XAS (X-ray Absorption Spectroscopy) spectroscopy and Multiple Scattering Theory: method and applications

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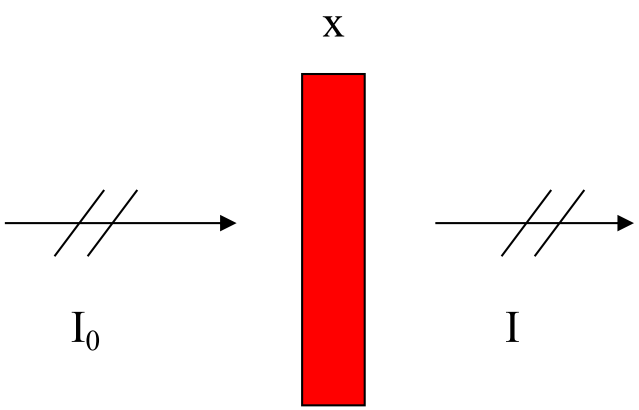
Plan of the talk

- general aspects of MS theory and XAS
- the XANES energy region and structural applications
- time-dependend analysis
- molecular dynamics and XANES

XAS – X-Ray Absorption Spectroscopy from core levels



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

E is in the X-ray energy range

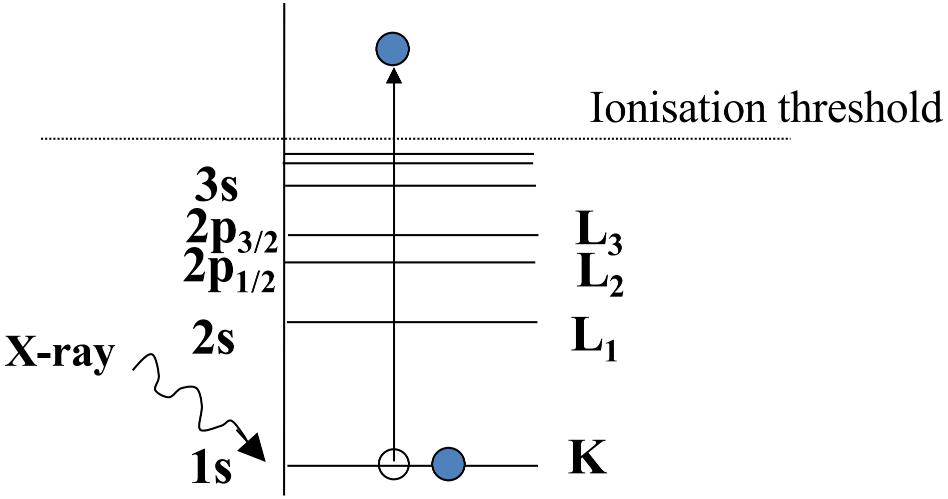
$$\mu(E) = n_{abs}\, \sigma(E)$$

Density of absorption medium

Photoabsorption cross section

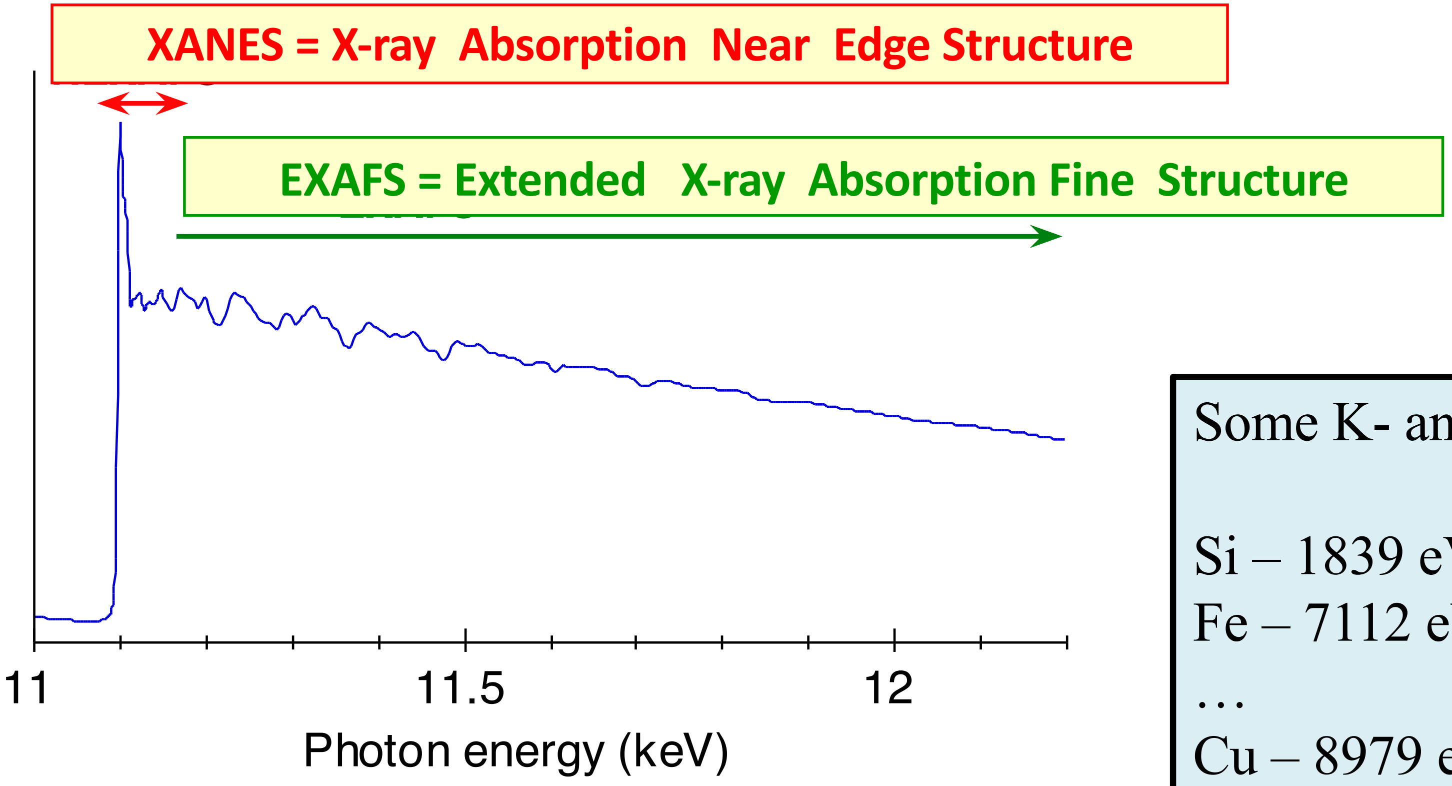
physical process: excitation of core-level electron to continuum states

There are other scattering processes with and without energy loss we must normalize the data to isolate the XAS signal.



typical XAS normalized spectrum

K-edge → 1s
L$_1$-edge → 2s
L$_2$-edge → 2p
……


XANES = X-ray Absorption Near Edge Structure

EXAFS = Extended X-ray Absorption Fine Structure

Some K- and L$_2$- edges

Si – 1839 eV – 99.8eV
Fe – 7112 eV – 719.9 eV
…
Cu – 8979 eV – 952.3 eV
Ge – 11103 eV – 1248.1 eV
…..

XAS is mainly used to get three-dimensional structural information around a few tens of angstroms from the photoabsorbing atom.

- 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

Fermi "golden rule" to calculate the total cross-section

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

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

ψ_f ⟶ w.f. in the final state

ψ_c ⟶ core w.f. spatially localized

we use multiple scattering theory (MS) to get the final state w.f.
we only need the final state ψ_f in the absorbing site

MS Theory

It is a method to solve the S.E. in real space without the need to have any symmetry. Introduced in the literature by K. H. Johnson since ’60-’70 to calculate bound states in small molecules

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

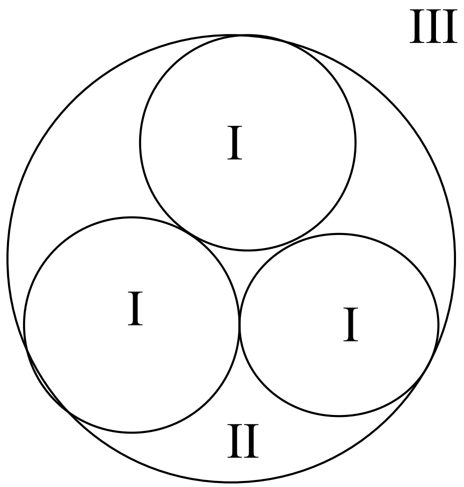
$$V(\vec{r}) = V_c(\vec{r}) + V_{exc}(\vec{r})$$

Some approximation must be done – we use the HL potential within a quasi-particle scheme

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

Sum of free atomic potential ⟷ cluster of atoms

How to build the MS theory



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 value - The average is over the interstitial volume

V_{III} has a spherical average form respect to the atomic cluster center
It depends to the physical problem to be solved.

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 ⟶ Ψ_{II} is a combination of Bessel and Neumann functions

In the outer sphere region (region III)

$$\Psi_{III} = \sum_{L,L'} [A_L^{III} f_l^{III}(kr_0)\,\delta_{LL'} + B_{LL'}^{III} g_{l'}^{III}(kr_0)]\, Y_{L'}(\hat{r}_0)$$

relative to the center of the entire molecule

This is a very general expression - The asymptotic behavior of f_l and g_l 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

$$B^i_L(\underline{L}) + t^i_l \sum_{j\neq i} \widetilde{G}^{ij}_{LL'} B^j_{L'}(\underline{L}) = -t^i_l J^{io}_{L\underline{L}} \Gamma_{\underline{L}}$$

valid for both bound and continuum states

$$\widetilde{G}^{ij}_{LL'} = G^{ij}_{LL'} - \sum_{L''} J^{i0}_{LL''} t^0_{l''} J^{oj}_{L''L'}$$

$$G^{ij}_{LL'} = -4\pi i \sum_{L''} i^{l''+l'-l} C^L_{L'L''} h^+_{l''}(kR_{ij}) Y_{L''}(\hat{R}_{ij})$$

Gaunt coefficient

$$t^i_l = W[j_l, R^i_l] / W[-ih^+_l, R^i_l] = e^{i\delta^i_l} \sin\delta^i_l$$

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

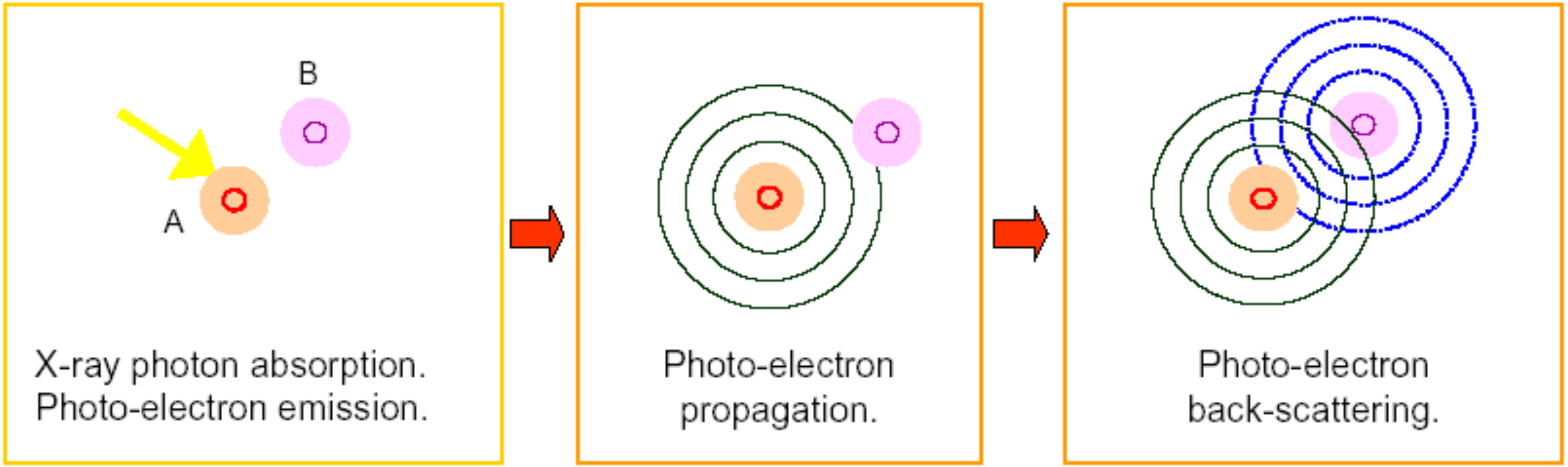
$\mathrm{J}^{i0}_{\mathrm{L}\underline{\mathrm{L}}}$ → Exciting wave referred to site i

