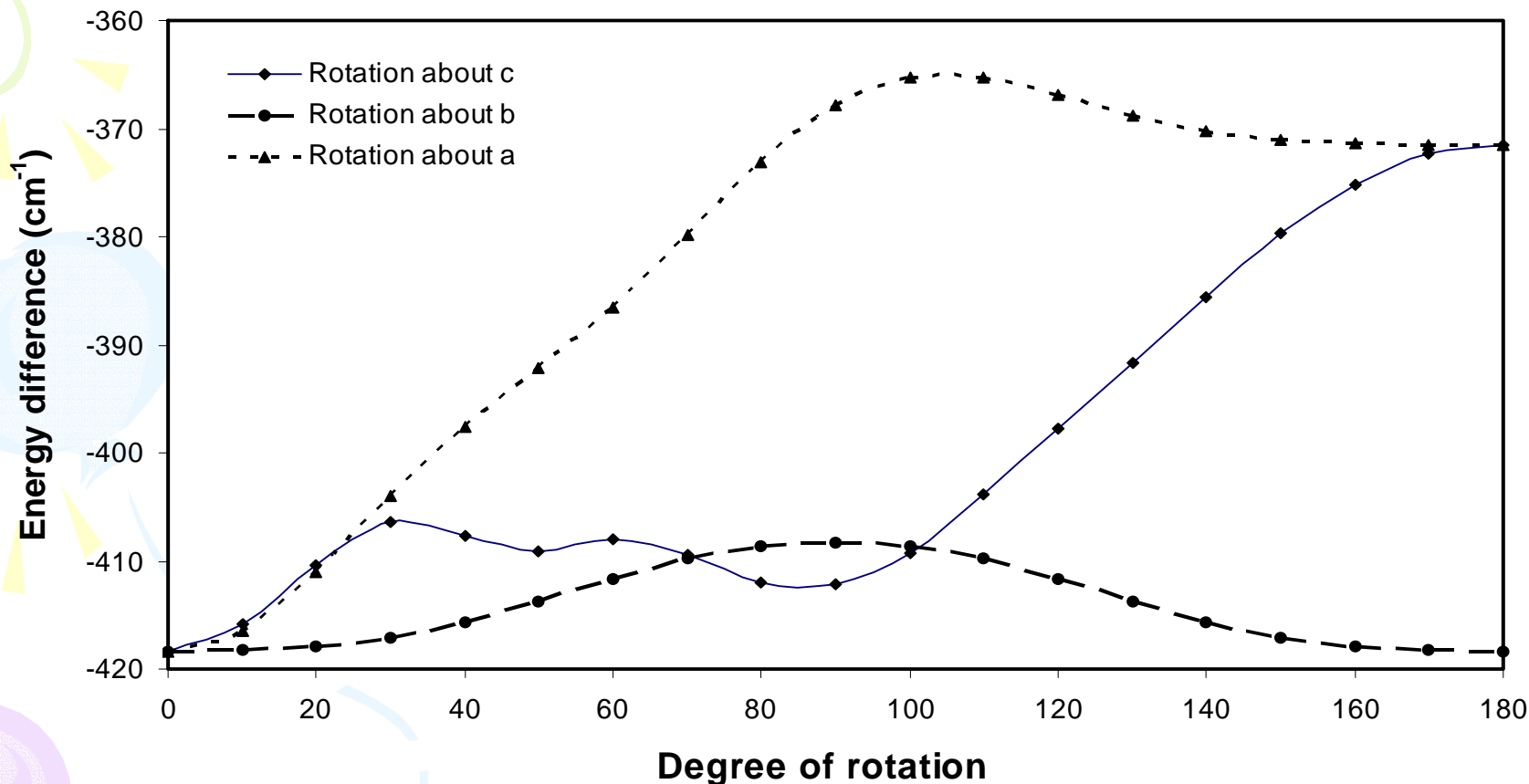
❖ C_{2v} symmetry and two indistinguishable Ar nuclei imply that some rotational levels will be missing

oo and *oe* levels are not allowed.

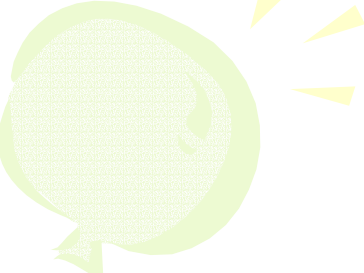


The Ar_2 center to H distances are 1.547 Å and 1.401 Å
Both H are closer to Ar_2

Barrier for internal rotation of H₂S



Potential is anisotropic, rotation about axes that break "H bonds" have higher barrier



Now that we have reliable distances, what do we do with them?



Can we determine a hydrogen bond radius?

Pauling defined different radii for atoms



(L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1960)

Covalent Radius

Ionic Radius

Metallic Radius

van der Waals Radius

Bonding:

Covalent

Ionic

Metallic

van der Waals

Hydrogen bonding

Is there a Hydrogen bond radius??

CAN THERE BE A HYDROGEN BOND RADIUS?



- Jeffrey in his book "Introduction to hydrogen bonding" Oxford University Press 1997, page 14 comments:
"it is not possible to separate hydrogen bond distances into hydrogen bond atomic radii, as Pauling did so successfully for covalent and ionic radii in *The Nature of Chemical Bond*"

CAN THERE BE A HYDROGEN BOND RADIUS?



- A. J. Stone in his book "The Theory of Intermolecular Forces" Oxford University Press 1996, page 116 comments on the Buckingham-Fowler (Can. J. Chem. 1985) model: "The Hydrogen atom forming the hydrogen bond is not assigned a radius; it is contained within the van der Waals sphere of the heavy atom to which it is attached"

Why no hydrogen bond radius so far?

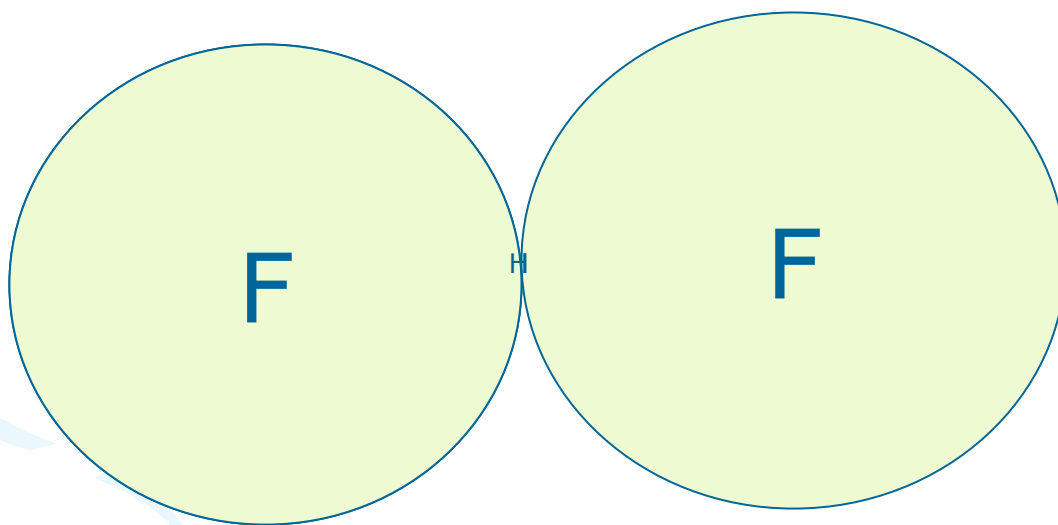


- Unlike other 'bonding' involving two atoms, hydrogen bond involves at least 3 if not more, $X-H\cdots Y$.
- Li Bian (JPC-A 2003, **107**, 11517) says H bond donors dominate the properties and acceptors don't. Can we define it for various donors?

Is that the only problem?

