Chemical speciation with high resolution x-ray spectroscopy

Dimosthenis Sokaras

SLAC National Accelerator Laboratory

SSRL

U.S. DEPARTMENT OF ENERGY
Office of Science

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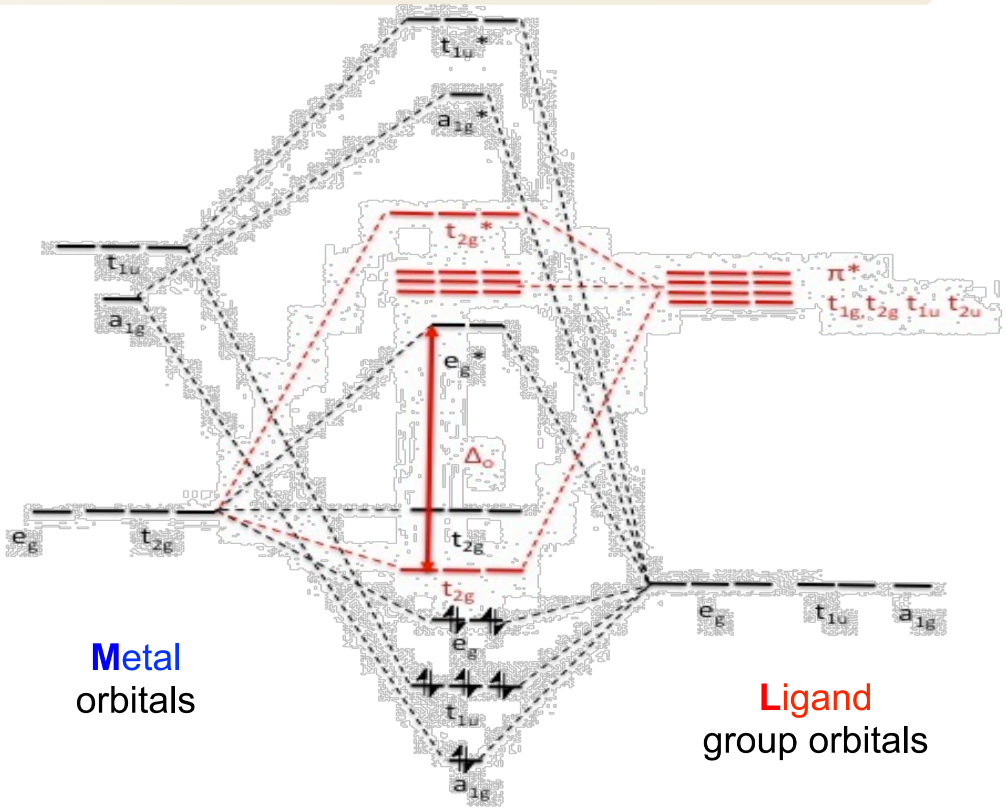
X-ray Spectroscopy → Electronic Structure characterization



Employing electronic transitions for deciphering the electronic structure of materials

Probing Chemical environment via **Energy**, **Intensity** and **Symmetry** of transitions

X-ray Spectroscopy

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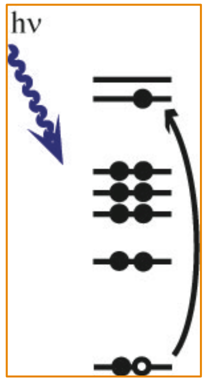
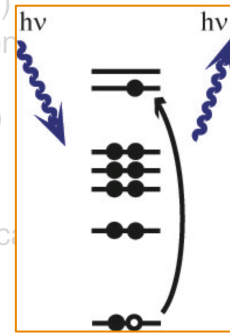
X-ray Absorption Spectroscopy (XAS)

- Near-Edge XAS (NEXAFS, XANES)
- Extended XAS (EXAFS)
- Detection via:
  - Electrons: TEY, PEY, AEY
  - Radiative: TFY, PFY, XES
- Combined with Imaging
  - Scanning (STXM)
  - Full-Field (TXM)



Inelastic X-ray Scattering (IXS)

- Nuclear Resonant Scattering (Mössbauer)
- Collective Dynamics Excitation (Relaxation Sound)
- Non-res Valence-to-Valence (UV-vis IXS)
- Non-res Core Excitations (X-ray Raman)
- Resonant Excitations (RIXS)
  - Charge Transfer, Hybridization, Loca
- Momentum Resolved RIXS
  - Spin Excitations, *d-d* excitations
- Detection via:
  - Gratings (Soft)
  - Crystal Optics (Hard)

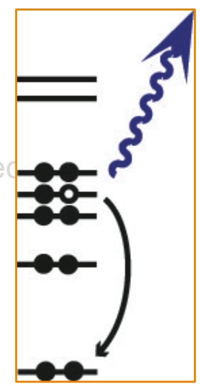


X-ray Photoelectron Spectroscopy (XPS)

- Ultra-Violet PES (UPS)
- Soft X-ray PES (PES, XPS)
- Hard X-ray PES (HXPS, HAXPES)
- Detection via Electrostatic Hemispheres, Cylinders
- Combined with:
  - Mott Detector (Spin-Resolved)
  - Imaging lens (PEEM)
  - Time-of-Flight Detector (TOF-PES)
  - Momentum Dispersion (ARPES)
- Resonant Excitation
  - Resonant Photoemission (RPES)
  - Resonant Auger (RAES)
  - Core-Hole Clock

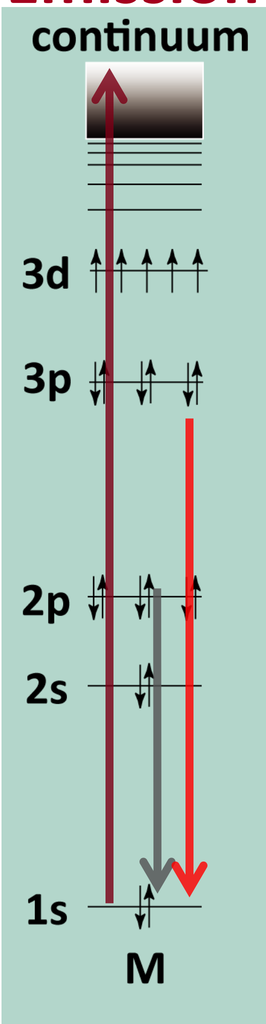
X-ray Emission Spectroscopy (XES)

- Non-Resonant Core-to-Core XES
- Non-Resonant Valence-to-Core XES
- Detection via:
  - Gratings (Soft)
  - Crystal Optics (Hard)
- High Energy Resolution Fluorescence Detec (HERFD)
- Resonant Excitation +
  - X-ray emission = RXES
  - Inelastic Scattering = RIXS



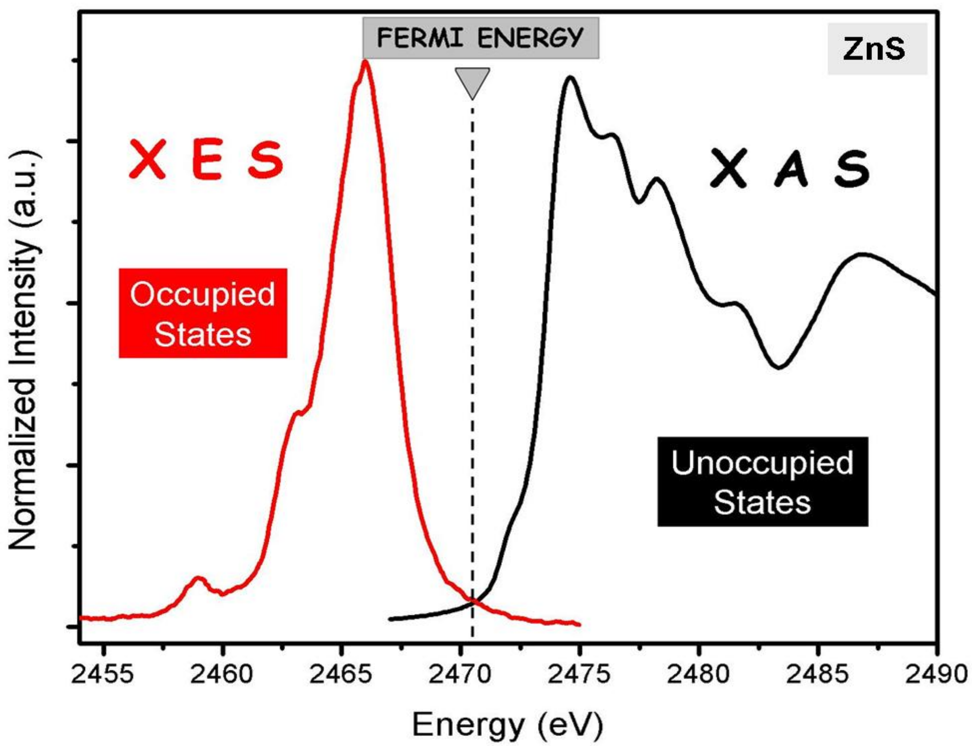
X-ray Emission and X-ray Absorption Spectroscopies

Emission

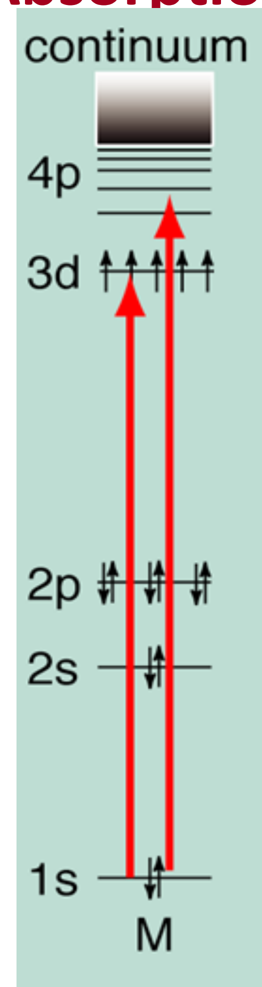


Different **information** from **different transitions**

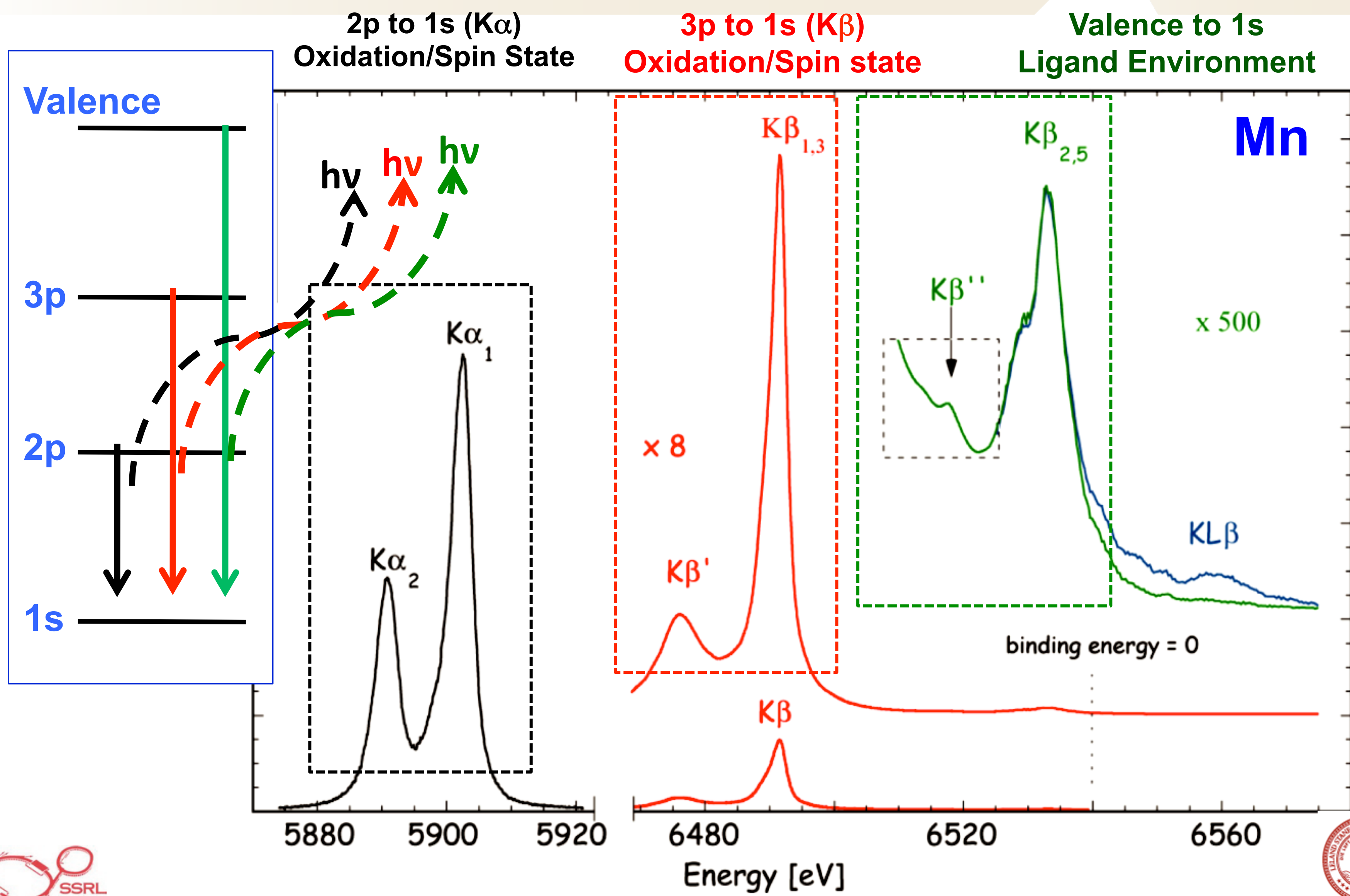
Oxidation state
Ligand environment
Coordination / Bond dist.



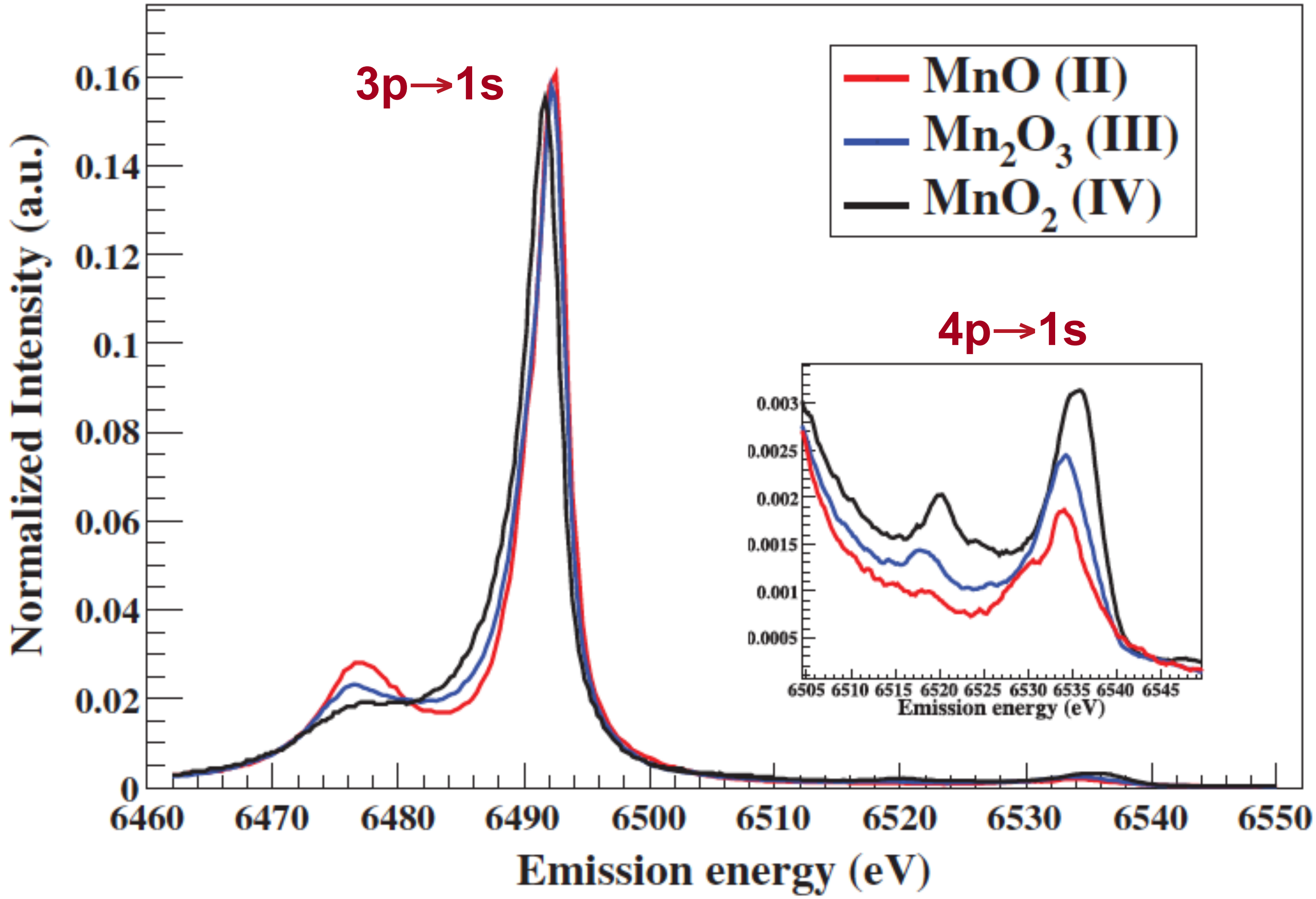
Absorption



Chemical Sensitivity of X-ray Emission Spectroscopy

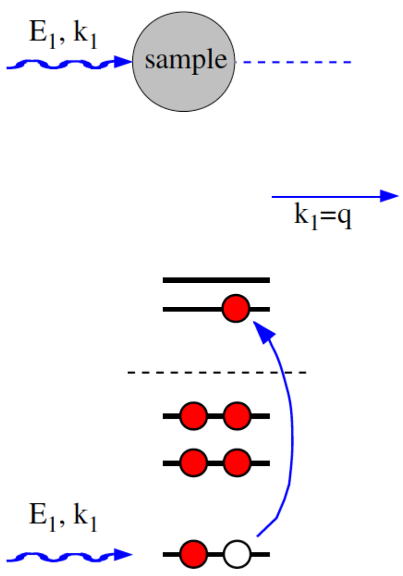


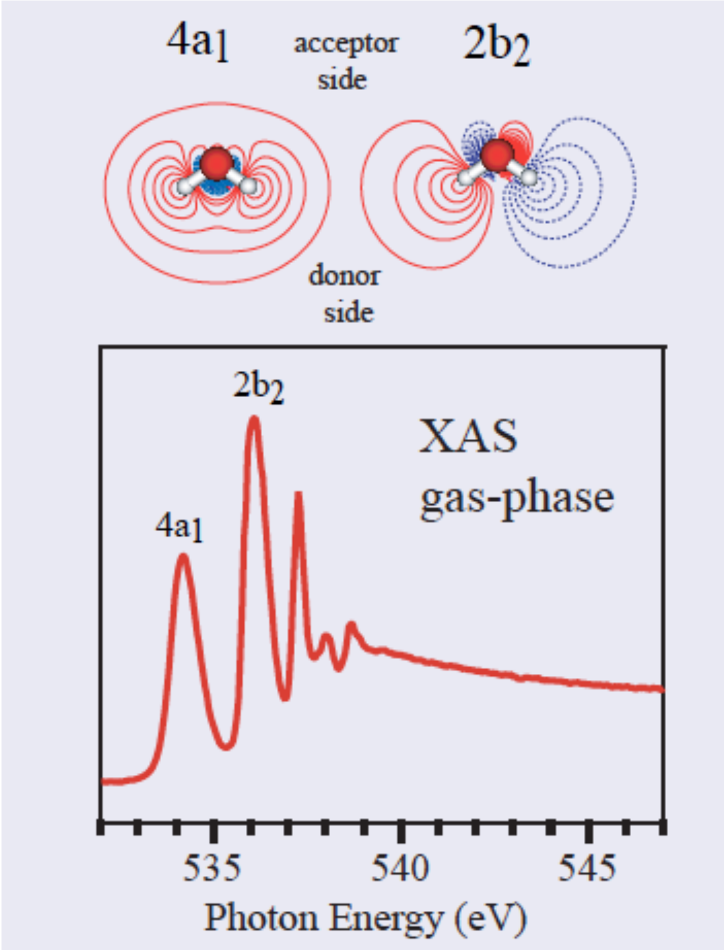
Chemical Sensitivity of X-ray Emission Spectroscopy



spin-state sensitivity of K$\beta_{1,3}$ emission lines due to the *3p*-*3d* exchange interaction

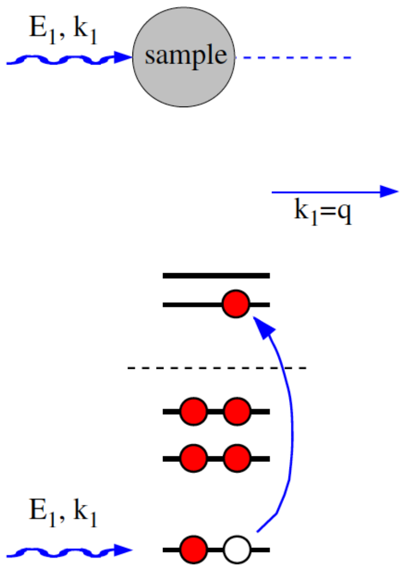
X-ray Absorption Spectroscopy



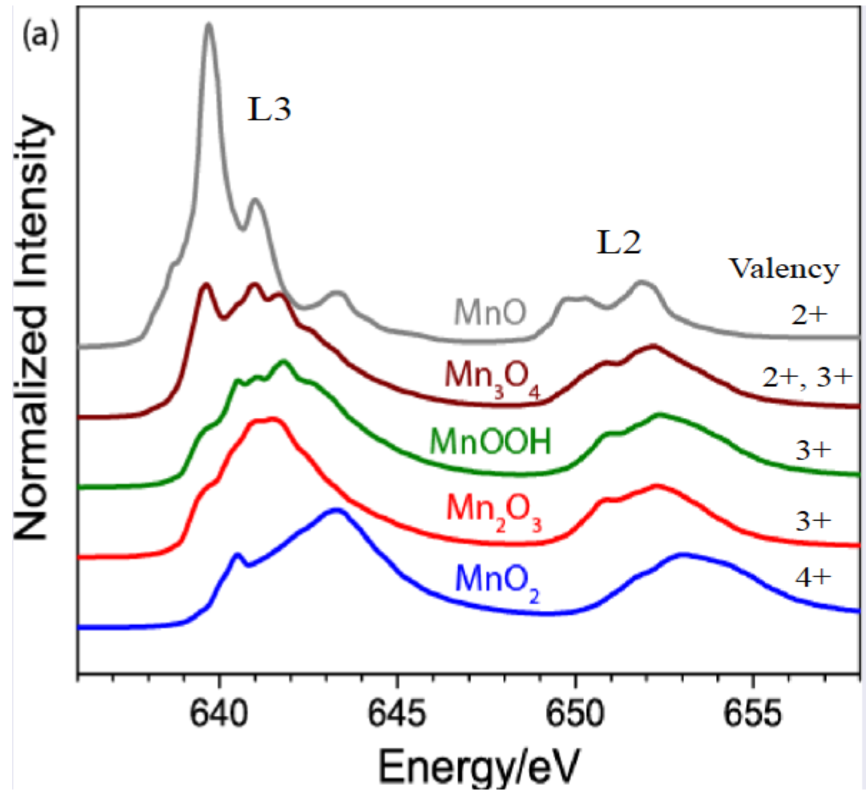


- Probes lower unoccupied states
- Element Specific
- Frozen Geometry

X-ray Absorption Spectroscopy



- Probes lower unoccupied states
- Element Specific
- Frozen Geometry
- Information on
  - **Oxidation State**



ACS. Catal. 2, 2687 (2012)

X-ray Absorption Spectroscopy

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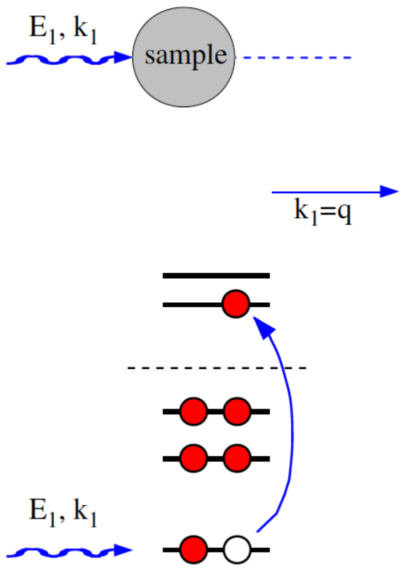
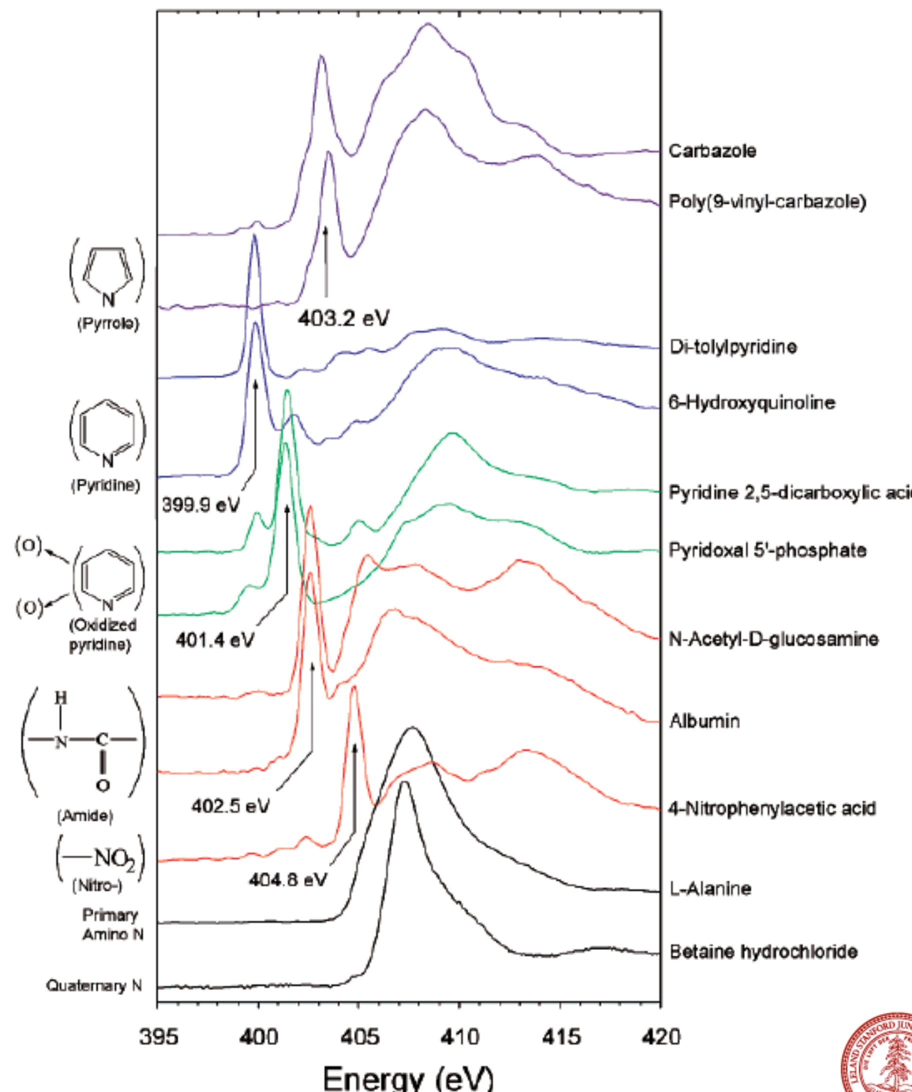


- Probes lower unoccupied states
- Element Specific
- Frozen Geometry
- Information on
    - **Oxidation State**
    - **Chemical Environment**



