Water clusters $(H_2O)_n$- toward the revealing the mysteries of water?

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Motivations

- **1. Water is ubiquitous; it is the third most common molecule in the Universe (after H_2 i CO)**
- **2. Water is the most atypical as a liquid, with its properties at low temperature quite different from its properties when hot.**
- **3. Water is crucial for all life. Life depends on these anomalous properties of water.**

The anomales of water

- **1. the density maximum at 4°C. Its density, however is not as great as that of closely packed isoelectronic liquid neon. The high density is due to the cohesive nature of the H-bonded network.**
- **2. at 4°C water expandes on heating or cooling while it is usual for liquid to expand when heated, at all temperat. This means that the freezing of rivers, lakes and oceans is from the top down, so permitting survival of the bottom ecology.**
- **3. high heat of vaporization (40.7 kJ /mol) – gives resistance to dehydration and considerable evaporative cooling.**
- **4. large heat capacity – allows the oceans and seas to act as heat reservoirs such that sea temperature vary only a third as much as land temperature and so moderate our climate.**

The anomales of water

- **5. high melting point – is over 100 K higher than expected by extrapolation of the m.p. of other group 6A hydrides.**
- **6. high dielectric constant (78.4 at 25C) – together with its polarity and small size make water as an excellent solvent. Water ionizes and allows easy proton transfer exchange between molecules, so contributing to the richness of the ionic interactions in biology.**
- **7. high surface tension – plus its expansion on freezing makes the erosion of rocks gives soil minerals.**

How can a liquid have a structure?

- **Structure when appplied to liquid has a different meaning to when it is applied to solid:**
- **The structure determined for water depends on the time and size-scales over which it is determined.**
- **In liquid, the X-ray and neutron diffraction pattern corresponds to the time-averaged positions of the molecules within the volume corresponding to the potential range of this short-range order.**

Structure of liquid

* **The neutron scattering - give information on the distribution of nuclei within a liquid sample. The nucleus-nucleus pair correlation function $g_{OO}(r)$, $g_{OD}(r)$, $g_{DD}(r)$ – is extracted from diffrection measurements on heavy water.**
* **An X-ray scattering experiment – probes the electronic density distribution within the fluid. The measured scattering cross section reveals essentially the position of oxygen atoms.**

Models for water

- **The philosophy of these investigations:**

  if the known model can successfully predict the physical properties of liquid water then the unknown structure of liquid water is determined.

General characteritics of the models

- **A large number of hypothetical models for water have been developed in order to discover its structure. Generally, each model is developed to fit well with one particular physical structure or parametres.**

- **It has been commonly been stated that no single model is able to explain all of its properties. A recent review listed 46 distinct models, so indirectly indicating their lack of success in quantitatively reproducing the properties of real water.**

About milestones in the saga of models...

- **1933 – Bernal&Fowler – the first simple potential was supposed to be able to explan tetrahedral arrangement**
- **1953 – Metropolis&Rosenbluth – the first Monte Carlo sampling scheme**
- **1969 – Rahman&Stillinger – the first computer simulations**

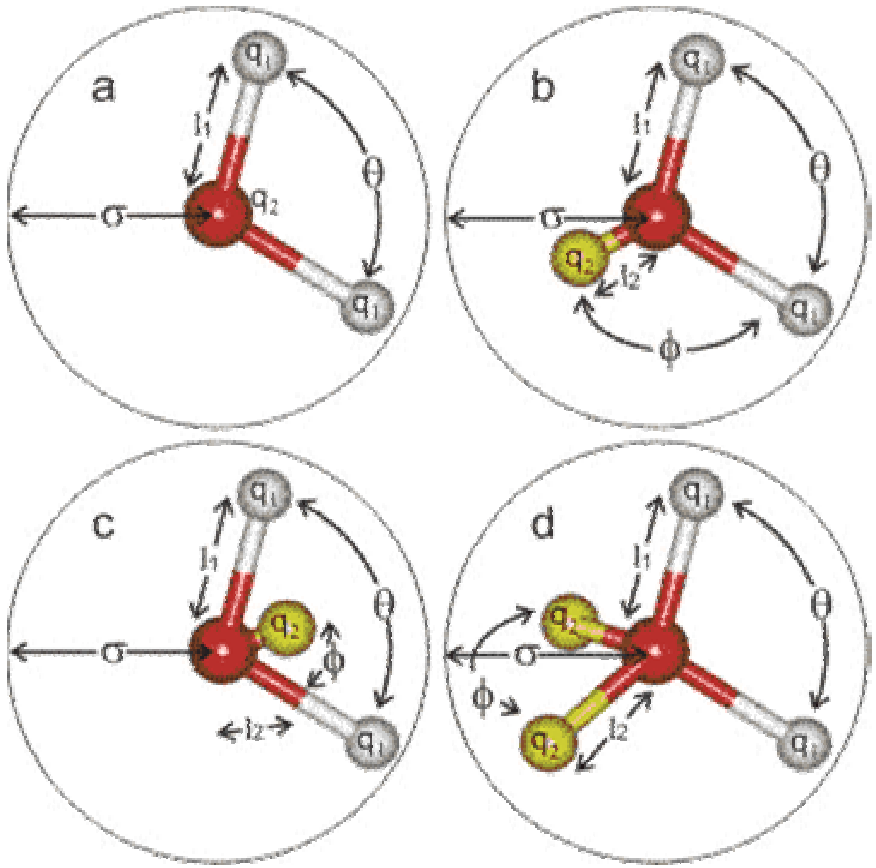
1976 – Clementi et al. – the first pair potential from *ab initio*

1981-1983 – simple pair potentials

1993 – Parinello&Car – the first *ab initio*+MD calculations for liquid

2000 – Szalewicz et al., Xantheas et al. Nonadditive three-body *ab initio* potentials

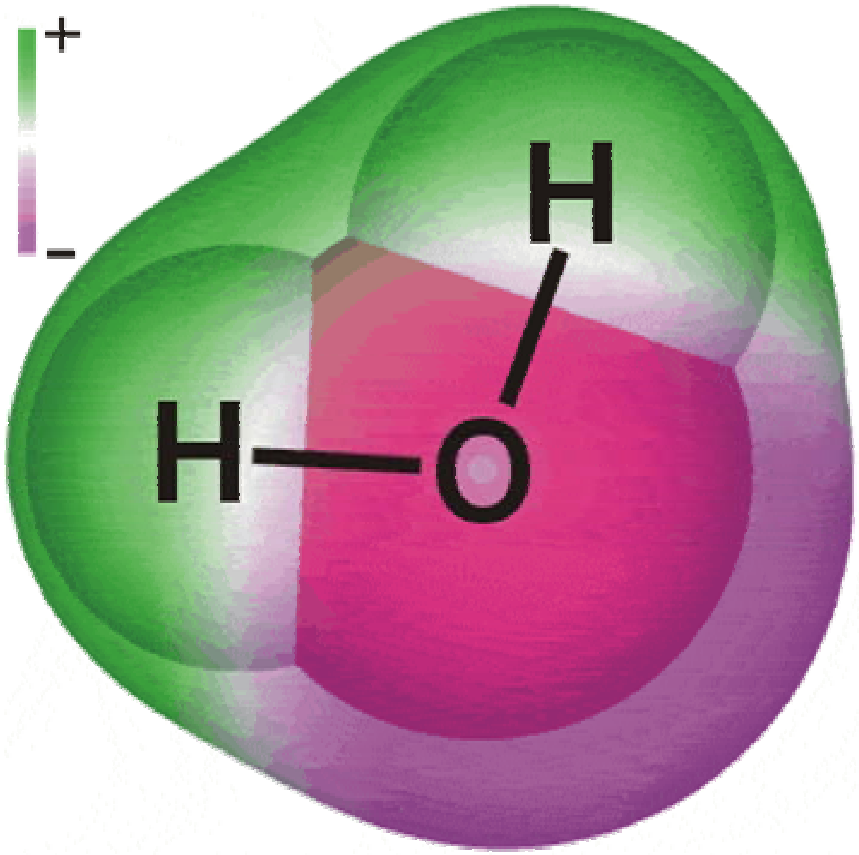
Model for empirical potentials



Is there still room for improvement?

- **Bernal&Fowler proposed a simple electrostatic model, which was supposed to be able to explain the tetrahedral arrangement of water. This picture was prophetic and its correctness waited nearly fifty years before to be proved by computer simulations.**
- **Dispite many efforts, the difficulty to reproduce in every details the properties of water demonstrates the extreme complexity of the water force field and their influences on the macroscopic properties of the condensed phase.**
- **There are many pieces of evidence indicating that the time-averaged hydrogen-bonded network possesses a large extent of order.**

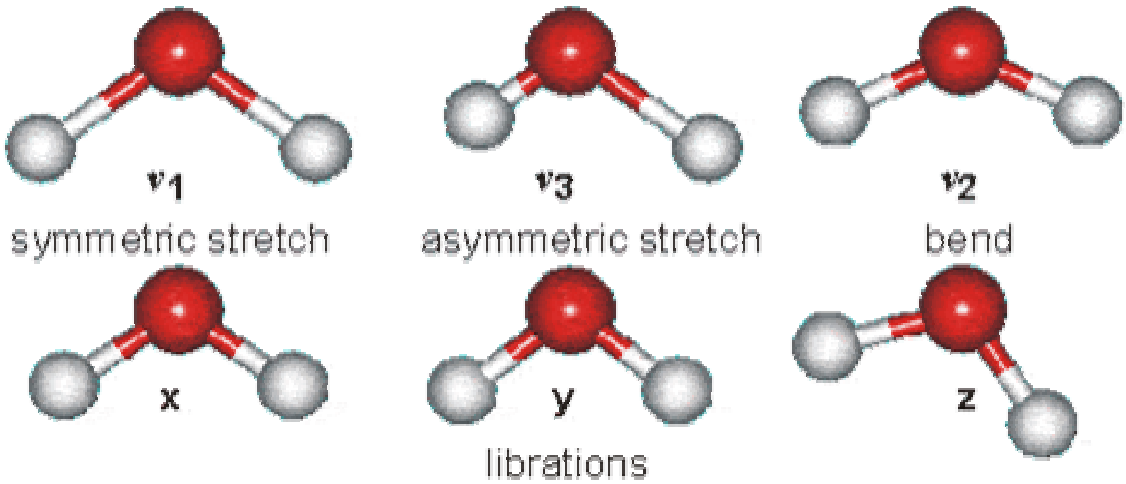
Water monomer – electron density



IR spectroscopy of the OH stretch region

- **The main value of the OH-stretch spectrum is its high sensitivity to the OH-stretch frequency.**
- **The spectrum is sensitive to the geometry of hydrogen bond spieces, its coordination numbers and cooperative effects.**

The vibration modes of water monomer



Why clusters are so interesting?

- **There are many pieces of evidence indicating that the time-averaged hydrogen-bonded network possesses a large extent of order. There are:the diffration data, MW dielectric relaxation and IR spectra that have indicated the presence of large clusters.**

- **The study of gaseous water clusters has become an important branch of water research.**

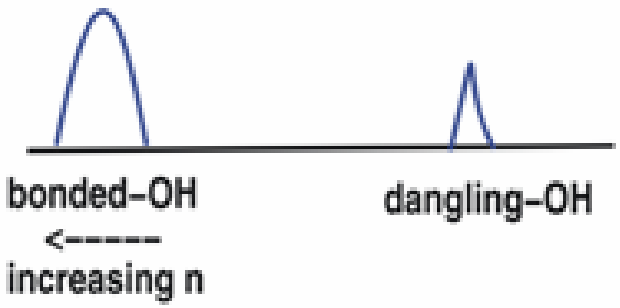
- **The excitement in clusters research lies in investigating the fundamental phenomena through clusters, and also in the possibility of connecting what is known about the gaseous and condensed states by exploring states lying between them.**

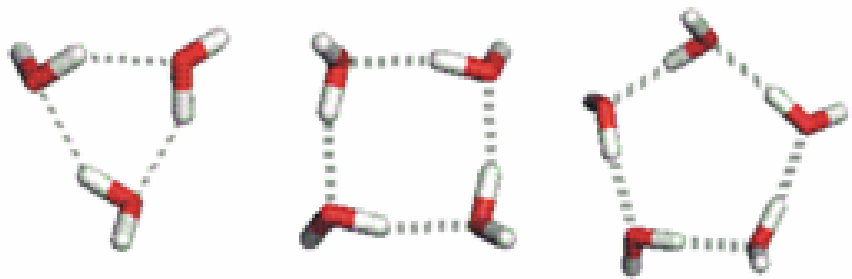
Why clusters are so interesting?

