XANES: MXAN and FPMS codes

Keisuke Hatada

CNRS-Université de Rennes1

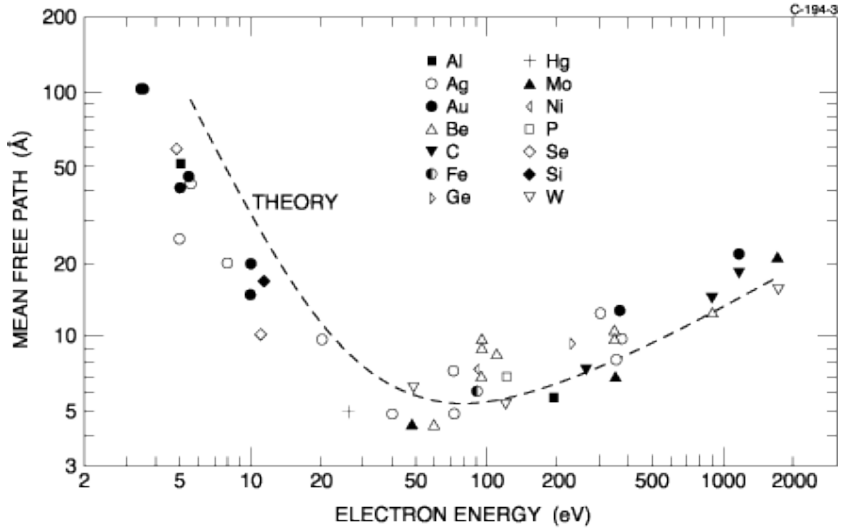
Programs related to Frascati school

- GNXAS (A. Di Cicco & A. Fillipponi, Univ. Camerino & l'Aquila)
  EXAFS
- MXAN (M. Benfatto & S. Della Longa, LNF-INFN & Univ. l'Aquila)
  XANES
- FPMS (My code)
  XANES
- MsSpec (D. Sébilleau, CNRS-Univ. Rennes1)
  X-ray photo electron emission (angle resolved)

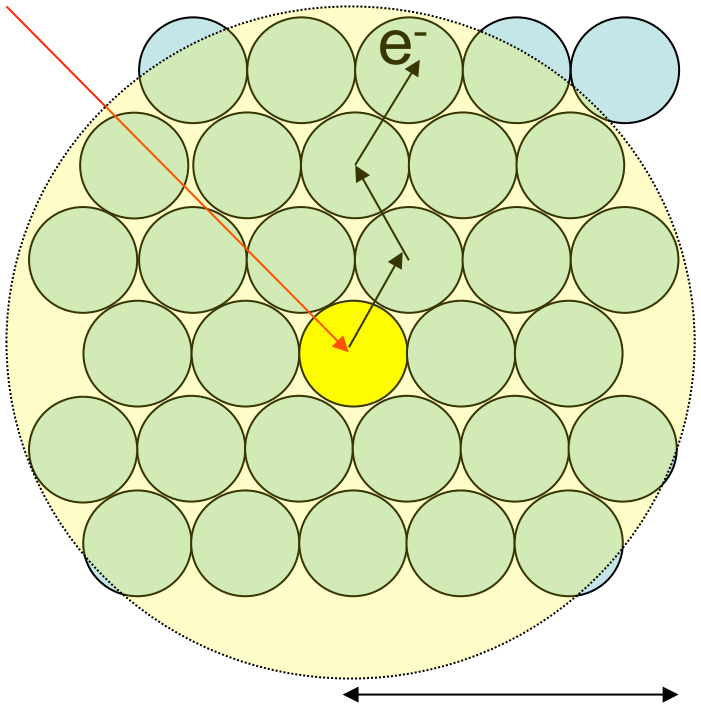
Introduction to core-electron spectroscopies

Absorption

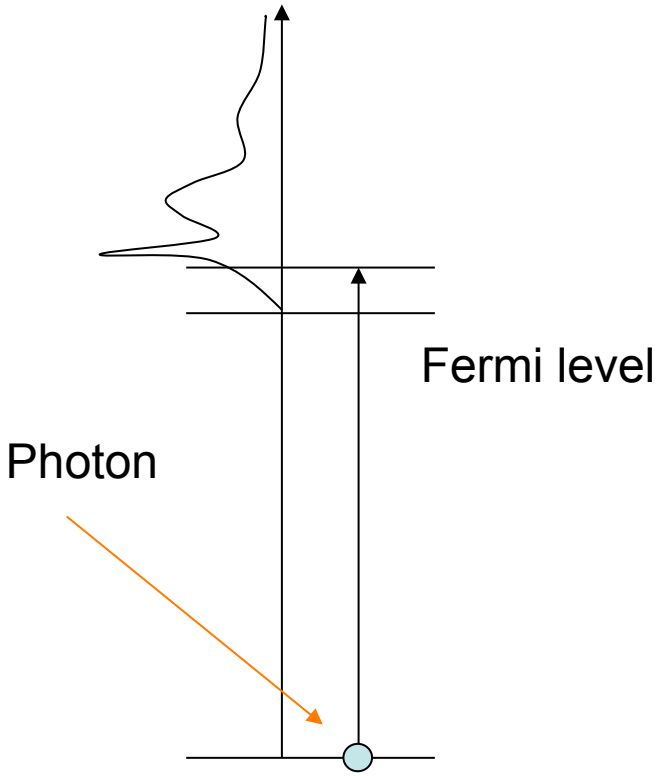
- Due to a finite lifetime of corehole and a mean free path of excited electron, it can travel only up to a few Å (depending on energy)



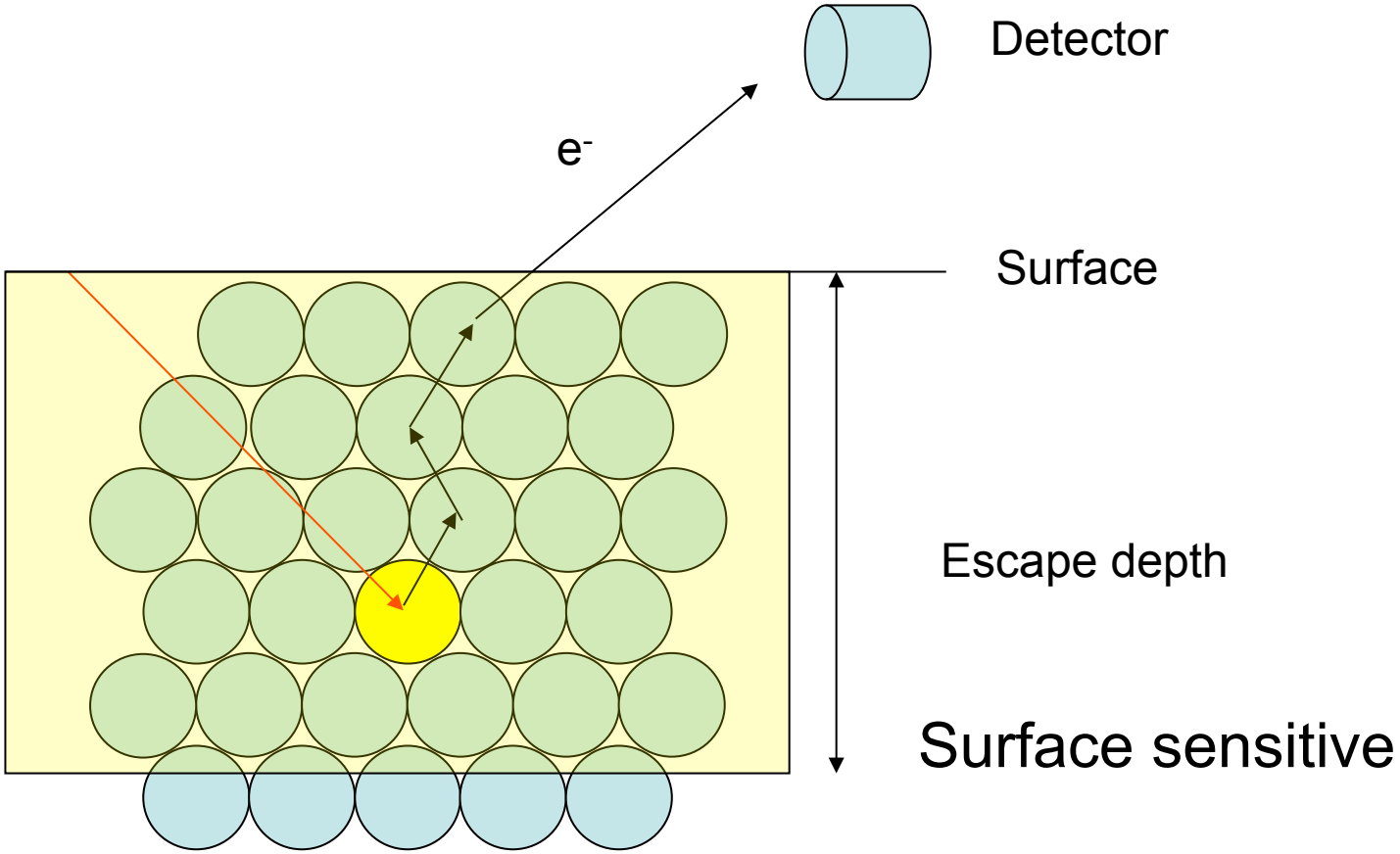
Photon



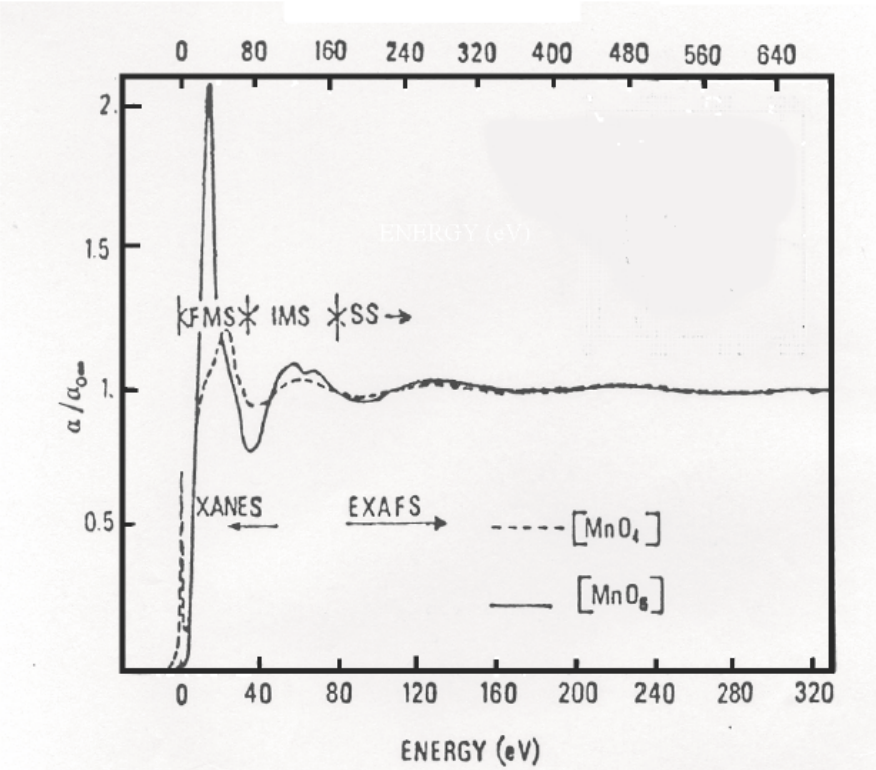
5~10 Å



Emission



Mn K-edge



The energy scale are in the ratio 0.47 to account for the different distance between Mn and O in MnO_6 and MnO_4

The amplitude has been corrected for the different number of neighbourings

The two spectra are the same beyond 150 eV → MS contributions

M. Benfatto et al. Phys. Rev B34, 5774 (1986)

	Structure	atomic species	Debye-Waller
EXAFS	1d distance	not so sensitive	sensitive
XANES	3d structure	sensitive	not much

For EXAFS, Multiple Scattering (MS) is just for improvement, while for XANES MS is unavoidable for scattering theory.

