WATCHING THE ULTRAFAST – ULTRASMALL WORLD WITH PUMP-PROBE X-RAY EXPERIMENTS

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X-ray Neutron Summer School, Argonne National Laboratory, 26 July 2018
STOP-ACTION PHOTOS IN “DAILY” LIFE

Xu, Zhang, Nagel, PRL 94, 184505 (2005)
Splashing on Dry Smooth Surface

Lei Xu, Wendy W. Zhang, Sidney R. Nagel

University of Chicago
SEE THE ATOMS AND ELECTRONS MOVE

Chemical reactions in solution

Photosystem II

Light-induced superconductivity
for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy

“Immeasurably fast reactions”

“Flash photolysis”

Manfred Eigen

Ronald George Wreyford Norrish

George Porter

Pressure
Electric field
Temperature
NOBEL PRIZE CHEMISTRY 1999

for his studies of the transition states of chemical reactions using femtoscond spectroscopy

Ahmed Zewail

Kinetics to Dynamics

- Coherent excitation
- Localized wavepacket formation
- ~“single molecule trajectory”

Femtosecond real-time probing of reactions

Demonstrate wavepacket formation in molecular systems!
ICN$^*$ → I•••CN$^{*+} →$ I ($^2P_{3/2}$) + CN ($^2\Sigma^+$) + $E_{tr}$

M. Dantos et al., JCP 84, 2395 (1987).
S.O. Williams & D. Imre, JPC 92, 6648 (1988)
M. Rosker, M. Dantos, Zewail JCP 89,6113 (1988)

Pump: 308 nm
Probe: 388-390 nm
Probing rxn dynamics on multiple surfaces

\[ \text{NaI}^* \rightarrow \text{Na} + \text{I} \rightarrow \text{Na}^+ + \text{I}^- \]

- Vary the probe wavelength to view dynamics of dissociation at different positions along the reaction coordinate (R).
- Detect resonance motion between ionic and covalent forms
- Timescales for reaction and wavepacket spreading (initial localization to ~0.1Å)
- Establish concept of single molecule trajectories
Pump-probe time-domain spectroscopy

Vibrational and rotational wavepacket recurrences yield molecular parameters through Fourier Transform of time domain data

- Wavepacket w/ two vibrational states
- Anharmonicity causes beating
  - $\nu = 3.3$ THz, (13.5 meV)
  - $\Delta \nu = 0.1$ THz, (0.41 meV)

But ….

optical domain ultrafast pump/probe spectroscopies
do not provide direct structural information
do not reach the electronic timescale
REVOLUTION IN ULTRASHORT X-RAY PULSES

High harmonic generation

Accelerator-based sources

$10^5$ x-rays/pulse/1% BW @ 1 keV
~1 fs
Current world record ~ 50 as

$10^{13}$ x-rays/pulse/1% BW @ 1 keV
~100 fs
Current record ~ 200 as
THE PUMP-PROBE CONCEPT – USING X-RAYS

Mapping valence electron rearrangements during chemical rxns

Ph. Wernet, PCCP (2011)
X-RAY SPECTROSCOPIC PROBES

All can be used in the time domain to track dynamics

- Photoelectron spectroscopy
  - binding energies (UPS,XPS)
  - prompt response
- Absorption spectroscopy
  - unoccupied orbitals (XANES)
  - local structure (EXAFS)
- Emission spectroscopy (XES)
  - occupied orbitals
  - spin-state sensitivity
- RIXS
  - spectroscopy w/o core-hole broadening
Orbital time 1s electron in hydrogen atom: 150 as
\[ T_{\text{orb}} = \frac{2\pi a_0}{(\alpha c)} \left[ \frac{n^3}{Z^2} \right] \]

Vibrational period in \( H_2 \) : 4160 cm\(^{-1} \) \( \sim \) 8 fs
\[ T_{\text{vib}} = 2\pi(\mu/k)^{1/2} \]

Rotational period in \( H_2 \) : 60 cm\(^{-1} \) \( \sim \) 0.55 ps
\[ T_{\text{rot}} = 2B_e = \frac{\hbar}{(2\pi)^2 \mu R_e^2} \]
Fundamental timescales in condensed matter

