ROTATIONAL SPECTRA AND STRUCTURE OF HYDROGEN BONDED COMPLEXES: TOWARDS A HYDROGEN BOND RADIUS

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

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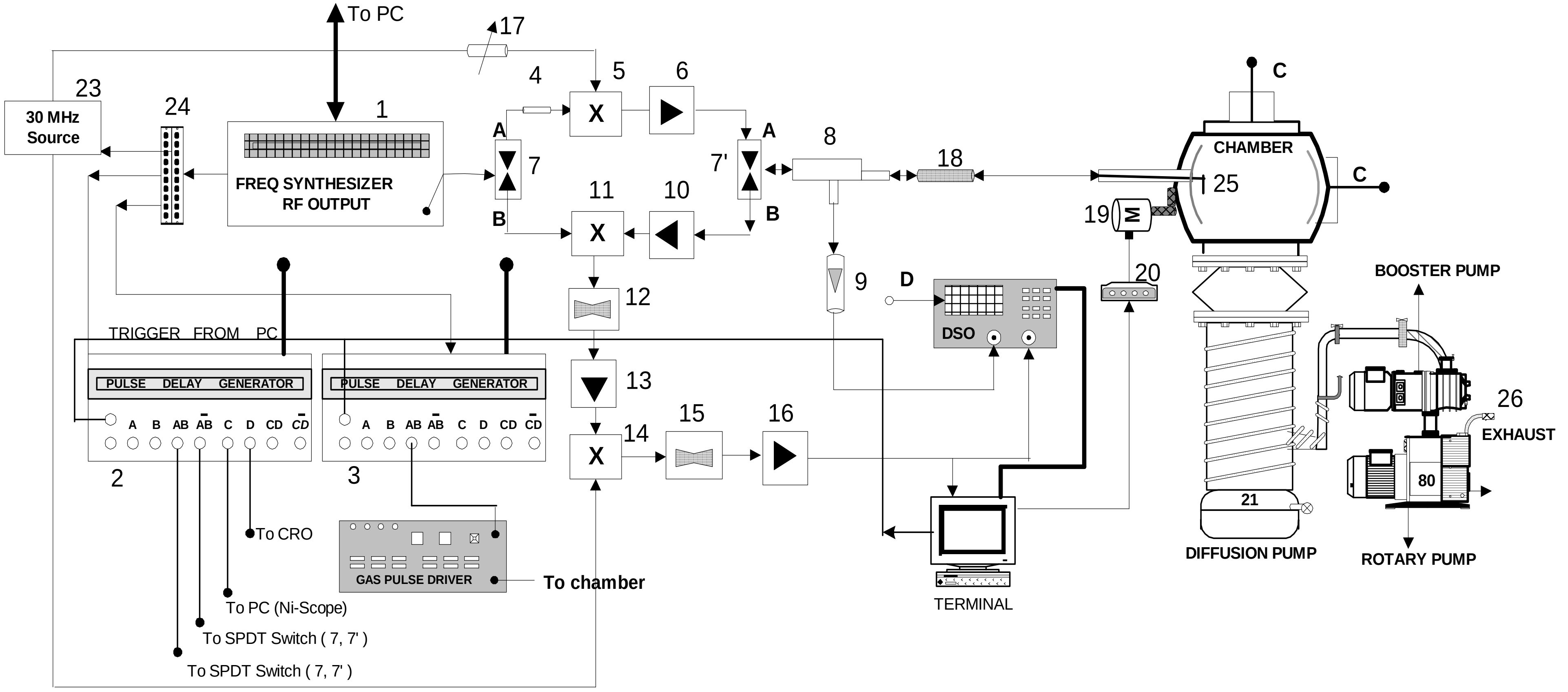
IUPAC WORKSHOP, PISA

Outline

- Pulsed Nozzle Fourier Transform Microwave Spectrometer.
- 'Hydrogen bonded complexes':
  - C_6H_6-H_2O (O-H••• π),
  - C_6H_6-HCN and C_6H_6-C_6H_6 (C-H••• π)
  - C_6H_6-H_2S (S-H••• π)
  - C_2H_4-H_2S (S-H••• π)
  - Ar_2-H_2S (H bond?)
- Definition of a Hydrogen bond radius for several HX groups.
- Conclusions

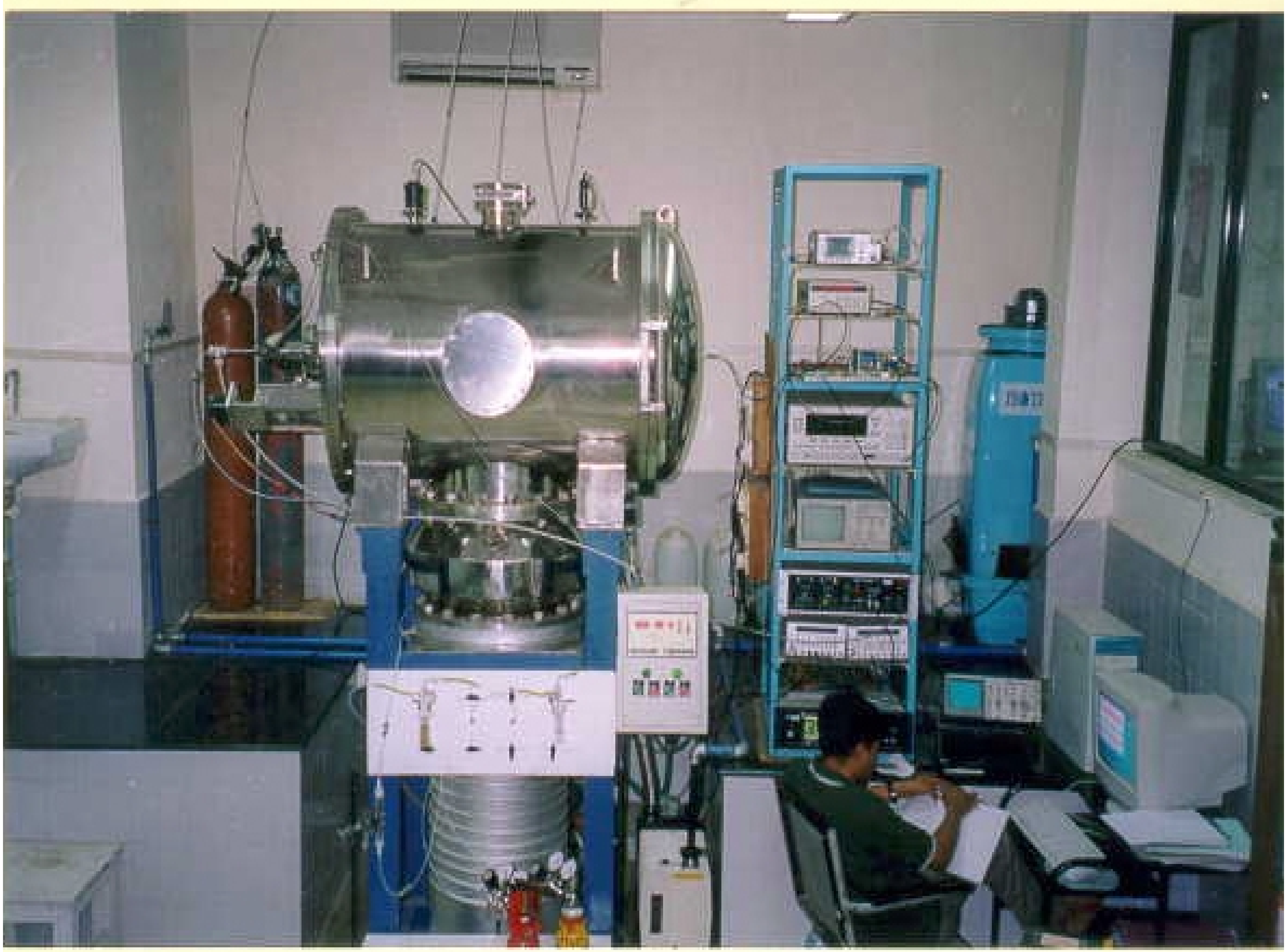
Pulsed Nozzle Fourier Transform Microwave Spectrometer



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 ≤ 1MHz before digitization

Balle and Flygare, 1979

E. Arunan et al. Curr. Sci. 2002



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

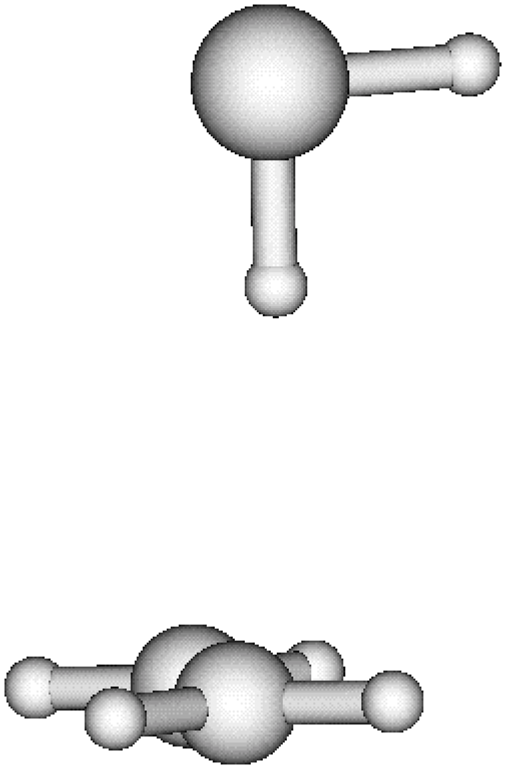
B	HF	H_2O	HCl	H_2S
Ar	3065.7	2988.2	1678.5	1681.4
Ar_2	3576.5 1739.1 1161.0	3457.2 1731.8 1144.6	1733.9 1667.9 844.5	1733.1 1617.7 830.3
Ar_3	1188.2	1172.1	843.9	819.0
C_6H_6	2048.5	1994.8	1237.7	1168.5
C_2H_4	24122 4368.0 3898.7	25960 3823.6 3452.1	25457 2308.1 2168.0	? ? ?

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 at7685.3 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 C_2H_4-H_2S

	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 C_2H_4-H_2S

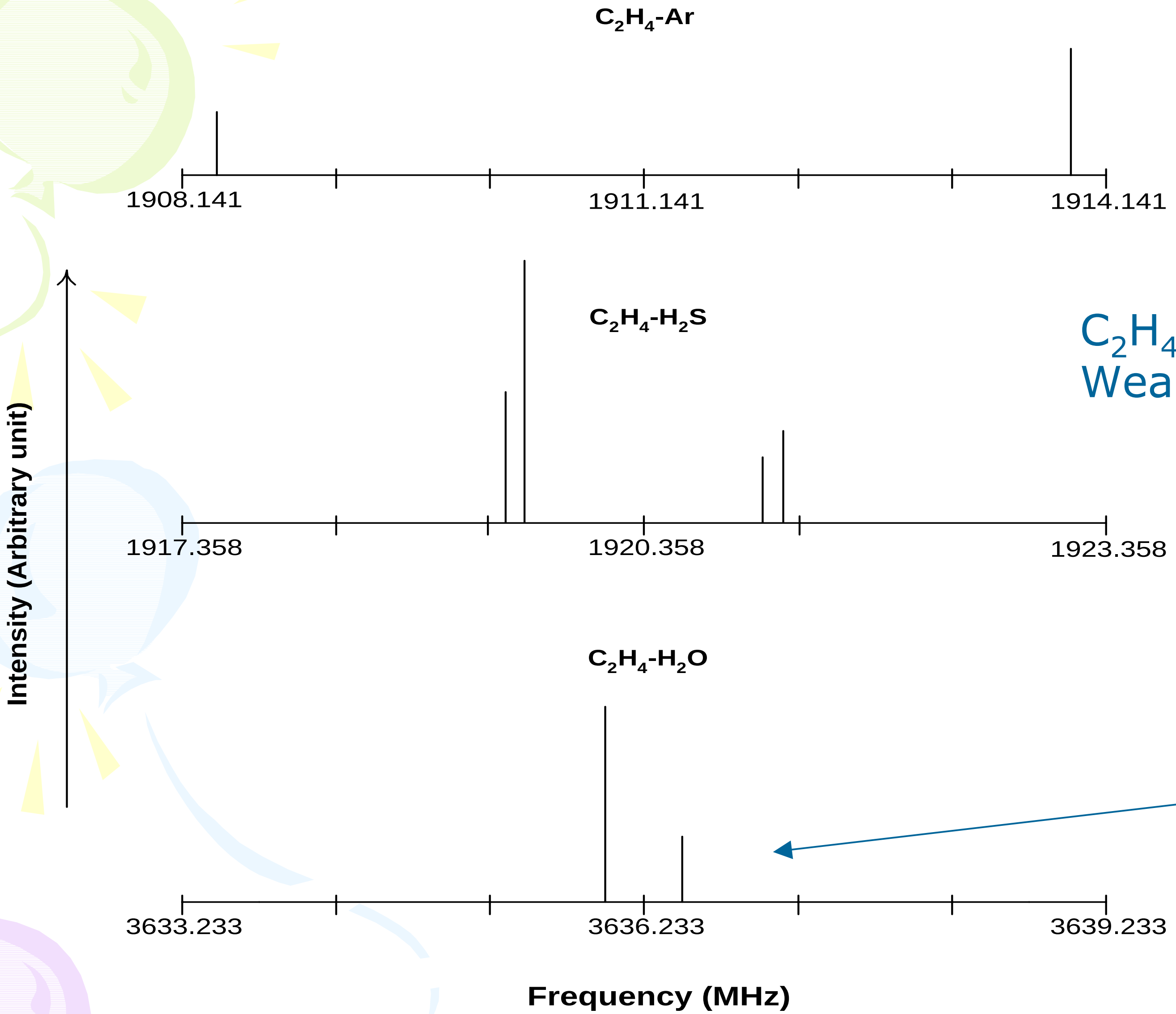
Parameters	L1	L2	U1	U2
A (MHz)	25961(34)	25968(42)	26189(55)	26204(61)
B (MHz)	1972.682(2)	1972.937(2)	1974.891(3)	1975.178(3)
C (MHz)	1866.658(2)	1866.646(2)	1867.732(3)	1867.715(3)
d_1(kHz)	-0.80(2)	-0.82(2)	-0.74(3)	-0.76(4)
d_2(kHz)	-0.21(2)	-0.22(2)	-0.24(3)	-0.24(3)
D_J (kHz)	14.30(2)	14.31(2)	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 deuteriation.