MXAN code: fitting structural and electronic properties by XANES spectra for molecule, protein and amorphous. (disordered system)

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

- XANES (X-ray Absorption Near Edge Structure) from edge to ~150 eV
- 3 dimensional information, sensitive to atomic species

Many applications have been done.

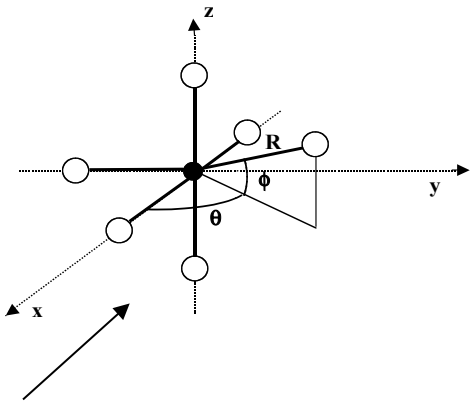
Main developers

Maurizio Benfatto[1]
Stefano Della Longa[2]
Calogero R. Natoli[1]
Kuniko Hayakawa[1]
Keisuke Hatada[3]

[1] INFN Laboratori Nazionali di Frascati
[2] Università L'Aquila
[3] CNRS-Université de Rennes1

To perform structural fits

- Initial geometrical configurations
- Exp. data



We generate hundred of theor.
spectra by moving atomic coordinates

The potential is calculated at each step

Minimization of error function by MINUIT

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

By comparison with exp. data we can fit relevant structural parameters

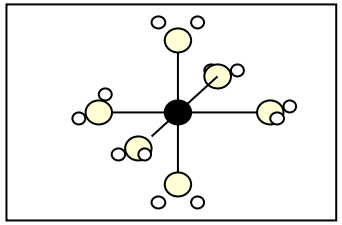
M. Benfatto and S. Della Longa (2001) J. Synch. Rad. 8, 1087
K. Hayakawa, K. Hatada, P. D'Angelo, S. Della Longa and M. Benfatto, AIP Conf. Proc. 882, 111 (2007)

- S. Della Longa et al. Biophy. Jour. 85, 549 (2003)
- P. Frank et al. Inorganic Chemistry 44, 1922 (2005)
- C Monesi et al. PRB 72, 174104 (2005)
- R. Sarangi et al. Inorganic Chemistry 44, 9652 (2005)
- P. D'Angelo et al. JACS 128, 1853 (2006)
- S. Marino et al. Biophy. Jour. 93, 2781 (2007)
- ....
- M. Bortolus et al. JACS 132, 18057 (2010)

Examples of MXAN analysis

Transition metals in water solution

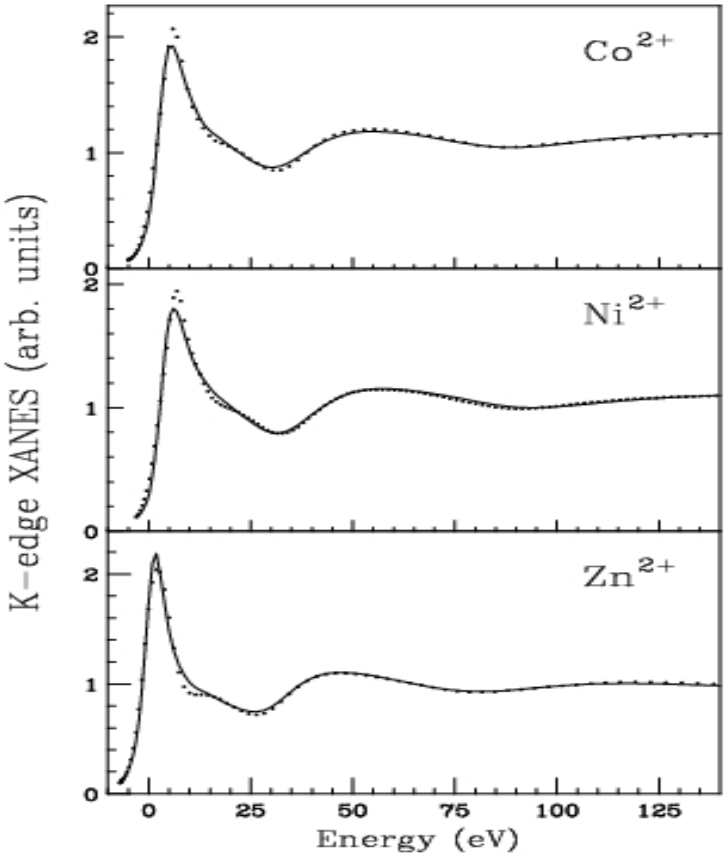
fits include Hydrogen atoms



MXAN

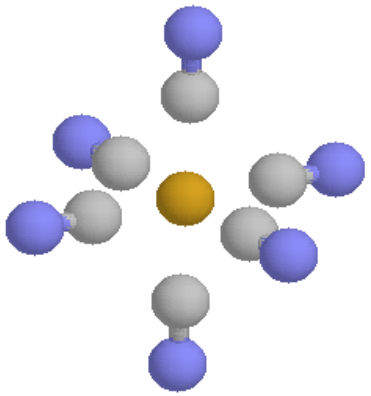
GNXAS

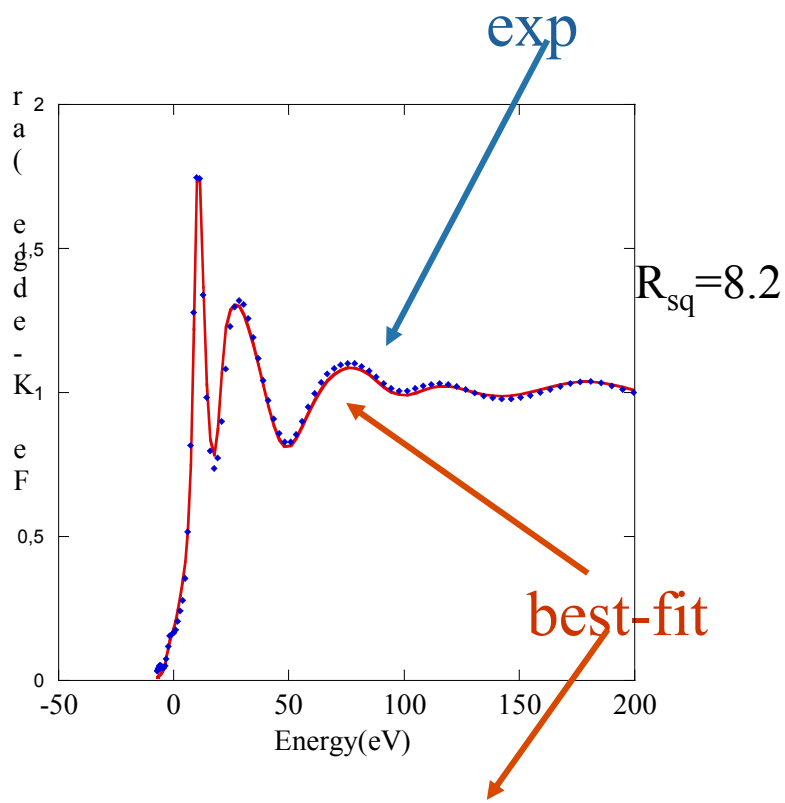
	R(Å)	R(Å)
Co^{2+}	2.06(0.03)	2.092(0.002)
Ni^{2+}	2.04(0.03)	2.072(0.002)
Zn^{2+}	2.06(0.02)	2.078(0.002)



P. D'Angelo et al. PRB (2002)

$Fe(CN)_6$ in water

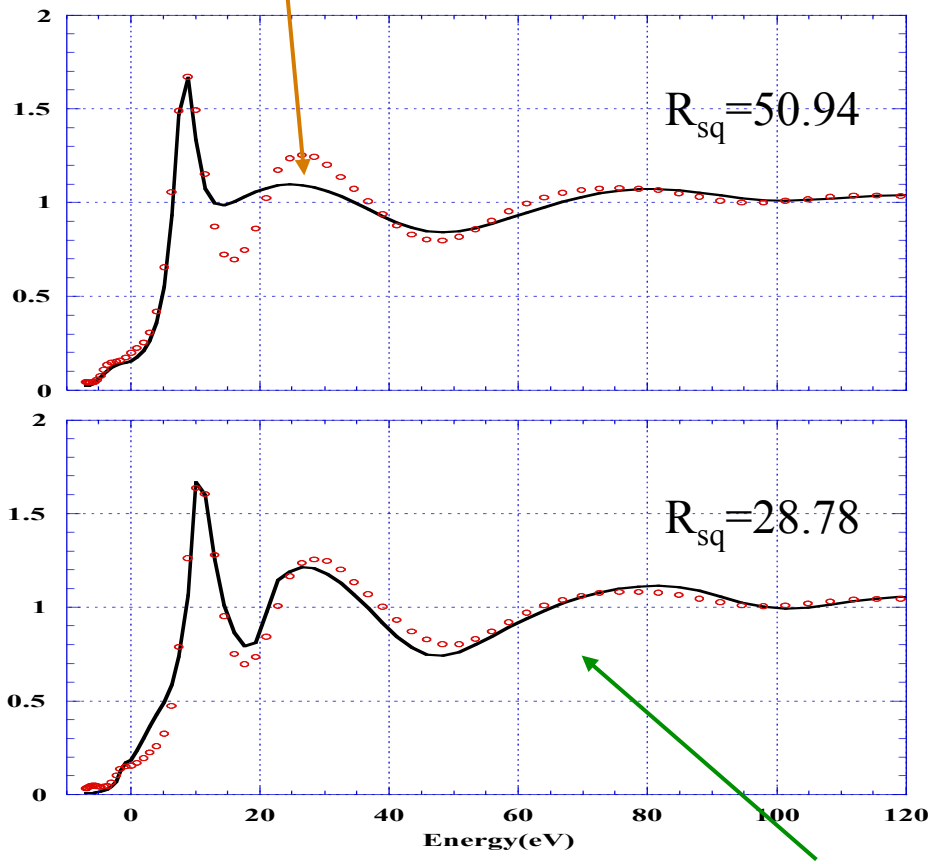




The best-fit condition corresponds to an octahedral symmetry with Fe-C distance of 1.92(0.01) Å and C-N distance of 1.21(0.01) Å

