Alamgir Lab

X-ray Absorption at the Near-edge and Its Applications

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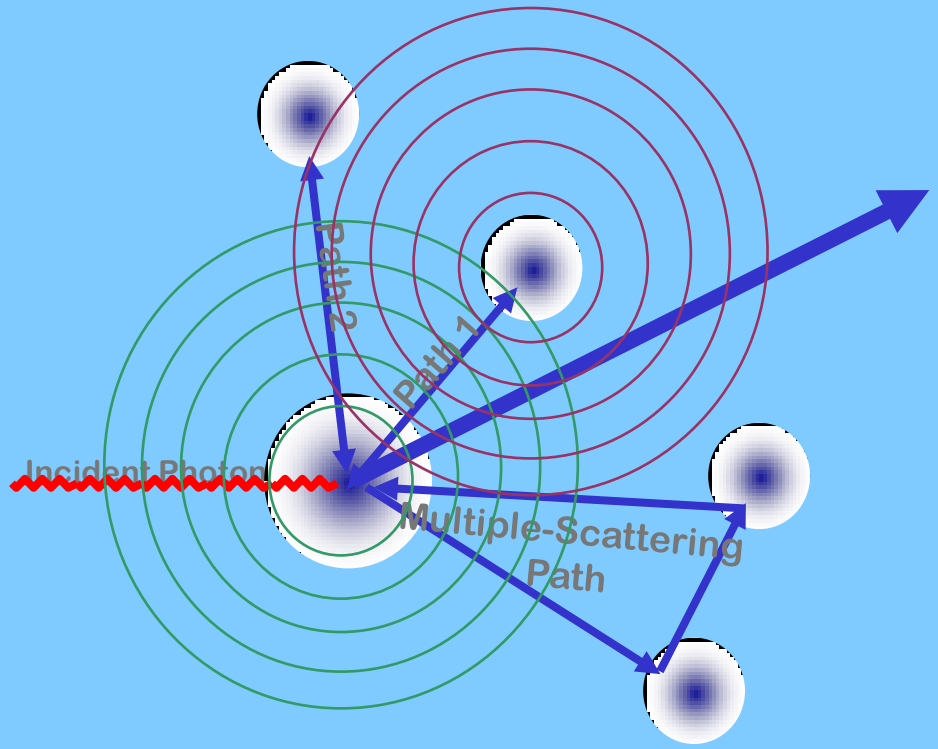
Cartoon of XAS

I_0 at

of X-rays
(synchrotron)

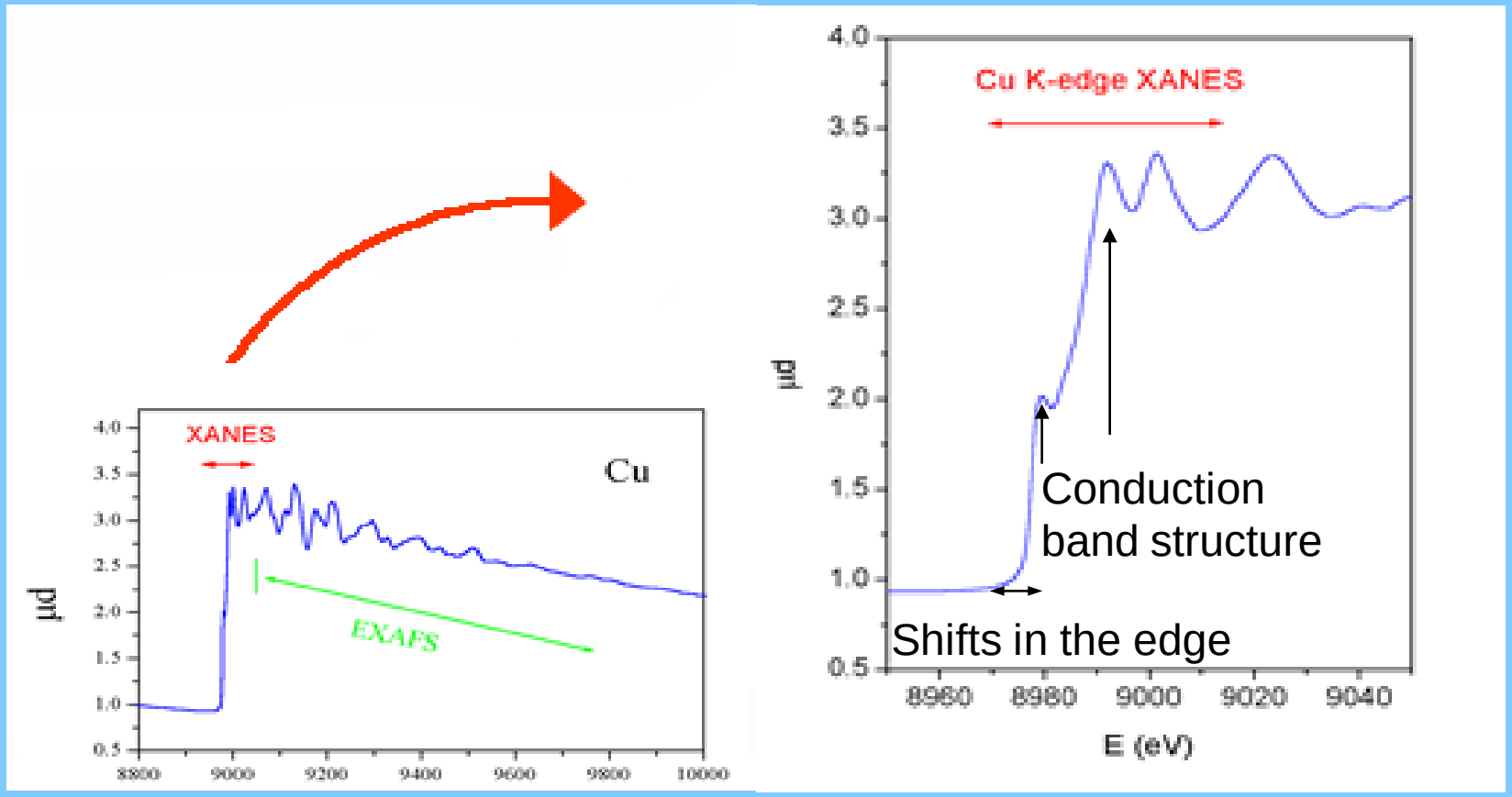


$\ln(I_0/I_t)$ or
I_f/I_0

measured by
ionization

chambers in XAS

Near edge X-ray Absorption Spectroscopy is too Often Neglected



Resources Available Online on XAS – XAFS Training Module

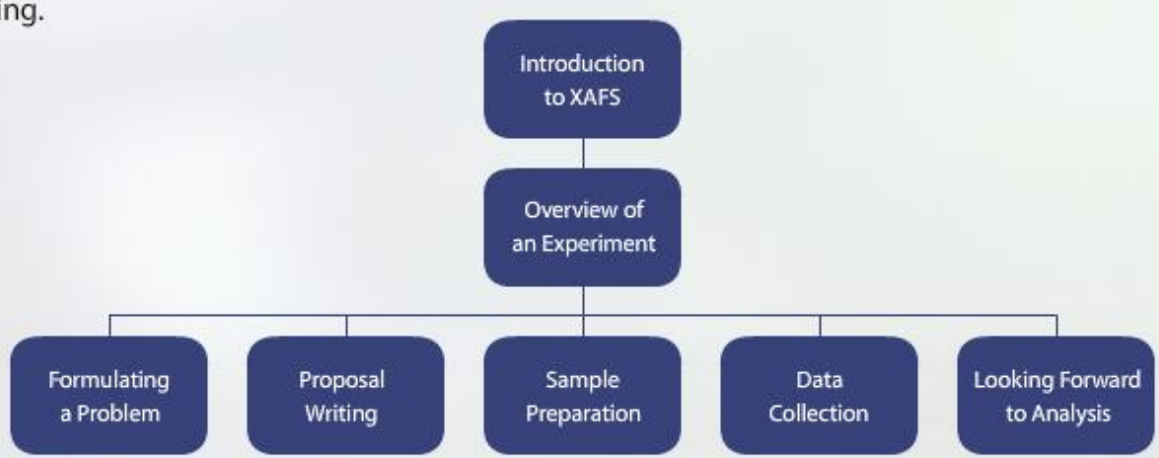
NSLS

NATIONAL SYNCHROTRON LIGHT SOURCE

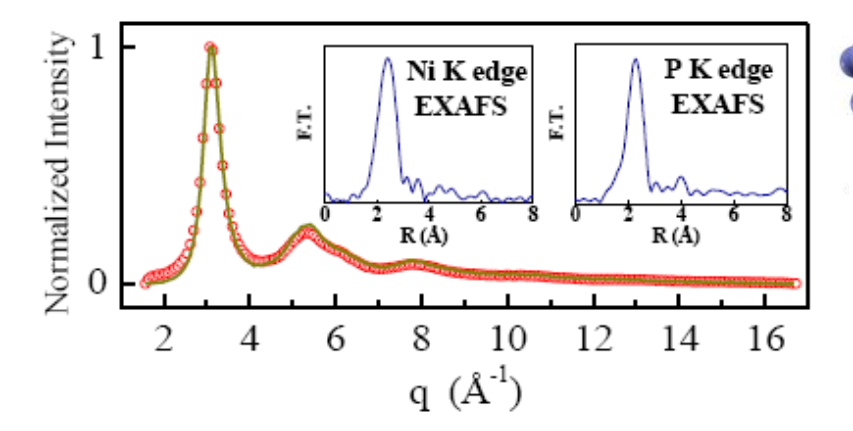
XAFS Online Orientation

Welcome to the X-Ray Absorption Fine Structure Online Orientation!

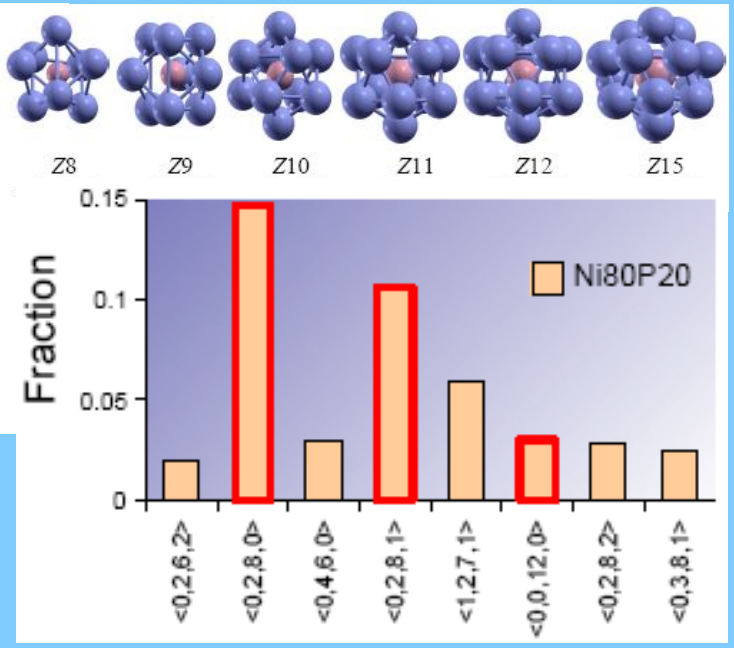
This orientation will provide you with tips that will help you conduct a successful x-ray absorption fine-structure spectroscopy (XAFS) experiment at the National Synchrotron Light Source (NSLS). We strongly recommend that you explore it whether you are new to XAFS, new to the NSLS, or just want to get the most out of your application for beam time. You may also want to come back to this orientation from time to time to refresh yourself on important points. From this page, you can choose any of the modules below. Working through the orientation typically takes about an hour, and does not need to be done at one sitting.



