MXAN approach to XANES
strenght and limits

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Some years ago we have developed the MXAN method, based on MS theory, to fit the XANES energy region (from edge to about 200 eV) to obtain *quantitative structural* information

Many time we have only this energy region

Because EXAFS does not contain many structural information and/or damage of the sample – biological applications

Because of the signal/noise ratio at high energy like for example in the time-depended XAS experiment in the ps-fs time domain

………..

Plan of the talk

- Theoretical background
- Applications: applications to catalysis - time-dependend analysis
- XANES and Molecular Dynamics DMXAN approach

Using the Fermi Golden-rule to calculate the photo-absorption cross within the dipole approximation we can write for the absorption cross section

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

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

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

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

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

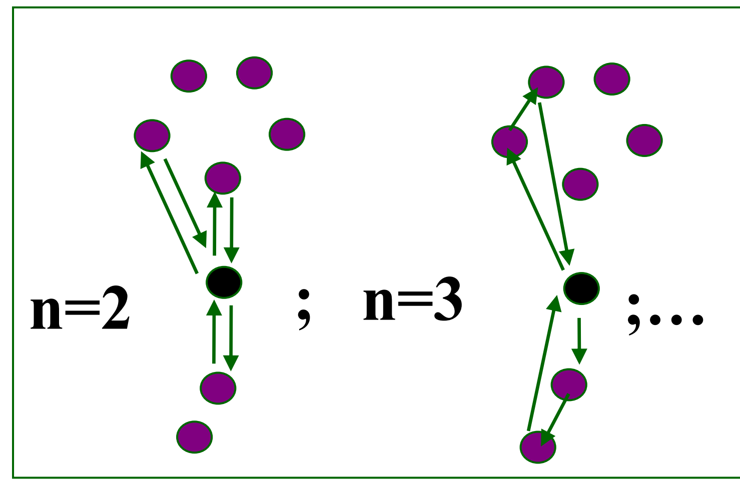
scattering path operator – it contains all the structural and electronic information

Two ways to calculate the scattering path operator

by series:

Exactly: all MS contributions are included

$$\sigma(E) = \sigma_0(E) + \sigma_2(E) + \ldots + \sigma_n(E)$$



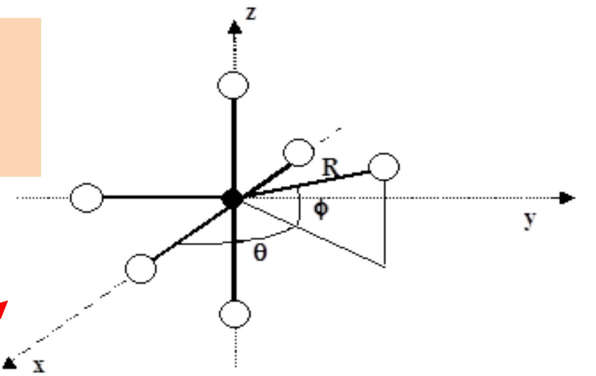
Most of the actually sotware packages to fit EXAFS data

MXAN

i) We work in the energy space
ii) We can start from the edge
iii) We can use polarization dependent spectra
iv) No DW factors are included

To perform structural fits

- Initial geometrical configurations
- Exp. data



We generate hundred of theoretical spectra by moving atomic coordinates

The potential is calculated at each step

By comparison with exp. data we can fit relevant structural parameters minimizing the error function

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

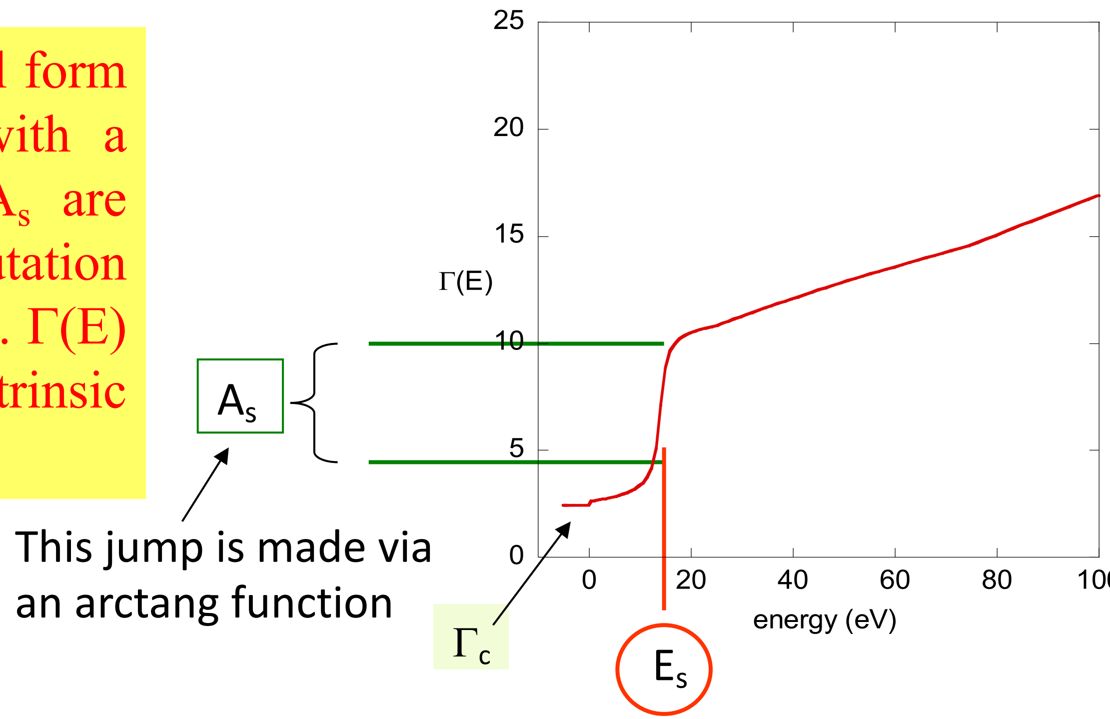
M. Benfatto and S. Della Longa J. Synch. Rad. **8**, 1087 (2001)
S. Della Longa et al. PRL **87**, 155501 (2001)
M. Benfatto et al. J. Synch. Rad. **10**, 51 (2003)

EXCHANGE and CORRELATION PART

Complex HL potential + Lorentzian function with constant Γc to account for the core-hole and the experimental resolution give rise to problems at low energy, typically in the energy range from the edge to 50 eV

The Exchange and Correlation part of the potential is calculated on the basis of a phenomenological approach $\longrightarrow$ real HL potential + convolution via a Lorentzian function with $\Gamma_{tot}(E)=\Gamma_c+\Gamma(E)$

$\Gamma(E)$ behaves like the universal form and starts from energy E_s with a jump A_s. Both E_s, Γ_c and A_s are derived at each step of computation on the basis of Monte Carlo fit. $\Gamma(E)$ contains all the intrinsic and extrinsic inelastic processes



• we have generalized the MS theory to treat the case where several electronic configurations are present MC-MS theory

• we have also demonstrated that if just one electronic configuration dominates we can eliminate from the set all channels which give rise to similar inter-channels potential

• from many body to an effective one particle problem – it is convenient to use the Green function formalism

$$\sigma(E) \approx Im G_{00}(E - I_c)$$

$$[\nabla^2 + E - V_c(\vec{r}) - \Sigma_{exc}(\vec{r}, E)] G_{00}^{+}(\vec{r}, \vec{r}\,', E) = \delta(\vec{r} - \vec{r}\,')$$

$$\Sigma_{exc}(\vec{r}, E) = V(\vec{r}, E) + i\Gamma(\vec{r}, E)$$

For a muffin-tin potential

$$G_{00}^{+}(\vec{r}, \vec{r}\,', E) = -k \sum_{L,L'} R_L^0(\vec{r}) \tau_{L,L'}^{00} R_{L'}^0(\vec{r}\,') + \sum_L R_L^0(\vec{r}) S_L^0(\vec{r}\,')$$

usual scattering path operator - complete equivalence between Green function and MS

C.R. Natoli, M. Benfatto et al. Phys. Rev **B42** 1944(1990); T. Tyson et al. Phys. Rev **B46** 5997(1992); C.R. Natoli, M. Benfatto et al. Jour. Synch. Rad. **10** 26 (2003)

If only one electronic channel (the elastic one) dominates the corresponding G_0 Green's function obeys to a Dyson-like equation with a suitable complex optical potential $\Sigma^{opt}(r,r';E)$

With some approximation (locality, homogeneous systems ..) this is equivalent to a "real" calculation convoluted by a Lorentzian function of suitable energy dependent width.

We also note that in the sudden limit of the MC-MT theory

$$\mu = \sum_n \mu_n \xrightarrow[\Delta E \to 0]{} \int \mu(\omega - \omega') A(\omega') \, d\omega'$$

Lorentzian function

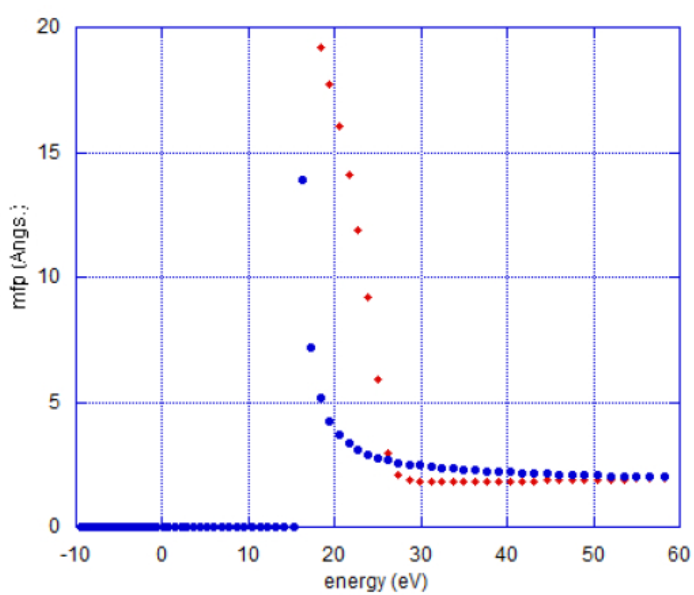
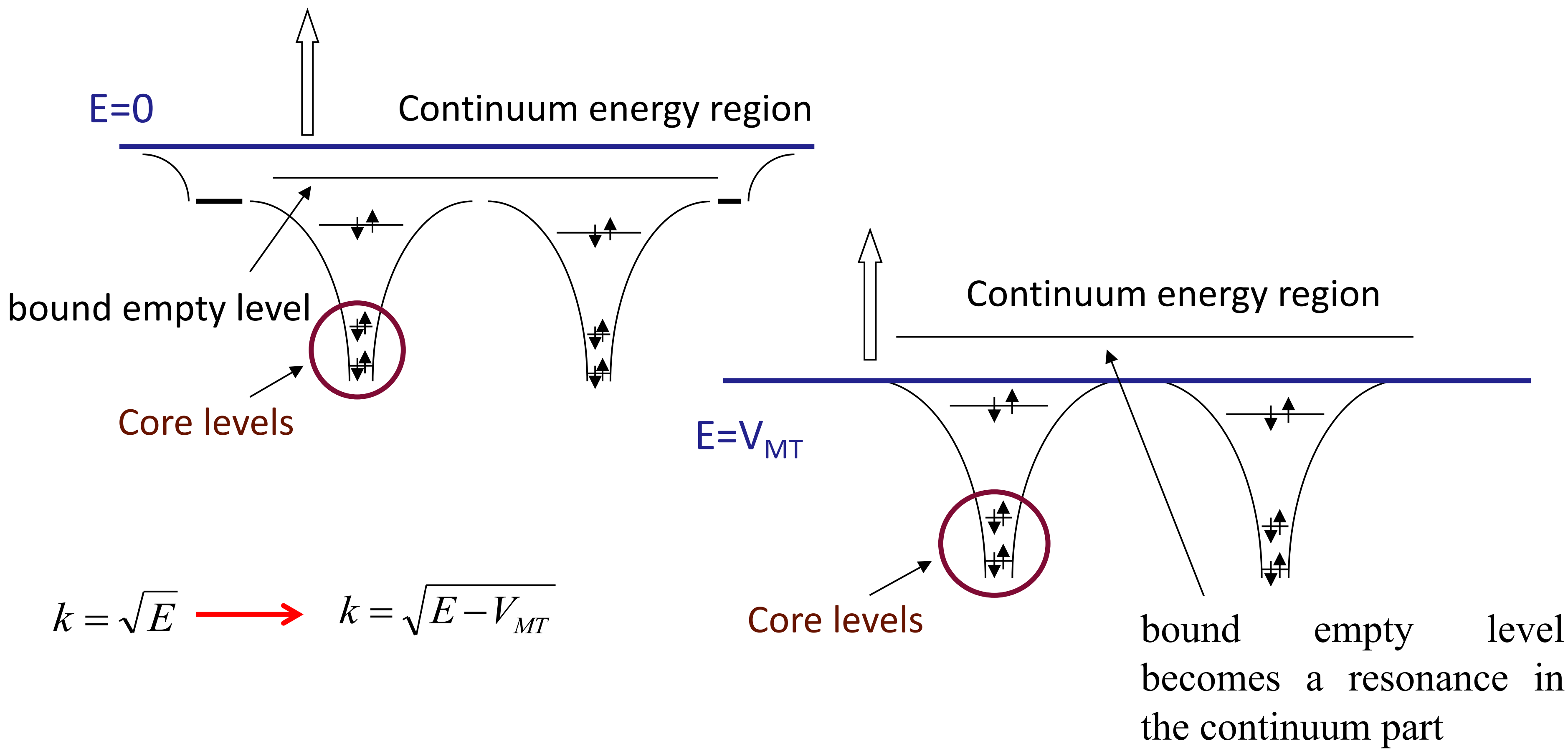


Fig. 7.2 Comparison between the mean free path calculated by the complex part of the HL potential (*blue circles*) and the one coming by the phenomenological approach (*red points*). These values come from the best fit of Ni *K*-edge in water solution

S.H. Chou et al. PRB (1987) **35**, 2604; J.J. Rehr and R.C. Albers (2000) Rev. Mod. Phys. **72**, 621; C.R.Natoli et al. (1990) PRB **42**, 1944; M. Benfatto et al. Springer Proceeding in Physics 204 (2017).