Environ. Sci. Technol. 2002, 36, 3050

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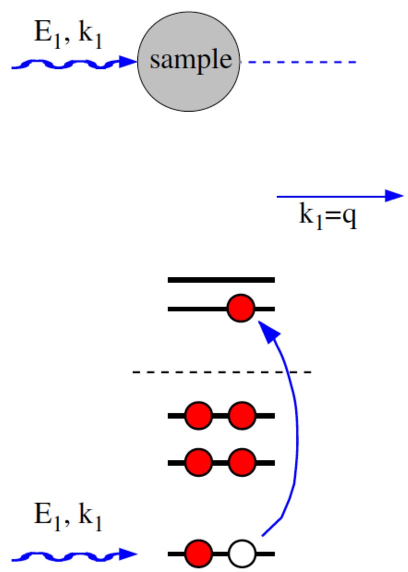
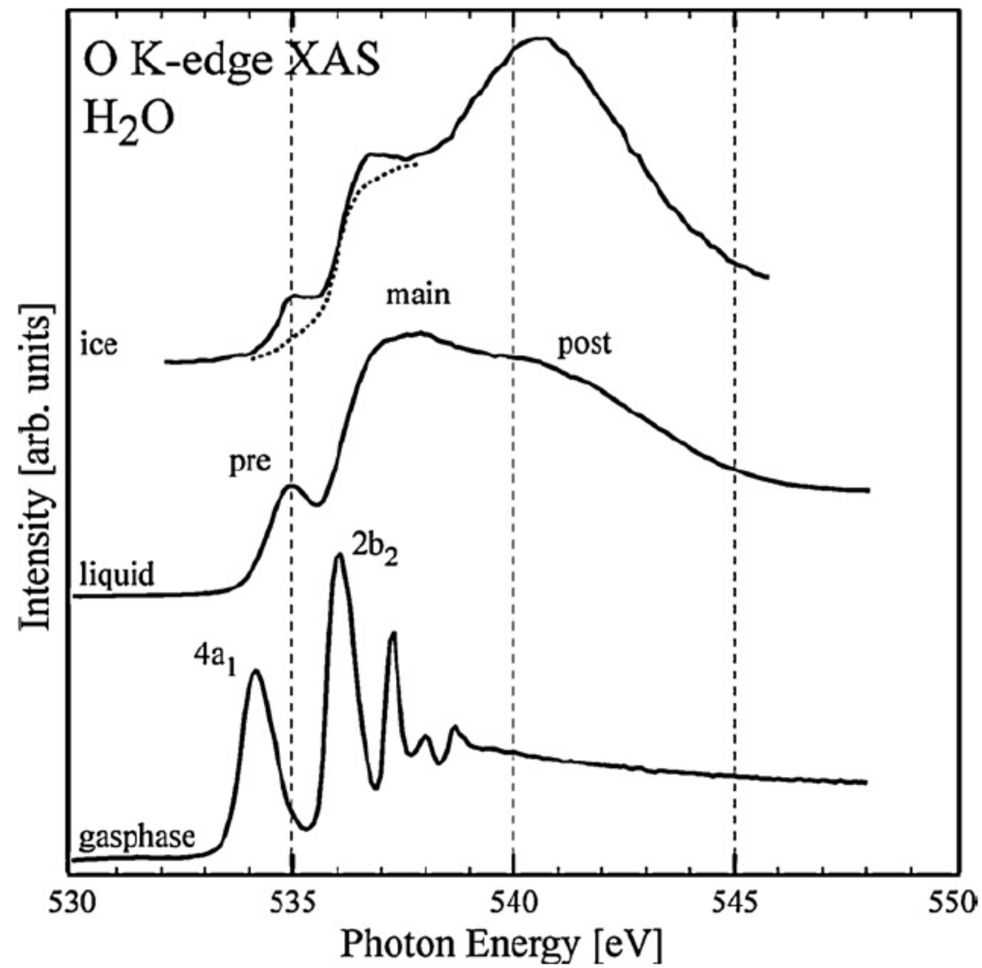
X-ray Absorption Spectroscopy



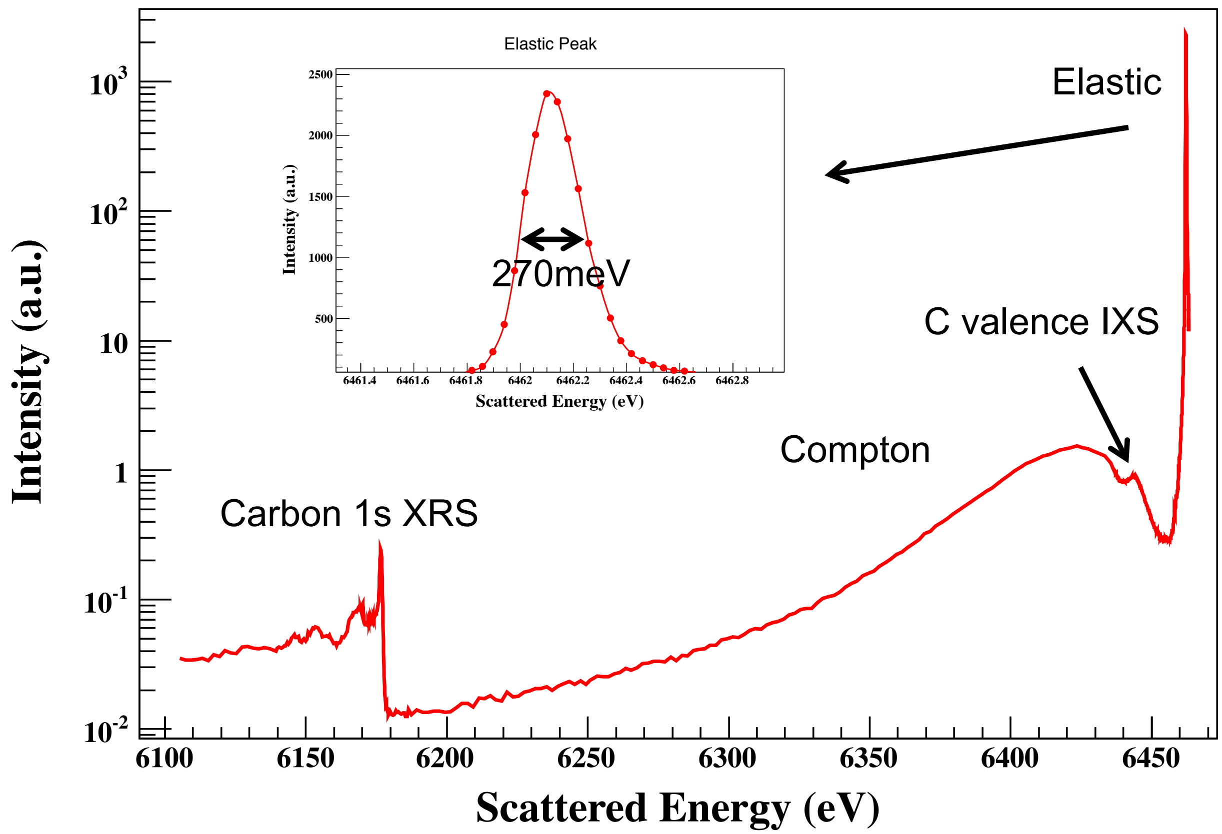
- Probes lower unoccupied states
- Element Specific
- Frozen Geometry
- Information on
  - **Oxidation State**
  - **Chemical Environment**
  - **Weak Bonding (e.g. H-bonds)**



J. El. Spec. Rel Ph. 177, 99 (2010)

Inelastic X-ray Scattering mechanisms

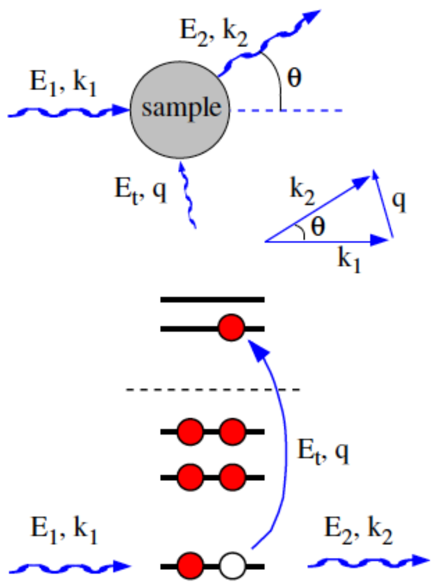
Carbon XRS



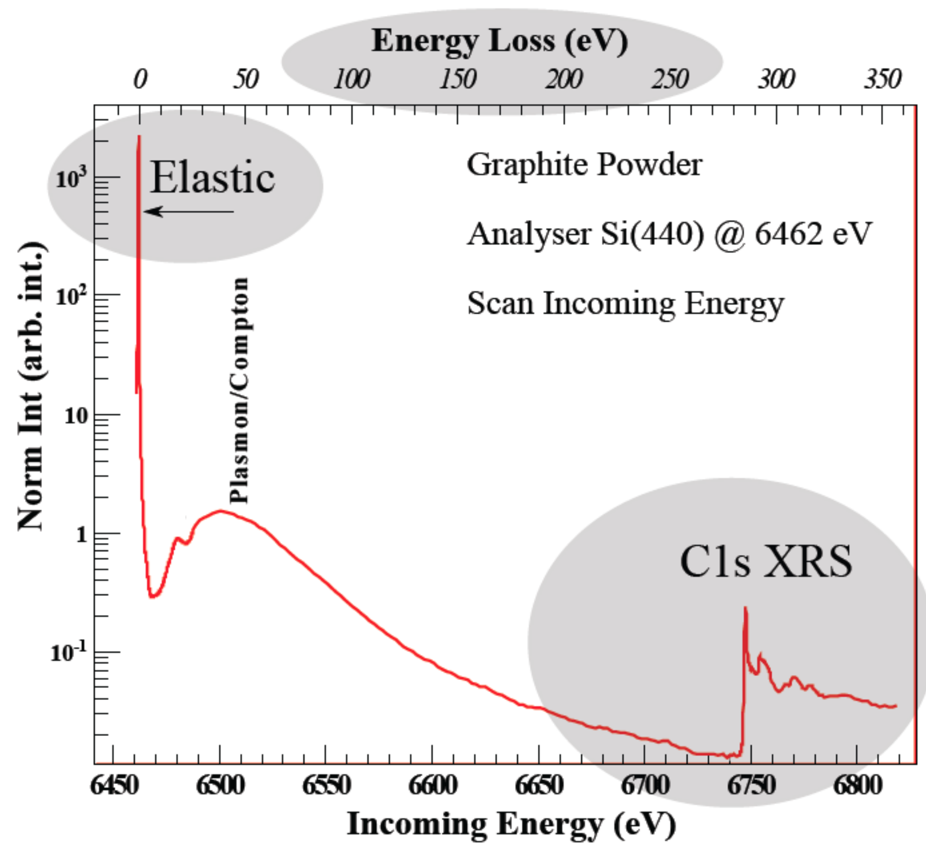
Scattering of 6462 eV photons on bulk Carbon target

Schematic of the X-ray Raman Spectroscopy – An inelastic X-ray Scattering Process

Detecting **photon-energy loss** and **NOT absolute photon-energy**

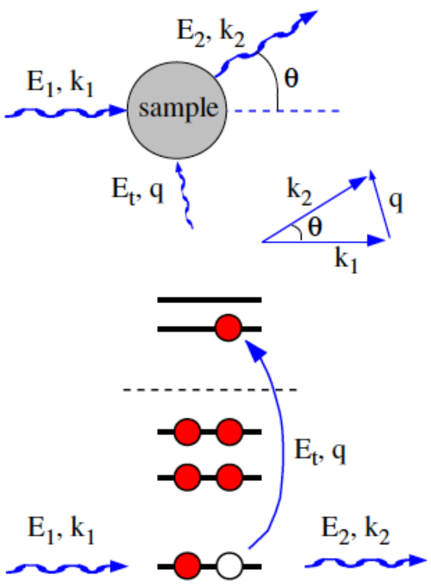


$$S(\mathbf{q},\omega)^{IXS} \sim |<i|e^{-i\mathbf{q}\cdot\mathbf{r}}|f>|^2$$

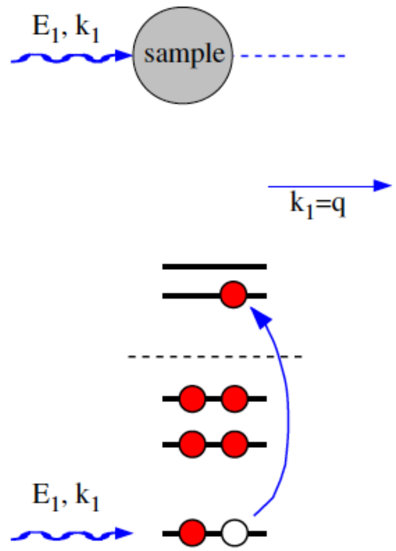


Dipole approx.: $e^{i\mathbf{qr}} \rightarrow \mathbf{q}\cdot\mathbf{r}$, similar matrix diagram as **soft x-ray absorption**.

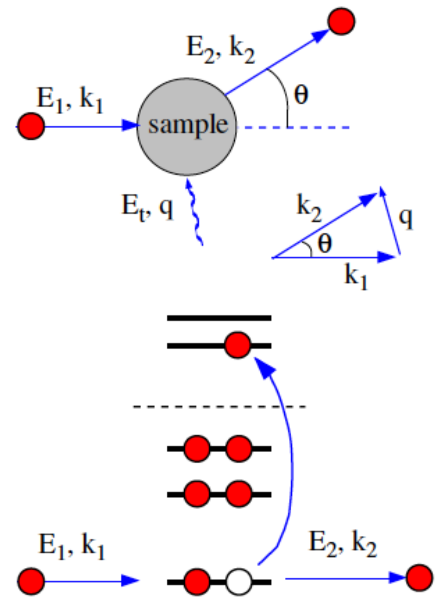
Principle of X-ray Raman Scattering (XRS)



XRS (hard x-rays)



XAS (soft x-rays)



EELS TEM (~100 keV)

X-ray Spectroscopy

Core-Level X-ray Spectroscopy = X-rays + Core-Level Transitions

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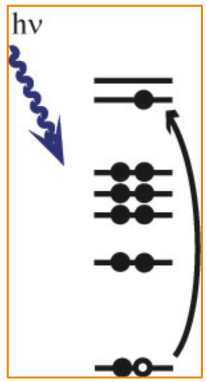
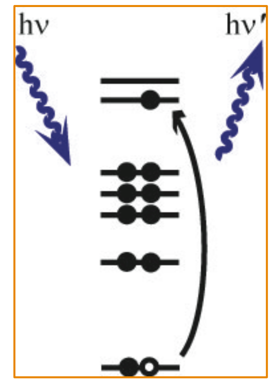
X-ray Absorption Spectroscopy (XAS)

- Element/Site Specific
- Frozen Geometry
- Local unocc. electronic structure
- Sensitivity to
  - Weak bond (e.g. H-bond)
  - Chemical Environment
  - Oxidation State / Valency
  - Symmetry
  - Spin



Resonant Inelastic X-ray Scatt (RIXS)

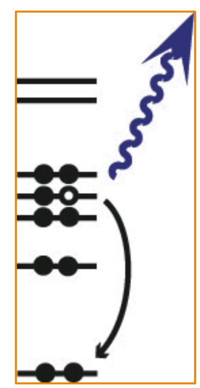
- Element/Site Specific
- Local electronic structure
- Low-Energy Excitations
  - *d-d*
  - charge transfer
- Momentum Resolved
  - Dispersion
- Increased Resolution
  - ΔE/E < core-hole (HERFD-XAS)



- **X-ray**
  - Penetration Depth
  - Flexible Sample Environment
- **Core-Level Transitions**
  - Element/Site Specificity
  - Selection Rules
  - Local Electronic Structure
    - partial DOS
    - valency
    - symmetry
    - spin

X-ray Emission Spectroscopy (XES)

- Element/Site Specific
- Frozen Geometry
- Local occ electronic structure
- Simple Final State
- Sensitivity to
  - Chemical Environment
  - Oxidation State/Valency
  - Symmetry
  - Spin



X-ray Spectroscopy

Core-Level X-ray Spectros... ...Level Transitions

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X-ray Absor... **...Scatt (RIXS)**

- Elemen...
- Fro...
- I...
-

“Peel-Off” Electronic Structure

Probe electronic structure locally

⇒ **Element specific**

⇒ **Site specific**

Resolve partial **density of states**

⇒ **Hybridization**

⇒ **Valency**

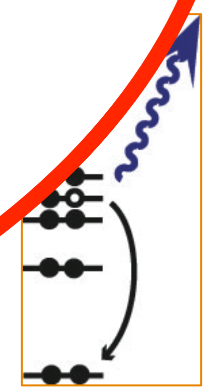
⇒ **Symmetry**

⇒ **Spin**

X-ray ⇒ Flexible Environment

Core-hole ⇒ Specificity & Sensitivity

***10^{-18}sec* transition ⇒ Dynamic Range (sec to femtosec)**



○

- v...
- symme...
- spin

X-ray Spectroscopy

X-rays Offers Flexible Environment

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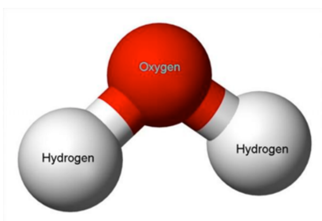
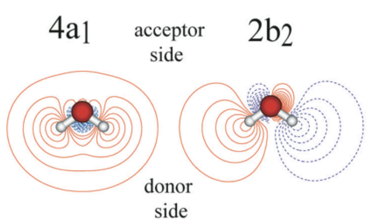
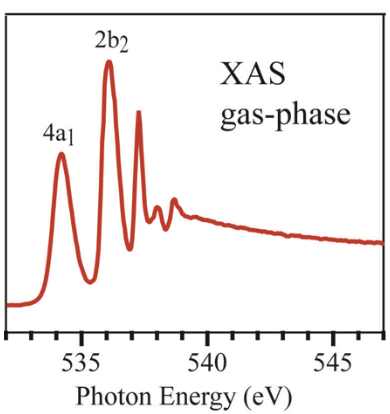
X-rays Can Probe All Phases

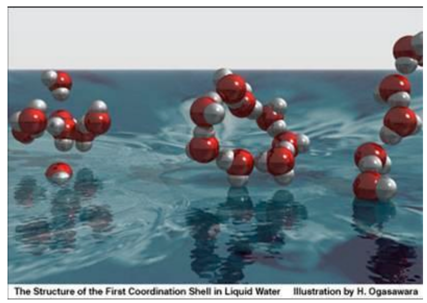
Gas-Phase

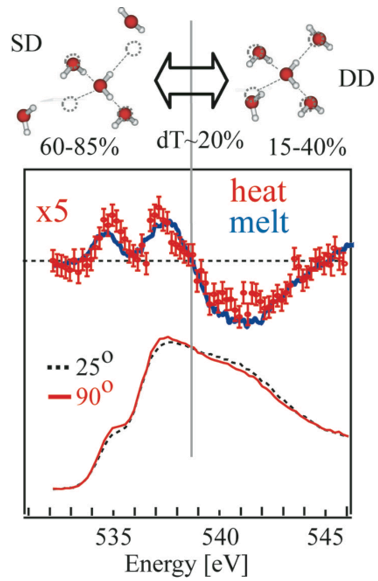




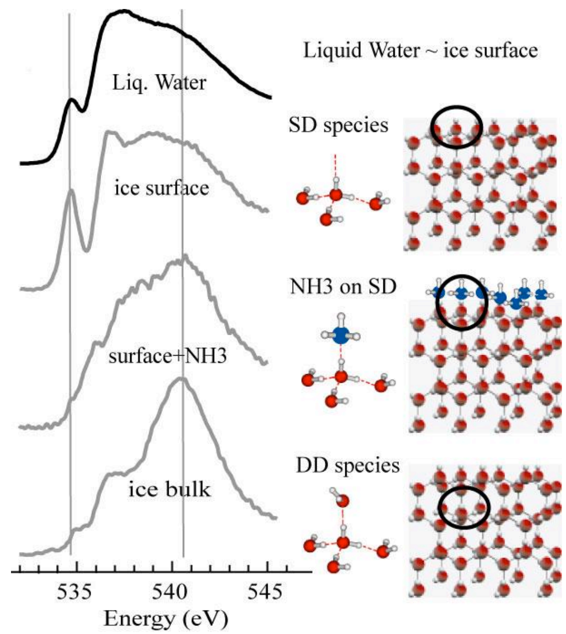


Liquid Phase





Solid Phase

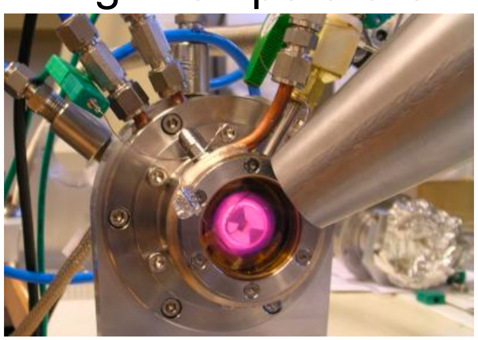


X-rays Can Probe Elaborate Environments

Extreme Conditions

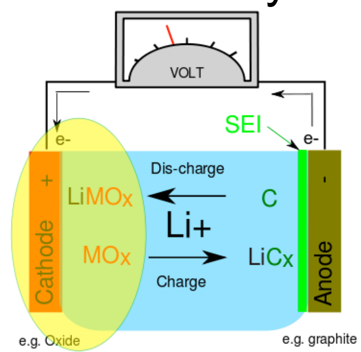
High Pressure

High Temperature

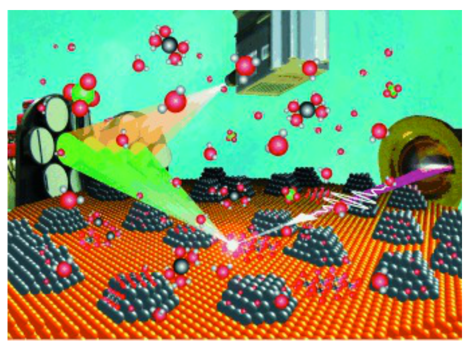


In Situ

Battery



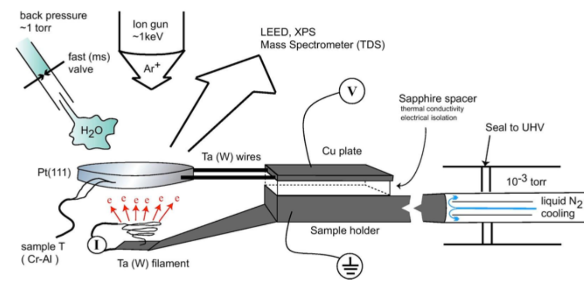
Electrochemistry



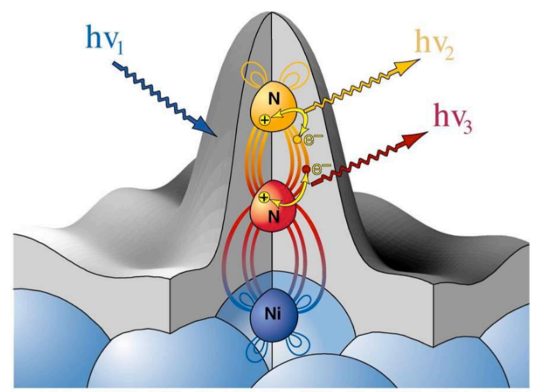
Courtesy of D. Friebel

In Vacuum

in-situ preparation...



..of well-defined systems

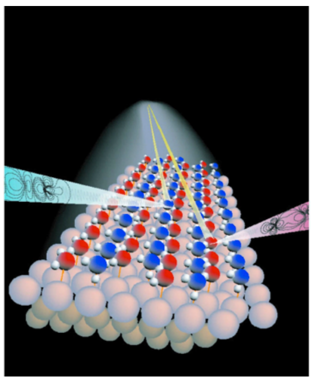


Courtesy of A. Foehlish

Element and Site Specificity: Probe Locally

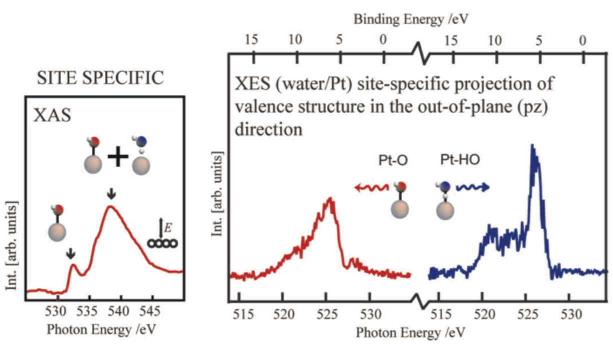
Adsorbates/Interfaces

Locally at the interface (H_2O/Pt)



PRL 89, 276102 (2002)

Specific site (hydrogen up/down)

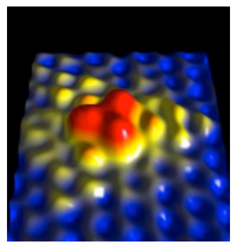


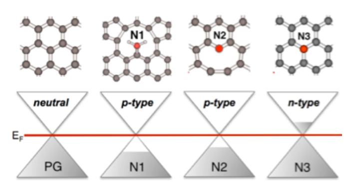
Nordlund (2004)

Dopants/Defects

Local Electronic Structure govern Workfunction & Bandgap

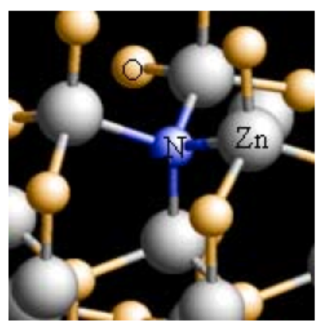
N/graphene





Science 333, 999 (2011)

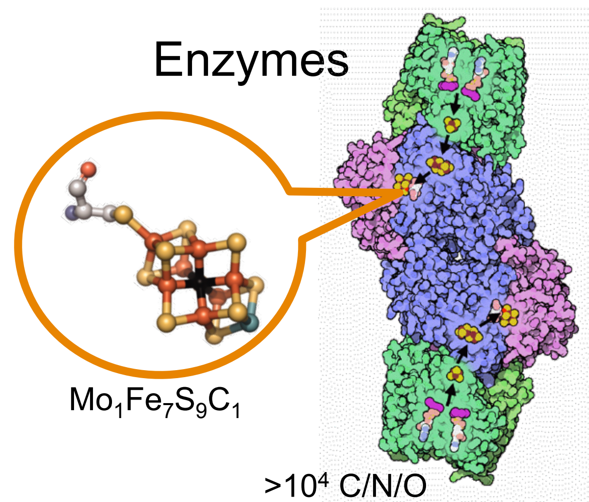
Electron/Hole mobility



NREL

Active Center

Enzymes



Science 334, 974-977 (2011)

N-fixation

Nitrogenase vs *Haber-Bosch*

$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$

C-fixation

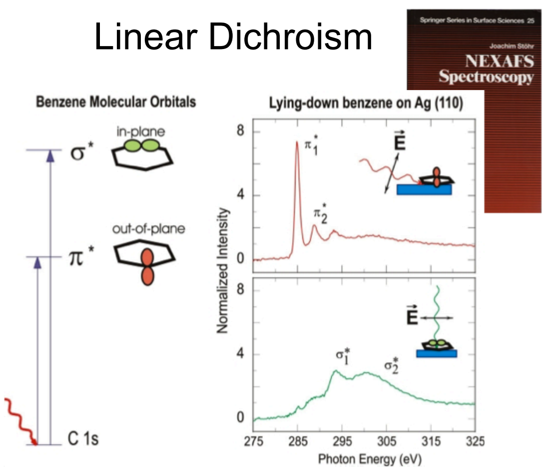
Photosynthesis vs *Fischer-Tropsch*

$6CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

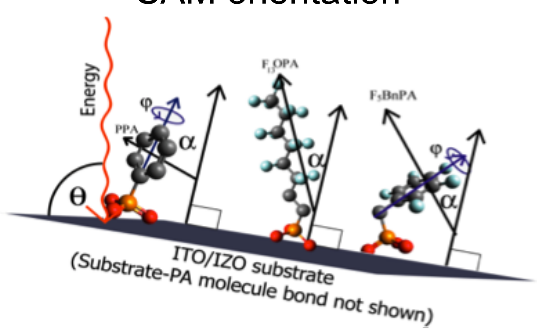
Core Level Transitions Involves Strong Selection Rules

