

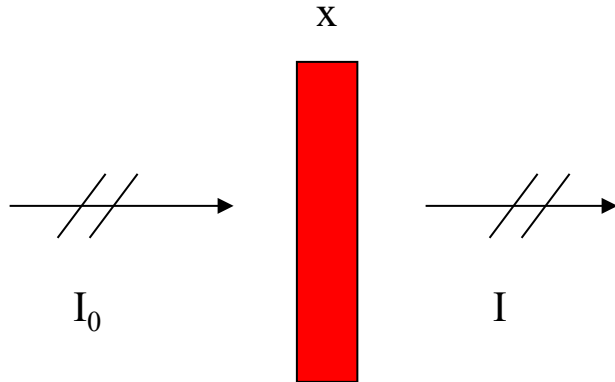
X-ray Absorption Spectroscopy and Multiple Scattering Theory

M. Benfatto

Istituto Nazionale Fisica Nucleare, Via E.Fermi 40, I-00044 Frascati, Italy

maurizio.benfatto@lnf.infn.it

The experiment



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

E is in the X-ray energy range

$$\mu(E) = n_{abs} \sigma(E)$$

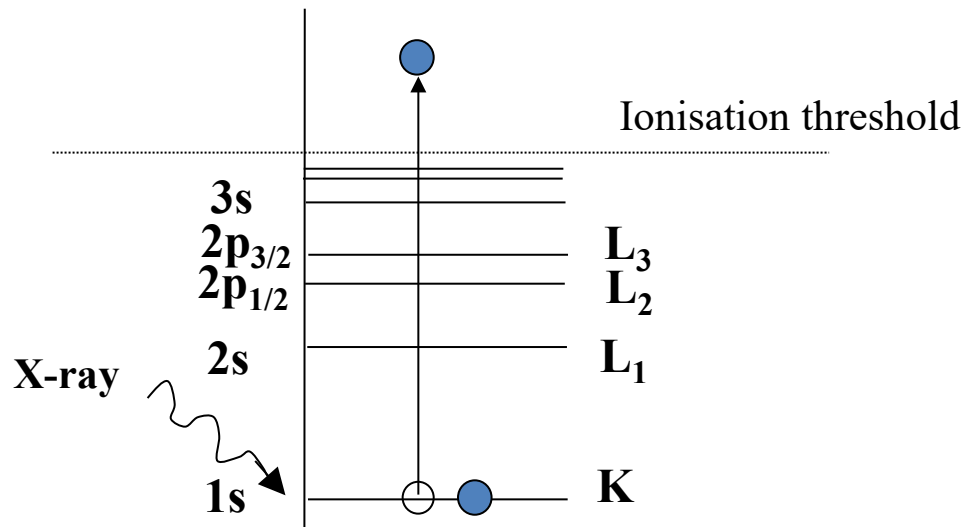
Density of absorption medium

Photoabsorption cross section

excitation of core-level electron to continuum states

There are other scattering processes with and without energy loss

we must normalize the data to isolate the XAS signal

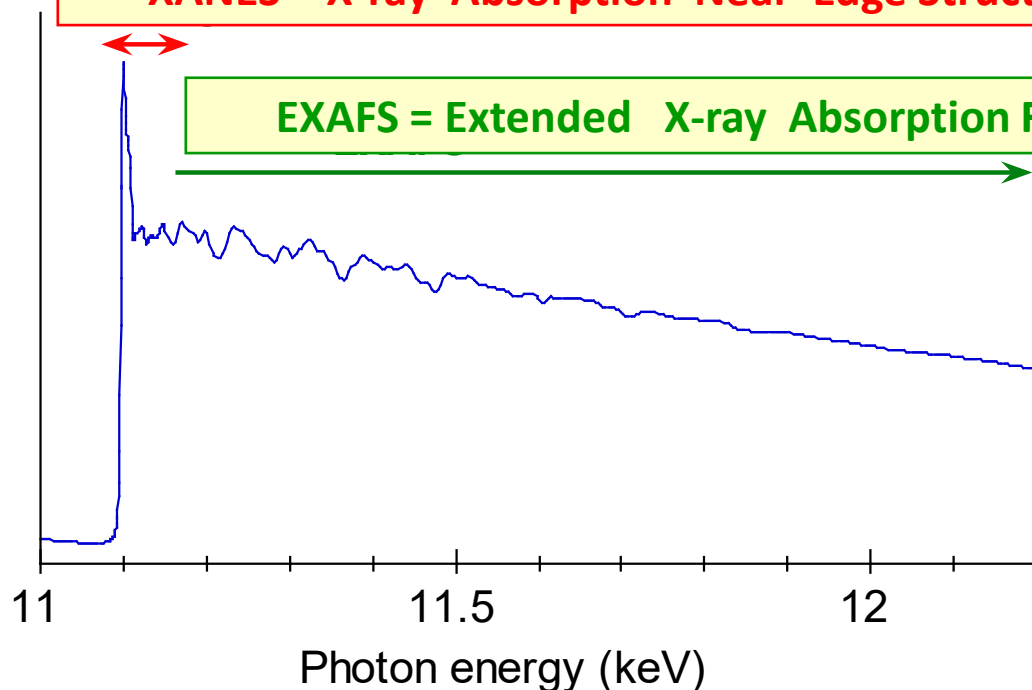


XAS normalized spectrum

K-edge $\longrightarrow$ 1s
L₁-edge $\longrightarrow$ 2s
L₂-edge $\longrightarrow$ 2p
.....

XANES = X-ray Absorption Near Edge Structure

EXAFS = Extended X-ray Absorption Fine Structure



Some K- and L₂- edges

Si - 1839 eV - 99.8 eV

Fe - 7112 eV - 719.9 eV

...

Cu - 8979 eV - 952.3 eV

Ge - 11103 eV - 1248.1 eV

.....

Fermi golden rule

$$\sigma(E) = 4\pi^2 \alpha E \sum_f |\langle \psi_f | \vec{\epsilon} \cdot \vec{r} | \psi_c \rangle|^2 \delta(E - E_f + E_c)$$

Dipole approximation $\longleftrightarrow$ $\frac{\sigma_q(E)}{\sigma_d(E)} \sim \frac{1}{100}$

$\psi_f \longrightarrow$ w.f. of final state

$\psi_c \longrightarrow$ w.f. of core

The core wave function is spatially localized

MS Theory

It is a method to solve the S.E. in real space without the need to have any symmetry.

$$[-\nabla^2 + V(\vec{r})] \Psi(\vec{r}) = E \Psi(\vec{r})$$

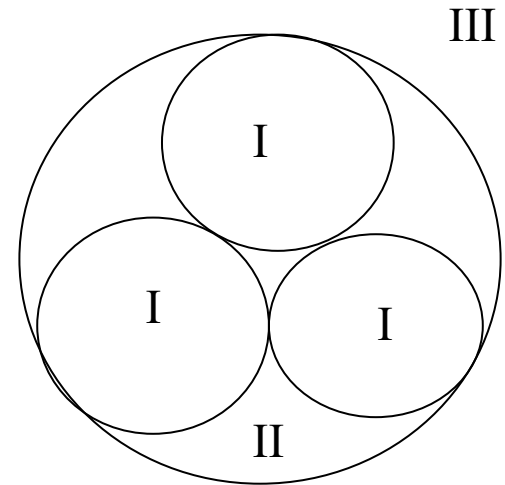
$$V(\vec{r}) = V_c(\vec{r}) + V_{exc}(\vec{r})$$

$$V_c(\vec{r}) = \sum_j V^j(\vec{r} - \vec{R}_j)$$


Sum of free atomic potential  cluster of atoms

Muffin-Tin approximation

The space is divided in three regions



$$V_I(\vec{r}) = \sum_L V_L(r) Y_L(\hat{r}); L \equiv l, m$$

Only the $L=0$ is used

$$V_{II}(\vec{r}) = V_{MT} = \frac{1}{\Omega_{II}} \int_{\Omega_{II}} V(\vec{r}) d\vec{r}$$

V_{MT} is a constant average value

V_{III} has a spherical average form respect to the atomic cluster center

We must solve the S.E. with this potential

The total w.f. can be written as: $\Psi = \sum_j \Psi_I^j + \Psi_{II} + \Psi_{III}$

- In each atomic region (region I) the w.f. is developed into spherical harmonics:

$$\Psi_I^J(\vec{r}) = \sum_L B_L^J R_L^J(E; r) Y_L(\hat{r})$$

- V_{MT} is constant $\rightarrow \Psi_{II}$ is a combination of Bessel and Neumann functions
- In the OS region we use a very general expression that allow us to go from bound to continuum states

We impose the continuity of wave function Ψ and its first derivate at the border of the different regions



Compatibility equations between B_L^j coefficients



- full energy spectrum (bound and continuum part) of the molecular cluster
- w.f. in the various regions
- Spectroscopy quantities

$$B_L^i(\underline{L}) + t_l^i \sum_{j \neq i} \tilde{G}_{LL'}^{ij} B_{L'}^j(\underline{L}) = -t_l^i J_{L\underline{L}}^{io} \Gamma_{\underline{L}}$$

The amplitude of the w.f. at each atomic site i is formed by the one coming from the center plus all arriving from the other sites.

The model is a multiple scattering model for several centers with free propagation in the interstitial region

$$\tilde{G}_{LL'}^{ij} = G_{LL'}^{ij} - \sum_{L''} J_{LL''}^{i0} t_{l''}^0 J_{L''L'}^{oj}$$

$$G_{LL'}^{ij} = -4\pi i \sum_{L''} i^{l''+l'-l} C_{L'L''}^L h_{l''}^+(kR_{ij}) Y_{L''}(\hat{R}_{ij})$$

$$G_{LL'}^{ii} \equiv 0$$

 Gaunt coefficient

It describes the propagation of the electronic wave in the atomic cluster  geometry

$$t_l^i = W[j_l, R_l^i] / W[-ih_l^+, R_l^i] = e^{i\delta_l^i} \sin \delta_l^i$$

$$W[f(x), g(x)] = f(x) \frac{d}{dx} g(x) - g(x) \frac{d}{dx} f(x)$$

It depends on the solution inside the atomic spheres  chemistry

It is possible to write the total cross section as

$$\sigma(E) \propto \text{Im} \sum_{L L'} (M^*)^0_L \tau_{LL'}^{00} M^0_{L'}$$

$$M^0_L = \int \phi_{L_0}^0(\vec{r}) \hat{\varepsilon} \cdot \vec{r} R_L^0(\vec{r}) d^3r$$

$$\tau_{L,L'}^{00} = ([T_a^{-1} - \tilde{G}]^{-1})_{L,L'}^{00} = ([I - T_a \tilde{G}]^{-1} T_a)_{L,L'}^{00}$$



$$\begin{pmatrix} .. & & \tilde{G}_{ij} \\ & (t_\ell^i)^{-1} & \\ \tilde{G}_{ji} & & .. \end{pmatrix}^{-1}$$

$$T_a = \begin{pmatrix} t_l^0 & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & t_l^n \end{pmatrix}$$

scattering path operator - it contains all the structural and electronic information

