Investigation of ultrafast structural changes in complex chemical systems using X-ray FELs


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Ultrafast structural changes in complex chemical systems by X-ray FELs

Ultrafast photochemistry

Understand complexity of structural dynamics

- modify potential (new materials)
- optimize excitation process fitting ($\lambda$, $\Delta t$, coherent control)
Ultrafast structural changes in complex chemical systems by X-ray FELs

Understand and copy bacteria light harvesting

Photosynthetic membrane | Reaction center | Chromophores
What can X-ray FELs contribute?

Spatial resolution
- use of hard (6 - 15 keV) x-rays enables sub-atomic resolution of the electron distribution

Temporal resolution
- 10’s of fs
- possibly below

Variety of sample preparations
- ‘real’ chemical reactions happen in liquid or solid phase, are irreversible

Intensity
- optimize signal by matching optical excitation depth → small signal

Ultrafast structural changes in complex chemical systems by X-ray FELs

Thomas Tschentscher, European XFEL, Mai 3, 2009
Ultrafast structural changes in complex chemical systems by X-ray FELs

Experimental techniques obtaining structure

**X-ray diffraction**
- Single crystal diffraction (monochromatic & Laue)
- Powder diffraction
- Small-angle diffraction
- Disordered/liquid system diffraction
- Single molecules/particles
Experimental techniques obtaining structure

**X-ray spectroscopy**

- Near-edge XAS (NEXAFS or XANES)
- Extended range XAS (EXAFS)
- Raman spectroscopy
- X-ray emission spectroscopy (XES)
- (Resonant) Inelastic x-ray scattering ((R)IXS)

→ light Z elements XAS, mono E
Outline

X-ray FELs and the European XFEL

Structural dynamics of complex systems studied by x-ray diffraction

Prospects and considerations for X-ray FEL experiments
Ultrafast structural changes in complex chemical systems by X-ray FELs

FEL performance depends exponentially on electron beam ($\varepsilon, I_p$)

$P \propto \exp\left(\frac{z}{L_G}\right)$

$L_{Gain} = \frac{\lambda_{und}}{4\pi\rho} \propto \left(\frac{\varepsilon}{I_p}\right)^{1/3}$
Ultrafast structural changes in complex chemical systems by X-ray FELs

Basic properties of FEL radiation

Peak brilliance = \frac{\text{Number of photons}}{\Delta x \Delta y \Delta \nu \times \text{bandwidth} \times \Delta t}

10^{12}(X) - 10^{14}(sX)

6 \times 10^{-11} \text{m}(X) \sim \lambda/2 \quad 100 \text{ fs eV}(X) \sim 25 \hbar

25 \text{ fs, 13 nm}

100 \text{ fs, 0.1 nm}

1.2 \text{ fs, 1.5 nm}
Ultrafast structural changes in complex chemical systems by X-ray FELs

Current status

FLASH

LCLS

- extremely exciting for hard X-ray FEL performance and its further development
Ultrafast structural changes in complex chemical systems by X-ray FELs

see www.xfel.eu for details

Accelerator ~ 2 km
Beam distribution/FELs ~ 1.4 km

status
Apr 30, 2009
↓
↓
↓
2013
Ultrafast structural changes in complex chemical systems by X-ray FELs

High repetition rate at European XFEL

- Optical laser
  - match repetition rate
  - provide ~mJ excitation energy

- Sample delivery
  - match repetition rate
  - positioning

- Photon diagnostics
  - on-line & single-shot
  - match repetition rate

- Detectors
  - match frame rate
  - large data amounts

High repetition rate: 10 Hz, up to 5 MHz (bunchtrain)
- high average brilliance
- distribution of pulses to many instruments quasi-simultaneous
- stabilisation of electron/x-ray beam in space & time
Ultrafast structural changes in complex chemical systems by X-ray FELs

