Electronic and geometric structure of matter probed under in-situ conditions by means of x-ray spectroscopy techniques

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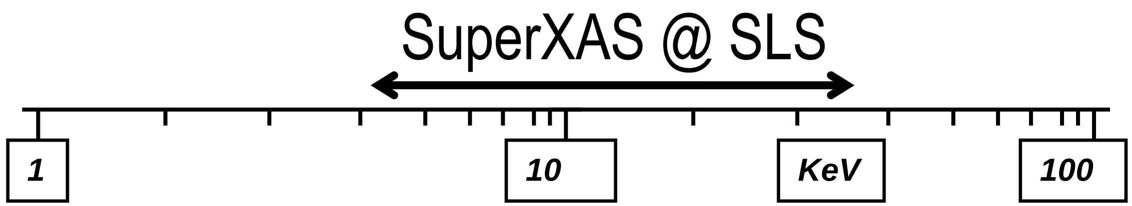
In-situ X-ray absorption & X-ray emission spectroscopy

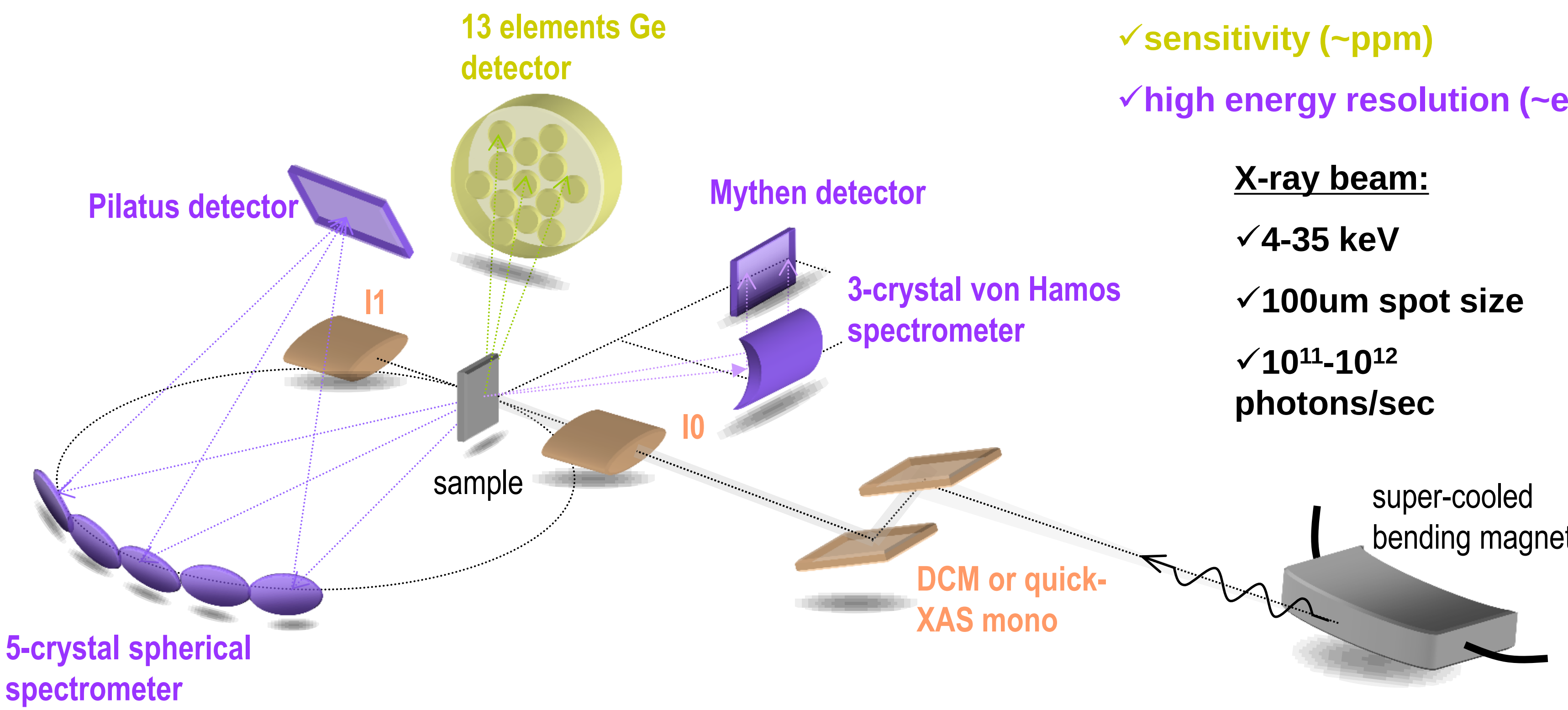


Key points:

- ✓time resolution (~msec)
- ✓sensitivity (~ppm)
- ✓high energy resolution (~eV)

X-ray beam:

- ✓4-35 keV
- ✓100um spot size
- ✓10^{11}-10^{12} photons/sec



State-of-the-art XAS and XES at SuperXAS

Development strategy

Multi-modal detection

fluorescence detected XAS/XES

time resolved XAS

high resolution XAS/XES

13 elements Ge detector

- high sensitivity
- low detection limits

quick-XAS monochromator

- msec time resolution
- transmission XAS

5 crystal spectrometer

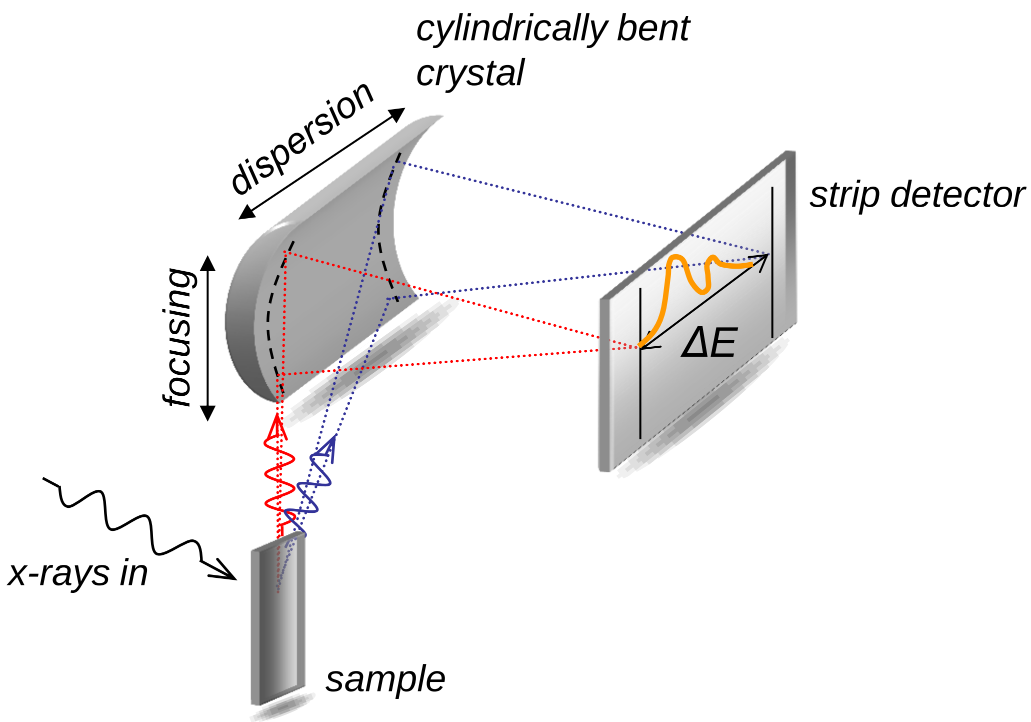
- sub eV energy resolution
- high resolution XAS

time resolution & energy resolution

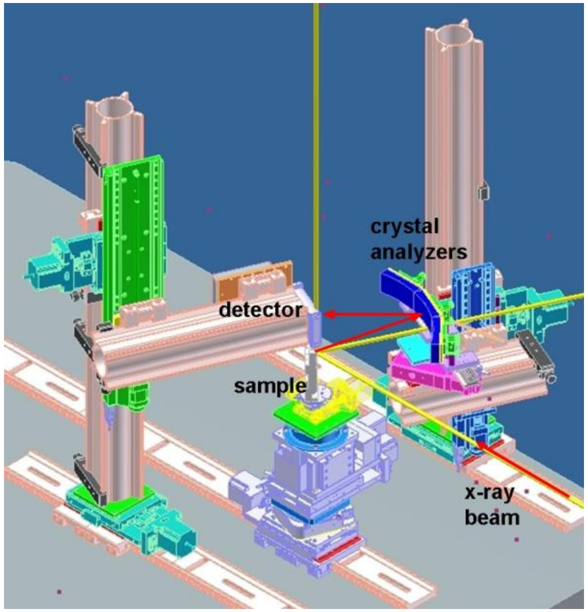
energy resolution – sensitivity to chemical state

time resolution -sensitivity to intermediates

X-ray spectrometer for time resolved spectroscopy



Spectrometer design @ SuperXAS



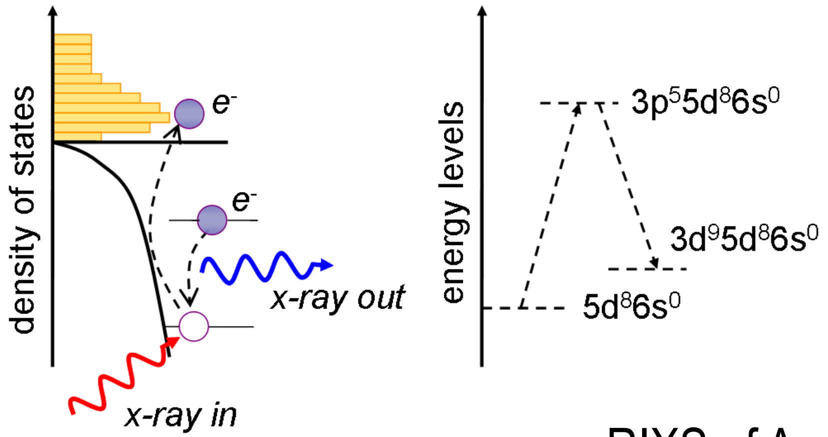
- resolution ~eV
- large energy bandwidth for single measurement
- single-shot capability
- vertical or horizontal scattering geometry
- easy adaptation to shorter/longer radiuses

L. von Hamos, Naturwiss. 20, 705 (1932).

J. Szlachetko et al., Rev. Sci. Instrum. 83, 103105 (2012).

Resonant inelastic x-ray scattering (RIXS)

RIXS spectroscopy



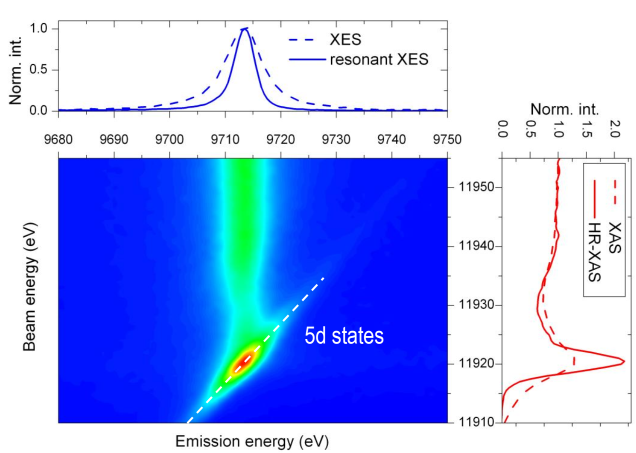
RIXS: photon-in photon-out technique, a combination of XAS and XES spectroscopy

XAS = unoccupied density of states

XES = occupied electronic states.

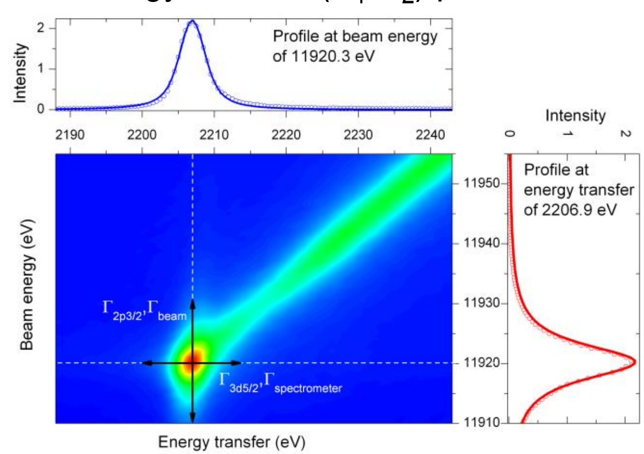
RIXS of Au_2O_3

RIXS plane



-detailed information about unoccupied electronic structure

Energy transfer (E_1-E_2) plane



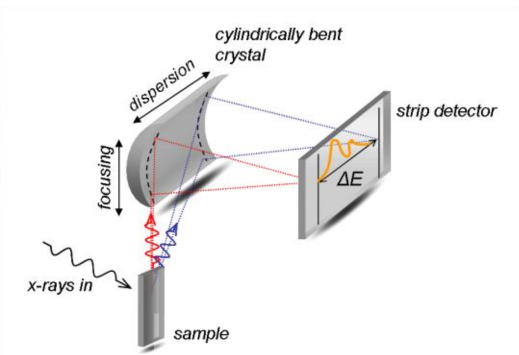
-final state energies and quantitative analysis

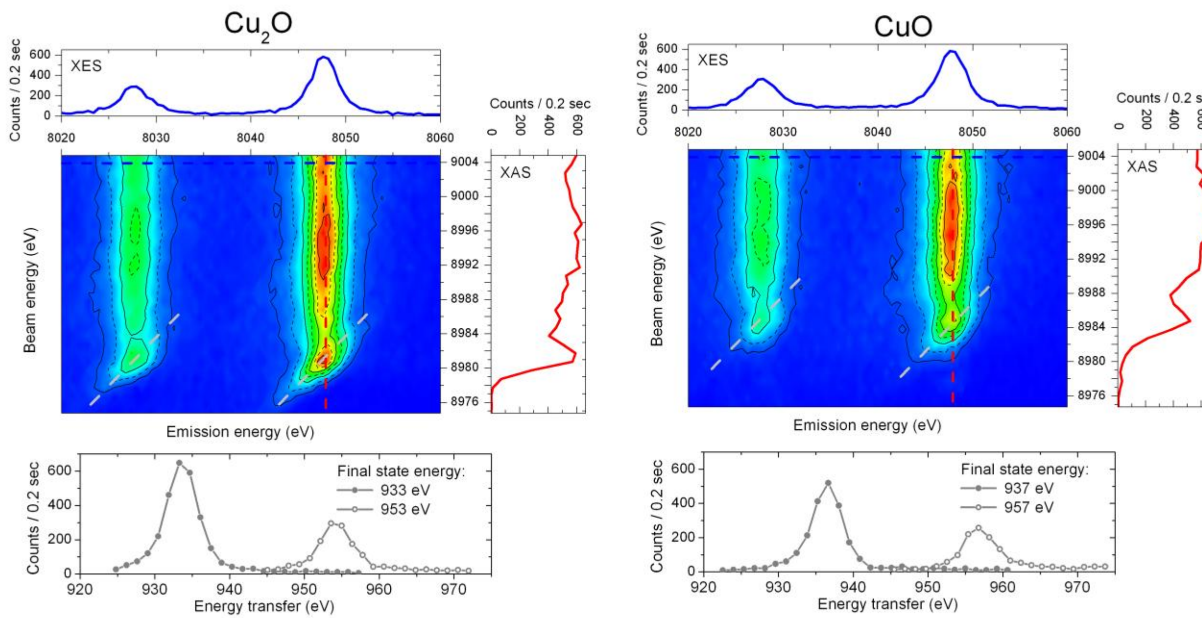
J. Szlachetko et al., 10.1016/j.elspec.2012.11.002 (2013).

Quick-RIXS spectroscopy

The main advantage of an X-ray spectrometer in the von Hamos geometry is the dispersive-type of detection, which allows recording a XES spectrum without any scanning components.

In combination with fast scanning of the incident energy axis, a RIXS plane can be collected within few seconds.