The scattering path operator can be calculated exactly or by series

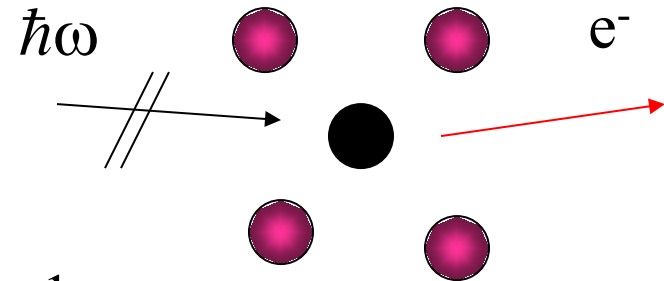
$$(I - T_a G)^{-1} = \sum_{n=0} (T_a G)^n$$

$$\tau = T_a + T_a G T_a G T_a + T_a G T_a G T_a G T_a + \dots$$

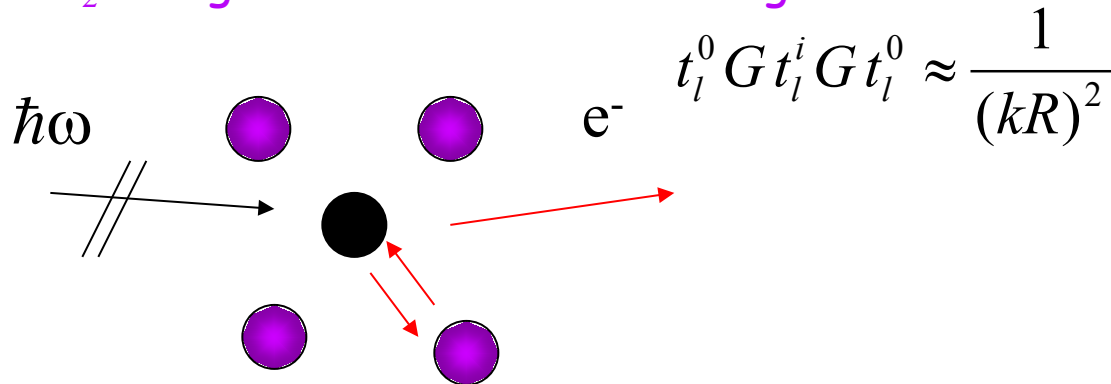

$$G_{LL'}^{ii} \equiv 0 \quad \text{we start from } n=2$$

MS paths

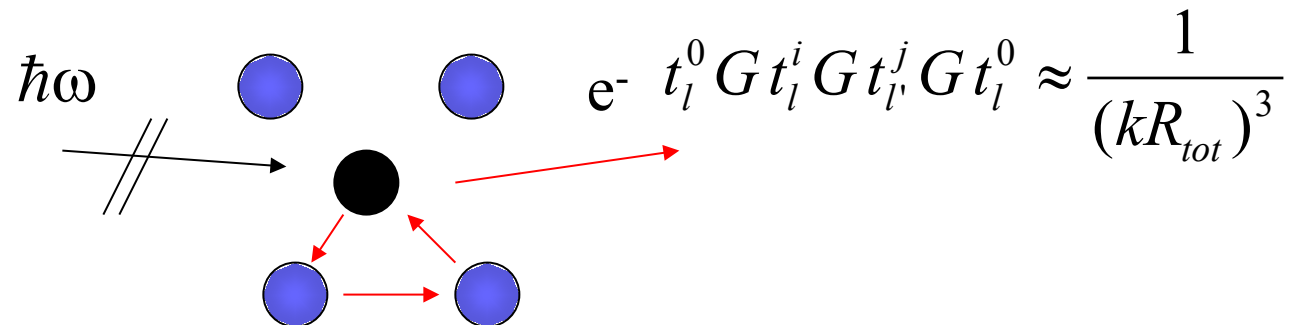
σ_0 – smooth atomic contribution



σ_2 – single diffusion - EXAFS region



σ_3 – double diffusion - high order correlation functions



We need to account for other physical processes

- inelastic excitations suffered by the photoelectron
- electronic excitations due to the creation on core-hole
- finite core hole width
-



finite lifetime of the photoelectron
in the final state

It is possible to built a MS multi-channels theory to include many-body effects

$$\sigma(E) \propto \text{Im} |S_0(E)|^2 \sum_{L L'} (M^*)_L^0 \tau_{LL'}^{00} M_{L'}^0$$

complex potential

$$G_{LL'}^{ij} \approx \frac{e^{ikR_{ij}}}{k R_{ij}}$$

- If $k = k_r + i k_i$ we have a decreasing exponential
- there is a damping in the elastic signal

We use the complex Hedin-Lundqvist potential that has an imaginary part able to reproduce the observed mean free path in metal

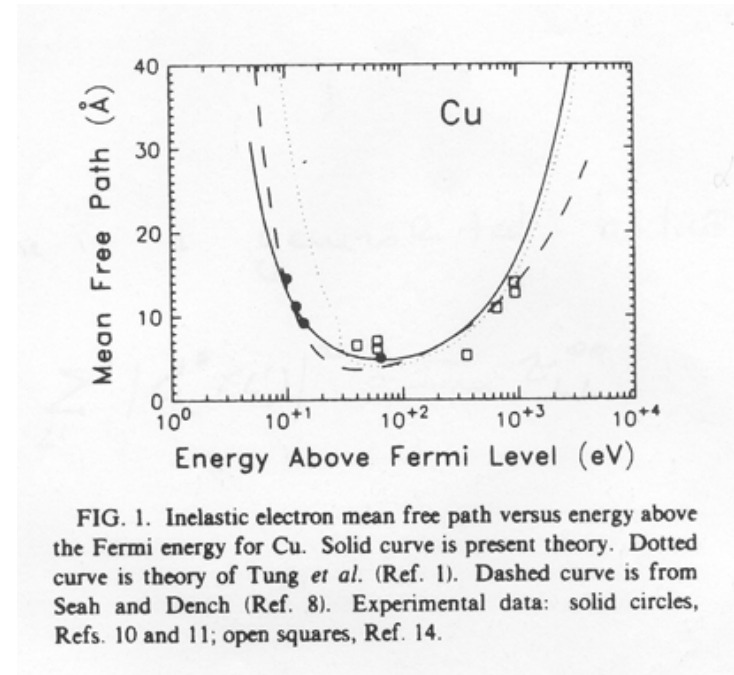
$$\lambda_{tot} = \frac{k}{\Gamma_{tot}(E)}$$

Where

$$k = \sqrt{E - E_0}$$

$$\Gamma_{tot} = \frac{1}{2}\Gamma_{c-h} + |\Gamma_i(E)|$$

$$V_{exc}(\vec{r}) \rightarrow \Sigma_{exc}(\vec{r}; E) = V(\vec{r}; E) + i\Gamma_i(\vec{r}; E)$$

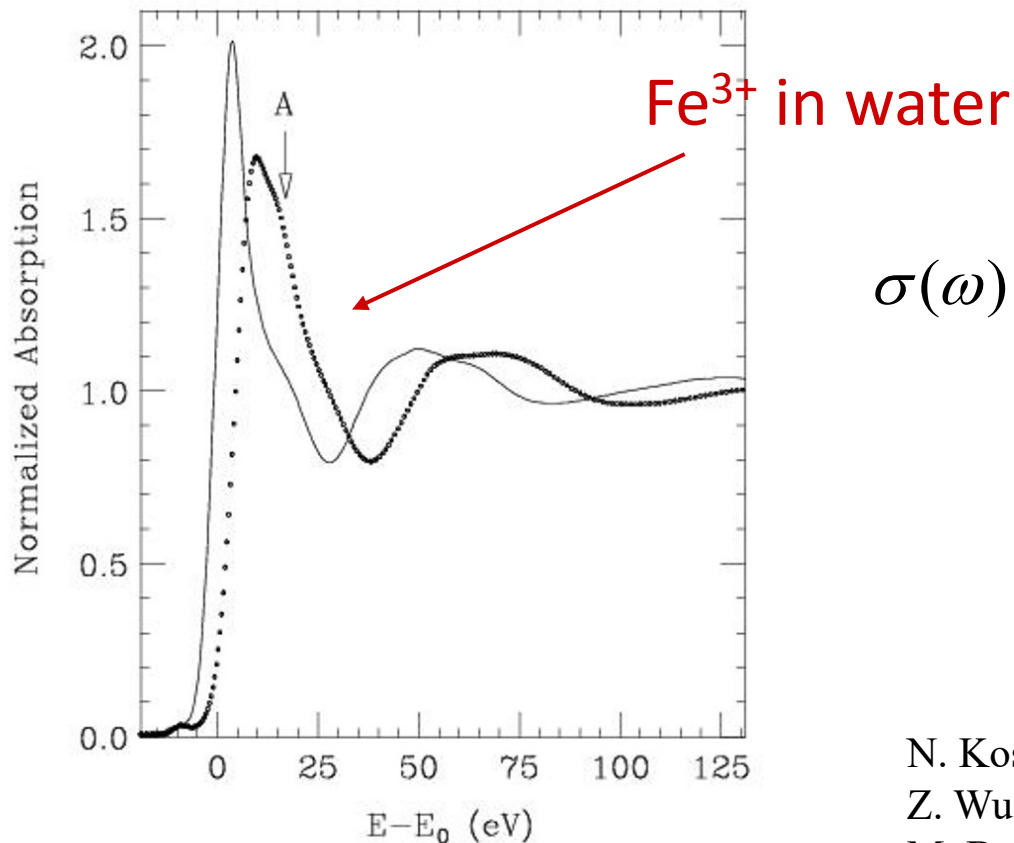


- we see only few shells around the absorber
- typically 5-10 at the edge

- no needs for crystal - sample in any type of conditions
- atomic selectivity - we can choose the site by tuning the energy
- short range three-dimensional structural information

The case of several electronic configurations

Several systems can generate K-edge XANES with “extra” peaks due to the presence of different electronic configurations



$$\sigma(\omega) = a^2 \sigma_0(k_0) + b^2 \sigma_1(k_1) + \dots$$

$$k_0^2 = \hbar\omega - I_c$$

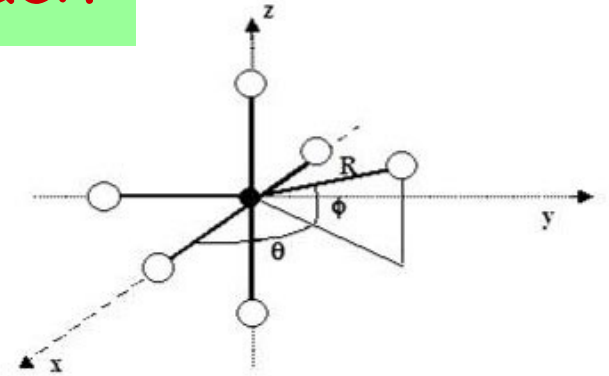
$$k_1^2 = \hbar\omega - I_c - \Delta E_1$$

N. Kosugi et al. (1989) Chem Phys. **135**, 149

Z. Wu et al. (1996) PRB **54**, 13409

M. Benfatto et al. (2002) Chem. Phys. **282**, 441

XANES part - the MXAN approach



MXAN is a software package able to fit the low energy part of the XAS spectrum, the XANES energy region, spectra in terms of structural parameters

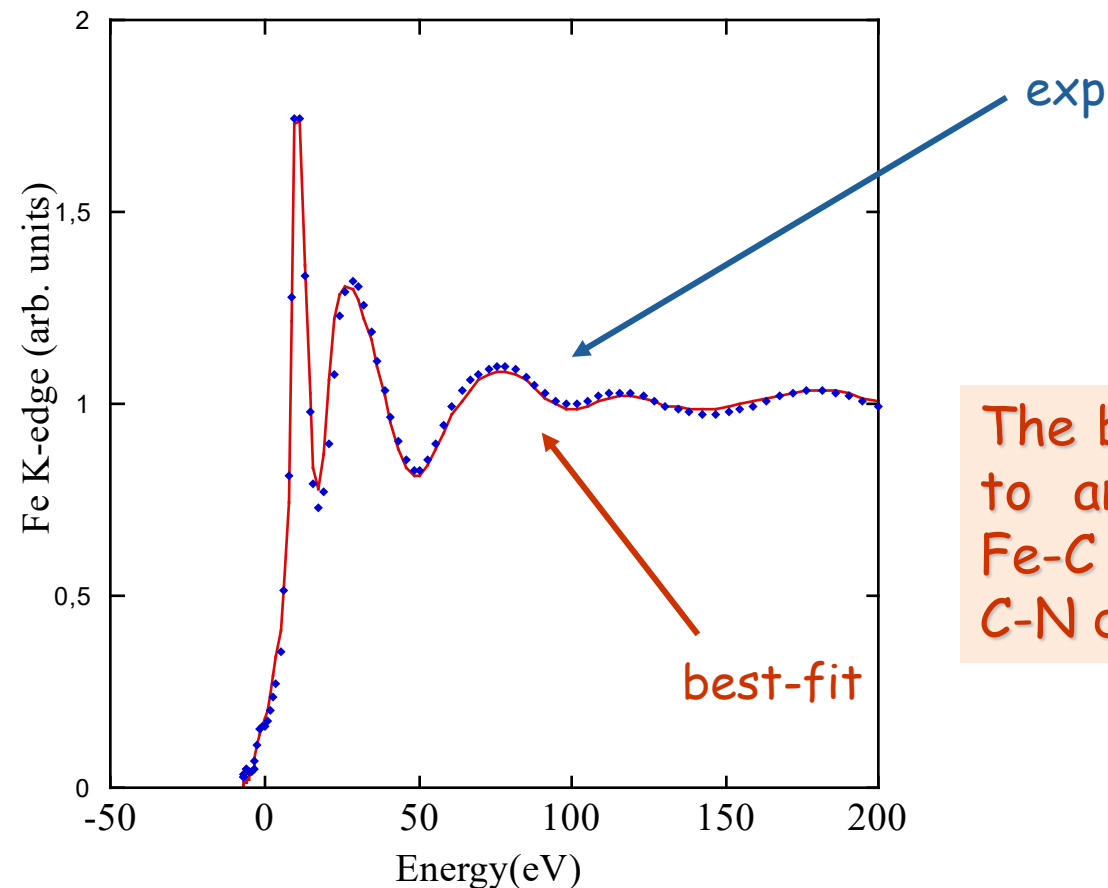
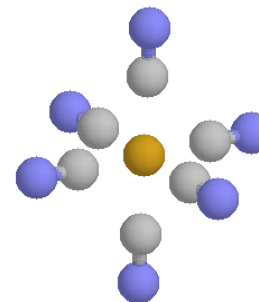
- work in the energy space
- start from the edge
- No DW factors are included