Orbital Orientation

Linear Dichroism



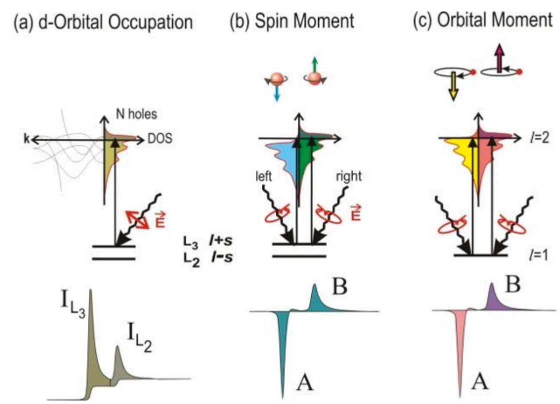
SAM orientation



Langmuir 29 (2013) 2166

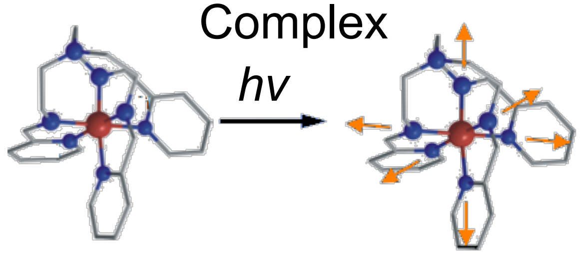
Spin and Symmetry

Circular Dichroism / Magnetism



Courtesy of J. Stöhr

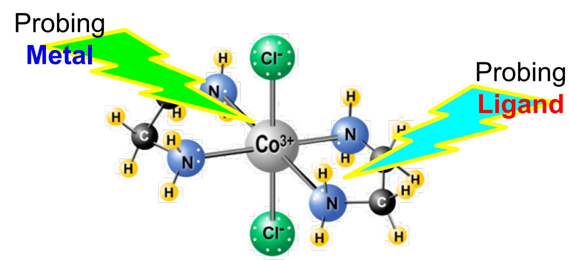
Spin Crossover Complex

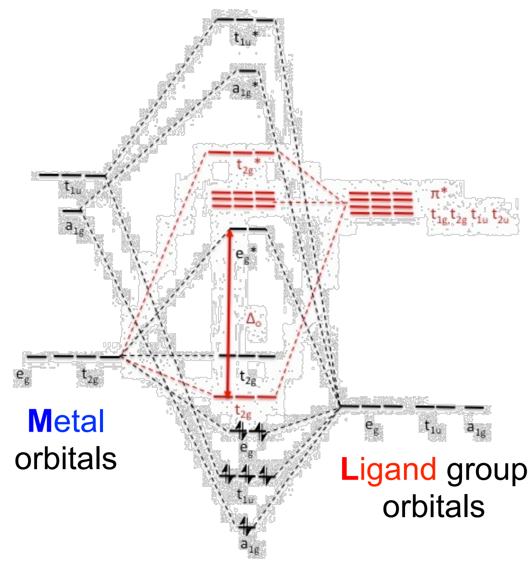


low spin **high spin**

Experimental LCAO

Metal-Ligand Chemical Bond





X-ray Spectroscopy

X-ray transition is fast (10^{-18}sec) which offers Dynamic Range (sec to femtosec)

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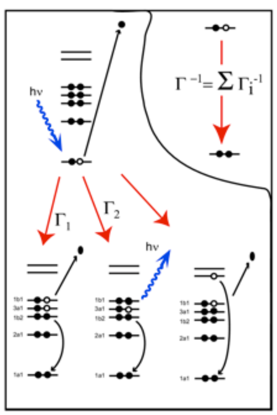
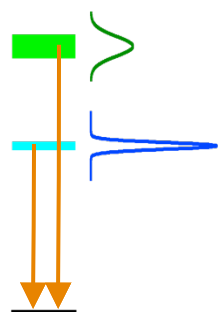
(Core-Hole) Intrinsic Lifetime and Energy Resolution

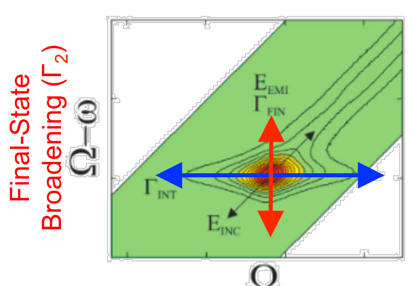
Time-Energy Uncertainty

Natural Line Width



$\Delta E \bullet \Delta t \geq \hbar/2$

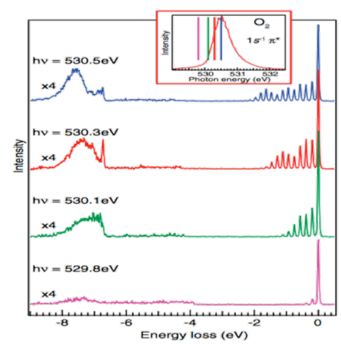




J. Elec. Spectrosc. 188, 17 (2013)

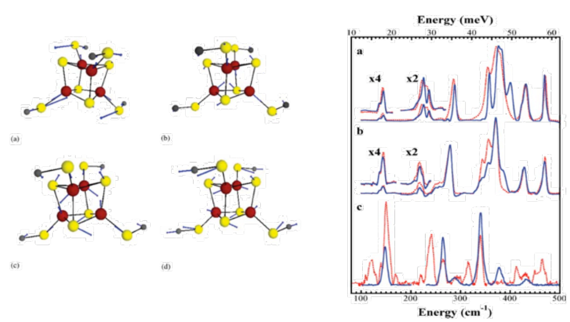
Time-domain

Potential Energy Surface of Oxygen Gas Molecule



PRL 104, 19302 (2010)

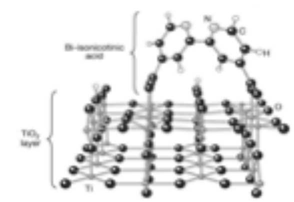
Nuclear Resonance Vibrational Spectroscopy



Dalton Trans. 2192-2201 (2006)

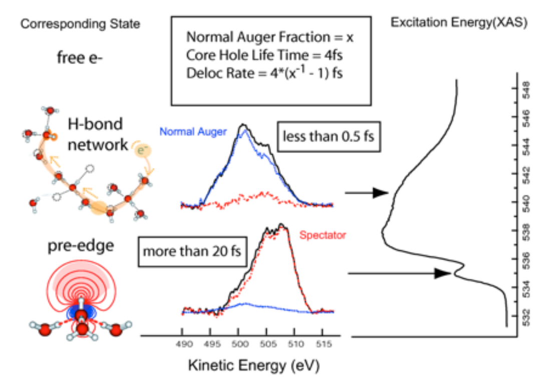
Core-Hole Clock

Dye to Semiconductor



Schnadt, Nature (2002)

Localized States (e⁻ water)



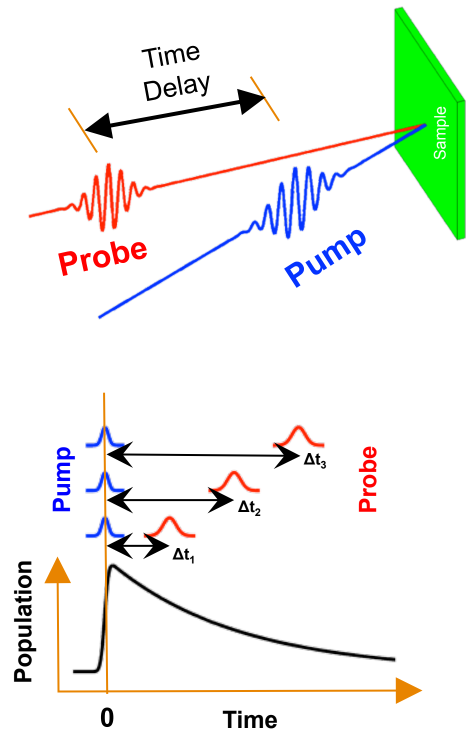
"Probing the electron delocalization in liquid water and ice at attosecond time scales" Nordlund, Ogasawara, Bluhm et al, Phys. Rev. Lett 99 (2007)

X-ray Spectroscopy

X-ray transition is fast (*10^{-18}sec*) which offers Dynamic Range (sec to femtosec)

Time-Resolved X-ray Spectroscopy: Ultrafast Pump-Probe

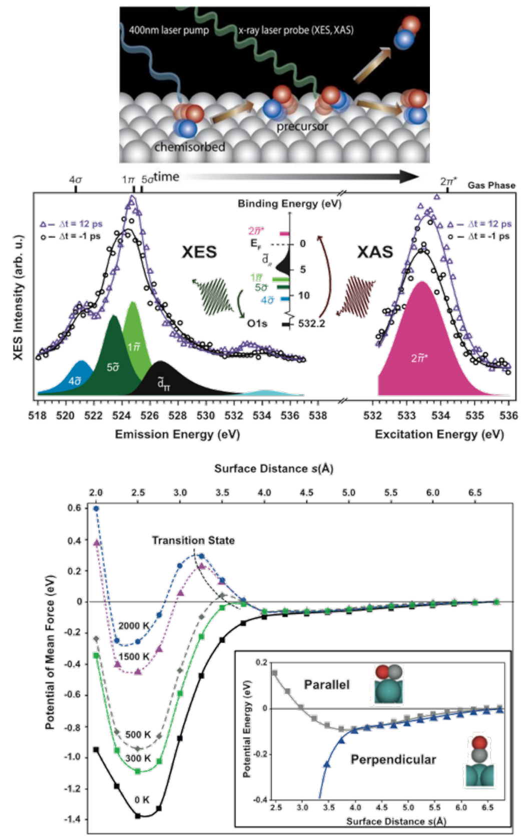
Pump-Probe



- LCLS : δt ~ 50 *fs*
- SSRL (low-alpha) : δt ~ 5 *ps*

Thermal Activation

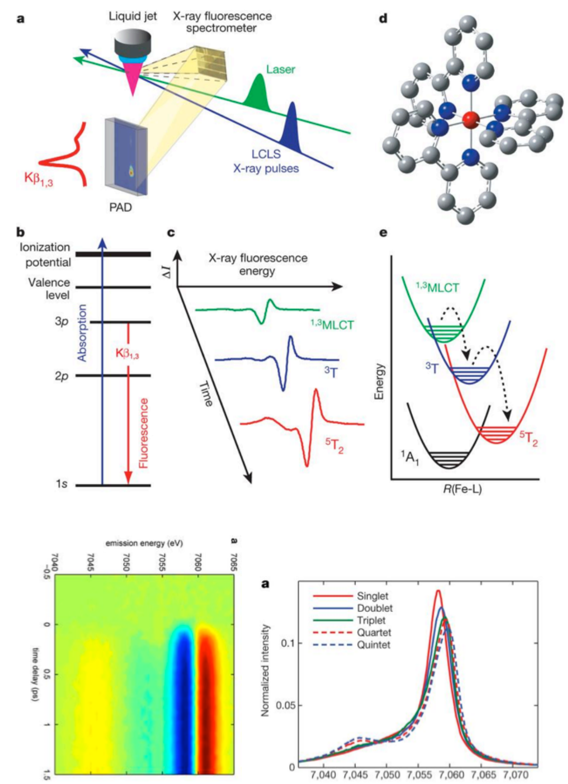
CO desorption



Science 339, 1302-1305 (2013)

Valence Excitation

Spin Dynamics



Nature 509, 345-348 (2013)

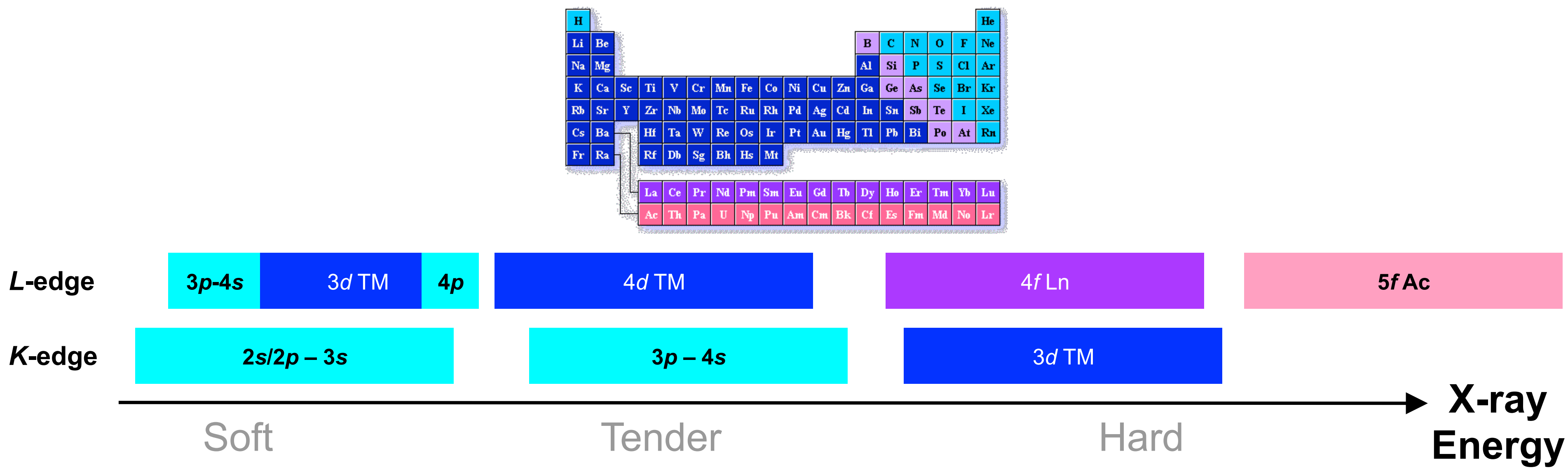
X-ray Spectroscopy requires Intense X-ray Sources

SLAC

SSRL: 3 GeV, 500 mA
LCLS: Hard X-ray FEL

SSRL

X-ray Spectroscopy at SLAC
Across Periodic Table

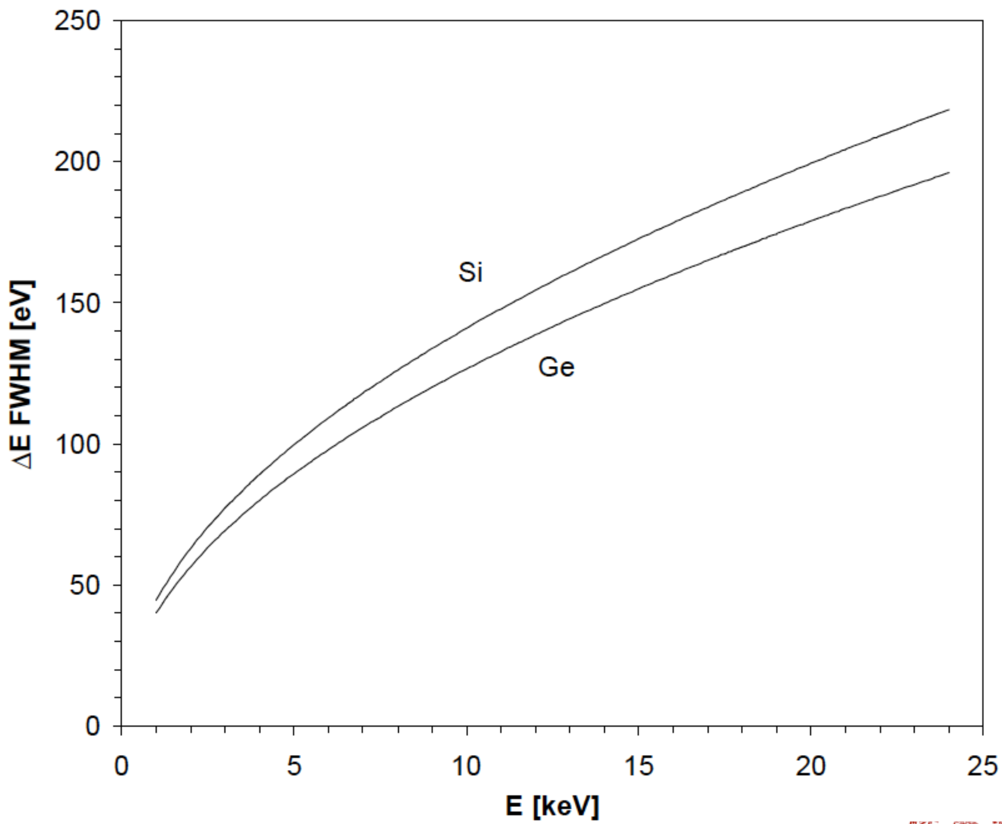


X-ray detection schemes

- Current Integration Detectors: PhotoDiodes or Ionization Chamber (no energy resolution)

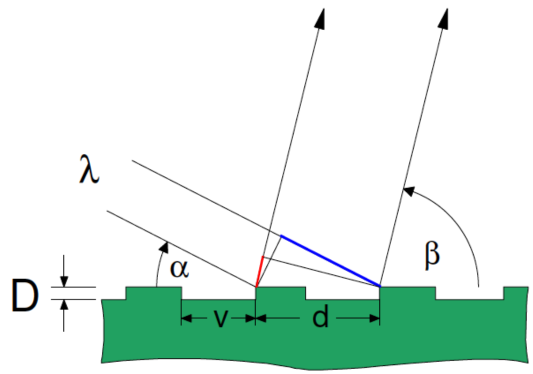
•Semiconductors (Si, Ge) with amplifying electronics

- •Single photon detection
- •High efficiency/solid angle
- •Detecting extended range
- •For Si, Fano Factor restricts the energy resolution to a physical minimum of ~115eV (@ 5.89keV)



Resolving x-rays with a high energy resolution – Diffractive x-ray optics

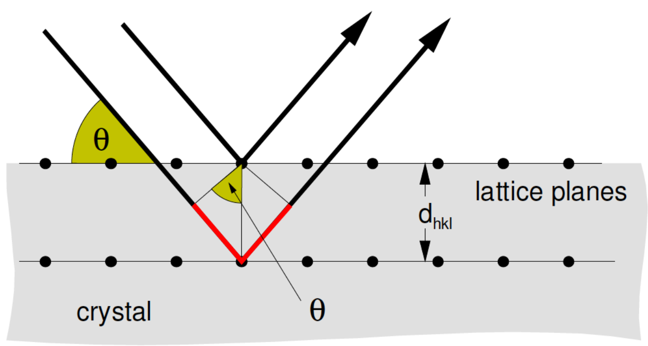
- Diffraction Gratings



$$m\frac{\lambda}{d} = (\sin\alpha + \sin\beta)$$

soft x-rays

- Bragg-type x-ray crystal optics

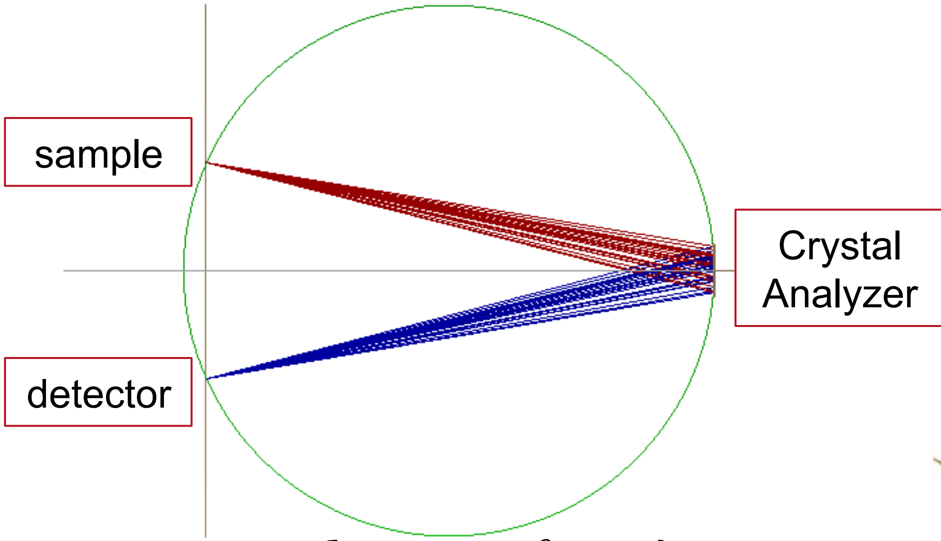


$$2d_{hkl}\sin\theta = \lambda$$

hard x-rays

Hard X-rays: Johann geometry with spherically bent

SLAC

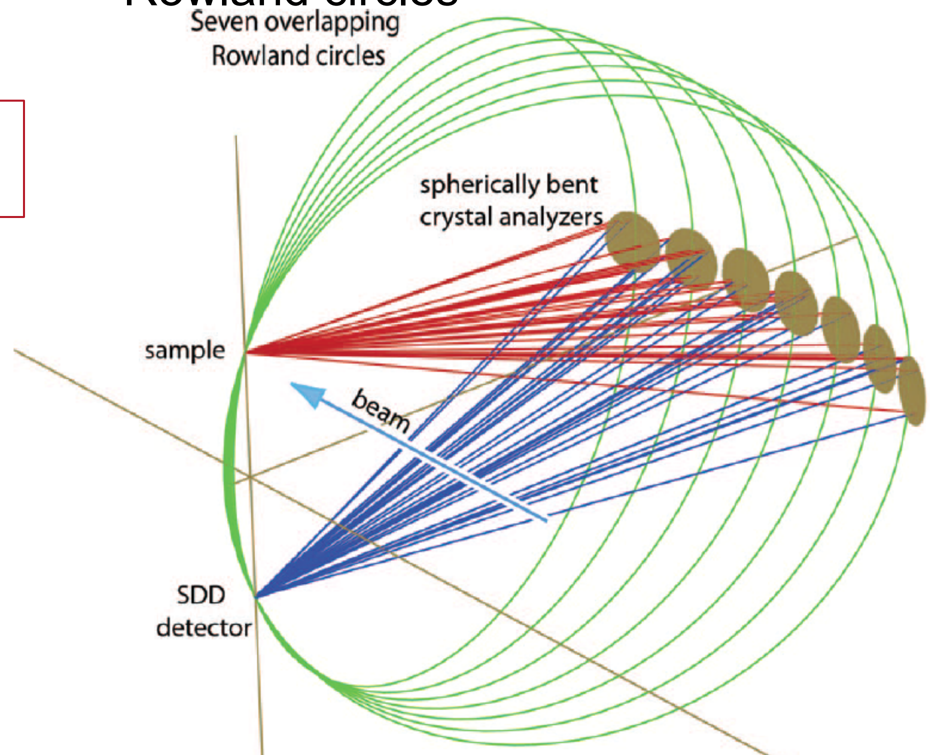


$$2d_{hkl}\sin\theta = \lambda$$

Johann Geometry:

- Spherically bended Bragg crystals
- Point-to-point focus
- Optimum resolution ➔ 90° (backscattering)
- For backscattering E/ΔE > 10^4

Multicrystal Spectrometer:
Crystals arranged on overlapping Rowland circles

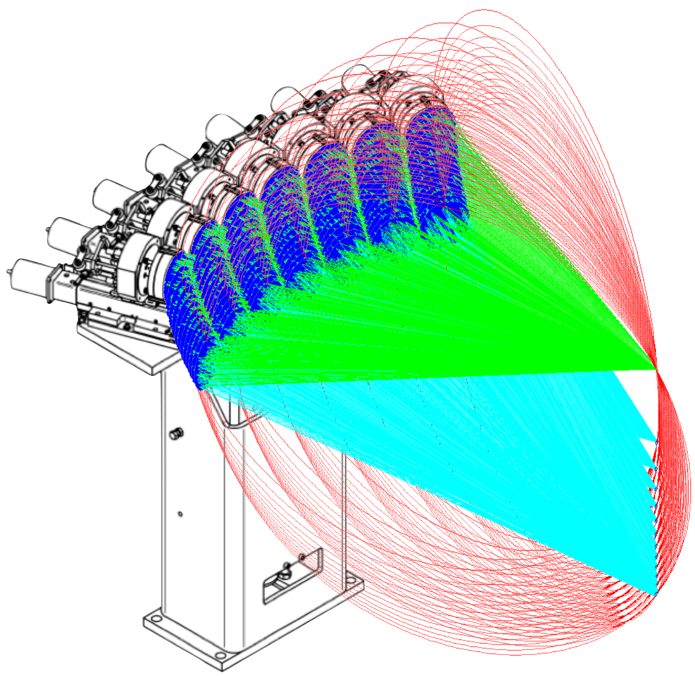


Overlapping focusing
signal/background ratio ➔ UP !!