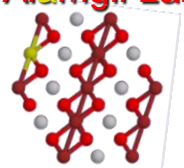
Structure from Each Constituent Element of a Glass System



Nature, Vol 439|26 January 2006, p. 419-425



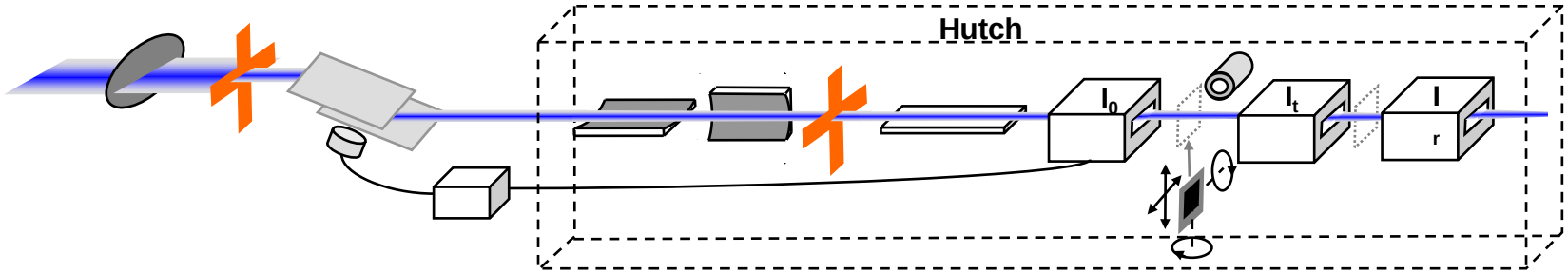
- Atomic specificity
- Local scattering
- Dual information:
  - a) the softness of neighboring atoms (XANES) and
  - b) their position (EXAFS).



Near-edge Information

- Oxidation State
  - Direct fingerprinting
  - Theory-backed (eg. FEFF 8)
- Reaction pathways
  - Statistical tools
- LUMO occupancy
  - Polarization alignment to MO

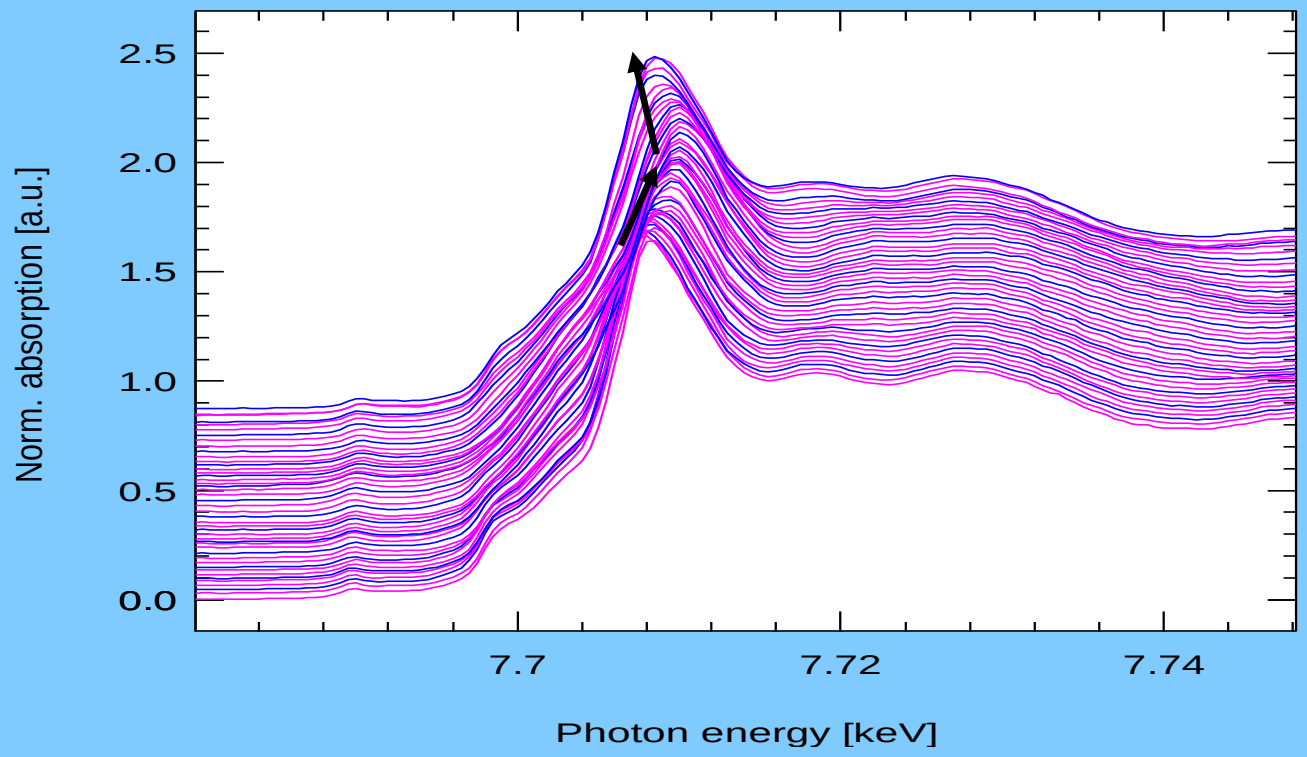
How Complicated is an XAS Experiment?



- Window
- Double crystal monochromator (mono)
- (Entrance/Exit) beam defining aperture
- Piezoelectric crystal
- Focusing mirror(s)
- Harmonic rejection mirror
- Ionization chamber
- Fluorescence detector
- Sample stage

