MEX high-resolution spectrometers

Jeremy Wykes

High resolution?

- Energy resolution of the order of core-hole lifetime broadening

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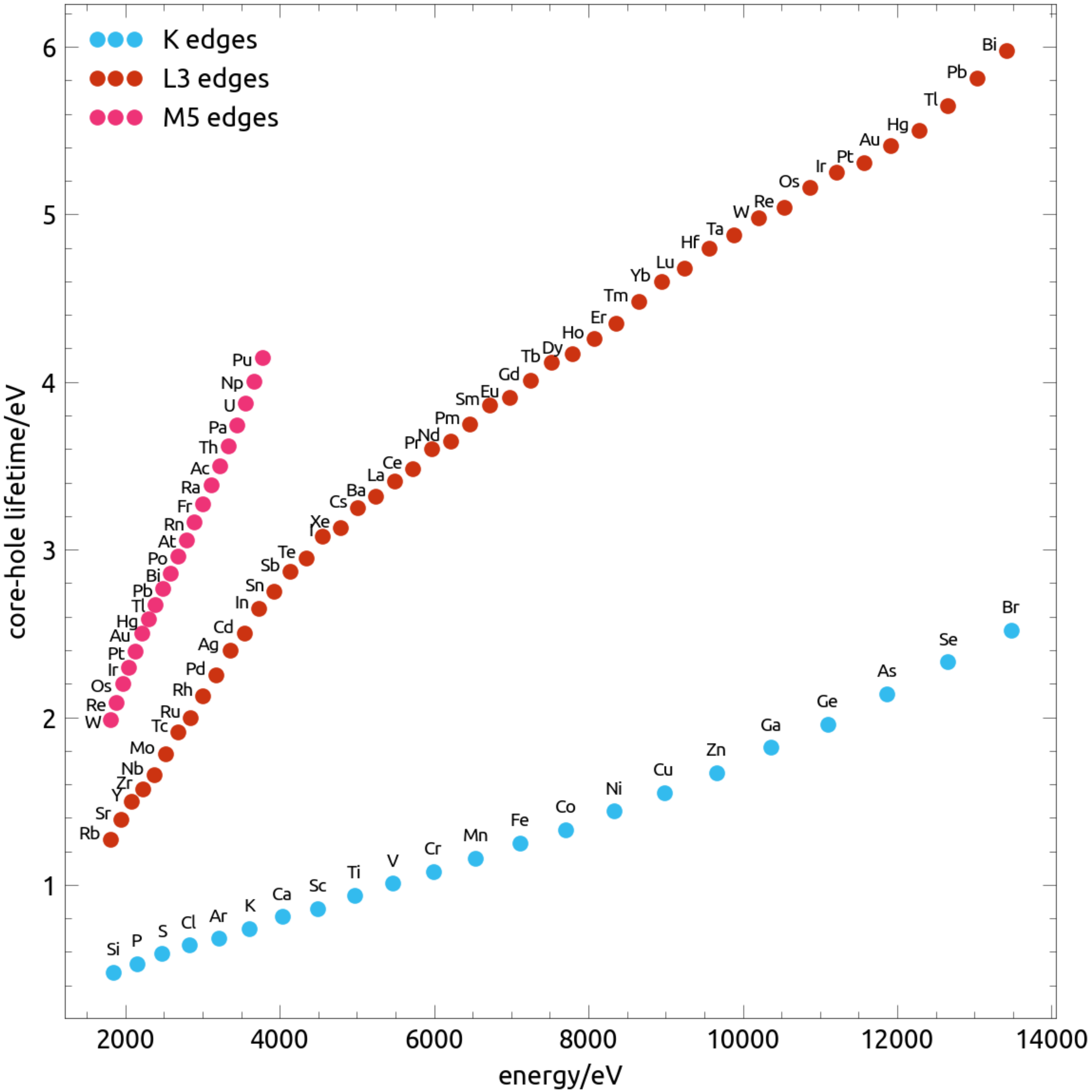
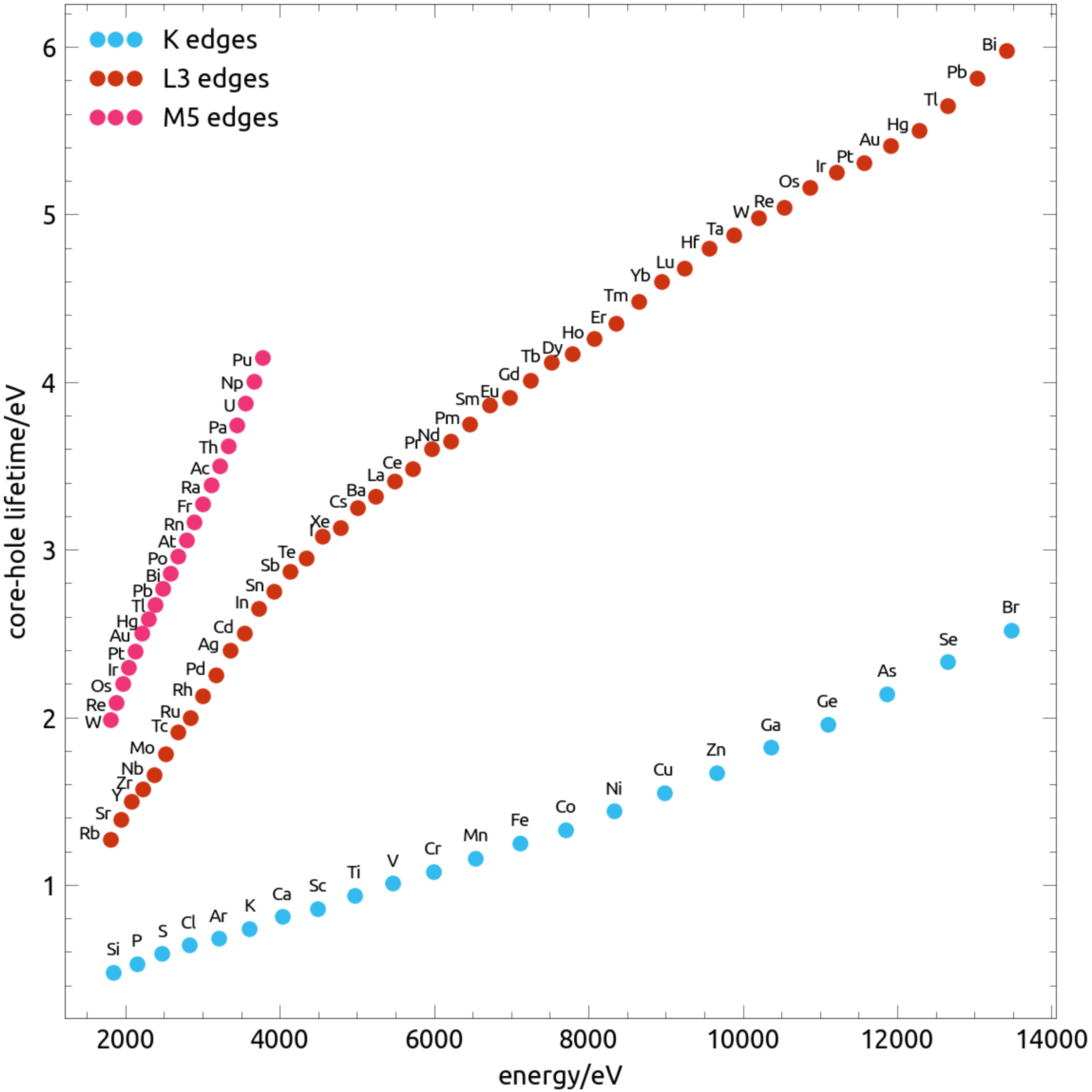


High resolution?

- Energy resolution of the order of core-hole lifetime broadening
- EDS detector
  - ΔE ≈ 125 → 250 eV



High resolution?

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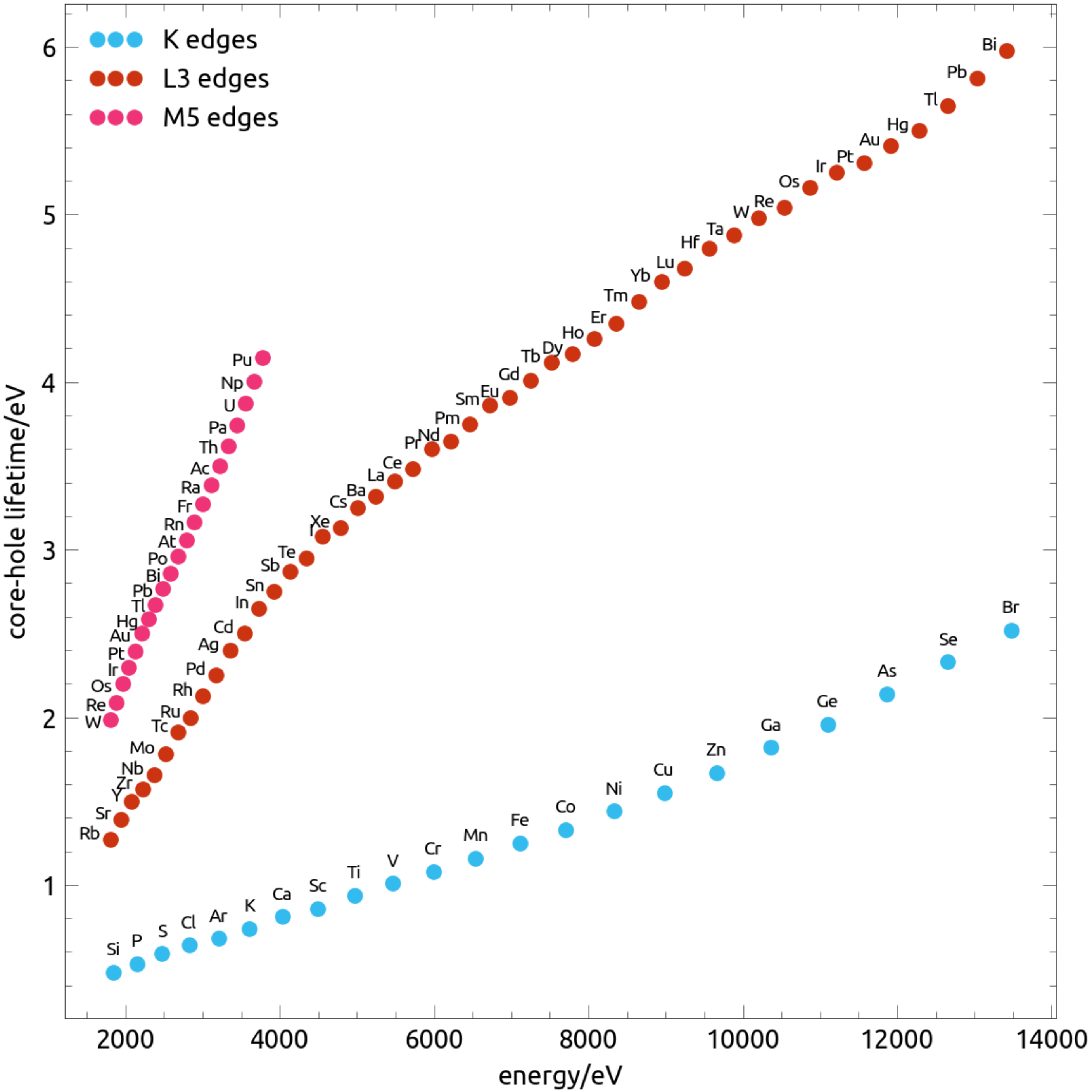
  - ΔE ≈ 125 → 250 eV
- How to do better?



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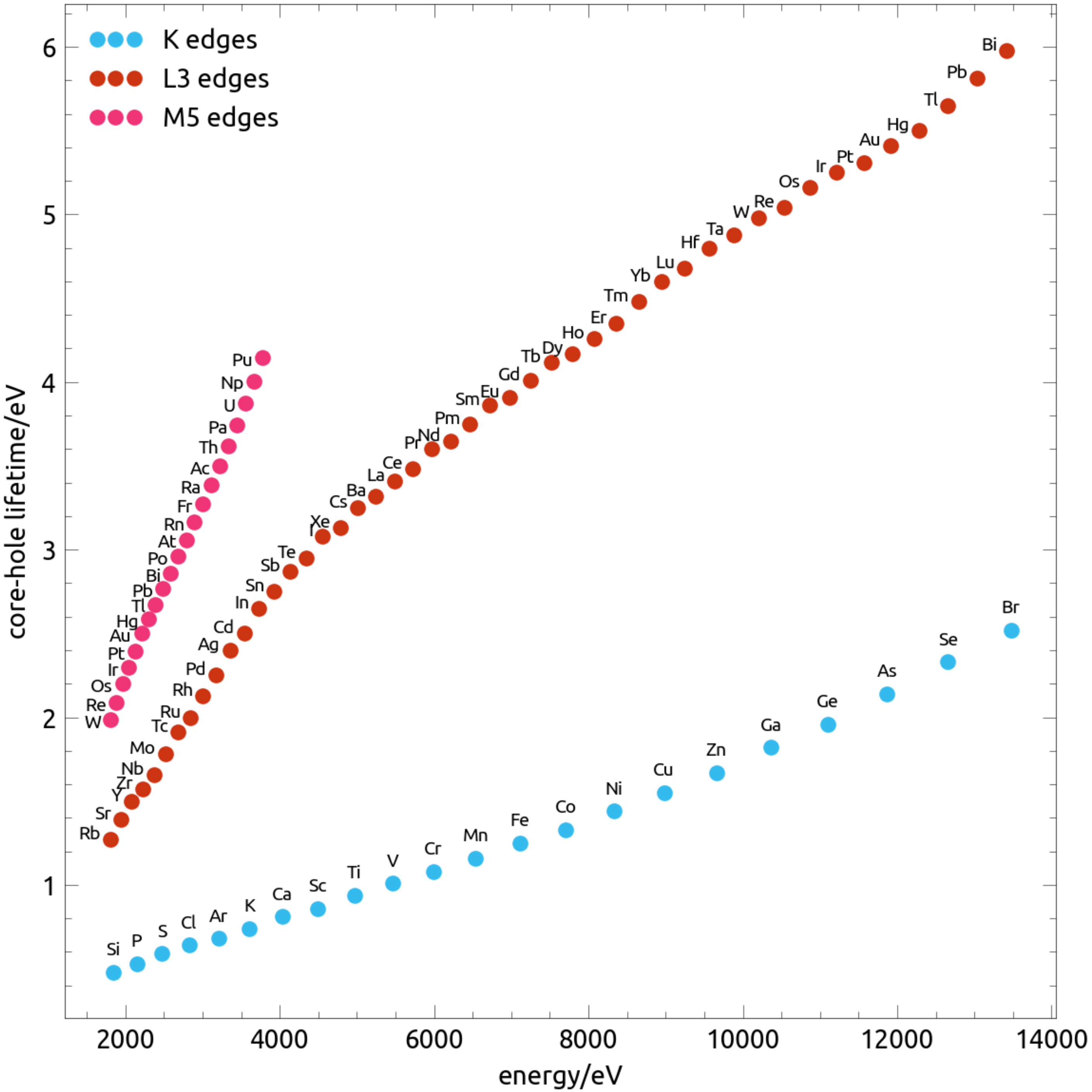
  - Bragg diffraction from perfect crystals
  - ΔE ≈ eV



High resolution?

