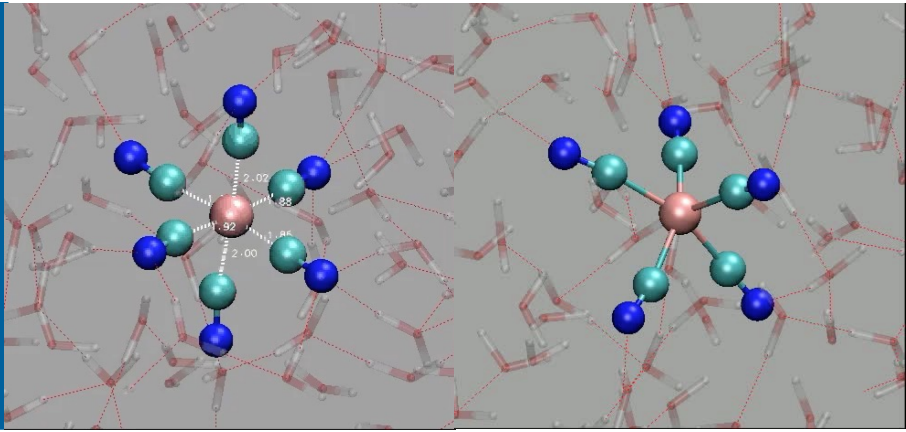
Probing Ultrafast Dynamics with X-rays



ANNE MARIE MARCH
Physicist
AMO Physics Group
Chemical Science and Engineering Division
Argonne National Laboratory

August 16, 2023
NX Summer School

U.S. DEPARTMENT OF ENERGY
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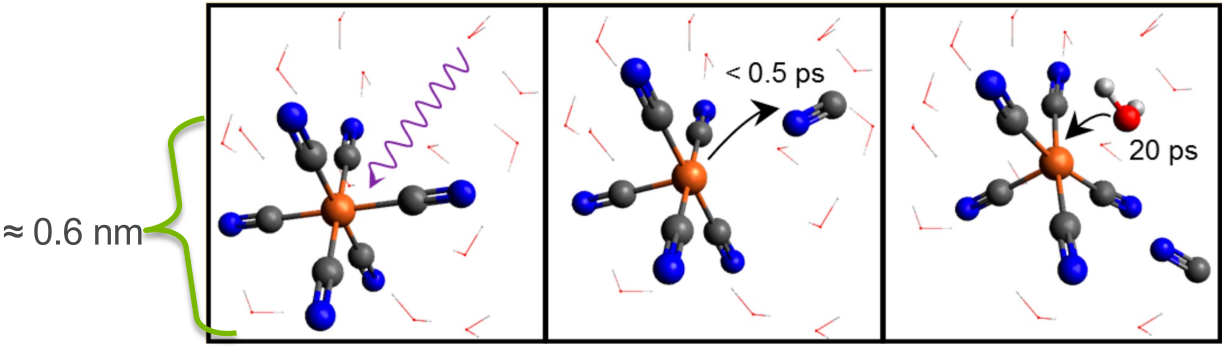
My research interests: ‘Seeing’ how molecules react after absorbing light

What happens after $[Fe(CN)_6]^{4-}$ (dissolved in water) absorbs light?



M. Reinhard *et al.* JACS **139**, 7335 (2017)

very small length scales
1 nanometer
10^{-9} m
0.000000001 m

very short time scales
<20 picoseconds
20 x 10^{-12} s
0.000000000020 s

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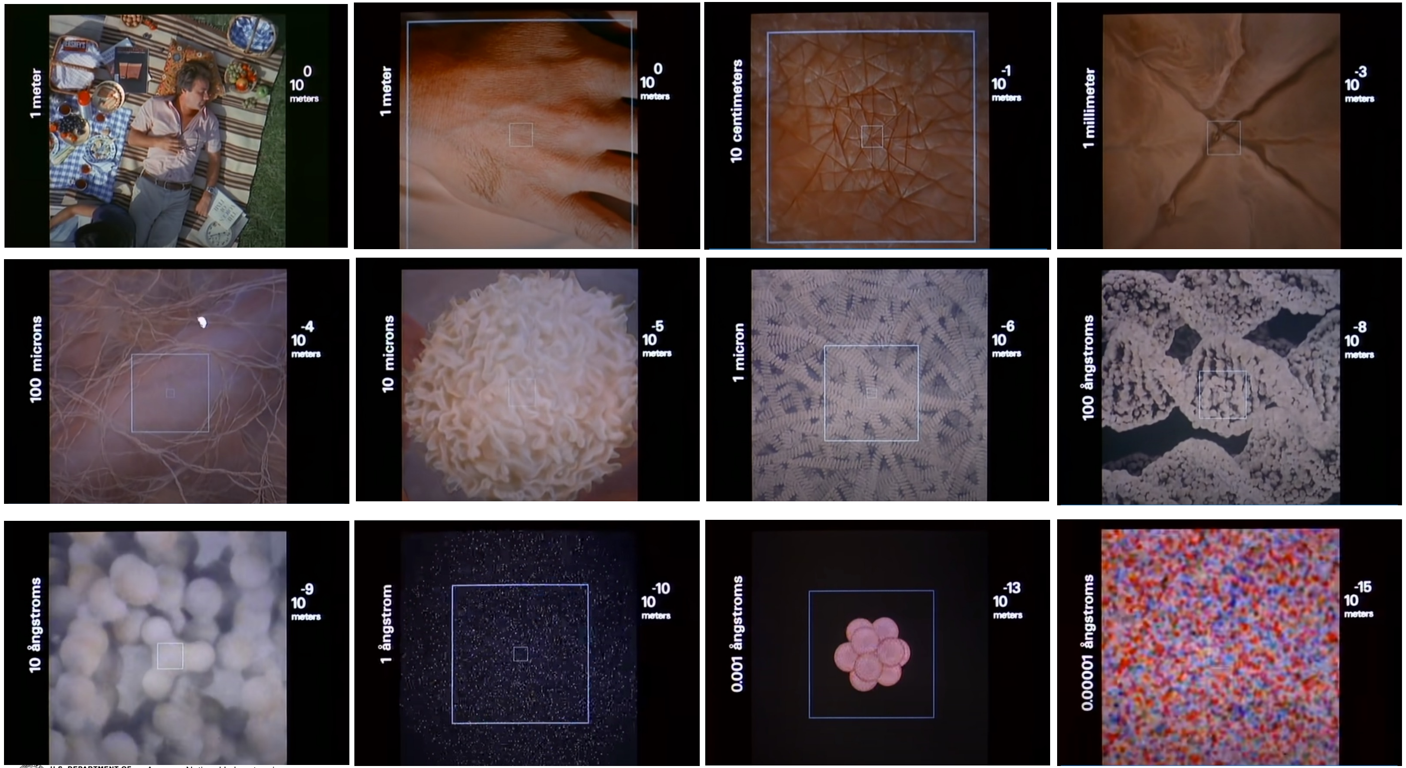
Legendary film “Powers of Ten”

by Charles and Ray Eames (1977)

a journey through the vast spatial dimension of the universe




© 2013 Eames Office, LLC (eamesoffice.com)

https://www.youtube.com/watch?v=0fKBhvDjuy0

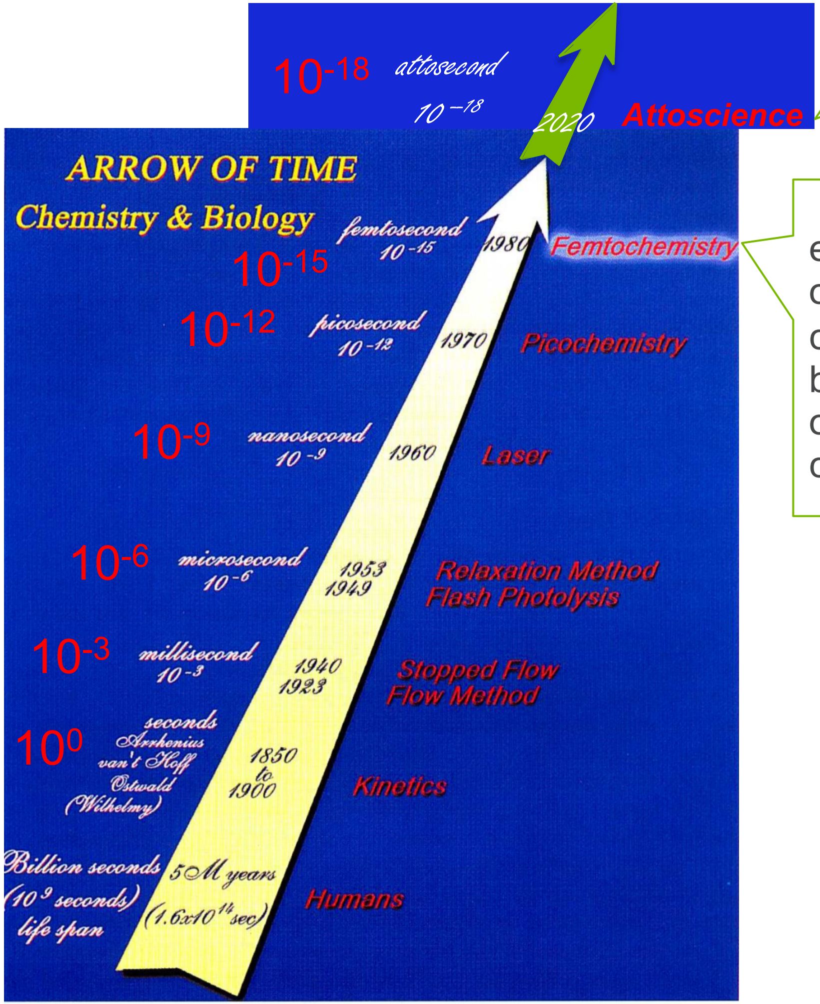
Watch the zoom-in portion of film

What about time?

(a laser physicist's/chemist's perspective)

Ahmed Zewail, 1999 Nobel Prize in Chemistry
"for his studies of the transition states of chemical reactions using femtosecond spectroscopy"

figure from his Nobel lecture



electron dynamics

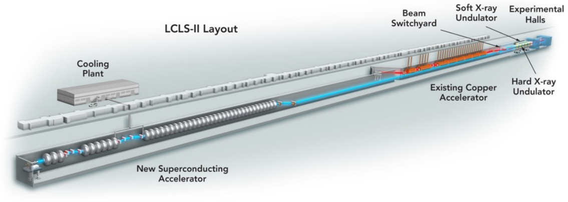
enabled observations of chemical bonds breaking, forming, or geometrically changing

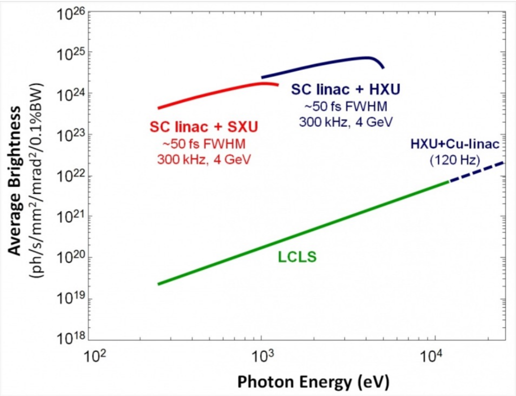
Exciting upgrades of x-ray facilities

We're entering a new era in x-ray science: exploration across a huge range of timescales!

LCLS-II

increased brightness and repetition rate

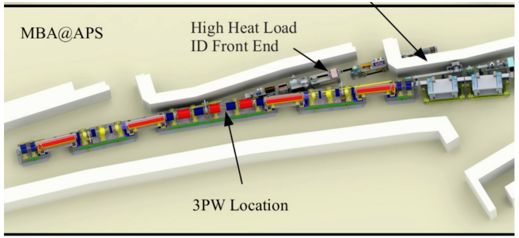


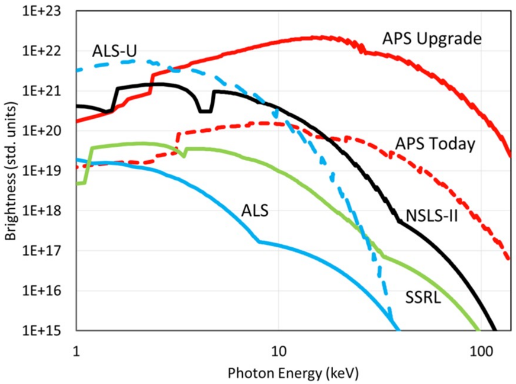


as fs ps

APS-U

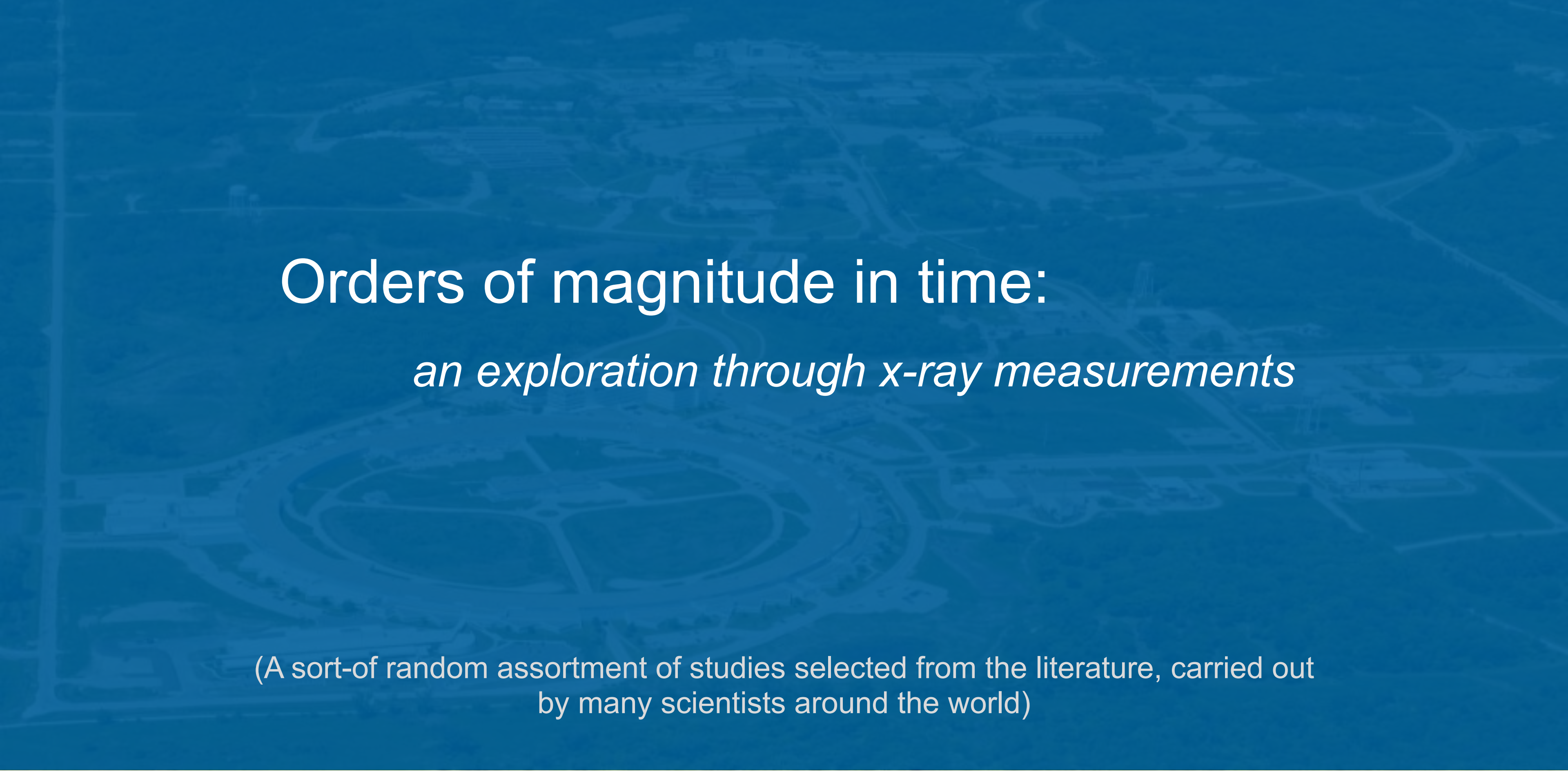
increased brightness and coherence





10's ps ns µs ms s

time



Orders of magnitude in time:

an exploration through x-ray measurements

(A sort-of random assortment of studies selected from the literature, carried out by many scientists around the world)

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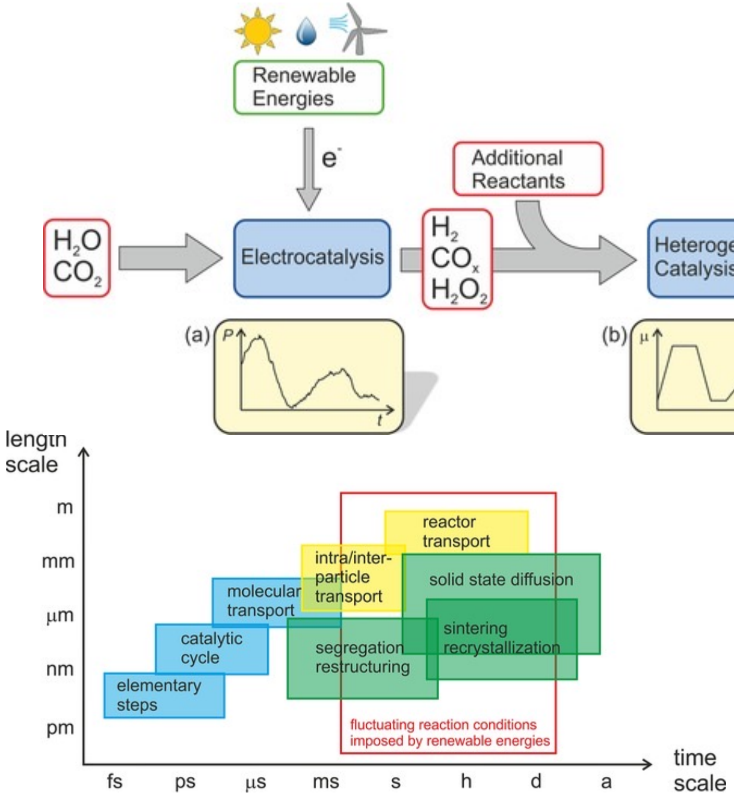
Scientific Problem: Future Challenges in Catalysis

10^0
seconds

Understanding Heterogenous Catalysts under Dynamic Reaction Conditions



For a world entirely based on renewable energies, we will need chemical and electrochemical catalysts more tolerant against an alternating supply of energy and raw materials

K. F. Kalz *et al.*, *ChemCatChem* **2017**

https://doi.org/10.1002/cctc.201600996

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Example: Spatiotemporal Operando XAS