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



C_2H_4 tunneling
Weak van der Waals bond

Both C_2H_4 and H_2S
Tunnel! Internal
Rotation!?

H_2O tunneling

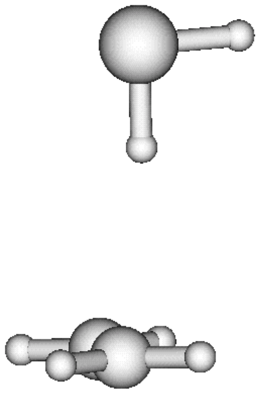
Other C_2H_4-HX (X = F, Cl) show no doubling of energy levels! Hydrogen bond is too strong. Larger the barrier smaller the splitting!

Splitting observed for H_2S, HDS and D_2S

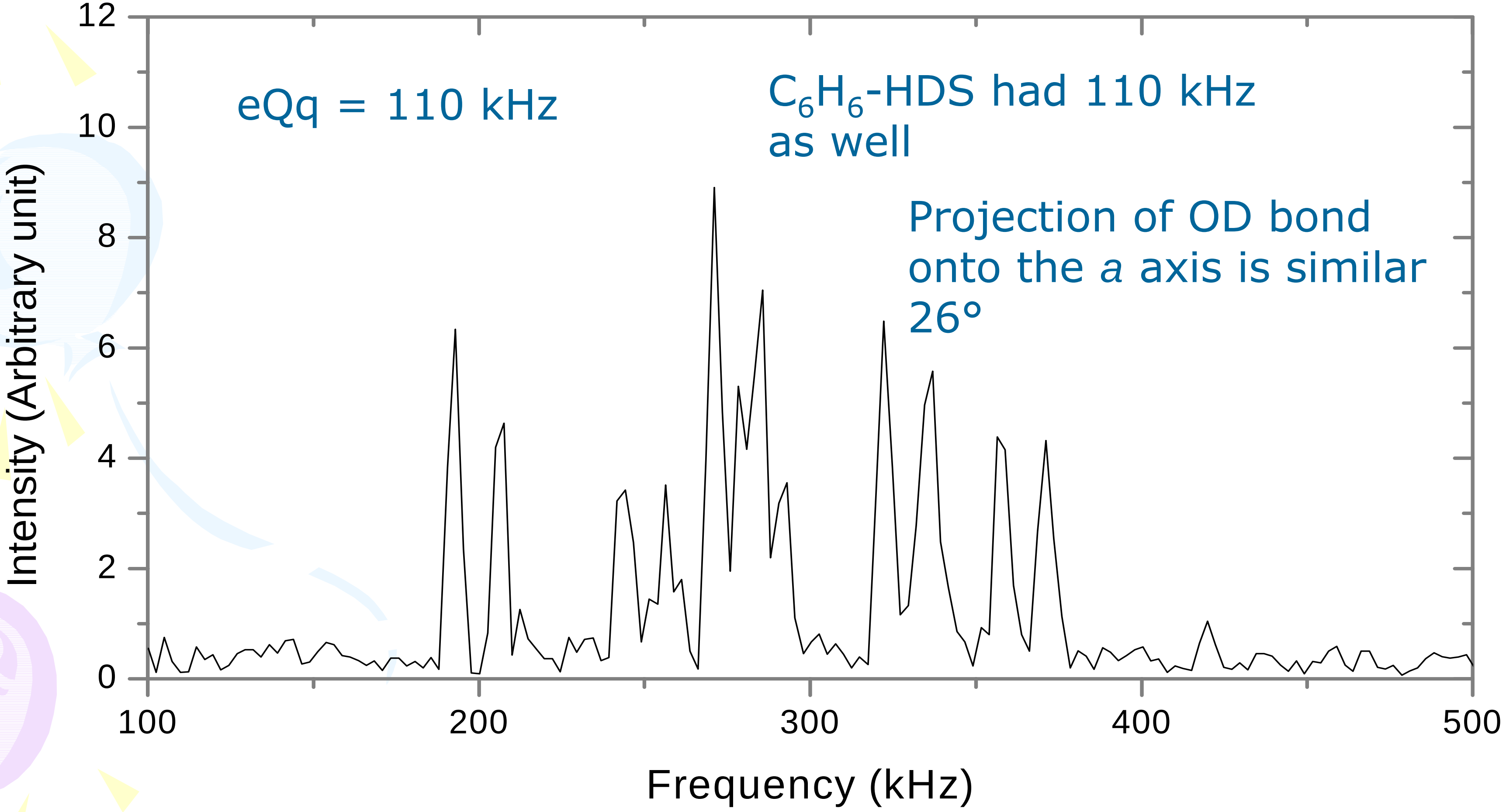
Isotop-Omer	Smaller MHz	Larger MHz
H_2S	0.14	1.67
$H_2{}^{34}S$	0.12	1.33
HDS	0.035	-
D_2S	0.035	3.11

SH bond in H_2S moves as C_2H_4 rotates

Deuterium bond is stronger than Hydrogen bond



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



eQq = 110 kHz

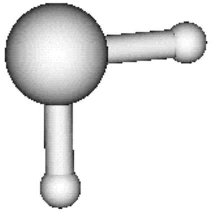
C_6H_6-HDS had 110 kHz as well

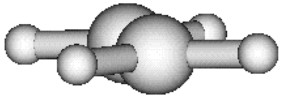
Projection of OD bond onto the *a* axis is similar 26°

Substitution analysis

H_2S/HDS/D_2S/$H_2{}^{34}S$ 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

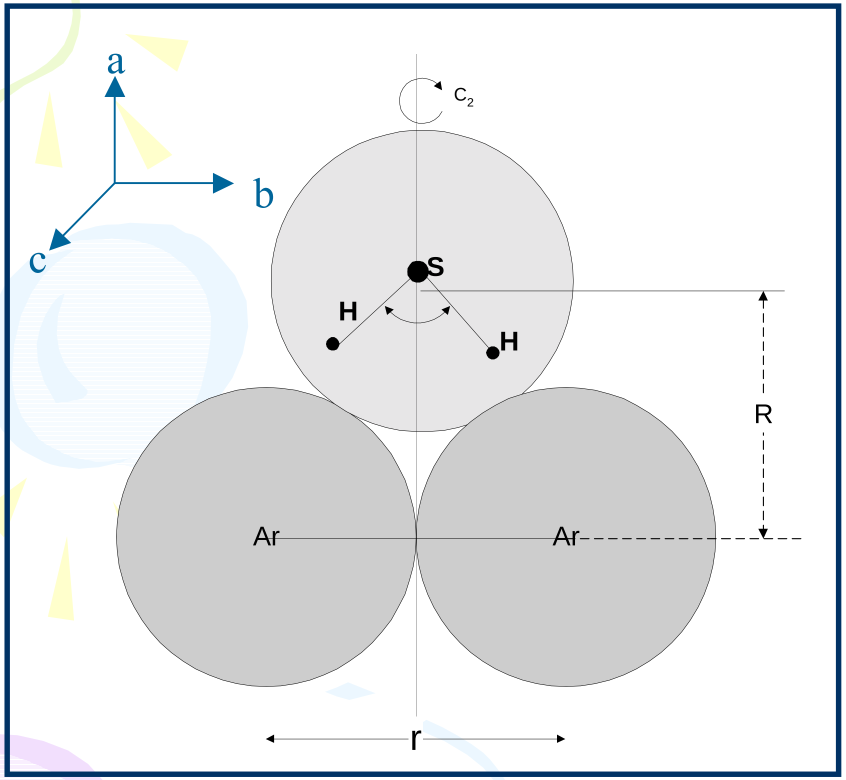
	S-H symmetric stretching	S-H asymmetric stretching
H_2S	2818	2838
Ar-H_2S	2817	2836
Ar_2-H_2S	2818	2837
H_2S-H_2S(a)	2817	2836
H_2S-H_2S(d)	2806	2830
C_2H_4-H_2S	2807	2829

Thiophenol in benzene solution shows a 16 cm^{-1} red shift!

Ar_2-H_2S

- Ar_m-H_2O 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?

Ar_2-H_2S asymmetric top



- Assuming H_2S to be effectively spherical, implies that only *a* dipole is present

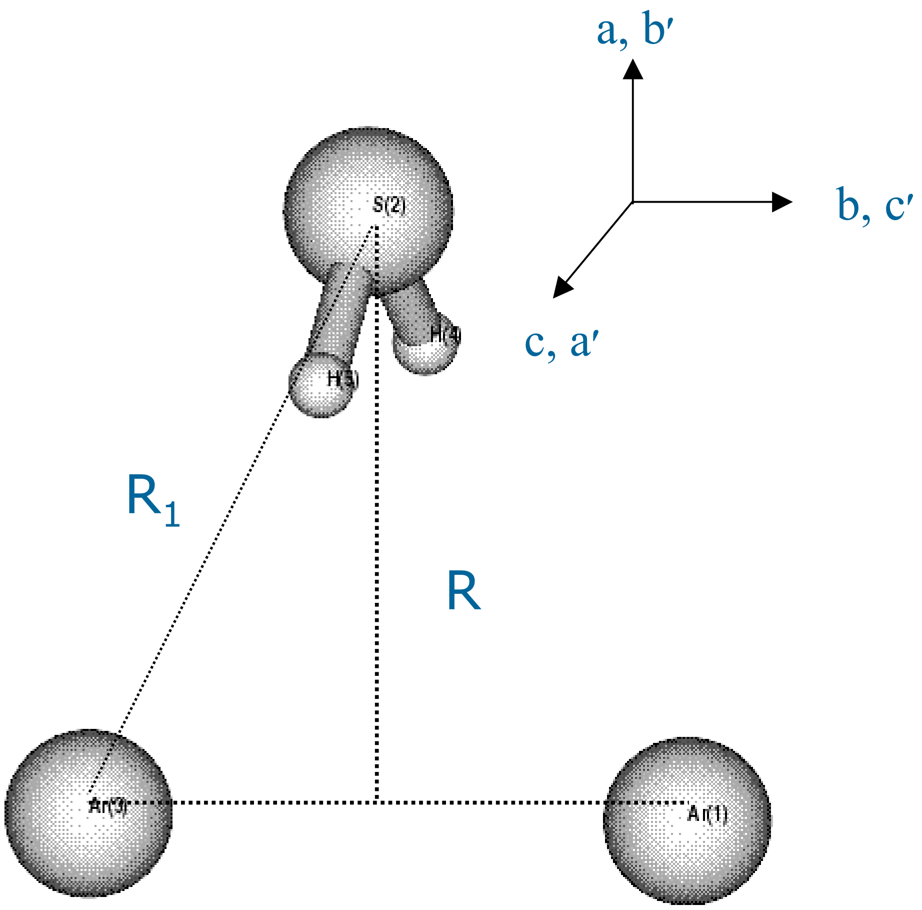
$$ee \leftrightarrow eo \text{ and } oo \leftrightarrow oe$$

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

oo and *oe* levels are not allowed.