M. Benfatto and S. Della Longa J. Synch. Rad. **8**, 1087 (2001)

S. Della Longa et al. PRL **87**, 155501 (2001)

M. Benfatto et al. Computer Phy. Comm. **265**, 107992 (2021)

Fe (CN)₆ in water

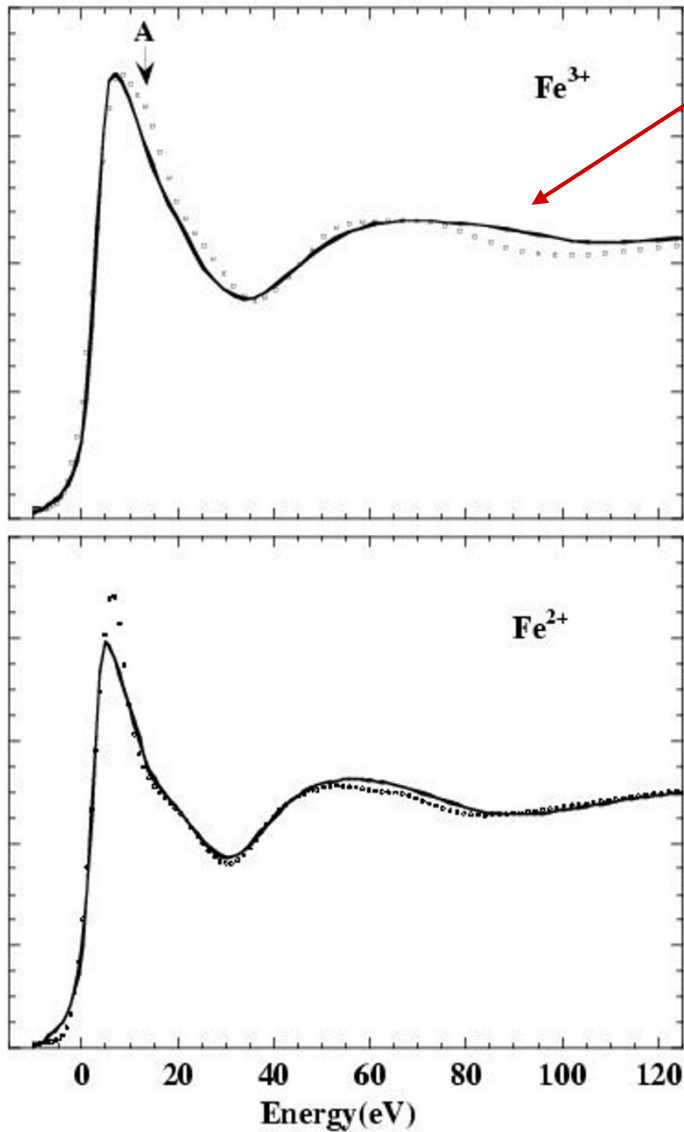


The best-fit condition corresponds to an octahedral symmetry with Fe-C distance of 1.92(0.01) Å and C-N distance of 1.21(0.01) Å

Previous GNXAS analysis (Westre et al. JACS 117 (1995)) reports Fe-C and Fe-N distances of 1.92 Å and 1.18 Å respectively

The MXAN methods fails for the Fe^{3+} case

No way to get a fit



about the MT approximation

we note that it is always possible to write a non-MT theory as

$$\sigma_t \approx \text{Im}(T + H)^{-1} \quad \begin{array}{l} T = (T_a)^{-1} + \Delta T \\ H = H_{MT} + \Delta H \end{array}$$

$$\sigma_t \approx \text{Im} \left\{ \sum_{n=0} (-1)^n [(T_a^{-1} + H_{MT})^{-1} \Delta]^n (T_a^{-1} + H_{MT})^{-1} \right\}$$

$$\sigma_t \approx \sigma_{MT} + \text{corr}(E; V_{\text{int}}) \quad \Delta = \Delta T + \Delta H$$

This also suggest how to minimize the effects of the non-MT corrections: by optimization of the MT radii and the interstitial potential – MXAN does this now within the structural loop.

C.R. Natoli, M.Benfatto and S. Doniach (1986) PRA **34**; R. Sarangi et al. (2005) Inorganic Chemistry **44**; M.Benfatto, S. Della Longa and P. D'Angelo (2005), Physica Scripta T115, 3

many different applications

from the coordination geometry of metal site in proteins to the time-depended spectra in the fs time domaine (data from LCLS facility).

S. Della Longa et al. Biophy. Jour. (2003) **85**, 549

P. Frank et al. Inorganic Chemistry (2005) **44**, 1922

C Monesi et al. PRB **72**, 174104 (2005)

P. D'Angelo et al. JACS (2006) **128**, 1853

.....

M. Bortolus et al. JACS (2010) **132**,18057

R. Sarangi et al. Journal of Chemical Physics (2012), 137, 2015103

.....

P. Frank et al. Journal of Chemical Physics (2015), 142, 084310

G. Chillemi et al. Journal of Physical Chemistry A (2016), 120, 3958

H.T. Lemke et al. Nature Communication (2017), 8, 15342

C. Evangelisti et al. ChemPhysChem (2017), 18, 1921

A. Zitolo et al. Nature Communication (2017), 8, 957

.....

MXAN and difference spectra

$$\Delta A(E, \Delta t) = f(\Delta t)[\mu_{ex}(E, \Delta t) - \mu_{gs}(E)]$$

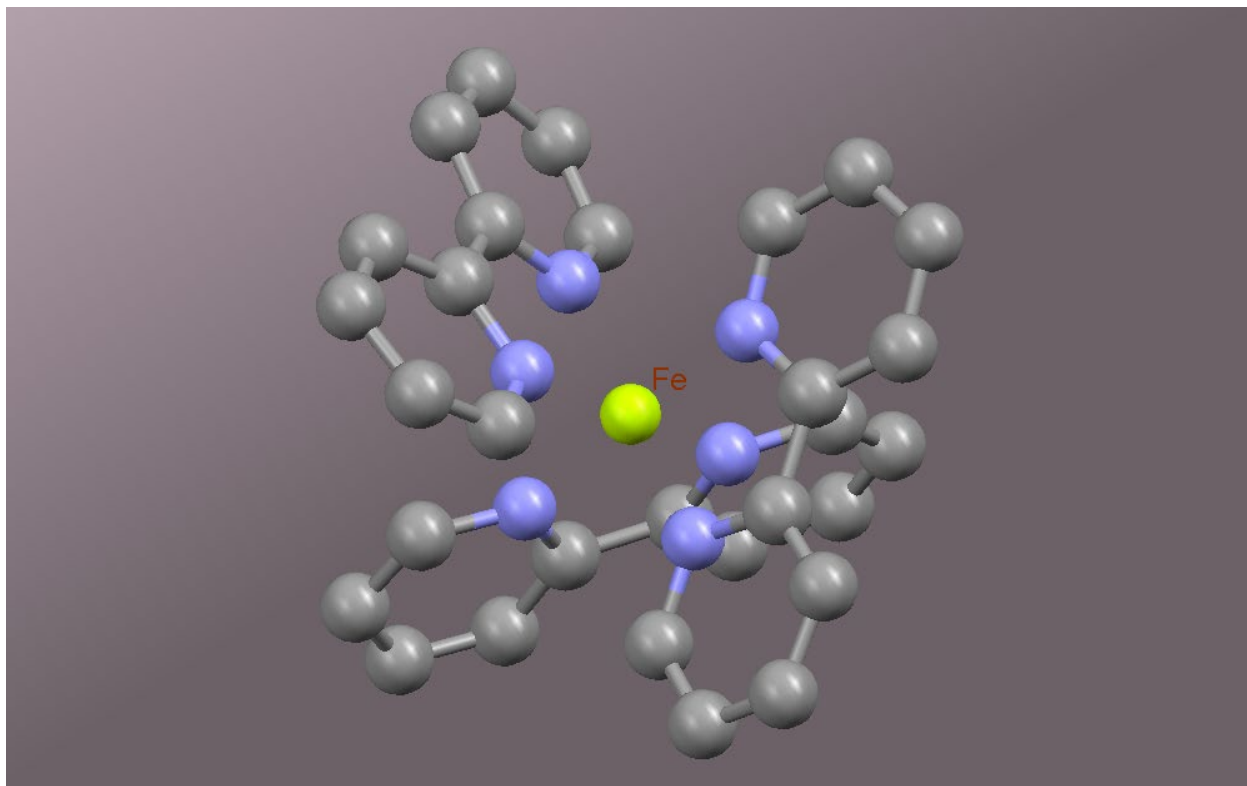
$f(\Delta t)$ ← is the fractional population of the ex-state at time delay Δt

To see (small) structural changes due to physical/chemical reasons in pump-probe experiments

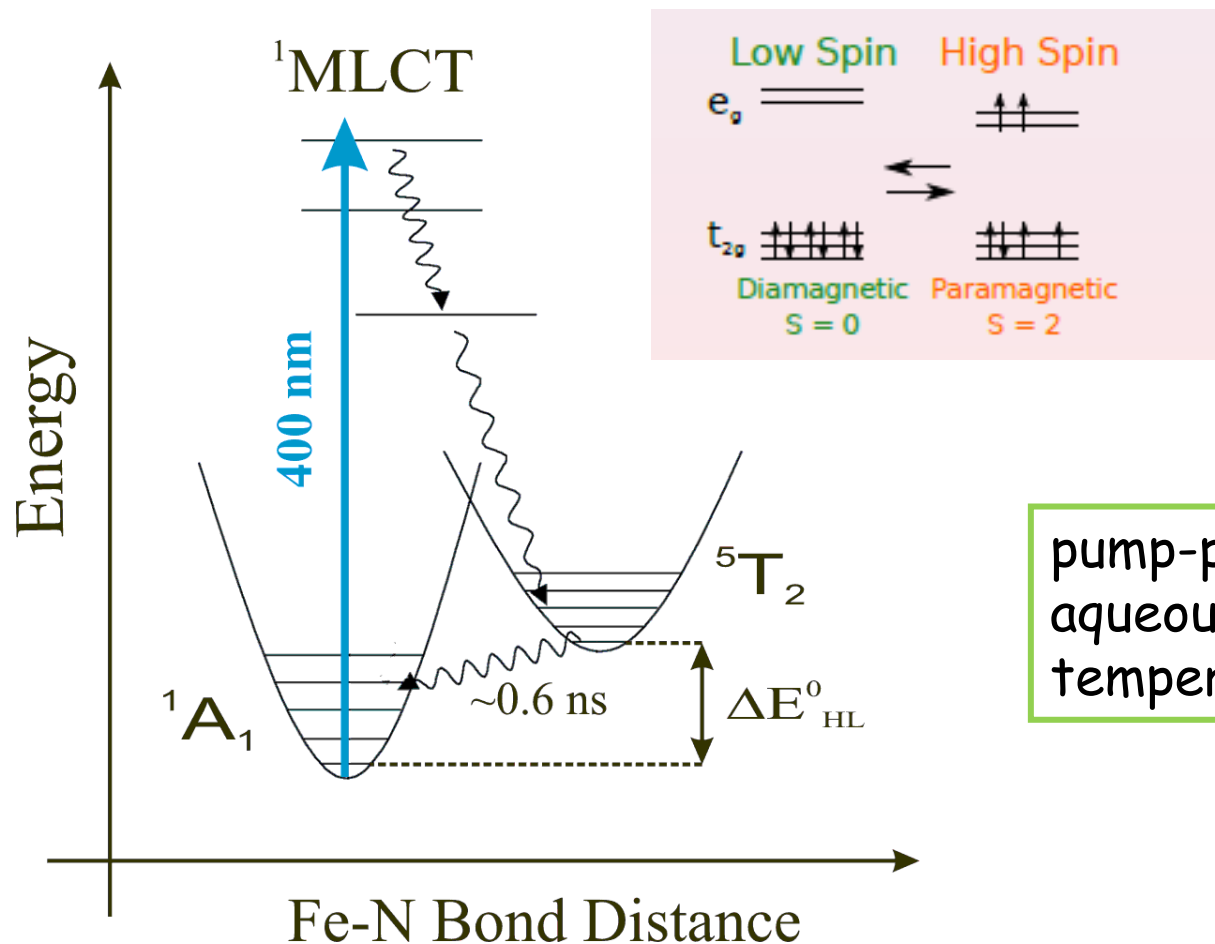
- time resolved experiment
- changes of chemical-physical and/or thermo-dynamical conditions