A full RIXS plane recorded with 7sec acquisition time

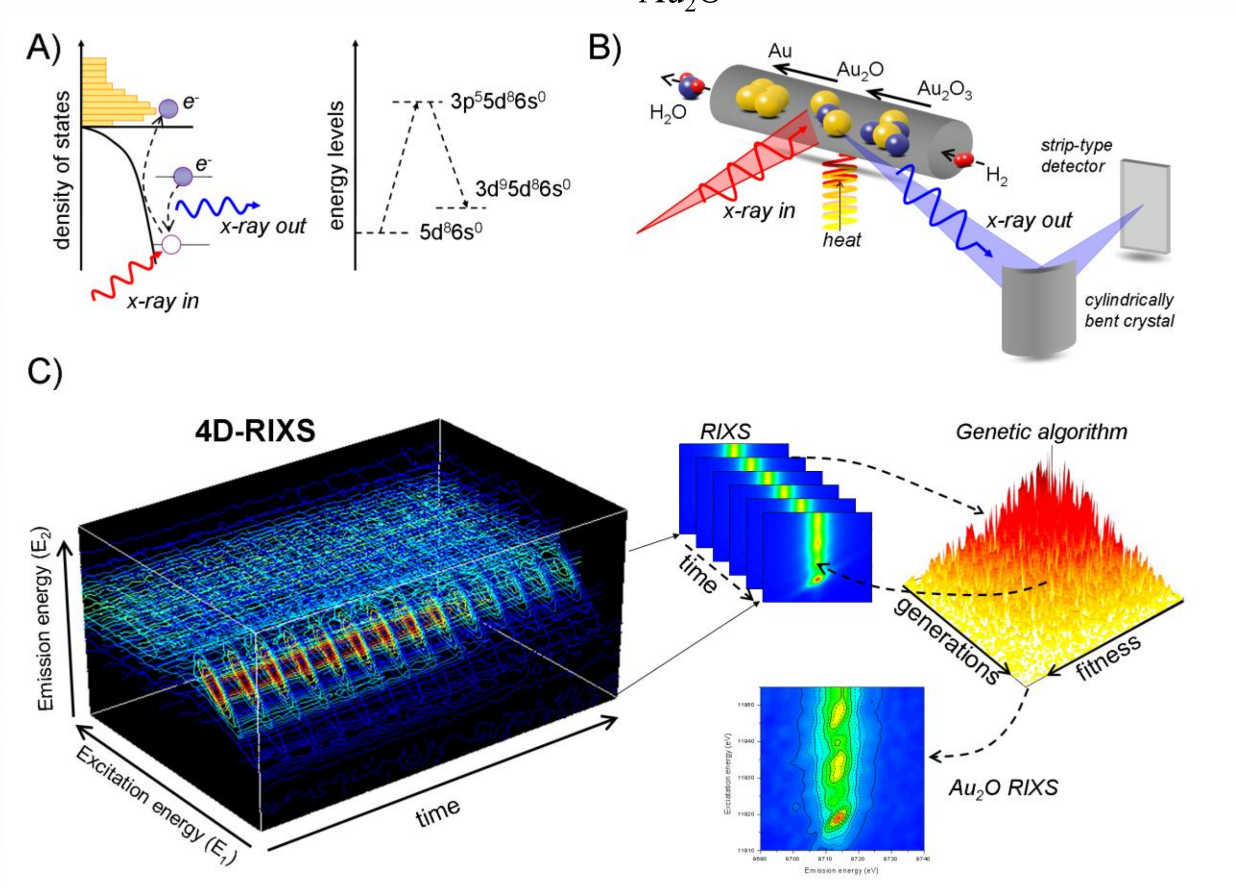
J. Szlachetko et al., Rev. Sci. Instrum. 83, 103105 (2012).

In-situ quick-RIXS spectroscopy

Temperature programmed reduction (TPR) of Au(III) oxide

$$Au_2O_3 \xrightarrow[\textit{intermediate?}]{\sim 120^\circ} Au$$

$$Au_2O_3 \rightarrow Au_2O \rightarrow Au$$

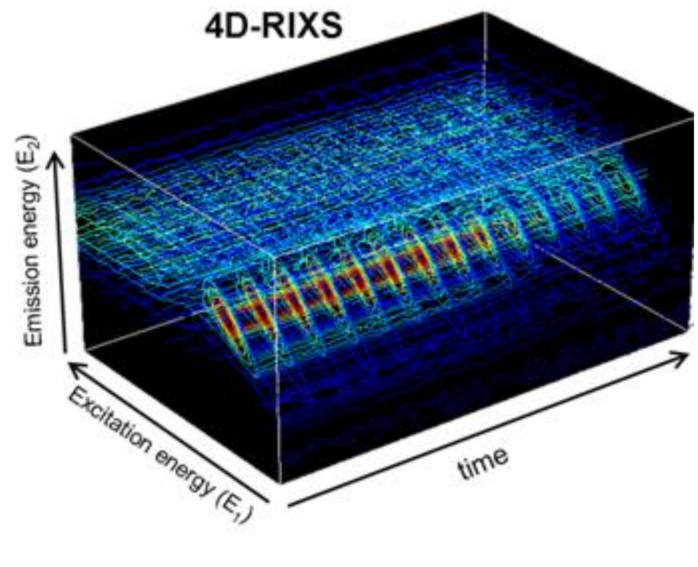


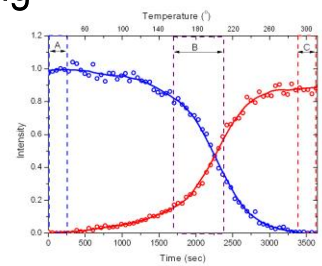
- The TPR technique was applied to monitor changes of the electronic structure of Au_2O_3 induced by temperature.
- The Au_2O_3 sample was heated, at a ramp of 5 degrees/minute, from 20°C up to 300°C.
- In-situ RIXS planes were recorded continuously with an acquisition time of 55 seconds per RIXS map. In total, 70 full RIXS planes were recorded at different temperatures, covering a total experiment time of about 60 minutes.

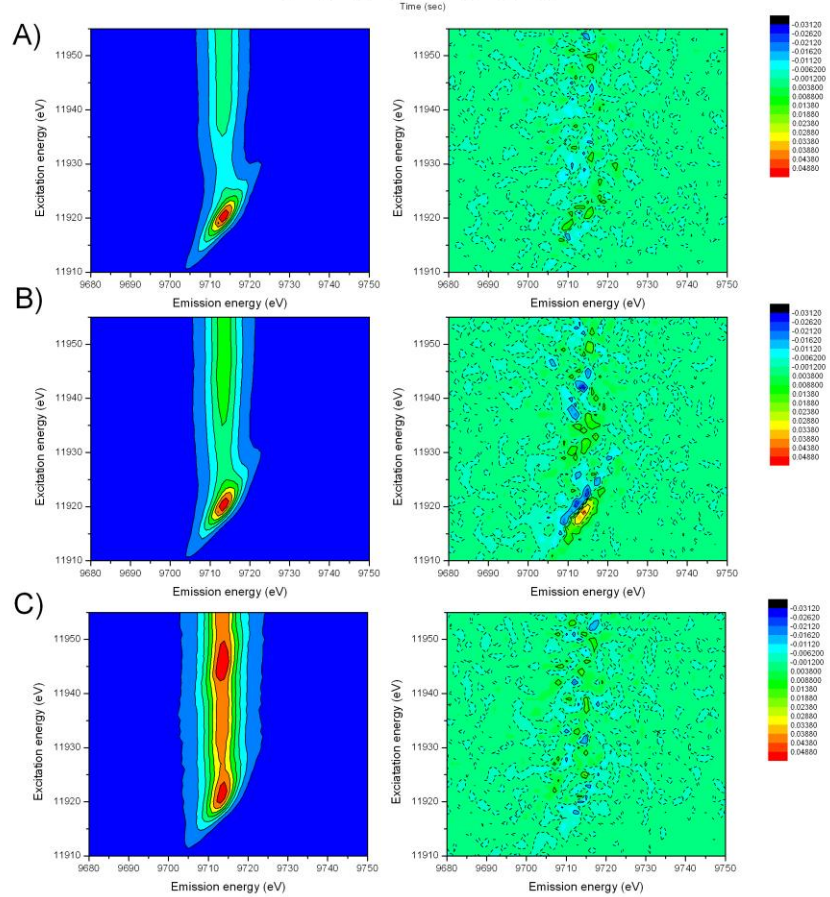
J. Sa & J. Szlachetko et al., submitted Nat. Matter (2013).

Quick-RIXS spectroscopy

TPR of Au(III) – results of 2D-RIXS fitting





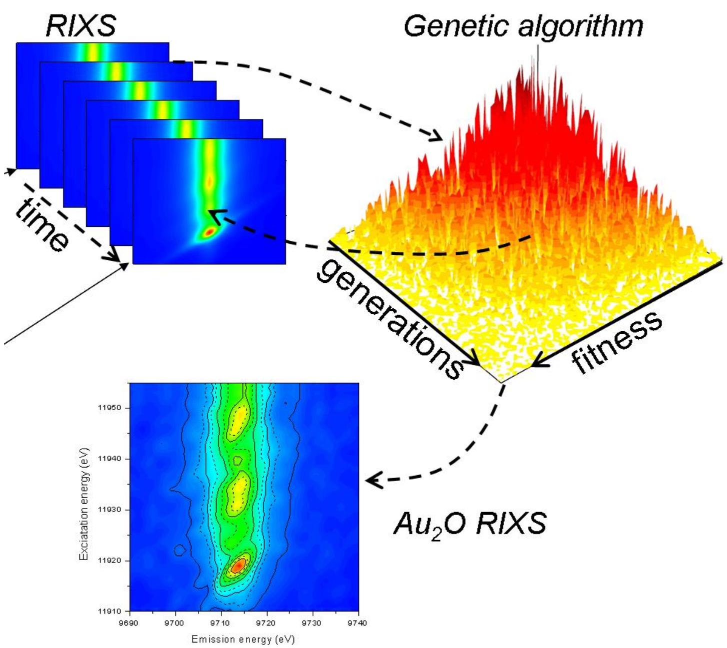


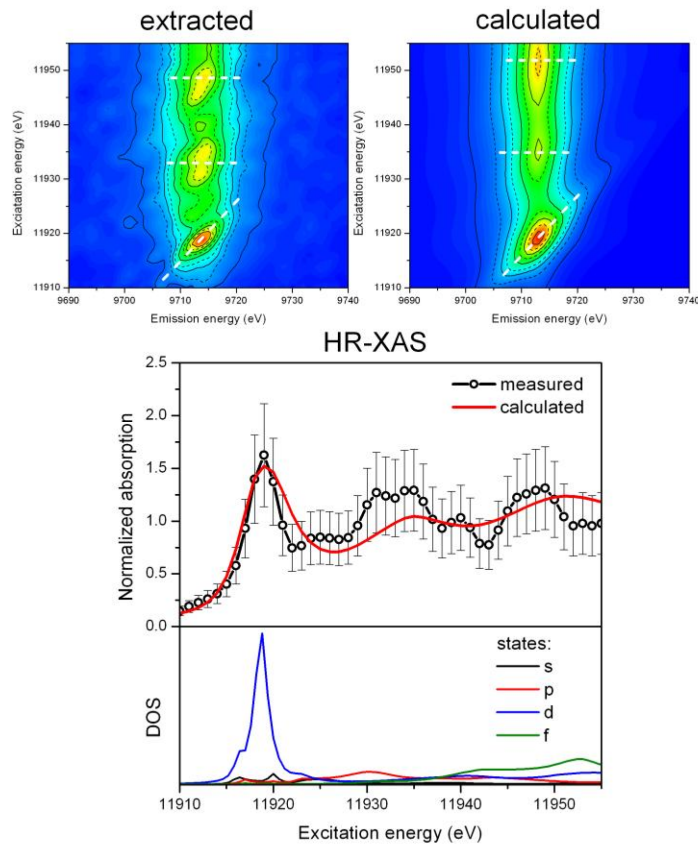
Result of RIXS fitting using a two component model. Top) The fitted intensities of Au_2O_3 and Au versus time/temperature. A) left: the RIXS plane for region A and right) fit residuals. B) and C) the same as A), but for regions B and C, respectively (marked in top panel). As shown the two component fit can not reproduce the RIXS spectra in the intermediate zone B.

Quick-RIXS spectroscopy

TPR of Au(III) – results of Genetic Algorithm analysis

Extracted RIXS plane of the intermediate compound using Genetic Algorithm procedure. For comparison the calculated Au_2O RIXS is shown on the right. Bottom) extracted from RIXS plane the high-resolution XAS is compared to calculated DOS contributions.



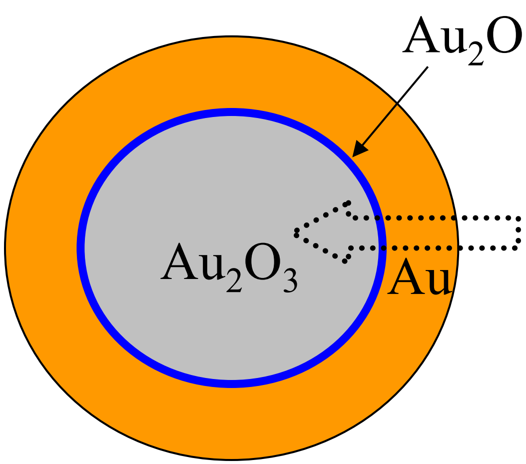


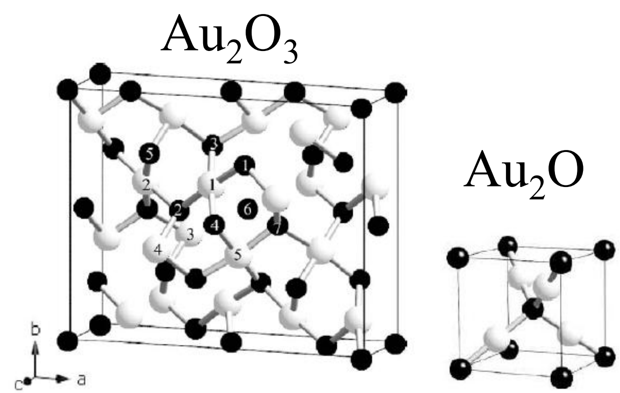
➢**Calculated RIXS plane include lattice expansion from 4.8A to 5.3A.**

Au(III) reduction: theory vs experiment

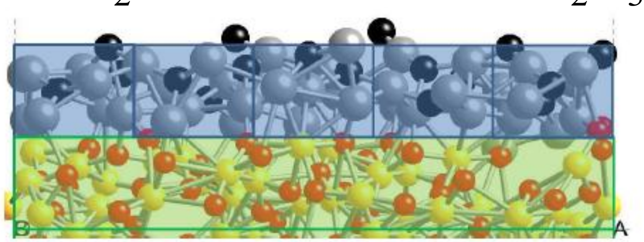
- Theory Au_2O → 4.8Å
- RIXS experiment → 5.3Å

Reaction mechanism: shell-to-core reduction





Au$_2$O termination on Au$_2$O$_3$ structure:

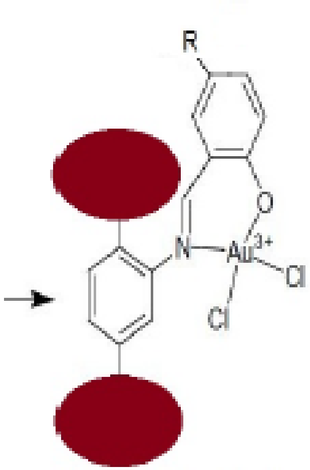


- Theory Au_2O → 5.34Å
- RIXS experiment → 5.3Å

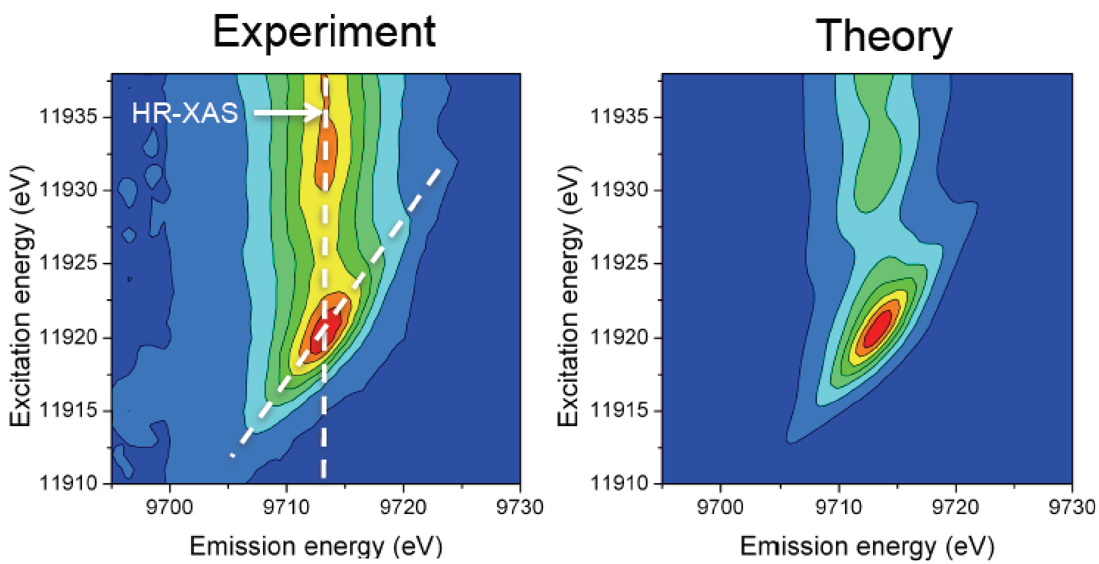
in collaboration with Prof. Cathy Stampfl

