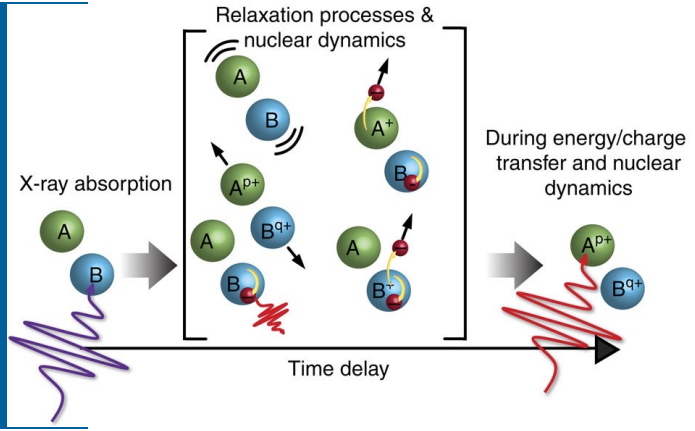
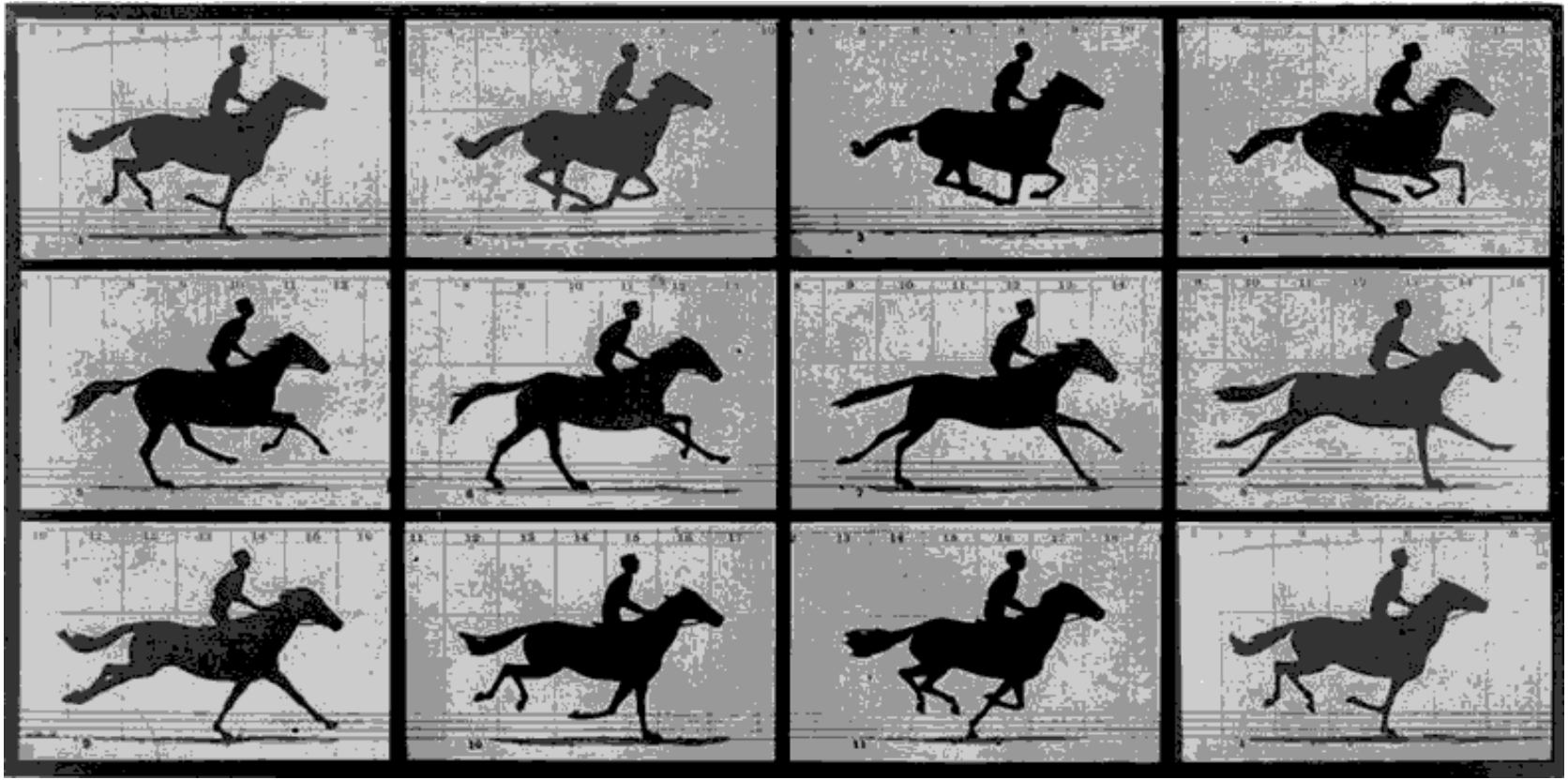
Probing ultrafast dynamics



LINDA YOUNG
Argonne National Laboratory
The University of Chicago

X-ray Neutron Summer School, Argonne National Laboratory, 20 July 2022

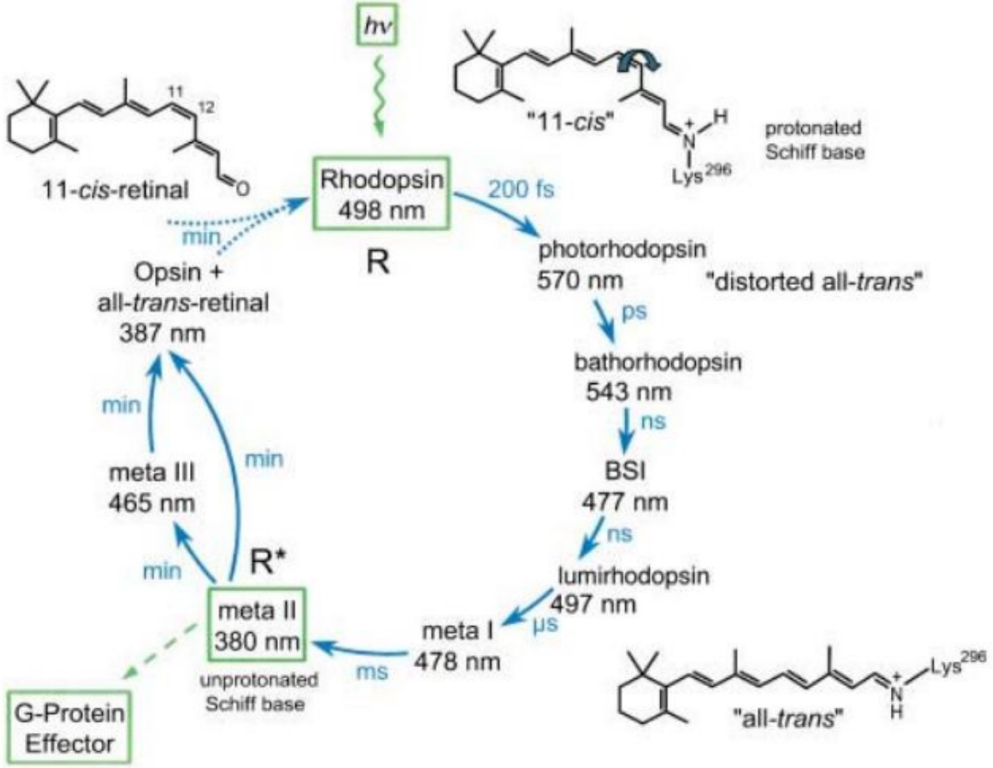
How fast a process can a human eye resolve?