.....

the case of iron-(II)-tris-bypyridine $[\text{Fe}^{\text{II}}(\text{byp})_3]^{2+}$



see the structural changes going from LS to HS state



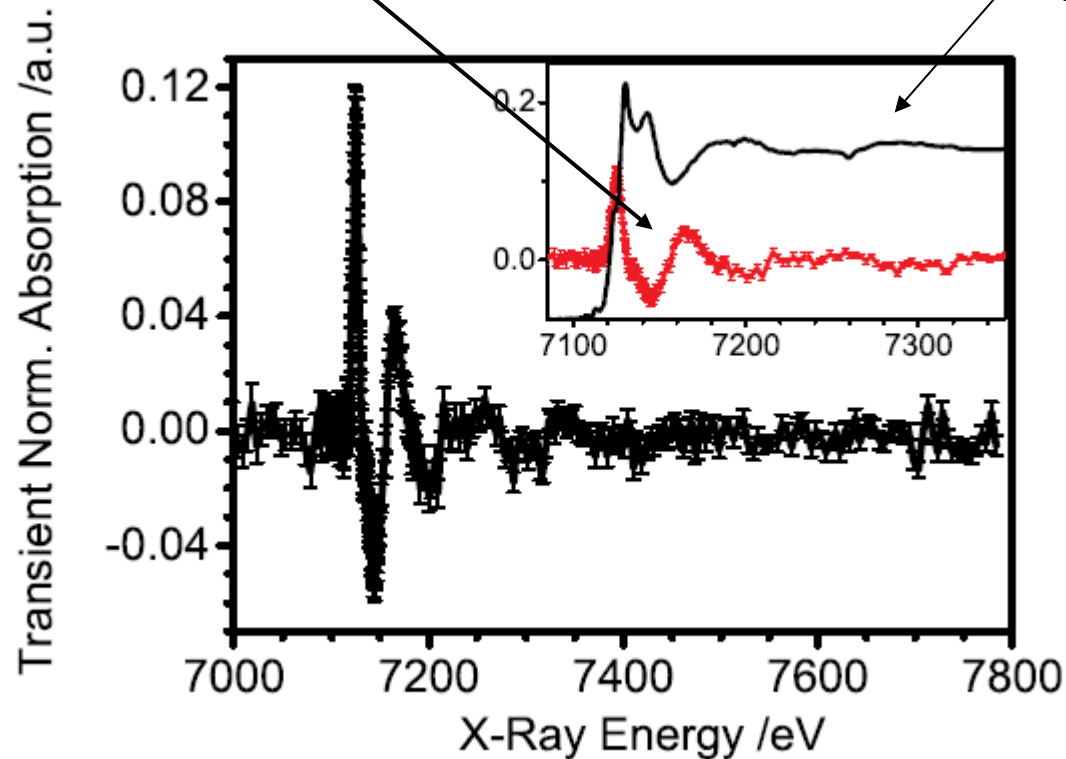
pump-probe experiment in aqueous solution and room temperature

The detected signal is directly the quantity $\Delta A(E, \Delta t)$

experimental data

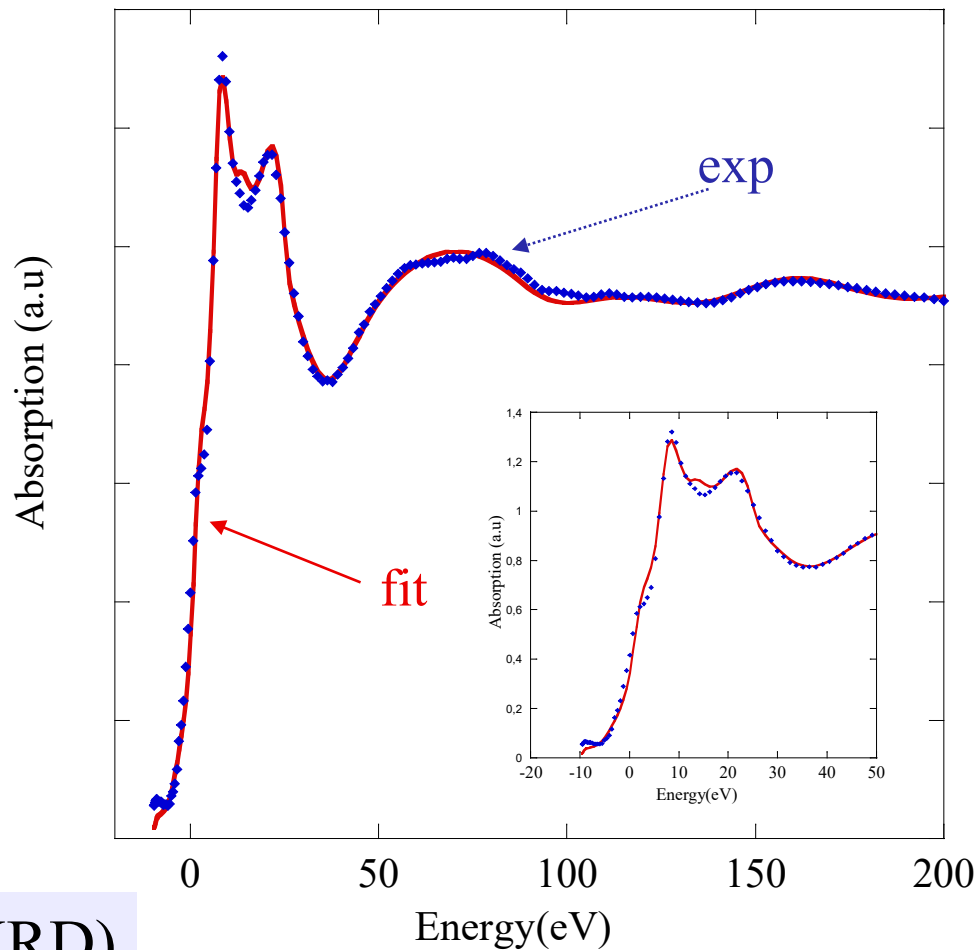
HS transient data at $\Delta t = 50$ ps

LS gs data



LS ground state fit

$$R_{\text{Fe-N}} = 2.00 \pm 0.02 \text{ \AA}$$



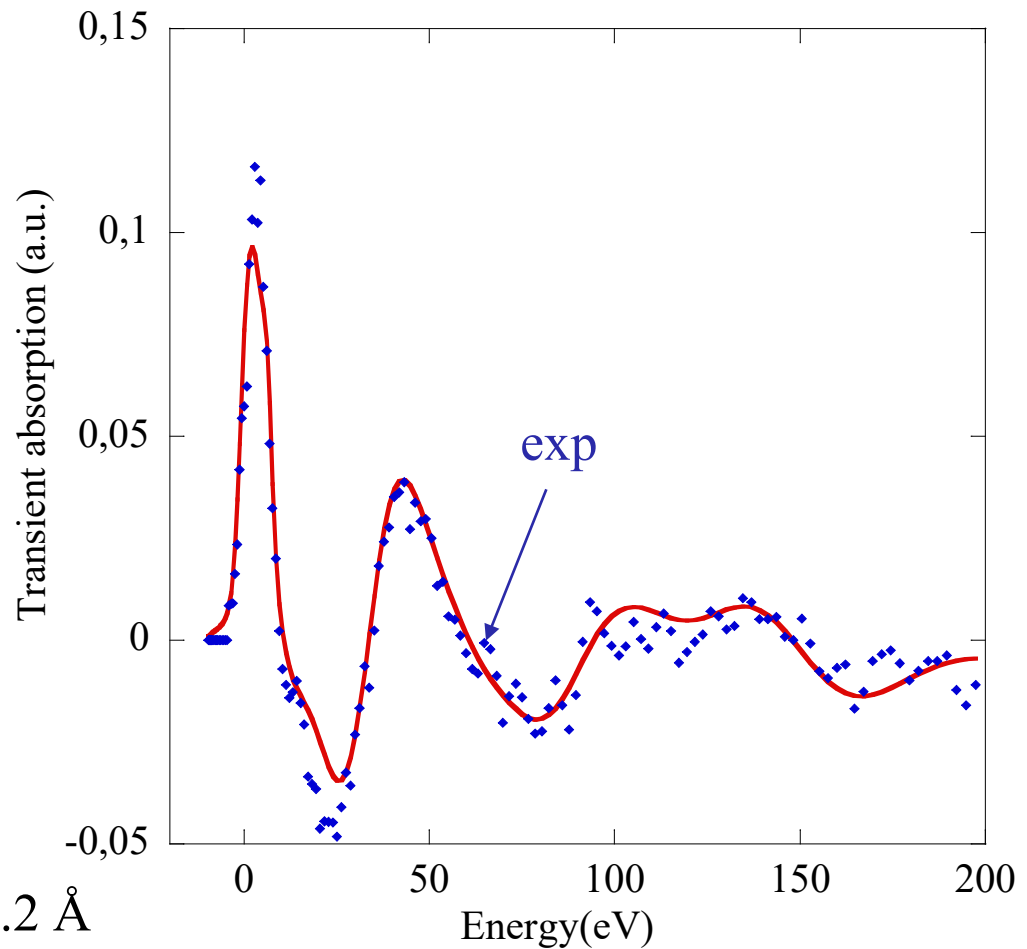
$$R_{\text{Fe-N}} = 1.967 \pm 0.006 \text{ \AA (XRD)}$$

$$R_{\text{Fe-N}} = 1.99 \pm 0.02 \text{ \AA (DFT)}$$

HS excited state fit by transient data

$$\Delta R_{\text{Fe-N}} = 0.20 \pm 0.05 \text{ \AA}$$

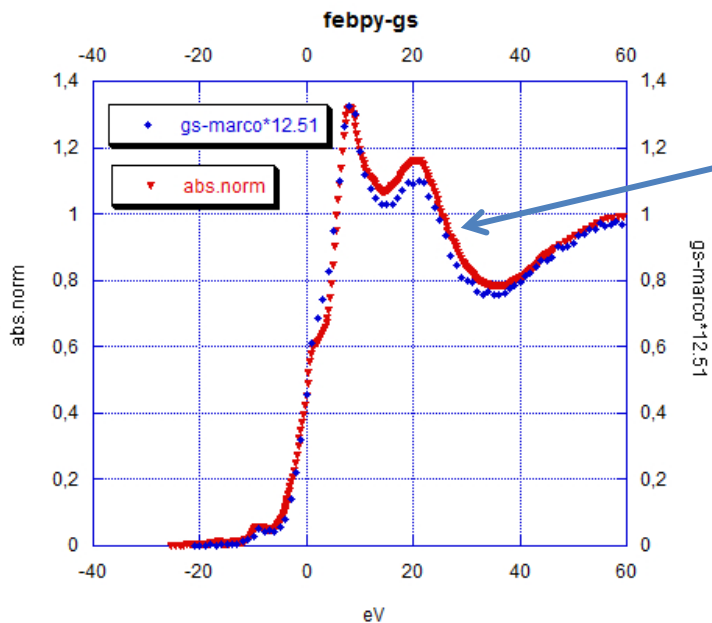
DFT calculations indicate $\sim 0.2 \text{ \AA}$



going to the fs time scale FEL experiment

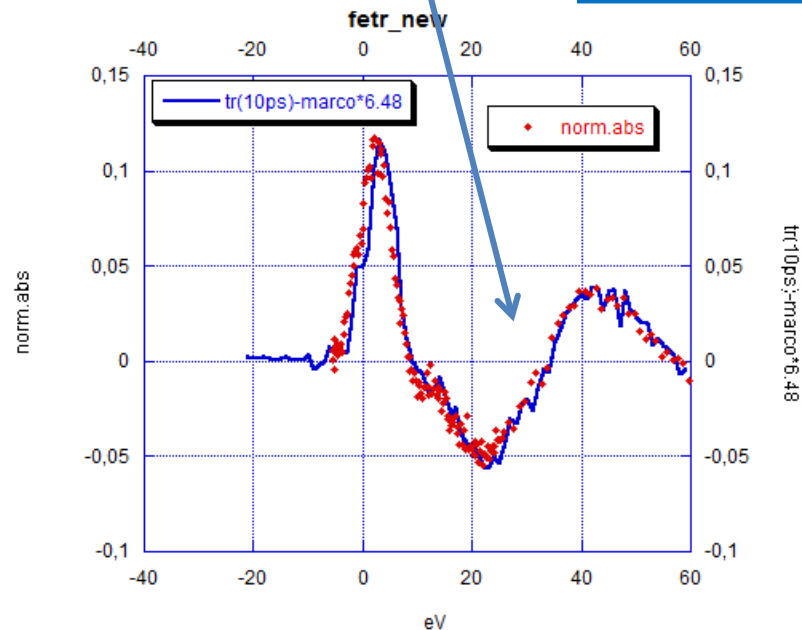
iron-(II)-tris-bypyridine $[\text{Fe}^{\text{II}}(\text{byp})_3]^{2+}$