RIXS sensitivity – application to metal-organic frameworks

Goal: fine-tuning of gold electronic structure to improve catalytic performances



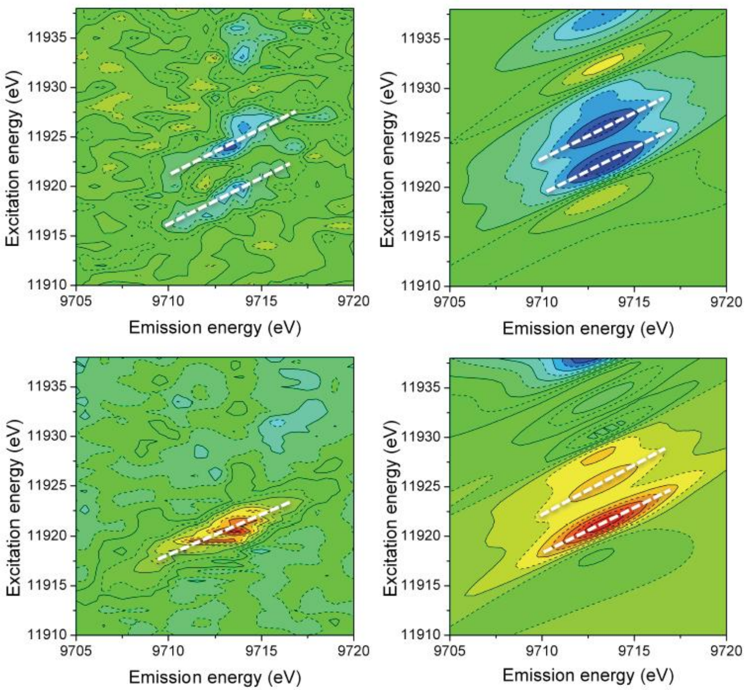
IRMOF-3-Si-Au



RIXS sensitivity – metal-organic frameworks

Δ-RIXS

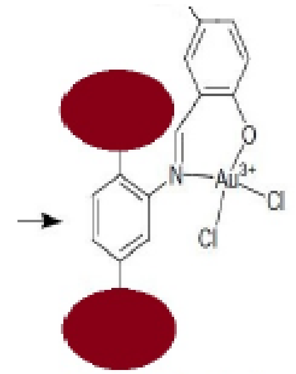
Experiment | Theory



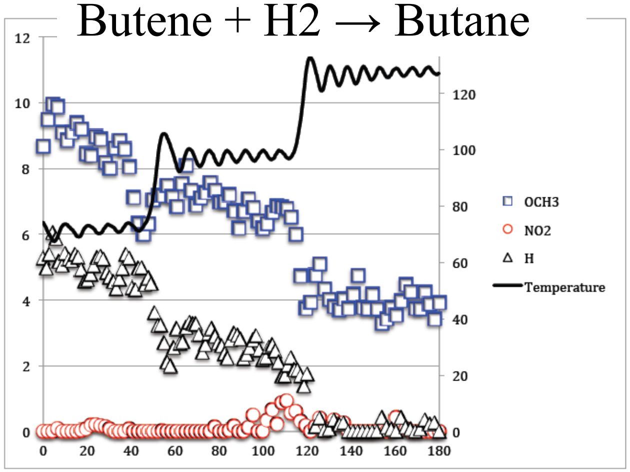
NO2 vs H

OCH3 vs H

H/NO2/OCH3



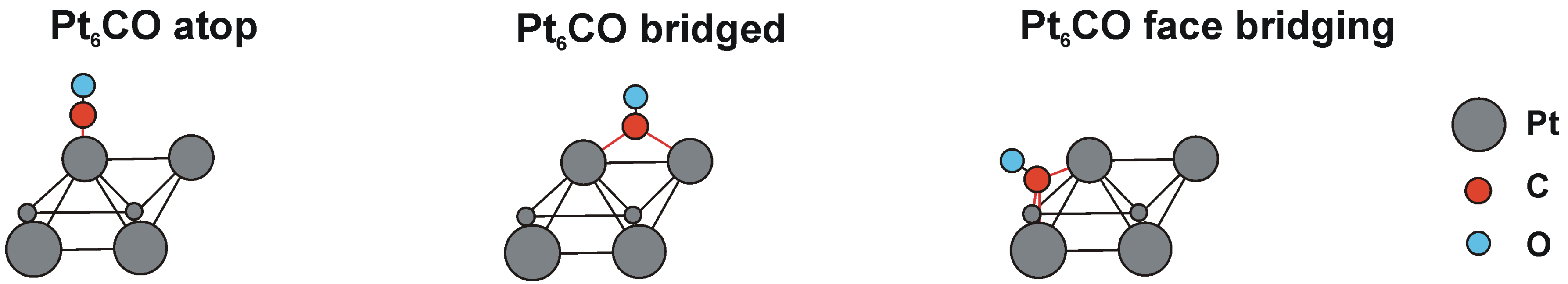
IRMOF-3-Si-Au



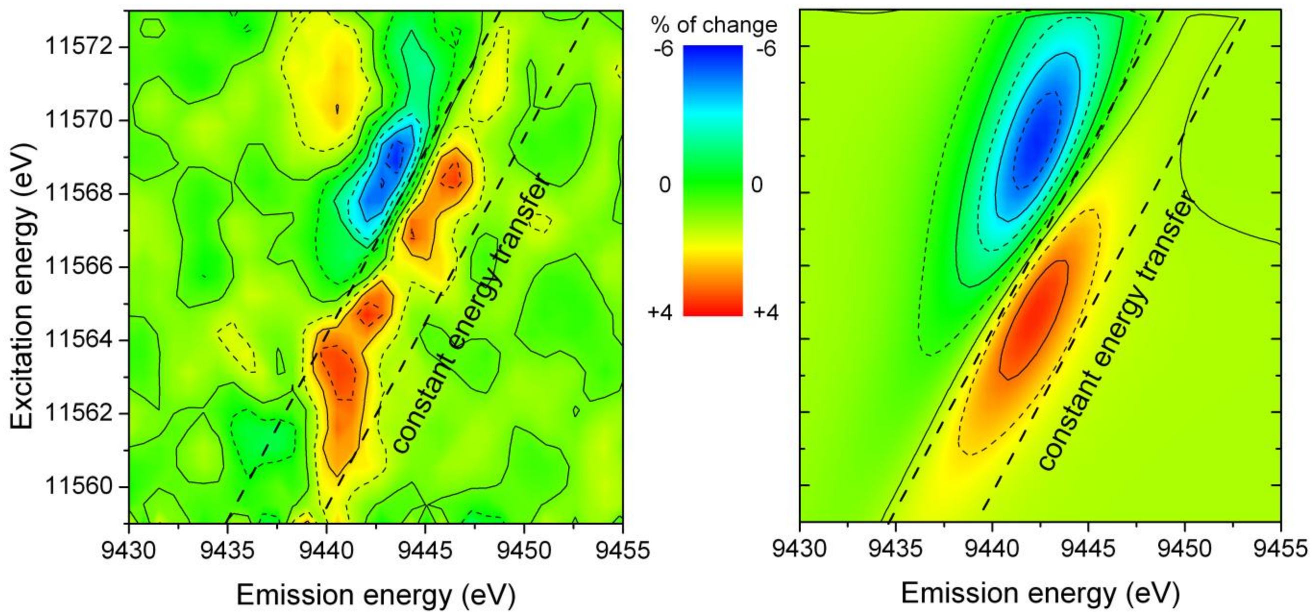
J. Sa, J. Szlachetko et al., accepted in RSC Advances (2013).

In-situ RIXS – molecule adsorption geometries

CO adsorption on Pt-nanoparticles

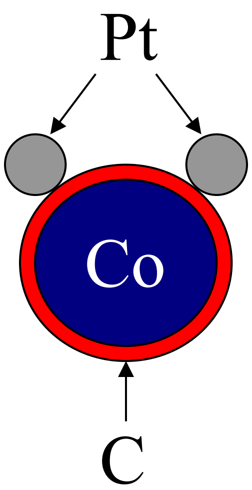


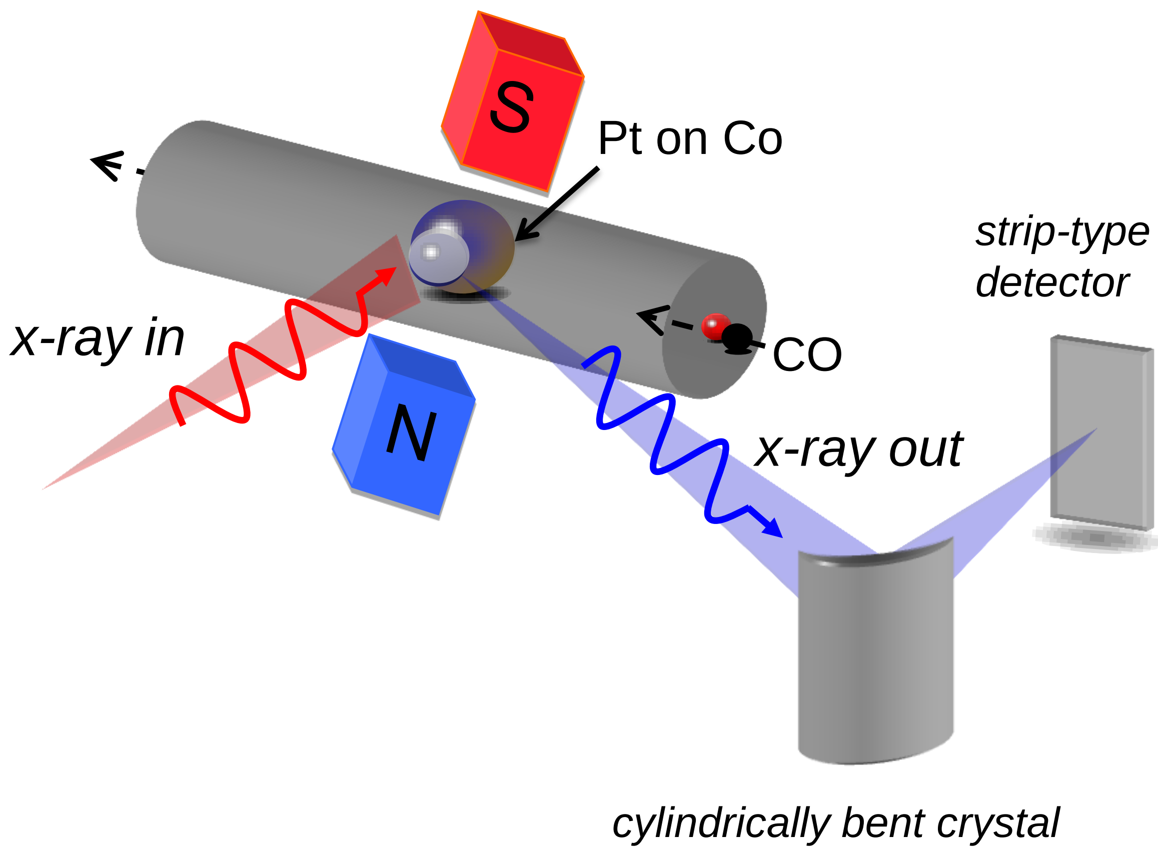
Δ-RIXS



In-situ RIXS –molecule adsorption geometries

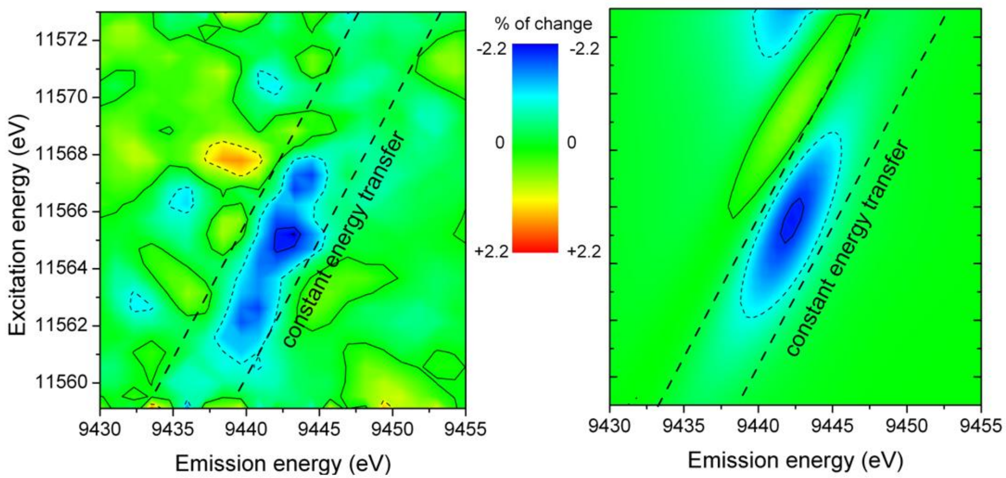
CO adsorption on Pt/Co@C

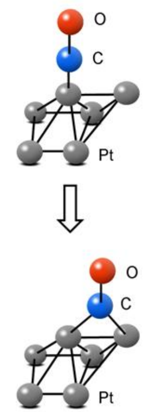


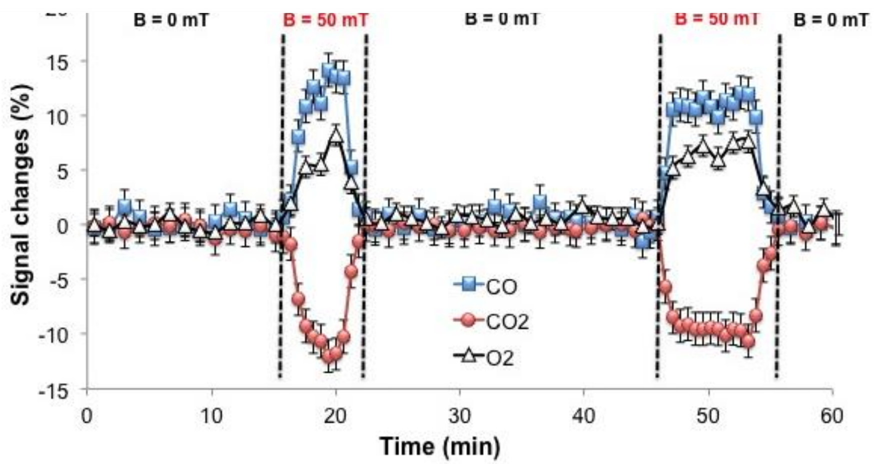


In-situ RIXS – magnetic manipulation of molecule adsorption

CO adsorption on Pt/Co@C





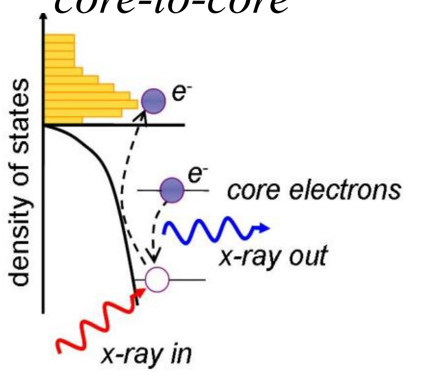


~11% change in adsorption geometry

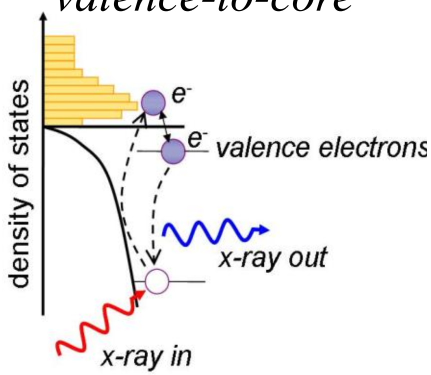
J. Sa, J. Szlachetko et al., accepted in Nanoscale (2013).

Valence-to-core (v2c) RIXS spectroscopy

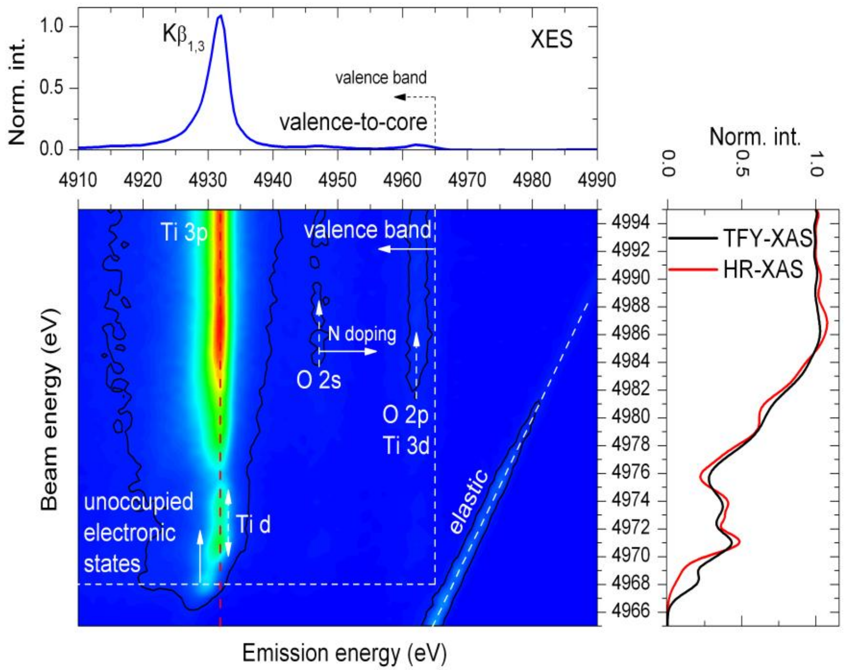
core-to-core



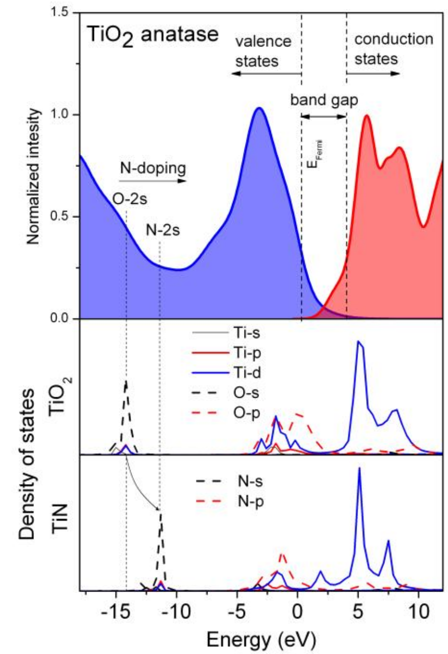
valence-to-core



v2c-RIXS of TiO_2



projected-DOS of TiO_2



v2c-RIXS →Detailed information about low energy unoccupied and occupied electronic structure

J. Szlachetko and J. Sa, CrystEngComm 15, 2583-2587 (2013).

J. Szlachetko and J. Sa et al., J. Chem. Sci. invited paper (2013).

RIXS spectroscopy

-RIXS was applied to in-situ time resolved chemical speciation (4D-RIXS)

- RIXS proves the sensitivity to very low changes in the electronic configuration of metal site

- RIXS is sensitive to molecule adsorption geometry

- RIXS allow for mapping lowest unoccupied and highest occupied states

High energy resolution off-resonant spectroscopy

High energy resolution off-resonant spectroscopy (HEROS)

Off-resonant excitations

$E_{beam} << E_{edge}$

Kramers-Heisenberg formalism (1925):

$$\frac{d\sigma(\omega_1)}{d\omega_2} \approx 2\pi r_0^2 \int \frac{\omega_2}{\omega_1} \frac{(\omega_{initial}-\omega_{final})\, g_{final\to initial}(\omega_{initial}+\omega)\cdot \frac{dg_{initial}}{d\omega}}{(\omega_{initial}+\omega-\omega_1)^2+\Gamma^2_{initial}/4\hbar^2} \times \frac{\Gamma_{final}/2\hbar}{(\omega_1-\omega_{final}-\omega-\omega_2)^2+\Gamma^2_{final}/4\hbar^2}\, d\omega$$

XAS

XES

Tulkki & Aberg J. Phys. (1982).

