MAX PLANCK INSTITUTE
FOR CHEMICAL ENERGY CONVERSION

Application of an in house von Hamos EXAFS spectrometer to NH_3 decomposition studies

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DeBeer Group – MPI CEC, Germany

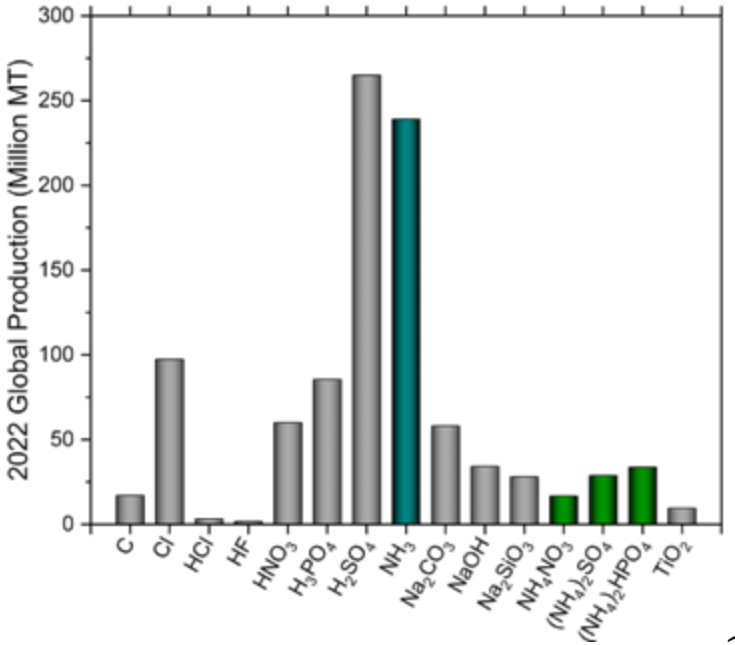
lab-X^3: 3rd Workshop on High-energy-resolution Laboratory X-ray Spectroscopy

03.10.2024

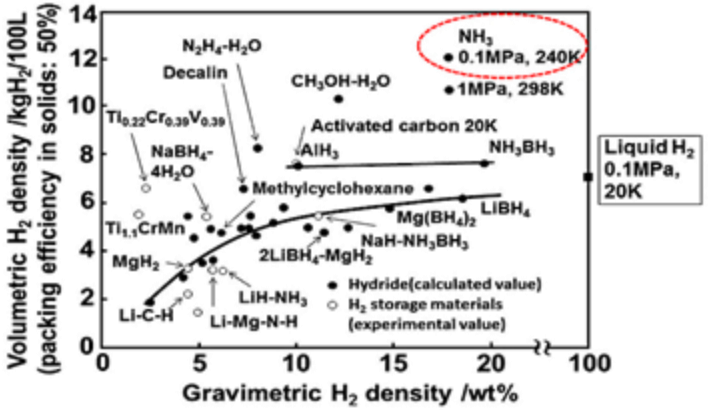
OUTLINE

1. Overview of NH_3 Decomposition
2. EXAFS in Catalysis Research
3. In house von Hamos EXAFS spectrometer
4. Assessment of current spectrometer performance
    a) Benchmarking studies
    b) Impact of detector-related parameters
    c) Estimation of relative error
    d) Updates on the *in situ* cell setup
5. Summary & Outlook

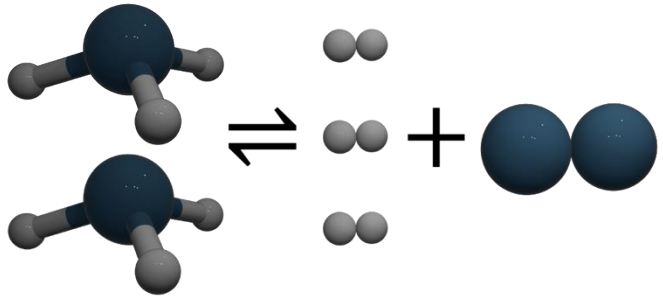
CATALYTIC NH_3 DECOMPOSITION: OVERVIEW



Statista ©, "Global production of Inorganic Chemicals", accessed 13.01.2024

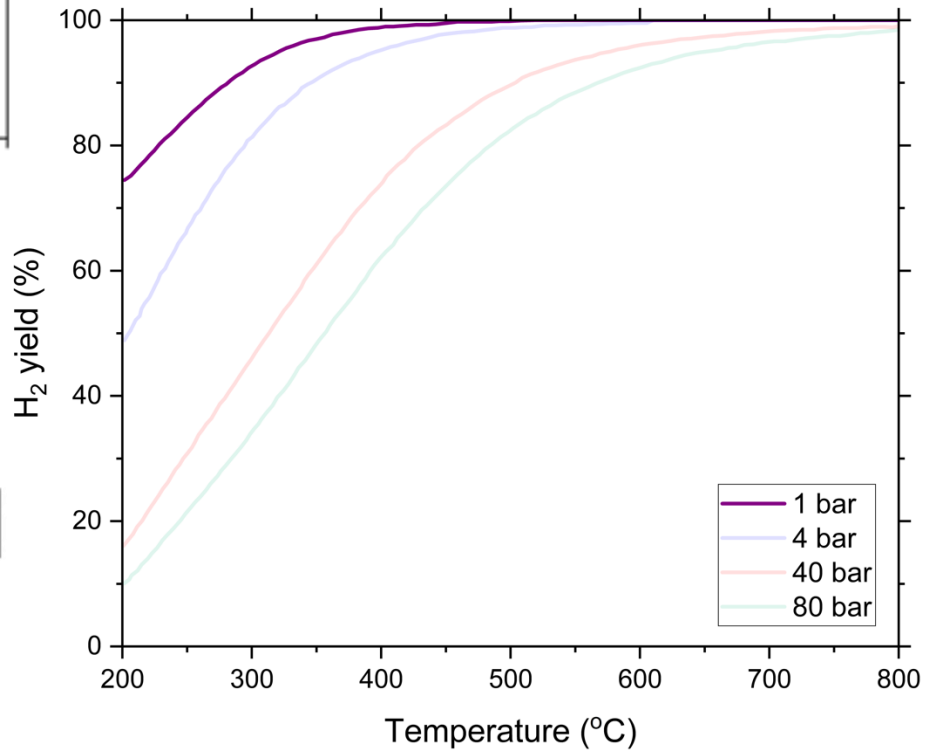


Energies **2021**, *14*(13), 3732.

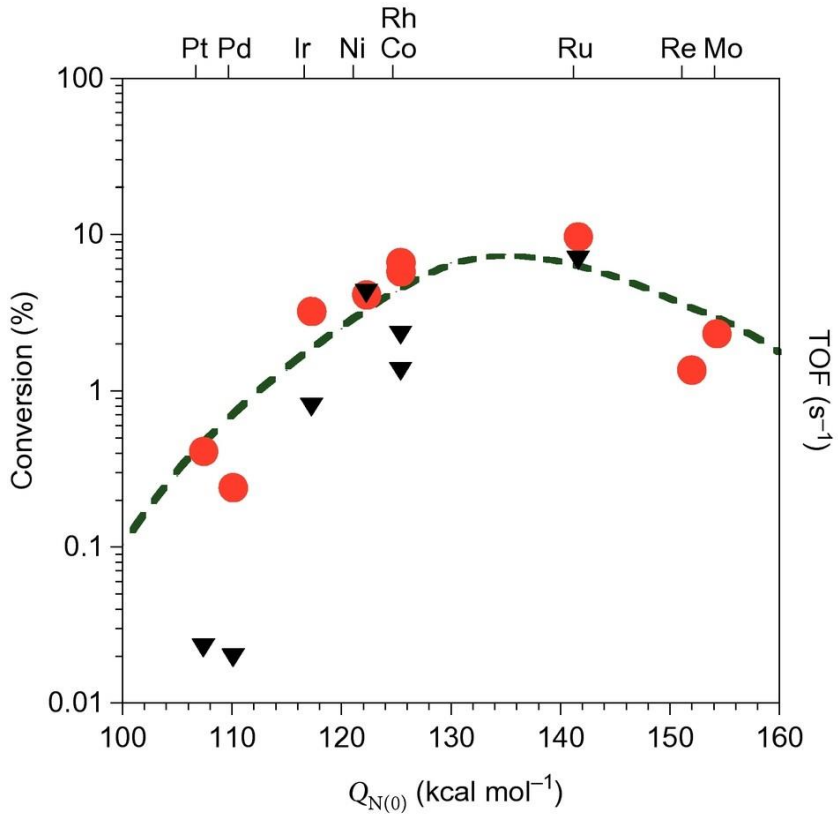


$$2NH_3 \rightleftharpoons 3H_2 + N_2$$

$$\Delta H_o = 46.2 kJ/mol_{NH_3}$$



replotted from: Chemie Ingenieur Technik 94 **2022**, *10*, 1413-1425.



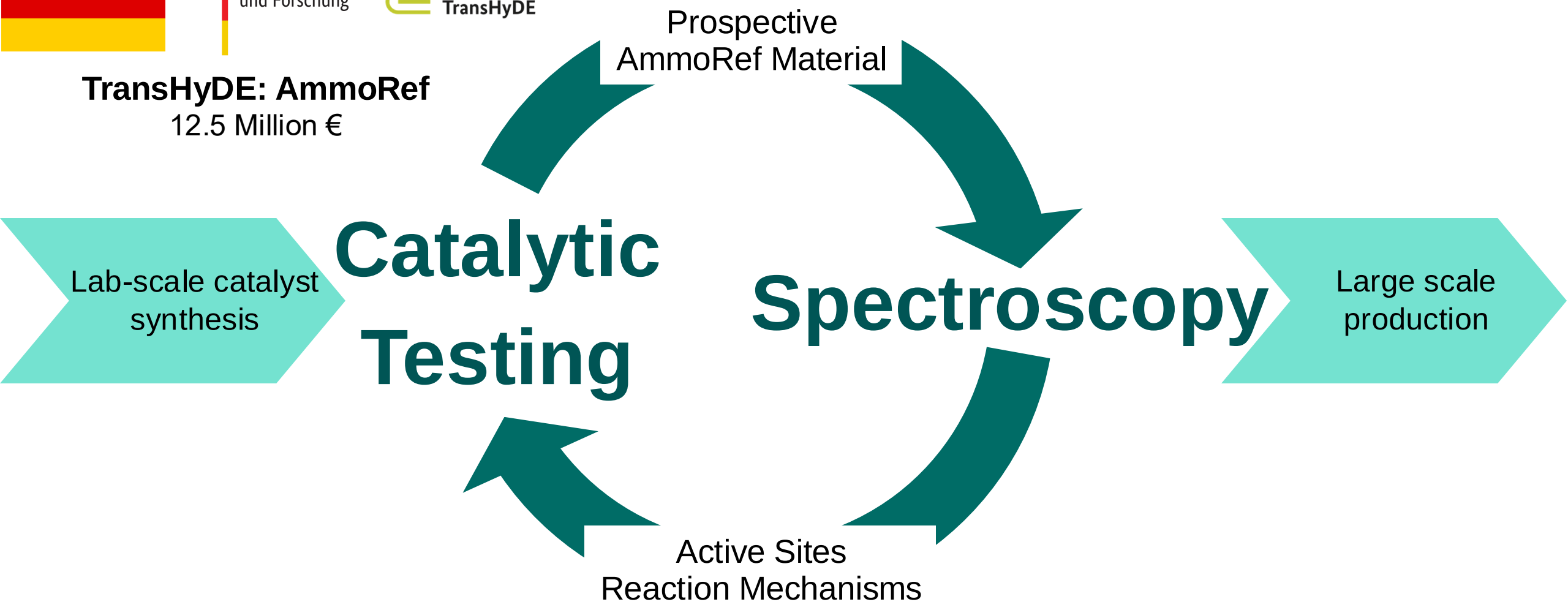
Nat. Chem. **2010**, *2*, 484-489.

