National Synchrotron Light Source II

XANES analysis

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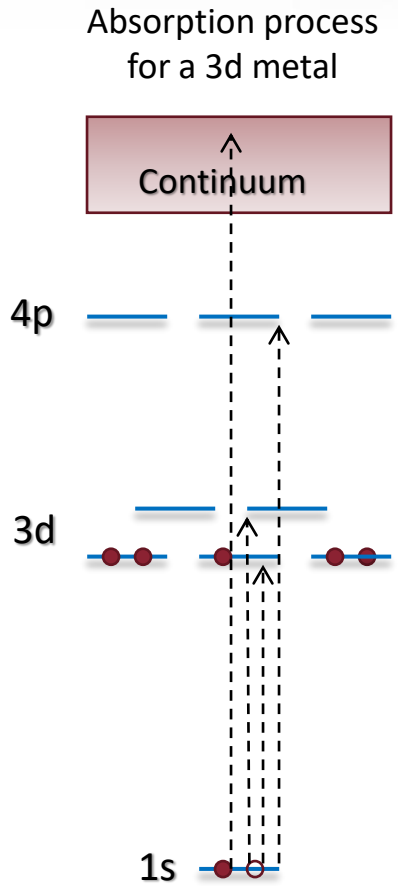
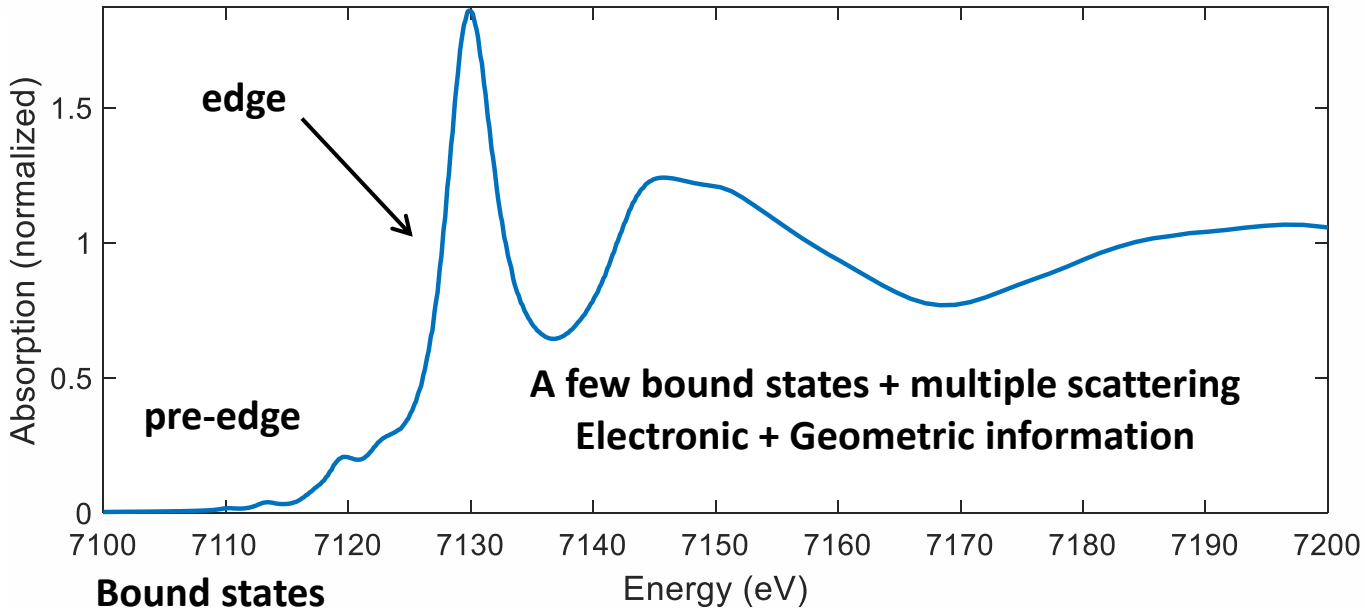
NSLS-II, BNL

U.S. DEPARTMENT OF ENERGY | Office of Science

BROOKHAVEN NATIONAL LABORATORY

XANES region





Bound states
Electronic structure

Why does it look like this?

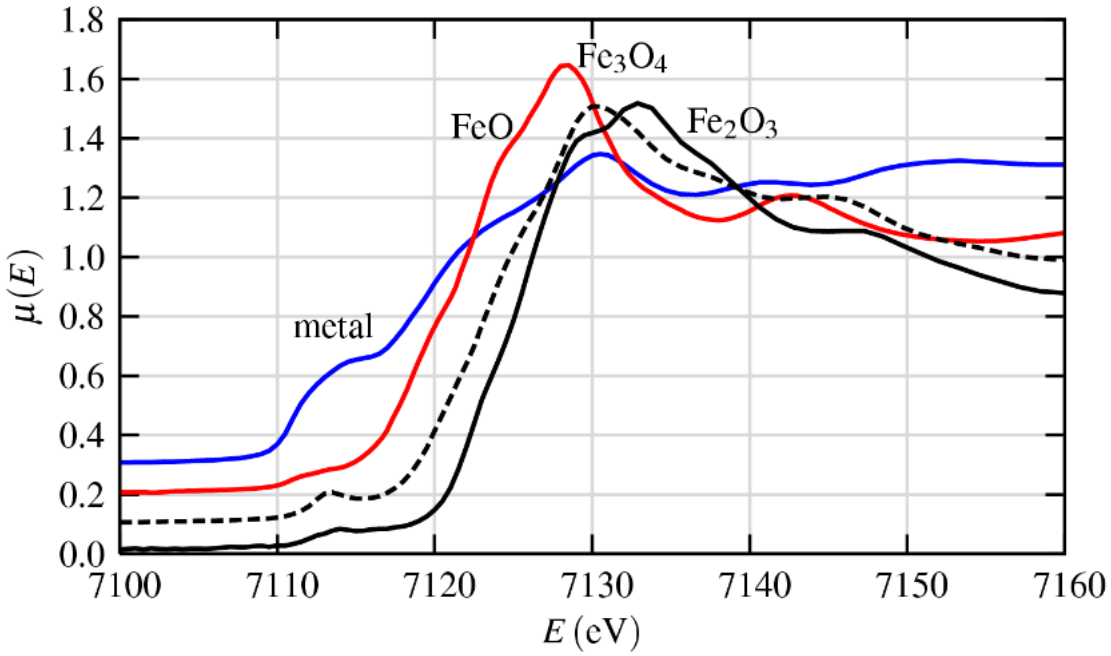
- Oxidation state
- Symmetry
- Bonding

Dealing with mixtures and harnessing large datasets:

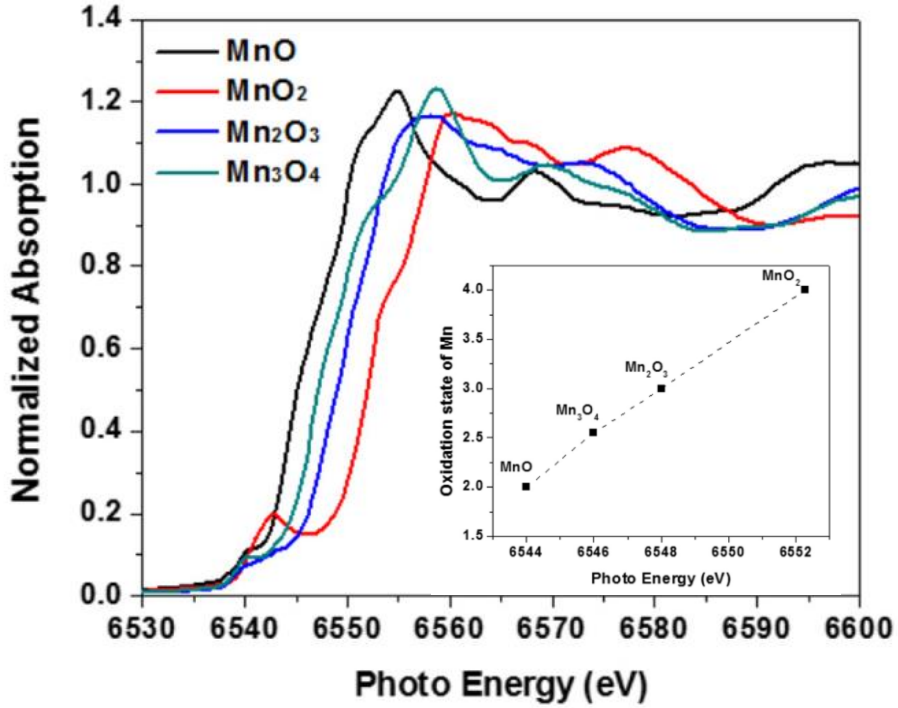
- Linear combination fitting
- Factor analysis

XANES: why does it look like this?

XANES is sensitive to formal oxidation state

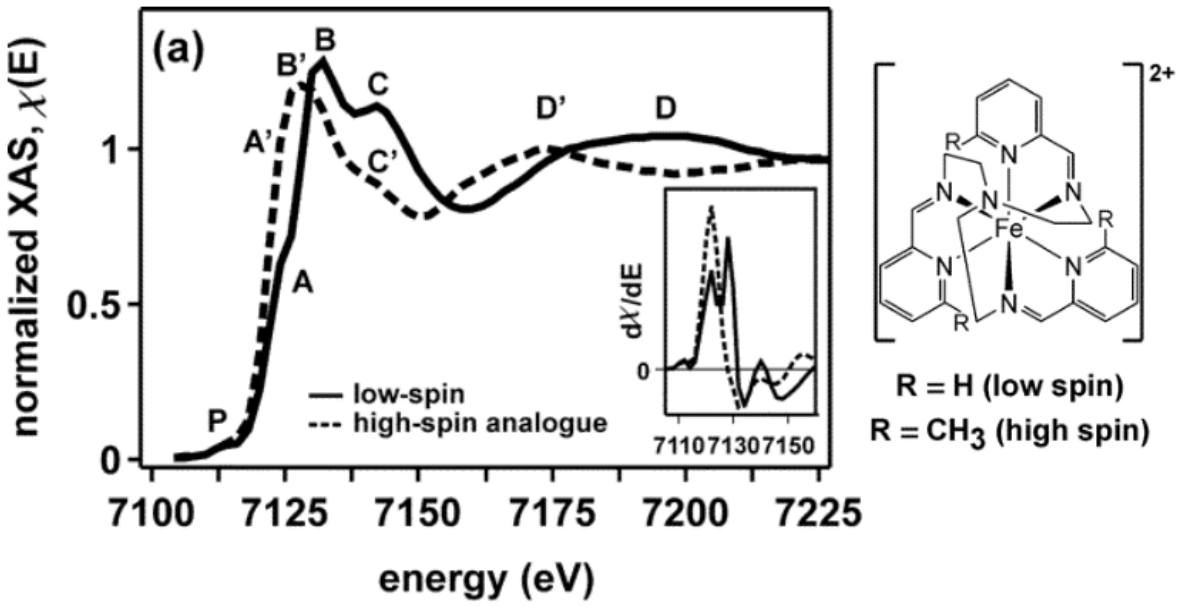


Fundamentals of XAFS, Matt Newville



Chem. Commun., 2015, 51, 5951--5954

XANES is sensitive to local structure

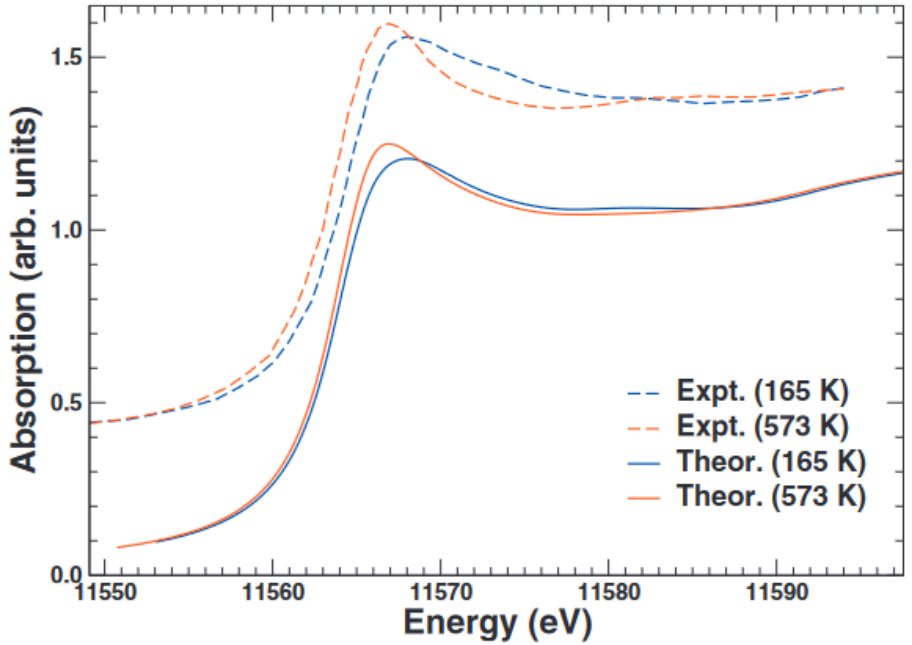


Both Fe(II)-N_6, but different spin and Fe-N distance

Low spin: R ≅ 2.0 Å

High spin: R ≅ 2.2 Å

J. Phys. Chem. A, Vol. 110, No. 1, 2006

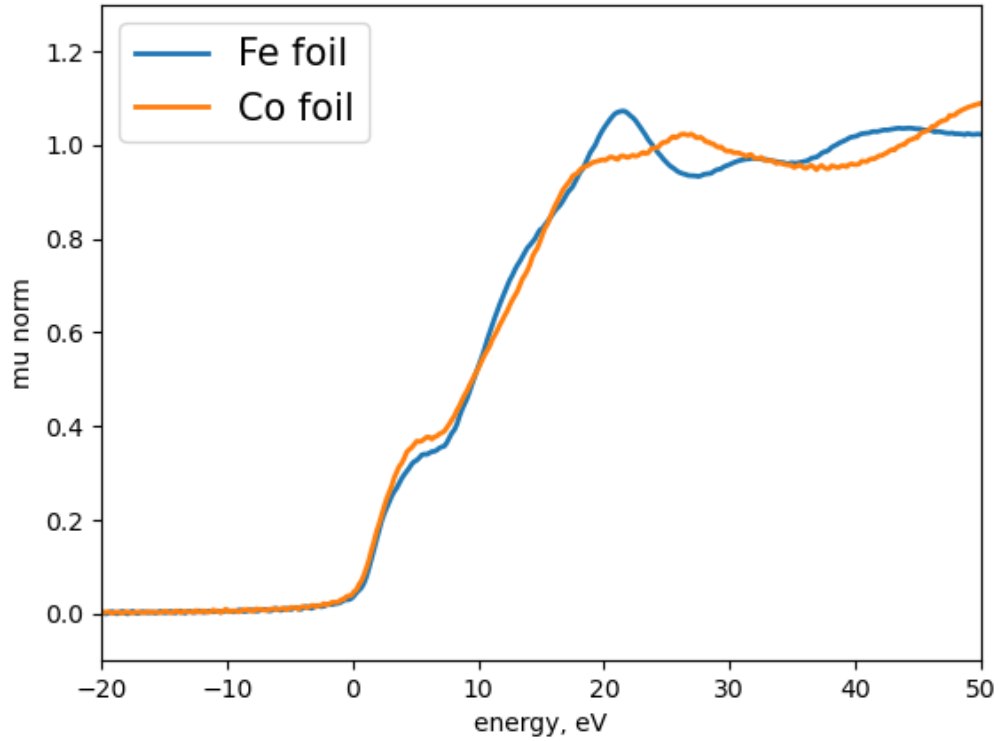


Pt nanoparticles

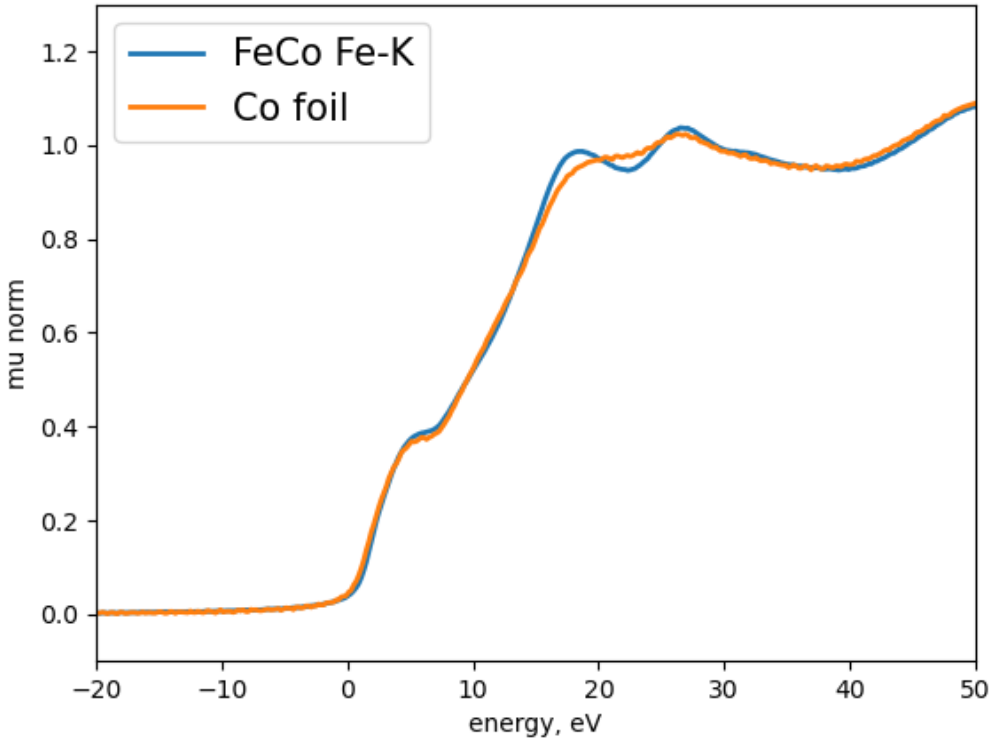
Pt-Pt distances increase with temperature