Photon beam systems startup scope

<table>
<thead>
<tr>
<th>Source</th>
<th>Instruments</th>
<th>Photon beam line characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>SASE 1</td>
<td>SPB, MID</td>
<td>FEL radiation ~12 keV; High coherence; Spont. radiation (3\textsuperscript{rd}, 5\textsuperscript{th} harm.)</td>
</tr>
<tr>
<td>SASE 2</td>
<td>FDE, HED</td>
<td>FEL radiation 3-12 keV; High time-resolution; Spont. radiation (3\textsuperscript{rd}, 5\textsuperscript{th} harm.)</td>
</tr>
<tr>
<td>SASE 3</td>
<td>SQS, SCS</td>
<td>FEL radiation 0.25 – 3 keV; High flux</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FEL radiation 0.25 – 3 keV; High resolution</td>
</tr>
</tbody>
</table>
Ultrafast structural changes in complex chemical systems by X-ray FELs

Scientific instruments

Ultrafast Coherent Diffraction Imaging of Single Particles, Clusters, and Biomolecules (SPB)
- Structure determination of single particles: atomic clusters, bio-molecules, virus particles, cells.

Materials Imaging & Dynamics (MID)
- Structure determination of nano-devices and dynamics at the nanoscale.

Femtosecond Diffraction Experiments (FDE)
- Time-resolved investigations of the dynamics of solids, liquids, gases

High Energy Density Matter (HED)
- Investigation of matter under extreme conditions using hard x-ray FEL radiation, e.g. probing dense plasmas

Small Quantum Systems (SQS)
- Investigation of atoms, ions, molecules and clusters in intense fields and non-linear phenomena

Soft x-ray Coherent Scattering (SCS)
- Structure and dynamics of nano-systems and of non-reproducible biological objects
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**X-ray diffraction provides structural information**

Bragg scattering of undisturbed crystal

Overall reduction of lattice parameter

Crystal with varying lattice parameter

Disorder

⇒ additional diffuse scattering
- precipitations (impurities, defects)
- clustering
- near-/far-field ordering

Ensemble of integrated peak intensities provides the possibility to refine the electron density distribution inside the cell

⇒ 3D molecule structure
Ultrafast structural changes in complex chemical systems by X-ray FELs

Examples of complex systems

Use XRD with sub-atomic resolution to investigate the photochemistry of complex chemical systems

- exploration of fs sources suitable for this work: SR & acc.-based sources

Molecular solids

- p-FCA → photo-dimerisation; irreversible
- TTF-derivates (-CA & -TCNQ) → reversible, photo-induced phase trans.
- MAMC → submicron crystals powder diffraction
- liquid crystals → ultrafast & large d-spacing

p-FCA  
\[ \text{p-formyl-trans-cinnamic acid} \]

TTF-CA  
\[ \text{Tetrathiafulvalene-Chloranil} \]

MAMC  
\[ \text{Methylammonium-Tetrachloromanganate} \]

Liquid crystal

\[ <4.2\text{Å} \]
**Ultrafast structural changes in complex chemical systems by X-ray FELs**

**Non-reversible chemical reactions**

*p*-formyl-*trans*-cinnamic acid: *p*-FCA

- photo-dimerisation
- applications:
  - nano-actuator
  - chiral synthesis

**Slow structural transition**
- peak broadening & splitting
- amorphisation

**Ultrafast transient change**
- fast signal near resolution limit

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**Graphs**

- **Left graph**:
  - Intensity vs. 2θ (degree)
  - Samples: 
    - t = 0 min
    - t = 28 min
    - t = 42 min
    - t = 54 min

- **Right graph**:
  - Intensity vs. τ (ps)
  - Sample labels:
    - sample 1 (< t<sub>slow</sub> > = 20 min)
    - sample 2 (< t<sub>slow</sub> > = 26 min)
    - sample 3 (< t<sub>slow</sub> > = 34 min)

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Ultrafast structural changes in complex chemical systems by X-ray FELs

Photo-induced reversible phase transitions

Tetrathiofulvalene-Chloranil: TTF-CA

- neutral-to-ionic phase transition
- applications:
  - organic opto-electronic materials
  - energy conversion in solar cells
  - isolator-conductor: switches & SC

Neutral phase

\[ \begin{align*}
  & D^0 A^0 D^0 A^0 \\
  & D^0 A^0 D^0 A^0 \\
  & D^0 A^0 D^0 A^0 \\
\end{align*} \]

