X-ray Spectroscopy and Scattering Studies of Water

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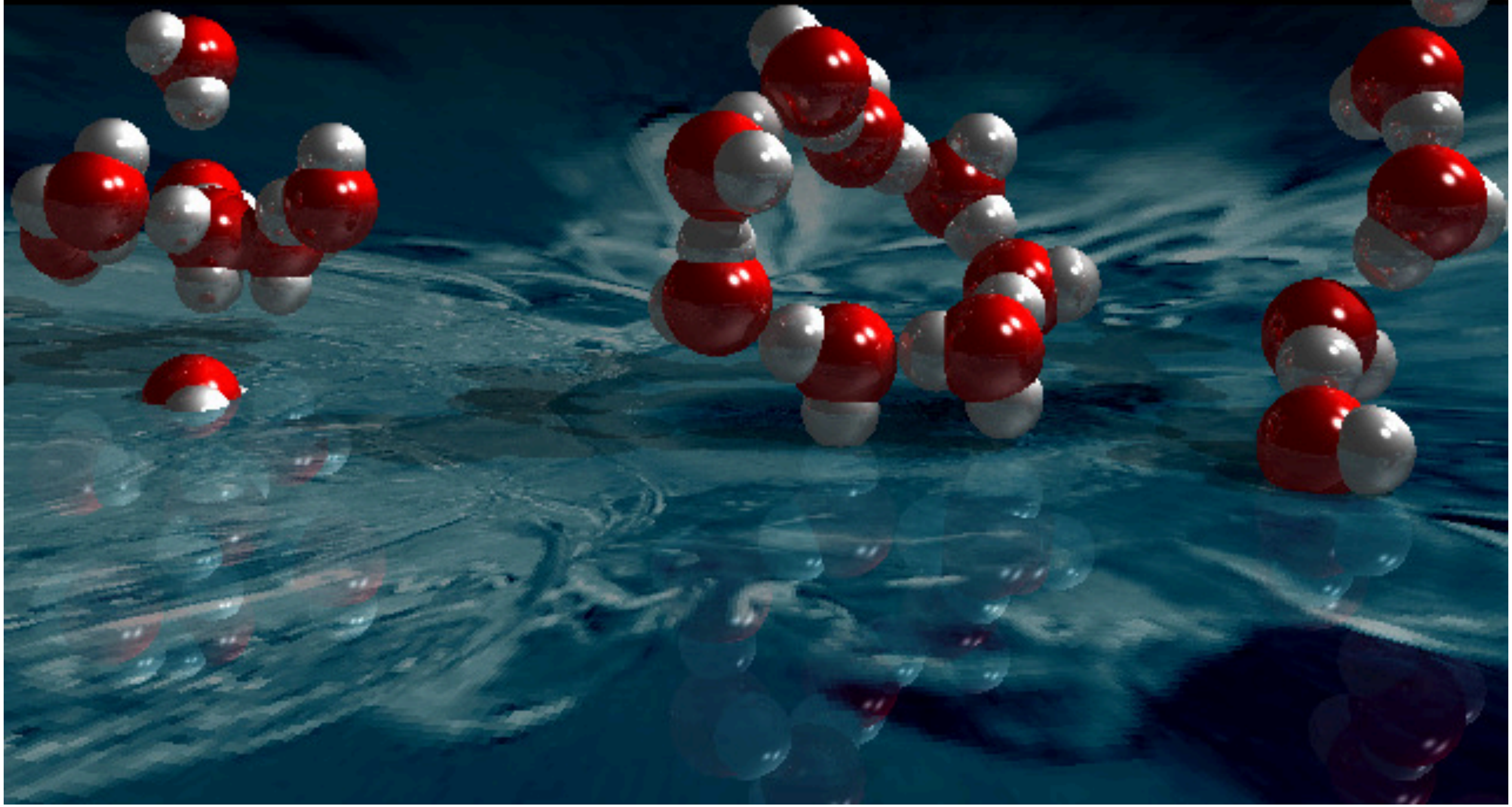

Coworkers, Funding and Experiments

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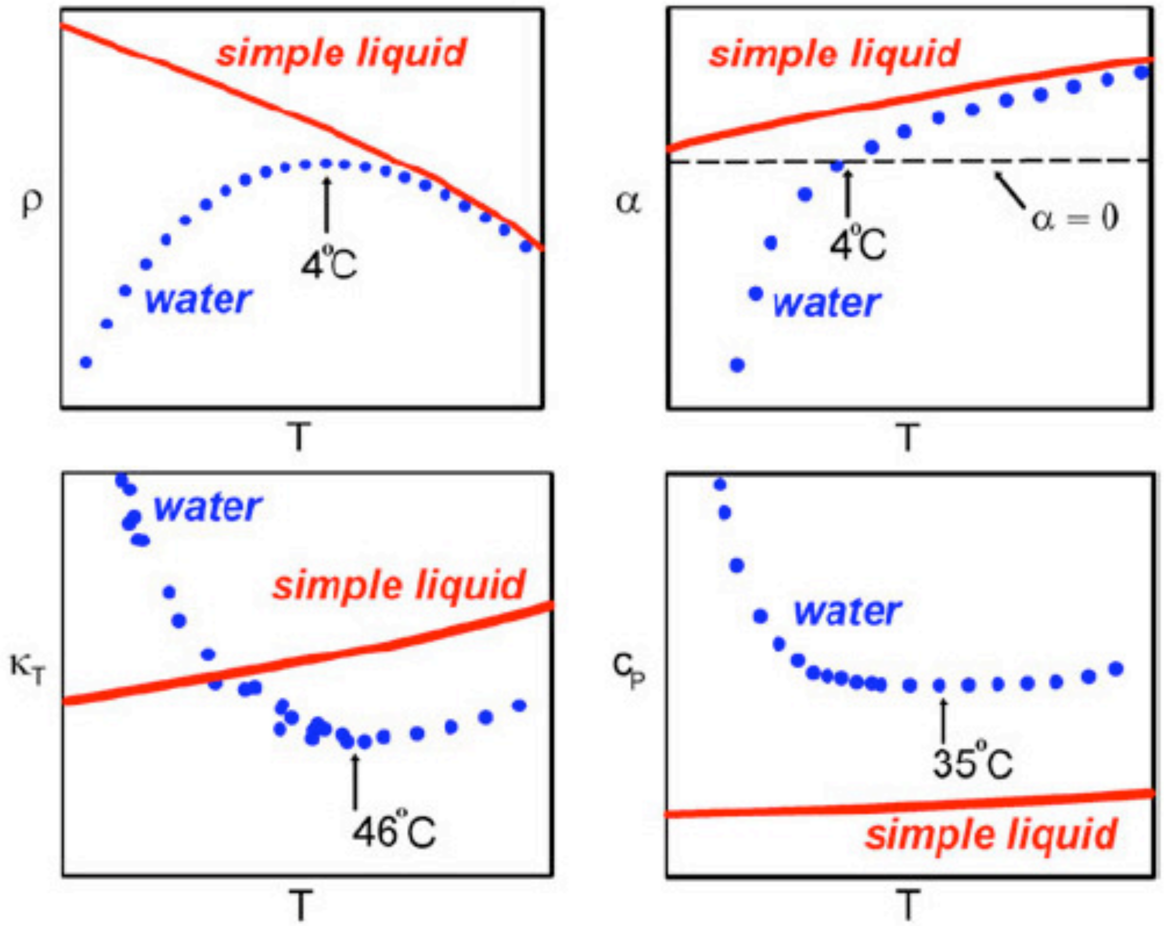
Anomalous Properties of Water

Density

Thermal expansion

$\langle(\delta S\ \delta V)\rangle = V k_B T \alpha$



Isothermal Compressibility

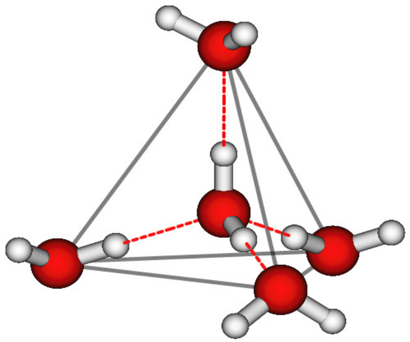
$\langle(\delta V)^2\rangle = V k_B T \kappa_T$

Heat Capacity

$\langle(\delta S)^2\rangle = N k_B c_p$

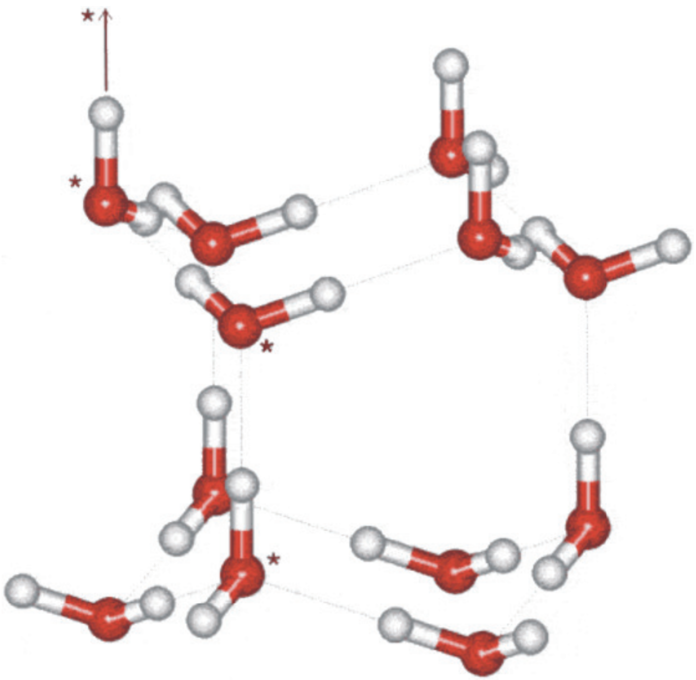
. [P. G. Debenedetti, *J. Phys.: Condens. Matter* **15**, R1669 (2003)]

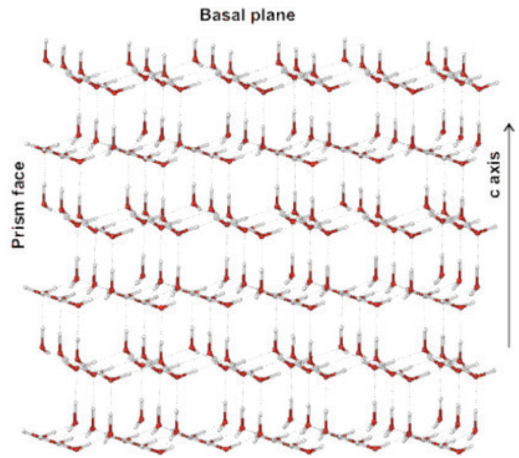
Ice

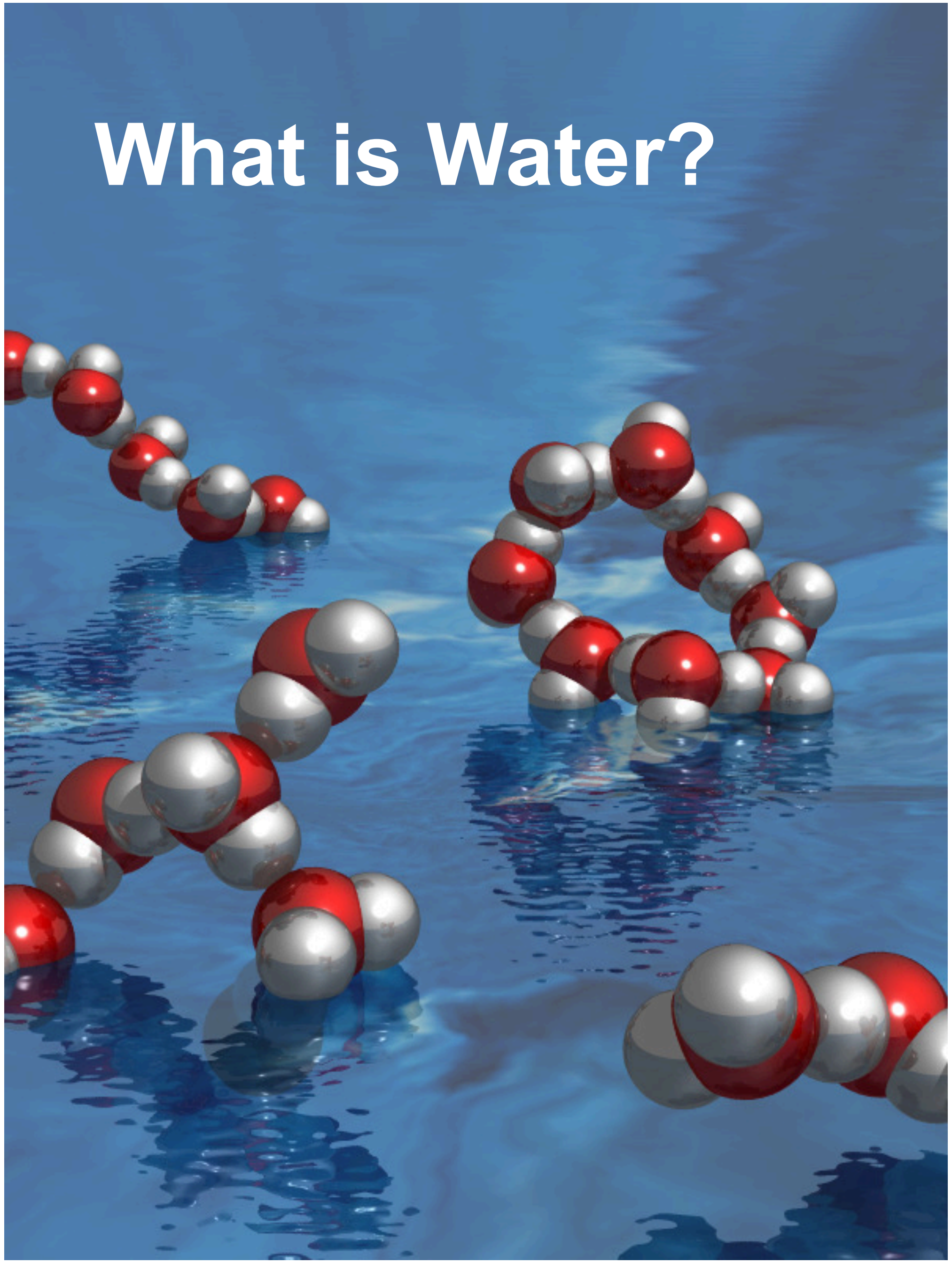


Open spaces where no molecules are present

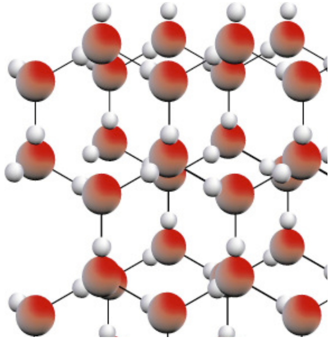
If molecules move to fill the open space there will be an increase in the density






What is Water?

Mixture or Continuum Models



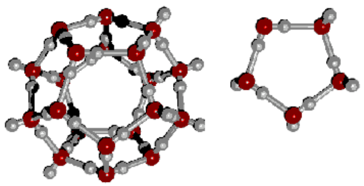
Ice Ih
Tetrahedral structure

Old debate prior to 1980

Two extreme models for water

Mixture models

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

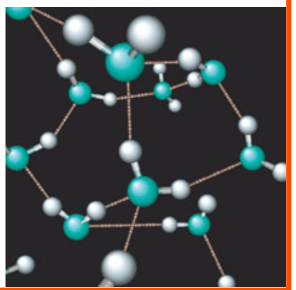


Röntgen 1892

Continuum Models

"Infinite Network of disordered tetrahedral water."

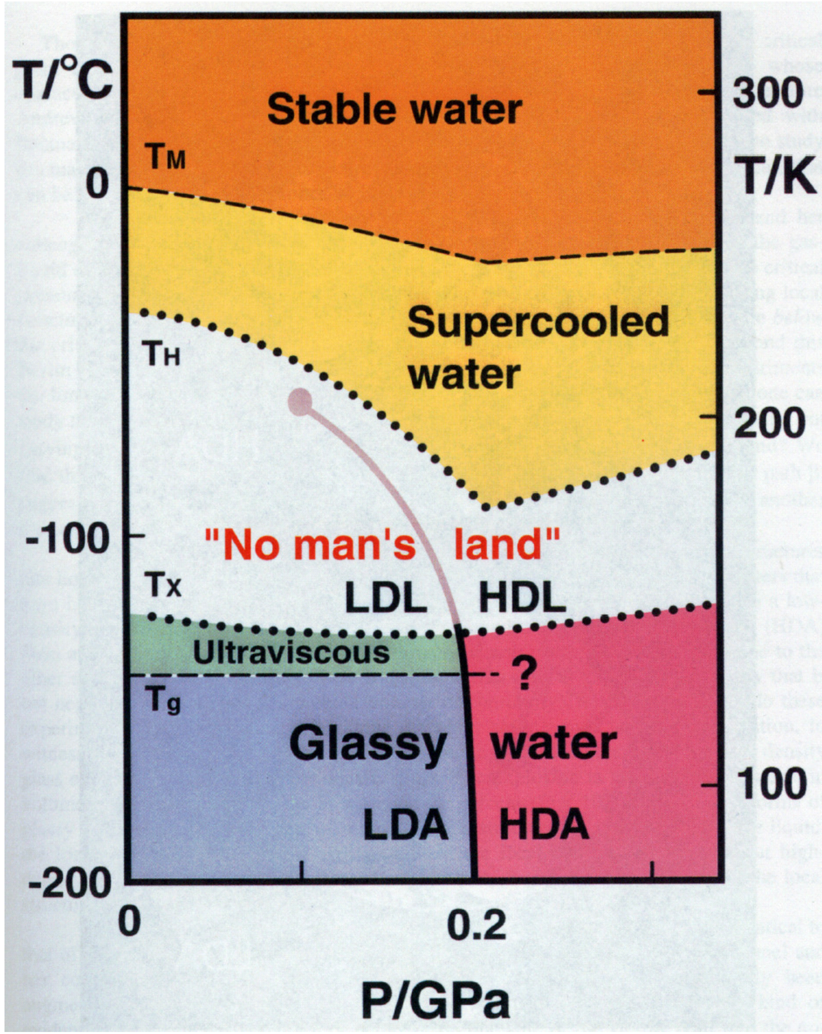
MD simulations! →



~3.5 HB/molecule

Mostly accepted picture

Polyamorphism and two liquids



ρ(HDA)=1.17 g/cm^3

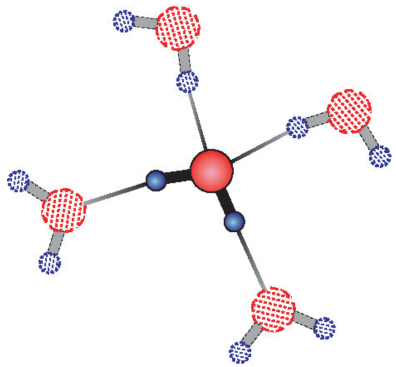
ρ(LDA)=0.94

ρ(Ih)=0.92

ρ(Ic)=0.92

H. E. STANLEY “Mysteries of Water” Les Houches Lecture, May 1998
Originally Proposed P. H. Pool and H. E. Stanley et.al Nature 360, 324 (1992)

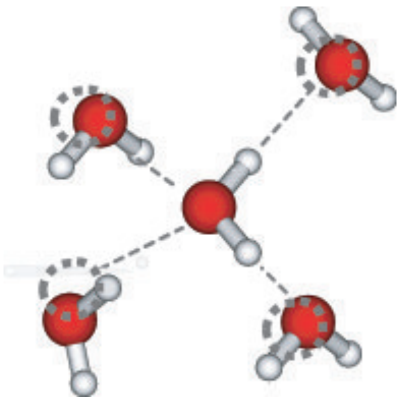
Local Structures



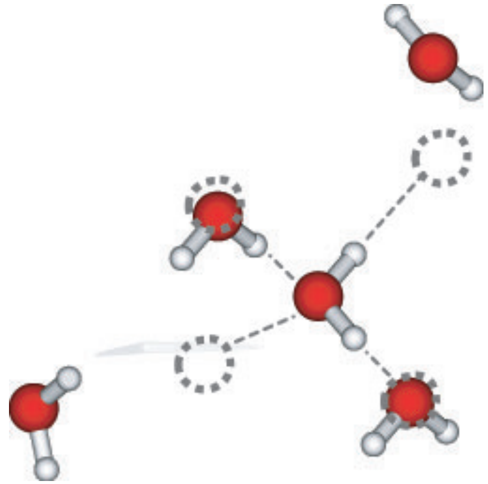
Ice

Tetrahedral Coordination

Energy



Distorted Component Water



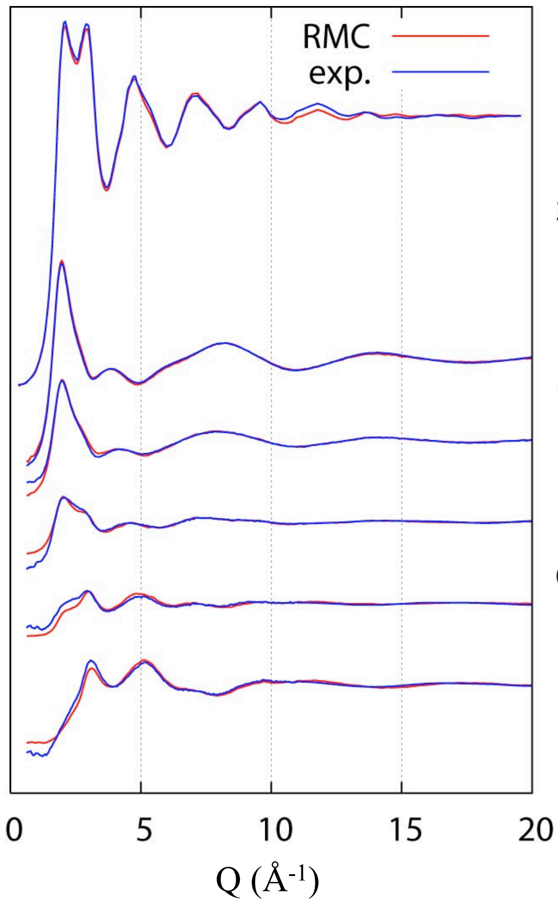
Symmetrical distortions

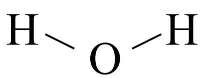
Tetrahedral model

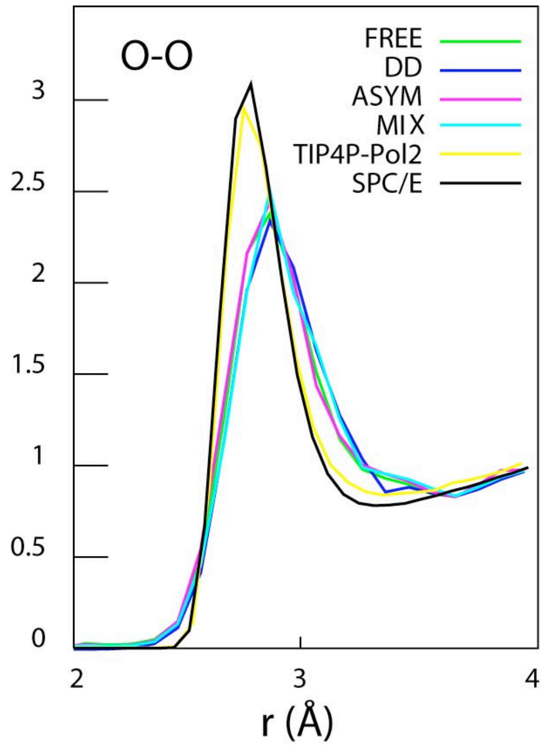
Asymmetrical distortions

Diffraction allow for many different structures

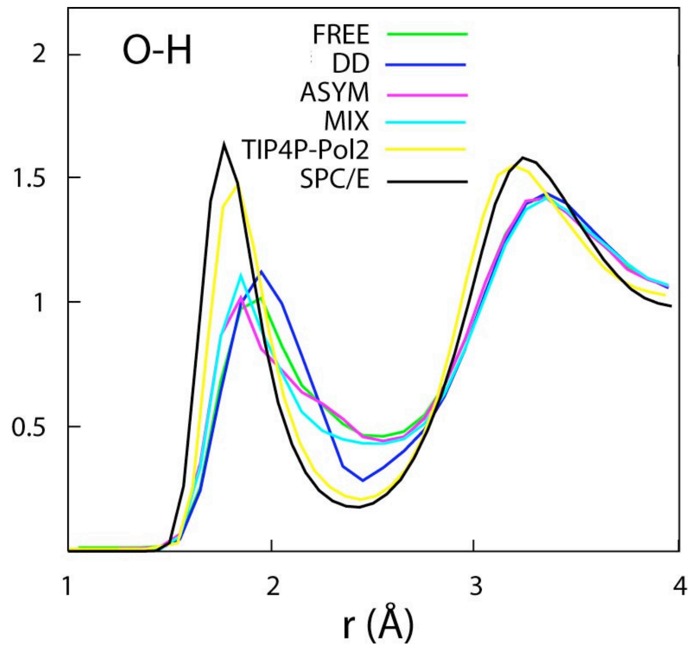
Reverse Monte Carlo fitting of new x-ray diffraction and neutron data







x-ray diffraction leads to robust O-O correlations

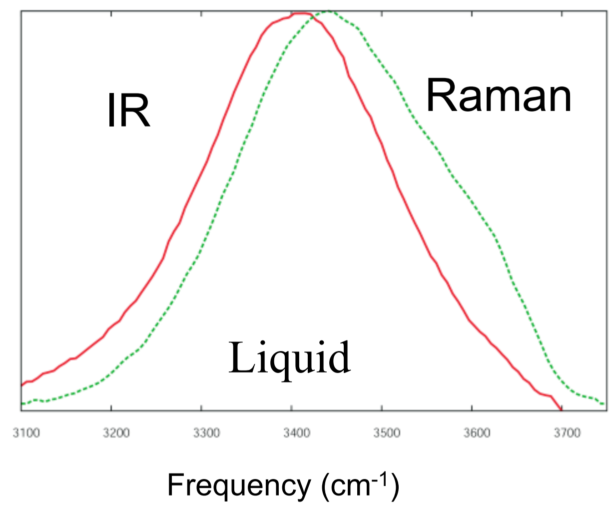


less sensitivity in neutron diffraction leads to large variations on O-H and H-H

Wikfeldt et al.