Exp data taken at LCLS

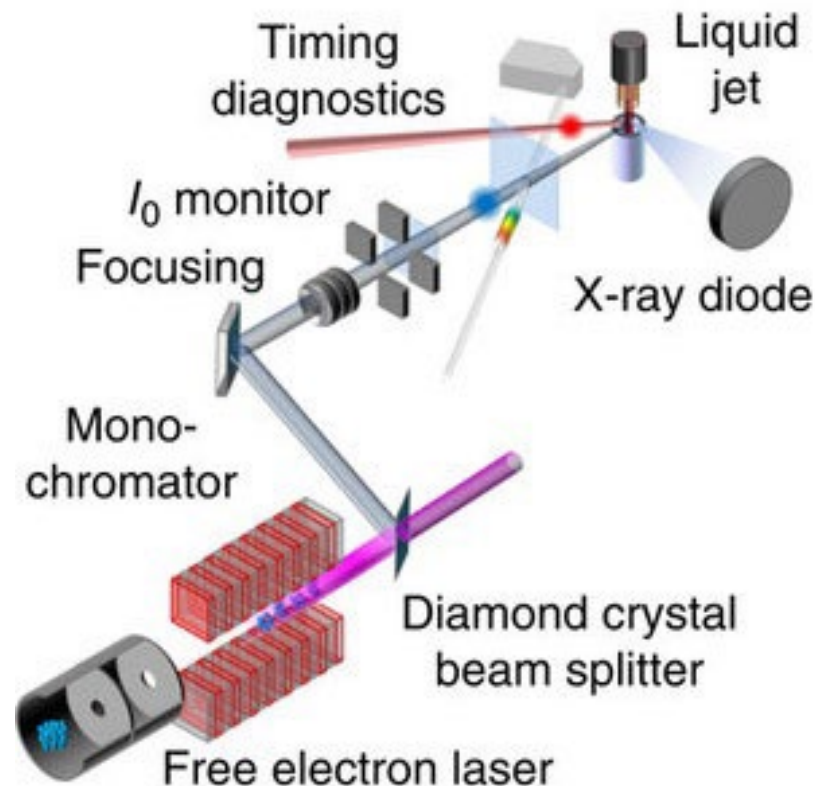


MXAN fits of such data give the results previously obtained within the statistical error

transient at 10 ps

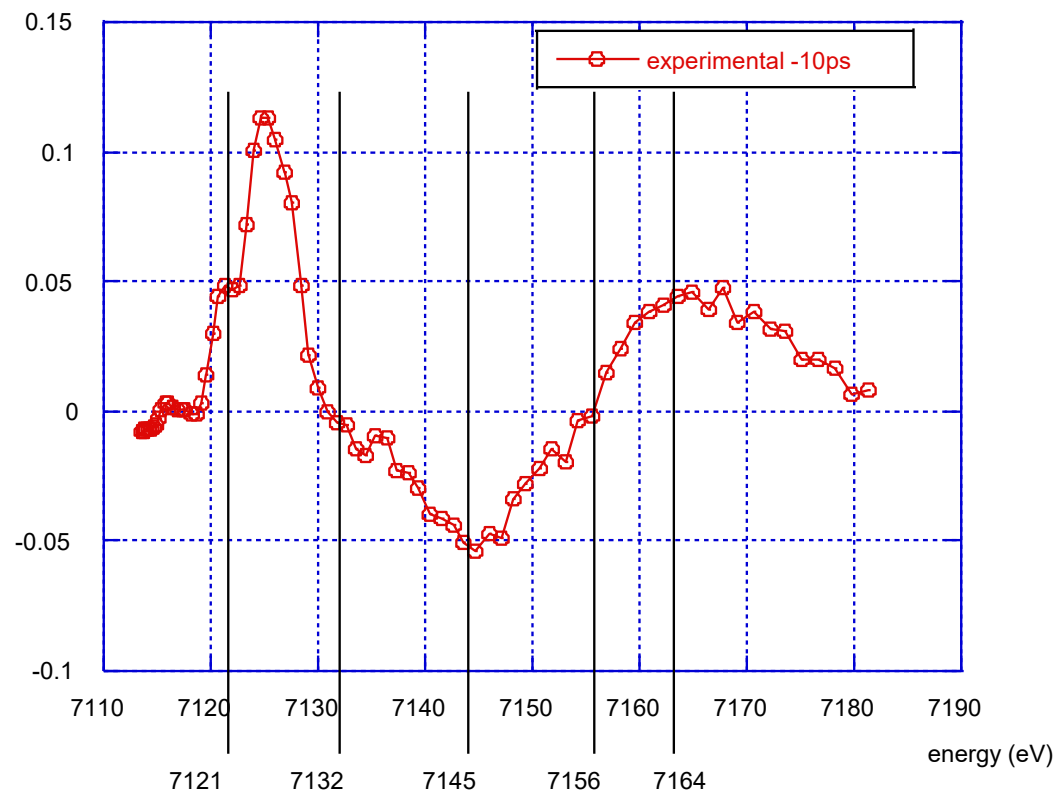


experimental set-up at LCLS – time resolution ≈ 25 fs
– the light is monochromatized by a double diamond (111) crystal – focus on sample ≈ 10 μm



at the fs time scale it is impossible to take extended experimental data – they must be taken at fixed energy

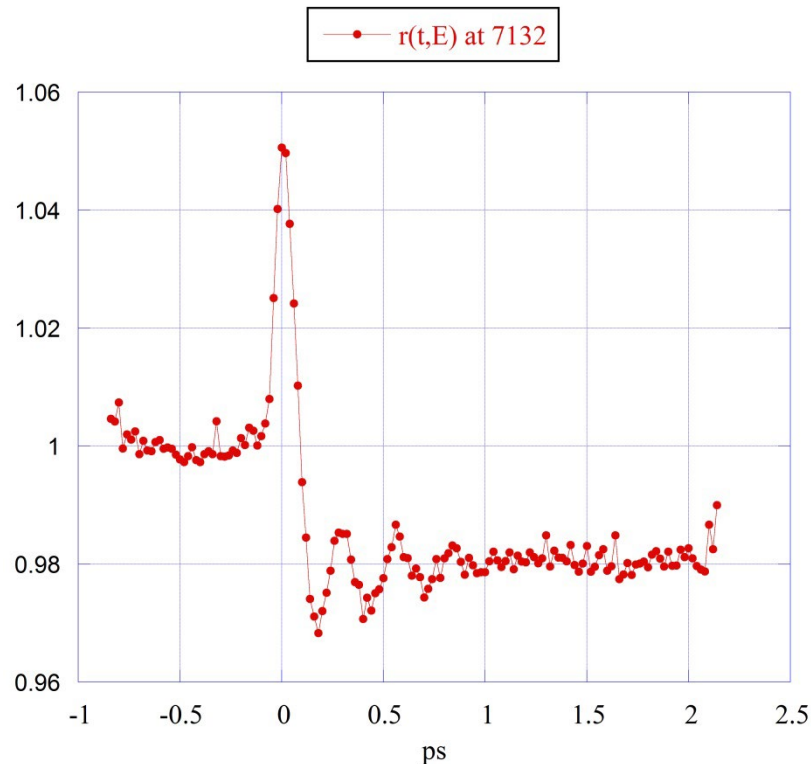
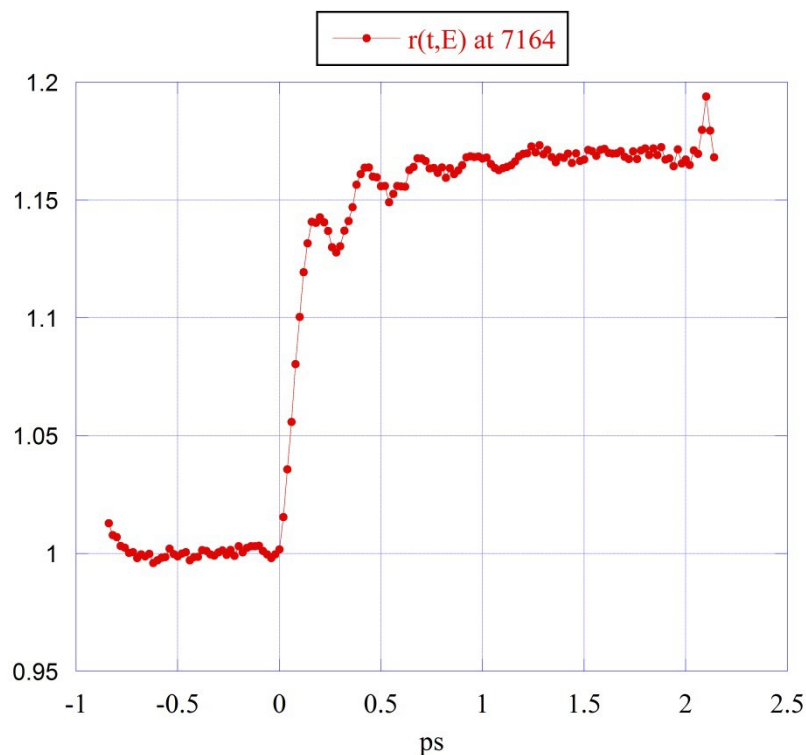
the transient data are taken as function of time but at fixed energy, in particular at 7121, 7132, 7145, 7156 and 7164 eV



