Structure Refinement of Neutron and X-ray Diffraction Data on Glassy Systems for Liquid and Glassy Systems

Daniel T. Bowron

ISIS Facility, Rutherford Appleton Laboratory,
Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom

Outline

(1)Brief summary of diffraction experiments

(2)Neutrons and X-rays and the structure of silica glass.

(3)Checking the model – EXAFS and a partial structure view.

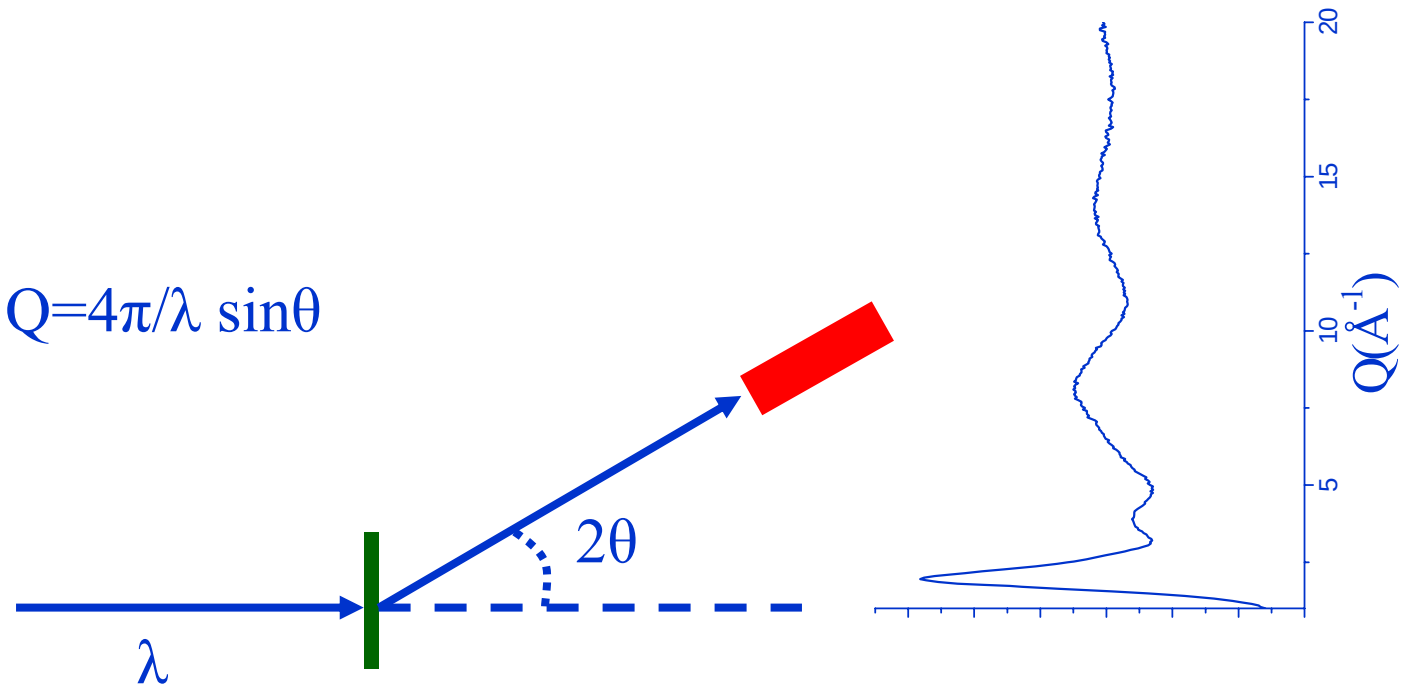
(4)The structure of a aqueous electrolyte solution

(5)Fine tuning an atomic potential

(6)From local structure to the mesoscale

(7)Conclusions: New possibilities for the structure refinement of disordered systems

Schematic of a neutron or X-ray scattering experiment



The neutron diffraction experiment

Total Structure Factor

Atomic concentrations and scattering lengths

$$F(Q) = \sum_{\alpha\beta} c_\alpha c_\beta b_\alpha b_\beta S_{\alpha\beta}(Q)$$

Partial Structure Factors

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^\infty r^2 \left[g_{\alpha\beta}(r) - 1 \right] \frac{\sin(Qr)}{Qr} dr$$

Atomic density

Partial Pair Distribution Functions

The X-ray diffraction experiment

Total Structure Factor

Atomic concentrations and scattering form factors

$$F(Q) = \sum_{\alpha\beta} c_\alpha c_\beta f_\alpha(Q) f_\beta(Q) S_{\alpha\beta}(Q)$$

Partial Structure Factors

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho_e \int_0^\infty r^2 \left[g_{\alpha\beta}(r) - 1\right] \frac{\sin(Qr)}{Qr} dr$$

Electronic density

Partial Pair Distribution Functions

The structure of silica glass: an under-determined problem

$$F_{SiO_2}(Q) = c_{Si}^2 b_{Si}^2 \left[S_{SiSi}(Q) - 1\right] + 2c_{Si}c_O b_{Si} b_O \left[S_{SiO}(Q) - 1\right] + c_O^2 b_O^2 \left[S_{OO}(Q) - 1\right]$$

By neutrons: No isotopic variation in scattering length of silicon or oxygen

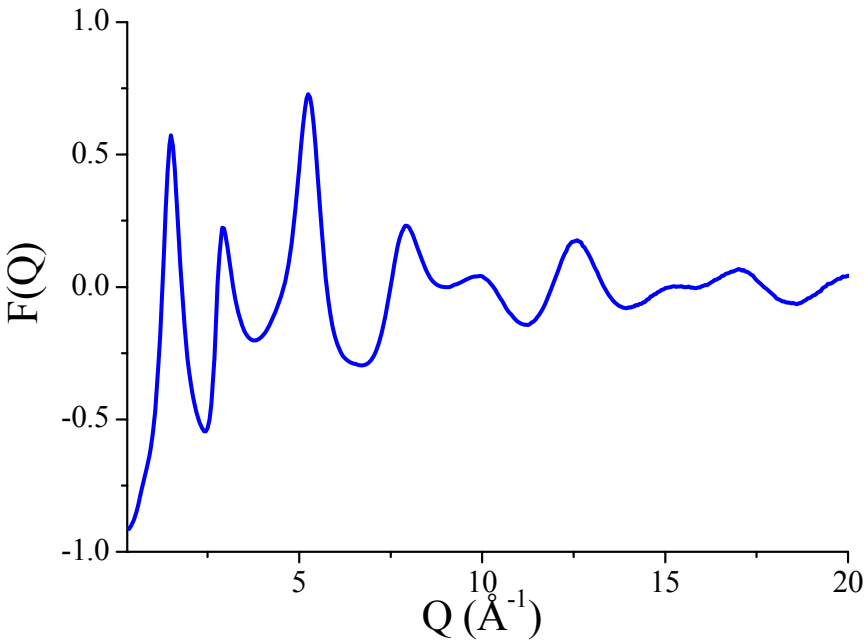
By X-rays: Silicon and oxygen absorption edges at too low an energy to make feasible anomalous X-ray scattering techniques

By neutrons and X-rays

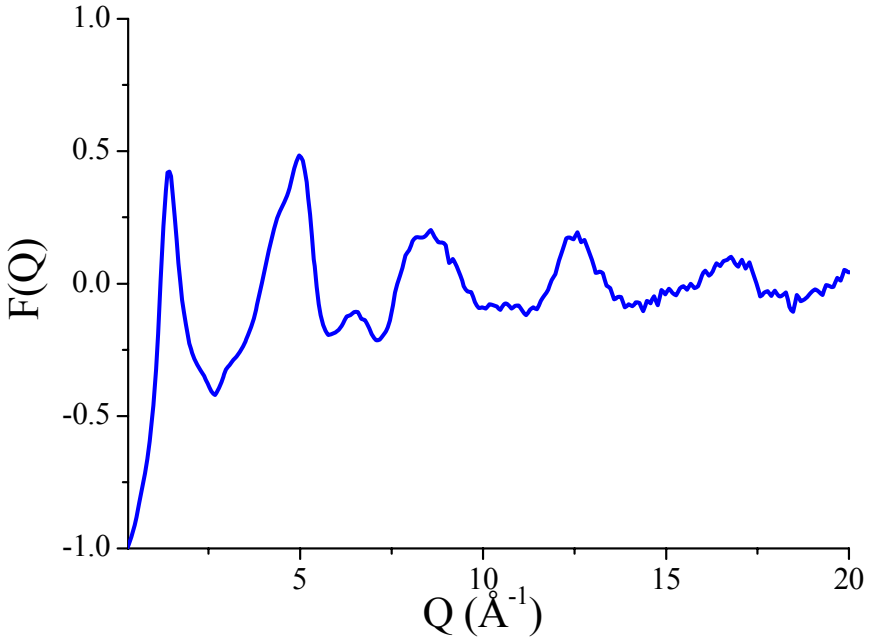
$$F_{SiO_2}(Q) = c_{Si}^2 f_{Si}^2(Q)\left[S_{SiSi}(Q) - 1\right] + 2c_{Si}c_O f_{Si}(Q) f_O(Q)\left[S_{SiO}(Q) - 1\right] + c_O^2 f_O^2(Q)\left[S_{OO}(Q) - 1\right]$$

The measured structure factors for silica

Neutron

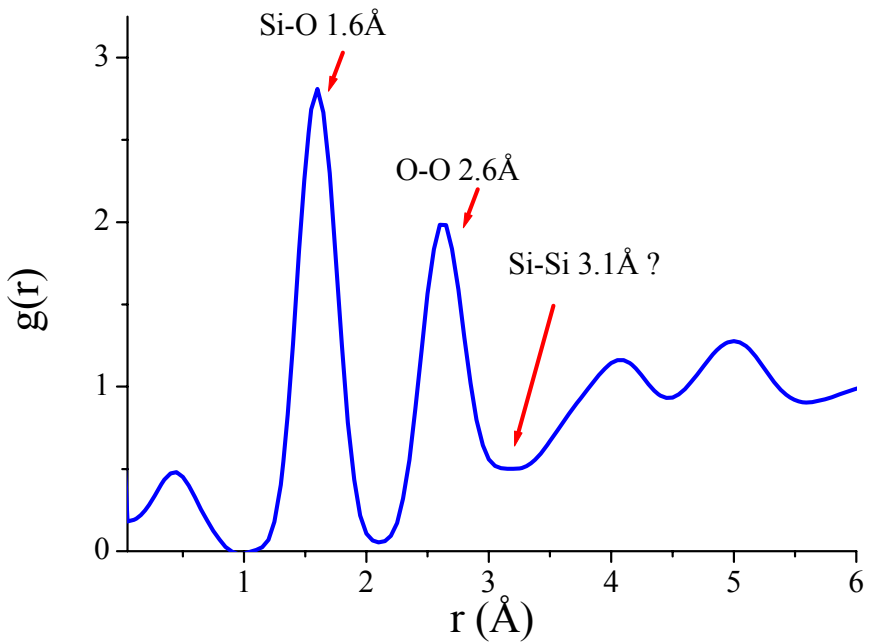


X-ray

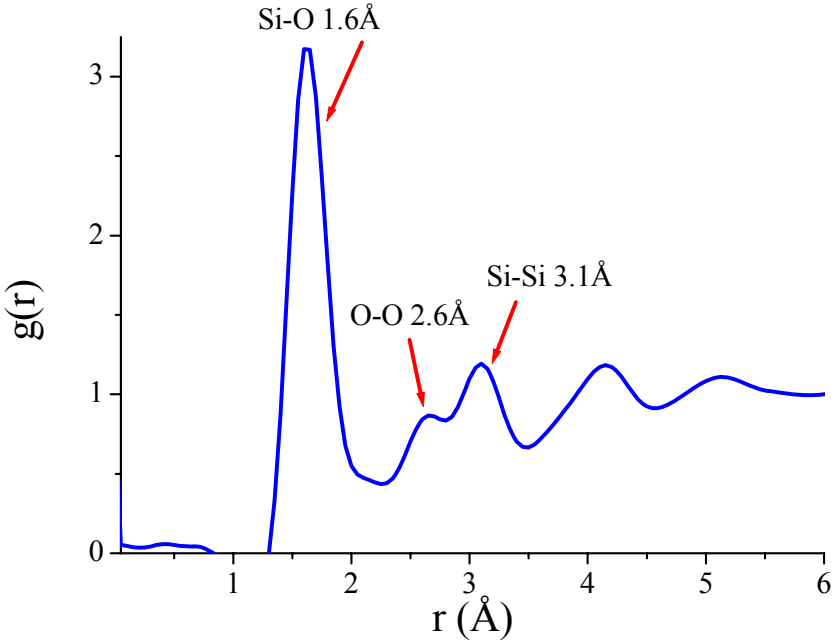


The neutron and X-ray total radial distribution functions for silica

Neutron

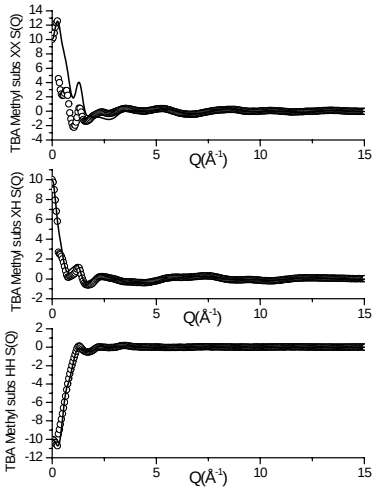


X-ray

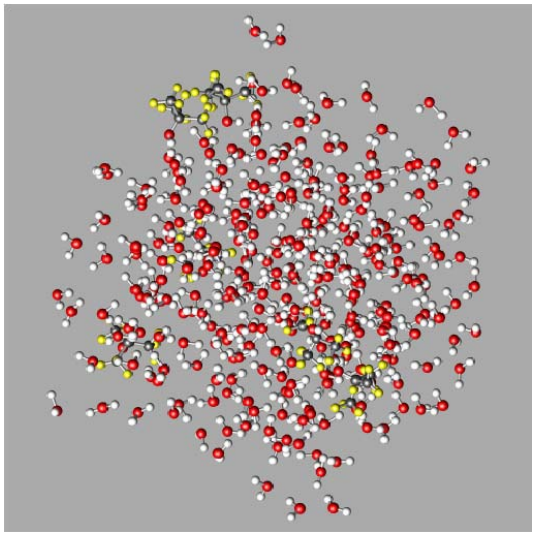


Empirical Potential Structure Refinement

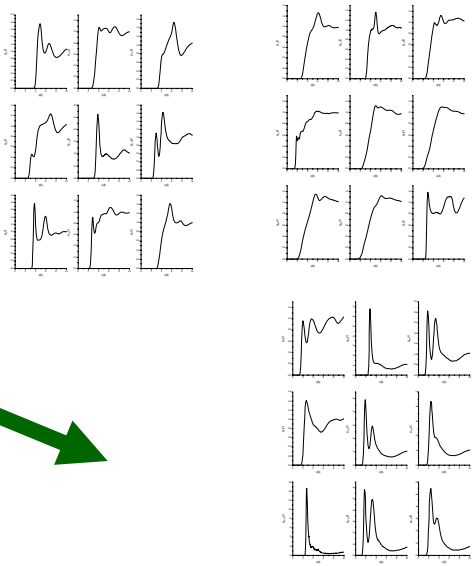
INPUT

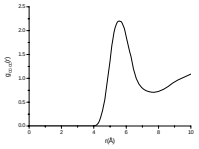


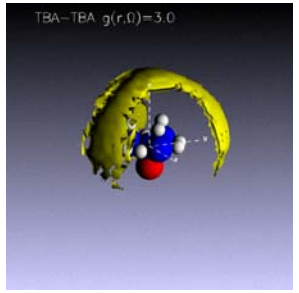
EPSR



OUTPUT







Constraints such as:
Density
Molecular geometry

$$U_{\alpha\beta}^{N} = U_{\alpha\beta}^{O} + kT\left(\ln\left(\frac{g_{\alpha\beta}(r)}{g_{\alpha\beta}^{D}(r)}\right)\right)$$

$$U_{\alpha\beta}^{N}(r) \approx U_{\alpha\beta}^{O}(r)$$

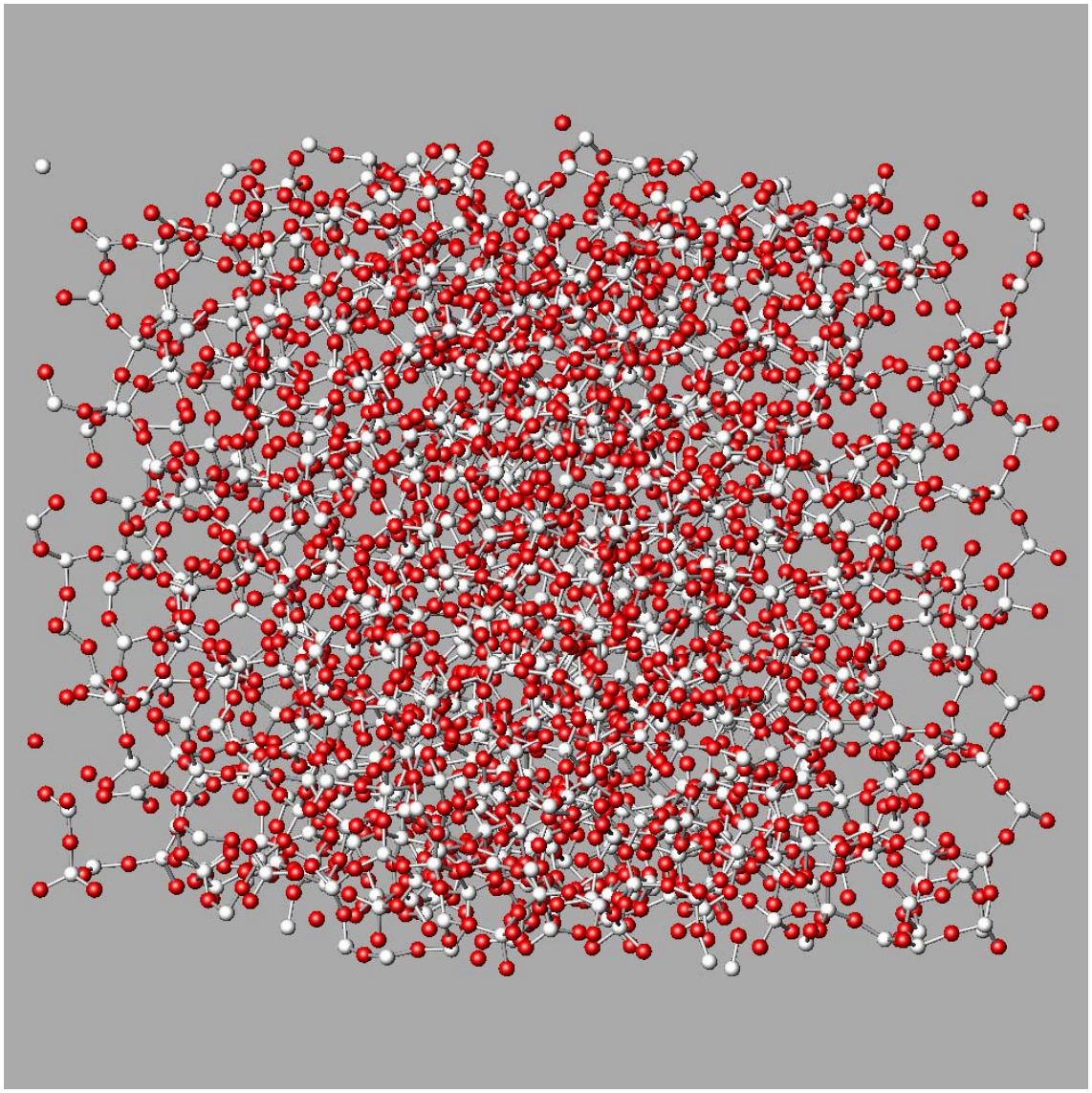
$$g_{\alpha\beta}(r) \approx g_{\alpha\beta}^{D}(r)$$

