

# S K-edge XAS: Theory and Data Collection

(Scope, Advantages and Pitfalls)

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Stanford Synchrotron Radiation Lightsource

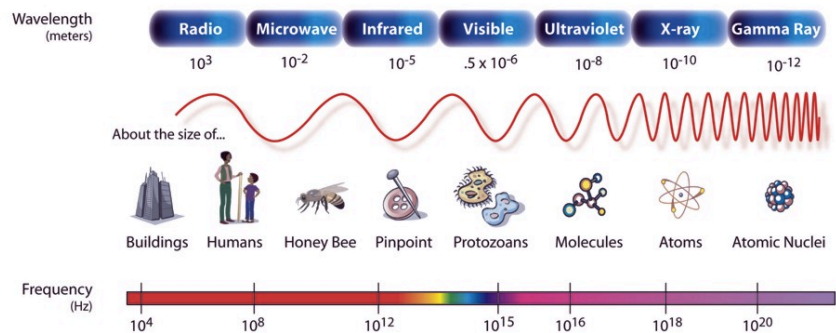
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February 4, 2010



## Electromagnetic Spectrum

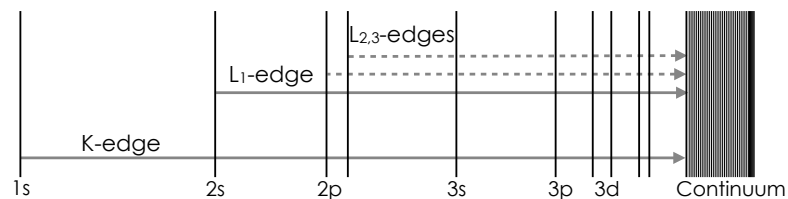
Spectroscopy	EPR,NMR Endor	Rotational	Raman	CD,MCD,Abs	PES	XPS, XAS	Mossbauer
Time scale(s)	$10^{-1}$ - $10^{-5}$	$10^{-4}$ - $10^{-9}$	$10^{-11}$ - $10^{-14}$	$10^{-14}$ - $10^{-16}$		$10^{-16}$ - $10^{-17}$	$10^{-5}$ - $10^{-8}$



## X-ray Absorption Edge

An XAS edge discontinuity results when a core electron absorbs energy equal to or greater than its binding energy.

Edges are labeled according to the shell the core electron originates from.

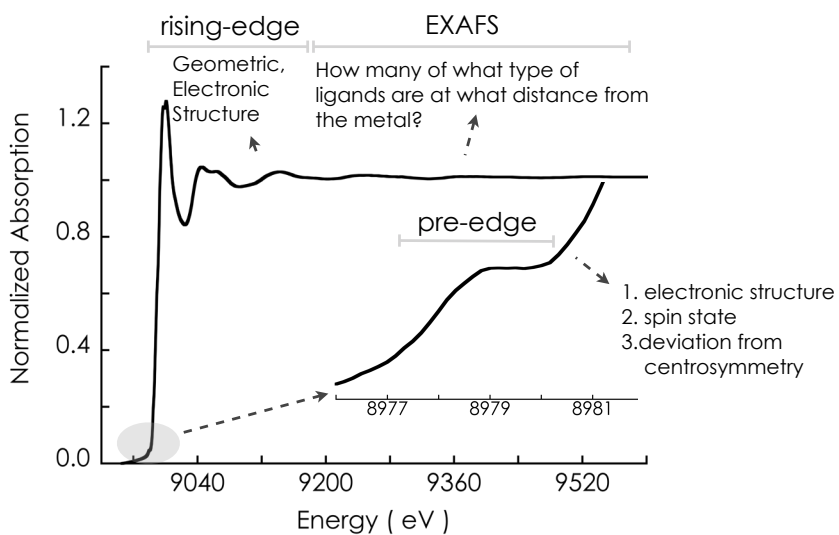


S K-edge ~2400 eV	Cu K-edge ~9000 eV	Fe K-edge ~7000 eV
S L-edges ~160-230 eV	Cu L-edges ~930 eV	Fe L-edges ~720 eV
	Cu M-edges ~70-120 eV	Fe M-edges ~50-100 eV