CATALYTIC NH_3 DECOMPOSITION: AmmoRef NETWORK

Bundesministerium für Bildung und Forschung

Leitprojekt TransHyDE

TransHyDE: AmmoRef
12.5 Million €



CATALYTIC NH_3 DECOMPOSITION: AmmoRef NETWORK

Spectroscopic Technique	Chemical Information
XANES	Local ligand field
	Oxidation state
	Site symmetry
EXAFS	Type of nearest neighbor
	Near neighbor distances
	Coordination number
	Thermal vibrations, Static disorder
VtC-XES	Ligand identity & nature
	Ligand-metal bonding
	Coordination environment
XRD	Chemical composition
	Crystal structure & properties
NAP-XPS & NEXAFS	Identity of surface species
	Surface oxidation state

Spectroscopy

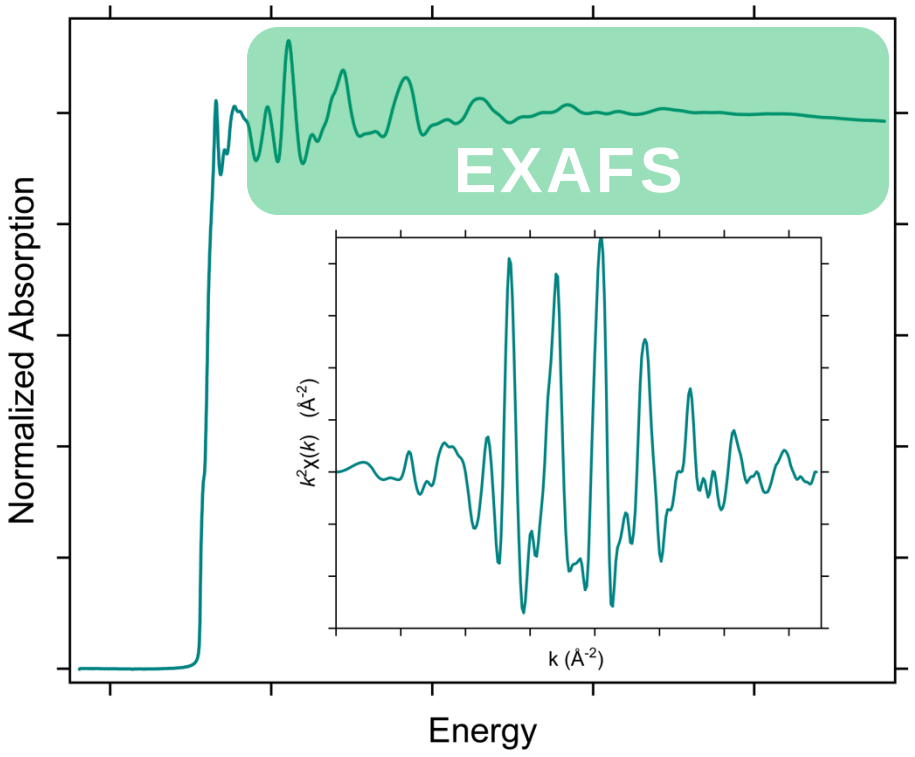
EXAFS IN CATALYSIS RESEARCH

Spectroscopic Technique	Chemical Information
XANES	Local ligand field
	Oxidation state
	Site symmetry
EXAFS	Type of nearest neighbor
	Near neighbor distances (R)
	Coordination number (N)
	Thermal vibrations, Static disorder (σ^2)
NEXAFS	Surface oxidation state

- Sensitive to short range structural order.
- Can accommodate wide range of sample types (e.g., liquids, amorphous solids).

∴ EXAFS can serve as a complementary technique to X-ray diffraction.

Extended X-ray absorption fine structure



$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} sin[2kR_j + \delta_j(k)] S_0^2$$

EXAFS IN CATALYSIS RESEARCH

Spectroscopic Technique	Chemical Information
XANES	Local ligand field
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EXAFS	Type of nearest neighbor
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- Sensitive to short range structural order.
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∴ EXAFS can serve as a complementary technique to X-ray diffraction.

Why EXAFS in NH_3 decomposition?

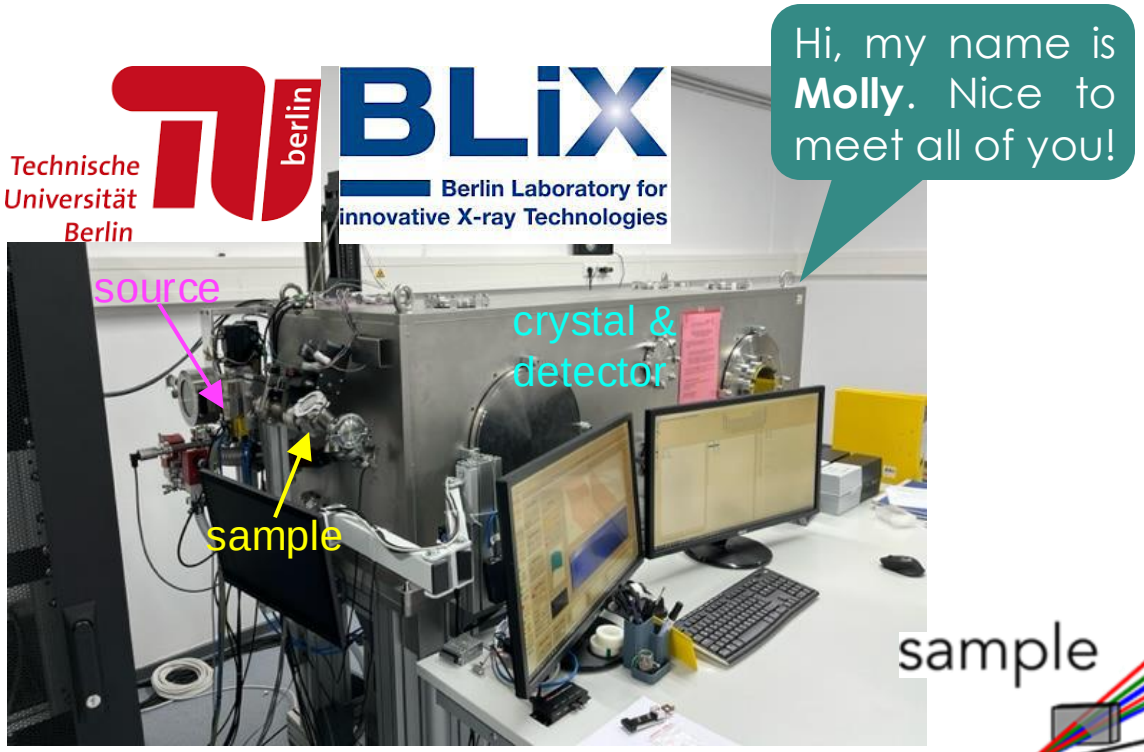
- starting materials undergo reconstruction during activation/pre-treatment‡
  - $MgFe_2O_4 \longmapsto Fe/MgO$
  - $MgFeCoO_4 \longmapsto FeCo/MgO$
- bulk nitride formation can occur during reaction§
  - $Fe \longmapsto Fe_xN_y$ (e.g., ε-Fe_3N_{1+z}, γ-Fe_4N_{1-z})

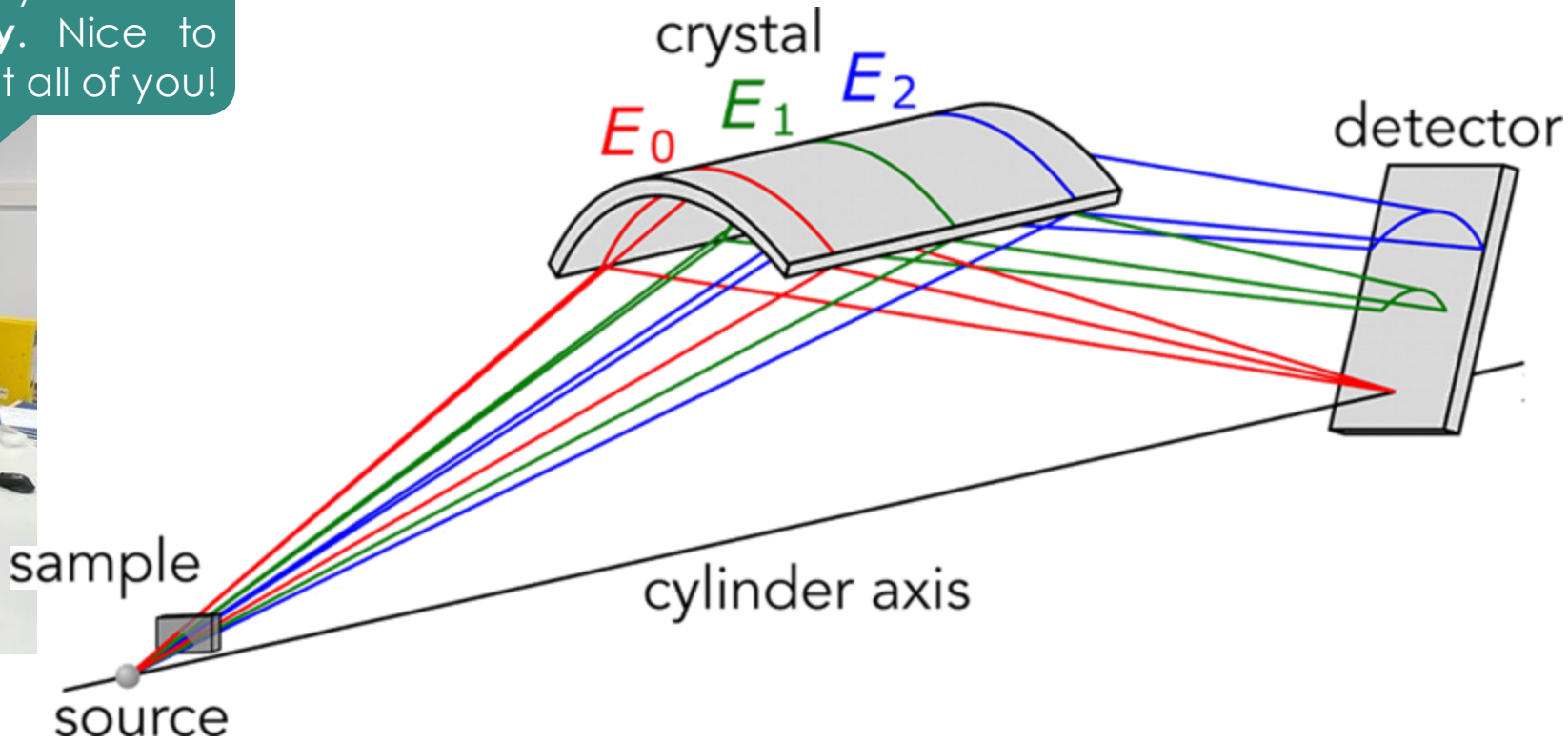
‡ Nat. Commun., **2024**, *15*, 871.

§ Ind. Eng. Chem. Res., **2021**, *60*, 18560−18611.

LABORATORY-BASED EXAFS

In house von Hamos spectrometer at MPI CEC

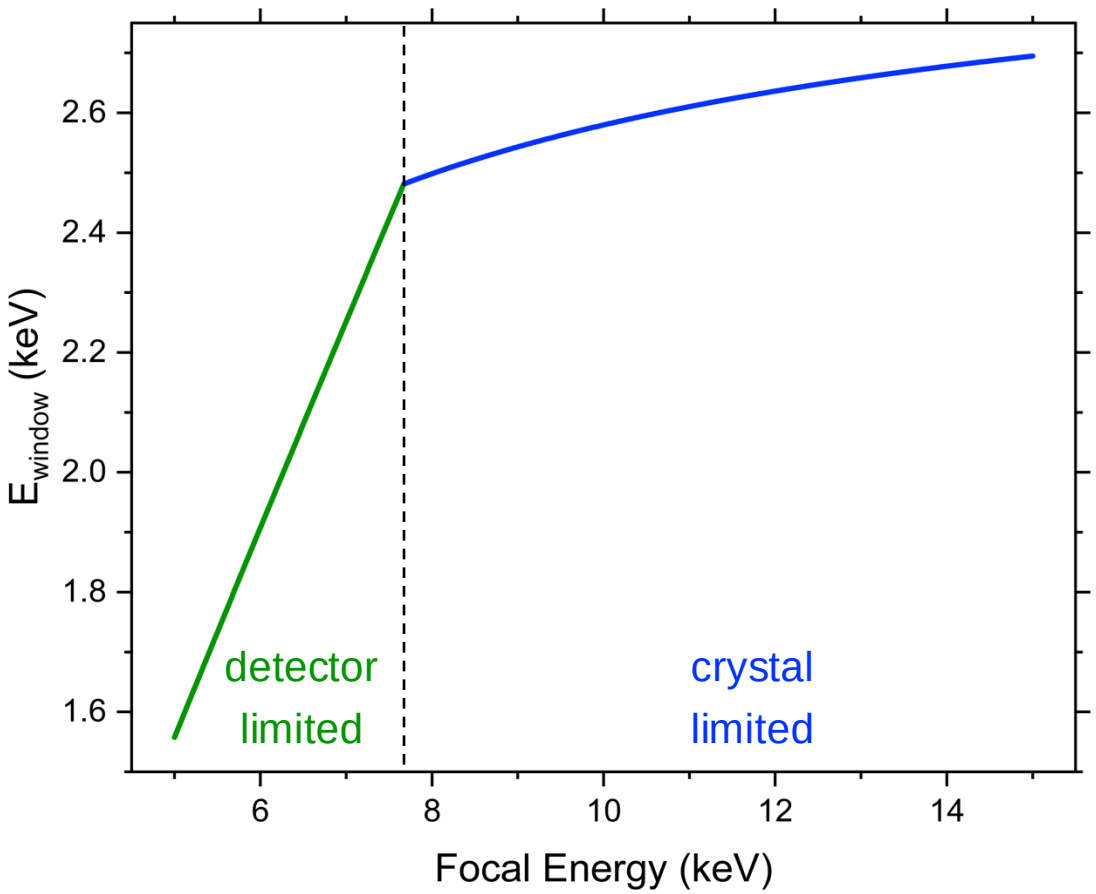




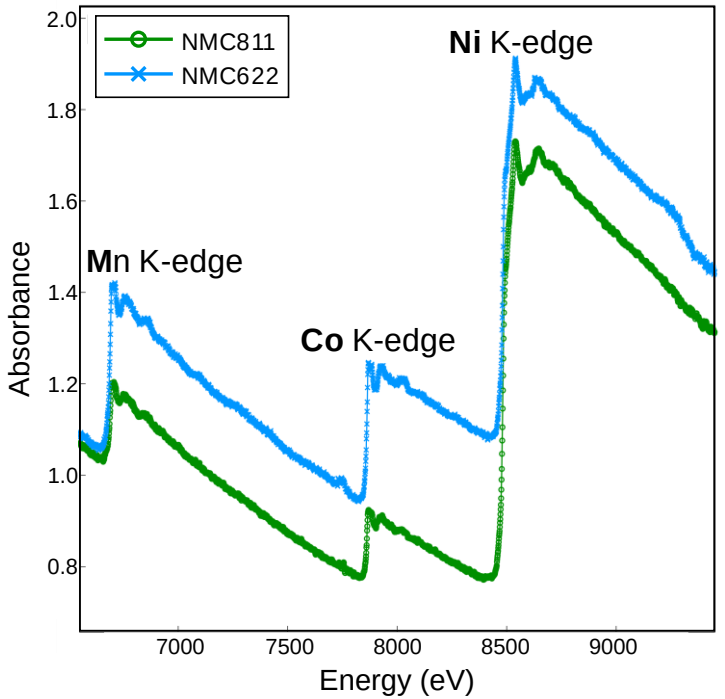
Spectrochim. Acta Part B: At. Spectrosc., **2021,** *177*, 106101.; Naturwissenschaften, **1932**, *20*, 705–706.; J. Appl. Cryst., **1988**, *21*, 79.

