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

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Sham's Group Meeting (Oct. 16, 2013)

Real Space Multiple Scattering

EXAFS spectrum μ(E):

$$\mu(\mathrm{E}) = \int_{Ef}^{\infty} dE'\, \tilde{\mu}(E')\, \frac{\Gamma}{\pi(E-E')^2 + \Gamma^2}$$

$$\tilde{\mu}(E) \propto -\frac{2}{\pi}\,\mathrm{Im}\left\langle i\left|\varepsilon\cdot\mathbf{r}'G(\mathbf{r}',\mathbf{r},E)\varepsilon\cdot\mathbf{r}\right|i\right\rangle$$

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

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

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

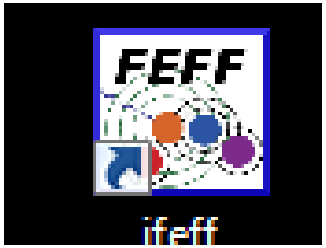
$$G^{SC}(\mathbf{r}',\mathbf{r},E) = -2p\sum_{L,L',\alpha} R_{L'}{}^{\alpha}(\mathbf{r}')\, G_{L'C,LC}{}^{SC}(E)\, R_{L'}{}^{\alpha}(\mathbf{r})$$

$$R_{L}{}^{\alpha}(\mathbf{r}) = i^{l}e^{i\delta_l}R_{l}{}^{\alpha}(r)Y_{lm}(r)$$

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

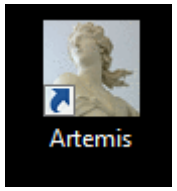
Programs

- Feff9:

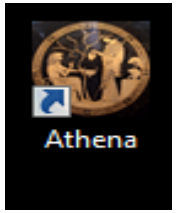


- http://www.feffproject.org/
- Operating system:
  - Microsoft windows (need Java 6)
  - unix or linux
  - All distances are in angstroms (A) and energies are in electron-volts (eV).

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

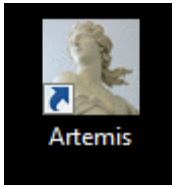


- Athena:

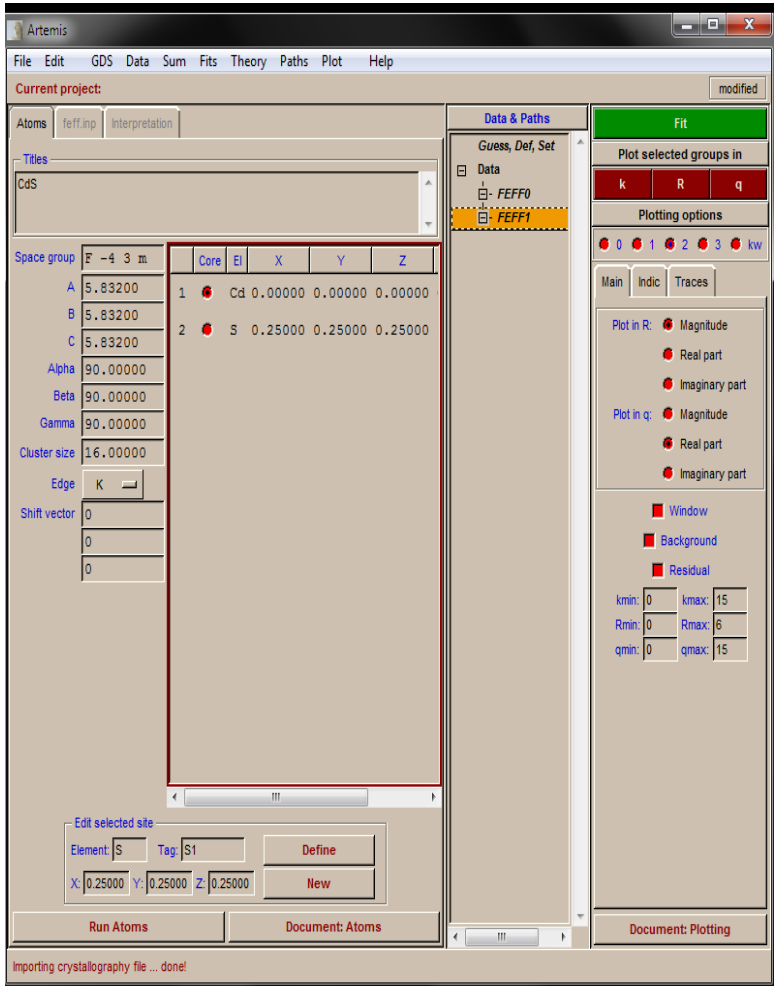


- http://cars9.uchicago.edu/ifeffit
- http://bruceravel.github.io/demeter/
- Operating system:
  - Microsoft windows
  - unix or linux

Artemis



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

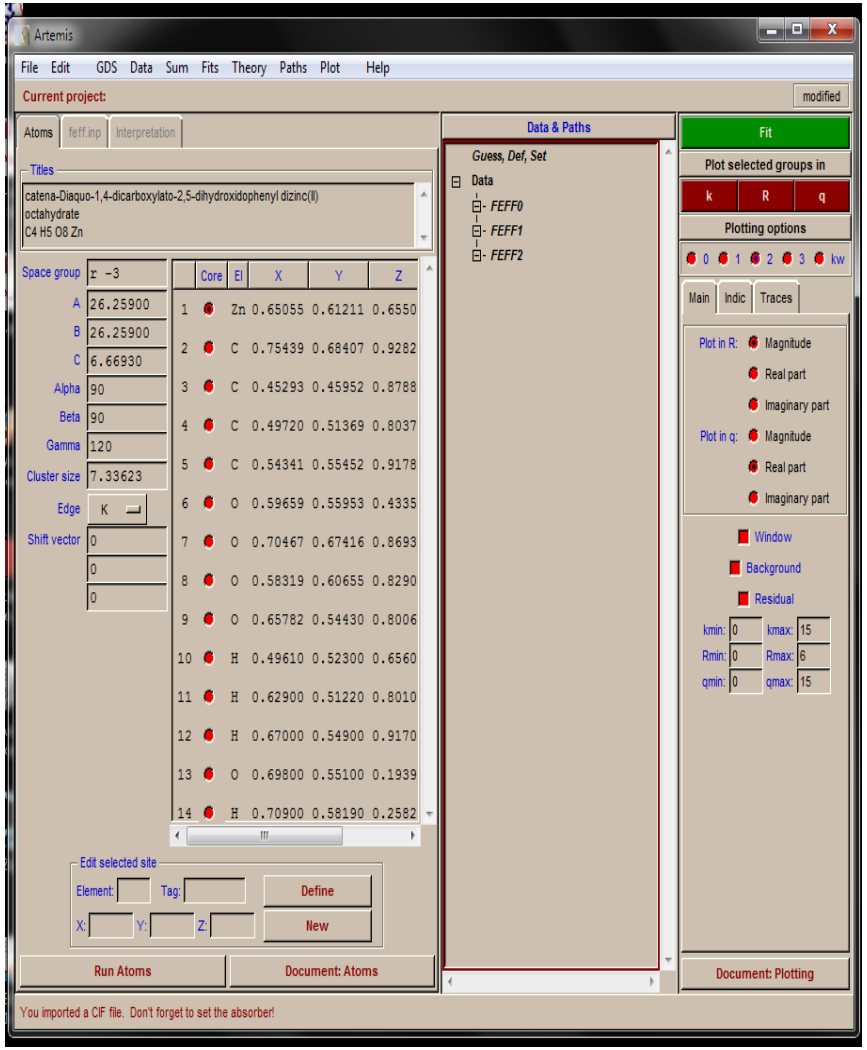


Input File of Artemis for CdS (B3 Structure): CdS_Cd.inp

- 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



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 c ore 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 rdirec]

    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 μ(E).
    - column 6: EXAFS fine structure χ .
    - column 5: atomic background μ0.
  - ldos00.dat
  - ldos01.dat

