IUPAC Workshop
"Hydrogen Bonds and Other Molecular Interactions"
Pisa 5-9 September 2005

Characterising Hydrogen Bonds
Cooperativity, Electron Density Topology

Roger A. Klein

Institute for Physiological Chemistry

University of Bonn

universitätbonn
RHEINISCHE FRIEDRICH-WILHELMS-UNIVERSITÄT

R.A. Klein, IUPAC Pisa September 2005

The 'simple' Pauling definition

- partially electrostatic

- resonance hybrid

- partially covalent (Isaacs et al. (1999))

- interaction of the type -X...H-Y-, where both X and Y are electronegative atoms

- geometry dependent

Not suitable for rigid formalisation

"... 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)

The more rigorous theoretical definition too confining

"...We have previously taken the position that the intramolecular hydrogen bonding between adjacent ring OH are definably hydrogen bonds, having strong interaction energy and showing synergistic effects in cellobiose..."

"...There is some evidence suggesting that these interactions should not be called hydrogen bonds because they do not demonstrate a bond critical point (BCP) of correct (3,-1) topology. Although this definition is theoretically very critical we will continue to use the term hydrogen bonding for these terms since most scientists in the field of carbohydrate chemistry will find the more rigorous theoretical definition too confining..."

Anonymous Author (2004)

R.A. Klein, IUPAC Pisa September 2005

Roald Hoffmann suggests that a chemical bond lies beyond the domain of physics and is incapable of precise physical understanding

"...And yet the concept of a chemical bond, so essential to chemistry, and with a venerable history, has a life, generating controversy and incredible interest. Even if we can't reduce it to physics .... Push the concept to its limits, accept that a bond will be a bond by some criteria, maybe not by others, respect chemical tradition, have fun with the richness of something that cannot be defined clearly, and spare us the hype..."; Whether physics does or does not offer a definition of a *chemical bond*, it does set out the necessary and sufficient conditions for two atoms to be *chemically bonded* to one another, conditions summarised by Slater in terms of the two theorems that are essential to the physics of bonding: *"... both the virial theorem and Feynman's theorem are exact consequences of wave mechanics. Both interpretations agree in pointing to the existence of overlap charge density as the essential feature in the attraction between the atoms..."*;

this article makes a modest proposal: reserve the name and concept of a *bond* for use by those who believe that chemistry lies beyond the scope of physics (in spite of their reliance on molecular orbitals and valence bond structures), and reserve the concept of *bonding* for use by those intent on the pursuit and understanding of chemistry using the tools of quantum mechanics;

Cortes-Guzman & Bader (2004) quoting Roald Hoffmann at the ACS Symposium on "Contemporary Aspects of Chemical Bonding" in September 2003

R.A. Klein, IUPAC Pisa September 2005

The Controversy

- Should an interaction such as O...H-O be called a 'Hydrogen Bond'?

- The German 'Wasserstoffbrücke' means a 'hydrogen bridge'- perhaps more accurate and inclusive as more descriptive

- if we wish to maintain the term 'Hydrogen Bond' we need to define precisely what is meant by a 'bond' in quantum mechanical terms

The Controversy

- How far can we rely on *small* experimental spectroscopic shifts?

- DFT and electron density topology

- Computed and experimentally determined electron density topologies show remarkable agreement

- are classic van der Waals atomic radii (Pauling or Bondi) appropriate?

Answers?

- Is COOPERATIVITY diagnostic of hydrogen bonding as opposed to other types of relatively weak interactions (dispersive, dipole-dipole or van der Waals interactions)?

- Should we define hydrogen bonding in terms of electron density topology?
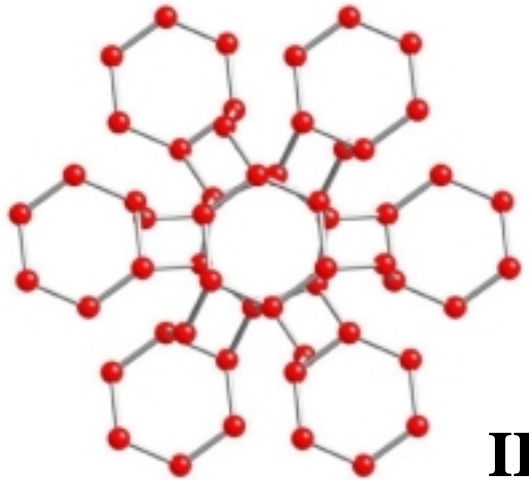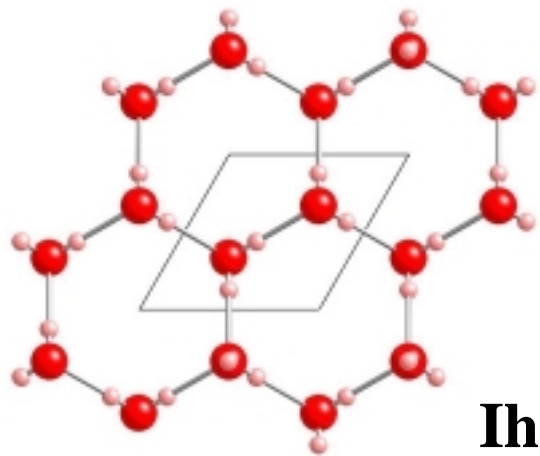
Benchmarking

- ## Three lemmas:
    - ### EXIST - Intermolecular or intramolecular hydrogen bonds that satisfy geometrical criteria and have a (3,-1) bond critical point (BCP)
        - Water clusters and clathrate cages - also enols, o-hydroxybenzoic acids, nucleic acids, peptide α-helices and β-pleated sheets, etc.
    - ### ASSUMED -Intramolecular hydrogen bonds with marginal geometry and <u>no</u> (3,-1) BCP although with minimal NMR and IR shifts
        - diols and sugars, specifically glucopyranose.
    - ### CANNOT EXIST - Hydrogen bonds in which the hydrogen atom cannot interact with the oxygen lone pairs on geometrical grounds <u>but which do have</u> (3,-1) BCPs
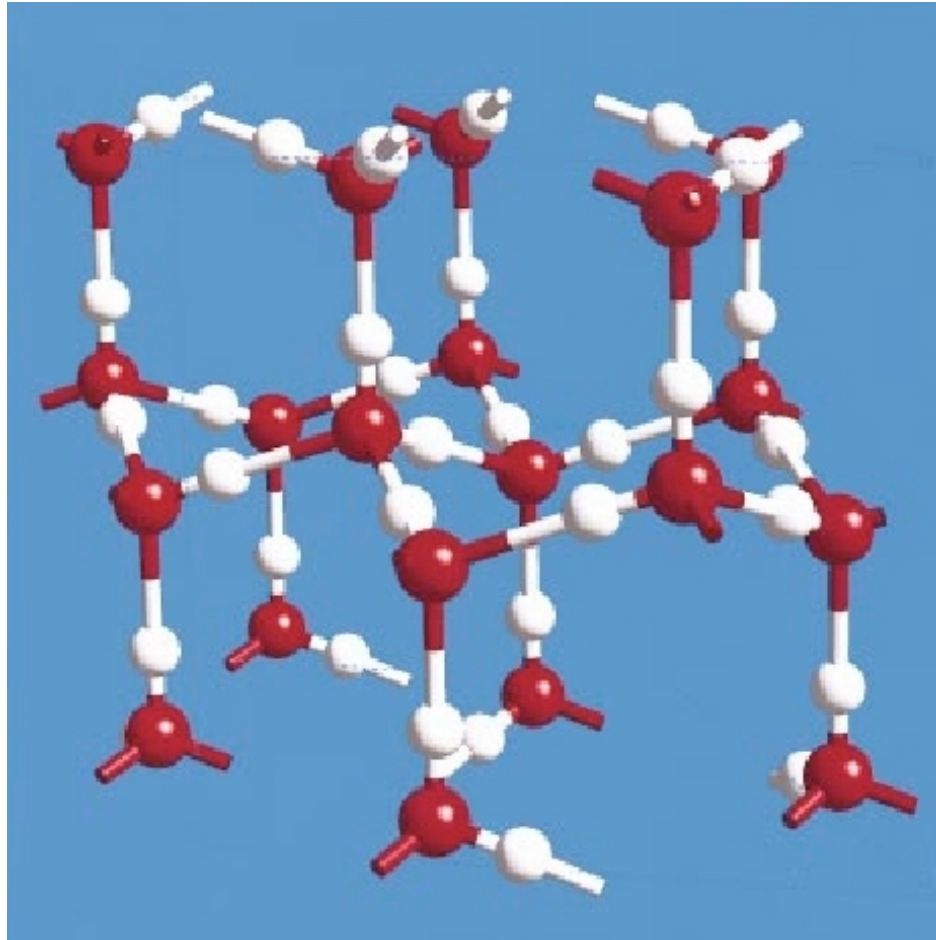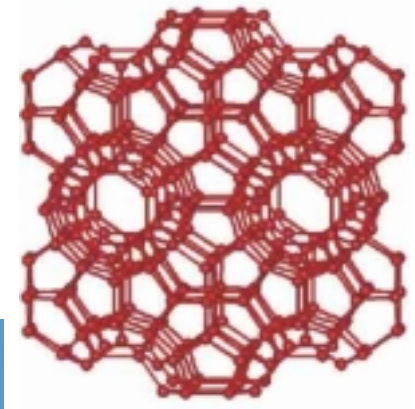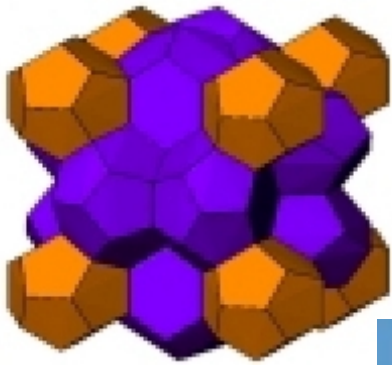   - Methane 5^{12} eicosamer and $6^2 5^{12}$ tetracosamer clathrates.

R.A. Klein, IUPAC Pisa September 2005

Data Generation

GAUSSIAN
G98 or G03
opt=tight
[calcfc]

Wavefunction
output=wfn 6D 10F
*.wfn
Cartesians

MORPHY98

AIM2000

critical point analysis

atomic basin integration

molecular paths

critical points

CRIT

INTE

electron density
Laplacian

kinetic energy
potential energy

electrostatic multipole
analysis

atomic volume
energy

Natural Bond Orbital Analysis
Fortran Unit 47 (*.47)
edit

NBO 5.0
*.nbo

occupancy

interaction energy

NCSA

Water Clusters
and
Clathrate Cages

R.A. Klein, IUPAC Pisa September 2005

Ice Polymorphs

Ih

II

XII

Ih

R.A. Klein, IUPAC Pisa September 2005

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

0°

90°

Cooperativity in Rings
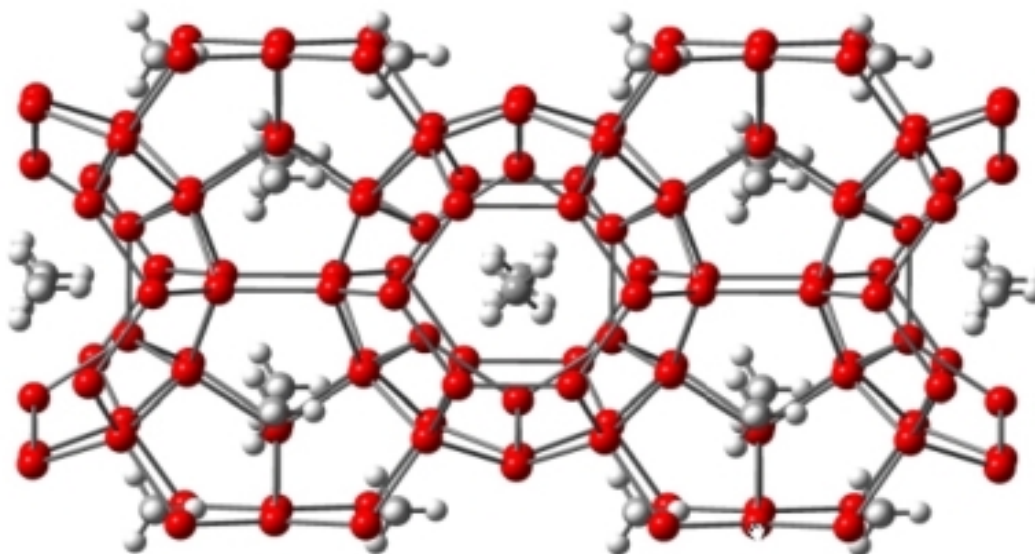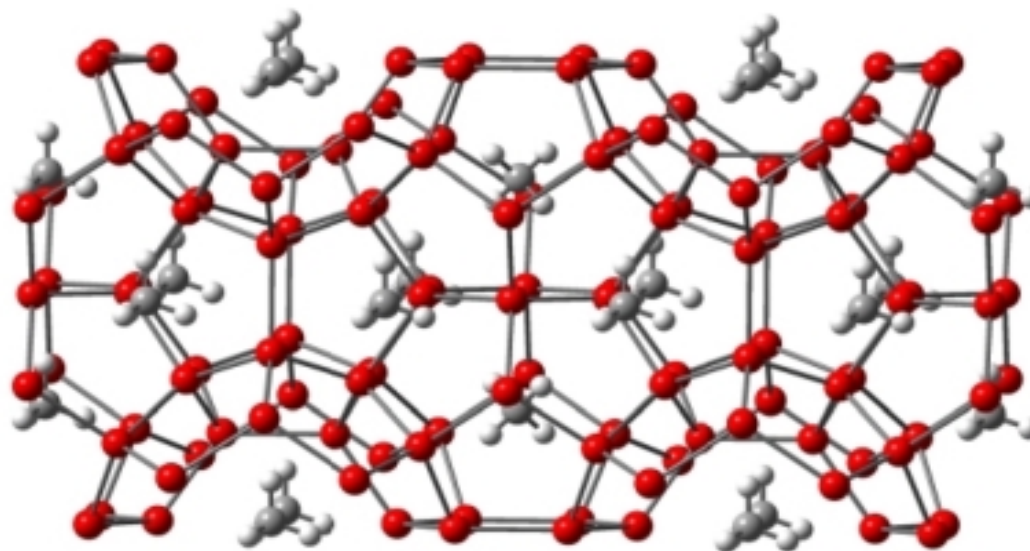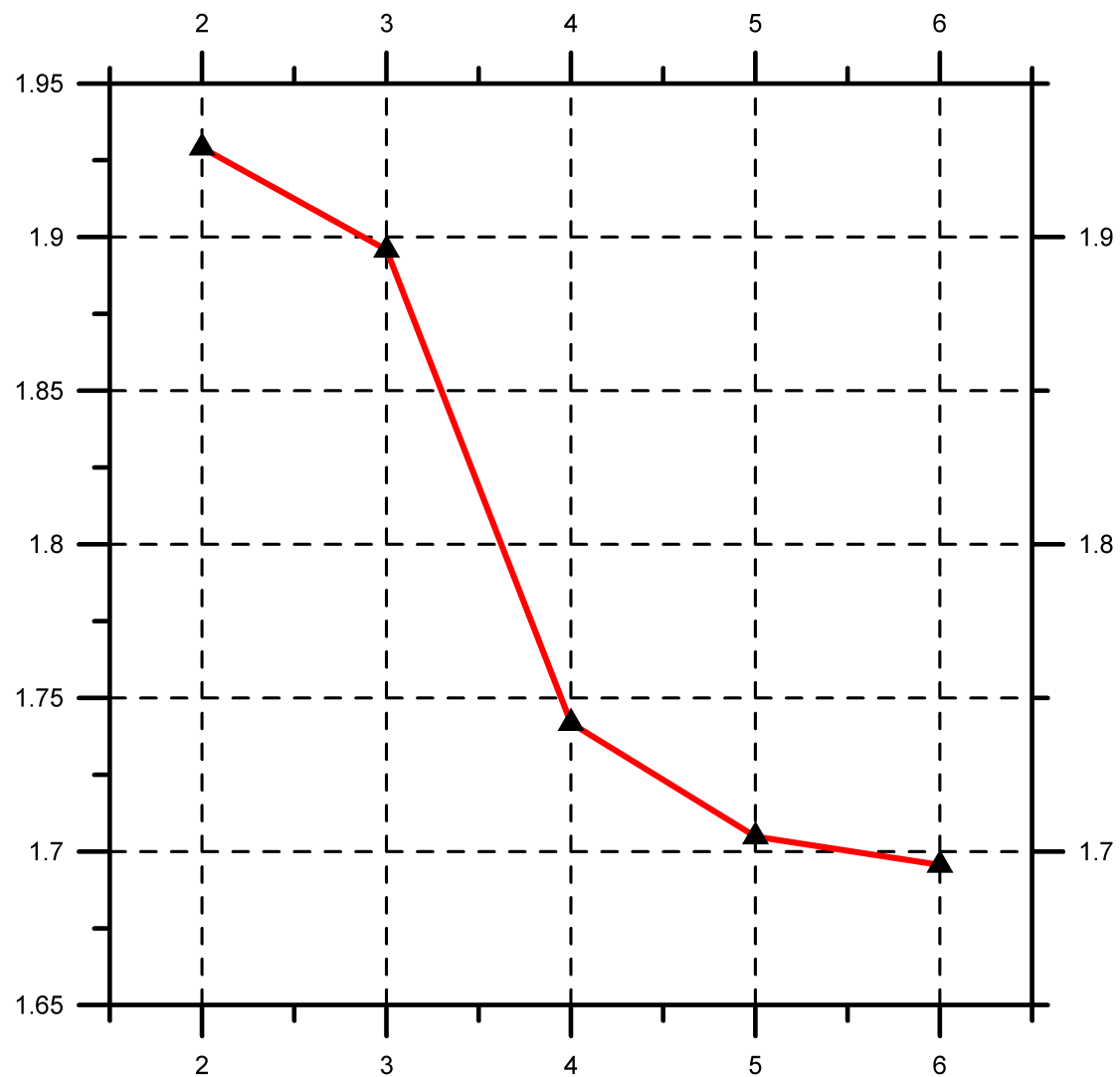
R.A. Klein, IUPAC Pisa September 2005