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  - ΔE ≈ 125 → 250 eV
- How to do better?
  - Bragg diffraction from perfect crystals
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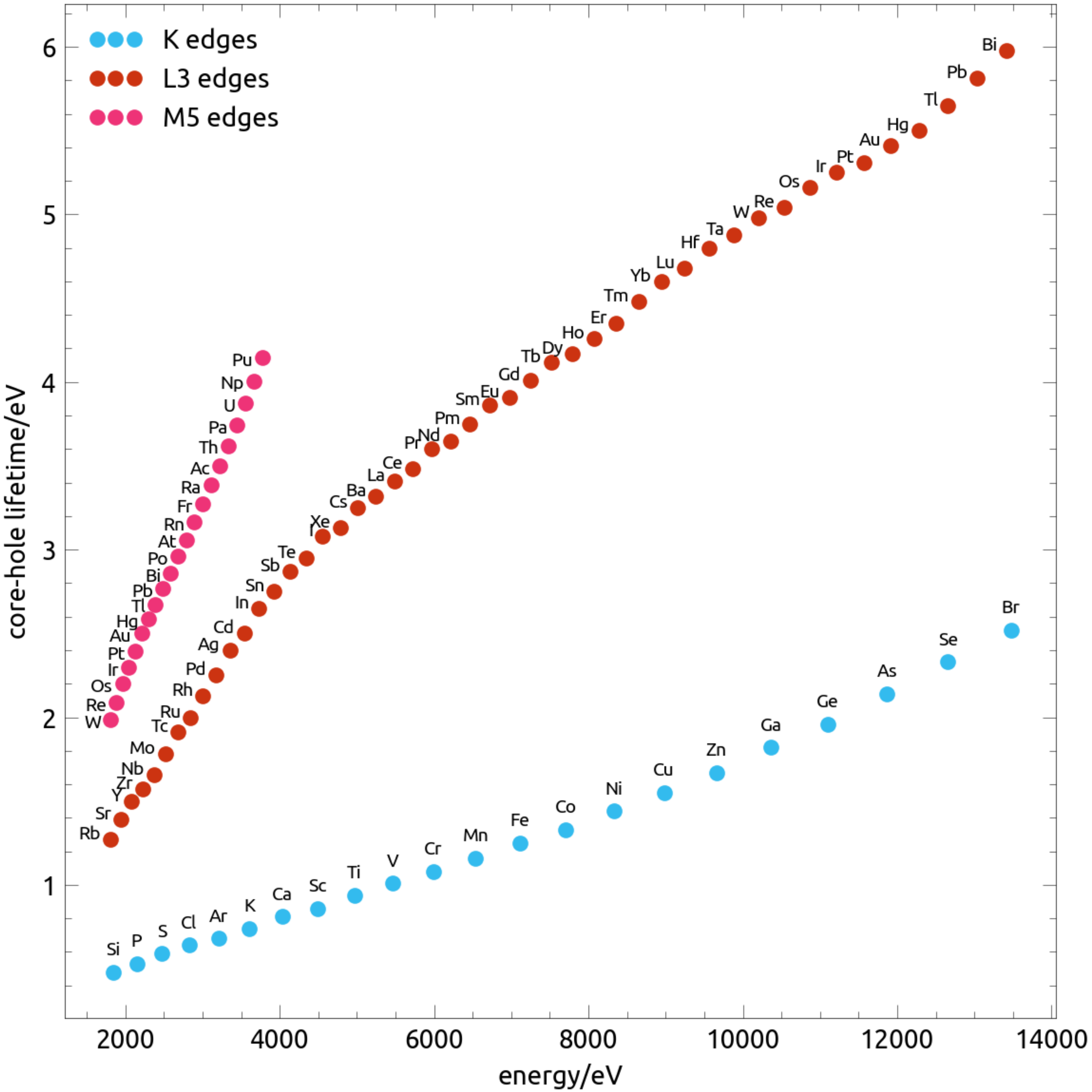
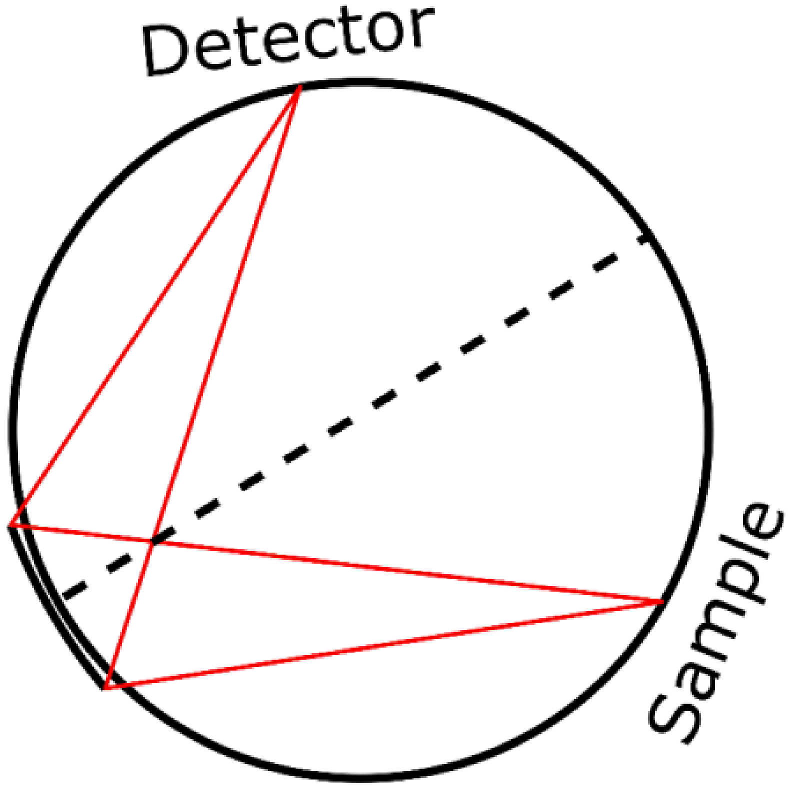
Why lifetime in eV?

- Heisenberg Uncertainty Principle
- $\Delta E \Delta t = \frac{\hbar}{2}$
- t≈10^{-15} seconds
- $\hbar$ = 6.5821 × 10^{-16} eV.s



Point-to-point Rowland circle geometry



Energy we want

Crystal cut

Bragg angle

$$n\lambda = 2d \sin\theta$$

Change these

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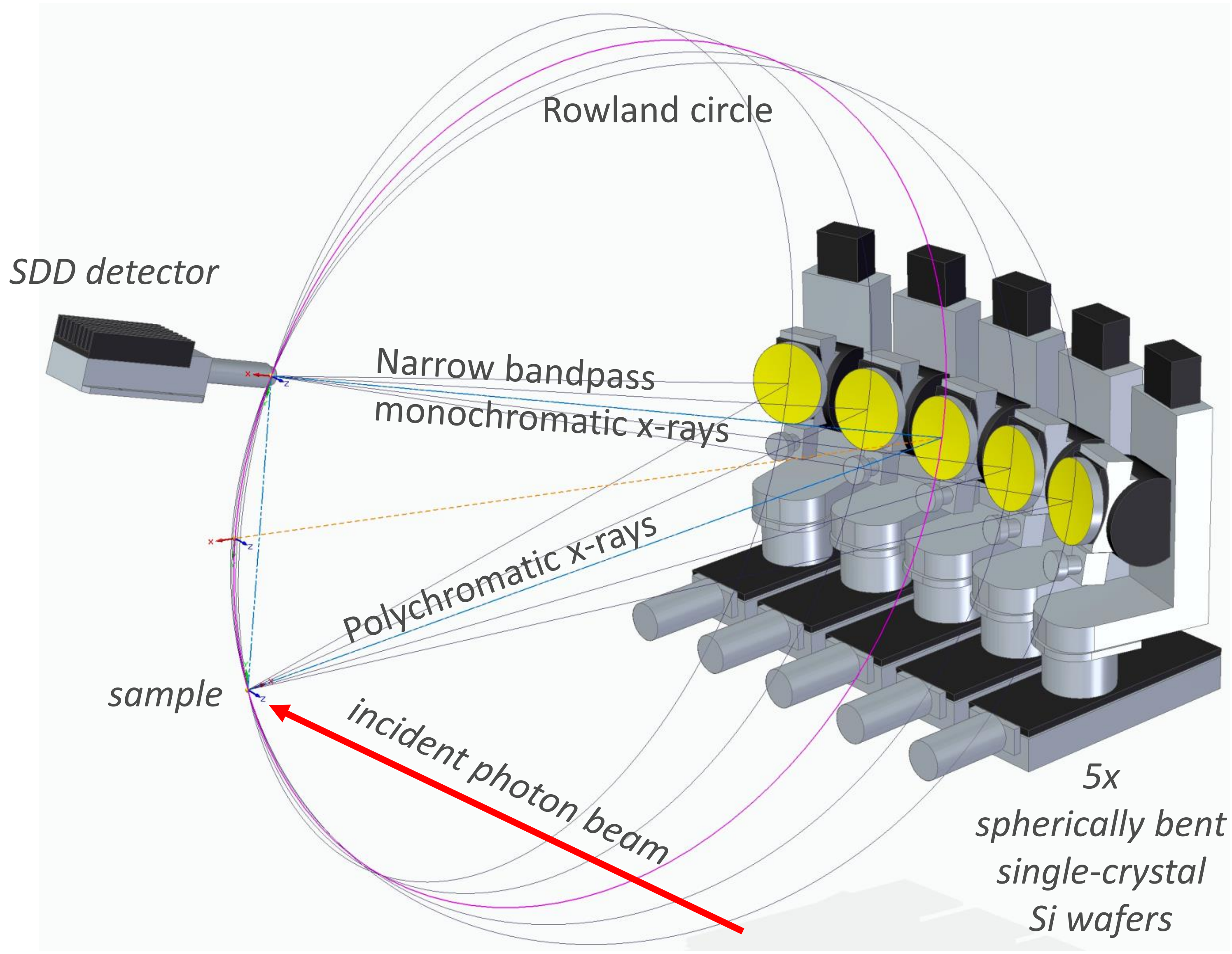
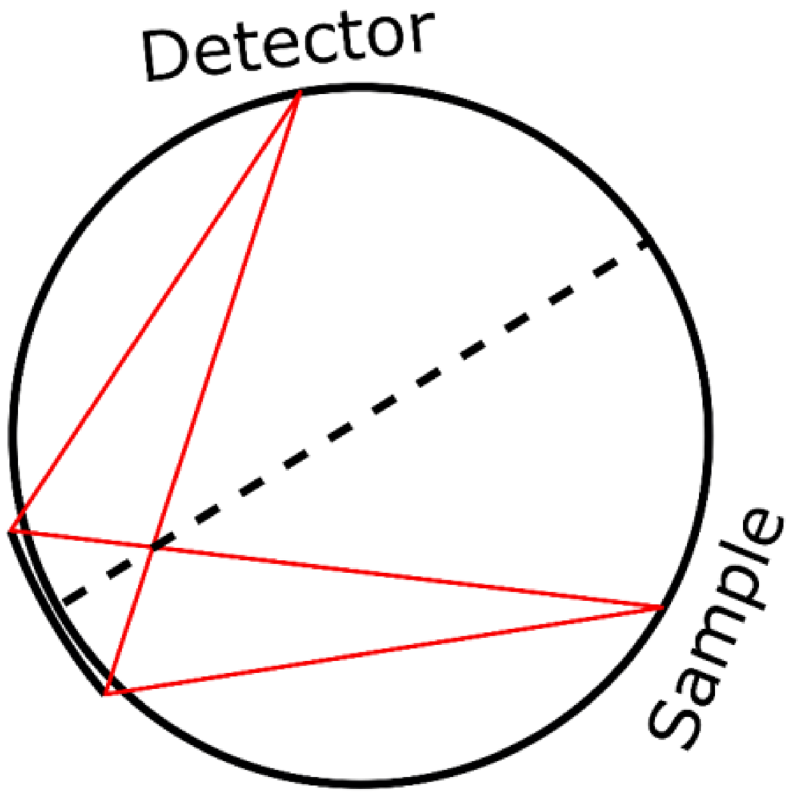
Point-to-point Rowland circle geometry





Energy we want Crystal cut

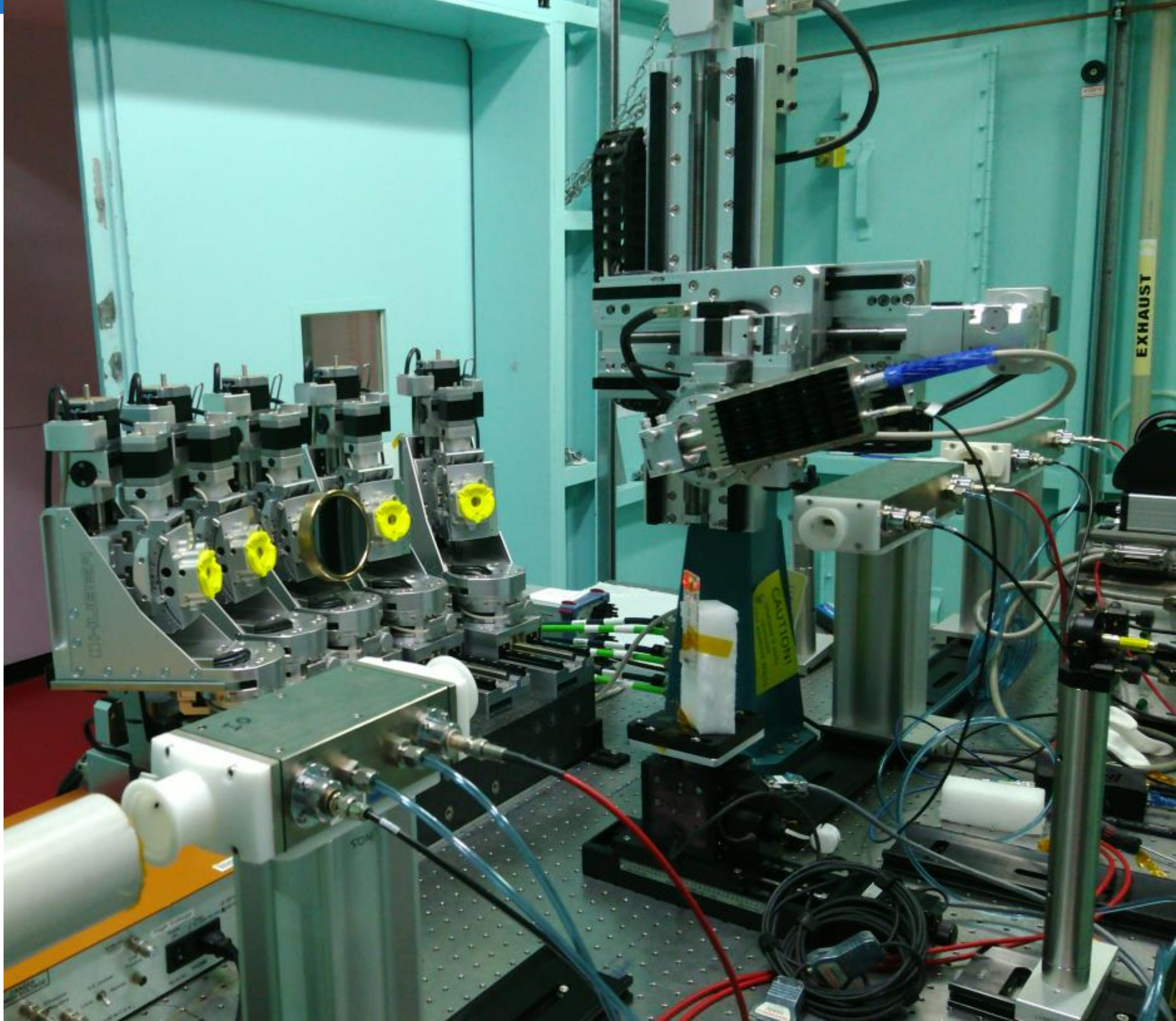
Bragg angle

$n\lambda = 2d \sin\theta$

Change these

spectroMEX

- 0.5 m Rowland circle diameter
- 5 x crystals
  - 100 mm diameter
  - spherically bent
  - 0.5 m bending radius
  - Johann-type
- Mechanics by Huber
- Single element Ketek SDD
- XGLab Dante DPP



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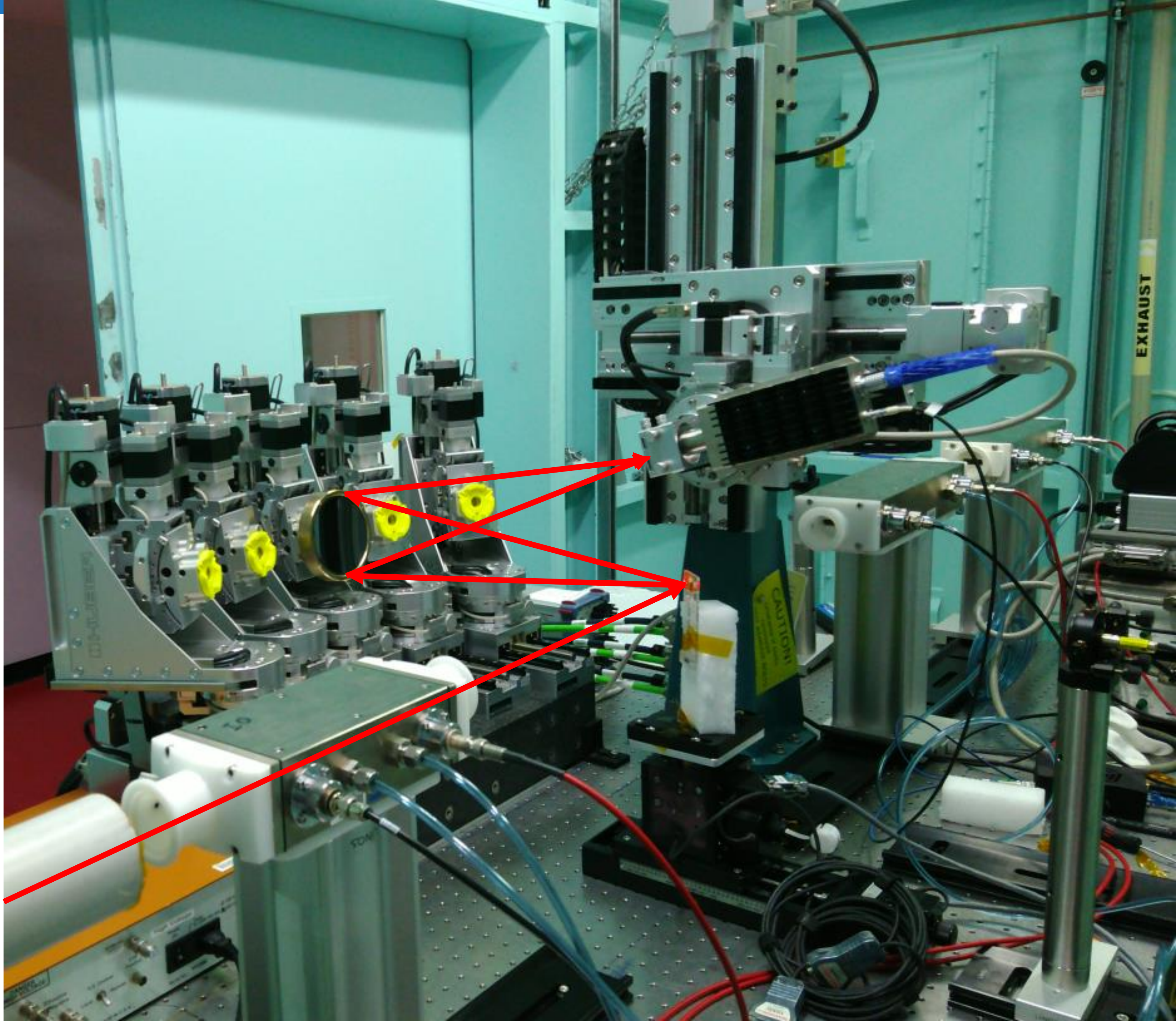

Why high resolution?

