中性子およびX線回折実験による液体水の構造解析

Structure of liquid water studied by neutron and X-ray diffraction methods

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水・蒸気性質シンポジウム2025
2025年6月2日（月）
大阪大学 基礎工学国際棟

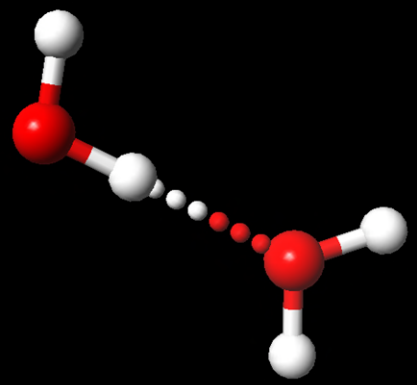
Aim of This Study

- Obtain Experimental Partial Structure Factors, $a_{HH}(Q)$, $a_{OH}(Q)$, and $a_{OO}(Q)$, and Partial Pair Correlation Functions, $g_{HH}(r)$, $g_{OH}(r)$, and $g_{OO}(r)$.

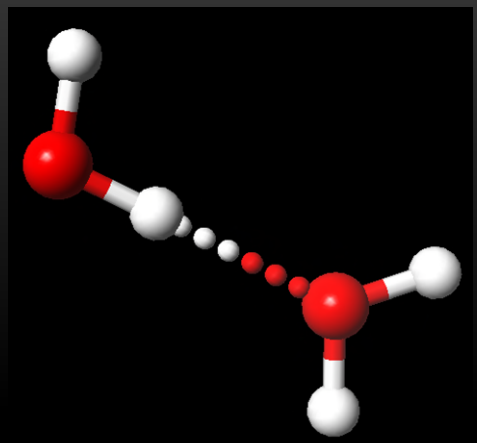
- Compare These Structure Functions with Those Obtained from SANDALS Spectrometer (ISIS).

- Comparison with Those Calculated by MD Simulations.

- Comparison with the X-ray Structure Factor
  → Electron Distribution within Liquid Water



Partial Structure Factors of Liquid Water



H-H Structure: $a_{HH}(Q)$, $g_{HH}(r)$
O-H Structure: $a_{OH}(Q)$, $g_{OH}(r)$
O-O Structure: $a_{OO}(Q)$, $g_{OO}(r)$

Interference term observed from neutron diffraction measurements, $i_N(Q)$
$= 4b_H^2[a_{HH}(Q)-1] + 4b_O b_H[a_{OH}(Q)-1] + b_O^2[a_{OO}(Q)-1]$

At least 3 Samples with different b_H values
→ $a_{HH}(Q)$, $a_{OH}(Q)$, and $a_{OO}(Q)$

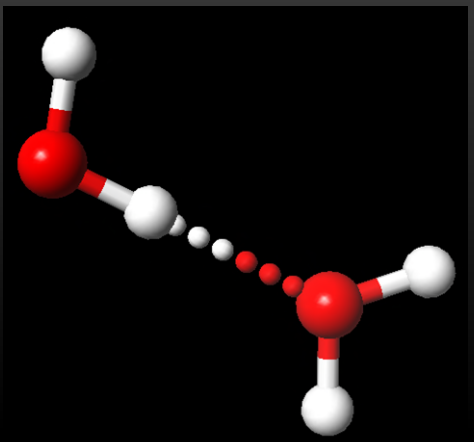
Problems: Inelasticity correction
Multiple scattering correction
Higher statistical accuracy required

‘Standard’ Neutron Data

Author: A. K. Soper

Diffractometer: SANDALS (ISIS Facility, UK)

Data Analysis Method: EPSR fit



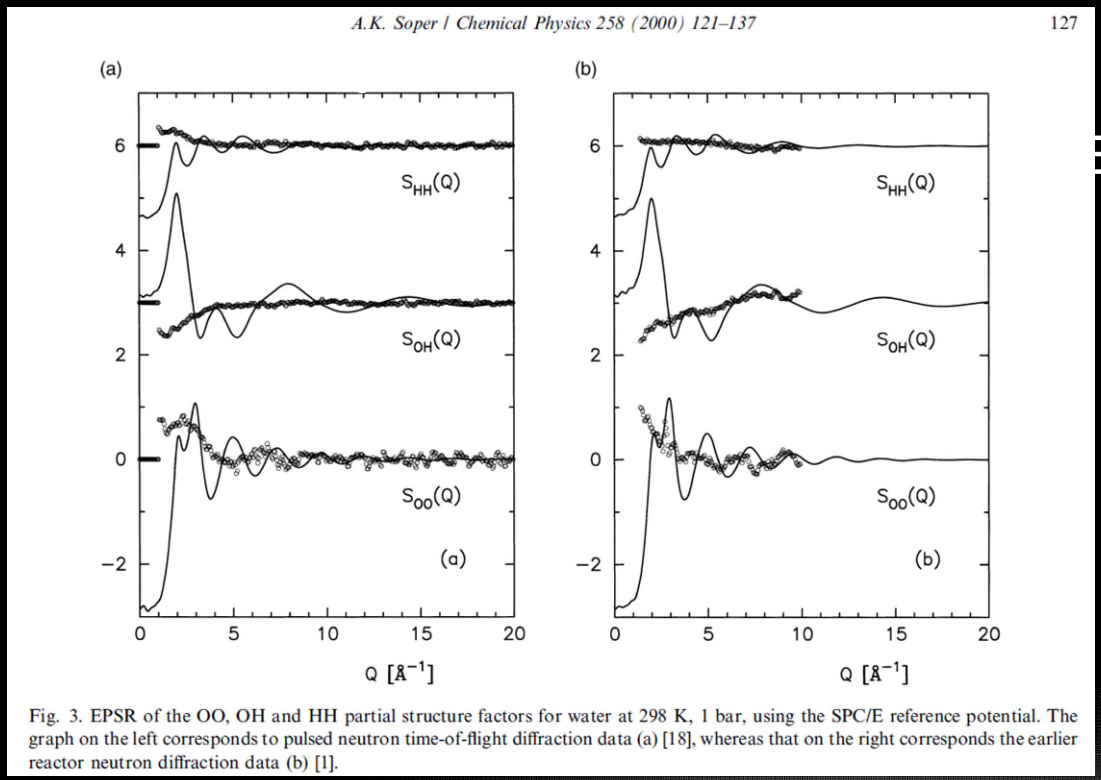


Fig. 3. EPSR of the OO, OH and HH partial structure factors for water at 298 K, 1 bar, using the SPC/E reference potential. The graph on the left corresponds to pulsed neutron time-of-flight diffraction data (a) [18], whereas that on the right corresponds the earlier reactor neutron diffraction data (b) [1].

EPSR fit:

Monte Carlo simulation

Reference potential

→ Partial structure factor

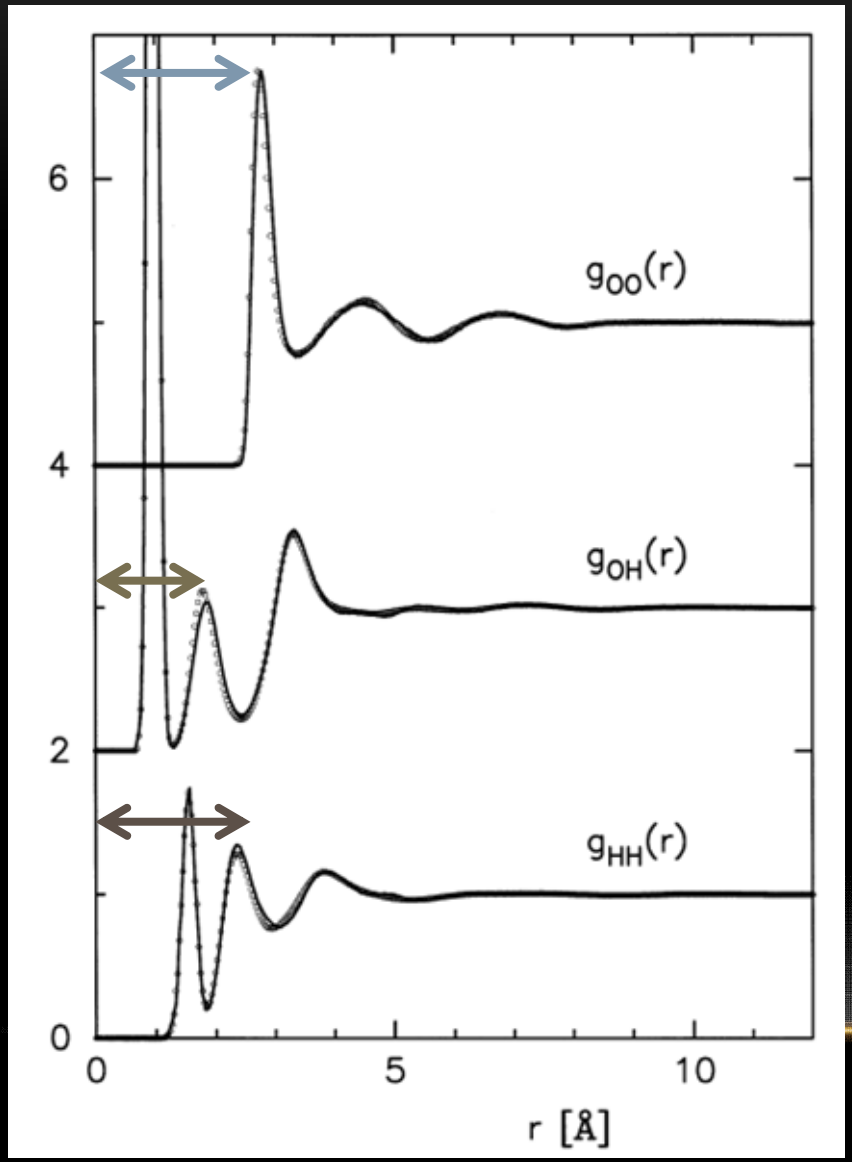
\+ Inelasticity residual

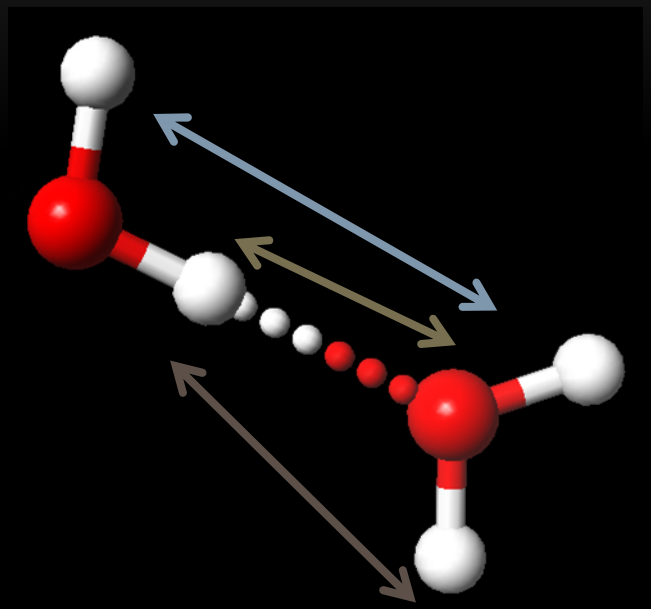
\+ Statistical Noise

A. K. Soper, (2000).

‘Standard’ Neutron Data

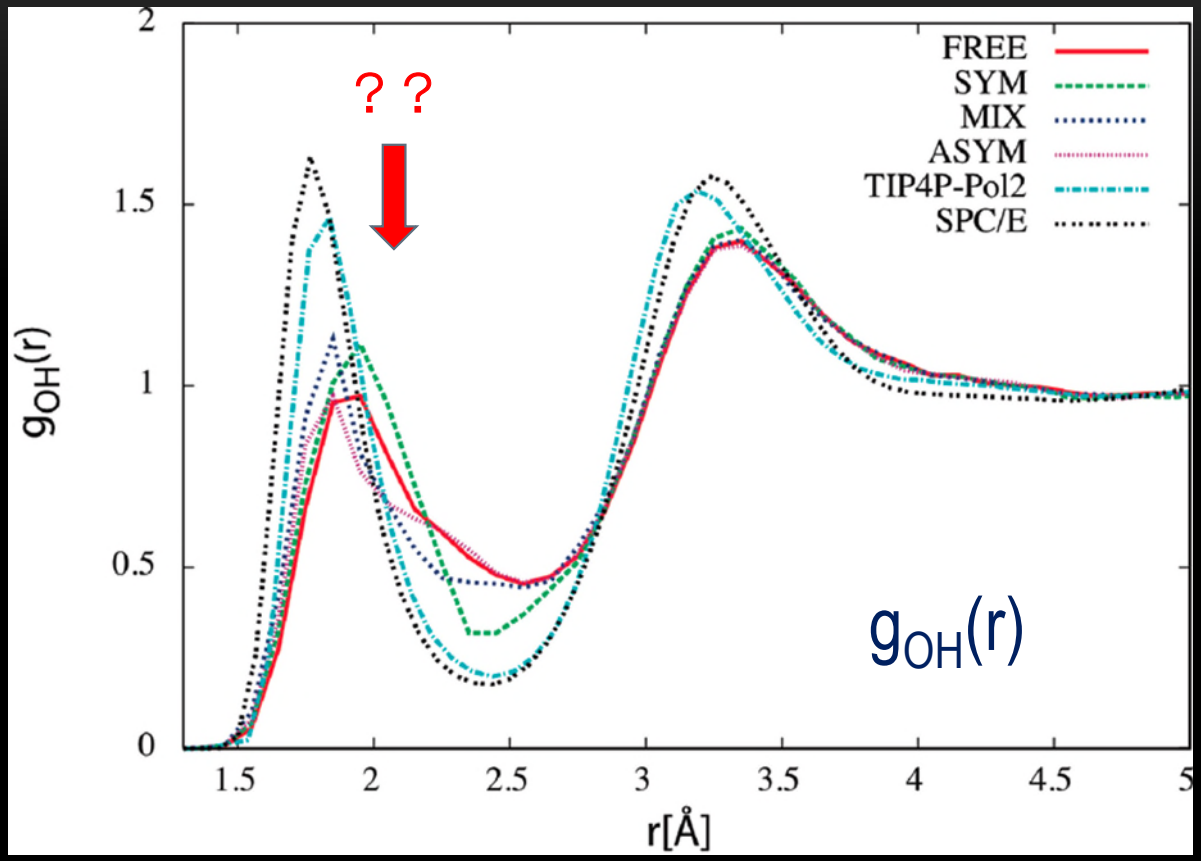
Partial pair correlation functions, $g_{HH}(r)$, $g_{OH}(r)$, and $g_{OO}(r)$