- **Detailed spectroscopic data are available for $(H_2O)_n$ in a broad size range**
- **A combination of theoretical and experimental investigations on water clusters are a valuable source of informations on interations between water molecules**
- **Clusters can be considered as a bridge between the gas and the condensed phase**
- **Clusters play an important role in atmospheric and space chemistry**

Infrared OH–stretch spectra of cyclic water clusters $(H_2O)_n$ n=3–5 (Huisken et al, incomplete size selection):

– Dangling OH band ~3700 cm–1
– H–bonded band: freq. decreases with n





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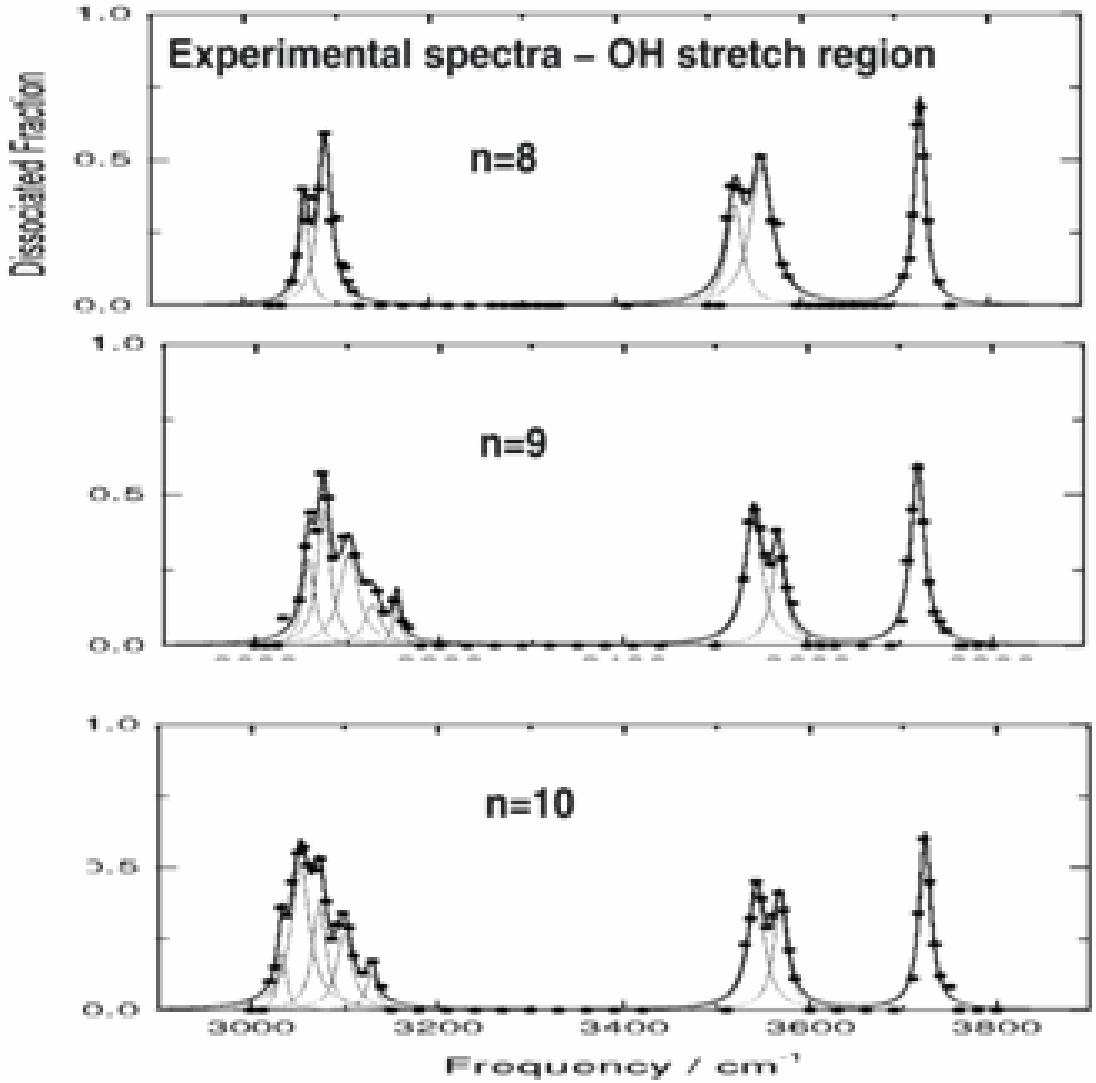

– Three well separated bands
– Similar spectra for n=8,9,10

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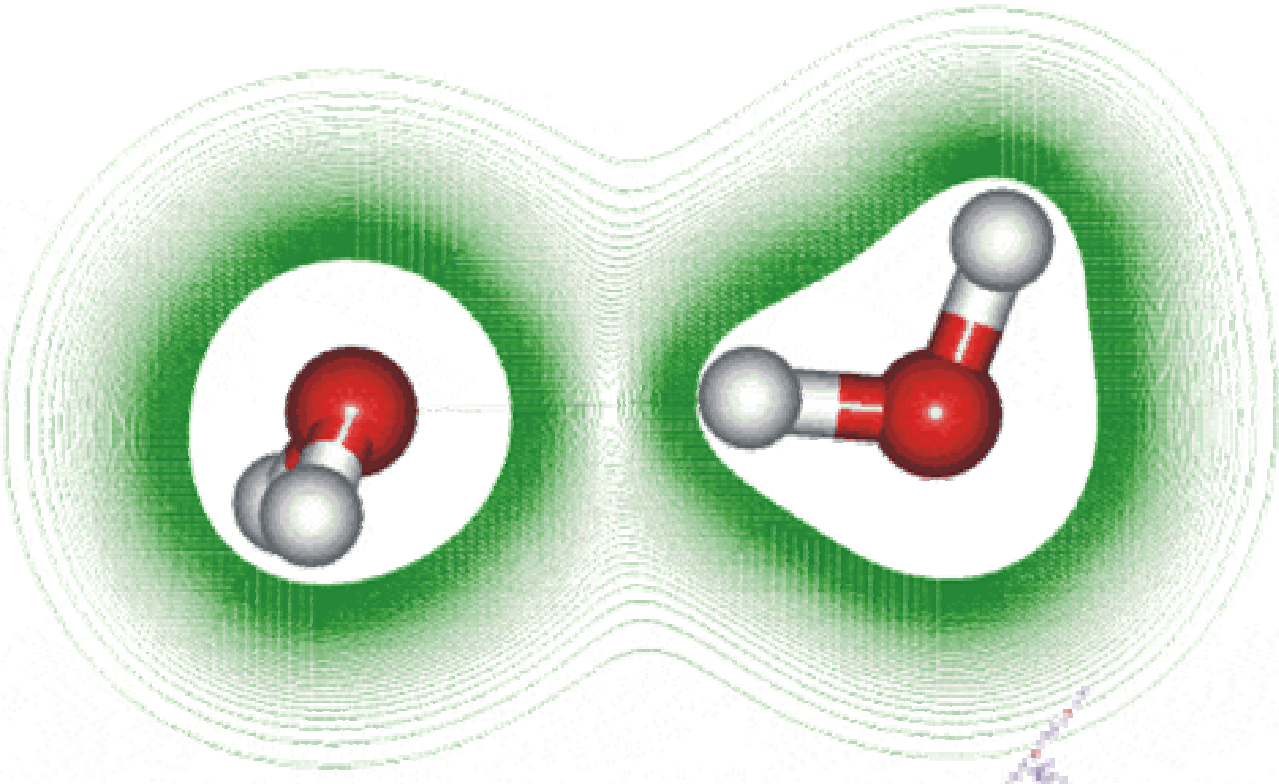
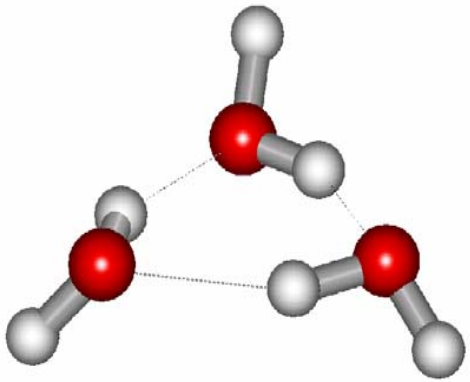
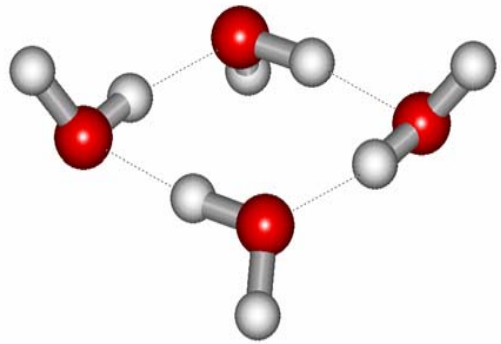
Dimer wody $(H_2O)_2$