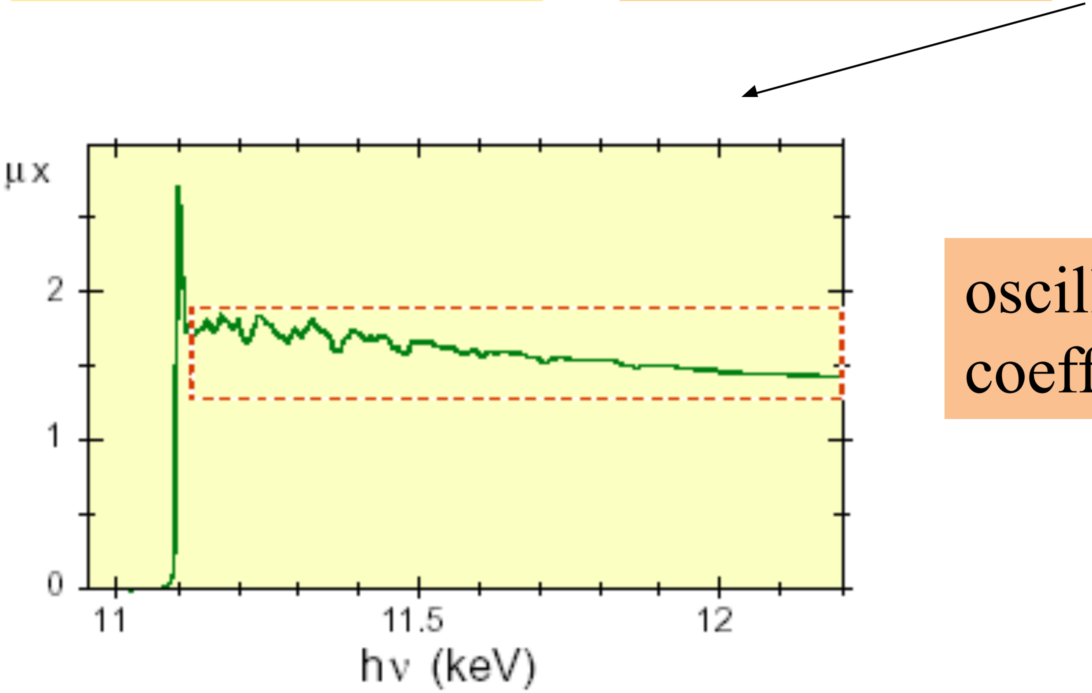
$$B_L^i(\underline{L}) + t_l^i \sum_{j \neq i} \widetilde{G}_{LL'}^{ij} B_{L'}^j(\underline{L}) = -t_l^i J_{L\underline{L}}^{io} \Gamma_{\underline{L}}$$

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

T. Tyson et al. Phys. Rev B46 5997 (1992)





oscillations in the absorbing coeffiecient

We need to know the final state wave function at absorbing site 0 because of the localization of the core wave function

$$\sigma(\omega) \approx \sum_{\underline{L},L,m_\gamma,m_0} \left|B_L^0(\underline{L})\right|^2 \left|(R_L^0(\vec{r}_0)\,|\,r_0 Y_{lm_\gamma}(\hat{r}_0)\,|\,\phi_{l_0}^0(r_0) Y_{L_0}(\hat{r}_0))\right|^2$$

coefficient of the development in spherical harmonics of the w.f. in the absorber site 0

Optical theorem

$$\sum_{\underline{L}} [B_L^0(\underline{L})]^* [B_{L'}^0(\underline{L})] = \mathrm{Im}[(I - T_a \widetilde{G})^{-1} T_a]_{LL'}^{00}$$

It is possible to rewrite the the total cross section as

$$\sigma(E) = -4\pi\alpha\, E \sum_{L\,L'} Im\,[(M^*)^0_L\, \tau^{00}_{LL'}\, M^0_{L'}]$$

$$M^0_L = \int \phi^0_{L_0}(\vec{r})\,\hat{\varepsilon}\cdot\vec{r}\,R^0_L(\vec{r})\,d^3r$$

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

↓

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

$$T_a = \begin{pmatrix} t^0_l & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & t^n_l \end{pmatrix}$$

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

it is possible to separate the atomic contribution to the oscillating part

$$\sigma(E)=(l+1)\sigma_0^{l_0+1}(E)\,\chi^{l_0+1}(E)+l\sigma_0^{l_0-1}(E)\,\chi^{l_0-1}(E)$$

$$\chi^l(E)=\frac{1}{(2l+1)\sin^2\delta_l^0}\sum_m \operatorname{Im}\tau_{lmlm}^{00}$$

dipole selection rule $1 = 1_0 \pm 1$

$$\sigma_0^l(E)=\frac{8\pi^2}{3}\alpha k\,(E+I_0)\sin^2\delta_l^0\left[\int_0^\infty r^3 R_l(r)\phi_{l_0}(r)\,dr\right]^2$$

atomic cross section - almost without structures

The scattering path operator can be calculated exactly or by series

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

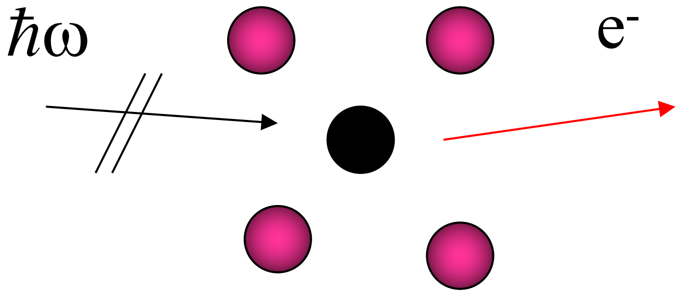
$$\tau = T_a + T_a G T_a G T_a + T_a G T_a G T_a G T_a + \ldots..$$

$$\mathrm{G}^{\mathrm{ii}}_{\mathrm{LL'}} \equiv 0$$

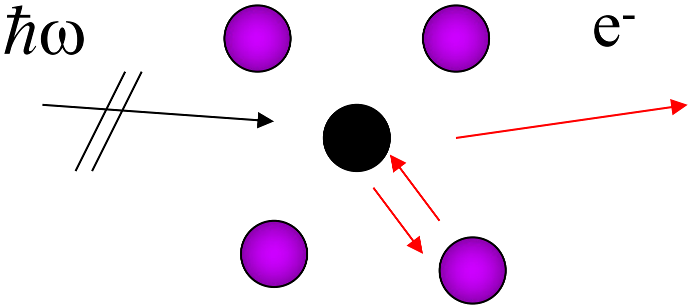
we start from n=2

MS paths

σ_0 – smooth atomic contribution

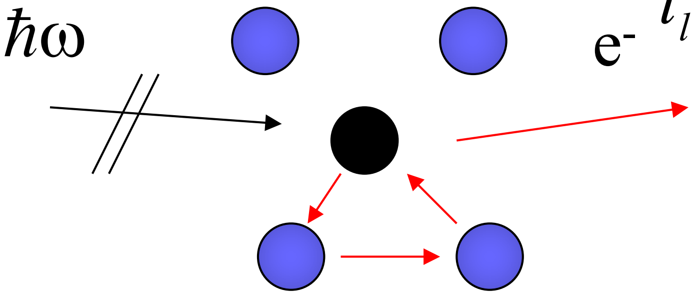


σ_2 – single diffusion – EXAFS region



$$t_l^0 \, G \, t_l^i \, G \, t_l^0 \approx \frac{1}{(kR)^2}$$

σ_3 – double diffusion – high order correlation functions



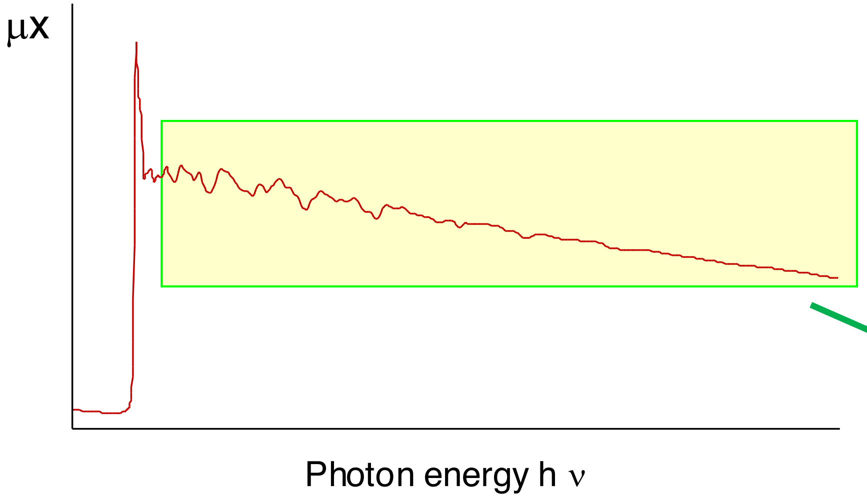
$$t_l^0 \, G \, t_l^i \, G \, t_{l'}^j \, G \, t_l^0 \approx \frac{1}{(kR_{tot})^3}$$

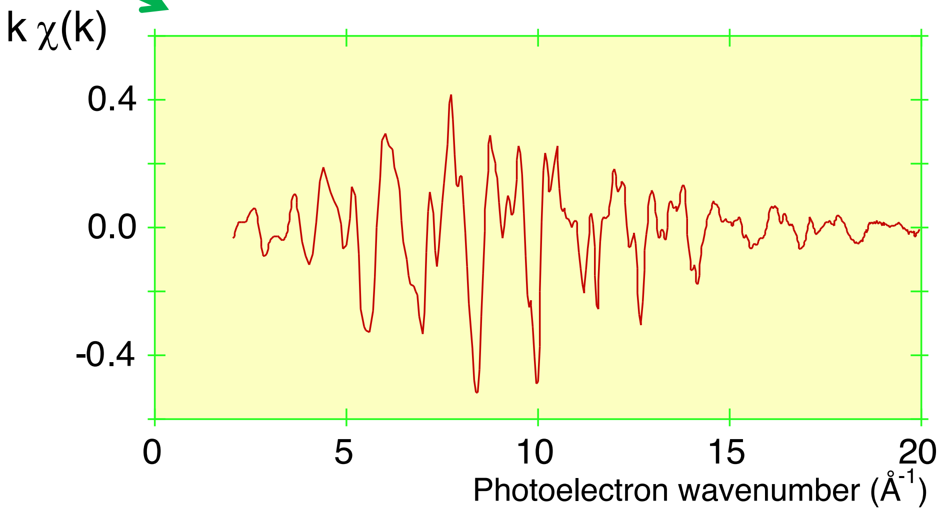
EXAFS part

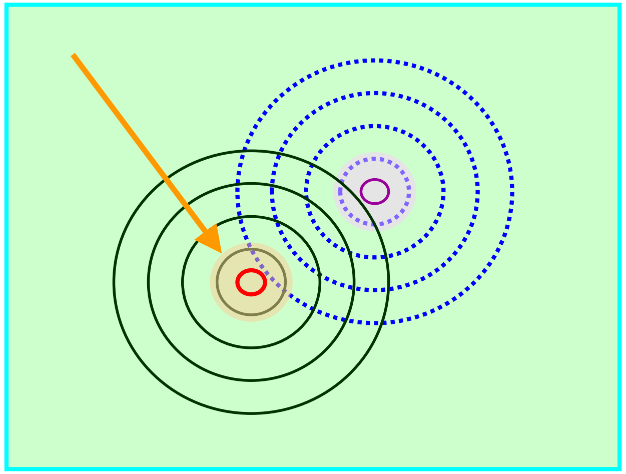
$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$

k is the photoelectron k-vector related to the photon energy by

$$k = \sqrt{\frac{8\pi^2 m}{h^2}(E - E_0)}$$







Interatomic distances – coordination numbers

The calculation of the EXAFS signal

$$\chi_2^l = \frac{1}{2l+1} \sum_{j \neq 0} \sum_{mm'l'} \mathrm{Im}\{ e^{2i\delta_l^0} G^{0j}_{lml'm'} \, t^j_{l'} \, G^{j0}_{l'm'lm} \}$$

$$\chi_2^l = (-1)^l \sum_{j \neq 0} \sum_{l'} \mathrm{Im}\{ e^{2i\delta_l^0} \, (i)^{2l'+1} \, t^j_{l'} \, (2l'+1) \, H(l, l', kR_{j0}) \}$$

$$\boxed{H(l, l', kR_{j0}) = \sum_{l''} (i)^{l''} \, (2l''+1) \begin{pmatrix} l \; l' \; l'' \\ 0 \; 0 \; 0 \end{pmatrix}^2 \, (h^+_{l''}(kR_{j0}))^2}$$

this part carries an amplitude and a phase
the phase depends on the interatomic distances

