# A multiple-scattering approach to the S K-edge analysis: problems and possibilities

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# plan of the talk

- **MS Theory and the MXAN approach**

  Generalities and examples

- **XAS spectroscopy of S compounds**

  Some examples

- **Quantitative analysis of the XANES energy region: the case of cysteine**

# MS Theory

**It is a method to solve the Sch. Equation in real space** and it does not need any particular symmetry. Introduced in the literature by K. H. Johnson since ’60-’70 to calculate bound states in small molecules

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

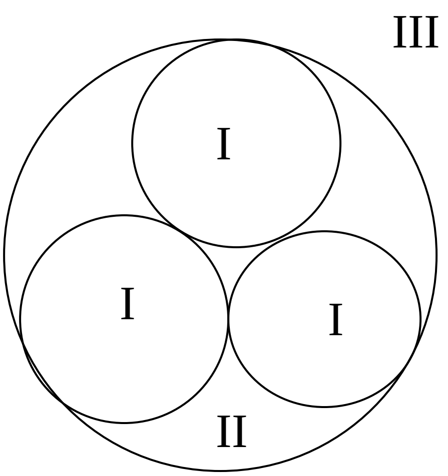
$$V(\vec{r})=V_{c}(\vec{r})+V_{exc}(\vec{r})$$

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

# 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 considered

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

$V_{MT}$ is a constant value - The average is over the interstitial volume

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

We must solve the Sch. equation with this potential

The total w.f. can be written as:

$$\Psi = \sum_{i} \Psi_{I} + \Psi_{II} + \Psi_{III}$$

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

$$\Psi_{I}^{J}(\vec{r}) = \sum_{L} B_{L}^{J} R_{l}^{J}(E; r) Y_{lm}(\hat{r})$$

- $V_{MT}$ is constant $\longrightarrow$ $Y_{II}$ 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

↓

i) Eigen-values of the bounded molecular states
ii) w.f. in the various regions
iii) Spectroscopy quantities

Starting from the Lippmann-Schwinger equation and using the Green’s theorem, we have demonstrated that

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

valid for both bound and continuum states

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

○ corrections due to the OS sphere, region III

$$t^i_l = e^{i\delta^i_l} \sin\delta^i_l$$

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

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

Gaunt coefficient

$J^{i0}_{L\underline{L}}$

Exciting wave referred to site i

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

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

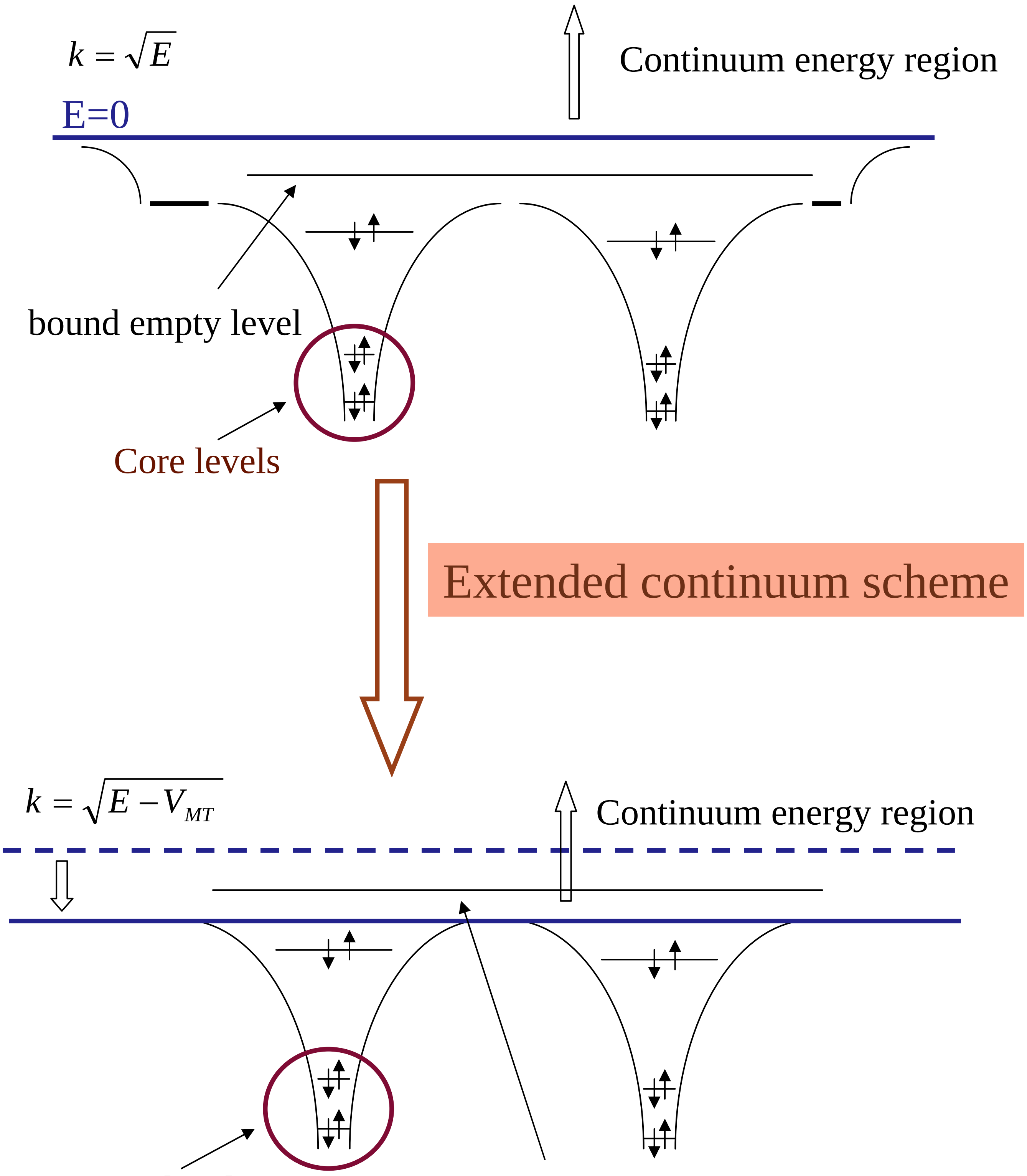
The model is a multiple scattering model for several centers with free propagation in the interstitial region

We have also demonstrated that it is possible to eliminate the OS by changing the normalization – the so-called “extended continuum” scheme

bound states can be found as continuum resonances, in other words for E > $V_{MT}$ (it is a negative value) we can found all the possible states as continuum states

unique energy scale from the pre-edge to the EXAFS energy region

S. Doniach et al. Proceedings of “EXAFS and Near Edge Structure III” Stanford (1984)
M. Benfatto et al. Phys. Rev **B34** 5774 (1986)
T. Tyson et al. Phys. Rev **B46** 5997(1992)



$k = \sqrt{E}$

E=0

Continuum energy region

bound empty level

Core levels

**Extended continuum scheme**

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

Continuum energy region

Core levels

bound empty level becomes a resonance in the continuum part

# We use the Fermi Golden-rule to calcolate the photoabsorption cross

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

$$\alpha = \frac{1}{137}$$ Fine structure constant

Dipole approximation ⟷ $\frac{\sigma_q(\omega)}{\sigma_d(\omega)} \approx \frac{1}{100}$

$\psi_f$ → continuum part of the w.f.

$\psi_c$ → core w.f. spatially localized

$$\sigma(\omega)=A(\omega)\sum_{\underline{L},L,m_\gamma,m_0}\left|B^0_L(\underline{L})\right|^2\left|(R^0_L(\vec{r}_0)\,|\,r_0 Y_{lm_\gamma}(\hat{r}_0)\,|\,\phi_{l_0}(r_0)Y_{L_0}(\hat{r}_0))\right|^2$$

$$A(\omega) = 2\pi\alpha\omega(4\pi/3)^2\frac{k}{\pi} \quad \begin{cases} k = \sqrt{E - V_{MT}} \\ E = \omega - I_0 \end{cases}$$

un-polarized photo-absorption cross section

Optical theorem

$$\sum_{\underline{L}} [B^{0}_{L}(\underline{L})]^{*} [B^{0}_{L'}(\underline{L})] = \mathrm{Im}[(I - T_{a} G)^{-1} T_{a}]^{00}_{LL'}$$

$$\tau^{00}_{LL'} = [(I - T_{a} G)^{-1} T_{a}]^{00}_{LL'}$$

$$\Downarrow$$

$$\begin{pmatrix} .. & & G_{ij} \\ & (t^{i}_{\ell})^{-1} & \\ G_{ji} & & .. \end{pmatrix}^{-1}$$

$$\Uparrow$$

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

complete equivalence between band structure,Green function and MS approach

## The photo-absorption cross section becomes

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

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

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

atomic cross section - almost without structures and independent from the energy

Final angular momentum according dipole selection rule

$$\mathrm{l}=\mathrm{l}_0\pm 1$$

# 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
- ……….

They drain away amplitude from the elastic channel and must be included in any realistic calculation

↓

finite lifetime of the photoelectron in the final state

↓

many-body treatment of the photoabsorption process

- 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

$$\boxed{\sigma(E) \propto \mathrm{Im}\, G_{00}(E - I_c)}$$

$$\left[\nabla^2 + \mathrm{E} - \mathrm{V}_c(\vec{\mathrm{r}}) - \Sigma_{\mathrm{exc}}(\vec{\mathrm{r}};\mathrm{E})\right] \mathrm{G}^{+}_{00}(\vec{\mathrm{r}},\vec{\mathrm{r}}\,';\mathrm{E}) = \delta(\vec{\mathrm{r}} - \vec{\mathrm{r}}\,')$$

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

For a muffin-tin potential

$$\mathrm{G}^{+}_{00}(\vec{\mathrm{r}},\vec{\mathrm{r}}\,';\mathrm{E}) = -\mathrm{k} \sum_{\mathrm{L,L'}} \mathrm{R}^{0}_{\mathrm{L}}(\vec{\mathrm{r}})\, \tau^{00}_{\mathrm{LL'}}\, \mathrm{R}^{0}_{\mathrm{L'}}(\vec{\mathrm{r}}\,') + \sum_{\mathrm{L}} \mathrm{R}^{0}_{\mathrm{L}}(\vec{\mathrm{r}}) \mathrm{S}^{0}_{\mathrm{L}}(\vec{\mathrm{r}}\,')$$

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

C.R. Natoli, M. Benfatto et al. Phys. Rev **B42** 1944(1990)
R. Gunnella et al. Solid. State Comm. **76** 109 (1990)
T. Tyson et al. Phys. Rev **B46** 5997(1992)
C.R. Natoli, M. Benfatto et al. Jour. Synch. Rad. **10** 26 (2003)

The use of complex potential automatically introduces a damping in the the elastic signal

$$G^{i\,j}_{L\,L'} \approx \frac{e^{ikR_{i\,j}}}{k\,R_{i\,j}}$$

If $k = k_r + i\,k_i$ we have a decreasing exponential

we choose the Hedin-Lundqvist (HL) potential extending its validity in to the atomic core region

it has an imaginary part that is able to reproduce the observed mean-free path in metal. This part starts at the plasmon energy

↓

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

Within some conditions the use of an optical potential is completely equivalent to a convolution of a real calculation with a Lorentzian function having a suitable energy dependent width

# Two ways to calculate the scattering path operator

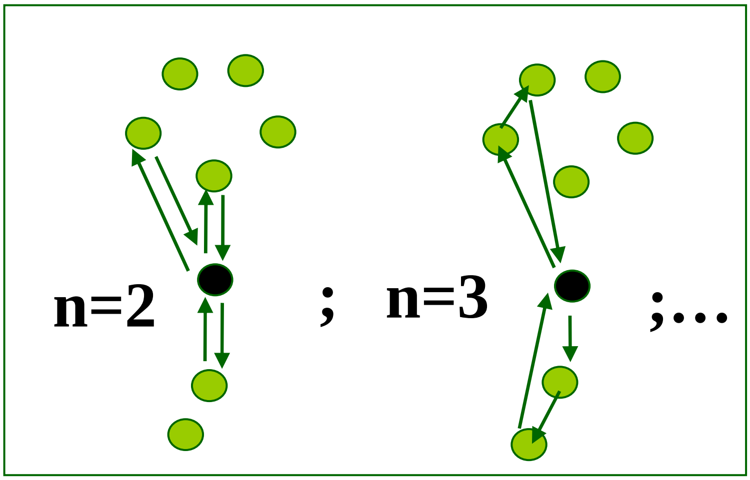
$$\tau^{00}_{LL'} = [(I - T_a G)^{-1} T_a]^{00}_{LL'}$$

Exactly: all MS contributions are included

MXAN

By series:

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



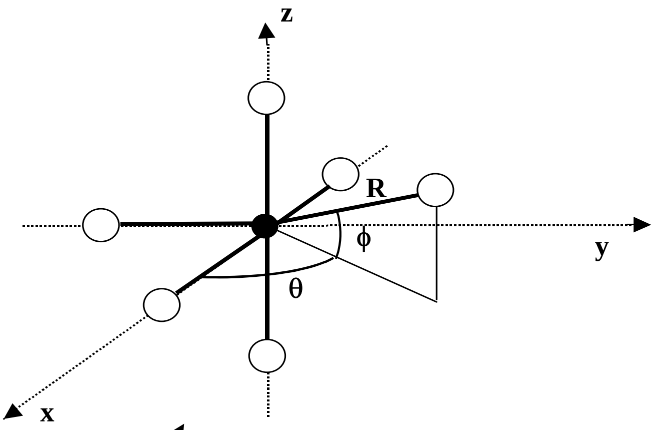
Most of the actually sotware packages to fit EXAFS data

- **i) We work in the energy space**
- **ii) We can start from the edge**
- **iii) We can use polarization dependent spectra**

