Christian Bressler, *Femtosecond X-ray Experiments (FXE) Instrument* European XFEL

**XFEL User Meeting, Hamburg, Jan 29, 2014**
Solvation dynamics using the FXE instrument

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

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”
2007 : Decided to build science instrument dedicated to

**Femtosecond Diffraction Experiments** –

Time-resolved structural dynamics investigations of solids, liquids, gases using various techniques: diffraction, scattering

2009 : The scientific scope was refined in a science scope Workshop (Budapest, Dec. 2009) for the

**Femtosecond X-ray Experiments** instrument –

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

Targets:

» electronic rearrangements (charge transfer/transport)

» spin state changes

» nuclear rearrangements (including the solvation cage)

…and all this simultaneously (→ single shot)
What are the fundamental timescales?

- **Femtochemistry, Photosynthesis and Catalysis**
- **Solid State Dynamics**
- **Vision**
- **Molecular Vibrations**
- **Protein Folding**
- **Molecular Rotations**

Time / seconds

- Harpo: $10^{-27}$
- Yacto: $10^{-24}$
- Zepto: $10^{-21}$
- Atto: $10^{-18}$
- Femto: $10^{-15}$
- Pico: $10^{-12}$
- Nano: $10^{-9}$
- Micro: $10^{-6}$
- Milli: $10^{-3}$
FXE: Make use of all incident x-ray photons

Combine Femtosecond
- XRD
- XAFS (XANES)
- XES, RIXS, ...
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,...

- **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→nd excitation)

- **X-Ray Raman Spectroscopy**
  - Access K-edges of light elements (N, O, C...) constituting solvent molecules

- **X-Ray Diffuse Scattering**
  - Short- and medium-range geometric environment, solute + solvent (cage) contributions to the structural factor
FXE Instrument – a suite of complementary x-ray tools for ultrafast structural dynamics in condensed matter systems

Exploiting complementary techniques

UDECS collaboration at work!
Sector 7ID @ APS, Argonne (3.26 MHz)

The FXE Instrument (5 – 20 keV)
Find single OM position/angle (5 – 20 keV) (maintain flexibility towards changes)

Use Si(111) 4-bounce for startup

→ Emphasis for „on-axis“ configuration
FXE Instrument: Overall

Top view of FXE hutches (SASE1)

- **FXE Control Hutch**
  - Upstream optics bench

- **FXE Optics**

- **FXE Experiments**
  - Laser beam
  - X-ray beam

- **FXE Laser Lab**

- **Central Sample Environment Area**
  - More flexibility, ambient conditions
  - Compatible with vacuum chamber
  - Secondary spectrometers
  - Pump beam conditioning

- **Downstream area provides space for diagnostics, vacuum chamber option and SAXS.**
Femtosecond X-Ray Experiments at the European XFEL

European XFEL Users' Meeting, Jan 29-31, 2014
Christian Bressler, FXE Instrument, European XFEL

FXE Instrument: Optics Bench + Sample Environment

- Large Pixel Detector (LPD)
- Robot tower
- He interface
- Clean-up slits
- BIU
- Slits
- Be lenses
- BIU
- Spectrum analyzer
- Attenuators
- Beam imaging
- TAD
- I₀
- Slits

Diagram labels: Clean-up slits, I₀, BIU, He interface, Spectrum analyzer, Attenuators, Robot tower, Large Pixel Detector (LPD), Beam imaging, TAD.
X-ray Absorption studies at FXE

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

- 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)

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A. Galler *et al.*, I/H$_2$O @ XPP-LCLS (January 2013)
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 (different Si and Ge crystals)
- The aim is to cover main 1st row TMs and some 2nd and 3rd 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

K₂PtCl₆ K₂PtCl₄

Kα XES of Fe(bpy)₃/H₂O

P. Glatzel et al. (ESRF)
Femtosecond X-ray experiments at the European XFEL

Femtosecond XAS/XES/XDS

...at LCLS

- XAS
- XES
- XDS
- Diode
- Rowland-circle
- Analyzer crystal
- APD
- Energy / keV

8 keV, 50 fs, 100 µm spot size

400 nm, 40 fs, 0.2 mJ, 150 µm spot size
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 Self-normalized → crucial! Energy resolution → 1-1.2 eV (segmented analyzers ca. 0.3 eV)

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
Femtosecond X-Ray Experiments at the European XFEL

**Femtosecond Kβ XES during Spin Transition:**
First Observation of Intermediate States

X-ray Diffuse Scattering: towards probing the solvation dynamics

Wide-angle X-ray scattering delivers global geometric structural dynamics of the solute and the surrounding solvent

- Requires large area detector $\rightarrow$ 1 Mpix LPD detector
- LPD $\rightarrow$ 4.5 MHz output, 5120 images/sec
- No monochromatization needed $\rightarrow$ pink beam compatible
- Moderate focusing requirements $\rightarrow$ < pixel size (0.5 mm)
- High repetition rate desired!
- Variable sample-detector distance desired $\rightarrow$ WAXS/SAXS
- He environment compatible
- High dynamics range (single photon $\rightarrow$ $10^5$ photons/pixel)

Diffuse scattering rings reflect the disordered nature of the liquid
Radially integrated scattering factor $\rightarrow$ mainly due to the solvent
Difference scattering factor $\Delta S$ $\rightarrow$ solute and solvent changes
Feasibility: solvated molecules (here: H2O)

Photons/s
Photons/s (SR)
Photons (XFEL)
Summary: simultaneous ultrafast X-ray tools at FXE

XES

XAS

XDS

Optical laser beam

XFEL beam
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- Christian Mammen et al. (JJ X-Ray)