

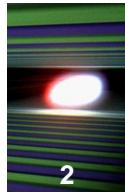
# FXE Scientific Instrument

C. Bressler

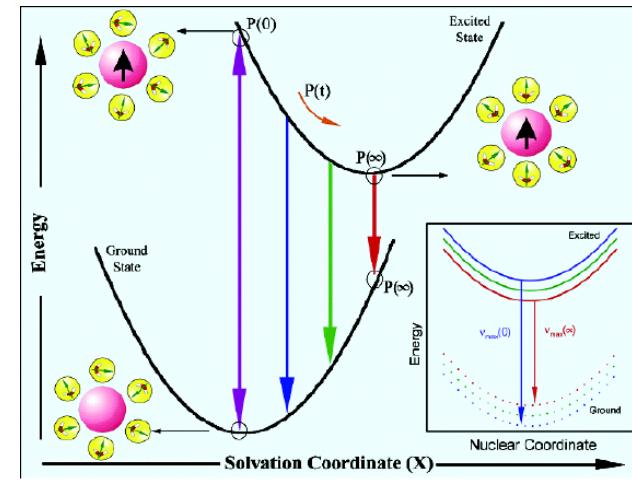
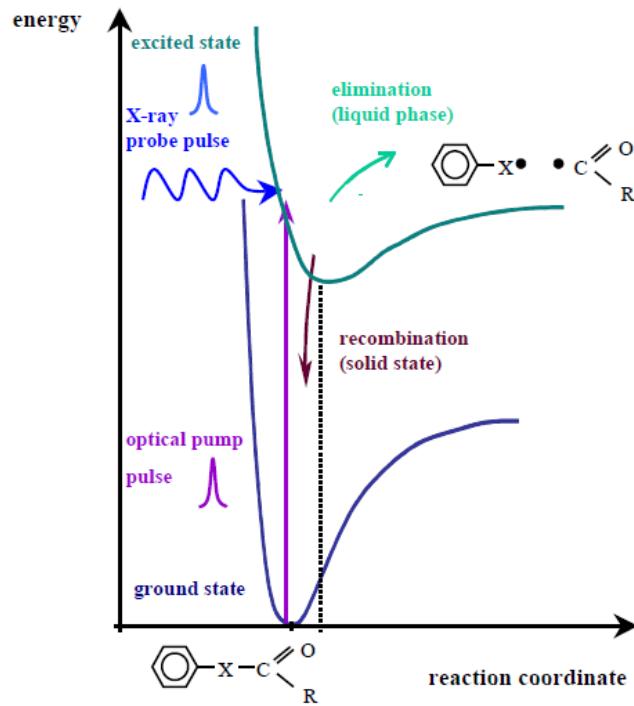
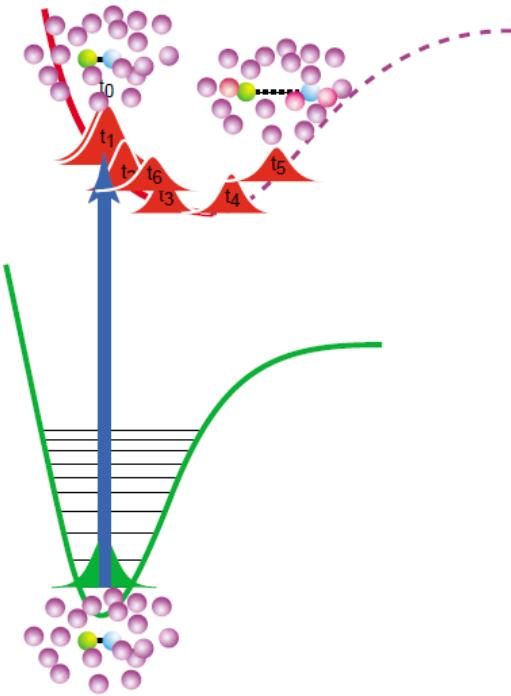
*Femtosecond X-ray Experiments (FXE)*

*European XFEL*

*christian.bressler@xfel.eu*



# Chemical Dynamics Applications...



# European XFEL FXE instrument

2007 : Scientific instrument dedicated to

## Femtosecond Diffraction Experiments –

Time-resolved structural dynamics investigations of solids, liquids, gases using x-ray diffraction + scattering

2009 : scientific scope refined following FXE Workshop (Budapest, Dec. 2009) for the

## Femtosecond X-ray Experiments instrument –

emphasizing the **combination** of X-ray **scattering** and X-ray **spectroscopies** to study liquid & solvation dynamics.

Target Observables:

- » electronic (charge transfer/transport)
- » spin
- » nuclear movements

...and all this **simultaneously**

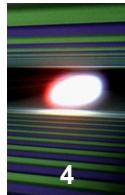
(→ single shot)

2016 : „From Picoseconds to Femtosecond X-Ray Experiments“

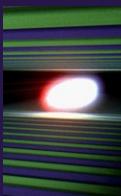


Late 2016: FXE early operation workshop (in planning stage)

# Workshop: From Picoseconds to Femtosecond X-Ray Experiments, Jan 26, 8:30 – 18:00

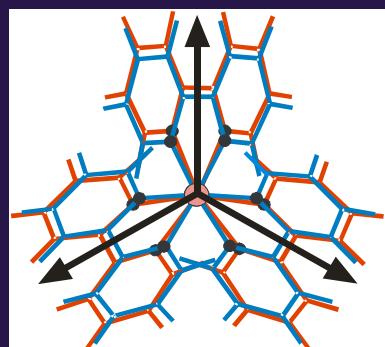
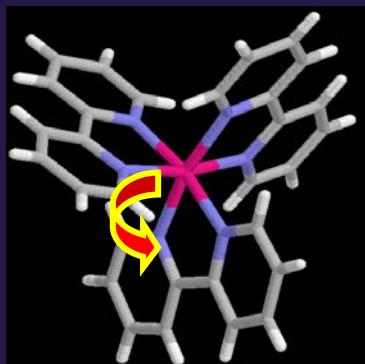


■ 142 Registered

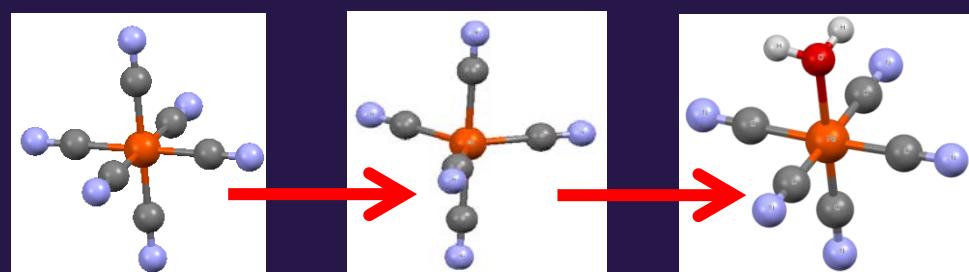


# FXE Mission: Nuclear, Charge and Spin Dynamics during an ongoing reaction „Elementary Steps in Photochemistry“

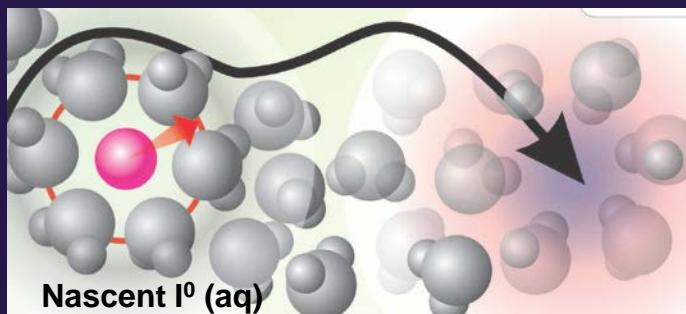
## Intramolecular Charge Transfer



## Ligand Detachment/Association

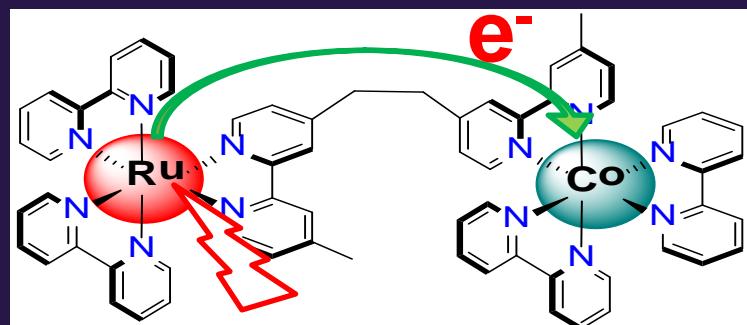


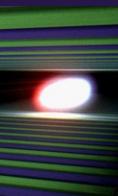
## Solvation Dynamics



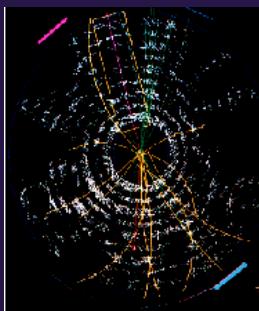
Nascent I<sup>0</sup> (aq)

