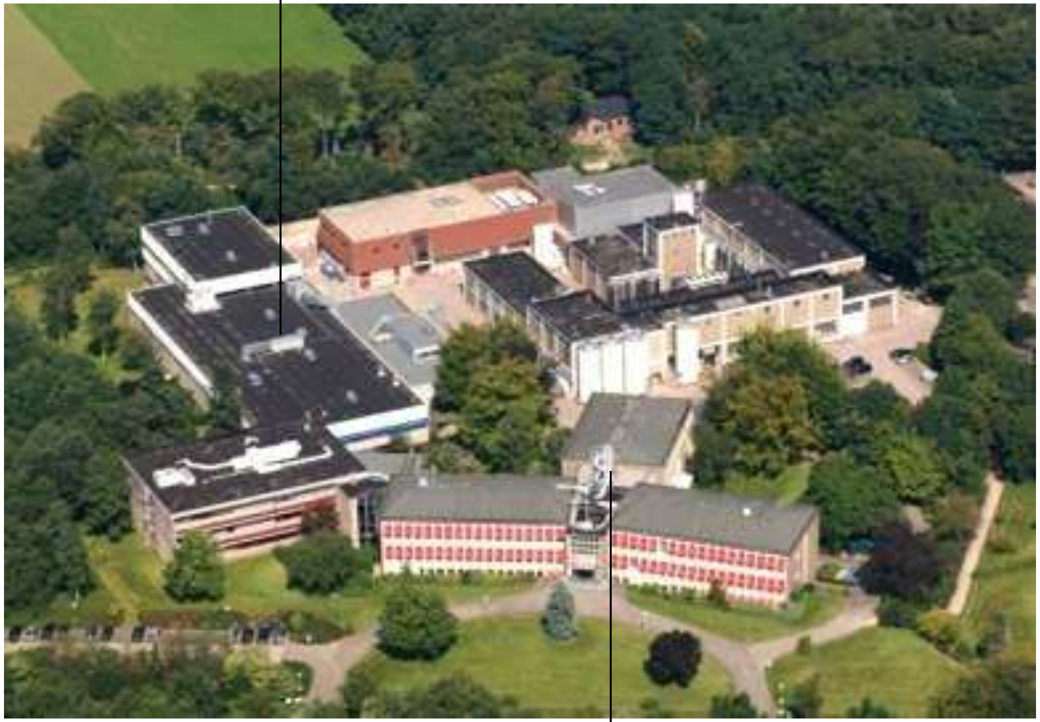
Hydrogen bonds studied by wide angle neutron scattering

Hans Tromp@NIZO.NL

Introducing **NIZO food research**

- Independent, private contract research company for the food industry
- Formerly the Dutch Institute of dairy research
- 200 employees



Application & Processing centre

Research centre

Outline

- Theory in brief
- Experimental results (Highlights)
- Future work

Isotopic substitution

Scattering cross section of a chemical mixture

$$\frac{d\sigma_{coh}(\theta)}{d\Omega} = \sum_{k,l} f_k f_l \langle b_k \rangle \langle b_l \rangle \left\langle \sum_{i(k)}^{N_k} \sum_{j(l)}^{N_l} e^{i\vec{Q}\cdot(\vec{r}_i - \vec{r}_j)} \right\rangle = N \sum_{k,l} f_k f_l \langle b_k \rangle \langle b_l \rangle S_{kl}(Q)$$

f_k= number fraction of atom k
$S_{kl}(Q)$=partial structure factor of atom pair [k,l]
N=total number of scatterers

- A structure function $S_{kl}(Q)$ for each pair of elements
- $\langle b_k \rangle$ scattering length of element k
- $\langle b_k \rangle$ dependent on isotopic composition of element k *(averaged over spin states)*
- Isotopes can be varied without changing the structure

Isotopic substitution

Convenient isotope pairs

	%		$<b>$ [fm]	
$^{1}H/^{2}H$	99.985	0.015	-3.37	6.67
$^{58}Ni/^{62}Ni$	68.27	3.59	14.1	-8.7
$^{35}Cl/^{37}Cl$	75.77	24.23	11.65	3.08
$^{40}Ca/^{44}Ca$	96.94	2.09	4.80	1.42
$^{63}Cu/^{65}Cu$	69.17	30.83	6.43	10.61
$^{54}Fe/^{56}Fe$	5.8	91.7	4.2	9.94

Isotopic substitution

E.g. for a $NiCl_2$ solution:

f = atomic number fraction

$$\frac{d\sigma_{coh}(\theta)}{d\Omega} =$$

$$f_{Ni} f_O b_{Ni} b_O S_{NiO}(Q)$$

$$+ f_{Ni} f_H b_{Ni} b_H S_{NiH}(Q)$$

$$+ f_H f_O b_H b_O S_{HO}(Q)$$

$$+ f_{Ni} f_{Cl} b_{Ni} b_{Cl} S_{NiCl}(Q)$$

$$+ f_{Ni}^2 b_{Ni}^2 S_{NiNi}(Q)$$

$$+ f_O^2 b_O^2 S_{OO}(Q)$$

$$+ f_H^2 b_H^2 S_{HH}(Q)$$

$$+ f_{Cl}^2 b_{Cl}^2 S_{ClCl}(Q)$$

Stay the same after isotopic substitution of Ni

Data processing

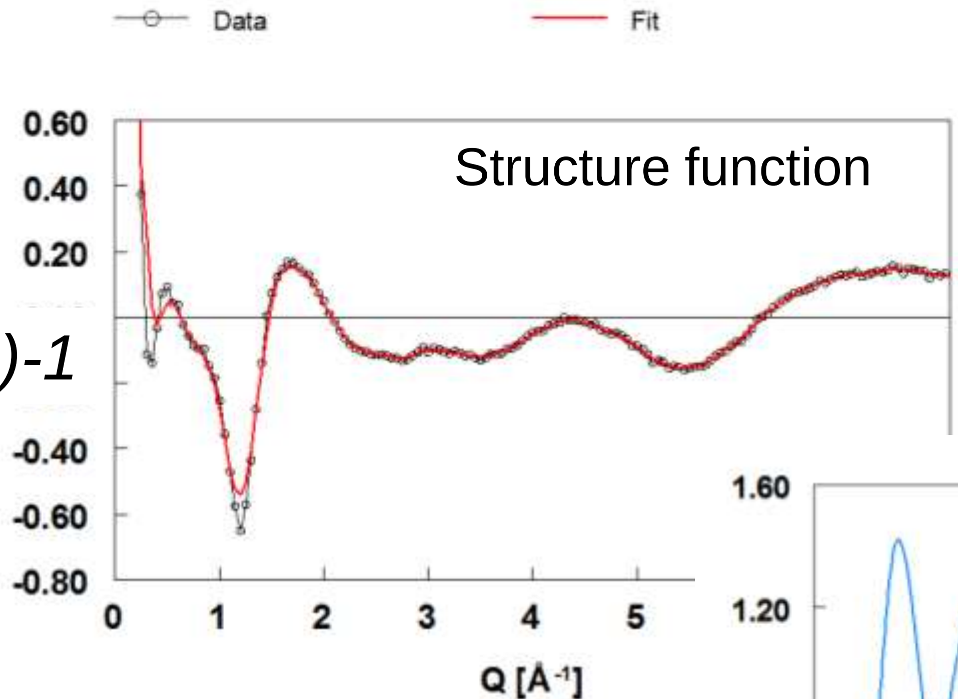
$$\frac{d\sigma(\theta)}{d\Omega} = N\frac{\sigma_{inc}}{4\pi} + N\frac{\sigma_{coh}}{4\pi}S(Q) =$$

$$N\frac{\sigma_{inc}}{4\pi} + N\sum_{i(k)}^{N_k}\sum_{j(l)}^{N_l} f_k f_l \langle b_k\rangle\langle b_l\rangle S_{kl}(Q)$$