Eadweard Muybridge 1872[2] ——› PC Gamer 2017

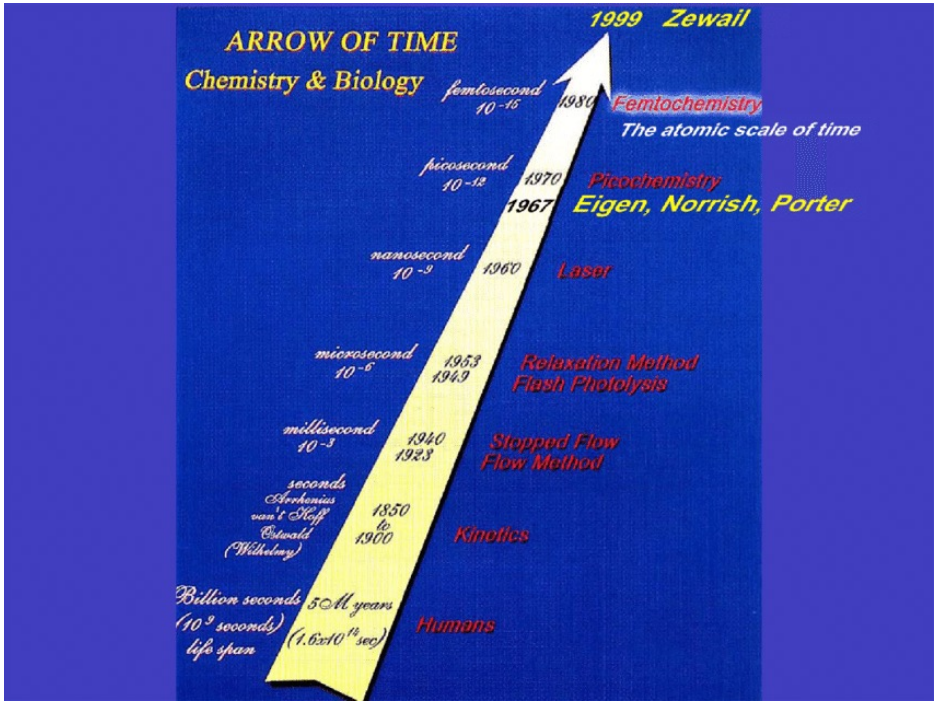
Argonne NATIONAL LABORATORY

PHOTOCHEMISTRY OF VISION



DECADES AND MILESTONES IN TIME

1967 Eigen, Norrish & Porter
"*for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy*"

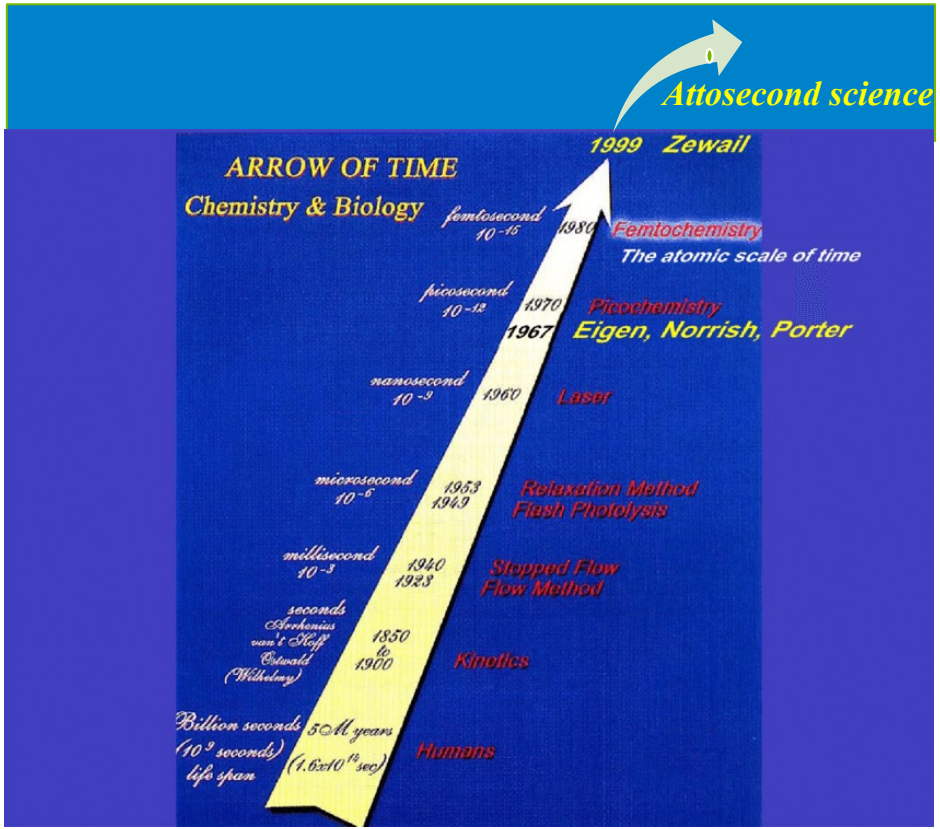


1999 Zewail
"for his *studies of the transition states of chemical reactions using femtoscond spectroscopy*"

Zewail's 1999 Nobel lecture

DECADES AND MILESTONES IN TIME

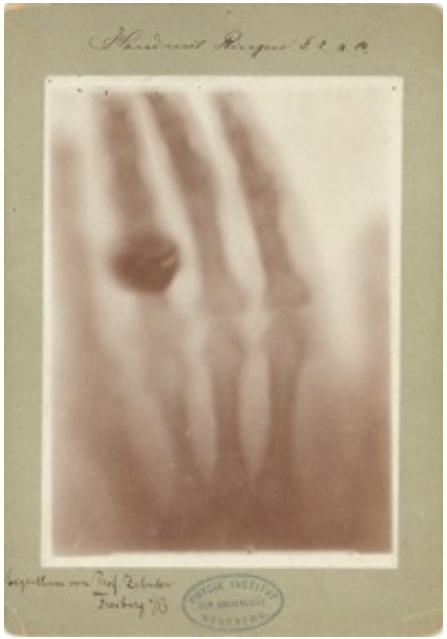
Strickland, Mourou
2018 Nobel
"for their method of generating high-intensity, ultra-short optical pulses"



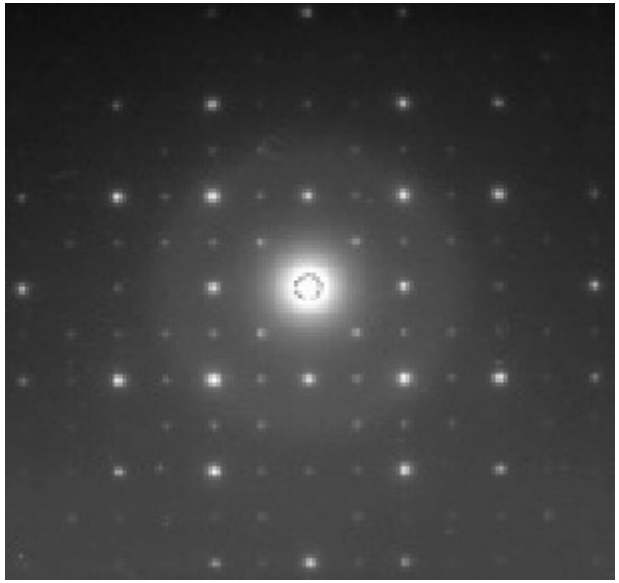
Corkum, Krausz, L'Huillier
2022 Wolf Prize

