New Perspective on structure and bonding in water using XAS and XRS

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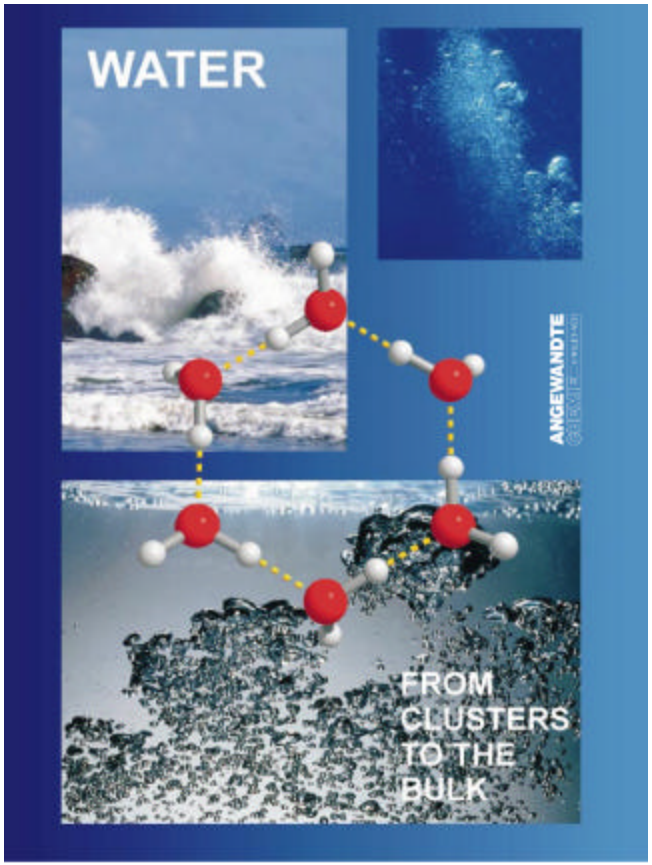

R. Ludwig Angew. Chem. 40, 1808 (2001)

Philippe Wernet/SSRL

Klas Andersson/SSRL

Uwe Bergman/SSRL

Lars Pettersson/SU

Matteo Cavalleri/SU

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Clemens Heske/UW

Lars Ojamäe/LU

Satish Myneni/PU

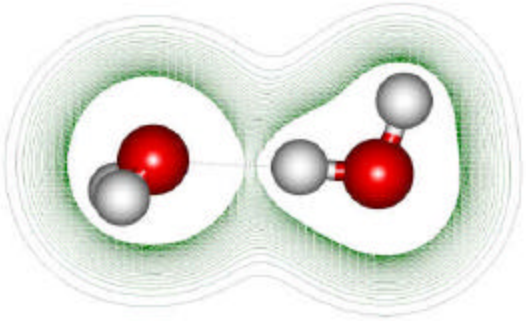
Yi Luo/KTH

Zahid Hussein/ALS

Rich Saykally/UCB

Kevin Wilson/UCB

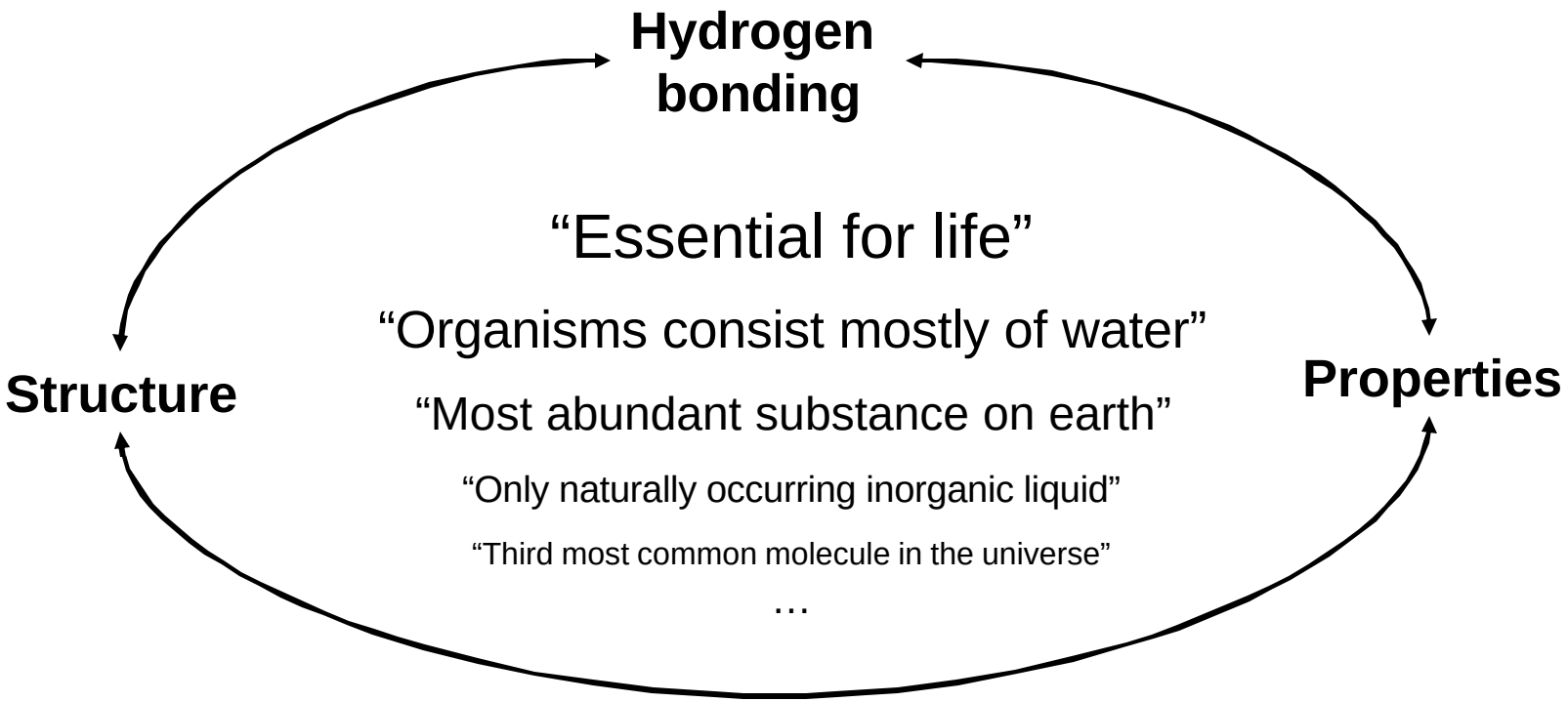
Hydrogen Bonding and Water



H-bonds are formed between H and N, O and F atoms

They are weak and easily broken and reformed

The valence electrons are strongly affected by H-bonds and can be probed using X-ray spectroscopy



Water: many questions

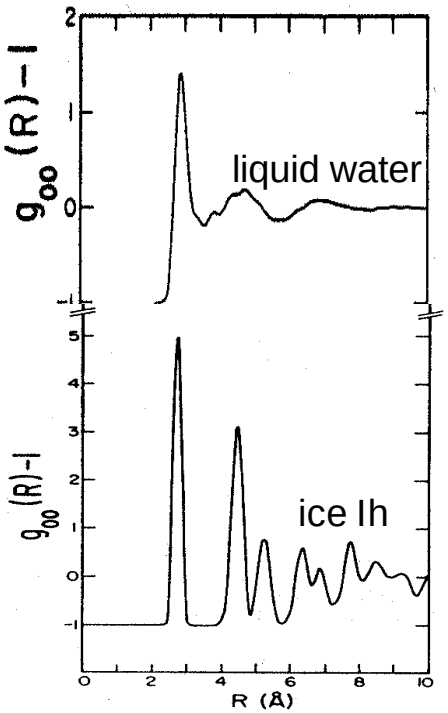
- Ice, water monomer, clusters: reference/model system, how far/close to liquid water?
- **Structure of water at ambient conditions:** more than 100 years of debate, new experimental evidence is needed!
- **Supercritical water:** “extensive … no hydrogen bonding” in sc water?
- Water at surfaces and interfaces: ordering vs. disordering, hydrophobic effect?
- Confined water: enhanced vs. reduced ordering for confined water?
- “Biowater”: water in biological systems, its structure, role, hydrophobic effect…?
- …

Gerald H. Pollack: "Cells, Gels and the Engines of Life. A New, Unifying Approach to Cell Function"

…remain to be answered and established methods cannot help...