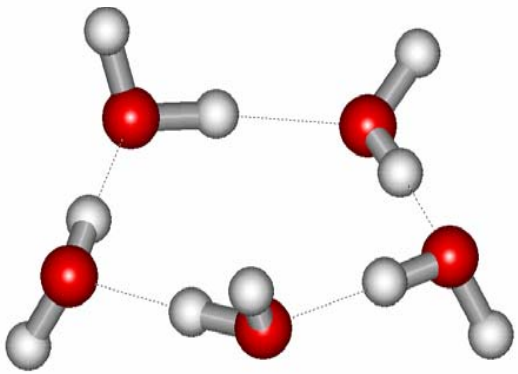
Models of cyclic clusters



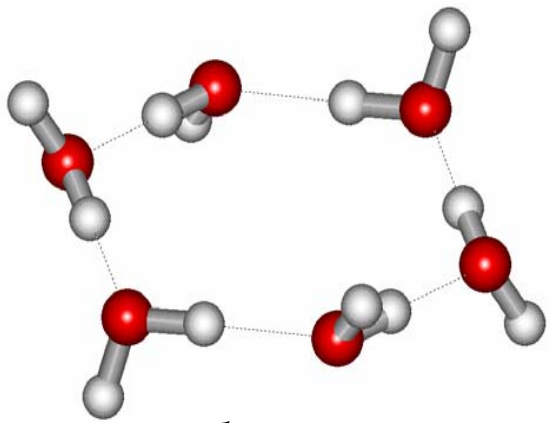
trimer



tetramer

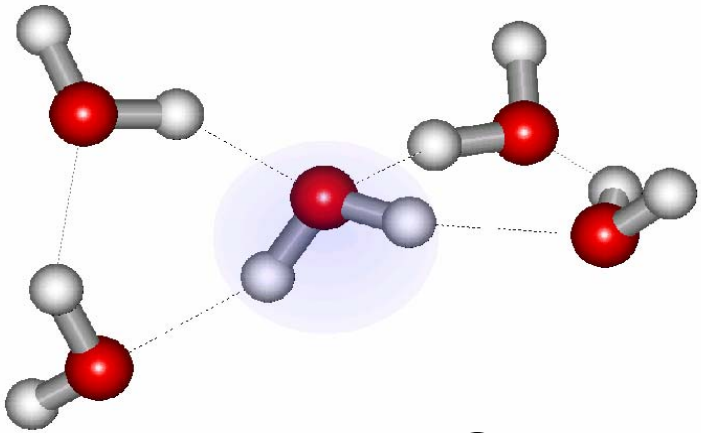


pentamer

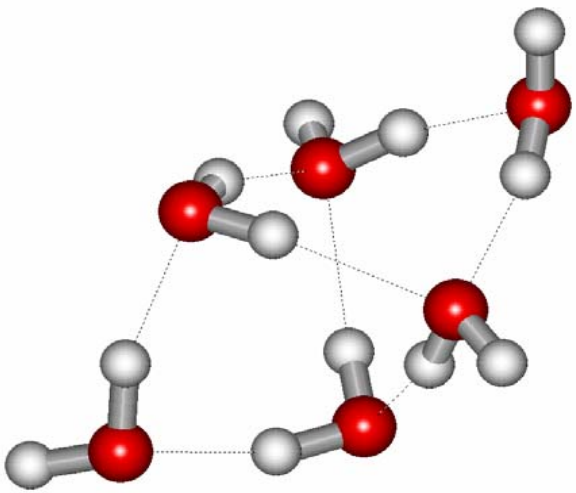


hexamer

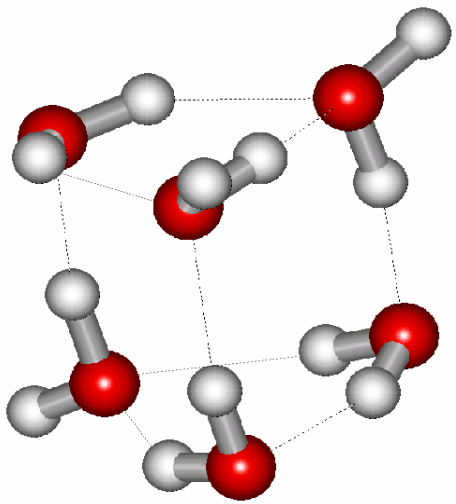
Models of 3D, n=5 tetra, n=6,7



pentamer C_2

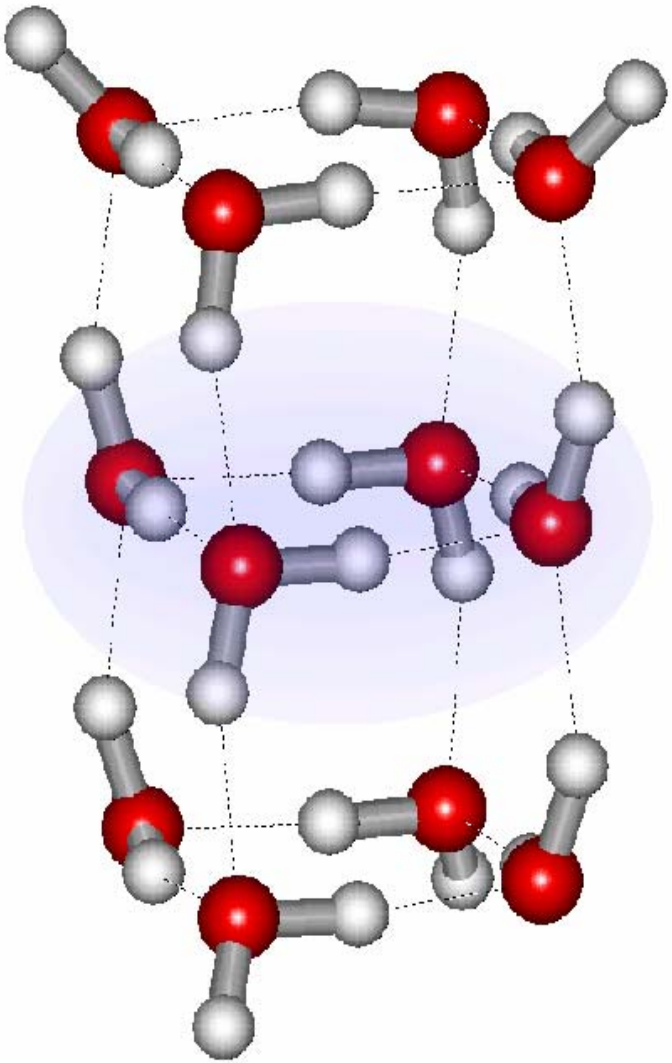


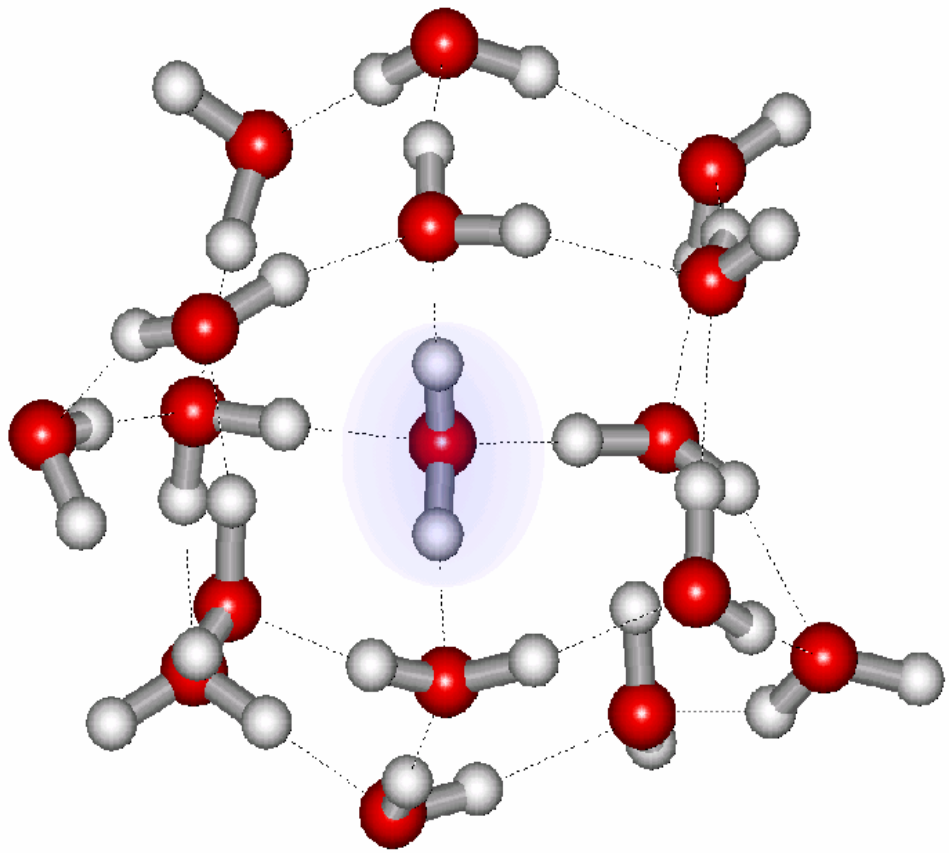
hexamer cage



hexamer prism

Models of 3D clusters, n=12 i n=17





n=12

n=17

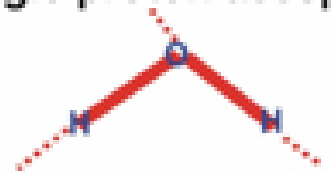
For the each 3D clusters with n=...

1. **The O-structure: the skeleton of the oxygen atoms determines the shape of the cluster, the number of hydrogen bonds and the H-bond coordination of the individual water molecules**
2. **The H-structure: the position of the H-atoms within the network of the hydrogen bonds**
3. **Each O-structure is associated with numerous distinct potential minima, corresponding to different H-structures.**

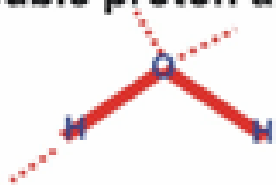
GENERAL FEATURES OF STRUCTURES, SPECTRA $(H_2O)_n$, n=8–10

– Numerous low lying minima
– 3D structures, dominated by 3–coordinated H_2O

Two varieties of 3–coordinated:
(a) double proton donor, single proton acceptor (DDA, with a dangling–O)



(b) single proton donor, double proton acceptor (DAA, with a dangling–H):

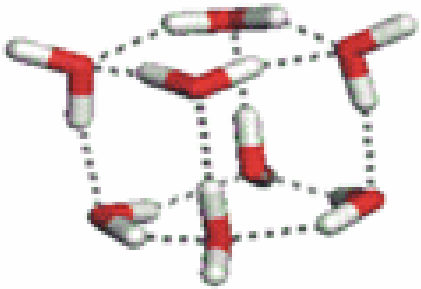


O..O DISTANCES IN H–BONDS EMANATING FROM DDA LONGER THAN BONDS EMANATING FROM DAA, HIGHER OH BOND FREQUENCIES:

PHYSICAL REASON:
– more directional hydrogen bonding via H than via O
– DAA molecules optimize H–bond geometry of a single bonded H–atom better than DDA molecules with two bonded H

OBSERVABLE RESULT: three OH stretch bands
– DAA band: ~3100 cm^{-1}
– bonded DDA band: ~3550 cm^{-1}
– dangling OH DAA band: ~3700 cm^{-1}

OCTAMER n=8 LOWEST (CUBIC) MINIMA:



D2d
–71.27 kcal/mol
–8.91 kcal/mol/H2O

S4
–71.32 kcal/mol
–8.92 kcal/mol/H2O

$D_{e,S}=D_{e,D}-0.05$ kcal/mol
$D_{o,S}=D_{o,D}-0.14$ kcal/mol (70K)

– DAA molecules connected only to DDA, and vice versa.
– Three well separated OH stretch bands

DAA DOUBLET BAND, ~3100 cm–1
Each isomer: a single infrared active DAA mode,
≡ collective oscillation of 4 bonded OH
– Observed doublet, split by ~20 cm–1:
SPLITTING DUE TO TWO ISOMERS!
– Calculated splitting:
30 cm–1 (EMP); 47 cm–1 (MP2/DZ1P)
Spectroscopic evidence for two isomers seen in octamer – benzene complex (Zwier et al. 1997).

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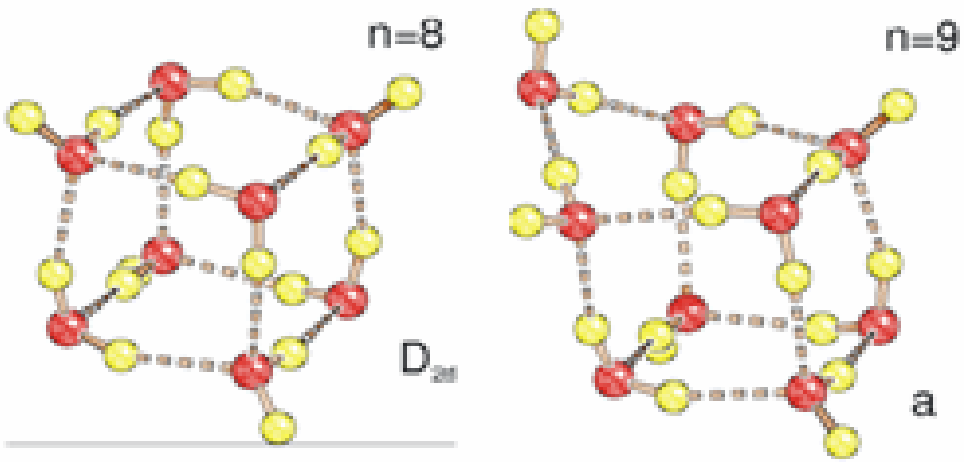
NANOMER n=9

LOWEST MINIMUM:
–80.54 kcal/mol (EMP)
–8.95 kcal/mol/H2O

– two rings 4+5 fused by 4 hydrogen bonds; opposite orientation of OH bonds
– or: D2d octamer, with extra 2–coordinated DA molecule inserted into an edge

– clear separation to three narrow spectral bands, in contrast to higher minima
– a 2–coordinated molecule contributes at 3200 cm–1.

