Spectroscopie d'absorption X dans les systèmes désordonnés: *méthodes numériques d'analyse*

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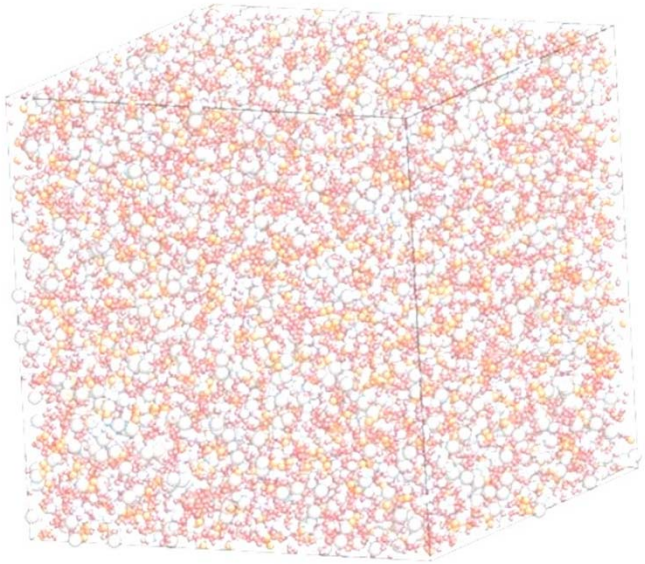


Modélisation des verres, Journées Thématiques CNRS, Marcoule, 12-13 Mai 2011

XAS (in disorded systems)

- brings structural and electronic information
- a complementary (to diffraction) and useful structural probe
- a chemically-selective probe (wide applicability to almost all the elements)
- highly sensitive to dilute quantities
- « easy to do » experiments
- sometimes, XAS is the only structural probe which might be doable: diluted samples, chemically complex systems, high pressure and/or high temperature environments …

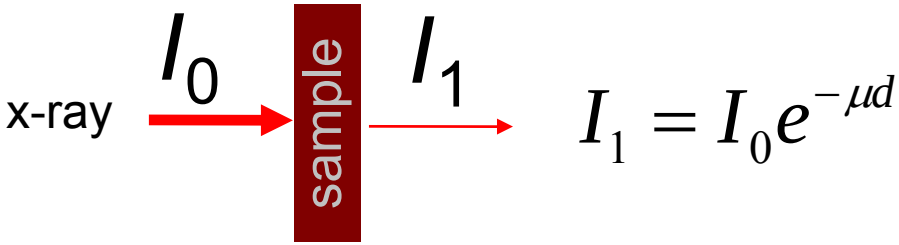
But:

- interpreting/analysing the data can be tricky or even misleading
- XAS is of limited interest if you know nothing (or almost) of your system

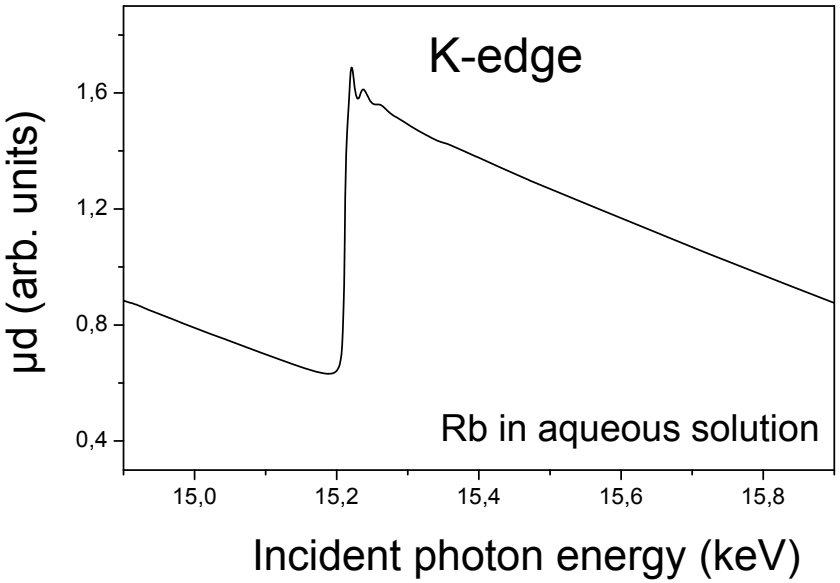
⇒ The use of external information (e.g. MD, diffraction) is highly desirable

Basics of x-ray absorption spectroscopy (XAS)

transmission experiment



$$I_1 = I_0 e^{-\mu d}$$



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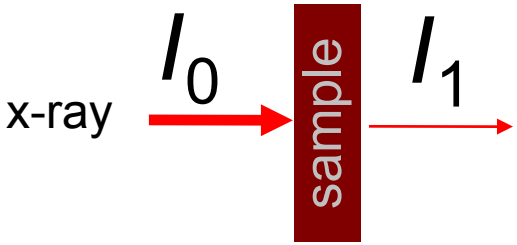

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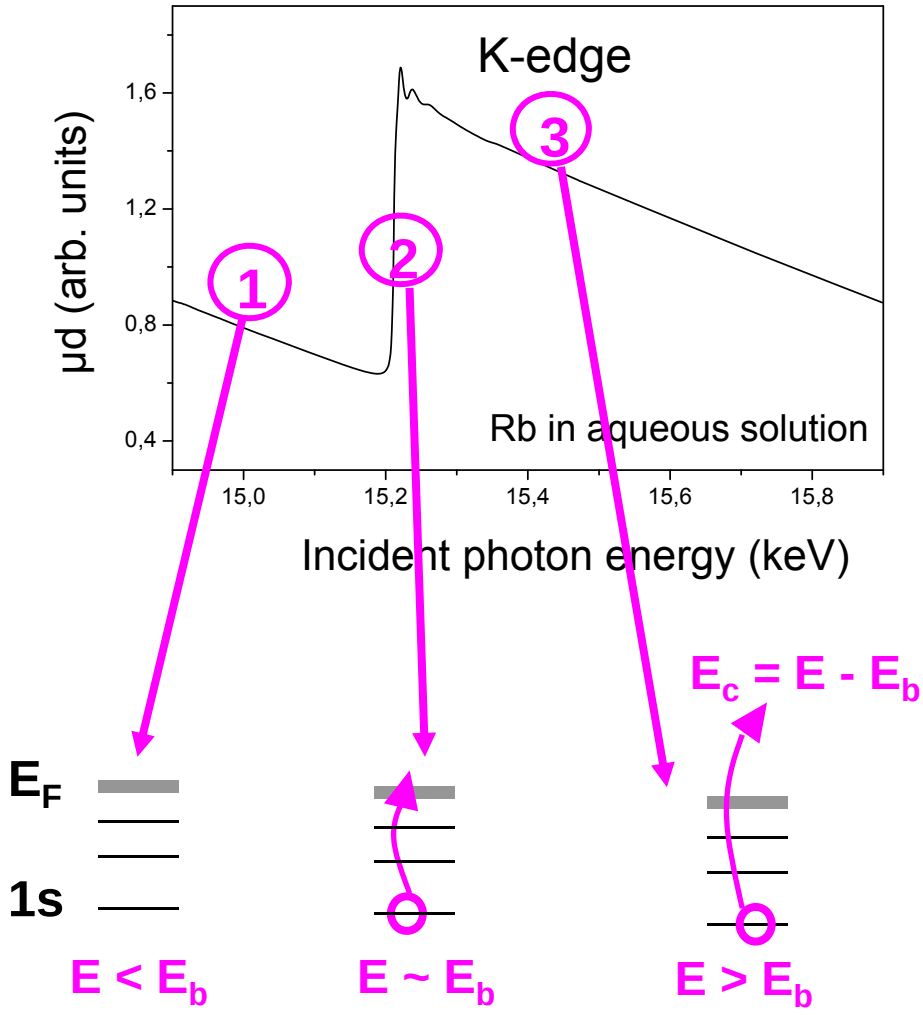

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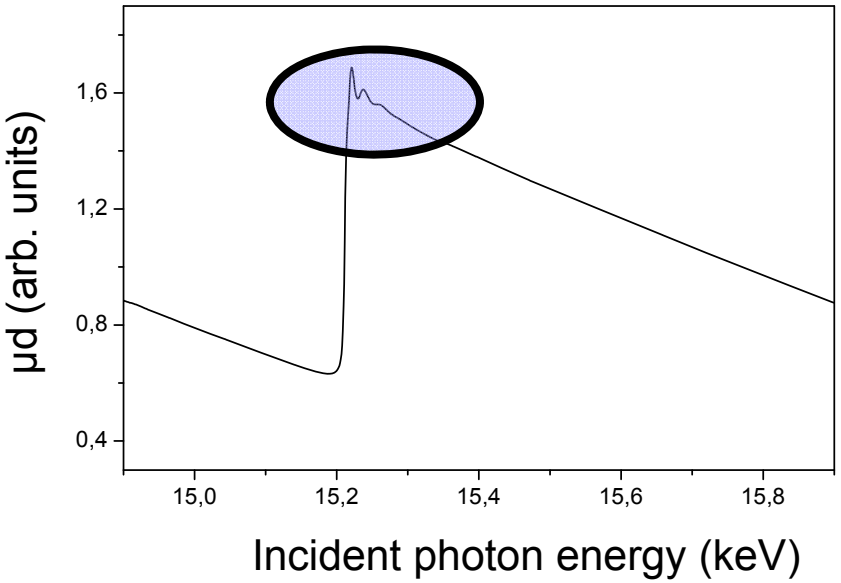

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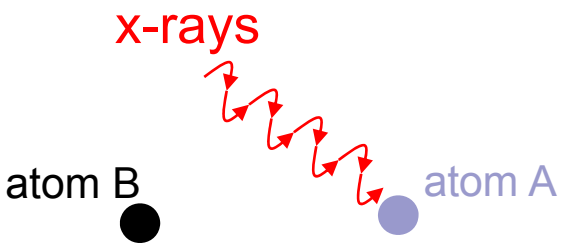

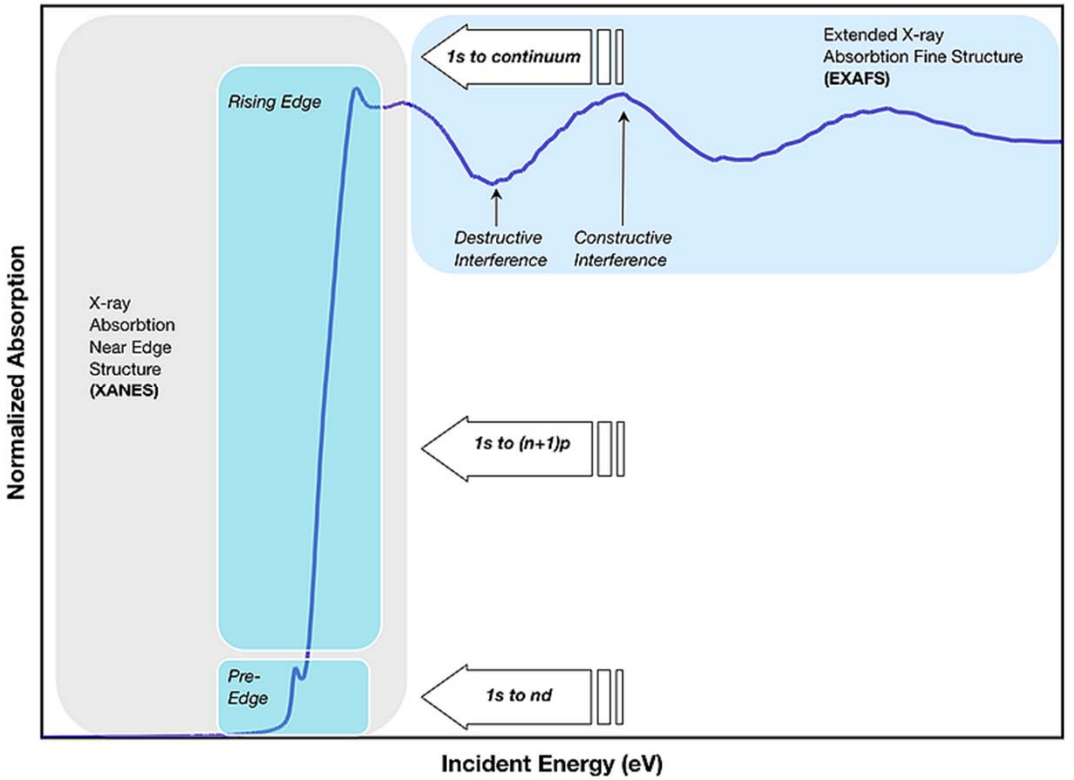

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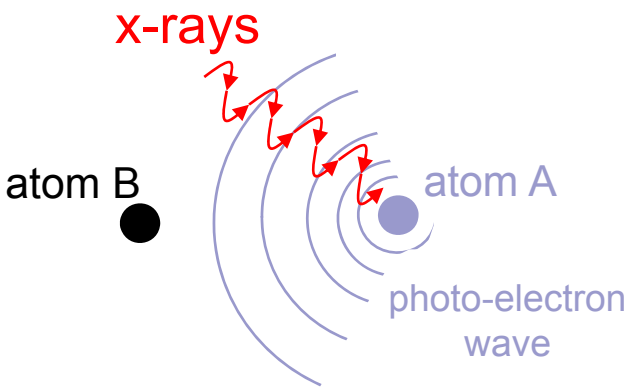

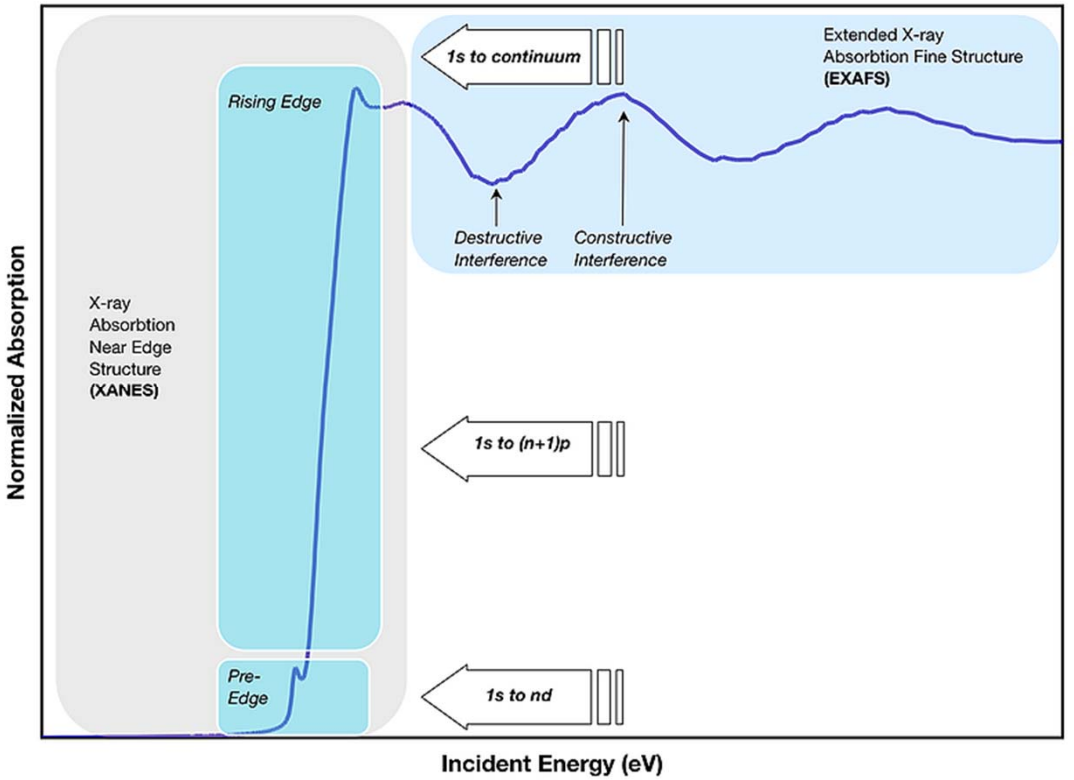

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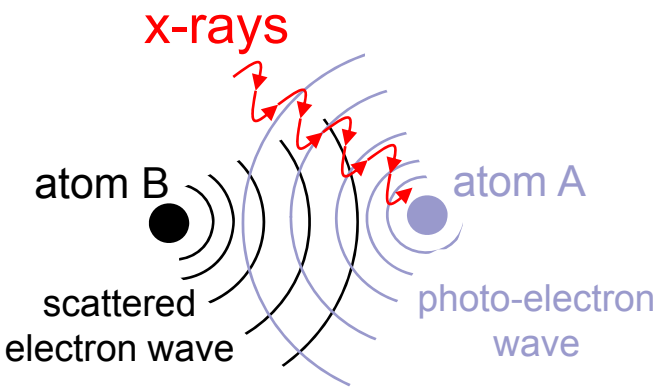
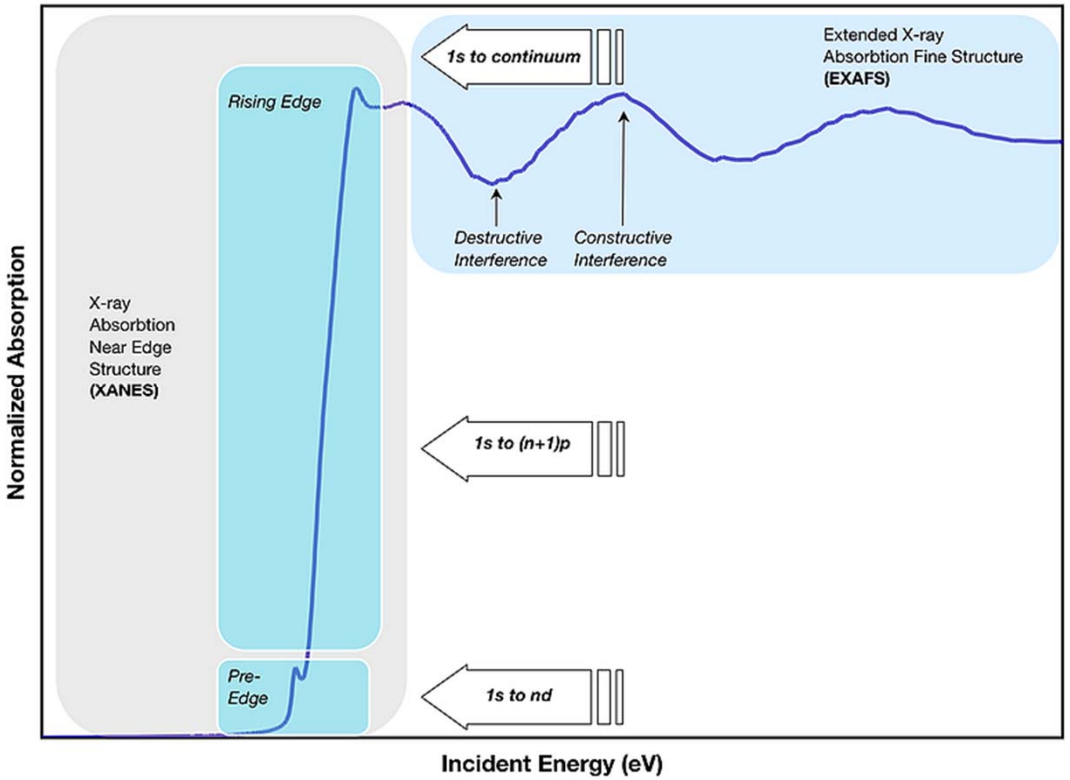


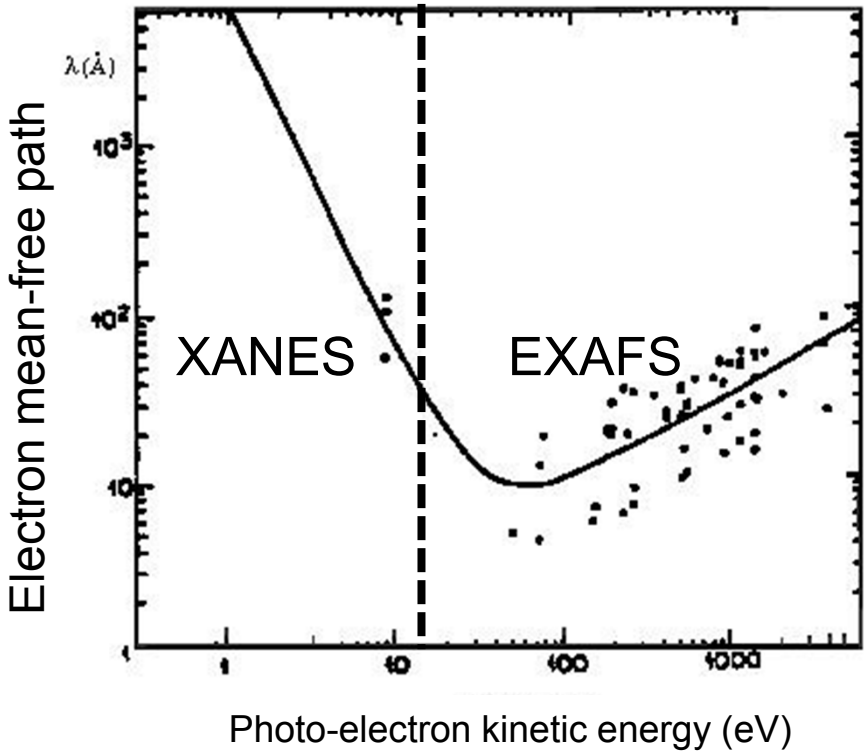


Fermi's Golden Rule (in *one-electron* approximation):

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E - E_f + E_i)$$

$|i\rangle$ is an initial deep core state (*e.g.* 1*s*).
$\langle f|$ is an unoccupied state in the presence of a core hole.
H_{int} is the electron transition operator.