- No, locating H is not easy. X-ray data is unreliable.
- Neutron data is reliable but scarce.
- Microwave structural data are limited to gas phase complexes. Location of H is difficult, but possible.
 - Quadrupole coupling, dipole moment, spin-spin coupling and rotational constants

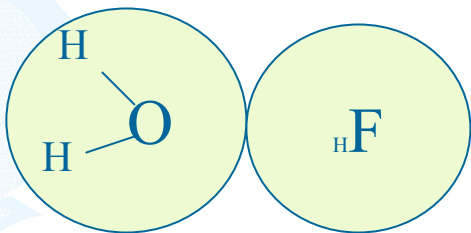
Pauling's H bond FHF⁻



Two F⁻ interacting simultaneously with H⁺
Size of H⁺ is 0.66 fm. F-F distance nearly the
twice the fluoride ion radii

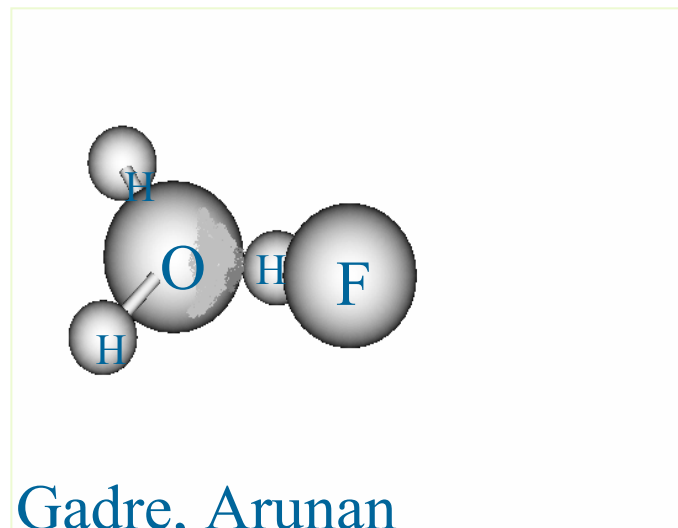
What about HF complexes?

Which of the two cartoons represent $\text{H}_2\text{O}\cdots\text{HF}$ complex truly?



Buckingham and Fowler

van der Waals spheres of F and O
in contact. H is immersed in F



Gadre, Arunan

Hydrogen occupies some space

H in HF is certainly not H^+

B---HX

B: H-bond acceptor **HX:** Donor



Buckingham and Fowler interpreted the intermolecular distances between A and HX as the sum of the van der Waals radii of A and X.

(*Can. J. Chem.* 1985, 62, 2018)

B	B---HF		B---HCl		B---HBr	
	r(A---F)	$\sigma(A) + \sigma(F)$	r(A---Cl)	$\sigma(A) + \sigma(Cl)$	r(A---Br)	$\sigma(A) + \sigma(Br)$
H ₂ S	3.246	3.20	3.809	3.65	3.991	3.80
HCN	2.805	2.85	3.405	3.30	3.610	3.45
CH ₃ CN	2.751	2.85	3.294	3.30	3.494	3.45
H ₂ O	2.684	2.75	3.215	3.20	3.414	3.35
H ₃ N	2.71	2.85	3.136	3.30	3.255	3.45

A is the atom in B, H-bonded to HX. For B---HF, r(A---X) is within 0.1 Å of the sum of the van der Waals radii of A and X. For B---HCl and B---HBr it is within 0.2 Å or more.



*Do A---H distances mean anything?

Gadre and Bhadane

- $R_{A-H} = R_E(A) + R_V(H)$

$R_E(A)$ is the distance from the acceptor atom/centre to the electrostatic minimum in the monomer

$R_V(H)$ van der Waals radius of H

JCP 107, 5625 (1997)

Mandal and Arunan

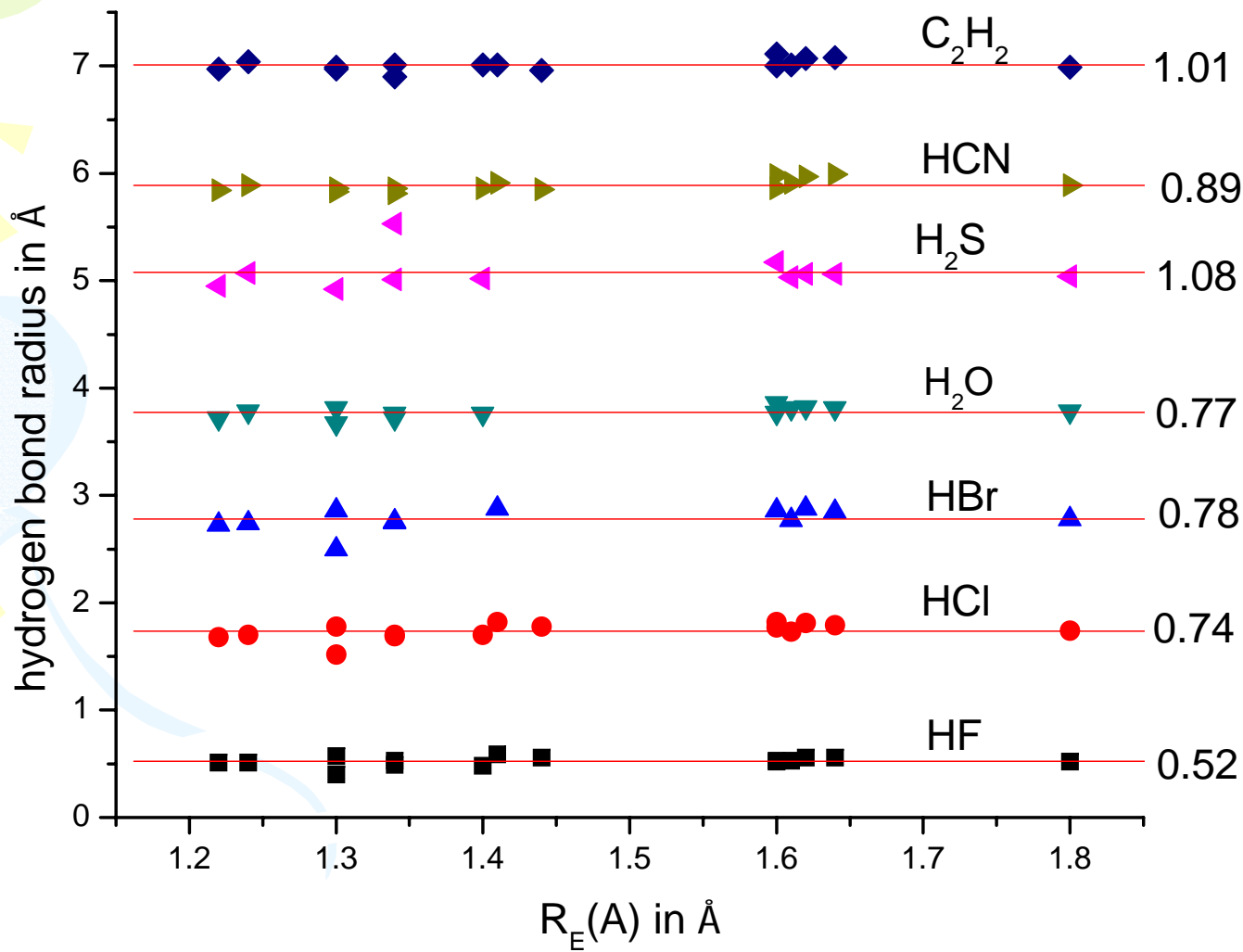
- $R_{A-H} = R_E(A) + R_H(DH)$

$R_E(A)$ is the distance from the acceptor atom/centre to the electrostatic minimum in the monomer

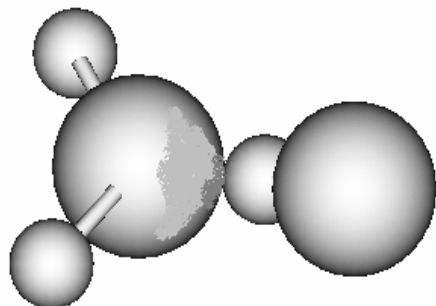
$R_H(DH)$ is the hydrogen bond radius for DH

JCP, **114**, 3880 (2001) Empirical analysis with experimental distances and theoretical $R_E(A)$

