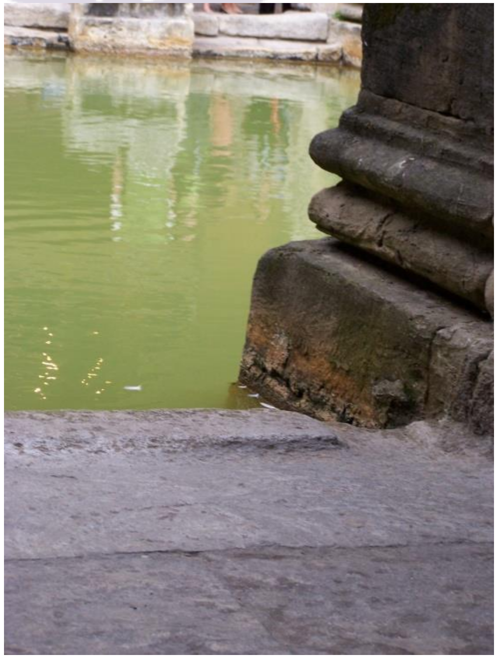
The structure of water



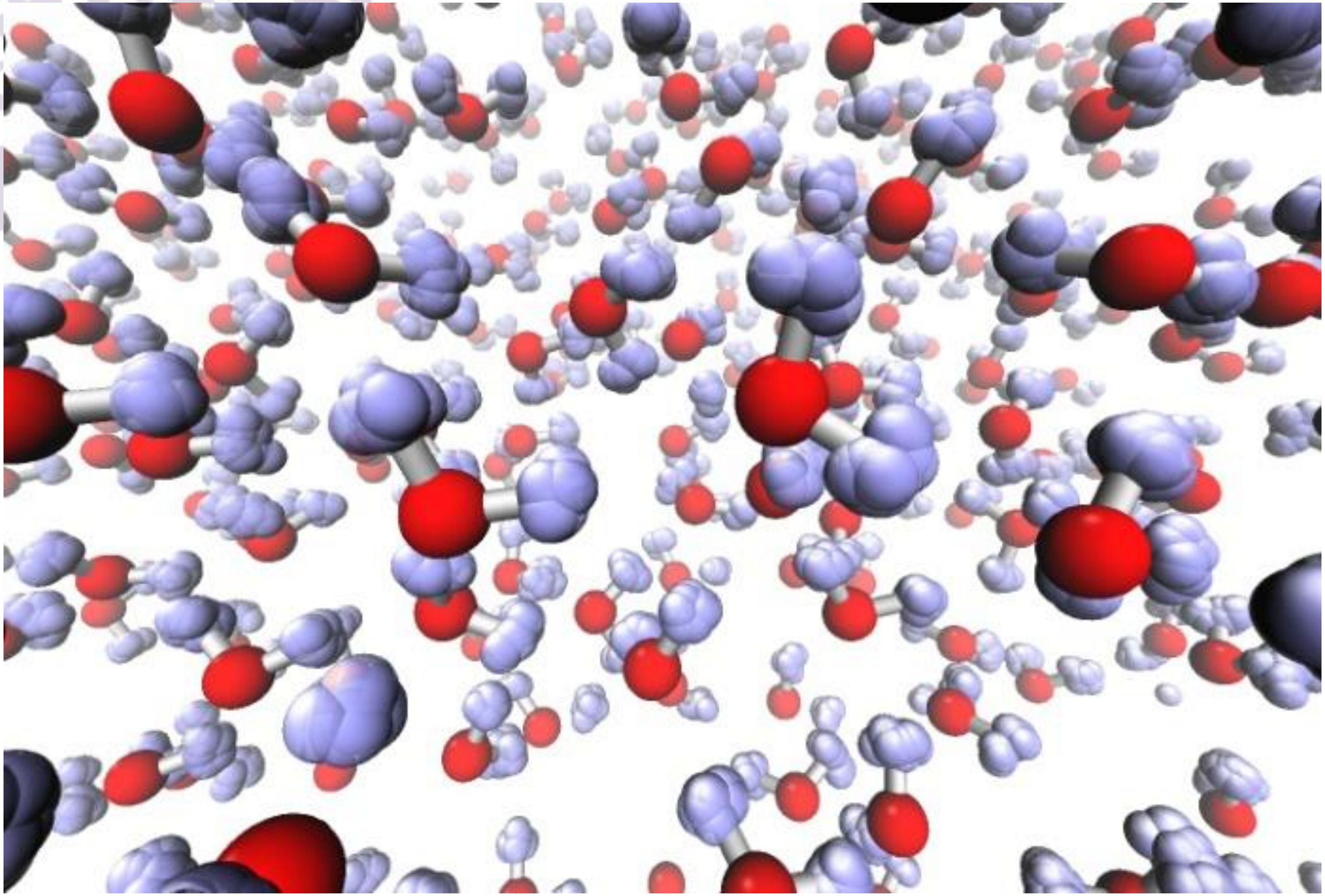
Anita Zeidler

University of Bath

- Philip S. Salmon (University of Bath)
- Henry E. Fischer (ILL, Grenoble)

ADD 21/03/2019

Formula: H_2O



Outline

- Issues with measurement of structure
- Neutron diffraction with H/D isotope substitution at a reactor source
- Oxygen substitution
- Down in *T* (ice)

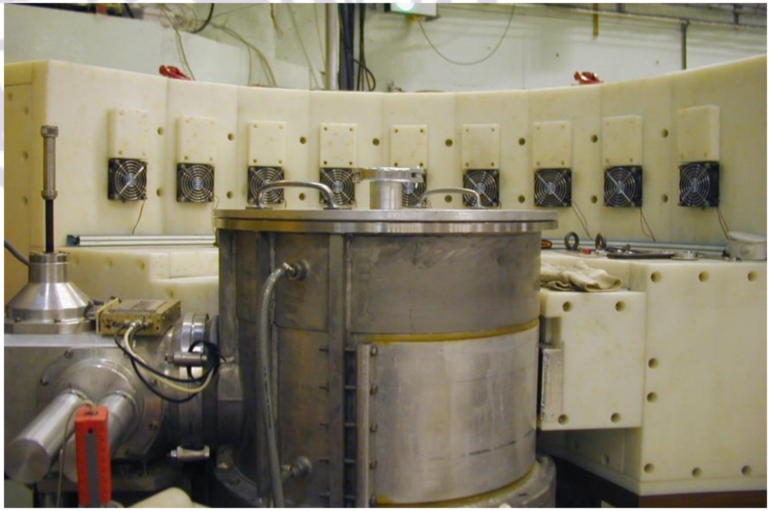
Water issues

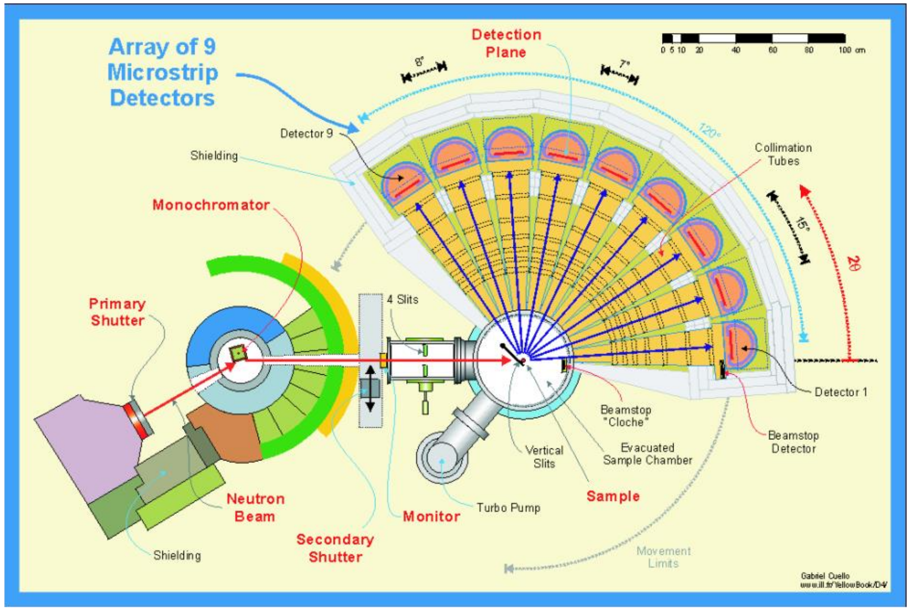
- X-rays scatter from electrons
  - H electron displaced towards O
- Mass of neutrons ~ mass of proton
  - Large inelastic scattering
- D has twice the mass of H
  - H_2O & D_2O truly isostructural?

NDIS (in principle)

- Measure at least 3 total structure factors for water with different H/D ratios
    - b_H = -3.7406(11) fm, b_D = 6.671(4) fm, b_O = 5.805(4) fm
- Combine to calculate 3 partial structure factors
- Or: mix H_2O & D_2O to obtain $b_{\text{"H"}} = 0$
    - Measure $S_{OO}(q)$ directly
- Or: mix H_2O & D_2O to obtain $b_{\text{"H"}} = b_O$
    - Measure $S_{NN}(q)$ directly