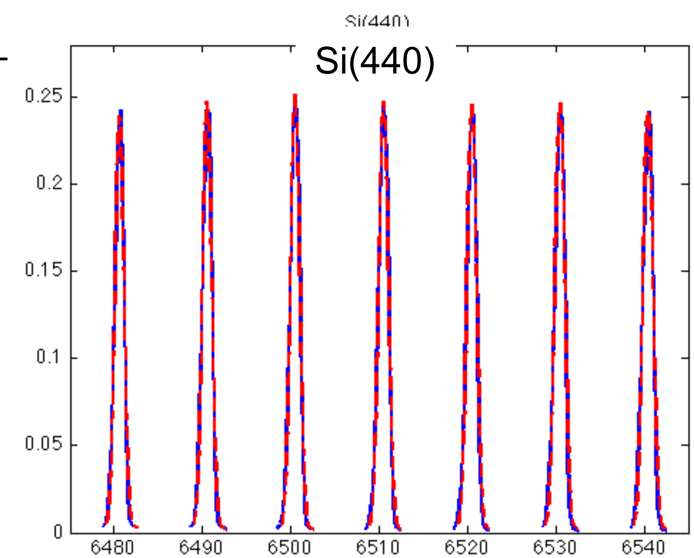
SSRL

Hard X-rays: a 7-crystal X-ray Emission Spectrometer

SLAC

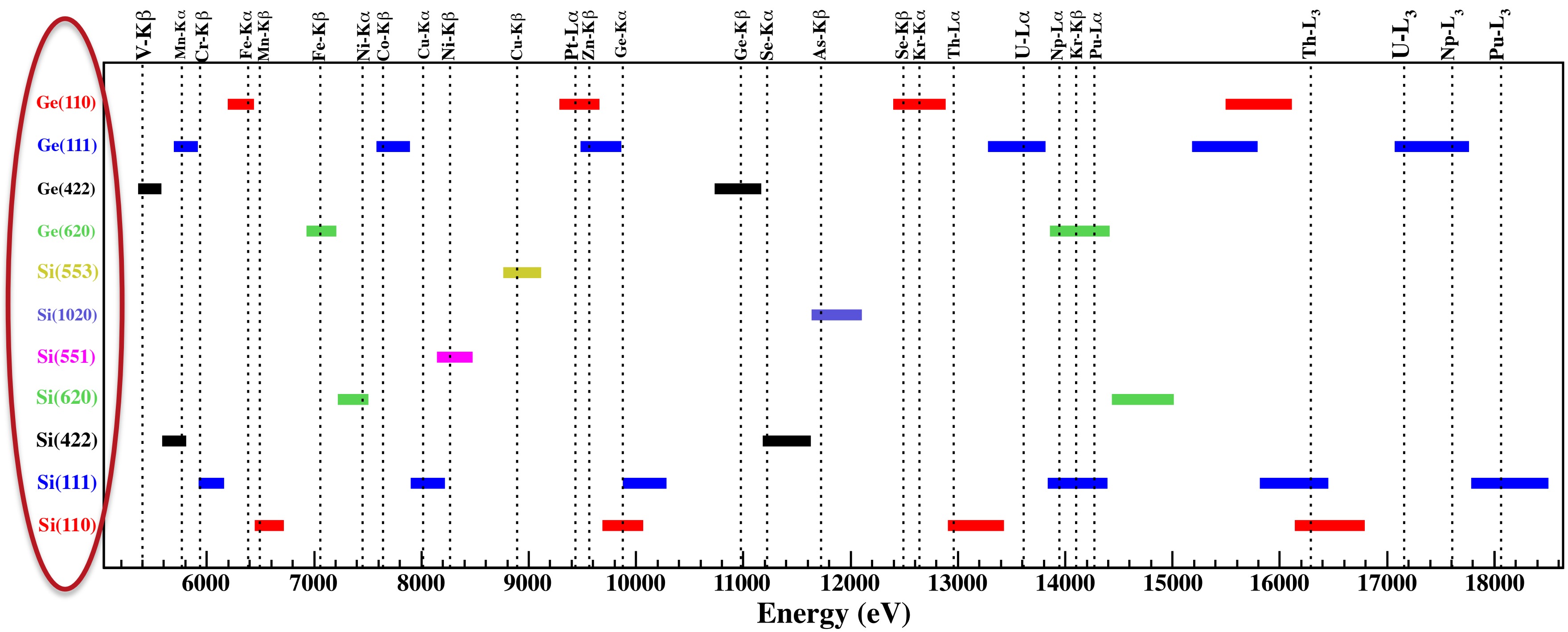


- 7-element XES spectrometer operates **on *Rowland* circle** throughout entire scan range
  - Energy resolution < 1 eV for 3*d* TM
  - High throughput (milions of cps on concetrated samples



SSRL

SSRL's crystal bank for the 7-crystal XES spectrometer



Various crystal cuts are required for analyzing the different x-ray energies along the 75-88 deg of backscattering angle

The high-resolution & high-throughput x-ray spectroscopy end-station at SSRL

XRS (low-q) @ 88º

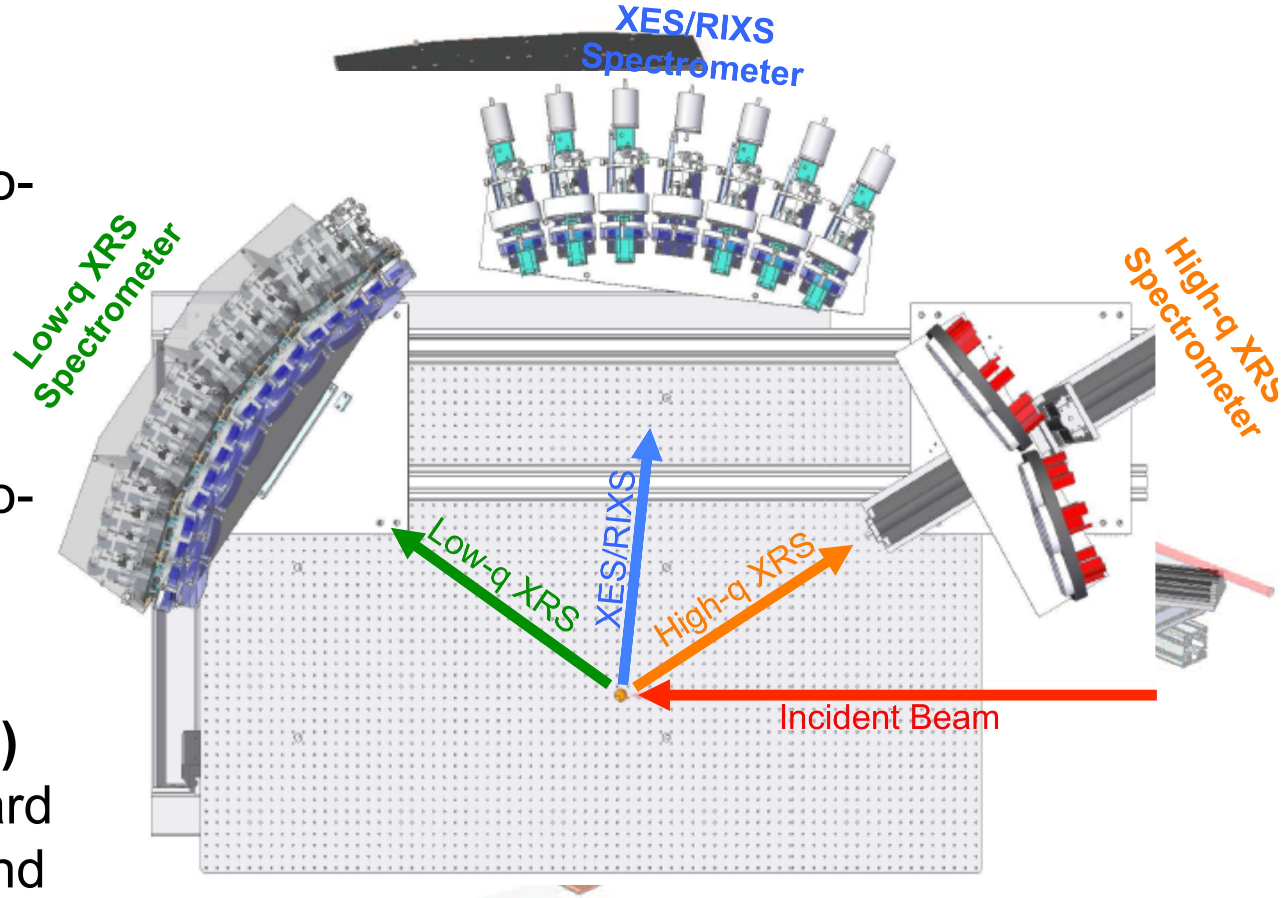
- 40-crystal spectrometer for X-ray Raman spectroscopy of light elements

XRS (high-q) @ 87.4º

- 14-crystal spectrometer for X-ray Raman spectroscopy of non-dipole transitions

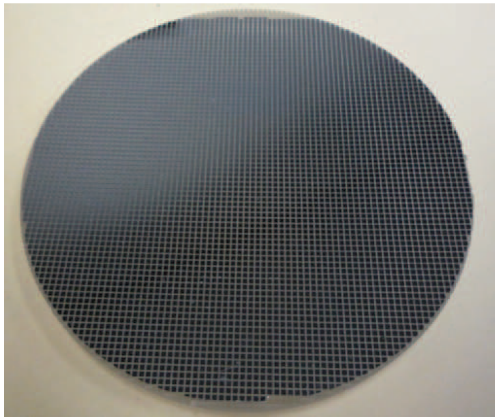
XES/RIXS/XAS (74º-88º)

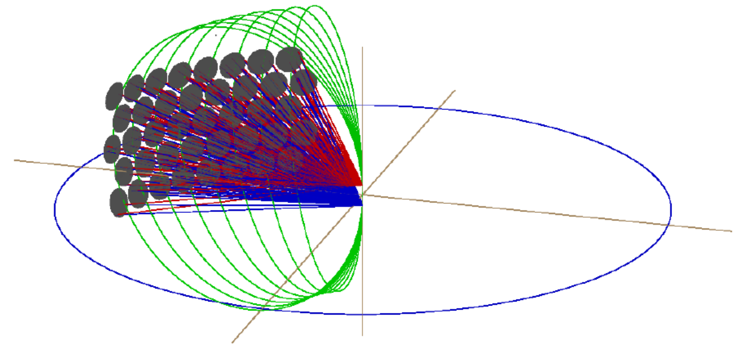
- 7-crystal analyzer for hard X-ray emission, RIXS and High energy resolution fluorescence detection



Rev. Sci. Instrum. 83, 043112 (2012)
Rev. Sci. Instrum. 84, 053102 (2013)

40- Crystal Spectrometer Performance





Crystal Analyzers

- Si (110) single crystal
- 88^o deg (Fixed energy)
- Si(440): 6460 eV
  Si(660): 9690 eV
- Spherically bent (1m radius)

Diced Crystals

- $1x1mm^2$ diced crystal
- Release of crystal stress (d-spacing)
- Improved resolution (<**250meV** at 6500 eV)

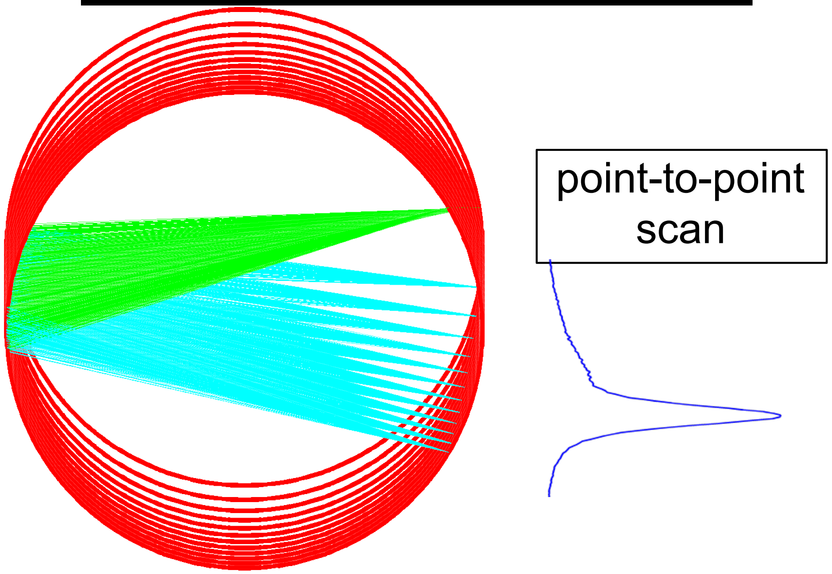
Johann Geometry

- Sample and Detector on Rowland circle
- In-air setup (helium bag for minimizing attenuation)
- Overall resolution (40-crystals) **270meV** @ 6460eV (with Si311 mono)

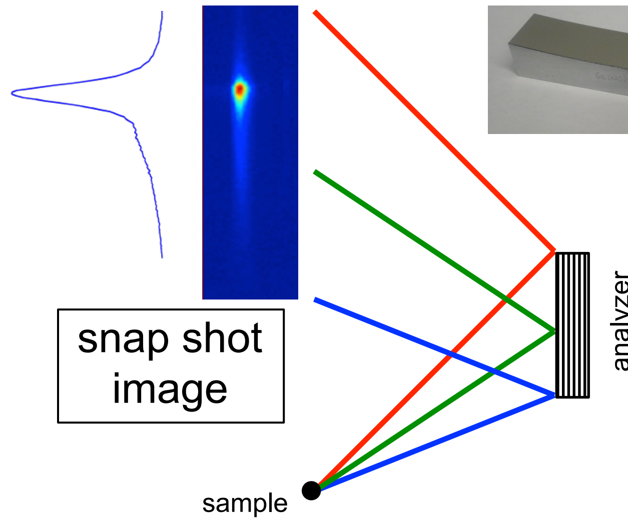
SDD detector can resolve analyzed signal from diffused scattering

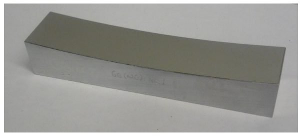
Hard X-rays: Point-to-Point vs Dispersive Geometry

Monochromatic analyzer

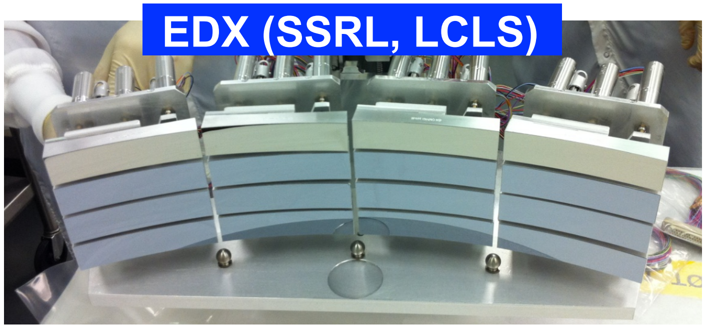


Dispersive analyzer





Rowland geometry



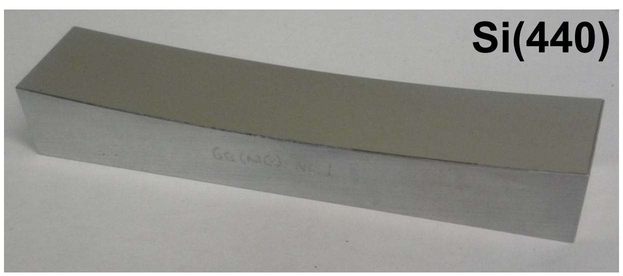
von Hamos geometry

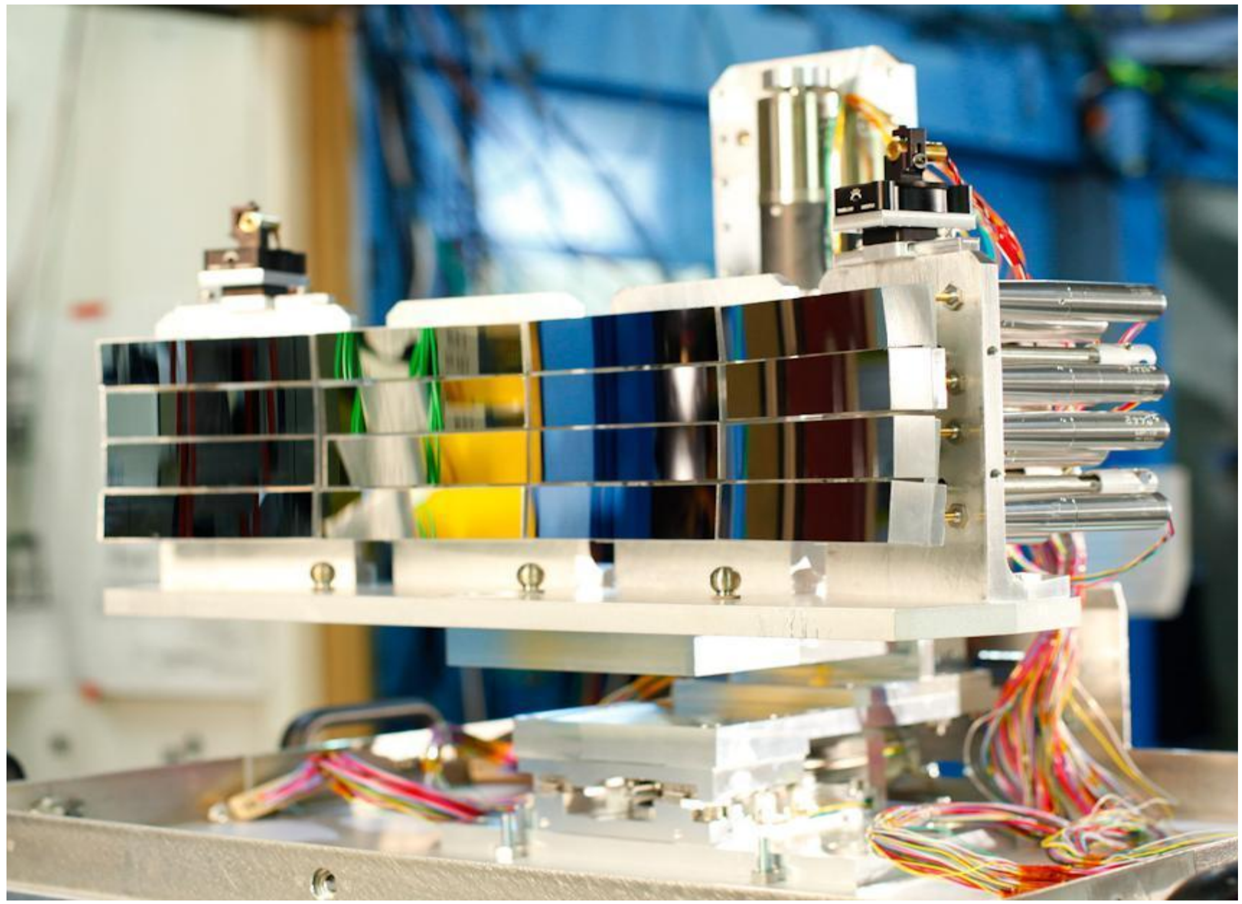
Hard X-rays: 16-Crystal Energy Dispersive Spectrometer

SLAC

Photon-In Photon-Out: XES – RIXS - XRS

- 16 cylindrical crystals
- 500 mm radius
- Large solid angle
- Resolution ~ 0.5 eV
- Vacuum compatible
- Portable / stand-alone





Rev. Sci. Instrum. 83, 073114 (2012)
PNAS 109, 19103 (2012)

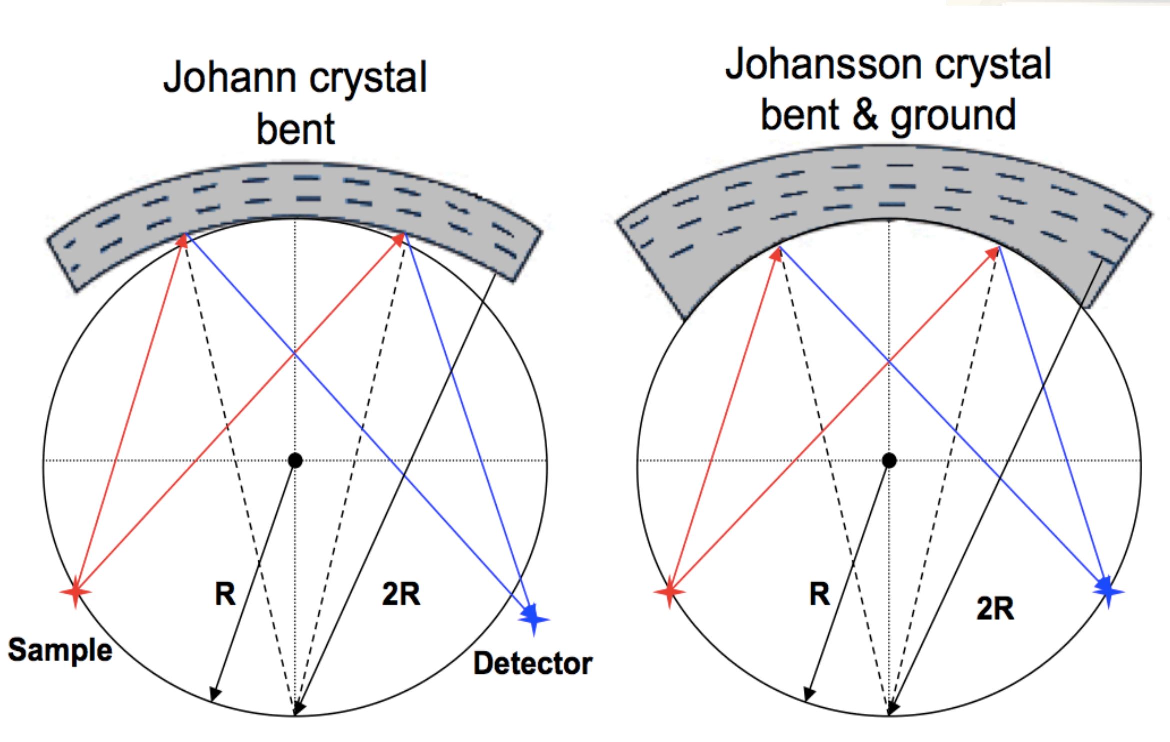
SSRL

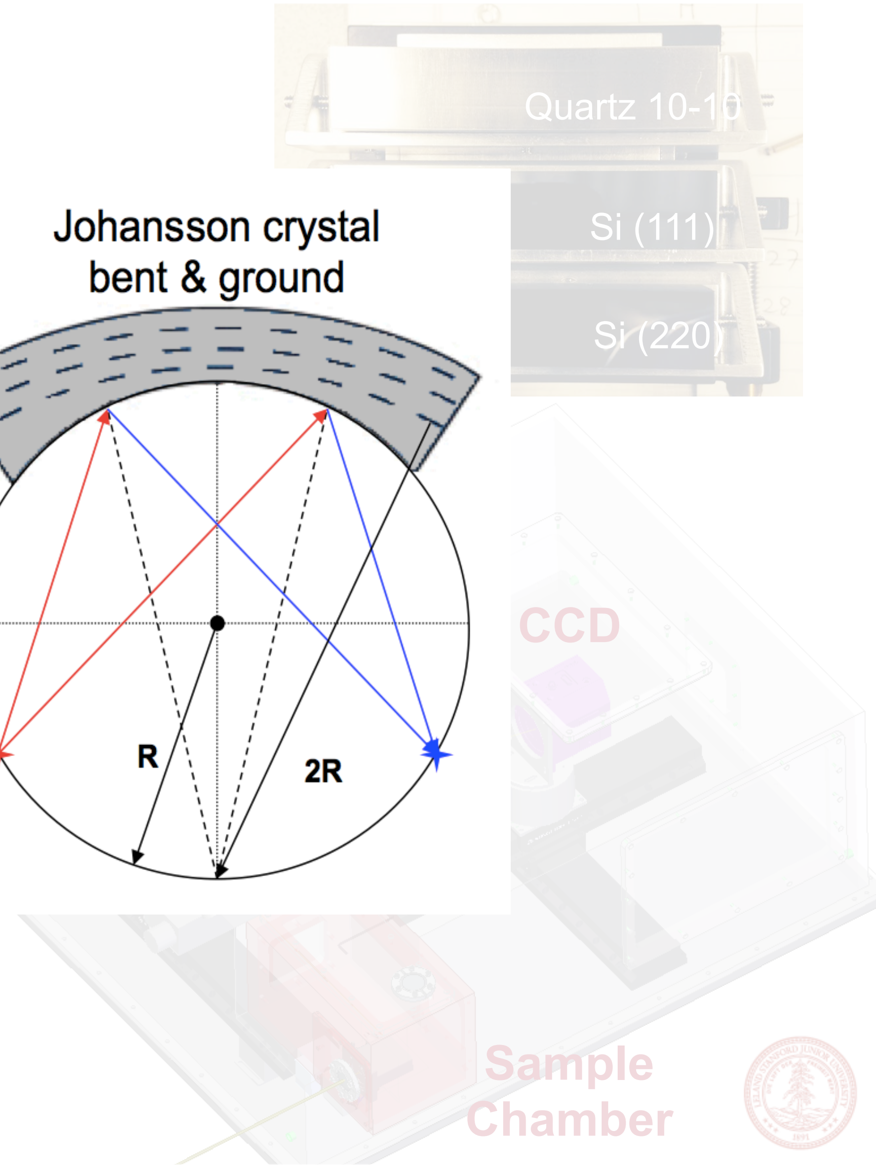
Tender X-rays: Johansson Spectrometer (~1.6-6.5 keV)

SLAC

Instrument Details

- 0.5m Rowland Circle
- Bragg ar
- **1.5 – 6.5**
  chamber
  - 3 Joha
    (10-10
- Large Sp
  - > Mov
- Spectrur
  - 25x25
- Versatile
  - Decou
    Sampl





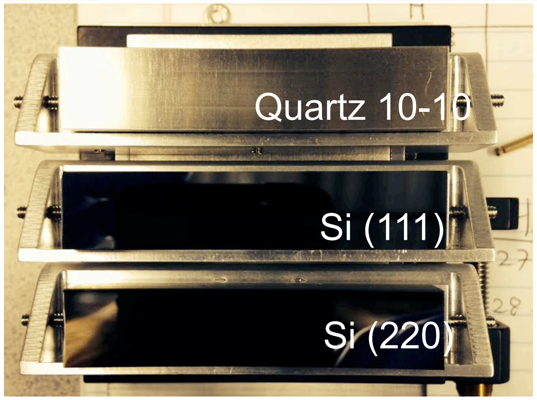
SSRL

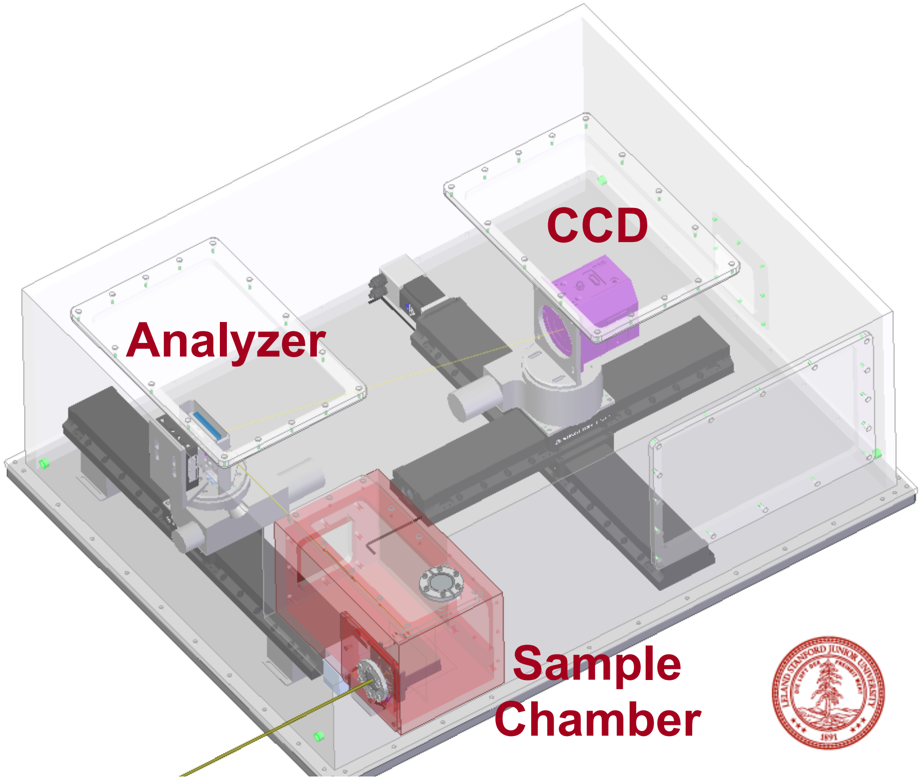
Tender X-rays: Johansson Spectrometer (~1.6-6.5 keV)

SLAC

Instrument Details

- 0.5m Rowland Circle
- Bragg angles: 30º-65º deg
- **1.5 – 6.5** keV (He and Vacuum chamber)
  - 3 Johansson Crystals (Quartz (10-10), Si (110), Si(111)
- Large Spot, Beamline 4-3
  - > Move inside Rowland Circle
- Spectrum Recorded with PSD
  - 25x25mm^2 Andor CCD
- Versatile Sample Enviroment
  - Decoupled Spectrometer and Sample environment





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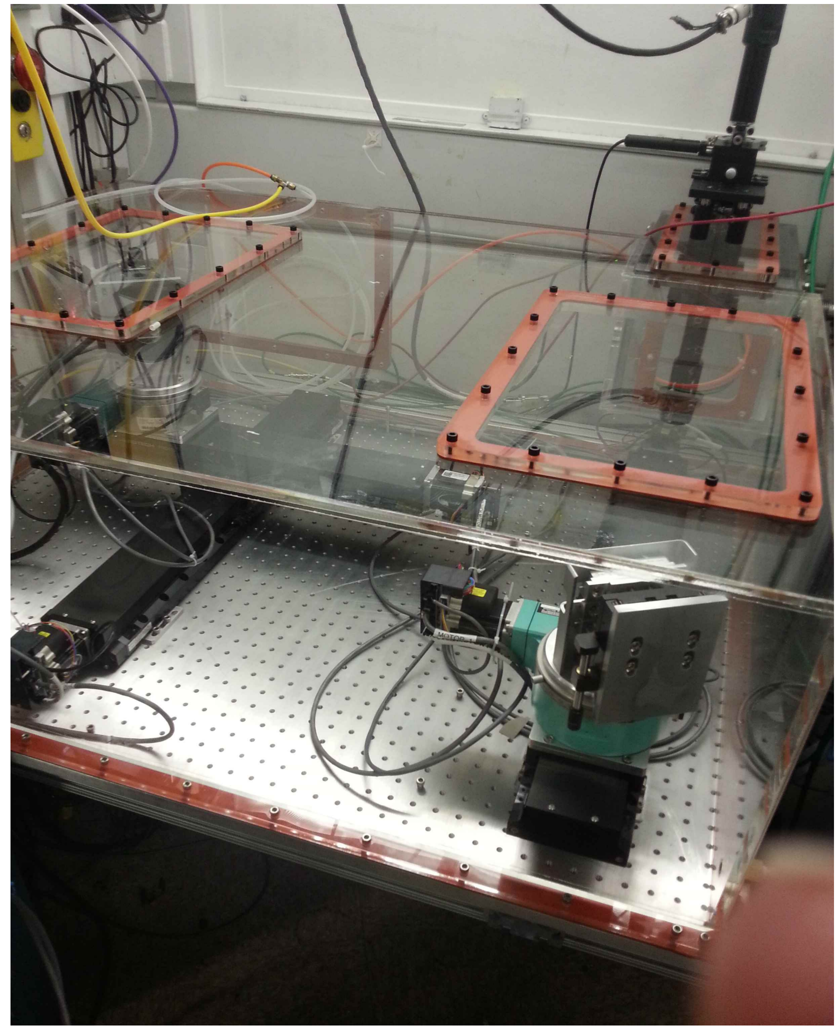

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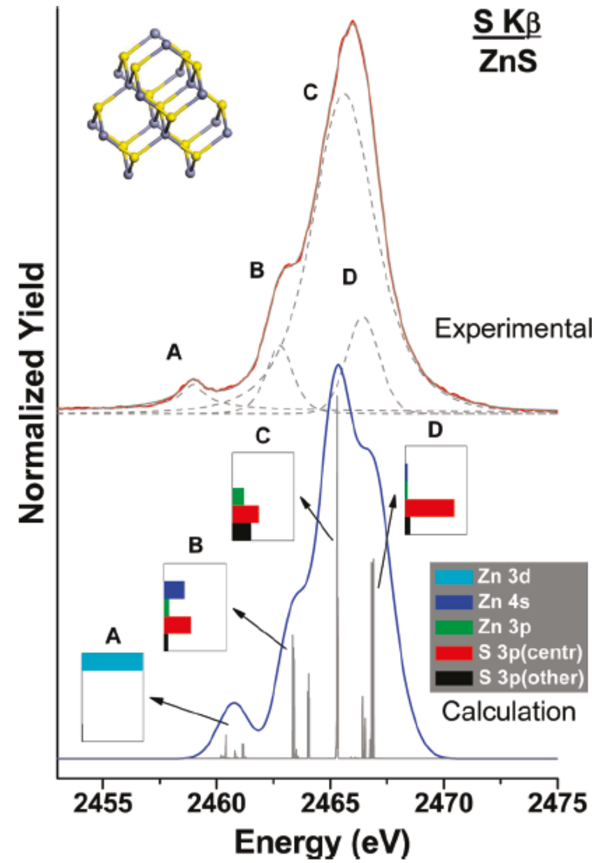


R. Alonso-Mori et al., Inorganic Chemistry 49, 6468 (2010)
R. Alonso-Mori et al., Anal. Chem. 81, 6516 (2009)

SSRL

X-ray Detection Techniques for Soft and Hard X-ray Core-Level Spectroscopy

SLAC

Hard X-rays (e.g.)