Rotational and Centrifugal Distortion constants for Ar_2-H_2S isotopomers

Parameters	Ar_2-H_2S	Ar_2-HDS	Ar_2-D_2S
A (MHz)	1733.0982 (11)	1734.2134 (14)	1735.441 (5)
B	1617.6570 (05)	1604.4189 (07)	1594.506 (2)
C	830.2755 (03)	827.0251 (03)	824.068 (2)
D_1 (kHz)	9.269 (05)	8.853 (07)	7.48 (2)
D_2	25.577 (19)	40.278 (26)	82.0 (1)
D_J	22.200 (10)	21.365 (14)	18.09 (5)
D_{JK}	3.336 (41)	33.263 (57)	114.5 (4)
D_K	6.172 (82)	-22.25 (11)	-86.3 (9)
H_J (Hz)	--	--	1.2(3)
H_{JK}	--	--	-54(7)
H_K	--	--	652(28)
Sd (kHz)	2.3	3.1	7.2



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

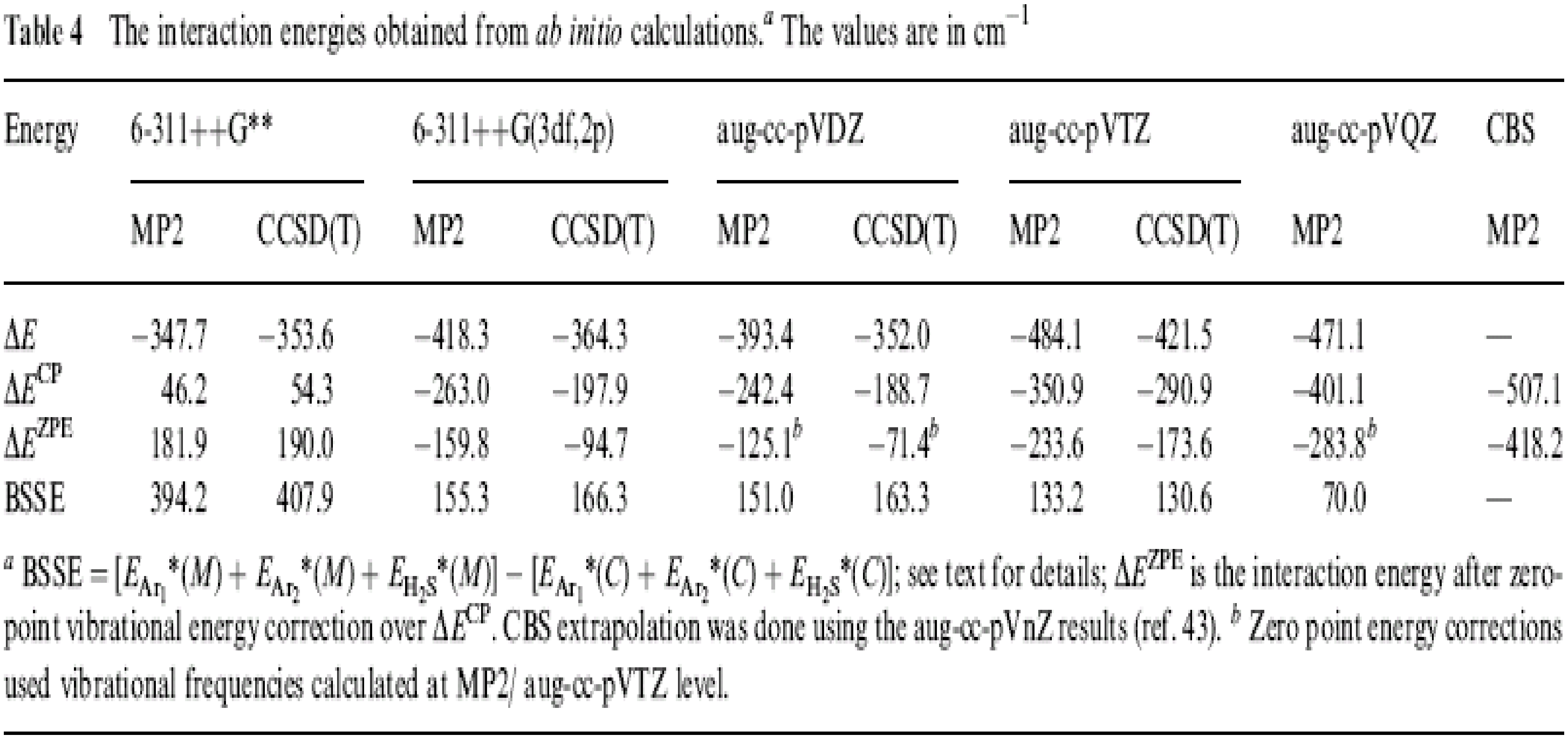
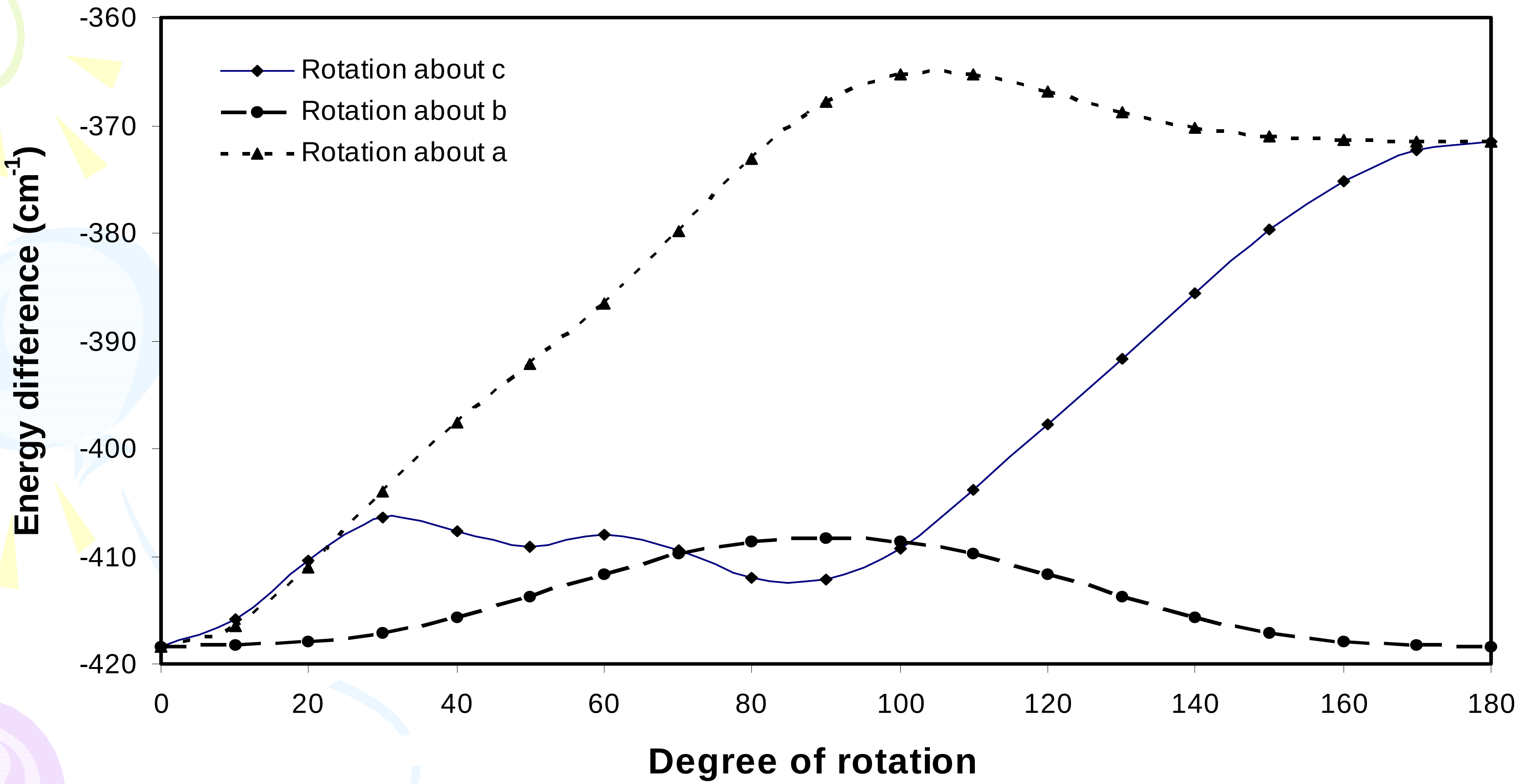


Table 4 The interaction energies obtained from *ab initio* calculations.[a] The values are in cm^{-1}

Energy	6-311++G**		6-311++G(3df,2p)		aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ	CBS
	MP2	CCSD(T)	MP2	CCSD(T)	MP2	CCSD(T)	MP2	CCSD(T)	MP2	MP2
ΔE	−347.7	−353.6	−418.3	−364.3	−393.4	−352.0	−484.1	−421.5	−471.1	—
ΔE^{CP}	46.2	54.3	−263.0	−197.9	−242.4	−188.7	−350.9	−290.9	−401.1	−507.1
ΔE^{ZPE}	181.9	190.0	−159.8	−94.7	−125.1[b]	−71.4[b]	−233.6	−173.6	−283.8[b]	−418.2
BSSE	394.2	407.9	155.3	166.3	151.0	163.3	133.2	130.6	70.0	—

[a] BSSE = $[E_{Ar_1}{}^*(M) + E_{Ar_2}{}^*(M) + E_{H_2S}{}^*(M)] - [E_{Ar_1}{}^*(C) + E_{Ar_2}{}^*(C) + E_{H_2S}{}^*(C)]$; see text for details; ΔE^{ZPE} is the interaction energy after zero-point vibrational energy correction over ΔE^{CP}. CBS extrapolation was done using the aug-cc-pVnZ results (ref. 43). [b] Zero point energy corrections used vibrational frequencies calculated at MP2/ aug-cc-pVTZ level.

Barrier for internal rotation of H_2S



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

Table 5 All the vibrational frequencies (in cm^{-1}) of Ar_2–H_2S, bending and stretching frequencies of H_2S in H_2S-H_2S (both H-bond donor and acceptor) and free H_2S, calculated at the MP2 level of theory

	MP2/6-311++G(3df,2p)			MP2/aug-cc-pVTZ		
Vibrational modes	Ar_2–H_2S	H_2S-H_2S^a	H_2S	Ar_2–H_2S	H_2S-H_2S^a	H_2S
Intermolecular bending	26	—	—	32	—	—
Intermolecular stretching (Ar–Ar)	26	—	—	26	—	—
Torsion about '*b*'-axis of H_2S	27	—	—	19	—	—
Intermolecular stretching (Ar_2–H_2S)	37	—	—	45	—	—
Torsion about '*c*'-axis of H_2S	43	—	—	43	—	—
Torsion about '*a*'-axis of H_2S	49	—	—	63	—	—
H–S–H bending	1214	1223/1215	1217	1209	1216/1209	1212
S–H symmetric stretch	2776	2741/2773	2776	2773	2729/2769	2771
S–H asymmetric stretch	2794	2786/2792	2795	2792	2783/2789	2791

[a] First entry is for the donor H_2S and the second entry is for acceptor H_2S.