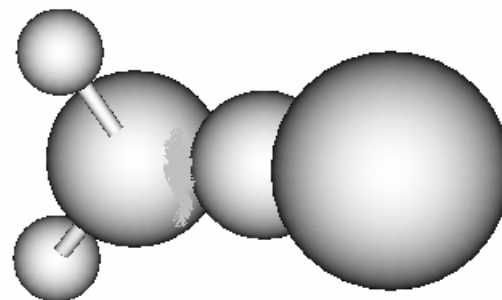
$R_{A-H} - R_E(A)$ vs $R_E(A)$ plots



Models of $\text{H}_2\text{O} \cdots \text{HX}$



$\text{H}_2\text{O} \cdots \text{HF}$



$\text{H}_2\text{O} \cdots \text{HCl}$

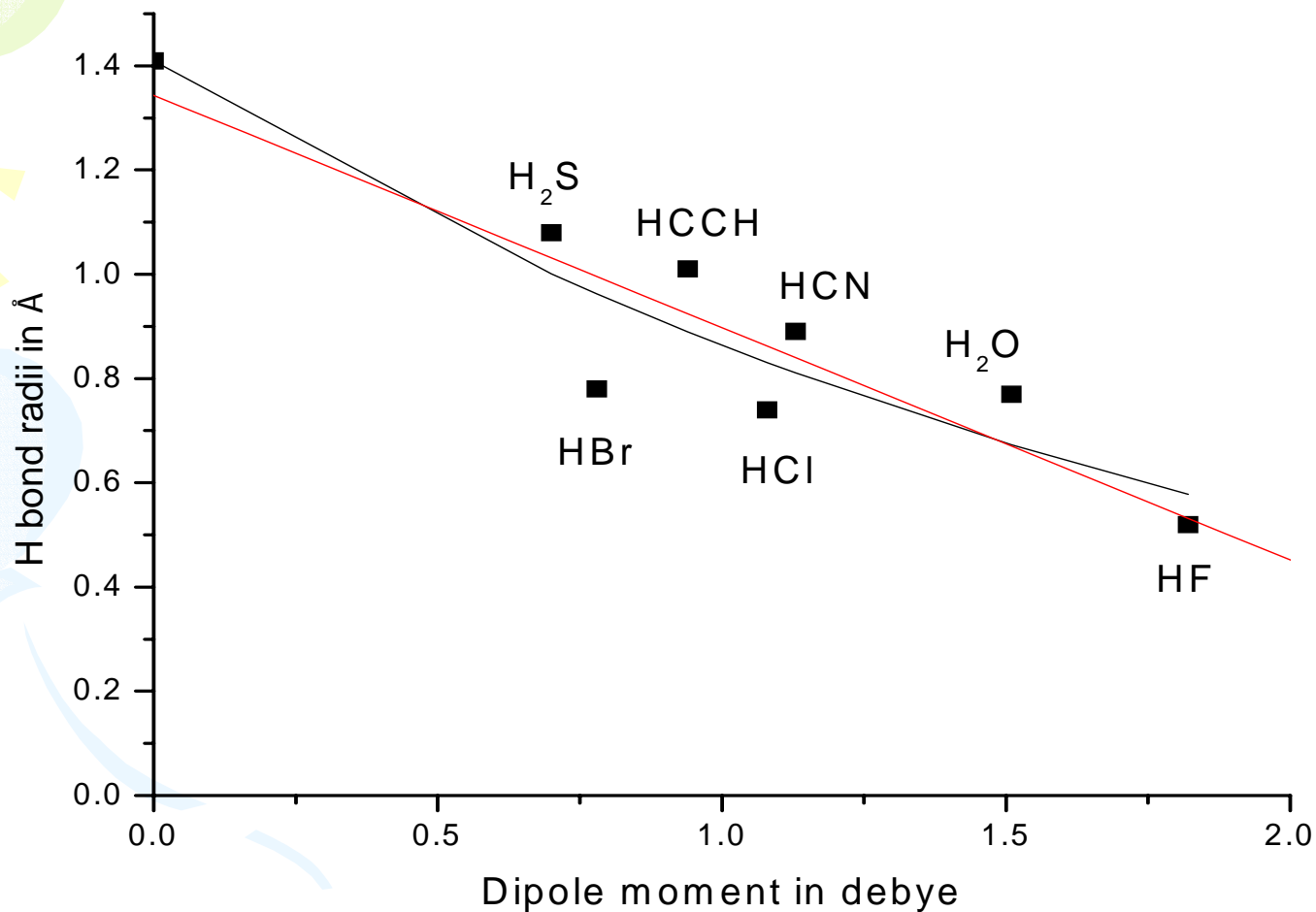


$\text{H}_2\text{O} \cdots \text{HBr}$

Hydrogen in HX has certain effective size(r_{eff}) and it increases from HF to HI.

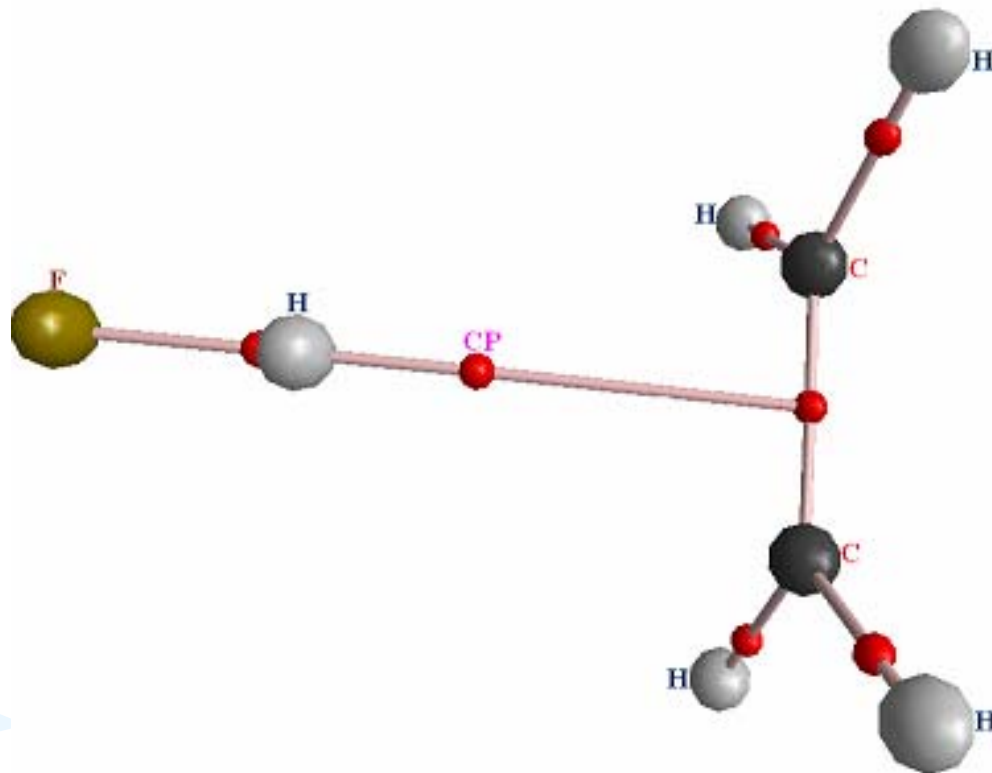
(Figures are not to scale)

Hydrogen bond radius vs dipole moment



Covalent radius of H is 0.32 Å van der Waals radius of H atom 1.2 Å
Hydride ion radius is 1.5 Å

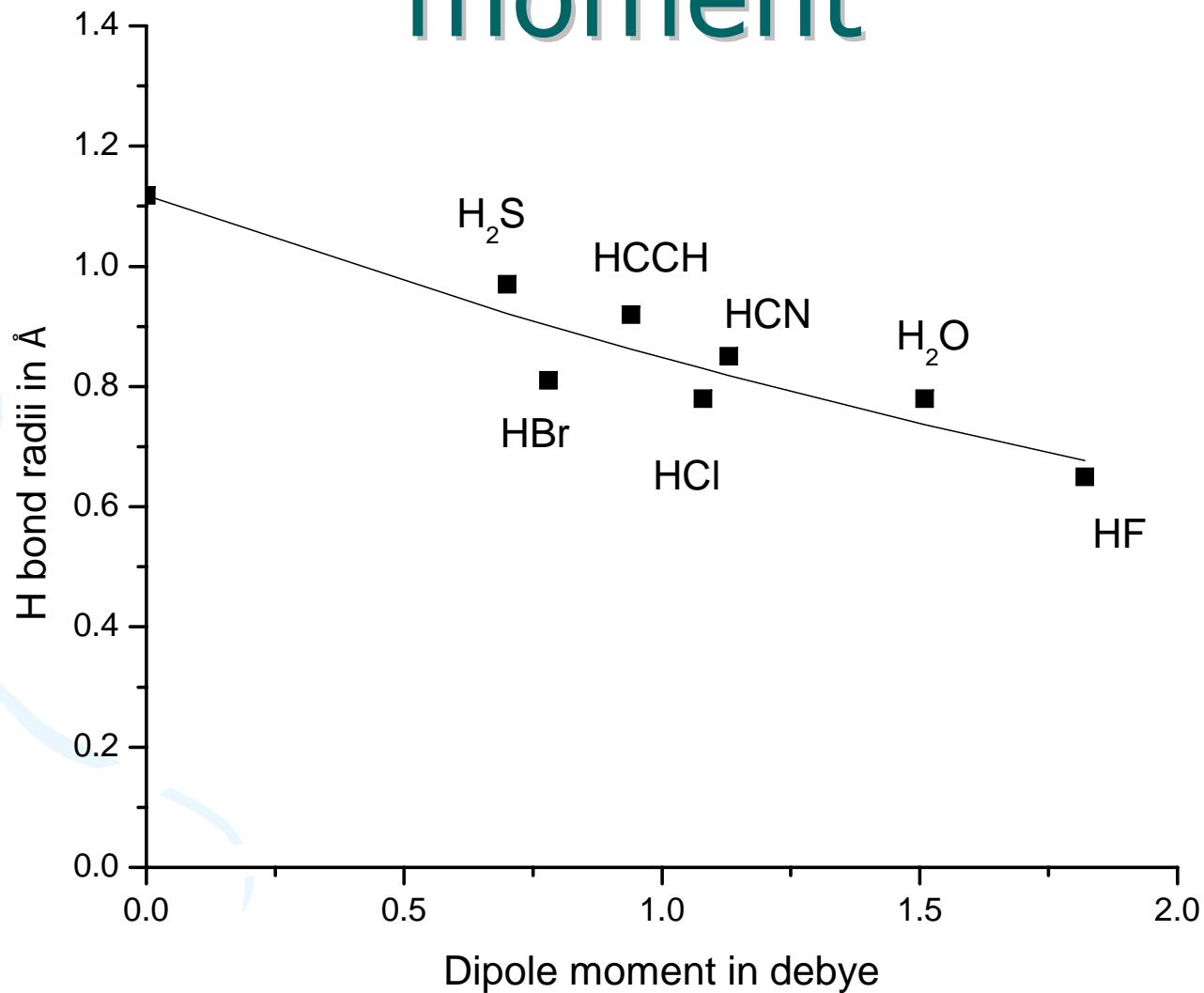
Atoms in Molecules Theory and Hydrogen bond radius



