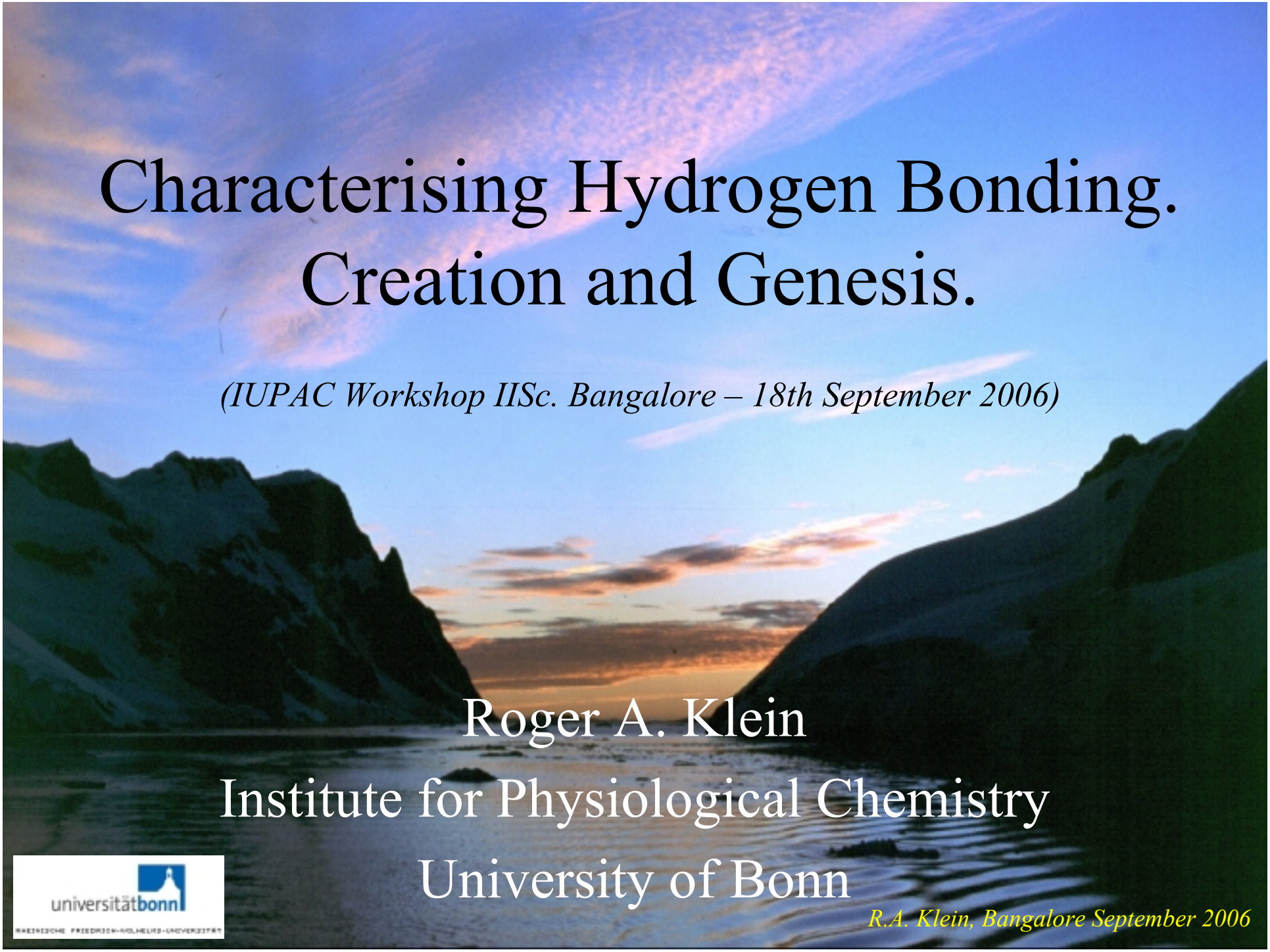


Characterising Hydrogen Bonding. Creation and Genesis.

(IUPAC Workshop IISc. Bangalore – 18th September 2006)

Roger A. Klein
Institute for Physiological Chemistry
University of Bonn

based on:

Klein, R.A.; Pacheco, V.; *Journal of Physical Chemistry A* **2001**, 105 (40) 9298.
Diols and Water Structure

Klein, R.A.; *Journal of Computational Chemistry* **2002**, 23, 585.
Diol Intramolecular Hydrogen Bonding

Klein, R.A.; *J. Amer. Chem. Soc.* **2002**, 124, 13931.
Glucopyranose and Hydrogen Bonding

Klein, R.A.; *Journal of Computational Chemistry* **2003**, 24, 1120.
Diol IR and NMR versus Hydrogen Bonding

Klein, R.A.; Mennucci, B.; Tomasi, J.; *Journal of Physical Chemistry A* **2004**, 108 (27) 5851.
^{17}O NMR of water clusters

Klein, R.A.; NIC Symposium Series **2006**, 32, 65; John von Neumann Institute for Computing, Jülich.
Cooperativity in Water Clusters

Klein, R.A.; *Chem. Phys. Lett.* **2006**, 423, 413.
Modified Atomic Radii

Klein, R.A.; *Chem. Phys. Lett.* **2006**, 425, 128.
Double-Barrelling

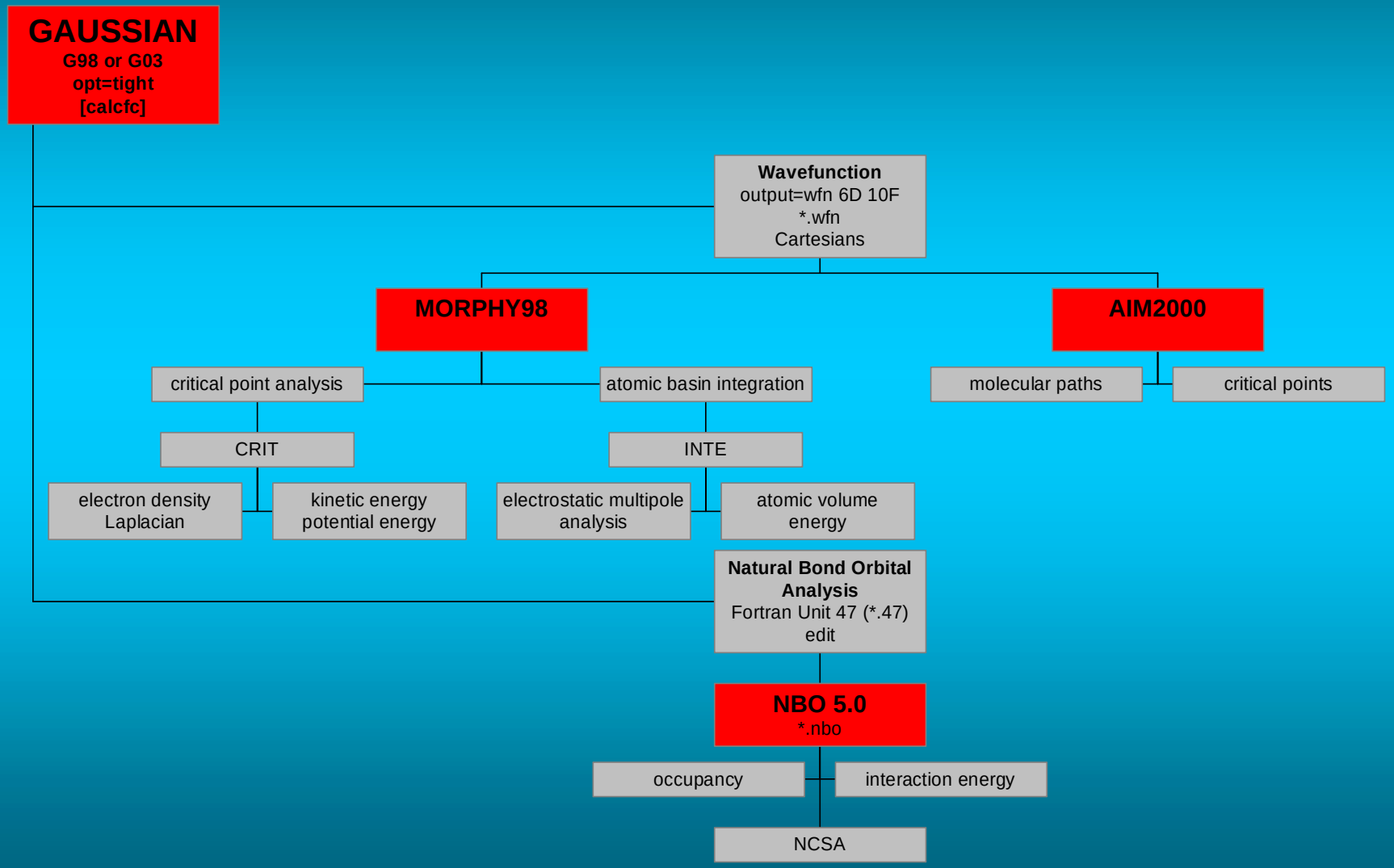
Klein, R.A.; *Chem. Phys. Lett.* **2006**, 429, in press.
Strained Cyclic Diols

Klein, R.A.; Zottola, M.A.; *Chem. Phys. Lett.* **2006**, 419, 254; 2006, 421, 595.
Pople versus Dunning basis-sets

Summary

- Diols and water structure
- Intramolecular hydrogen bonding in
  - Open-chain diols and other 2-substituted ethanols
  - Cyclic 1,2-diols
  - Glucopyranose
- VDW atomic radii
- Topological fold catastrophes
- Cooperativity in water clusters

Data Generation



Gaussian 98 / Gaussian 03

- MPW1PW91/6-311+G(2d,p)
- output=wfn 6D 10F
- NMR prop
- $NBO archive plot print=2 file=*name* $END

Diols and Water Structure

Structuring and de-structuring

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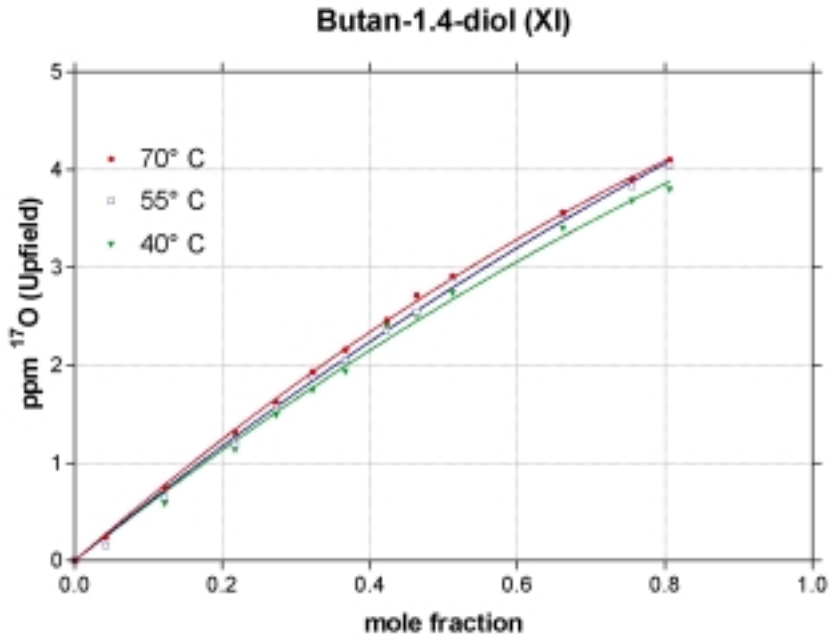
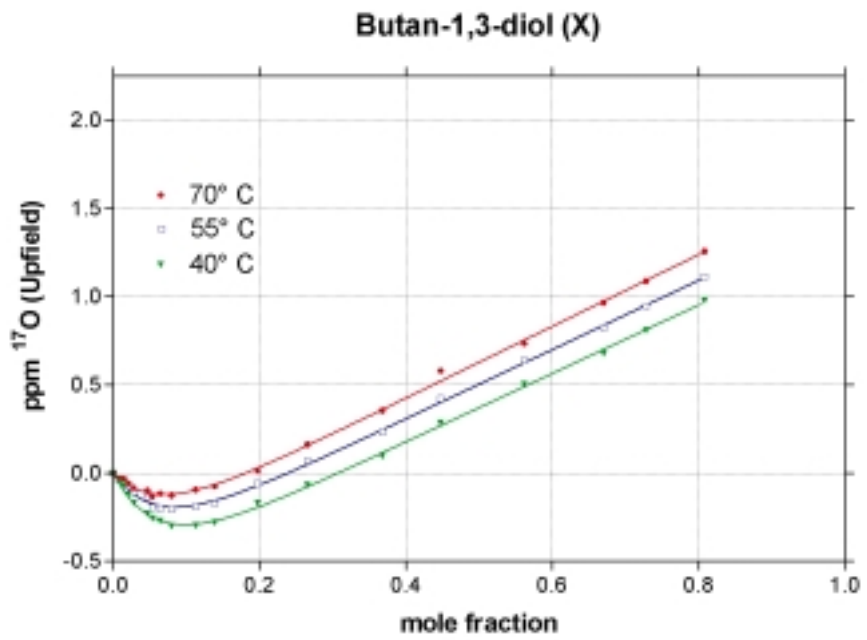
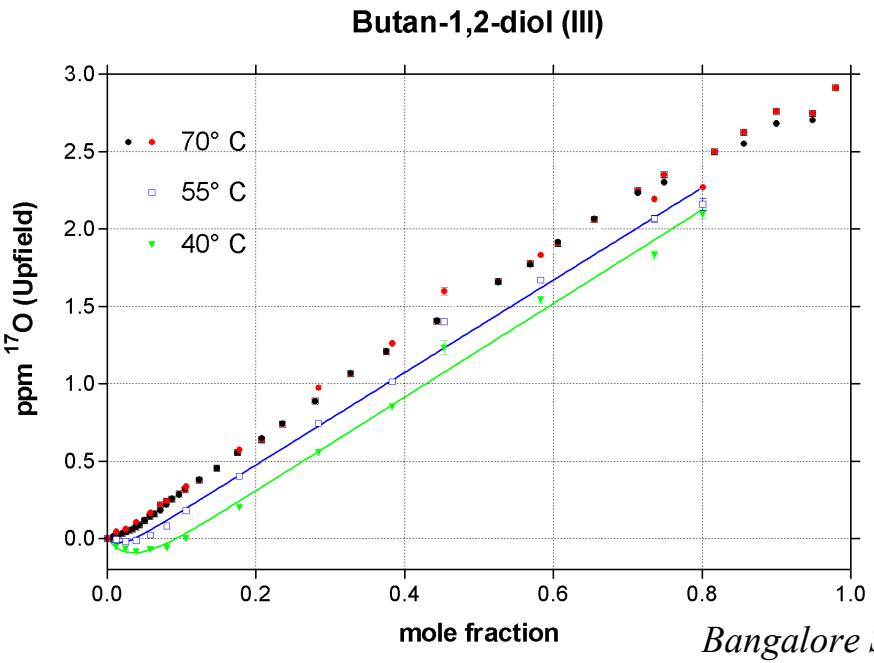
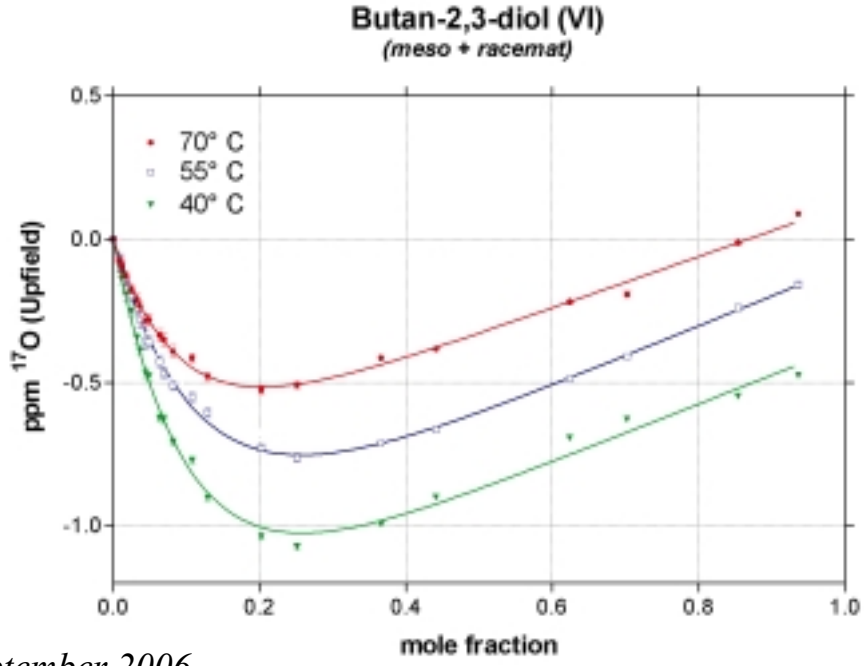

Butan-1.4-diol (XI)
70° C
55° C
40° C
ppm 17O (Upfield)
mole fraction

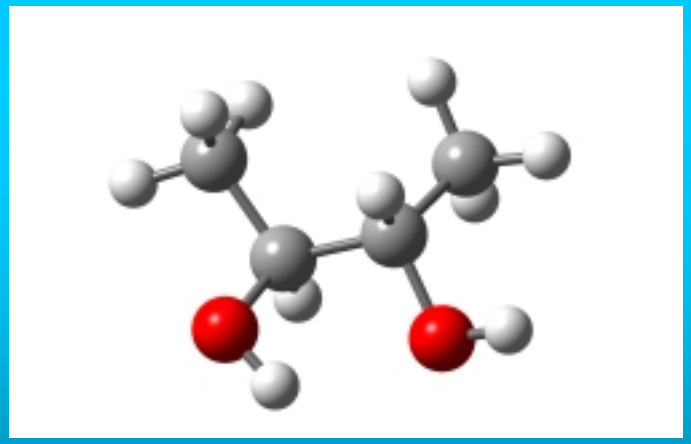

Butan-1,3-diol (X)
70° C
55° C
40° C
ppm 17O (Upfield)
mole fraction


Butan-1,2-diol (III)
70° C
55° C
40° C
ppm 17O (Upfield)
mole fraction


Butan-2,3-diol (VI)
(meso + racemat)
70° C
55° C
40° C
ppm 17O (Upfield)
mole fraction

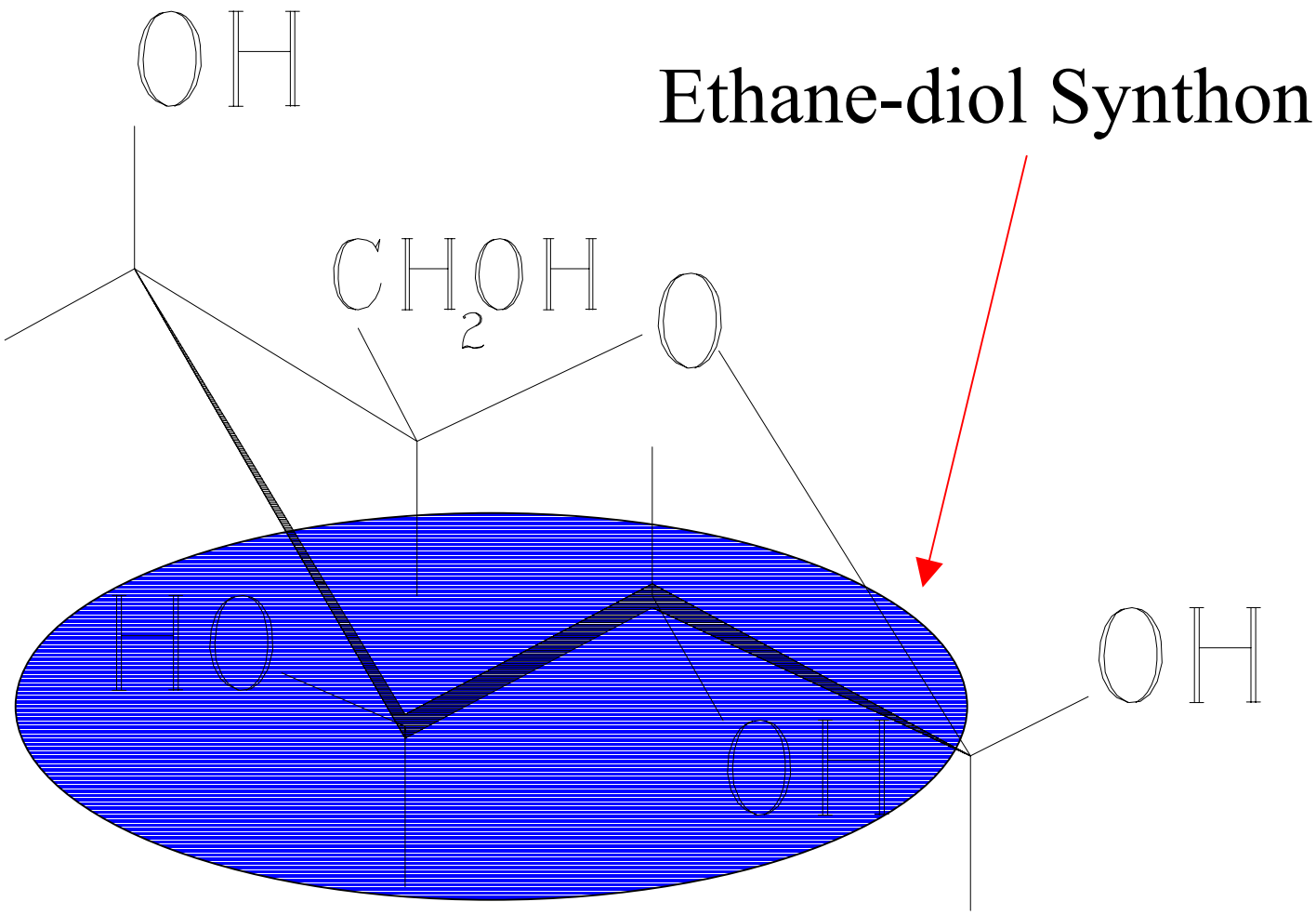
^{17}O Chemical Shift as a Measure of Water Structure in Binary Glycol-Water Systems

- Type I (upfield) = 'destructuring' - all glycols but structure-dependent



- Type II (downfield) = 'structuring' - only glycols containing the methylcarbinol group, CH_3CHOH

$^4C_1$-Galactopyranose



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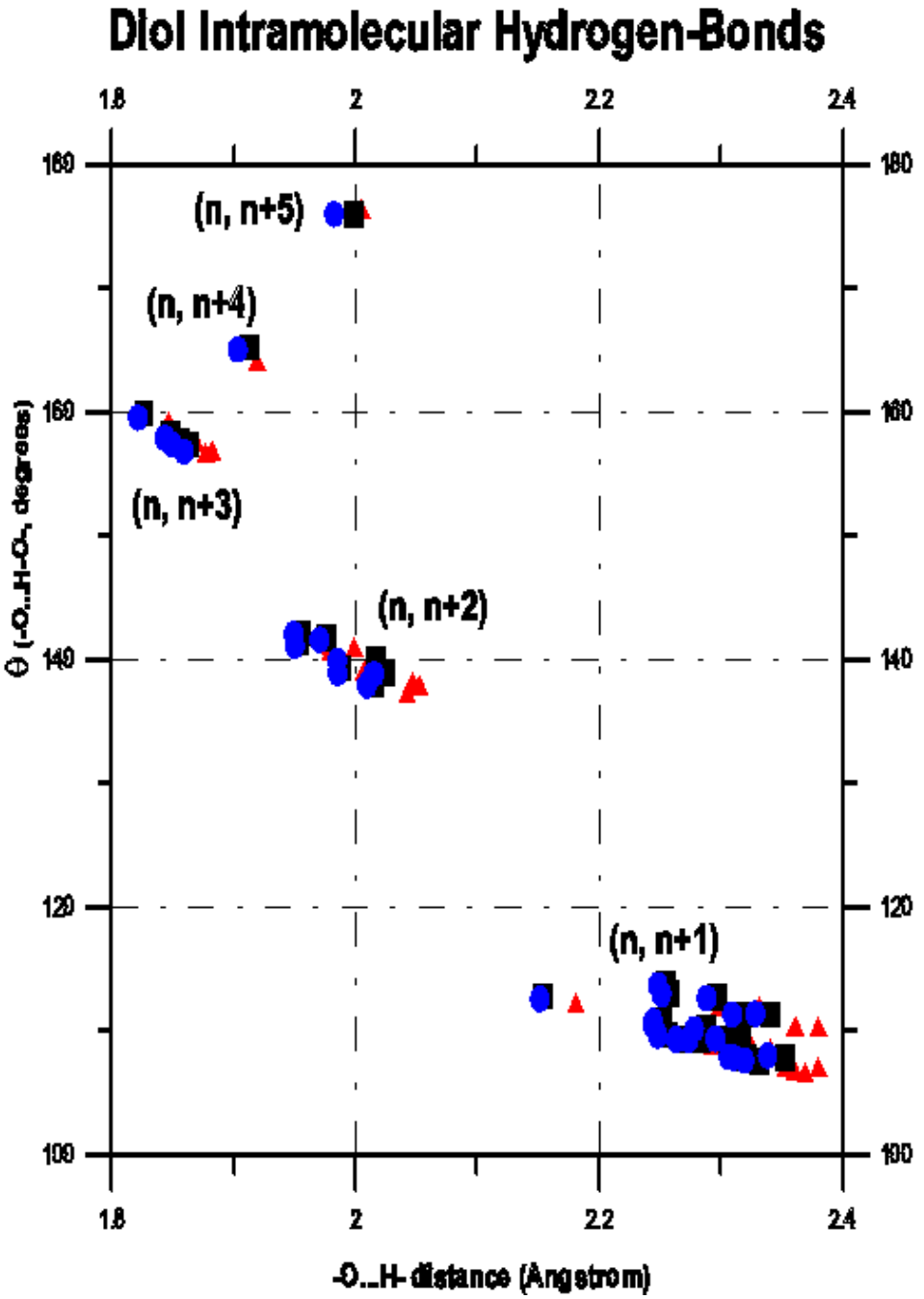
Intramolecular Hydrogen Bonding

- open-chain diols and 2-substituted ethanols

Diols

- (n,n+1)
  - 12ED, 23BD
- (n,n+2)
  - 13BD, 25PD
- (n,n+3)
  - 14BD, 25HD
- (n,n+4)
  - 15PD
- (n,n+5)
  - 16HD