Neutral phase

\[ \begin{align*}
  & D^+ A^- D^+ A^- \\
  & D^+ A^- D^+ A^- \\
  & D^+ A^- D^+ A^- \\
\end{align*} \]

Metastable phase

\[ \begin{align*}
  & D^+ A^- D^+ A^- \\
  & D^+ A^- D^+ A^- \\
  & D^+ A^- D^+ A^- \\
\end{align*} \]

Metastable phase

Ionic phase

\[ \begin{align*}
  & D^+ A^- D^+ A^- \\
  & D^+ A^- D^+ A^- \\
  & D^+ A^- D^+ A^- \\
\end{align*} \]

Photoinduced neutral-ionic phase transition

- Observed strong variation in reflections which are explained by non-equilibration effects
- complete trans. of sample → coop. process
- threshold behaviour → number of domains
- delayed start → domain formation

Increase time-resolution to study primary processes

- how is energy transferred into the crystal
- how does the structural order change depend on parameters

Use 80 fs, $10^6$ photons/pulse (SPPS)

- crystals Ø~80 µm
- 2% signal, instant rise of signal

C. Blome, S. Techert, Th. Tschentscher et al., unpublished
Ultrafast structural changes in complex chemical systems by X-ray FELs

Parallel data-taking

Laue diffraction
- use bandwidth of few %
- record many reflections in parallel
- requirements
  - small mosaicity
  - well char. instrument & spectrum

Advantages
- high signals even for very small crystals
- much faster collection of complete data sets
- fewer exposures / pp-cycles
- self-calibration of reflections

M. Messerschmidt, Th. Tschentscher, S. Techert et al., in prep.
Ultrafast structural changes in complex chemical systems by X-ray FELs

Time-resolved measurement on TTF-CA

Measurement
- 10-20 μm thick samples
- 30 exposures/angle @ 20 Hz
- 1 – 90 deg, ±1 deg
- ~2 min or 2700 shots/delay

Analysis & results

s. crystal
90 K
800 nm
5 mJ/cm²

to be published
to be published
Ultrafast structural changes in complex chemical systems by X-ray FELs

Lattice response in TTF-CA

The change of lattice parameters (spacing, angles, symmetry) can be observed from the movement of the Bragg spots

- we observe such a response only for $\Delta t > \sim 10$ ns
- crystal recovers before next optical/x-ray pulse arrives

dependence on laser fluence

M. Messerschmidt, Th. Tschentscher, S. Techert et al., in prep.

Thomas Tschentscher, European XFEL, Mai 3, 2009
From the variation of the integrated intensities of the Bragg reflections we can refine rearrangements inside the unit cell

- we find a fast response (limited to time resolution of the setup)
- following the system does not evolve until it decays
- new transient phase

**Photo-excited (50 ps)**
- 90 K
- 2700 single pulses
- 800 nm, 107 uJ, 20Hz

for comparison:

**Static (78 K – 70 K)**
- lab source
- minutes exposures

M. Messerschmidt, Th. Tschentscher, S. Techert et al., in prep.
Observed new transient structure
- forming instantly after excitation (time-resolution limited)
- symmetric difference structure varies significantly from difference structure between thermal equilibrium static states
- non-equilibrium structure, probably due to bond-softening
- observation possible due to Laue method enabling much higher accuracy in determining integrated intensities and shifts of Bragg position
- Laue method enabled further to use much smaller crystals with improved signal-to-noise ratio

Lattice response
- much reduced and observable only at late times (>10 ns)

Next steps
- Use FEL radiation to improve time-resolution to ~100 fs
- Need to develop schemes to measure high quality crystals
Laue diffraction provides the bandwidth to follow changes

- FELs need to operate at larger bandwidth
  - one possibility is chirping the electron beam
  - ~$10^{-4}$ within coherence length
  - maybe 1, 2, … % are possible

Powder diffraction samples simultaneous all orientations

- case studies to exploit using 1D-detectors
- maintain high angular resolution
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Powder diffraction using FELs

Methylammonium tetrachloromanganate: MAMC

- rich t-dependent phase diagram
- varying macroscopic properties
- applications:
  - inorganic opto-electronic materials