LABORATORY-BASED EXAFS

Advantages of the von Hamos geometry's broad E_{window}



Simultaneous measurements for multi-metallic catalysts



Courtesy: Y. Kayser

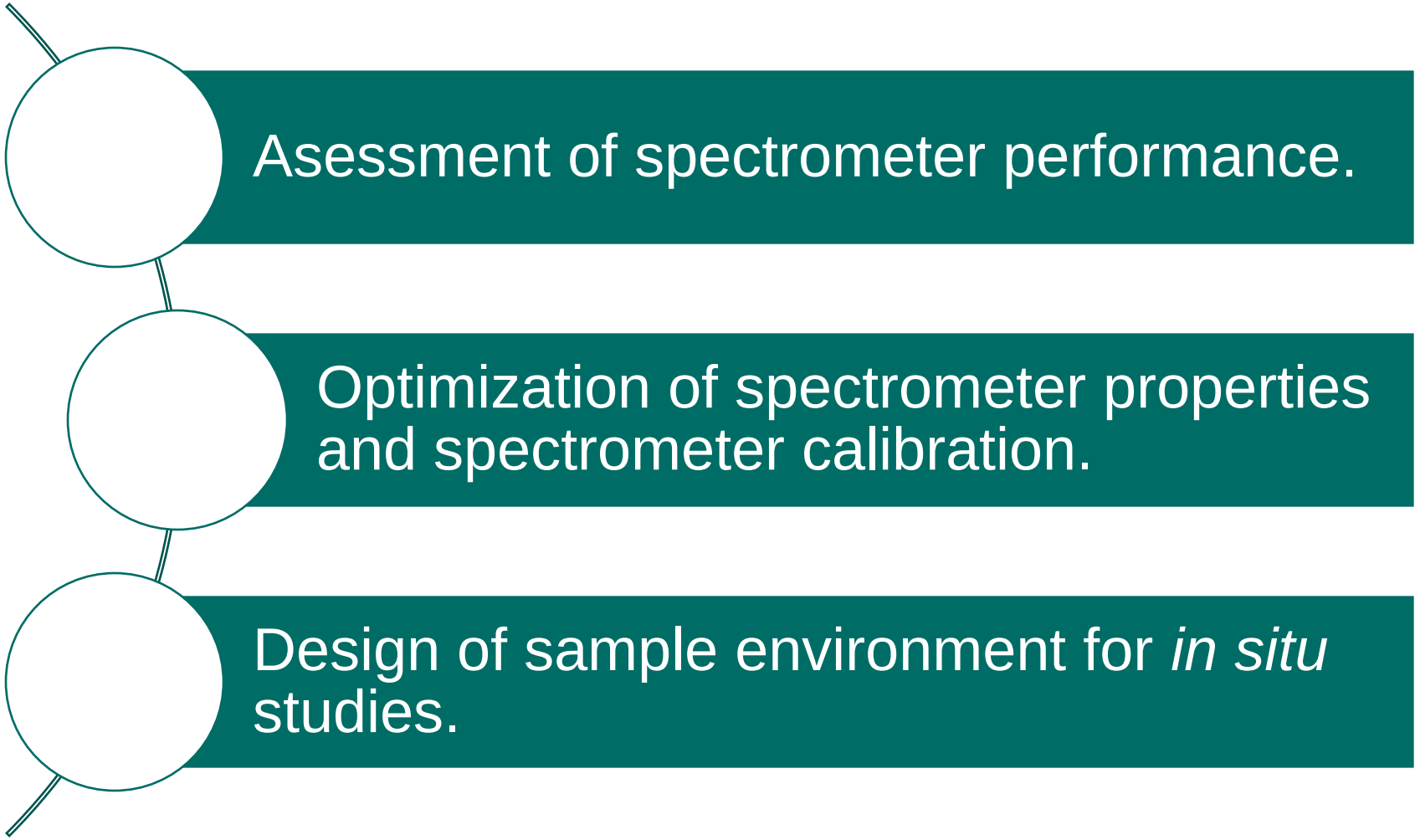
FT-EXAFS resolution is dependent on k_{range} transformed.

$$E_{window} \propto \Delta k$$

$$\mathbb{R} = \frac{\pi}{2\Delta k}$$

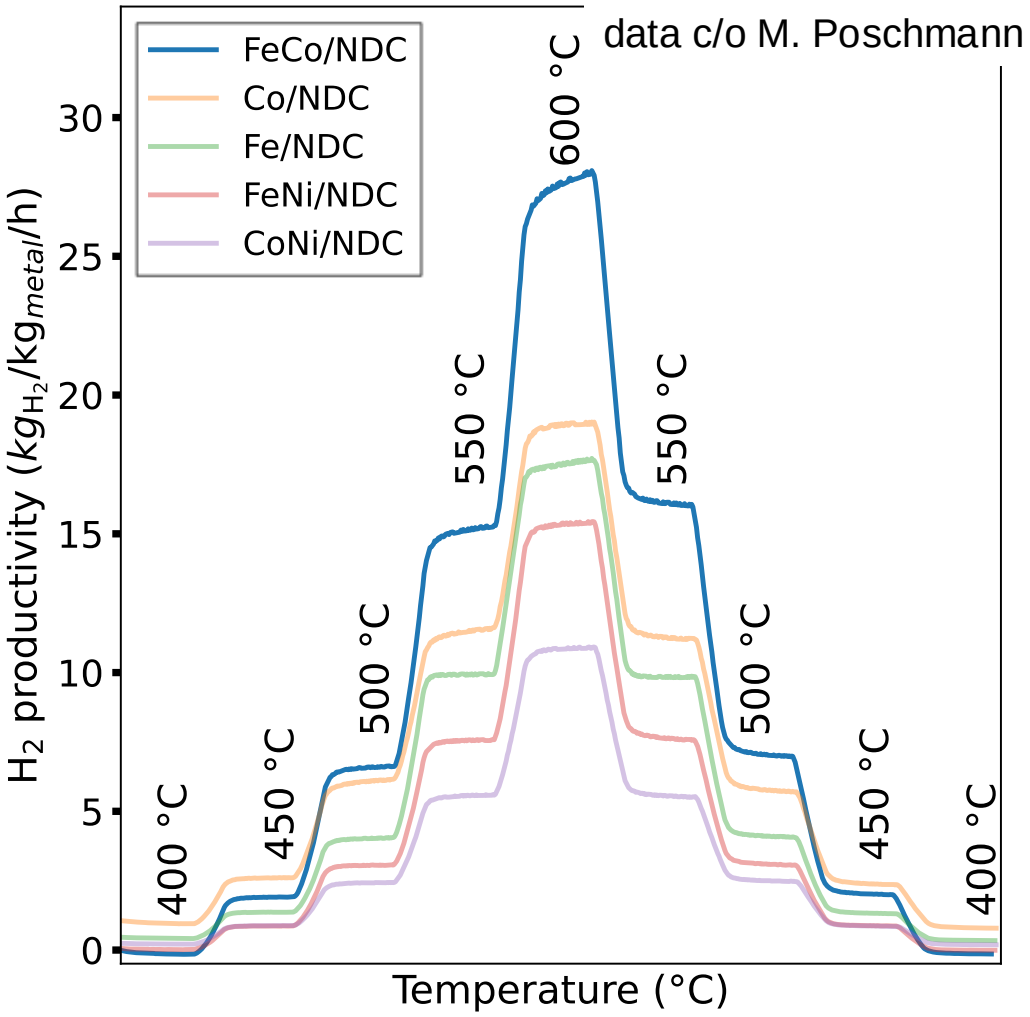
$\mathbb{R}$: smallest distance between two scattering shells that can be resolved

PROJECT OBJECTIVES



ASSESSMENT OF SPECTROMETER PERFORMANCE

Benchmarking laboratory measurements to synchrotron data



Reference Material (i.e., metal foil)

EXAFS Fitting: N (fixed), R, σ^2, S_0^2

Supported metal catalyst (M/NDC)