O_A...H_D distance in Å

2-coordinated rings

electron density ρ(r) at BCP
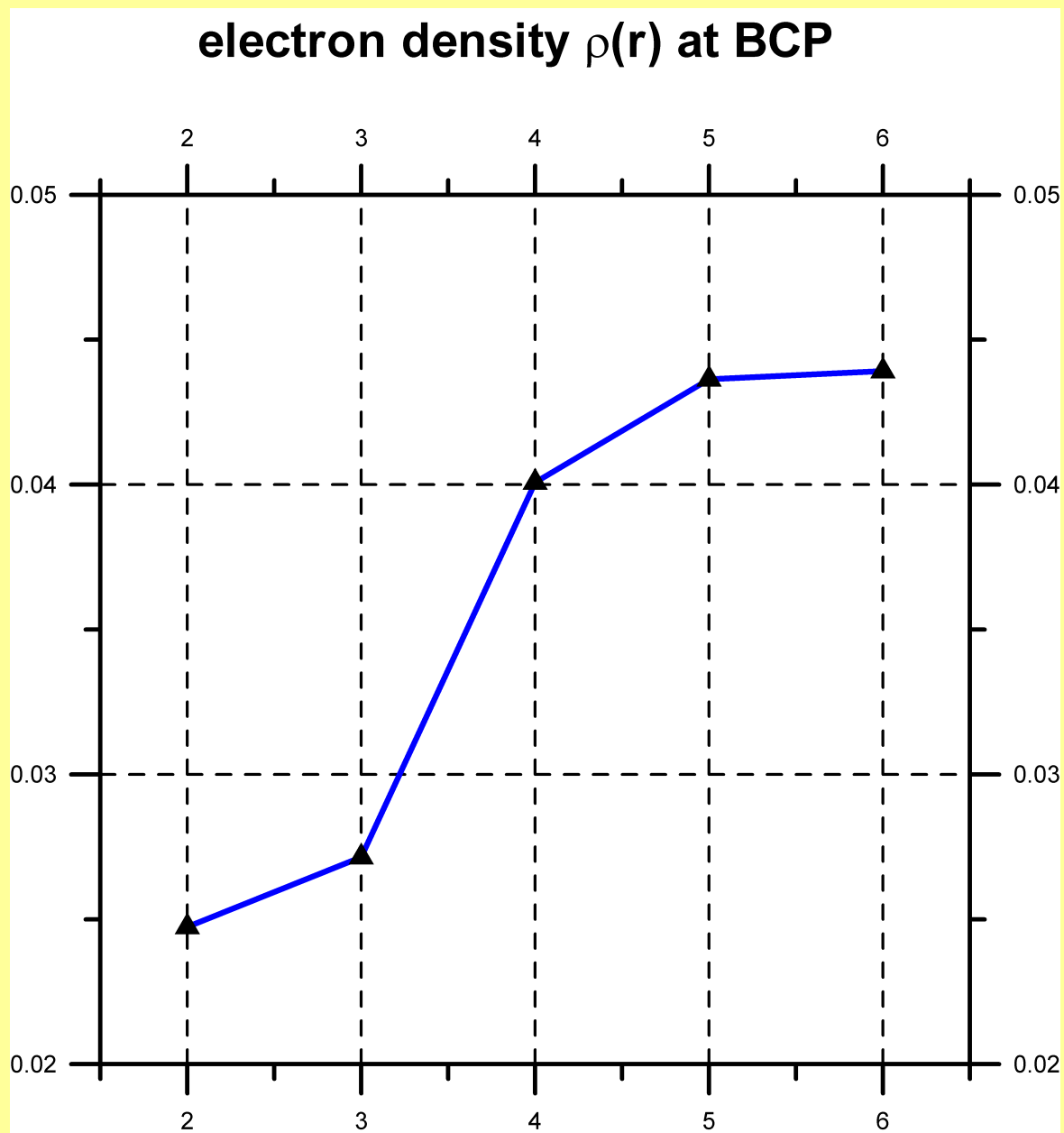
2-coordinated rings
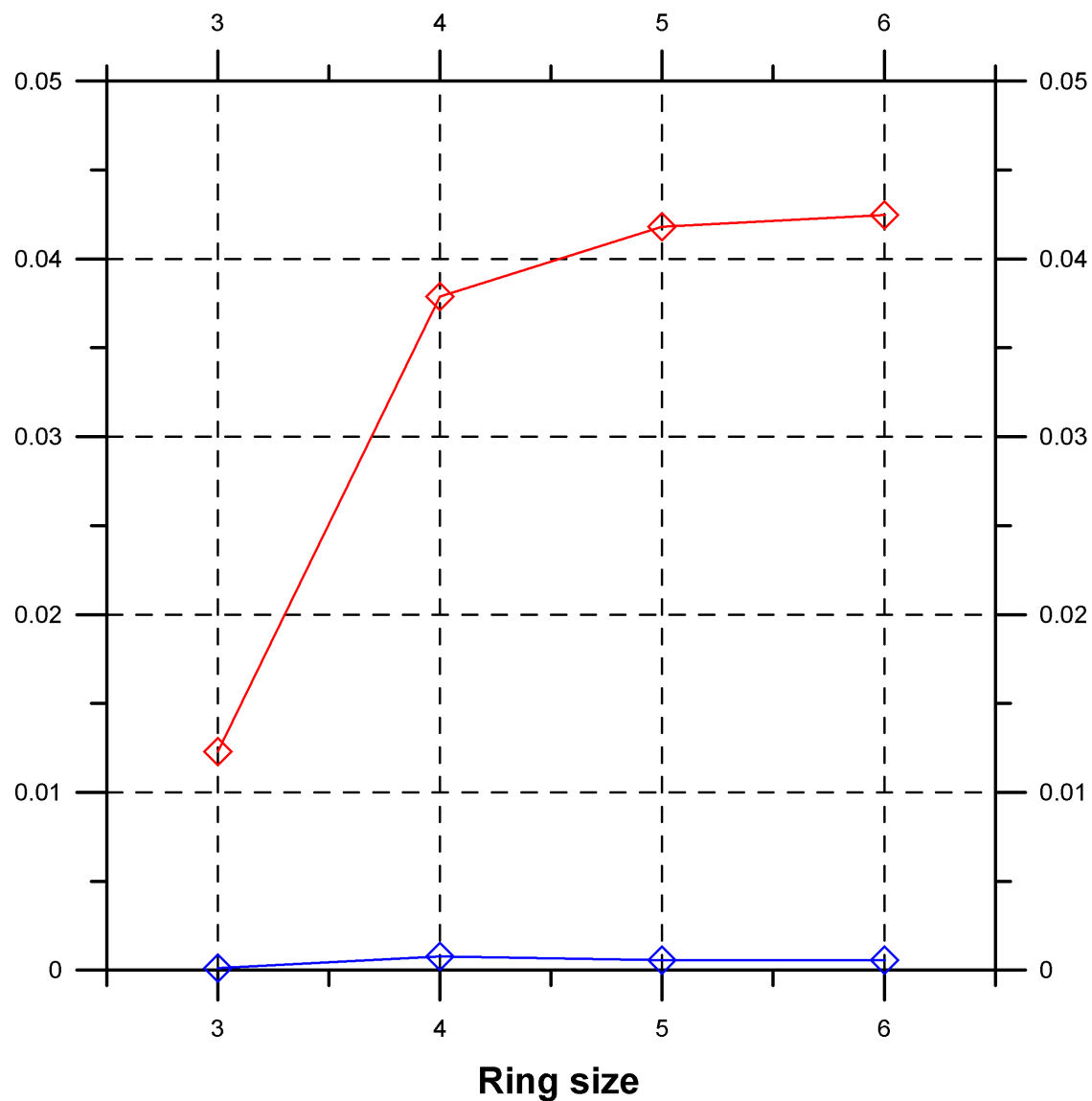
R.A. Klein, IUPAC Pisa September 2005

Laplacian of $\rho(r)$ at BCP
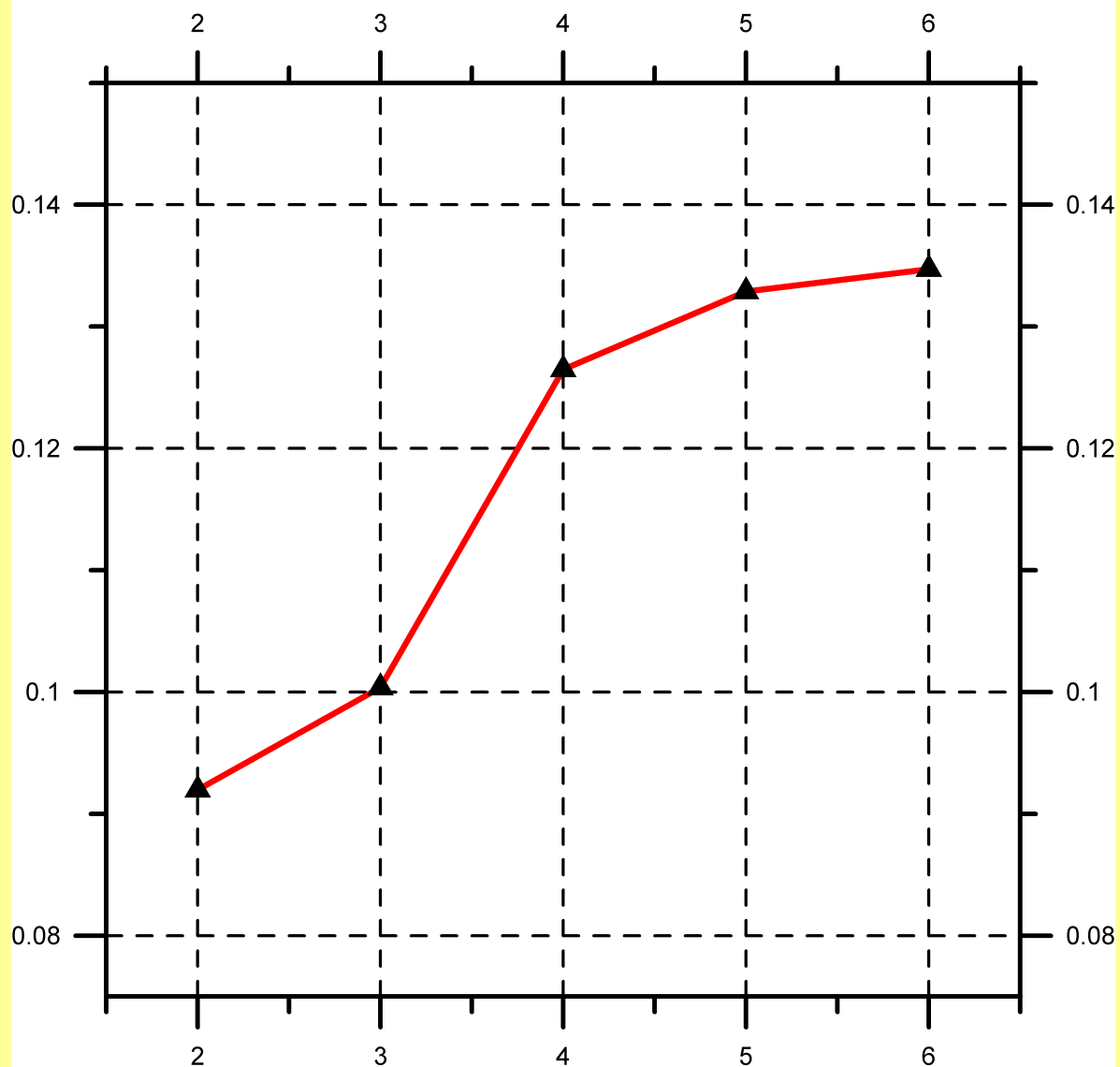
2-coordinated rings

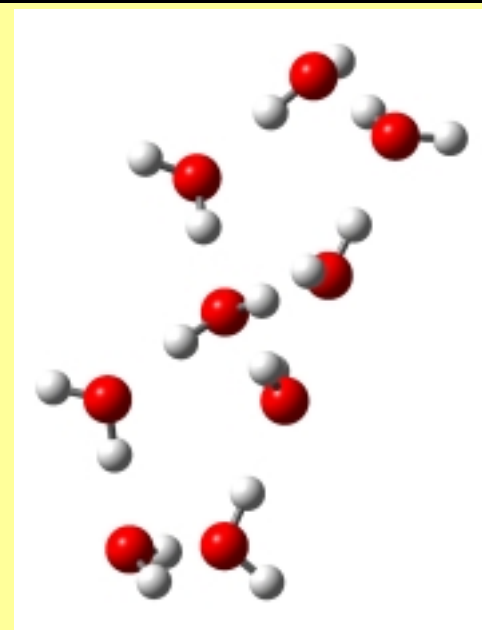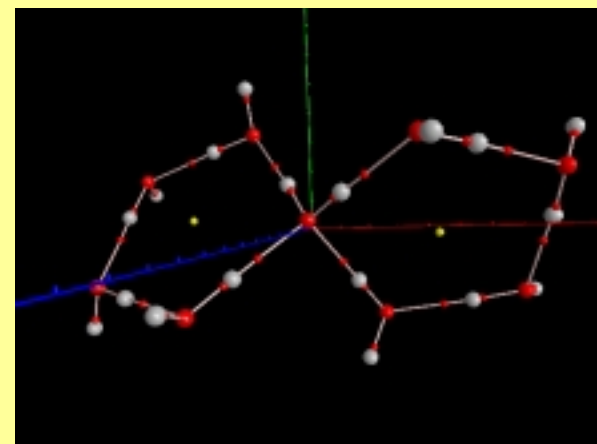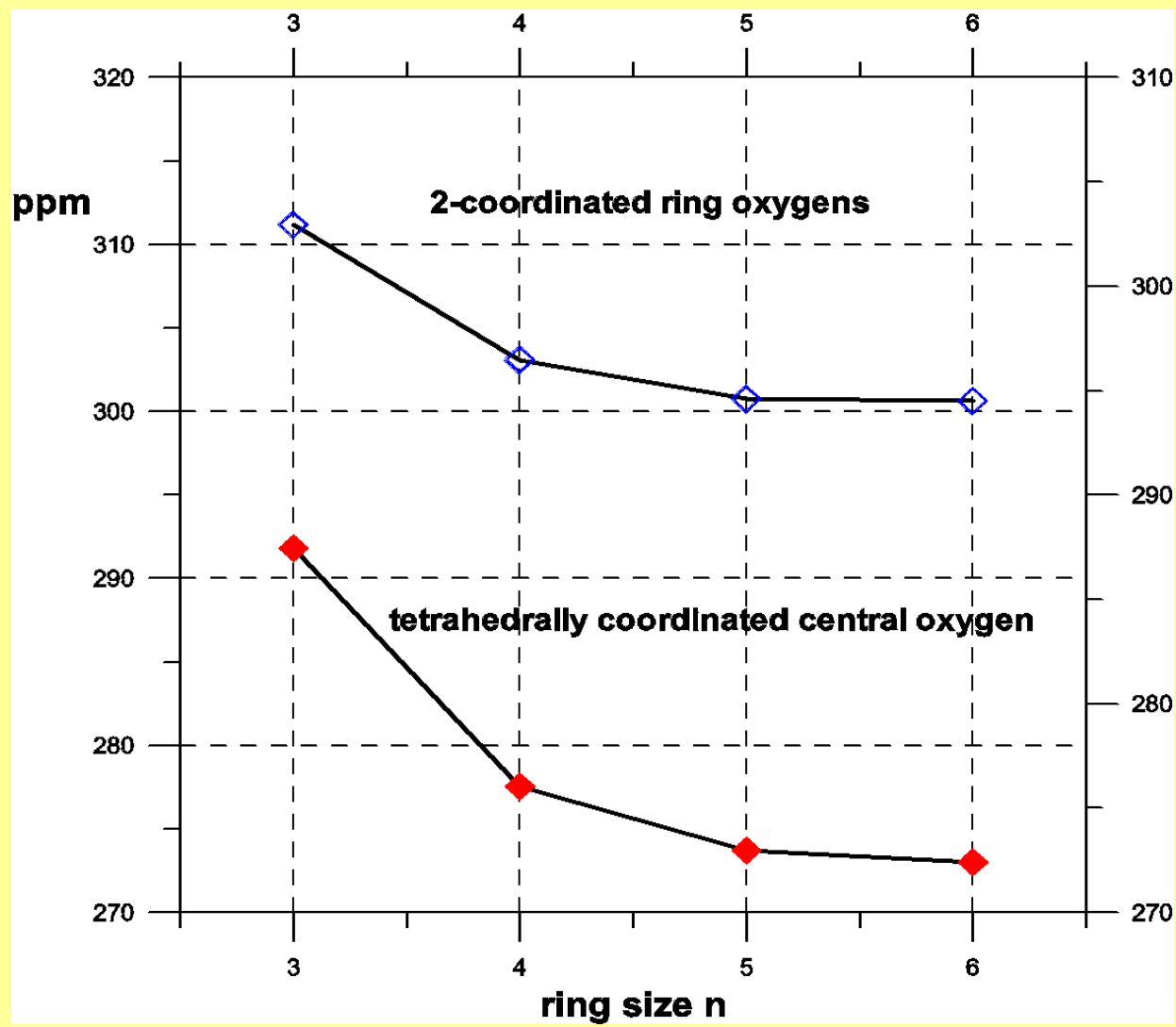*R.A. Klein, IUPAC Pisa September 2005*

NBO Occupancies for σ*O-HD (red) and σ*OA-H (blue)