Reduced thermal damping effects – we do not include DW factors

# 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 – Norman criterion

Minimization of error function

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

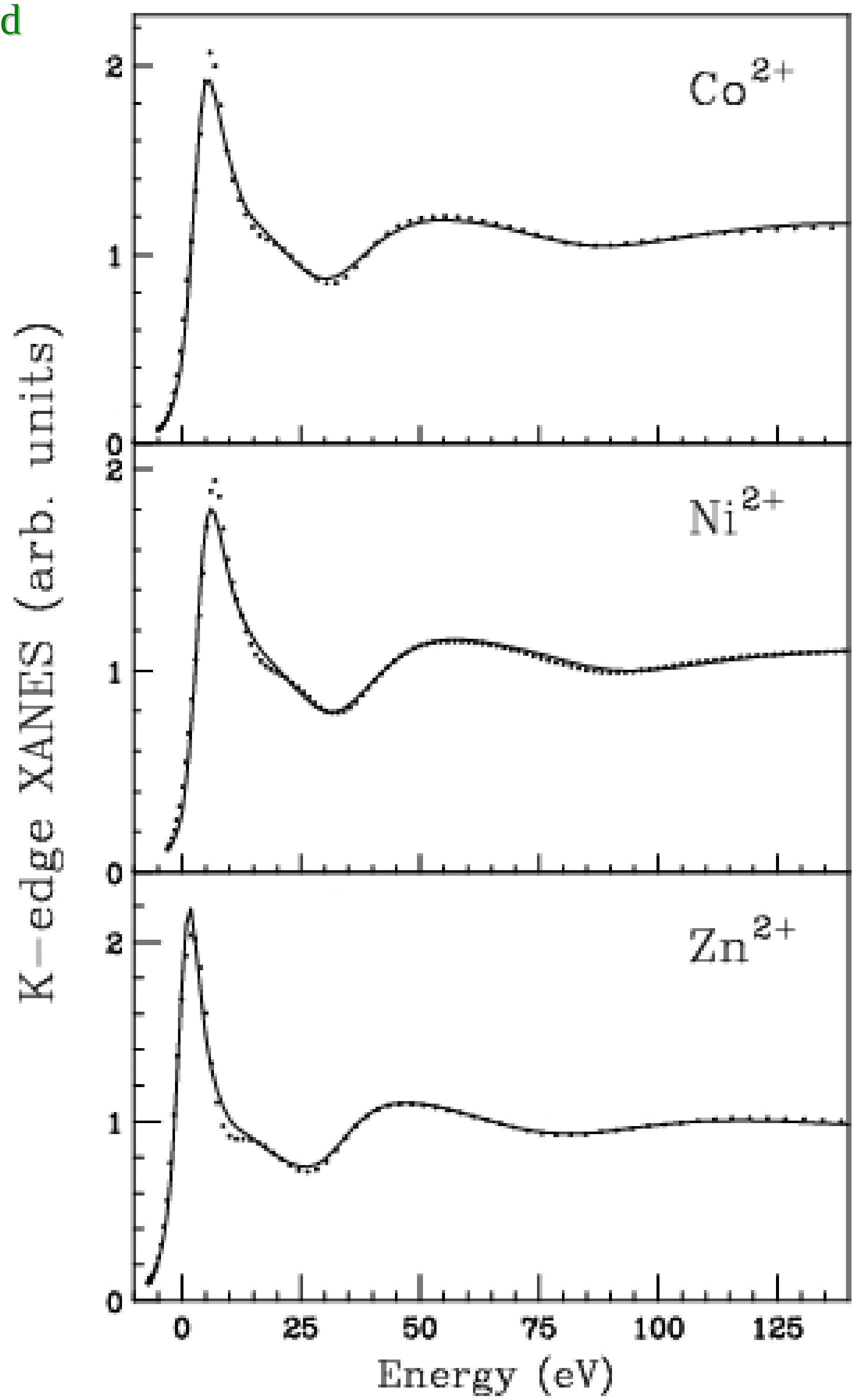
By comparison with exp. data we can fit relevant structural parameters

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)

# Transition metals in water solution

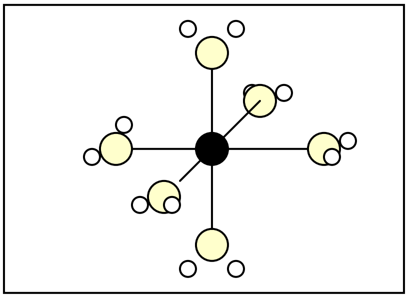
-Starting condition: distorted orthorhombic symm.

-The fits include Hydrogen atoms



# Best fit conditions

Octahedral symmetry

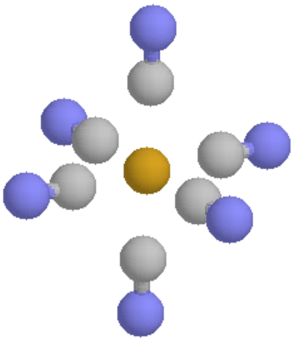


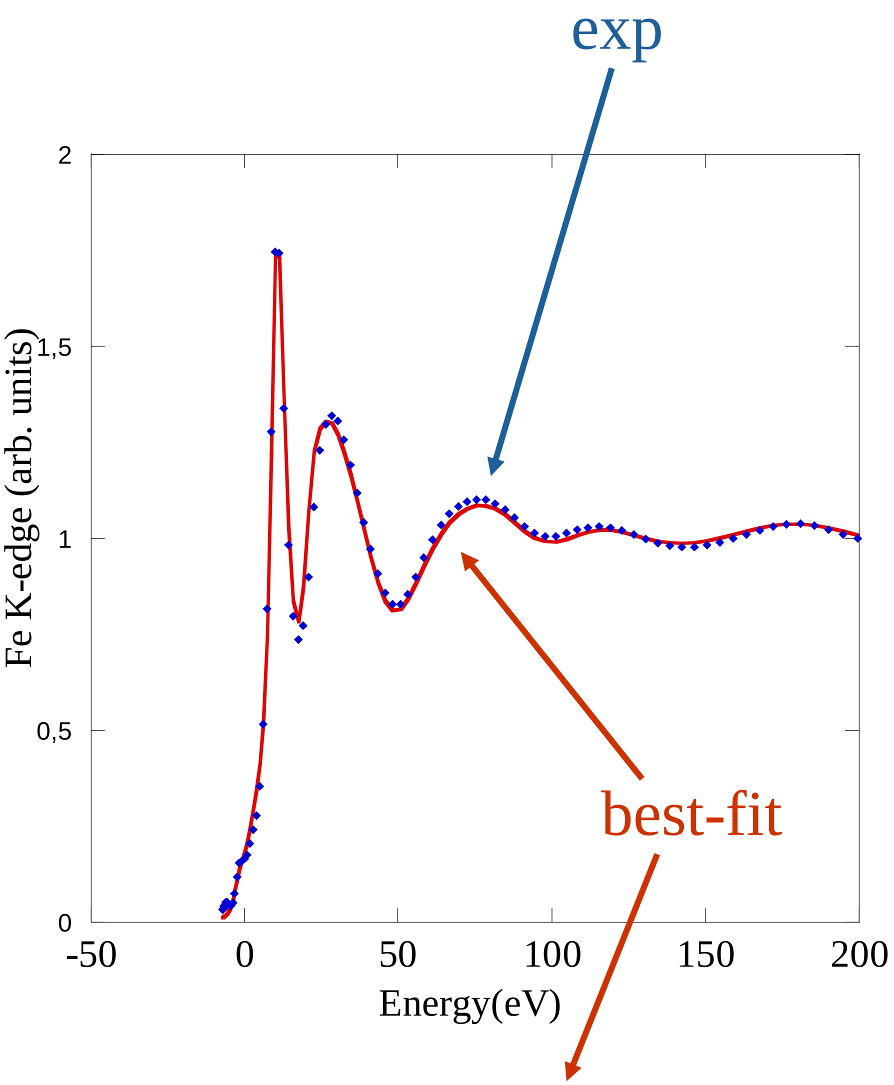
| | R(Å) | R(Å) |
|---|---|---|
| **$Co^{2+}$** | 2.06(0.03) | 2.092(0.002) |
| **$Ni^{2+}$** | 2.03(0.03) | 2.072(0.002) |
| **$Zn^{2+}$** | 2.06(0.02) | 2.078(0.002) |

MXAN

GNXAS

# Fe $(CN)_6$ in water

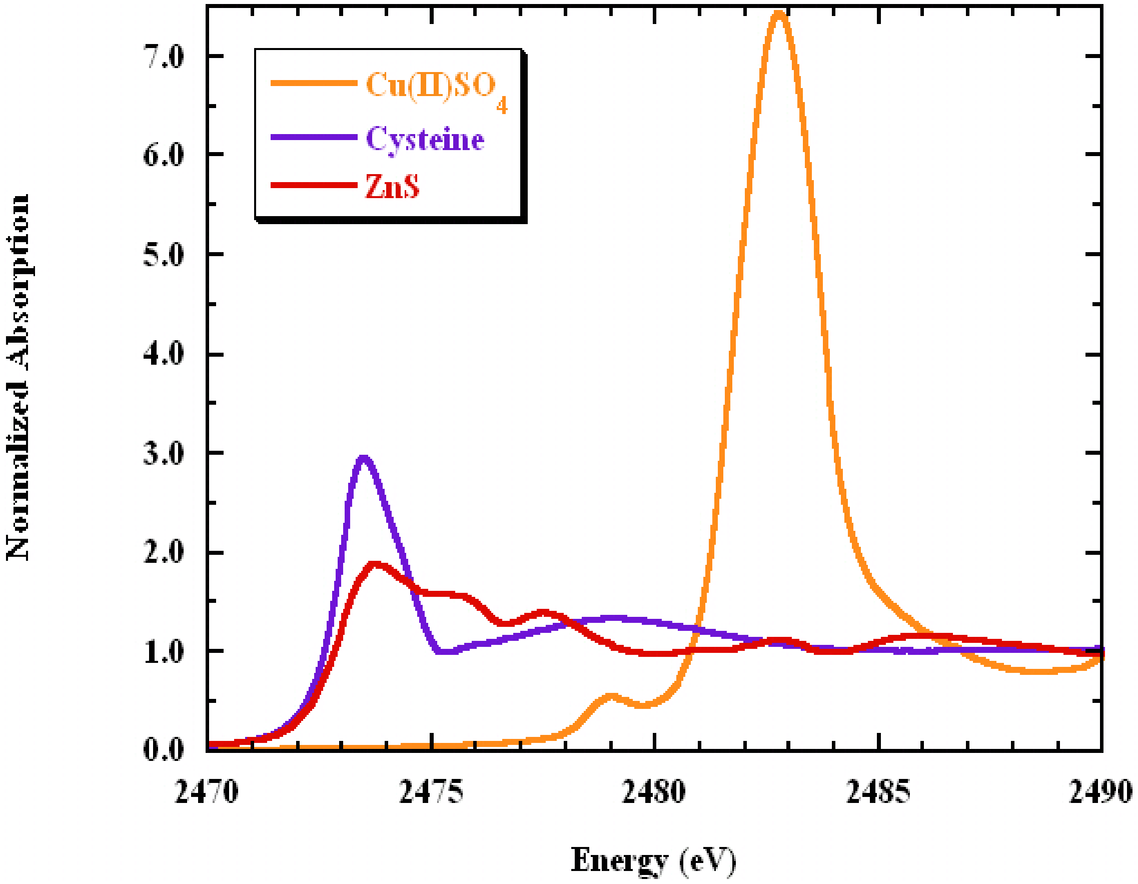




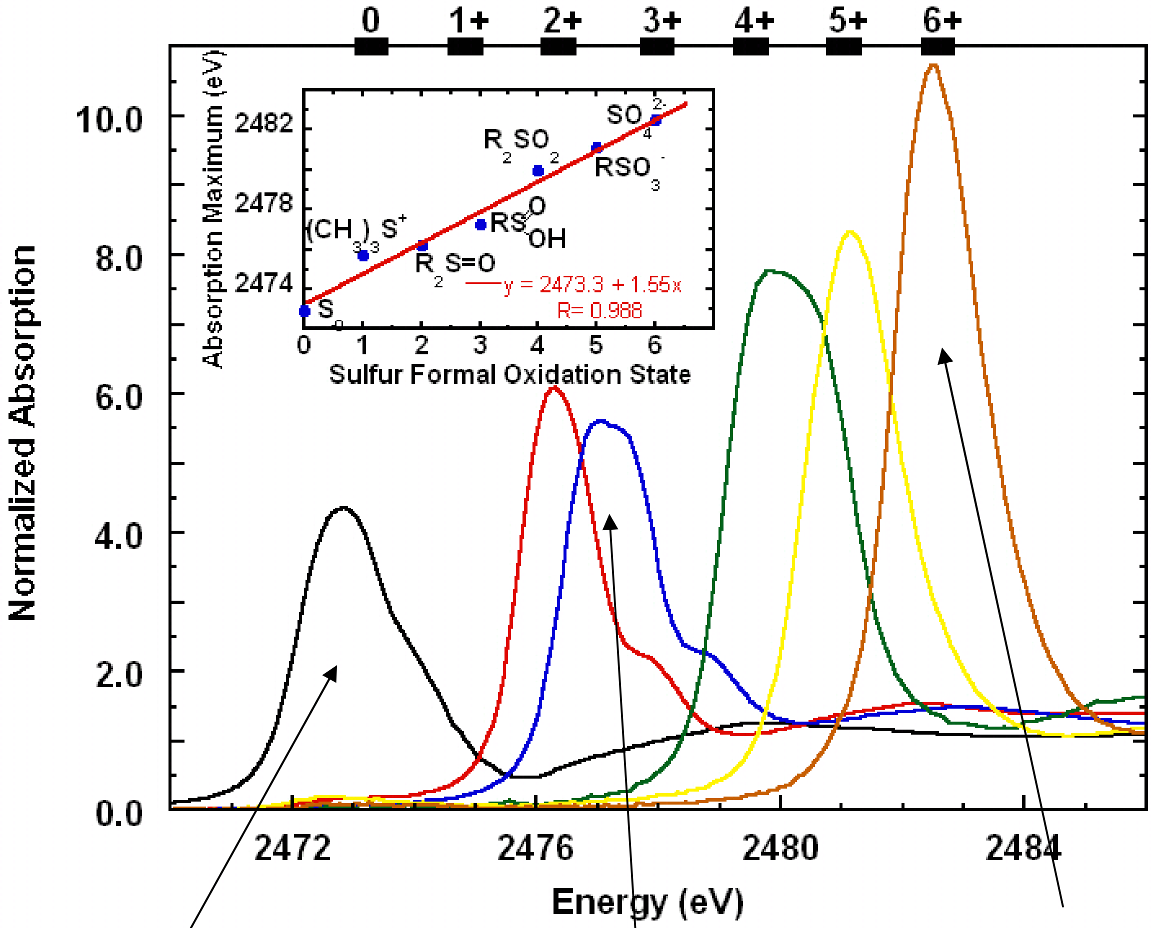
The best-fit condition corresponds to an octahedral symmetry with Fe-C distance of 1.92(0.01) Å and C-N distance of 1.21(0.01) Å

