Tracking chemical reactions using combined time-resolved x-ray spectroscopies and scattering

Workshop on MXAN code for XANES analysis
IP PAS, Warsaw, Poland
April 8, 2014

Alexander Britz and Tadesse Assefa
European XFEL
Tracking chemical reactions using combined time-resolved x-ray spectroscopies and scattering

Outline of the talk

European XFEL and FXE Instrument (A. Britz)
- Resolving dynamics
- The European XFEL
- The FXE instrument: combining time-resolved x-ray spectroscopy and scattering

Why do we need pump-probe experiments?

What can be done using XFELs?

Time-resolved x-ray absorption spectroscopy (T. Assefa)
- Static XANES + XAFS for Fe-based complexes
- Time-resolved x-ray absorption spectroscopy
- Time-resolved XAFS analysis

What do we measure during XAS experiment?

How to extract information from TR-XAS data?
Capturing dynamics

Menlo Park (Stanford, 1878)

Hamburg (2011)
What are the fundamental timescales?

Chemistry and Biochemistry

- Photosynthesis
- Vision
- Molecular Vibrations
- Protein Folding
- Molecular Rotations
- Electron dynamics
- Particle Collisions
- Strings, Cosmology
- Horse movement

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 $10^{-3}$
- 1
Tracking chemical reactions using combined time-resolved x-ray spectroscopies and scattering

Optical laser pump-probe

[Image: Optical laser pump-probe diagram]

Spin Transition

[Fe^{II}(bpy)_3]^{2+}

Need structural tools

Ch. Bressler et al. Science 323 (2009)
High flux: $10^{16} - 10^{17} \text{ ph/s}$
- Synchrotrons: $< 10^{14} \text{ ph/s}$

Short pulses: 1-100 fs
- Synchrotrons: ~100 ps

Coherence
- Synchrotrons: no/low coherence
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Optical laser pump – x-ray probe

Laser
Sample
Detector
Delay Scan -> Kinetics

Focusing optics
Monochromator
X-rays

XAFS -> Time Resolved Structure

Delay Scan -> Kinetics

Δt = 50 ps

665 ps
70 ps

[Fe^{II}(bpy)_3]^{2+}

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Hard x-ray FELs: elsewhere

**LINAC COHERENT LIGHT SOURCE (LCLS)**
- 2009 - 120 p/s
- 2011 - 60 p/s

**SACLA (SPring-8 Angstrom Compact Laser)**
- 2009 - 120 p/s

**Swiss XFEL (2016)**
- 100 pulses/s

**Korean XFEL, (2015)**
- 60 pulses/s

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The European XFEL

Undulator/Photon Tunnels

Experiment Hall in Schenefeld

Linear Accelerator
1.7 km
17.5 GeV

Injector at DESY campus

Adapted from M. Altarelli

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### Scientific Instruments

<table>
<thead>
<tr>
<th>SASE1</th>
<th>SPB: Ultrafast Coherent Diffraction Imaging of Single Particles, Clusters, and Biomolecules</th>
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<tbody>
<tr>
<td></td>
<td>Structure determination of single particles: atomic clusters, bio-molecules, virus particles, cells.</td>
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<td><strong>FXE:</strong> Femtosecond X-ray Experiments</td>
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<td>Time-resolved investigations of the dynamics of solids, liquids, gases, by pump-probe expts.</td>
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<tr>
<td>SASE2</td>
<td><strong>MID:</strong> Materials Imaging &amp; Dynamics</td>
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<td>Structure/dynamics at the nanoscale by photon correlation and speckle techniques</td>
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<td><strong>HED:</strong> High Energy Density Matter</td>
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<td>Investigation of matter under extreme conditions using hard X-ray FEL radiation, e.g. probing dense plasmas</td>
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<tr>
<td>SASE3</td>
<td><strong>SQS:</strong> Small Quantum Systems</td>
</tr>
<tr>
<td></td>
<td>Investigation of atoms, ions, molecules and clusters in intense fields and non-linear phenomena</td>
</tr>
<tr>
<td></td>
<td><strong>SCS:</strong> Soft x-ray Coherent Scattering/Spectroscopy</td>
</tr>
<tr>
<td></td>
<td>Electronic and real structure, dynamics of nano-systems and of non-reproducible biological objects</td>
</tr>
</tbody>
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Overall view of the FXE instrument

Towards an Ultimate High Speed Molecular Camera
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
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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., $\ce{I/H2O}$ @ XPP-LCLS (January 2013)
X-ray Emission Spectroscopy 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 (different Si and Ge crystals)
- The aim is 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)
X-ray Diffuse Scattering for probing solvation cage

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

- Requires large area detector → 1 Mpix LPD detector
- LPD → 4.5 MHz output, 5120 images/sec
- 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)
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  - The FXE instrument: combining time-resolved x-ray spectroscopy and scattering

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  - Time-resolved x-ray absorption spectroscopy
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Why do we need pump-probe experiments?
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X-ray absorption and emission spectroscopy

Mn k-edge XAS

vtc XES spectra of Mn

1s core-hole life time\(^1\) = 1.16 eV

\(^1\)M. O. Krause and J. H. Oliver J. Phys. Chem, 1979

Courtesy: P. Glatzel
[Fe(CN)$_6$]$^{4-}$/H$_2$O

1) **Element specific:**
   - Absorption edge

2) **Electronic structure:**
   - Density of unoccupied states
   - Valence orbitals
   - Degree of oxidation
   - Local symmetry

3) **Bond distances/angles:**
   - **Multiple scattering:** (low-energy photoelectrons) Resonances above ionization threshold

**XANES**

M. Benfatto *et al.* JACS, 2004
A. Bianconi *et al.* PRB, 1982

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Element specific; through the absorption edge
- Dominated by single scattering amplitudes
- Geometric structure: Single Scattering (high energy photoelectrons)
Measuring chemical reactions using combined time-resolved x-ray spectroscopies and scattering

**Static XAFS on Fe-based complexes**

- Measured around Fe-k edge
- XAFS oscillations are molecular fingerprints.

\[
\text{Fe(CN)}_6^{4-} / \text{H}_2\text{O} \quad \text{[Fe(dcpp)]}^{2+} / \text{CH}_3\text{CN} \quad \text{[Fe(terpy)]}^{2+} / \text{H}_2\text{O}
\]


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Why do we do time-resolved experiments?

We would like to get finger-prints of Photoinduced excited states of a molecule.

Pump: Laser pulse
Probe: X-ray
We can capture a snapshot of transient states created by pump laser pulse.

Time-delay has to be less than lifetime of transient state.
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Time-resolved XAFS on Ferrocyanide molecule

\[ \text{[Fe(CN)\textsubscript{6}]^{4-} / H\text{\textsubscript{2}}O} \]

If you know the excited state fraction nail-down to single digits

\[ ES = \text{Laser OFF} + \frac{\text{Transient}}{f} \]

*ES*: excited state spectra

*\( f \)*: excited state fraction

*Transient*: difference signal

\[ \Delta \tau = 100 \text{ ps} \]

\[ 60 \times 10^{-3} \]

\[ \text{Difference signal} \]

\[ \text{Laser ON} \]

\[ \text{Laser OFF} \]

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Pump-probe techniques allow measuring dynamics

European XFEL opens up new possibilities in research with x-rays

XFELs and synchrotrons probe time resolved structures

XAFS data analysis helps us to get photoinduced geometrical changes in the molecule
Tracking chemical reactions using combined time-resolved x-ray spectroscopies and scattering

Collaborators

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Stephen H. Southworth
Thank you for your attention!