Neutron Diffraction Experiment

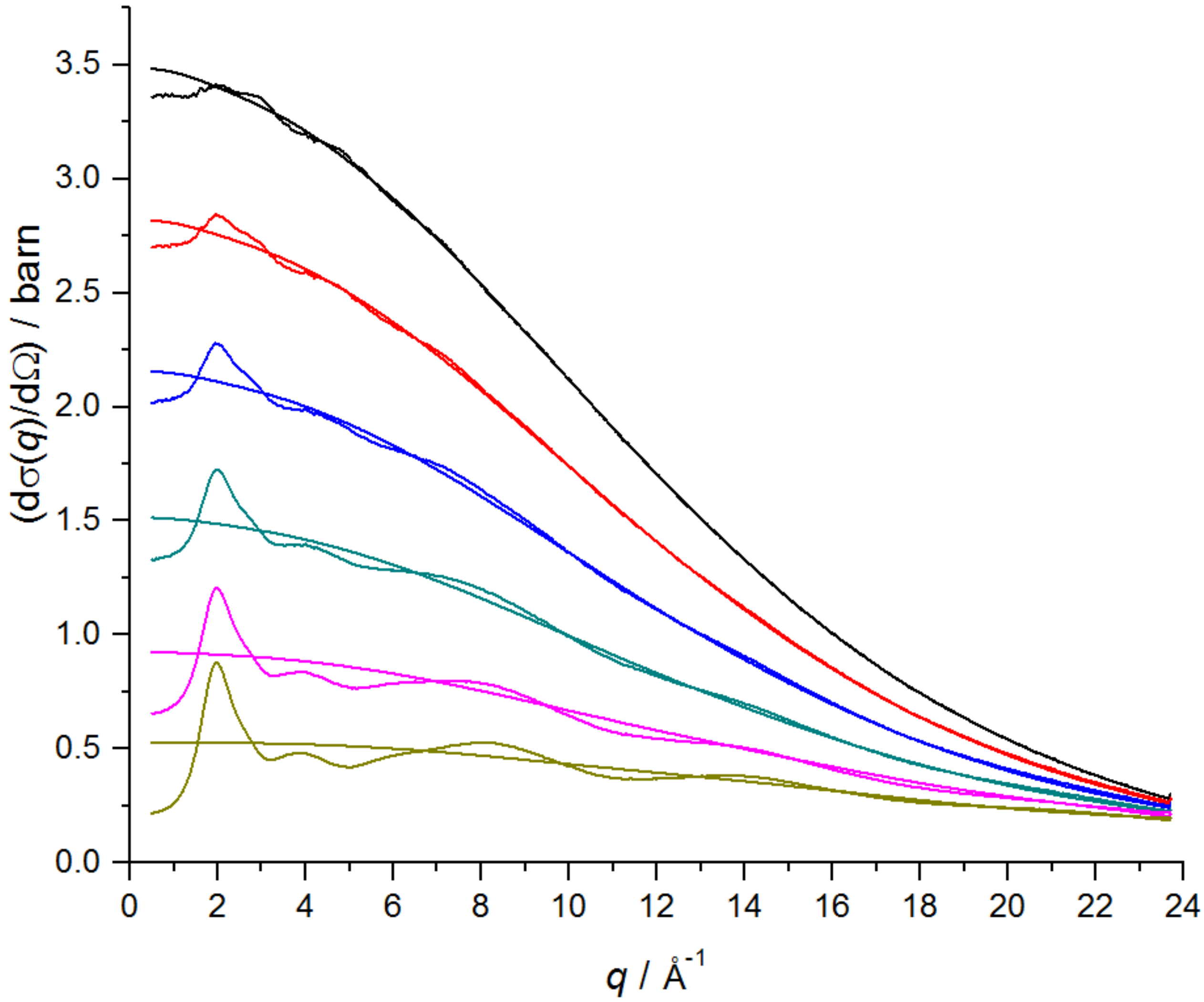




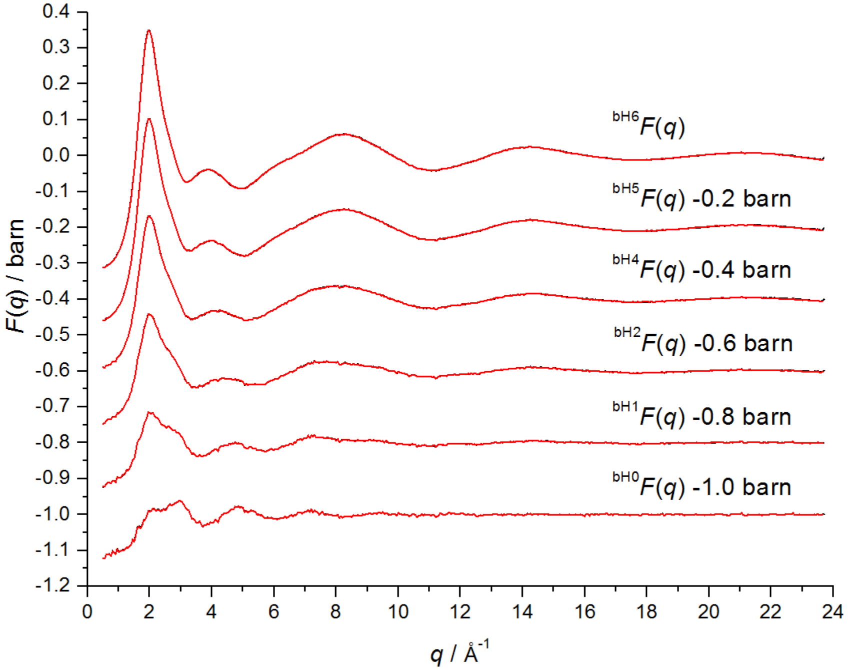
Intensity measured as function of angle at fixed wavelength

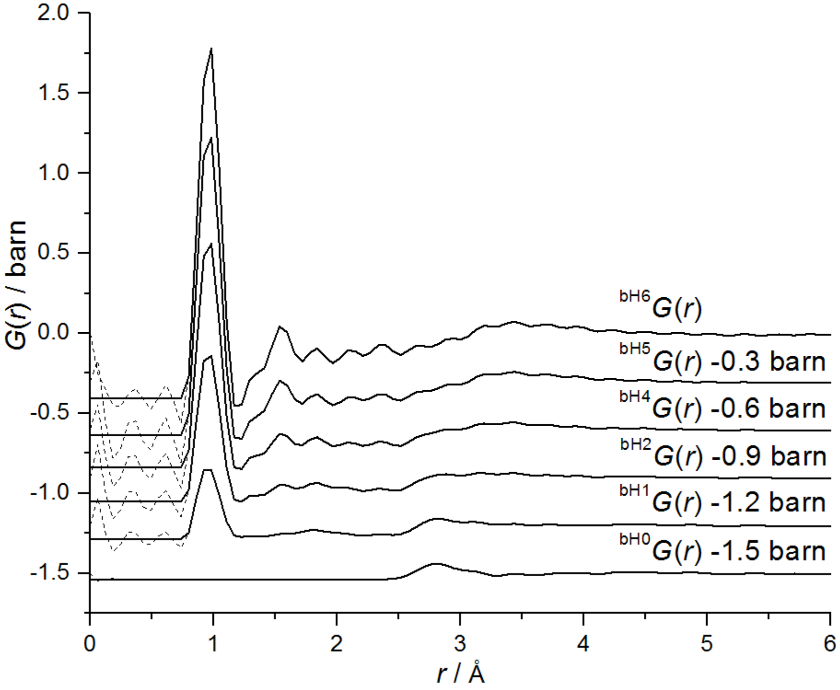
$$q = \frac{4\pi \sin(\theta)}{\lambda}$$

Water Diffraction



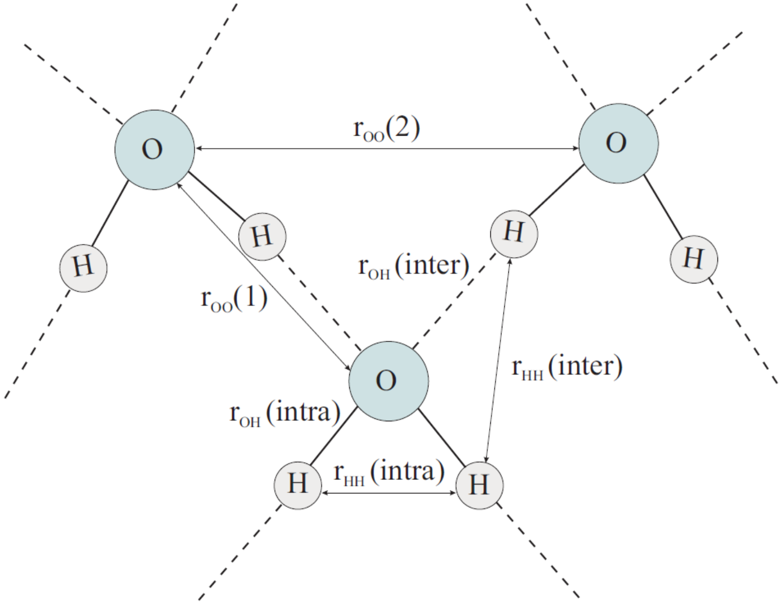
Water Diffraction



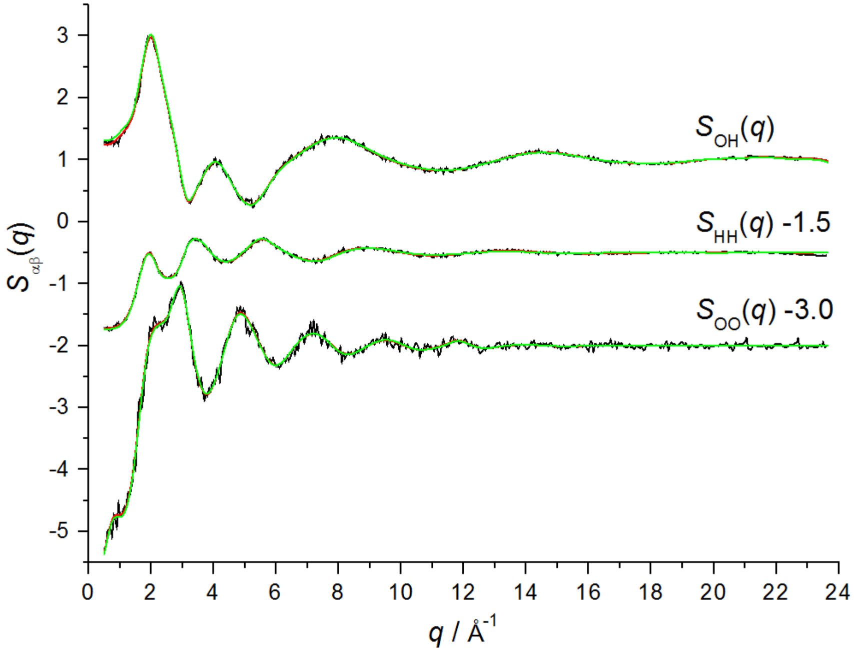


Use SVD method to get partials

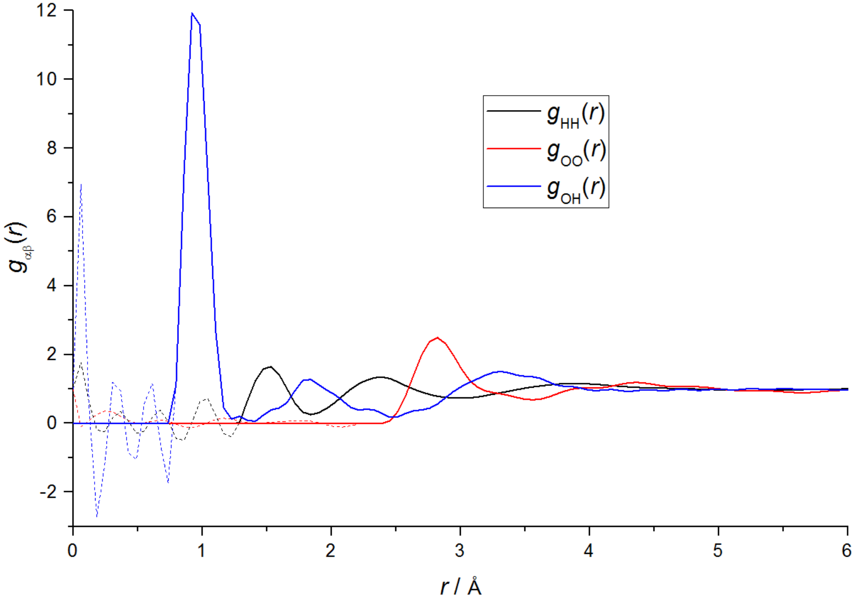
Partials



O
O
O
H
H
H
H
H
H
$r_{OO}(2)$
$r_{OO}(1)$
r_{OH} (inter)
r_{HH} (inter)
r_{OH} (intra)
r_{HH} (intra)



$S_{OH}(q)$
$S_{HH}(q)$ -1.5
$S_{OO}(q)$ -3.0
$S_{\alpha\beta}(q)$
q / Å^{-1}
3
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8
10
12
14
16
18
20
22
24



$g_{HH}(r)$
$g_{OO}(r)$
$g_{OH}(r)$
$g_{\alpha\beta}(r)$
r / Å
12
10
8
6
4
2
0
-2
0
1
2
3
4
5
6

Neutron Diffraction Experiment

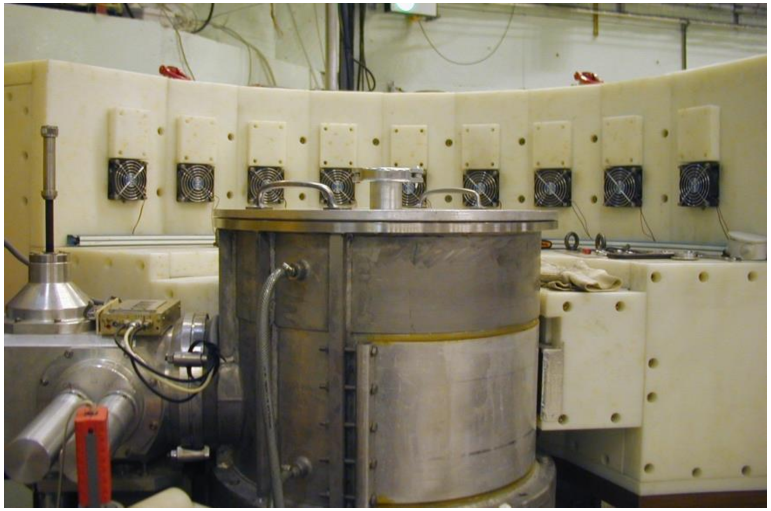
- The structure of water at the partial structure factor level had so far only been investigated using H/D substitution
- Use of oxygen isotope substitution should eliminate main effects due to inelastic scattering in NDIS experiments
- The difference in structure between H_2O and D_2O can be investigated by calculating suitable difference functions

Why is there a need for more ND experiments on H_2O/D_2O?