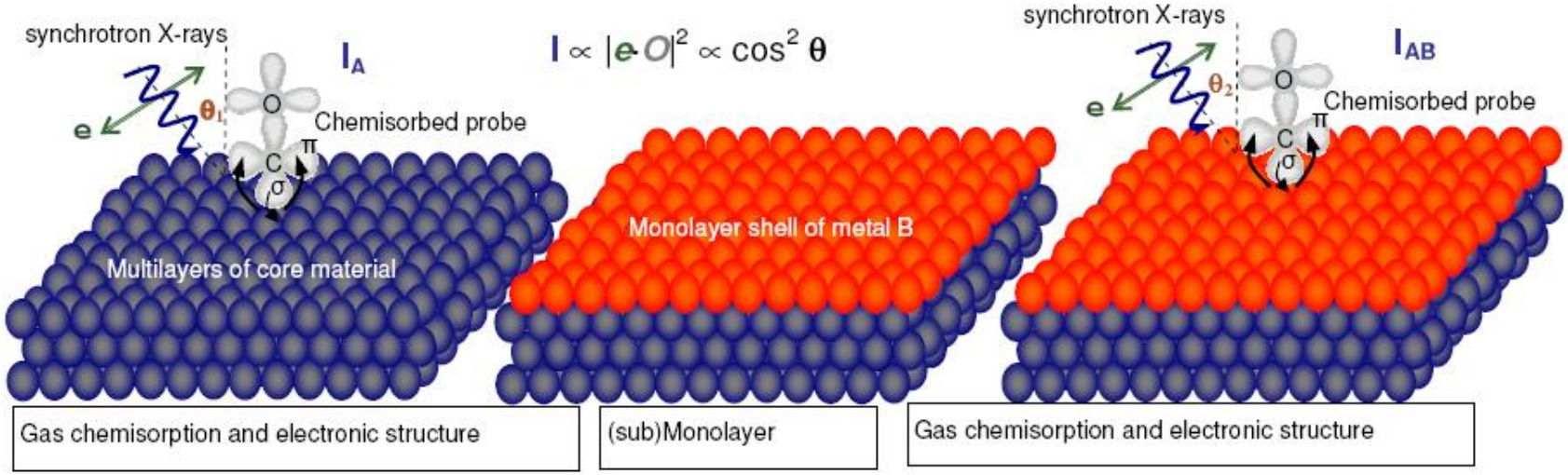
Near-edge Information

- Reaction Pathways

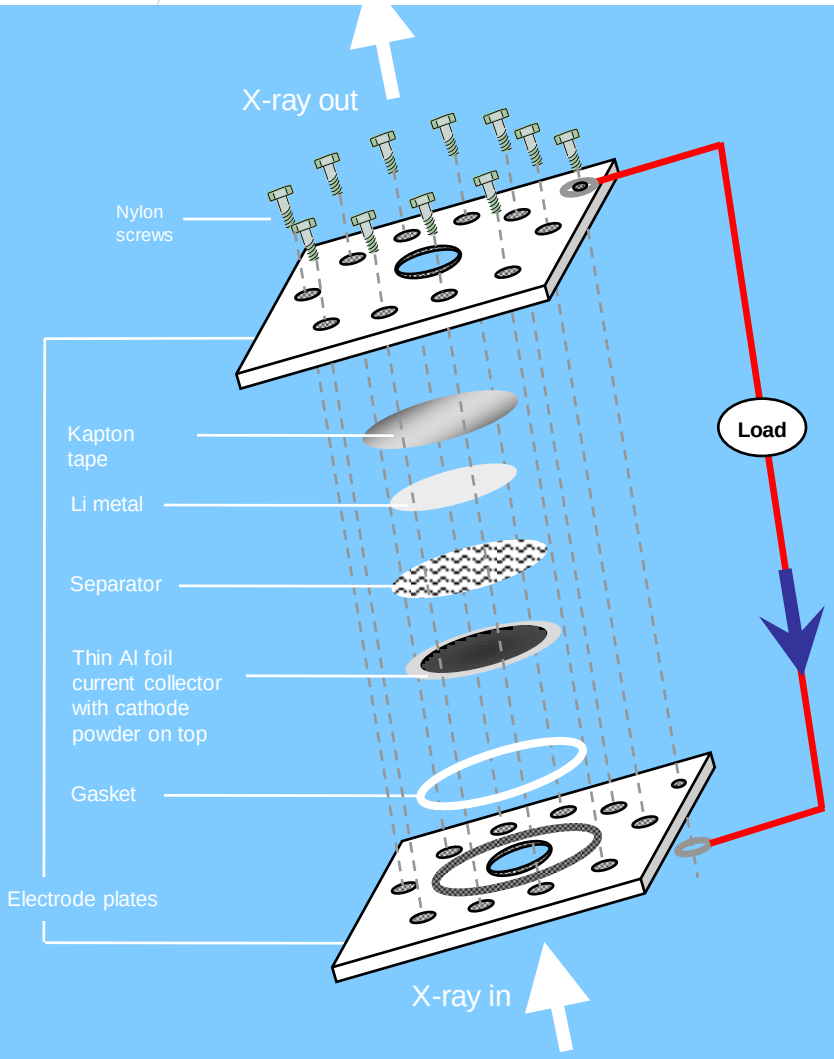


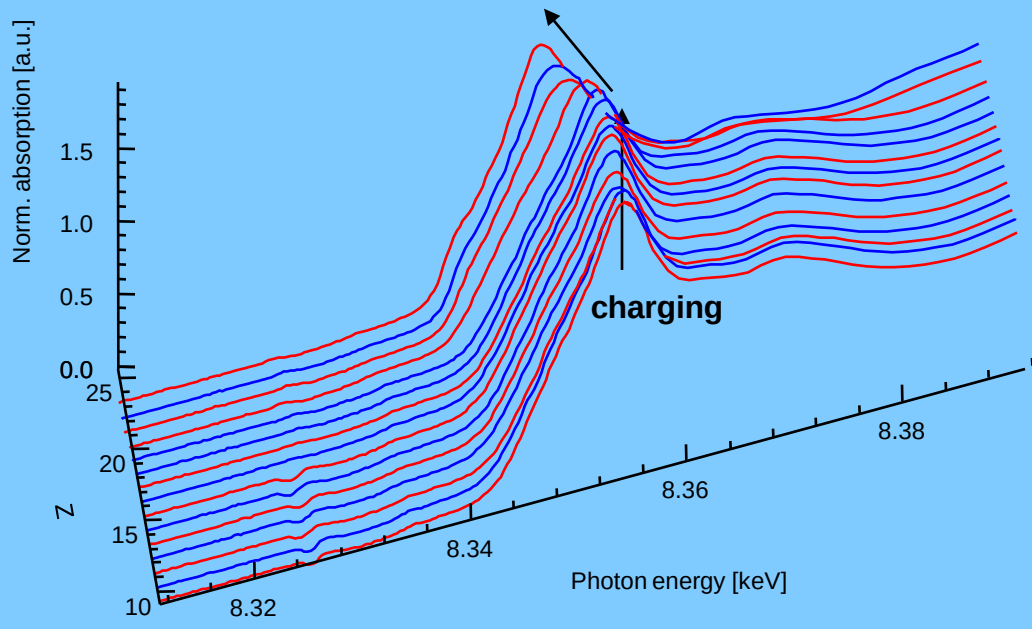
Near-edge Information

- LUMO occupancy



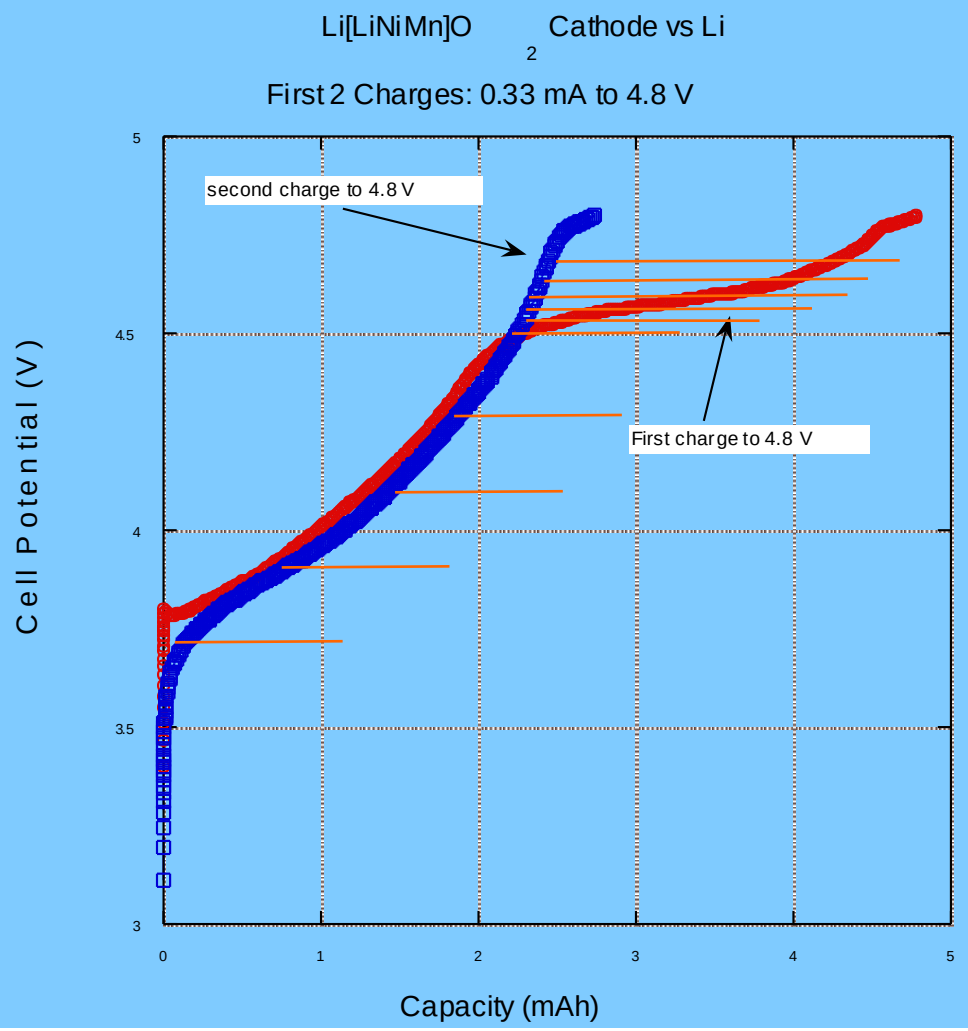
In-situ XAS experiment



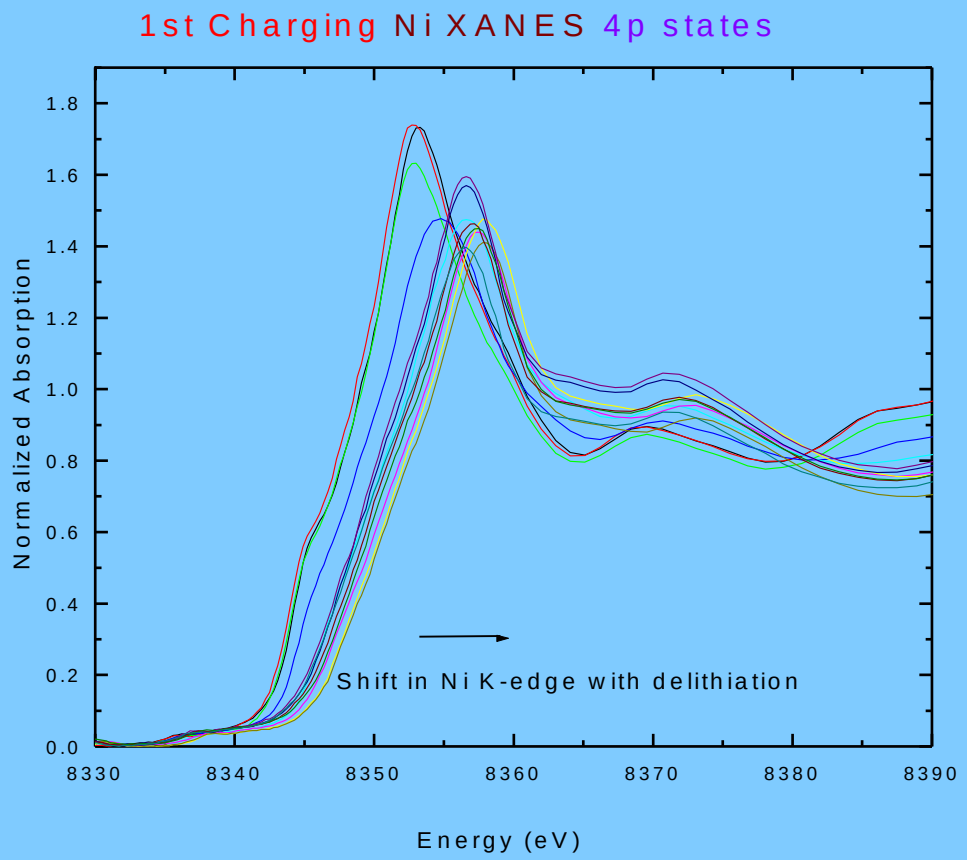


Atomic and electronic structure can be measured as a function of the state of charge.

