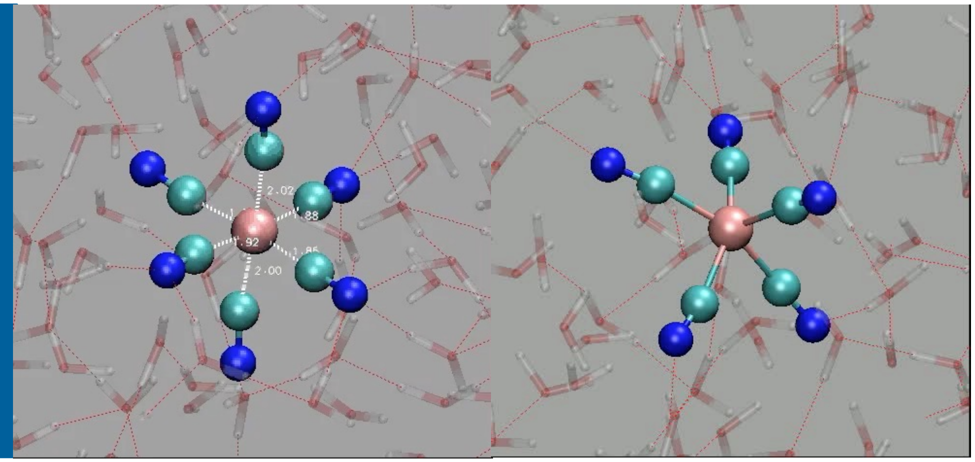
Probing Ultrafast Dynamics with X-rays



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

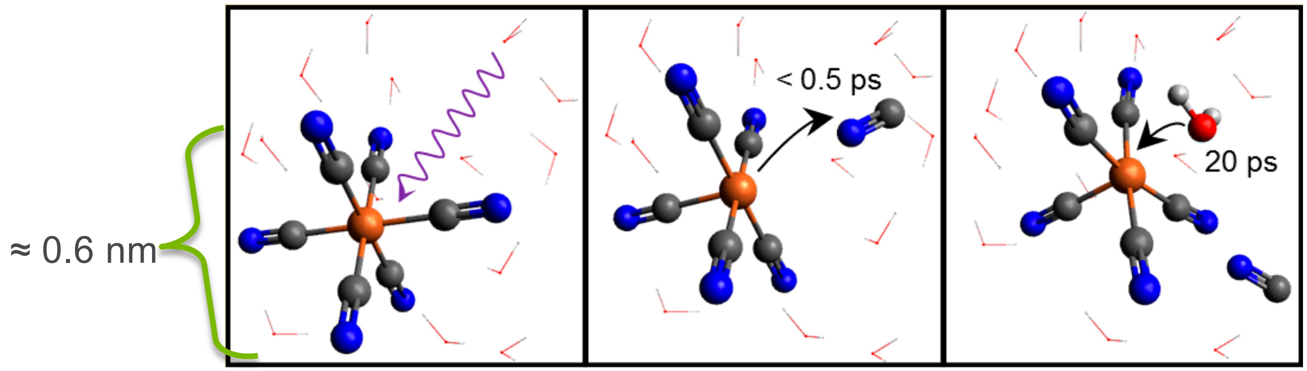
amarch@anl.gov
(I'm happy to receive your questions!)

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

July 31, 2024
NX Summer School

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

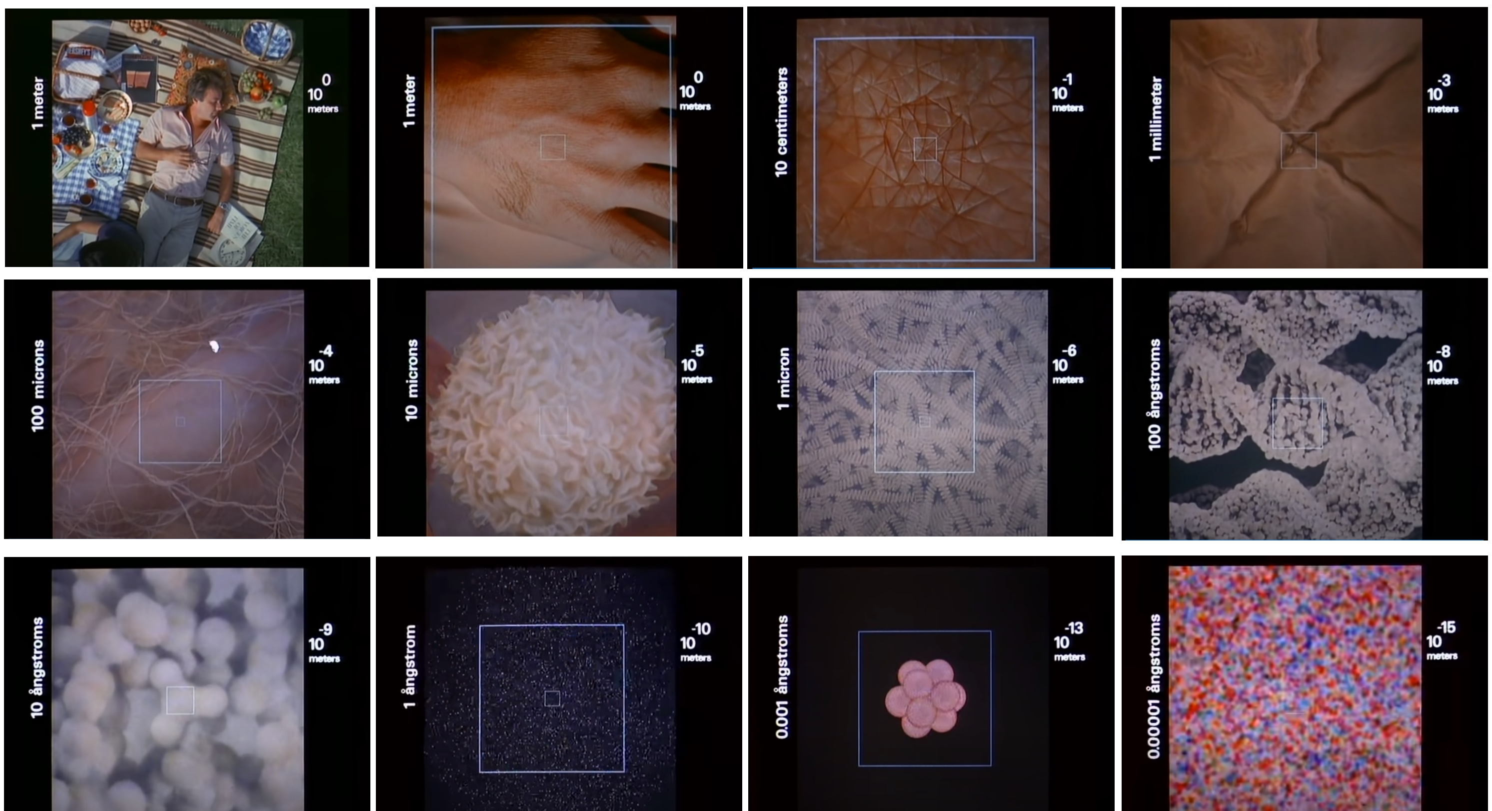
very short time scales
<20 picoseconds
20 x 10^{-12} s
0.000000000020 s

Legendary film “Powers of Ten”

by Charles and Ray Eames (1977)

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

a journey through the vast spatial dimension of the universe



Charles and Ray Eames: responsible for groundbreaking contributions in architecture, furniture design, industrial design, manufacturing design, and photographic arts.

Watch the zoom-in portion of film

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

(I highly recommend watching the whole thing, including the zoom-out portion, later!)

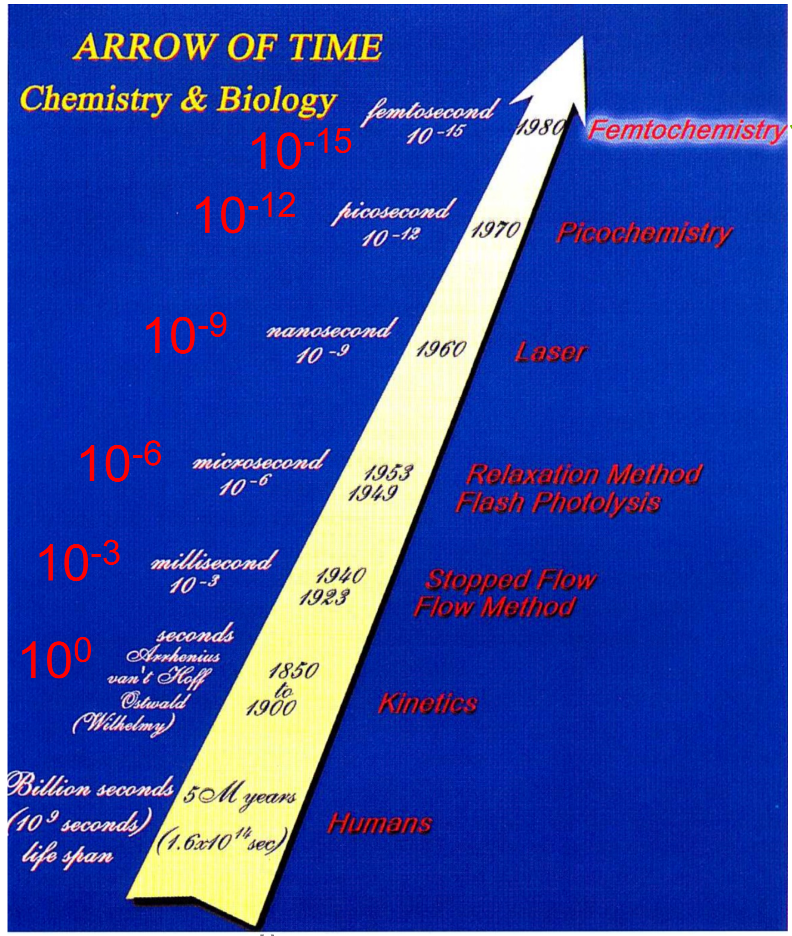
What about time?

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



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

What about time?

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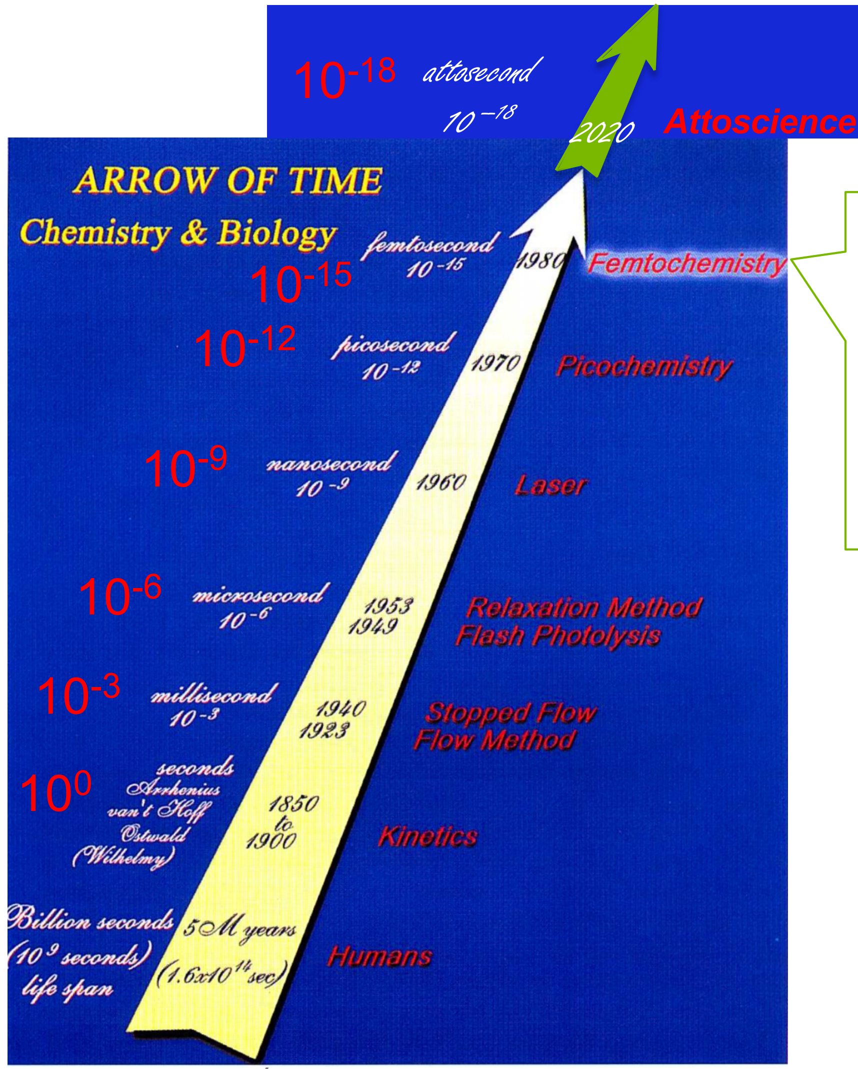


electron dynamics

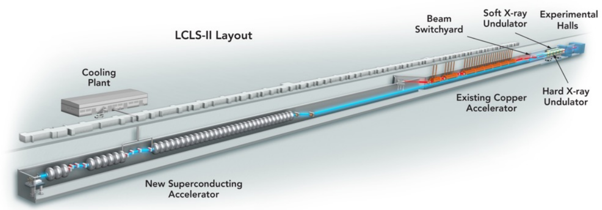
enabled observations of chemical bonds breaking, forming, or geometrically changing

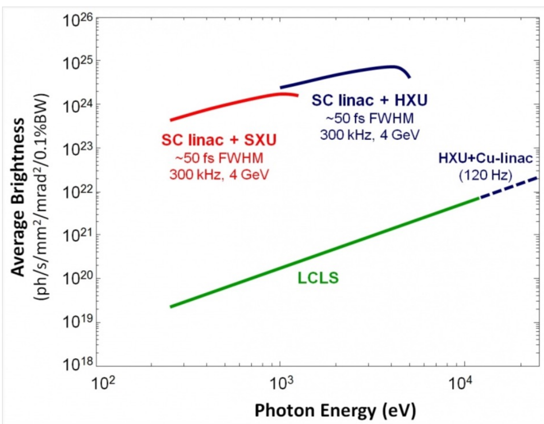
Exciting upgrades of x-ray facilities

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

LCLS-II

increased brightness and repetition rate

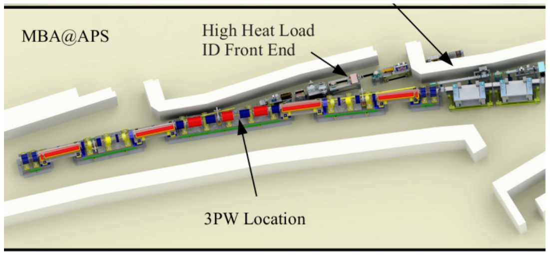


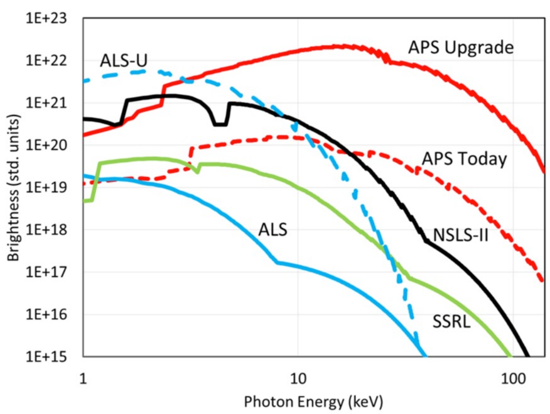


as fs ps

APS-U

increased brightness and coherence





10's ps ns µs ms s

time

This lecture:

Orders of magnitude in time:

an exploration of ultrafast dynamics through x-ray measurements

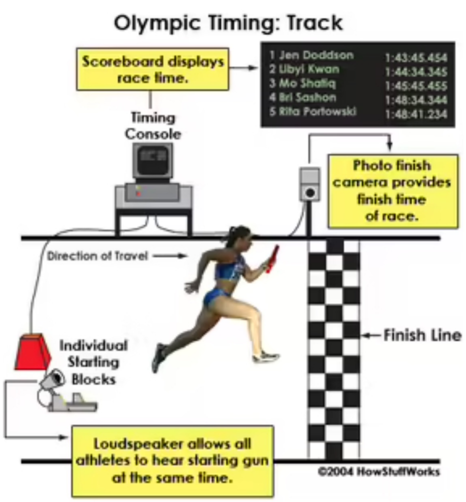
10^{-3} seconds	10^{-6} seconds	10^{-9} seconds	10^{-12} seconds	10^{-15} seconds	10^{-18} seconds

(A super quick overview of a sort-of random assortment of studies selected from the literature, during which we hope to gain general insights into how one can capture ultrafast dynamics with x-rays)

But first, Olympics timing technology!