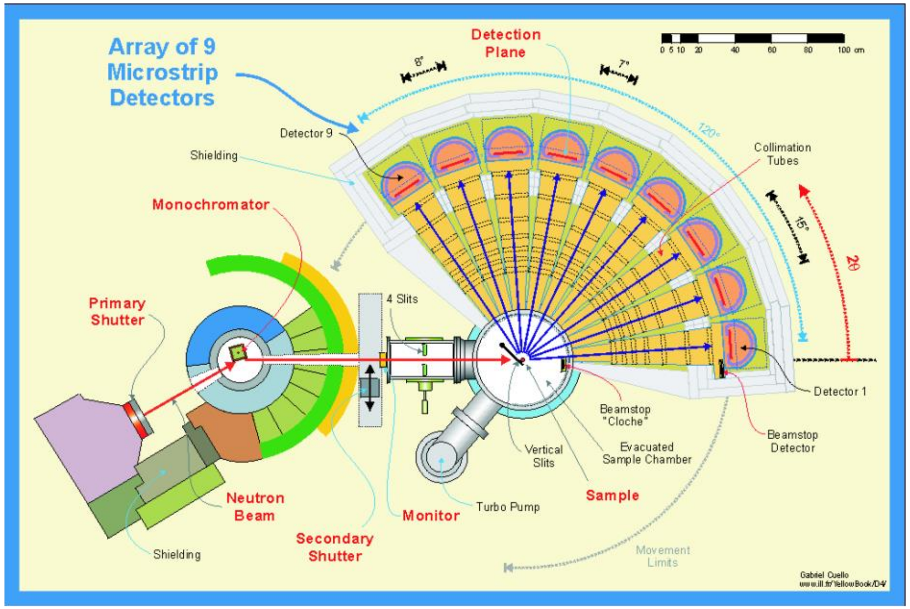
- Differences in structure and dynamics of H_2O vs. D_2O (due to quantum effects) lead to e.g. changes in melting/boiling point, temperature of maximum density, interactions with biological systems
- There exists no purely experimental measurement on the difference between the O-H and O-D bond lengths in liquid water
- Much cited PRL* that models a combination of x-ray and neutron data finds O-H bond to be ~ 3 % longer than O-D bond (larger than any theoretical prediction)

* AK Soper and CJ Benmore (2008) *PRL* **101** 065502

D4C Experiment (ILL Grenoble)

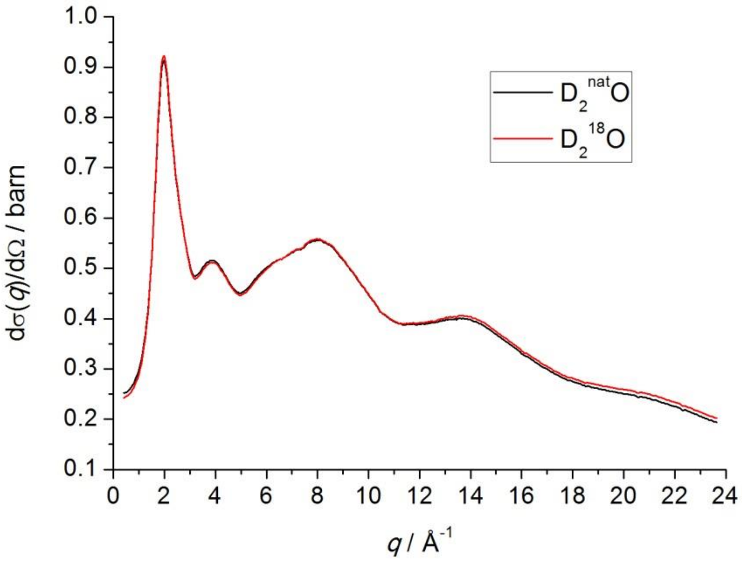


- Measured
  - $D_2{}^{nat}O$ and $D_2{}^{18}O$
  - $H_2{}^{nat}O$ and $H_2{}^{18}O$
- Wavelength of ~0.5 Å
- $0.35 \leq q/\text{Å}^{-1} \leq 23.5$
- $b_{natO} = 5.805(4)$ fm
- $b_{18O} = 6.009(5)$ fm

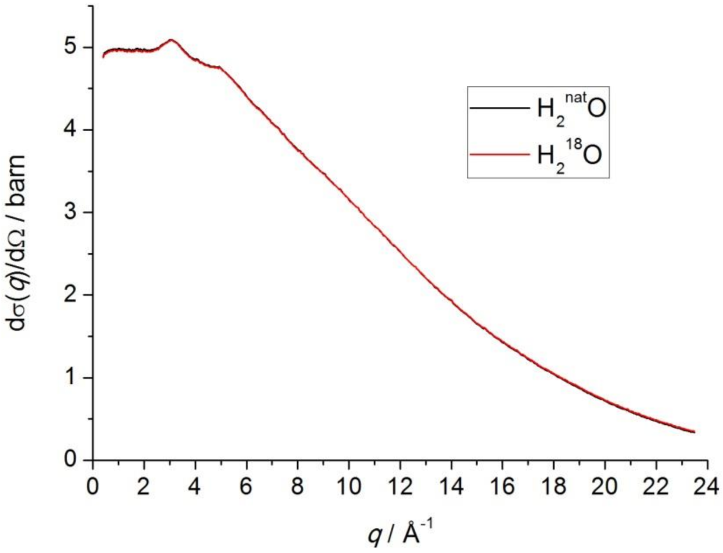


NDIS experiment

Differential scattering cross-sections for $D_2{}^{nat}O$ and $D_2{}^{18}O$



Differential scattering cross-sections for $H_2{}^{nat}O$ and $H_2{}^{18}O$



$$\frac{d\sigma(q)}{d\Omega} = F(q) + \sum_{\alpha} \frac{c_{\alpha}\sigma_{s,\alpha}}{4\pi}\left(P_{\alpha}(q)+1\right)$$

Maths

$$\Delta F_H(q) = \left(\frac{\mathrm{d}\sigma(q)}{\mathrm{d}\Omega}\right)_{H_2{}^{18}O} - \left(\frac{\mathrm{d}\sigma(q)}{\mathrm{d}\Omega}\right)_{H_2{}^{nat}O} + \Delta P_H(q)$$

$$= F_{H_2{}^{18}O}(q) - F_{H_2{}^{nat}O}(q)$$

$$= c_O^2\left(b^2_{^{18}O} - b^2_{^{nat}O}\right)\cdot\left(S_{OO}(q)-1\right) + 2c_H c_O b_H\left(b_{^{18}O} - b_{^{nat}O}\right)\cdot\left(S_{OH}(q)-1\right)$$

$$\Delta F_D(q) = \left(\frac{\mathrm{d}\sigma(q)}{\mathrm{d}\Omega}\right)_{D_2{}^{18}O} - \left(\frac{\mathrm{d}\sigma(q)}{\mathrm{d}\Omega}\right)_{D_2{}^{nat}O} + \Delta P_D(q)$$

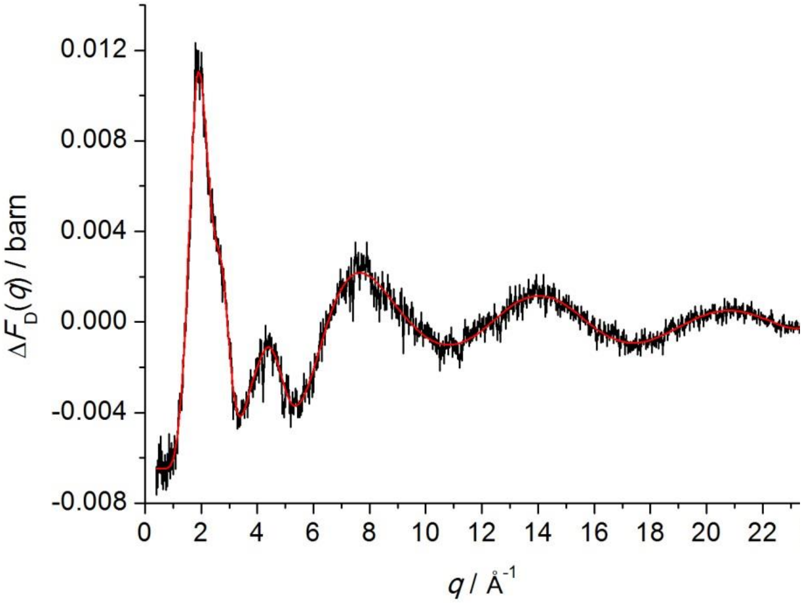
$$= F_{D_2{}^{18}O}(q) - F_{D_2{}^{nat}O}(q)$$

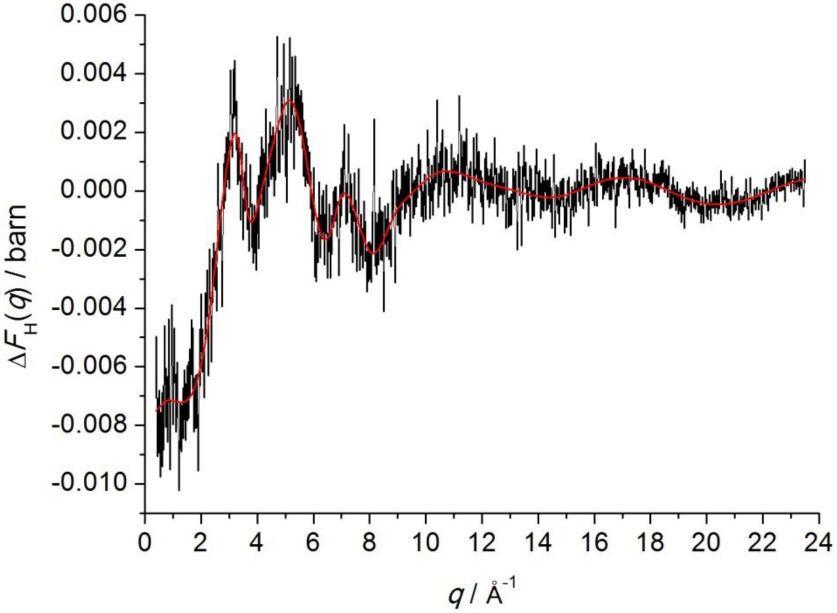
$$= c_O^2\left(b^2_{^{18}O} - b^2_{^{nat}O}\right)\cdot\left(S_{OO}(q)-1\right) + 2c_D c_O b_D\left(b_{^{18}O} - b_{^{nat}O}\right)\cdot\left(S_{OD}(q)-1\right)$$