Basics of x-ray absorption spectroscopy (XAS)



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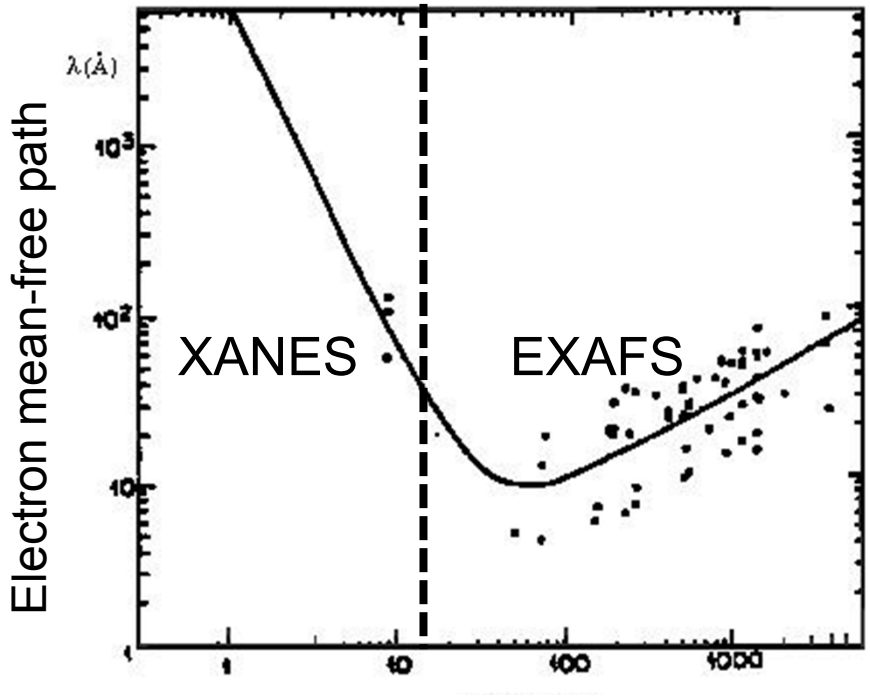
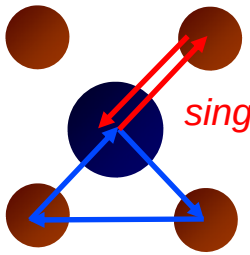


EXAFS:

- dominated by single-scattering (SS) paths
  (+ short multiple-scattering (MS) paths)



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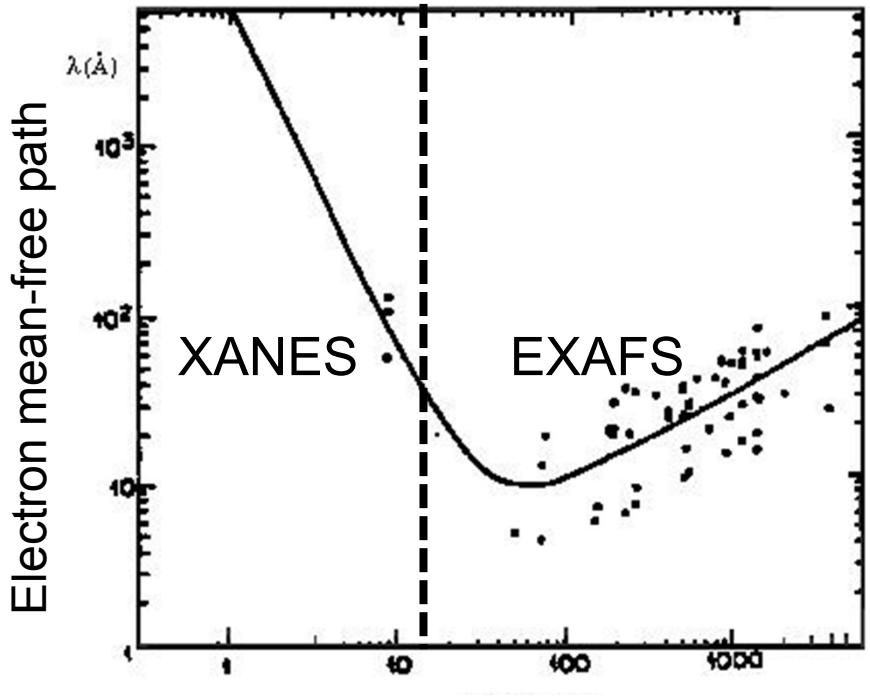
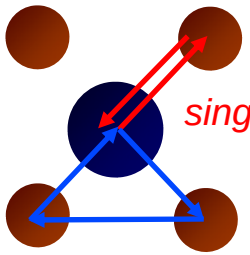


XANES:

- dominated by multiple-scattering terms
- close to the edge : reflects the eDOS of empty levels at the absorbing sites convoluted by core-hole effects

EXAFS:

- dominated by single-scattering (SS) paths
(+ short multiple-scattering (MS) paths)



The *standard* EXAFS formula

(restricted to single-scattering contributions)

$$\chi(k) = S_0^2 \sum_{shell\, i} \frac{N_i}{kR_i^2} \left| f_i\ (k) \right| e^{-2R_i / \lambda(k)} \sin\left[2kR_i + \Phi_i(k) + 2\delta_c(k)\right] e^{-2k^2\sigma_i^2}$$

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

$f_i\ , \Phi_i$: scattering amplitude and phase of atom type *i*

$\lambda(k)$: photo-electron mean free path

S_0^2 : reduction factor (0.75-1.00) due to many-body effects

N_i, R_i, σ^2_i : structural parameters of shell *i*

Dale E. Sayers, Edward A. Stern, and Farrel W. Lytle, *"New Technique for Investigating Noncrystalline Structures : Fourier Analysis of the Extended X-Ray Absorption Fine Structure",* Phys. Rev. Lett. **27**, 1204–1207 (1971).

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Non-structural parameters

- f_i, Φ_i: scattering amplitude and phase of atom type *i*
- $\lambda(k)$: photo-electron mean free path
- S_0^2: reduction factor (0.75-1.00) due to many-body effects

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N_i, R_i, σ^2_i : structural parameters of shell *i*

- strong correlations between E_0 – R and N – S_0^2
- limited *k* range [2.5:20] Å^{-1}. Structural solutions hardly univoque
- *standard* formula valid only in the case of small and gaussian disorder

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Theory of XAS

- Reduction of the photo-absorption *many-body* problem into that of an electron moving in an optical potential (that takes into account both the extrinsic and intrinsic losses).

  Aim : construction of the effective optical potential and solution of the associated Green's function equation for the calculation of the *one-electron* cross-section.

- Construction of the local charge density by overlapping neutral atomic charge densities; relaxation of the density around the core hole (optionally in a self-consistent way).
- Ansatz for the optical potential (*e.g.* Hedin-Lundqvist: self-energy of an electron embedded in a locally uniform interacting electron gas).

  Real part : scattering from atomic sites described through *k*-dependent partial wave phase shifts for different angular momenta *l.* Imaginary part : gives mean free path.
- Solve the Schrödinger equation for continuum states. Often (but not necessarily) using the *muffin-tin* scheme (reasonable approx. for EXAFS but might be too coarse at low energies).

Polarisation averaged XAS cross-section for transitions to a dipole selected final state:

$$\mu(E) = \mu_0 \left[\mathrm{Im} \frac{1}{\mathrm{Im}(t_0^{l_0})} \frac{1}{2l_0+1} \sum_{m_0} \left[T(1-GT)^{-1} \right]_{0,0}^{L_0,L_0} \right]$$

atomic cross-section

scattering and propagator matrices

A. Filipponi *et al.*, Phys. Rev. B **52** 15122 (1995)

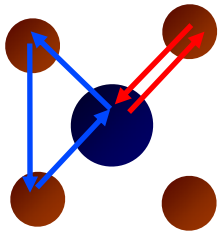
Multiple-Scattering Theory of XAFS

$$\mu(E) = \mu_0 \left[\mathrm{Im} \frac{1}{\mathrm{Im}(t_0^{l_0})} \frac{1}{2l_0+1} \sum_{m_0} \left[T(1-GT)^{-1} \right]_{0,0}^{L_0,L_0} \right]$$

$$if \left\| GT \right\| < 1, \; then \quad T(I-GT)^{-1} = T(I+GT+GTGT+GTGTGT+\ldots)$$

$$\mu(E) = \mu_0 \left[1 + \sum_{i \neq 0} \chi_2^{0i0} + \sum_{\substack{i \neq j \\ i \neq 0, j \neq 0}} \chi_3^{0ij0} + \sum_{\substack{i \neq j \neq k \\ i \neq 0, k \neq 0}} \chi_4^{0ijk0} + \ldots \right]$$

(SS) (3-leg) (4-leg)



with $\chi_n(k) = A(k,R)\sin\left[kR_{tot} + \Phi(k)\right]$

Limitations:

- valid only in the weak scattering regime, *i.e.* at high energies (EXAFS)
- path proliferation problem (need for *ad hoc* filtering criteria)

A. Filipponi *et al.*, Phys. Rev. B **52** 15122 (1995)

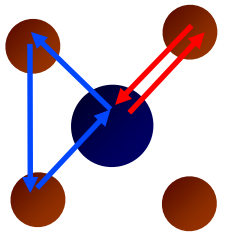
Multiple-Scattering Theory of XAFS

$$\mu(E) = \mu_0(E)\left[1 + \chi(E)\right]$$

μ can be factored in terms of an atomic background μ_0 and an oscillatory part χ

with $$\chi = \sum \chi_2 + \sum \chi_3 + \sum \chi_4 + \ldots$$

(SS) (3-leg) (4-leg)



For each path Γ:

$$\chi_\Gamma(k) = S_0^2 \frac{1}{kR_\Gamma^2} \left| f_\Gamma^{eff}(k) \right| e^{-2R_\Gamma/\lambda(k)} \sin\left[2kR_\Gamma + \Phi_\Gamma(k) + 2\delta_c(k)\right] e^{-2k^2\sigma_\Gamma^2}$$

$f_\Gamma^{eff}, \Phi_\Gamma$: *effective* scattering amplitude and phase of path Γ

R_Γ : *effective* path length (= $R_{tot}/2$)

σ^2_Γ : mean-square fluctuation in path Γ

FEFF code : Ankudinov *et al.* Phys. Rev. B **58**, 7565 (1998)

Theory of XAS: irreducible *n*-body contributions

$$\mu(E) = \mu_0 \left[1 + \sum_{i \neq 0} \chi_2^{0i0} + \sum_{\substack{i \neq j \\ i \neq 0, j \neq 0}} \chi_3^{0ij0} + \sum_{\substack{i \neq j \neq k \\ i \neq 0, k \neq 0}} \chi_4^{0ijk0} + \ldots \right]$$

(SS) (3-leg) (4-leg)

$$\mu(E) = \mu_0 \left[1 + \sum_{i} \underbrace{\gamma^{(2)}(0,i)} + \sum_{(i,j)} \underbrace{\gamma^{(3)}(0,i,j)} + \sum_{(i,j,k)} \underbrace{\gamma^{(4)}(0,i,j,k)} + \ldots \right]$$

two-body three-body four-body

$$\gamma^{(n)} = \mu^{(n)} / \mu_0$$

μ_0 : atomic cross-section

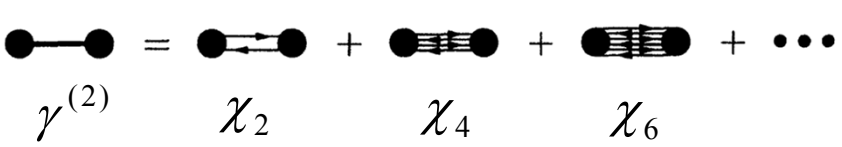
$\mu(0,i)$: cross-section of the structure including atoms 0 and *i* only

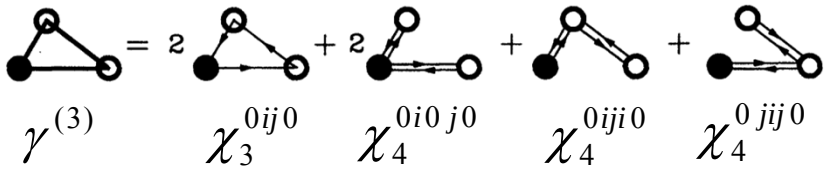
$\mu(0,i,j)$: cross-section of the structure including atoms 0, *i* and *j*

Irreducible *n*-body cross-sections:

$$\mu^{(2)}(0,i) = \mu(0,i) - \mu_0$$

$$\mu^{(3)}(0,i,j) = \mu(0,i,j) - \mu^{(2)}(0,i) - \mu^{(2)}(0,j) - \mu_0$$





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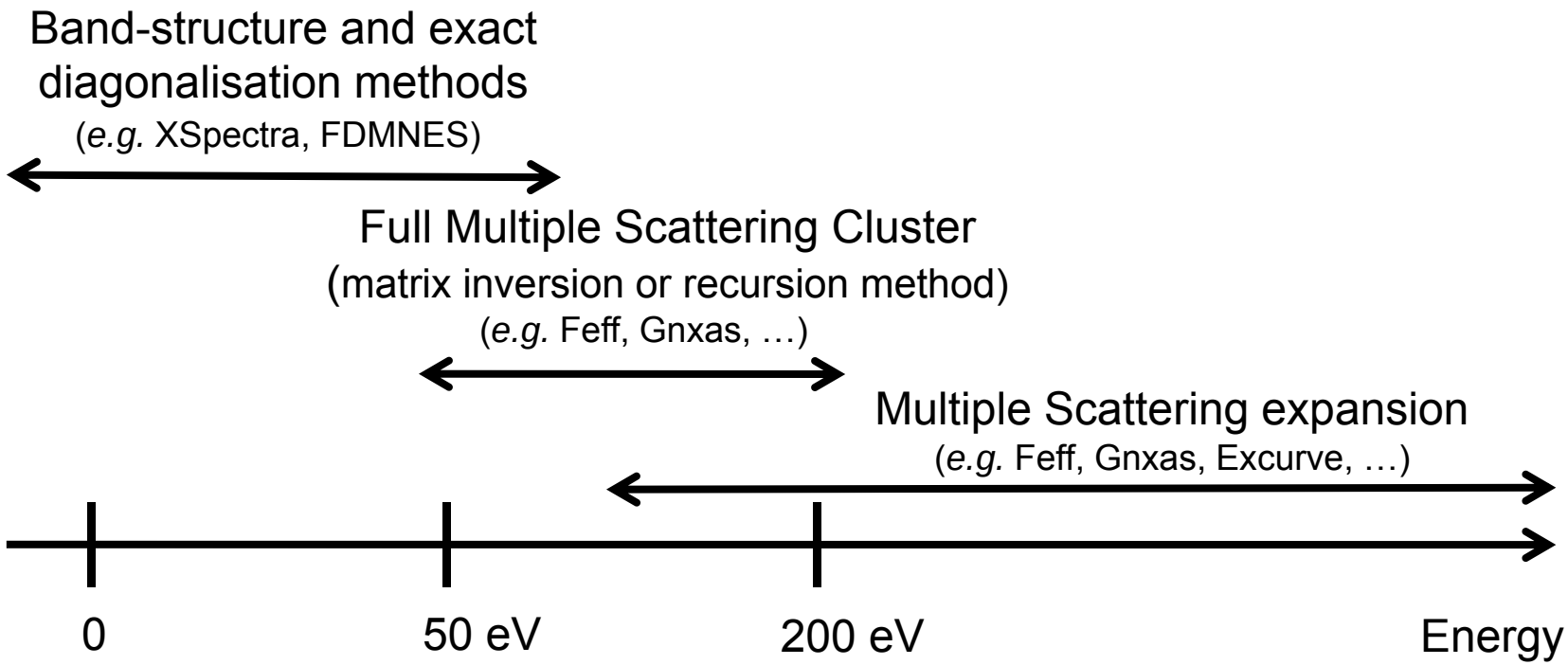
Theoretical approaches to XAS



Pros:
- accurate electronic charge densities and potentials
- accurate Fermi energy
- exact treatment of curved-wave effects and MS to all orders

Cons:
- computationally inefficient; nb of basis-set functions and orbital angular momentum components rapidly increase with E
- structural and electronic information not disentangled

Pros:
- computational efficiency
- geometrical interpretation of XAFS

Cons:
- untractable and inaccurate at low energies

Configurational average

using the *n*-body contributions

For a mono-atomic system:

$$\langle \chi(k) \rangle = 4\pi\rho \int_0^{R_{\max}} r^2 g_2(r) \gamma^{(2)}(k,r) dr$$

$$+ 8\pi^2 \rho^2 \int r_1^2 r_2^2 \sin(\phi) g_3(r_1, r_2, \phi) \gamma^{(3)}(k, r_1, r_2, \phi) dr_1 dr_2 d\phi$$

$$+ \ldots$$

with $\gamma^{(n)}$: irreducible *n*-body contributions

- the above configurational average is of general validity (crystals, glasses, liquids)
- the ability to probe g_n (n>2) is a unique feature of XAS
- however, the inversion of χ to get the g_n functions is a *ill-defined* problem

"The radial distribution function probed by x-ray absorption spectroscopy"
A. Filipponi, J. Phys.: Condens. Matter, **6**, 8415-8427 (1994)

Configurational average

using weak-disorder approximations

i) The *standard* EXAFS formula (don't use it!):

$$\langle \chi(k) \rangle = S_0^2 \sum_{shell\, i} \frac{N_i}{kR_i^2} \left| f_i\ (k) \right| e^{-2R_i / \lambda(k)} \sin\left[2kR_i + \Phi_i(k) + 2\delta_c(k)\right] e^{-2k^2\sigma_i^2}$$

N_i, R_i, σ^2_i : structural parameters of shell *i*

- valid only in the case of small and gaussian disorder

ii) Cumulant expansion of the prob. distribution p(r) (refrain from using it…):

$$\left\langle e^{i2k(r-R)} \right\rangle = \exp \sum_{n=0}^{\infty} \frac{(2ik)^n}{n!} \sigma^{(n)} = \exp(-W + i\Phi)$$

$$\sigma^{(1)} = \langle (r-R) \rangle$$
$$\sigma^{(2)} = \langle (r-R)^2 \rangle$$
$$\sigma^{(3)} = \langle (r-R)^3 \rangle$$

$$W(k) = 2\sigma^{(2)}k^2 - \tfrac{2}{3}\sigma^{(4)} + \ldots$$
$$\Phi(k) = 2k\sigma^{(1)} - \tfrac{4}{3}\sigma^{(3)}k^3 + \ldots$$

- valid only in the case of weak anharmonic disorder
- may produce unphysical distributions

Configurational average

using weak-disorder approximations

iii) Gamma-like distributions (gnxas)

$$p(r) = \frac{2}{\sigma|\beta|\Gamma(4/\beta^2)}\left(\frac{4}{\beta^2} + \frac{2(r-R)}{\sigma\beta}\right)^{(4/\beta^2)-1} \exp\left[-\left(\frac{4}{\beta^2} + \frac{2(r-R)}{\sigma\beta}\right)\right]$$

$\Gamma(4/\beta^2)$: Euler function

R, σ^2, β : average, variance and skewness ($\beta = C_3/\sigma^3$) of the distribution

Then, $<\chi>$ obtained using Taylor expansions for amplitudes and phases around the average distance R.

- not to be used for broad distributions (wider than ~ 1 Å)

Diffraction versus XAS

For a mono-atomic system:

Diffraction: $$S(k) = \frac{4\pi\rho}{k} \int_0^\infty r(g_2(r) - 1)\sin(kr)dr$$

- probes the full *r* range
- obeys the compressibility sum rule
- multi-component system : N(N+1)/2 partials contributing

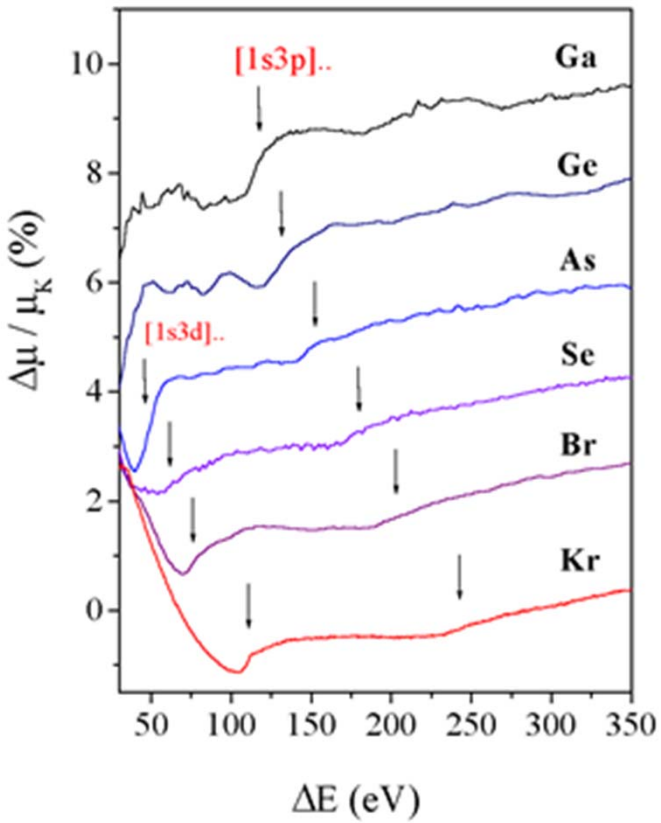
XAS: $$\chi(k) = 4\pi\rho \int_0^{R_{\max}} r^2 g_2(r)\gamma^{(2)}(k,r)dr$$

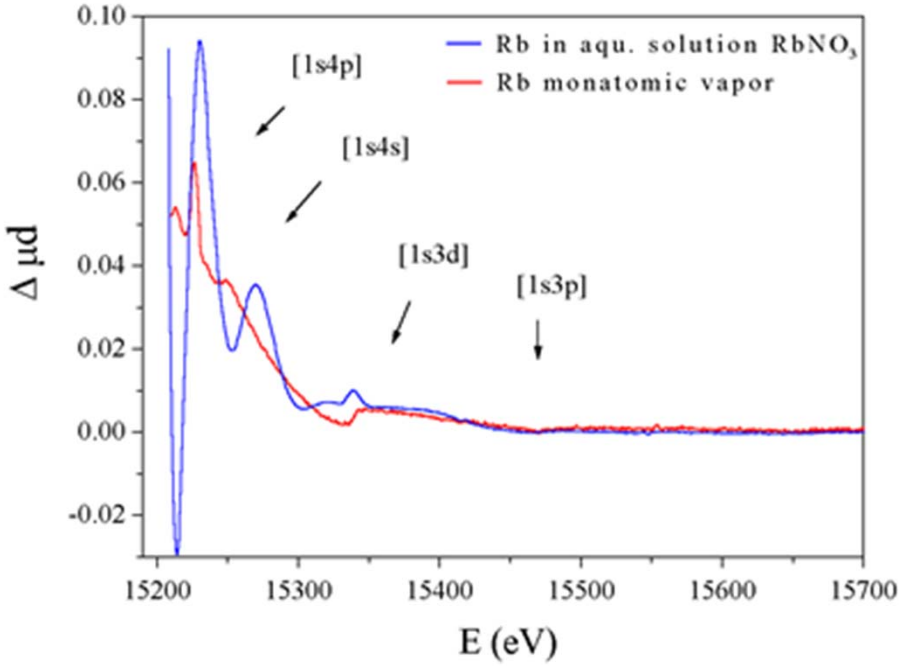
with $$\gamma^{(2)} = A(k,r)\sin(2kr + \phi\ (k,r))$$

- short-sighted ($R_{max} \sim \lambda$)
- EXAFS $k \cong$ twice Diffraction k
- multi-component system : N partials contributing

"The radial distribution function probed by x-ray absorption spectroscopy"
A. Filipponi, J. Phys.: Condens. Matter, **6**, 8415-8427 (1994)

Multi-electronic excitations





Taken from http://www.p-ng.si/~arcon/xas

- positions in energy are well-known but not their shape and intensity (~ few %).
- taken into account empirically (usually by arc-tangent like functions).
- shake-up, shake-off resonances produce an amplitude reduction factor S_0^2

with respect to the *one-electron* calculation.