- Can we understand emergent phenomena (high Tc superconductivity, colossal magnetoresistance…) in systems with strongly interacting degrees of freedom?
- Can we control material properties in correlated systems
  - light, fields, pressure, composition…

Coupled degrees of freedom
Time domain x-ray spectroscopies provide access to low energy collective excitations

Spin orbit, phonon, magnons…

$\Delta E = 1\text{–}100 \text{ meV}$
$T \sim 4000 \text{ – } 40 \text{ fs}$

$S(q,t)$ rather than $S(q,\omega)$
Time-domain phonon spectroscopy

X-ray diffuse scattering

- $\Delta I(t)$ for different momentum xfers (pixels) oscillates with phonon frequency
- Phonon dispersion obtained from Fourier transform of $\Delta I(t)$
- Access to very low energy modes w/ fs pulses

Transform-limited Gaussian pulse
$\Delta E \Delta T \sim 1.8 \text{ eV fs}$ (FWHM)

M. Trigo et al., Nat. Phys. 9, 790 (2013)
Chemical systems exhibit complicated photoexcited state potential energy landscapes. 4d, 5d vs 3d transition metals complexes of interest for solar energy.

Ponseca ... Sundstrom, Chem Rev 117,10940 (2017)
OUTLINE – FOUR EXAMPLES

- Watching chemical reactions in solution
  - Laser-pump / x-ray probe spectroscopies (TR-RIXS)

- Elucidating the oxygen evolution mechanism in Photosystem II
  - Laser-pump / x-ray probe diffraction and spectroscopy

- Emergent superconductivity
  - Laser-pump / x-ray probe diffraction plus laser-pump / UV probe-photoemission

- Inner-shell electronic dynamics
  - X-ray pump / x-ray probe recoil ion spectroscopy
Example 1: watching chemical reactions in solution

LETTER

Orbital-specific mapping of the ligand exchange dynamics of Fe(CO)$_5$ in solution

Ph. Wernet$^1$, K. Kunnus$^{1,2}$, I. Joseffson$^3$, I. Rajkovic$^4$$^\dagger$, W. Quevedo$^4$$^\dagger$, M. Beye$^1$, S. Schreck$^{1,2}$, S. Grübels$^4$$^\dagger$, M. Scholz$^4$, D. Nordlund$^5$, W. Zhang$^6$$^\dagger$, R. W. Hartsock$^6$, W. F. Schlotter$^7$, J. J. Turner$^7$, B. Kennedy$^8$$^\dagger$, F. Hennies$^8$, F. M. F. de Groot$^9$, K. J. Gaffney$^8$, S. Techert$^{4,10,11}$, M. Odellus$^3$ & A. Föhlisch$^{1,2}$
A classic light-induced chemical reaction in soln

Photoexcitation @ 295 nm: \( \text{Fe(CO)}_5 \rightarrow \text{Fe(CO)}_4 + \text{CO} \)

Study w/ UV pump/IR probe transient absorption
- singlet v triplet reactivity (spin barrier?)
- establish timescale for rxn (~40 ps MeOH)
- no evidence of singlet

P.T. Snee et al., JACS 123, 6909 (2001)
P.T. Snee et al., JACS 123, 2255 (2001)
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Revisit with x-rays focused on metal-ctr orbitals

Photoexcitation @ 266 nm: Fe(CO)$_5$ $\rightarrow$ Fe(CO)$_4$ + CO

Valence molecular orbital diagram of Fe(CO)$_5$

K. Kunnus et al., Struct Dyn (2016)
FeCO$_5$ photochemistry in solution - ethanol

The primary species involved

Fe(CO)$_5$ $^1A_1$'

Fe(CO)$_4$ $^1B_2$

Fe(CO)$_4$-EtOH $^1A'$

Fe(CO)$_4$ $^3B_2$
RIXS probes orbital evolution during Fe(CO)$_5$ ligand exchange

Excite 2p $\rightarrow$ LUMO and via IXS monitor the $d_{\pi} \rightarrow d_{\sigma^*}$ Fe-centered frontier orbitals on fs timescale