Plane wave approximation

$$(i)^l\, h_l^+(kR) \to \frac{e^{ikR}}{kR}$$

$$\chi_2^l = (-1)^l \sum_{j\neq 0} \mathrm{Im}\{e^{2i\delta_l^0}\, \frac{e^{2ikR_{j0}}}{(kR_{j0})^2}\, F_j(k)\}$$

$$\boxed{F_j(k) = \frac{1}{k}\sum_l (i)^{2l+1}(2l+1)\, e^{i\delta_l^j}\, \sin\delta_l^j}$$

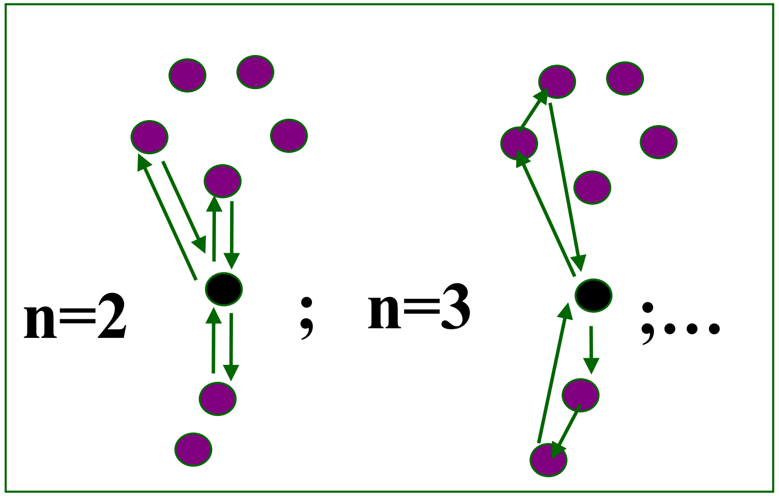
The phase does not depend by the distance two ways to calculate the scattering path operator

- exactly including all MS contributions
- by series up to some order

$$\sigma(E) = \sigma_0(E) + \sigma_2(E) + \cdots \sigma_n(E) + ..$$

MXAN

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

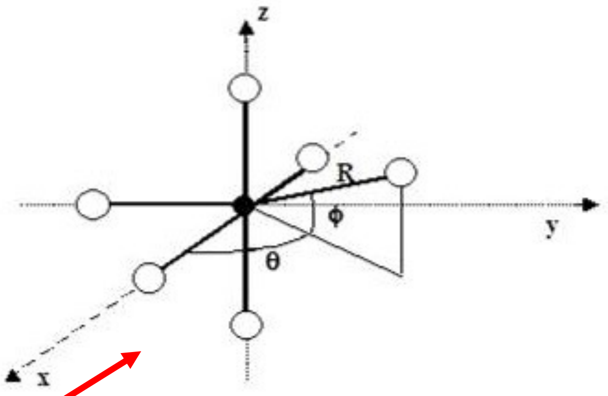


Most of the actually sotware packages to fit EXAFS data

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. J. Synch. Rad. **10**, 51 (2003)
M. Benfatto et al. Computer Phy. Comm. **265**, 107992 (2021)

XANES part – the MXAN approach

- Initial geometrical configurations
- Exp. data



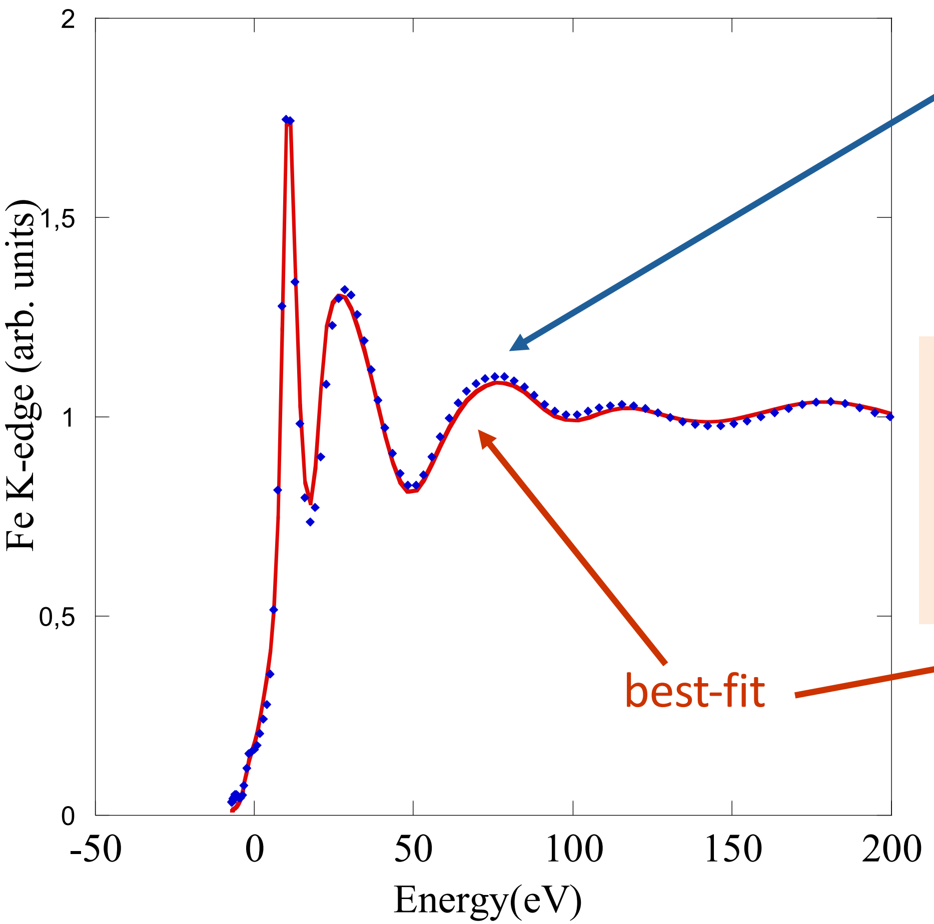
we generate hundred of theoretical spectra by moving atoms and/or groups of atoms

we can fit relevant structural parameters minimizing the error function

$$R_{sq}^{2} = \sum_{i=1}^{N} \{[y_i^{th.}(..r_n,\theta_n,..) - y_i^{exp.}]^2 / \varepsilon_i^2\} w_i \Big/ \sum_{i=1}^{N} w_i$$

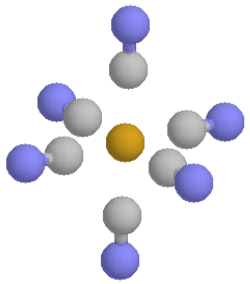
- work in the energy space
- start from the edge
- No DW factors are included

$Fe (CN)_6$ in water



exp

best-fit



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

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

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
…….

about the MT approximation

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

$$\sigma_t \approx \mathrm{Im}\,(T+H)^{-1}$$

$$T=(T_a)^{-1}+\Delta T$$

$$H=H_{MT}+\Delta H$$

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

$$\sigma_t \approx \sigma_{MT} + corr\,(E;V_{\mathrm{int}})$$

$$\Delta = \Delta T + \Delta H$$

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

MXAN and difference spectra

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

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

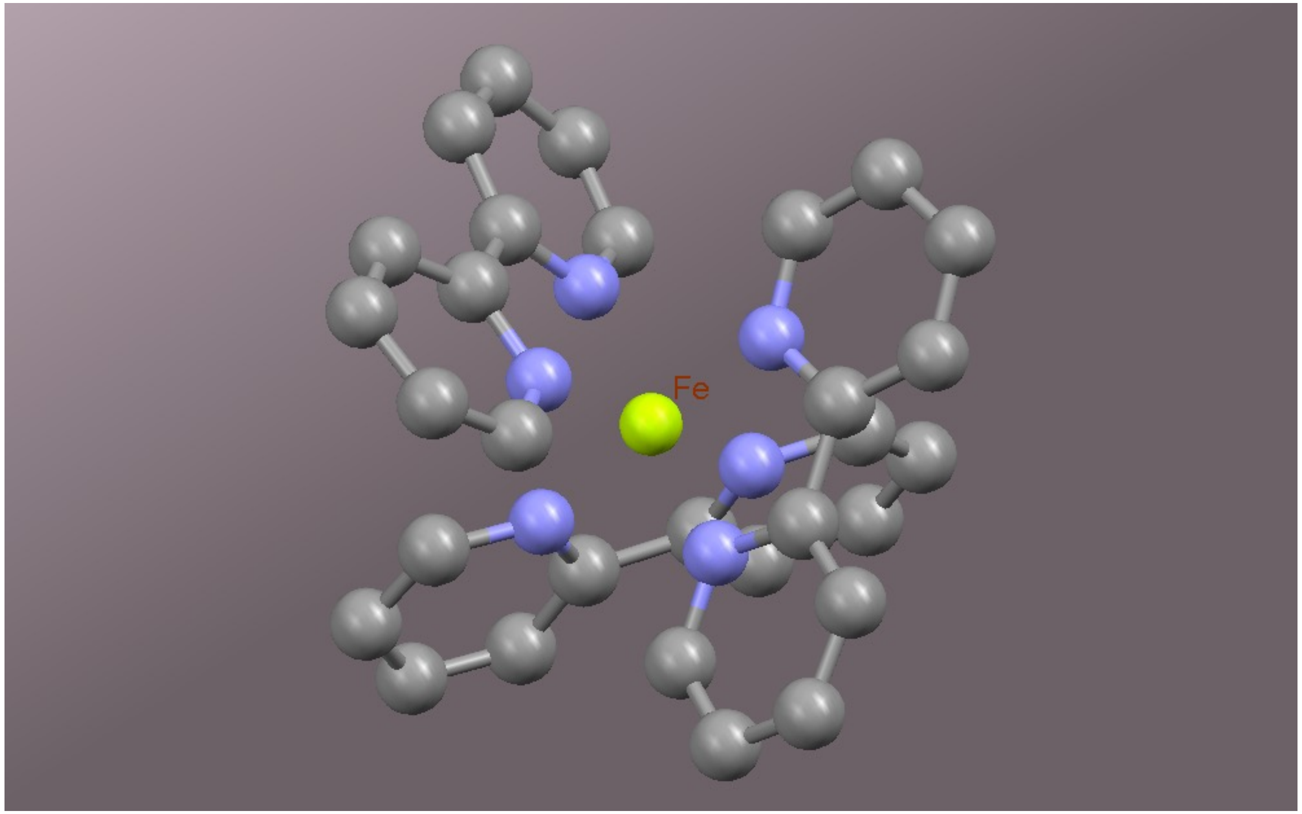
To see (small) structural changes due to physical/chemical reasons in pump-probe experiments

Fields of application:

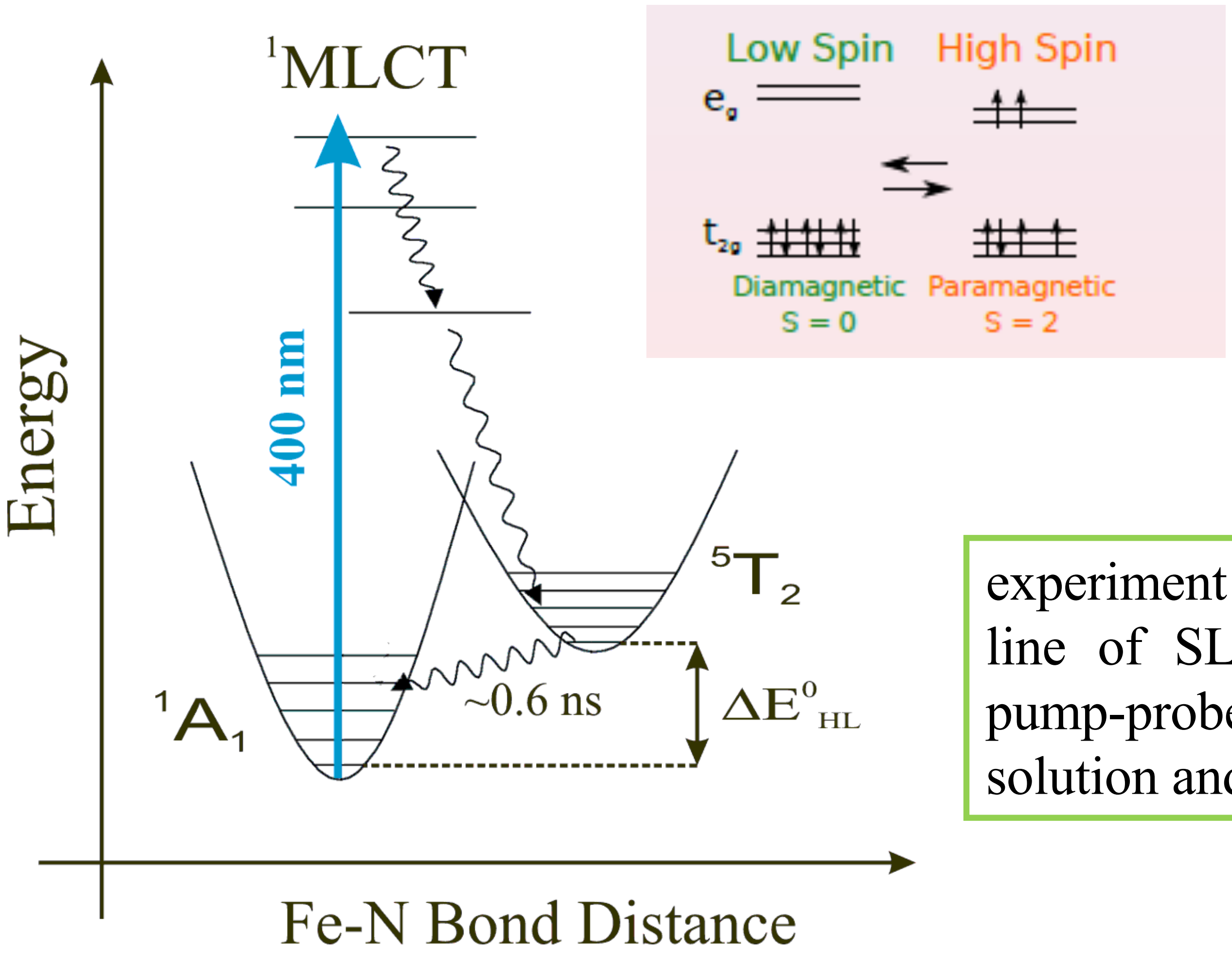
time resolved experiment
changes of chemical-physical and/or thermo-dynamical conditions
………….