PHYSICAL REVIEW B 78, 121404R 2008

XANES is sensitive to local structure - continued

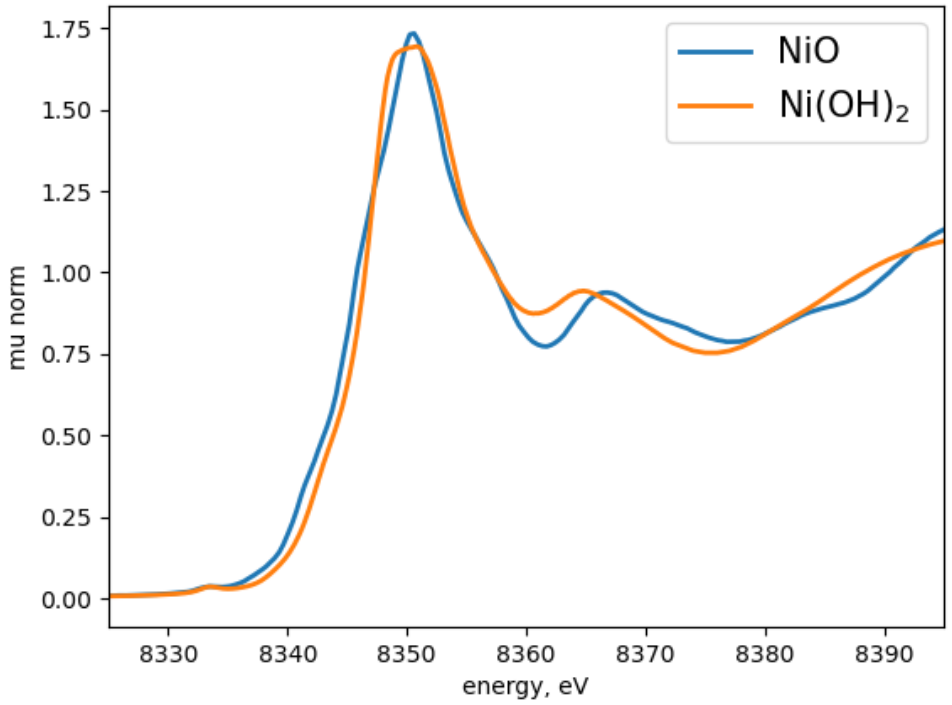


Fe – bcc structure
Co – hcp/fcc mix



Fe in Fe/Co thin film shows XANES similar to that of Co

XANES is sensitive to bonding

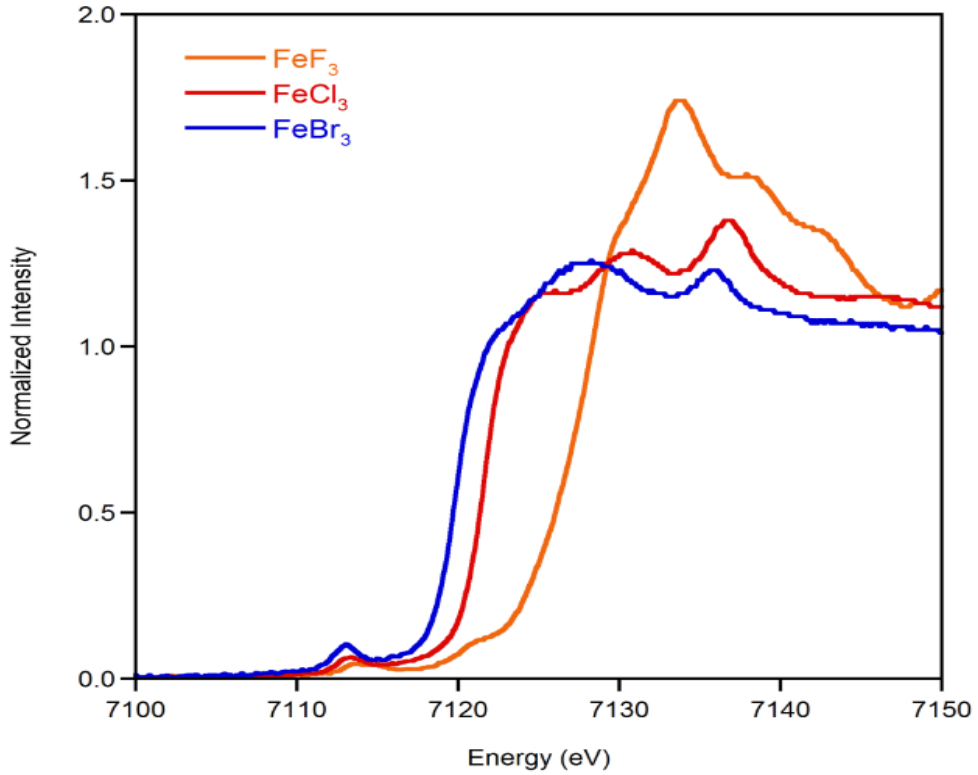


Both Ni(II), coordinated with 6 oxygen atoms

NiO: Ni-O ~ 2.09 A

$Ni(OH)_2$ ~ 2.07 A

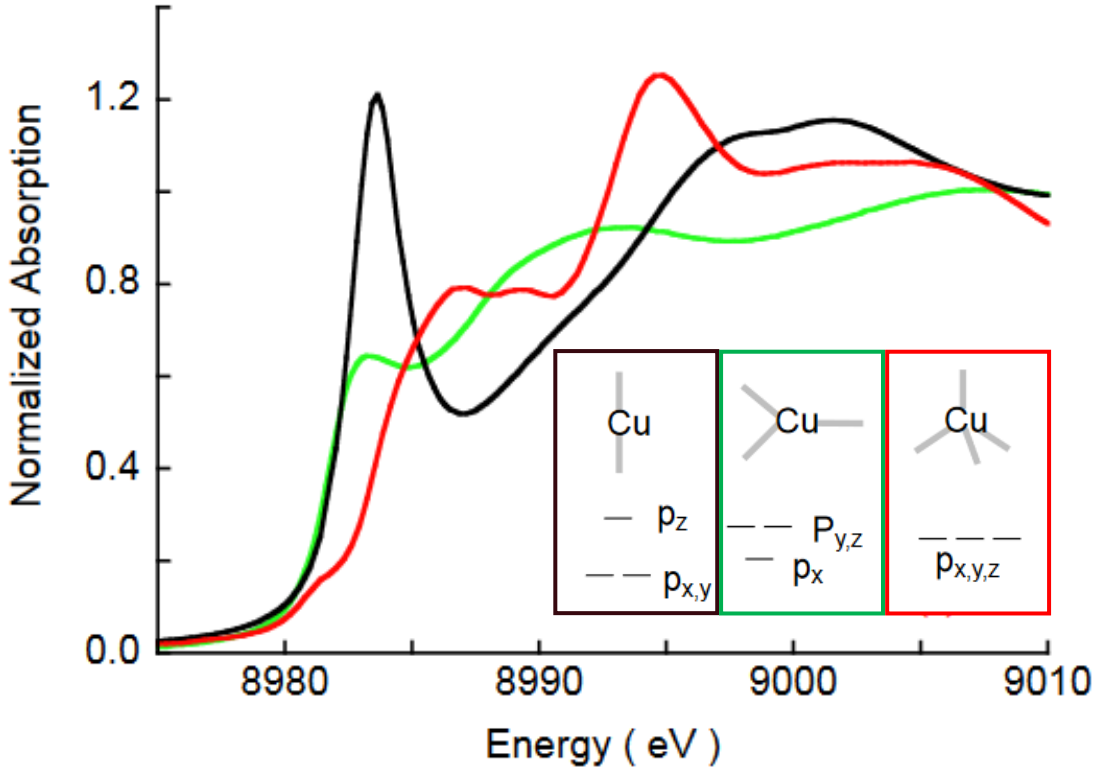
Data: Akhil Tayal



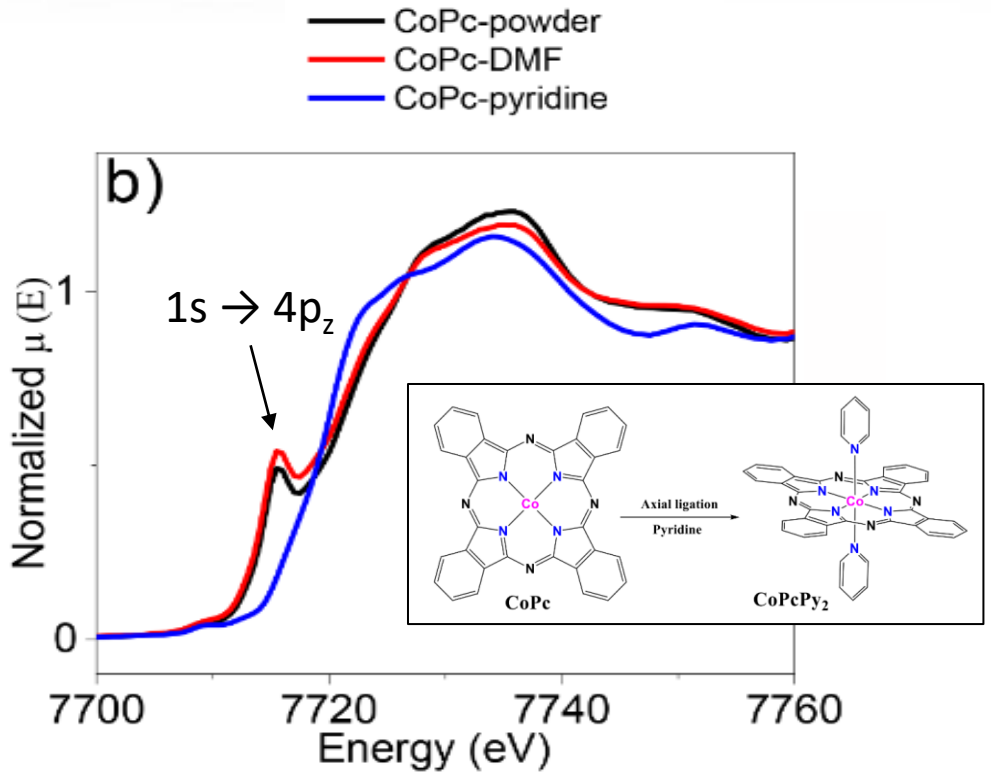
All Fe(III) compounds

J. Am. Chem. Soc., Vol. 119, No. 27, 1997

XANES is sensitive to local symmetry

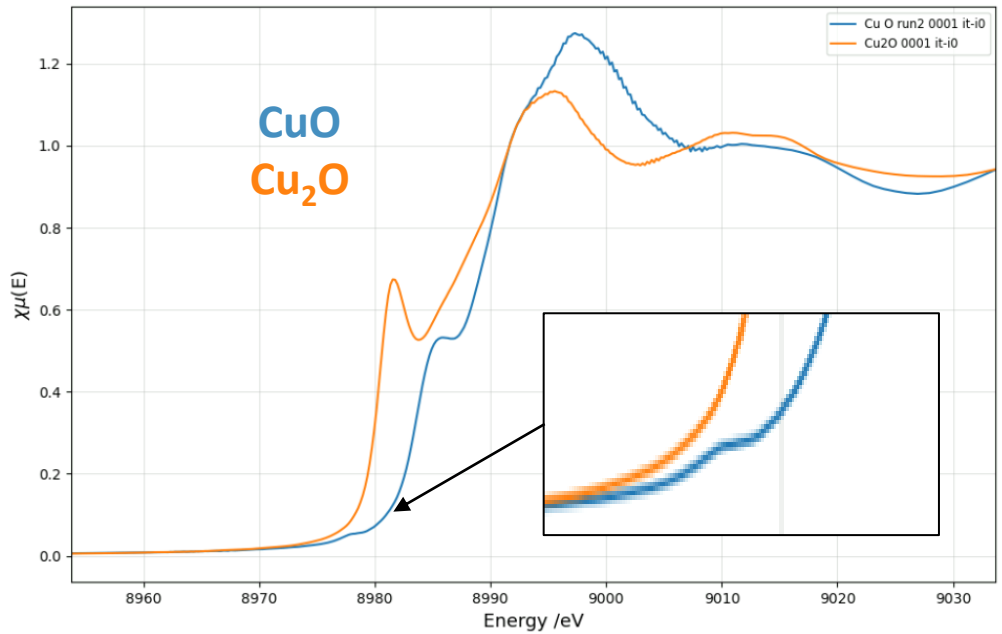


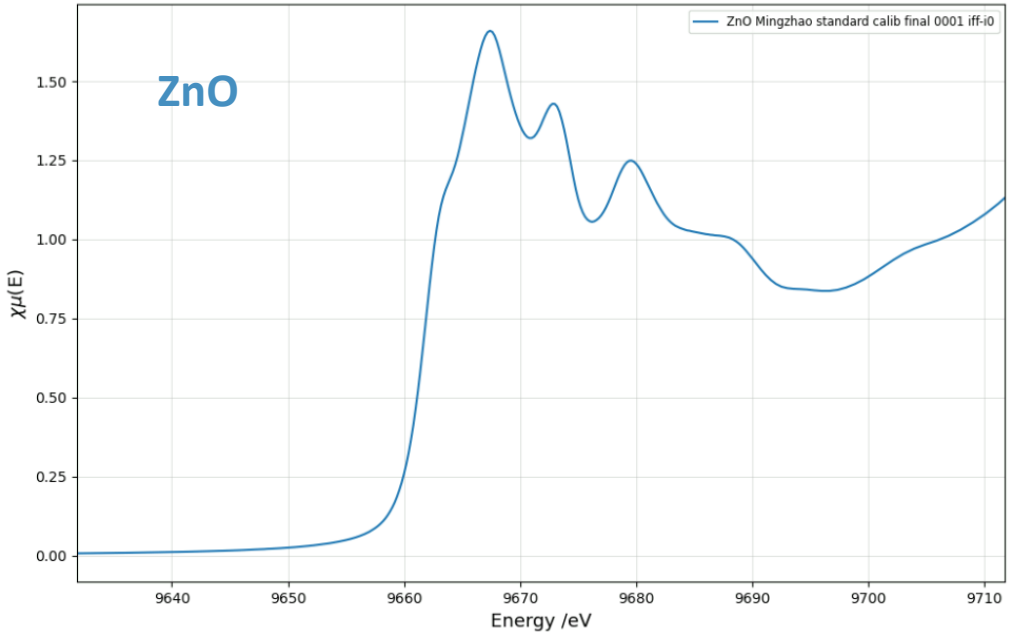
M.L. Baker et al. / Coordination Chemistry Reviews 345 (2017) 182–208



Journal of Photochemistry and Photobiology 11 (2022) 100132

Pre-edge features: quadruple allowed transitions

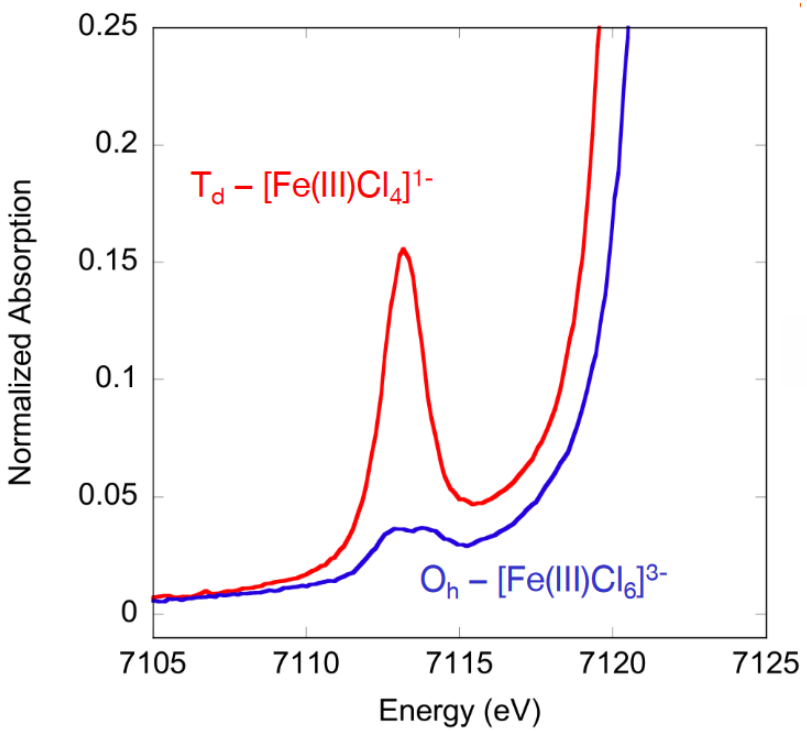




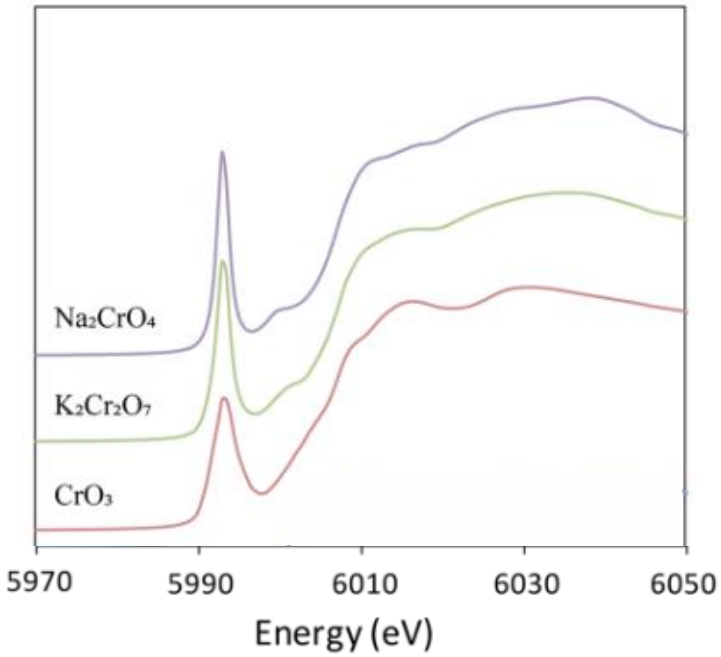
Cu_2O, ZnO - d^{10} systems - do not have any pre-edge

CuO – d^9 system – has one!