Silica simulation box

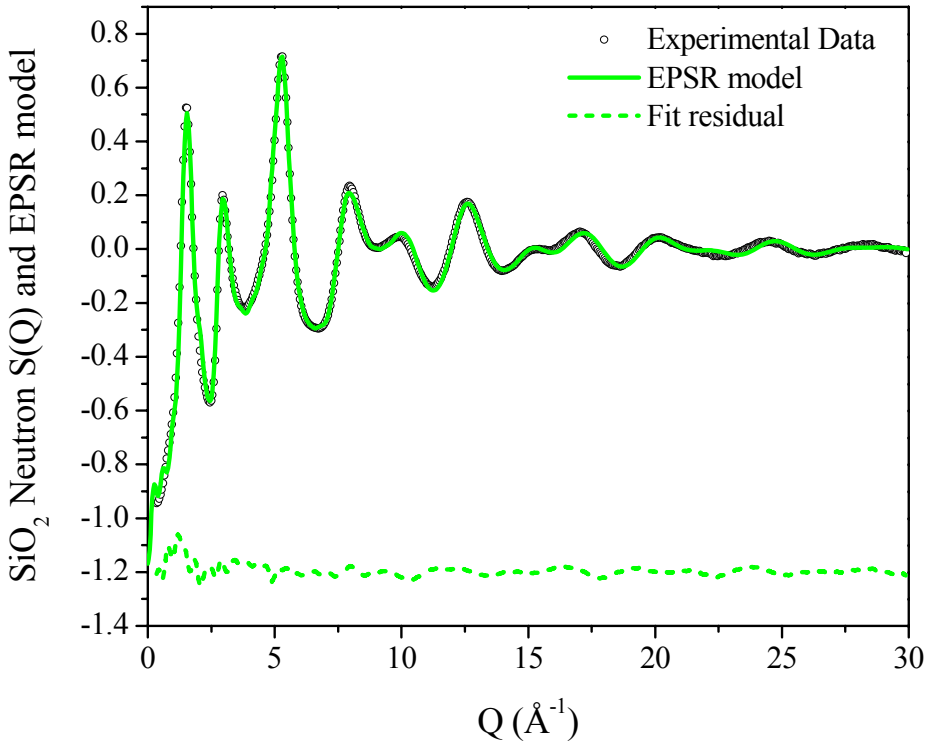
1000 Si atoms
2000 O atoms

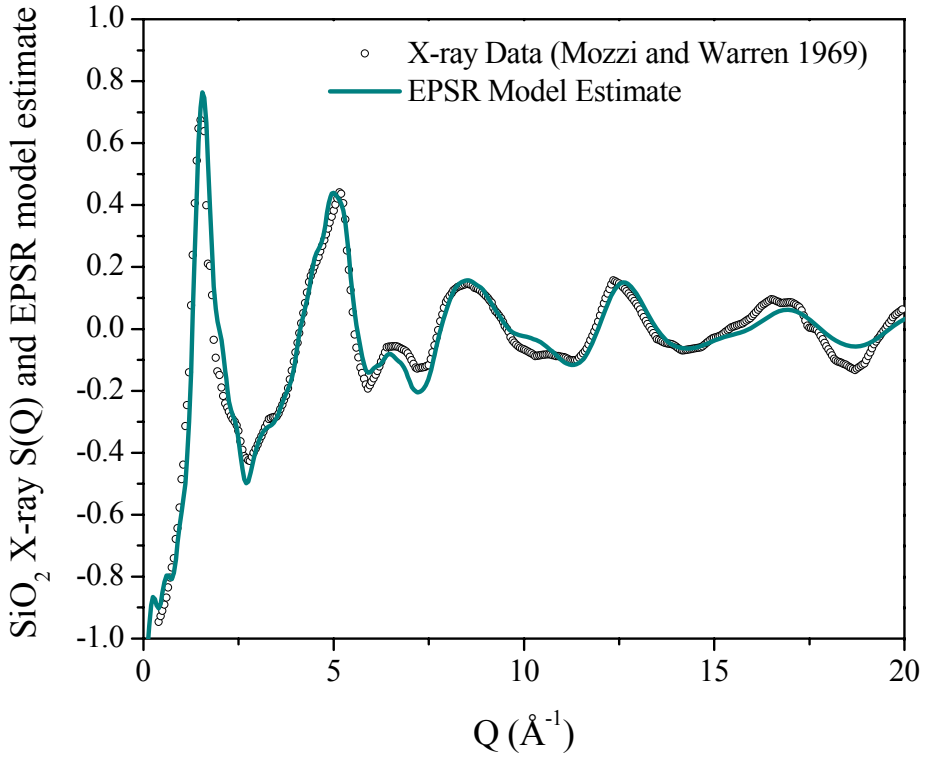
Box side: 35.62Å

Density: 0.0664 ats/Å^3

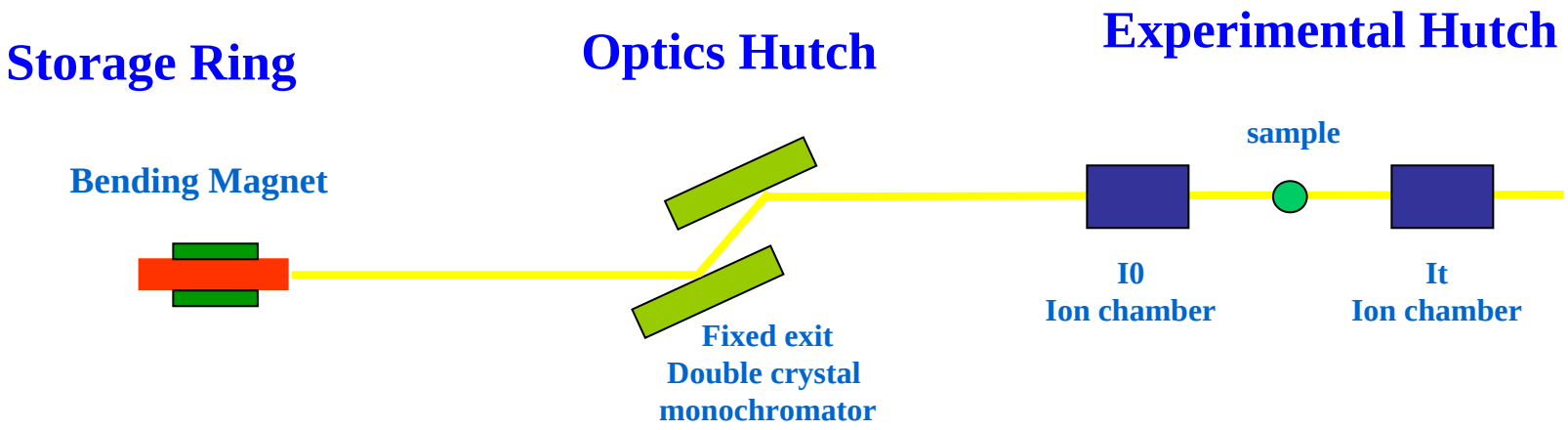


EPSR model fits to the neutron and X-ray data for silica





EXAFS measurements: One route to partial structure information



$I_t = I_0 \, e^{-\mu(E)x}$

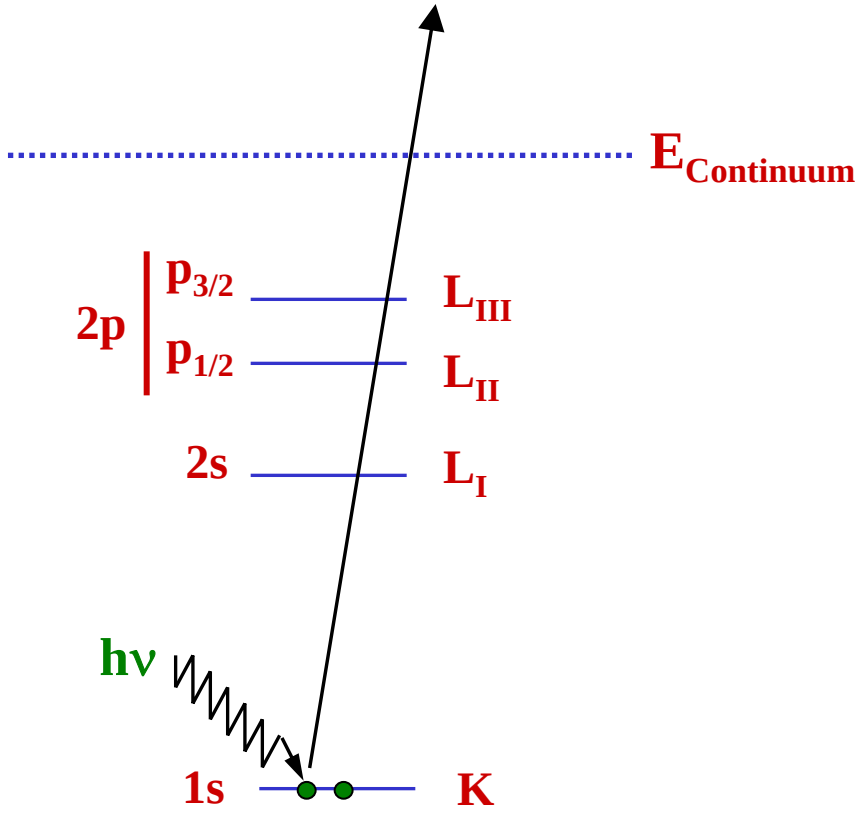
Where x: thickness of the sample

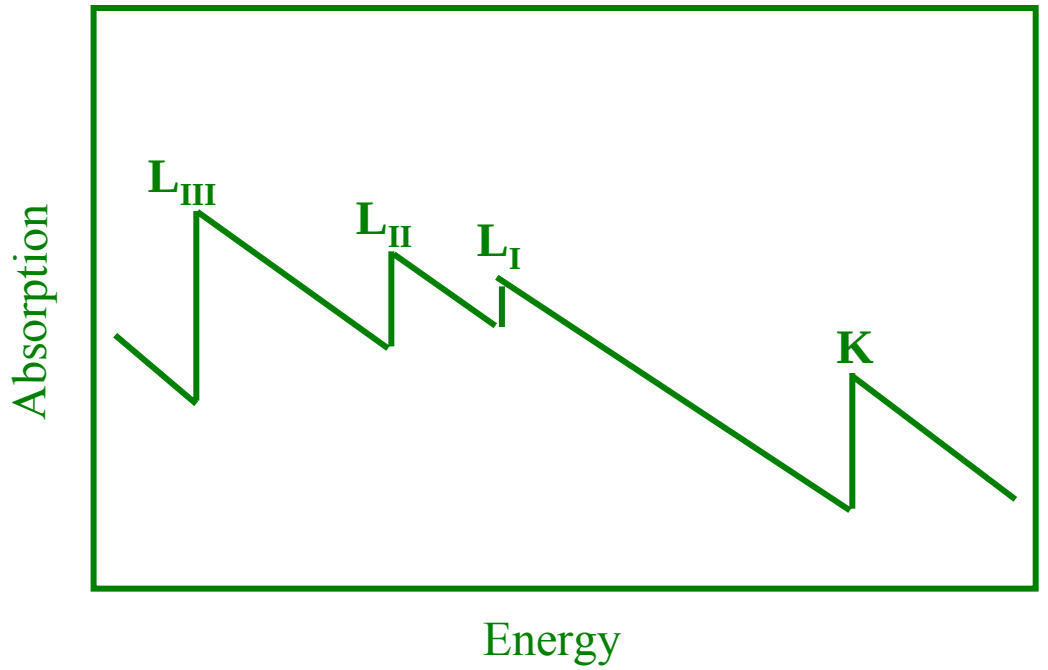
μ: absorption coefficient

EXAFS

$\mu(E)x = \ln (I_0/I_t)$ $\mu(E) = \mu_0(E) \{ 1 + \chi(k) \}$

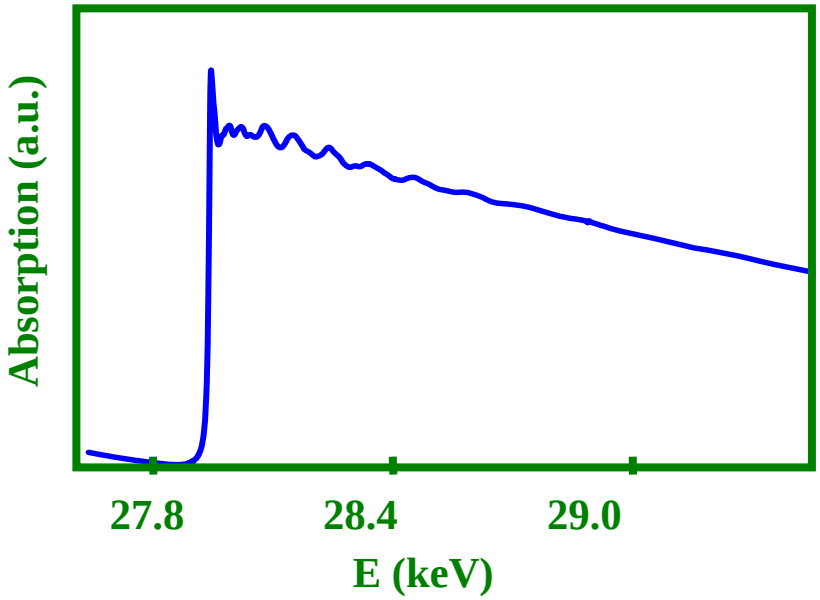
X-ray Absorption Spectroscopy

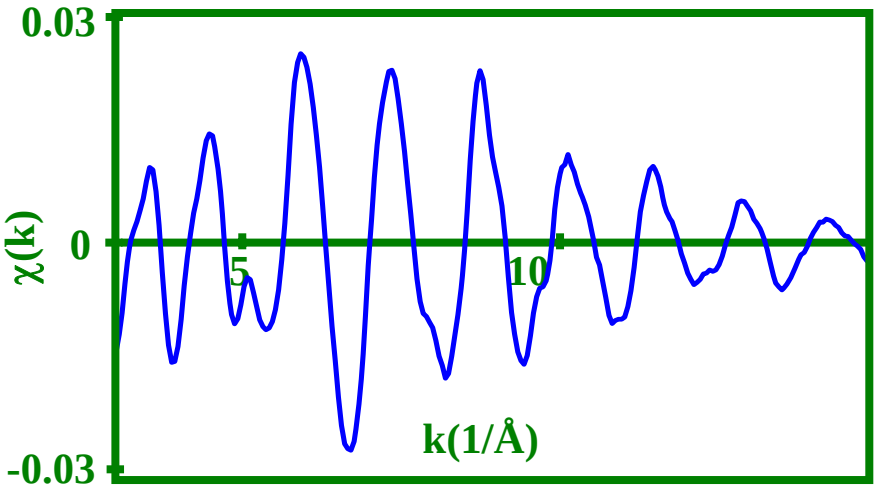


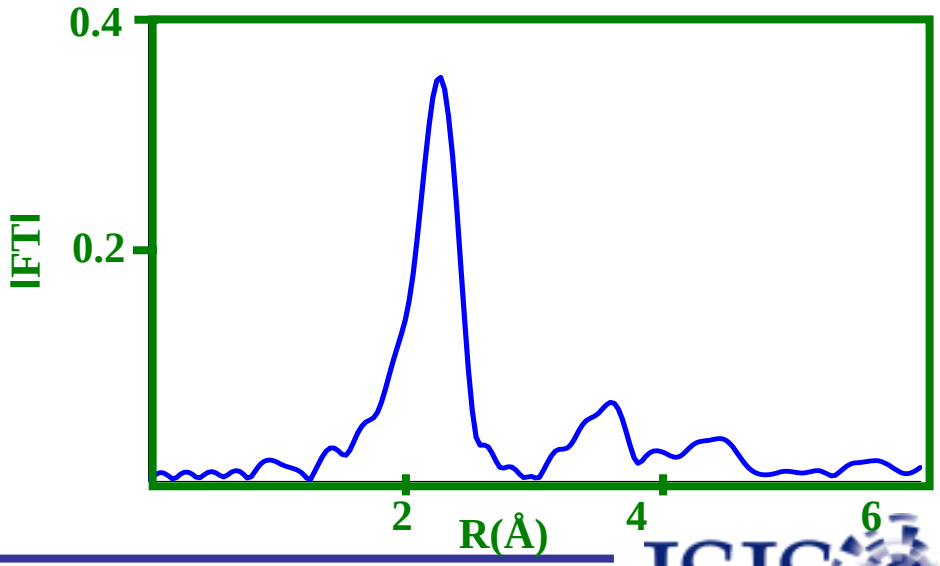


Permitted transitions → Selection rules → $\Delta l = \pm 1$

EXAFS





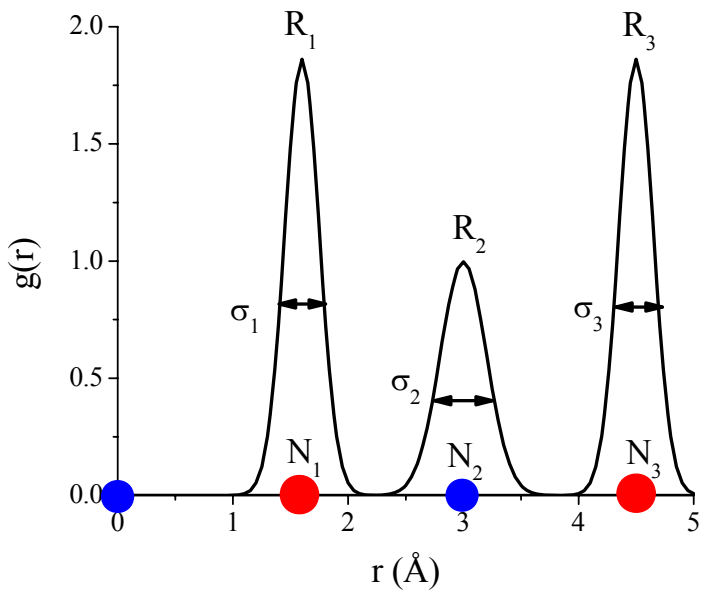


Information about:

- Type of neighbors
- Number of neighbors
- Radial distribution around the absorbing atom
- Disorder.