How accurate are these frequencies? Experimental Centrifugal distortion constants can help

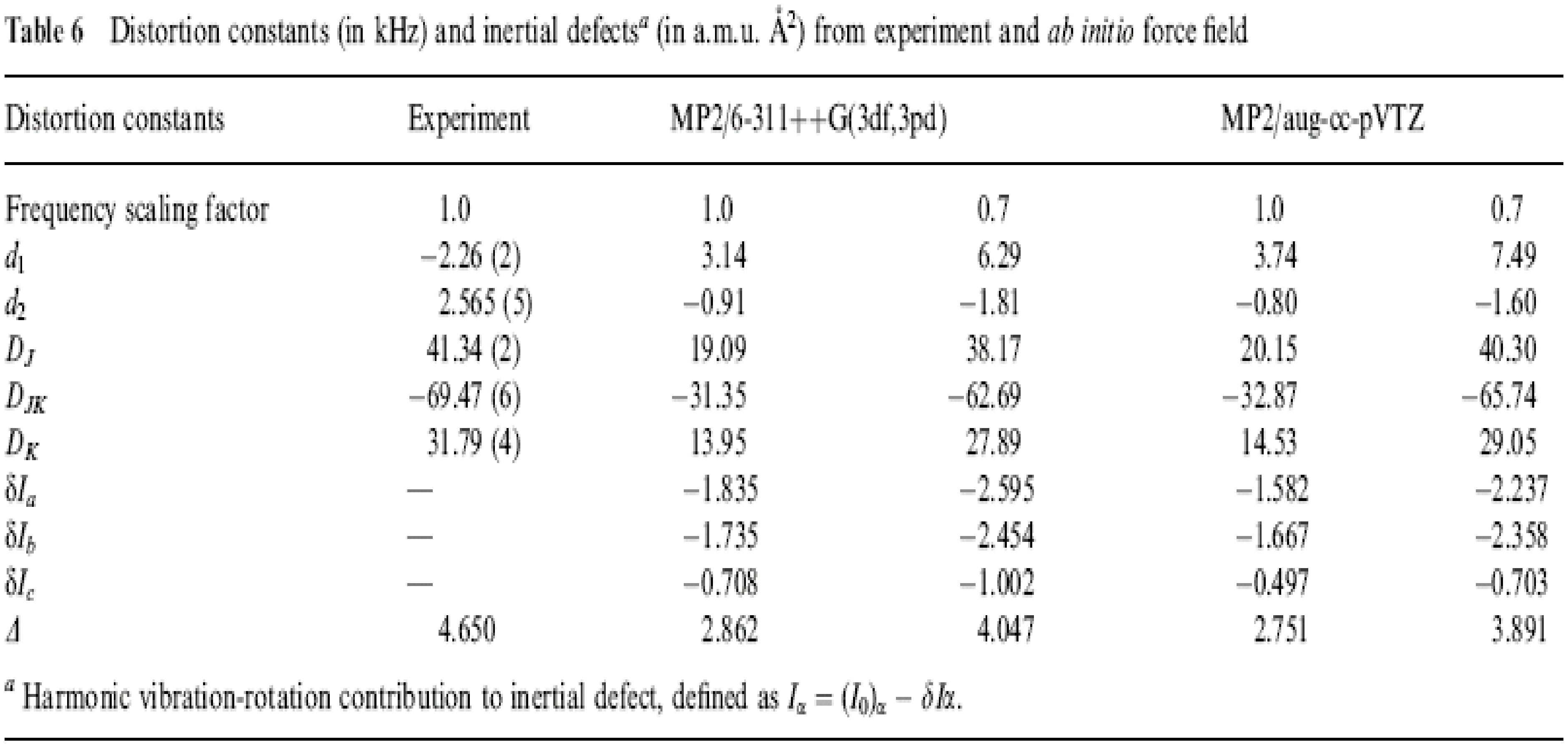


Table 6 Distortion constants (in kHz) and inertial defects[a] (in a.m.u. Å^2) from experiment and *ab initio* force field

Distortion constants	Experiment	MP2/6-311++G(3df,3pd)		MP2/aug-cc-pVTZ	
Frequency scaling factor	1.0	1.0	0.7	1.0	0.7
d_1	−2.26 (2)	3.14	6.29	3.74	7.49
d_2	2.565 (5)	−0.91	−1.81	−0.80	−1.60
D_J	41.34 (2)	19.09	38.17	20.15	40.30
D_{JK}	−69.47 (6)	−31.35	−62.69	−32.87	−65.74
D_K	31.79 (4)	13.95	27.89	14.53	29.05
δI_a	—	−1.835	−2.595	−1.582	−2.237
δI_b	—	−1.735	−2.454	−1.667	−2.358
δI_c	—	−0.708	−1.002	−0.497	−0.703
Δ	4.650	2.862	4.047	2.751	3.891

[a] Harmonic vibration-rotation contribution to inertial defect, defined as $I_\alpha = (I_0)_\alpha - \delta I\alpha$.

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, Ithaka, 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” commented that it will not be possible to define a hydrogen bond radius as C-OH is different from P-OH as donor and C=O is different from C_2-O as an acceptor.

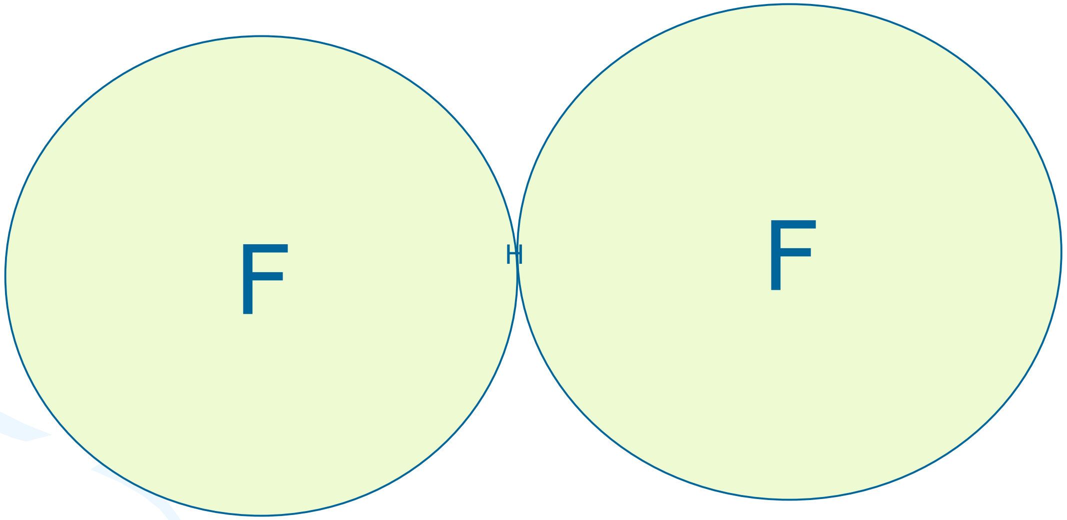
Why no hydrogen bond radius so far?

- Unlike other ‘bonding’ involving two atoms, hydrogen bond involves at least 3, X-H•••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^-

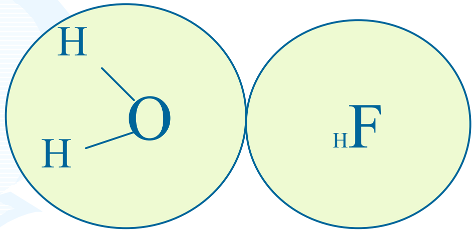


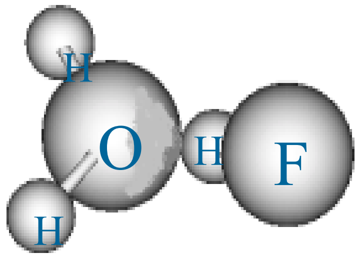
Two F^- interacting simultaneously with H^+

Size of H^+ is 0.66 fm

What about HF complexes?

Which of the two cartoons represent H_2O---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 *Z* and HX as the sum of the van der Waals radii of Z and X.

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

B	**B---HF**		**B---HCl**		**B---HBr**	
	r(Z---F)	$\sigma(Z) + \sigma(F)$	r(Z---Cl)	$\sigma(Z) + \sigma(Cl)$	r(Z---Br)	$\sigma(Z) + \sigma(Br)$
H_2S	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_3CN	2.751	2.85	3.294	3.30	3.494	3.45
H_2O	2.684	2.75	3.215	3.20	3.414	3.35
H_3N	2.71	2.85	3.136	3.30	3.255	3.45

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

*Do Z---H distances mean anything?

Comparison of structural properties observed for C_6H_6--HX dimers

Dimer	B_0 (MHz)	D_J (kHz)	D_{JK} (kHz)	r^a (Å)	θ (deg)
C_6H_6-HF	2048.540	3.1	74	2.25	22
C_6H_6-HCl	1237.684	1.22	13.4	2.32	23.0
C_6H_6-HCN	1219.911	1.12	18.0	2.41	15.2

[a] C_6H_6 c.m. to H distance

Gutowsky, Arunan *et al., J. Chem. Phys.* **103,** 3917 (1995)

Gadre and Bhadane interpretation :

[*J. Chem. Phys.* **107**, 5625 (1997)]

B---H distances are the sum of van der Waals radii of B and H.

* **Molecular Electrostatic Potential(MESP)** at a point ‘r’, due to nuclear charge $\{Z_A\}$ at $\{R_A\}$ and electron density ρ(r) is defined as:

$$V(r) = \sum_{A}^{N} Z_A / |r - R_A| - \int \rho(r') \, d^3r' / |r - r'|$$

* **MESP minima** symbolize the electron localization in a molecule.

* $\mathbf{r_{ESP}}$ is the distance between Z and MESP minima; Z is the atom or centre in B, bonded to the H.

They studied the B---HF complexes and obtained the correlation:

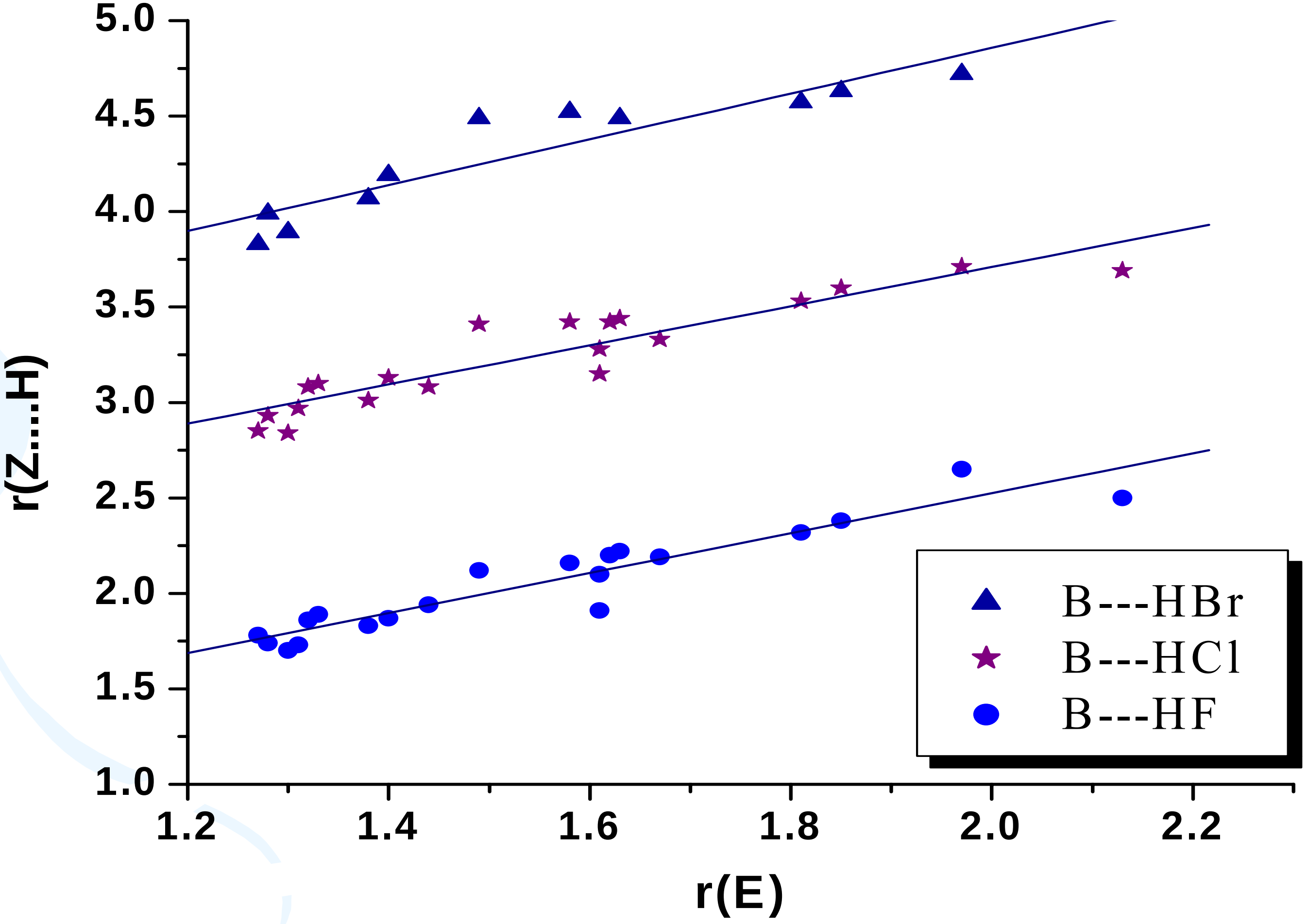
$$r_{HYD} = (r_{ESP} \times 1.04) + 0.47$$

* $\mathbf{r_{HYD}}$ is the Z---H distance in the complex B---HX.