- Increased sensitivity
- New techniques
  - **HERFD** XANES
    - **H**igh **E**nergy **R**esolution **F**luorescence **D**etected XANES
  - **XES**
    - (non-resonant) **X**-ray **E**mission **S**pectroscopy
  - **RIXS/RXES**
    - **R**esonant **I**nelastic **X**-ray **S**cattering/**R**esonant **X**-ray **E**mission **S**pectroscopy
  - **XRS**
    - **X**-ray **R**aman **S**pectroscopy

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    - ~~**X**-ray **R**aman **S**pectroscopy~~

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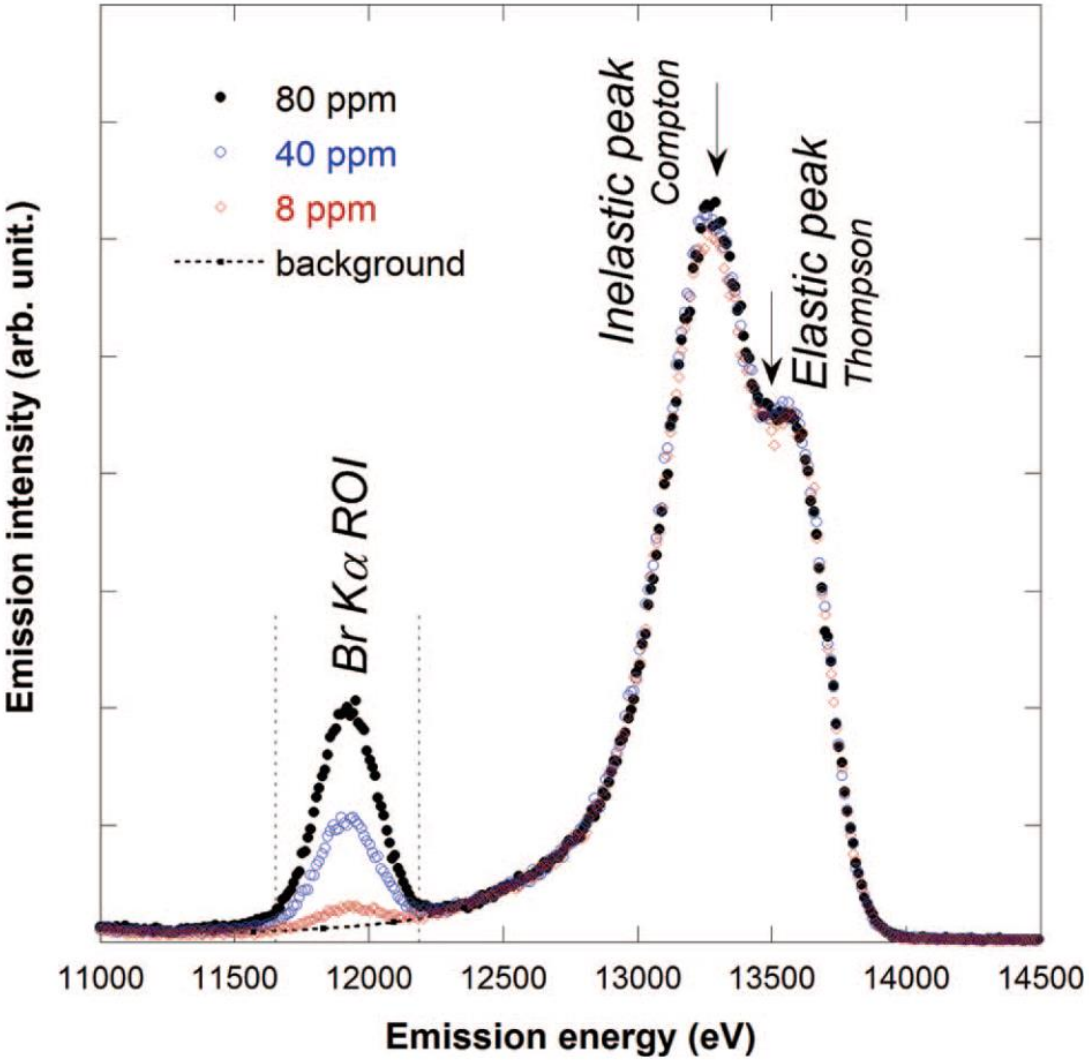
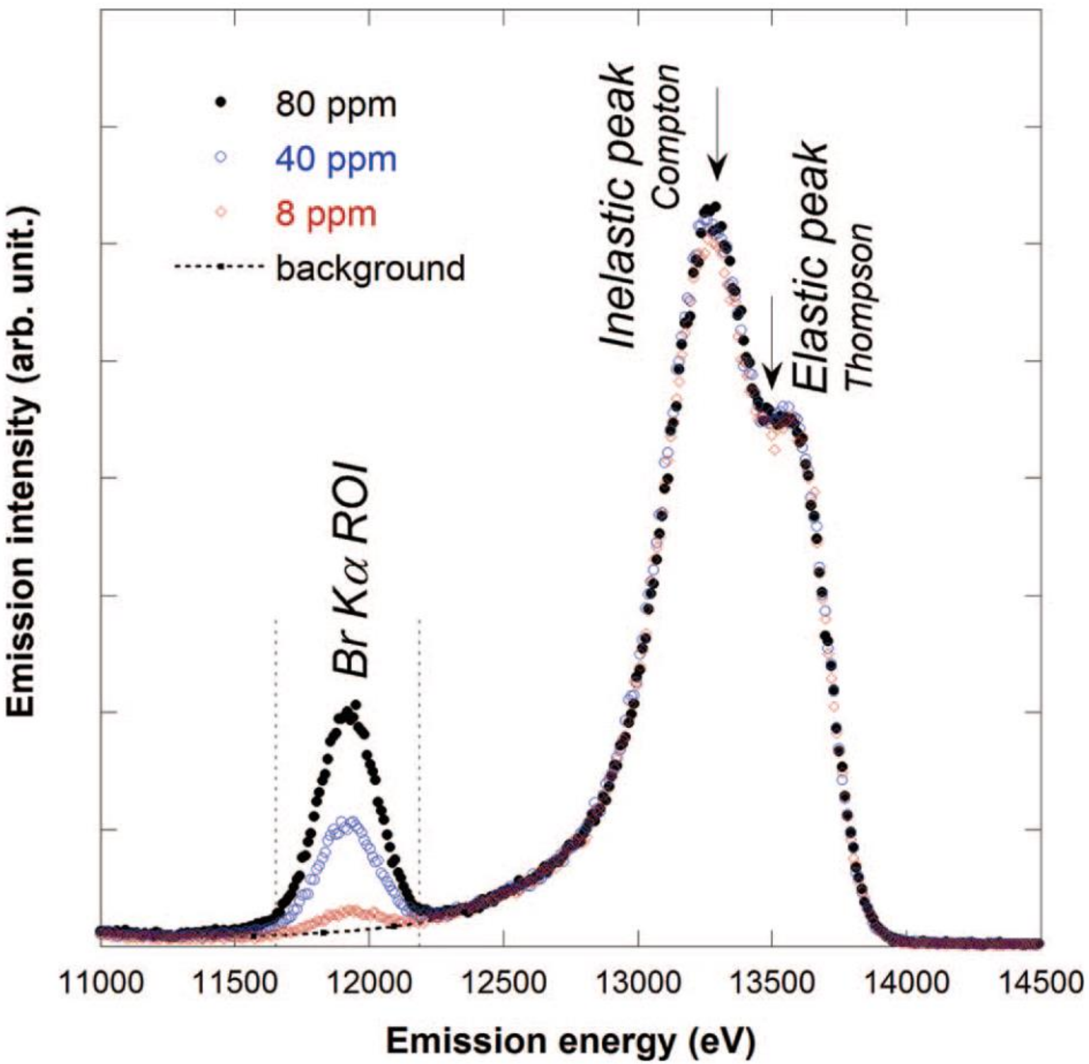
Increased sensitivity



Br K-edge: 13474 eV

Llorens, I. *et al.* (2012). High energy resolution five-crystal spectrometer for high quality fluorescence and absorption measurements on an x-ray absorption spectroscopy beamline. *Review of Scientific Instruments* **83**, 063104.

Increased sensitivity



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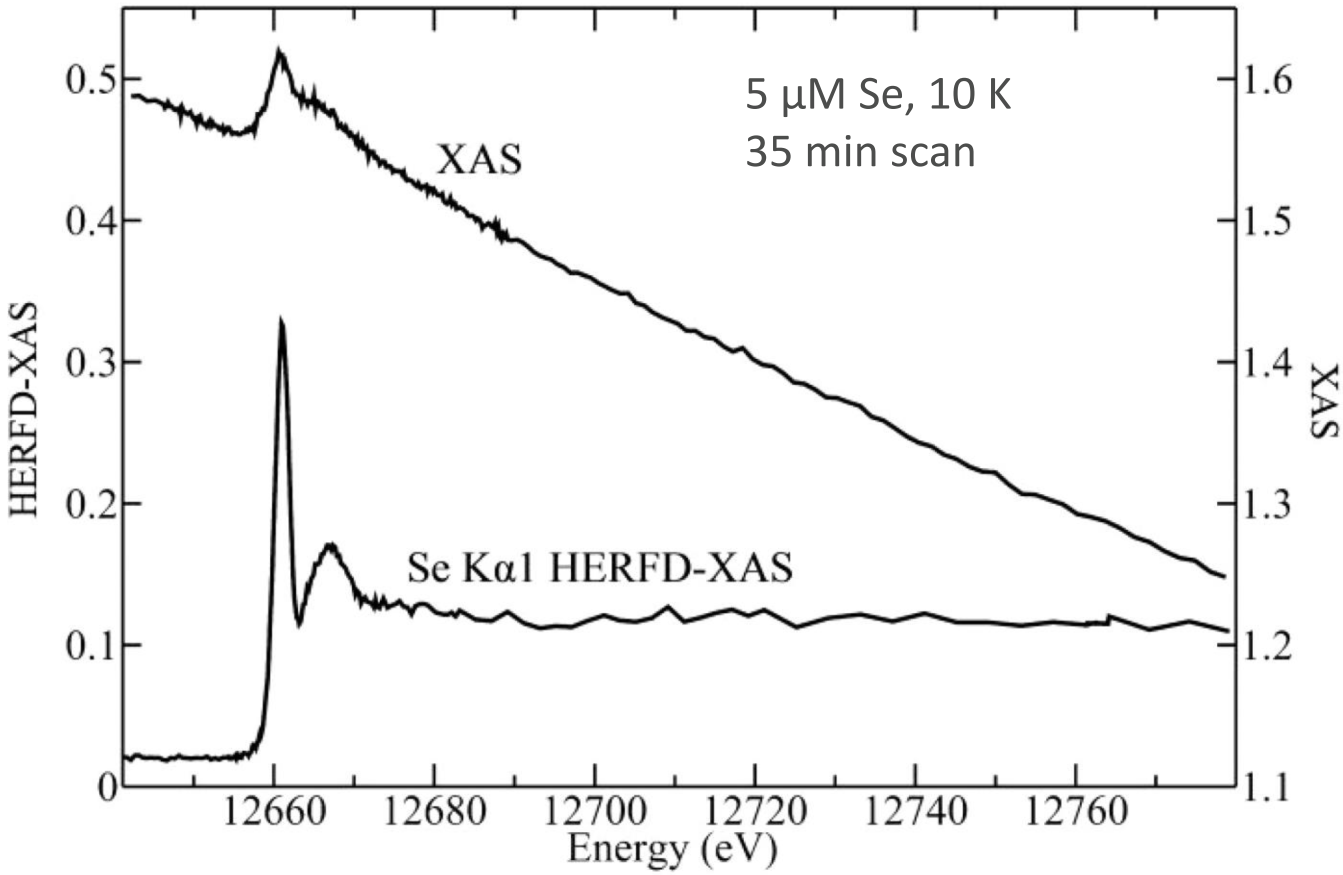
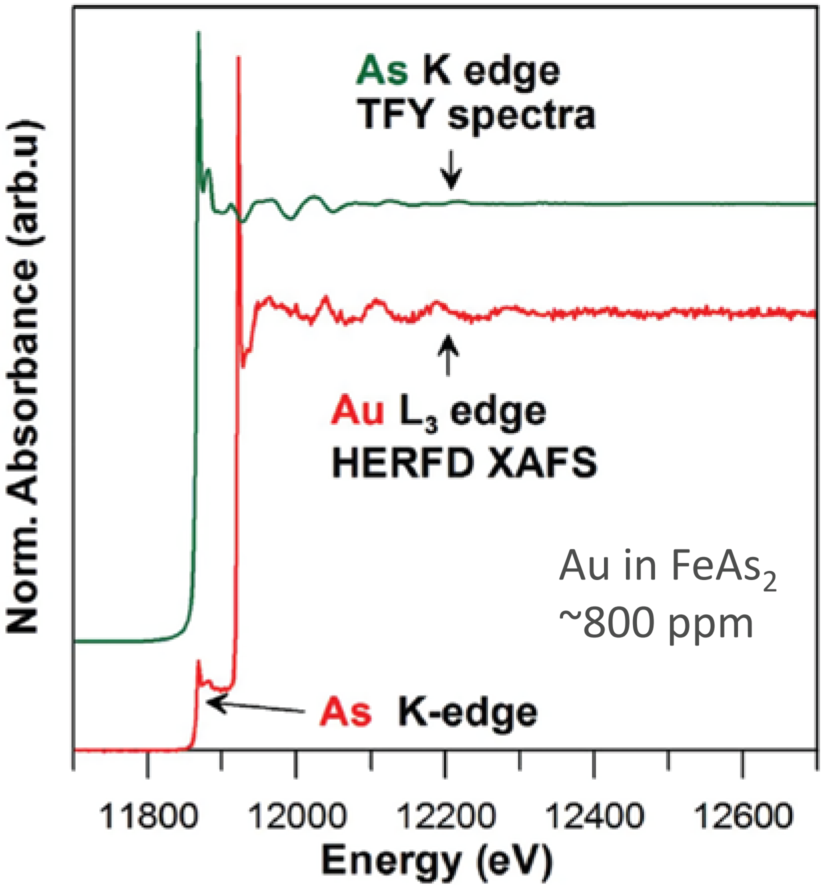
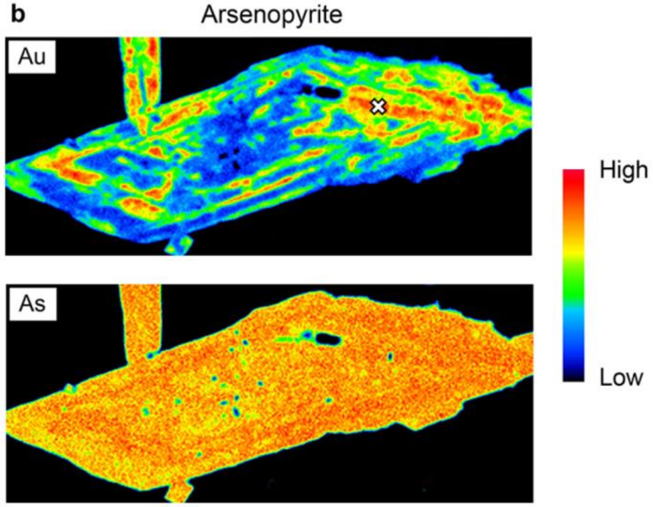


Nehzati, S., Dolgova, N. V., James, A. K., Cotelesage, J. J. H., Sokaras, D., Kroll, T., George, G. N. & Pickering, I. J. (2021). High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy: An Analytical Method for Selenium Speciation. *Analytical Chemistry*. American Chemical Society **93**, 9235–9243.

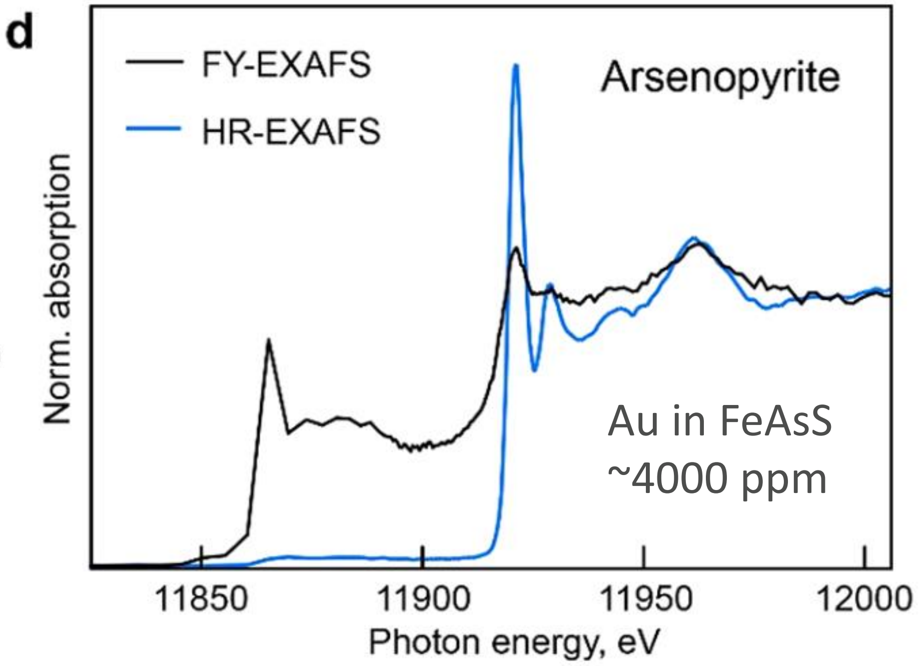
Increased sensitivity

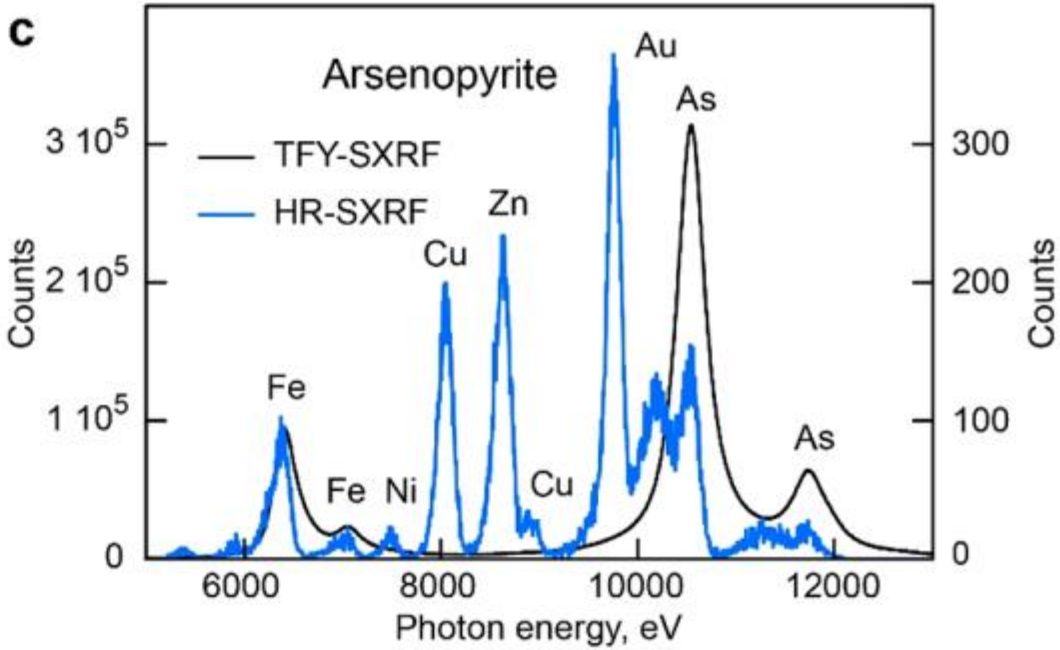


Trigub, A. L., Tagirov, B. R., Kvashnina, K. O., Chareev, D. A., Nickolsky, M. S., Shiryaev, A. A., Baranova, N. N., Kovalchuk, E. V. & Mokhov, A. V. (2017). X-ray spectroscopy study of the chemical state of "invisible" Au in synthetic minerals in the Fe-As-S system. *American Mineralogist* **102**, 1057–1065.