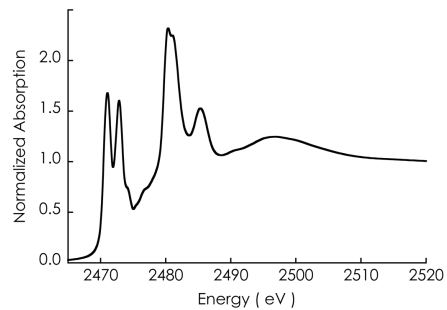
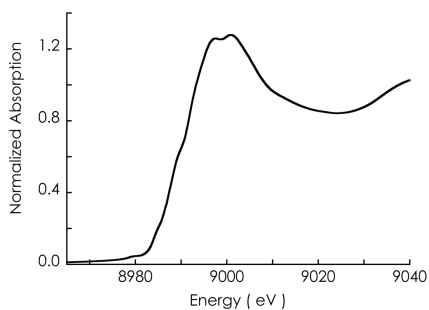
XAS is an element specific technique



## Regions of the XAS Spectra



## Metal K- vs S K-Edge



1. Pre-edge feature is dipole-forbidden : 1s to 3d transition

2. At higher energy the peaks are broader. e.g at 9000 eV (Cu), the natural width is 1.55 eV

1. Pre-edge feature is dipole-allowed : 1s to 3p&4p transition

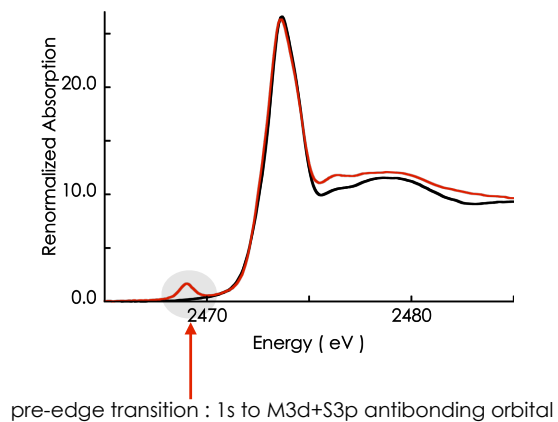
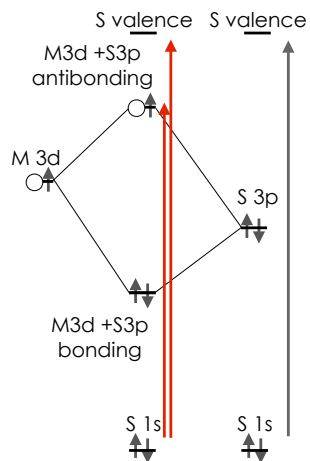
2. At S K-edge energies the peaks are sharper. the natural width is 0.59 eV

The result is an inherently sharper, feature-rich S K-edge spectrum



## S in Open Shell Environments

In molecules where the S 3p orbital(s) gains "hole" character, a low-energy pre-edge transition may be observed.



## Pre-edge Analysis

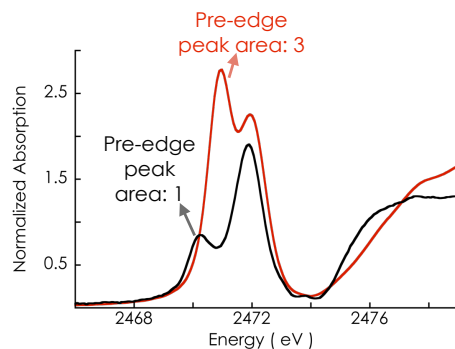
The Pre-edge energy position and intensity can be used to determine

1. Covalency &/or Bond Strength
2. Ligand Field
3. Effective Charge on S

In this Example:

Red is 3 times more intense than Black:  
Red probably has a stronger Metal-S overlap.

Red pre-edge is higher in energy: Red probably has a stronger ligand field.



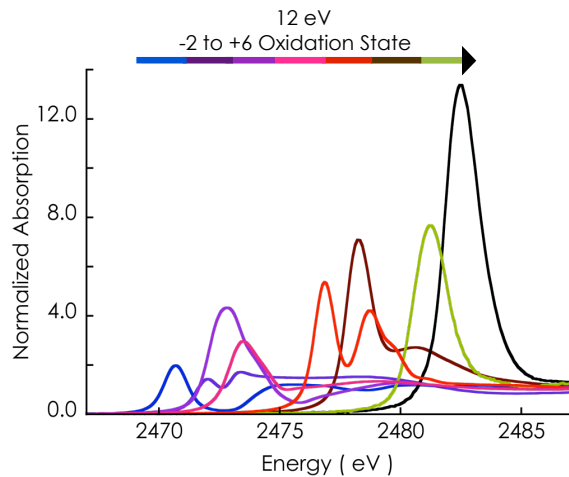
Applications of pre-edge:

- a) Covalency determination in Electron Transfer Proteins.
- b) Ligand-Metal Overlap estimation in systems with non-innocent ligands.
- c) Determination of oxidation state of the metal site (Indirect)
- d) Determination of oxidation state of S



## Effect of Oxidation State

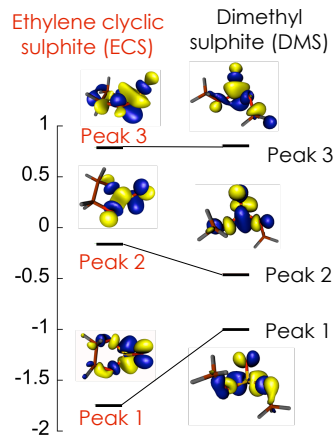
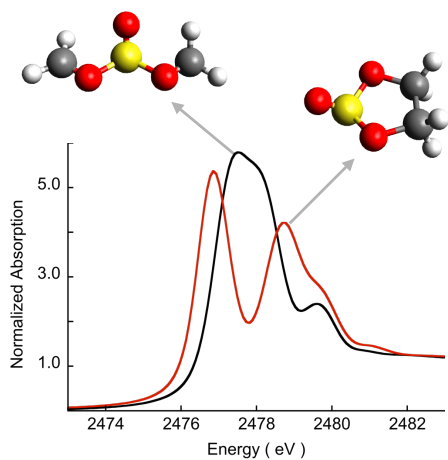
Large energy shifts associated with oxidation state changes



Excellent for fingerprinting & speciation analysis in a sample containing a mixture of S containing species



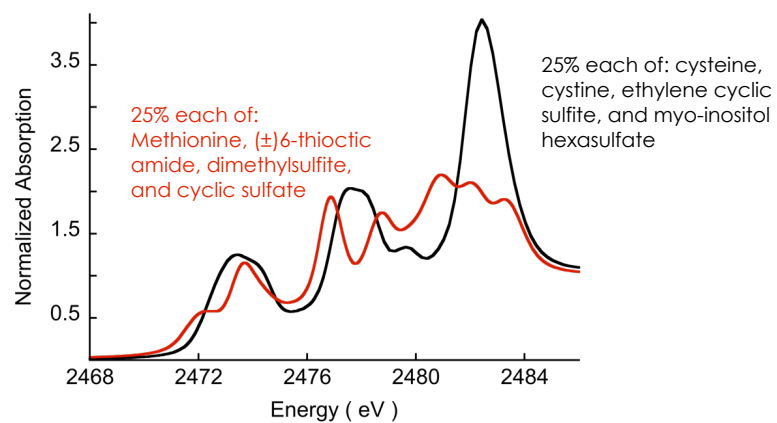
## Differences in Spectral Shape



- Spectral differences are due to 0.02 Å difference in the single bond S-O distances: 1.70 in ECS vs 1.72 in DMS
- Small changes in bonding can lead to large shifts in valence MO energy levels and hence strikingly different spectral shapes.

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## Complications with Unknowns



- Need some chemical information to perform speciation analysis.
- Or have an extensive database of standards to choose from.

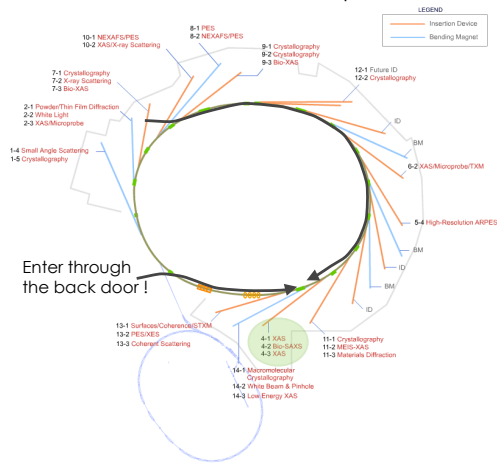
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# The Facility

Stanford Synchrotron Radiation Lightsource



SSRL Beamline Map



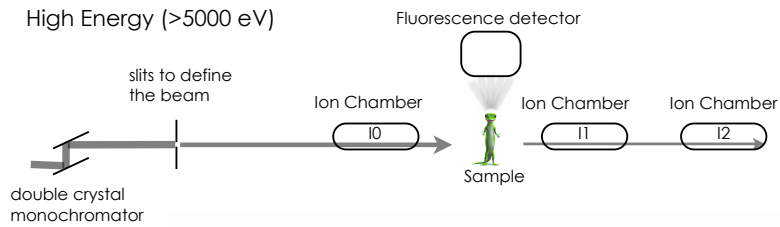
Enter through the back door!