M. Benfatto et al. J. Phys. Chem. B (2006), 110 14035

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



see the structural changes going from LS to HS state



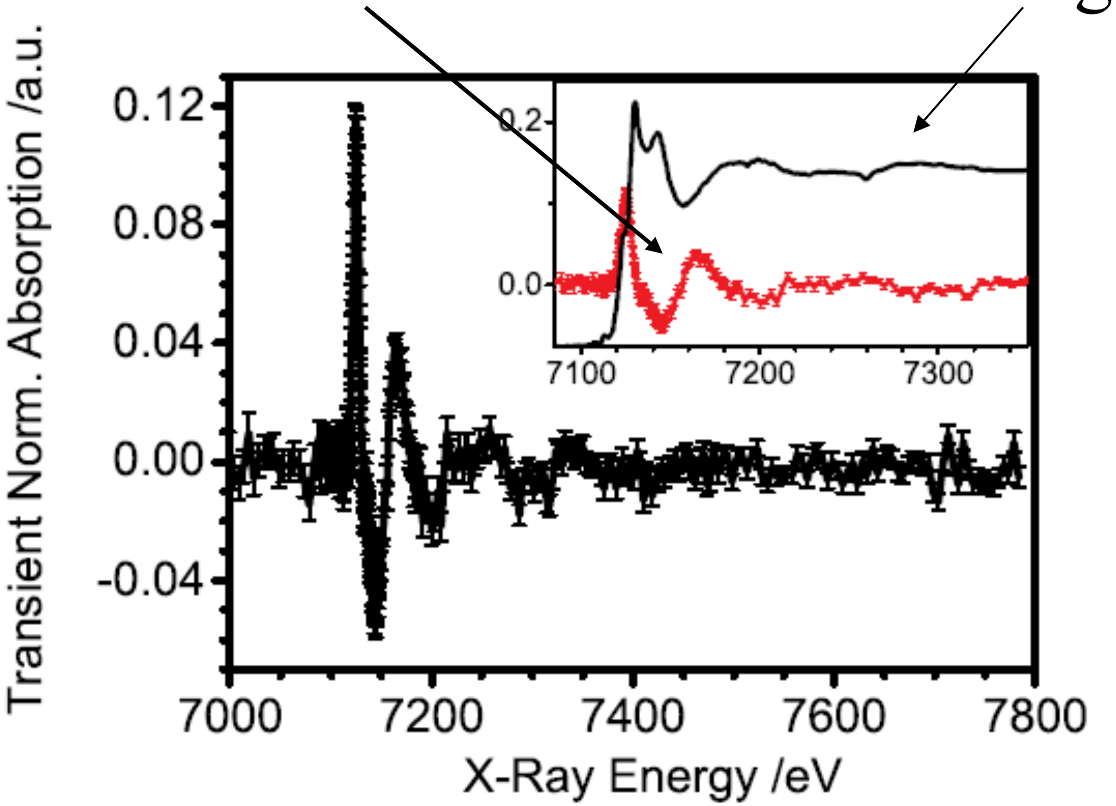
experiment done at the micro-XAS line of SLS by Chergui's group - pump-probe experiment in aqueous solution and room temperature

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

experimental data

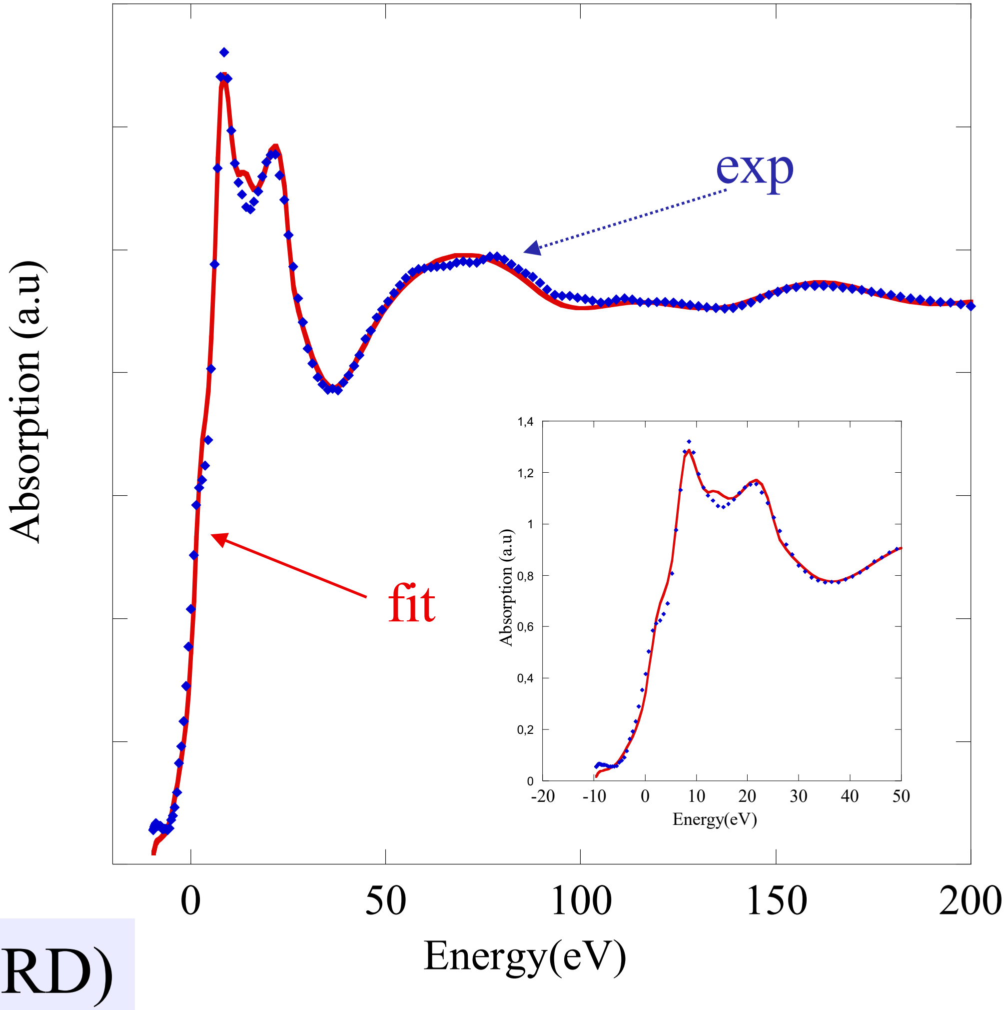
HS transient data at Δt = 50 ps

LS gs data



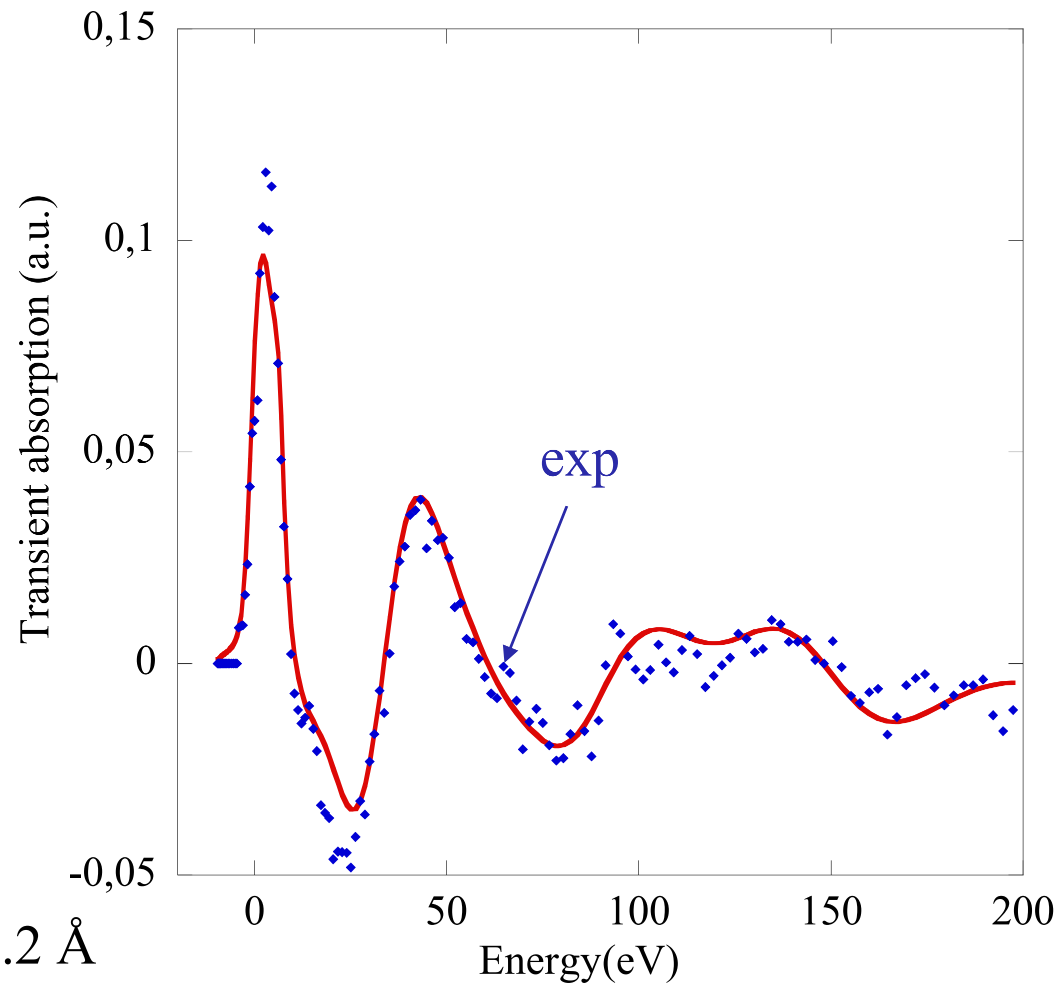
LS ground state fit

$R_{Fe\text{-}N} = 2.00 \pm 0.02$ Å



$R_{Fe\text{-}N} = 1.967 \pm 0.006$ Å (XRD)
$R_{Fe\text{-}N} = 1.99 \pm 0.02$ Å (DFT)