* **CONCLUSION:** 0.47Å is the van der Waals radius of H

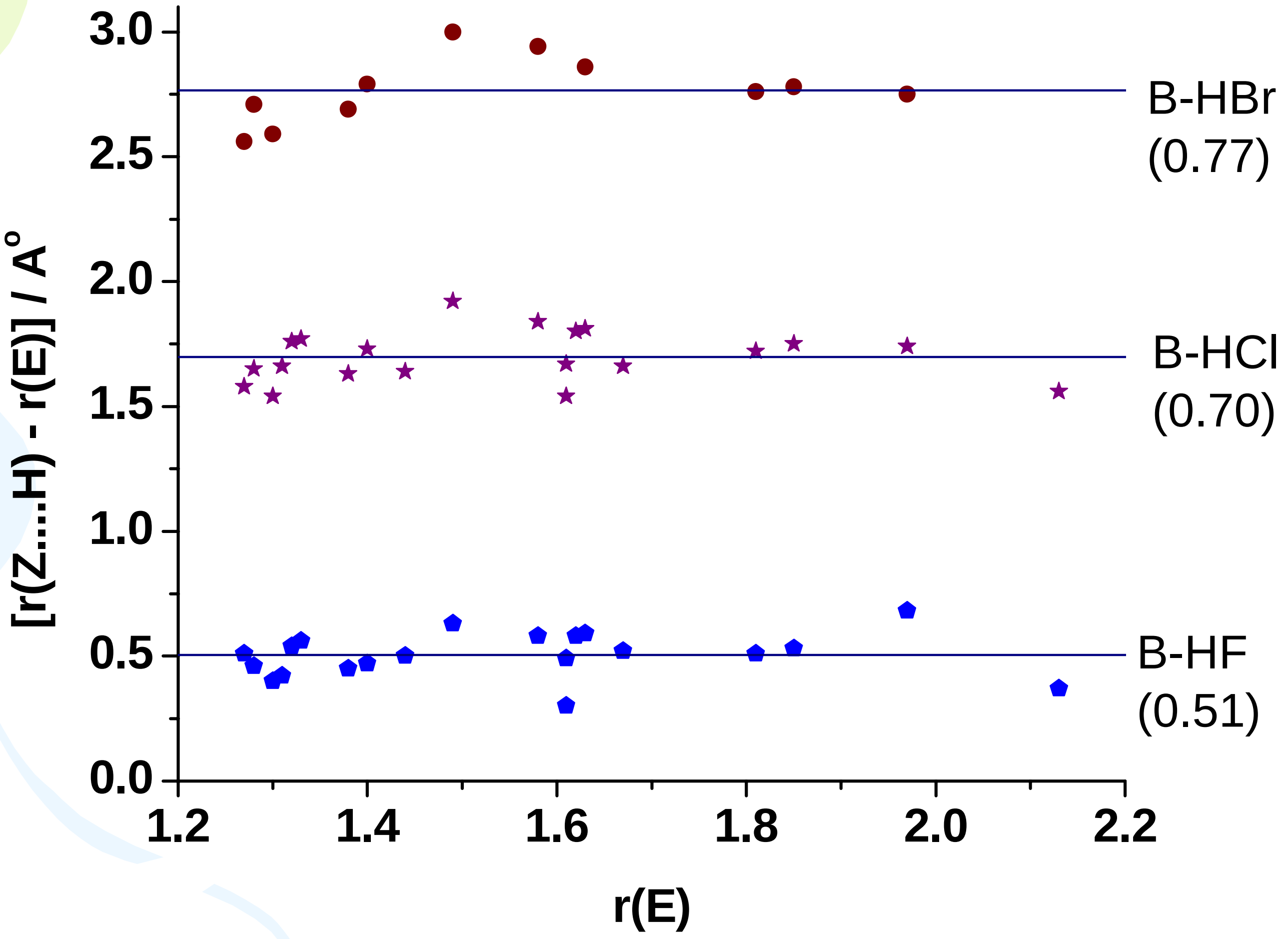
NB: Pauling suggested the van der Waals radius of H to be 1.2 Å.

r(Z...H) vs r(E)



B-HX, X = F, Cl, Br, CN, CCH, OH and SH (*ab initio*)

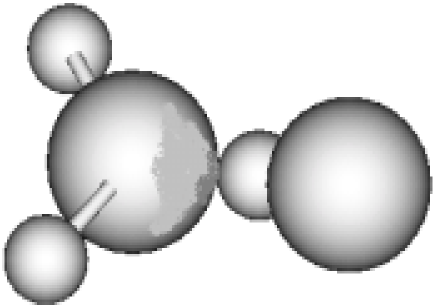
[r(Z…H) – r(E)] vs r(E)



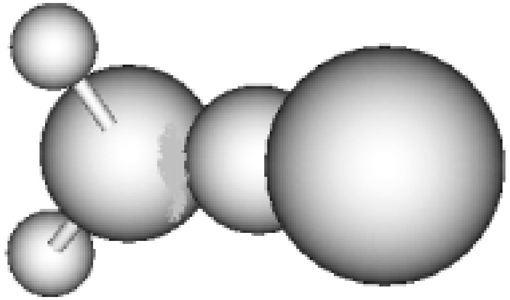
“Hydrogen Bond Radius”

r(Z…H) = r(E) +r(H)

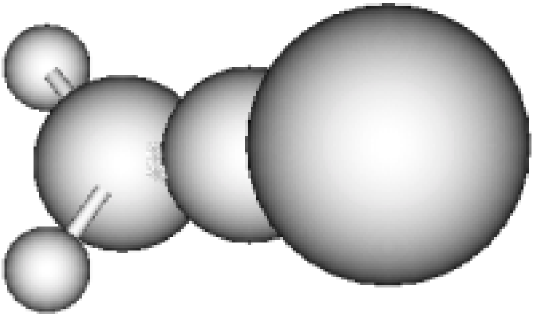
Models of H_2O---HX



H_2O---HF



H_2O---HCl

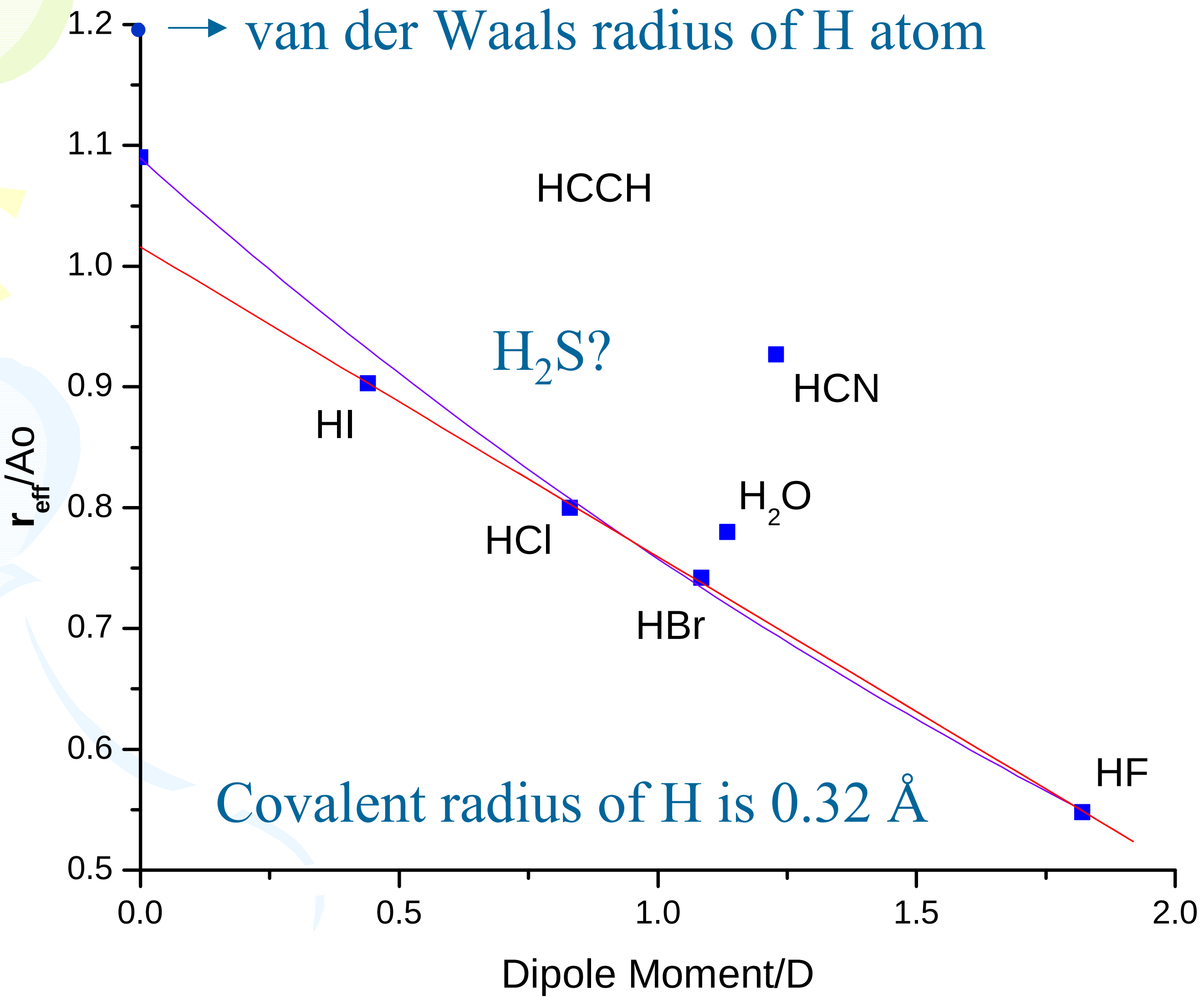


H_2O---HBr

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



→ van der Waals radius of H atom

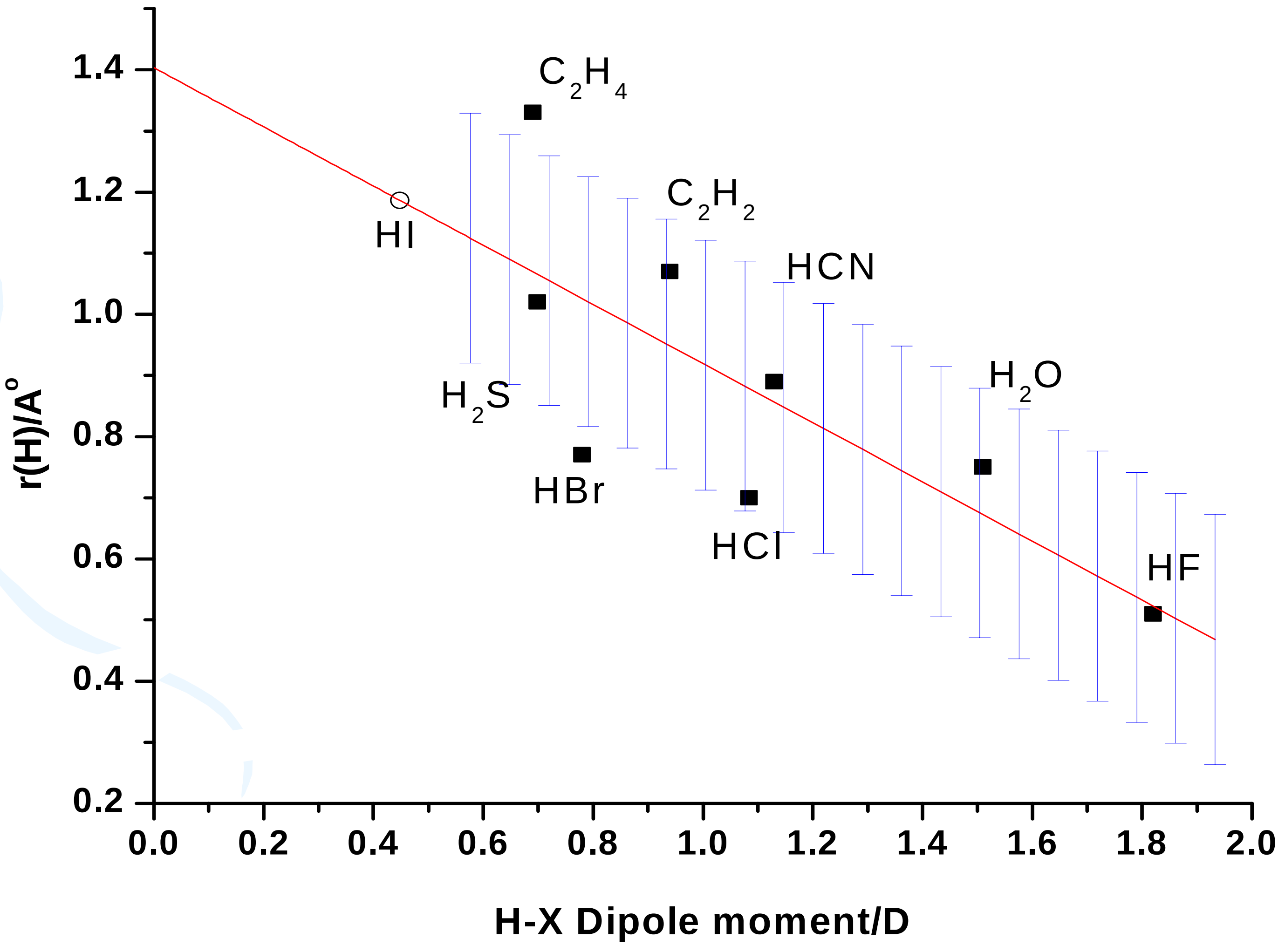
H_2S?