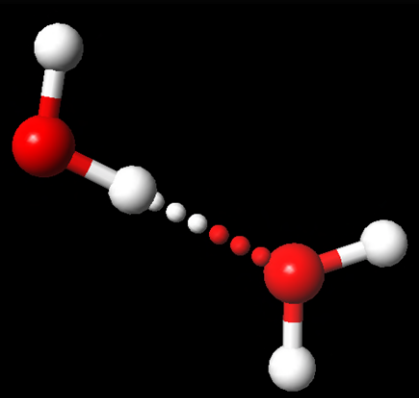


A. K. Soper, *Chem. Phys*. **2000**, *258*, 121.

Recent Literatures

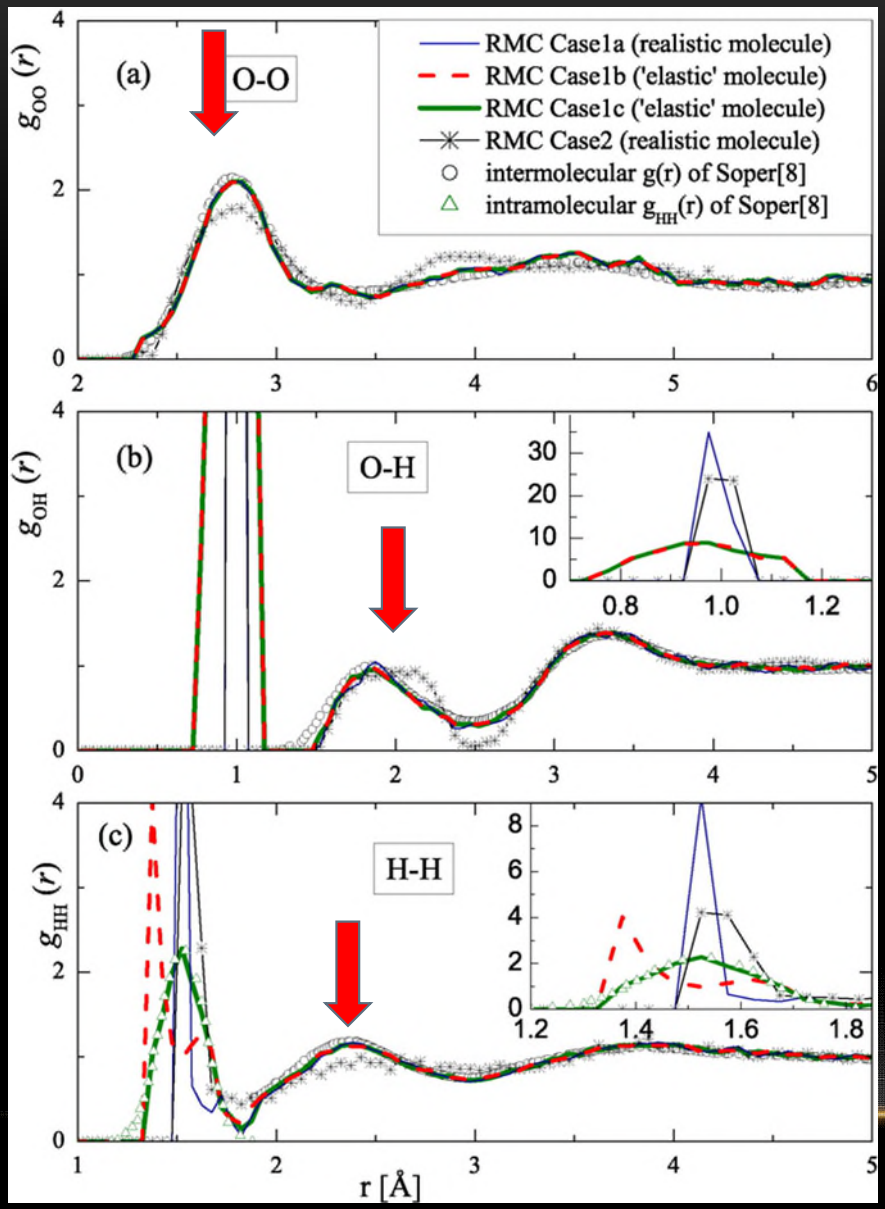


RMC analysis
SANDALS data + X-ray data

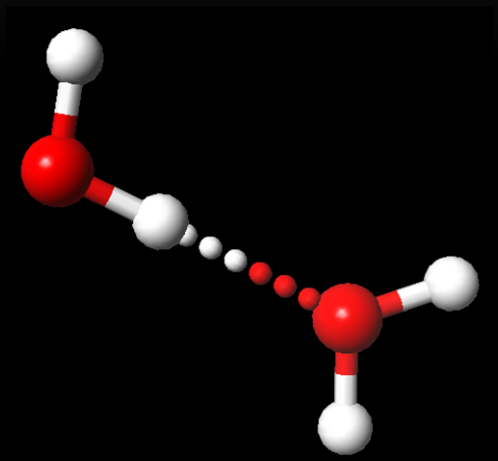


K. T. Wirkfeldt et al. (2009).

Recent Literatures

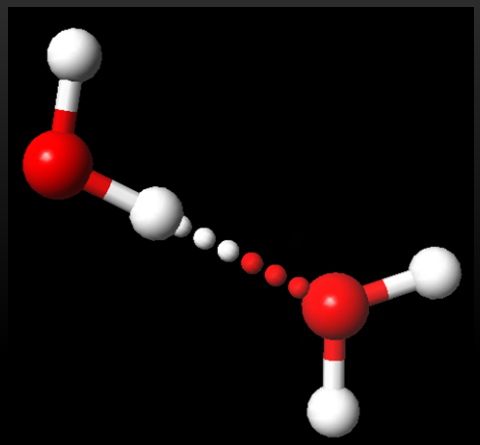


RMC analysis
SANDALS data

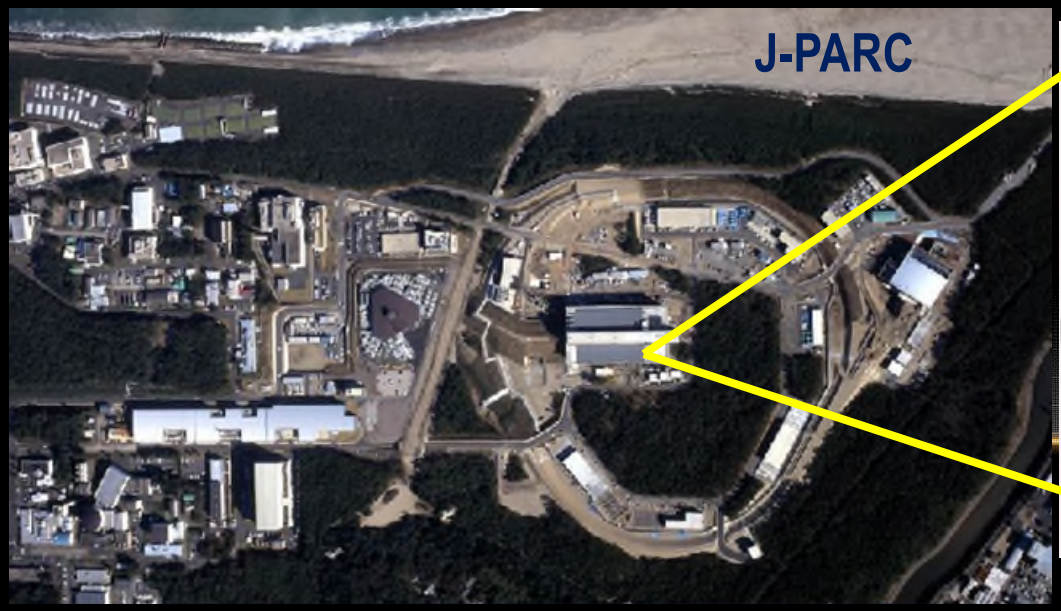


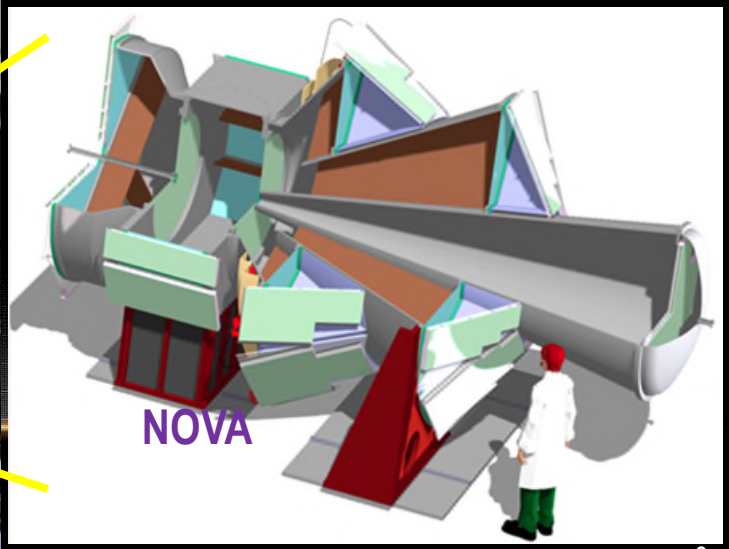
I. Pethes and L. Pusztai (2015).

NOVA Measurements



- Reduce scattering from sample cell
  → Use thin-walled vanadium cell
- Reduce multiple scattering intensity
  → Cell with 1～2 mm in thickness
- Excellent statistical accuracy
  → High power neutron source (MLF, J-PARC)
  High performance diffractometer (NOVA)





NOVA experiments

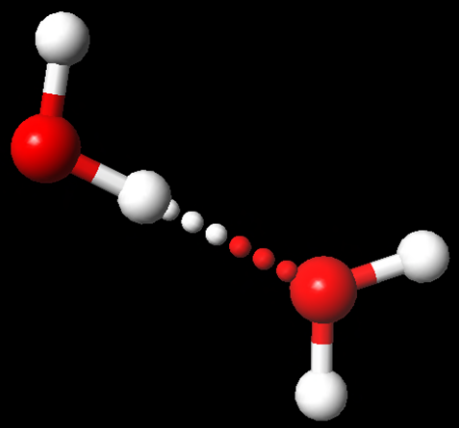
Samples: D_2O
HDO
H_2O
^0H_2O → Inelasticity correction

→ $a_{HH}(Q)$, $a_{OH}(Q)$, $a_{OO}(Q)$

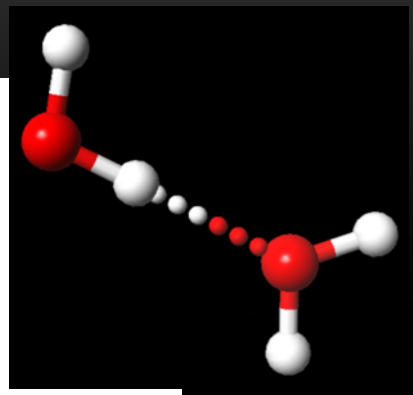
Cell: Vanadium cell (2mmt × 14mmW × 40mmH)