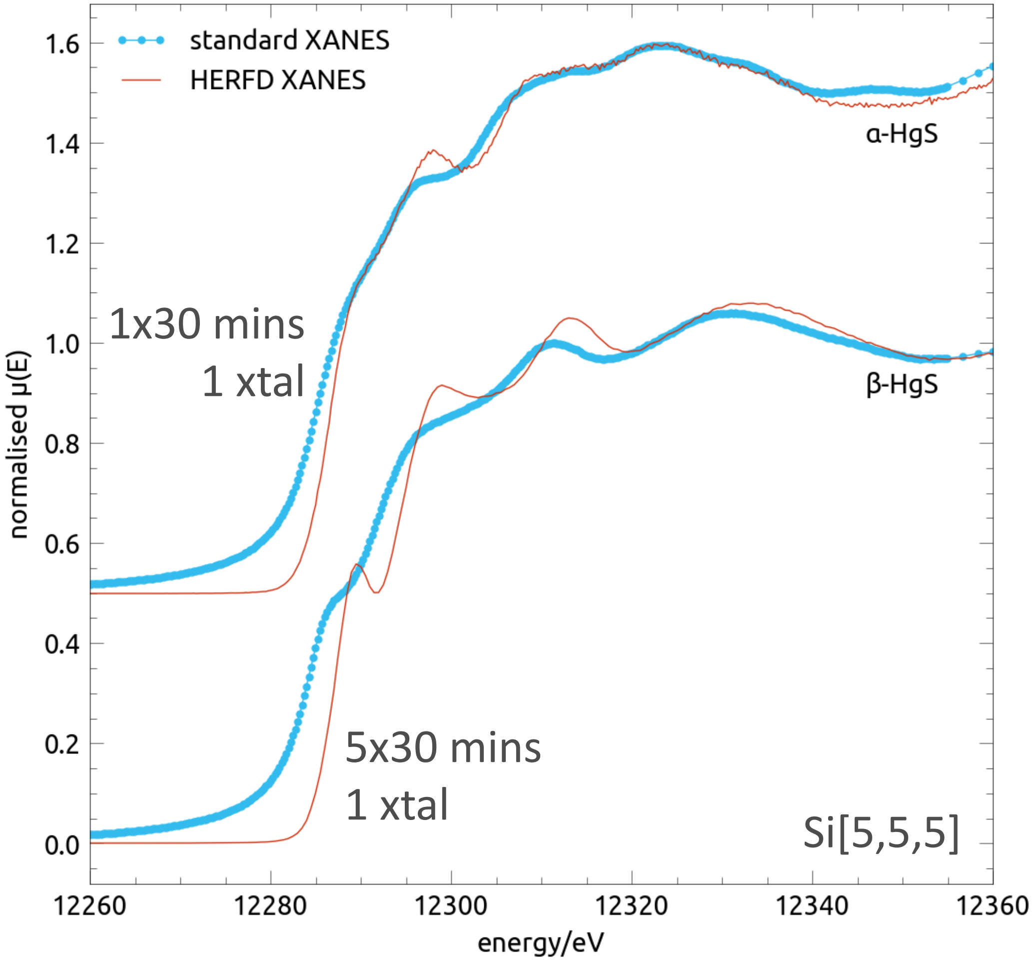


Merkulova, M., Mathon, O., Glatzel, P., Rovezzi, M., Batanova, V., Marion, P., Boiron, M.-C. & Manceau, A. (2019). Revealing the Chemical Form of "Invisible" Gold in Natural Arsenian Pyrite and Arsenopyrite with High Energy-Resolution X-ray Absorption Spectroscopy. *ACS Earth and Space Chemistry*. American Chemical Society **3**, 1905–1914.

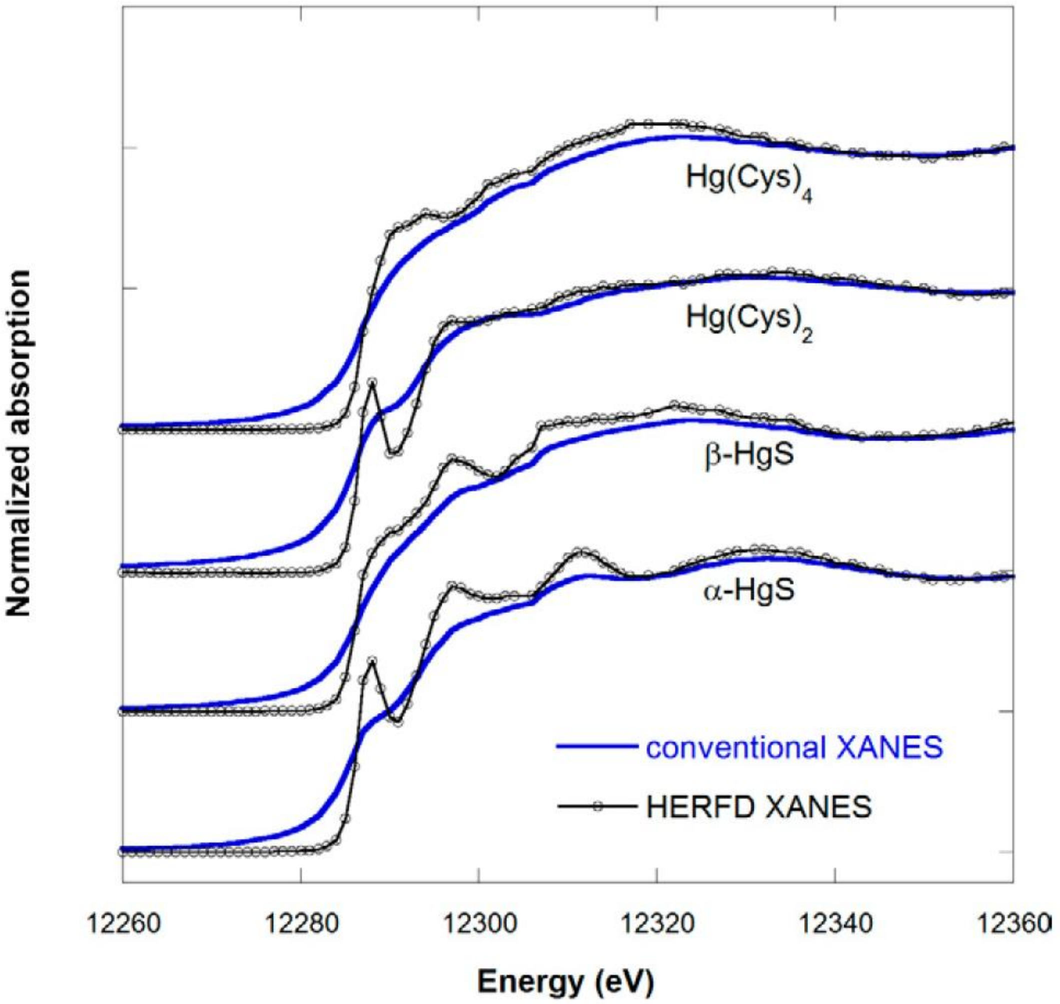




HERFD XANES: spectral sharpening

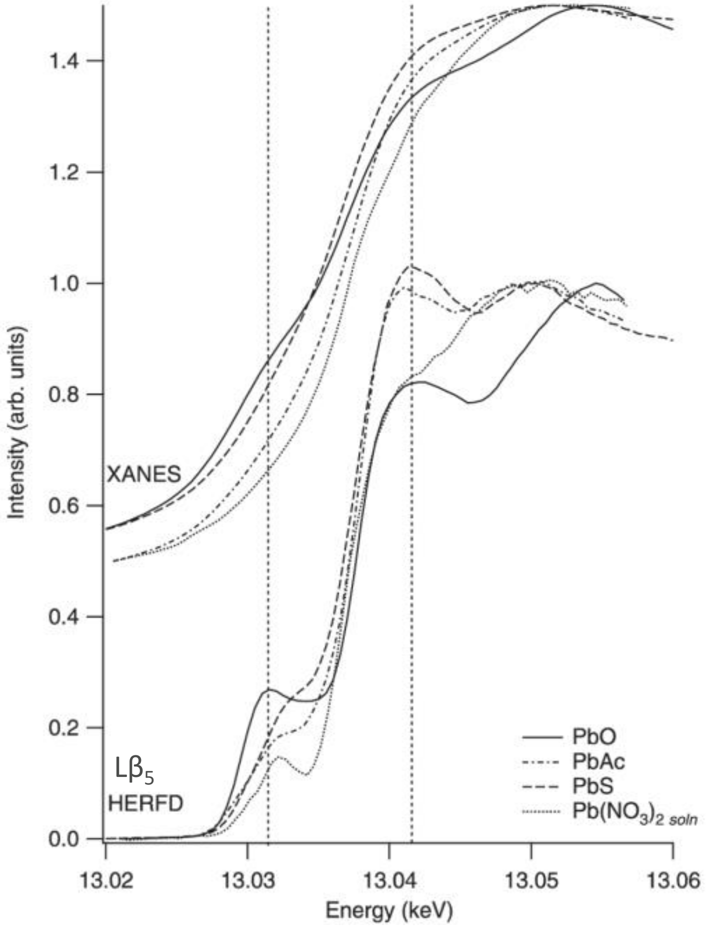


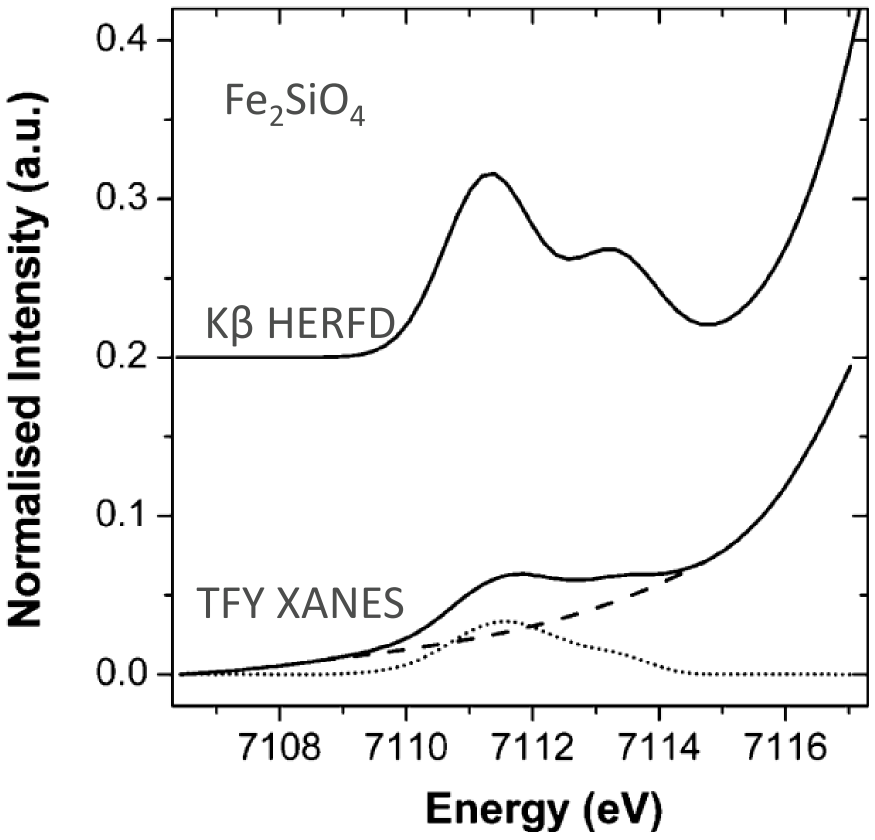
spectroMEX, 2021, unpublished

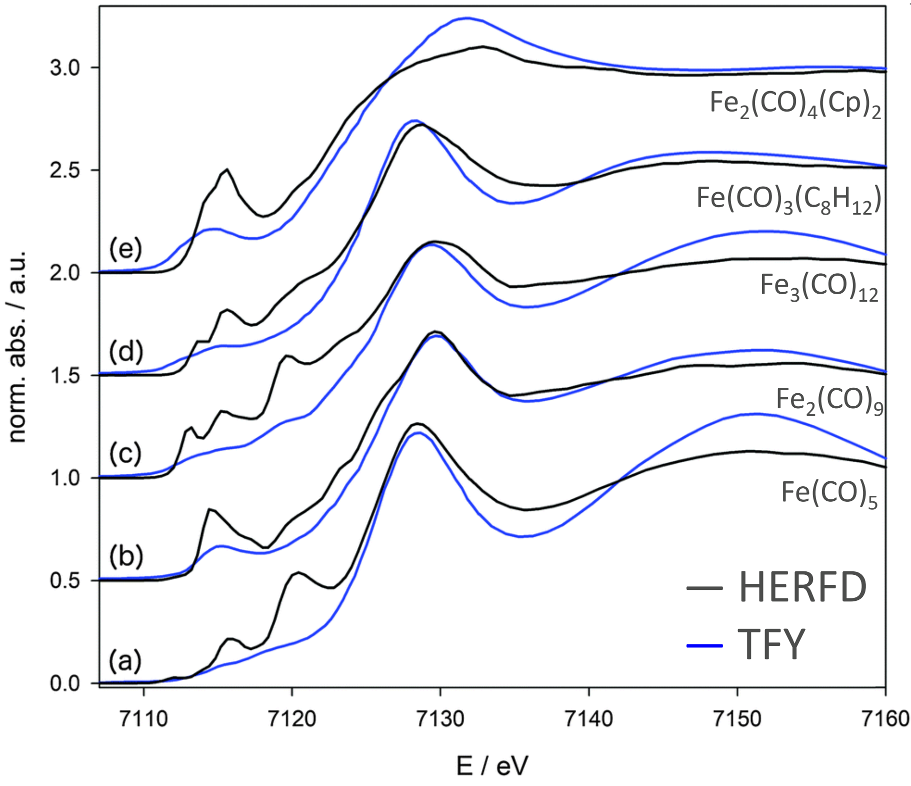


Proux, O. *et al.* (2017). High-Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy: A Powerful New Structural Tool in Environmental Biogeochemistry Sciences. *Journal of Environmental Quality* **46**, 1146–1157.

HERFD XANES: pre-edge sharpening







Swarbrick, J. C., Skyllberg, U., Karlsson, T. & Glatzel, P. (2009). High Energy Resolution X-ray Absorption Spectroscopy of Environmentally Relevant Lead(II) Compounds. *Inorganic Chemistry*. American Chemical Society **48**, 10748–10756.

Heijboer, W. M., Glatzel, P., Sawant, K. R., Lobo, R. F., Bergmann, U., Barrea, R. A., Koningsberger, D. C., Weckhuysen, B. M. & de Groot, F. M. F. (2004). Kβ-Detected XANES of Framework-Substituted FeZSM-5 Zeolites. *The Journal of Physical Chemistry B* **108**, 10002–10011.

Atkins, A. J., Bauer, M. & Jacob, C. R. (2015). High-resolution X-ray absorption spectroscopy of iron carbonyl complexes. *Physical Chemistry Chemical Physics*. The Royal Society of Chemistry **17**, 13937–13948.