(Next minimum, 0.3 kcal/mol above lowest – same OH orientation in fused cycles)



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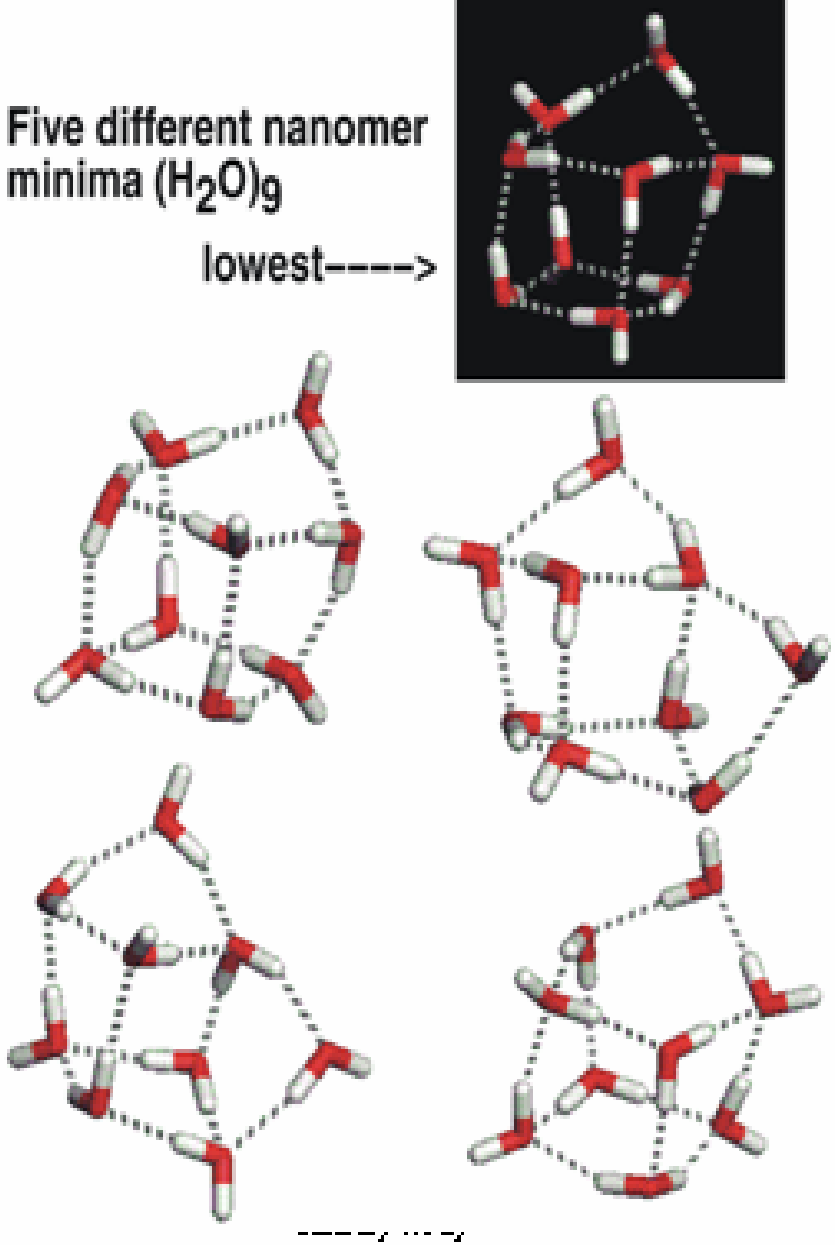

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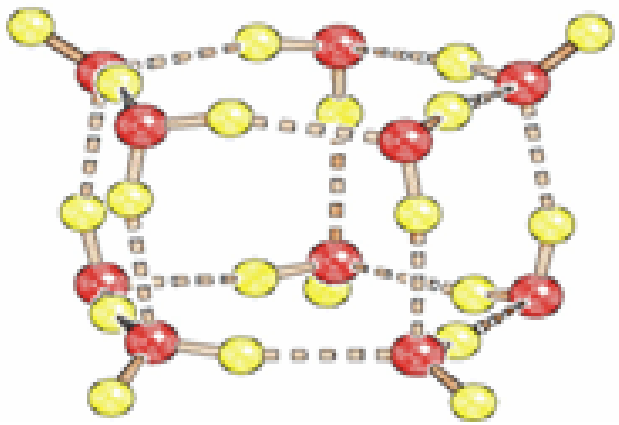
DECAMER n=10

TWO LOWEST MINIMA:
PENTAMER "CAGES"

–92.01 & –91.93 kcal/mol (EMP)
–9.20 & –9.19 kcal/mol/H2O
– two fused pentamers;
– all molecules 3–coordinated;
– same and the opposite orientation of OH bonds in the two cycles
Discrepancy with experiment:
features near 3400 cm–1
from adjacent molecules of the same kind DDA–DDA–DAA–DAA



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DECAMER n=10

Better agreement with experiment:
"BUTTERFLY" MINIMUM:

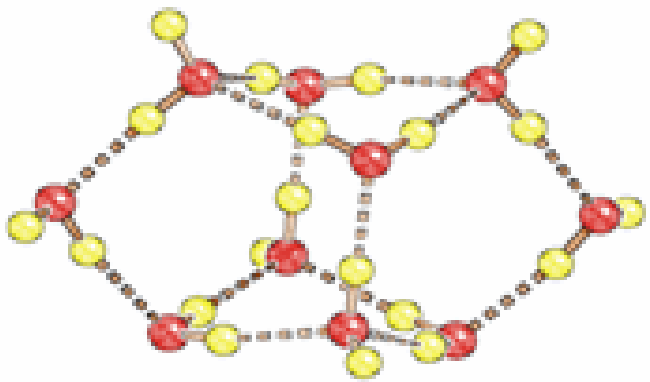
–89.67 kcal/mol (EMP)
–8.97 kcal/mol/H2O

– D2d octamer,
with two extra 2–coordinated DA molecules,
inserted at opposite edges

ZERO–POINT ENERGY EFFECT:
reduction of energy gap between cage and butterfly

$D_{e,cage}=D_{e,but}$ –2.3 kcal/mol
$D_{o,cage}=D_{o,but}$ –0.3 kcal/mol

(in reality, butterfly energy is lower(?),
errors ~0.3% in PES not unexpected)



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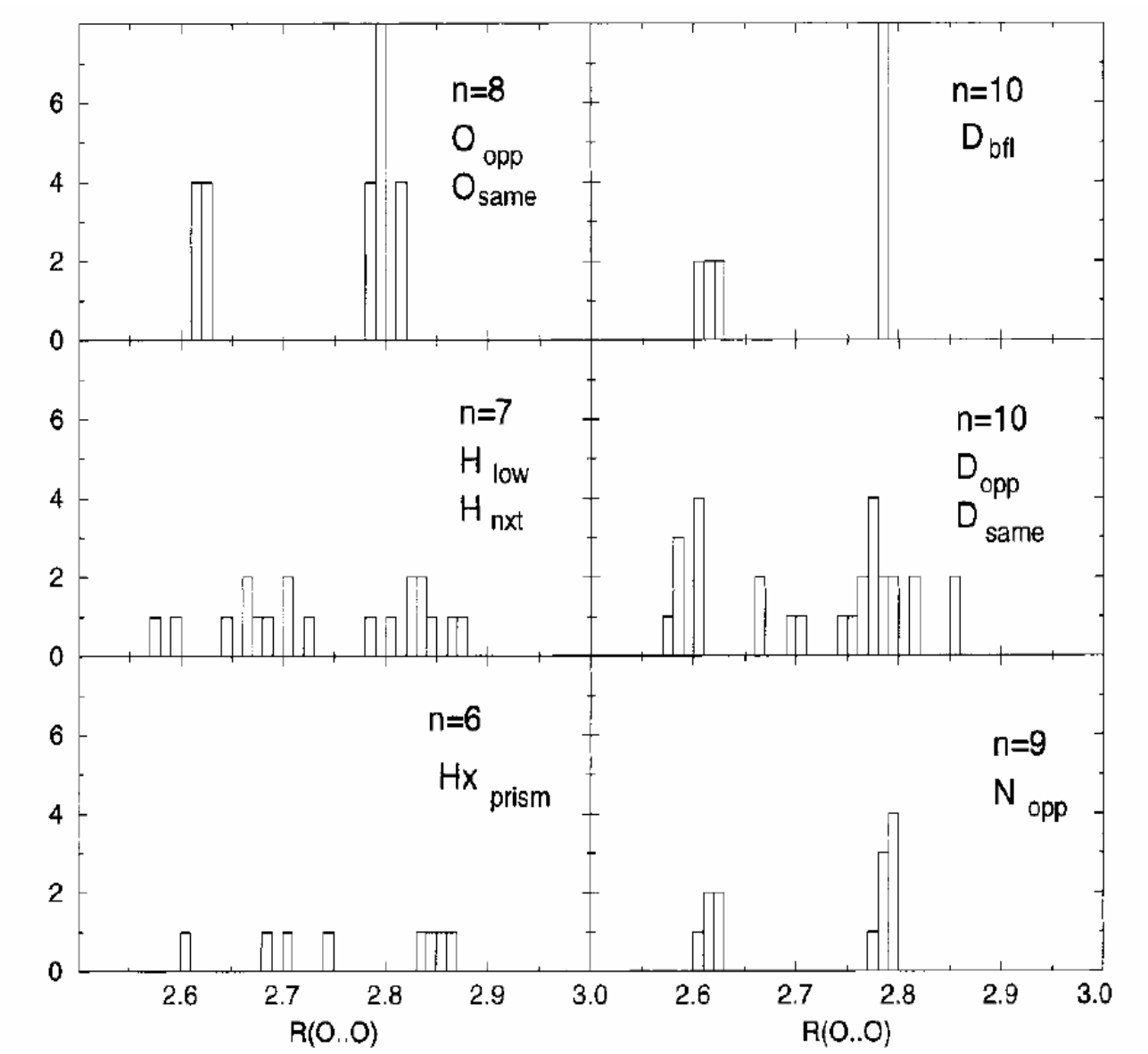
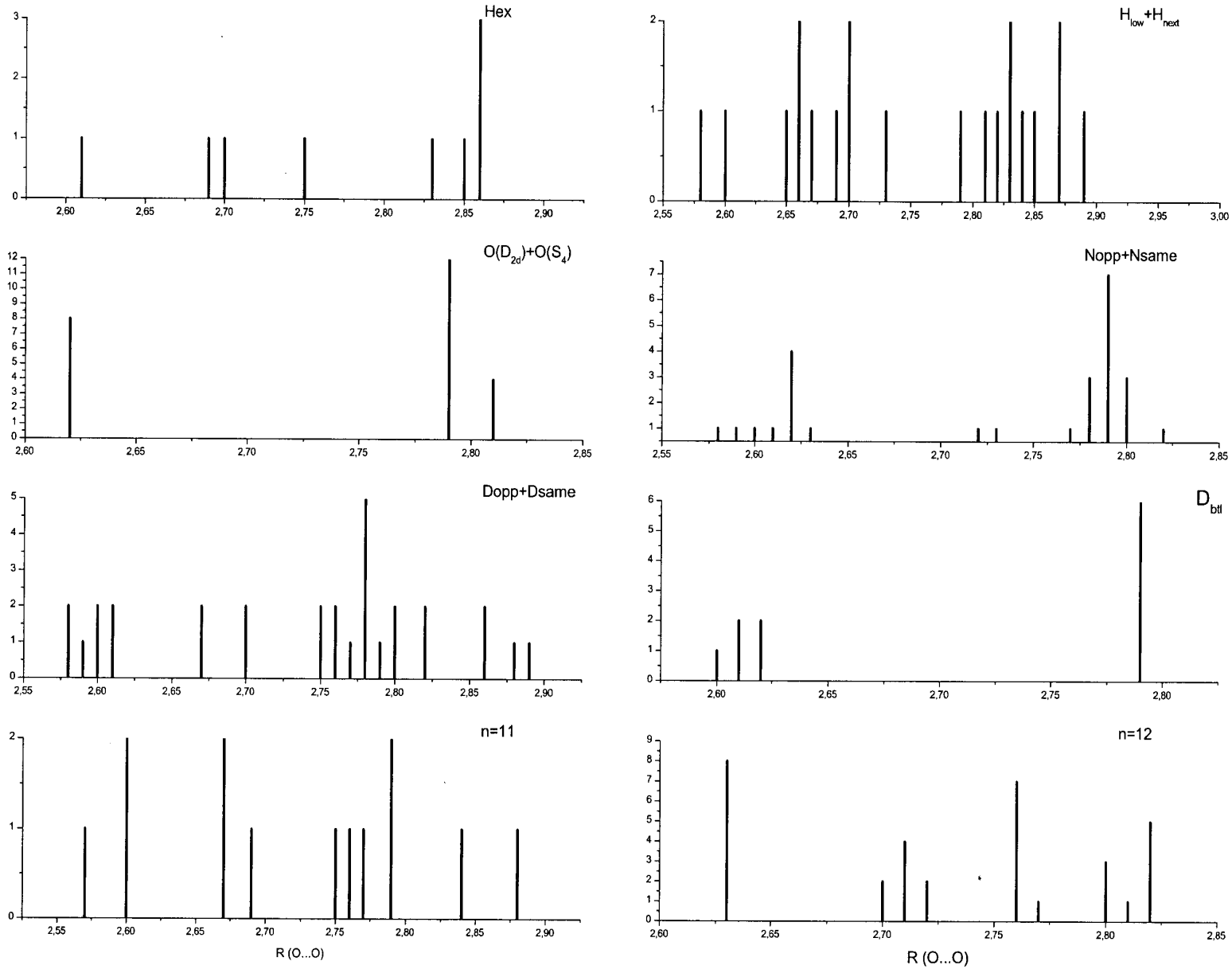
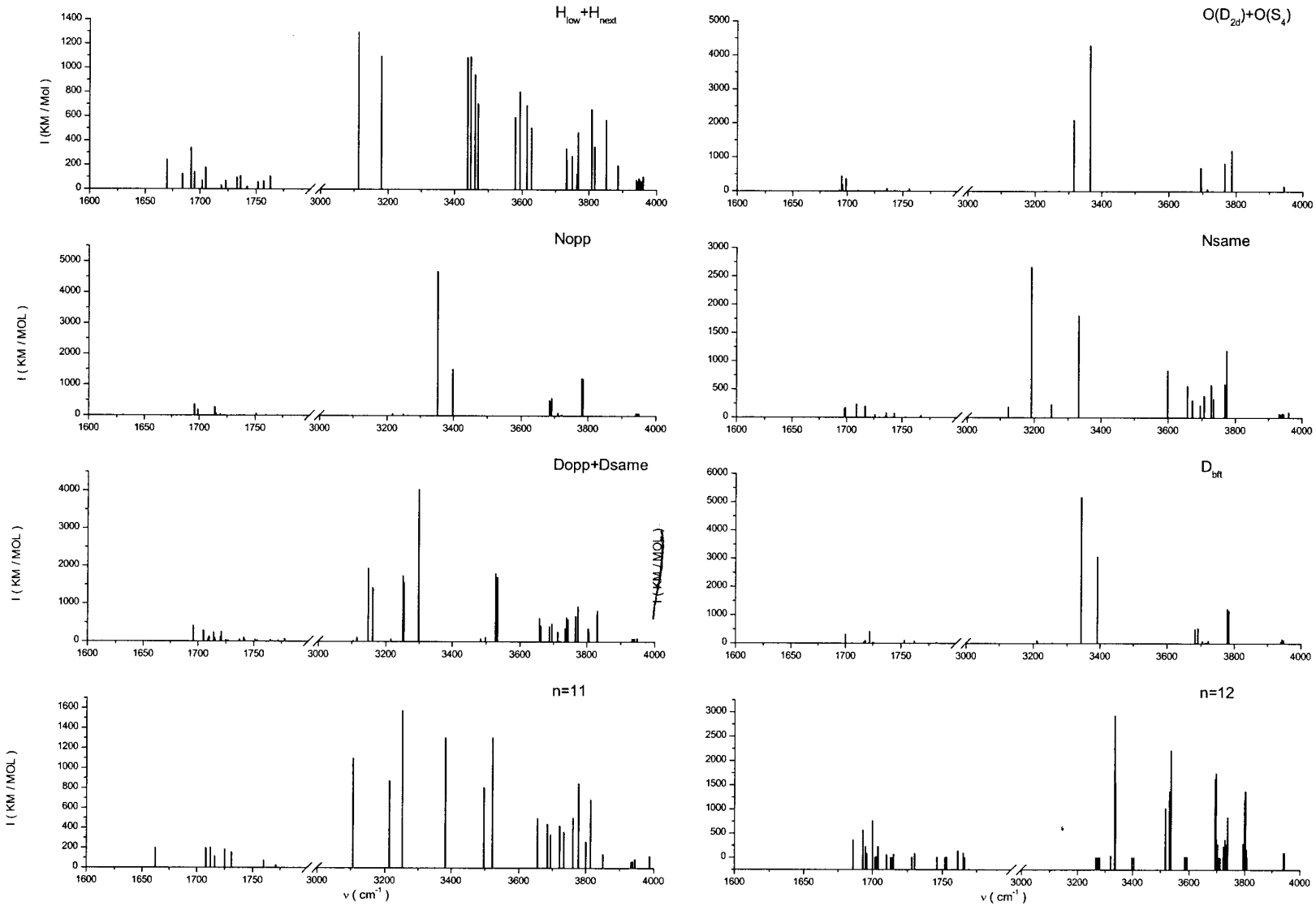
The distribution of R(O⋯O) for 3D clusters



