

Calculation for XANES and XAFS: Part I. Real Space Multiple Scattering

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Real Space Multiple Scattering

EXAFS spectrum $\mu(E)$:

$$\mu(E) = \int_{E_f}^{\infty} dE' \tilde{\mu}(E') \frac{\Gamma}{\pi(E - E')^2 + \Gamma^2}$$
$$\tilde{\mu}(E) \propto -\frac{2}{\pi} \text{Im} \langle i | \boldsymbol{\varepsilon} \cdot \mathbf{r}' G(\mathbf{r}', \mathbf{r}, E) \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle$$

$$G(\mathbf{r}', \mathbf{r}, E) = G^C(\mathbf{r}', \mathbf{r}, E) + G^{SC}(\mathbf{r}', \mathbf{r}, E)$$

$$G^{SC} = G^0(1 - tG^0)^{-1}$$

$$G^0(\mathbf{r}', \mathbf{r}, E) = -\frac{e^{ip|\mathbf{r}'-\mathbf{r}|}}{4\pi p|\mathbf{r}'-\mathbf{r}|}$$

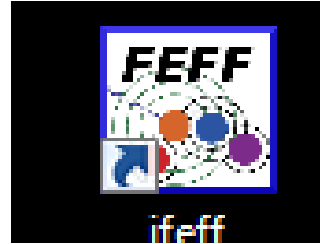
$$G^{SC}(\mathbf{r}', \mathbf{r}, E) = -2p \sum_{L, L', \alpha} R_{L'}^{\alpha}(\mathbf{r}') G_{L', L}^{SC}(E) R_L^{\alpha}(\mathbf{r})$$

$$R_L^{\alpha}(\mathbf{r}) = i^l e^{i\delta} R_l^{\alpha}(r) Y_{lm}(r)$$

$$t_l = e^{i\delta} \sin \delta_l$$

Programs

- Feff9:



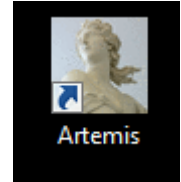
- <http://www.feffproject.org/>

- Operating system:

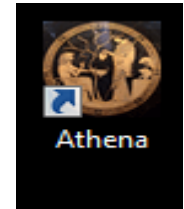
- Microsoft windows (need Java 6)
- unix or linux
- All distances are in angstroms (Å) and energies are in electron-volts (eV).

- Artemis:

- Input file:
 - atom.inp
 - *.cif



- Athena:



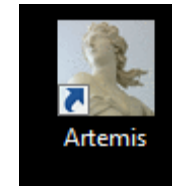
- <http://cars9.uchicago.edu/ifeffit>

- <http://bruceravel.github.io/demeter/>

- Operating system:

- Microsoft windows
- unix or linux

Artemis



- Input file:
 - CdS_Cd.inp
- Command:
 - Run atoms
- Output file:
 - feff.inp
- Preparation for FEFF9 input file:
 - Modified feff.inp

The screenshot shows the Artemis software interface. The 'Atoms' panel displays the following data:

Space group	F	-4	3	m	Core	EI	X	Y	Z	
A	5.83200				1	•	Cd	0.00000	0.00000	0.00000
B	5.83200				2	•	S	0.25000	0.25000	0.25000
C	5.83200									

The 'Data & Paths' panel shows the 'Data' section with 'FEFF0' and 'FEFF1' selected. The 'Fit' panel on the right shows 'Plot selected groups in' with 'k', 'R', and 'q' selected, and 'Plotting options' with 'Magnitude', 'Real part', and 'Imaginary part' selected for both 'Plot in R' and 'Plot in q'. The 'Window', 'Background', and 'Residual' checkboxes are also visible. At the bottom, there are buttons for 'Run Atoms', 'Document: Atoms', and 'Document: Plotting'.