Ring size

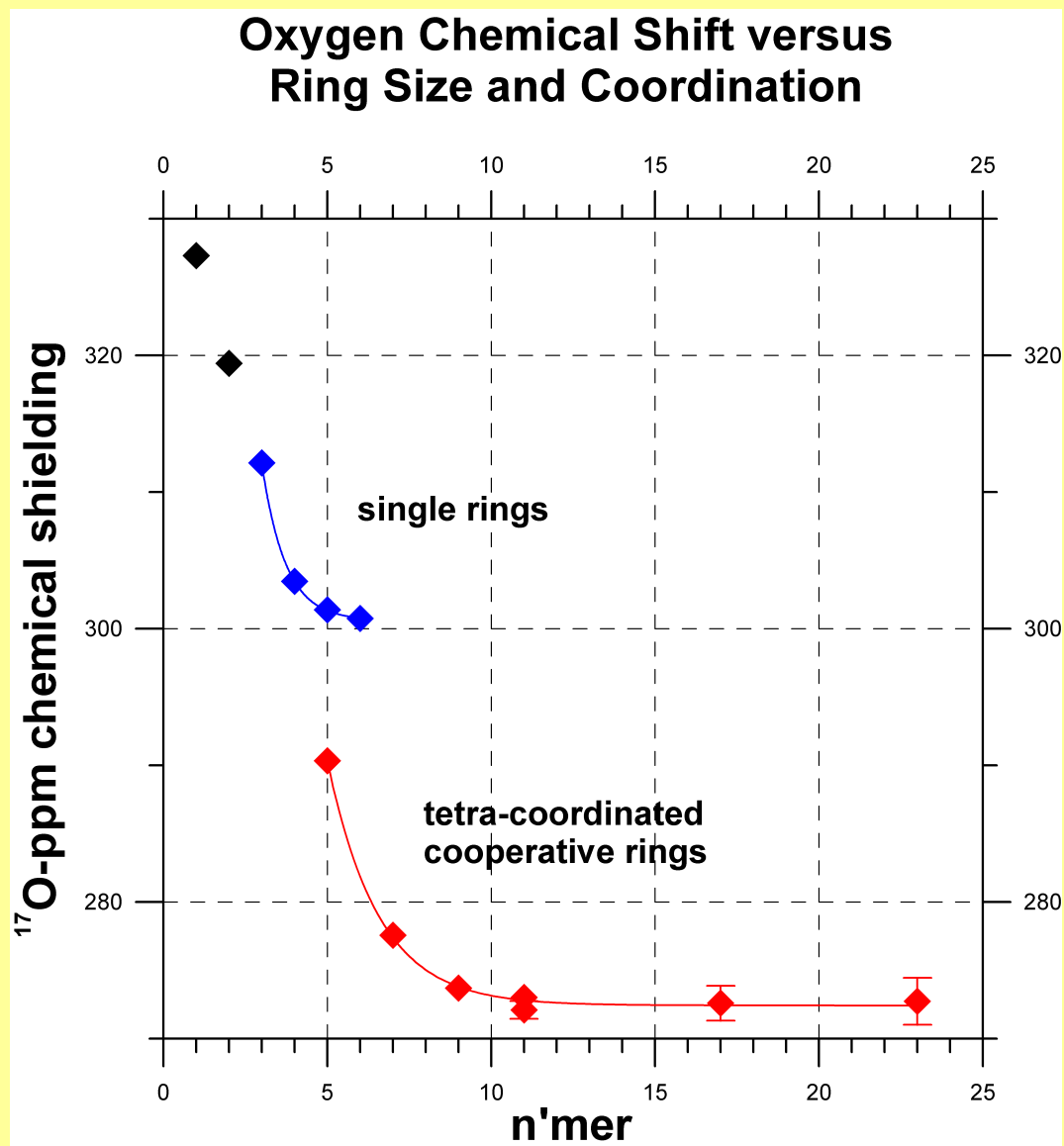**2-coordinated rings**

R.A. Klein, IUPAC Pisa September 2005

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

R.A. Klein, IUPAC Pisa September 2005

Cooperativity in rings

Oxygen Chemical Shift versus Ring Size and Coordination

single rings

tetra-coordinated cooperative rings

^{17}O-ppm chemical shielding

n'mer

Cooperativity in Ring Systems

R.A. Klein, IUPAC Pisa September 2005

Pentamer ring

R.A. Klein, IUPAC Pisa September 2005

R.A. Klein, IUPAC Pisa September 2005
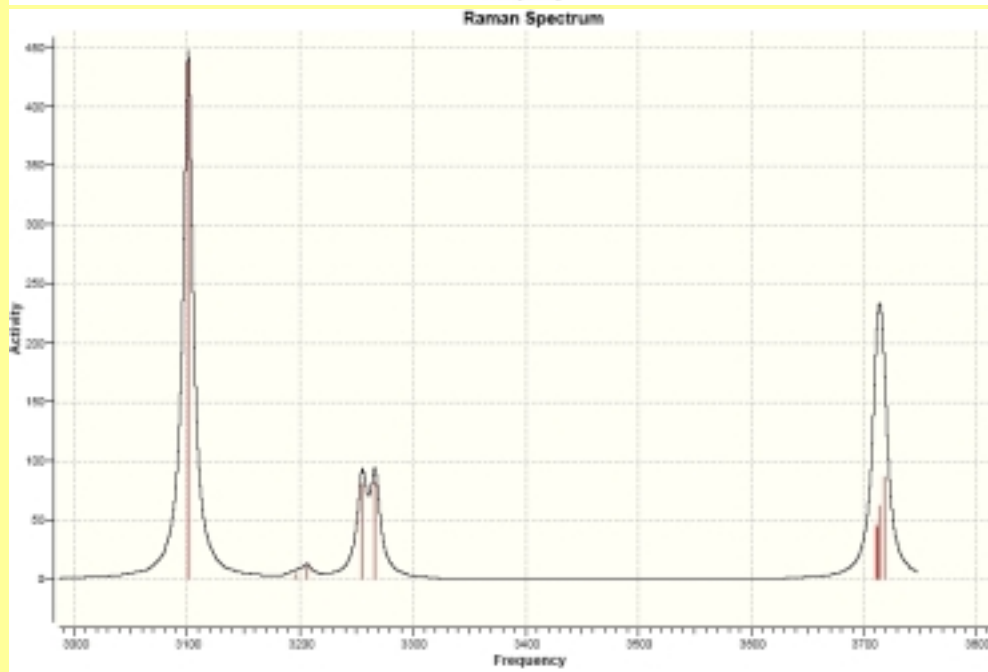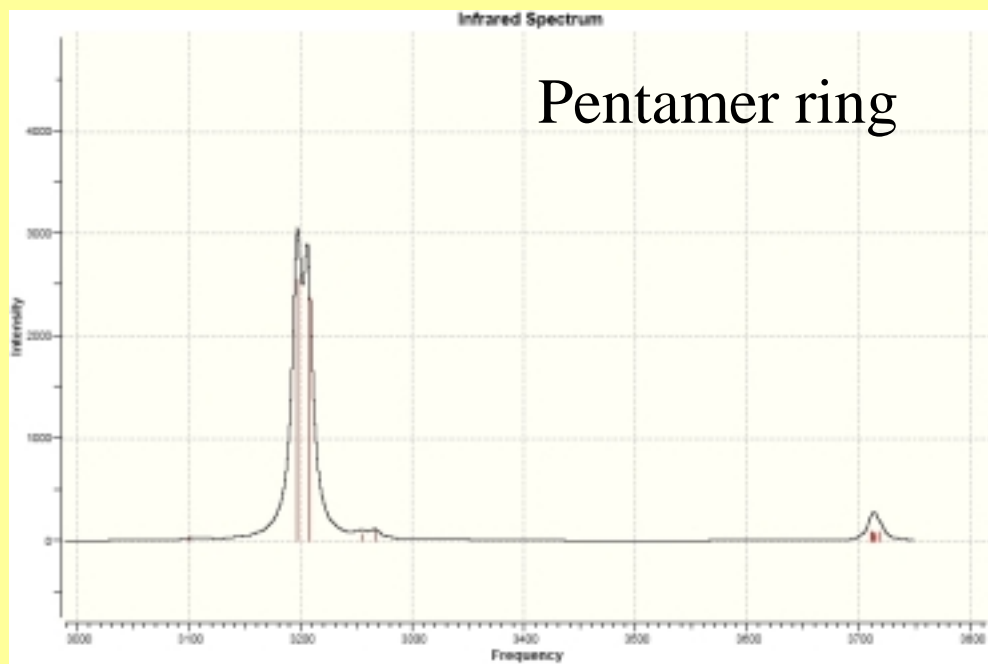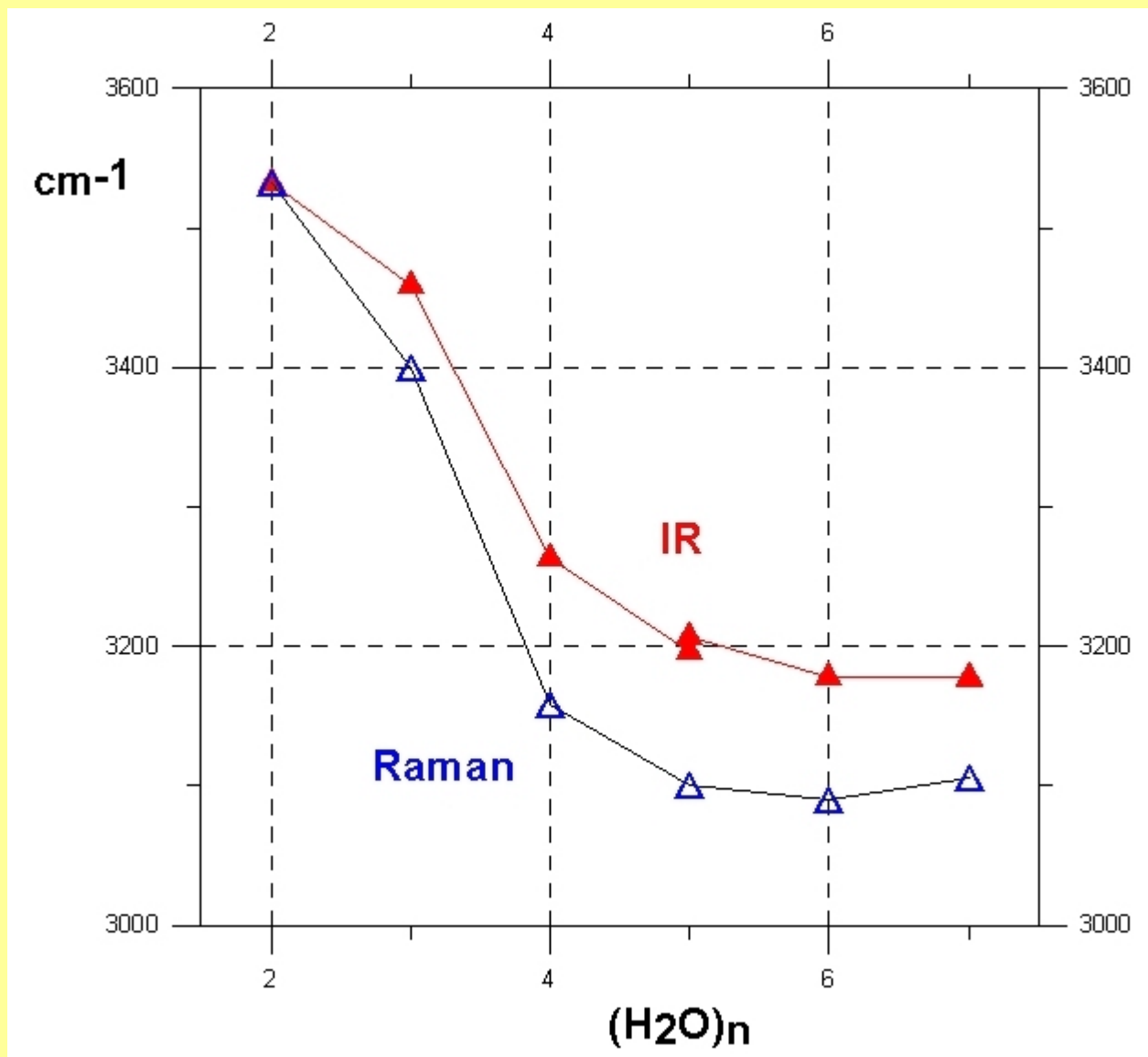
Raman in-phase / in- and out-of-phase