## Elementary Steps in Charge Transport

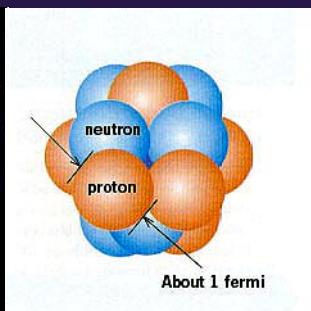




# What are the fundamental timescales?

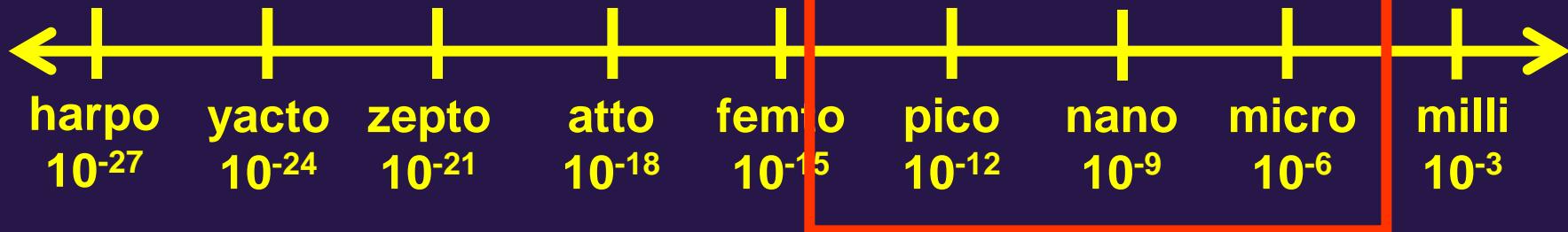


Strings,  
Cosmology



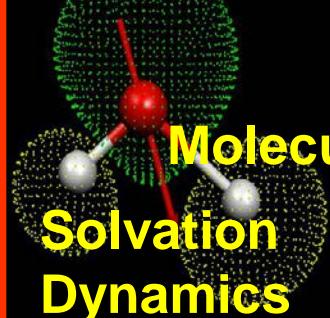
Particle  
Collisions

Electron dynamics

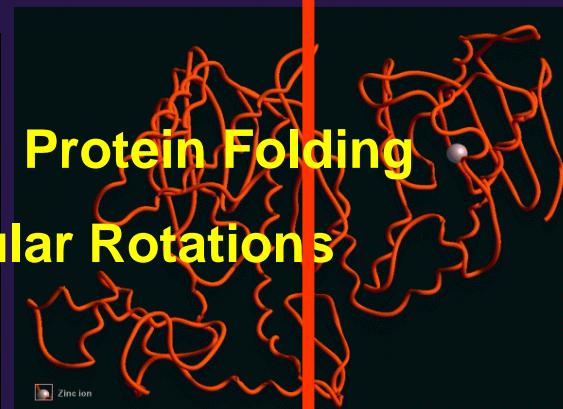


Femtochemistry, Photosynthesis and  
Catalysis

Molecular  
Vibrations



Molecular  
Rotations  
Solvation  
Dynamics



Protein Folding  
Molecular Rotations

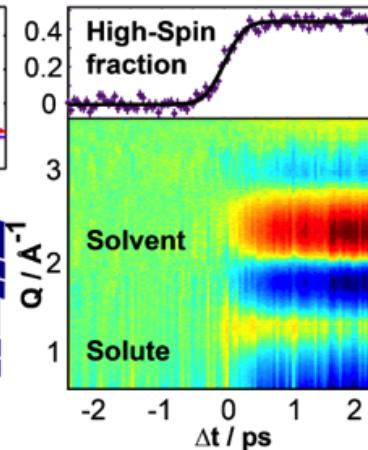
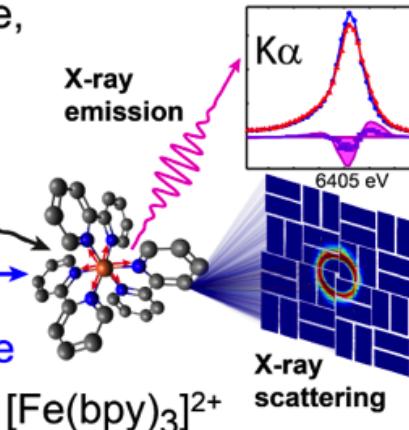
Zinc ion

Time /seconds

# Simultaneous ultrafast X-ray tools at XFELs

Laser pump pulse,  
400 nm, < 100 fs

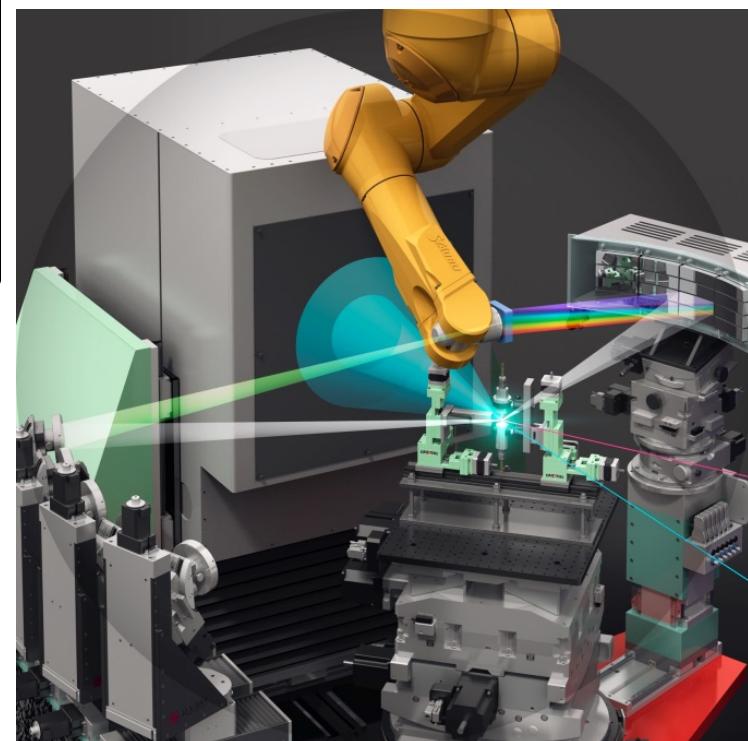
LCLS X-ray probe  
8 keV, < 100 fs



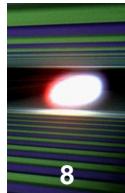
K. Haldrup et al., *J. Phys. Chem. B*, Just Accepted (2016)

Benchmark experiments at both worldwide existing XFEL facilities

Make use of complementary observables  
→ employ different experimental techniques)



Courtesy by European XFEL/Rey.Hori



# Simultaneous Techniques at the FXE instrument

## ■ X-Ray Absorption Spectroscopy

XANES: oxidation state changes, valence orbitals, DOS...

EXAFS: coordination shells (geometric)

## ■ X-Ray Emission Spectroscopy

spin momentum of the absorber, charge state, molecular orbitals,...

## ■ X-Ray Diffuse Scattering

Short- and medium-range geometric environment, solute + solvent (cage) contributions to the structural factor

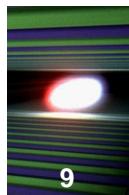
## ■ Resonant Inelastic X-Ray Scattering (RIXS)

Low energy excitations (d-d, charge transfer, even phonons), tunable to different final states, i.e. 3d orbitals (dipole-forbidden for  $1s \rightarrow nd$  excitation)

## ■ X-Ray Raman Spectroscopy

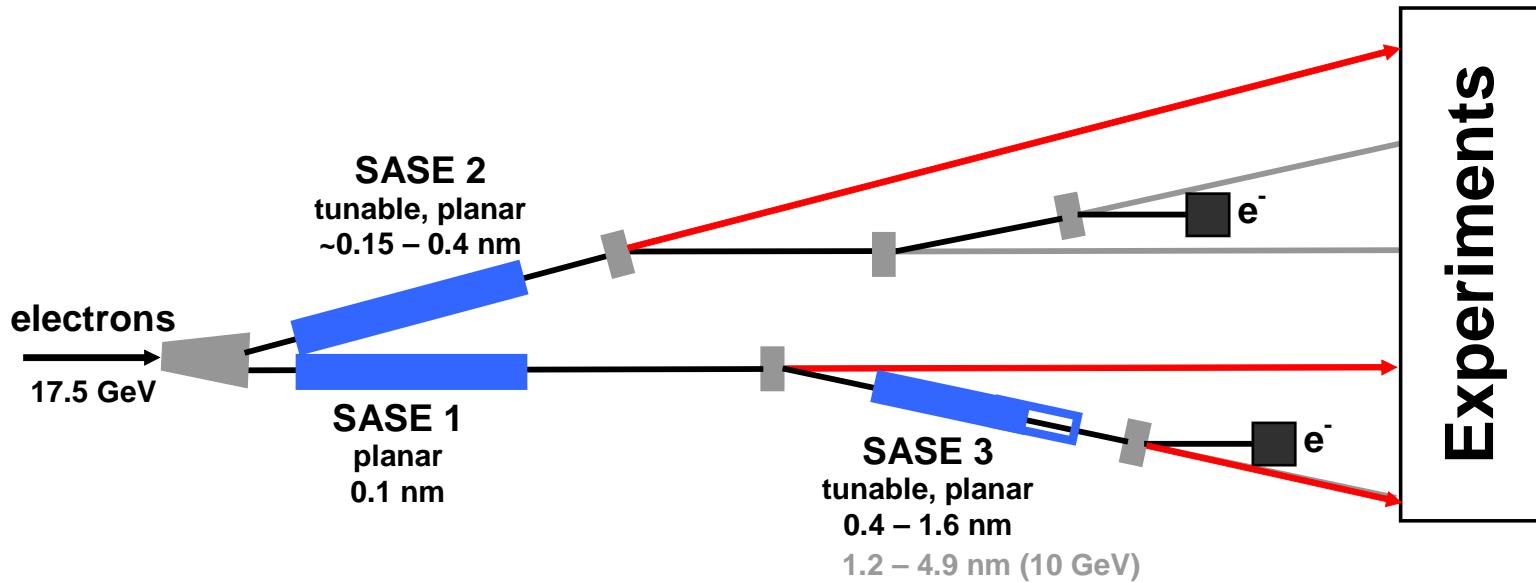
Access K-edges of light elements (N, O, C...) constituting solvent molecules