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

# Is it possible to use the same methods to analyze the Sulphur K-edges ?



Big changes in the XANES from one compound to others associated to big differences of bond distances between S and first neighbors: S-O in $CuSO_4$ is 1.55 Å, S-Zn in ZnS is 2.34 Å while S-C and S-H in cysteine is 1.85 Å and 1.35 Å respectively



elemental sulfur S$^0$

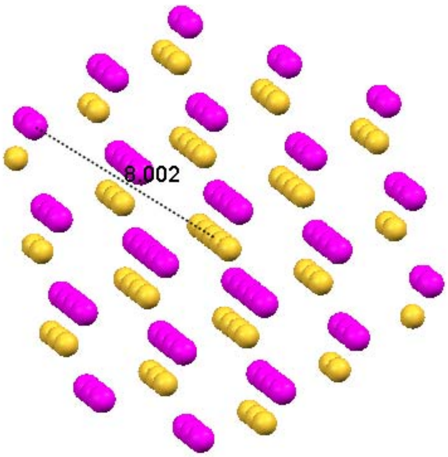
solution sulfate S$^{+6}$

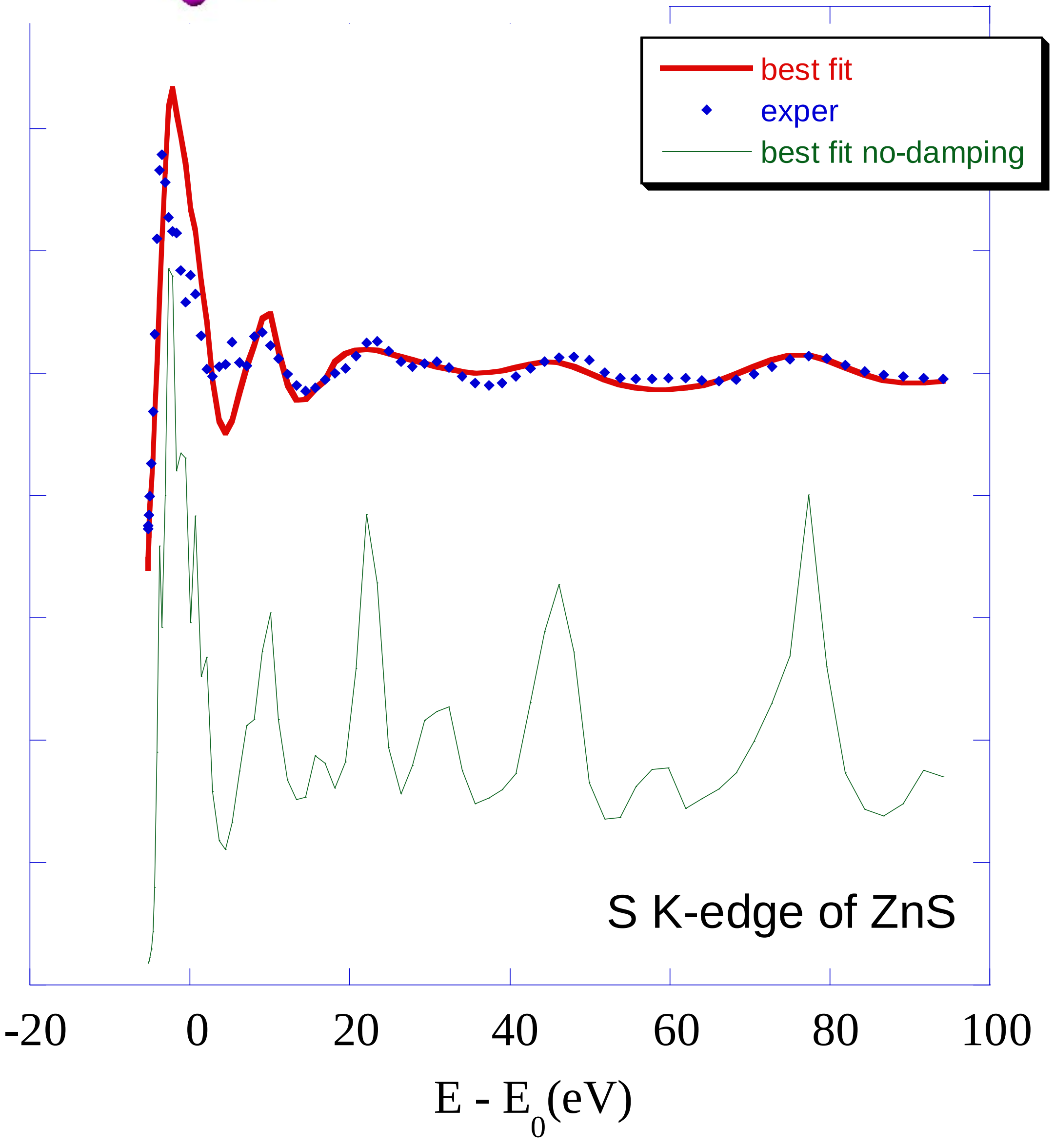
methionine sulfoxide S$^{+2}$

Spectra are dominated by transitions from 1s to 3p-like bound empty levels

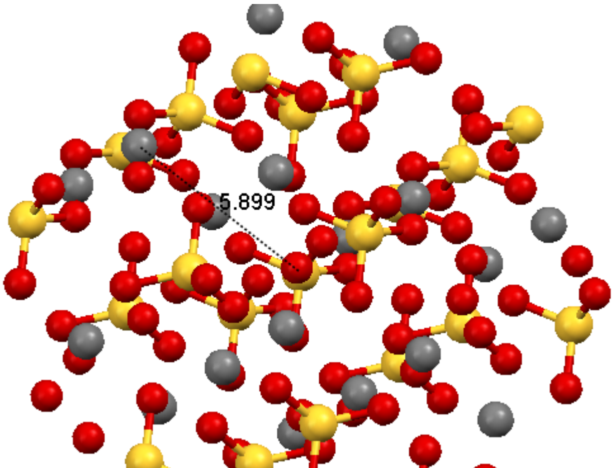
P. Frank, B. Hedman, et al. Biochemistry **26**, 4975 (1987).
Hedman, B, Frank, P, et al. Nucl. Instrum. Methods Phys. Res., Sect. **A 246**, 797 (1986)

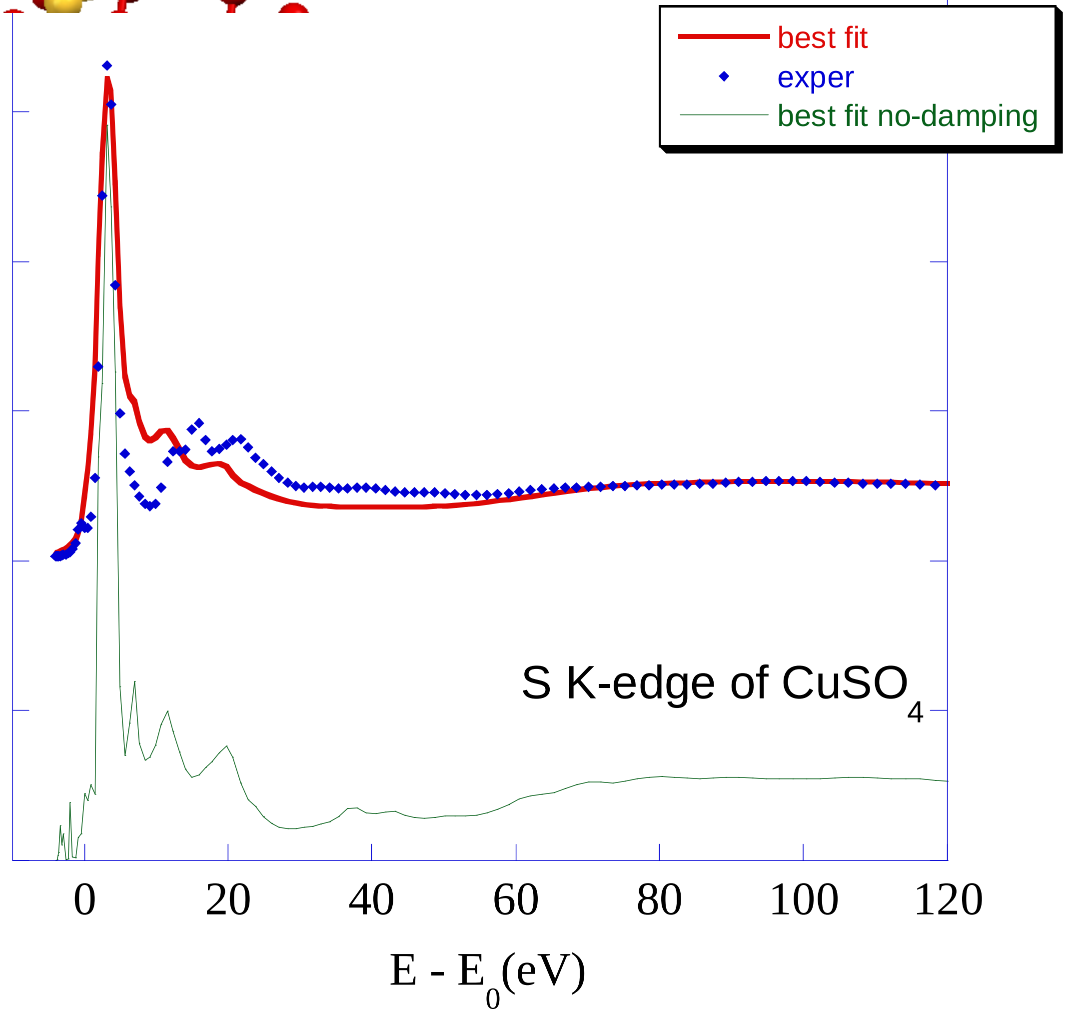
124 atoms, up to 8.0 Å

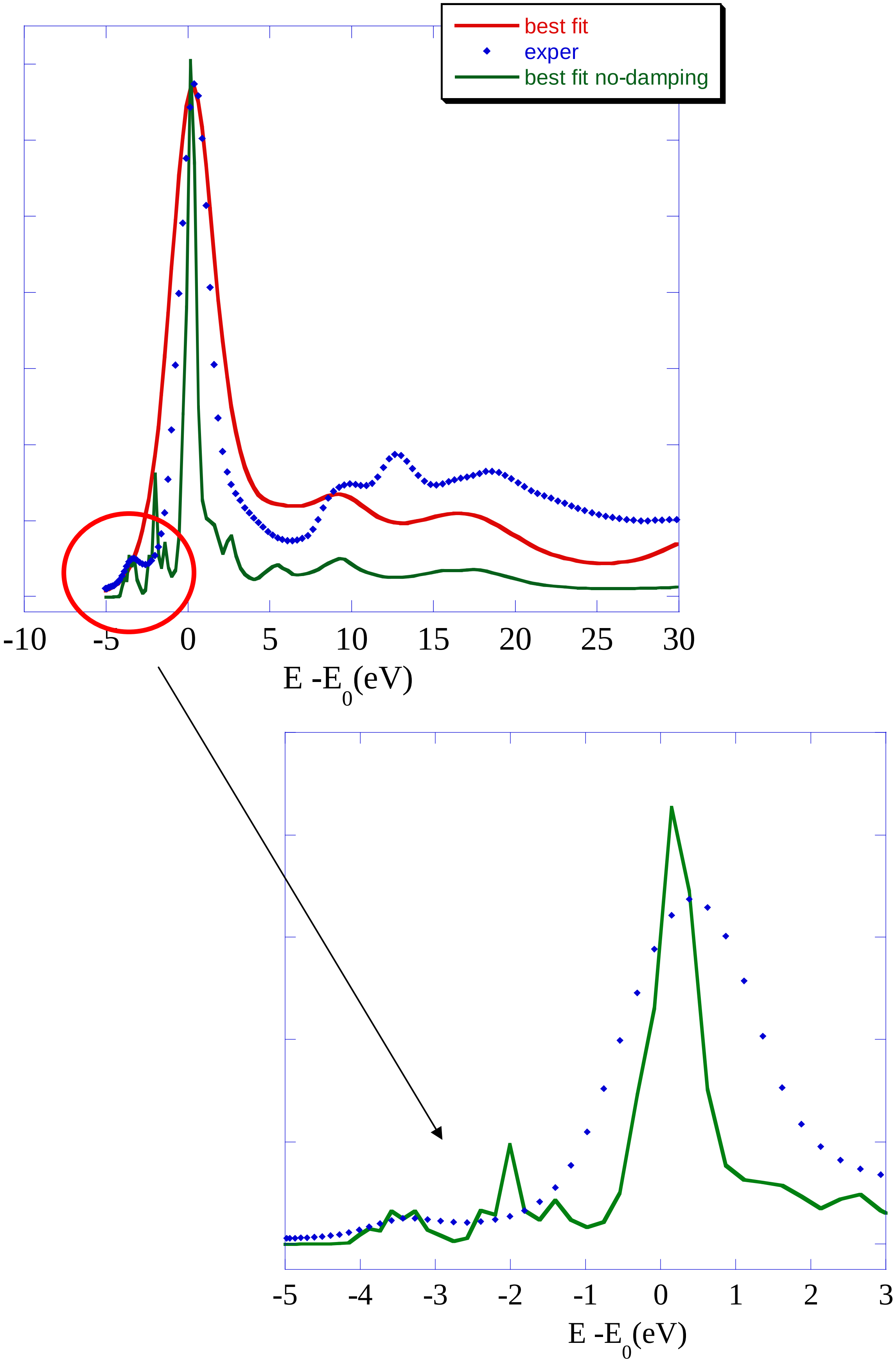




# 80 atoms, up to 5.8 Å






best fit
exper
best fit no-damping
-10
-5
0
5
10
15
20
25
30
E -E$_0$(eV)
-5
-4
-3
-2
-1
0
1
2
3
E -E$_0$(eV)

Although we are able to simulate all peaks in the spectrum, the presence of huge transitions to bound states creates some problems in the MXAN fitting procedure because the use of the “extended continuum” approach to simulate these transitions.