The average distance between H and CP could be compared to the H bond radius

The distance between acceptor atom/centre and CP can be compared to $R_E(A)$ assumed to be constant in ab initio/empirical analysis

H bond radius vs dipole moment

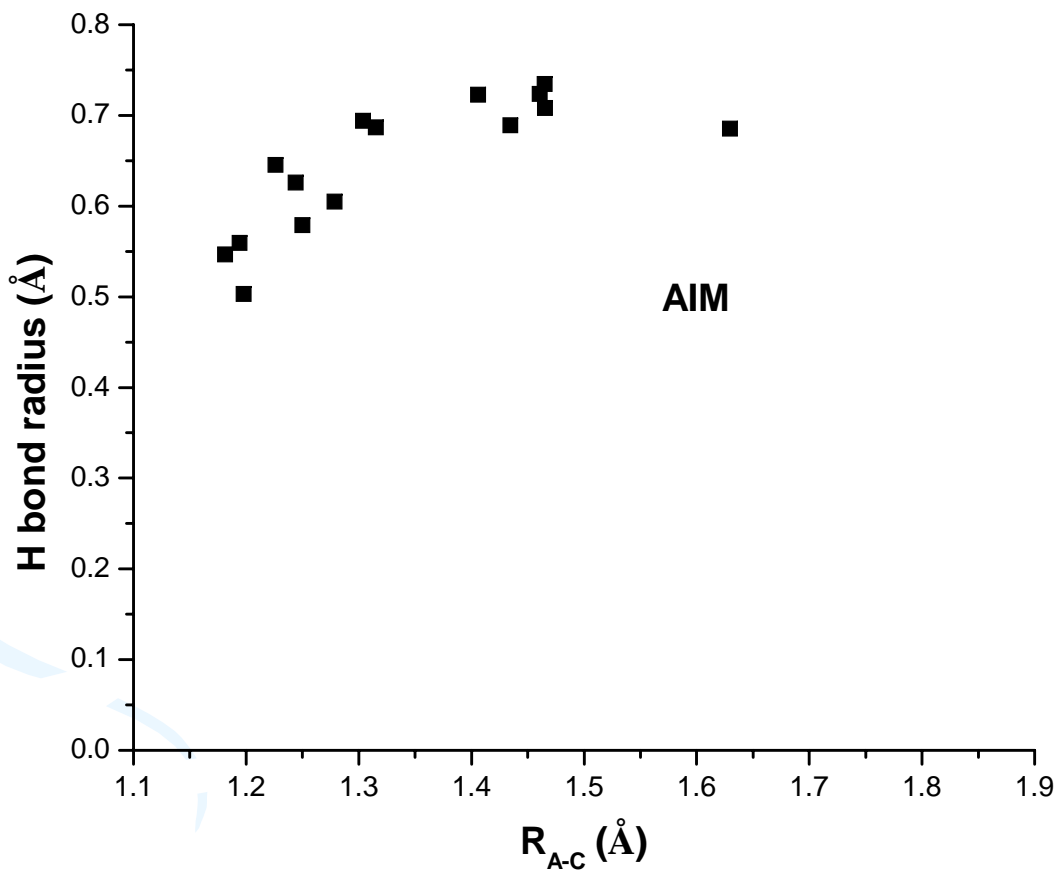


Comparison

Donor	Empirical	<i>Ab initio</i>	AIM
HF	0.51 ± 0.09	0.52 ± 0.04	0.65 ± 0.07
HCl	0.70 ± 0.10	0.74 ± 0.08	0.78 ± 0.09
H ₂ O	0.75 ± 0.09	0.77 ± 0.05	0.78 ± 0.08
HBr	0.77 ± 0.13	0.78 ± 0.11	0.81 ± 0.11
HCN	0.89 ± 0.12	0.89 ± 0.05	0.85 ± 0.08
HCCH	1.07 ± 0.08	1.01 ± 0.05	0.92 ± 0.07
H ₂ S	--	1.08 ± 0.16	0.97 ± 0.13
DH ^{av}		1.41	1.12

For *ab initio* and AIM R_{A---H} distance is the same. The fact that H bond radius is smaller for weak Donors such as HCCH and H₂S implies the Acceptor radius must be larger

AIM Results



Donor radius plateaus, approaches a maximum always below Van der Waals radius of H atom

Table V. Comparison of $R_E(A)$ for the monomers with R_{A-C} from AIM theoretical calculations.

Accetor	$R_E(A)$	$\langle R_{A-C} \rangle$	$R_{A-C} (1)$	$R_{A-C} (2)$	$R_{A-C} (3)$	R_{A-C}^{\oplus}
H ₂ O	1.22	1.29 ± 0.07	1.18	1.26	1.36	1.43±0.07
H ₂ CO	1.24	1.32 ± 0.08	1.19	1.28	1.40	
HF	1.30	1.32 ± 0.05	1.23	1.32	1.36	1.43±0.05
H ₃ N	1.30	1.33 ± 0.10	1.20	1.26	1.44	1.48±0.13
CH ₃ CN	1.34	1.38 ± 0.08	1.25	1.35	1.46	1.55±0.08
SO ₂	1.34	1.36 ± 0.12	1.24	1.31	1.37	
HCN	1.40	1.42 ± 0.08	1.28	1.38	1.48	
N ₂ O	1.41	1.38 ± 0.04	1.32	1.37	1.42	
CO ₂	1.44	1.38 ± 0.06	1.30	1.37	1.44	
OC	1.60	1.60 ± 0.09	1.43	1.58	1.68	
N ₂	1.60	1.51 ± 0.06	1.41	1.50	1.57	
*C ₃ H ₆	1.61	1.55 ± 0.08	1.47	1.50	1.64	
*C ₂ H ₂	1.62	1.60 ± 0.07	1.46	1.57	1.67	1.76±0.07
*C ₂ H ₄	1.64	1.60 ± 0.08	1.46	1.57	1.69	1.77±0.09
H ₂ S	1.80	1.76 ± 0.07	1.63	1.73	1.83	1.91±0.07

1 for HF, 2 for HCl, HBr and H₂O and 3 for HCN, HCCH and H₂S

SIGNIFICANT OBSERVATIONS



- Both donor and acceptor radii are different for strong, medium and weak hydrogen bonds.
- Using a single van der Waals radius should be discouraged.
- Results from 105 complexes have been condensed to recommend donor and acceptor radii for several atoms

H bond radii for donor and acceptor atoms



Atom	Strong	Medium	Weak	Limit [®]	Pauling
H	0.73	0.89	1.07	1.26	1.20
F	1.23	1.32	1.36	1.43	1.35
O	1.25	1.32	1.40	1.43	1.40
N	1.24	1.33	1.46	1.55	1.50
C [*]	1.46	1.55	1.67	1.77	1.70
C	1.43	1.58	1.68	1.77	
S	1.63	1.73	1.83	1.91	1.85