Time-Resolution of In-situ XAS Experiment

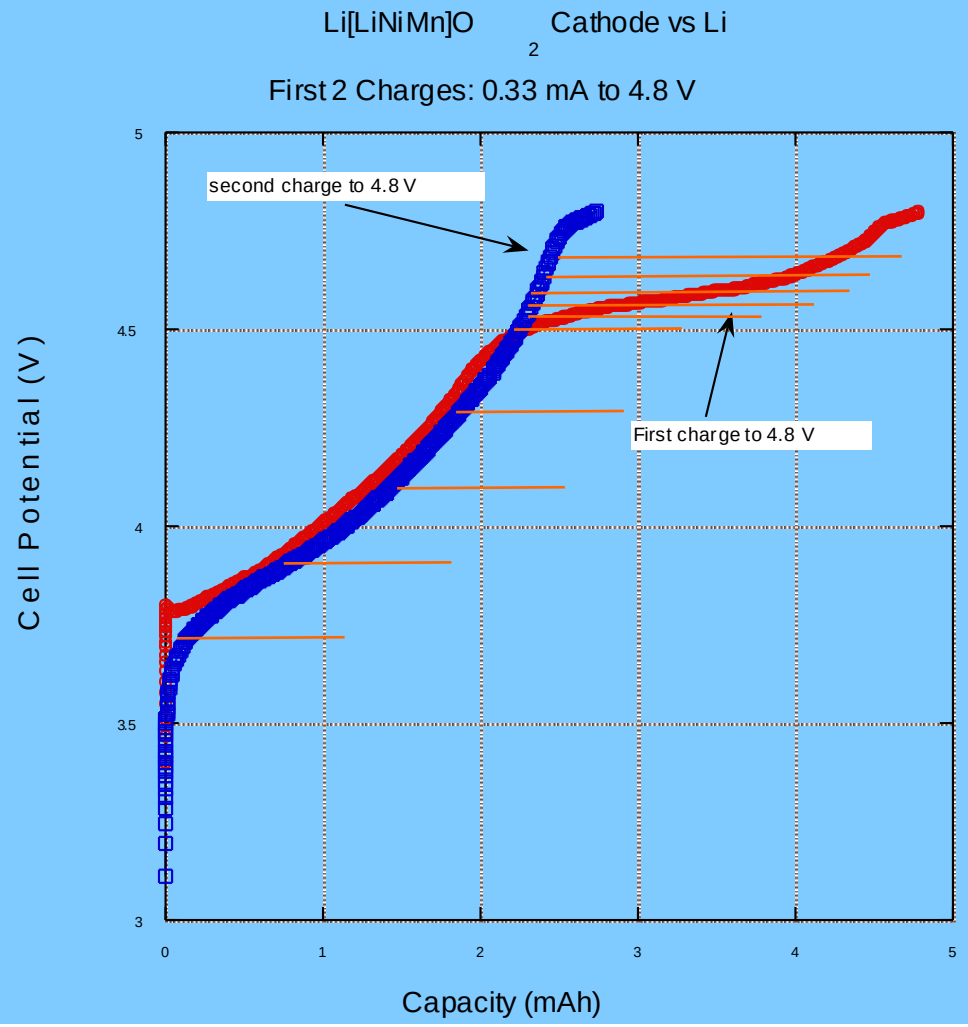


XAS of Ni K-edge from 3.7 V - 4.8 V

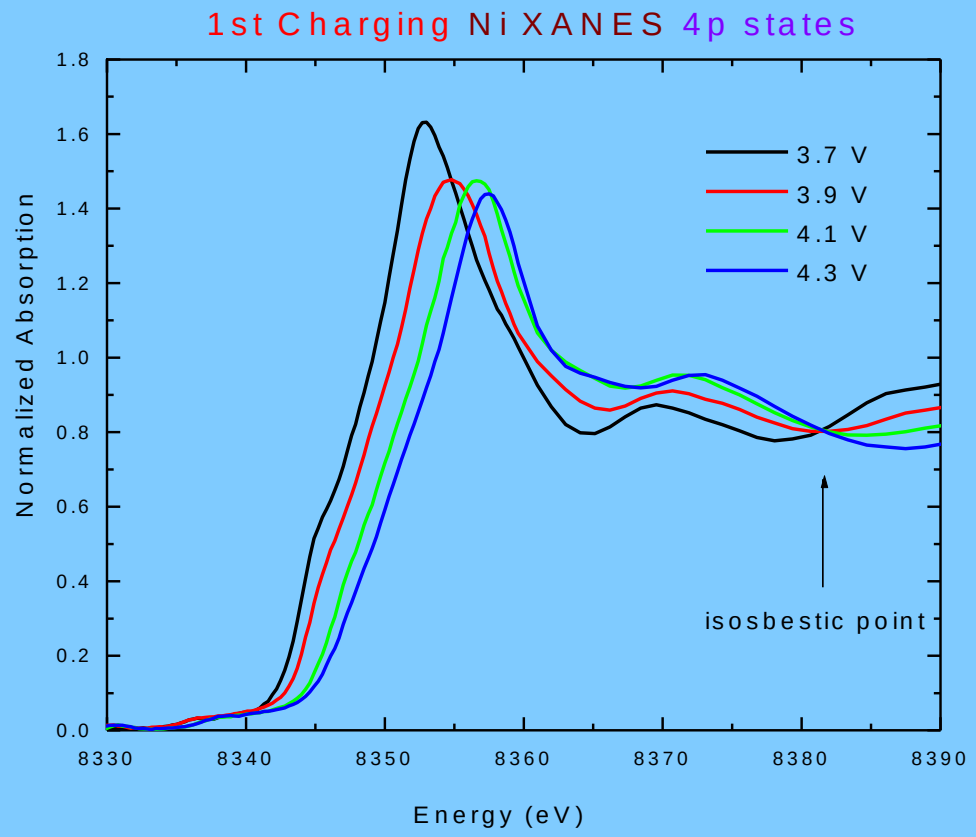


Ni is certainly oxidized, but this picture needs a closer look

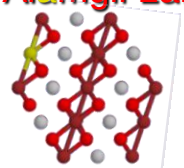
In-situ XAS Experiment: Narrower Focus on a Single Plateau



XAS of Ni K-edge from 3.7 V - 4.3 V: 1st plateau



What does the isosbestic point indicate?



Isosbestic Points

If the reactants and the products have equal light absorbtion coefficient at a specific energy (i.e. $\alpha A = \alpha B = \alpha$), and the analytical concentration remains constant, then we have an isosbestic point.

For the reaction:
$A \rightarrow B$, where one mol. of reactants produces one mol of products,

the analytical concentration is the same at any point in the reaction:
$c_A + c_B = c$

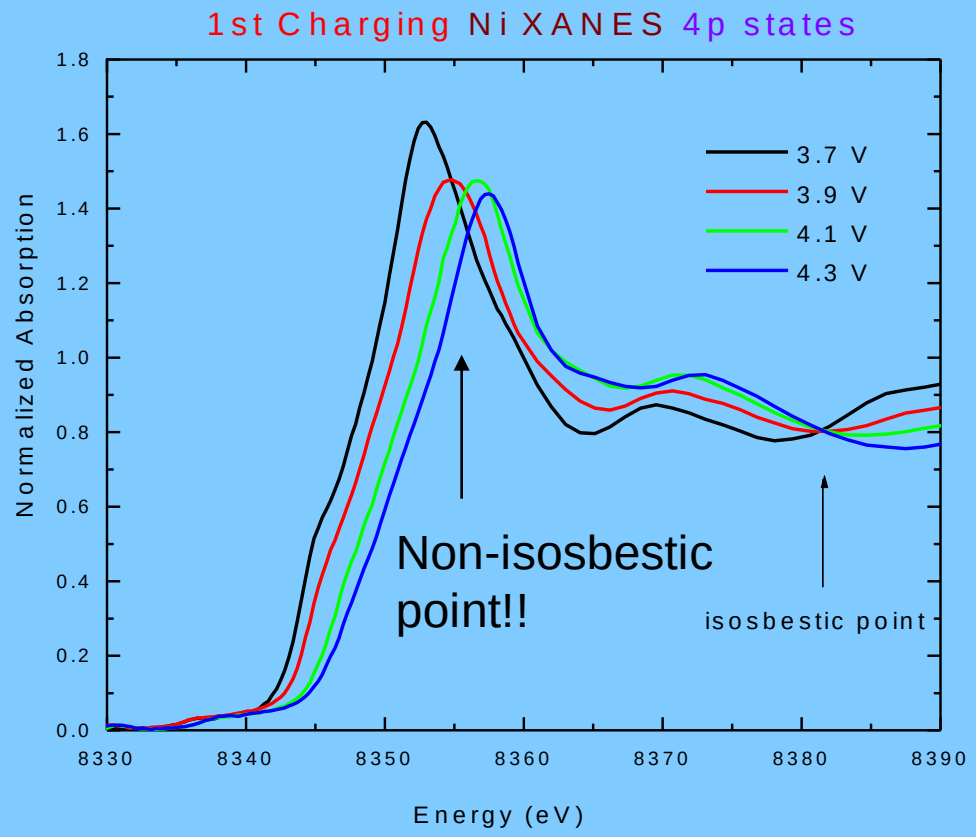
.

The absorption coefficient is:
$\mu = p\,(\alpha_A\, c_A + \alpha_B\, c_B) = p\,\alpha\ \ (cA + cB) = p\,\alpha\, c$

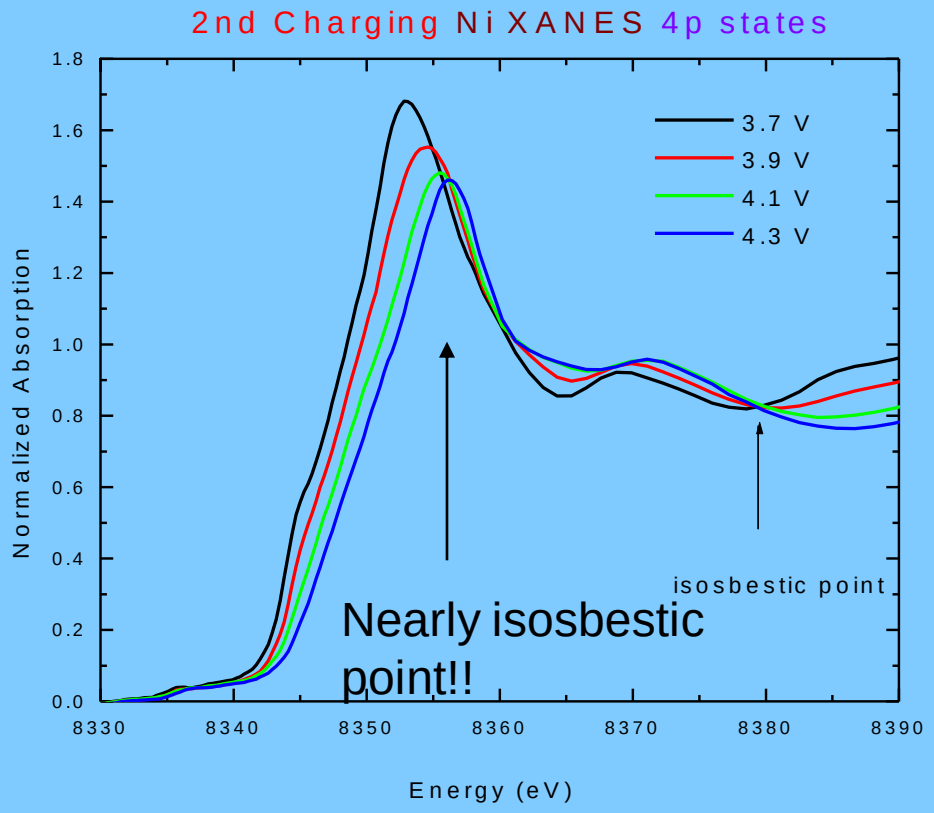
.

Hence, the absorption coefficient at that point remains constant.