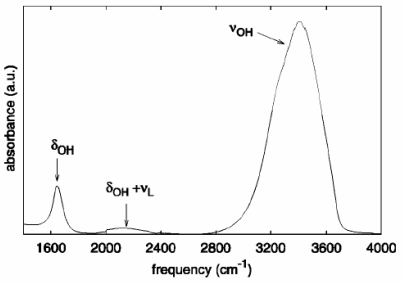
- X-ray and neutron diffraction
- Infrared spectroscopy (linear absorption, Raman and fs-pump-probe)
- Molecular dynamics and other simulations
- Water structure models and concepts
- …

Most common techniques and current belief



x-ray, neutron diffraction

IR absorption

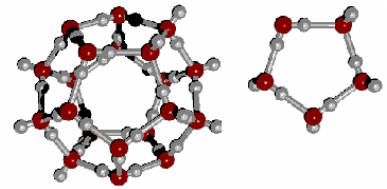


Lock et al., JCP **117**, 1708 (2002)

- X-ray (and neutron) diffraction provide O-O (and O-H and H-H) radial distribution functions (RDF) – uncertainties in analysis, debated
- Infrared absorption and Raman spectroscopy of OH stretching band - ambiguous
- Molecular Dynamics (MD) simulations using classical pair potentials or ab initio derived forces, test versus RDF's – results depend strongly on potentials

Mixture models

"Small number of different species with well defined bond angles/lengths."

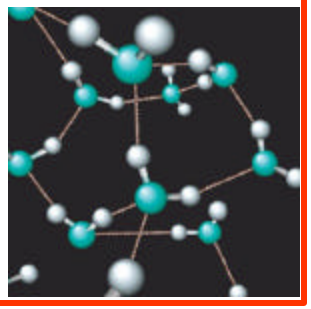


Continuum Models

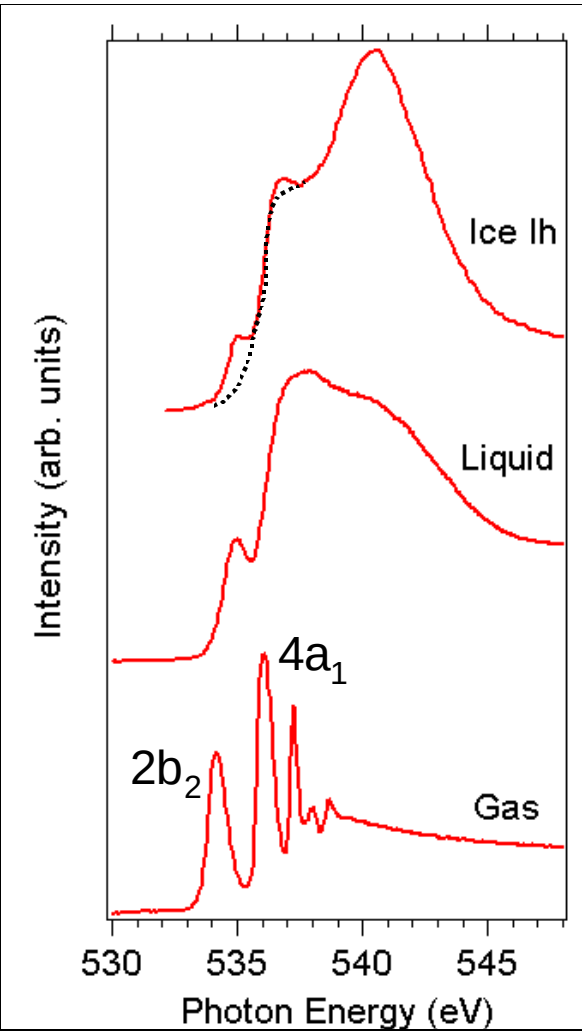
"Infinite Network of disordered tetrahedral water."

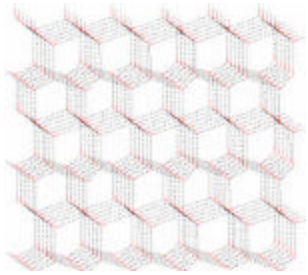
MD simulations! ⟶

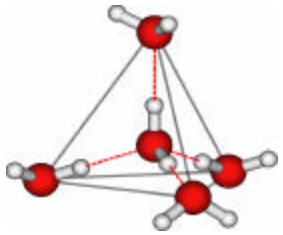
~3.5 HB/molecule



X-ray Absorption Spectroscopy of Water



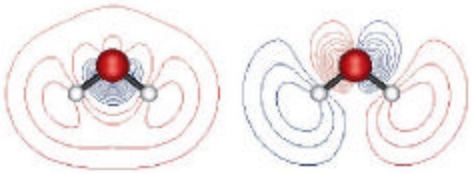




"…making and breaking of H-bonds…"

⇩

?



$4a_1$ $2b_2$

Hydrogen bonding

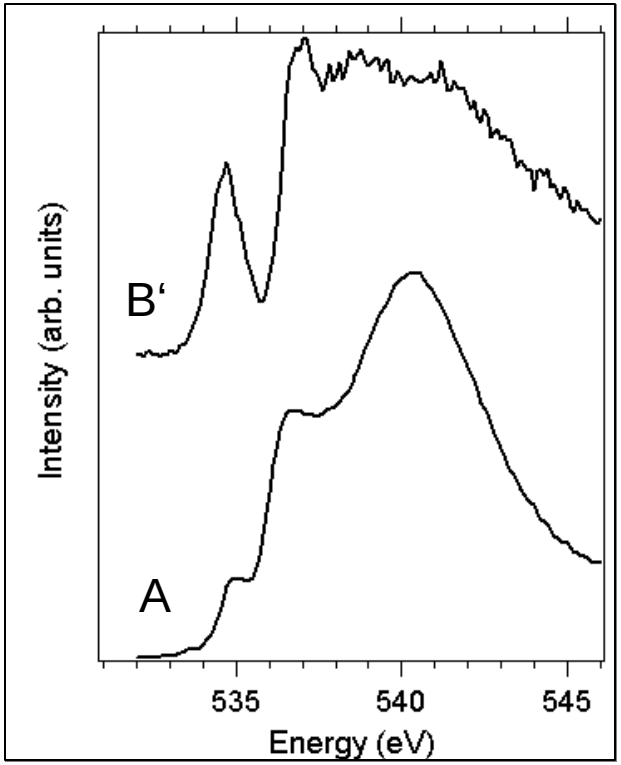
Conduction band formation
Local symmetry

⇩

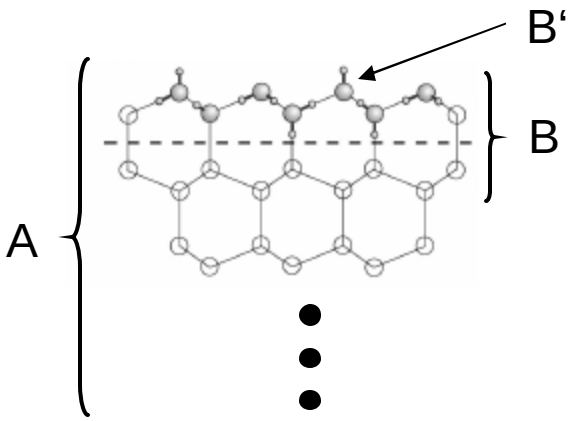
O K-edge XAS:

ultra-fast, element-specific, symmetry-sensitive and local probe for the structure of water.