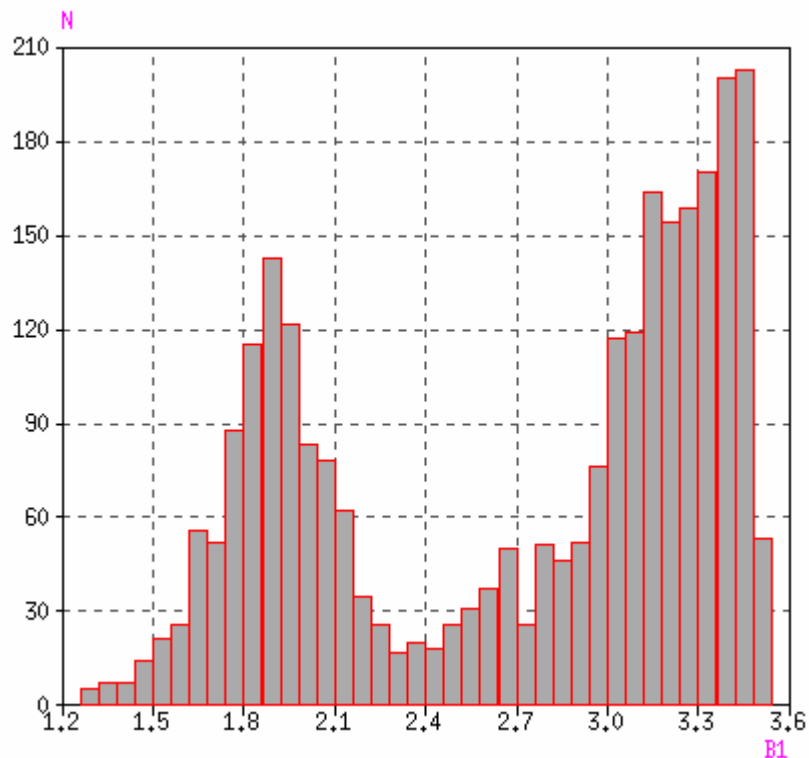
Strong for HF, medium for HCl, HBr and H₂O and weak for HCN, HCCH and H₂S Raghavendra, Mandal and Arunan PCCP accepted for publication

What about condensed phase?



- Is hydrogen bond radii transferable to condensed phase?
- Can we determine it for NH donors for which gas phase data are scarce?
- CCSD analysis answers in the affirmative for both questions

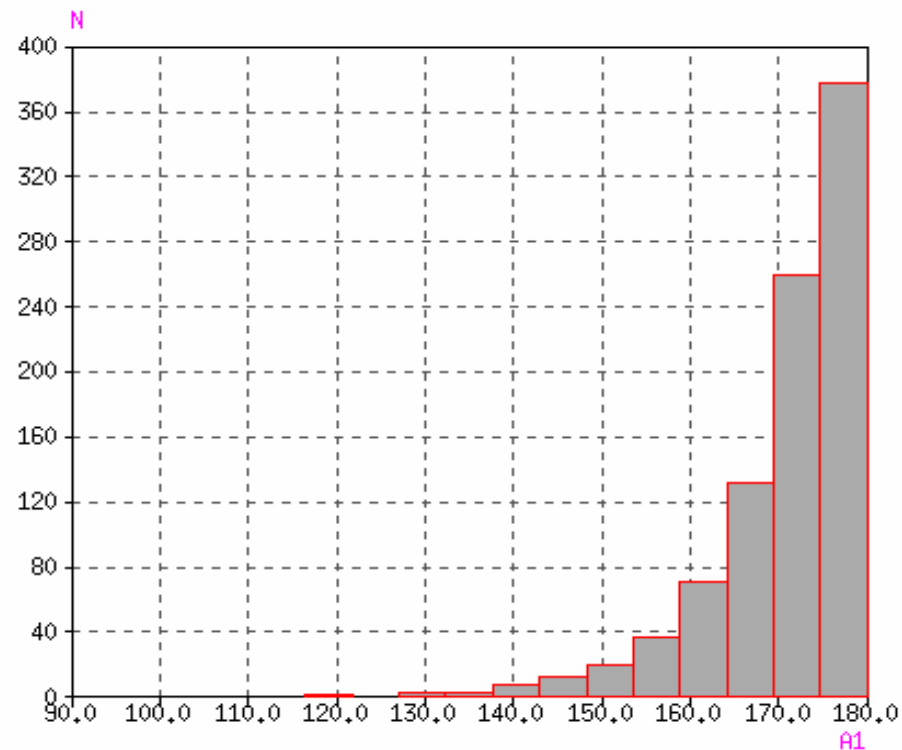
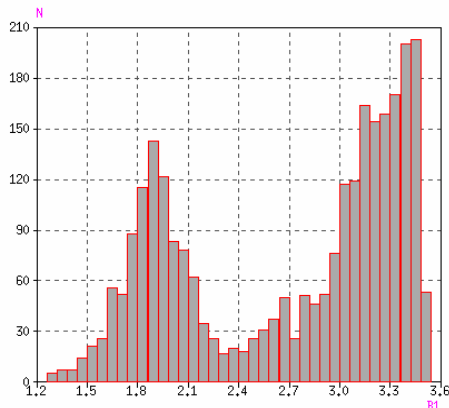
N•••H distance in O-H---pyrdinic N contact



The peak distance could be used to determine the H bond radius

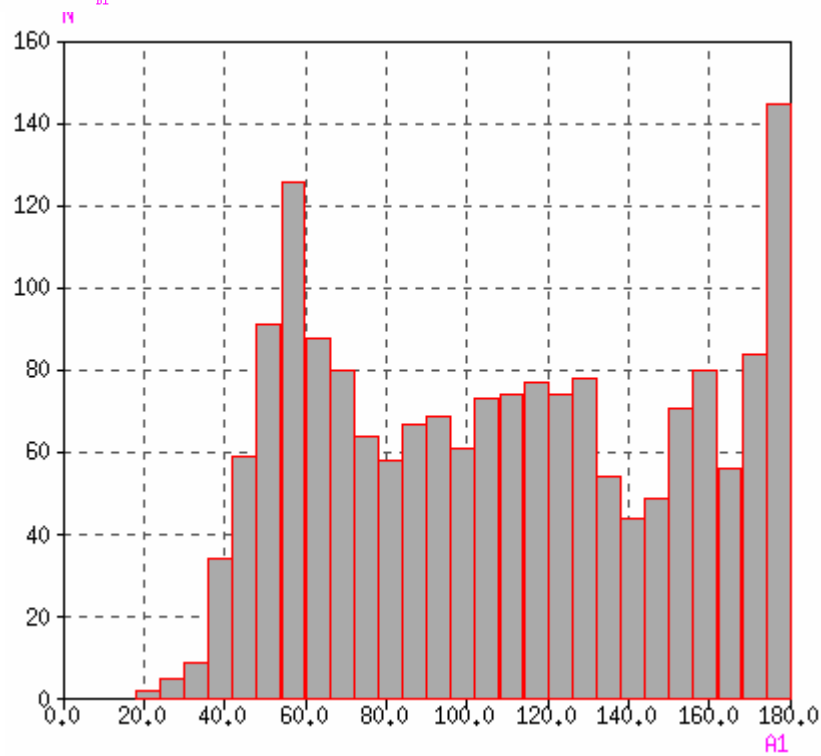
Important observations

- For OH, the condensed phase radius is typically 0.1-0.2 Å smaller than that of gas phase.
- For CH, the radii for condensed phase and gas phase are closer.
- For NH, the radius from condensed phase data yields 0.8 ± 0.1 Å
- Directionality is observed for all!