More quantitative analysis of TR-RIXS data

Experimental data

Ab initio Fe L₃ RIXS for relevant species

Deduced kinetic model for ligand exchange

Three component model: Excited Singlet, Triplet and Ligated Fe(CO)₄

Summary
- Primary rxn steps involve singlet in soln as in gas phase
- Sub-ps ISC to triplet
- Triplet persistent to 3 ps – Competing channels of spin-crossover and ligation

TR-RIXS provides capability to correlate orbital symmetry with spin multiplicity and reactivity

Expt’l details: RIXS orbital specific mapping of ligand exchange

Fe(CO)$_5$ in ethanol solution, 1 M, 20 µm jet

Laser pump:
4.66 eV (266 nm)
5 µJ, 100 fs, 100x400 µm$^2$

X-ray probe:
703-715 eV, dE = 0.5 eV
1.6x10$^{10}$ photons/pulse
20 x 300 µm$^2$

RIXS resolution
0.7 eV incident
1.2 eV energy transfer

Mn-based catalysts for CO$_2$ reduction

Understanding photodegradation mechanisms in order to make inexpensive and earth-abundant catalysts – x-ray spectroscopy probes mechanism over wide timescales

- Reduction of CO$_2$ to CO provides a promising source of renewable fuels and chemical feedstock
- Rhenium tricarbonyl complexes are efficient and stable catalysts, but too toxic and expensive for large-scale applications
- Manganese analogues are promising alternatives but suffer photodegradation that must be overcome

C. Elles and J. Blakemore (U Kansas)
A.M. March and G. Doumy (ANL)

Photosystem II – structure and mechanism

Slides courtesy Junko Yano
Water oxidation reaction in photosystem II

2 \( \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \)

- Where and how the O-O bond formation occurs?
- How substrate water comes in?
- How the protein environment modulates the catalytic reaction?
Understanding the mechanism of the water oxidation reaction in Photosystem II

Status prior to XFEL experiments:
• High-resolution crystal structure of the dark (S\textsubscript{1}) state.
• Information from various advanced spectroscopies (EPR, IR, Optical, and X-ray) of the stable S (S\textsubscript{1}, S\textsubscript{2}, S\textsubscript{3}, and S\textsubscript{0})-states at cryo. temp. that predict possible structure and electronic structure of those states.
• Proposed water oxidation mechanisms from theoretical studies.

Gaps:
• Requires high-resolution room temperature structure of each S-state as well as time-points during the transitions.
• Capability (methods) for interpreting structural information together with spectroscopic data.
• Charge/spin localization/delocalization between metals and ligands during the catalytic cycle.
• Theoretical capabilities to simulate detailed electronic structures, in particular, for multinuclear complexes, and at room temperature.
Simultaneous x-ray crystallography and spectroscopy at RT

- **X-ray diffraction** (protein structure)
- **X-ray emission spectroscopy** (catalytic center)

Alonso-Mori et al., (2012) RSI
Alonso-Mori et al., (2012) PNAS
Kern et al., (2012) PNAS
Kern et al., (2013) Science
High resolution structure of OEC in light activated state!

Enabled by improved sample delivery and data collection efficiency

Structure of the oxygen evolving Mn$_4$Ca complex in photosystem II in the S1 and S3 state at RT to 2.25 Å.

Future Outlook

- High-resolution data collection of the **transient states** to understand the **sequence of events** and the role of **protein dynamics** that enable the multielectron catalysis.

- Application of metal L-edge XAS and RIXS to understand the evolution of the Mn electronic structure at room temperature.

- High rep. rate of LCLS-II realizes some of the photon-hungry spectroscopy of dilute protein samples.