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

Fit with NO molecules
Fe-N =1.91Å and N-O =1.16Å

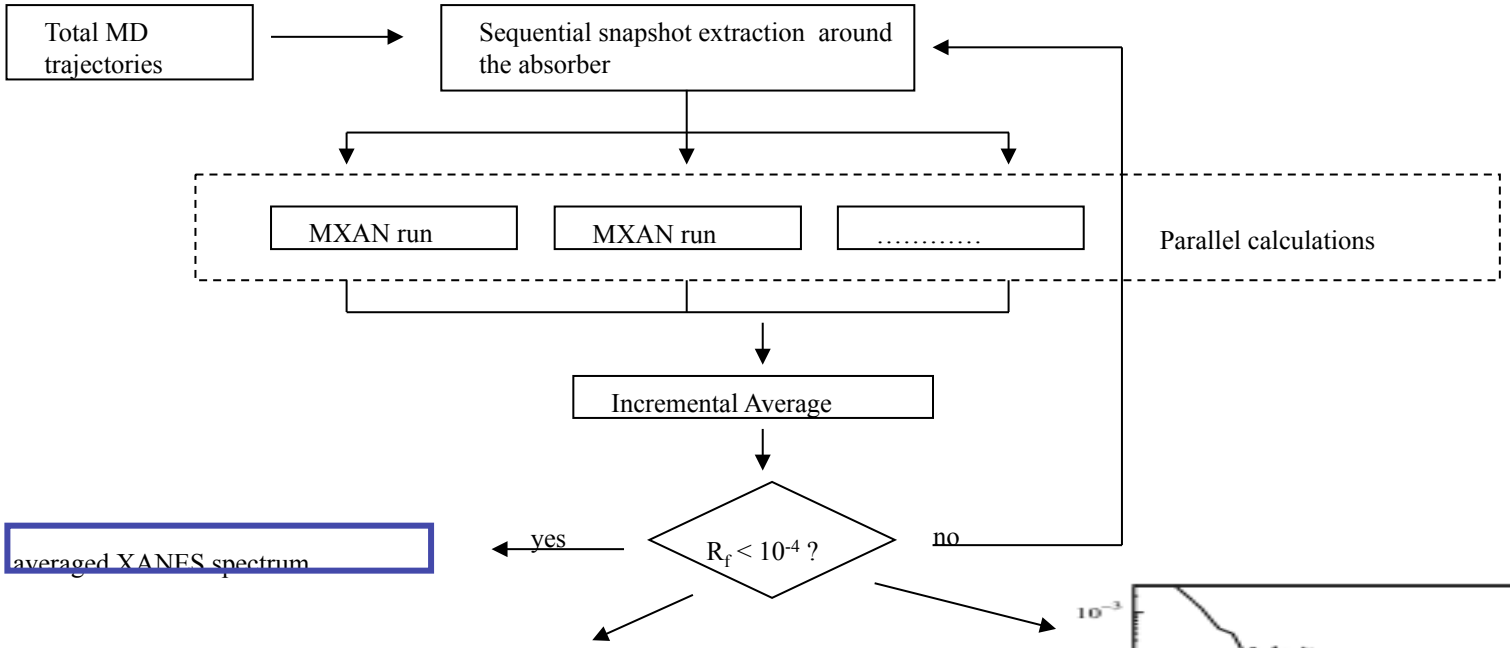


Fit with CO molecules
Fe-C =1.94Å and C-O =1.11Å

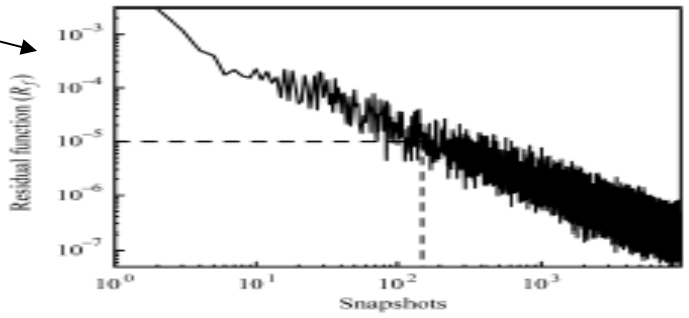
Chemical sensitivity

thermal and structural disorder

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

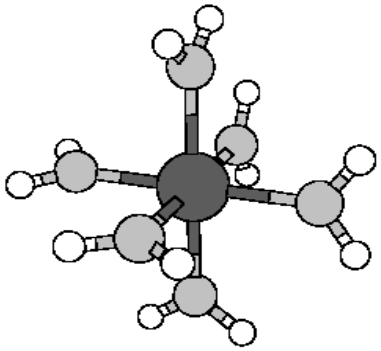


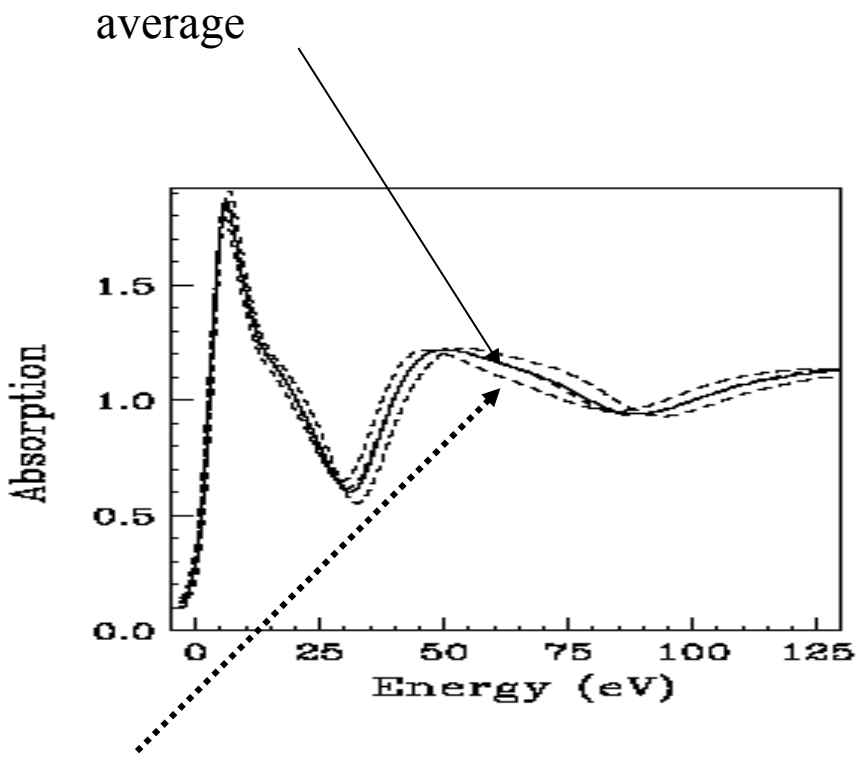
$$R_f(N) = \left[\sum_i [\sigma^N(E_i) - \sigma^{N-1}(E_i)]^2 \right]^{1/2}$$



Merkling et al. JACS 124 (2002)
Campbell et al. Jour.Synch.Rad. 6 (1999)

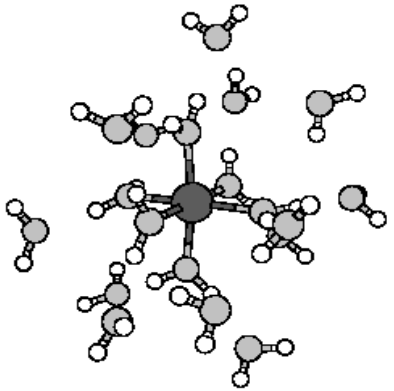
Ni^{2+} in water – Ni Kedge

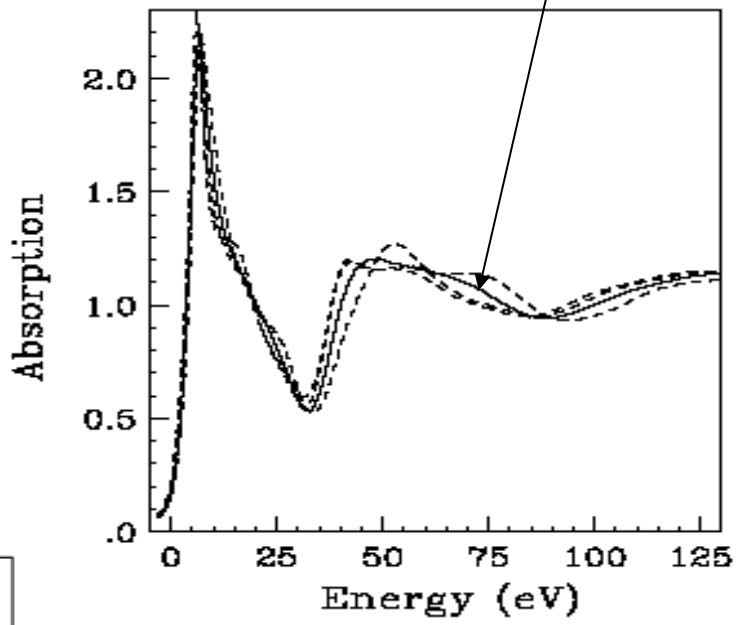


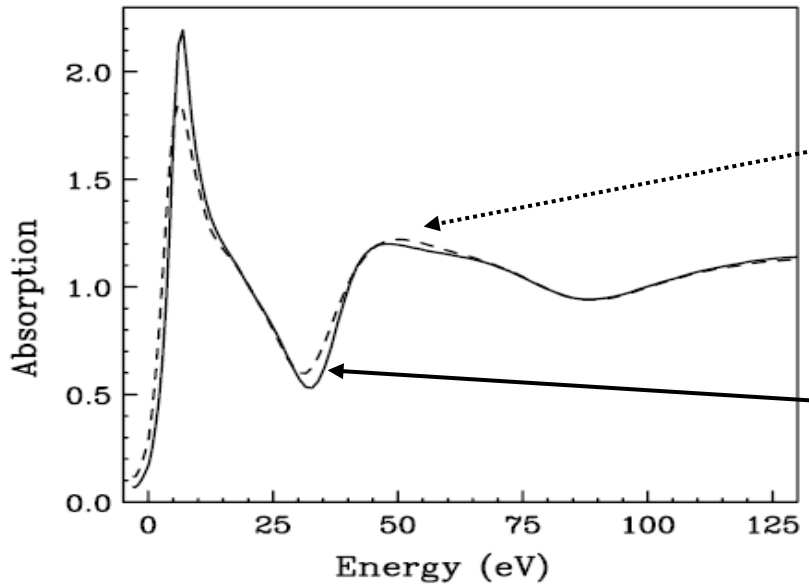


Calculations for some particular snapshots

including the second shell

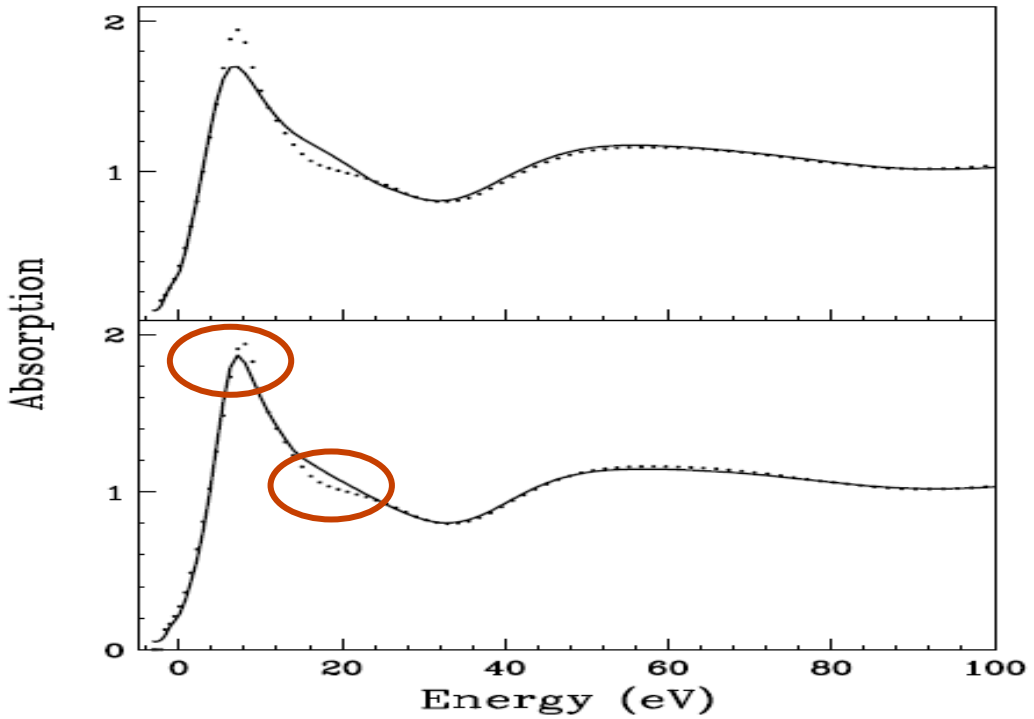






first shell average

first + second shells average



one shell fit

two shells fit

sizeable effects in the energy range 0 - 30 eV

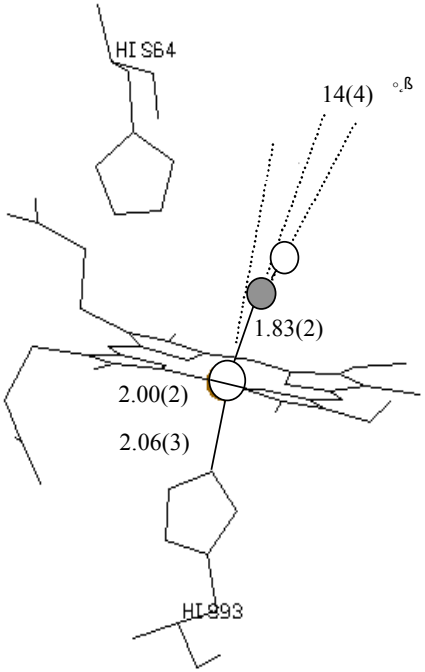
P. D'Angelo et al. JACS 128 (2006)