MD/MC simulations:

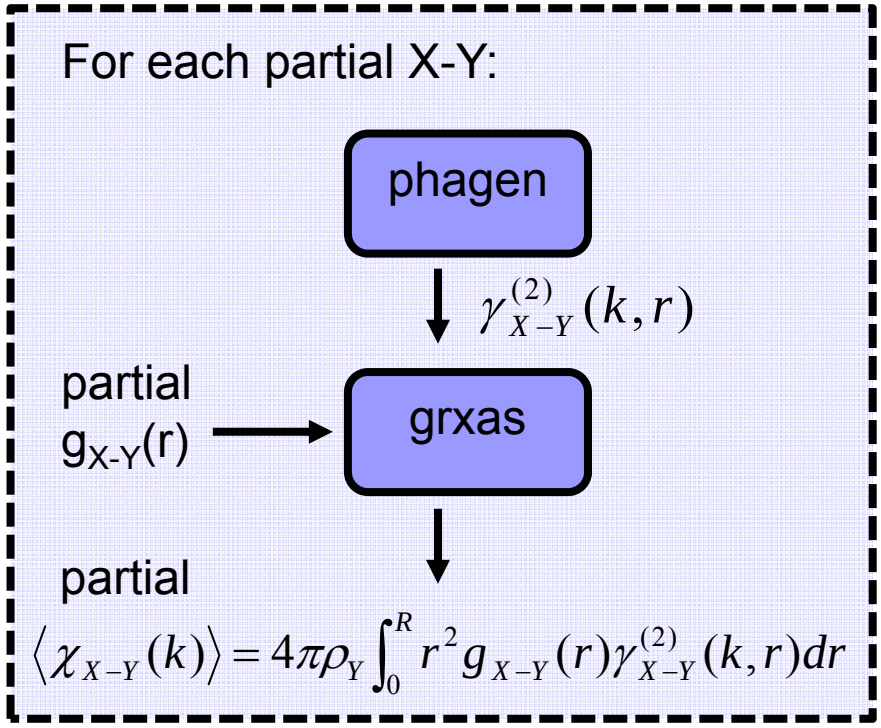
✓ To sample the system phase space and get an *energetically constrained* model

✓ To assist the XAS analysis :

- in a complex system : which species are contributing to the XAS signal and how
- configurational average (intrinsic account of the disorder)
- avoids the proliferation problem of fitting parameters:
  all structural parameters are fixed by the model (only two unknowns: ΔE_0 and S_0^2)
- to provide an initial model which may be refined (e.g. RMC/EPSR, gnxas)
- to probe the data sensitivity

✓ To get information beyond the first shells of neighbours

Configurational average from the *n*-body distributions: in practice



Pros:
- staighforward calculation (very fast)
- straightforward evidence of each atomic type contribution

Cons:
- cumbersome for *n*-body contributions > 2

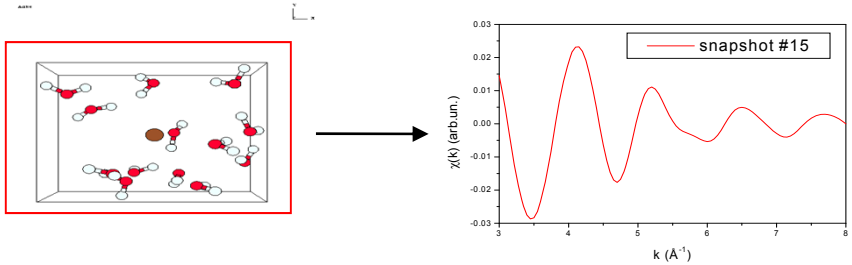
Then, summation over the partials to get the total signal:

$$\langle \chi_X(k) \rangle = \sum_Y \langle \chi_{X-Y}(k) \rangle$$

The Gnxas package: free but not open-source

Configurational average from a series of paths

MS paths average over a clusters ensemble



For each absorbing atom in each snapshot:

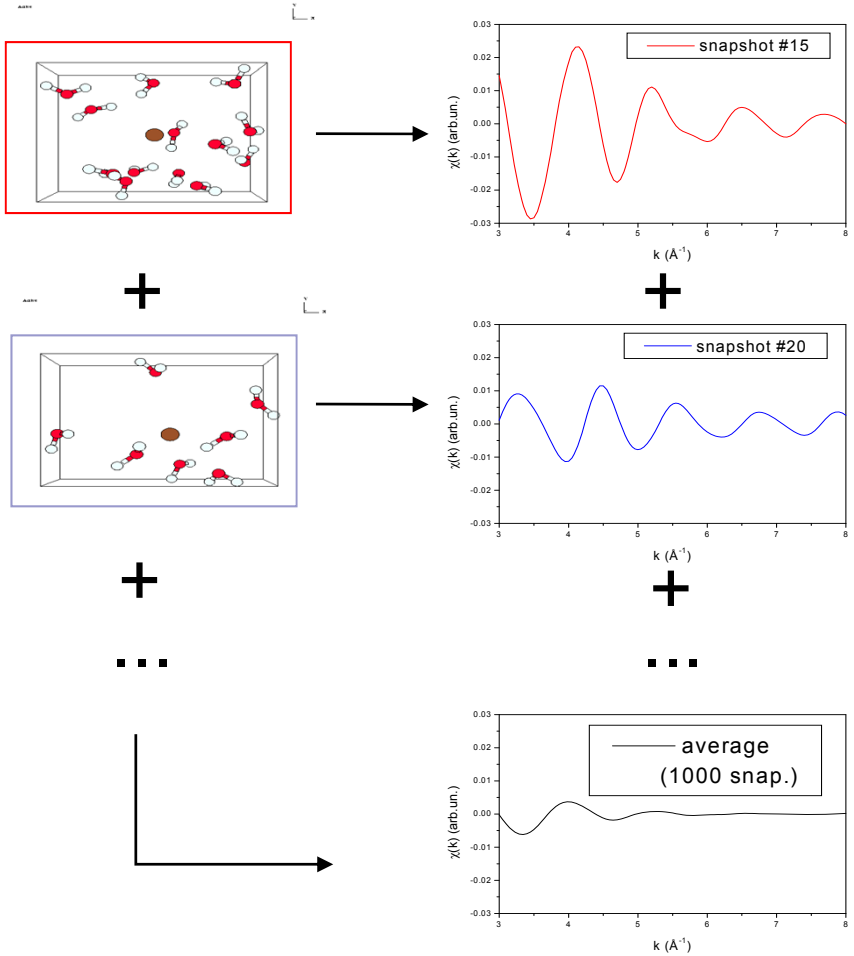
$$\chi^{cluster}(k) = \sum_{\Gamma} \frac{1}{kR_{\Gamma}^{2}} \left| f_{\Gamma}^{eff}(k) \right| e^{-2R_{\Gamma}/\lambda(k)} \sin\left[2kR_{\Gamma} + \Phi_{\Gamma}(k)\right]$$

- Note that $\sigma = 0$ in $\chi^{cluster}$

"Direct Modelling of EXAFS Spectra from Molecular Dynamics Simulations", Bruce J. Palmer, David M. Pfund, John L. Fulton, J. Phys. Chem. **100** 13393-13398 (1996)

Configurational average from a series of paths

MS paths average over a clusters ensemble



For each absorbing atom in each snapshot:

$$\chi^{cluster}(k) = \sum_{\Gamma} \frac{1}{kR_{\Gamma}^{2}} \left| f_{\Gamma}^{eff}(k) \right| e^{-2R_{\Gamma}/\lambda(k)} \sin\left[2kR_{\Gamma} + \Phi_{\Gamma}(k)\right]$$

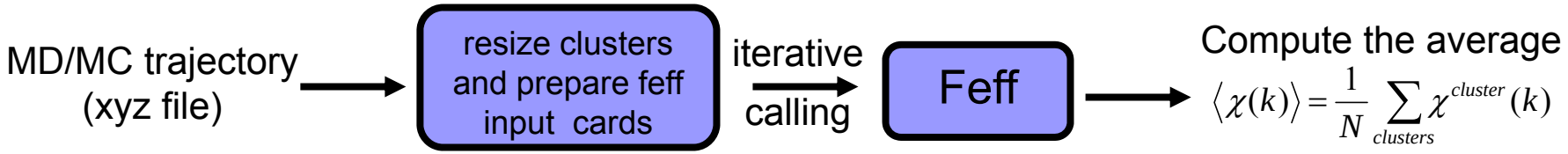
- Note that $\sigma = 0$ in $\chi^{cluster}$

- $N_{cluster} = N_{abs} * N_{snapshot}$

$$\left\langle \chi(k) \right\rangle = \frac{1}{N} \sum_{clusters} \chi^{cluster}(k)$$

"Direct Modelling of EXAFS Spectra from Molecular Dynamics Simulations", Bruce J. Palmer, David M. Pfund, John L. Fulton, J. Phys. Chem. **100** 13393-13398 (1996)

Configurational average from a set of clusters: in practice



Pros:

- easy to evidence the MS contributions
- allows to study the influence of fluctuations (space/time)
- allows a site-by-site study

Cons:

- need a lot of clusters for convergence (~ 100 – 10000)

(Each non-SCF calculation ~ 1 mn; each SCF calculation ~ 20 mn)

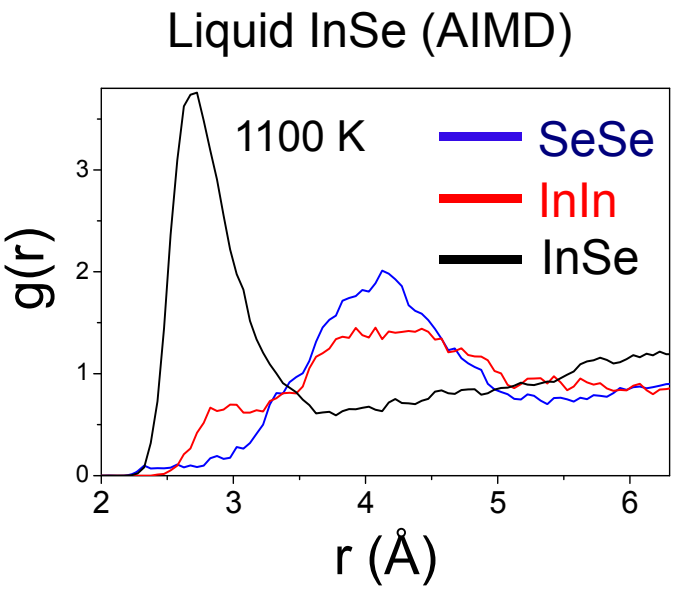
- the identification of the contribution from a given atomic type of neighbours is not straightforward

The Feff code: open-source but not free

Feff input card :

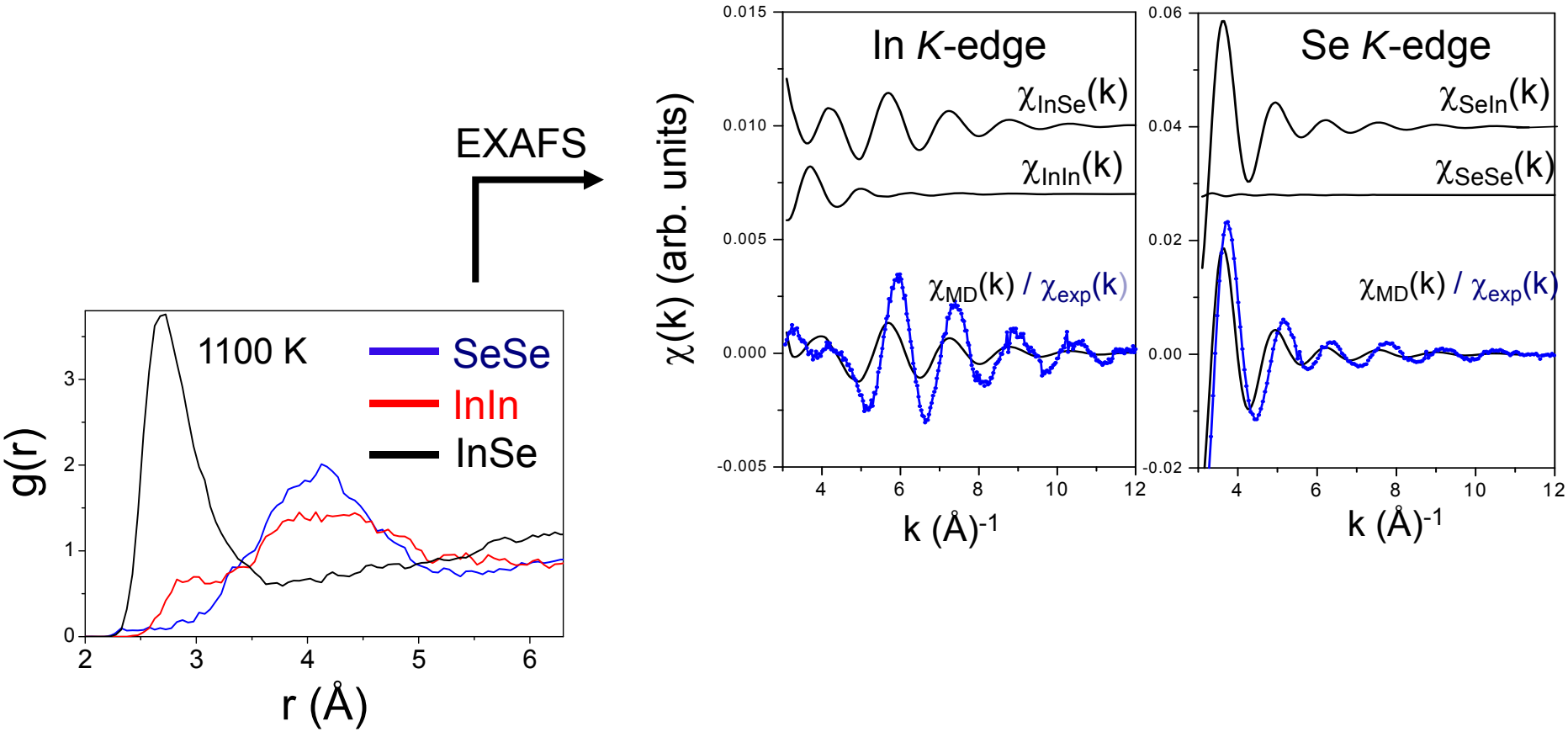
```
TITLE  B2O3
FMS    5.4
SCF  2.
XANES 3.5 0.02 0.1
EXCHANGE  0  15.0  0.
* INTERSTITIAL  0  1.54

HOLE 1    1.0      1=k edge, s0^2=1.0

*          mphase,mpath,mfeff,mchi
CONTROL  1  1  1  1  1  1
PRINT  1  1  1  1  1  1
*EXCHANGE  0  0.0  1.0

*RPATH  6.00
*NLEG 6
*CRITERIA  0.0  0.0

*CFAVERAGE  1  0  0

POTENTIALS
      0     8   O
      1     5   B
      2     8   O

ATOMS
  0.0000  0.0000  0.0000   0        0.0000
  1.4471 -2.5124  0.5889   1        2.9585
  2.4620  1.2119  2.1127   1        3.4632
  0.8030 -0.2017  1.0141   1        1.3092
 -2.5546  1.1179  0.0400   1        2.7888
  1.6372 -3.3372 -1.5782   1        4.0383
  1.2655 -1.4588  1.3792   2        2.3731
  0.2835 -1.3982  4.8152   2        5.0221
  4.0443 -0.2331 -1.5382   2        4.3332
 -2.9343 -0.0511  3.4524   2        4.5312
  6.3408 -2.6830  1.8606   2        7.1320
 -6.3712 -2.7319 -2.6600   2        7.4250
  4.9827 -1.5803  0.2125   2        5.2316
  3.9690  3.3181 -2.9755   2        5.9679
 -5.9054  4.5961  1.7051   2        7.6749
 -4.0397  5.2007  0.1859   2        6.5879
 -3.4902 -6.3865  1.1689   2        7.3712
 -3.7613  4.0487  2.2324   2        5.9601
  4.9661  4.4801 -1.1787   2        6.7914
END
```

Refining the initial (MD) model



G. Ferlat *et al.* Phys. Rev. B, **69**, 155202 (2004)

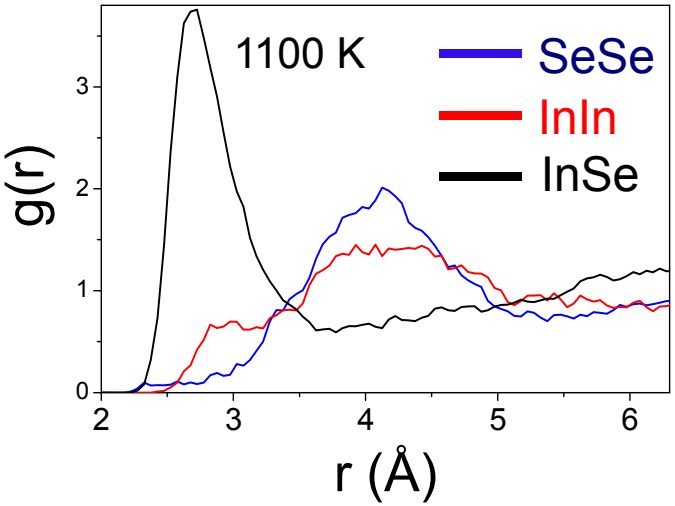
Refining the initial (MD) model

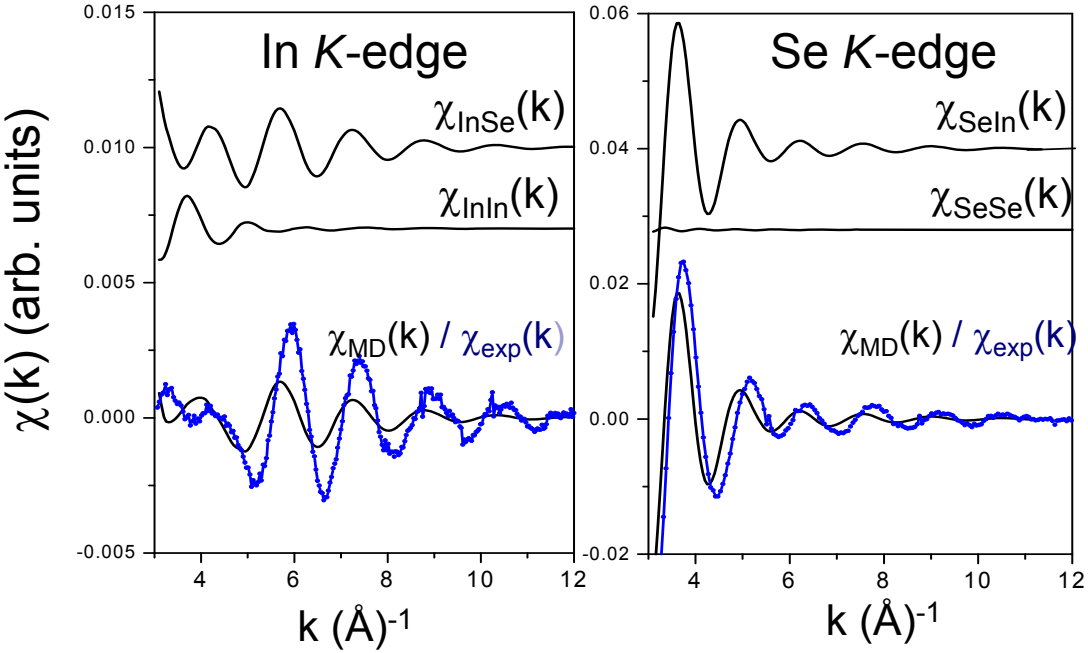


G. Ferlat *et al.* Phys. Rev. B, **69**, 155202 (2004)

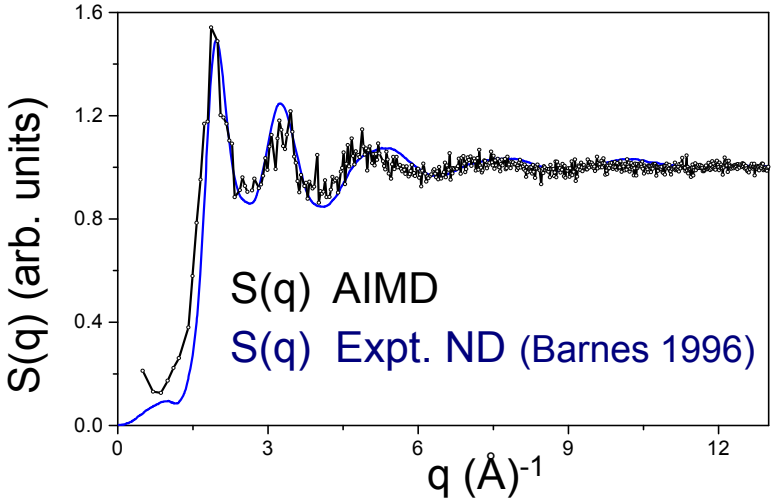
Refining the initial (MD) model

EXAFS





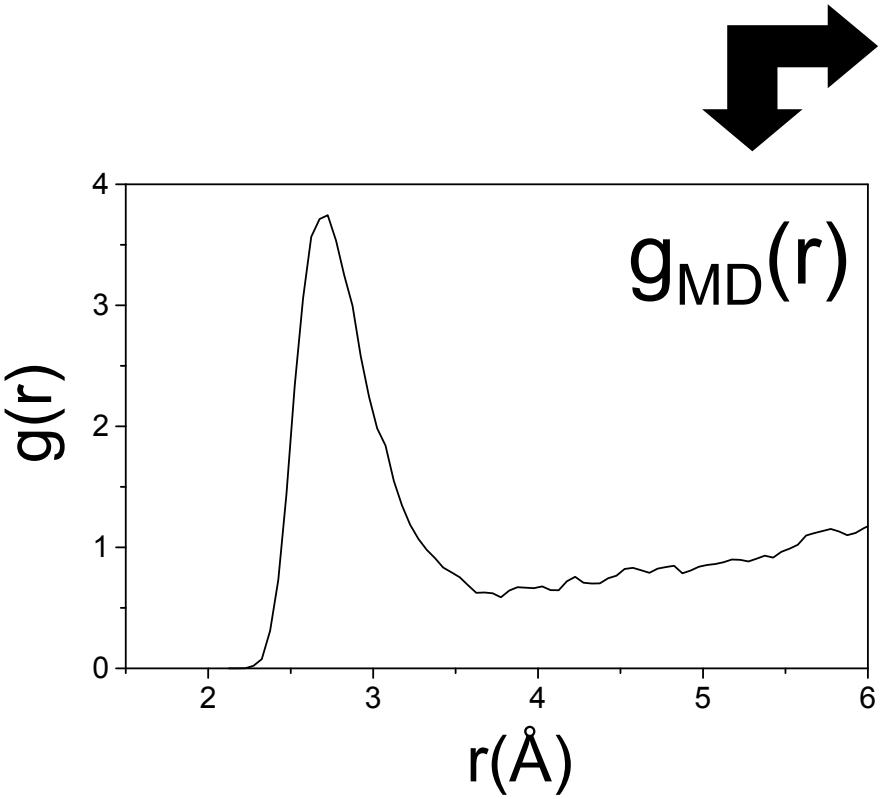
ND

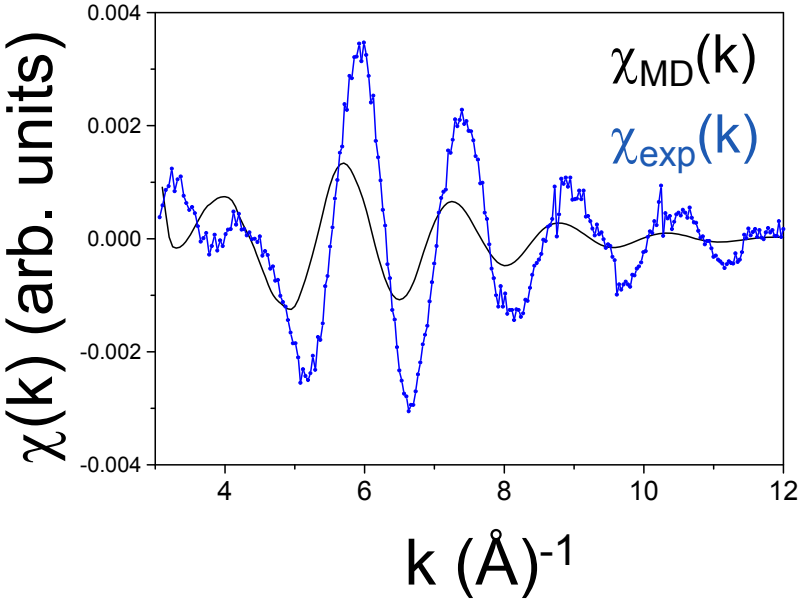


✓The initial model (AIMD) needs to be refined

G. Ferlat *et al.* Phys. Rev. B, **69**, 155202 (2004)

Refining the initial (MD) model: g(r) refinement (using gnxas)

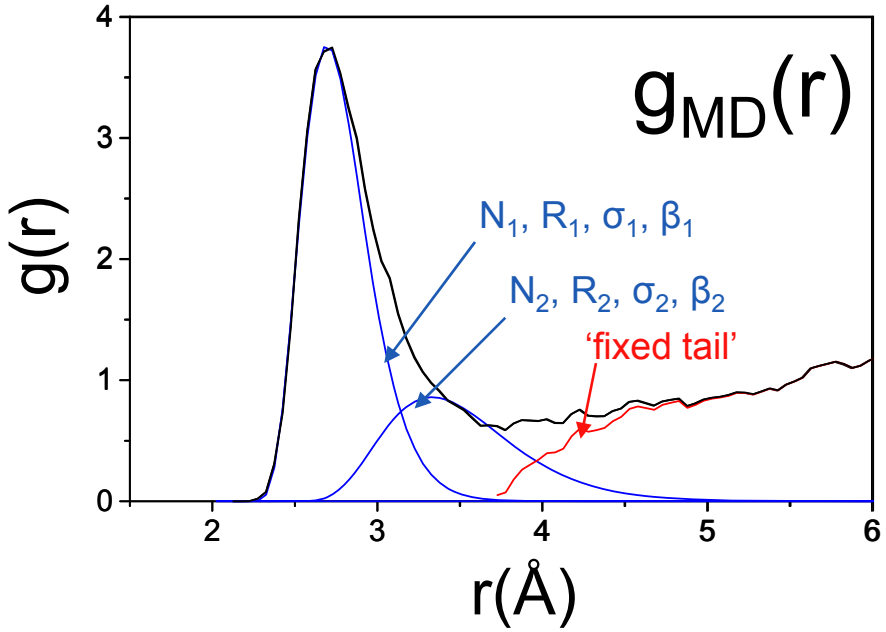




✓The initial model g(r)'s (which do not well reproduce the XAS data)

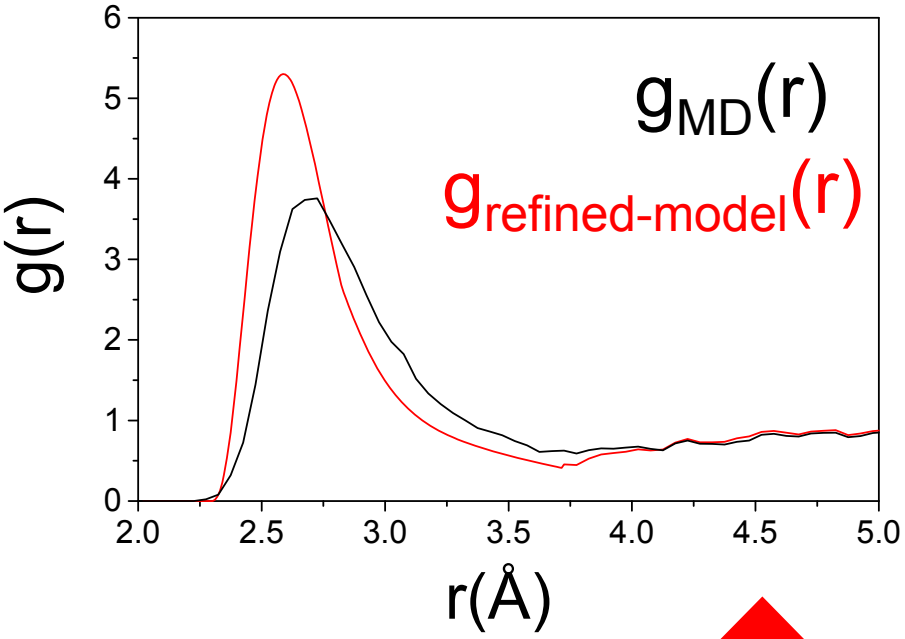
...