20 pole 2T Wiggler Beamline 4-3

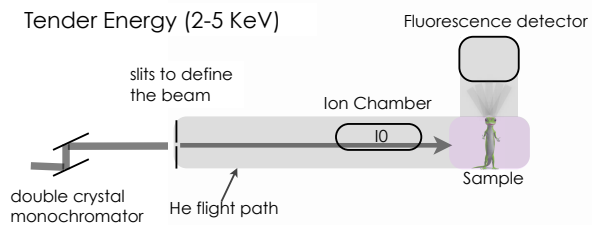


# The Experimental Setup

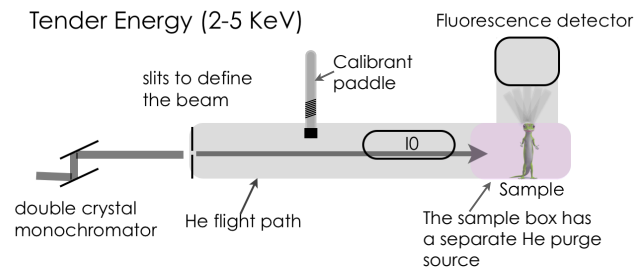
High Energy (>5000 eV)



Tender Energy (2-5 KeV)



## The Experimental Setup



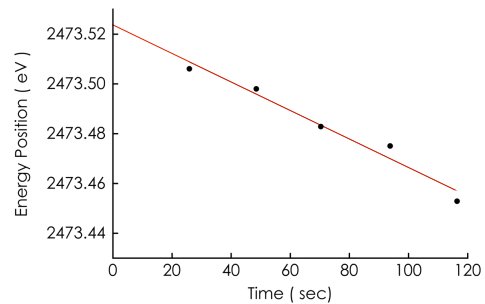
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## The Calibration Issue

- No I1 or I2 = No Internal Calibration
- Calibration is achieved by measuring the standard before and after the sample.
- For S, the typically used calibrant is  $\text{Na}_2\text{S}_2\text{O}_3$  (lowest energy peak at 2472.02 eV)
- Higher error in estimating true energy position

If the goal is to know small energy shift between spectra very accurately- the following method should be used:

Calibration	filename	time
2472.050	SCALIB_053.001	12:10:20
2473.506	LCYST_054.001	12:36:11
2473.498	LCYST_054.002	12:58:49
2473.483	LCYST_054.003	13:21:27
2473.475	LCYST_054.004	13:44:06
2473.453	LCYST_054.005	14:06:44
2472.000	SCALIB_053.001	14:28:10



Energy of the peak in your data: 2472.522 eV

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## The Calibration Issue

Other calibration methods commonly used and associated errors

Calibration filename  
2472.050 SCALIB\_053.001  
2473.506 LCYST\_054.001  
2473.498 LCYST\_054.002  
2473.483 LCYST\_054.003  
2473.475 LCYST\_054.004  
2473.453 LCYST\_054.005  
2472.000 SCALIB\_053.001

Method	Error
Interpolation of energy shift between the 2 calibrants and applying a linear shift per scan.	Artificial broadening of the average spectrum
Using only 1 before-calibration scan and applying the energy shift to the first scan of data.	Error in energy position.
Using an average of the before and after calibrant and applying it to each spectrum.	Error in energy position if large variations in mono energy.



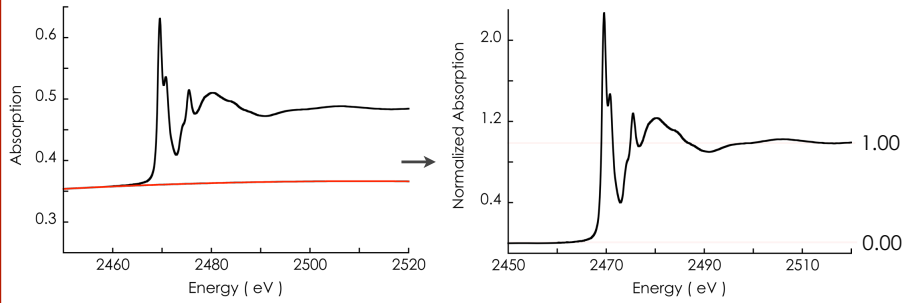
## Sample Considerations

- Amorphous solid samples ground to a very small particle size.  
Conc > 100 ppm.
- Homogeneous solution samples.  
Conc > 5mM in S, 200 uL
- Whole samples. e.g: Leaves, wood, soil. etc. Specific sections of the sample can be targeted to see differences in speciation.
- Solid samples with high S concentrations should be applied as a thin layer.
- Solution samples have to be placed within thin x-ray transparent windows- (4-5um polypropylene or other S-free film)
- For quantitative analysis : Homogenous S site structure
- For speciation analysis : The sample and the standards should be measured under the same experimental condition.