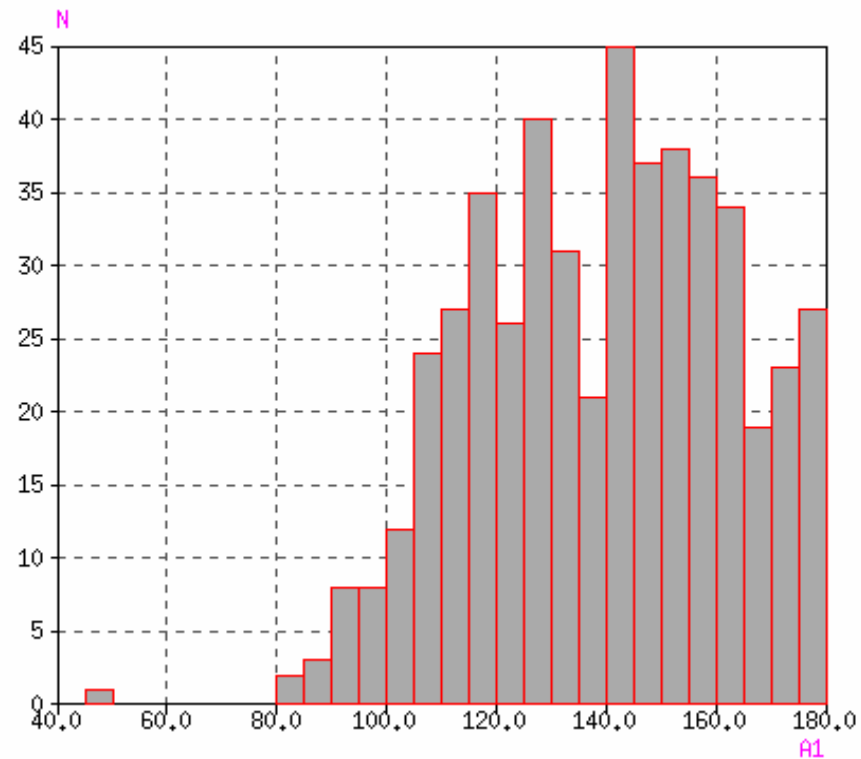
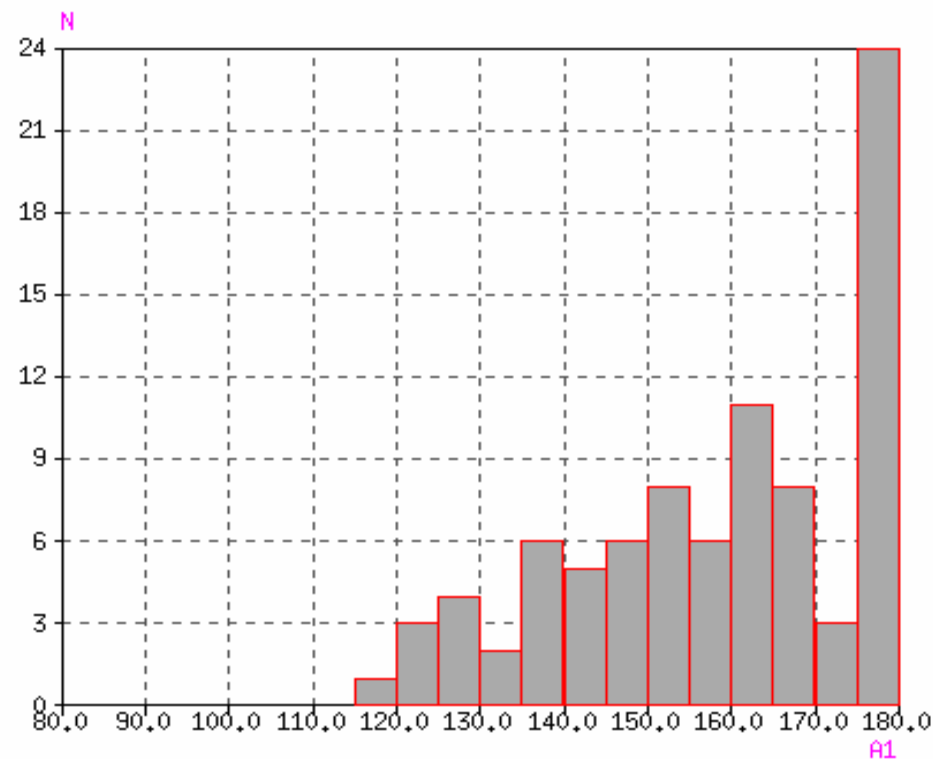
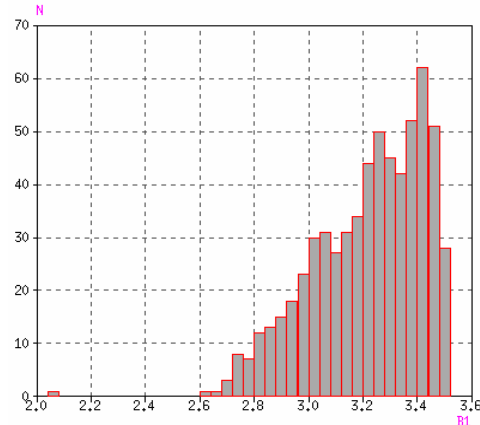
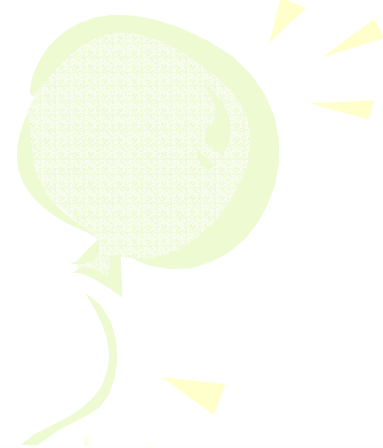
PyN---H-O

Hydrogen bond peak



PyN---H-O

($B_1 > 2.4 \text{ \AA}$)



$(B_1 > 2.6-3.0 \text{ \AA})$



$(B_1 > 3.0-3.5 \text{ \AA})$

Is H bond radius real?

- Klein, has come to similar conclusions recently based on electron density topology
 - R. Klein J. Computational Chem. 2003, Chem. Phys. Lett. 2006
- Gillespie has come to a similar conclusion i.e. the radius of H is different for OH, NH and CH by analyzing structural data for several ligands and they are amazingly close
 - Gillespie Inorg. Chem. 2004

Is H bond radius needed?

- Desiraju and Steiner's book argues that there can be H bonds at C-O distances of 3.25 to 3.3 Å

- According to our H bond radius

$$\begin{aligned}R_{\text{C-O}} &= R_{\text{CH}} + R_{\text{H}}(\text{CH}) + R_{\text{H}}(\text{CO}) \\ &= 1.0 + 1.1 + 1.4 = 3.5 \text{ \AA}\end{aligned}$$

Is H bond radius needed?

- A recent paper from JACS (2006), 128, 10646-10647 titled "A single CH/ π weak hydrogen bond governs stability and the photocycle of the photoactive yellow protein" notes the following:

The C-C distance is 3.78 Å, greater than the reported value for the CH/ π hydrogen bond 3.5 (no reference). For this hydrogen bond we get

$$\begin{aligned} R_{\text{C-C}} &= R_{\text{CH}} + R_{\text{H}}(\text{CH}) + R_{\text{H}}(\text{C}) \\ &= 1.0 + 1.1 + 1.7 = 3.8 \text{ \AA} \end{aligned}$$

Did any one else think about hydrogen bond radius Before?



Acta Cryst. (1962). **15**, 758

Hydrogen-Bond Radii

BY S. C. WALLWORK

Department of Chemistry, University of Nottingham, England

(Received 23 October 1961)

A table of classified average intermolecular hydrogen-bond distances ($Y-H \cdots Z$) is presented. It is shown that these average distances can be represented, to a sufficient degree of accuracy, by the sums of two hydrogen-bond radii, one a constant for each donor group $Y-H$ and one a constant (approximately equal to the van der Waals radius) for each acceptor group Z .

Wallwork assumed that the heavy atom distances are sum of van der Waals radii of acceptors and H bond radii of donors. However, he was disappointed not to find any correlation with the donor properties

Conclusions

- A home-made PNFTMW spectrometer has been used to obtain rotational spectrum for several H_2S complexes.
- $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ and $\text{Ar}_2\text{-(H}_2\text{S)}$ complexes have been identified.
- Both these complexes may be classified as hydrogen bonded, depending on the definition used.
- A hydrogen bond radius has been defined. Consistent with both gas phase and condensed phase structural data.
- Using van der Waals radii for confirming/ruling out hydrogen bonding could be misleading

Evolving definition of hydrogen bond



- Hydrogen bonding occurs when a hydrogen that is covalently bonded to an atom, has an attractive interaction with another electron-rich region either within the same or with another molecular entity
- The hydrogen bond is an attractive interaction between a group D–H and an atom or a group of atoms A, in the same or different molecules, when there is evidence of such bond formation.

Three stylized balloons are positioned on the left side of the slide. The top balloon is green, the middle one is light blue, and the bottom one is purple. Each balloon has a white string and several yellow triangular shapes radiating from its base, suggesting light or movement.

Thanks for listening

NH and SH groups

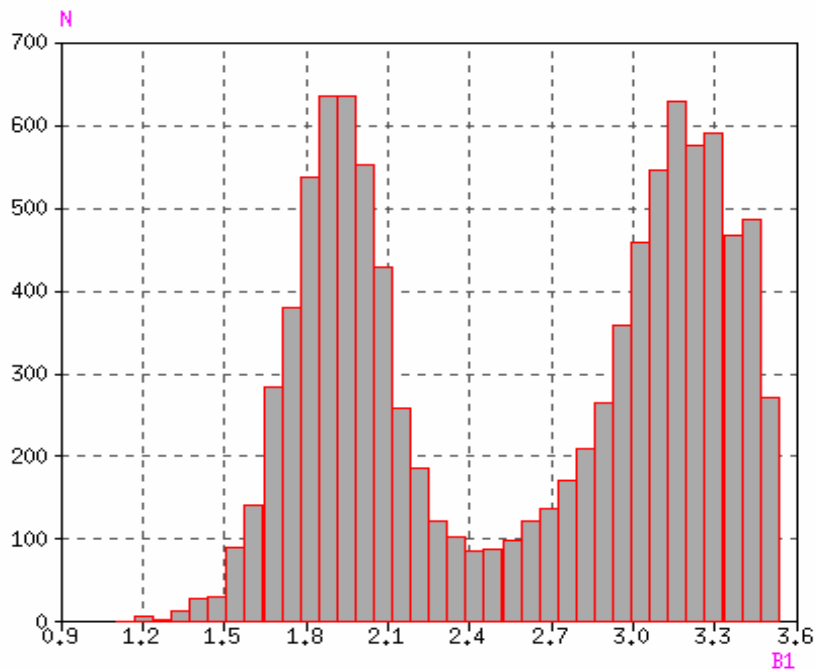
- Gas phase data do not exist. And there is not much hope of generating a data base either!
- NH_3 acts as a proton donor in only two cases $(\text{NH}_3)_2$ and $\text{C}_6\text{H}_6\text{-NH}_3$.
- Our laboratory is looking at a series of H_2S complexes. Will need a few more years!