Reciprocal space first order difference functions

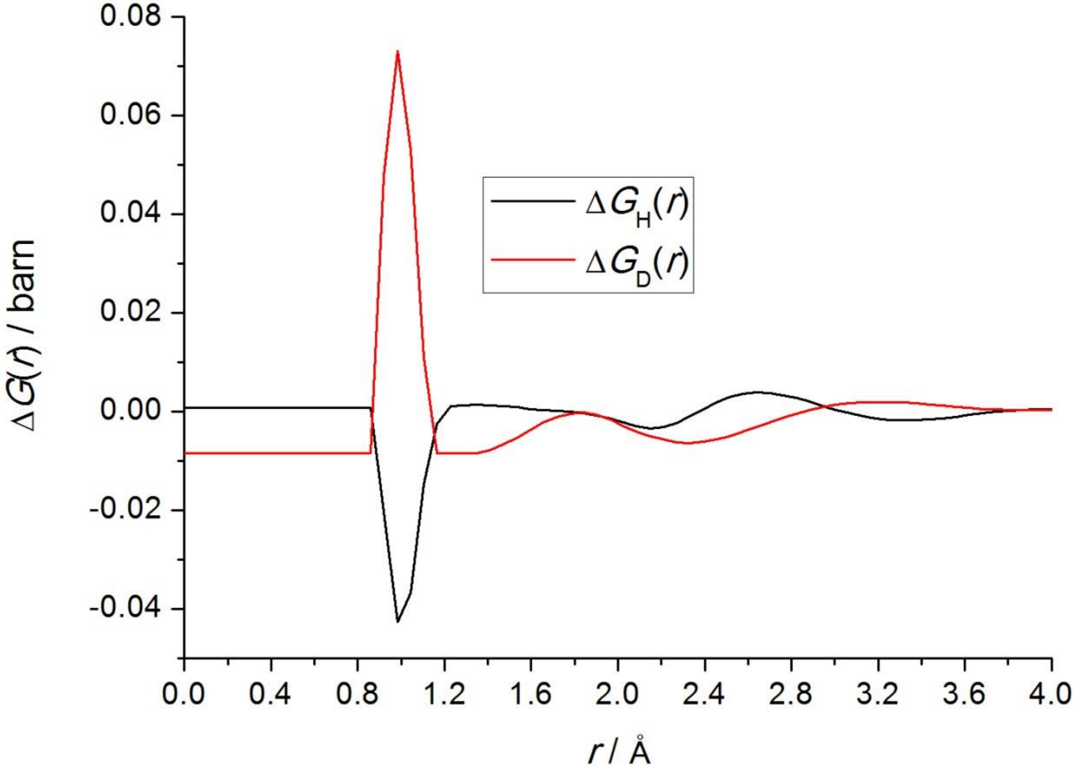
- after residual inelasticity correction

$$\Delta P(q) = a + bq^2 + cq^4$$





Real space first order difference functions



r_{OD} = 0.985(5) Å

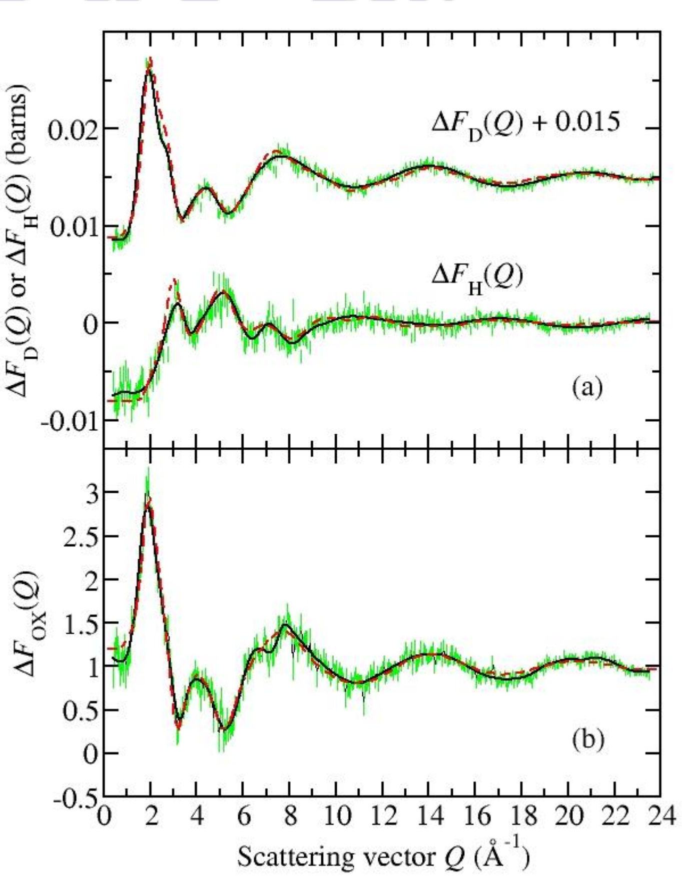
r_{OH} = 0.990(5) Å

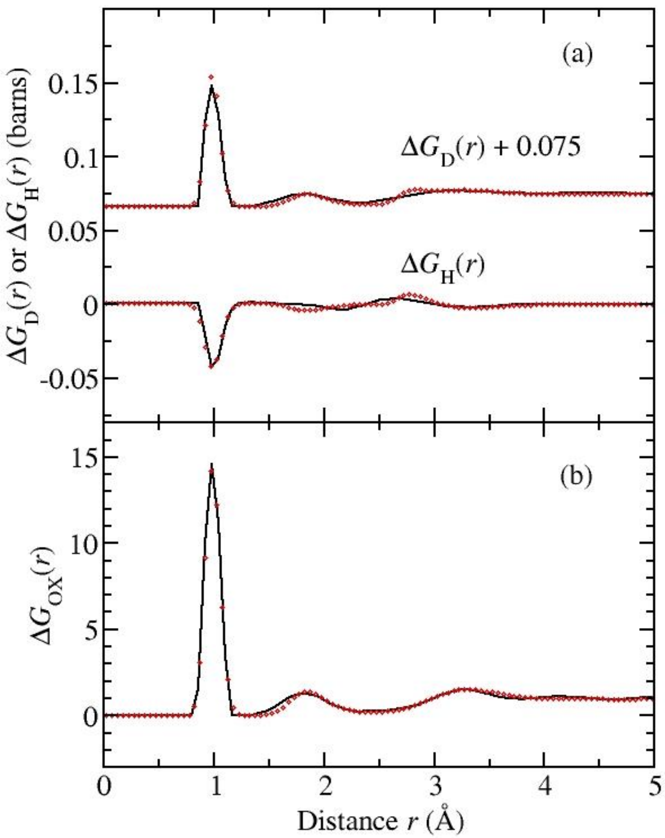
Difference ~ 0.5 %

First time ever this was **measured**.

Comparison with TTM3-F model simulation

PIMD simulations take into account quantum effects





TTM3-F model

- Polarisable & flexible
- Reproduces accurately O-H stretch region of IR absorption spectrum of liquid water as well as its diffusion coefficient
- Supports “competing quantum effects model”
  - Inter-molecular zero point energy and tunnelling weaken hydrogen bond network
  - Quantum fluctuations in anharmonic intra-molecular O-H bond increase its length and hence the dipole moment of molecule which increases binding between molecules (i.e. strengthens network)
  - Net effect is much smaller than originally suggested from rigid water simulations

Conclusions (O substitution)

- Oxygen isotope substitution in ND is feasible and can be applied to measure liquid and glassy oxide materials
- First entirely experimental evaluation of the difference in O-H and O-D bond lengths in liquid water
- Intra-molecular difference in bond length ~ 0.5 %
- So H/D substitution is valid for ambient water
- Path integral molecular dynamics simulations using TTM3-F model for water agree best with our diffraction results
- Results support a “competing quantum effects model” for water

Quantum weirdness makes life possible

Lisa Grossman

WATER'S life-giving properties exist on a knife-edge. It turns out that life as we know it relies on a fortuitous, but incredibly delicate, balance of quantum forces.

Water is one of the planet's weirdest liquids, and many of its most bizarre features make it life-giving. For example, its higher density as a liquid than as a solid means ice floats on water, allowing fish to survive under partially frozen rivers and lakes. And unlike many liquids, it takes a lot of heat to warm water up even a little, a quality that allows mammals to regulate their body temperature.

But computer simulations show that quantum mechanics nearly robbed water of these life-giving features. Most of them arise due to weak hydrogen bonds that hold H_2O molecules together in a networked structure. For example, it is hydrogen bonds that hold ice molecules in a more open structure than in liquid water, leading to a lower density. By contrast, without hydrogen bonds, liquid molecules move freely and take up more space than in rigid solid structures.

Yet in simulations that include quantum effects, hydrogen bond lengths keep changing thanks to the Heisenberg uncertainty principle, which says no molecule can have a definite position with respect to the others. This destabilises the network, removing many of water's special properties. "It breaks down big time," says Philip Salmon of the University of Bath in the UK.

JON HURSA / EPA/CORBIS

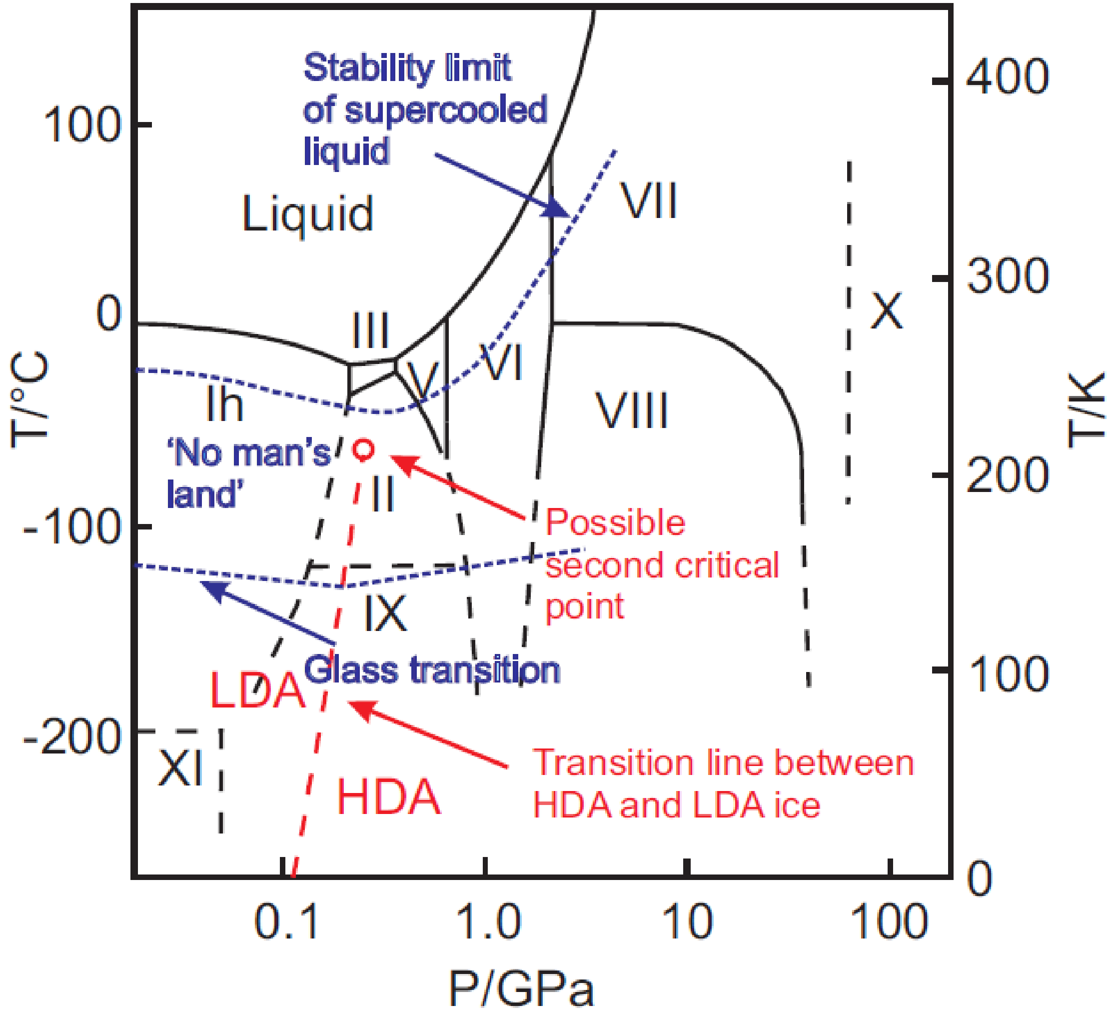
Water very nearly wasn't like this

neutron as well as a proton. The extra bulk makes it less vulnerable to quantum uncertainties. "It's like turning the quantum mechanics half off," says Chris Benmore, of the Argonne National Laboratory in Illinois, who was not involved in the study.