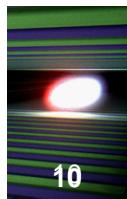


# The European XFEL

- First beam 31/12/2016
- Start of operation early 2017



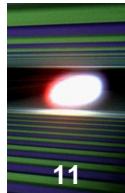
# Experimental Hall



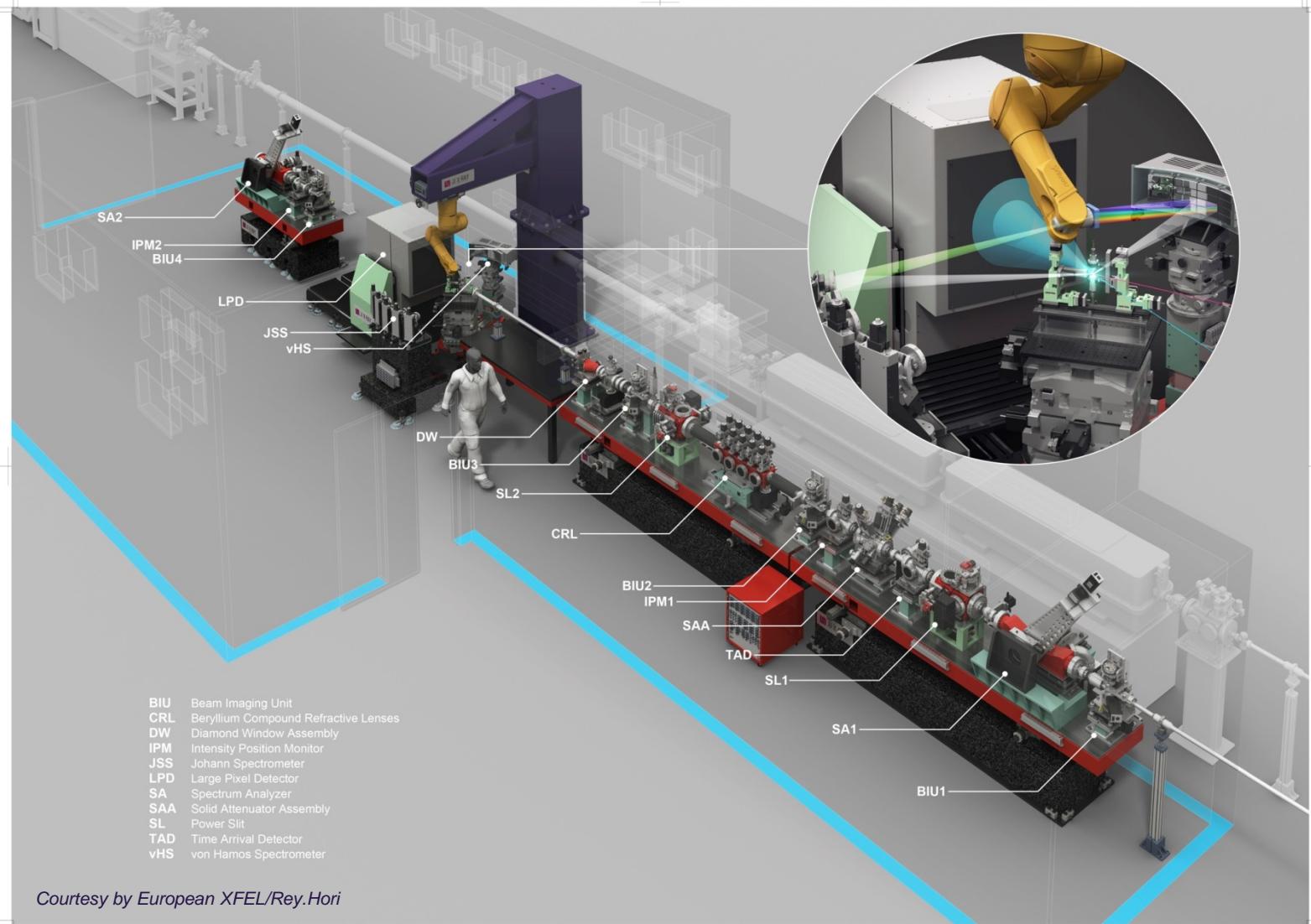
# FXE



# FXE Instrument (Jan. 2016)

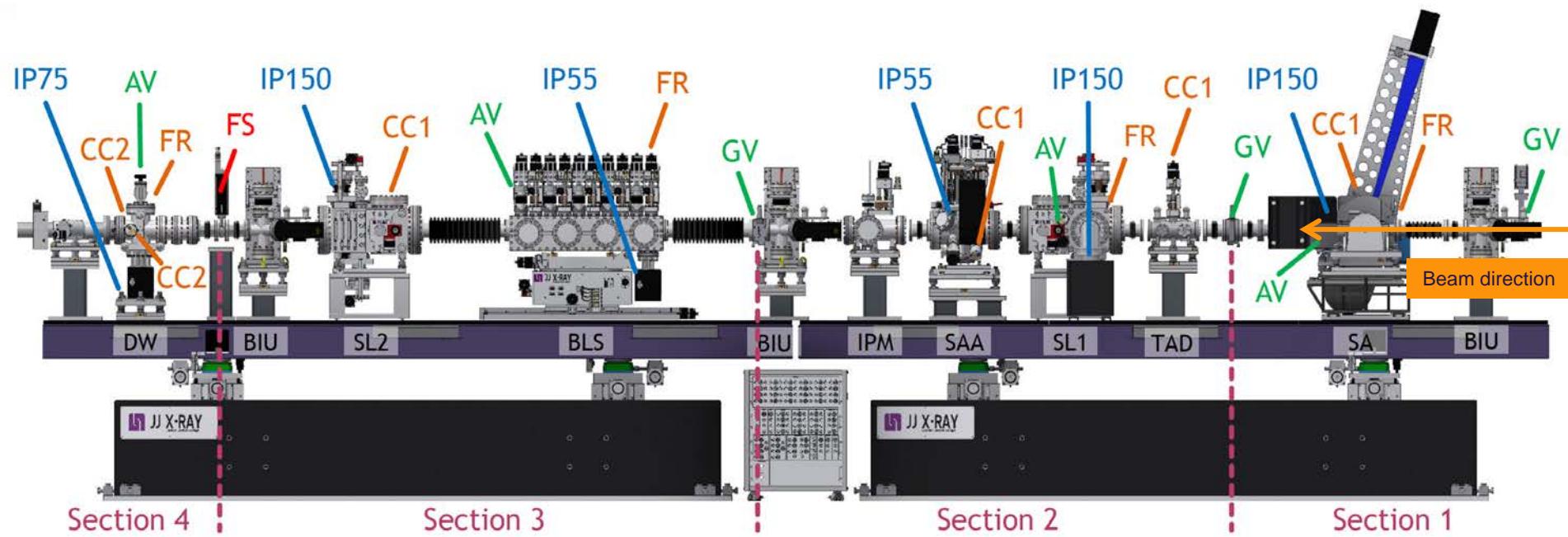


11

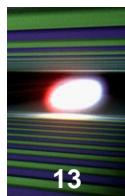


Courtesy by European XFEL/Rey.Hori

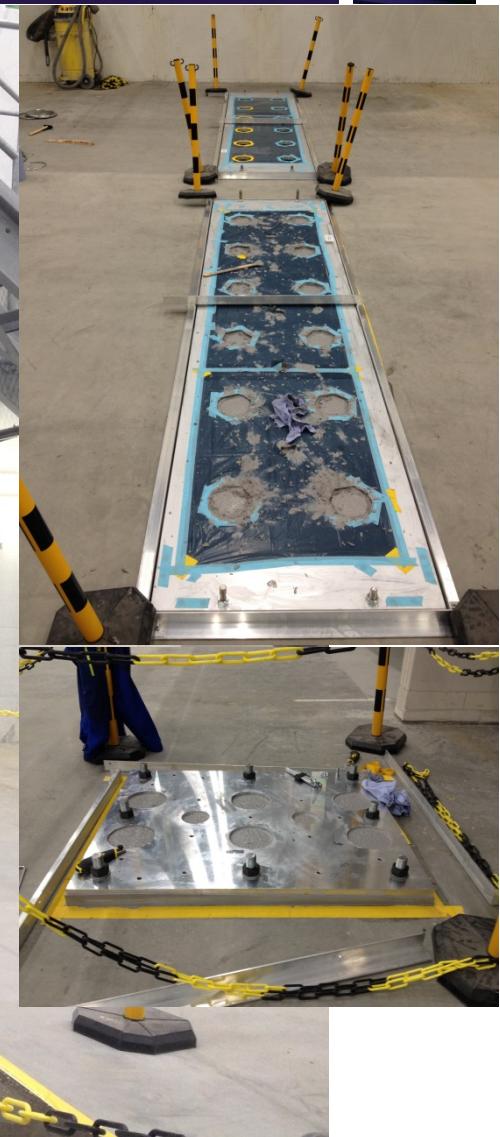
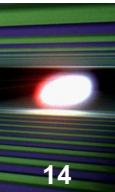
# FXE Optics Section



Feb 2015



March 2015

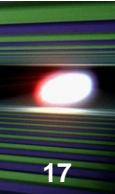


# The flying robot tower (Aug 2015)





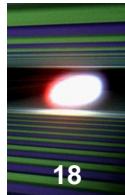
# FXE exp hutch (Sep 2015)

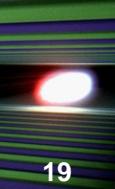


17



# Production well underway at JJ X-Ray (Sep 2015)



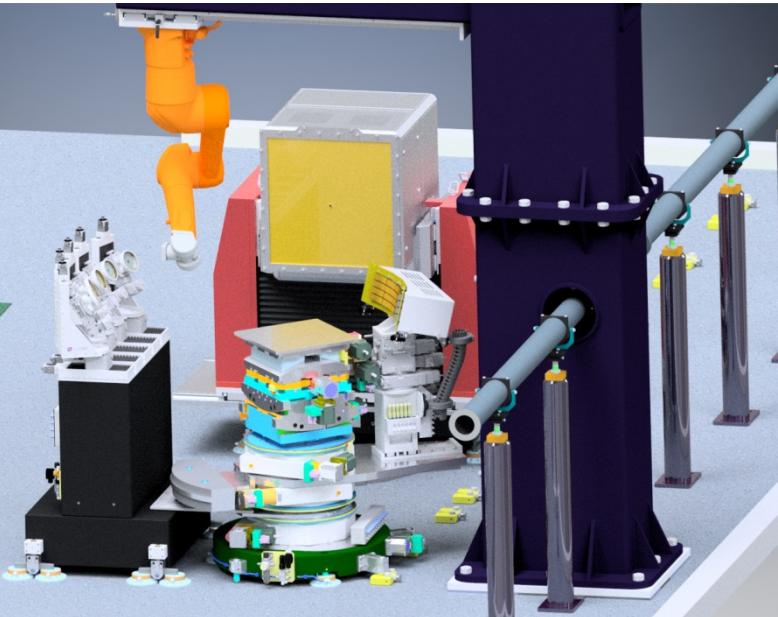
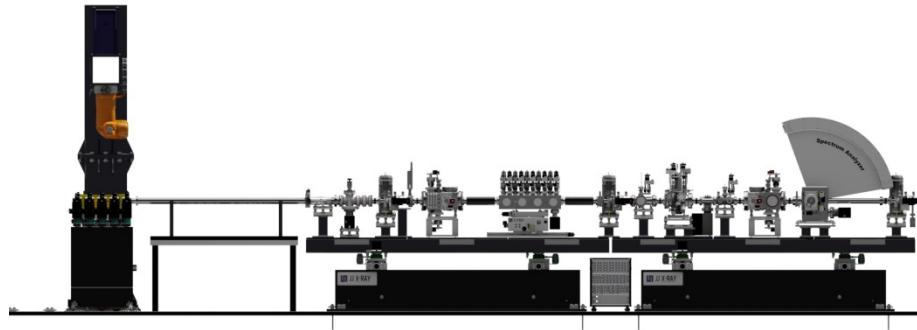