Raman Spectrum

R.A. Klein, IUPAC Pisa September 2005

Raman ring frequency (symm) against
-O-H...O- distance in Å

cm-1

-O-H...O- distance in Angstrom

Infrared Spectrum

Eicosamer

Infrared Spectrum

Tetracosamer

Raman Spectrum

Eicosamer

Raman Spectrum

Tetracosamer

R.A. Klein, IUPAC Pisa September 2005

Undecamer

Heptadecamer

Tricosamer

Undecamer

Heptadecamer

Tricosamer
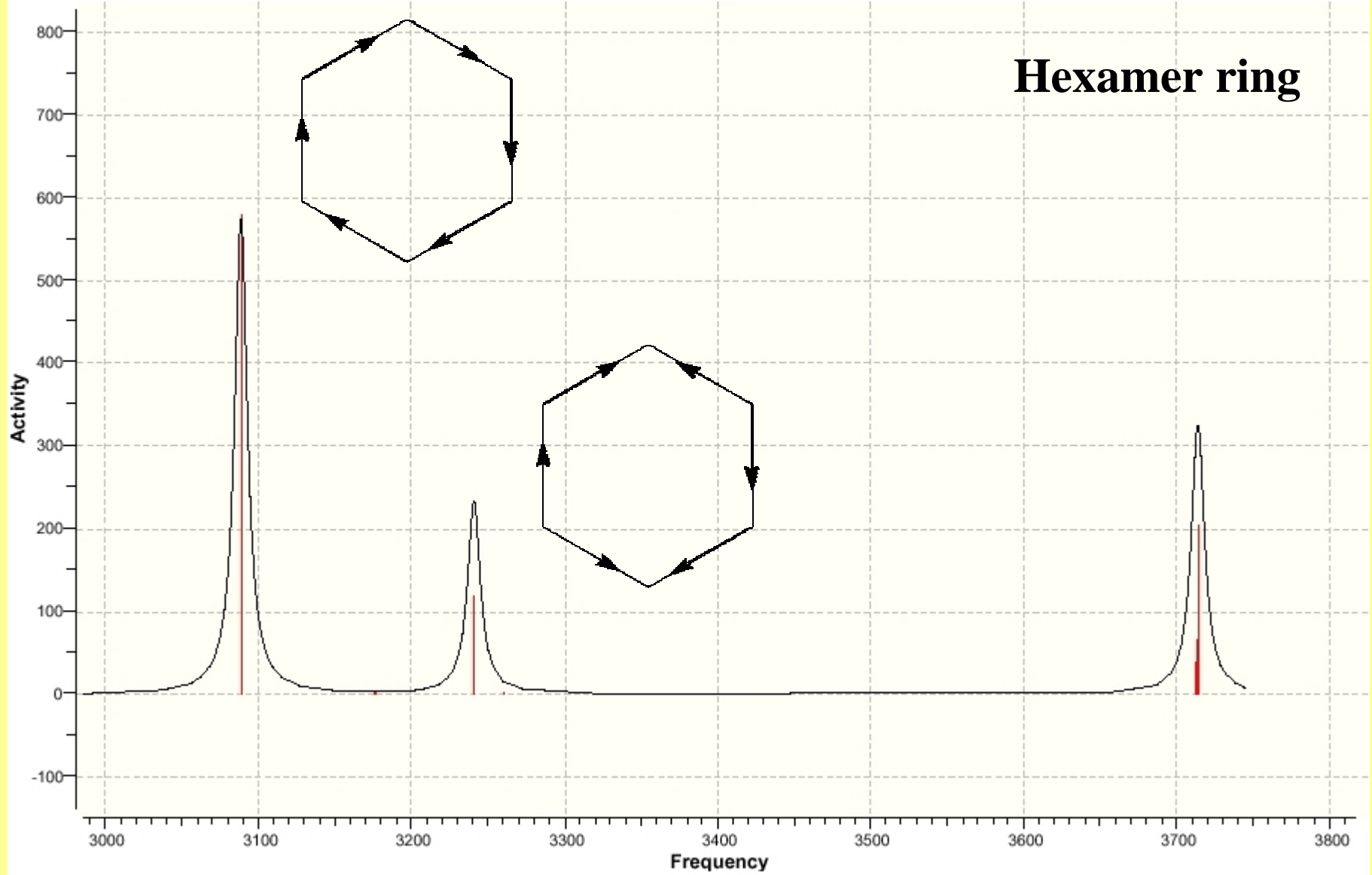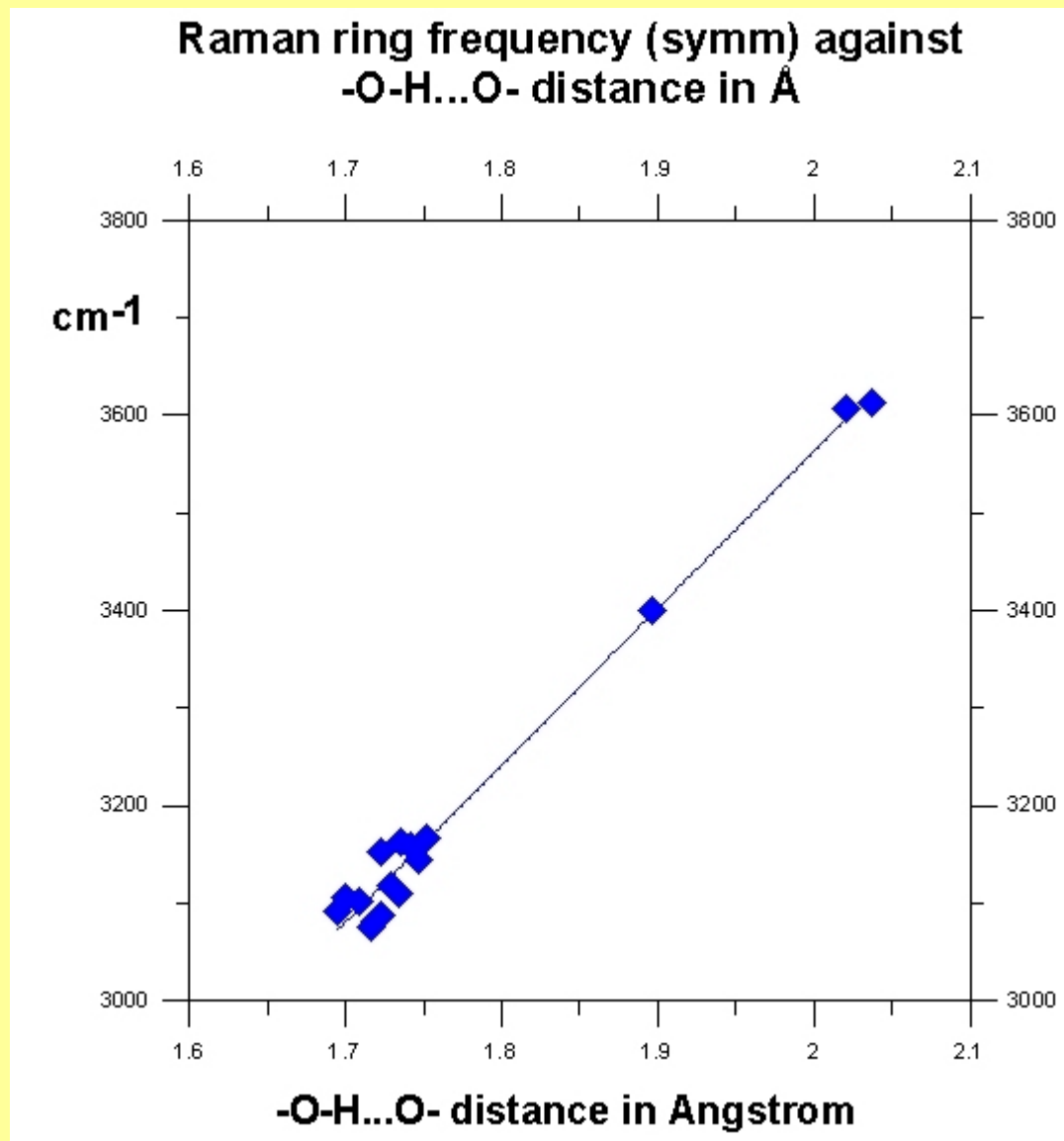
Fig. 4. Raman spectra of the new ice phase compared with ices I, II, III, V, VI, and water measured in situ in the diamond cell. Ice I is proton disordered; ice II is proton ordered; ice III is partially proton disordered but has a proton-ordered form (ice IX); ice V is partially proton disordered. We suggest that ice VI is partially ordered as well. The spectrum of supercooled water is in good agreement with previous work [for example (27)]. Weak peaks <100 cm^{-1} in that spectrum arise from spurious scattering. The tick marks denote characteristic Raman peaks discussed in the text: bands at 192, 490, 3215, and 3410 cm^{-1} for the new phase; 145 and 157 cm^{-1} for ice VI; and 95 and 190 cm^{-1} for ice III. Intensity is given in arbitrary units. Detailed analysis of the spectra of the additional phases will be presented elsewhere.
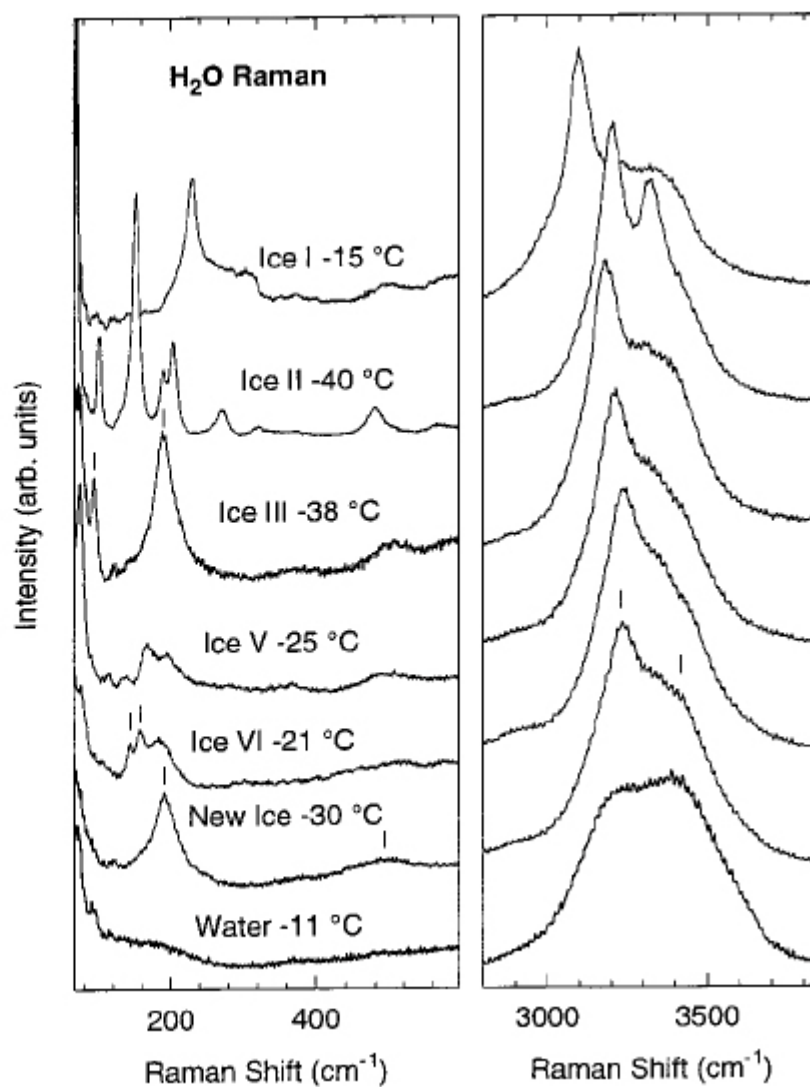
from Chou et al.; *Science* (1998) 281, 809
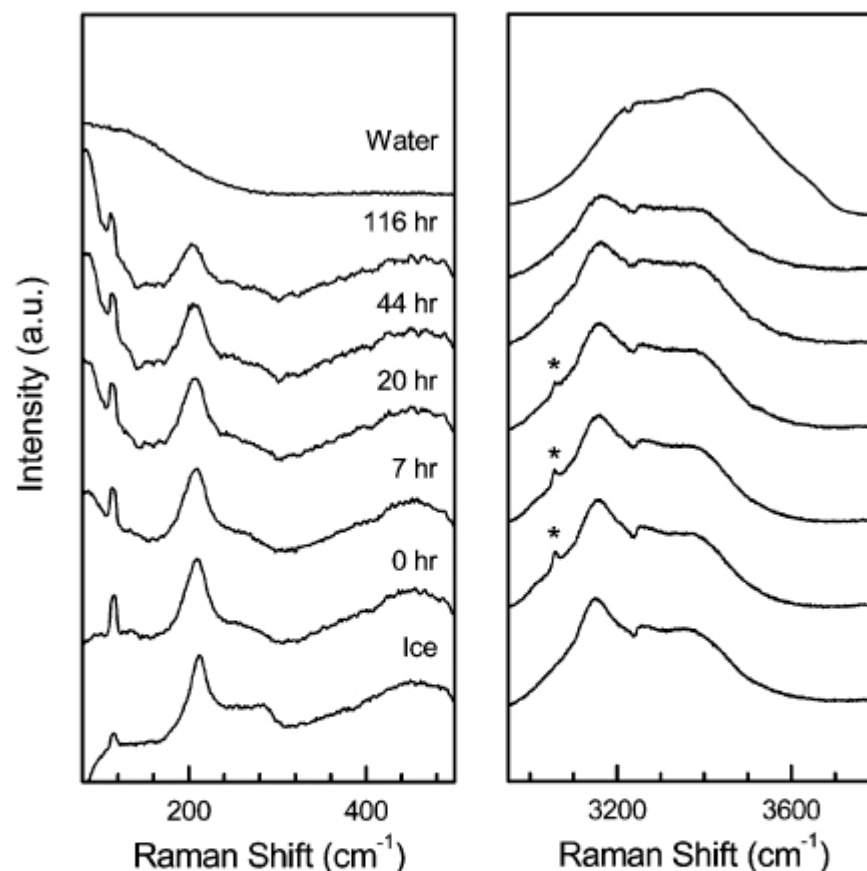
Figure 2. Raman spectra of lattice vibrations and O−H vibrations around 100−400 and 3000−4000 cm^{-1}, respectively, of sI hydrate. The asterisks denote characteristic Raman peaks for weak C−H vibration of methane molecules in the cages of the sI hydrate discussed in the text. For comparison, the intensity for hydrate samples is reduced in a same scale, even though it is given in arbitrary units. The experimental conditions for replacement are 278 K and 3 MPa (CO_2).

from Yoon et al.; *J. Phys. Chem. A* (2004) 108,5057

Water and Ice
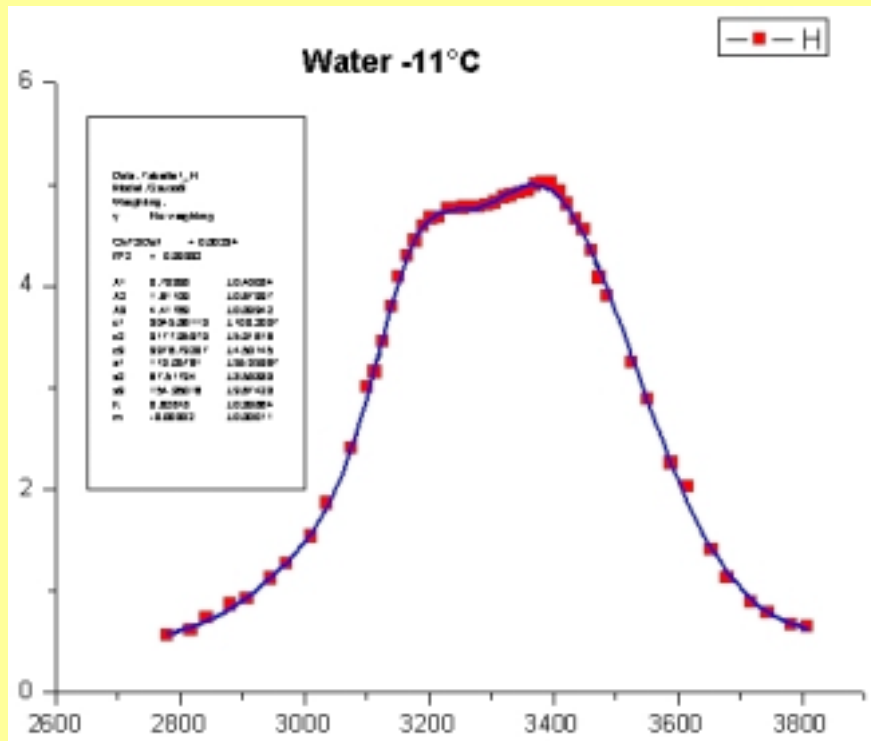
Experimental data (red) from
Chou et al. (1998) *Science* 281, 809

sI Methane Clathrate

Data: Tabelle1_D
Model: Gauss4
Weighting:
y   No weighting

Chi^2/DoF = 0.01259
R^2 = 0.99651

A1	3.15421	±0.47885
A2	0.6053	±0.25733
A3	1.83361	±0.24352
A4	3.40444	±0.40941
c1	3146.0535	±21.61208
c2	3057.87985	±6.48354
c3	3152.69664	±1.94015
c4	3356.95768	±21.18582
s1	104.67222	±21.95232
s2	10.0843	±6.01007
s3	29.30242	±3.25394
s4	103.02929	±9.67876
K	-2.31641	±2.03537
m	0.00063	±0.00055
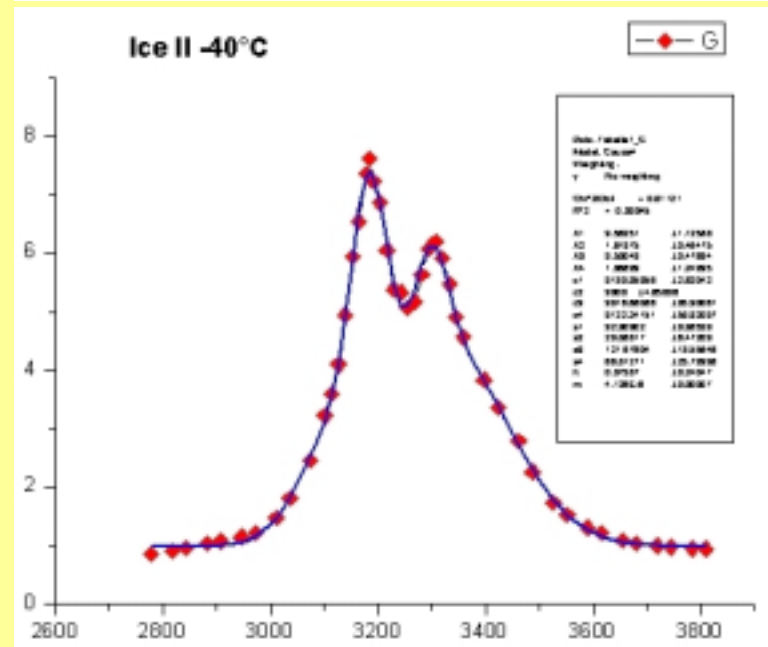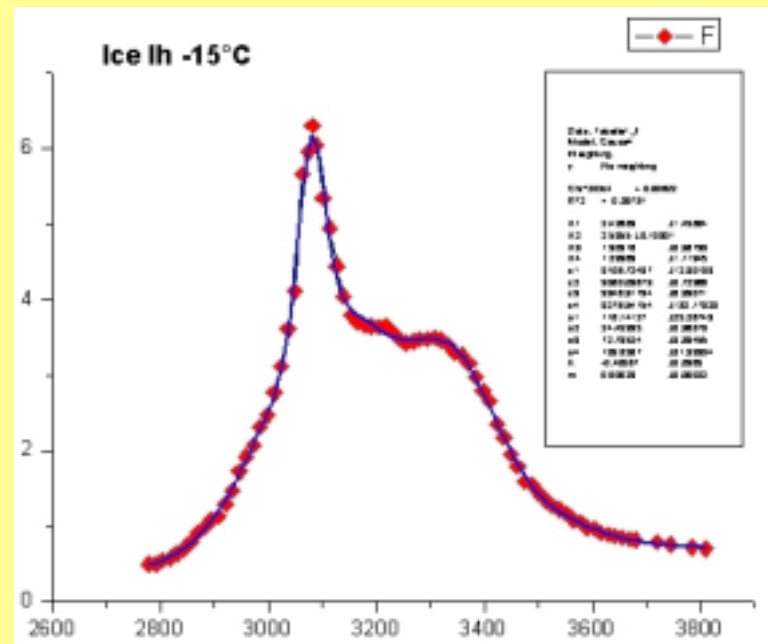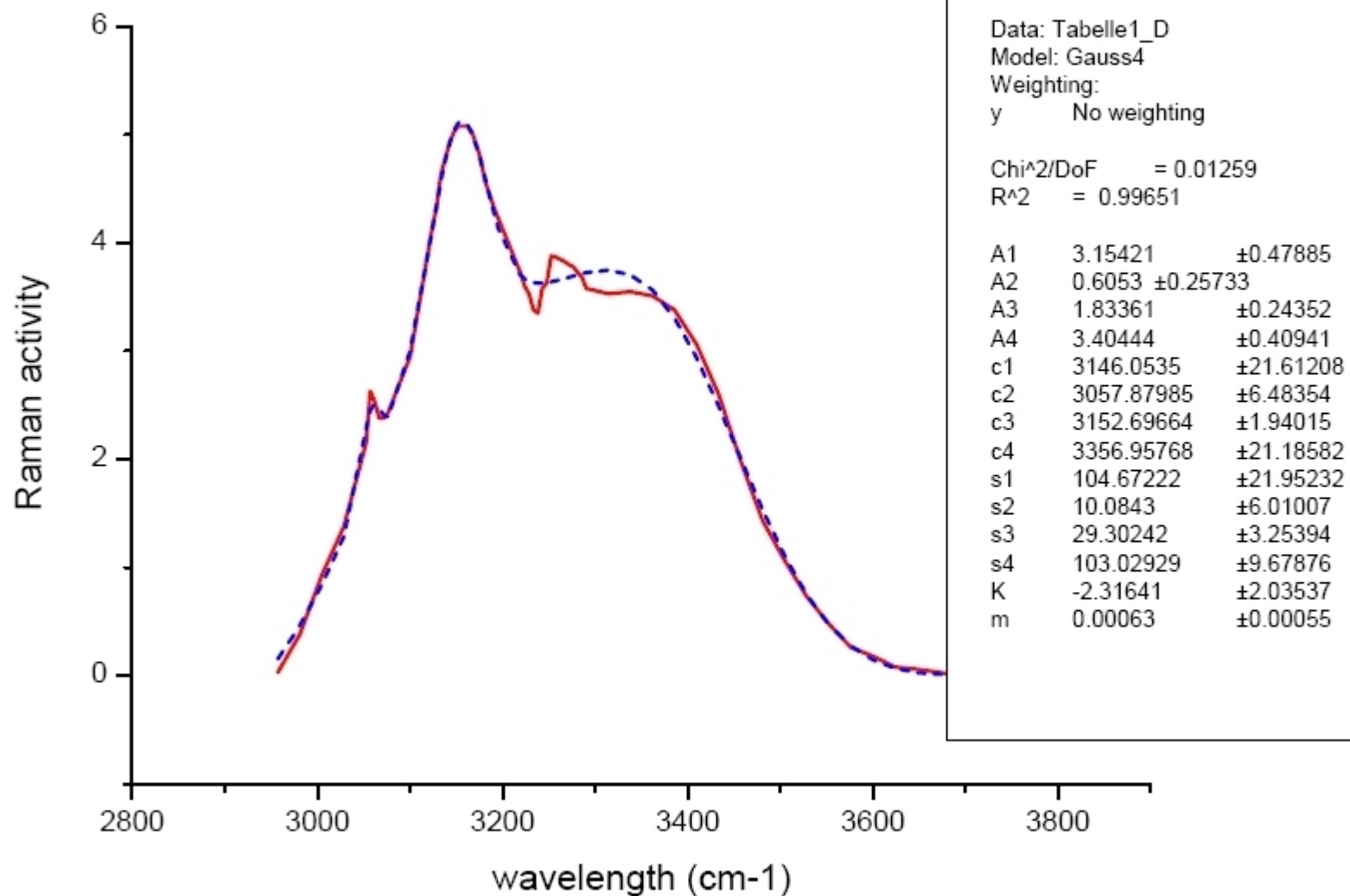
Experimental data (red) from Yoon et al. (2004) *J. Phys. Chem.* A 108, 5057