Spectroscopy

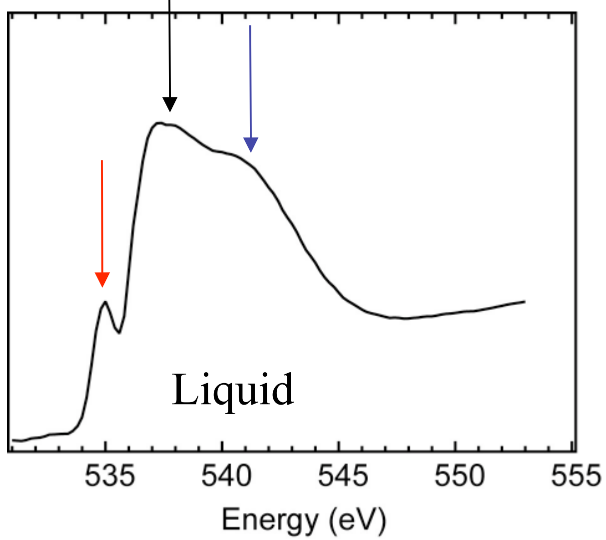
OH stretch with HOD in D_2O



No spectral fine structure
Large number of interpretations

J. D. Smith et al. PNAS 102, 14171 (2005)

X-ray Absorption Spectroscopy

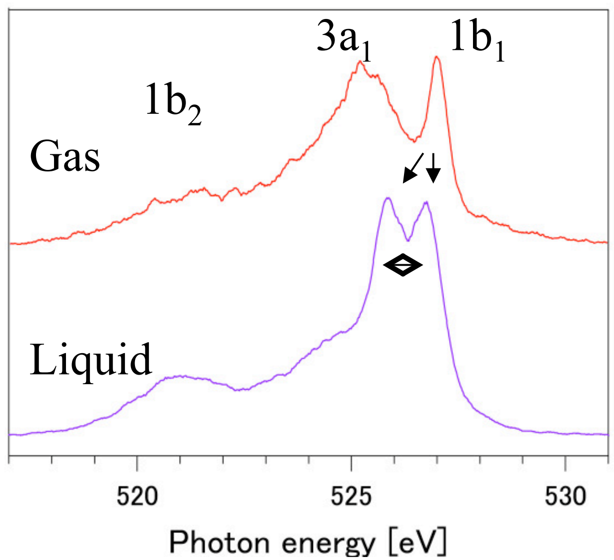


Wernet et al, *Science* **304** (2004) 995

More spectral fine structure!

Spectroscopic interaction time
Ultrafast no H-bond changes

X-ray Emission Spectroscopy

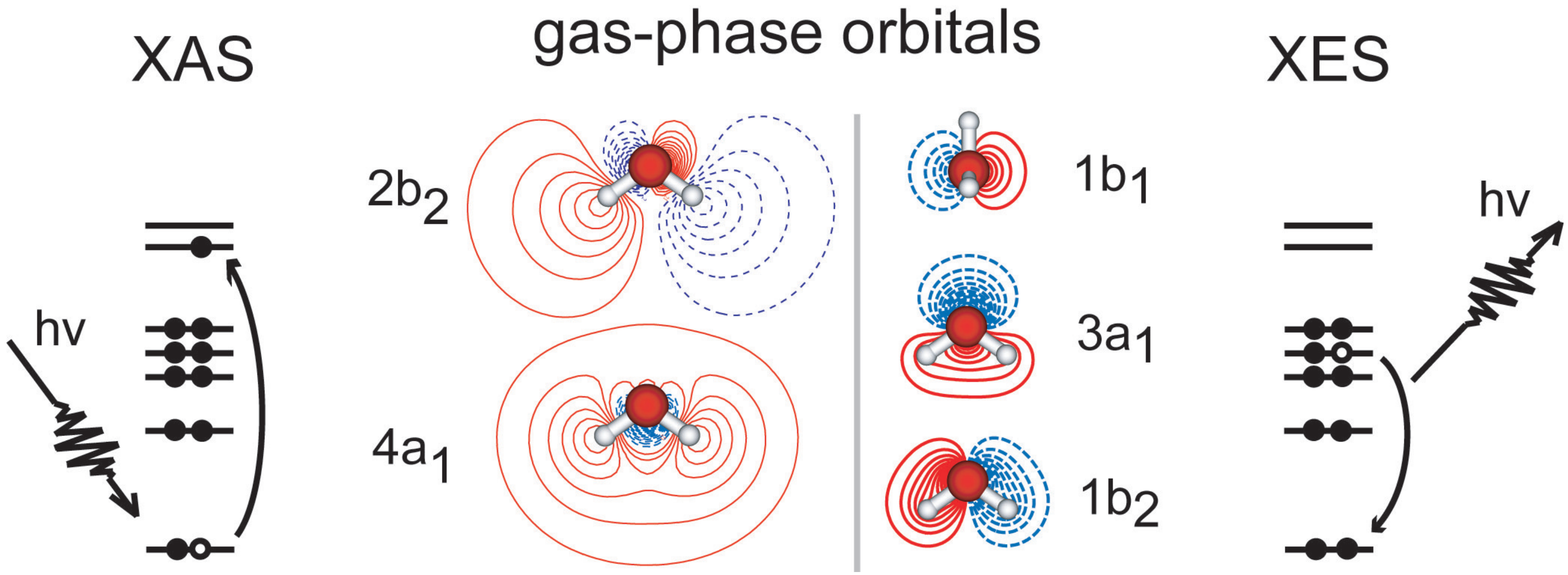


Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

Probing Valence Electrons

The hydrogen bond is directional

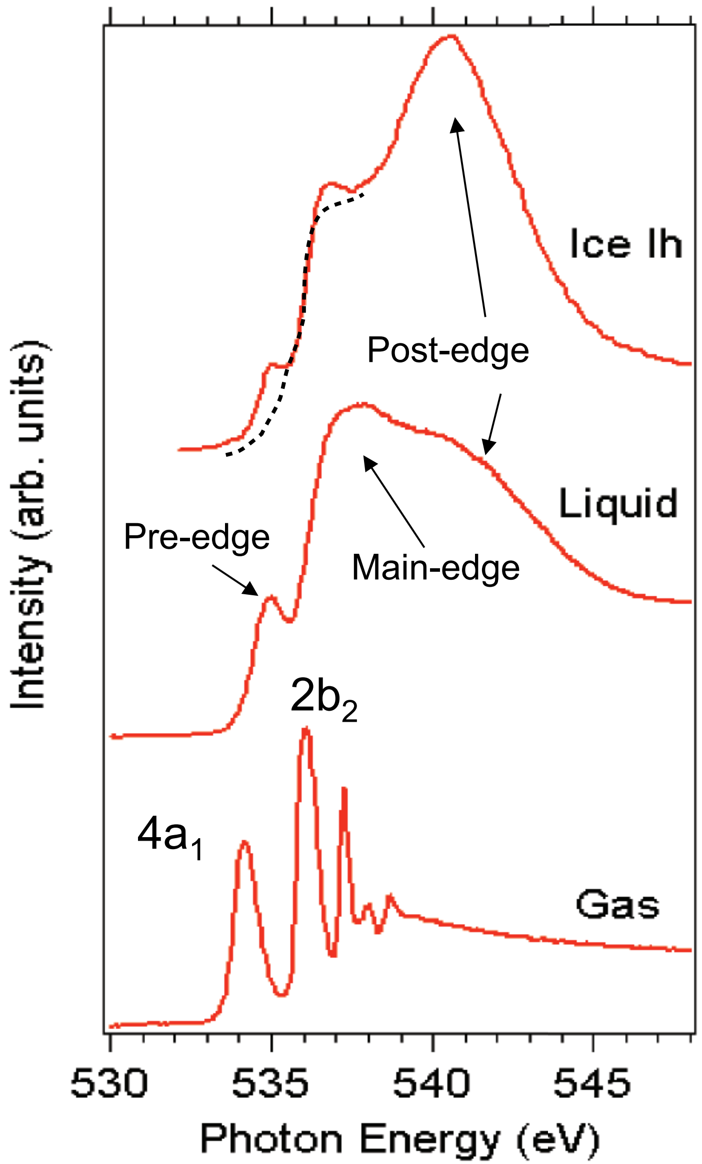
Probing of valence electrons



X-ray Absorption Spectroscopy
Probes Unoccupied Orbitals

X-ray Emission Spectroscopy
Probes Occupied Orbitals

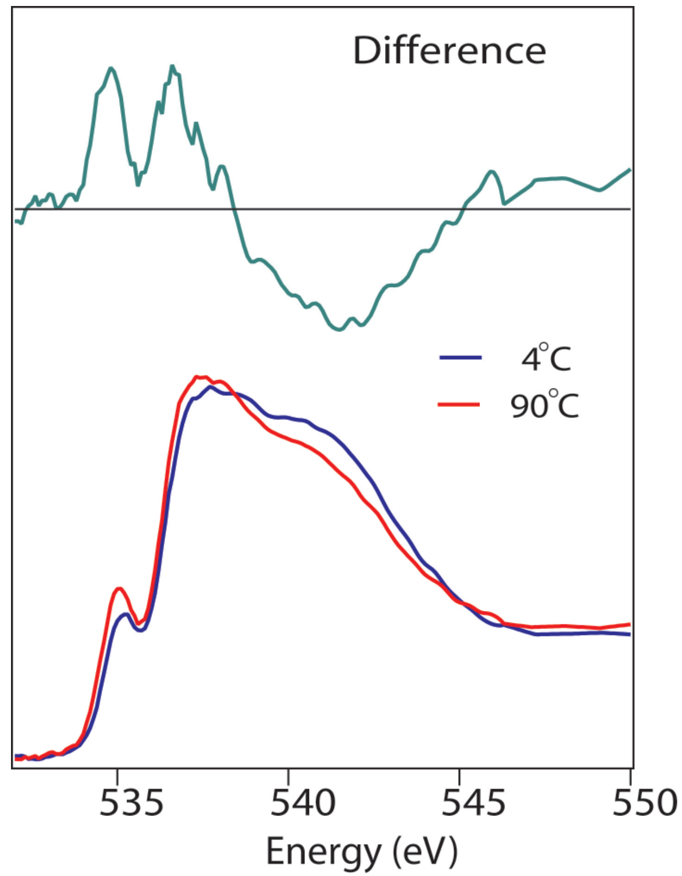
X-ray Absorption Spectroscopy of Water



Wernet et al, *Science* **304** (2004) 995

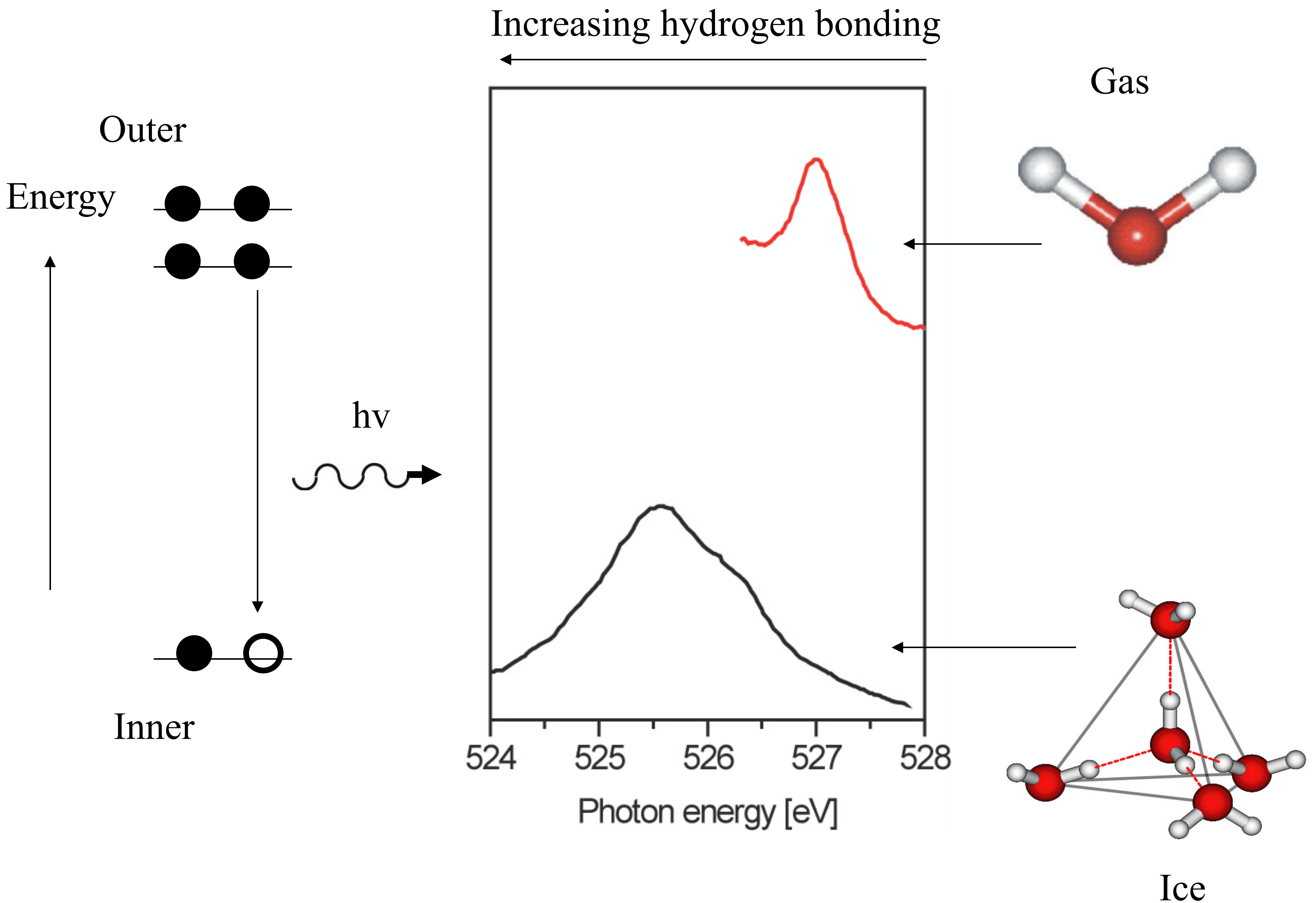
Myneni et.al. *J. Phys. Condens. Matter* **14** (2002) 213

X-ray Raman Scattering



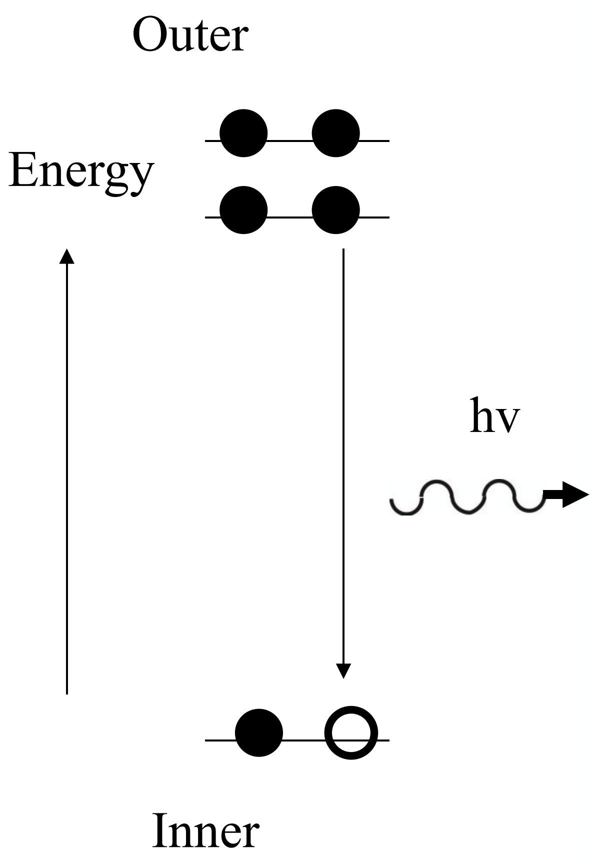
Huang *et al*., PNAS. **106** (2009) 15214

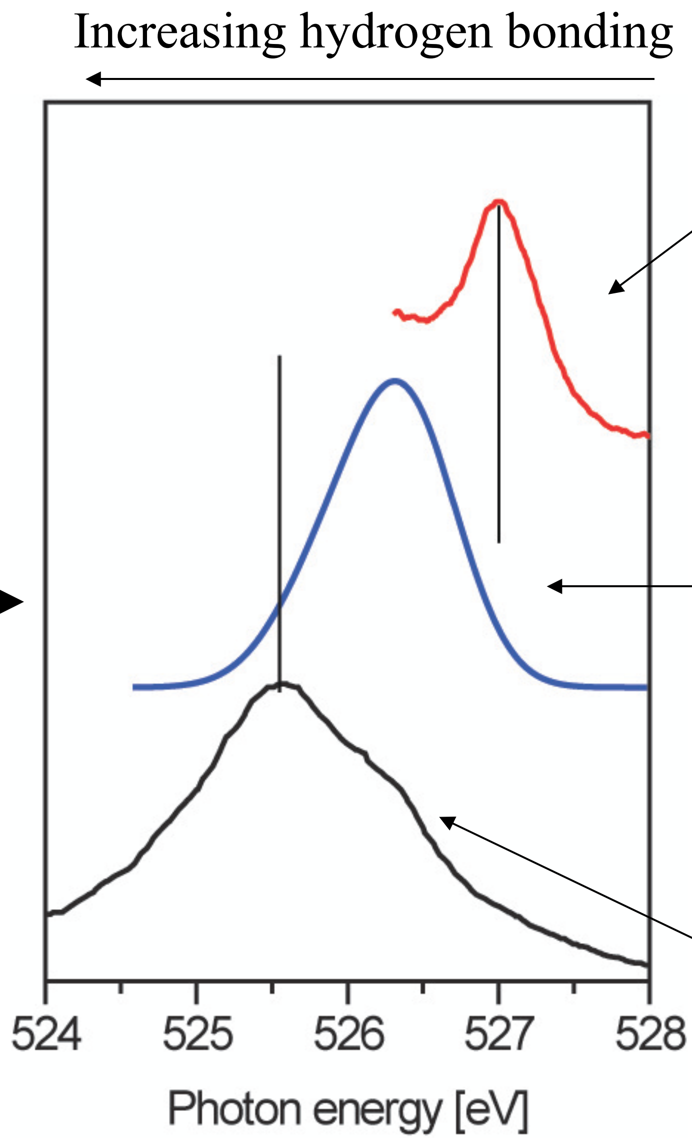
X-ray Emission Spectroscopy

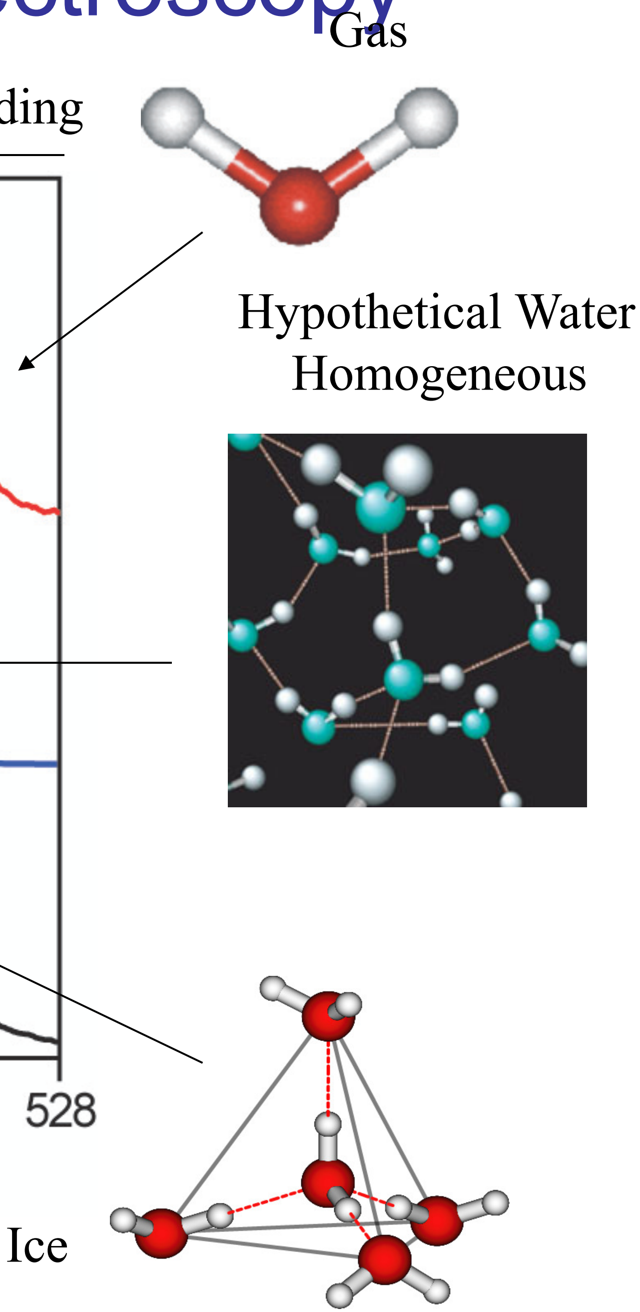


Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

X-ray Emission Spectroscopy

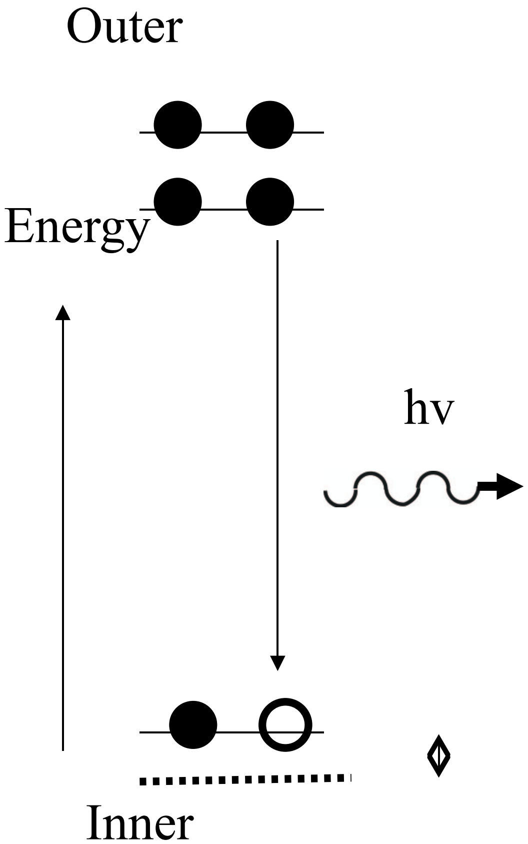


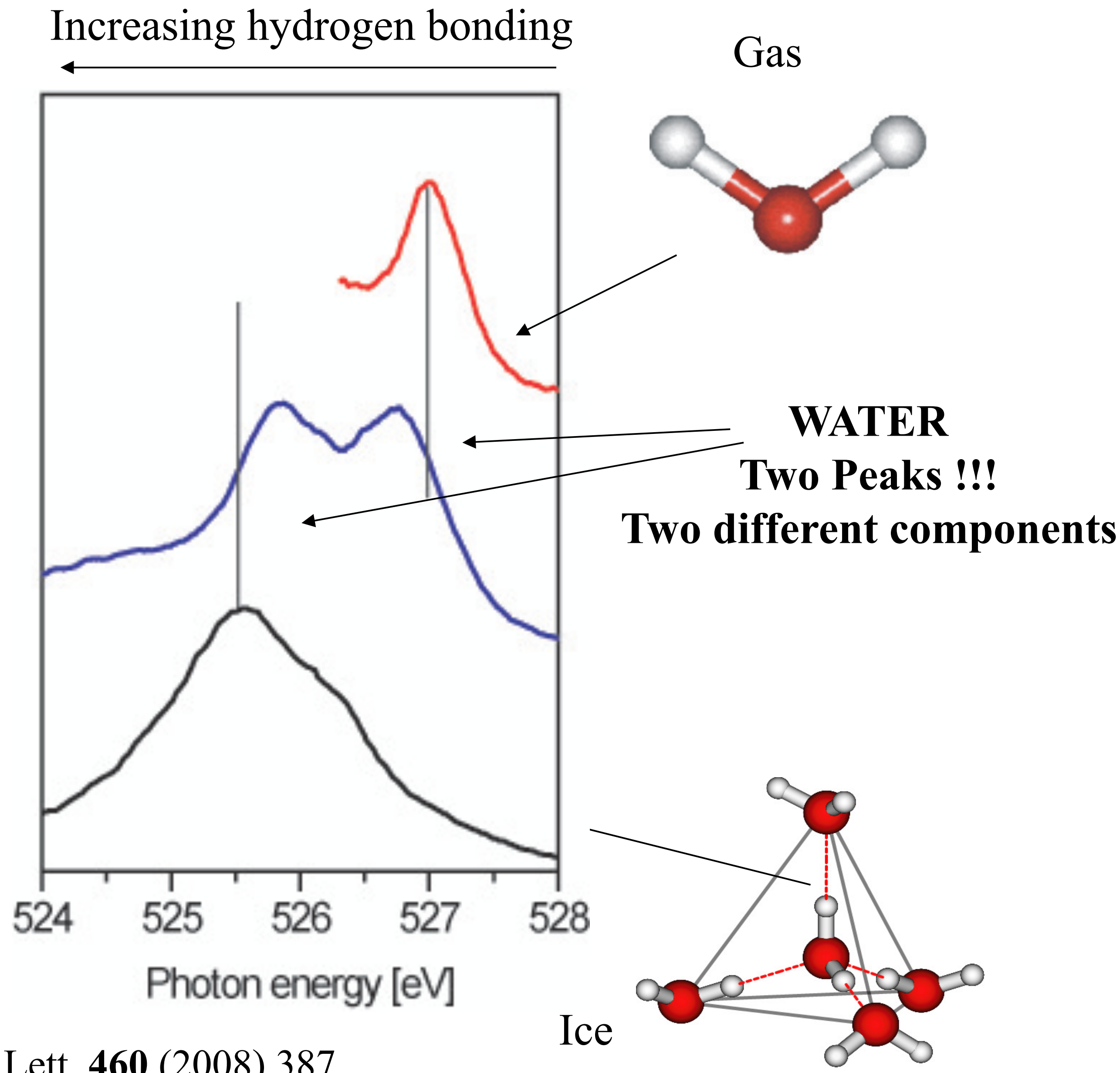




Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

X-ray Emission Spectroscopy





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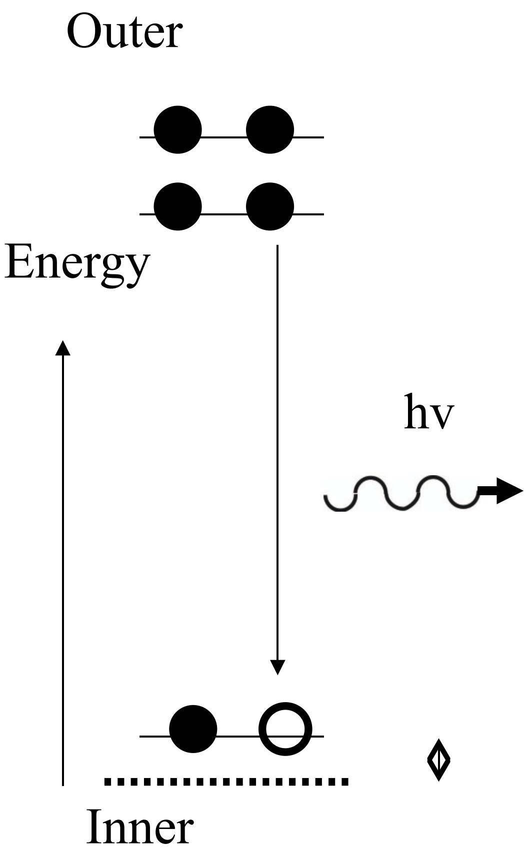