Refining the initial (MD) model: g(r) refinement (using gnxas)

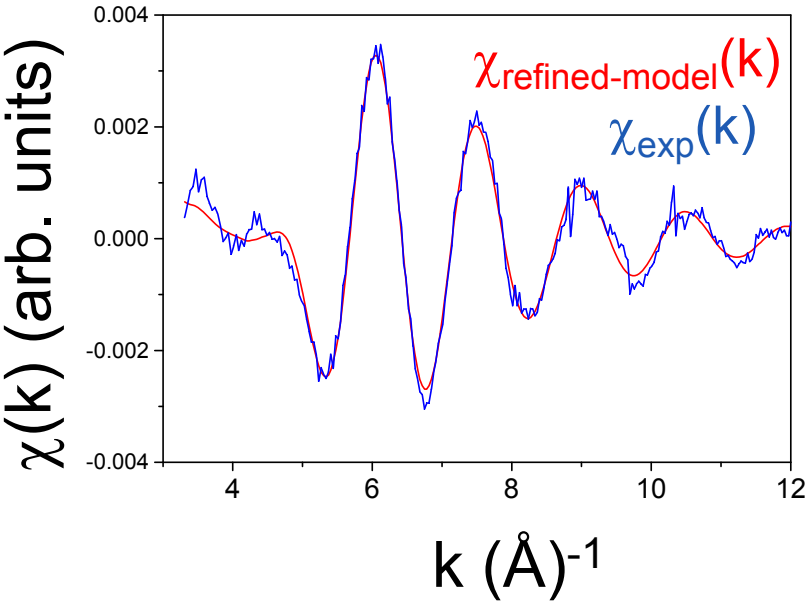


✓... are decomposed into short-range peaks plus a long-range tail. The parameters describing the short-range peaks are then freed in a fitting procedure ...

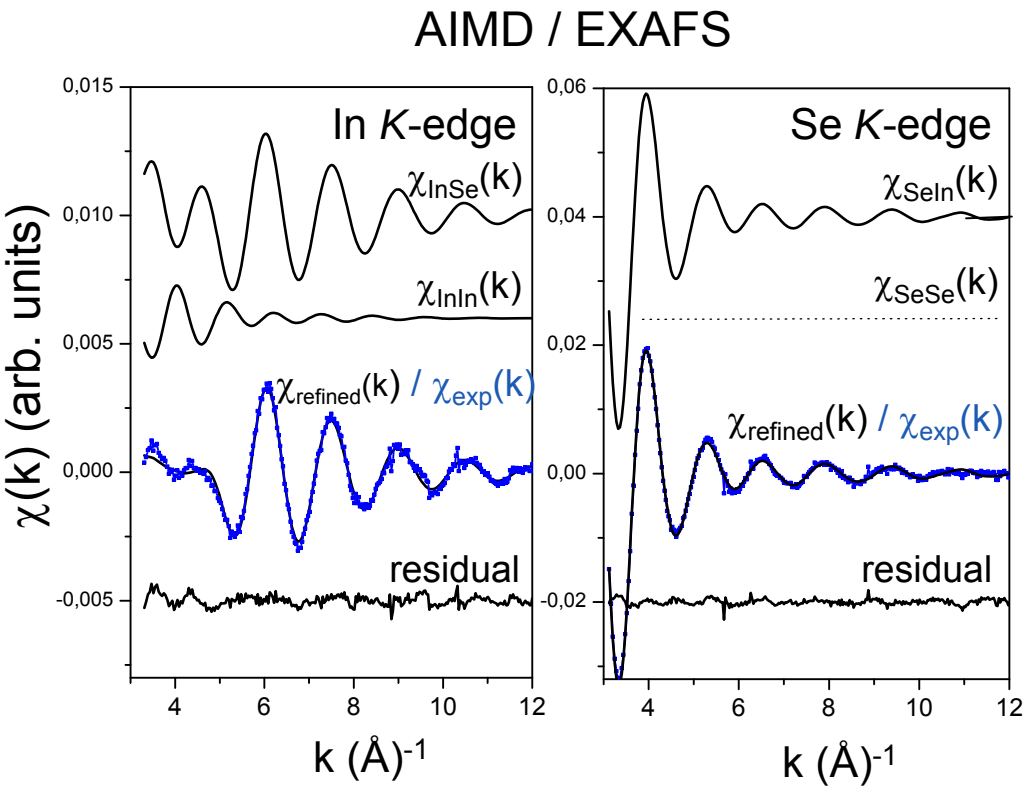
Refining the initial (MD) model: g(r) refinement (using gnxas)



✓... until agreement is achieved between the experimental $\chi_{exp}(k)$ and the XAS signal computed from the refined model $\chi_{refined\text{-}MD}(k)$.



Refining the initial (MD) model: g(r) refinement (using gnxas)



Multiple-edge analysis :

$$\chi_{In}(k) = \chi_{In-Se}(k) + \chi_{In-In}(k)$$

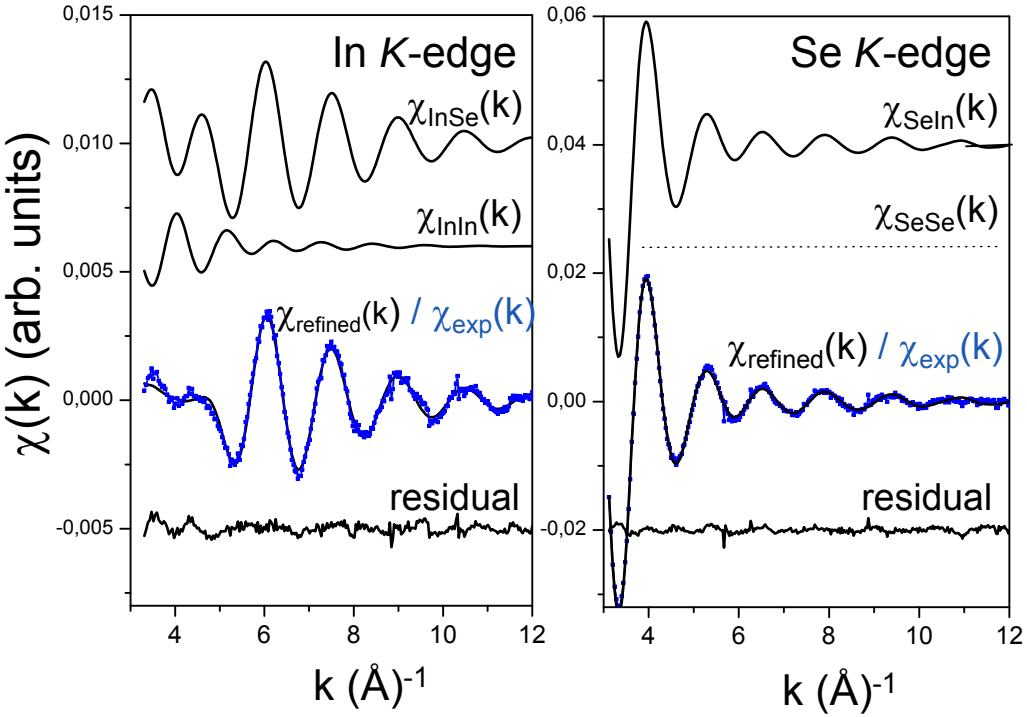
$$\chi_{Se}(k) = \chi_{Se-In}(k) + \chi_{Se-Se}(k)$$

✓better constrain of the In-Se contribution

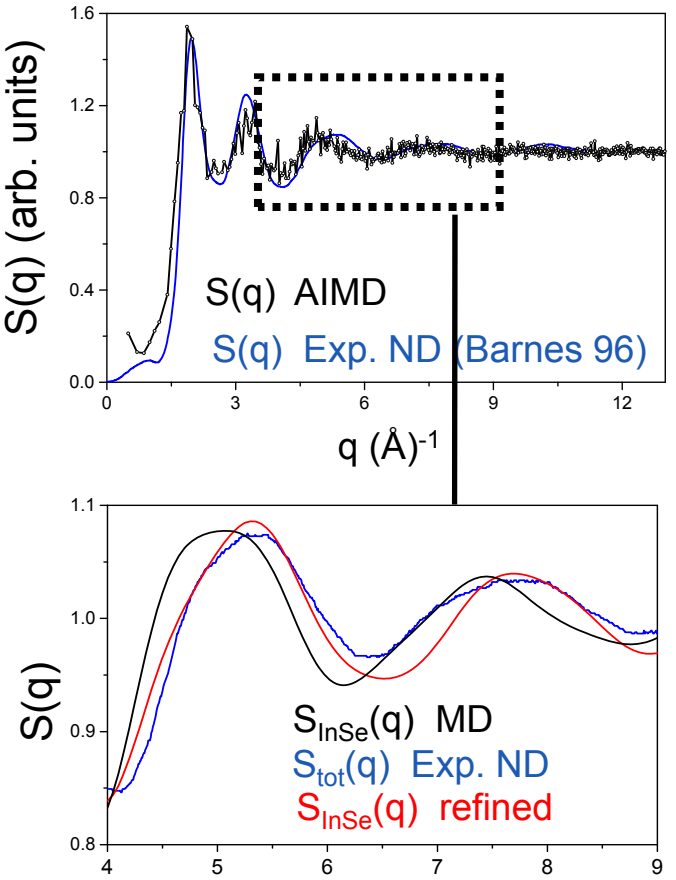
✓The refinement can be driven by a multiple-edge fitting of the XAS data

Refining the initial (MD) model: g(r) refinement (using gnxas)

AIMD / EXAFS



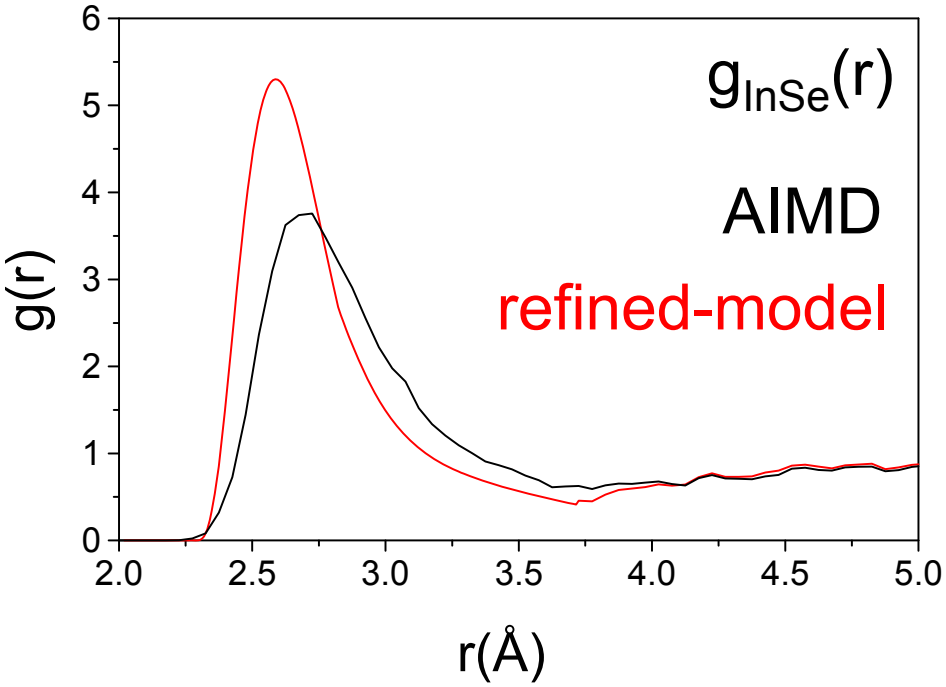
AIMD / ND



✓The refinement (which was driven by XAS only) is validated *a posteriori* by the ND data.

G. Ferlat *et al.* Phys. Rev. B, **69**, 155202 (2004)

Refining the initial (MD) model: g(r) refinement (using gnxas)



More on the methodology, see:

- A. Filipponi, J. Phys.: Condens. Matter, **6**, 8415-8427 (1994)
- P. D'Angelo *et al.*, J. Chem. Phys. **100**, 985 (1994)
- A. Trapananti & A. DiCicco, Phys. Rev. B, **70**, 014101 (2204)

Drawback of this method:

• empirical refinement of the g(r) shape: the microscopic 3-D information is lost

-> RMC-GnXAS: A. Di Cicco *et al.* Phys. Rev. Letters (2003)

Refining the model: RMC/EPSR

First RMC-XAS: S. J. Gurman, R. McGreevy, J. Phys. : Condens. Matter, **2**, 9463 (1990)

RMC should not be driven by XAS only. It should include long-range constraints such as diffraction data :

A. Di Cicco *et al.*, Phys. Rev. Letters, **91**, 135505 (2003): RMC-GnXAS(ND+EXAFS)
M. V. Coulet *et al.,* Phys. Rev. B, **72**, 174209 (2005) : RMC(ND + EXAFS)
D. T. Bowron, Pure Appl. Chem., **80**, 1211 (2008): EPSR(ND/XRD + EXAFS)
…

MD-XAS studies of liquids and glasses: selected examples

I) Zr environment in borosilicate glasses (weak disorder, multi-component system, many-body contributions)

II) Ions in aqueous solutions (strong disorder)

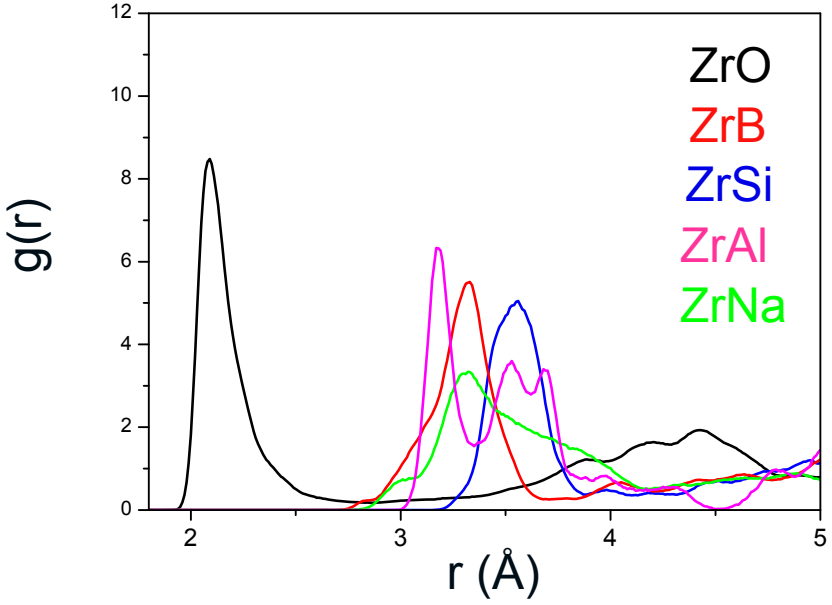
Environment of Zr in borosilicate glasses

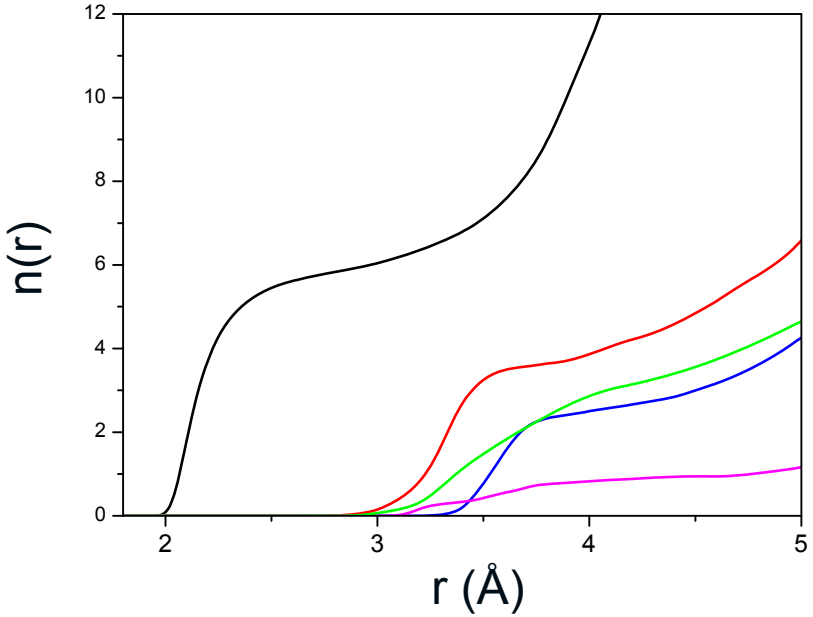
SiO_2-B_2O_3-Na_2O-Al_2O_3-ZrO_2
(40% - 30% - 20% - 5% - 5%)

- Empirical MD simulations:

Born-Mayer-Huggins (BMH) potentials + 3-body terms (on network formers)

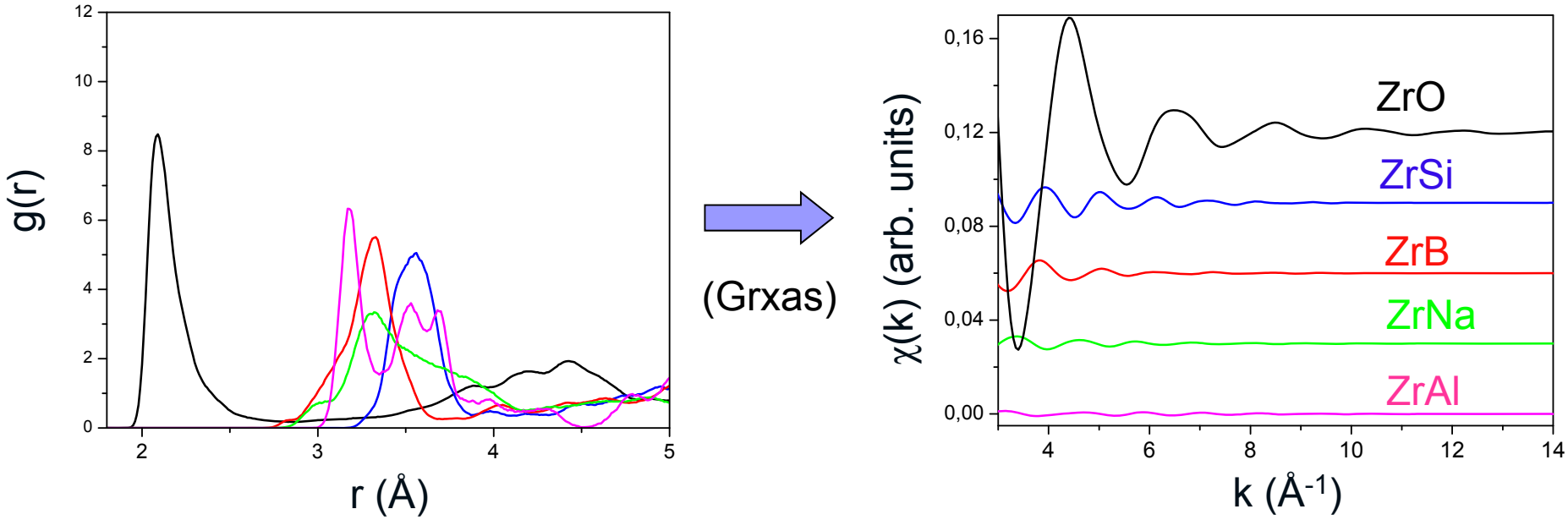
Time step: 1 fs ; Equilibration at 300 K: 70 ps
N = 2400 atoms; Box length ~ 30 Å





Environment of Zr in borosilicate glasses

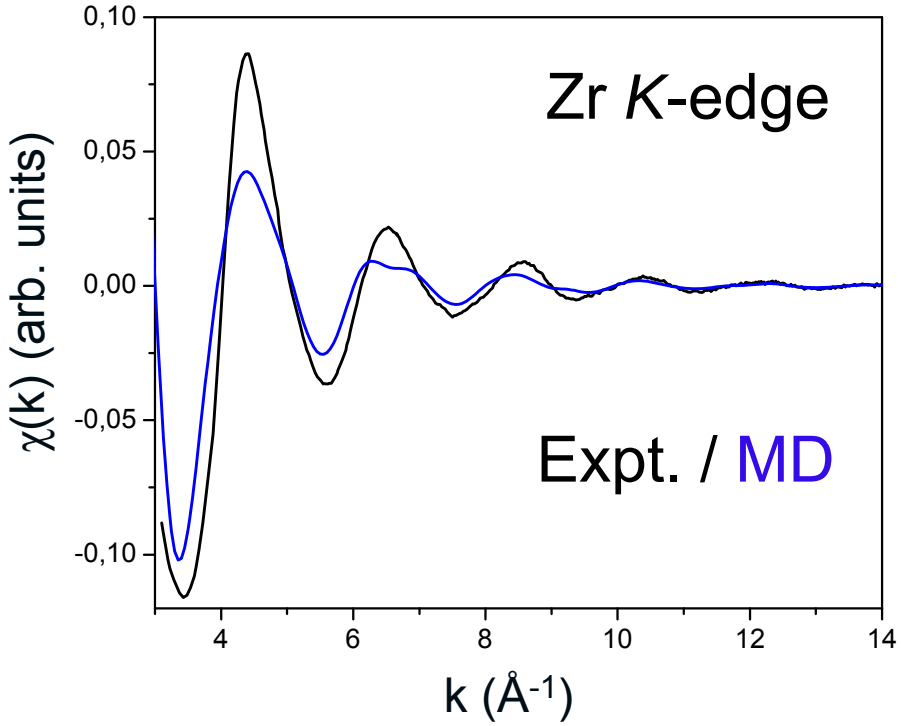
- MD-EXAFS calculations:



✓ MD simulations allow to evidence the dominant contributions to the XAS signal

Environment of Zr in borosilicate glasses

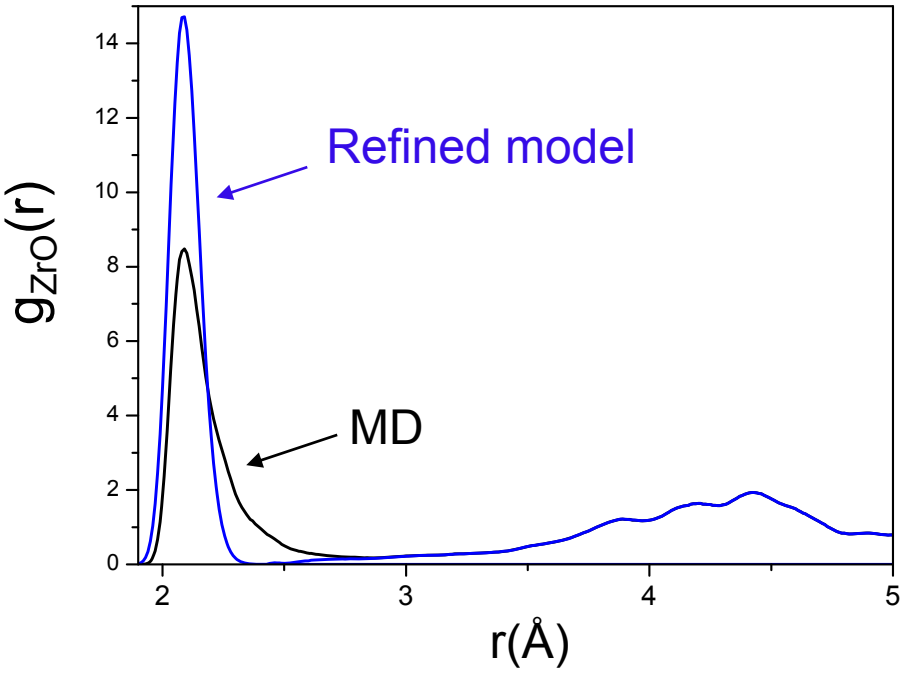
- MD-EXAFS versus Expt.:



✓ Qualitative agreement. The MD structural model needs to be refined

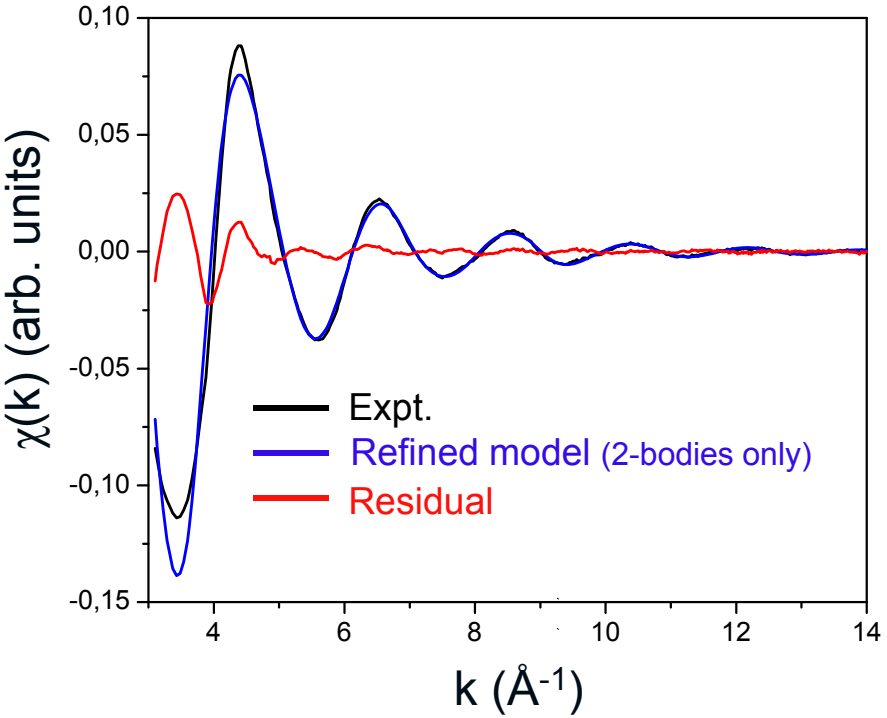
Environment of Zr in borosilicate glasses

- Refining the MD model



✓ Sharp 1^{rst} peak in the Zr-O distribution

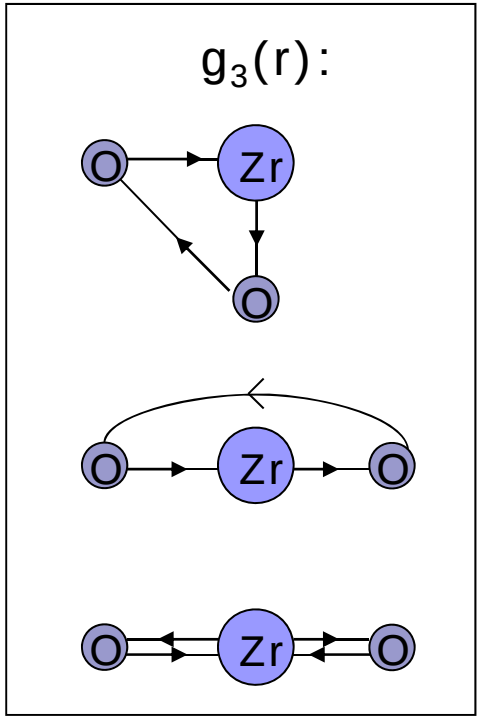
✓ N_{ZrO} ~ 6 ⟶ ZrO_6 octahedra

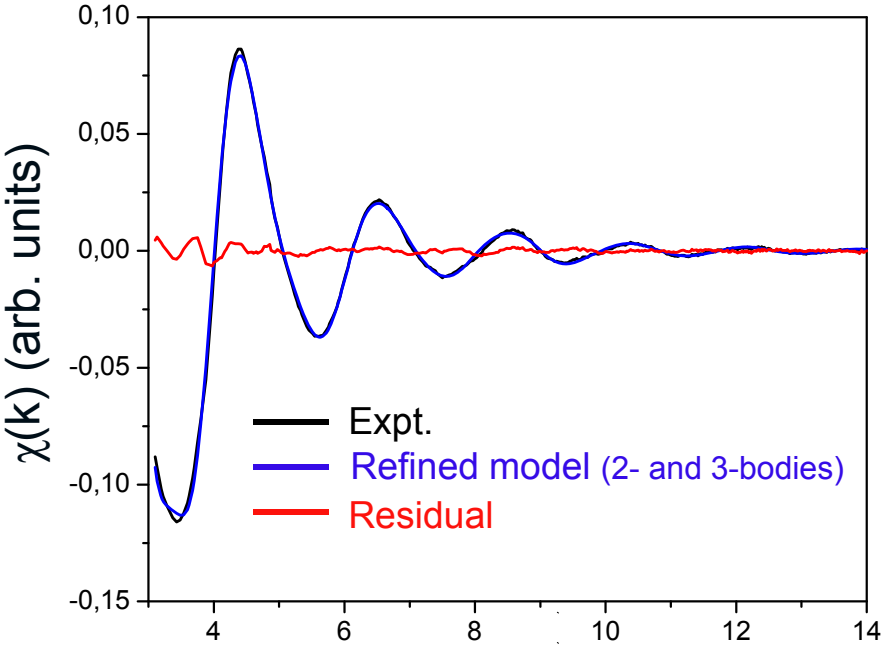


✓ Significant residual:
evidence for three-body contributions

Environment of Zr in borosilicate glasses

- Refining the MD model

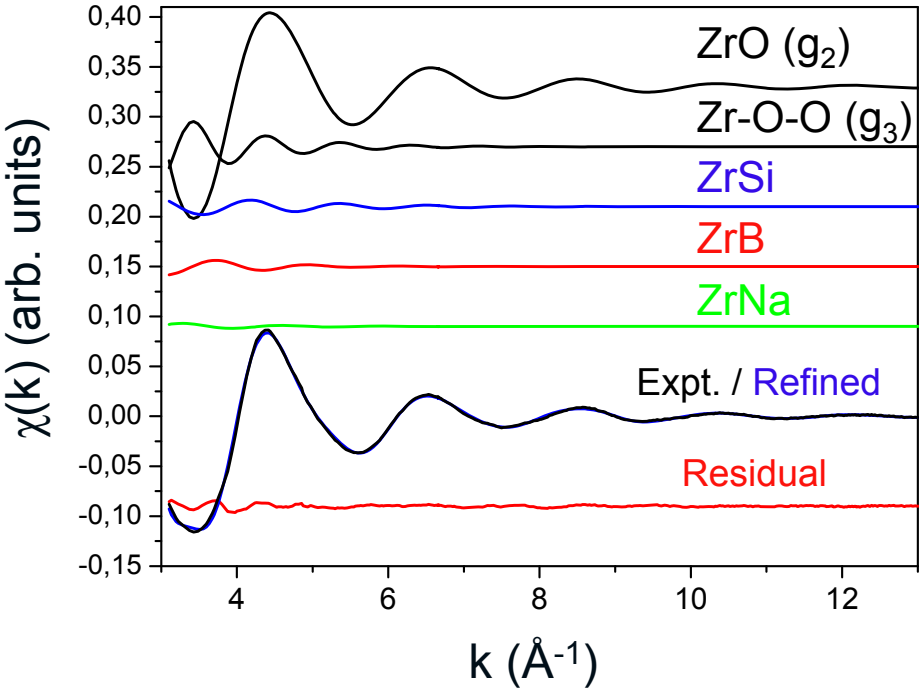


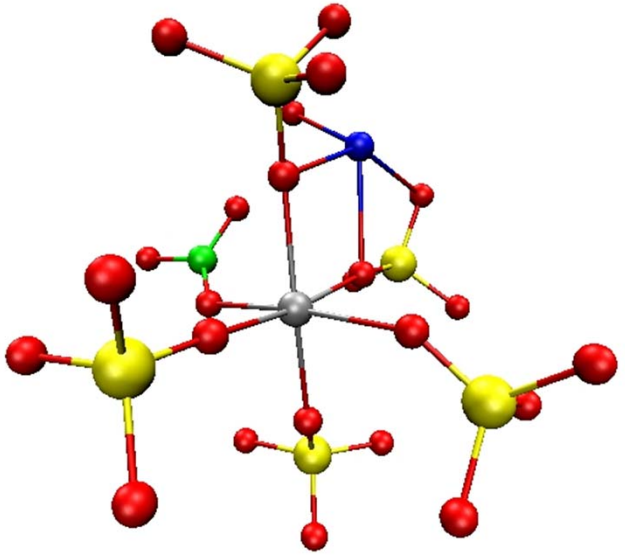


✓ Significant three-body contributions from intra-octahedra paths

Environment of Zr in borosilicate glasses

- Refining the MD model



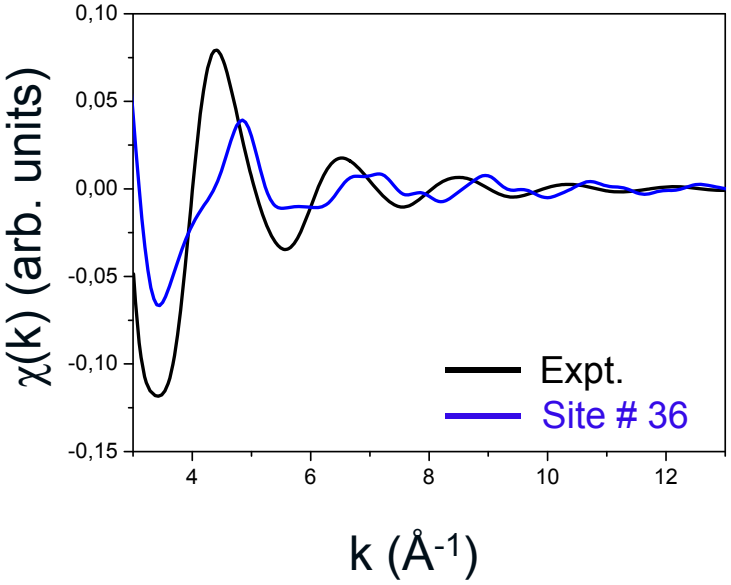


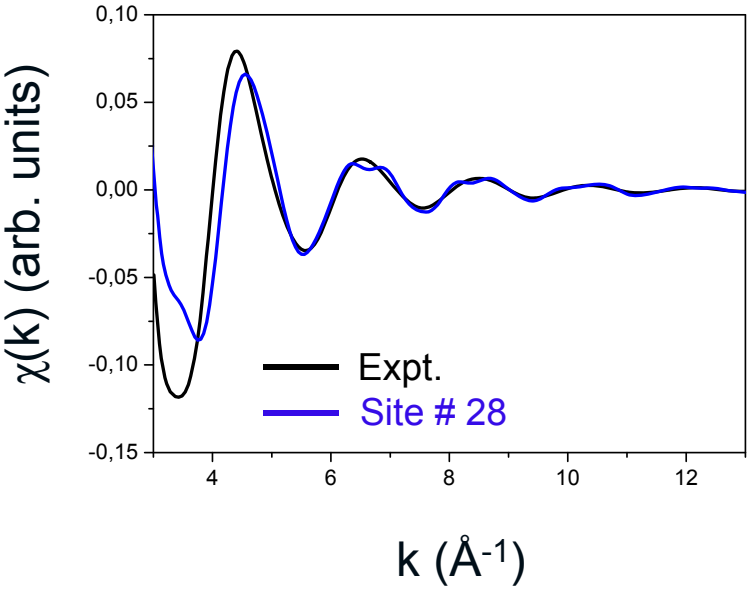
✓ The 3-body contributions are larger than the 2nd shells 2-bodies signals
✓ Determining the next-nearest neighbours distributions from XAS is still challenging

G. Ferlat *et al.*, Phys. Rev. B, **73**, 214207 (2006)

Environment of Zr in borosilicate glasses

Site by site inspection of the individual spectra:





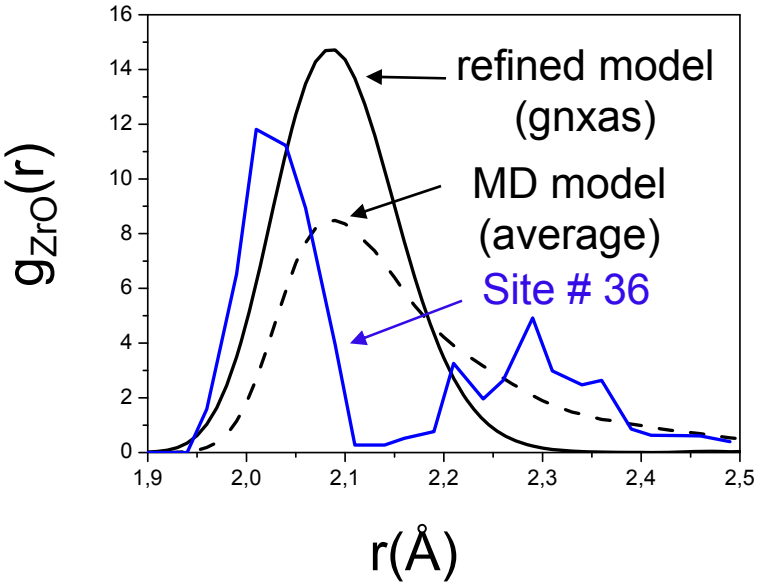
"bad" site

"good" site

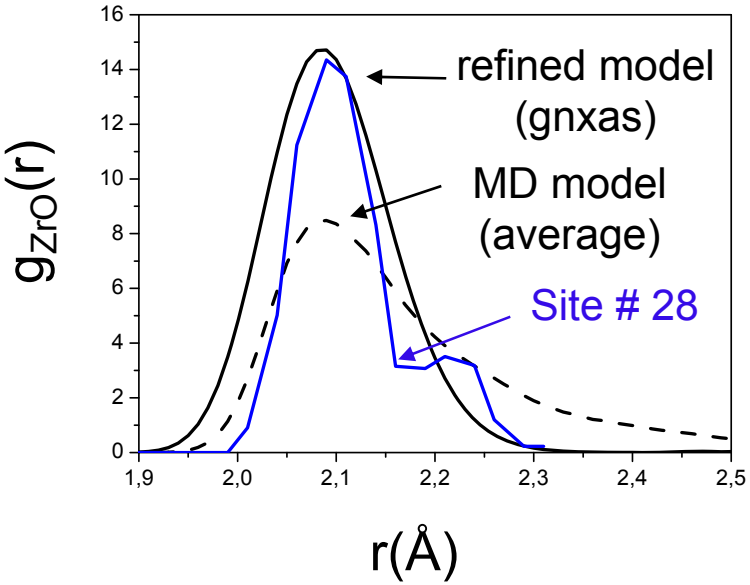
Moderately disorded environment: an individual site by site analysis is possible.

Environment of Zr in borosilicate glasses

Site by site inspection of the radial distribution functions:



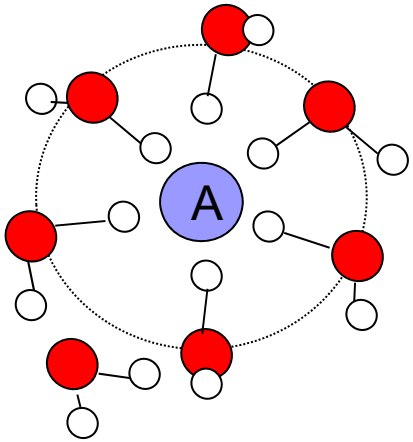
“bad” site



“good” site

The site by site analysis corroborates the g(r) refinement.

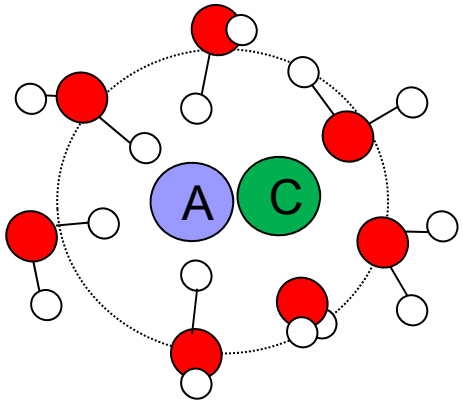
Ions in aqueous solutions: hydration



	Ambient	*Supercritical*
Simulations: (NaCl)	n ~ 6	**~ 6**
Expt (EXAFS):[(1)] (RbBr)	n ~ 7	~ 2

1) S.L. Wallen et al., J. Phys. Chem., **101**, 9632 (1997)

Ions in aqueous solutions: complexation



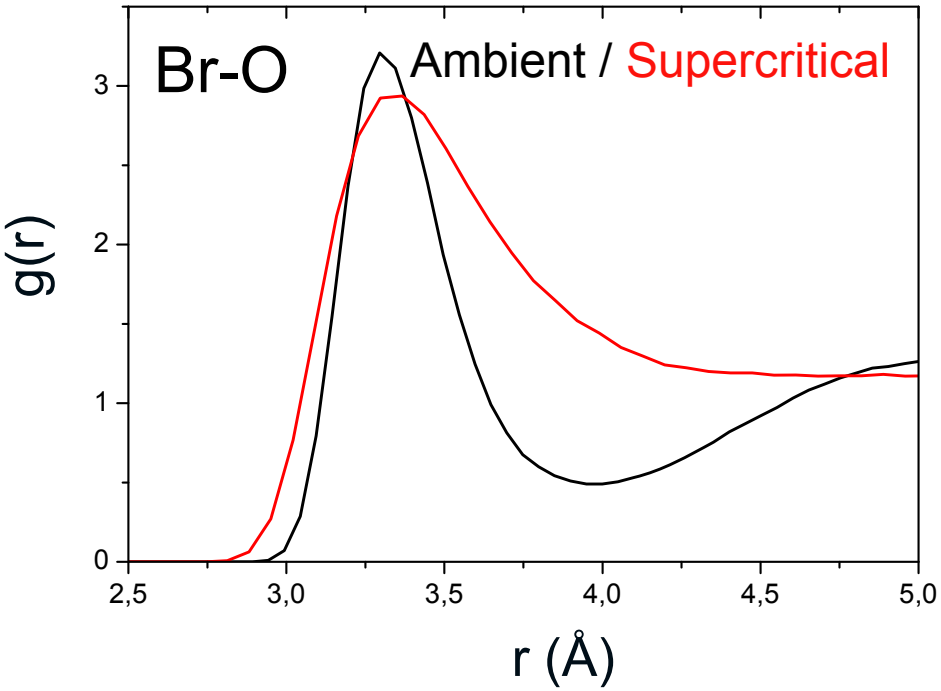
	Ambient	*Supercritical*
Simulations: (NaCl)	~ 0	30%[2]
Expt (EXAFS):[1] (RbBr)	~ 0	0 ? (m=0.02-1.5 kg/mol)

1) S.L. Wallen et al., J. Phys. Chem., **101**, 9632 (1997)

2) E. Oelkers, H. Hegelson, Science, **261**, 888 (1993)

Ions in aqueous solutions: hydration

- MD simulations of diluted 1:1 aqueous electrolytes



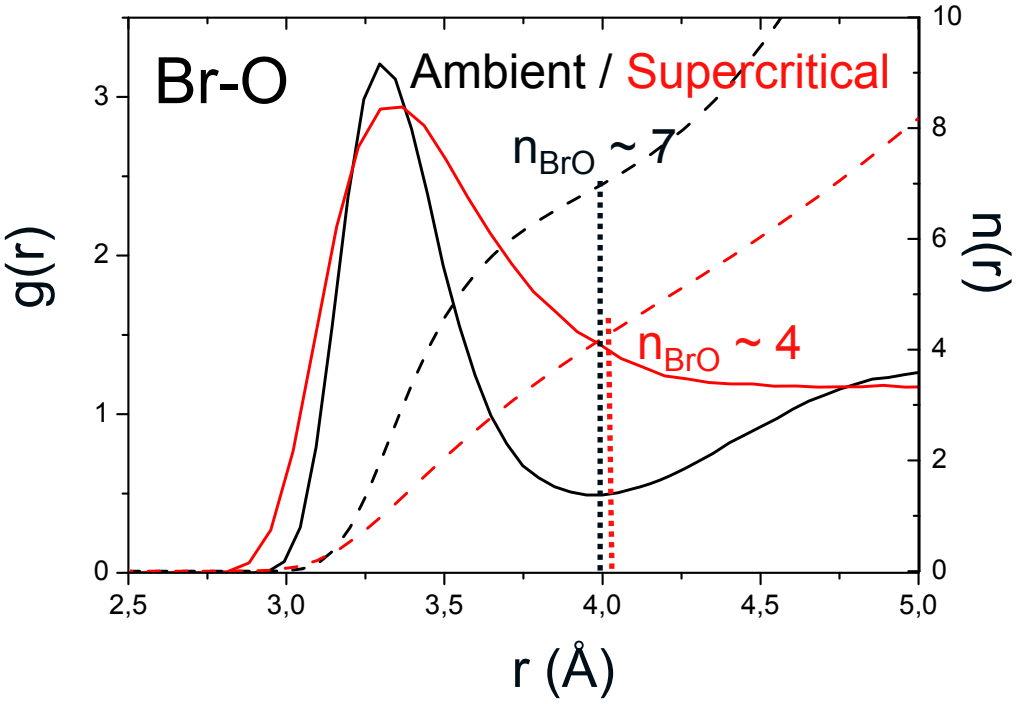
$(RbBr)_{0.4}$ - $(H_2O)_{99.6}$ (m=0.2)

Ambient: ρ ~ 1. g.cm^{-3}, T = 30°C
Supercritical: ρ ~ 0.4 g.cm^{-3}, T = 450°C
potentials: LJ + Coulomb (ions);
SPC/E (water)
Box size: 452 H_2O + 2 RbBr pairs
Time step: 2 fs
Simulation duration: ~ 1 ns

✓ Expansion of the first hydration shell in supercritical conditions

Ions in aqueous solutions: hydration

- MD simulations of diluted 1:1 aqueous electrolytes



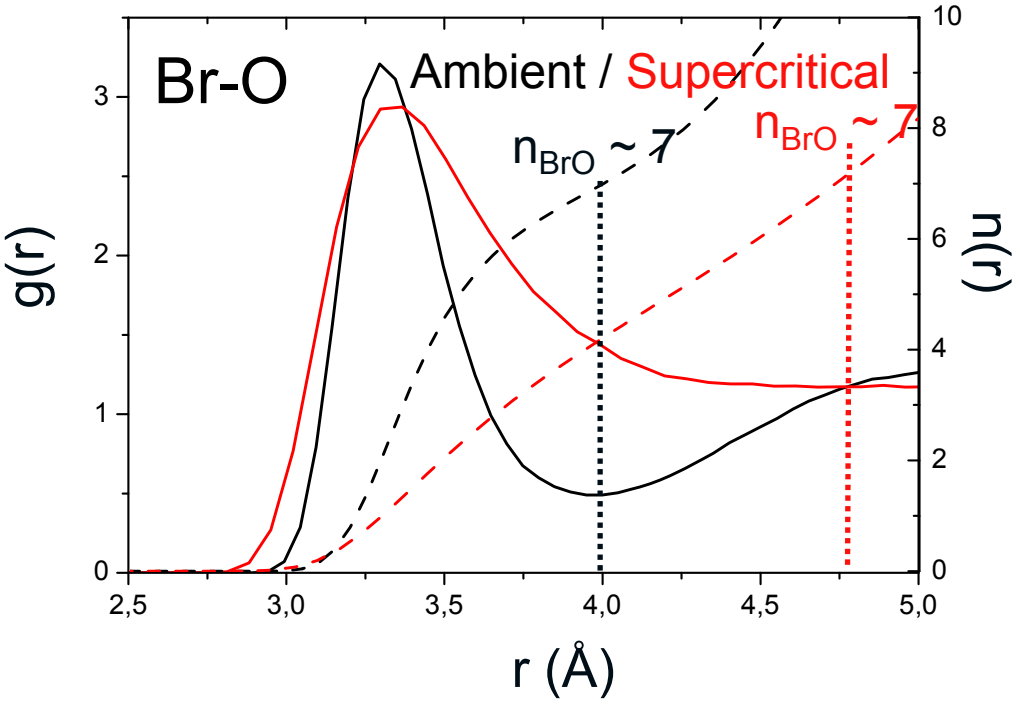
$(RbBr)_{0.4}$ - $(H_2O)_{99.6}$ (m=0.2)