# Fast Valve FAT



# Flexible sample environment

## Sample Environment



- He Environment (ambient conditions, liquid jets)
- Solid State Chamber

# Dispersive XES and X-ray Raman at FXE

## Single-shot NXES and RXES

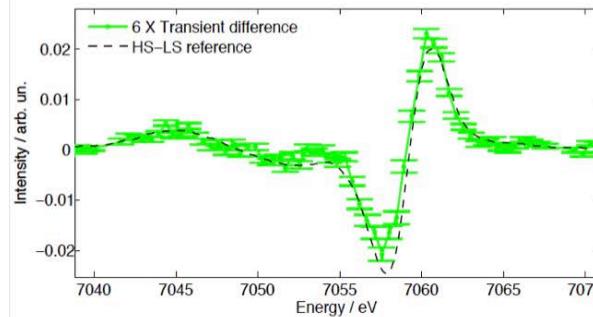
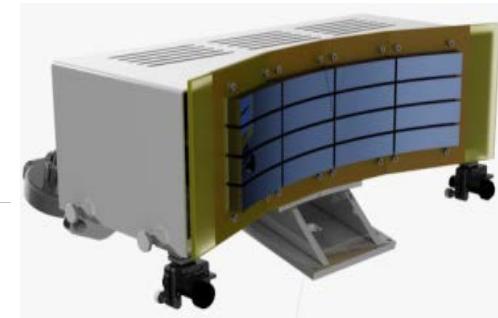
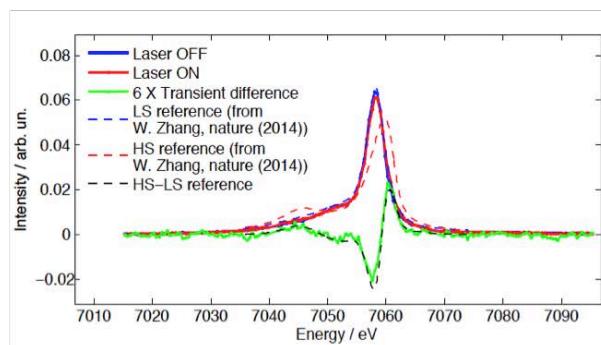
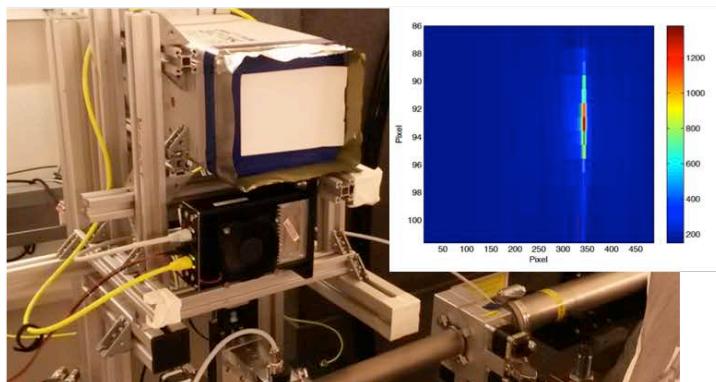
Does not require scanning the Bragg angle

Multiple analyzer crystal can be used to record simultaneously different emission lines

Extension to RXES → scanning the incident x-ray photon energy

Self-normalized → crucial!

Energy resolution → 1-1.2 eV (segmented analyzers ca. 0.3 eV)



Test beamtimes at Petra III  
(see poster session!!)

APS (7ID)  
DELTA

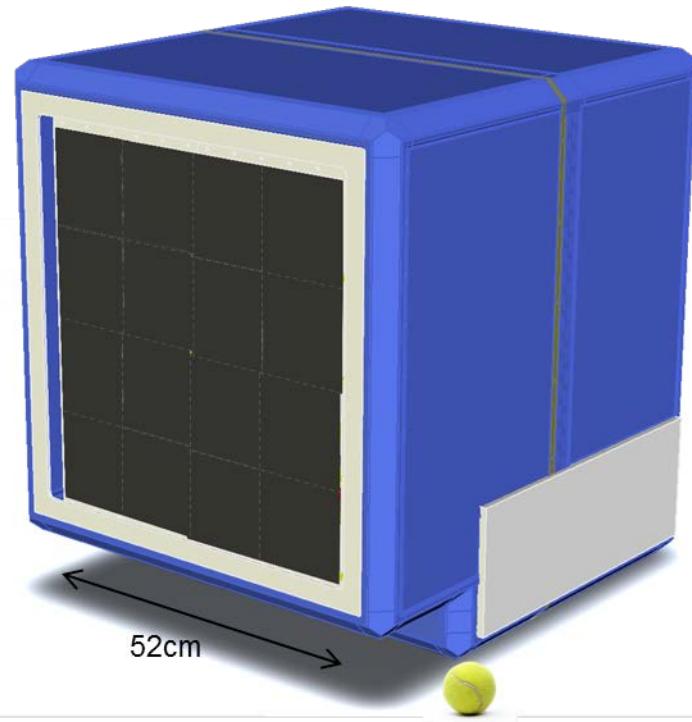
# LPD for Wide-Angle X-ray Scattering

## Large Pixel Detector

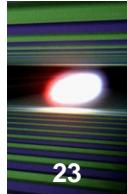
- Built by STFC for the European XFEL
- **1 Megapixel** - 500um pixels
- **4.5MHz frame rate**
- **High dynamic range**, 1 to  $1 \times 10^5$  photons per pixel per pulse. Using parallel gain stages (1x, 10x, 100x)
- **512 frame memory depth**  
continuously stores all three gains, overwriting whenever a veto is received.
- Output data rate **~10GByte/s** per megapixel



Science & Technology  
Facilities Council

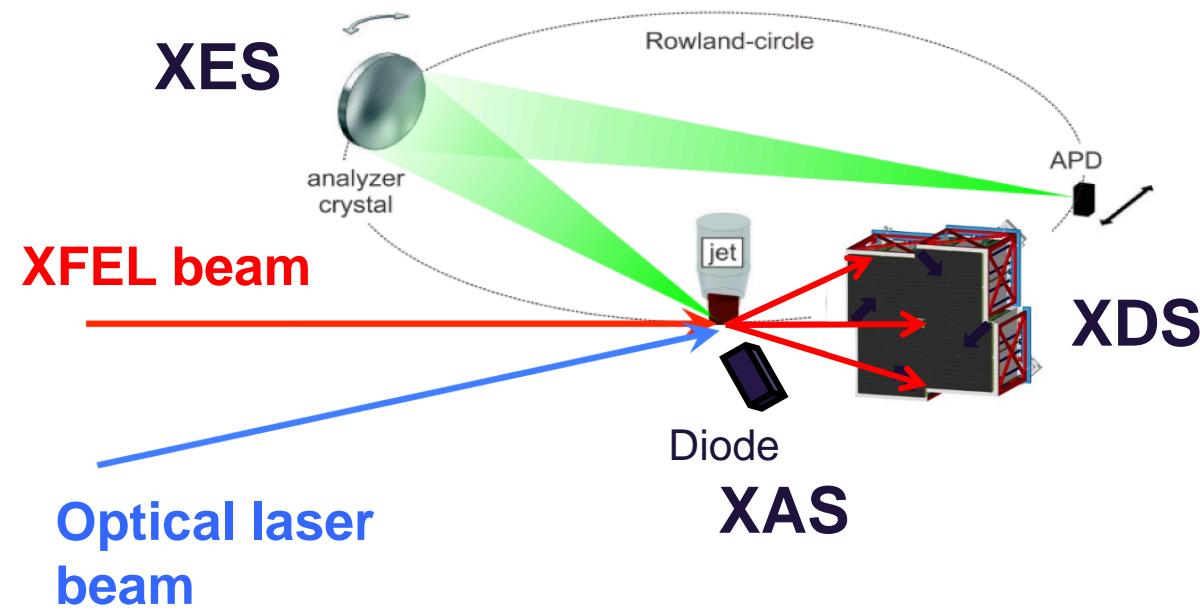


LPD megapixel detector consists of:  
⑩ 16 Super Modules  
⑩ 256 Detector Tiles  
⑩ 2048 ASICs



# A few science examples...

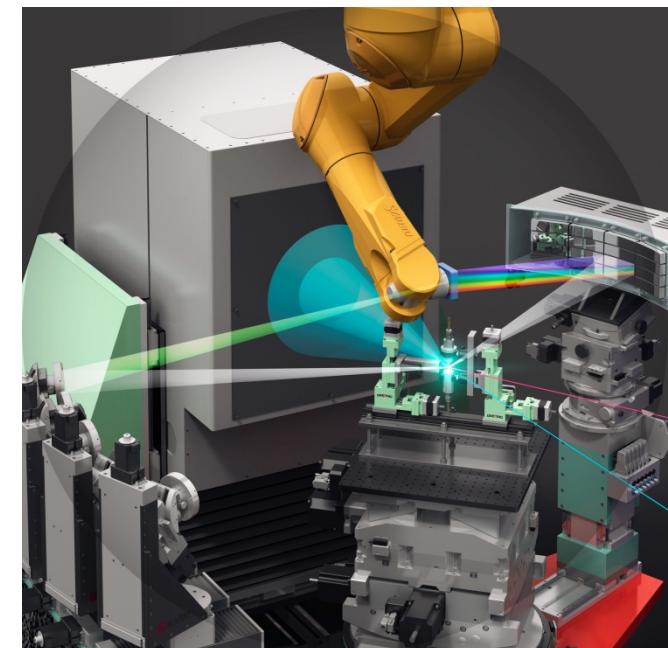
# Summary: Towards a High-Speed Molecular Camera for tracking chemical reaction dynamics



User operation in 2017!

A Suite of Simultaneous X-Ray Tools available:

- XAS
- Non resonant XES
- Resonant XES (RIXS)
- X-Ray Raman Scattering
- Wide(Small)-Angle X-ray Scattering
- ...



Courtesy by European XFEL/Rey.Hori

# Day -1 Experimental Conditions

- 1) WAXS (=XDS) experiment on solvated chromophores.
- 2) XES experiment on solvated chromophores
- 3) And each of the above Time-Resolved (< 1 ps)
- 4) TR-XANES (with 4-bounce mono)

## Experimental Conditions for Incident Beam

12 keV, 15, 20 keV

Pink Beam, mono (for 4)

Single Pulse (10 Hz), 100 kHz, 4.5 MHz

## Experimental Conditions for TR Experiment

Synchronized PP Laser at same rep-rate as XFEL beam

**Backup:** FXE Tangerine laser (synchronizable, gatable, tunable)

(may also be borrowed from other instruments)

## Available Instrumentation

Femtosecond Laser System (10 uJ, 1 mJ), synch'ed to XFEL

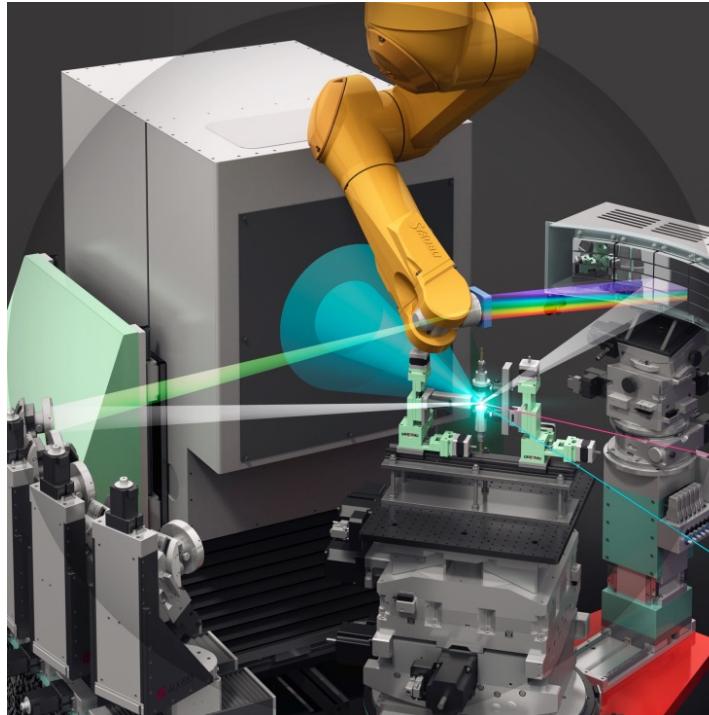
Liquid Jet collection (flat sheet)

1 LPD

2 strip detectors, various diodes, MHz DAQ schemes,...