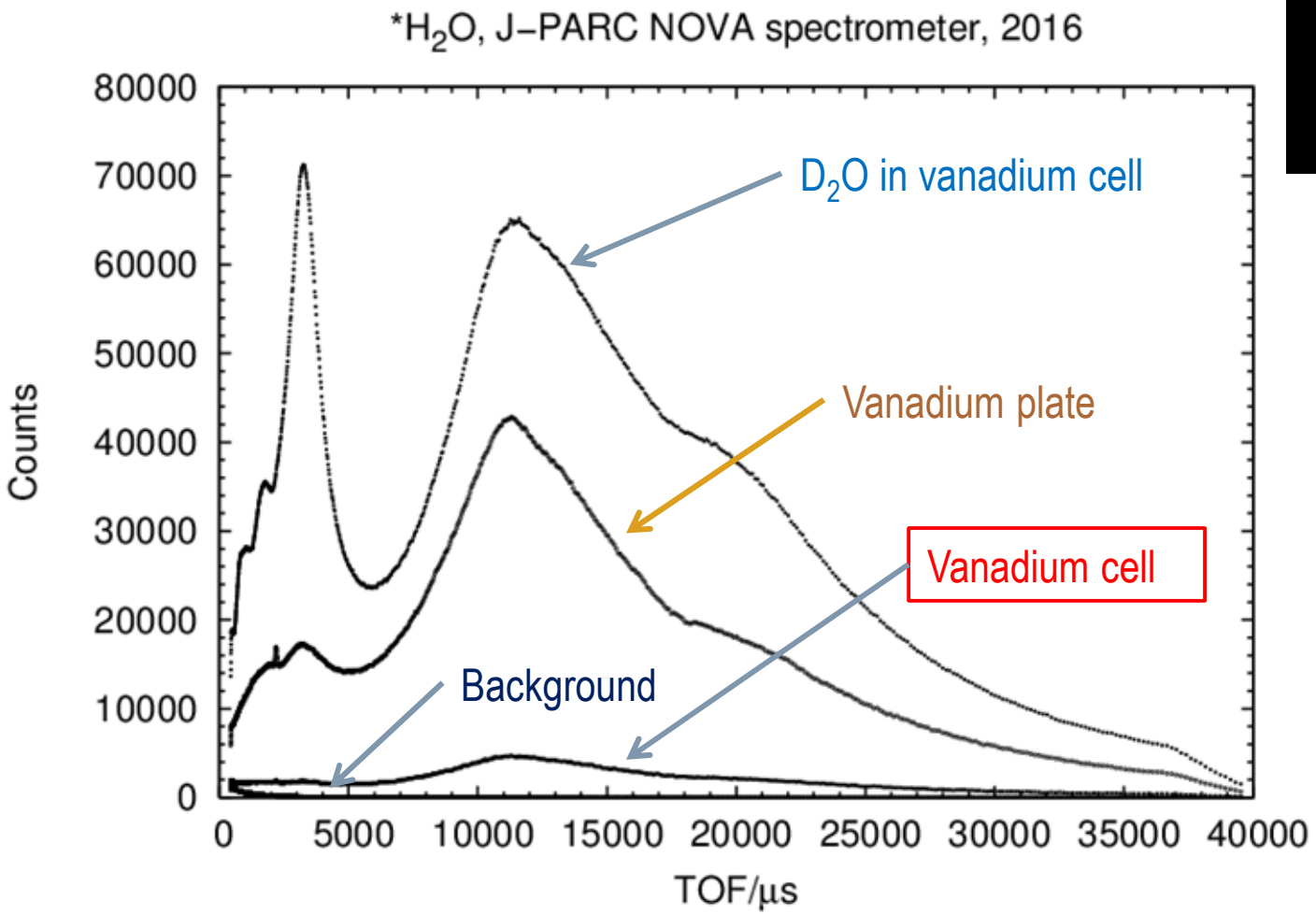
Exposure time: 9h/sample

Forward angle detector pixels

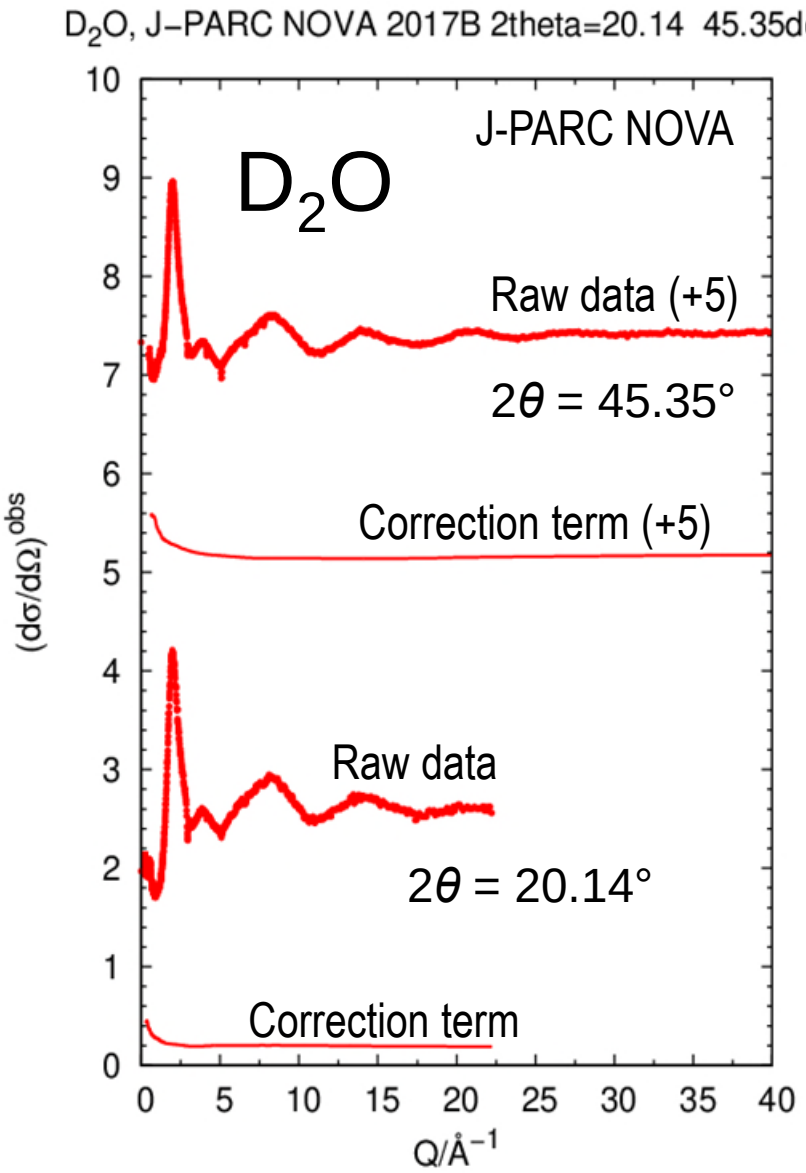


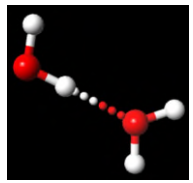
Observed Time-of-Flight Spectra (2θ = 13.06°)

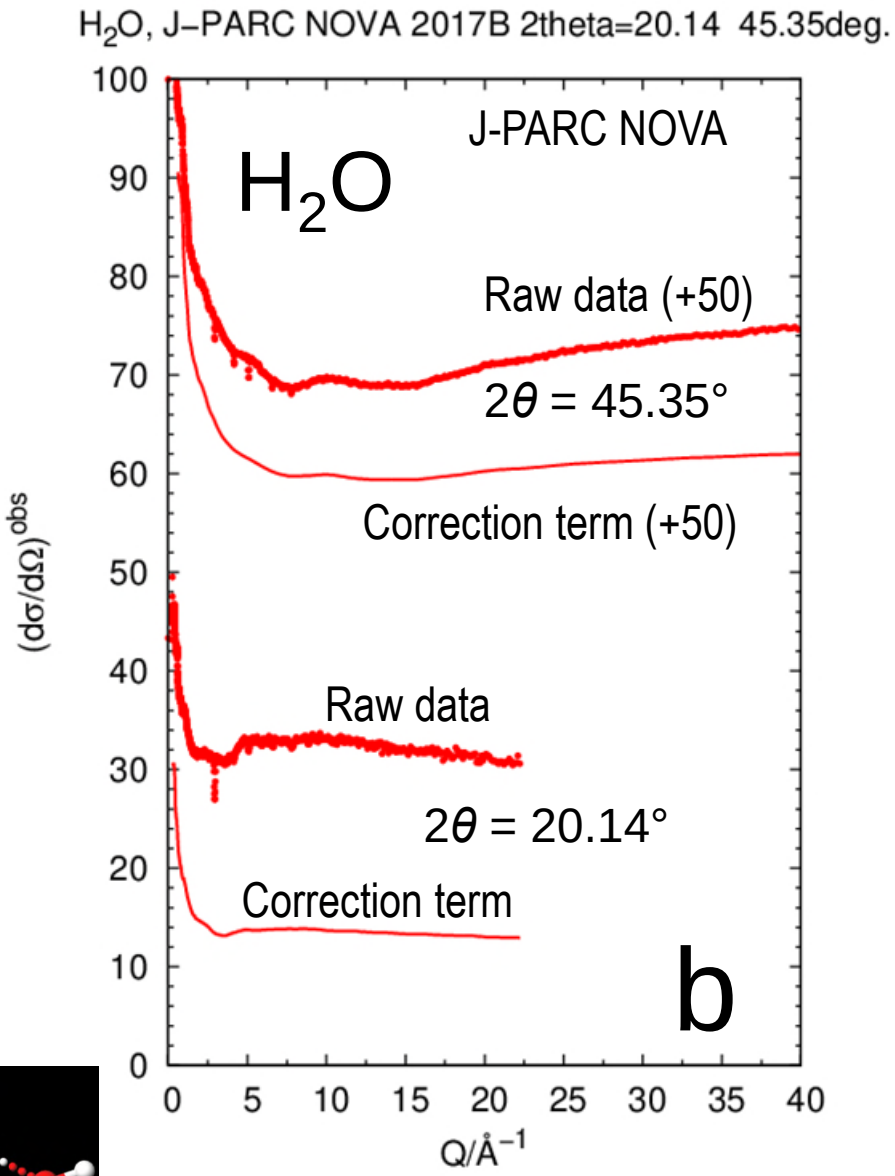


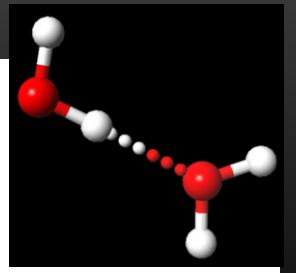


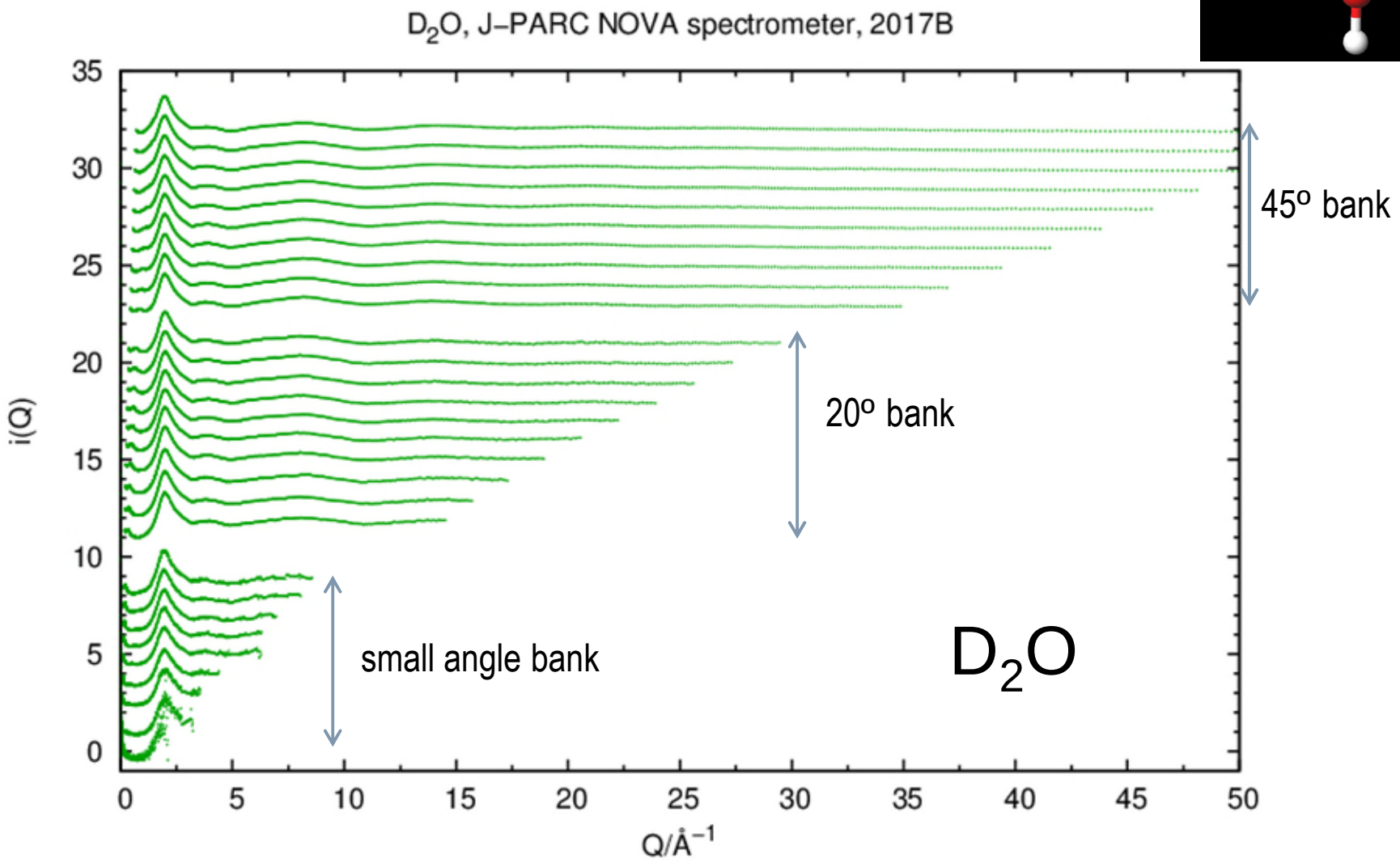
Inelasticity correction using scattering intensity of $^{0}H_2O$