It is possible to demonstrate using the scattering theory that deeper is the bound state broader is the resonance calculated with this approach

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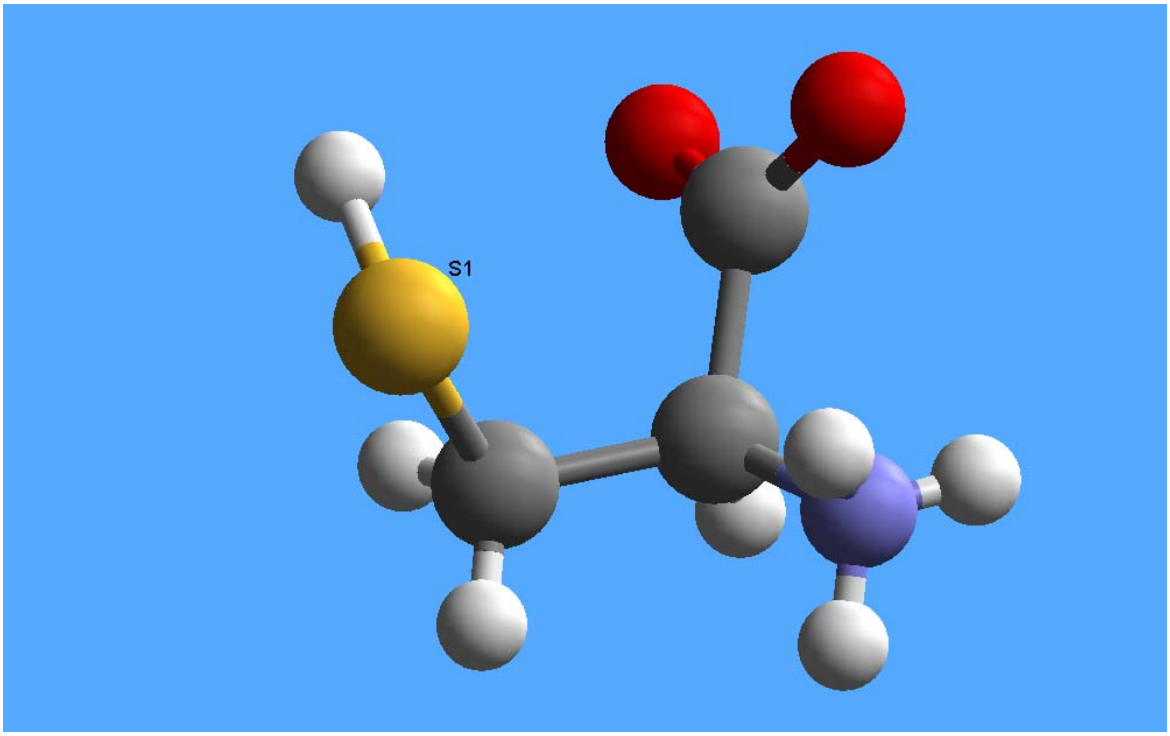
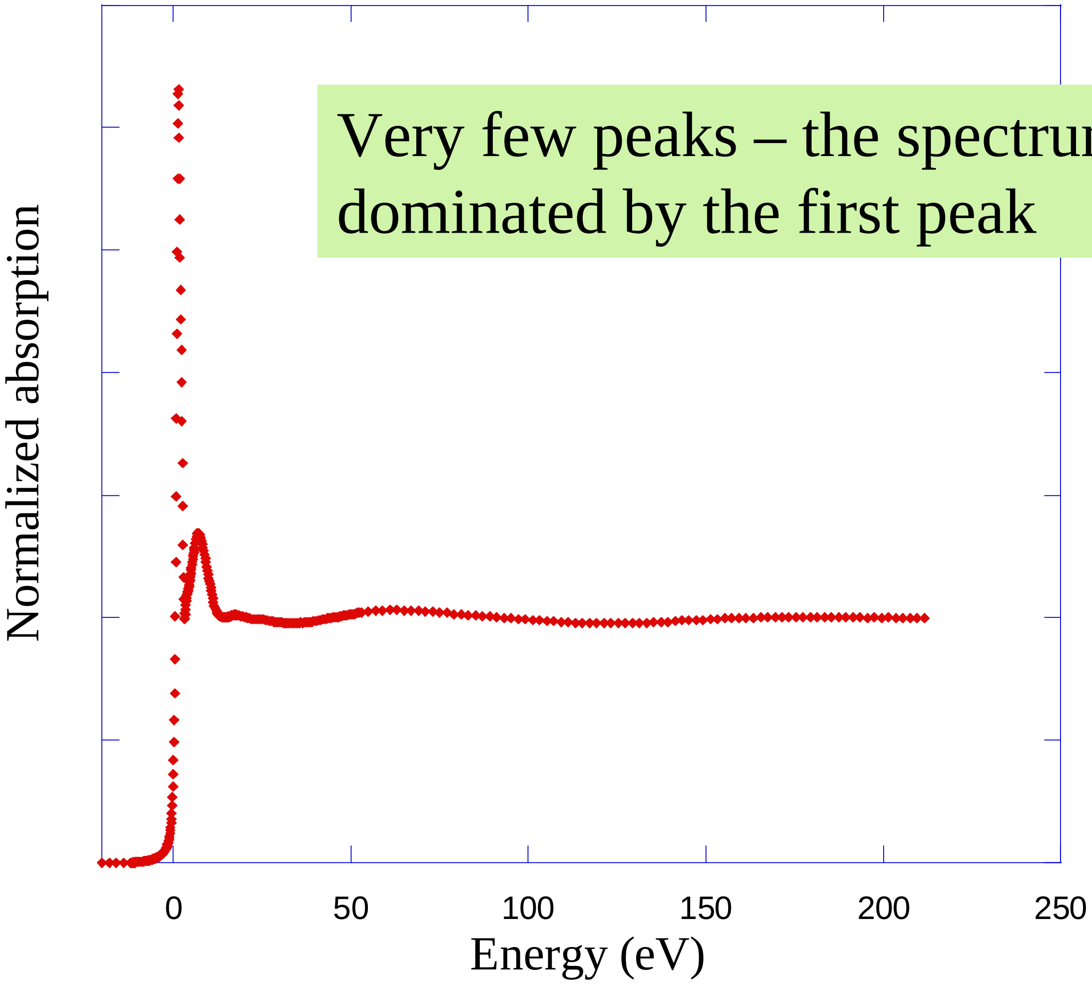
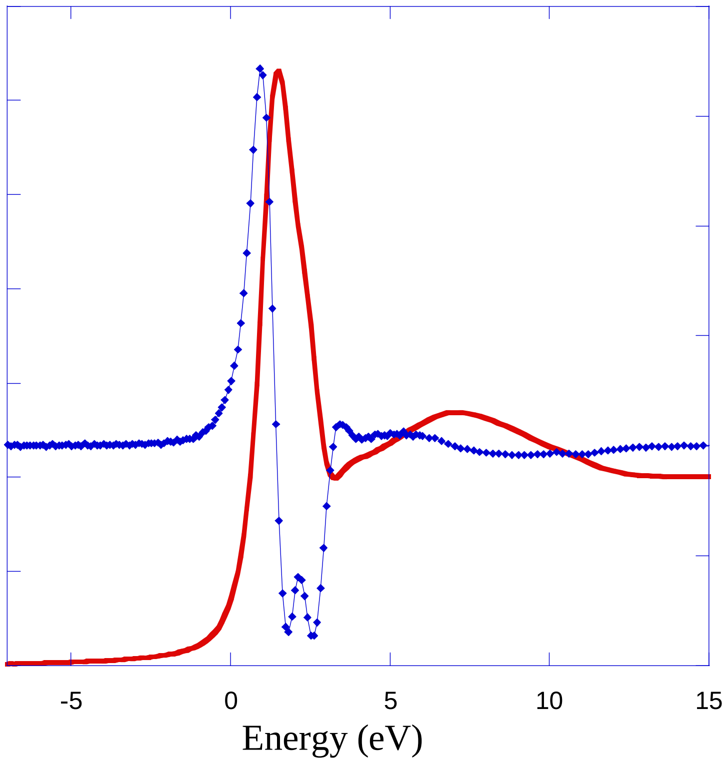
One possibility for making fit to obtain quantitative structural information is to eliminate such transitions from the fit

# The case of sulphur K-edge XANES of cysteine





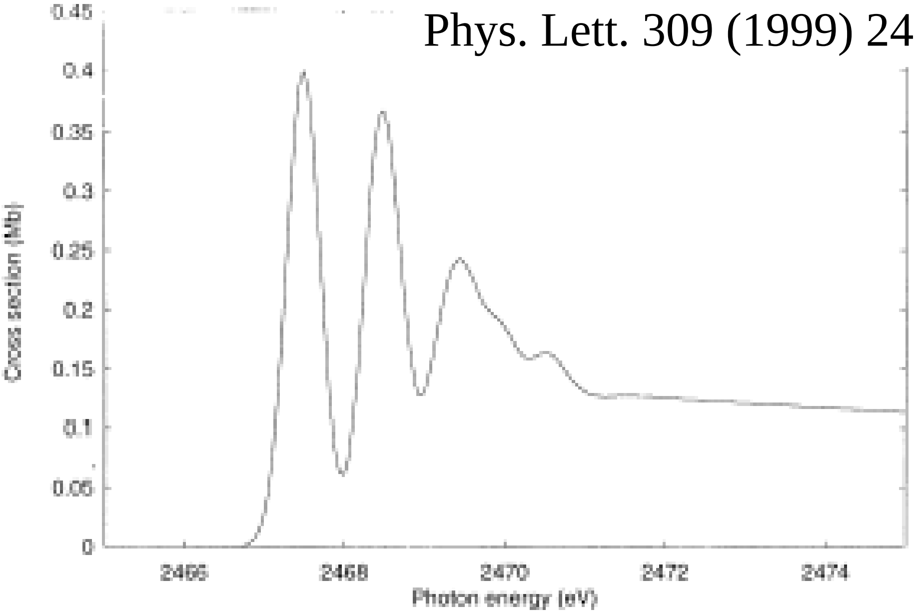
Very few peaks – the spectrum is dominated by the first peak



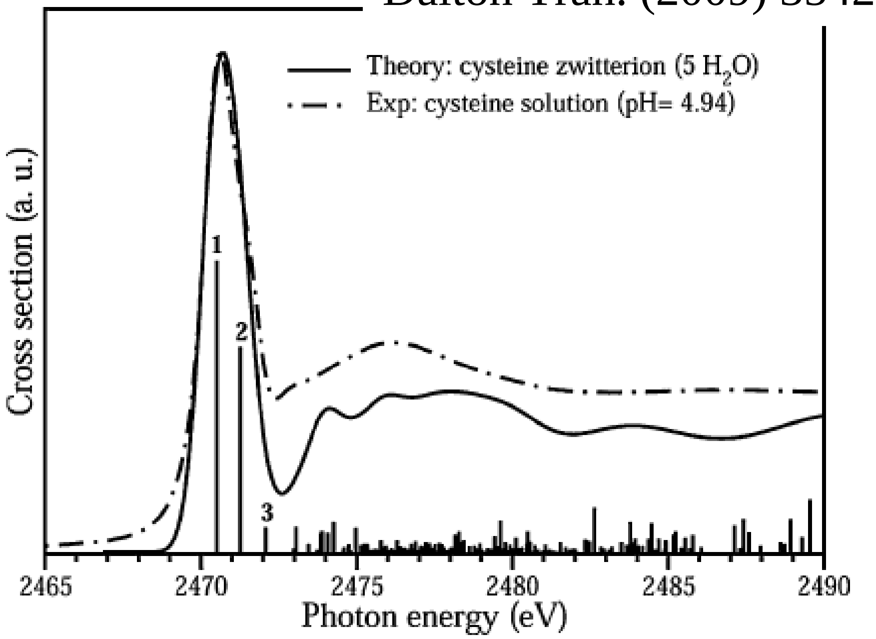
SSRL Beam line 4-3, fluor. detector

100mM L-cysteine solution at ph 7.2

HF calculation by Y. Mochizuki et al. Chem. Phys. Lett. 309 (1999) 241



StoBe DFT code by E.D. Risberg et al. Dalton Tran. (2009) 3542



## DFT details:

Structures are optimized by Gaussian03 package using Gradient-corrected spin-unrestricted density functional calculations.

Polarizable Continuum Model was used to model a solvation sphere of $H_2O$.