Covalent radius of H is 0.32 Å

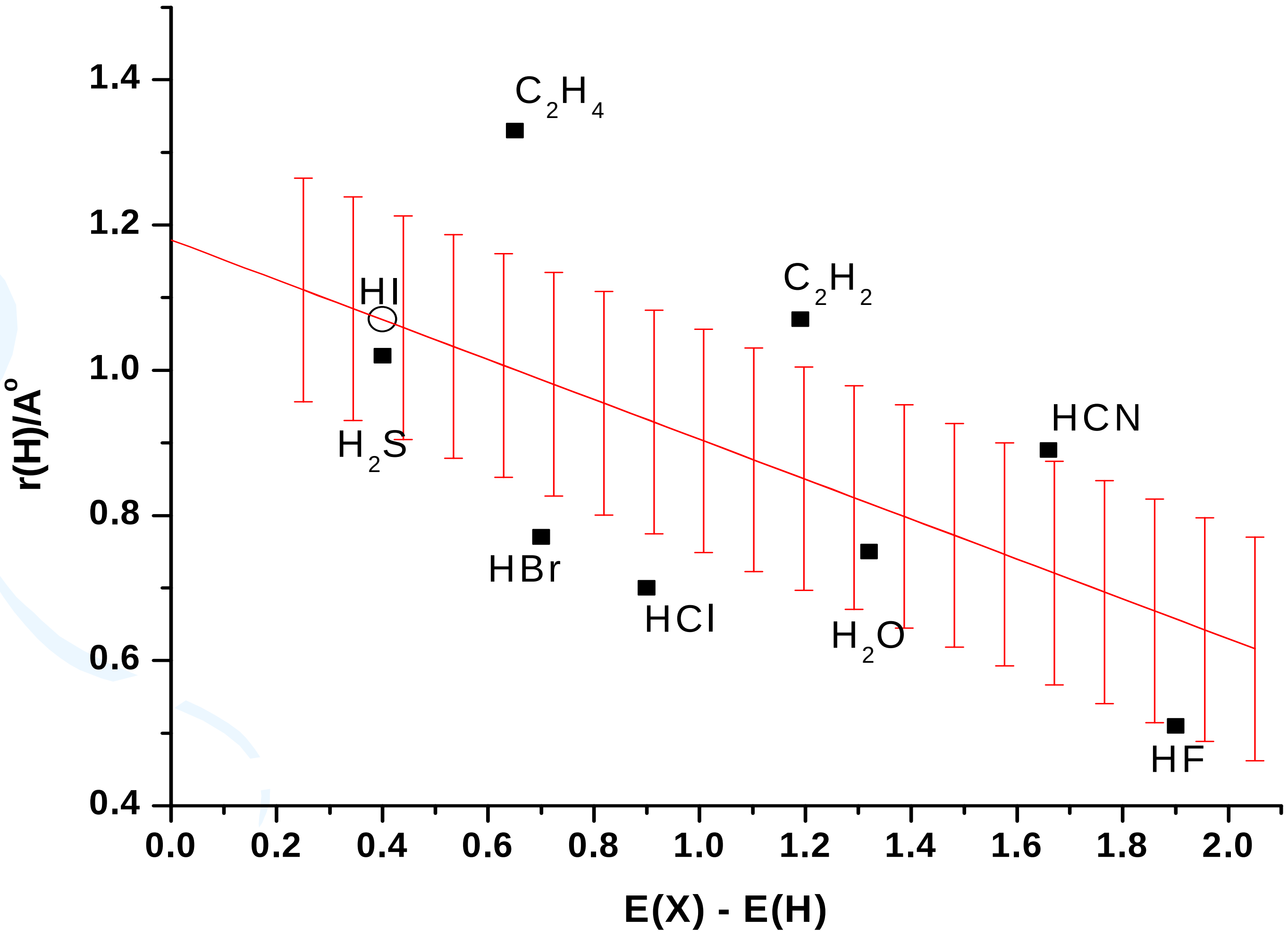
r(H) values from empirical and theoretical analysis

	Empirical		MP2	B3LYP	
r(E)	HF	MP2	MP2	HF	MP2
HF	0.54 ± 0.07	0.51 ± 0.09	0.50 ± 0.06	0.48 ± 0.04	0.46 ± 0.05
HCl	0.73 ± 0.08	0.70 ± 0.10	0.69 ± 0.10	0.67 ± 0.10	0.63 ± 0.10
HBr	0.79 ± 0.11	0.77 ± 0.13	--	--	--
HCN	0.92 ± 0.08	0.89 ± 0.12	--	--	--
H_2O	0.78 ± 0.06	0.75 ± 0.09	0.76 ± 0.08	0.76 ± 0.08	0.75 ± 0.08
HCCH	1.08 ± 0.07	1.07 ± 0.08	--	--	--
H_2S	--	--	1.02 ± 0.10	1.05 ± 0.12	1.03 ± 0.13

r(H) vs Dipole moment



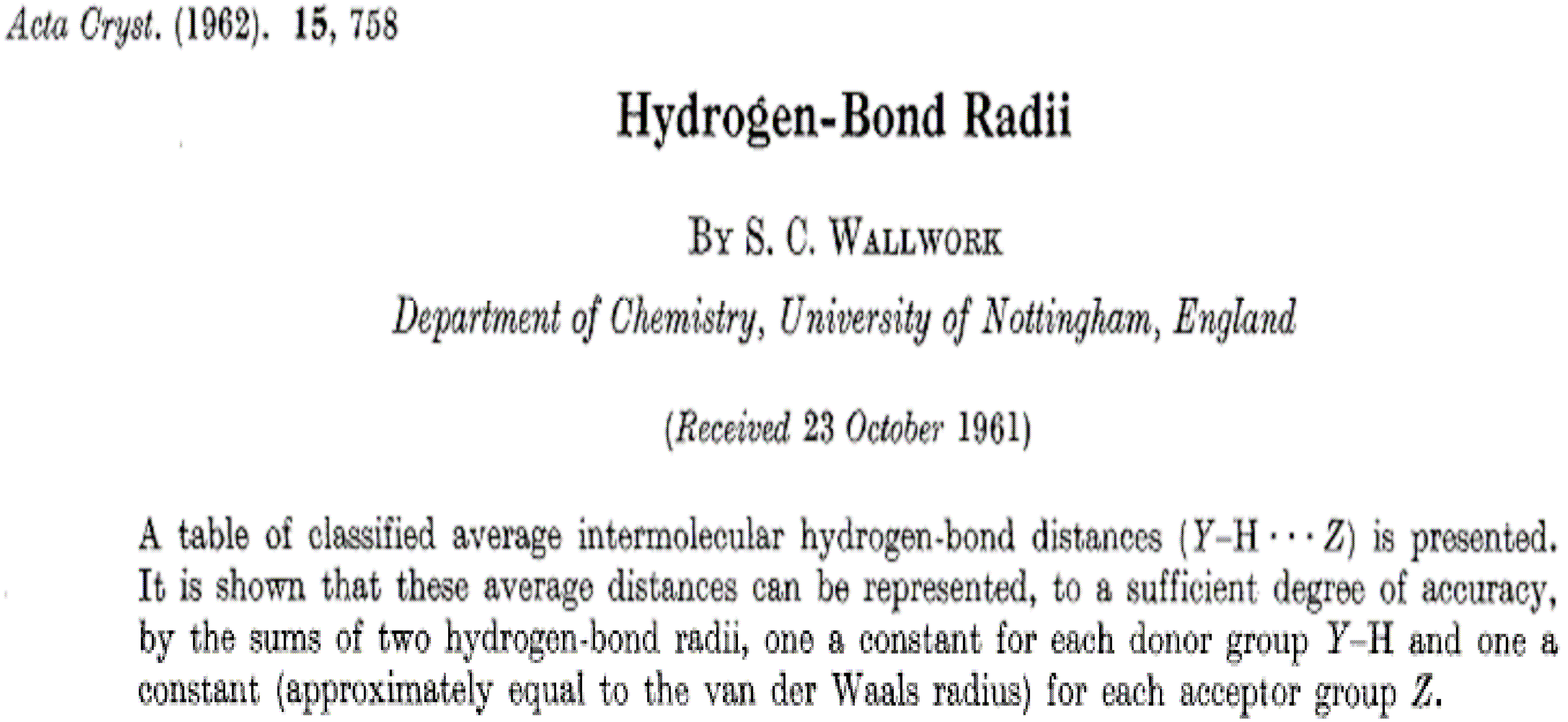
r(H) vs Electronegativity difference



Is H bond radius real?

- Klein, has concluded recently by Atoms in Molecules theory that H bonded to O should be assigned a radius of 0.8 Å, instead of 1.2 Å
  - R. Klein J. Computational Chem. 2003
- Gillespie has come to a similar conclusion for OH by analyzing structural data for several ligands
  - Gillespie Inorg. Chem. 2004

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.
- C_2H_4-H_2S and Ar_2-(H_2S) 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.

Acknowledgements

- P. K. Mandal, Mausumi Goswami, Raghavendra, Aiswarya and Dharmendar Ramdass (FTMW work)
- B. Lakshmi and Sujeetha (CSD analysis)
- DST, CSIR, Director IISc.
- Profs. S.R.Gadre, A.G.Samuelson, and P.C. Mathias

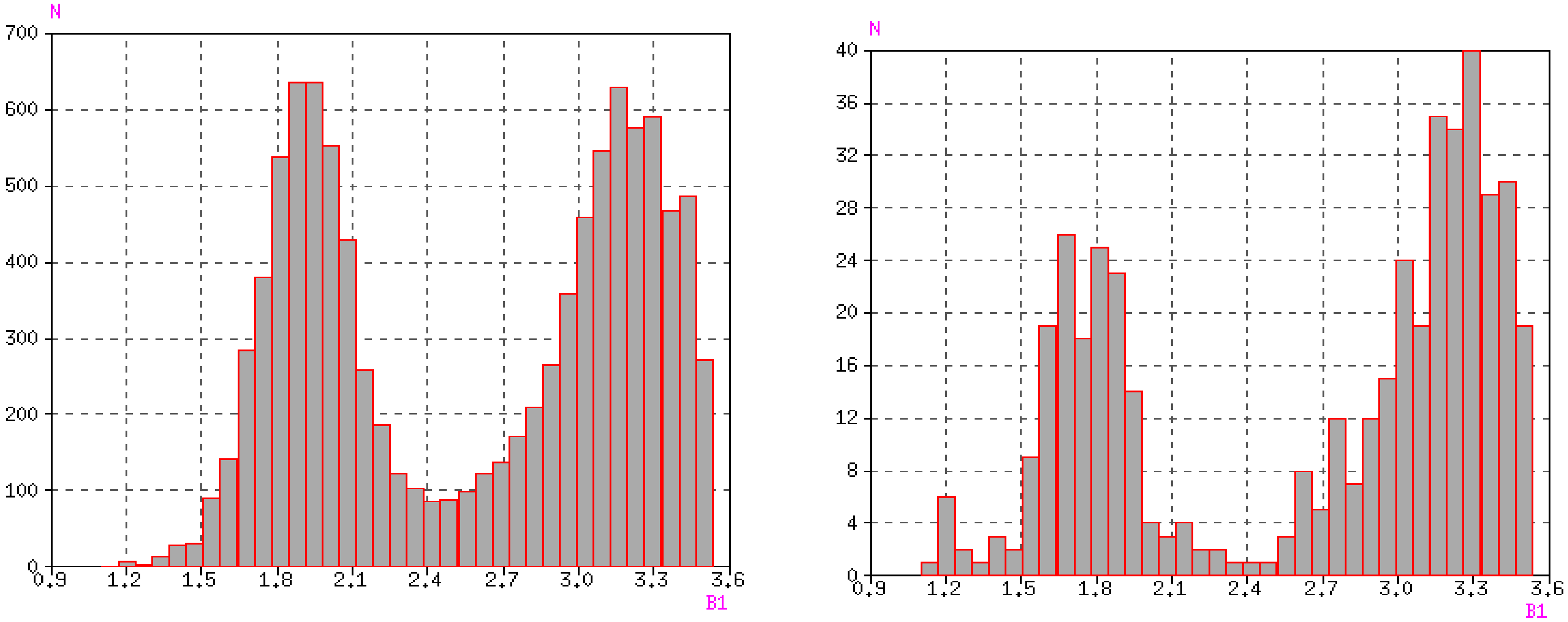
NH and SH groups

- 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 $(NH_3)_2$ and C_6H_6-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!