$$S_{kl}(Q) = 1 + \frac{4\pi N_k}{VQ}\int_0^\infty [g_{kl}(r)-1]r\sin(Qr)dr$$

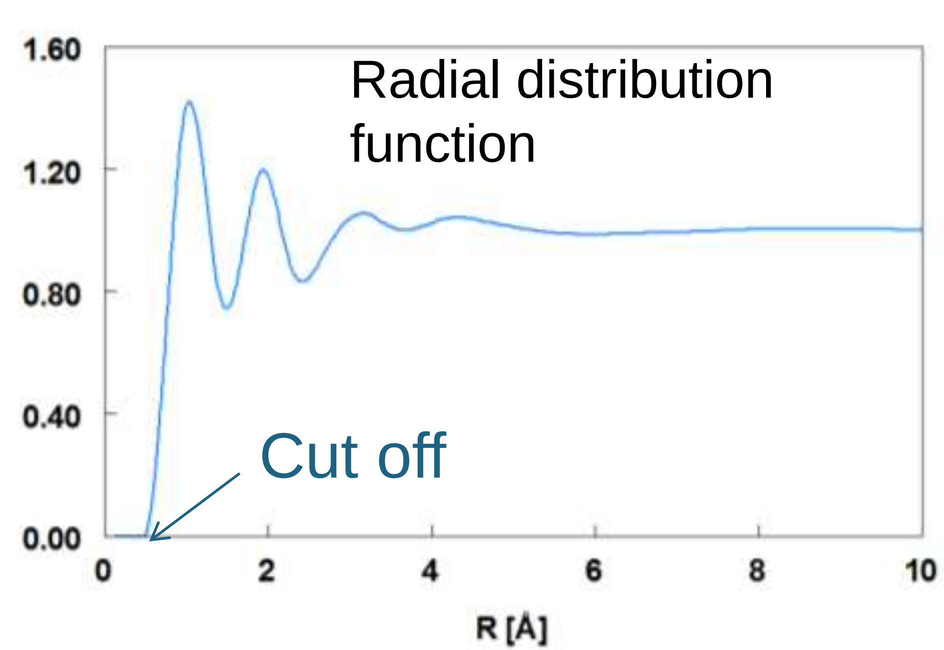
$$g_{kl}(r) = 1 + \frac{V}{2\pi^2 N_k}\int_0^\infty [S_{kl}(Q)-1]Q\sin(Qr)dQ$$

Data processing



$S_{kl}(Q)$-1

$g_{kl}(R)$



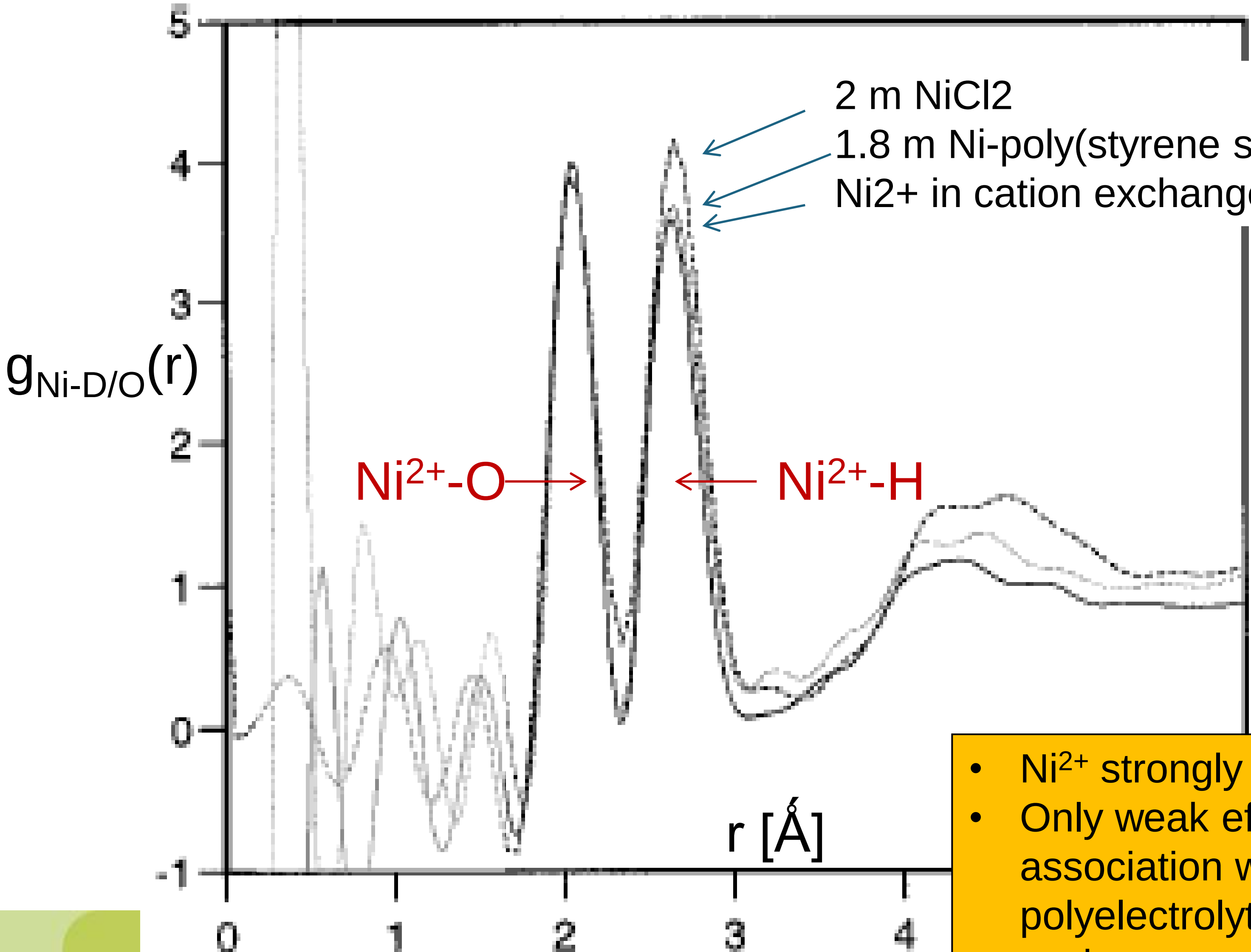
Best smooth fit with constraints:
- Low Q limit of *S(Q)*
- Low R cut-off of *g(R)*
- High R level of *g(R)*