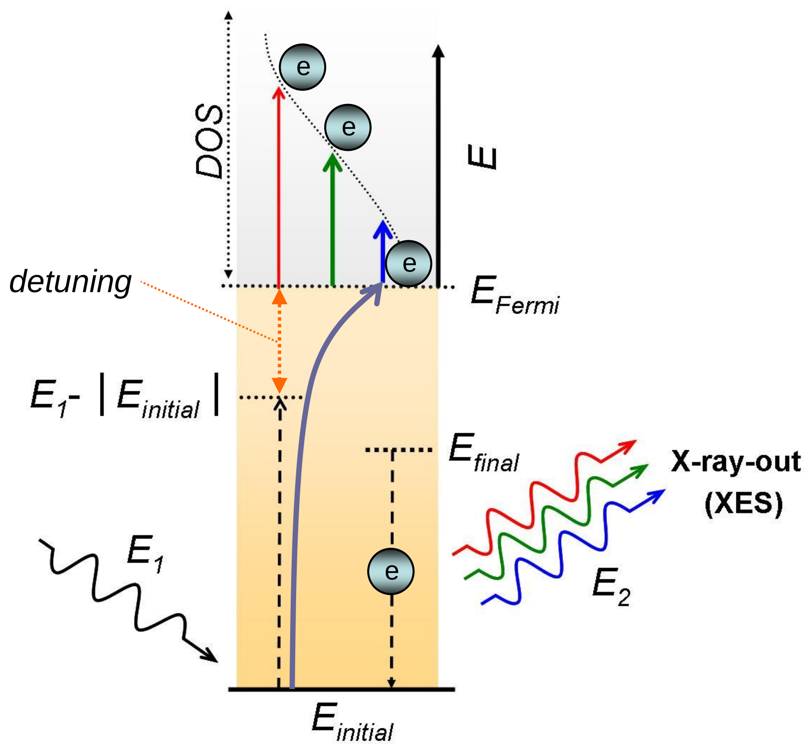
for below edge excitations the shape of the x-ray emission spectrum:

- is proportional to DOS of an atom
- independent on initial state broadening

PAUL SCHERRER INSTITUT

Off-resonant excitations

Energy diagram

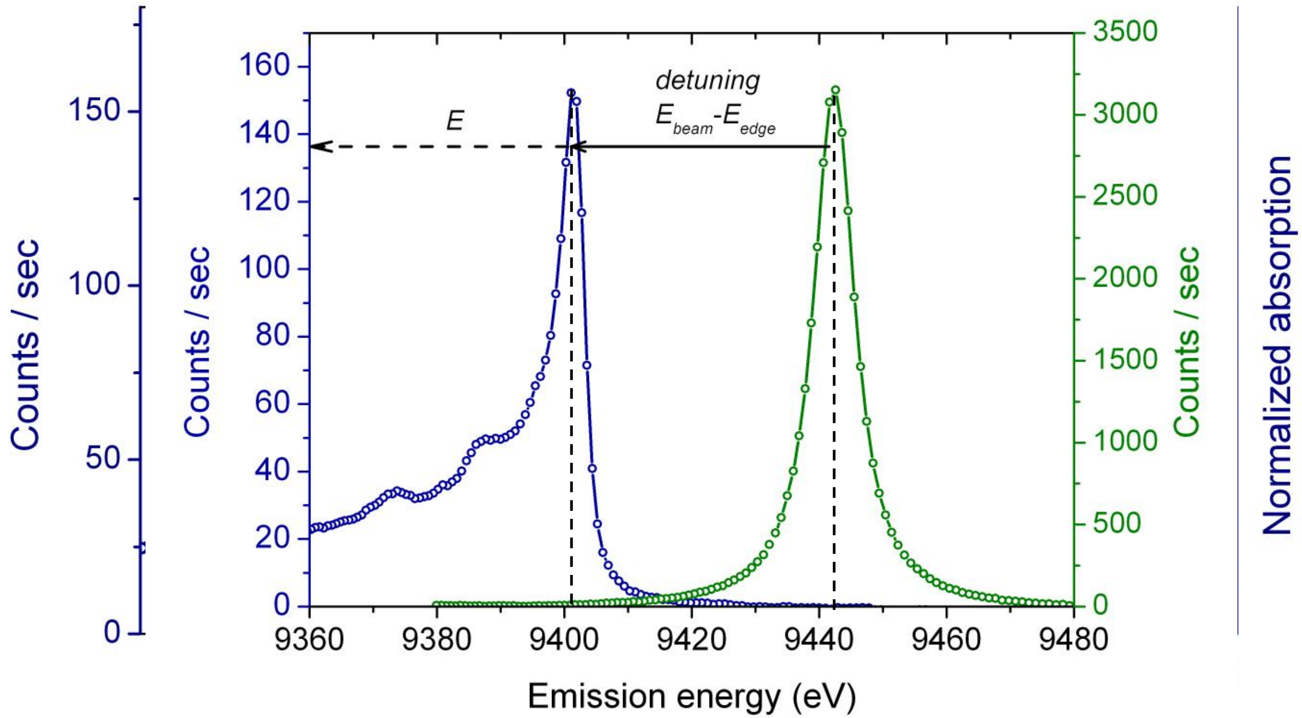


$$E_2 \;=(E_{fluo} - E_{Detuning}) - \; E_{electron}$$

fixed

High energy resolution off-resonant spectroscopy (HEROS)

X-ray emission spectrum Pt $3d_{5/2} \rightarrow 2p_{3/2}$ ($L\alpha_1$)

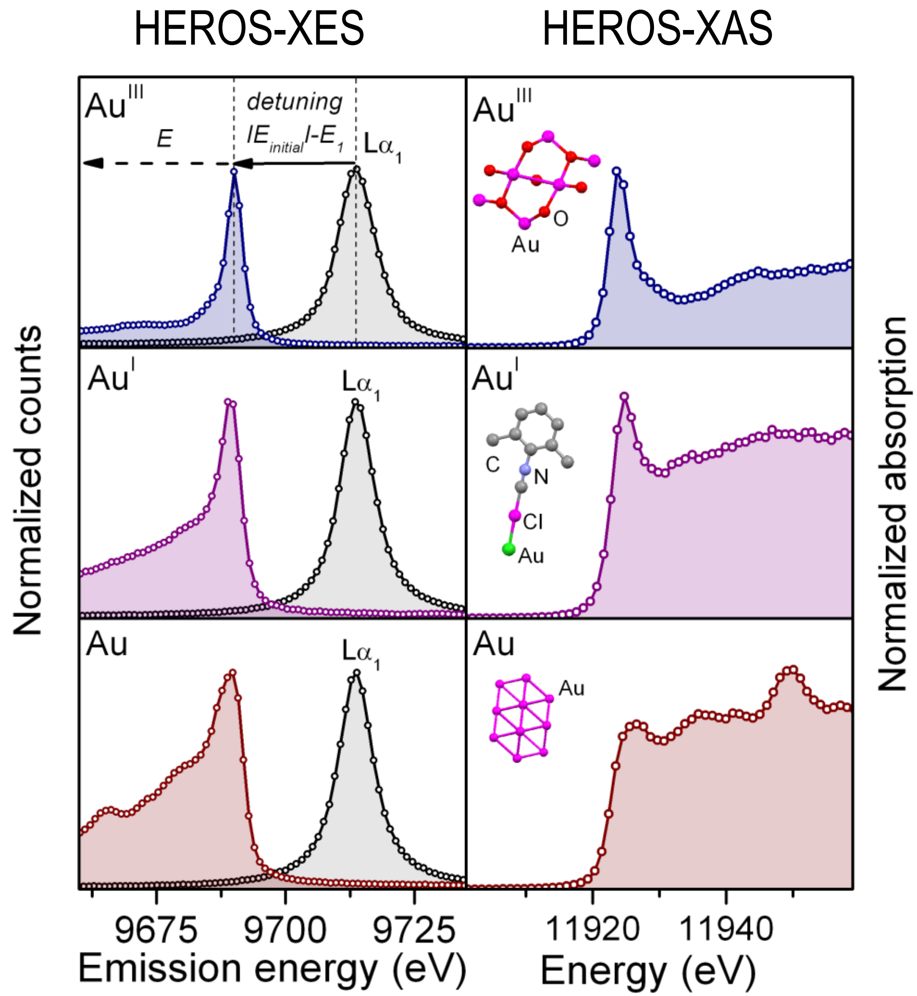


dispersive-type spectrometer: XAS can be obtained for fixed beam energy excitation without moving any optical components

high energy resolution – more detailed structure as compared to conventional XAS

High energy resolution off-resonant spectroscopy (HEROS)

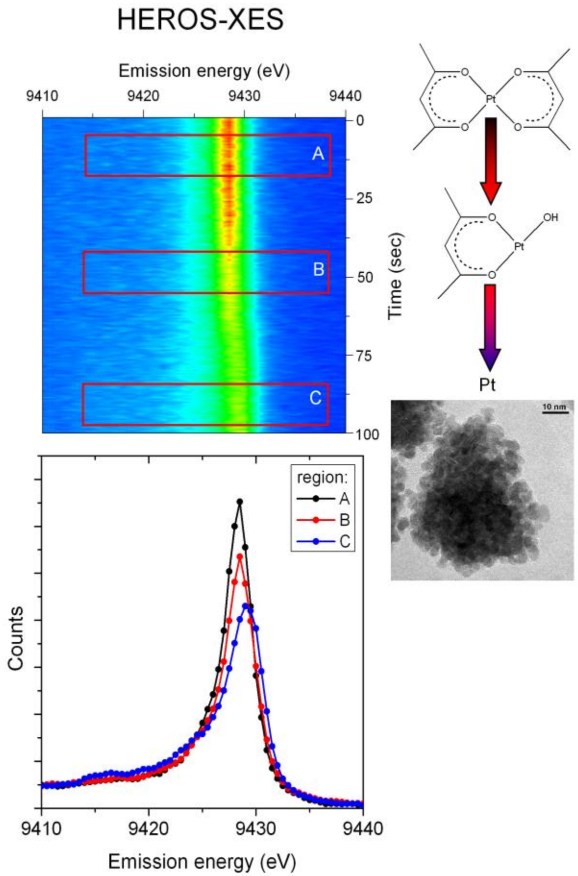
Chemical sensitivity

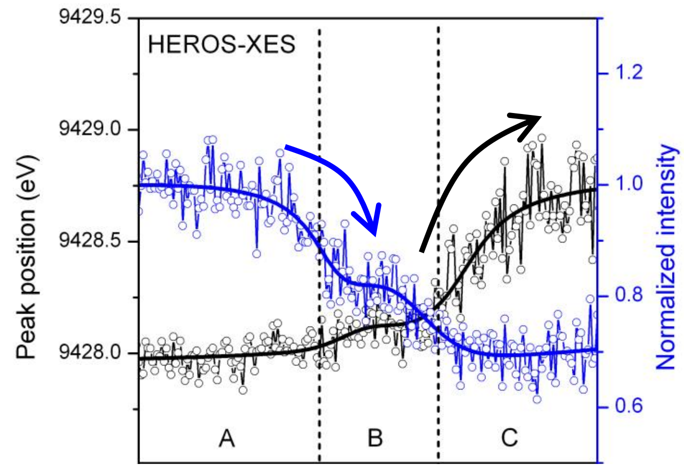


High energy resolution off-resonant spectroscopy

($Pt(acac)_2$) decomposition: 500msec time resolution

In situ decomposition of $Pt(acac)_2$ under 5% H_2 in He induced by flash heating at 150 ^oC





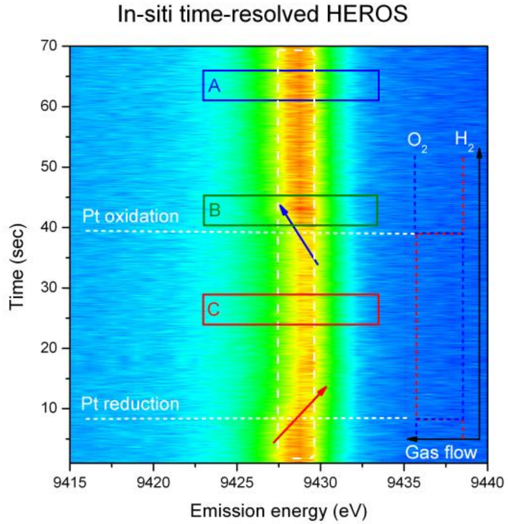
The spectral shape in intermediate zone B indicates changes in the chemical environment, such as change of the ligand of the Pt site that however do not correspond to a change in oxidation state.

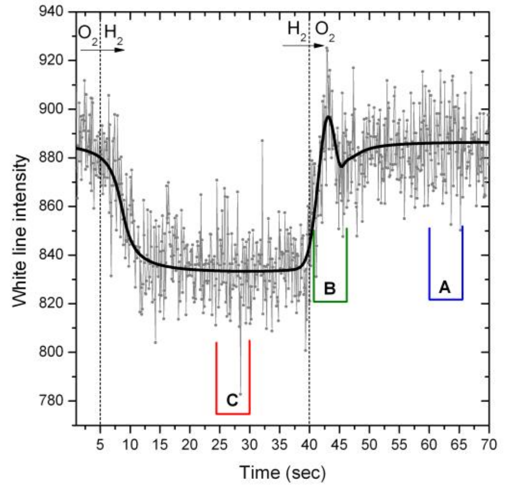
J. Szlachetko, M. Nachtegaal, J. Sa et al., Chem. Comm., 48, 10898 (2012).

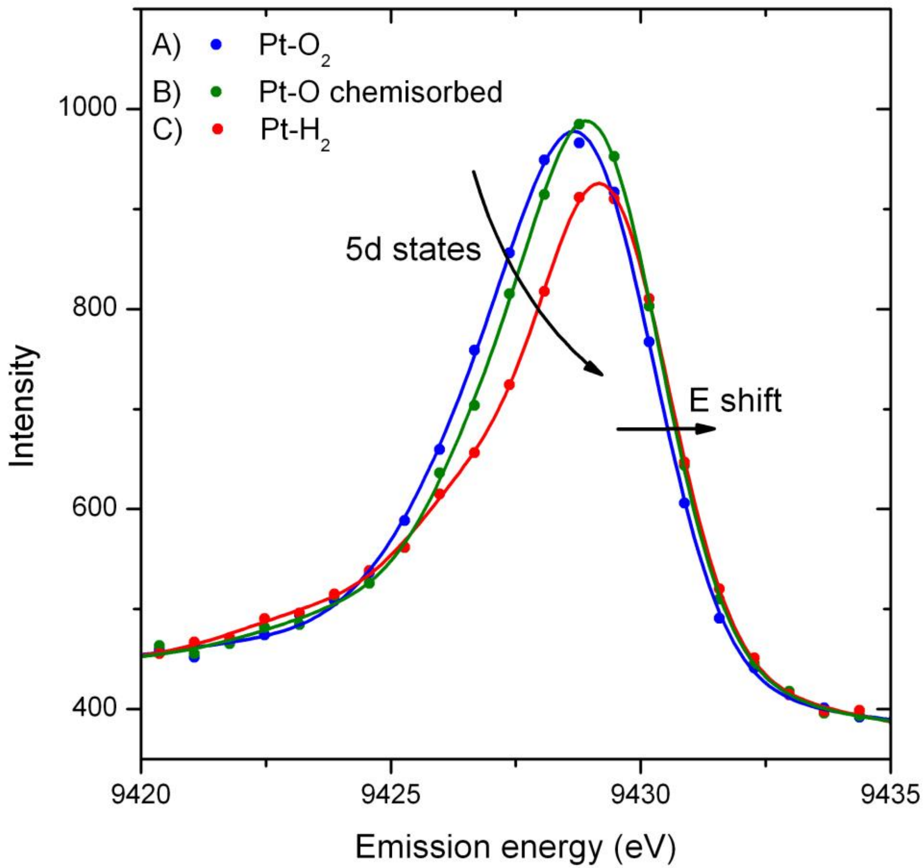
High energy resolution off-resonant spectroscopy

Pt reduction/oxidation: 100msec time resolution

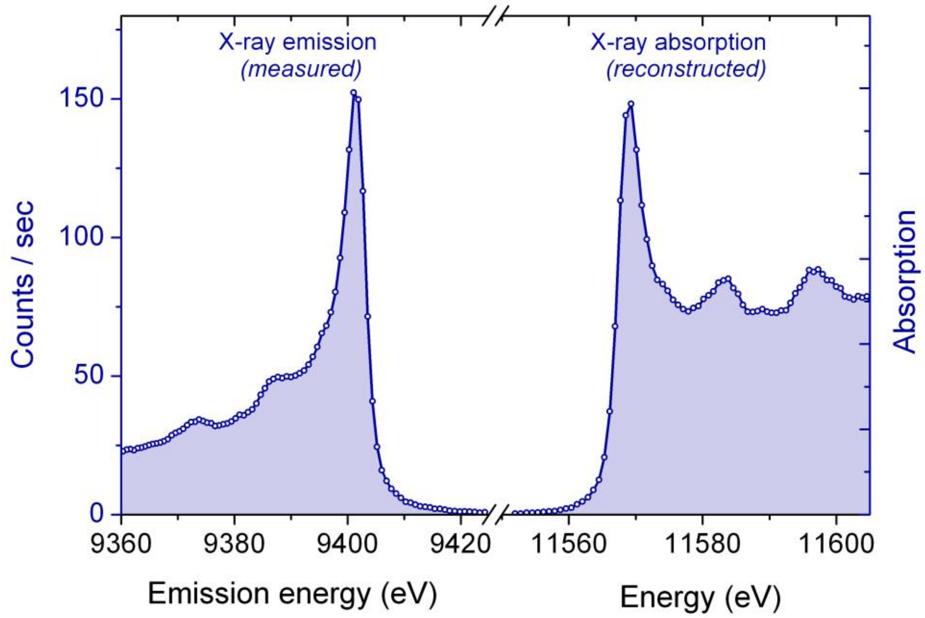
In situ reduction/oxidation of Pt by gas switching at 200 ^{o}C