Input File of Artemis for CdS (B3 Structure): CdS_Cd.inp

- title CdS
- space F -4 3 m
- rmax 16. a 5.832 b 5.832 c 5.832
- alpha 90. beta 90. gamma 90.
- core=Cd1
- atoms
- Cd 0.0000 0.0000 0.0000 Cd1
- S 0.2500 0.2500 0.2500 S1

Artemis

- Input file:
 - CPO-27-Zn-H₂O_ChemEurJ_2008(1).cif

The screenshot displays the Artemis software interface. The main window is titled 'Artemis' and contains a menu bar (File, Edit, GDS, Data, Sum, Fits, Theory, Paths, Plot, Help) and a 'Current project' section. The 'Atoms' panel shows a table of atoms with columns for 'Space group', 'Core', 'El', 'X', 'Y', and 'Z'. The 'Data & Paths' panel shows a tree view of data files (FEFF0, FEFF1, FEFF2). The 'Fit' panel includes a 'Plot selected groups in' section with buttons for 'k', 'R', and 'q', and a 'Plotting options' section with radio buttons for 'Magnitude', 'Real part', and 'Imaginary part'. The 'Window' panel has buttons for 'Window', 'Background', and 'Residual'. The 'Document: Atoms' panel has buttons for 'Run Atoms' and 'Document: Atoms'. The status bar at the bottom reads 'You imported a CIF file. Don't forget to set the absorber!'.

Space group	Core	El	X	Y	Z
A 26.25900	1	Zn	0.65055	0.61211	0.6550
B 26.25900	2	C	0.75439	0.68407	0.9282
C 6.66930	3	C	0.45293	0.45952	0.8788
Alpha 90	4	C	0.49720	0.51369	0.8037
Beta 90	5	C	0.54341	0.55452	0.9178
Gamma 120	6	O	0.59659	0.55953	0.4335
Cluster size 7.33623	7	O	0.70467	0.67416	0.8693
Edge K	8	O	0.58319	0.60655	0.8290
Shift vector 0	9	O	0.65782	0.54430	0.8006
0	10	H	0.49610	0.52300	0.6560
0	11	H	0.62900	0.51220	0.8010
0	12	H	0.67000	0.54900	0.9170
	13	O	0.69800	0.55100	0.1939
	14	H	0.70900	0.58190	0.2582

feff.inp vs. Modified feff.inp

feff.inp

- TITLE CdS
- HOLE 1 1.0 * Cd K edge (26711.0 eV), second number is S0^2
- * mphase,mpath,mfeff,mchi
- CONTROL 1 1 1 1
- PRINT 1 0 0 0

- RMAX 16.0

- *CRITERIA curved plane
- *DEBYE temp debye-temp
- NLEG 4

- POTENTIALS
- * ipot Z element
- 0 48 Cd
- 1 48 Cd
- 2 16 S

- ATOMS * this list contains 705 atoms
- * x y z ipot tag distance
- 0.00000 0.00000 0.00000 0 Cd1 0.00000
- 1.45800 1.45800 1.45800 2 S1_1 2.52533
- -1.45800 -1.45800 1.45800 2 S1_1 2.52533

Modified feff.inp

- TITLE CdS
- HOLE 1 1.0 * Cd K edge (26711.0 eV), second number is S0^2
- * mphase,mpath,mfeff,mchi
- CONTROL 1 1 1 1 1 1
- PRINT 0 0 0 0 0 0
- RMAX 16.0
- * This feff6 input file was generated by Artemis 0.8.012
- LDOS -10 50 0.1
- SCF 3.7 0 30 0.05 10
- FMS 5.1 1
- *AFOLP 1.0
- XANES 6.0 0.05
- *CRITERIA curved plane
- *DEBYE temp debye-temp
- NLEG 4
- POTENTIALS
- * ipot Z element
- 0 48 Cd
- 1 48 Cd
- 2 16 S

- ATOMS * this list contains 705 atoms
- * x y z ipot tag distance
- 0.00000 0.00000 0.00000 0 Cd1 0.00000
- 1.45800 1.45800 1.45800 2 S1_1 2.52533

Feff Input Cards

• EDGE

- EDGE L3 0.0
- S02 0.0
- S02 is a square of determinant of overlap integrals for core orbitals calculated with and without core hole.
- If S20 is less than 0.1, S20 will be estimated from atomic overlap integrals.

• COREHOLE

- COREHOLE RPA (RPA screened core hole)
- COREHOLE none (No core hole)
- COREHOLE FSR *or omit the card
 - a final state rule (non-screened) core hole

• LDOS (81 points limit)

- LDOS -20. 20. 0.05 *first run, -20->20 eV
- LDOS 20. 60. 0.05 *second run, 20->60eV

• REAL

- do a real-space calculation (the default mode).