HS excited state fit by transient data



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

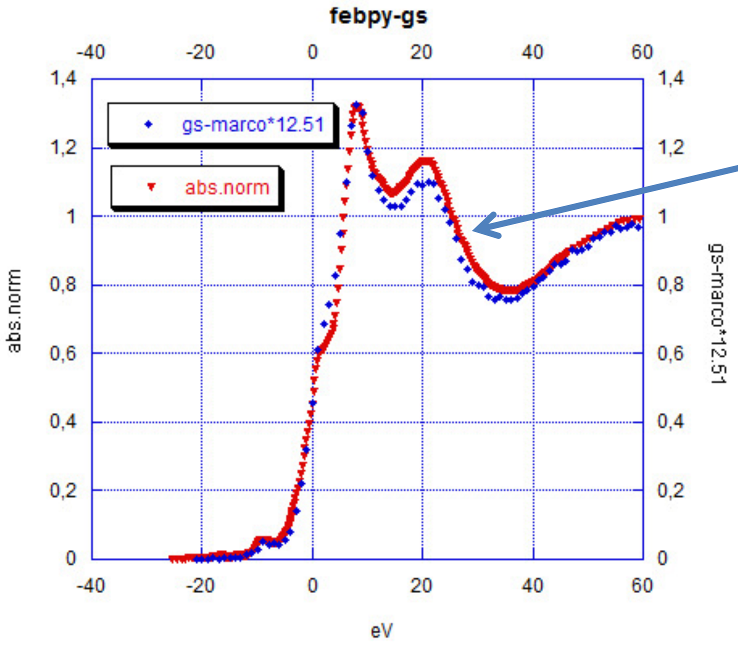
DFT calculations indicate ~ 0.2 Å

W. Gawelda et al. PRL (2007) 98, 057401

going to the fs time scale FEL experiment

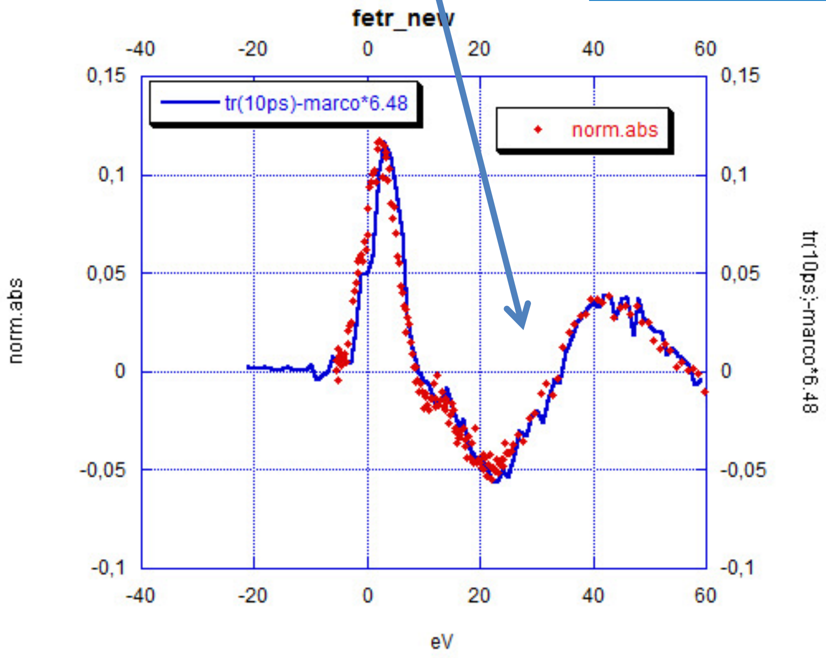
iron-(II)-tris-bypyridine $[Fe^{II}(byp)_3]^{2+}$

Exp data taken at LCLS

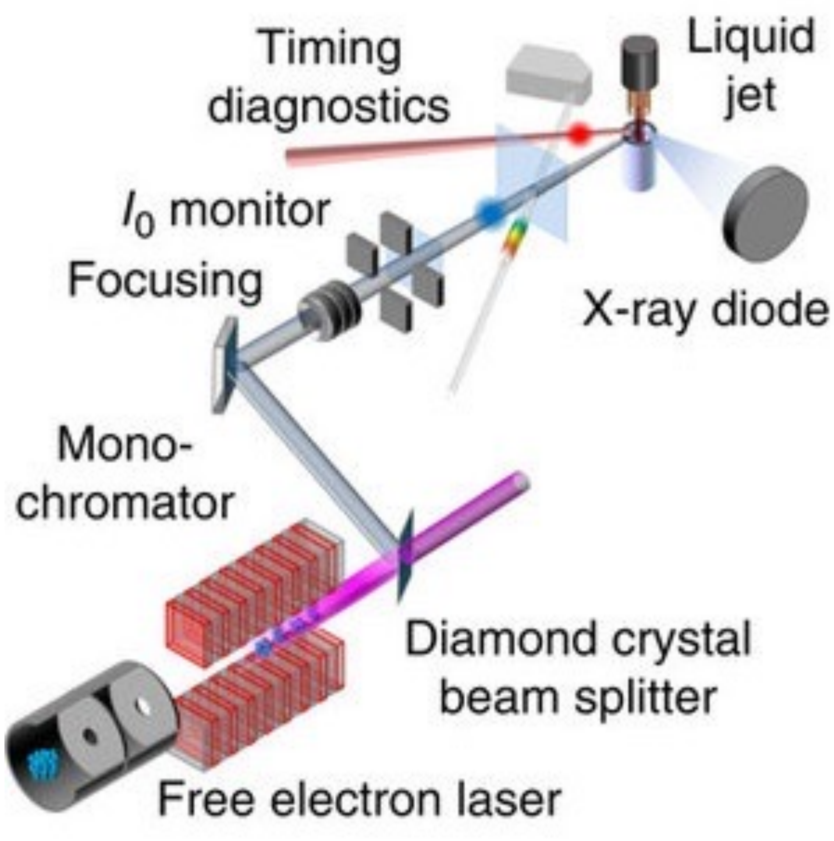


MXAN fits of such data give the results previously obtained within the statistical error

transient at 10 ps

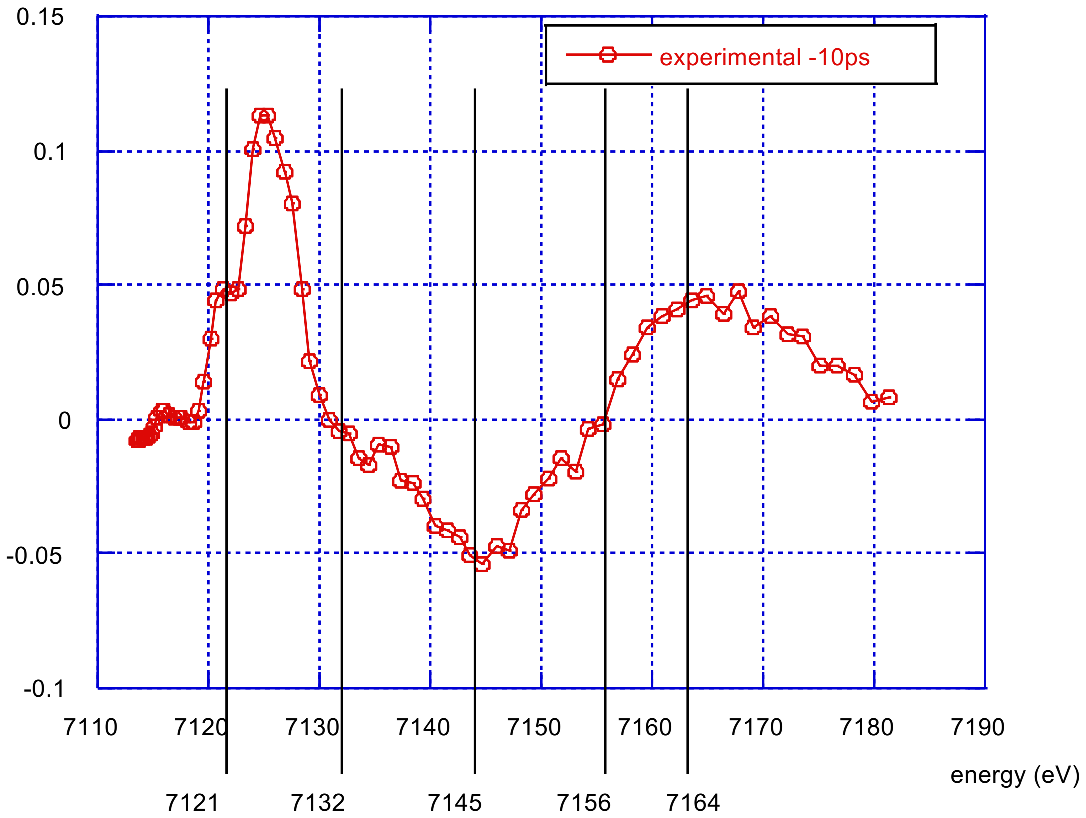


experimental set-up at LCLS – time resolution ≈ 25 fs – the light is monochromatized by a double diamond (111) cristal – focus on sample ≈ 10 μm



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

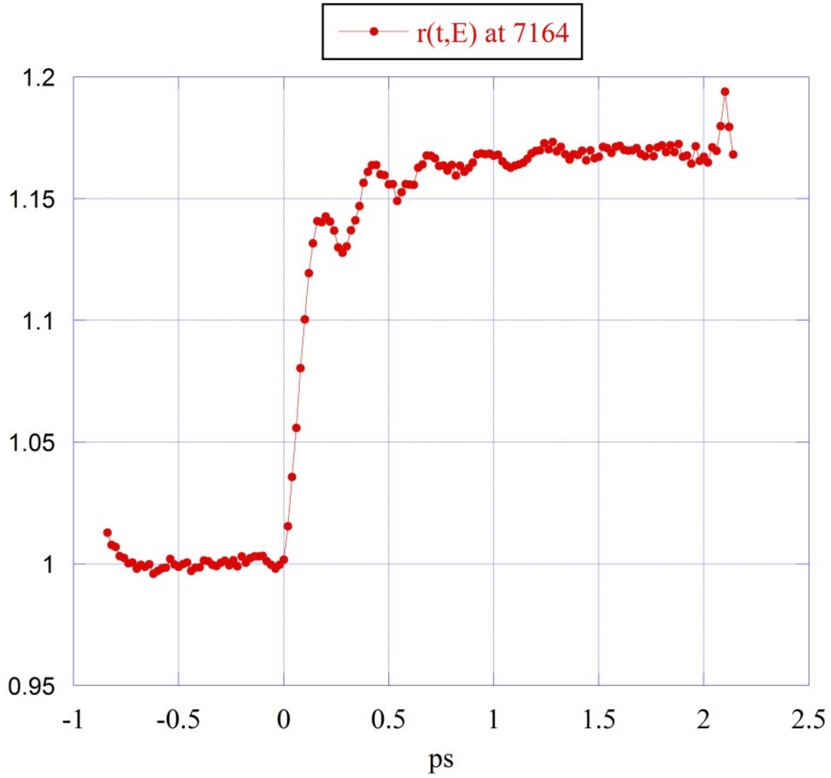
the transient data are taken as function of time but at fixed energy, in particular at 7121, 7132, 7145, 7156 and 7164 eV