Sperm whale myoglobin single crystal

Low temperature
photolysis of myoglobin

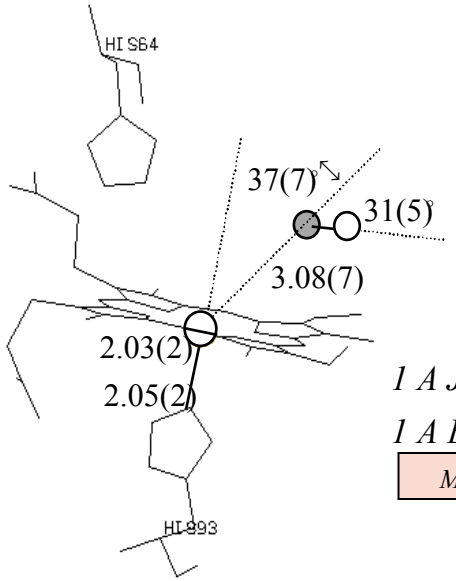
Fe K-edge XANES

$$MbCO \xrightarrow[T < 40K]{hn} Mb^{*}CO$$



MbCO

	Fe - Np	Fe - Nhis	Fe - C	a	b	C - O
1MBC 1.5Å	1.97	2.19	1.92	3	38	1.17
1BZR 1.1Å	1.98	2.06	1.73	4	7	1.12
1A6G 1.1Å	1.98	2.06	1.82	9	9	1.09
MXAN fit	2.00(2)	2.06(3)	1.83(2)	--	14(4)	1.07



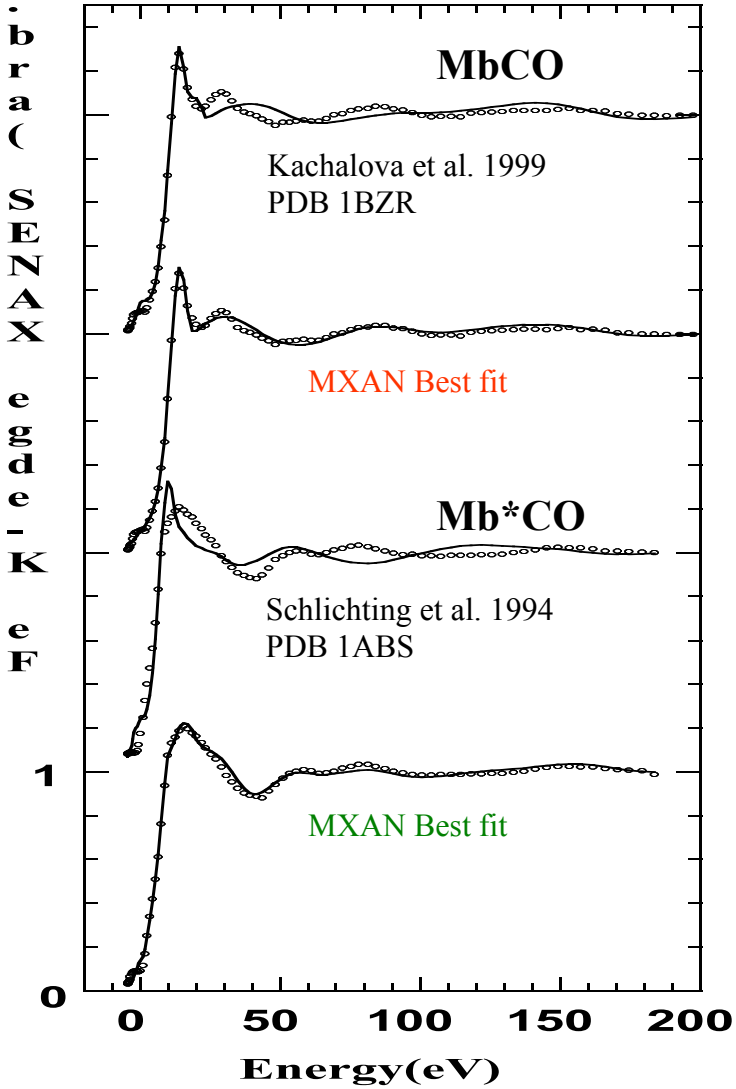
Mb*CO

	Fe - Np	Fe - Nhis	Fe - C	a	b	C - O
1AJH 1.7Å	2.00	2.11	2.84	23	45	1.21
1ABS 1.5Å	1.97	2.25	3.60*	27*	54	1.12
MXAN fit	2.03(2)	2.05(2)	3.08(7)	37(7)	31(5)	1.24

S. Della Longa et al. PRL (2001)

High XANES sensitivity to the CO position

Fe K-edge XANES



Analyzing the difference spectrum

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

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

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

Fields of application:

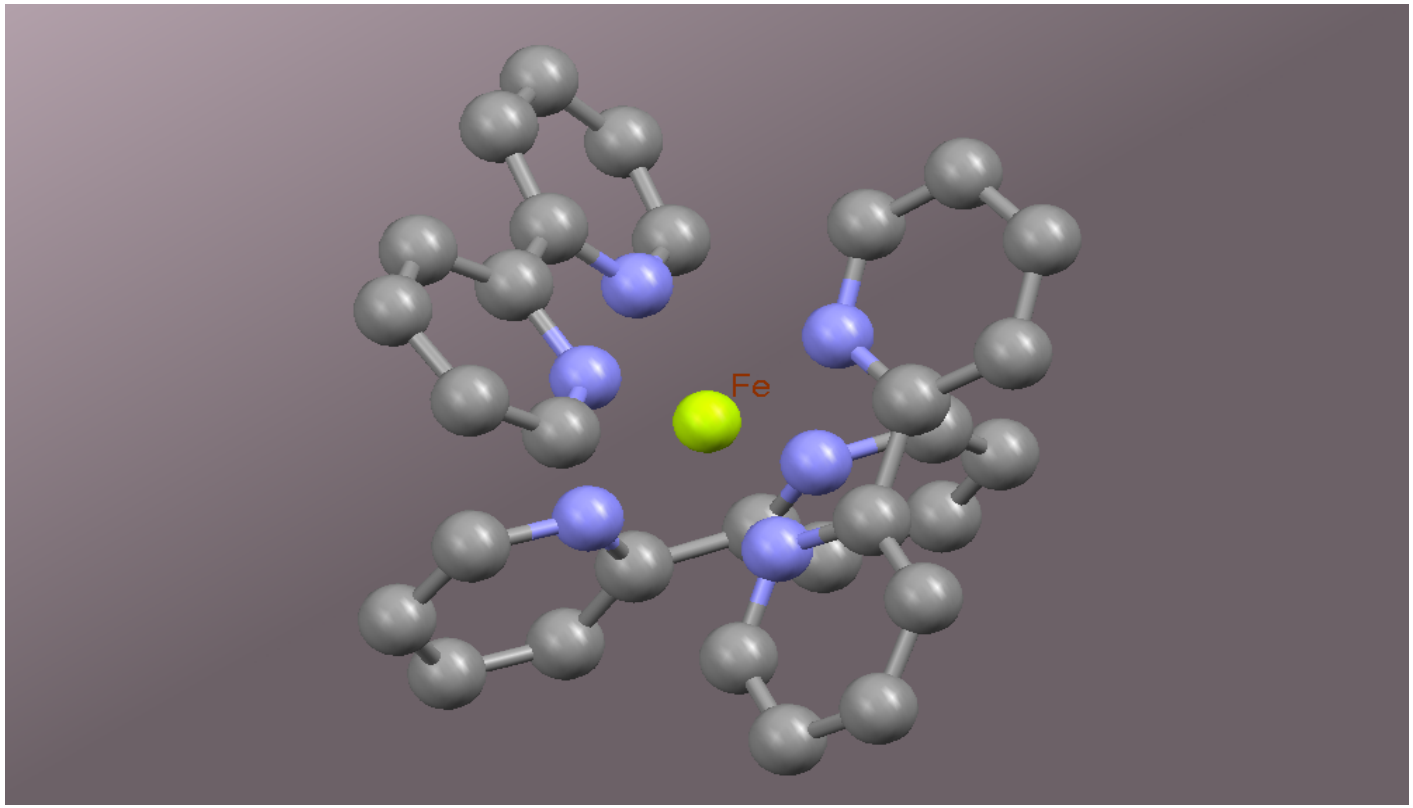
time resolved experiment

changes of chemical-physical and/or thermo-dynamical conditions

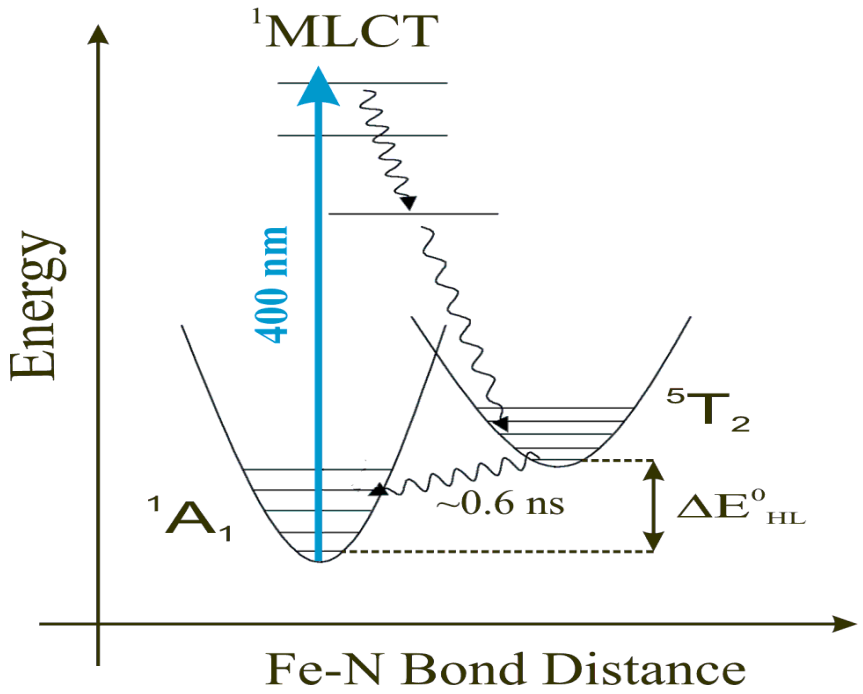
……

J. Phys. Chem. B (2006)

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



see the structural changes going from LS to HS state

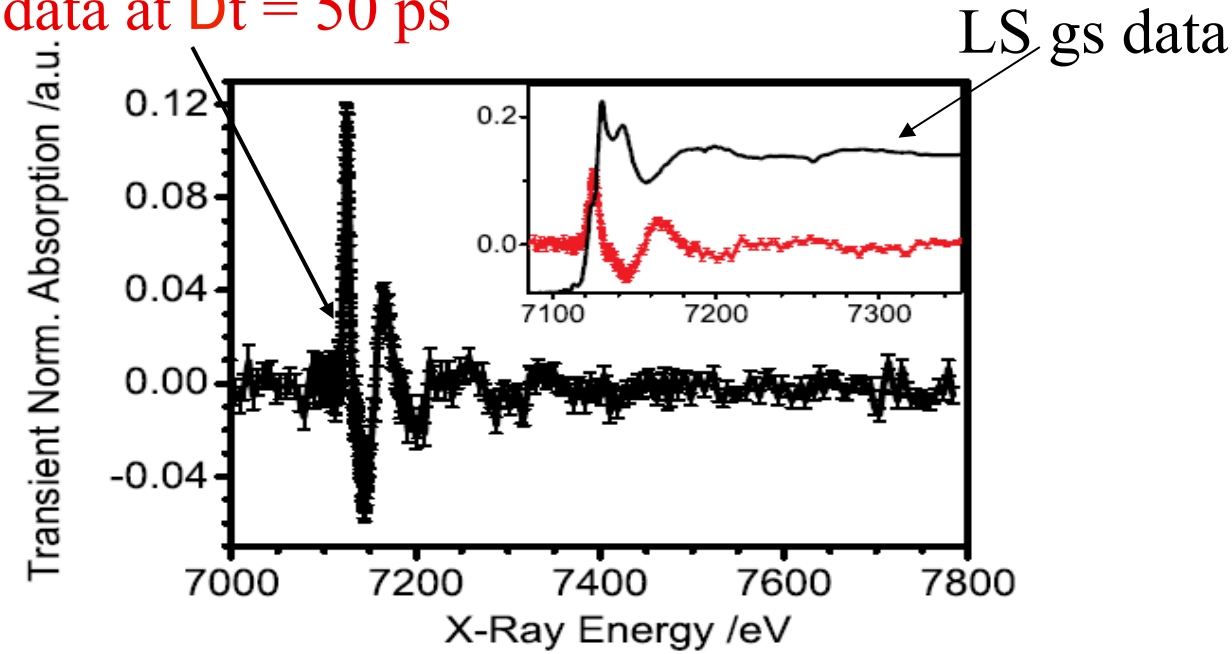


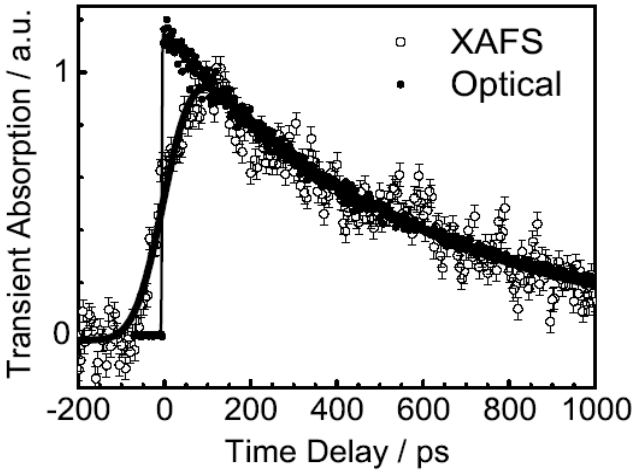
experiment done at the micro-XAS line of SLS by Chergui's group - pump-probe experiment in aqueous solution and room temperature

The detected signal is directly the quantity DA(E,Dt)

experimental data

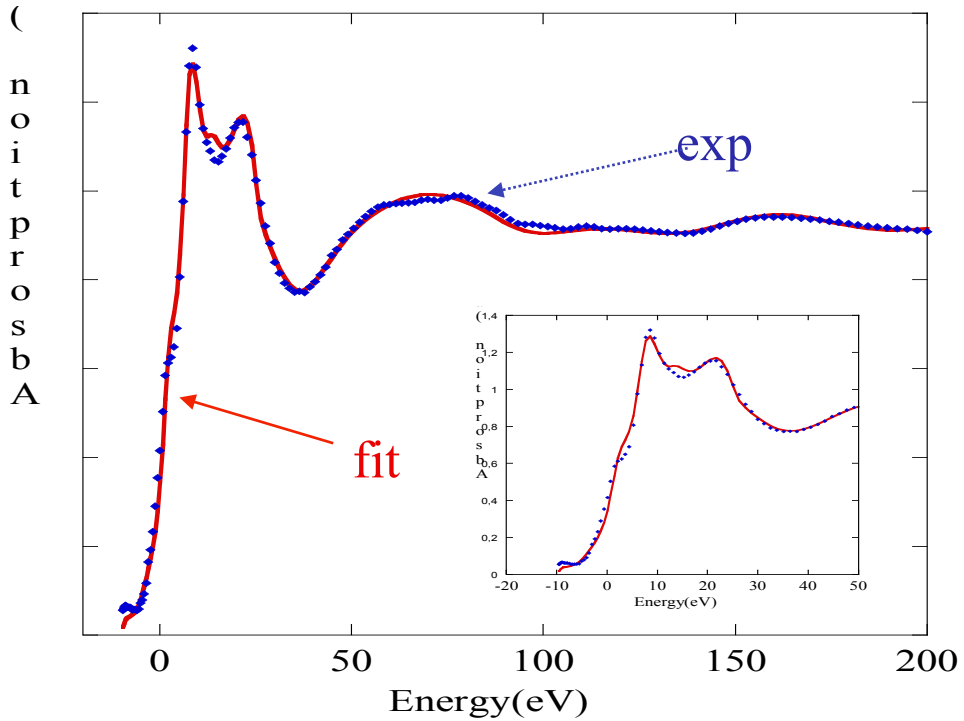
HS exs transient data at Dt = 50 ps





Kinetics of transient XAS and optical signals

LS ground state fit

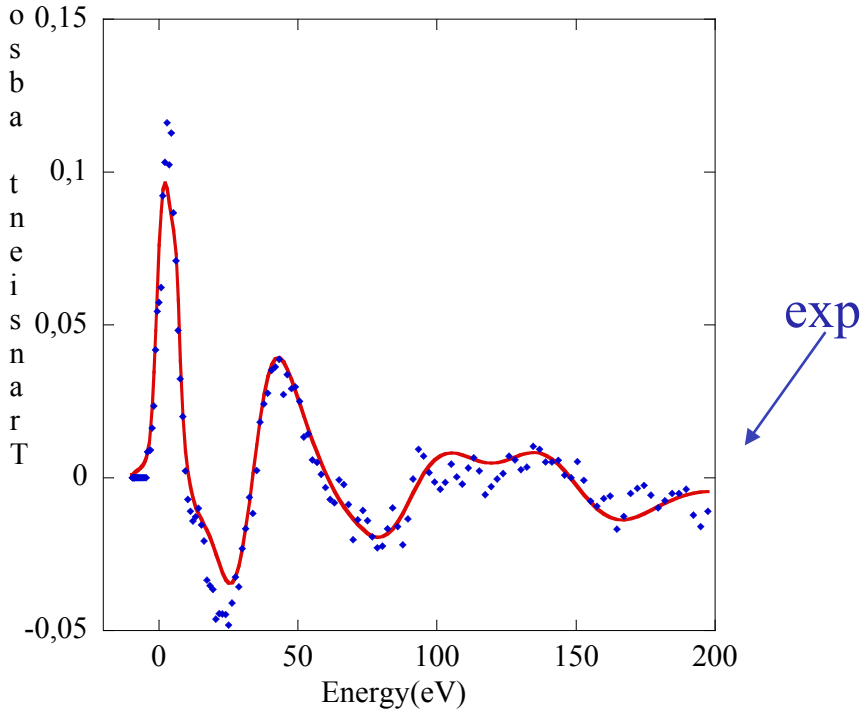


$R_{Fe\text{-}N} = 2.00 \pm 0.02$ Å

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

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

HS excited state fit by transient data



supposing a chemical shift DE = -2.5 ± 0.5 eV

$DR_{Fe\text{-}N} = 0.20 \pm 0.05$ Å

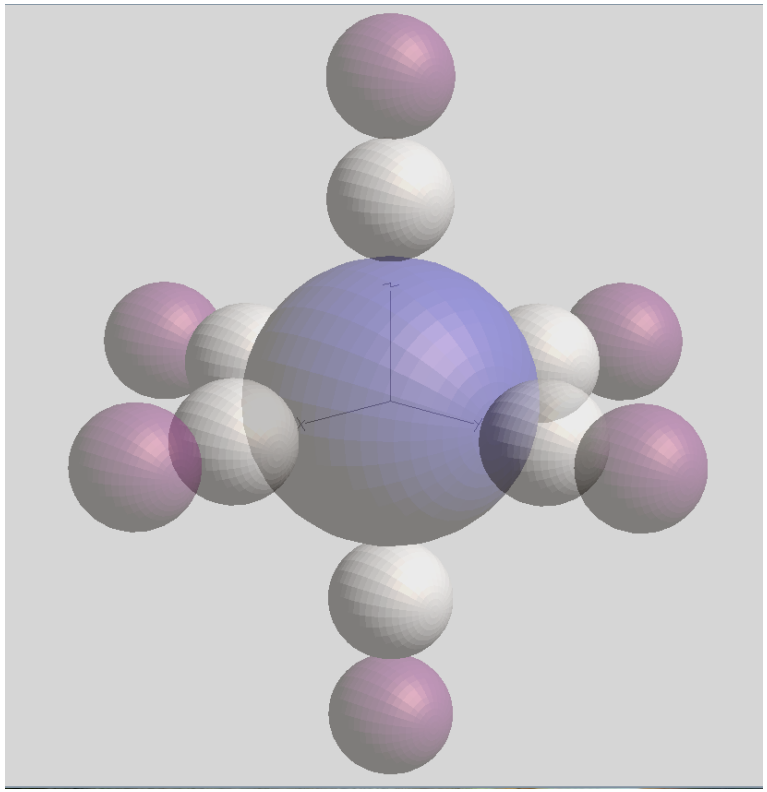
DFT calculations indicate ~ 0.2 Å

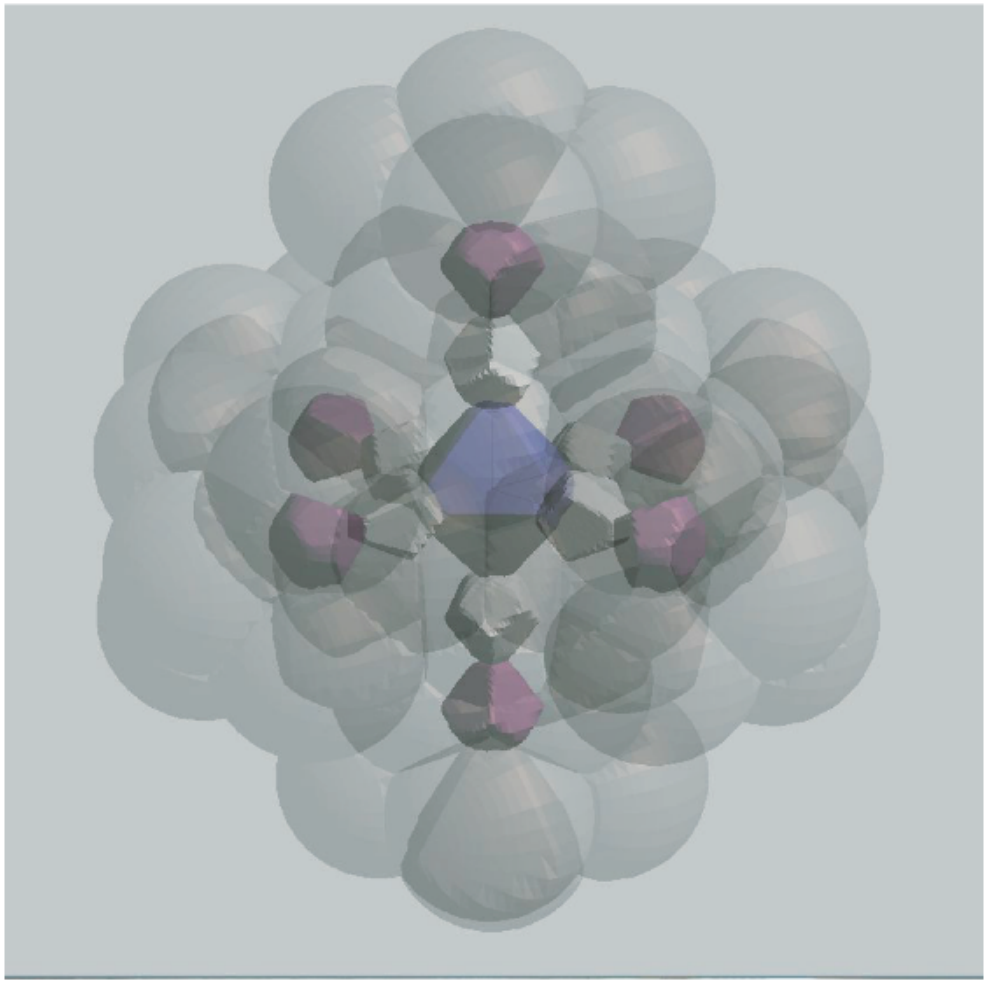
W. Gawelda et al. PRL (2007) 98, 057401

FPMS (Full Potential Multiple Scattering)