The Gaussian shell model for EXAFS analysis

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} e^{2R_j/\lambda_j(k)} \left| f_j(k,\pi) \right| \sin\left(2kR_j + 2\delta_l'(k) + \phi_j(k)\right) e^{-2\sigma_j^2 k^2}$$



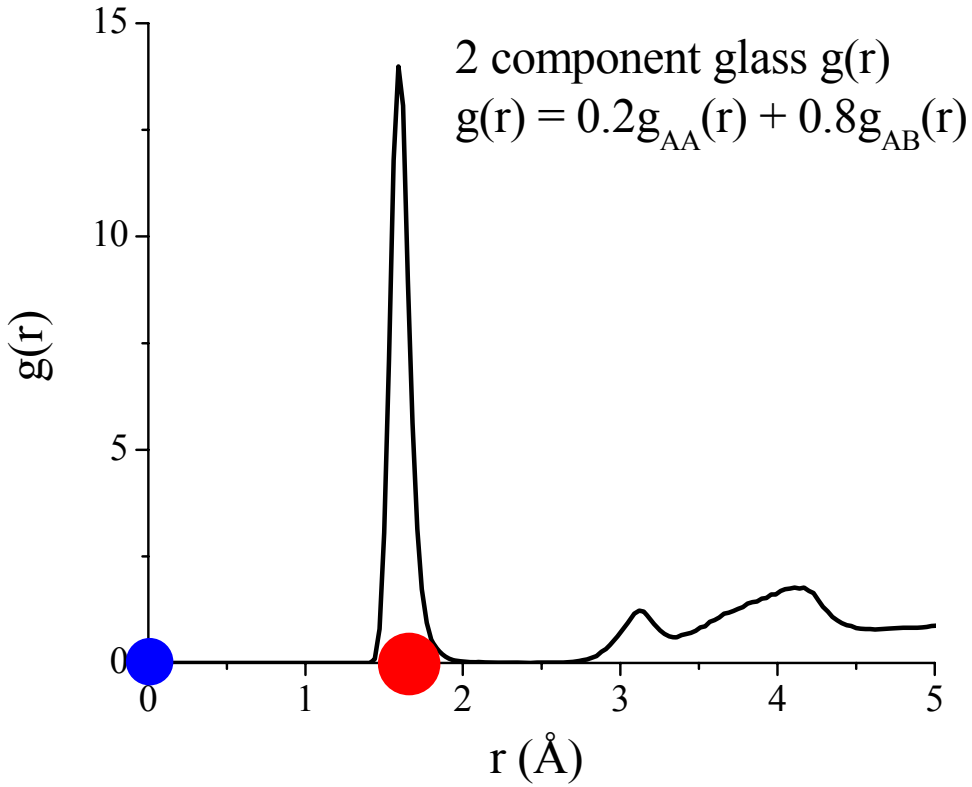
Convenient for peak fitting analysis based on a (significant) number of free parameters

R_j = Distance of photo-absorber to shell j
N_j = Number of atoms in shell j
$\exp(-2\sigma^2_j k^2)$ = Debye-Waller disorder for shell j
$|f_j(k,\pi)|$ = Backscattering amplitude of shell j
$\phi_j(k)$ = Backscattering phase function of shell j
$\delta_l'(k)$ = Photo-absorber phase function
λ_j = Mean-free path term for inelastic losses

Works well for crystalline solids and well defined molecular structures

Breakdown of the EXAFS shell model

Liquids and disordered materials are best characterised by the radial distribution function g(r)



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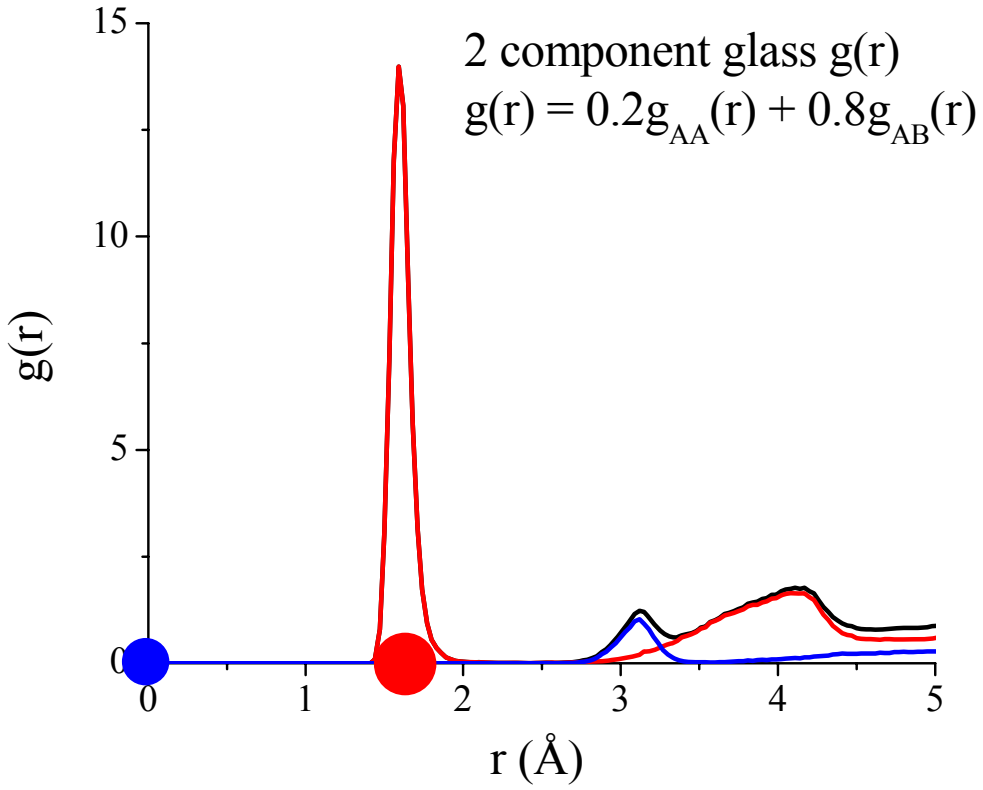

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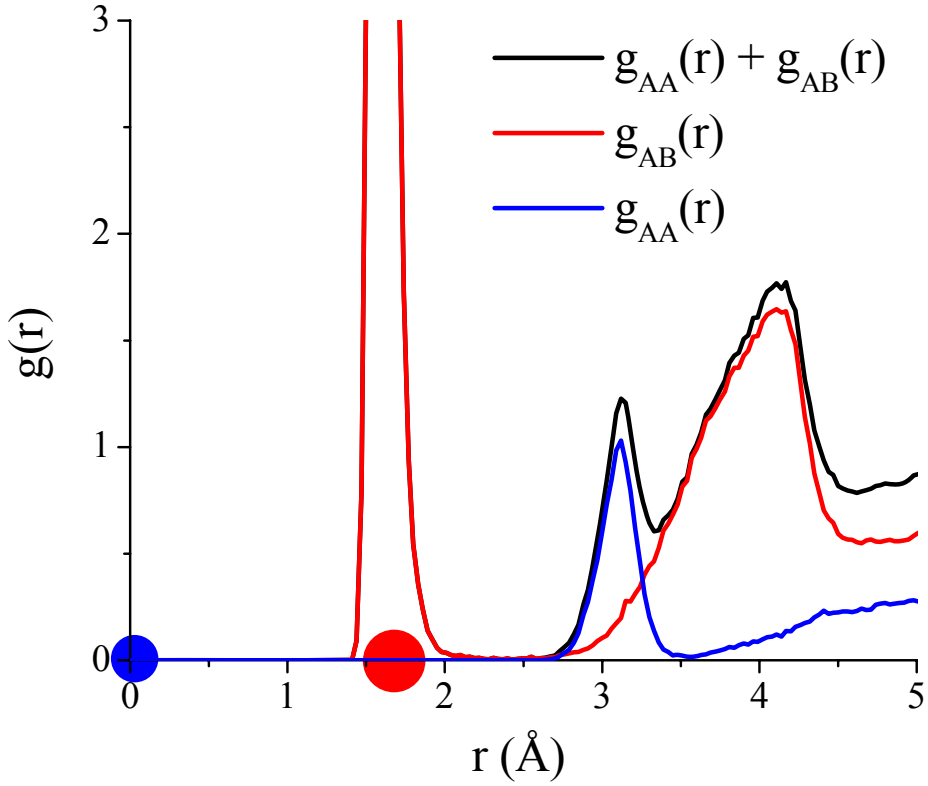


Reformulation of the EXAFS equation as a configurational average

$$\chi(k) = \sum_i \gamma^{(2)}(0,i)$$

$\gamma^{(2)}$ is the EXAFS signal associated with a single neighbour atom at a distance r from the photo-absorber.

$$\langle \chi(k) \rangle = \int_0^\infty dr\, 4\pi r^2 \rho g(r) \gamma^{(2)}(r,k)$$

$\langle \chi(k) \rangle$ is the ensemble average of the pair-wise atomic configurations characterised by the radial pair distribution function, g(r), centred on the photo-absorber. This function intrinsically incorporates the static and dynamic disorder in the local environment.

A.Filipponi, *J. Phys. Condens. Matter*, **13**, R23 (2001)

Reformulation of the EXAFS equation

$$\langle \chi(k) \rangle = \int_0^\infty dr\, 4\pi r^2 \rho g(r) \gamma^{(2)}(r,k)$$

$\gamma^{(2)}$ contains the chemically specific phase and backscattering amplitude information

Phase term

$$\gamma^{(2)}(r,k) = A(k,r)\sin\left(2kr + \phi(k,r)\right)$$

Atom, energy and distance dependent loss term

Backscattering amplitude

$$A(k,r) = \frac{f(k,r)}{kr^2}\exp\left(-r/\lambda(k,r)\right)$$

A.Filipponi, *J. Phys. Condens. Matter*, **6**, 8415 (1994)

Complementarity between Diffraction and EXAFS

A diffraction experiment probes the pair correlation function g(r):

$$S(Q) = 1 + \frac{4\pi\rho}{Q}\int_0^\infty (g_2(r) - 1) r \sin(Qr) dr$$

For a fixed atom configuration around a photoabsorber, the EXAFS can be written as:

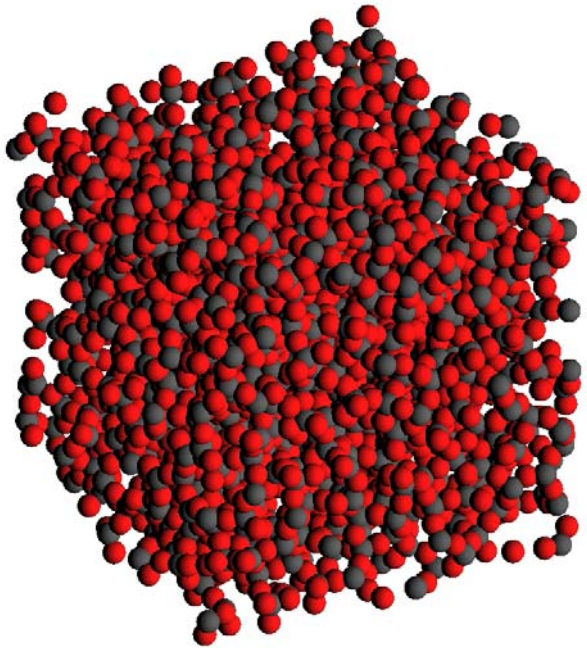
$$\chi(k) = \sum_i \gamma^{(2)}(0,i) + \sum_{i,j} \gamma^{(3)}(0,i,j) + \ldots$$

To apply this to a real system we need to ensemble average to include structural and dynamic disorder. This is achieved through the inclusion of the pair and higher order correlation functions:

$$\langle \chi(k) \rangle = \int_0^\infty dr\, 4\pi r^2 \rho g(r) \gamma^{(2)}(r,k) + \int dr_1 dr_2 d\phi\, 8\pi^2 r_1^2 r_2^2 \sin(\phi) \rho^2 g_3(r_1, r_2, \phi) \gamma^{(3)}(r_1, r_2, \phi, k)$$

A.Filipponi, *J. Phys. Condens. Matter*, **13**, R23 (2001)

EXAFS from an EPSR model



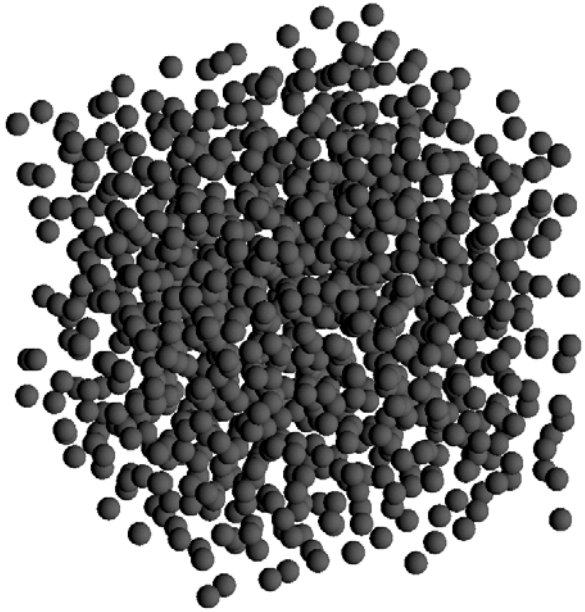
Step 1: select a photoabsorbing atom within the simulation box and place at origin

Step 2: identify neighbouring atom coordinates within a radius of 6Å (cluster for potential, phase shift and scattering path calculations)

Step 3: Calculate theoretical EXAFS signal using no Debye-waller broadening (e.g. FEFF 8) and all significant paths

Step 4: repeat for all photoabsorbing atoms in the box, and average signals

EXAFS from an EPSR model



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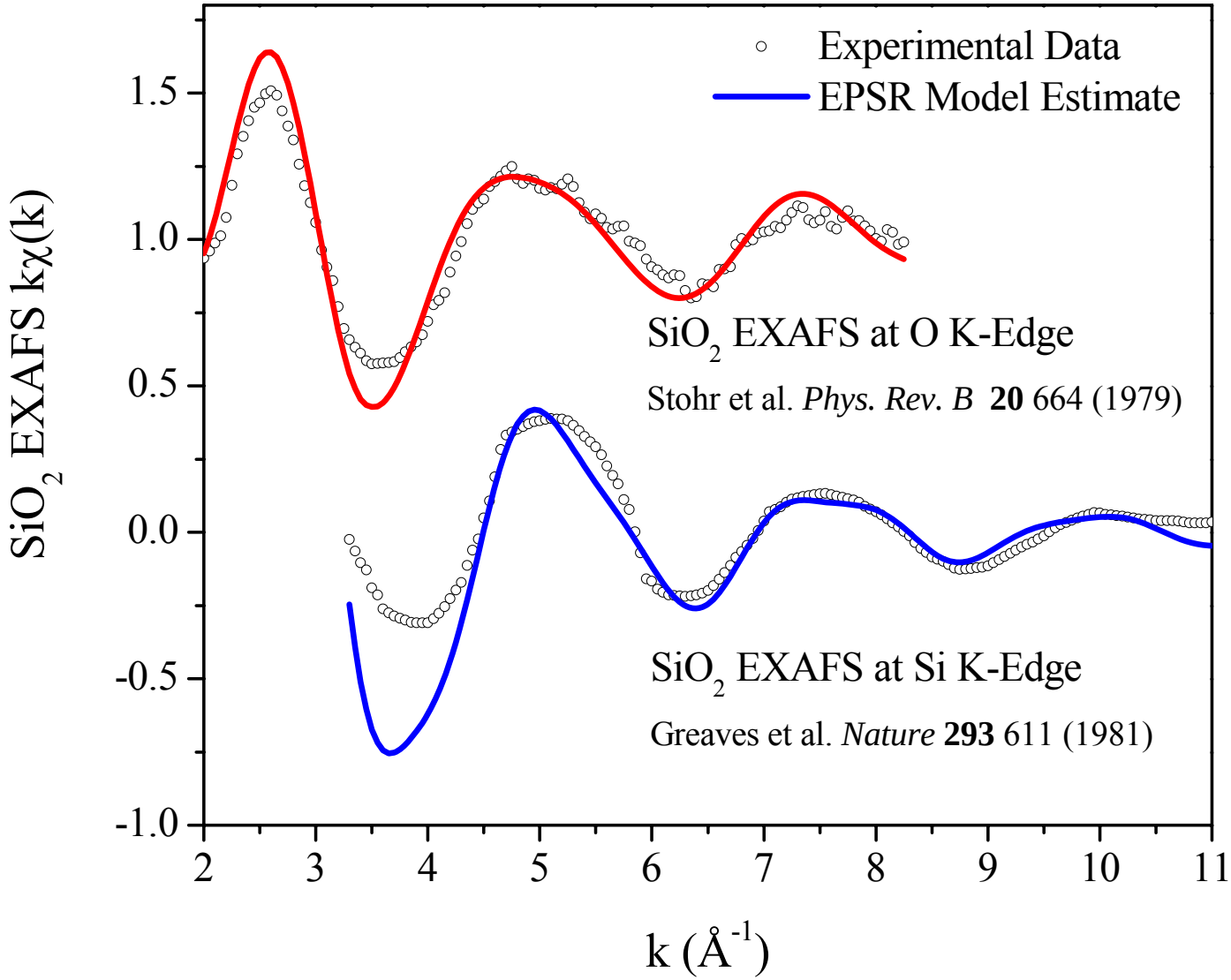
Si and O K-edge EXAFS calculated from EPSR refinement of SiO_2 glass