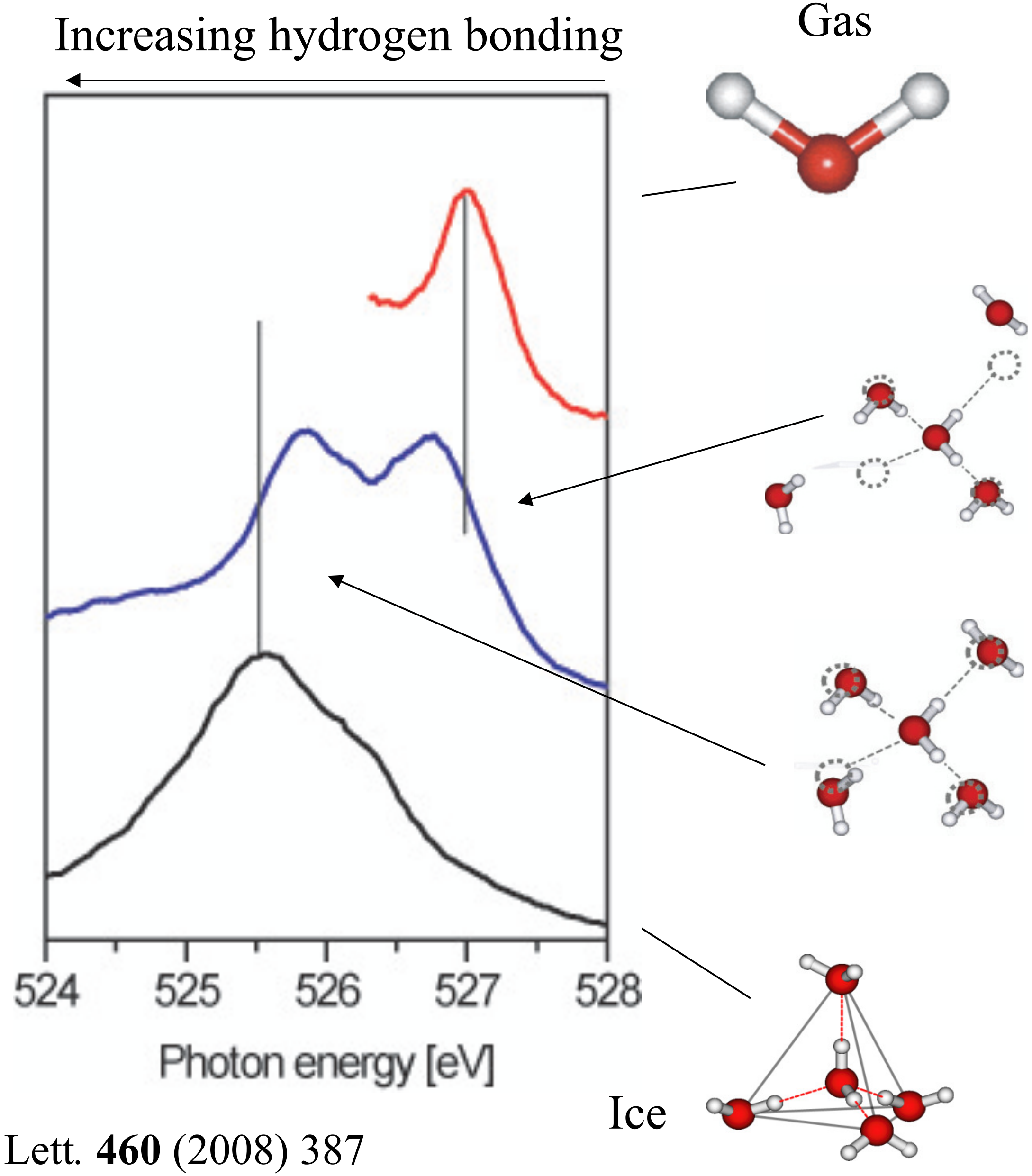

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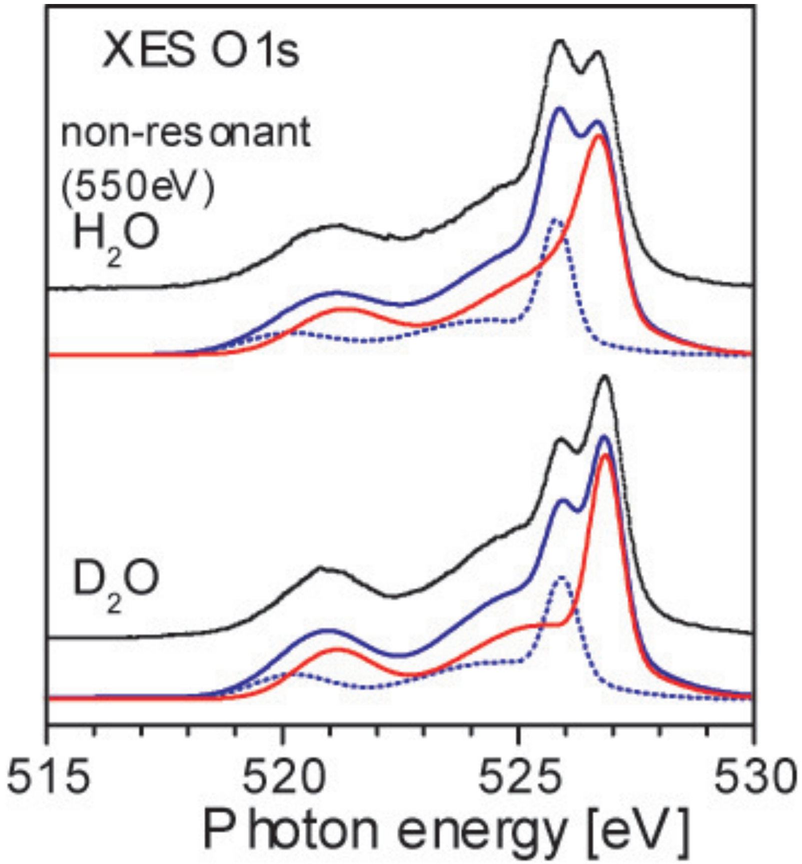
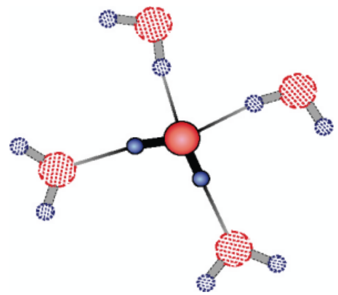
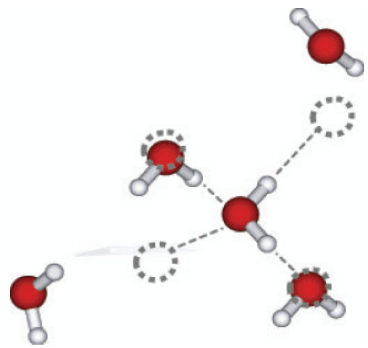
Curve Fitting





20-30 %



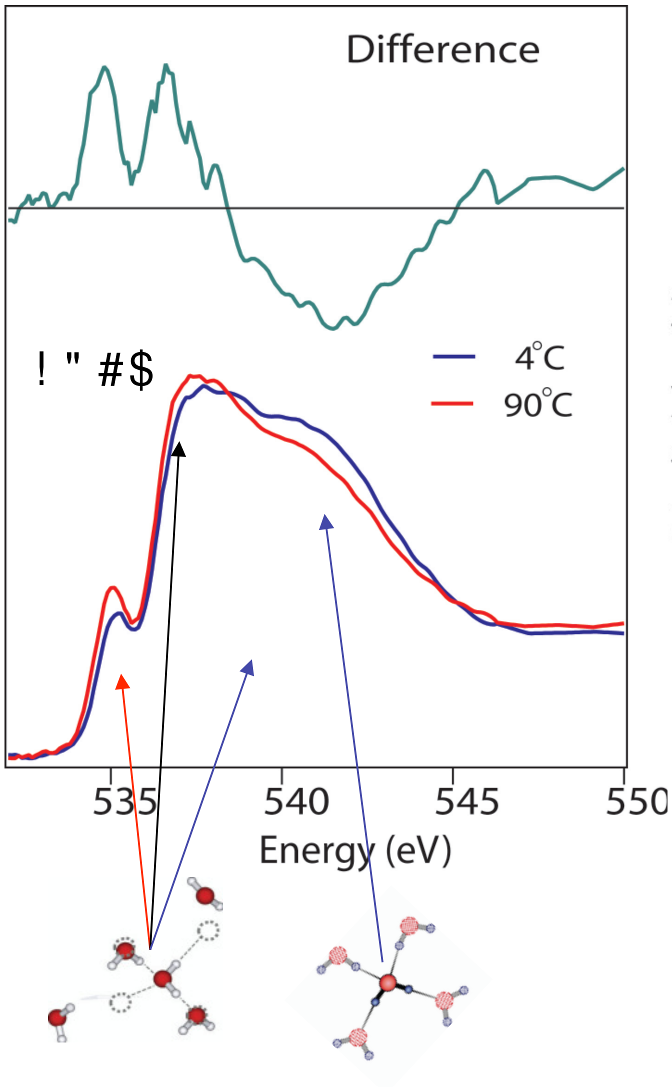
70-80 %

Different line shape due to ultrafast dynamics leading to dissociation

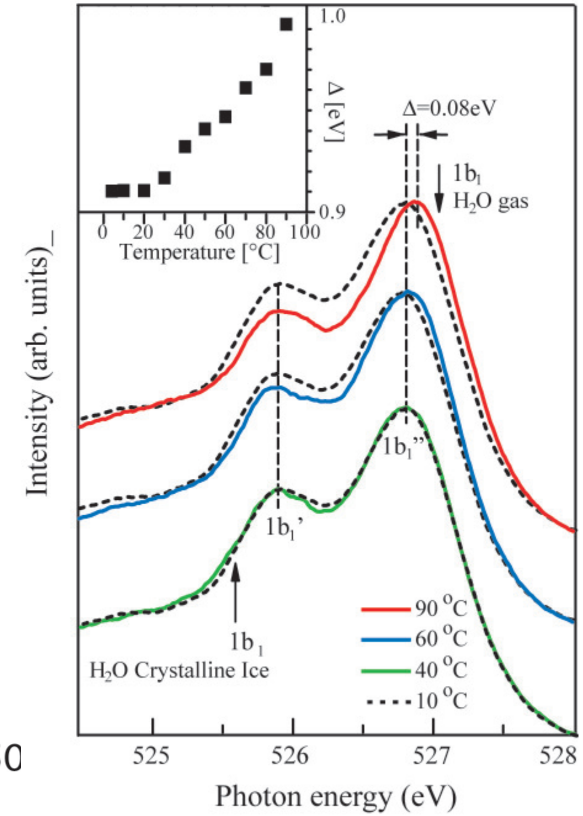
Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

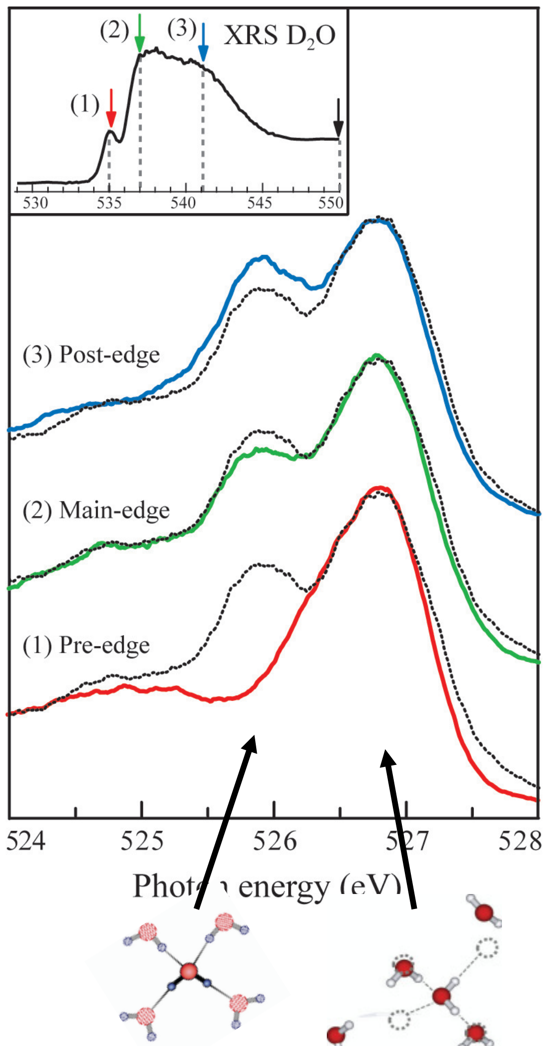
Connection between XAS/XRS

X-ray Absorption Spectroscopy



X-ray Emission Spectroscopy





Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

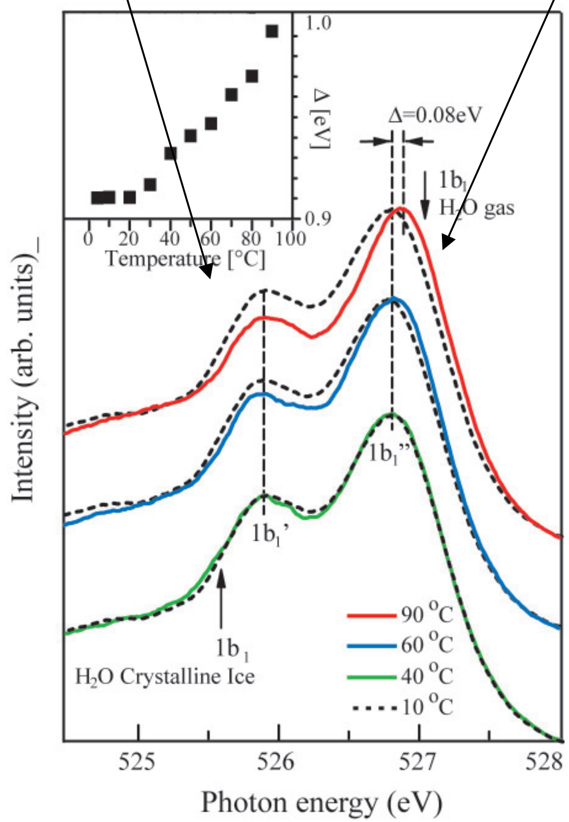
Huang *et al*., PNAS. **106** (2009) 15214

Temperature Changes of Distorted Component

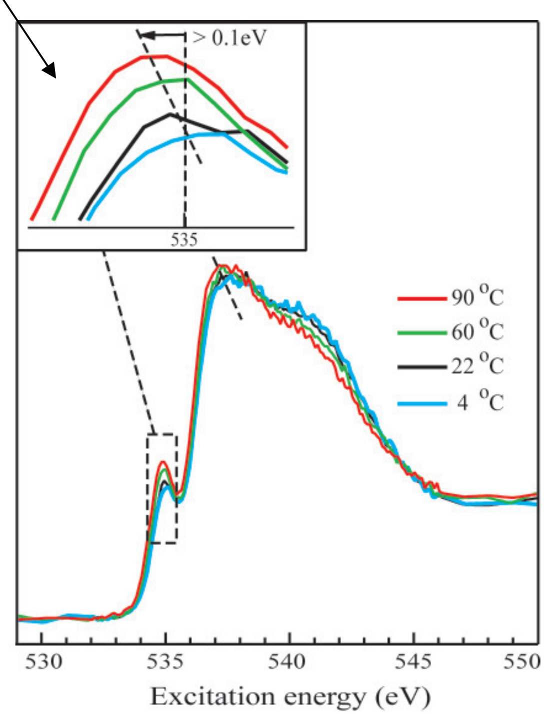
Shifts towards gas phase with increasing temperature

Fixed

XES D_2O



XAS H_2O



Distorted species changes with temperature
Tetrahedral fixed

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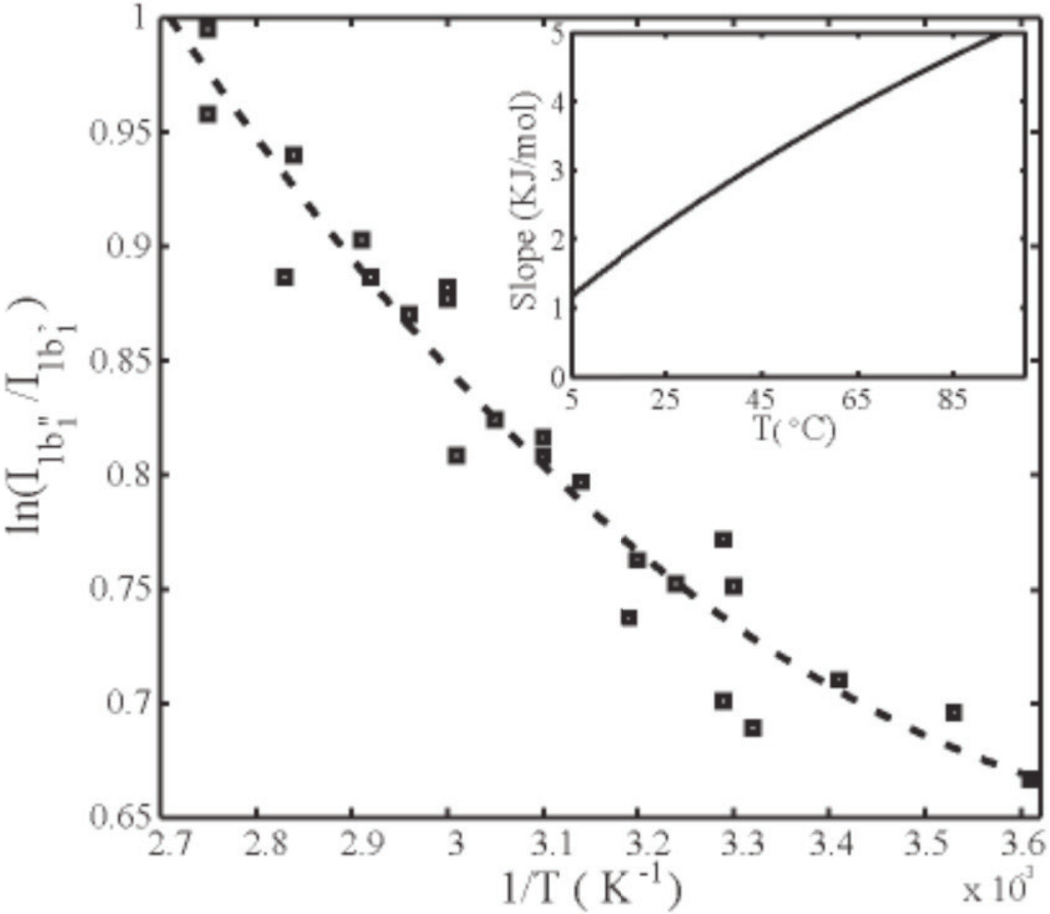
Energy Difference: Tetrahedral vs. Distorted



Decompose as two core-level shifted XES spectra

Boltzmann analysis

$$\frac{N_{distort}}{N_{tetrahed}} = A\exp(\Delta E / RT + \Delta S / R)$$

Plot ln(b_1'/b_1") vs 1/T

NOT a straight line → Energy difference *increases and/or changes in entropy* with temperature (90 °C~2x10 °C)

2±1 kJ/mole at 25 °C

Distorted component thermally excited and expands

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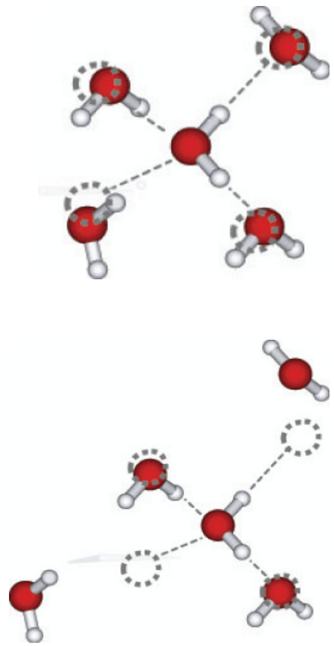
Enthalpy vs. Entropy

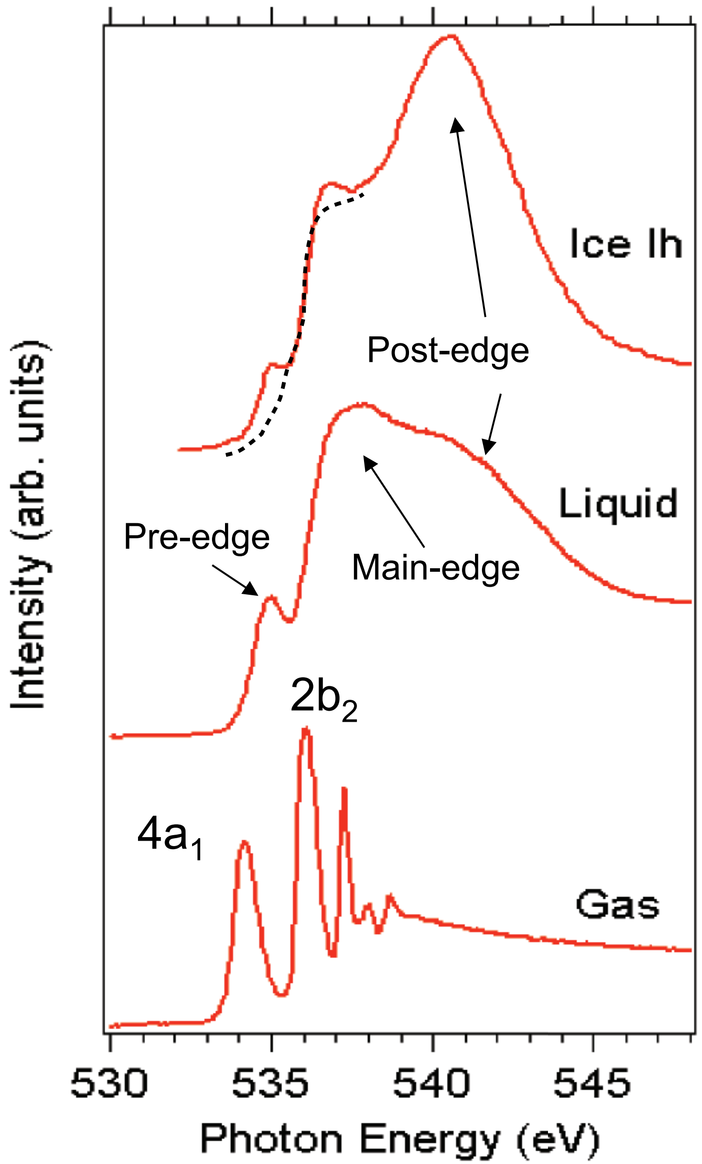


- Tetrahedral loses intensity with temperature, but peak at fixed energy
- Distorted gains intensity and disperses with temperature
- Energy taken up through:
  - Thermal excitation of distorted species
  - Breaking up a fraction of tetrahedral species

Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

Huang *et al*., PNAS. **106** (2009) 15214

X-ray Absorption Spectroscopy of Water



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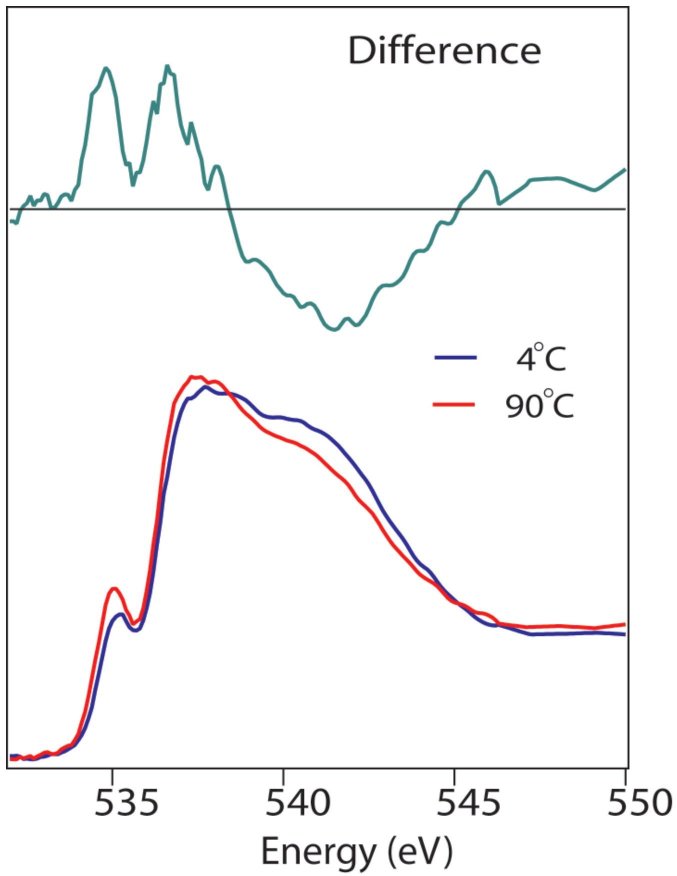
X-ray Raman Scattering

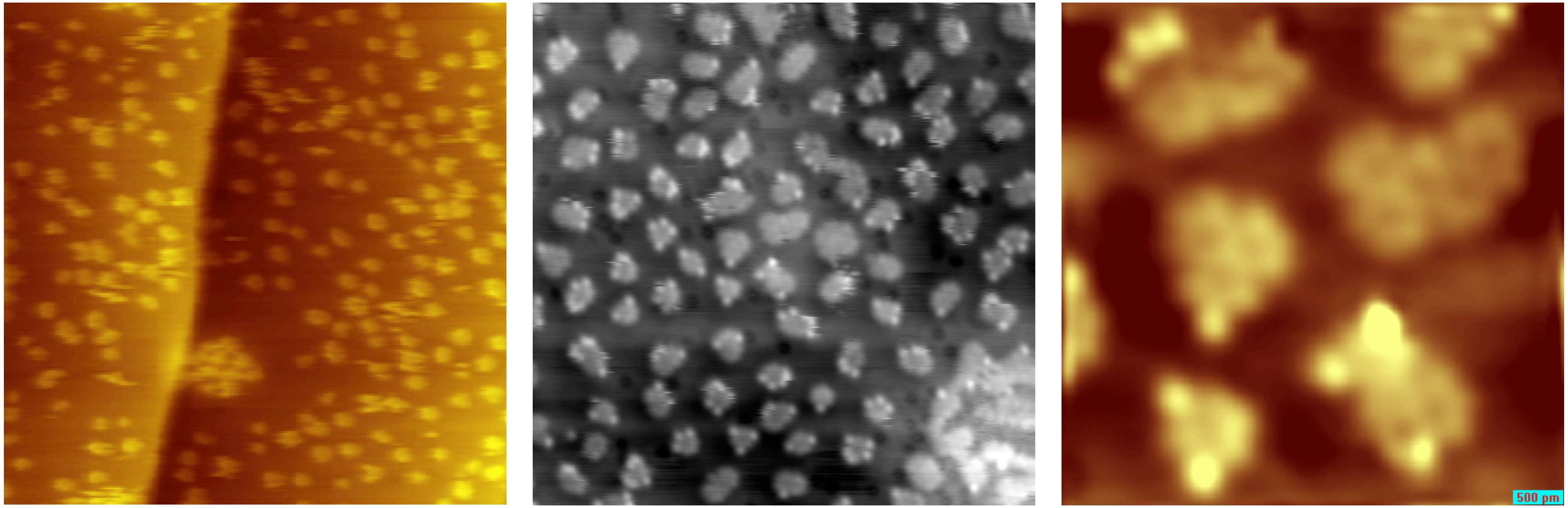


Huang *et al*., PNAS. **106** (2009) 15214

Water Clusters on Surfaces

Scanning Tunneling Microscopy (STM) of Water on Ru(0001)