X-RAY MILESTONES

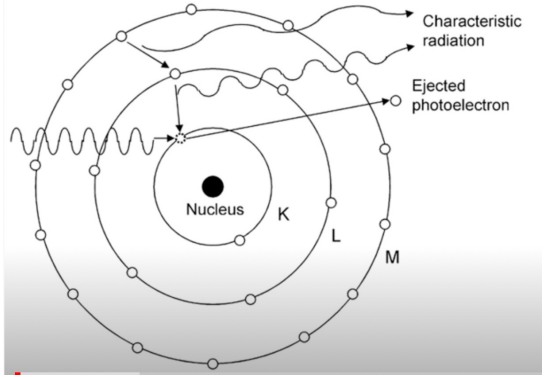
Imaging --- Scattering --- Spectroscopy



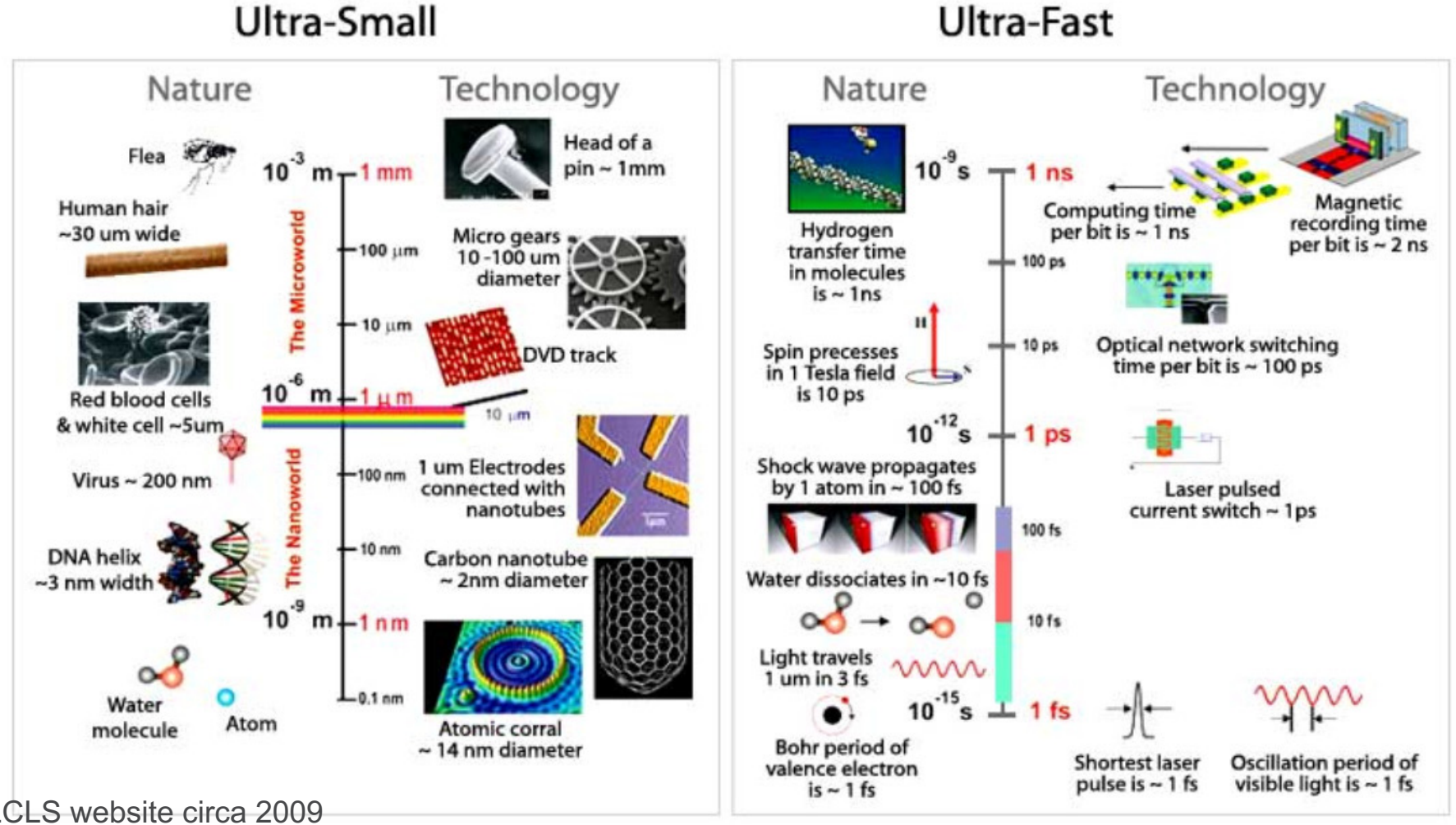
Discovery 1895 Roentgen
Nobel prize 1901