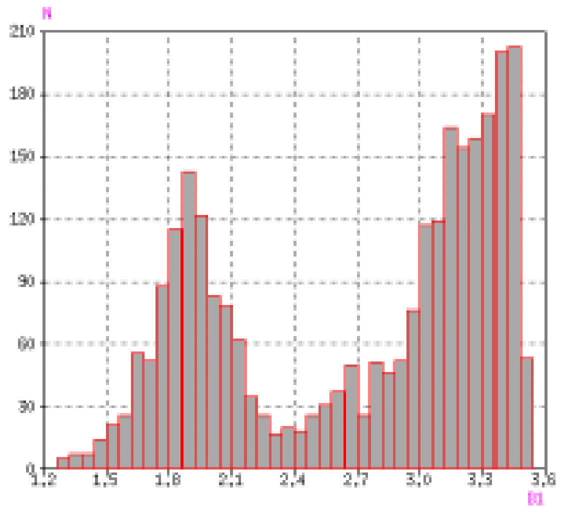
H---O Distances from the database



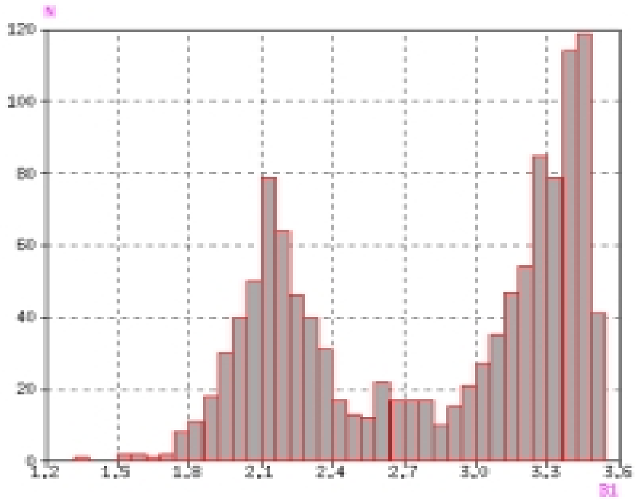
X-ray diffraction

Neutron diffraction

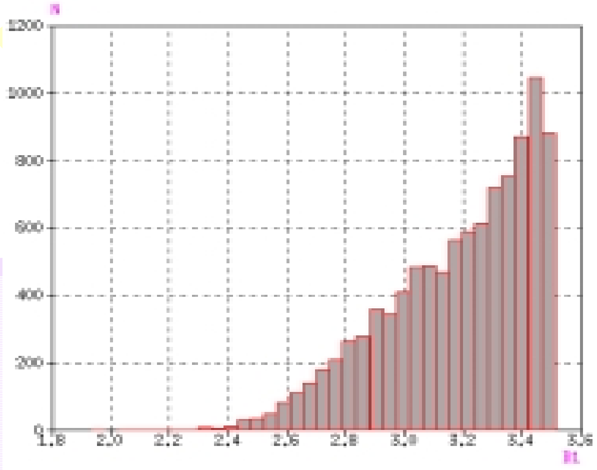
O-H---O=C contacts



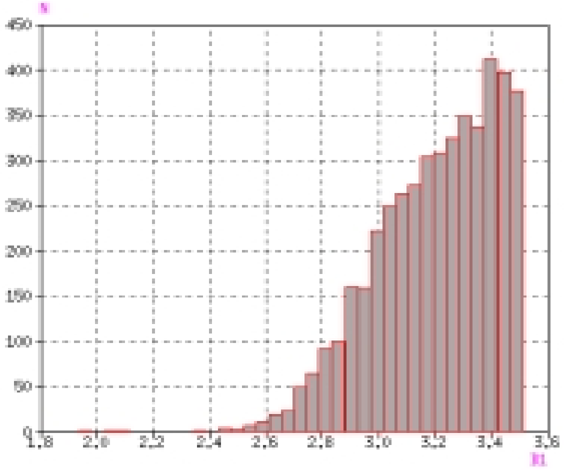
PyN---H-O



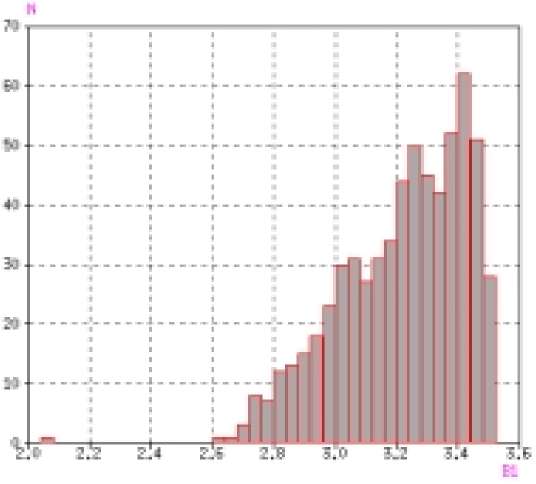
PyN---H-N



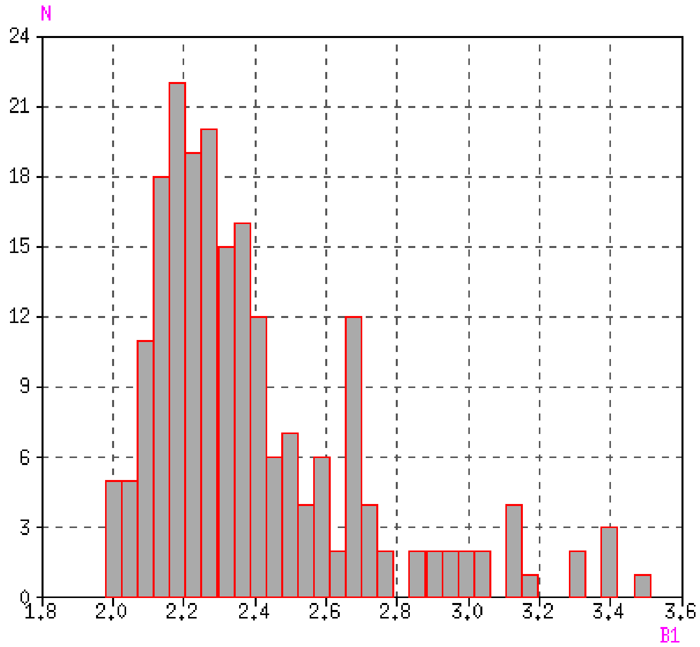
PyN---H-C



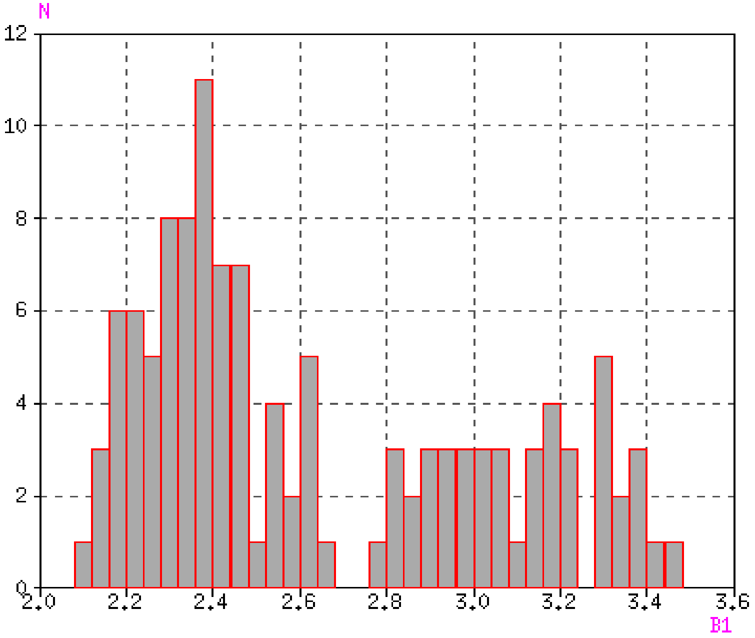
PyN---H-CH$_2$-C



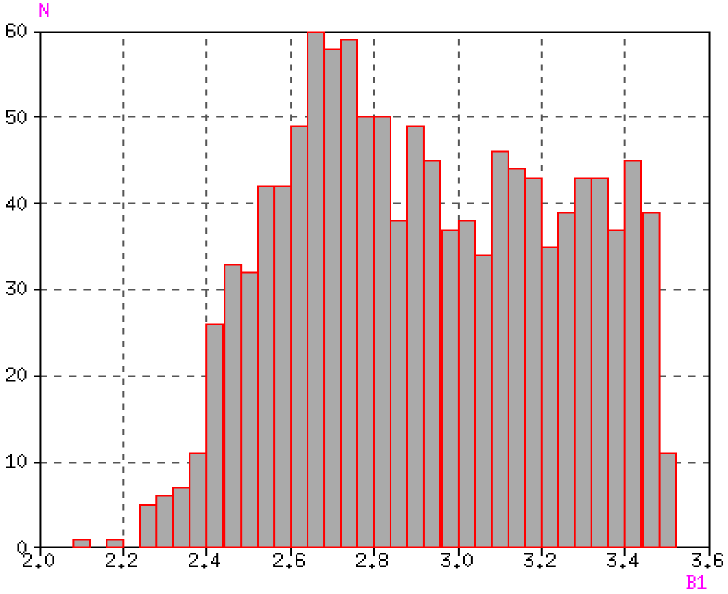
PyN---H-CH$_2$-CH$_2$



C=O---H-CCl$_3$



C=O---H-C≡ C

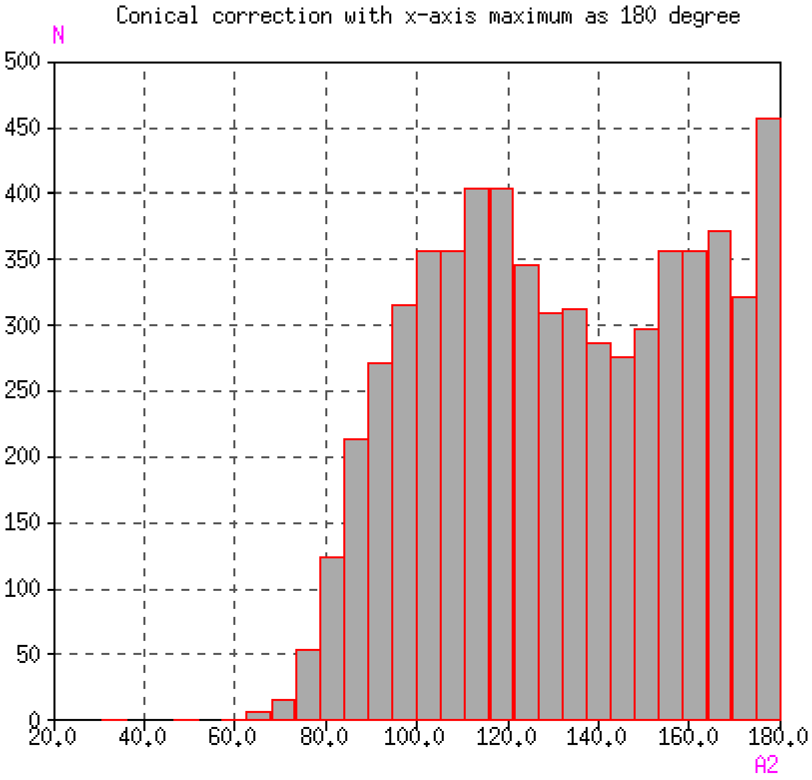


C=O---H-C=O

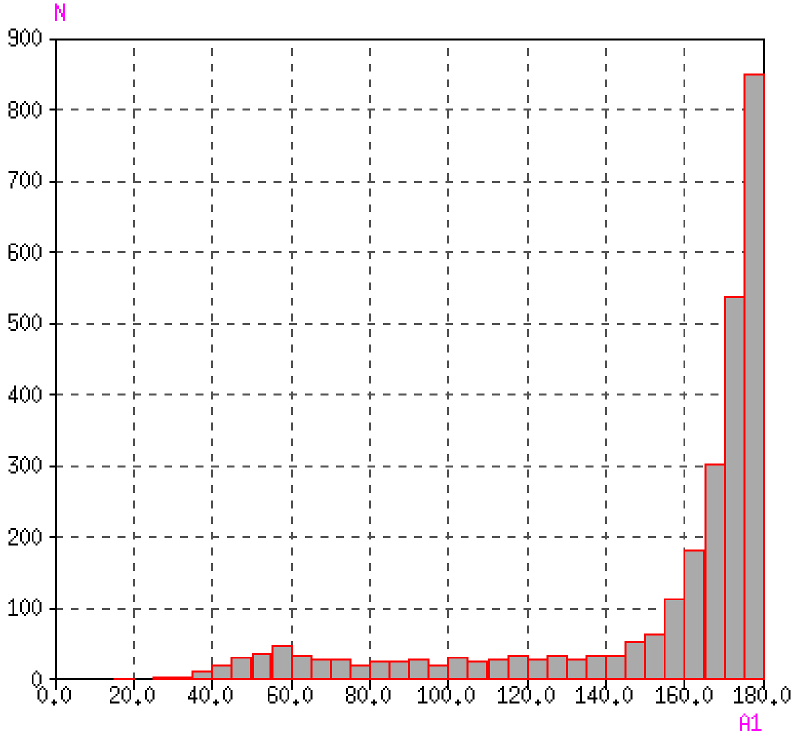
So, what about CH groups without electronegative substituents?

- 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!