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)



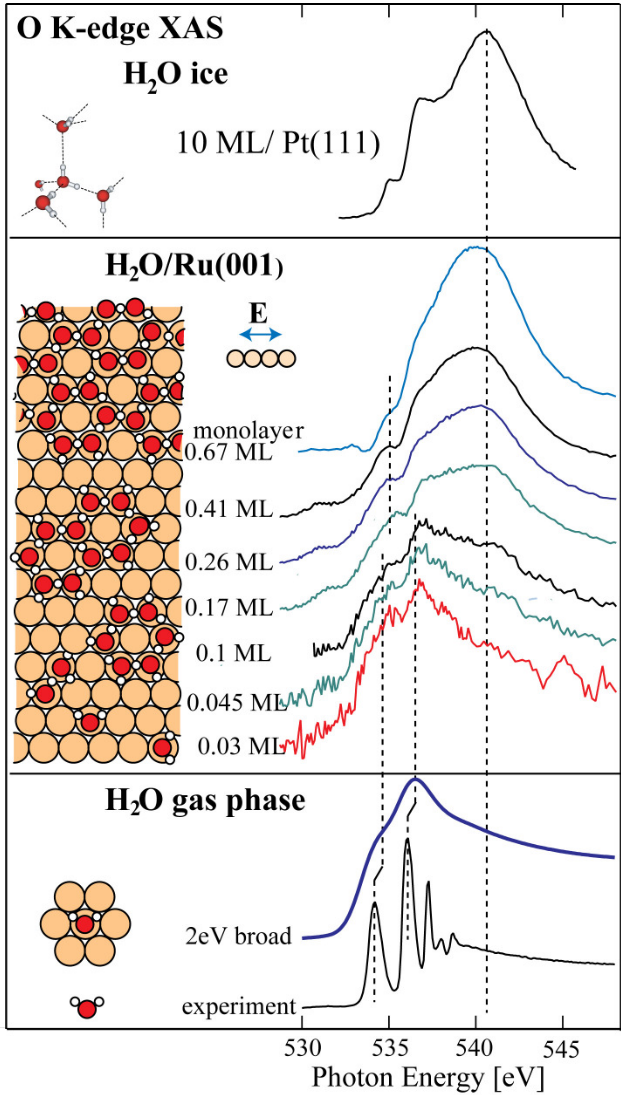
Deposited at 50 K

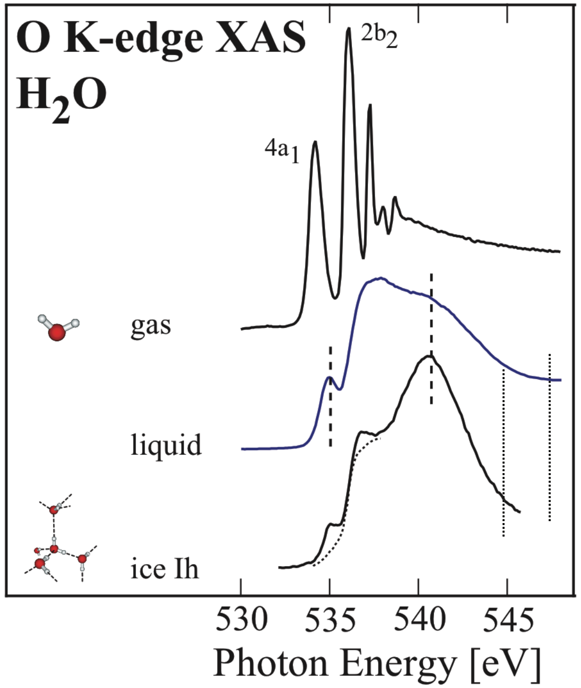
Annealed to 130 K imaged at 50 K

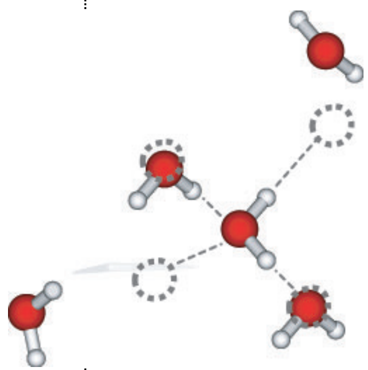
IR shows that water molecules are adsorbed flat with the HOH plane parallel to the surface

A. Hodgson et.al. unpublished

Two Dimensional Water Structures



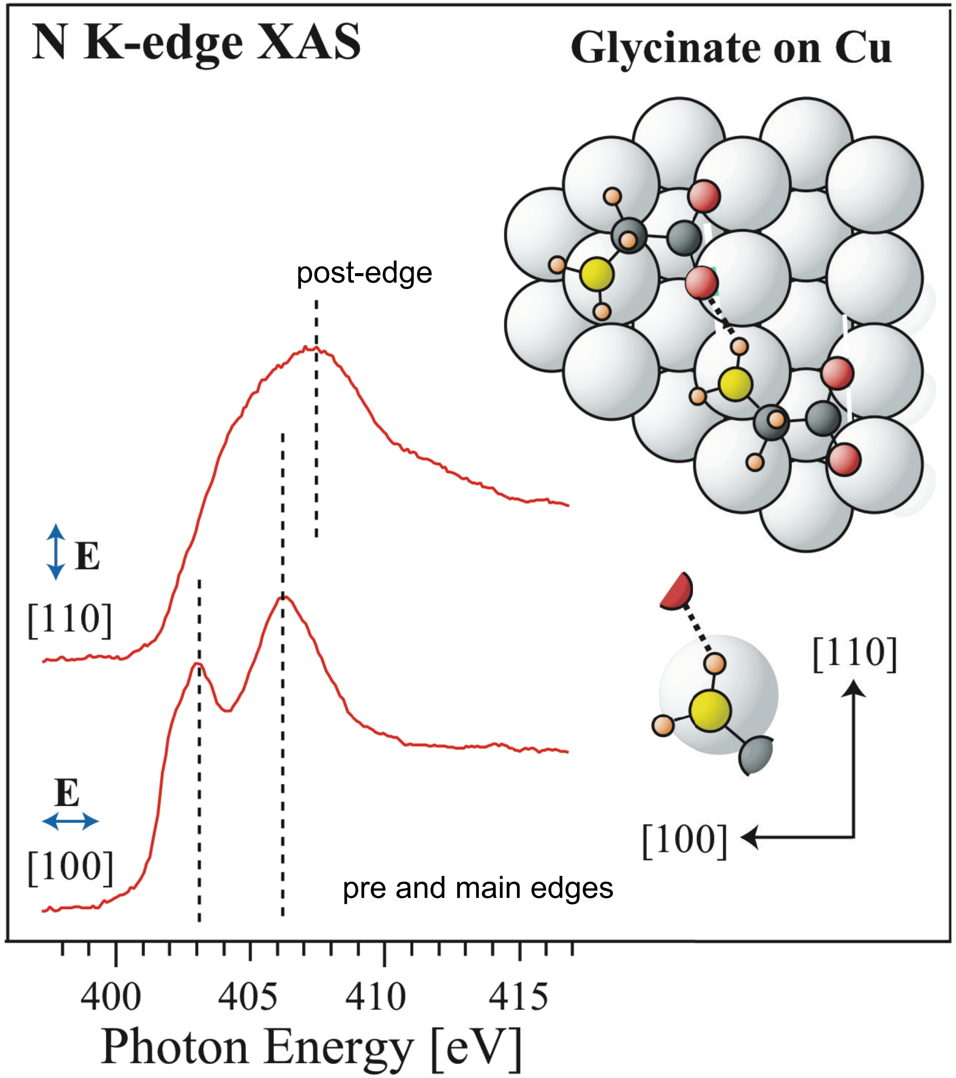


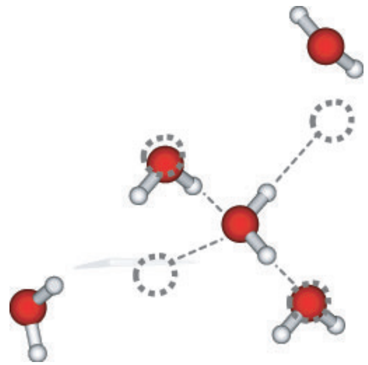


Asymmetrical distortions

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)

Similar local symmetry; Glycine



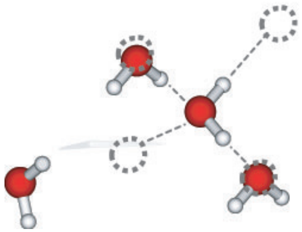


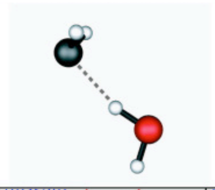
Asymmetrical distortions

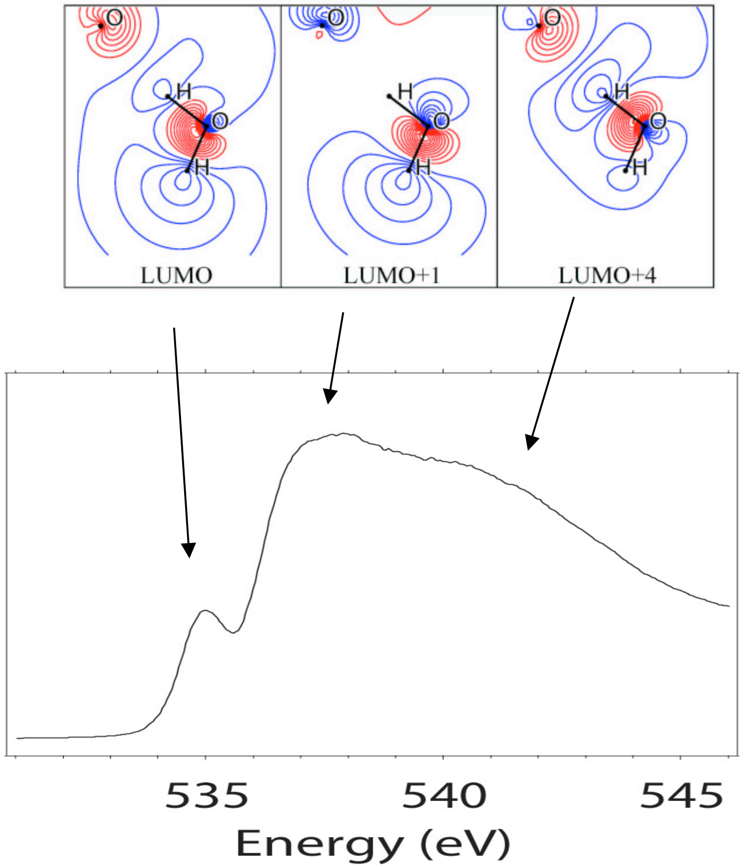
Interpretation of Water Spectrum

Breaking of symmetry

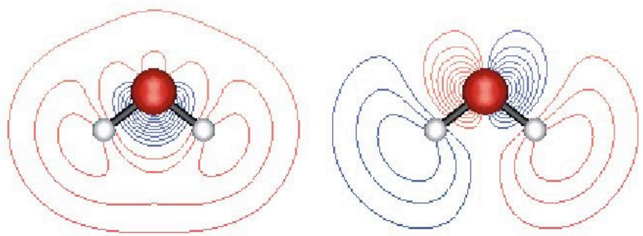
OH group orbital localization





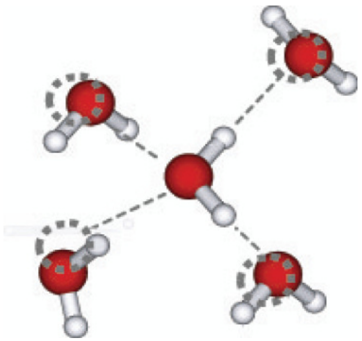


Free molecule
MO

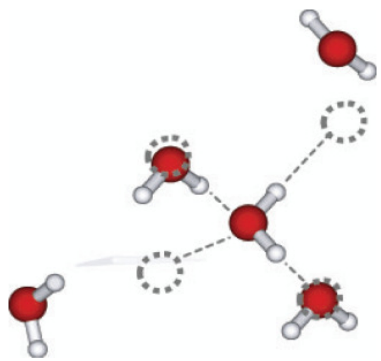


Cavalleri et.al. Chem. Phys. Lett. **364**, 363 (2002)

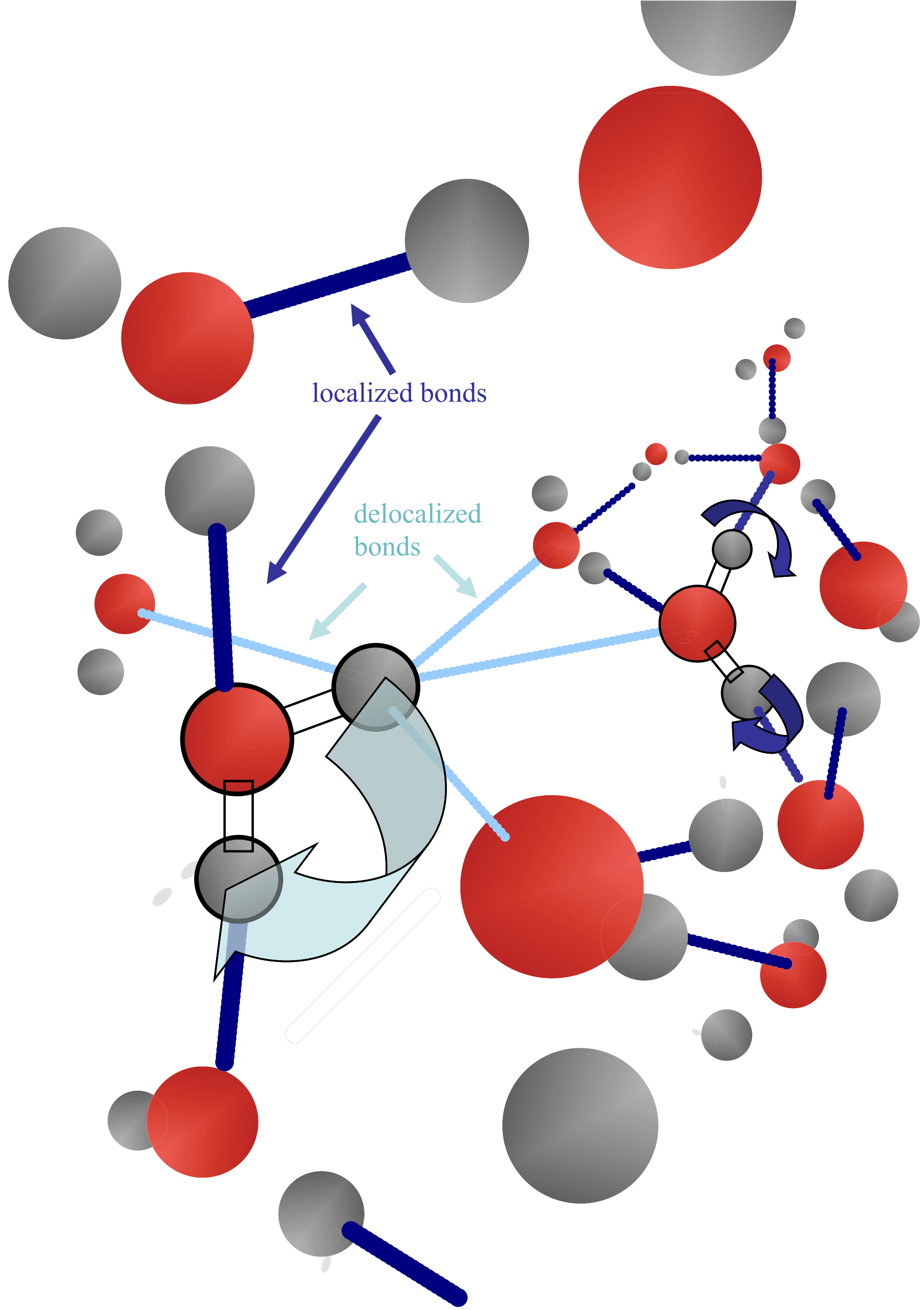
Bonds vs. Entropy



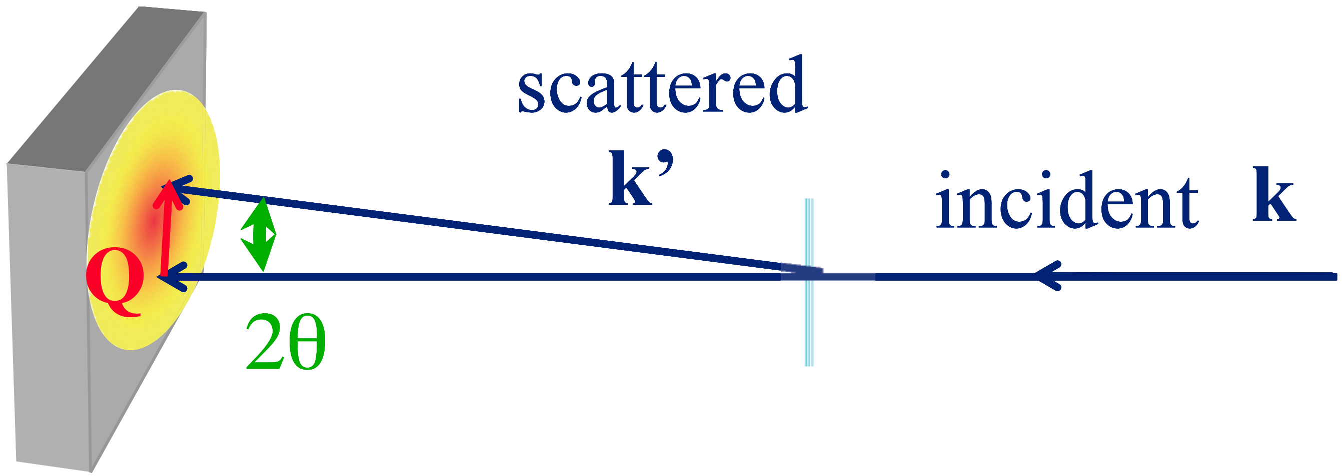
Bond Energy

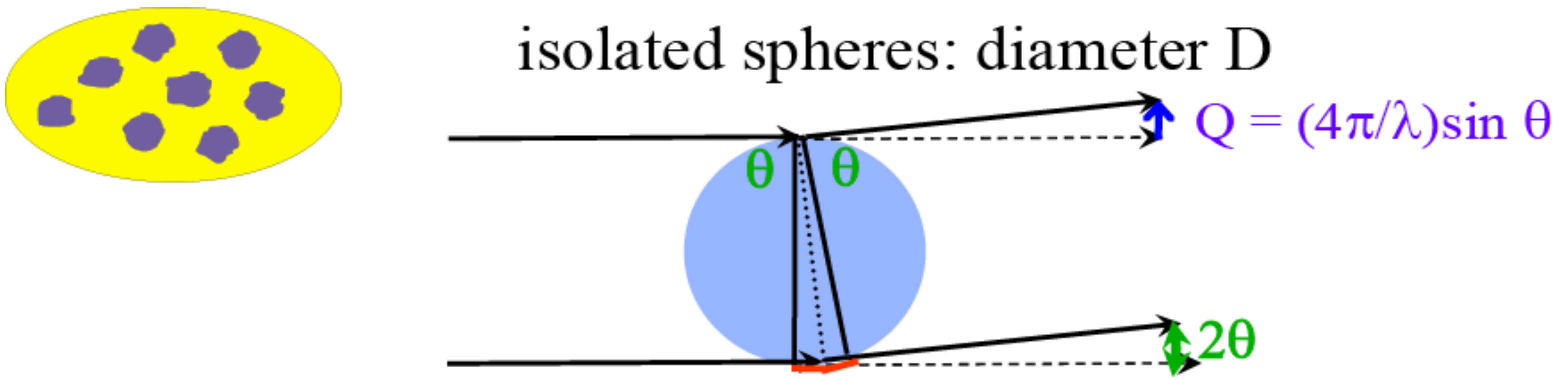


Entropy

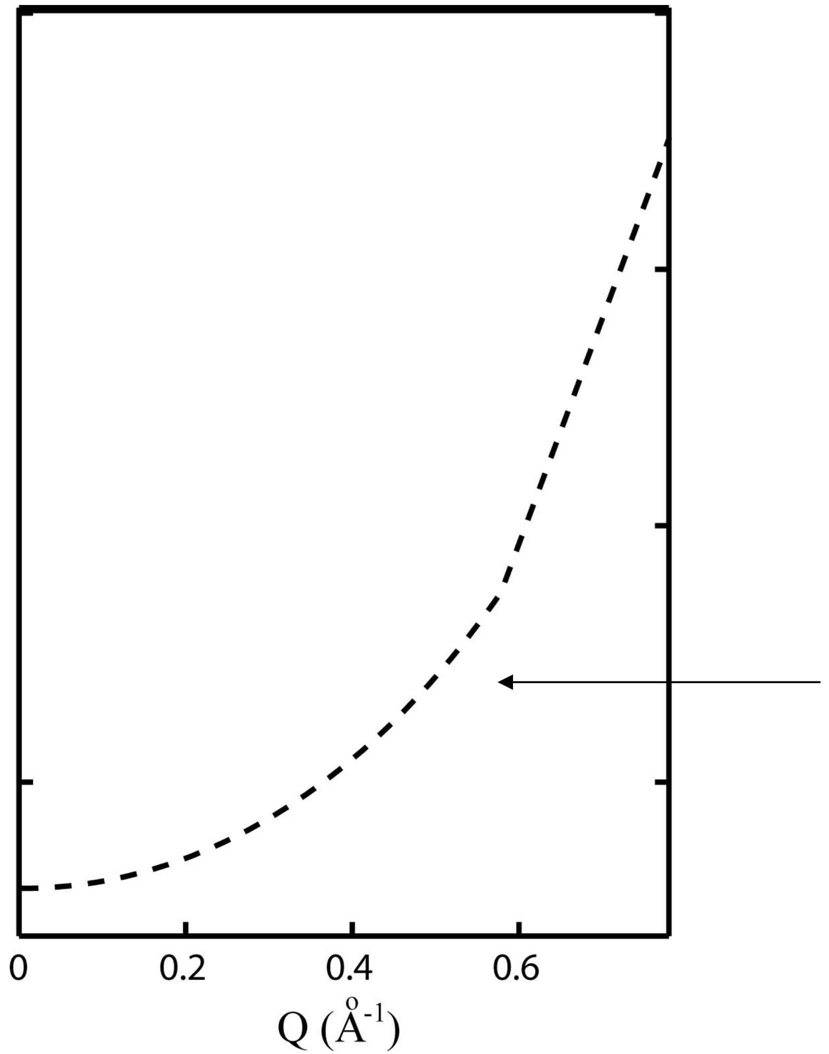


Small Angle X-ray Scattering (SAXS)