The "extended continuum" scheme

Slightly changing the MS theory we can found bound states as resonances in the continuum part of the spectra which starts at negative energy, the muffin-tin value V_{MT}



$$k = \sqrt{E} \longrightarrow k = \sqrt{E - V_{MT}}$$

We can calibrate on the same energy scale the bound state features relative to the continuum features without the need to perform ionization energy calculation - unique energy scale from the pre-edge energy region to the EXAFS part.

The energy separation between the different features is correct but we pay the price that the calculated intensity of the transitions from core to empty bound levels could be incorrect.

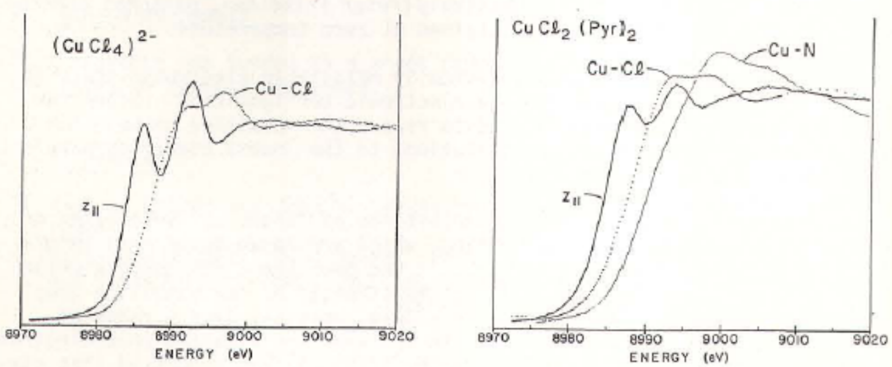


Fig. 1: K-edge absorption spectra as a function of E-polarization for (C -bis creatinium (left panel) and $Cu-Cl_2$-di-pyridine (right panel). The instrumental resolution is lower (∿ 4 eV) in the right panel than in the left panel (∿ 1 eV).

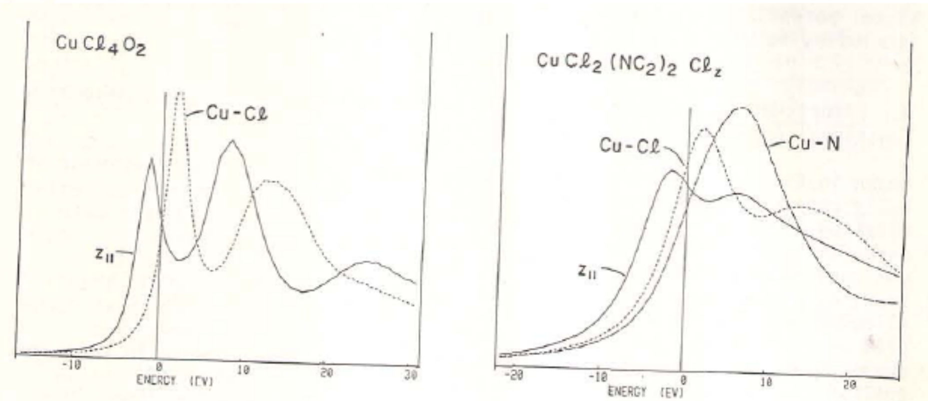


Fig. 2: Absorption cross sections as a function of E-polarization calculated for model clusters using the 'extended continuum' approach. Note the effect of the axial O-ligand producing an extra bump at +23 eV in the $(CuCl_4)^{2-}$ cluster.

S. Doniach et al. Proceedings of "EXAFS and Near Edge Structure III" Stanford (1984)
M. Benfatto et al. Phys. Rev B (1986); T. Tyson et al. Phys. Rev B (1992)

about the MT approximation

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

$$\sigma_t \approx \mathrm{Im}\,(T+H)^{-1} \qquad T=(T_a)^{-1}+\Delta T \qquad H=H_{MT}+\Delta H$$

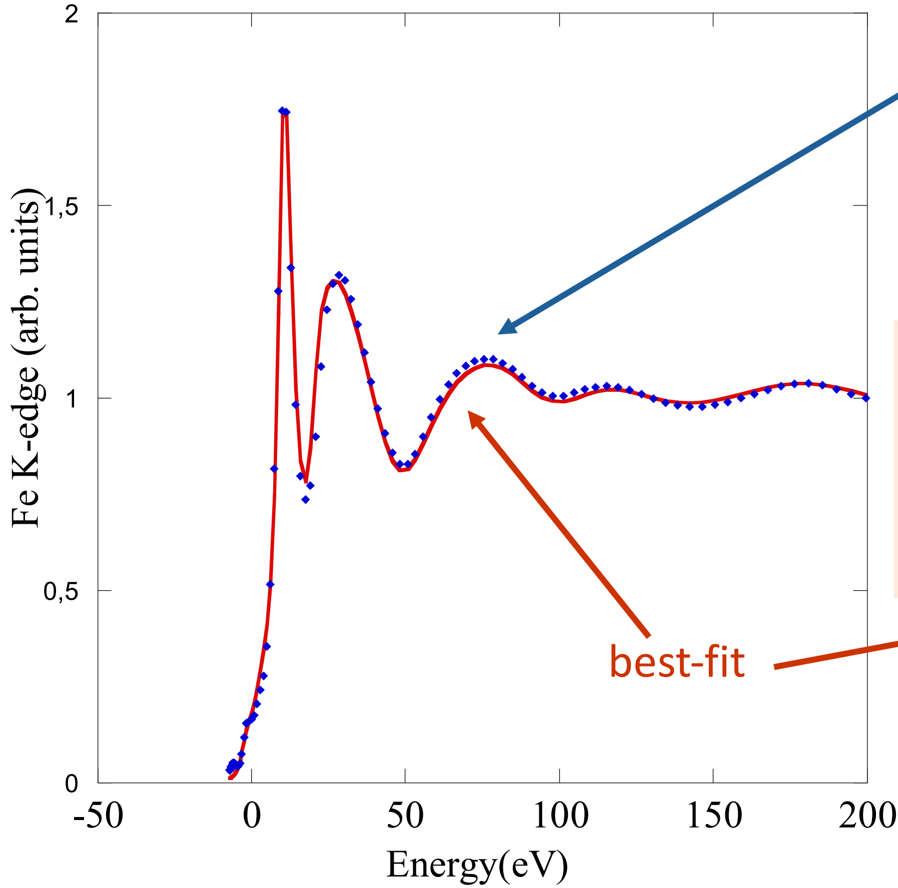
$$\sigma_t \approx \mathrm{Im}\left\{\sum_{n=0}(-1)^n\,[(T_a^{-1}+H_{MT})^{-1}\Delta]^n\,(T_a^{-1}+H_{MT})^{-1}\right\}$$

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

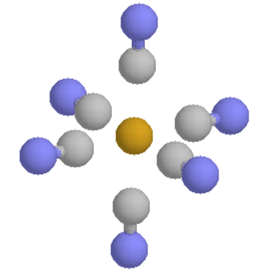
This also suggest how to minimize the effects of the non-MT corrections: by optimization of the MT radii and the interstitial potential – MXAN does this now within the structural loop.

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

Fe $(CN)_6$ in water



exp



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

Many different applications

From the coordination geometry of metal site in proteins to the time-dependend 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)
R. Sarangi et al. Inorganic Chemistry (2005) **44**, 9652
P. D'Angelo et al. JACS (2006) **128**, 1853
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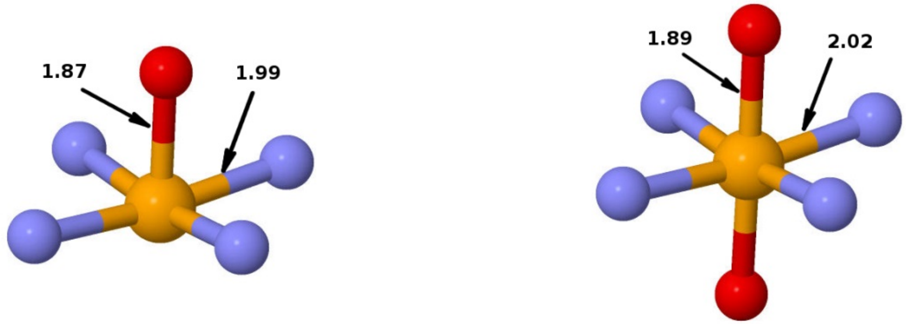
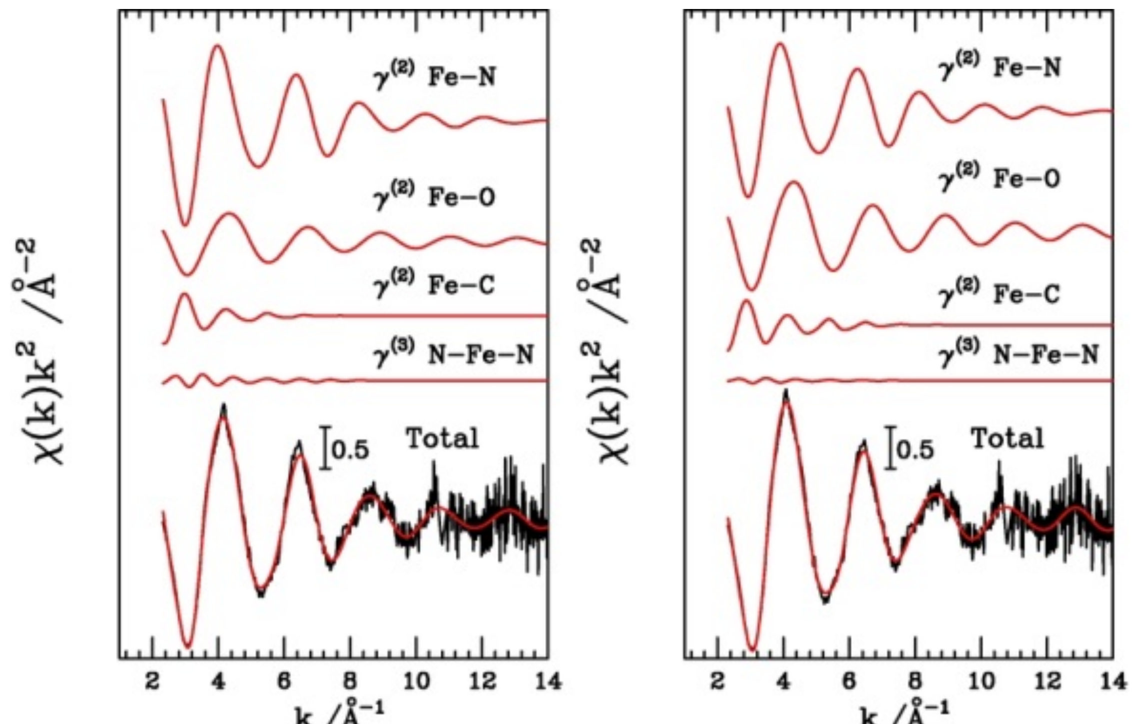
M. Bortolus et al. JACS (2010) **132**,18057
R. Sarangi et al. Journal of Chemical Physics (2012), 137, 2015103
.....
P. Frank et al. Journal of Chemical Physics (2015), 142, 084310
G. Chillemi et al. Journal of Physical Chemistry A (2016), 120, 3958
M. Antalek, et al. Journal of Chemical Physics (2016), 145, 044318.
H.T. Lemke et al. Nature Communication (2017), 8, 15342 doi:10.1038

Fe-N-C catalyst for Oxygen Reduction Reaction - The active site of Fe-N-C catalysts is investigated by XAS analysis.