Outline

- Theory in brief
- Experimental results (highlights)
- Future work

Hydration of Ni^{2+}

^{58}Ni and ^{60}Ni

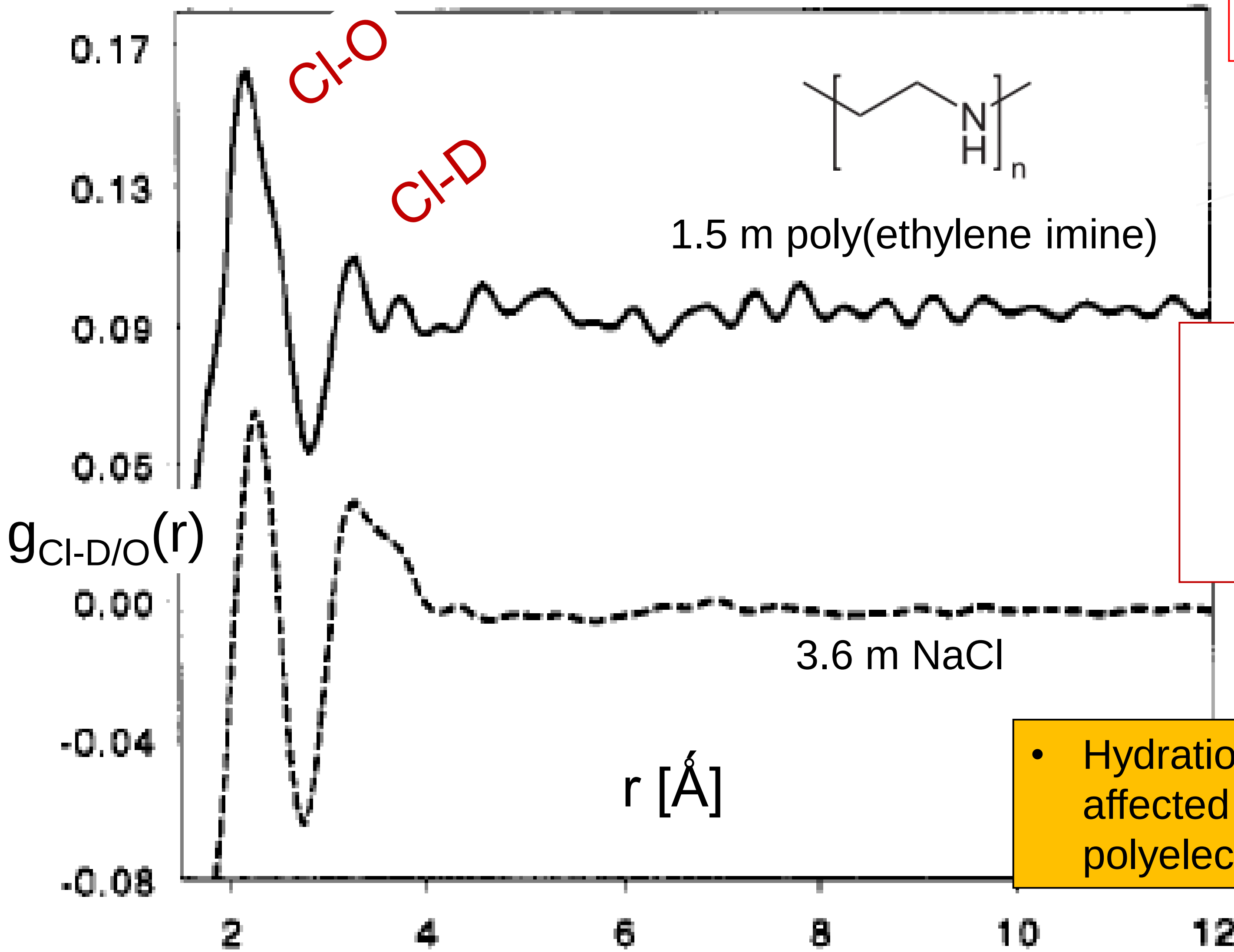


- Ni^{2+} strongly hydrated
- Only weak effect of association with polyelectrolyte or cation exchange resin

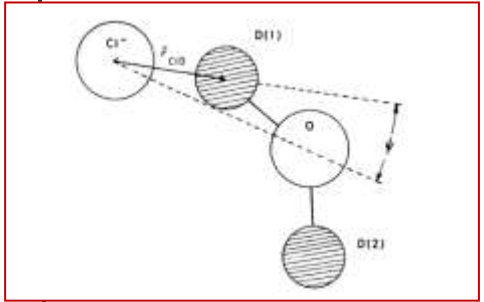
Tromp and Neilson J. Phys. Chem., Vol. 100, No. 18, 1996

Hydration of Cl^-

^{35}Cl and ^{37}Cl



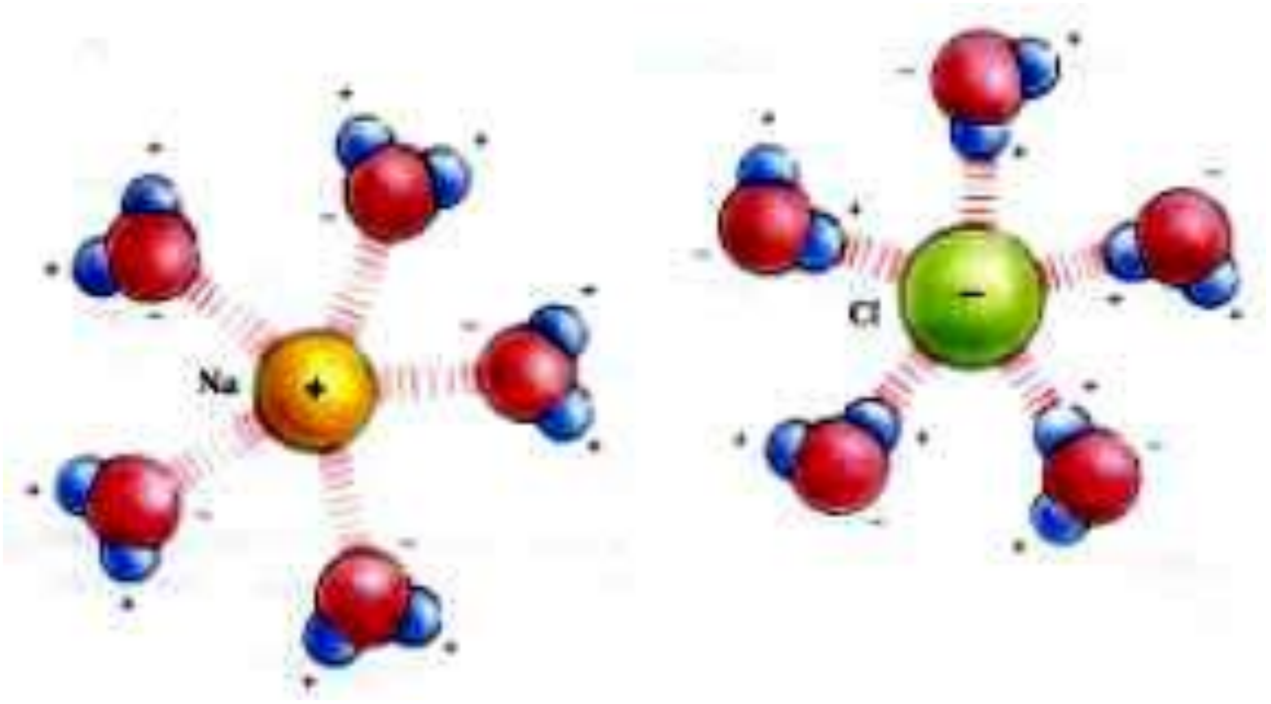
D.H. Powell et al. *Faraday Discuss Chem. Soc*. **85**, 137 (1988)



- Hydration of Cl^- weakly affected of association with polyelectrolyte

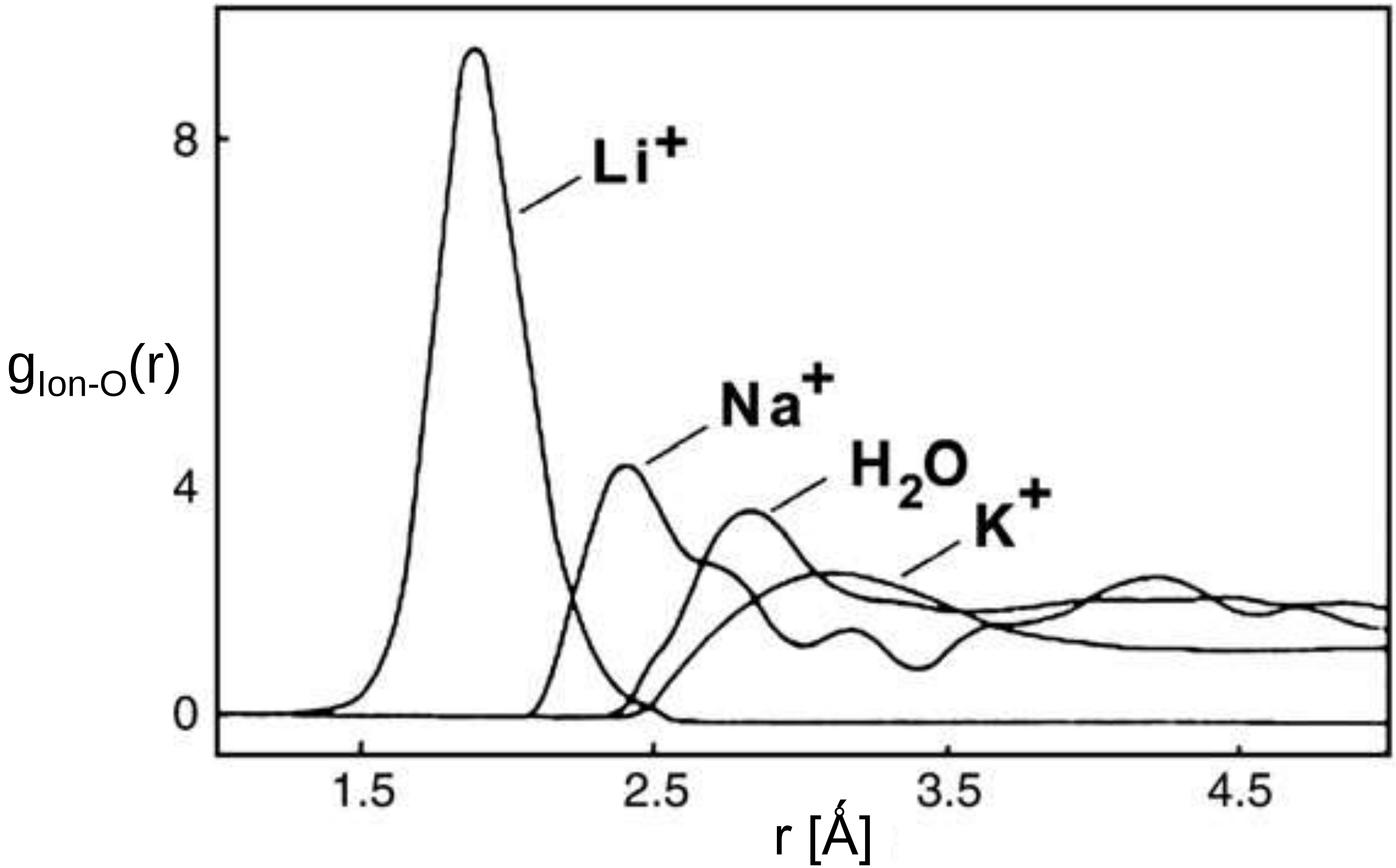
Bieze at al.J. Phys. Chem.,**98**, 4454 (1994)