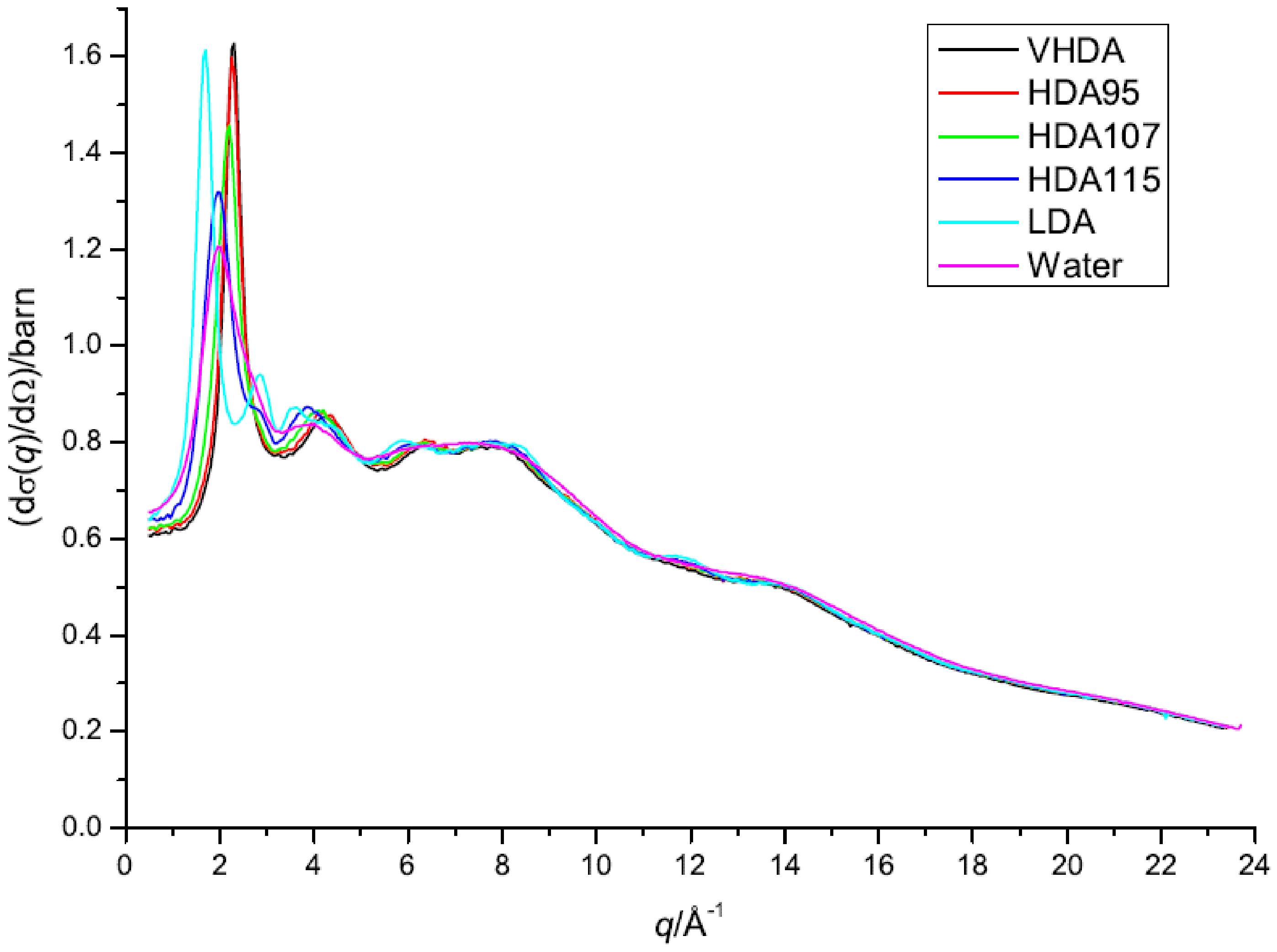
Ice (outline)

- Amorphous ice and its various forms
- Ice Ih
- comparison

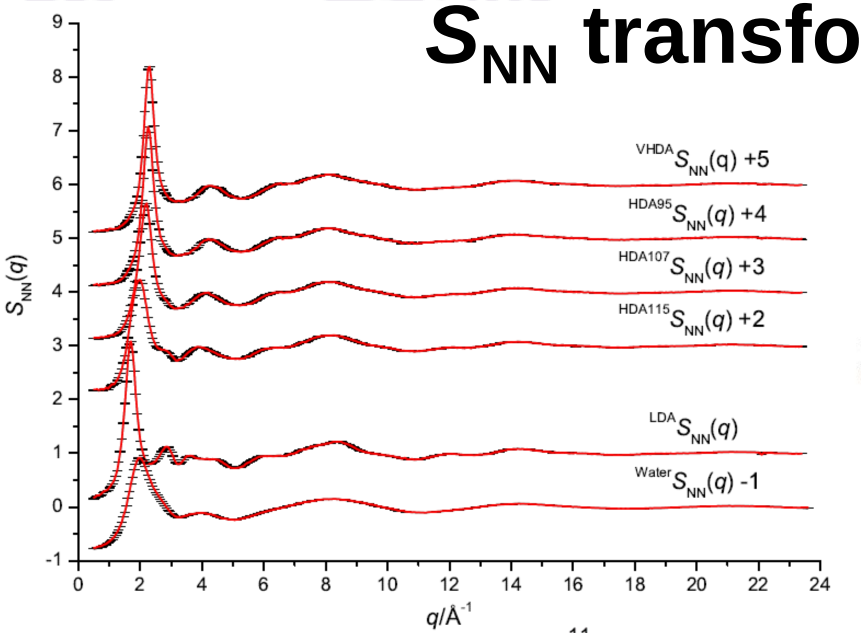
Phase diagram

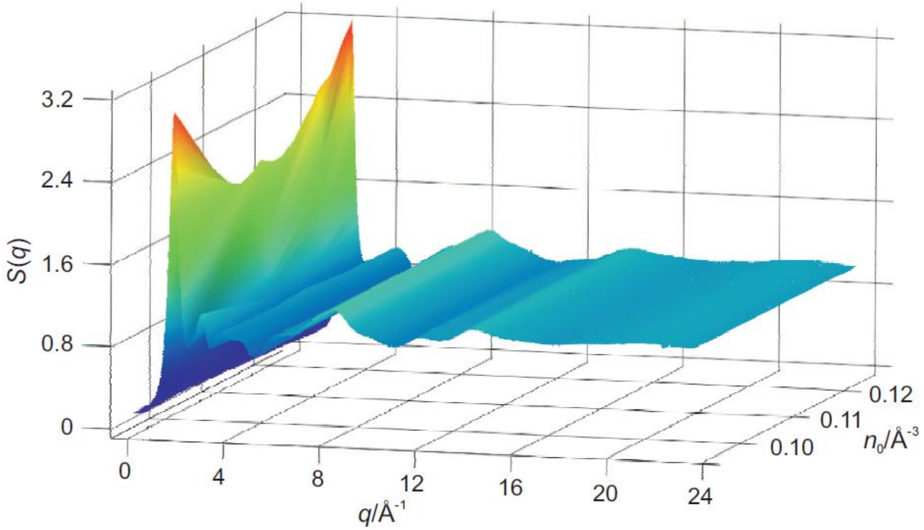


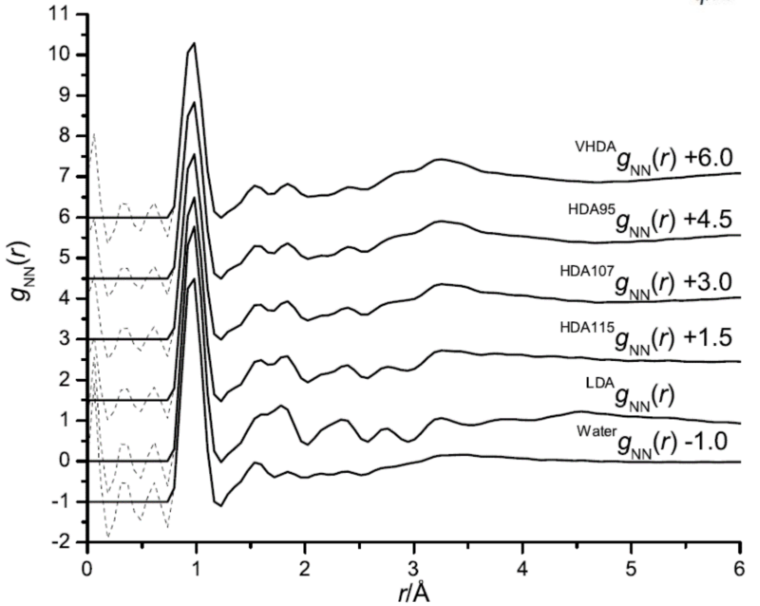
Amorphous ice (S_{NN})