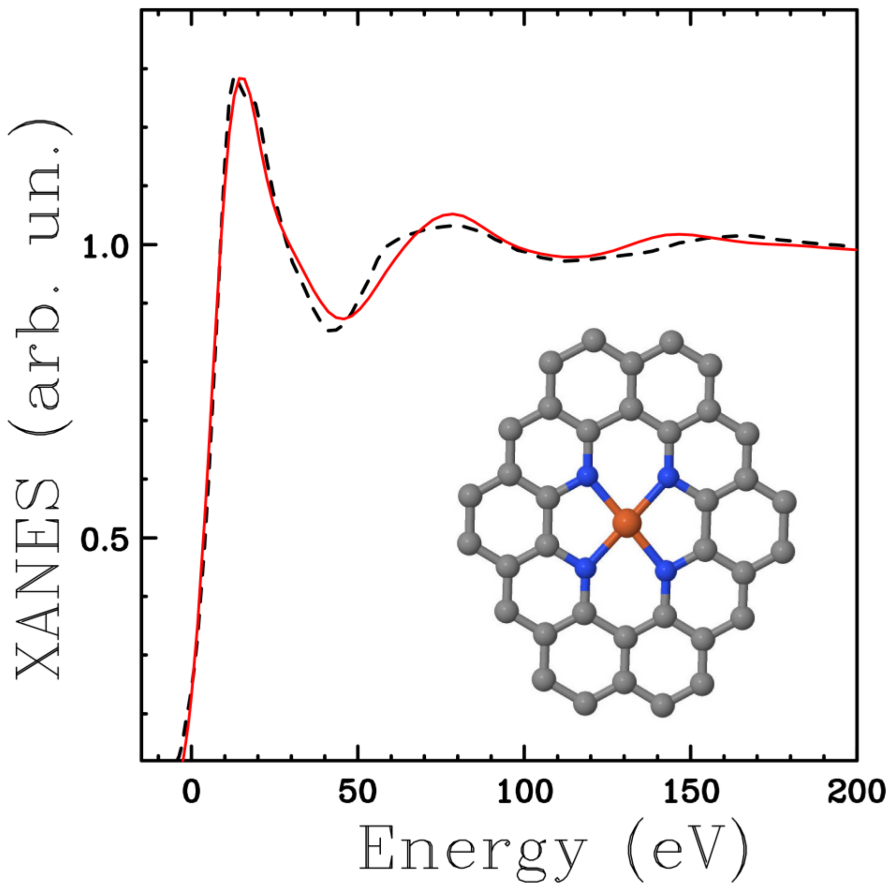


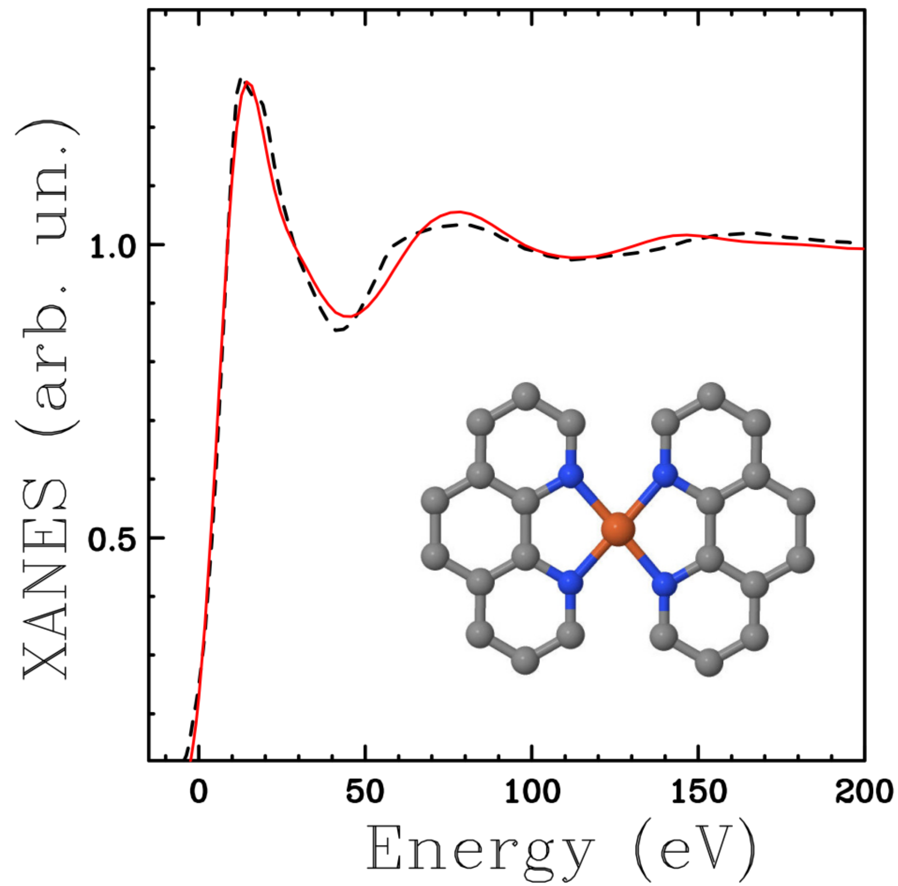
5 or 6-fold coordination
The same behavior of the Cu in water



Zitolo, A. *et al*. *Nat. Mater*. **2015**, *14*, 937–942.

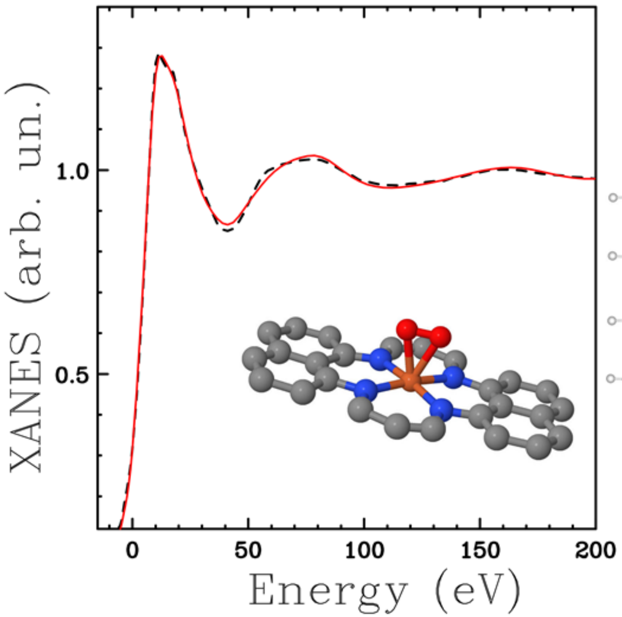
The old proposed model

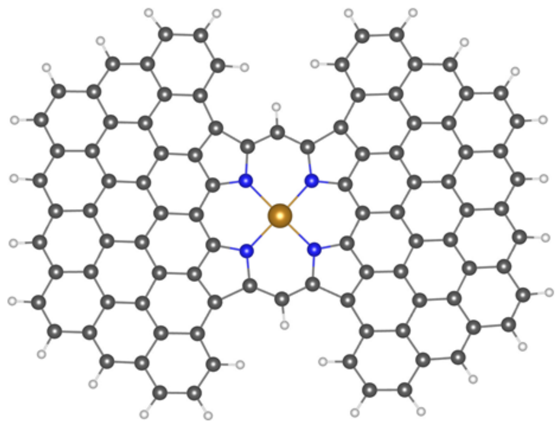


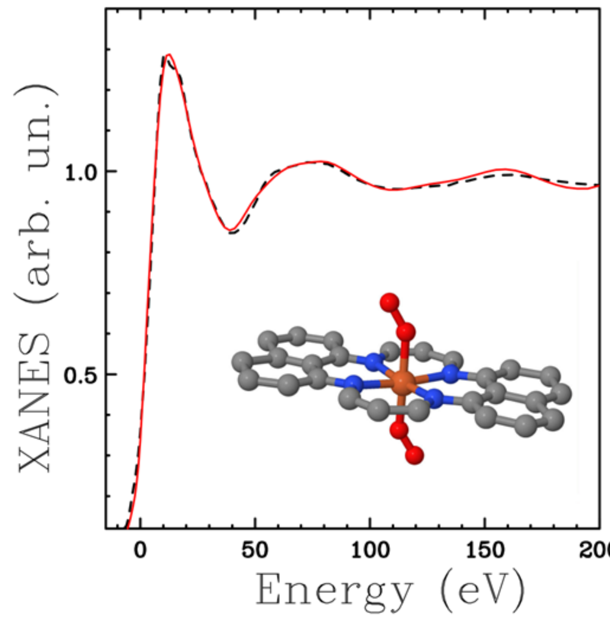


R_{sq} of the order of 3

The porphyrinic model







R_{sq} of the order of 1.1

Fe-N = 1.93(3) Å
Fe-O = 2.00(4) Å

Fe-N = 2.03(3) Å
Fe-O = 1.87(4) Å

This is better in agreement with EXAFS results

Zitolo, A. *et al*. in *Nat. Mater*. **2015**, *14*, 937–942.

‘ …..In conclusion, the quantitative analysis of the EXAFS and XANES regions on Fe–N–C catalysts free or almost free of Fe crystalline structures has revealed the existence of porphyrin- like FeN4 C12 moieties, in strong contrast with the previously assumed FeN_xC_y moieties based on nitrogen atoms included in six- membered rings. The electrochemical investigation shows that such moieties catalyse the four-electron reduction of dioxygen to water. Owing to their geometric structure, porphyrinic moieties may either form in strongly disordered graphene sheets or between zigzag graphene edges defining a micropore…..’

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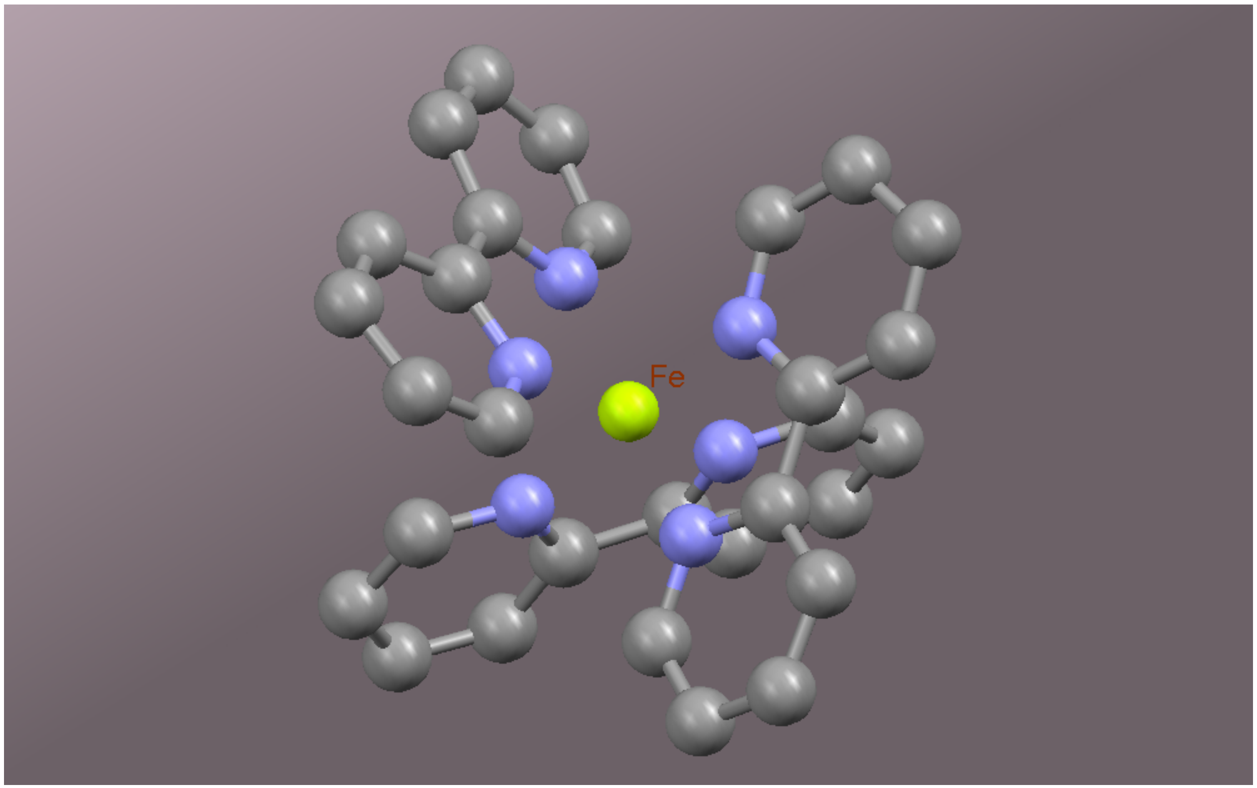
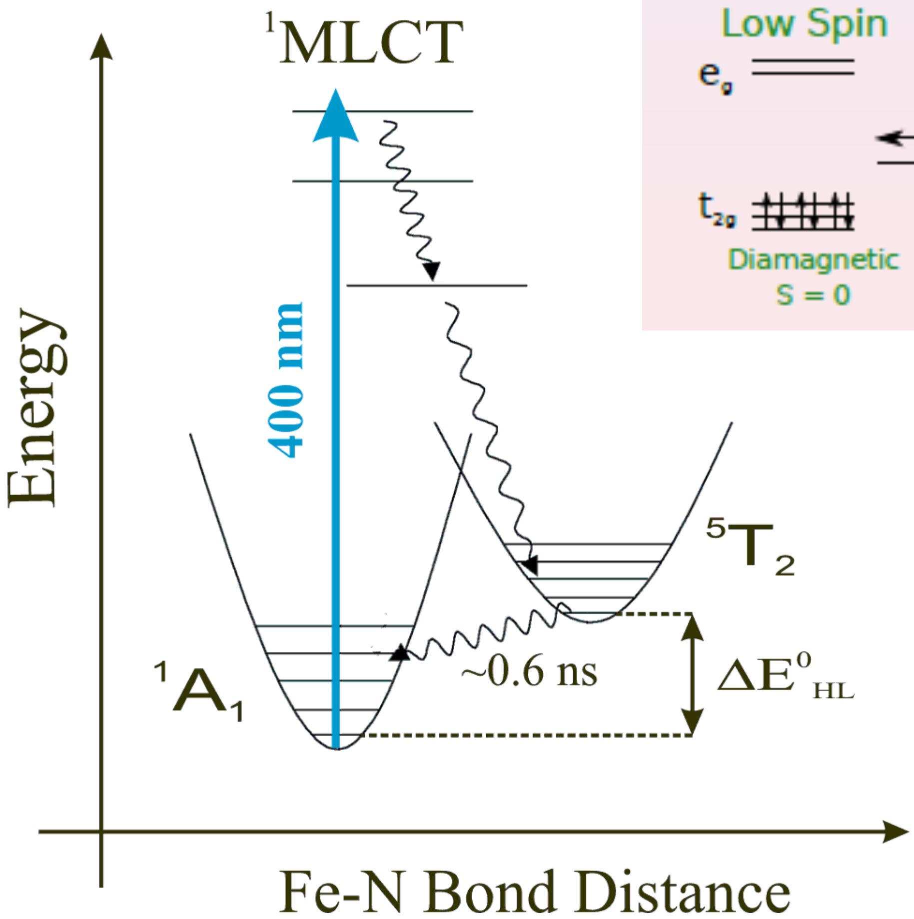
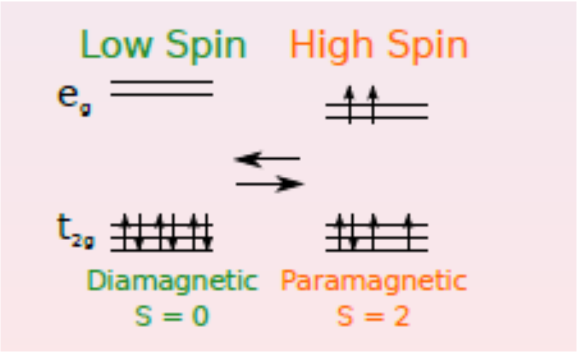
M. Benfatto et al. J. Phys. Chem. B (2006), 110 14035