## Acknowledgments FXE group

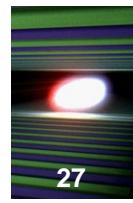
- Christian Bressler (Group leader)
- Wojciech Gawelda
- Andreas Galler
- Dmitry Khakhulin
- Martin Knoll
- Sebastian Schulz
- Peter Zalden
- Christina Bömer
- Alexander Britz
- Tadesse Assefa
- Michael Diez



- Christian Mammen et al. (JJ X-Ray)
- Martin M Nielsen (DTU)

### Funding (since 2009):

European XFEL  
DFG (SFB925, TPA4)  
BMBF (VP302)  
CUI Hamburg  
Uni Hamburg  
PIER Hamburg  
IMPRS-UFAST  
EU-CRISP (- 2014)  
EUCALL (2015 -)



# Molecular dynamics using the FXE instrument

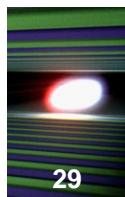
| Parameter                                  | Monochromatic   | Pink beam   |
|--|---|---|
| Energy range                               | 5-20(25) keV  | 5-20(25) keV  |
| Beam position                              | Sample (fixed)  | Sample (fixed)  |
| Energy bandwidth                           | $1.4 \times 10^{-4}$ Si(111) $3 \times 10^{-5}$ Si(311)                 | 0.3-1 %   |
| Bunch charge                               | $\leq 250$ pC   | $\leq 250$ pC   |
| X-ray pulse duration                       | < 25 fs   | < 25 fs   |
| Optical pulse duration                     | 15 fs   | 15 fs   |
| Sample delivery:<br>Liquid flat-sheet jets | Up to 15 m/s (sapphire nozzles)<br>Up to 100 m/s (colliding $\mu$ jets) | Up to 15 m/s (sapphire nozzles)<br>Up to 100 m/s (colliding $\mu$ jets) |
| X-ray beam spot                            | 1-10 $\mu$ m in focus<br>Up to 0.1 mm out of focus                      | 1-10 $\mu$ m in focus<br>Up to 0.1 mm out of focus                      |
| Energy resolution                          | ca. 1 eV (cylindrical)<br>0.3 - <1eV (spherical)                        | ca. 1 eV (cylindrical)<br>0.3 - <1eV(spherical)                         |
| Q range ( XDS)                             | 0.7 – 13 $\text{\AA}^{-1}$  | 0.7 – 13 $\text{\AA}^{-1}$  |

## FXE Overview Specifications

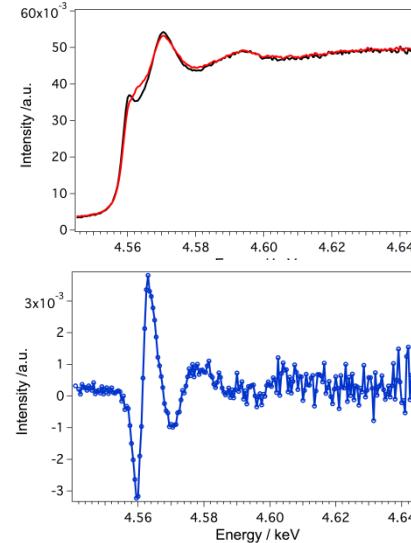
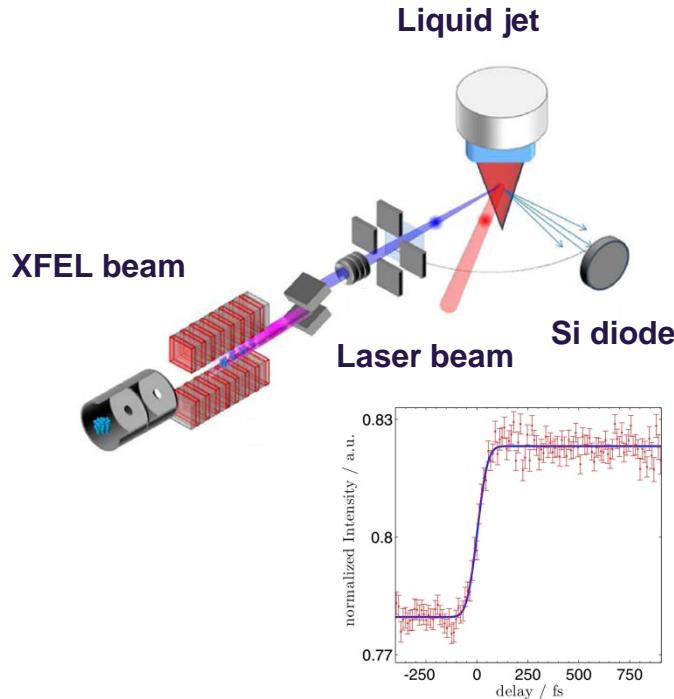
- FXE will offer world-wide unique and versatile end station for dynamical studies of guest-host interactions
- It will exploit the high repetition rate, x-ray photon flux and ultrashort pulse duration of the European XFEL
- FXE will offer a flexible sample environment optimized for liquid-phase photochemistry using a suite of complementary x-ray spectroscopic and scattering techniques in pump-probe arrangement.
- Simultaneous measurements of several observables deliver a more complete picture of the dynamics both of the solute (guest) and solvent molecules (host).

**Coupled electronic, spin and nuclear changes of solute and solvent molecules can be resolved in “real-time”**

# X-ray Absorption Spectroscopy (XAS) at FXE



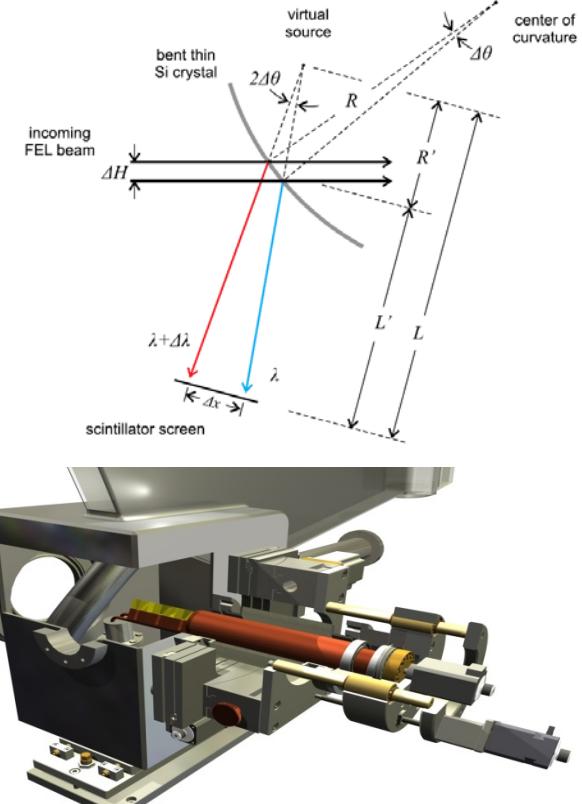
## Point-by-point XAS (scanning mode)



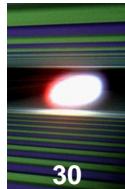
A. Galler et al., I/H<sub>2</sub>O @ XPP-LCLS  
(January 2013)

- Scanning mode → 4-bounce monochromator
- Beam focusing chromaticity → transfocator
- Requires reliable intensity normalization!
- (Single energy @ time delay) /shot
- Gated point detector (APD)

## Dispersive XAS (single-shot mode)



- Single-shot measurements → require 2 Spectrum Analyzers (SA)
- Pink beam would provide up to 1% bandwidth
- (Entire XANES spectrum @ time delay) /shot
- Self-normalization!
- Requires a fast readout gated 1D detector (Gotthard)



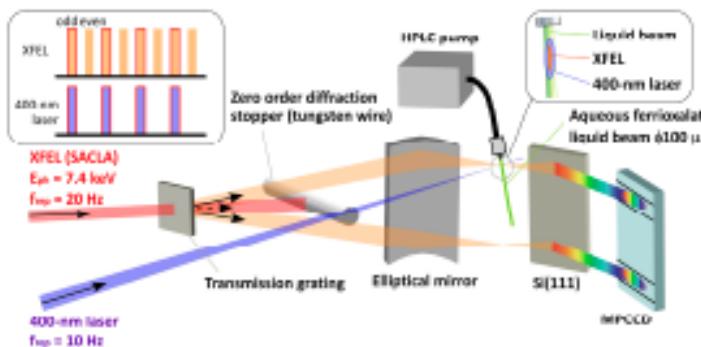
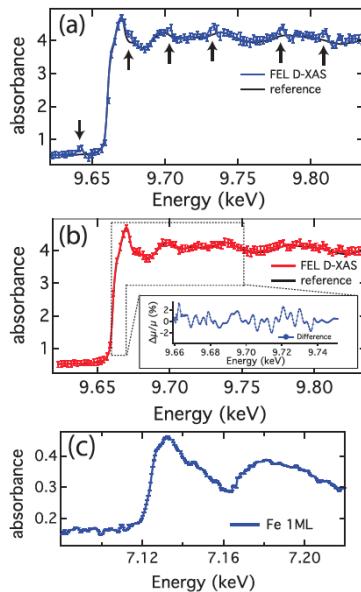
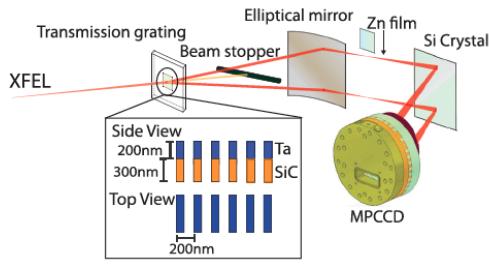
# Dispersive XAS at XFELs

APPLIED PHYSICS LETTERS 103, 131105 (2013)