Pre-edge features: effect of 4p/3d mixing



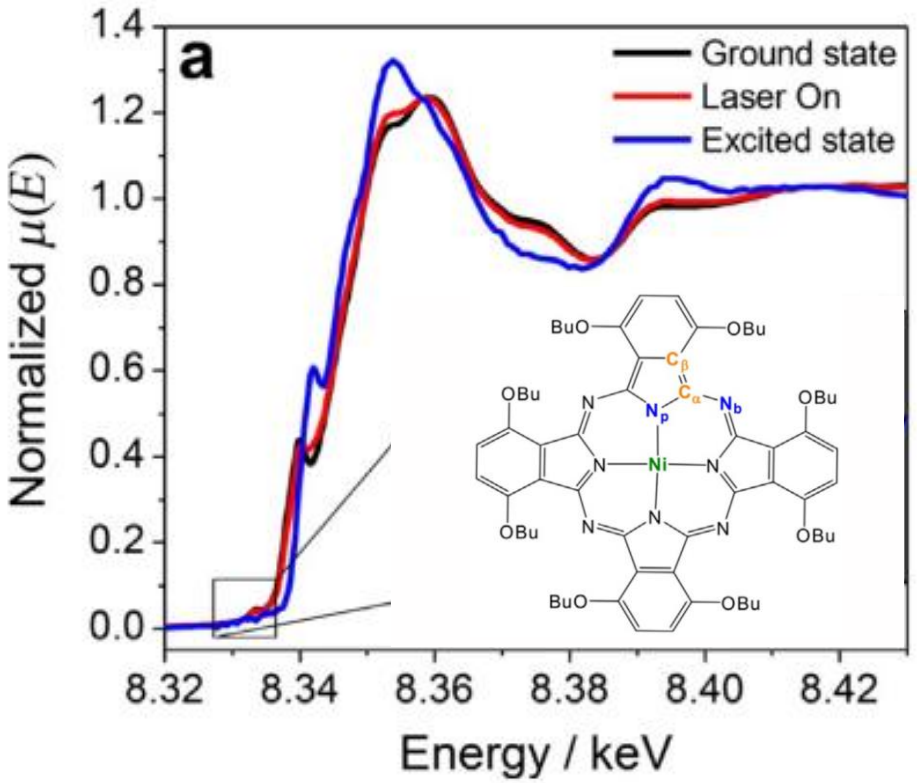
Serena DeBeer, 2nd Penn State Bioinorganic Workshop, 2012
J. Am. Chem. Soc., Vol. 119, No. 27, 1997

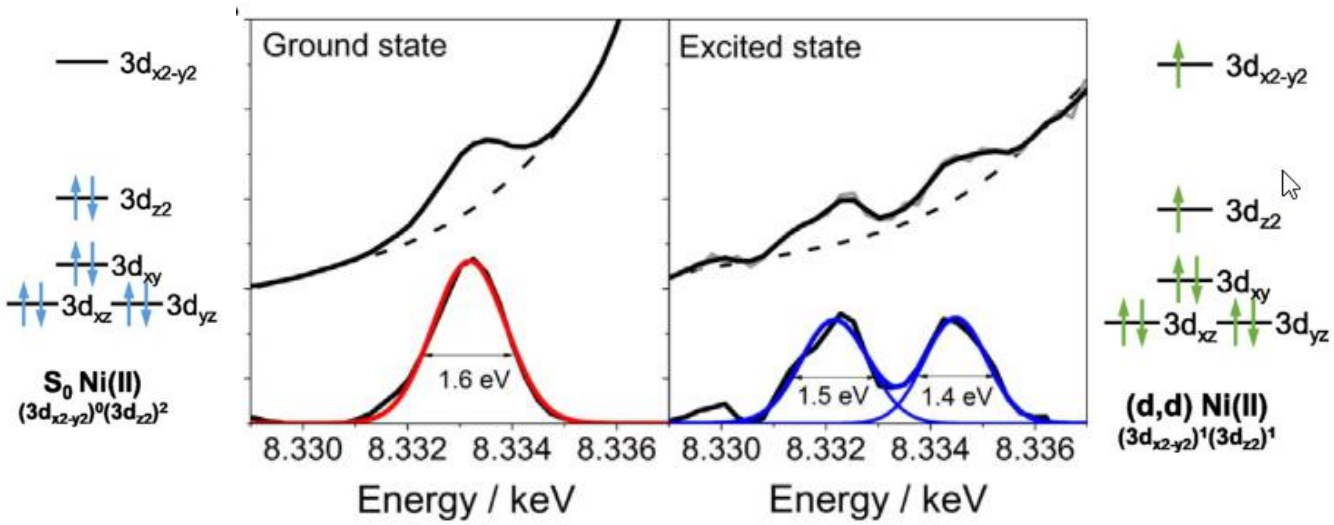


Scientific Reports (2018) 8:8603

- Oh coordination has inversion symmetry – low mixing, quadruple only
- Td coordination 4p and 3dxy, xz, yz orbitals have the same symmetry – high mixing, intense pre-edge
- More pre-edge intensity -> more distortion from centrosymmetric geometry

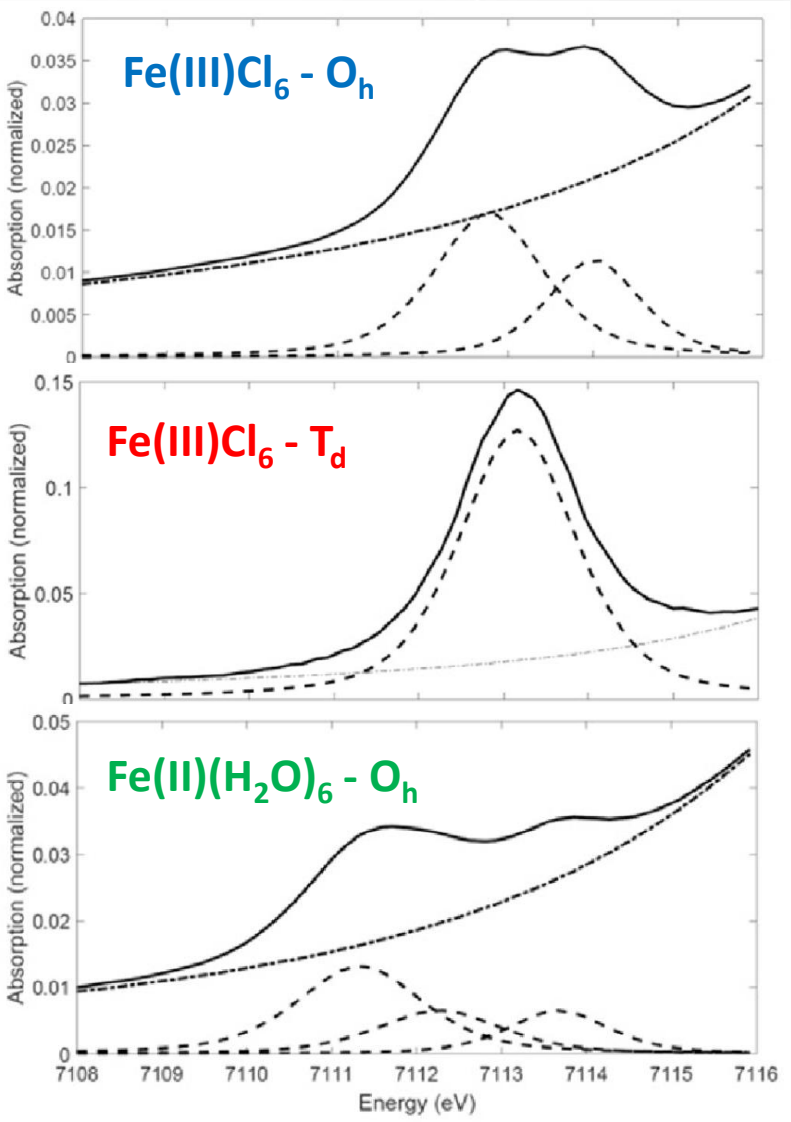
Pre-edge features: electronic structure fingerprinting

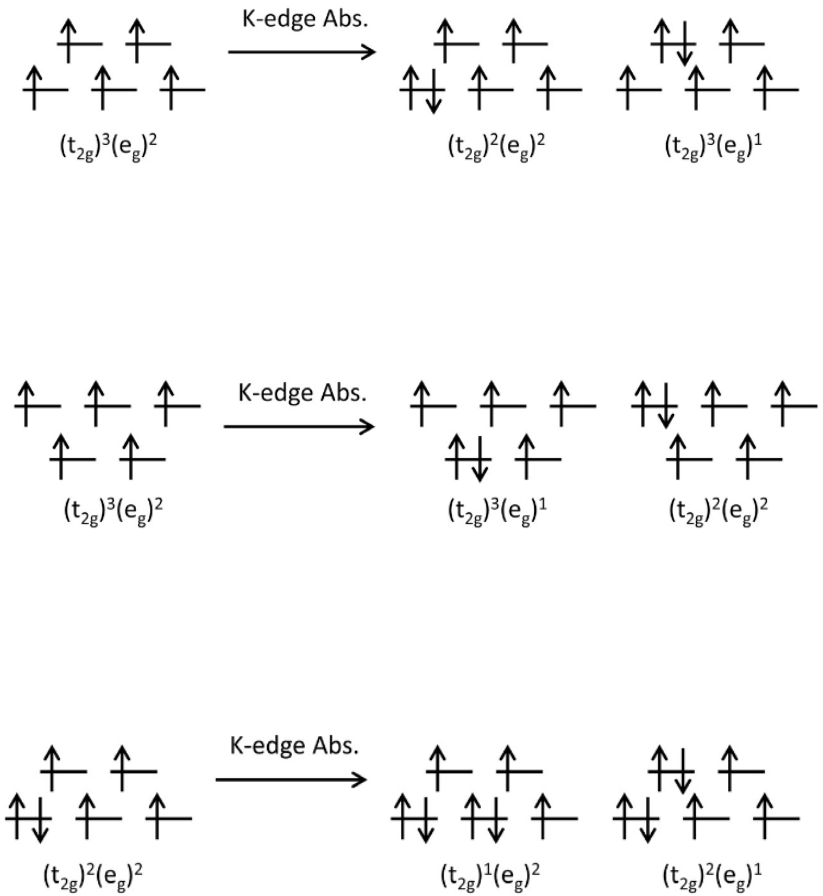


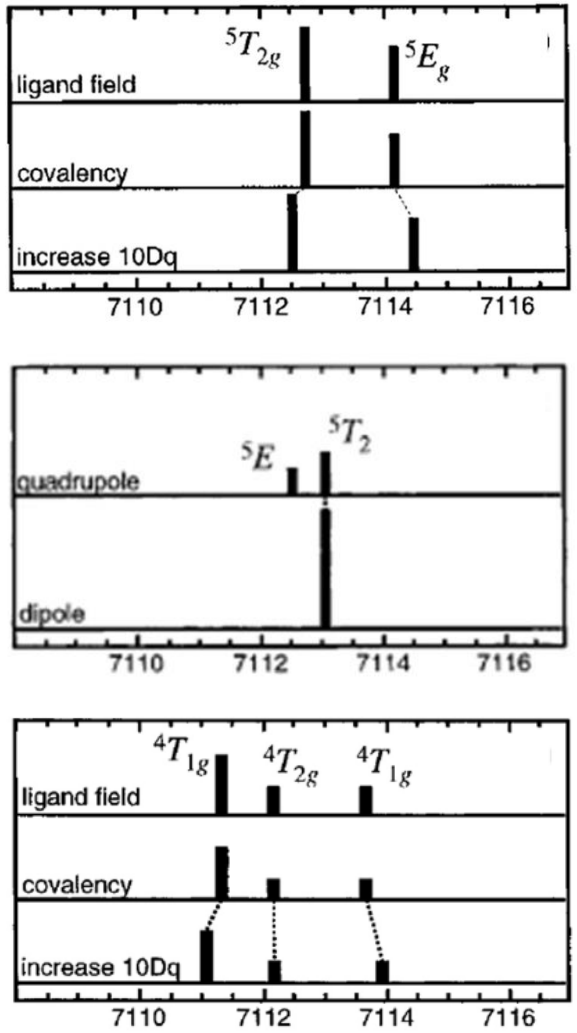


ChemSusChem 2018, 11, 2421 –2428

Pre-edge features: multiplet structure effects







M.L. Baker et al. / Coordination Chemistry Reviews 345 (2017) 182–208

Pre-edge & XANES is sensitive to…

- Oxidation state
- Spin
- Multiplet structure
- Symmetry
- Bond lengths
- Covalency

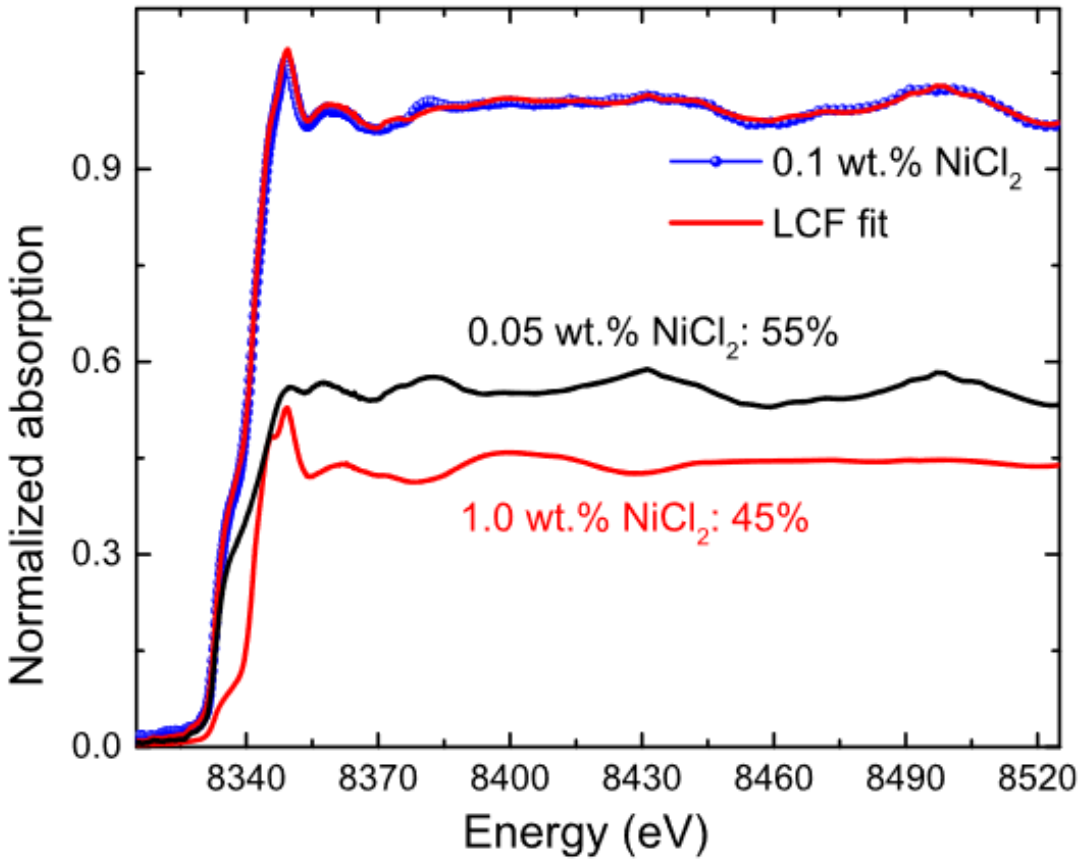
XANES Software:
FEFF
Ocean
MXAN

Pre-edge: DFT

XANES analysis of mixtures & Harnessing large datasets

XANES analysis of mixtures

- Real samples rarely contain only one species
- Composition of a sample can be analyzed using a set of reference spectra