Von Laue -1914
Bragg & Bragg -1915



Barkla -1917 .
Siegbahn -1924

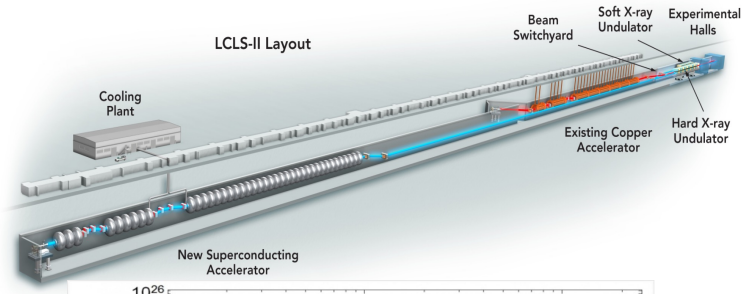


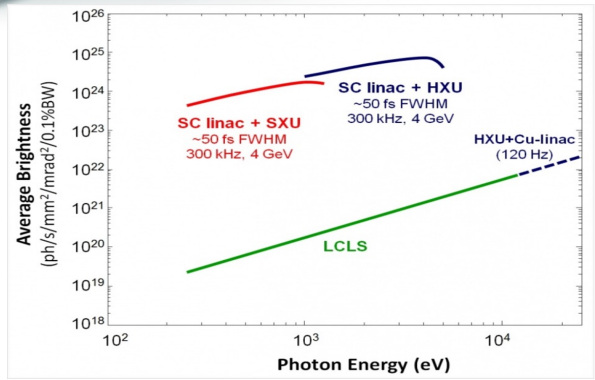
LCLS website circa 2009

Upgraded American x-ray facilities coming soon

LCLS-II

increased brightness and repetition rate

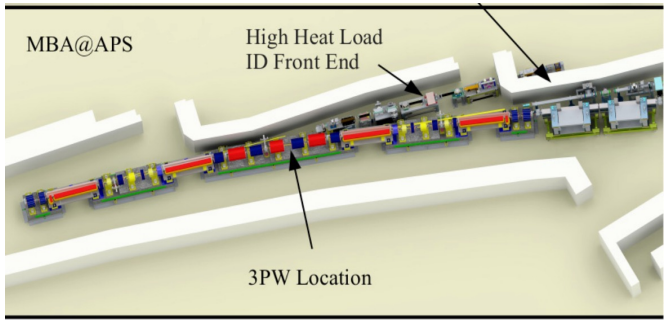


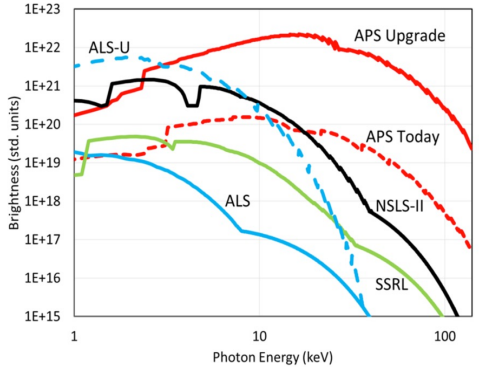


as fs ps

APS-U

increased brightness and coherence

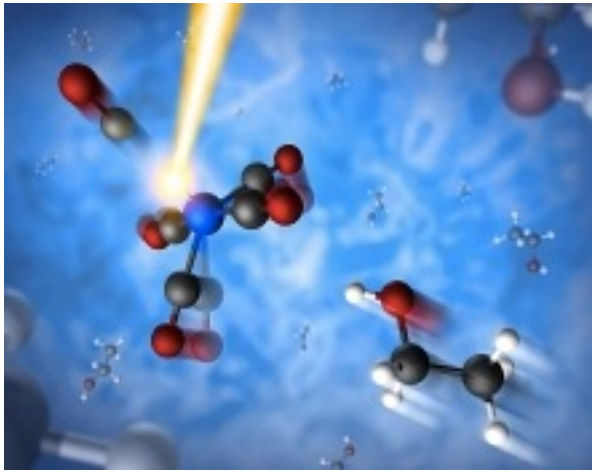




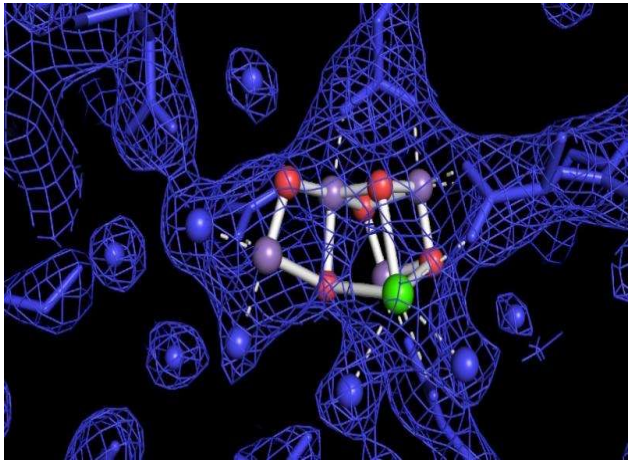
10's ps ns µs ms s

Break for questions

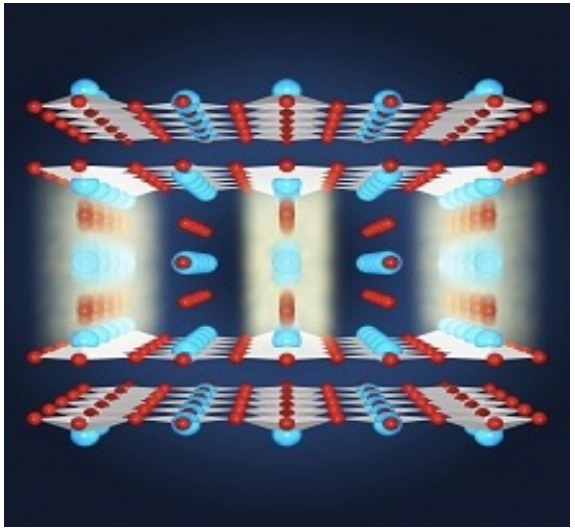
X-RAYS SEE THE ATOMS AND ELECTRONS MOVE



Chemical reactions
in solution



Photosystem II



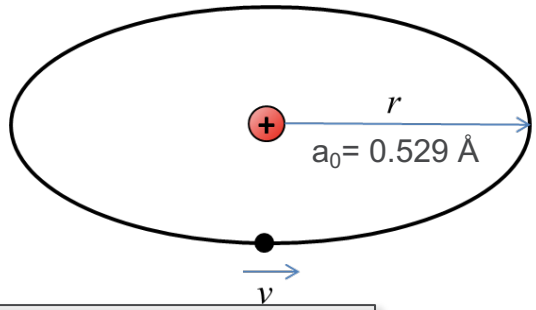
Light-induced
superconductivity

FUNDAMENTAL TIMESCALES

Orbital time 1s electron in hydrogen atom: 150 as

$T_{orb} = 2\pi a_0/(\alpha c)\ [n^3/Z^2]$

Hydrogen atom

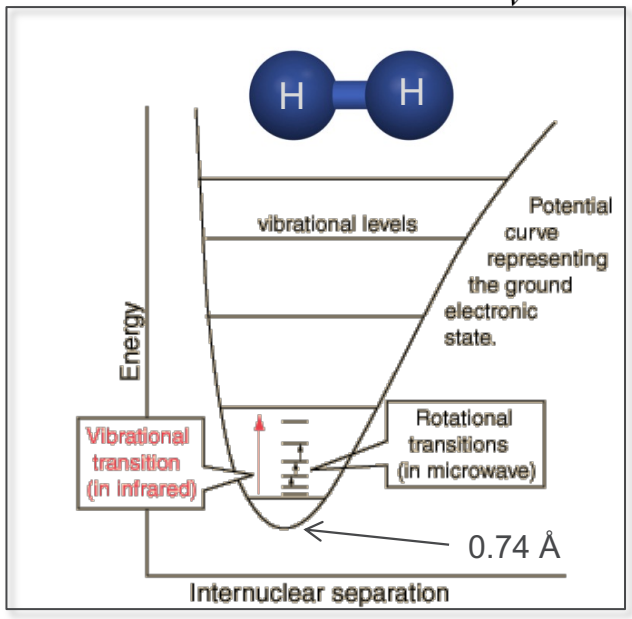


Vibrational period in H_2 : 4160 cm^{-1} ~ 8 fs

$T_{vib} = 2\pi(\mu/k)^{1/2}$

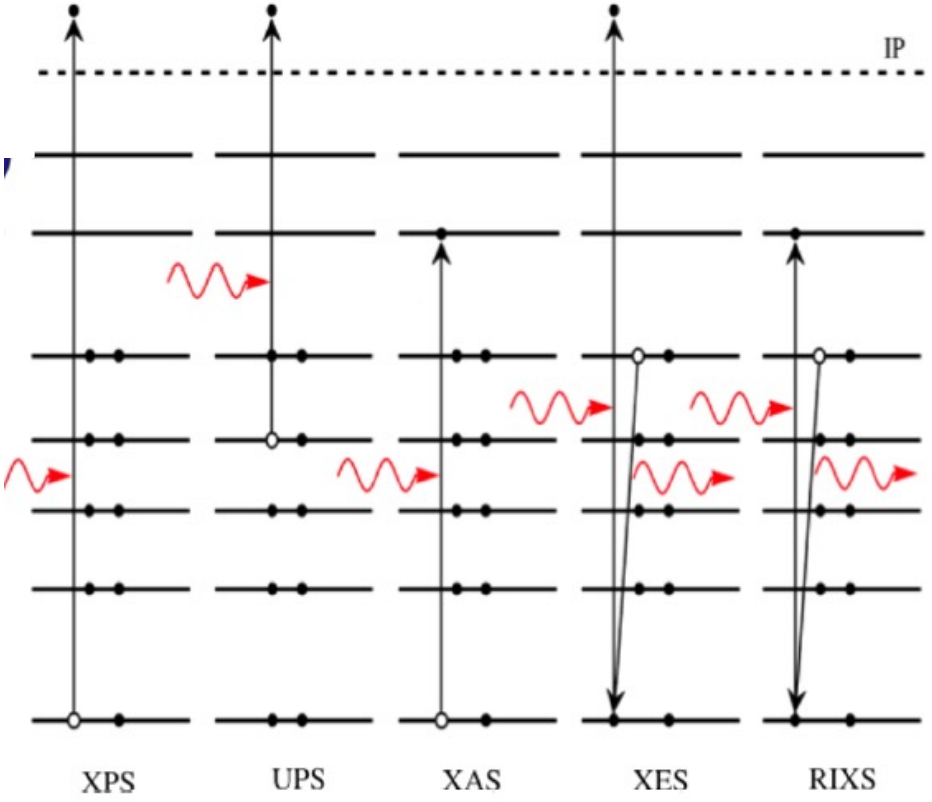
Rotational period in H_2 : 60 cm^{-1} ~ 0.55 ps

$T_{rot} = 2B_e = h/(2\pi)^2\mu R_e^2$



X-RAY SPECTROSCOPIC PROBES

All can be used via pump-probe to track dynamics



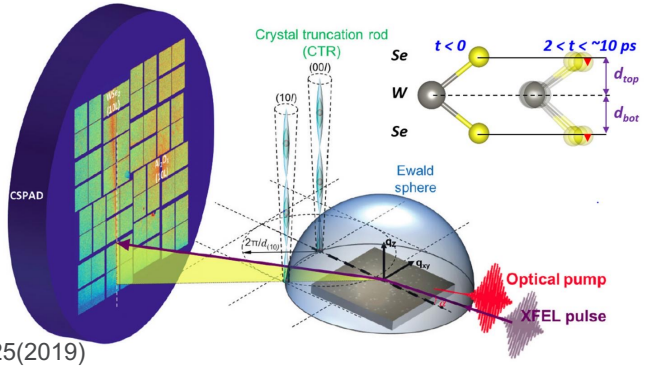
- Photoelectron spectroscopy
  - binding energies (UPS,XPS)
  - prompt response
- Absorption spectroscopy
  - unoccupied orbitals (XANES)
  - local structure (EXAFS)
- Emission spectroscopy (XES)
  - occupied orbitals
  - spin-state sensitivity
- RIXS
  - spectroscopy w/o core-hole broadening

X-RAY SCATTERING PROBES

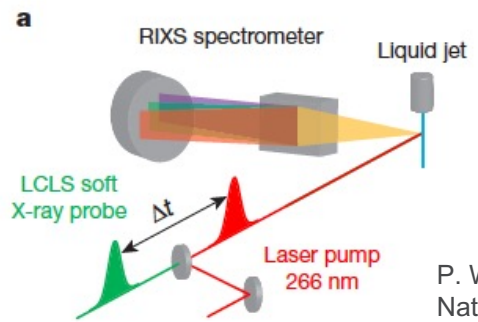
All can be used via pump/probe to track dynamics