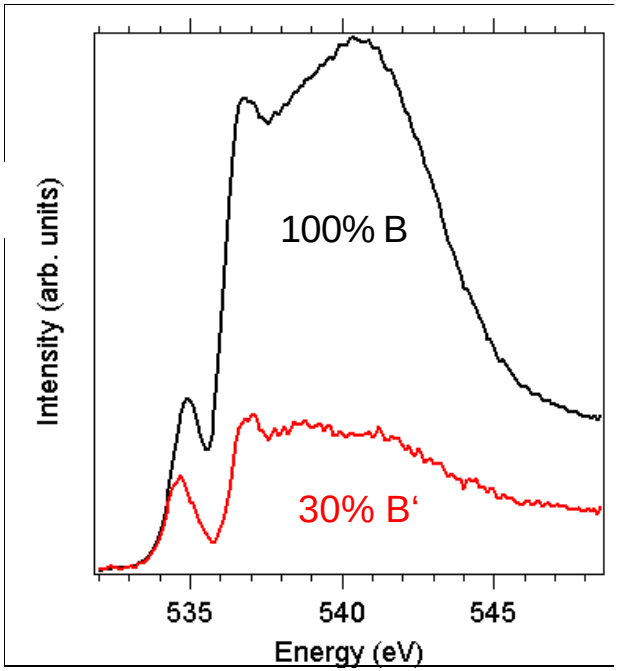
Surface model systems



ice
surface and bulk



Wei et al., Phys. Rev. B **66**, 085401 (2002)



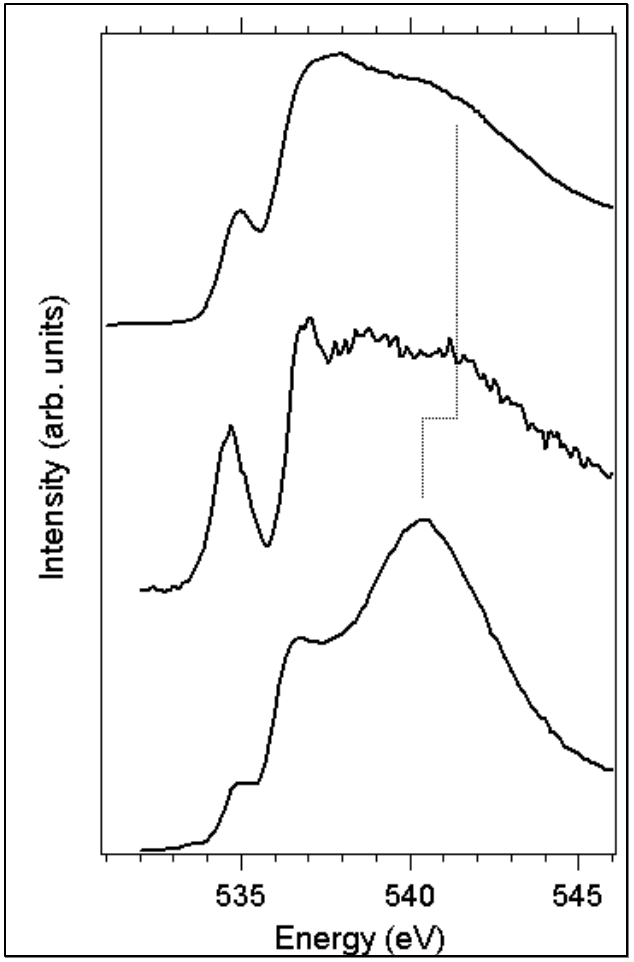
Probing depth

B’	1 ± 0.7 Å
A	≥ 50 Å

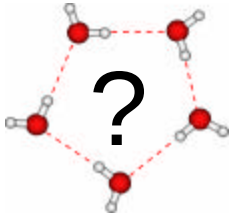
Ice samples:

- Thin films
- Grown epitaxially on Pt(111)
- Kept at 100K

Liquid water similar to the surface of ice

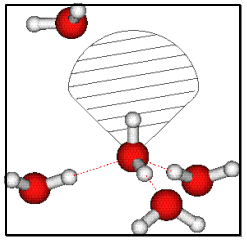


Liquid water



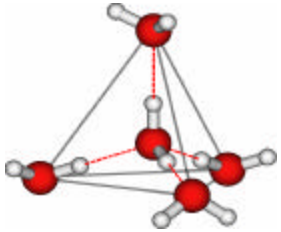
Liquid water and ice surface have a similar local structure.

One free O-H bond at the ice surface



Most molecules in liquid water have one non-H-bonded OH group

Fully coordinated in bulk ice



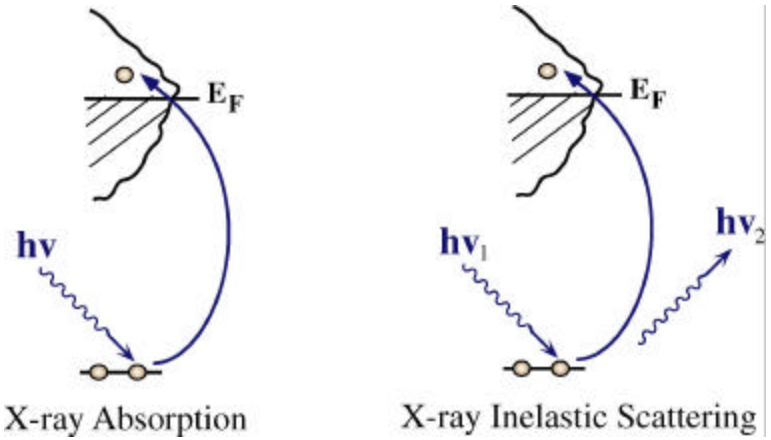
~10% are fully coordinated

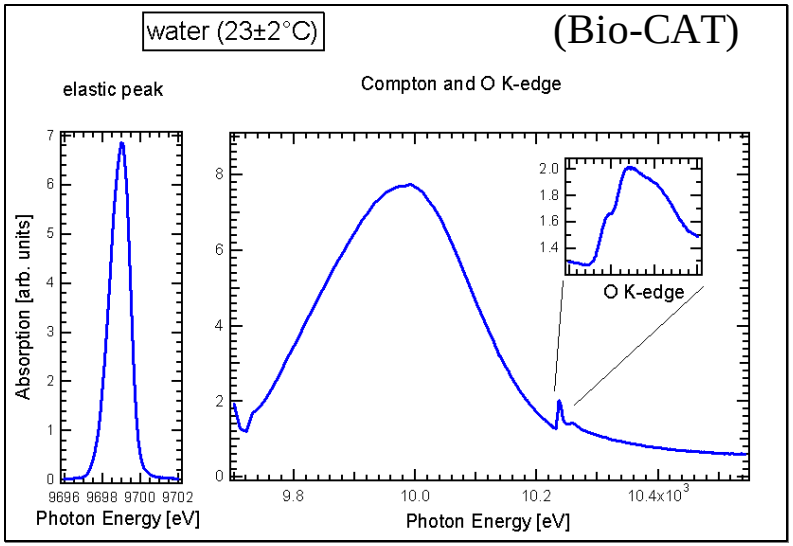
Surface effects in water x-ray absorption, temperature/pressure effects…?