## Data Processing



Fluorescence data from beamline 4-3.  
Red line mimics the background

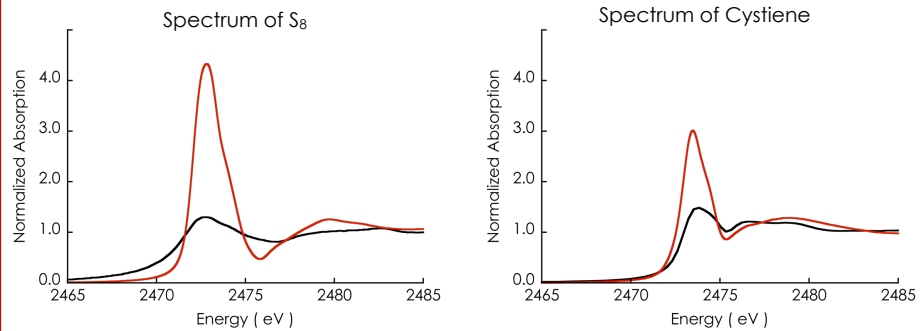
Post edge should pass through 1.00  
Pre-edge should pass through 0.00

Our favourite softwares are often slightly off with normalization. Recheck manually in excel or other graphing software.

## Self Absorption

Self Absorption is observed in a spectrum of too concentrated a sample due to variations in penetration depth that affects the fluorescence yield.

Concentrated samples can only be measured reliably with fluorescence where the sample thickness is comparable to or smaller than  $1/e$  absorption depth.

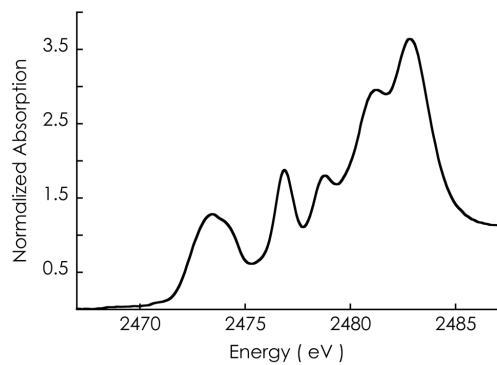


## Data Analysis

- Linear Combination Analysis (DATFIT)
- Peak Deconvolution Analysis (EDG\_FIT, PEAKFIT)
- EXAFS Analysis
- Structure Determination using Near-edge Analysis (MXAN)
- DFT calculation of electronic structure and simulation of spectra (STOBE)
- DFT and TD-DFT methods to simulate XAS spectra (ORCA, Gaussian)

## Linear Combination Analysis

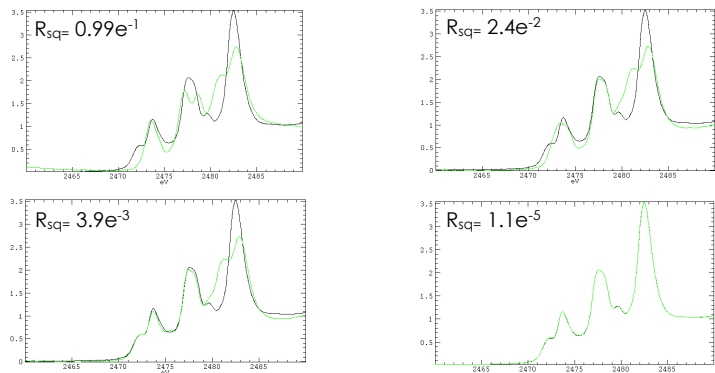
- Program: DATFIT (Part of EXAFSPAK) or other peak fitting software
- Data: 2 Column data file. (Energy and background subtracted normalized data)
- Standards: A complete set of standard data on species expected to be similar to those in the unknown mixture



Range of oxidation states?  
Are data self absorbed?  
Are so many peaks expected?