Elastic scattering

- X-ray diffraction
  - Crystal structure
- Small angle x-ray scattering (<5°)
  - Structure in nm to μm range
- Wide angle x-ray scattering
  - Sub-nm structure



I.C. Tung …,
Nat Photon.**13**, 425(2019)



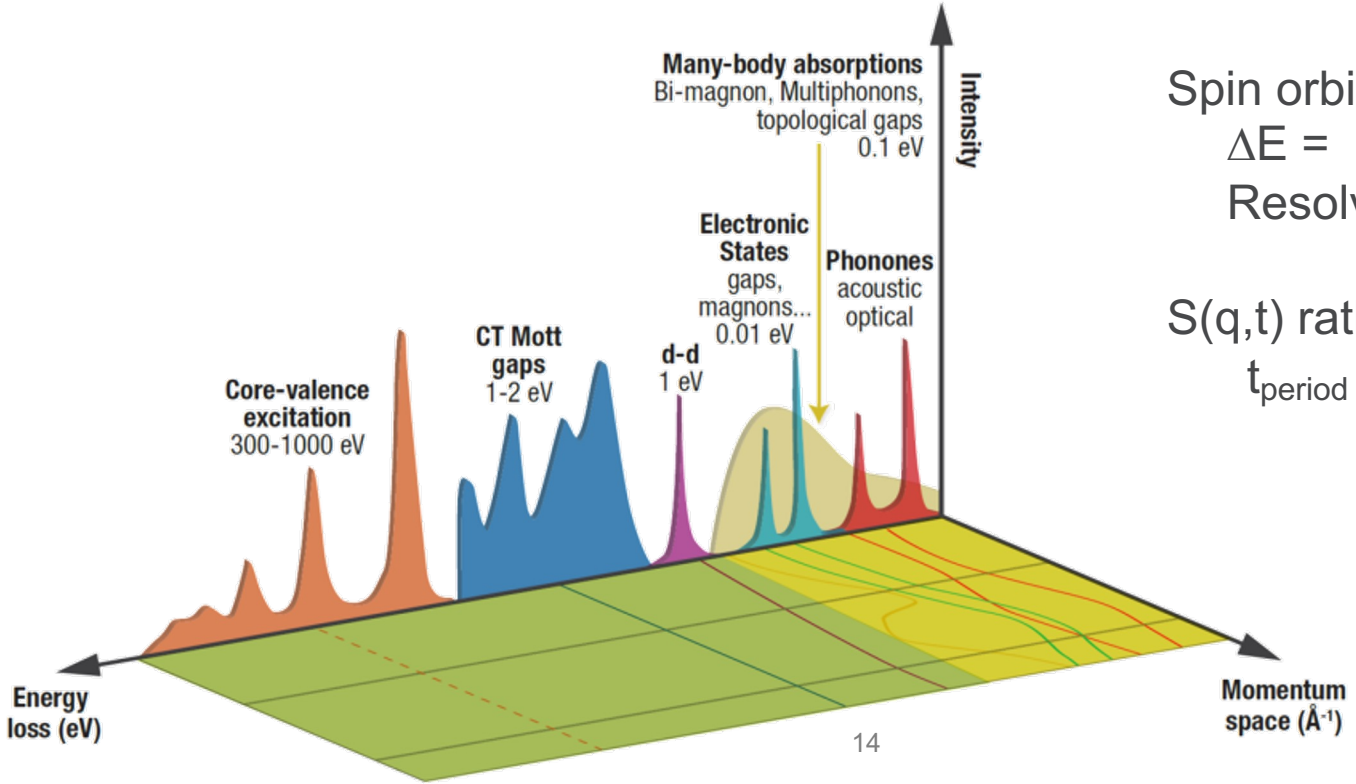
P. Wernet …
Nature **520**, 78 (2015)

Inelastic scattering

- Raman scattering
  - Absorption Edge Structure,
  - Bonding, Valence
- Compton scattering
- RIXS, NRIXS

Probe of low-energy collective excitations requires extremely high resolving power

Time-domain methods can also be employed for very low energy ΔE



Spin orbit, phonon, magnons…

$\Delta E =$ 1-100 meV

Resolving power ~ 40000

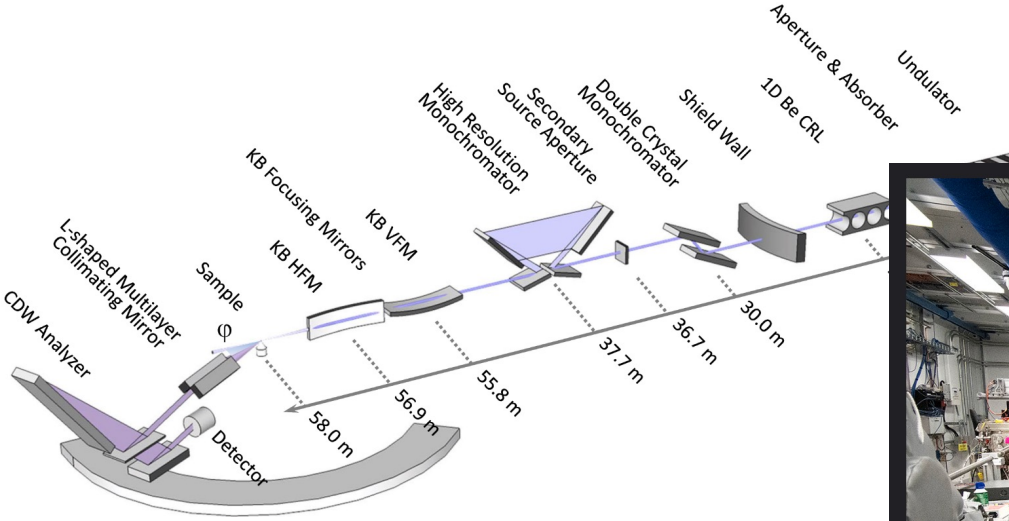
S(q,t) rather than S(q,ω)

t_{period} ~ 4000 – 40 fs

$$\hbar = 0.66 \text{ eV fs}$$

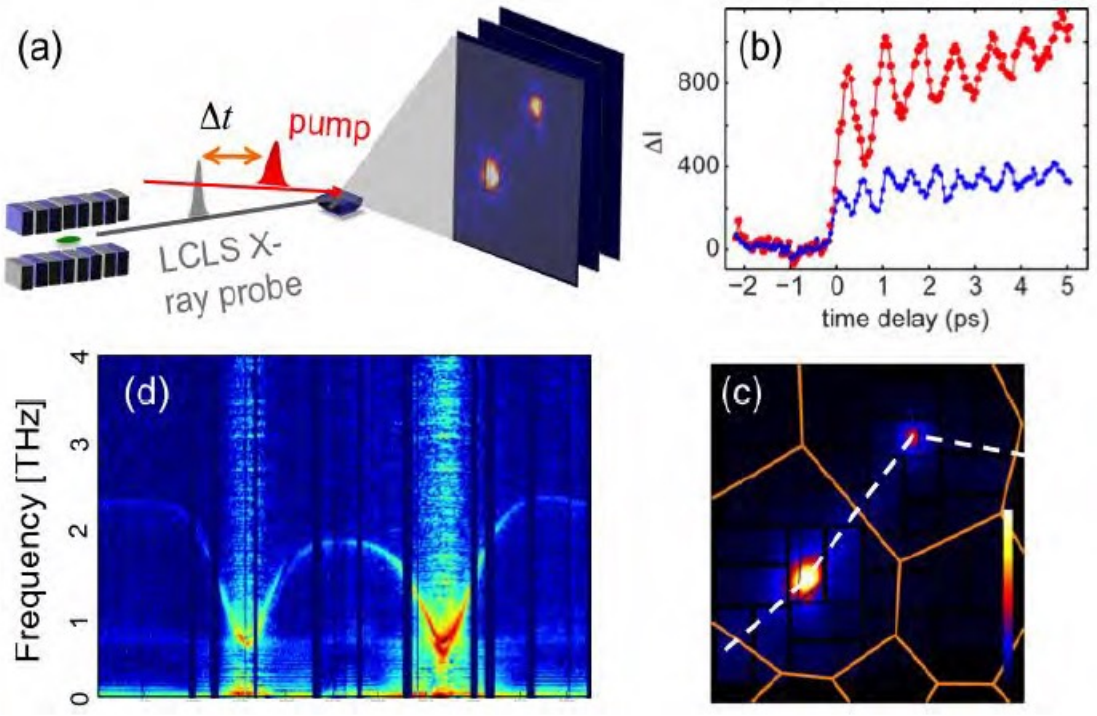
A high-res inelastic x-ray scattering beamline