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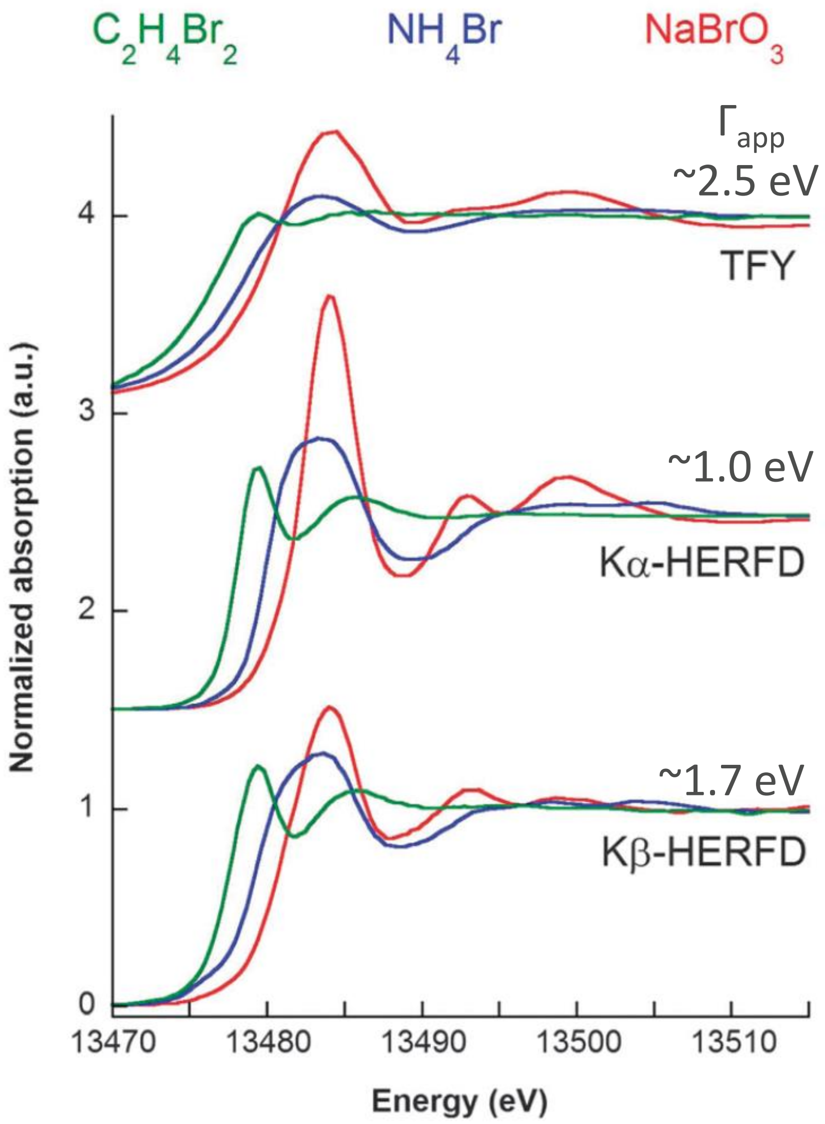
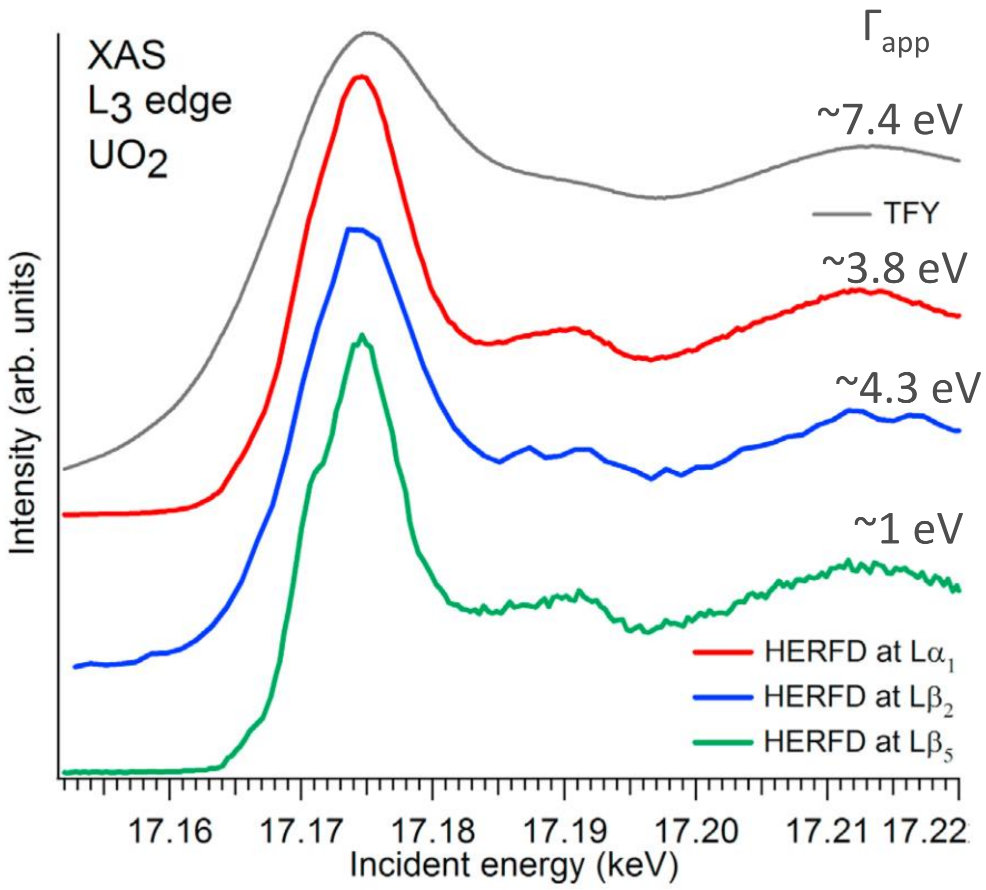
HERFD XANES: spectral sharpening



Bordage, A., Pápai, M., Sas, N. S., Szlachetko, J., Nachtegaal, M. & Vankó, G. (2013). On the sensitivity of hard X-ray spectroscopies to the chemical state of Br. *Physical Chemistry Chemical Physics* **15**, 11088.



Glatzel, P., Weng, T.-C., Kvashnina, K., Swarbrick, J., Sikora, M., Gallo, E., Smolentsev, N. & Mori, R. A. (2013). Reflections on hard X-ray photon-in/photon-out spectroscopy for electronic structure studies. *Journal of Electron Spectroscopy and Related Phenomena* **188**, 17–25.

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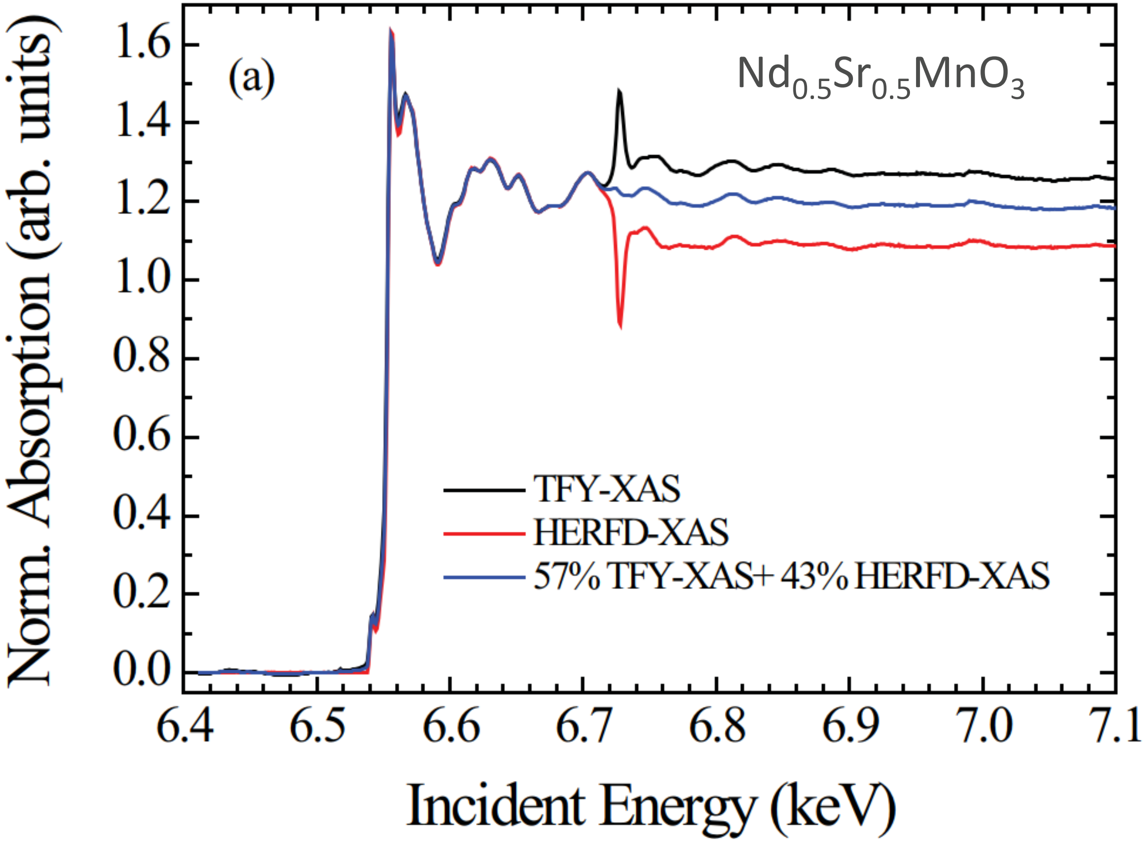
'range-extended' EXAFS



- Avoiding unwanted edges by combining HERFD and TFY
  - Mn *K*-edge HERFD shows drop in intensity at Nd L_2 edge
  - Nd L_2-edge feature is not high resolution
  - Weighted sum of HERFD and TFY to remove Nd L_2 signal

Lafuerza, S., García, J., Subías, G., Blasco, J. & Glatzel, P. (2016). High-resolution Mn K-edge x-ray emission and absorption spectroscopy study of the electronic and local structure of the three different phases in Nd0.5Sr0.5MnO3 *Physical Review B*. American Physical Society **93**, 205108.

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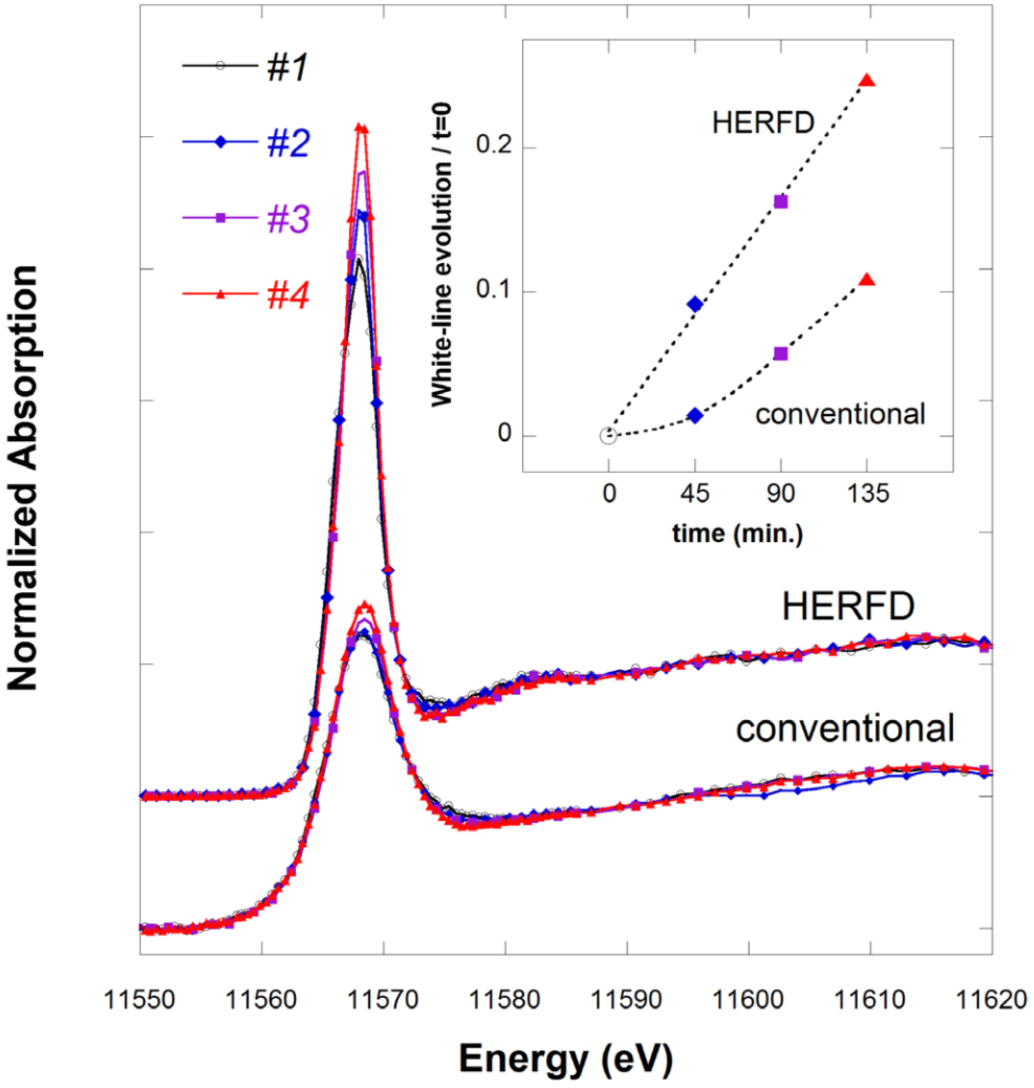
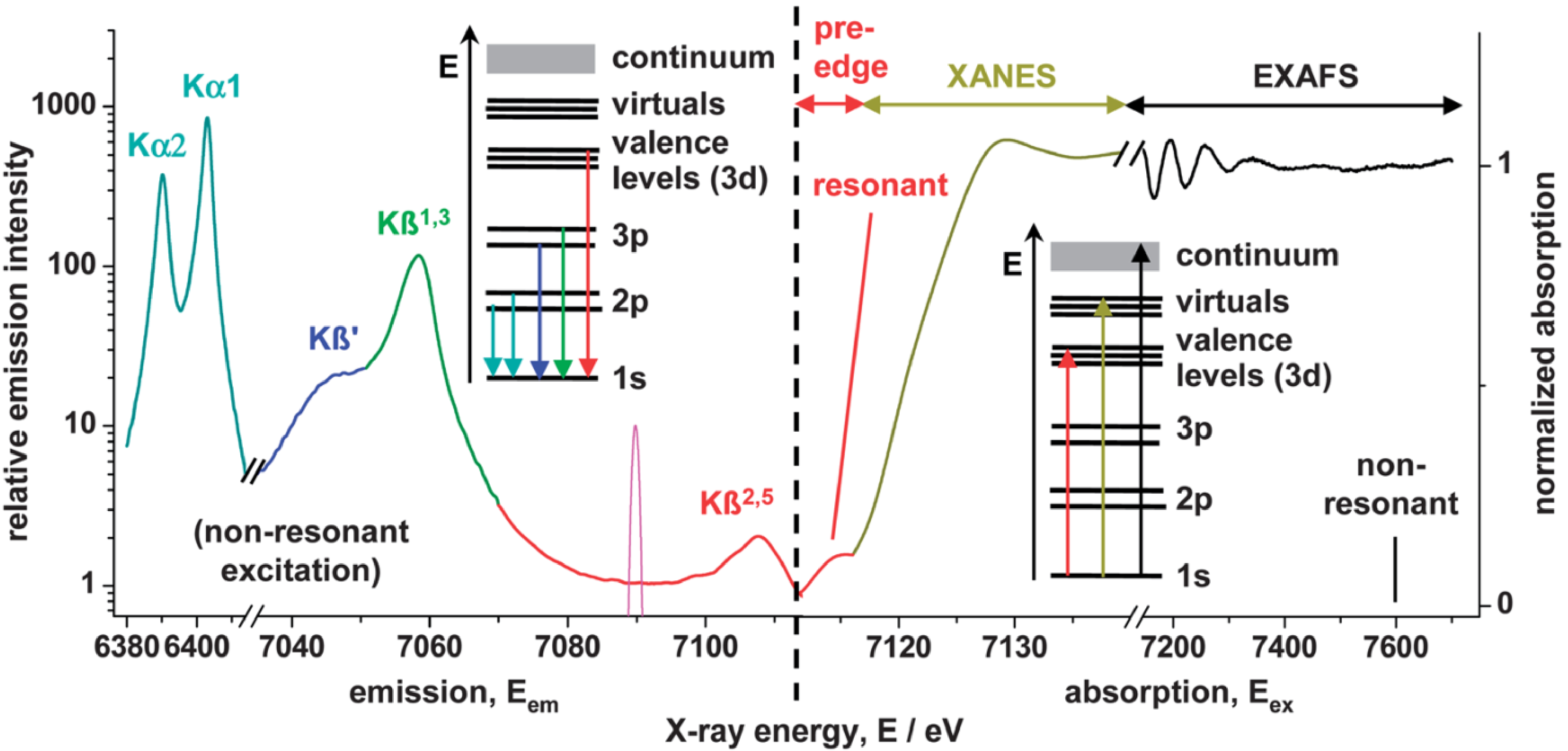
Beam damage



- Shaper spectral features means radiation damage is more obvious
- Lower efficiency of HERFD can mean longer exposure…
- Background rejection can mean shorter exposure time…
- Background rejection means more dilute samples can be measured…
- Even more dilute samples take longer…

Proux, O. *et al.* (2017). High-Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy: A Powerful New Structural Tool in Environmental Biogeochemistry Sciences. *Journal of Environmental Quality* **46**, 1146–1157.

X-ray Emission Spectroscopy



Lambertz, C., Chernev, P., Klingan, K., Leidel, N., Sigfridsson, K. G. V., Happe, T. & Haumann, M. (2014). Electronic and molecular structures of the active-site H-cluster in [FeFe]-hydrogenase determined by site-selective X-ray spectroscopy and quantum chemical calculations. *Chem. Sci.* **5**, 1187–1203.