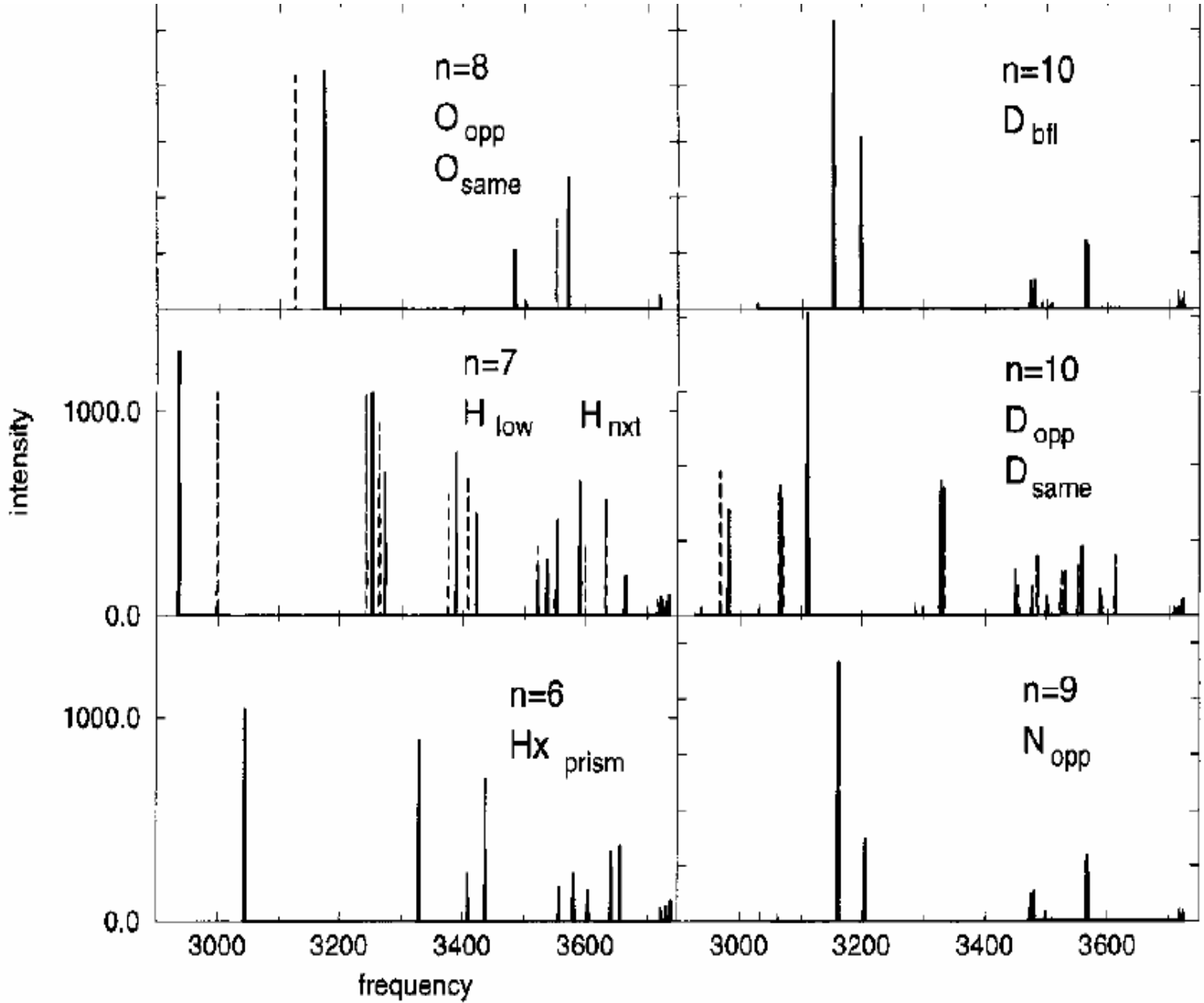
The distribution of R(O…O) for 3D clusters



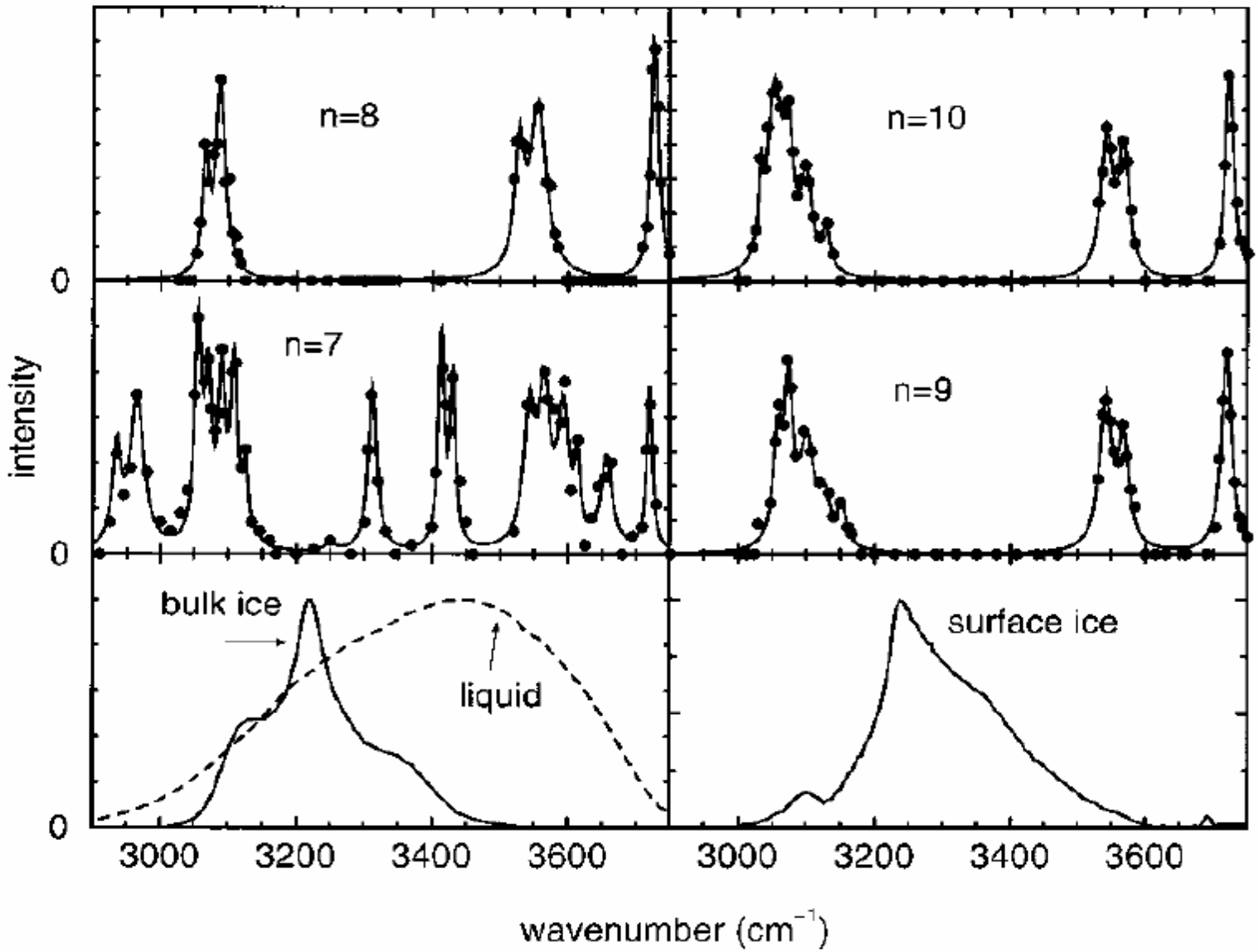
Harmonic frequences for 3D clusters



Harmonic frequences for 3D clusters



IR experimental spectrum for 3D clusters, liquid and ice



Clusters $(H_2O)_n$, n=6-12

Crystal-like

- O(S4), O(D2d), Nopp, Dbtf, Dopp
- R(O...O) 2.69 A for DAA
  2.79 A for DDA
  2.72-2.76 for DDAA