• AFOLP

- AFOLP 1.0 (touching muffin-tins)
- Automatic overlapping of muffin tin spheres:
Default folpx=1.15

• XANES + FMS

- XANES 6 0.05 0.3 (xkmax, xkstep, vixan)
 - If FMS calculations are being made, note that these are not accurate beyond about $k = 6$;
- SCF 3.7 0 30 0.05 10
 - SCF rfms1 [lfms1 nscmt ca nmix]
 - By default: lfms1=0, nscmt=30, ca=0.2, nmix=1
- FMS 5.1 1
 - FMS rfms [lfms2 minv toler1 toler2 rdirac]
 - Gtot = Gfms + G0tiG0 + G0tiG0tjG0 +
 - full multiple scattering, appropriate for near-edge absorption spectra

• EXAFS + RPATH

- EXAFS 20 (k edge up to 20 Å⁻¹)
- RPATH 10

• DEBYE

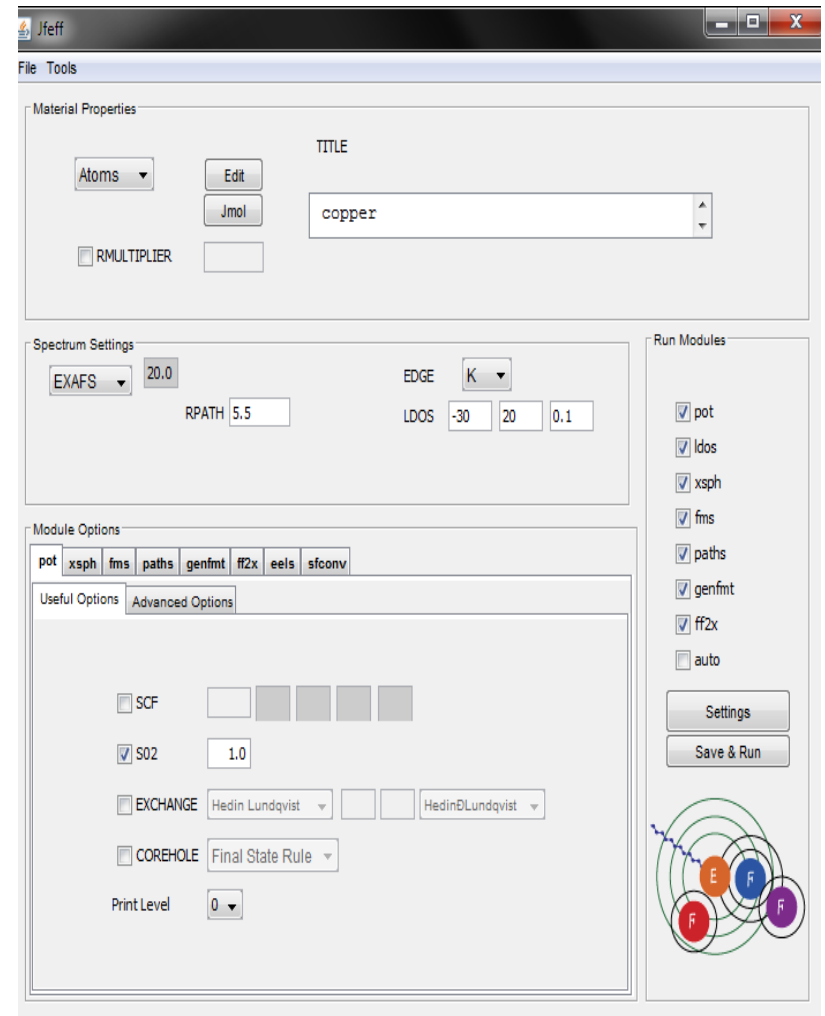
- DEBYE 150 176 (temp Debye-temp)

• EXCHANGE

- EXCHANGE 0 2. 1.
 - *Hedin-Lundqvist -2eV edge shift and 1eV expt broadening (default)
- EXCHANGE 1 3. 5.
 - *Dirac-Hara exchange -3 eV edge shift and 5 eV optical potential

FEFF 9

- <http://www.feffproject.org>
- <http://cars9.uchicago.edu/ifeffit>
- Input file: feff.inp (with no symmetry requirements)
- Output files:
 - xmu.dat:
 - column 4: total EXAFS spectrum $\mu(E)$.
 - column 6: EXAFS fine structure χ .
 - column 5: atomic background μ_0 .
 - ldos00.dat
 - ldos01.dat



Cloud computing is not a free service.
So run in PC or workstation.