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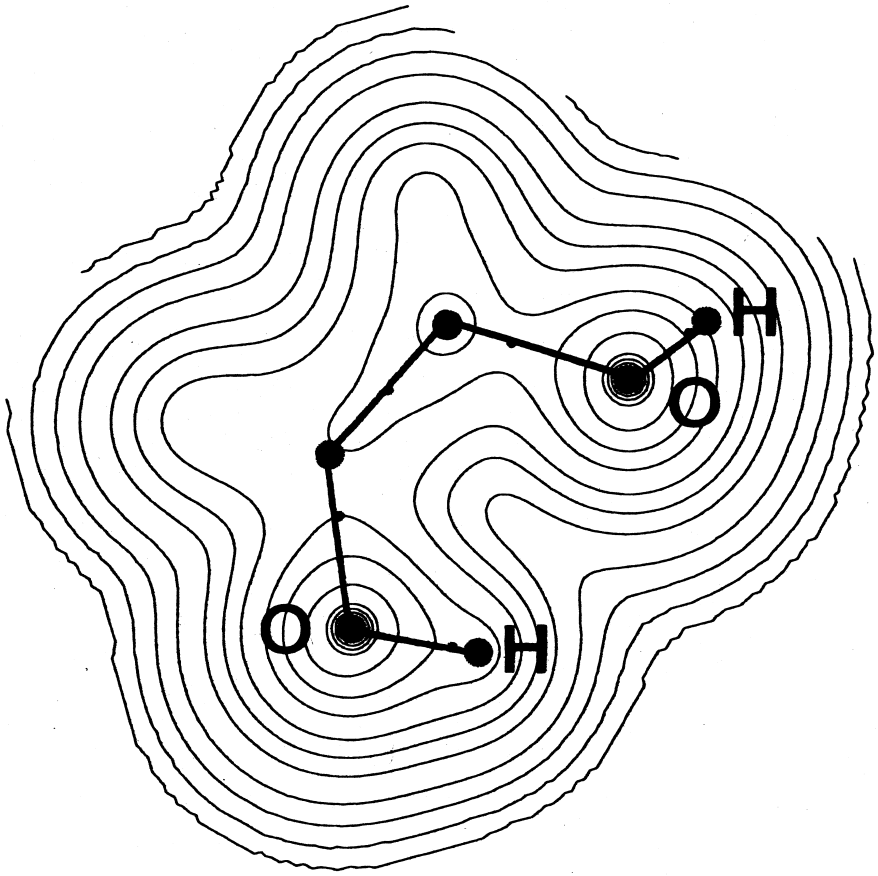
Electron Density



Ethane-1,2-diol

MPW1PW91/6-311+G(2d,p) 6D 10F

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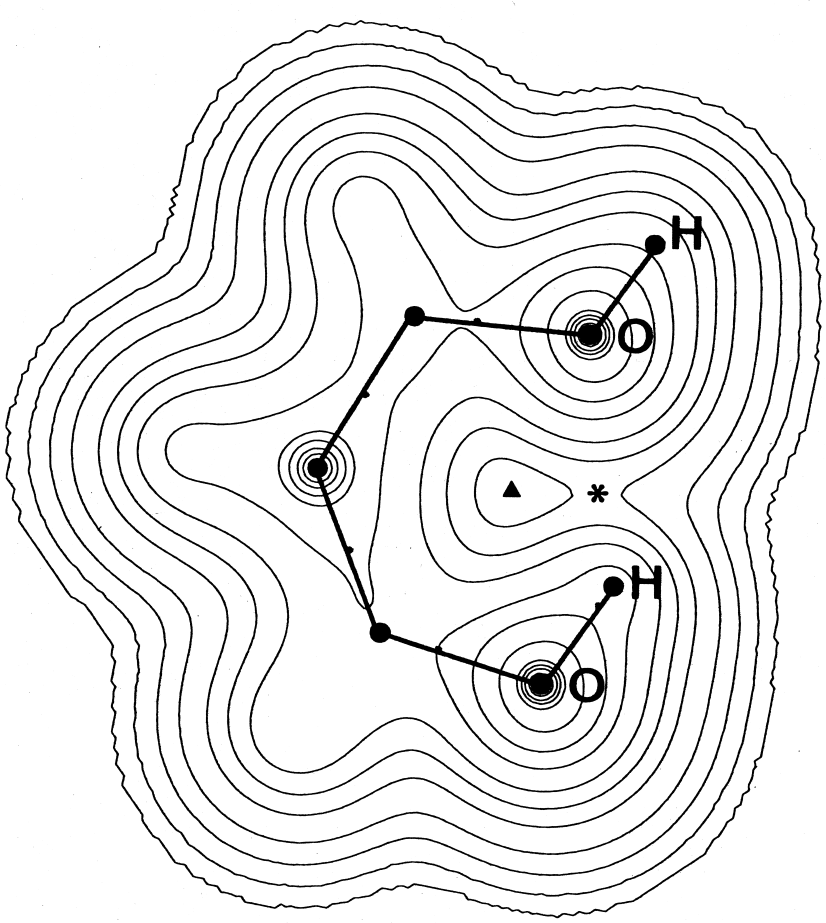
Electron Density



Propane-1,3-diol

MPW1PW91/6-311+G(2d,p) 6D 10F

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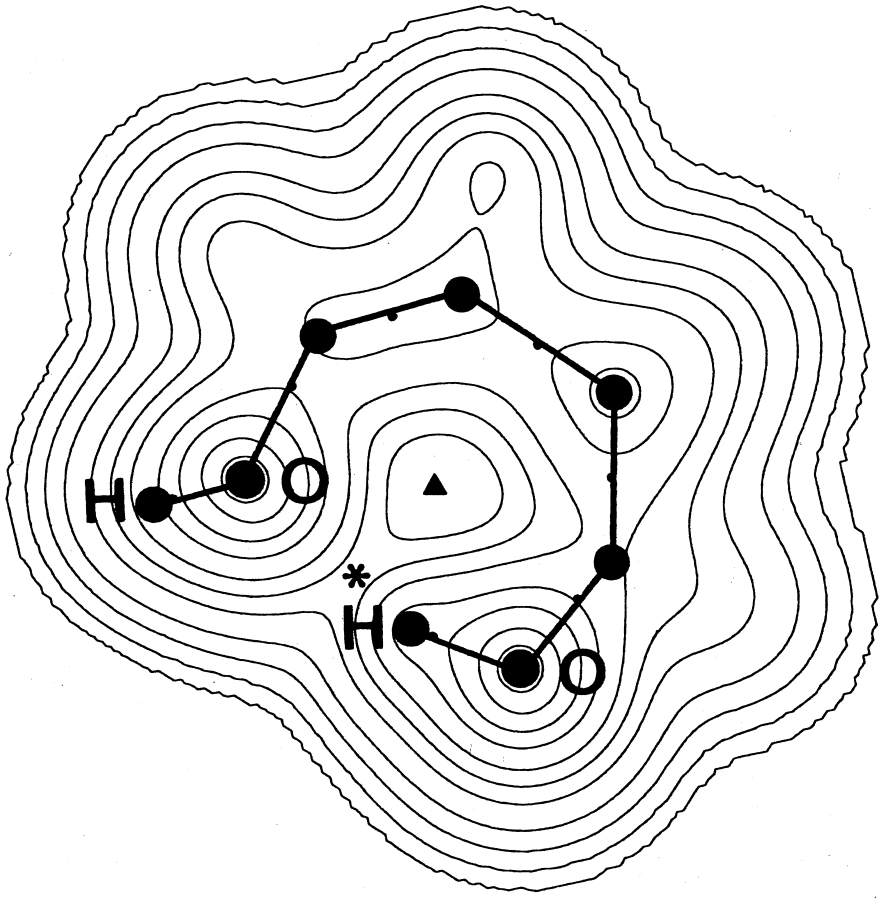
Electron Density



Butane-1,4-diol

MPW1PW91/6-311+G(2d,p) 6D 10F

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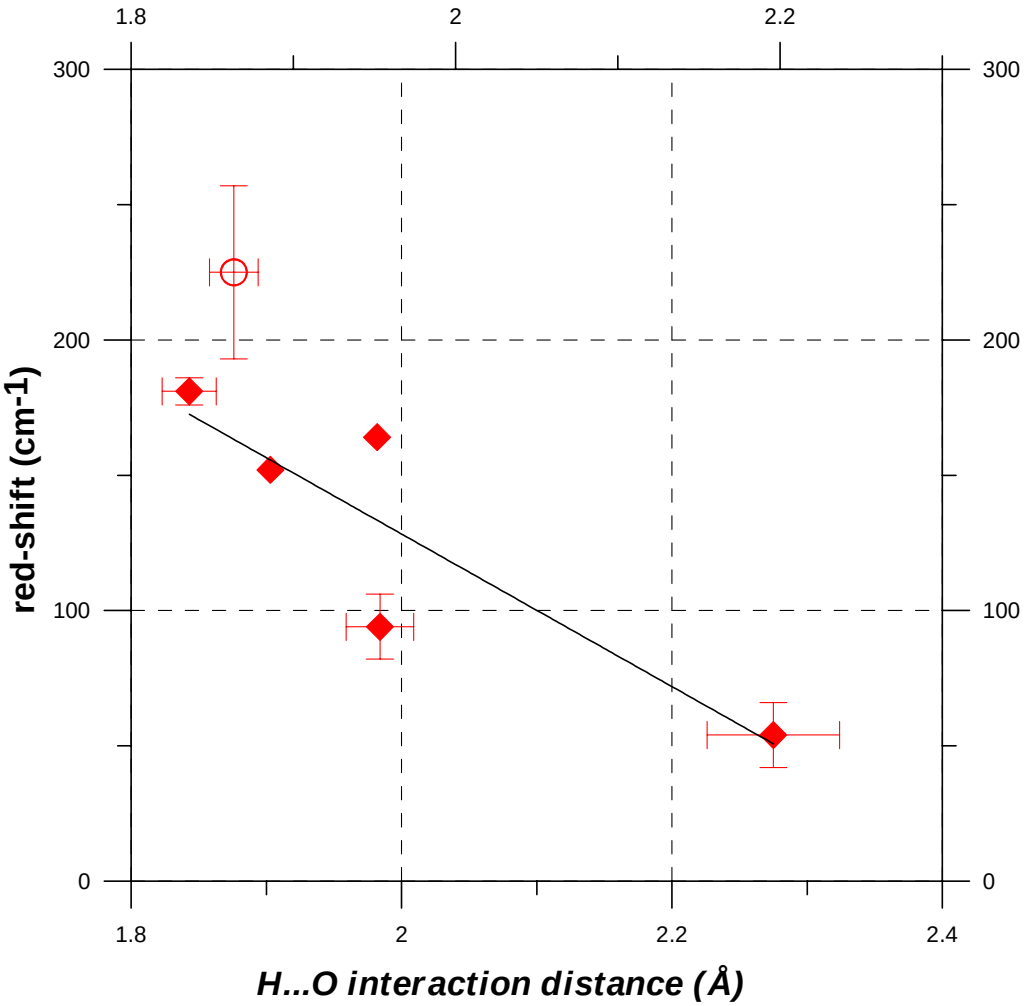
BCP Electron Density and Laplacian

Diol	rho	∇^2rho	f(h)	ellipt.	BCP
12EG	--	--	--	--	no
13PG	0.02163	+0.0845	0.3713	0.02293	yes
14BD	0.03186	+0.1128	0.3479	0.04764	yes
15PD	0.02576	+0.0987	0.3532	0.06160	yes
16HD	0.02282	+0.0802	0.3513	0.02240	yes

IR red-shift for -O-H_D



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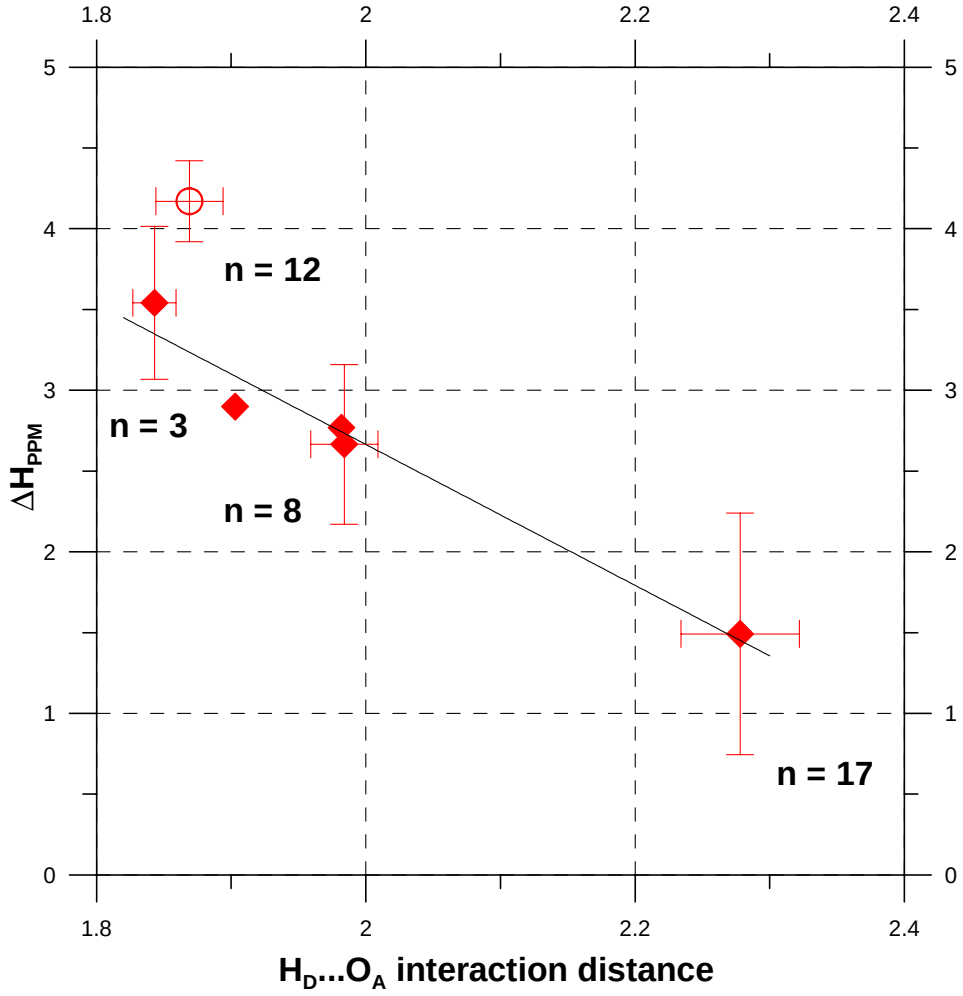
NMR downfield shift for -O-H_D



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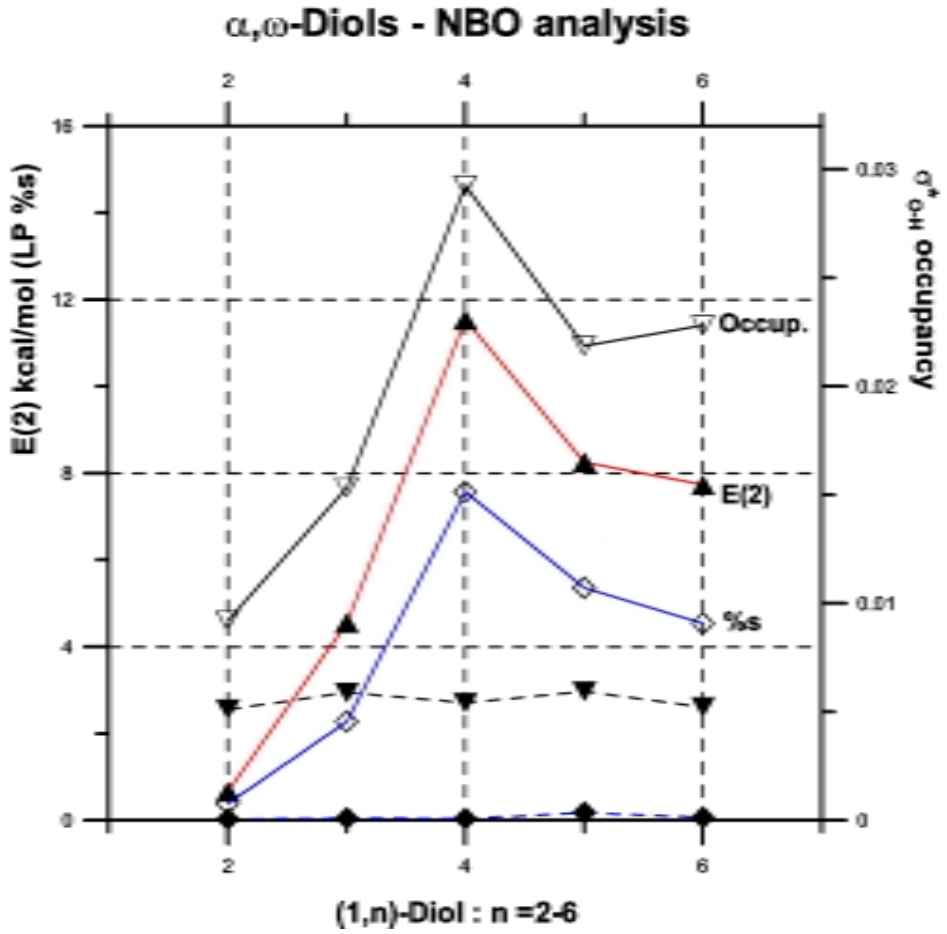
α,ω-Diols - NBO Analysis



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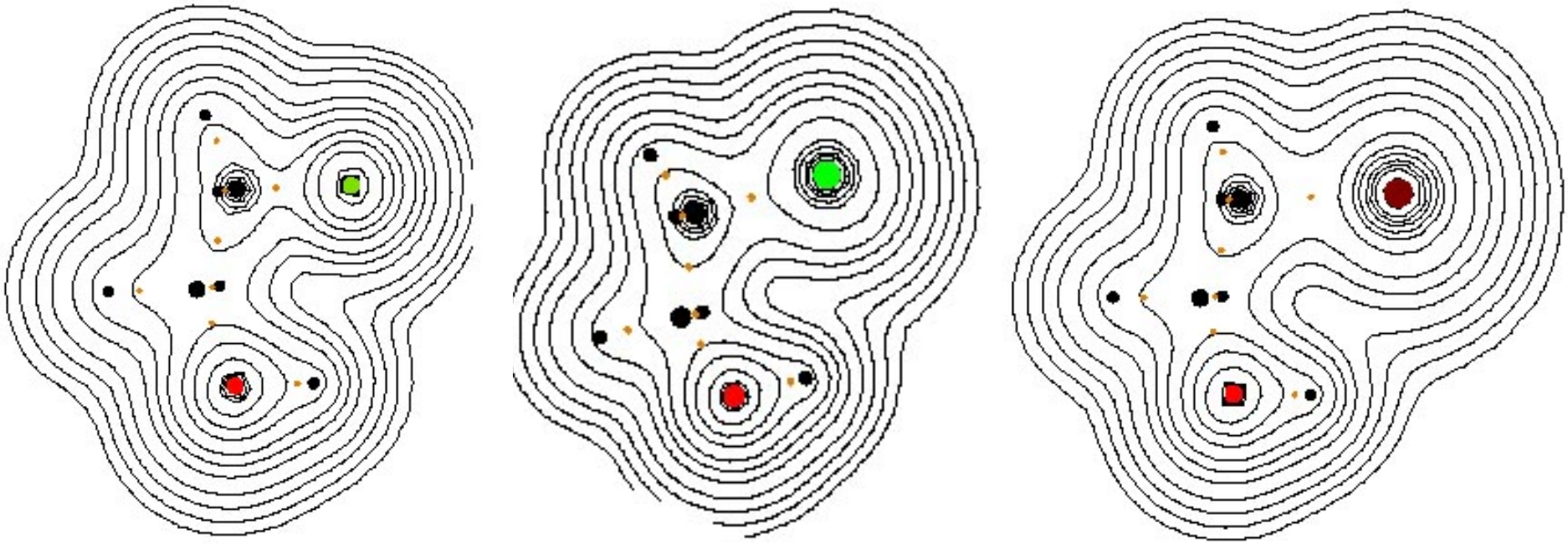
2-Haloethanols

F **Cl** **Br**



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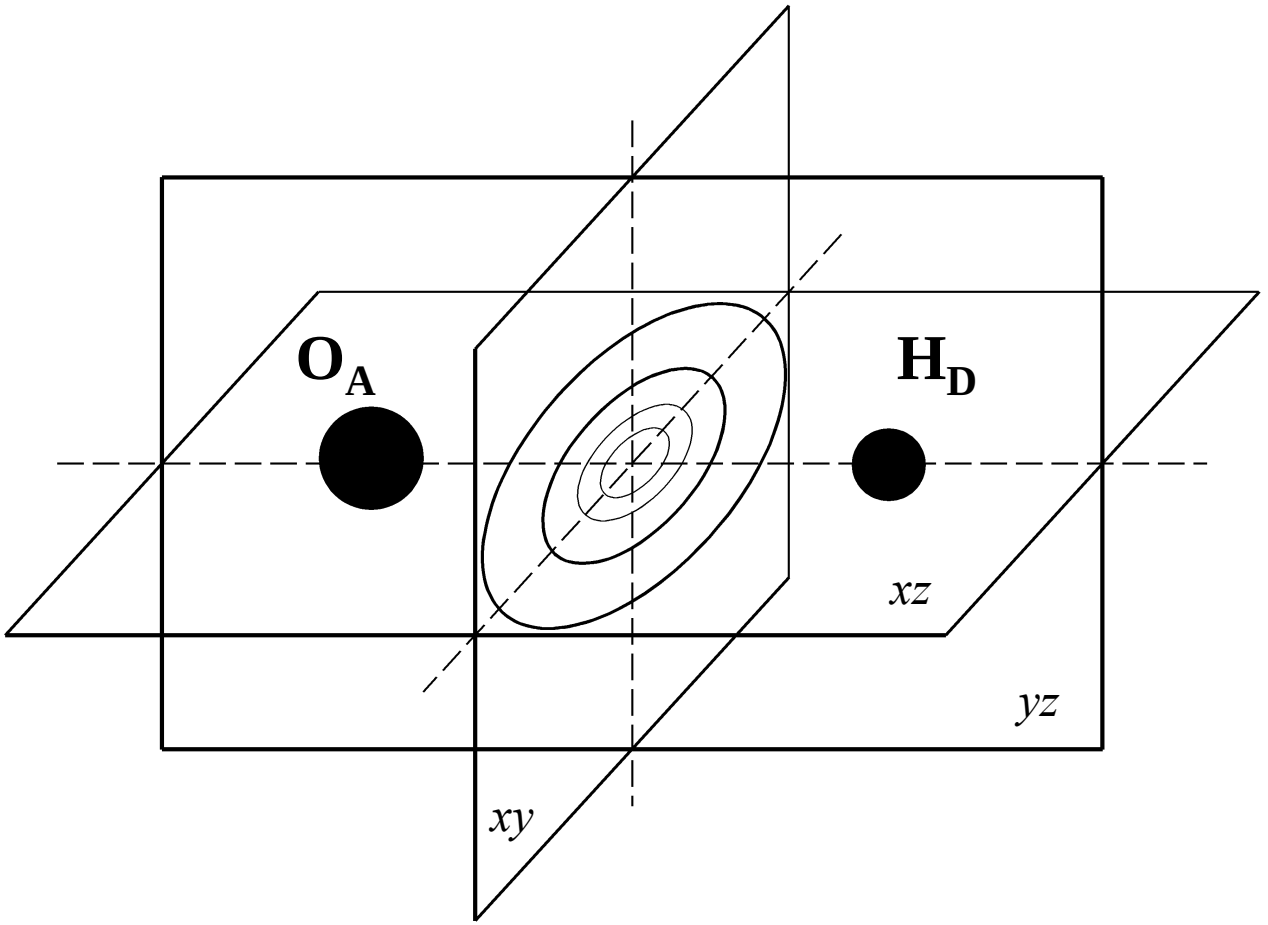
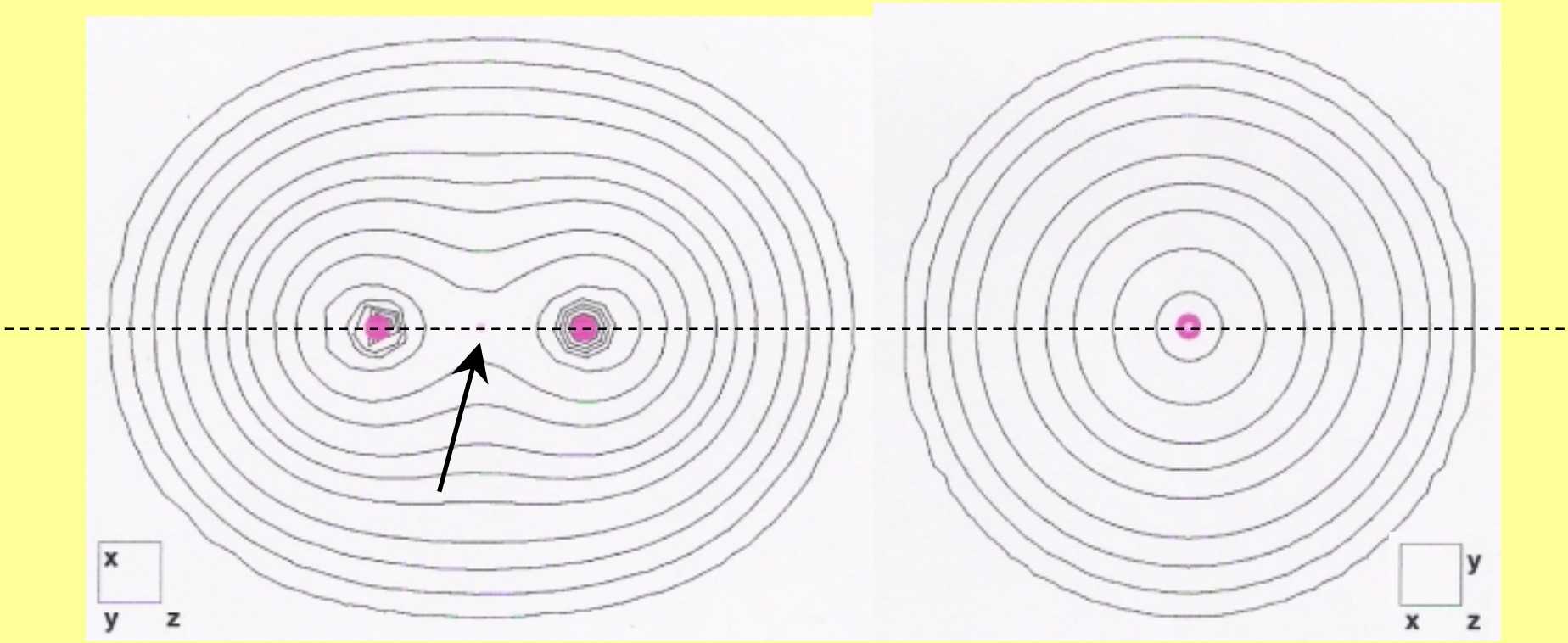
Internuclear axes



Bond Critical Point (BCP)



O_2 MP2/aug-cc-pVDZ

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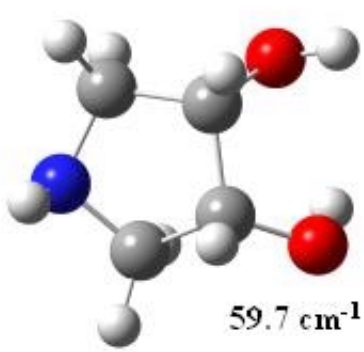
Intramolecular Hydrogen Bonding

- open-chain diols and 2-substituted ethanols
- strained cyclic 1,2-diols

Cyclic 1,2-Diols

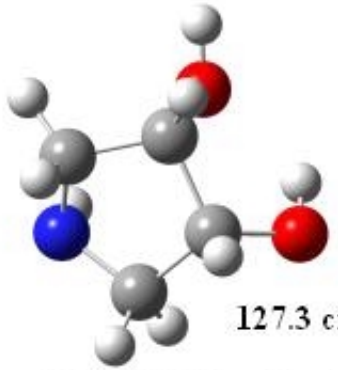
- Simple cyclic diols such as:
  - Dihydroxycyclopropane (C3):
  - 1,2-Dihydroxycyclobutane (C4):
  - 1,2-Dihydroxycyclopentane (C5):
  - 1,2-Dihydroxycyclofuran (C4O);
  - 1,2-Dihydroxycyclohexane (C6);
  - 1,2-Dihydroxybenzene (C6);
- do not form an intramolecular –O…H-O- hydrogen bond as evidenced by a (3,-1) BCP.