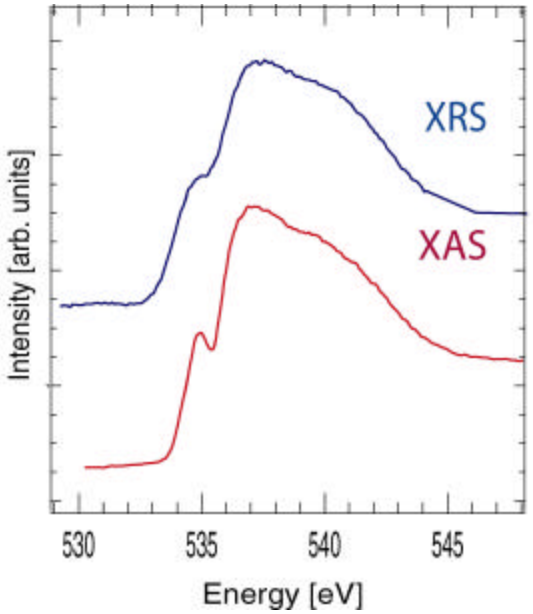
X-ray Raman Spectroscopy

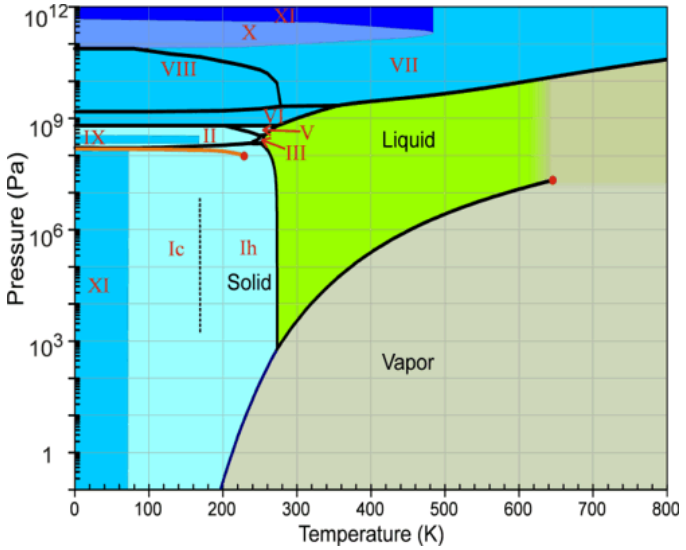
Soft X-ray NEXAFS using hard X-rays

APS beamline 18-ID
(Bio-CAT)





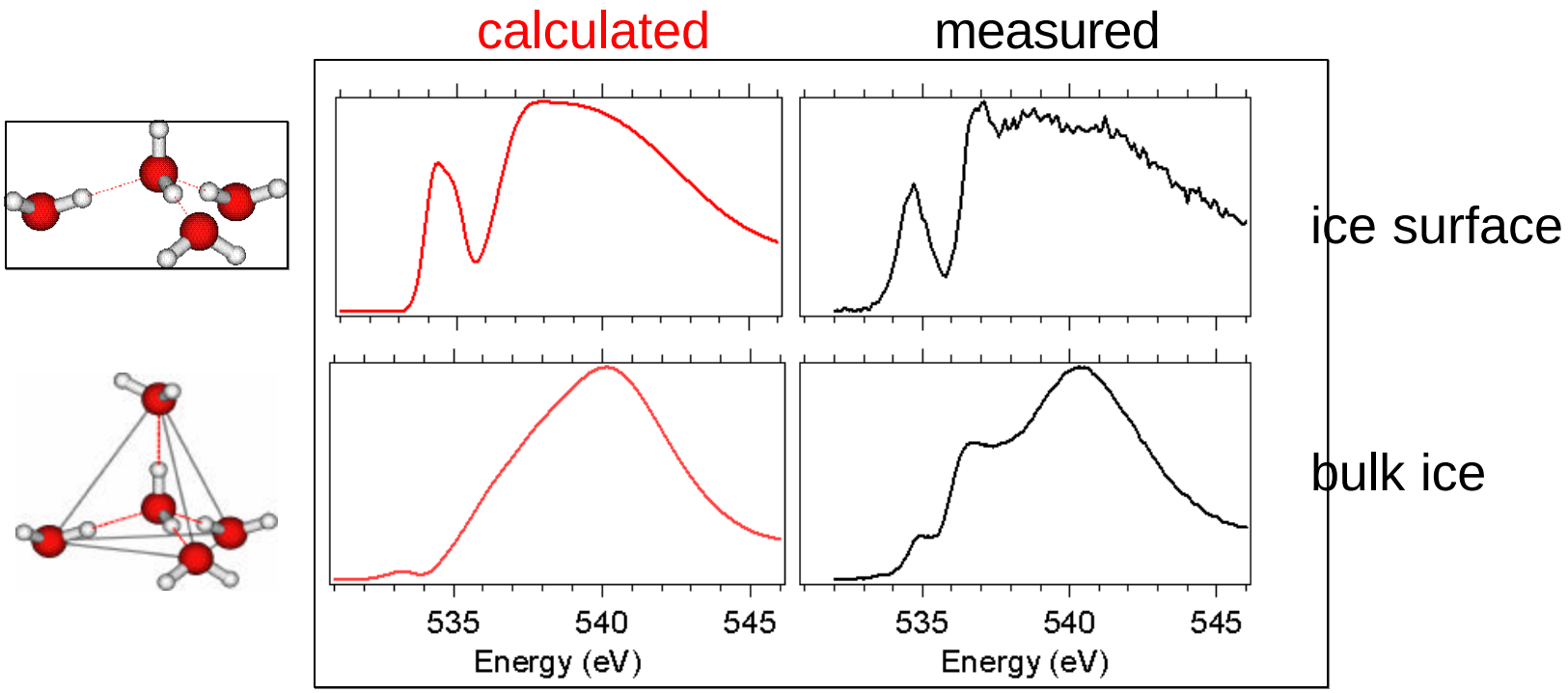




Model calculations

Systematic variation of local structure in model cluster:

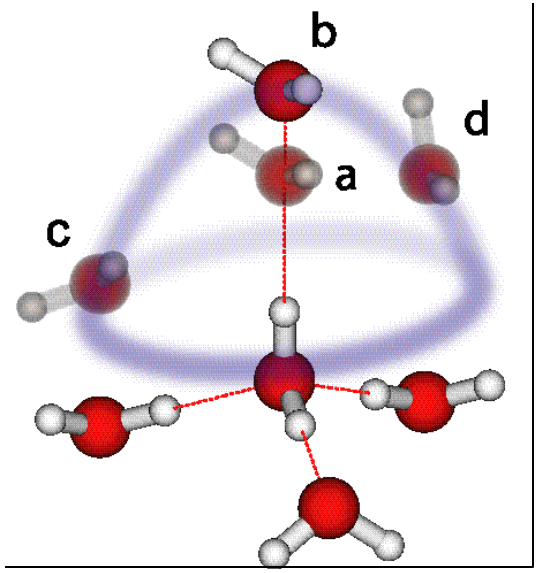
- 11 molecules
- DFT calculation
- Transition potential method