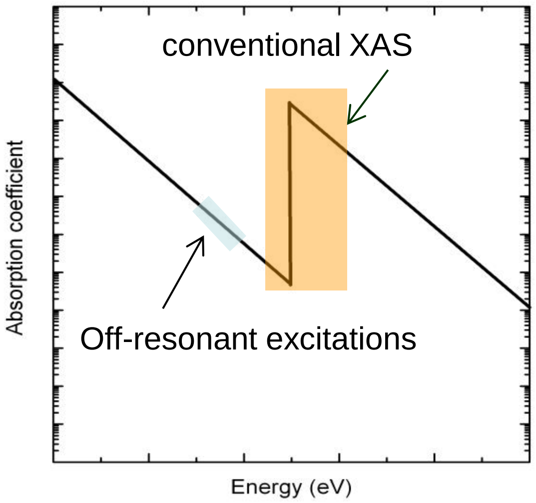




High energy resolution off-resonant spectroscopy



I) HEROS shape is independent on I_0 fluctuations



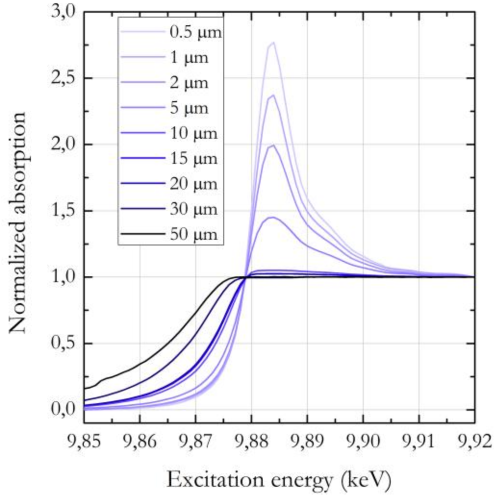
II) HEROS shape is independent on self-absorption process

High energy resolution off-resonant spectroscopy

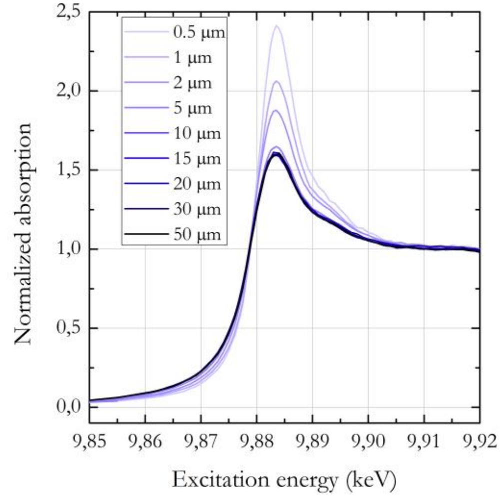
XAS shape modifications by sample concentration/thickness

Ta L_3-XAS

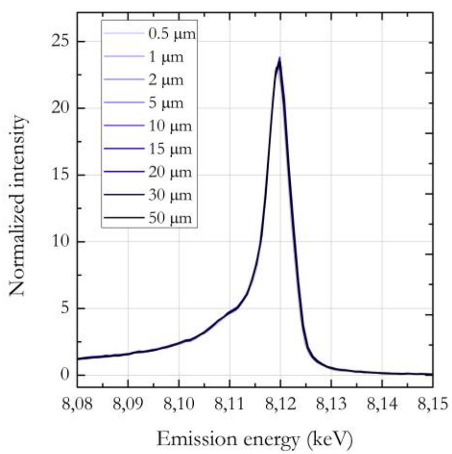
transmission XAS



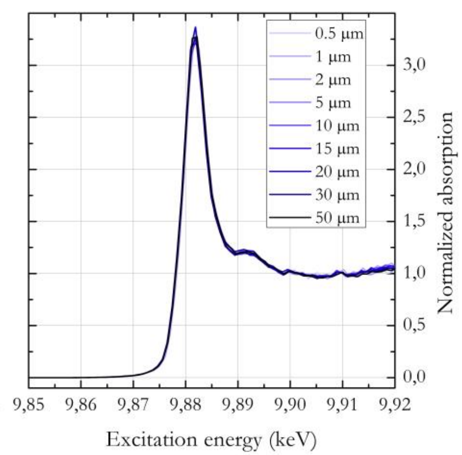
TFY-XAS



HEROS-XES



HEROS-XAS



HEROS spectroscopy

-HEROS allows for XAS-like studies at unlimited time resolution

-HEROS spectra are of high energy resolution

-HEROS is ideal technique to be applied for pulsed x-ray sources

Preliminary results from x-ray free electron laser experiment (LCLS)

XFEL radiation

	XFEL	SLS
No of pulses per sec:	1 -100	104 000
Pulse length:	10-50 femtosec	50 picosec, 960 nanosec
No of photons / pulse:	10^{12}	10^{4}, 10^{6}
No of photons / sec:	10^{12}-10^{14}	10^{12}-10^{14}

Single-shot off-resonant spectroscopy

XFEL project devoted to study the interaction of short x-ray pulses with mater

Experimental setup LCLS-CXI end station:

x-ray energy: 8.9-9.6keV

pulse length 20-50 fsec

10^{12} photons / pulse

beam size 0.1-0.3 um^2

Photon fluencies:

up to **10^4 photons/(atom·fsec)**

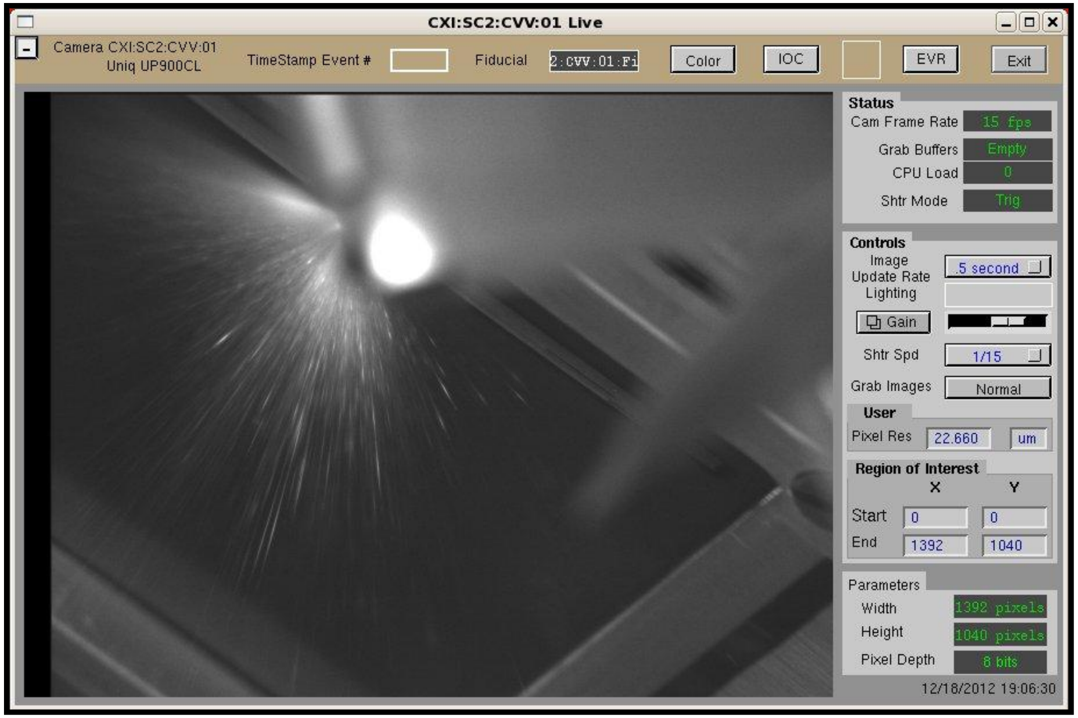


Figure: Photograph of Cu-foil during the XFEL irradiation. Material sputtering induced by short and intense x-ray pulses was observed.

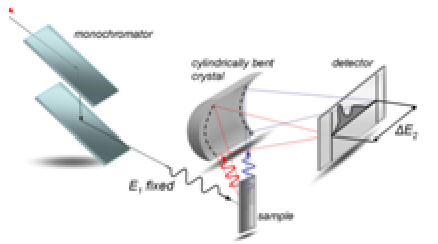
Single-shot off resonant spectroscopy

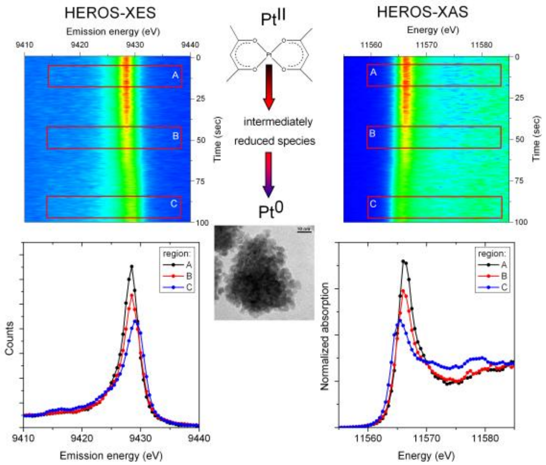
XFEL project devoted to study the interaction of short x-ray pulses with matter

Goal: probe unoccupied electronic structure with HEROS and decay channels (occupied states) by XES.

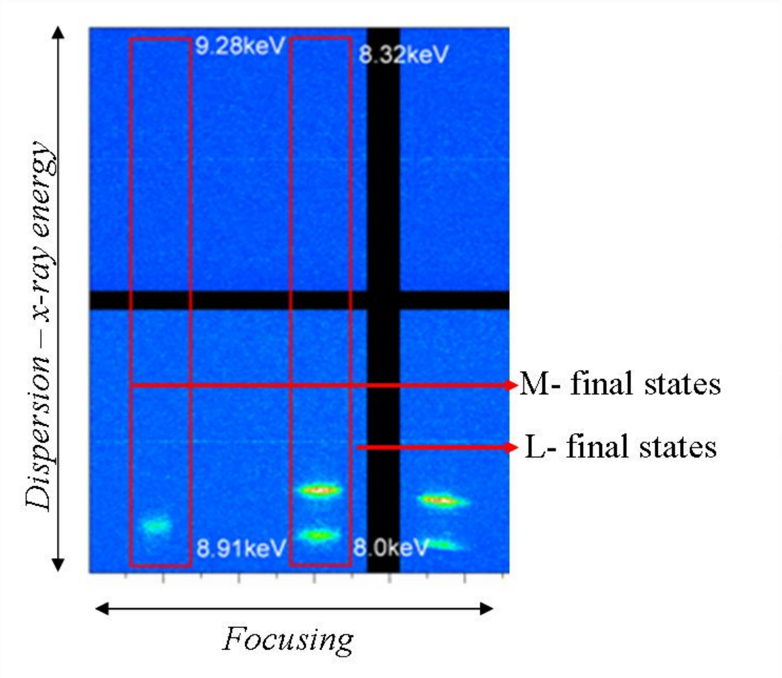
Experimental approach: Multi-wavelength detection experimental scheme in the von Hamos geometry, recently developed at SuperXAS of SLS.

High energy resolution off-resonant spectroscopy (HEROS)





Multi-wavelength detection at LCLS



J. Szlachetko et al, Rev. Sci. Instr., 83, 103105 (2012).

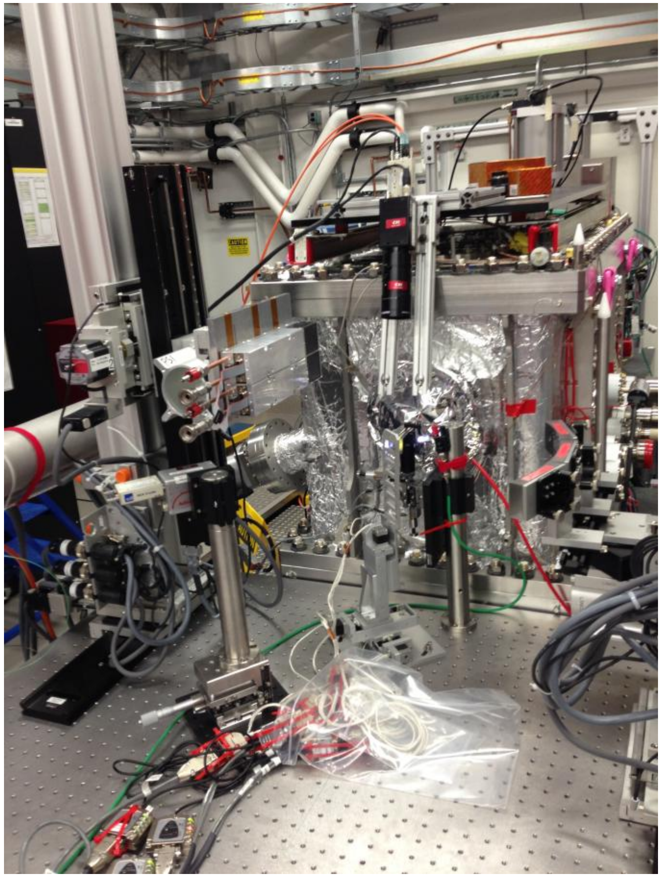
J. Szlachetko et al, Chem. Comm., 48, 10898 (2012).

J. Szlachetko et al, J. Electron. Spectrosc. Relat. Phenom. doi:11.002 (2012)

Single-shot off-resonant spectroscopy

XFEL project devoted to study the interaction of short x-ray pulses with mater

Experimental setup LCLS-CXI end station:



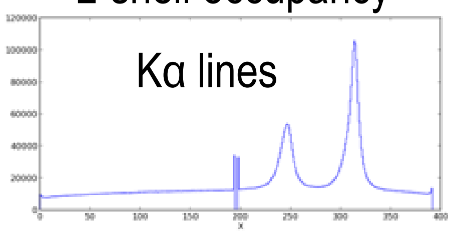
XFEL experiment – preliminary spectra

Imaging the atom electronic structure and electron rearrangements at fsec time scales

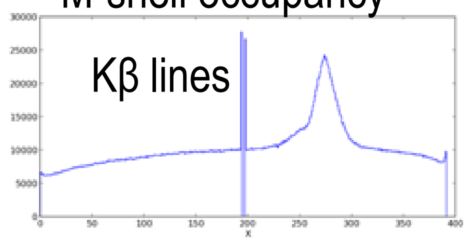
XES spectra

low fluencies < 0.1 photons/(atom·fsec)

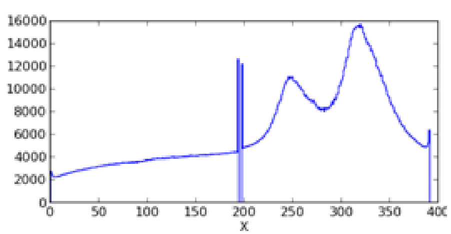
L-shell occupancy



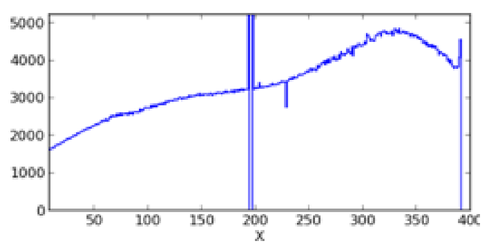
M-shell occupancy



high fluencies > 10^4 photons/(atom·fsec)



line broadening
+ signal dump



no signal

Data suggest ion creation up to Cu^{25+}. Detailed analysis will allow to determine steps in hole-transfer and electron rearrangement processes within femtosecond time resolution.