Dihydroxypyrrolidine conformers



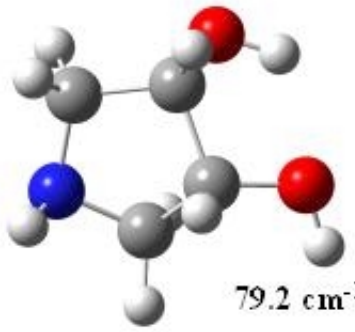
59.7 cm^{-1}

NO (+0.45 kcal/mole)



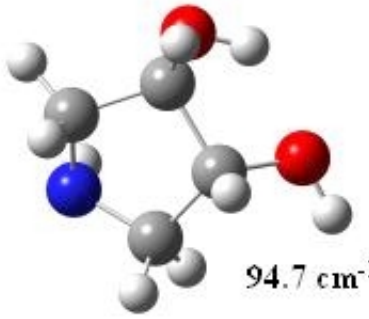
127.3 cm^{-1}

YES (+0.65 kcal/mole)



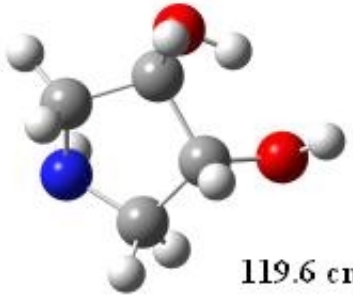
79.2 cm^{-1}

NO (+0.90 kcal/mole)



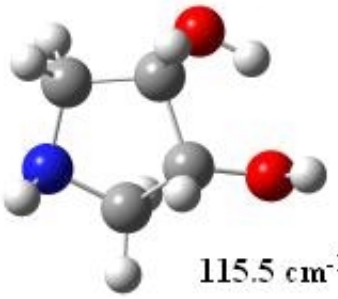
94.7 cm^{-1}

YES (+0.25 kcal/mole)



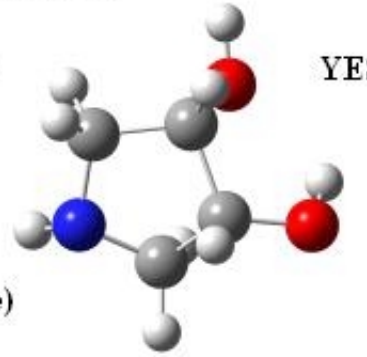
119.6 cm^{-1}

YES (+0.00 kcal/mole)



115.5 cm^{-1}

YES (+1.02 kcal/mole)



94.6 cm^{-1}

NO (+0.56 kcal/mole)

unscaled (ν_1-ν_2)

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Dihydroxypyrrolidine conformers

DHCPyr	O_A-H	O-H_D	HB?
A1	*26.0*	*82.3*	*N*
A2	-4.8	115.3	Y
B1	*10.7*	*85.4*	*N*
B2	5.8	95.1	Y
C1	22.8	135.5	Y
C2	13.9	122.8	Y
D1	*0.6*	*89.8*	*N*
D2	*26.0*	*82.4*	*N*

Scaled IR red-shifts in cm^{-1} referenced to 12EG_confA

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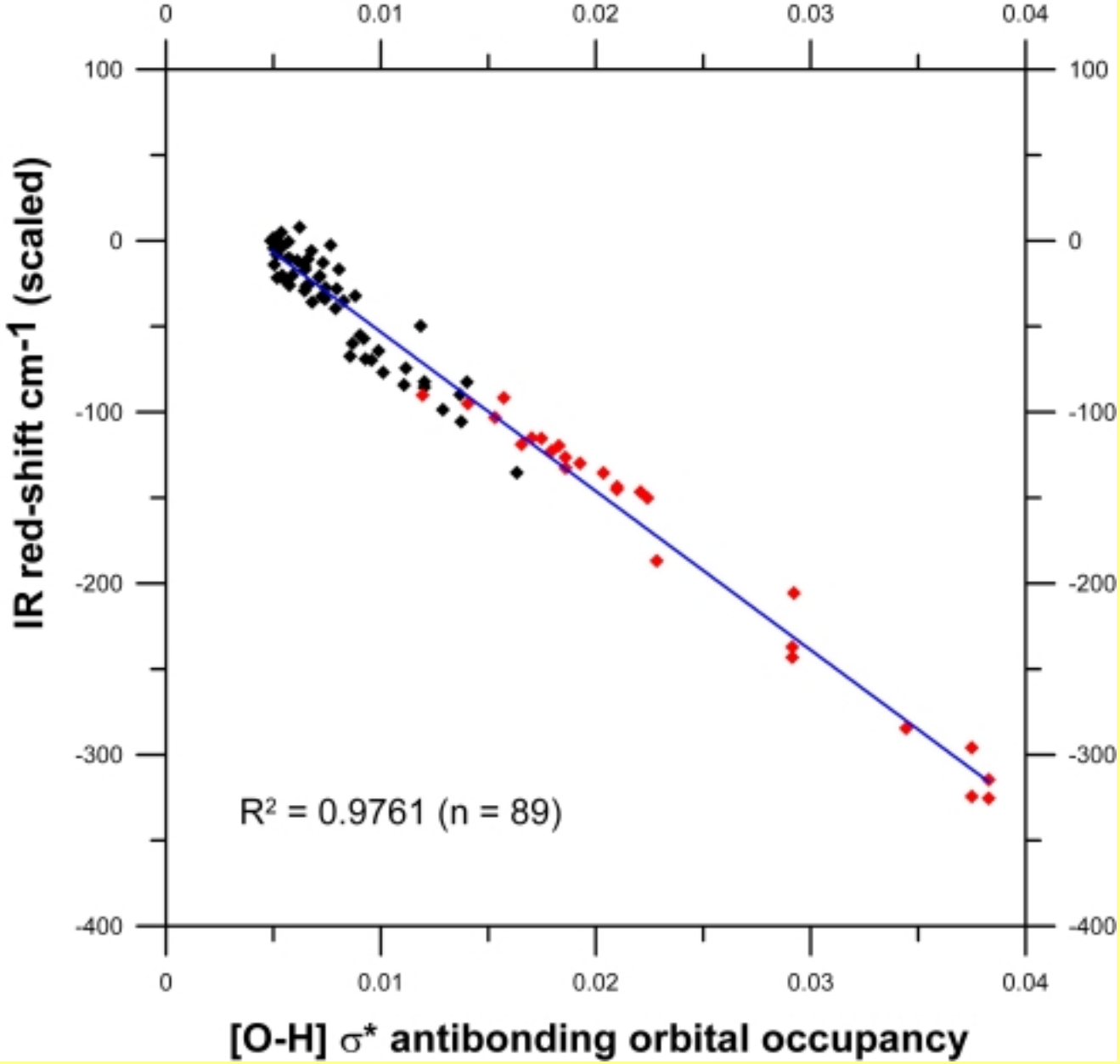
Diol [O-H] σ* occupancies



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IR red-shifts and antibonding orbital occupancies without hydrogen bonding

Ethanediol Conformer	kcal/mol	ν cm^{-1}	shift cm^{-1}	occupancy σ*[O—H]
tTt	2.35	3690.5 (s)	**0.0**	0.00489
		3691.0 (a)		
gTt	2.52	3687.0	**-3.2**	0.00520
		3669.6	**-21.2**	0.00730
gTg	2.72	3664.6 (a)	**-26.4**	0.00769
		3665.5 (s)	**-25.1**	
gTg'	2.52	3668.0 (a)	**-23.0**	0.00718
		3669.4 (s)	**-21.2**	
tGt	2.58	3693.5 (a)	**+2.5**	0.00492
		3693.7 (s)	**+3.2**	
g'Gg'	0.74	3675.9 (a)	**-15.1**	0.00641
		3677.4 (s)	**-13.2**	
g'G'g'	4.95	3659.0 (a)	**-32.0**	0.00778
		3659.9 (s)	**-30.7**	
g'Pg'	2.18	3644.5 (s)	**-46.1**	0.00902
		3648.0 (a)	**-43.0**	
g'Gt (min)	(00.0)	3636.9	**-53.9**	0.00920
		3690.8	**0.0**	0.00512

Average for 1,2-diols = -29.9 ± 9.6 cm^{-1}

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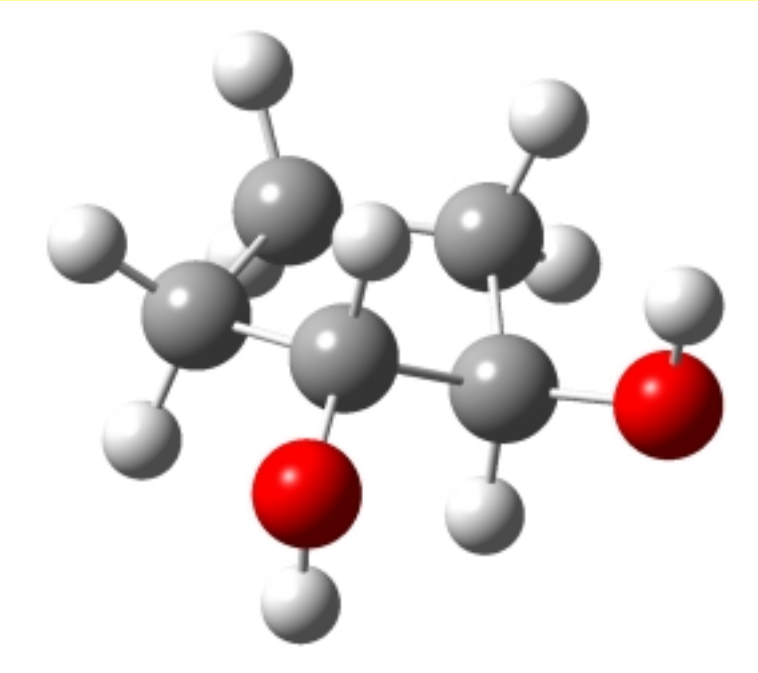
IR red-shifts and antibonding orbital occupancies without hydrogen bonding

1,2-dihydroxycyclopentane



red-shift = 40.0 cm^{-1}

σ^*[O-H] = 0.00907

C-H => σ^*[O-H]
= 2.99 kcal/mole

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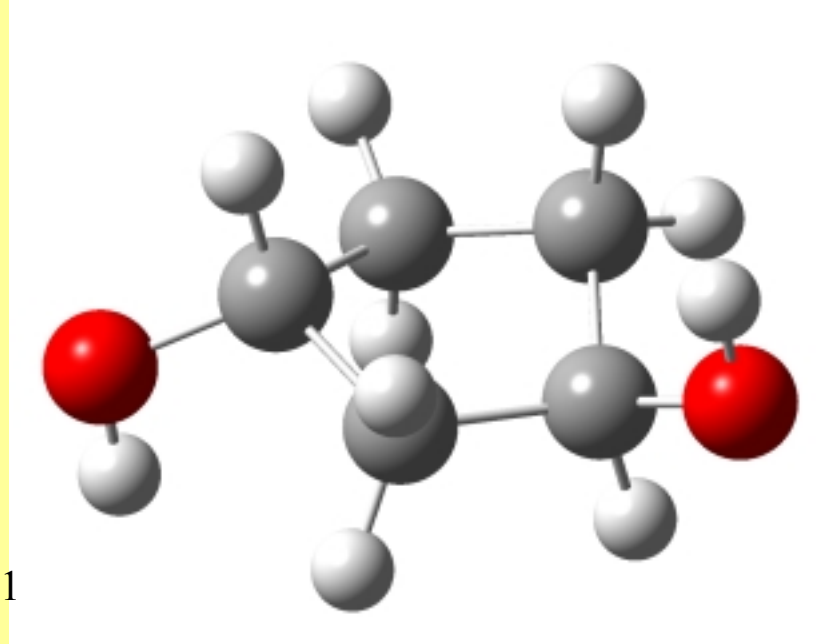
IR red-shifts and antibonding orbital occupancies without hydrogen bonding

1,3-dihydroxycyclopentane



red-shift = 43.5 cm^{-1}

σ^*[O-H] = 0.00944

C-H => σ^*[O-H]
= 3.04 kcal/mole

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Hyperconjugation and Steric Effects

(a.k.a. Pauli Exchange Repulsion)

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σ_{CH} - σ_{CH}^* in Ethane

(Weinhold & Landis, 2005)

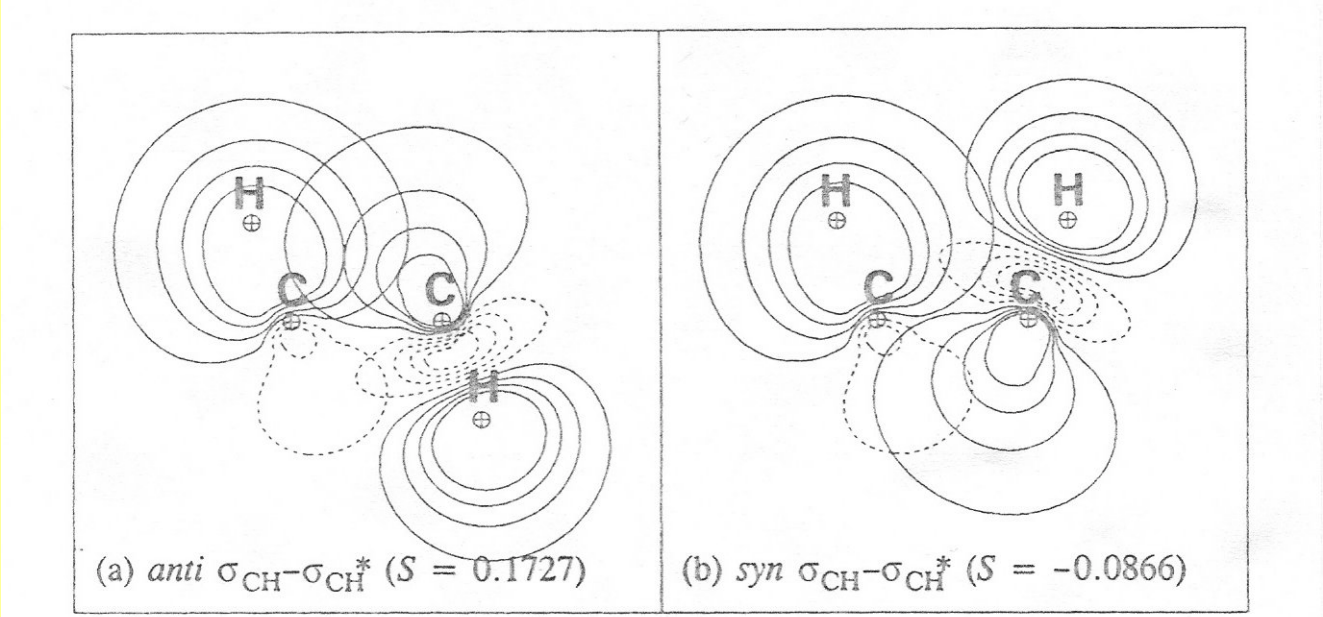

Figure 3.55 Leading σ_{CH}–σ_{CH}^* hyperconjugative donor–acceptor interactions in the staggered (left) and eclipsed (right) conformers of ethane.

Numerical overlap integral (S) larger by a factor of two for the *anti*-periplanar arrangement compared to the *syn*-periplanar one.

n_o => [O-H]σ* hyperconjugation in 1,2-diols

	HB?	kcal/mole		HB?	kcal/mole
12EGb	*N*	*0.54*	DHCP A1	*N*	*1.76*
12EGd	*N*	*0.98*	DHCP A2	Y	3.96
13PG	Y	4.55	DHCP B1	*N*	*1.77*
14BD	Y	11.57	DHCP B2	Y	2.68
15PD	Y	8.06	DHCP C1	Y	4.63
16HD	Y	7.64	DHCP C2	Y	3.65
NB2OH	Y	3.52	DHCP D1	*N*	*2.06*
NB4OHex	Y	5.28	DHCP D2	*N*	*1.33*
NB4OHen	Y	7.02	Ribose A	Y	3.19
NB4OHm	Y	5.37	Ribose B	*N*	*1.60*
NB4OHdi	Y	3.19			

Average σ => σ* stabilisation = 4.41 ± 0.38 kcal/mole

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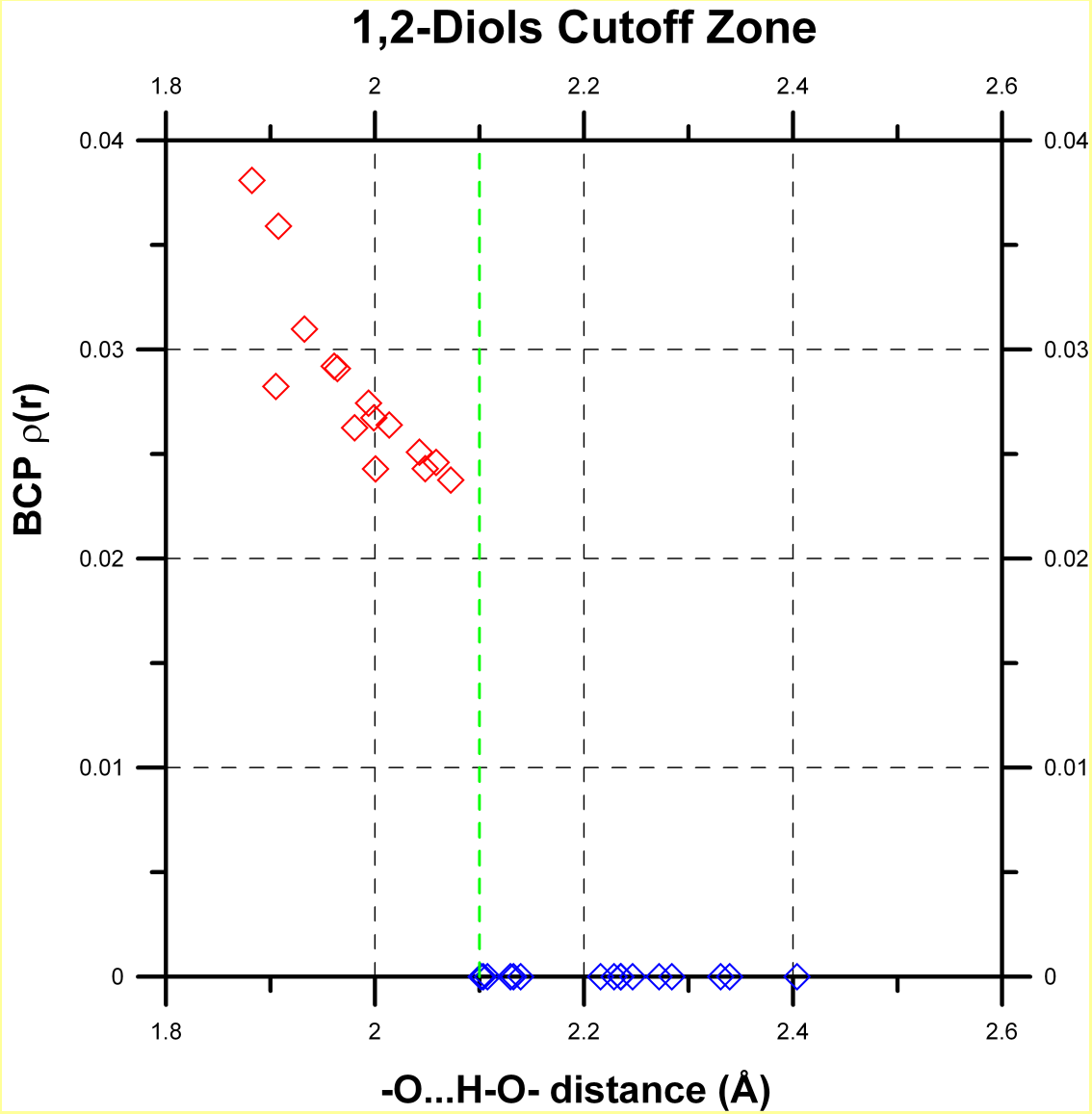
Geometric Cutoff Point



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Hyperconjugation v. Pauli Exchange

Structure	[S*]	[S]	$\Delta E_{n=>\sigma^*}$	$\Delta E_{exchange}$	ΔE_{diff}
12EG *(tGg')*	0.0601	**0.1066**	-0.54	+1.29	+0.75
12EG *(gGg')*	0.0817	**0.1024**	-0.98	+1.56	+0.58
12PG *(tG'g)*	0.1038	**0.1335**	-0.87	+1.95	+1.08
12PG *(tGg')*	0.0899	**0.1166**	-0.71	+1.57	+0.86
23BD (meso)	0.1166	**0.1388**	-1.00	+2.08	+1.08
13PG *(tGG'g)*	**0.2596**	0.1836	-4.55	+4.52	-0.03
13BD ***(A)***	**0.2860**	0.2034	-5.63	+5.48	-0.15
13BD *(B)*	**0.2473**	0.1785	-5.64	+5.74	+0.10
2M13PG *(A)*	**0.2602**	0.1881	-4.53	+4.67	+0.14
24PD *(dl)*	**0.2789**	0.2082	-4.90	+5.48	+0.58
24PD *(meso)*	**0.3027**	0.2250	-6.13	+6.41	+0.28
14BD	**0.3687**	0.2298	-11.57	+9.00	-2.57
25HD *(dl)*	**0.3801**	0.2542	-12.60	+10.62	-1.98
25HD *(meso)*	**0.3658**	0.2415	-11.29	+9.43	-1.86
15PD	**0.3441**	0.2108	-8.06	+6.40	-1.66
16HD	**0.3068**	0.1915	-7.64	+5.51	-2.07

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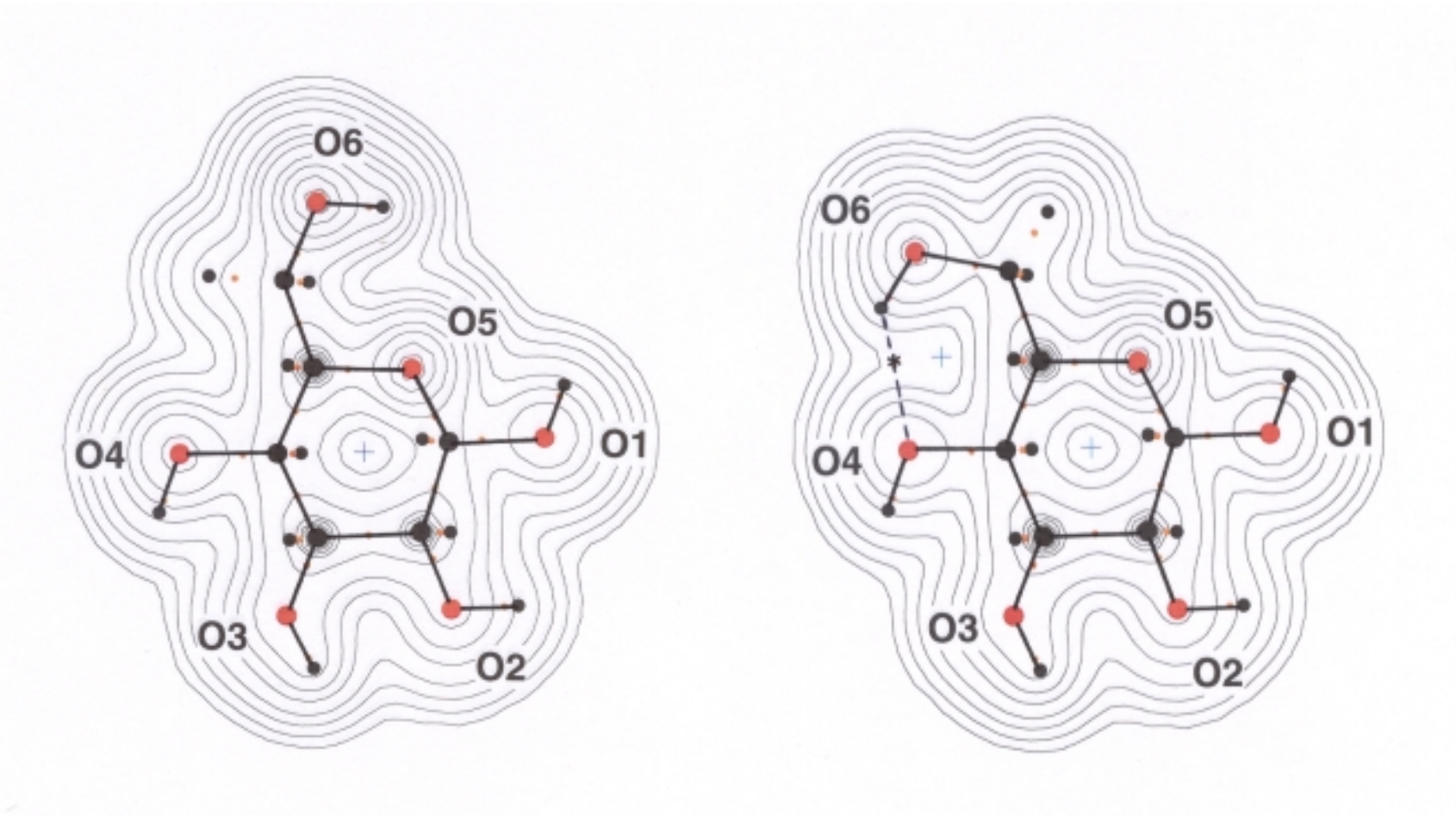
Intramolecular Hydrogen Bonding