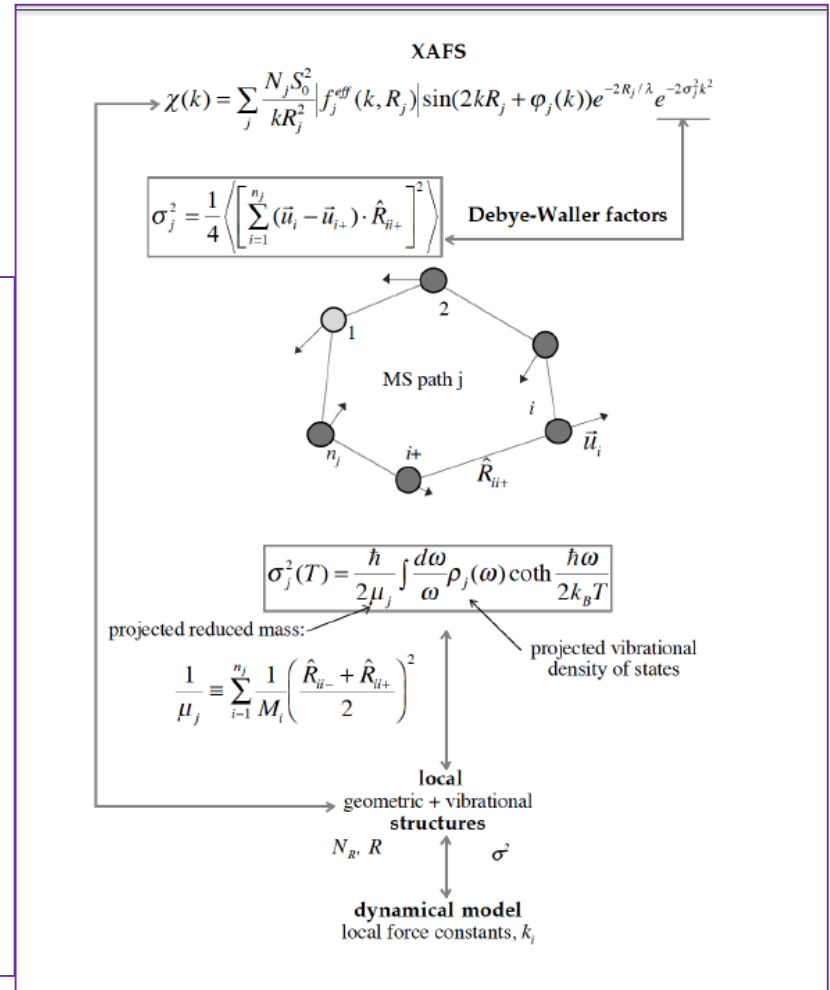
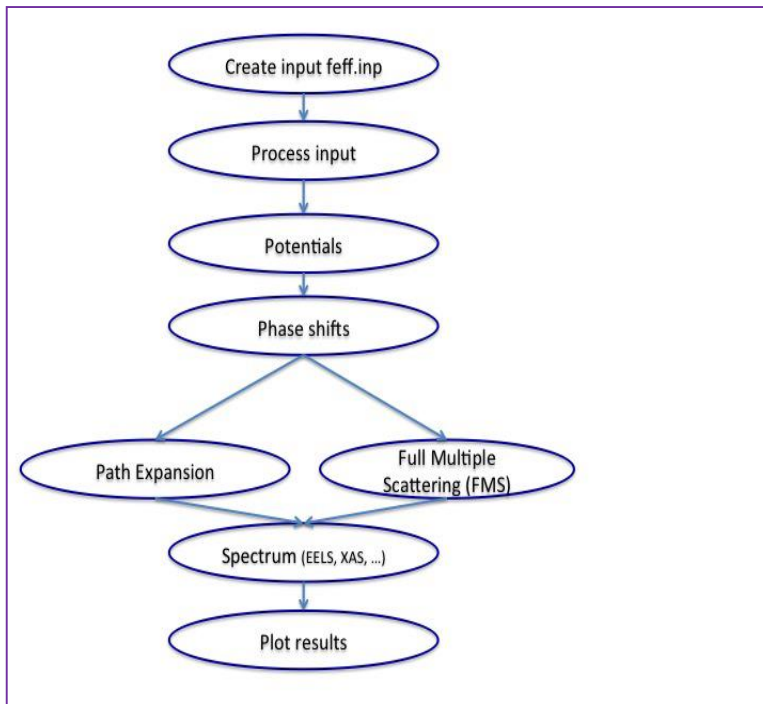
Flow Charts of feff

Debye-Waller factor

EXAFS regime: important.