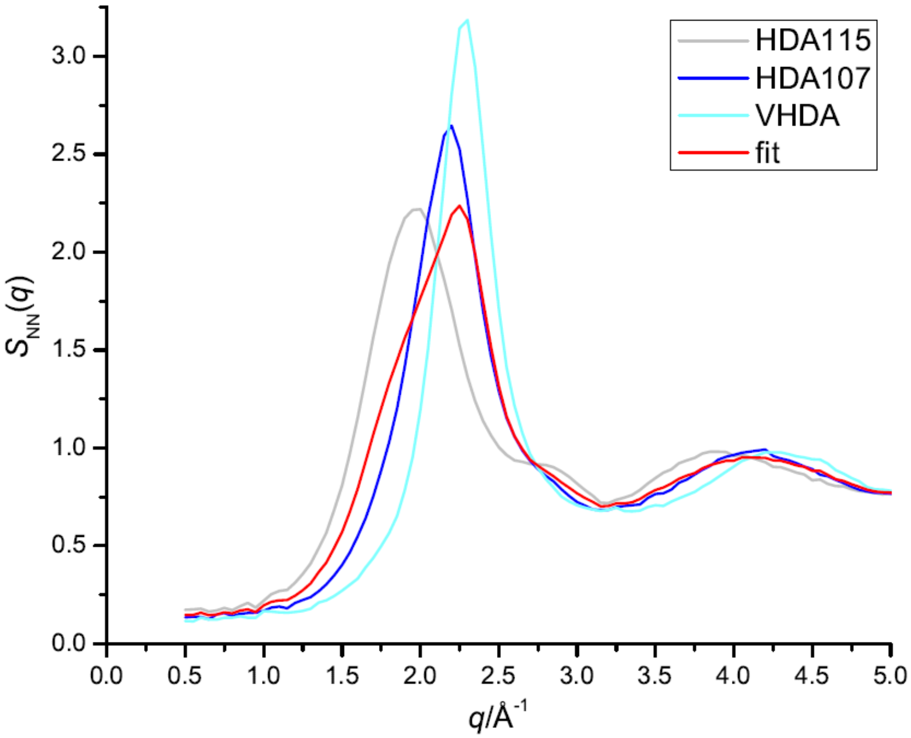
S_{NN} transformation

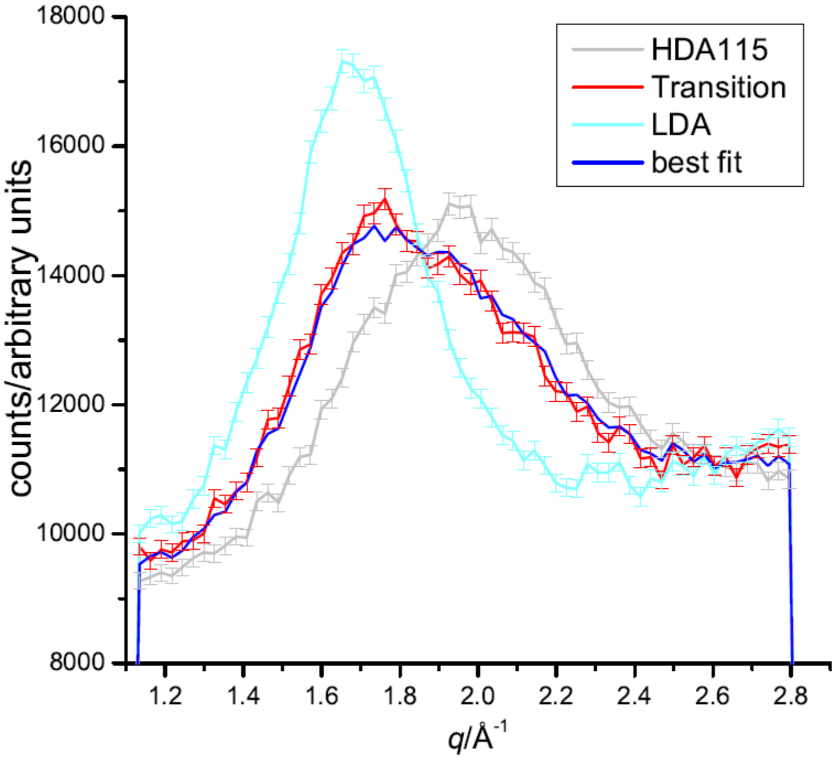




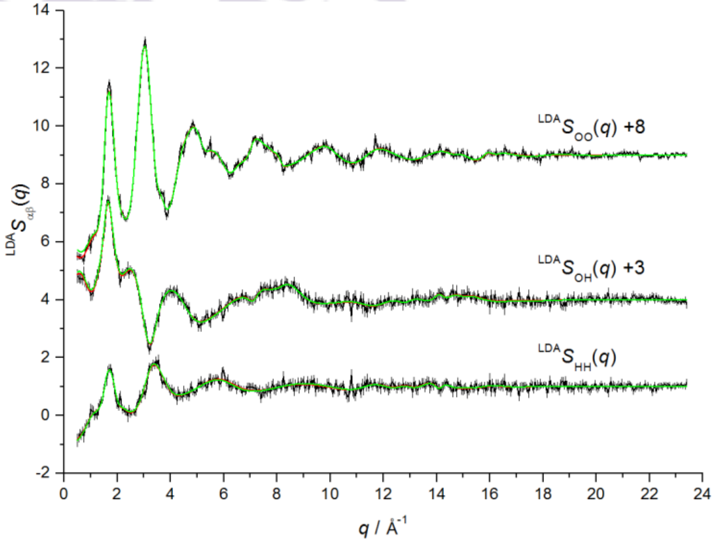


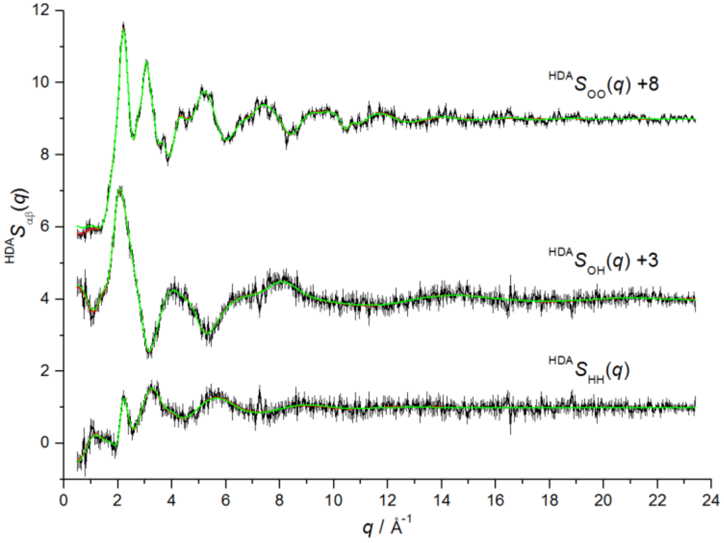
Transformations

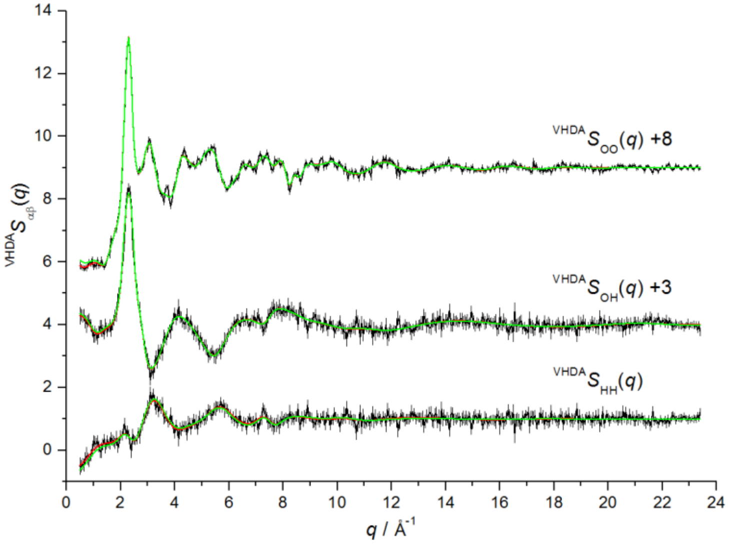




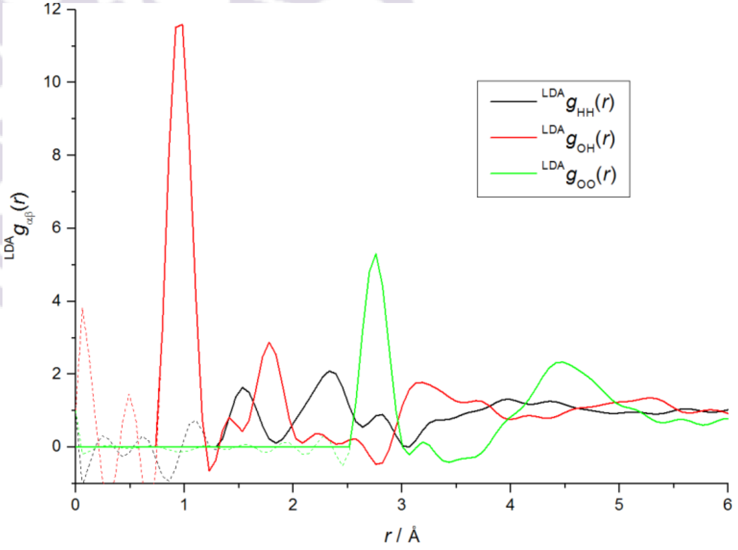
Partials (reciprocal)

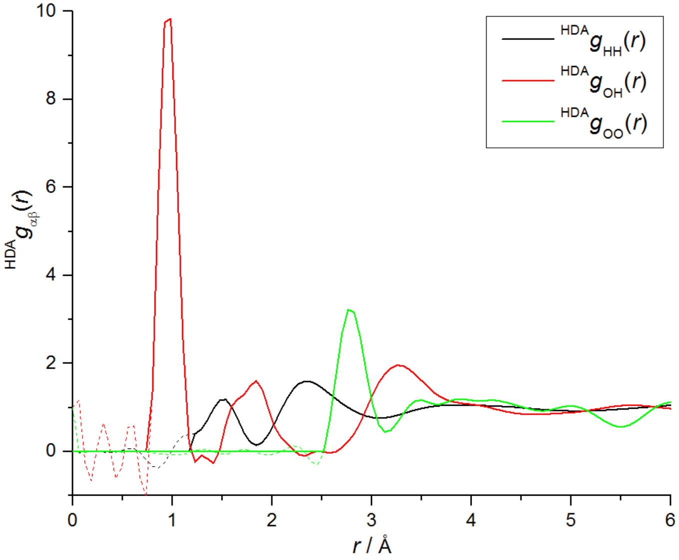


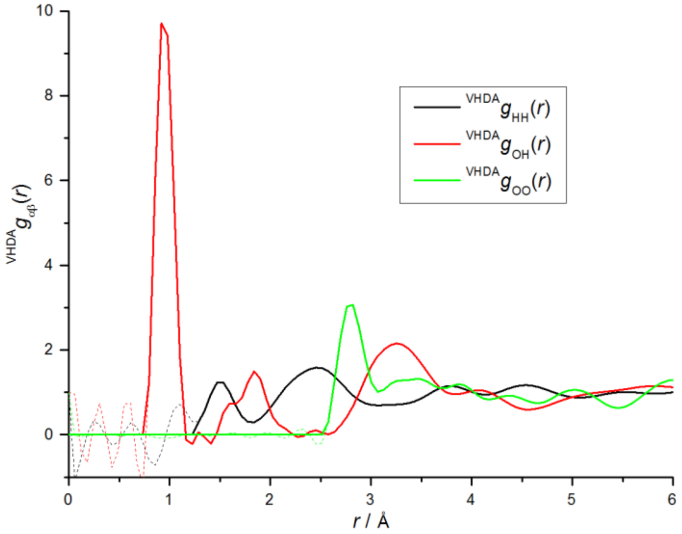




Partials (real)



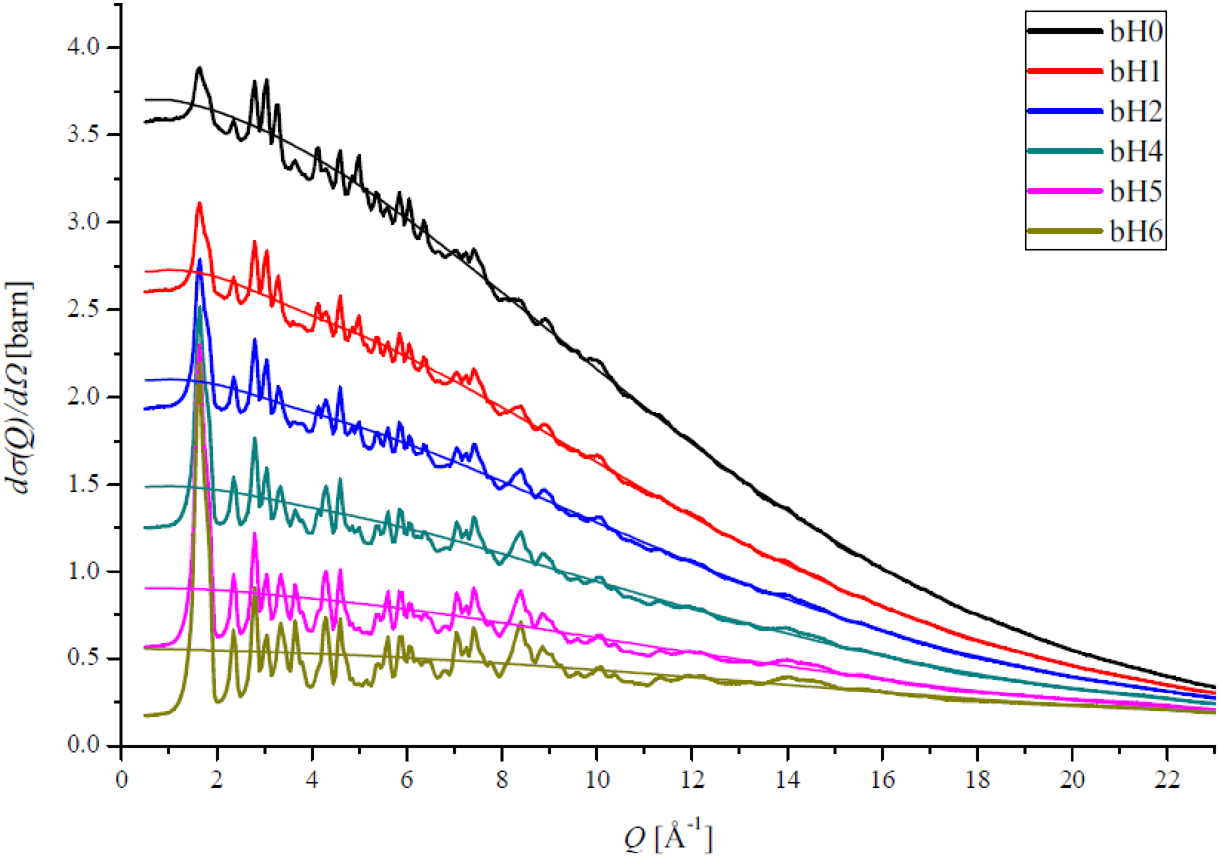




Summary (amorphous ice)