here the exp. data is the ratio

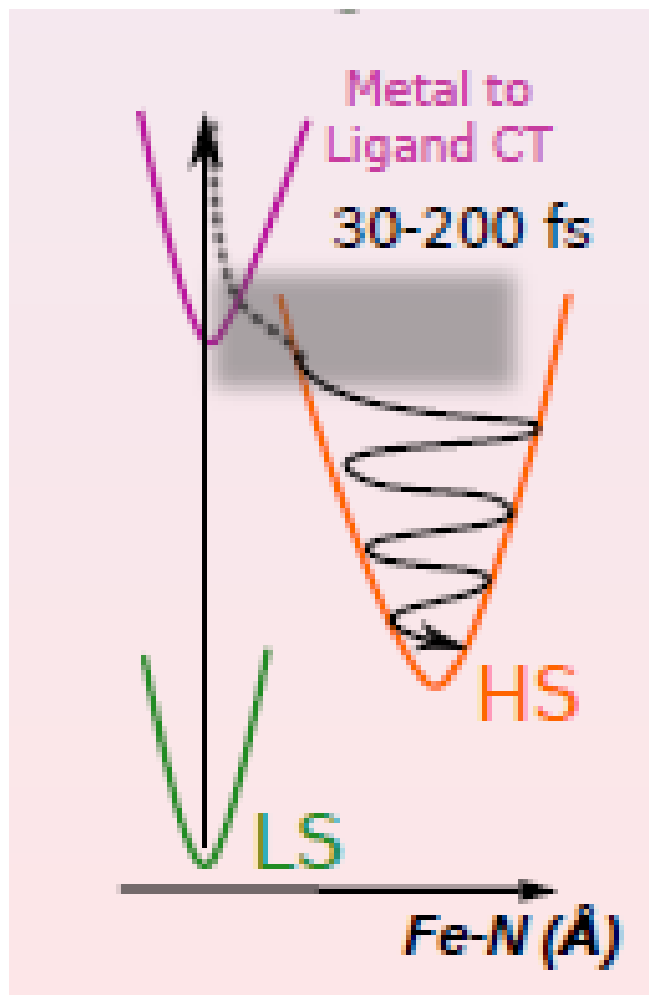
we get data as function of time

$$r(t, E) = S(t, E) / S_{GS}(E)$$



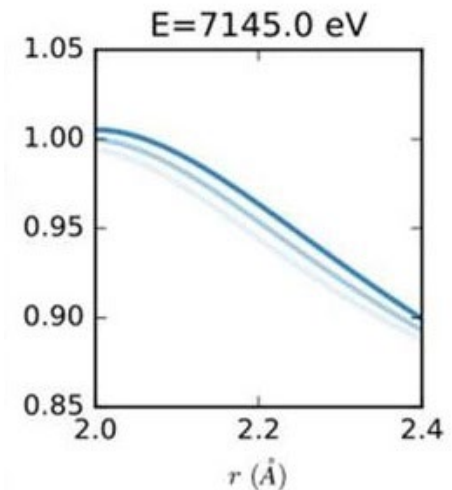
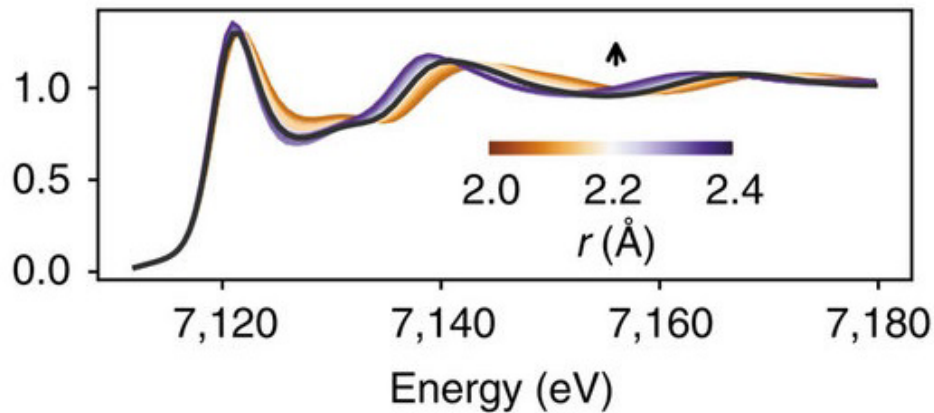
oscillations up to 2ps with a period of about 0.265 ps corresponding to 126 cm^{-1} - the system is in the HS state after 2ps.

all data shows a rapid change within 30-200 fs followed by an oscillating phase up to 1-2 ps. After this we reach the HS state.



how to analyze these data?

we see how the calculated spectrum change as function of Fe-N distance

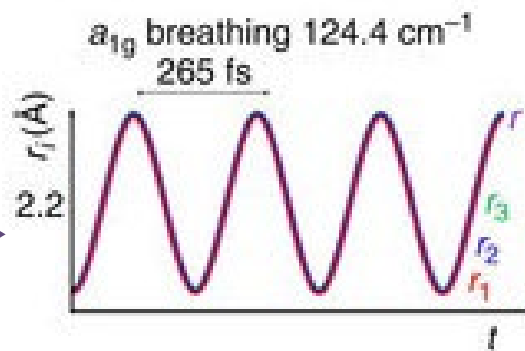
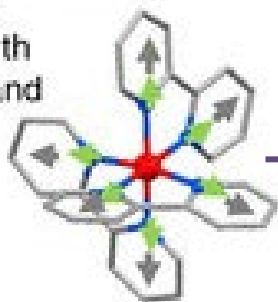


with these calculations we build the signal

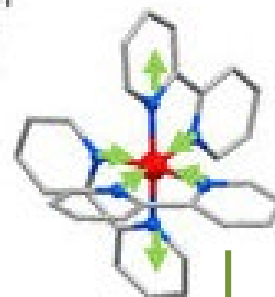
where $S(E, r)$ is the calculated signal for a given E and r
 $g(r, t)$ is a numeric time-dependent distance distribution coming from the breathing mode at $124,4 \text{ cm}^{-1}$

$$I(t, E) = \int S(E, r) g(r, t) dr$$

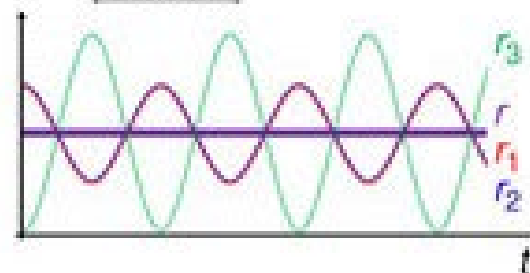
a_{1g} 124.4 cm^{-1}
breathing mode in
phase Fe-N
stretching with
rigid bpy ligand



e_g 115.9 cm^{-1}
out of phase
Fe-N
stretching

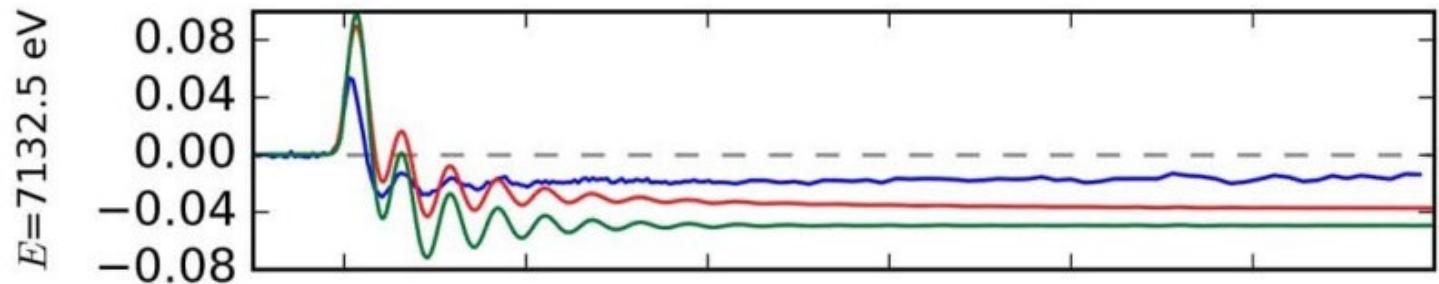


e_g mode 115.9 cm^{-1}
288 fs

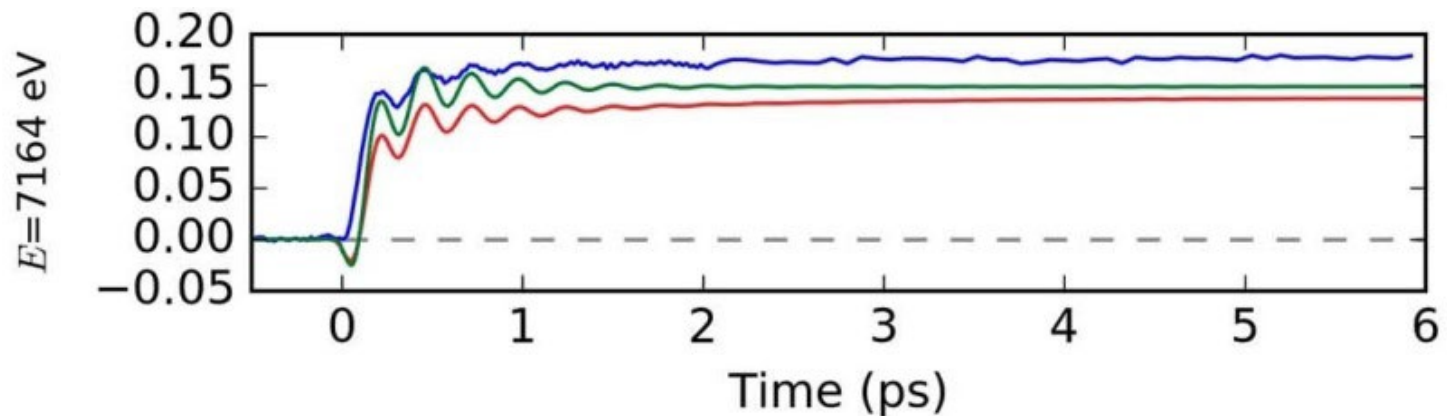


here we plot $[I(t, E_i) - I(E_i)_{off}] / I(E_i)_{off}$

— Exp. data — with $I(t, E_i)$ — with $I(t, E_i, \bar{r})$



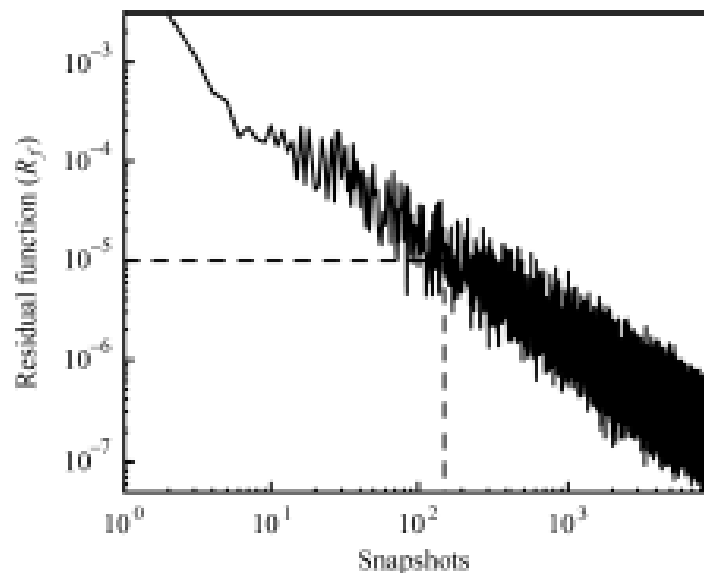
.....



MXAN and Molecular Dynamics

we use MD to generate thousands of geometrical configurations, each one, taken every 50 fs, is used to generate one XANES spectrum – the averaging procedure stops when $R_f(N)$ is below 10^{-5} - typically about 10^4 geometrical configurations.

$$R_f(N) = \left[\sum_i [\sigma^N(E_i) - \sigma^{N-1}(E_i)]^2 \right]^{1/2}$$

P. D'Angelo et al. (2006) JACS ,128, 1853

MD details

- classical MD – solve the Newton's equations of motion for a given force field - GROMACS
- two body potential formed by two parts: bonded and nobonded interactions (LJ and Electrostatic interactions) – if needed, corrections to account QM effects