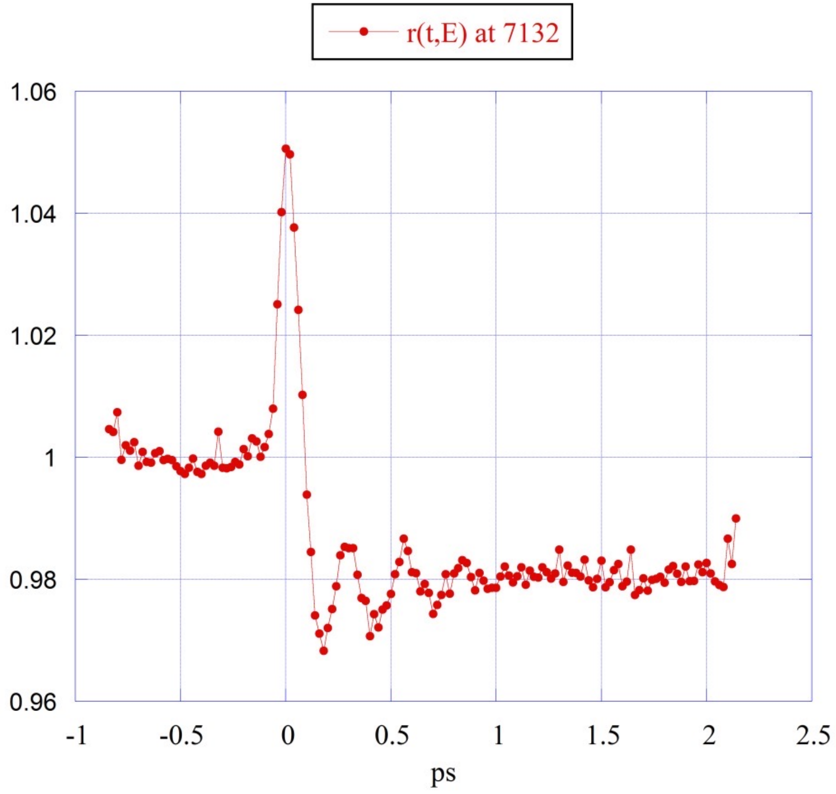


here the exp. data is the ratio

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

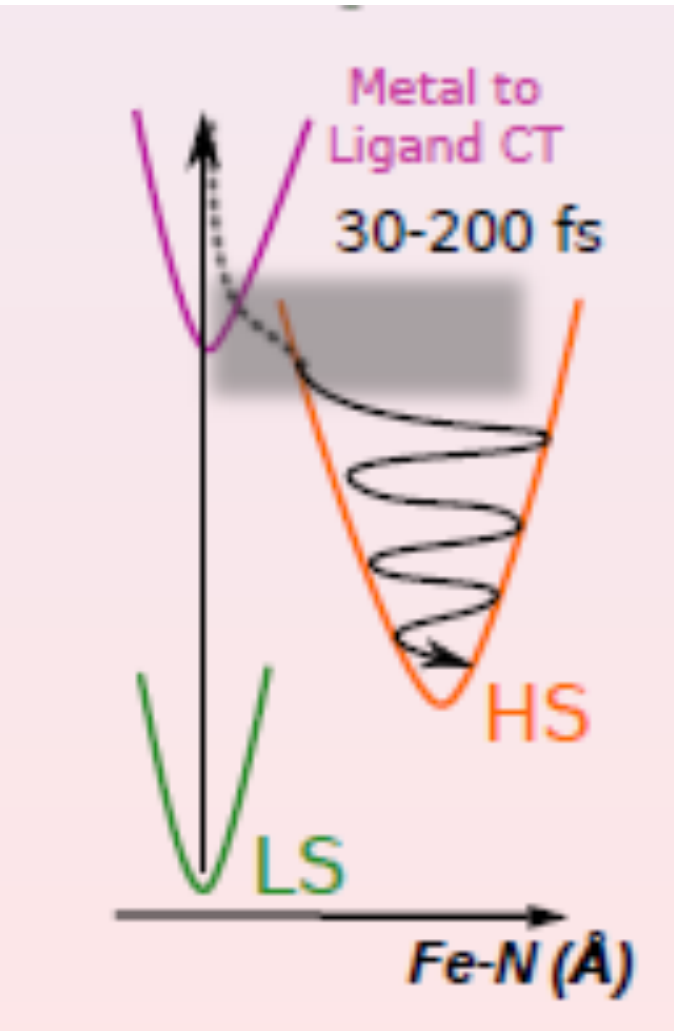
we get data as function of time





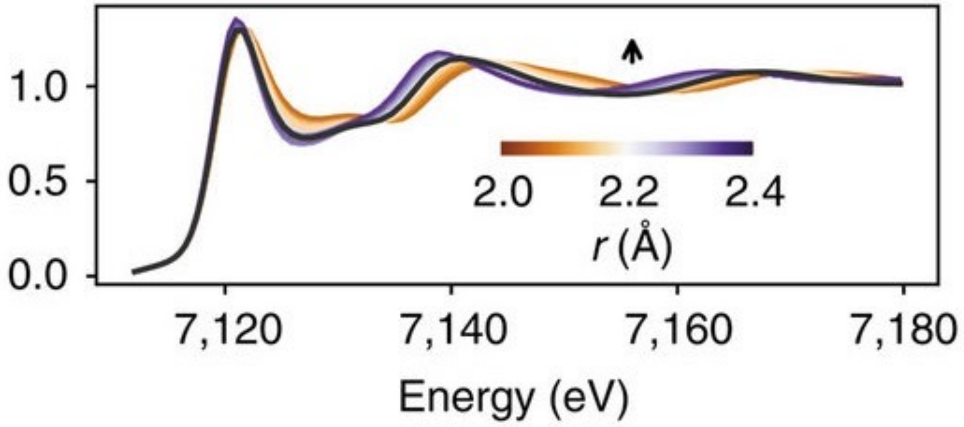
oscillations up to 2ps with a period of about 0.265 ps correspondig to 126 cm^{-1} - the system is in the HS state after 2ps.

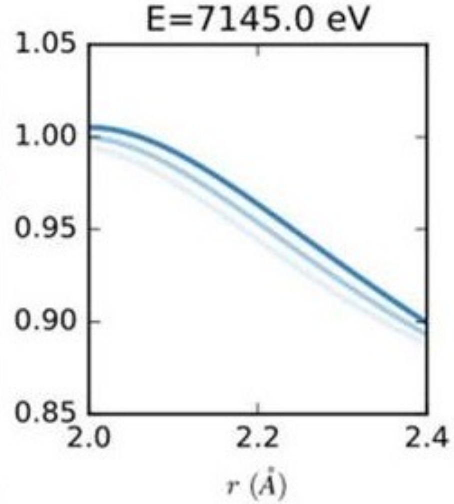
all data shows a rapid change within 30-200 fs followed by an oscillating phase up to 1-2 ps. After this we reach the HS state.



how to analyze these data?

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

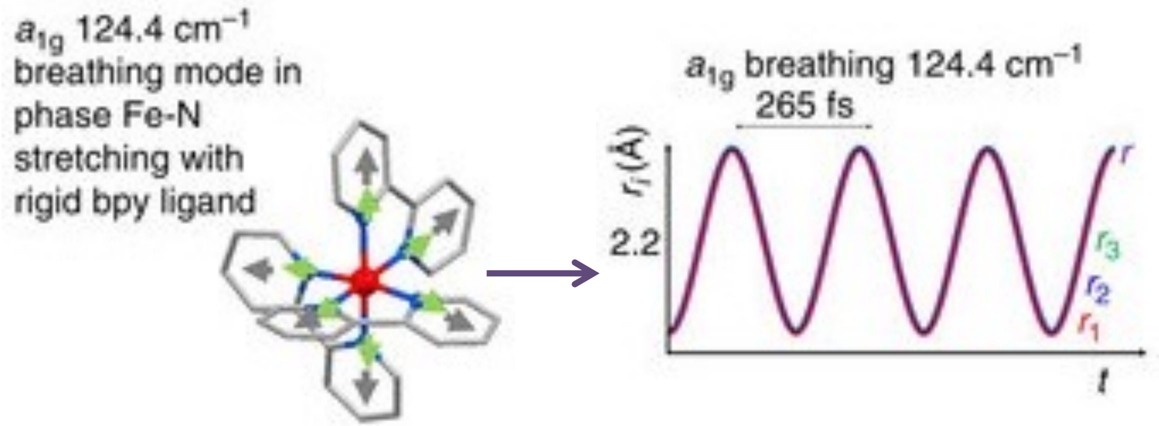


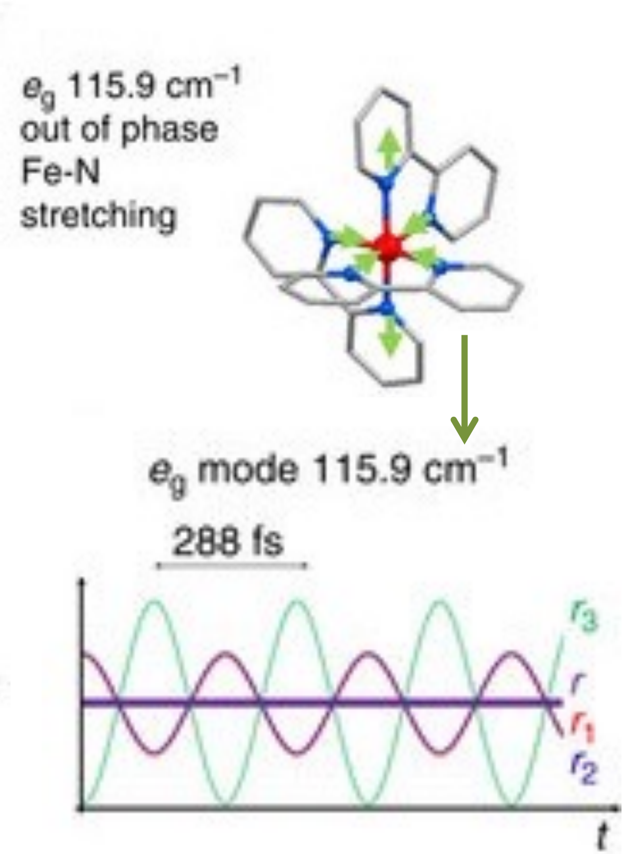


with these calculations we build the signal

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 cm^{-1}

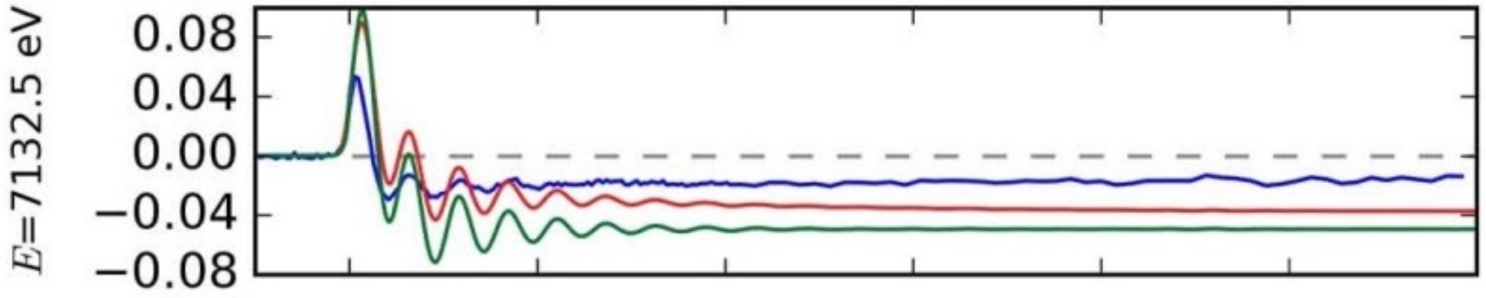
$$I(t,E) = \int S(E,r)g(r,t)dr$$





H.T. Lemke et al. Nature Communication (2017), 8, 15342 here we plot $\left[I(t,E_i)-I(E_i)_{off}\right]/I(E_i)_{off}$

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



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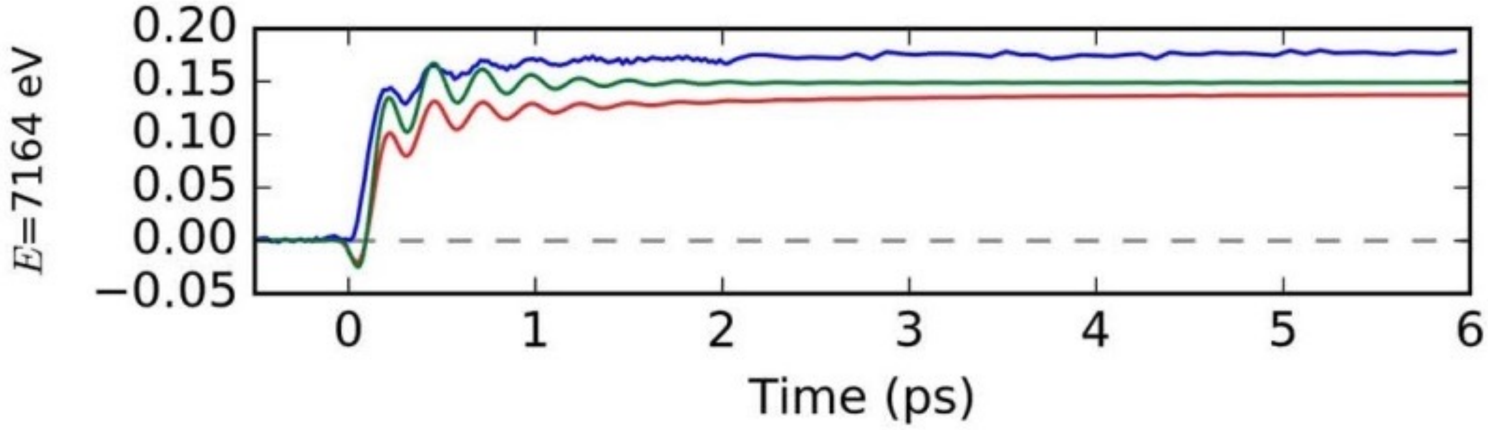
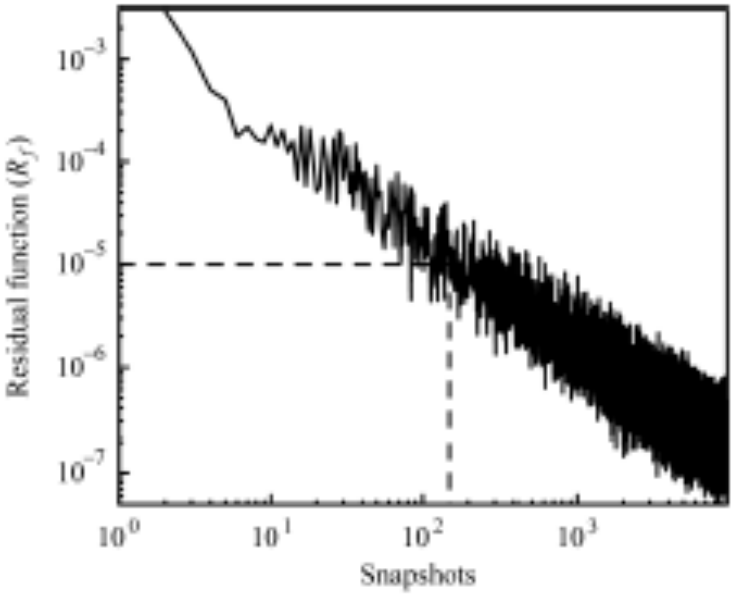