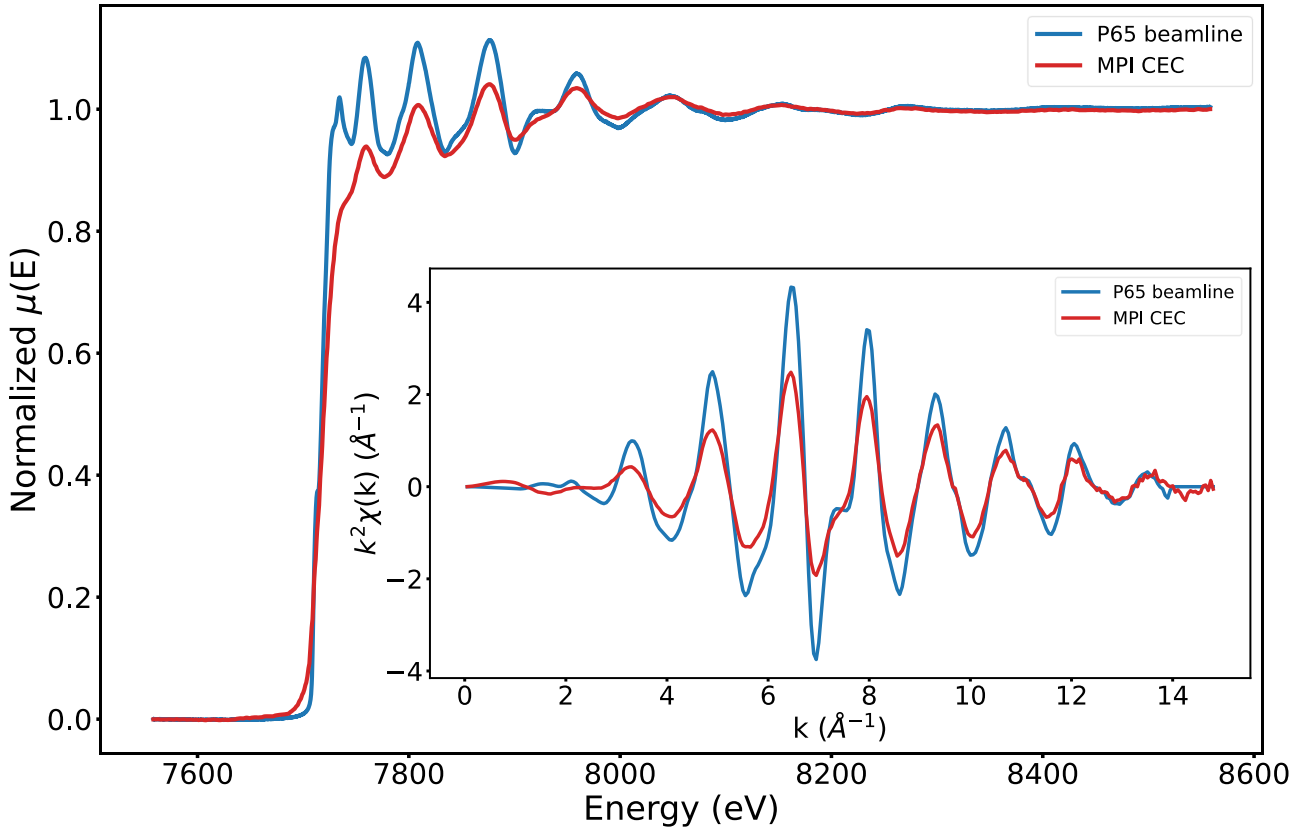
EXAFS Fitting: S_0^2 (fixed), R, σ^2, N

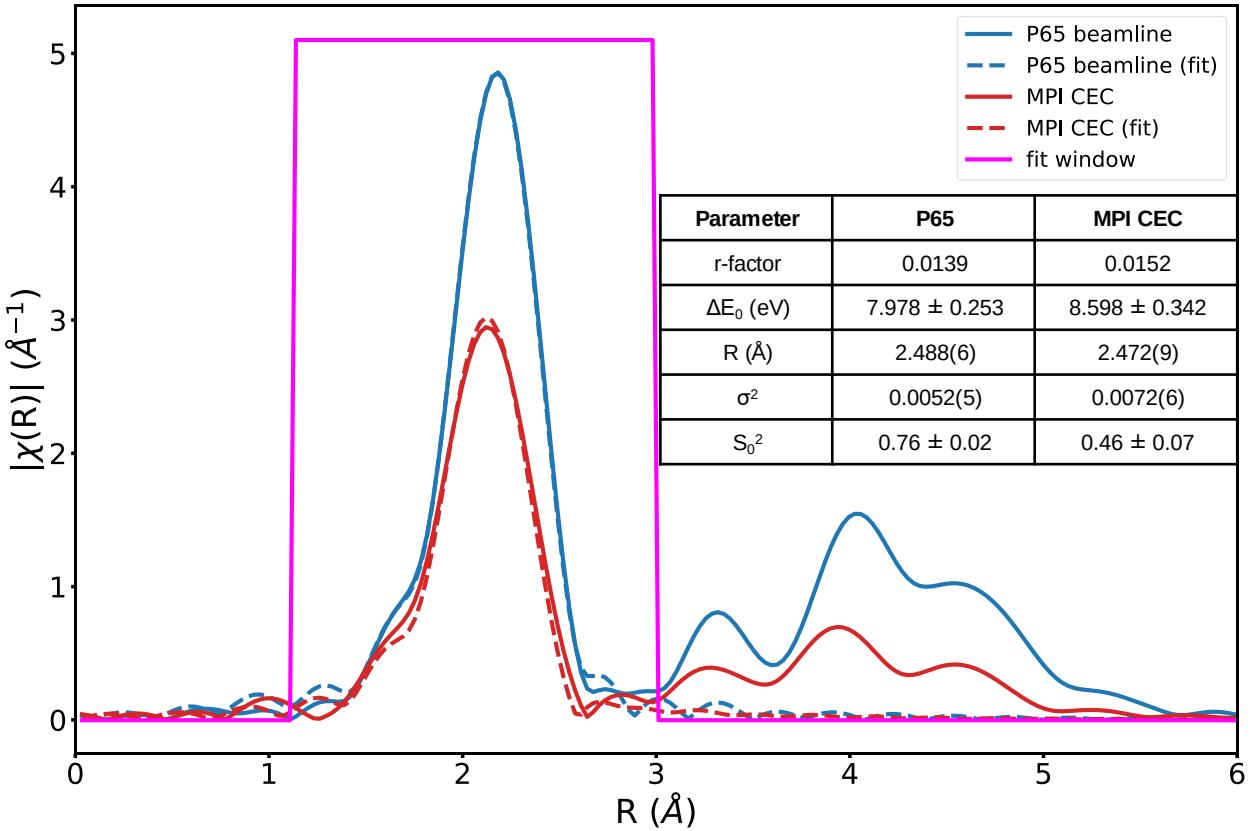
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} sin[2kR_j + \delta_j(k)] S_0^2$$

ASSESSMENT OF SPECTROMETER PERFORMANCE

Benchmarking laboratory measurements to synchrotron data

Co foil measurements



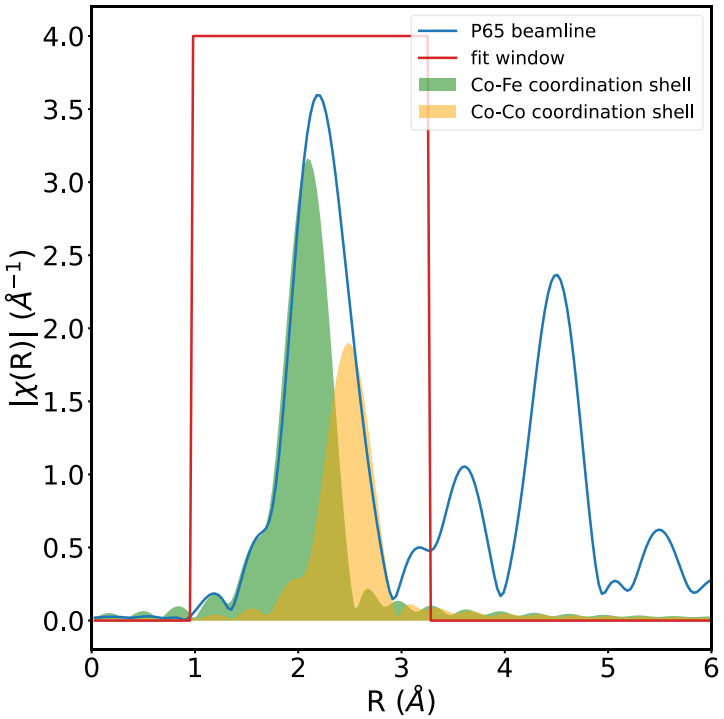


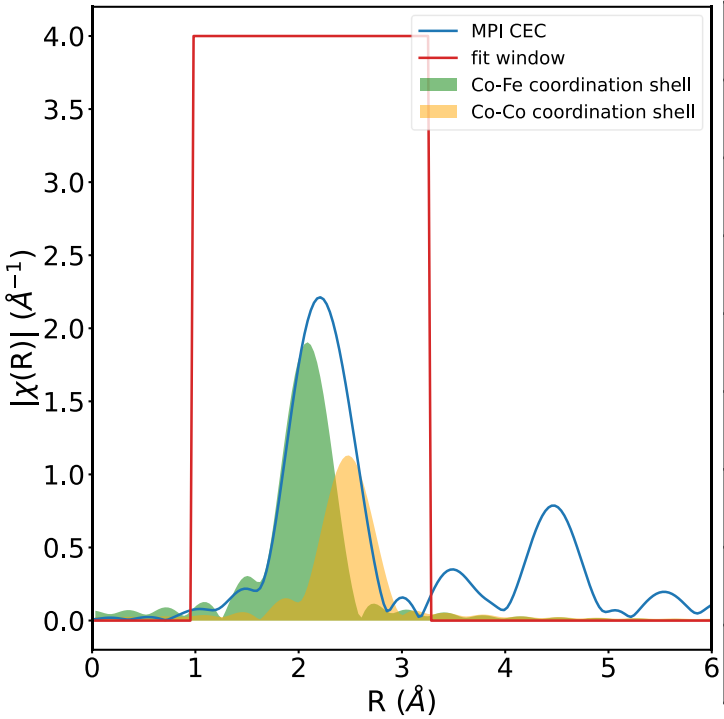
Parameter	P65	MPI CEC
r-factor	0.0139	0.0152
ΔE_0 (eV)	7.978 ± 0.253	8.598 ± 0.342
R (Å)	2.488(6)	2.472(9)
σ^2	0.0052(5)	0.0072(6)
S_0^2	0.76 ± 0.02	0.46 ± 0.07

ASSESSMENT OF SPECTROMETER PERFORMANCE

Benchmarking laboratory measurements to synchrotron data

Co K-edge of CoFe/NDC catalyst (as prepared)





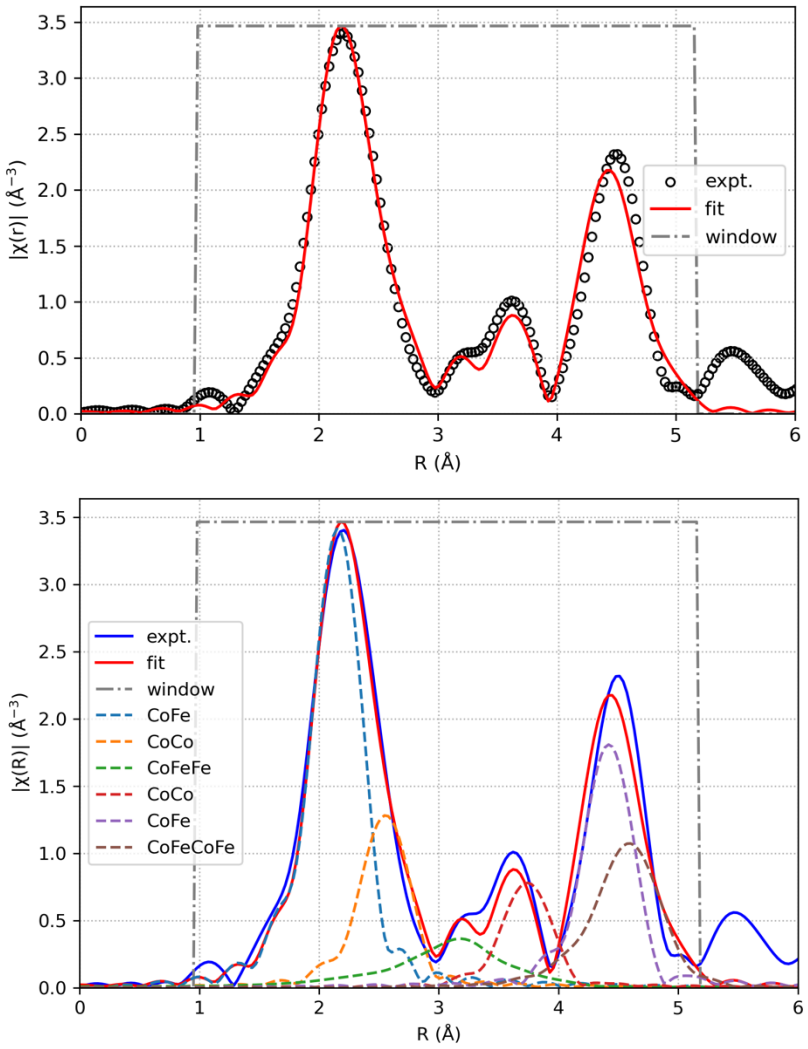
Parameter	P65 Beamline	MPI CEC
S_0^2 ‡	0.76 ± 0.02	0.46 ± 0.07
r-factor	0.0179	0.0192
ΔE_0 (eV)	4.215 ± 2.167	5.432 ± 2.932
σ^2	0.0047(3)	0.0056(8)
R_{Co-Fe} (Å)	2.45(5)	2.47(4)
R_{Co-Co} (Å)	2.82(9)	2.81(8)
N_{Co-Fe}	6.3 ± 0.6	6.5 ± 0.9
N_{Co-Co}	5.5 ± 0.8	5.6 ± 1.4

‡ from EXAFS fitting of Co foil measured at the P65 Beamline and at MPI CEC

ASSESSMENT OF SPECTROMETER PERFORMANCE

Benchmarking laboratory measurements to synchrotron data

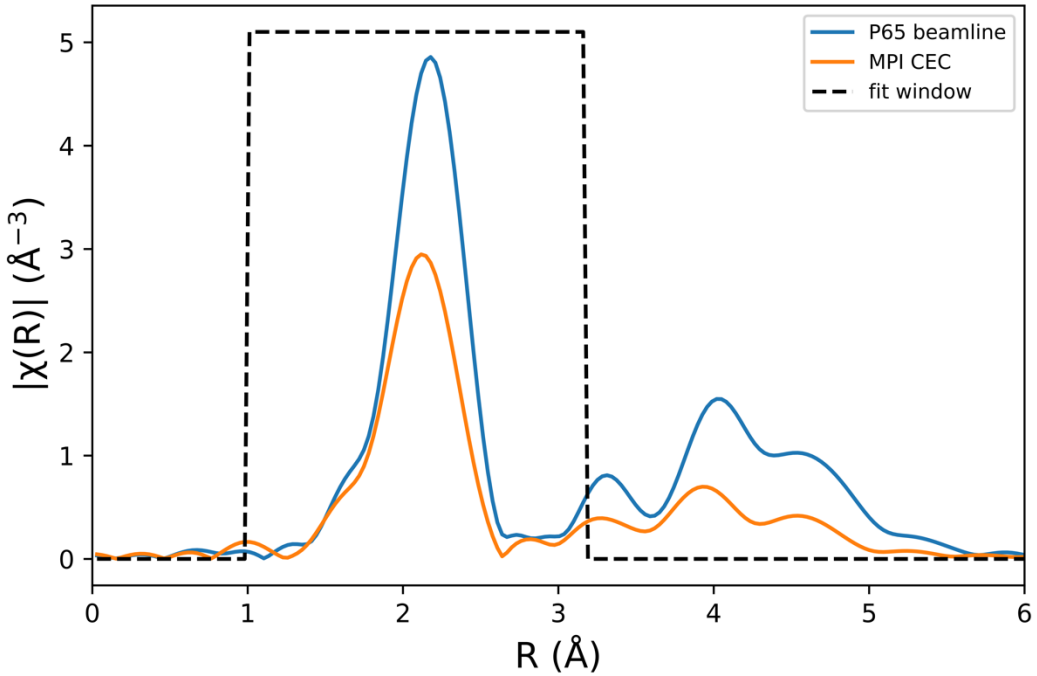
What happens to a wider fitting window?