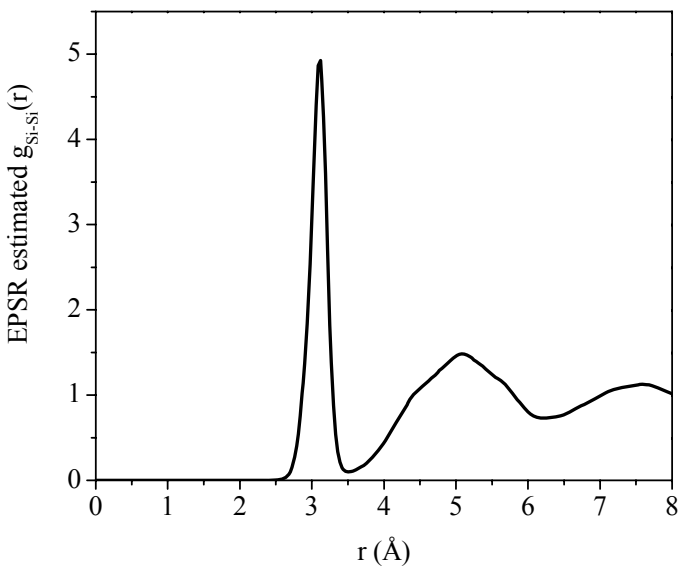


O-O and O-Si correlations

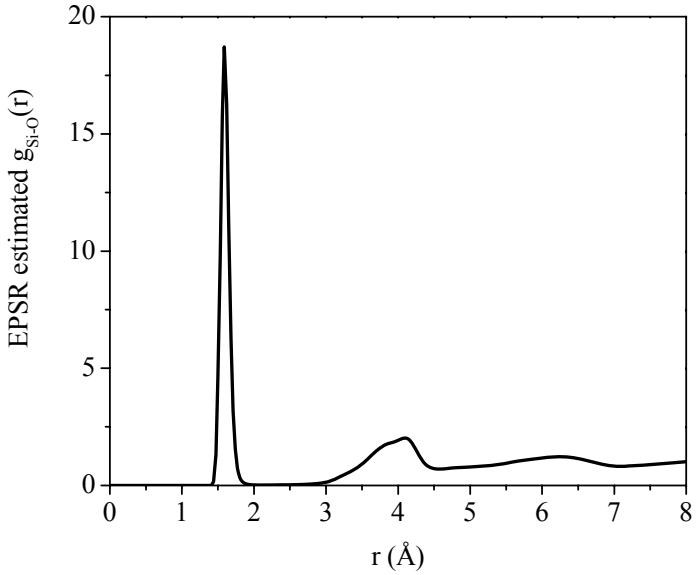
Si-Si and Si-O correlations

EPSR derived partial pair distribution functions

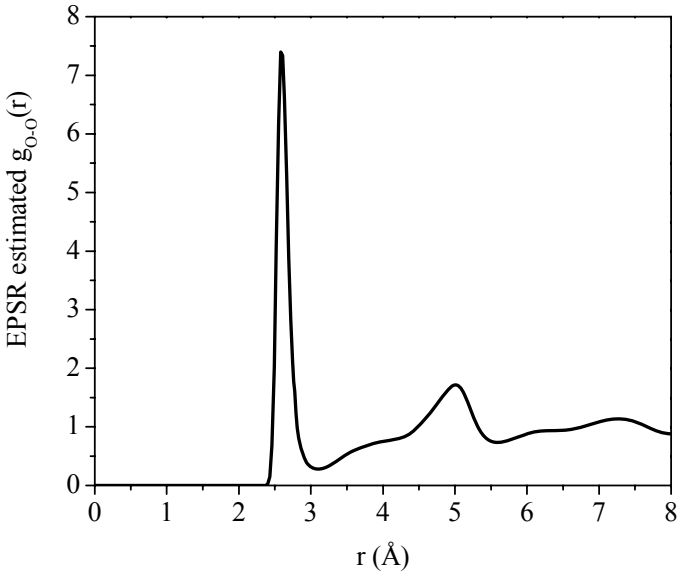
Si-Si



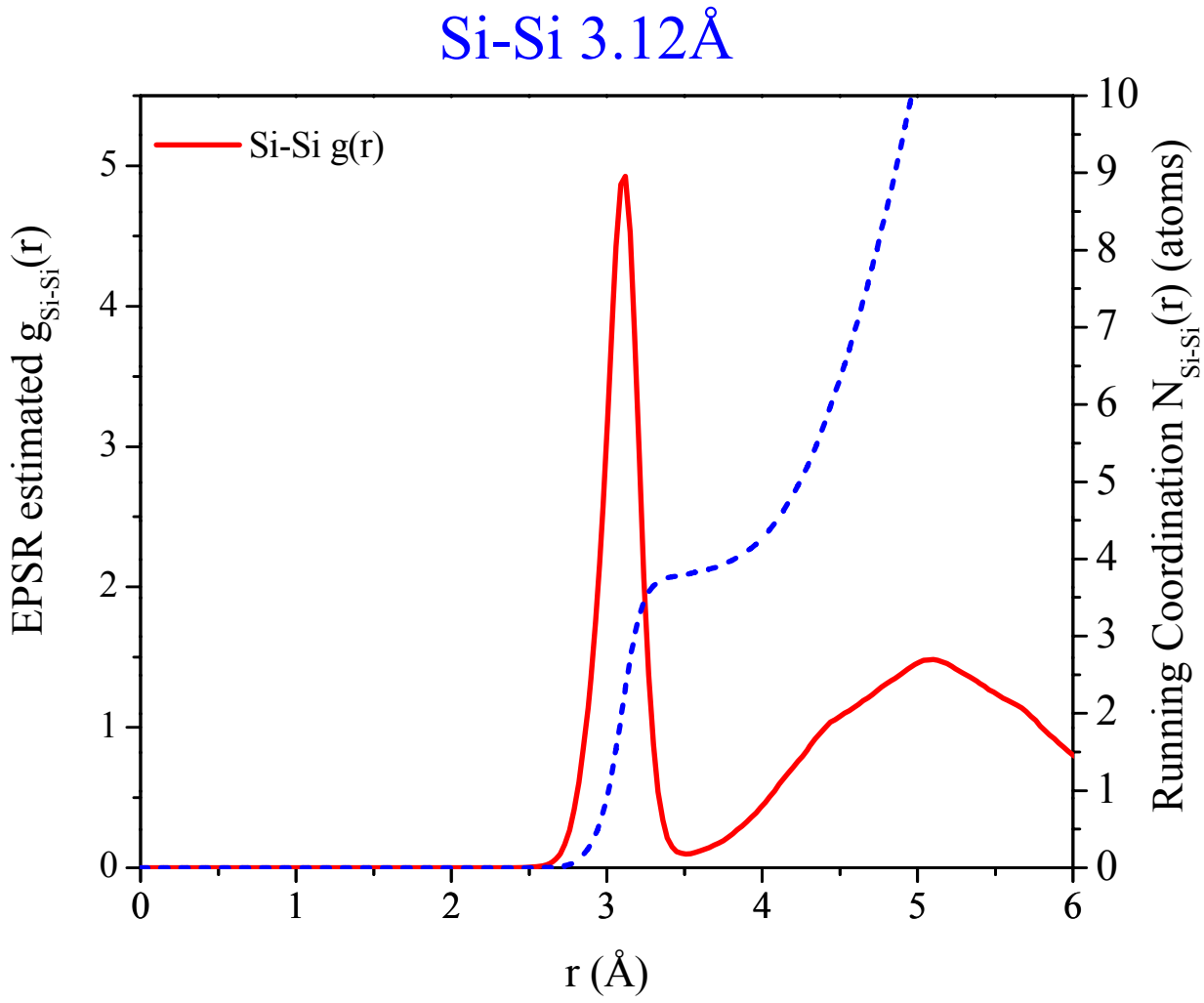
Si-O



O-O

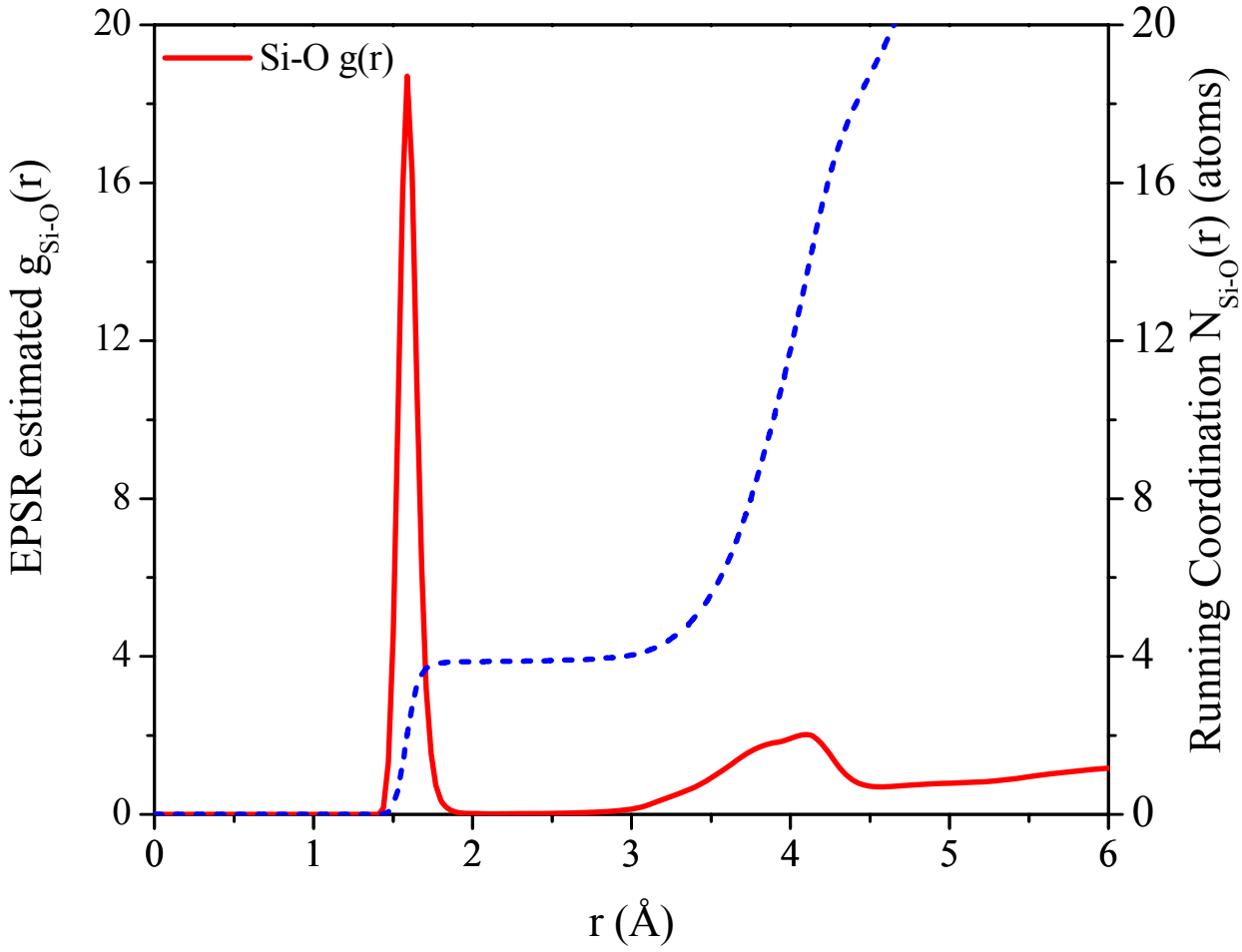


Silicon-silicon pair distribution function



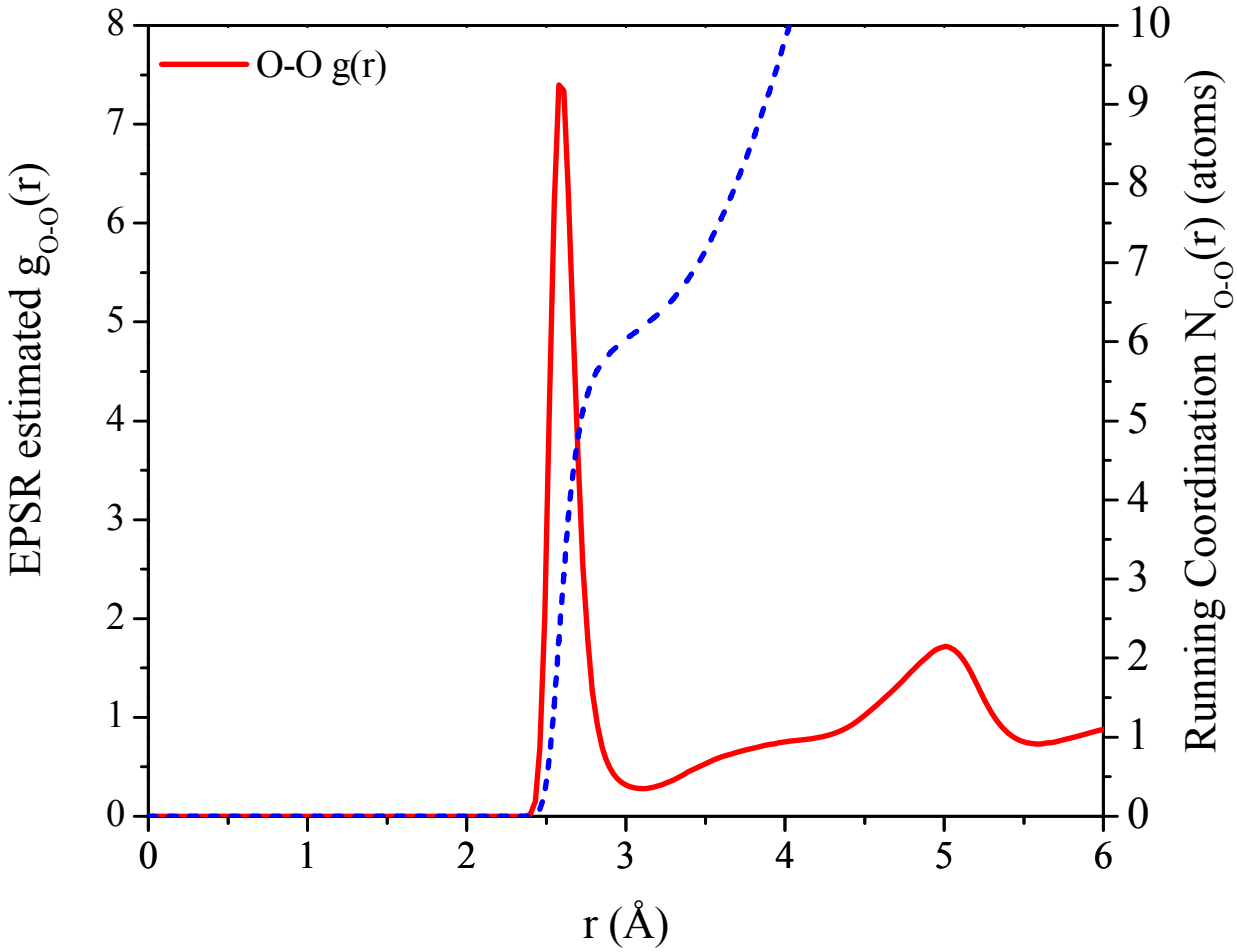
Silicon-oxygen pair distribution function

Si-O 1.60Å

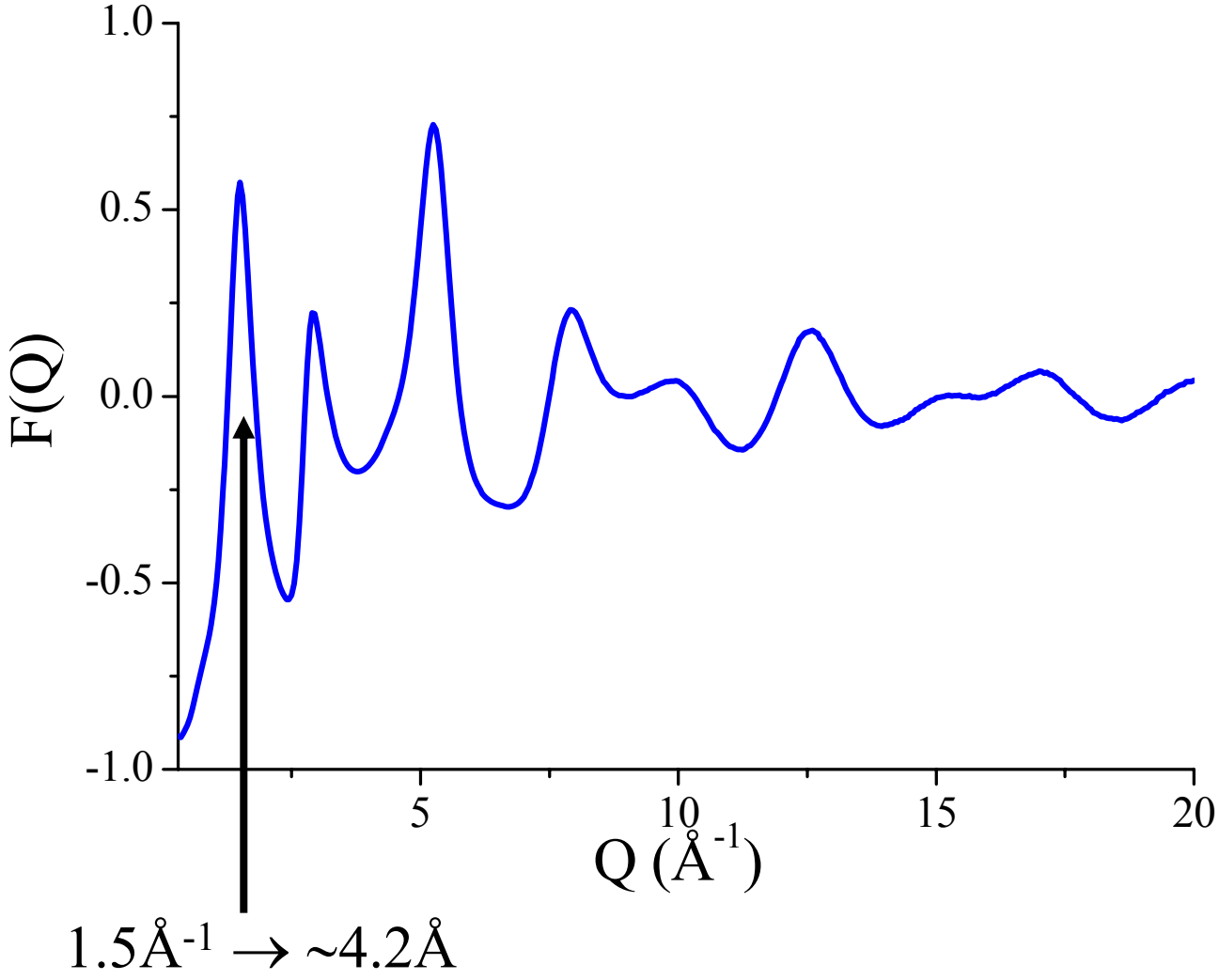


Oxygen-oxygen pair distribution function

O-O 2.61Å



Intermediate Range Order in Pure Silica Glass



Intermediate Range Order in Pure Silica Glass from Faber-Ziman to Bhatia-Thornton Structure Factors

$$F_{SiO_2}(Q) = c_{Si}^2 b_{Si}^2 \left[S_{SiSi}(Q) - 1\right] + 2c_{Si}c_O b_{Si} b_O \left[S_{SiO}(Q) - 1\right] + c_O^2 b_O^2 \left[S_{OO}(Q) - 1\right]$$

$S_{NN}(Q)$ reflects correlations between atomic sites irregardless of chemical species

$S_{cc}(Q)$ reflects correlations between chemical species and

$S_{Nc}(Q)$ represents the cross correlations between number density and chemical species

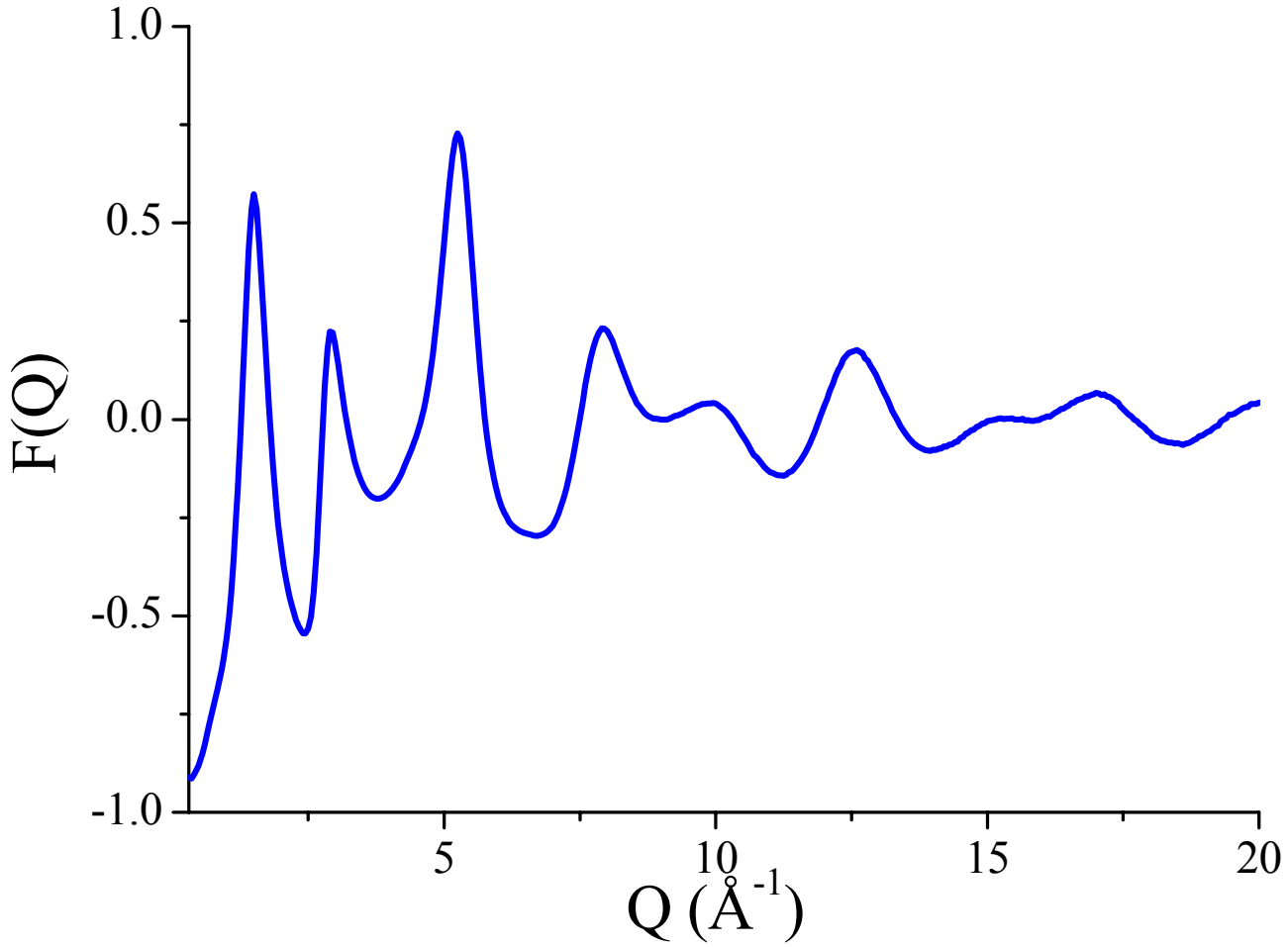
$$S_{NN}(Q) = c_{Si}^2 S_{SiSi}(Q) + c_O^2 S_{OO}(Q) + 2c_{Si}c_O S_{SiO}(Q)$$

$$S_{Nc}(Q) = c_{Si}c_O \left[c_{Si}\left(S_{SiSi}(Q) - S_{SiO}(Q)\right) - c_O\left(S_{OO}(Q) - S_{SiO}(Q)\right)\right]$$