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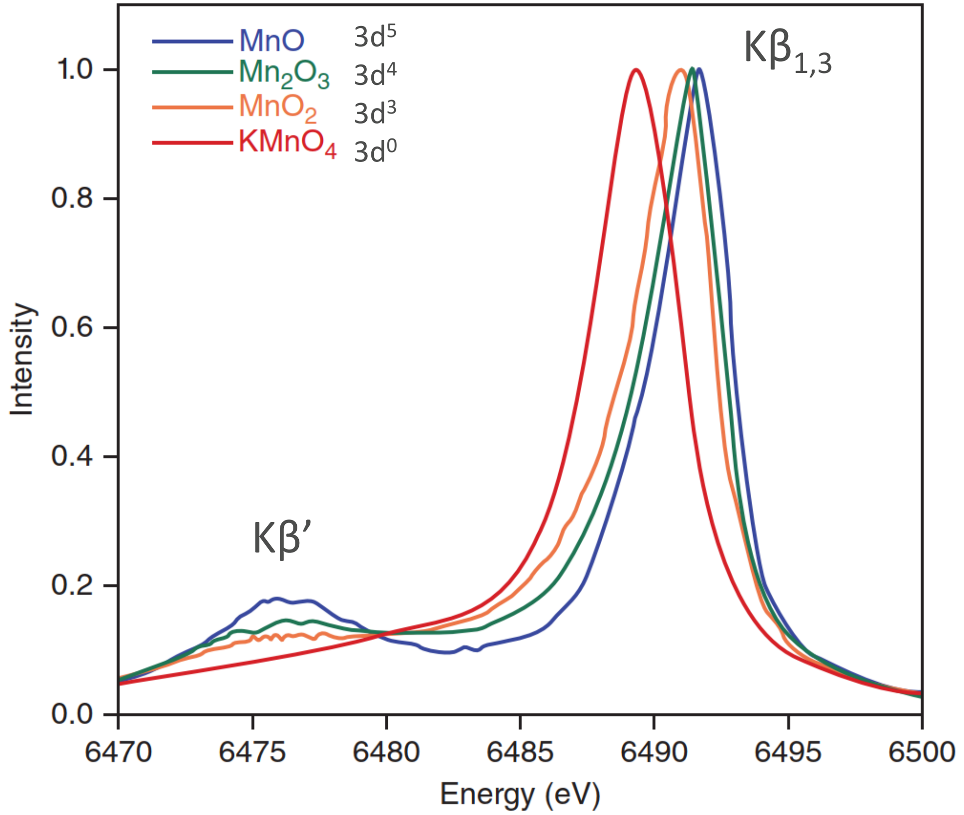
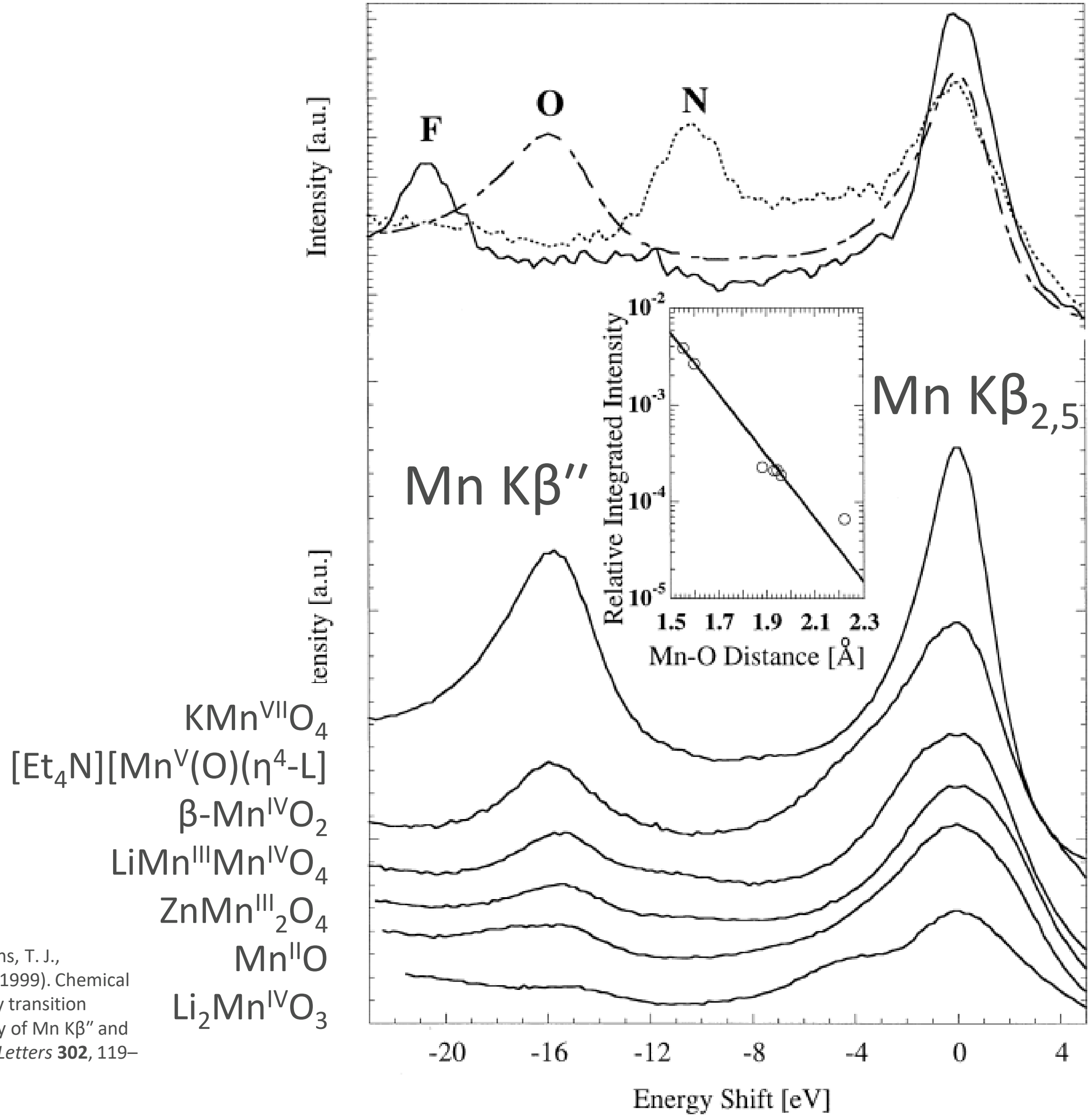
X-ray Emission Spectroscopy

Kβ mainline



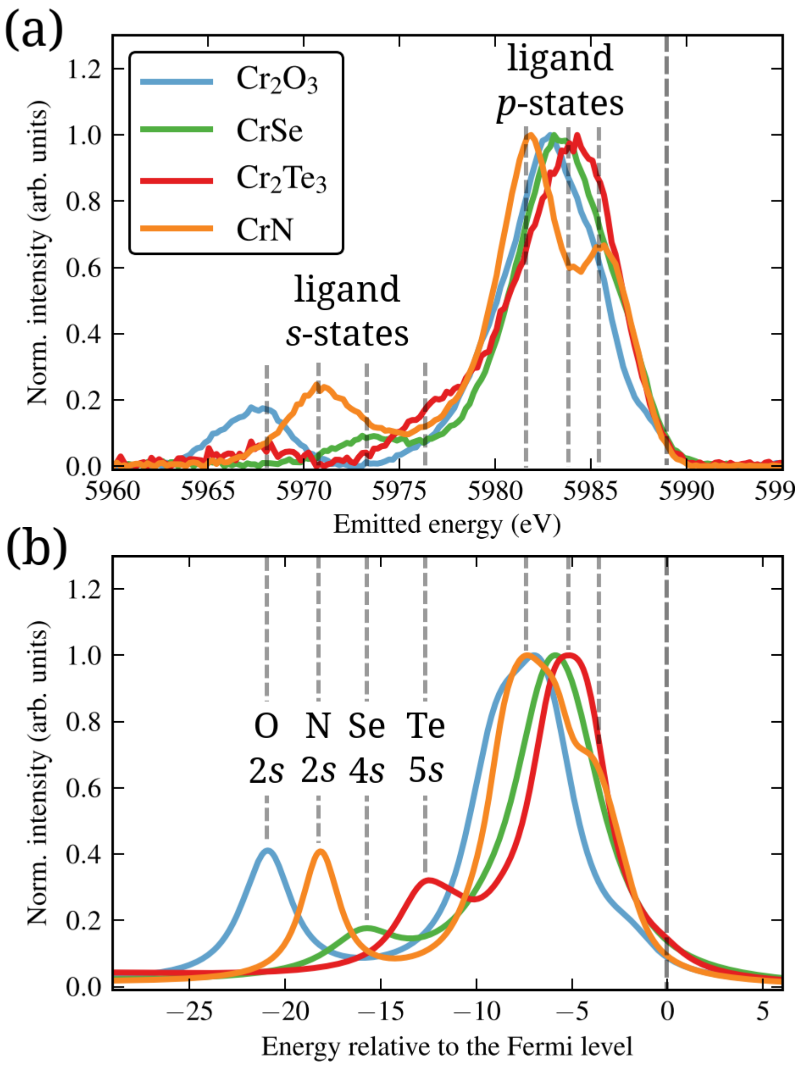
DeBeer, S. & Bergmann, U. (2011). X-Ray Emission Spectroscopic Techniques in Bioinorganic Applications. *Encyclopedia of Inorganic and Bioinorganic Chemistry*. John Wiley & Sons, Ltd.

Kβ satellite/vtc-XES

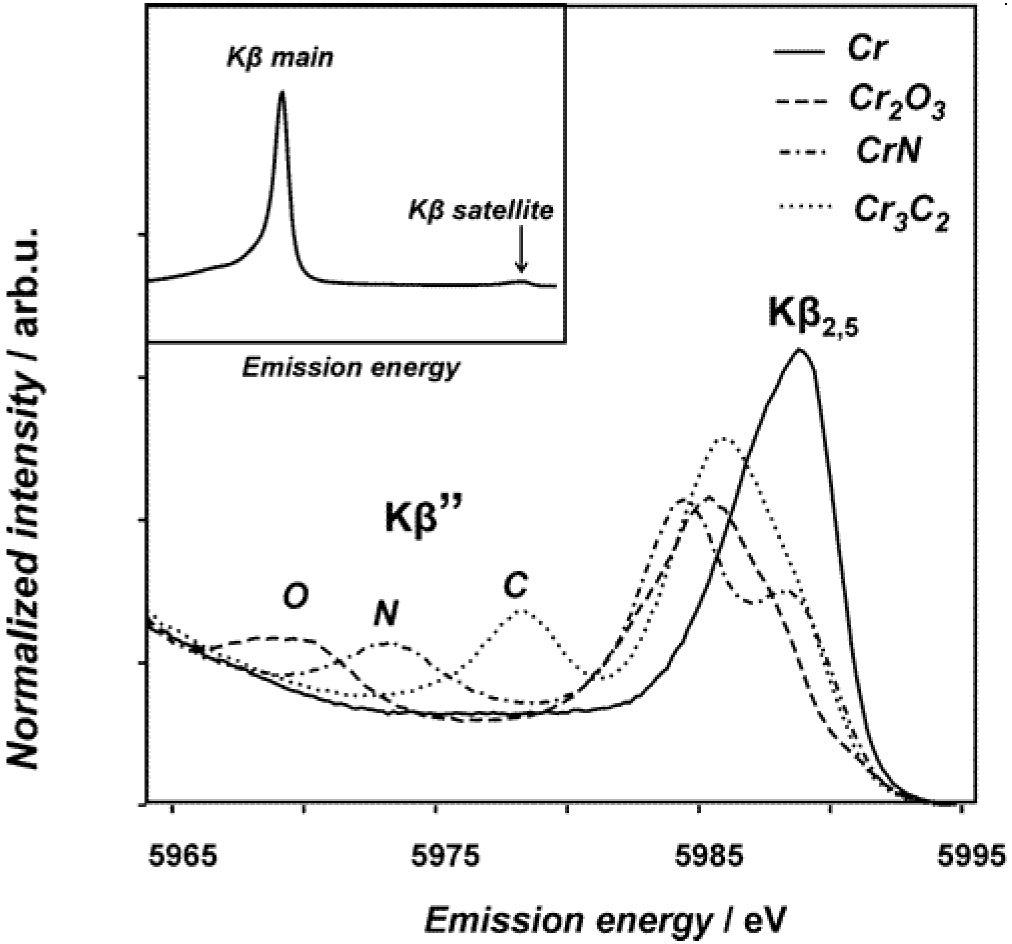


Bergmann, U., Horne, C. R., Collins, T. J., Workman, J. M. & Cramer, S. P. (1999). Chemical dependence of interatomic X-ray transition energies and intensities – a study of Mn Kβ'' and Kβ2,5 spectra. *Chemical Physics Letters* **302**, 119–124.

vtc-XES

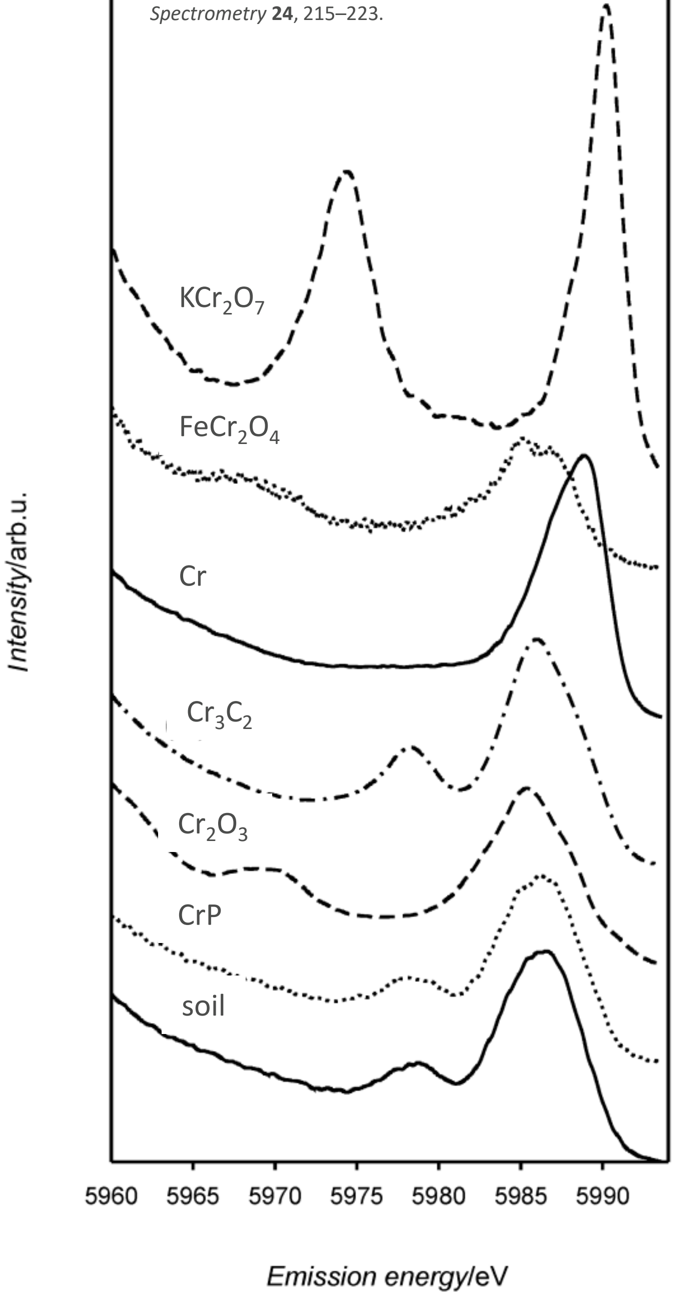


Rovezzi, M. & Glatzel, P. (2014). Hard x-ray emission spectroscopy: a powerful tool for the characterization of magnetic semiconductors. *Semiconductor Science and Technology* **29**, 023002.



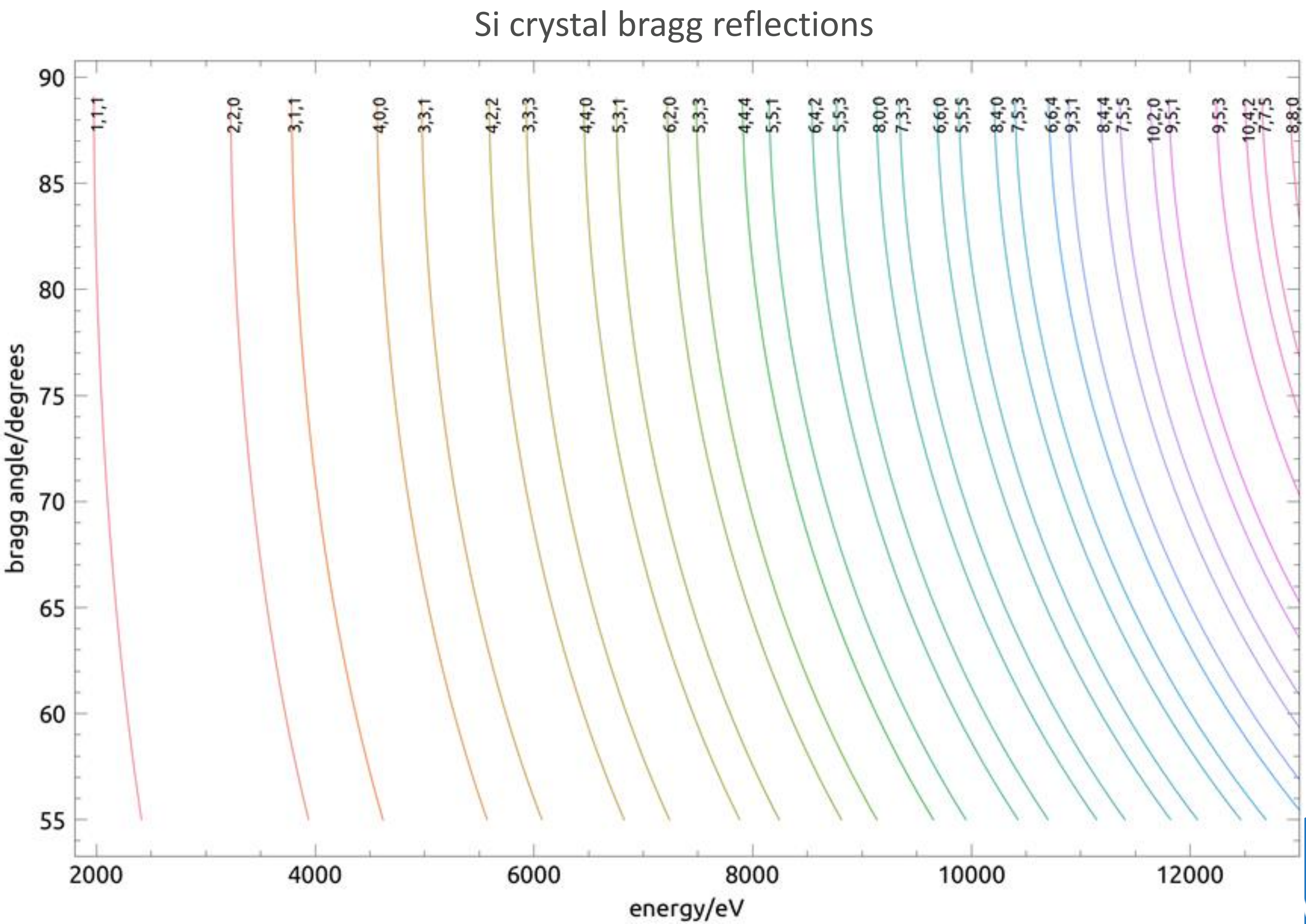
Safonov, V. A., Vykhodtseva, L. N., Polukarov, Y. M., Safonova, O. V., Smolentsev, G., Sikora, M., Eeckhout, S. G. & Glatzel, P. (2006). Valence-to-Core X-ray Emission Spectroscopy Identification of Carbide Compounds in Nanocrystalline Cr Coatings Deposited from Cr(III) Electrolytes Containing Organic Substances. *The Journal of Physical Chemistry B* **110**, 23192–23196.