Ambient: ρ ~ 1. g.cm^{-3}, T = 30°C
Supercritical: ρ ~ 0.4 g.cm^{-3}, T = 450°C
potentials: LJ + Coulomb (ions);
SPC/E (water)
Box size: 452 H_2O + 2 RbBr pairs
Time step: 2 fs
Simulation duration: ~ 1 ns

✓ Expansion of the first hydration shell in supercritical conditions
✓ Locally, slight dehydration (at constant cutoff)

Ions in aqueous solutions: hydration

- MD simulations of diluted 1:1 aqueous electrolytes



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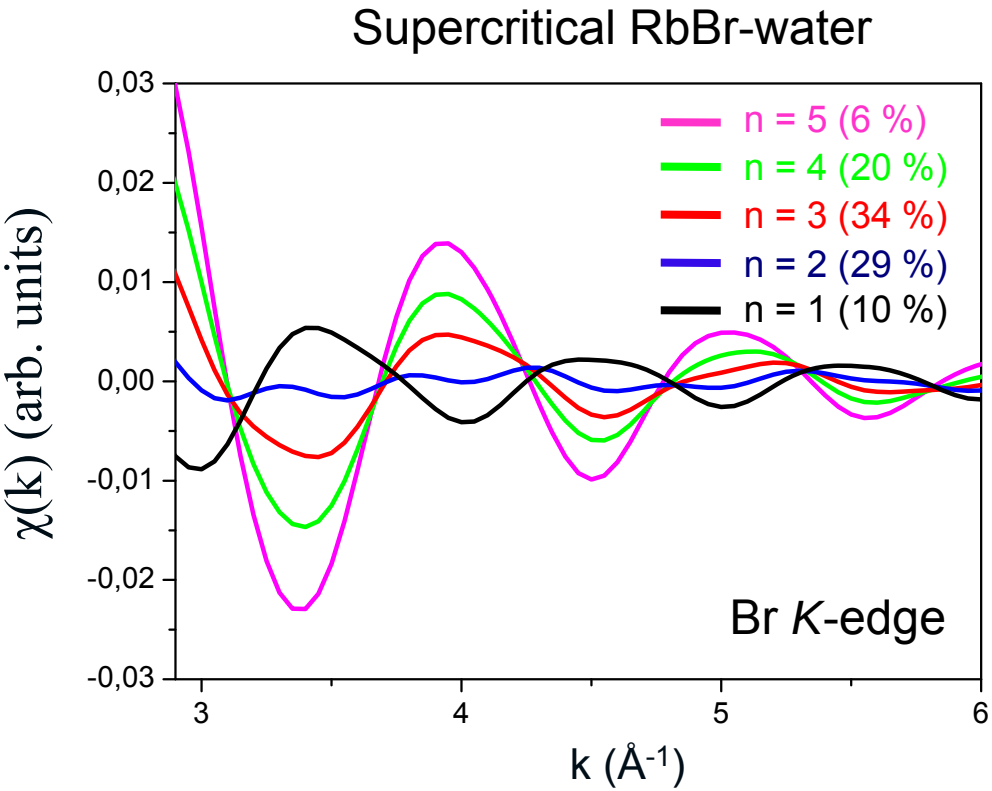
Box size: 452 H_2O + 2 RbBr pairs
Time step: 2 fs
Simulation duration: ~ 1 ns

✓ Expansion of the first hydration shell in supercritical conditions
✓ Locally, slight dehydration (at constant cutoff)
✓ However, total number of water molecules unchanged (~ 7)

Ions in aqueous solutions: MD-XAS



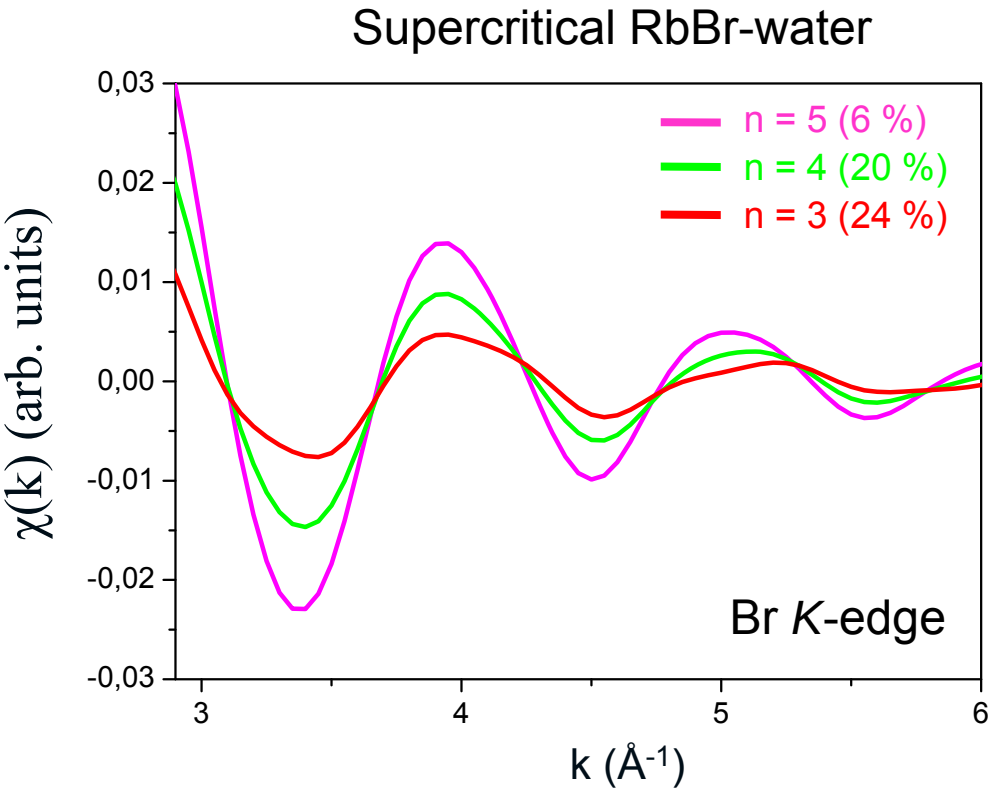
Cluster analysis:
- 8000 individual MD-XAS computed spectra (sampled every 0.2 ps).
- clusters classified according to the nb of neighbours at a given cutoff (3.55 Å).

✓ Drastically different local environments (none of them being representative of the average)

✓ Significantly interfering signals (~ 50 % of the clusters will give a ~ zero contribution)

G. Ferlat *et al.*, Phys. Rev. B, **63**, 134202 (2001); *ibid* ,High Pressure Research (2002)

Ions in aqueous solutions: MD-XAS



Cluster analysis:
- 8000 individual MD-XAS computed spectra (sampled every 0.2 ps).
- clusters classified according to the nb of neighbours at a given cutoff (3.55 Å).

✓ Significantly interfering signals (~ 50 % of the clusters)

✓ The inversion of the average EXAFS signal is *ill-defined* (can give different solutions)

G. Ferlat *et al.*, Phys. Rev. B, **63**, 134202 (2001); *ibid* ,High Pressure Research (2002)

Ions in aqueous solutions: hydration

- MD-XAS calculations at the Br *K*-edge

$$(RbBr)_{0.4}\text{-}(H_2O)_{99.6}$$

$$\langle \chi_{Br}(k) \rangle = \langle \chi_{Br-O}(k) \rangle + \cancel{\langle \chi_{Br-H}(k) \rangle} + \cancel{\langle \chi_{Br-Rb}(k) \rangle}$$

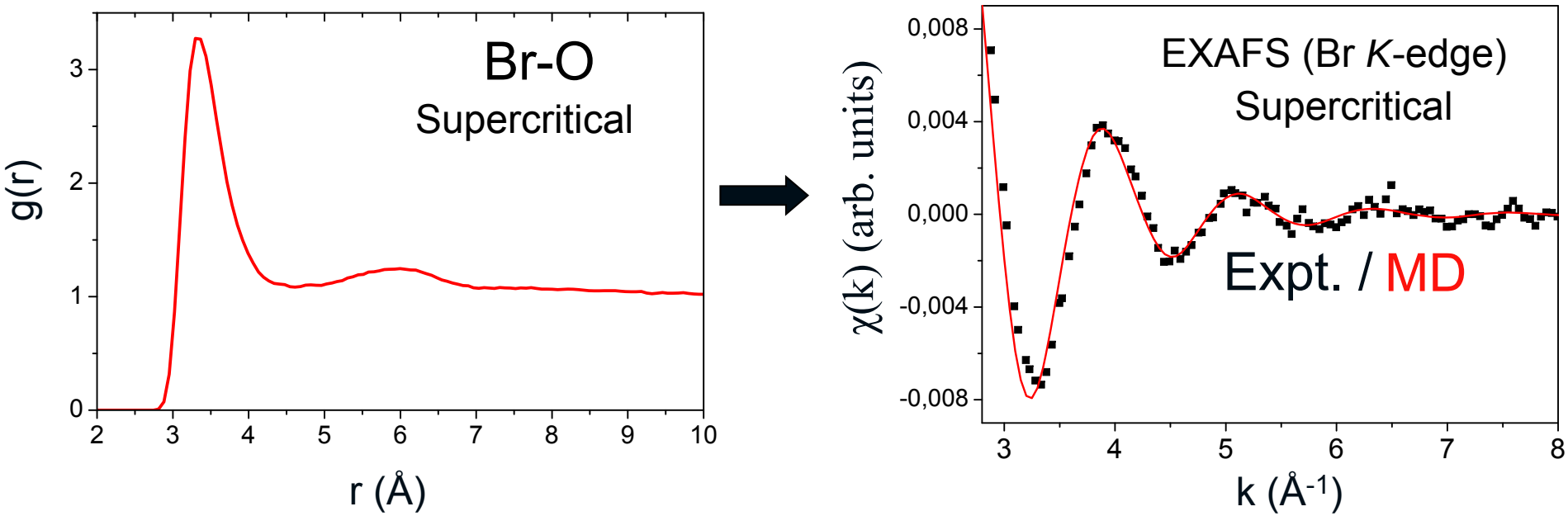
$$\langle \chi_{Br}(k) \rangle = 4\pi\rho_O \int_0^R r^2 g_{BrO}(r) \gamma^{(2)}_{BrO}(k,r) dr$$

with $\gamma^{(2)}_{BrO} = A_O(k,r)\sin(2kr + \phi_{BrO}(k,r))$

Supercritical aqueous solutions: hydration

- MD-XAS calculations

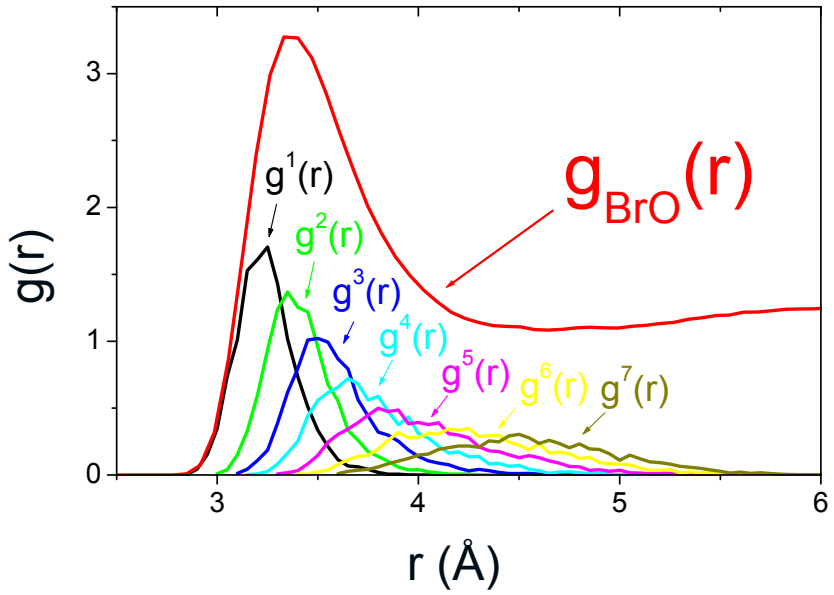
$(RbBr)_{0.4}$ -$(H_2O)_{99.6}$



✓ The MD model reproduces quite well the experimental data. However, let's check the sensitivity of the XAS data to the g(r) ...

Supercritical aqueous solutions: hydration

- MD-XAS calculations:

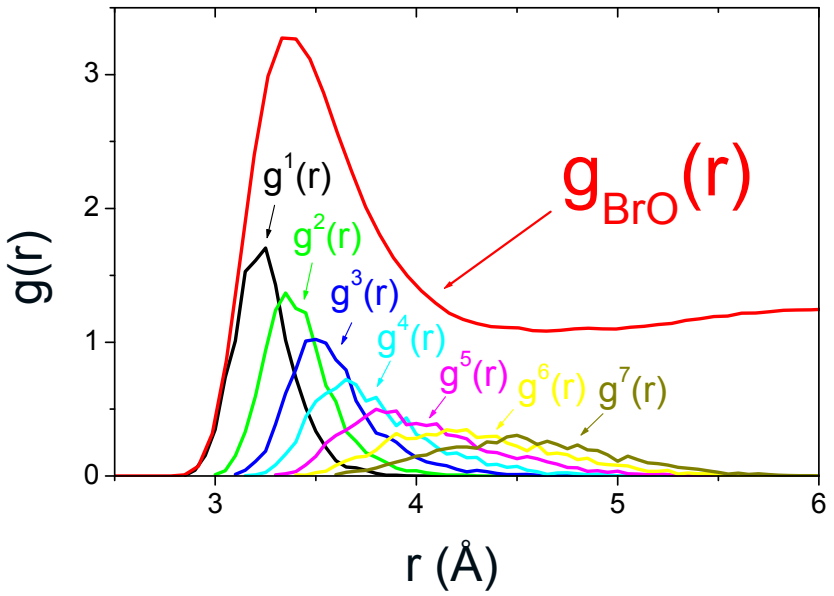


n-coordinated g(r)

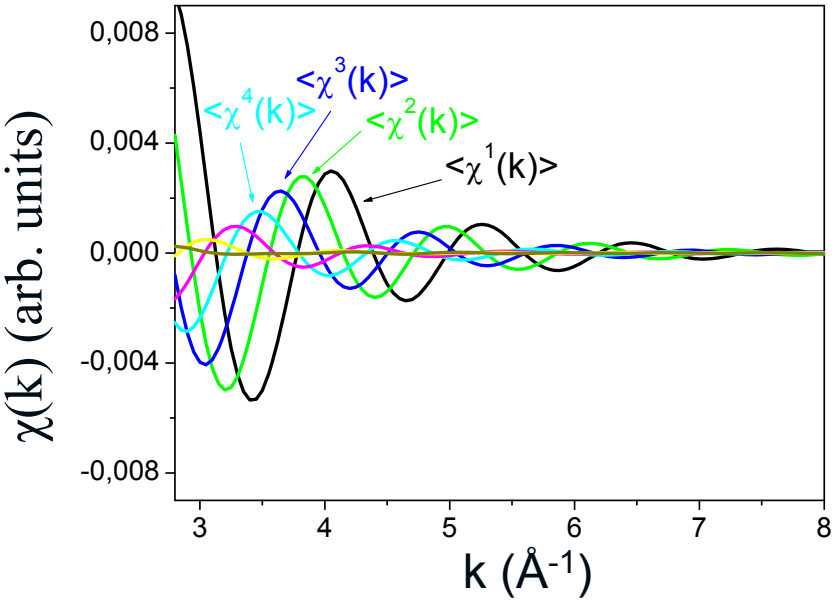
✓ To test the XAS sensitivity, the MD g(r) is decomposed into subgroups ...

Supercritical aqueous solutions: hydration

- MD-XAS calculations:



n-coordinated g(r)



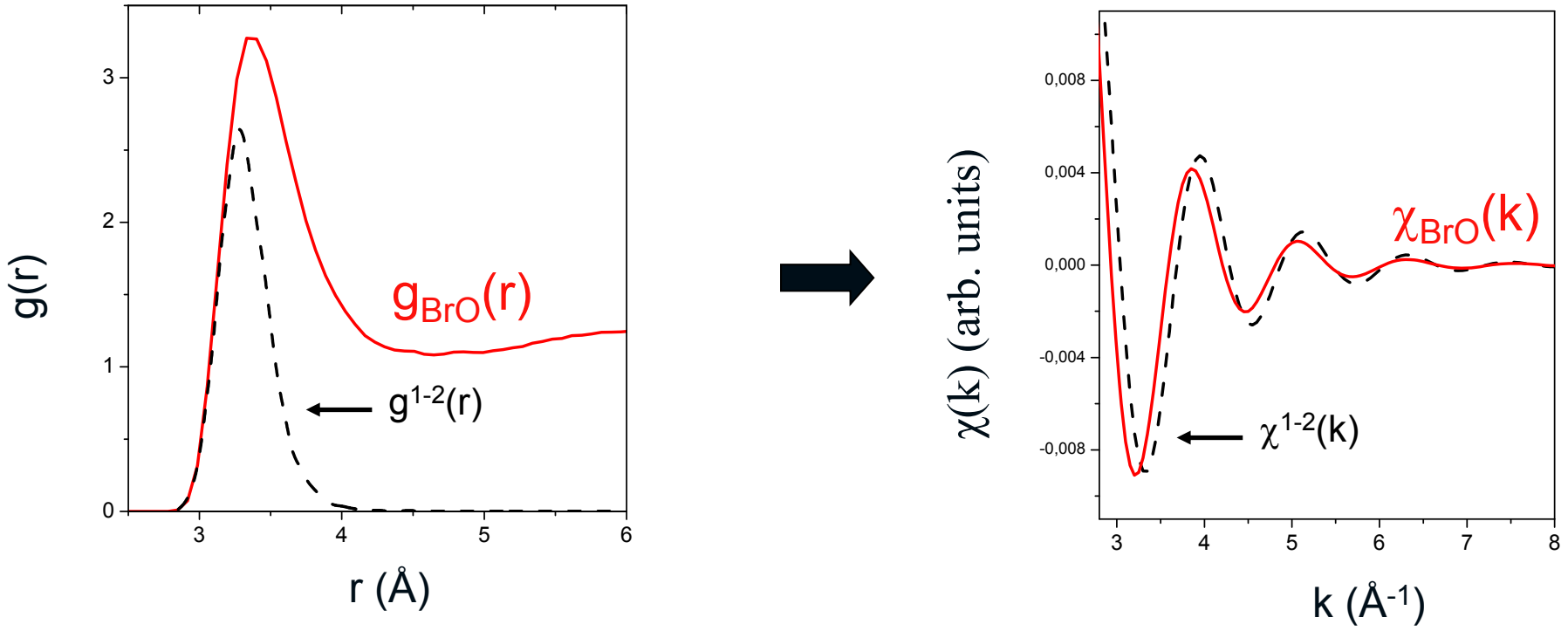
n-coordinated $\chi(k)$

✓ To test the XAS sensitivity, the MD g(r) is decomposed into subgroups ...

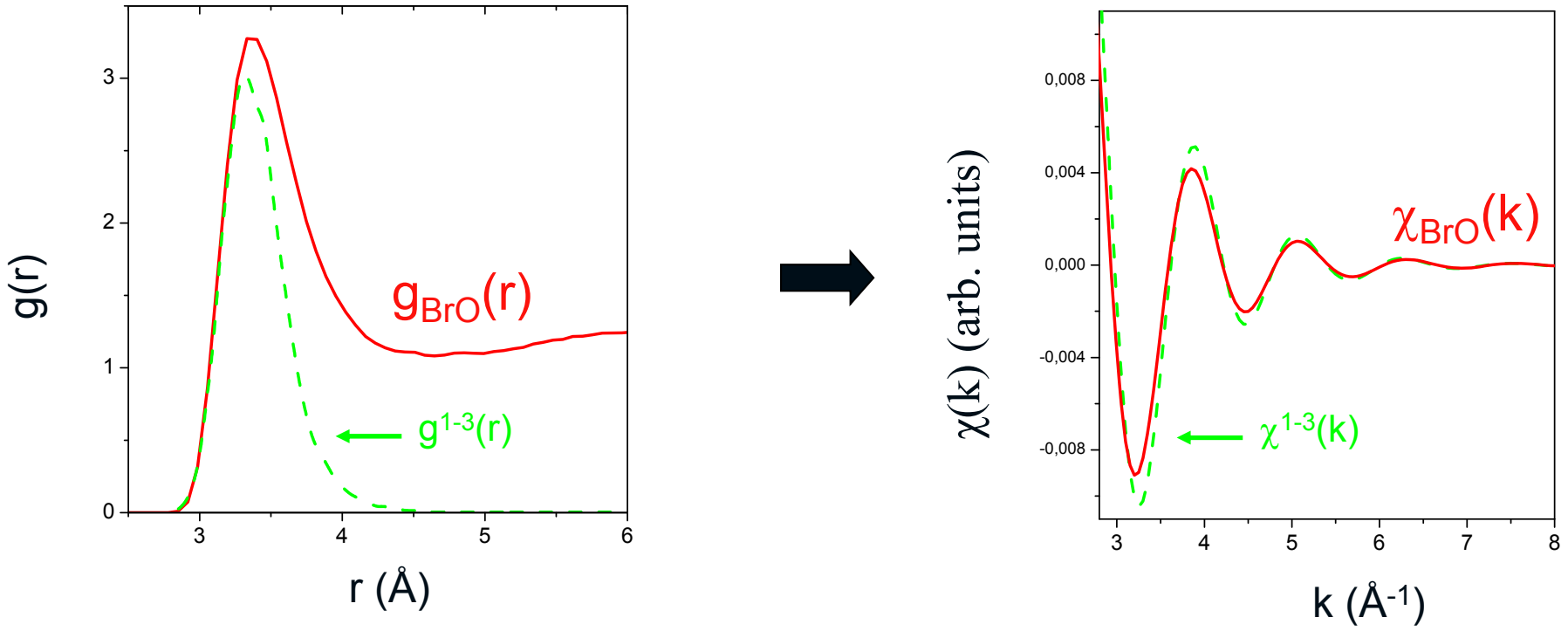
✓ ... and the corresponding XAS signals are computed

Supercritical aqueous solutions: hydration

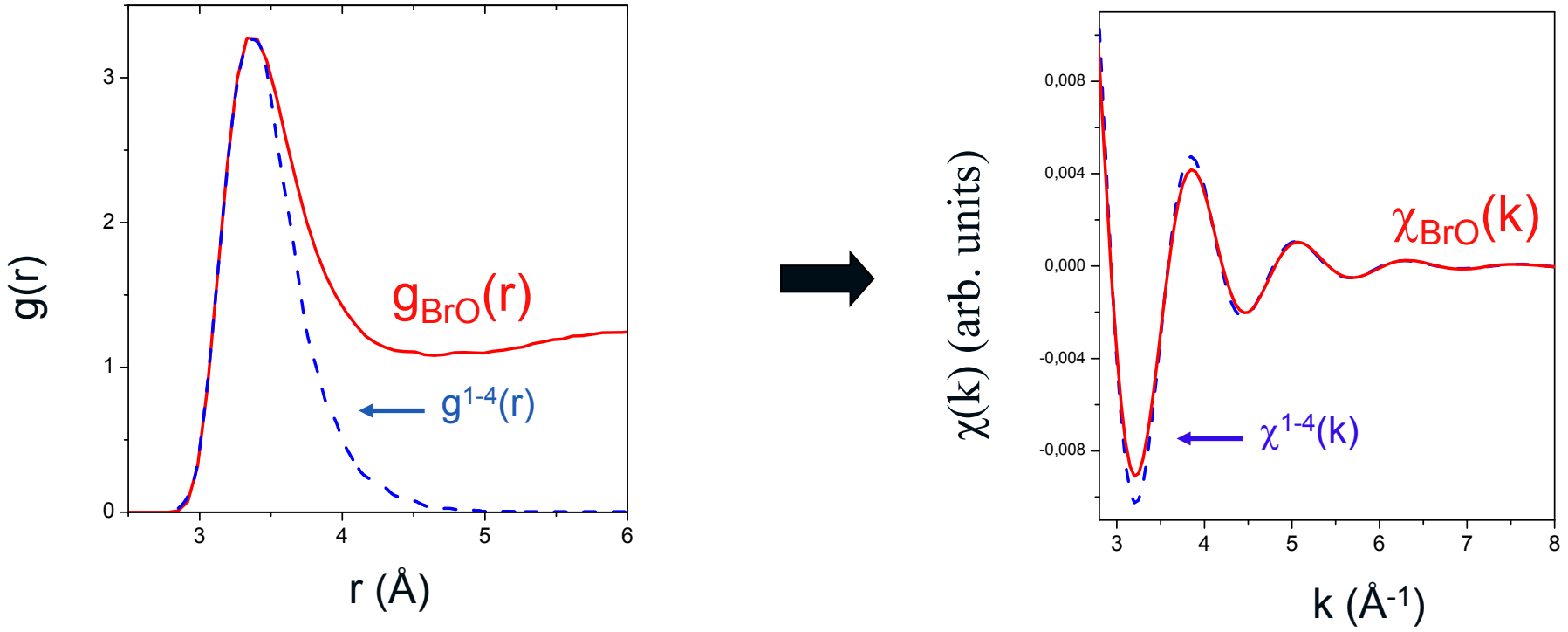
How fast does the total XAS signal converged wrt to the partial $\chi^{1-n}(k)$?