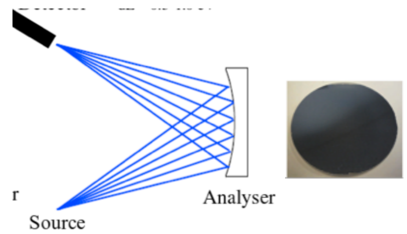
- 3*d* Metal 1*s* (K-edge)
- 5d Metal 2*p* (L-edge)
- Ln 2*p* (L-edge)
- An 2*p* (L-edge)

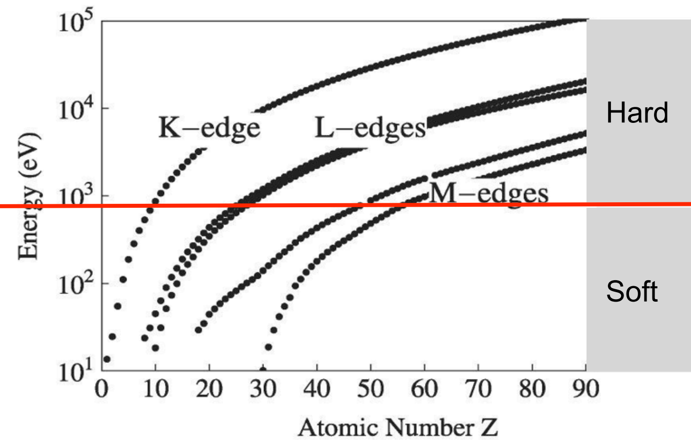
Tender X-rays (e.g.)

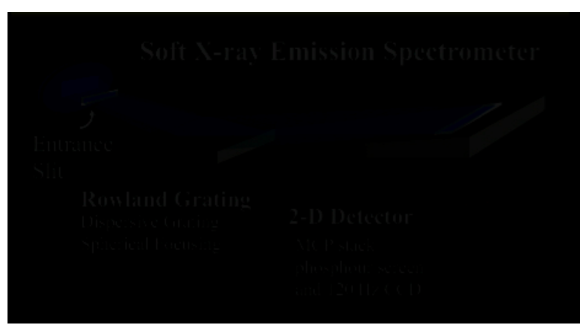
- Sulphur 1*s* (K-edge)
- 4*d* Metal 2*p* (L-edge)

Soft X-rays

- Light Element 1*s* (K-edge)
- 3*d* Metal 2*p* (L-edge)







High Energy Resolution

Bent Bragg Crystals
E/dE ~ 10000
Fluoresc Yield ~ 35%
Efficiency ~ 10%
Solid Angle ~ 0.1% of 4pi sr

High Energy Resolution

Grazing Incidence Gratings
E/dE ~ 1000
Fluoresc Yield ~ 1%
Efficiency ~ 2%
Solid Angle ~ 0.01% of 4pi sr

Soft X-ray Detection: Conventional Method

Soft X-ray Grazing Incidence Grating Spectrometers and its limitations

SLAC

Conventional Soft X-ray Grating Spectrometer

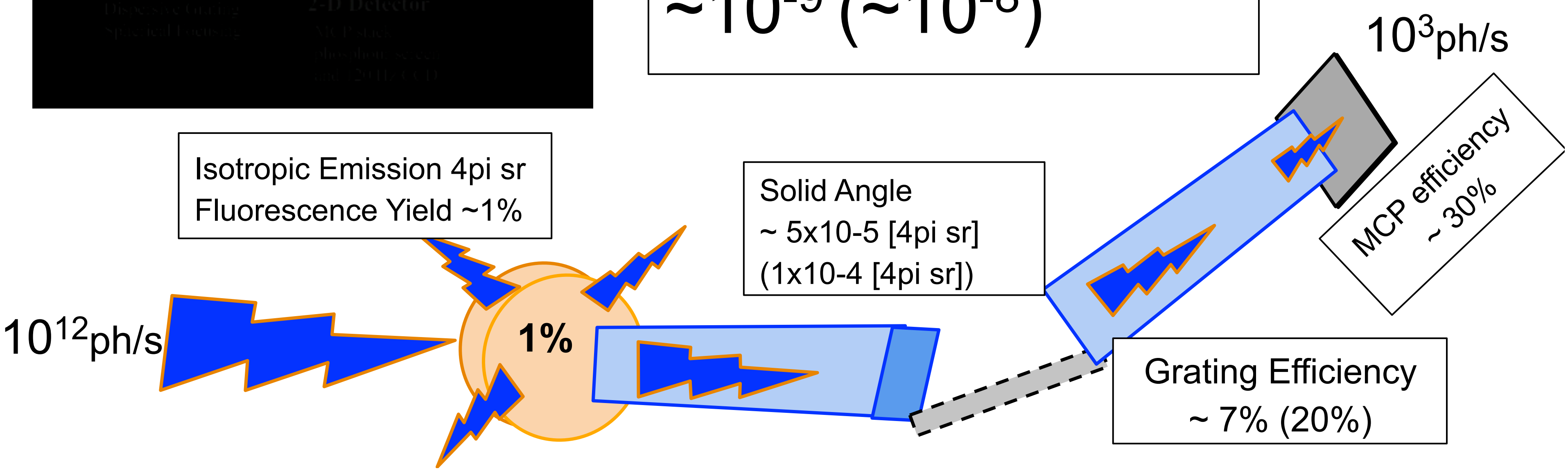
- Limited Solid Angle
- Low Detection Efficiency
- High Resolution Possible (at a cost)
- Small Spot Size

Fraction Detected

Rad Yield **x** Sol. Angle **x** Efficiency =

1% x 5x10^{-5} x 7% x 30%

~10^{-9} (~10^{-8})



X-ray Detection Techniques for Soft and Hard X-ray Core-Level Spectroscopy

SLAC

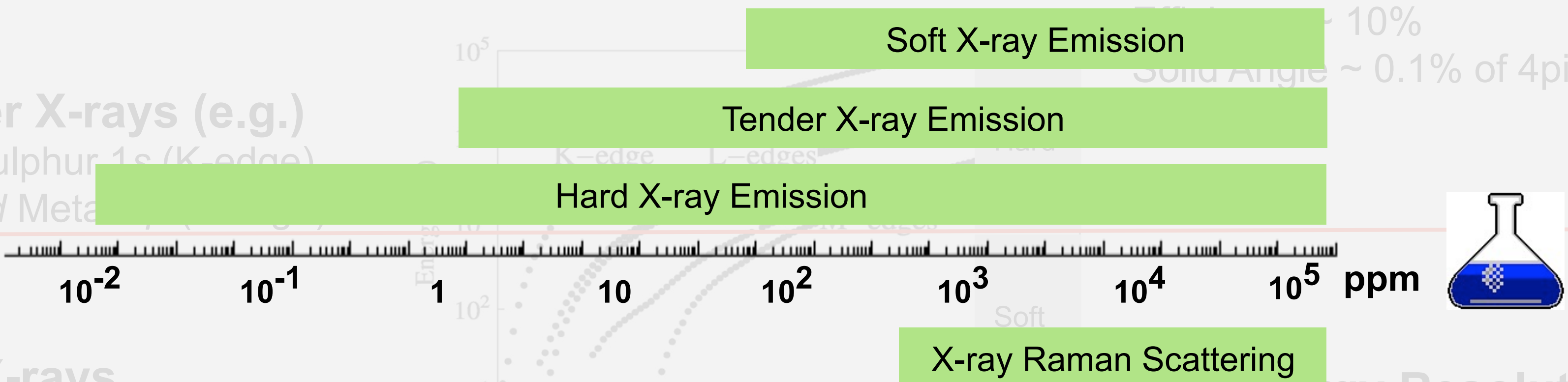
Hard X-rays (e.g.)
- 3*d* Metal 1*s* (K-edge)
- 5d Metal 2*p* (L-edge)
- Ln 2*p* (L-edge)
- An 2*p* (L-edge)

Tender X-rays (e.g.)
- Sulphur 1s (K-edge)
- 4*d* Meta...

Soft X-rays
- Light Element 1*s* (K-edge)
- 3*d* Metal 2*p* (L-edge)

High Energy Resolution

Bent Bragg Crystals
E/dE ~ 10000
Fluoresc Yield ~ 35%
... ~ 10%
... ~ 0.1% of 4pi

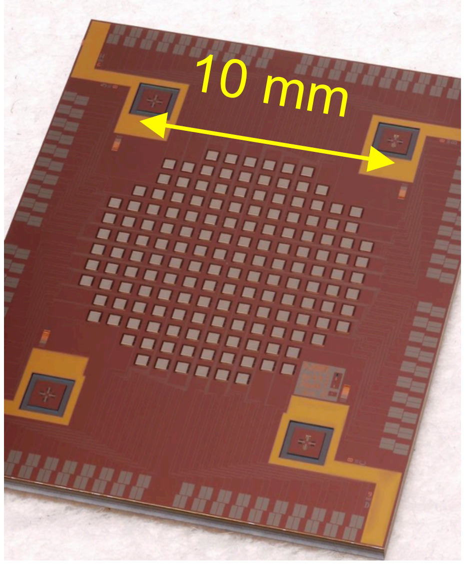


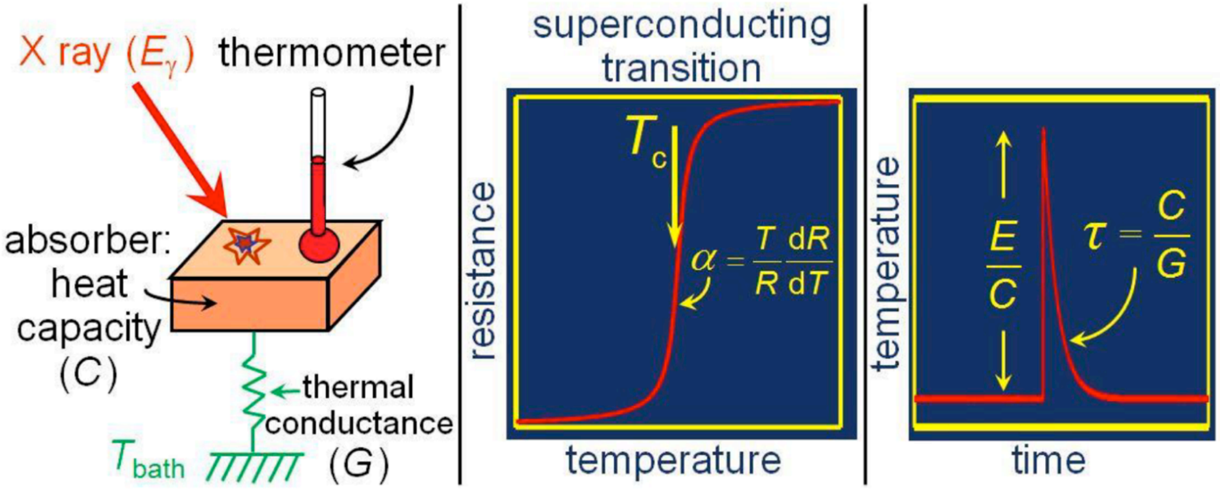
High Energy Resolution

Grazing Incidence Gratings
E/dE ~ 1000
Fluoresc Yield ~ 1%
Efficiency ~ 2%
Solid Angle ~ 0.01% of 4pi sr

Soft X-rays: Unprecedented Sensitivity with Transition Edge Sensors (TES)

- ★ **Superconductive Thin Film**
  - Extremely sensitive to small dE
- ★ **Detect Individual X-ray Energy (XES)**
  - Large Energy Range (no scanning)
  - Saturation energy tunable
  - Energy Resolution ~1eV
- ★ **Fabrication into arrays is now possible**
  - **Large scale detectors! (240 pixels)**



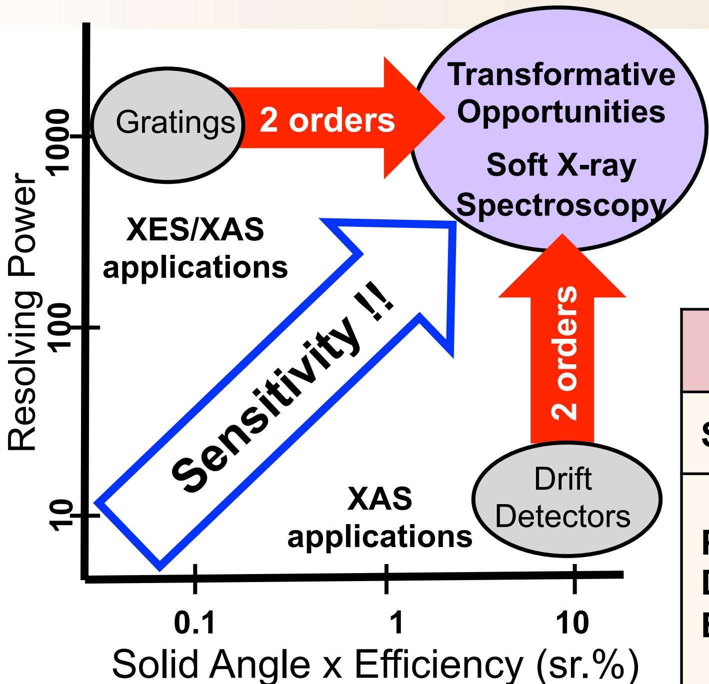


$$\Delta E \propto \sqrt{k_B T E_{max}}$$

Ongoing LDRD Project: D. Nordlund, et al

Soft X-rays: LDRD-funded TES Spectrometer for SSRL

SLAC



- 240 pixel array
- 100 Hz x-ray event rate at each pixel

	TES Spectrometer	Grating Spectrometer
Solid Angle	**0.02 sr**	0.0013 sr
Photon Detection Efficiency	**33% N *K*, 58% O *K*, 90% Cu *L*** (dominated by x-ray windows)	<5%
Measurement Energy Range	**250-1000 eV (multiple edges simultaneously)**	~100 eV (single edge, time consuming alignment)
X-ray Beam Focus	None Required	Tight Focus (~few um)
Energy Resolution	1 eV	0.7 eV typical*

*Can be significantly better, but with much lower efficiency and smaller solid angle

Soft X-rays: Ultra-Sensitive Detection

Enabling Ultra-low Concentrations in soft X-ray Region (ppm)

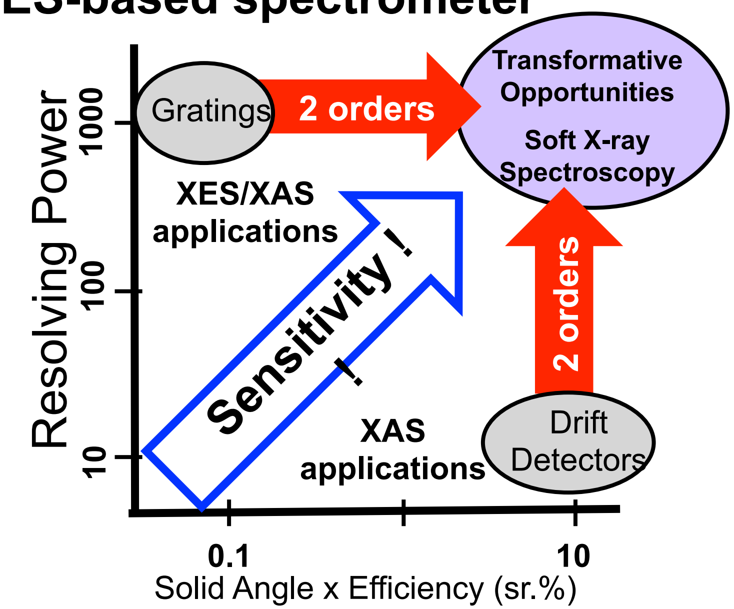
SLAC

Defects/Dopants	10^{19}-10^{20}/cm^3	=>10^{17}-10^{18}/cm^3
Surface Sensitivity	1-10% monolayer	=>0.01-0.1% ML
Solute Sensitivity	10-100 mM	=>100-1000 uM
Spot Size	10-100um	=> 1-10mm

New Science Opportunities in Material Science, Chemistry, and Biology!

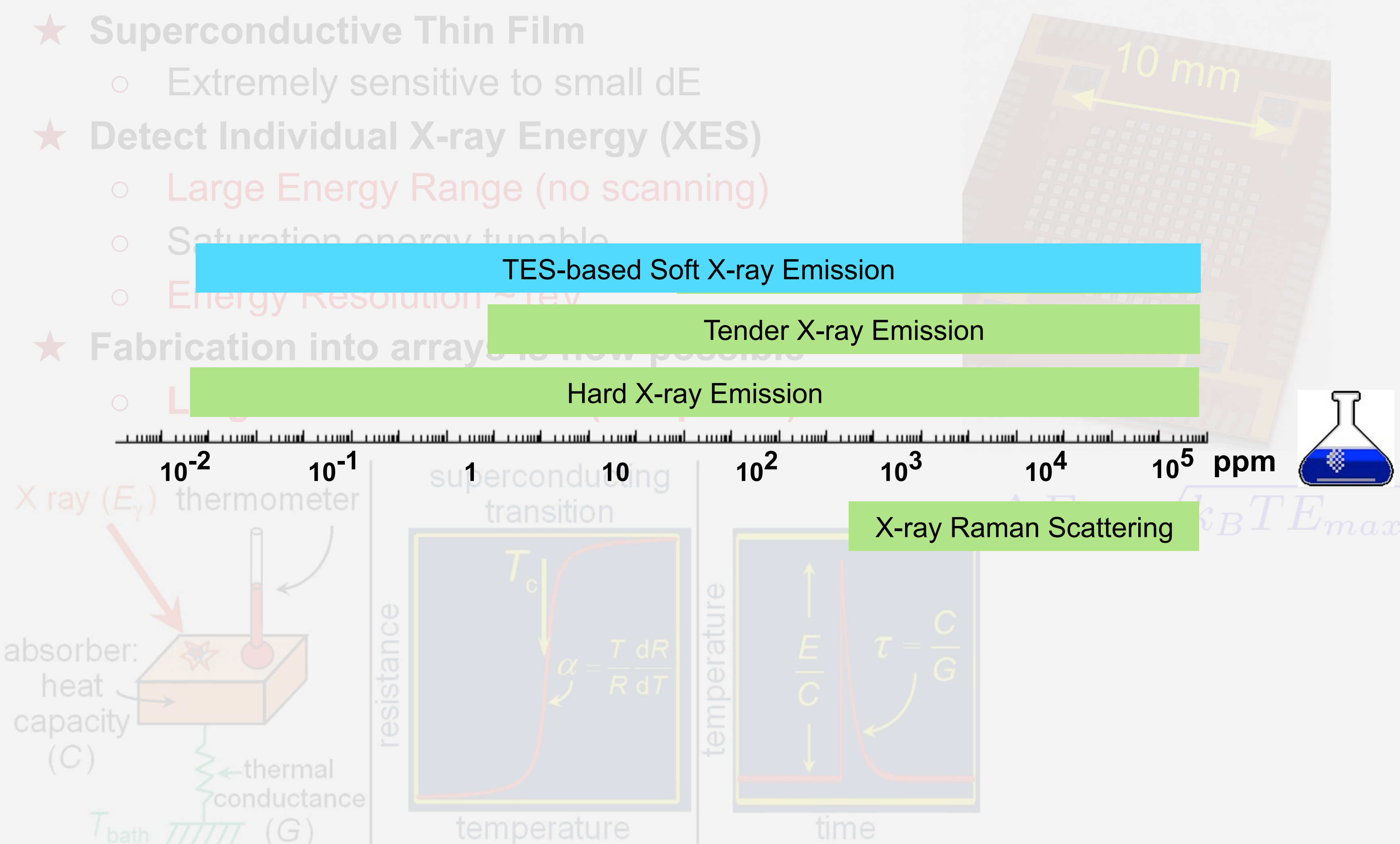
Grating Spectrometer

TES-based spectrometer



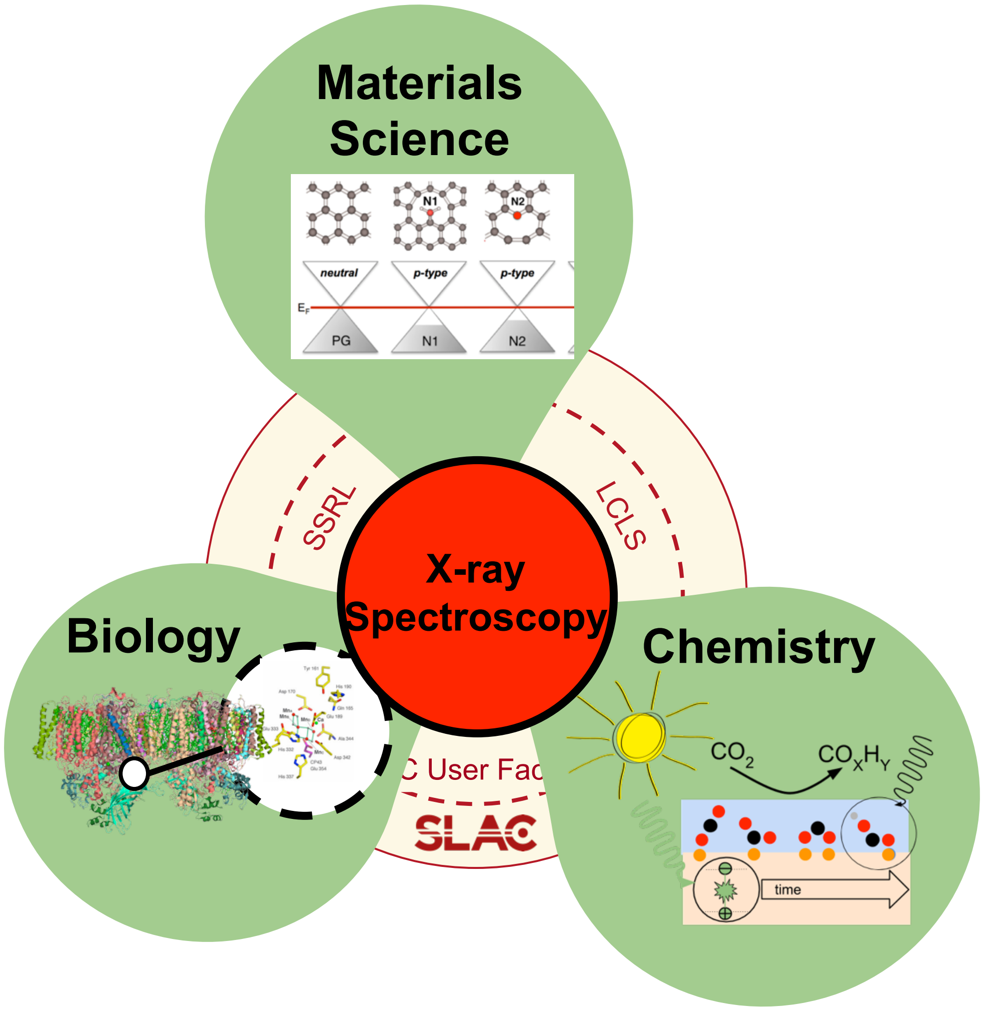
Soft X-ray Spectroscopy at SLAC

Unprecedented Sensitivity with Transition Edge Sensors (TES)



Ongoing LDRD Project: D. Nordlund, K. Irwin, et al

X-ray Spectroscopy at SLAC
A Multidisciplinary Research Program

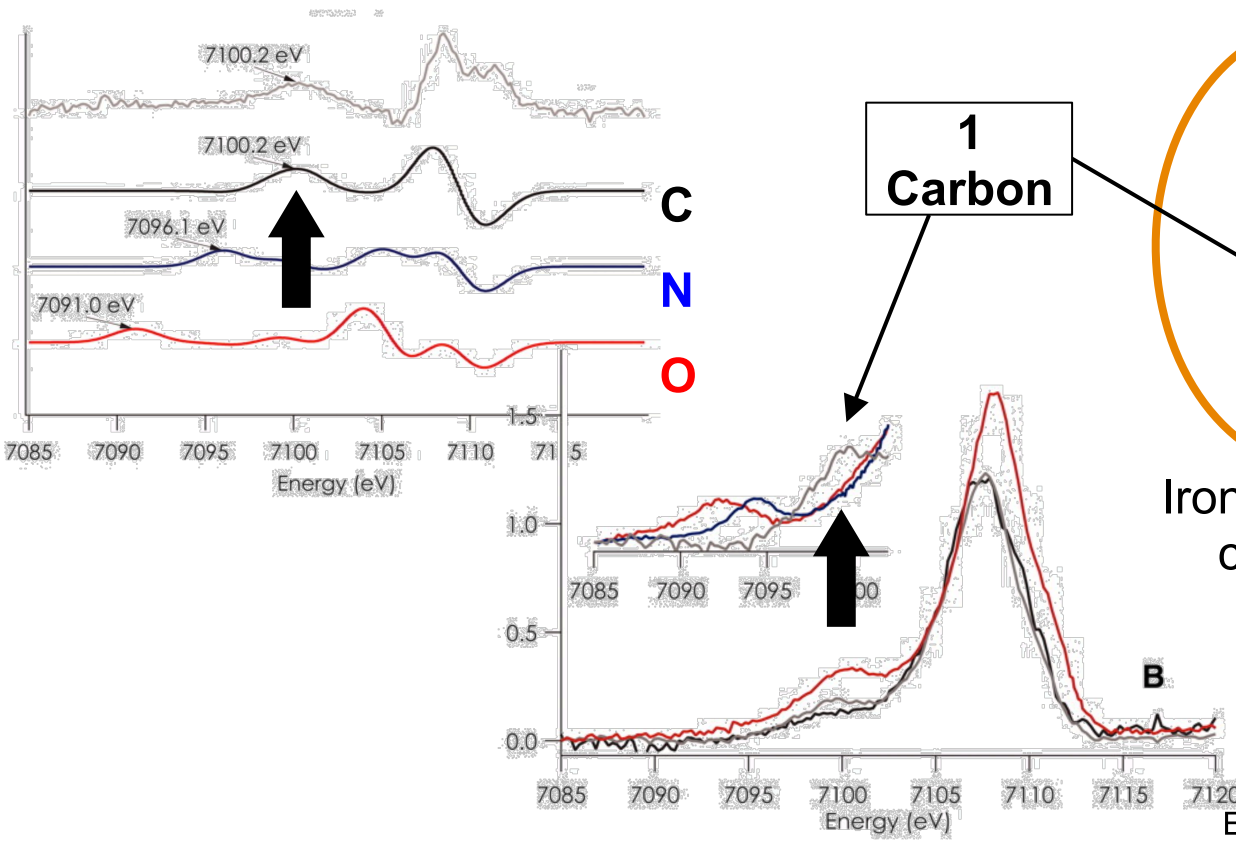


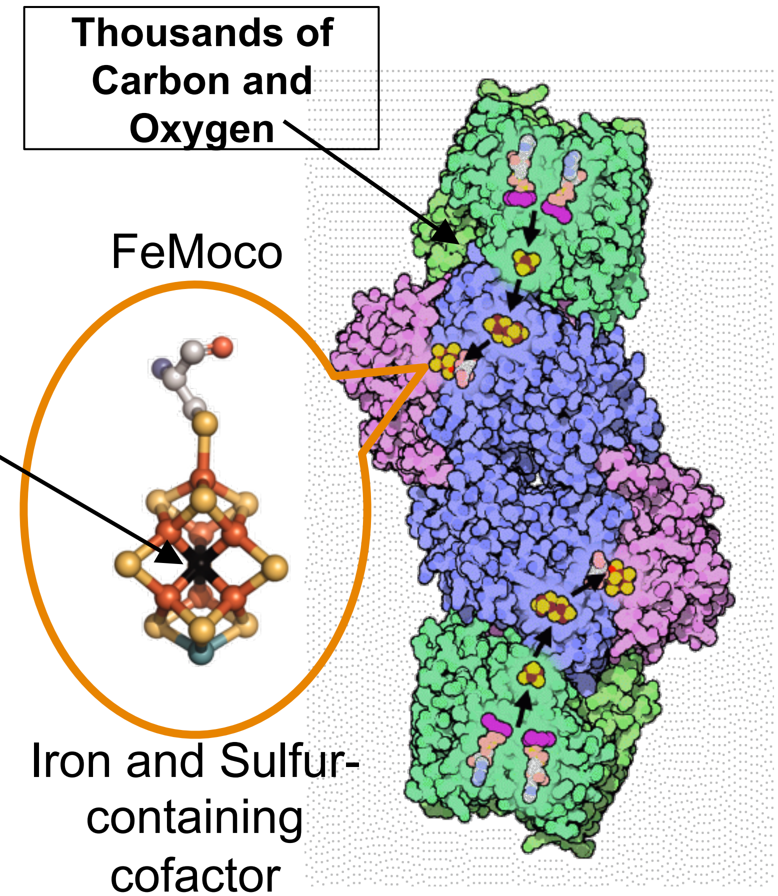
Valence X-ray Emission : Ligand Identification in Nitrogenase