R.A. Klein, IUPAC Pisa September 2005

Raman-active Vibrations
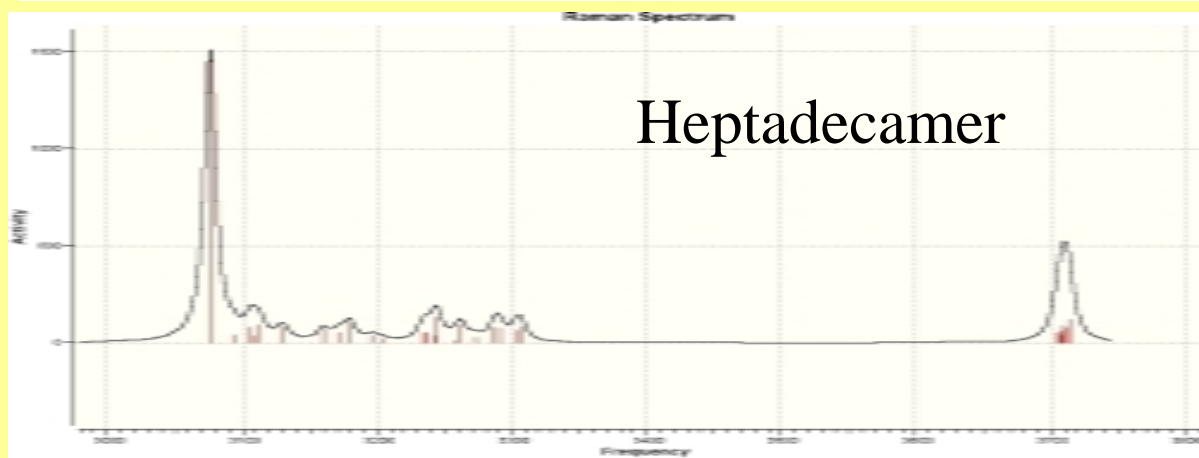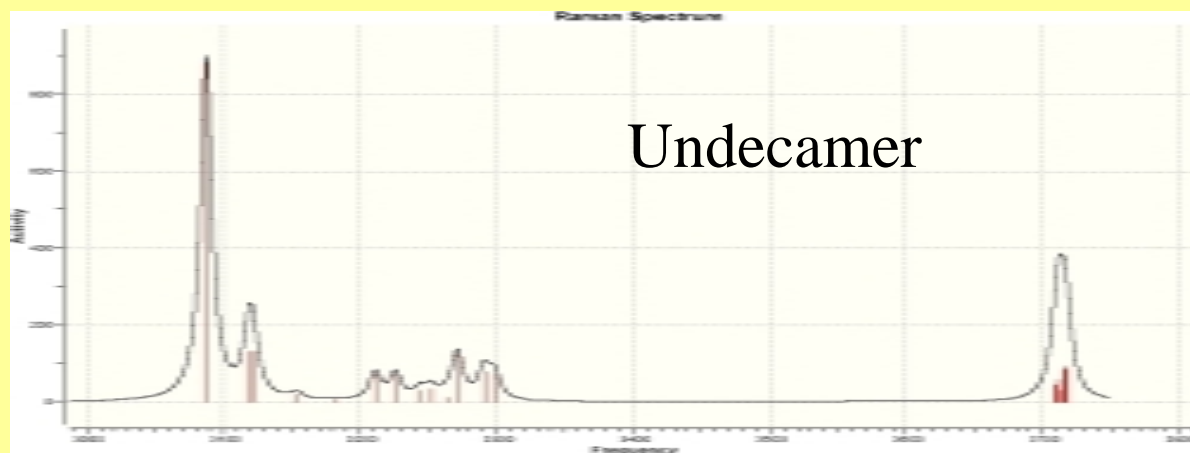
- Water -11°C
  - 3046 ± 113 cm^{-1} (11%)
  - 3177 ± 68 cm^{-1} (24%)
  - 3378 ± 155 cm^{-1} (65%)

- Ice Ih -15°C
  - 3080 ± 24; 3107 ± 116 cm^{-1} (66%)
  - 3277 ± 200; 3347 ± 73 cm^{-1} (34%)

- Ice II -40°C
  - 3182 ± 31; 3119 ± 62 cm^{-1} (47%)
  - 3300 ± 27; 3307 ± 125 cm^{-1} (53%)

- sI Methane Hydrate
  - 3058 ± 10 cm^{-1} (7%)
  - 3146 ± 105; 3153 ± 29 cm^{-1} (55%)
  - 3357 ± 103 cm^{-1} (38%)

**all peaks obtained by fitting experimental data

Calculated Raman Vibrations

- Rings 3-7
  - cooperative in-phase -   3090-3400 cm^{-1}
  - cooperative in- and out-of-phase -   3240-3460 cm^{-1}

- Undecamer/Heptadecamer/Tricosamer
  - cooperative in-phase -   3075-3087 cm^{-1}
  - cooperative in- and out-of-phase -   3107-3121 cm^{-1}
  - cooperative in- and out-of-phase -   3100-3320 cm^{-1} (broad multiple)

- Eicosamer/Tetracosamer
  - cooperative annular and polar -   3143-3168 cm^{-1}
  - cooperative in- and out-of-phase -   3220-3300 cm^{-1}

**MPW1PW91/6-311+G(2d,p)

IR and Raman Spectroscopy

- [pentamer](#) and [hexamer](#) ring
- [undecamer](#)
- [heptadecamer](#)
- [tricosamer](#)
- [tetracosamer](#)

-O...H-O- Cooperativity

- vibrational relaxation 740 ± 25 femtoseconds;

- for resonant intermolecular energy transfer (RIET), inter-action 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

Diols and Glucopyranose

R.A. Klein, IUPAC Pisa September 2005

[1,n]-Diols

12EG(B)　　　　　12EG(D)

13PG　　　　　14BD

15PD　　　　　16HD
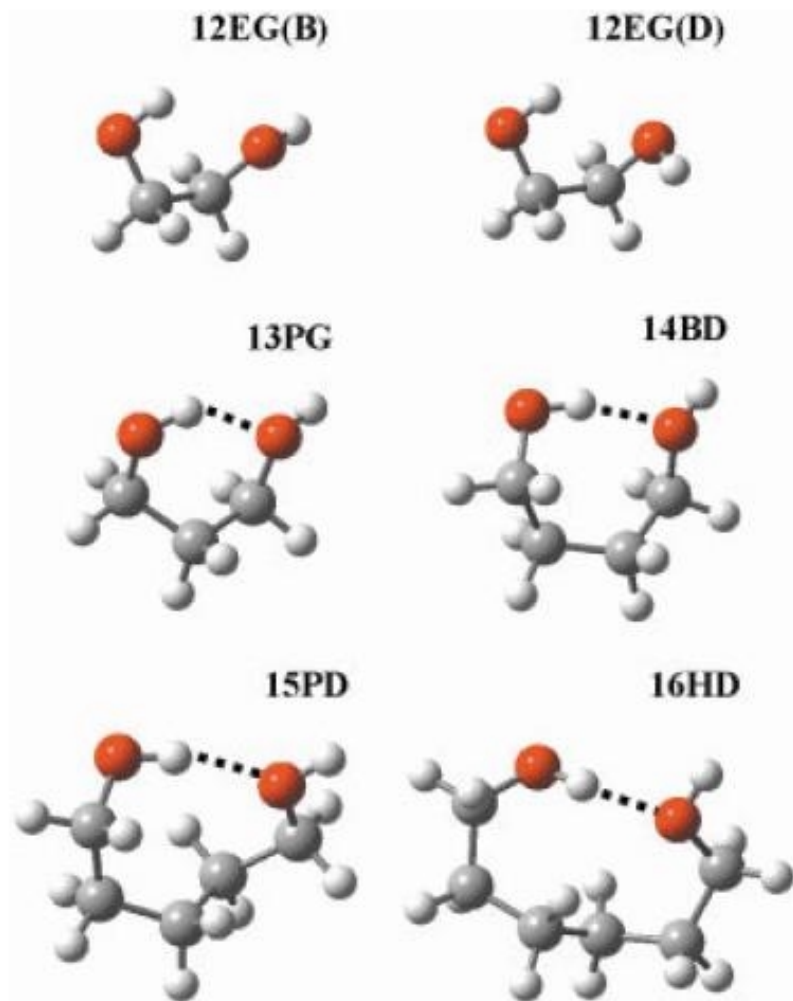
Scheme 1. Three-dimensional, minimised structures for the (α, ω)-diols discussed in detail in this article, namely: ethane–1,2-diol (12EG); propane–1,3-diol (13PG); butane–1,4-diol (14BD); pentane–1,5-diol (15PD); and hexane–1,6-diol (16HD).

[1,n]-Diols - Geometry
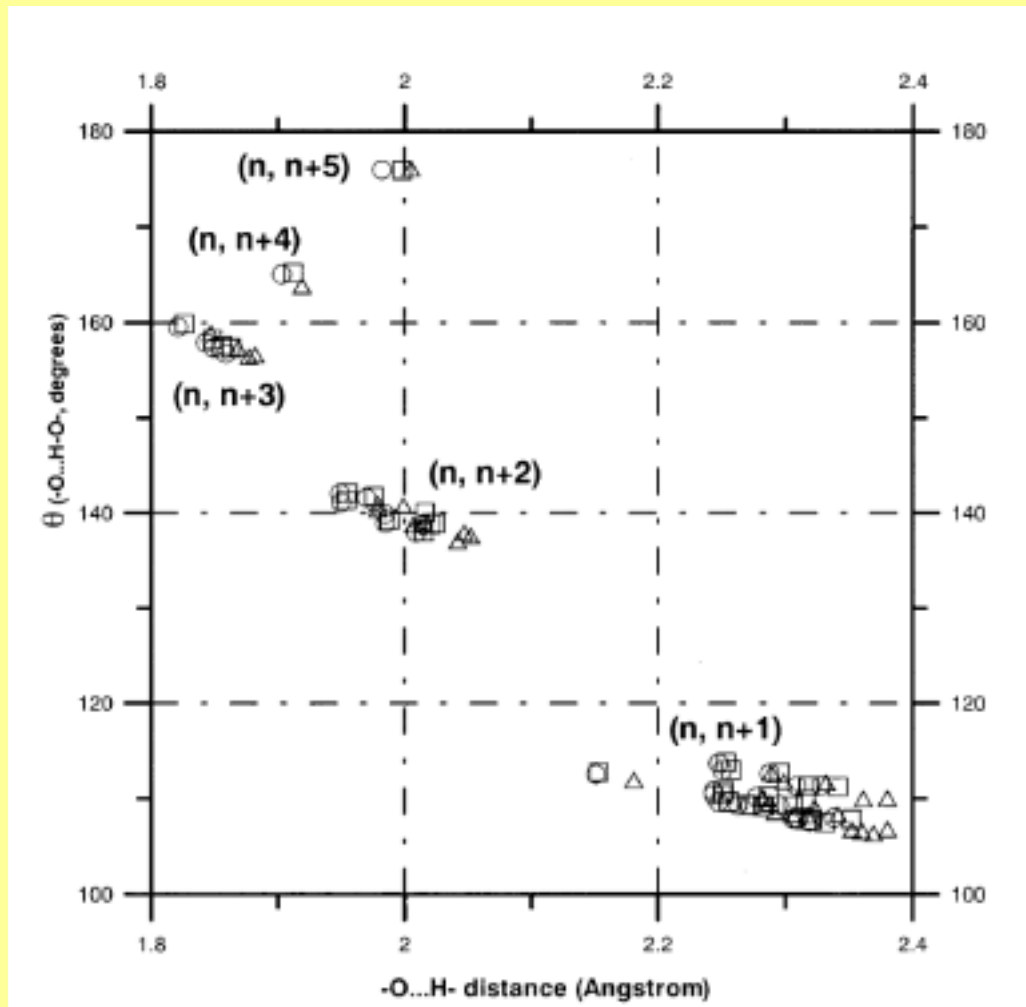
Topological analysis of the bond critical points (BCP), with topology (3,-1), for the intra-molecular hydrogen-bond O-H...O in diols excluding 1,2-diols and butane-2,3-diol. Geometries were obtained using MPW1PW91/6-311+G(2d,p); (d) is the electron density at the BCP in a.u.; ∇^2 (d) its Laplacian in a.u.; BCPs were located 34-35% of the bond length from the H atom; ellipticities were in the range 0.02 - 0.09.

Diol	Electron density (ρ)	Laplacian $\nabla^2 (\rho)$
13PG	0.02163	0.08452
13BDa	0.02381	0.09300
13BDb	0.02373	0.08511
2M13PGa	0.02200	0.08620
2M13PGb	0.02361	0.09273
14BD	0.03186	0.11280
15PD	0.02576	0.09879
16HD	0.02282	0.08024
m24PD	0.02487	0.09756
L24PDa	0.02282	0.09075
L24PDb	0.02479	0.09743
m25HD	0.03124	0.11070
L25HD	0.03394	0.11890

Bond critical points (BCPs)

12EG
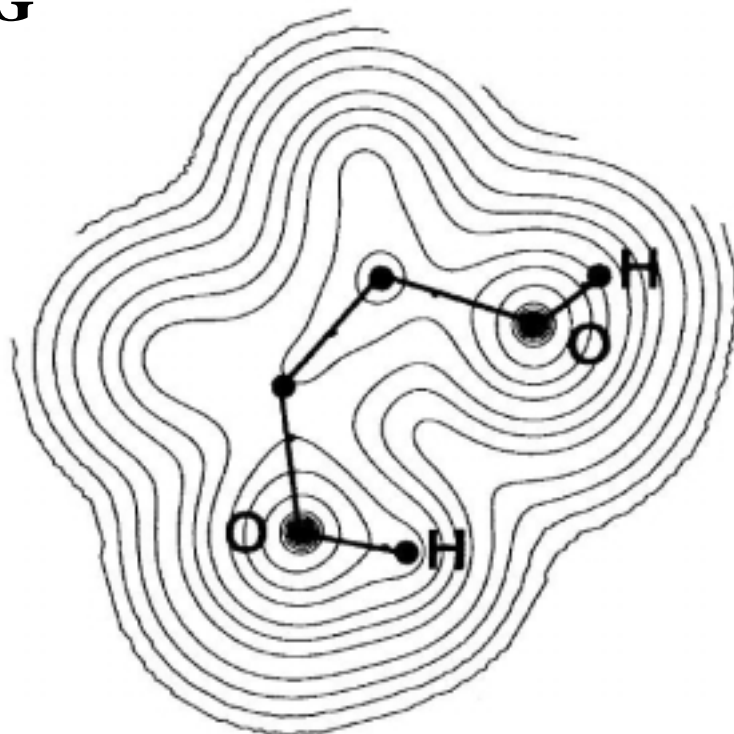
Figure 3. Electron density plot for ethane-1,2-diol with geometry optimized at the MPW1PW91/6-311+G(2d,p) level, followed by the generation of a wave function file (6D 10F). Contours are shown for a geometrical scale from 1e10-2 to 8e10+6. The oxygen and hydrogen atoms involved in the putative intramolecular hydrogen bond are marked; unmarked atoms are carbon atoms. Bond critical points (BCP) with (3,−1) topology are marked with an asterisk (*), points with (3,+1) topology with a triangle (▲).

14BD

Figure 4. Electron density plot for butane-1,4-diol. Details are as given in the legend to Figure 3.

R.A. Klein, IUPAC Pisa September 2005

Table 9. Integrated Atomic Properties for the O—H Atoms in Representative $(n, n + m)$-Diols, for $n = 1, 2$ and $m = 1$–5.

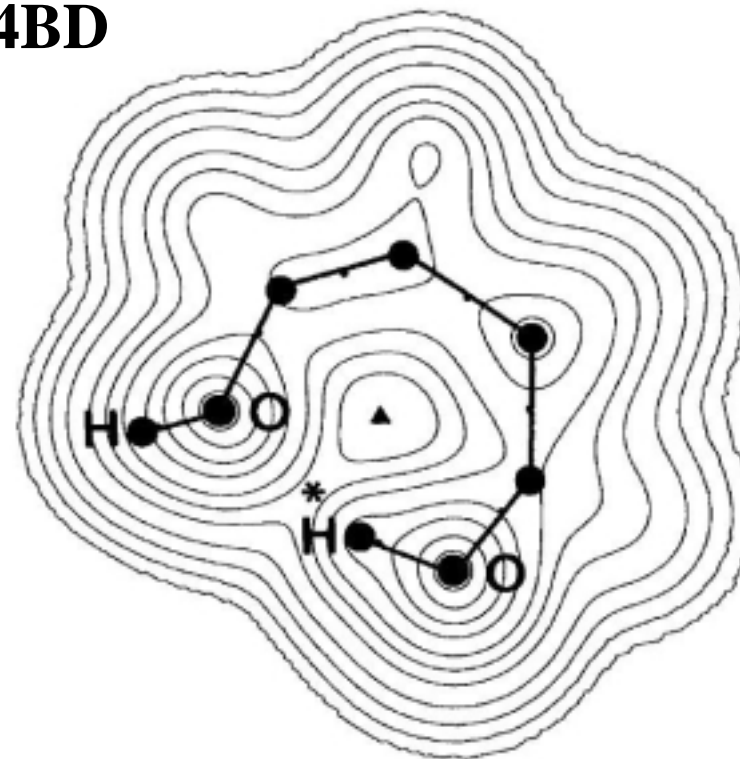| Diol	H Atom	$E(\Omega)$	$q(\Omega)$	$\mu(\Omega)$	Vol(Ω)	BCP
12EG (B)	O—H$_D$	−0.3872	0.5665	0.1567	21.2113	No
	O$_A$—H	−0.3940	0.5577	0.1628	22.8329	
12PG (A)	O—H$_D$	−0.3854	0.5688	0.1553	20.6514	No
	O$_A$—H	−0.3961	0.5550	0.1623	22.9274	
12PG (B)	O—H$_D$	0.3855	0.5690	0.1557	20.7952	No
	O$_A$—H	−0.3956	0.5523	0.1652	23.1882	
13PG	O—H$_D$	−0.3765	0.5866	0.1391	16.8615	Yes
	O$_A$—H	−0.3921	0.5589	0.1624	22.7929	
12BD	O—H$_D$	−0.3864	0.5675	0.1565	21.0780	No
	O$_A$—H	−0.3932	0.5525	0.1628	21.9069	
13BD (A)	O—H$_D$	−0.3764	0.5871	0.1365	16.2861	Yes
	O$_A$—H	0.3926	0.5596	0.1621	22.8109	
13BD (B)	O—H$_D$	−0.3771	0.5837	0.1411	16.9087	Yes
	O$_A$—H	−0.3942	0.5505	0.1693	23.7924	
m23BD (B)	O—H$_D$	−0.3859	0.5677	0.1558	20.7362	No
	O$_A$—H	−0.3961	0.5509	0.1670	23.3739	
2M13PG (A)	O—H$_D$	−0.3778	0.5845	0.1396	16.8912	Yes
	O$_A$—H	−0.3929	0.5593	0.1621	22.7031	
2M13PG (B)	O—H$_D$	−0.3762	0.5879	0.1375	16.4937	Yes
	O$_A$—H	−0.3926	0.5595	0.1623	22.7305	
14BD	O—H$_D$	−0.3732	0.5917	0.1290	14.3823	Yes
	O$_A$—H	−0.3914	0.5606	0.1616	22.6916	
12PD	O—H$_D$	−0.3891	0.5637	0.1567	21.2651	No
	O$_A$—H	−0.3948	0.5530	0.1630	21.9432	
15PD	O—H$_D$	−0.3724	0.5938	0.1290	14.4315	Yes
	O$_A$—H	−0.3915	0.5616	0.1610	22.5602	
m24PD	O—H$_D$	−0.3744	0.5901	0.1360	16.0912	Yes
	O$_A$—H	−0.3964	0.5515	0.1651	23.2529	
12HD	O—H$_D$	−0.3883	0.5648	0.1564	21.1668	No
	O$_A$—H	−0.3938	0.5545	0.1625	21.7989	
16HD	O—H$_D$	−0.3752	0.5853	0.1340	14.8101	Yes
	O$_A$—H	−0.3927	0.5593	0.1617	22.6310	
m25HD	O—H$_D$	−0.3745	0.5888	0.1303	14.4607	Yes
	O$_A$—H	−0.3931	0.5555	0.1653	23.1626	