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



see the structural changes going from LS to HS state





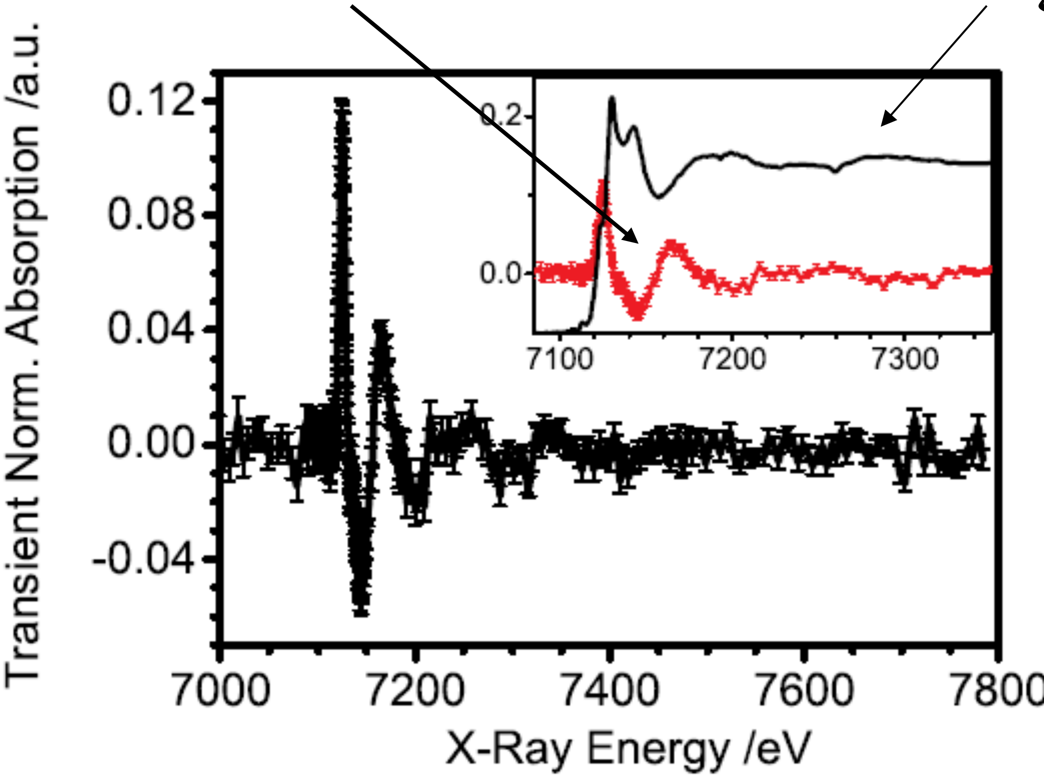
experiment done at the micro-XAS line of SLS by Chergui's group - pump-probe experiment in aqueous solution and room temperature

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

experimental data

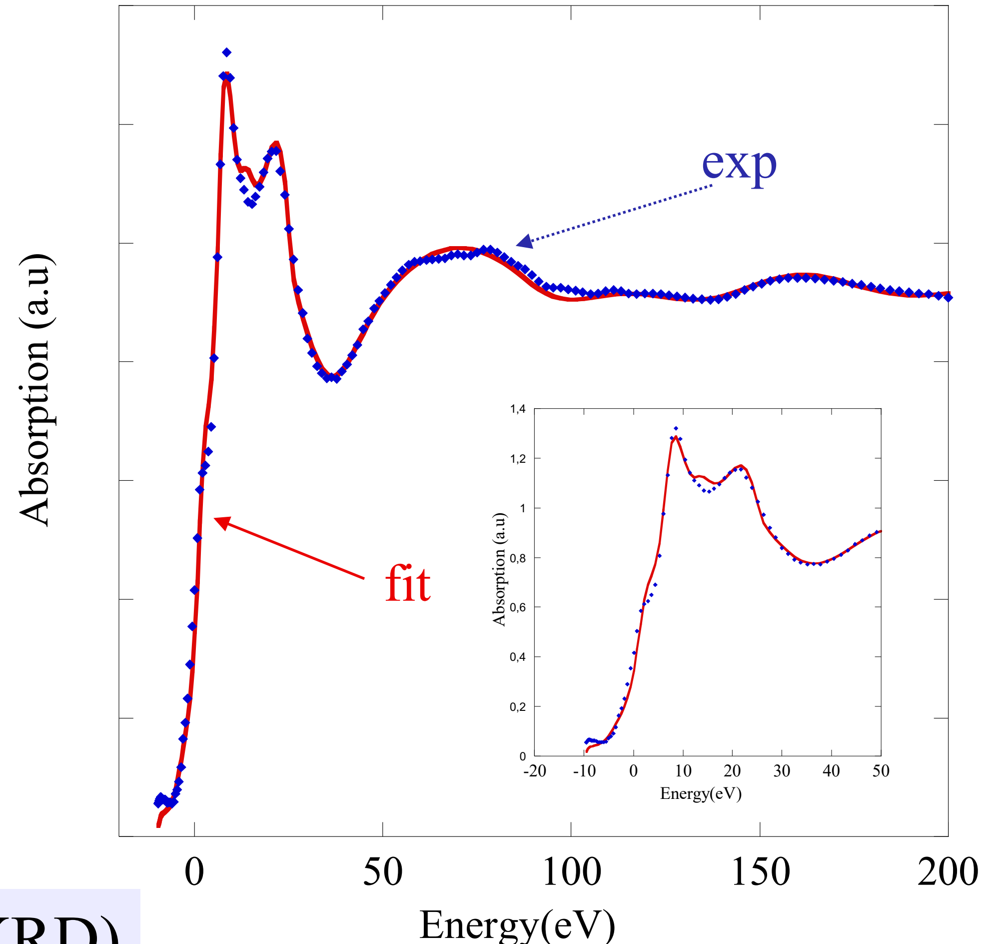
HS transient data at Δt = 50 ps

LS gs data



LS ground state fit

$R_{Fe\text{-}N} = 2.00 \pm 0.02$ Å



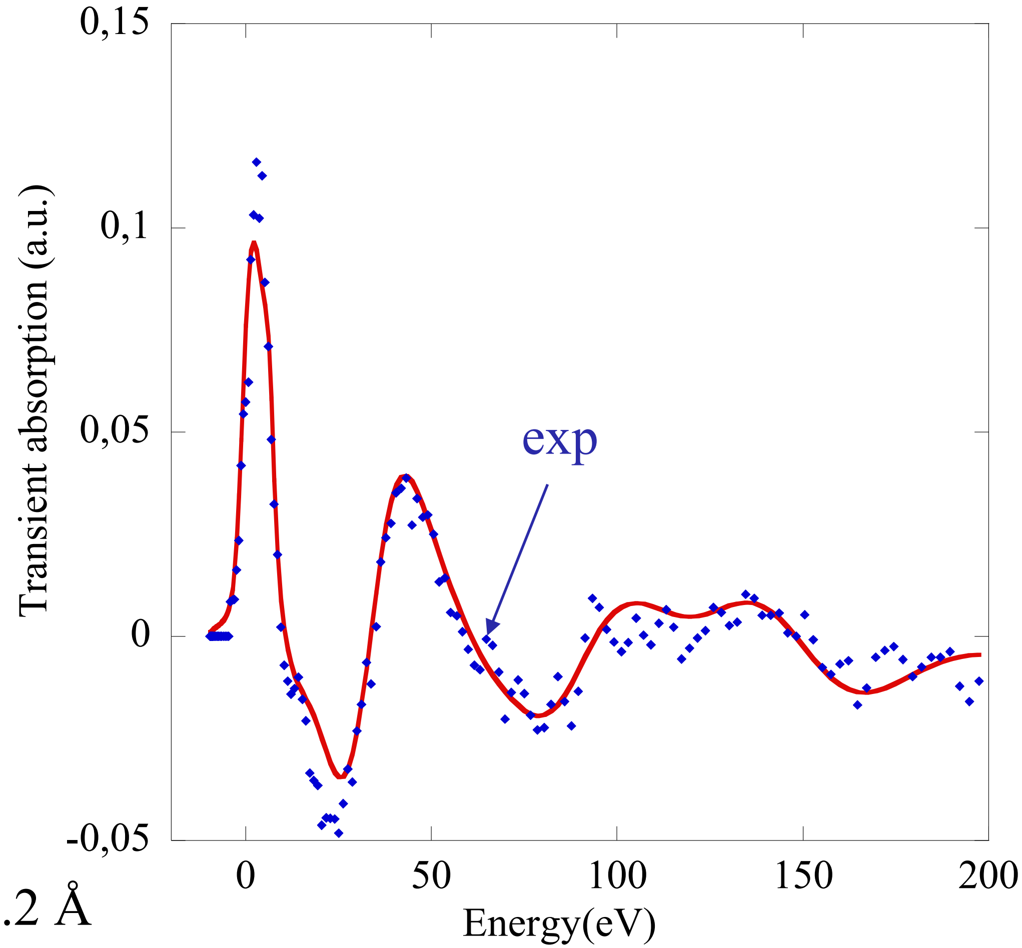
$R_{Fe\text{-}N} = 1.967 \pm 0.006$ Å (XRD)
$R_{Fe\text{-}N} = 1.99 \pm 0.02$ Å (DFT)

HS excited state fit by transient data

supposing a chemical shift
$\Delta E = -2.5 \pm 0.5$ eV

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

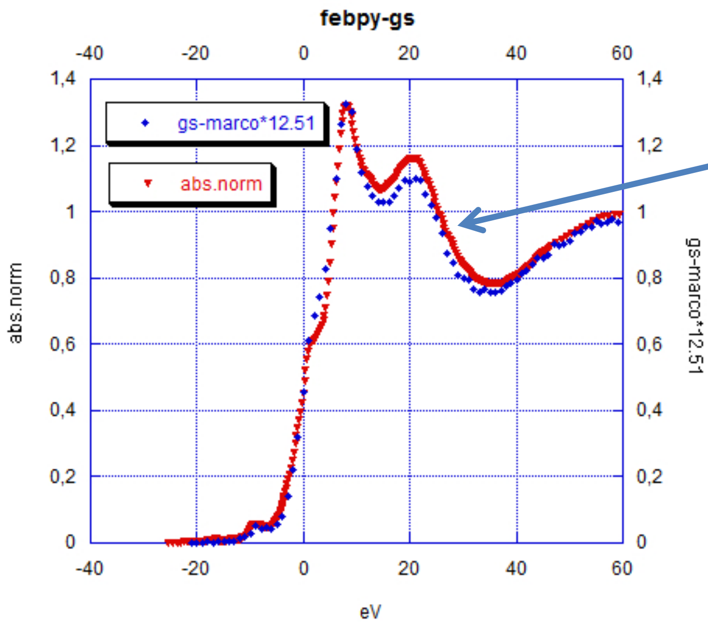
DFT calculations indicate ~ 0.2 Å



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

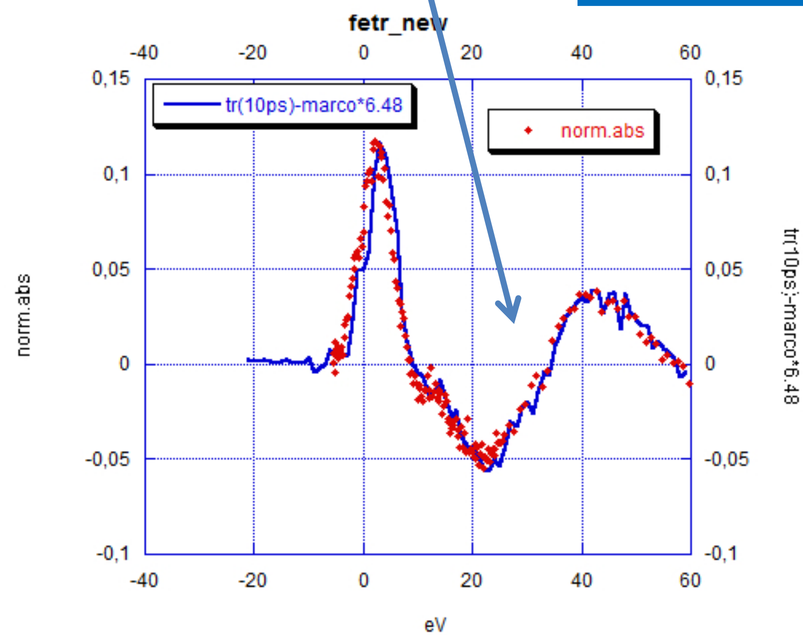
Going to the fs time scale FEL experiment