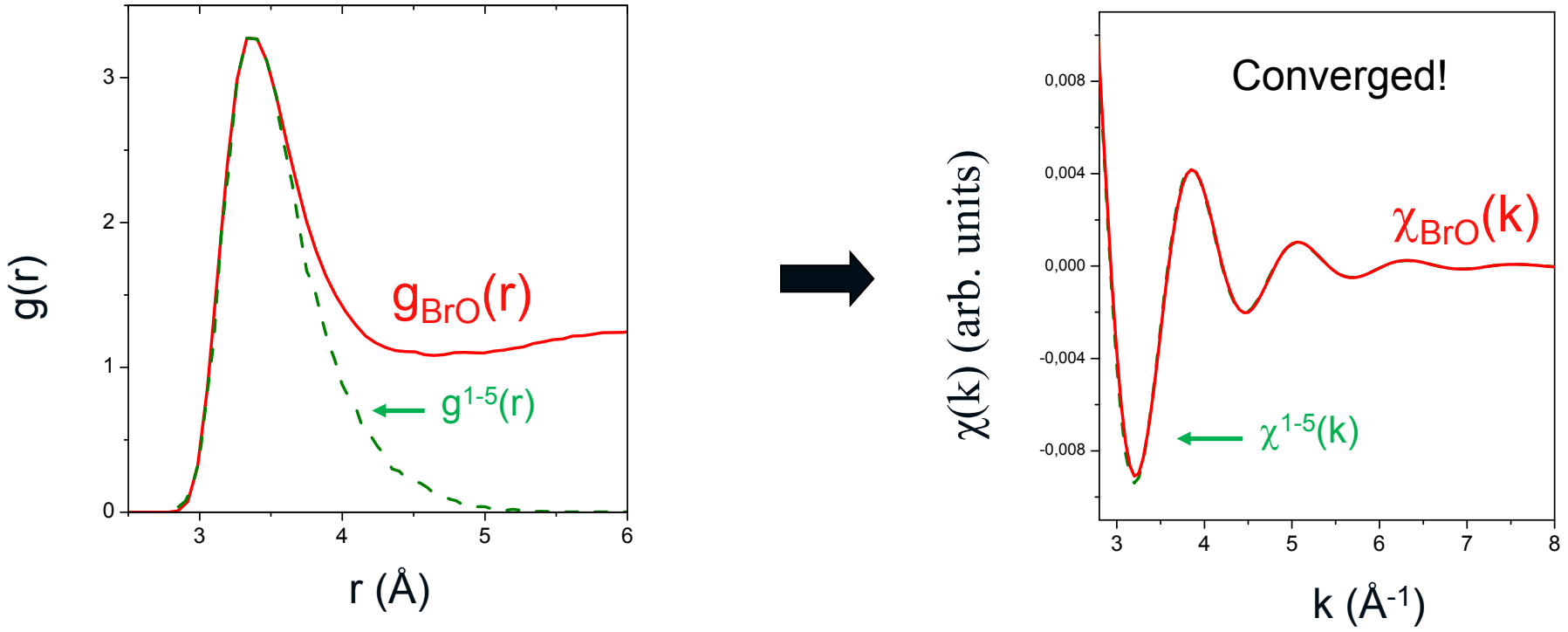
Supercritical aqueous solutions: hydration



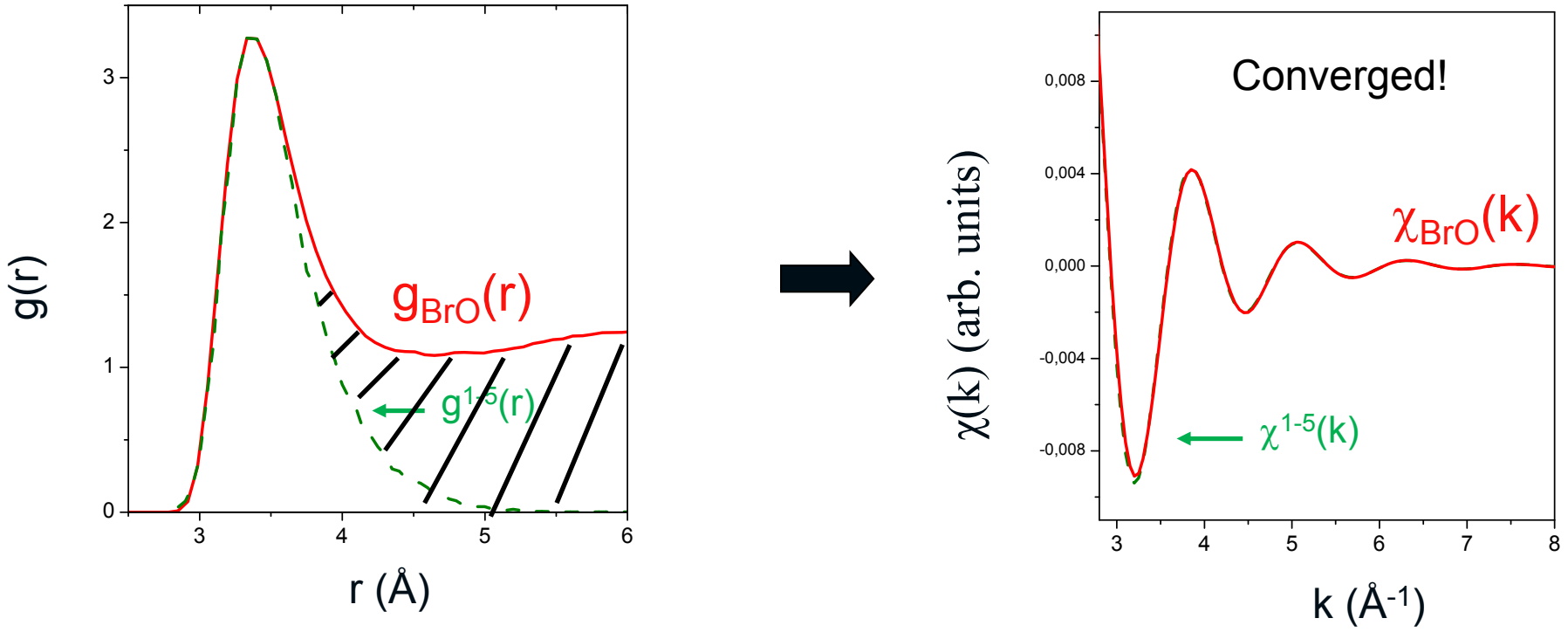
Supercritical aqueous solutions: hydration



Supercritical aqueous solutions: hydration



Supercritical aqueous solutions: hydration

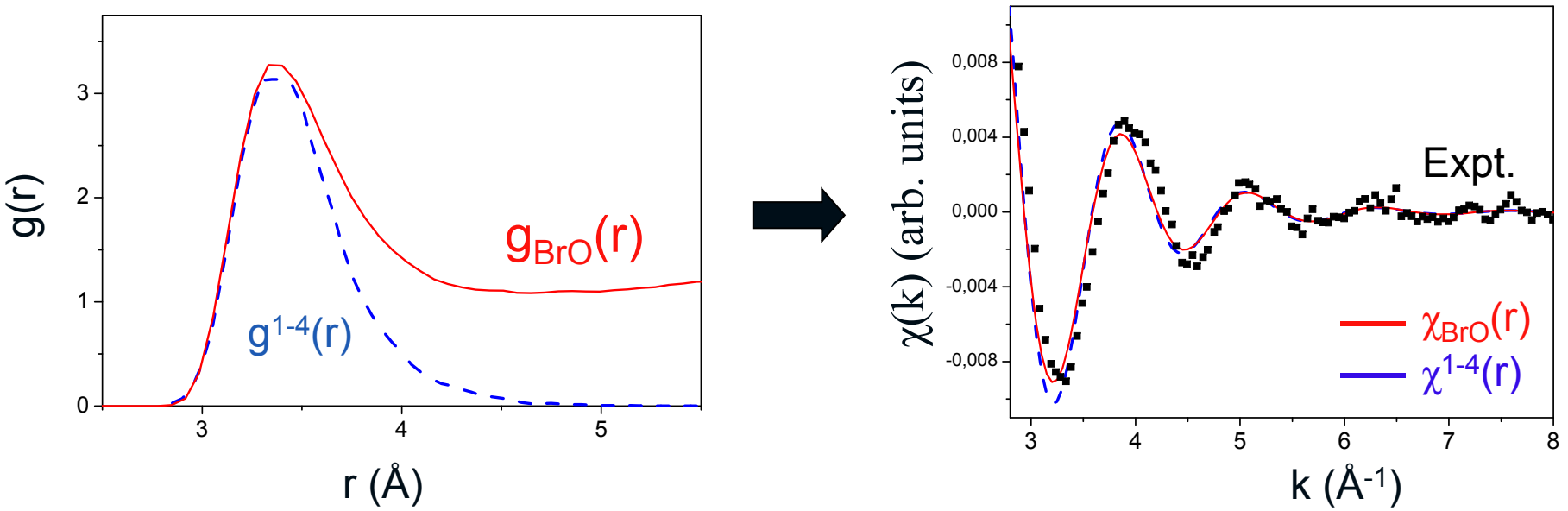


✓ The convergence is quite fast

✓ The high-r part of the g(r) is *not contributing* to the XAS signal

Supercritical aqueous solutions: hydration

- MD-XAS calculations:



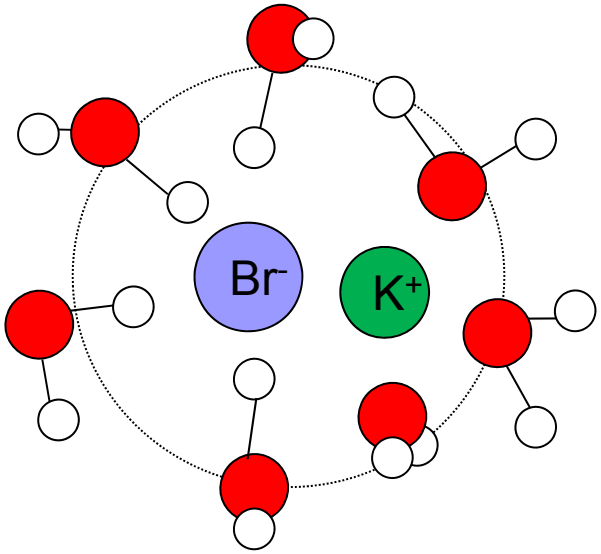
✓ Considering only a fraction of the full g(r) is sufficient to reproduce the expt. data: this shows that the inversion of the EXAFS $\chi(k)$ is a *ill-defined* problem and that conventional approaches (cumulant or peak-fitting) should not be trusted !

G. Ferlat *et al*., J. Phys. : Condens. Matter, **17**, S145 (2005)

Ions in aqueous solutions: complexation

A « differential » XAS analysis

XAS at Br K-edge in { *KBr-H_2O*, *$RbBr$-H_2O*, *$CsBr$-H_2O* }



$$\langle \chi(k) \rangle = \langle \chi_{BrO}(k) \rangle + \langle \chi_{BrX}(k) \rangle$$

?

G. Ferlat *et al.*, J. Mol. Liquids, **101**, 127 (2002)

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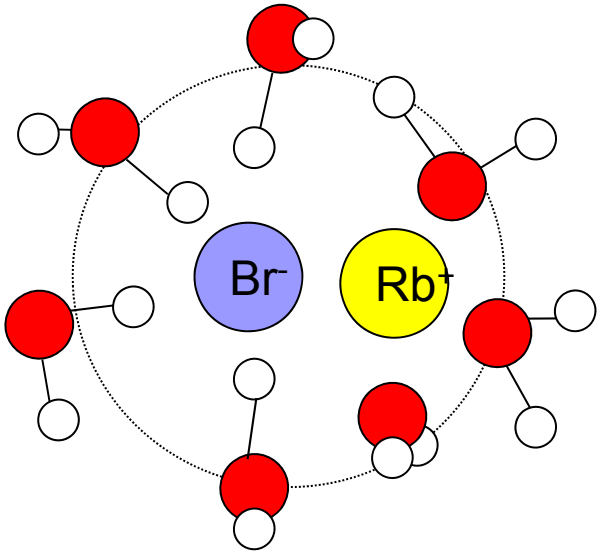

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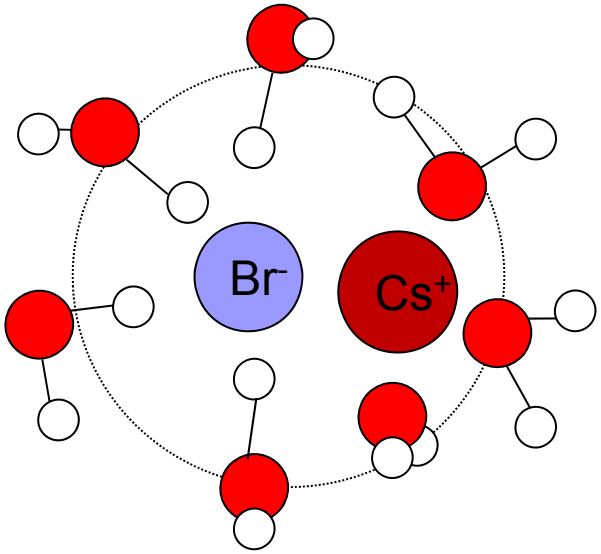
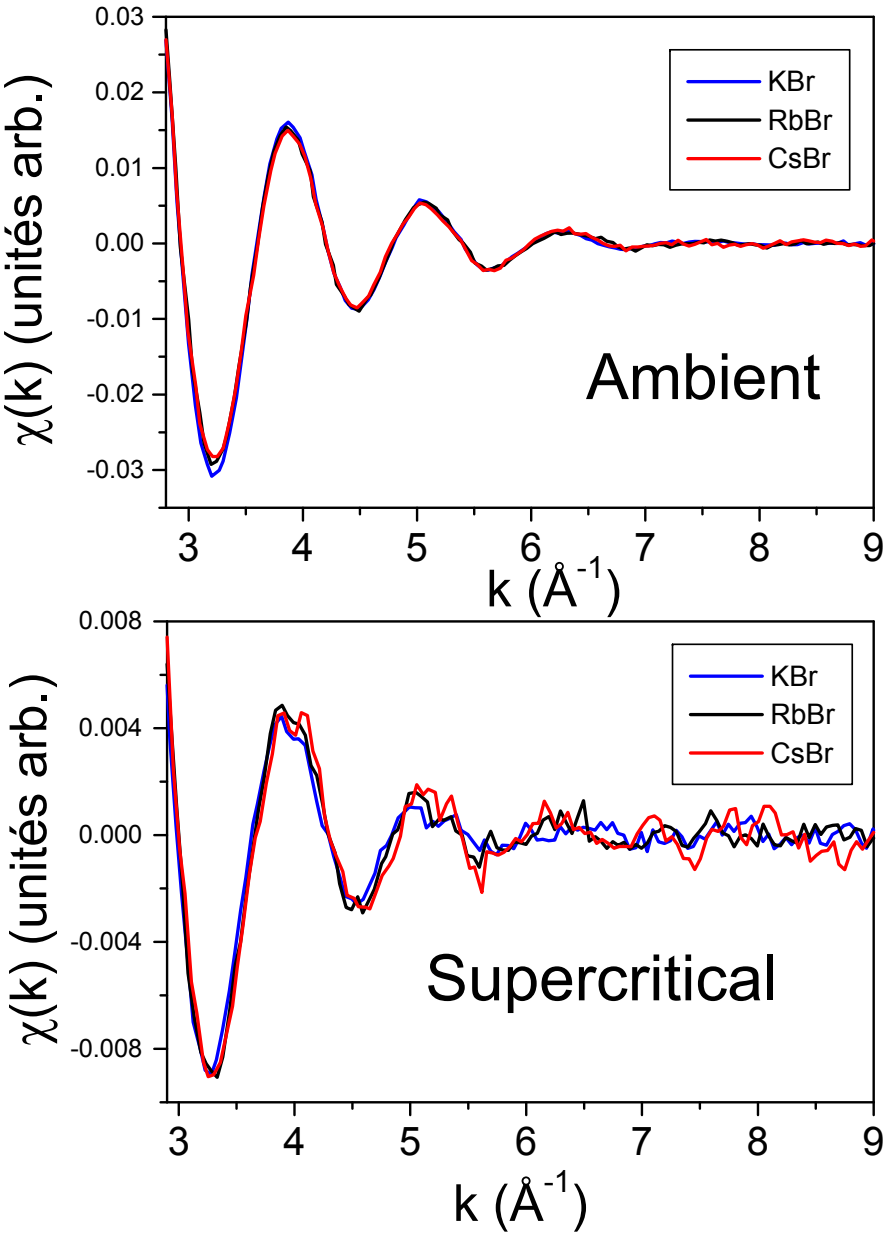


$$\langle \chi(k) \rangle = \langle \chi_{BrO}(k) \rangle + \langle \chi_{BrX}(k) \rangle$$

?

G. Ferlat *et al.*, J. Mol. Liquids, **101**, 127 (2002)

“Differential XAS”: Expt.

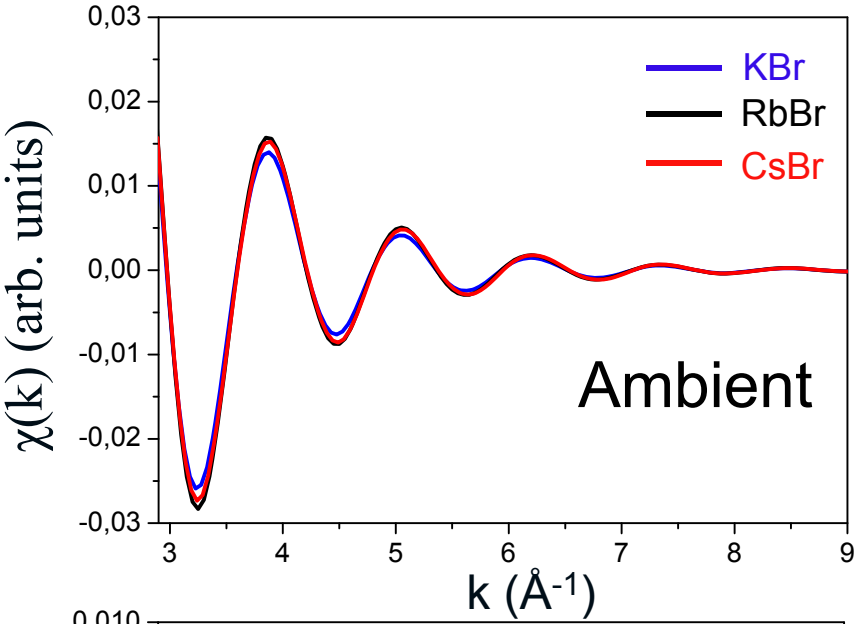


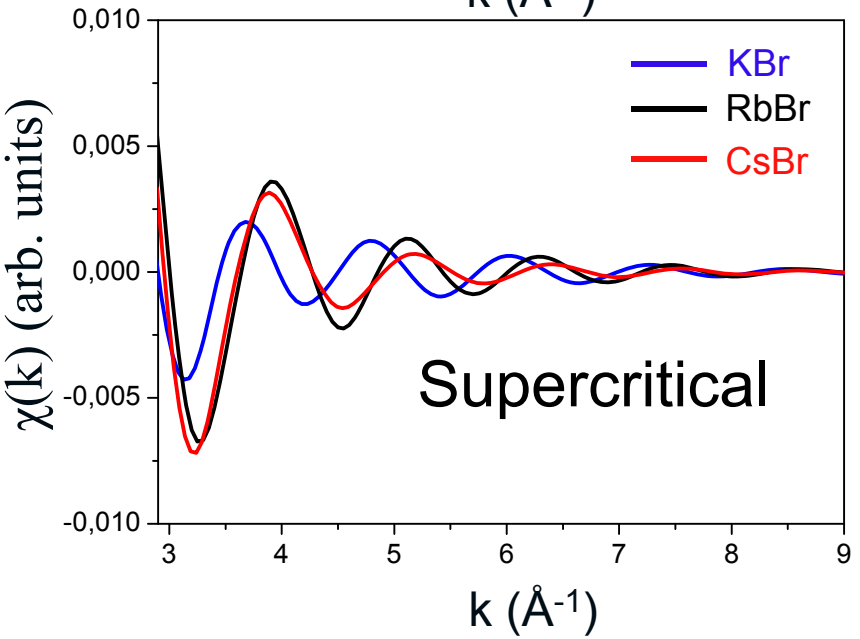
XAS at Br K-edge in { *KBr-H_2O*, *$RbBr$-H_2O*, *$CsBr$-H_2O* }

✓ No significative differentiation of the signals neither in ambient nor in SC.

✓ no differentiation <-> no ion-pairs? (what are the sensitivity limits?)