BNL 10-ID- IXS: ~2 meV inelastic scattering



Energy Range:	5 ~ 15 keV for DCM; 9.1 keV +/- 300 meV for HRM
Flux:	~4 x 10^9 photons/sec/meV @ 9.13 keV @ 400 mA RC
Mono Crystal Grating:	Si(111) DCM / 4B HRM
Resolution:	1.3 eV with DCM; ~1 meV @ 9.13 keV with HRM
Spot Size:	~10 (V) x 10 (H) um^2
Total Angular Acceptance:	~20 (H) x 7.5 (V) $mrad^2$

Time-domain phonon spectroscopy



X-ray diffuse scattering

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

Transform-limited Gaussian pulse
ΔEΔT ~ 1.8 eV fs (FWHM)

M. Trigo et al., Nat. Phys. 9, 790 (2013)

Break for questions

OUTLINE – THREE EXAMPLES

- Watching chemical reactions in solution
  - Laser-pump / x-ray probe spectroscopies (TR-XAS, TR-XES) @ APS

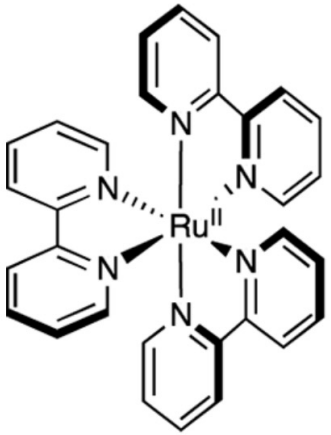
- Elucidating the oxygen evolution mechanism in Photosystem II
  - Laser-pump / x-ray probe diffraction and spectroscopy

- Inner-shell electronic dynamics
  - X-ray pump / x-ray probe spectroscopies

from 2021 Nobel Lecture – David MacMillan

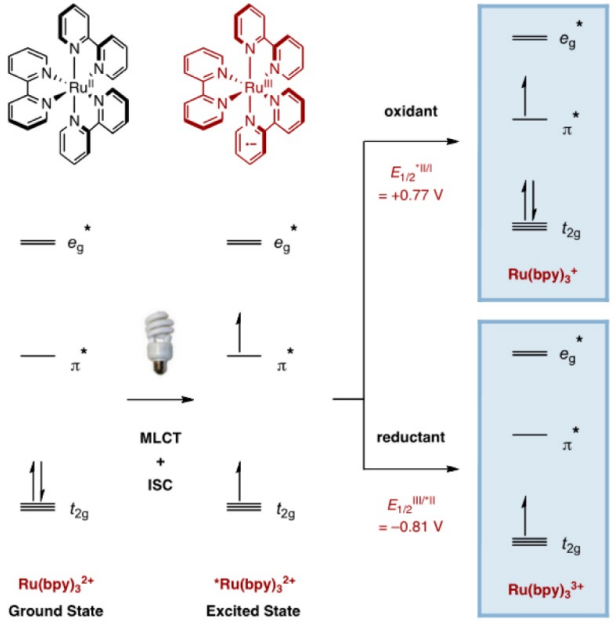
Photochemistry of transition metal complexes

Inexpensive visible light photocatalyst: splitting of water, reduction of CO2, dye-sensitized solar cells …



$Ru(bpy)_3^{2+}$

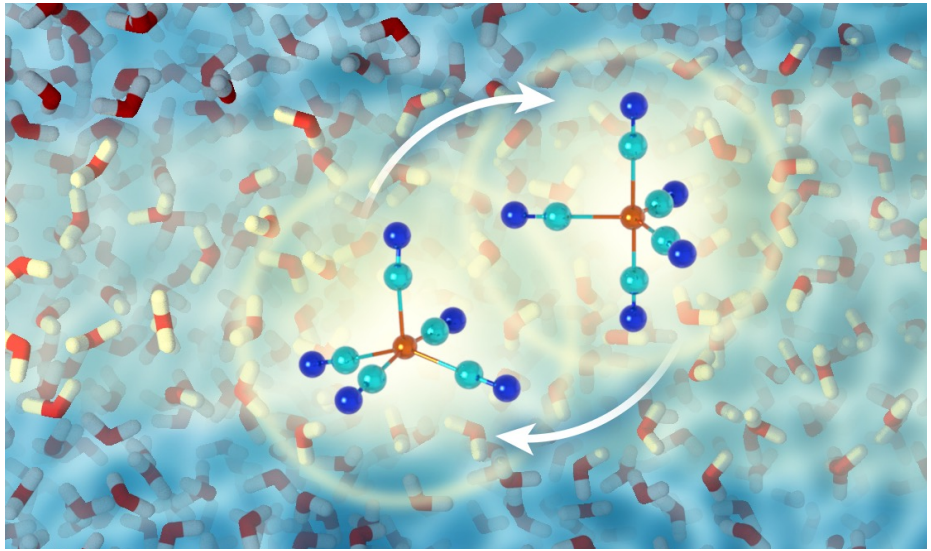
Scheme 1. Simplified Molecular Orbital Depiction of $Ru(bpy)_3^{2+}$ Photochemistry[1]



…MacMillan Chem. Rev. 2013, 113, 5322−5363

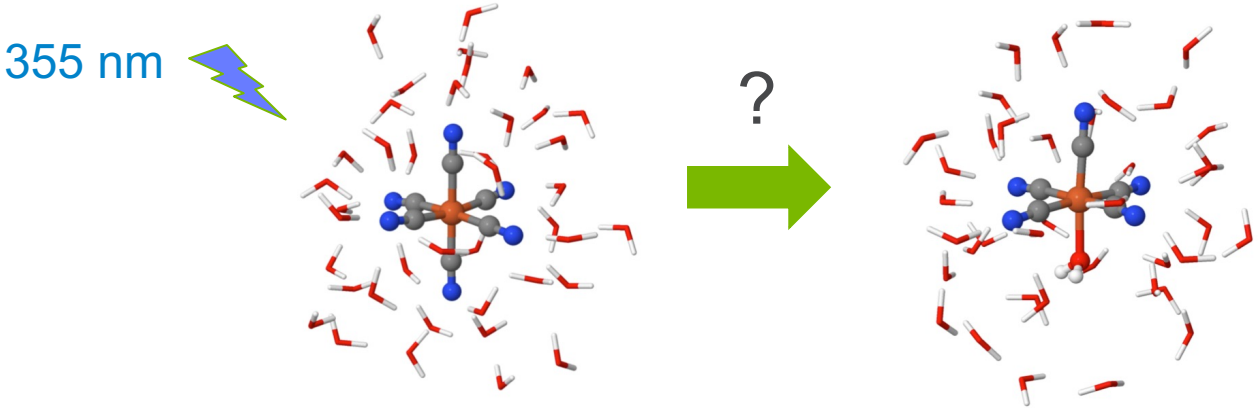
Elucidating reaction mechanisms for photoexcited transition metal complexes in solution

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



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

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



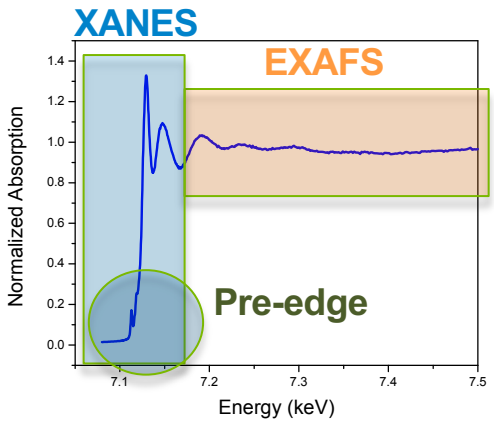
- highlights the power of high-flux, very stable, MHz-repetition-rate synchrotron x-rays
- detection of reaction intermediates with lifetimes shorter than the x-ray pulse duration