XAS of Ni K-edge from 3.7 V - 4.3 V: 1st plateau

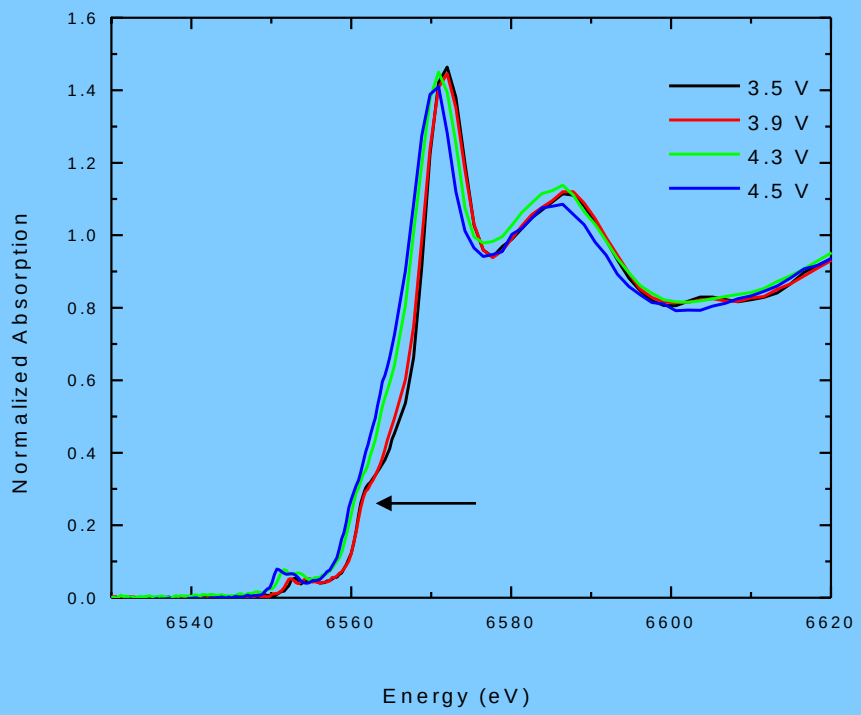


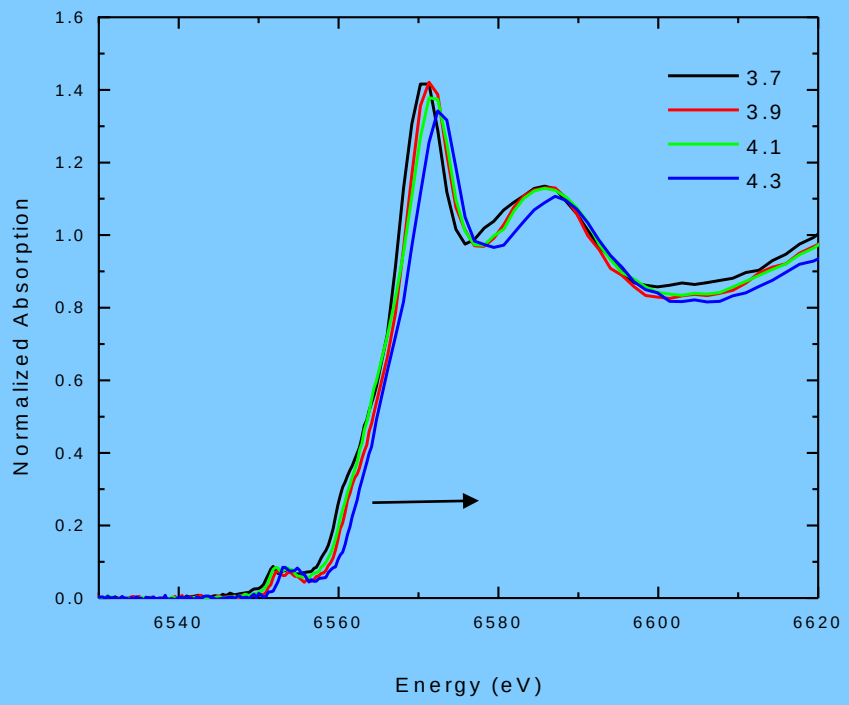
XAS of Ni K-edge from 3.7 V - 4.3 V during 2nd charge



Isosbestic point indicates a single reaction. Ni is oxidized.

XAS of Mn K-edge from 3.5 V - 4.5 V: 1st & 2nd charge

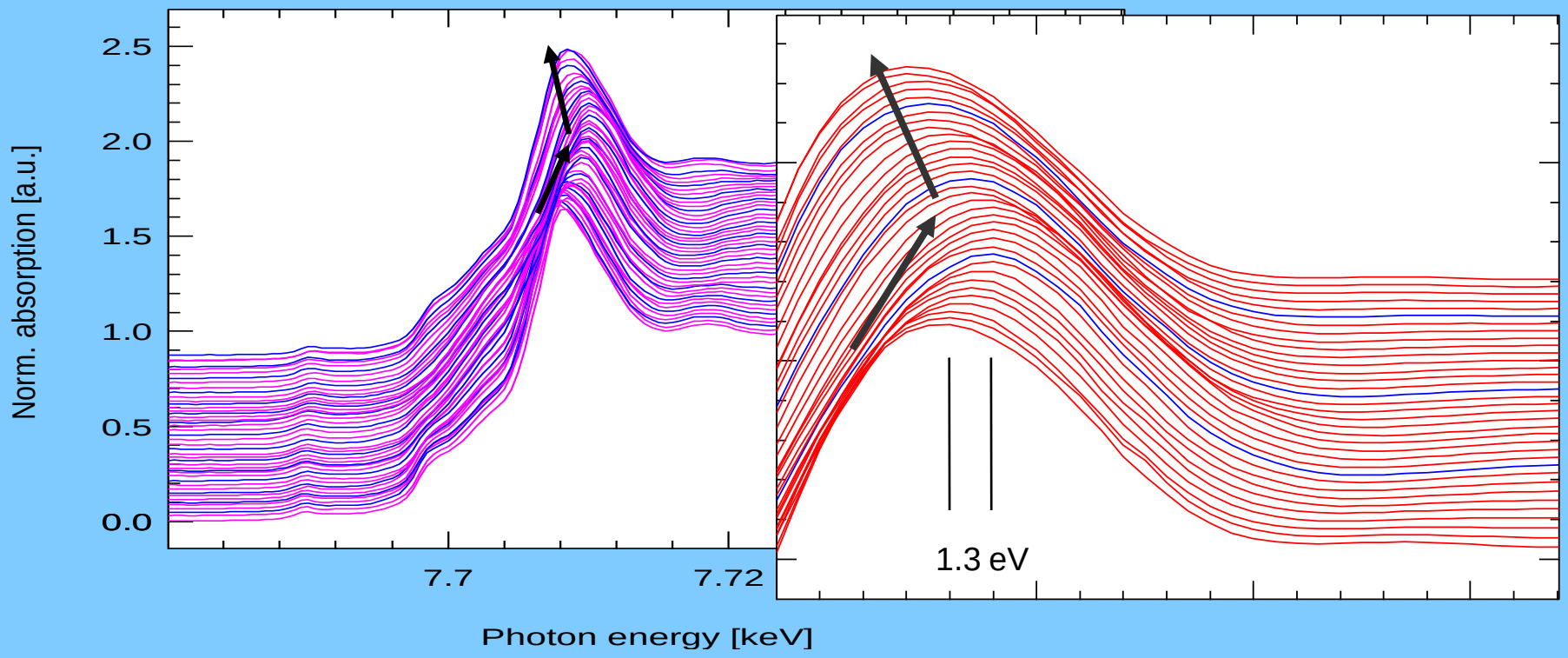




Mn gets reduced in the 1st charge; -ve shift in binding energy!

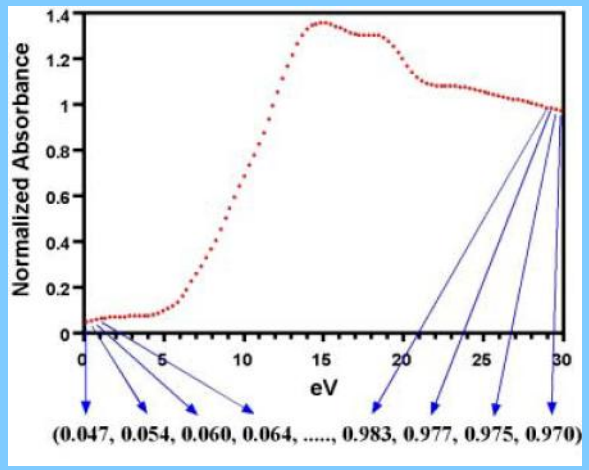
In the 2nd cycle Mn participates in the charge compensation process.

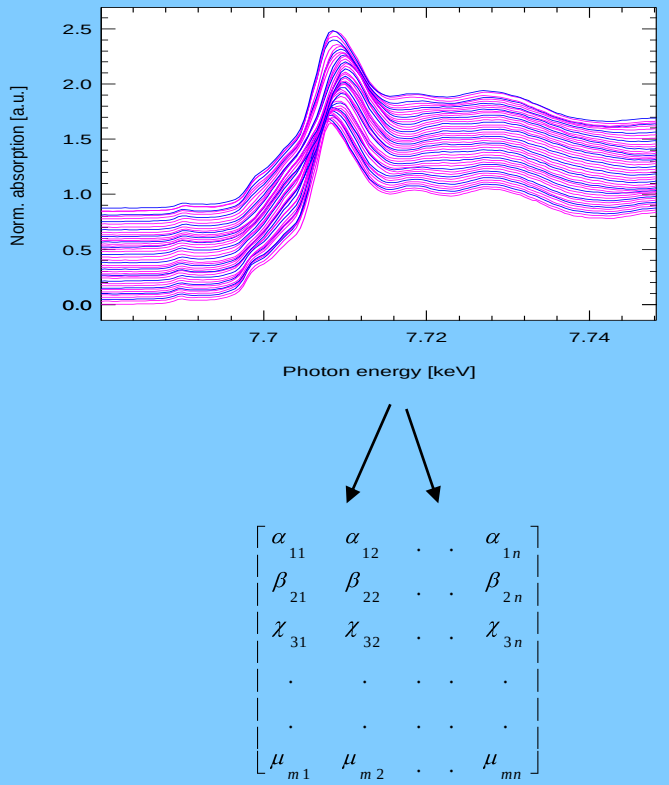
X-ray absorption near-edge structure of Co



- The white line of the near-edge undergoes a shift of ~1.3 eV
- similar shift for a $Li_xNi_{0.8}Co_{0.2}O_2$ cell has been reported [Johnson and Kropf].