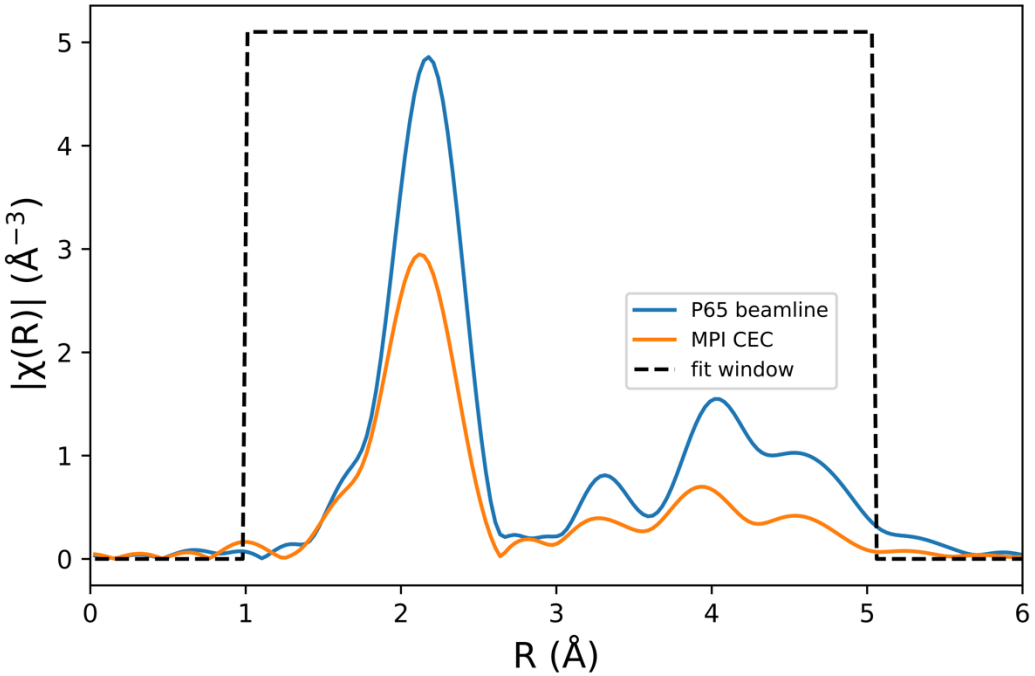


Parameter	P65 Beamline	MPI CEC
S_0^2	0.80 ± 0.05	0.48 ± 0.09
r-factor	0.0215	0.0344
ΔE_0 (eV)	9.832 ± 0.869	10.657 ± 1.269
$N_{Co\text{-}Fe}$	6.4 ± 0.9	5.9 ± 1.2
$N_{Co\text{-}Co}$	4.2 ± 0.7	3.7 ± 2.8
$N_{Co\text{-}Fe\text{-}Fe}$	78.3 ± 22.7	62.5 ± 15.6
$N_{Co\text{-}Co'}$	6.4 ± 1.9	9.3 ± 1.5
$N_{Co\text{-}Fe'}$	20.8 ± 3.8	18.7 ± 2.7
$N_{Co\text{-}Fe\text{-}Co\text{-}Fe}$	9.2 ± 3.1	7.4 ± 4.5
$R_{Co\text{-}Fe}$ (Å)	2.48(5)	2.49(9)
$R_{Co\text{-}Co}$ (Å)	2.86(5)	2.88(7)
$R_{Co\text{-}Fe\text{-}Fe}$ (Å)	3.91(8)	3.94(2)
$R_{Co\text{-}Co'}$ (Å)	4.05(8)	4.07(6)
$R_{Co\text{-}Fe'}$ (Å)	4.75(9)	4.79(2)
$R_{Co\text{-}Fe\text{-}Co\text{-}Fe}$ (Å)	4.94(9)	4.98(7)
σ^2 (s.s)	0.0047(9)	0.0058 ± 0.023
σ^2 (n.l.s)	0.0074(1)	0.0088 ± 0.014
σ^2 (m.s)	0.0056(2)	0.0126 ± 0.011

ASSESSMENT OF SPECTROMETER PERFORMANCE

Benchmarking laboratory measurements to synchrotron data





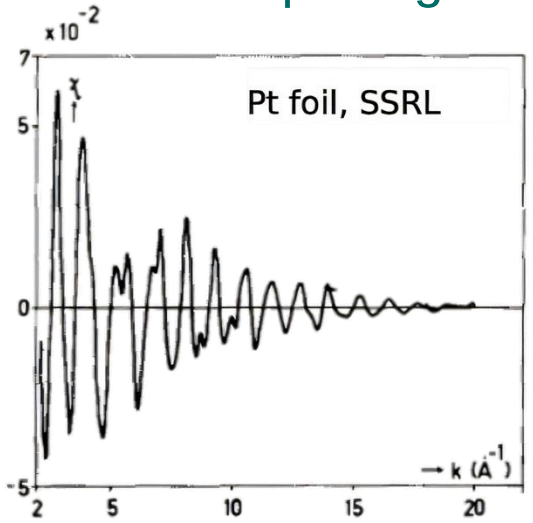
Fitting Window (Å)	RMSE§
1 − 3.3 Å	0.0303
1 − 5.2 Å	0.0461

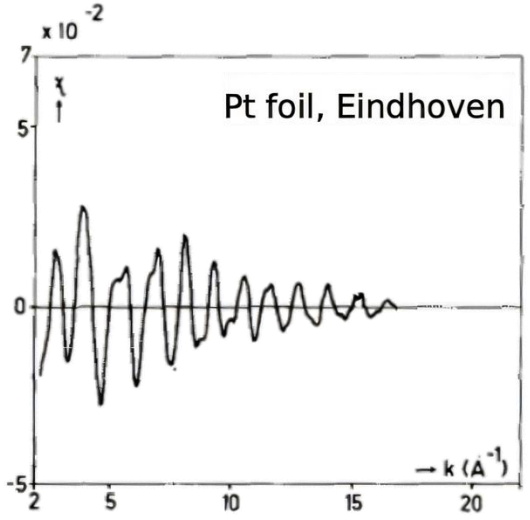
§ statistical measure of ‘similarity’ between the shape of SR & lab EXAFS

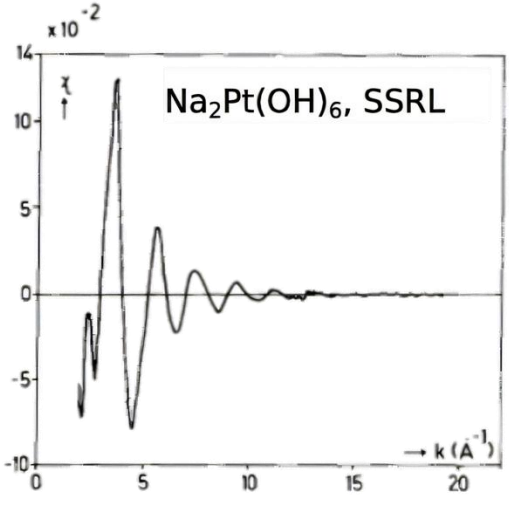
∴ S_0^2 and overall shape of the EXAFS data dictate the degree of similarity of extracted chemical information from SR and lab measurements.

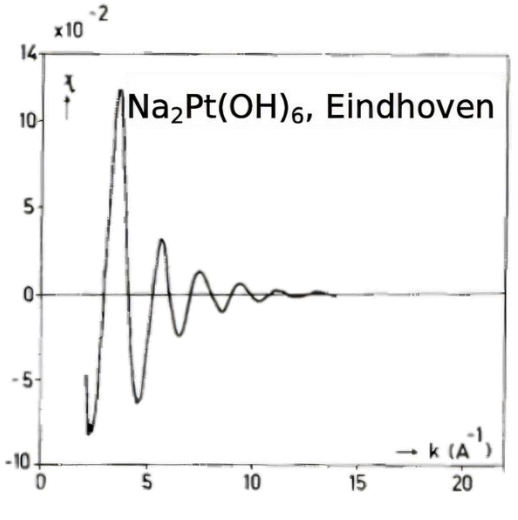
ASSESSMENT OF SPECTROMETER PERFORMANCE

Dampening in EXAFS features: not a new observation in lab-based instrumentation.

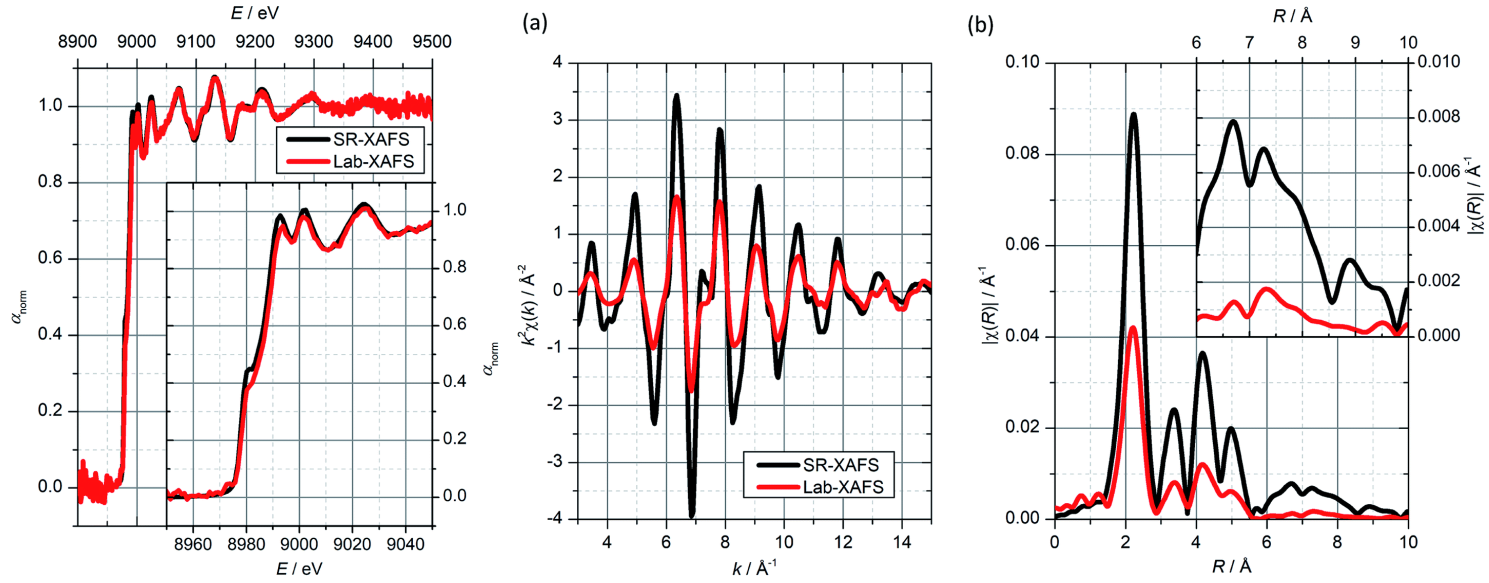








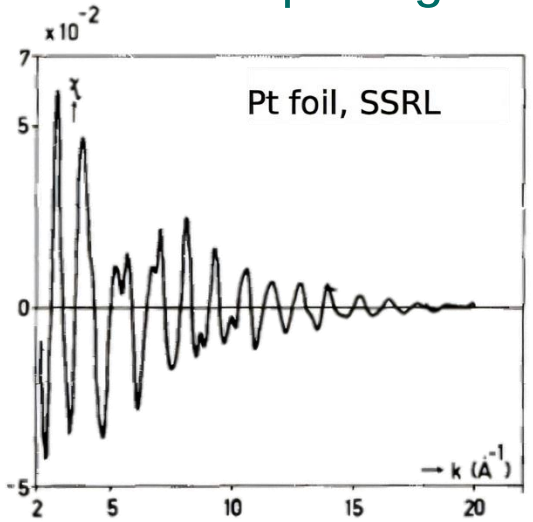
Solid State Ionics, **1985**, *16*, 55-64.