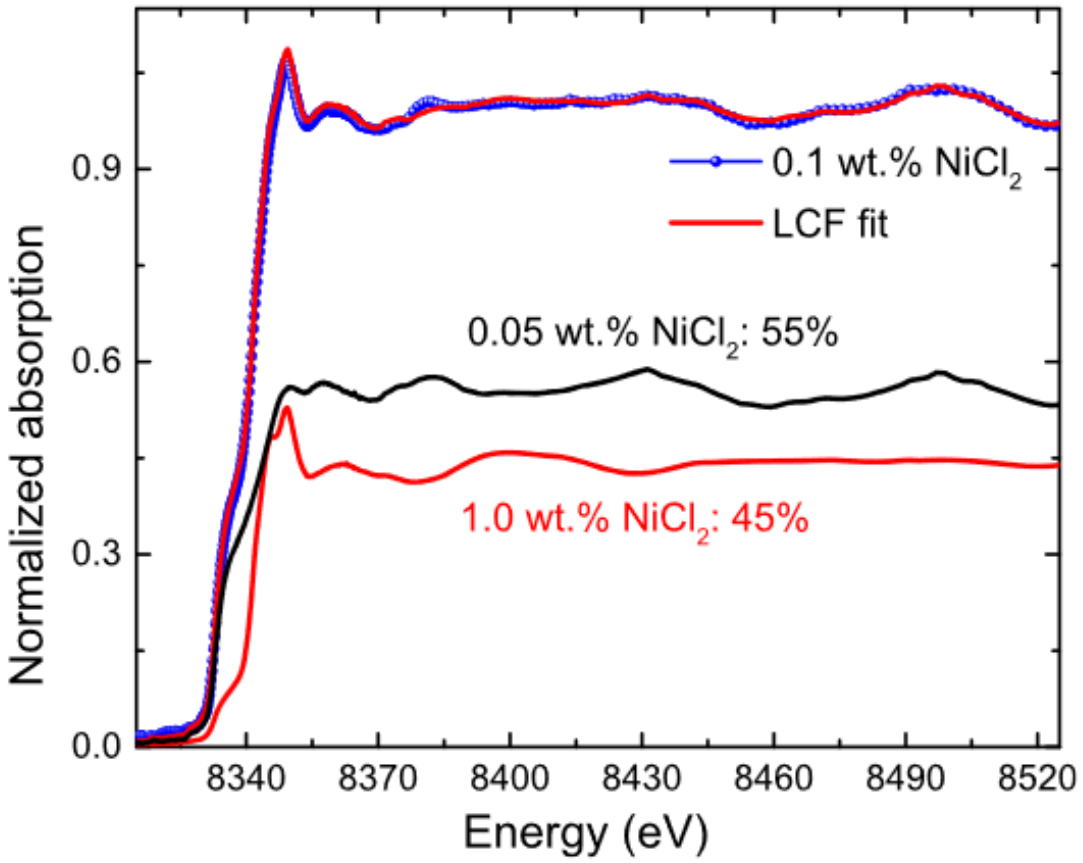


J. Phys. Chem. Lett. 2021, 12, 157−164

Linear Component Fitting – 2 components

- Linear component fitting is a way to compare sample XAS with a combination of reference spectra:

$$\mu_{sample}(E) = c_1\mu_1(E) + c_2\mu_2(E)$$



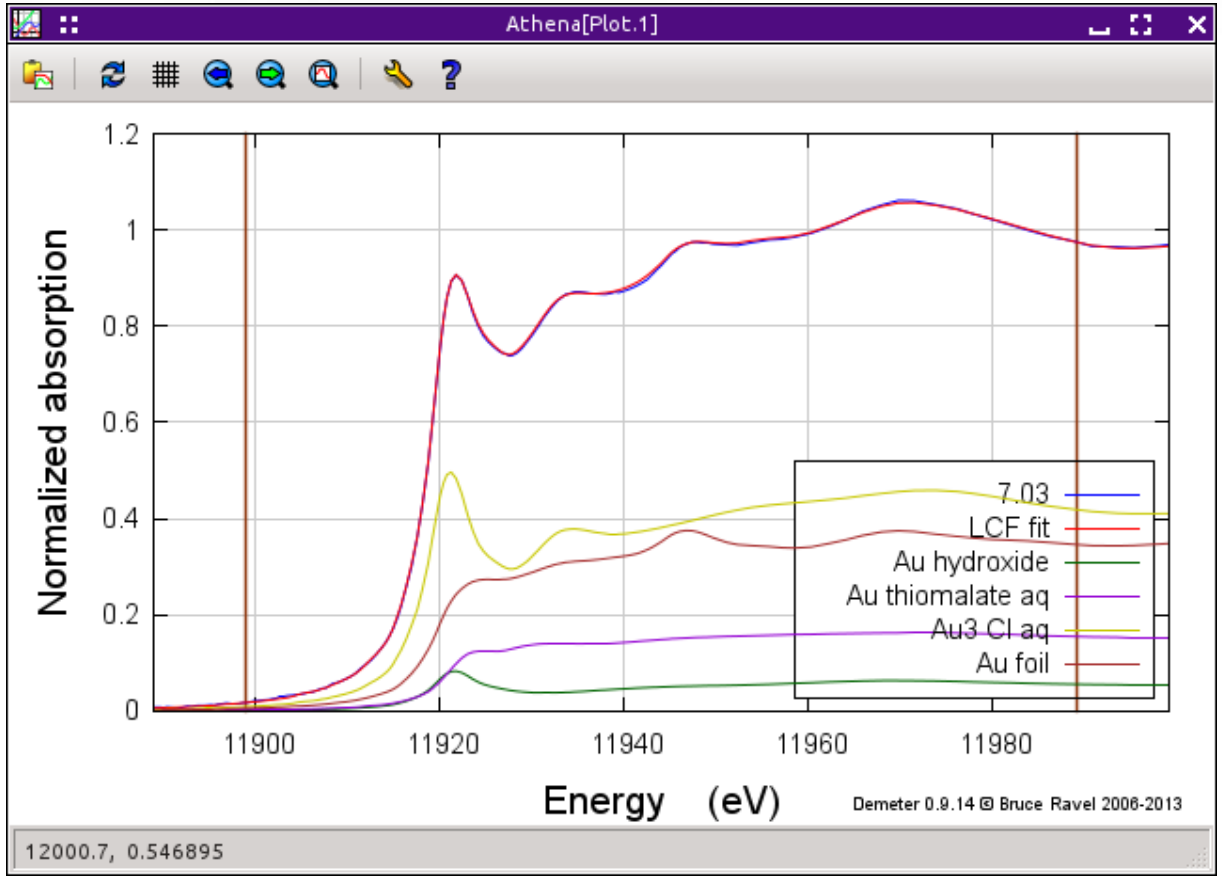
J. Phys. Chem. Lett. 2021, 12, 157−164

Linear Component Fitting – N components

- LCF with more components:

$$\mu_{sample}(E) = \sum_i c_i \mu_i(E)$$

- If many components are present in the sample, you might need to run many different combinations to figure out which one fits the best

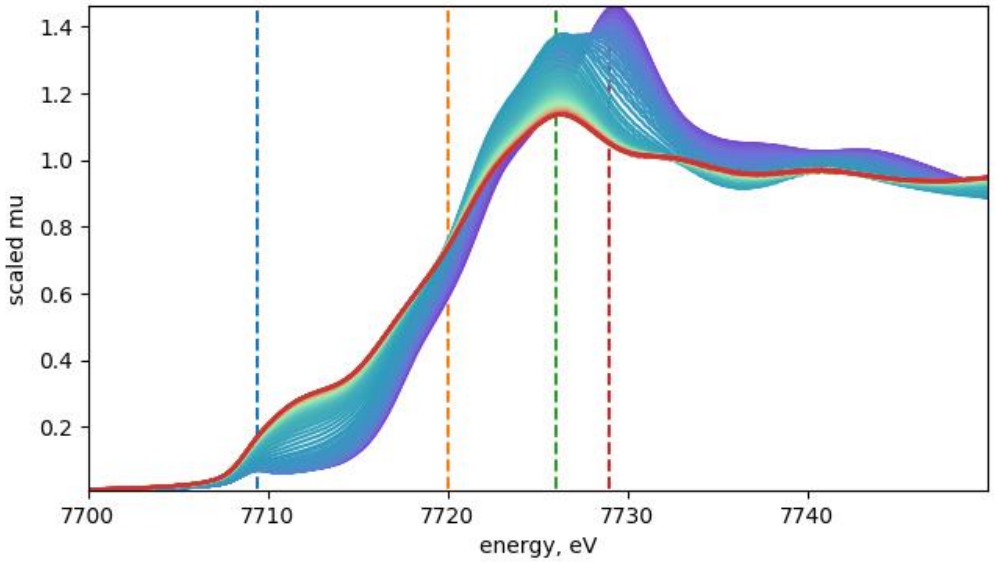


From Athena documentation

Linear Component Fitting - shortcomings

- Results get unreliable when the sample contains phases not represented by the reference data, e.g. in situ data
- Analysis gets tedious with a large set of candidate reference spectra (combinatorics)
- Analysis gets tedious with large datasets

A typical in situ dataset that users take home from ISS



What can be done?

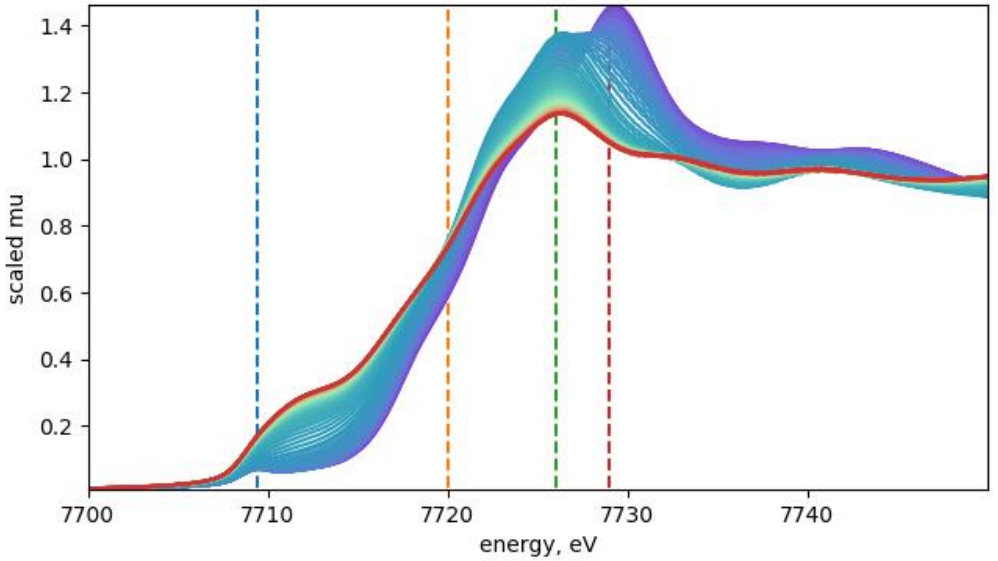
How many components are present in a given dataset?

Can we extract spectral components for the species not present in our reference data? E.g. intermediate states? Their concentrations?

The answer is yes!

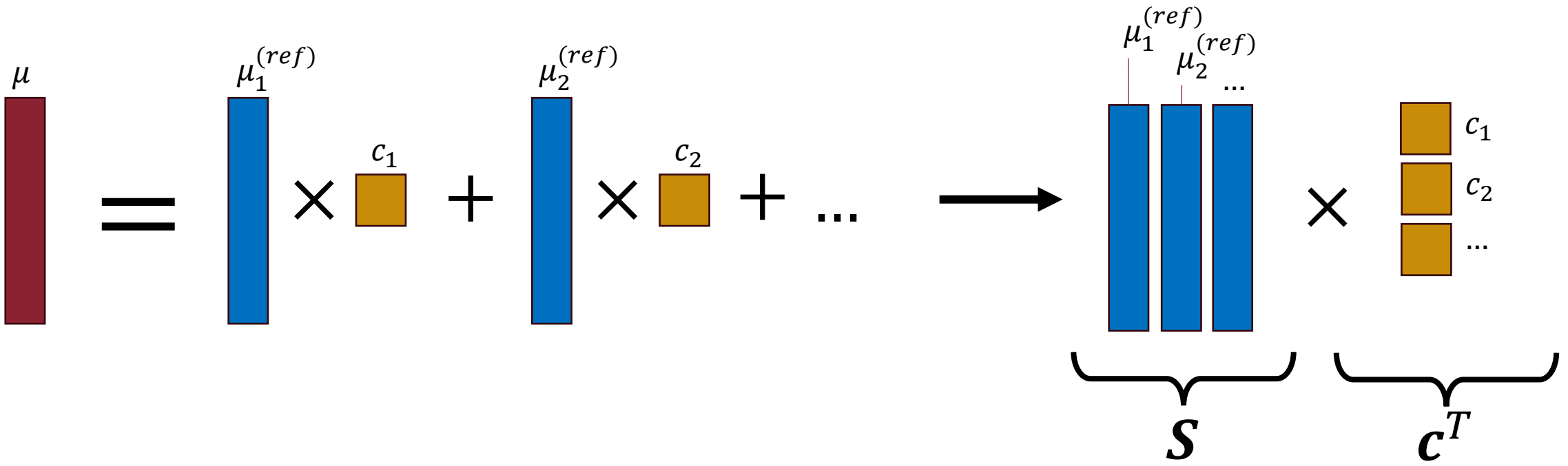
Let’s take a look at the problem from the **linear algebra perspective**

A typical in situ dataset that users take home from ISS



One spectrum as a sum of several components

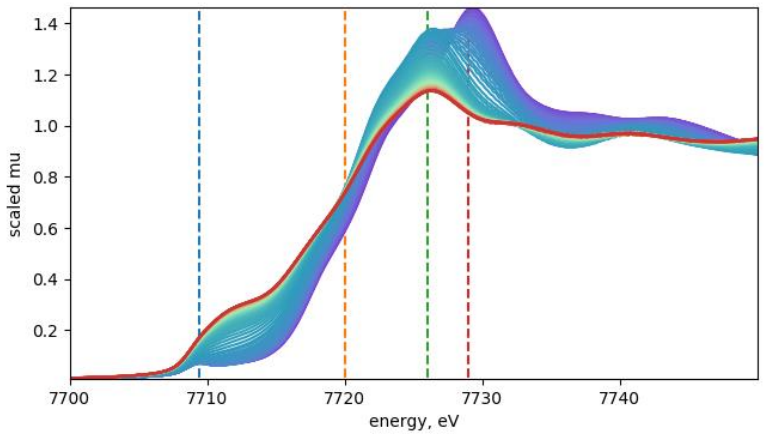
$$\mu_{sample}(E) = c_1\mu_1(E) + c_2\mu_2(E) + \cdots \longrightarrow \mu = \boldsymbol{S}\boldsymbol{c}^T$$



A set of spectra as a sum of contributions

This is called **Factorization**

A bunch of spectra $\{\mu_i(E)\}$



$\mu_1 \quad \mu_2 \quad \mu_3 \quad \ldots$

$\boldsymbol{A}$

$=$

$\mu_1 \quad \mu_2 \quad \ldots$

$\boldsymbol{S}$

$\times$

c_1

c_2

$\ldots$

$\boldsymbol{C^T}$

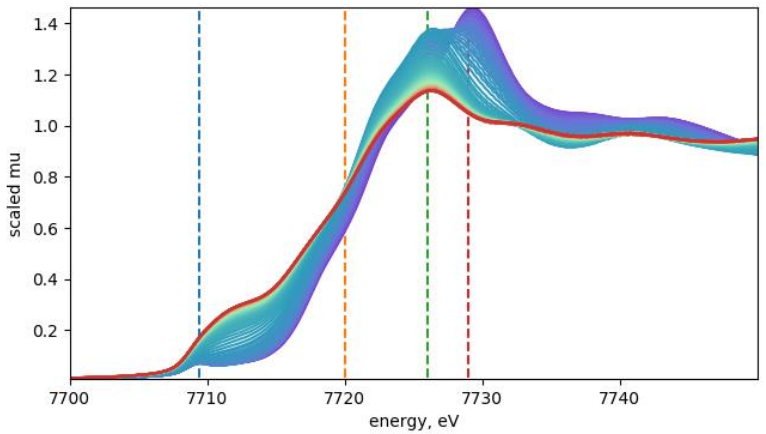
What can be done? – again, but in a matrix form

How many components are present in a given dataset?

How many columns?

How many rows?

A bunch of spectra $\{\mu_i(E)\}$



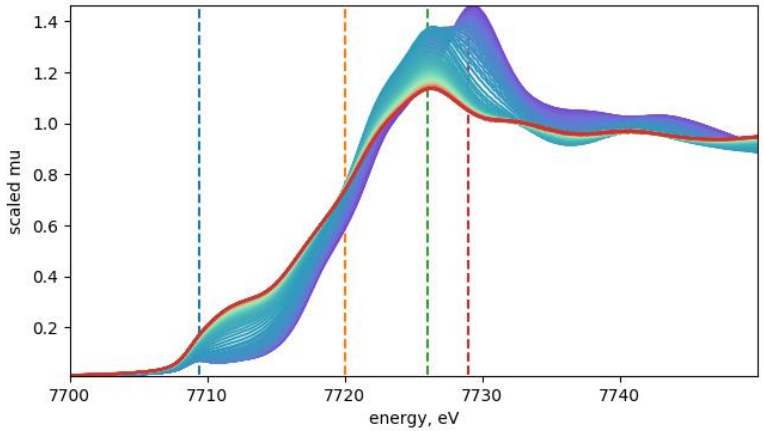
$$\rightarrow \underbrace{\begin{matrix}\mu_1 & \mu_2 & \mu_3 & \dots\end{matrix}}_{\boldsymbol{A}} = \underbrace{\begin{matrix}\mu_1 & \mu_2 & \dots\end{matrix}}_{\boldsymbol{S}} \times \underbrace{\begin{matrix}c_1 \\ c_2 \\ \dots\end{matrix}}_{\boldsymbol{C}^T}$$

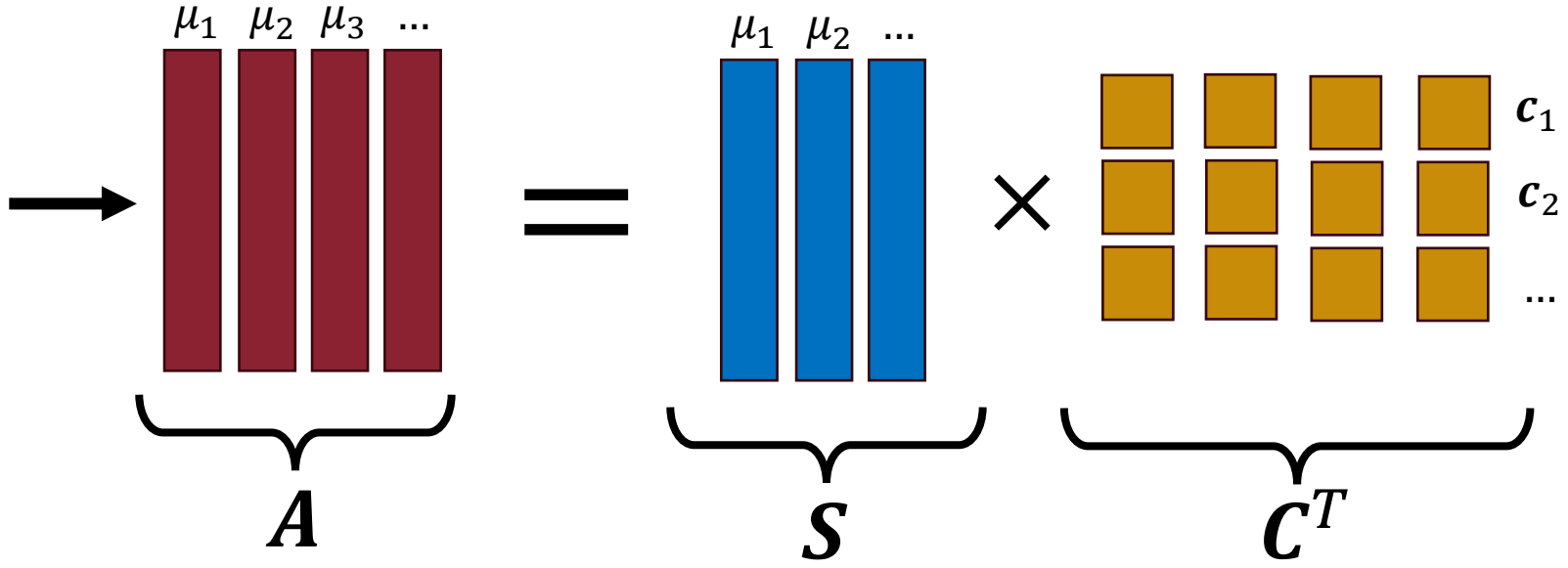
Can we extract component spectra?