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



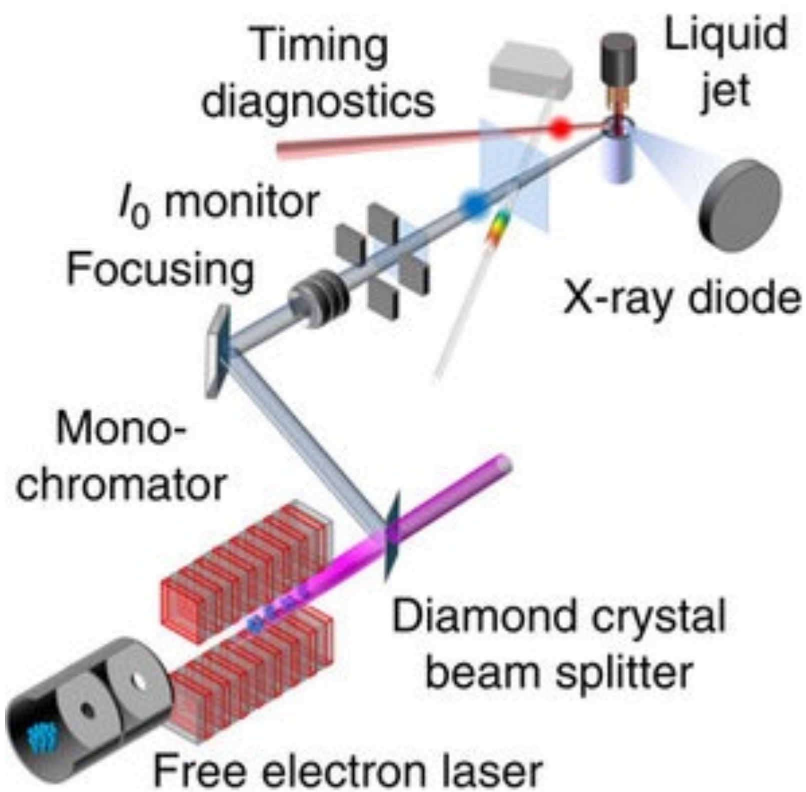
Exp data taken at LCLS

transient at 10 ps



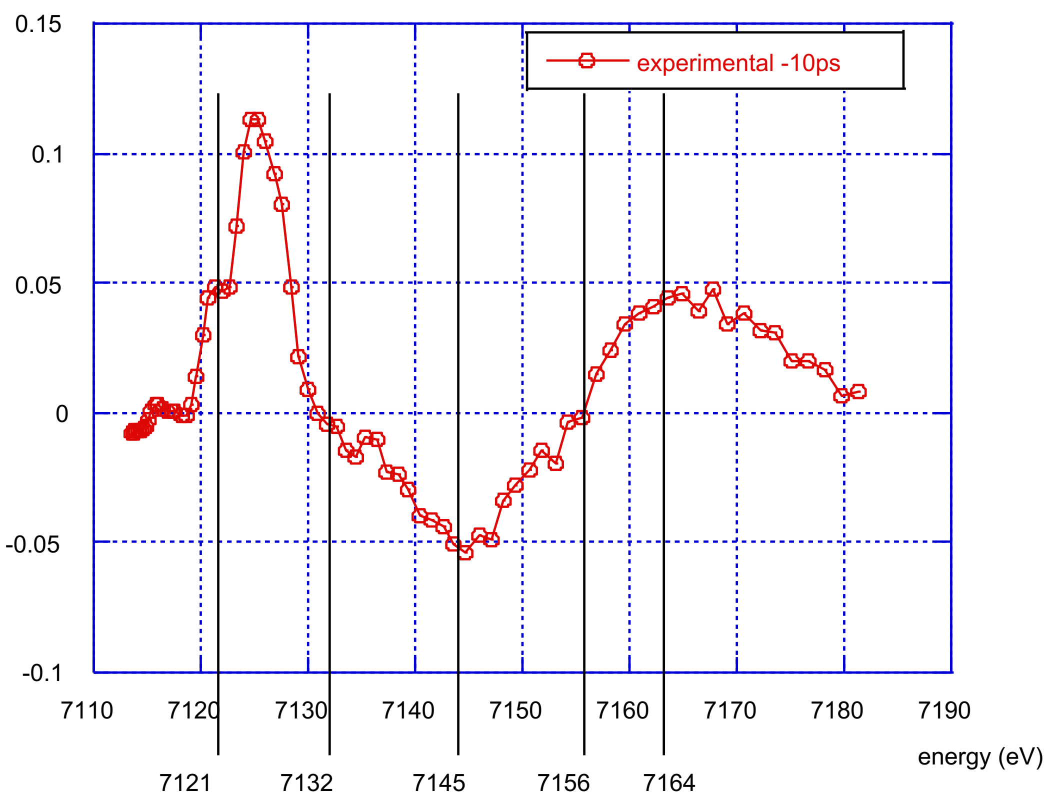
MXAN fits of such data give the results previously obtained within the statistical error

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



H.T. Lemke et al. Nature Commun. **8**, 15342 (2017) at the fs time scale it is impossible to take extedend experimental data – they must be taken at fixed energy

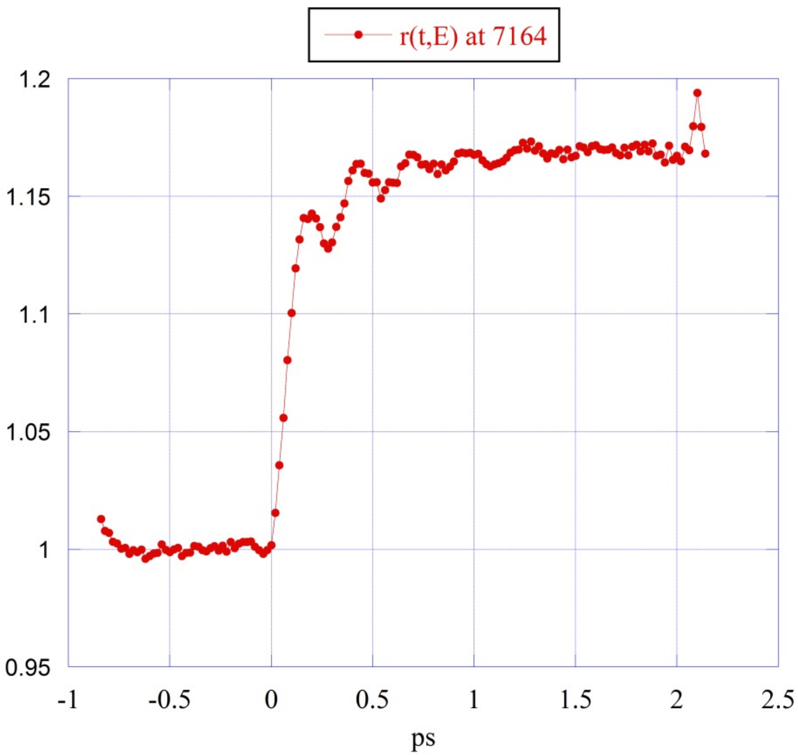
the transient data are taken as function of time but at fixed energy, in particular at 7121, 7132, 7145, 7156 and 7164 eV

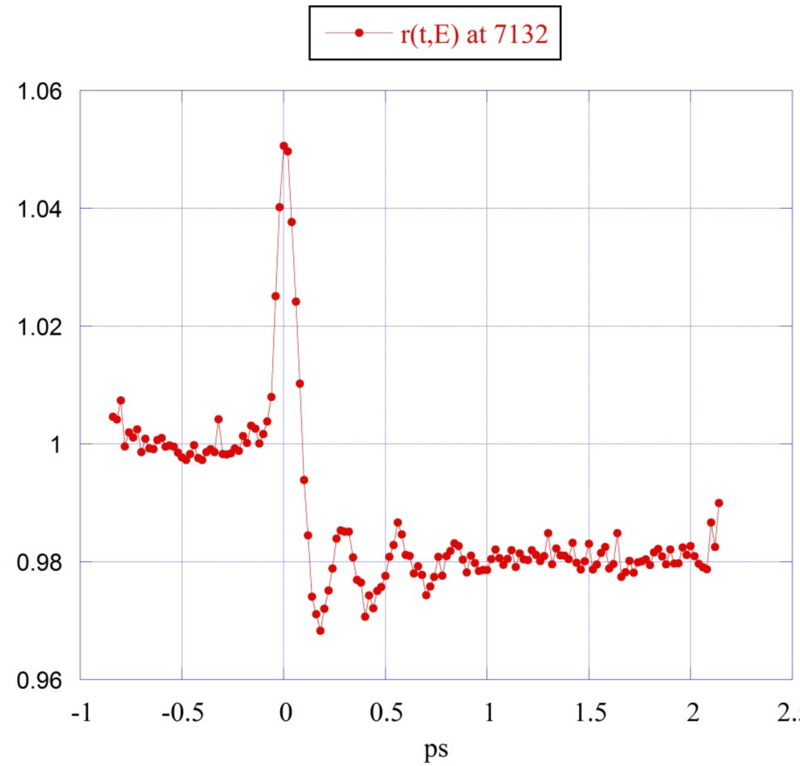


Here the exp. data is the ratio

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

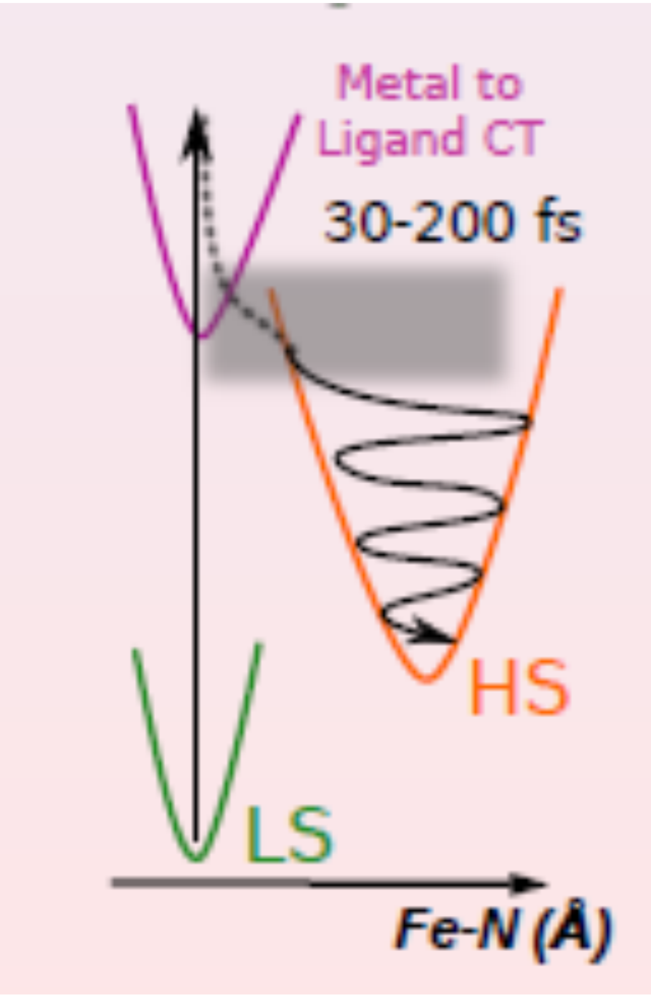
We get data as function of time





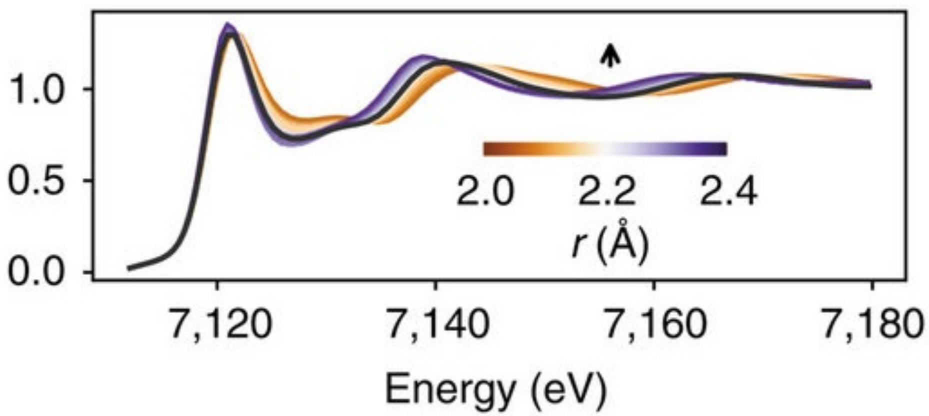
oscillations up to 2ps with a period of about 0.265 ps correspondig to 126 cm^{-1} - the system is in the HS state after 2ps.

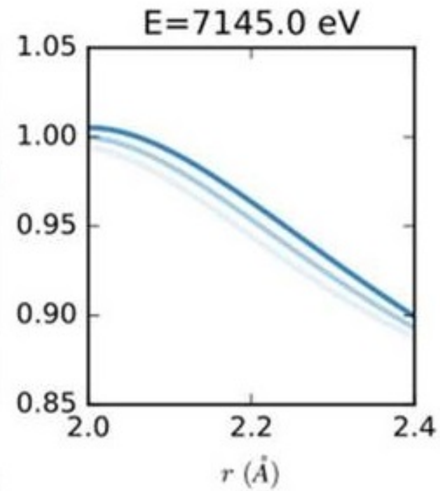
All data shows a rapid change within 30-200 fs followed by an oscillating phase up to 1-2 ps. After this we reach the HS state.



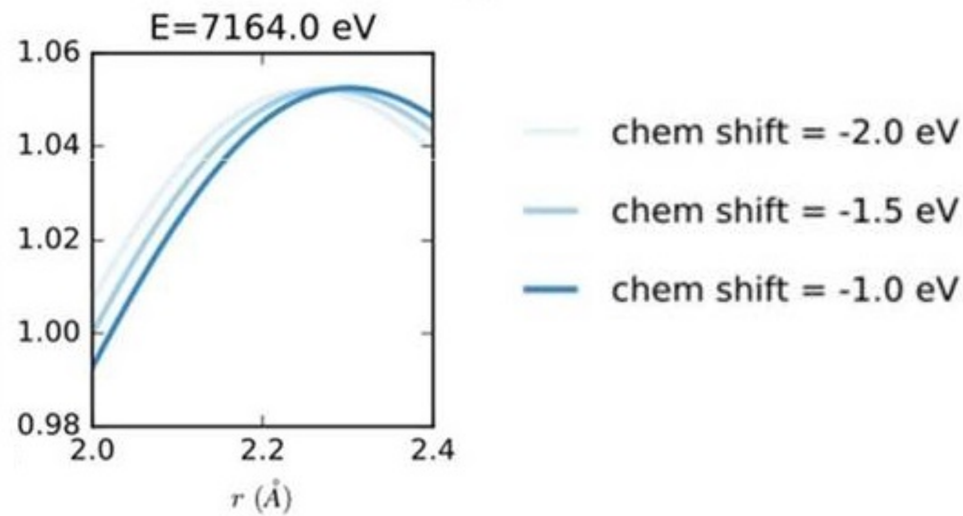
How to analyze these data?