Four different starting models were considered for geometry optimization:

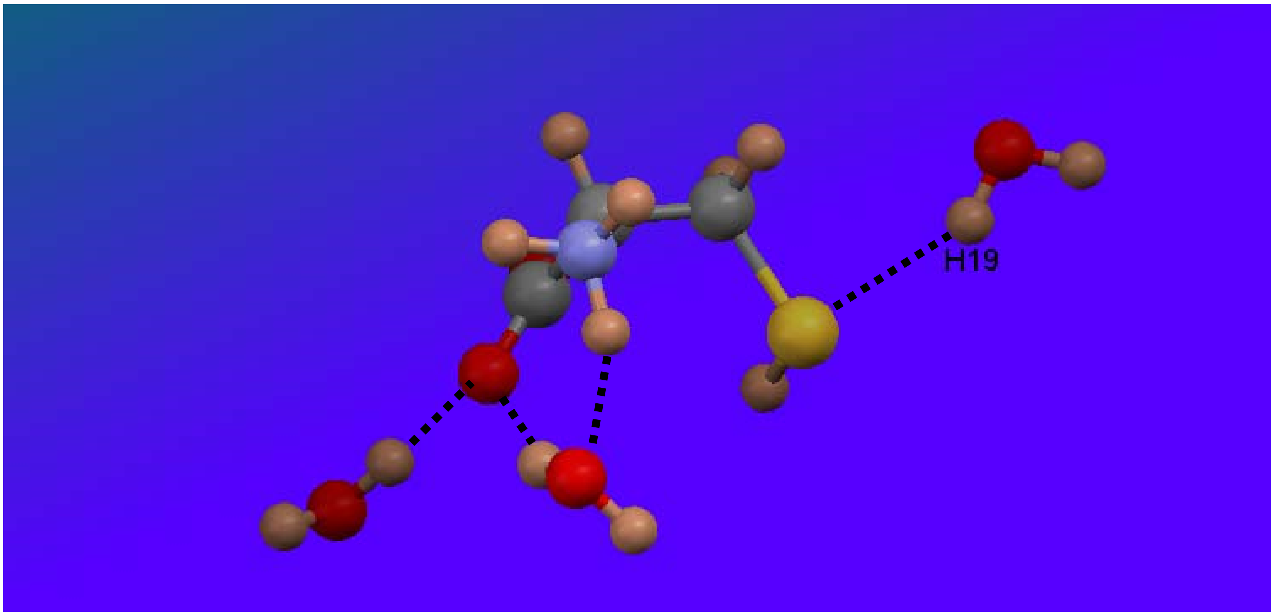
cysteine

cysteine + 1 water in H-bonding distance to the S of cystine (1w model)

cysteine + 2 water in H-bonding distance to the S of cysteine and the $-CO_2-$ group (2w model)

cysteine + 3 water in H-bonding distance to the S of cystine, the $-CO_2-$ and the $–NH^{3+}$ groups (3w model).

3 waters DFT model

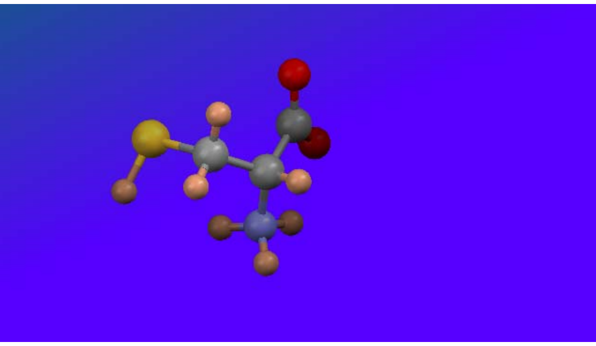


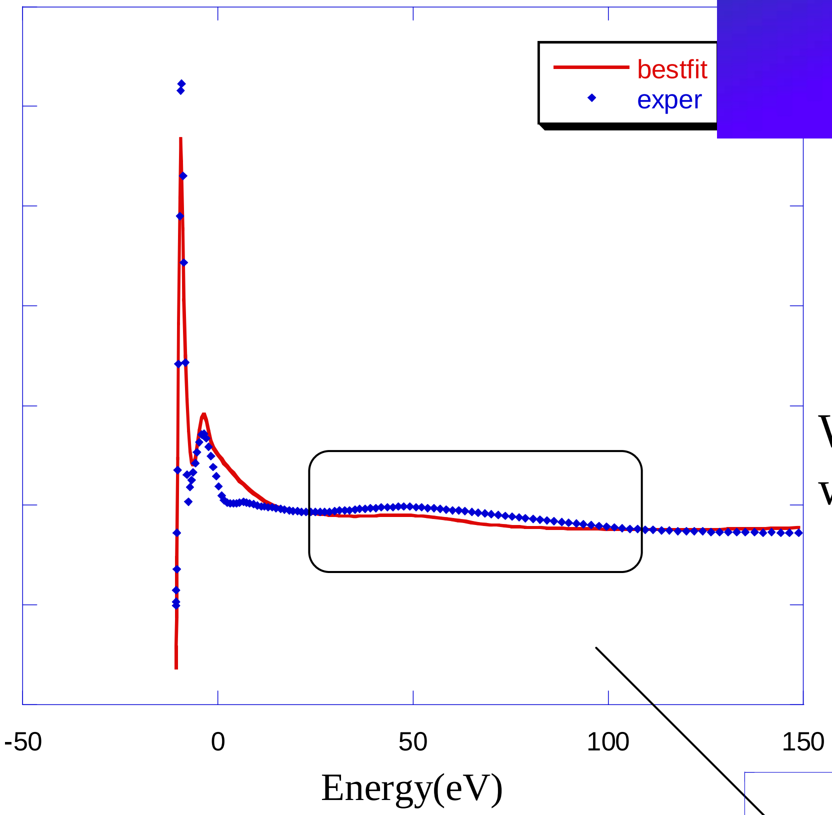
The structural parameters of cysteine are in good agreement with the reported crystal structure data.

The structure optimizes to the zwitterionic form of cysteine The optimized S---H hydrogen bond distances (atom H19) ranges from 2.7 to 2.5 Å depending by the models.