The abbreviation O—H$_D$ refers to the donor H atom; O$_A$—H to the acceptor O atom; $E(\Omega)$, the total energy; $q(\Omega)$, the atomic charge; $\mu(\Omega)$, the dipolar polarization; and Vol(Ω), the atomic volume. All values are given in atomic units. BCP indicates whether a bond critical point of (3,−1) topology was detected for the hydrogen bond.
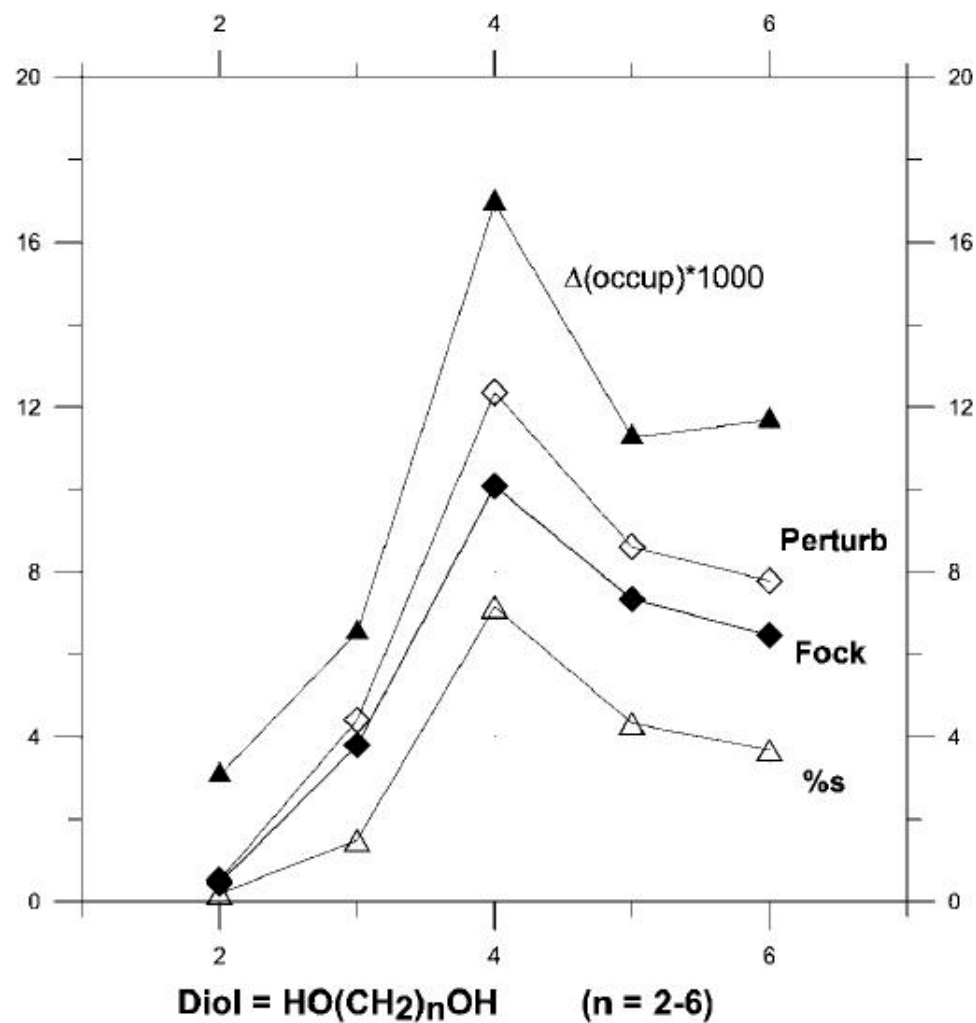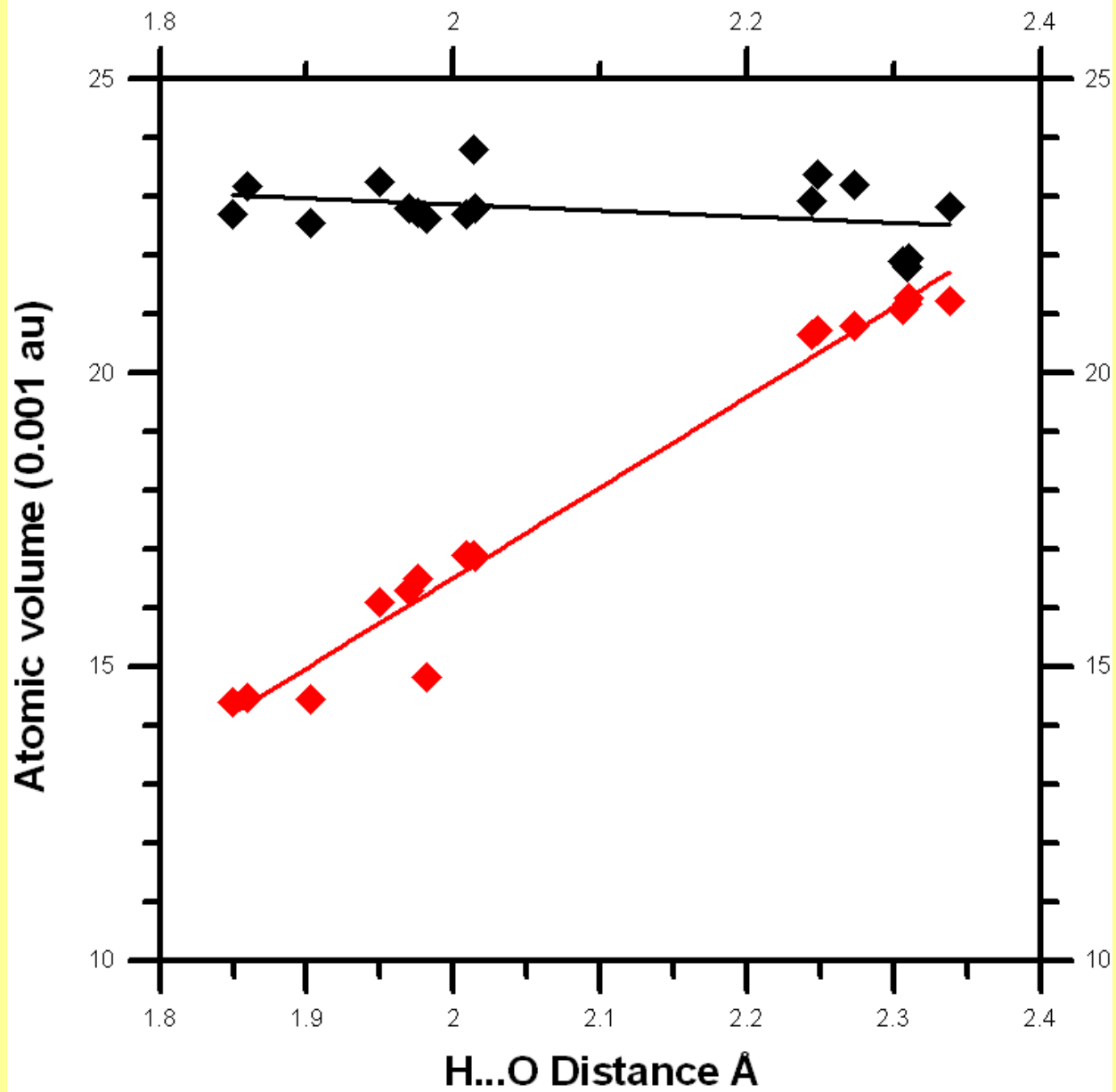
Figure 7. The relationship between the number of carbon atoms in (α, ω)-diols (n = 2–6) against the change in occupancy of the OH σ^* antibonding orbital (▲), the stabilization energy calculated by second-order perturbation analysis (◇) or Fock-matrix element deletion (◆), and the percentage s-character for the interacting LP electrons (△), for the —O—H_D . . . O_A— interaction determined as described in the text.

Hydrogen atomic volume

R.A. Klein, IUPAC Pisa September 2005

Hydrogen dipolar polarisation

R.A. Klein, IUPAC Pisa September 2005
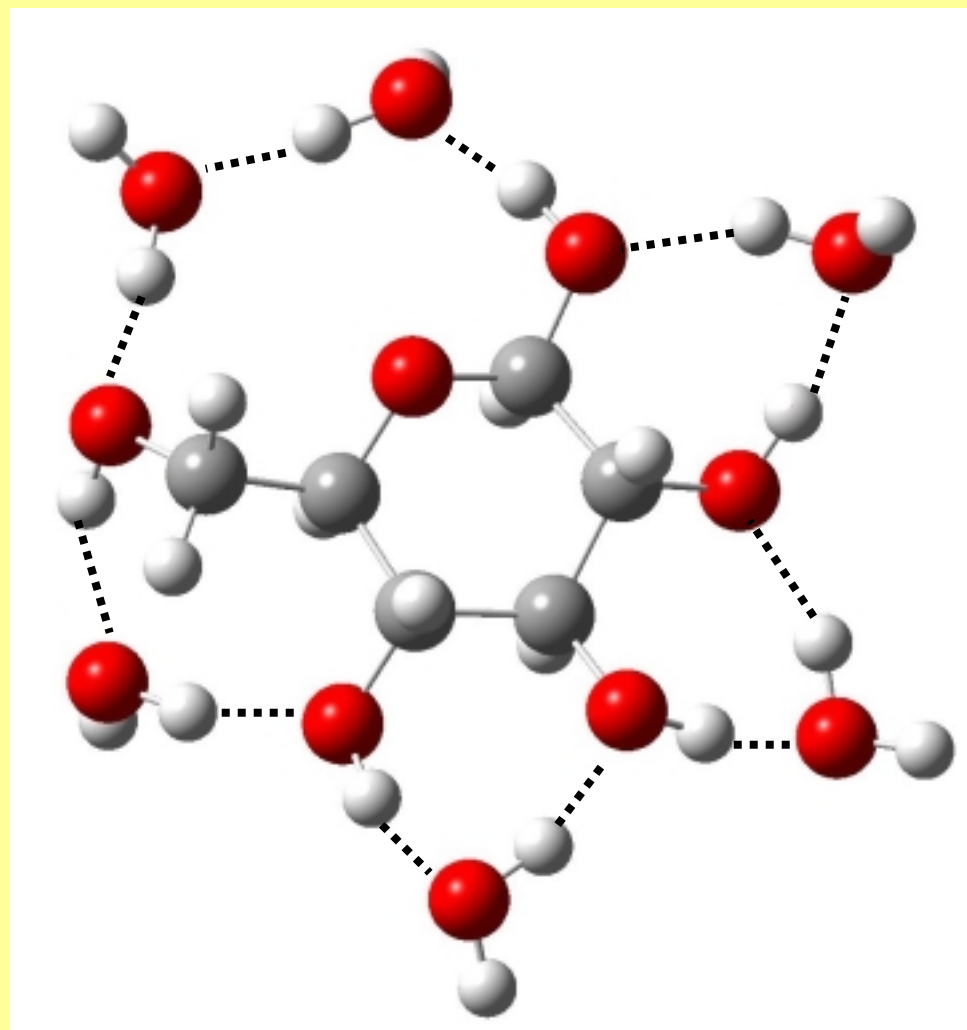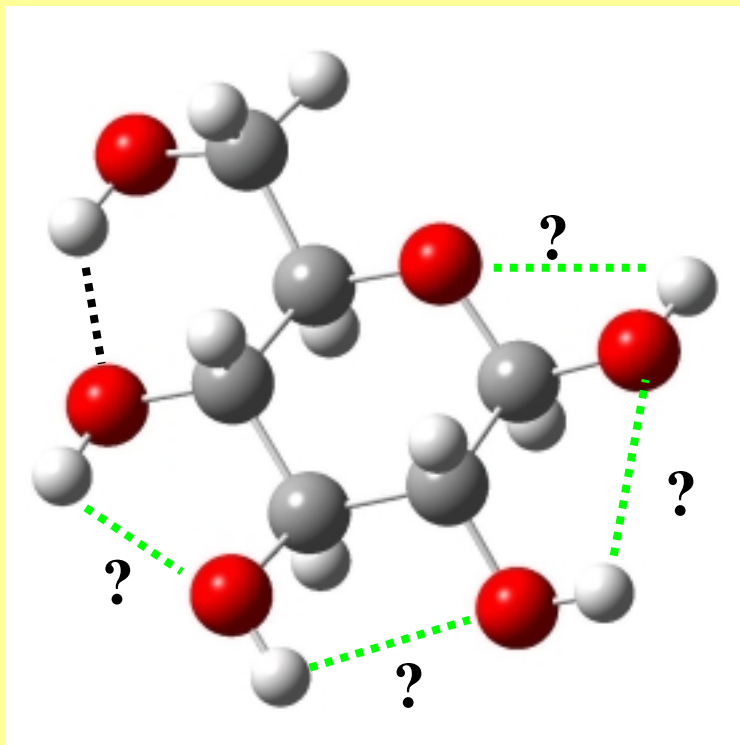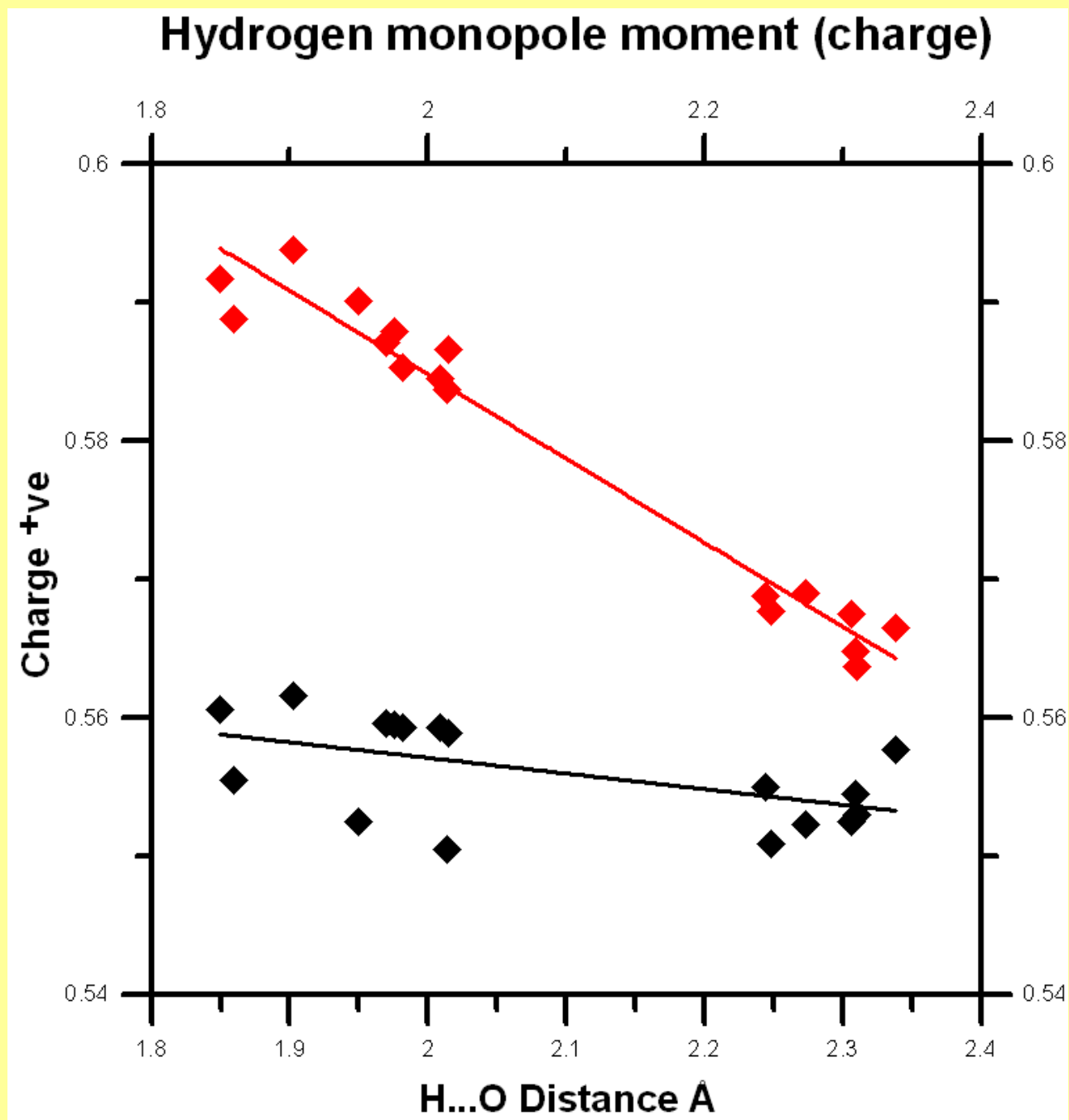
Glucose.6H₂O

Glucose

R.A. Klein, IUPAC Pisa September

Hydrogen monopole moment (charge)