- open-chain diols and 2-substituted ethanols
- strained cyclic 1,2-diols
- carbohydrate rings, e.g., hexopyranose

Glucopyranose $^4C_1$ *g*+ / *trans*



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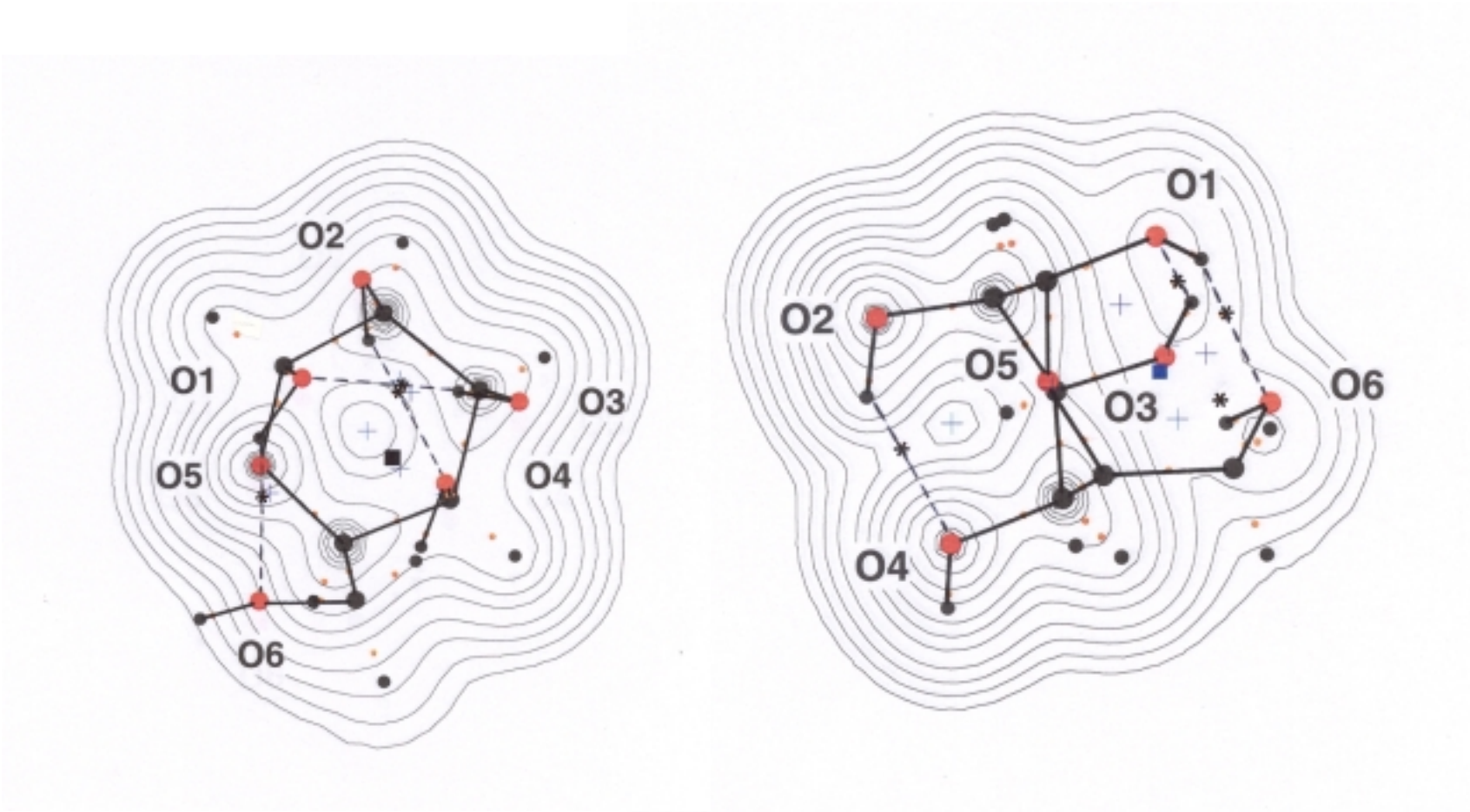
Glucopyranose $^{1}C_{4}$ *g*+



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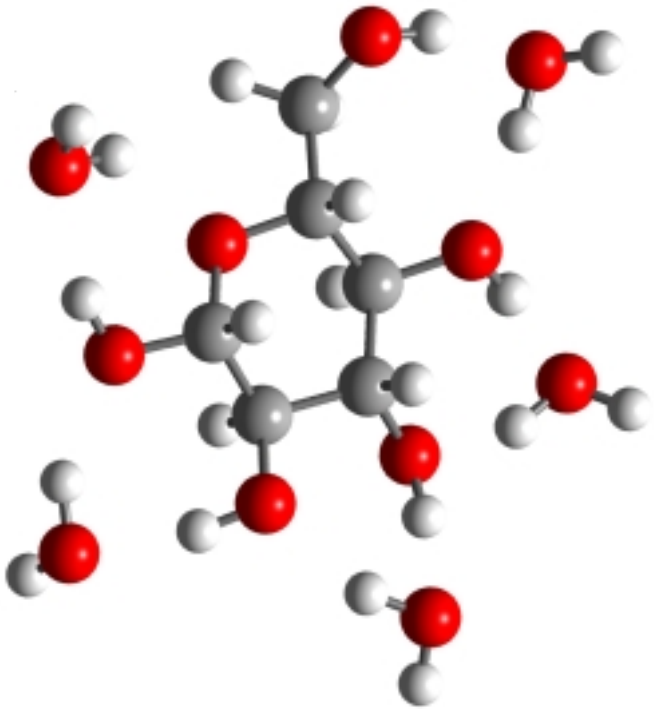
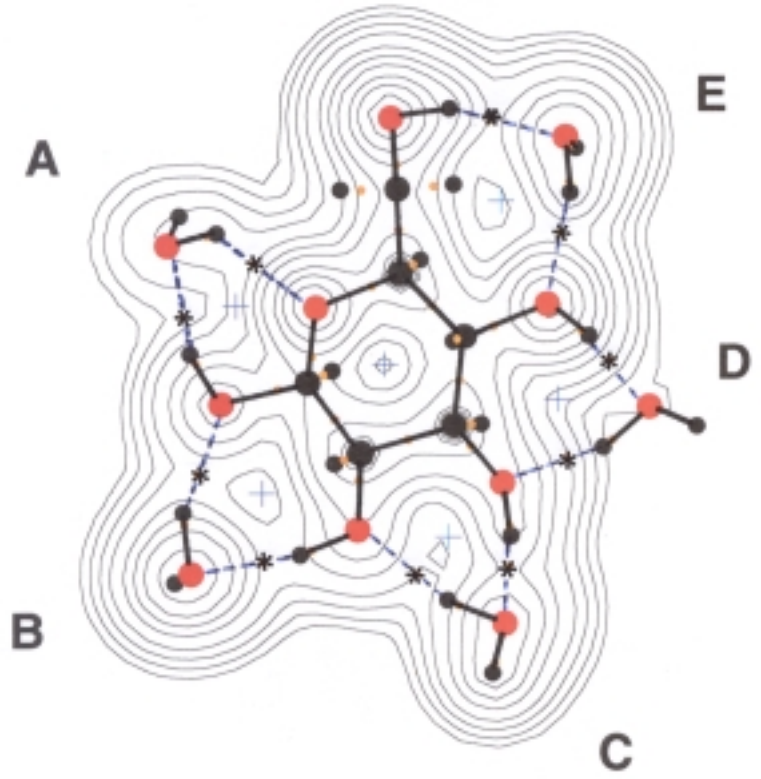
Hydrogen Bond Cooperativity





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Diols and Water Structure

VDW atomic radii and interpenetration

R. A. Klein, Bangalore September 2006

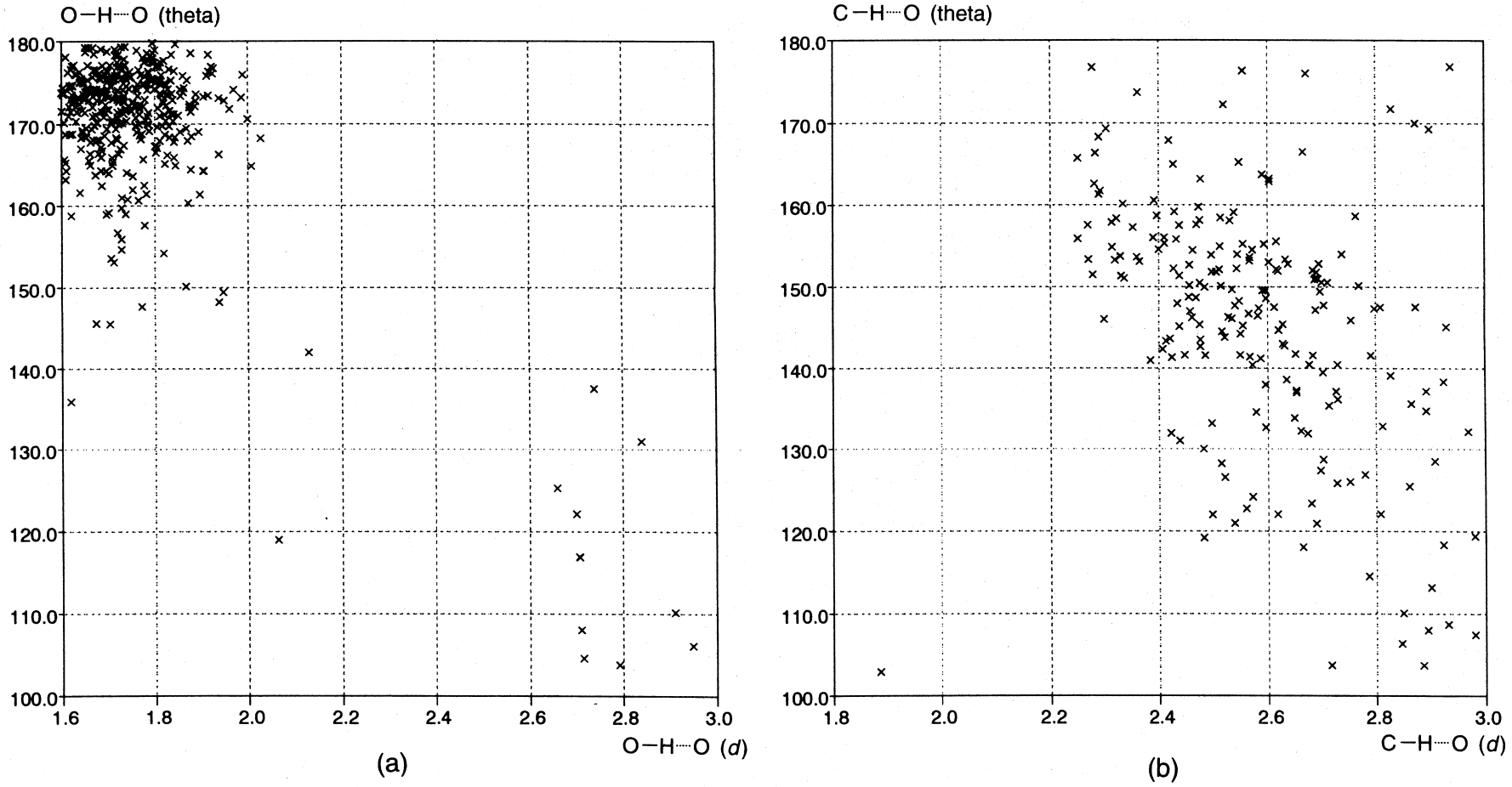

Fig. 1.5. Difference between strong and weak hydrogen bonds. θ–d scatterplots for (a) O—H···O and (b) C—H···O hydrogen bonds in synthons **4** and **5**, respectively (CSD data). The weak hydrogen bonds span much wider ranges of angles and distances than the tightly grouped sample of strong hydrogen bonds. Note, however, the roughly inverse θ–d correlation in the right hand side plot, that is characteristic of a hydrogen bonding interaction.

from Desiraju, G.R.; Steiner, T. (1999)

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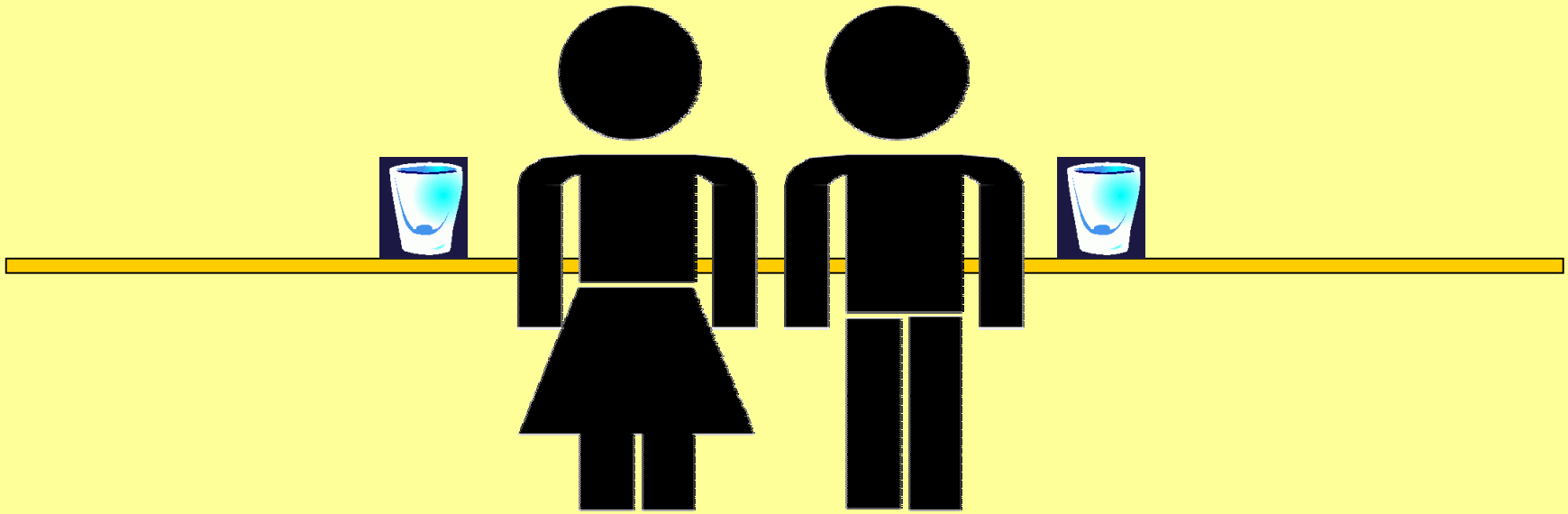
Distance Criteria?

What information can be extracted from separation distance?

Distance Criteria?

Interaction likely!



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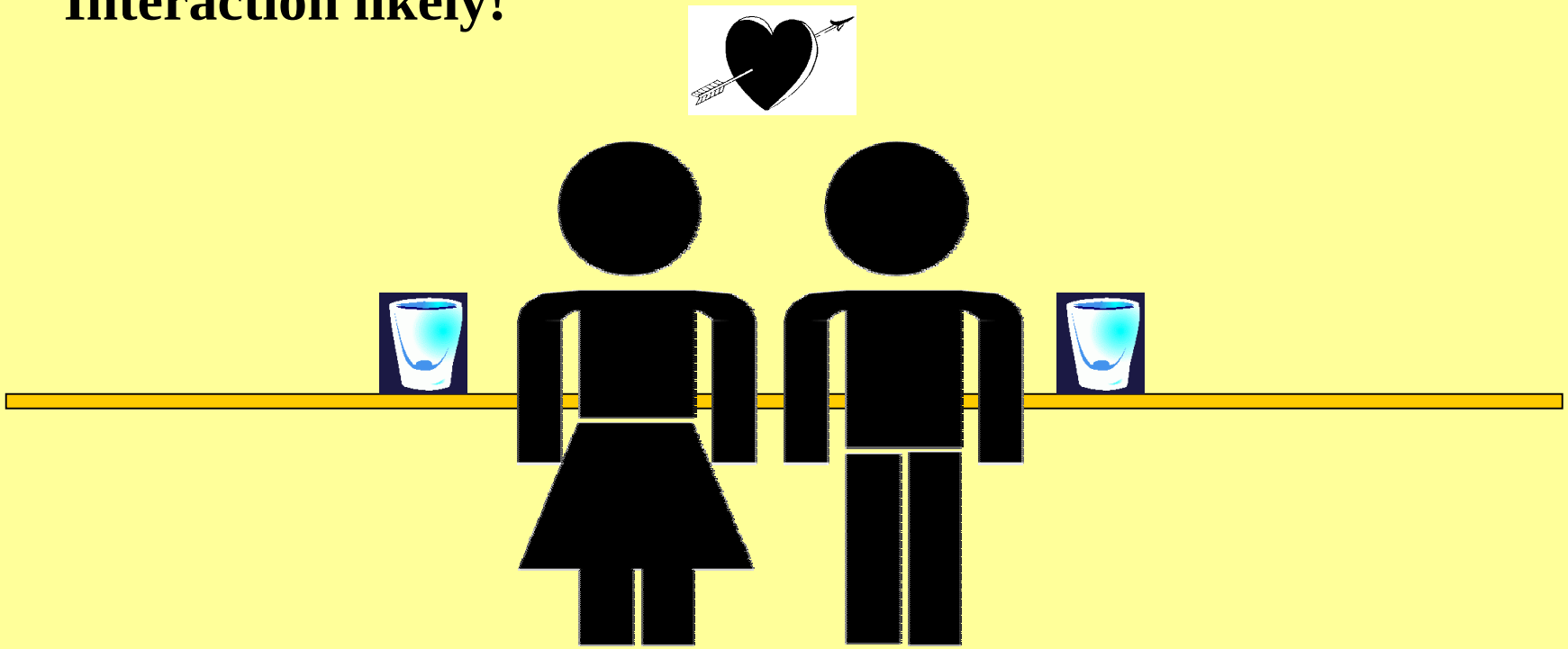
Distance Criteria?

Interaction likely!



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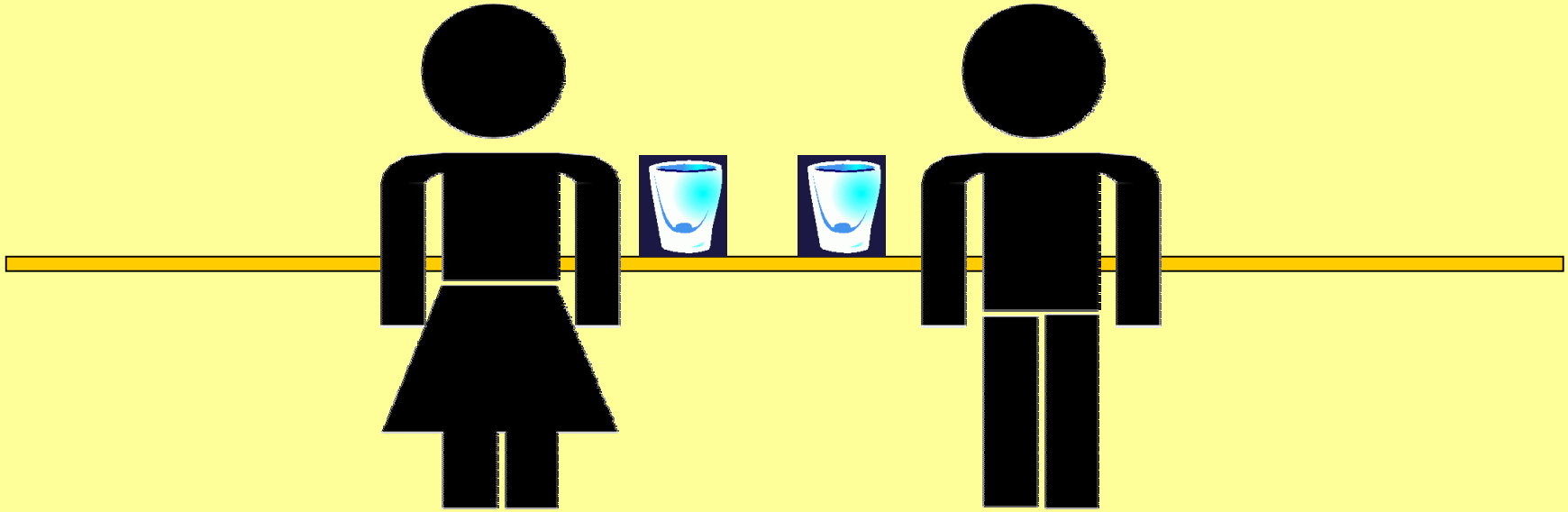
Distance Criteria?

Interaction possible!



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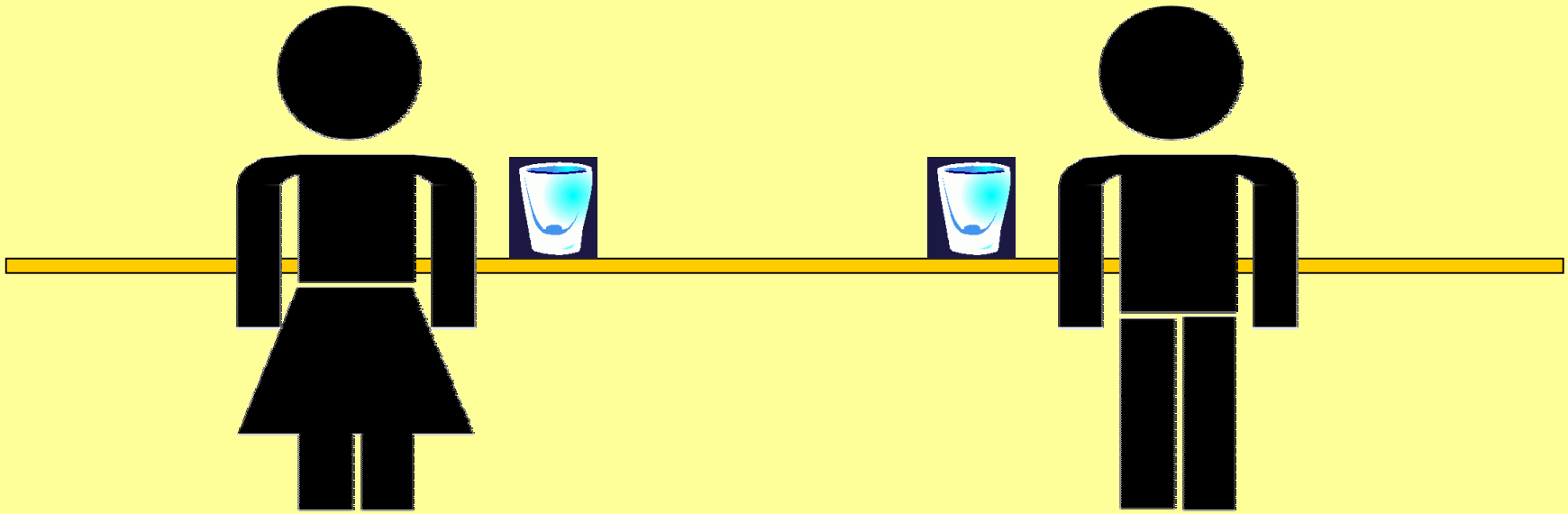
Distance Criteria?

May talk to one another



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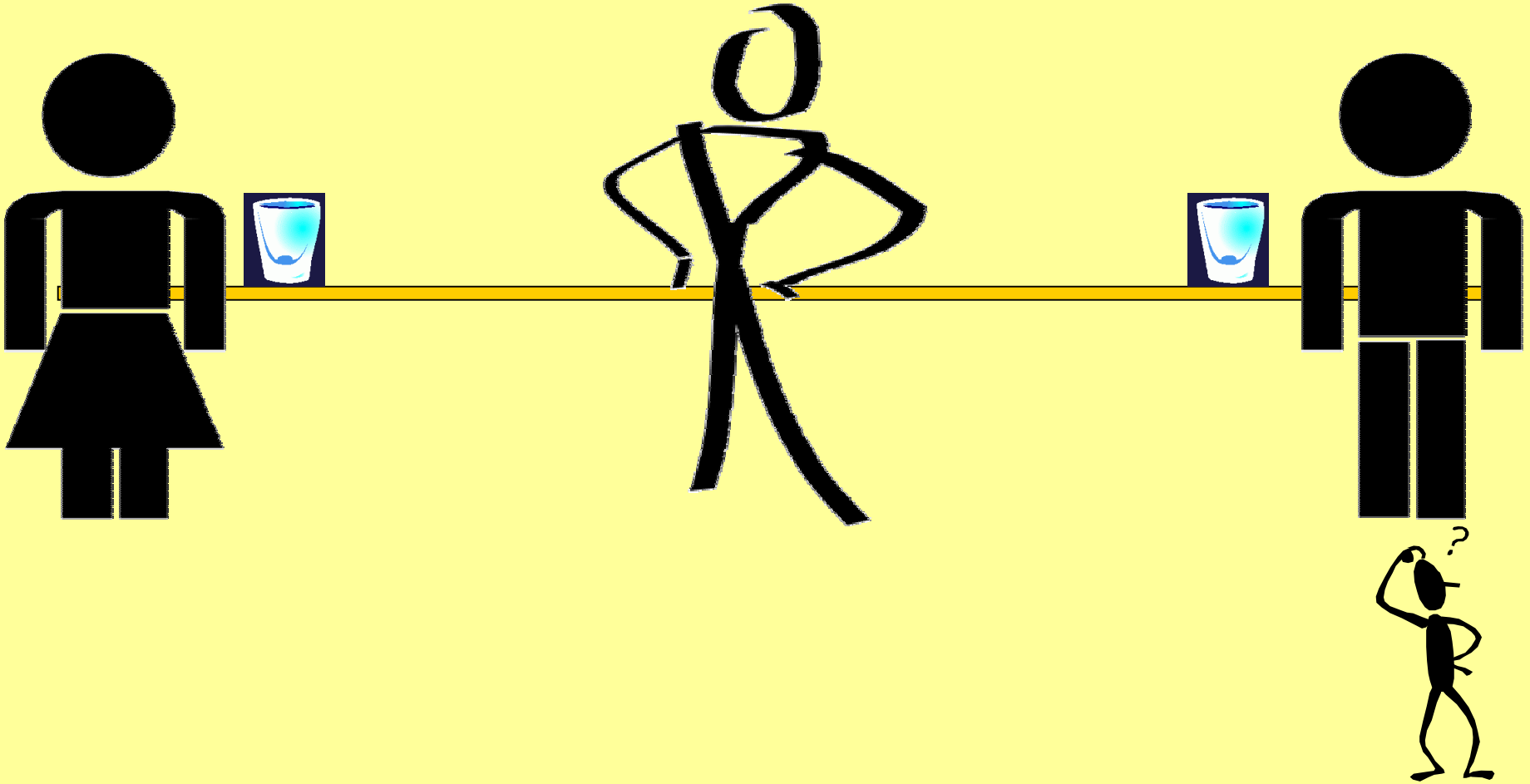
Distance Criteria?