Spectrum

3100 cm^{-1} DAA
3500 cm^{-1} DDA
3600 cm^{-1} dangling OH
3330 cm^{-1} DDAA

Amorphous

- Hxprism, Hlow, Dsame
- R(O...O) 2.58-2.89 broad distribution

Spectrum

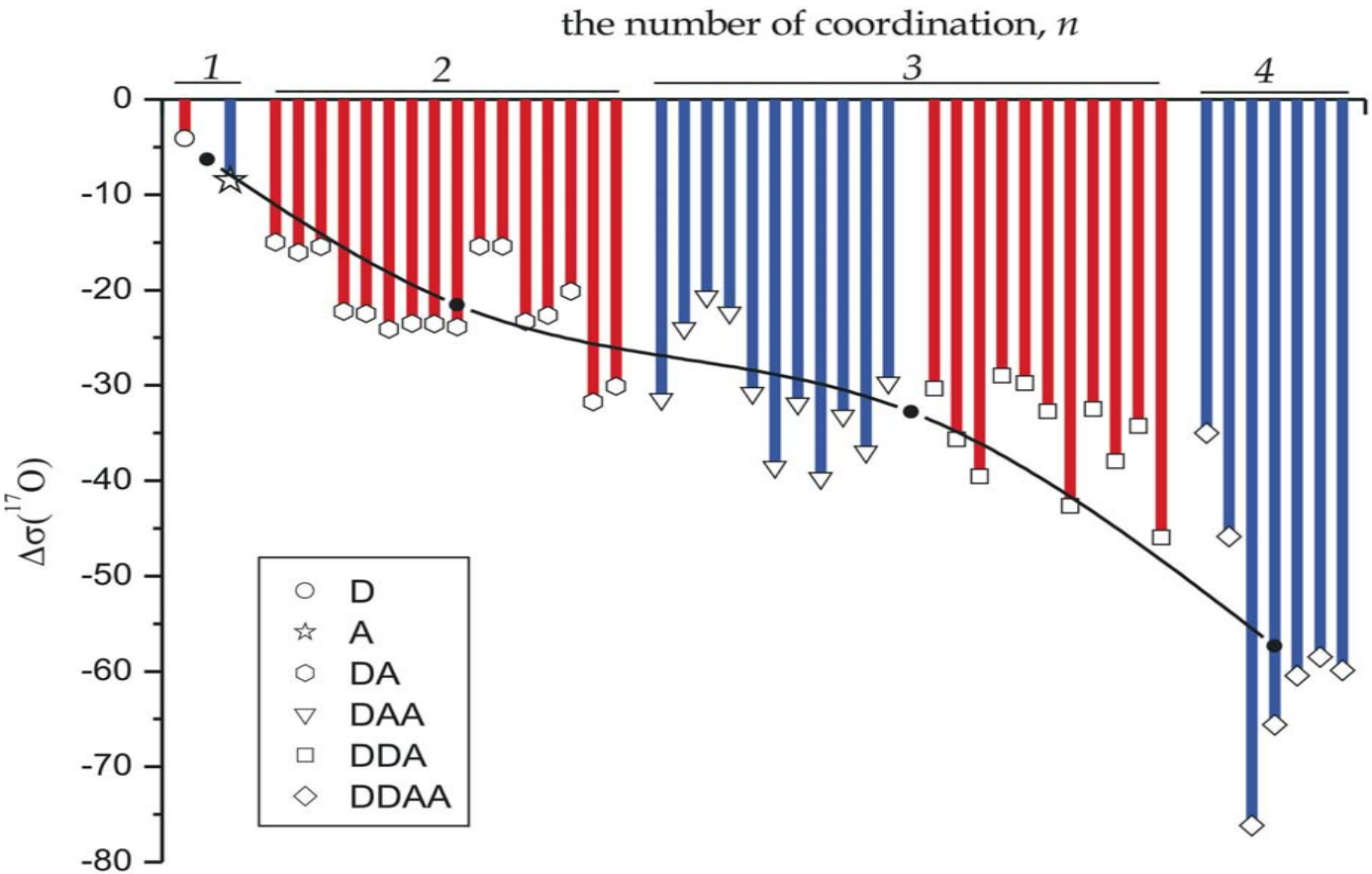
- Except three bands there are bands between 3200-3600 cm^{-1}

Gas-to-liquid chemical shift for water???

- **Experimental gas-to-liquid chemical shifs are for water: –4.26 ppm (^{1}H) and –36.1 ppm for ^{17}O.**
- **The continuum models (SCRF or PCM) fail to predict the correct magnitude for the ^{17}O chemical shift but also give the wrong absolute sign (upfield shifts-R. Klein, B.Mennuci, J. Tomasi)**
- **Does supramolecular model of clusters, could describe the deshielding of ^{17}O on going from gas to liquid?**

Change of the shielding constants of ^{17}O depends on .....?

- **Size of the cluster and the topology of the hydrogen bonding:**



^{17}O chemical shifts in 3D water clusters

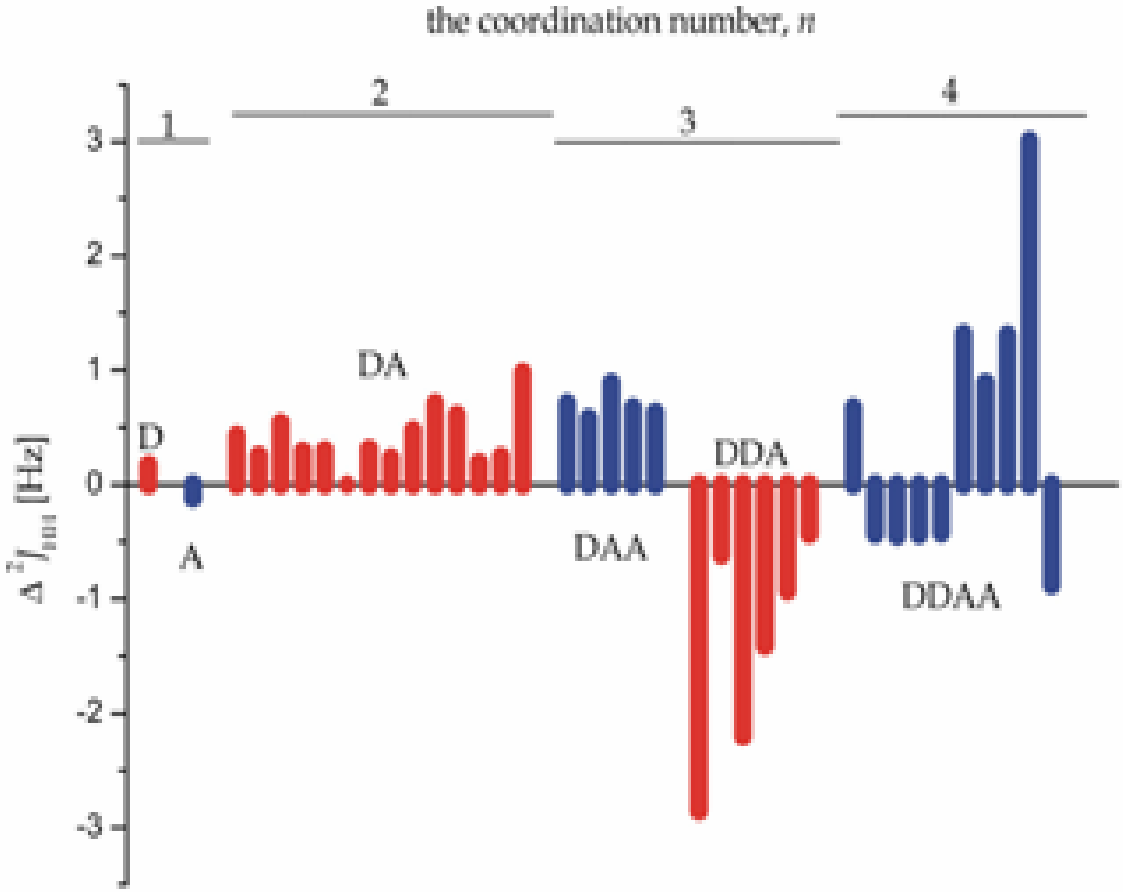
The ^{17}O shielding constants decrease as the cluster size increases,

- **These changes depend on the environment: in pentamer n=5, for oxygen atom of the type DDAA: $\Delta\sigma(^{17}O)$=-35 ppm, while for n=17, $\Delta\sigma(^{17}O)$=-76 ppm.**
- **But... averaging over all oxygen atoms of the DDAA-type in cluster n=12, $\Delta\sigma(^{17}O)$=-36 ppm; there is a lack of the experimental data for ice,**
- **But... averaging over the cluster n=931, which have 755 DDAA, 78 DDA, 68 DAA i 18 DA oxygen atoms we obtained $\Delta\sigma(^{17}O)$=-50 ppm.**

The calculations of the nuclear spin-spin coupling constants

- **We investigated couplings between three nuclei involved in H-bonds and the analysis is focused mainly on their presumed correlation with the topology of the clusters and with the geometrical parametrs of H-bonds.**
- **The complexation-induced changes in the intramolecular proton-proton coupling $^{2}J_{HH}$ cover a range between -2.9 and 3.0 Hz. For DA and DAA types we observe a decrease of $^{2}J_{HH}$, while for DDA the changes are negative. The descrimination between water molecules of the DDA and DAA types occurs also for other parameters.**

Spin-spin coupling constants calculations for water clusters...



$^{1h}J_{OH}$ and $^{2h}J_{OO}$ couplings

- **The hydrogen-bond transmitted coupling constants are substantial. The increase of $^{1h}J_{OH}$ coupling is connected with the elongation of the intramolecular O-H bond and the shortening of the intermolecular separations.**
- **The intermolecular coupling $^{2h}J_{OO}$ transmitted through two bonds cover the range between -0.6 and 7.5 Hz. The largest and smallest values are observed for the shortest and longest internuclear O...O separation, respectively.**

$^{1h}J_{OH}$ and $^{2h}J_{OO}$ couplings

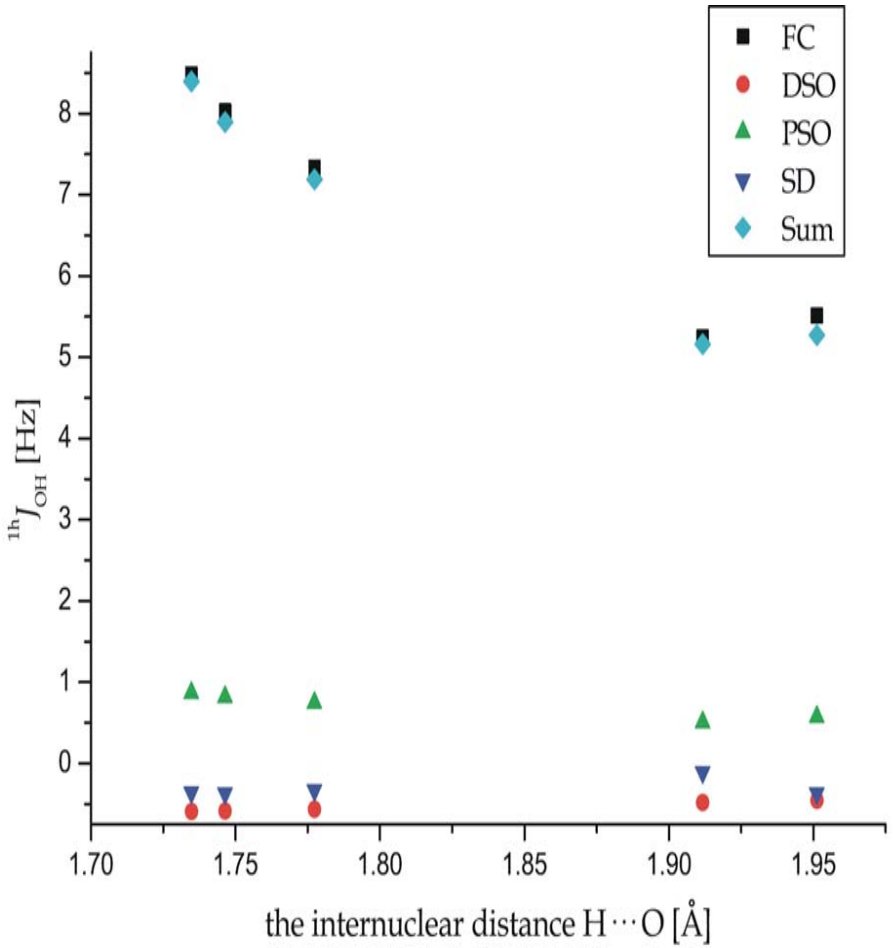


Fig. 6. The dependence of the changes in the average intermolecular $^{1h}J_{OH}$ spin–spin coupling constant [Hz] on the H···O internuclear separation [A] in cyclic clusters $n = 2$–6 [Å].