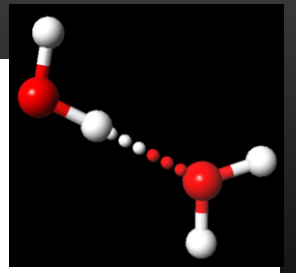


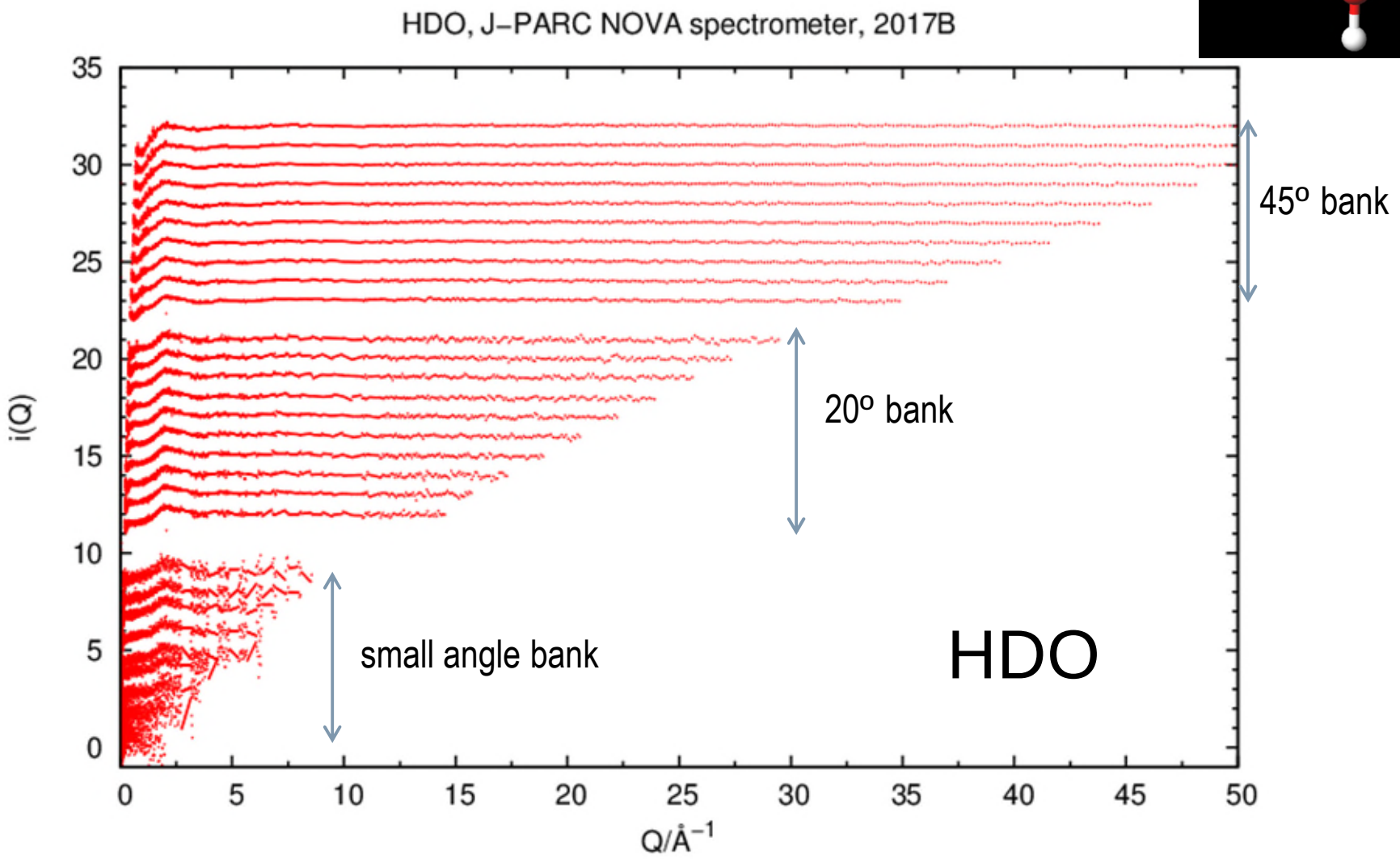


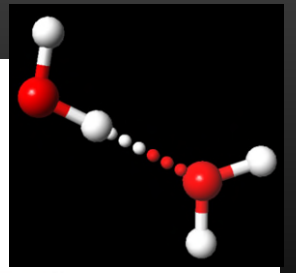


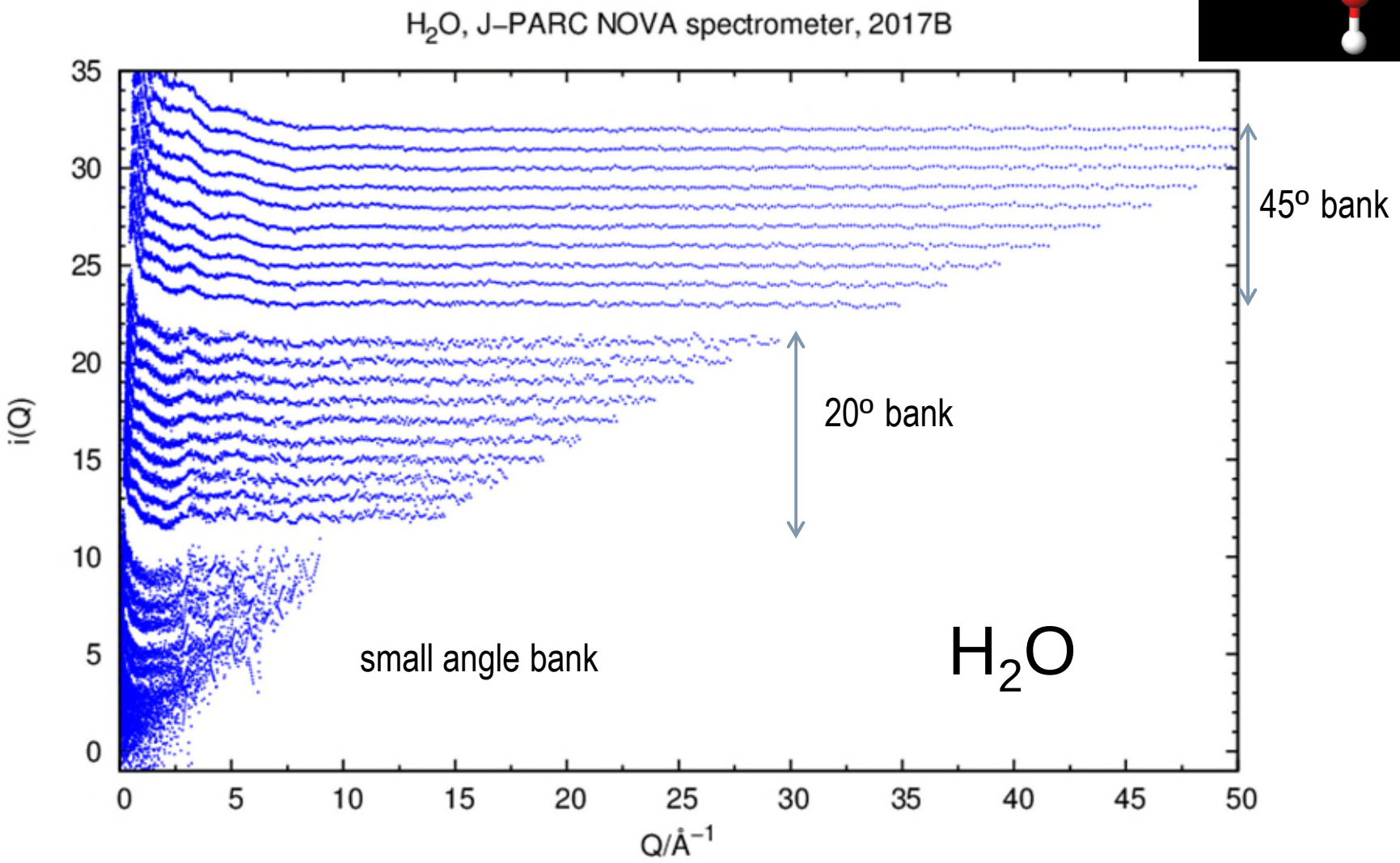



D2O, J-PARC NOVA spectrometer, 2017B
i(Q)
Q/Å−1
0
5
10
15
20
25
30
35
40
45
50
45º bank
20º bank
small angle bank
D2O

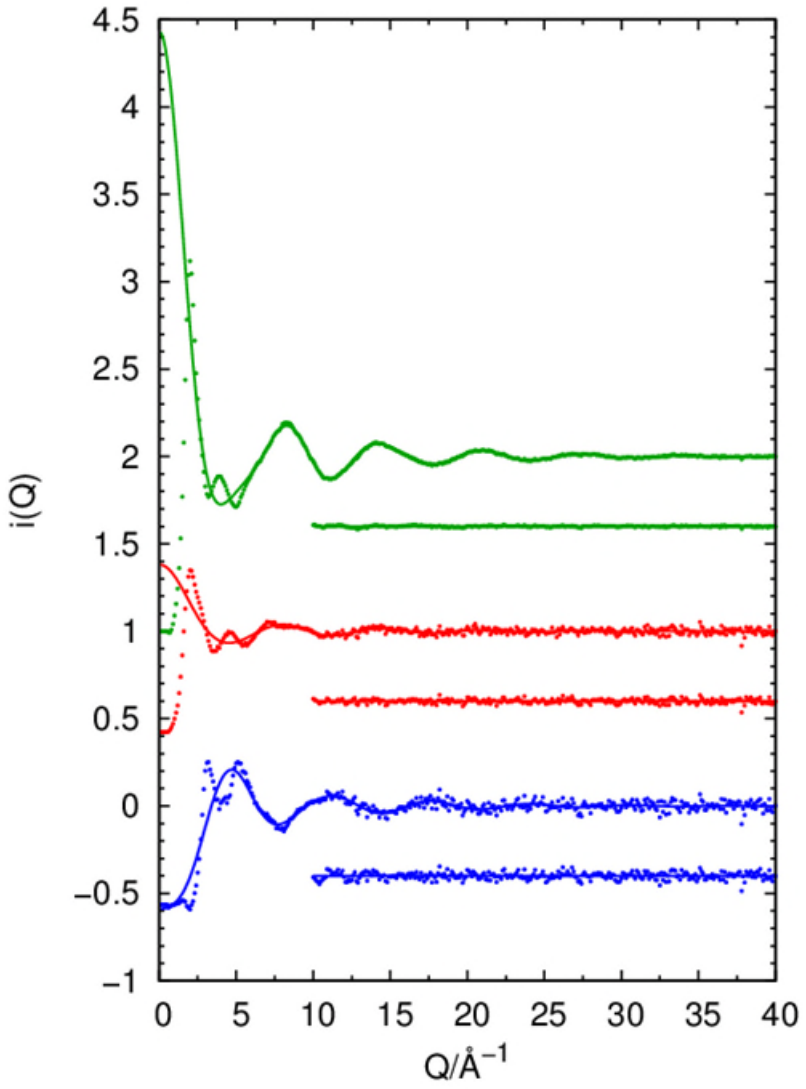


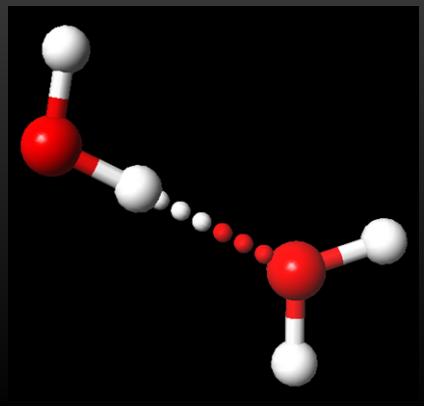

HDO, J–PARC NOVA spectrometer, 2017B
i(Q)
Q/Å^{-1}
0
5
10
15
20
25
30
35
40
45
50
45º bank
20º bank
small angle bank
HDO




H2O, J–PARC NOVA spectrometer, 2017B
i(Q)
Q/Å−1
0
5
10
15
20
25
30
35
40
45
50
45º bank
20º bank
small angle bank
H2O

Total interference term





Results of the least squares fitting analyses of intramolecular interference terms

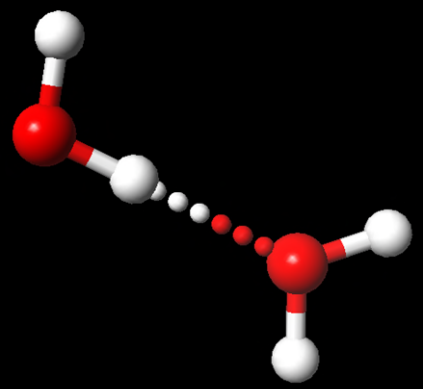
Sample	D_2O	H_2O	HDO
r_{OH}/Å	0.970(1)	0.969(1)	0.967(3)
l_{OH}/Å	0.061(1)	0.063(2)	0.062(4)
r_{HH}/Å	1.55(1)	1.59(2)	1.53(8)
l_{HH}/Å	0.12(1)	0.10(1)	0.09(6)
α	0.98(1)	0.98(2)	1.04(5)

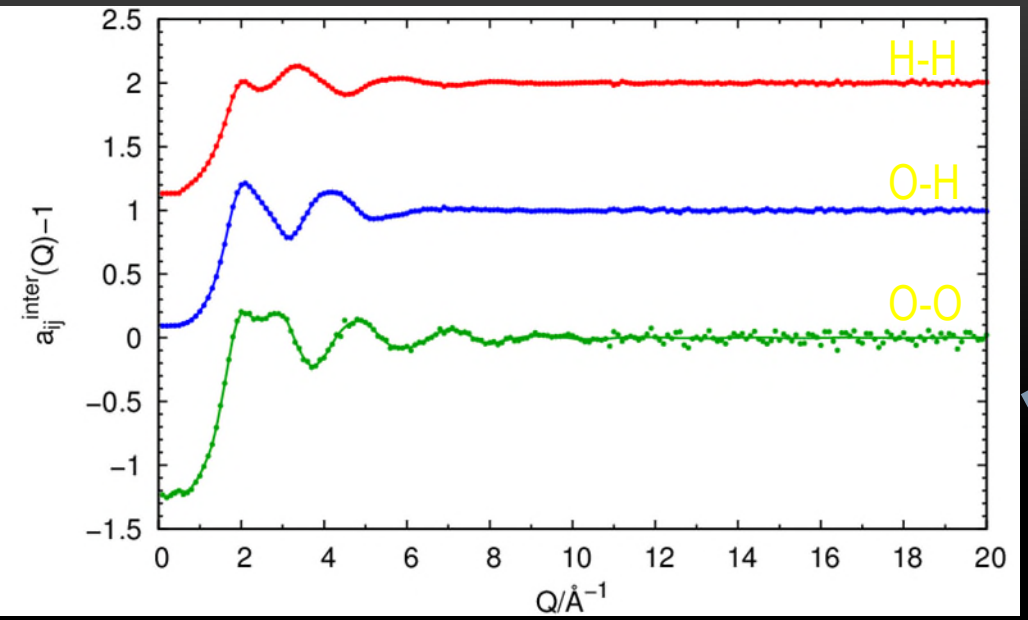
Partial Structure Factors, $a_{HH}(Q)$, $a_{OH}(Q)$, and $a_{OO}(Q)$