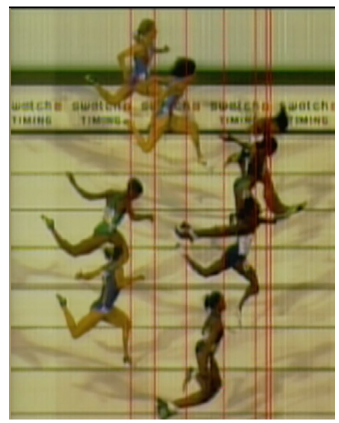
Timing athletes to 1/100th (or 1/1000th) of a second

Precise synchronization



All aspects are electronic, including the starting gun and starting blocks (FAT: fully automatic timing). Speakers behind each athlete to ensure no delays due to speed of sound.
Clock(s) with sufficient precision required. (Omega's 'Quantum Timer' is the clock used for Paris 2024.)

Detectors with sufficient speed



Devers vs. Ottey 100m (Atlanta 1996)
Devers wins gold by <0.01 s

Human vision
How fast? ~30 ms, ~30-50 Hz

Fast video
For gaming, or sports where slow motion reply is important:
Frame rate = 60 Hz, 120 Hz, 240 Hz
Exposure rate set to be twice the frame rate (exp. times ~8 ms, ~4 ms ~ 2 ms)

Photo finish
Composite of tall, 1-pixel wide images of the finish line, taken at a very fast frame rate (~ 10kHz)
In the composite, distance can be used to precisely measure time (1 pix width = ~0.1 m s)

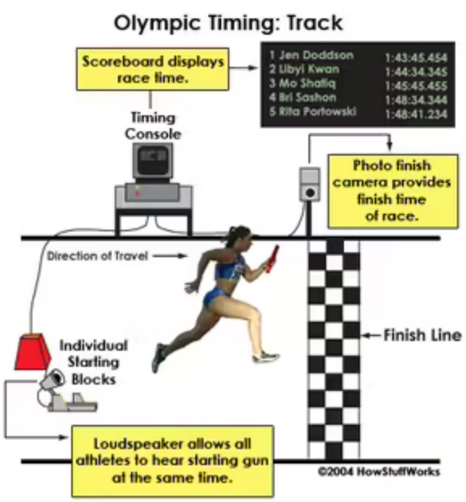
Omega's Scan'O'Vision Utlimate is being used at the 2024 Olympics and captures 40,000 Hz at the finish line.

But first, Olympics timing technology!

Timing athletes to 1/100th (or 1/1000th) of a second

PARIS 2024

Precise synchronization



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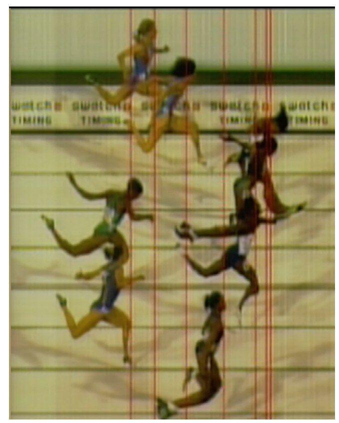

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Fast video
For gaming, or sports
is important:
Frame rate = 60 Hz or
Exposure rate set to be
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Generally, the more pixels in an image, the slower the frame rate

Photo finish
Composite of tall, 1-pixel wide images of the finish line, taken at a very fast frame rate (~ 10kHz)
In the composite, distance can be used to precisely measure time (1 pixel width = ~0.001 s)

Omega's Scan'O'Vision Utlimate is being used at the 2024 Olympics and captures 40,000 Hz at the finish line.

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

10^{-3} seconds

Dipteran flies 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*

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

Time-resolved X-ray tomographic microscopy

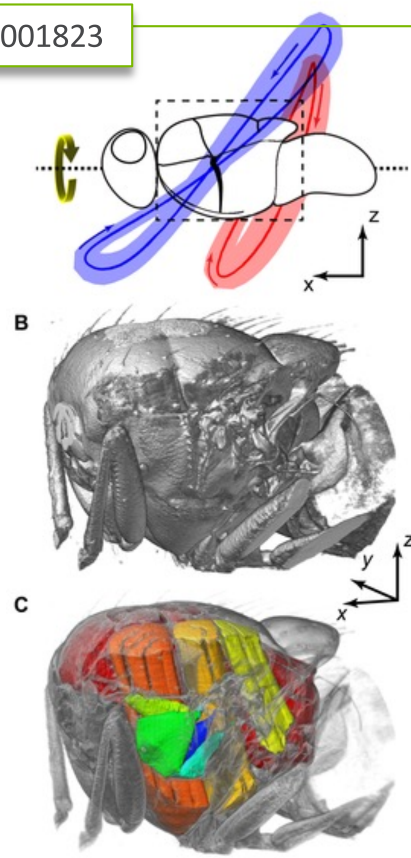
10^{-3} seconds

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

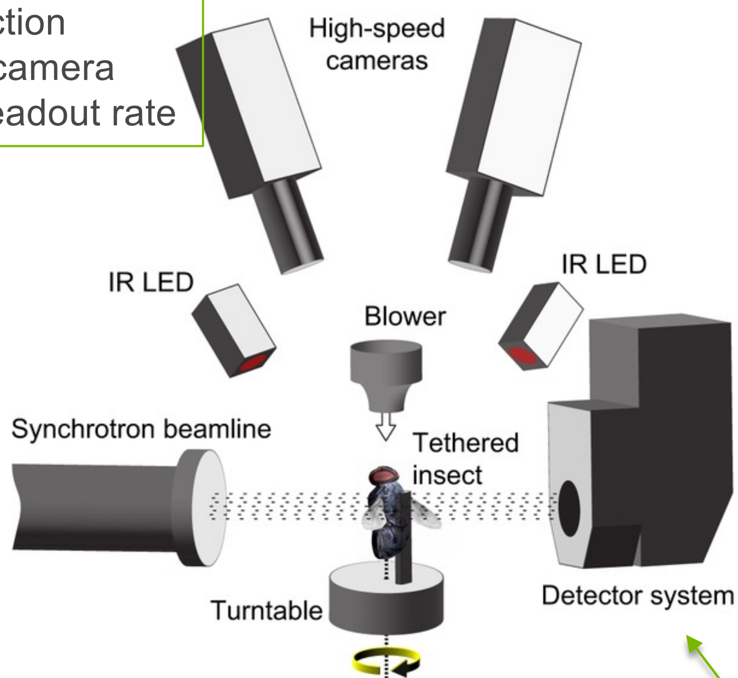
External visualization of the fly's thorax

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

Time-resolved microtomographic imaging

Measurement details

- IR detection
- CMOS camera
  4 kHz readout rate



- Ce-doped LuAG scintillator converts x-ray to visible
- CMOS camera, 2 kHz readout rate

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

TOMCAT beamline of the Swiss Light Source

- tethered fly, 4 revolutions per 4s recording
- Wingbeat: 145 Hz; ~ 600 wingbeats per recording
- ~8,000 radiographs per recording
- Simultaneously, two high-speed cameras record IR images to yield 3D wingtip position vs. time
- x-ray images (i.e. radiographs) grouped according to the wingtip position, tomograms reconstructed for 10 evenly spaced phases of the wingbeat
- End result: one composite wingbeat with 10 time steps, where every time step pools radiographs from ~600 wingbeats

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

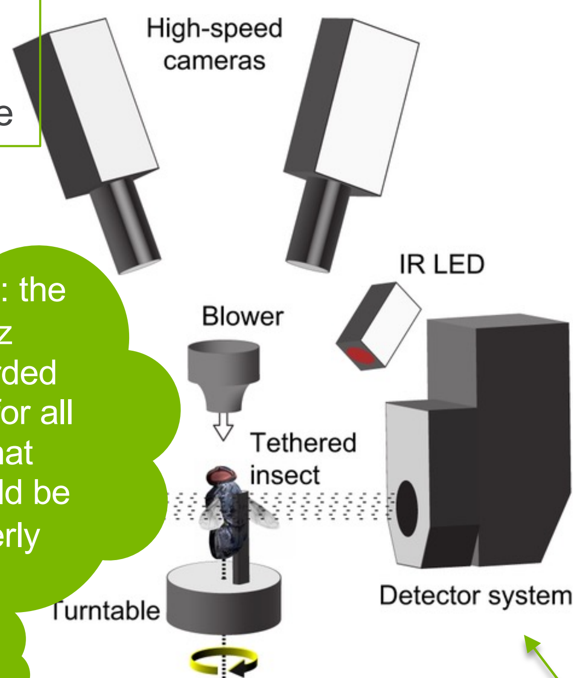
Time-resolved microtomographic imaging

Measurement details

10^{-3}
seconds

- IR detection
- CMOS camera
  4 kHz readout rate

Synchronization: the DAQ (80 kHz sampling) recorded exposure times for all cameras so that radiographs could be grouped properly



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  time steps, where
  radiographs from

Time resolution governed by frame rate

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- CMOS camera, 2 kHz readout rate

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

Time-resolved microtomographic imaging

videos

10^{-3}
seconds

https://www.psi.ch/en/news/media-releases/x-rays-film-inside-live-flying-insects-in-3d

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

Time-resolved microtomographic imaging

More to explore

10^{-3}
seconds

Using X-ray tomoscopy to explore the dynamics of foaming metal (200 tomograms per second!)
https://www.nature.com/articles/s41467-019-11521-1

Fast *in situ* 3D nanoimaging: a new tool for dynamic characterization in materials science (nanoimaging!)
https://doi.org/10.1016/j.mattod.2017.06.001

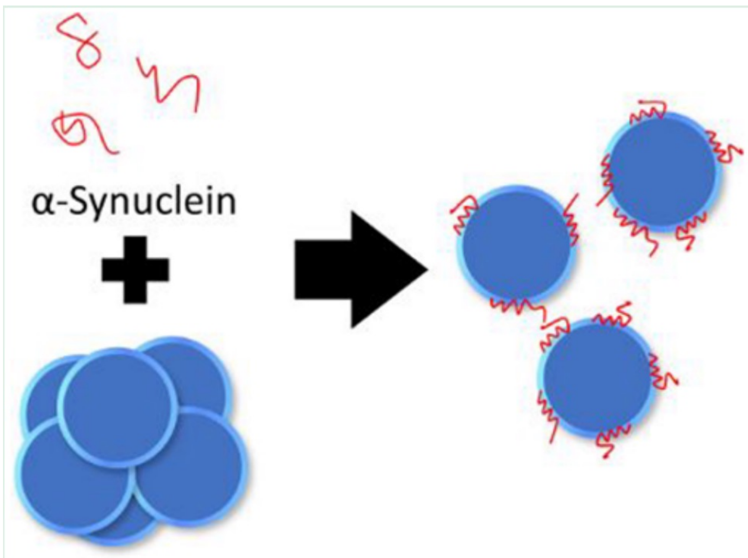
Recent blowfly study (no x-rays, but machine learning and robotics!)

Machine learning reveals the control mechanics of an insect wing hinge
Melis, J.M., Siwanowicz, I. & Dickinson, M.H., *Nature* **628**, 795–803 (2024)
https://doi.org/10.1038/s41586-024-07293-4

https://youtu.be/J-guci0Exz8?si=aFbEwha5YLYnt1yE

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

10^{-6} seconds



- 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
- These authors used 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?)

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

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

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

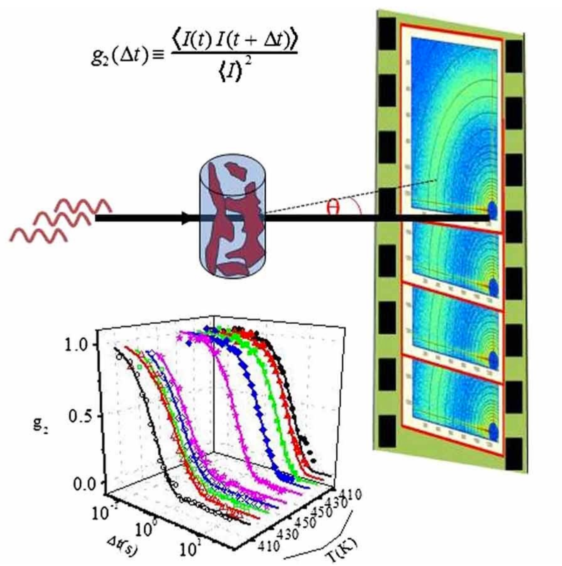
Corresponding author:

Prof. Ka Yee C. Lee

THE UNIVERSITY OF CHICAGO

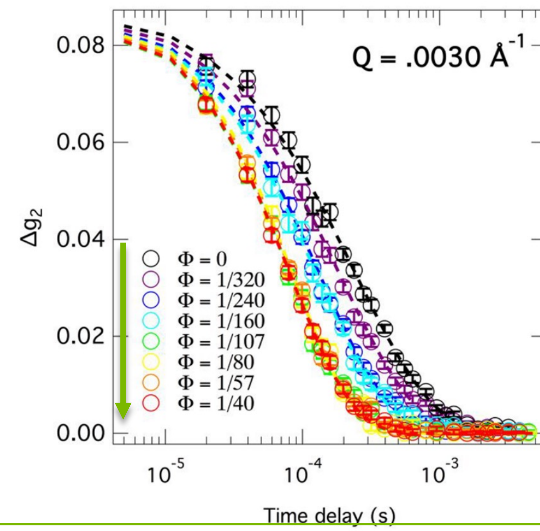
XPCS basics

$$g_2(\Delta t) \equiv \frac{\langle I(t)\, I(t+\Delta t)\rangle}{\langle I\rangle^2}$$



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

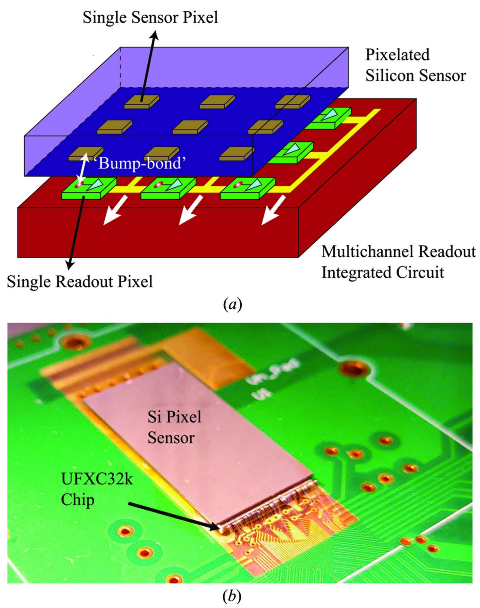


XPCS reveals increasing α-synuclein enhances diffusivity of the spherical nanoparticle lipid bilayers

α-Synuclein Sterically Stabilizes Spherical Nanoparticle-Supported Lipid Bilayers

Measurement details

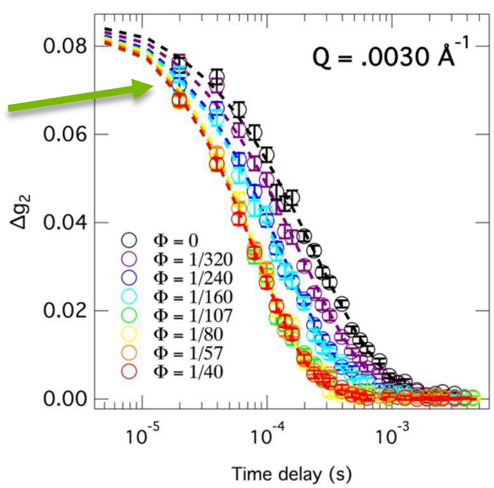
10^{-6} seconds



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



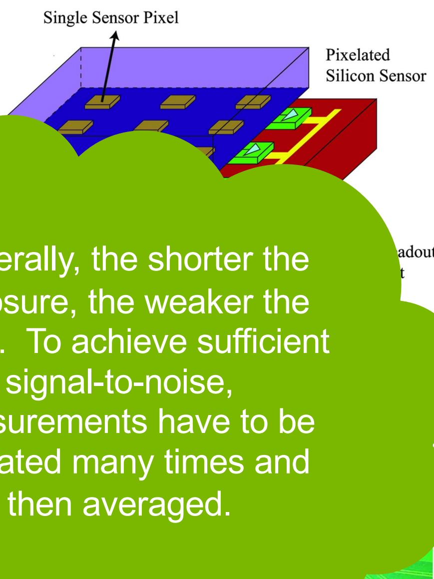
- 10.91 keV, $4x10^{10}$ ph/s
- 4 μm (v) x 15 μm (h) x-ray spot
- fresh spot on sample, 4 s acquisition of images
- 300 acquisitions yield final autocorrelation function

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

α-Synuclein Sterically Stabilizes Spherical Nanoparticle-Supported Lipid Bilayers

10^{-6} seconds

Measurement details



Generally, the shorter the exposure, the weaker the signal. To achieve sufficient signal-to-noise, measurements have to be repeated many times and then averaged.