3d images of MT & NMT

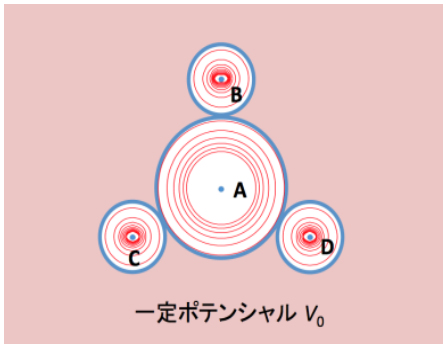
$Fe(CN)_6$



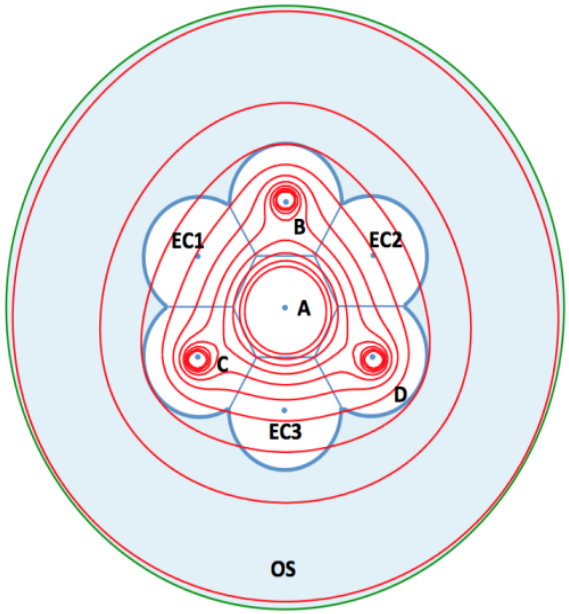


Separation by cells

(a) Spherical approximation
(Muffin-tin approximation)

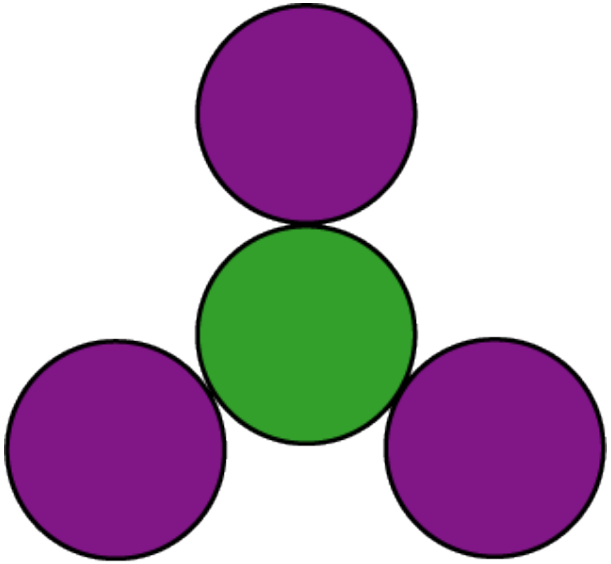


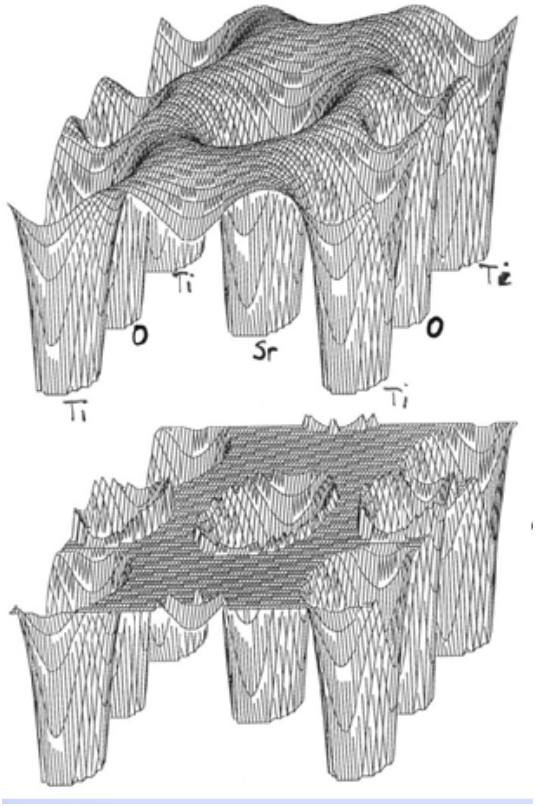
(b) non-spherical full potential



X線吸収分光法-XAFSとその応用 第2版
Ohta, Yokoyama, Asakura

Approximation of potential: Muffin-tin (MT) approximation





Spherical shaped

Spherical averaged

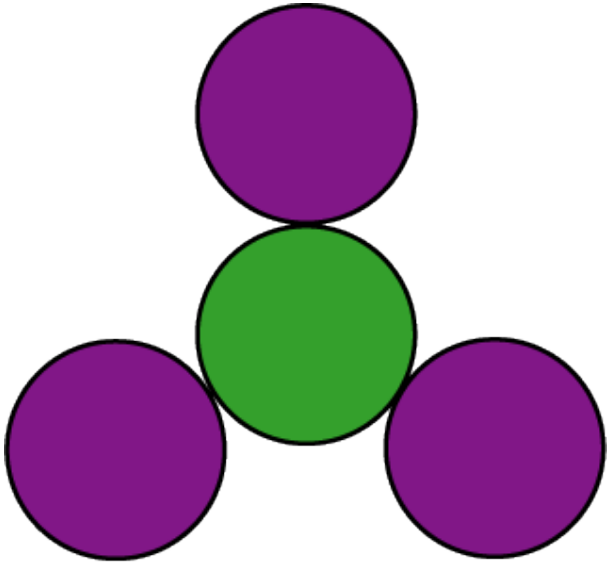
Constant in interstitial region

This approximation works well for :

Closed packed system

Higher energy region ~20 eV

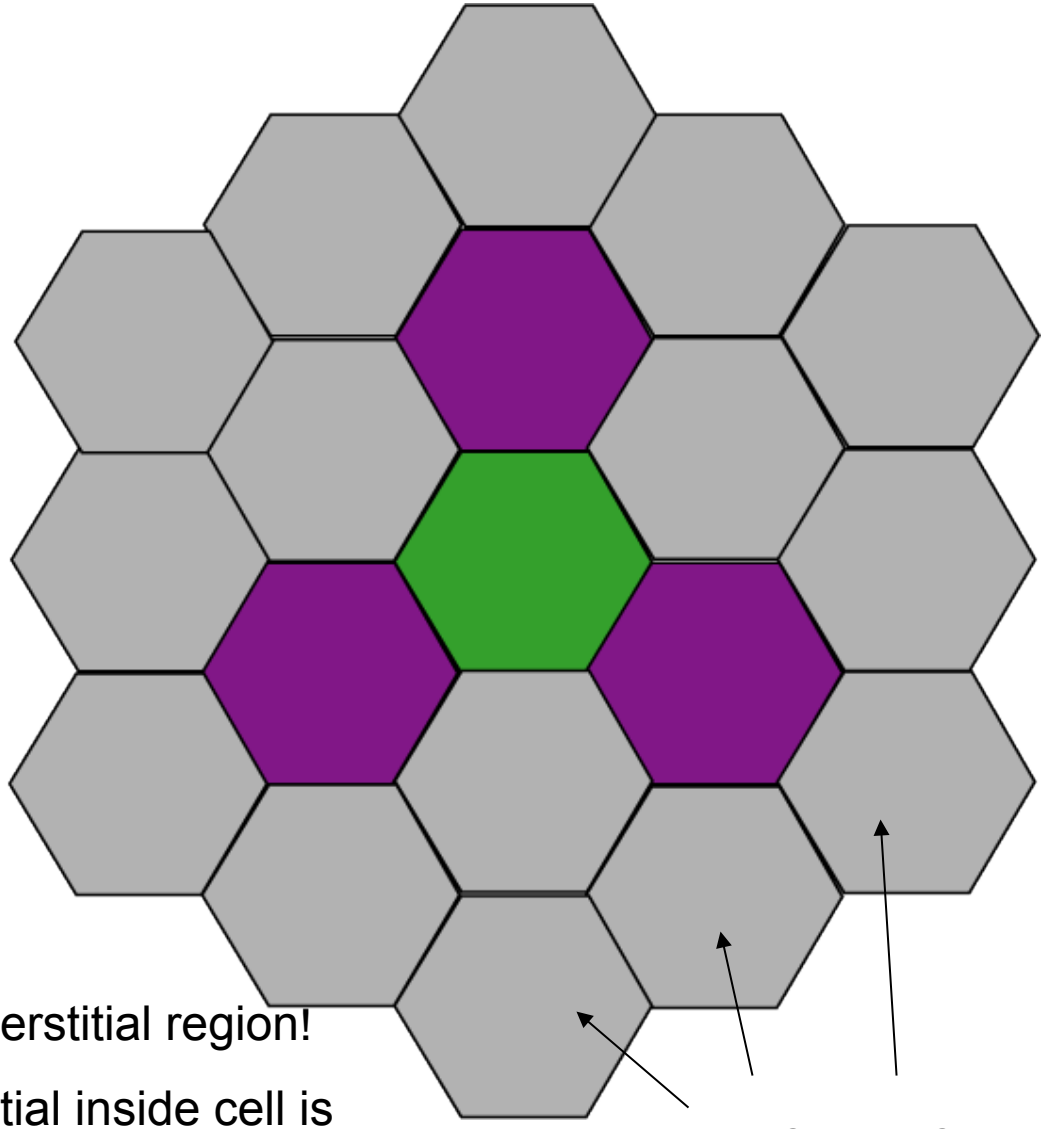
MT approximation (MXAN)



Use spherical shaped and averaged potential

outside the cells potential is flat

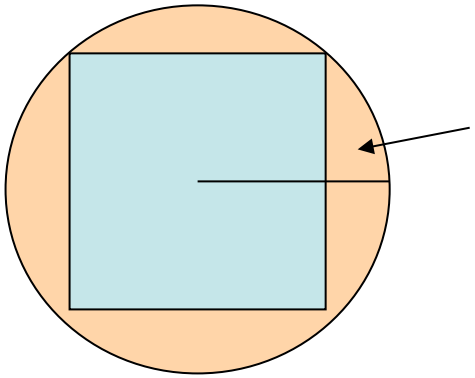
Non-MT (FPMS)



No interstitial region!

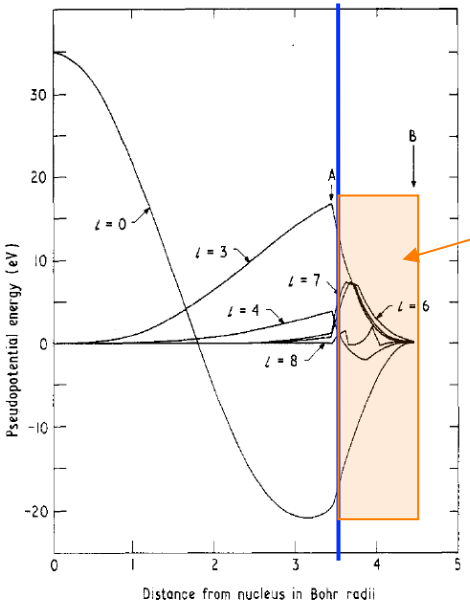
Potential inside cell is anisotropic

FPMS



So called moon region.
In this region
expansion by
spherical harmonics
never converges.

$$V(\mathbf{r}) = \sum_{L} V_L(r) Y_L(\hat{\mathbf{r}}) \quad (L=(l,m))$$



For discontinued function
spherical harmonics
expansion
never converges in
practice.

