ULTRAFAST TIME-RESOLVED X-RAY ABSORPTION SPECTROSCOPY

Frederico Alves Lima

Ecole Polytechnique Fédérale de Lausanne
Swiss Light Source - Paul Scherrer Institut
Outline

- Introduction
  - Structure vs. function
  - Ultrafast phenomena
- How to obtain structural information
  - XAS and time-resolved XAS
- Interesting results
  - Spin-crossover model - \([Fe^{ll}(bpy)_3]^{2+}\)
  - Photo-detachment of Myoglobin
- Summary
Is function structure or dynamics?

**Structure**
- X-ray crystallography
- electron microscopy
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy
- NMR

**Dynamics**
- Laser spectroscopy
- NMR
- time-resolved diffraction
- X-ray absorption spectroscopy

Side view of the light-harvesting complex II in chlorophyll (PDB)

Rotating hydrated myoglobin molecule

http://uweb.cas.usf.edu/chemistry/faculty/space/
B. Space & J. Belof (University of South Florida)
1. Laserblitz löst Reaktion aus

Energie

angeregter Zustand

kurzlebige Übergangszustände

Gleichgewichtszustand

2. Laserblitz macht Momentaufnahme

zeitlicher Ablauf der Reaktion

http://bilder.desy.de
What are the length scales involved?

http://www.newgrounds.com/portal/view/525347
What are the timescales involved?

- **Attoseconds** ($10^{-18}$ s)
  - Electron motion
  - Core-hole lifetimes

- **Femtoseconds** ($10^{-15}$ s)
  - Motion of nuclei
  - Molecular vibrations
  - Optical phonons
  - Molecular bond formation

- **Picoseconds** ($10^{-12}$ s)
  - Rotation of molecules
  - Vibrational dephasing
  - Electronic relaxation

- **纳oseconds** ($10^{-9}$ s)
  - Fluorescence
  - Thermal effects

- **Microseconds** ($10^{-6}$ s)
  - Large-scale protein motion
  - Phosphorescence

- **Milliseconds** ($10^{-3}$ s)
  - Protein folding
  - Chemical kinetics

**X-rays**

- High-harmonic generation
- Laser plasma
- Laser-slicing
- X-FELs
- Synchrotrons
- Electronics
- Lasers

110 as delay between electron emission from conduction band and lower-lying states in Tungsten upon irradiation.

The Fe K-edge core-hole lifetime is 4 fs.

Period of the symmetric stretch in H$_2$O is $10$ fs.

Hemoglobin R->T transition takes microseconds.

Camera shutter speeds range from ms through to seconds.
Where can we do that?
Synchrotron radiation

Synchrotron radiation → relativistic accelerated charges
Synchrotron radiation

http://www.diamond.ac.uk/Home/About/Films/technology.html
The Swiss Light Source

- 3rd generation synchrotron light source located one hour from Zürich
- 2.4 GeV energy, operating on top-up mode
- Up to Sept. 2009 only femtosecond hard x-ray source in the world
Ultrafast X-ray Sources: picosecond

**MicroXAS beamline**
- tunable hard x-ray in-vacuum undulator (4-20 keV)
- Si (111), Ge(111) & Si(311) monochromator crystals
- micro-focus capability (< 1mm²)
- $10^{12}$ photons/second

**PHOENIX beamline**
- tunable ‘tender’ x-ray in-vacuum undulator (0.8-8 keV)
- Si (111), KTP, Be, InSb monochromator crystals
- micro-focus capability (< 1mm²)
- $10^{11}$-$10^{12}$ photons/second

Using fast avalanche photodiodes and either boxcar integrators or track-and-hold circuits we can selectively measure using only the camshaft pulse giving us 70 ps time resolution.
Ultrafast X-ray Sources: femtosecond

- An ultrashort (fs) laser pulse co-propagate with an electron bunch causing a modulation on its energy
- Electrons with different energy are further separate in space via dispersive elements on the synchrotron ring

The FEMTO slicing source at the SLS
- tunable from 4 to 14 keV
- 140 ± 30 fs x-ray pulse duration
- timing stability of < 30 fs RMS over days
- $10^5$ photons/second

How the (time-resolved) experiments are done
Ultrafast time-resolved X-ray Absorption Spectroscopy

Frederico Alves Lima


\[ \Delta A(E, t) = f(t) \cdot [A_{\text{Pumped}}(E, t) - A_{\text{Unpumped}}(E)] \]

signal
fraction of excited species

X-ray Absorption Spectroscopy

- An x-ray photon is absorbed by an atom when its energy is transferred to a core-level electron which is ejected from the atom.