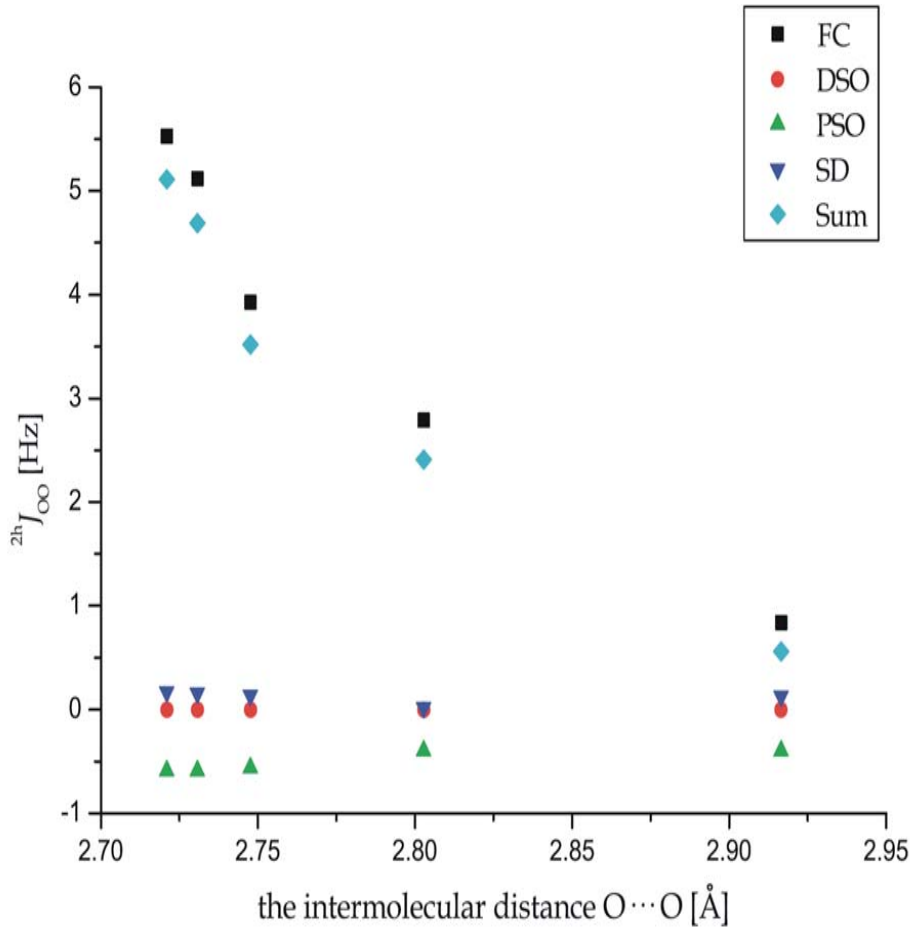


Fig. 7. The dependence of the changes in the average intermolecular $^{2h}J_{OO}$ spin–spin coupling constant [Hz] on the O···O internuclear separation [A] in cyclic clusters $n = 2$–6 [Å].

The network of the hydrogen-bonding

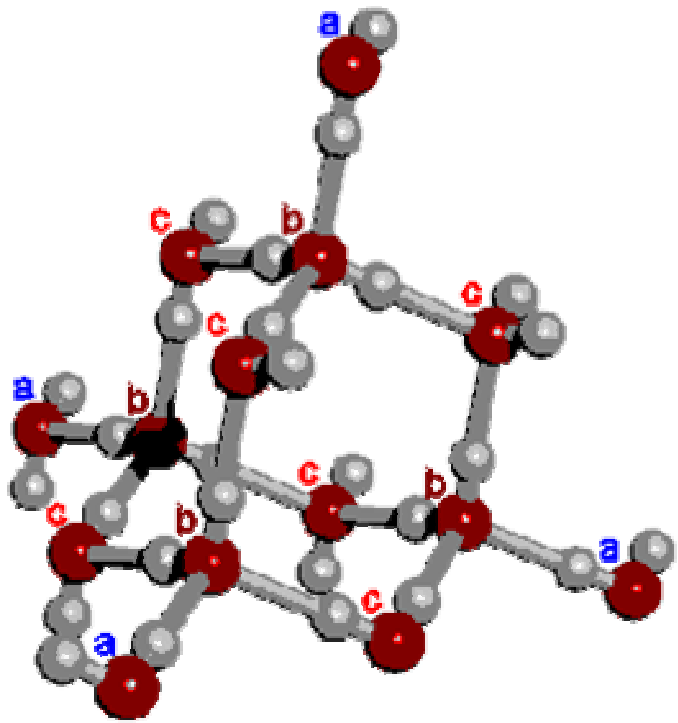
- **It is thought by some that the instantaneous degree of hydrogen-bonding is very high (>95% at 0 C and ca 85% at 100 C) and gives rise to extensive network, aided by bonding cooperativity. There is evidence (the fine structure of diffraction data, MW dielectric relaxation, vibrational spectra) that the time-averaged network possesses a large extent of order.**

- **The cooperative nature of the H-bond means that acting as an acceptor strengthens the water molecule acting as a donor.**

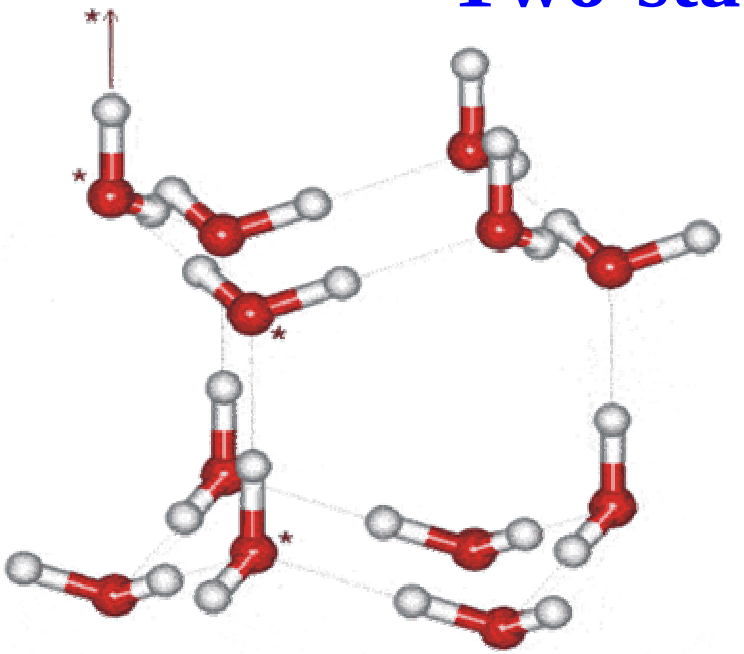
- **The network should be related to the small clusters. It was the first idea to explaine the maximum of density with the existance of the region of the low and high-density space.**

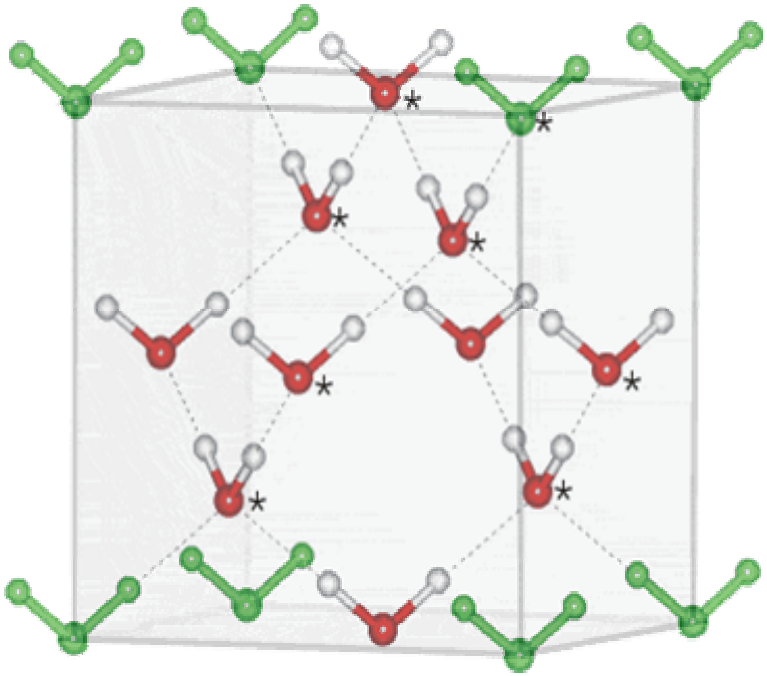
Water as a two-state network model...

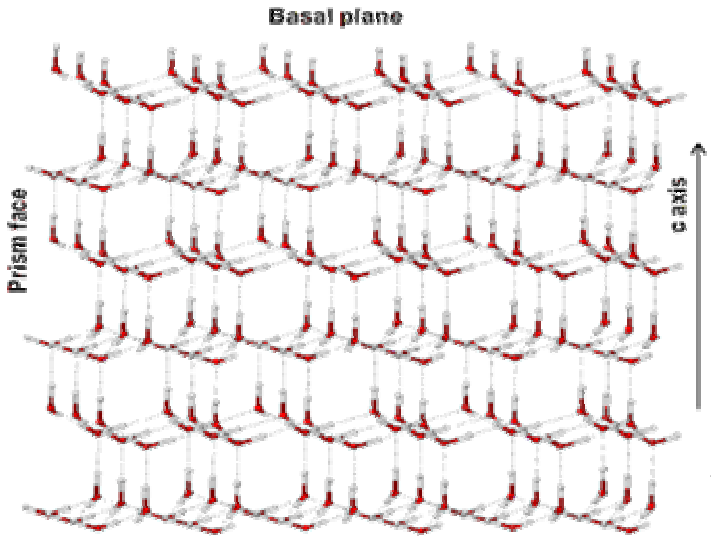
- **the „two-states” model - Ih hexagonal ice and Ic cubic ice form altering sheets from these boat (from Ih ice) and chair (from Ic ice) water hexamer.**



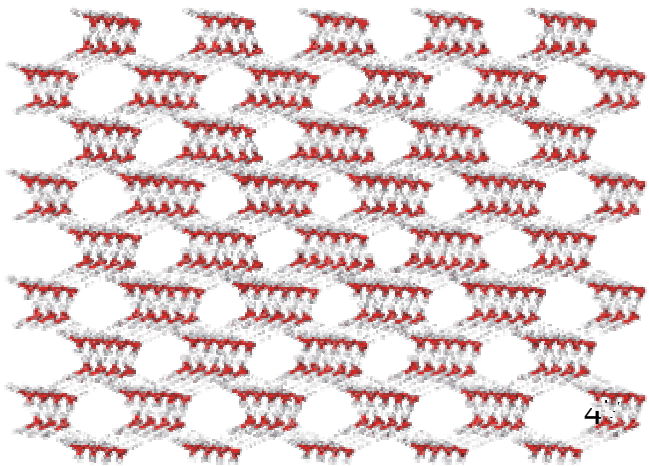
Two-state model...