X-ray and neutron diffraction

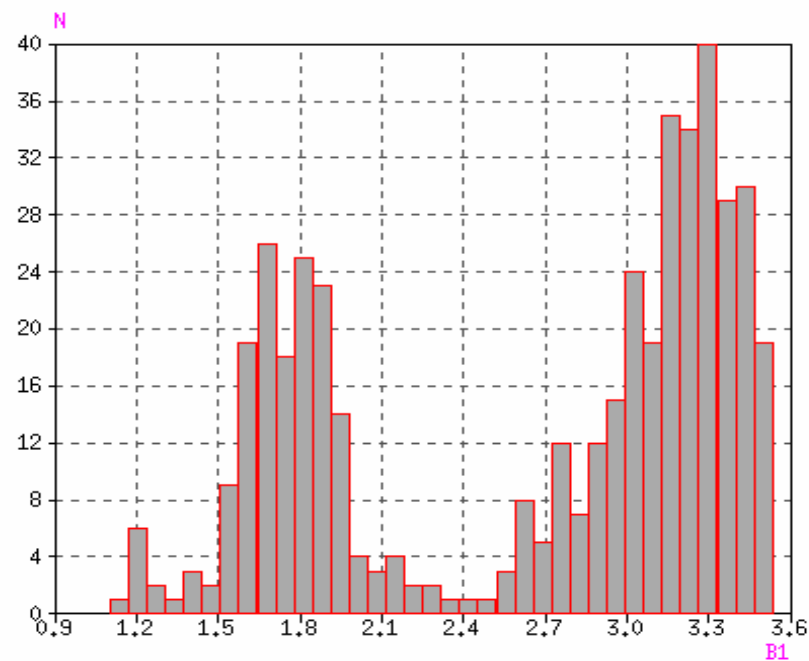


- Cambridge crystal structure database analysis!
- A wealth of information!
- Could define hydrogen bond radius for OH, NH and CCH groups
- How?
- X-ray diffraction is less reliable for locating H. Hence, in the past heavy atom distances were only interpreted!