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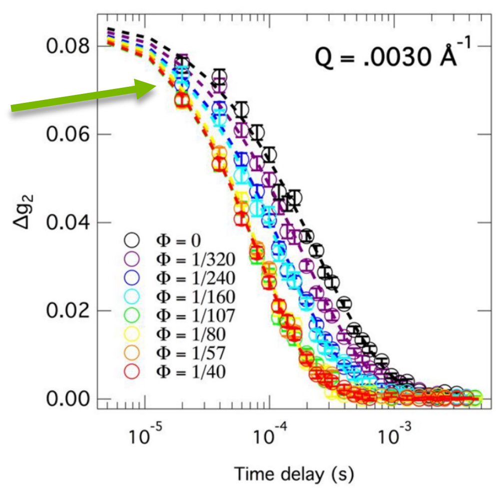


https://pubs.acs.org/doi/pdf/10.1021/acsabm.8b00774

X-ray Photon Correlation Spectroscopy

More to explore

10^{-6}
seconds

X-ray photon correlation spectroscopy

Oleg G Shpyrko , J. Synchrotron Rad. (2014). 21, 1057-1064
https://doi.org/10.1107/S1600577514018232

Sub-Microsecond Resolved Multi-Speckle X-Ray Photon Correlation Spectroscopy with a Pixel Array Detector

Zhang, Q.; Dufresne, E. M.; Narayanan, S.; Maj, P.; Koziol, A.; Szczygiel, R.; Grybos, P.; Sutton, M.; Sandy, A. R.. J. Synchrotron Radiat. 2018, 25, 1408−1416.

X Ray Photon Correlation Spectroscopy for the study of polymer dynamics

Aurora Nogales, Andrei Fluerasu, European Polymer Journal
Volume 81, August 2016, Pages 494-504 https://doi.org/10.1016/j.eurpolymj.2016.03.032

Nanosecond X-Ray Photon Correlation Spectroscopy on Magnetic Skyrmions

M. H. Seaberg, *et al.* Phys. Rev. Lett. **119**, 067403 (2017)
https://doi.org/10.1103/PhysRevLett.119.067403 (LCLS)

Alpha-synuclein

https://www.youtube.com/watch?v=ns2ynOpHYh8

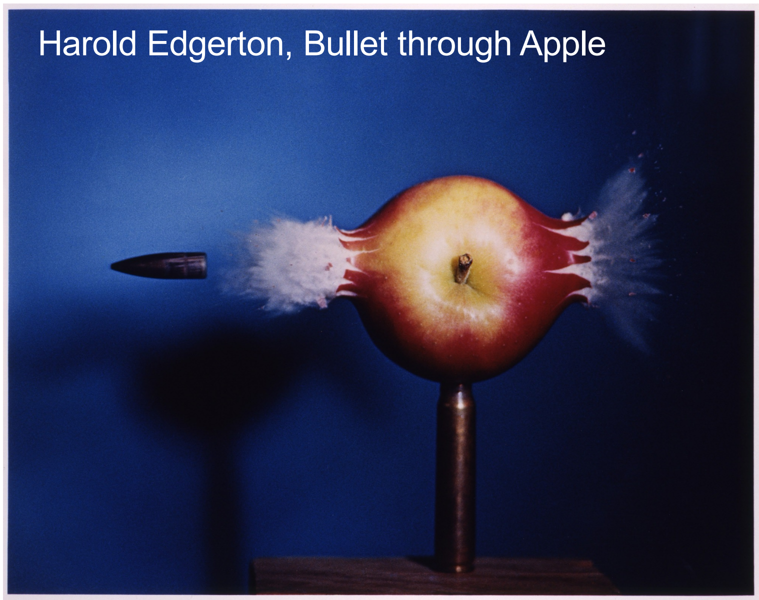
https://youtu.be/29r6WFnaAT8?si=vOUWVBp2Yp-KS-IG

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



Camera's shutter speed is too slow to capture motion

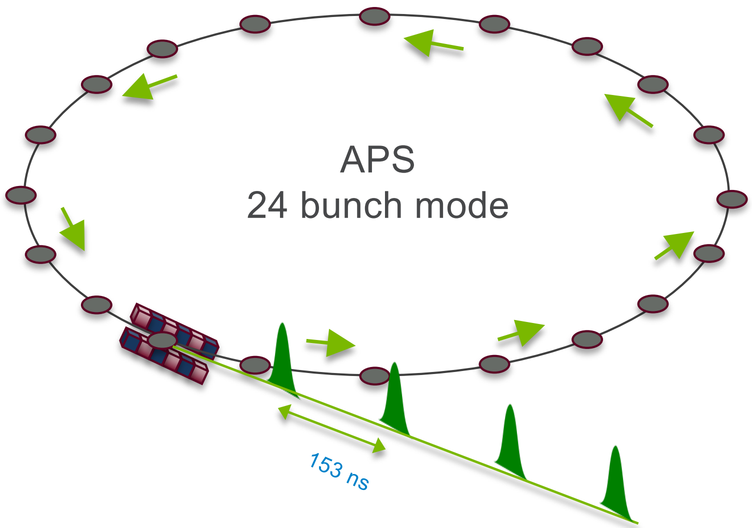
Flash duration is short enough

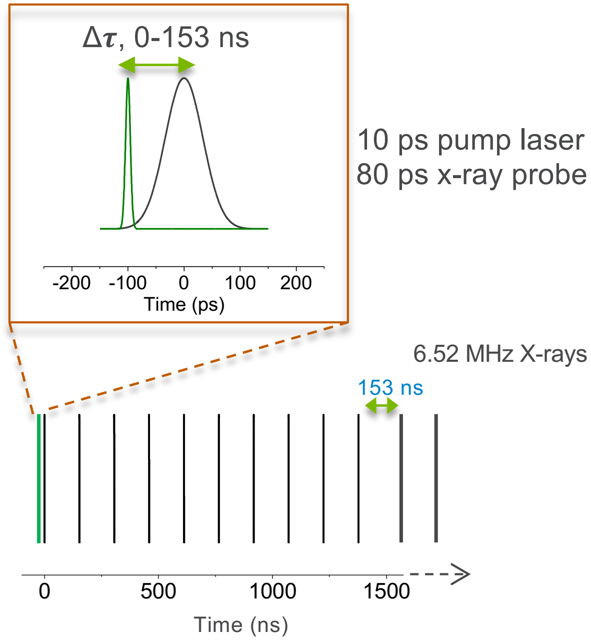
flash duration: ~300 ns

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

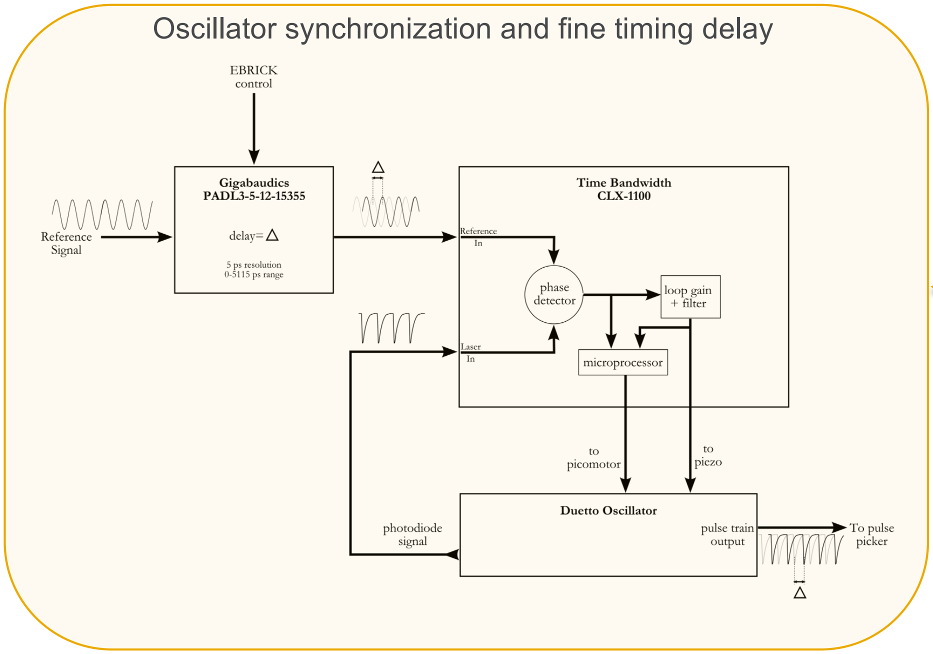


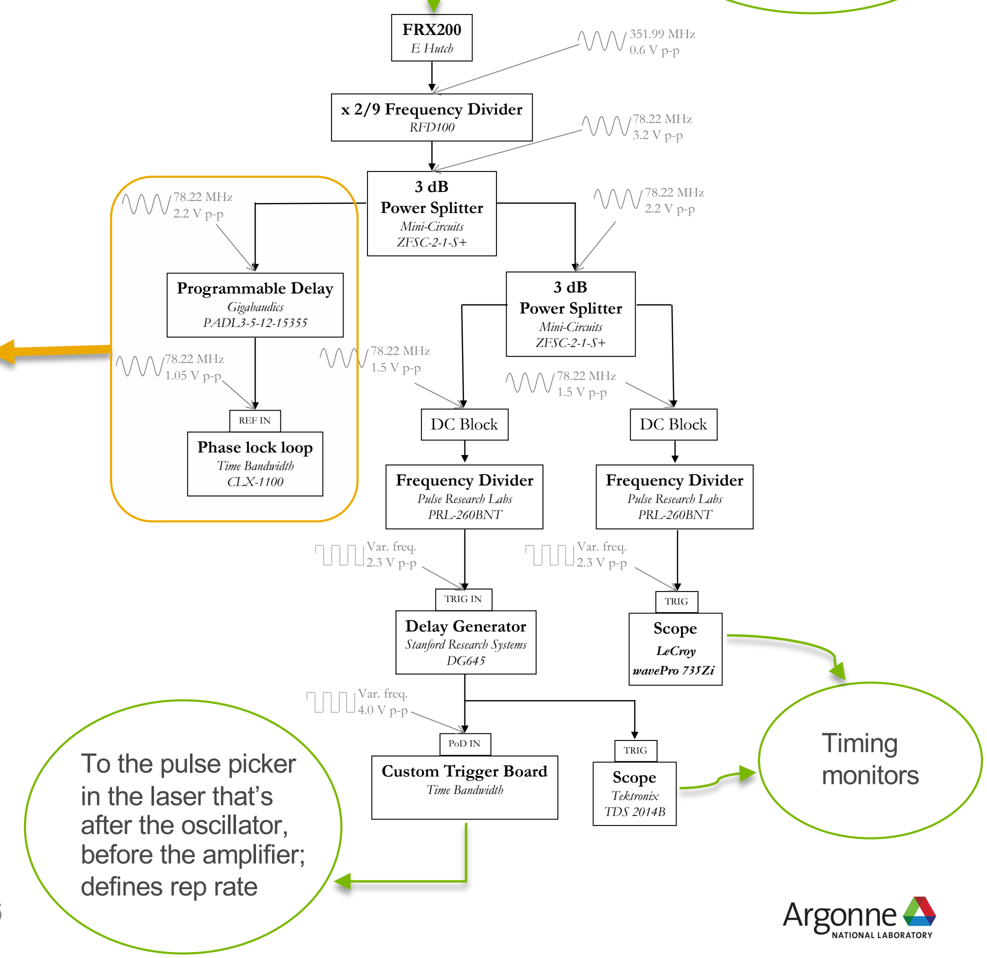


- need detectors that can isolate individual pulses (or groups of pulses)
- variable repetition rate pump laser to access different temporal regimes
- pump laser is temporally “locked” to the storage ring RF (352 MHz)
- control of laser delays with respect to the x-ray pulses is done electronically
-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

Synchronizing the laser and x-rays to ~few ps

Synchrotron-laser timing schematic for the Duetto laser system at the APS

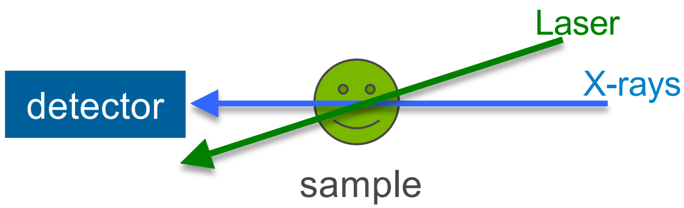




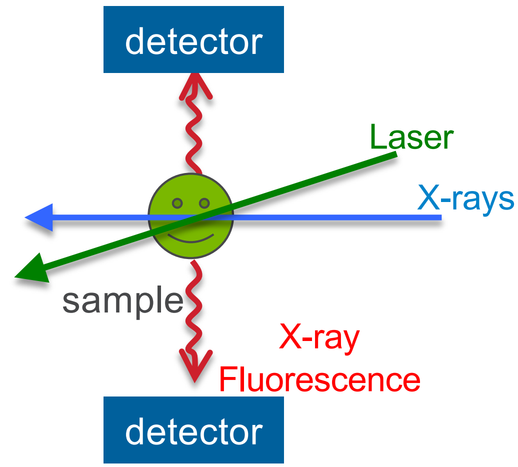
Laser-pump, synchrotron-x-ray-probe basics

spatial considerations

scattering, diffraction, imaging…

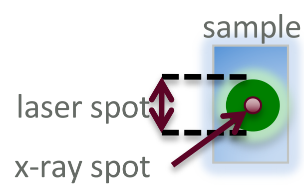


fluorescence detection (XAS)



- precisely overlap x-rays and laser at sample

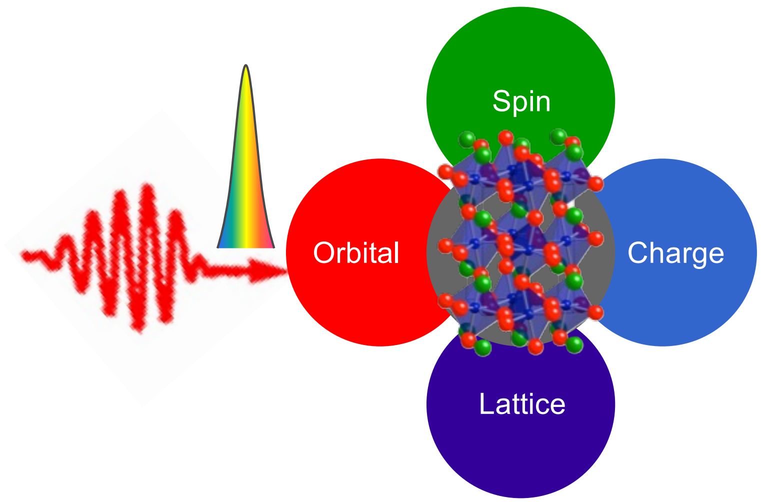
- x-rays smaller than laser spot to probe volume with highest excitation fraction



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

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
- Understanding often requires following several degrees of freedom through time-resolved 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:

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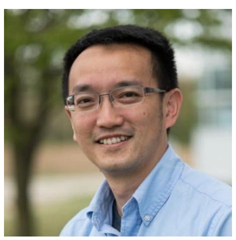
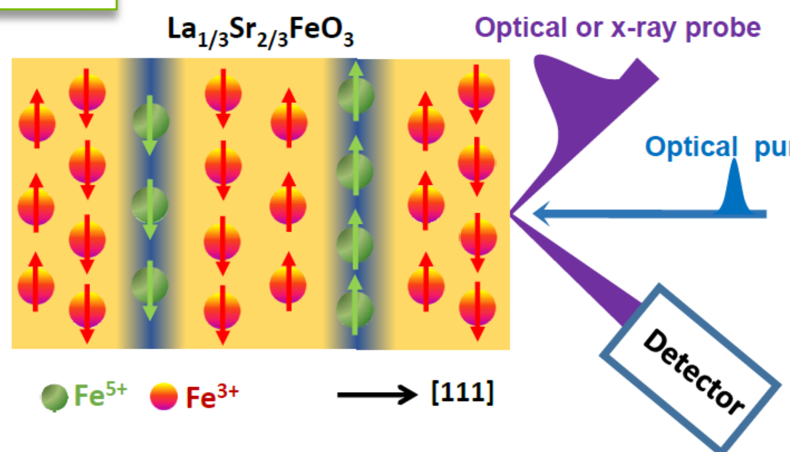
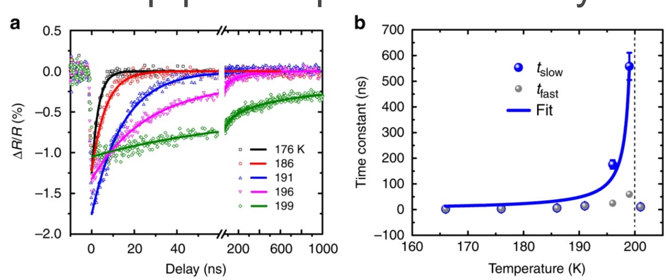


Argonne NATIONAL LABORATORY



Pump-probe optical reflectivity



- $La_{1/3}Sr_{2/3}FeO_3$ (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)