<table>
<thead>
<tr>
<th>Phases</th>
<th>Crystal structure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature (HT)</td>
<td>Tetragonal</td>
<td>394 K &lt; T</td>
</tr>
<tr>
<td>Room temperature (RT)</td>
<td>Orthorhombic</td>
<td>257 K &lt; T &lt; 394 K</td>
</tr>
<tr>
<td>Low temperature (LT)</td>
<td>Pseudotetragonal</td>
<td>94 K &lt; T &lt; 257 K</td>
</tr>
</tbody>
</table>

1 mrad angular res. needed

C. Blome, Th. Tschentscher, S. Techert et al., JSR 12, 812(2005); AIP CP879 (2007)
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Outline

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Structural dynamics of complex systems studied by x-ray diffraction

Prospects and considerations for X-ray FEL experiments
Time resolution of 10 fs corresponds to 3 µm in length
- mechanical precision of light paths
- tilting of wavefronts needs to be adapted

Group velocities differ significantly for optical dense matter
- $\Delta v \leq c/4 = 0.75 \times 10^8$ m/s
- 10 fs resolution $\rightarrow$ 12 µm sample thickness
High intensity x-ray beams are expected to damage sample
- consider hard x-rays \(\sim 12\) keV
- \(2\) mJ, \(10^{12}\) phts in \(100\) fs \(\rightarrow\) \(20\) GW
- \(100\) µm beam spot \(\rightarrow\) \(2.5 \times 10^{14}\) W/cm\(^2\)

We have simulated the energy absorption per … for the case of MAMC
(C. Blome, Th. Tschentscher, J. Davaasambuu, P. Durand, S. Techert, AIP CP879, 2007)
- \(1\)% absorption in sample
- \(\sim 50\) meV/molecule/pulse \(\rightarrow\) \(10\) K temperature jump
- pulse trains with \(5\) MHz repetition rate will alter samples considerably

Experiments at ESRF-ID09 are routinely carried out with \(10^{10}\) phts/pulse
(\(=10^{13}\) phts/s) on the sample
- increase of 1 to 2 orders of magnitude
- \(100\) ps instead of \(100\) fs
**Sample exchange schemes**

**Single crystals**
- translation, rotation, replacement (speed !)
  - $1 \text{ MHz} \ & \ 100 \ \mu\text{m} \rightarrow 100 \ \text{m/s}$
- issue with pre-alignment & accuracy of placement

**Jets for solutions**
- stable operation shown
- speed of 10s of m/s feasible

**but X-ray radiation will interact with jets too !**

XUV pump –opt. laser probe
$\rightarrow$ solvated electrons in $\text{H}_2\text{O}$

to be published

*figure & data courtesy S. Techert group*
If we can photo-excite samples by ionising electrons to unoccupied high lying states we could think of this new type of ultrafast pump-probe exp.

- intrinsic synchronization
- match of excitation & probing depth
- still might require 2-color scheme
  - e.g. 1st & 3rd harmonic

1st hard x-ray design available & tested now
- thin single crystal monochromators
- combine Bragg & Laue geometry

figure & data courtesy W. Rosecker, G. Grübel, et al.
Dynamical diffraction could affect temporal profile

C 111 reflection
0.1 nm, 25 µm thickness
⇒ Δt = 5 fs

Time response
0.1 µm – 11 µm thickness
X-ray FELs turn on now and are expected to start a new era of time-resolved x-ray experiments!!!

Investigation of structural dynamics in complex chemical systems following photo-excitations is an important field of application

This requires high resolution, which can be matched by using Bragg diffraction

Picosecond time-resolution experiments reach high spatial resolution and indicate already ultrafast responses below resolution limit

Lattice response requires further investigation

Single crystal experiments using extremely brilliant radiation require further development for sample delivery and data collection schemes
Acknowledgement

- Co-workers at DESY: C. Blome, C. Sager, M. Messerschmidt, A. Meents
- Collaboration with group of S. Techert (MPI biophysical Chemistry, Göttingen)
- Data from ESRF (ID09), FLASH, APS and SPPS
- Contributors to TDR and its workshops
- The European XFEL team & DESY