Hydration spheres of simple ions



http://www.biog1105-1106.org/demos/105/unit1/waterasasolvent.html

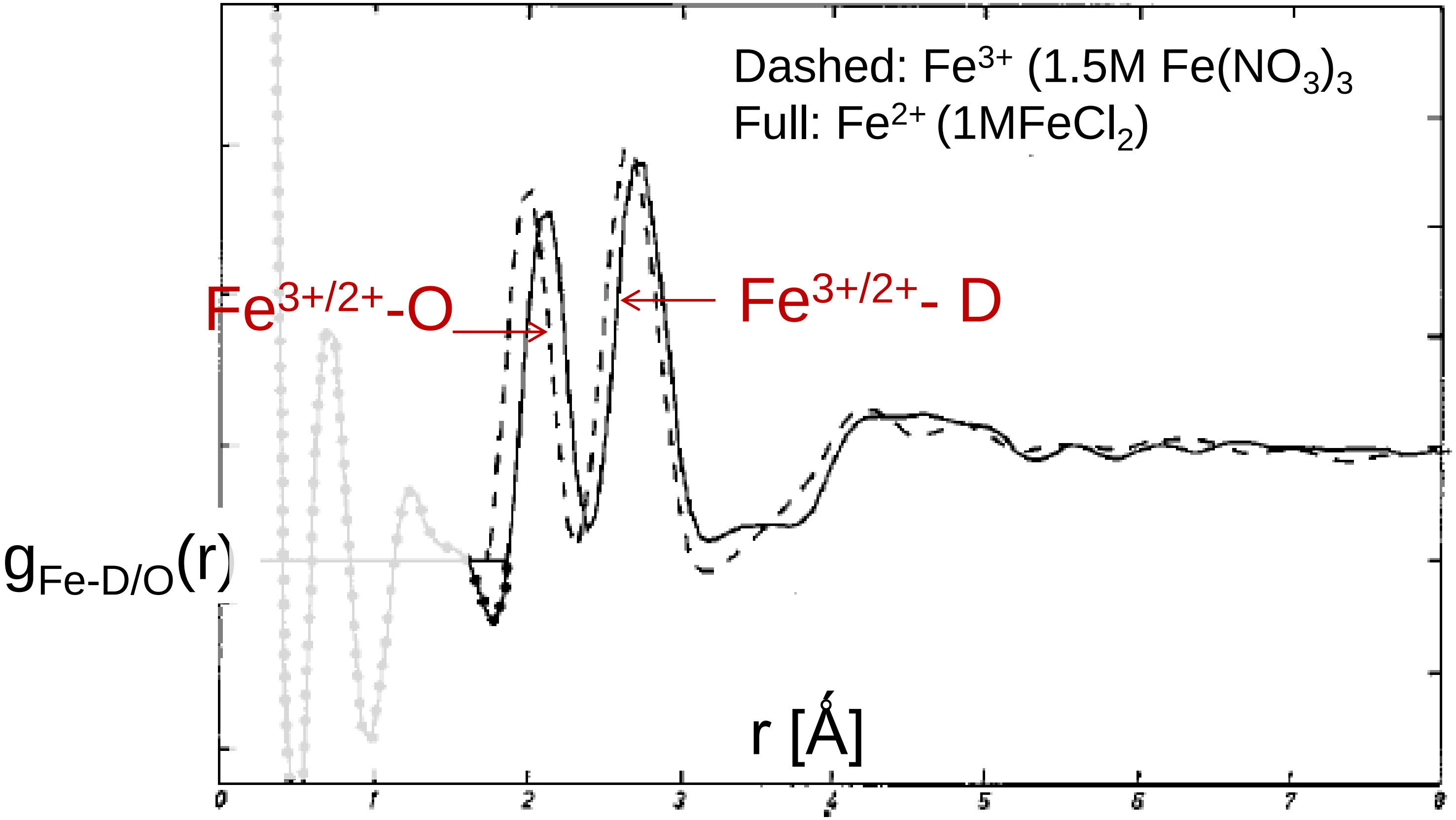
Metal ion-oxygen correlation



N.T. Skipper, G.W. Neilson, *J. Phys., Condens. Matter* **1** 4141 (1989) .