  Photo-electron effect

- The photo-electrons are emitted as spherical waves which are damped out rapidly due to inelastic effects caused by the extended valence orbitals of the nearby-lying atoms.

  XAS is a local probe!

http://xafs.org/
The (x-ray) absorption process depends whether or not there's an available state for the photo-electron.

Neighboring atoms scatter the emitted photo-electron modification of the absorption coefficient $\mu$. 
Aqueous $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$

- Light-induced spin crossover effect
- Porphyrin-like model system (Myoglobin)
- Magnetic switching and data storage
- Model system in the group of *polypyridine* photosensitizers

MLCT = metal-to-ligand charge-transfer

MLCT = metal-to-ligand charge-transfer

$\lambda_{\text{exc}} = 400 \text{ nm}$, $\lambda_{\text{em}} = 532 \text{ nm}$
Aqueous $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$

- Energy levels: $^1\text{T}_2$, $^3\text{T}_2$, $^1\text{A}_1$, $^5\text{E}$
- Transitions: $^{1,3}\text{MLCT}$, $^3\text{T}_2$ to $^5\text{T}_2$
- Timescales: ~30 fs, ~120 fs, 660 ps
- Change in Fe-N bond length: low spin, high spin
- Fluorescence: $^1\text{MLCT} \rightarrow \text{GS}$

Aqueous $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$

Aqueous $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$: Femtosecond XAS planning

With a loss of 4 orders of magnitude of x-ray photons we need to be smart about the experiment.

The largest transient signal is at the B feature which is a multiple-scattering feature sensitive to the Fe-N bond distance.

The picosecond experiments suggest it will take 30-60 minutes per data point to acquire S/N of $\sim 4:1$

**Proposal**
Tune the energy to the maximum transient signal (7126 eV) and perform a time scan.
Aqueous $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$: Femtosecond XAS results

The molecule arrives in the high-spin state directly from the $^3\text{MLCT}$ in ~150 fs.
Ultrafast time-resolved X-ray Absorption Spectroscopy
Frederico Alves Lima

Aqueous \([\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}\): Conclusions

- Picosecond EXAFS has successfully resolved the transient high-spin state structure of a spin-crossover molecular system in solution to sub-Å resolution.
- Femtosecond XANES has allowed us to watch the arrival of an excited molecular system in its high-spin state.

By combining ultrafast optical techniques and ultrafast x-ray techniques we have completely characterized the structure and dynamics of a molecular spin-crossover system.
Aqueous $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$ revised

- The newly-implemented MHz data scheme allows the collection of high-quality data.
- More details of the transient excited-state structures can be studied.


Fluorescence yield - 25 mM Fe(bpy)$_3$
The increased S/N allows the collection of high-quality data in less time.

Possibility to investigate subtle details of the transient structure.

Allows the measurement of highly-diluted systems, e.g., proteins in solution.
Myoglobin is an oxygen transport/storage protein that has the ability to bind small molecules such as $O_2$, CO, NO and CN.

Small changes in the ligand character have profound spectroscopic effects.

We can knock this ligand off with a photon of green or blue light.
Proof-of-principle: MbCO

- First ever time-resolved x-ray experiment \(^1\)
- Alternative data-collection strategy due to the high repetition rate and long photo-excited lifetime
- Liquid sample under physiological conditions

MbNO - dynamics of ligand detachment

- What’s the spin-state & electronic structure of the Fe atom on the transient structure?
- What’s the geometry of the transient structure?
- Is there more than one excited state structure?
- Can we see a bound MbON structure? ¹

- How fast is the geminate recombination?
- Existence of a 6-coordinate domed structure on MbNO? ²

² S. Kruglik et al. PNAS 107, 13678 (2010)
MbNO

Fast dynamics (ca. 200 ps) captured on the fly

Small discrepancy from the predicted signal might be an indication of a 30 ps domed ligated (6-coordinated) configuration. ¹

Summary

☑ The potential inherent to time-resolved XAS is enormous, we can measure structural changes in excited systems on the timescale of atomic motion

☑ Using higher data acquisition repetition rate we can study subtle details of the transient (excited) structures and/or more complex systems

☑ The ultrafast structural dynamics of excited-state biological systems under physiological conditions can be followed

☑ Extending the technique to the soft x-ray regime will allow the study of L-edges of transition metals and K-edges of C, N, O, etc