$$\mathbf{f}_i = m_i \cdot \mathbf{a}_i$$

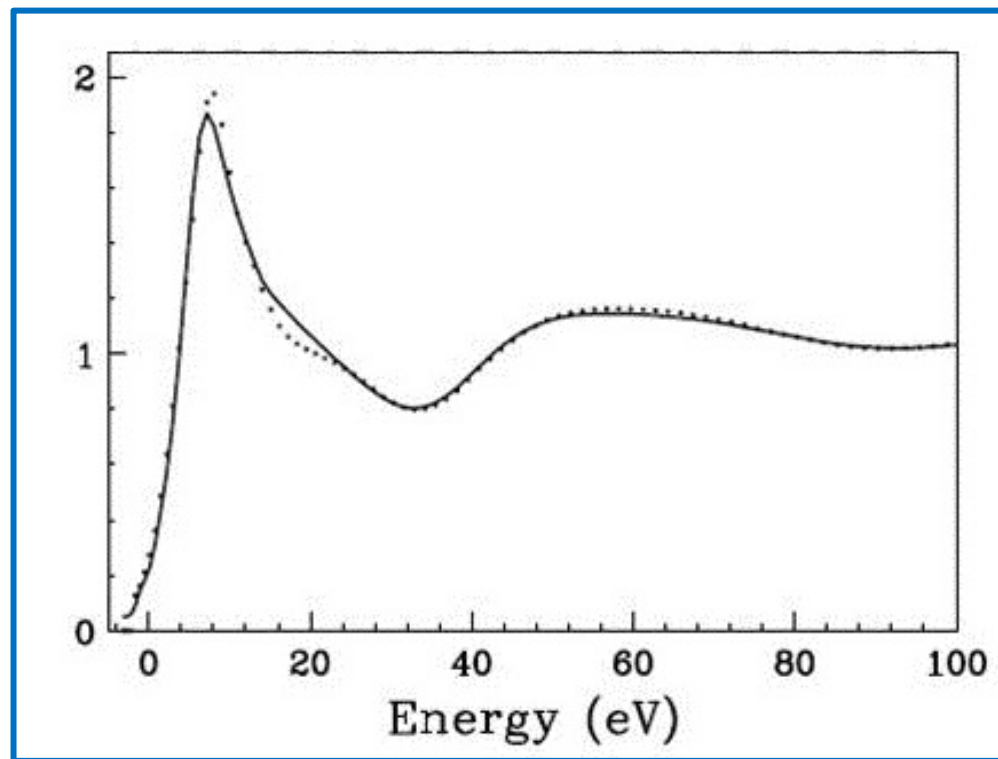
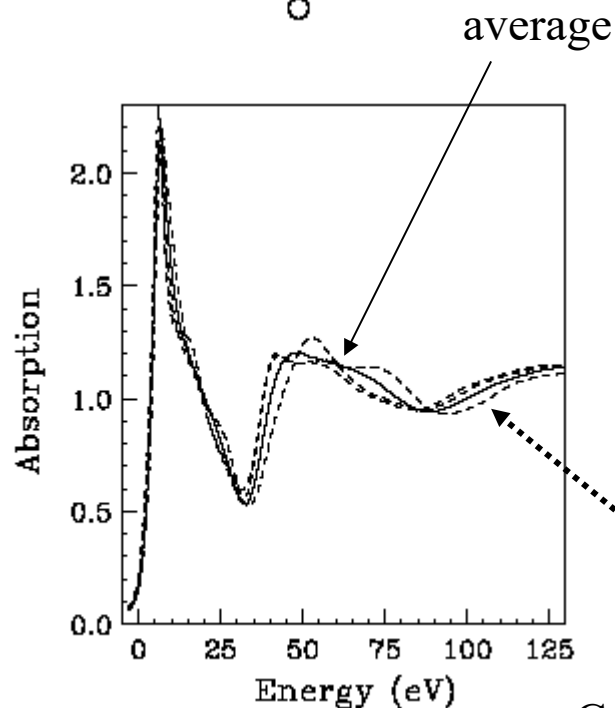
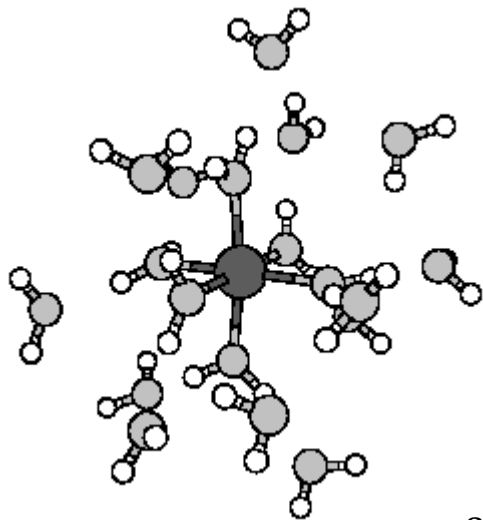
$$\mathbf{f}_i = -\frac{\delta V}{\delta \mathbf{r}_i}$$

$$\begin{aligned}
 V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = & \sum_{bond} \frac{1}{2} k_{b_0} (b_n - b_{0_n})^2 + \sum_{angle} \frac{1}{2} k_{\theta_0} (\theta_n - \theta_{0_n})^2 + \\
 & + \sum_{\substack{improper \\ dihedral}} \frac{1}{2} k_{\xi_0} (\xi_n - \xi_{0_n})^2 + \sum_{dihedral} 1 + \cos(m_n \phi_n - \delta_n)^2 + \\
 & + \sum_{\substack{nonbonded \\ pairs(ij)}} \left(\left(\frac{C_{ij}^{(12)}}{r_{ij}^{12}} - \frac{C_{ij}^{(6)}}{r_{ij}^6} \right) + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{\epsilon_r r_{ij}} \right)
 \end{aligned}$$

L-J potential $\longrightarrow$ Van der Waals interactions. $C^{(6)}$ is the constant in the term describing the dispersion attractive force between atoms; $C^{(12)}$ is in the term that describes interatomic electron cloud repulsion

Ni^{2+} in water – Ni Kedge

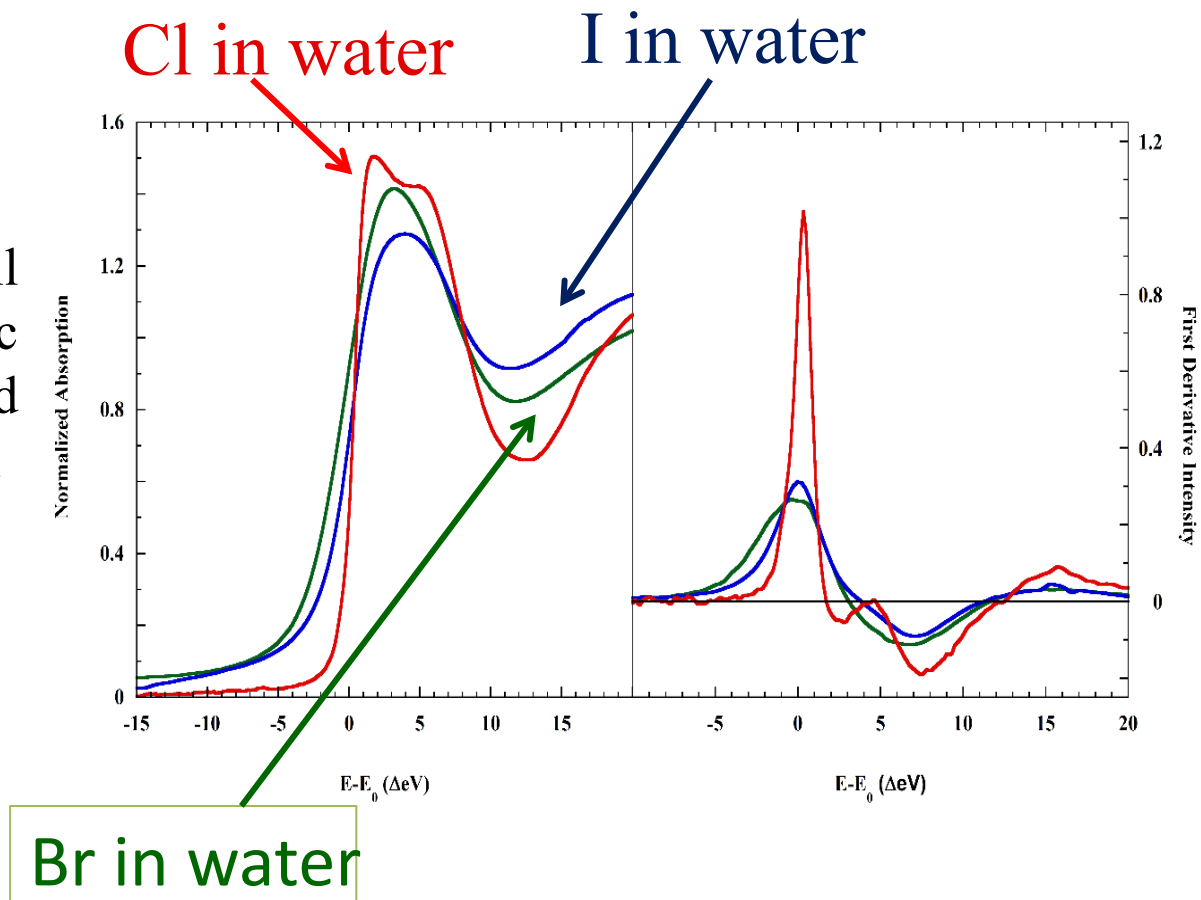
including the second shell



Calculations (without any damping) for some particular⁴² snapshots

the “strange case ” of Cl

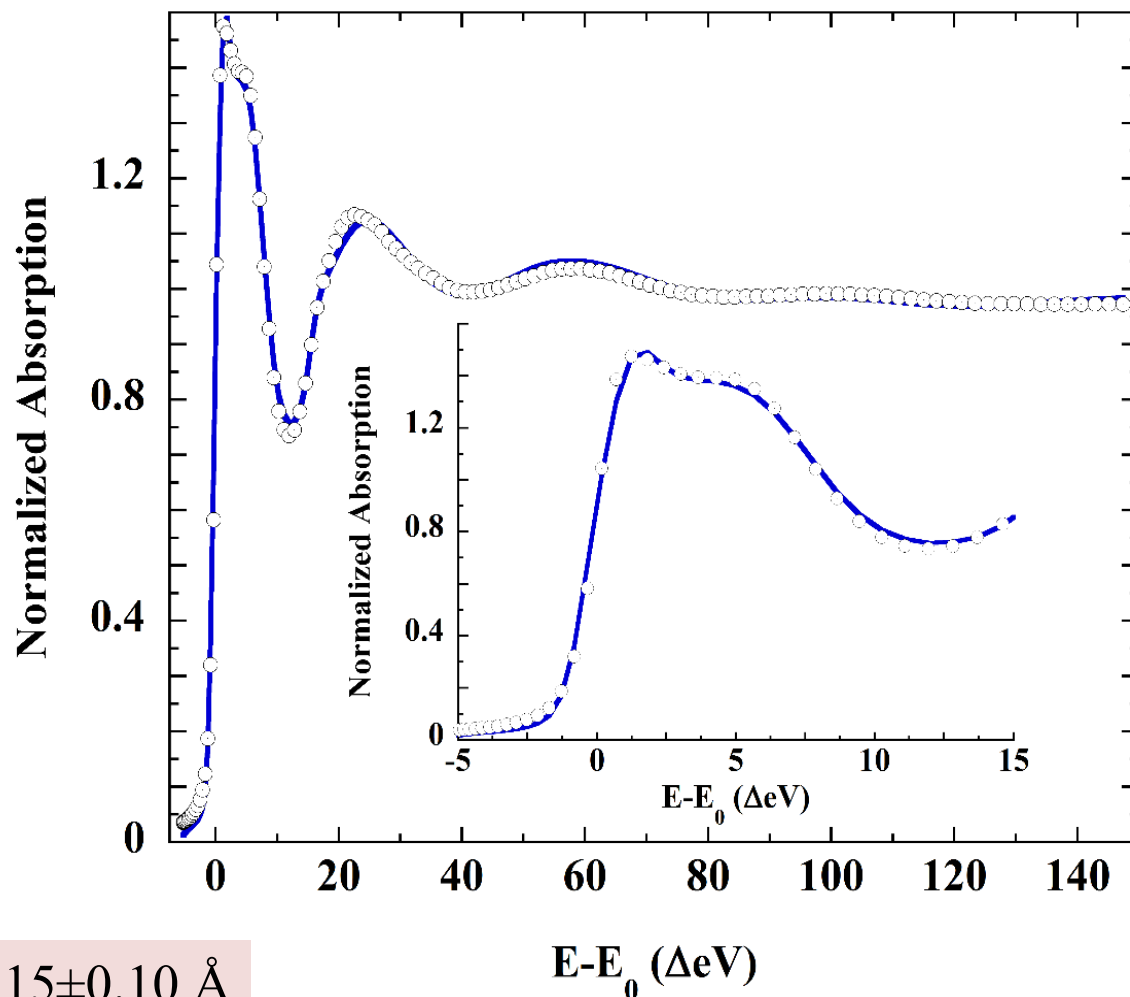
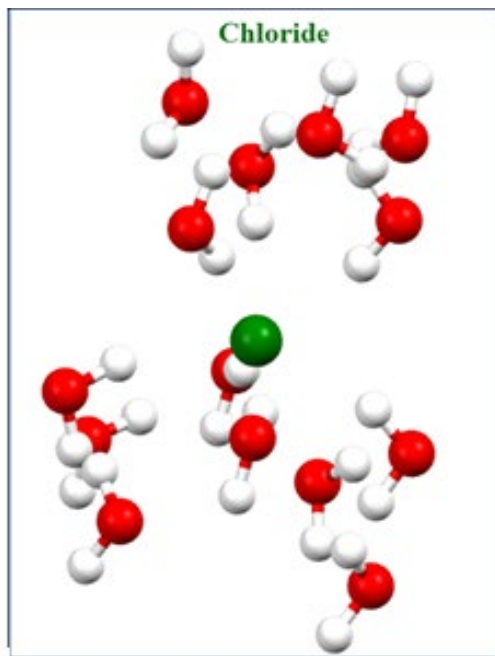
The three halide ions are all filled shell and iso-electronic ($3p^6$, $4p^6$, $5p^6$) – same ground state electronic configuration