SLAC

Nitrogenase is a complex enzyme that catalyzes the reduction of dinitrogen to ammonia (N-fixation)

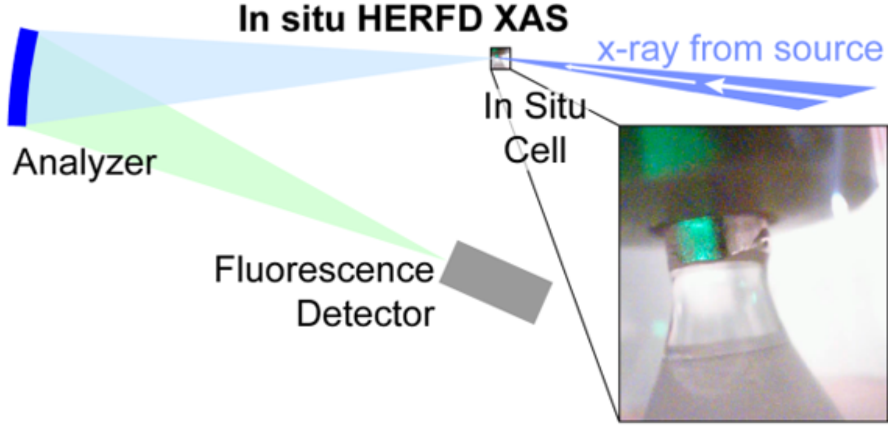
$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$





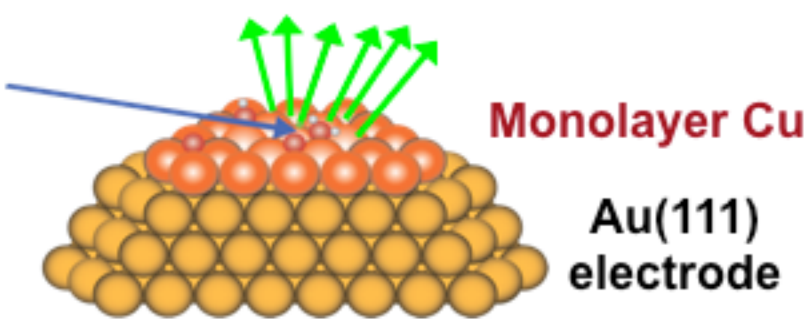
Einsle et al, Science, 297, 1696 (2002)
Lacaster et al, Science, 334, 974 (2011)

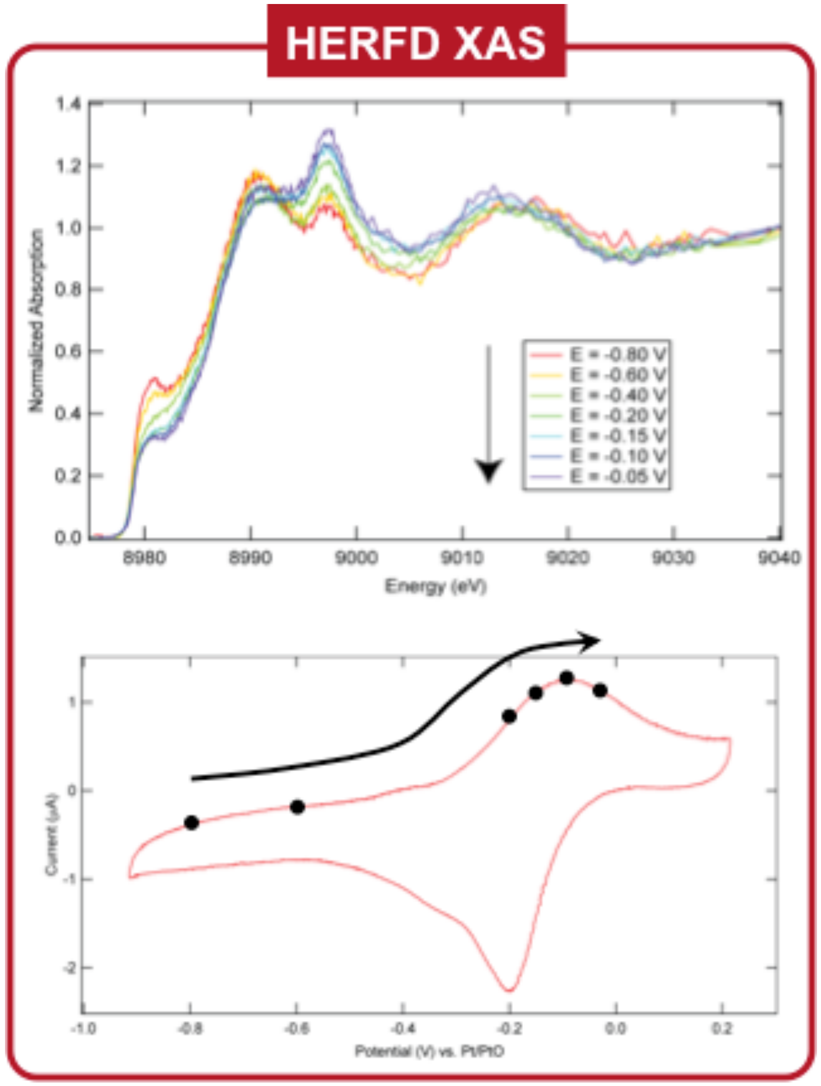
In-Situ Electro-catalysis – HERDF XAS



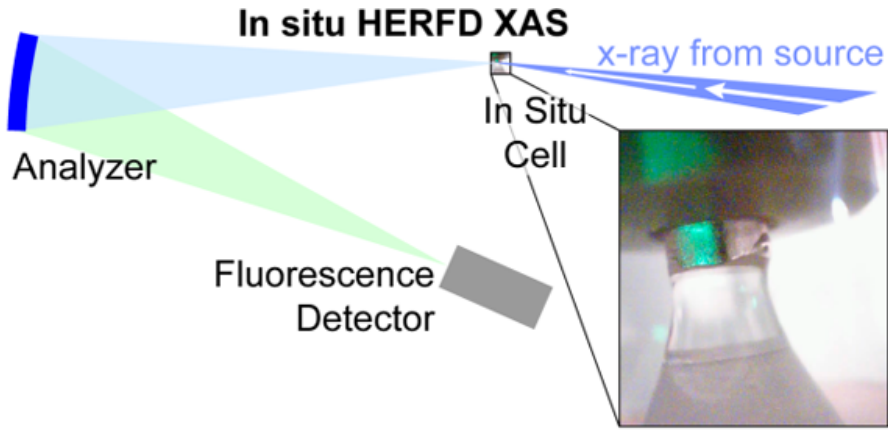
Solar-to-fuel conversion

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$





In-Situ Electro-catalysis – HERDF XAS

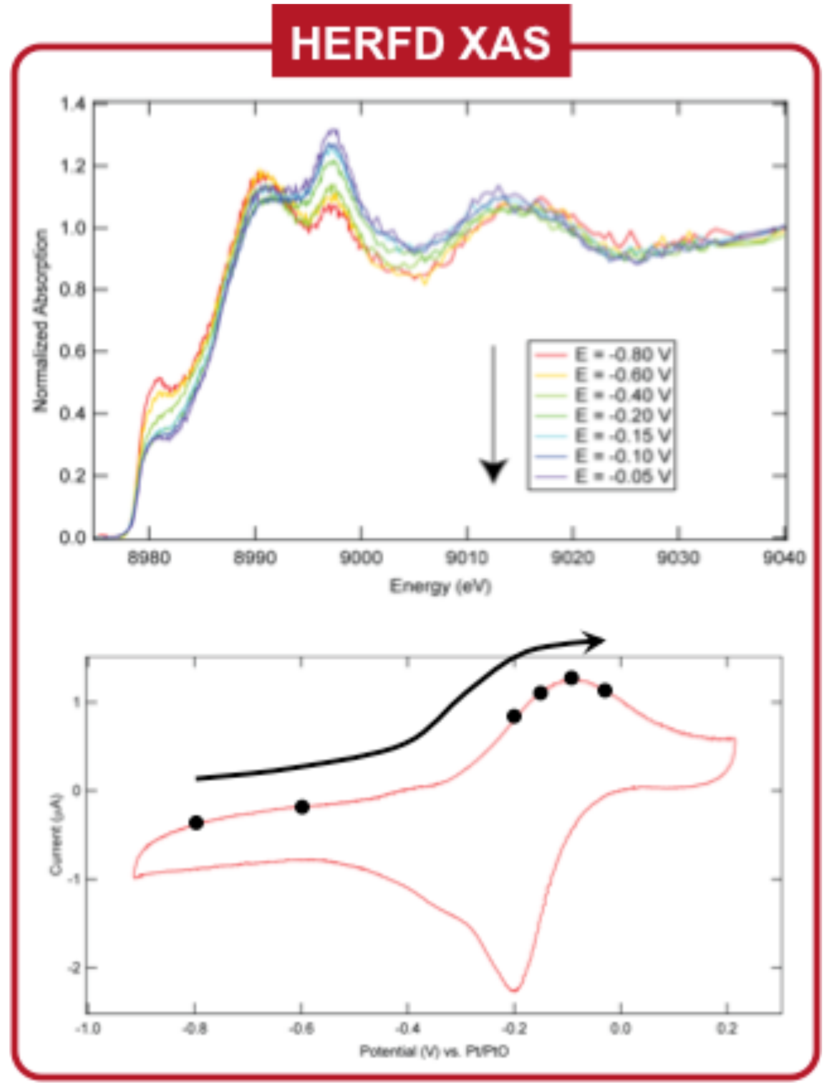


- Ultra-high sensitivity of XES detection for sub-/mono-layer surface coverage

- Catalyst on single crystal electrode:

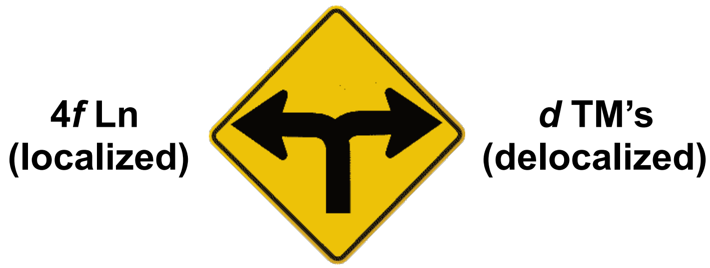
  catalytic activity vs. bimetallic interactions and strain

L. Merte et al, ACSCatal. 2, 2371 (2012)
D. Friebel et al, Phys.Chem.Chem.Phys. 15, 17460 (2013)
D. Friebel et al, J.Phys.Chem. C 118, 7954 (2014)



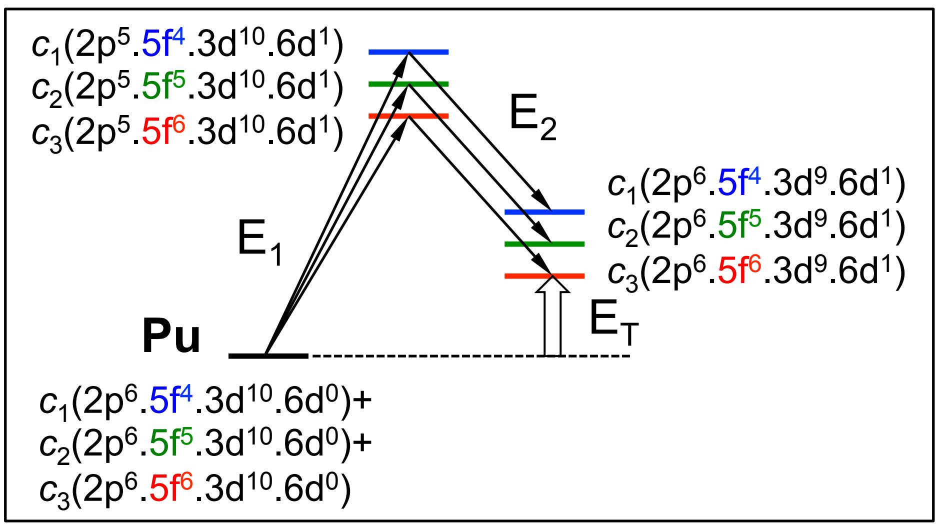
X-ray Spectroscopy at SLAC

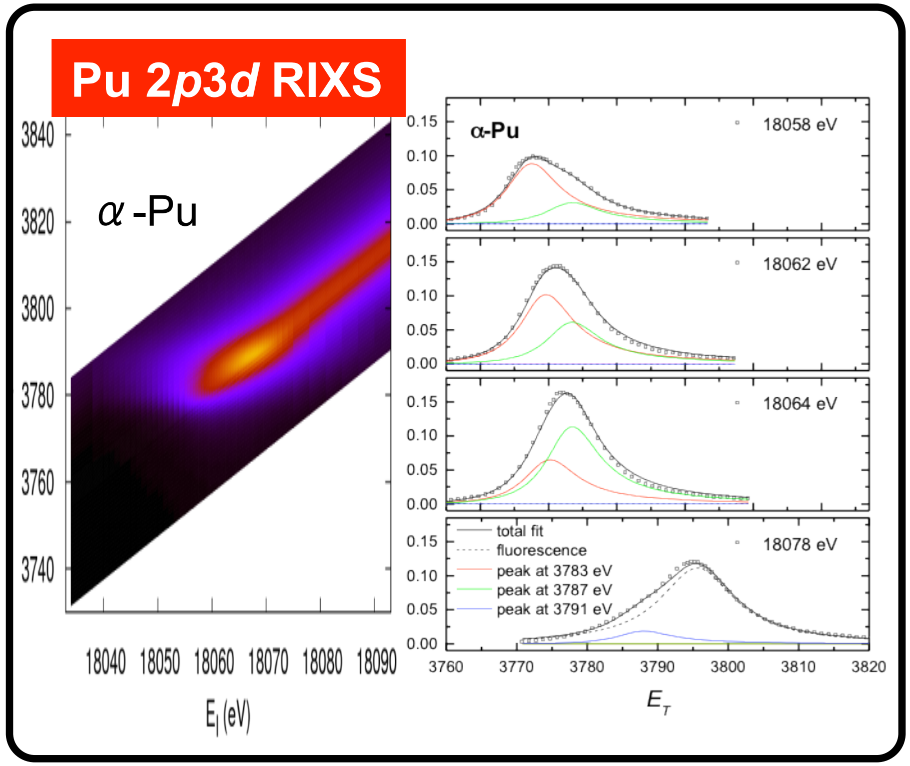
Highlight: Multi-configurational Nature of 5f Orbitals in Actinides



5*f*

U	**Np**	**Pu**





	n_f	f^4	f^5	f^6
δ -Pu	5.28	0.17	0.38	0.45
α -Pu	5.16	0.19	0.46	0.35

SSRL

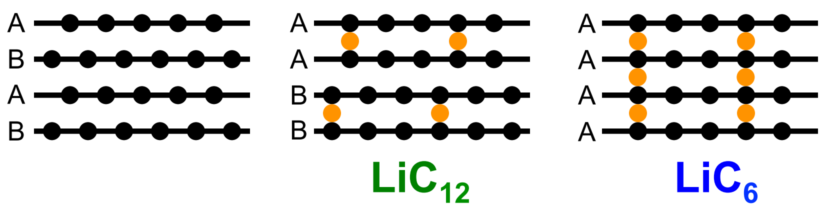
C. Booth, *et al.* PNAS, 109, 10205 (2012)

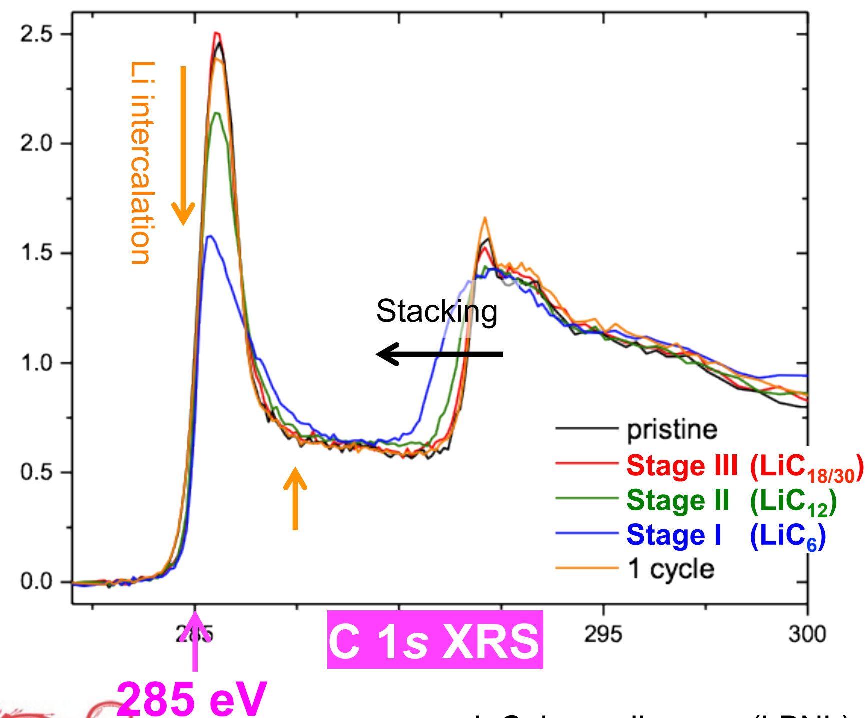
Lithium Ion Batteries – X-ray Raman Spectroscopy

SLAC

Anode

HOPG Lithiation



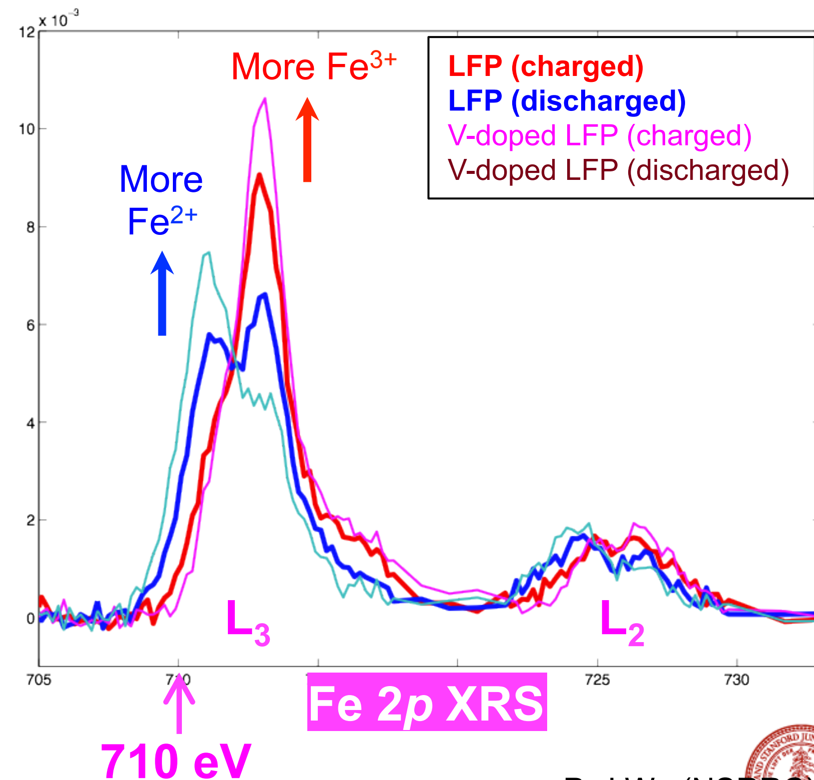


J. Cabana-Jimenez (LBNL)

Cathode

Battery capacity enhanced by dopant

$$LiFePO_4 \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} Li^+ + FePO_4$$



P.-J Wu (NSRRC)

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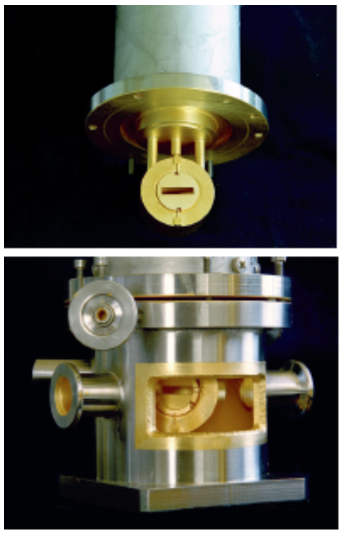
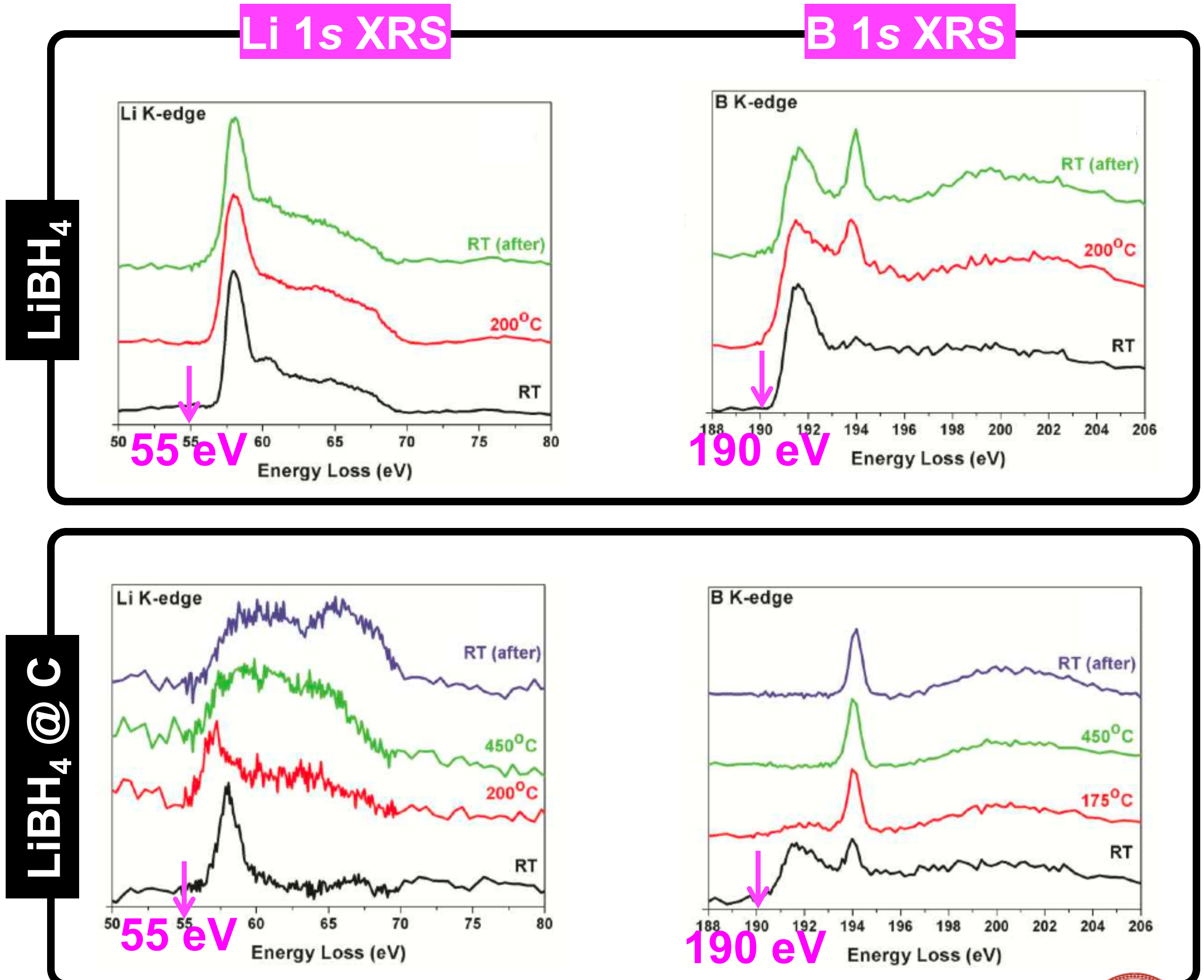
Hydrogen Storage Materials– X-ray Raman Spectroscopy

SLAC





- *In-situ*
- 5% H_2/He (1 bar)
- Kapton window

P. Miedema et al, Phys.Chem.Chem.Phys., 14, 5581 (2012)
P. Miedema et al, Phys.Chem.Chem.Phys., 16 , 22651 (2014)

SSRL

Time resolved studies – Need for Energy Dispersive X-ray Spectroscopy – Linac Coherent Light Source (LCLS)

	Current performance
Photon energy range	**280 eV to 10 keV**
Pulse length	**< 5 - 200 fs**
Pulse energy	**up to 5 mJ (~10^{12} ph/pulse @ 10 keV)**

LCLS operates at 120 Hz

Difficulties for scanning instruments since:

- New sample is required for each shot
- XFEL intensity jitters a lot from shot-to-shot