Fe^{2+} and Fe^{3+}

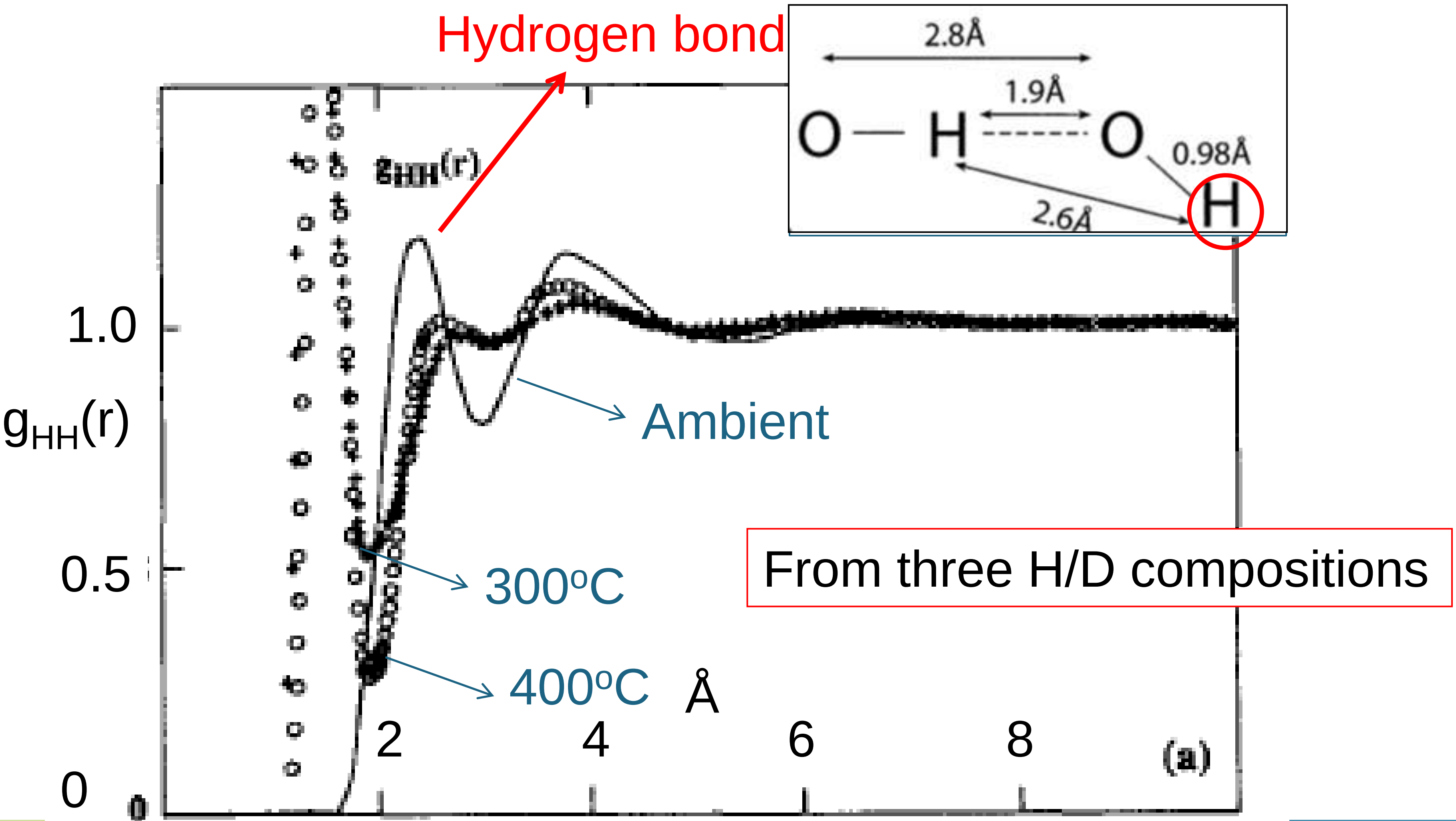
^{nat}Fe and ^{54}Fe



G. J. Herdman and G. W. Neilson J. Phys.: Condens. Matter **4,** 649 (1992)

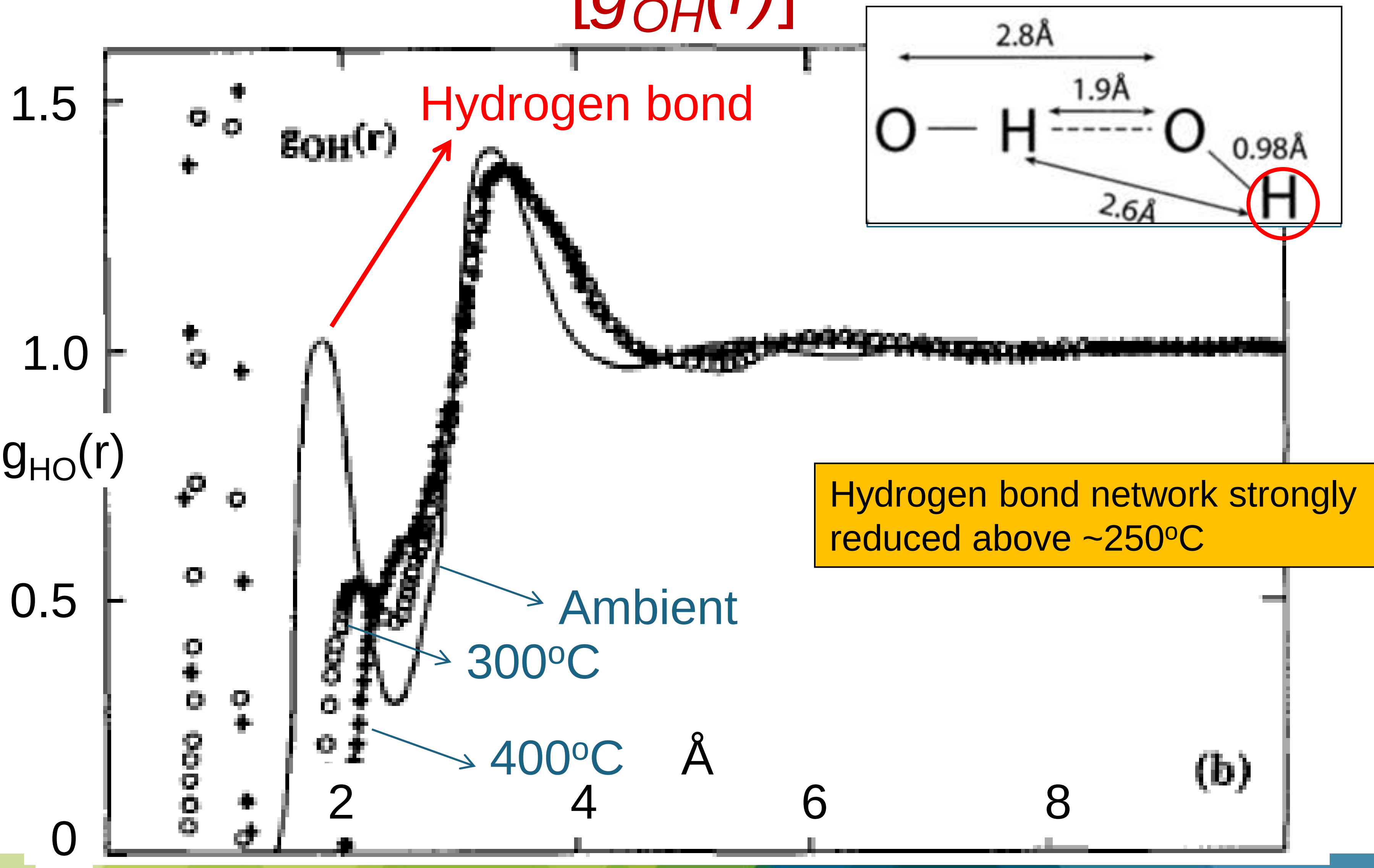
Hydration sphere for Fe^{3+} tighter than for Fe^{2+}

Hydrogen bonding in water [$g_{HH}(r)$]



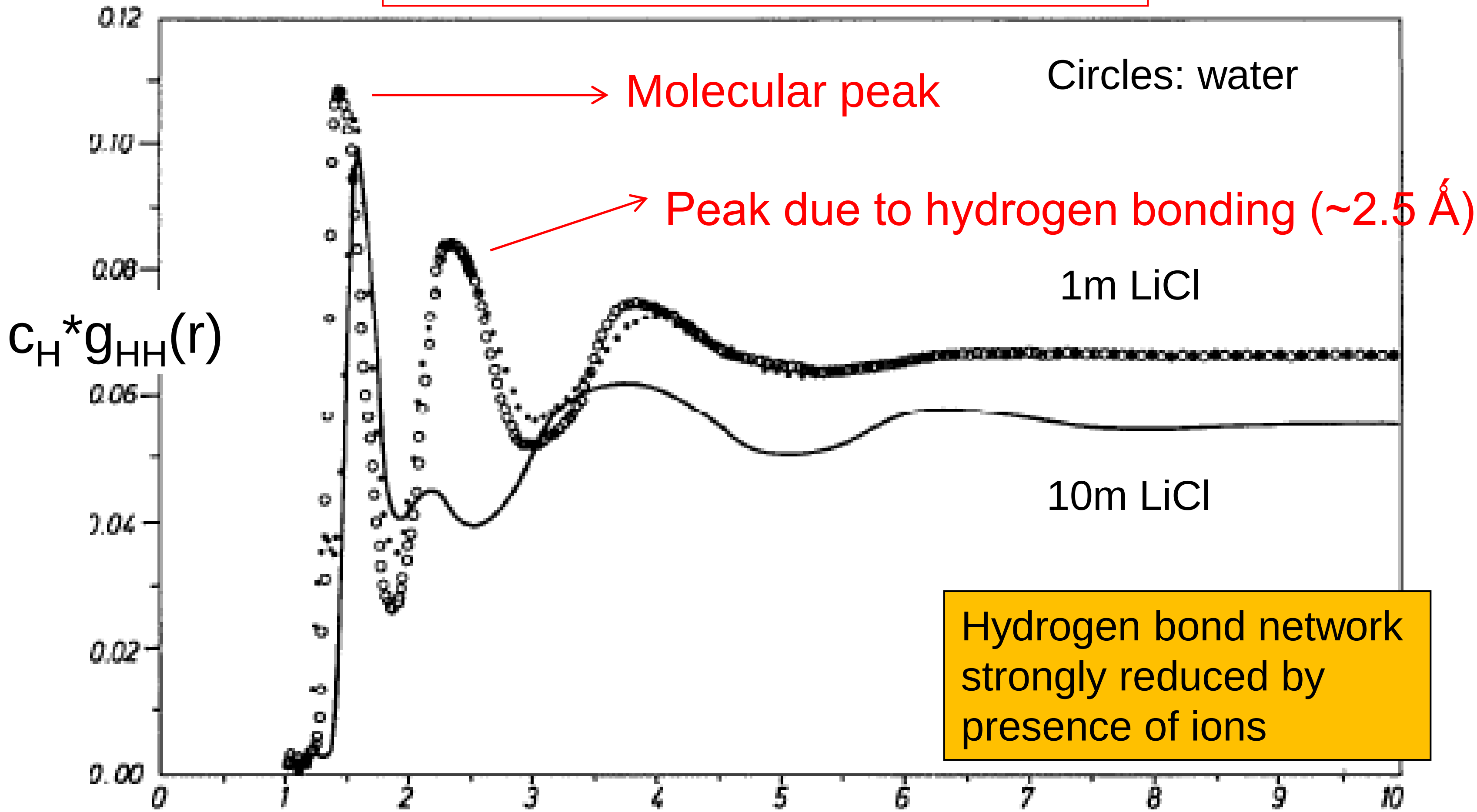
R. H. Tromp, P. Postorino, G. W. Neilson, M. A. Ricci, and A. K. Soper , J. Chem. Phys. **101**, 6210 (1994)

Hydrogen bonding in water [$g_{OH}(r)$]