To understand the ignition process of the catalytic partial oxidation of methane

10^0

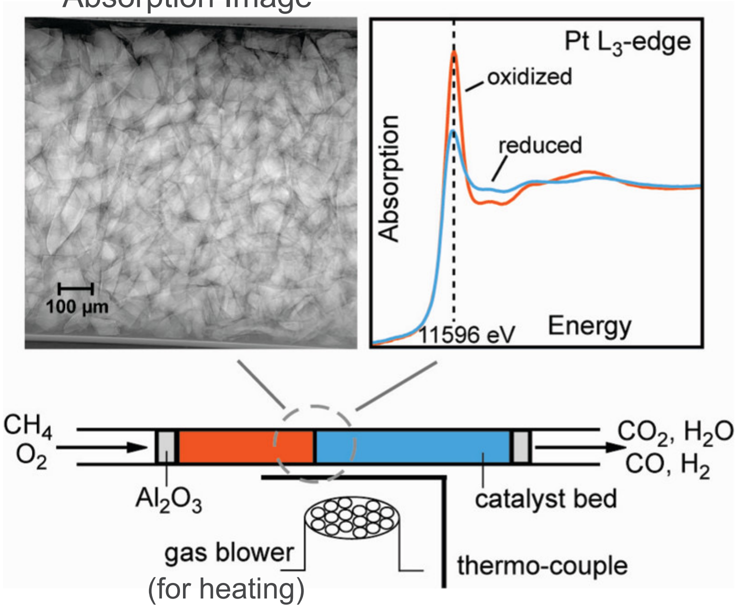
seconds

Kimmerle *et al.*, *J. Phys. Chem. C* 2009

https://doi.org/10.1021/jp810319v

Corresponding author:
Prof. Dr. Jan-Dierk Grunwaldt

Transmission X-ray Absorption Image



- conversion of hydrocarbons to CO and H_2
- full field XAS microscopy to track oxidation state of the Pt species as a function of time while reactor is heated
- X-rays: 11596 eV (Pt L_3 edge)

Example: Spatiotemporal Operando XAS

To understand the ignition process of the catalytic partial oxidation of methane

10^0
seconds

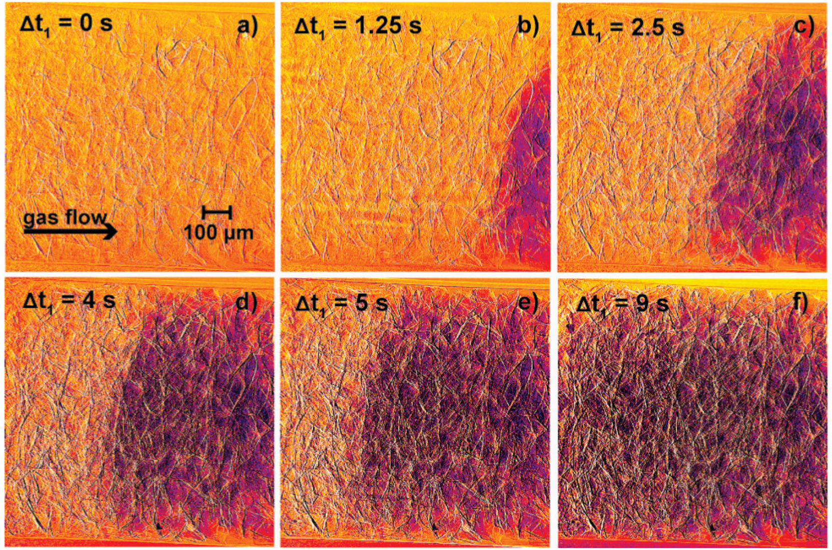
Kimmerle *et al., J. Phys. Chem. C* 2009

https://doi.org/10.1021/jp810319v

Corresponding author:
Prof. Dr. Jan-Dierk Grunwaldt

Karlsruhe Institute of Technology

Transmission X-ray Absorption Images



- conversion of hydrocarbons to CO and H_2
- full field XAS microscopy to track oxidation state of the Pt species as a function of time while reactor is heated
- X-rays: 11596 eV (Pt L_3 edge)
- orange: more absorption (oxidized Pt-containing species)
- Dark red: less absorption (reduced Pt-containing species)

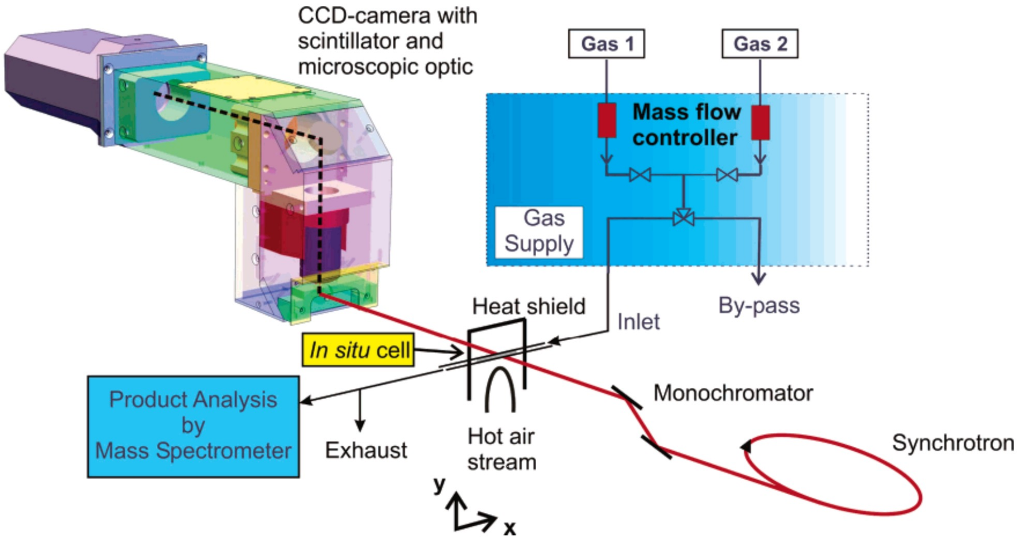
- reduction starts from end and moves toward the inlet

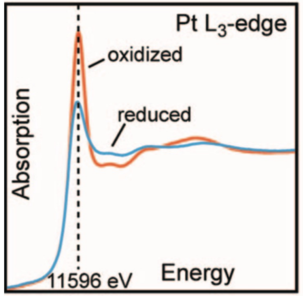
Go to movie (SI in paper)

Example: Spatiotemporal Operando XAS

10^0 seconds

Measurement details





ID26 at the ERSF

- fixed energy: 11596 eV
- 5×10^{12} ph/s, 1.7 eV bandwidth
- 1×1 mm^2 x-ray spot

- FReLoN (fast readout low noise camera, ESRF), ~kHz read out rate
- 4 images taken per second
- 0.5 µm spatial resolution

J.-D. Grunwaldt *et al*. J. Phys. Chem. B 2006

https://doi.org/10.1021/jp060371n

Scientific Problem: Looking to nature to inform design of new micromechanical devices

10^{-3} seconds

Dipteran flies (blowflies) are amongst the smallest and most agile of flying animals.

In one blink of the eye, the blowfly has beat its wings 50 times

The wingbeat is controlled by numerous tiny steering muscles that represent <3% of the total flight muscle mass

How do they modulate the output of much larger power muscles?

Fly With Metallic Blue - *Calliphora vicina*

Copyright © 2009 Mardon Erbland

High-speed 3D X-ray visualizations of the flight muscles of the blow fly

Time-resolved X-ray tomographic microscopy

10^{-3}
seconds

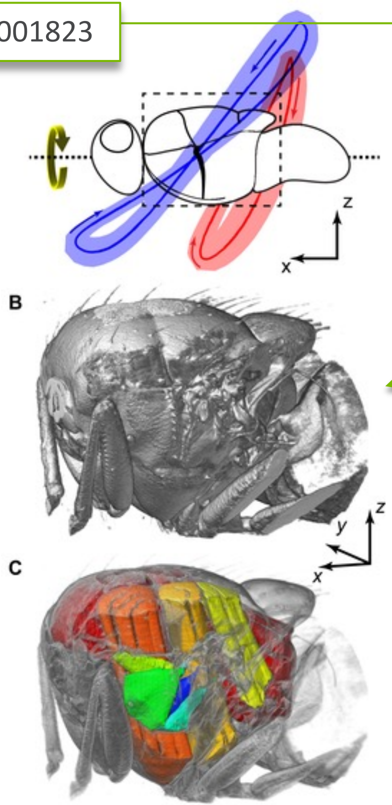
Walker SM, et al. (2014) PLoS Biol 12(3): e1001823

https://doi.org/10.1371/journal.pbio.1001823

Corresponding author:
Professor Graham Taylor

Department of
BIOLOGY

UNIVERSITY OF
OXFORD



Captured the dynamic internal mechanics of the blow fly wingbeat

External visualization of the fly's thorax

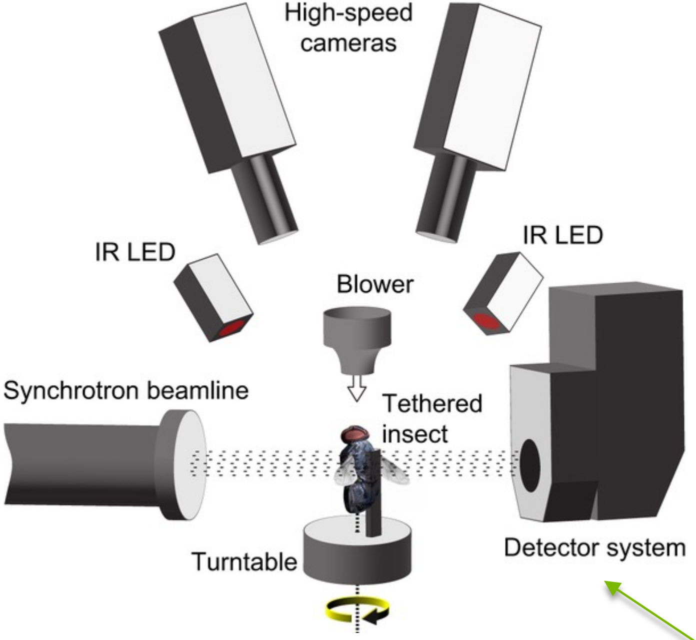
Cutaway visualization of the thorax showing the five steering muscles analyzed (green to blue) and the power muscles (yellow to red)

Go to movie

Time-resolved microtomographic imaging

Measurement details

10^{-3}
seconds



TOMCAT beamline of the Swiss Light Source

- tethered fly, 4 revolutions per recording
- x-ray images (i.e. radiographs) grouped according to the wingtip position, as captured by stereo high-speed photogrammetry
- tomograms reconstructed for 10 evenly spaced phases of the wingbeat
- each tomograms uses result from ~600 wingbeats and so represents an average state of the flight motor at each phase

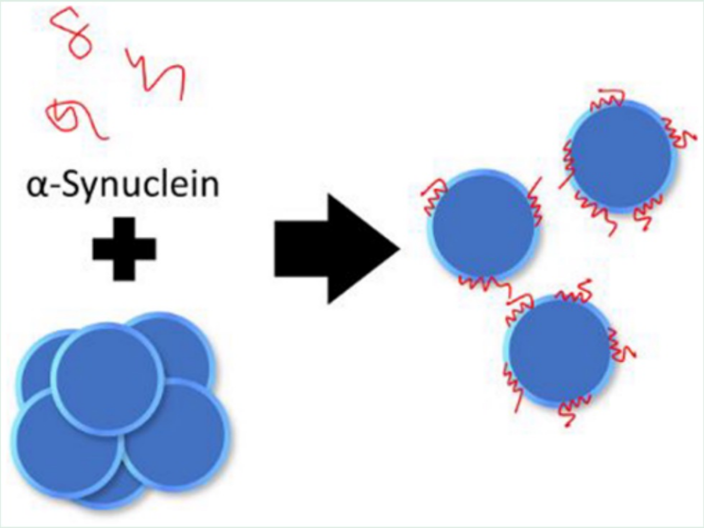
- Ce-doped LuAG scintillator converts x-ray to visible
- CMOS camera, kHz readout rate

Spatial resolution of ~3 μm
Temporal resolution of ~1 ms

https://doi.org/10.1371/journal.pbio.1001823

Scientific Problem: Following motion and force response in increasingly complex biological systems

10^{-6}
seconds



Ka Yee C. Lee *et al.* ACS Appl. Bio Mater. 2019, 2, 1413–1419

https://pubs.acs.org/doi/pdf/10.1021/acsabm.8b00774

- the neuronal protein **α**-synuclein is known to have a link to Parkinson’s disease
- it binds to highly curved and highly charged lipid membranes, but beyond binding, its biological function is unknown
- it has an intrinsically disordered nature making it challenging to study
- use spherical nanoparticle lipid bilayers (SSLBs) to mimic membranes of organelles
- Use XPCS and SAXS to understand how the addition of **α**-synuclein affects inter-organelle interactions (does it modulate interactions between membranes?)

X-ray Photon Correlation Spectroscopy

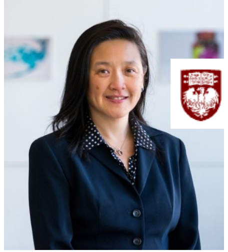
Needs coherent x-ray flux → APS-U revolutionizes technique!

10^{-6}
seconds

Ka Yee C. Lee *et al.* ACS Appl. Bio Mater. 2019

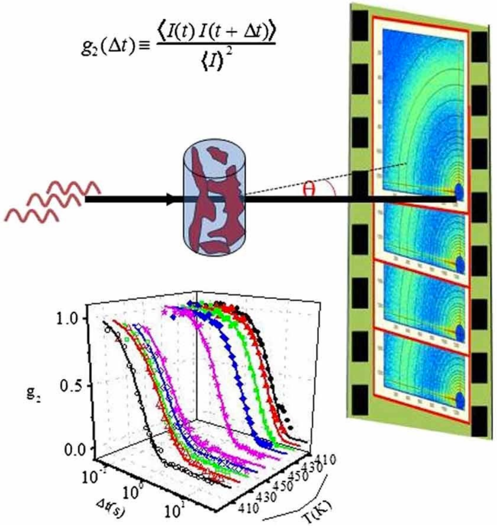
DOI: 10.1021/acsabm.8b00774

Corresponding author:
Prof. Ka Yee C. Lee



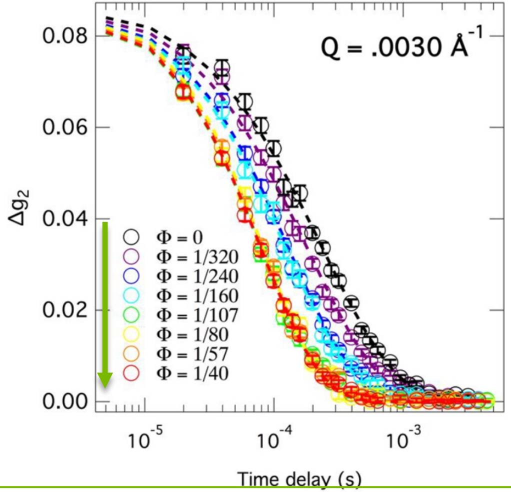
THE UNIVERSITY OF CHICAGO

XPCS basics



Review paper:
A. Nolgales, A. Fluerasu, Euro. Poly. J. (2016)
https://doi.org/10.1016/j.eurpolymj.2016.03.032

normalized intensity time autocorrelation function of SSLBs at a selected wavevector and as a function of added α-synuclein

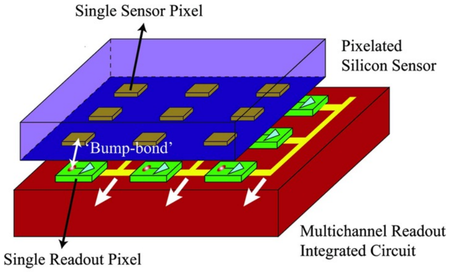


XPCS reveals increasing α-synuclein enhances diffusivity of the spherical nanoparticle lipid bilayers

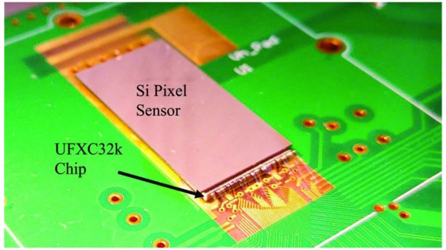
α-Synuclein Sterically Stabilizes Spherical Nanoparticle-Supported Lipid Bilayers

10^{-6}
seconds

Measurement details



(a)



(b)

- 10.91 keV, 4x10^{10} ph/s
- 4 µm (v) x 15 µm (h) x-ray spot
- fresh spot on sample, 4 s acquisition of images
- 300 acquisitions yield final autocorrelation function

8-ID APS

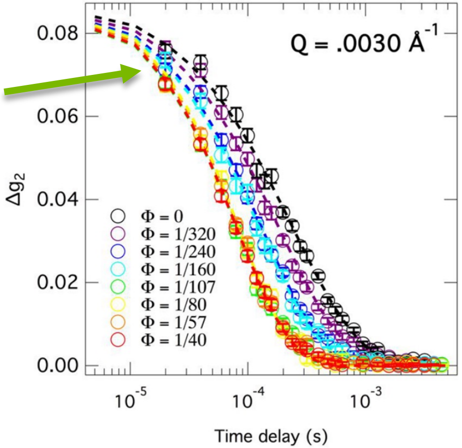
- custom 2D area detector, 50 kHz frame rate

  UFXC32k detector

  Q. Zhang *et al.*, J. Synch. Rad. 2016

  https://doi.org/10.1107/S1600577516005166

20 µs limit defined by frame rate of detector



https://pubs.acs.org/doi/pdf/10.1021/acsabm.8b00774

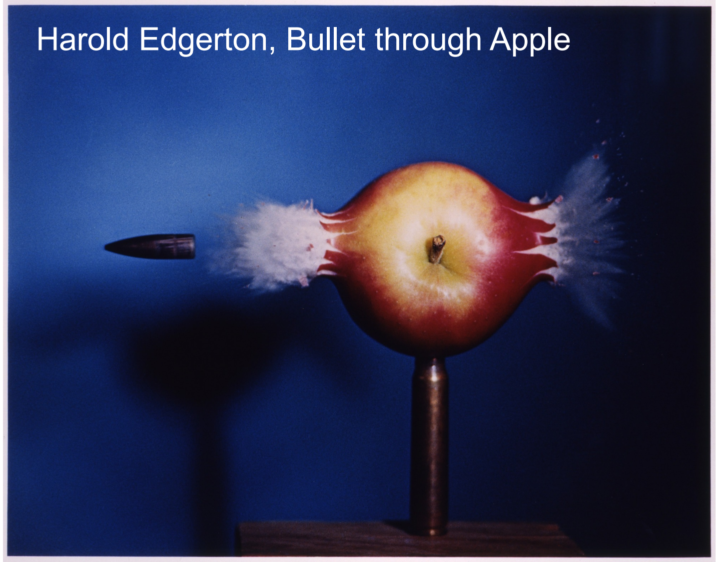
10^{-9}

seconds

We have now reached a temporal regime where our typical detectors are likely too slow to resolve what we want to observe