(Gibbs phenomenon)

Radial component oscillates!

Figure 8. Spherical harmonic components of the pseudopotential of Cohen and Bergstresser.
A, muffin tin radius; B, radius of circumscribed sphere.

=> We expand the wave function.

$$\Phi(\mathbf{r}) = \sum_L R_L(r) Y_L(\hat{\mathbf{r}}) \qquad (L=(l,m))$$

Since the wave function and its first derivative are continuous, the series converges uniformly even with truncated potential.

Kellog, *potential theory* (1967)

$$L^2\Phi(\mathbf{r}) = \sum_L l(l+1) R_L(r) Y_L(\hat{\mathbf{r}})$$

We treat it as inhomogeneus term in Schrödinger equation.

To solve the equation efficiently, we developed modified Numerov method.

K. Hatada et al, PRB (2007)

Applications of FPMS

PHYSICAL REVIEW A VOLUME 22, NUMBER 3 SEPTEMBER 1980

First-principles calculation of x-ray absorption-edge structure in molecular clusters

C. R. Natoli,* D. K. Misemer, and S. Doniach
Department of Applied Physics and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305

F. W. Kutzler
Department of Chemistry, Stanford University, Stanford, California 94305
(Received 30 July 1979)

We report initial results of a systematic study of the calculation of near-edge features in the x-ray absorption spectra of an atom in a molecular cluster as a function of different chemical environments and of varying prescriptions for the effective molecular potential of the excited electron. For a test-case comparison of the K edges of $GeCl_4$ and GeH_4, we find that the chemically induced changes in the molecular potential lead to large changes in the occurrence and strengths of bound-state and shape-resonance spectral features, in semiquantitative agreement with observation.

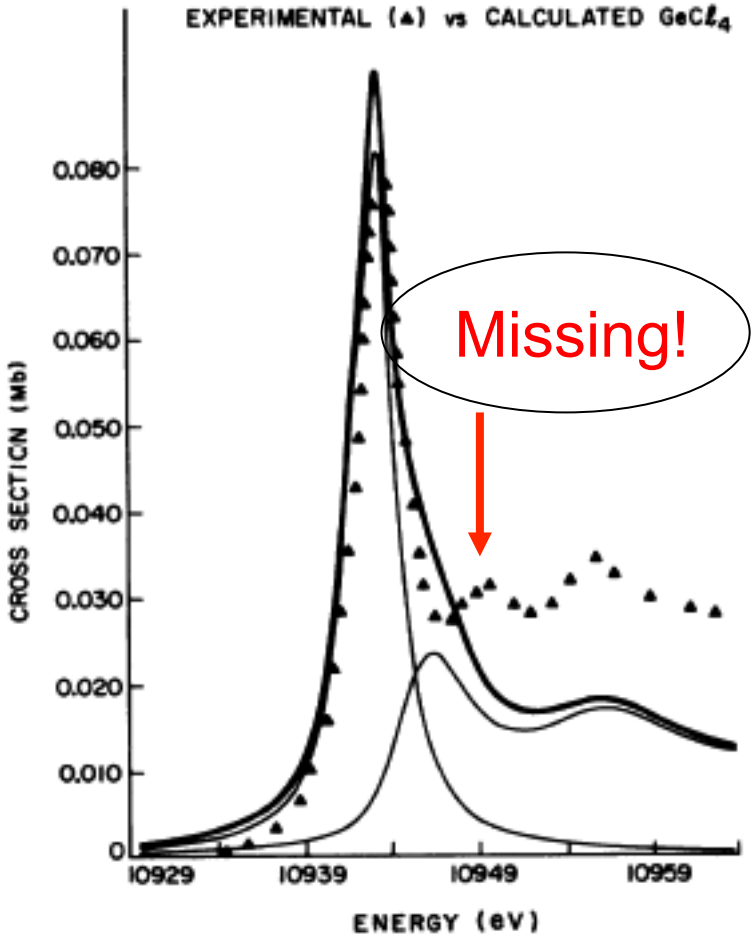
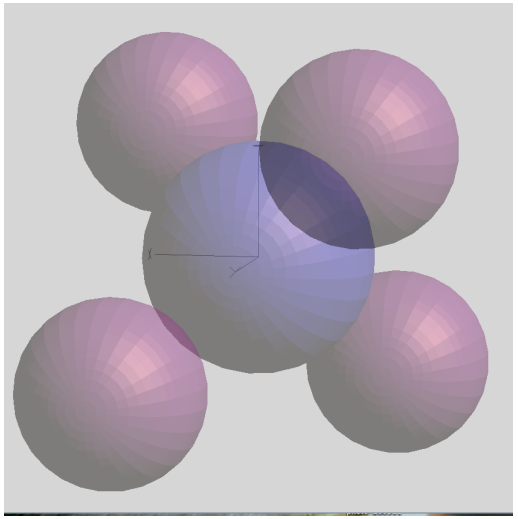
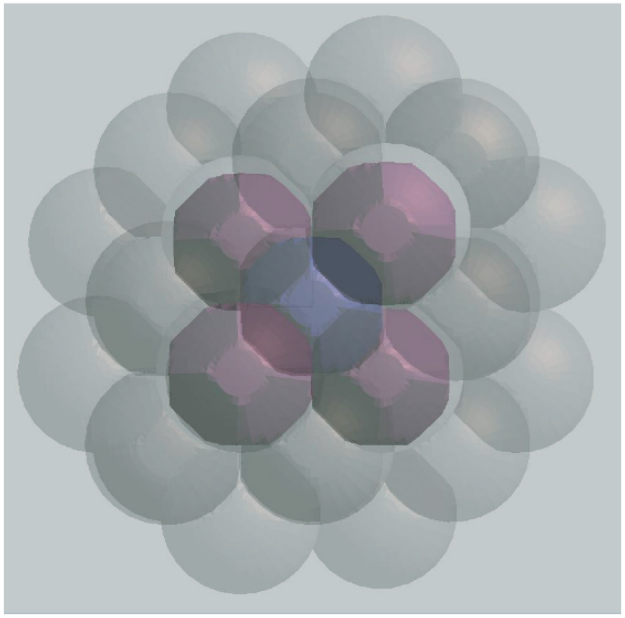


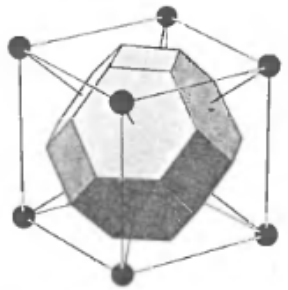
FIG. 1. Computed K-absorption spectra for Ge in GeH_4 (upper panel) and $GeCl_4$ (lower panel) after convolution with a Lorentzian to represent lifetime and experimental resolution effects. The light curves represent the bound-state and continuum contributions separately, while the heavy curves give the sum of the two. The energy placement of the experimental points has been adjusted for a reasonable fit (see text). Note that inelastic effects will generally be expected to increase the total cross section over the results given by the present calculation.

As far as energy dependence goes, the overall vertical scale of the experimental points shown in Fig. 1 for $GeCl_4$ has been adjusted by eye to give an overall "best fit." It may be noted that although the number and magnitude of the calculated spectral features are in qualitative agreement with experiment, the separation of the first and second continuum resonances is of order 10.0 eV compared to 6 eV seen experimentally. We ascribe this discrepancy to the inaccurate treatment of the interstitial potential by the use of the muffin-tin approximation.

Check Natoli's prediction of 30 years ago.