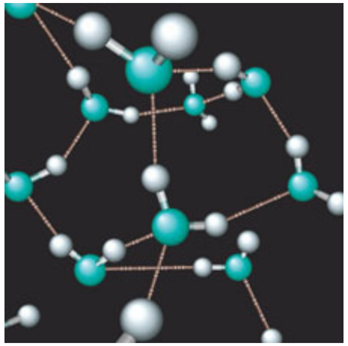




Theoretical curve for single component

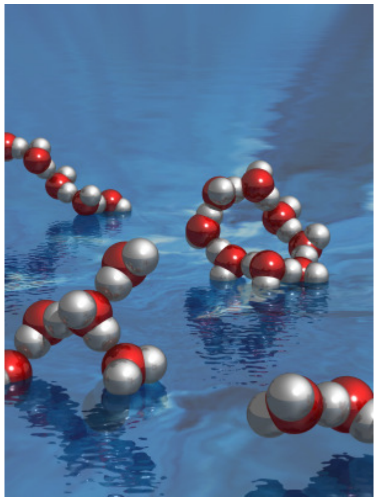


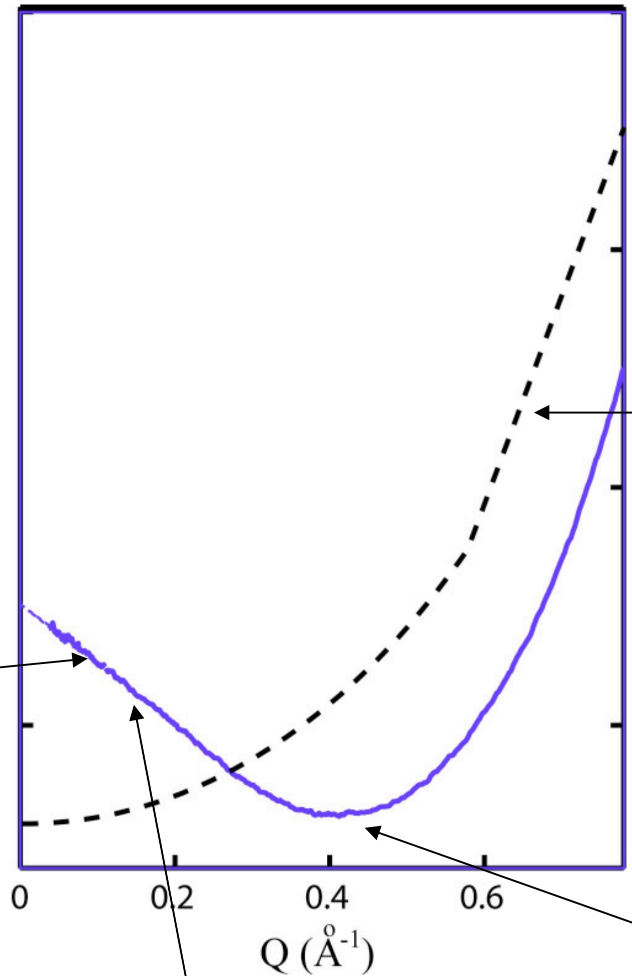
Hypothetical Water
Homogeneous



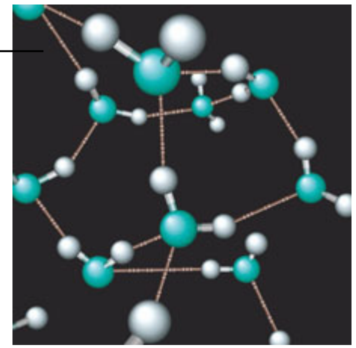
Surprising experimental result

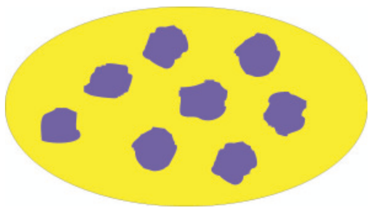
Experimental Water





Hypothetical Water
Homogeneous





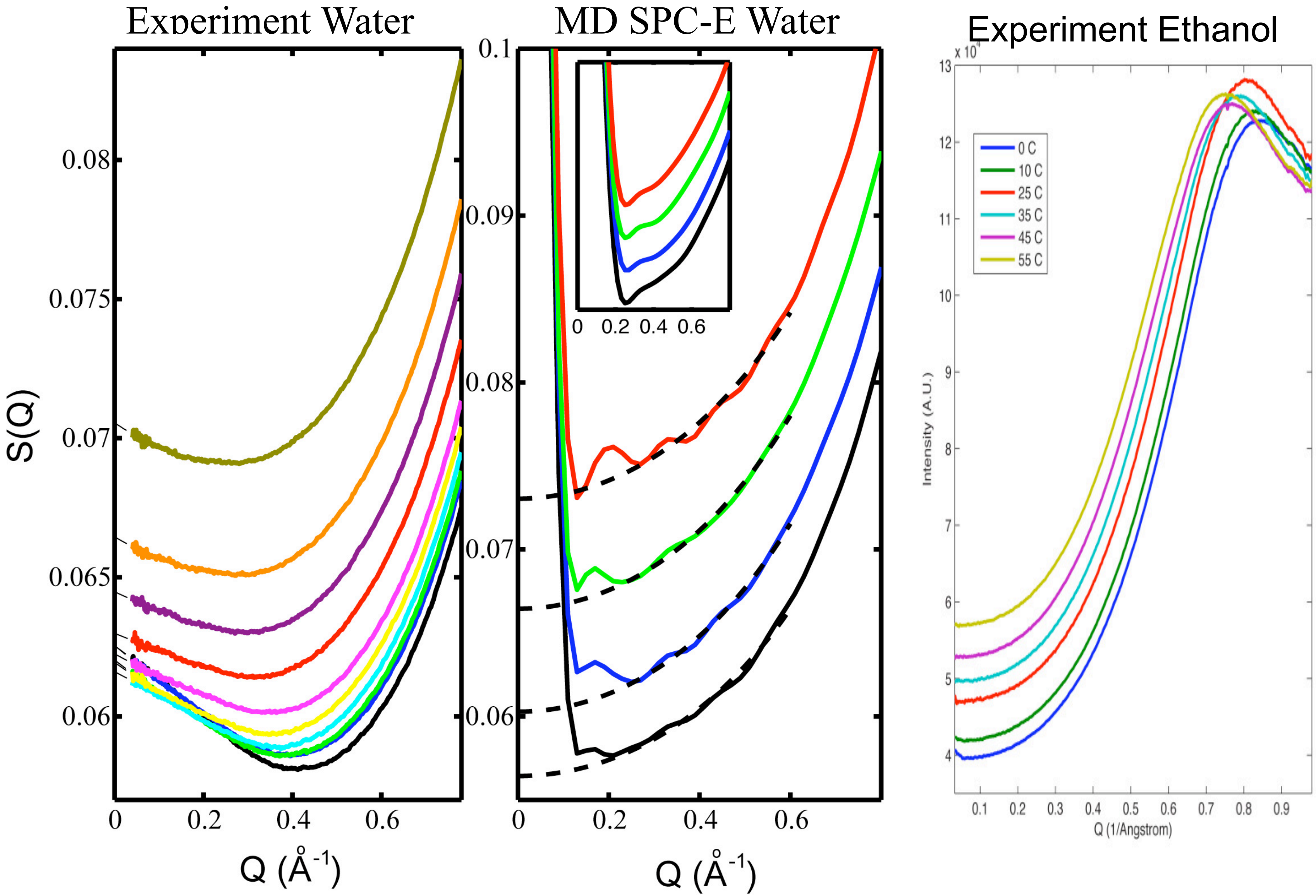
10-20 Ångström in Size

Minimum gives us size

Enhancement showing heterogeneity

Huang *et al*., PNAS. **106** (2009) 15214

Temperature dependence

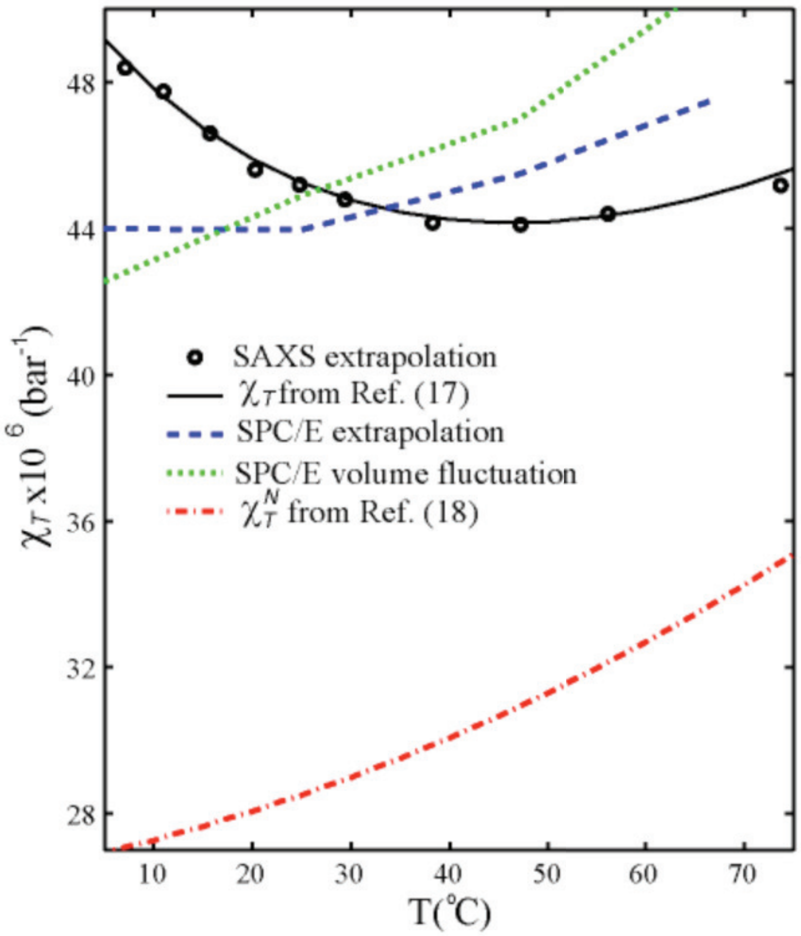


Huang *et al*., PNAS. **106** (2009) 15214

Connecting to isothermal compressibility

The isothermal compressibility,

$$S(0) = k_B T n \chi_T$$



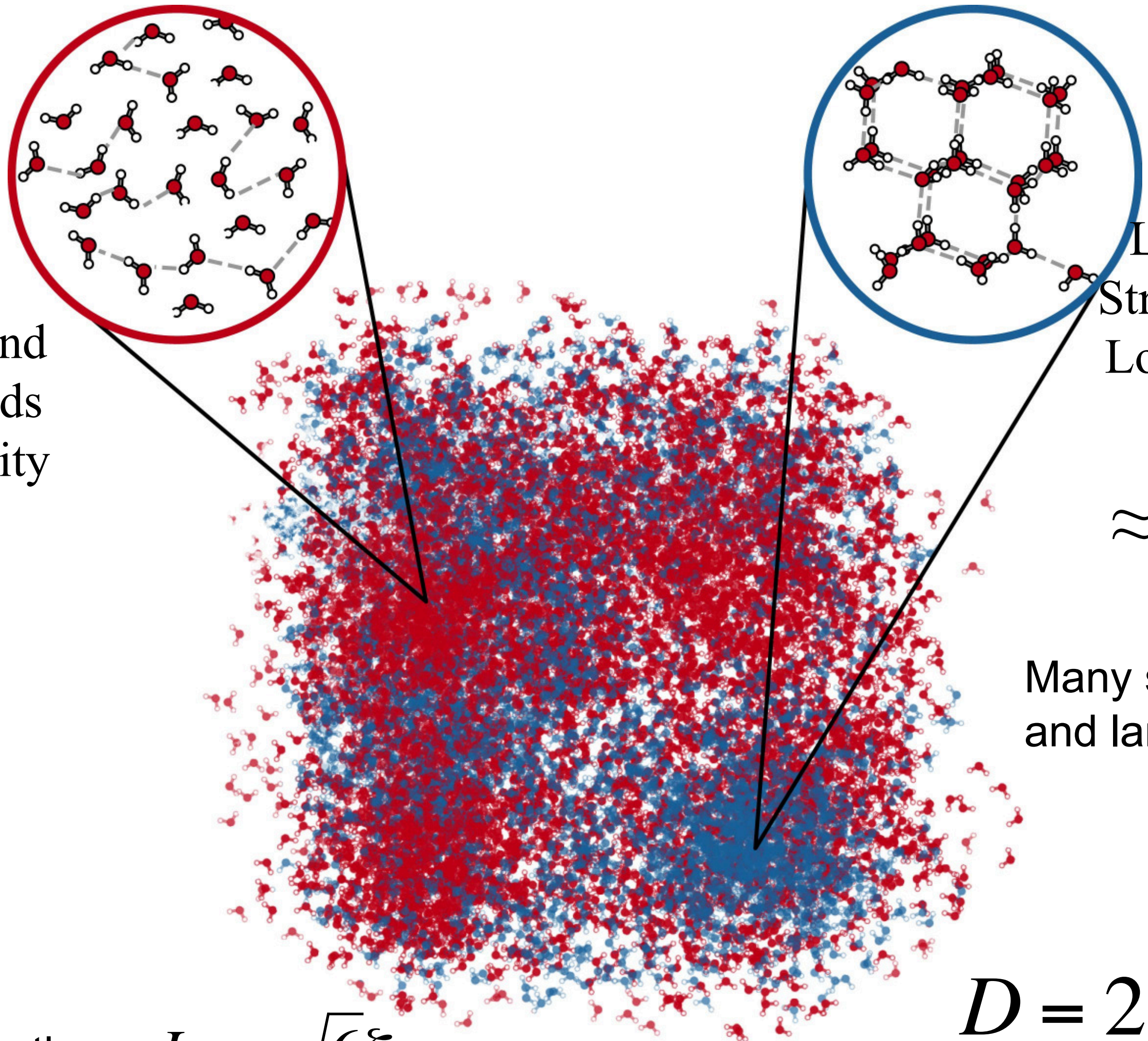
Density Fluctuations

Huang *et al*., PNAS. **106** (2009) 15214

Fluctuations in a bimodal distribution

Disordered

Tetrahedral



Moves Around
Weaker Bonds
Higher Density

Local Order
Stronger Bonds
Lower Density

≈ 10Å

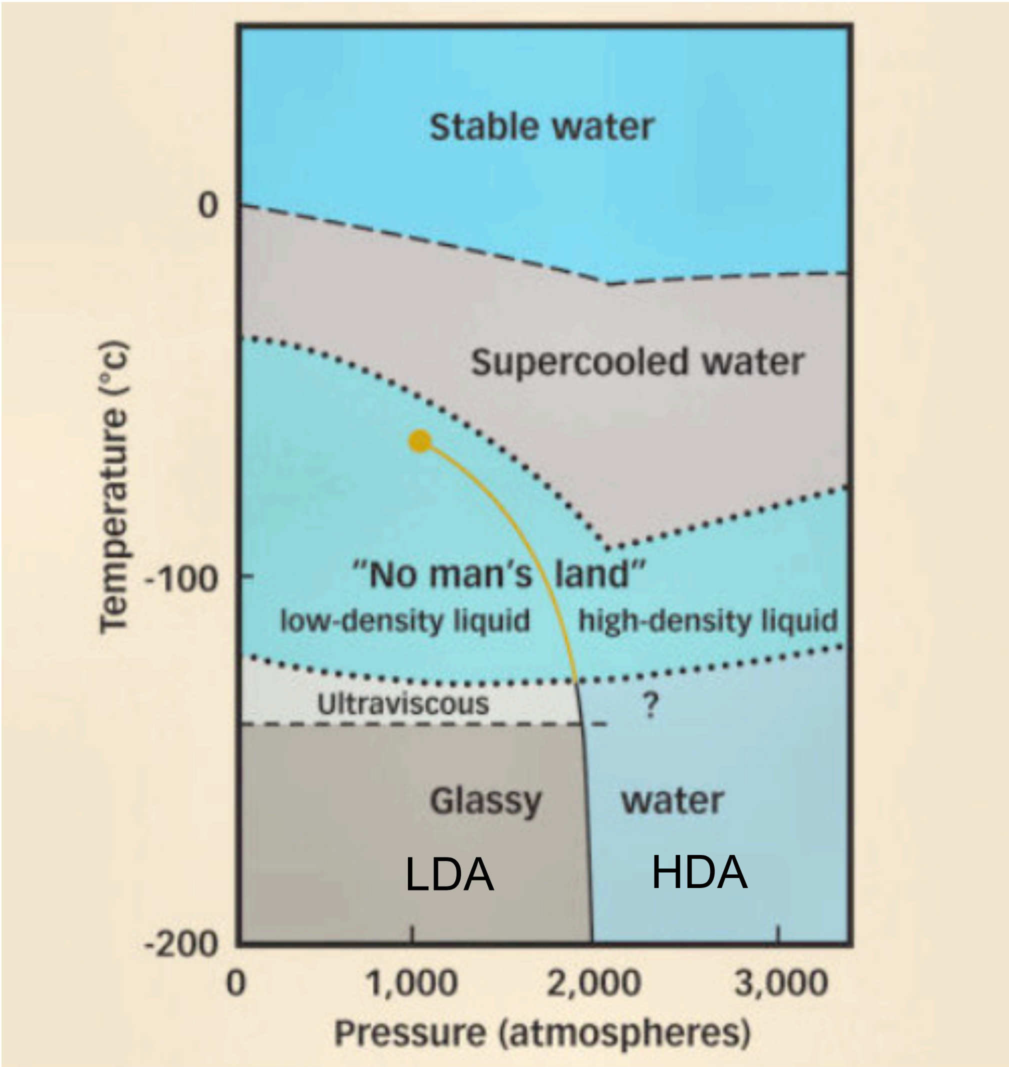
Many sizes smaller
and larger

Debey Length $L_D = \sqrt{6}\xi$

Spherical shape $D = 2.2L_D$

Huang *et al.*, PNAS. **106** (2009) 15214

Second Critical Point or 1st order phase transition

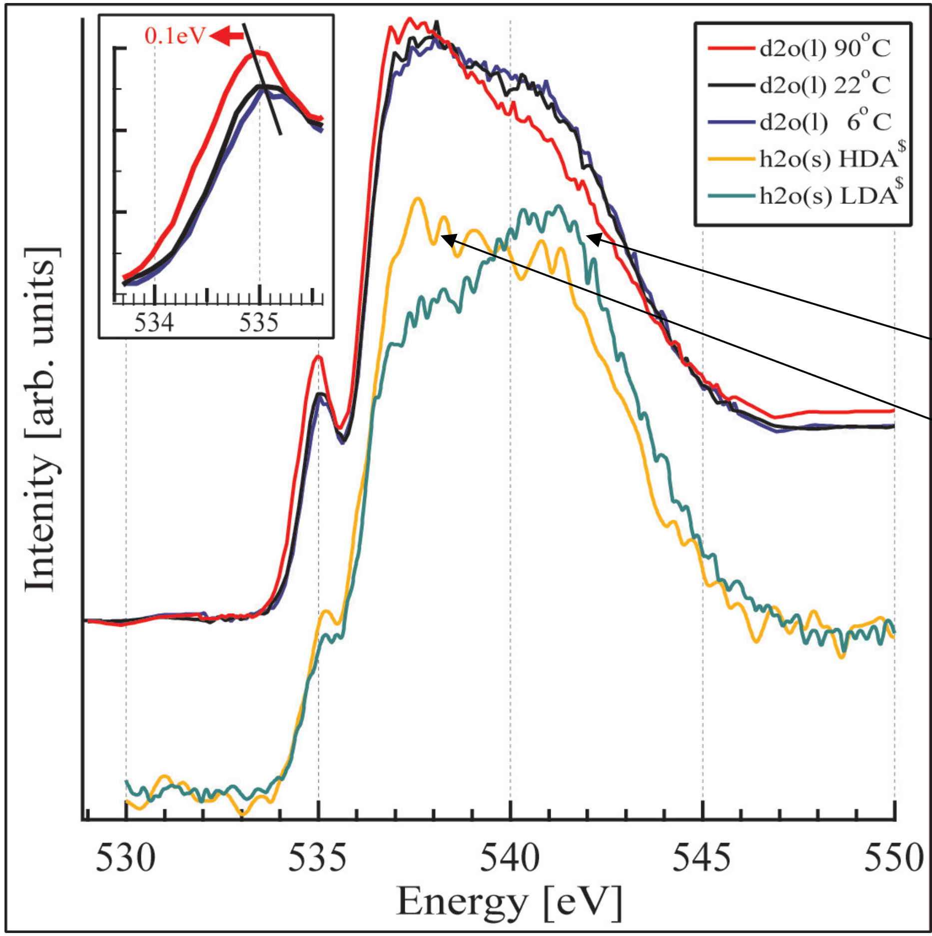


H. E. STANLEY "Mysteries of Water" Les Houches Lecture, May 1998

Originally Proposed P. H. Pool and H. E. Stanley et.al Nature 360, 324 (1992)

See also A. Angell, Science 319, 582 (2009)

X-ray Raman HDA and LDA

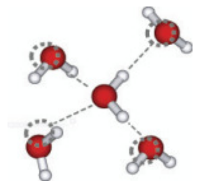


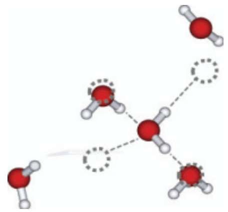
HDA spectrum resembles water

HDA similar to the distorted component

LDA

HDA





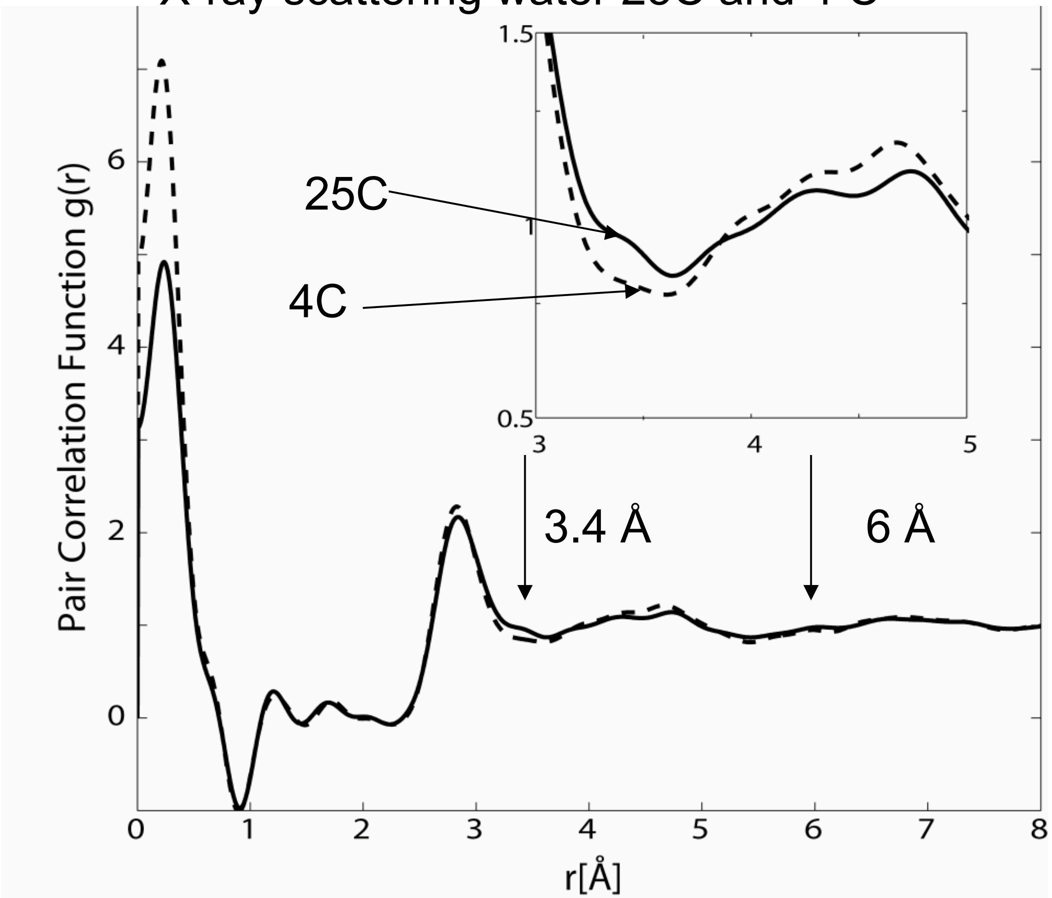
HDA and LDA J. Tse et.al Phys. Rev. Lett. 100, 095502 (2008)

Water, Huang *et al*., PNAS. **106** (2009) 15214

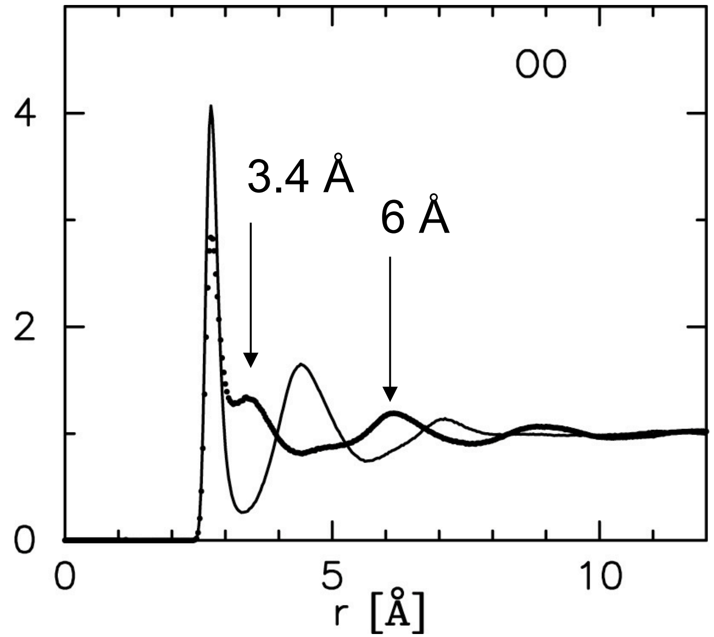
New high resolution x-ray diffraction

O-O pair correlation functions

X-ray scattering water 25C and 4 C



Extrapolated HDL and LDL structures from neutron diff
LDL full line
HDL dotted



L. Fu et al. J. Chem. Phys. **131**, 234702 (2009)

A. Soper et al Phys. Rev. Lett. **84**, 2881 (2000)

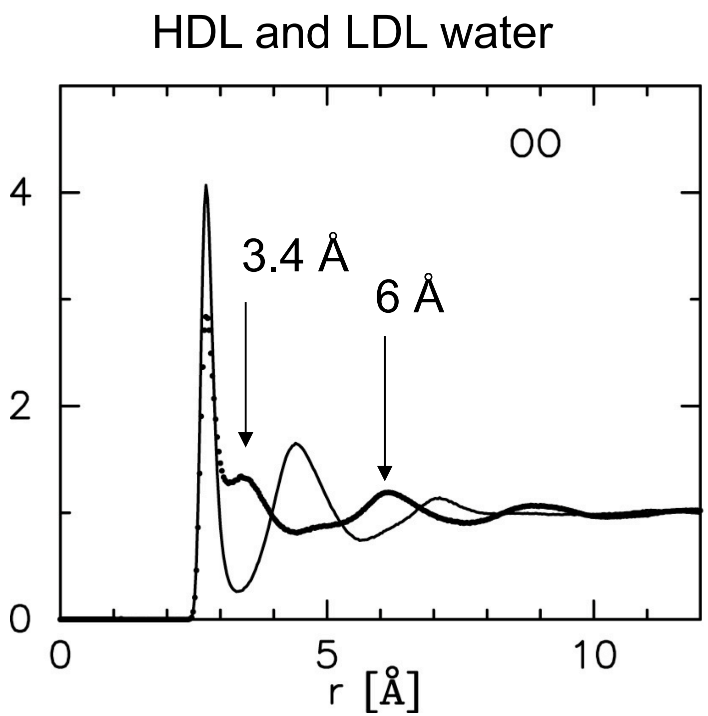
Signatures of HDL and LDL as distinct structures in diffractions !