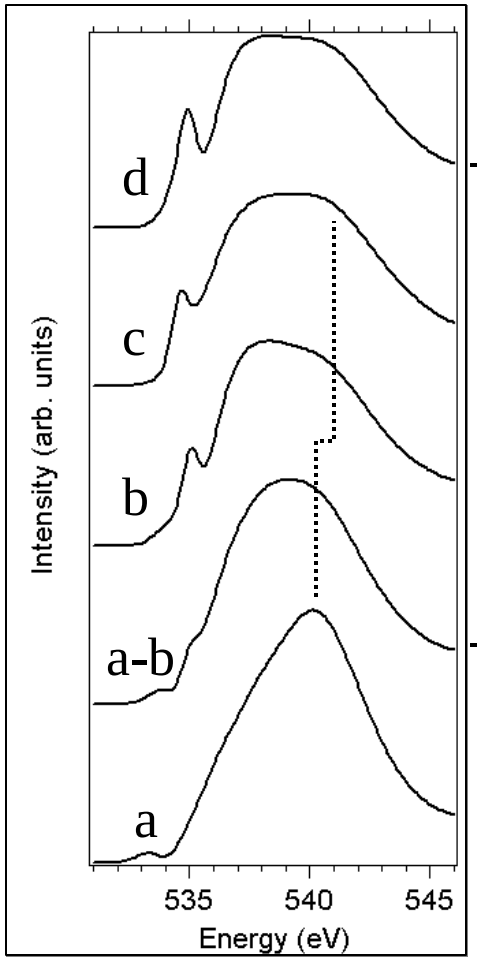


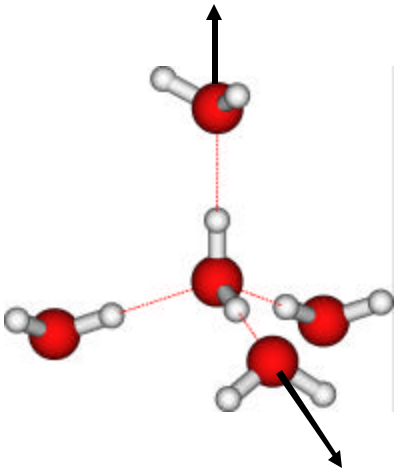
Breaking donor H-bonds

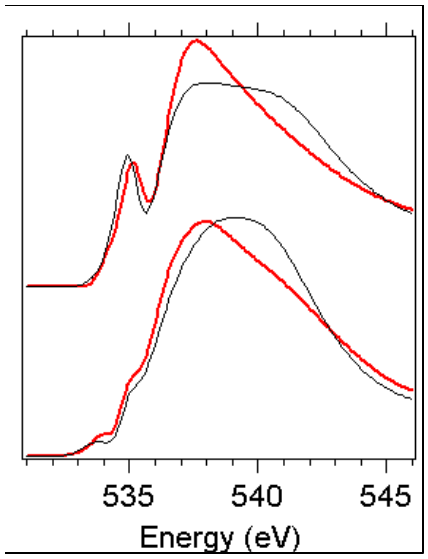
Move molecule on *one* H-side:

Move molecule on *both* H-sides:

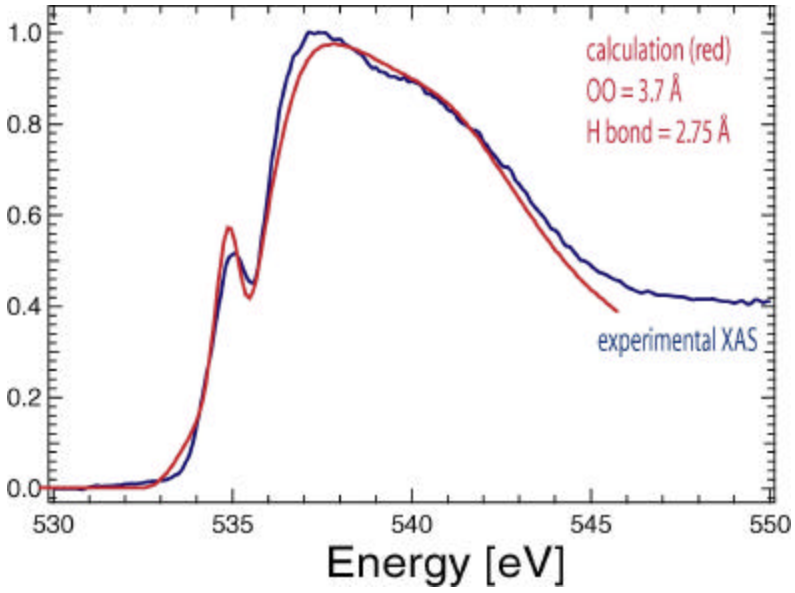




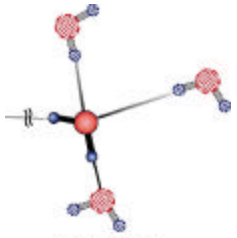




Nearly all waters are SD species

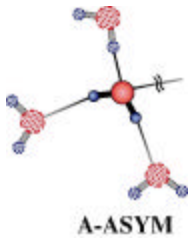


Comparing water spectrum with one theoretical spectrum

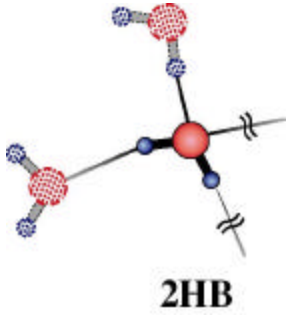


All waters SD species?

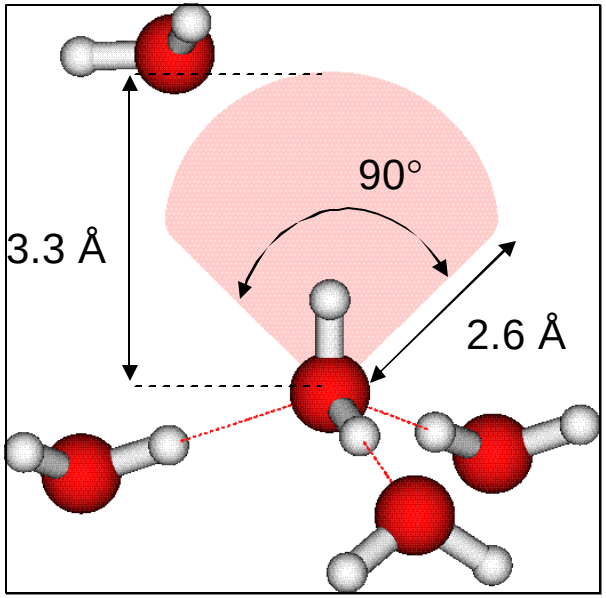
Symmetry requires the same amount broken H-bonds on oxygen side



Most water molecules in 2 hydrogen bonded structures with broken donor and acceptor on both molecule

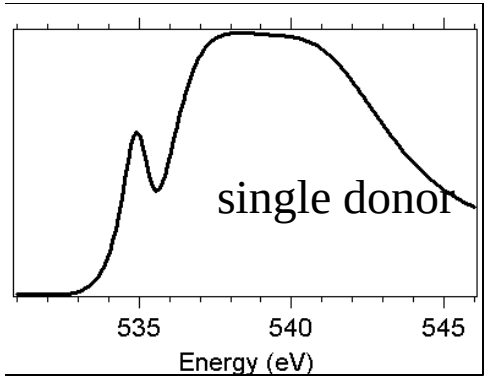


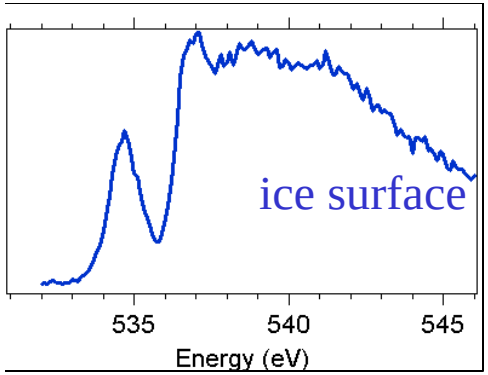
Electronic Structure Definition of a H-bond



Distortion beyond red zone

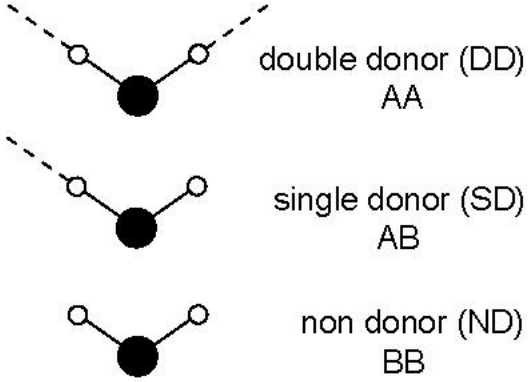
→ Characteristic shape (ice surface)
→ Broken donor H-bond





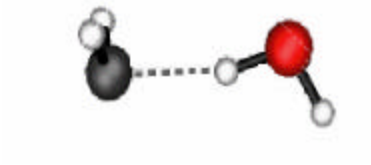
Three main configurations:

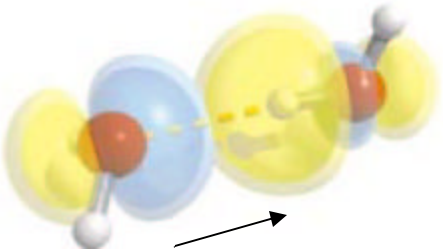
Double donor:	both in
Single donor:	1 in, 1 out
Non donor:	both out

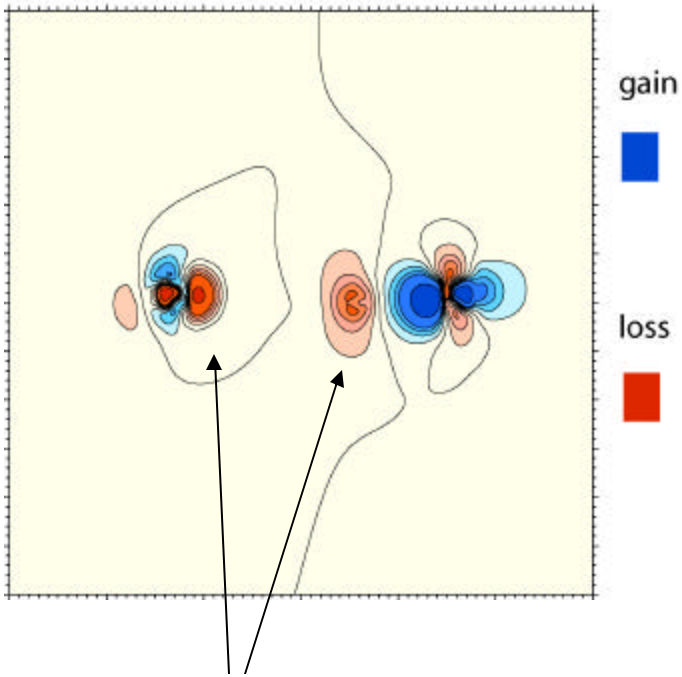


Quantify populations in liquid water and test molecular dynamics simulations!

Water Dimer Bonding

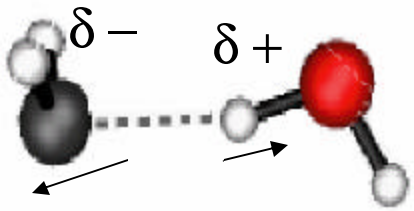






Charge transfer from lone pair
to antibonding O-H orbital

MINIMIZE REPULSIVE INTERACTION



Depletion of charge
between bonding units

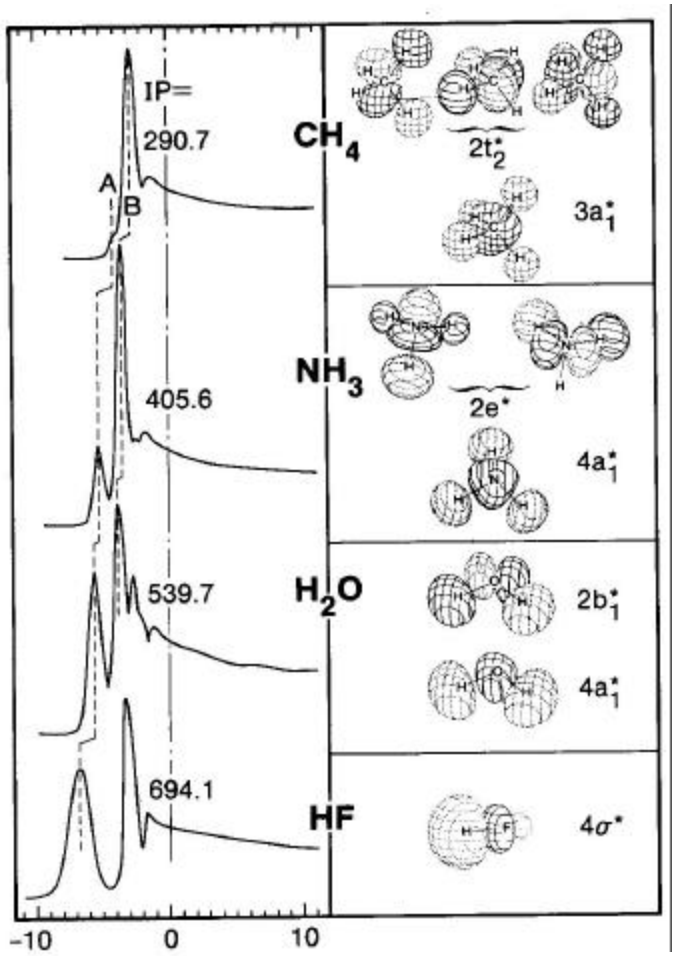
Charge transfer to decrease repulsive interaction

Weakening of O-H internal bond

H atom can get for maximum electrostatic interaction

Origin of the Pre-edge Peak: Theory

Dipole selection rule, O 2p contributions, s-p hybridization in MO's.



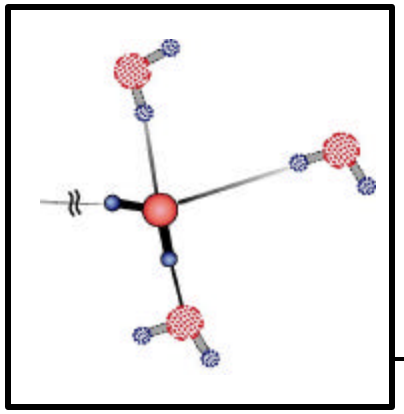
J. Stöhr, NEXAFS spectroscopy.