H---O Distances from the database

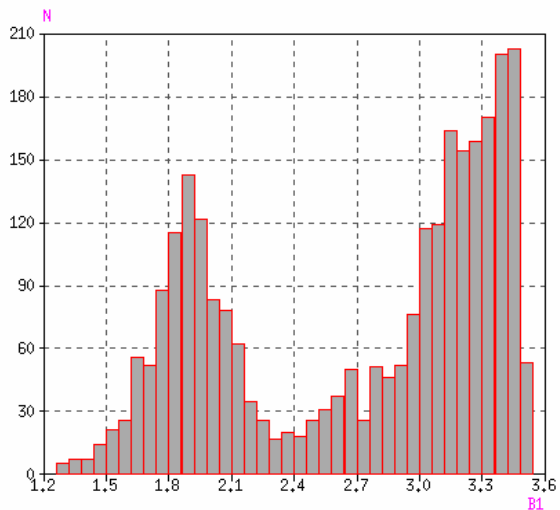


X-ray diffraction

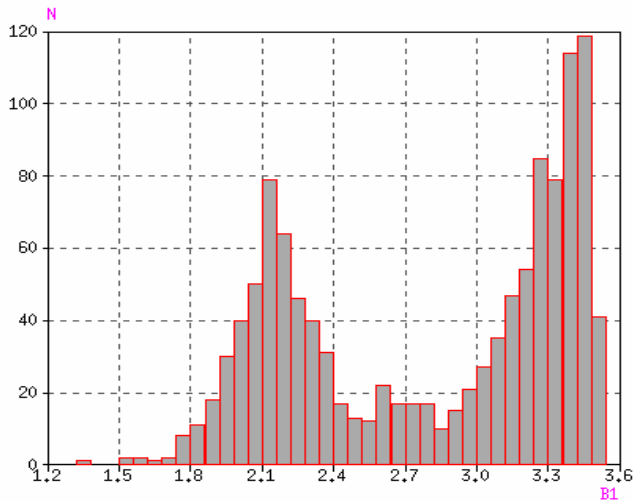


Neutron diffraction

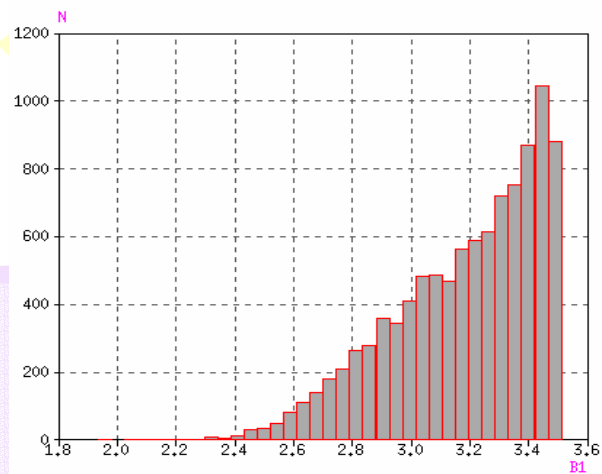
O-H---O=C contacts



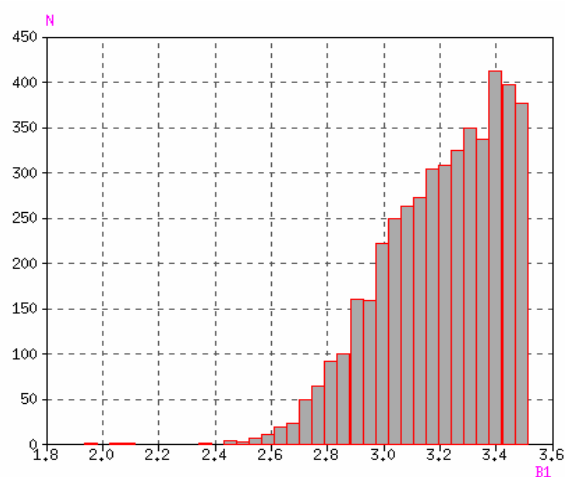
PyN---H-O



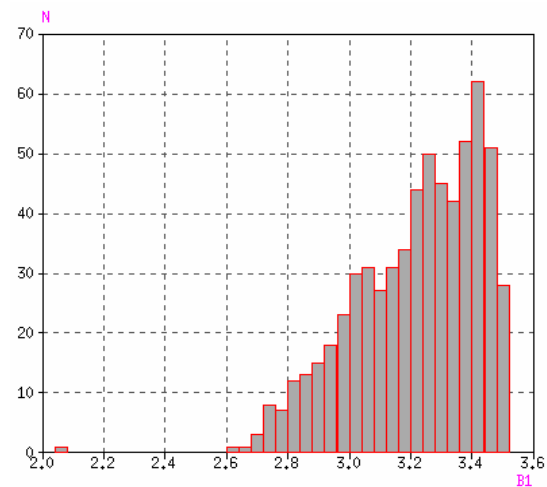
PyN---H-N



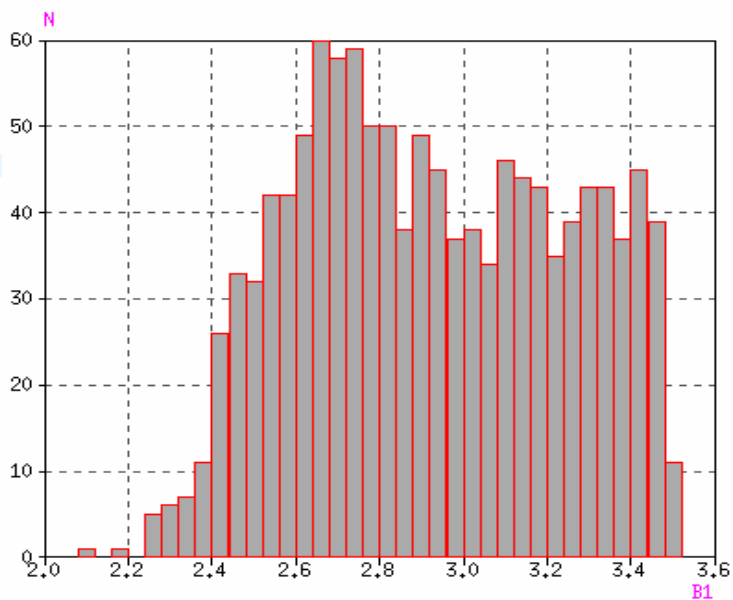
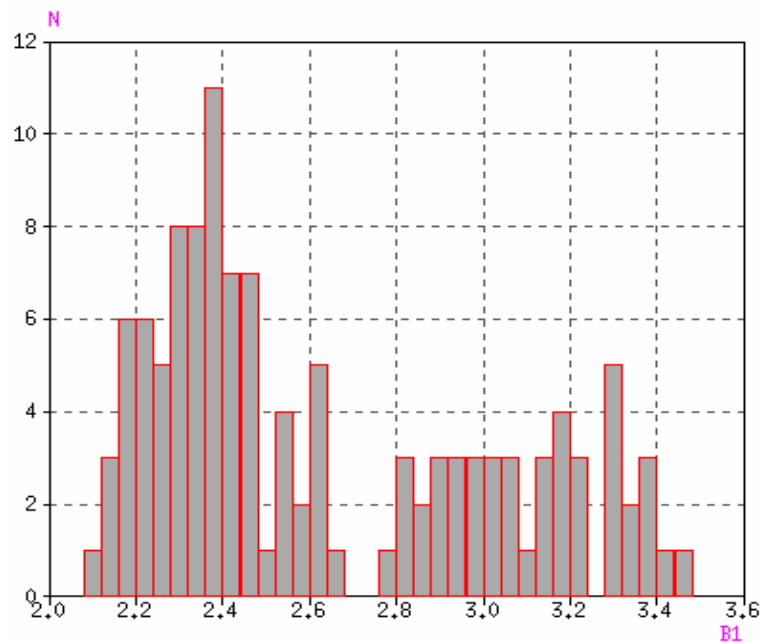
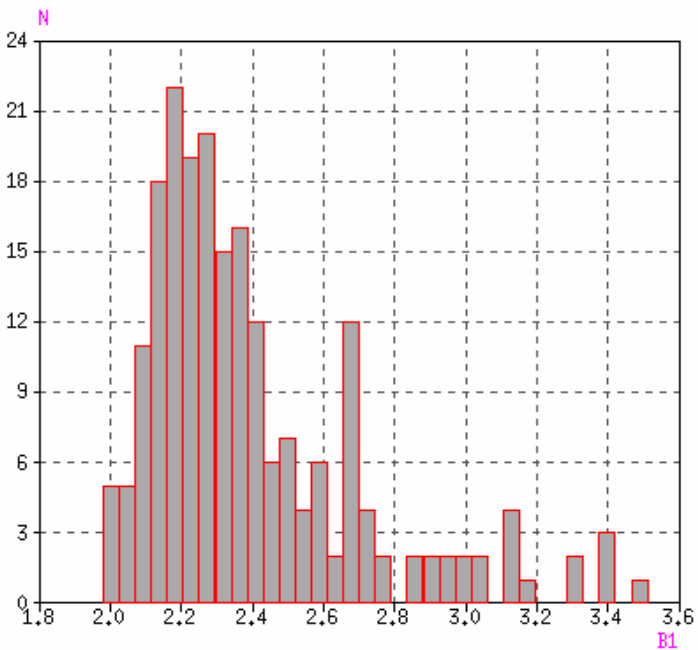
PyN---H-C



$\text{PyN---H-CH}_2\text{-C}$



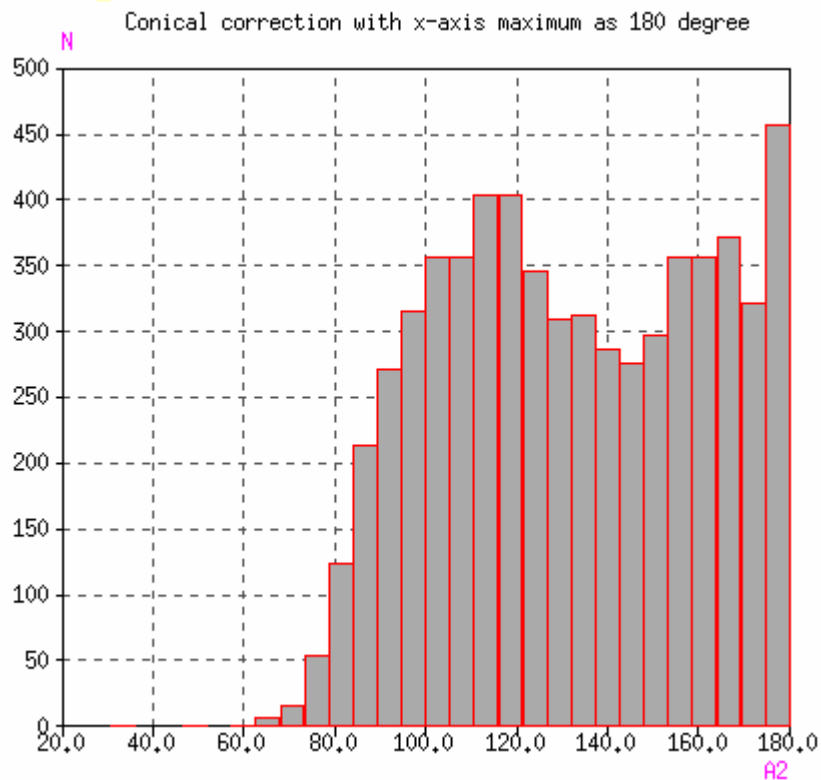
$\text{PyN---H-CH}_2\text{-CH}_2$



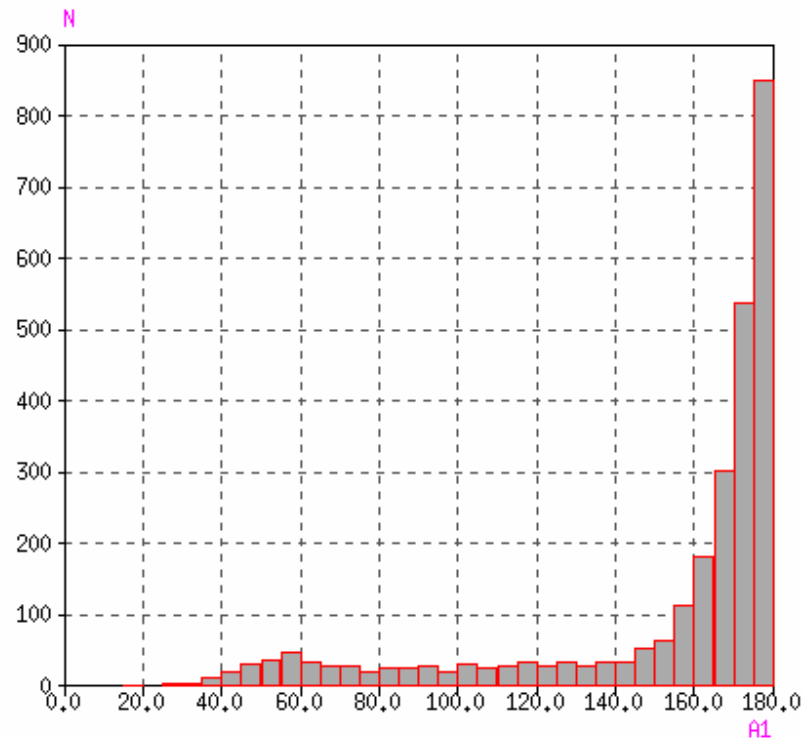
So, what about CH groups without electronegative substituents?

- Some believed in hydrogen bonding by such groups.
- Others did not. Controversial!
- Desiraju and Steiner looked at the hydrogen bond angles! They were convinced and most others are too!

N•••H-X angle distribution



Pyridine-H-CH₂-CH₂



Pyridine-HO

H bond radius from X-ray crystal structure database

H-X	CN (1.34)	Pyridine (1.27)	C ₂ O (1.22)	C=O (1.26)
H-O	0.64	0.59	0.76	0.59
H-N	0.86	0.83	0.83	0.72
H-C≡C	-	-	-	1.10
H-C=O	-	-	1.30	1.18
HCCl ₃	-	1.10	1.10	0.90