Unlikely to be talking



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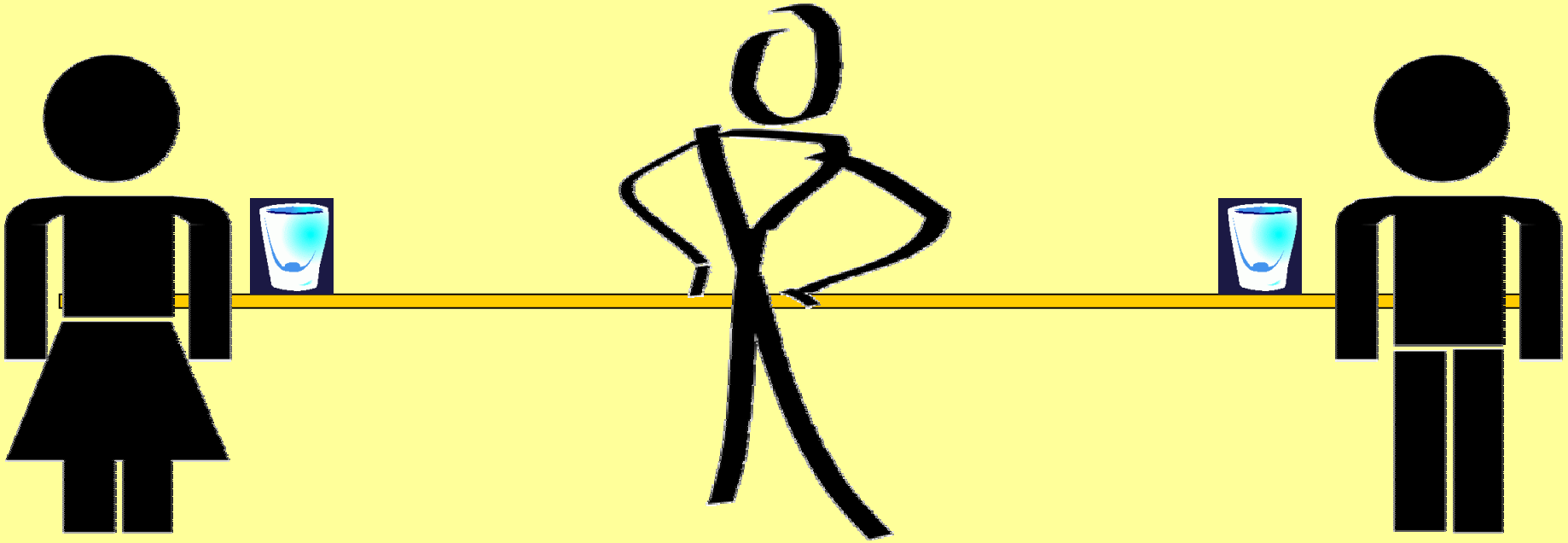
Distance Criteria?

Unlikely to be talking (probably married!)



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Modified Atomic Radii

Source	H	N	O	-H...N-	-H...O-
Bondi	1.2	1.55	1.52	2.75	2.72
Pauling	1.2	1.5	1.4	2.70	2.72
Rowland & Taylor	1.1	1.64	1.58	2.74	2.68
Yang & Davidson	1.06	1.36	1.27	2.42	2.33
Bader (a) (b)	1.52 1.34	1.77 1.62	1.68 1.55	3.29 3.08	3.20 2.89
Klein (a) (b) (c) (d)	1.34 1.18 0.98 0.82	1.87 1.66 1.46 1.31	1.68 1.50 1.33 1.20	3.21 2.84 2.44 2.13	3.02 2.68 2.31 2.02

from Klein, R.A.; Chem. Phys. Lett. 2006, 423, in press.

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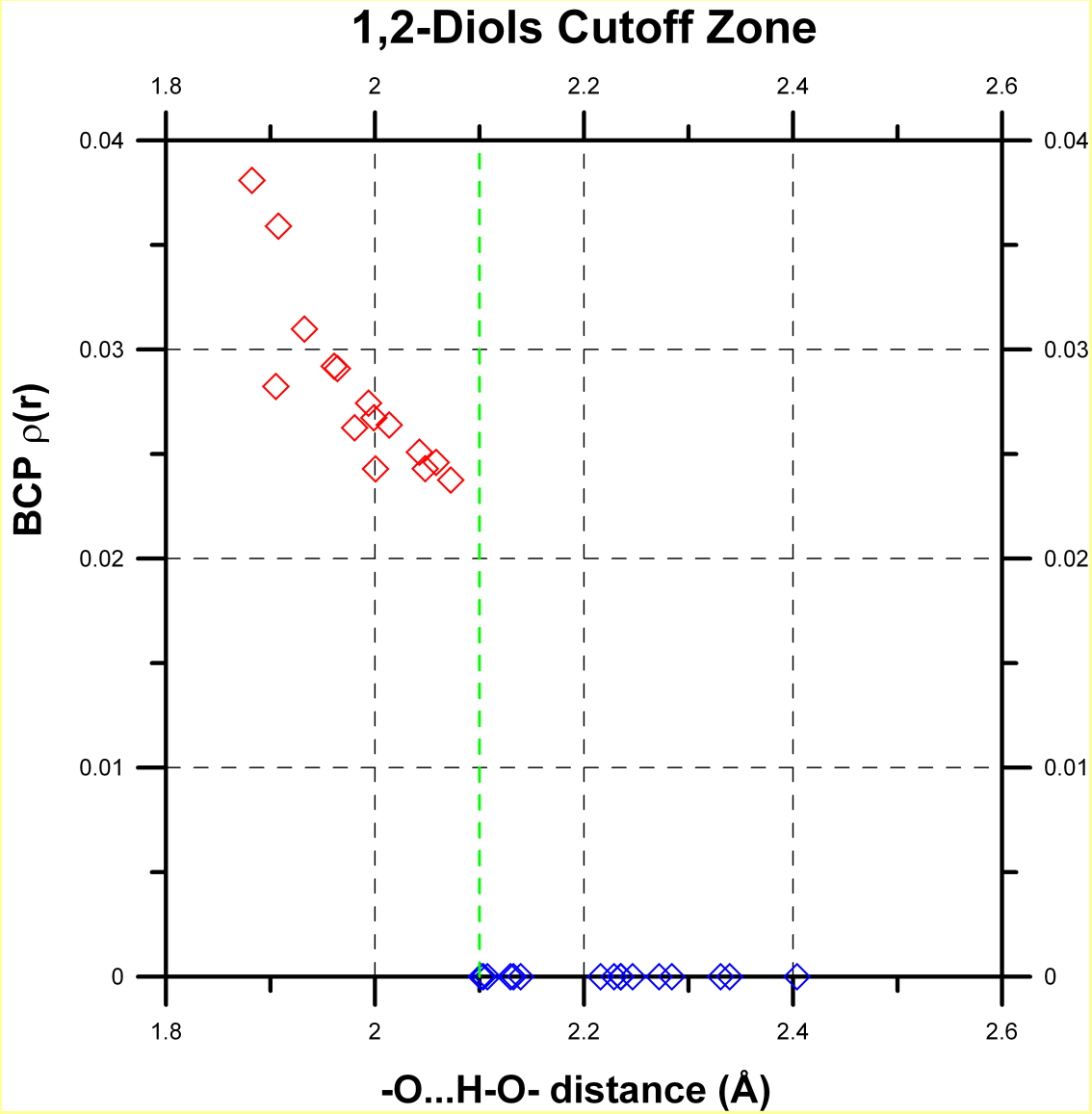
Diols and Water Structure

Topological fold catastrophes

R. A. Klein, Bangalore September 2006

Fold Catastrophe = BCP-RCP Coalescence



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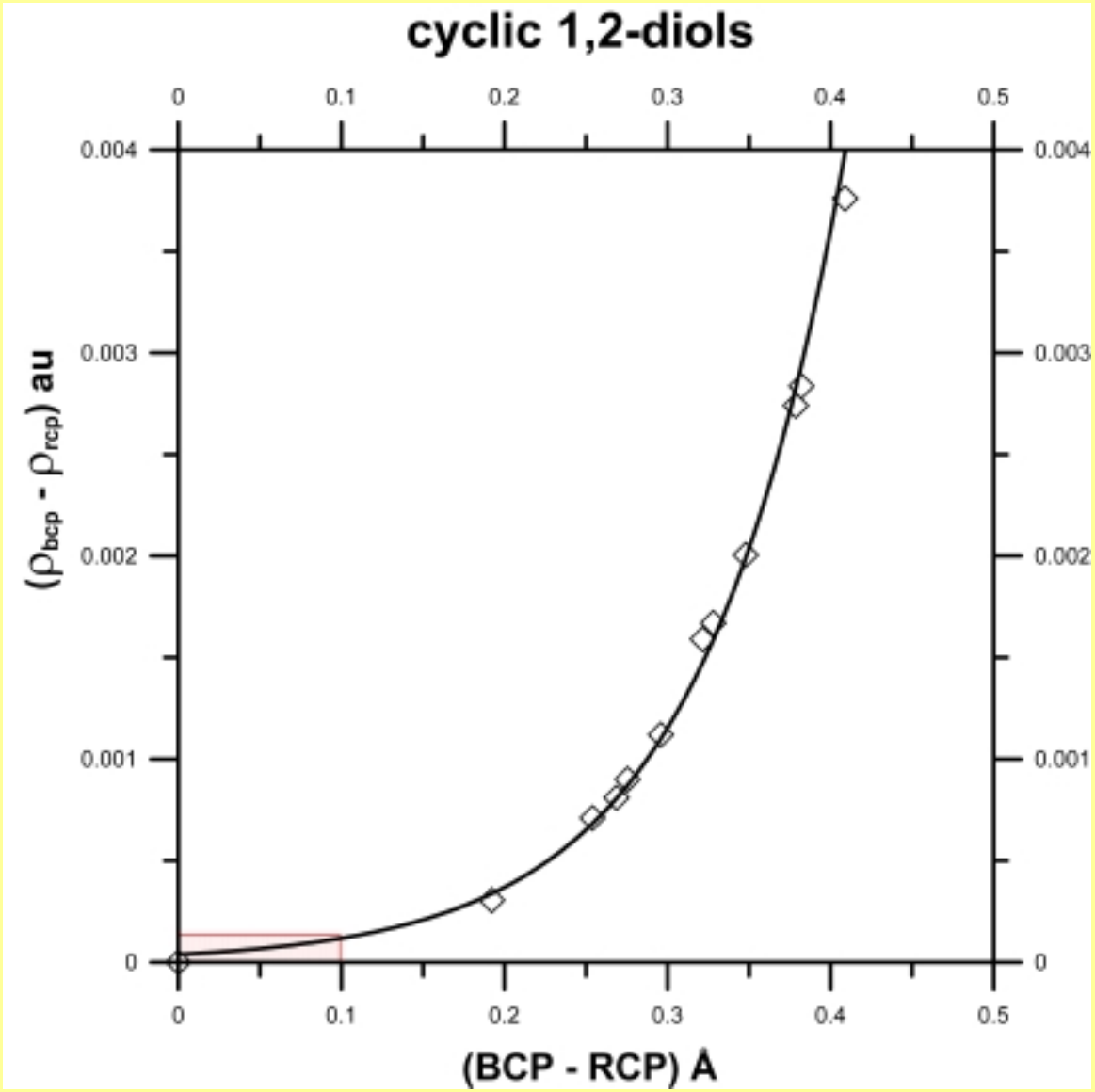
Fold Catastrophe = BCP-RCP Coalescence



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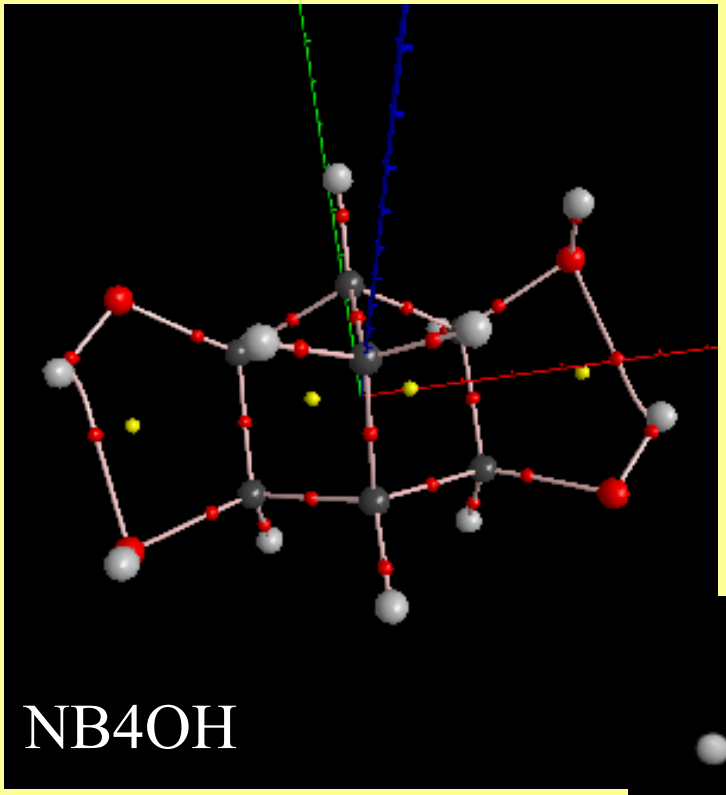
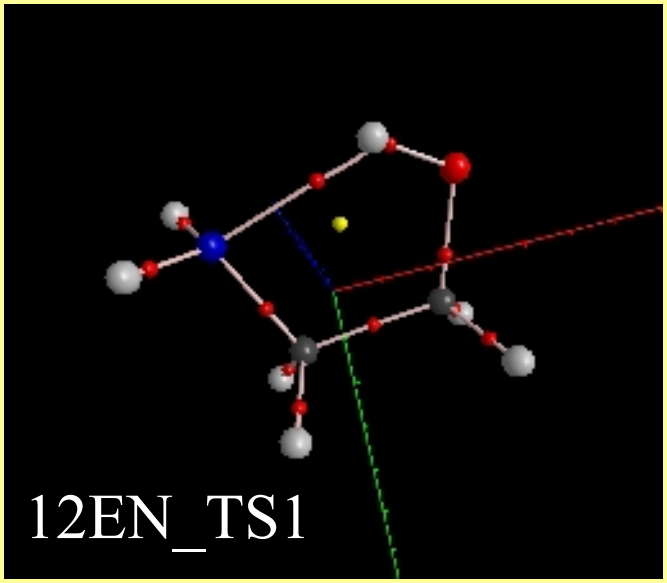
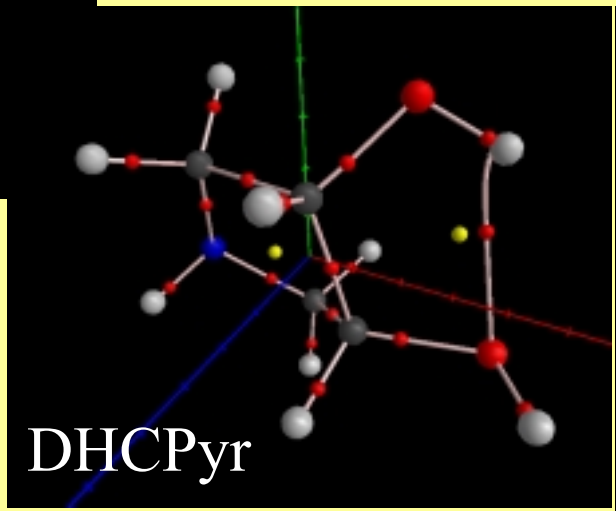
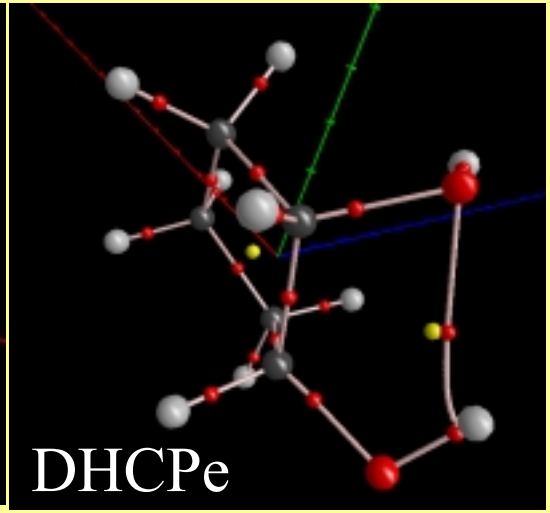
Fold Catastrophe = BCP-RCP Coalescence









DHCPe coalesces at higher levels of theory

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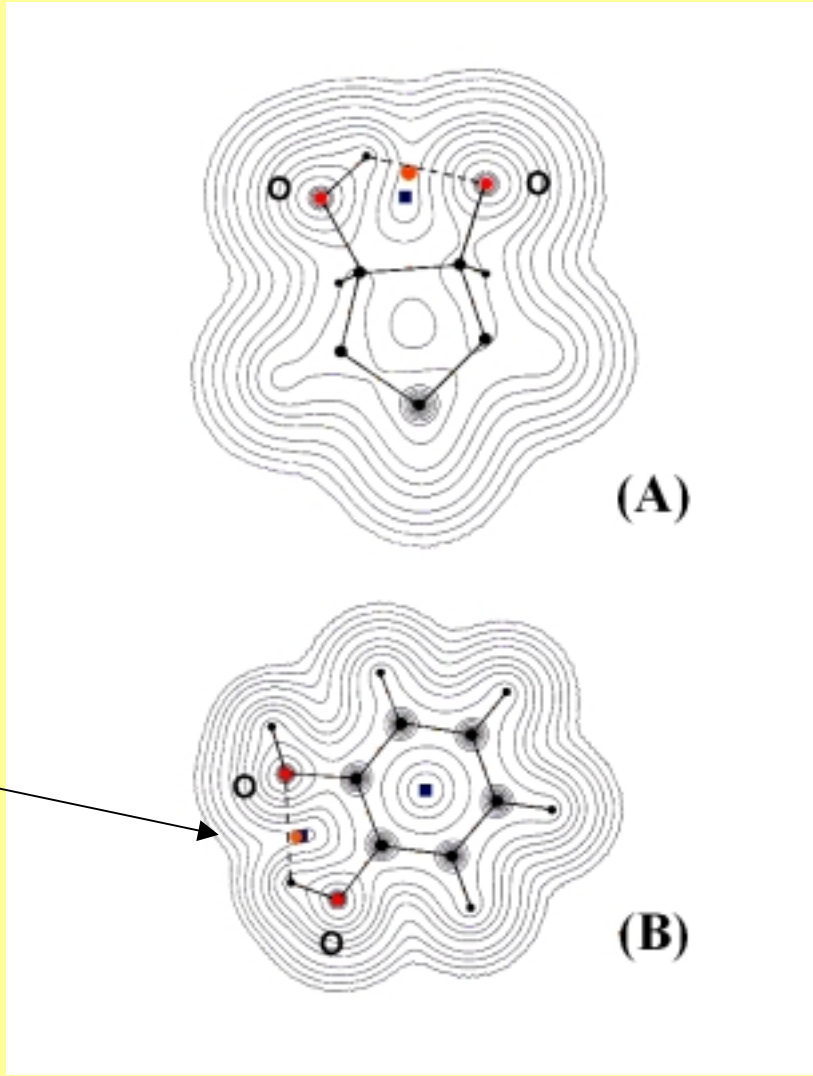
Fold Catastrophe = BCP-RCP Coalescence



NB4OH

DHBz coalesces at
higher levels of theory

DHBz

Figure 5. Electron density contour plots for (A) *endo*-2,3,5,6-tetrahydroxynorbornane calculated at MPW1PW91/6-311+G(2d,p), and (B) *ortho*-dihydroxybenzene at B3LYP/6-31+G(d,p).

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Fold Catastrophe = BCP-RCP Coalescence

- Always analyse the BCP and RCP;
- As the BCP and RCP coalesce the Hydrogen Bond ceases to exist, i.e., there is no longer concentration of electron density around the internuclear axis;
- A (BCP-RCP) distance of < 0.1 Å and an electron density difference ($\rho_{bcp} - \rho_{rcp}$) < 0.0002 au, should be treated with caution;
- If there is evidence of incipient BCP:RCP coalescence, then calculations must be made at higher levels of theory until a 'limit situation' is reached;
- Diffuse and polarisation functions as well as electron correlation are important in achieving invariant electron density profiles.

Diols and Water Structure

Cooperativity in water clusters

R. A. Klein, Bangalore September 2006

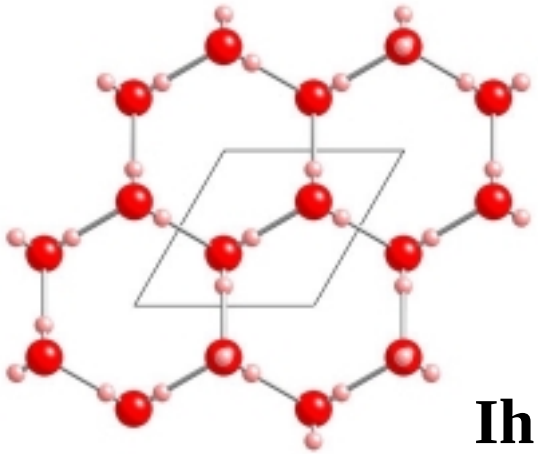
O—O in Clusters

- Calculated O—O in solid, highly structured, edged-fused pentagonal clusters for the O…H—O distance terminated by tetrahedrally coordinated H_2O molecules
- $= 2.72 \pm 0.01$ Å
- compare Bergmann EXAFS = 2.71-2.73 Å

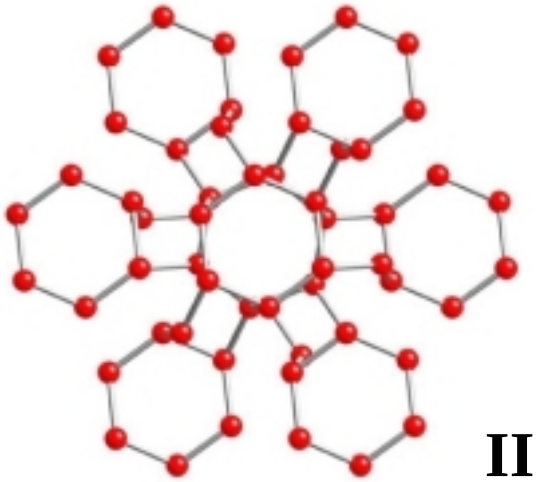
-O...H-O- Cooperativity

- vibrational relaxation 740 ± 25 femtoseconds;
- for resonant intermolecular energy transfer (RIET), interaction between H_2O molecules must be extremely strong;
- concentration dependence for rotational anisotropy decay shows that RIET occurs for the OH excitation:
- for dipole-dipole Förster-type interaction, rate of energy transfer, $k = T_1^{-1} * [r_0/r]^6$, where is the lifetime of the T_1 is the excited state and r_0 the Förster radius;
- experimental $T_1 = 4.0 \pm 0.4$ ps; $r_0 = 2.10 \pm 0.05$ Å comparable to O...O in liquid water implying that RIET will be very fast;
- also higher orders and anharmonic coupling;
- Woutersen, S.; Bakker, H.J.; (1999) *Nature* 402, 507

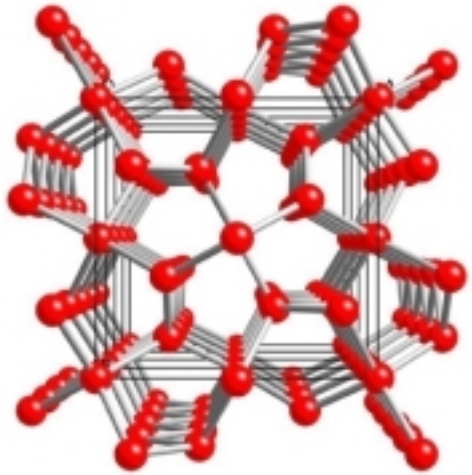
Ice Polymorphs



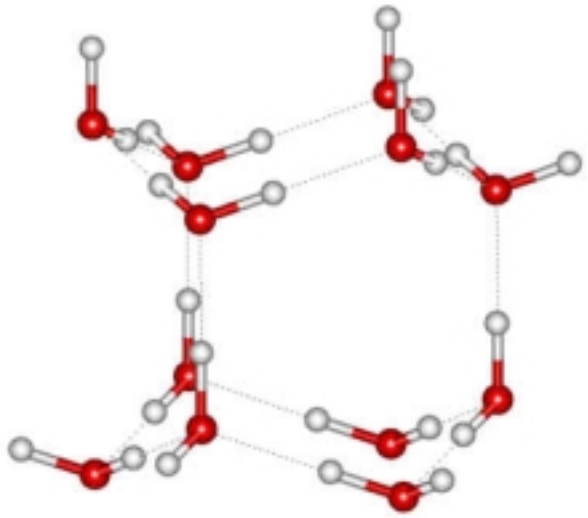
Ih



II



XII



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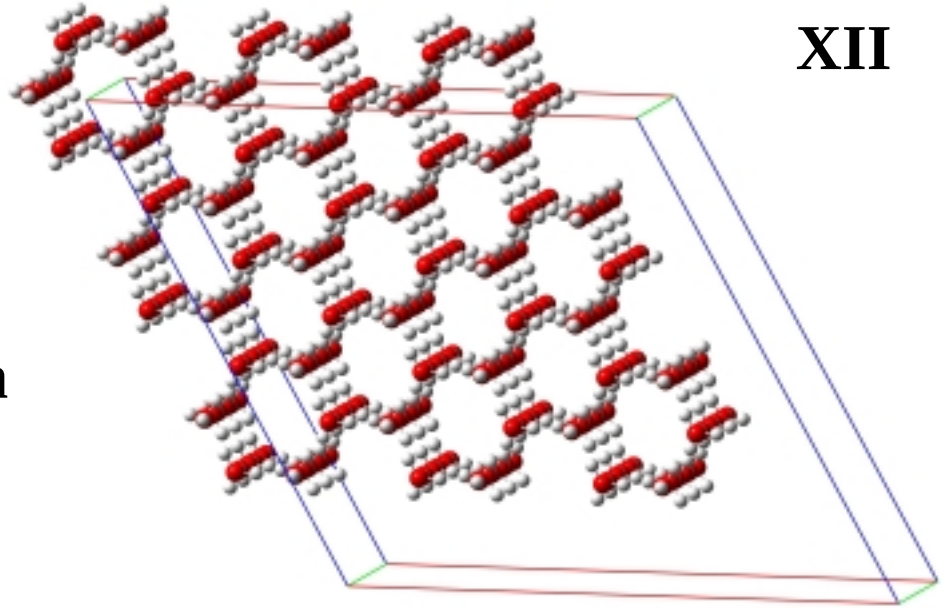