Courtesy J. Yano

Kubin et al. (2017)
Structural Dynamics
Condensed matter and materials
Excitations in strongly correlated materials

D. Basov et al, RMP 83, 471 (2011)
Combining TR-XRD + TR-ARPES yields orbitally-resolved electron-phonon coupling

Provides quantitative guidance for many-body theory

- Single mode response of $A_{1g}$ optical phonon allows “lock-in” of two separate time-resolved measurements
- Diffraction $\rightarrow$ atomic displacement
  ARPES $\rightarrow$ band structure $d_{xz/yz}$ and $d_{z^2}$
- Determination of potential seen by Fe electrons due to Se anion movement
- Measured value is an order of magnitude larger than DFT result $\rightarrow$ theory guidance

Gerber et al., Science 357, 71 (2017)
Light activated domain dynamics in ferroelectrics

APS: Nanofocused x-ray beam circumvents spatial averaging to reveal emergent phenomena on the mesoscale

- Domain-dependent gigahertz acoustic wave
- Photoinduced large surface electric field
- Derived domain wall speed of 2.5 m/s

7ID-C@APS

X-ray beam size: 400 nm
X-ray pulse duration: 100 ps

X-ray pump / x-ray probe studies

watching & controlling inner-shell electron motion
understanding radiation damage
X-ray pump/x-ray probe capabilities at LCLS

One e-bunch – two x-pulse – two color (Lutman et al., PRL 110, 134801 (2013))

Two e-bunch – two x-pulse – two color (Marinelli et al., Nat. Comm. 6, 6369 (2015))

Fresh-slice multicolor (Lutman et al., Nat. Photon. 10, 745 (2016))
Motivation: inner-shell vacancies initiate radiation damage

Radiation damage limits resolution in x-ray imaging applications
Localized damage can be used for therapies [Gohkberg..Cederbaum Nature (2015)]

Single K-shell vacancy in Xe can create Xe$^{8+}$
Cascade happens on tens of fs timescale
What happens in “complex” environment?

XeF$_2$

- Higher charge in molecule vs atom
- Evidence for “Interatomic Coulombic Decay”

R.W. Dunford et al., PRA 86, 033401 (2012)
TIME-RESOLVED X-RAY SPECTROSCOPY OF XeF₂

Early two-color SASE x-ray pump/probe: Lutman PRL (2013) scheme

Monitor competition
Auger decay
Charge redistribution
Coulomb Explosion

- Pump: 690 eV
  Xe 3d → εf shape resonance
- Probe: 683 eV
  F⁺, F²⁺ 1s → 2p
- 10-fs pulses
- Δt = 4, 29, 54 fs
- 33 µJ combined pulse energy
- 20% optics efficiency
- 5 µm² focal spot
- 1.3 x 10¹⁶ W/cm² peak intensity

THE $F^{2+}$ $Xe^{q+}$ $F^{3+}$ BREAKUP CHANNEL

Time-dependent dynamics manifest in recoil ion energies

- KERs modeled w/classical eqns of motion & Coulomb forces consistent w/observations
- KER is a ruler for internuclear distance
- 600,000 x-ray shots .... 800 $F^{2+}$ - $Xe^{q+}$ - $F^{3+}$ coincidences

Static + pump/probe KER observed
Outlook is bright for molecular movies

- Multiple timescales contain interesting scientific problems in chemistry, biology, materials science.

- For the nanoscale, mesoscale phenomena the picosecond - microsecond timescale and nanofocusing available at synchrotrons is ideal

- For atomic-scale phenomena the attosecond – femtosecond timescales available at XFELs is becoming more readily available with multiple XFELs just coming online.
Ultra-Small

Nature
- Flea
- Human hair ~30 um wide
- Red blood cells & white cell ~5um
- Virus ~200 nm
- DNA helix ~3 nm width
- Water molecule
- Atom

Technology
- Head of a pin ~1mm
- Micro gears 10-100 um diameter
- DVD track
- 1 um Electrodes connected with nanotubes
- Carbon nanotube ~2nm diameter
- Atomic corral ~14 nm diameter

Ultra-Fast

Nature
- Hydrogen transfer time in molecules is ~1ns
- Spin processes in 1 Tesla field is 10 ps
- Shock wave propagates by 1 atom in ~100 fs
- Water dissociates in ~10 fs
- Light travels 1 um in 3 fs
- Bohr period of valence electron is ~1 fs

Technology
- Computing time per bit is ~1 ns
- Optical network switching time per bit is ~100 ps
- Magnetic recording time per bit is ~2 ns
- Laser pulsed current switch ~1 ps
- Shortest laser pulse is ~1 fs
- Oscillation period of visible light is ~1 fs

LCLS website circa 2009
SEE THE ATOMS AND ELECTRONS MOVE

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