☑ More to come with new sources of ultrafast x-rays: XFEL
Acknowledgments

LSU
Chris Milne
Renske van der Veen
Hannelore Rittman-Frank
Marco Reinhard
Susanne Karlsson
Frank van Mourik
Majed Chergui

LSU alumni
Wojciech Gawelda
Christian Bressler
Dimali Amarasinghe
Amal El Nahhas
Van-Thai Pham
Andrea Cannizzo

FEMTO
Steve Johnson
Paul Beaud
Ekaterina Vorobeva
Andrin Caviezel
Gerhard Ingold
Alex Oggenfuss
Simon Mariager

MicroXAS
Daniel Grolimund
Camelia Borca
Marcus Willimann
Beat Meyer
Rafael Abela

PHOENIX
Markus Janousch
Thomas Huthwelker
Reto Wetter

Funding: Swiss NSF, SLS, EPFL

For more information on ultrafast structural dynamics visit http://lsu1.epfl.ch/dyna/
The intensity of an x-ray beam passing through a material of thickness $t$ is given by the absorption coefficient $\mu$.

Beer-Lambert law: $I = I_0 e^{-\mu t}$

$\mu$ depends strongly on x-ray energy $E$, atomic number $Z$, on the density $\rho$ and on the atomic mass $A$:

$$\mu \approx \frac{\rho Z^4}{AE^3}$$

X-ray absorption fine structure function:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)}$$
Fermi’s Golden Rule

\[ \mu(E) \propto |\langle i | H | f \rangle|^2 \]

\[ |f\rangle = |f_0\rangle + |\Delta f\rangle \]

\[ \mu(E) \propto |\langle i | H | f \rangle|^2 \left[ 1 + |\langle i | H | \Delta f \rangle| \frac{\langle f_0 | H | i \rangle}{|\langle i | H | f_0 \rangle|^2} + C.C. \right] \]

\[ \mu(E) = \mu_0(E)[1 + \chi(E)] \]
Aqueous $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$: (picosecond) Data analysis

- Optimize ground-state structures and parameters
- Generate a set of EXAFS spectra for a given model by moving specific coordinates
- Calculate the transient spectrum
  \[ \Delta \chi_i^{TH}(\Delta R_i, E') = \chi_i^{ES}(\Delta R_i, E') - \chi_i^{GS}(E) \]
- Minimize the reduced chi squared function
  \[ \chi_r^2(i, f, \Delta E_0) = \frac{1}{N-1} \sum_{j=1}^{N} \left( \frac{x_j/f - \Delta \chi_{i,j}^{TH}(\Delta R_i, E')}{\sigma_j^x/f} \right)^2 \]

<table>
<thead>
<tr>
<th>Fe-N (Å)</th>
<th>Error (Å)</th>
<th>f (%)</th>
<th>ΔE₀ (eV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>±0.02</td>
<td>22</td>
<td>-2.8±0.5</td>
<td>EXAFS analysis</td>
</tr>
<tr>
<td>0.19</td>
<td>±0.03</td>
<td>21.5±1.5</td>
<td>-2.5</td>
<td>MXAN analysis with fixed ΔE₀</td>
</tr>
<tr>
<td>0.2</td>
<td>±0.04</td>
<td>22</td>
<td>-2.5±0.5</td>
<td>MXAN analysis with fixed f</td>
</tr>
<tr>
<td>0.203</td>
<td>-0.035, +0.012</td>
<td>22±1</td>
<td>-2.5±0.5</td>
<td>this analysis with f=22% and ΔE₀=-2.5 eV</td>
</tr>
<tr>
<td>0.2005</td>
<td>-0.0165, +0.0135</td>
<td>17±1</td>
<td>-1.2±0.5</td>
<td>this analysis 90% confidence levels</td>
</tr>
<tr>
<td>0.203</td>
<td>±0.008</td>
<td>17±1</td>
<td>-1.2±0.6</td>
<td>this analysis 95% confidence levels</td>
</tr>
</tbody>
</table>

1 W. Gawelda, et al., JCP 124520, 130 (2009)
Ultrafast time-resolved X-ray Absorption Spectroscopy
Frederico Alves Lima
Myoglobin - expected signal on TR-XAS
MbCO - expected signal on TR-XAS
MbNO - expected signal on TR-XAS
Myoglobin - static XAS and radiation damage

F. Lima, D. Amarasinghe, C. Milne, private data 2009
Ultrafast time-resolved X-ray Absorption Spectroscopy
Frederico Alves Lima

☐ bla bla bla

☐ bla bla bla

☑ bla bla bla

☑ bla bla bla

☐ bla bla bla

☐ bla bla bla