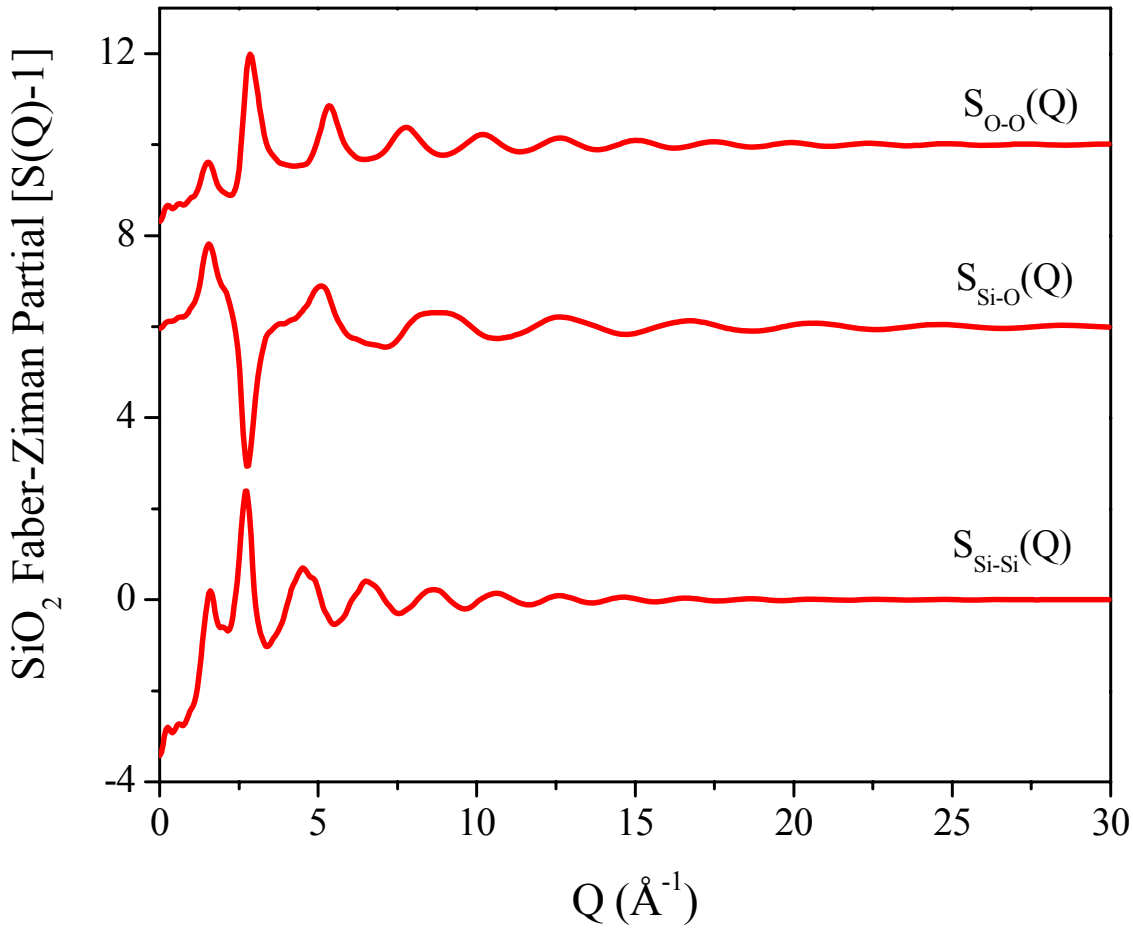
$$S_{cc}(Q) = c_{Si}c_O \left[1 + c_{Si}c_O\left(S_{SiSi}(Q) + S_{OO}(Q) - 2S_{SiO}(Q)\right)\right]$$

A.B.Bhatia and D.E.Thornton, *Phys. Rev. B* **2**, 3004, (1970)

Intermediate Range Order in Pure Silica Glass

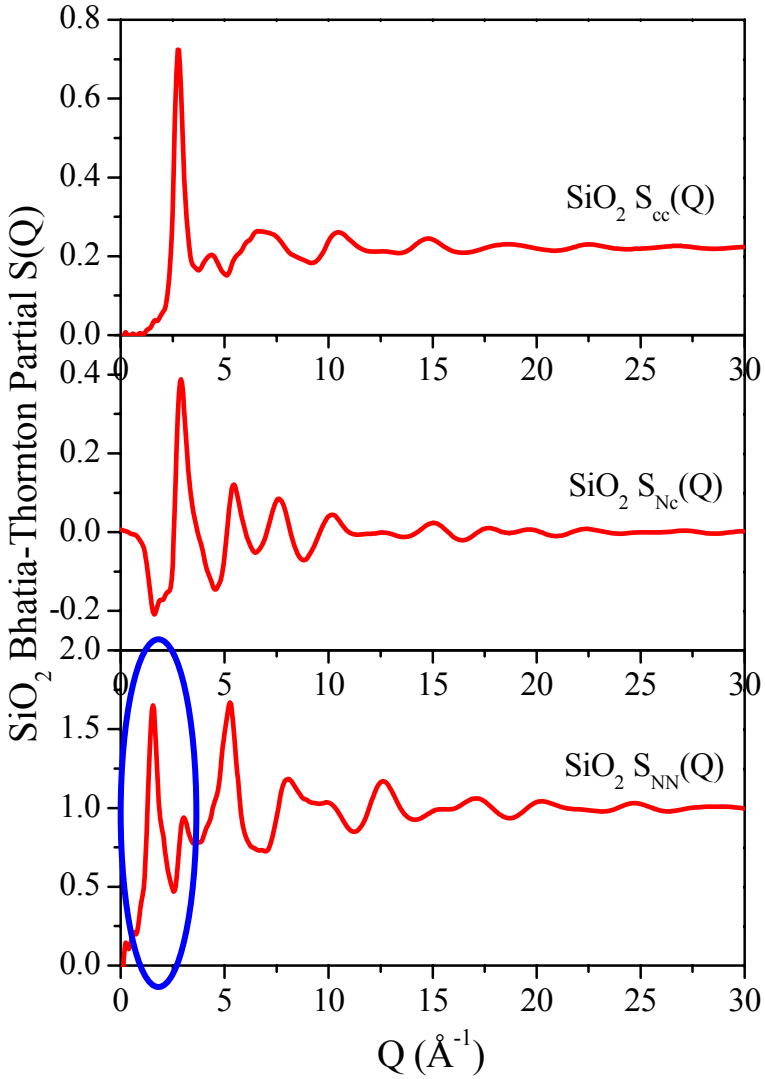


Intermediate Range Order in Pure Silica Glass

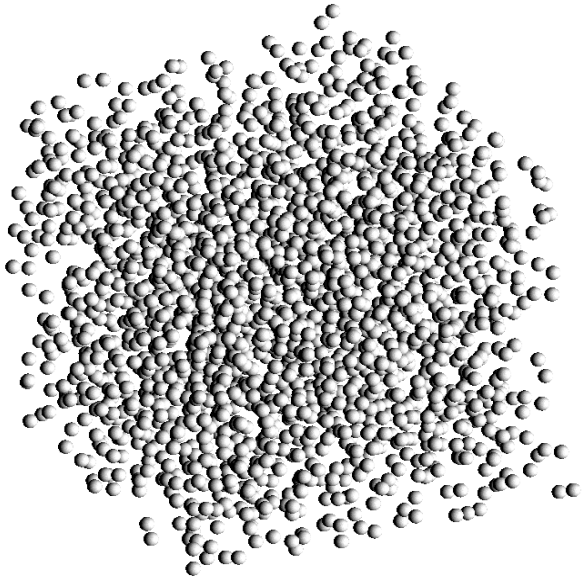


Intermediate Range Order in Pure Silica Glass

Intermediate range order correlates with fluctuations *general* atomic density i.e. it is not correlated with a specific chemical component (Si or O)



Bulk solution structure of 1m YCl_3 in water

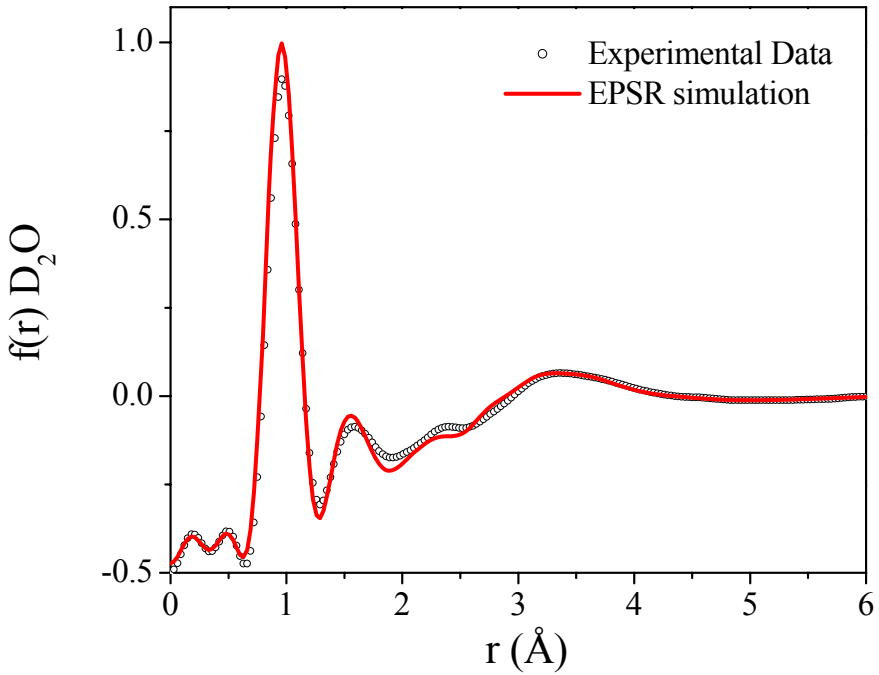


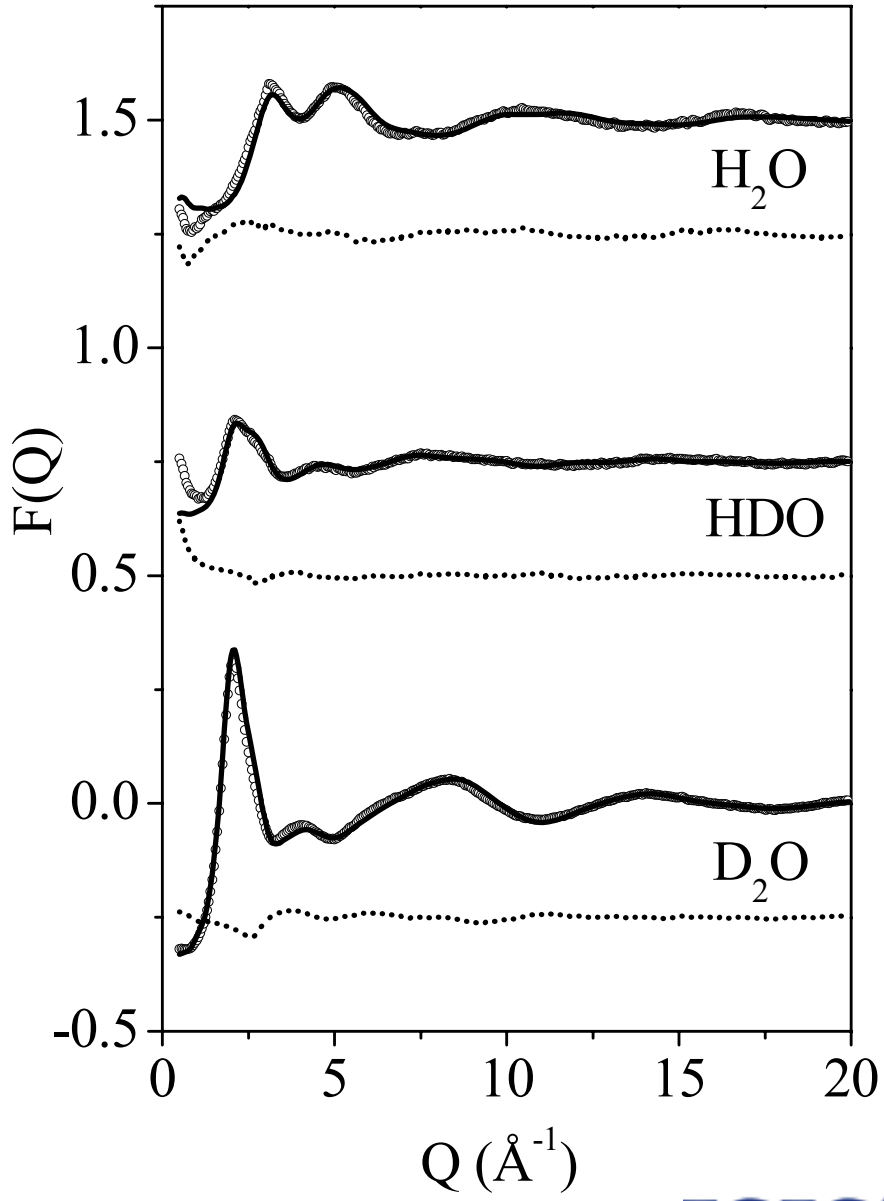
Correlation	Neutron Weights D_2O solution	Rel. Weight %
Y-Y	0.00002	0.004
Y-Cl	0.00015	0.036
Y-OW	0.00170	0.412
Y-HW	0.00392	0.951
Cl-Cl	0.00028	0.068
Cl-OW	0.00633	1.536
Cl-HW	0.01453	3.524
OW-OW	0.03547	8.603
OW-HW	0.16289	39.510
HW-HW	0.18699	45.355

H/D substitution to probe the solvent structure

D.T.Bowron and S.Diaz-Moreno, *J.Phys.Chem B* **111,** 11393 (2007)

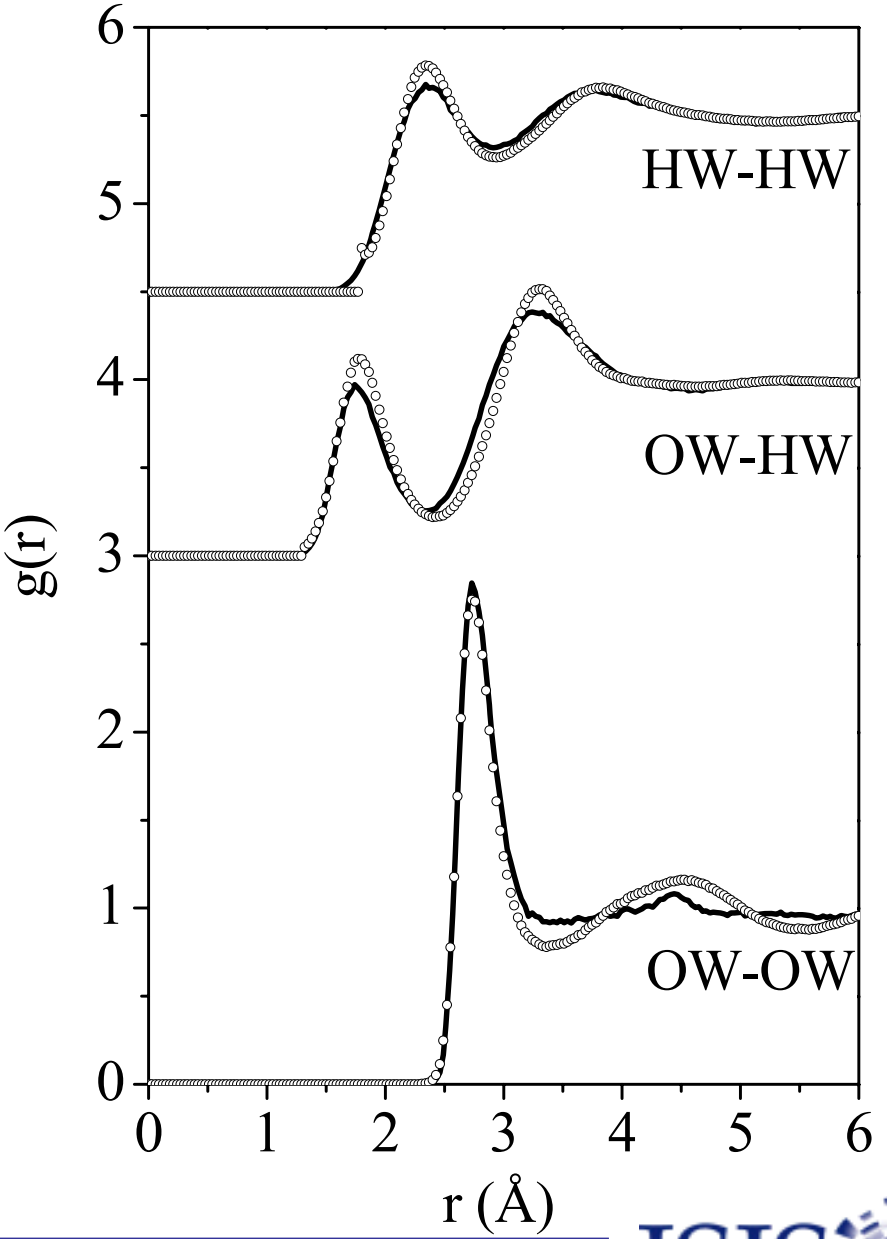
EPSR refinement of 1m YCl_3 in water



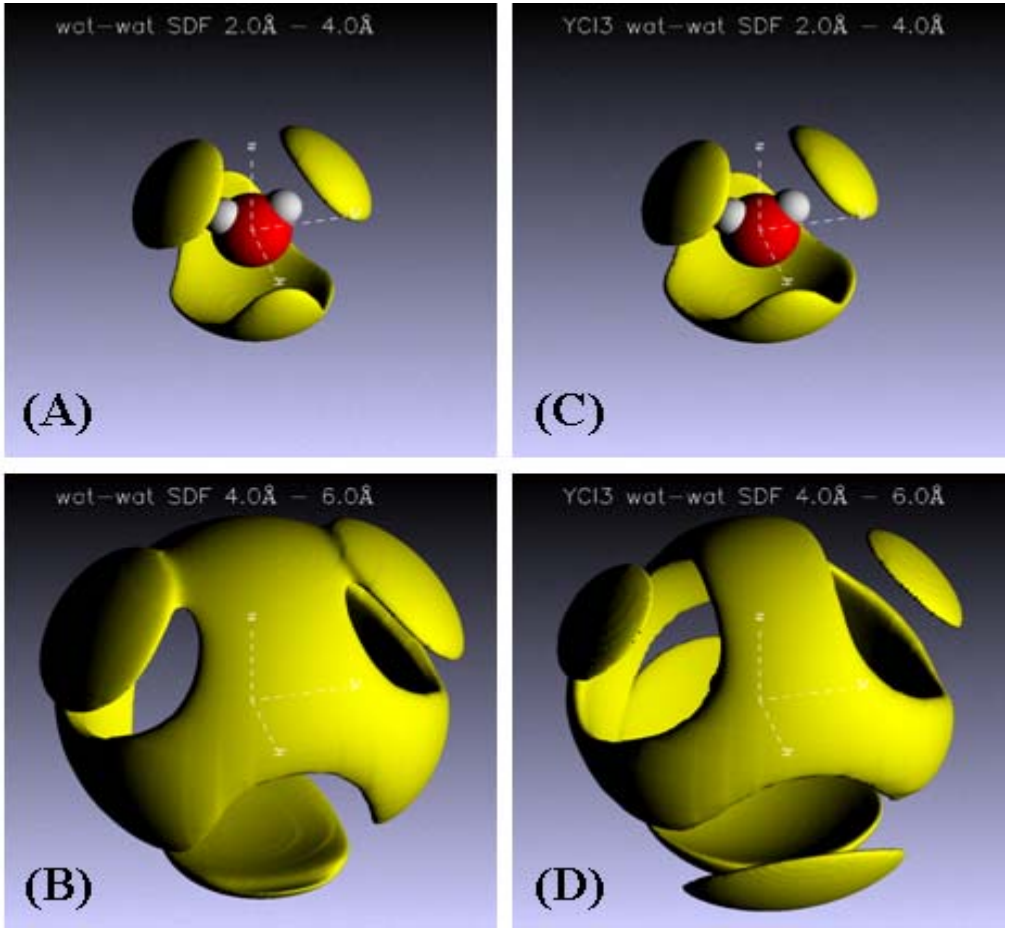


EPSR derived pair distribution functions for pure water and water in a 1m YCl_3 in water

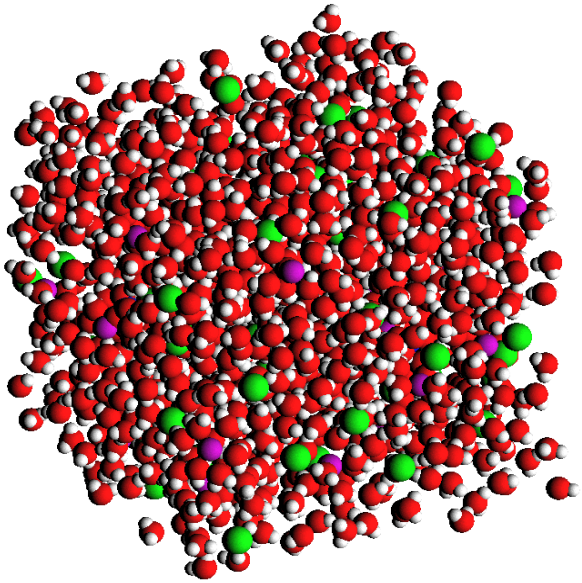
	Range Å	Pure Water	1m YCl_3 solution
OW-OW	2.3 - 3.3	4.3 ± 0.1	4.5 ± 0.1
OW-HW	1.4 - 2.5	2.0 ± 0.1	1.7 ± 0.1
HW-HW	1.5 - 3.0	5.6 ± 0.1	5.2 ± 0.1