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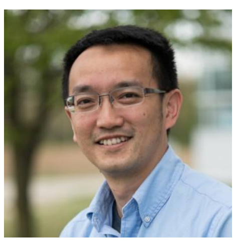
Anand Bhattacharya

Haidan Wen



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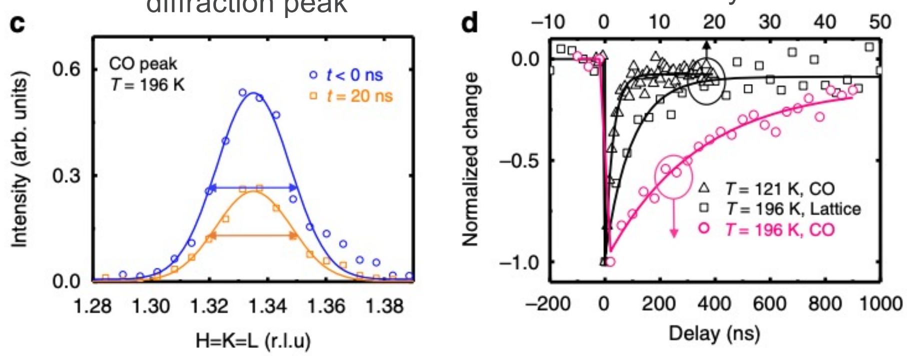
Measured intensities of 2 diffraction peaks as a function of pump-probe delay:

-One sensitive to charge ordering

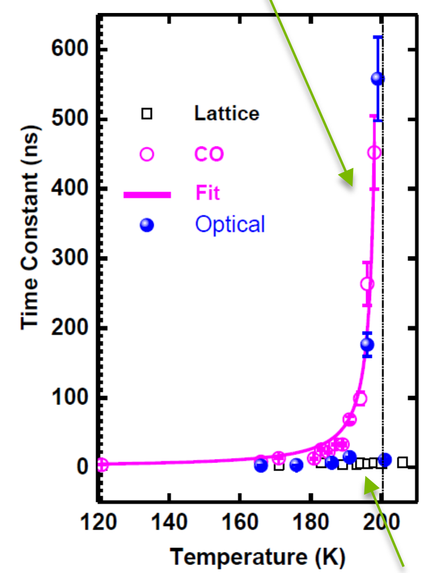
-The other sensitive to the lattice constant

Charge ordering diffraction peak

Peak intensity vs. p-p delay



Gets large



Stays small

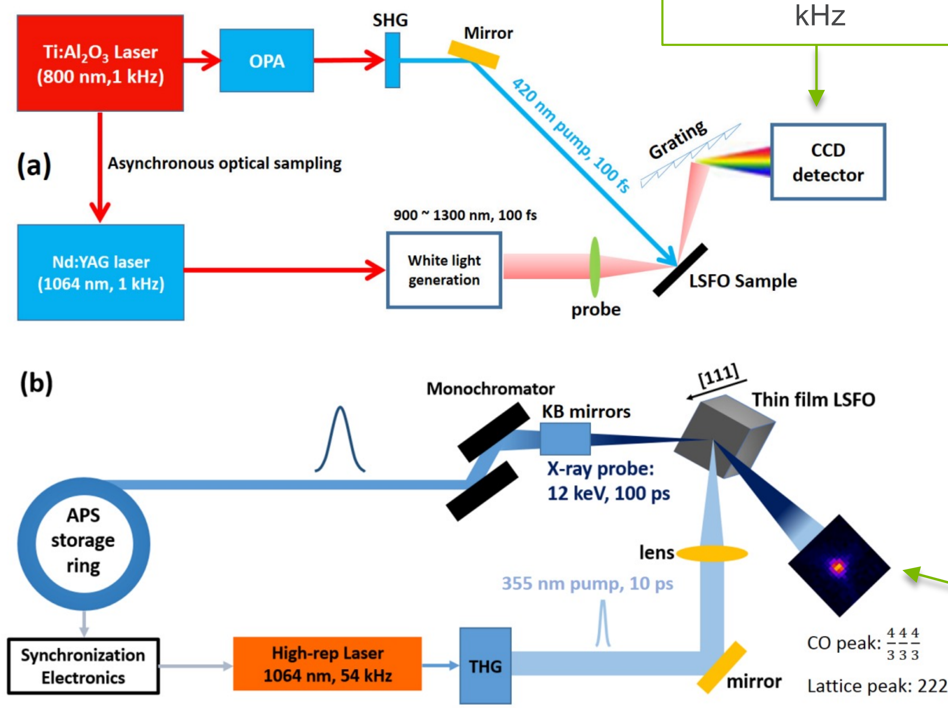
Charge order recovery *is* uncoupled to lattice cooling – First principles calculations point towards a magnetic interaction driven mechanism

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

Measurement details

10^{-9} seconds

Measures spectrum of probe light at 1 kHz



7-ID-C APS

Multimodal characterization:

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

Detected using the Pilatus100k, gated at 54 kHz

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

10^{-9} seconds

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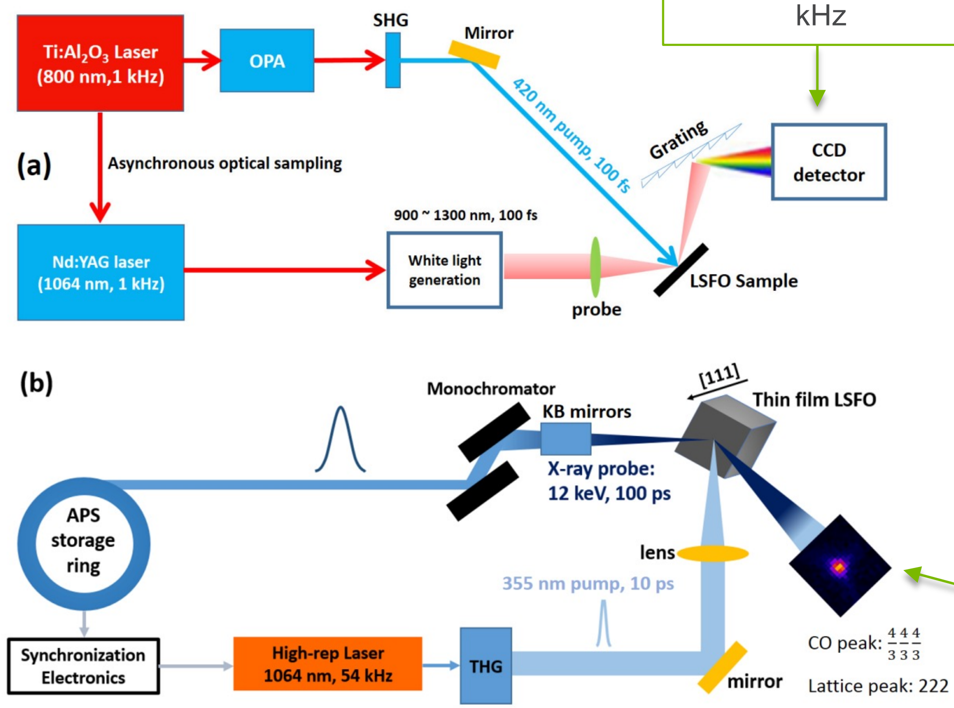


Detected using the Pilatus100k, gated at 54 kHz

7-ID-C APS

The probe pulses define the temporal resolution, not the detector.

...tion:

...bes

...tion rate optical ...mp crucial to observe small ...harge ordering diffraction peak

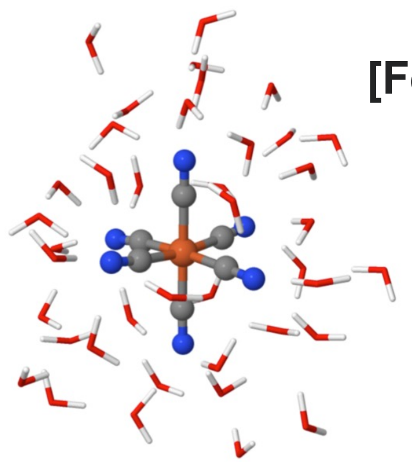
Zhu, Y., Hoffman, J., Rowland, C.E. *et al. Nat Commun* **9,** 1799 (2018). https://doi.org/10.1038/s41467-018-04199-4

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

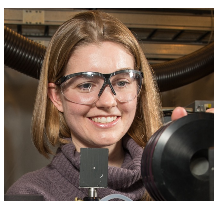
10^{-12} seconds

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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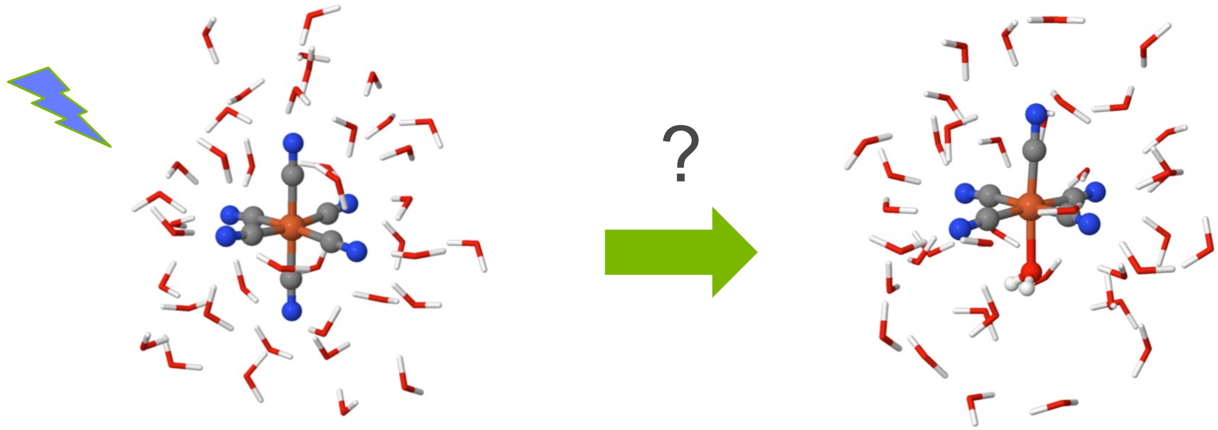
Pacific Northwest NATIONAL LABORATORY

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

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



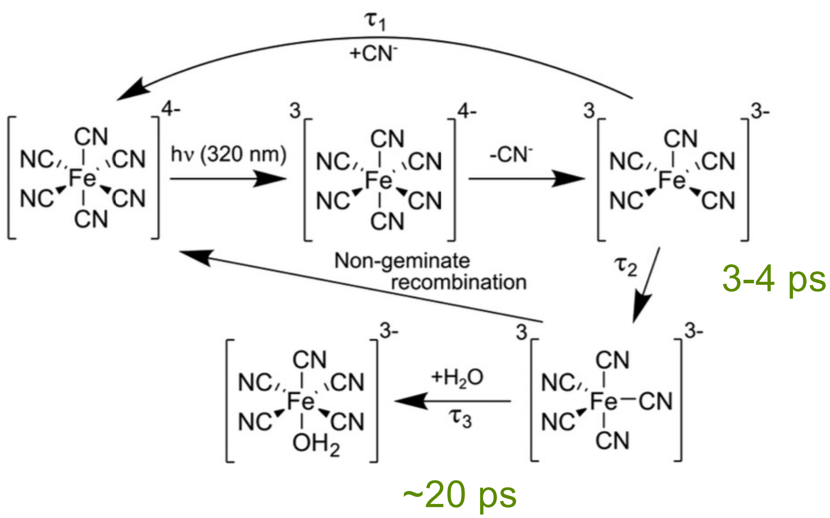
Ultrafast studies of the aquation reaction

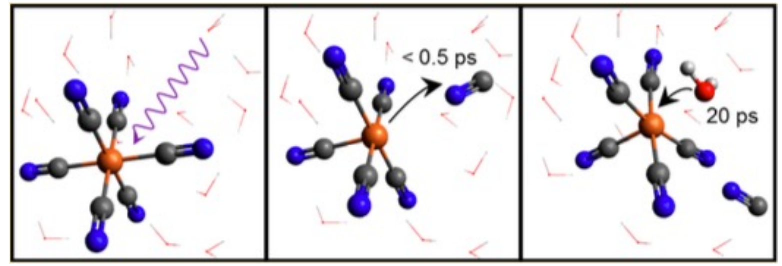
10^{-12} seconds

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

Proposed reaction scheme





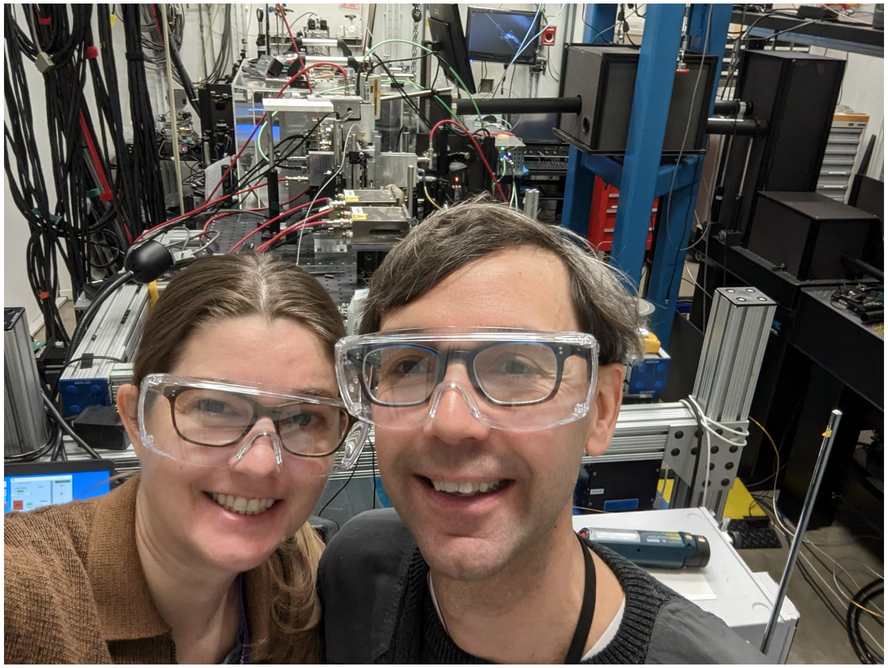
M. Reinhard *et al.* JACS **139**, 7335 (2017)
M. Reinhard *et al.* Struc. Dyn. **1**, 024901 (2014)
M. Chergui, Coord. Chem. Rev. **372**, 52 (2018)

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

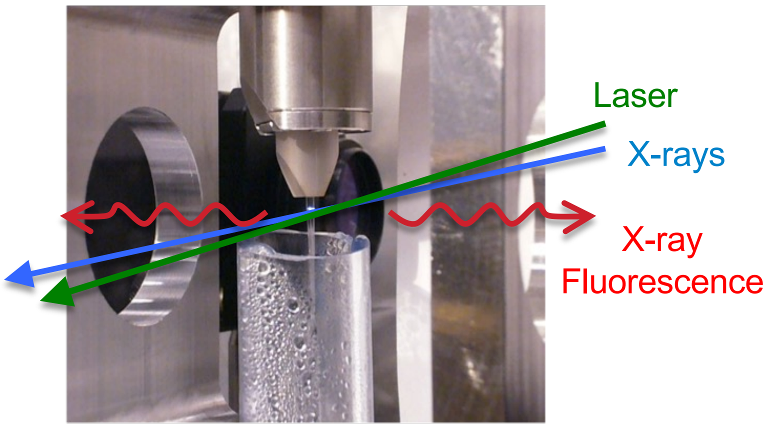
(presently being moved to the new 25-ID!)

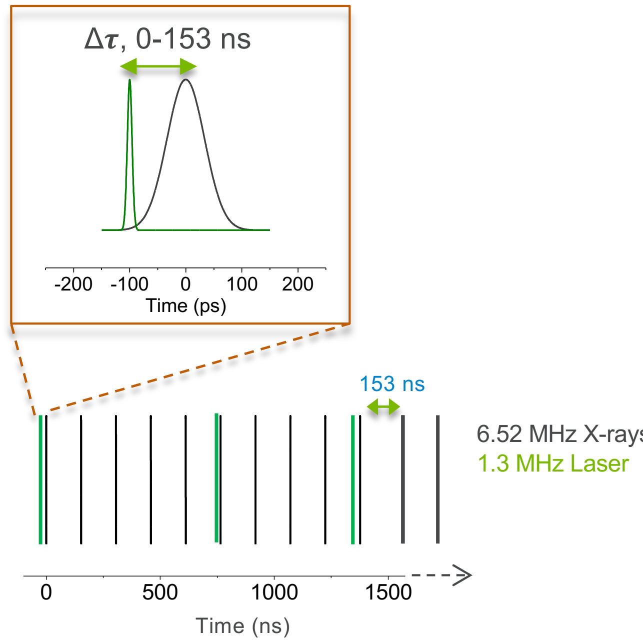
10^{-12} seconds

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

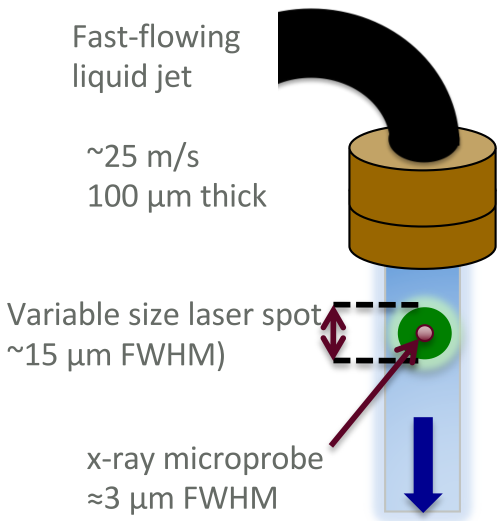
- electronic control of laser delay with respect to the x-ray pulses
- variable repetition rate pump laser

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.

