Ultrafast X-ray Spectroscopy of Solvated Transition-metal Complexes and Oxide Materials

Robert Schoenlein
Materials Sciences Division
Chemical Sciences Division - UXSL

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Fundamental Challenge – Condensed Matter

Understand the Interplay between Atomic and Electronic Structure
- Valence electronic structure – energy levels, charge distribution, bonding, spin
- Atomic structure – coordination, atomic arrangements, bond distances

Particularly in systems that challenge the standard paradigms:
- beyond single-electron band structure models, Landau-Fermi Liquid Theory
  complex materials exhibiting strong correlation among charges, and between charge, spin, orbit, and lattice

Atomic Structural Dynamics
atomic vibrational period: \( T_{\text{vib}} = 2\pi (k/m)^{1/2} \sim 100 \text{ fs} \)
\( k \sim \text{eV/a}^2 \quad m \sim 10^{-25} \text{ Kg} \)
- structural phase transitions
- chemical reactions

Electronic Structural Dynamics
- electron-phonon interaction \( \sim 1 \text{ ps} \)
- e-e scattering \( \sim 10 \text{ fs} \)
- e+ correlation time \( \sim 100 \text{ attoseconds} \) \( (a/V_{\text{Fermi}}) \)
- bond dynamics, valence charge flow
- electronic phase transitions
- correlated electron systems
Ultrafast X-rays: Quantitative Information on Electronic and Atomic Structure

time-resolved x-ray spectroscopy

- **XANES** – local electronic structure, bonding geometry (x-ray absorption near-edge structure)
- **XMCD, XMLD** – spin, magnetization – dichroism (x-ray magnetic/linear dichroism)
- **EXAFS** – local atomic structure and coordination (extended x-ray absorption fine structure)

- element specific
- symmetry/spin selective
- ferromagnetic/antiferromagnetic order
- molecular systems and reactions
- interfaces, complex/disordered materials

![Diagram of X-ray spectroscopy](image)

**Time-resolved x-ray diffraction**

atomic structure in systems with long-range order/periodicity
phase transitions, coherent phonons
Structural Dynamics in Solvated Transition-Metal Complexes
- spin-crossover transition – Fe(II) complex – EXAFS, Fe K-edge (atomic structure)
- spin-crossover – Fe(II) – XANES, Fe L-edge (electronic structure)

Structural Dynamics in Colossal Magnetoresistive (CMR) Manganites
- ultrafast photo- and vibrationally-induced insulator-metal transition in Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\)
- electronic structure – time-resolved XANES (O K-edge, Mn L-edge)

Future Directions, Ultrafast Soft X-ray Spectroscopy – LCLS
**Fe**II Spin-Crossover Molecules

Motivation:

- ligand field strength \((10Dq)\) ~ electron pairing energy
- relationship between structure, electronic, and magnetic properties

**Do the dynamic structural distortions facilitate the spin-crossover reaction?**

- electron transfer mechanistic role in biochemical processes (cytochrome P450)
- molecular electronics, opto-magnetic storage material

**Collaborator:** J.K. McCusker group – Michigan State
Fe$^{II}$ Time-resolved EXAFS

0.2 Å change in Fe-N bond distance within 70 picoseconds

Electronic Structure - Fe$^{II}$ Spin-Crossover Molecules

**Soft X-ray XANES - transmission**

Charge Transfer $\Rightarrow$ Ligand Bonding $\Rightarrow$ Spin State

Electronic structure: L-edge spectroscopy
- Metal-ligand bonding (high-spin vs. low spin)
- Fe 3$d$-electrons (N-2$p$)
- Spin state (S-O split Fe-2$p$)

Solvent influence
- Dielectric interaction with charge-transfer process
- Steric interaction with ligand distortions?

MLCT (charge-transfer state)

(low-spin state)

$\Delta S=2$

(high-spin state)

Fe-3$d$

$^{t_{2g}}^{6}$

Fe-2$p_{3/2}$

Fe-2$p_{1/2}$

$^{(t_{2g})^4 (e_g)^2}$

Fe[tren(py)$_3$]$^{2+}$ in acetonitrile

Lee, et al., JACS, 122, 5742, 2000
Electronic Structure - Fe$^{II}$ Spin-Crossover Molecules

Soft X-ray XANES - transmission

Interferrogram sample thickness

~0.5 µm thick liquid sample cell

100 nm Si$_3$N$_4$ windows

Solvent Transmission

UXSL Soft X-ray Endstation
**Electronic Structure - Fe^{II} Spin-Crossover L-edge XANES**

*Soft X-ray XANES – Fe L_{III}*

Fe[trepy]_{3}^{2+} in acetonitrile

**Differential Spectra**

- 150 ps delay
- 5 ns delay

**Time-Dependence**

- 708.0 eV
- 710.0 eV
- 706.25 eV

- Ligand field strength ~ electron pairing energy
- reduction in ligand field parameter 10Dq
- electronic structure evolution within 70 ps resolution
Future Directions - Fe$^\text{II}$ Spin-Crossover L-edge XANES

$L_{\text{III}}$ Transient Absorption Spectra

- Low-spin ground state
- Photo-excited high-spin state

**Theory:** (Brois et al., *JACS*, 117, 1995)
- ~0.55 eV reduction in 10$Dq$
- contribution from core-hole correlations

**Future Directions - Fe$^\text{II}$ Spin-Crossover L-edge XANES**

- Spin-Crossover L-edge XANES
  - Low-spin
  - Photo-high-spin

- Energy (eV)
- Absorption
- Delay (ps)