M. Antalek et al. (2016) The Journal of Chemical Physics 145 (4), 044318.

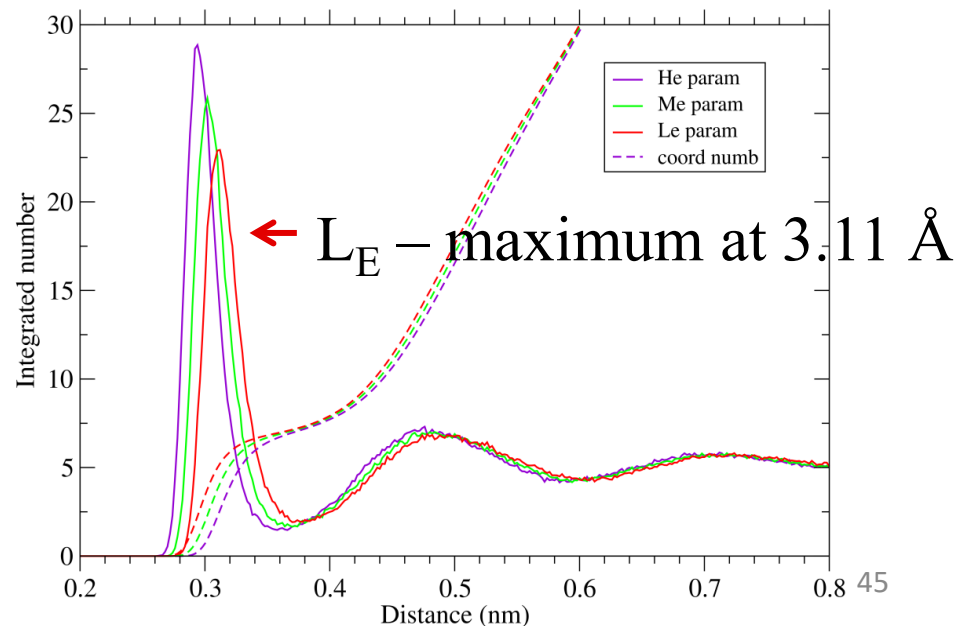
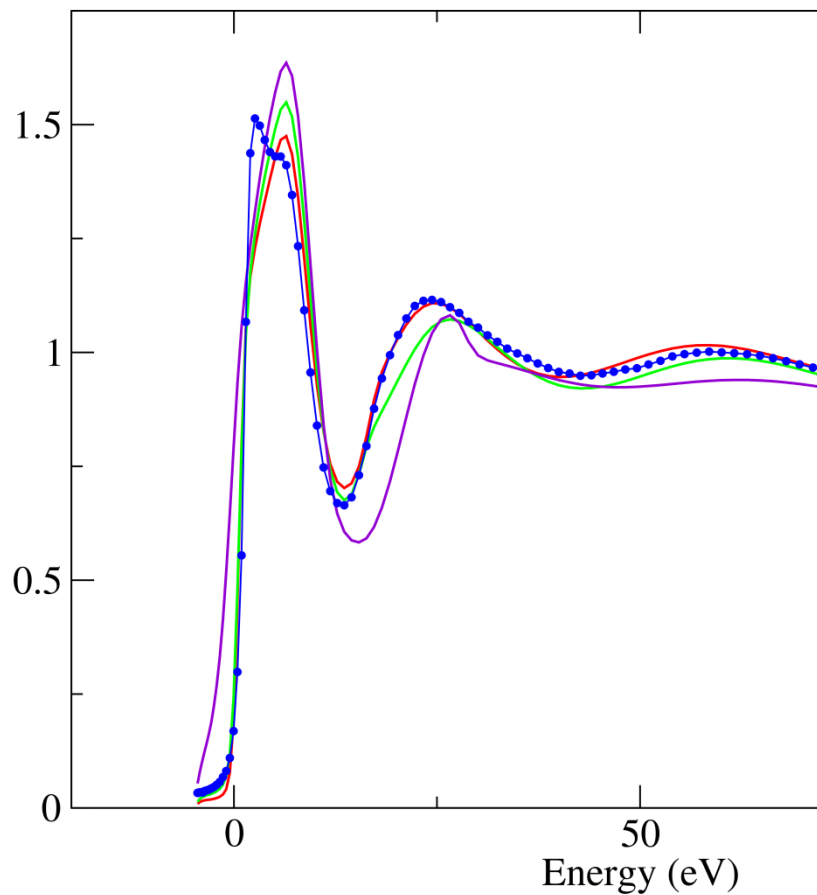
M. Benfatto et al. International Tables for Crystallography (2020). Vol. I, Edited by C. T. Chantler, F. Boscherini and B. Bunker

while Iodine and Bromine are well fitted with a first 8-fold coordination shell the Chloride needs two shells of 7+7 water molecules

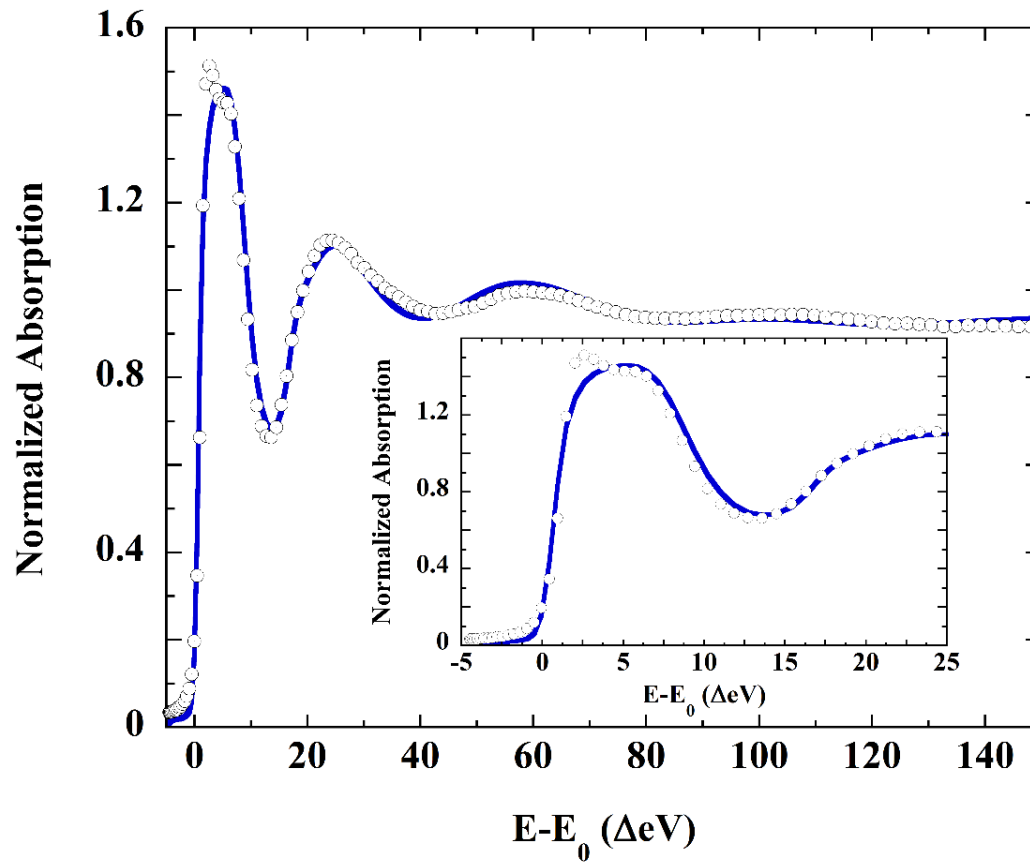


The fit gives a first shell at $3.15 \pm 0.10 \text{ \AA}$
and a second one at $4.14 \pm 0.31 \text{ \AA}$

DM of Cl in water - three different L-J parameters L_E , M_E , and H_E for the SPC/E water model by Reif and Hünenberger – only $C^{(12)}$ changes

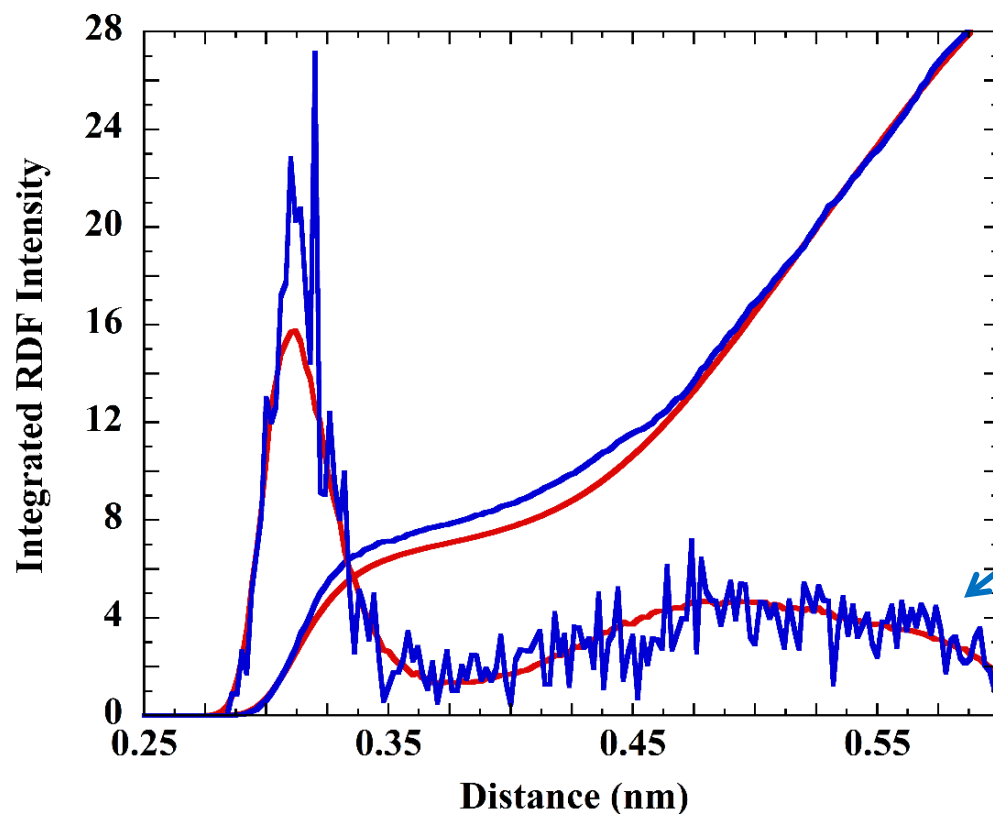


M. M. Reif, and P. H. Hünenberger, J. Chem. Phys. **134** 144104 (2011).



we have selected some frames from the total such as $R_{th} < 10^{-7}$. The R_{th} criterion selected 199 from the original 3190 frames. The value m is the total number of the energy points

$$R_{th} = \frac{\sqrt{\sum_{i=1}^m (\sigma_i^{MD} - \sigma_i^{th})^2}}{m}$$



Cl-O $g(r)$ obtained
with R_{th} criterion

it seems that to improve the theory we need a further compression of the second hydration shell.

this effect is not easy to obtain with a two-body classical potential, because an alteration of the Cl-water or water-water interaction parameters would also change the structure of the first hydration shell

conclusions

it is possible to fit the whole energy range of the XAS spectrum

the XANES energy range can be used from the edge to obtain quantitative structural information in particular for the time-depended spectra

MD combined with XANES can be a strong tool to go deeper in the analysis of experimental data

Acknowledgments

- E.Pace - LNF – Frascati
- G. Chillemi and N.Sanna - DIBAF - University of Viterbo “La Tuscia” – Viterbo
- P. D’Angelo – University of Rome “La Sapienza” - Roma
- P. Frank - Stanford University and SSRL
- B. Hedmann and K.Hodgson - Stanford University and SSRL
- M. Cammarata – CNRS - Rennes
- M. Chergui - EPFL – Lausanne