R.A. Klein, IUPAC Pisa September 2005
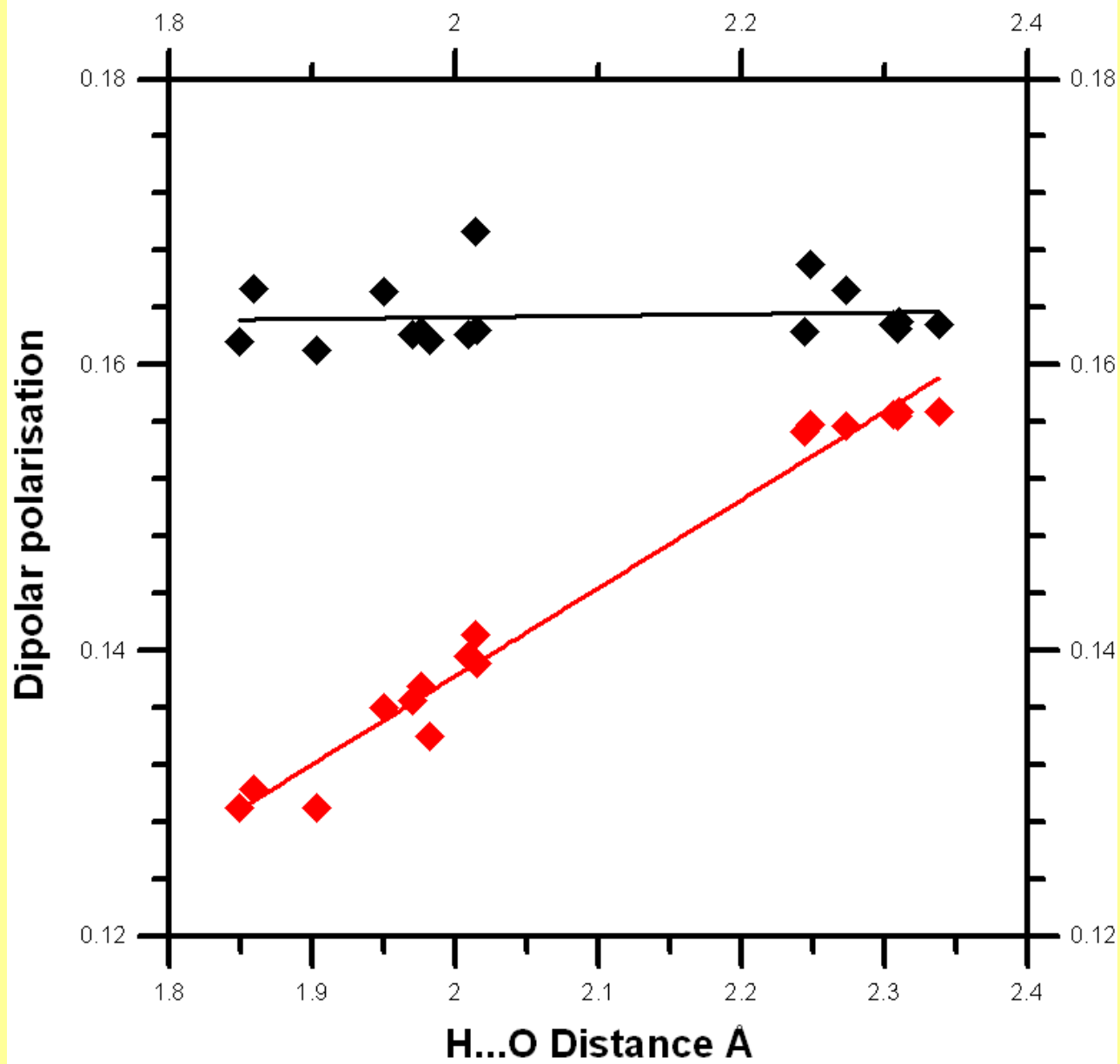
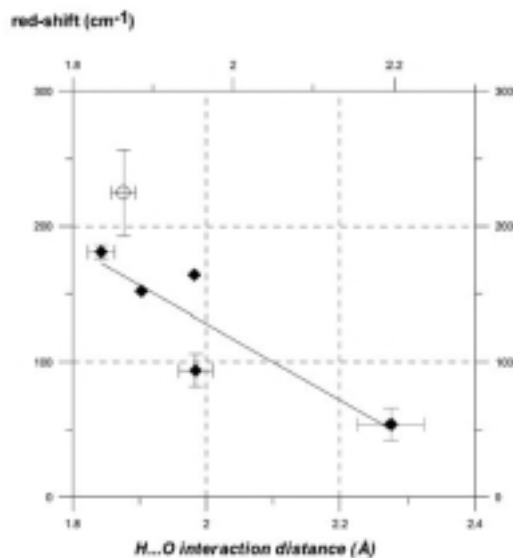# IR red-shifts and NMR downfield shifts are continuous

Figure 1B. Average difference (the 'red-shift') between the IR hydroxyl stretching frequencies for the -O$_A$-H and -O-H$_D$ bonds in each of diols studied plotted against the -O$_A$...H$_D$- interaction distance, based on the data shown in Figure 1A. The filled diamonds (♦) represent average data for 1,2-, 1,3-, 1,4-, 1,5- and 1,6-diols (the last two are single points); the open circle (○) indicates the average value for 1:1 complexes between the different conformers of ethane-1,2-diol, propane-1,2-diol and butane-2,3-diol, with water[2].
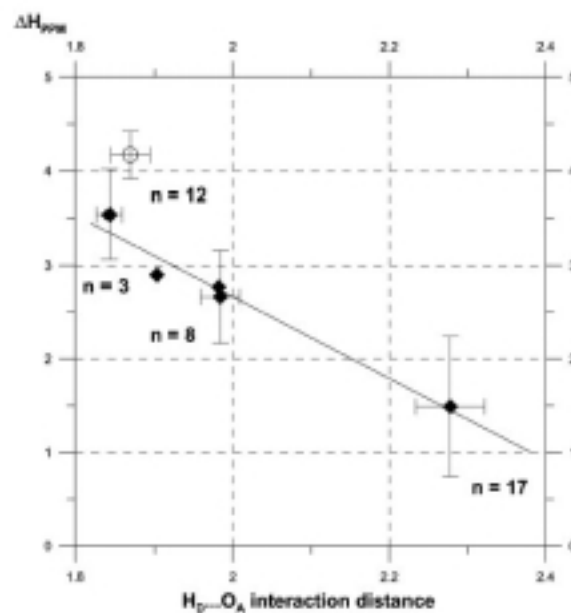
Figure 5. Average difference in DFT-GIAO calculated ^{1}H chemical shifts for the O-H$_D$ and O$_A$-H hydroxyl group hydrogen atoms in 1,2-, 1,3-, 1,4-, 1,5- and 1,6-diols (♦), and in cooperative 1:1 water-(n, n+1)-diol complexes (○).

from Klein, R.A.; (2003) J. Comp. Chem. 24, 1120

Glucose and Hydrated Glucose

R.A. Klein, IUPAC Pisa Septembe

Glucose-$^4C_1$ OH6O4

12eg_confB

Infrared Spectrum

Glucose-$^4C_1$ 6TIP3

12eg_confB_TIP3

R.A. Klein, IUPAC Pisa September 2005
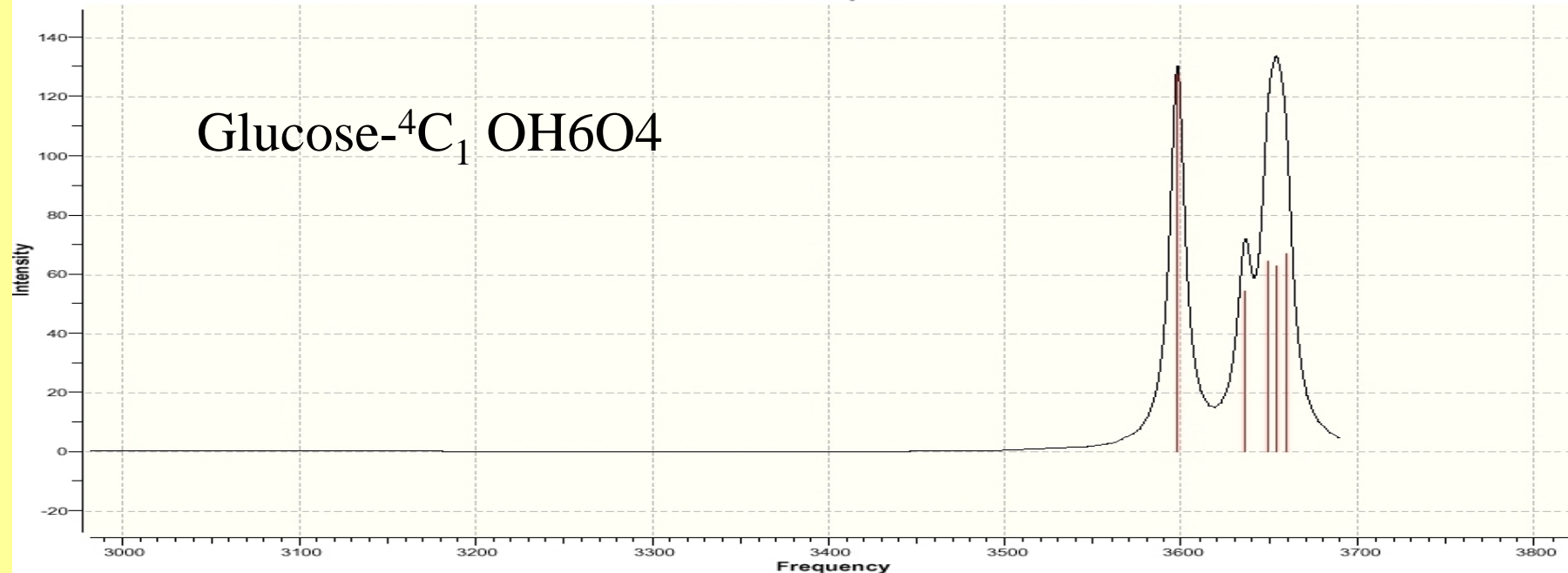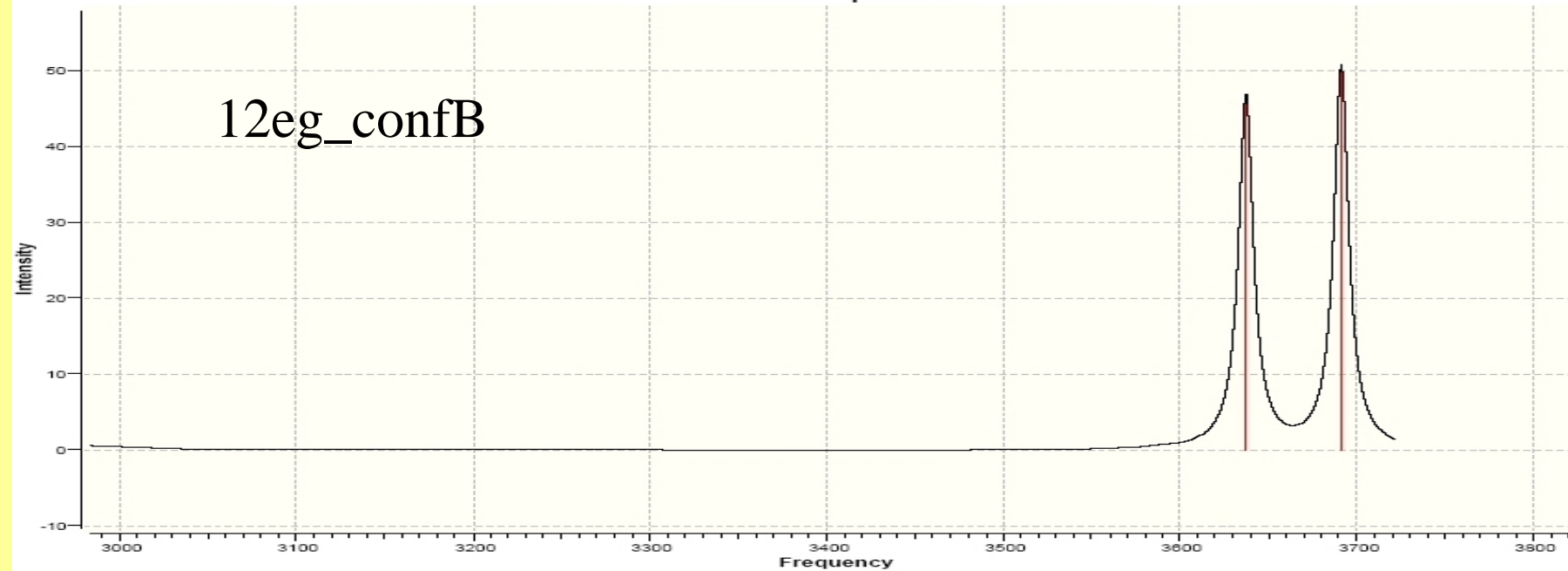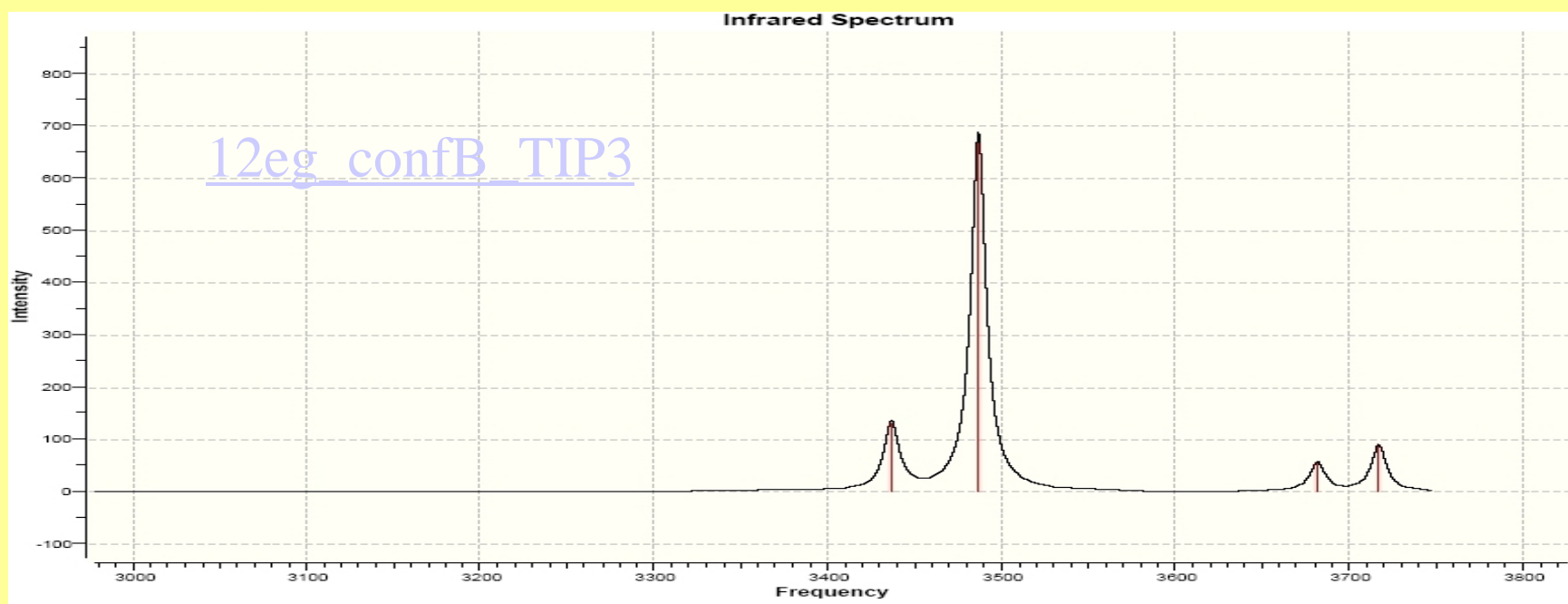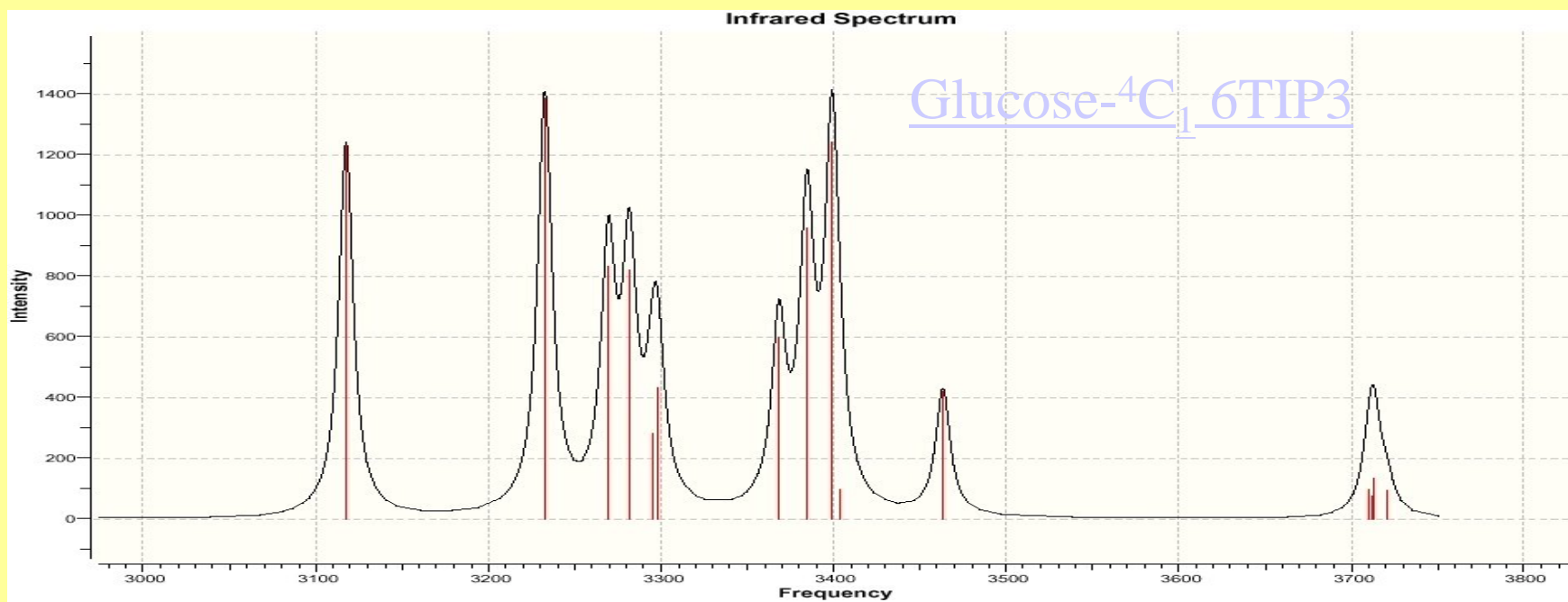
Table YY. OH stretching frequencies in cm^{-1} (relative intensity) for glucose hexahydrate. Assignments are shown for the various cooperative modes involving sugar hydroxyl groups and the bidentate hydrogen bonded water molecules.