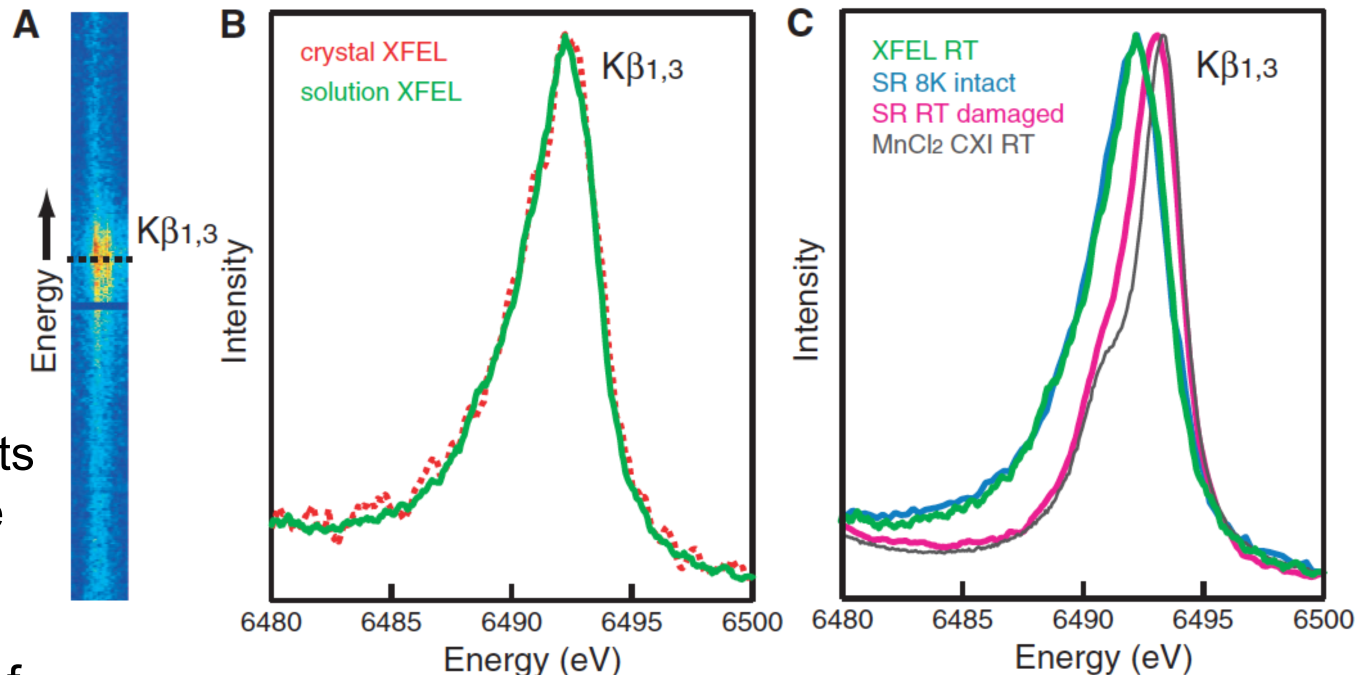
X-ray Emission at XFEL's - "probe-before-destroy"

SLAC

XES at XFEL

- XES is an Ultrafast probe
- Can probe matter before destroyed by FEL pulses
- Enables measurements on extremely sensitive systems to radiation damage on room Temperature instead of cryogenic conditions

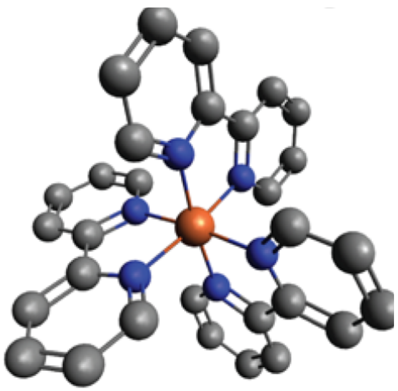
Mn-center at Photosystem II



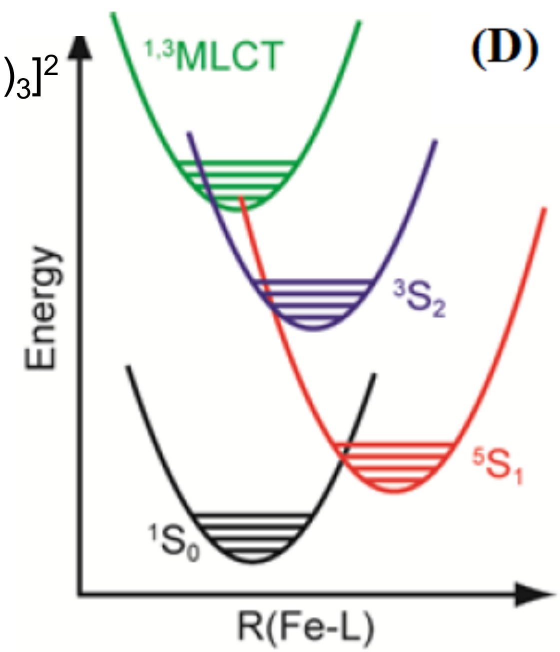
PNAS 109, 19103 (2012)
Science 340, 493 (2013)

SSRL

Ultrafast Spin Dynamics in Iron Coordination complexes



$[Fe(2,2'\text{-bipyridine})_3]^2$



Scientific Case:

- Spin dynamics on 3d metal complexes upon visible light MLCT excitation
- Elucidation and manipulation of the ultrafast relaxation mechanisms for the excited state
- Solar energy applications upon long lived charge transfer states

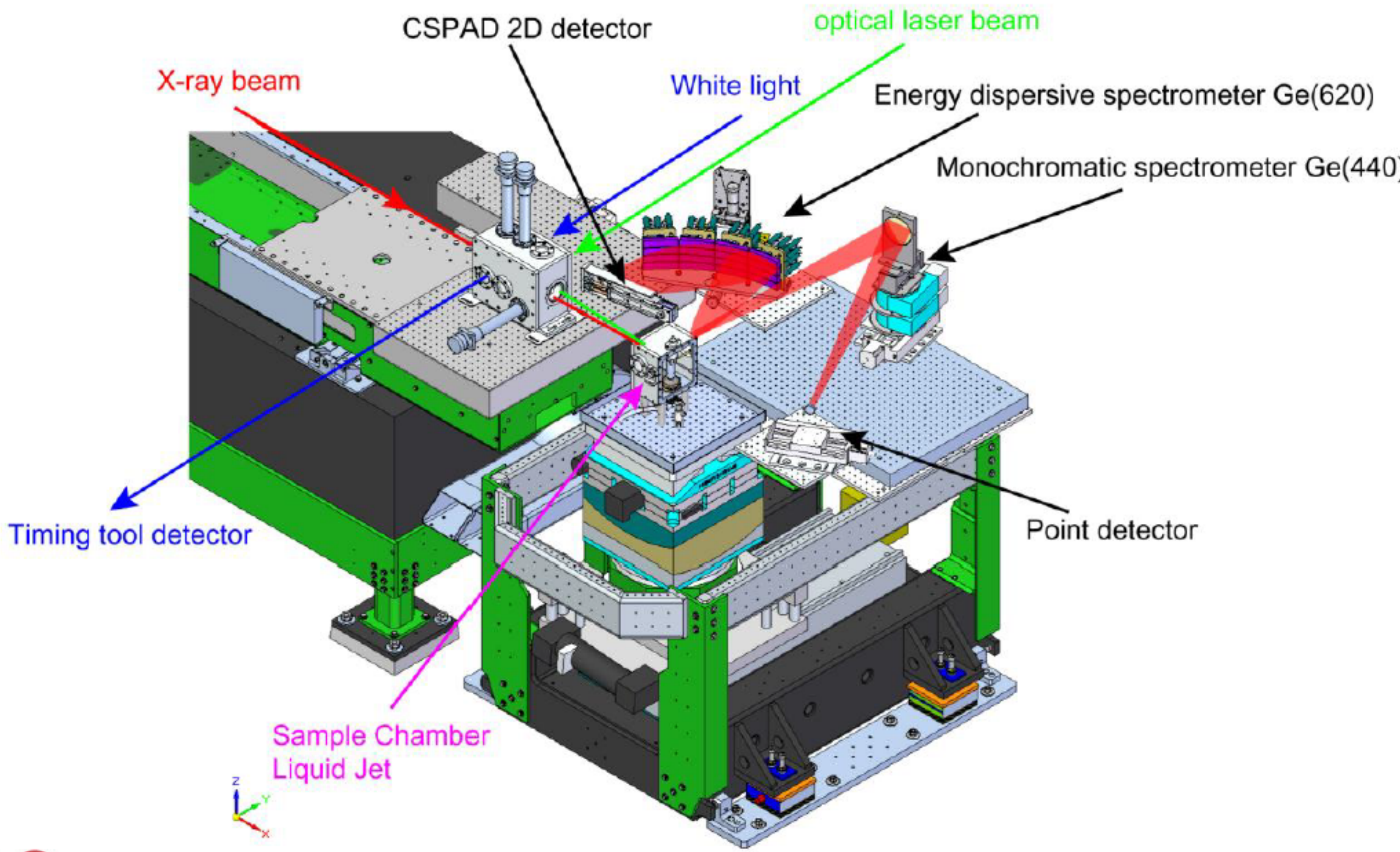
Methodology:

Femtosecond optical laser-pump / Kb XES probe at LCLS (150fs resolution)

Reference Kb XES at SSRL from various candidates intermediate states

Nature 509, 345 (2014)

XPP end-station @ LCLS: configuration with XES spectrometers

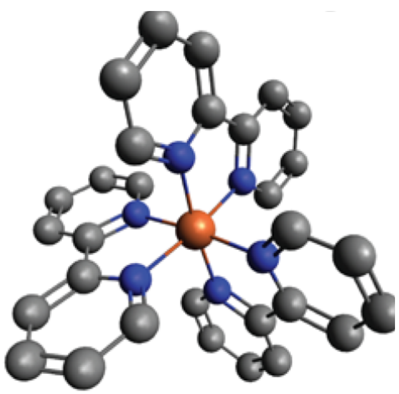


Nature 509, 345 (2014)

Ultrafast Spin Dynamics – XES at SSRL & LCLS

- Photoinduced metal-to-ligand charge transfer **MLCT**-excitations

- Ultrafast spin crossover dynamics elucidate with **Kβ XES spectroscopy**



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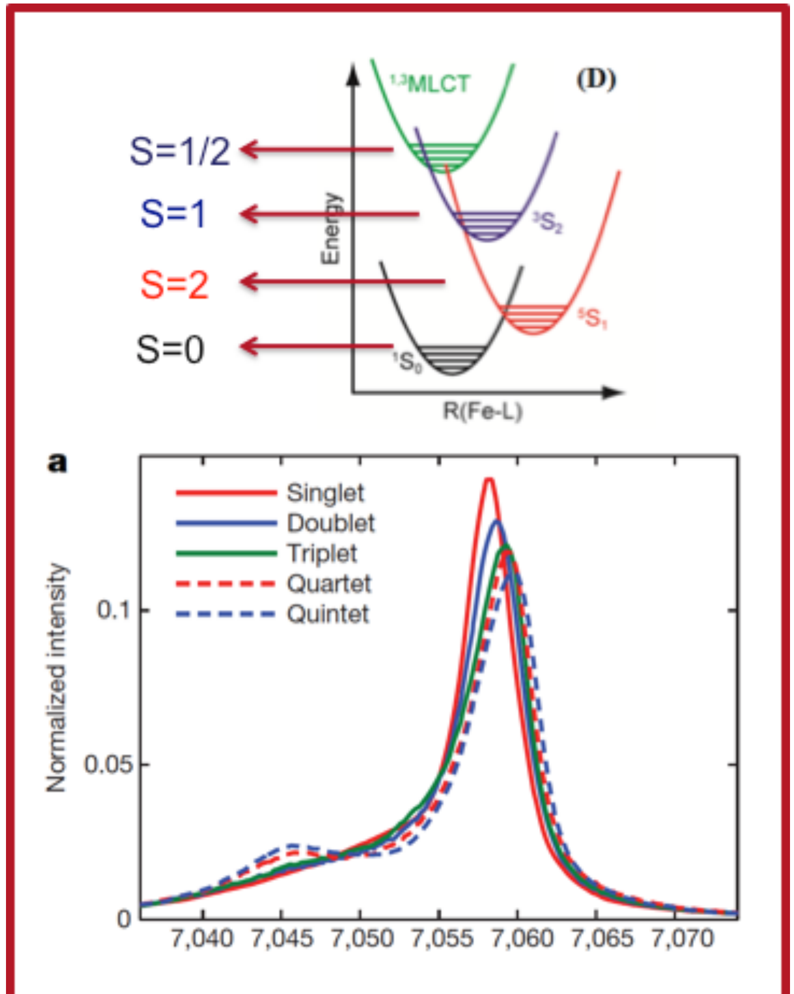
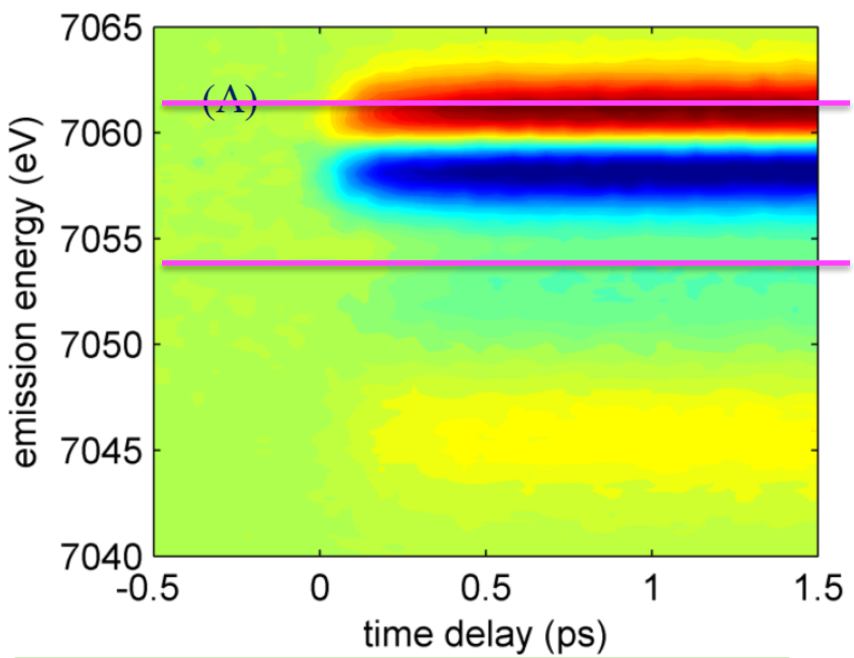
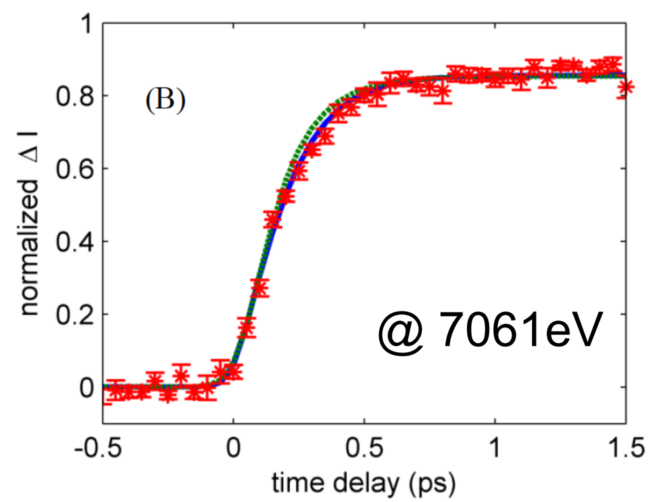
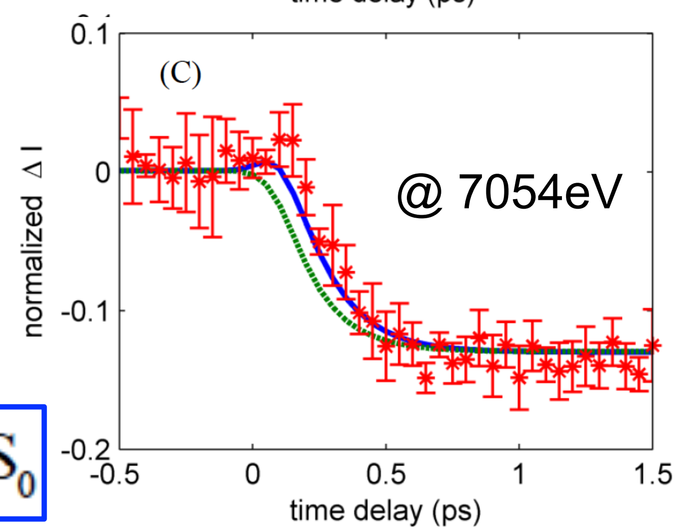


Time dependent optically-induced XES signal

$[Fe(2,2'\text{-bipyridine})_3]^{2+}$ (o) water







$$^{1,3}MLCT \xrightarrow{k_1} {}^5S_1 \xrightarrow{k_3} {}^1S_0$$

$$^{1,3}MLCT \xrightarrow{k_1} {}^3S_2 \xrightarrow{k_2} {}^5S_1 \xrightarrow{k_3} {}^1S_0$$

150±50fs 70±30fs

Nature 509, 345 (2014)

Summary

- High resolution x-ray spectroscopies are powerful tools for electronic structure characterization studies

- State-of-the-art instruments coupled with 3^{rd} generation beamlines or XFELs

- Multicrystal spectrometers provide high throughput and high energy resolution

- Besides direct XES and high resolution XAS, the X-ray Raman can provide soft XAS equivalent information using hard x-rays

- Hard x-rays provide *in-situ* capabilities

Summary

Thank you !

U.S. DEPARTMENT OF ENERGY
Office of Science

SLAC NATIONAL ACCELERATOR LABORATORY

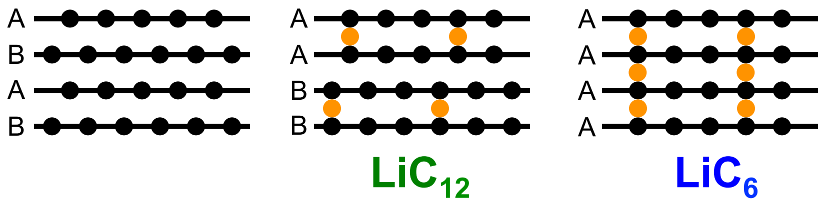
X-ray Spectroscopy at SLAC

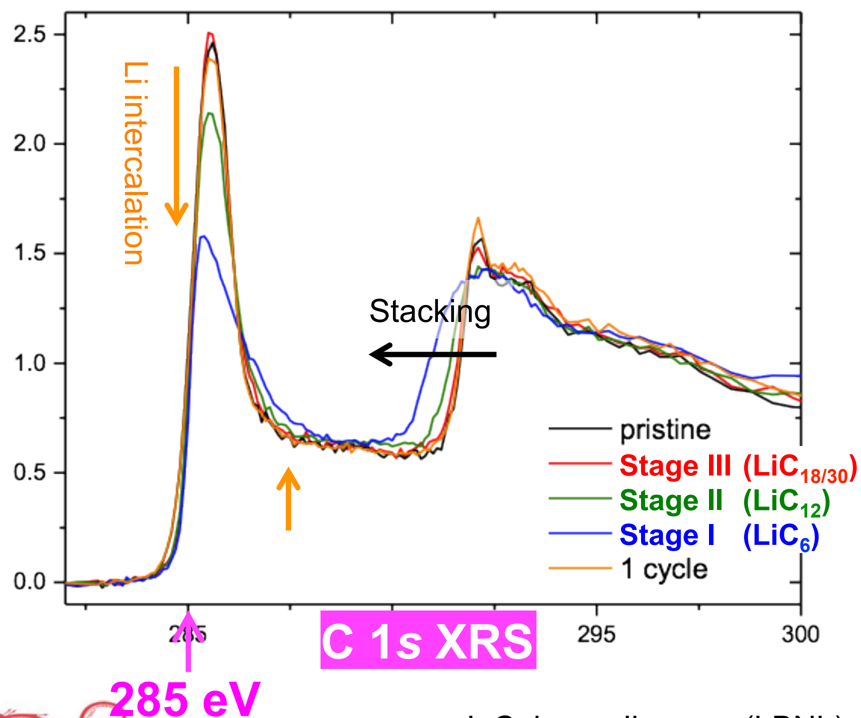
Highlight: Lithium Ion Batteries – X-ray Raman Spectroscopy

SLAC

Anode

HOPG Lithiation





J. Cabana-Jimenez (LBNL)

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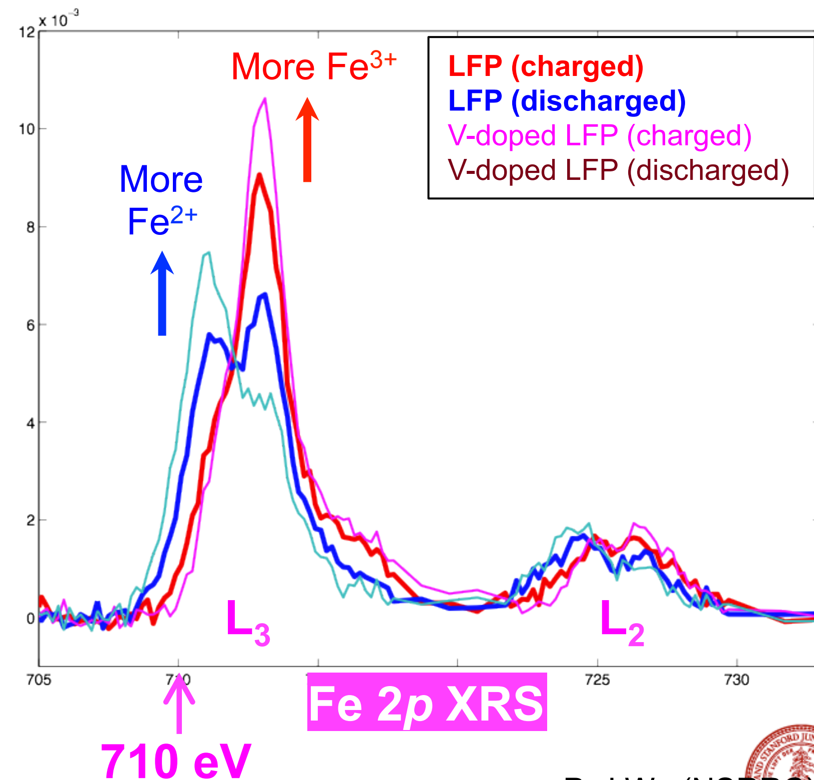
Battery capacity enhanced by dopant

$$LiFePO_4 \rightleftharpoons Li^+ + FePO_4$$

charging / discharging



P.-J Wu (NSRRC)

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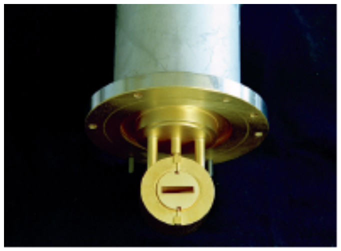
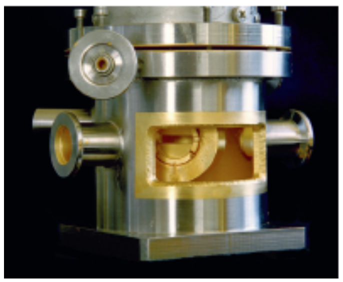
X-ray Spectroscopy at SLAC

Highlight: Hydrogen Storage Materials– X-ray Raman Spectroscopy

SLAC





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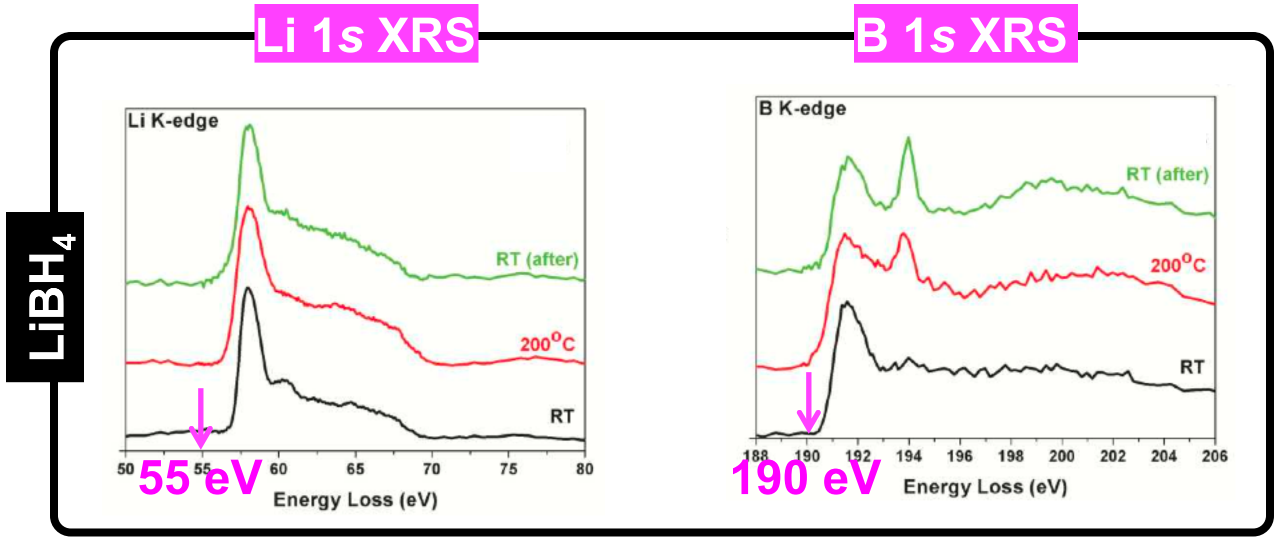