Hydrogen bonds affected by a salt

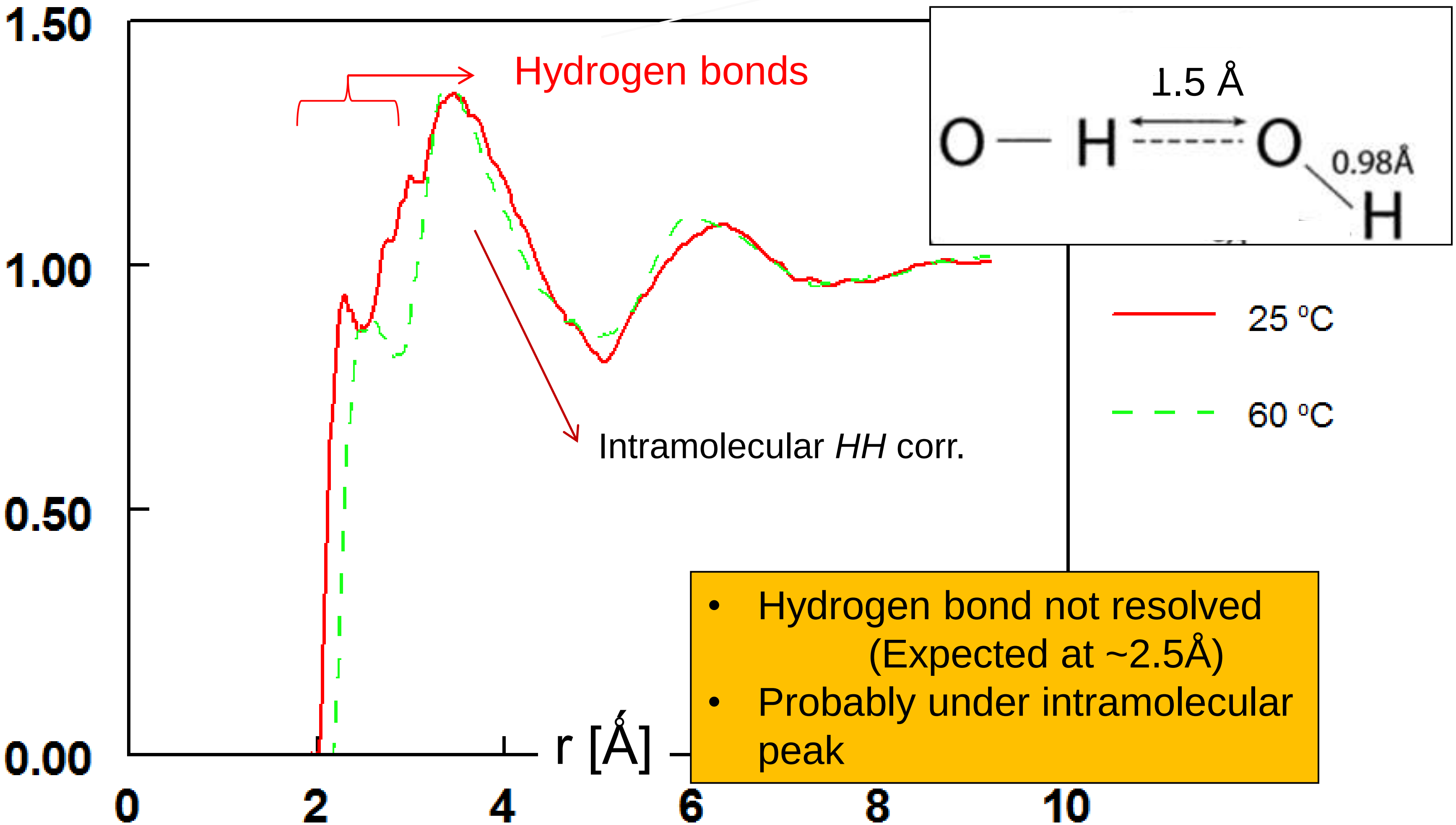
From three H/D compositions



R. H. Tromp, G.W. Neilson and A.K. Soper, *J.Chem.Phys* **98**, 8460, (1992)

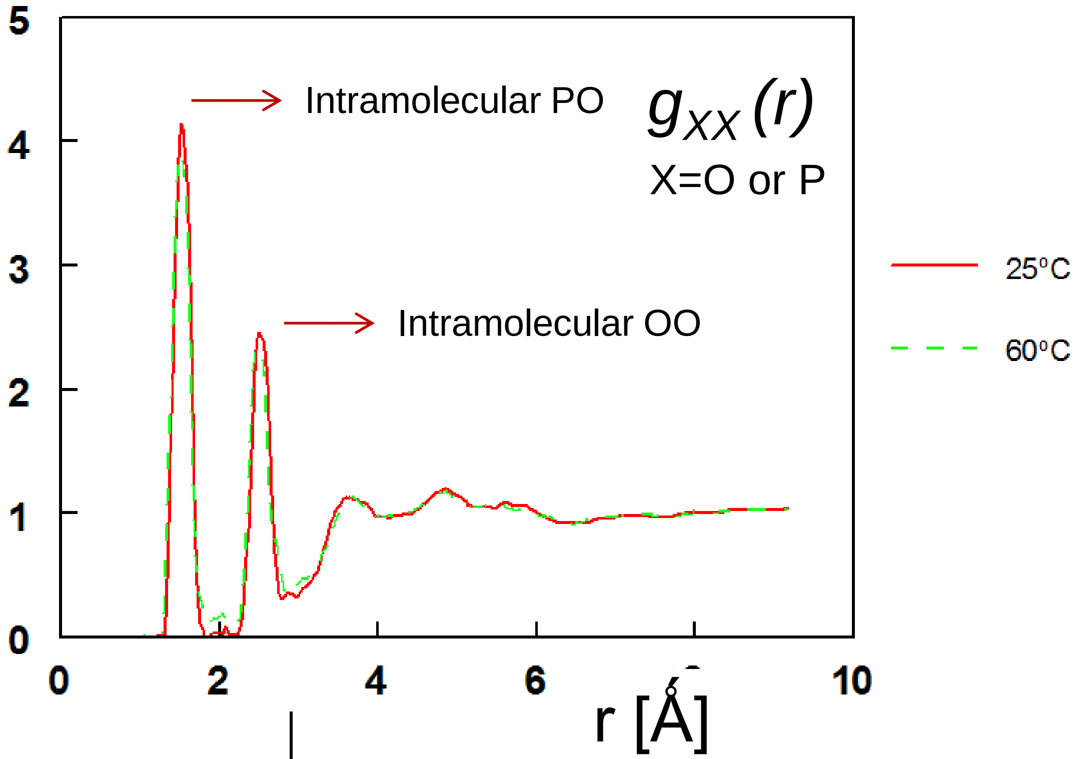
$g_{HH}(r)$ in pure phosphoric acid

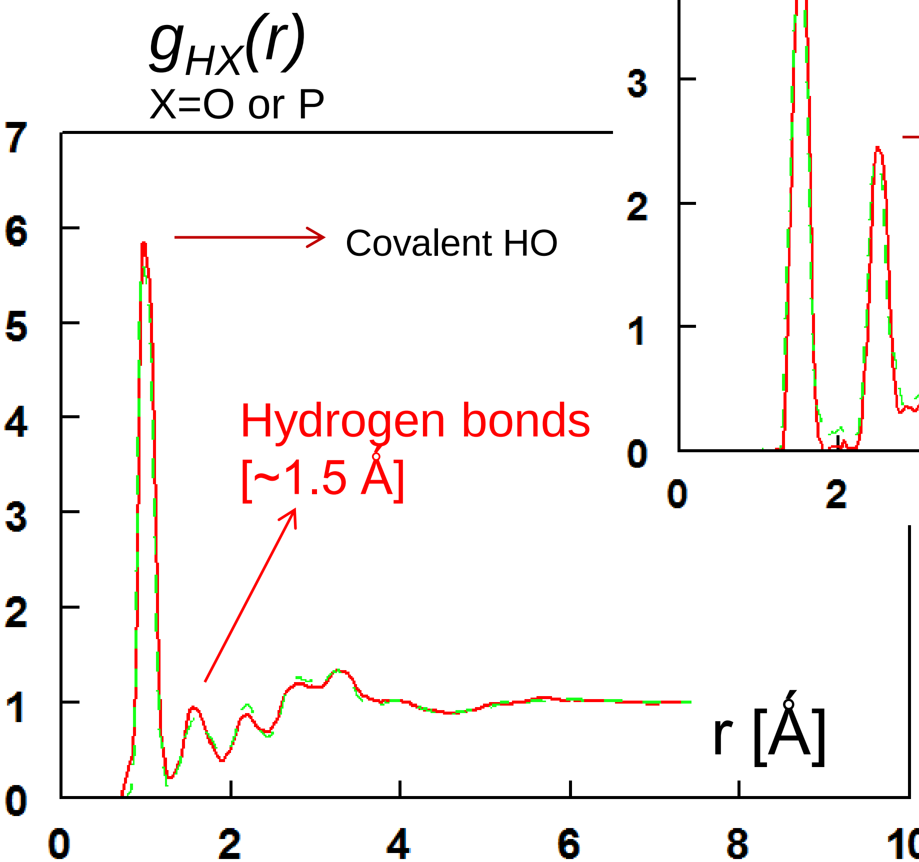
From three *H/D* compositions



- Hydrogen bond not resolved (Expected at ~2.5Å)
- Probably under intramolecular peak