The spatial density function of water, and water in a 1m YCl_3 solution

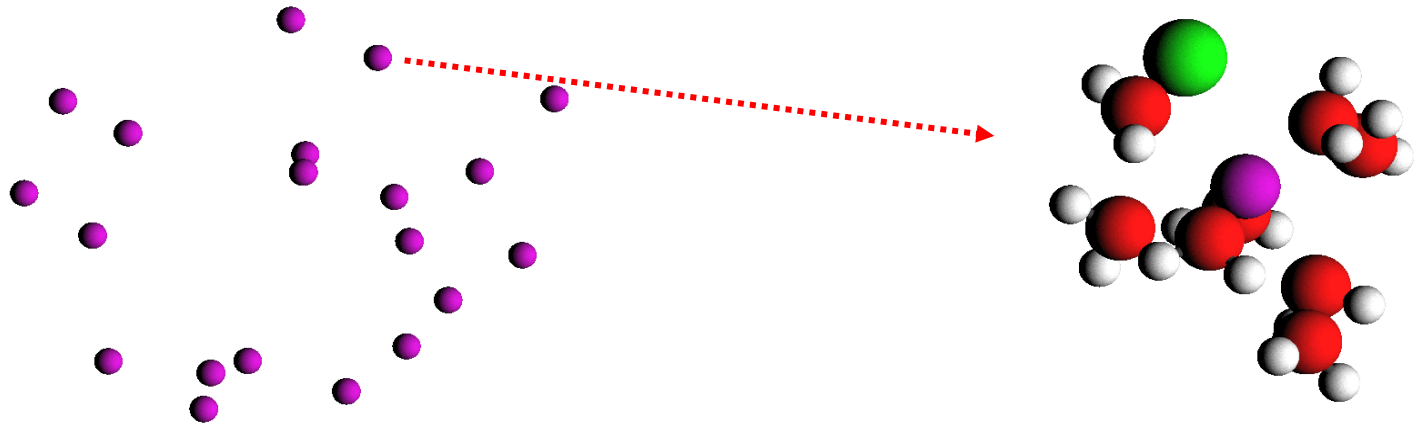


Local structure in 1m aqueous solution of YCl_3 and refining an atomic potential



EXAFS spectroscopy to investigate the Y^{3+} local structure

Local structure in 1m aqueous solution of YCl_3 and refining an atomic potential

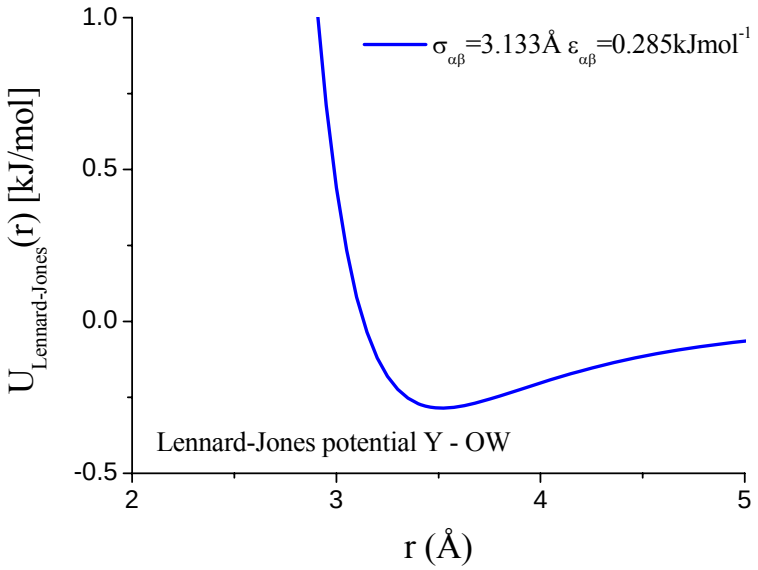


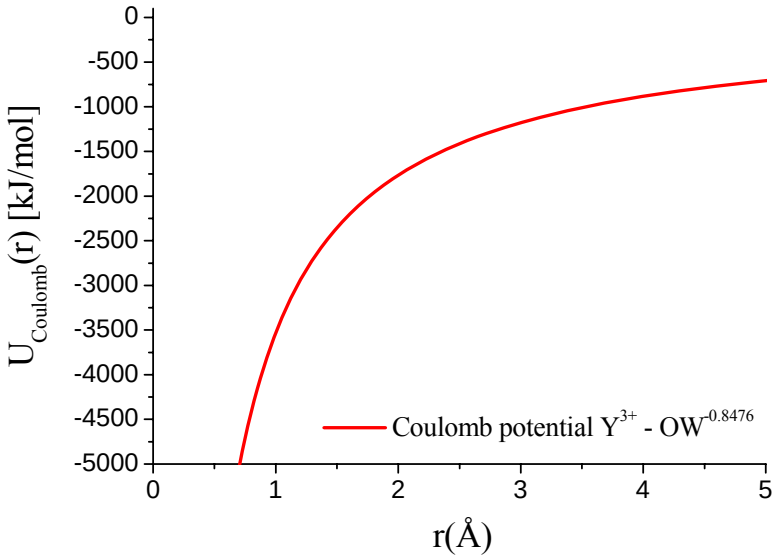
EXAFS spectroscopy to investigate the Y^{3+} local structure

Y^{3+}-OW interaction potential used in the structure refinement

$$U_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right] + \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r_{ij}}$$

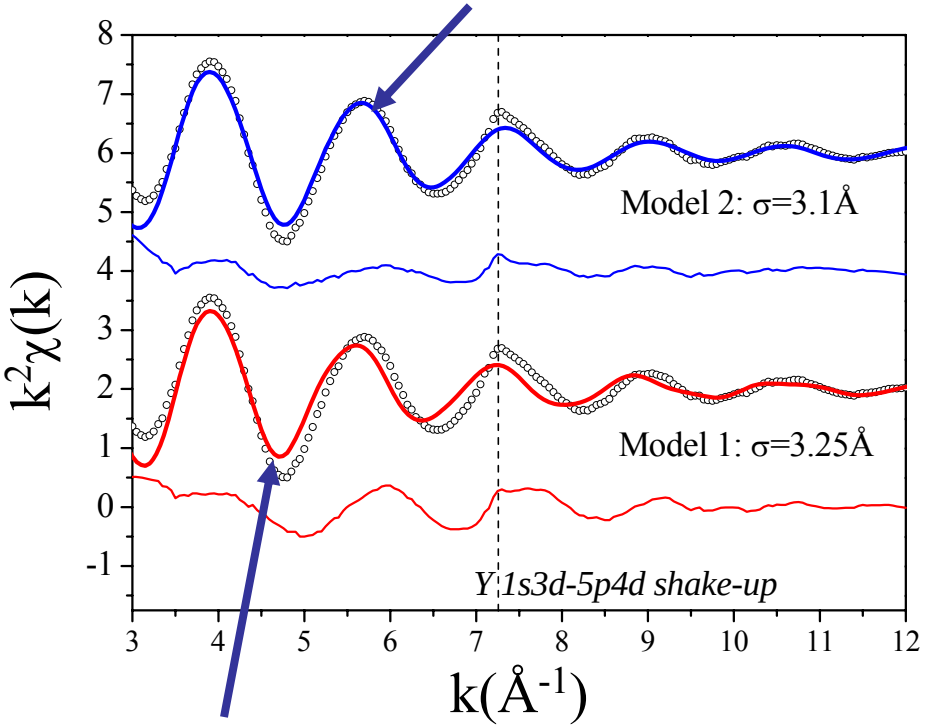
$$\varepsilon_{\alpha\beta} = \left(\varepsilon_\alpha \varepsilon_\beta\right)^{\frac{1}{2}} \qquad \sigma_{\alpha\beta} = \frac{1}{2}\left(\sigma_\alpha + \sigma_\beta\right)$$



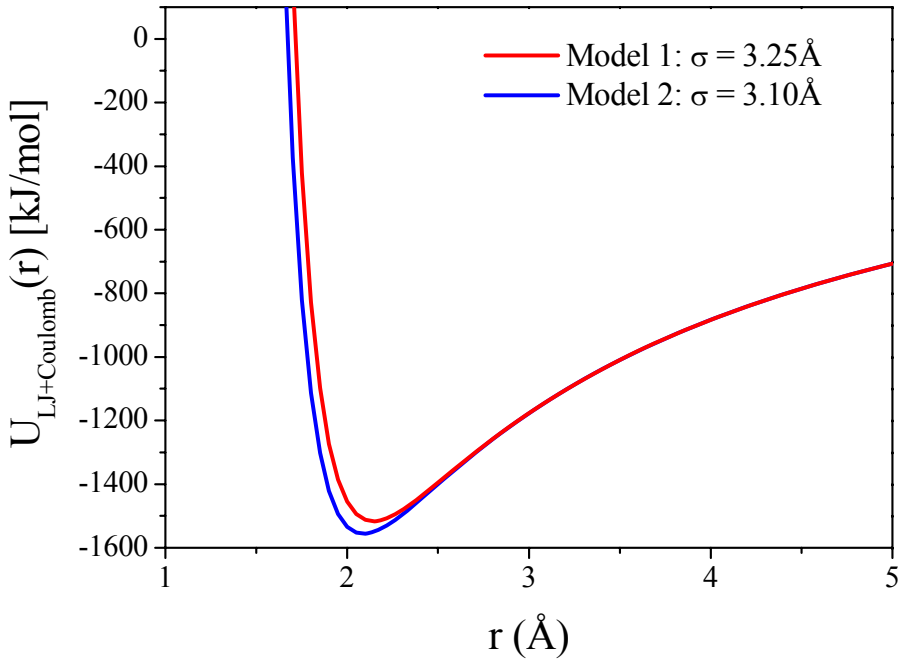


Y^{3+}-OW EXAFS optimised interaction potential

Y^{3+}-OW = 2.33Å



Y^{3+}-OW = 2.39Å

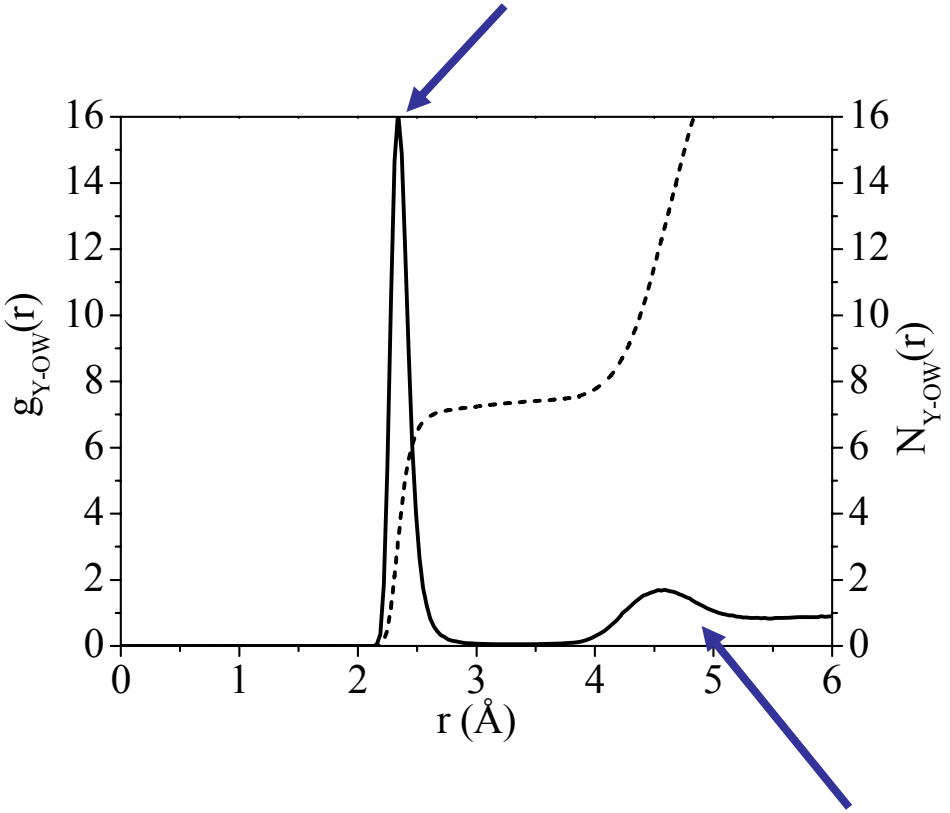


Only one free parameter in fit!
ΔE_0 The EXAFS energy scale offset
(In this study ΔE_0 = 4eV)

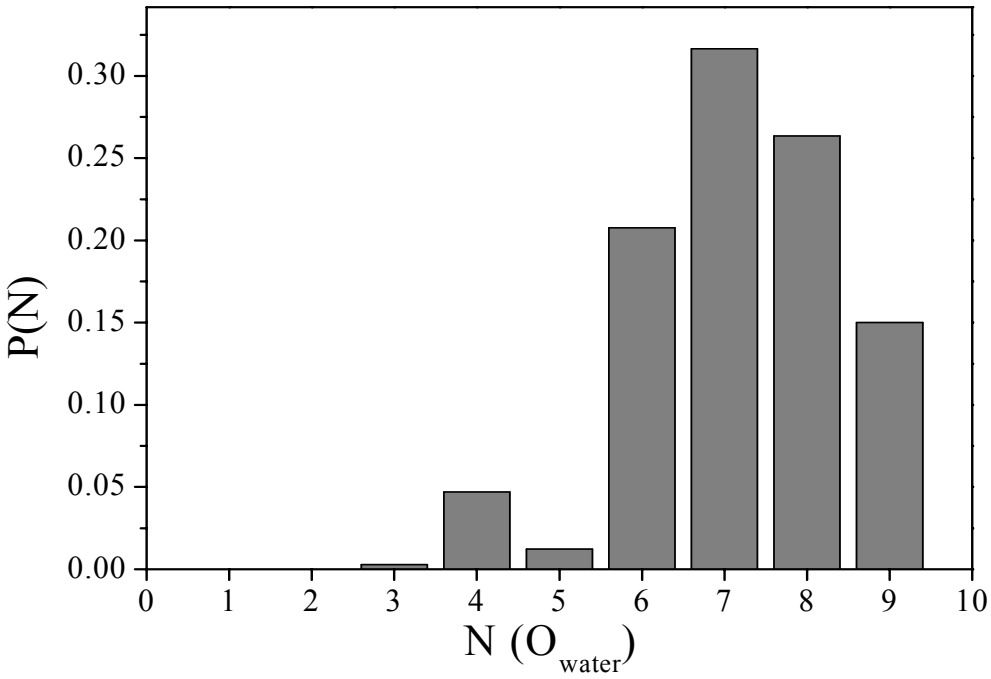
Experimental data: S.Díaz-Moreno, A.Muñoz-Paez and J.Chaboy, *J. Phys. Chem. A*, **104** 1278 (2000)

Local structure of the Y^{3+} hydration shell

Y^{3+}-OW = 2.33Å

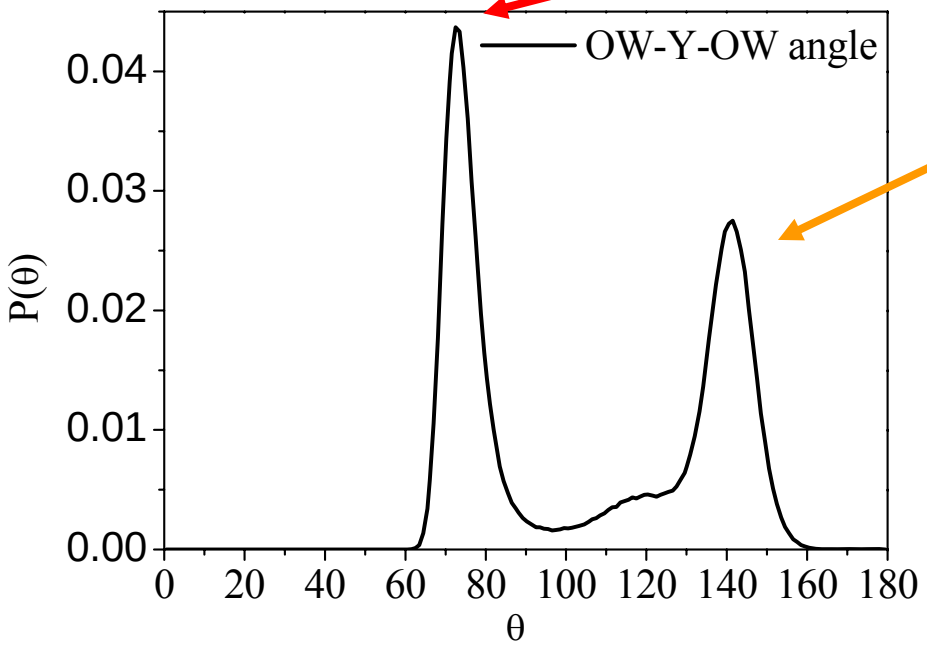


Y^{3+}-OW mean C.N. 7.4±0.5



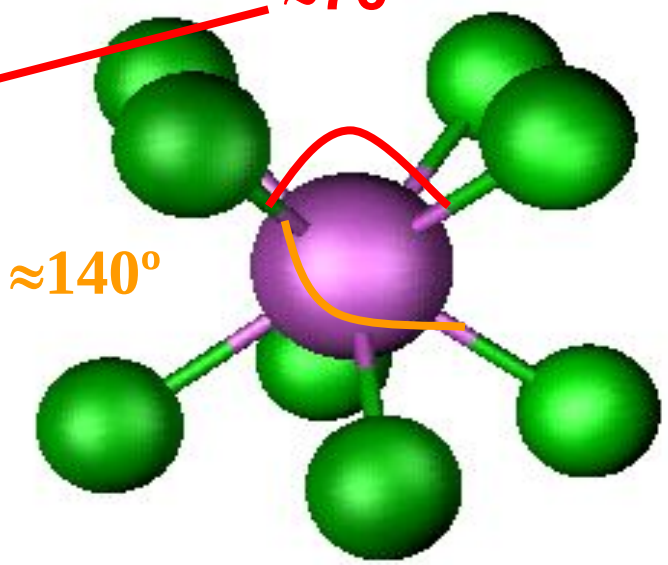
Well defined second hydration shell at ≈ 4.6Å

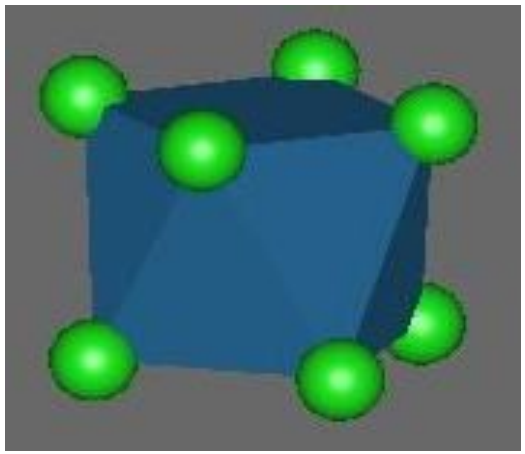
Local geometry of the Y^{3+} hydration shell