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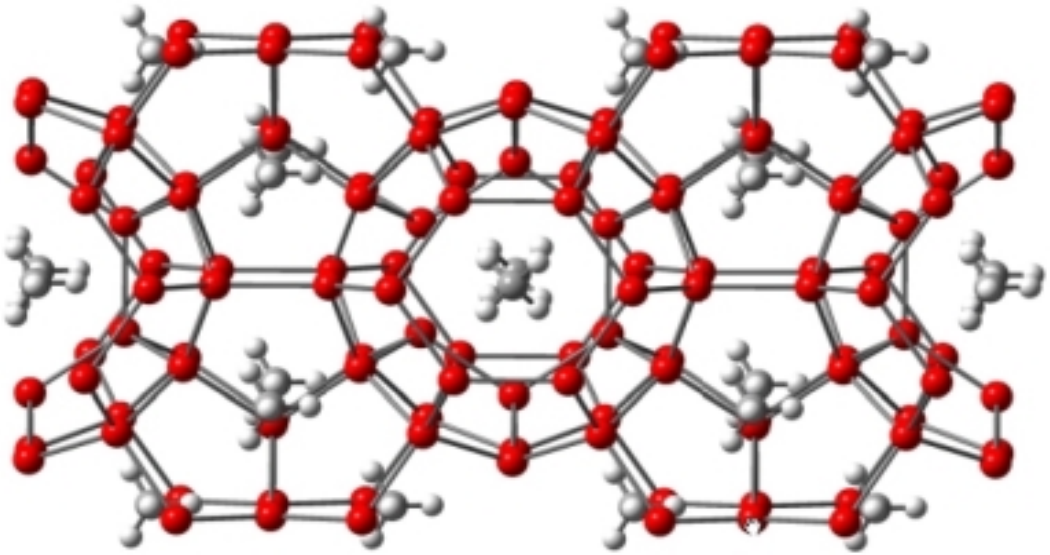
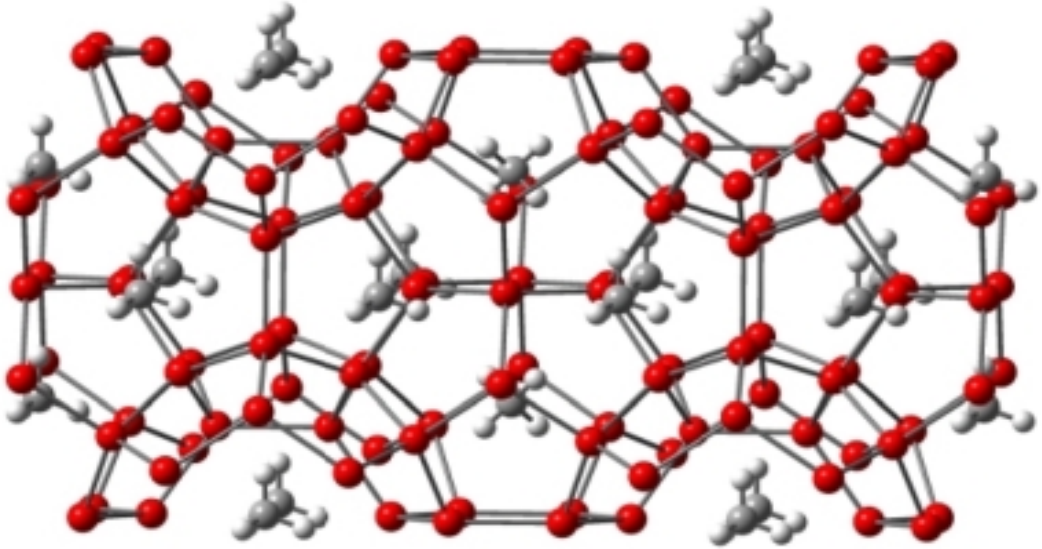
sI Clathrates (5^{12} and $5^{12}6^2$ cages)

0°



90°



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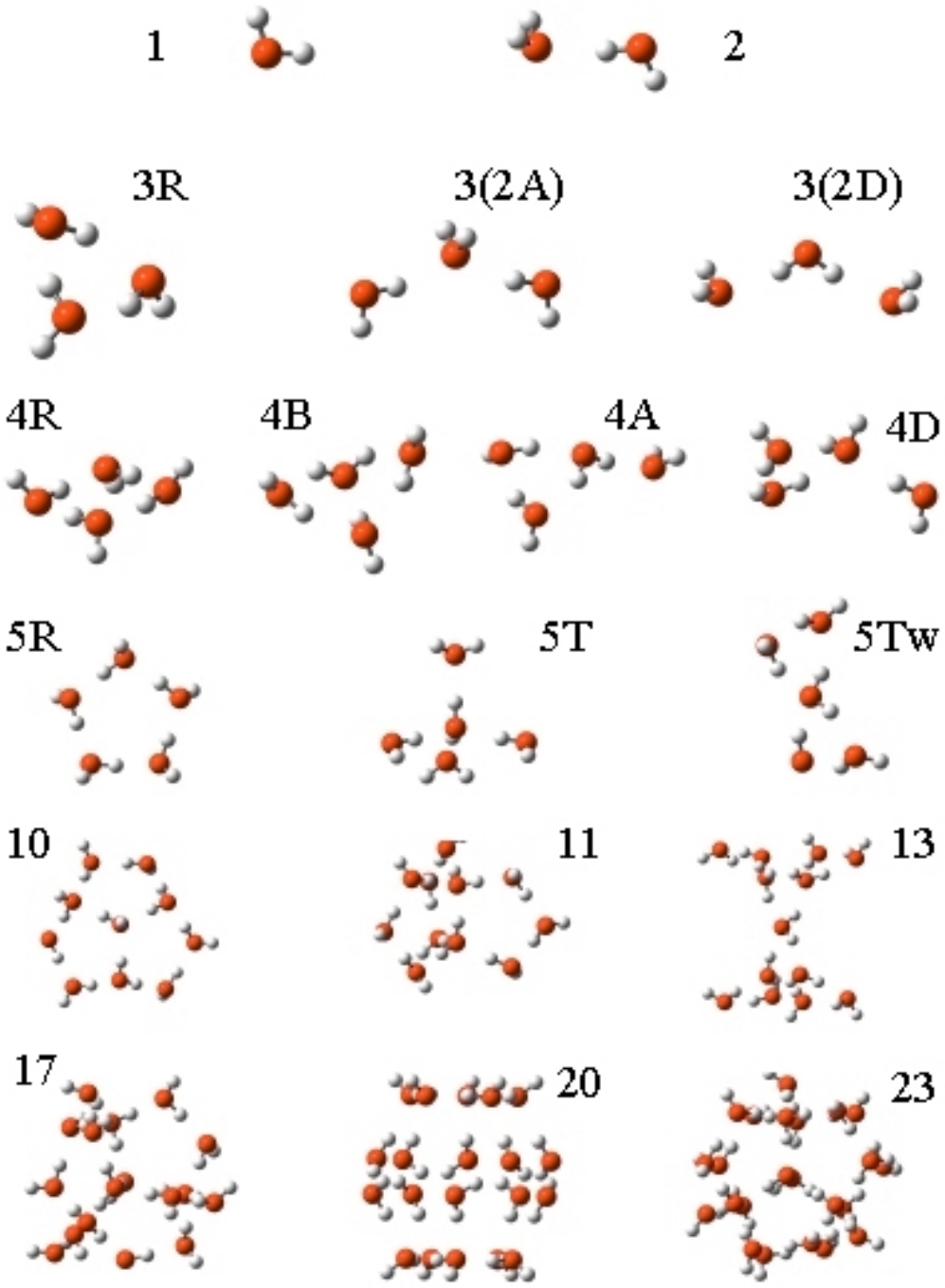
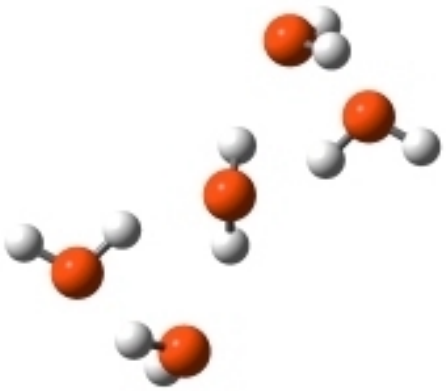

1
2
3R
3(2A)
3(2D)
4R
4B
4A
4D
5R
5T
5Tw
10
11
13
17
20
23



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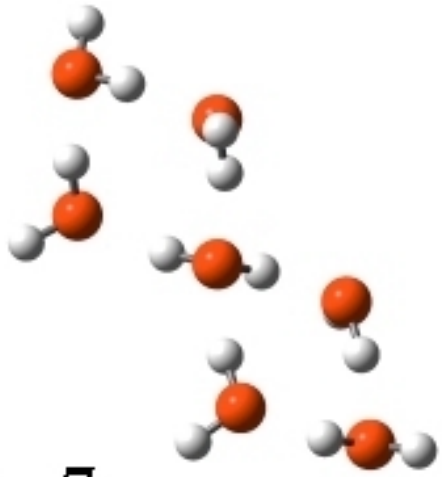
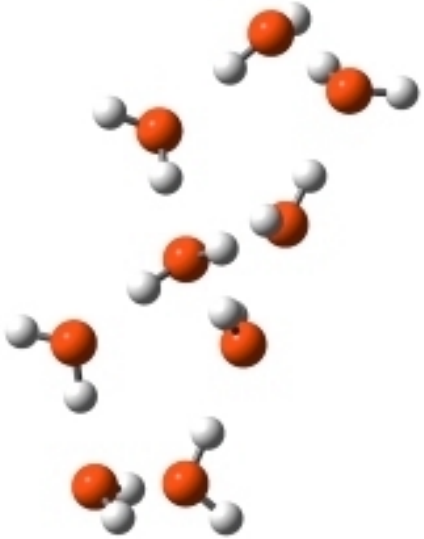
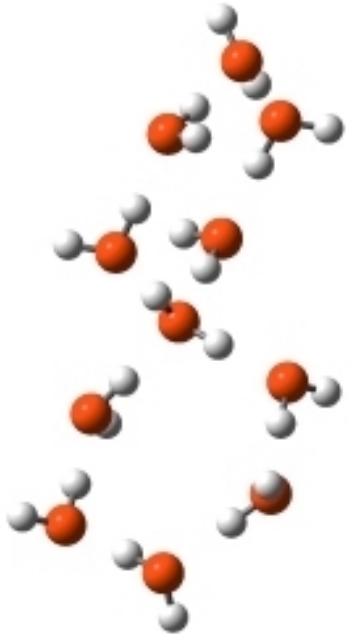