“Differential XAS”: MD-XAS



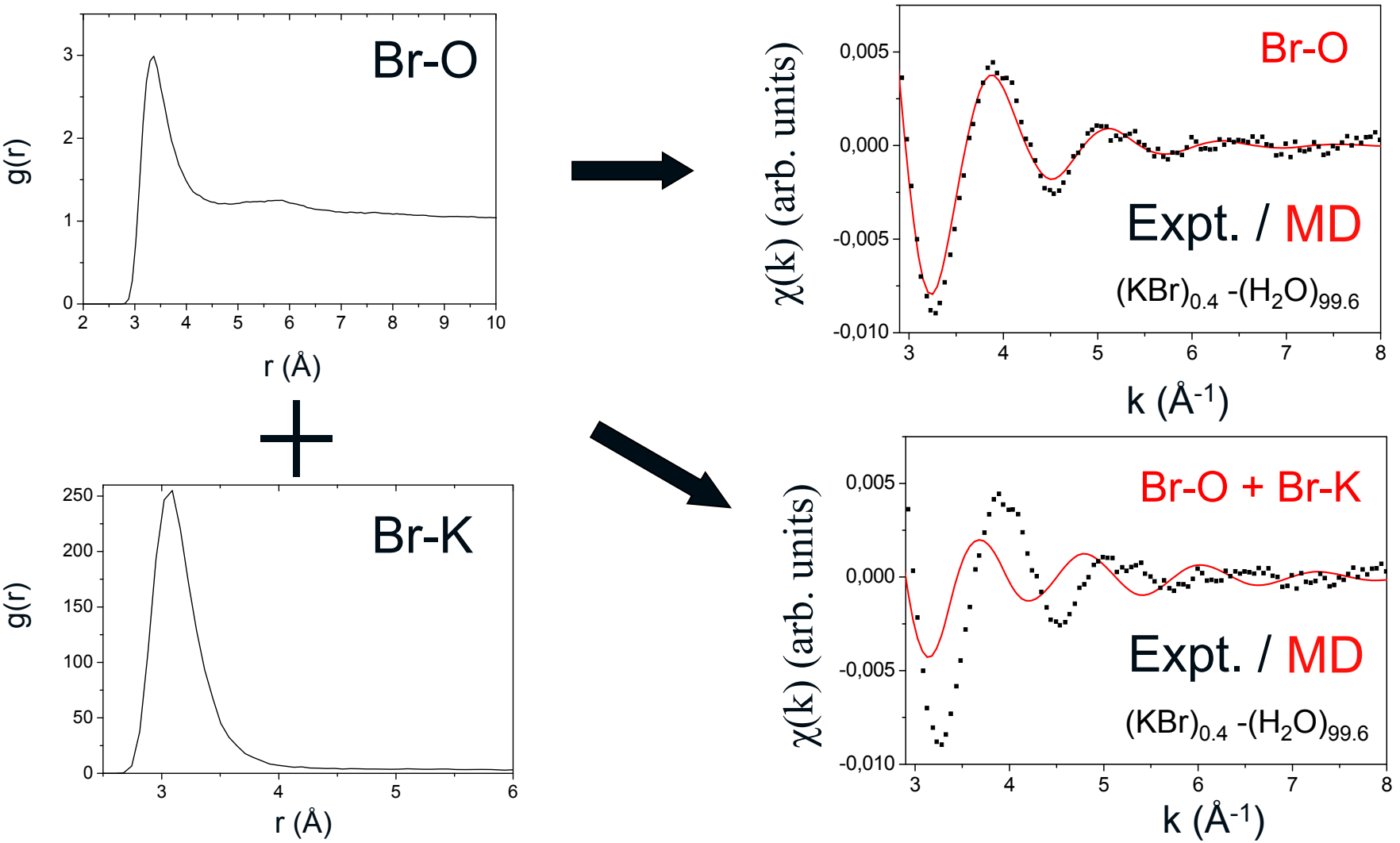


XAS at Br K-edge in { *KBr-H_2O*, *$RbBr$-H_2O*, *$CsBr$-H_2O* }

✓ No differentiation in Ambient (in agreement with expt. observations)

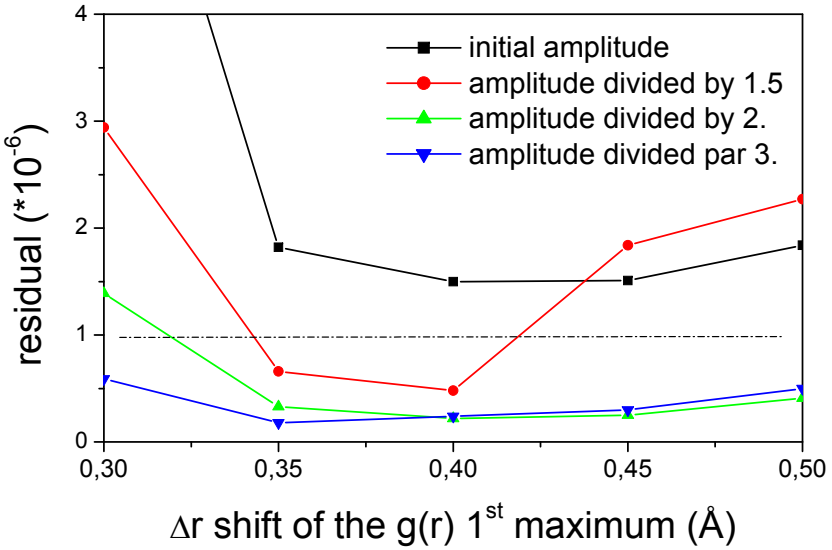
✓ However, strong differentiation in SC : overestimation of the ion-pairs in the MD model

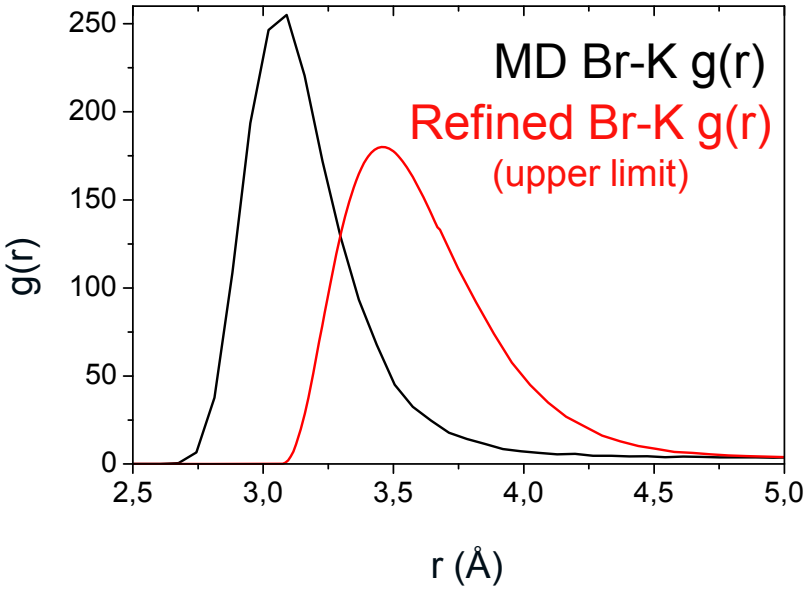
supercritical complexation: MD-XAS (KBr)



supercritical complexation: MD-XAS (KBr)

- Refining the ion-ion model





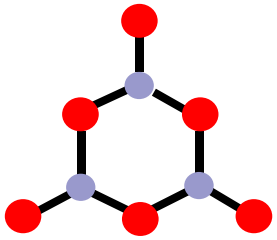
✓ Ion – ion correlations are *overestimated* in the MD model
✓ The MD-XAS combination allows to estimate an upper limit

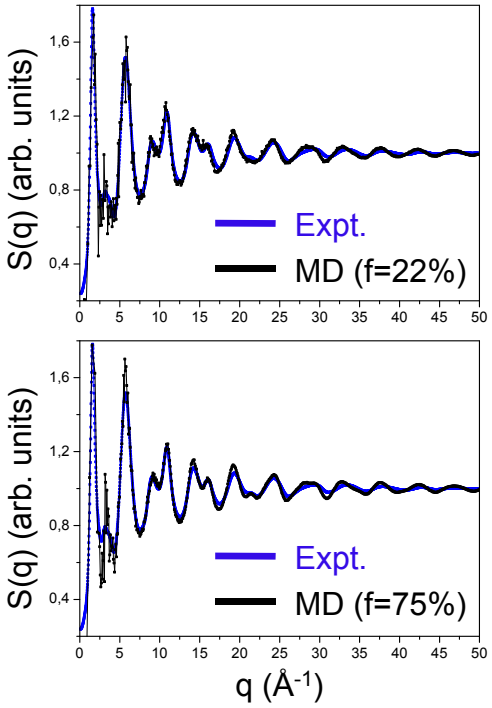
G. Ferlat *et al.*, J. Mol. Liquids, **101**, 127 (2002)

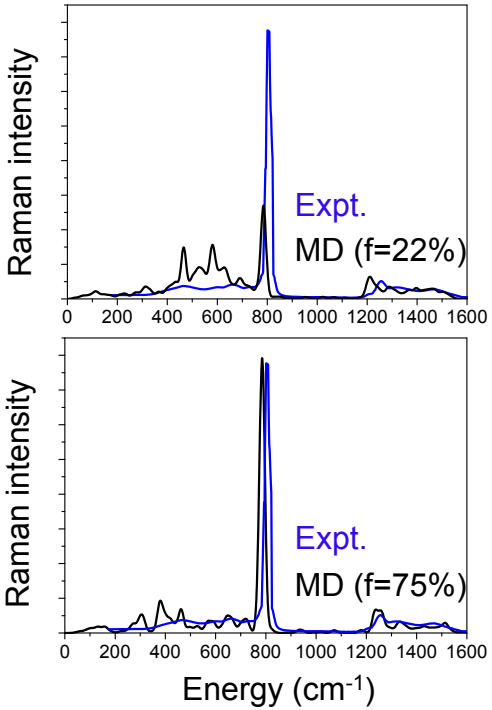
Beyond MD-XAS: MD-NMR, MD-Raman...

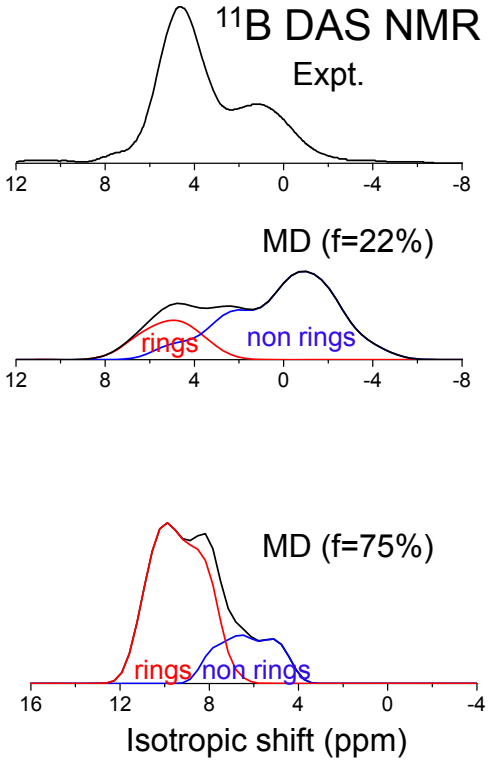
Boroxol-poor (BP) and boroxol-rich (BR) models tested against expt. probes:

- Static structure factor
- NMR ^{11}B and ^{17}O (DAS, MAS)
- XANES at B and O *K*-edges
- Raman
- Infra-red
- Heat capacity









Conclusions

- XAS has provided a very valuable, sometimes unique information in many disorded systems: triplet correlations, original coordination environments …
- The MD-MC/XAS symbiosis played a key role, especially for determining very subtle contributions (MS, …), to assess the limits of the technique sensitivity or to evidence inaccuracies in the MD/MC potentials.
- There are still difficulties to get reliable information beyond the first coordination shells but progress is being made

Critical reading of a XAS paper

- How was the experimental signal extracted (Fourier filtering, splines)?
- Were possible multi-electronic excitations considered?
- What is the available k range? Are the spectra in k space shown?
- Data analysis: how was the configurational average taken into account? Was some external information used to constrain the analysis?

References:

- www.xafs.org (Lectures, Tutorials, …)

- “A History of the X-ray Absorption Fine Structure” by R. Stumm von Bordwehr, Ann. Phys. Fr. vol. **14**, 377-466 (1989) (real author's name is Ch. Brouder).

- "Theoretical approaches to X-ray absorption fine structure", J.J. Rehr and R.C. Albers, Review of Modern Physics, vol. **72**, 621-654 (2000)

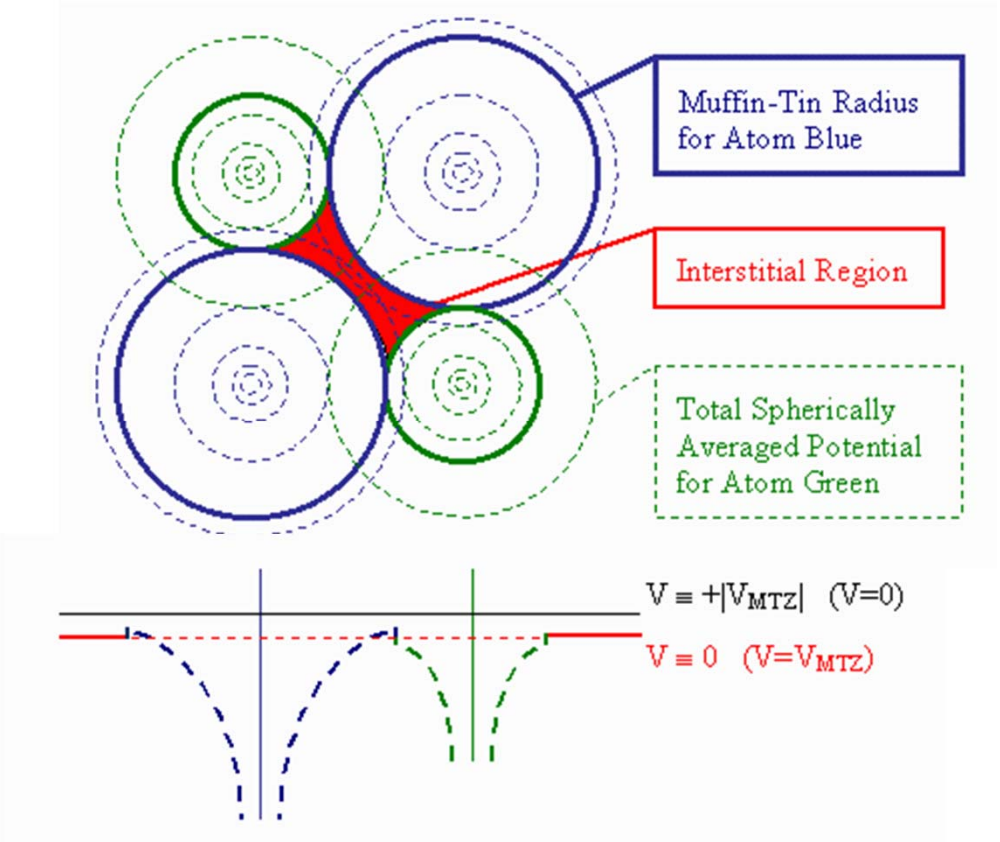
- “A review of the current status of XAFS spectroscopy”, E. Daryl Crozier, Nuclear Instruments and Methods in Physics, vol. **133**, 134-144 (1997)

- “EXAFS for liquids” A. Filipponi J. Phys.: Condens. Matter **13** R23-R60 (2001)

- “Combining EXAFS with numerical simulations for disordered systems”, G. Ferlat *et al.* , J. Phys.: Condens. Matter **17** S145-S157 (2005)

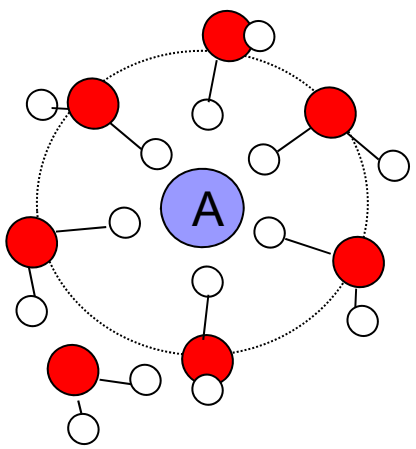
The *muffin-tin* (MT) approximation

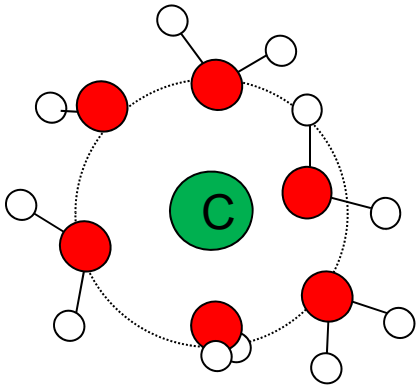
The potential is spherically averaged inside MT spheres around the atoms and averaged to a constant in the interstitial region :

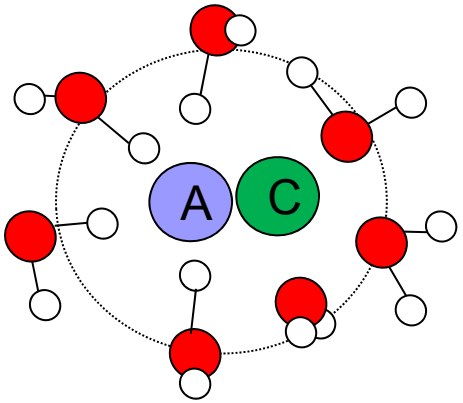


Justification : photo-electrons with high kinetic energies are essentially scattered by the core-regions and are almost free elsewhere (weakly sensitive to the potential details). However, it is now largely superseded by full potential techniques (from low to moderate energies).

Ions in aqueous solutions







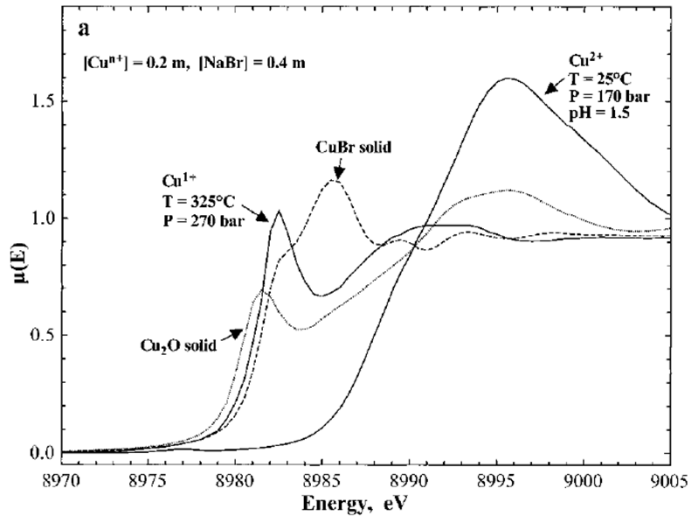
	Hydration		*Complexation*	
	Amb.	*SC*	*Amb.*	*SC*
Simulations: (NaCl)	n ~ 6	~ 6	~ 0	30%[2]
Expt (EXAFS):[1] (RbBr)	n ~ 7	~ 2	~ 0	0 ? (m=0.02-1.5 kg/mol)

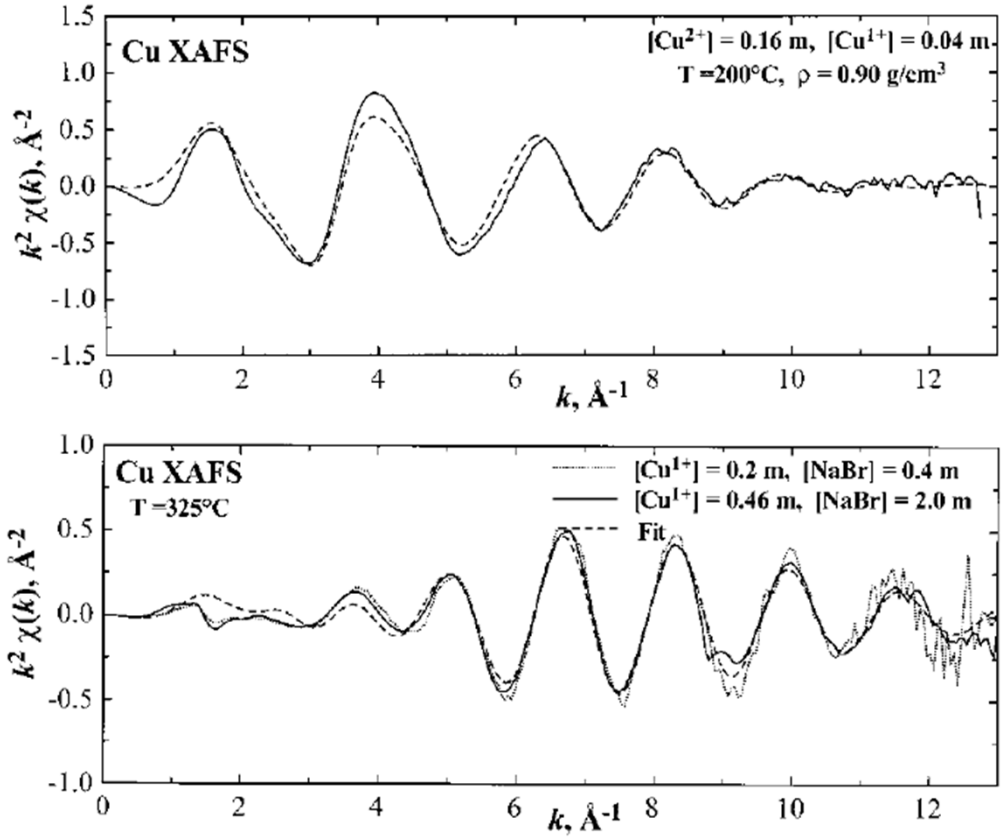
1) S.L. Wallen et al., J. Phys. Chem., **101**, 9632 (1997)

2) E. Oelkers, H. Hegelson, Science, **261**, 888 (1993)

Ion-pairing
(with decreasing density)

Low density -> low dielectric constant -> favours ion-pairing

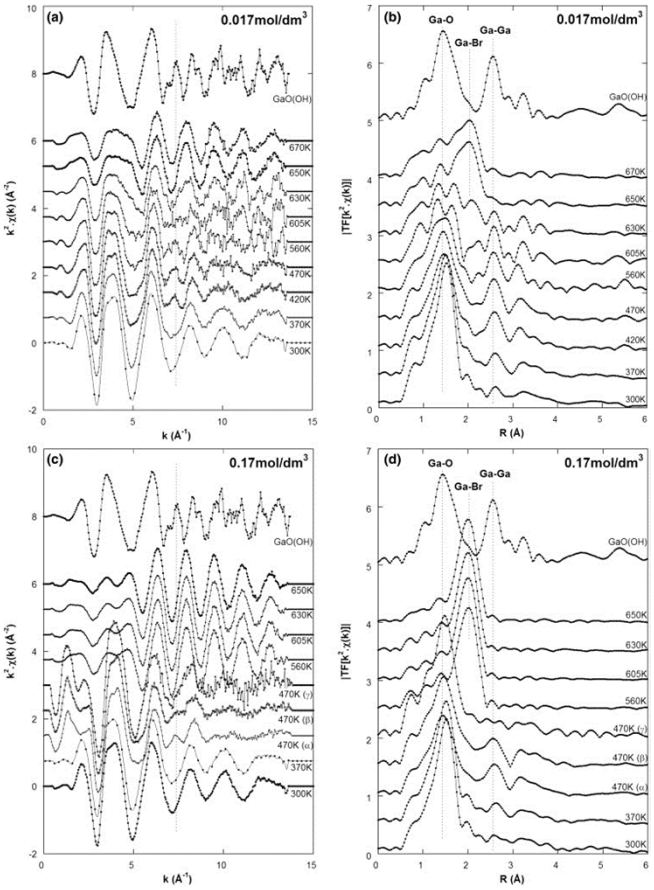




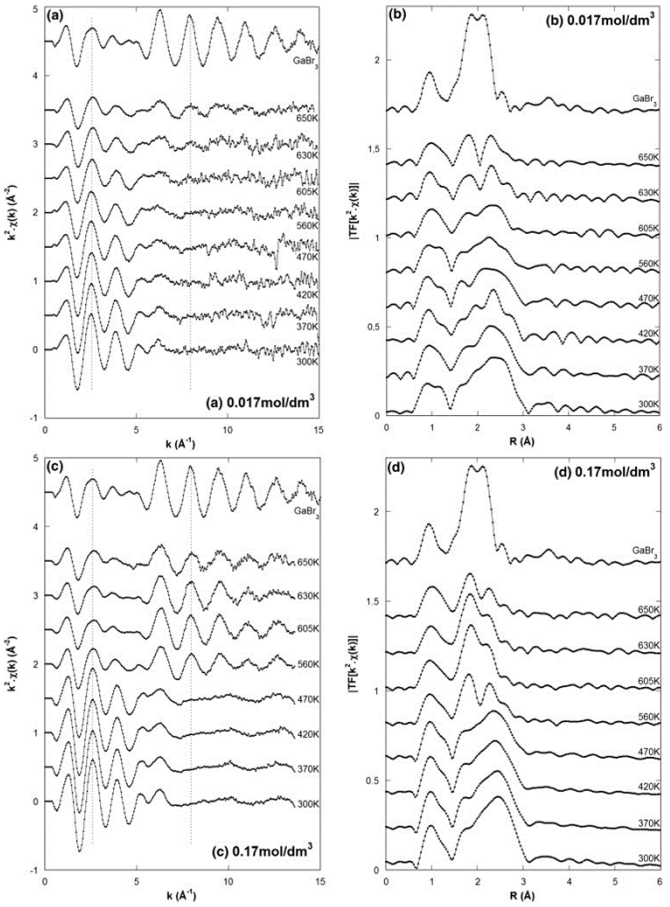
"Copper(I) and Copper(II) coordination structure under hydrothermal conditions at 325°C: an x-ray absorption fine structure and molecular dynamics study"
J. L. Fulton *et al.*, J. Phys. Chem. A, **104**, 11651 (2000)

Ion-pairing
(with decreasing density)

Ga *K*-edge



Br *K*-edge



"XAS study of solvation and ion-pairing in aqueous gallium bromide solutions at supercritical conditions"
C. Da Silva *et al.*, J. Mol. Liquids, **147**, 83 (2009)