MXAN and Molecular Dynamics

we use MD to generate thousands of geometrical configurations, each one, taken every 50 fs, is used to generated 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

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

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

$$V\left(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n\right)=\sum_{bond}\frac{1}{2}k_{b_0}\left(b_n-b_{0_n}\right)^2+\sum_{angle}\frac{1}{2}k_{\theta_0}\left(\theta_n-\theta_{0_n}\right)^2+$$

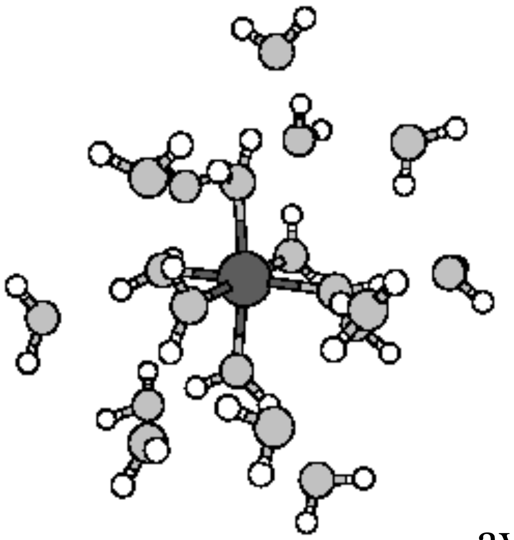
$$+\sum_{\substack{improper\\dihedral}}\frac{1}{2}k_{\xi_0}\left(\xi_n-\xi_{0_n}\right)^2+\sum_{dihedral}1+\cos\left(m_n\phi_n-\delta_n\right)^2+$$

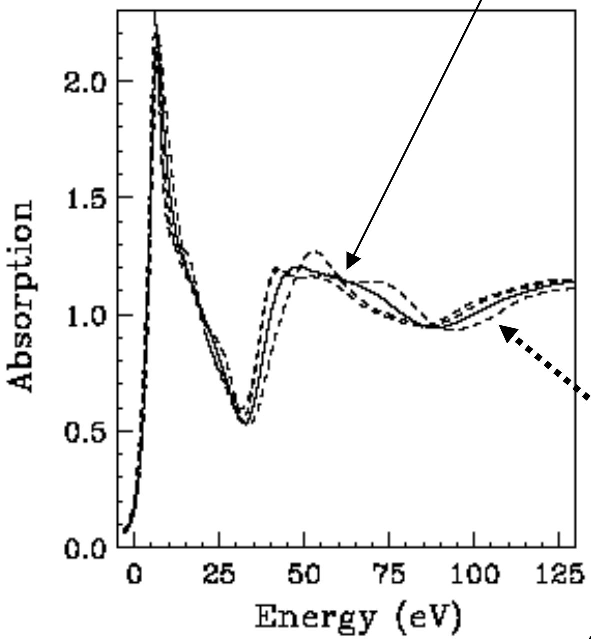
$$+\sum_{\substack{nonbonded\\pairs(ij)}}\left(\boxed{\left(\frac{C_{ij}^{(12)}}{r_{ij}^{12}}-\frac{C_{ij}^{(6)}}{r_{ij}^{6}}\right)}+\frac{1}{4\pi\varepsilon_0}\frac{q_iq_j}{\varepsilon_r r_{ij}}\right)$$

L-J potential → 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

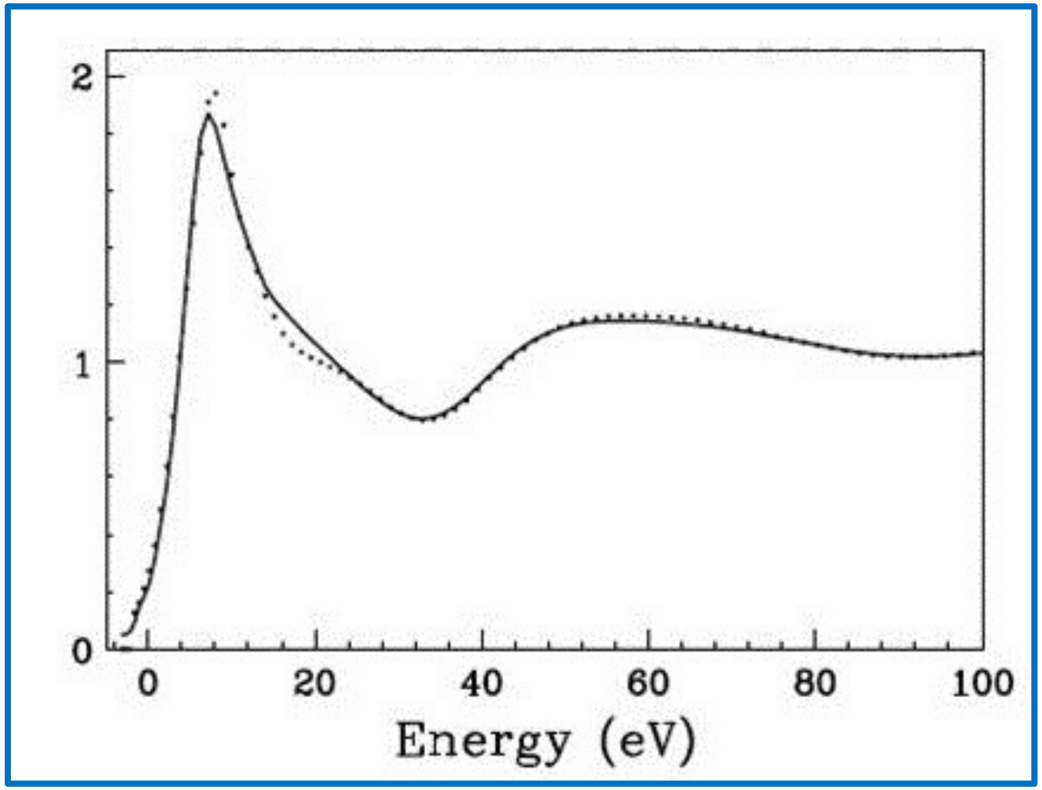
Ni^{2+} in water – Ni Kedge

including the second shell





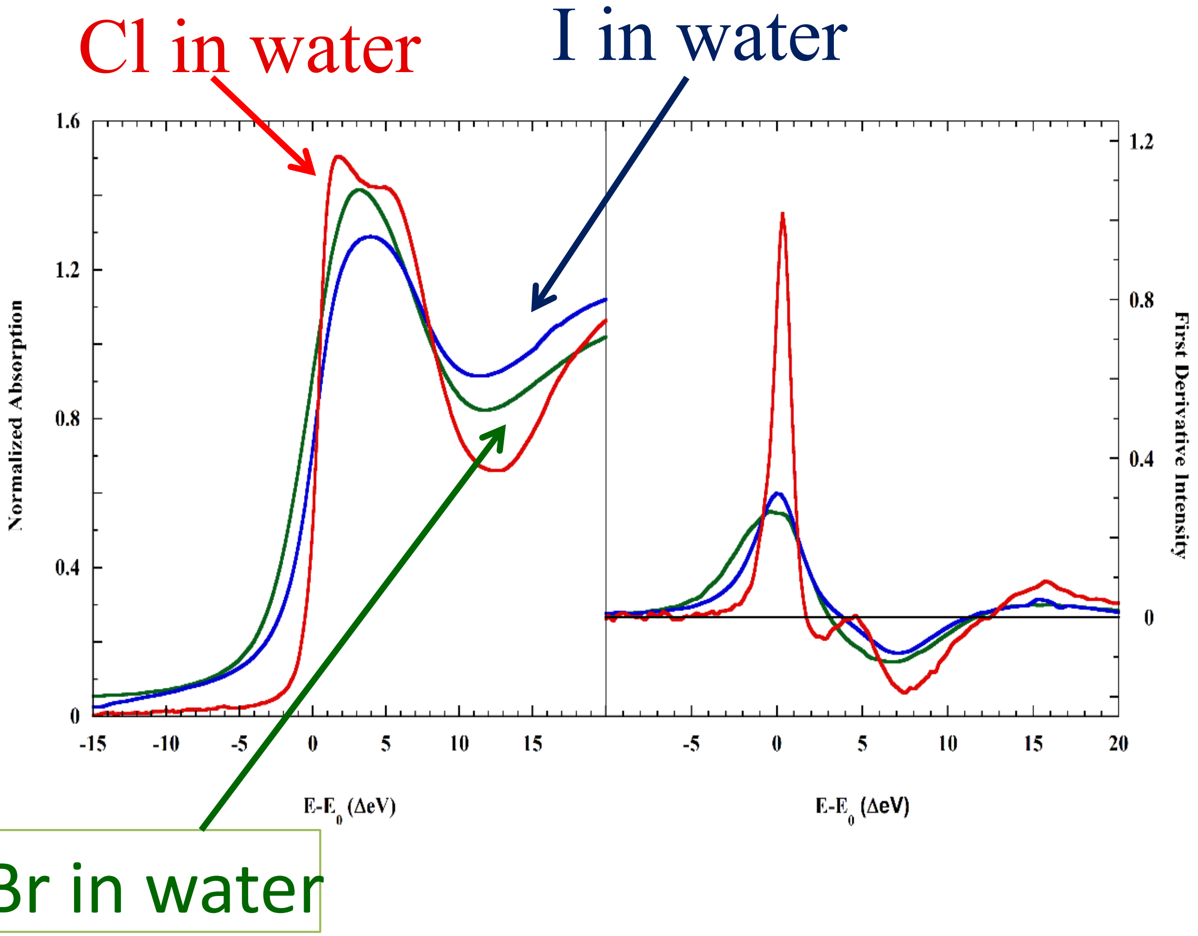
average



Calculations (without any damping) for some particular 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