When your detector’s too slow: Pump-probe technique

Similar to stroboscopic flash photography


Harold Edgerton, Bullet through Apple

Camera’s shutter speed is too slow to capture motion

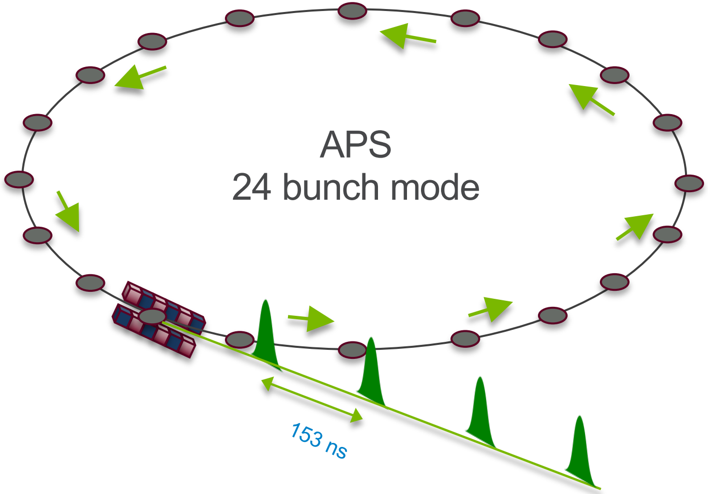
Flash duration is short enough

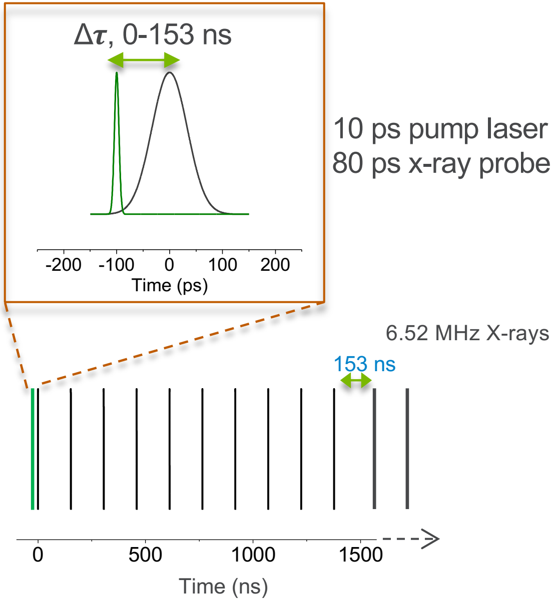
flash duration: ~300 ns

firing of gun	Camera flash	Camera sensor
↓	↓	↓
Laser pulse (initiates reaction)	X-ray pulse (80 ps)	X-ray detector

Laser-pump, synchrotron-x-ray-probe basics

temporal considerations



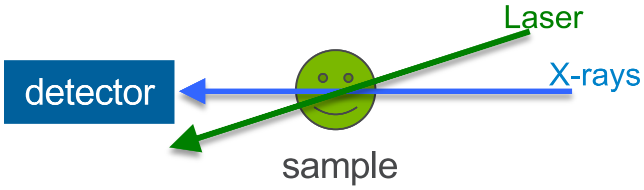


- need detectors that can isolate individual pulses (or groups of pulses)
- variable repetition rate pump laser to access different temporal regimes
- pump laser is temporally “locked” to the storage ring RF (352 MHz)
- control of laser delays with respect to the x-ray pulses is done electronically
- temporal jitter ~ few ps

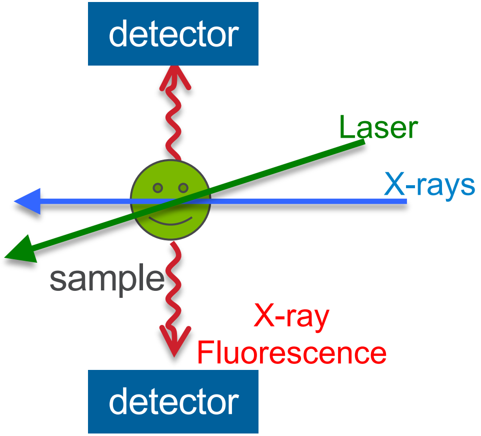
Laser-pump, synchrotron-x-ray-probe basics

spatial considerations

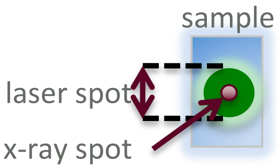
scattering, diffraction, imaging…



fluorescence detection (XAS)



- precisely overlap x-rays and laser at sample
- x-rays smaller than laser spot to probe volume with highest excitation fraction



- try to ensure even pumping and probing through probed sample volume
  - liquid samples – adjust concentration
  - solid samples – try grazing incidence

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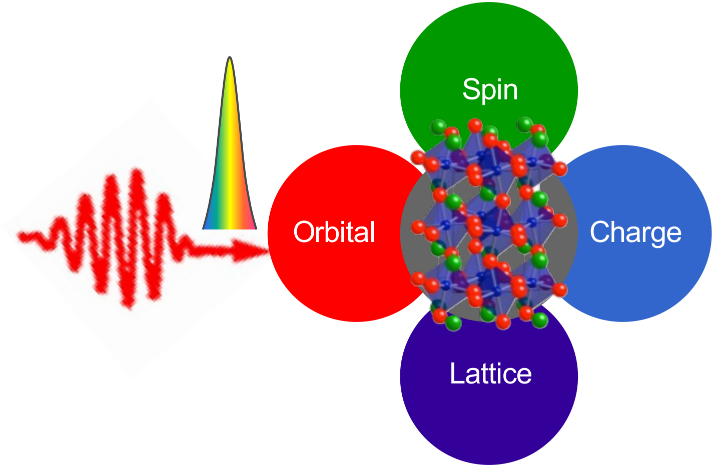
Scientific Problem: Understanding emergent phenomena in correlated materials

10^{-9}

seconds



- Interactions between electronic, spin, and structural degrees of freedom in correlated materials are the basis of emergent phenomena
- Hidden phases can be created by driving systems out of equilibrium
- Requires following several degrees of freedom simultaneously through multimodal measurements

Zhu, Y., Hoffman, J., Rowland, C.E. *et al. Nat Commun* **9,** 1799 (2018).   https://doi.org/10.1038/s41467-018-04199-4

Unconventional slowing down of electronic recovery in photoexcited charge-ordered $La_{1/3}Sr_{2/3}FeO_3$

pump-probe x-ray diffraction & optical reflectivity

10^{-9}

seconds

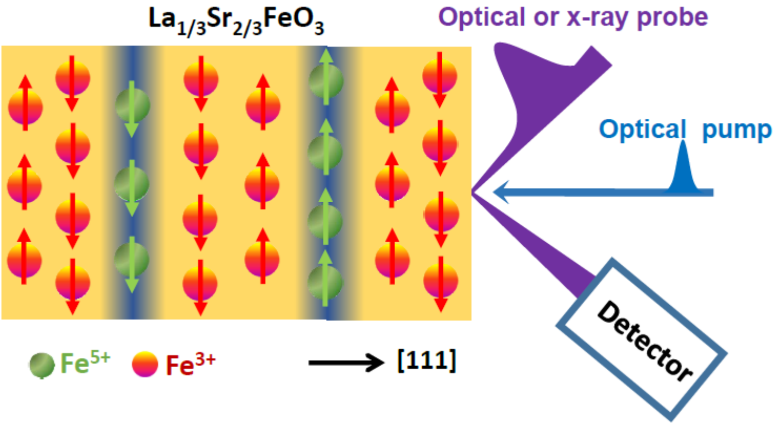
Yi Zhu *et al.*, *Nat Commun* **9,** 1799 (2018)

https://doi.org/10.1038/s41467-018-04199-4

Corresponding authors:

Anand Bhattacharya

Haidan Wen



- $La_{1/3}Sr_{2/3}FeO_3$ (a perovskite oxide)
- Below a critical temperature (200 K), exhibits charge ordering (along with a metal-insulator transition and paramagnetic to antiferromagnet transition)
- Disrupt the ordering with laser excitation and measure how long it takes to recover
- Transient optical probes show that near the critical temperature, recovery of the charge ordering following excitation becomes much slower than expected

Is this recovery decoupled from the lattice cooling?

Unconventional slowing down of electronic recovery in photoexcited charge-ordered $La_{1/3}Sr_{2/3}FeO_3$

pump-probe x-ray diffraction & optical reflectivity

10^{-9}
seconds

Nat Commun **9,** 1799 (2018)

https://doi.org/10.1038/s41467-018-04199-4

Corresponding authors:

Anand Bhattacharya

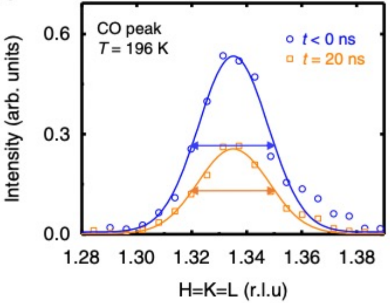
Haidan Wen

Measured intensities of 2 diffraction peaks as a function of pump-probe delay:

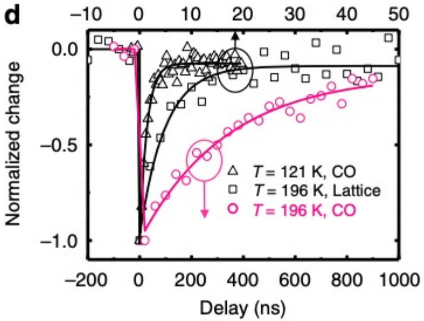
-One sensitive to charge ordering

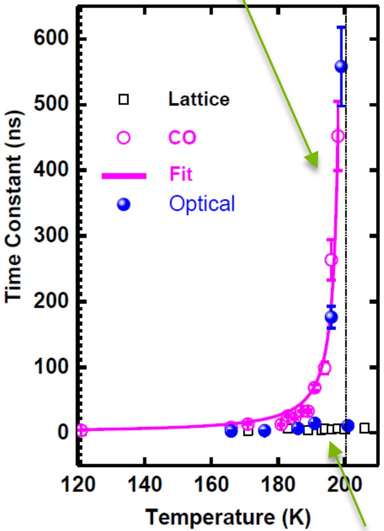
-The other sensitive to the lattice constant

Charge ordering diffraction peak



Peak intensity vs. p-p delay





Gets large

Stays small

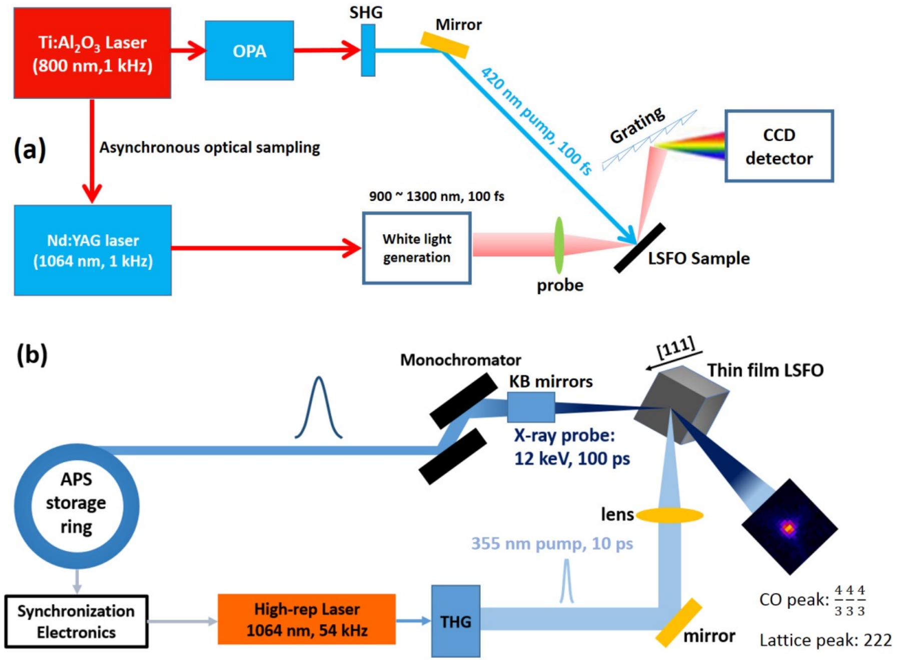
Charge order recovery *is* uncoupled to lattice cooling – First principles calculations point towards a magnetic interaction driven mechanism

Unconventional slowing of electronic recovery in $La_{1/3}Sr_{2/3}FeO_3$

Measurement details

10^{-9}

seconds



7-ID-C APS

Multimodal characterization:

- Optical reflection probes charge ordering
- High repetition rate optical pump crucial to observe small Charge ordering diffraction peak

Zhu, Y., Hoffman, J., Rowland, C.E. *et al. Nat Commun* **9,** 1799 (2018).

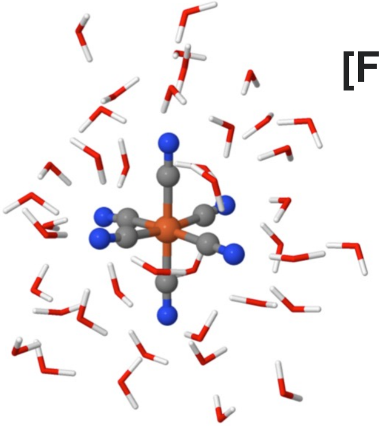
https://doi.org/10.1038/s41467-018-04199-4

Elucidating reaction mechanisms for photoexcited transition metal complexes in solution

10^{-12}
seconds

Fe hexacyanide in water

long-studied, but continues to intrigue and be investigated



$[Fe^{II}(CN)_6]^{4-}$

- small, highly charged ion – water "structure maker" Evan Williams *et al.* (Chem.Sci. 2017), Gerhard Schwaab *et al.* (Phys.Chem.Chem.Phys. 2017)
- environmental pollution Yunmei Wei *et al.* (Chemosphere 2020), Samir Fernando Castilla-Acevedo *et al.* (J. Environ. Chem. Eng. 2021)
- prebiotic chemistry of early Earth John Sutherland *et al.* (Chem.Commun. 2018)
- redox flow batteries T. Leo Liu *et al.* (Nano Energy 2017), J. Luo *et al.* (Joule 2019)
- thermogalvanic cells Leigh Aldous *et al.* Sustainable Energy Fuels 2020
- redox mediator for aqueous solar cells F.Bella, M.Grätzel et al. Chem.Soc.Rev. 2015
- Metal ion sorbents for radionuclide recovery T. Vincent *et al.* (Molecules 2015)
- model system for understanding information content of x-ray spectra

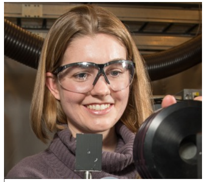
Elucidating reaction mechanisms for photoexcited transition metal complexes in solution

10^{-12}
seconds

A. M. March *et al.*, J. Chem. Phys. (2019)

https://doi.org/10.1063/1.5117318

Corresponding authors:


A.M. March


Niri Govind

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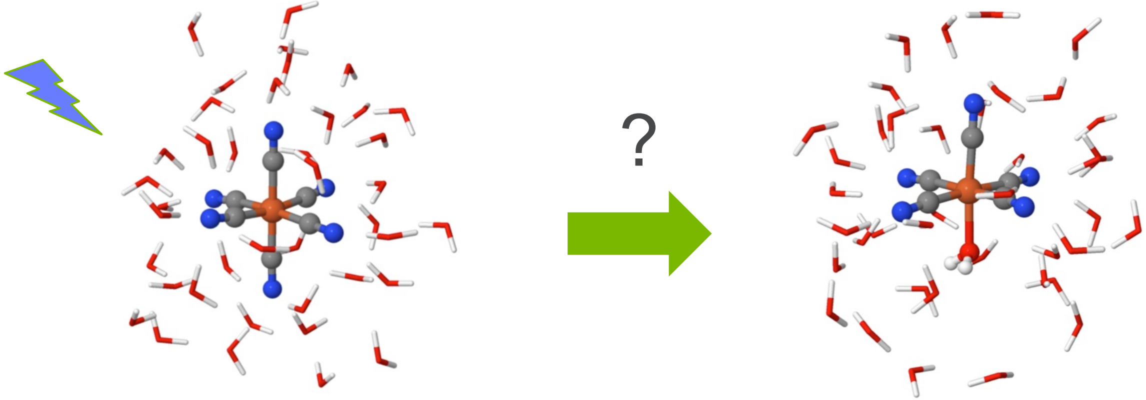
Pacific Northwest NATIONAL LABORATORY

Photoaquation reaction of aqueous $[Fe^{II}(CN)_6]^{4-}$

$$Fe^{II}(CN)_6^{4-} + h\nu \rightarrow Fe^{II}(CN)_6^{4-*} + H_2O \rightarrow Fe^{II}(CN)_5H_2O^{3-} + CN^-$$

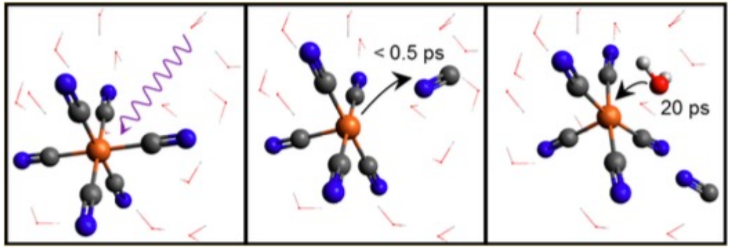


Ultrafast studies of the aquation reaction

10^{-12} seconds

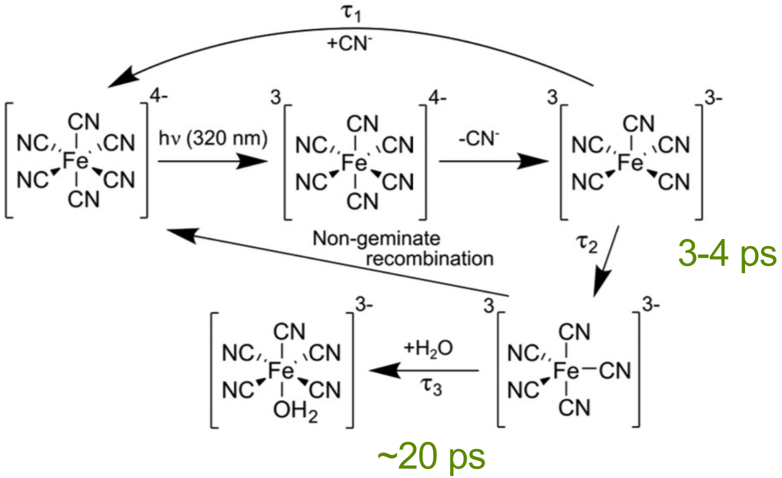
Chergui Group, EPFL, Switzerland

- 2D UV transient absorption spectroscopy
- UV pump/Visible probe transient absorption spectroscopy
- Time-resolved infrared transient absorption spectroscopy
- DFT
- laser-pump, X-ray-probe XAS



M. Reinhard *et al.* JACS **139**, 7335 (2017)
M. Reinhard *et al.* Struc. Dyn. **1**, 024901 (2014)
M. Chergui, Coord. Chem. Rev. **372**, 52 (2018)

Proposed reaction scheme



At APS can we capture the short-lived (20 ps) pentacoordinated intermediate species, determine its structure, and test the proposed reaction scheme?