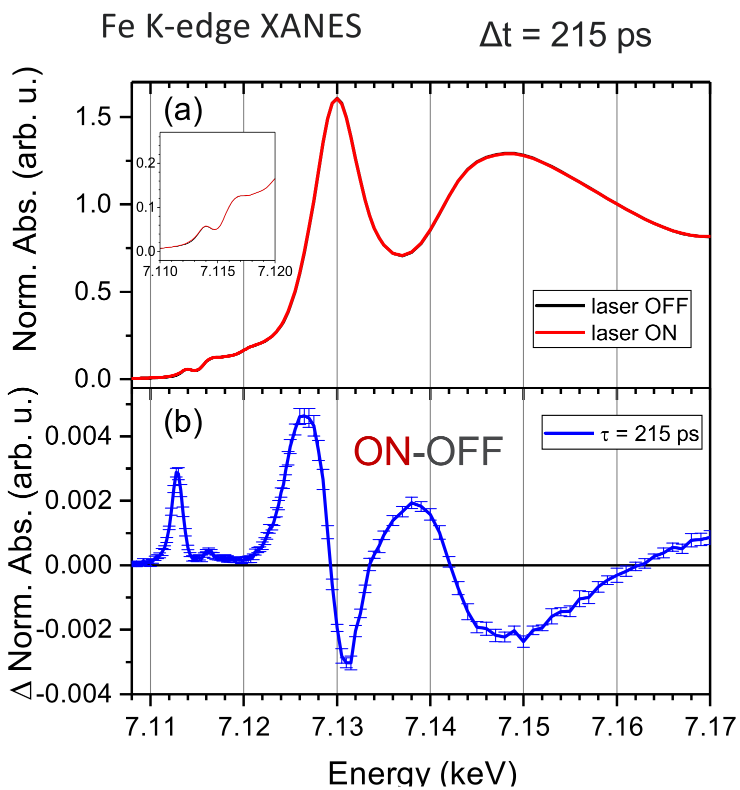
- To get "simultaneously" measured ground state (OFF) spectrum, need to refresh the sample volume between pump-probe cycles

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



XAS difference spectra

10^{-12} seconds



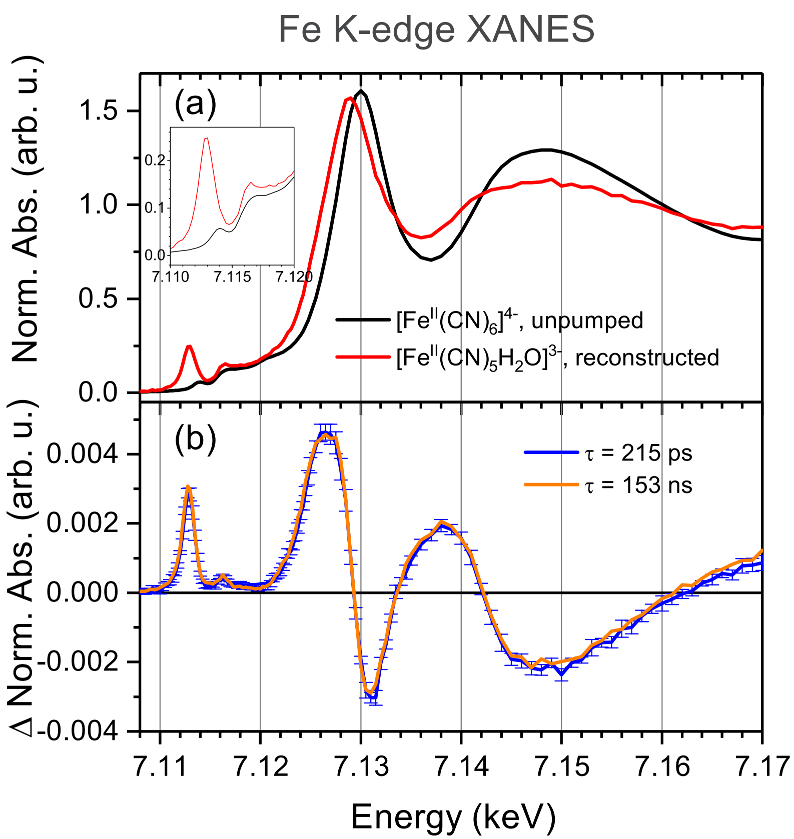
OFF = ground state spectrum

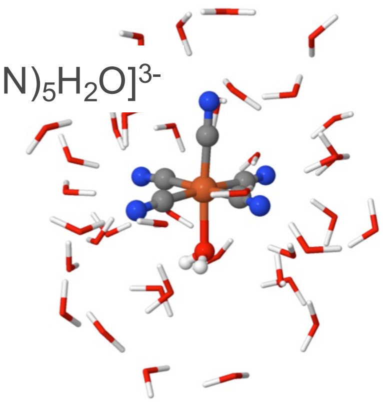
ON = (1-f)(ground state spectrum) + f (photoproduct(s) spectrum)

- 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

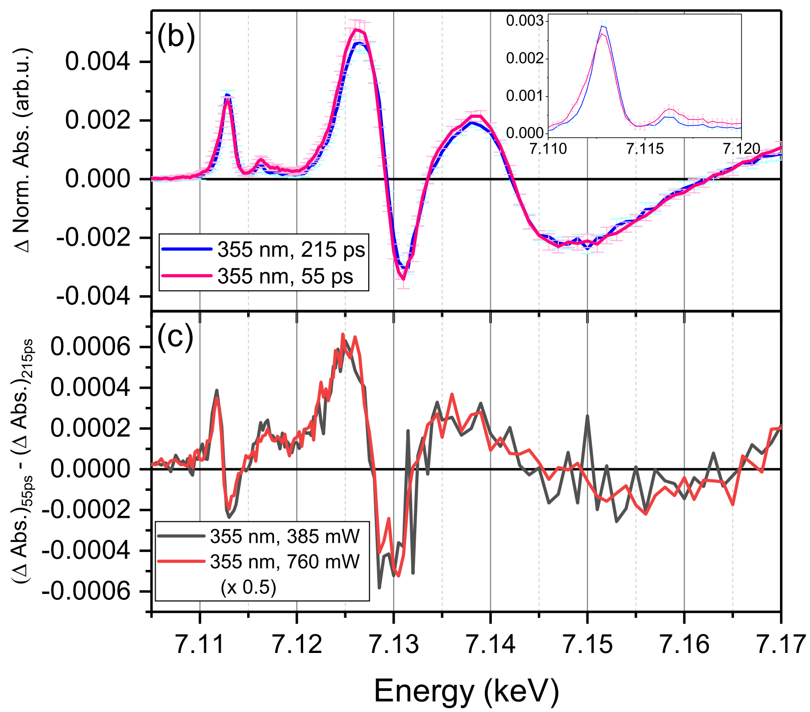
- long-lived (>2 μs)
- yield is small
- spectral features consistent with expectations

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

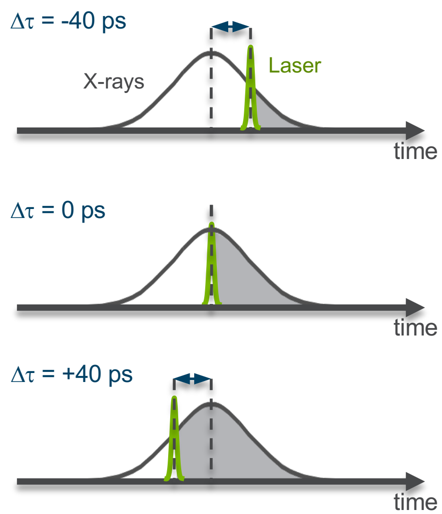
Observing sub-pulse-duration dynamics at the Advanced Photon Source

10^{-12} seconds

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

Time-slicing scheme

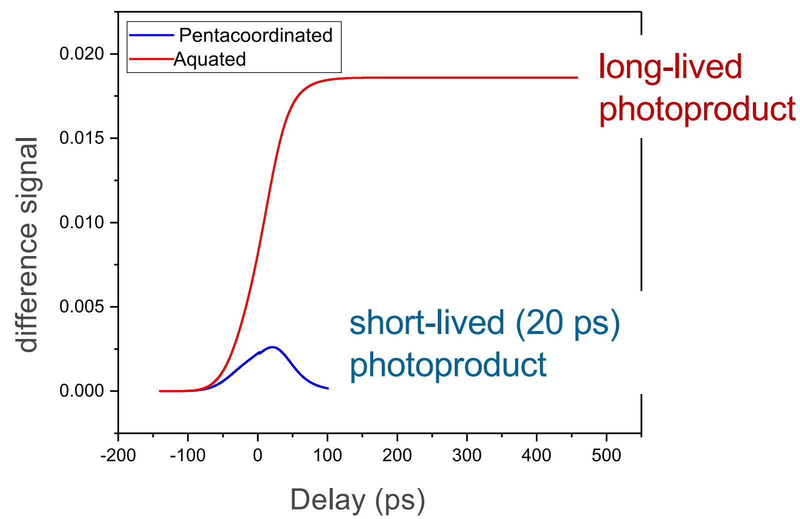
Enabled by dramatic gains in measurement efficiency



measured signal vs. time: convolution

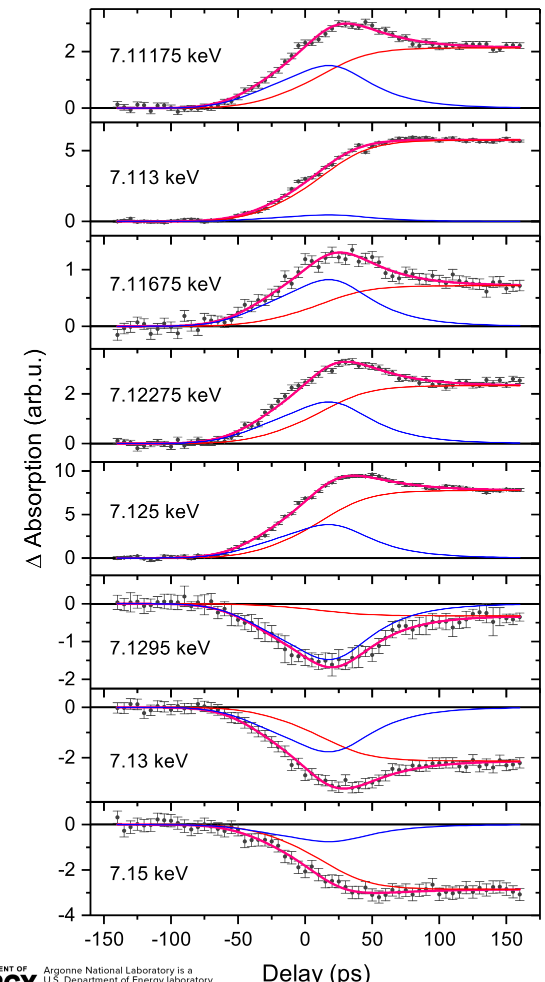
x-ray pulse temporal profile	⊗	temporal evolution of the population of the photoinduced species

"kinetic scan"



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

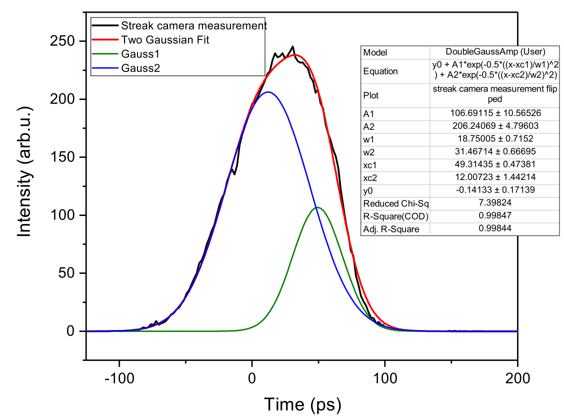
Global fit of kinetic scans



- kinetic model for time dependent concentrations:

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

- instrument response function:



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

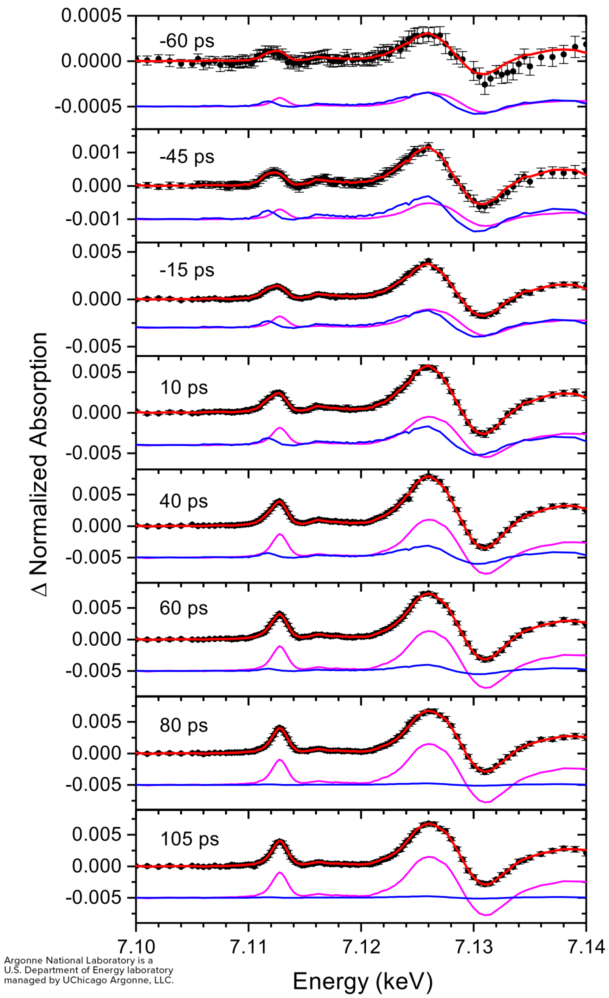
$[Fe^{II}(CN)_5]^{3-}$ growth: $\tau_1 \sim 1$ ps (fast)

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

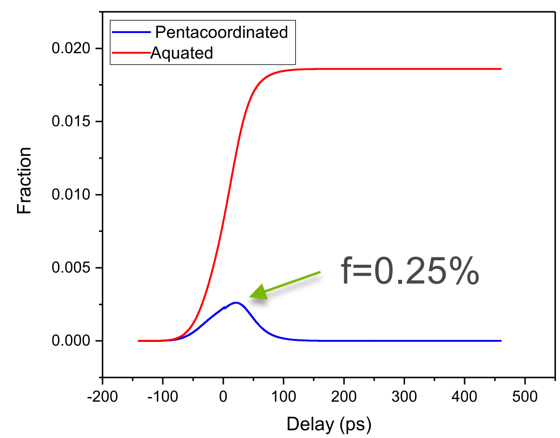
A. M. March *et al.*, J. Chem. Phys. (2019)