n = 7

n = 9



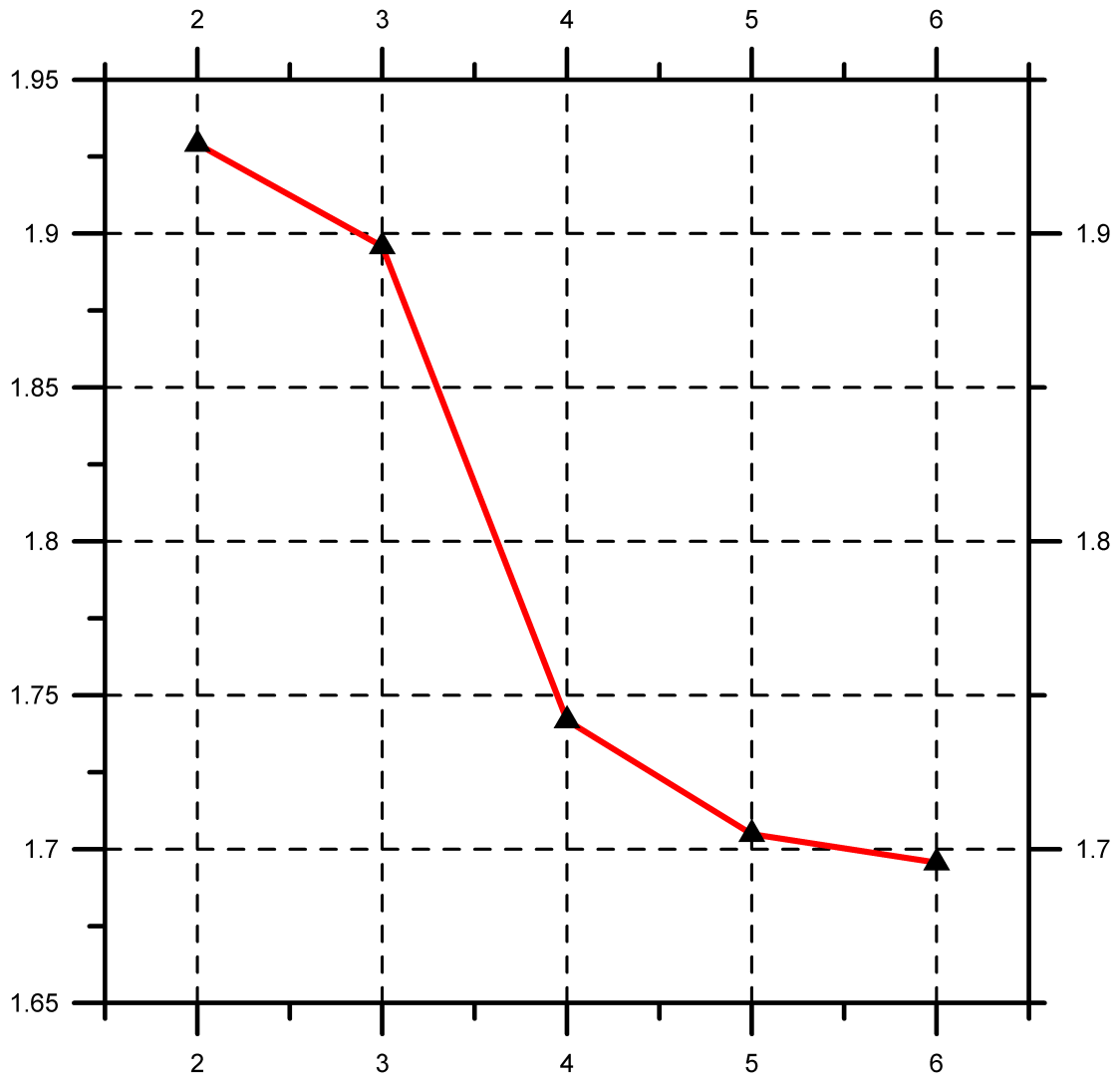


n = 11

R.A. Klein, February 2004

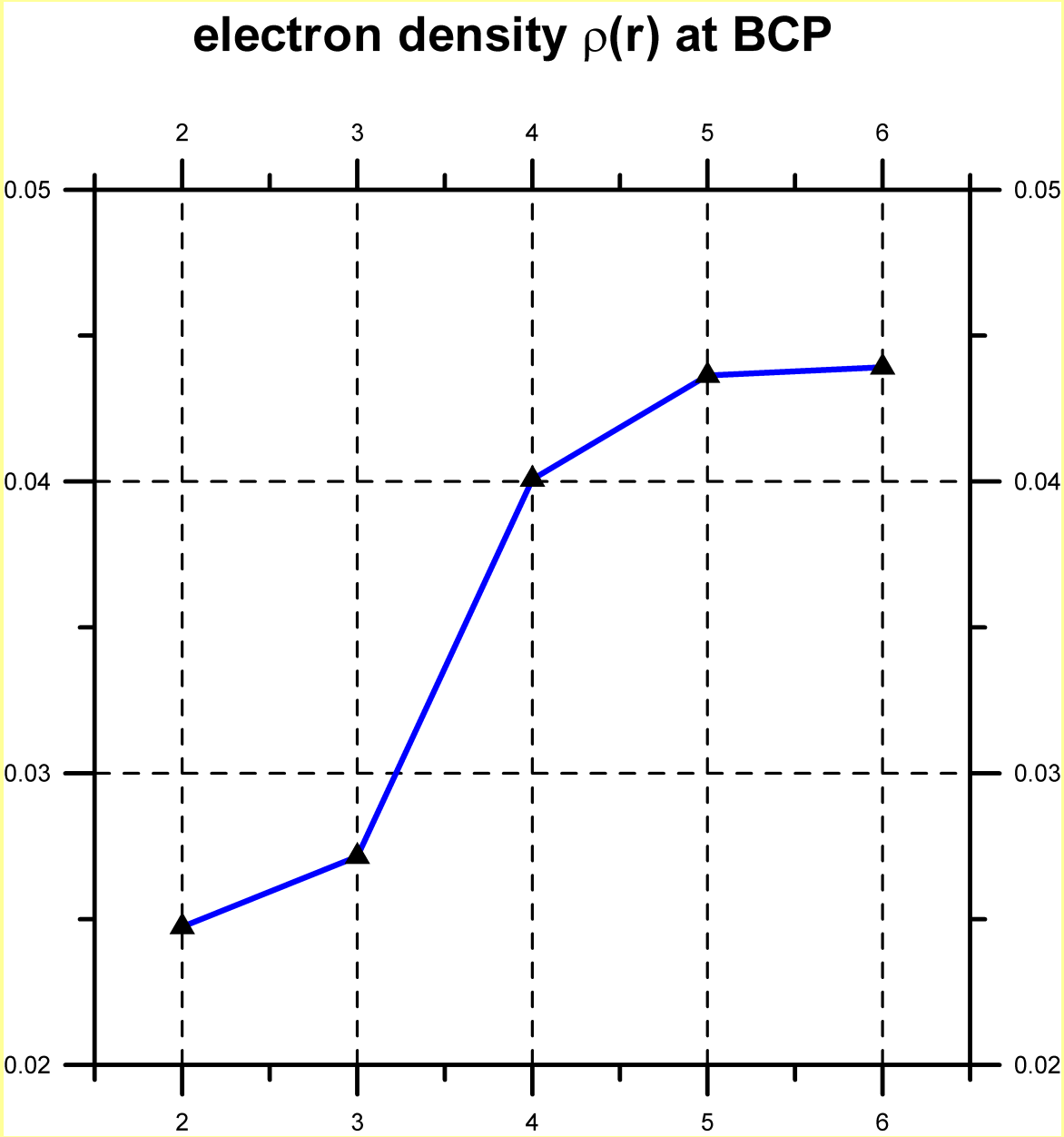
Cooperativity in Rings

R.A. Klein, Bangalore September 2006



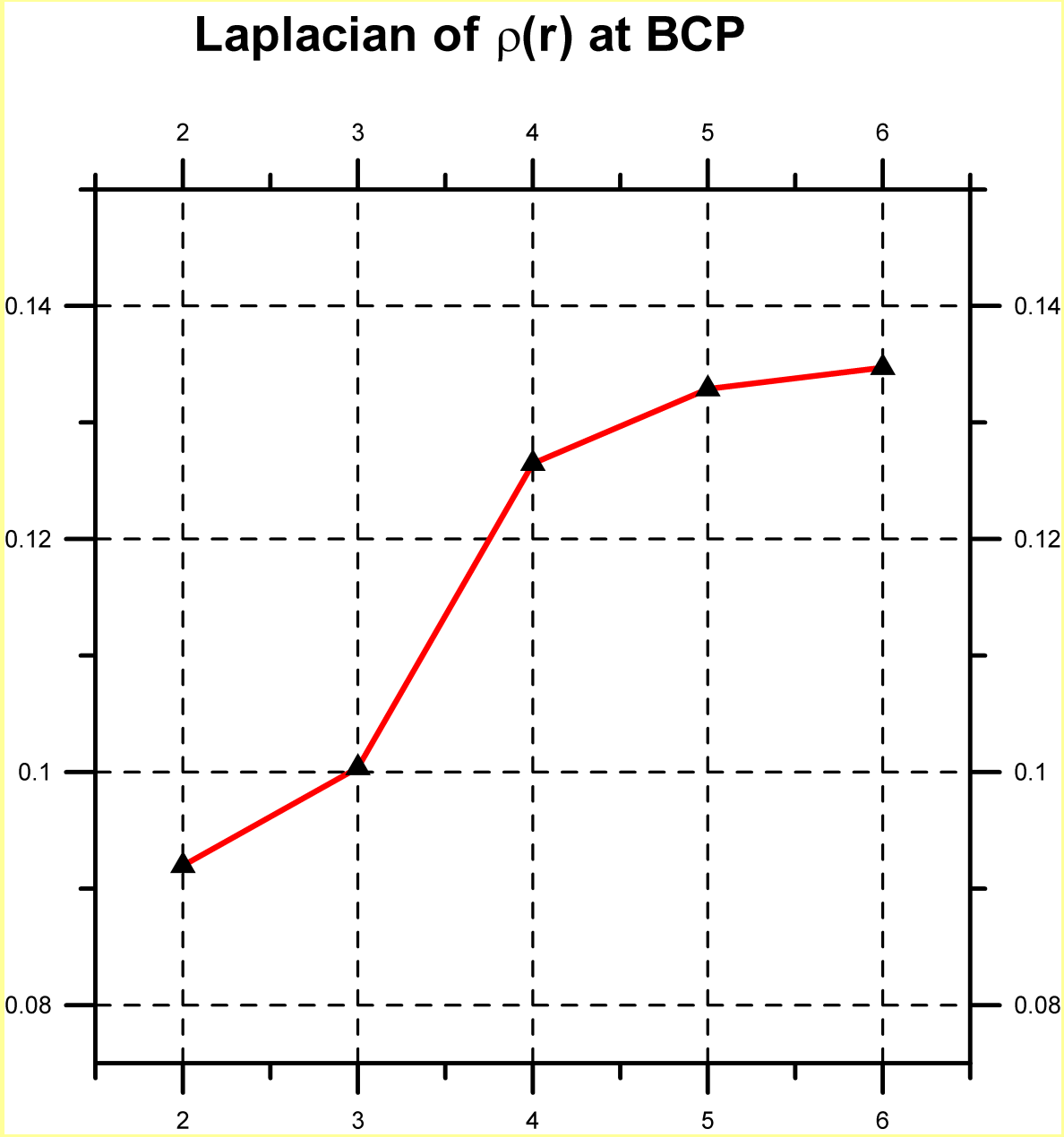
2-coordinated rings

R.A. Klein, Bangalore September 2006



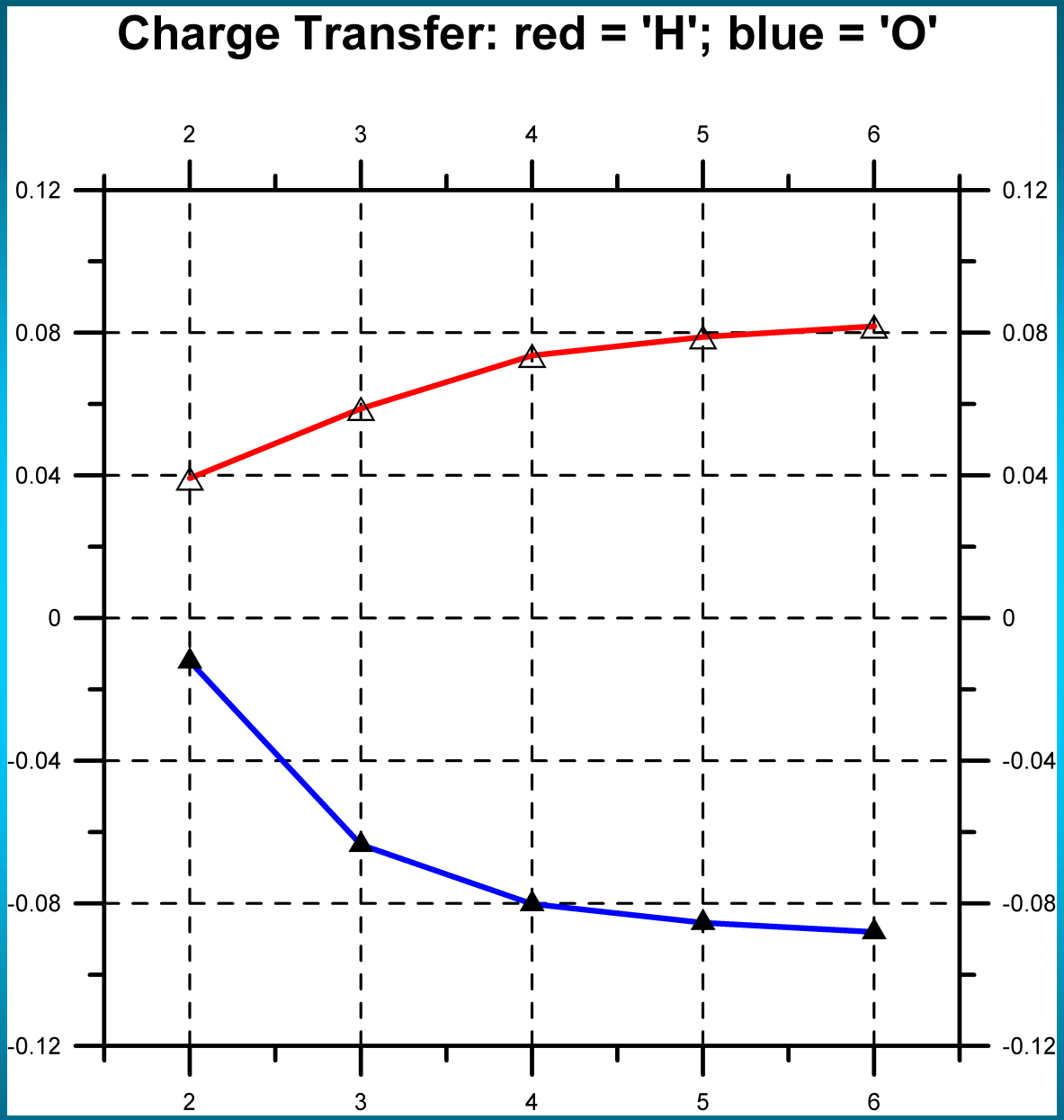
2-coordinated rings

R.A. Klein, Bangalore September 2006



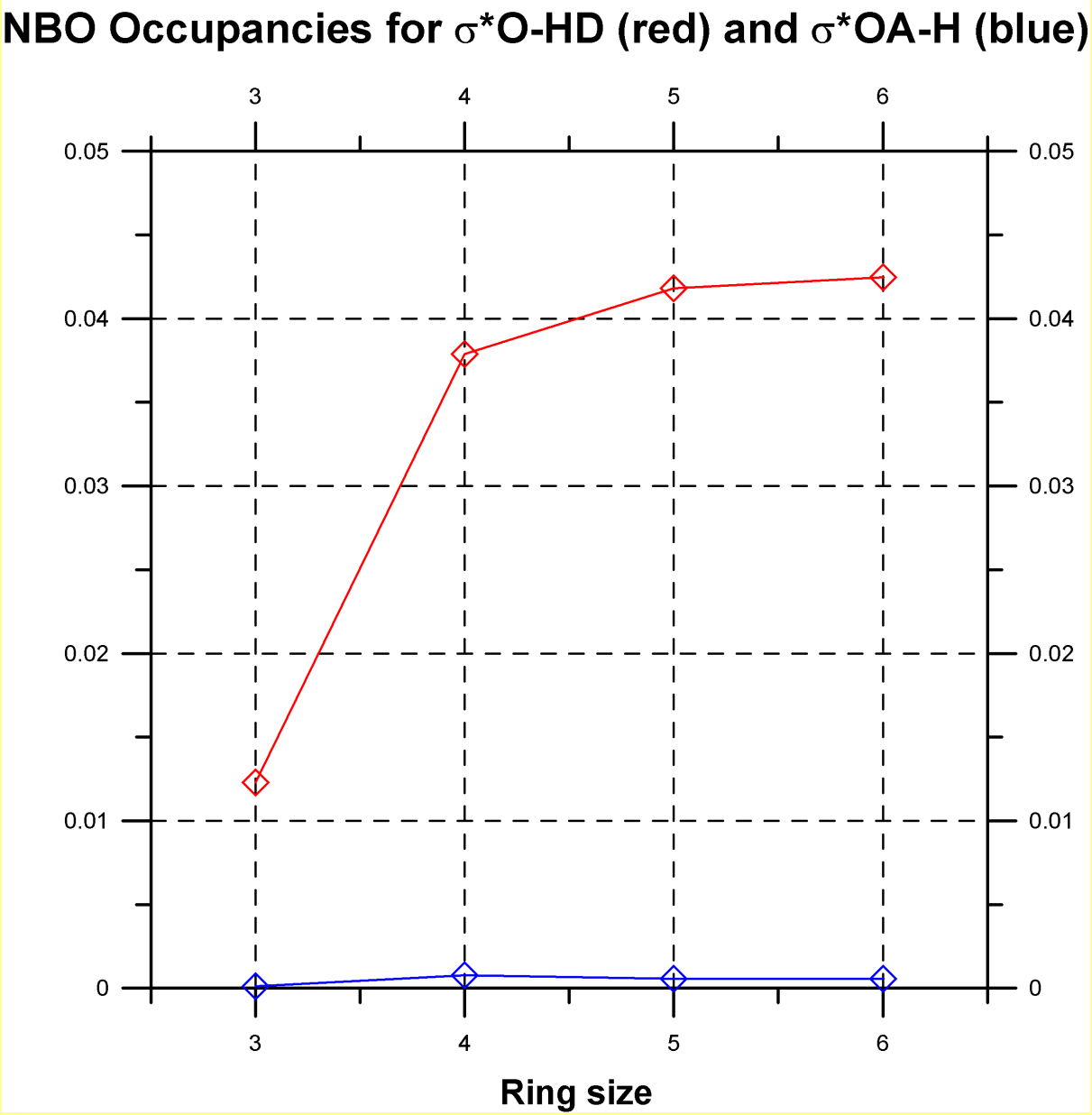
2-coordinated rings

R.A. Klein, Bangalore September 2006



2-coordinated rings

Bangalore September 2006



2-coordinated rings

R.A. Klein, Bangalore September 2006

^{17}O-NMR Chemical Shielding

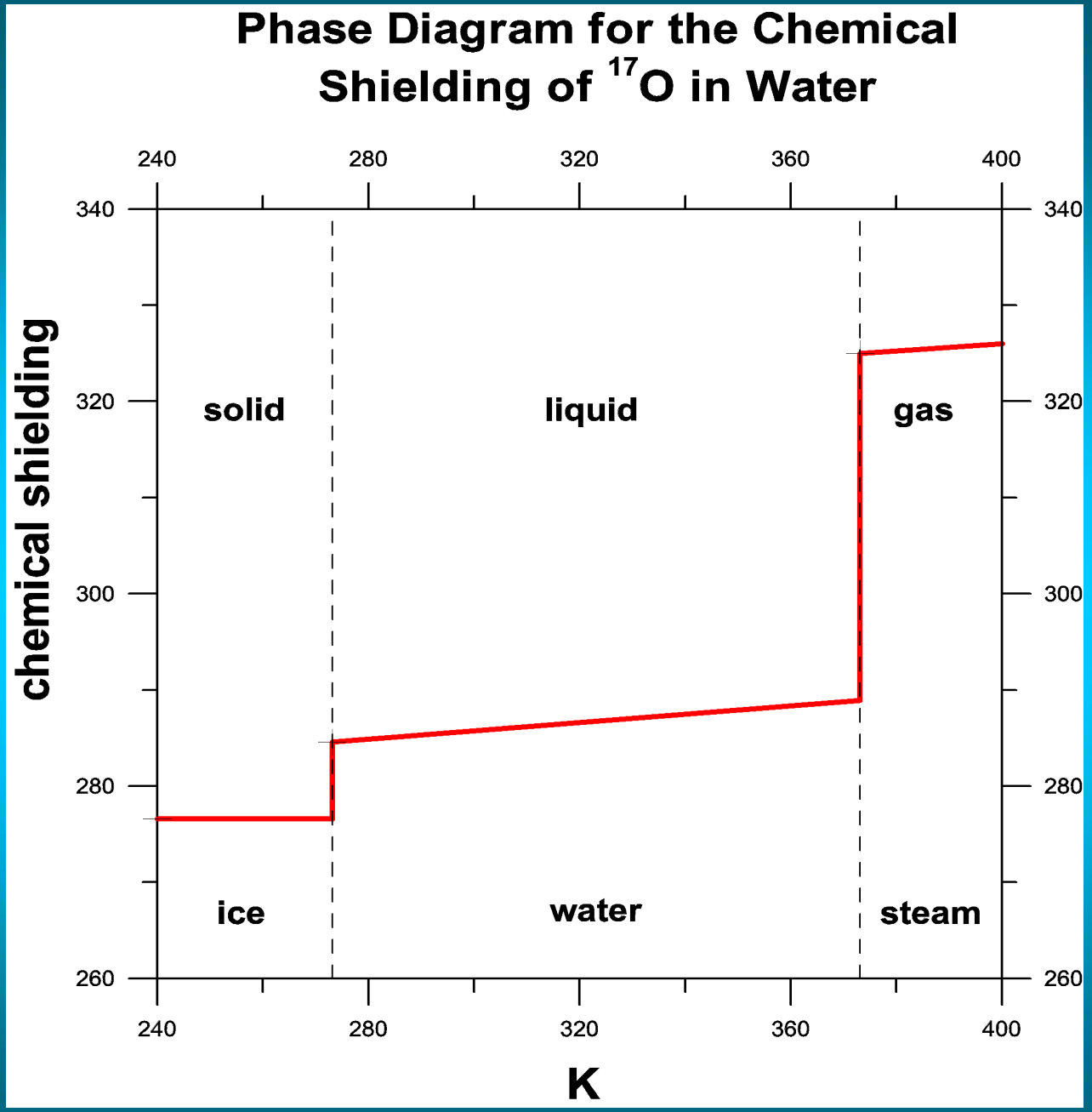
Bangalore September 2006

^{17}O Chemical Shift Tensor

Our value of **327.3 ± 0.2 ppm** for ^{17}O in monomeric water in the gas-phase compares well with the values given by Vaara, Lounila, Ruud and Helgaker (1998) *Journal of Chemical Physics* 109(19), 8388-8397, namely:

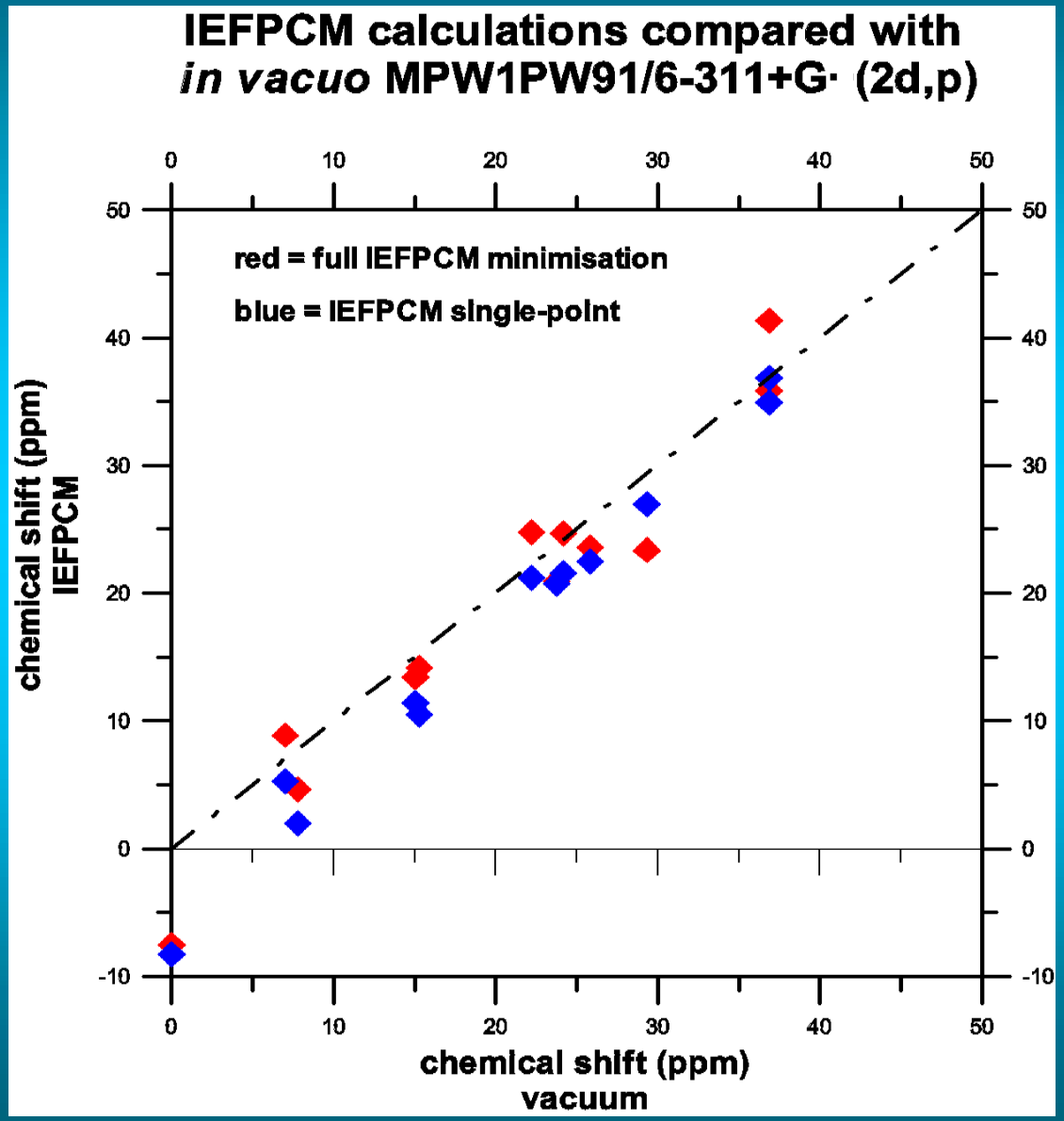
(i) asymptote without rovibrational correction = 327.7 ± 0.3 ppm

(ii) with rovibrational correction = 324.0 ± 1.5 ppm

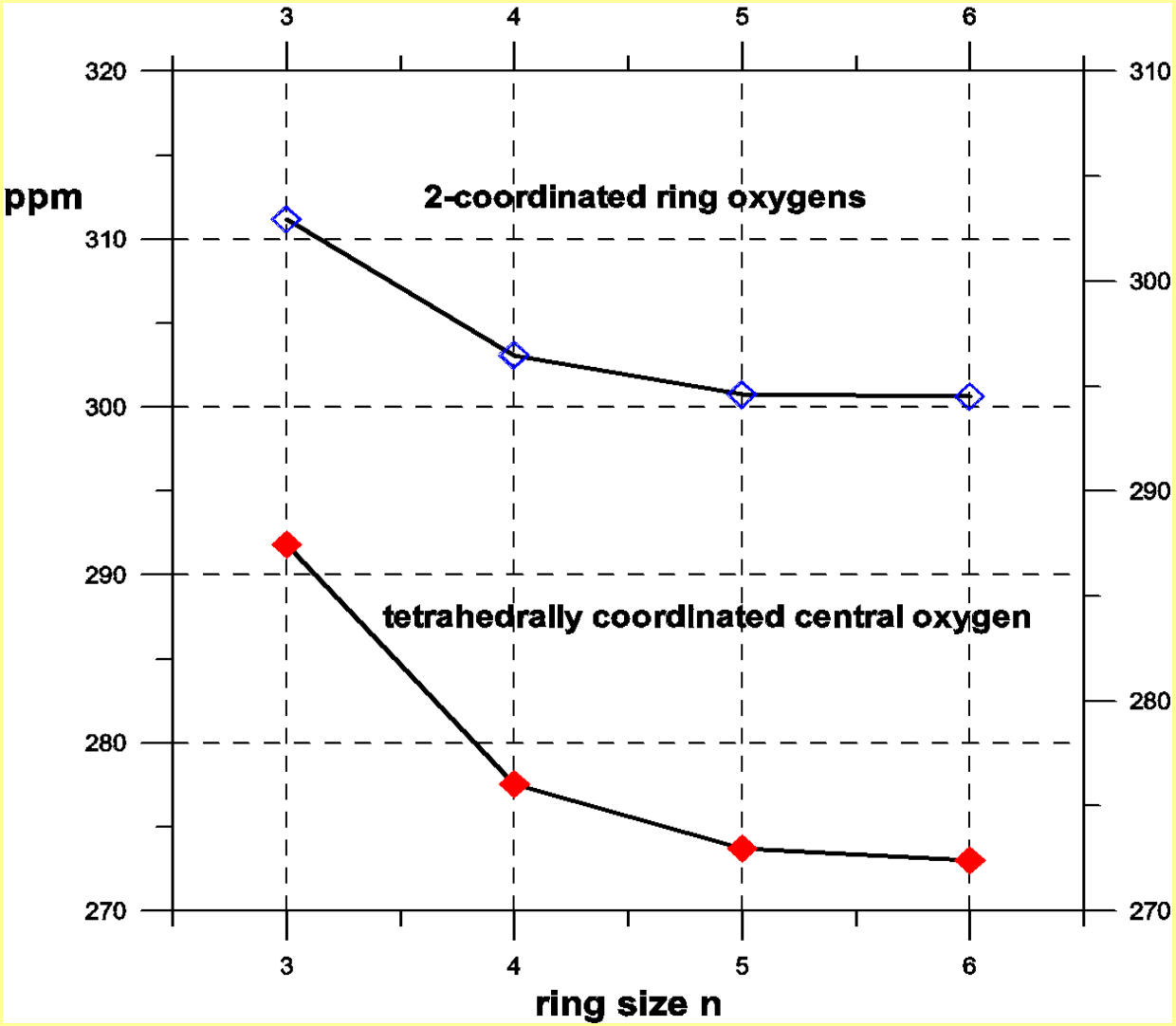


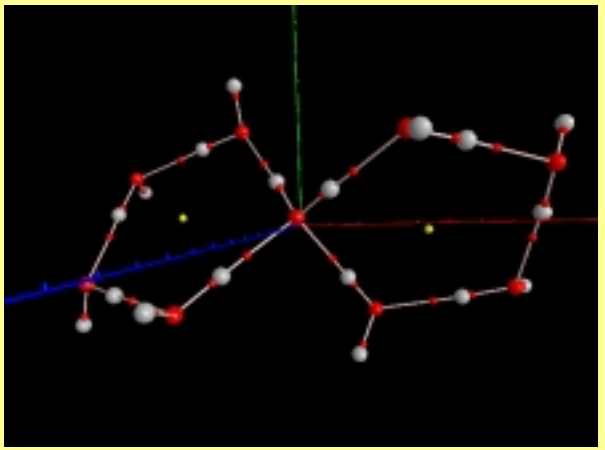
Bangalore September 2006

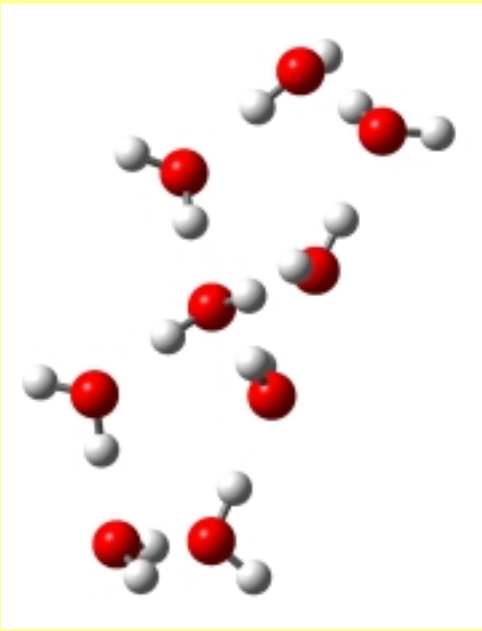
PCM ‘solvation’ fails!



Fused 2-ring Systems ([2n-1]mer)