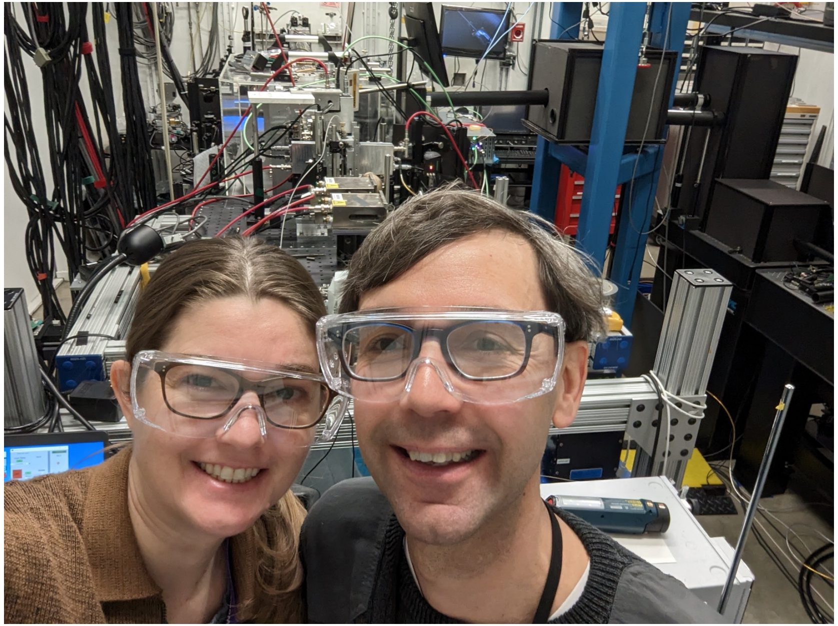
Laser-pump, x-ray-probe at 7ID-D

(presently being moved to the new 25-ID!)

10^{-12}

seconds

Photos from our last beamtime before the shutdown, March 2023



Laser-pump, x-ray-probe at 7ID-D

(presently being moved to the new 25-ID!)

10^{-12}

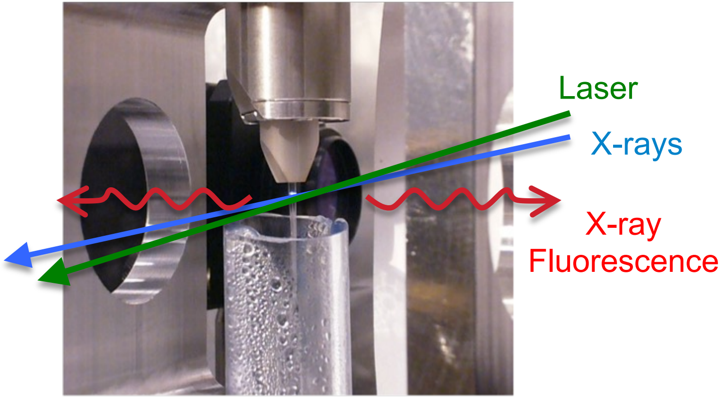
seconds

Photos from our last beamtime before the shutdown, March 2023

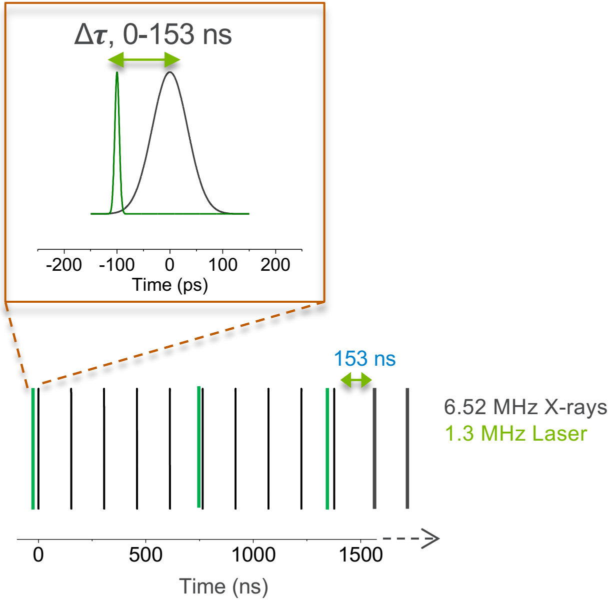
Laser-pump, x-ray-probe at 7ID-D

(presently being moved to the new 25-ID!)

10^{-12} seconds



- sample: fast flowing jet
- spatially and temporally overlap laser beam and x-rays at the jet



- electronic control of laser delay with respect to the x-ray pulses
- variable repetition rate pump laser

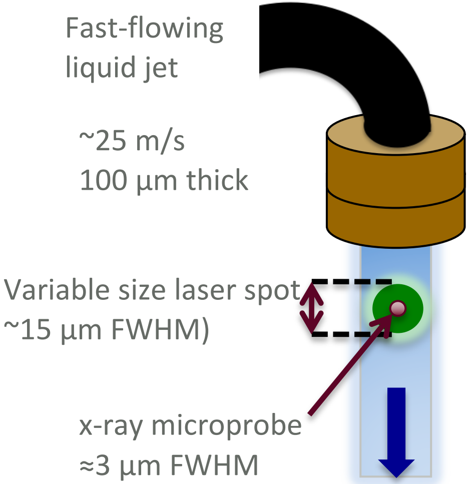
Go to other power point for ‘fancy’ animation

Technical considerations

- Need uniform pumping and probing through the thickness of the sample
  - drastically different absorption cross sections for x-rays (~kb) and optical light (~Mb)
  - Chose sample concentration that yields OD ~ 1 (pump absorption in sample is about 90%). This produces dilute samples for x-ray absorption.

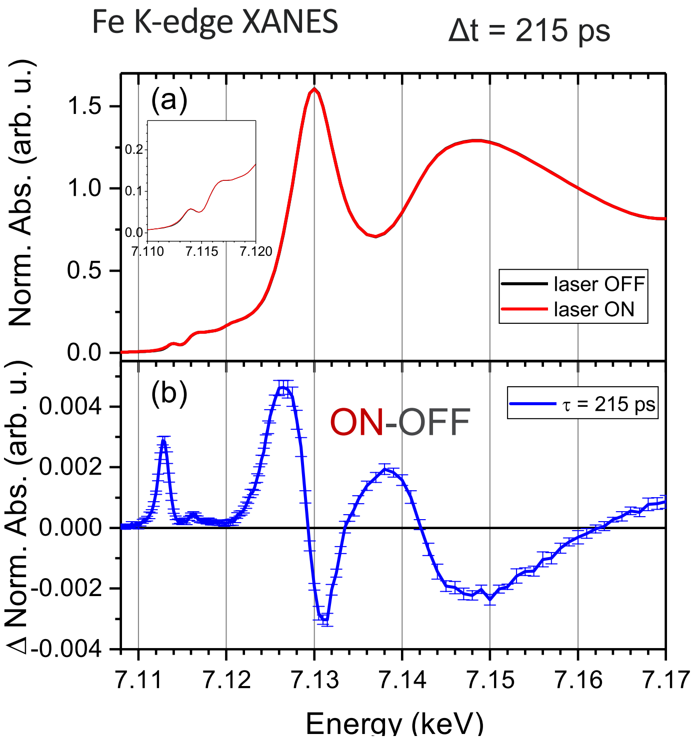
- To get “simultaneously” measured ground state (OFF) spectrum, need to refresh the sample volume between pump-probe cycles

typical operating conditions: can refresh for 1.3 MHz pump-probe repetition rate



XAS difference spectra

10^{-12} seconds



OFF = ground state spectrum

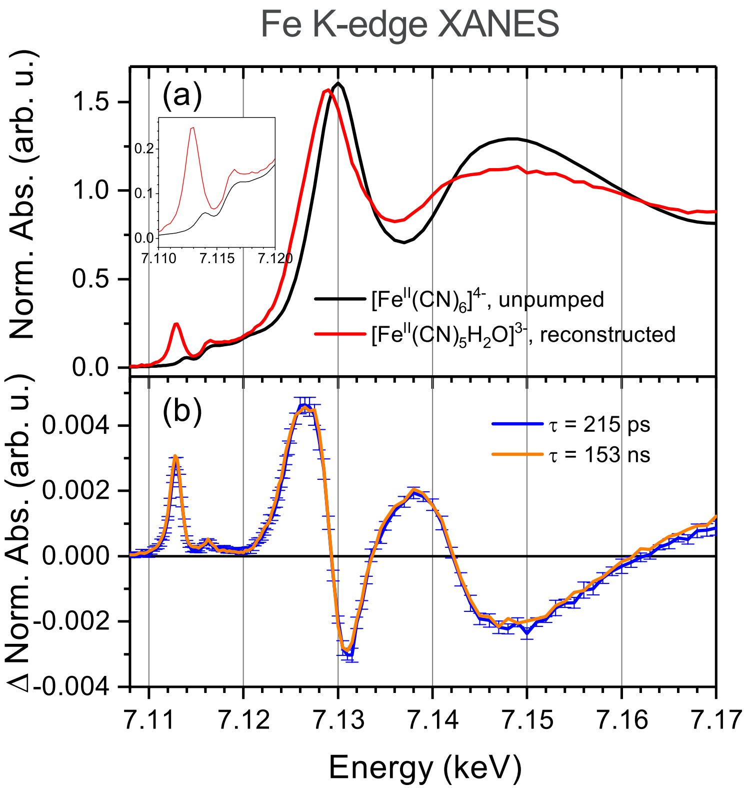
ON = (1-f)(ground state spectrum) + f (photoproduct(s) spectrum)

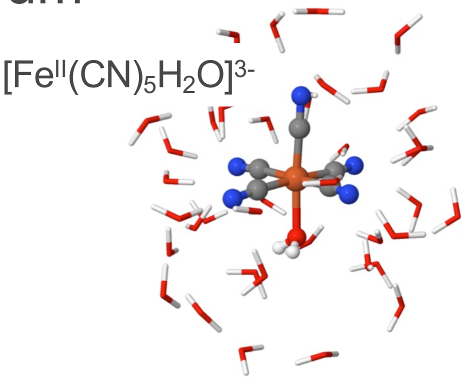
- If we know the excitation fraction (f), we can reconstruct the spectrum for the photoproduct(s)

Capturing the aquated photoproduct spectrum

10^{-12}

seconds





f = 1.3%

optical-pump, x-ray-probe, optical-probe measurement

- long-lived (>2 μs)
- yield is small
- spectral features consistent with expectations

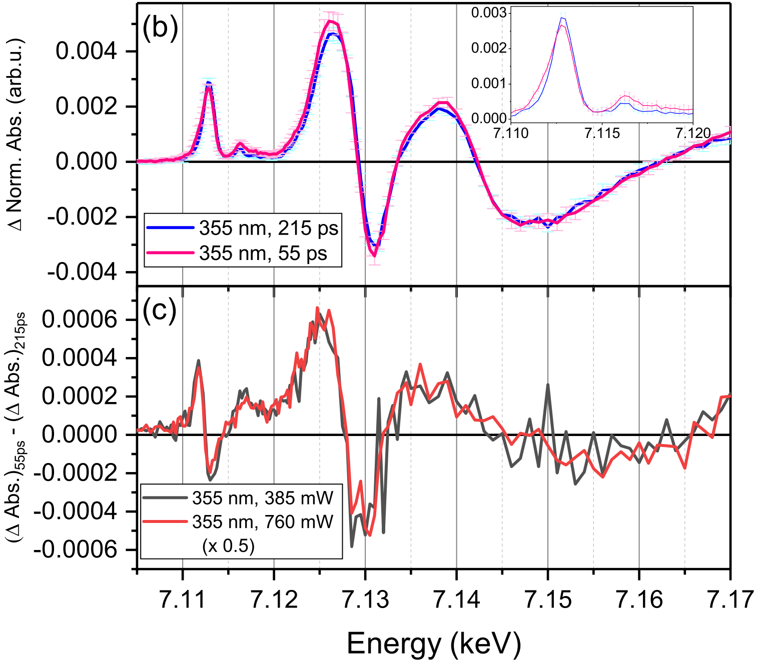
A. M. March *et al.*, J. Chem. Phys. (2019)

Subtle signs of an additional species

At pump-probe delays <80 ps (the x-ray pulse duration)

10^{-12}

seconds



- differences in the 50 ps transient signal compared to later times

- differences are linearly dependent on the laser fluence (not due to multiphoton processes)

signatures of the pentacoordinated intermediate?

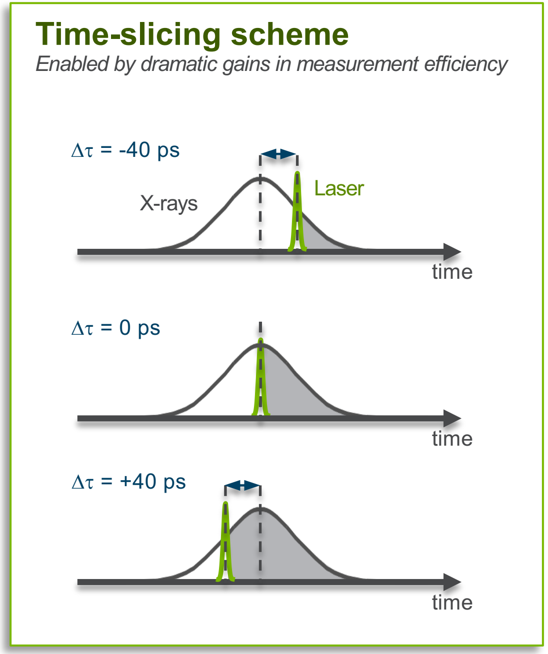
A. M. March *et al.*, J. Chem. Phys. (2019)

Capturing a short-lived species with long X-rays pulses

Observing sub-pulse-duration dynamics at the Advanced Photon Source

10^{-12}
seconds

X-rays: 80 ps FWHM
Laser: 10 ps FWHM



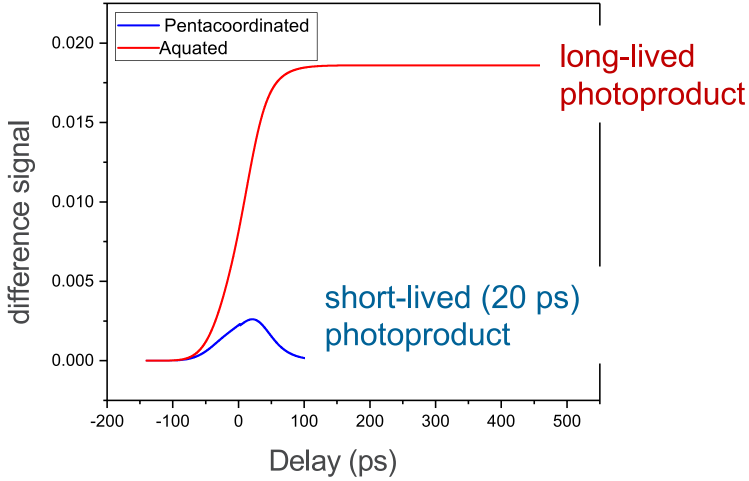
Time-slicing scheme

Enabled by dramatic gains in measurement efficiency

measured signal vs. time: convolution

x-ray pulse temporal profile ⊗ temporal evolution of the population of the photoinduced species

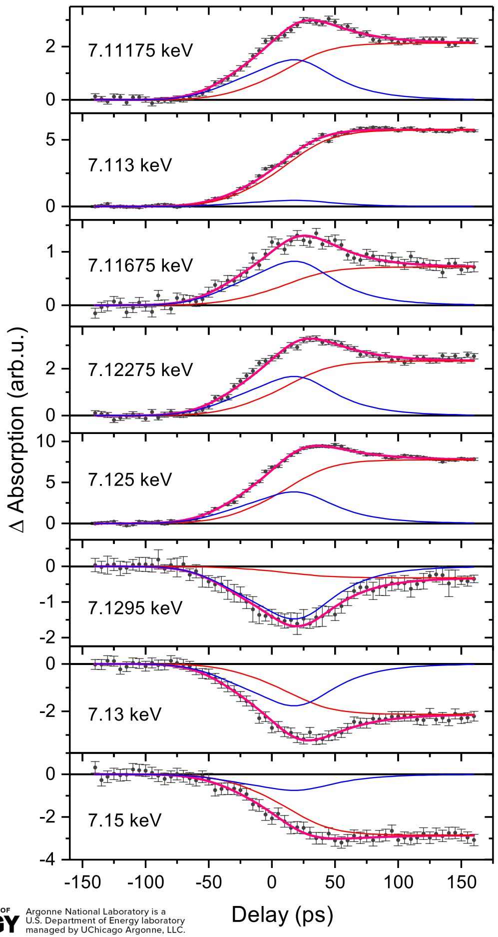
"kinetic scan"



A. M. March *et al.*, J. Chem. Phys. (2019)

Global fit of kinetic scans

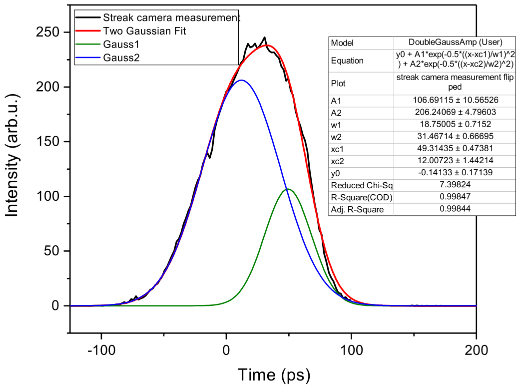
10^{-12}
seconds



- kinetic model for time dependent concentrations:

$$^{*}[\mathrm{Fe^{II}(CN)_6}]^{4-} \xrightarrow{\tau_1} [\mathrm{Fe^{II}(CN)_5}]^{3-} \xrightarrow[+\mathrm{H2O}]{\tau_2} [\mathrm{Fe^{II}(CN)_5\,H_2O}]^{3-}$$

- instrument response function:



Model	DoubleGaussAmp (User)
Equation	y0 + A1*exp(-0.5*((x-xc1)/w1)^2) + A2*exp(-0.5*((x-xc2)/w2)^2)
Plot	streak camera measurement flipped
A1	106.69115 ± 10.56526
A2	206.24069 ± 4.79603
w1	18.75005 ± 0.7152
w2	31.46714 ± 0.66695
xc1	49.31435 ± 0.47381
xc2	12.00723 ± 1.44214
y0	-0.14133 ± 0.17139
Reduced Chi-Sq	7.39824
R-Square(COD)	0.99847
Adj. R-Square	0.99844