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

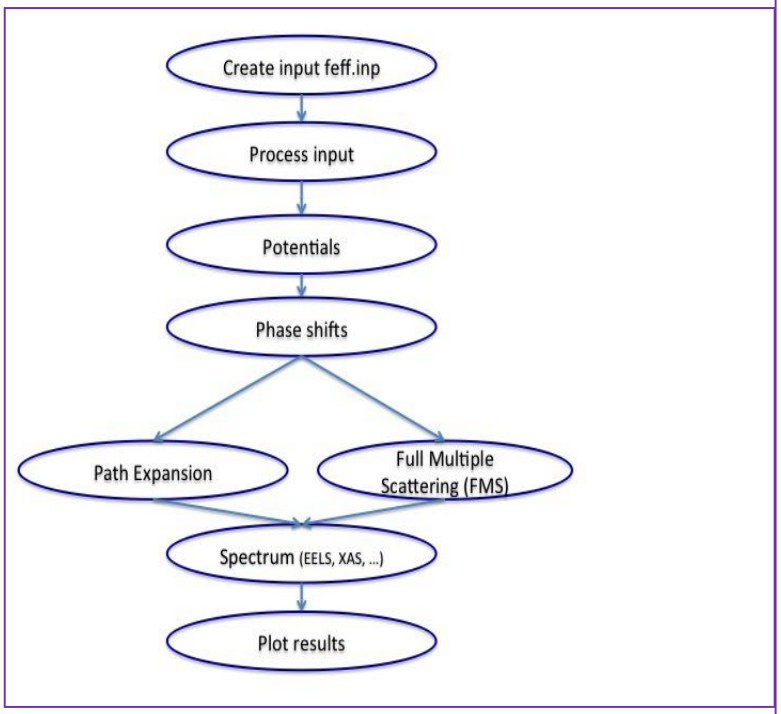
Flow Charts of feff

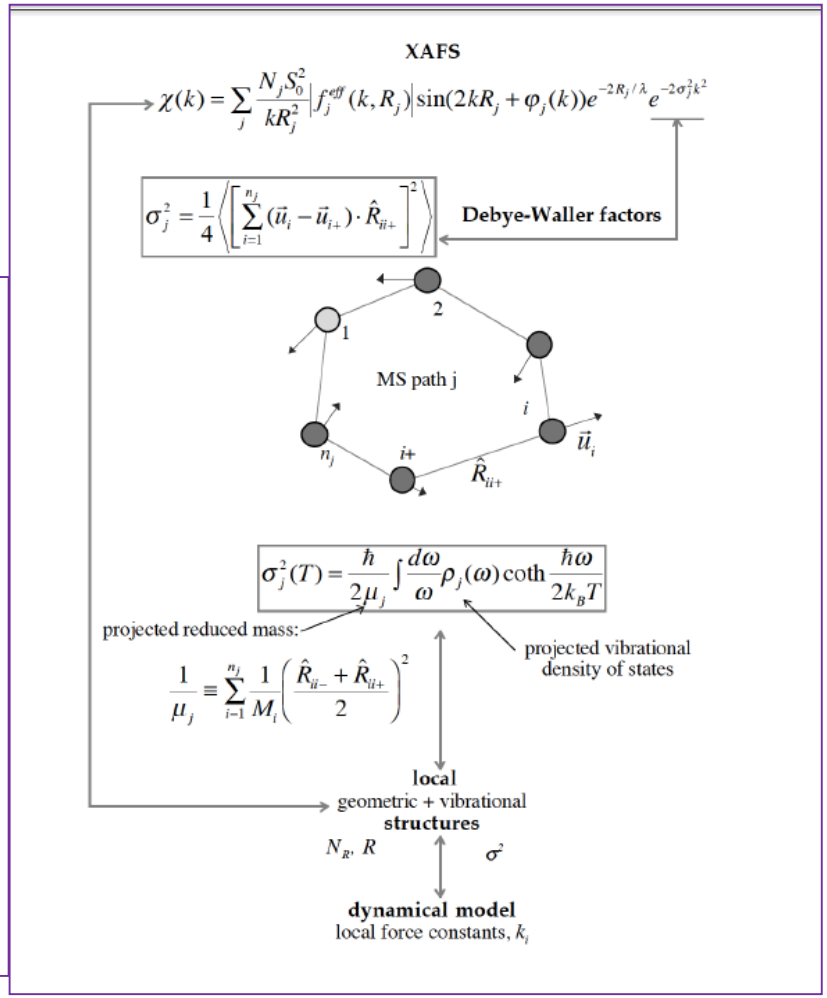
Debye-Waller factor

EXAFS regime: important.

XANES regime:

may be less sensitive.





XAFS (X-ray Absorption Fine Structure)

- XAFS fine structure χ(k):

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

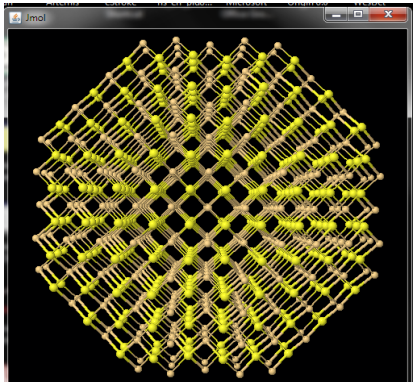
- Debye-Waller factor

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

- 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]]