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





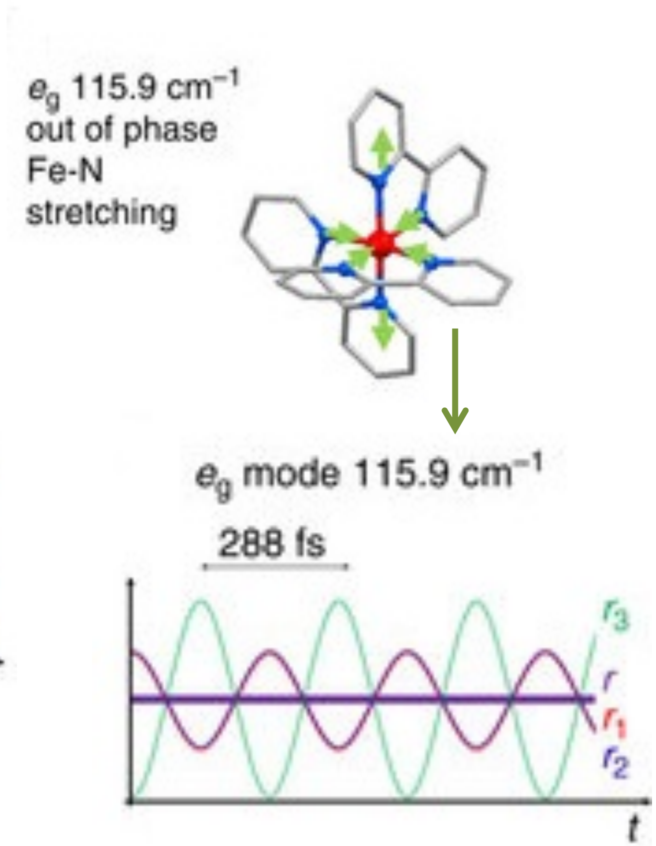
We plot the dependence of the $S(E,r)$ signal at given energy for different chemical shifts

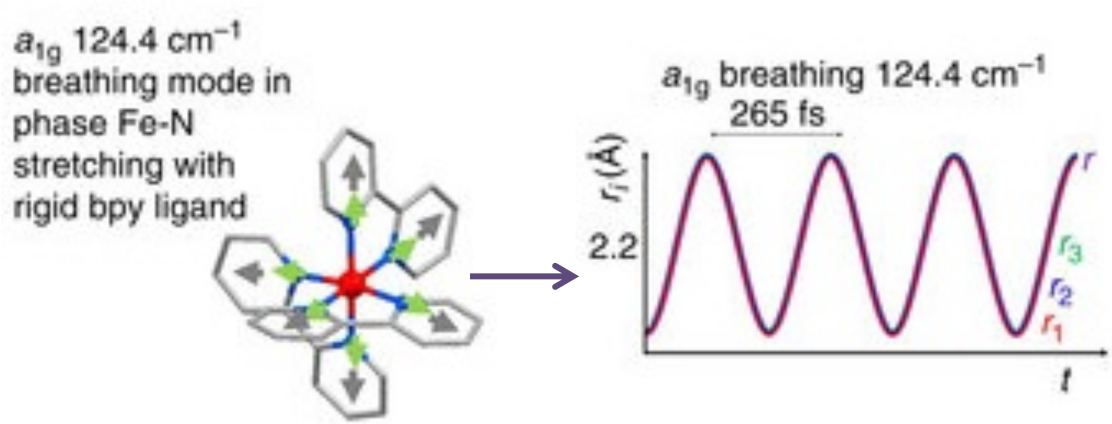


With these calculations we build the signal

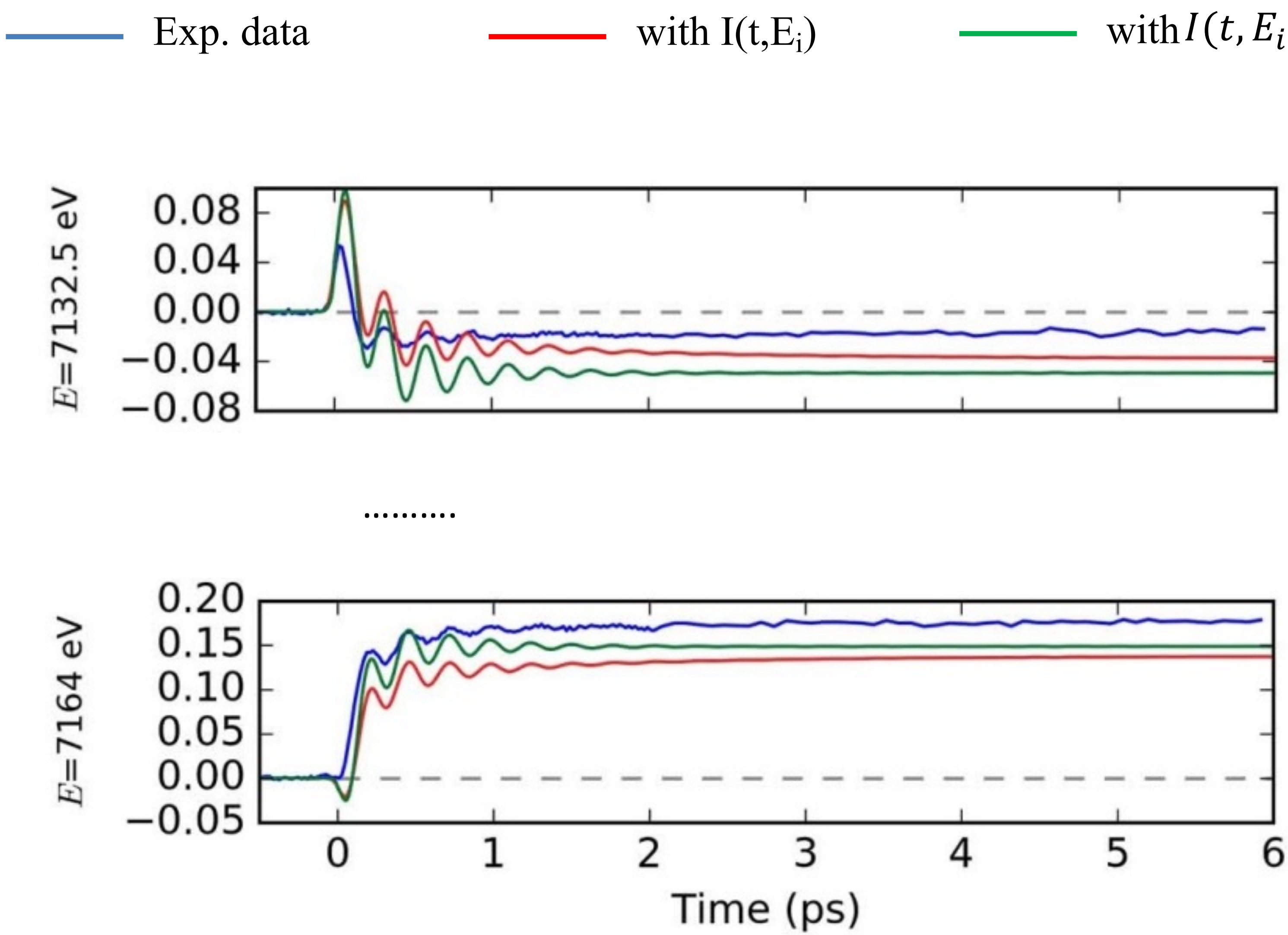
Where $S(E,r)$ is the calculated signal for a given E and r $g(r,t)$ is a numeric time-dependent distance distribution coming from the breathing mode at 124,4 cm^{-1}

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





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



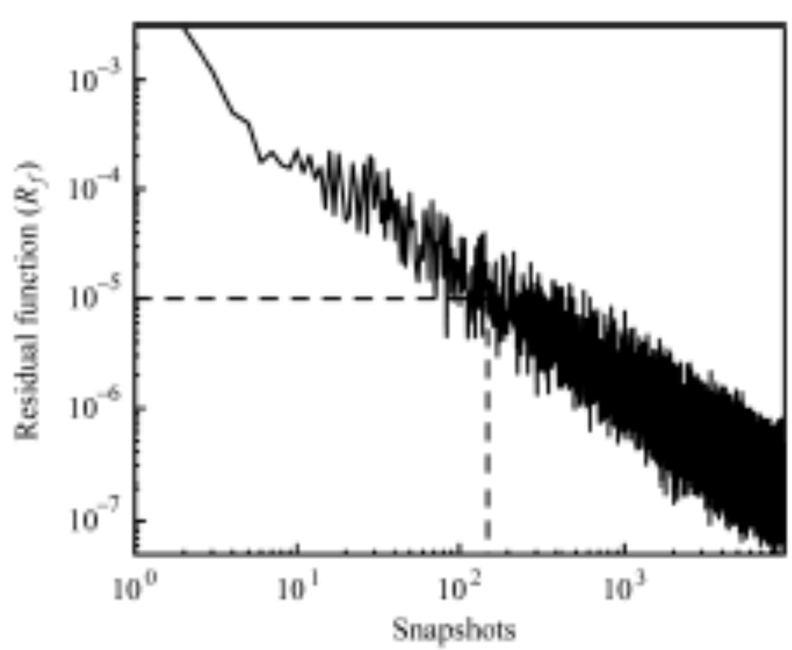
We are able to have a complete description of the experimental data from the excitation to the triplet state looking in details to the dynamic

The discrepancies between experimental data and the theoretical simulations indicates at least the need to include in the calculations the contributions of normal mode different from the breathing one

XANES and Molecular Dynamics D-MXAN approach

We use MD to generate thousands of geometrical configurations – each snapshot with a time step of 50 fs is used to generated one XANES spectrum – average using ~ 10^4 geometrical configuration

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



MD details

- Classical MD – solve the Newton's equations of motion for a given Force field
- Two body potential formed by two parts: bonded and nobonded interactions (LJ and Electrostatic interactions) if needed corrections to account QM effects
- GROMACS
- Time steps of 2 fs
- Before to extract the trajectories the system is thermal equilibrated for several ps by using a thermal bath at a given temperature

More details

$$\mathbf{f}_i = m_i \cdot \mathbf{a}_i \qquad \mathbf{f}_i = -\frac{\delta V}{\delta \mathbf{r}_i}$$

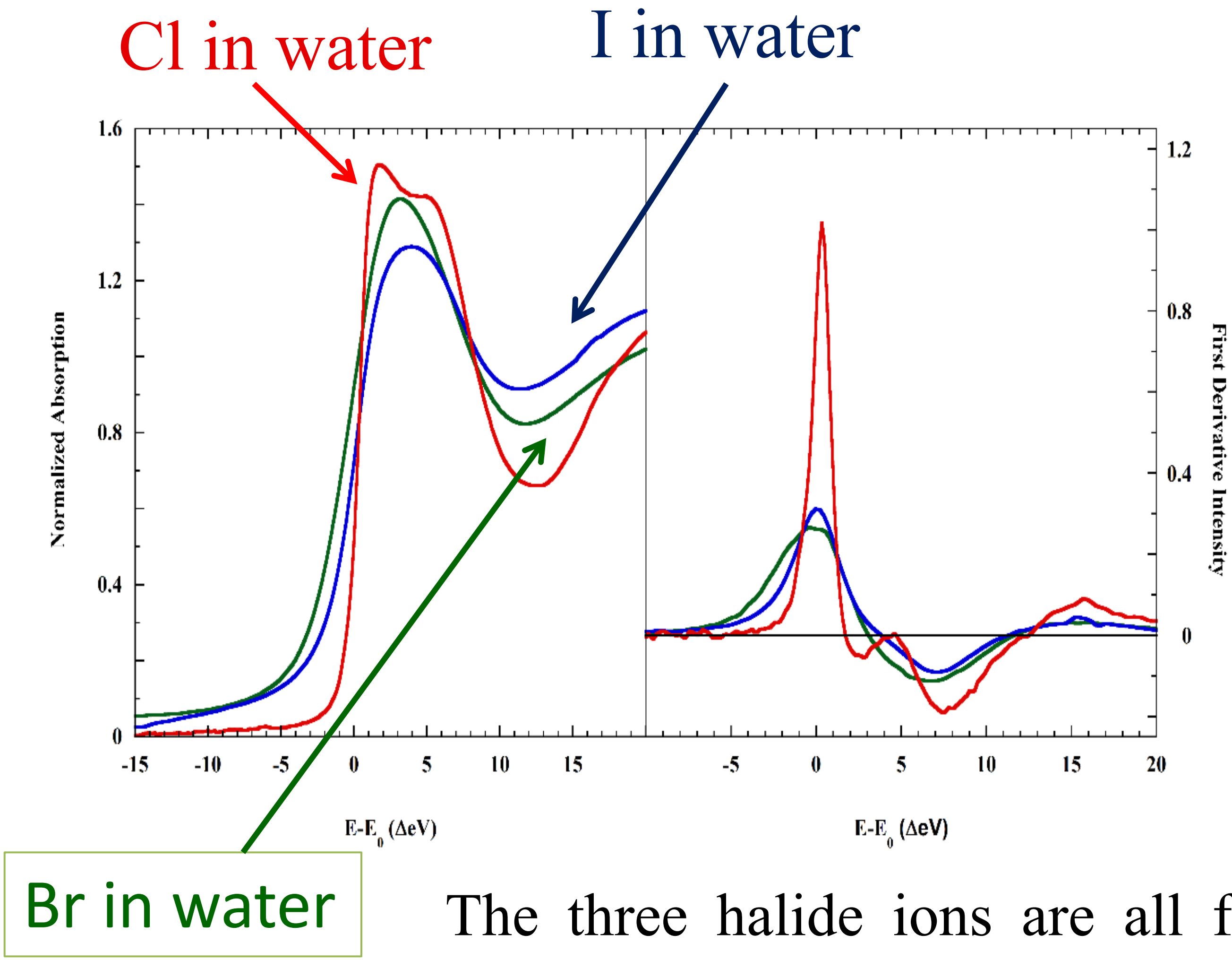
$$V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \sum_{bond} \frac{1}{2} k_{b_0} \left(b_n - b_{0_n}\right)^2 + \sum_{angle} \frac{1}{2} k_{\theta_0} \left(\theta_n - \theta_{0_n}\right)^2 +$$