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

X-ray photon-in photon-out spectroscopies

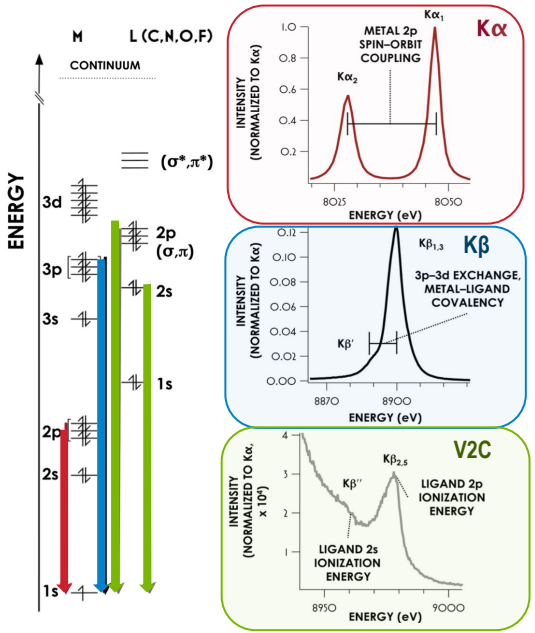
Elemental, chemically specific information on electronic & geometric structure

X-ray absorption spectroscopy (XAS)



- **EXAFS**: distances to neighboring atoms
- **XANES**: oxidation state, geometry, coordination environment
- **Pre-edge**: valence orbital occupancy

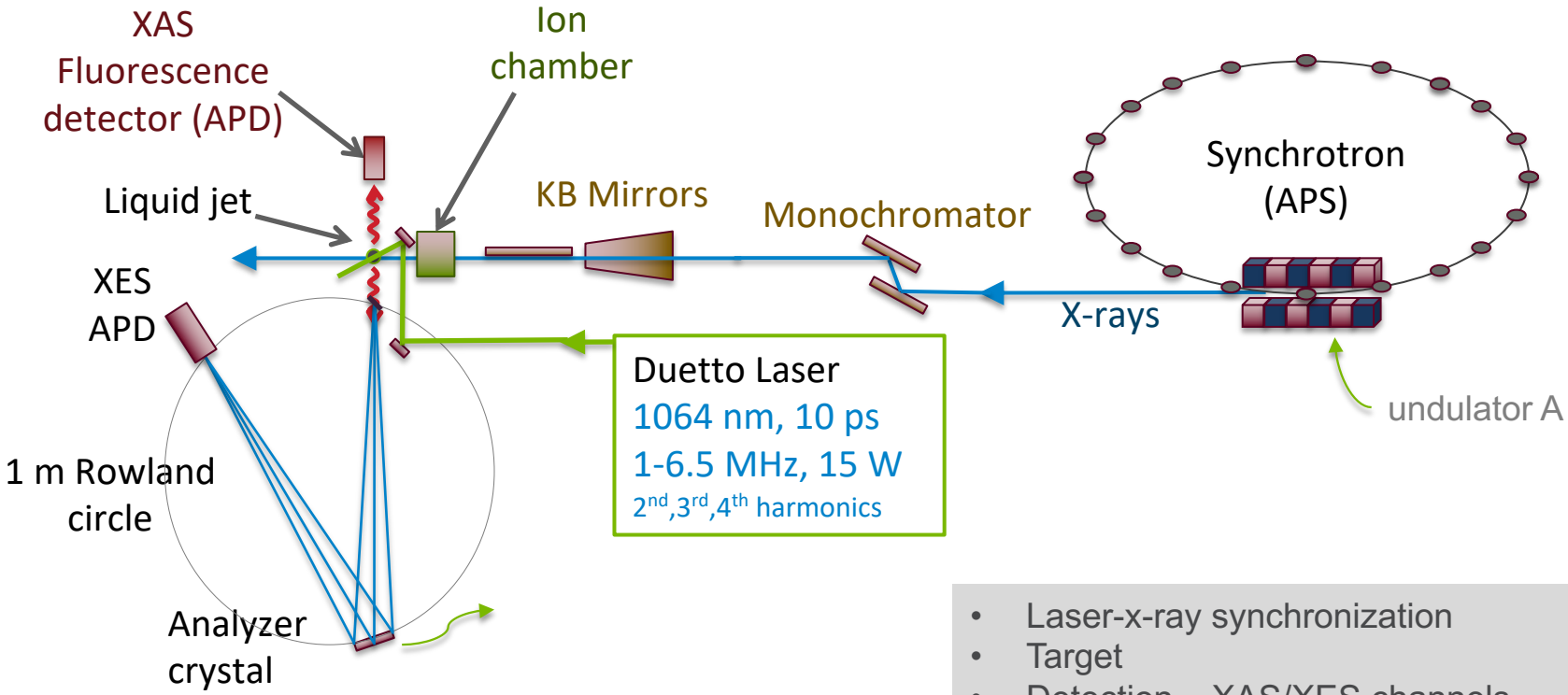
X-ray emission spectroscopy (XES)



- occupied orbitals, spin state, covalency, ligand identity

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

Essential ingredients: laser pump/x-ray probe spectroscopies ps - µs

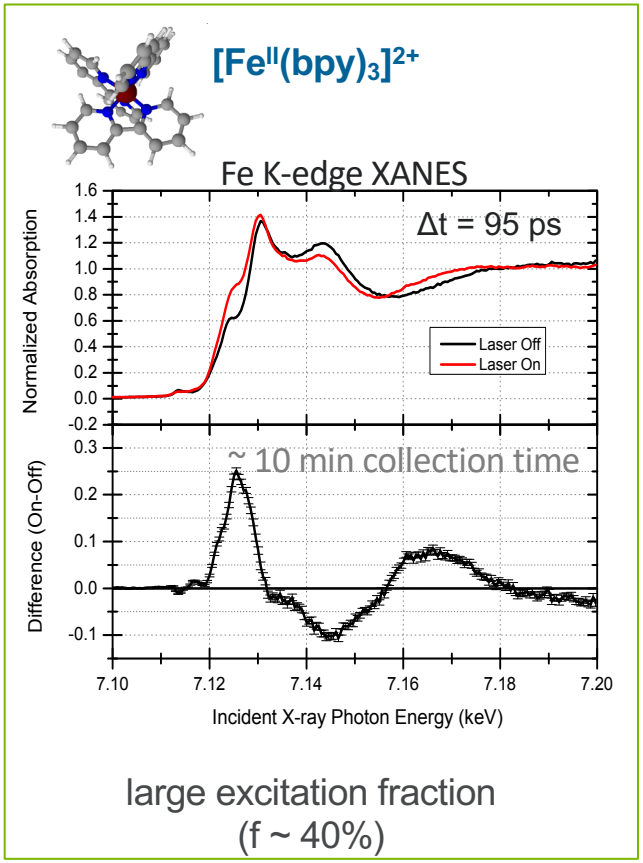


- Laser-x-ray synchronization
- Target
- Detection – XAS/XES channels
  - Pump on/pump off simultaneouS

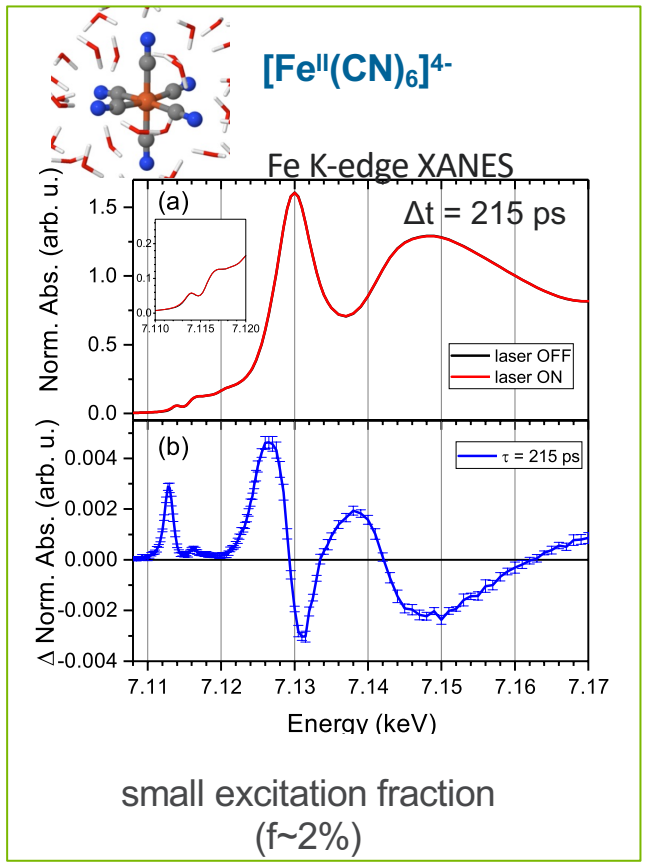
Sector 7 TR-spectroscopy implementation

Example XAS difference spectra

OFF = ground state spectrum ON = (1-f)(ground state) + f (excited state)