≈70°

≈140°

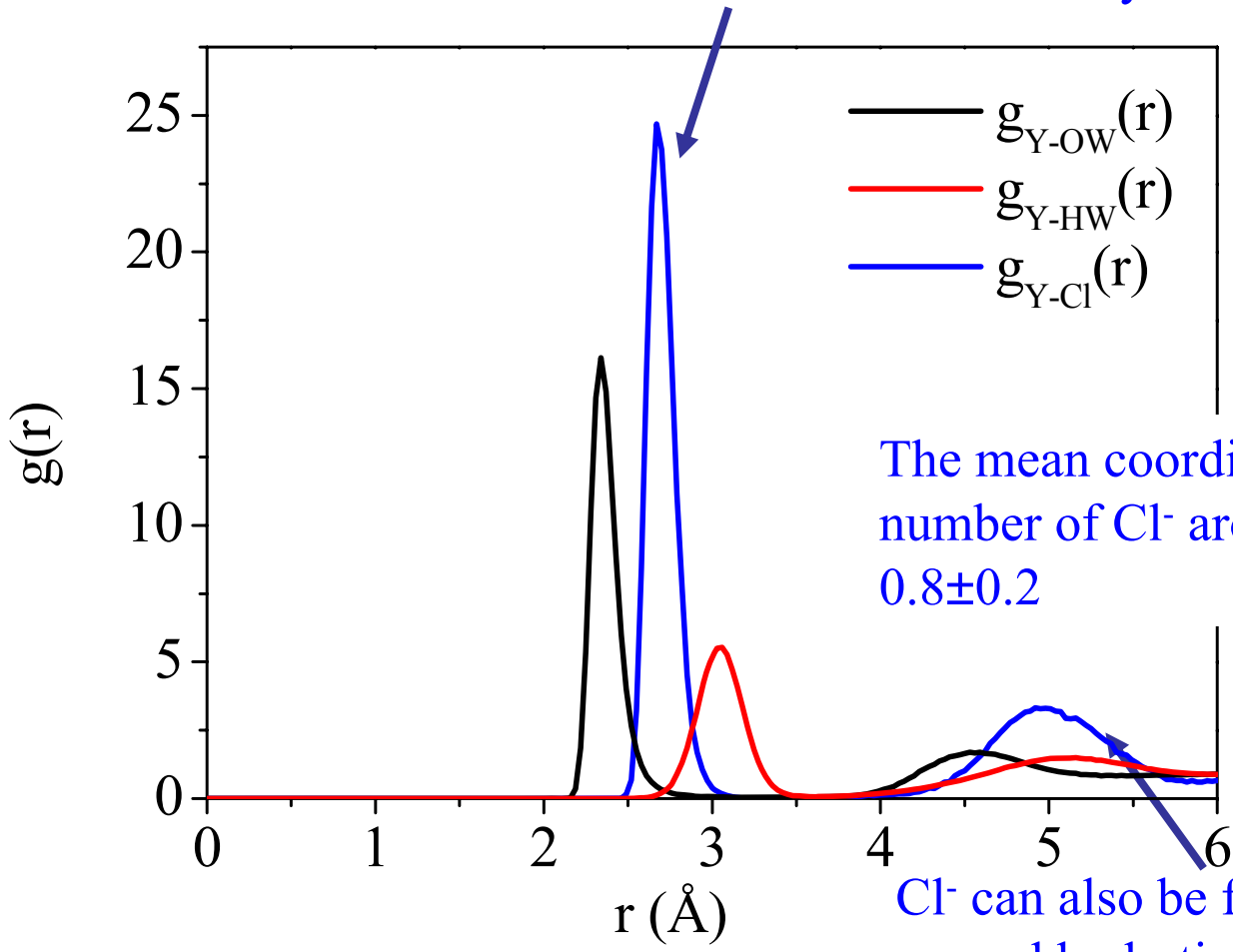




Square antiprism

Ion-ion interactions in the Y^{3+} hydration shell

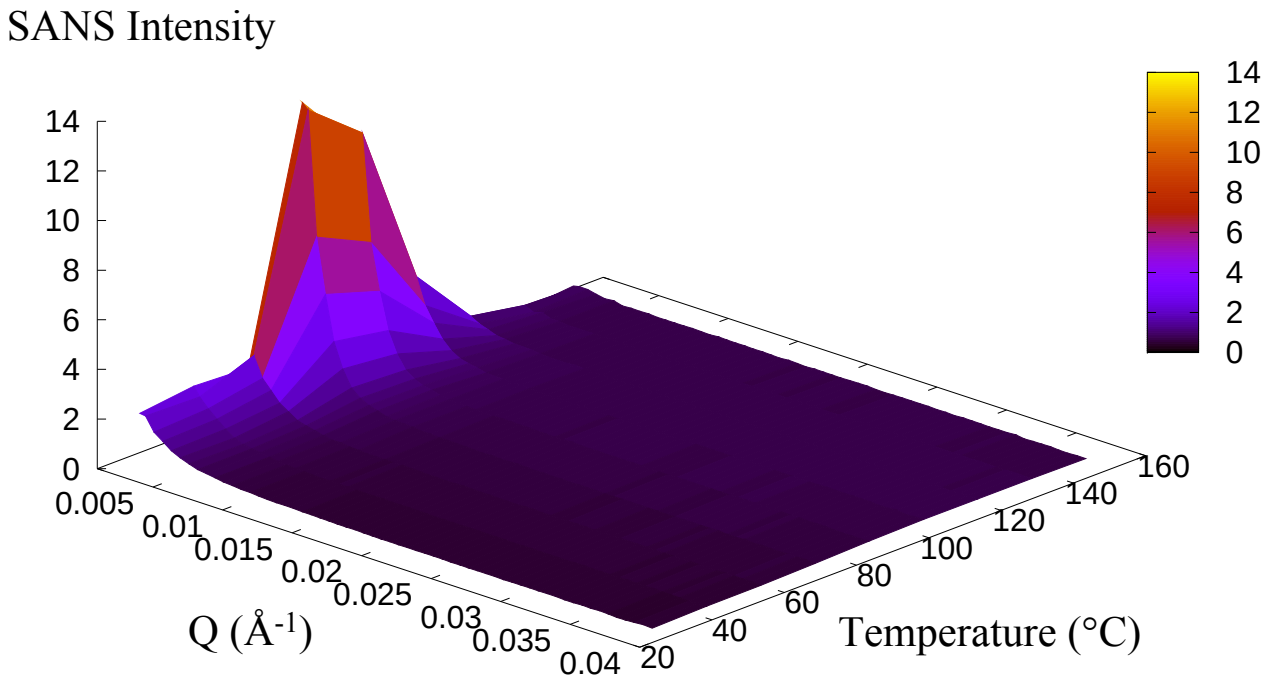
The model tells us that Cl^- anions can be found in the first hydration shell



The mean coordination number of Cl^- around Y^{3+} is 0.8±0.2

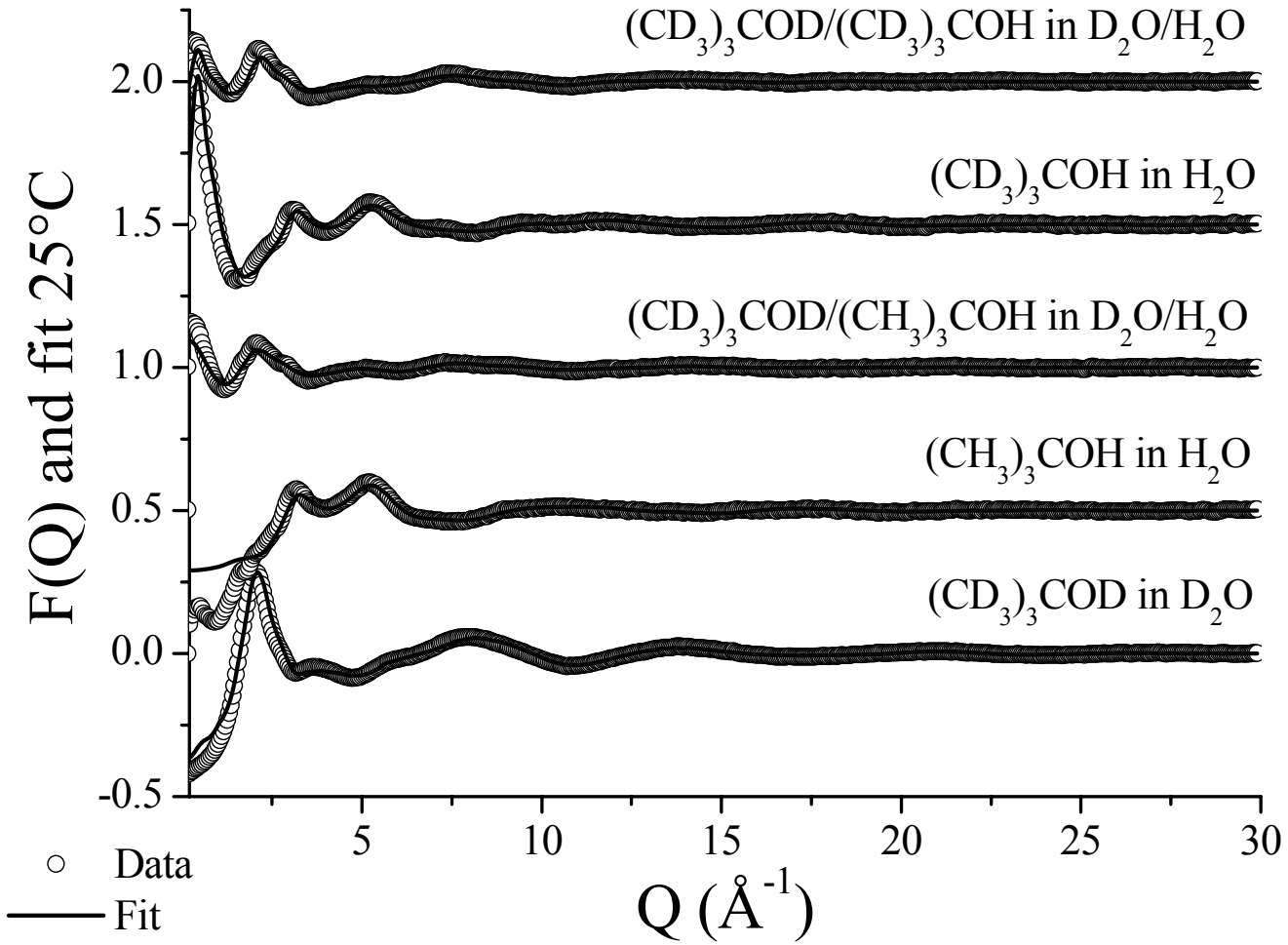
Cl^- can also be found in the second hydration shell of Y^{3+}

Mesoscale structure in 0.04 mole fraction tert. butanol – water solutions

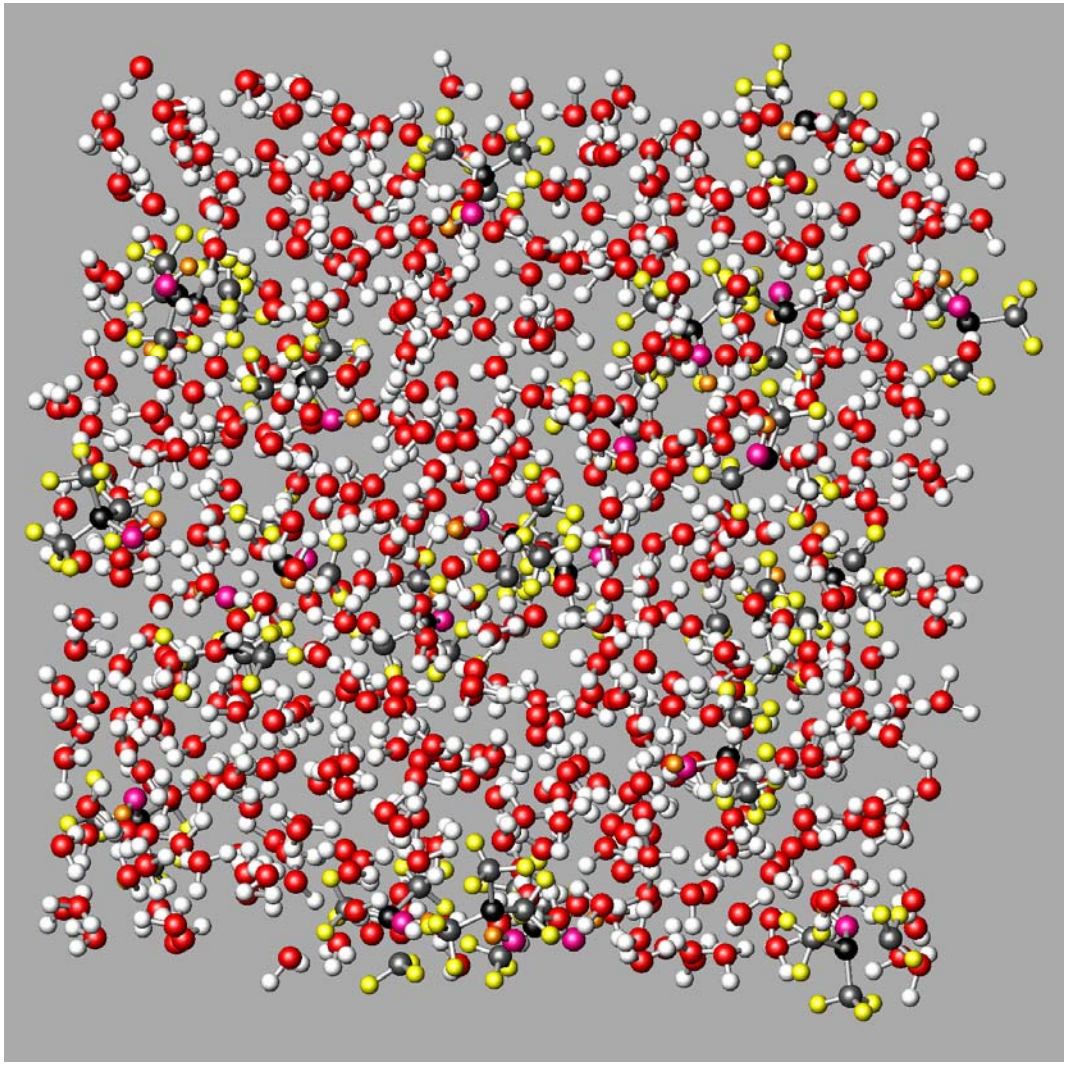


D.T.Bowron and J.L.Finney, *J.Phys.Chem B* **111** 9838 (2007)

Mesoscale structure with atomistic resolution

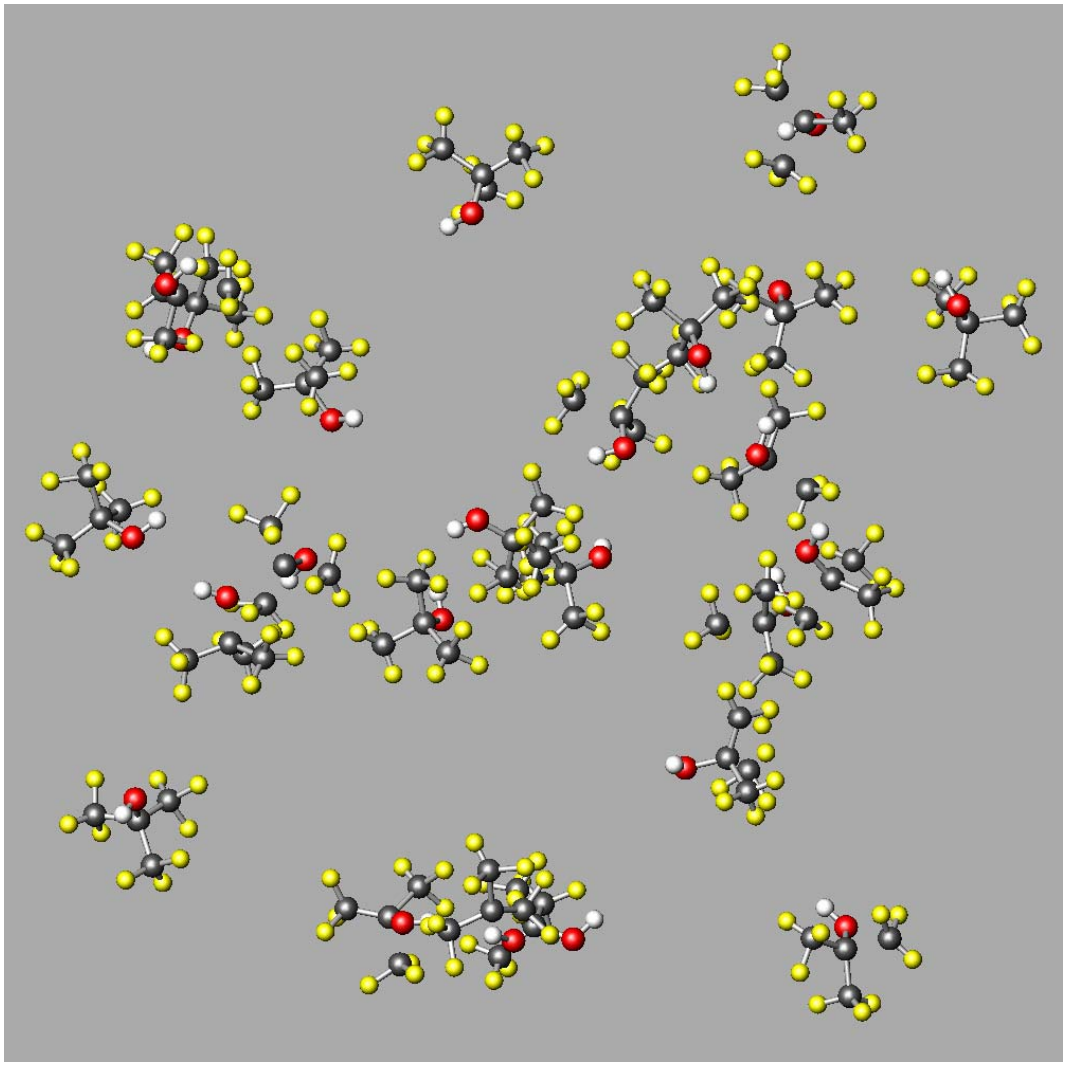


Mesoscale structure with atomistic resolution



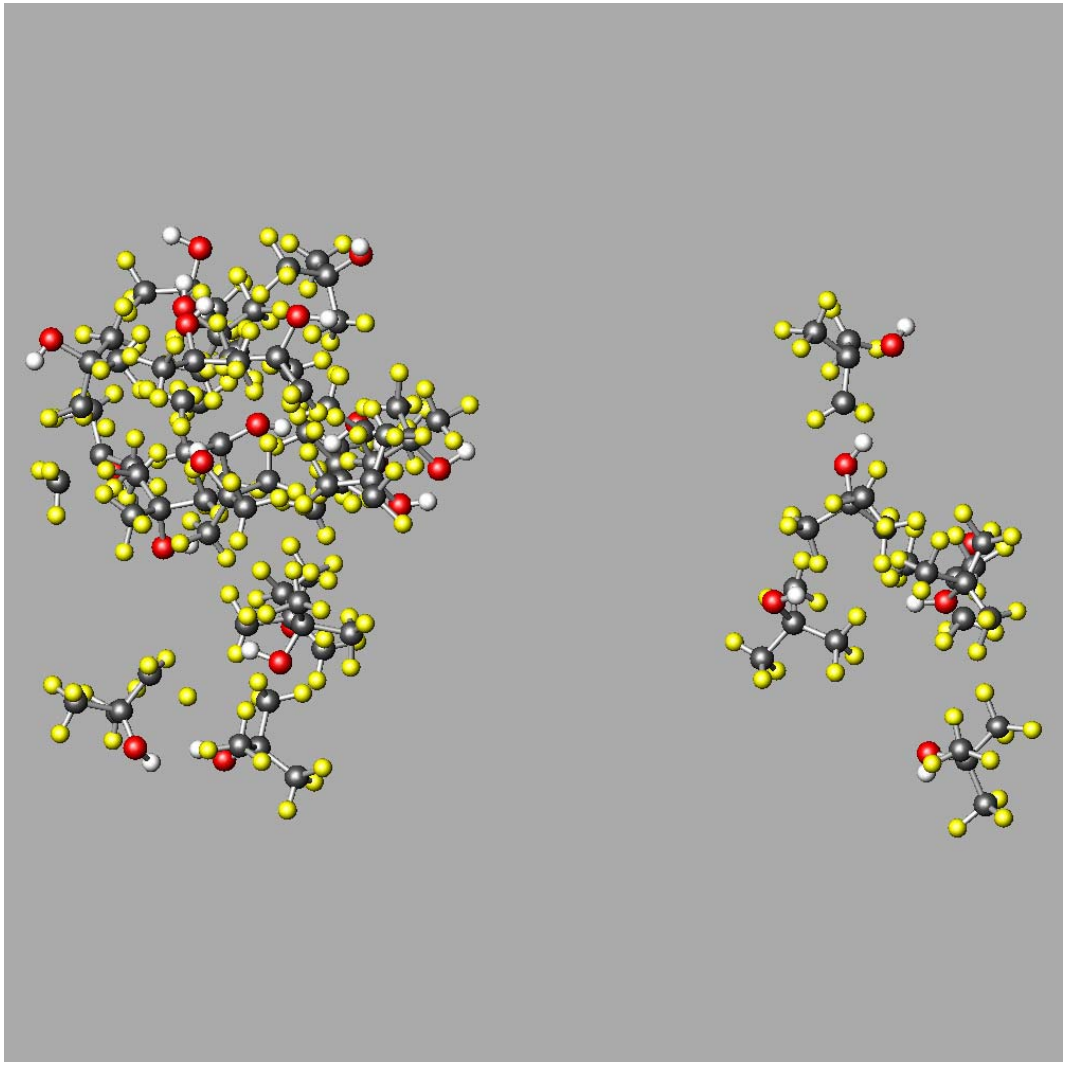
Mesoscale structure with atomistic resolution