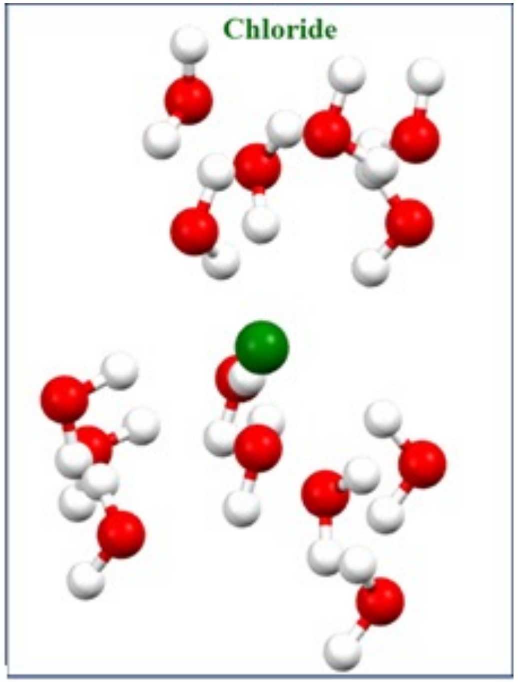

Cl in water

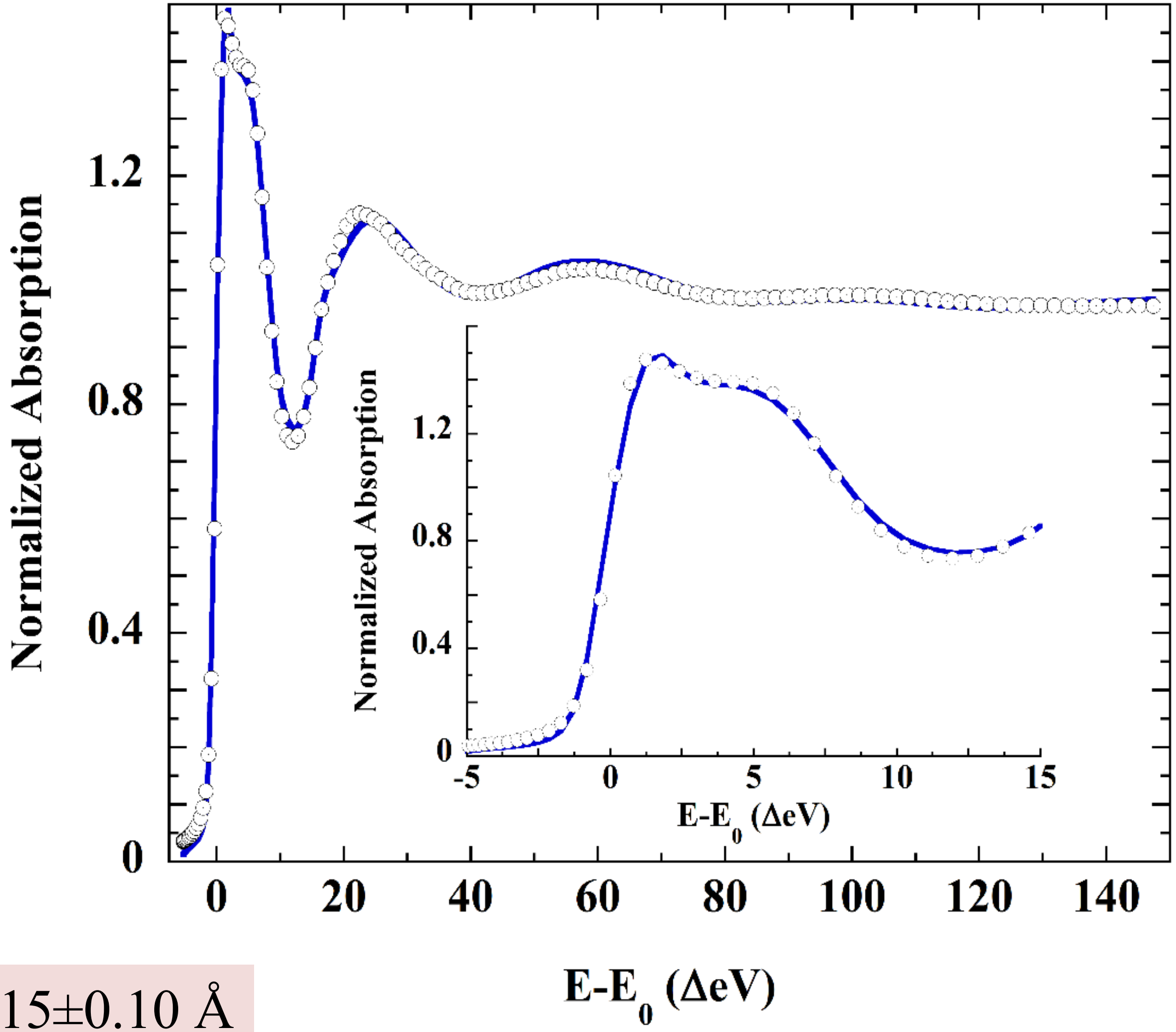
I in water

Br in water

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

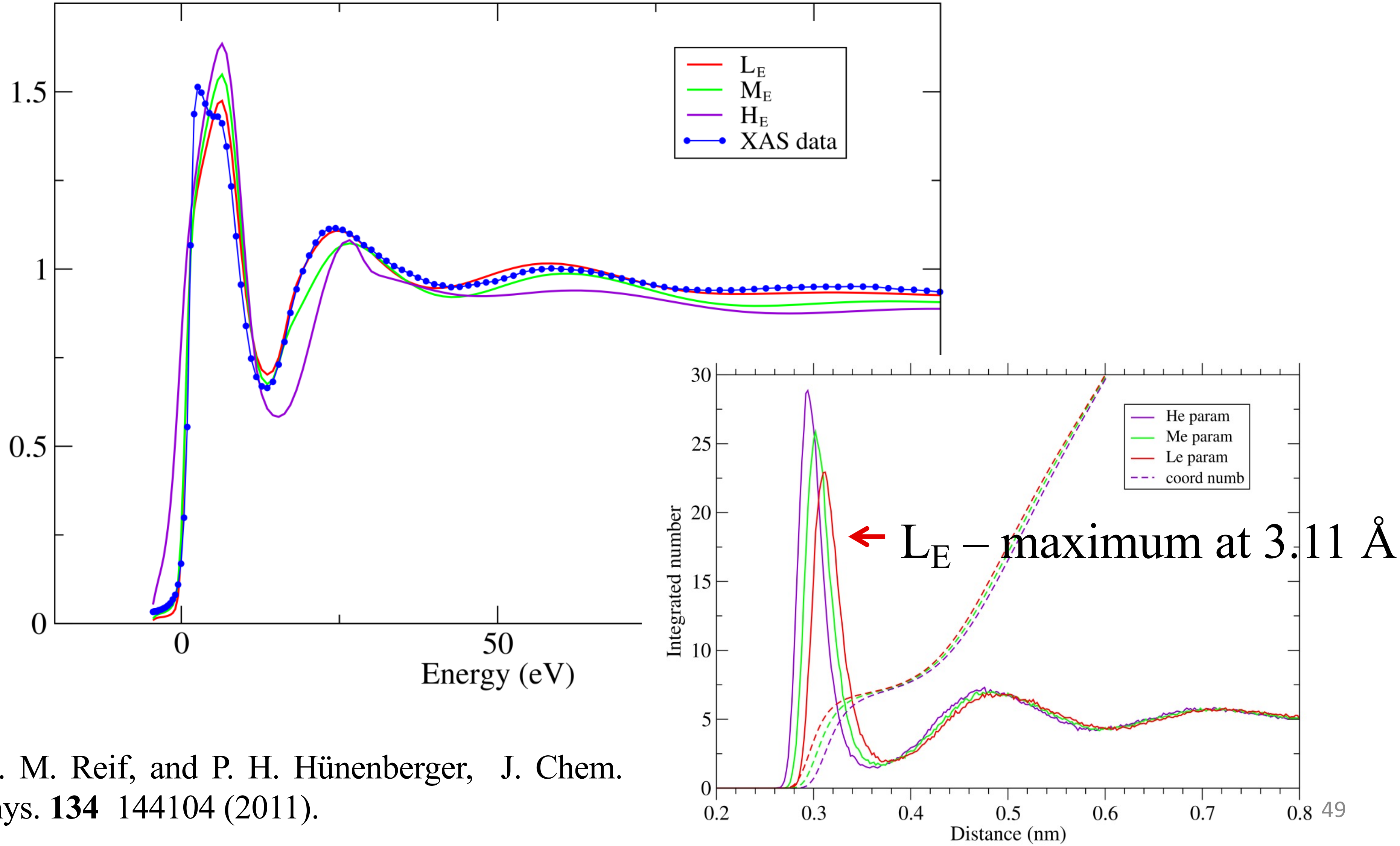
while Iodine and Bromine are well fitted with a first 8-fold coordination shell the Chloride needs two shells of 7+7 water molecules





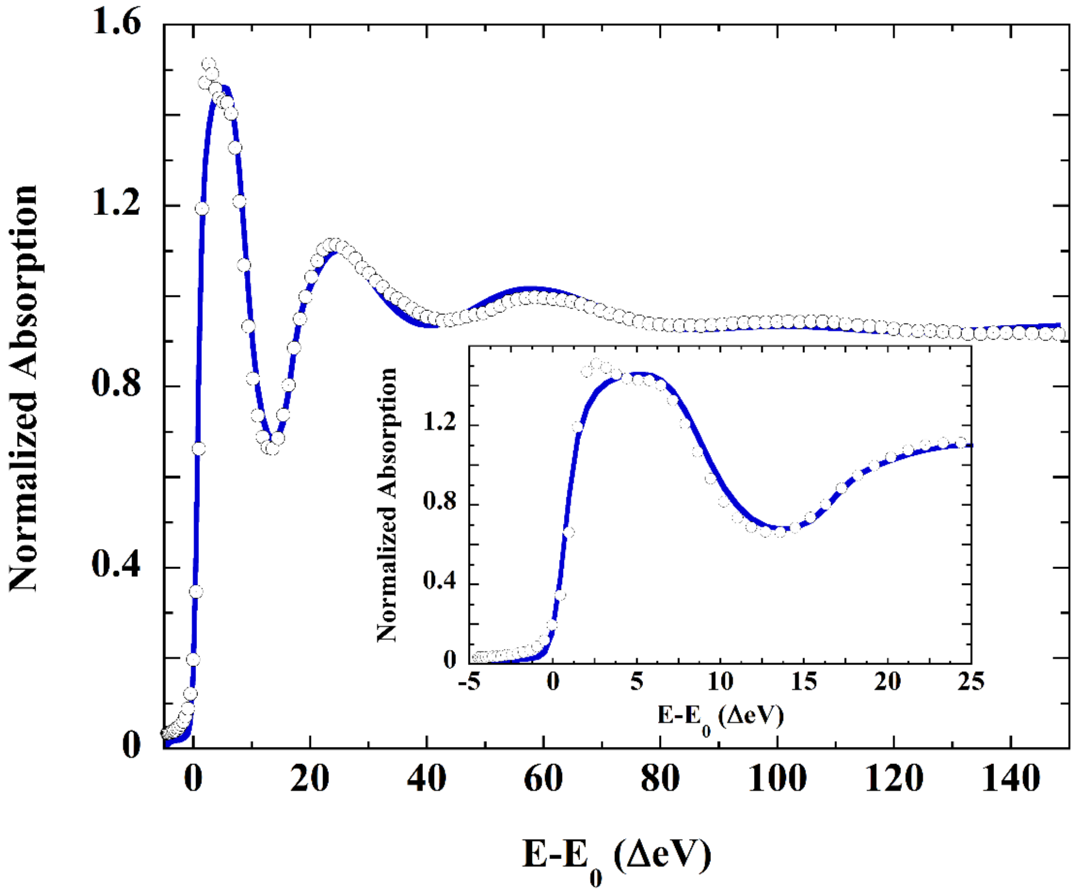
The fit gives a first shell at 3.15±0.10 Å and a second one at 4.14±0.31 Å

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



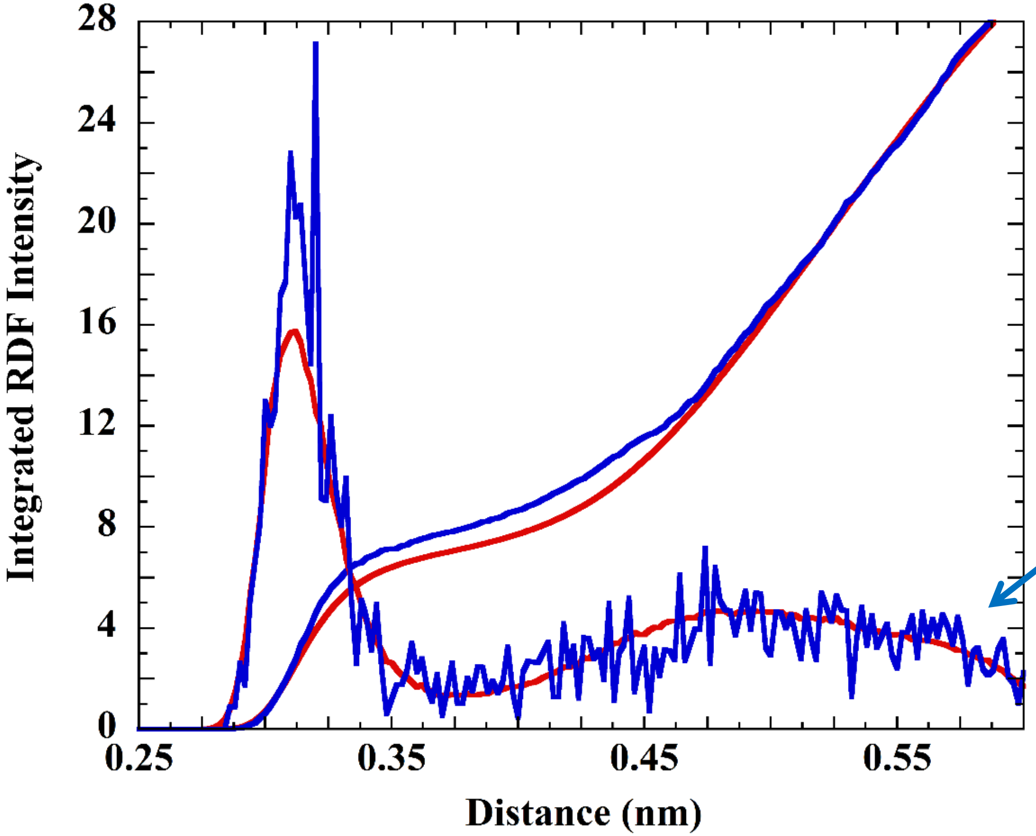
L_E – maximum at 3.11 Å

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

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