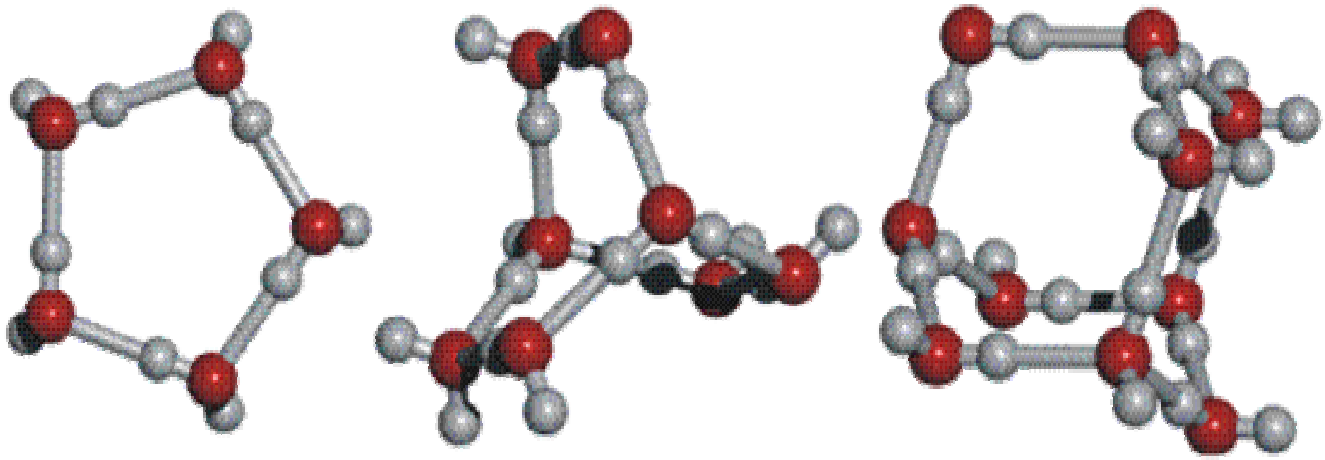


Water clusters



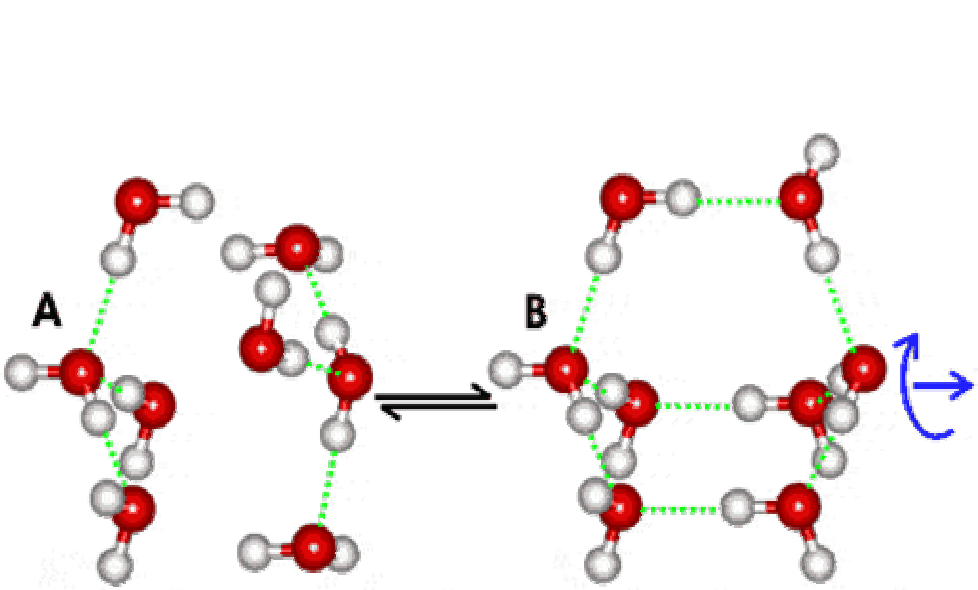
Clusters in water....

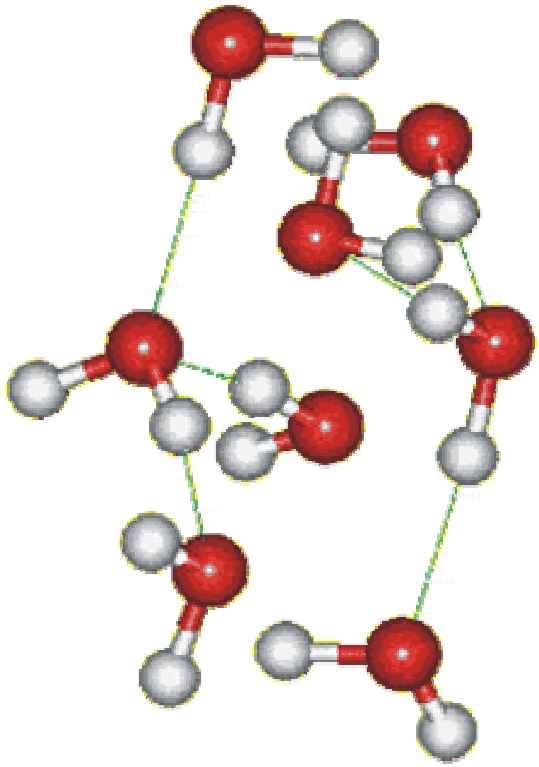
small clusters could form bicyclo-octamers



- **The bicyclo-octamers may cluster further to form highly symmetric icosahedral clusters**

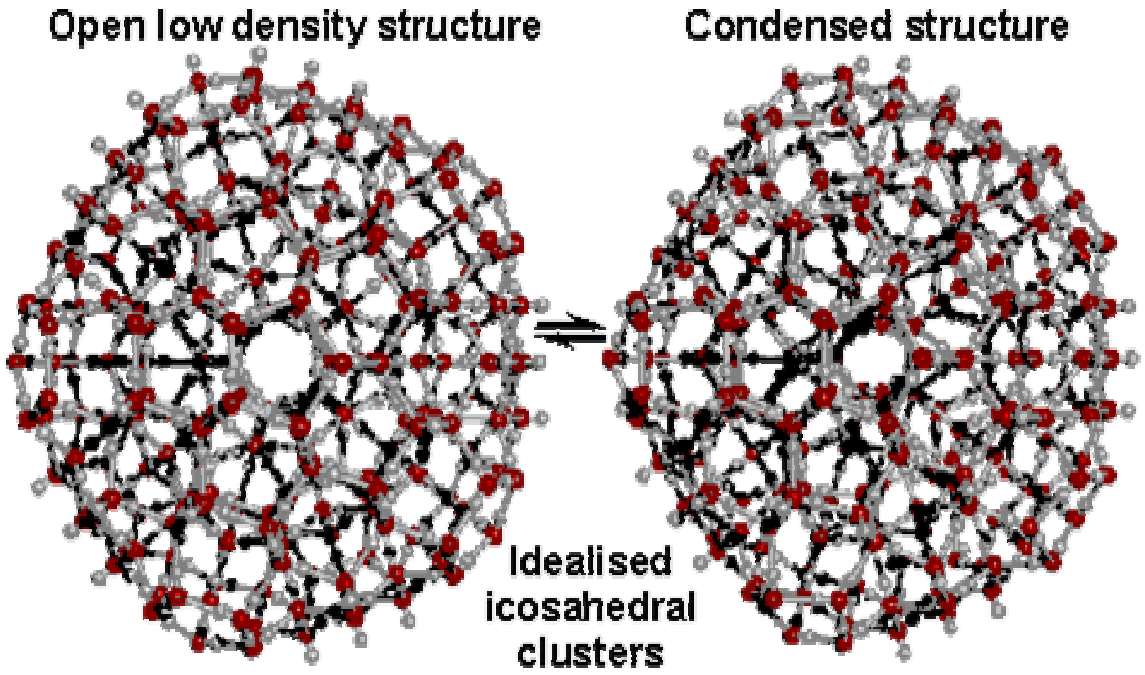
Icosahedral clusters..





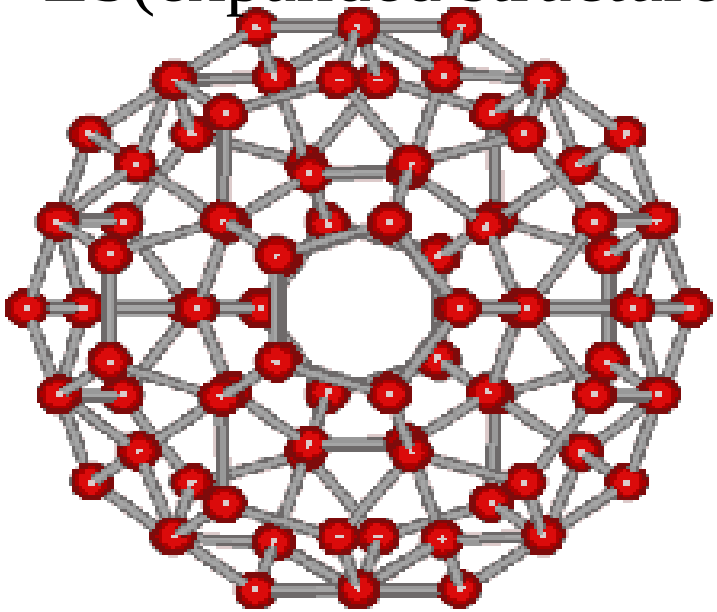
Icosahedral clusters

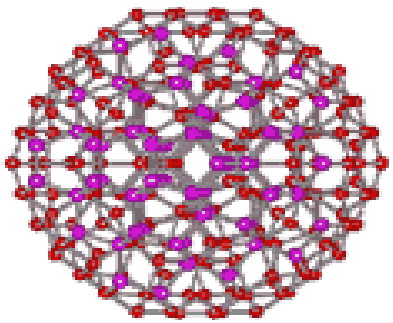
first proposed to exist in liquid water in 1998 and found in water nanodrops



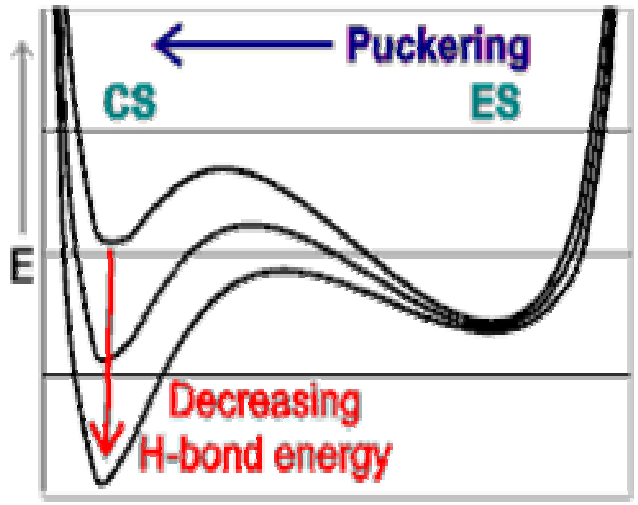
Icosahedral clusters

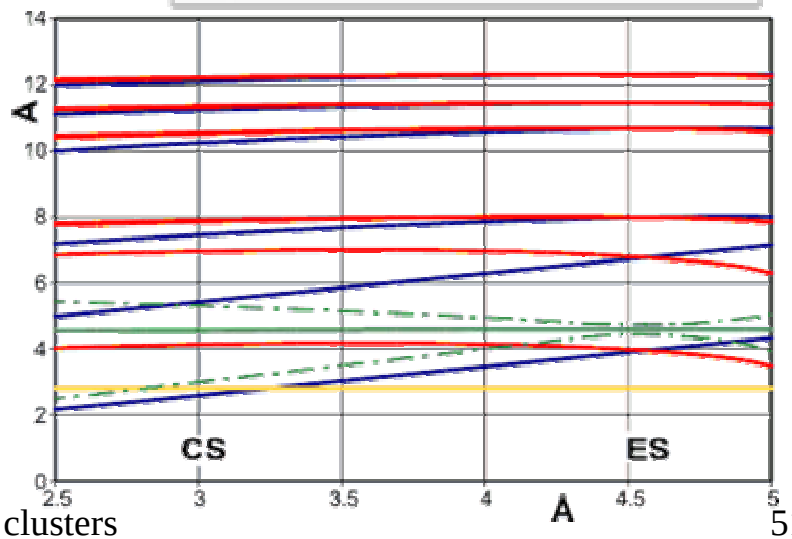
ES(expanded structure)





CS(collapsed structure)





The conclusion...

- **One difficulty...**

Does these clusters realy exists in liquid water?

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