25ºC



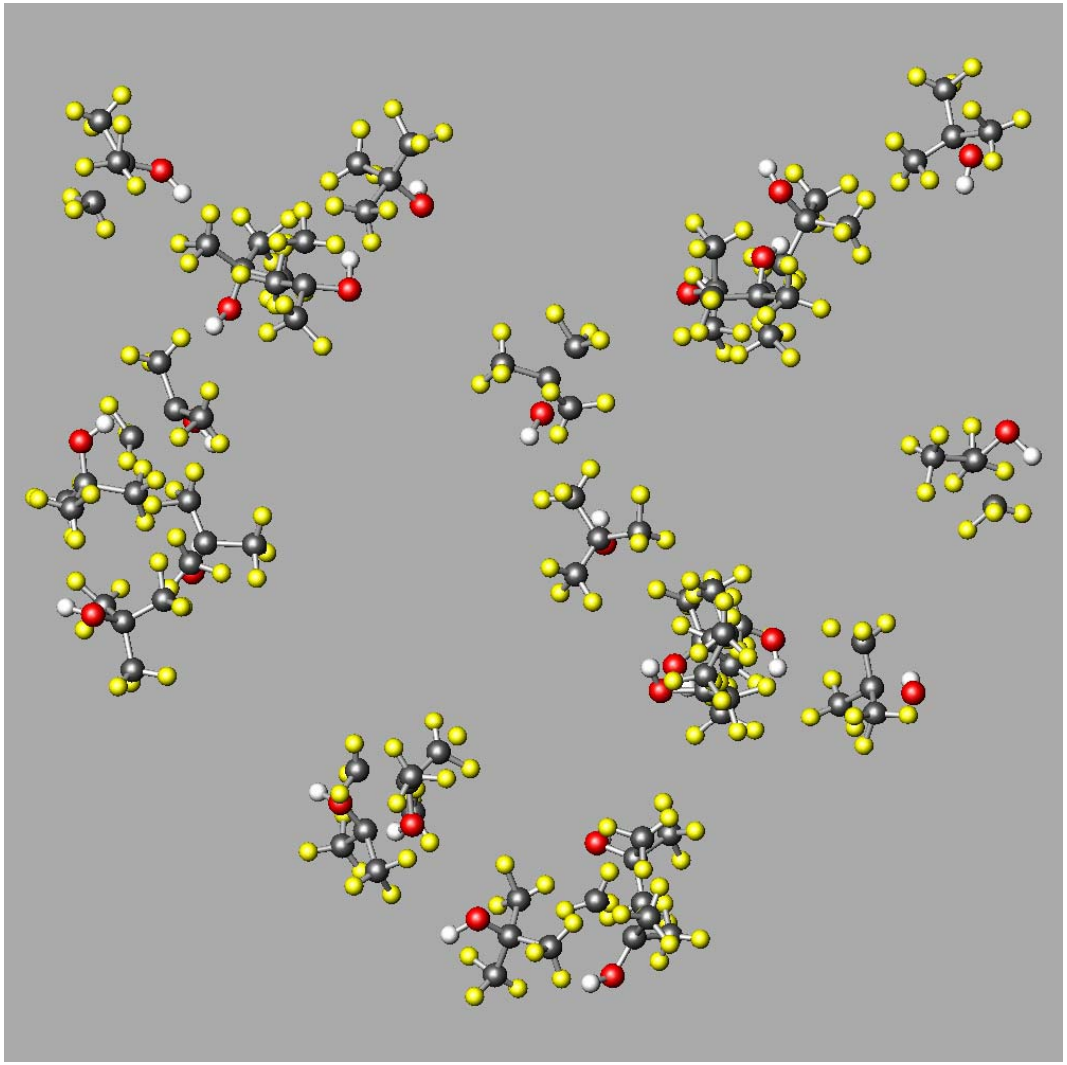
Mesoscale structure with atomistic resolution

80ºC

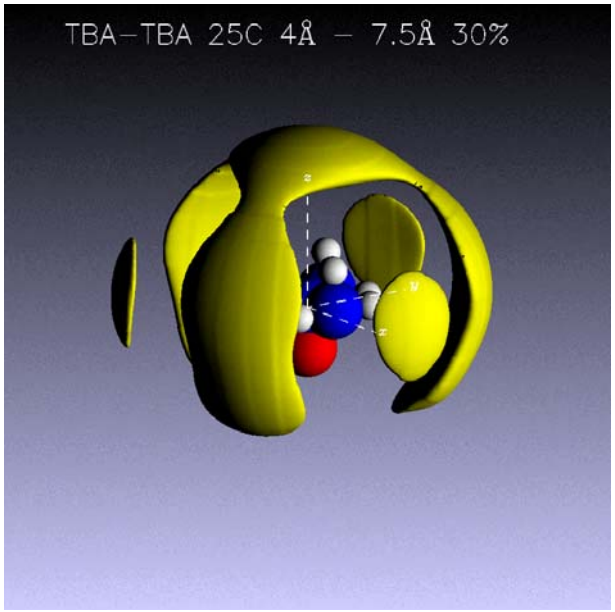


Mesoscale structure with atomistic resolution

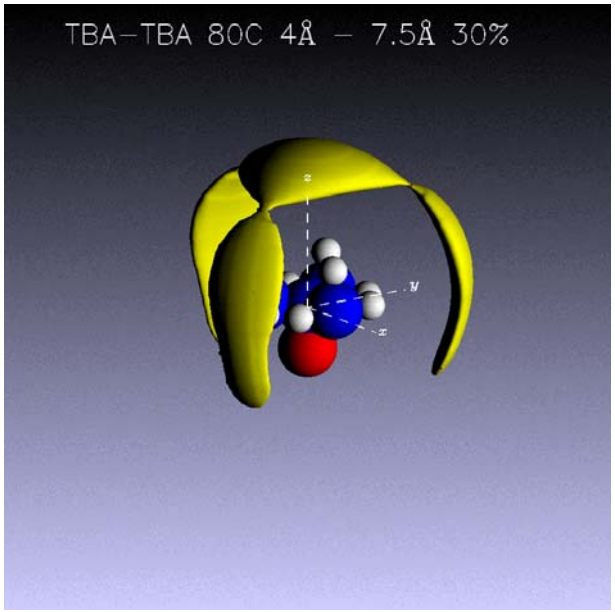
106ºC



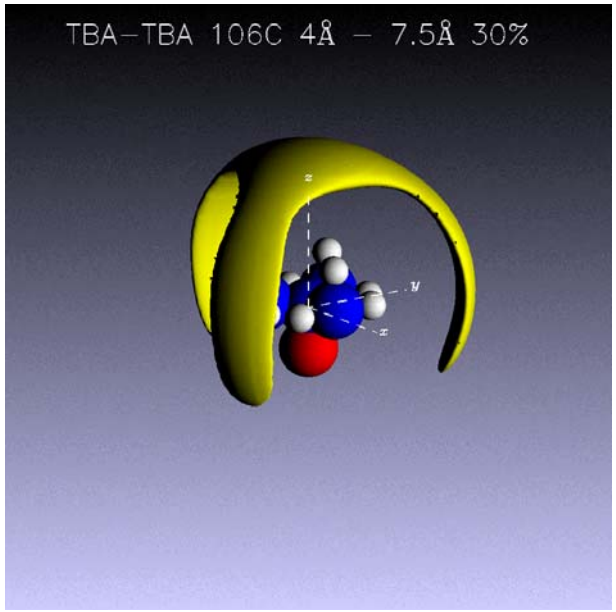
Alcohol-alcohol interactions



25ºC



80ºC



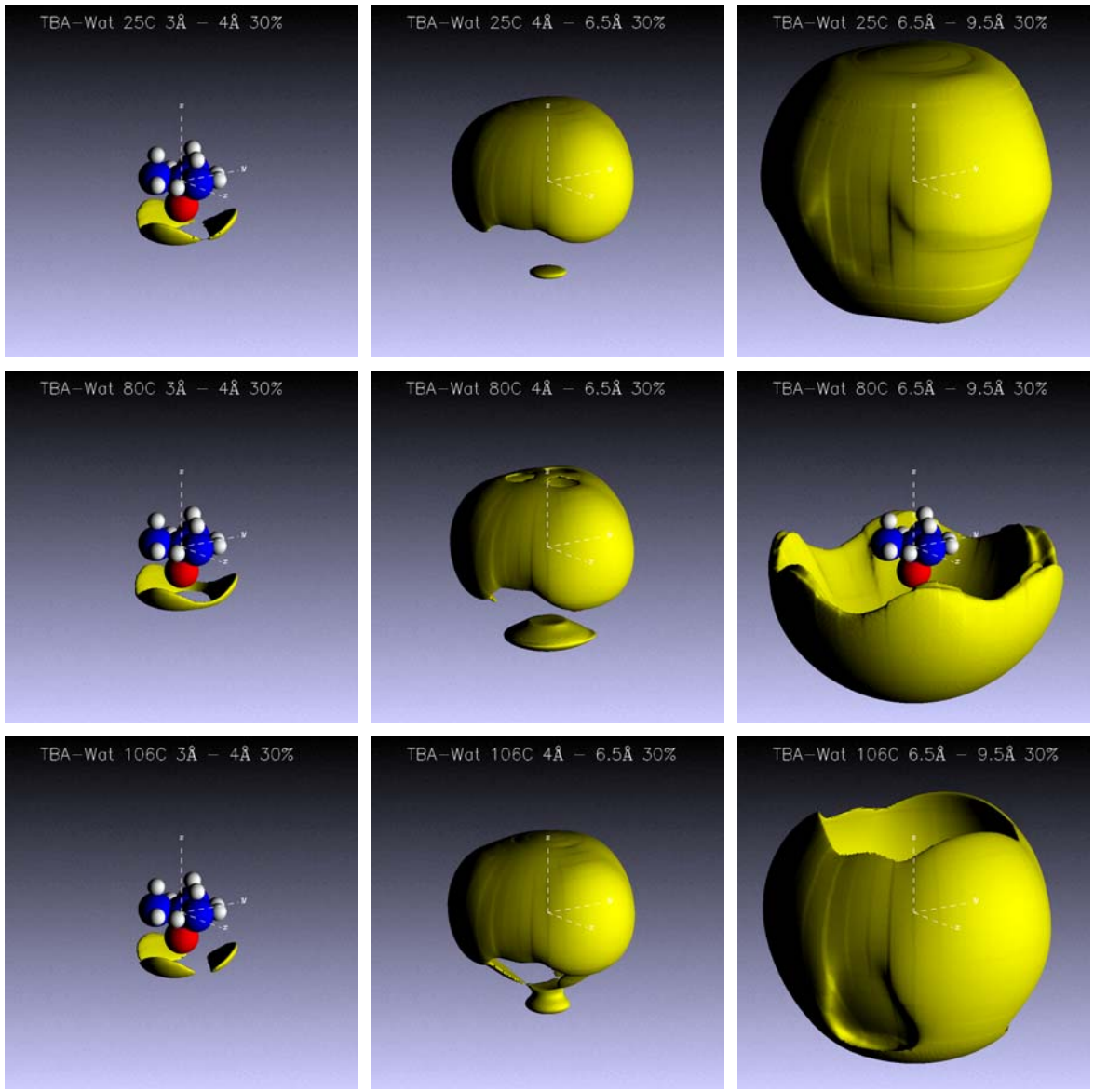
106ºC

Alcohol-water interactions

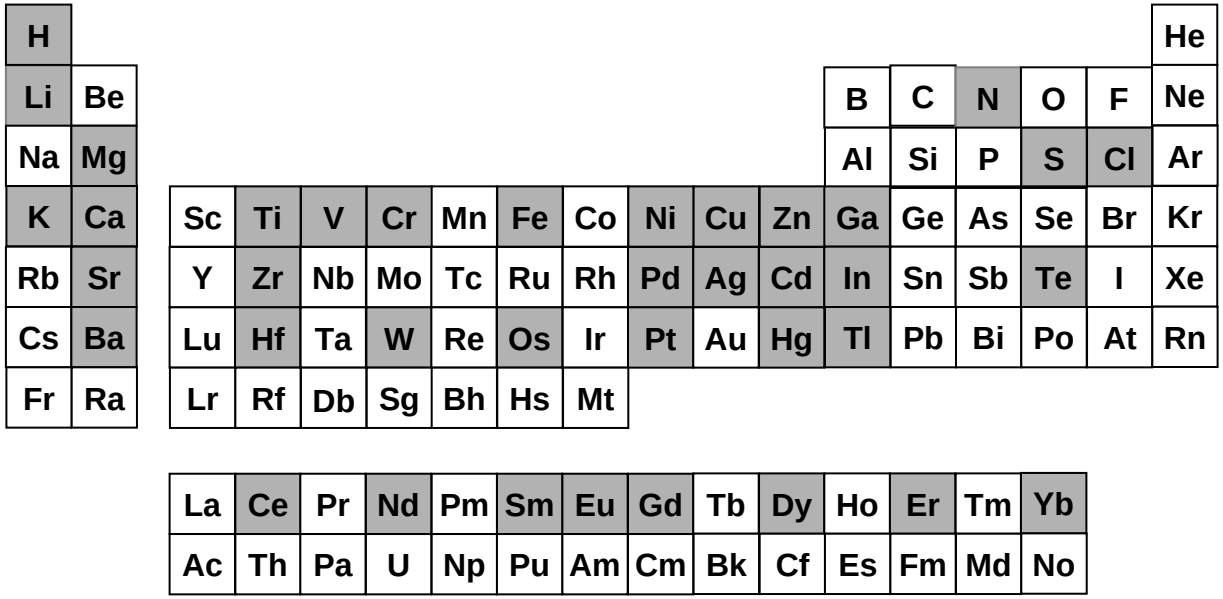
25ºC

80ºC

106ºC

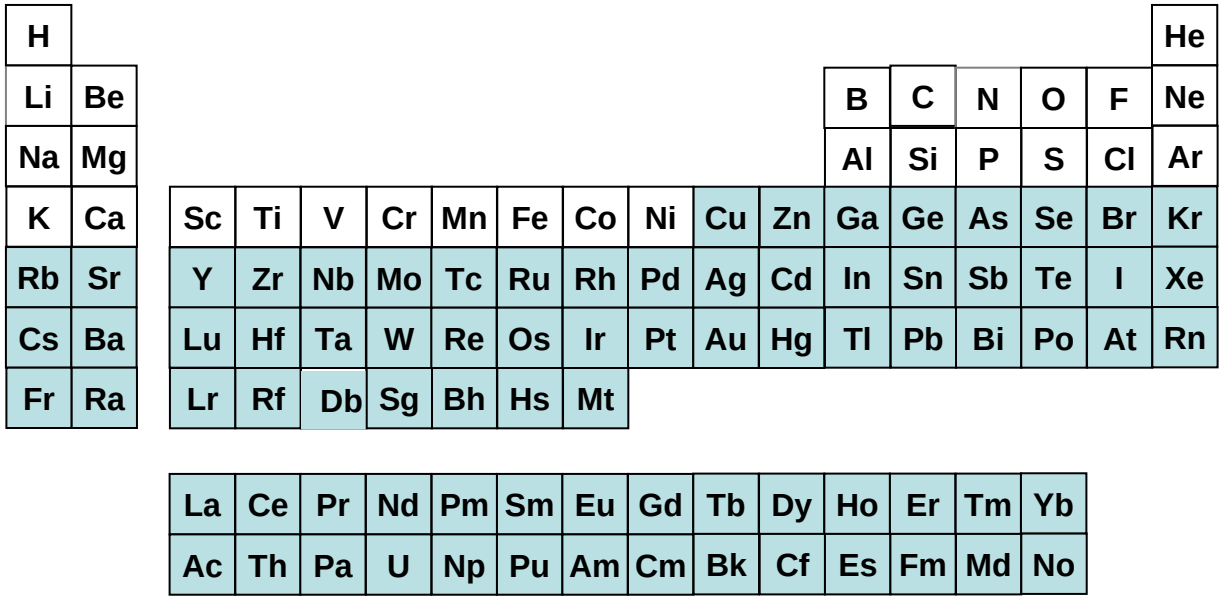


Isotopes and absorption edges – routes to chemical specificity



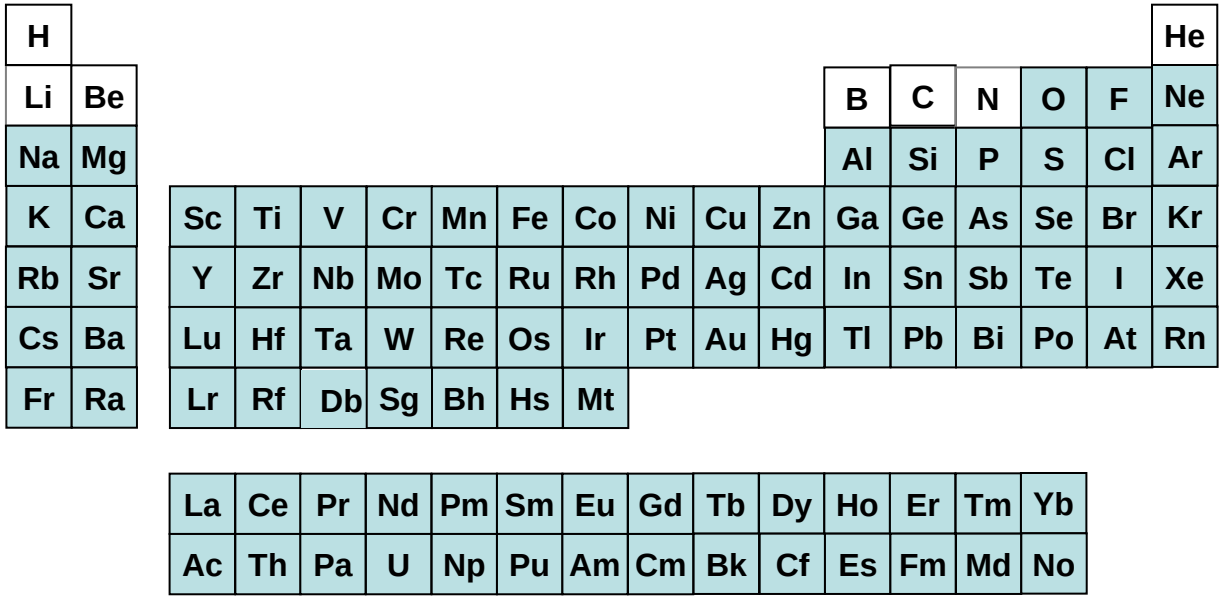
Elements with isotopes that potentially can be used for NDIS ion solvation studies ($\Delta b_c \geq 1$fm)
J.E.Enderby, *Chem. Soc. Revs.* 159 (1995)

Isotopes and absorption edges – routes to chemical specificity



Elements with absorption edges suitable for atomic resolution Anomalous X-ray Scattering investigation of local structure in solutions

Isotopes and absorption edges – routes to chemical specificity



Elements with absorption edges suitable for EXAFS investigation of local structure in solutions

Concentration limits: Diffraction 1 to 10 atom %
Spectroscopy ~0.01 atom %

Benefits of the neutron (or X-ray) scattering plus EXAFS, EPSR analysis approach

(1) Produces a model that is consistent with both bulk and local structural information.

(2) Brings dilute component sensitivity of the spectroscopic probe to bulk structural models.

(3) Circumvents the traditional limitations of direct EXAFS analysis of disordered materials data:

(i) No need for peak shape approximations

(ii) No need for Debye-Waller factor models

(iii) Reduces the number of free parameters in the model to 1

(iv) Provides an unambiguous means to incorporate higher order correlation functions into a disordered materials analysis – sensitivity to the local atomic environmental geometry

Benefits of the neutron scattering plus EXAFS, EPSR analysis approach

(4) Allows pair potential models to be investigated and refined
(5) Is cheaper, more sensitive and more versatile than neutron scattering with exotic isotopic substitution methods for the investigation of ionic species
(6) Experimentally much simpler and more sensitive than Anomalous X-ray Scattering techniques

If the scattering and spectroscopy data exist, the method can be applied.