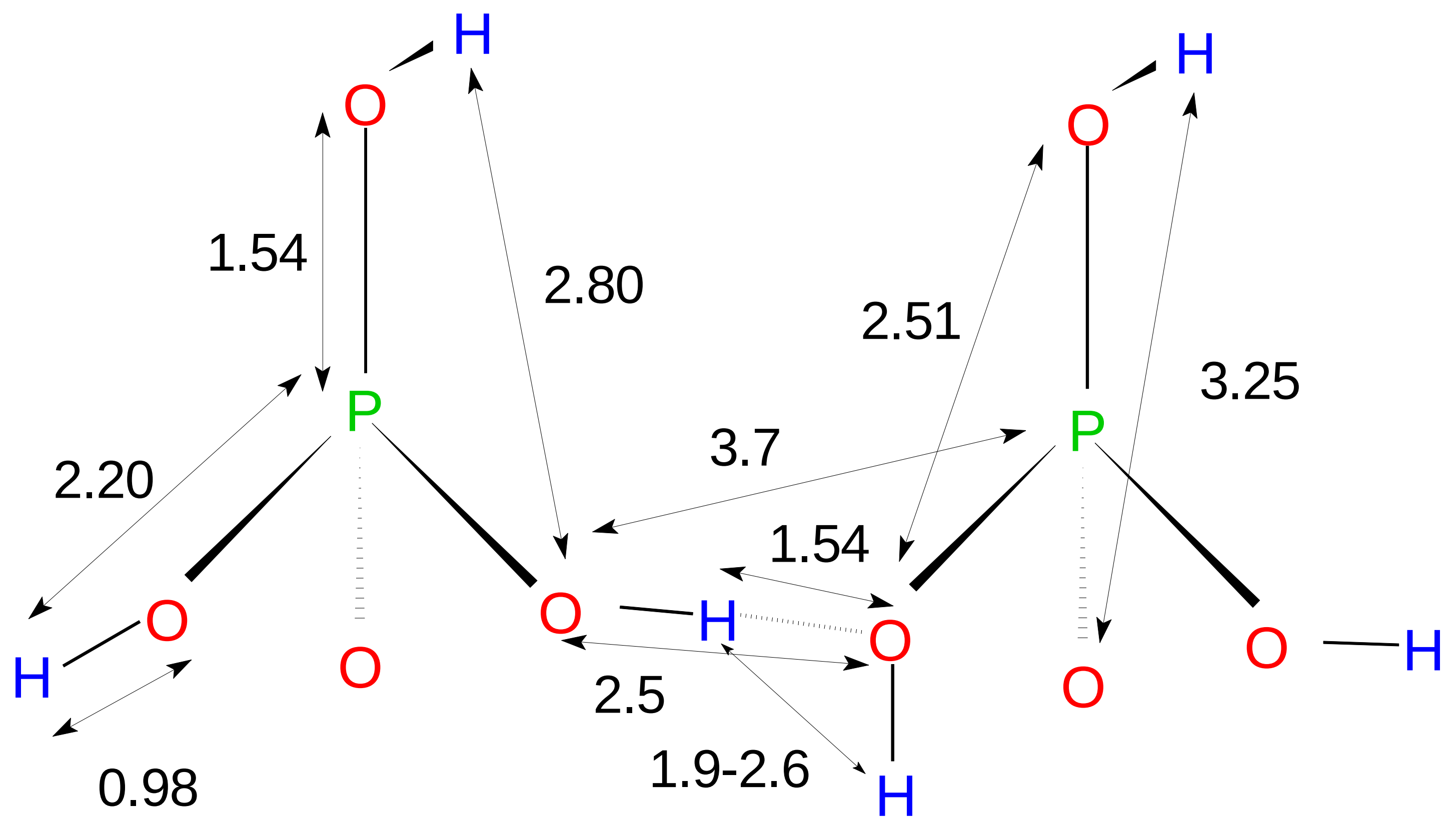
Mixed correlations in pure phosphoric acid





- Hydrogen bond shorter (1.5 Å) than in water (1.8 Å)
- Hydrogen bond unaffected by temperature
- PO_4 tetraeder unaffected by temperature

Model phosphoric acid

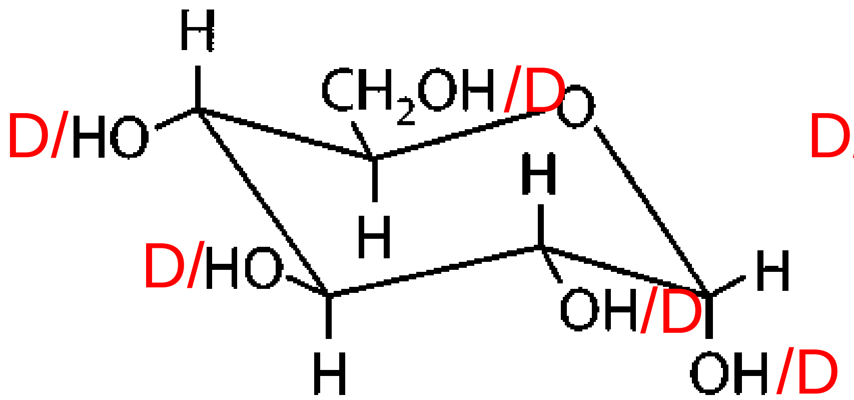


Hydrogen bonds in liquid and glassy glucose

H/D substitution in exchangeable H atoms

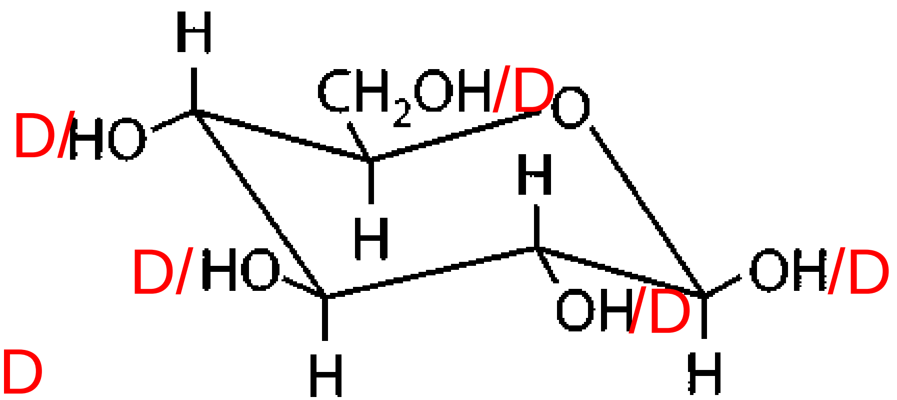
- Glucose-H_5
- Glucose-D_5
- 50/50 Glucose-D_5/ Glucose-H_5