Can we extract component concentrations?

Data factorizations: Linear component fitting

A bunch of spectra $\{\mu_i(E)\}$

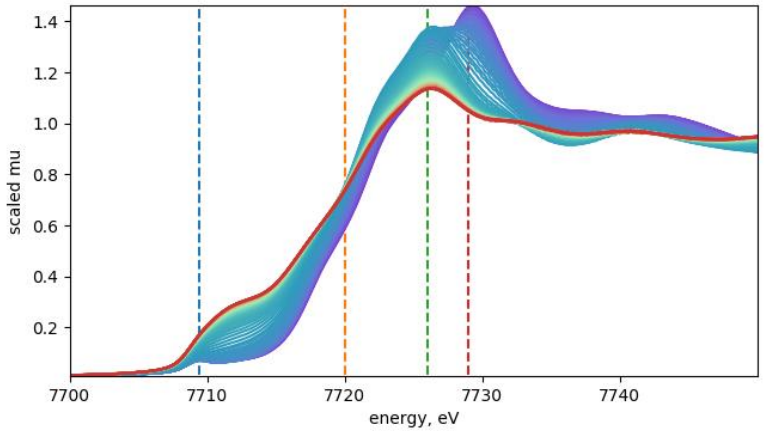


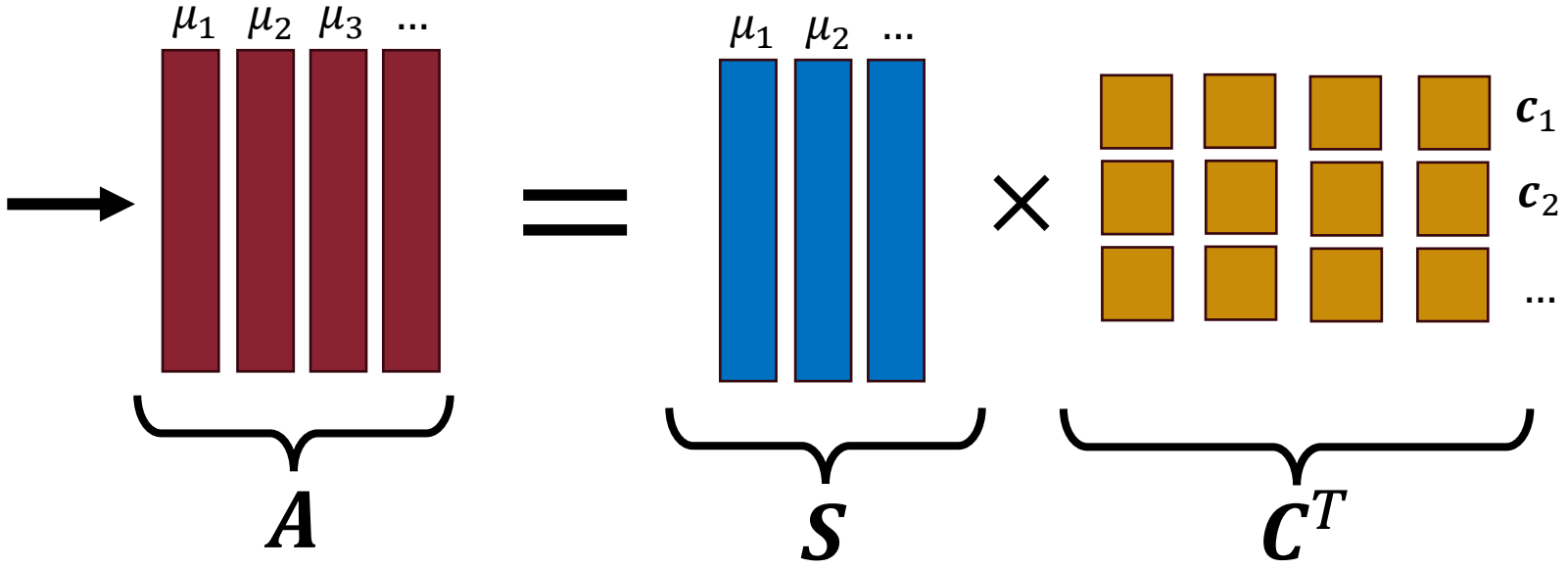


Linear component fitting (LCF):
You have references → you have S → solve for C

Data factorizations: Multivariate curve resolution (MCR)

A bunch of spectra $\{\mu_i(E)\}$



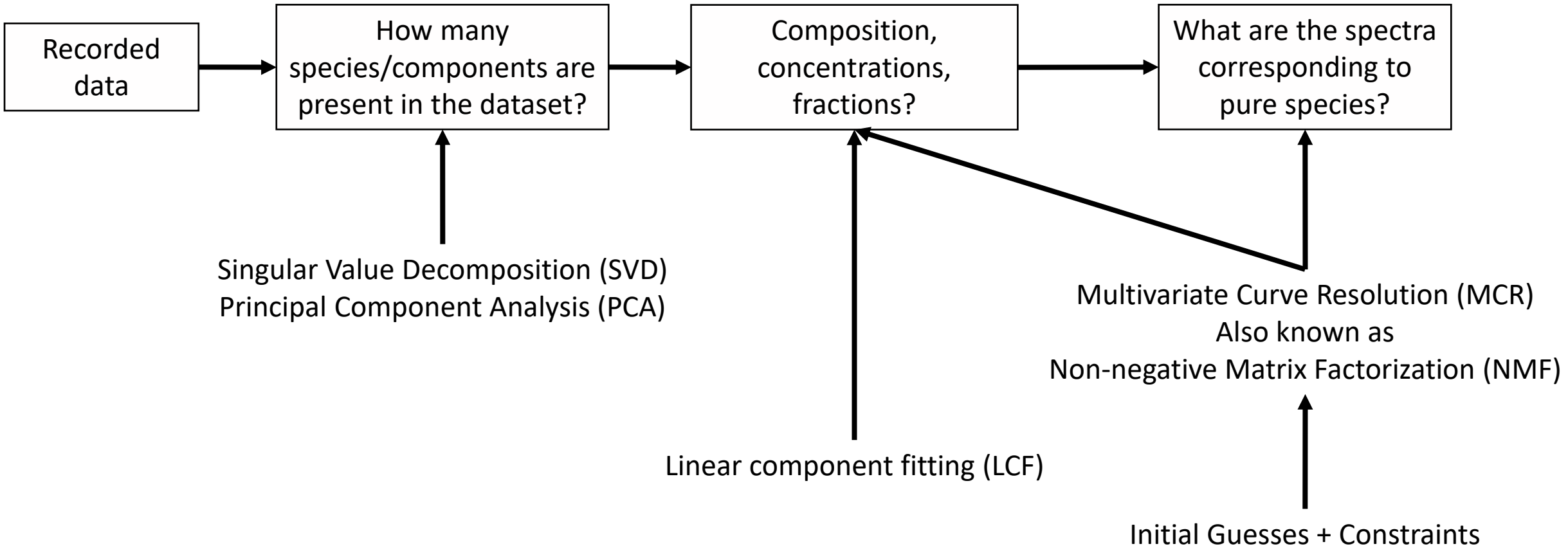


Multivariate curve resolution (MCR):

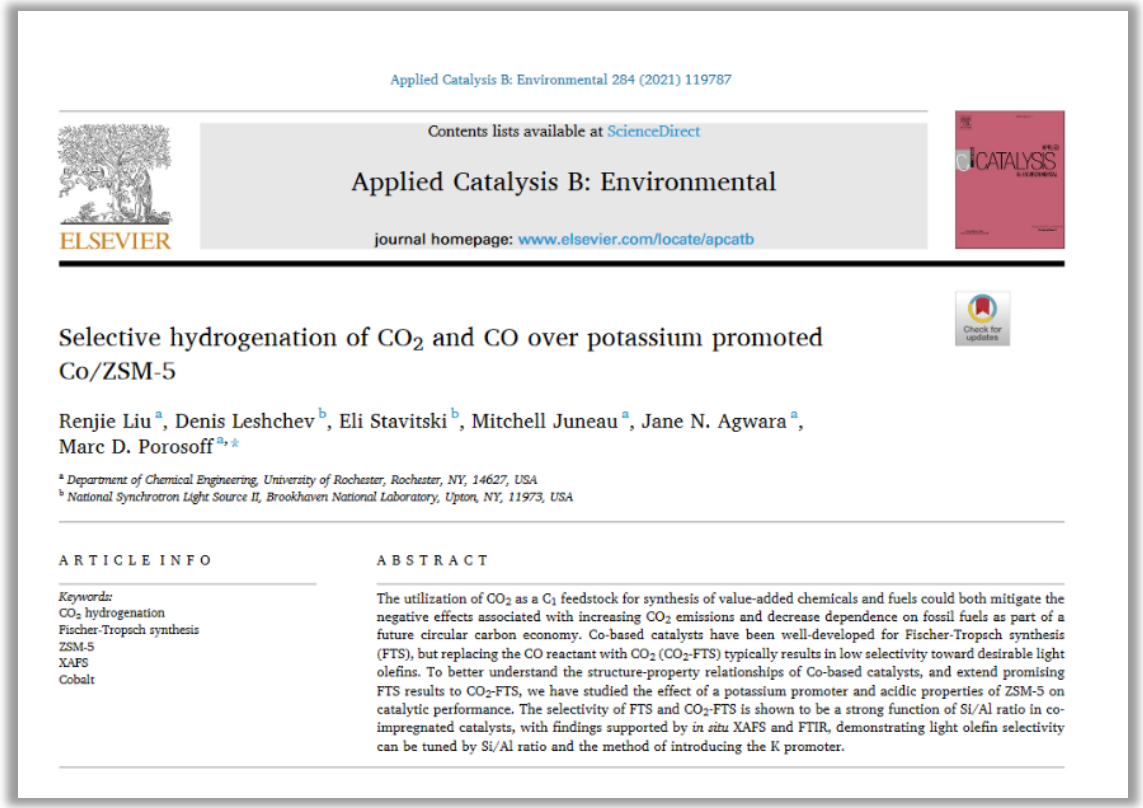
You have references → you have S → solve for C → solve for S (with constraints)

Until convergence

General analysis workflow for large datasets



Some examples from ISS



Applied Catalysis B: Environmental 284 (2021) 119787

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Selective hydrogenation of CO_2 and CO over potassium promoted Co/ZSM-5

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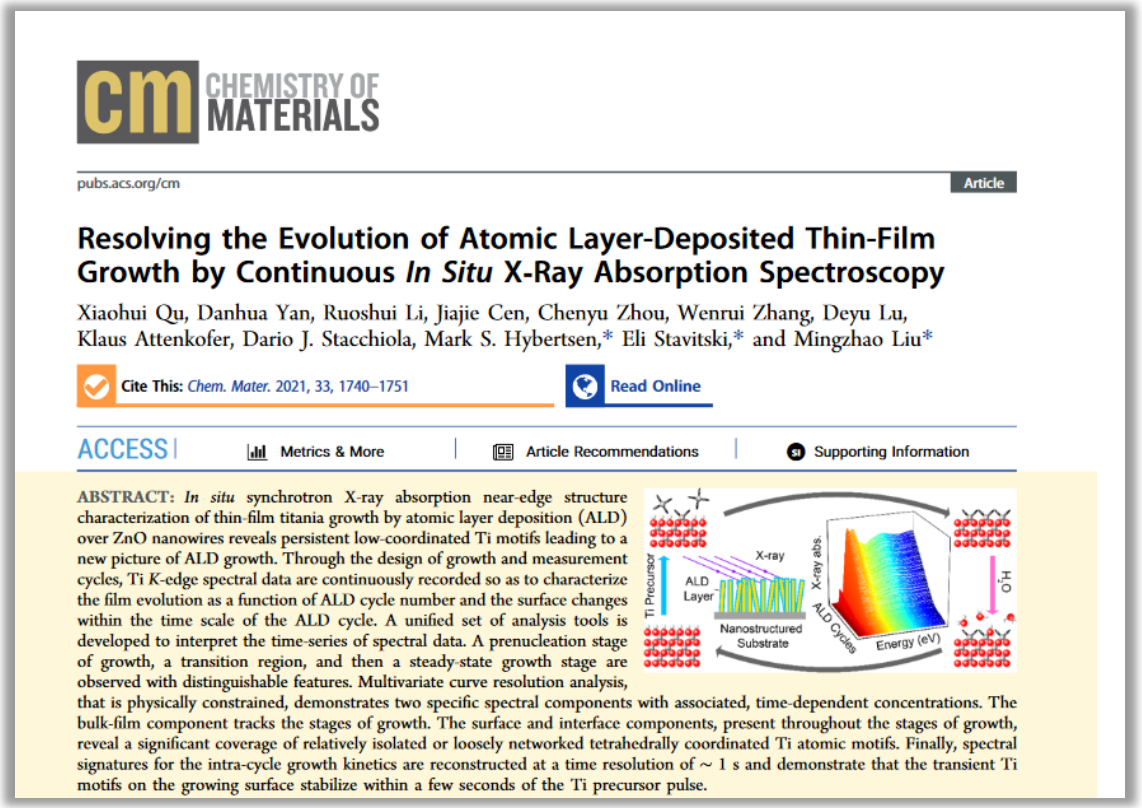
ARTICLE INFO

Keywords:
CO_2 hydrogenation
Fischer-Tropsch synthesis
ZSM-5
XAFS
Cobalt

ABSTRACT

The utilization of CO_2 as a C_1 feedstock for synthesis of value-added chemicals and fuels could both mitigate the negative effects associated with increasing CO_2 emissions and decrease dependence on fossil fuels as part of a future circular carbon economy. Co-based catalysts have been well-developed for Fischer-Tropsch synthesis (FTS), but replacing the CO reactant with CO_2 (CO_2-FTS) typically results in low selectivity toward desirable light olefins. To better understand the structure-property relationships of Co-based catalysts, and extend promising FTS results to CO_2-FTS, we have studied the effect of a potassium promoter and acidic properties of ZSM-5 on catalytic performance. The selectivity of FTS and CO_2-FTS is shown to be a strong function of Si/Al ratio in co-impregnated catalysts, with findings supported by *in situ* XAFS and FTIR, demonstrating light olefin selectivity can be tuned by Si/Al ratio and the method of introducing the K promoter.

R. Liu et al, Appl. Catal. B, 284 (2021), 119787



CHEMISTRY OF MATERIALS

pubs.acs.org/cm Article

Resolving the Evolution of Atomic Layer-Deposited Thin-Film Growth by Continuous *In Situ* X-Ray Absorption Spectroscopy

Xiaohui Qu, Danhua Yan, Ruoshui Li, Jiajie Cen, Chenyu Zhou, Wenrui Zhang, Deyu Lu, Klaus Attenkofer, Dario J. Stacchiola, Mark S. Hybertsen,* Eli Stavitski,* and Mingzhao Liu*

Cite This: *Chem. Mater.* 2021, 33, 1740−1751 Read Online

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ABSTRACT: *In situ* synchrotron X-ray absorption near-edge structure characterization of thin-film titania growth by atomic layer deposition (ALD) over ZnO nanowires reveals persistent low-coordinated Ti motifs leading to a new picture of ALD growth. Through the design of growth and measurement cycles, Ti *K*-edge spectral data are continuously recorded so as to characterize the film evolution as a function of ALD cycle number and the surface changes within the time scale of the ALD cycle. A unified set of analysis tools is developed to interpret the time-series of spectral data. A prenucleation stage of growth, a transition region, and then a steady-state growth stage are observed with distinguishable features. Multivariate curve resolution analysis, that is physically constrained, demonstrates two specific spectral components with associated, time-dependent concentrations. The bulk-film component tracks the stages of growth. The surface and interface components, present throughout the stages of growth, reveal a significant coverage of relatively isolated or loosely networked tetrahedrally coordinated Ti atomic motifs. Finally, spectral signatures for the intra-cycle growth kinetics are reconstructed at a time resolution of ~ 1 s and demonstrate that the transient Ti motifs on the growing surface stabilize within a few seconds of the Ti precursor pulse.