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

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

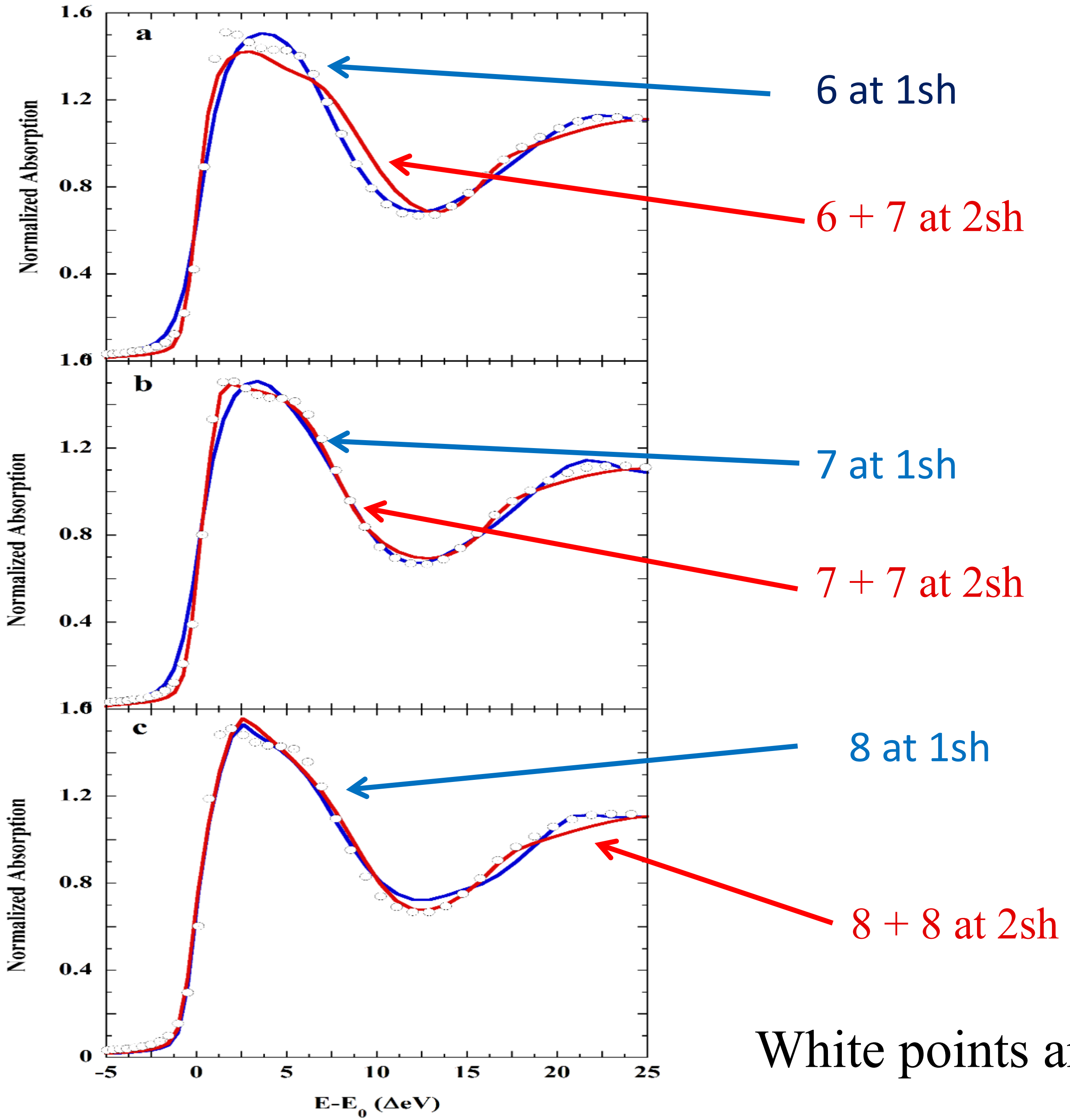
L-J potential - $C^{(6)}$ is the constant in the term describing the dispersion attractive force between atoms; $C^{(12)}$ is in the term that describes interatomic electron cloud repulsion

the "strange case " of Cl



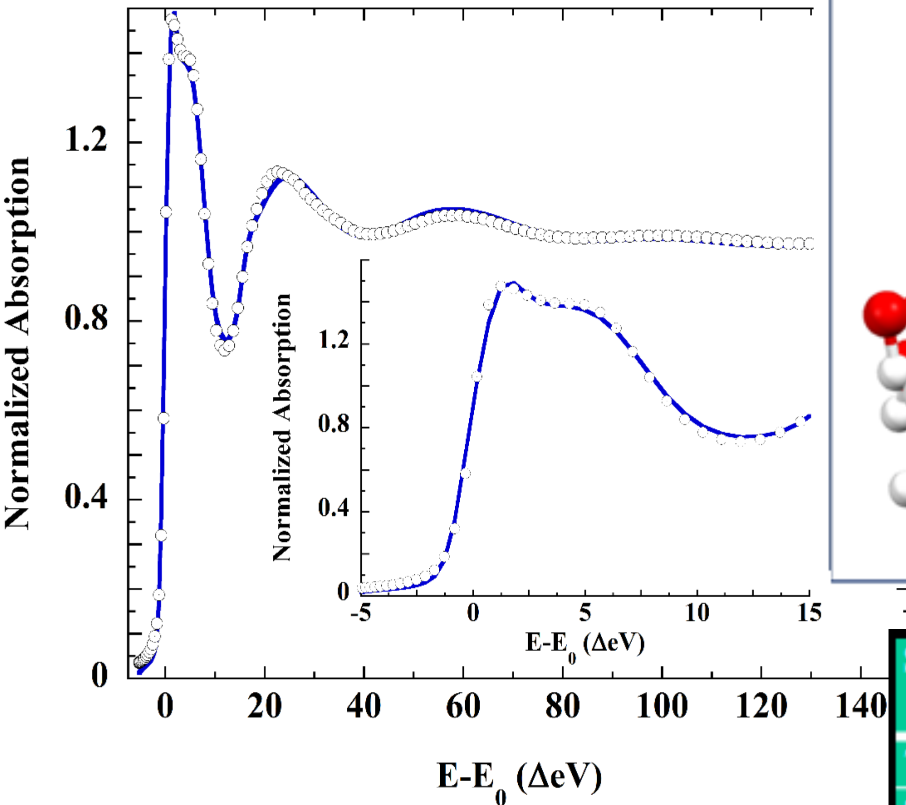
The three halide ions are all filled shell and iso-electronic ($3p^6$, $4p^6$, $5p^6$) – same ground state electronic configuration

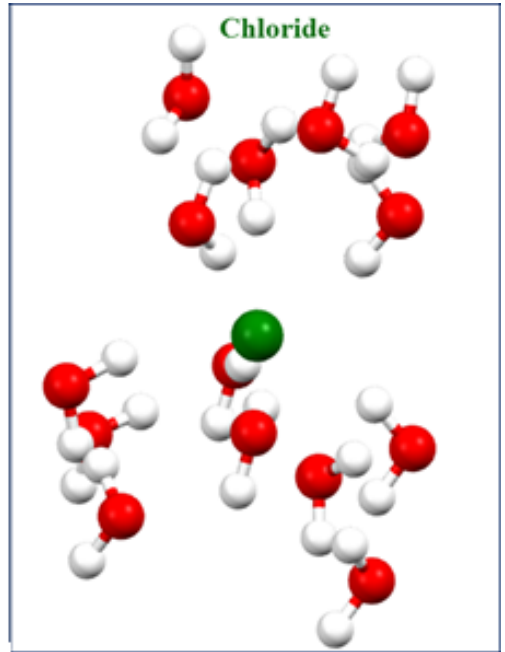
Static analysis



White points are the exp. data

Further refinement of the second shell



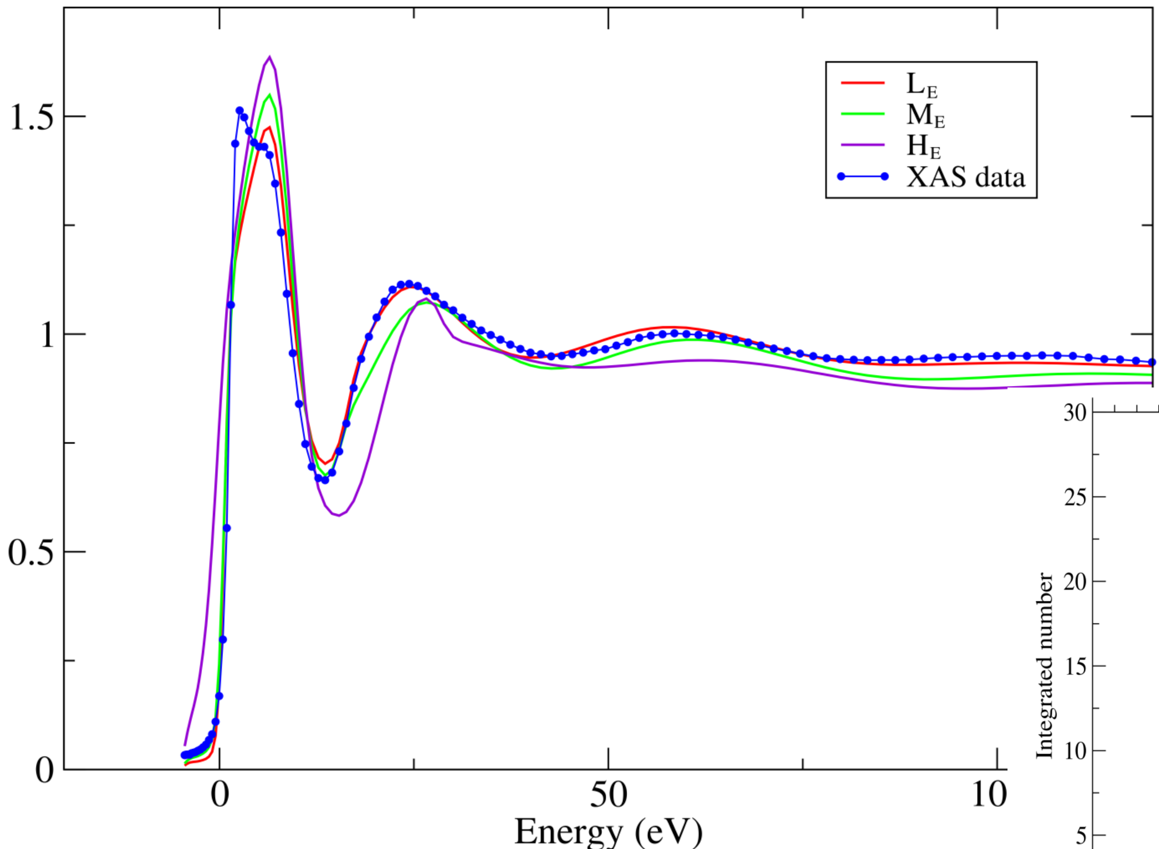


Shell	Cl-O (Å)[a,b]	Cl-H_{near} (Å)[a]	Cl-H_{far} (Å)[a]
7 waters	3.15±0.10	2.18±0.10	3.50±0.10
7 waters	4.14±0.31	3.76±0.38	4.89±0.30
Prior Work			
CN[d]	Cl-O (Å)	Cl-H_{near} (Å)	Method[e]
6±1	3.1	2.2	ND,XRD
6.4±0.3	3.1±0.01	2.28±0.03	ND
6.4	3.3	2.28	AXD
---	3.14±0.02	---	SAXS
6.4	3.14±0.02	2.23±0.04	EXAFS

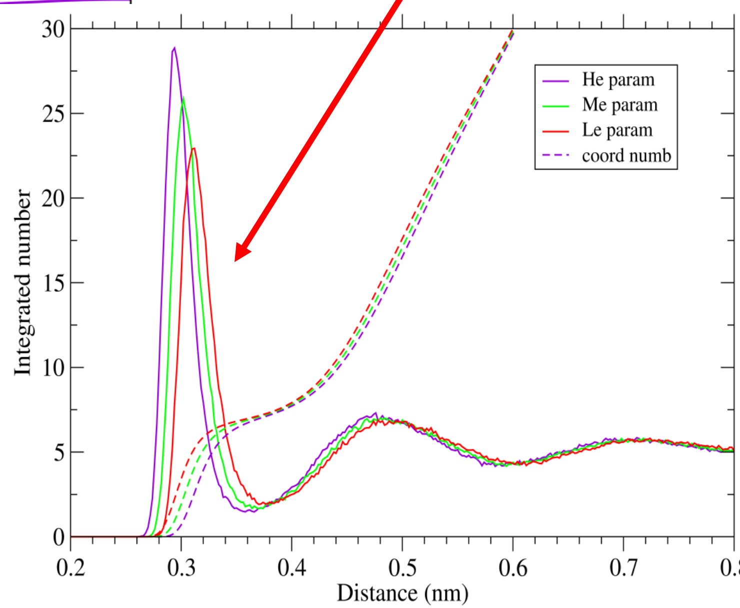
M. Antalek, E. Pace, B. Hedman, K. Hodgson et al. (2016) The Journal of Chemical Physics 145 (4), 044318.