- dominated by x-ray profile
- skewed profile approximated by two Gaussians

$[\mathrm{Fe^{II}(CN)_5}]^{3-}$ growth: τ_1 ~ 1 ps (fast)

$[\mathrm{Fe^{II}(CN)_5}]^{3-}$ decay: $\tau_2 = 19\ (\pm\ 5)$ ps

A. M. March *et al.*, J. Chem. Phys. (2019)

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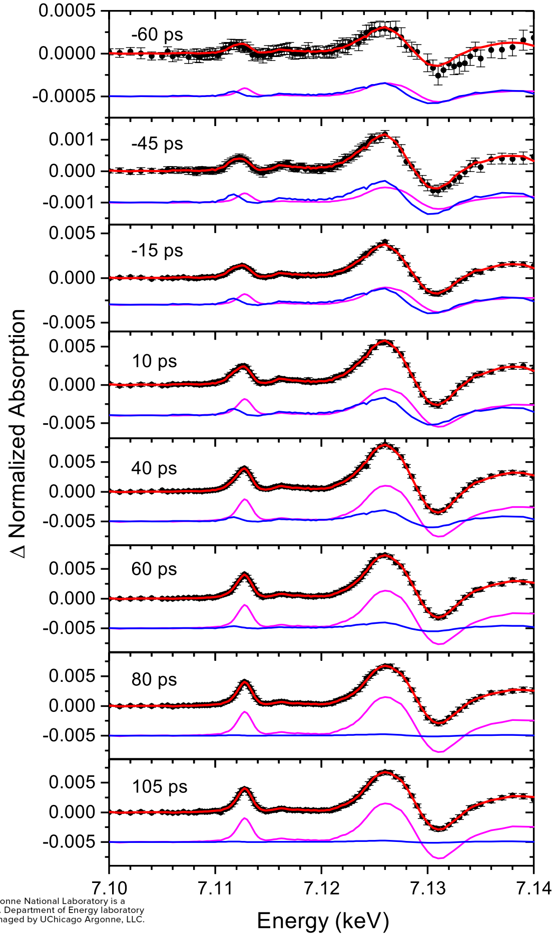
Argonne NATIONAL LABORATORY

Isolating the $[Fe^{II}(CN)_5]^{3-}$ spectrum

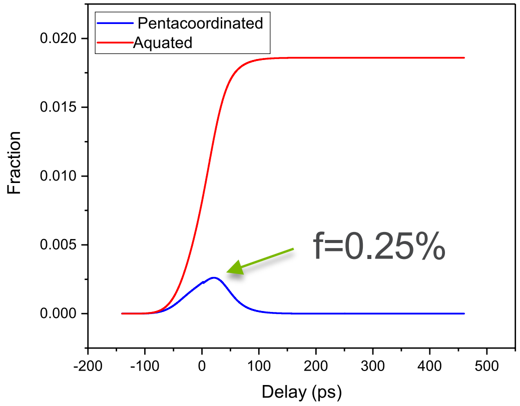
10^{-12}

seconds



- SVD analysis indicates 2 components

- known $[Fe^{II}(CN)_5H_2O]^{3-}$ spectrum and kinetic model provide constraints for SVD
  - → obtain spectral shape for the $[Fe^{II}(CN)_5]^{3-}$ difference signal



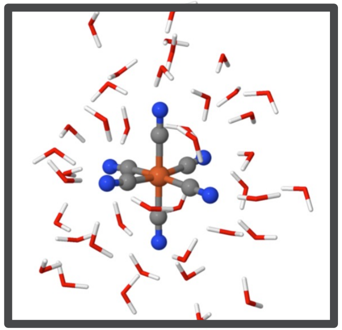
- known $[Fe^{II}(CN)_5H_2O]^{3-}$ fraction and kinetic model yields $[Fe^{II}(CN)_5]^{3-}$ fraction

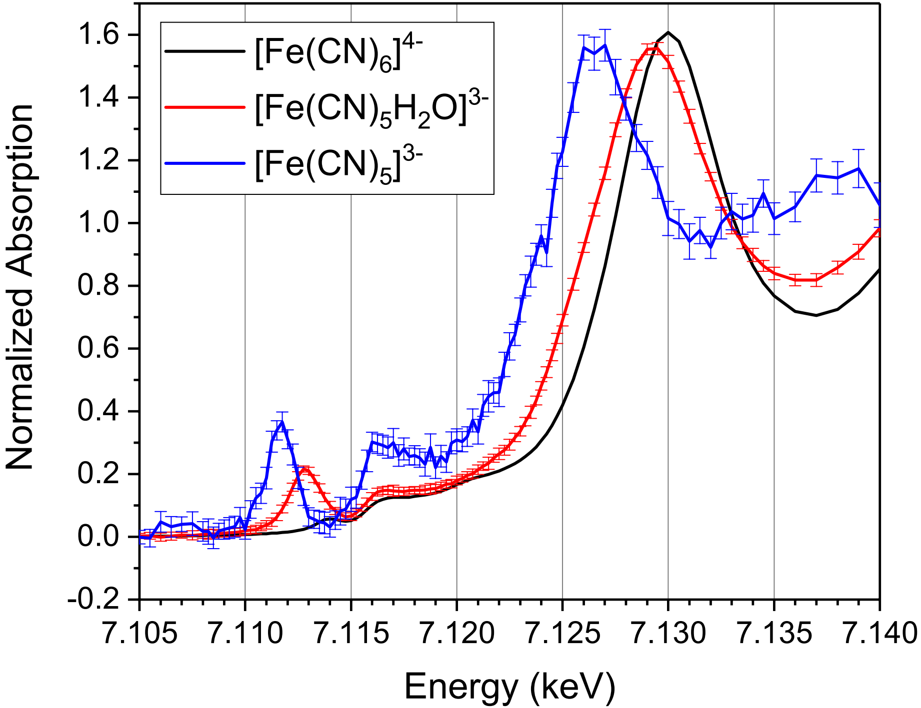
A. M. March *et al.*, J. Chem. Phys. (2019)

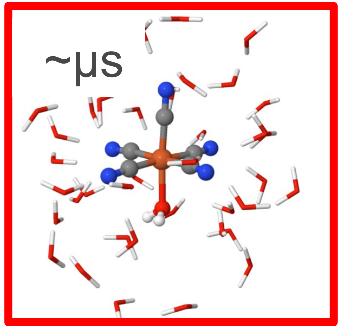
Reconstructed $[Fe^{II}(CN)_5]^{3-}$ spectrum

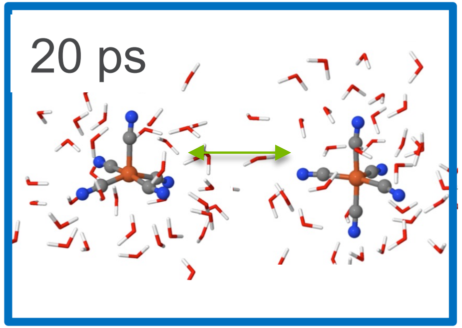
10^{-12}

seconds





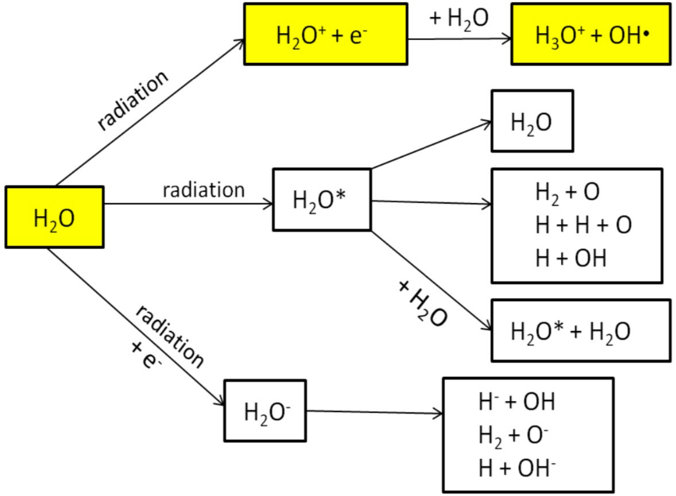




A. M. March *et al.*, J. Chem. Phys. (2019)

Tracking the primary chemical reaction that follows ionization of liquid water

10^{-15}
seconds



B. C. Garrett *et al*., Chem. Rev. **105**, 355 (2005).

- Ionization of liquid water a universal phenomena accompanying interaction of radiation with matter

- Cascade of electrons, ions and radicals forms basis of solution and interfacial chemistry in aqueous environments

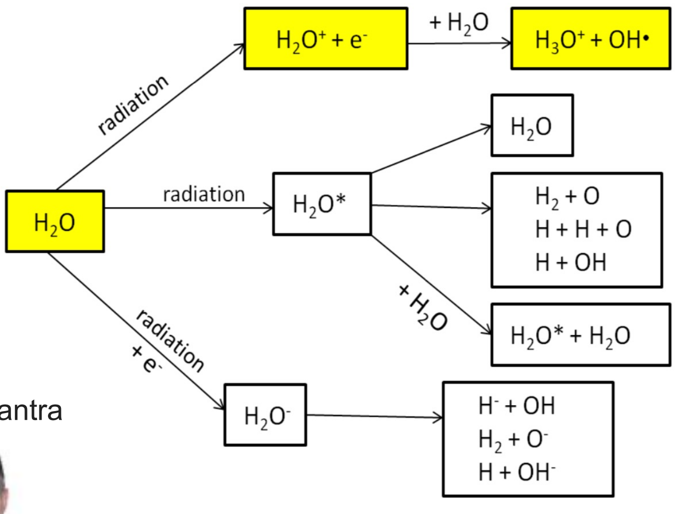
- Water major component in cells – biological damage triggered by ionization of water

Tracking the primary chemical reaction that follows ionization of liquid water

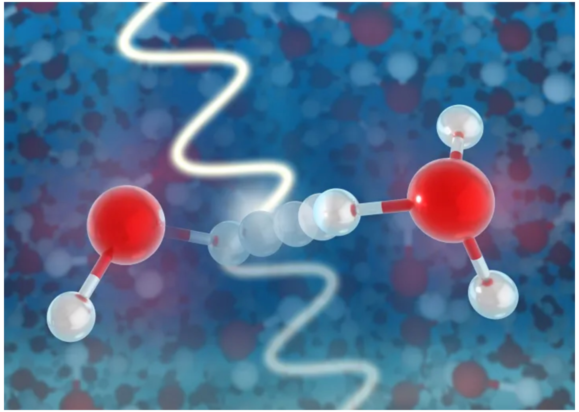
10^{-15}
seconds

Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

DOI: 10.1126/science.aaz4740



LCLS soft x-ray absorption spectroscopy to look for the elusive H_2O^+



Corresponding authors:

Zhi-Heng Loh

Linda Young

Robin Santra

NANYANG TECHNOLOGICAL UNIVERSITY
SINGAPORE

Argonne NATIONAL LABORATORY

CFEL SCIENCE
CFEL-DESY Theory Division

Linac Coherent Light Source

SLAC National Lab

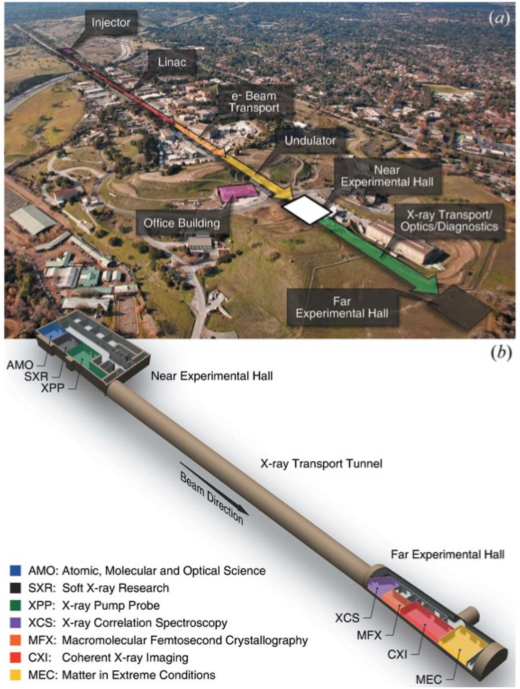
10^{-15}

seconds

Soft x-rays: 250 eV – 2 keV
Hard x-rays: 3 keV – 11 keV

~10^{12} photons/pulse

~5 fs to 300 fs



- X-rays created through a stochastic process, self-amplified stimulated emission (SASE)
- Each shot can have different temporal, spectral, and spatial properties

Other XFELS:

SACLA (Japan)
FLASH (Germany)
FERMI@Elettra (Italy)
European XFEL (Germany)
Swiss-FEL (Switzerland)
PAL-XFEL (Korea)

U.S. DEPARTMENT OF ENERGY Argonne National Laboratory is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC.

LCLS Experimental Team

LR01- Dynamics and coherence in strong-field ionized water: Transient spectroscopy in the water window

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Steve Southworth
Phay Ho
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Marc Simon

LCLS
Bill Schlotter
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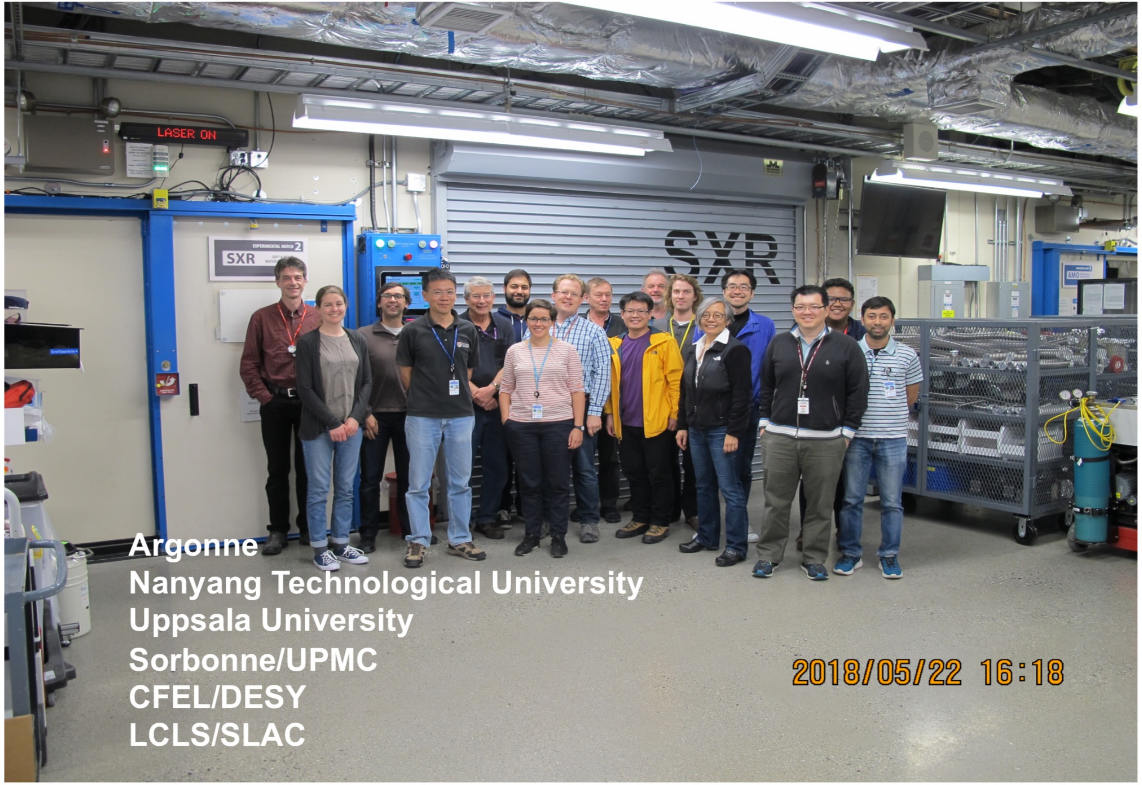
Giacomo Coslovich
Jake Koralek
Dan DePonte

LR-01 EXPERIMENTAL TEAM

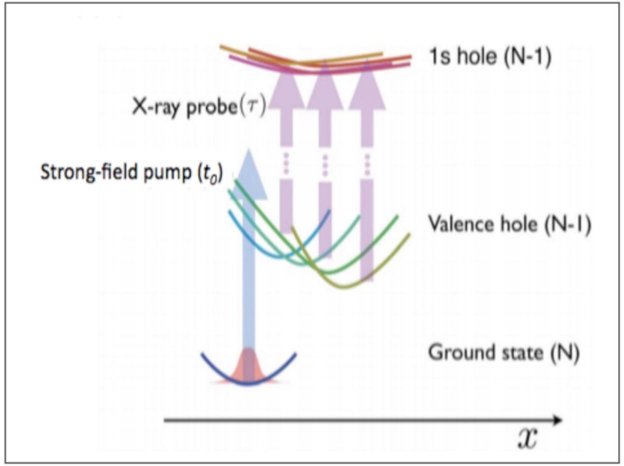


Argonne
Nanyang Technological University
Uppsala University
Sorbonne/UPMC
CFEL/DESY
LCLS/SLAC

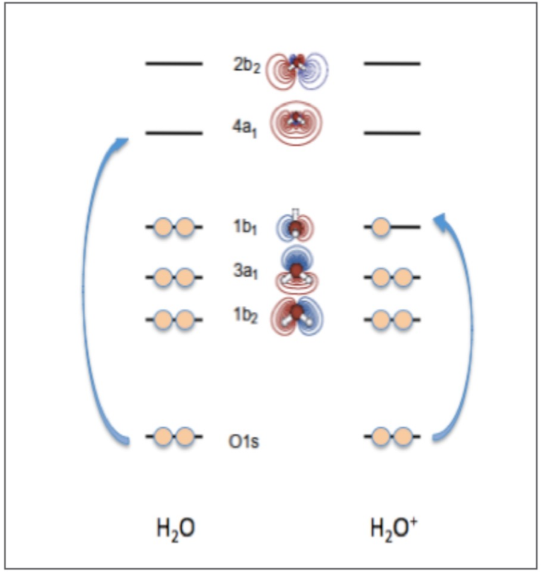
2018/05/22 16:18

Strong-field ionization + ultrafast x-ray absorption

Prompt production and clean detection of H_2O^+ (and OH)



- 800-nm ionization pump ($2x10^{13}W/cm^2$)
- Nine-photon process
- Deposition of 14 eV > Vertical IP (11.16)
- Electron ejection length ~35Å