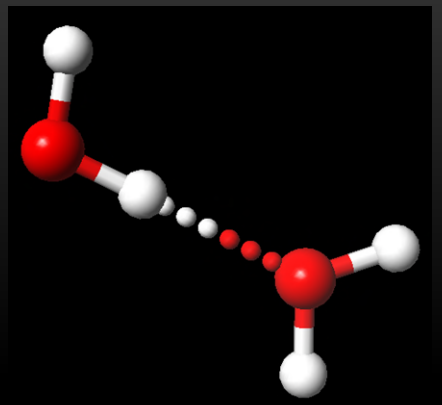
$$i_{H2O}(Q) + i_{D2O}(Q) - 2i_{HDO}(Q) = 2(b_D - b_H)^2[a_{HH}(Q)-1]$$

$$(b_D+3b_H)i_{D2O}(Q) + (3b_D+b_H)i_{H2O}(Q) + 2(b_D-b_H)i_{HDO}(Q) = -4(b_D-b_H)^2 b_O[a_{OH}(Q)-1]$$

$$2(b_D+b_H)b_H i_{D2O}(Q) - 4b_H b_D i_{H2O}(Q) + 2b_D(b_D-b_H)i_{HDO}(Q) = 2b_O^2(b_D^2+b_H^2-2b_D b_H)[a_{OO}(Q)-1] = 2b_O^2(b_D-b_H)^2[a_{OO}(Q)-1]$$



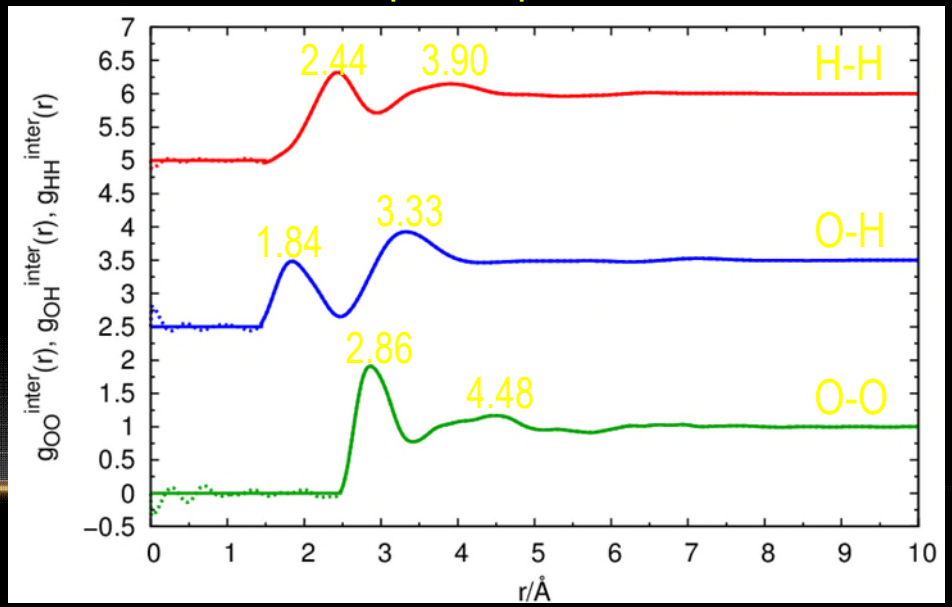


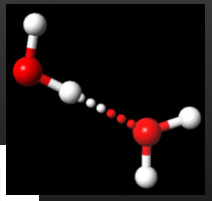


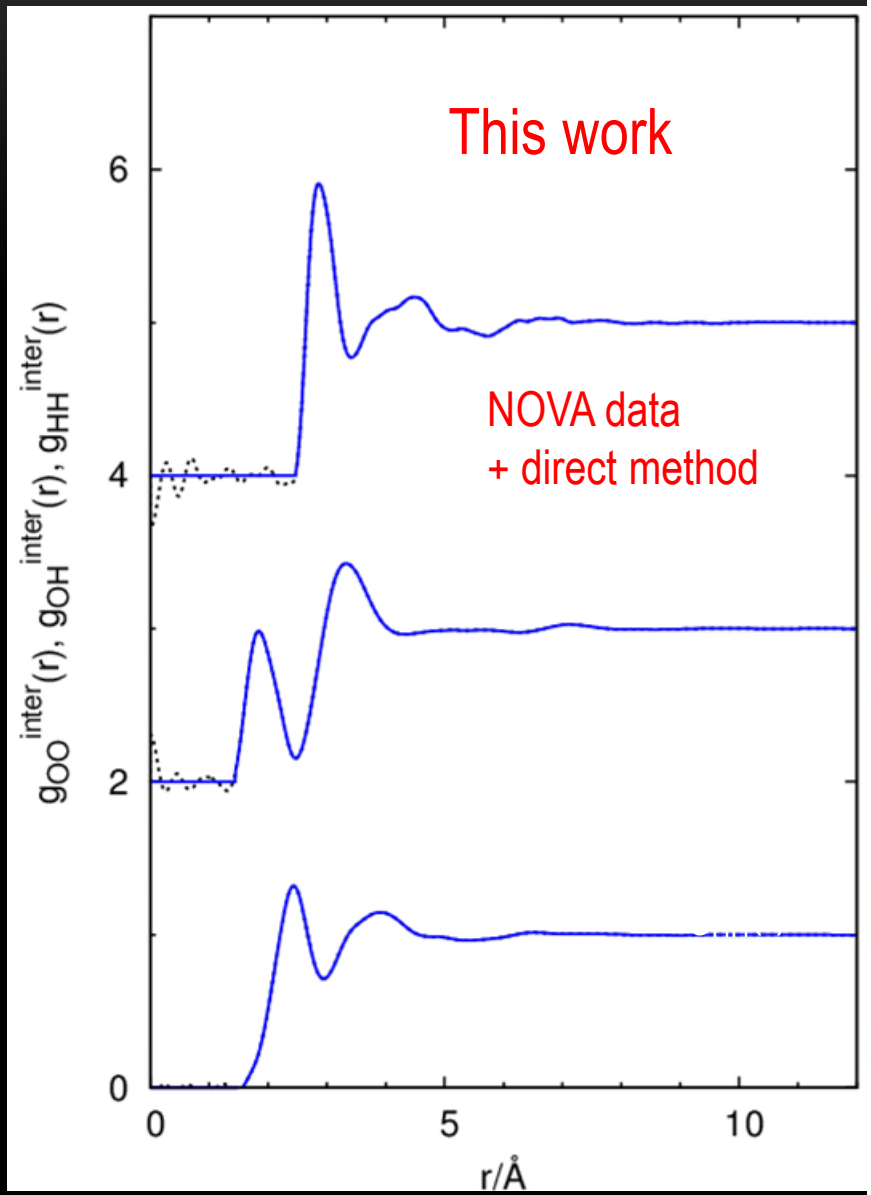
Fourier transform

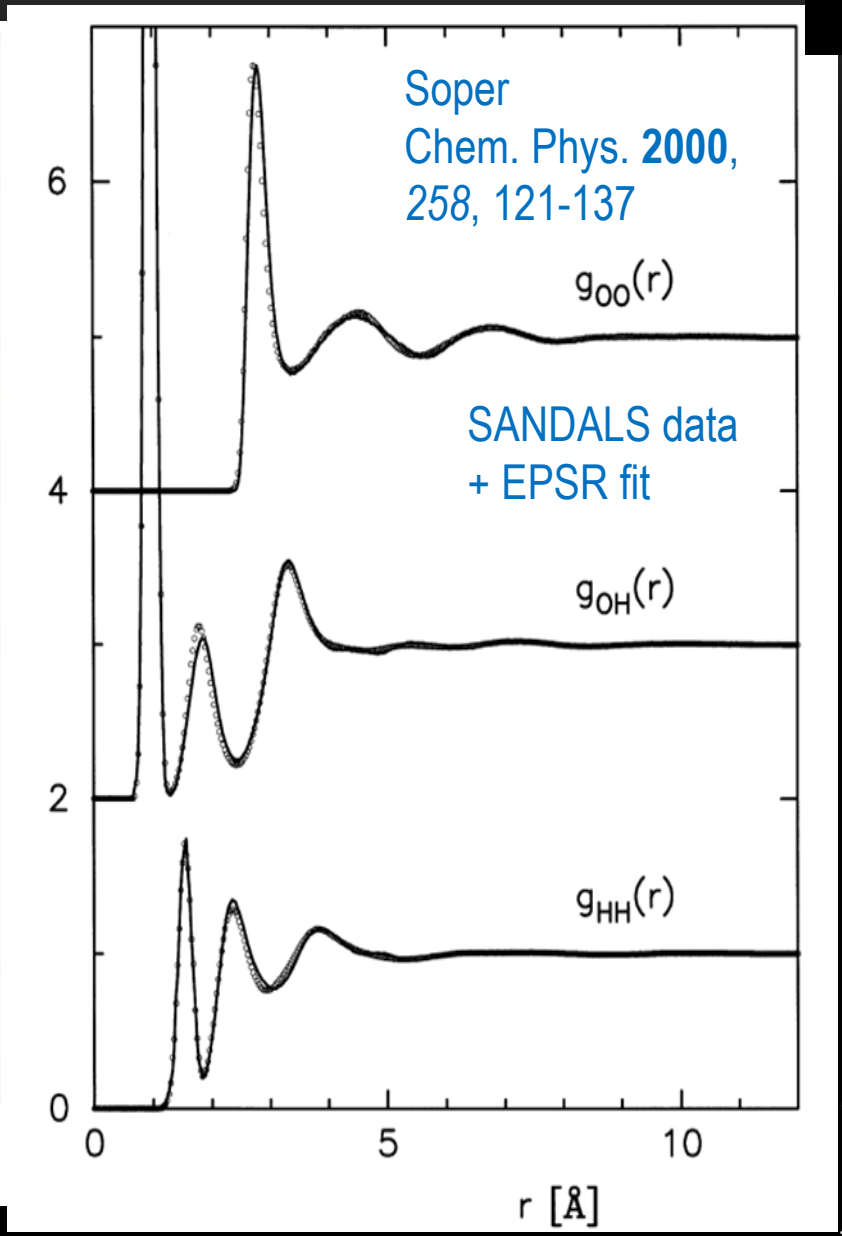
Intermolecular partial structure factors

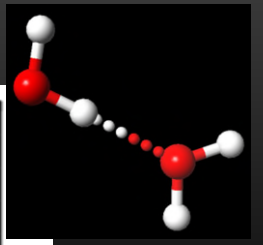
Intermolecular partial pair correlation functions