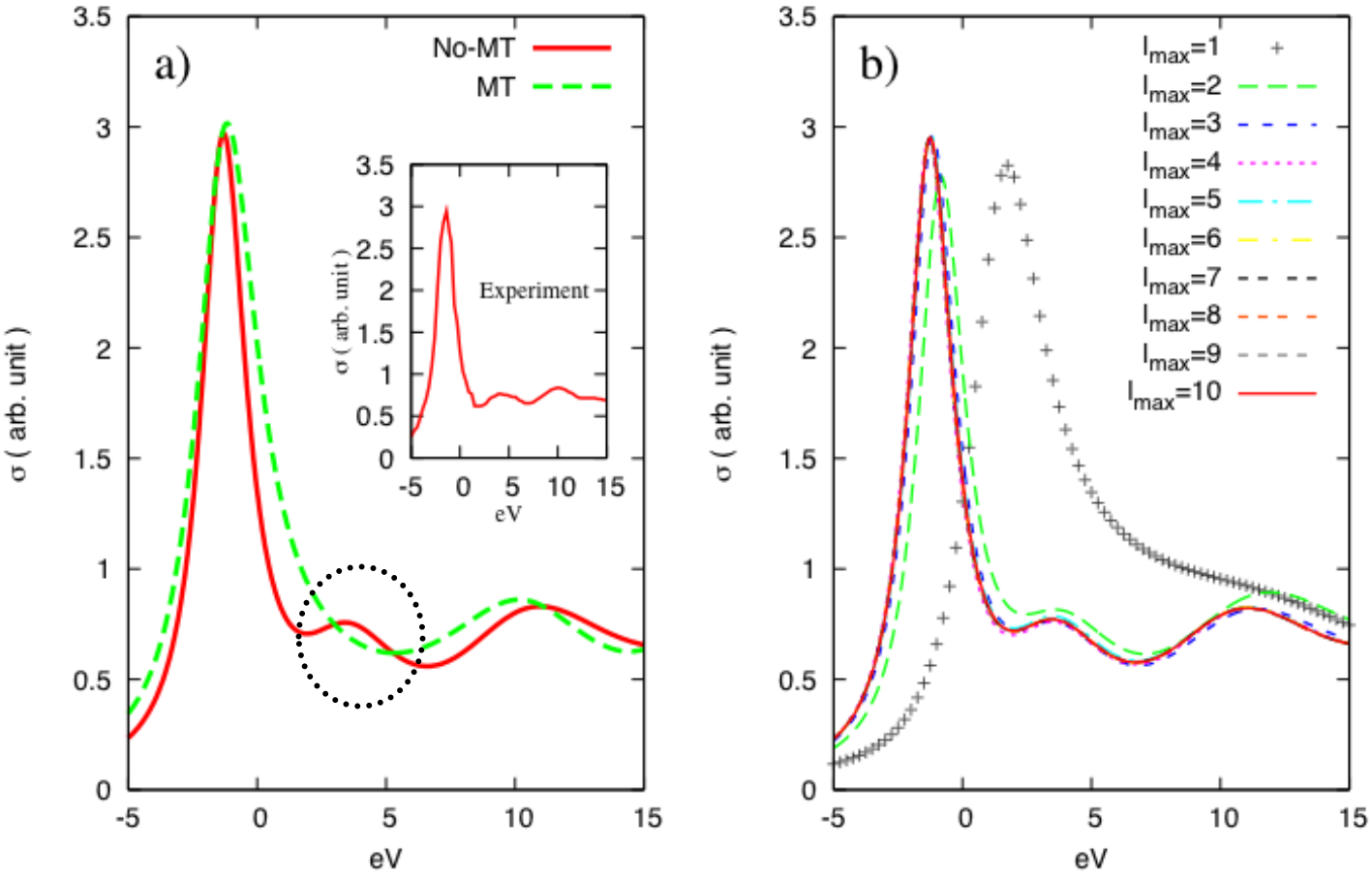
Muffin-Tin approximation

Potentials are Takoyaki like

Non-Muffin-tin

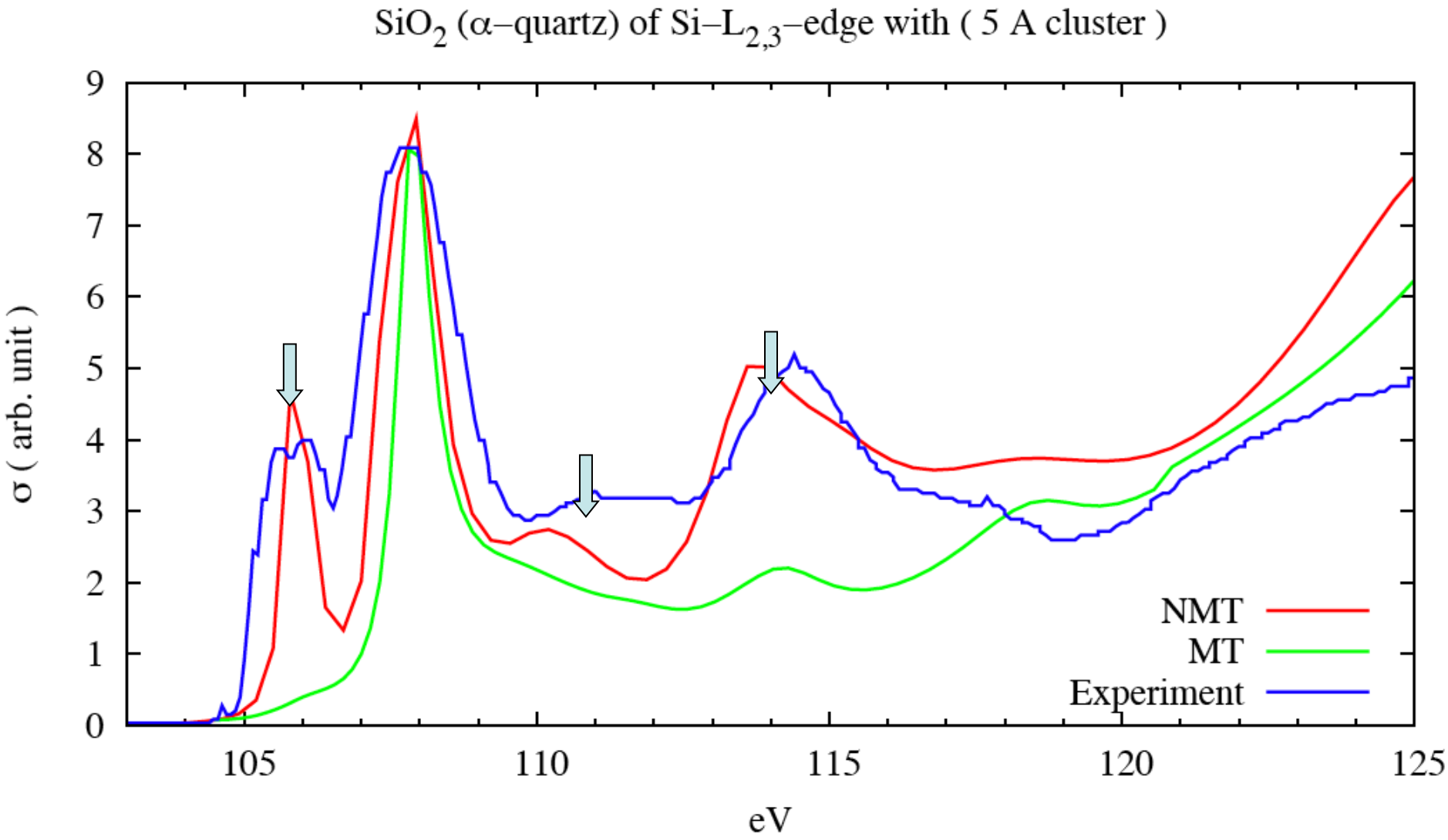
Voronoi shape

Ge K-edge of $GeCl_4$



Hatda. et. al. PRB-Rapid (2007)

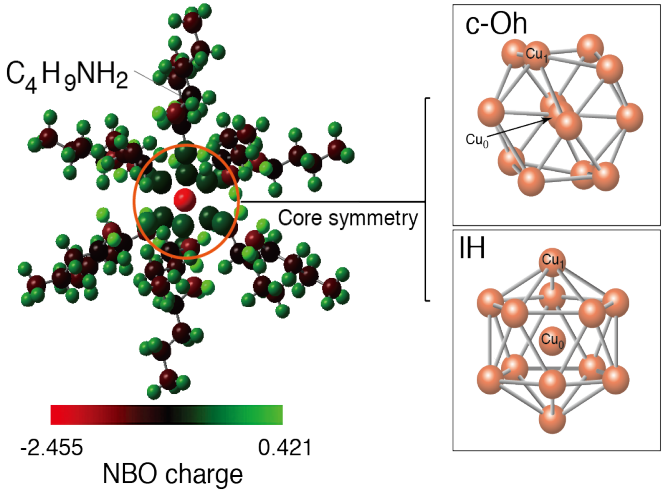
ELNES (NMT vs MT)



K. Hatada et. al, J. Phys. Cond. Matt. (2009)

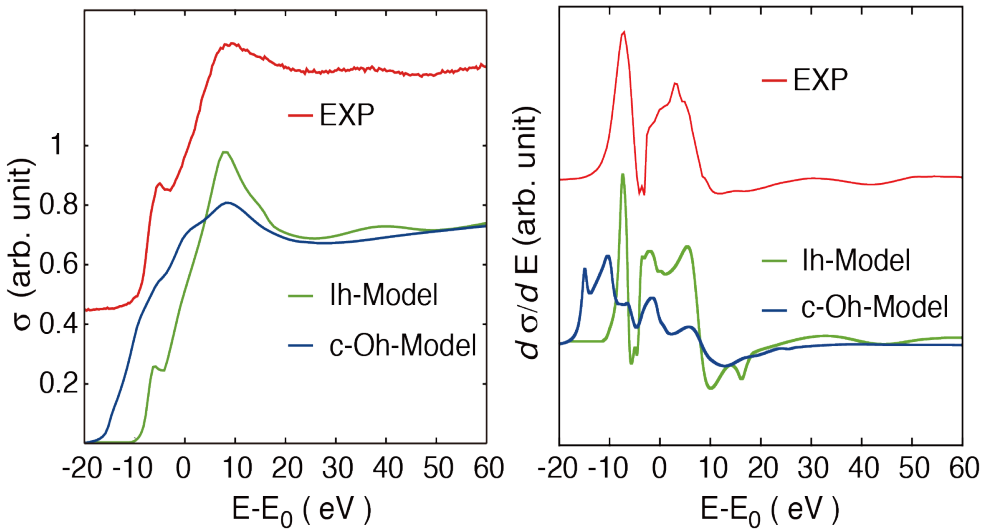
Cu Nano Cluster

(a)



icosahedron (*Ih*)
cubo-octahedron (*c-Oh*)

(b)



Oyanaghi, Orimoto et. al.

Interface of use of VASP charge density

- Calogero R. Natoli

LNF-INFN (Italy)

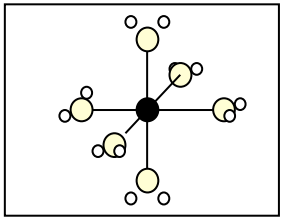
- Peter Kruger

Chiba Univ. (Japan)

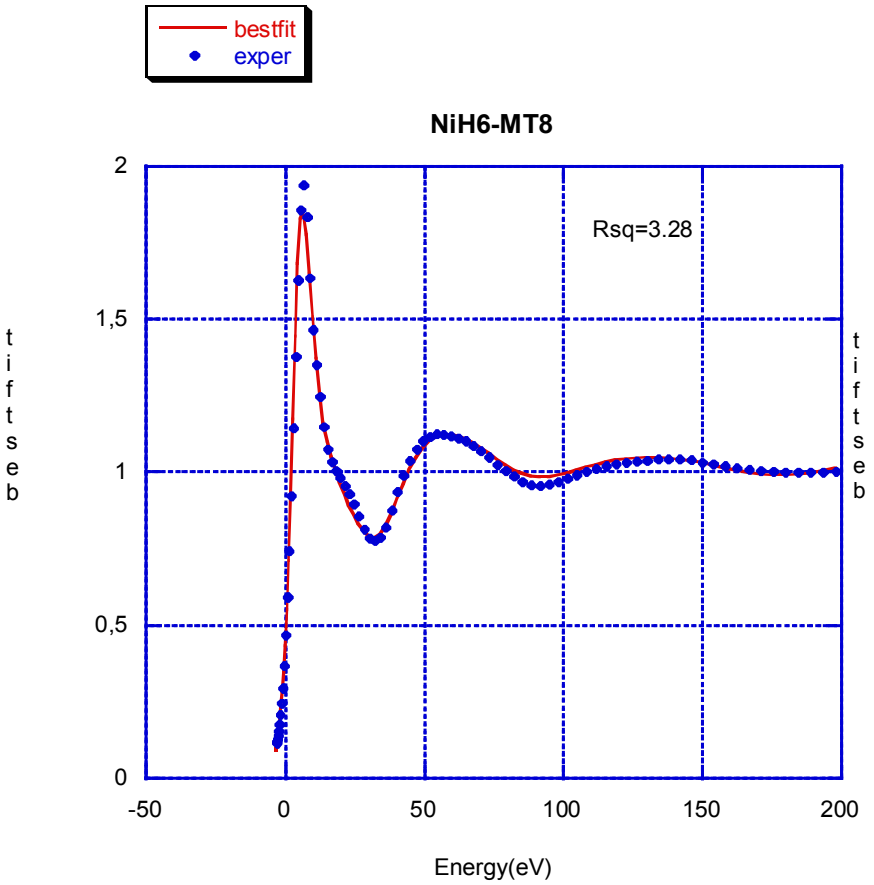
- Junqing Xu

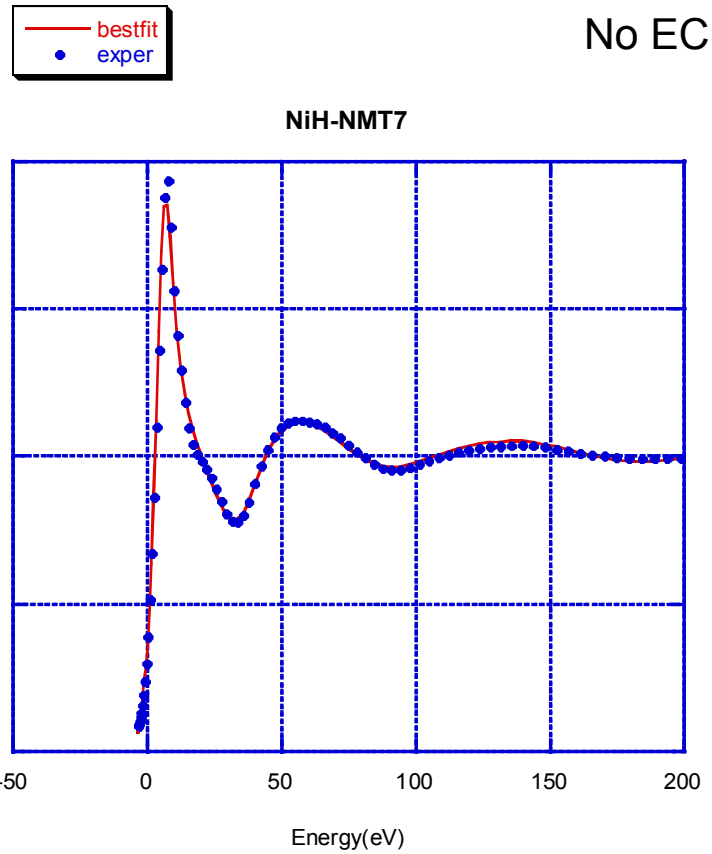
University of Science and Technology of China (China)

FP-MXAN
Structural Fitting over $Ni(OH_2)_6$



No EC's





R_{sq}=3.28
Ni-O : 2.0327 ± 0.025 Å

R_{sq}=2.49
Ni-O : 2.038±0.023 Å

EXAFS: 2.072 ±0.002 Å (by GNXAS)

Improvement!

Conclusion

- MXAN works well for predicting the structure from the fitting
- For highly anisotropic systems and low dimensional systems, eg. nano cluster and surface, FPMS is needed.
- Full potential is more important than SCF calculation for continuum state calculations

Thank you for your attention