- HOMO-LUMO gap 8 eV
- H_2O^+ resonance in water window

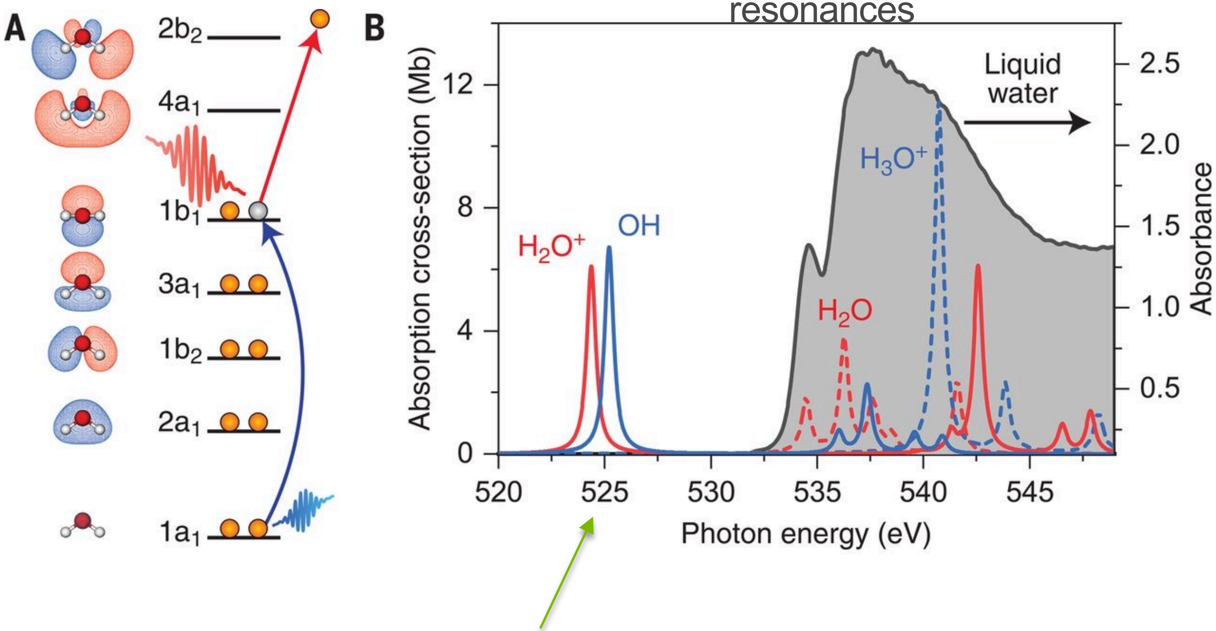
Ultrafast x-ray probe

10^{-15} seconds

enables tracking of the primary chemical reaction following ionization

$$H_2O^+ + H_2O \rightarrow OH + H_3O^+$$

calculated gas phase absorption resonances

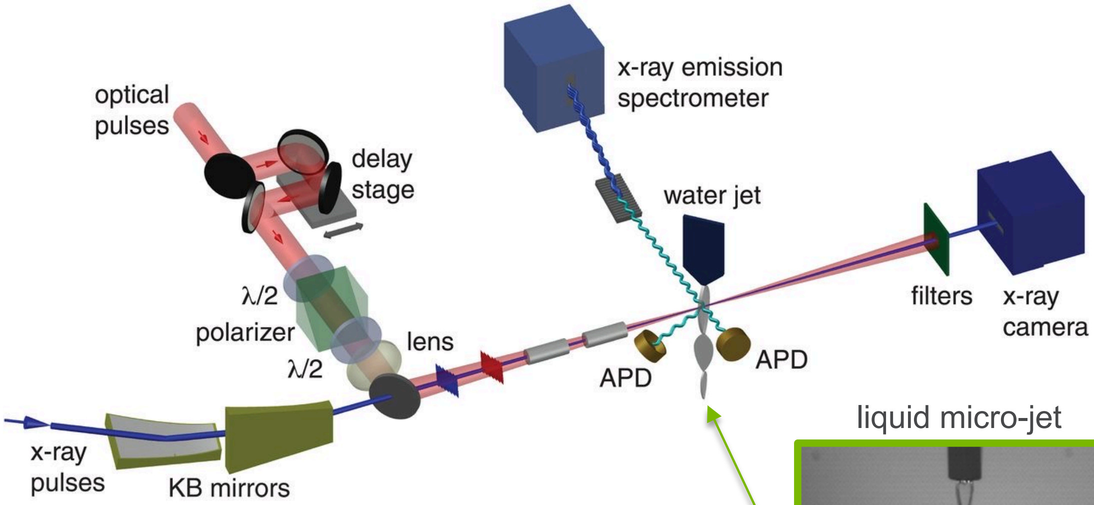


absorption lines fall cleanly in the water window

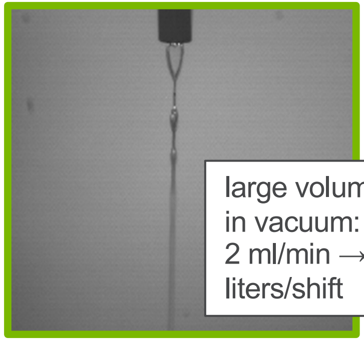
Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

Experimental Details @ LCLS-SXR

**Simultaneous detection in three channels:
transmission, fluorescence, dispersed emission (RIXS)**



liquid micro-jet



large volume of water in vacuum:
2 ml/min → 2 liters/shift

Laser: 800 nm, ~60 fs, 60 μm spot
X-rays: 520-540 eV, 20 fs, 0.2 eV, ~20 μm spot

Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

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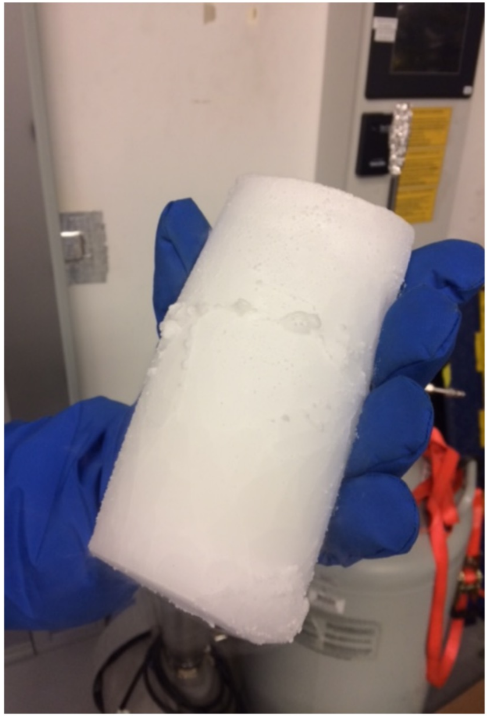
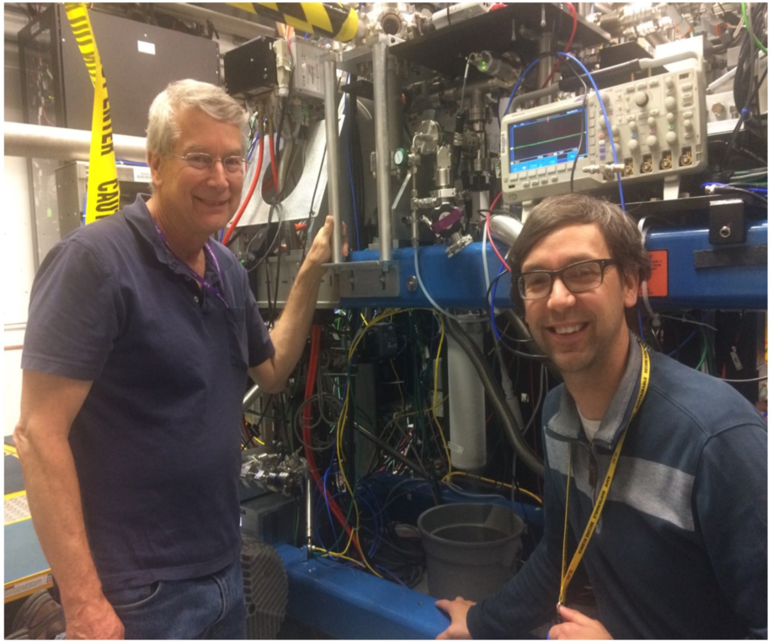
Water after 6 hr run



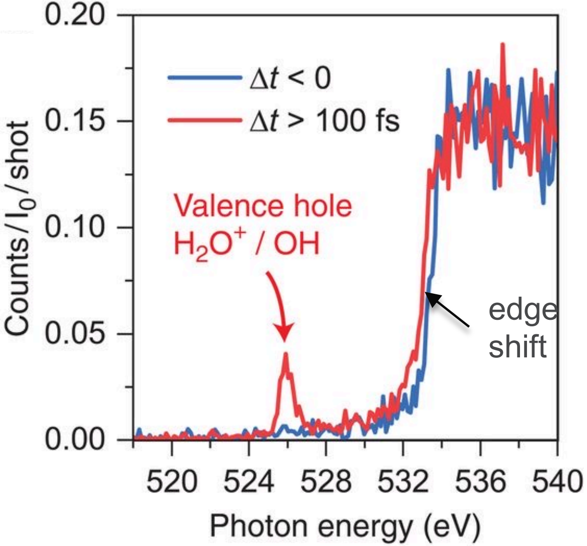
Experimenters at end of run



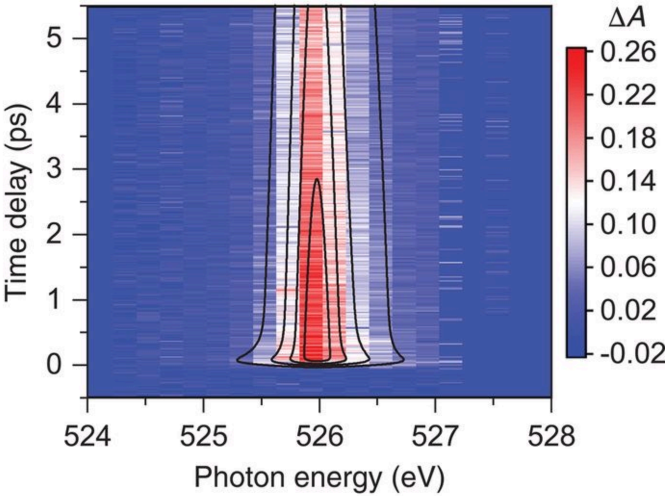
Time-resolved signatures appear in all three channels:

transmission, total fluorescence and dispersed emission

Absorption before and after ionization



Time-resolved differential absorption spectrum



fit, sequential kinetics:

τ_1 = 0.18 +/- 0.02 ps → OH vibrational cooling

τ_2 = 14.2 +/- 0.4 ps → OH radical decay

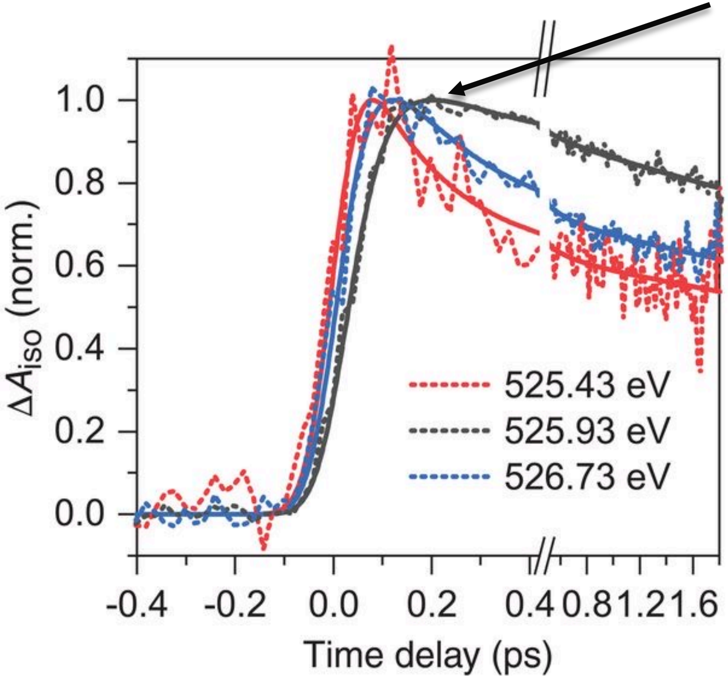
Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

Delay scans reveal additional time constant

10^{-15}

seconds

delayed rise: suggests additional ultrafast process



τ_1 = 0.16 +/- 0.03 ps

(0.18 +/- 0.02 ps → OH vibrational cooling)

τ_2 = 9.2 +/- 1.3 ps

(14.2 +/- 0.4 ps → OH radical decay)

τ_{growth} = 46 +/- 10 fs

↓

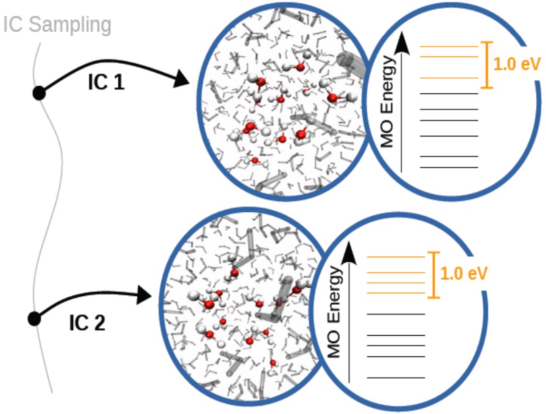
growth of OH, lifetime for H_2O^+

Z. H. Loh *et al.* Science **367**, 179-182 (2020)

QM/MM excited-state molecular dynamics simulation of liquid water following strong field ionization

10^{-15}
seconds

- Considered initial ionization in the upper 1.5 eV of the valence band and averaged across 107 initial geometries of liquid water
- Non-Born-Oppenheimer effects taken into account by Tully's fewest-switches surface hopping approach
- Combined QM description of a $(H_2O)_{12}^+$ cluster with a MM description of surrounding water molecules
- Electronic structure obtained at Hartree-Fock level of theory using Koopman's theorem to obtain singly ionized states and using the 6-31G basis set (as implemented in XMOLECULE)



calculations confirm experimentally observed timescale for the proton transfer step (~40 fs)

Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

Robin Santra, Caroline Arnold

Water experiment at LCLS

10^{-15}

seconds

Water experiment at LCLS

10^{-15}
seconds

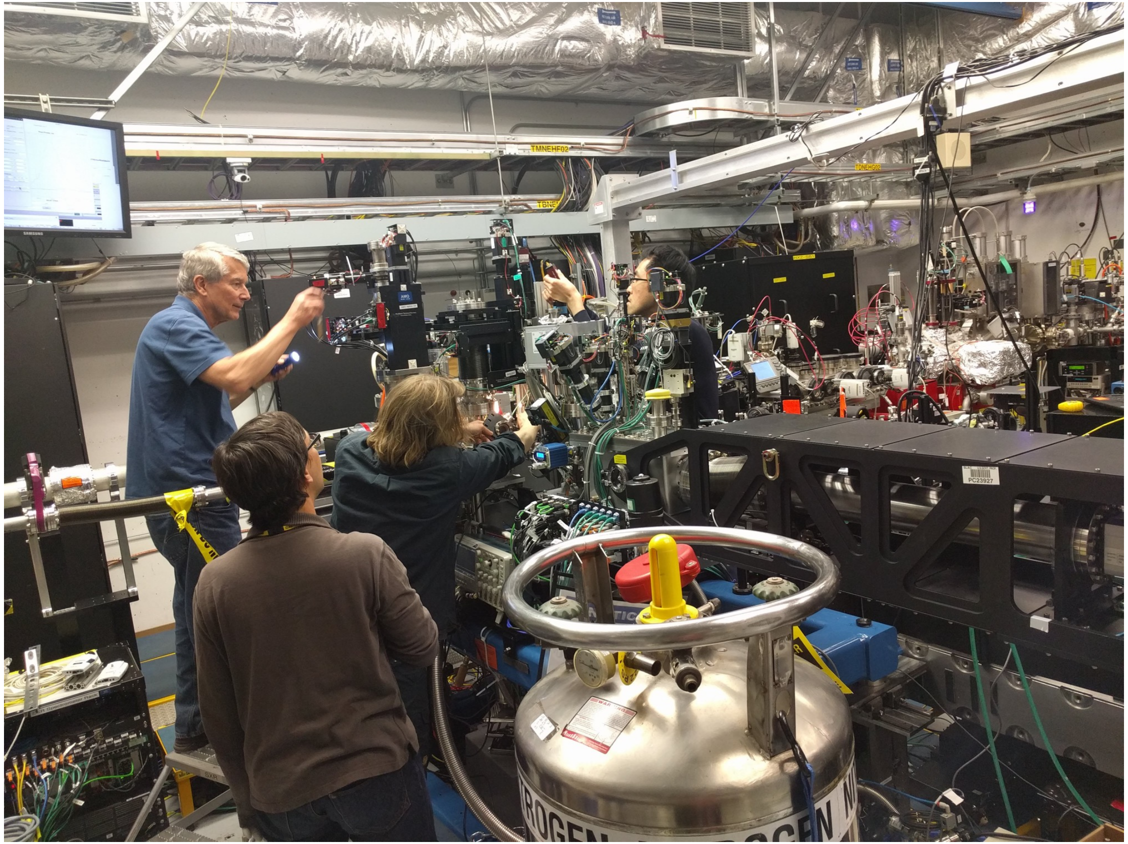
Water experiment at LCLS

10^{-15}

seconds

Water experiment at LCLS

10^{-15}
seconds



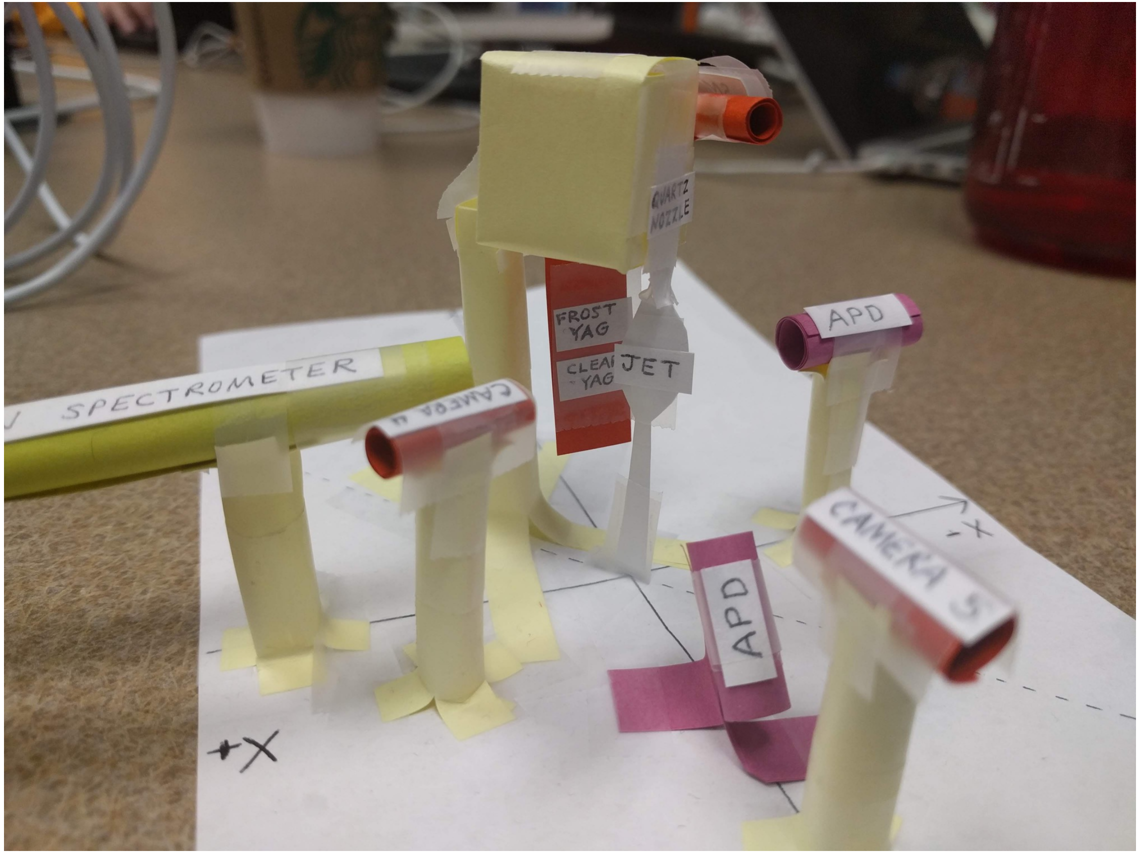
Water experiment at LCLS

10^{-15}
seconds

Water experiment at LCLS

10^{-15}

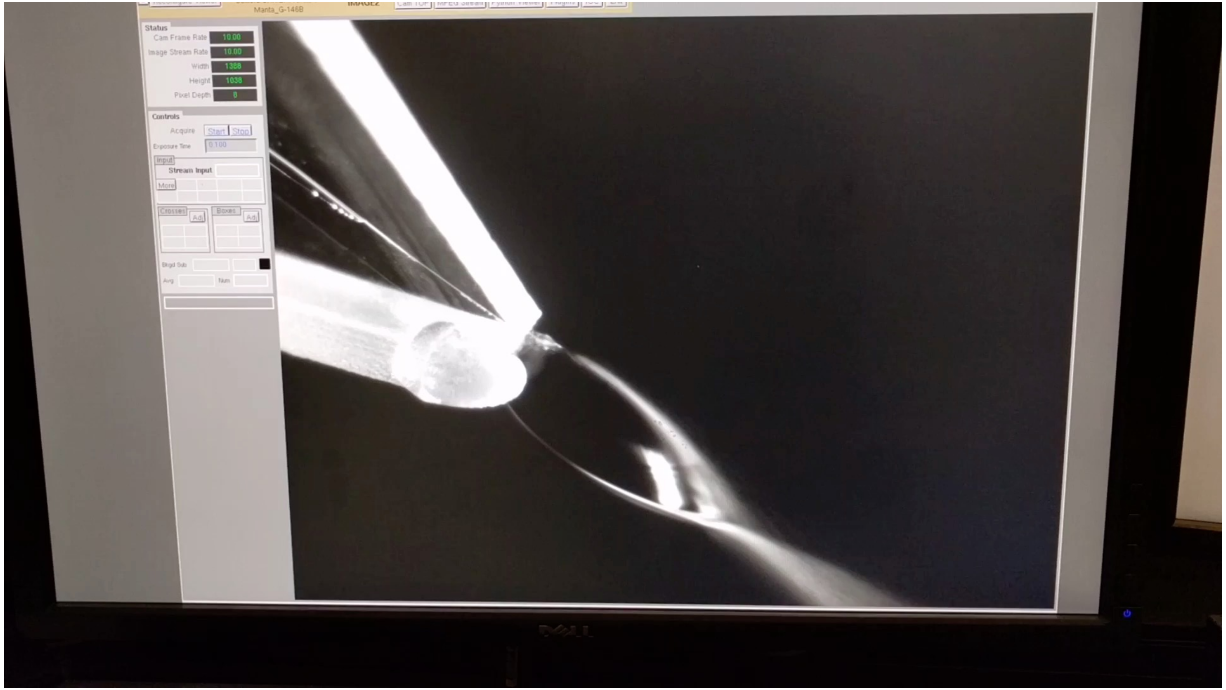
seconds



Water experiment at LCLS

10^{-15}

seconds



Manta_G-146B

Status
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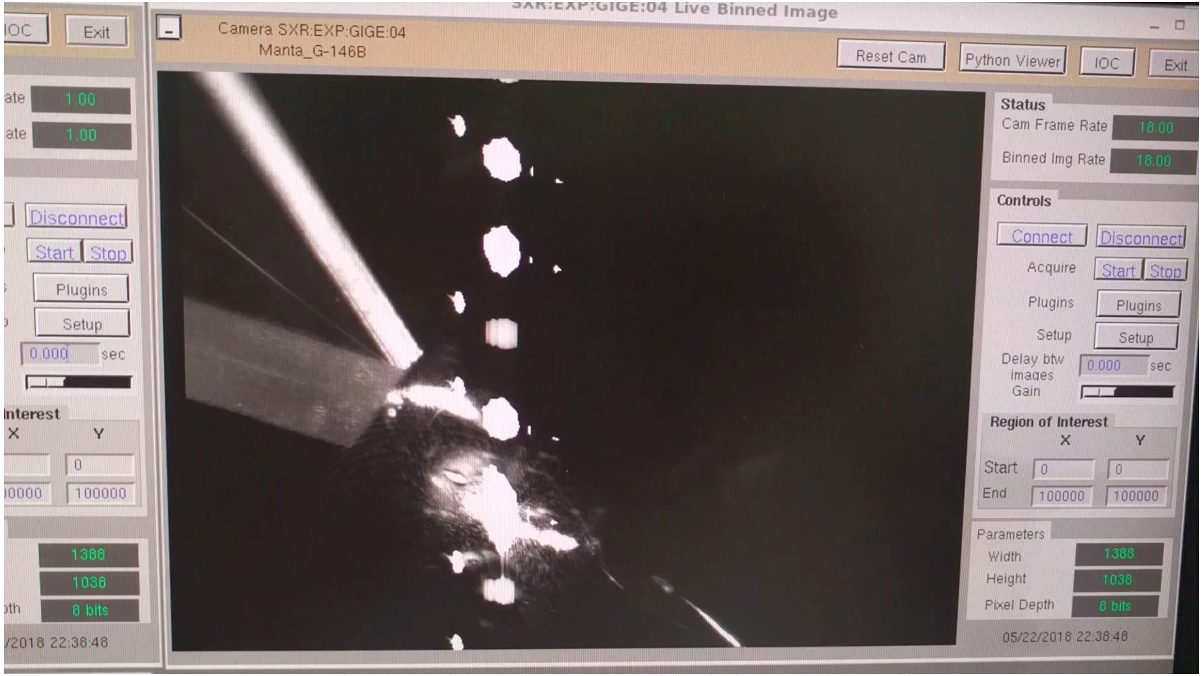
Image Stream Rate 10.00
Width 1388
Height 1038
Pixel Depth 8

Controls
Exposure Time 0.100

Water experiment at LCLS

10^{-15}
seconds



Camera SXR:EXP:GIGE:04
Manta_G-146B

Cam Frame Rate 18.00
Binned Img Rate 18.00

Acquire: Start Stop
Delay btw images 0.000 sec
Gain

	X	Y
Start	0	0
End	100000	100000

Width 1388
Height 1038
Pixel Depth 8 bits

05/22/2018 22:38:48

Tunable isolated attosecond X-ray pulses with gigawatt peak power from a free-electron laser

10^{-18}

seconds

A. Marinelli *et al.*, Nature Photonics **14** 30-36 (2020)

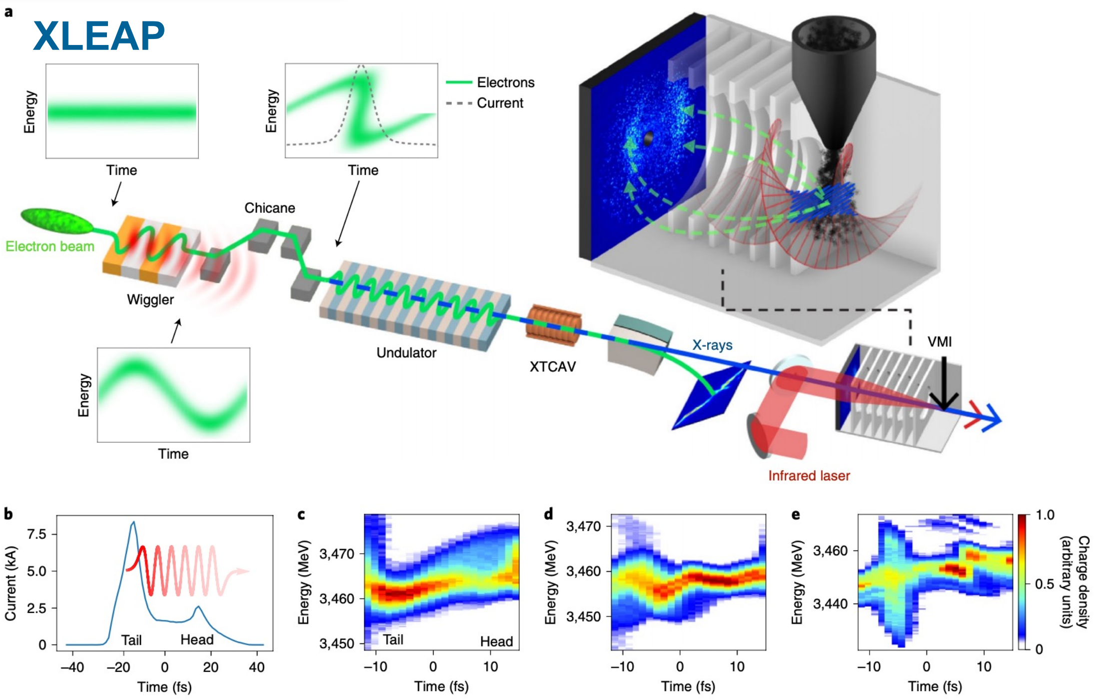
https://www.nature.com/articles/s41566-019-0549-5

Corresponding authors:

James P. Cryan

Agostino Marinelli

SLAC Stanford University



Attosecond coherent electron motion in Auger-Meitner decay

10^{-18}

seconds

Siqi Li *et al.*, Science **375** 285-290 (2022)

DOI: 10.1126/science.abj2096

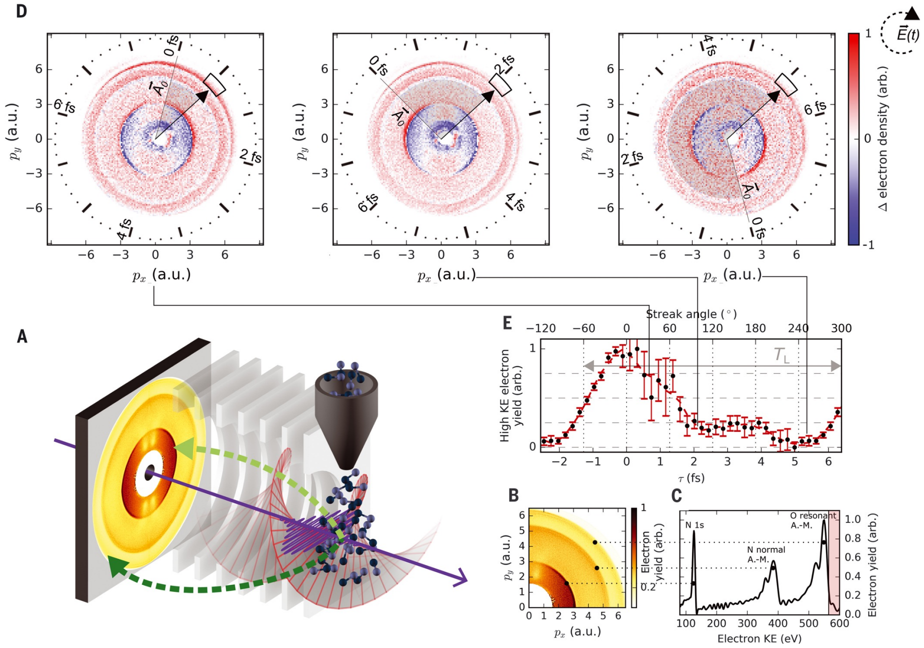
Corresponding authors:

James P. Cryan

Agostino Marinelli

SLAC Stanford University

First results using XLEAP attosecond pulses



X-rays are extraordinarily powerful probes of matter across many orders of magnitude in time.

New, brighter X-ray facilities promise exciting new discoveries ahead!

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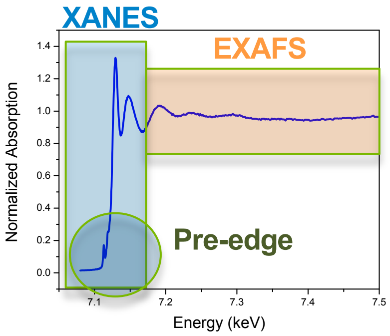
Thank you for your attention!

X-ray photon-in/photon-out spectroscopies

Element selectivity and a wealth of information on electronic and geometrical structure

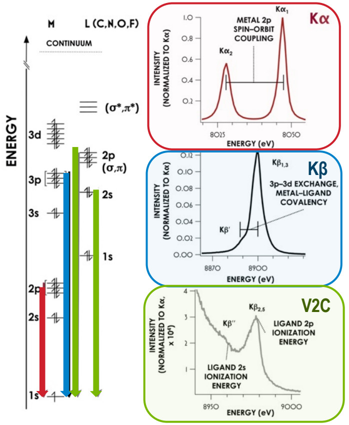
X-ray absorption spectroscopy (XAS)



- Bond distances, oxidation state, geometry, coordination environment, unoccupied orbitals

RXES
HERFD-XAS

X-ray emission spectroscopy (XES)



- occupied orbitals, spin state, covalency, ligand identity

valence-to-core XES

S. N. MacMillan and K. M. Lancaster, ACS Catal. 7, 1776−1791 (2017)

At 7ID-D:

- x-ray microprobe and MHz pump laser
- have expanded the pump-probe toolkit to include all these techniques

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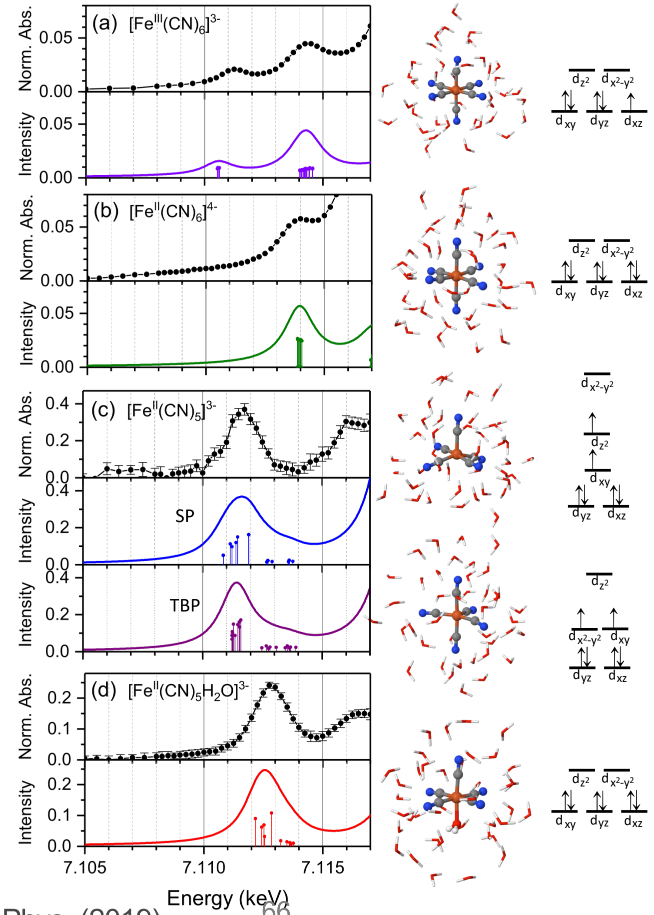
Comparison to simulated spectra

Pre-edge peaks

D. R. Nascimento, A. Andersen,
N. Govind (PNNL)



A. M. March *et al.*, J. Chem. Phys. (2019)

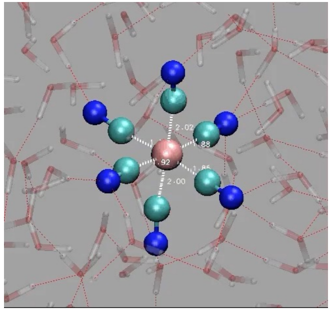
QM/MM MD simulations

D. R. Nascimento, A. Andersen, N. Govind (PNNL)

I.

$$^{3}[\mathrm{Fe^{II}(CN)_6}]^{4-} \xrightarrow[1.3\ \mathrm{ps}]{-\mathrm{CN}^-} {}^{3}[\mathrm{Fe^{II}(CN)_5}]^{3-}_{\mathrm{SP}}$$

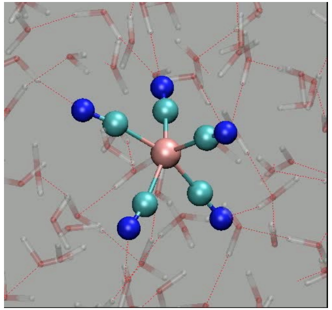
- CN^- dissociation takes place in ~1.3 ps



II.

$$^{3}[\mathrm{Fe^{II}(CN)_5}]^{3-}_{\mathrm{SP}} \overset{3\,\mathrm{ps}}{\longleftrightarrow} {}^{3}[\mathrm{Fe^{II}(CN)_5}]^{3-}_{\mathrm{TBP}}$$

- interconversion between square pyramidal geometry and trigonal bipyramidal geometry on 3-4 ps timescale



III.