Very High Density Amorphous Ice

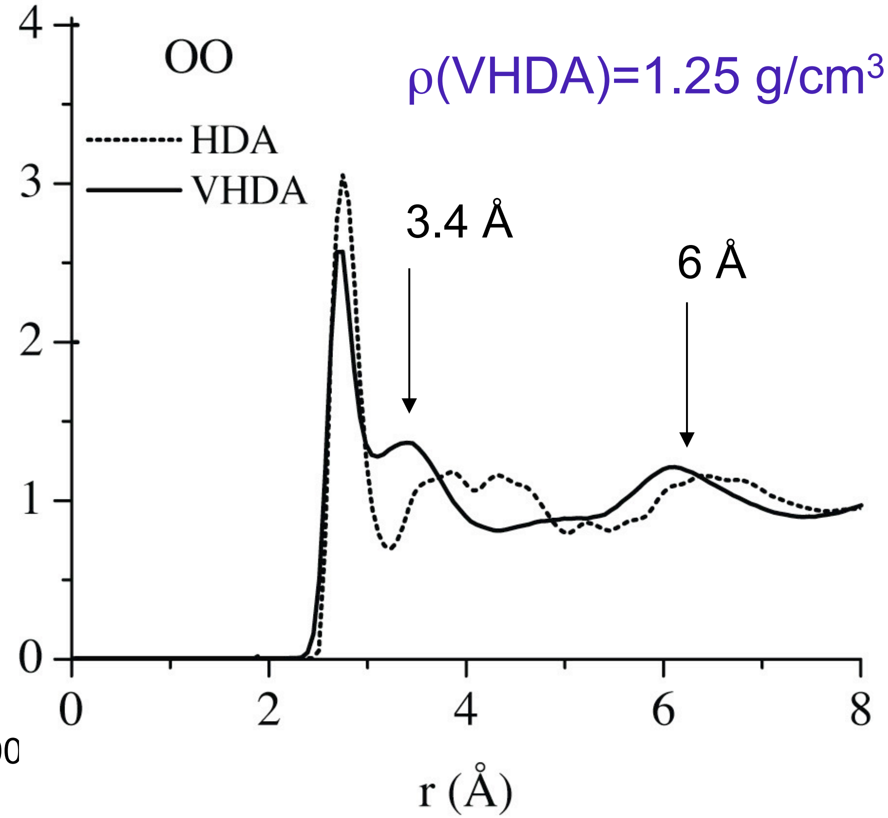
ρ(HDA)=1.17 g/cm^3

ρ(LDA)=0.94

ρ(VHDA)=1.25 g/cm^3

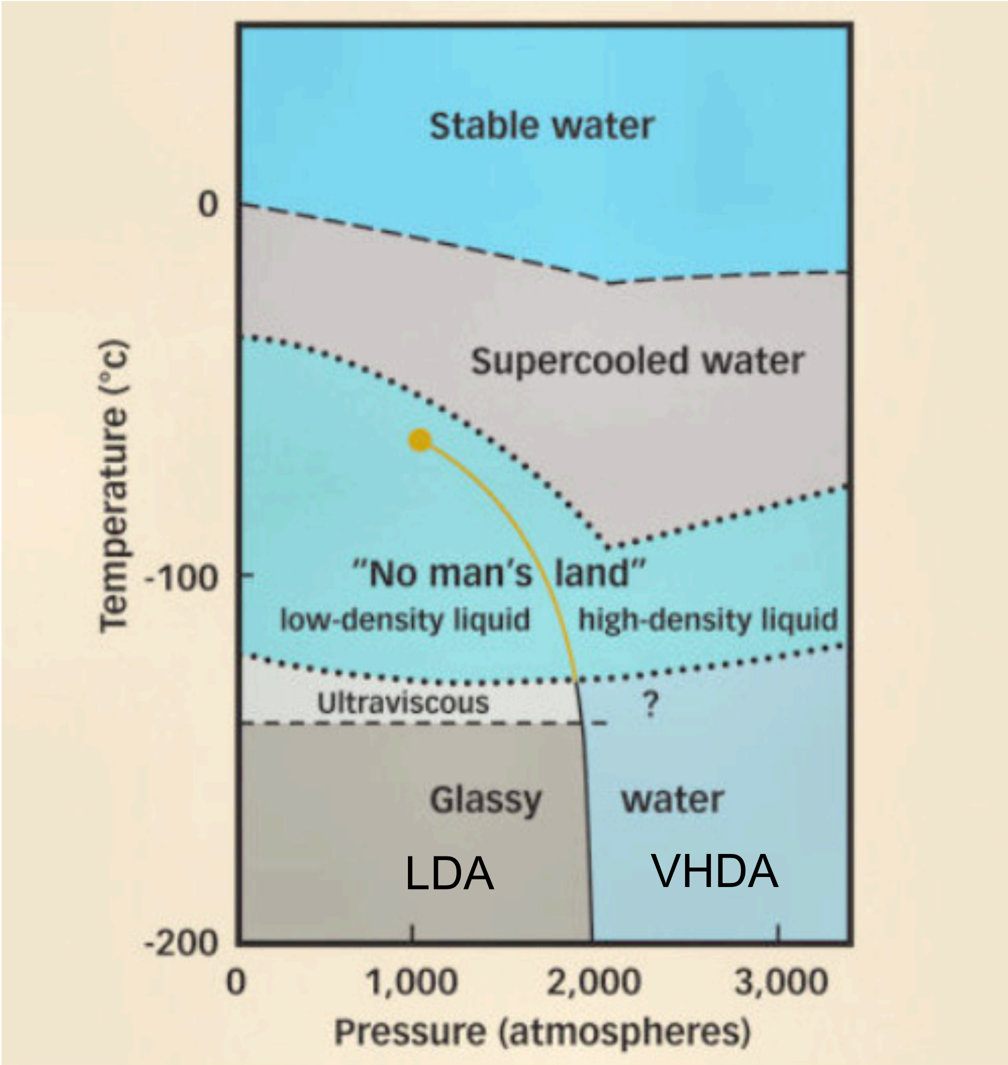


A. Soper et al Phys. Rev. Lett. **84**, 2881 (2000



J. L. Finney et al Phys. Rev. Lett. **89**, 205503 (2002)

Second Critical Point or 1st order phase transition



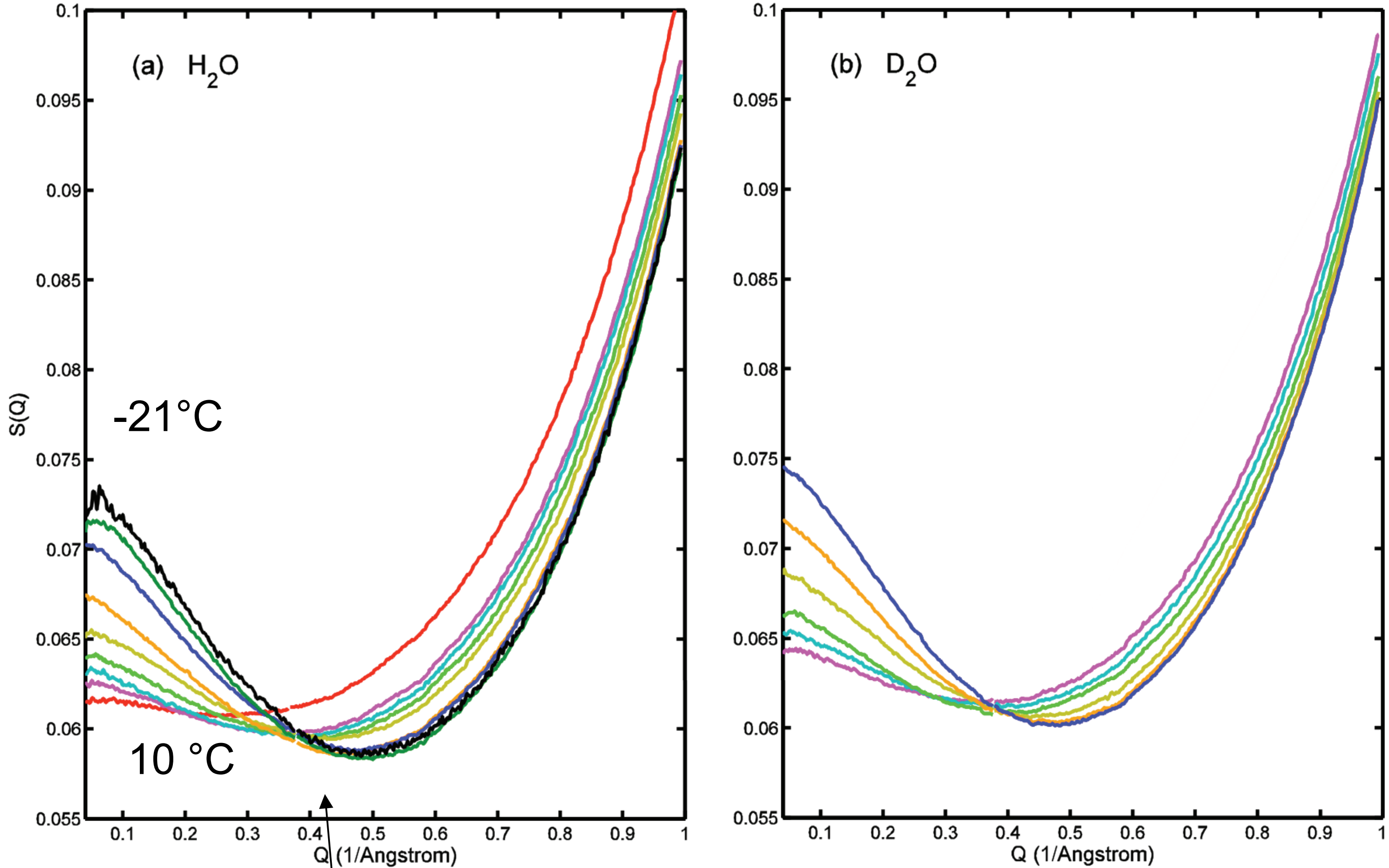
H. E. STANLEY "Mysteries of Water" Les Houches Lecture, May 1998

Originally Proposed P. H. Pool and H. E. Stanley et.al Nature 360, 324 (1992)

See also A. Angell, Science 319, 582 (2009)

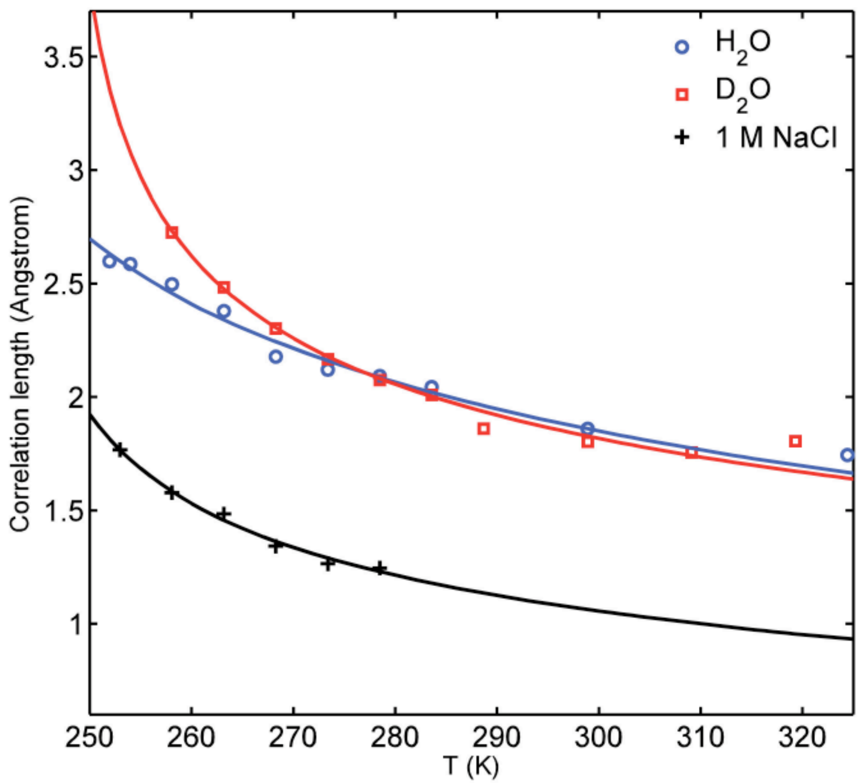
Supercooled water

SAXS



Isobestic point ?

Correlation length and fitted power law



As approaching a critical point

$$\xi = \xi_0 \varepsilon^{-\gamma}$$

where reduced temperature

$$\varepsilon = T / T_c - 1$$

	ξ_0	T_c	γ
H_2O	1.3	228	0.32
D_2O	1.0	233	0.44
NaCl	0.54	228	0.52

Recent MD model

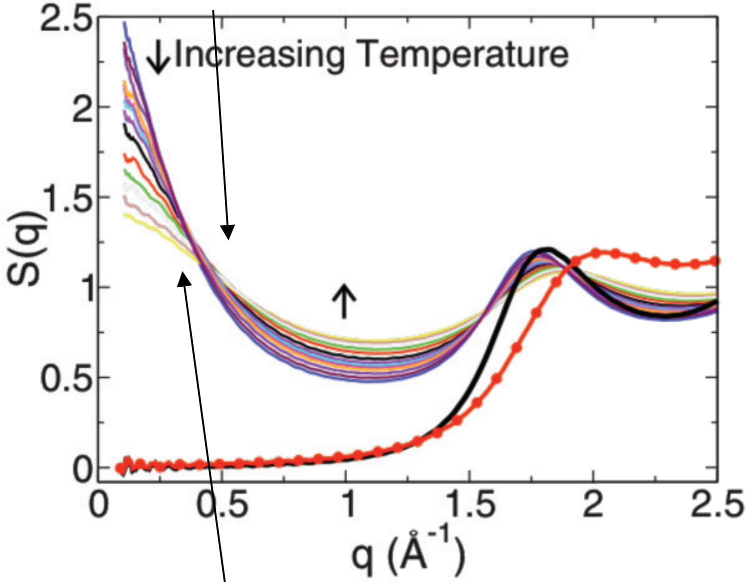
Coarse grain MD

Potential with a balance of tetrahedral bonding and high packing

≈300,000 molecules in the box

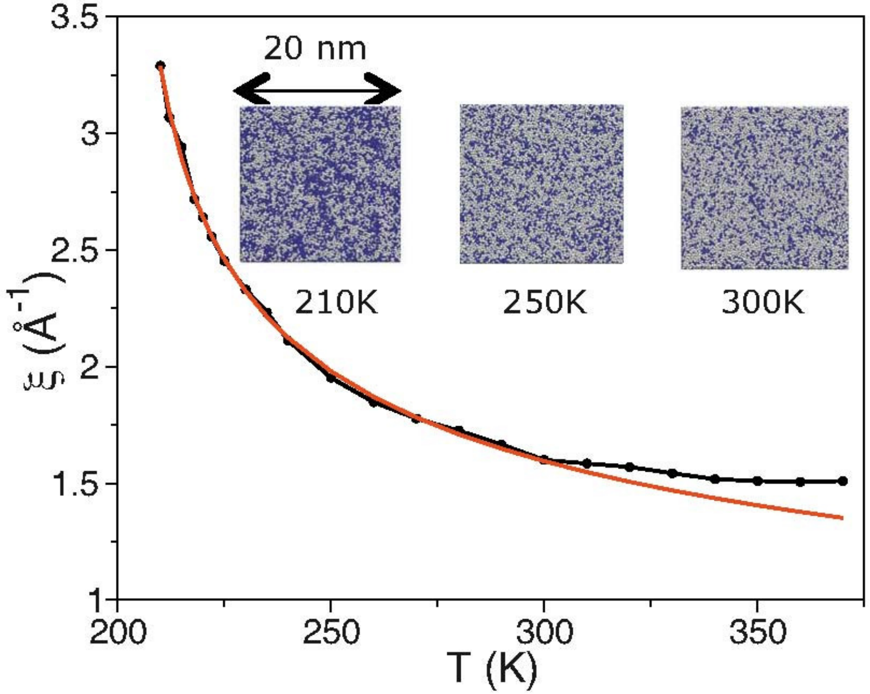
Negliable density difference

Only tetrahedral structures



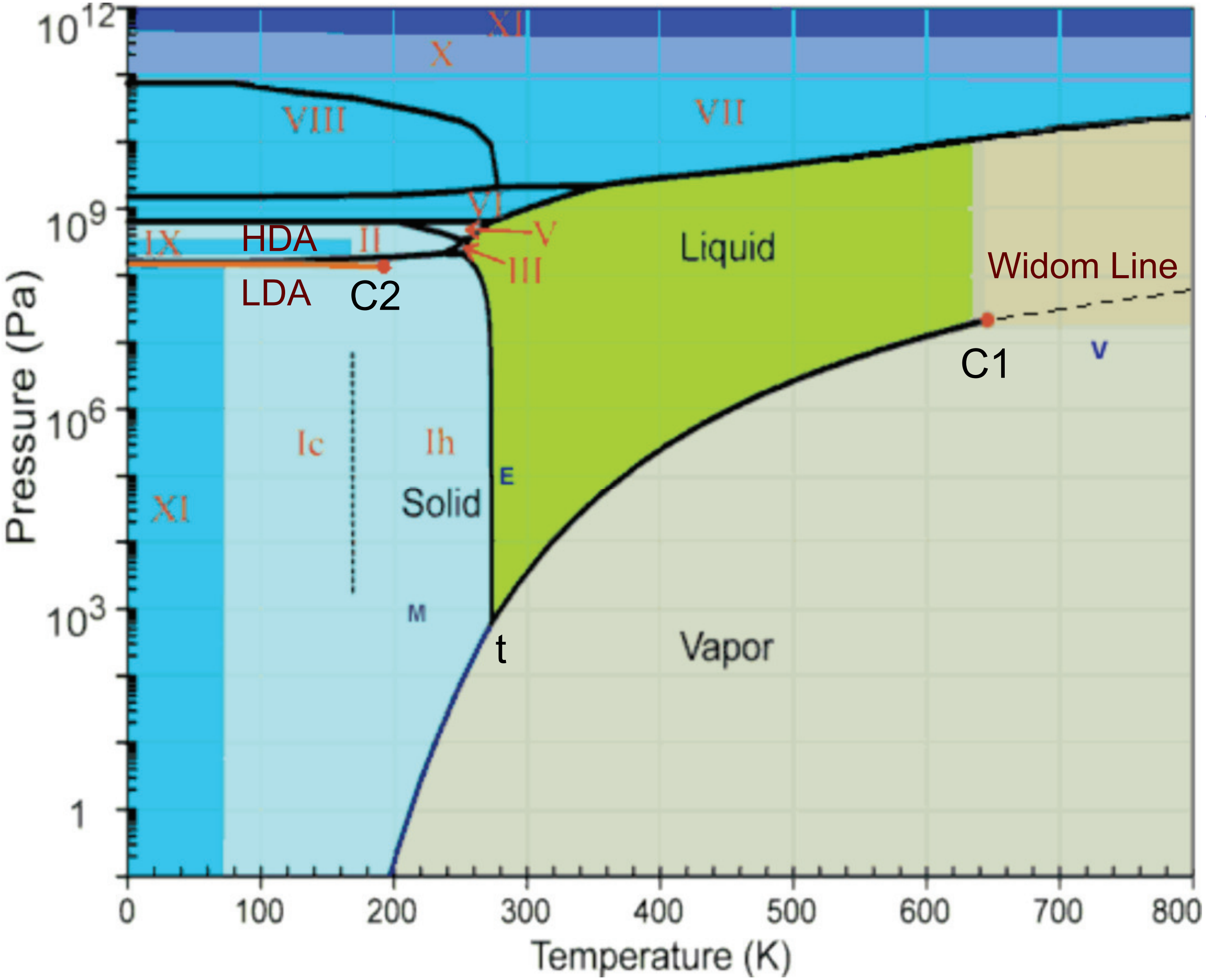
Isobestic point ?

Heterogeneity



E. B. Moore JCP 130, 244505 (2009)

Phase Diagram of Water and Ice



15 Ice Polymorphs

2 Amorphous Ices

LDA & HDA,VHDA

ρ(HDA)=1.17 g/cm^3

ρ(VHDA)=1.25

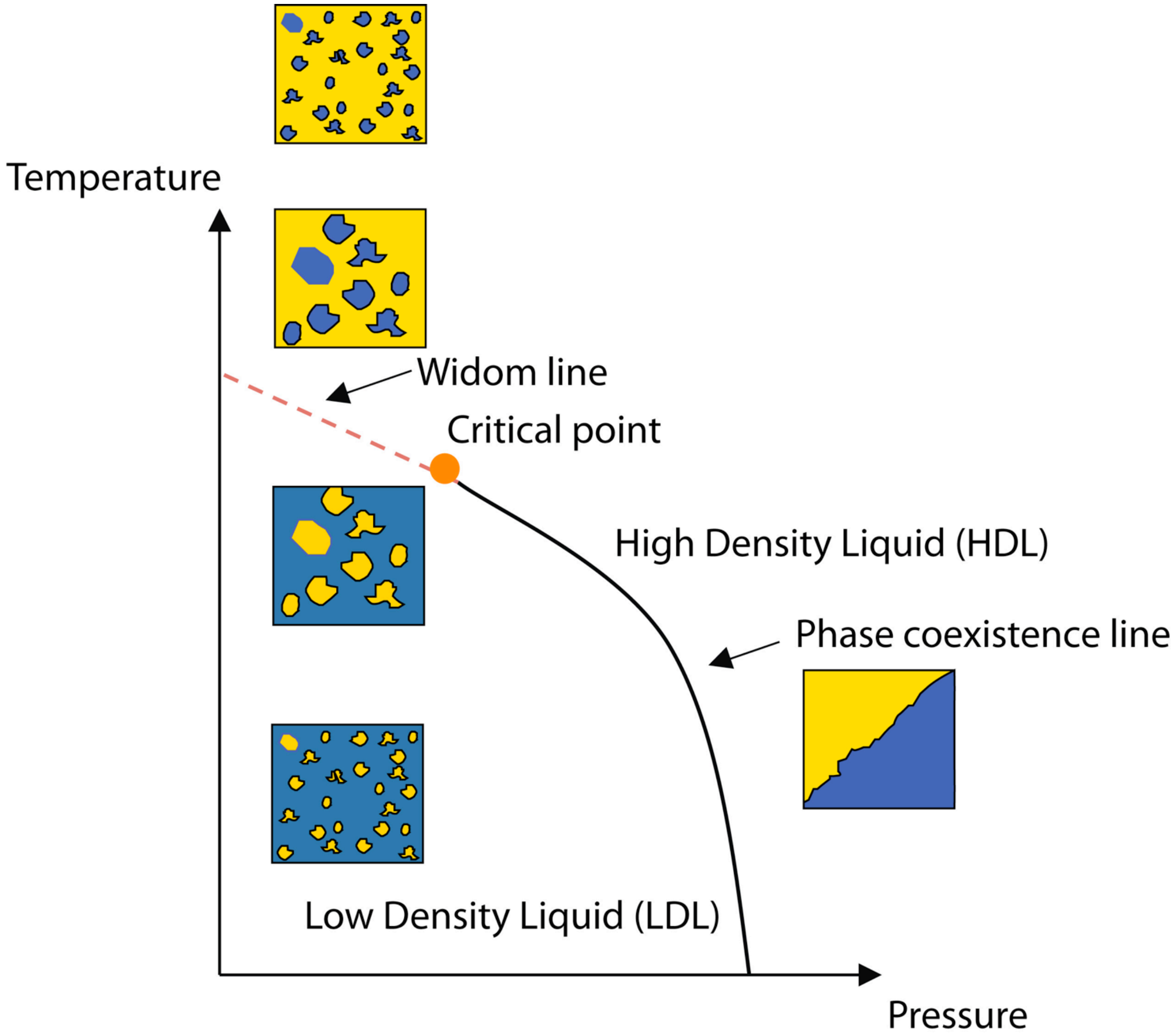
ρ(LDA)=0.94

ρ(Ih)=0.92

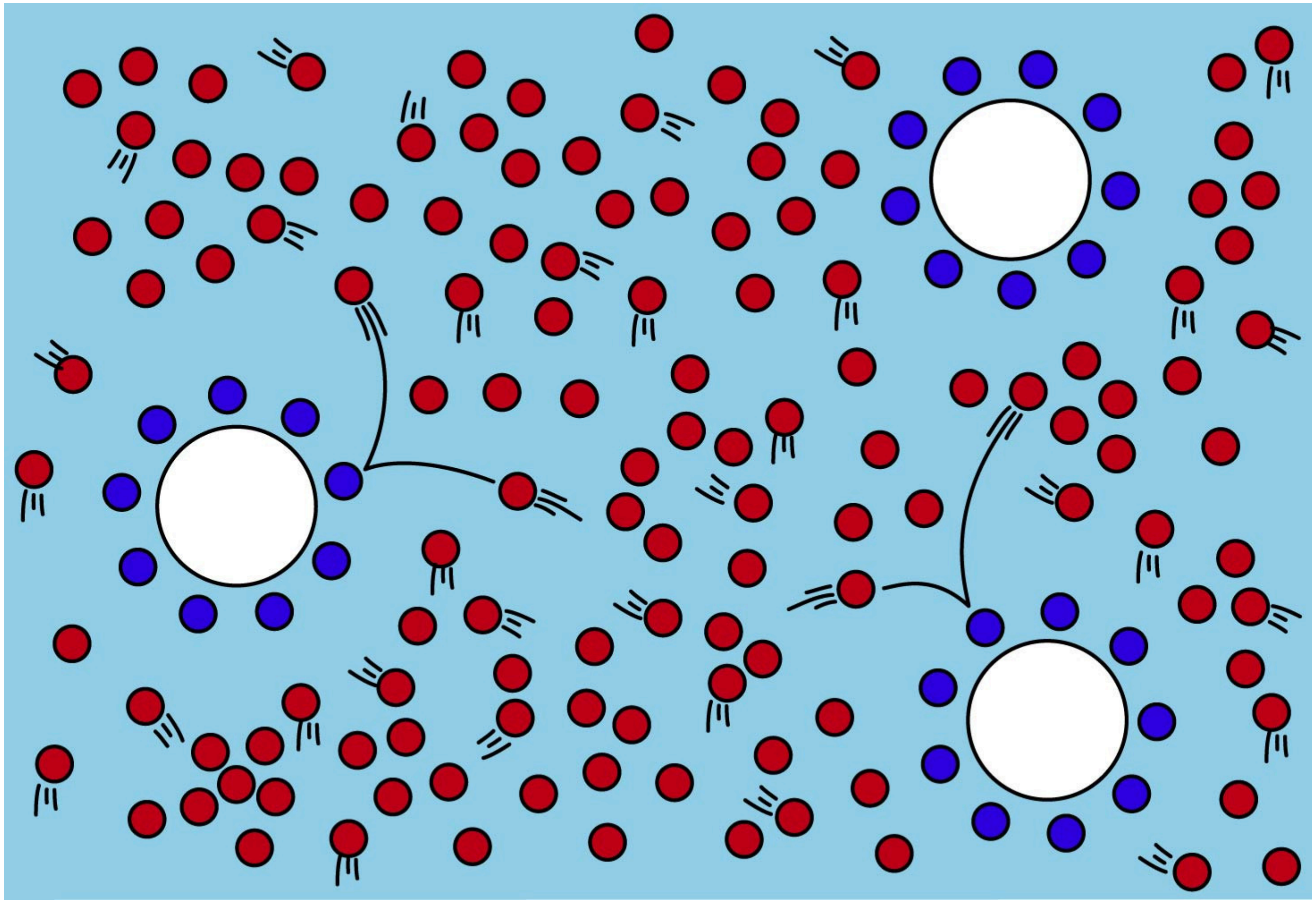
ρ(Ic)=0.92

ρ(C1)=0.322

Widom Line and 2nd Critical Point

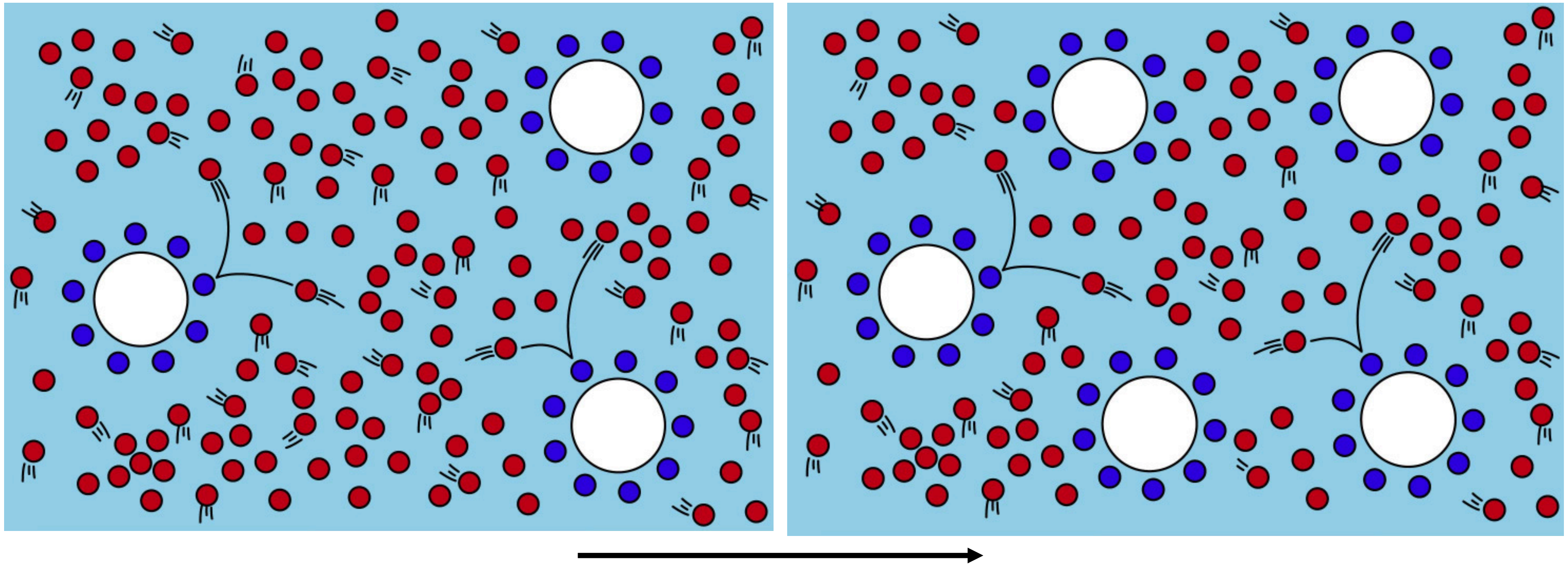


Dance Restaurant



People at the table are more socially bonded, local order, low density
People dancing are disordered but excited and moves around, higher density
Exchange between dancing and sitting people