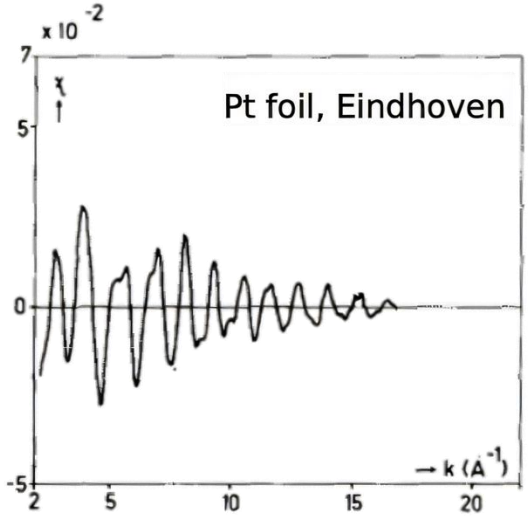


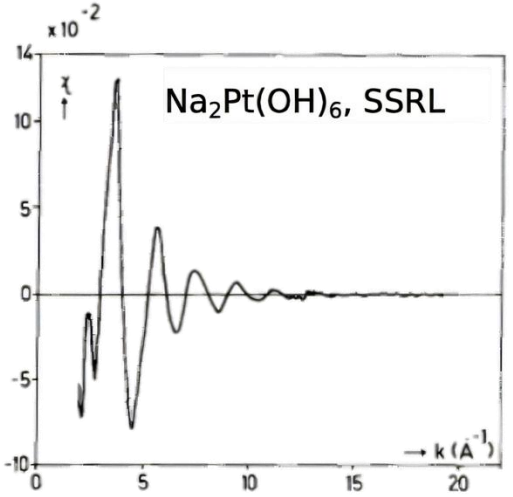
J. Anal. At. Spectrom. **2020**, *35*, 2298.

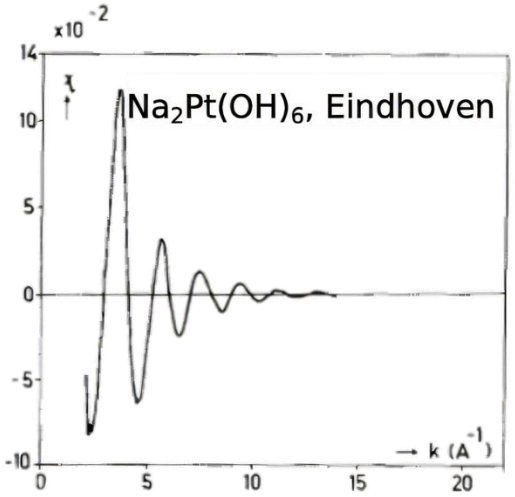
ASSESSMENT OF SPECTROMETER PERFORMANCE

Dampening in EXAFS features: not a new observation in lab-based instrumentation.





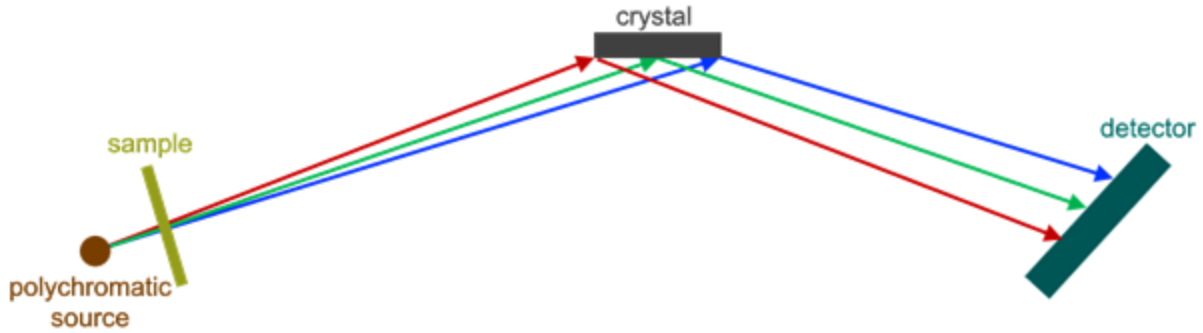




Solid State Ionics, **1985**, *16*, 55-64.

∴ instrument resolution influences degree of dampening

$$\frac{\Delta E}{E}_{overall} = \sqrt{\left(\frac{\Delta E}{E}_{source}\right)^2 + \left(\frac{\Delta E}{E}_{crystal}\right)^2 + \left(\frac{\Delta E}{E}_{detector}\right)^2}$$



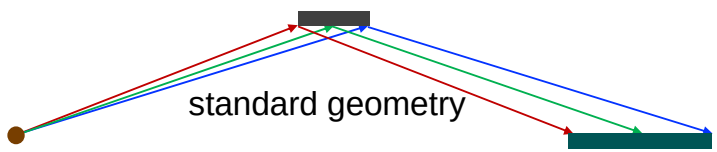
detector-related parameters:

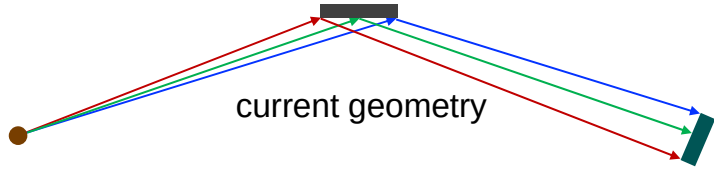
- detector orientation
- focal energy (E_0)
- image processing

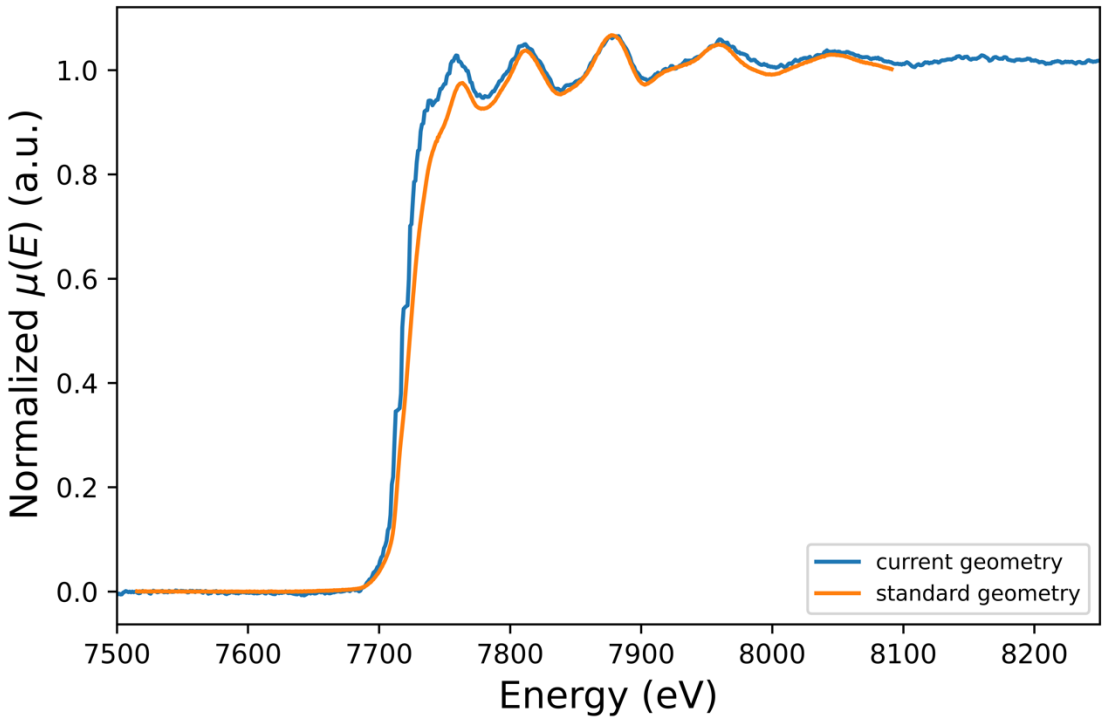
ASSESSMENT OF SPECTROMETER PERFORMANCE

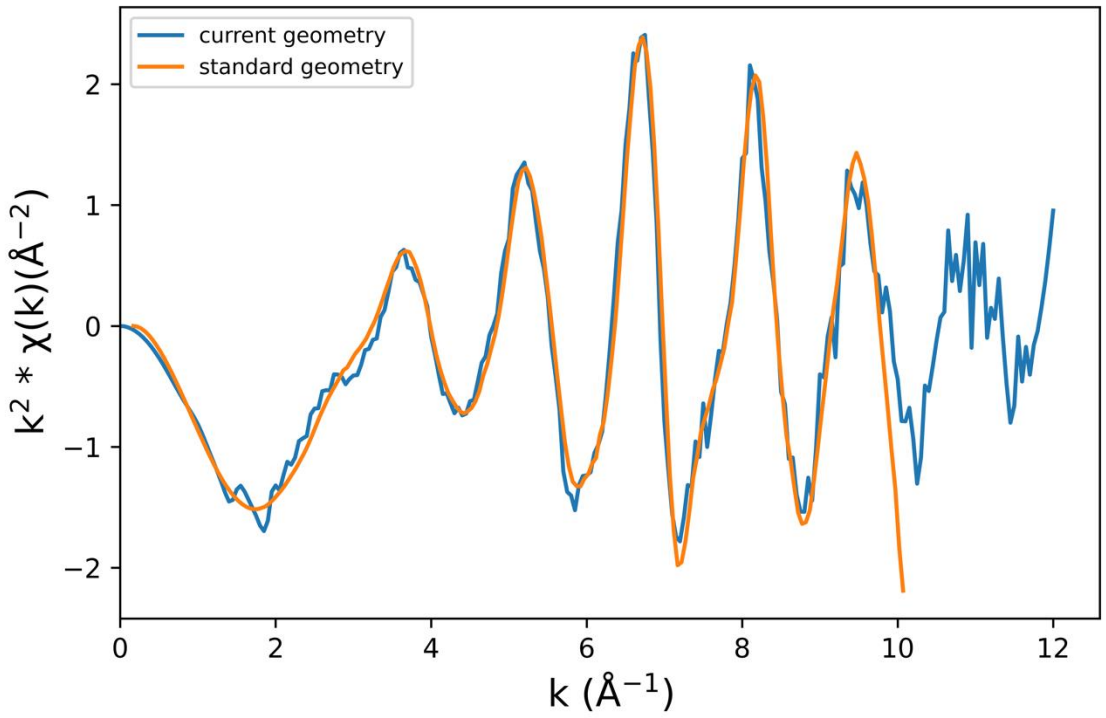
Impact of detector-related parameters to S_0^2 and overall shape of EXAFS.