- 720 eV
- $\Delta T/T$ normalized
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Future Directions, Ultrafast Soft X-ray Spectroscopy – LCLS
Colossal Magnetoresistive Manganites

Pr$_{1-x}$Ca$_x$MnO$_3$

- Magnetic control of electronic structure (magneto-transport)
- Rich phase diagram – order/symmetry breaking competing ground states
- New physics, correlation effects other complex materials

**Distorted Perovskite structure ↔ Rich Phase Diagram**

**Rich Phase Diagram**

- COI - charge ordered insulator
- PI – paramagnetic insulator
- AFI – antiferromagnetic insulator
- CAFI – canted antiferromagnetic insulator
Vibrationally-Driven Phase Transition in Manganites

Tolerance Factor: Orthorhombic Distortion of Cubic Perovskite Structure

\[ \Gamma = \frac{d_{Pr-O}}{\sqrt{2} \cdot d_{Mn-O}} \]

Related to the Mn-Mn electron hopping rate

small tolerance factor \( \leftrightarrow \) tendency to charge localization

Ground-state vibrational pumping \( \text{Pr}_{0.7} \text{Ca}_{0.3} \text{MnO}_3 \)
- transient sample conductivity measurements

Changes of sample resistance
- depend on resonant phonon excitation

No current is observed when pumping at 8.5 \( \mu \)m

M. Rini, et al.
*Nature*, 2007

Collaborator: A. Cavalleri – Oxford, DESY CFEL

mid-IR 10-24 \( \mu \)m
1 \( \mu \)J, 200 fs
1 mJ/cm\(^2\)

Conductivity \( [\Omega \cdot cm] \) Delay \( [ns] \)

[Graph showing conductivity and delay]

\( \rho_{\text{PEAK}} = 1.1 \times 10^3 \Omega \cdot \text{cm} \)

\( \rho_{\text{INIT}} = 2.8 \times 10^7 \Omega \cdot \text{cm} \)
Vibrationally Driven I-M Transition in a Manganite via coherent THz excitation

Phase Transition
- vibrational excitation
  - long-lived changes in reflectivity
- well-defined fluence threshold and saturation


Collaborator: A. Cavalleri – Oxford, DESY CFEL
Static XAS - Insulator/Metal Transition in Manganites

O K-edge: $1s \rightarrow 2p$
Pre-edge: unoccupied states of mixed O-2$p$ and Mn-3$d$ character

Mn L-edge: $2p \rightarrow 3d$
Predominantly metal-3$d$ character

Mannella et al. PRB (2005)
Time-resolved XAS
Insulator/Metal Transition in Manganite (PCMO)

M. Rini, Y. Zhu, R. Schoenlein – LBNL Materials Sciences
S. Wall, R. Tobey, A. Cavalleri - Oxford

800 nm, 100 fs
30 mJ/cm², s-pol

X-Rays, 70 ps
530-560 eV

channeltron

\[ \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \]

\[ \text{Mn}^{3+} \quad \text{Mn}^{4+} \quad \text{Mn}^{3+} \]

Insulator

\[ \text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \]

- XAS evidence of I-M transition, DOS spectral weight transferred to absorption threshold
- Mn-3d/O-2p hybridization
- Modification of 10Dq crystal field splitting

\[ \alpha \text{ (a.u.)} \]

\[ \Delta \alpha/\alpha \]

\[ \text{Energy (eV)} \]

\[ \text{Delay (ps)} \]

\[ 530 \quad 531 \quad 532 \quad 533 \quad 534 \quad 535 \quad 536 \]

\[ 0.00 \quad 0.02 \quad 0.04 \quad 0.06 \quad 0.08 \]

\[ -0.02 \quad -0.01 \quad 0.00 \quad 0.01 \quad 0.02 \]

\[ \text{PROBE: 532 eV} \]

\[ \text{FWHM: 65 ps} \]
**Photoinduced XAS Changes - Evidence of IM Transition**

**Photo-induced vs. Thermally-induced Phase Transition:**

The DOS change in the conduction band appears in the O 1s XAS spectrum and spectral weight is transferred to the absorption threshold.

**PHOTOINDUCED:**

![Graph showing photoinduced transition](image1)

**THERMALLY INDUCED:**

![Graph showing thermally induced transition](image2)

XANES experiments on the thermally-induced IM phase transition
Summary

Structural Dynamics in Solvated Transition-Metal Complexes

*Ligand field coupling between molecular structure and electronic properties*

- spin-crossover transition – Fe(II) complex – EXAFS, Fe K-edge (atomic structure)
  - atomic/molecular dynamics – EXAFS (0.2 Å change in ligand bond within 70 ps)
- spin-crossover – Fe(II) – XANES, Fe L-edge (electronic structure)
  - electronic structural dynamics – Fe L-edge XANES
  - ~0.55 eV reduction in 10Dq

Structural Dynamics in Colossal Magnetoiresistive (CMR) Manganites

*THz vibrational control of correlated electron phases – tolerance factor*

- ultrafast photo- and vibrationally-induced insulator-metal transition in Pr$_{1-x}$Ca$_x$MnO$_3$
  - targeting specific vibrational modes - Mn-O stretch, modulation of the tolerance factor
- electronic structure – time-resolved XANES (O K-edge, Mn L-edge)
  - changes in DOS spectrum – ultrafast insulator-metal transition