Cooling

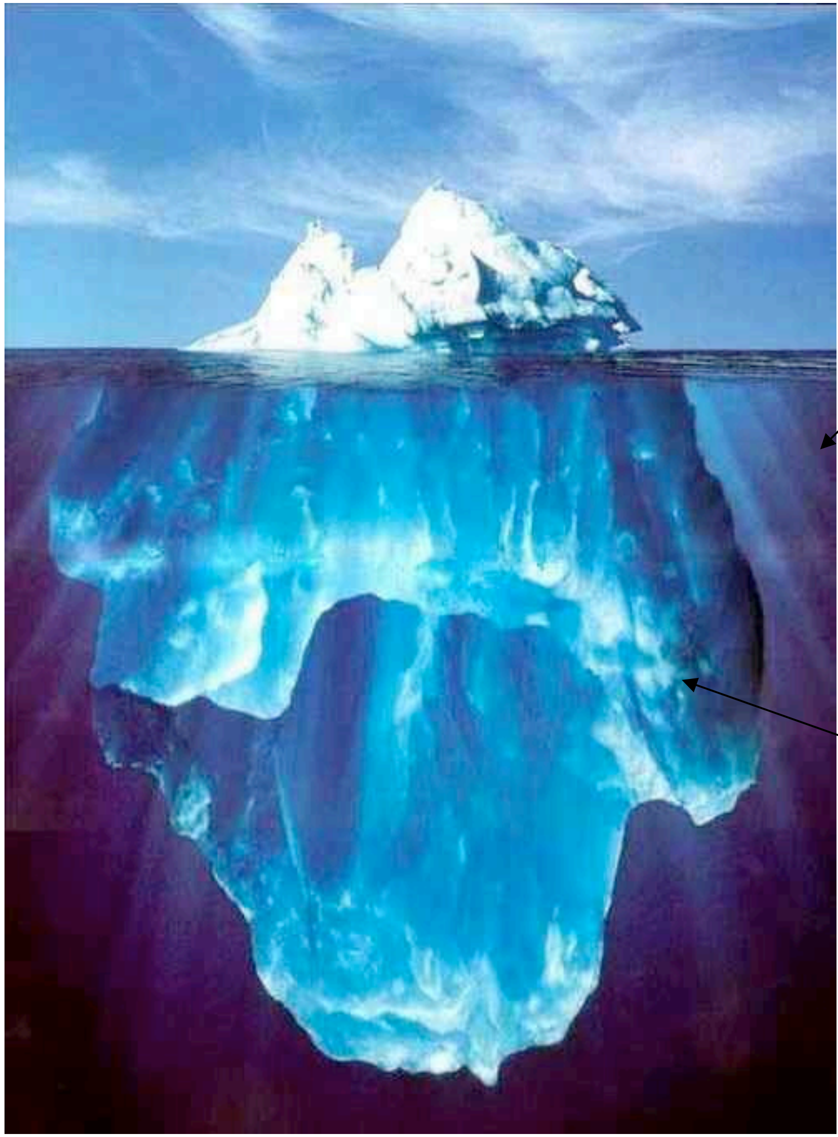


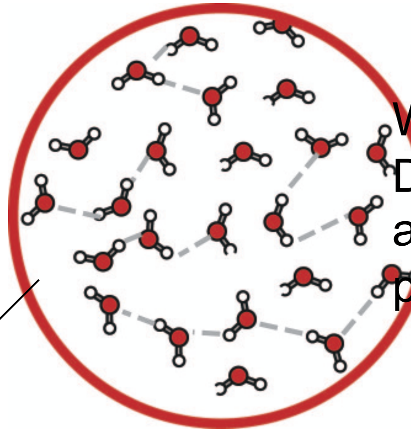
lowering temperature

Bond Energy in Tetrahedral becomes more important

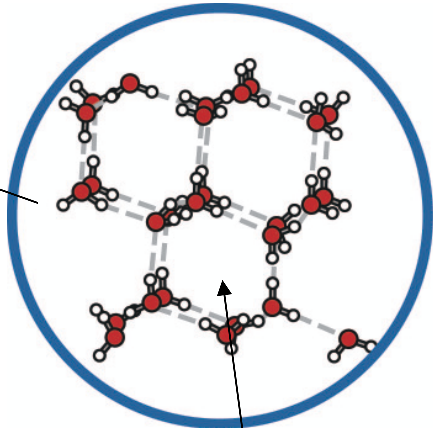
Converting some Disordered structures to ice-like structures

Water denser than the solid

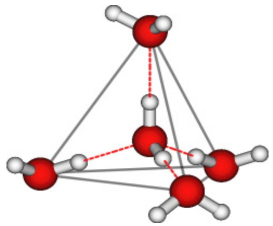




Water, higher density
Disordered structure
allows more dense
packing

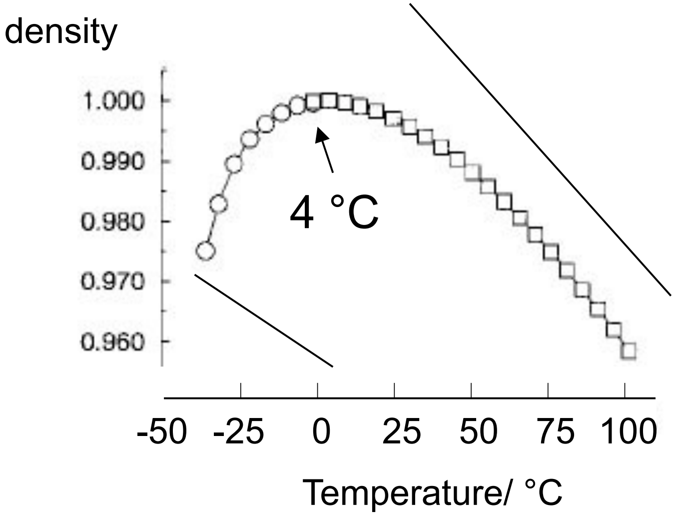


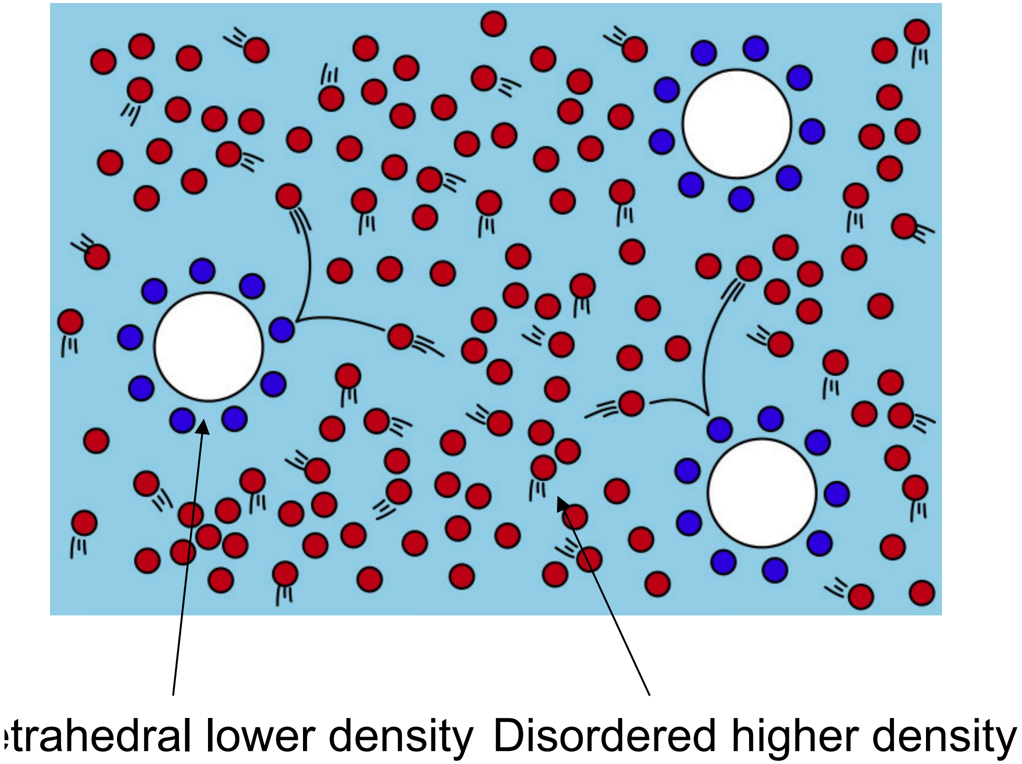
Ice, lower density
More open space



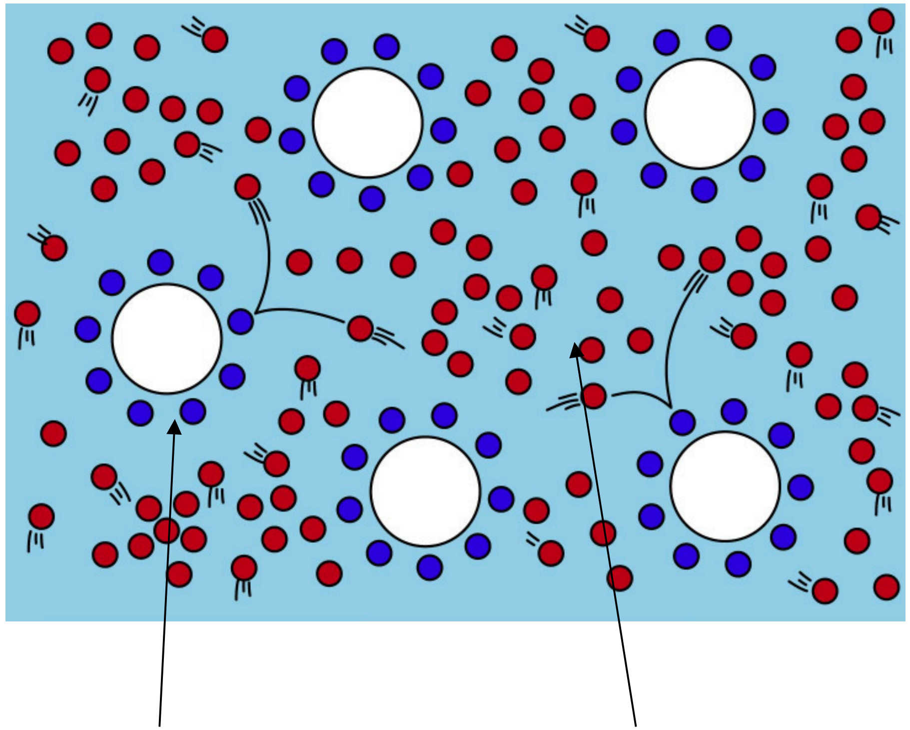
Open space inside the rings

Density Maximum



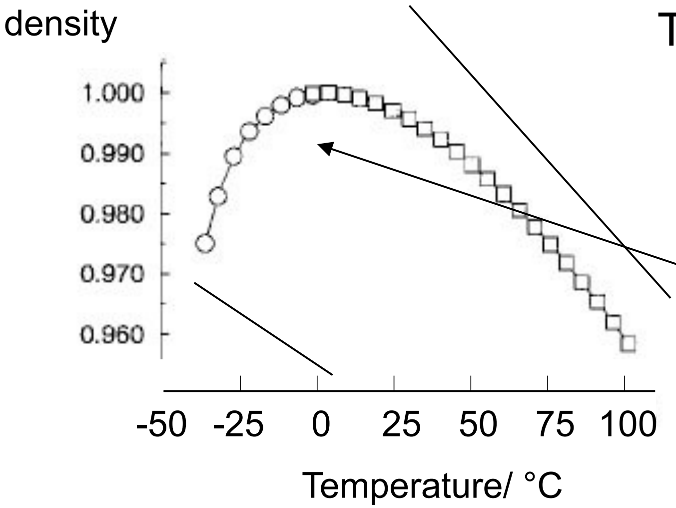


Density Maximum



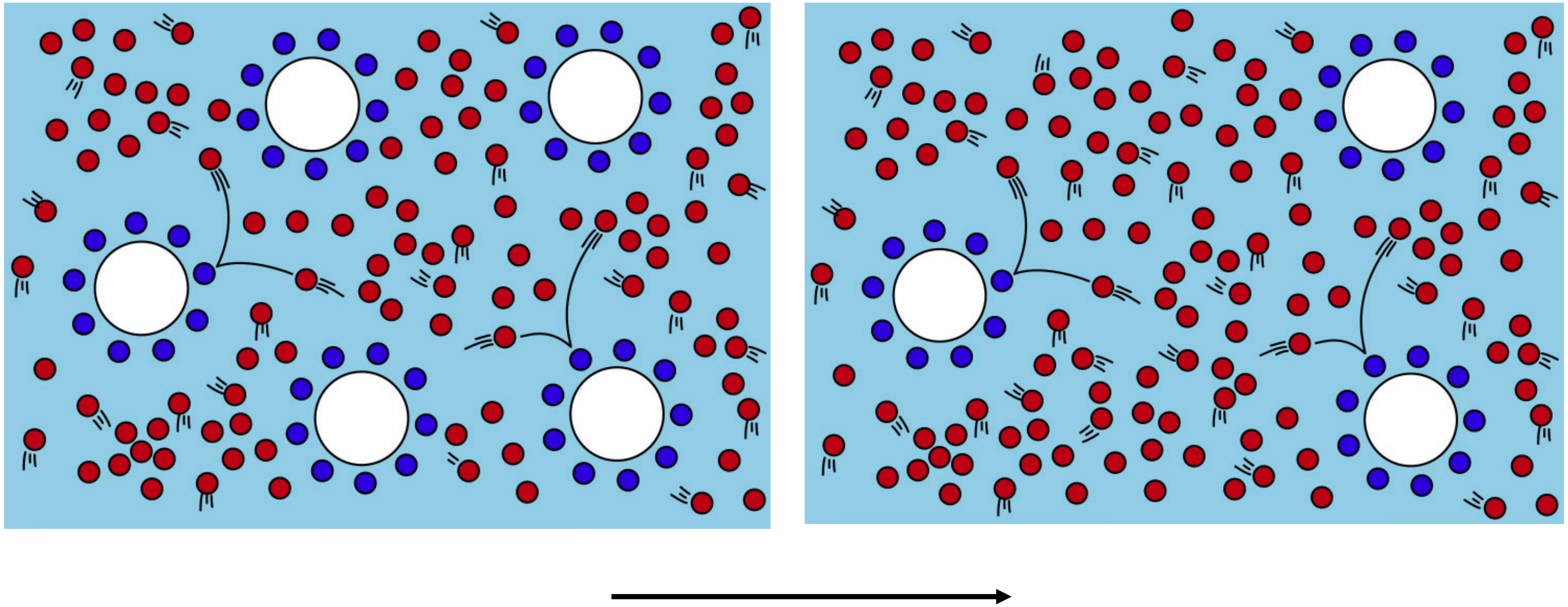
Tetrahedral lower density

Disordered higher density



With decreasing temperature we increase the number of tetrahedral structures which have lower density

High Heat Capacity

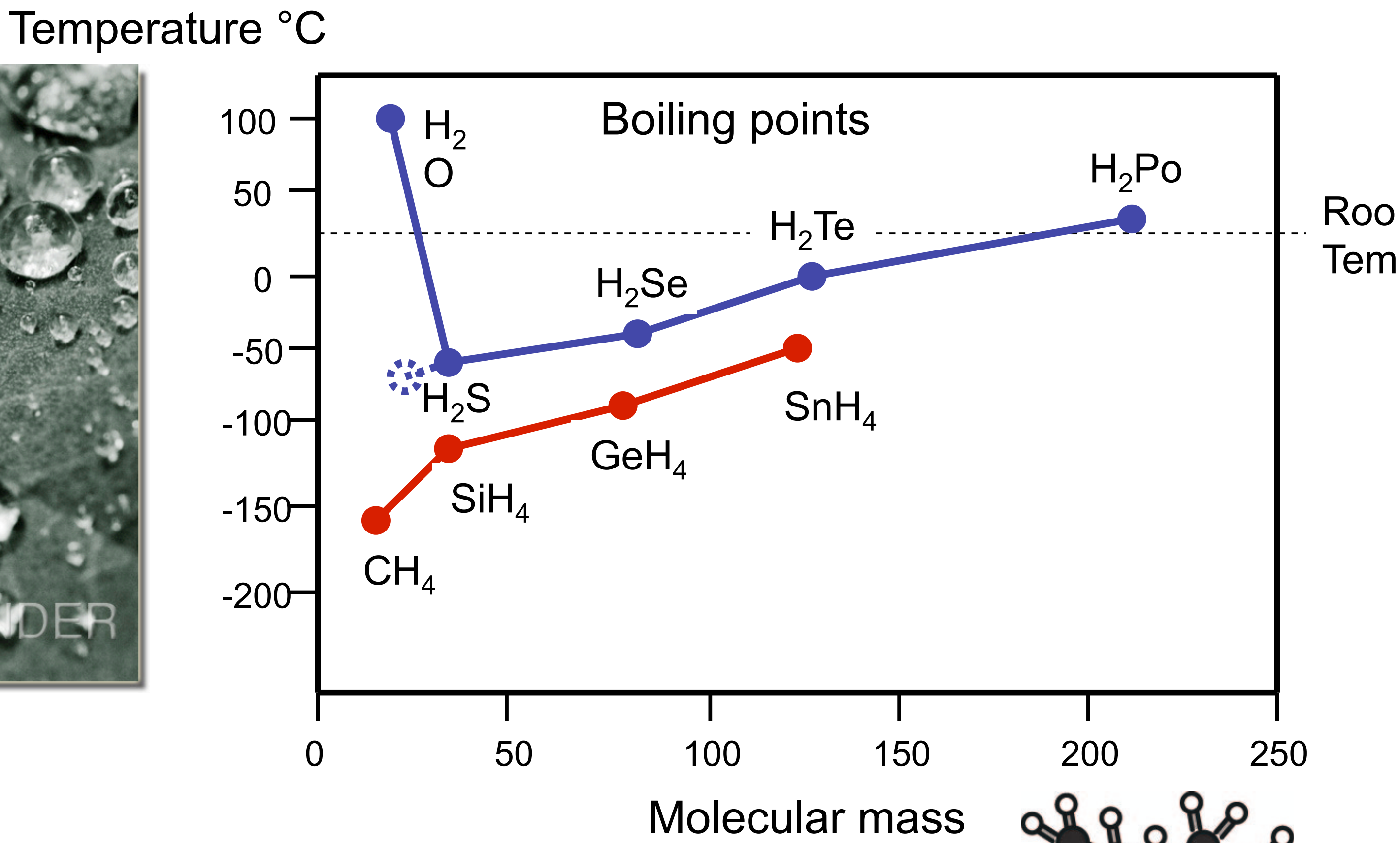


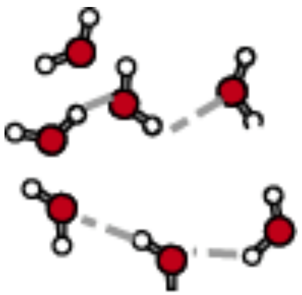
increasing temperature

Temperature related to kinetic energy of particles

Normal liquid heat is increasing kinetic energy
Water is additional energy required to convert tetrahedral to disordered
Additional heat required to increase temperature
HIGH HEAT CAPACITY

High Surface Tension





Hydrogen bonds in water makes the glue

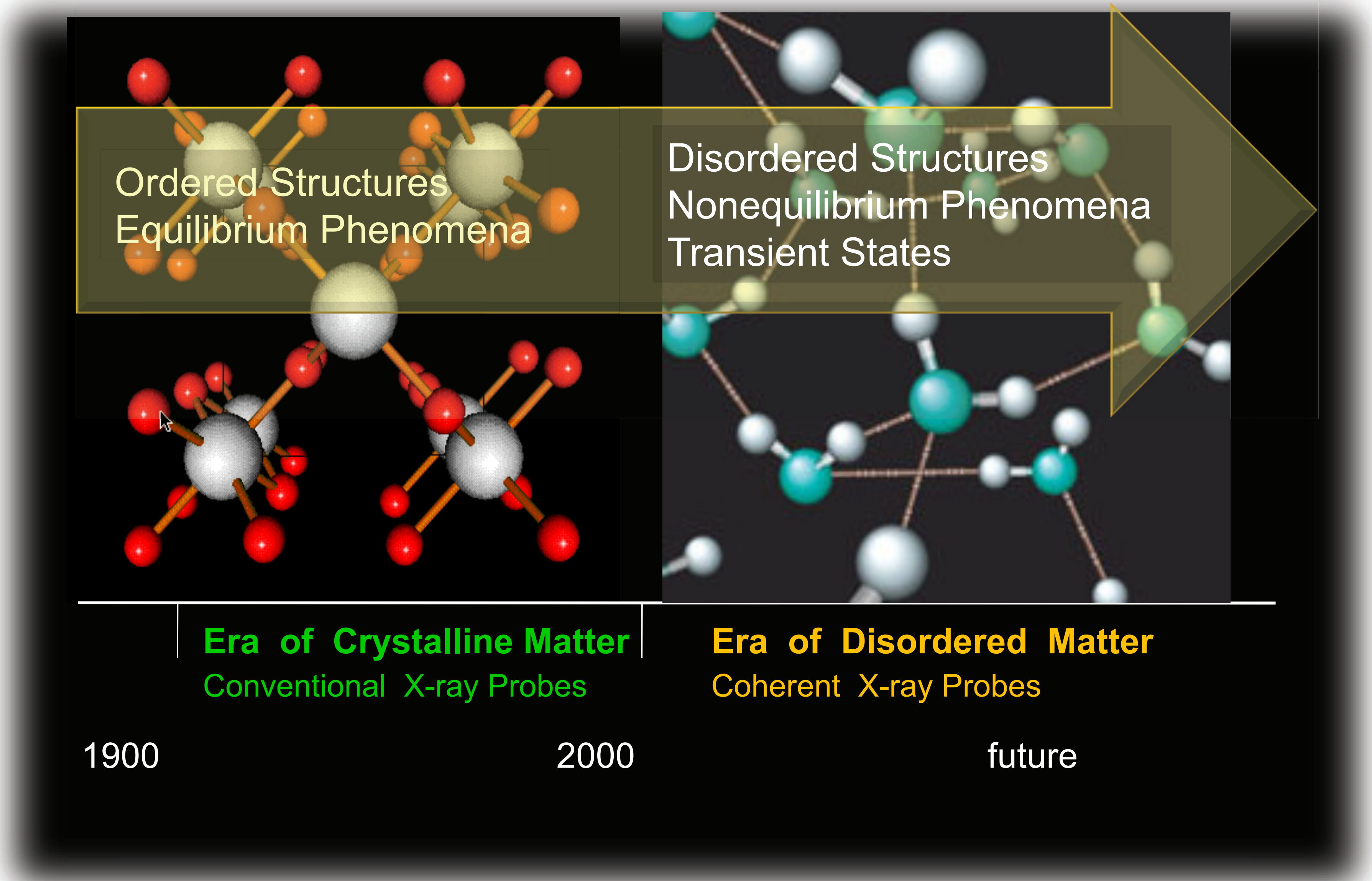
Molecular mass makes gasoline a liquid but weak bonding in between the molecules

6 February 2010

Conclusions

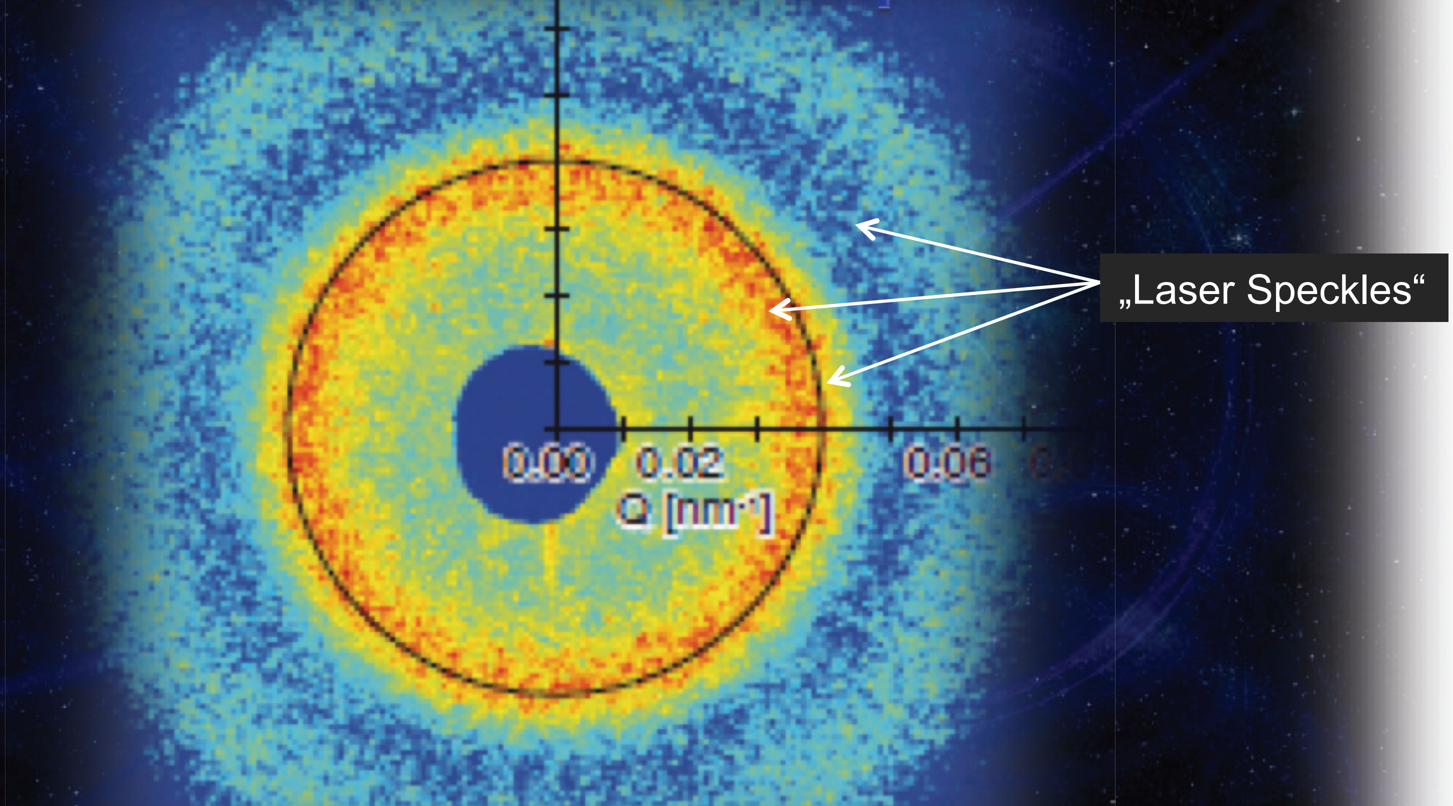
- Two components maximizing either enthalpy (tetrahedral, low-density) or entropy (non-specific H-bonding, higher density)
- Interconvert discontinuously
- Ratio depends on temperature
- Density fluctuations on 1 nm length scale
- Increasing size in supercooled region, critical exponents
- Connection to Widom line and 2nd critical point