Eeckhout, S. G., Safonova, O. V., Smolentsev, G., Biasioli, M., Safonov, V. A., Vykhodtseva, L. N., Sikora, M. & Glatzel, P. (2009). Cr local environment by valence-to-core X-ray emission spectroscopy. *Journal of Analytical Atomic Spectrometry* **24**, 215–223.



What emission lines can I measure?

- MEX1 energy range
  - 3500 – 13400 eV
- spectroMEX bragg range
  - 65-90 degrees
- Best performance
  - 80-88 degrees
- MEX budget
  - ≠∞



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What emission lines can I measure?

- Si[1,1,1] × 5
- Si[2,2,0] × 1
- Si[4,0,0] × 1
- Si[4,2,2] × 1
- Si[3,3,1] × 1
- Si[6,2,0] × 1
- Si[5,3,1] × 1

spectroMEX crystals

Jeremy Wykes jeremyw@ansto.gov.au
2021.07.13

The MEX crystal spectrometer has a library comprising the following crystals:

- Si[1,1,1] x 5
- Si[2,2,0] x 1
- Si[4,0,0] x 1
- Si[4,2,2] x 1
- Si[3,3,1] x 1
- Si[6,2,0] x 1
- Si[5,3,1] x 1

This document provides tables outlining which emission lines are accessible via which bragg reflection of which cut. The document has two sections, the first comprises tables for each crystal cut; the second comprises tables for each element.

Fe

line	energy/eV	cut	bragg reflection	bragg angle
Fe_Ka3	6267.4	1,1,1	3,3,3	71.15
Fe_Ka2	6392.1	1,1,1	3,3,3	68.11
Fe_Ka1	6405.2	1,1,1	3,3,3	67.82
Fe_Kb3	7059.3	5,3,1	5,3,1	73.06
Fe_Kb1	7059.3	5,3,1	5,3,1	73.06
Fe_Kb3	7059.3	2,2,0	4,4,0	66.16
Fe_Kb1	7059.3	2,2,0	4,4,0	66.16
Fe_Kb5	7110.0	5,3,1	5,3,1	71.76
Fe_Kb5	7110.0	2,2,0	4,4,0	65.25

Co

line	energy/eV	cut	bragg reflection	bragg angle
Co_Ka3	6783.9	5,3,1	5,3,1	84.52
Co_Ka3	6783.9	2,2,0	4,4,0	72.14
Co_Ka2	6915.8	2,2,0	4,4,0	69.01
Co_Ka2	6915.8	5,3,1	5,3,1	77.54
Co_Ka1	6930.9	5,3,1	5,3,1	76.99
Co_Ka1	6930.9	2,2,0	4,4,0	68.69
Co_Kb1	7649.1	6,2,0	6,2,0	70.70
Co_Kb3	7650.1	6,2,0	6,2,0	70.68
Co_Kb5	7706.0	6,2,0	6,2,0	69.52

Ni

line	energy/eV	cut	bragg reflection	bragg angle
Ni_Ka3	7324.4	6,2,0	6,2,0	80.27
Ni_Ka3	7324.4	5,3,1	5,3,1	67.22
Ni_Ka2	7463.0	6,2,0	6,2,0	75.31
Ni_Ka1	7480.3	6,2,0	6,2,0	74.82
Ni_Kb3	8265.0	1,1,1	4,4,4	73.10
Ni_Kb1	8266.8	1,1,1	4,4,4	73.06
Ni_Kb5	8329.0	1,1,1	4,4,4	71.71

Cu

line	energy/eV	cut	bragg reflection	bragg angle
Cu_Ka3	7882.3	6,2,0	6,2,0	66.33
Cu_Ka2	8026.7	1,1,1	4,4,4	80.14
Cu_Ka1	8046.3	1,1,1	4,4,4	79.37

Zn

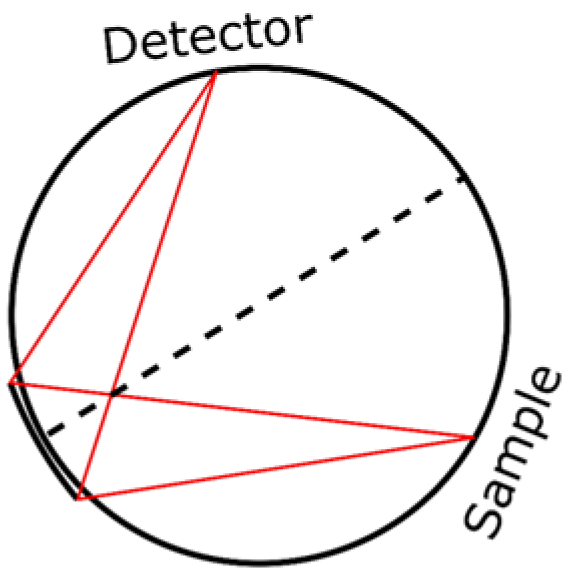
line	energy/eV	cut	bragg reflection	bragg angle
Zn_Ka3	8462.8	1,1,1	4,4,4	69.14
Zn_Ka2	8614.1	1,1,1	4,4,4	66.64
Zn_Ka1	8637.2	1,1,1	4,4,4	66.29
Zn_Kb3	9567.6	4,0,0	8,0,0	72.64
Zn_Kb1	9570.4	4,0,0	8,0,0	72.58
Zn_Kb5	9648.8	4,0,0	8,0,0	71.15

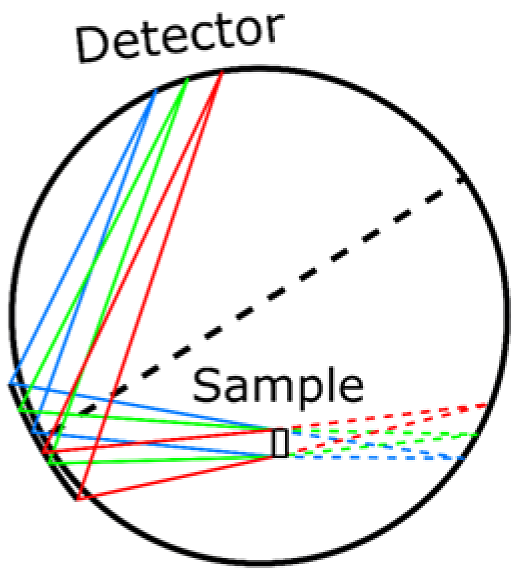
https://www.ansto.gov.au/medium-energy-x-ray-absorption-spectroscopy-beamline

ANSTO

MEX2 'Brimstone' spectrometer

- Dispersive Rowland Refocusing
  - DRR
  - Large beam, off circle
  - All areas of the sample contribute at all energies
  - Position sensitive detector
    - Energy = position





MEX2 ‘Brimstone’ spectrometer

REVIEW OF SCIENTIFIC INSTRUMENTS **88**, 073904 (2017)

A compact dispersive refocusing Rowland circle X-ray emission spectrometer for laboratory, synchrotron, and XFEL applications

William M. Holden,[1] Oliver R. Hoidn,[1] Alexander S. Ditter,[1] Gerald T. Seidler,[1,a)] Joshua Kas,[1] Jennifer L. Stein,[2] Brandi M. Cossairt,[2] Stosh A. Kozimor,[3] Jinghua Guo,[4] Yifan Ye,[4] Matthew A. Marcus,[4] and Sirine Fakra[4]
[1]*Physics Department, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Chemistry Department, University of Washington, Seattle, Washington 98195-1560, USA*
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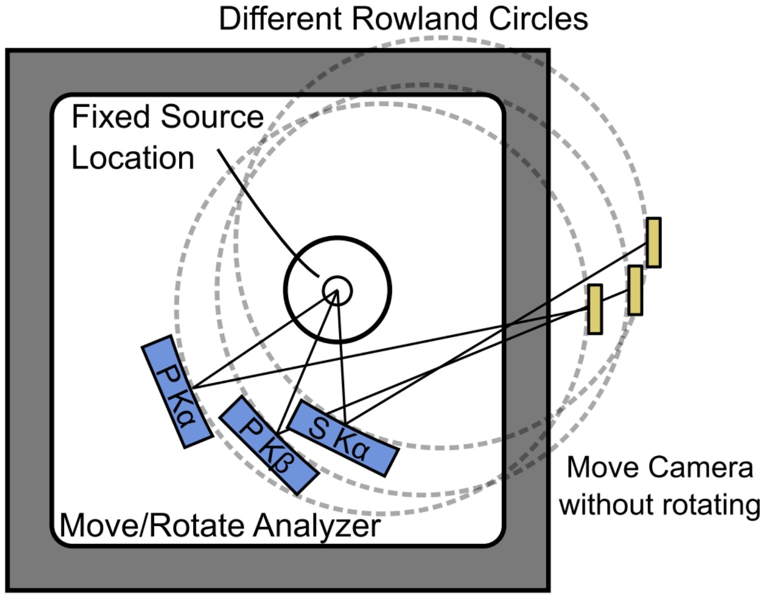
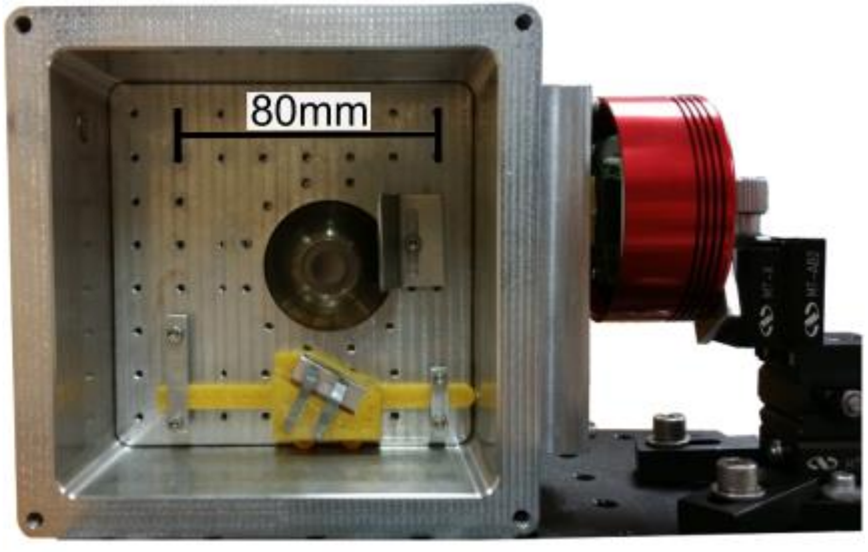
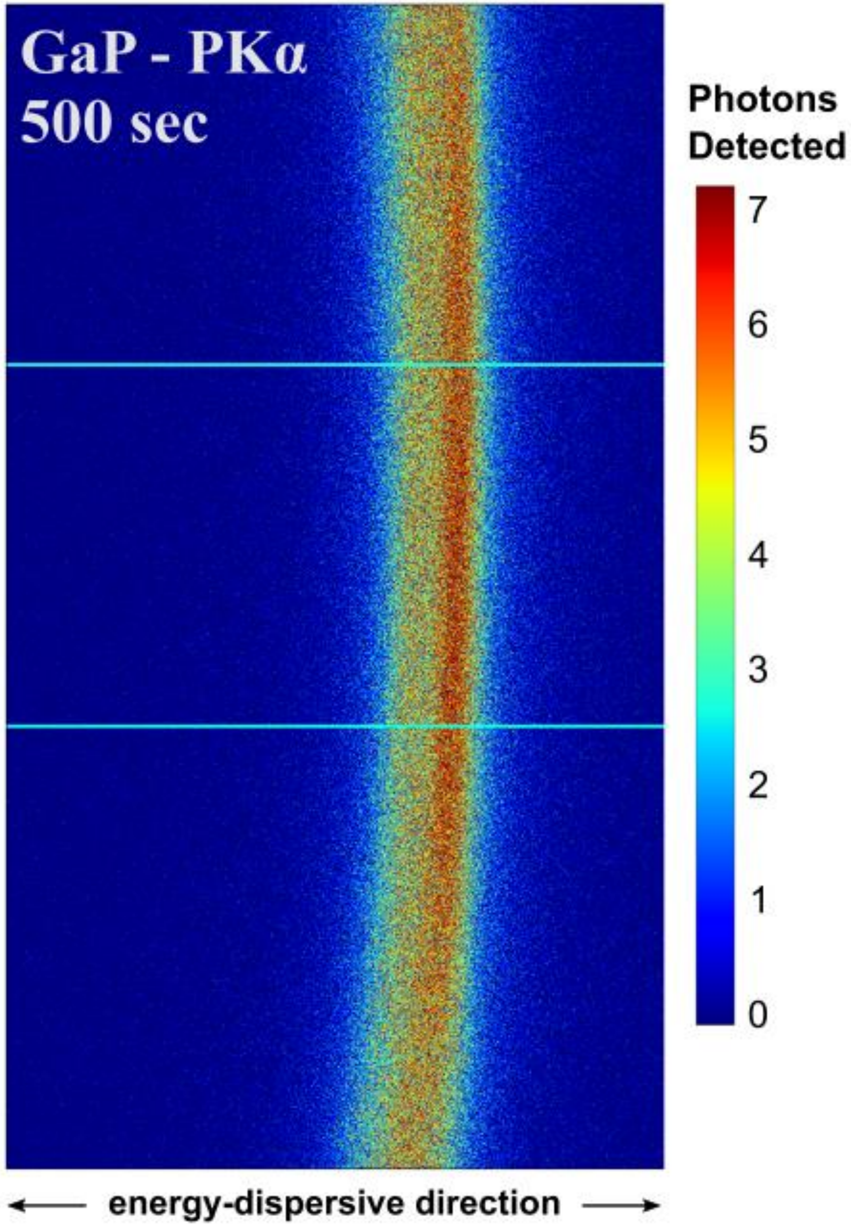
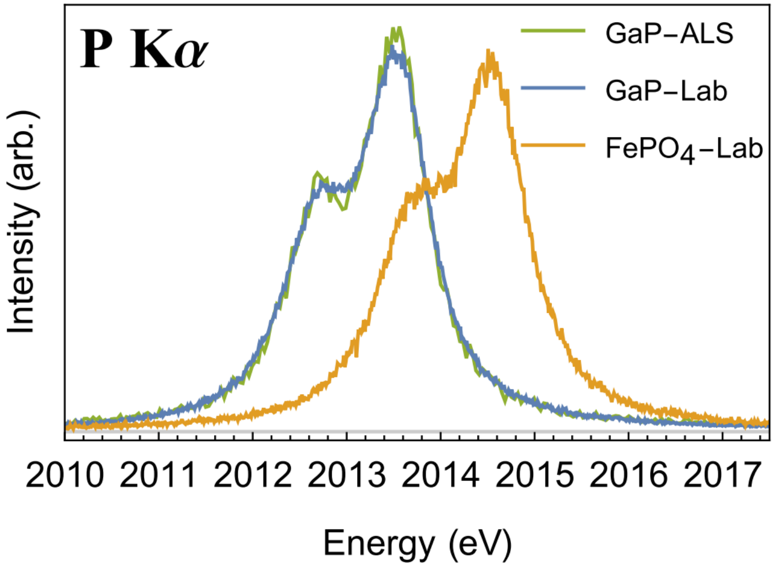
100 mm bending radius
cylindrically bent Si[1,1,1]