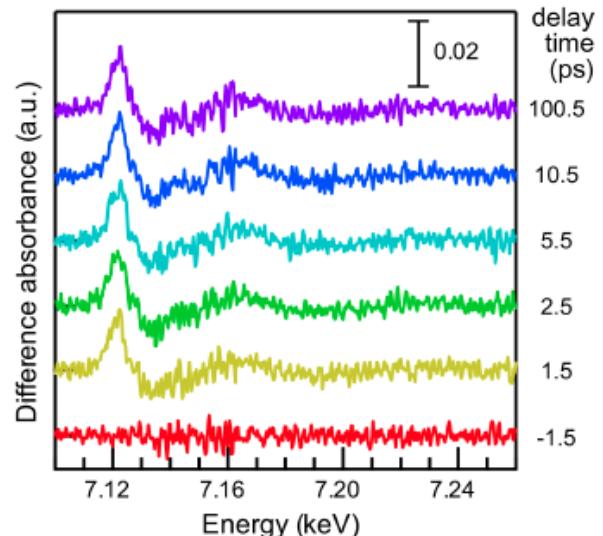


## Femtosecond x-ray absorption spectroscopy with hard x-ray free electron laser

Tetsuo Katayama,<sup>1</sup> Yuichi Inubushi,<sup>2</sup> Yuki Obara,<sup>3</sup> Takahiro Sato,<sup>2,a)</sup> Tadashi Togashi,<sup>1</sup> Kensuke Tono,<sup>1</sup> Takaki Hatsui,<sup>2</sup> Takashi Kameshima,<sup>1</sup> Atanu Bhattacharya,<sup>4,b)</sup> Yoshihiro Ogi,<sup>5</sup> Naoya Kurahashi,<sup>4</sup> Kazuhiko Misawa,<sup>3</sup> Toshinori Suzuki,<sup>4,5</sup> and Makina Yabashi<sup>2,c)</sup>



Y. Obara *et al.*,  
Optics Express, 22 (2014) 1105



# X-ray Emission Spectroscopy (XES) at FXE

**Non-resonant XES with moderate energy resolution (0.3 - 2 eV) – Johann geometry**

**High Energy Resolution Fluorescence Detected (HERFD) - XAS**

5 spherical analyzers focus the fluorescence on the same detector (Si and Ge crystals)

The aim is cover main 1<sup>st</sup> row TMs and some 2<sup>nd</sup> and 3<sup>rd</sup> row as well

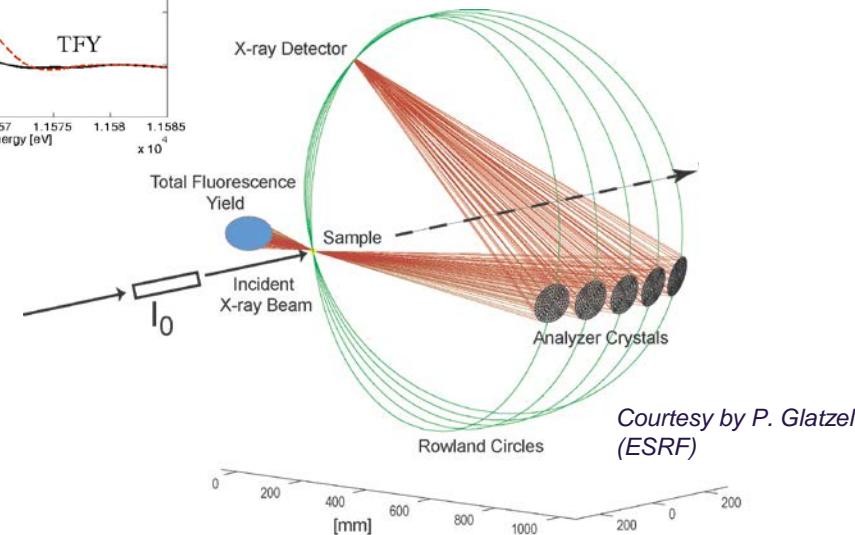
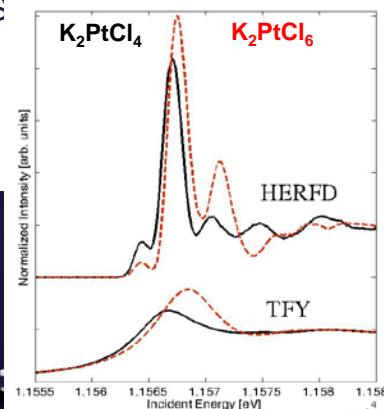
Exact tracking of individual Rowland circles required

Variable Rowland radii → extension to high energy resolution XES → RXES

Variable scattering angle → opportunity to record RIXS

Both pink and monochromatic beam compatible

Large solid angle coverage/energy interval



# Dispersive XES and X-ray Raman at FXE

## Single-shot NXES and RXES

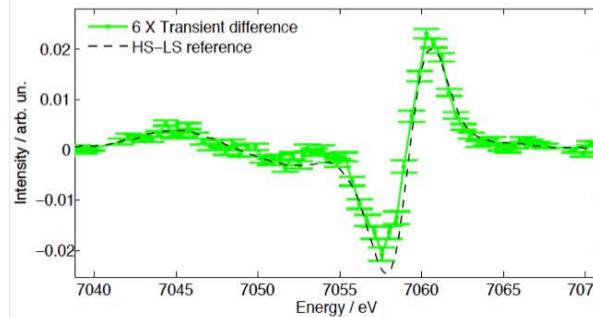
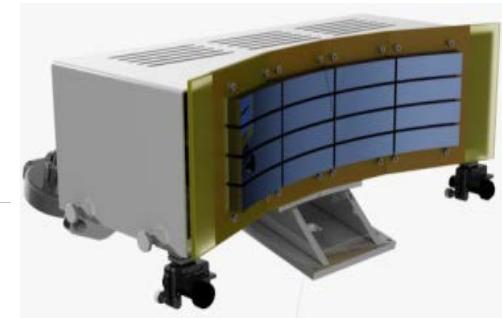
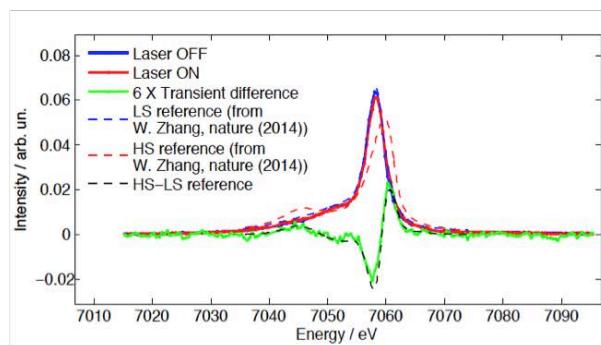
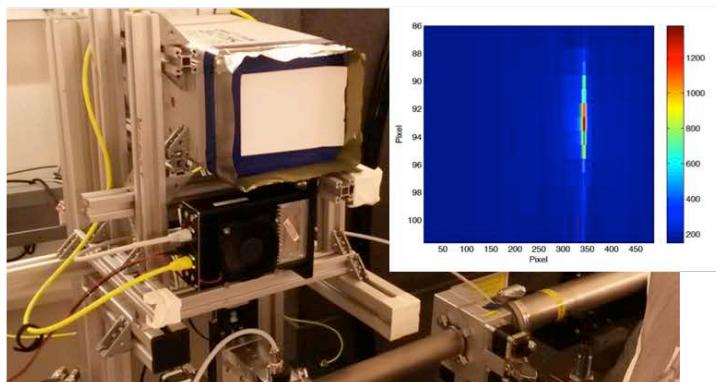
Does not require scanning the Bragg angle

Multiple analyzer crystal can be used to record simultaneously different emission lines

Extension to RXES → scanning the incident x-ray photon energy

Self-normalized → crucial!

Energy resolution → 1-1.2 eV (segmented analyzers ca. 0.3 eV)



Test beamtime at Petra III  
(August 2015)

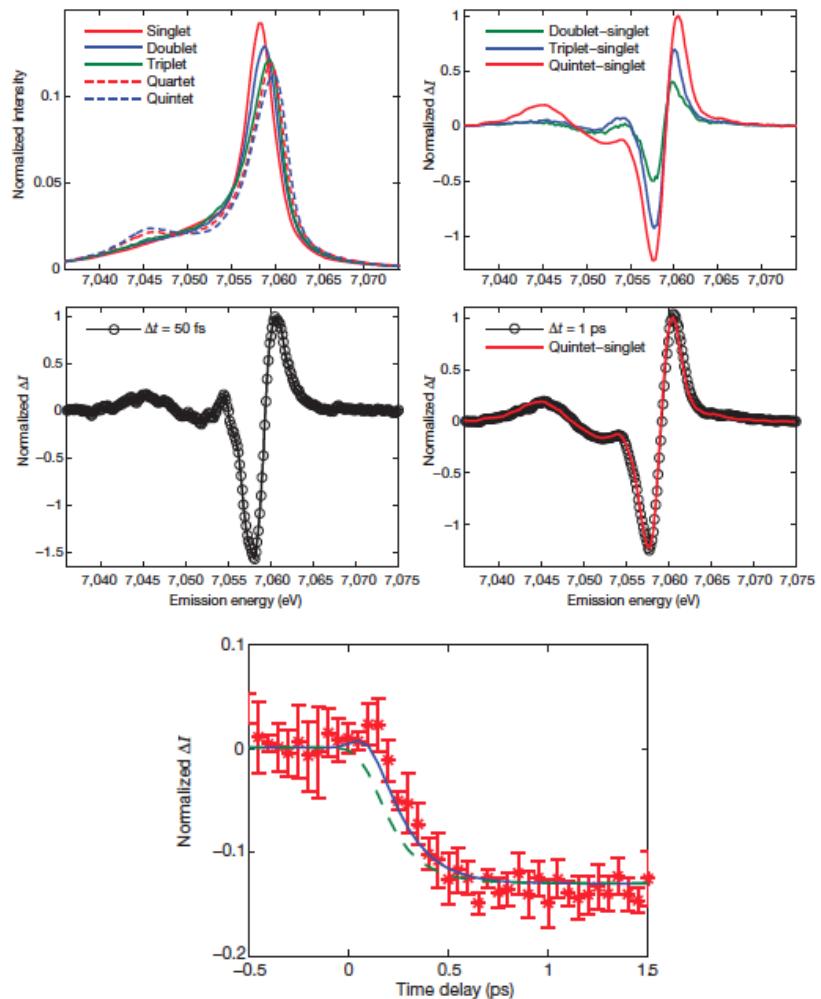
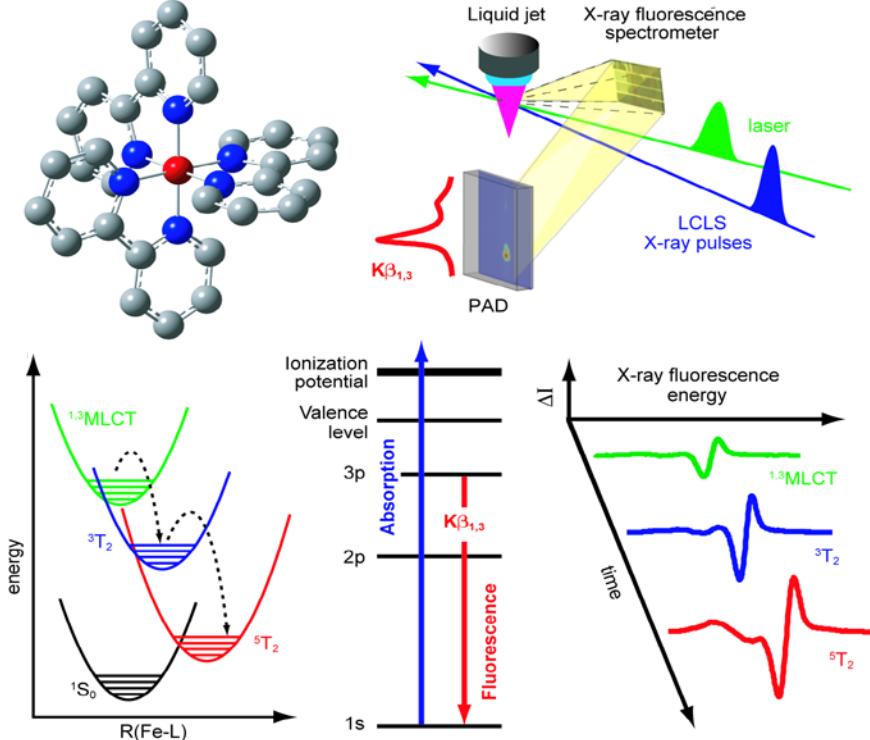
# Femtosecond XES reveals “hidden” excited states