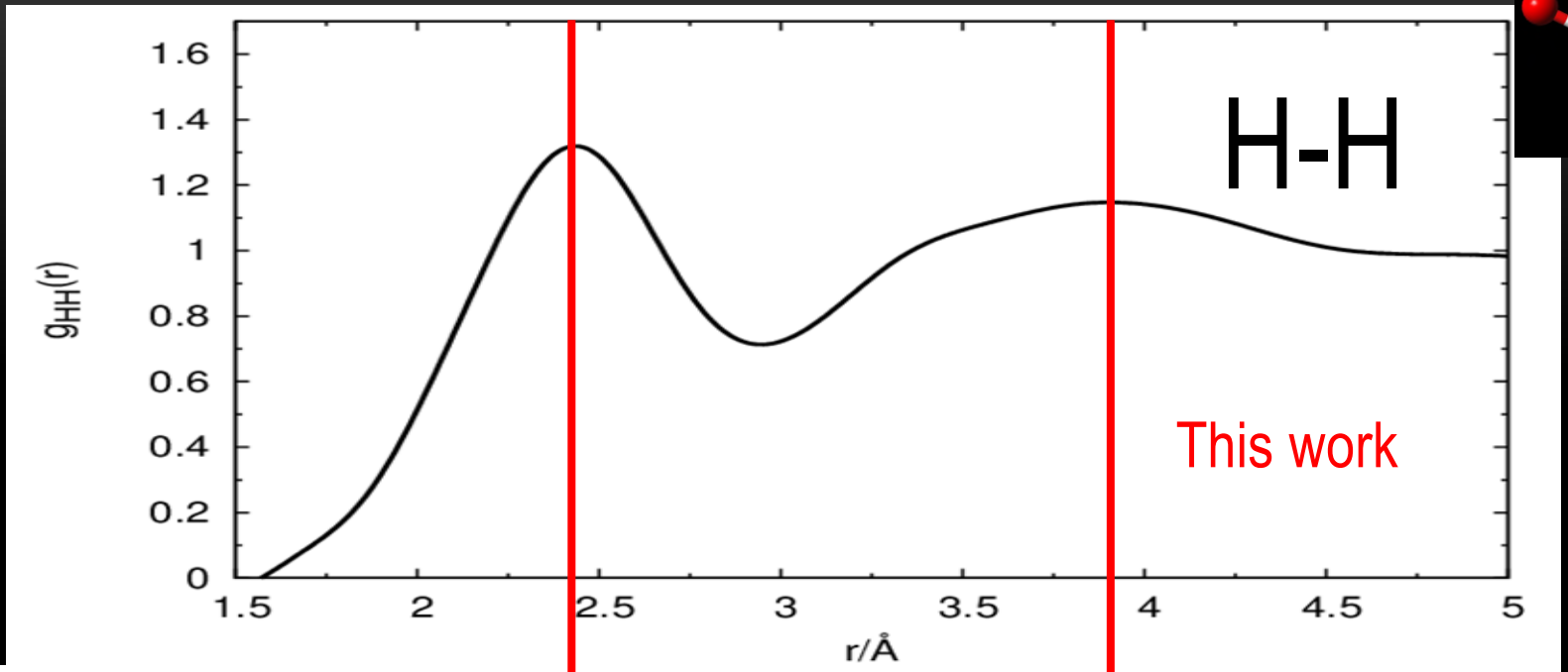


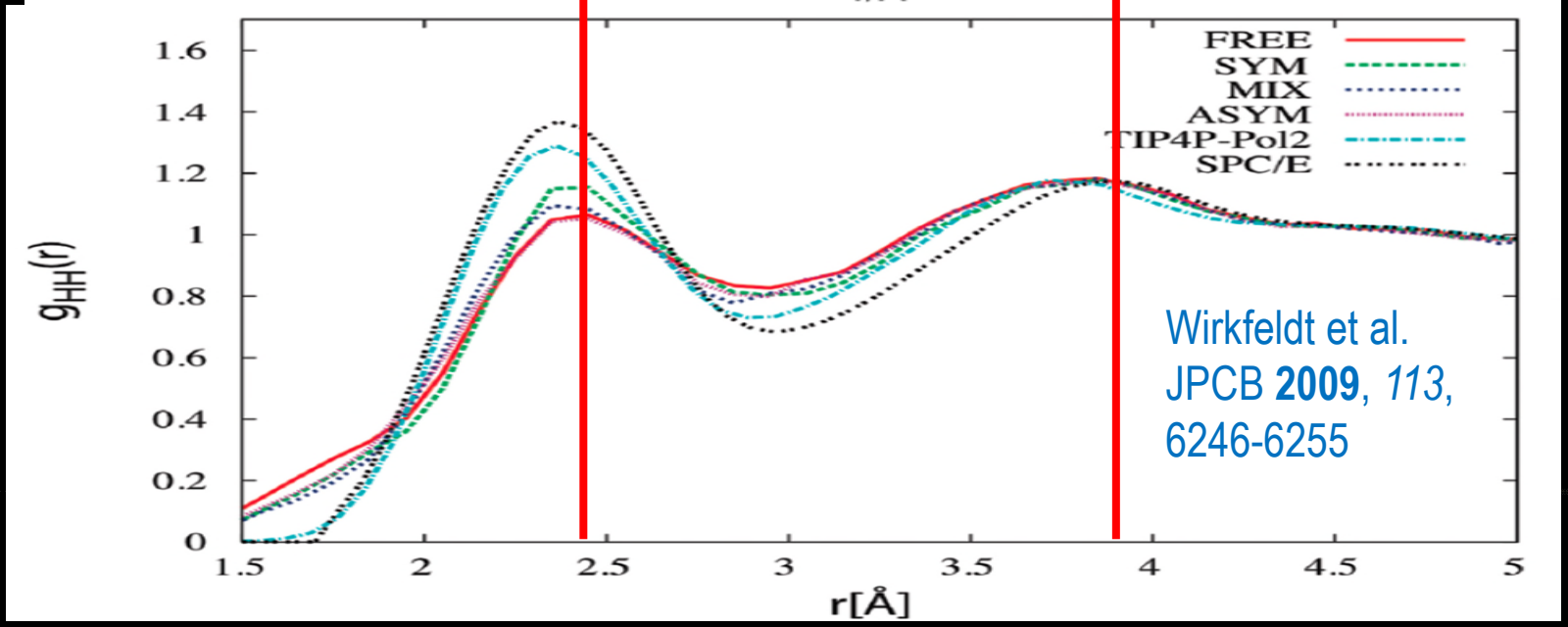


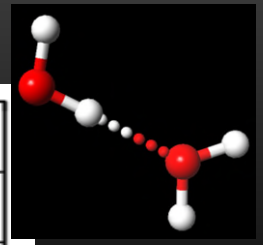

This work
NOVA data
+ direct method
$g_{OO}^{inter}(r)$, $g_{OH}^{inter}(r)$, $g_{HH}^{inter}(r)$
0
2
4
6
0
5
10
r/Å

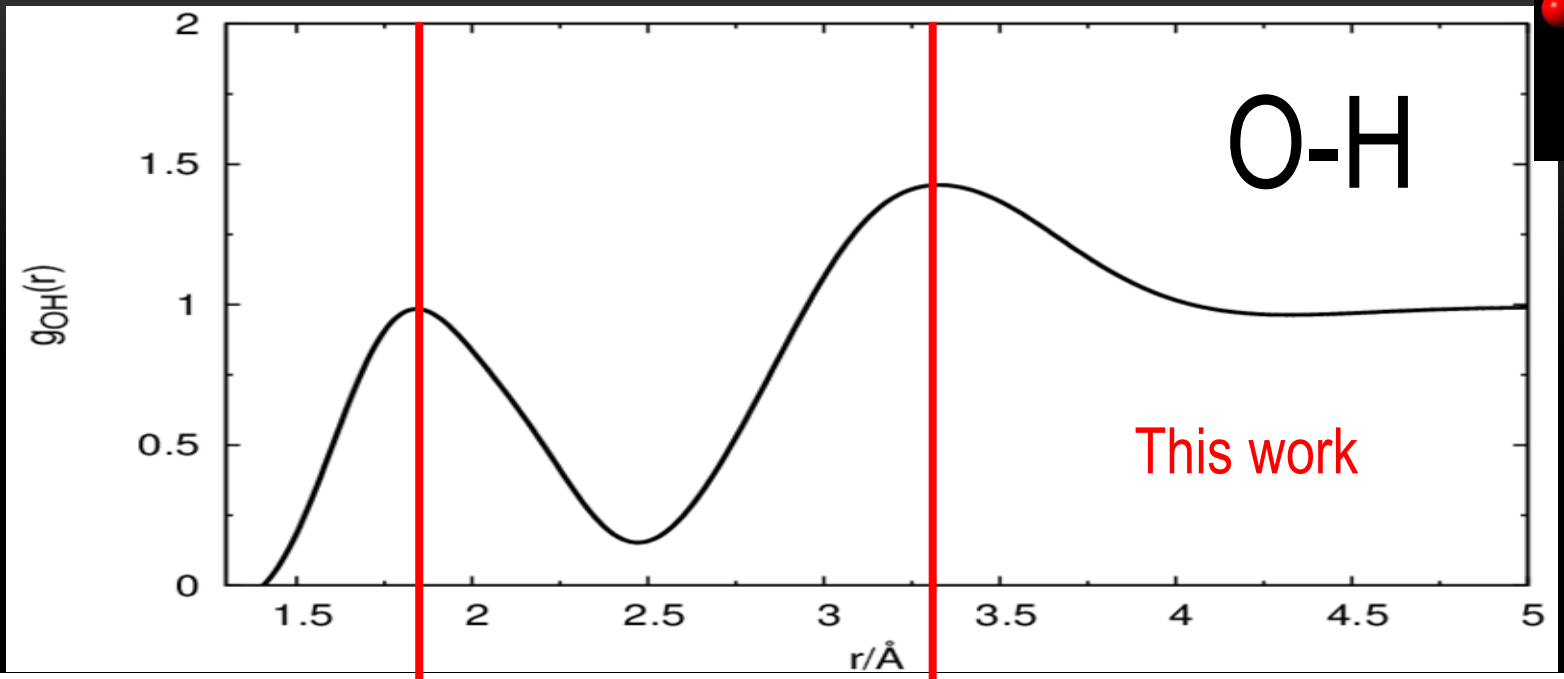

Soper
Chem. Phys. **2000**,
258, 121-137
$g_{OO}(r)$
SANDALS data
+ EPSR fit
$g_{OH}(r)$
$g_{HH}(r)$
0
2
4
6
0
5
10
r [Å]

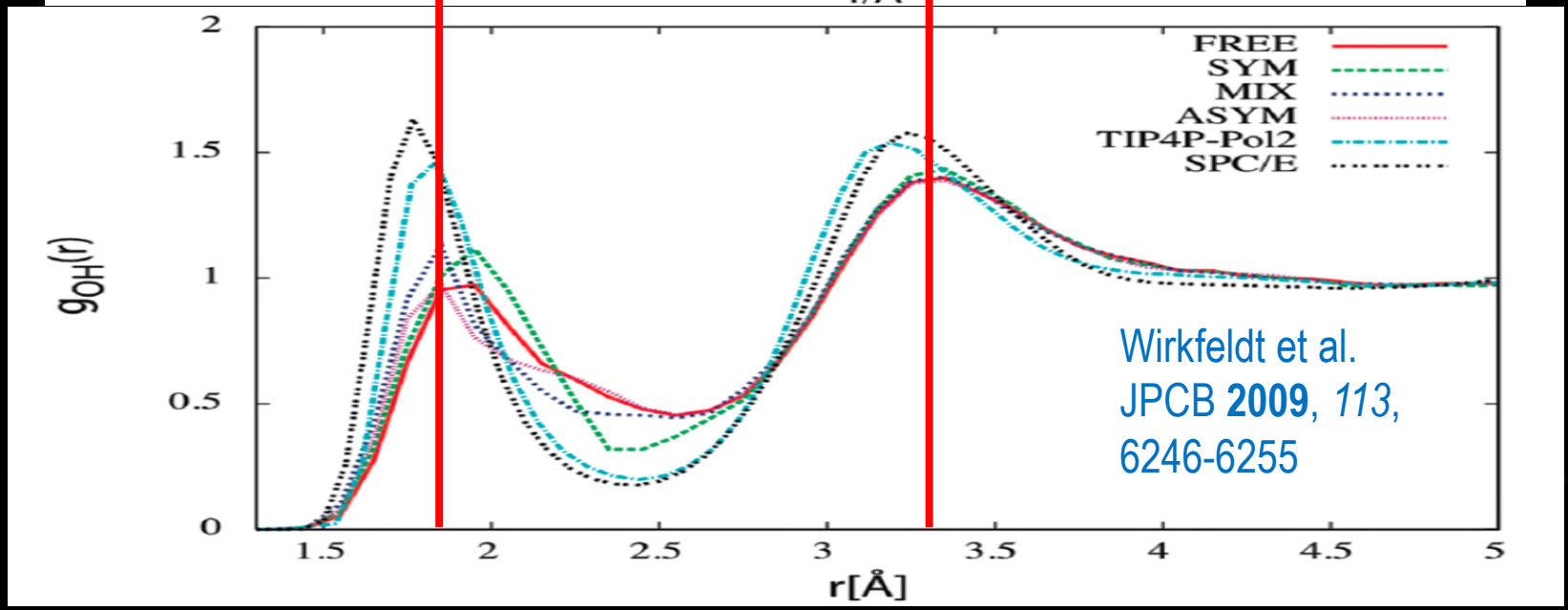



H-H
This work
$g_{HH}(r)$
r/Å


FREE
SYM
MIX
ASYM
TIP4P-Pol2
SPC/E
$g_{HH}(r)$
r[Å]
Wirkfeldt et al.
JPCB **2009**, *113*,
6246-6255




O-H
This work
$g_{OH}(r)$
r/Å


FREE
SYM
MIX
ASYM
TIP4P-Pol2
SPC/E
$g_{OH}(r)$
r[Å]
Wirkfeldt et al.
JPCB **2009**, *113*,
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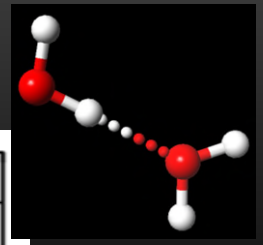
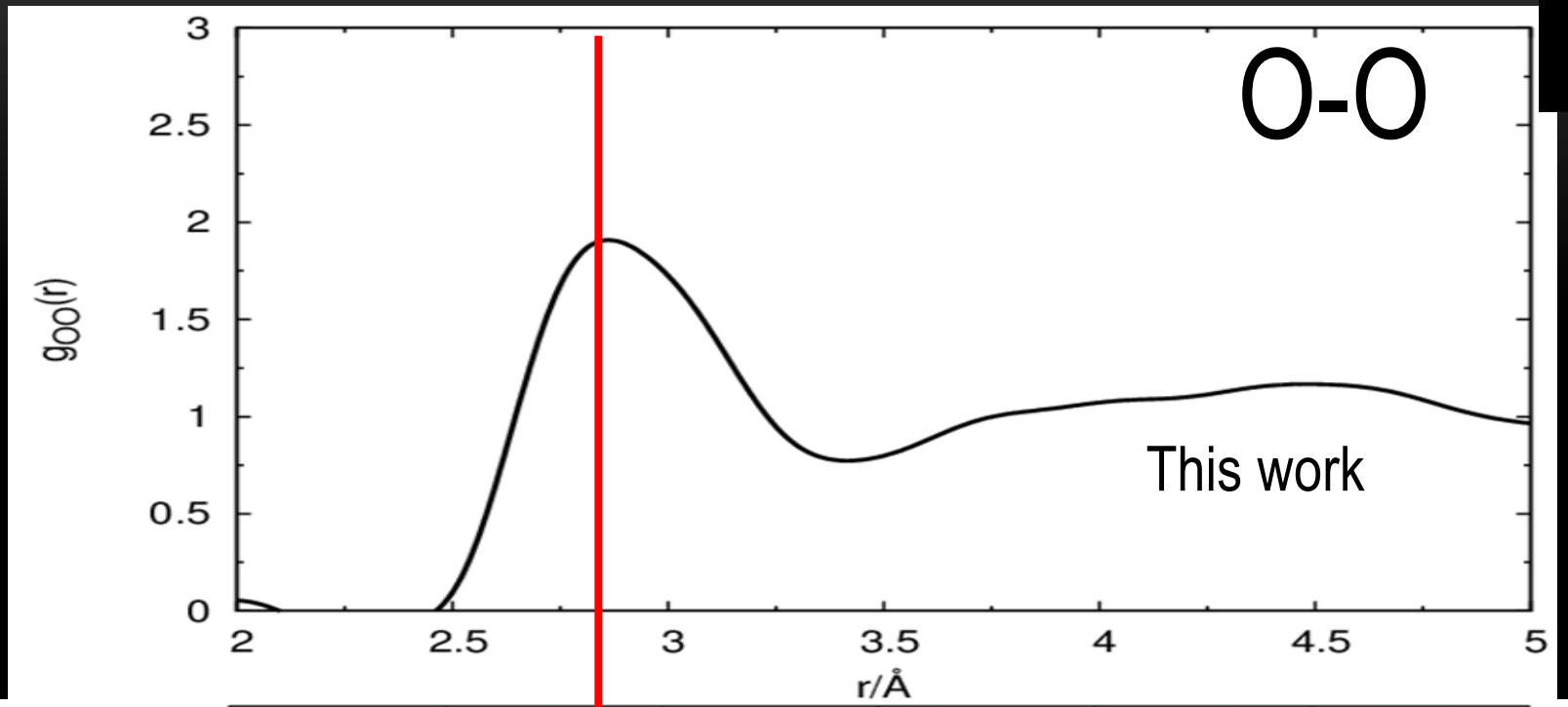
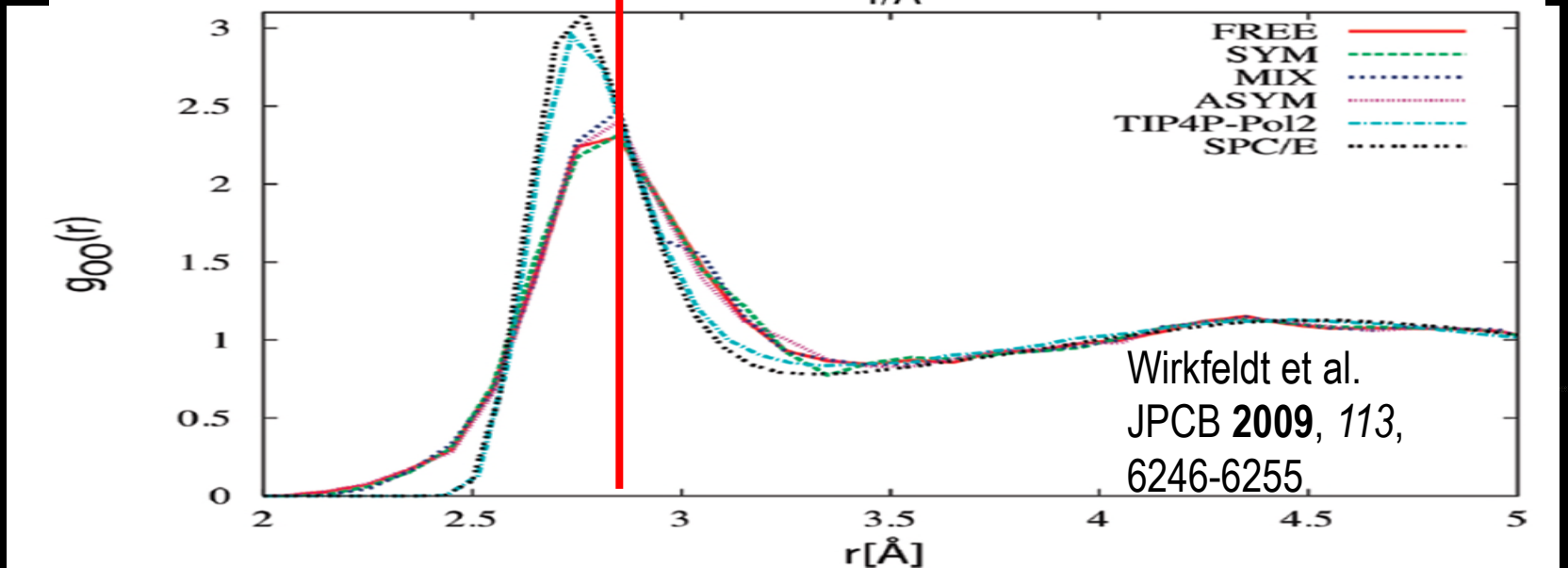