Broken local symmetry

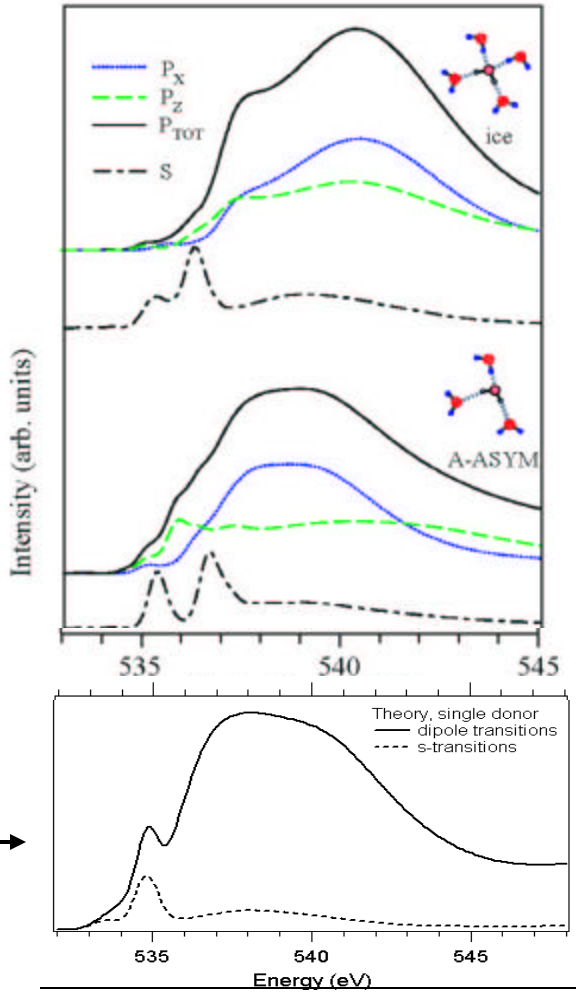
↓

s-p mixing

dipole selection rule 1s → 2p

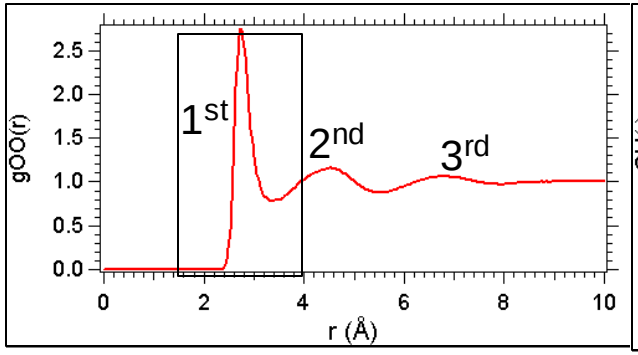


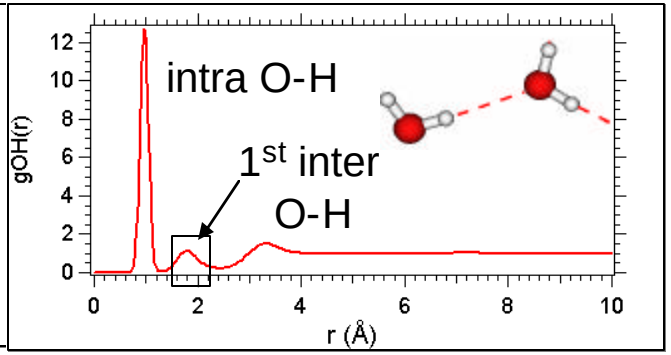
Projection of water spectra in s, p_x and p_z components.



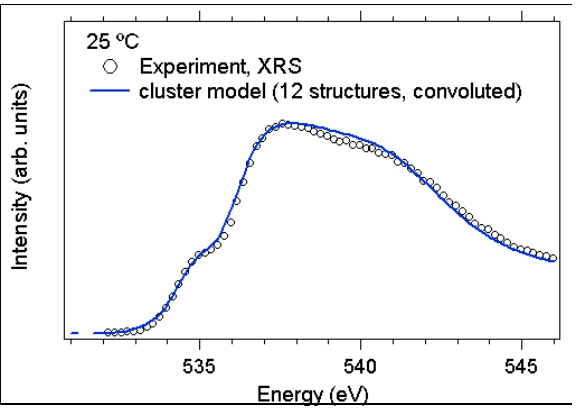
Cavalleri et al., Chem. Phys. Lett. **364**, 363 (2002).

Local structure of water at 25 ºC

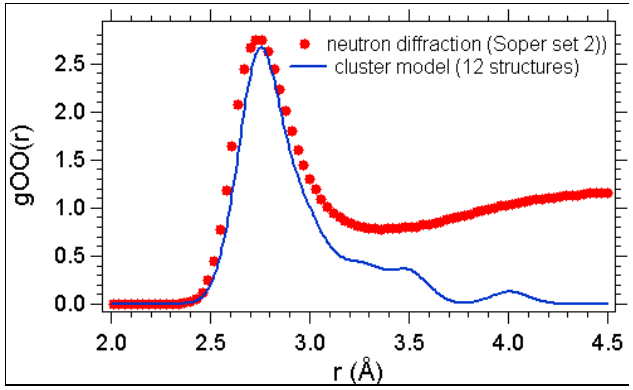




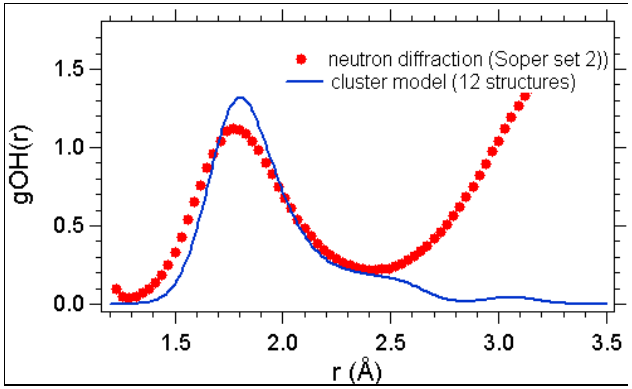
XRS



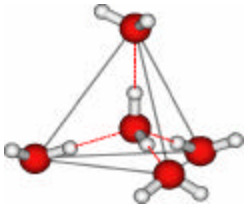
O-O RDF

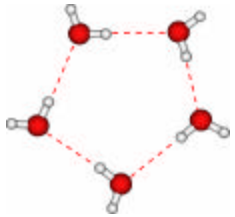


O-H RDF

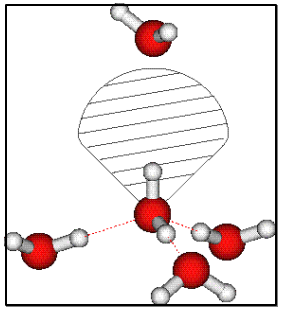


Best combination **10% double donor** **85% single donor** **5% non donor**





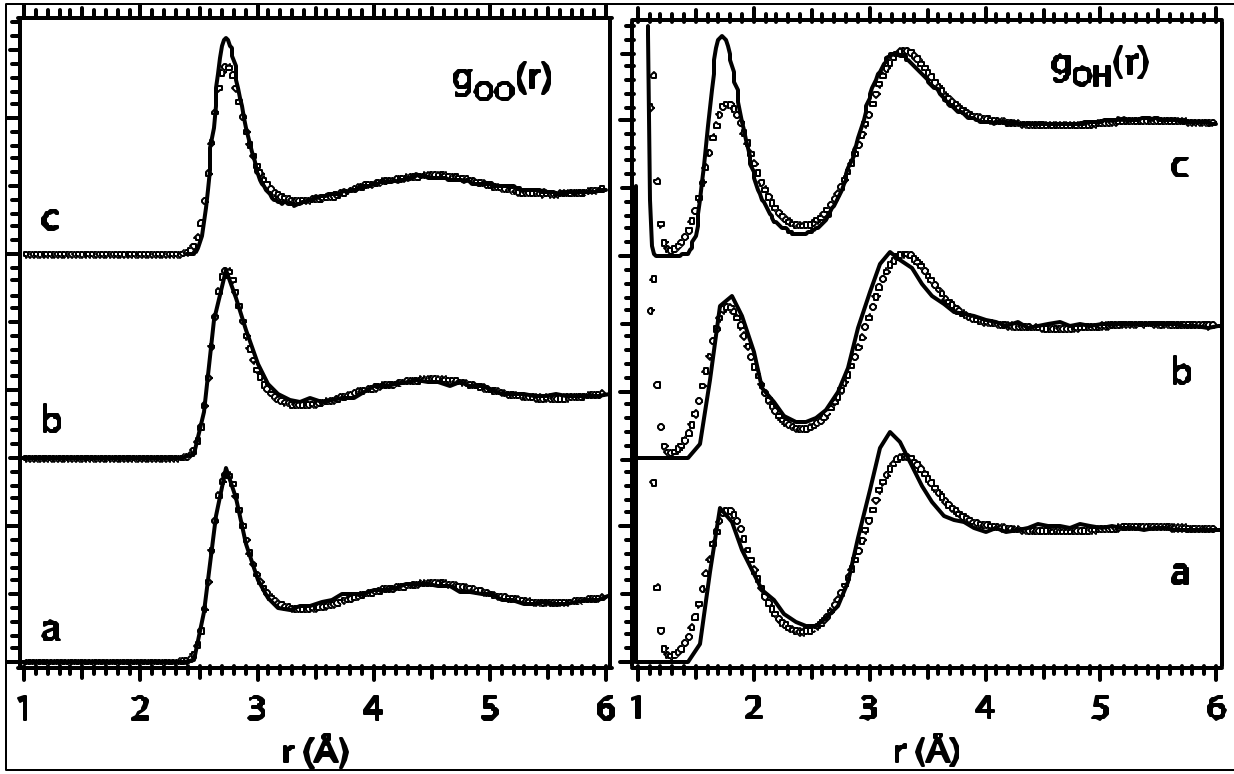
Extended Models



Case A: Artificial MD simulation by not allowing molecules to be in the cone, Results consistent with XAS