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

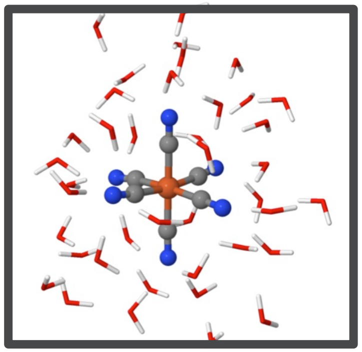


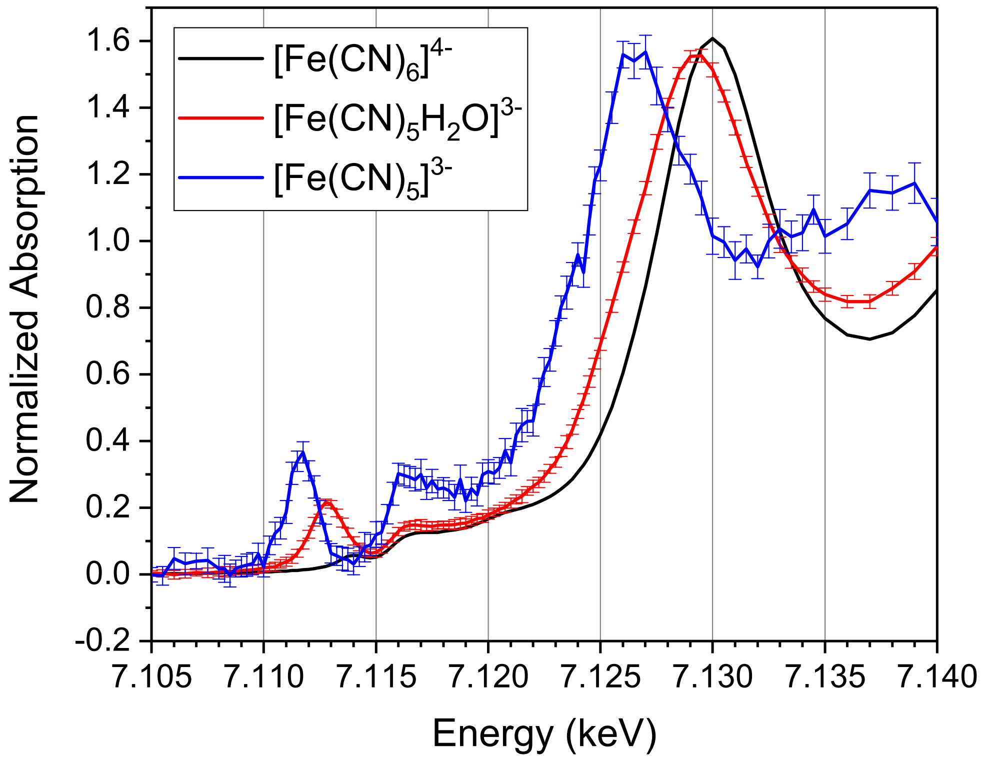
- known $[Fe^{II}(CN)_5H_2O]^{3-}$ fraction and kinetic model yields $[Fe^{II}(CN)_5]^{3-}$ fraction

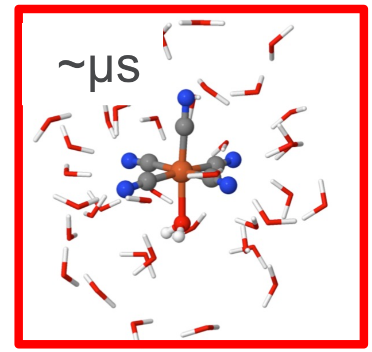
A. M. March *et al.*, J. Chem. Phys. (2019)

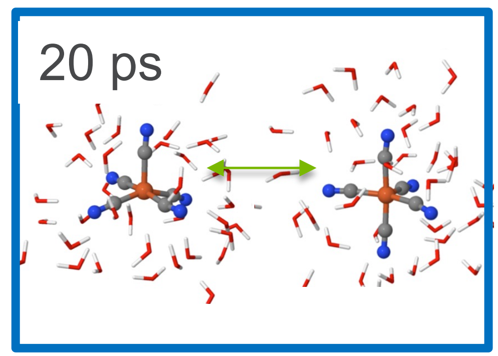
Reconstructed $[Fe^{II}(CN)_5]^{3-}$ spectrum

10^{-12}
seconds





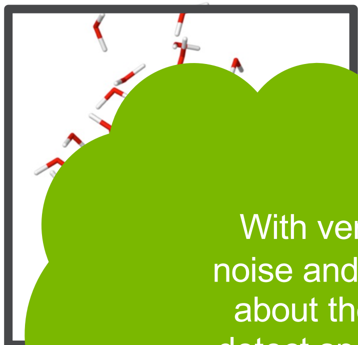


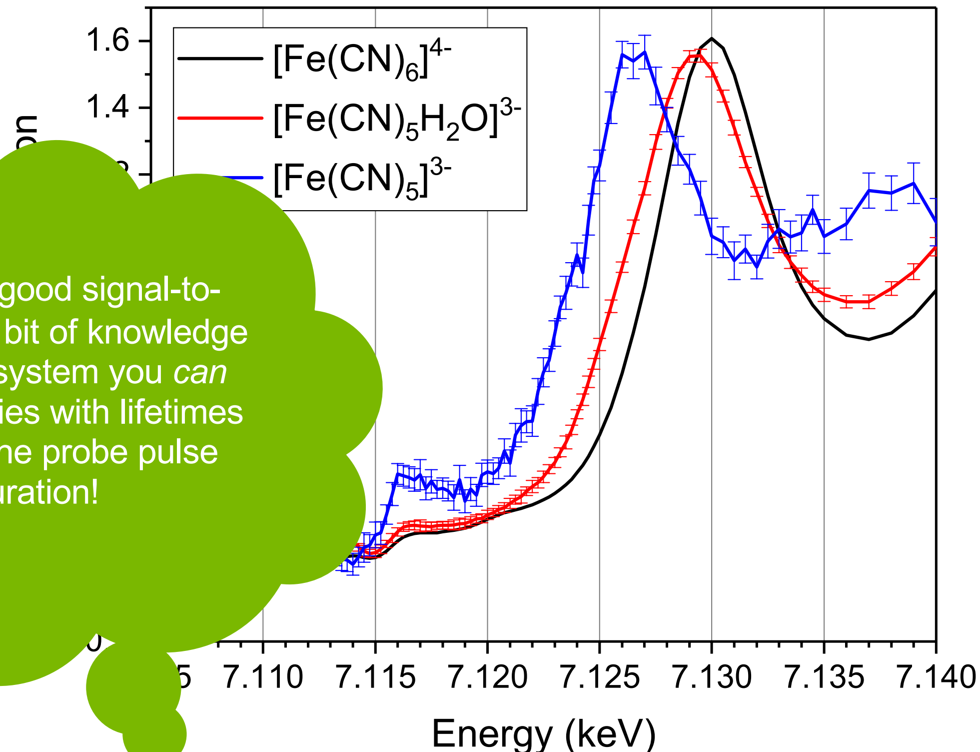


A. M. March *et al.*, J. Chem. Phys. (2019)

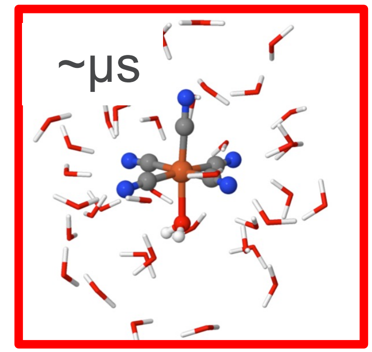
Reconstructed $[Fe^{II}(CN)_5]^{3-}$ spectrum

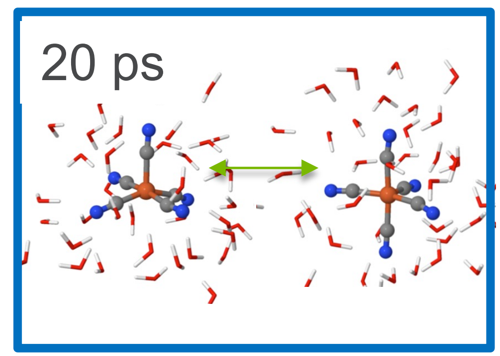
10^{-12} seconds





With very good signal-to-noise and a bit of knowledge about the system you *can* detect species with lifetimes less that the probe pulse duration!

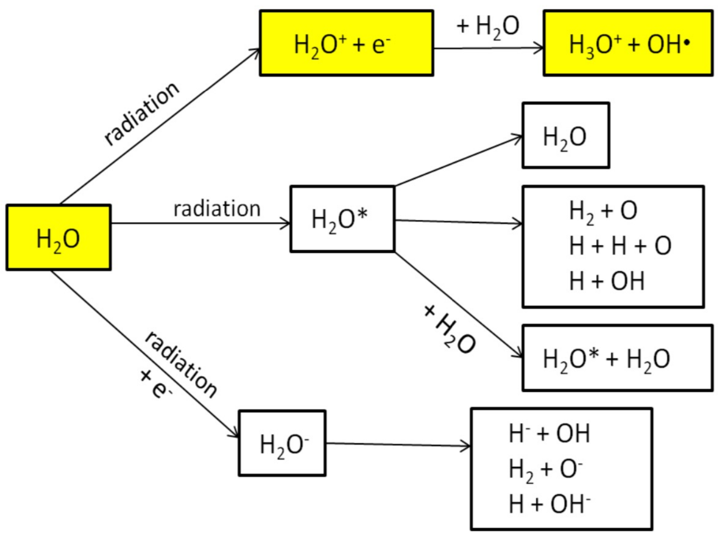




A. M. March *et al.*, J. Chem. Phys. (2019)

Tracking the primary chemical reaction that follows ionization of liquid water

10^{-15}
seconds



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

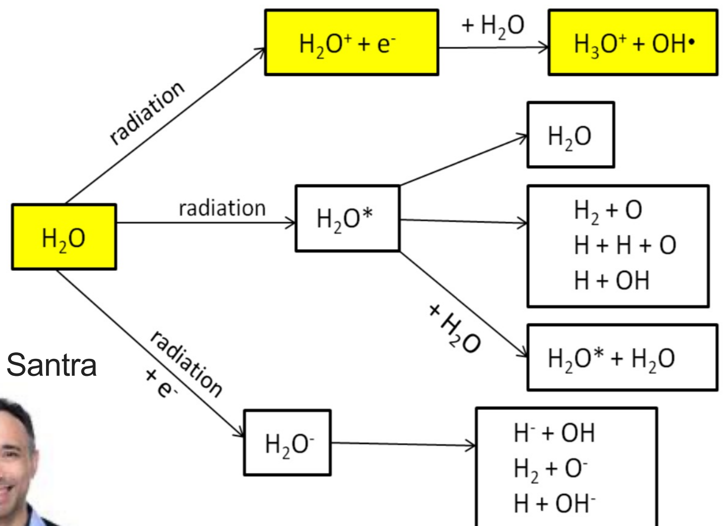
- Ionization of liquid water a universal phenomena accompanying interaction of radiation with matter
- Cascade of electrons, ions and radicals forms basis of solution and interfacial chemistry in aqueous environments
- Water major component in cells – biological damage triggered by ionization of water

Tracking the primary chemical reaction that follows ionization of liquid water

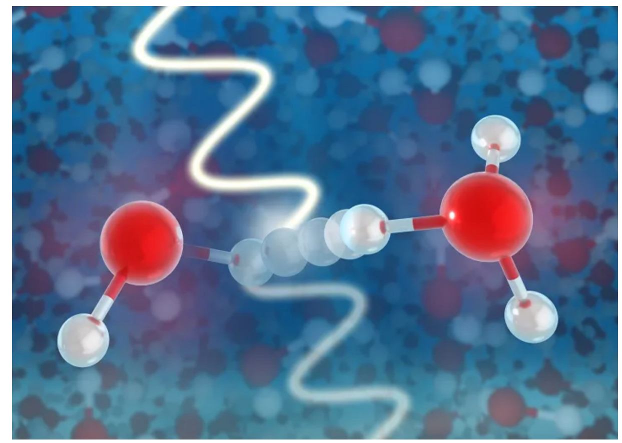
10^{-15} seconds

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:

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Robin Santra

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Argonne NATIONAL LABORATORY

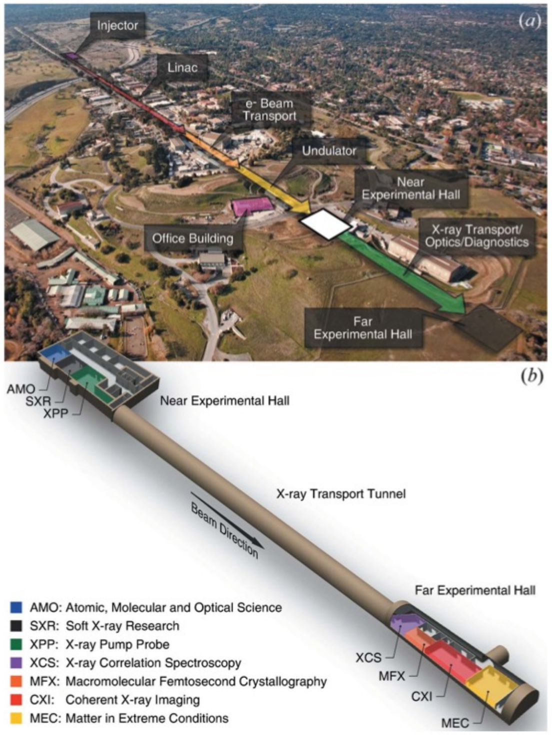
CFEL SCIENCE

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)

LCLS Experimental Team

10^{-15} seconds

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

Argonne
Gilles Doumy
Steve Southworth
Phay Ho
Anne Marie March
Andre Al Haddad
Yoshiaki Kumagai
Ming-Feng Tu
Linda Young

NTU
Zhi-Heng Loh
Tushar Debnath
M. Al-Shafiq

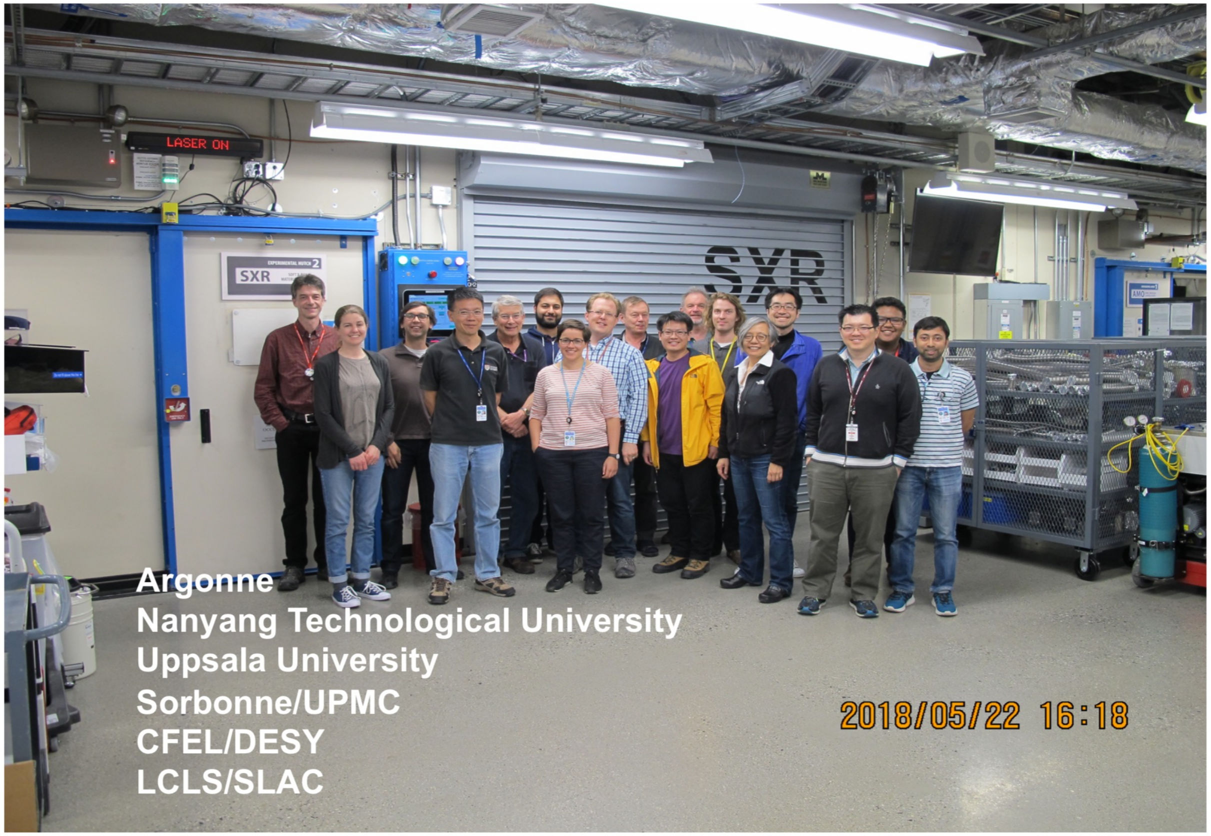
CFEL
Robin Santra
Caroline Arnold
Ralph Welsch
Ludger Inhester

Uppsala
J-E. Rubensson
Ludvig Kjellsson

Sorbonne-UPMC
Marc Simon

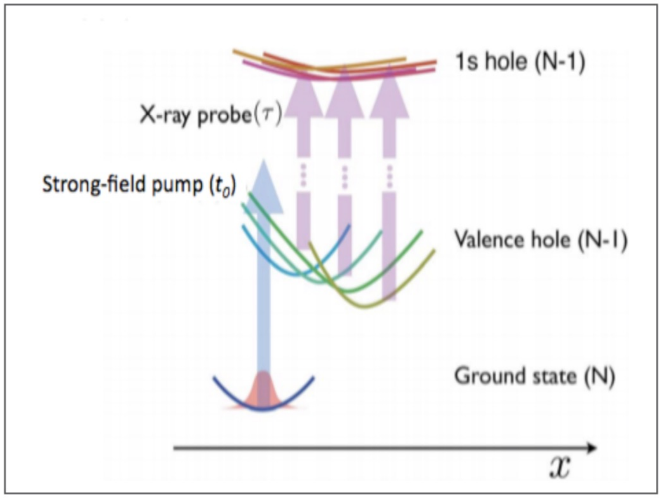
LCLS
Bill Schlotter
Stefan Moeller
Giacomo Coslovich
Jake Koralek
Dan DePonte