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

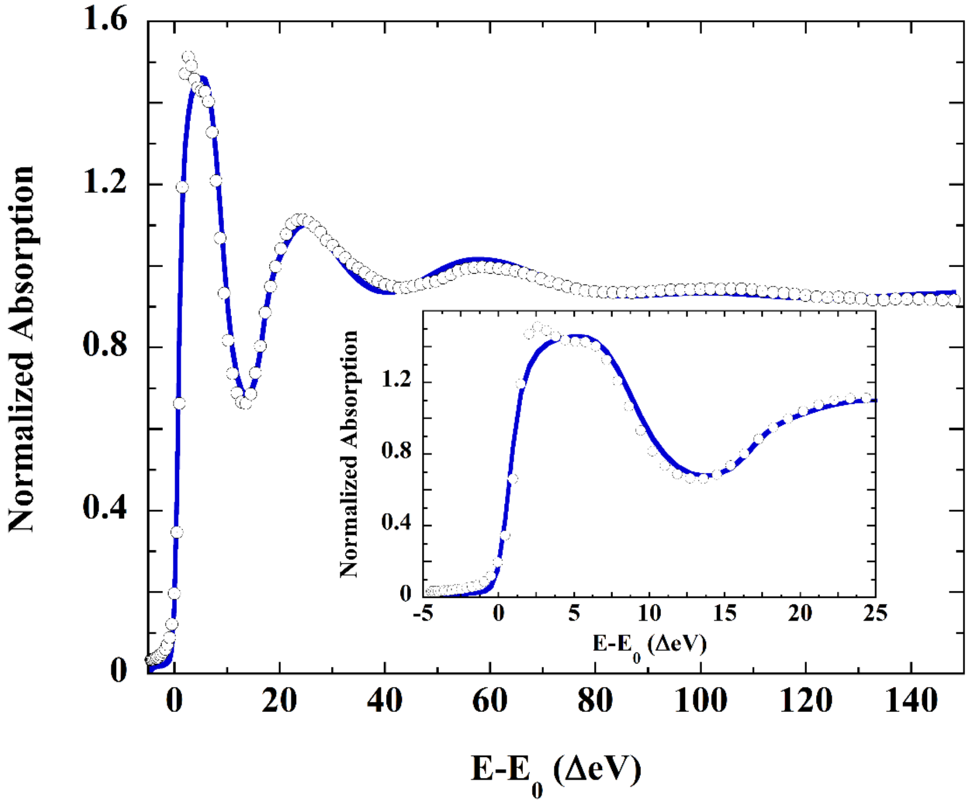
$$\left(\frac{C_{ij}^{(12)}}{r_{ij}^{12}} - \frac{C_{ij}^{(6)}}{r_{ij}^{6}} \right)$$



L_E – maximum at 3.11 Å

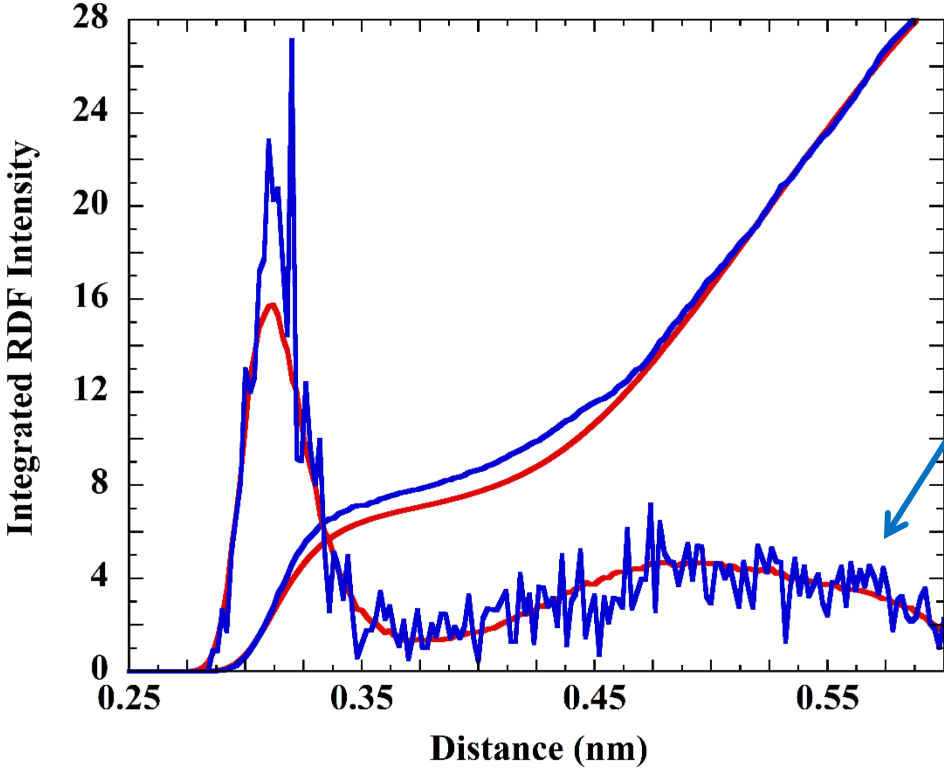


M. M. Reif, and P. H. Hünenberger,
J. Chem. Phys. **134** 144104 (2011).



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

Spectrum calculated from the set of $R_{th} < 10^{-7}$ - R_{sq} decreases to 7.1 - The R_{th} criterion selected 199 from the original 3190 frames.



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

We have done several other DMXAN analysis

- First and second shell of Ni in Water (2006)
- First solvation shell of Hg(II) in water (2007)
- Dynamic of the axial ligands of Cu in water (2016)
- New dynamic force field for myoglobin (2018)
- .....

Problems

Systems with "extra" peaks due to the presence of different electronic configurations

Some cuprates – the Cu K-edge – $3d^9 + 3d^{10}\underline{L}$

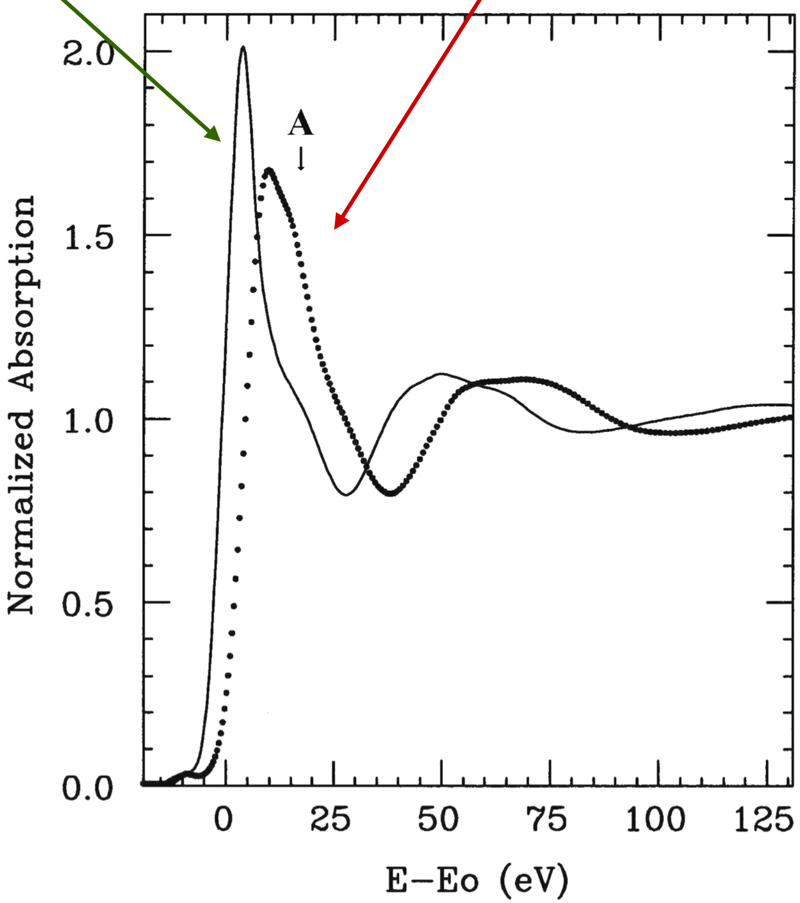
The K-edge of Fe^{2+} and Fe^{3+} in water solution

In principle we can treat these situations by MCMS theory

C.R. Natoli, M. Benfatto et al. Phys Rev B42, 1944 (1990)

Fe^{2+} in water

Fe^{3+} in water



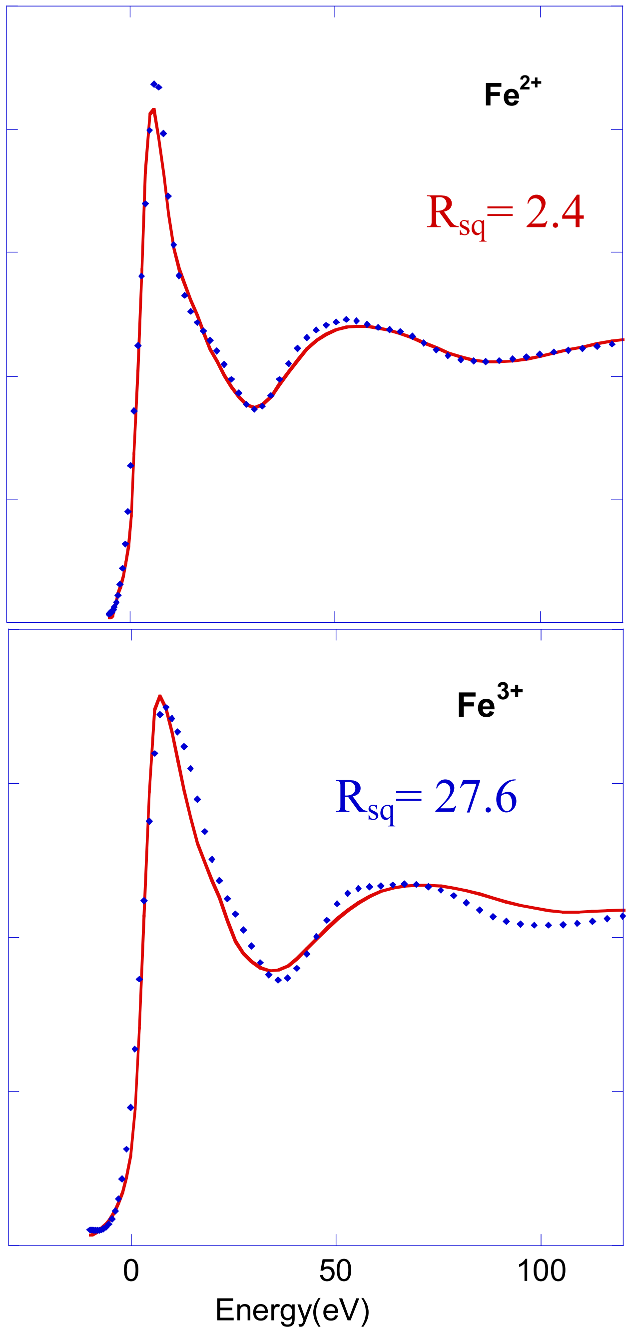
The extra feature A is explained by the presence a second electronic configuration generated by moving one electron from low- to high-t_{2g} level. SCF calculation gives an energy separation ΔE=5 eV

The different channels decouple at high energy and more in general in the sudden limit

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

$$k_0^2 = \hbar\omega - I_c \quad k_1^2 = \hbar\omega - I_c - \Delta E_1 \quad \ldots$$

The total cross section is the sum of independent spectra shifted in energy



MXAN fails to fit the Fe^{3+} spectrum

No way to get a fit

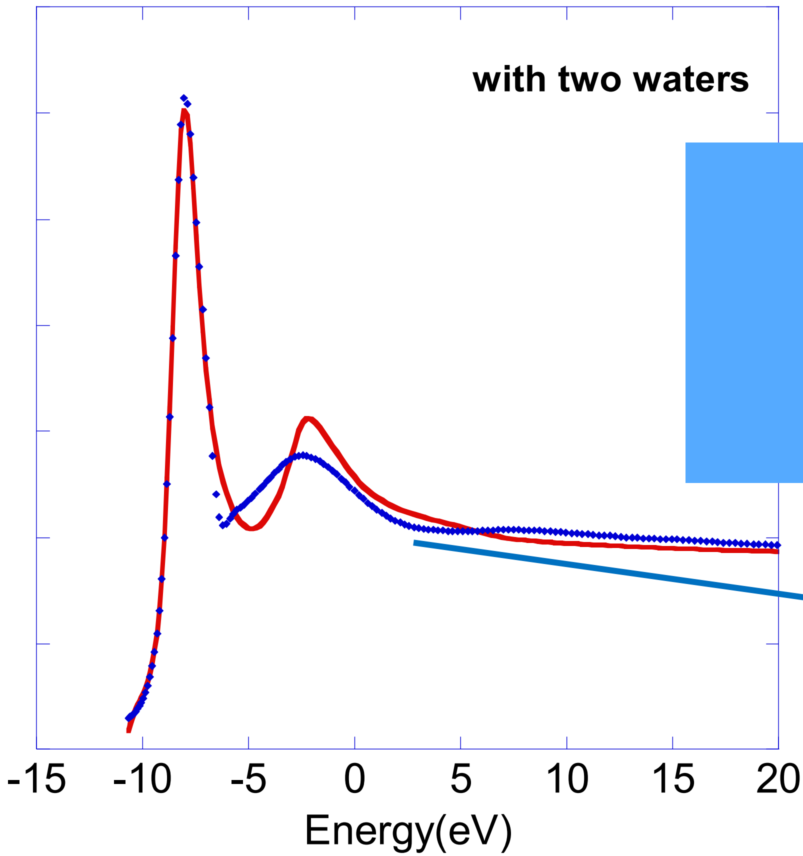
M. Benfatto et al. (2002) Chem. Phys. **282**, 441

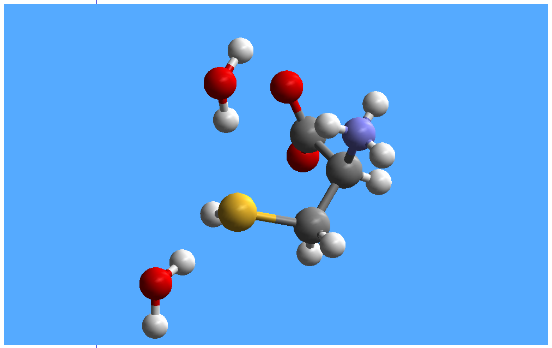
systems with strong resonance at the edge

L-edges, K-edges of light elements…..

The K-edge of sulphur of cysteine

EXAFS is very weak or even absent





Experimental data

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

some conclusions

It is possible to fit the XANES energy region starting from the edge to obtain quantitative structural information

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

Future: we would like to do a new version of MXAN to improve the speed, to have a better description of the EXC potential, go beyond the Muffin-tin approximation, to analyze the new type of data……..

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