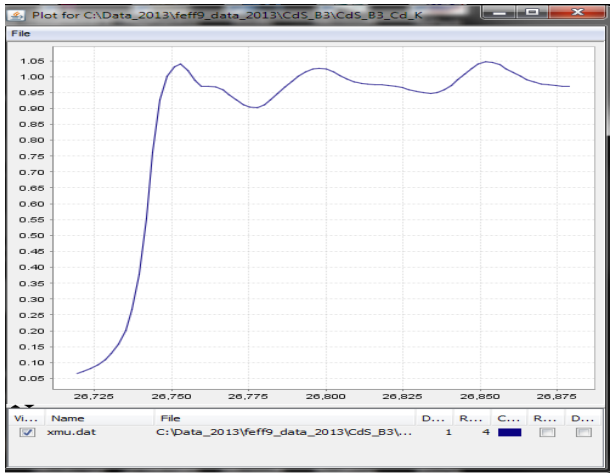
FEFF 9

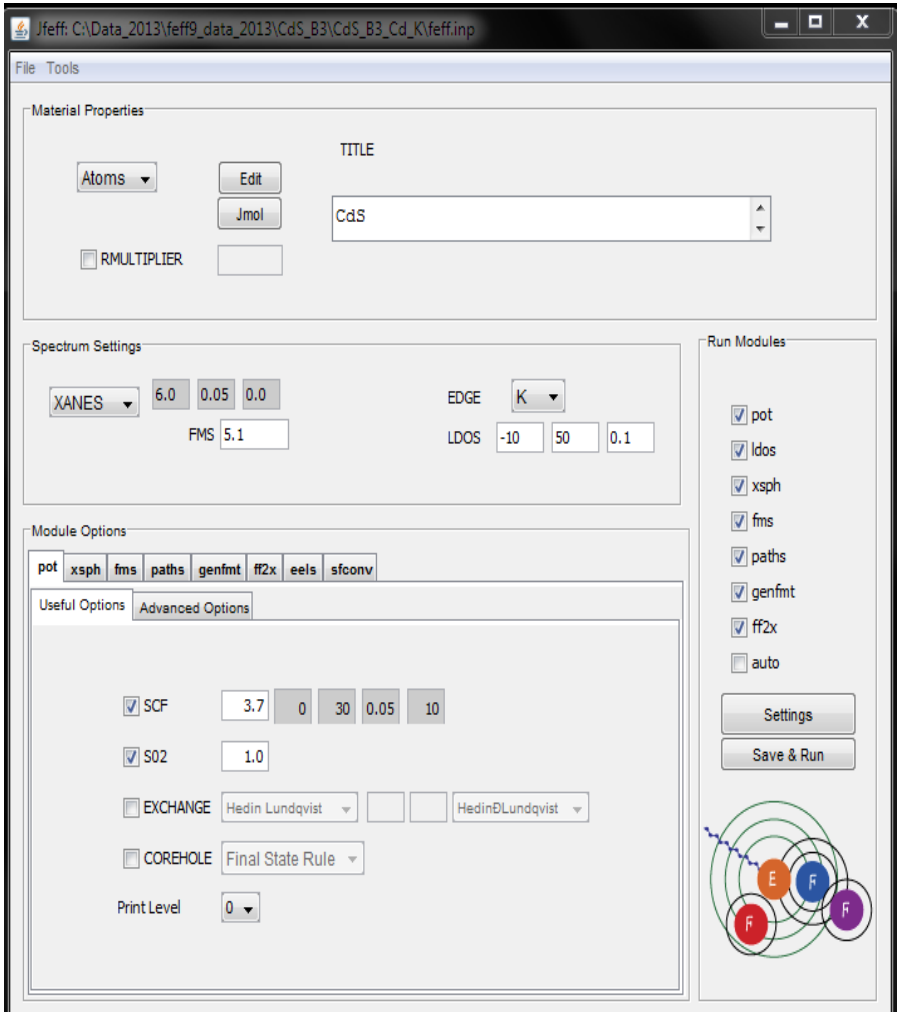
Jmol



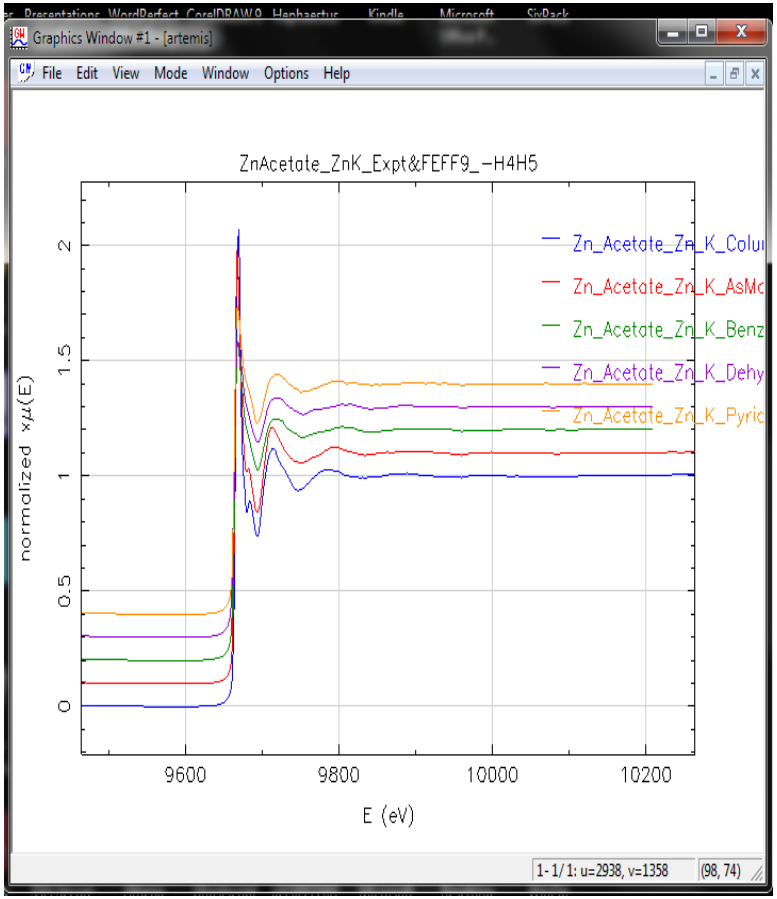
Save & Run

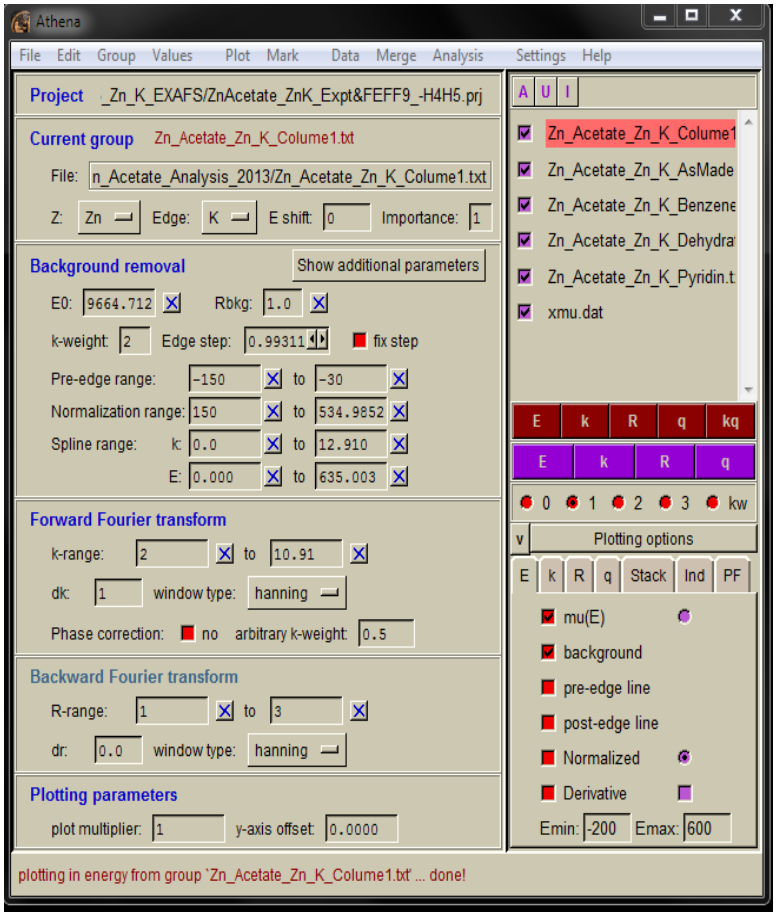
Tools: new plot



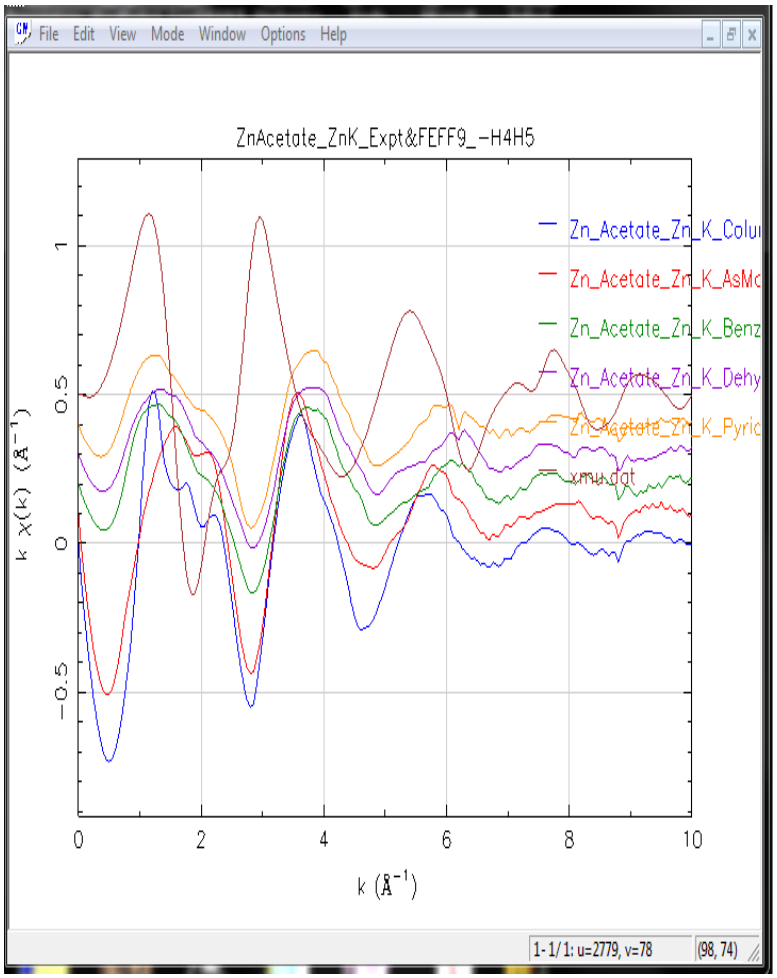