Principal Component Analysis: Representation of XAS Spectra as an **m** x **n** Matrix





$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \cdots & \alpha_{1n} \\ \beta_{21} & \beta_{22} & \cdots & \beta_{2n} \\ \chi_{31} & \chi_{32} & \cdots & \chi_{3n} \\ \vdots & \vdots & \cdots & \vdots \\ \vdots & \vdots & \cdots & \vdots \\ \mu_{m1} & \mu_{m2} & \cdots & \mu_{mn} \end{bmatrix}$$

- An XAS spectrum can be represented as a series of coordinates
- An XAS data set can be expressed as an **m** x **n** matrix

PCA Formulation and Interpretation in XAS

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & . & . & \alpha_{1n} \\ \beta_{21} & \beta_{22} & . & . & \beta_{2n} \\ \chi_{31} & \chi_{32} & . & . & \chi_{3n} \\ . & . & . & . & . \\ . & . & . & . & . \\ \mu_{m1} & \mu_{m2} & . & . & \mu_{mn} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & . & . & a_{1n} \\ b_{21} & b_{22} & . & . & b_{2n} \\ c_{31} & c_{32} & . & . & c_{3n} \\ . & . & . & . & . \\ . & . & . & . & . \\ m_{m1} & m_{m2} & . & . & m_{mn} \end{bmatrix} \bullet \begin{bmatrix} v_{11} & 0 & . & 0 \\ 0 & v_{22} & . & 0 \\ . & . & v_{ij} & . \\ 0 & 0 & . & v_{nn} \end{bmatrix} \bullet \begin{bmatrix} w_{11} & w_{12} & . & w_{1n} \\ w_{21} & w_{22} & . & w_{2n} \\ . & . & . & . \\ w_{n1} & w_{n2} & . & w_{nn} \end{bmatrix}$$

[A] = [B] • [v] • [w]^t

Data Components Eigenvalues weighting

- Purely statistical
- Provides an objective view of chemical transformation during cycling
- Useful as a preliminary analysis prior to invoking physical knowledge

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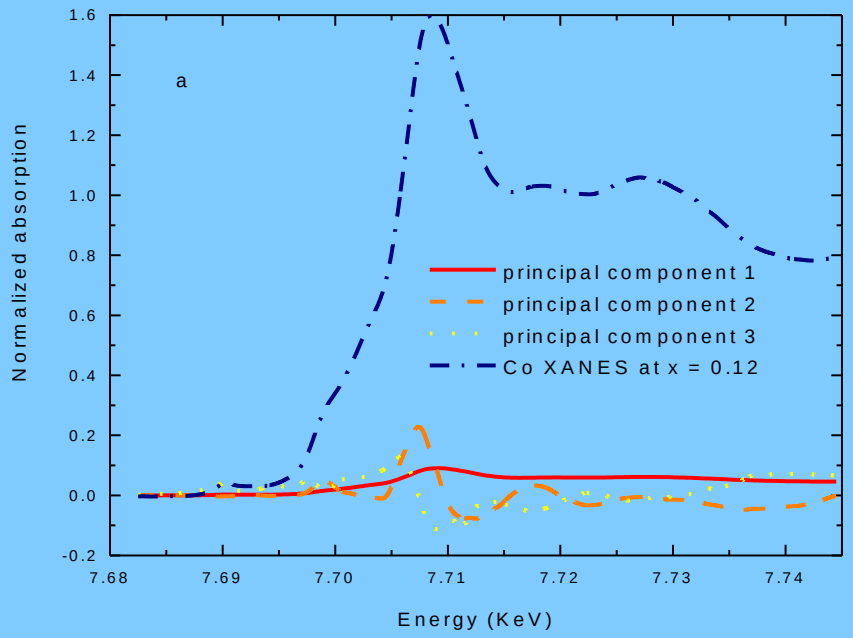
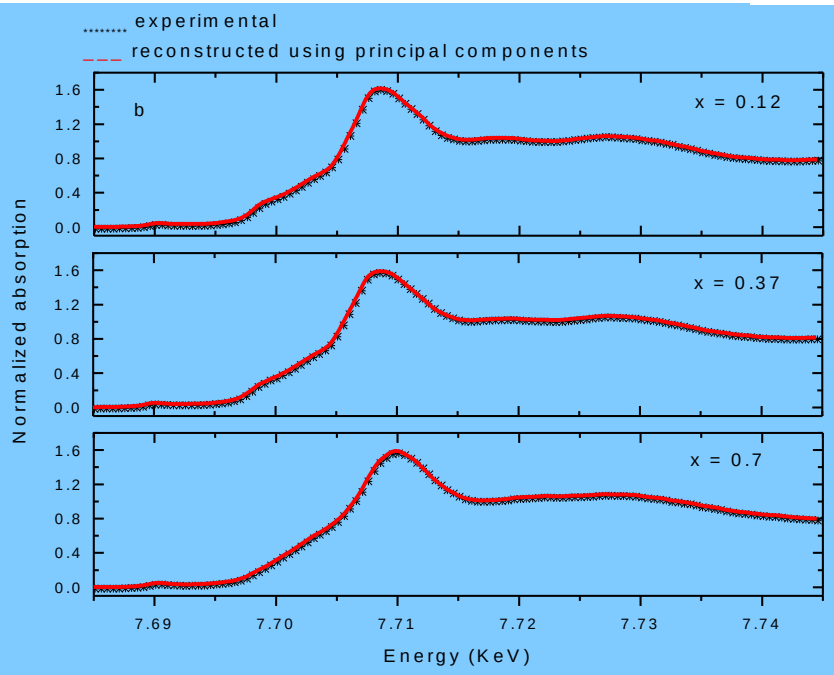
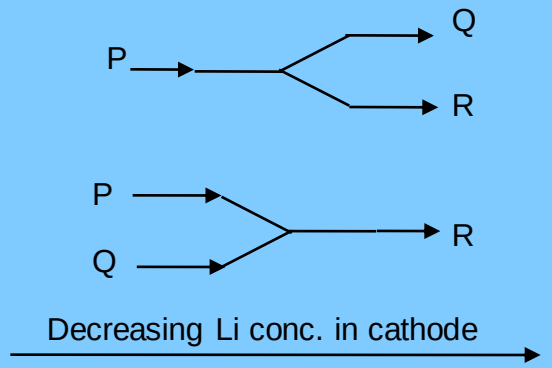
PCA: Components and Reconstruction





- Three principal components found
- Sufficient to reconstruct data at various stages of delithiation
- Two possible reaction pathways



The So-Called Pre-Edge: Co K-edge in $Li_{(1-x)}CoO_2$

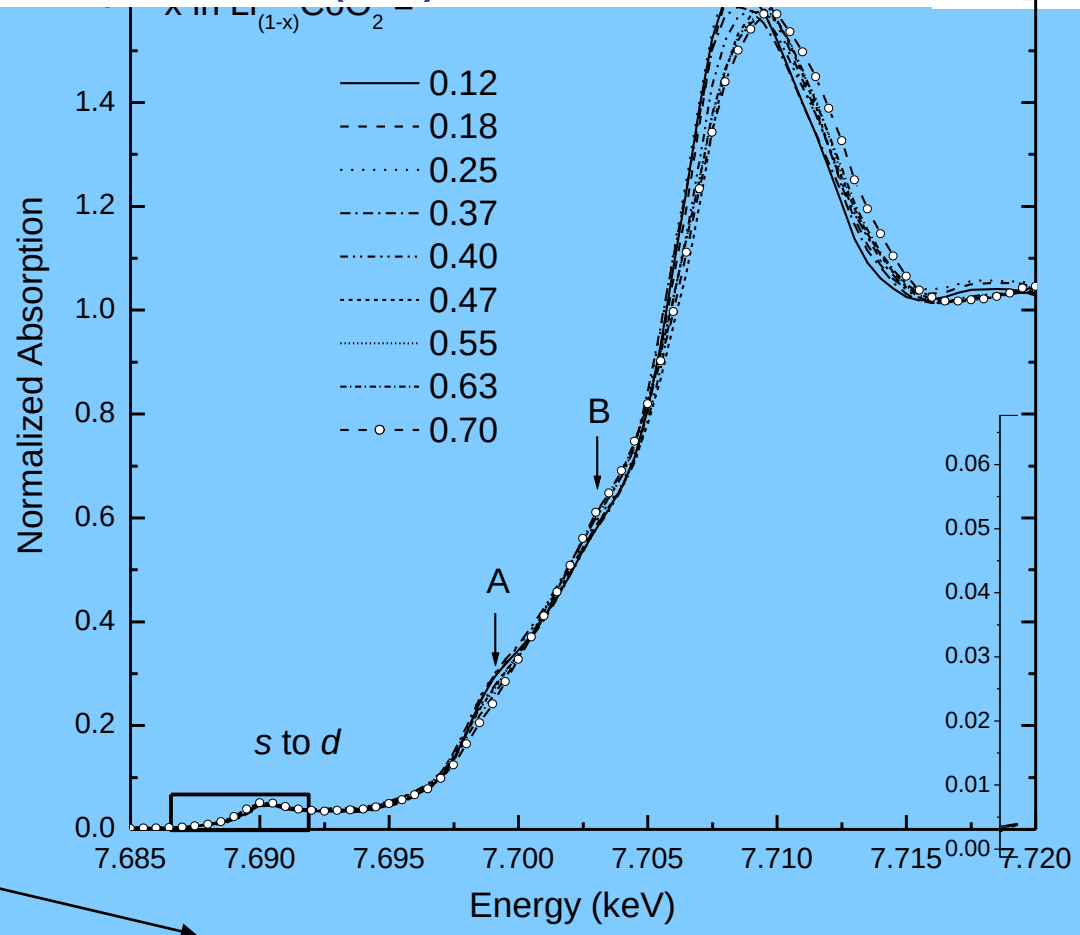
The Co K-edge XANES in $Li_{(1-x)}CoO_2$ as a function of x.

The *s to d* transition and *s to p* transition (A, B and C) are labeled.

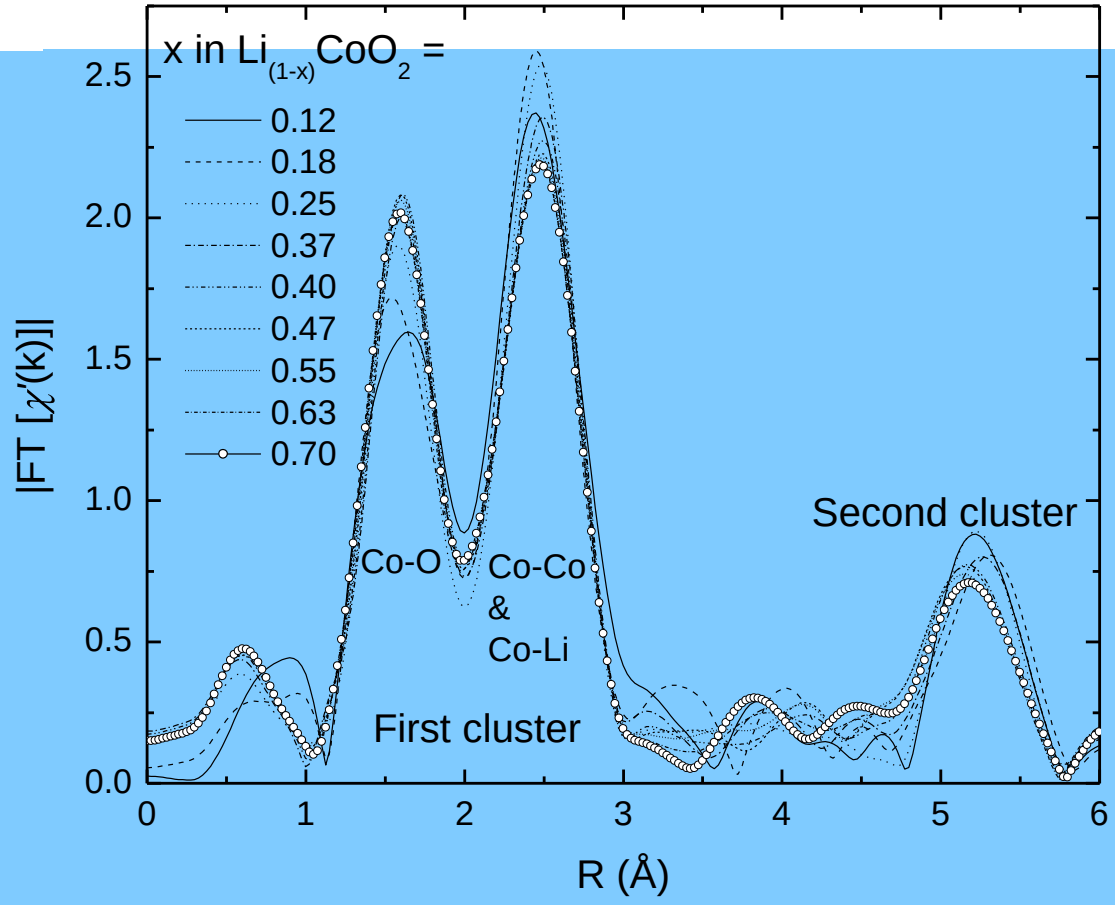
Co does appears to be involved in charge recompensation