Unique Opportunity with FEL for Water Research



Courtesy of H. Dosch

Coherent snapshot diffraction from liquid



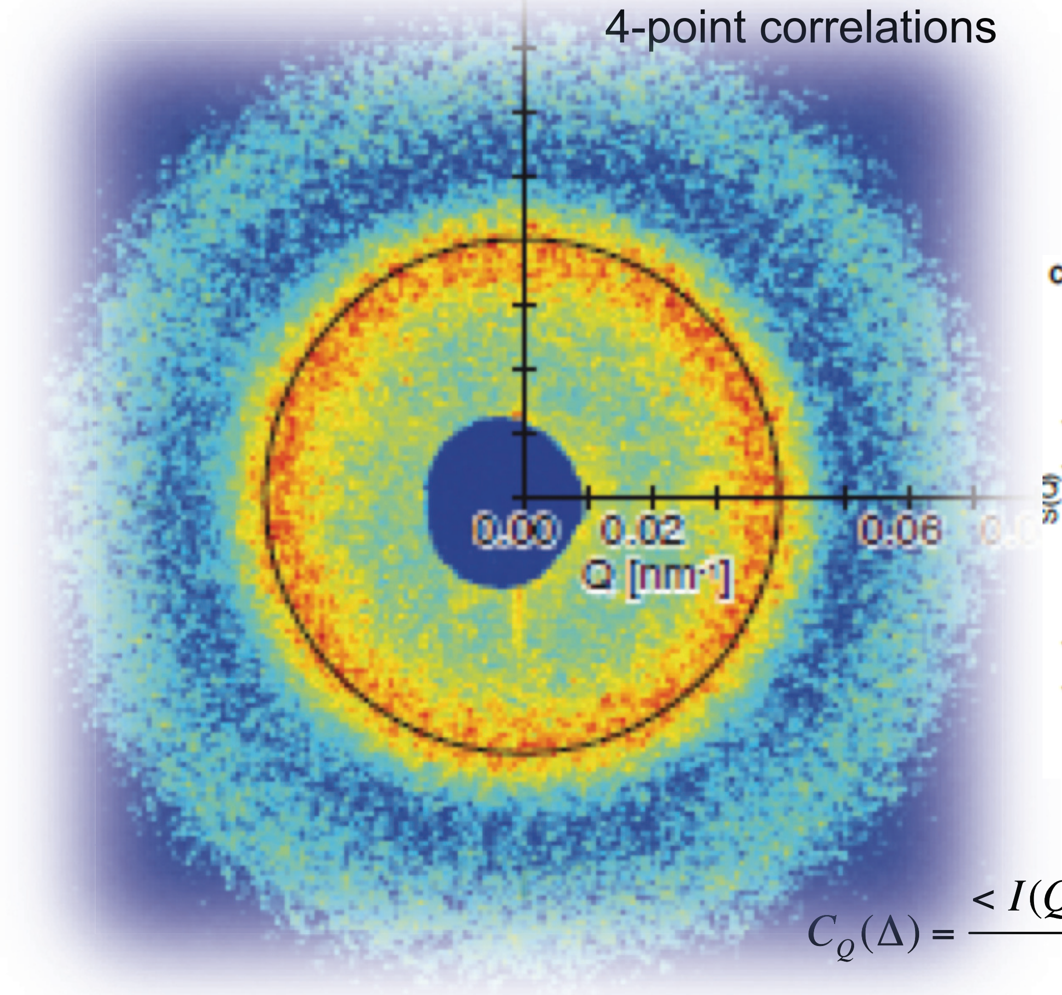
Coherent Diffraction Pattern
obtained from frozen liquid (glass)
P. Wochner et al., PNAS **106**, 11511 (2009)

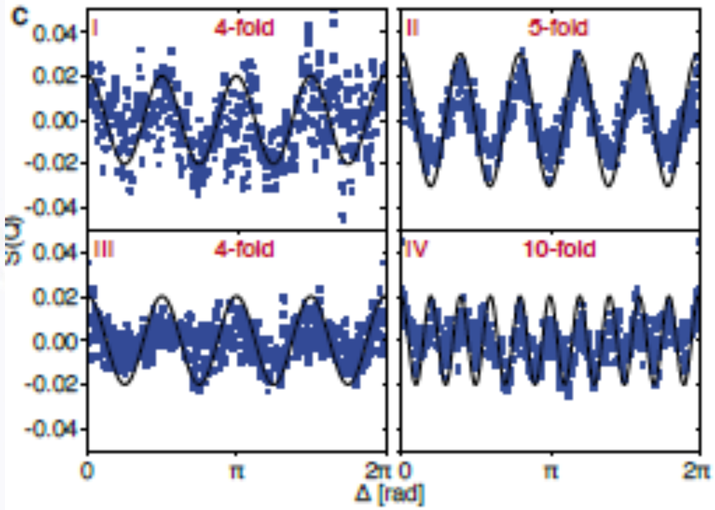
cognitivedistortion.com

Hidden Local Symmetries from Higher-Order Correlation Functions

4-point correlations

MPI-MF DESY ESRF
P. Wochner et al.
PNAS **106**, 11511 (2009)





$$C_Q(\Delta) = \frac{< I(Q,\varphi) I(Q,\varphi+\Delta) >_\varphi - < I(Q,\varphi) >_\varphi^2}{< I(Q,\varphi) >_\varphi^2}$$

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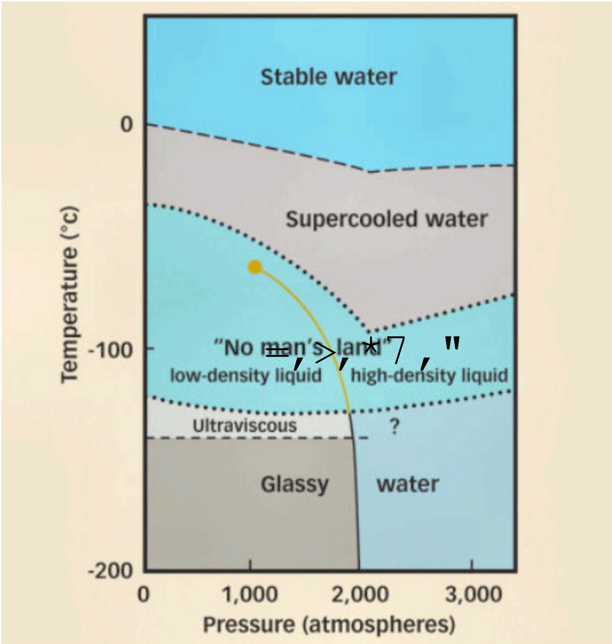

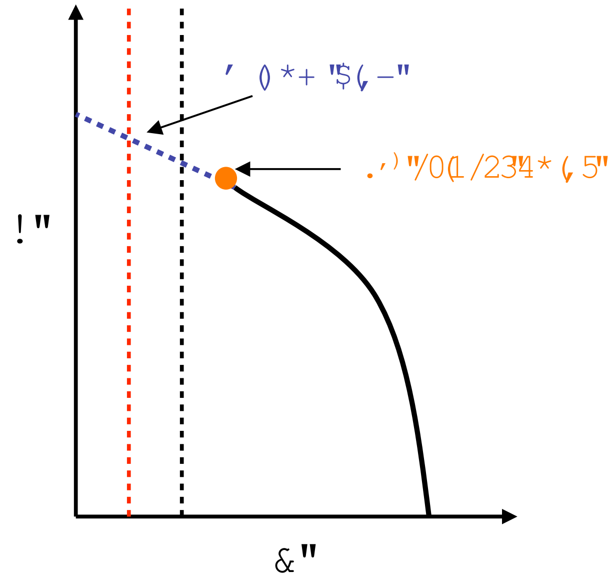

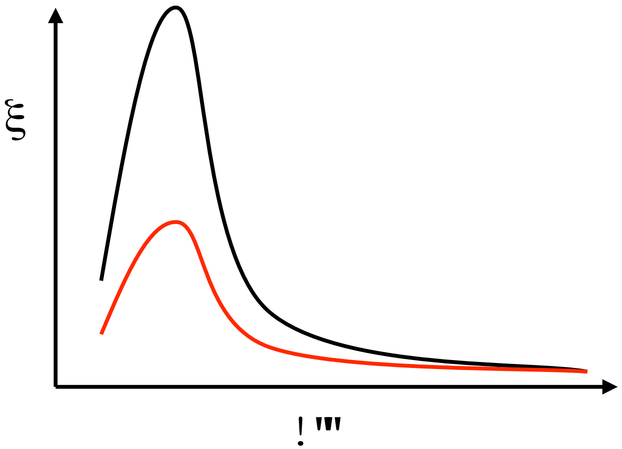

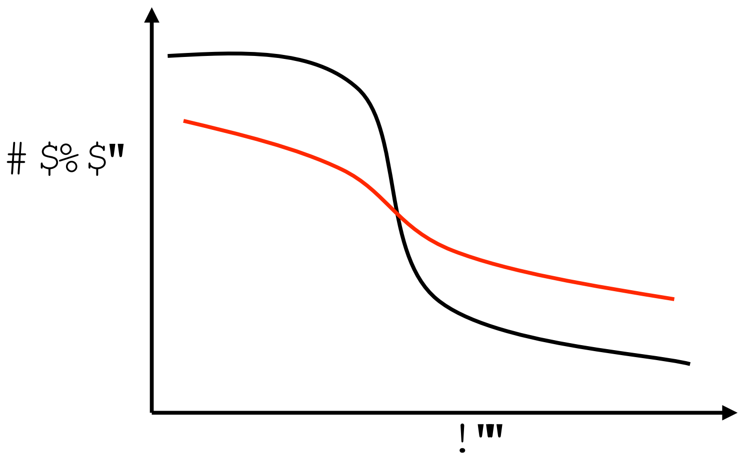

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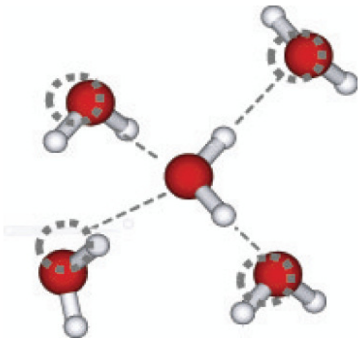
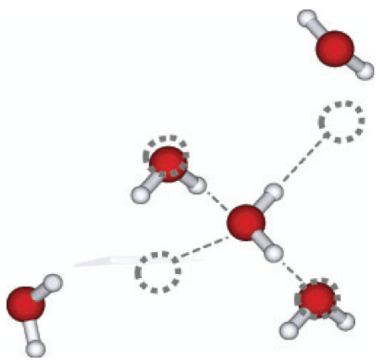
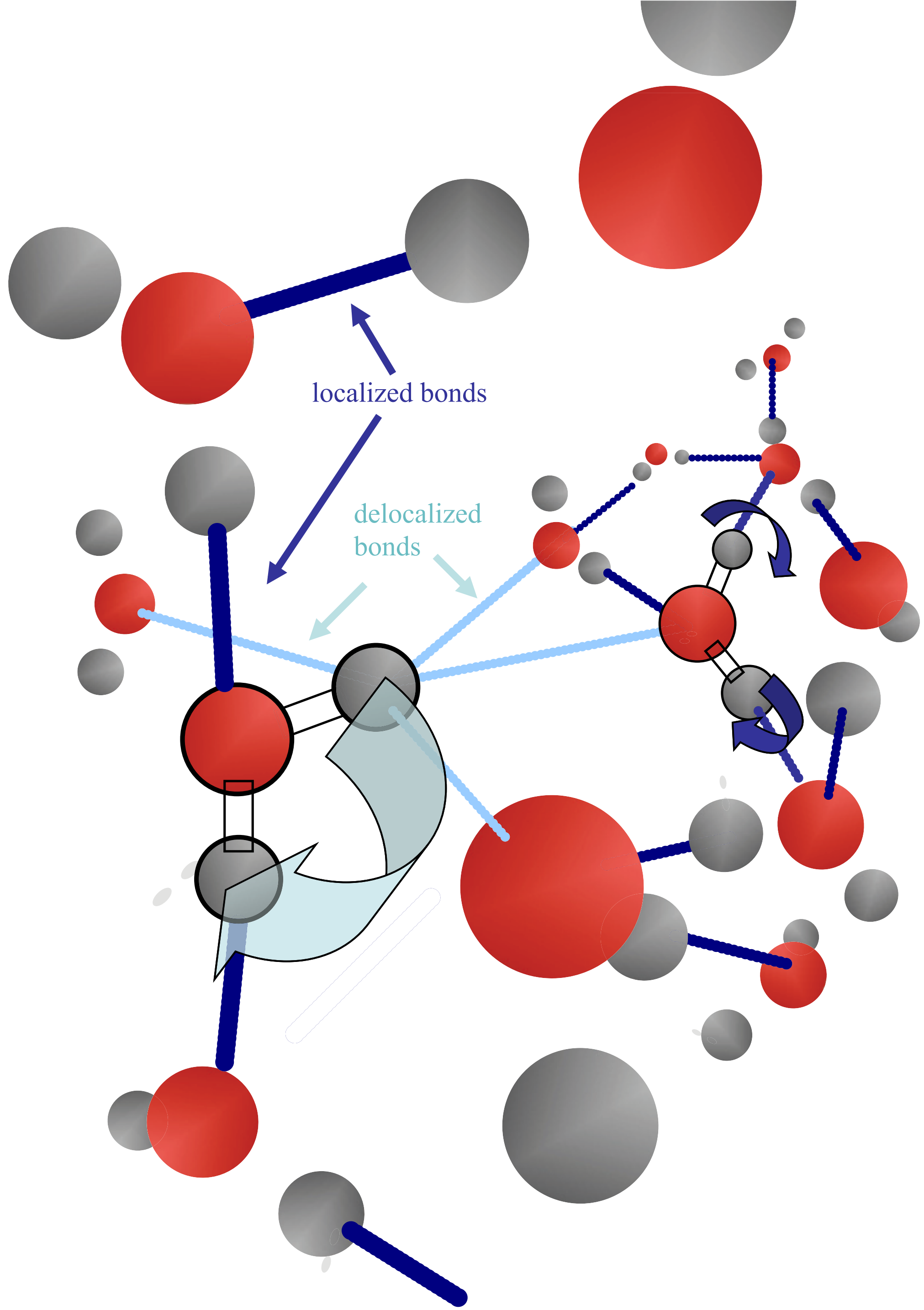


Bond Energy



Entropy



Pump-probe

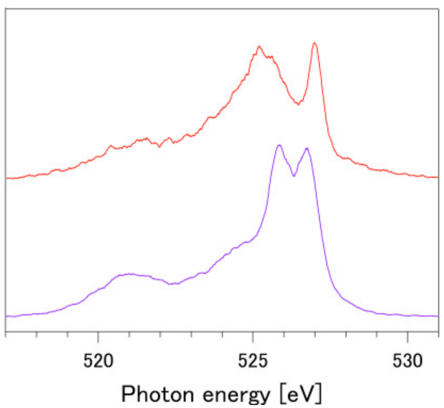
Perform pump-probe
IR-THz and x-ray

Probe stabilty and dynamics of
Tetrahedral and disordered

High repetition rate machine
Minimum beam damage

Nordlund, Nilsson, Lindenberg, Gaffney

XES



IR spectra

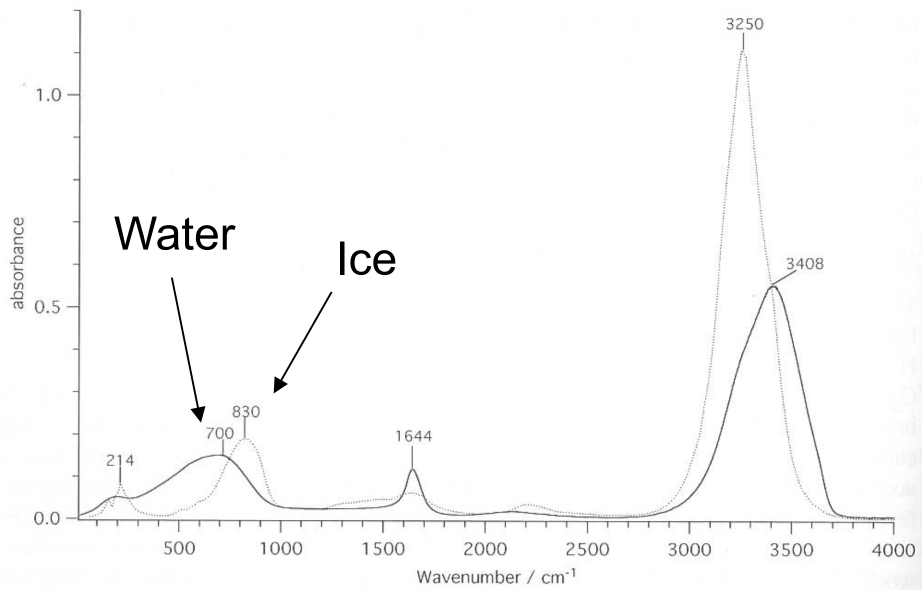


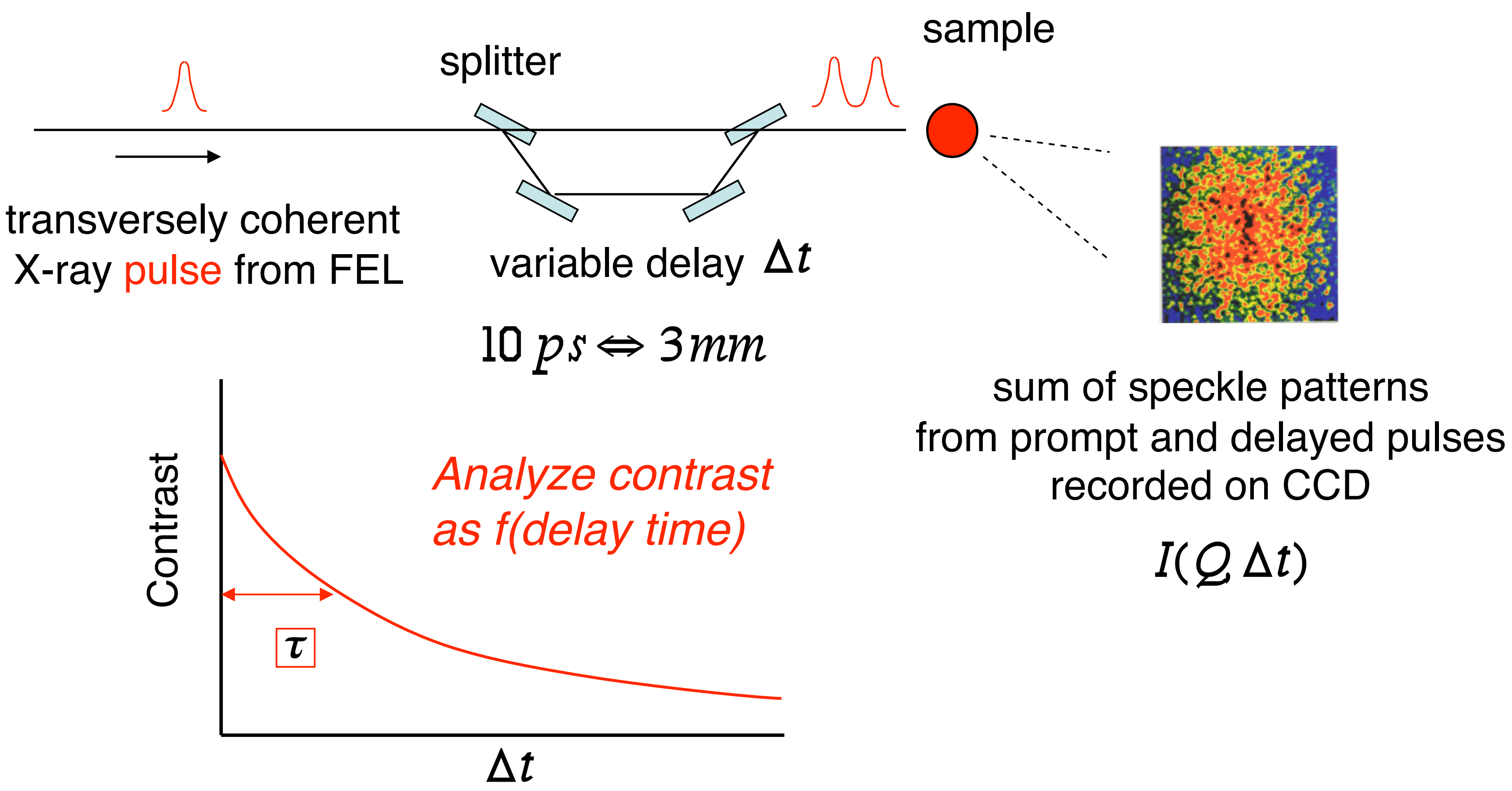
Figure 9.2 Infrared absorption spectra of 1-μm thick films of liquid water at room temperature (solid line) and of ice at −7 °C (dotted line). Absorbances $\log(I_0/I)$ for both species are calculated from the values of the absorption coefficient $k(\tilde{\nu})$, using eq. (5.A8) written in the form: $\log(I_0/I) = 4\pi\tilde{\nu}k(\tilde{\nu})l\log(e)$, with $l = 10^{-4}$ cm and wavenumbers $\tilde{\nu}$ expressed in cm^{-1}. Values of k for ice are those given by Warren (16). Values of k for liquid water are calculated from ATR spectra (17) in the mid-IR region ($\tilde{\nu} > 550\ cm^{-1}$) and are those given by Zelsmann (18), as calculated from absorption spectra, in the FIR region ($\tilde{\nu} < 600\ cm^{-1}$).

From Y. Maréchal, *The Hydrogen Bond and the Water Molecule*, Elsevier (2007)

Ultrafast XPCS using ‘Split Pulse’ Mode

Femtoseconds to nanoseconds time resolution

Uses high *peak* brilliance



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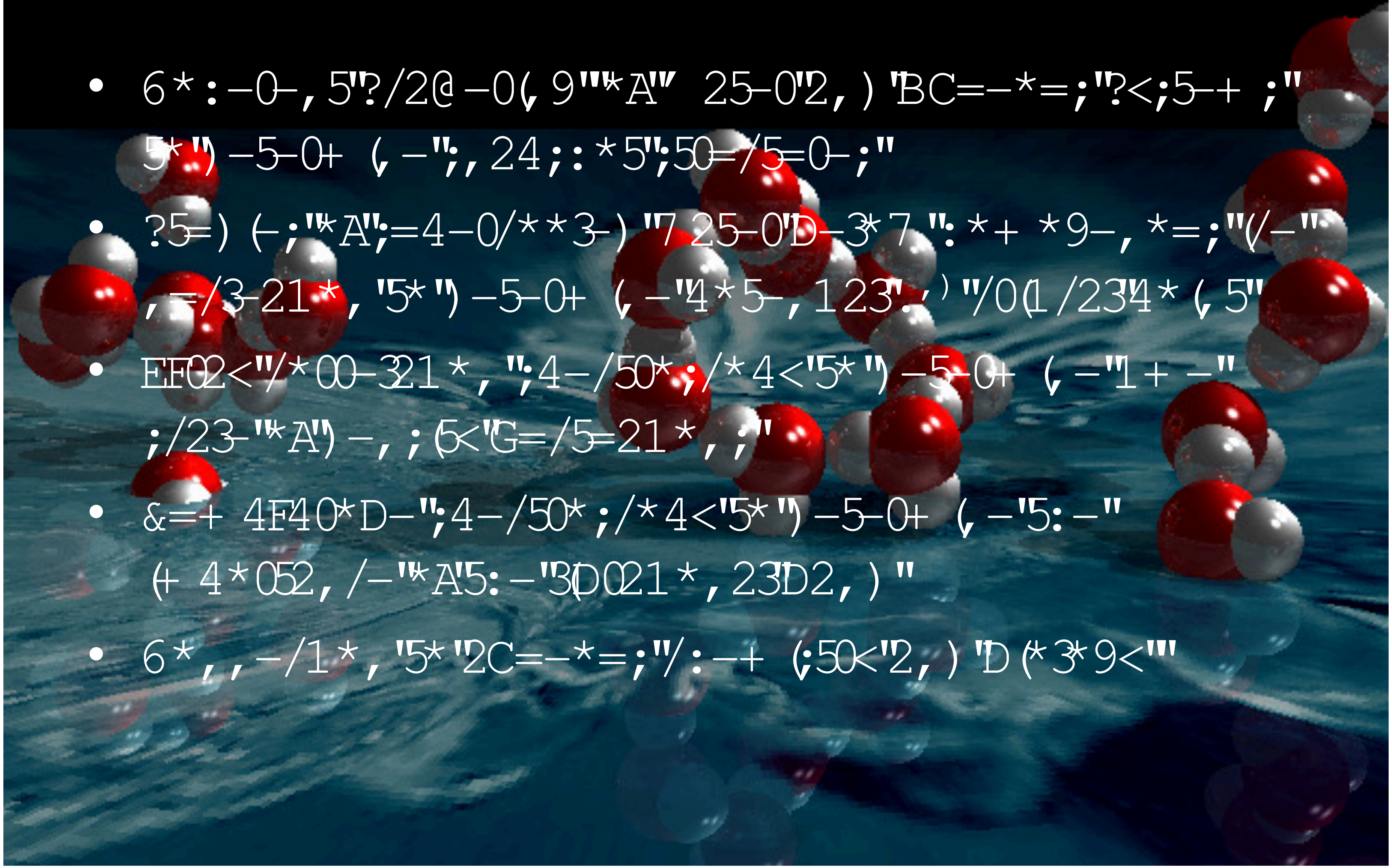

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- EF02<"/*00-321*,";4-/50*;/*4<"5*")-5-0+ (,-"1+-" ;/23-"*A")-,;(5<"G=/5=21*,;"
- &=+ 4F40*D-";4-/50*;/*4<"5*")-5-0+ (,-"5:-" (+ 4*052,/-"*A"5:-"3(D021*,23"D2,)"
- 6*,,-/1*,"5*"2C=-*=;"/:-+ (;50<"2,)"D(*3*9<""