# MXAN analysis of the DFT models

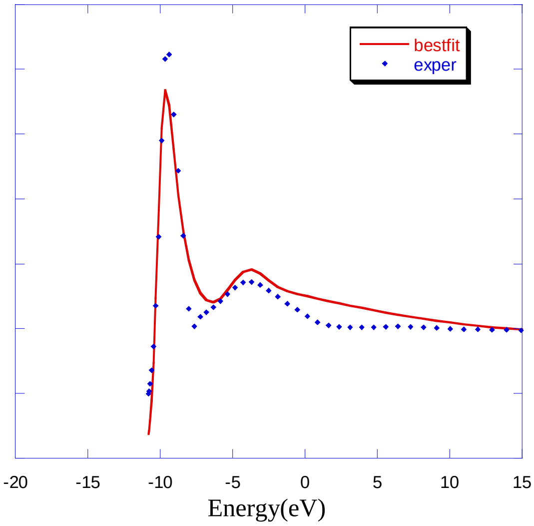
0 waters model

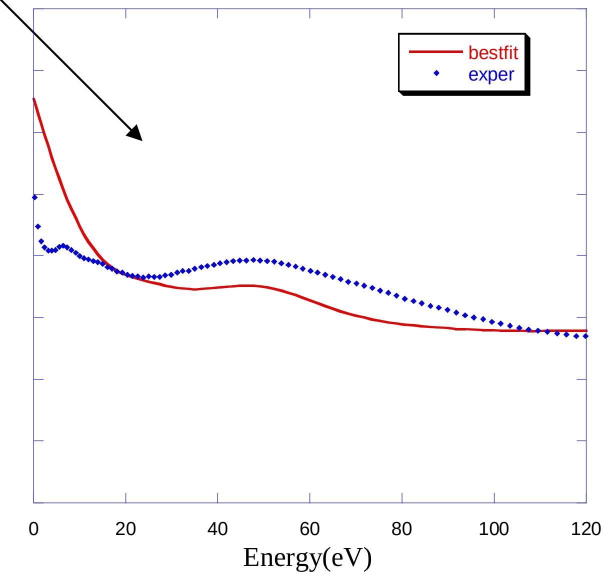




We reproduce the shape but with several discrepancies

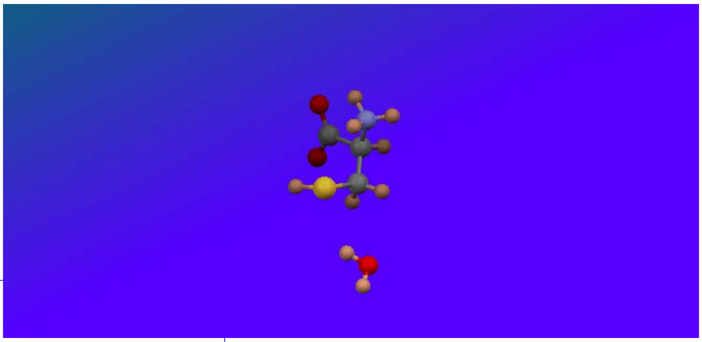
Rsq=37.3

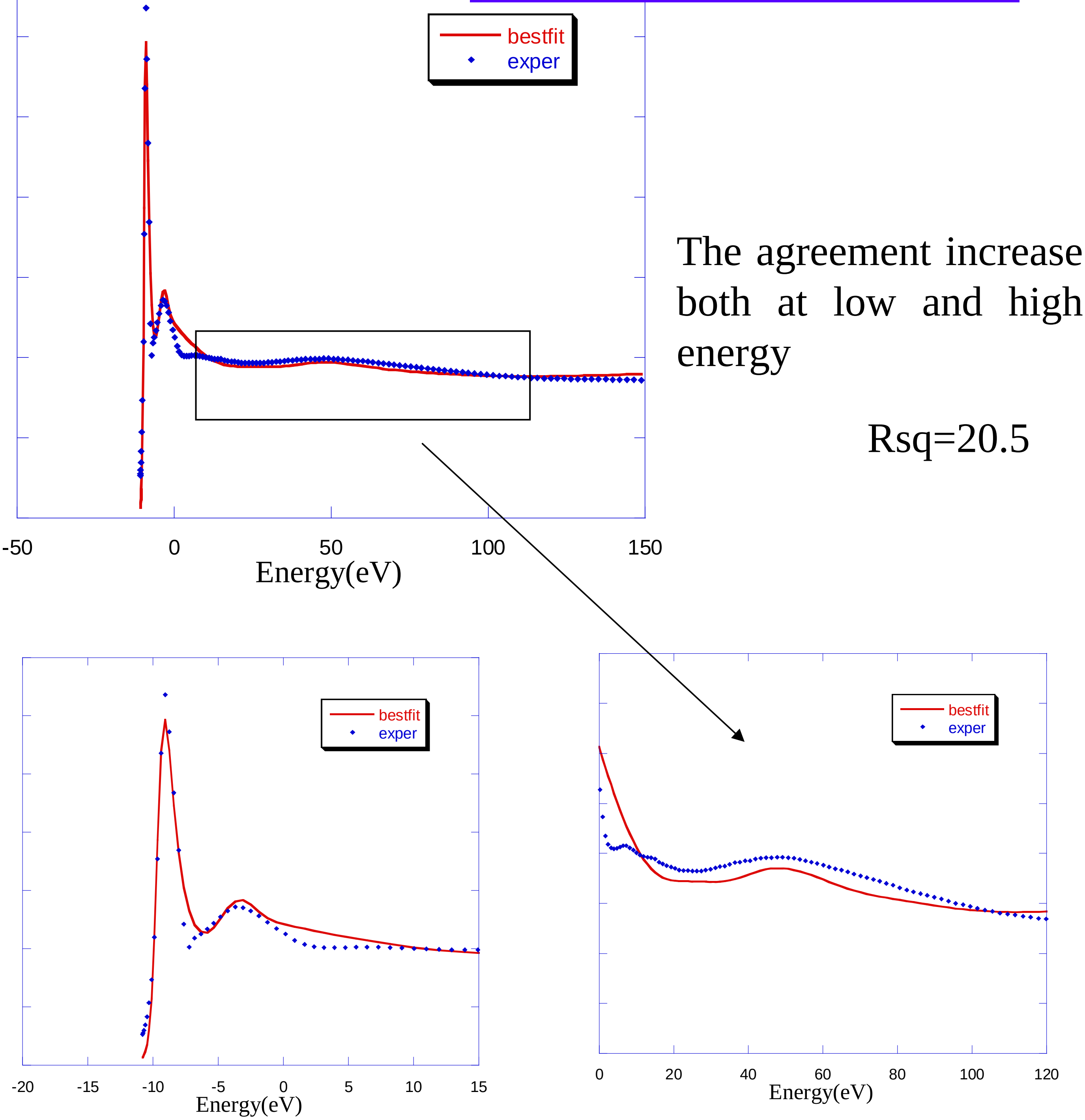




# 1 water model

The H of the water at 2.7 Å

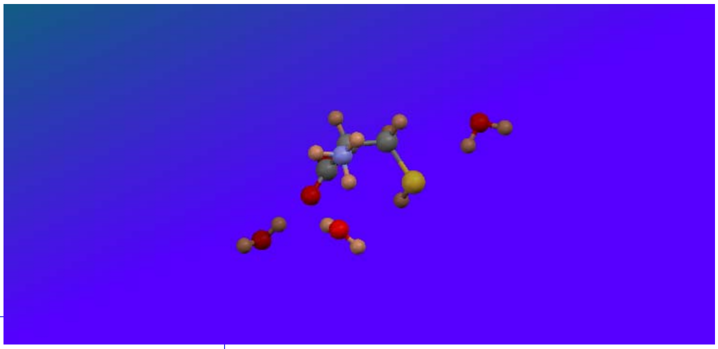


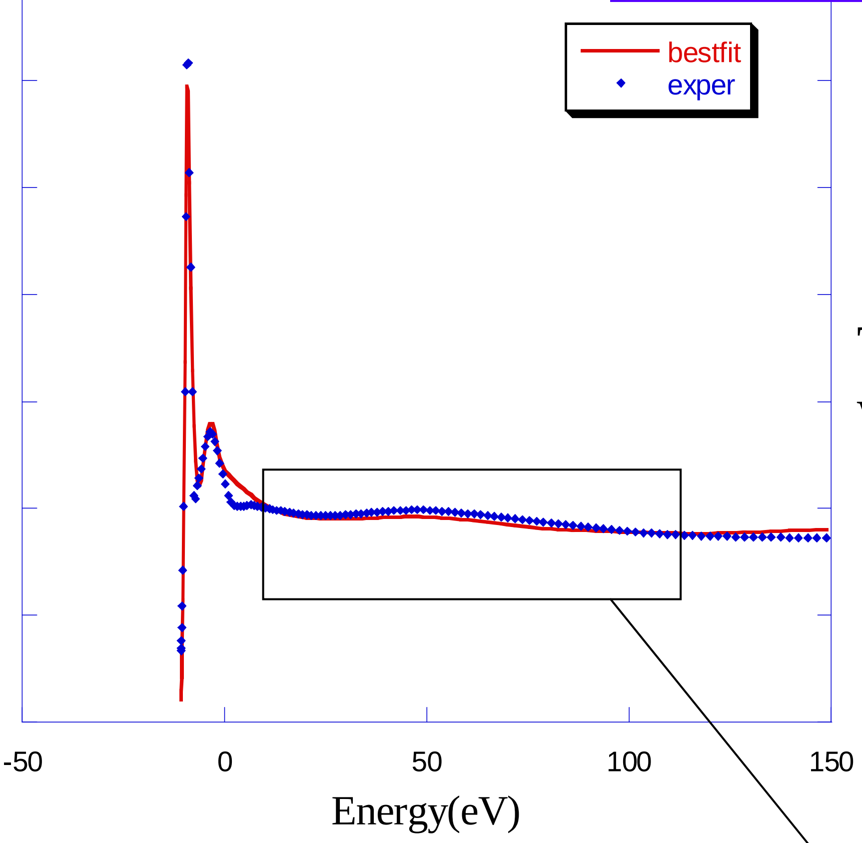


The agreement increase both at low and high energy

Rsq=20.5

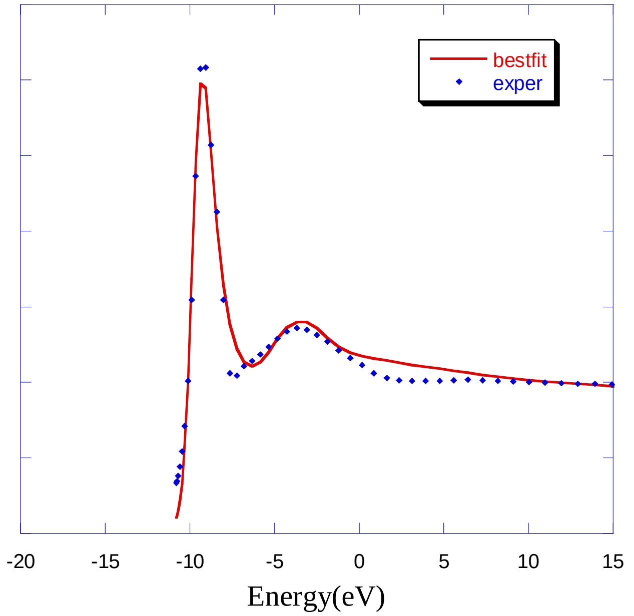
# 3 waters model

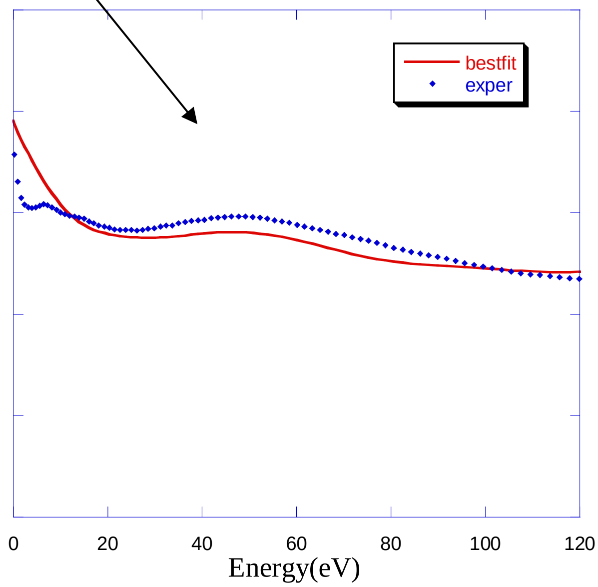




The agreement increase with

Rsq=15.6





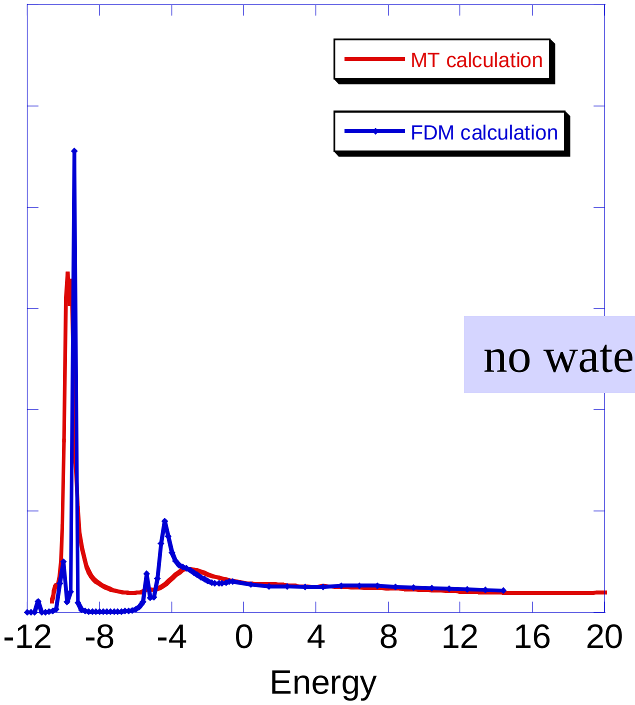
Going from 0 to 3 waters the agreement between theory and experiment increases

Rsq=37.3 → Rsq=15.6

but we are still far from the “standard” agreement we have normally obtained up to now with Rsq of the order of the unit – moving atoms from the DFT positions does not improve the fit

We have indications that the non-MT corrections does not play a sizeable role

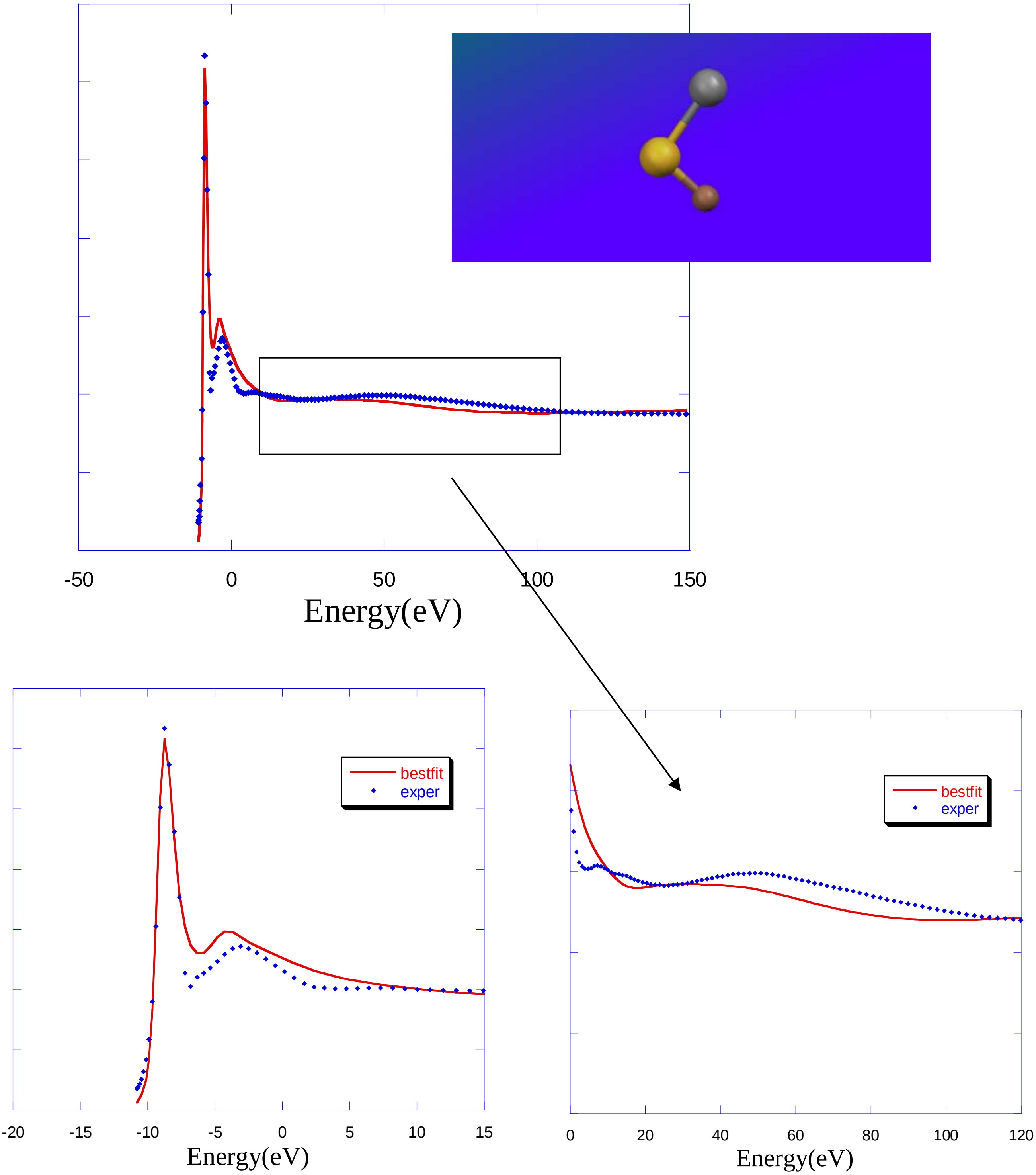
The energy separation between A and B is 6.0 eV in MT, 4.9 in no-MT face to about 5.7 which is the exp. value.



no waters

# Some problems

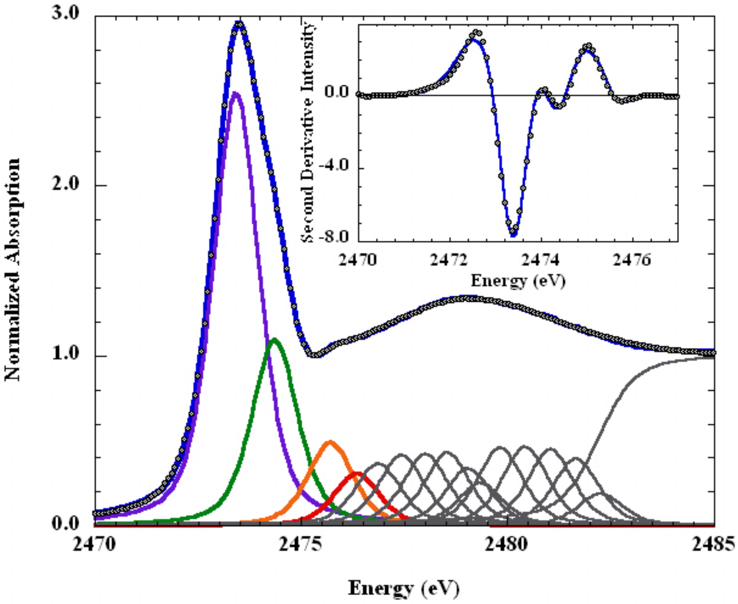
The spectrum is dominated by the first 3 atoms:



This makes quite difficult to fit the water positions from the XAS data

There is also the possibility to have several geometrical configuration of the water around the cysteine

The first peak is made by bound to bound transitions

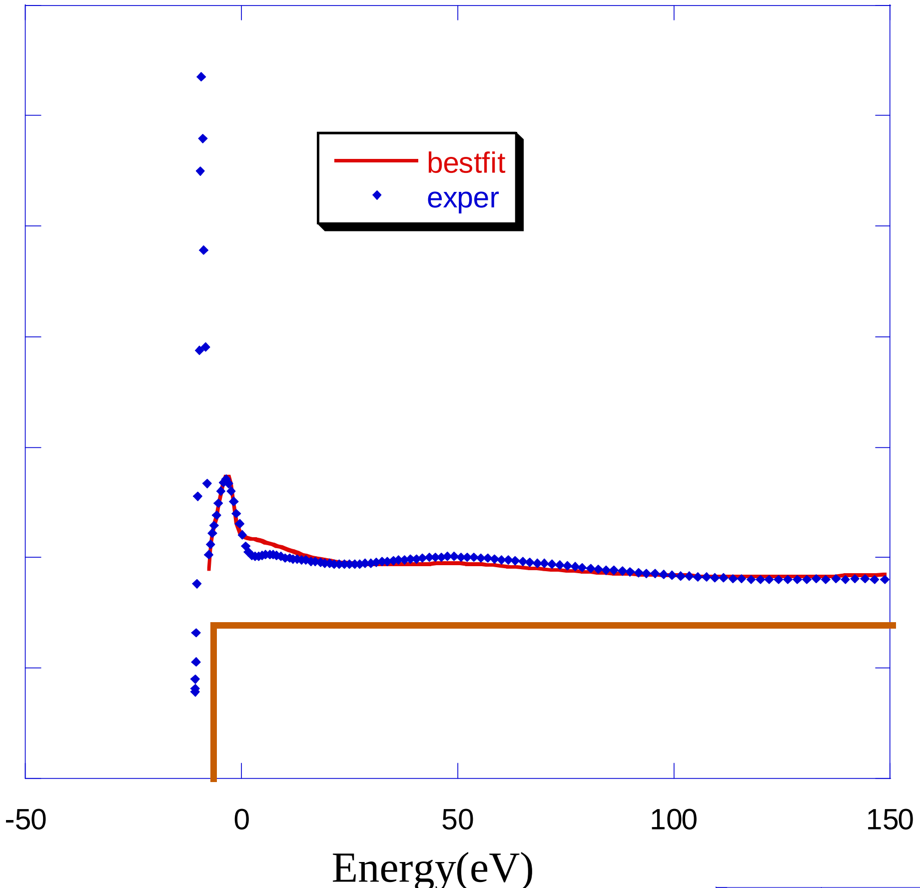


This fit with pseudo-voight functions indicates three contributions – purple, green and orange