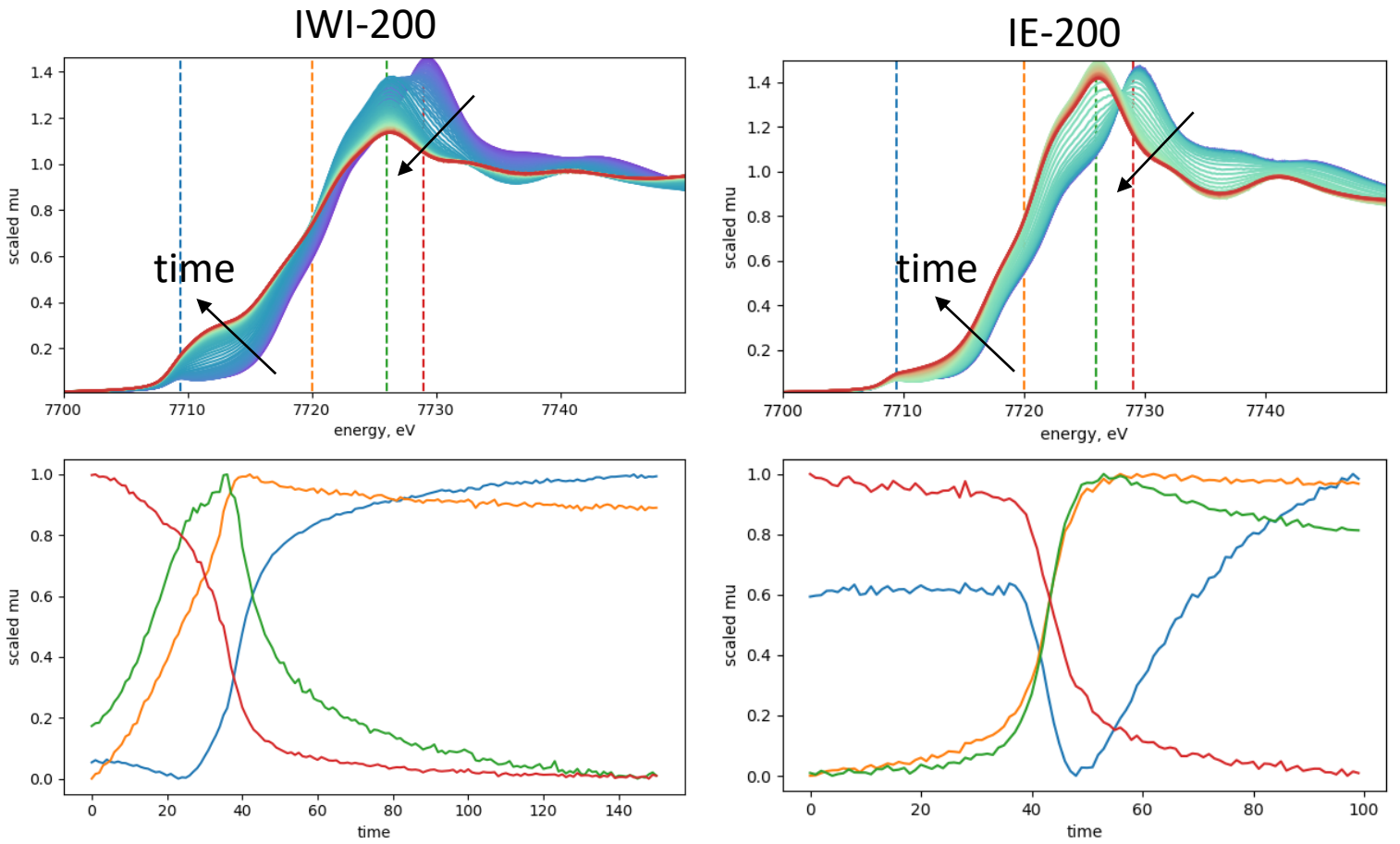
X. Qu et al, Chem. Mater. (2021)
DOI: 10.1021/acs.chemmater.0c04547

In situ study of Co/ZSM catalyst reduction

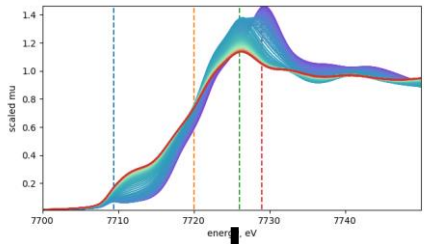
- Co is embedded in zeolite ZSM-5 framework
- The catalyst performance was tested against method of K impregnation for Si/Al = 200 ratio
  - Incipient Wetness Impregnation (IWI) synthesis
  - Ion Exchange (IE) synthesis
- What is the kinetics of reduction and what is the degree of reduction at the end of the process?

Overview of the IWI and IE datasets

- Both datasets qualitatively show the signs of reduction
- Complex multi-stage kinetics can be observed in both cases
- How do we analyze such datasets?



Singular Value Decomposition



data → $A = USV^T$

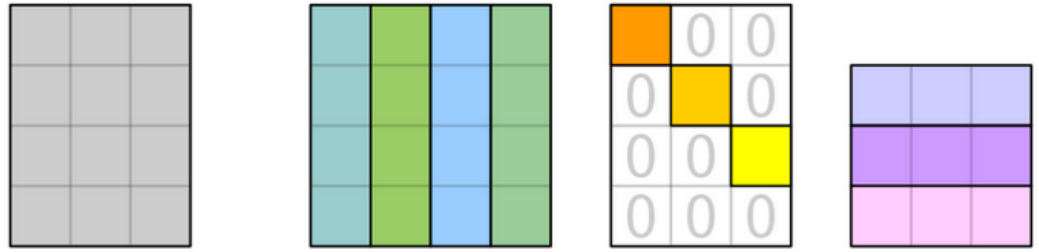
Left singular vectors
Eigen-spectra

Singular values
Indicate the amplitude of the contribution of the component

Right singular vectors
Eigen-kinetic traces

Components are sorted according to their significance

yet another way to factorize your data
Model free!



$A = U \quad S \quad V^T$

$m \times n \quad m \times m \quad m \times n \quad n \times n$

Picture: wikipedia

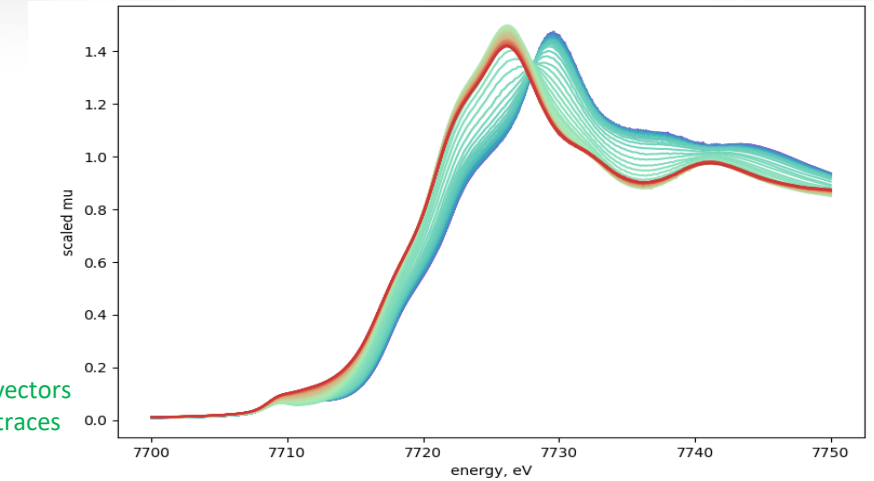
Singular Value Decomposition analysis of IE-200 dataset

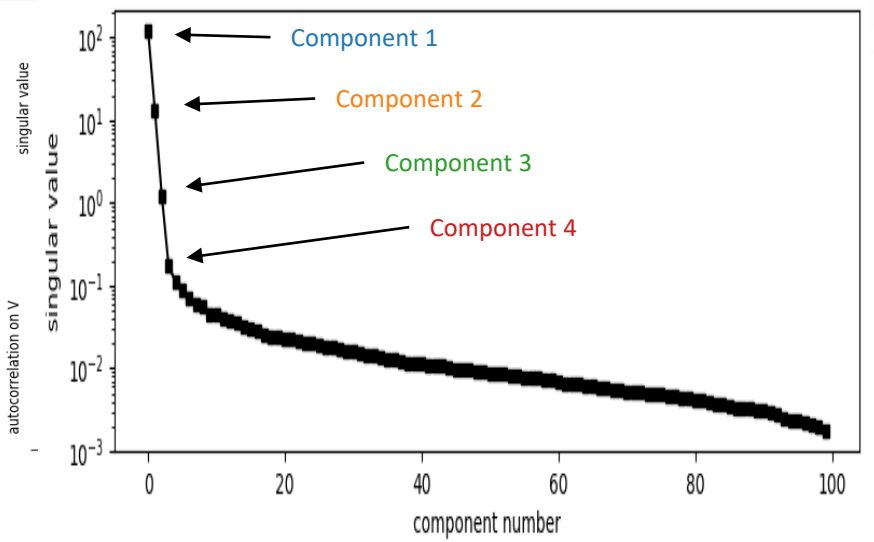
data → $A = USV^T$

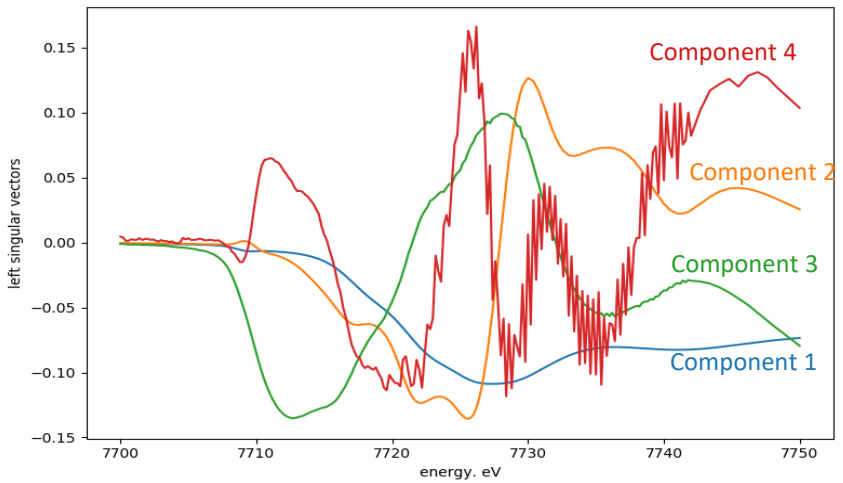
Left singular vectors
Eigen-spectra

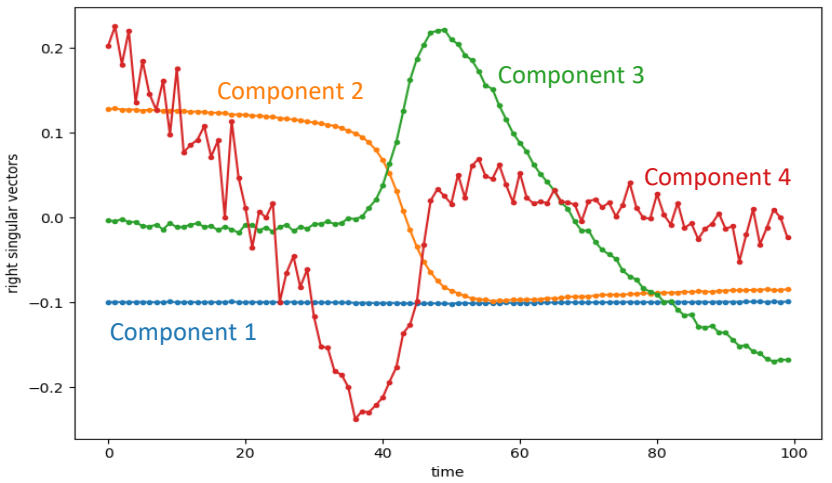
Singular values
Indicate the amplitude of the contribution of the component

Right singular vectors
Eigen-kinetic traces

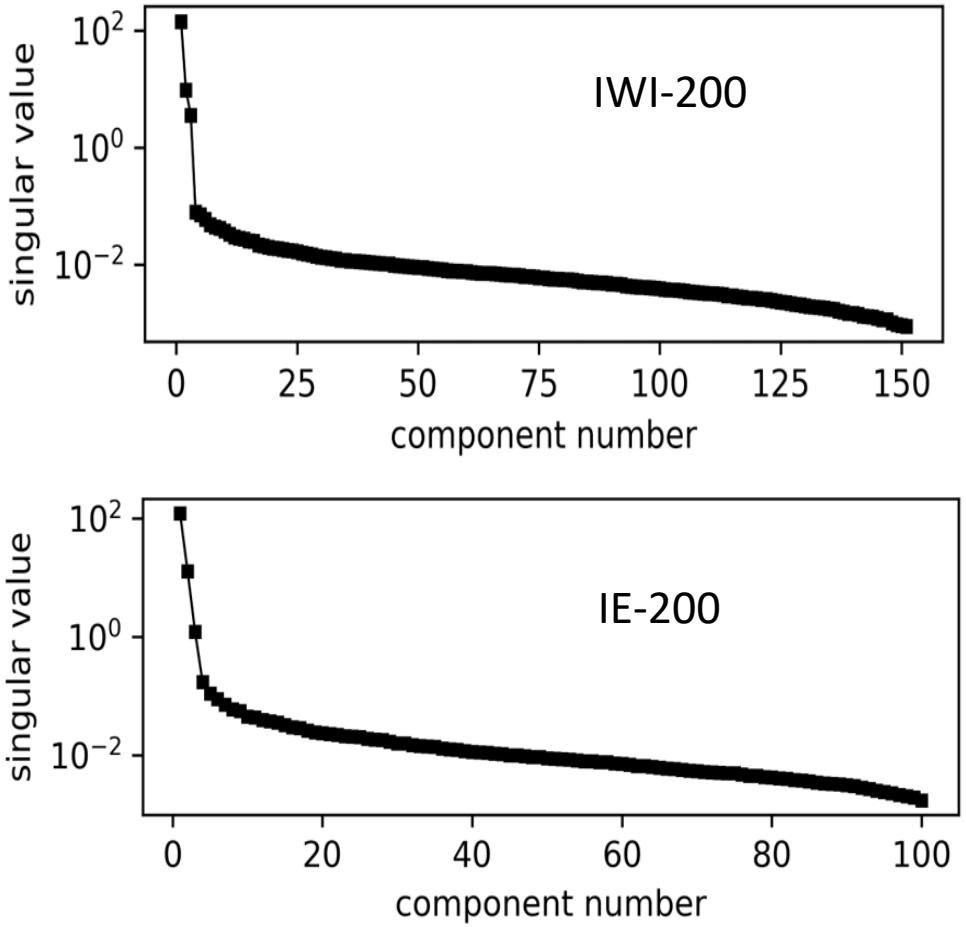








Number of significant components: scree plot



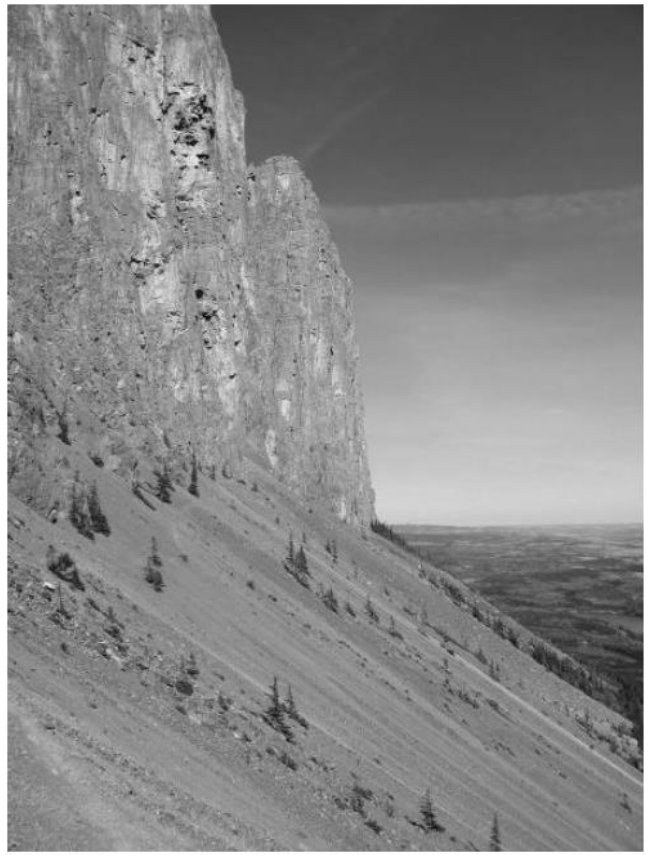
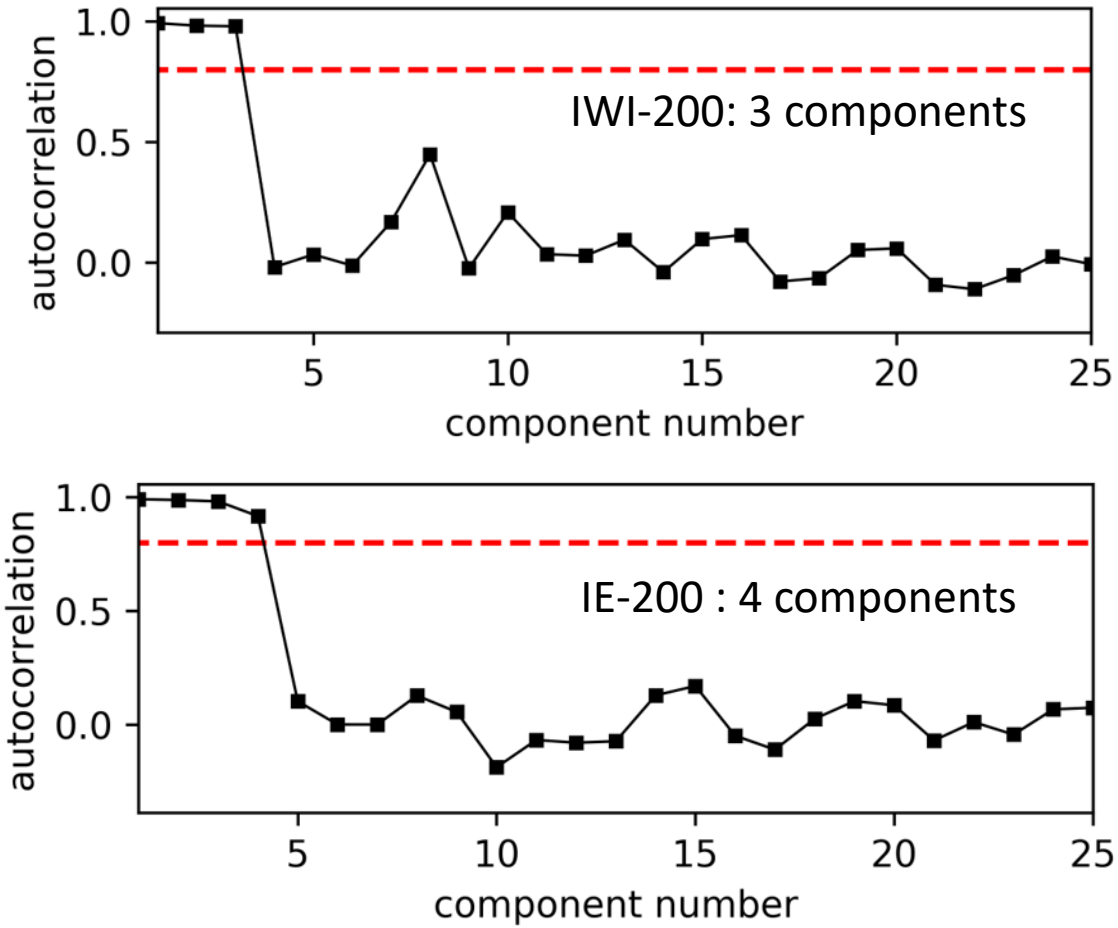


Figure 8.12 Yamnuska, a mountain in the Canadian Rockies. Note how the steep mountain side gives ways to a gentler slope made up of scree, which is a material made of rock fragments weathered from the mountain. Kevin Lenz. This photo is licensed under the Creative Commons Attribution-Share Alike 2.5 Generic license.