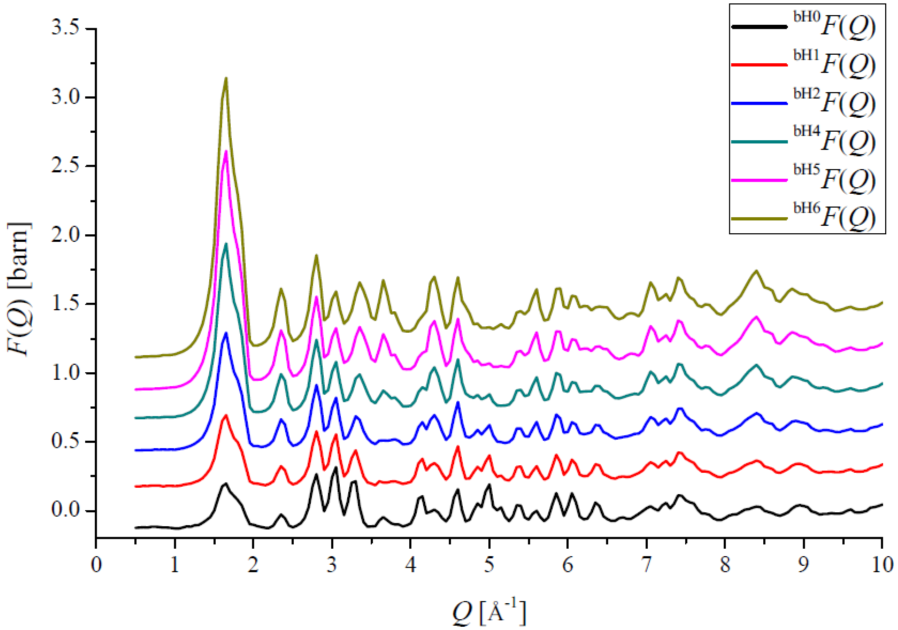
- 3 forms of amorphous ice
- Transition LDA → HDA first order like
- Transition HDA → VHDA continuous
- Local bonding arrangement (water molecules connected via H-bonds) remains intact
- O coordination increases with density

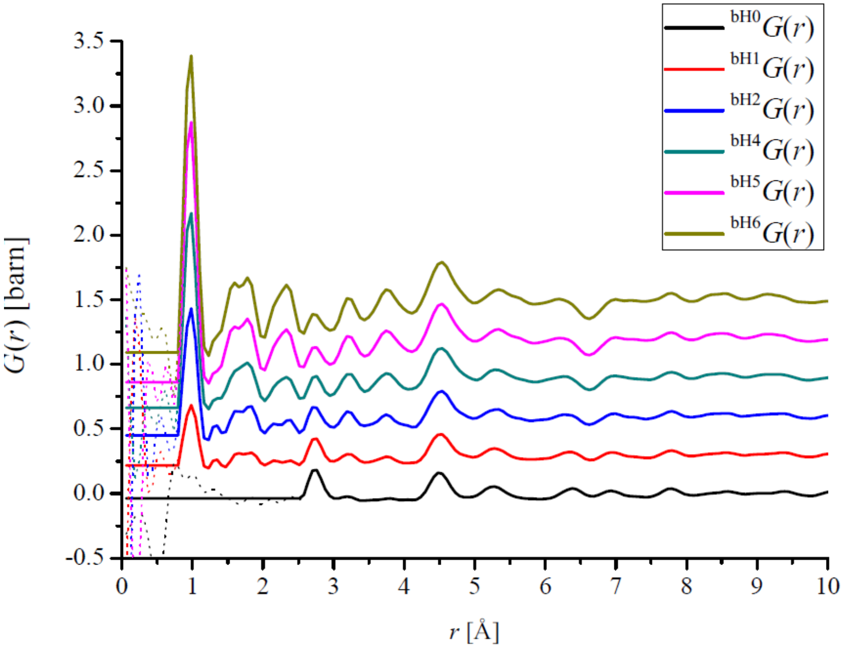
Ice Ih



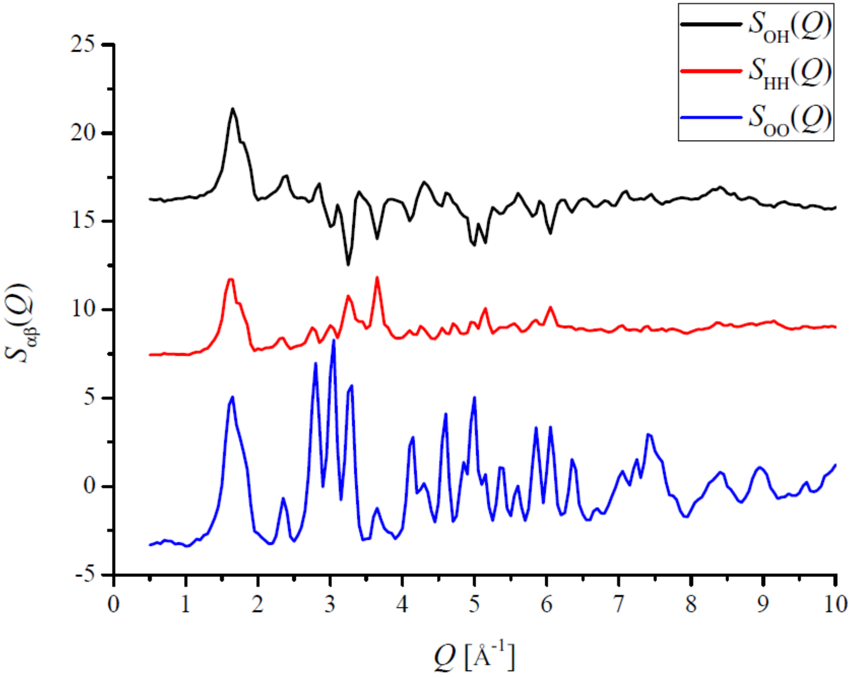
bH0
bH1
bH2
bH4
bH5
bH6
$d\sigma(Q)/d\Omega$ [barn]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
2
4
6
8
10
12
14
16
18
20
22
Q [Å^{-1}]

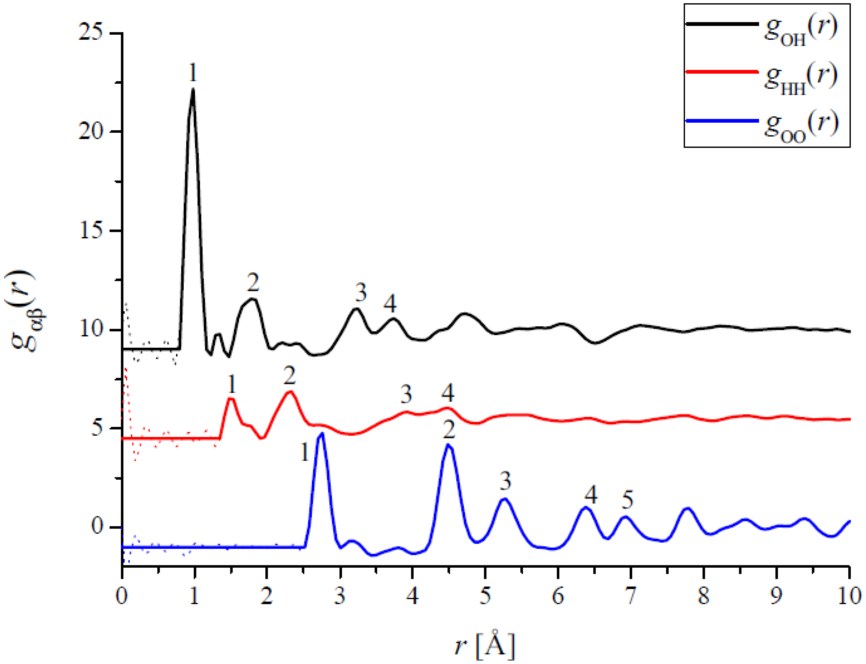
Totals (ice Ih)



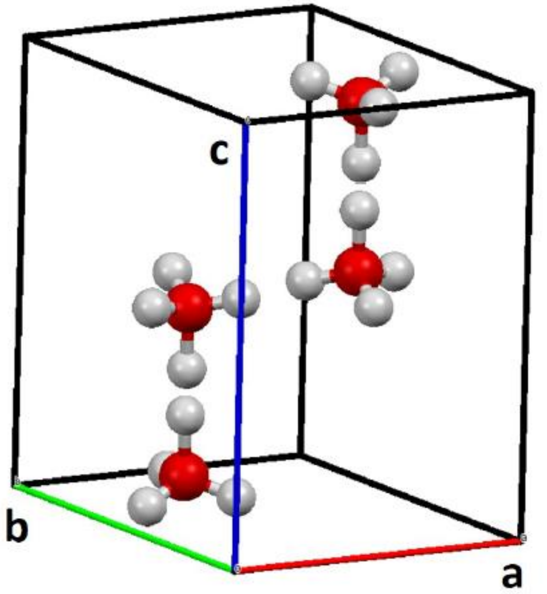


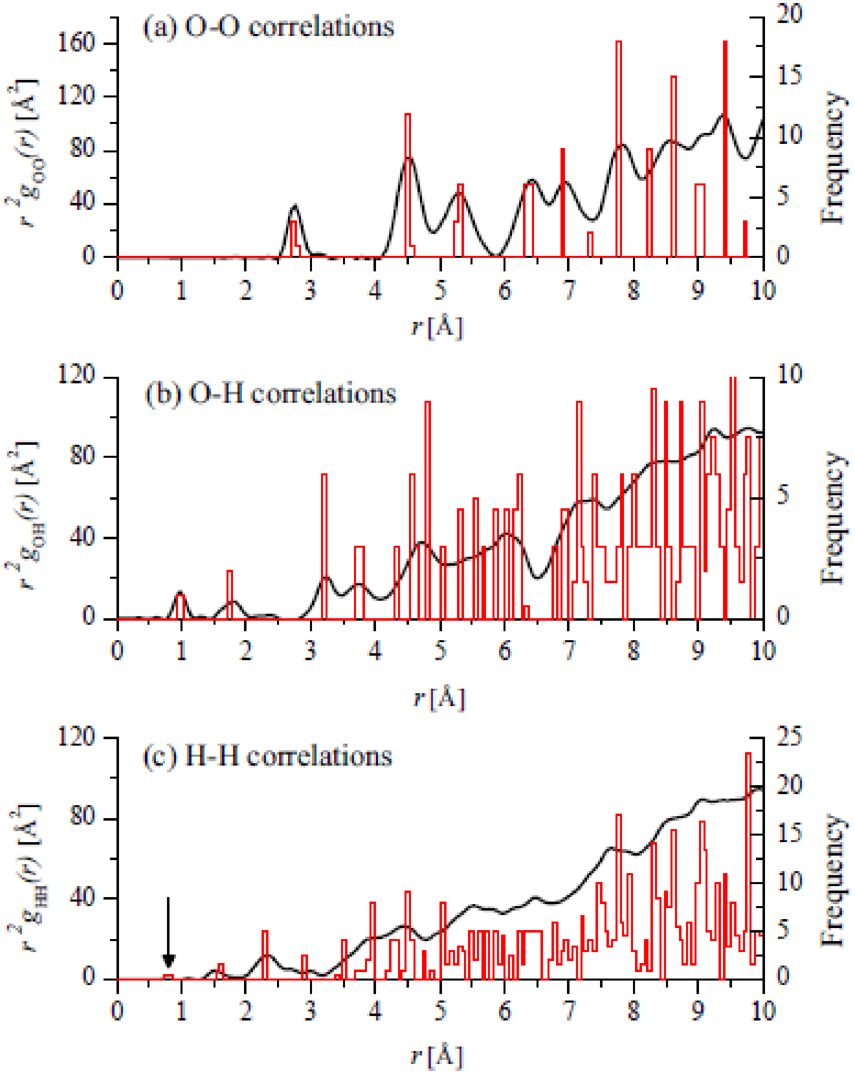
Totals (ice Ih)