O-O
This work
$g_{OO}(r)$
r/Å


FREE
SYM
MIX
ASYM
TIP4P-Pol2
SPC/E
$g_{OO}(r)$
r[Å]
Wirkfeldt et al.
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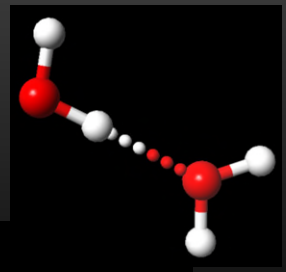
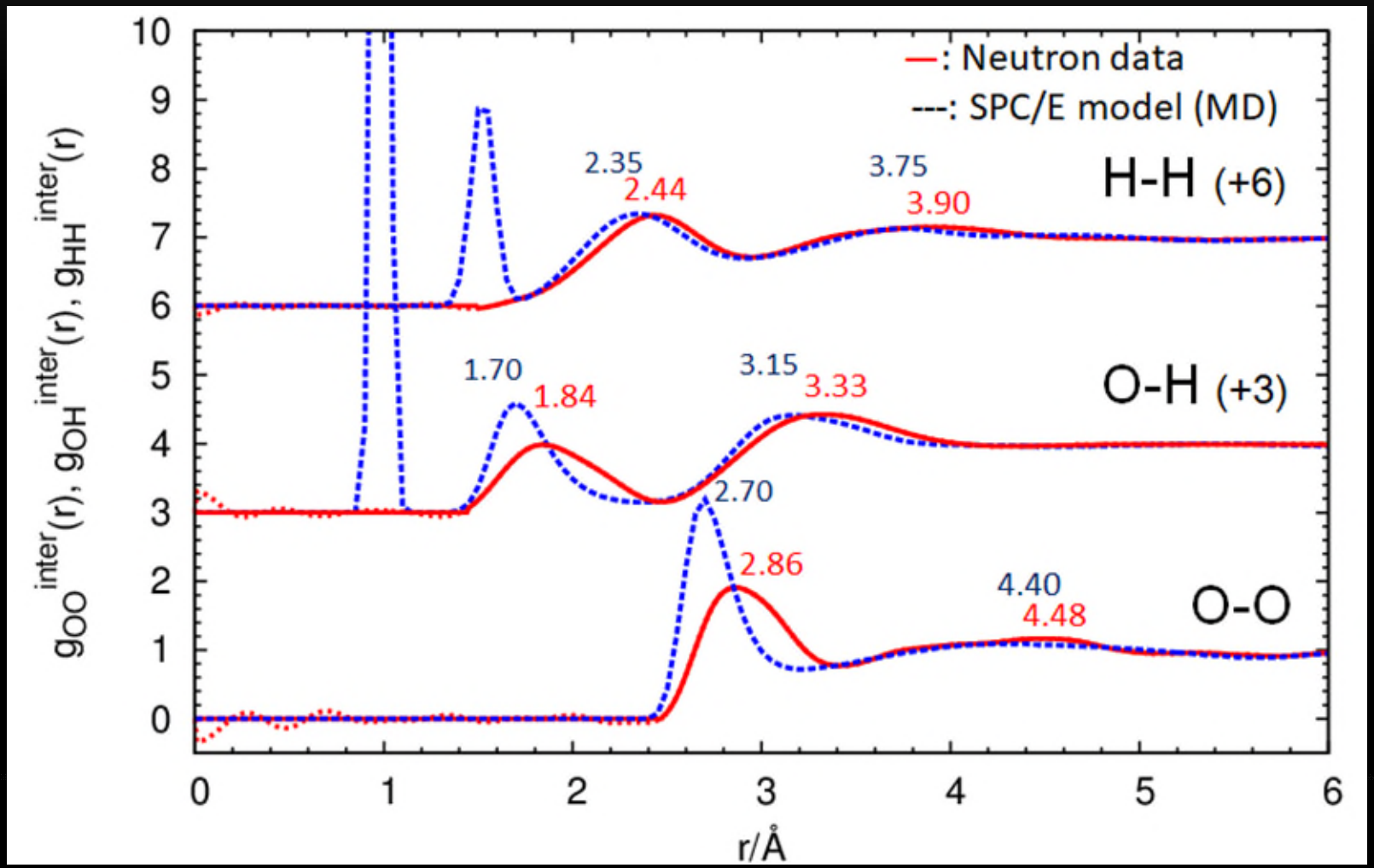
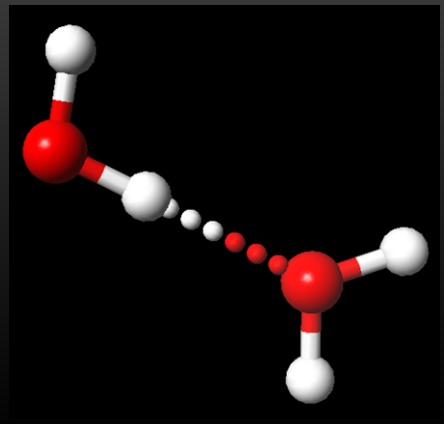


Comparison with MD simulation (SPC/E potential)



Combination with X-ray diffraction data



X-ray data → Distribution of electrons
Neutron data → Distribution of nuclei

$a_{HH}(Q)$, $a_{OH}(Q)$ and $a_{OO}(Q)$ ← Neutron data

$$I_{XN}(Q) = \{4f_H(Q)^2[a_{HH}(Q)-1] + 4f_O(Q)f_H(Q)[a_{OH}(Q)-1] + f_O(Q)^2[a_{OO}(Q)-1]\} / [2f_H(Q)+f_O(Q)]^2$$

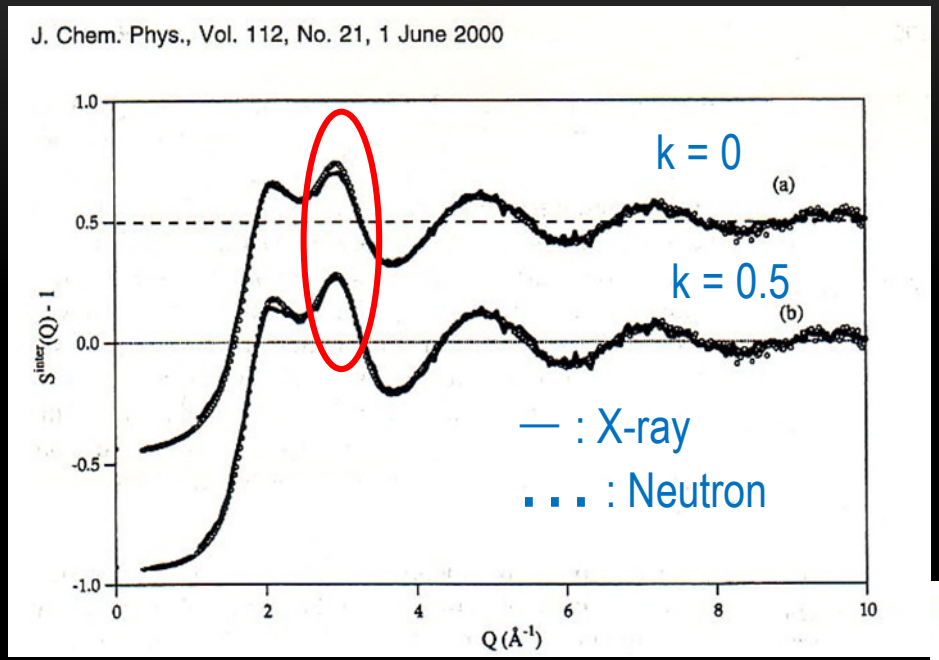
↕

X-ray interference term

↓

Information on electron distribution in the liquid state

Badyal et al. *J. Chem. Phys*. **2000**, *112*, 9206-9208.



$f_H(Q) \rightarrow (1-k)f_H(Q)$

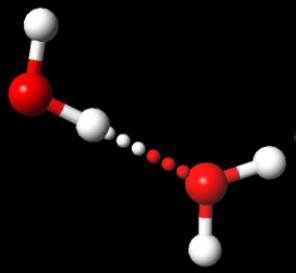
$f_O(Q) \rightarrow f_O(Q)+k[f_O{}^2\text{-}(Q) - f_O(Q)]$