Number of significant components: autocorrelation



Autocorrelation:

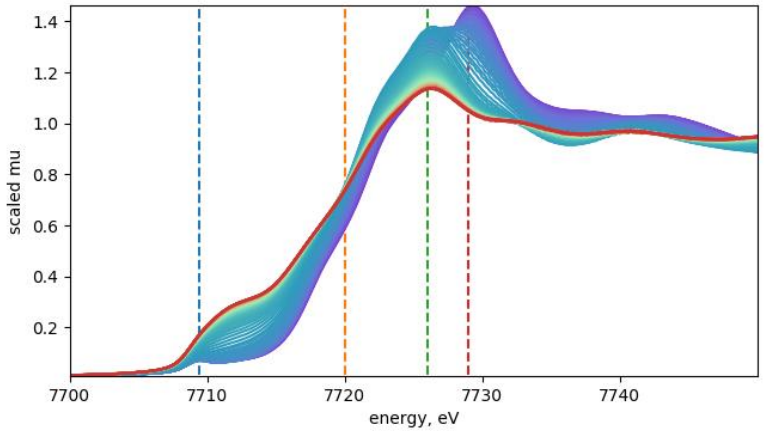
$$C_i = \sum_j V_{i,j} V_{i,j-1}$$

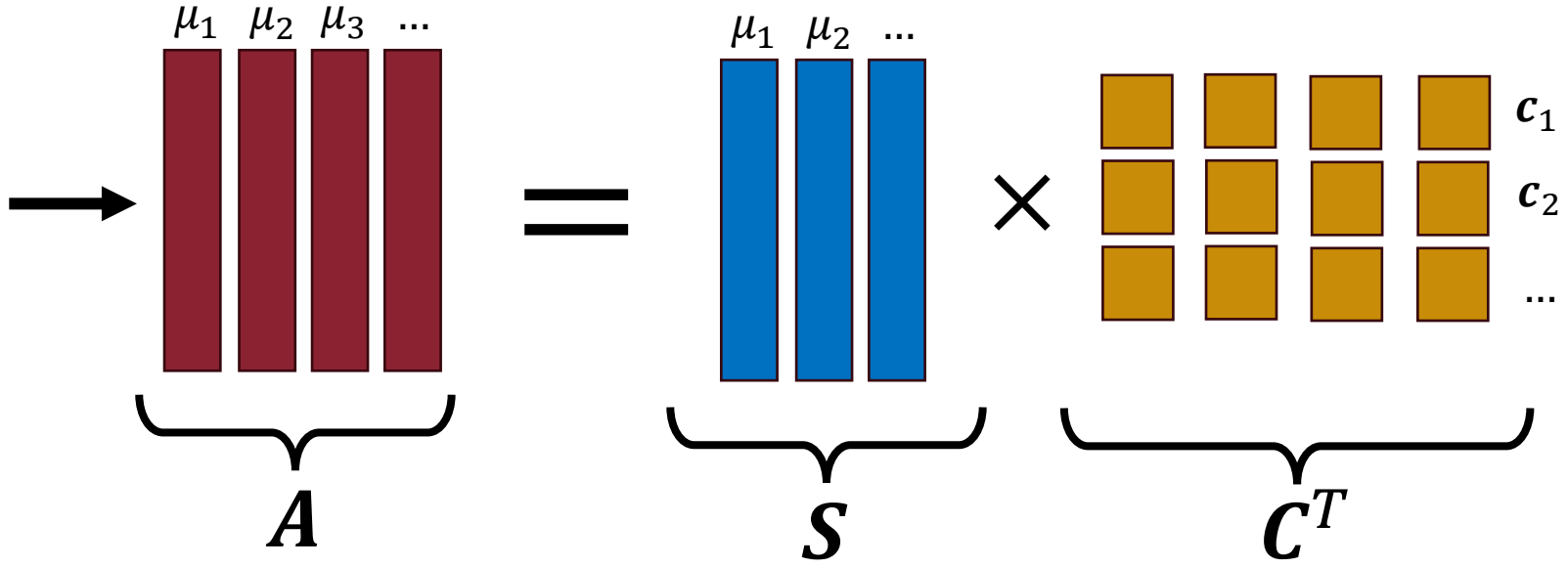
(Arbitrary) threshold: 0.8

Singular value decomposition: Application to analysis of experimental data
Methods in Enzymology
Volume 210, 1992, Pages 129-192

Data factorizations: Multivariate curve resolution (MCR)

A bunch of spectra $\{\mu_i(E)\}$





Multivariate curve resolution (MCR):

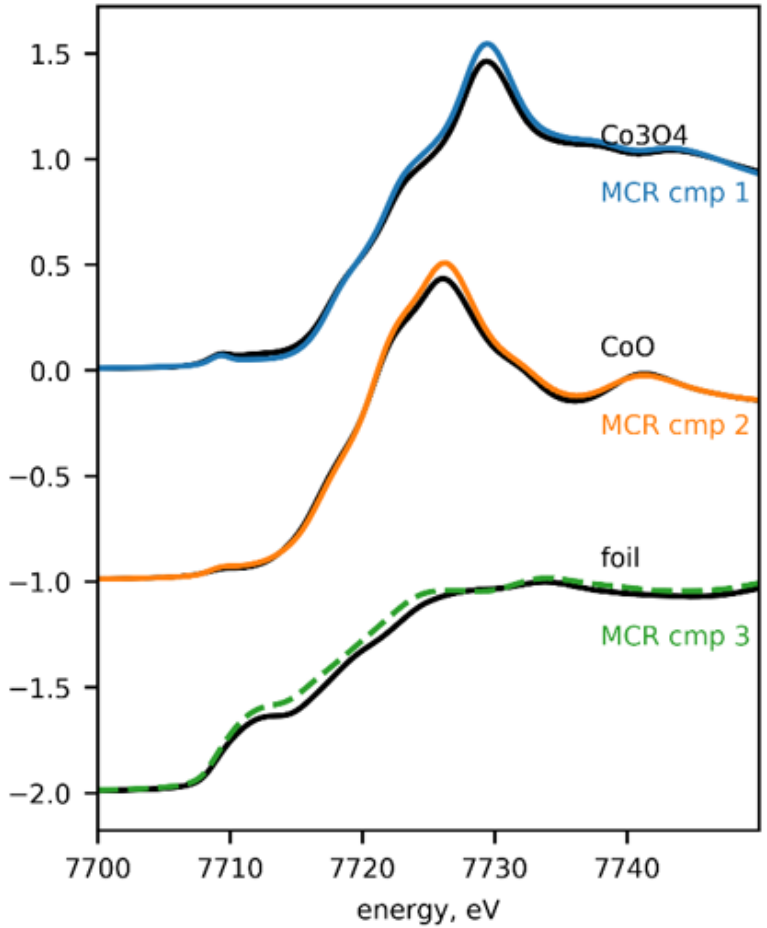
You have references → you have S → solve for C → solve for S (with constraints)

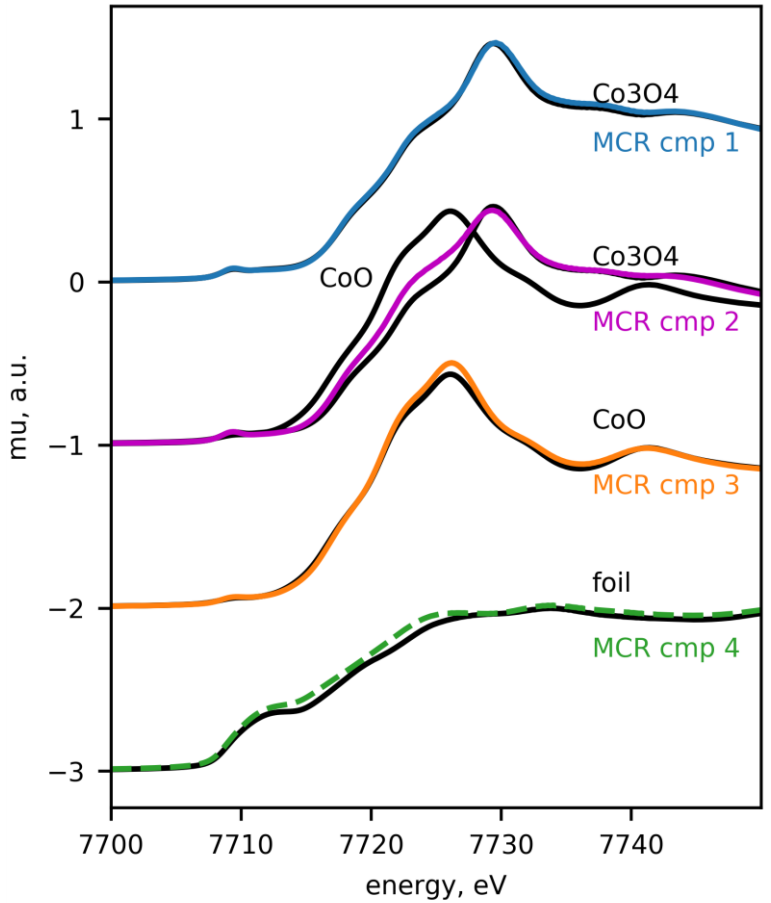
Until convergence

$$C = A^T S(S^T S)^{-1}$$

$$S = AC(C^T C)^{-1}$$

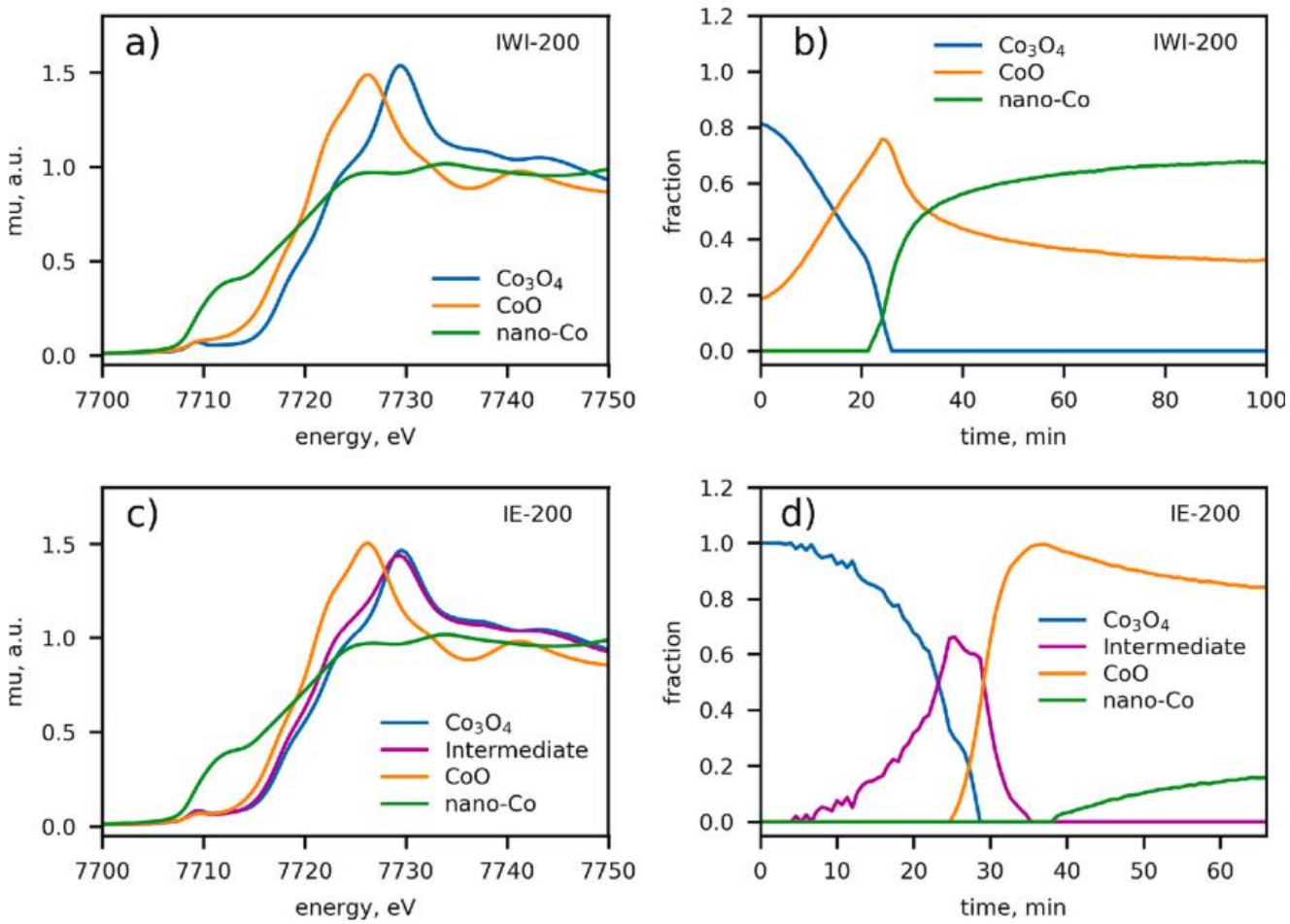
MCR-retrieved components VS starting solutions



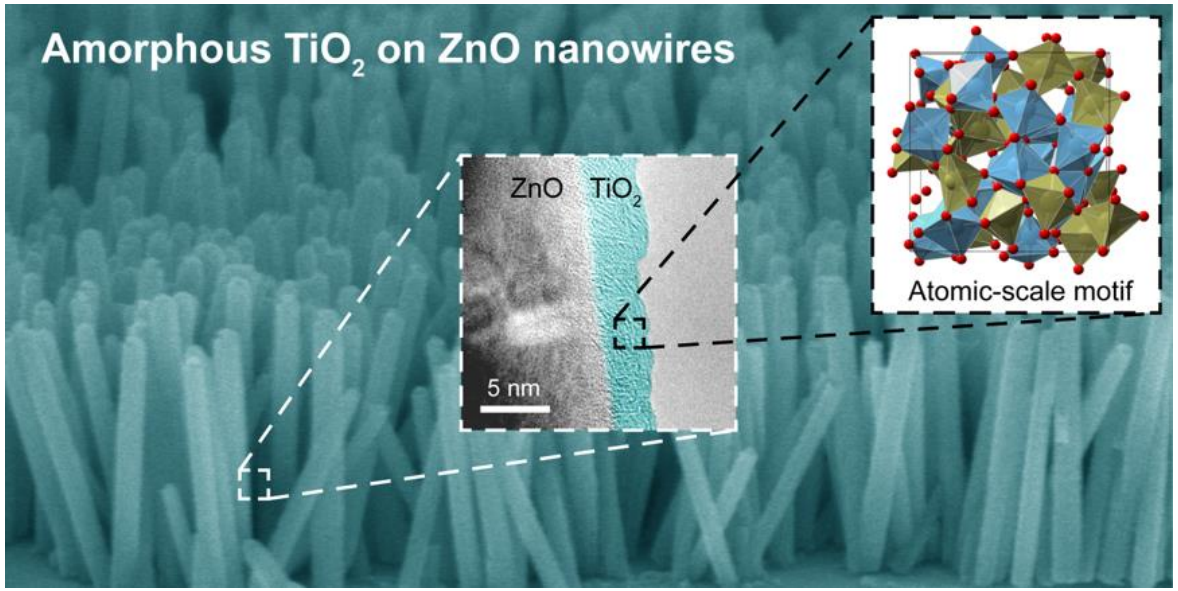


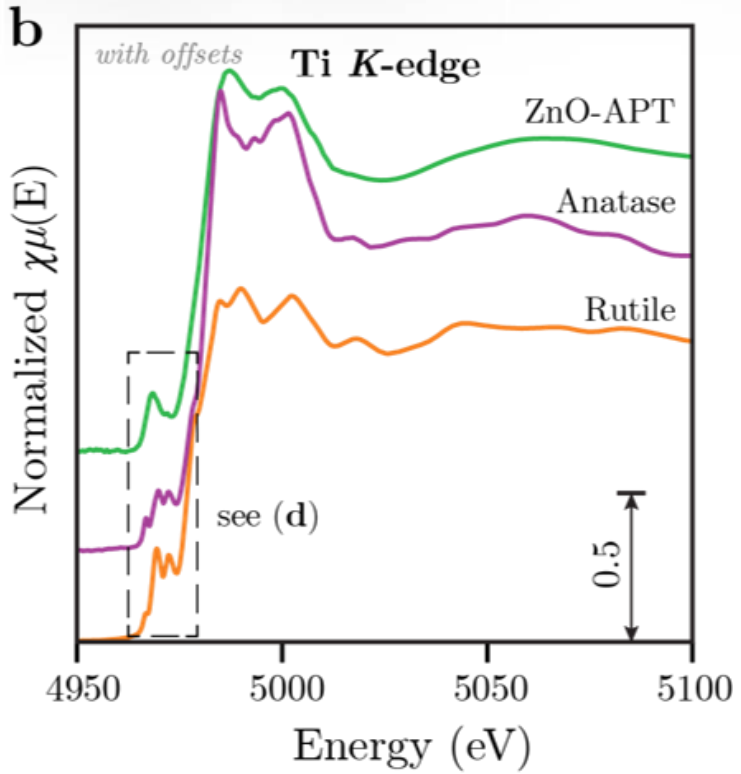
Components and fractions extracted from MCR

- IWI-200 dataset is successfully fitted using only non-negativity constraint
- IE-200 fitting was done with fixed metallic cobalt component and additional constraining of concentrations to be above 1.5% level improves the quality of retrieved spectra