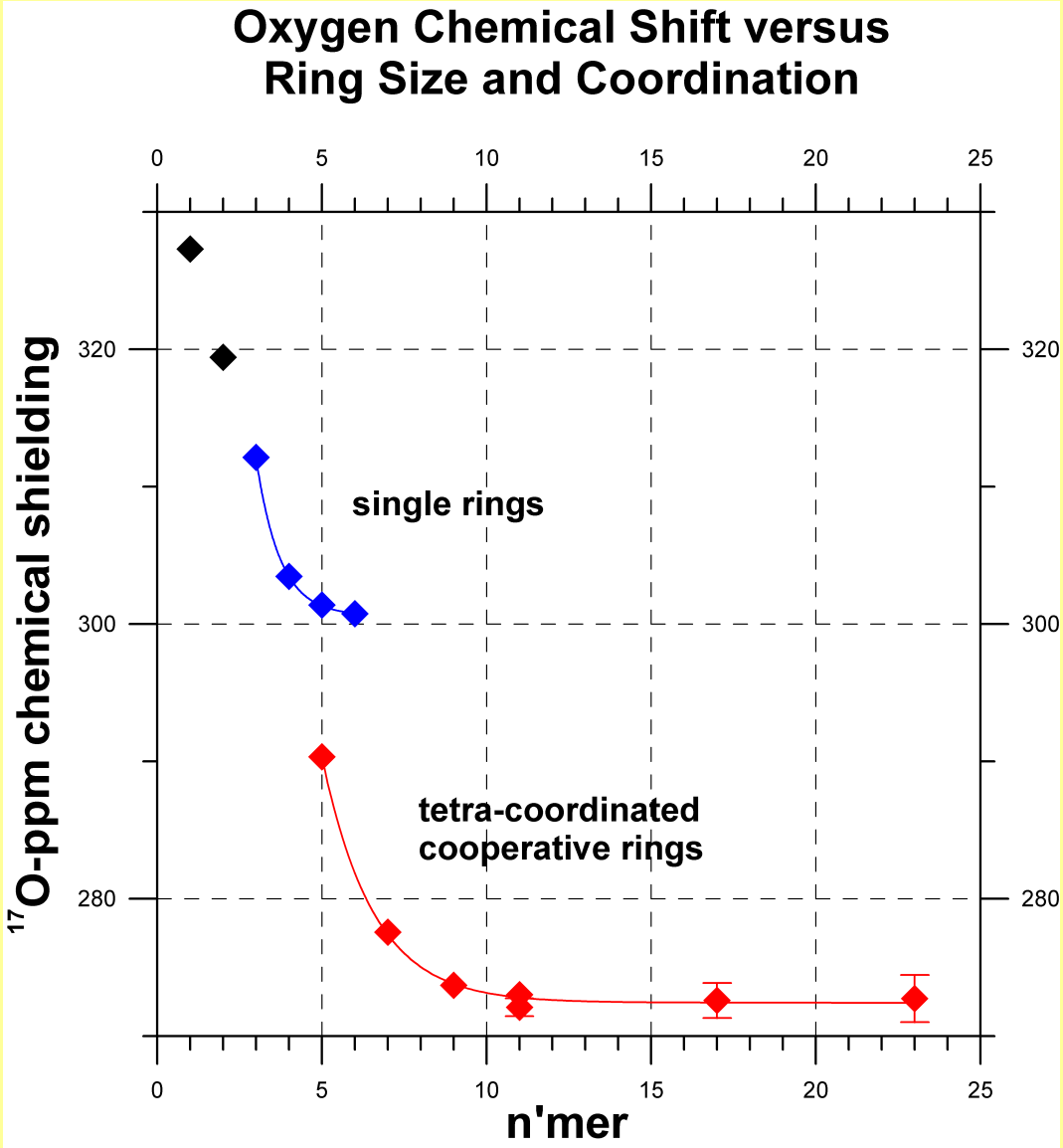




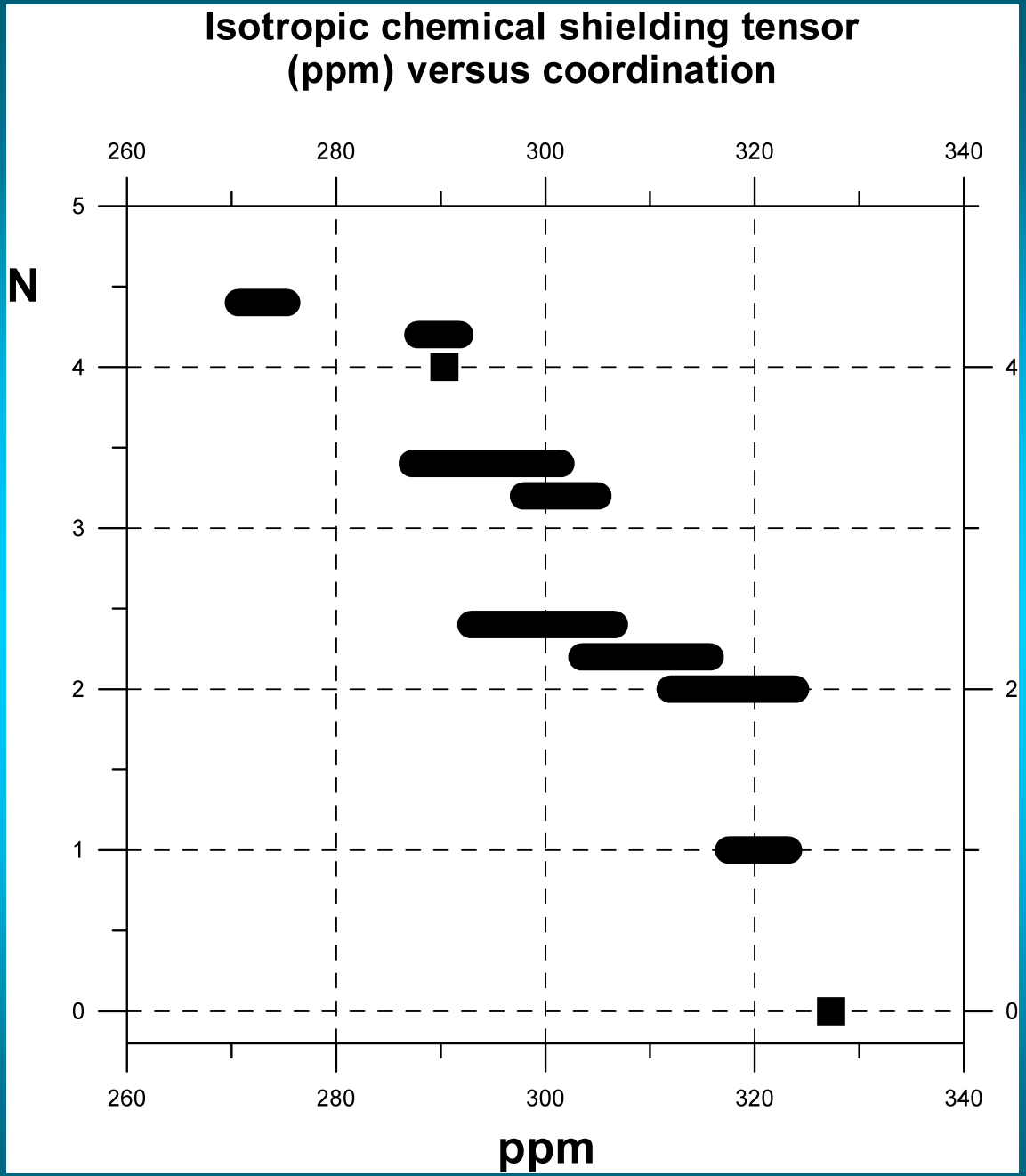


R.A. Klein, Bangalore September 2006

Cooperativity in rings

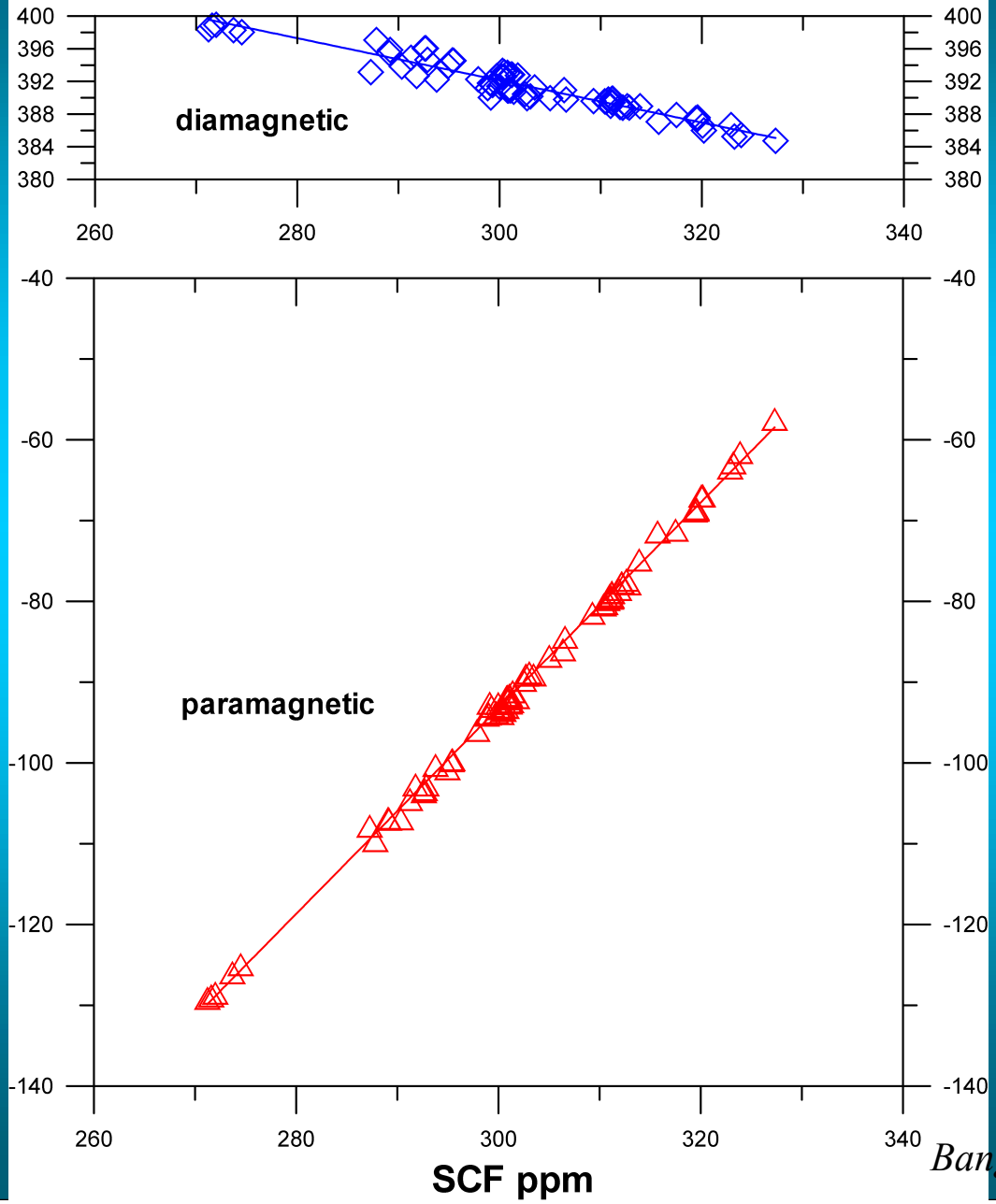


R.A. Klein, Bangalore September 2006

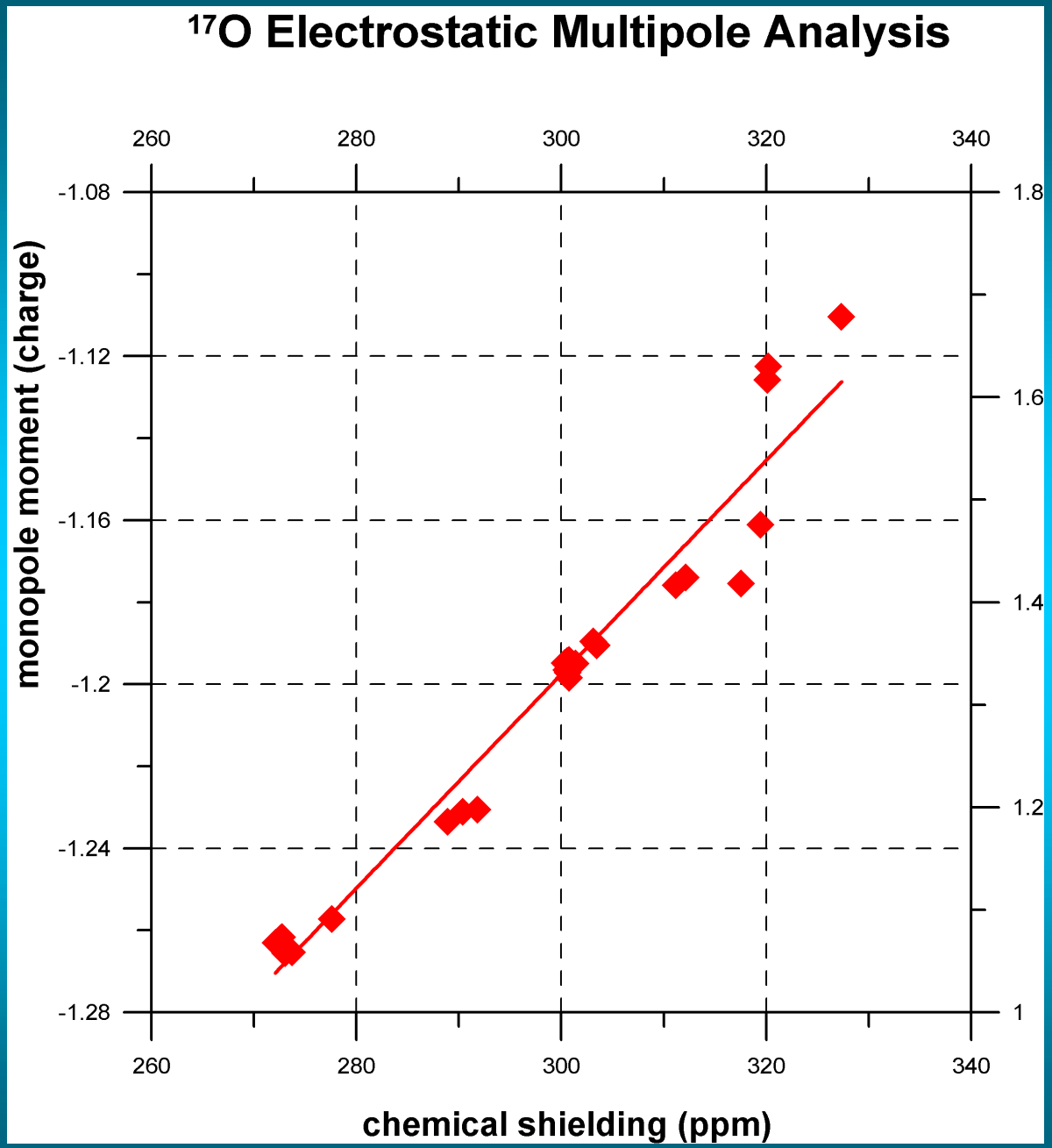


Bangalore September 2006

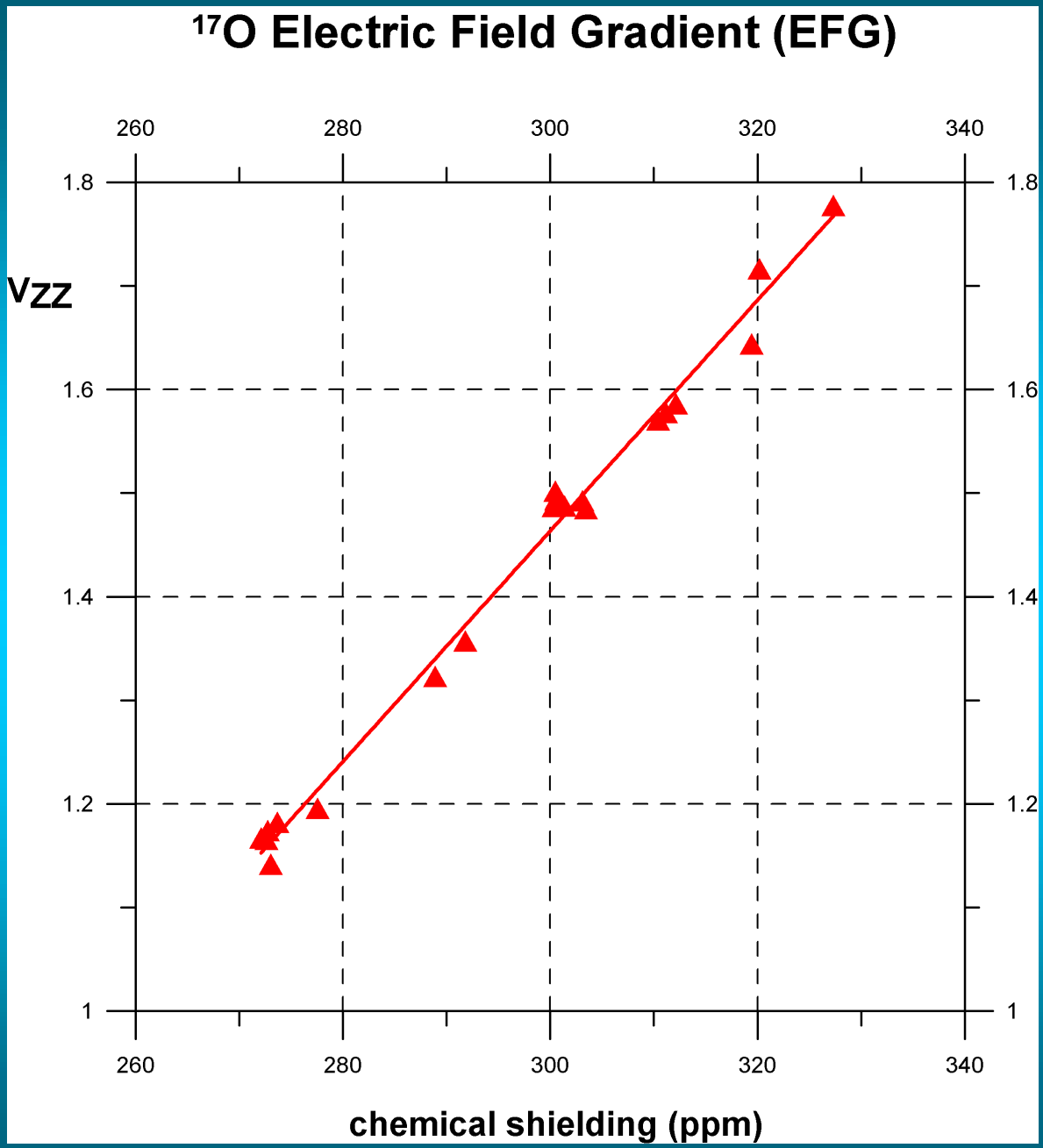
SCF ppm against NCSA paramagnetic/diamagnetic component (atomic origin)



Bangalore September 2006



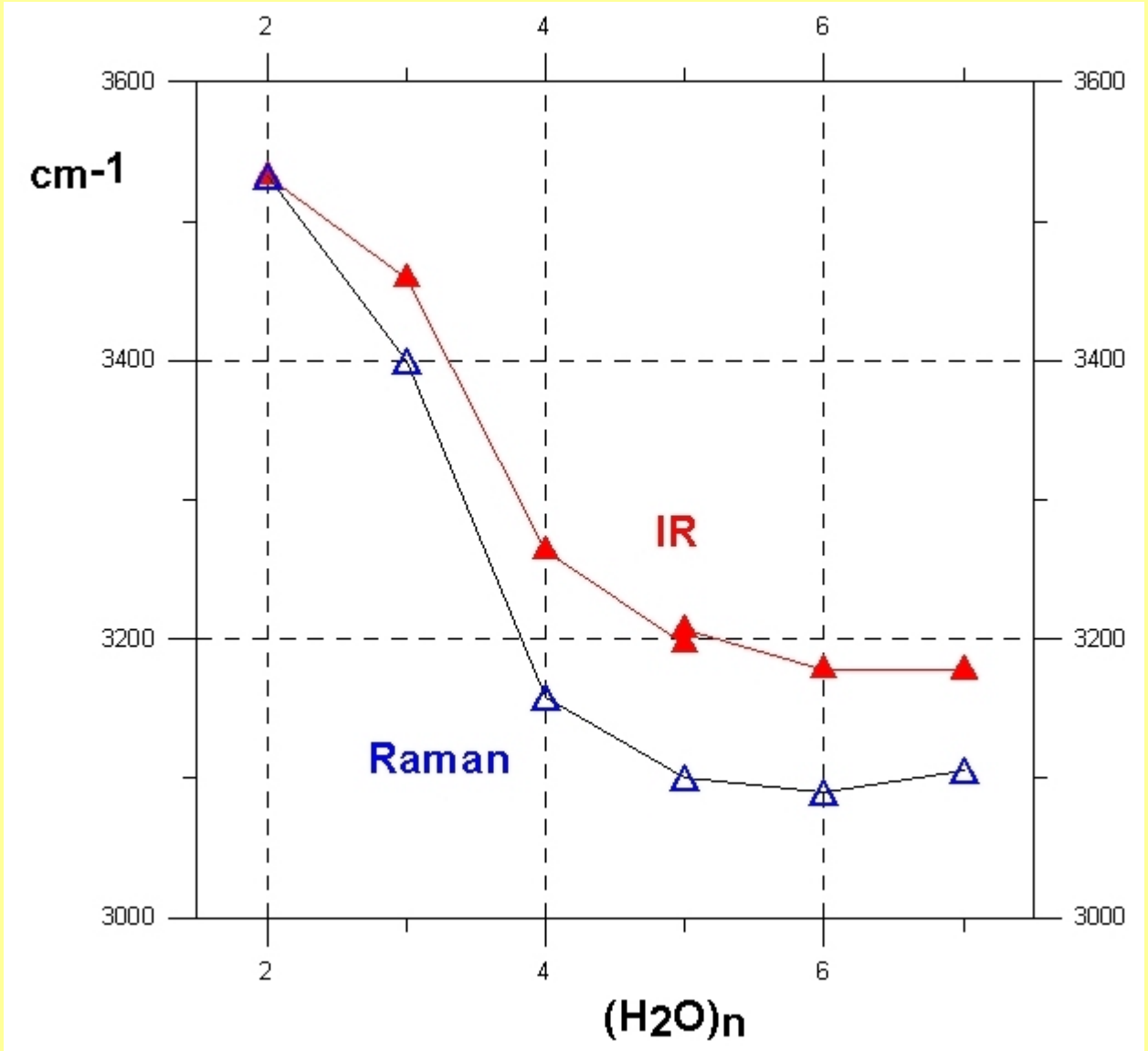
Bangalore September 2006



Bangalore September 2006

Cooperativity in Ring Systems (II)

R.A. Klein, Bangalore September 2006



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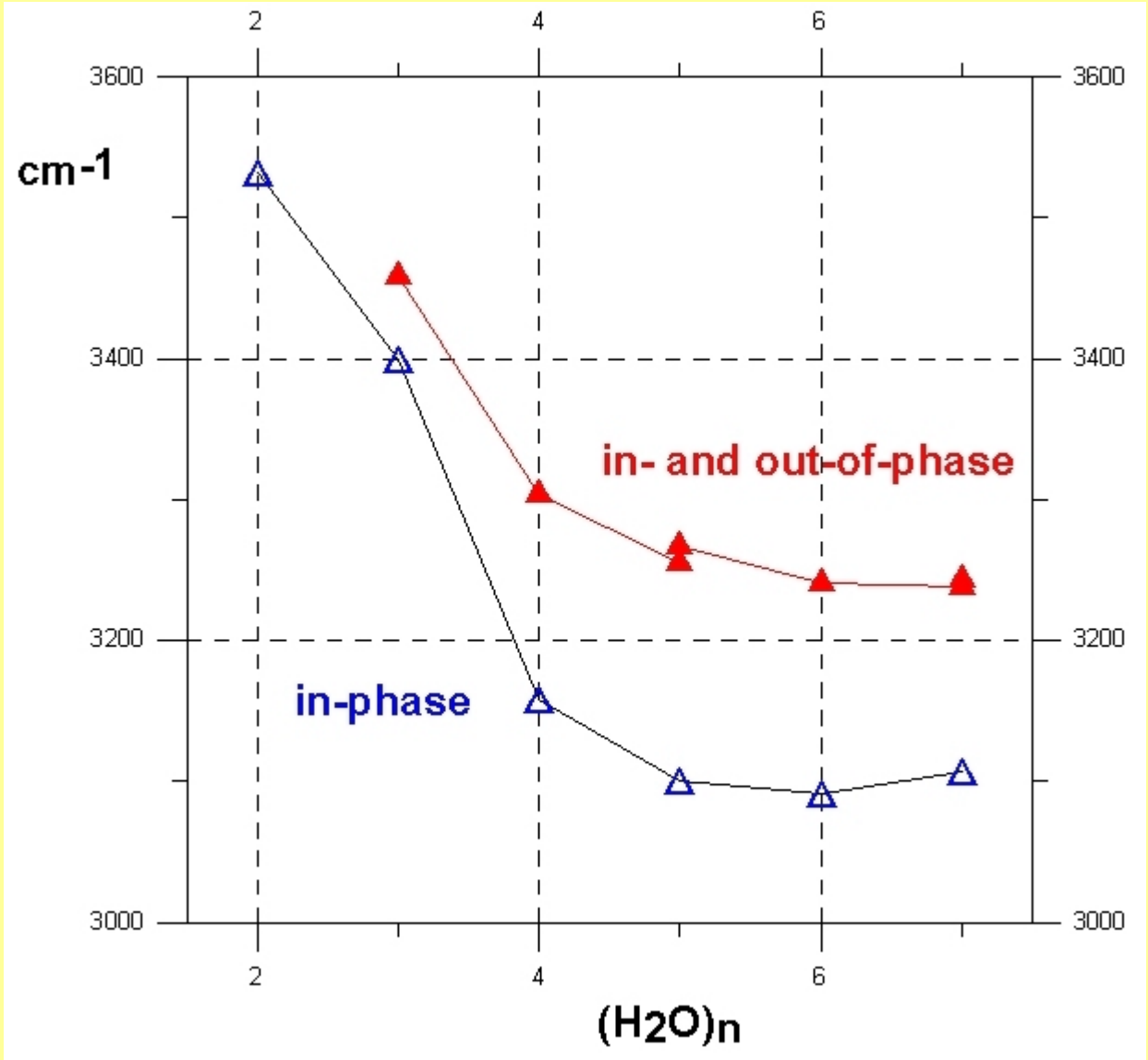
Raman in-phase / in- and out-of-phase



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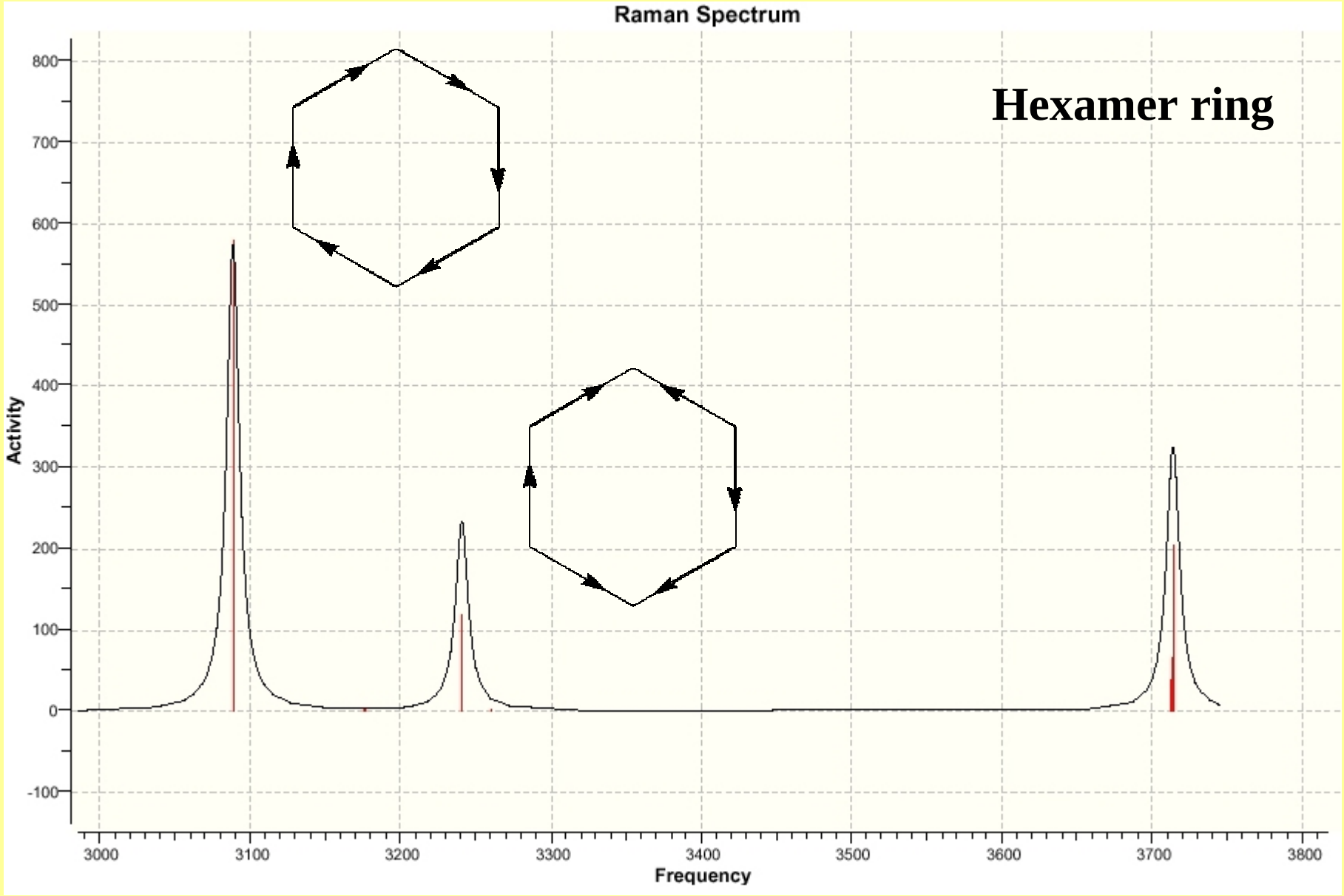

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What is a Hydrogen Bond?

IUPAC Task Group

"Categorizing Hydrogen Bonding and Other Molecular Interactions"

- 2004-2006 Project #2004-026-2-100
- Core Group
  - Arunan (co-chair), Desiraju, Scheiner (co-chair), Klein, Sadlej
- Other members
  - Alkorta, Clary, Crabtree, Dannenberg , Hobza, Kjaergaard, Kleinermanns, Legon, Mennucci, Nesbitt

IUPAC Task Group

"Categorizing Hydrogen Bonding and Other Molecular Interactions"

- Semantics?
- Philosophy?
- Metaphysics?

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Addresses the general problem of what is meant by hydrogen bonding and cooperativity:

"... Like most chemical concepts, this term [hydrogen bonding] is more or less universally understood by the practitioners in the field but is not precisely defined ....
.... This topic is one for interesting debates at tea or coffee times in chemistry departments around the world but is not .... suitable for rigid formalisation..."

An Unknown Referee (2004)

IUPAC Gold Book Definition

The current International Union of Pure and Applied Chemistry (IUPAC) definition of a hydrogen bond is contained in the IUPAC *Compendium of Chemical Terminology*, popularly referred to as the `Gold Book' in recognition of the initial efforts of the late Victor Gold. [1] The *Compendium* defines a hydrogen bond as

``...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}*)."*

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What Constitutes Evidence for Hydrogen Bonding?

- Nuclear separation – what distance is appropriate? $VDW_{(donor)} + VDW_{(acceptor)}$?
- IR red-shifts – how reliable are small shifts (~50 cm^{-1})?
- NMR downfield shifts – how large?
- Charge transfer – how much?
- Bond critical point (BCP) – theoretical and experimental electronic structural details

Conclusions

- Small IR red-shifts are not necessarily diagnostic of hydrogen bonding;
- Hyperconjugative effects can lead to significant IR red-shifts of the order of ~50-100 cm^{-1};
- IR red-shift and antibonding orbital occupancies are closely correlated;
- Levels of theory used must be “adequate”

Characterising a Hydrogen Bond (I)

- an interaction between a H-atom and an electron-rich atom or region;
- range of energies large: $CH_4 \ldots O$ to $[F \ldots H \ldots F]^-$
- geometric criteria must be specific for the given $X\text{-}H_D \ldots Y_A$ system = modified atomic radii;
- a (3,-1) bond critical point (BCP);
- $n_0 \Rightarrow \sigma^*$ hyperconjugation
  - > kT or 3/2kT (~ 1 kcal/mole) interaction energy
  - > 0.01-0.015 antibonding orbital occupancy;
- atomic properties of the H_D-atom
  - atomic volume; dipole polarisation; monopole moment;

Characterising a Hydrogen Bond (II)

- Spectroscopic shifts
  - IR red-shifts – hyperconjugative effects and antibonding orbital occupancies
    - » competition between n_o => σ^* and σ => σ^*
    - » difficult with certainty <~ 100 cm^{-1}
  - NMR downfield shifts – stereochemical effects
    - » > 1 ppm for ^{1}H, at least an order of magnitude greater for ^{13}C and ^{17}O
- Energies
  - calculated and experimental
- etc

and when attractive hyperconjugative effects exceed the Pauli exchange (steric) repulsion

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- IUPAC Task Group

Klein-Weinhold Definition

Hydrogen bond: *An attractive B···H-A interaction (partial B···H "bond") between an electron-rich Lewis base B, often lone pair-bearing, and a hydridic Lewis acid H-A, often involving electronegative A, that reflects partial sharing of the proton between A and B species. The H-bond may be quantified through a characteristic array of correlated structural, spectroscopic, and reactivity features: unusually short B···H distance and near-linear B···H-A geometry, pronounced shifts in IR and NMR frequencies and lineshapes, altered proton exchange reactivity, and so forth. In theoretical terms, it is best considered as a type of* $B\text{-}H^{+}\cdots A^{-}$ *resonance stabilisation, quantified by associated theoretical descriptors such as* b_{BH} *bond order, strength of* $n_B\text{-}\sigma^*_{AH}$ *charge delocalisation, existence of a topological BCP(3,-1) bond critical point, and so forth. Hydrogen bonds may be intermolecular or intramolecular, involving ions and radicals as well as closed-shell neutral species, and their strengths vary widely over the range 5-200 kJ* mol^{-1} *(i.e., from a little above kT to typical dative coordination bond values).*

R. A. Klein, Bangalore September 2006