- detector orientation







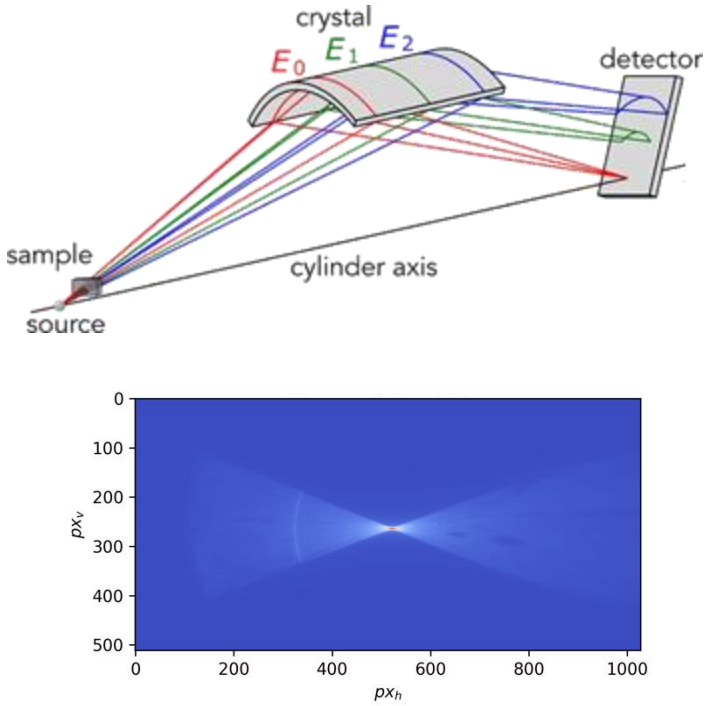


∴ orientation has minimal impact on S_0^2 and overall shape of EXAFS

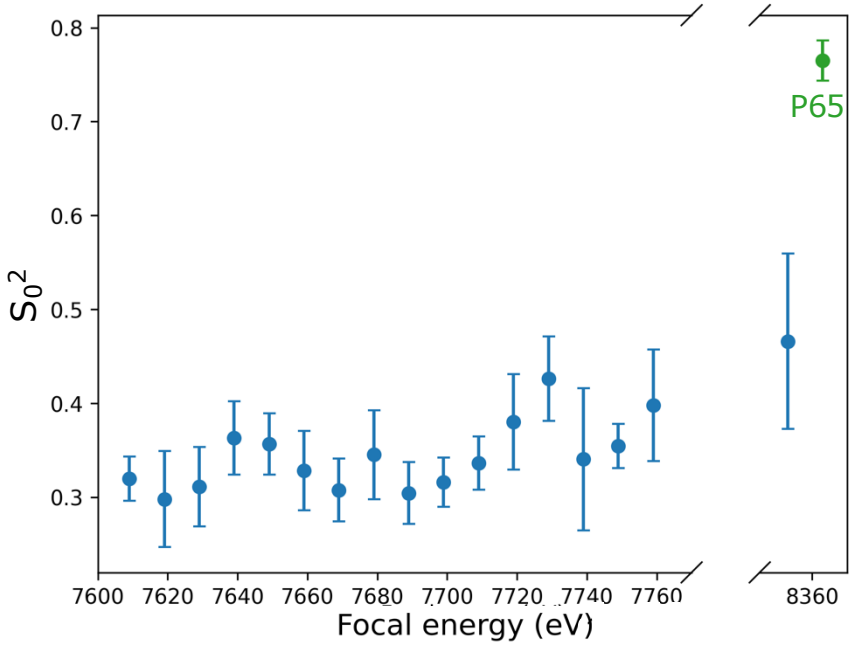
ASSESSMENT OF SPECTROMETER PERFORMANCE

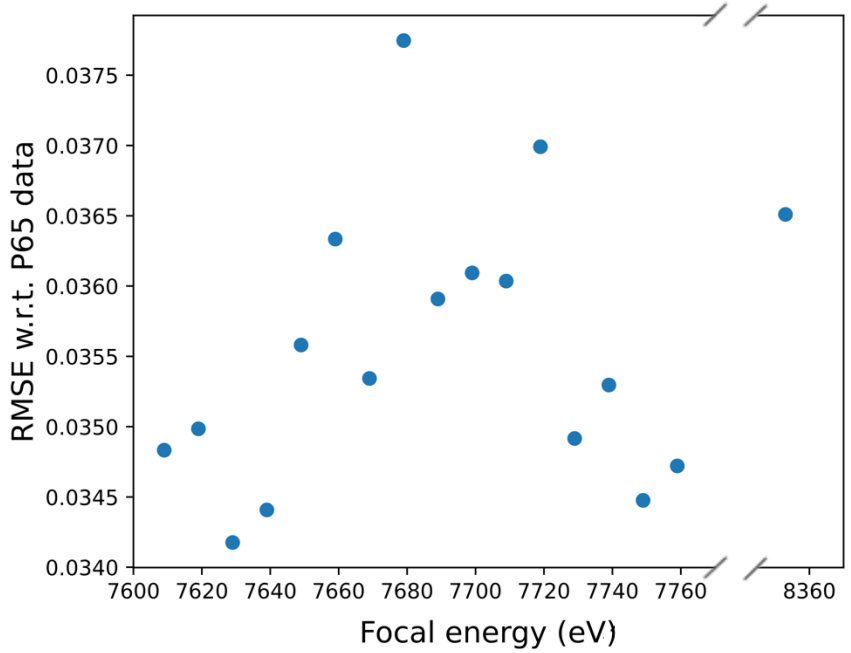
Impact of detector-related parameters to S_0^2 and overall shape of EXAFS.

- focal energy (E_0)



Co foil (1st shell fit: 1 − 3.3 Å)



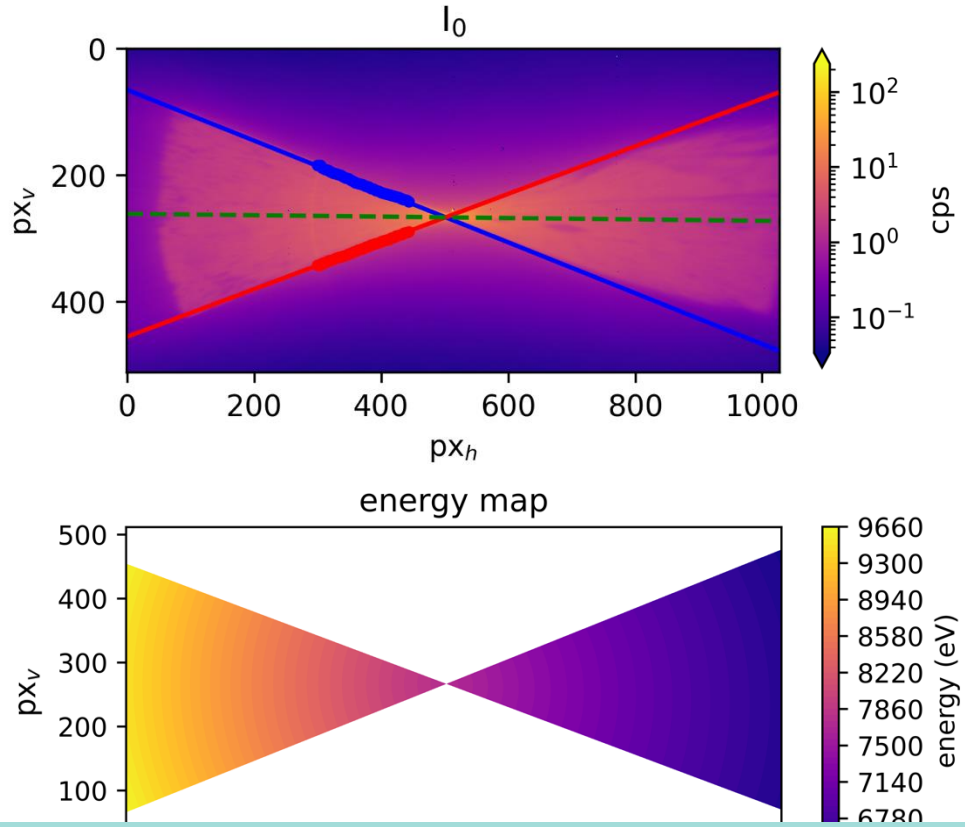


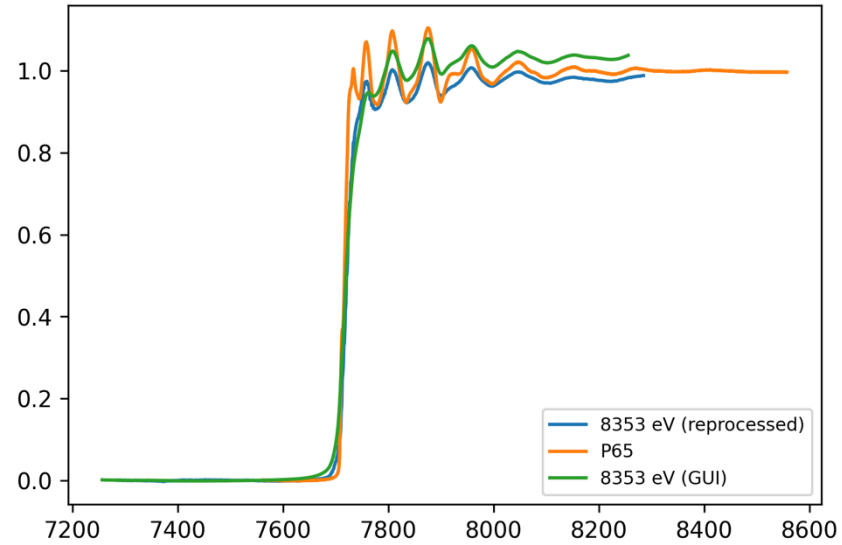
∴ E_0 has moderate impact on S_0^2 and overall shape of EXAFS but <u>no trend is observed</u>

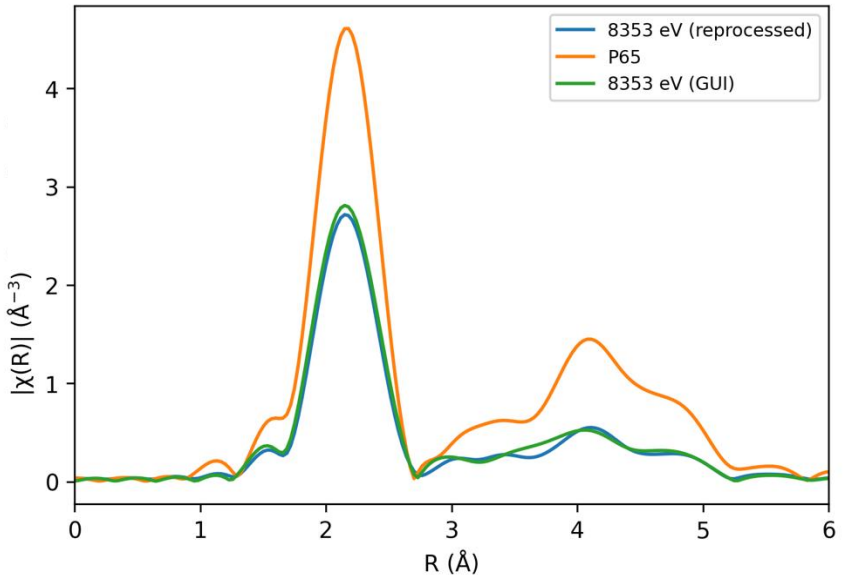
ASSESSMENT OF SPECTROMETER PERFORMANCE

Impact of detector-related parameters to S_0^2 and overall shape of EXAFS.

- image processing



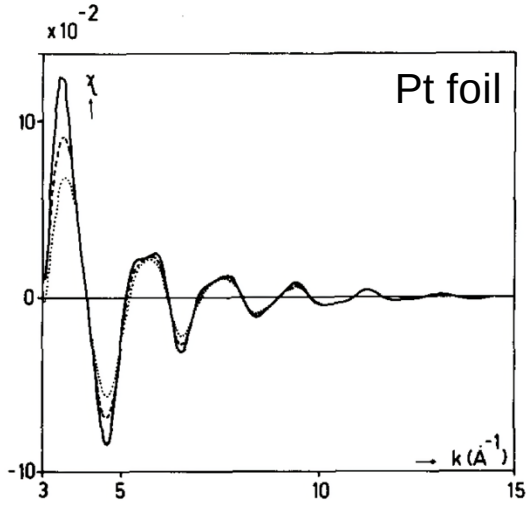


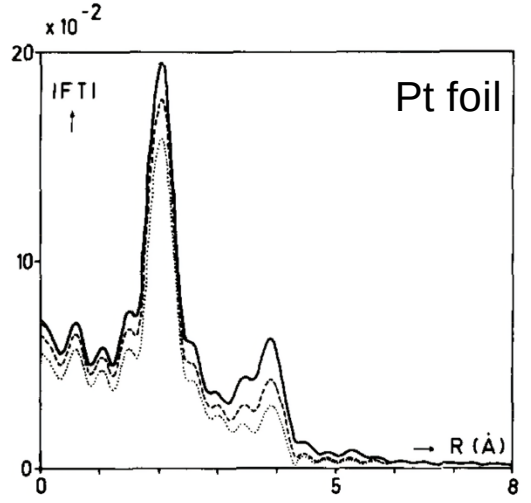


∴ image processing has minimal impact on S_0^2 and overall shape of EXAFS

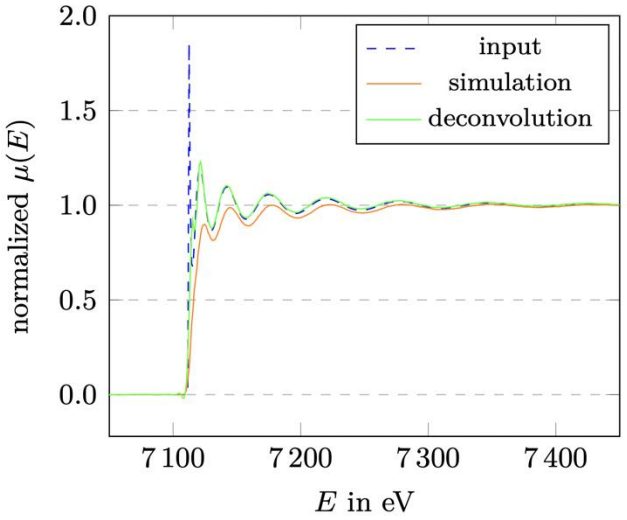
ASSESSMENT OF SPECTROMETER PERFORMANCE

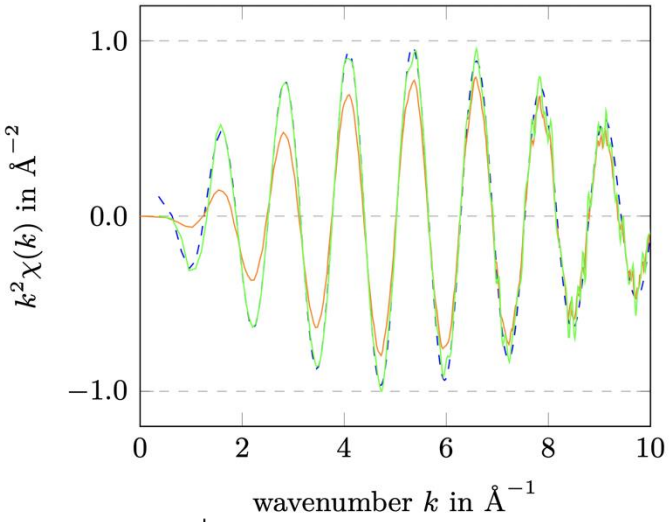
Next step: Deconvolution Studies





Solid State Ionics, **1985**, *16*, 55-64.





	input	deconvolution fit	measurement fit
N_0	2.0	(1.97 ± 0.06)	(1.46 ± 0.04)
R_0	2.5 Å	(2.502 ± 0.004) Å	(2.4949 ± 0.0027) Å
σ_0	0.1 Å^{-1}	(0.1013 ± 0.0013) Å^{-1}	(0.094 ± 0.002) Å^{-1}
δ_0	0.0 rad	(-0.01 ± 0.05) rad	(-0.11 ± 0.04) rad