## Linear Combination Analysis

DATFIT Interface



- Perform several fits by sequentially increasing number of standards.
- A best fit:
  - a) has least number of standards
  - b) fit over the entire energy range
  - c) makes chemical sense
- E.S.D: 3 times the value printed in DATFIT (if fit is very good).

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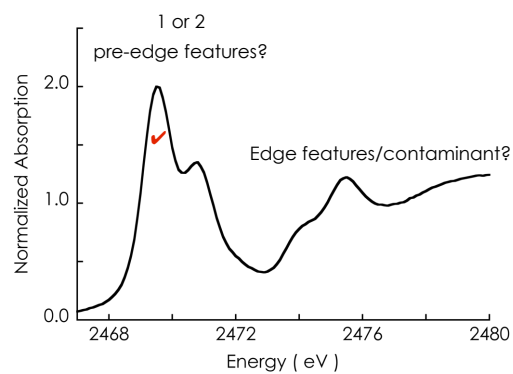
## Considerations

- Data and standards should be free of self absorption.
- Data and standards should be normalized to 1.00.
- Data and standards should have very near flat pre-edges and post-edges.
- Always have your chemists hat on when using linear combination analysis.

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## Peak Deconvolution Analysis

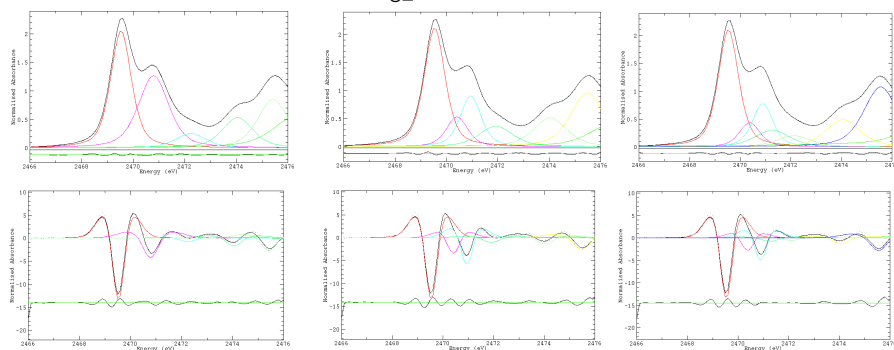
- Program: Edg\_Fit (Part of EXAFSPAK) or other peak fitting software
- Data: 2 Column data file. (Energy and background subtracted normalized data)
- Information: Some idea about the origin of the different spectral features



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## Peak Deconvolution Analysis

### Edg\_Fit Interface



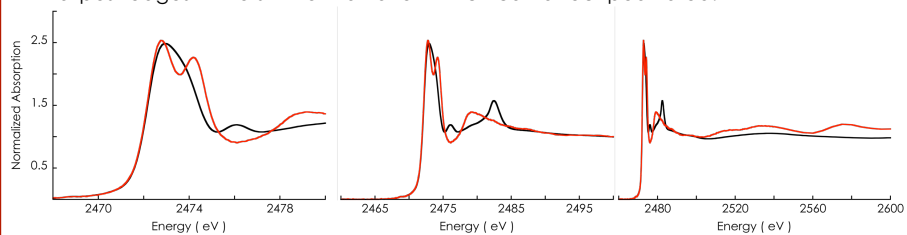
- Perform several fits by varying:
  - a) # of peaks
  - b) energy range
  - c) weight of second derivative
- A best fit:
  - a) has least number of unjustified peaks
  - b) fit over a reasonable eV range
  - c) a good fit to the second derivative.
- Error bar:

Is obtained by estimating standard deviation among chosen best fits.

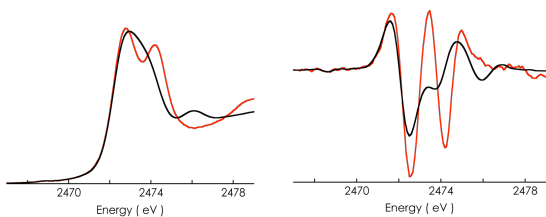
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## Considerations

- Data with strange backgrounds require special manipulation to obtain flat pre-edges & post-edges = Errors in normalization which can affect peak area.



- Using black box normalization methods= Differences in normalization in different data sets.



- Use 2nd derivative fitting method to separate overlaying peaks.



## Acknowledgements

Stanford Synchrotron Radiation Laboratory  
SLAC National Accelerator Laboratory

Thank You

Please direct additional questions to : [rifis@slac.stanford.edu](mailto:rifis@slac.stanford.edu)