Glass transition:35-39^{o}C



α-D-glucose

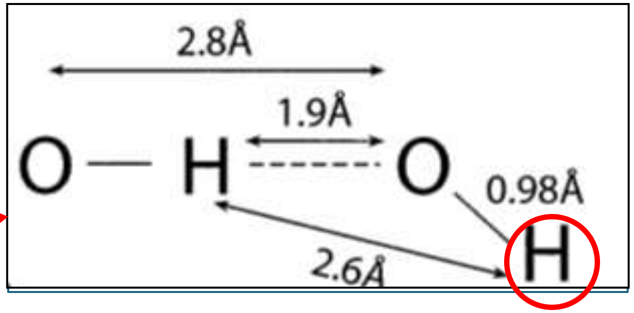
Melting point 146^{o}C

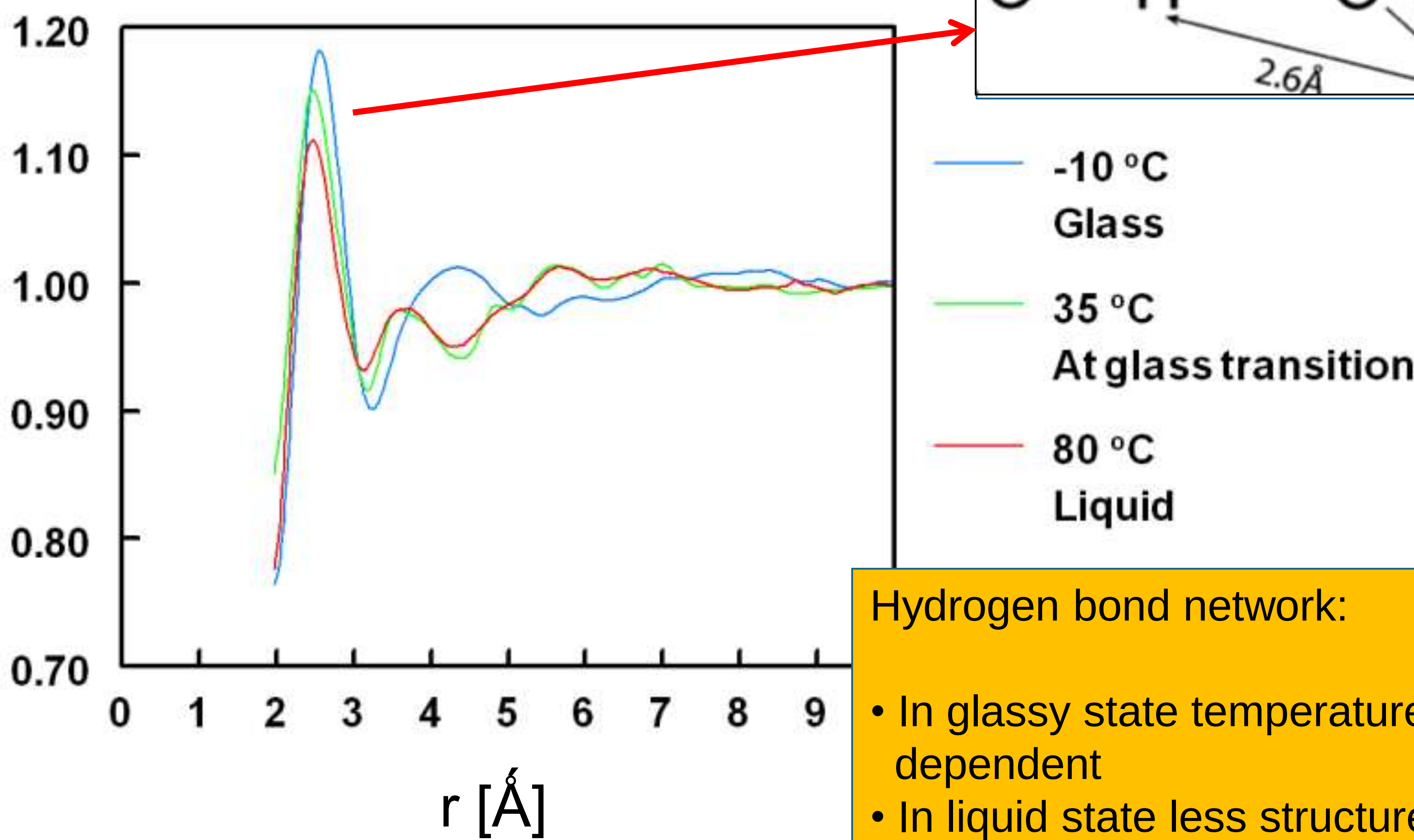


β-D-glucose

Melting point 150^{o}C

Hydrogen bonds in liquid and glassy glucose [$g_{HH}(r)$]

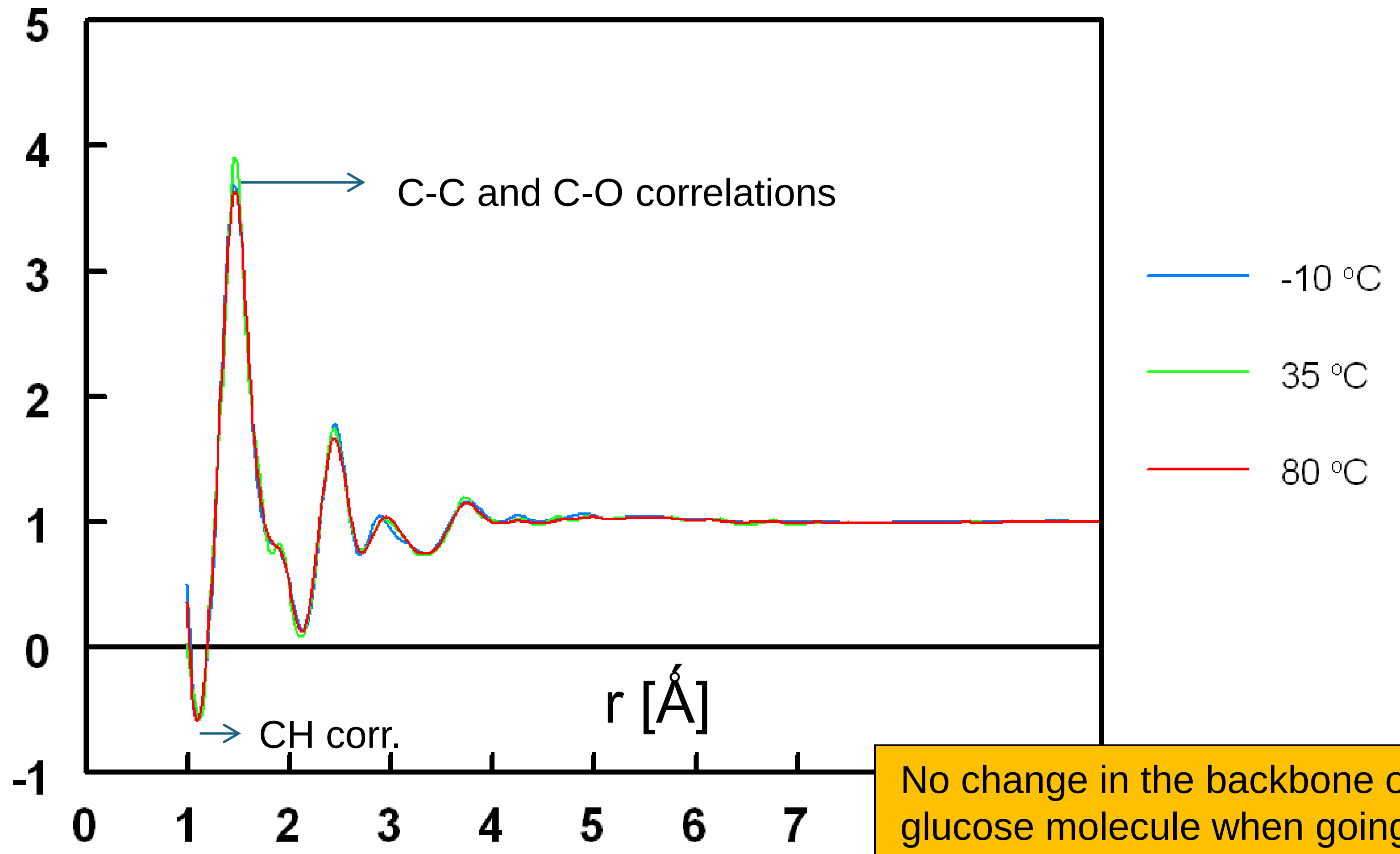




Hydrogen bond network:

- In glassy state temperature dependent
- In liquid state less structured than in glassy state

$g_{XX}(r)$ (X=O,C and covalent H) in glucose



No change in the backbone of the glucose molecule when going from glass to liquid

Issues for wide angle neutron scattering in food (among many others...)

- $^{40}Ca/^{44}Ca$ substitution to study
  - Calcium phosphate in casein
  - Interaction/hydration of calcium/pectin and calcium/alginate gels

- Water trapped in sugar glasses
  - Water distribution on a molecular level

- Salt in concentrated sugar solutions (K^+,Cl^-)

- Glycerol as a plasticizer
  - In starch
  - In protein films

Acknowledgements

- S. Ansell
- M.-C. Bellissant-Funel
- T. Bieze
- G. Neilson
- M.-A. Ricci
- Alan Soper