J.Grage, MS Thesis, TU Berlin, 30.04.**2024**

f(t) Ⓧ g(t) = h(t)

f(t) : SR-EXAFS
h(t) : lab-EXAFS
g(t) : convolution function

ASSESSMENT OF SPECTROMETER PERFORMANCE

Next step: Deconvolution Studies

Open questions:

- Does deconvolution improve the benchmarking results?
- How does the nature of sample influence the results of deconvolution?
- What instrument-related factors (e.g., E_0, $t_{measurement}$) impact the convolution function?
- What does the convolution function represent?

$$f(t) \circledast g(t) = h(t)$$

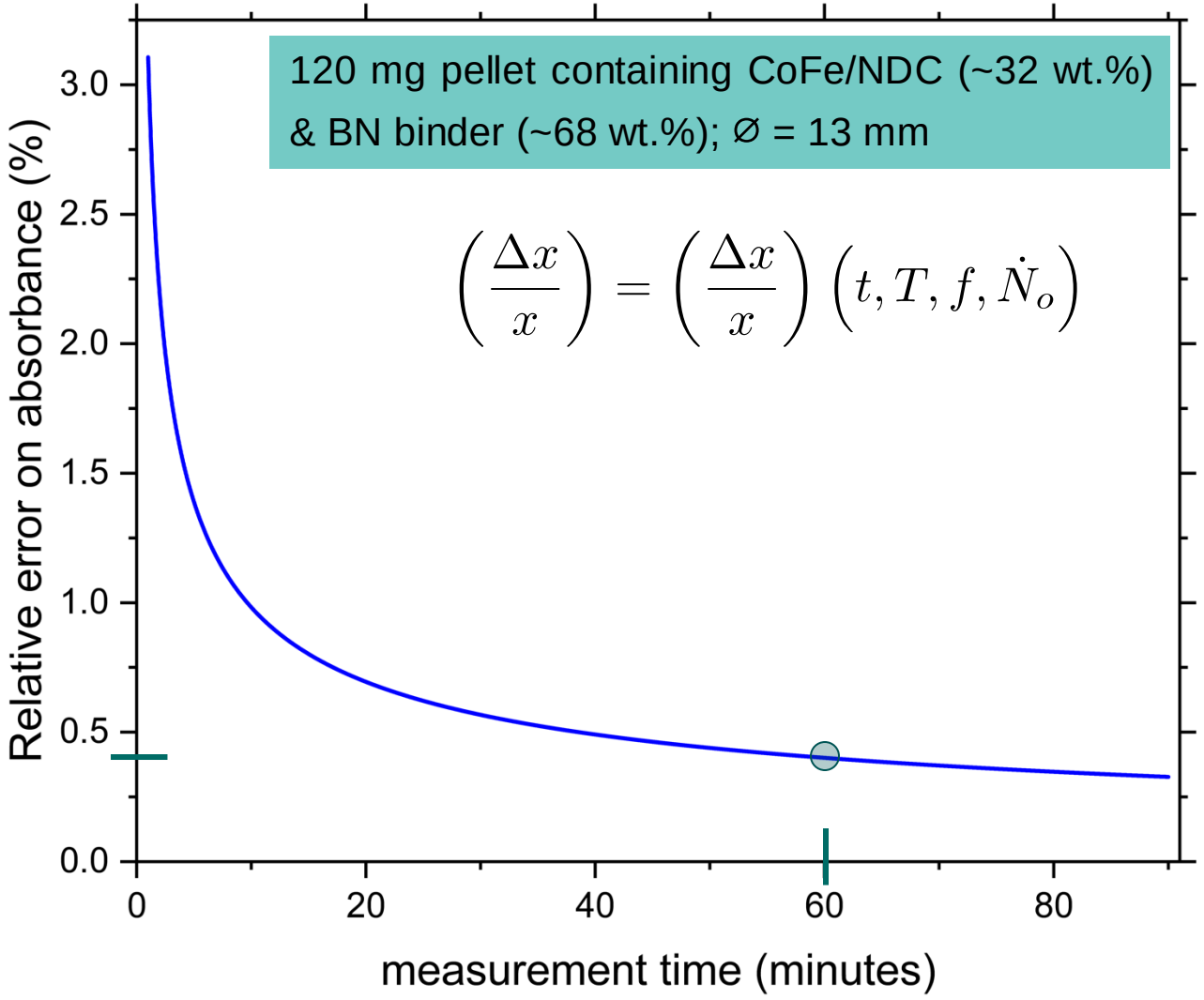
f(t) : SR-EXAFS
h(t) : lab-EXAFS
g(t) : convolution function

ASSESSMENT OF SPECTROMETER PERFORMANCE

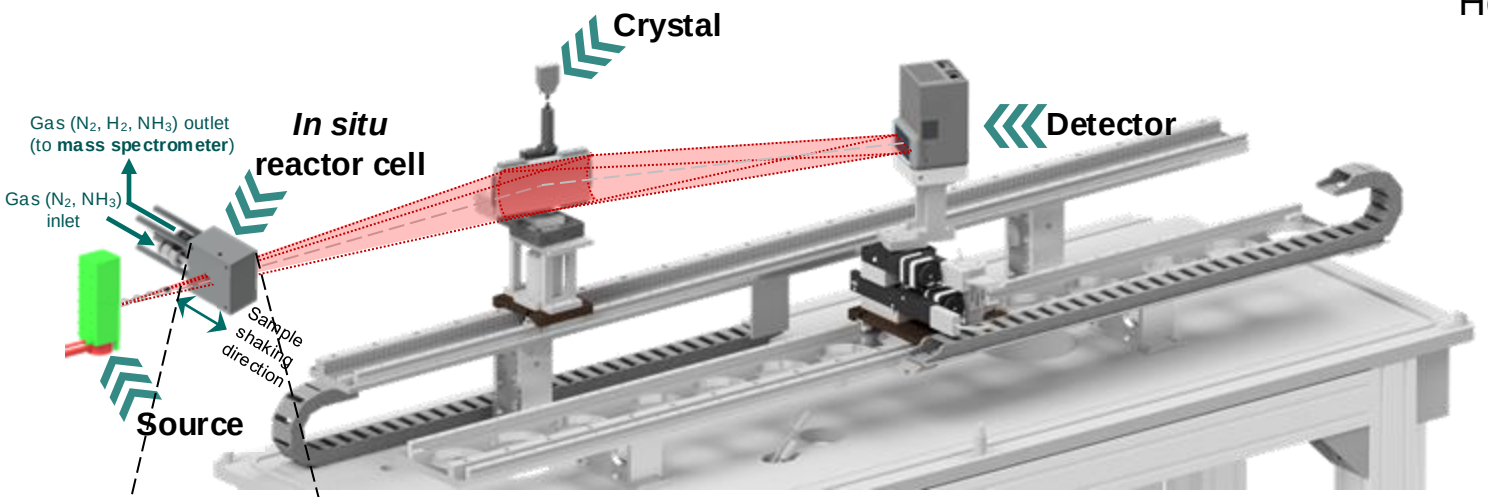
Estimation of measurement time for *in situ* experiments

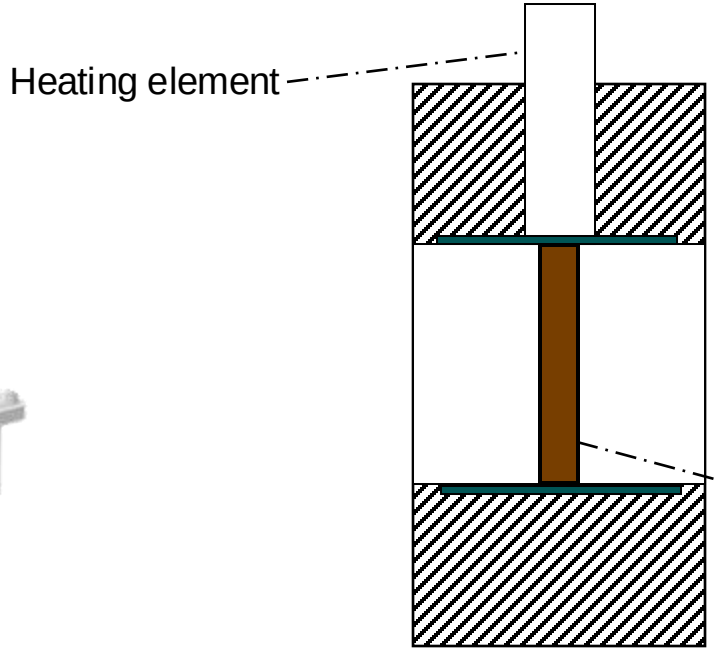
120 mg pellet containing CoFe/NDC (~32 wt.%) & BN binder (~68 wt.%); ∅ = 13 mm

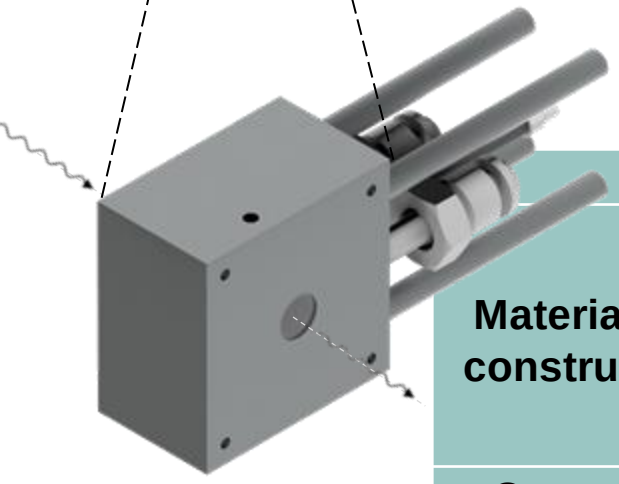
$$\left(\frac{\Delta x}{x}\right) = \left(\frac{\Delta x}{x}\right)\left(t, T, f, \dot{N}_o\right)$$



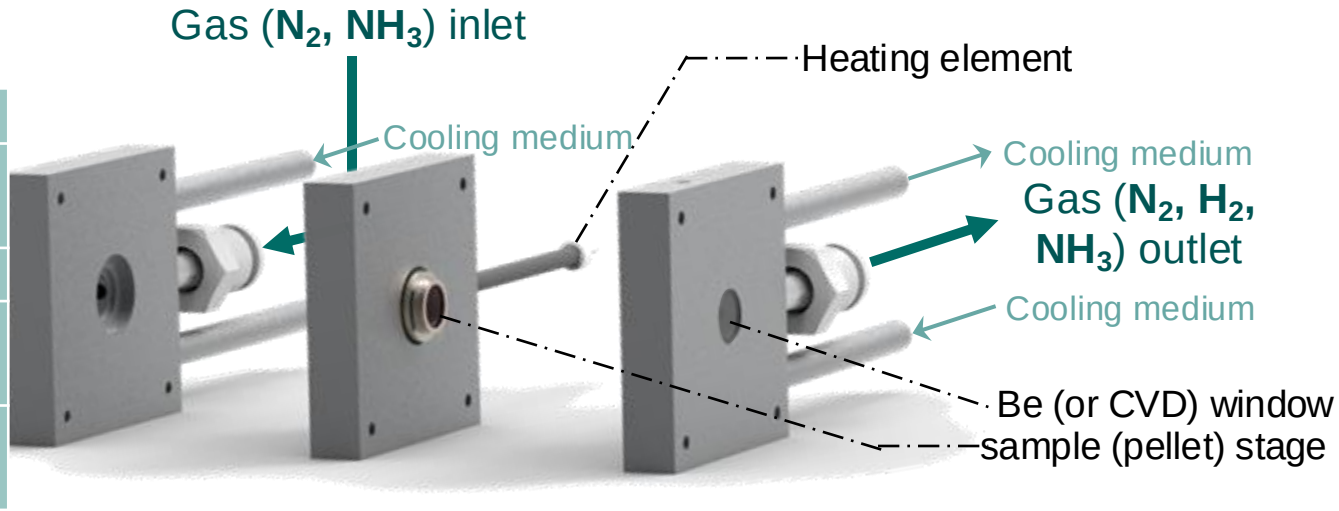
UPDATES ON *IN SITU* CELL SETUP







Cell characteristics	
Materials of construction	Stainless steel (SS 300) for housing & sample lid
	Copper (gaskets)
	Ceramic lids and cylinders (heat isolation)
Operating Temperatures	up to 873 K



SUMMARY AND OUTLOOK

- Lab-EXAFS in NH_3 decomposition: bulk structural changes on the catalyst
- Benchmarking with SR data: within a limited fitting window
- Detector-related parameters: no significant impact to S_0^2 and overall shape
- Deconvolution studies: improve data reliability? applicable to wider range of samples?
- *In situ* cell setup: commissioning measurements to follow

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ACKNOWLEDGMENTS

Thank you for your kind attention!

Questions, comments, and suggestions are more than welcome.

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DESY.

Technische Universität Berlin

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