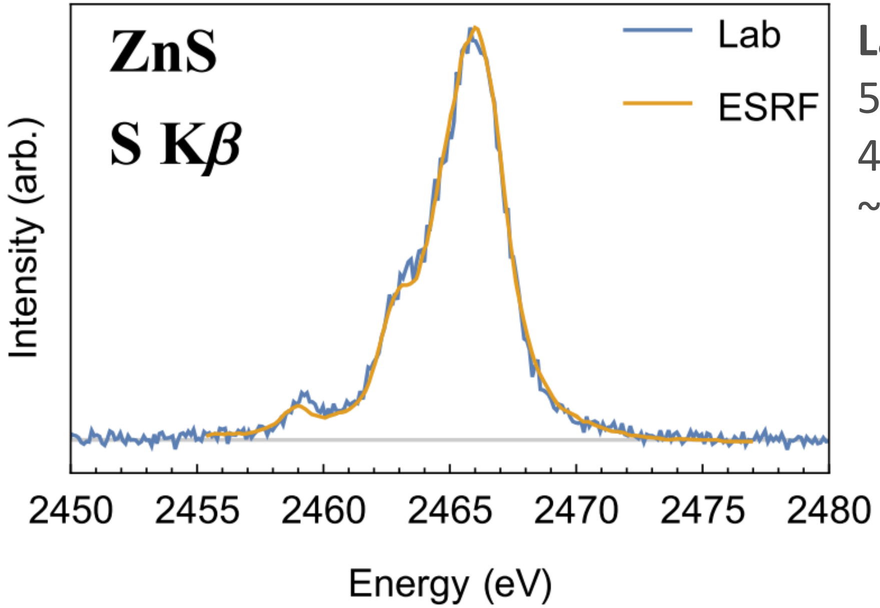




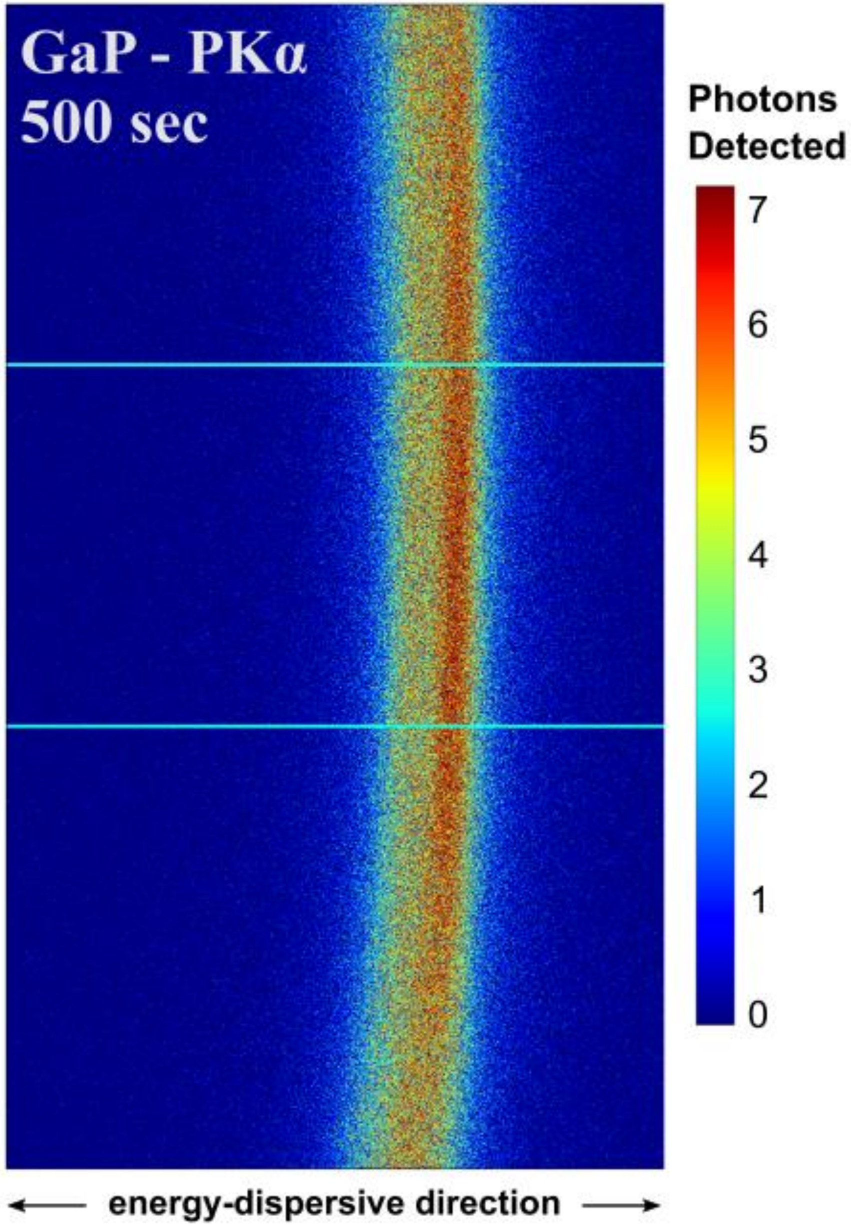
MEX2 'Brimstone' spectrometer



ALS 10.3.2
10^9 ph./sec.
2 hrs.
79° bragg
12 eV bandwidth

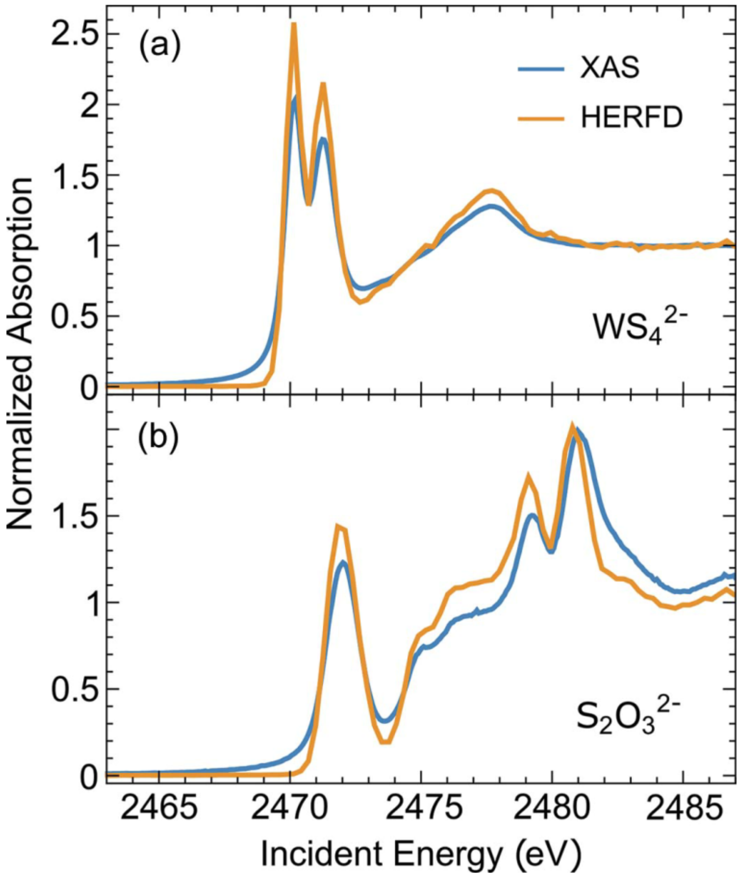


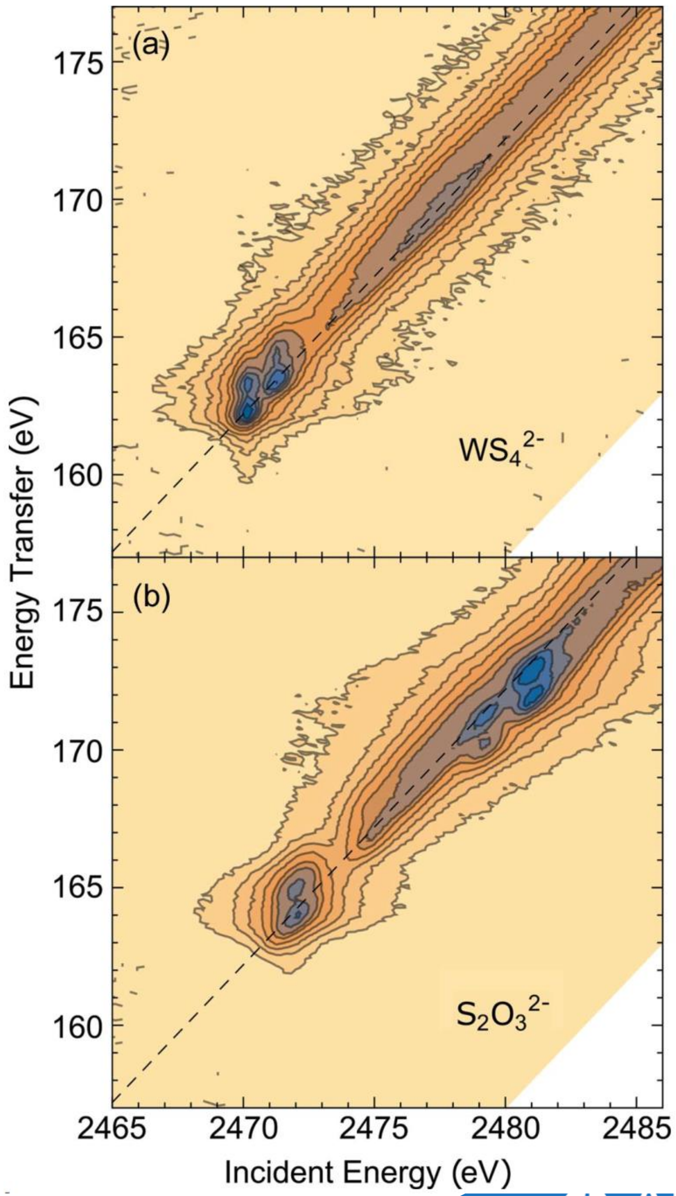
Lab source
59° bragg
46 eV bandwidth
~0.7 eV energy resolution



MEX2 ‘Brimstone’ spectrometer

- **S K-edge HERFD**
- SSRL BL 4-3
- 10^{12} photons/sec
- 5 min/incident energy point
- 0.5 eV incident energy step
- 5 hour RIXS plane
- 0.43 eV energy resolution
  - *cf.* S K-edge lifetime 0.53 eV





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Resonant inelastic X-ray scattering using a miniature dispersive Rowland refocusing spectrometer

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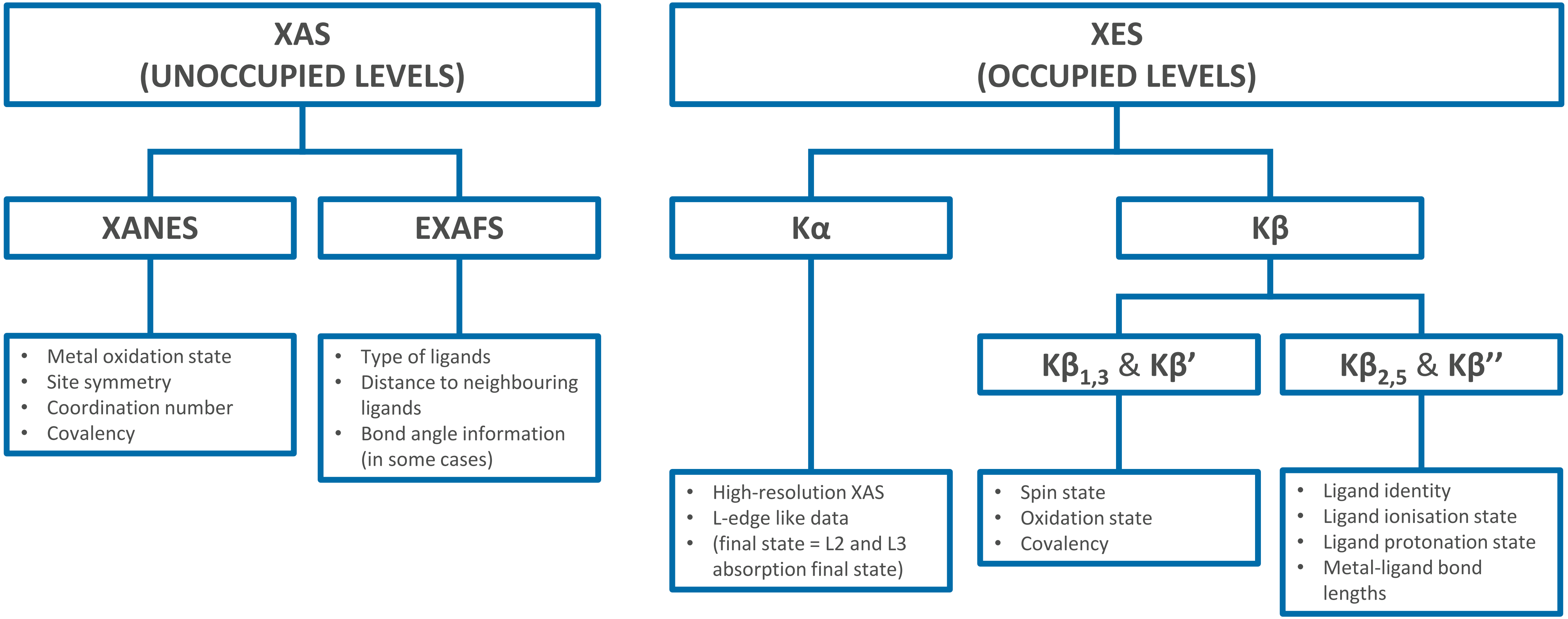
ANSTO

High resolution x-ray spectroscopy



Non-resonant XES not sensitive to self-absorption

Kowalska, J. & DeBeer, S. (2015). The role of X-ray spectroscopy in understanding the geometric and electronic structure of nitrogenase. *Biochimica et Biophysica Acta (BBA) - Molecular Cell Research* **1853**, 1406–1415.

ANSTO

Questions?

- Nehzati, S., Dolgova, N. V., James, A. K., Cotelesage, J. J. H., Sokaras, D., Kroll, T., George, G. N. & Pickering, I. J. (2021). High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy: An Analytical Method for Selenium Speciation. *Analytical Chemistry*. American Chemical Society **93**, 9235–9243.
- Castillo, R. G., Hahn, A. W., Van Kuiken, B. E., Henthorn, J. T., McGale, J. & DeBeer, S. (2021). Probing Physical Oxidation State by Resonant X-ray Emission Spectroscopy: Applications to Iron Model Complexes and Nitrogenase. *Angewandte Chemie* **133**, 10200–10209.
- Glatzel, P. *et al.* (2021). The five-analyzer point-to-point scanning crystal spectrometer at ESRF ID26. *Journal of Synchrotron Radiation* **28**, 362–371.
- Ditter, A. S., Holden, W. M., Cary, S. K., Mocko, V., Latimer, M. J., Nelson, E. J., Kozimor, S. A. & Seidler, G. T. (2020). Resonant inelastic X-ray scattering using a miniature dispersive Rowland refocusing spectrometer. *Journal of Synchrotron Radiation*. International Union of Crystallography **27**, 446–454.
- Lafuerza, S., Retegan, M., Detlefs, B., Chatterjee, R., Yachandra, V., Yano, J. & Glatzel, P. (2020). New reflections on hard X-ray photon-in/photon-out spectroscopy. *Nanoscale* **12**, 16270–16284.
- Zimmermann, P., Peredkov, S., Abdala, P. M., DeBeer, S., Tromp, M., Müller, C. & van Bokhoven, J. A. (2020). Modern X-ray spectroscopy: XAS and XES in the laboratory. *Coordination Chemistry Reviews* **423**, 213466.
- Rovezzi, M., Lapras, C., Manceau, A., Glatzel, P. & Verbeni, R. (2017). High energy-resolution x-ray spectroscopy at ultra-high dilution with spherically bent crystal analyzers of 0.5 m radius. *Review of Scientific Instruments* **88**, 013108.
- Proux, O. *et al.* (2017). High-Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy: A Powerful New Structural Tool in Environmental Biogeochemistry Sciences. *Journal of Environmental Quality* **46**, 1146–1157.
- Kowalska, J. K., Lima, F. A., Pollock, C. J., Rees, J. A. & DeBeer, S. (2016). A Practical Guide to High-resolution X-ray Spectroscopic Measurements and their Applications in Bioinorganic Chemistry. *Israel Journal of Chemistry* **56**, 803–815.
- Glatzel, P., Alonso-Mori, R. & Sokaras, D. (2016). 6. Hard X-ray photon-in/photon-out spectroscopy: instrumentation, theory and applications. *X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications*. John Wiley & Sons, Ltd., 125–152.
- Bokhoven, J. A. van & Lamberti, C. (eds) (2015). *X-ray absorption and X-ray emission spectroscopy: theory and applications*. Chichester, West Sussex: John Wiley & Sons, Inc.
- Heald, S. M. (2015). Strategies and limitations for fluorescence detection of XAFS at high flux beamlines. *Journal of Synchrotron Radiation* **22**, 436–445.
- Bauer, M. (2014). HERFD-XAS and valence-to-core-XES: new tools to push the limits in research with hard X-rays? *Physical Chemistry Chemical Physics* **16**, 13827–13837.
- Hall, E. R., Pollock, C. J., Bendix, J., Collins, T. J., Glatzel, P. & DeBeer, S. (2014). Valence-to-Core-Detected X-ray Absorption Spectroscopy: Targeting Ligand Selectivity. *Journal of the American Chemical Society* **136**, 10076–10084.
- Gallo, E. & Glatzel, P. (2014). Valence to Core X-ray Emission Spectroscopy. *Advanced Materials* **26**, 7730–7746.
- Rovezzi, M. & Glatzel, P. (2014). Hard x-ray emission spectroscopy: a powerful tool for the characterization of magnetic semiconductors. *Semiconductor Science and Technology* **29**, 023002.
- Lambertz, C., Chernev, P., Klingan, K., Leidel, N., Sigfridsson, K. G. V., Happe, T. & Haumann, M. (2014). Electronic and molecular structures of the active-site H-cluster in [FeFe]-hydrogenase determined by site-selective X-ray spectroscopy and quantum chemical calculations. *Chem. Sci.* **5**, 1187–1203.
- Glatzel, P., Weng, T.-C., Kvashnina, K., Swarbrick, J., Sikora, M., Gallo, E., Smolentsev, N. & Mori, R. A. (2013). Reflections on hard X-ray photon-in/photon-out spectroscopy for electronic structure studies. *Journal of Electron Spectroscopy and Related Phenomena* **188**, 17–25.
- Glatzel, P. & Juhin, A. (2013). X-ray Absorption and Emission Spectroscopy. *Local Structural Characterisation*. John Wiley & Sons, Ltd, 89–171.
- Bianchini, M. & Glatzel, P. (2012). A tool to plan photon-in/photon-out experiments: count rates, dips and self-absorption. *Journal of Synchrotron Radiation* **19**, 911–919.
- Llorens, I. *et al.* (2012). High energy resolution five-crystal spectrometer for high quality fluorescence and absorption measurements on an x-ray absorption spectroscopy beamline. *Review of Scientific Instruments* **83**, 063104.
- DeBeer, S. & Bergmann, U. (2011). X-Ray Emission Spectroscopic Techniques in Bioinorganic Applications. *Encyclopedia of Inorganic and Bioinorganic Chemistry*. John Wiley & Sons, Ltd.
- Singh, J., Lamberti, C. & van Bokhoven, J. A. (2010). Advanced X-ray absorption and emission spectroscopy: in situ catalytic studies. *Chemical Society Reviews* **39**, 4754.
- Rueff, J.-P. Inelastic X-Ray Scattering by Electronic Excitations under High Pressure. *Rev. Mod. Phys.* **2010**, *82* (1), 847–896.
- Glatzel, P., Sikora, M. & Fernández-García, M. (2009). Resonant X-ray spectroscopy to study K absorption pre-edges in 3d transition metal compounds. *The European Physical Journal Special Topics* **169**, 207–214.
- Hazemann, J.-L. *et al.* (2009). High-resolution spectroscopy on an X-ray absorption beamline. *Journal of Synchrotron Radiation* **16**, 283–292.
- Glatzel, P. & Bergmann, U. (2005). High resolution 1s core hole X-ray spectroscopy in 3d transition metal complexes—electronic and structural information. *Coordination Chemistry Reviews* **249**, 65–95.