LR-01 EXPERIMENTAL TEAM

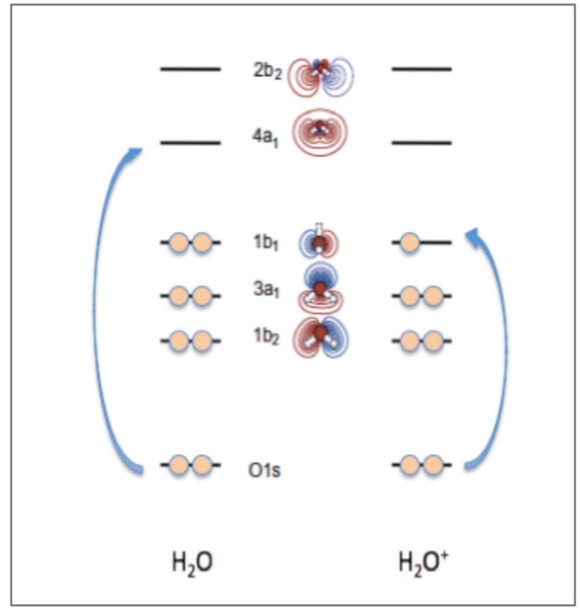


Strong-field ionization + ultrafast x-ray absorption

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

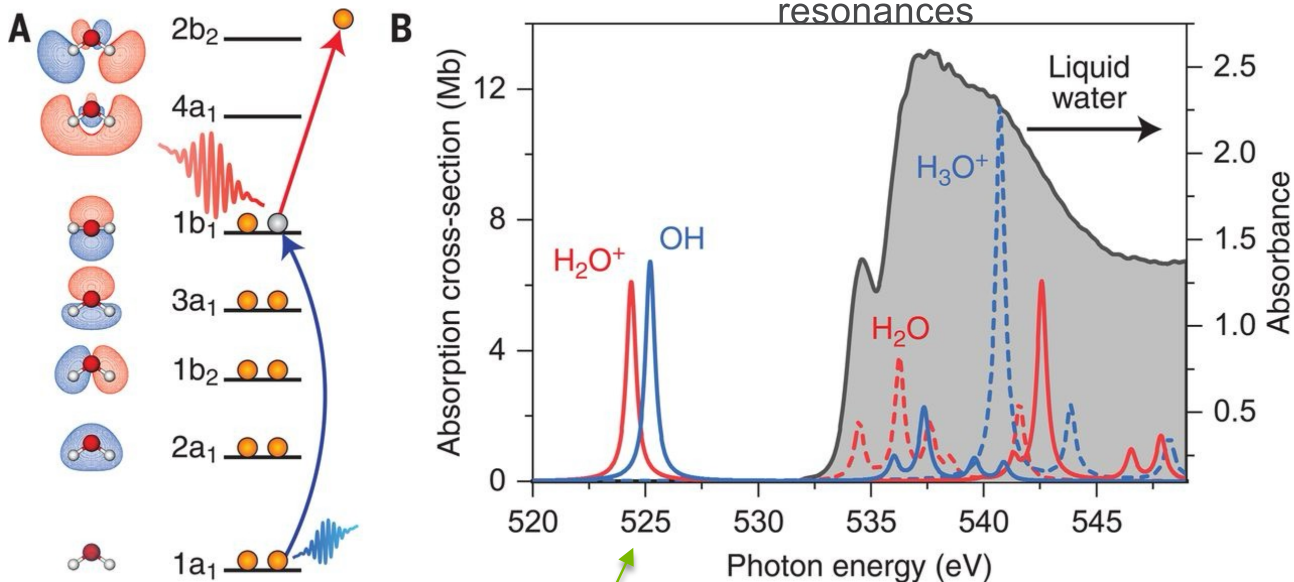
Ultrafast x-ray probe

enables tracking of the primary chemical reaction following ionization

10[-15] seconds

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

calculated gas phase absorption resonances



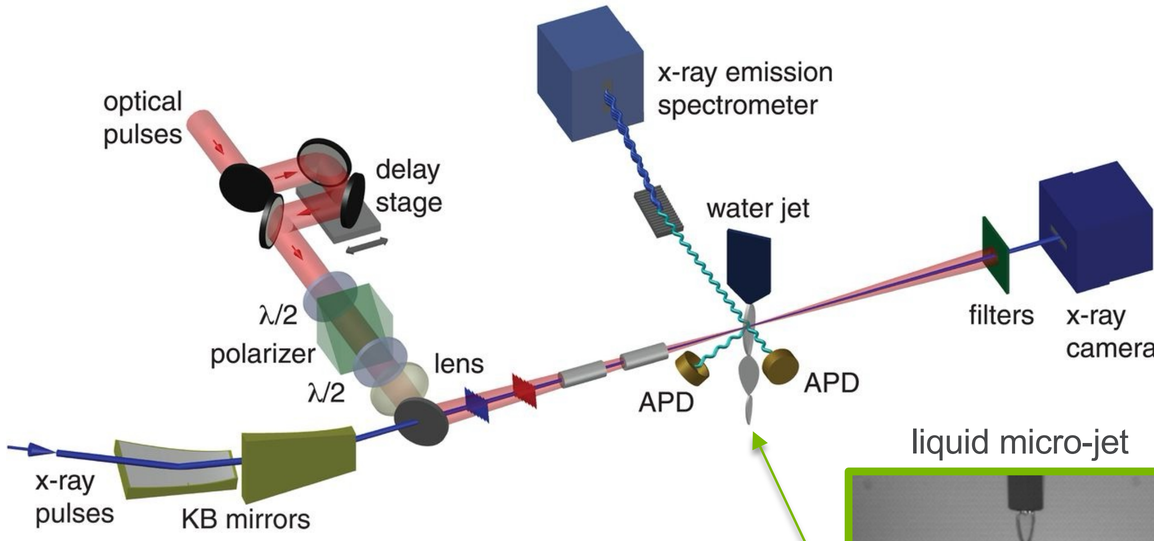
absorption lines fall cleanly in the water window

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

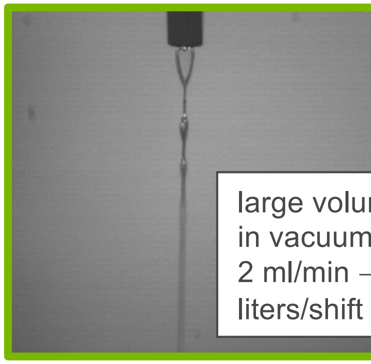
Experimental Details @ LCLS-SXR

10^{-15} seconds

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



liquid micro-jet

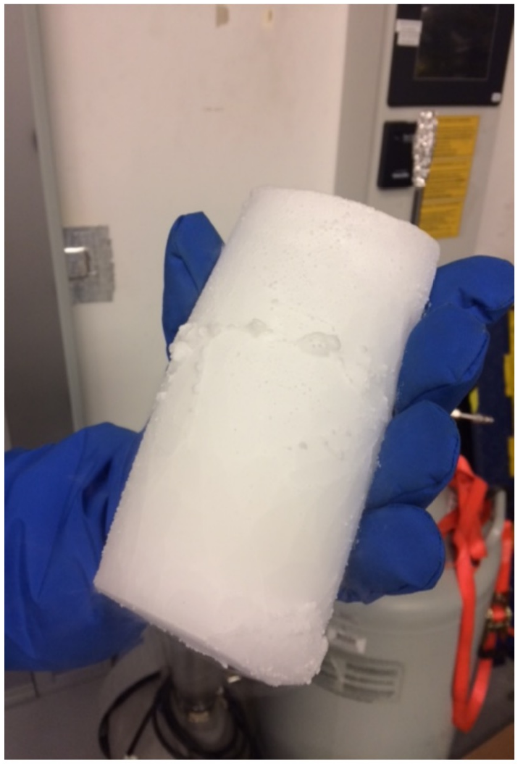


large volume of water in vacuum:
2 ml/min → 2 liters/shift

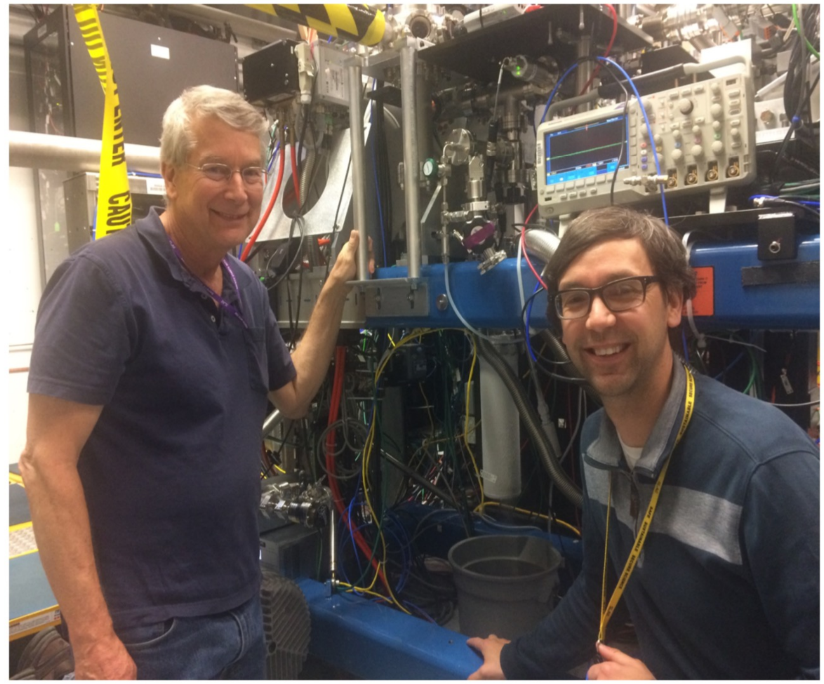
Laser: 800 nm, ~60 fs, 60 μm spot
X-rays: 520-540 eV, 20 fs, 0.2 eV, ~20 μm spot

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

Water after 6 hr run

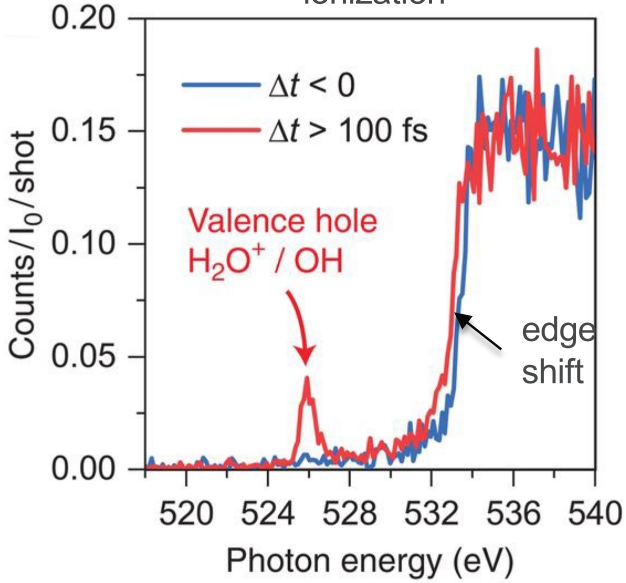


Experimenters at end of run

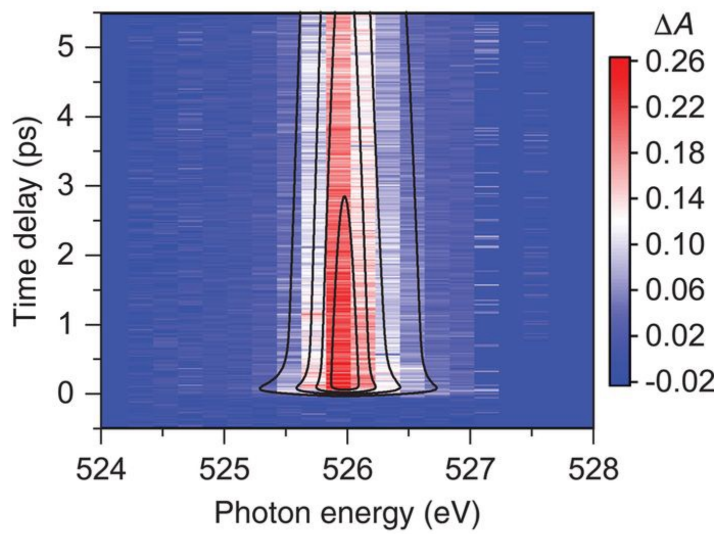


Time-resolved signatures appear in all three channels:
transmission, total fluorescence and dispersed emission

Absorption before and after ionization



Time-resolved differential absorption spectrum



fit, sequential kinetics:

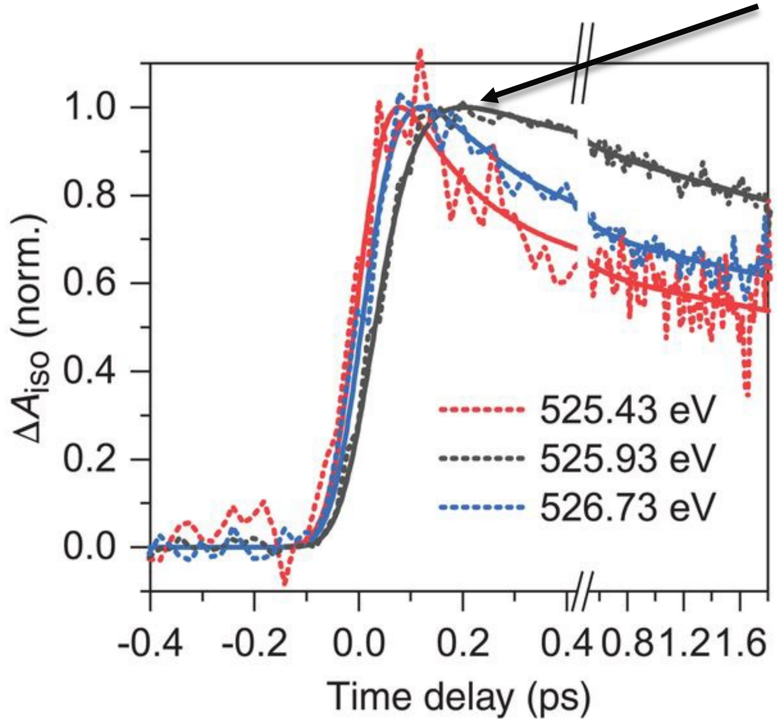
τ_1 = 0.18 +/- 0.02 ps → OH vibrational cooling

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

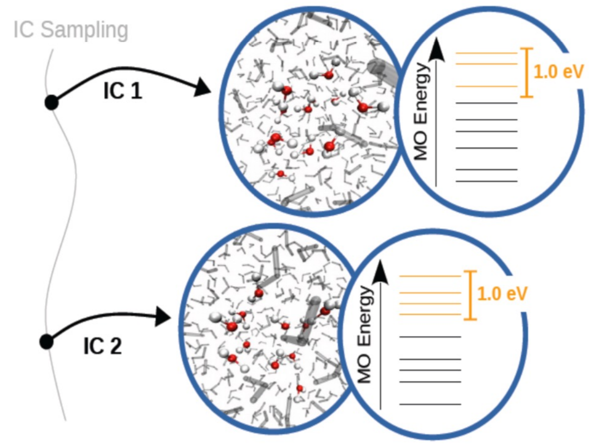
growth of OH, lifetime for H_2O^+

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)