XANES regime:

may be less sensitive.



XAFS (X-ray Absorption Fine Structure)

- XAFS fine structure $\chi(k)$:

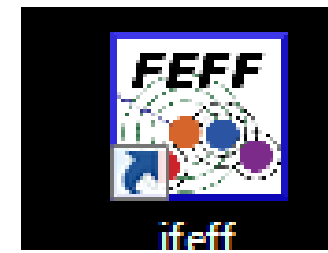
$$\chi(k) = \sum_j \frac{N_j S_j^2}{k R_j^2} |f_j^{eff}(k, R_j)| \sin(2kR_j + \varphi_j(k)) e^{-2R_j/\lambda} e^{-2\sigma_j k^2}$$

- Debye-Waller factor

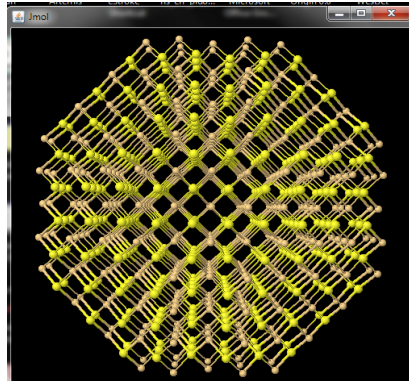
$$\sigma_j^2 = \frac{1}{4} \left[\sum_{i=1}^{n_j} (\vec{u}_i - \vec{u}_{i+}) \hat{R}_{ij+} \right]^2$$

- To calculate Debye-Waller factors from a dynamical matrix (or matrix of force constants or Hessian matrix) using the Lanczos recursive algorithm:
 - DEBYE Temp Debye_Temp [DW_Opt [dymFile DMDW_Order DMDW_Type DMDW_Route]]

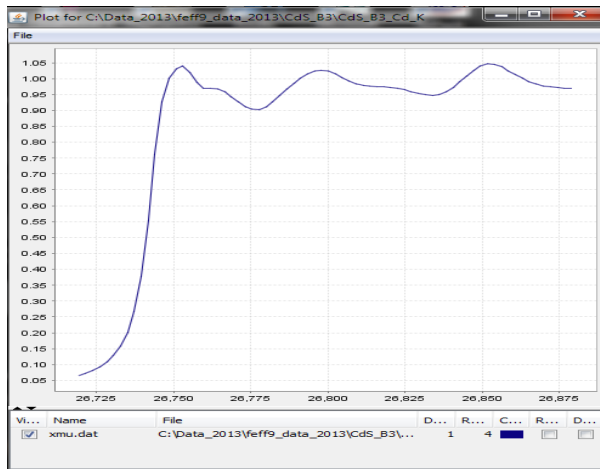
FEFF 9



Jmol



Save & Run
Tools: new plot



Material Properties

Atoms: TITLE: CdS

RMULTIPLIER

Spectrum Settings

XANES: EDGE: K

FMS: LDOS:

Module Options

pot xsph fms paths genfmt ff2x eels sfconv

Useful Options: SCF (3.7, 0, 30, 0.05, 10) S02 (1.0)

