Ultrafast X-Ray Absorption Spectroscopy

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What are the fundamental timescales?

- **Molecular Physics, Chemistry and Biochemistry**
- **Photosynthesis**
- **Vision**
- **Molecular Vibrations**
- **Protein Folding**
- **Molecular Rotations**
- **Electron dynamics**

Strings, Particle Collisions, Cosmology

- 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 $10^{-3}$

Time / seconds
Nature is dynamic, even at molecular and atomic scales

Motion can be observed by:
- Strobe light illumination (short pulses)
- Fast-shuttered cameras and high speed movies

We need short-wavelength x-ray light to “see” atomic structure

However, atoms cannot be “seen” directly, but only through patterns of scattered light, or variations in absorbed light, which reveal structure

Measurement of dynamics requires “phasing” by an initializing event (e.g., using laser pulses)
The hard currency for experimentalists: PHOTONS

1 kHz amplified laser system

100 MHz laser oscillator

this laser pointer

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The diagram shows a graph with the x-axis labeled "Pulse width / ps" ranging from 1000 to 0.01, and the y-axis labeled "Pulse intensity / photons (0.1 % b.w.)" ranging from $10^0$ to $10^{12}$. The graph includes the following labels:

- Synchrotron Radiation
- ERL
- X-FEL
- Time-Sliced SR
- X-Ray Plasma

The graph also features a red line and a black arrow indicating the relative pulse intensity and width for different laser systems.
Ultrafast EXAFS on Transition Metal Compounds

Structural Dynamics Research:

- Coordination Chemistry (Transition Metal Compounds)
- Artificial Solar Cells (charge delivery)
- Biologically relevant processes (porphyrins)
- Molecular switches (Bi-metallic devices)

- Solvation Dynamics
- Atomic Ions (Halides, Ag\textsuperscript{+}, diatomics, etc…)

- Gas Phase Atomic and Molecular Physics
  - attosecond charge redistribution
  - nonadiabatic wave packet dynamics

Ultrafast X-Ray Science at ETH Lausanne and SLS

Methodologies:
- Pulse-limited transient XAFS (+ shot-noise!)
- Streak Camera Development (SLS)
- Advanced XAFS Analysis Packages

Research Topics:
- Intramolecular Charge Transfer
- Light Induced Spin-Crossover
- Solvation Dynamics

In-House:
- Femtosecond to nanosecond laser spectroscopies
Why ultrafast X-ray Absorption Spectroscopy?

We want to measure transient STRUCTURES

- **Short time scales ↔ short distance scales**
- All media (gas, liquids, solids, biological samples, ...)
- Optically silent states

![Graph showing absorption spectra with time delay Δt = 50 ps and Ru(bpy)_3 as an example.]

- **Electronic Structure (DOS)**
- **Element specific (disordered media !!)**

Gawelda et al., JACS 128, 5001 (2006)

**MXAN (XANES)**

**Geometric Structure (EXAFS)**
Light-induced low spin to high spin transition in $[\text{Fe}^{II}(\text{bpy})_3]^{2+}/\text{H}_2\text{O}$

$[\text{Fe}(\text{bpy})_3]^{2+}(\text{aq})$: 
(LS) $\rightarrow$ (HS) ($<$1ps)

Application
(HS) $\rightarrow$ (LS) ($<$0.7 ns)
Summary of ultrafast laser studies

- 15 fs
- 120 fs
- 960 fs
- 665 ps
- Configuration Coordinate

A. Hauser (2006)
Structural Implications

Measure Structure

Understand High Spin Lifetimes in SCO Compounds

→ Time-Resolved X-Ray Absorption
Sample Time-Resolved XAFS Setup (Swiss Light Source)

Fluorescence Detection
Photon Statistics

Poisson Fit:
\[ \mu = 2.818 \pm 0.001 \]

per pulse
Low-Spin $\rightarrow$ High-Spin Crossover (and back)

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

static absorption

$\Delta t = 50$ ps

$\Delta t = 100$ ps

Transient Absorption / a.u.

Time Delay / ps
Low-Spin → High-Spin Transition (and back)

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

Normalized Absorption

$\Delta t = 50$ ps

Transitional Absorption / $\Delta \chi$

X-Ray probe Energy / eV

7000 7200 7400 7600 7800

Δt = 50 ps

665 ps

100 ps

Transient Absorption / a.u.

Time Delay / ps

0 1 2 3 4 5 6 7 8 9 10

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

0 200 400 600 800 1000

XAFS

Optical

1

0

-200 0 200 400 600 800 1000

0

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

static absorption
Fe(bpy)$_3$ K-edge XAFS: Experiment and Theory

Fit the transient data directly!!

$\Delta R = 0.19 \pm 0.03 \text{ Å}$

Gawelda et al., submitted to PRL (2006)
Solvation Dynamics

Condensed Phase Dynamics

\[
R(I^- - O) = 350 \text{ pm}
\]

\[
0 < t < 1 \text{ ps}
\]

\[
\text{CTTS - } e^-
\]

\[
\text{Inertial Response ?}
\]

\[
R(I^0 - O) = 300 \text{ pm} (?)
\]

\[
t >> 1 \text{ ps}
\]

Solvation Coordinate
Theoretical Prediction for Atomic Iodine Radicals

I in 183 water molecules

\[ g(r) \] - I - O Distance / Å

I. Tavernelli, unpublished results (2006)

 transient absorption / a.u.

laser experiment

Transient Absorption / a.u.

\[ I^- + h\nu \rightarrow I^0 + e^- \]
Theoretical Prediction for Atomic Iodine Radicals

I in 183 water molecules

\[ g(r) \] versus I - O Distance / Å

I. Tavernelli, unpublished results (2006)

Laser experiment

\[ \text{I}^- + h\nu \leftrightarrow \text{I}^0 + e^- \]

Transient Absorption / a.u.

Time Delay / ps
\[
\text{I}^- (5p^6) + (\text{H}_2\text{O})_n + h\nu \rightarrow \text{I}^0 (5p^5) + (\text{H}_2\text{O})_m + \text{e}^- (aq)
\]

- Partial Charge Back Transfer
- Solvation shell changes dramatically
- XAFS unique to detect all this!!

Next steps...
Pulsed X-Ray Sources: Present and the Future

XFEL radiation will open up new research possibilities

2-20 keV

Number of Photons for S/N = 1

Liquid Phase XAFS (1 mM)

Atomic Number Z
Summary

✓ Transient XAFS spectroscopy (ca. 50 ps)
✓ High(est) experimental sensitivity

- Electronic structure inferred from XANES (0-100% electron transfer detectable)
- Molecular structure from EXAFS (FEFF), XANES including Multiple Scattering (MXAN)
- Future experiments calibrated (feasibility)
  - 100 fs  →  1-100 ps  →  ps-μsec
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Photoelectron Wavevector $k / \text{Å}^{-1}$

$\Delta t < 0$

$\Delta \chi(k) \times k^2$

FEFF

Ground State

$\Delta t = 50 \text{ ps}$

$\Delta \chi(k) \times k^2$

Transitient fit (FEFF)

Fe-N Bond increase:

$\Delta R = 0.18 \pm 0.02 \text{ Å}$

Modifying FEFF for Transient XAFS Fits...