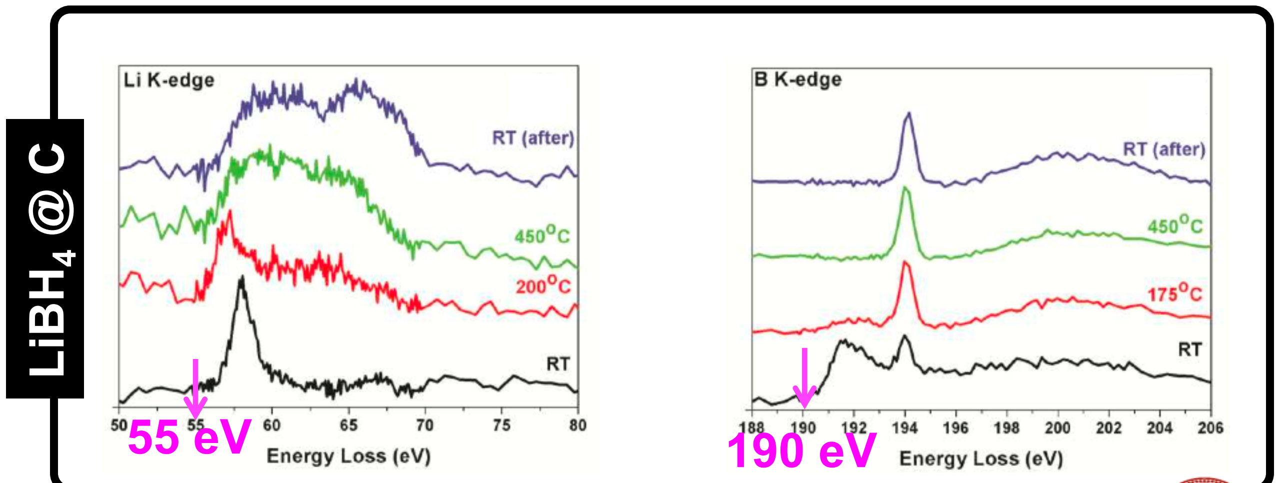

P. Miedema et al, Phys.Chem.Chem.Phys., 14, 5581 (2012)
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SSRL

X-ray Spectroscopy at SLAC

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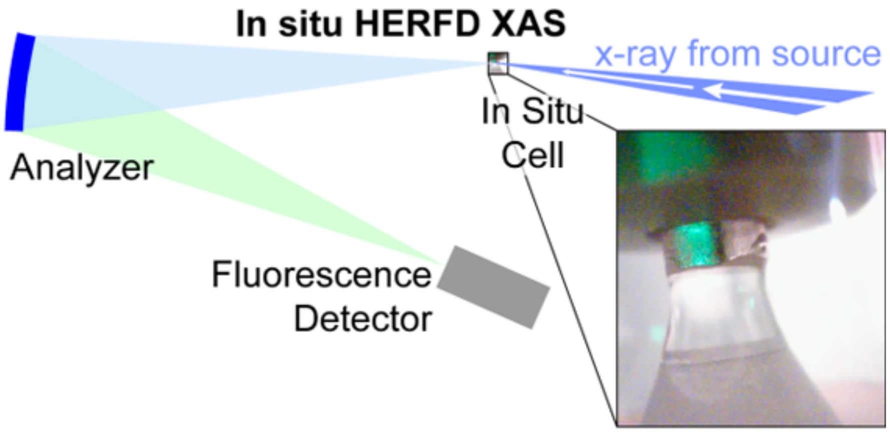
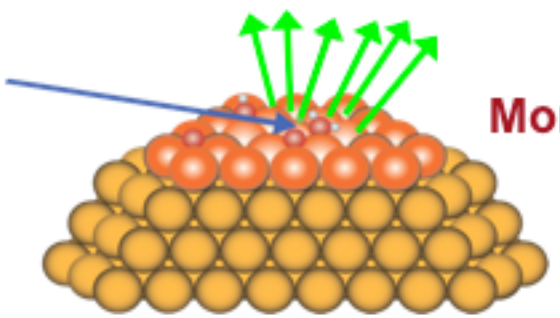
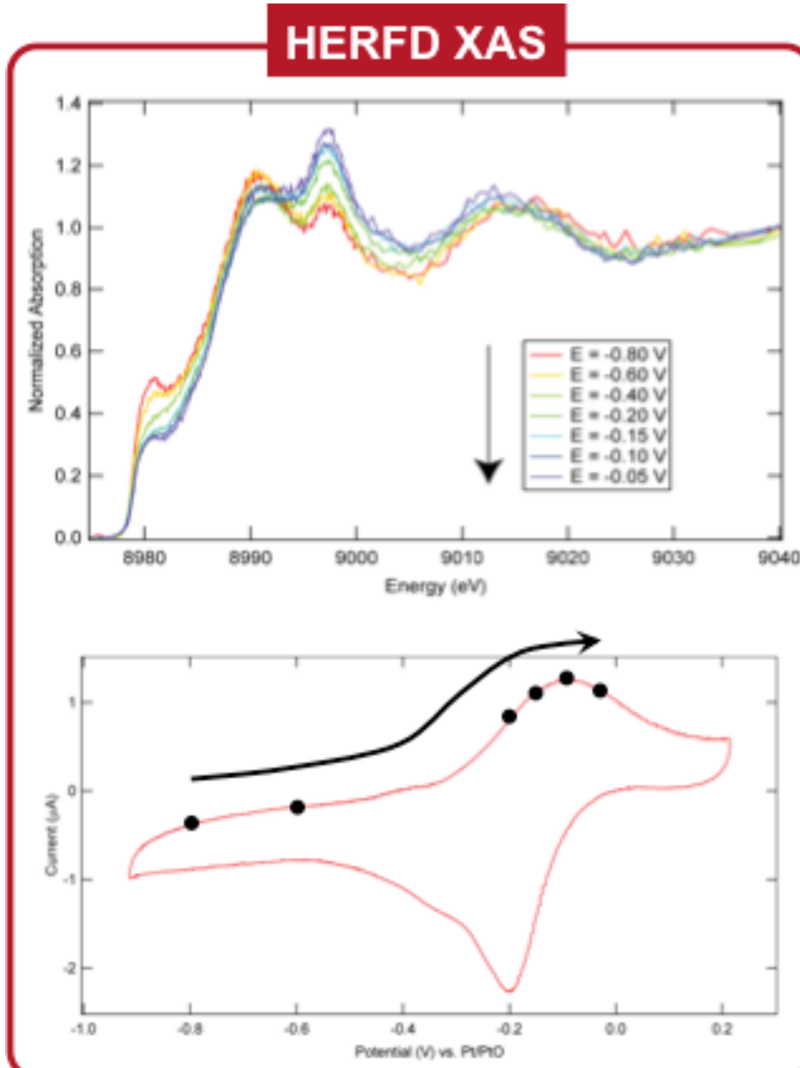


Solar-to-fuel conversion

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$

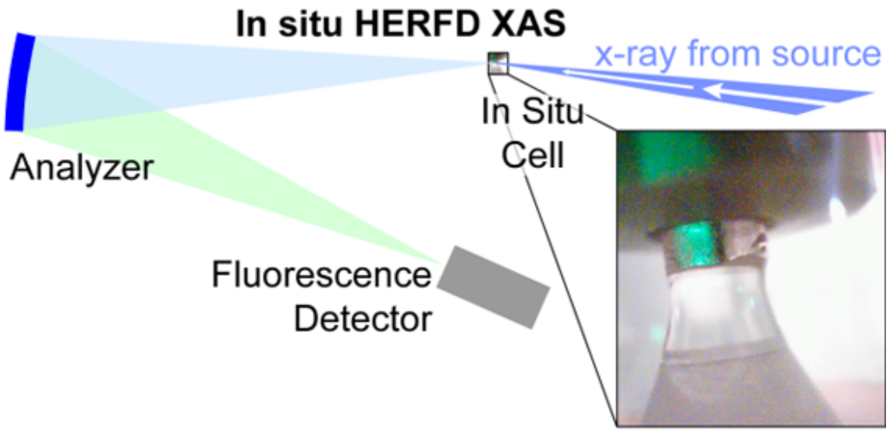




X-ray Spectroscopy at SLAC

Highlight: *In-Situ* Electro-catalysis – HERDF XAS

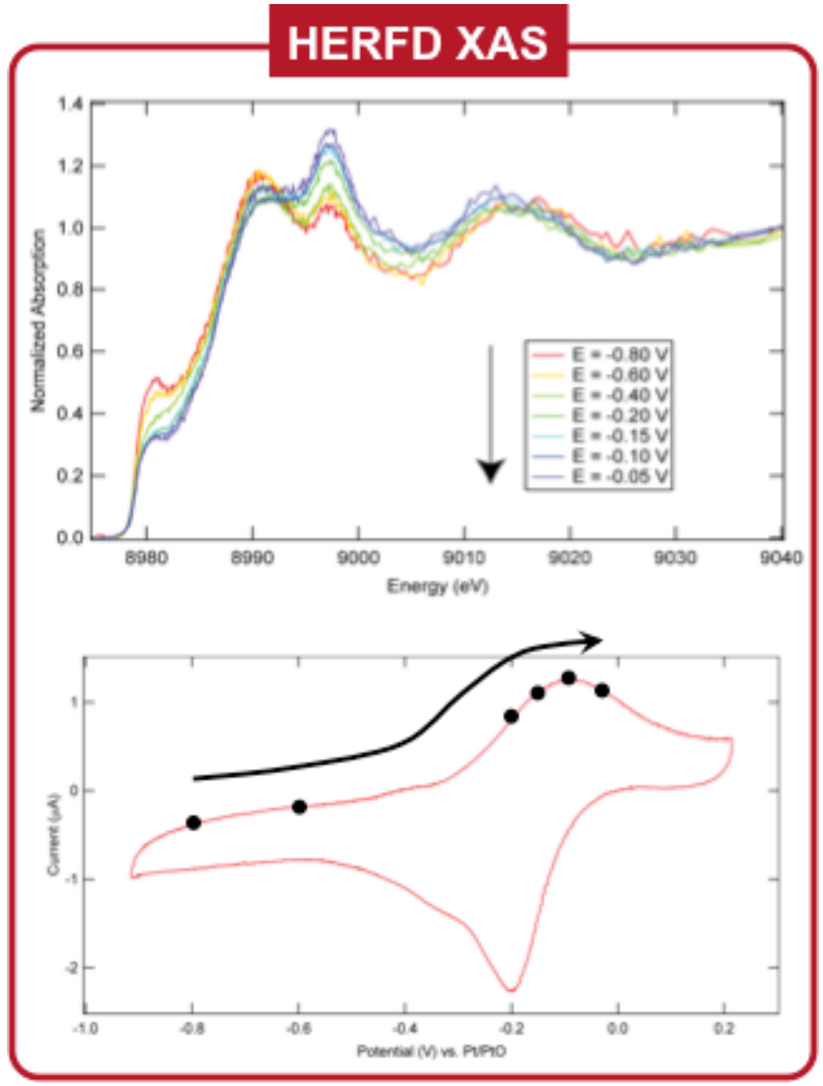
SLAC



- Ultra-high sensitivity of XES detection for sub-/mono-layer surface coverage

- Catalyst on single crystal electrode:

  catalytic activity vs. bimetallic interactions and strain



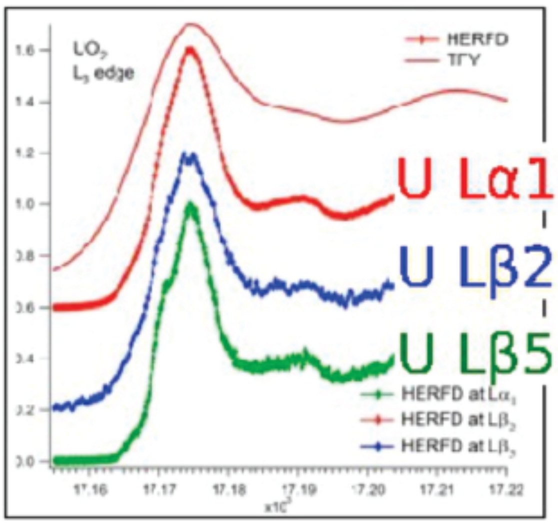
L. Merte et al, ACSCatal. 2, 2371 (2012)
D. Friebel et al, Phys.Chem.Chem.Phys. 15, 17460 (2013)
D. Friebel et al, J.Phys.Chem. C 118, 7954 (2014)

SSRL

High energy-resolution XAS – Fluorescence mode

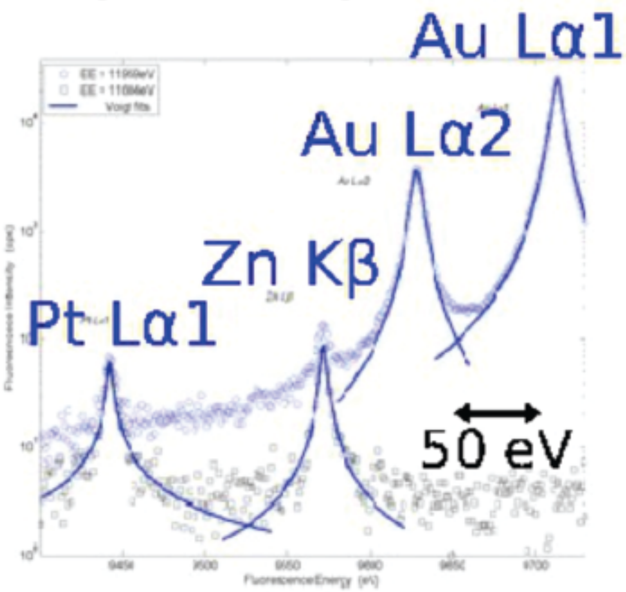
SLAC

Edge Sharpening



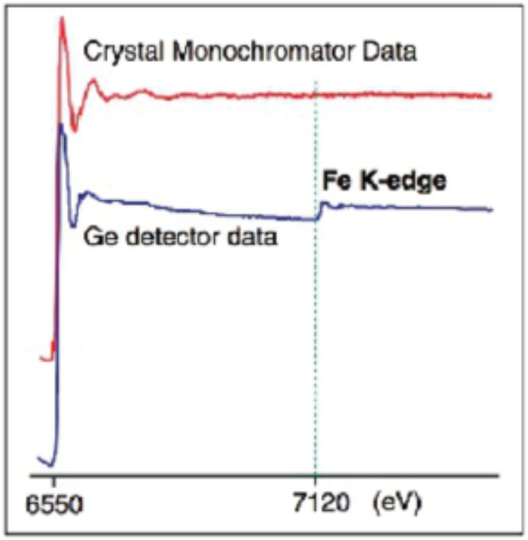
K. Kvashnina et al.

Signal/Background ratio



M. Sikora et al.

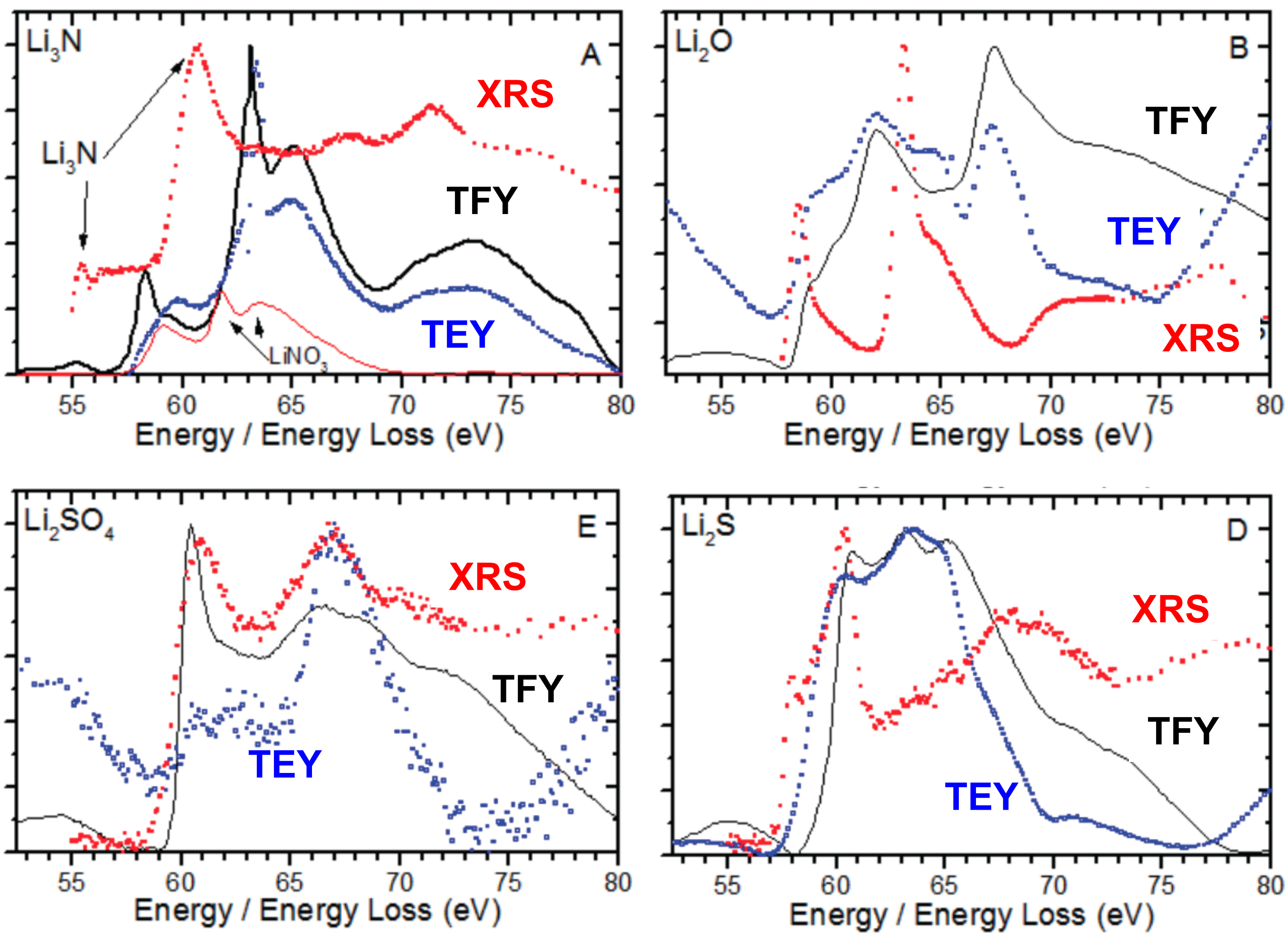
Range extended EXAFS



P. Glatzel et al.

SSRL

Lithium Pure Compounds:
Surface techniques (TEY, TFY) vs X-ray Raman (@ ~1.2$Å^{-1}$)

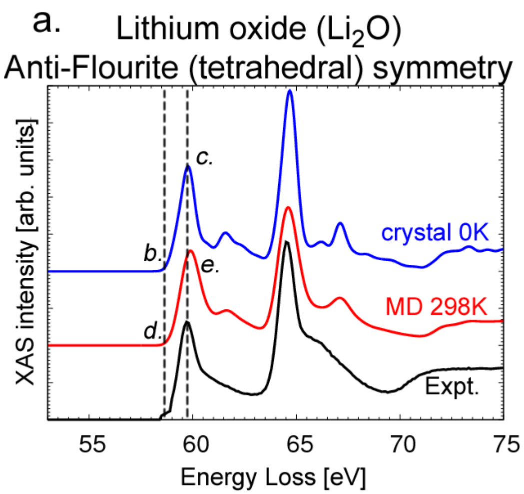


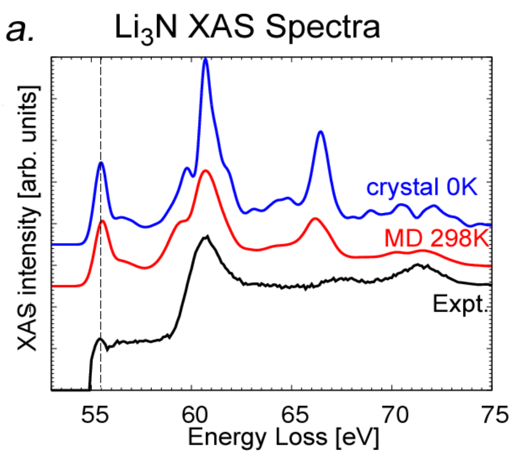
Significant differences among surface sensitive and bulk techniques!

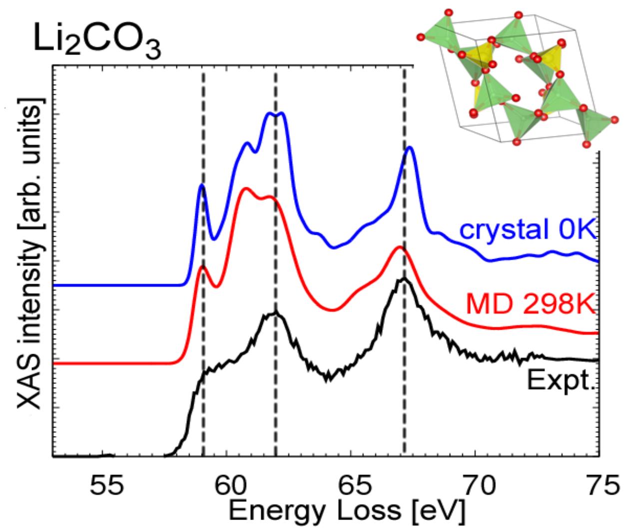
Contaminated Surfaces

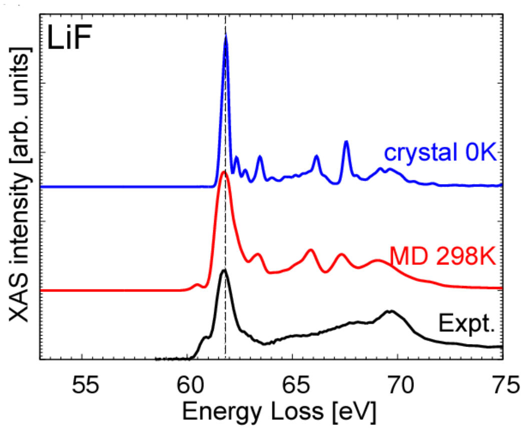
E. McDermott, A. Moewes, T. A. Pascal, D. Prendergast, J. Cabana, U. Bosenberg, et al

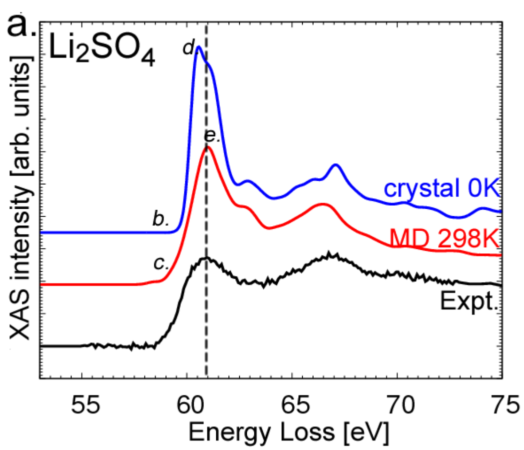
Li 1s XRS from model compounds + eXcited-state-Core-Hole (XCH) approach











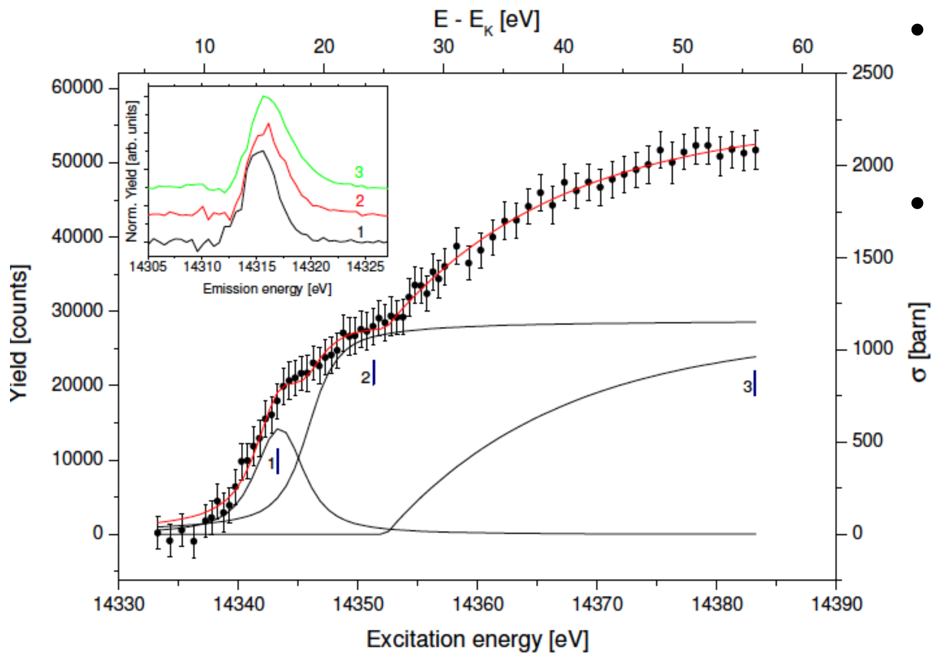
ab-initio theoretical approach

- Constrained *DFT (plane-waves)*
- XCH approach
- Molecular Dynamics Sampling

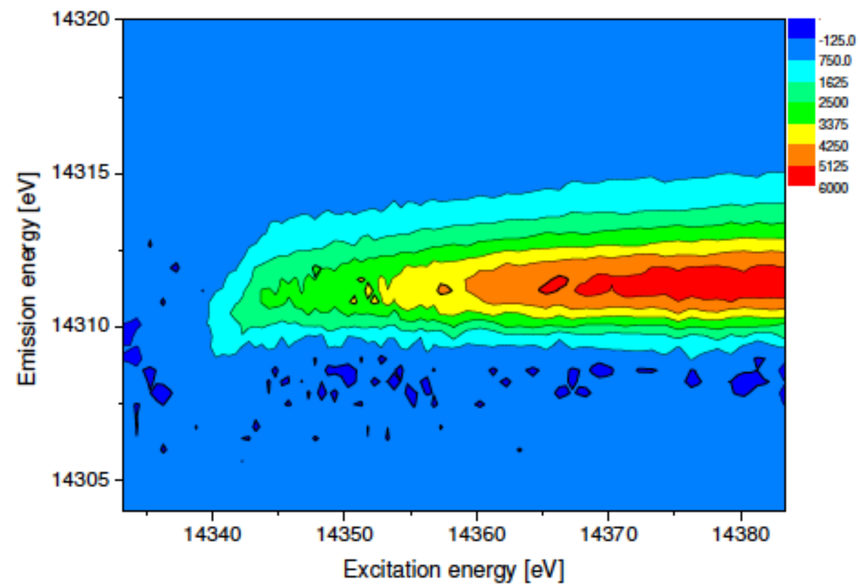
Great **Agreement** with XRS Data

J. Chem. Phys. 140 , 034107 (2014)

Two-electron photo-excitations in Kr - RIXS

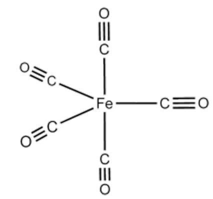


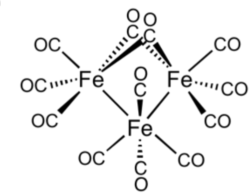
- *Kr* Gas
- High Resolution RIXS ➔ **isolated** [1*s*4*p*] and [1*s*3*d*] double excitations
- Very good agreement with theory



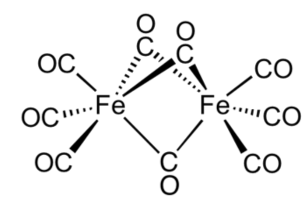
Project Description: Approach

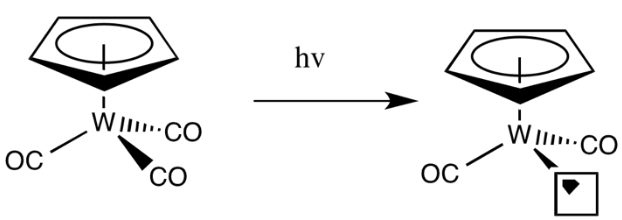
- Metal Carbonyls and derivatives in catalysis
  - *hydroformylation* (alkene to aldehyde)
  - hydrocarboxylation (alkyne to carboxylate)
  - C-C formation (acetylene to cycloalkne)

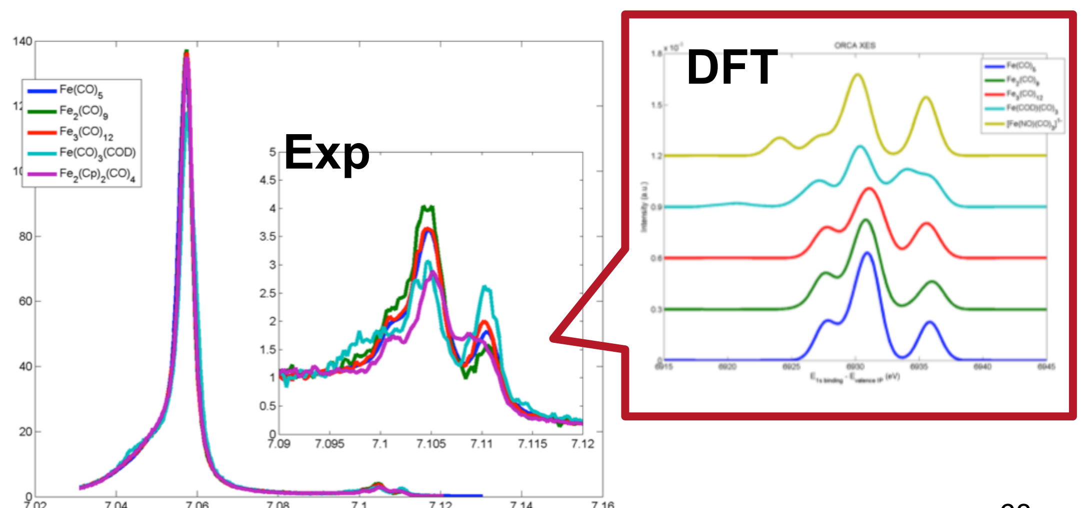




- Reactivity of Metal Carbonyls
  - CO substitution (e.g. NO, CN, CS, CNR)
  - CO *activation* (as an electrophile)







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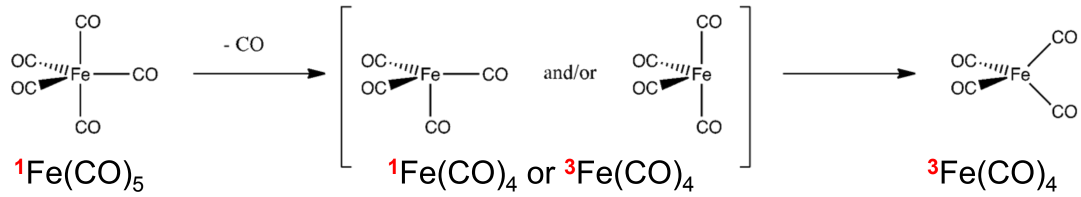

- **$Fe(CO)_5$ Photolysis**
  - Spin dynamics (LCLS)
    - understanding the energy surface of excited state to steer the reaction with helps from theory
  - CO replacement by solvent, substrate (SSRL BL15-2)
    - investigating factors (ligands, solvation) which control the chemical reactivity and kinetics