Water experiment at LCLS

10^{-15} seconds

Water experiment at LCLS

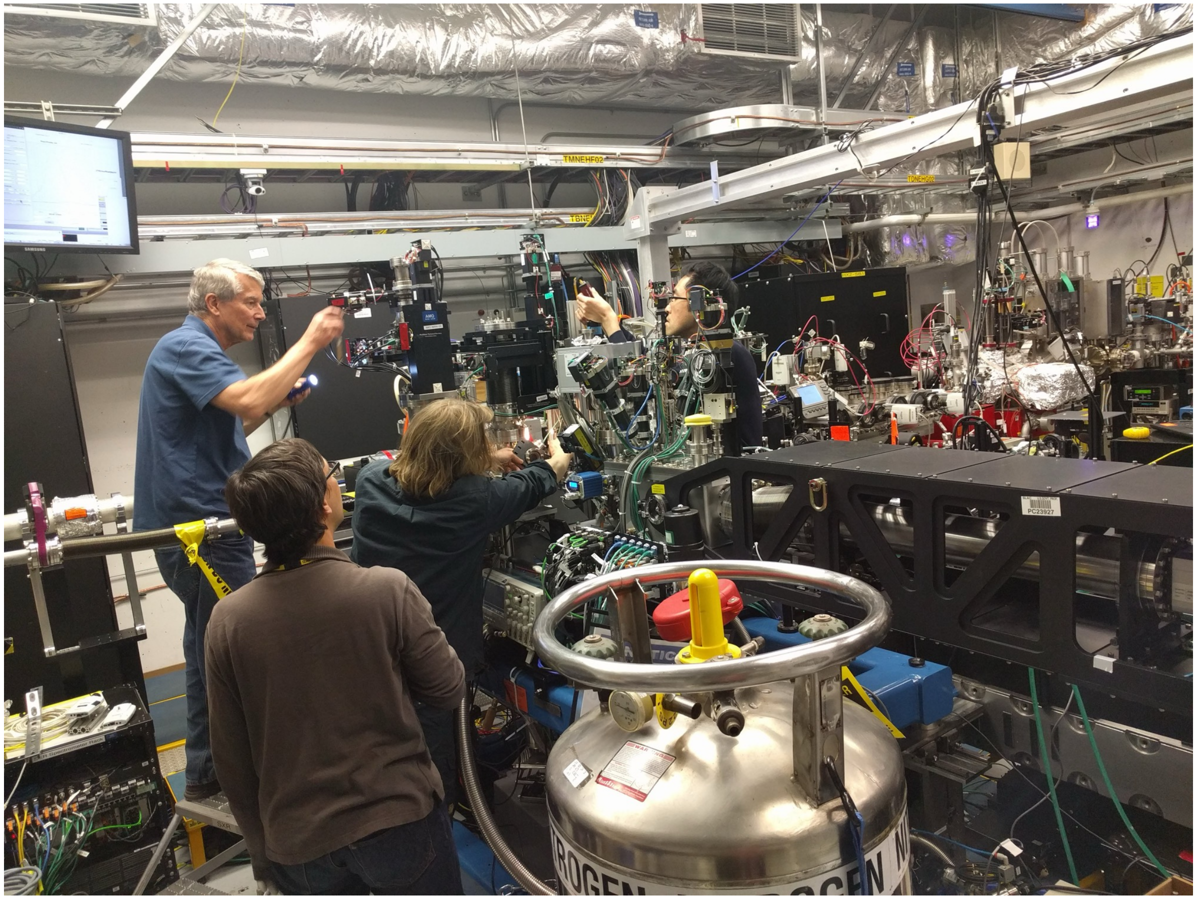
10^{-15} seconds

Water experiment at LCLS

10^{-15}
seconds

Water experiment at LCLS

10^{-15}
seconds

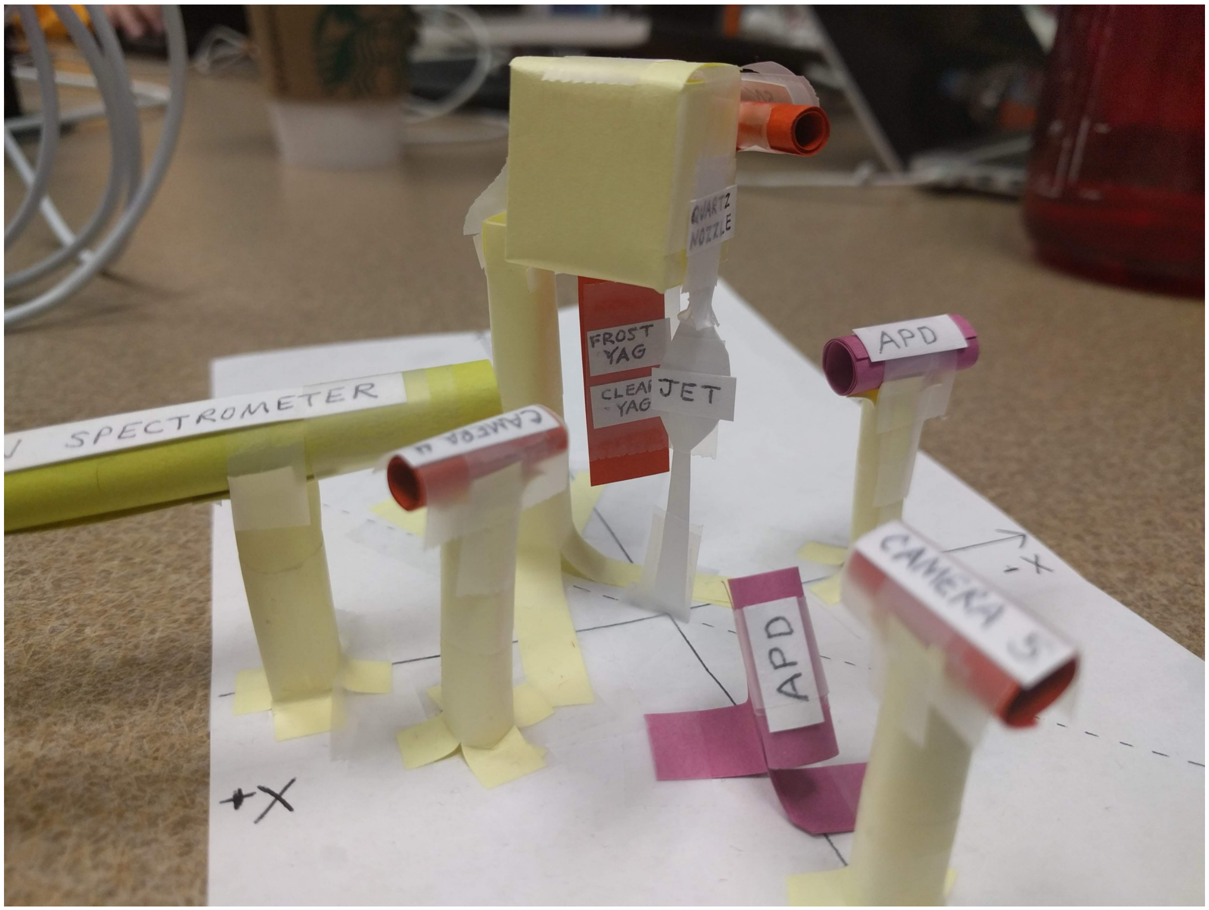


Water experiment at LCLS

10^{-15} seconds

Water experiment at LCLS

10^{-15}
seconds



Water experiment at LCLS

10^{-15}
seconds

Water experiment at LCLS

10^{-15}
seconds

Water experiment at LCLS

Subsequent experiments

10^{-15} seconds

Shuai Li, et al., "Attosecond-pump attosecond-probe x-ray spectroscopy of liquid water," Science 383, 1118 (2024). https://doi:10.1126/science.adn6059.

Arturo Sopena Moros et al. "Tracking Cavity Formation in Electron Solvation: Insights from X-ray Spectroscopy and Theory" J. Am. Chem. Soc. 2024, 146, 3262−3269 https://doi.org/10.1021/jacs.3c11857

2023 Nobel Prize in Physics

10^{-18}
seconds

The x-ray regime is where the shortest light pulses are possible!

A 100 as pulse requires *20 eV* phase-locked bandwidth

The bandwidth covering the visible (IR-UV) is only *3 eV*

https://www.lunduniversity.lu.se/research-and-innovation/nobel-prize

https://news.osu.edu/ohio-states-agostini-wins-nobel-prize-in-physics/

https://www.mpg.de/20915252/nobel-prize-physics-2023-ferenc-krausz

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

10^{-18} seconds

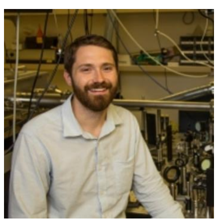
A. Marinelli *et al.*, Nature Photonics **14** 30-36 (2020)

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

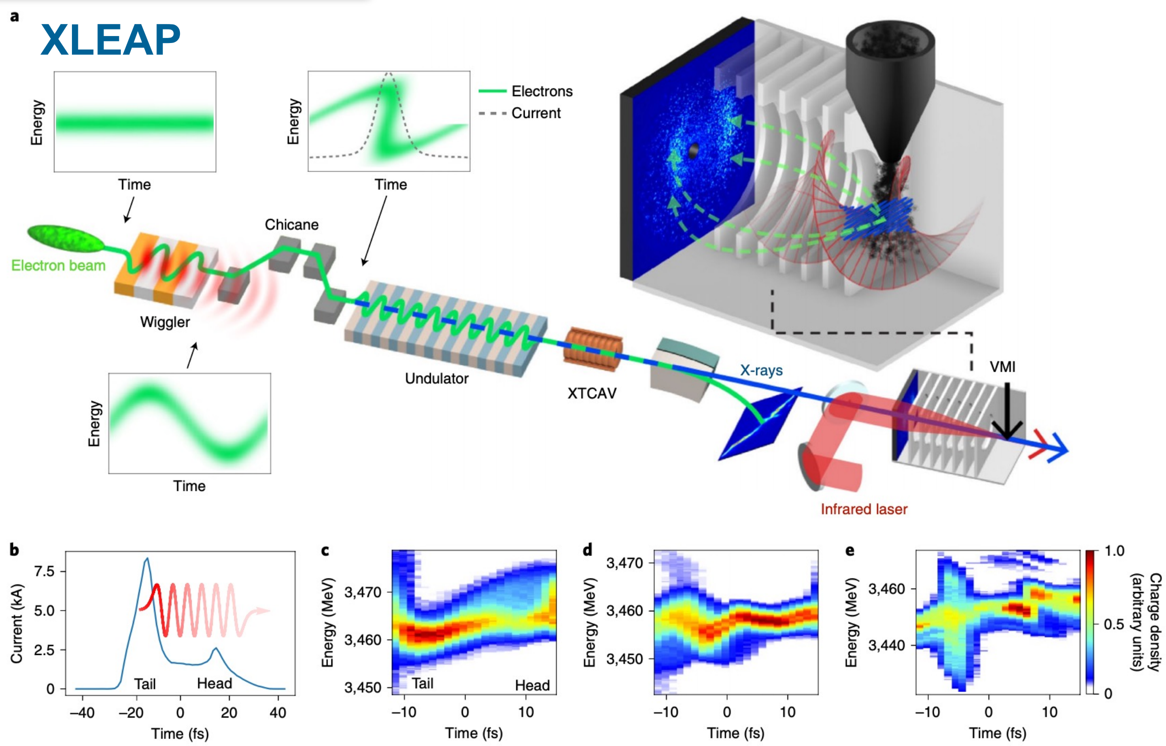
Corresponding authors:

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

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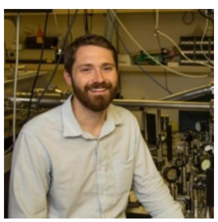
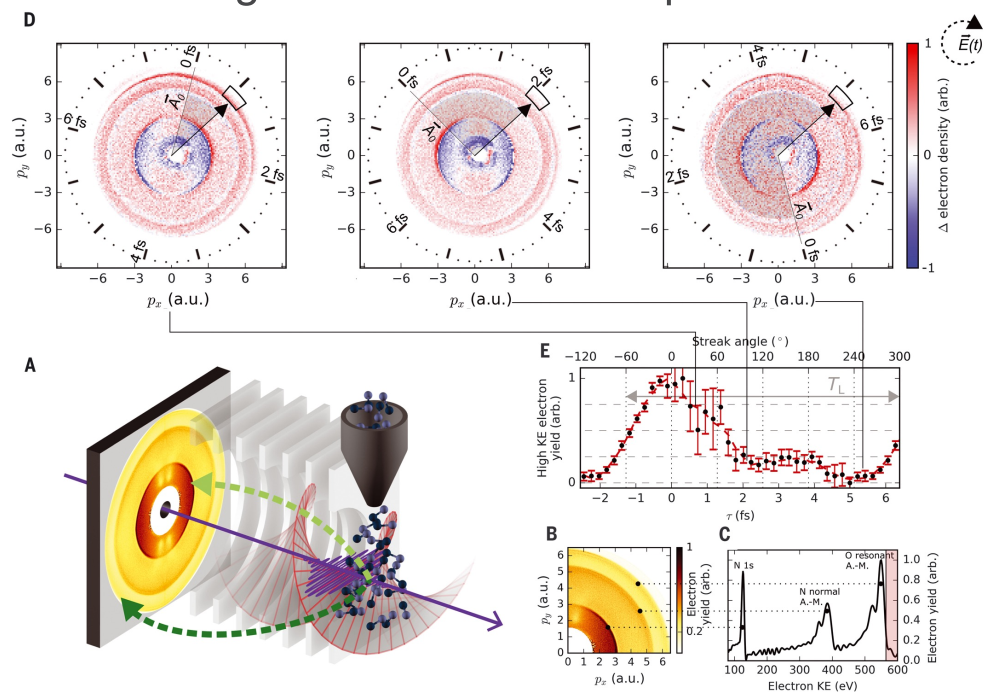
James P. Cryan

Agostino Marinelli



SLAC Stanford University

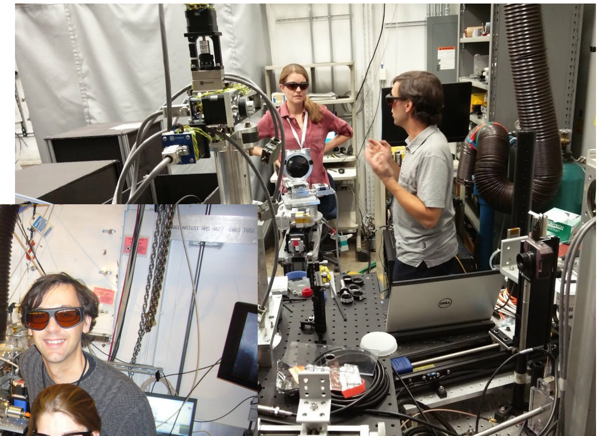
First results using XLEAP attosecond pulses

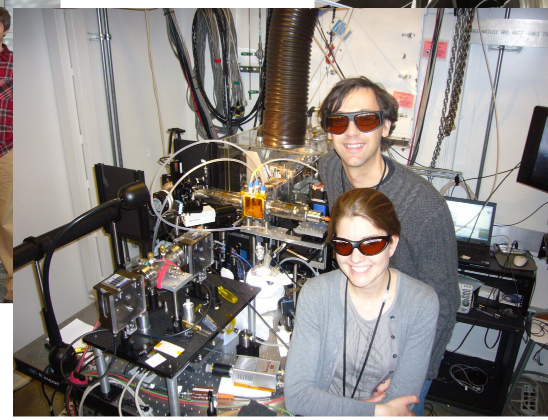


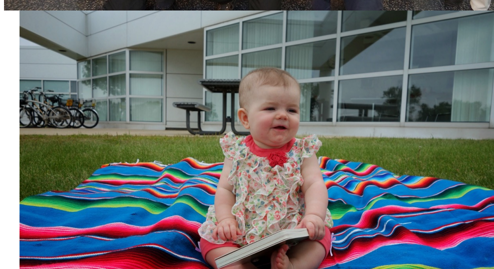
X-rays are extraordinarily powerful probes of matter across many orders of magnitude in time.

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

Thank you for your attention!







Please provide feedback!

https://forms.office.com/g/gkBpwVMivv

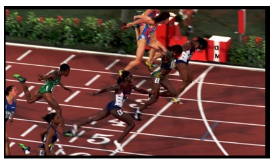
NXS Lecture - Anne Marie March: “Probing ultrafast dynamics with X-rays”

Appendix 1:

More Olympics fun!

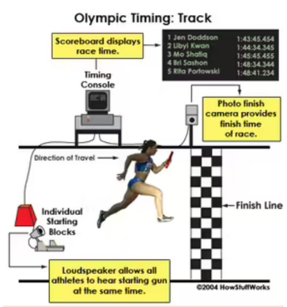
Tolan Wins Historic 100m Gold in Los Angeles 1932

https://olympics.com/en/original-series/episode/tolan-wins-historic-100m-gold-in-los-angeles-1932



Devers Pips Ottey in Dramatic 100M in Atlanta 1996

https://olympics.com/en/original-series/episode/devers-pips-ottey-in-dramatic-100m-in-atlanta-1996

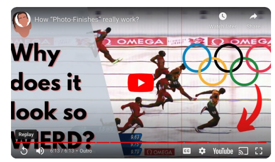


How Olympic Timing Works

https://entertainment.howstuffworks.com/olympic-timing.htm

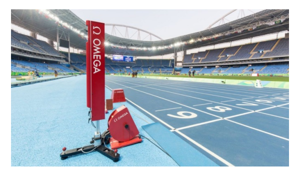
Photo Finish For Women's Triathlon in London 2012

https://olympics.com/en/original-series/episode/photo-finish-for-women-s-triathlon-in-london-2012



How "Photo-Finishes" really work?

https://www.youtube.com/watch?v=QGNgINohags



Olympic Timekeeping Goes High-Tech With Emerging Technologies

https://www.iotworldtoday.com/connectivity/olympics-2024-timekeeping-goes-high-tech-with-emerging-technologies

Appendix 2

Another awe-inspiring time video

The Scale of Time

https://youtu.be/nOVvEbH2GC0?si=_mR5OJv5B1afKAVQ

How We Built a Scale Model of Time

https://youtu.be/5lXxMmCCfCY?si=teebLQyE_Glyq3TD