EXCHANGE: HedIn Lundqvist HedInDLundqvist

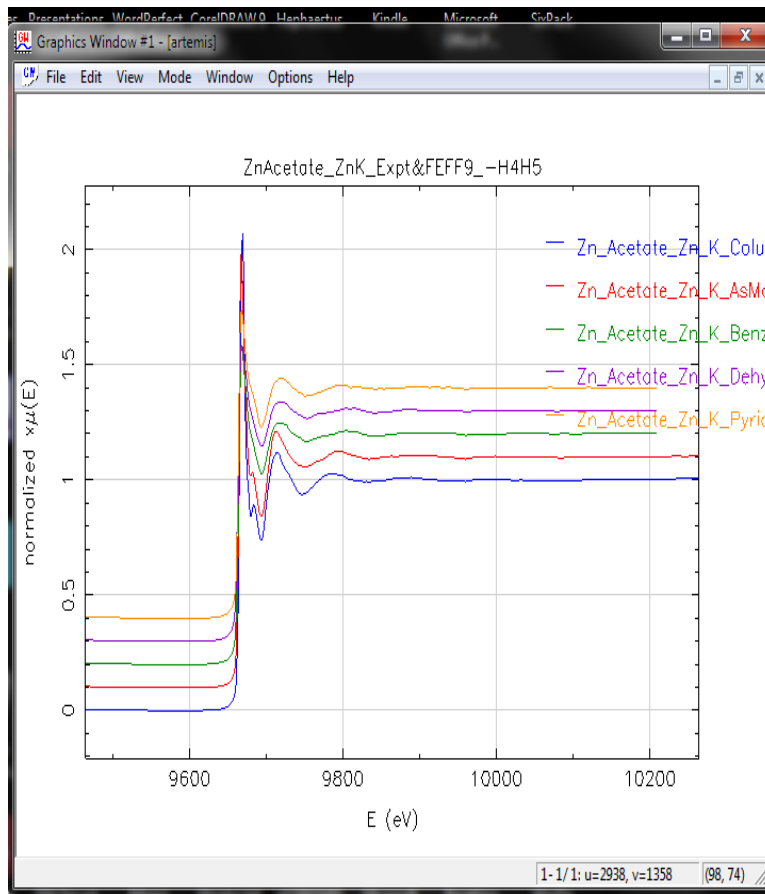
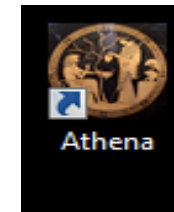
COREHOLE: Final State Rule

Print Level:

Run Modules

- pot
- ldos
- xsph
- fms
- paths
- genfmt
- ff2x
- auto

Athena



Athena

File Edit Group Values Plot Mark Data Merge Analysis Settings Help

Project _Zn_K_EXAFS/ZnAcetate_ZnK_Expt&FEFF9_-H4H5.prj

Current group Zn_Acetate_Zn_K_Colume1.txt

File: n_Acetate_Analysis_2013/Zn_Acetate_Zn_K_Colume1.txt

Z: Zn Edge: K E shift: 0 Importance: 1

Background removal Show additional parameters

E0: 9664.712 Rbkg: 1.0

k-weight: 2 Edge step: 0.99311 fix step

Pre-edge range: -150 to -30

Normalization range: 150 to 534.9852

Spline range: k: 0.0 to 12.910

E: 0.000 to 635.003

Forward Fourier transform

k-range: 2 to 10.91

dk: 1 window type: hanning

Phase correction: no arbitrary k-weight: 0.5

Backward Fourier transform

R-range: 1 to 3

dr: 0.0 window type: hanning

Plotting parameters

plot multiplier: 1 y-axis offset: 0.0000

plotting in energy from group 'Zn_Acetate_Zn_K_Colume1.txt' ... done!

UI

- Zn_Acetate_Zn_K_Colume1
- Zn_Acetate_Zn_K_AsMade
- Zn_Acetate_Zn_K_Benzene
- Zn_Acetate_Zn_K_Dehydra
- Zn_Acetate_Zn_K_Pyridin.t
- xmu.dat