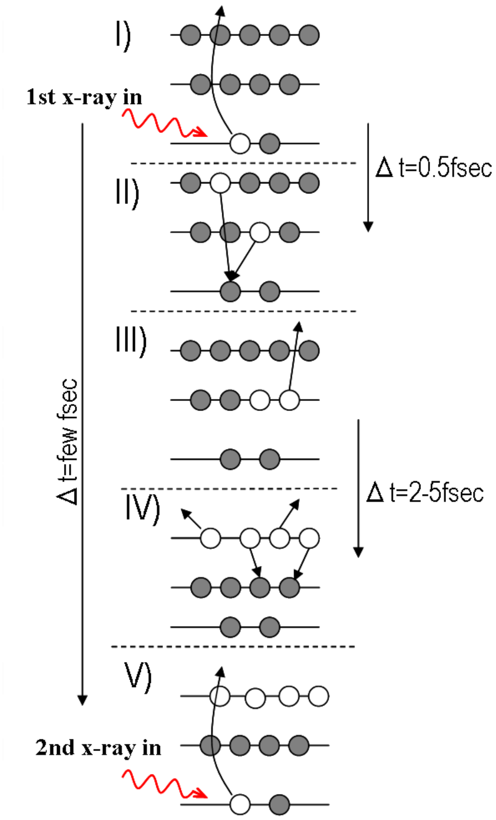


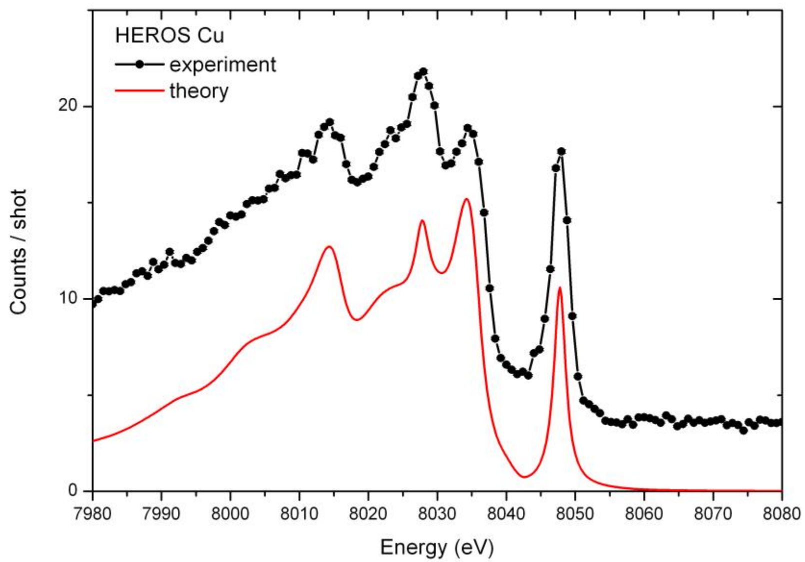
Figure: Schematic of electron rearrangement process induced by x-ray absorption of core electron.

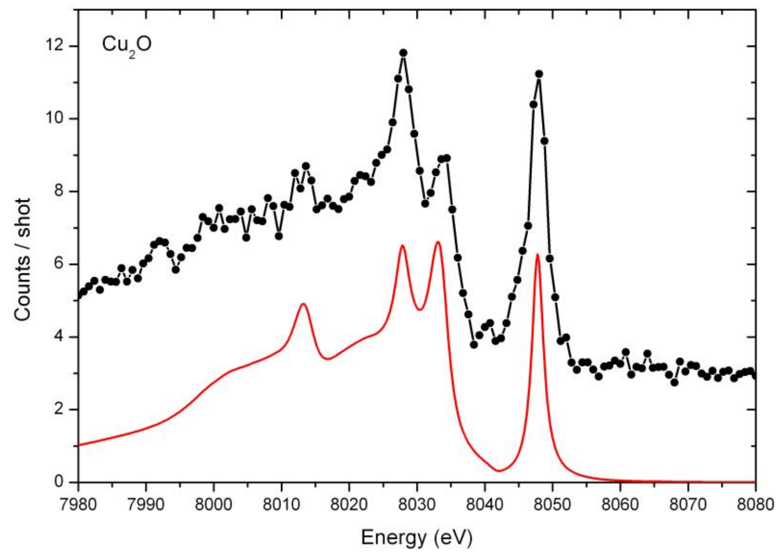
XFEL experiment – preliminary spectra

High energy resolution off-resonant spectroscopy (HEROS): Chemical speciation at femtosecond time scales.

HEROS provide information about unoccupied electronic states. Experimental approach allows for XAS-like studies on a shot-to-shot basis.

HEROS XFEL spectra, 50fsec pulses

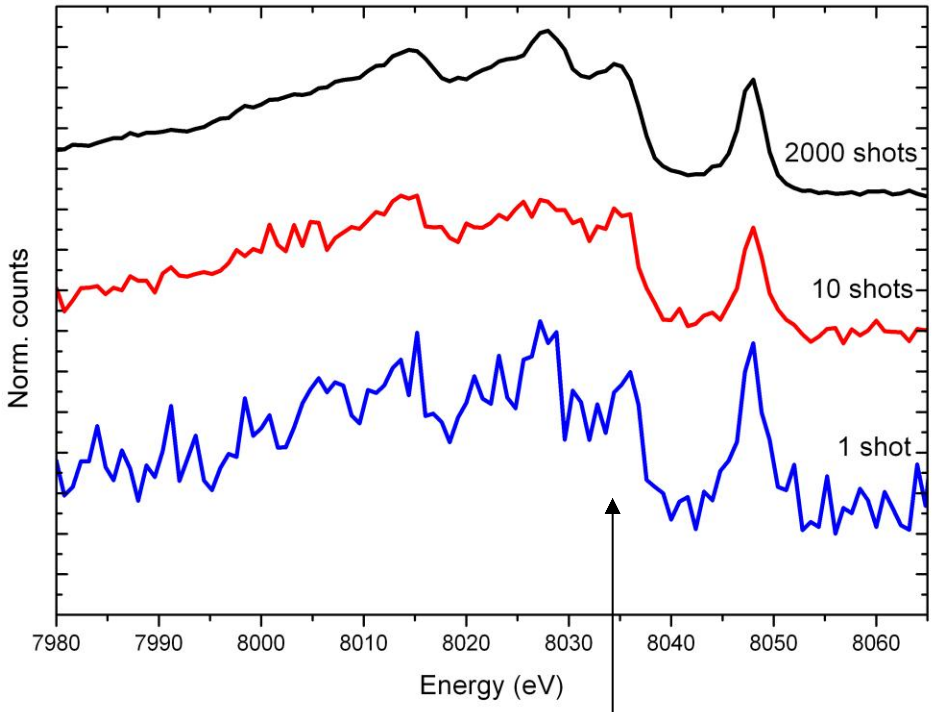




First time demonstration of HEROS applicability to XFEL sources

XFEL experiment – preliminary spectra

HEROS @ XFEL: single-shot capability



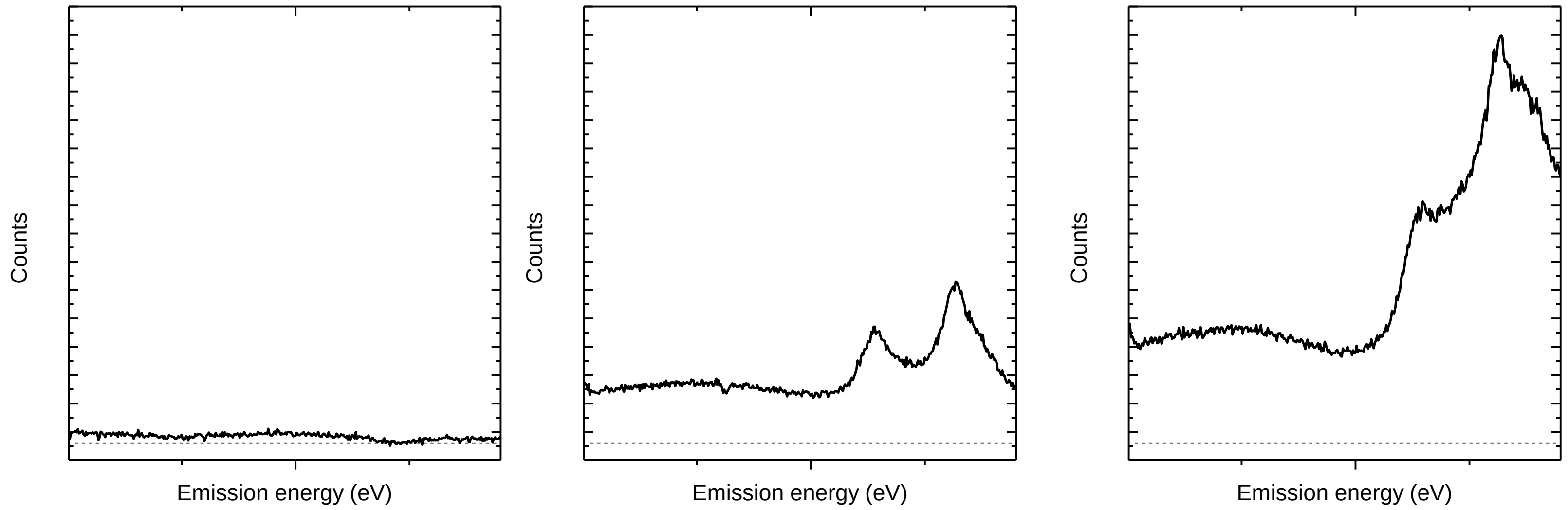
XAS-like spectrum with ONE 50fsec x-ray pulse

XFEL experiment – preliminary spectra

Non-linear x-ray absorption: fluency dependence studies

Incident x-ray energy << Ionization energy

0.1 ph/(atom x fsec) 100 ph/(atom x fsec) 10000 ph/(atom x fsec)

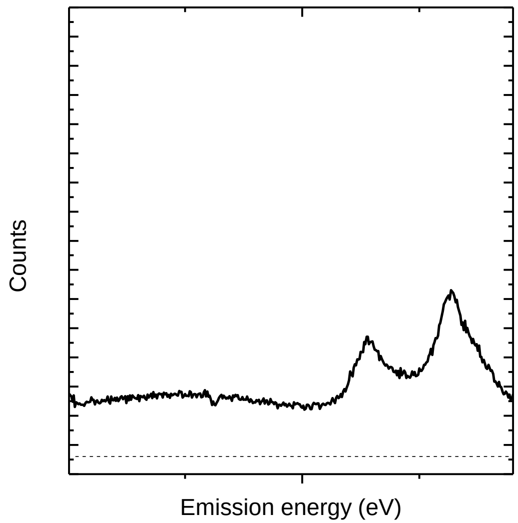


synchrotron flux: 0.000000000001 ph / (atom x fsec)

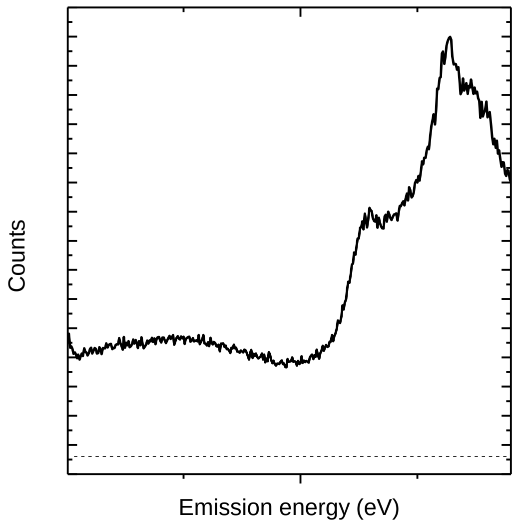
XFEL experiment – preliminary spectra

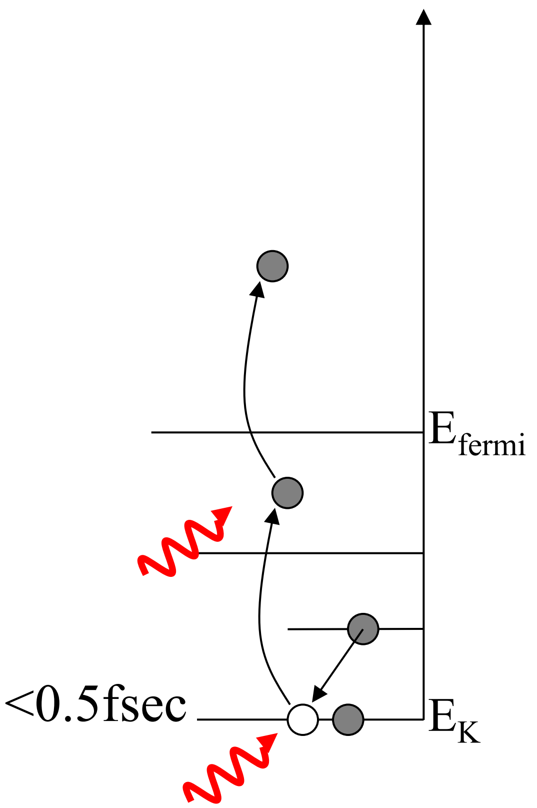
Non-linear x-ray absorption: fluency dependence studies

100 ph/(atom x fsec)



10000 ph/(atom x fsec)

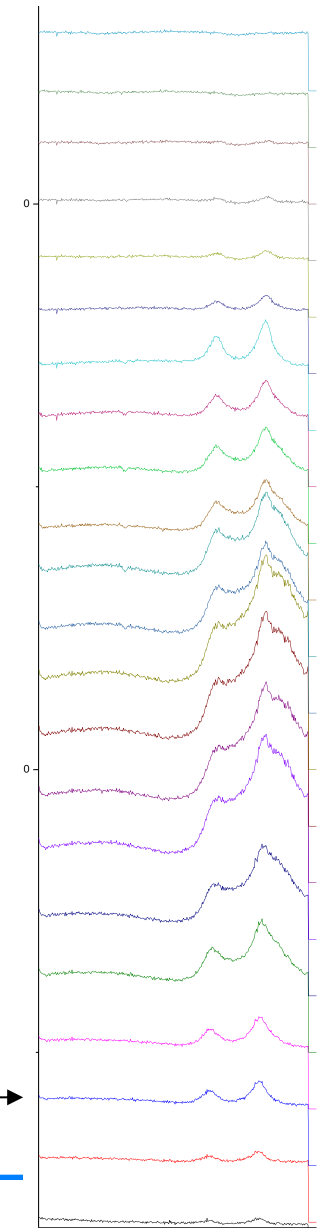




Thank you for your attention

XFEL experiment – preliminary spectra

Non-linear x-ray absorption: fluency dependence studies



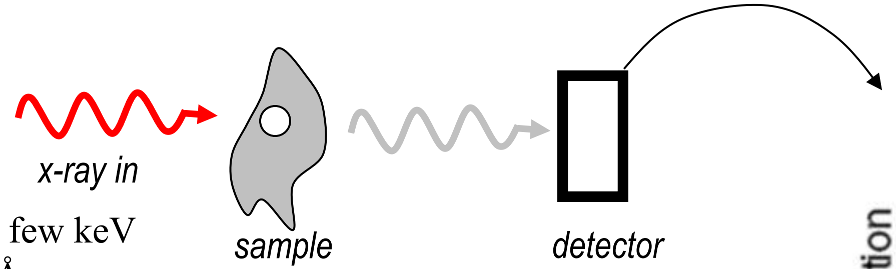
x-ray power

x-ray power

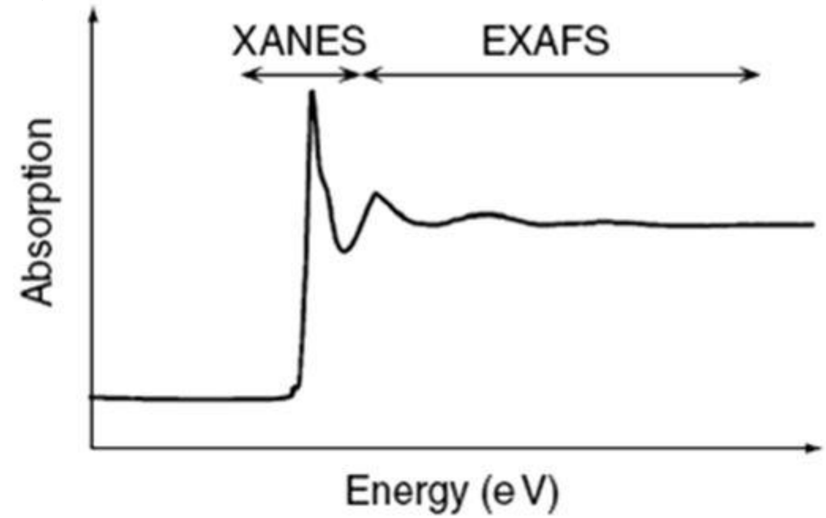
decay time 0.5 femtosec

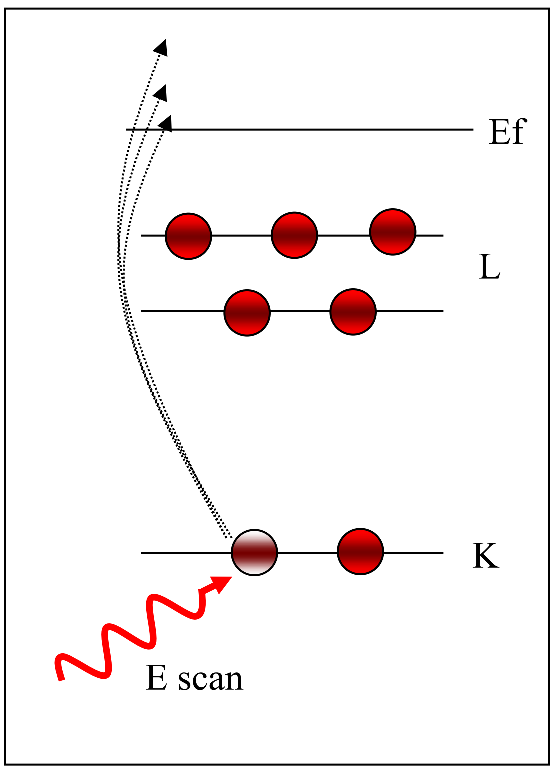
X-ray interaction with matter: absorption & emission