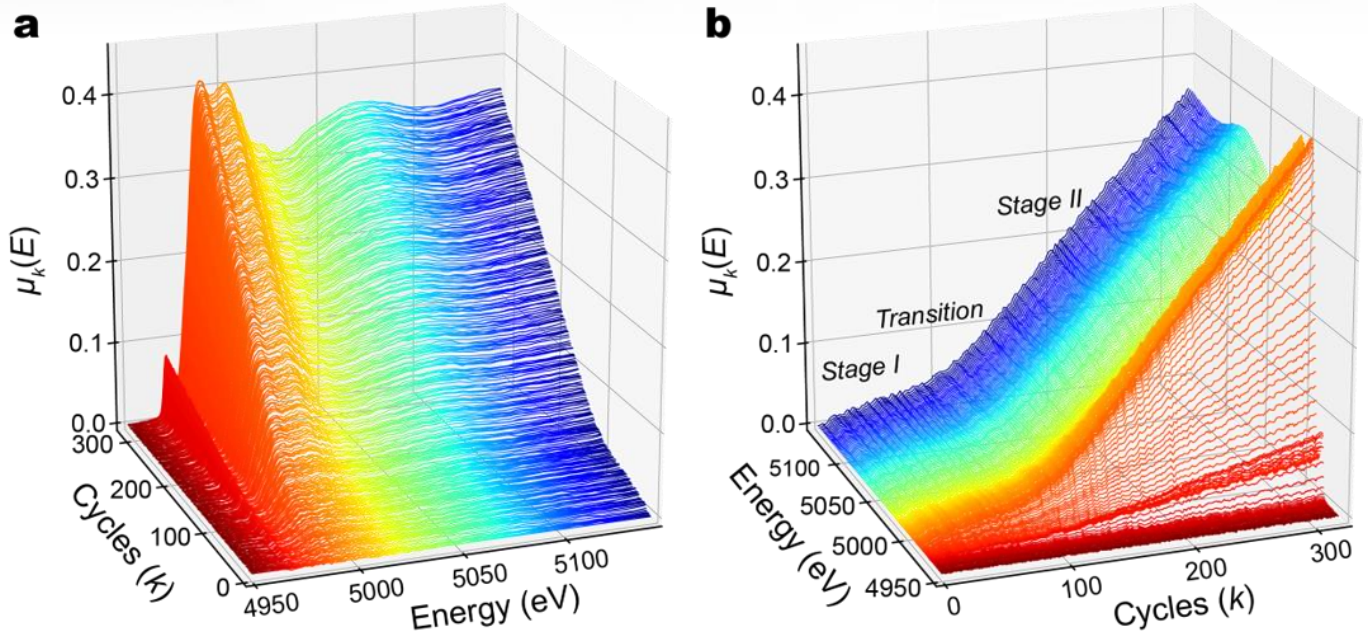
In situ study of TiO2 thin film growth over ZnO nanowires – Project 2





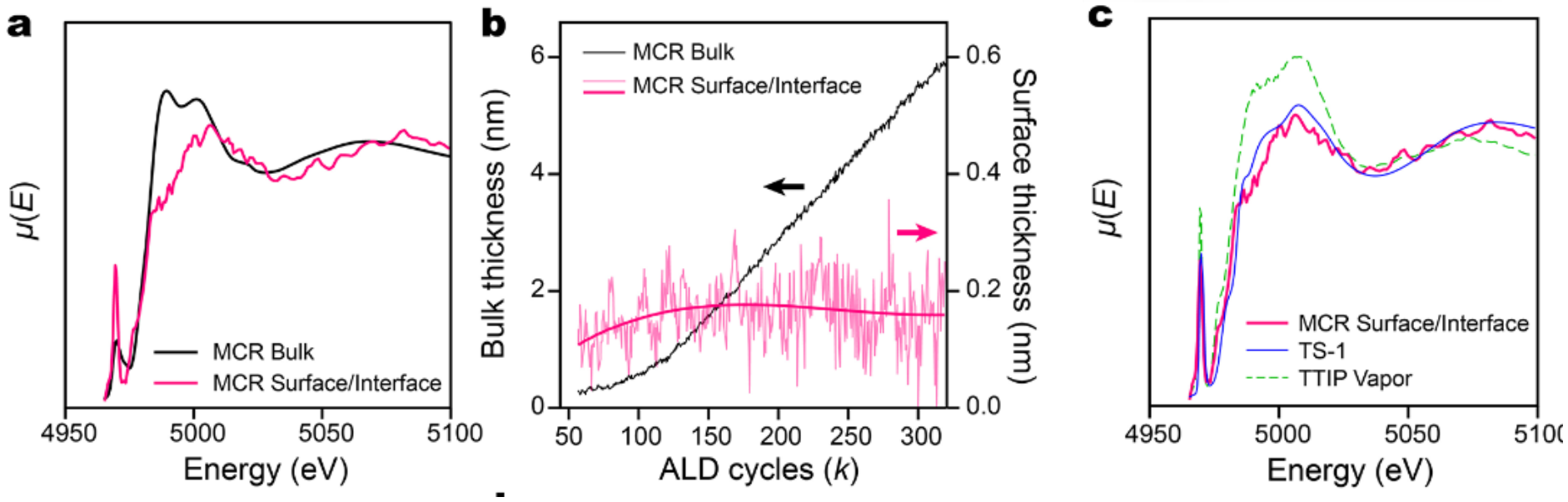
- Atomic layer deposition (ALD) was used to make thin films of TiO2 over ZnO nanowires
- Ex situ measurements demonstrate that TiO_2 is highly amorphous with distinctly different XANES from crystallin TiO_2 with half of Ti^{4+} under-coordinated (CN=4-5)

In situ XANES reveals different ALD growth stages



- XANES spectra were recorded as a function of the ALD cycle
- ALD cycle: titaniumisopropoxide (TTIP) and water are alternately introduced into the chamber as short pulses (~0.5s) separated by 60s
- The XANES spectral series readily demonstrates a two-stage growth process

MCR-ALS analysis of the XANES data

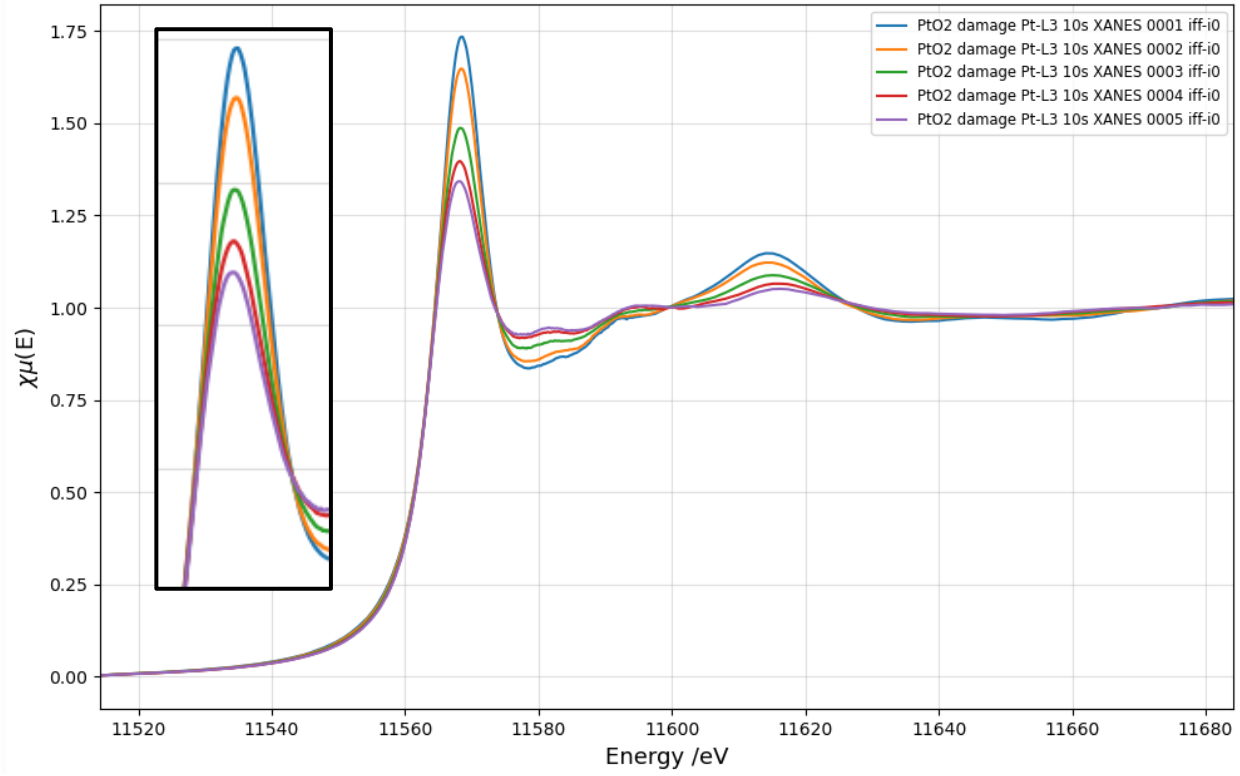


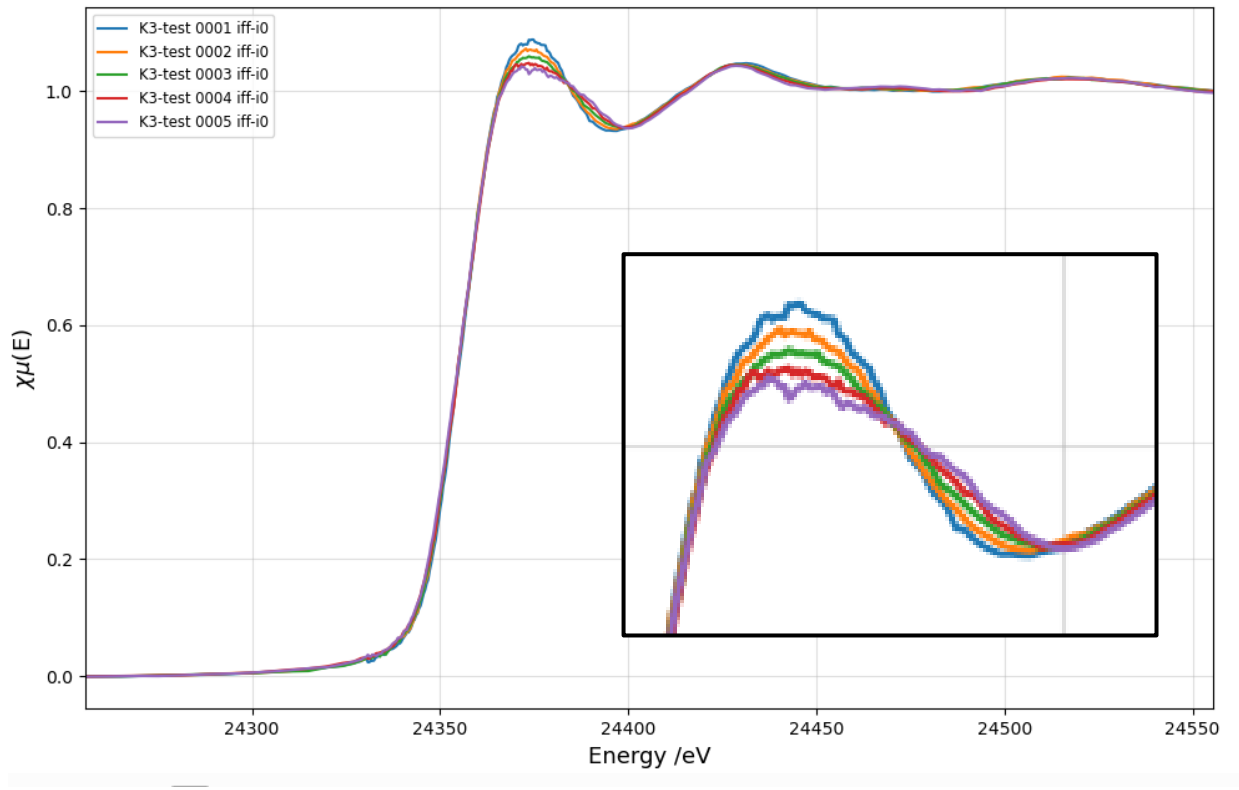
- The initial guesses were taken from the start end end of the series
- Non-negativity constraint and an additional concentration smoothness constraint were introduced to
- The recovered spectra correspond to the bulk and surface signals. The surface signal pre-edge feature intensity closely resembles the 4-coordinated Ti^{4+} in both TTIP and Titanosilicate

Mixed samples/Harnessing large datasets – Conclusions

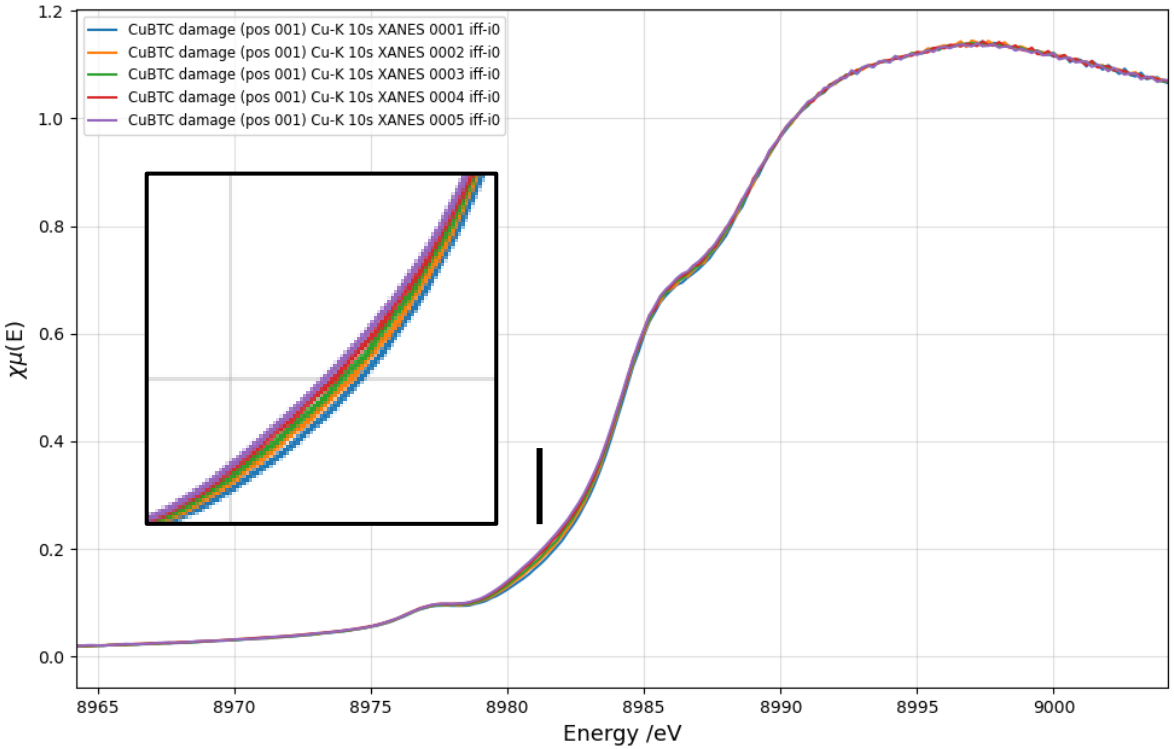
- LCF is a good first step to understand the sample composition
- PCA/SVD is a quick method to see how many components/species are in the spectral series
- MCR can be used to extract components/concentration profiles
- Components can be analyzed using our XANES intuition and/or comparing with references

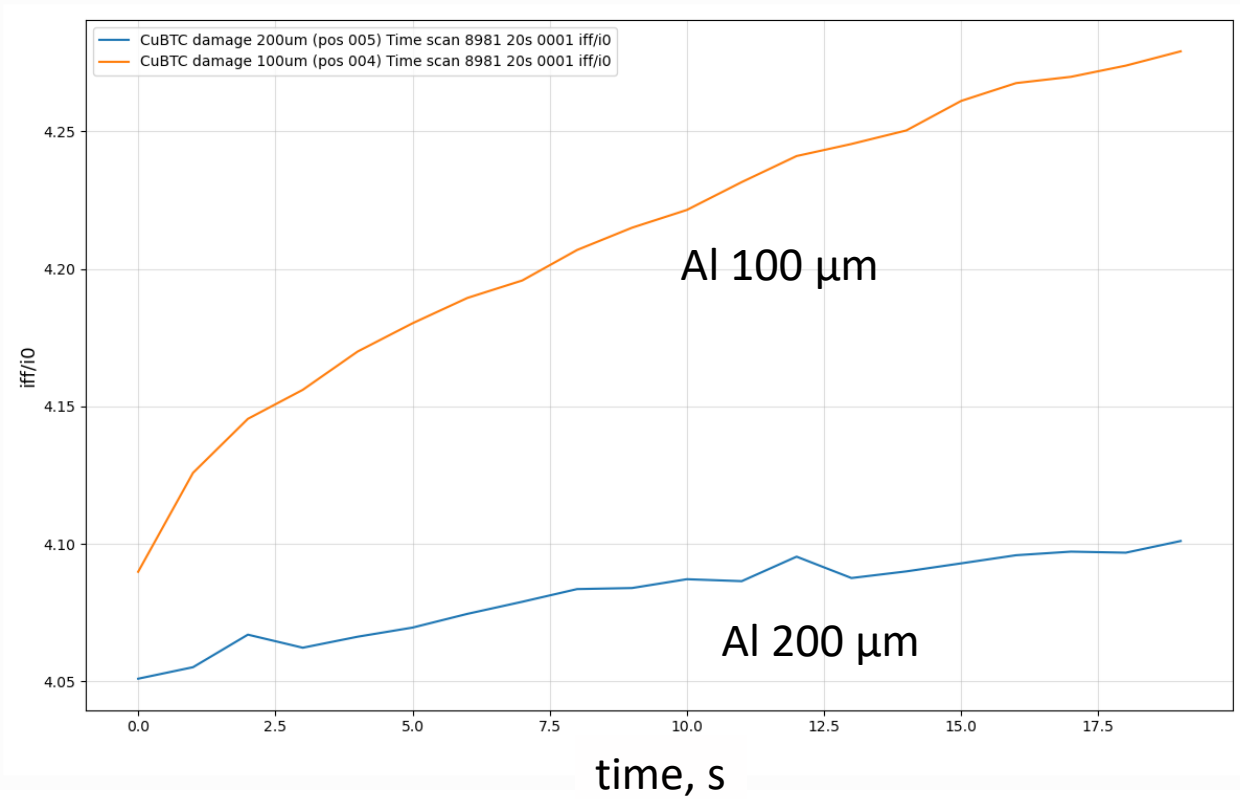
Bonus: XANES and radiation-induced damage (1)





Bonus: XANES and radiation-induced damage (2)





Bonus: XANES and radiation-induced damage (3)