…because

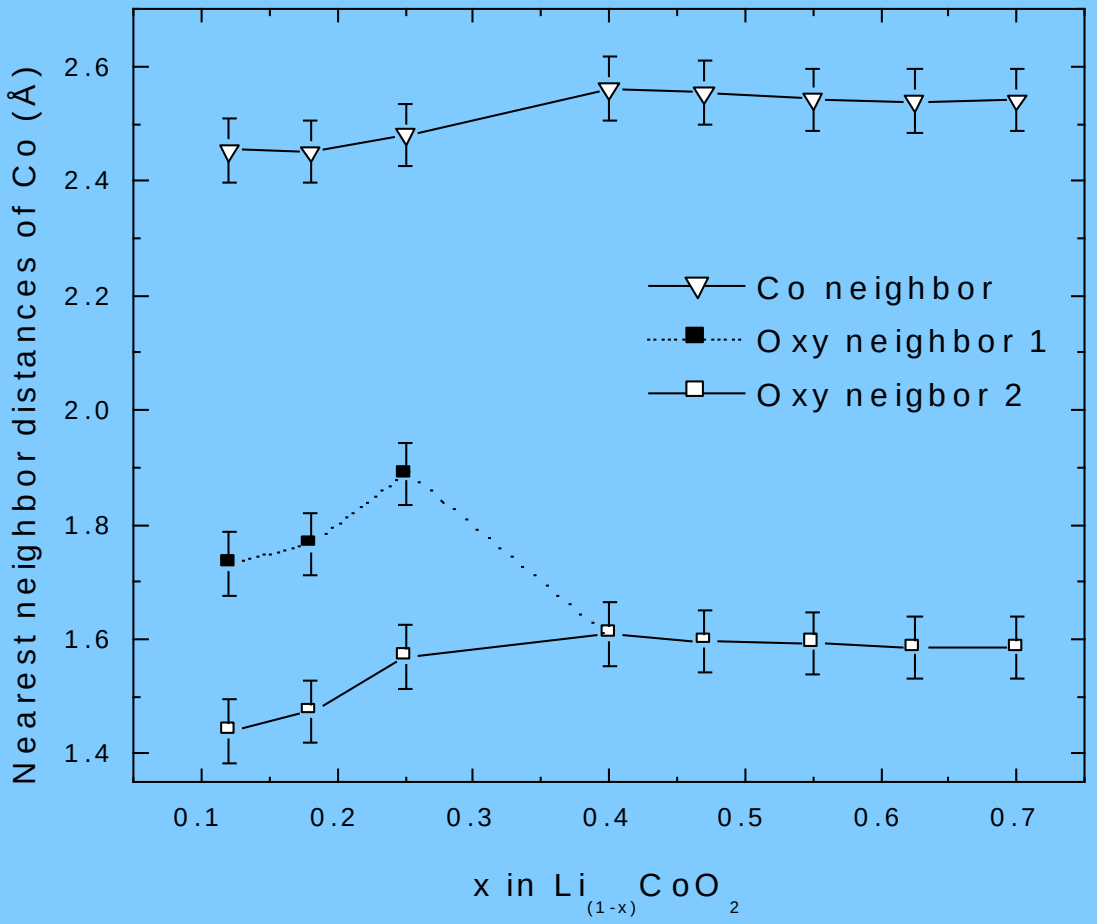
if the d-band occupancy of Co changes with increased delithiation, then this peak amplitude should increase



Theoretical fit to real-space data



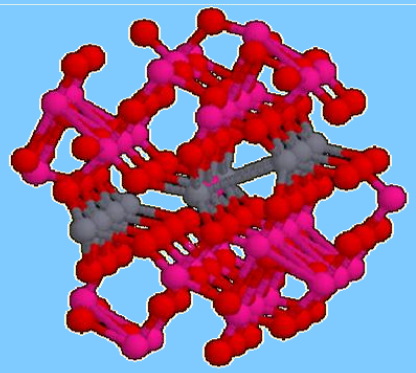
Theoretical fit to real-space data



The atomic structure around Co shows charge compensation occurs first by formation of O holes (for x<0.25).

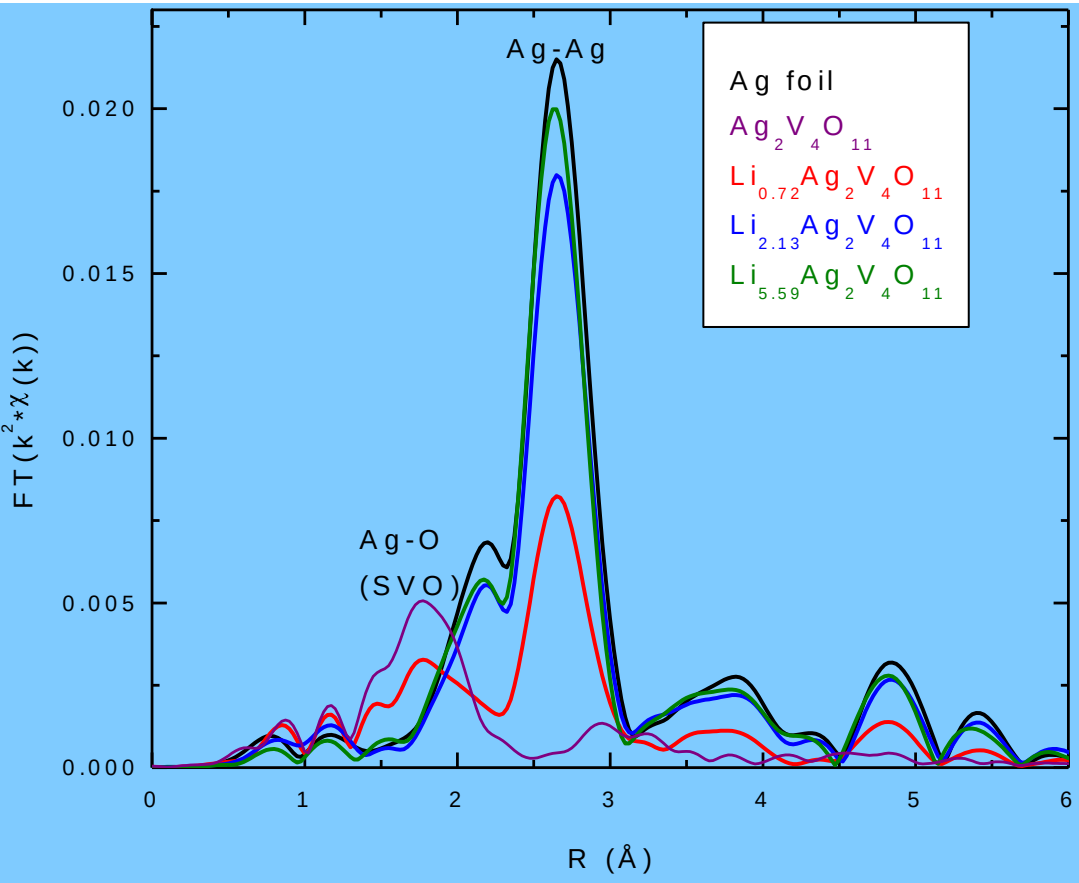
XANES shows us that for x>0.25, charge compensation occurs through Co d-hole formation.

Ex-situ Study of Li Intercalation in $Ag_2V_4O_{11}$



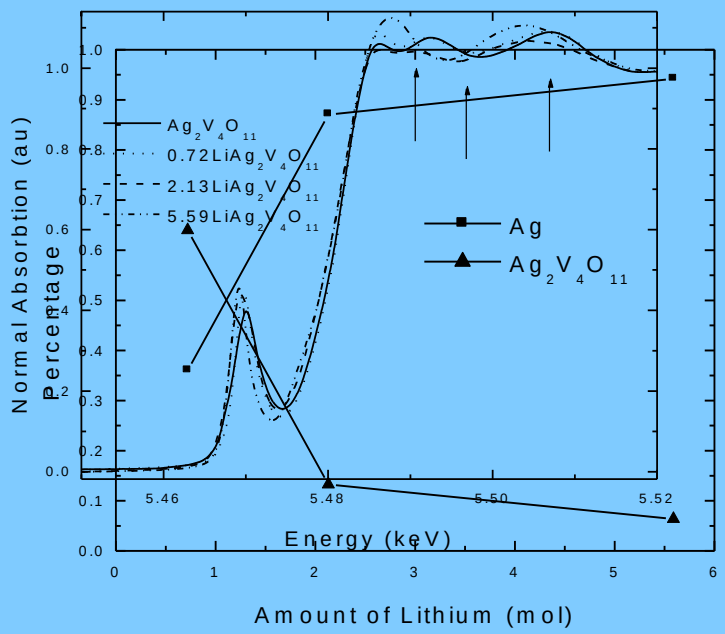
- Particularly useful in medical applications
- High power delivery
- Non-toxic

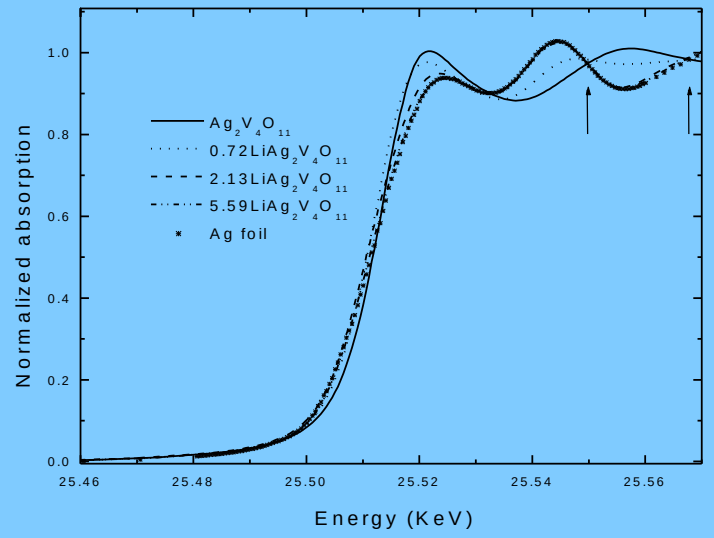
Ag K-edge analysis of $Li_xAg_2V_4O_{11}$



- FT {χ′} at the silver k-edge of the samples. Features of SVO are well resolved from those of metallic Ag.