LETTER

doi:10.1038/nature13252

## Tracking excited-state charge and spin dynamics in iron coordination complexes

Wenkai Zhang<sup>1</sup>, Roberto Alonso-Mori<sup>2</sup>, Uwe Bergmann<sup>2</sup>, Christian Bressler<sup>3</sup>, Matthieu Choller<sup>2</sup>, Andreas Galler<sup>3</sup>, Wojciech Gawelda<sup>3</sup>, Ryan G. Hadt<sup>4</sup>, Robert W. Hartsock<sup>1,4</sup>, Thomas Kroll<sup>4</sup>, Kasper S. Kjær<sup>5,6</sup>, Katharina Kubicek<sup>7,8</sup>, Henrik T. Lemke<sup>9</sup>, Huiyang W. Liang<sup>4,9</sup>, Drew A. Meyer<sup>1,4</sup>, Martin M. Nielsen<sup>6</sup>, Carola Purser<sup>1</sup>, Joseph S. Robinson<sup>2</sup>, Edward I. Solomon<sup>4,9</sup>, Zheng Sun<sup>1</sup>, Dimosthenis Sokaras<sup>9</sup>, Tim B. van Driel<sup>6</sup>, György Vankó<sup>10</sup>, Tsu-Chien Weng<sup>9</sup>, Diling Zhu<sup>2</sup> & Kelly J. Gaffney<sup>1</sup>



# Dispersive XES and X-ray Raman at FXE

**X-ray Raman Scattering (XRS) → study low-Z elements (solvent molecules) with hard x-rays.**

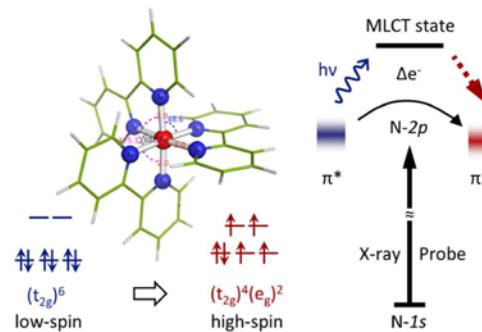
Measures inelastic energy loss in the sample → resonant with 1s core-hole excitation of light elements

Requires scanning the incident monochromatic beam energy

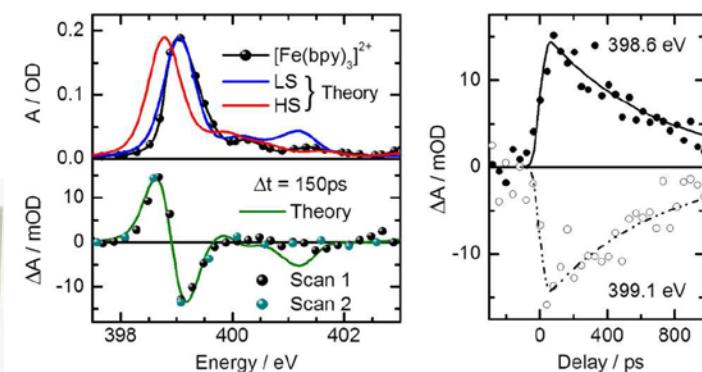
Von Hamos (dispersive) geometry allows to measure the entire spectrum in a single shot

Probe the electronic structure of charge transfer states via ligand absorptions directly, i.e. C, N or O absorption edges

Here N K-edge of a prototypical spin transition Fe(II) complex

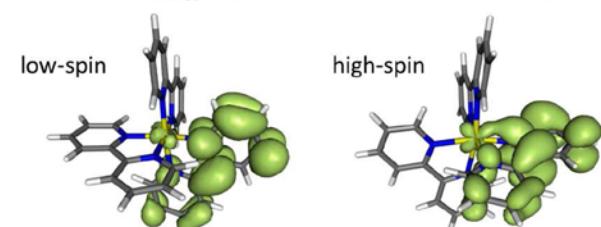
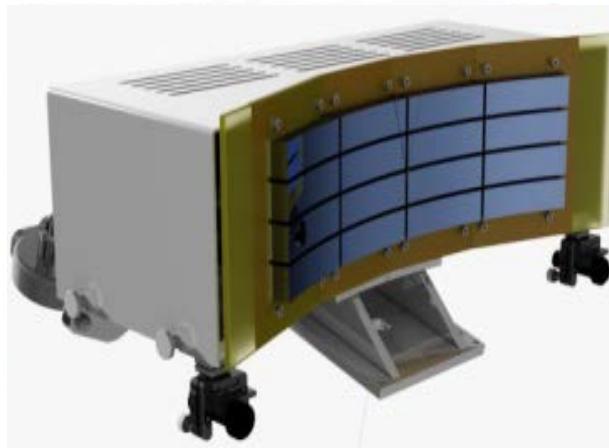
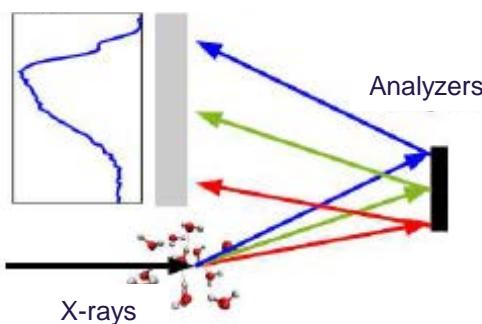


Nils Huse group (CFEL, Hamburg)



X-ray Raman K-edge spectrum of N

Gotthard Detector (1D)



B. E. Van Kuiken, et al., J. Phys. Chem. Lett. Just Accepted (2016)

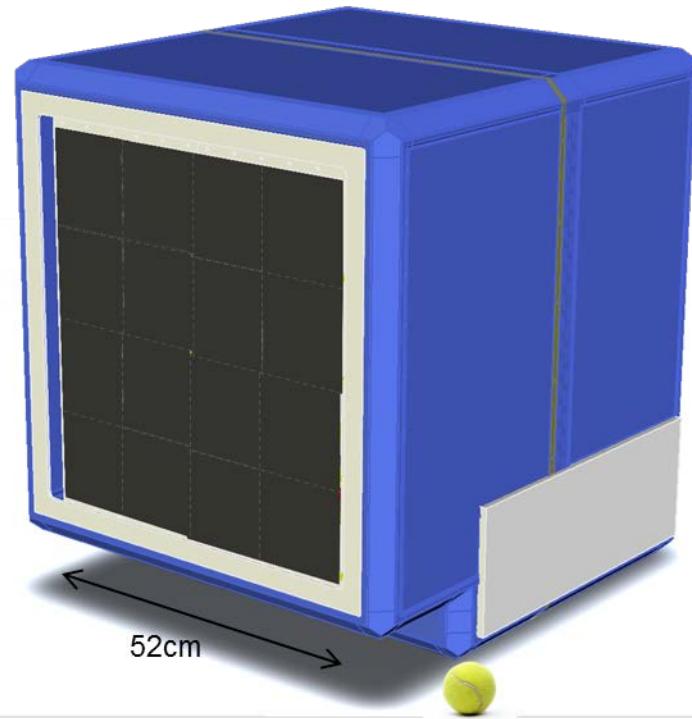
# LPD for Wide-Angle X-ray Scattering

## Large Pixel Detector

- Built by STFC for the European XFEL
- **1 Megapixel** - 500um pixels
- **4.5MHz frame rate**
- **High dynamic range**, 1 to  $1 \times 10^5$  photons per pixel per pulse. Using parallel gain stages (1x, 10x, 100x)
- **512 frame memory depth**  
continuously stores all three gains, overwriting whenever a veto is received.
- Output data rate **~10GByte/s** per megapixel



Science & Technology  
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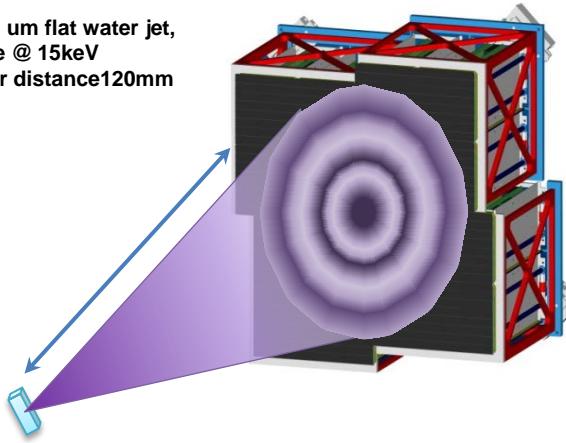
LPD megapixel detector consists of:

- 16 Super Modules
- 256 Detector Tiles
- 2048 ASICs

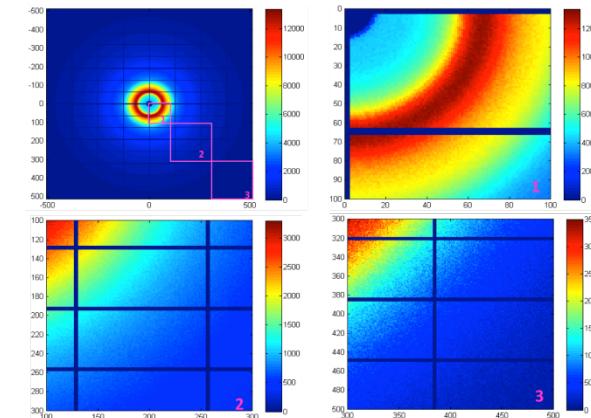
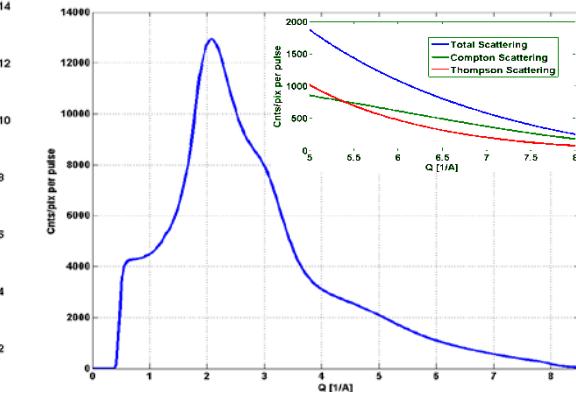
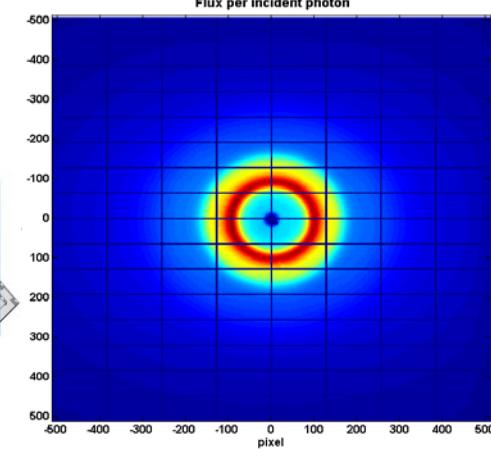
# Liquid WAXS for probing solvation cage

Wide-Angle X-ray Scattering (WAXS) delivers global geometric structural dynamics of the solute and the surrounding solvent

Scattering from 10  $\mu\text{m}$  flat water jet,  
 $10^{12}$  photons/pulse @ 15keV  
Sample-to-detector distance 120mm



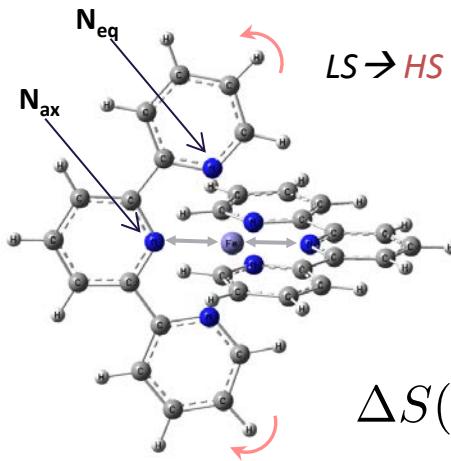
Estimate scattering from 10  $\mu\text{m}$  Water jet on LPD,  
 $E_{\text{x-ray}} = 12 \text{ keV}$ , sample-to-detector distance 150 mm,  
Flux per incident photon



- No monochromatization needed → pink beam compatible
- Moderate focusing requirements → < pixel size (0.5 mm)
- High repetition rate desired!
- Variable sample-detector distance desired → WAXS/SAXS
- He environment compatible
- High dynamics range (single photon →  $10^5$  photons/pixel)

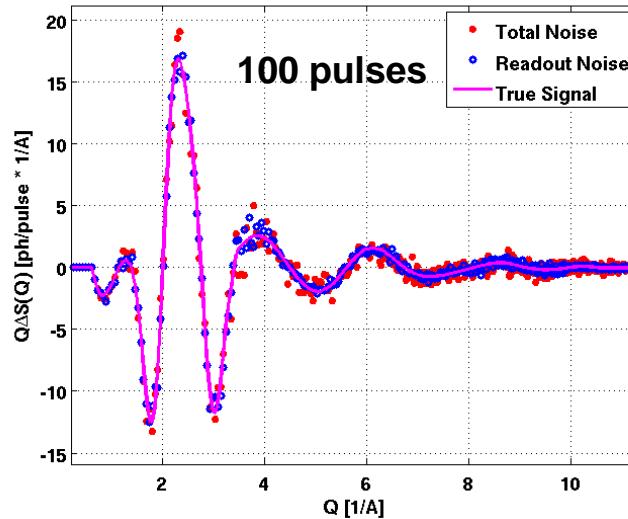
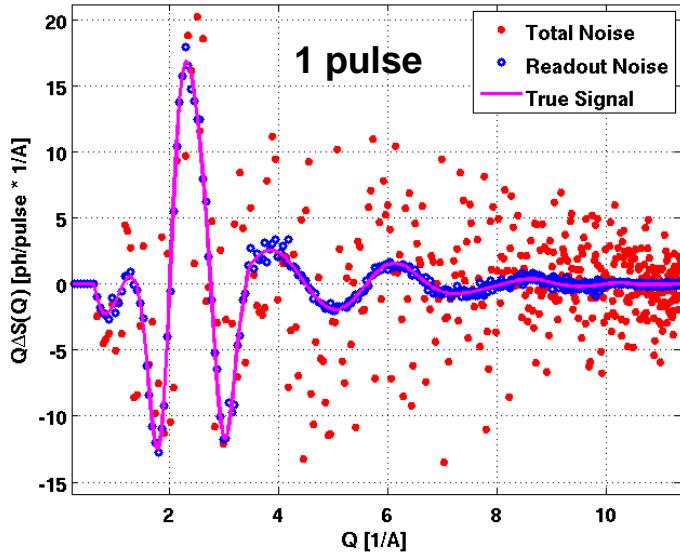
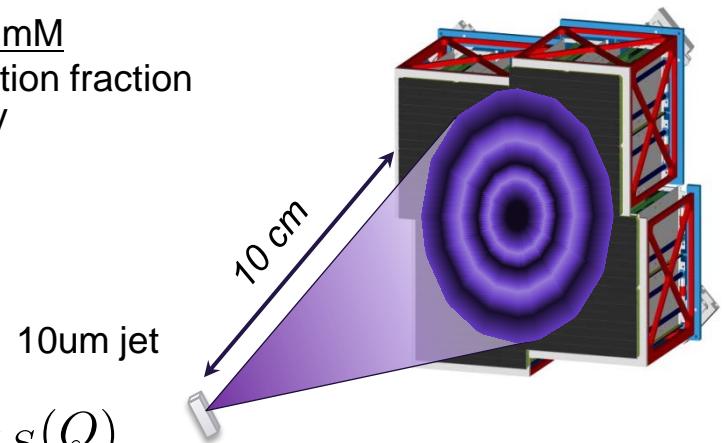


# Spin crossover in aqueous Fe(II) complexes

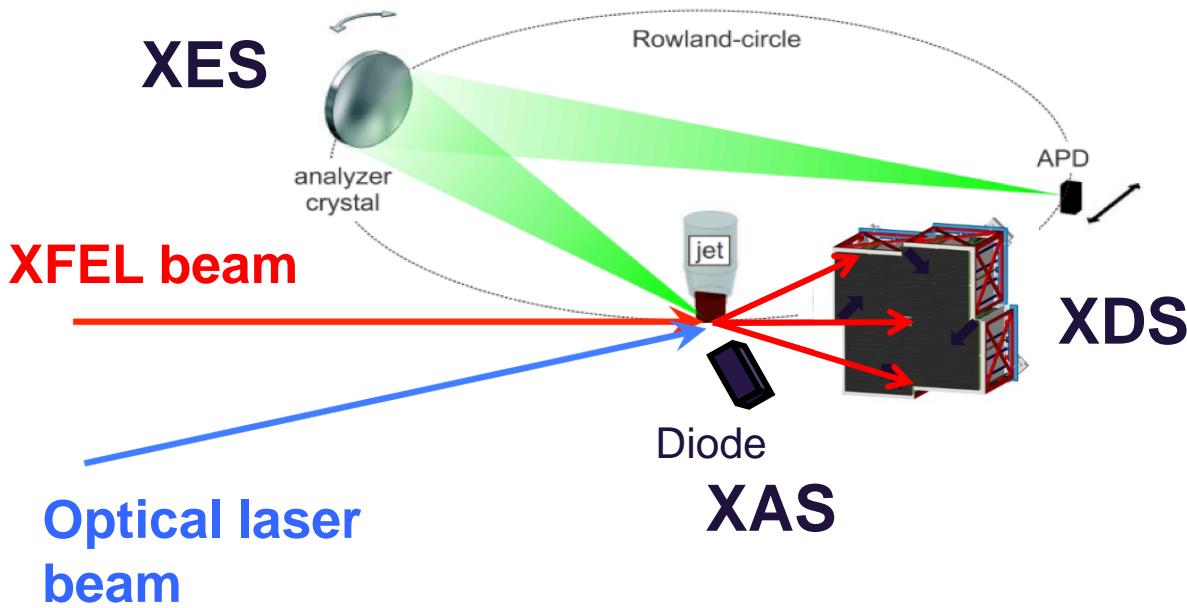
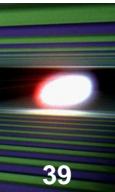


$$\Delta S(Q, t) = \Delta S_{HS}(Q, t) - \Delta S_{LS}(Q)$$

Aqueous solution, 15 mM  
10  $\mu\text{m}$  jet, 50% excitation fraction  
 $10^{12}$  ph/pulse@20keV

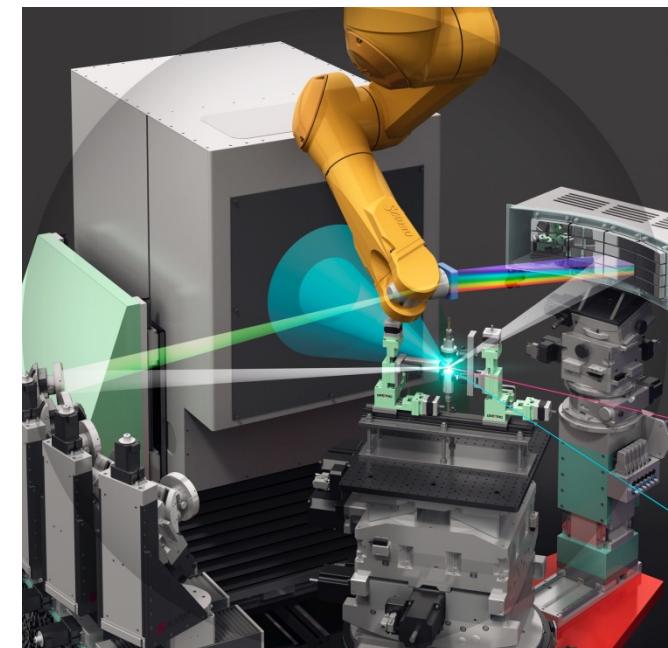


# Summary: Towards a High-Speed Molecular Camera for tracking chemical reaction dynamics



A Suite of Simultaneous X-Ray Tools available:

- XAS
- Non resonant XES
- Resonant XES (RIXS)
- X-Ray Raman Scattering
- Wide(Small)-Angle X-ray Scattering
- ...



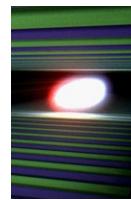
Courtesy by European XFEL/Rey.Hori

## Acknowledgments FXE group

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- **Martin M Nielsen (DTU)**
- ...

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EUCALL (2015 -)



# Thank you for your attention!