Frequency cm^{-1}	Assignment
3117 (0.90)	OH1; H_2O(f)
3233 (1.00)	OH1; H_2O(f); H_2O(e)
3269 (0.60)	OH2; OH3; OH4; H_2O(a,b,c)
3282 (0.59)	OH2; OH4; H_2O(a,b,c)
3295 (0.20)	OH2; OH3; OH4; H_2O(a,b,c,d,e,f)
3298 (0.31)	OH3; OH4; H_2O(e,f)
3368 (0.43)	OH4; H_2O(b,c,d)
3385 (0.69)	OH3; OH4; H_2O(a,b,c,d)
3399 (0.90)	OH2; OH3; OH4; OH6; H_2O(a,b,c,d)
3404 (0.07)	OH2; OH3; OH4; OH6; H_2O(a,b,c,d)
3463 (0.30)	OH6 ; H_2O(d)
3710 (0.07)	H_2O(f); H_{NB}
3712 (0.05)	H_2O(a,b); H_{NB}; asymm
3713 (0.20)	H_2O(b,c); H_{NB}; asymm+symm
3721 (0.07)	H_2O(d); H_{NB}; asymm

Table XX. O-H$_D$ bond lengths in Ångstrom and cooperativity for ethane-diol and glucose in the absence and presence of water of hydration.

Structure	Non-interacting OH	Interacting OH
Isolated diol 'synthon'		
Ethane-1,2-diol (tGg')	0.95806	0.96207
Ethane-1,2-diol (gGg')	0.96010	0.96298
Glucose-$^4C_1$	**0.9615 ± 0.00057**	
H$_2$O complexes		
Ethane-1,2-diol (tGg')	0.95903	0.97041
H$_2$O	0.95875	0.97215
Ethane-1,2-diol (gGg')	0.96070	0.97120
H$_2$O	0.95903	0.97248
Glucose-$^4C_1$	**0.98002 ± 0.00054**	
H$_2$O	0.95866	0.97903

# $^4C_1$-glucose shows *negative* synergism between OH groups

Natural bond orbital (NBO) analysis[aa] of a series of 1,n-diols (n = 2-6) with the two hydroxyls in the same conformation with respect to one another as in the tGg' conformer of ethane-1,2-diol, gives an average electron occupancy for the σ* anti-bonding orbital of the non-interacting O-H groups of 0.00550 ± 0.00033. Electron occupancies for the interacting OH σ* anti-bonding orbital rise from a value of 0.00921 for ethane-1,2-diol to a maximum of 0.02926 for butane-1,4-diol, decreasing to 0.02187 and 0.02045 for pentane-1,5- and hexane-1,6-diol, as reported previously[bb]. By contrast, in glucose-$^4C_1$ the σ* occupancies for the putatively hygrogen-bonded ring OH groups range from 0.00652 to 0.00908 with a mean value of 0.00755 ± 0.00085; these are significantly less than for ethane-1,2-diol, the reference structure, and are again in the *opposite direction* to that predicted on the basis of any possible cooperative hydrogen bonding. On the other hand, in hydrated ethane-1,2-diol or glucopyranose, where cooperative hydrogen bonding is possible, OH σ* anti-bonding orbital occupancies range from 0.02655 (diol OH) and 0.02109 (water OH) in the 1:1 ethane-1,2-diol/H_2O complex, to an average value as high as 0.04548 ± 0.01000 for the O-H bonds in glucose and 0.03695 ± 0.00541 for those of its associated waters underlining the degree of cooperativity attained. Cross-ring hydrogen bonding in $^1C_4$-glucose, involving OH1...O6, OH3...O1, and OH2...O4, gives rise to OH σ* anti-bonding orbital occupancies of 0.02115, 0.02270 and 0.01708, respectively.

$^4C_1$-glucose does not form intra-molecular hydrogen bonds

Thus based on all the criteria referred to above, $^4C_1$-glucopyranose does not form intra-molecular hydrogen bonds between the neighbouring or vicinal ring OH groups. This is not merely theoretical 'hair-splitting' as without evidence for hydrogen bond formation there are no grounds for invoking non-existent synergistic or cooperative effects, especially when conformational equilibria in aqueous solution are being considered, conditions under which the sugar ring will be completely hydrated and where donor-acceptor cooperativity is possible with the formation of a network of *inter-molecular* hydrogen bonds.

Methane Clathrates

Eicosamer 5^{12}

Clathrate 5x12 CH4
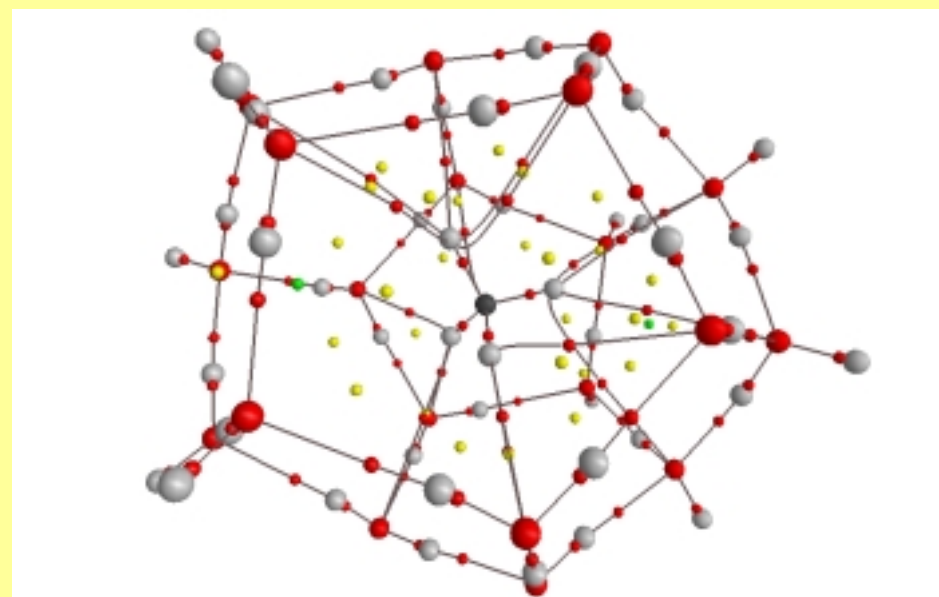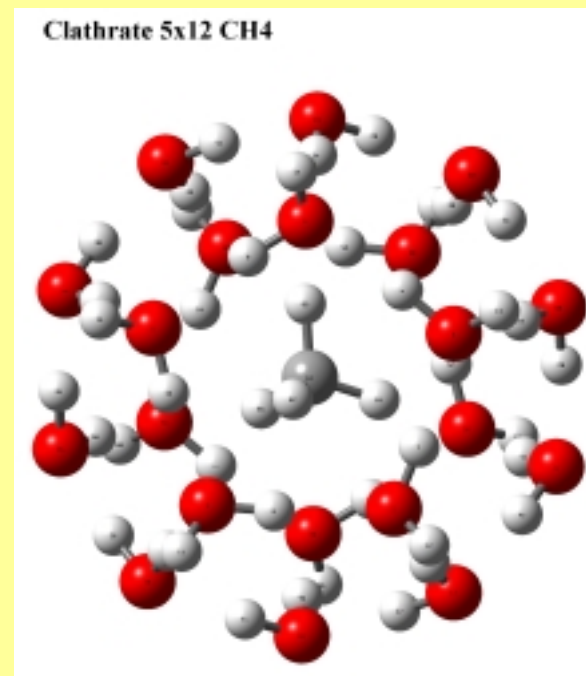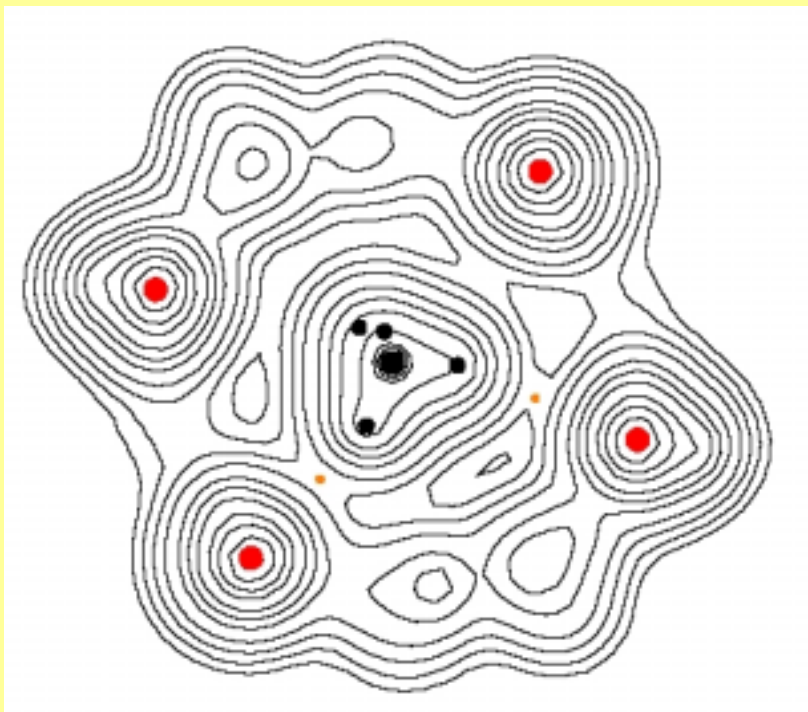
Tetracosamer (S4) $5^{12}6^2$
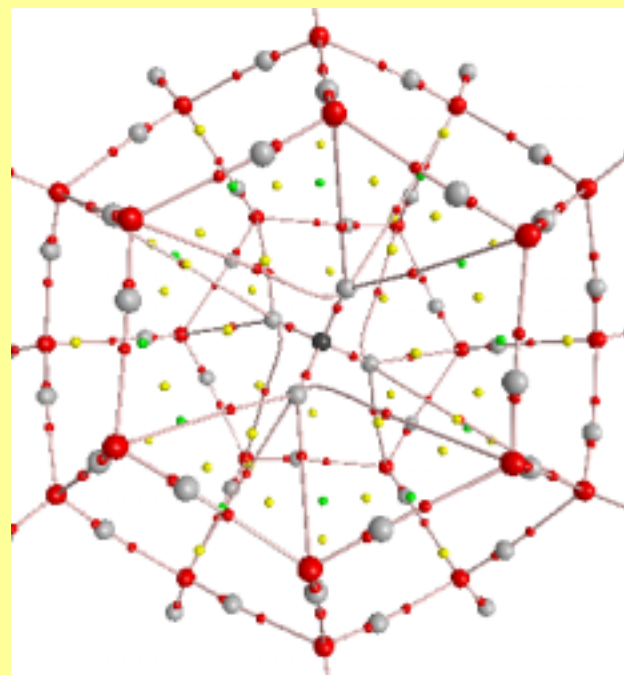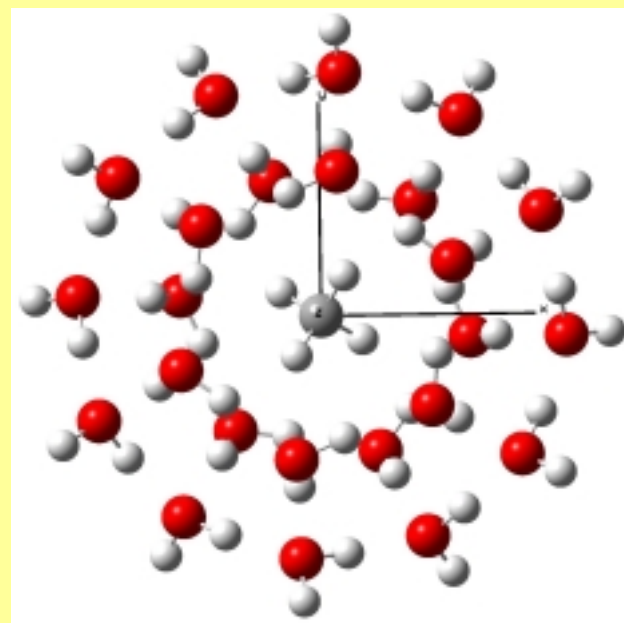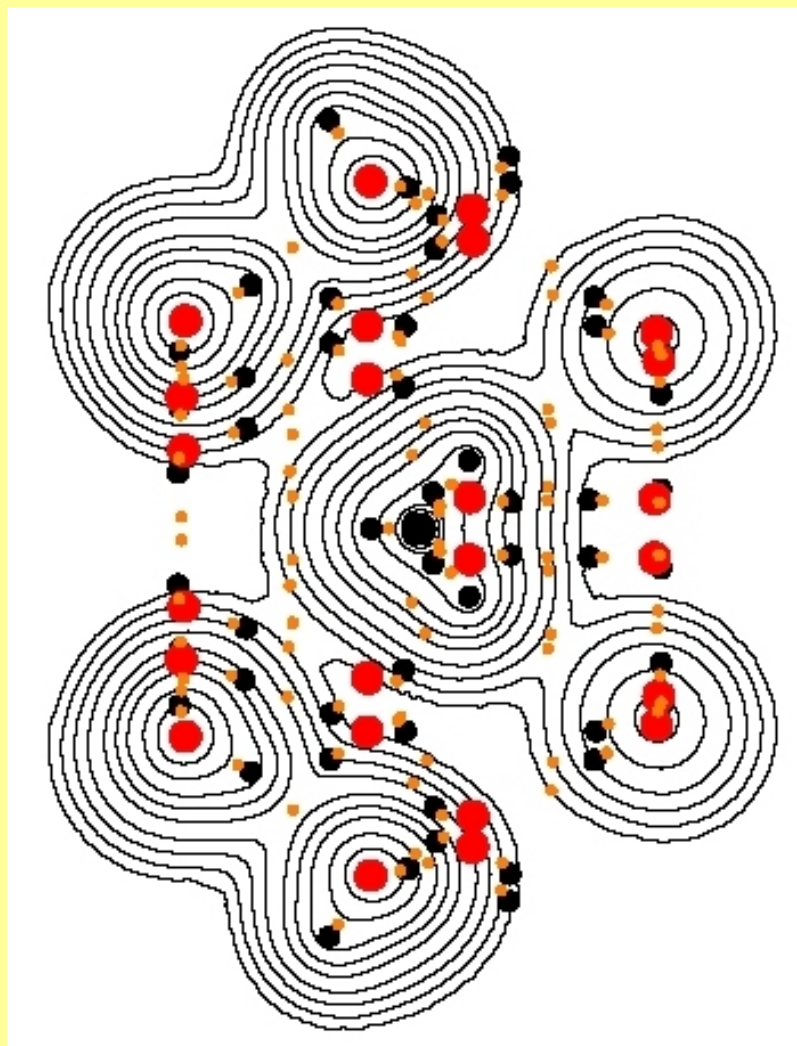
CH4...O Interactions

Tetracosamer 4x4

distance	3.1120 Å	3.2532 Å	3.6408 Å	3.8515 Å
$\rho(r)$	0.00297	0.00225	0.00139	0.00051
$\nabla^2 \rho(r)$	+0.00936	+0.00804	+0.00527	+0.00282
$G(r)$	0.00192	0.00155	0.00094	0.00038
$K(r)$	-0.00042	-0.00046	-0.00038	-0.00020
$V(r)$	-0.00150	-0.00109	-0.00056	-0.00018
$V(r)/G(r)$	-0.7813	-0.7032	-0.5979	-0.4737
ε	0.0567	0.4547	3.3539	1.04485
E_{HB} kcal	-0.471	-0.342	-0.176	-0.056

Methane
Electron Density Topology
Electrostatic Moments

	1.	2.	4.	8.	16.
CH_4 gas	-0.1027	0.0002	0.0008	4.1692	3.8348
CH_4 S4	-0.1072	0.0003	0.0702	3.9280	4.3642
CH_4 gas	+0.0257	0.1564	0.2289	0.3515	0.0798
CH_4 S4	+0.0253	0.1452	0.2516	0.3058	0.3356

Clathrate Vibrational Frequencies

	$\delta\text{Å}$	CH_4 as	CH_4 s	CH_4 as/s
$5^{12}6^2$ S4	-0.00059	+4.9	+1.5	-1.1
5^{12}	-0.00091	+10.0	+2.1	-3.5
IEFPCM	+0.00021	-3.5	-7.2	-5.9
sI large		-12.8		
sI small		-2.6		
sII small		-3.9		
sH small		-4.8		

Methane-Clathrate
^{13}C-NMR
Chemical Shielding Tensors

	Cage+CH_4	Ref. CH_4	13C ppm	Exper.
Eicosamer				
5^{12} sI small	188.70±0.14	193.17±0.04	4.47±0.16	*4.16*
Tetracosamer				
$5^{12}6^2$ sI large	190.54±0.05	193.09±0.02	2.55±0.07	*1.79*

Suitable and Sufficient?

- Hydrogen bonds
    - must satisfy certain geometrical criteria, i.e., donor-acceptor distances, -X:...H-Y- angle, H points towards a lone-pair
    - show elongation of the H-Y- bond associated with IR red-shifts and NMR downfield shifts (n.b.: bond shortening and blue-shifts)
    - demonstrate a (3,-1) bond critical point (BCP) both experimentally and theoretically
    - show charge-transfer between donor and acceptor
    - show changes in anti-bonding orbital occupancies

R.A. Klein, IUPAC Pisa September 2005

Suitable and Sufficient?

- ## Hydrogen bonds

    - and be characterised by **<u>cooperativity</u>** defined in terms of synergism resulting in greater than simple additivity of effects, i.e., bond length, electron density topology, and spectroscopic parameters.

References

- Jonsdottir, S.; Klein, R.A. (1997) *Fluid Phase Equilibria B* 132, 117
- Klein, R.A.; Pacheco, V. (2001) *J. Phys. Chem. A* 105, 9298
- Klein, R.A. (2002) *J. Comp. Chem.* 23, 585
- Klein, R.A. (2002) *J. Amer. Chem. Soc.* 124, 13931
- Klein, R.A. (2003) *J. Comp. Chem.* 24, 1120
- Klein, R.A.; Mennucci, B.; Tomasi, J. (2004) *J. Phys. Chem. A* 108, 5851

Acknowledgements

- Jacopo Tomasi (Pisa)

- Benedetta Mennucci (Pisa)

- Mark Zottola (Birmingham Alabama)

- Viktorya Aviyente (Istanbul)

- Ernst Bause (Bonn)

- Victor Pacheco (San Martin)

- Svava Jonsdottir (Lyngby)

Thank You

for your attention