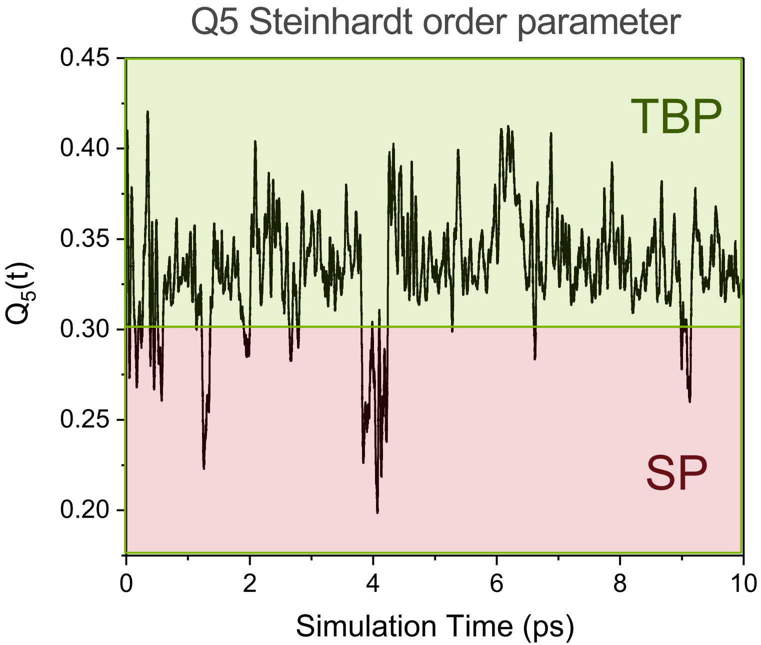
$$^{3}[\mathrm{Fe^{II}(CN)_5}]^{3-} \xrightarrow{+\mathrm{H_2O}} {}^{3}[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-} \xrightarrow[\sim 1\ \mathrm{ps}]{} {}^{3}[\mathrm{Fe^{II}(CN)_5}]^{3-}_{\mathrm{TBP}} + \mathrm{H_2O}$$

$$^{1}\,\mathrm{Fe^{II}(CN)_5}]^{3-} \xrightarrow{+\mathrm{H_2O}} {}^{1}[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-}$$

- aquated product formation requires a spin state change

Trigonal bipyramidal vs. square pyramidal character

A. Andersen, D. R. Nascimento, N. Govind (PNNL)



- pentacoordinated intermediate spends most of its time in TBP geometry
- SP geometry for ~500 fs, every 3-4 ps
- aquation can only occur in SP geometry
- small windows of time for aquation and required spin state change explain the “long” 20 ps lifetime

$$^3[\mathrm{Fe^{II}(CN)_5}]^{3-}_{\mathrm{SP}} \xleftrightarrow{3\,\mathrm{ps}} {}^3[\mathrm{Fe^{II}(CN)_5}]^{3-}_{\mathrm{TBP}} \xrightarrow[20\,\mathrm{ps}]{+\mathrm{H_2O}} {}^1[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-}$$

A. M. March *et al.*, J. Chem. Phys. (2019)

Pump-Probe Measurements Require a Large Team!

AMO Physics Group
Argonne National Laboratory

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Gilles Doumy
Stephen Southworth
Dimitrios Koulentianos
Linda Young
Alec Dinerstein
Joohee Bang
Ming-Feng Tu
Andre Al Haddad (PSI)
Yoshiaki Kumagai (Tokyo U.)
Christoph Bostedt (PSI, EPFL)

APS Sector 7

Don Walko
Anthony DiChiara

Pacific Northwest National Laboratory

Daniel Nascimento
Amity Andersen
Niri Govind

Lund University
Jens Uhlig

Wigner Research Centre for Physics
Hungarian Academy of Sciences

Zoltán Németh
György Vankó

European XFEL

Tadesse A. Assefa (BNL)
Alexander Britz (SLAC)
Andreas Galler
Wojciech Gawelda
Christian Bressler

Work was supported by the U.S. Department of Energy, Office of Science, Chemical Sciences, Geosciences, and Biosciences Division

New beamline at APS: Advanced Spectroscopy

Specialized for X-ray absorption and emission spectroscopy

- Both broad and narrow bandwith X-rays delivered along the same path

  -collect both nonresonant XES (with broadband) and XAS (with monoband) spectra during one beamtime

- Microprobe focusing

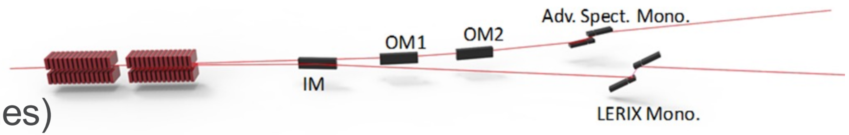
- Canted beamline (two branches)

  -Microprobe branch:

  4-32 keV (all elements K or L edges heavier than K)

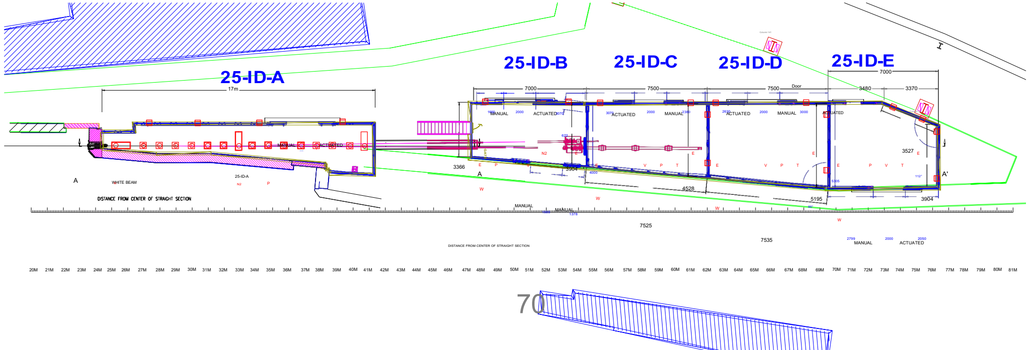
  -Lerix branch

  4-40 keV (covers a few applications above 32 keV)



Coming online in ~2021

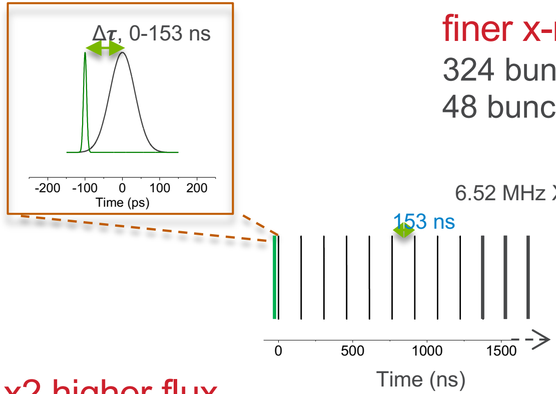
Sector 25



Looking ahead to APS-U

Optimal probe for following chemical reactions

- capture multiple temporal regimes simultaneously with pump-probe-probe-probe…



finer x-ray temporal combs

324 bunch mode: 88 MHz (11 ns spacing)
48 bunch mode: 13 MHz (77 ns spacing)

~20 ps to ns, µs, ms

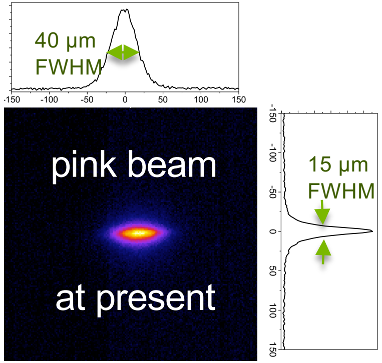
”time-slicing” limits:
324 bunch mode: 206 ps FWHM → ~20 ps
48 bunch mode: 240 ps FWHM → ~25 ps

x2 higher flux

24 bunches, 4 mA per bunch → 48 bunches, 4 mA per bunch

rounder x-ray spot

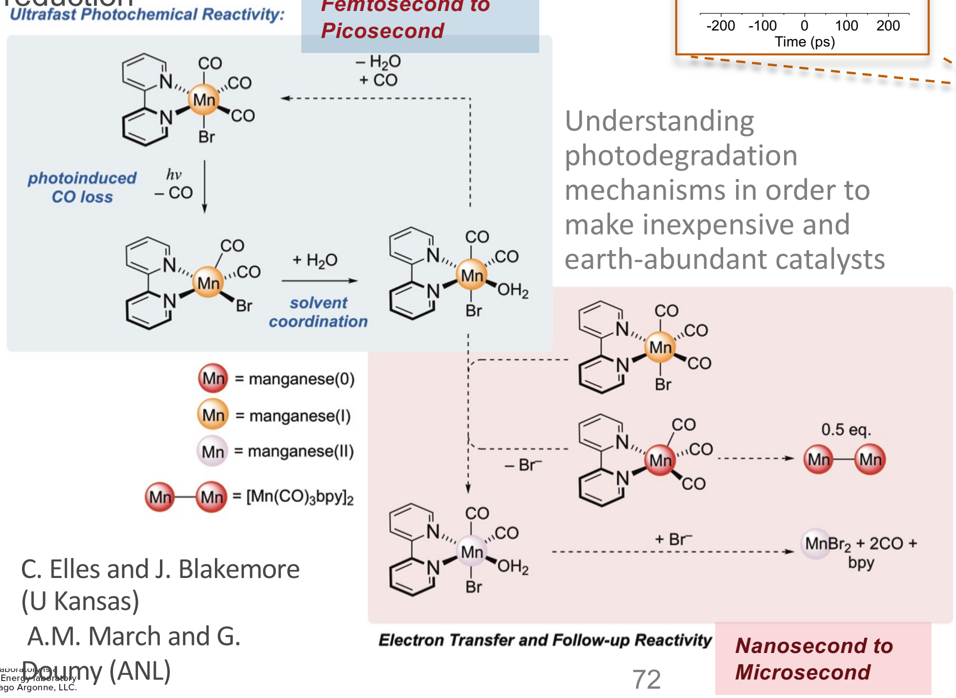
smaller laser power (reduce sample damage)
probe volume with higher excitation fraction



Opportunities using synchrotron X-rays

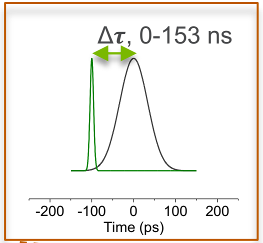
Pump-probe-probe-probe-… to capture multiple temporal regimes simultaneously

Mn-based catalysts for CO_2 reduction

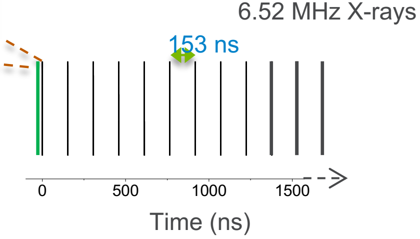


Understanding photodegradation mechanisms in order to make inexpensive and earth-abundant catalysts

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



Variable repetition rate pump lasers coupled with **MHz rep rate** X-ray temporal combs



stability

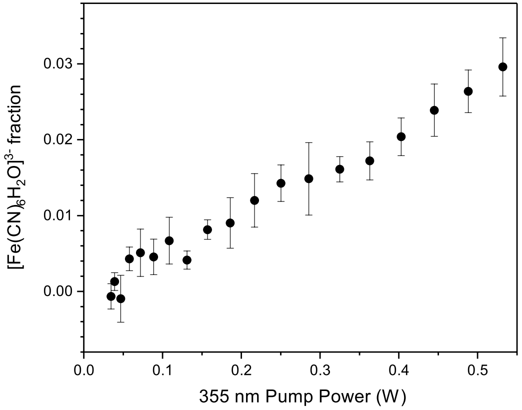
high flux
$10^{12} – 10^{15}$ ph/s

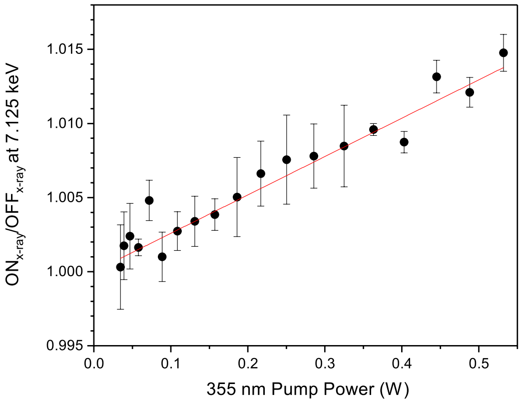
high precision measurements

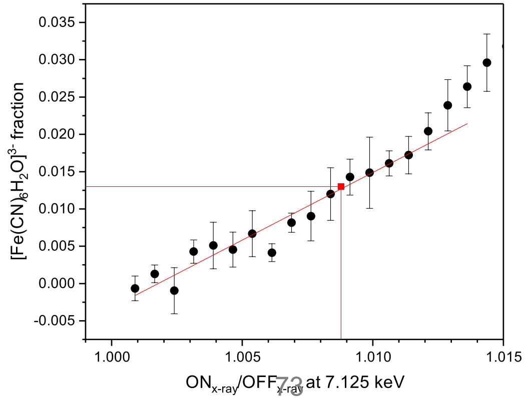
Measurement of excited state fraction

optical-pump, x-ray-probe, optical-probe

tuned to 450 nm absorption peak of $[Fe^{II}(CN)_5H_2O]^{3-}$







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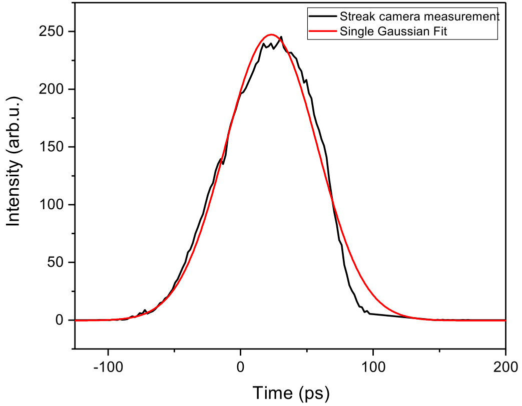
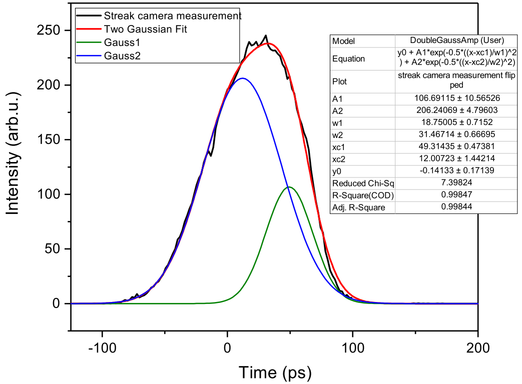
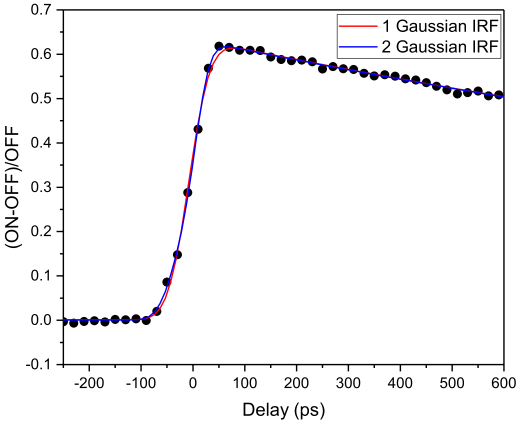
Determination of IRF





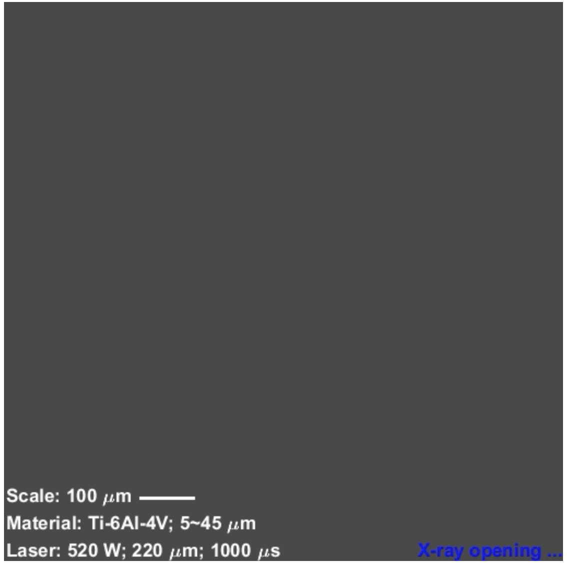
Model	DoubleGaussAmp (User)
Equation	y0 + A1*exp(-0.5*((x-xc1)/w1)^2) + A2*exp(-0.5*((x-xc2)/w2)^2)
Plot	streak camera measurement flipped
A1	106.69115 ± 10.56526
A2	206.24069 ± 4.79603
w1	18.75005 ± 0.7152
w2	31.46714 ± 0.66695
xc1	49.31435 ± 0.47381
xc2	12.00723 ± 1.44214
y0	-0.14133 ± 0.17139
Reduced Chi-Sq	7.39824
R-Square(COD)	0.99847
Adj. R-Square	0.99844



High speed detectors

2D detectors

laser powder bed fusion (LPBF) process
of Ti-6Al-4V *in situ* and in real time



C. Zhao *et al.* Sci.Rep. **7** 3602 (2017)

50 kHz frame rate, 340 ns exposure time

Point detectors

MSM photodetector (Hamamatsu)

30 ps response time
200 um active area

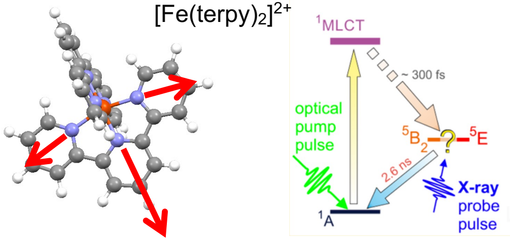
small detectors -> very small solid angle
-> negligible signal

Hard x-ray studies of transition metal complexes in solutions

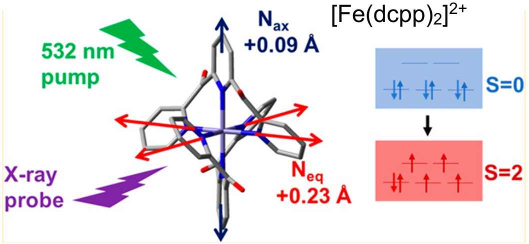
Complexity:

- **Coupled electronic, spin, and geometric degrees of freedom**
- **photochemical dynamics spanning orders of magnitude in time**

tracking spin with XES and structure with XAS in Fe photosensitizers

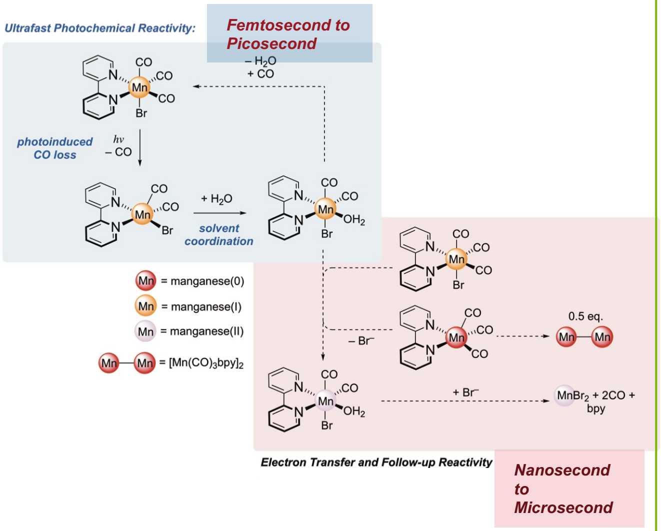


G. Vankó *et al.*, J. Phys. Chem. C **119**, 5888 (2015)



A. Britz *et al.*, Inorg. Chem. **58** 9341 (2019)

photodegradation of a CO_2 reduction catalyst



Blakemore, Elles, *et al. Inorg. Chem.* **59** *2178 (2020)*

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