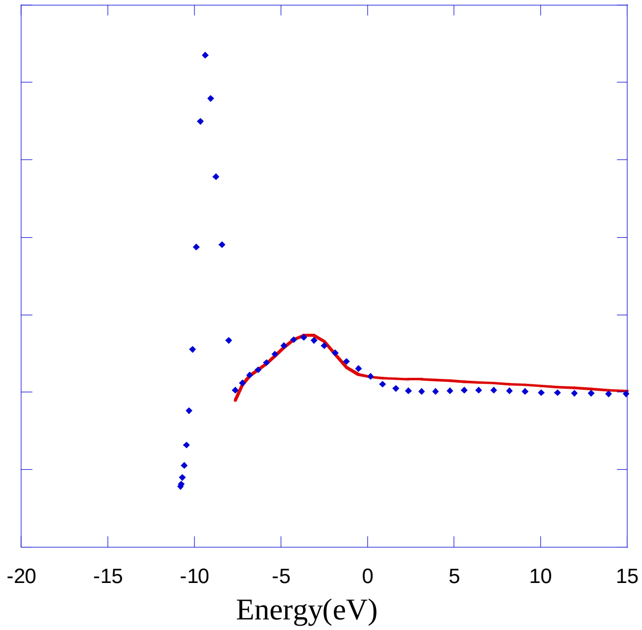
StoBe has three peaks

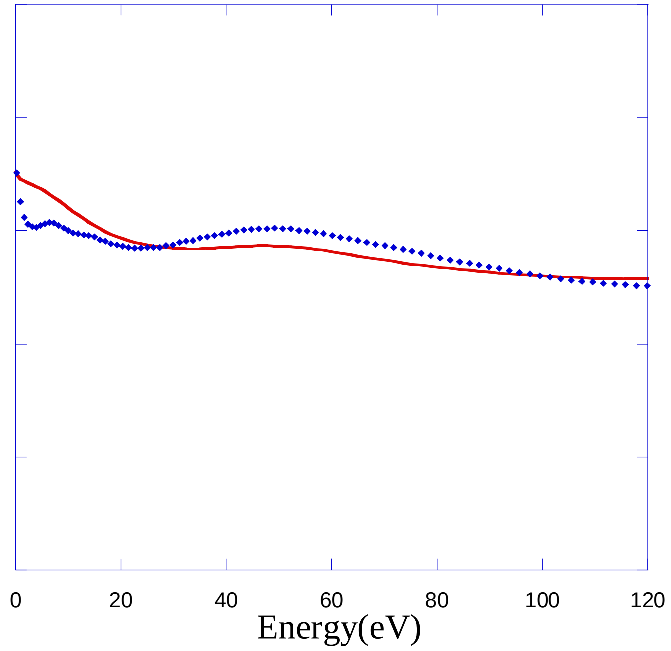
# 0 water model

Excluding the first peak by a step function the quality of the fit increases everywhere



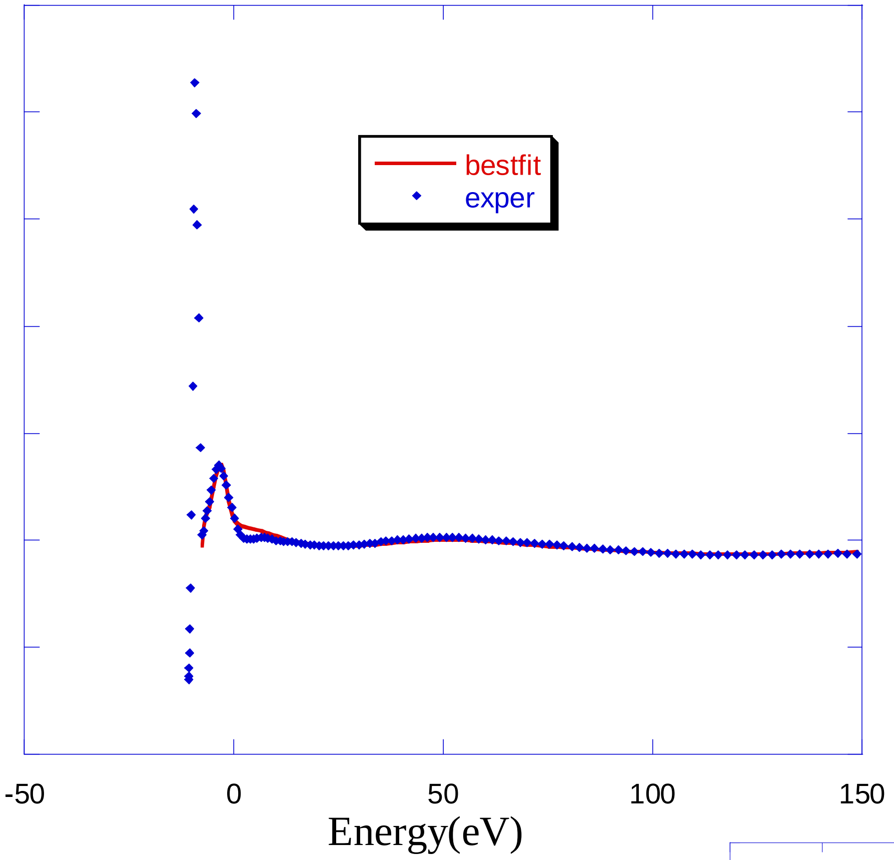
Rsq=5.4



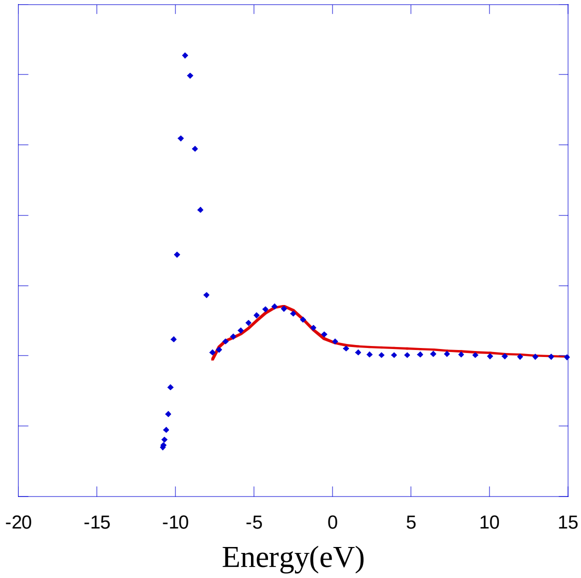


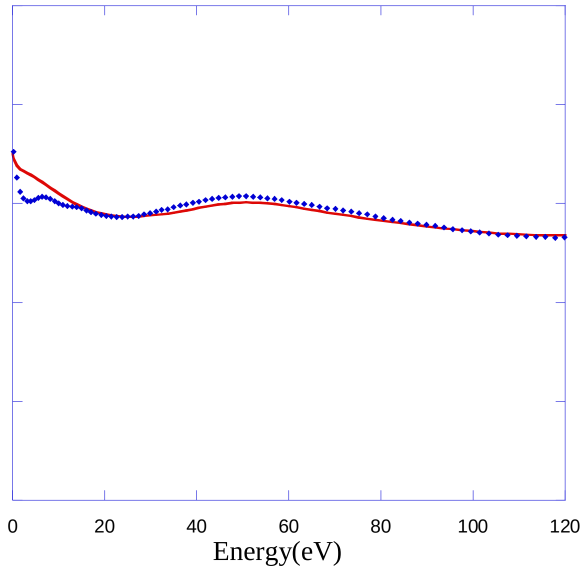
# 1 water model

With 1 water H at 2.7 Å and O at 3.5 Å – the fit is in quite good agreement with the experiment



Rsq=1.71

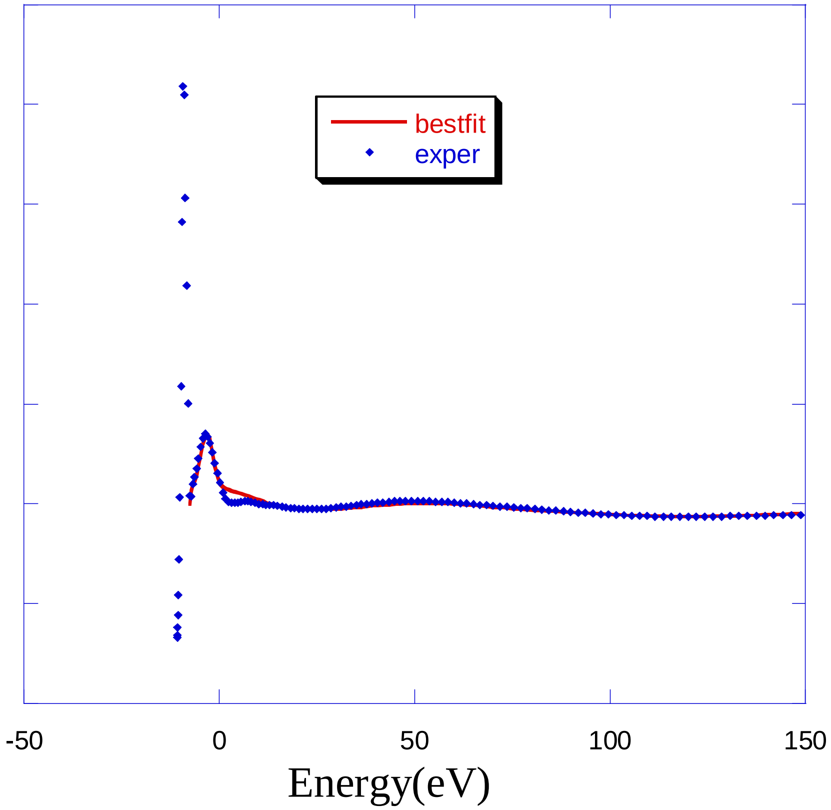


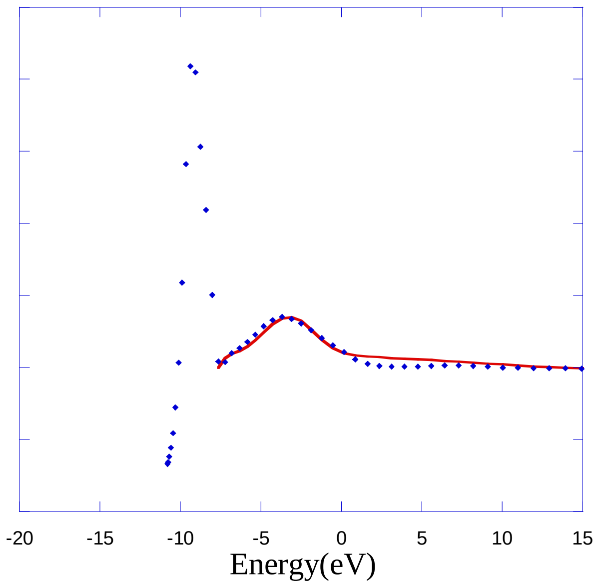


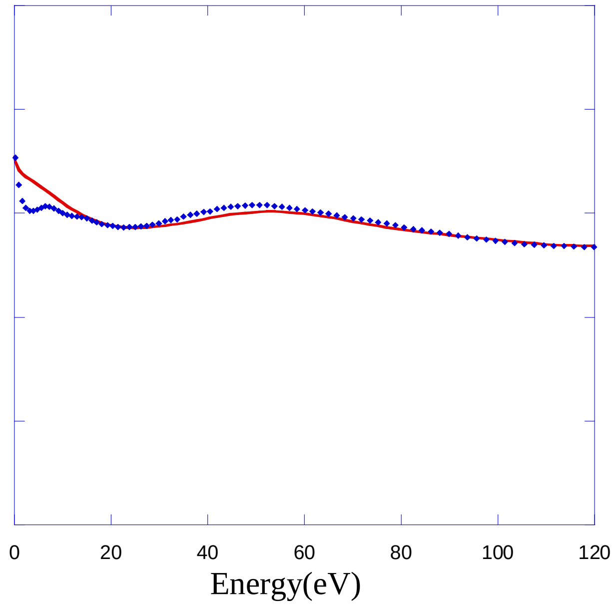
# 3 waters model

This fit is of the same quality of the one of the 1 water model

Rsq=1.80







We cannot discriminate between 1 and 3 waters model but this is not a surprising because in these models we have