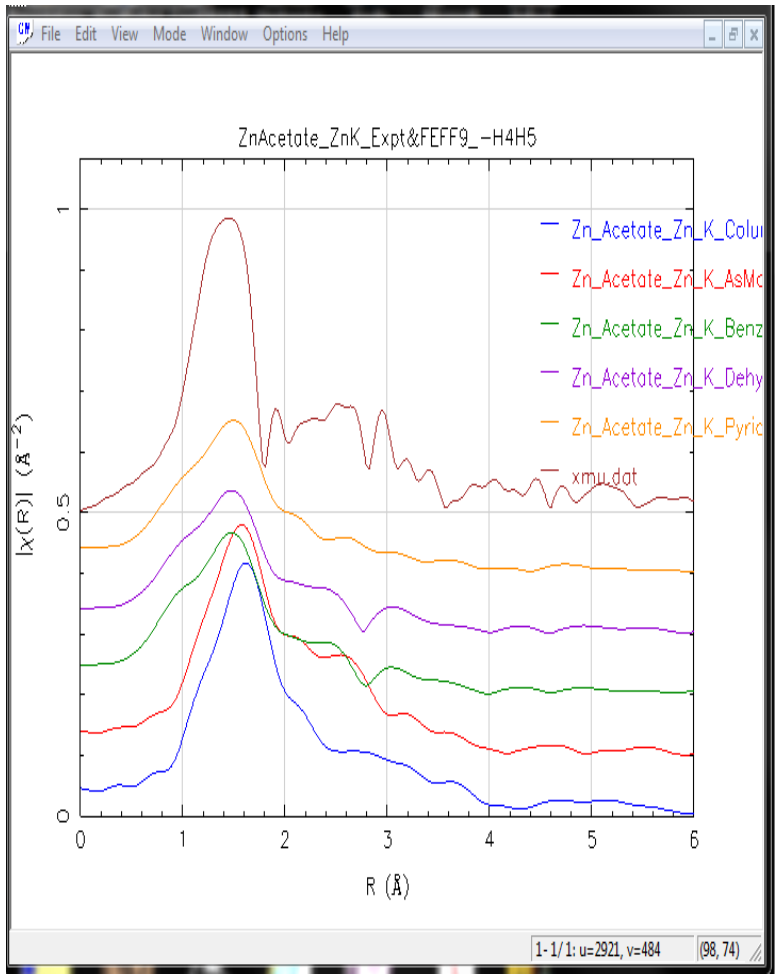
Athena


Graphics Window #1 - [artemis]
File Edit View Mode Window Options Help
ZnAcetate_ZnK_Expt&FEFF9_-H4H5
Zn_Acetate_Zn_K_Colu
Zn_Acetate_Zn_K_AsMc
Zn_Acetate_Zn_K_Benz
Zn_Acetate_Zn_K_Dehy
Zn_Acetate_Zn_K_Pyric
normalized xμ(E)
0
0.5
1
1.5
2
9600
9800
10000
10200
E (eV)
1-1/1: u=2938, v=1358
(98, 74)


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
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
Plotting options
E k R q Stack Ind PF
mu(E)
background
pre-edge line
post-edge line
Normalized
Derivative
Emin: -200 Emax: 600
plotting in energy from group 'Zn_Acetate_Zn_K_Colume1.txt' ... done!

Athena Plots





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