k : fraction of electron, H → O

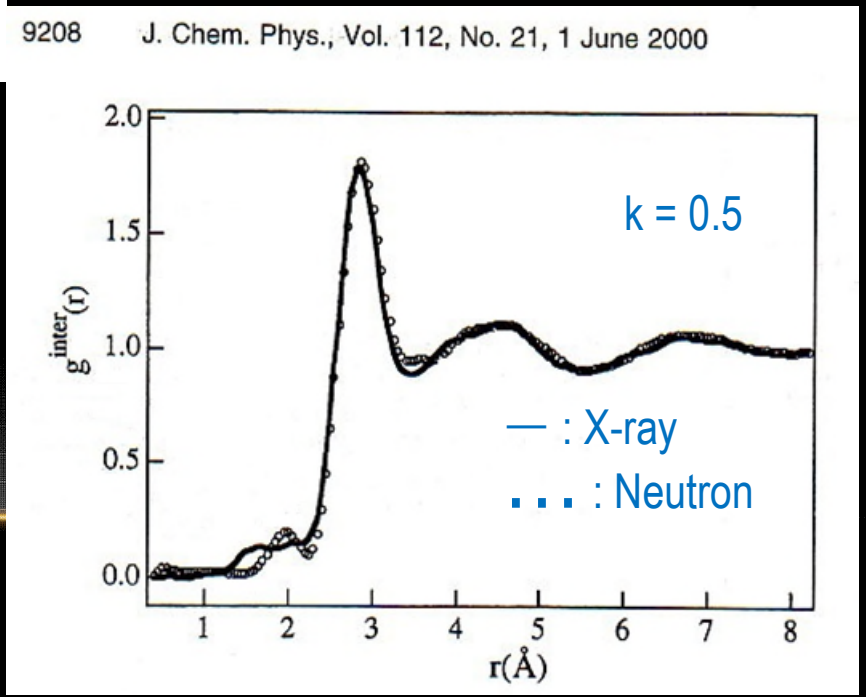
→ k = 0.5

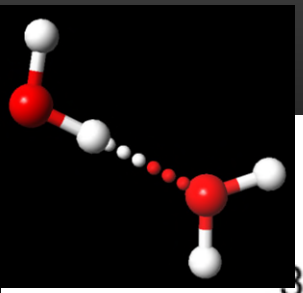
$S^{inter}(Q)$

$= \sum c_a c_b f_a(Q) f_b(Q) S^{inter}{}_{ab}(Q)$

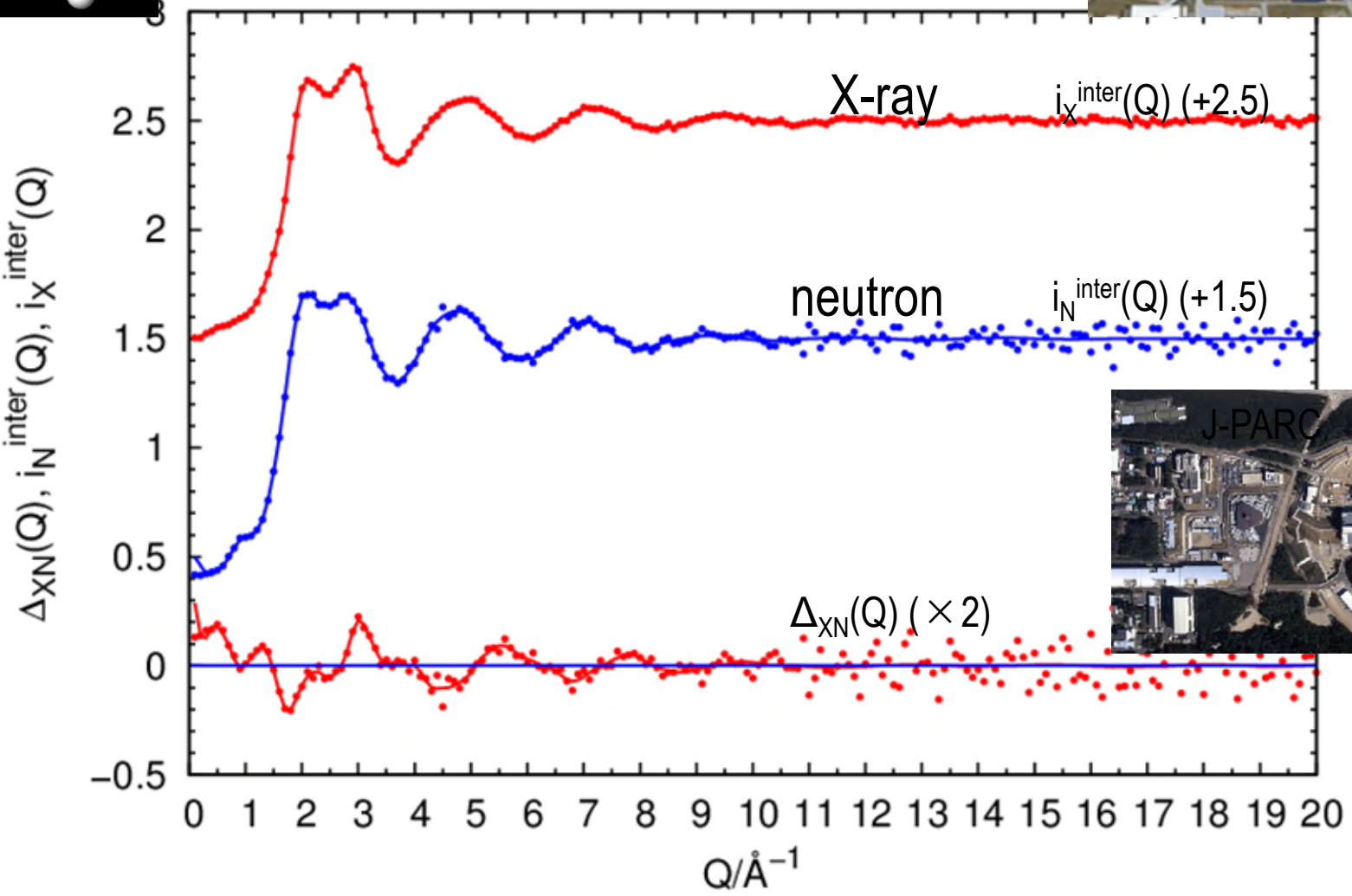


neutron data (SANDALS)

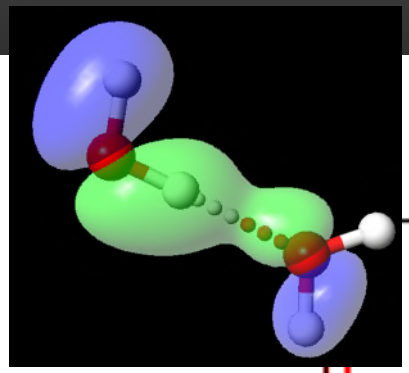


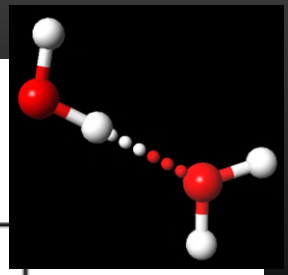


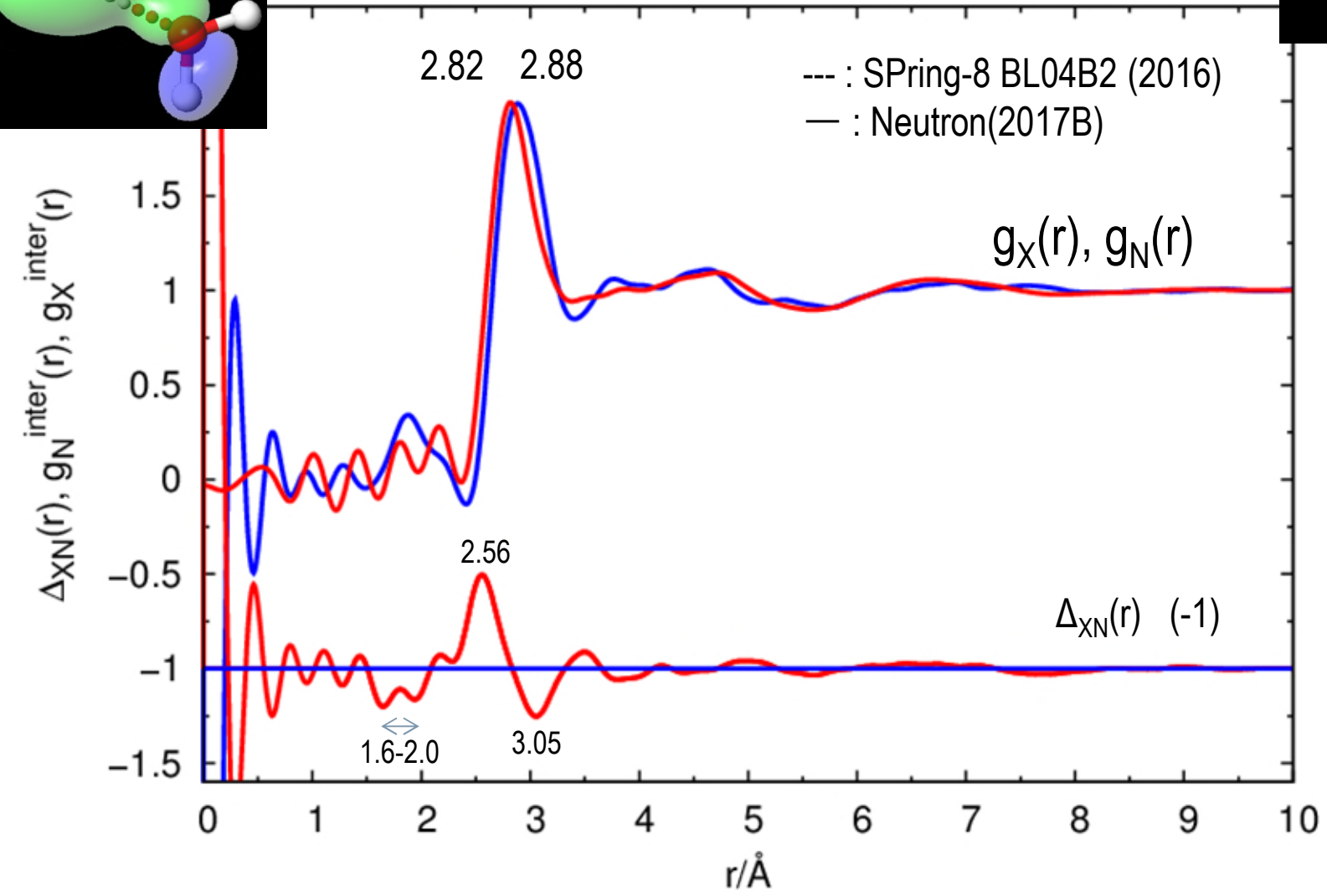

SPring-8

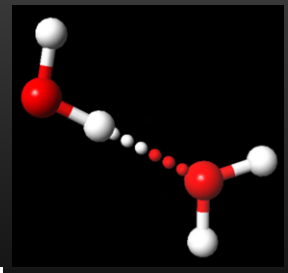

X-ray
$i_X^{inter}(Q)$ (+2.5)
neutron
$i_N^{inter}(Q)$ (+1.5)
$\Delta_{XN}(Q)$ (×2)
$\Delta_{XN}(Q)$, $i_N^{inter}(Q)$, $i_X^{inter}(Q)$
Q/Å^{-1}
2.5
2
1.5
1
0.5
0
−0.5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

J-PARC

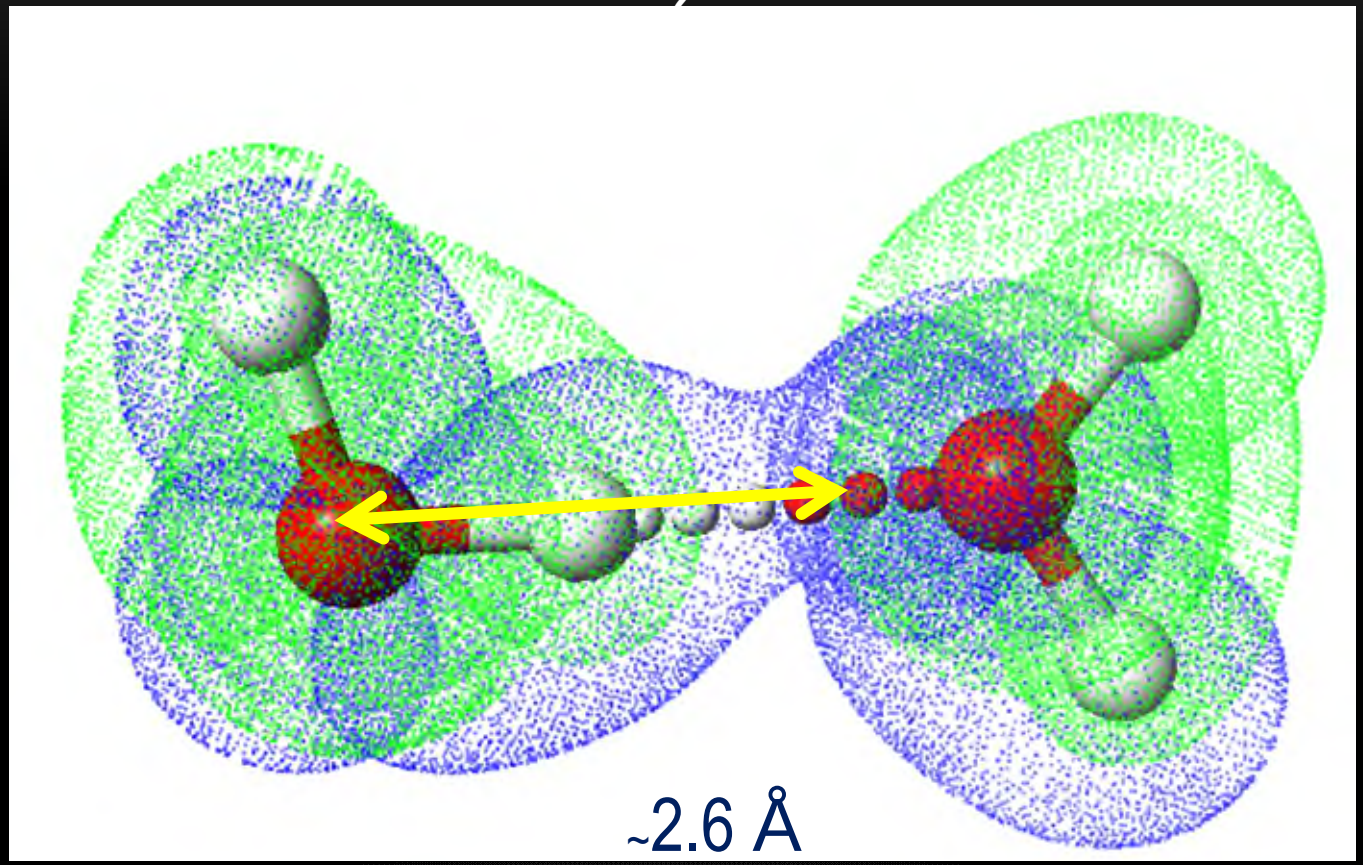




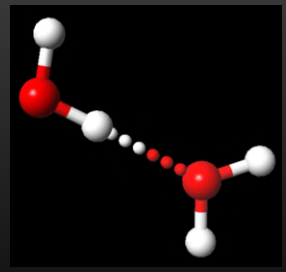

2.82
2.88
--- : SPring-8 BL04B2 (2016)
— : Neutron(2017B)
$g_X(r)$, $g_N(r)$
$\Delta_{XN}(r)$ (-1)
2.56
3.05
1.6-2.0
$\Delta_{XN}(r)$, $g_N^{inter}(r)$, $g_X^{inter}(r)$
r/Å
1.5
1
0.5
0
−0.5
−1
−1.5
0
1
2
3
4
5
6
7
8
9
10



Molecular Orbitals of H_2O Dimer



Conclusions



- Partial structure factors $a_{HH}(Q)$, $a_{OH}(Q)$ and $a_{OO}(Q)$ were successfully obtained from NOVA data
- There exist differences in the first intermolecular peak positions and intensities of $g_{ij}(r)$ between NOVA and SANDALS data.
- It is possible to extract information on electron distribution in liquid state by the combination of partial structure factors (neutron) and X-ray interference term.

Acknowledgements

We thank Prof. Kazutaka Ikeda (KEK) and Prof. Toshiya Otomo (KEK) for their help for neutron diffraction measurements using the NOVA spectrometer. We also thank Prof. Yasuhiro Umebayashi (Niigata Univ.) for providing the X-ray data measured with BL04B2 diffractometer at SPring-8 facility.