1 water

H at 2.7 Å
O at 3.5 Å
H at 4.2 Å

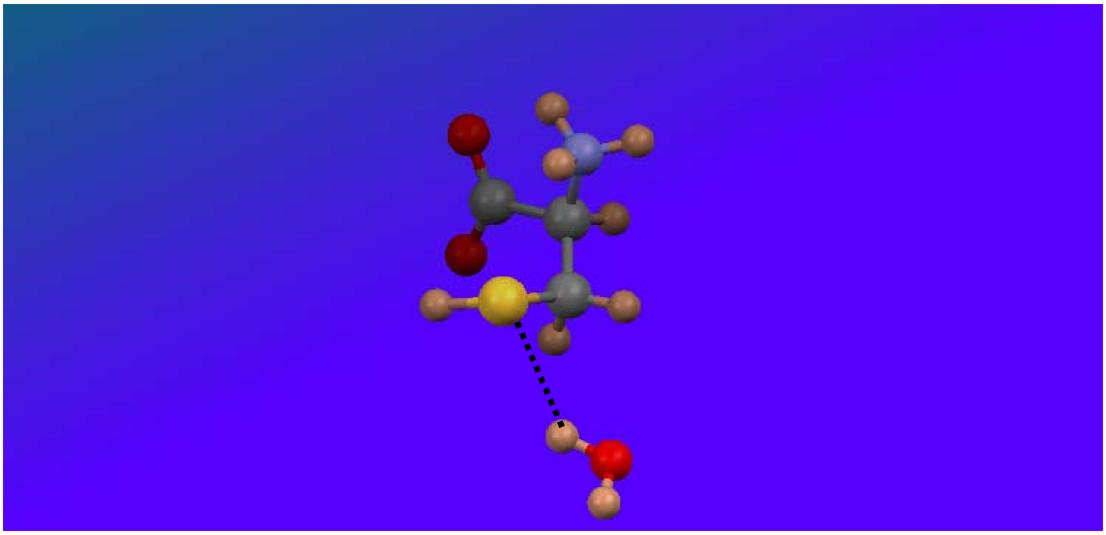
3 waters

H at 2.5 Å
O at 3.4 Å
H at 4.0 Å

H at 3.6 Å
O at 3.8 Å
H at 3.7 Å

H at 5.4 Å
O at 6.3 Å
H at 6.8 Å

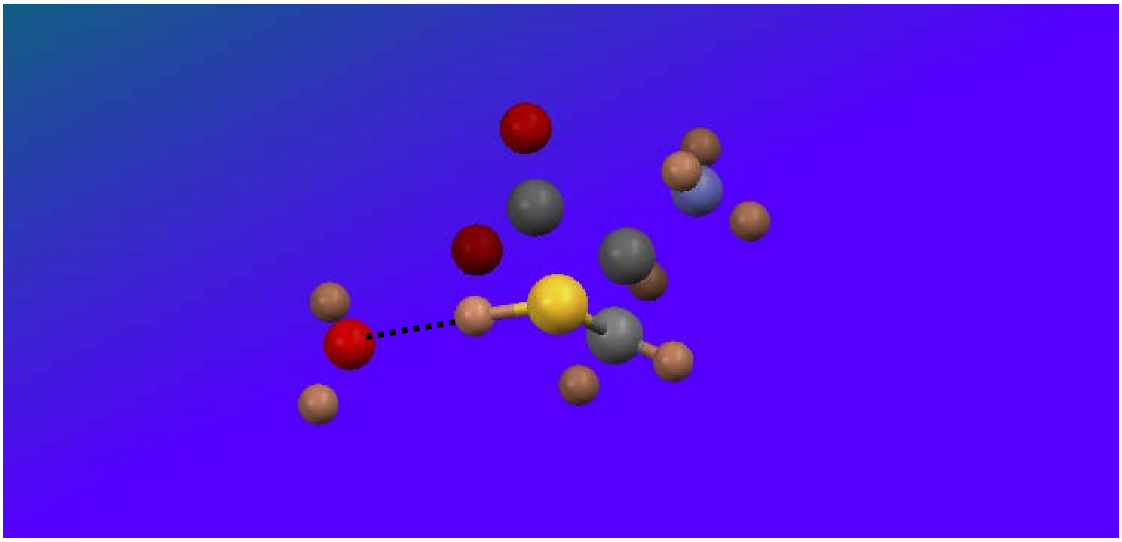
# but if we change the position of the closer water

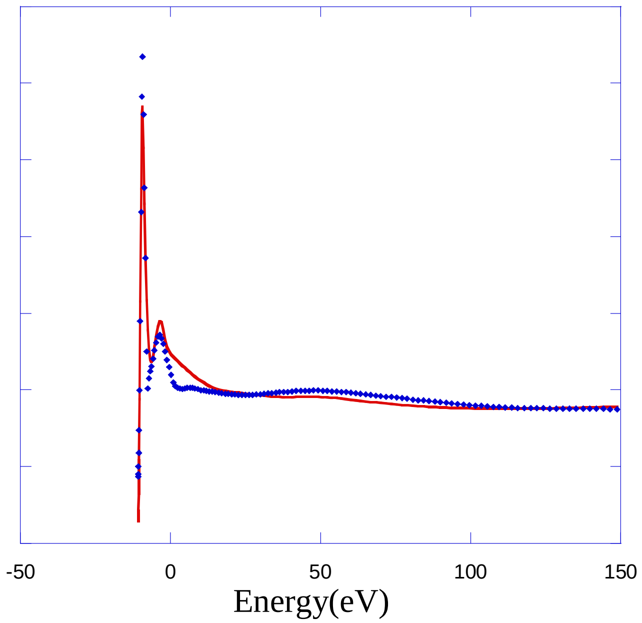


H at 2.7 Å
O at 3.5 Å
H at 4.2 Å

→

H at 3.8 Å
O at 3.3 Å
H at 4.0 Å

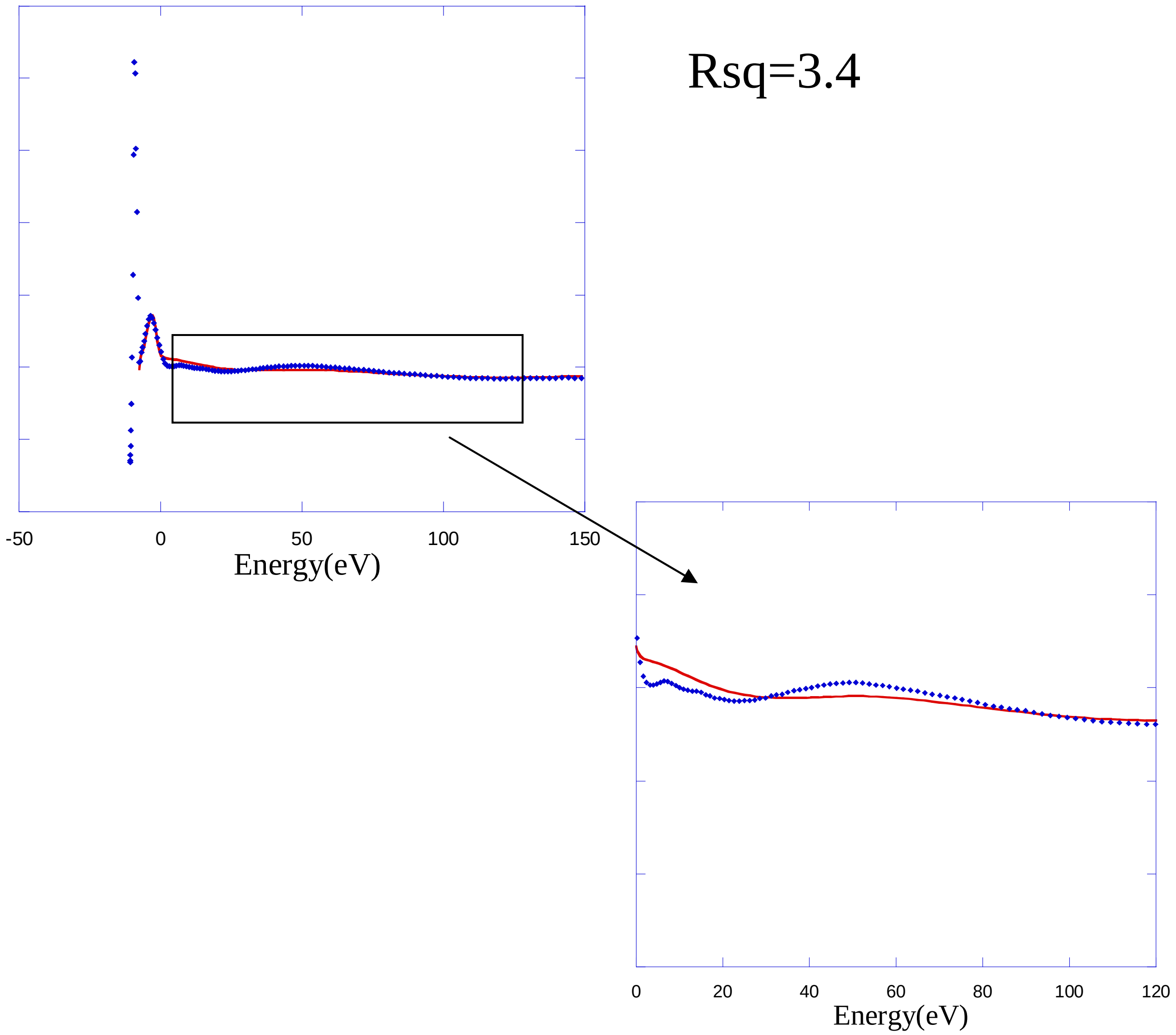




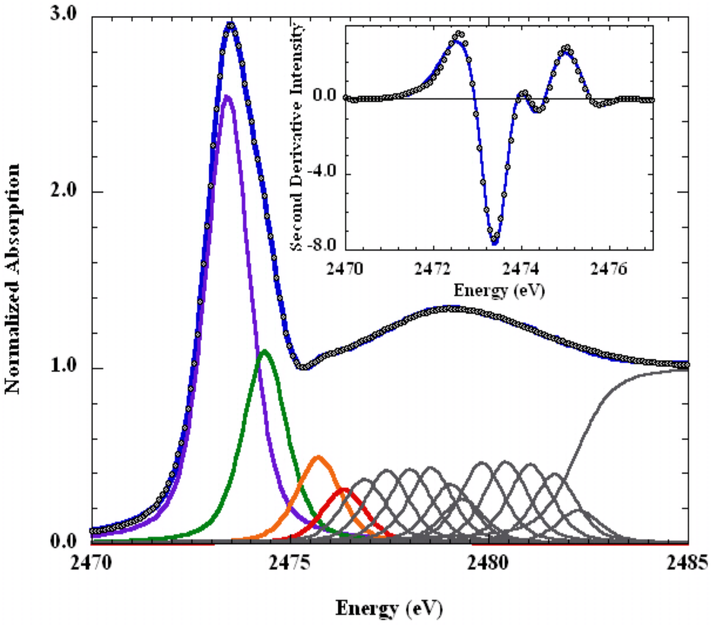
we can discriminate the two cases

Rsq=33.2

Rsq=3.4



# First peak



DFT spin density calculation

| Orbital | eV | S | H | C | Rest |
|---|---|---|---|---|---|
| LUMO | 0.201 | 20.52 | 13.05 | 0.70 | 64.85 |
| LUMO+1 | 0.574 | 34.62 | 3.25 | 10.66 | 52.37 |
| LUMO+2 | 0.737 | 7.72 | 30.18 | 13.53 | 53.70 |
| LUMO+3 | 1.311 | 11.24 | 23.66 | 12.51 | 56.42 |

LUMO and LUMO+1 are dominantly S

they produce the purple contribution of the intense peak

LUMO+2 and LUMO+3 have less S

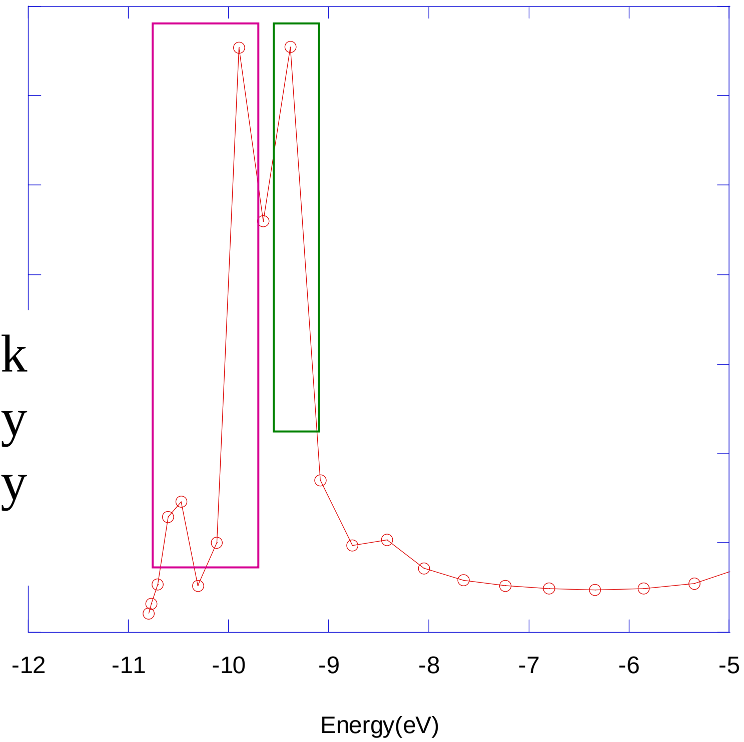
they produce the green contribution of the intense peak

They are heavily mixed with both S-C and S-H The S character in the first peak in the spectrum arises from orbitals with contribution from both S-H and S-C

The energy difference between the center of gravity of the LUMOs, weighted by the percent sulfur contribution, is 0.71 eV, which is a little small compared to the experimental value 0.94 eV

The intensity ratio is 2.9:1, which is close enough to the experimental value 2.3:1

MXAN first peak calculation without any damping – energy separation 0.66 eV



# Some conclusions

The MXAN approach can be used to get structural quantitative information although the presence of some problems at the rising edge.

The full spectrum can be taken into account by a combined DFT – MS approach.

For cysteine there is the need to check better the water positions but we have enough sensitivity to discriminate between models. We are performing MD simulations to go deeper in details