X-ray absorption spectroscopy in transmission



E ~ few keV
λ~ Å





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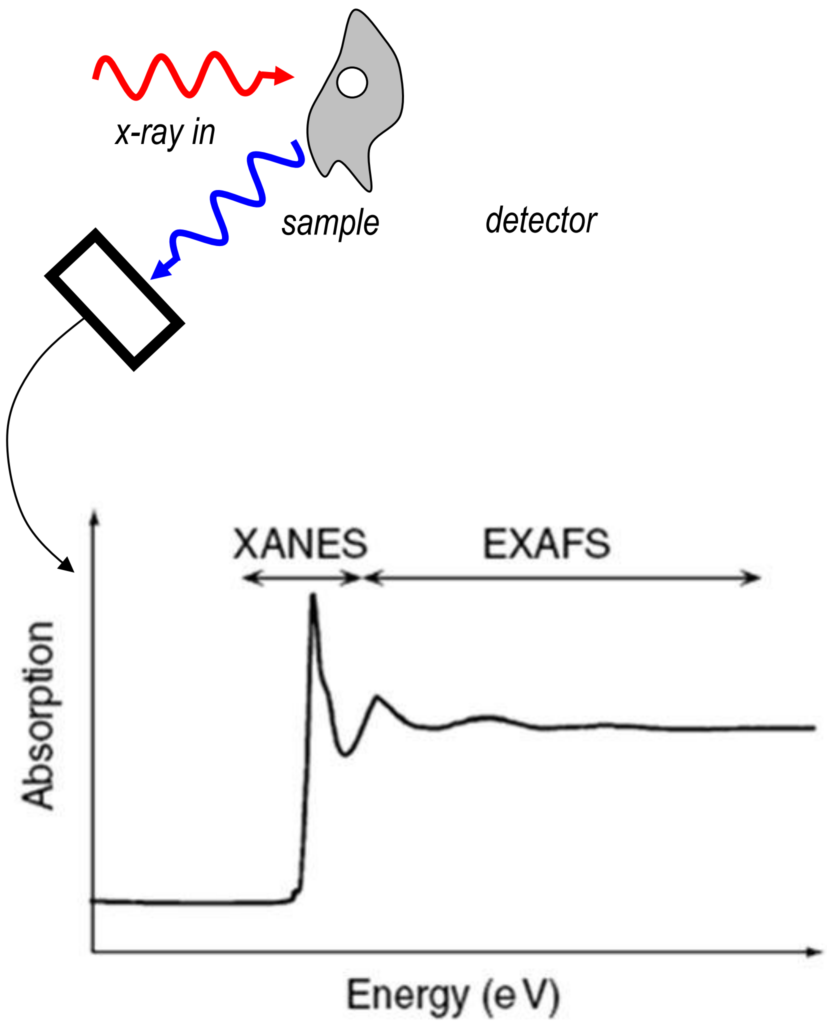
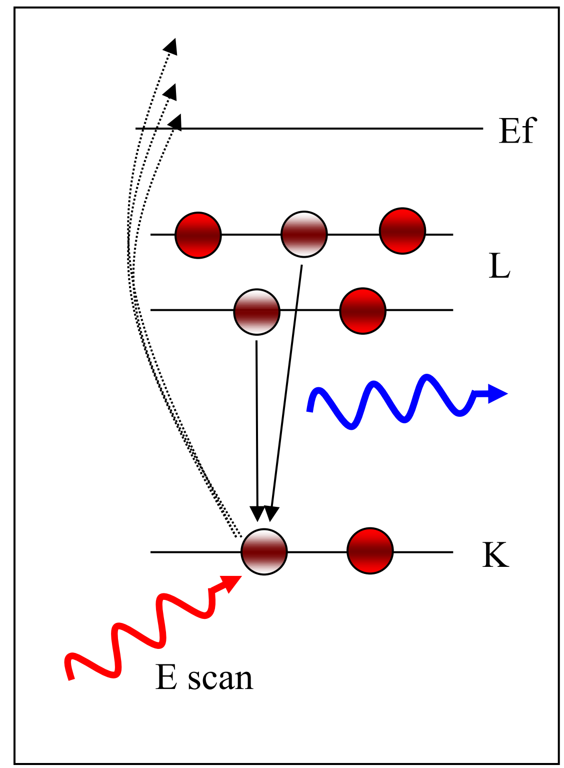
X-ray interaction with matter: absorption & emission

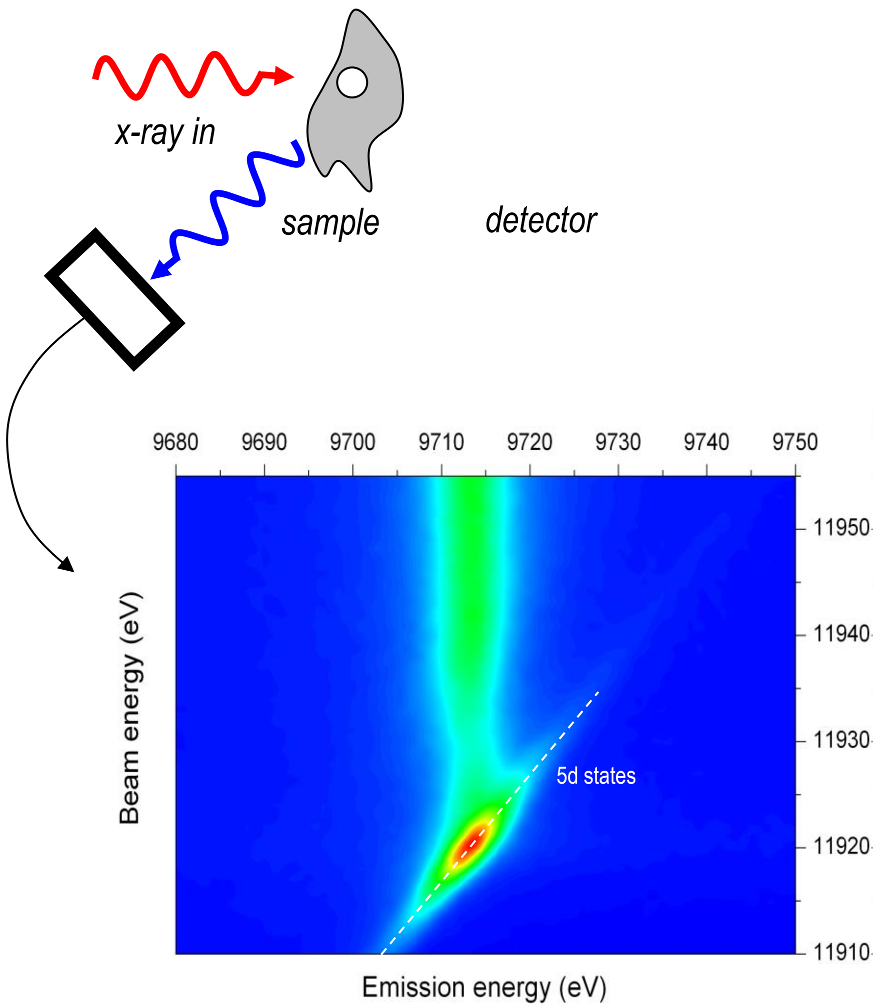
X-ray absorption spectroscopy in fluorescence

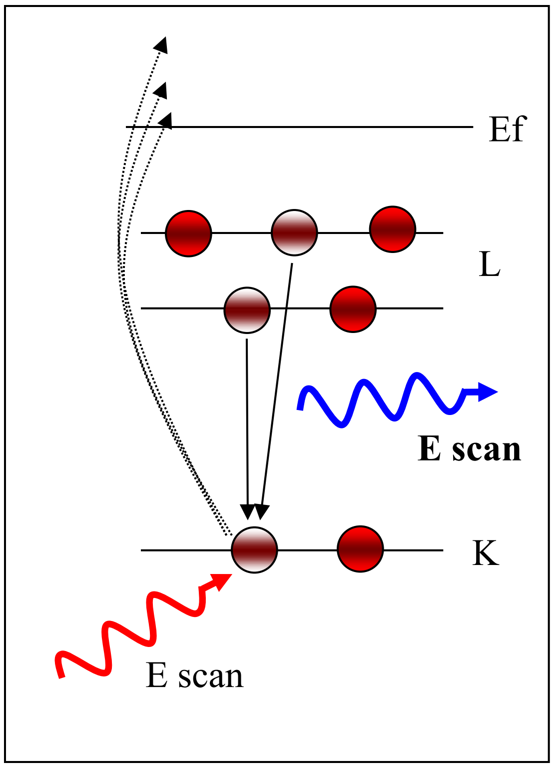




X-ray interaction with matter: absorption & emission

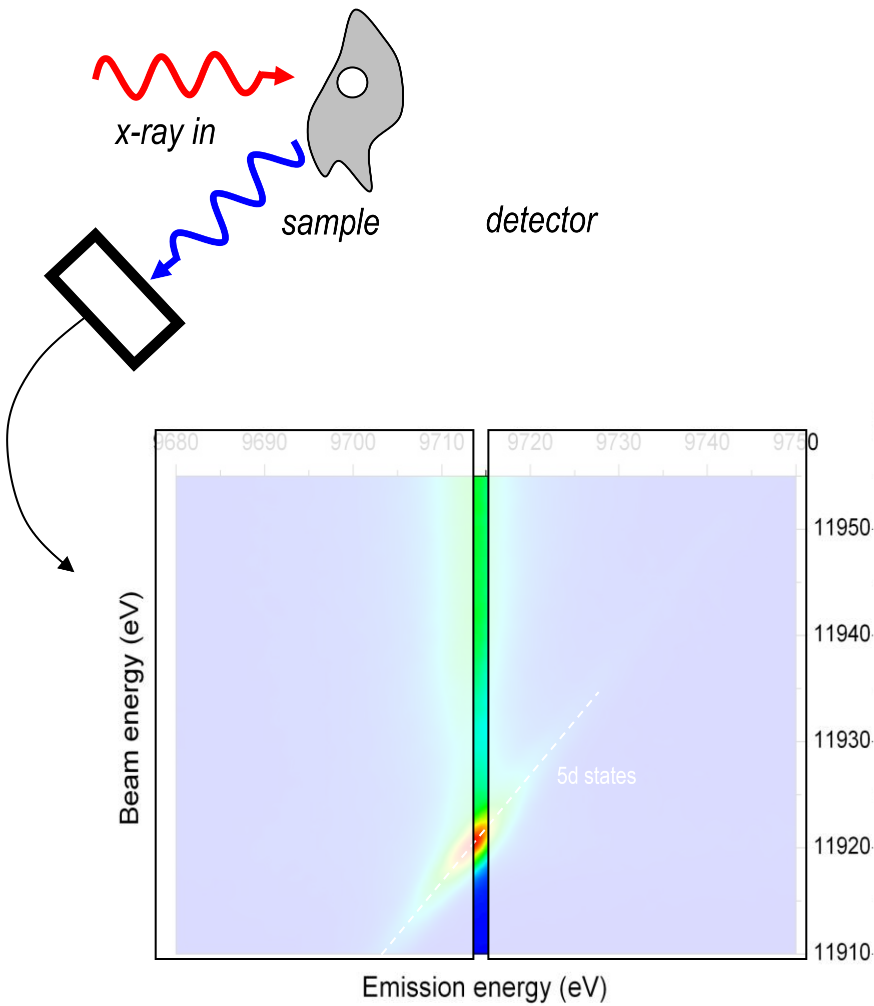
Resonant inelastic x-ray scattering (RIXS) spectroscopy

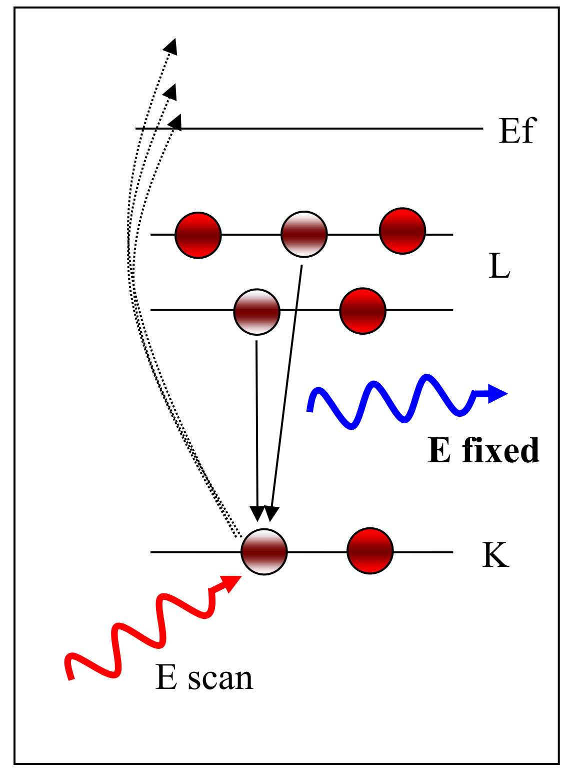




X-ray interaction with matter: absorption & emission

High energy resolution XAS spectroscopy





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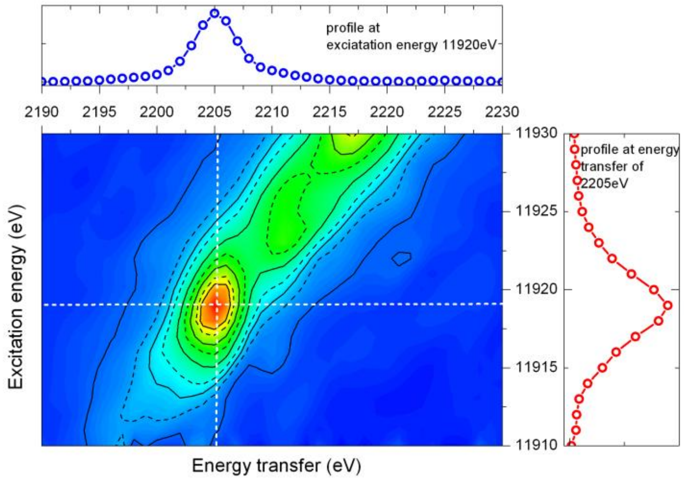
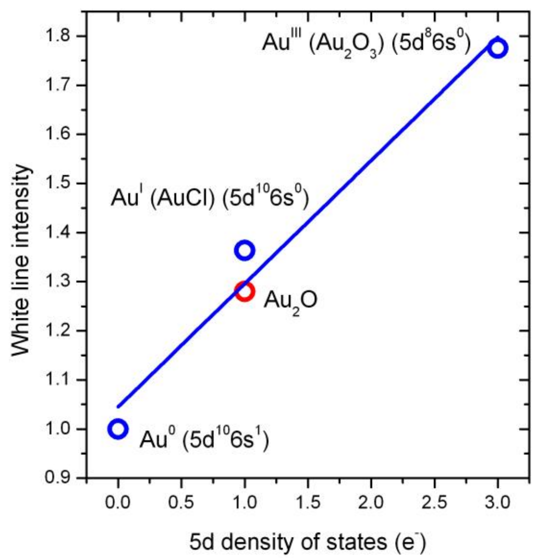
Quick-RIXS spectroscopy

TPR of Au(III) – quantitative analysis of 5d unoccupied states





Top) Energy transfer RIXS for extracted intermediate compound. The profiles at constant excitation energy and energy transfer are plotted on top and right panels, respectively. The profiles intensities were used for qualitative determination of 5d states of extracted Au2O compound.

Bottom) The extracted population of 5d states of intermediate Au2O are compared to Au-standards.

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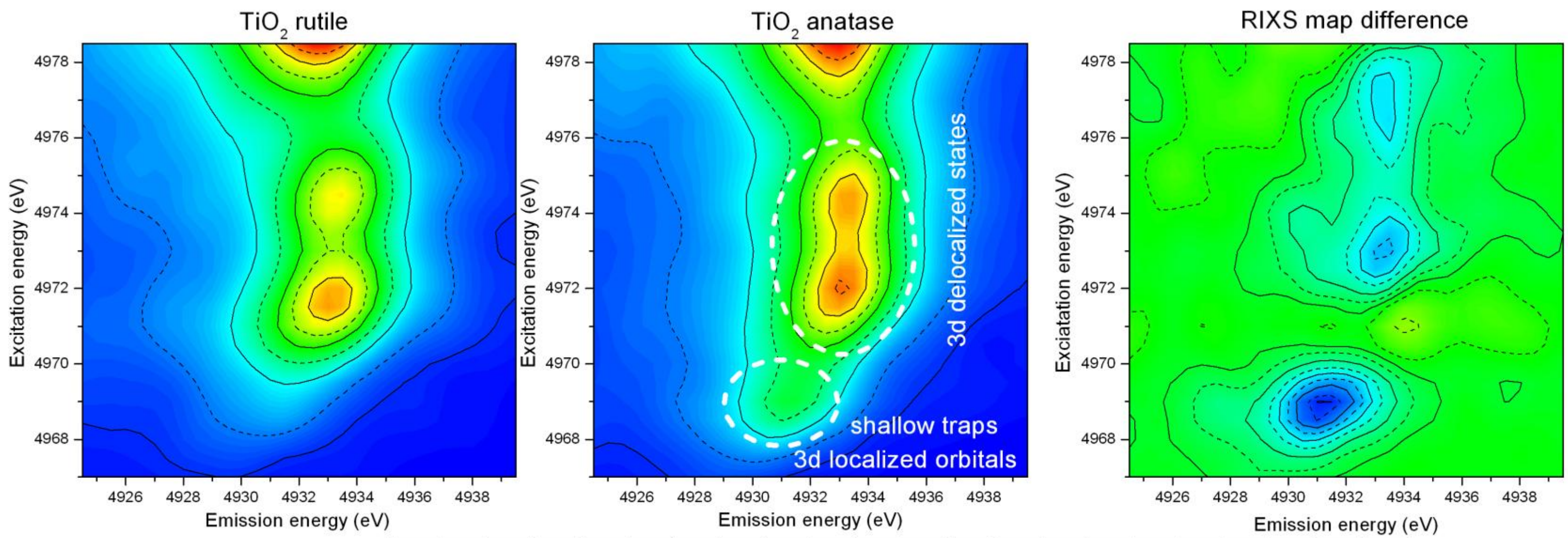
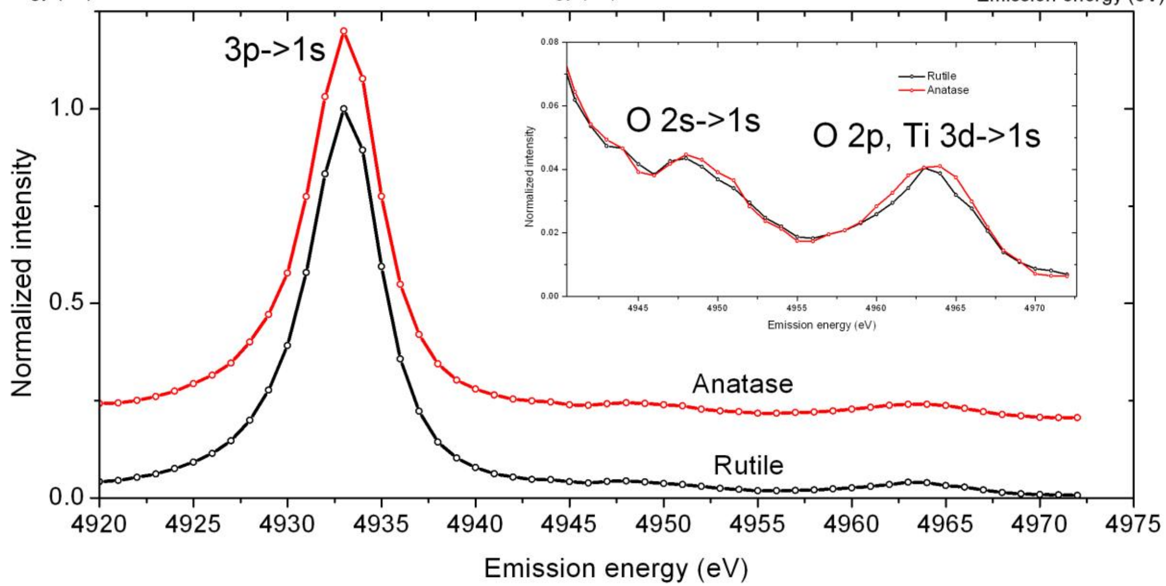
RIXS spectroscopy on Kb and v2c transitions