E k R q kq

E k R q

0 1 2 3 kw

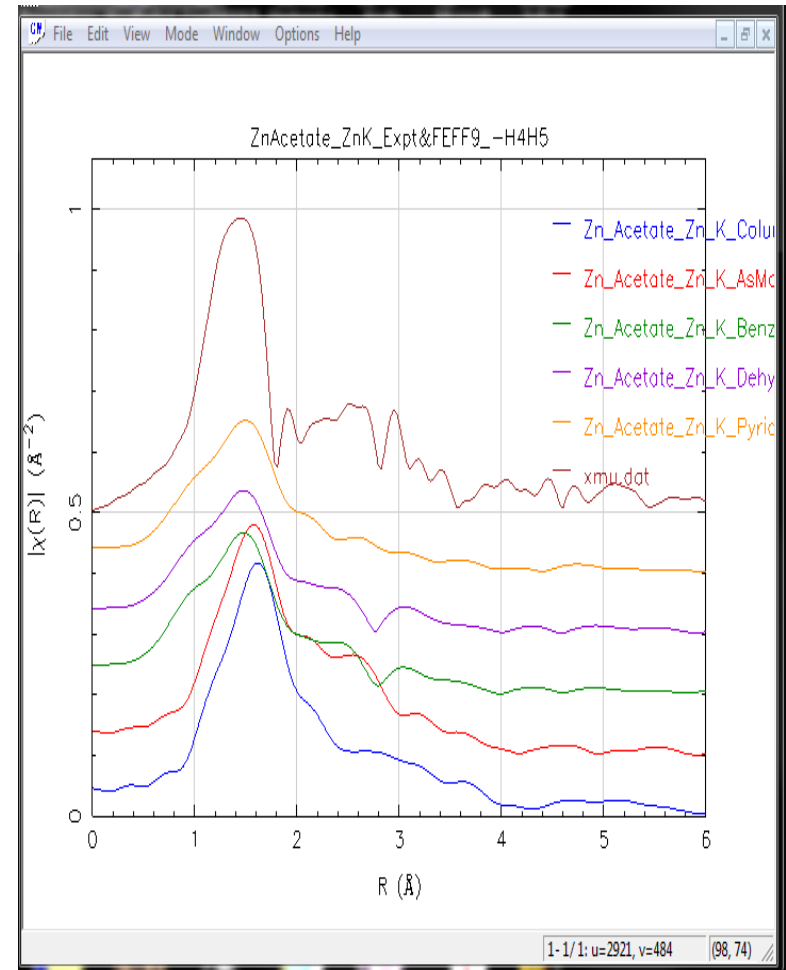
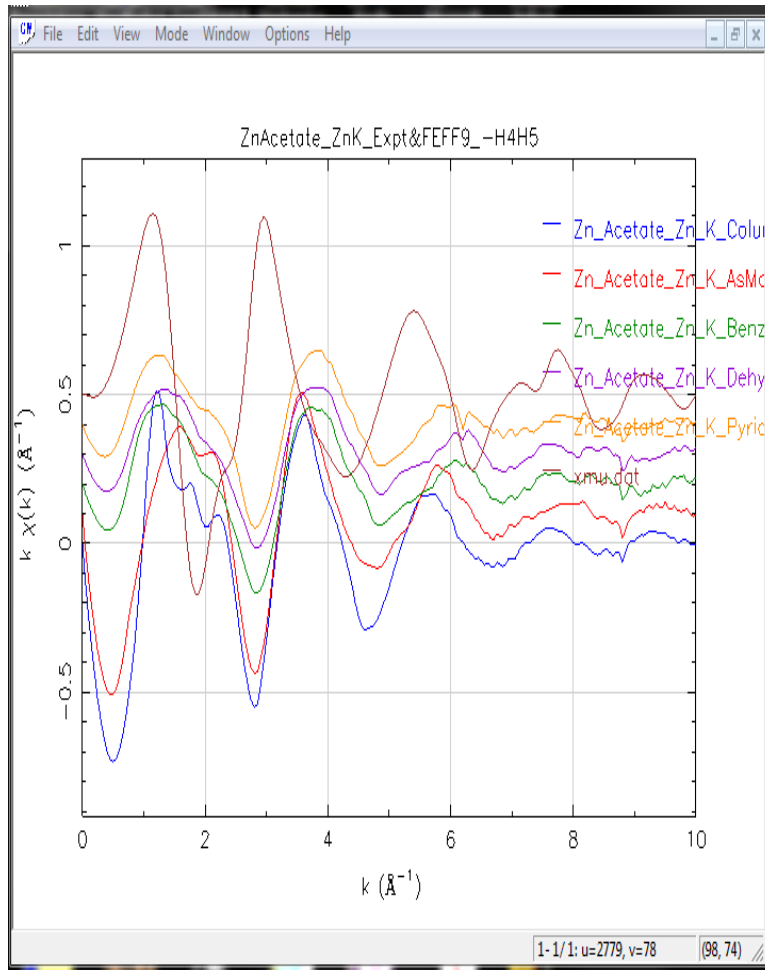
v Plotting options

E k R q Stack Ind PF

- mu(E)
- background
- pre-edge line
- post-edge line
- Normalized
- Derivative

Emin: -200 Emax: 600

Athena Plots



References

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[doi:10.1107/S0909049505012719](https://doi.org/10.1107/S0909049505012719)
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