Case B: TIPP5 standard MD simulation

Case C: SPC MD simulation

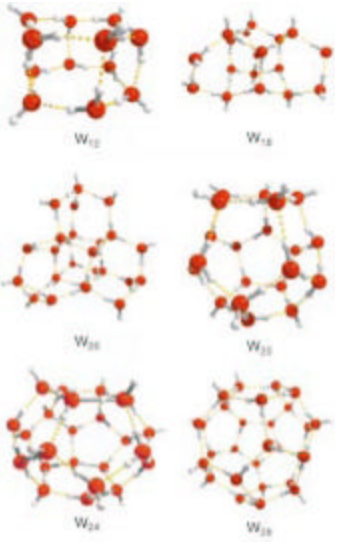


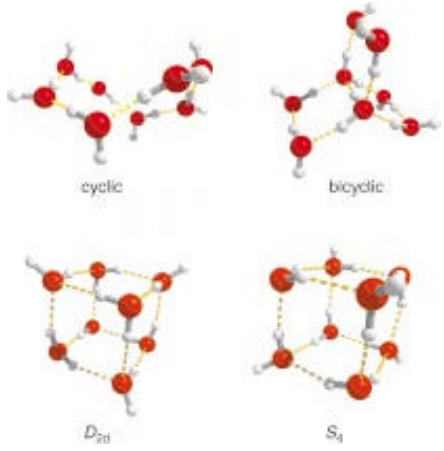
Method	EXP+FIT	a	b	c
DD	10^{+15}_{-10}	25		70
SD	$85^{+}_{-}15$	75		27
ND	$5^{+}_{-}5$	0		3
TOTAL	100	100		100
n_{HB}	$2.1^{+}_{-}0.4$	2.5		3.3

Cluster Equilibrium Theory

Weinhold et. al. J. Chem. Phys. 110, 508 (1999)

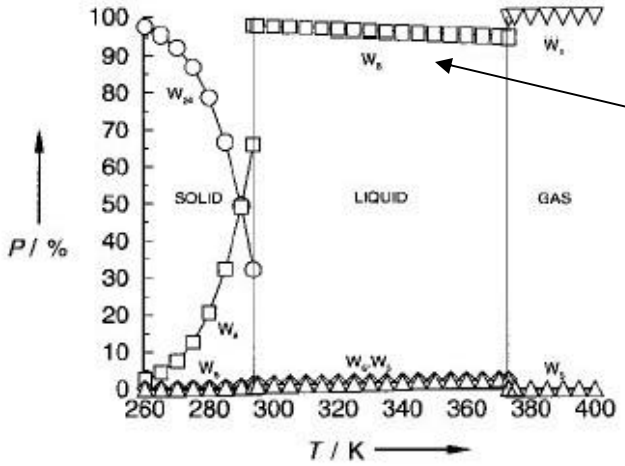
Renewal of old model

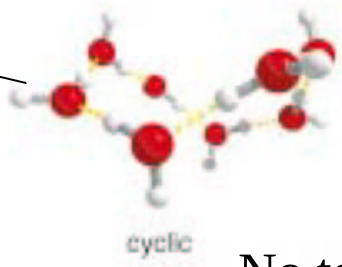




Thermodynamic equilibrium between different clusters

Properties of clusters obtained from quantum chemistry calculations





Cyclic Octamer dominates calculated distribution

All waters 2HB

No temperature dependence

Not consistent with MD simulations

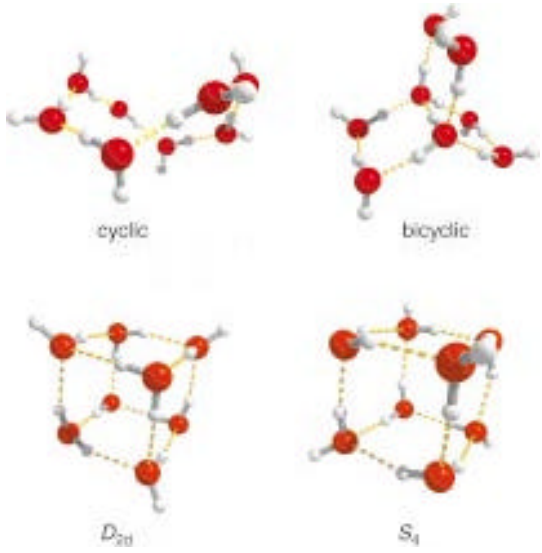
Stability of Clusters

Many Body Cooperativity effect

Hartree Fock Calculations by Wienhold

Large variation of H-bond strength

Cluster size	H-bond energy (a.u)
2	6.0
5	10.7
8 (ring)	11.4
8 (cube)	7.6
20	7.7
26	9.0

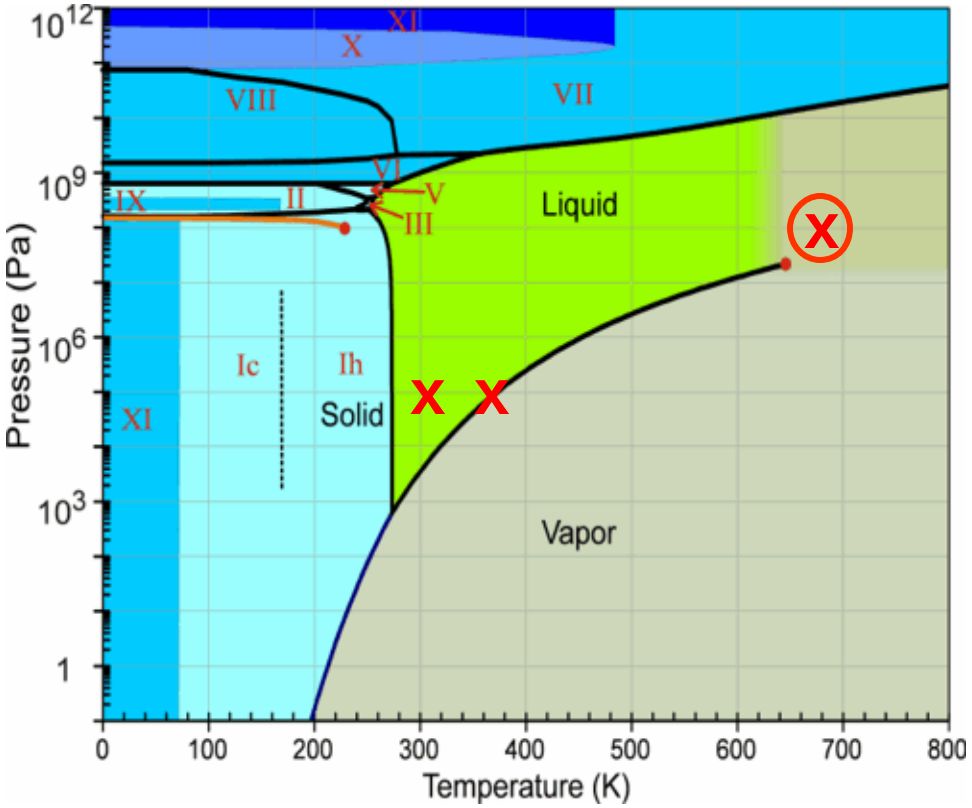


$$\Delta G = \Delta H - T\Delta S$$

S: Entropi numbers of ways to partition the energy

The cyclic octamer has more low energy modes of freedom compared with cubic octamer

Supercritical water



XRS

380 °C
300 bar
0.5 g/cm^3

- New phase
- Structure and bonding
- Properties of sc water
- Solvent for organics
- …

Outlook

X-ray Raman can probe the whole water phase diagram

High and low density ice

Supercooled water

Supercritical water

Water in confinement

Biological water

Aqueous solutions

pH dependence

Ions in solutions

CO_2 and CH_4 in water under pressure