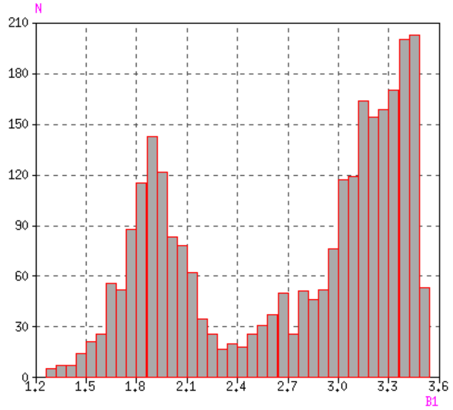
N•••H-X angle distribution

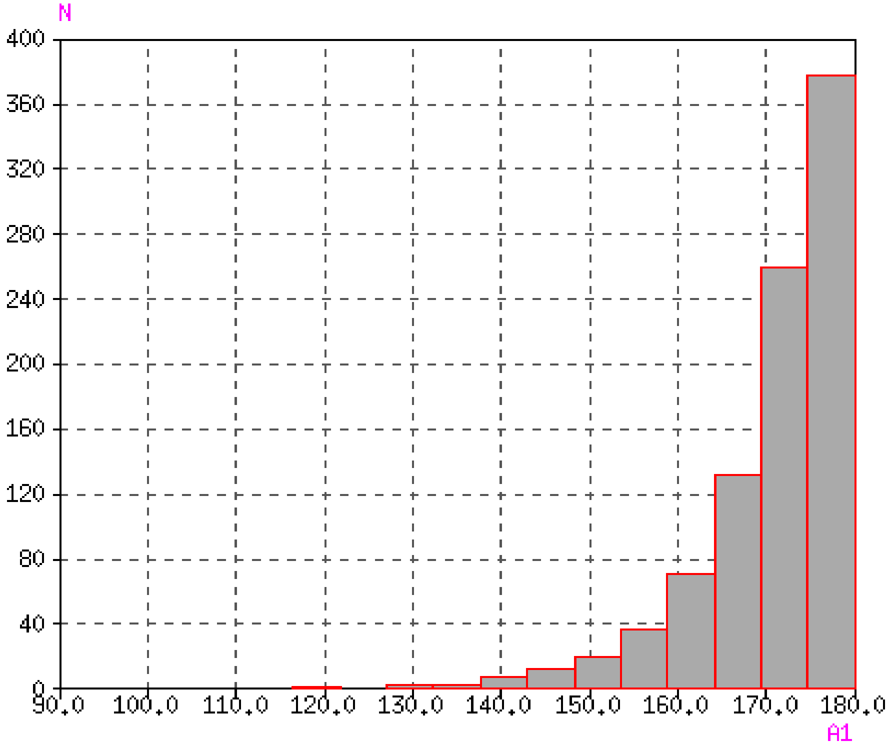


Pyridine-H-CH$_2$-CH$_2$



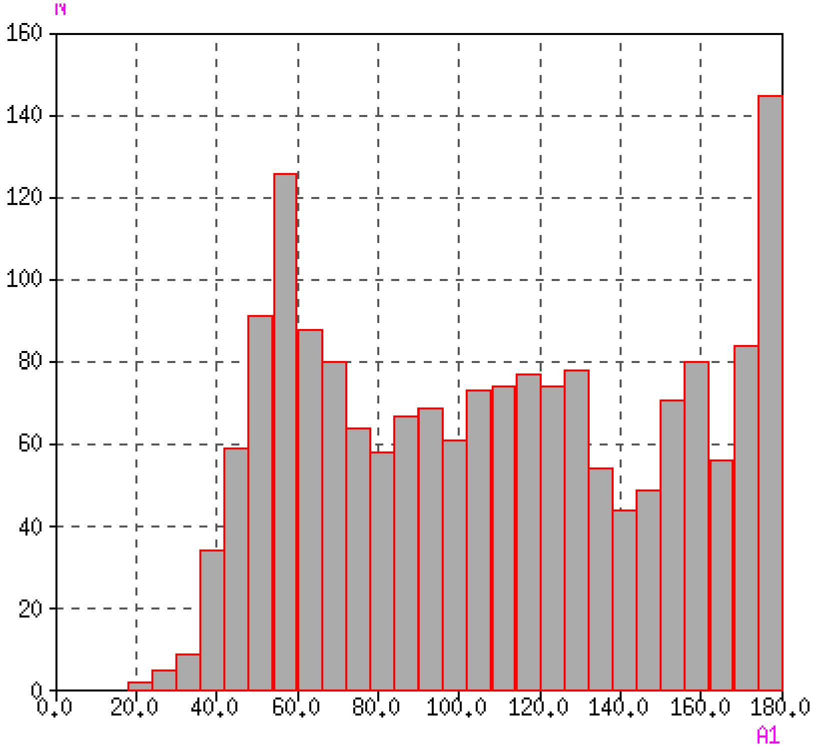
Pyridine-HO





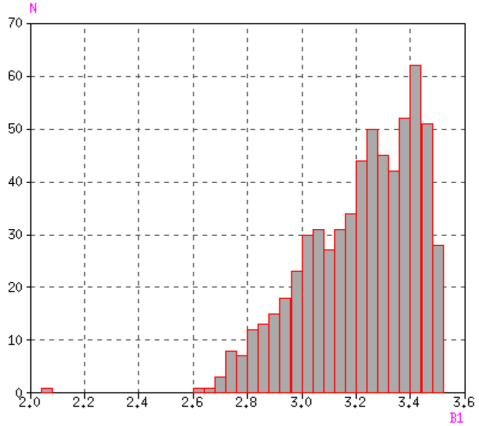
PyN---H-O

Hydrogen bond peak

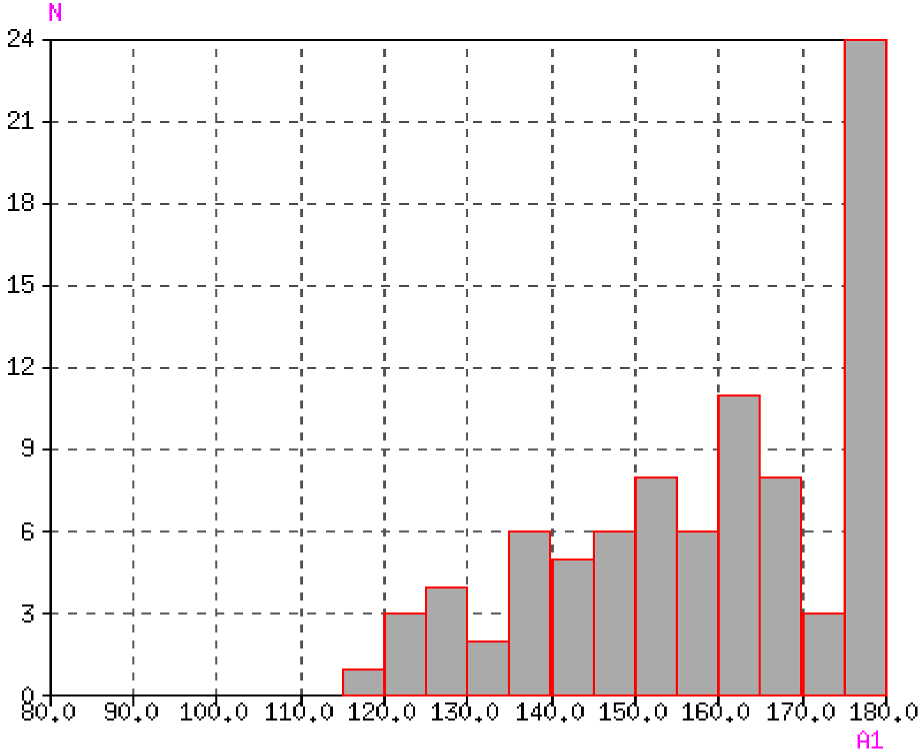


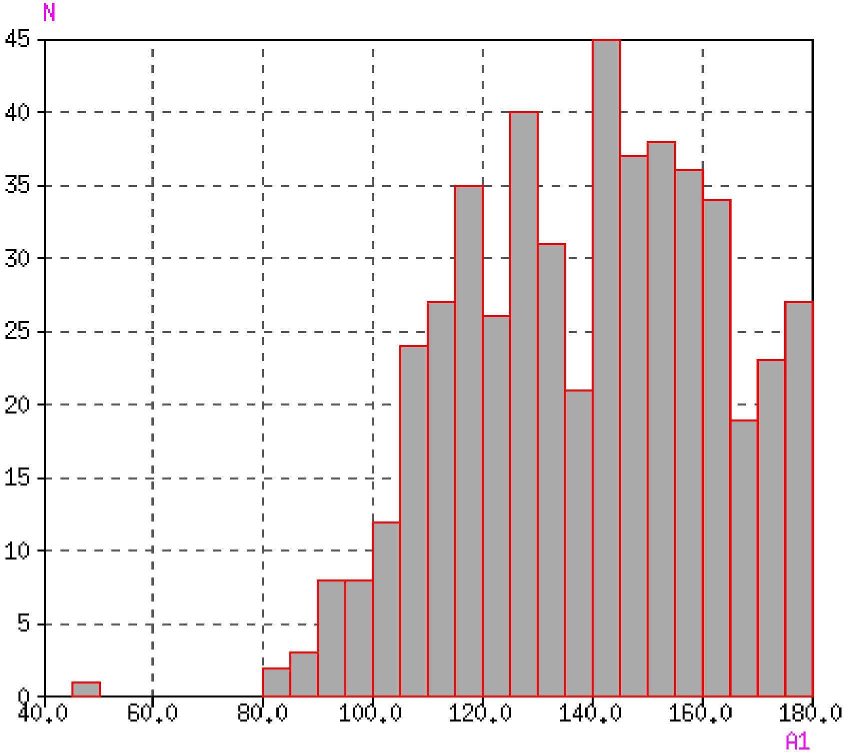
PyN---H-O

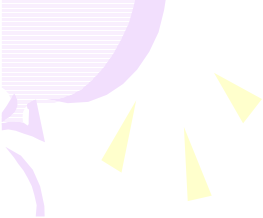
(B$_1$ >2.4 Å)



IISc







PyN---H-CH_2-CH_2

(B_1 > 2.6-3.0 Å)

PyN---H-CH_2-CH_2

(B_1 > 3.0-3.5 Å)

H bond radius from X-ray crystal structure database

H-X	CN (1.34)	Pyridine (1.27)	C_2O (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

Lakshmi, Samuelson, Jovan Jose, and Arunan *New J. Chem. 2005*