XANES Using SVO at Ag and V K-edges

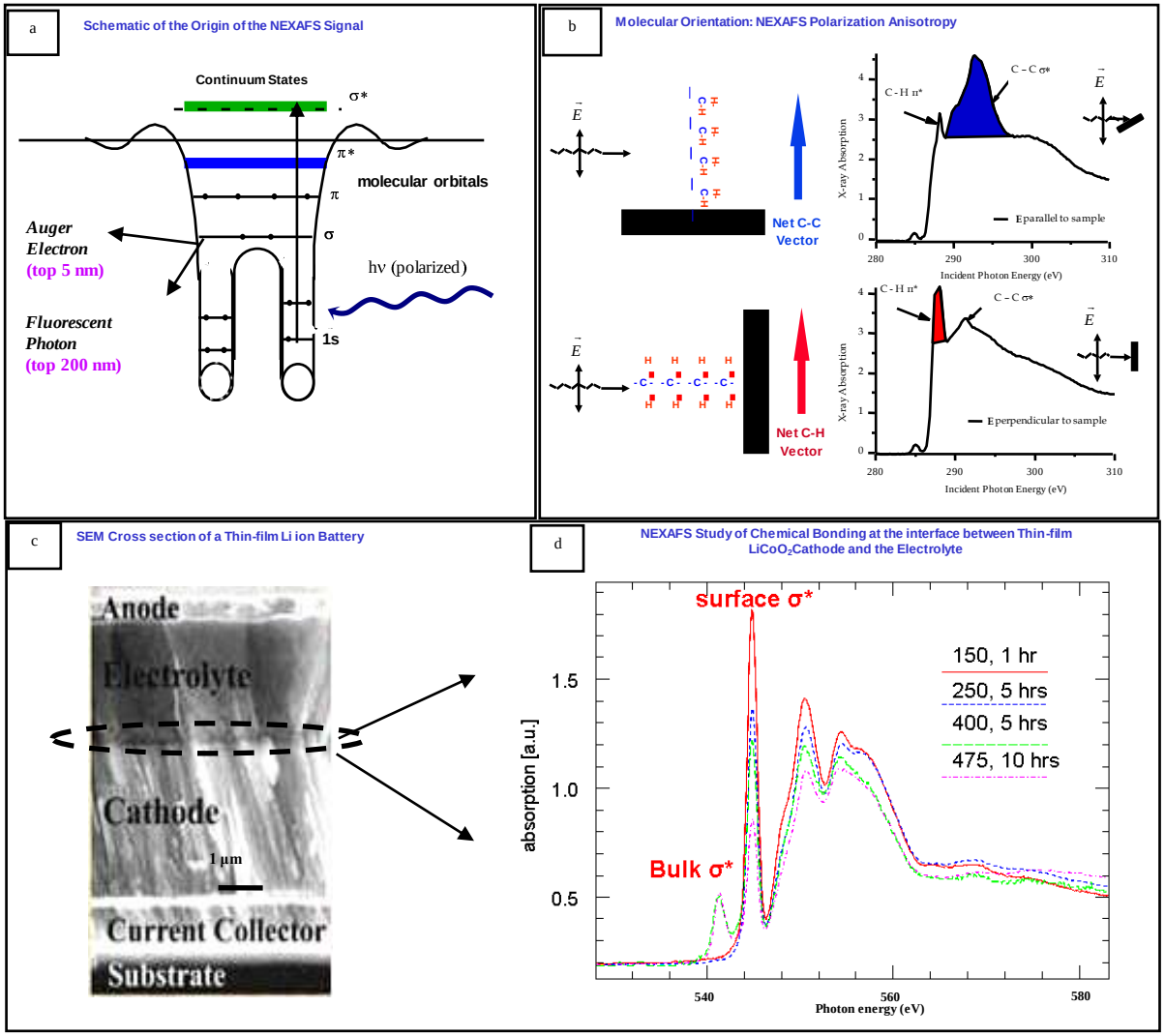




Linear Combination analysis of Ag K-edge XANES corroboration of phase segregation from Ag XANES

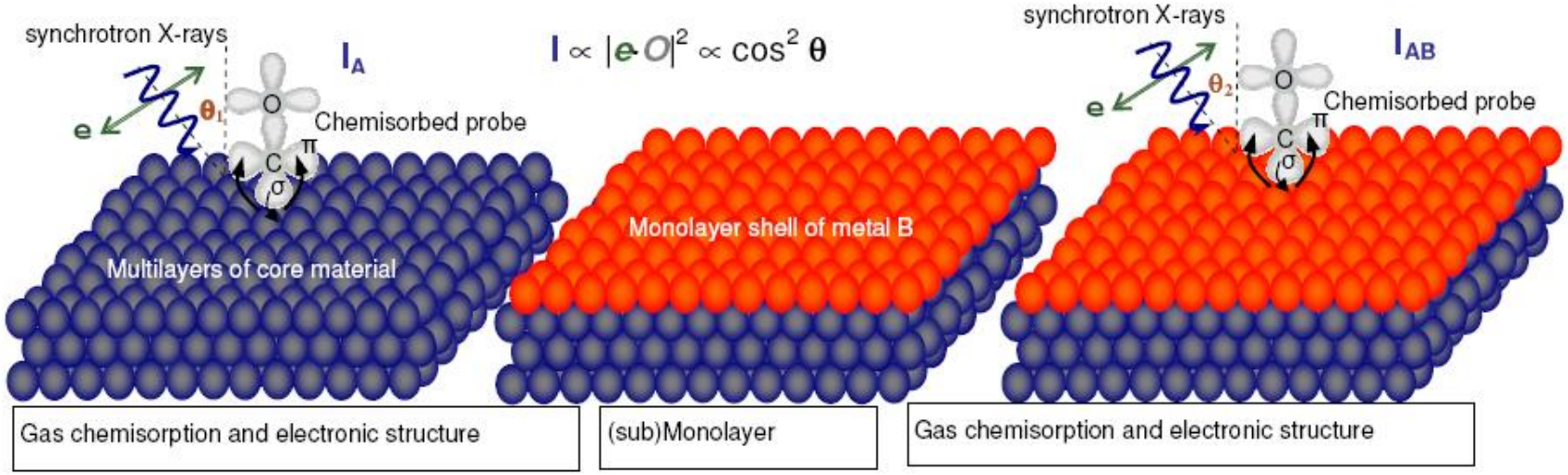
The XANES spectra at the V K-edge, unlike the case of Ag K-edge XANES, show no isosbestic points. Arrows indicate points where the plots fail to intersect isosbestically.

Soft X-ray XAS: Low-Z Atom-Specific Information



Sof X-ray XAS: LUMO occupancy

- LUMO occupancy
  - Orientation of molecular orbitals



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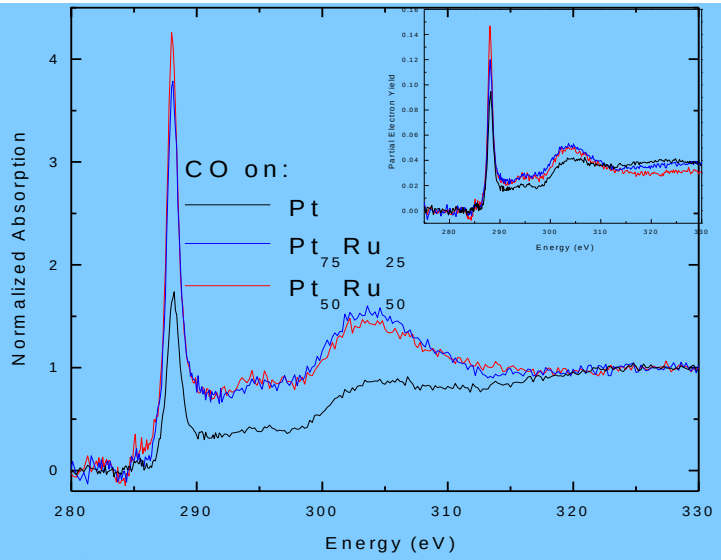
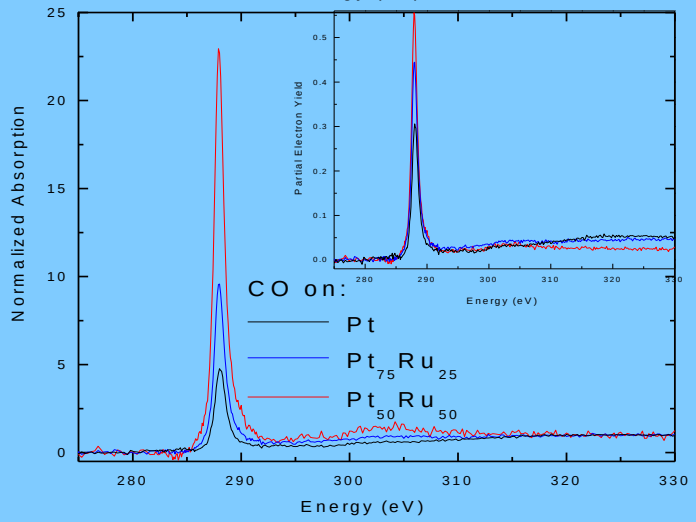
Sof X-ray XAS: LUMO occupancy

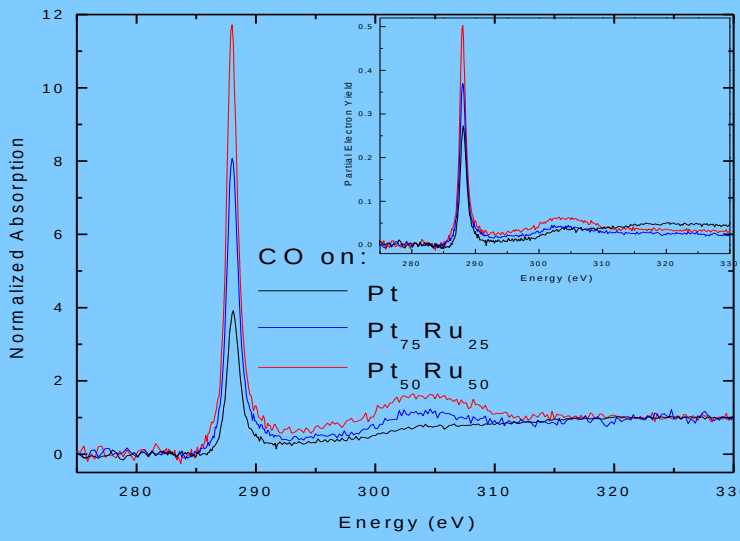
Grazing angle-angle; σ enhanced



Normal angle-angle; π* enhanced



Magic-angle; no orientation effects



Concluding Remarks

- Consider using XANES/NEXAFS in glass research
  - You can obtain
    - oxidation state information
    - molecular orbital information
    - time-resolved information
      - Lends itself to statistical analysis tools like PCA and LC