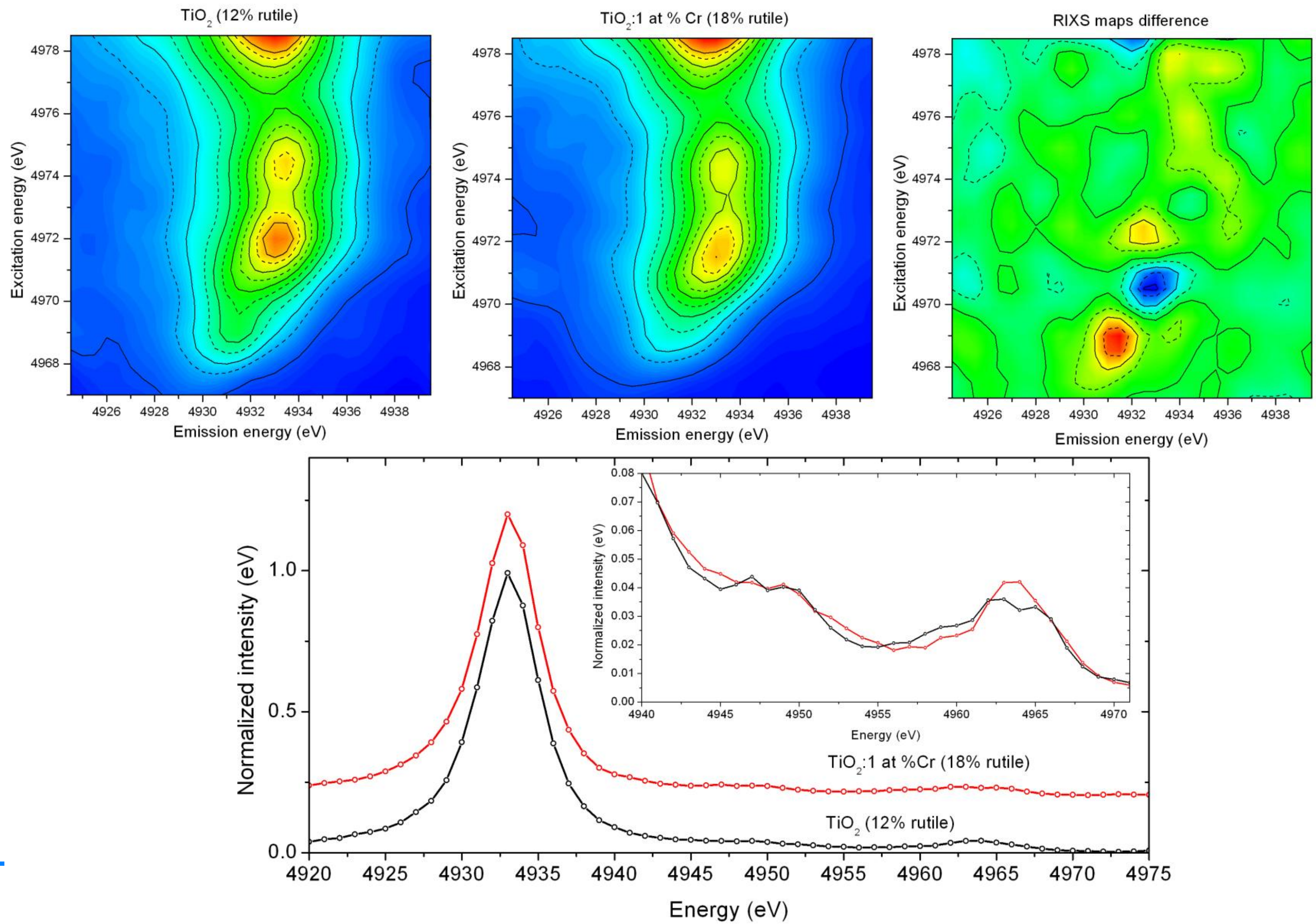
Valence-to-core transitions on TiO_2: anatase vs. rutile





RIXS spectroscopy on Kb and v2c transitions

Valence-to-core transitions on TiO_2 and doped-TiO_2



RIXS spectroscopy on Kb and v2c transitions

Valence-to-core transitions on TiO_2 and doped-TiO_2

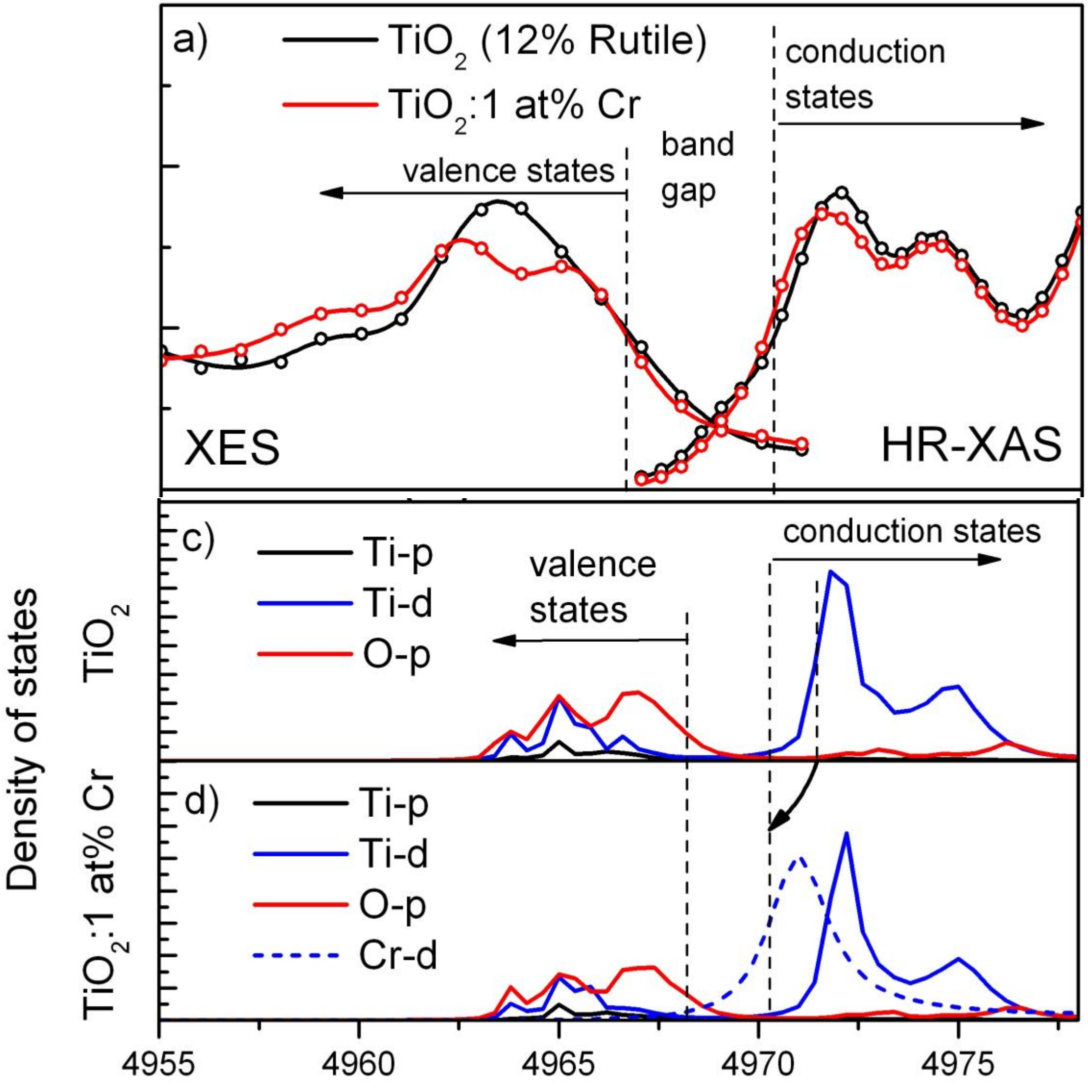


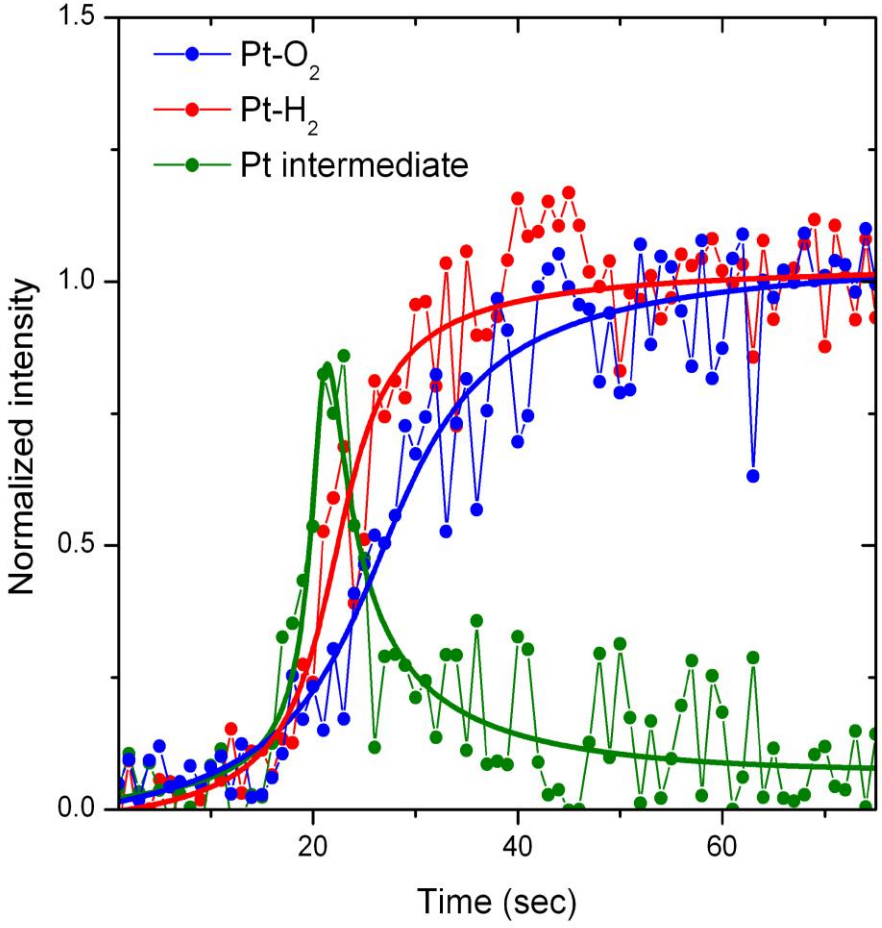
Table: Summary of extracted energy gaps between occupied and unoccupied states.

TiO2 rutile	3.7eV
TiO2 anatase	4.6eV
TiO2 anatase (12% rutile)	4.2eV
TiO2 Cr-doped	3.8eV

High energy resolution off-resonant spectroscopy

Pt reduction/oxidation: 100msec time resolution

In situ reduction/oxidation of Pt by gas switching at 200 ^{o}C



Result of 3 component fitting to the HEROS profiles. The data are binned to 400 msec time resolution for clarity of presentation. An intermediate profile is detected before the oxidation process. The fitted profiles also shows slower reaction kinetics in case of oxidation as compared to the reduction.

Single-shot x-ray spectroscopy

Summary and outlook:

XES and HEROS spectra were measured on a shot-to-shot basis.

Non-linear processes were observed and identified.

Electron rearrangement processes could be detected.

Sequential K-shell ionization mechanism was observed and corresponding x-ray transitions were detected.

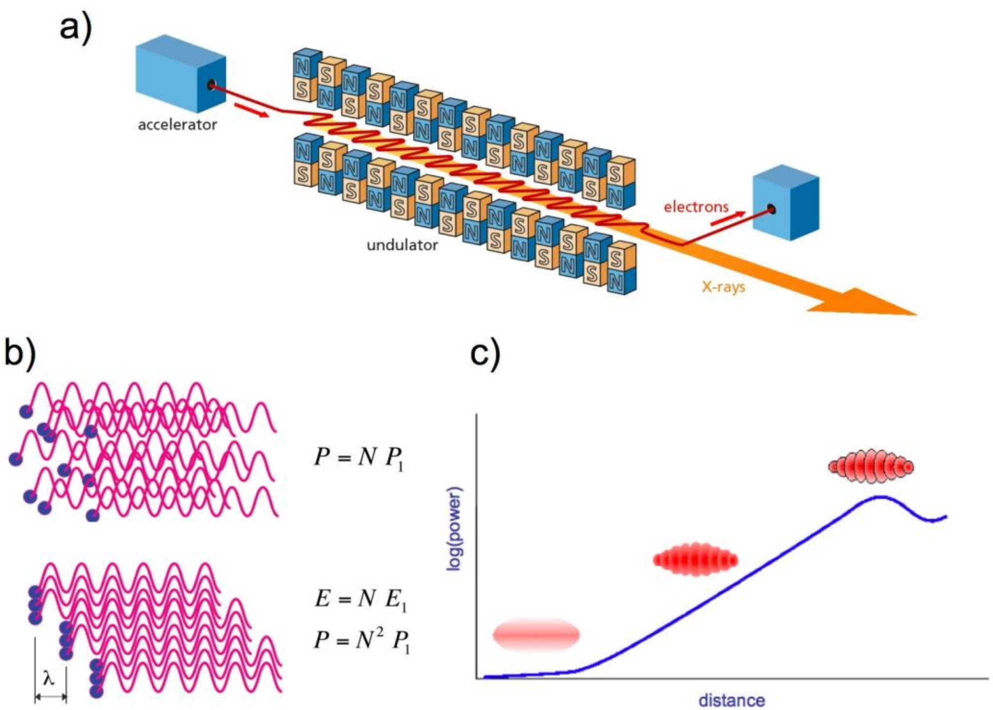
Capability of HEROS for single-shot chemical speciation was probed.

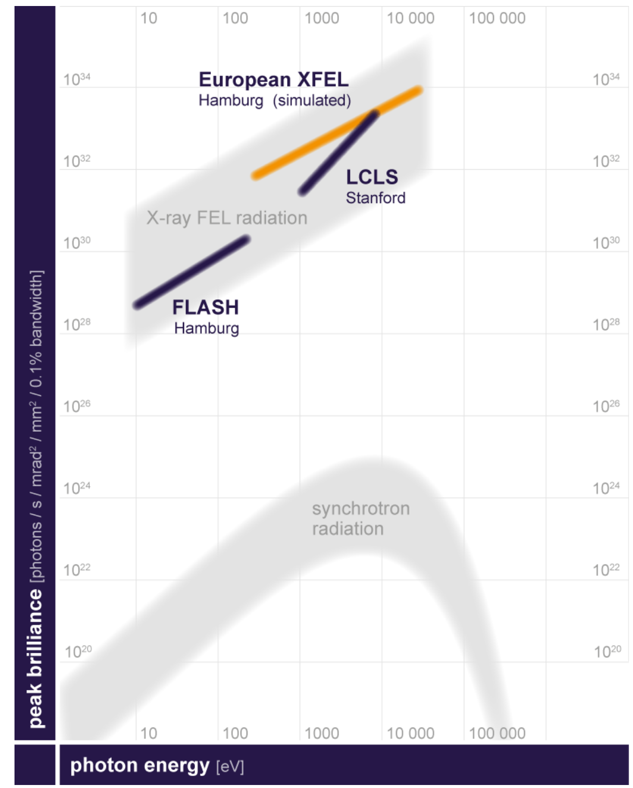
The experiment was a first step in understanding the electronic processes induced by XFEL pulses.

next step:

Radiation damage problems: test the experimental schemes for “probe-before-destroy” regime.

XFEL radiation





Number of photons on the sample: synchrotron 10^{12}-10^{13} ph/sec

XFEL 10^{14} ph/sec

RIXS spectroscopy on Kb and v2c transitions

Valence-to-core transitions on TiO_2 and doped-TiO_2

v2c-RIXS of TiO_2