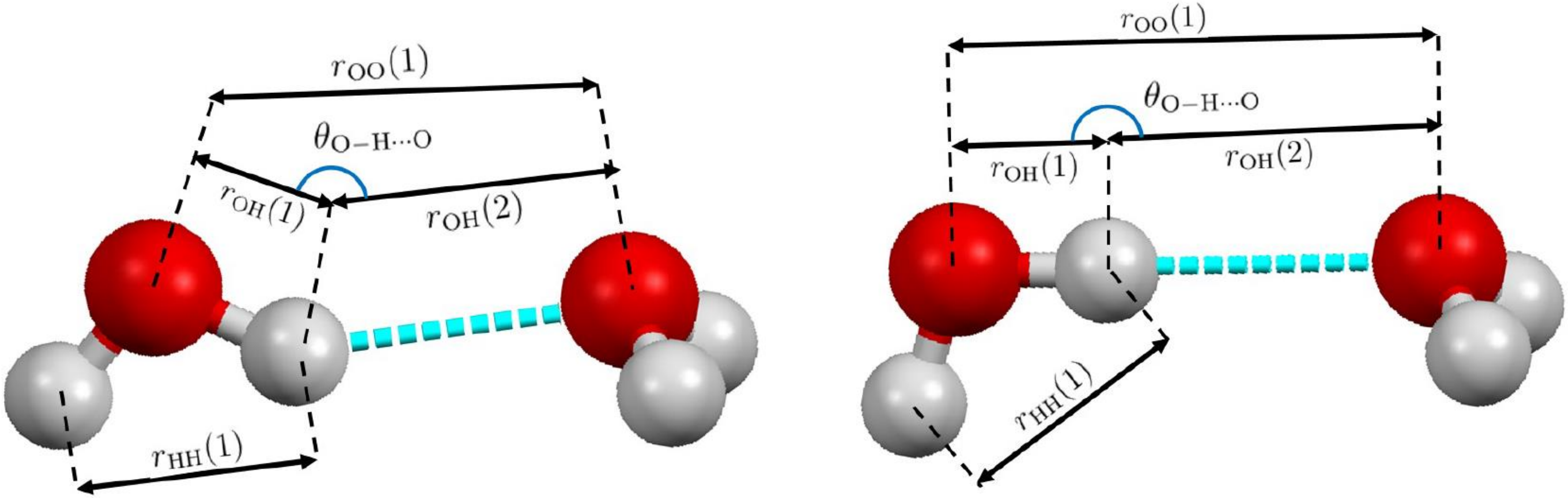


Comparison with crystallography



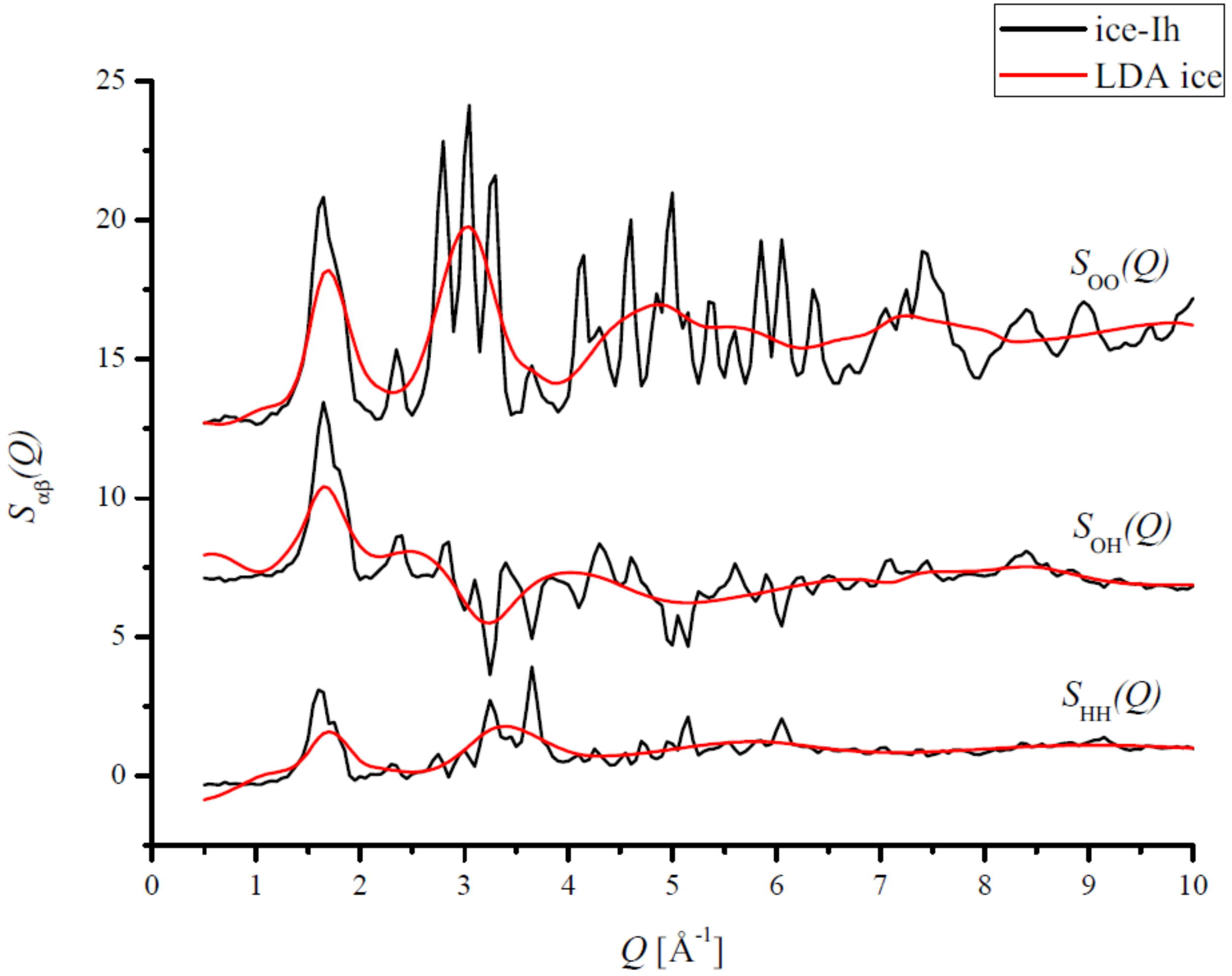


Bonding geometry

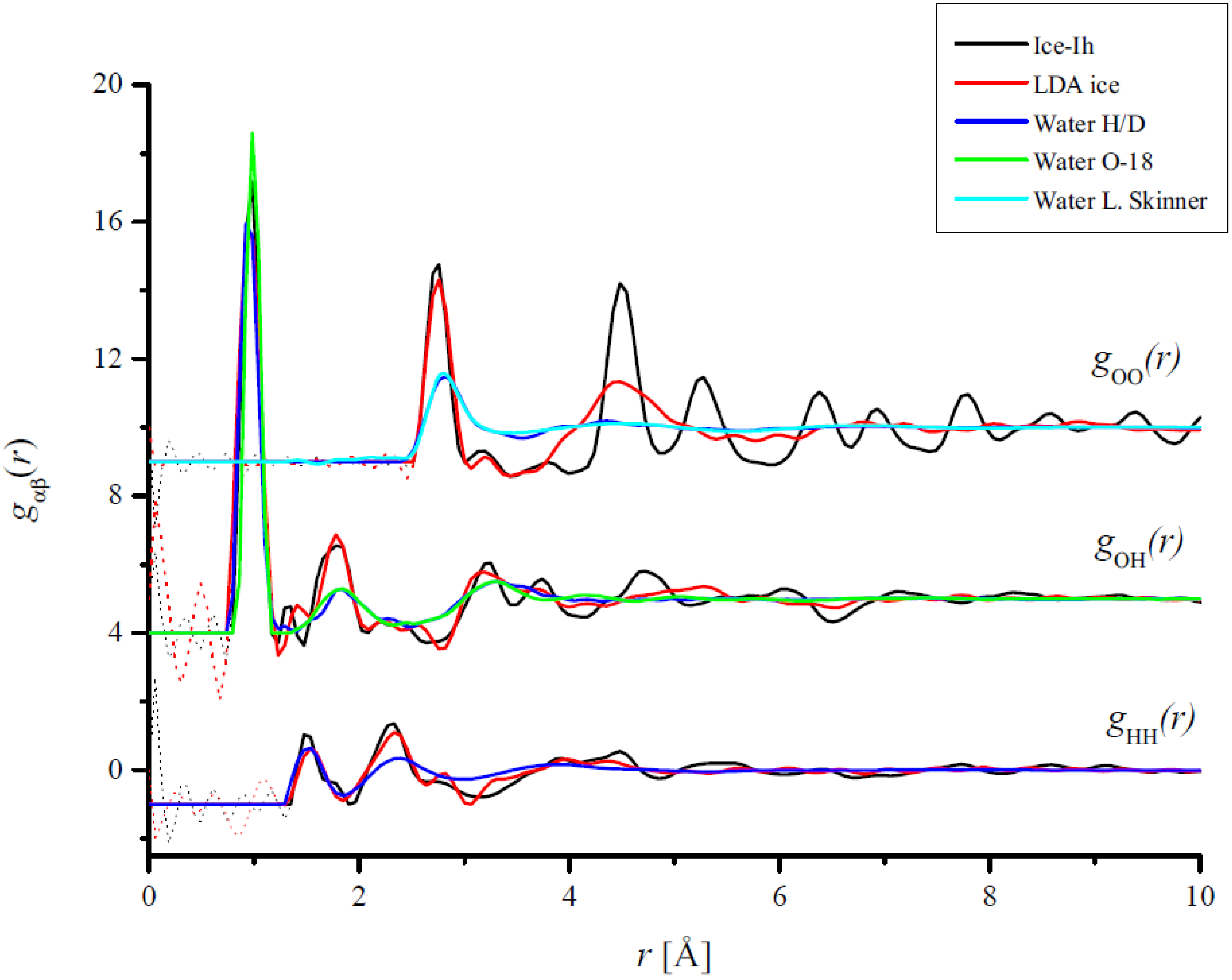


15 K	160.1(4.4) °
123 K	177.2(2.4) °

Comparison with amorphous ice



Comparison with amorphous ice



Conclusions

- Diffraction results agree with crystallography
- O-H···O bond angle was determined
    - 15 K 160.1(4.4) °
    - 123 K 177.2(2.4) °
- Diffraction patterns of LDA ice and ice Ih are very similar

Acknowledgements

- Chris Tulk
- Hartmut Lemmel
- Tom Markland
- Ruth Rowlands

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