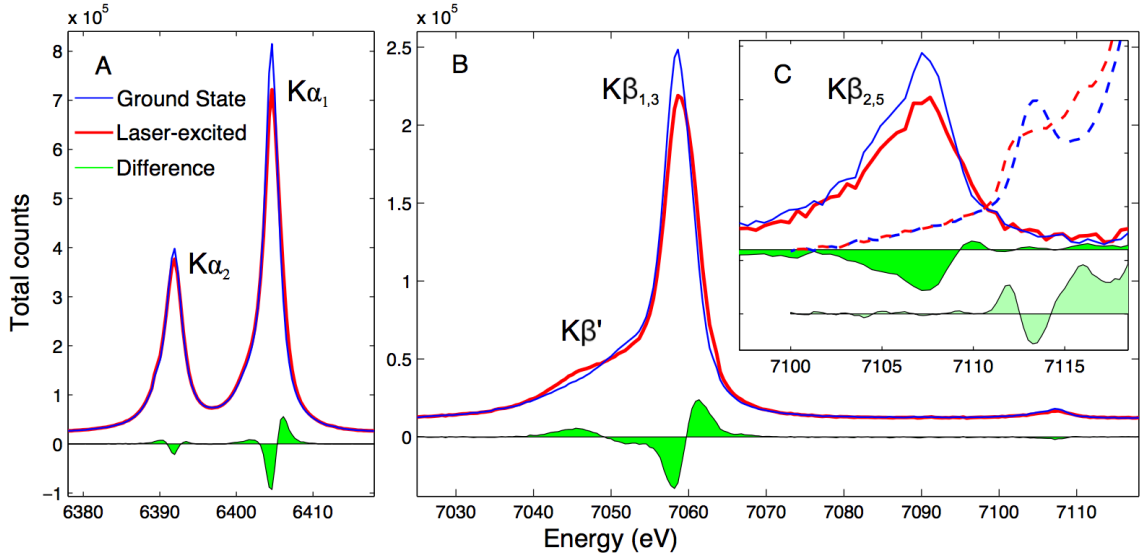
large excitation fraction
(f ~ 40%)



small excitation fraction
(f~2%)

Pump-probe x-ray emission spectroscopy

Complete Fe 1s XES of $[Fe(terpy)_2]^{2+}$, including valence-to-core



- "Core-to-core" Kα and Kβ emission lines reflect the LS to HS transition
- Changes in the valence-to-core region detected!

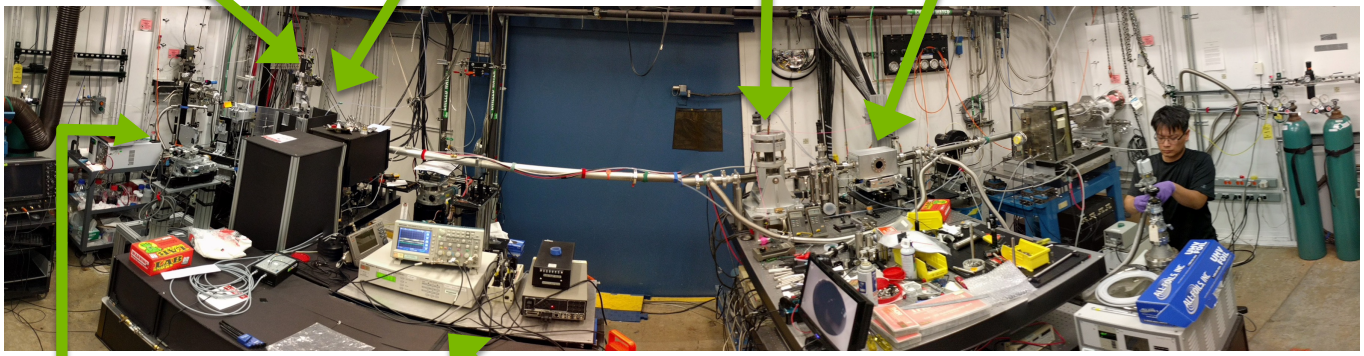
19 hours collection time

Still impractical for most samples of interest

A. M. March *et* al., J. Phys. Chem. C, **121**, 2620 (2017).

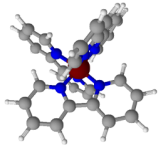
Pink beam pump-probe XES realization …

MHz pump-probe XES with pink beam 7ID-B hutch



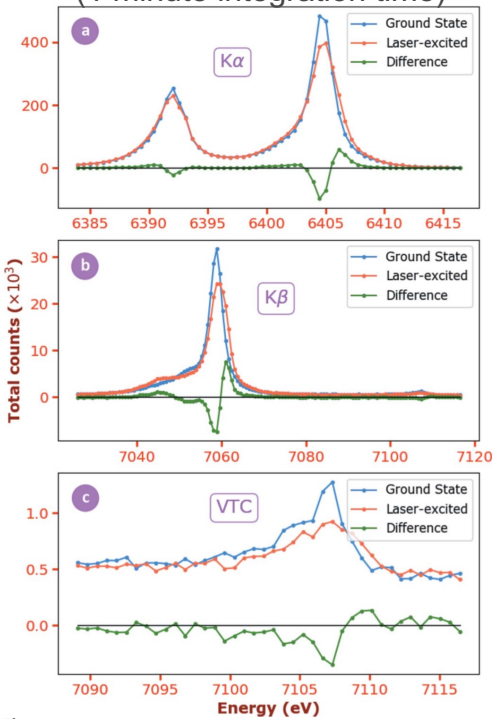
M.-F. Tu, G. Doumy, *et al.*, J. Synch. Rad. (2019)

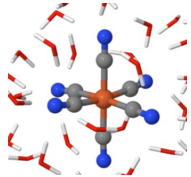
Pink beam XES measurements



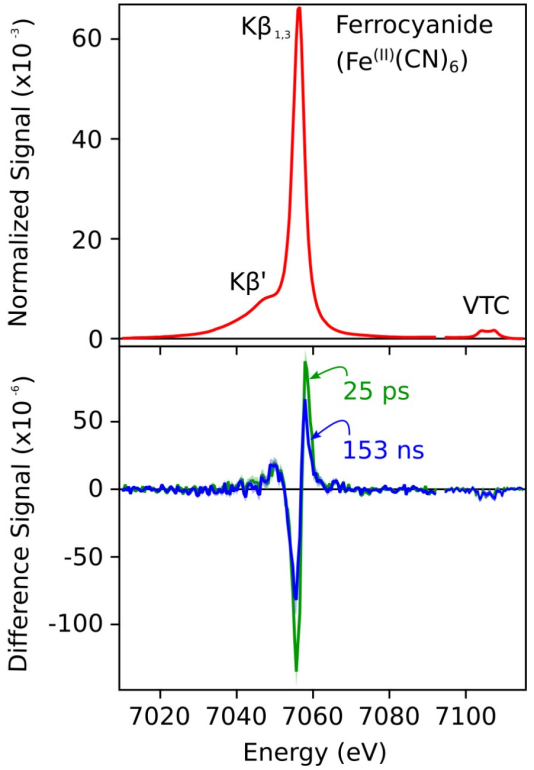
$[Fe^{II}(bpy)_3]^{2+}$

(1 minute integration time)



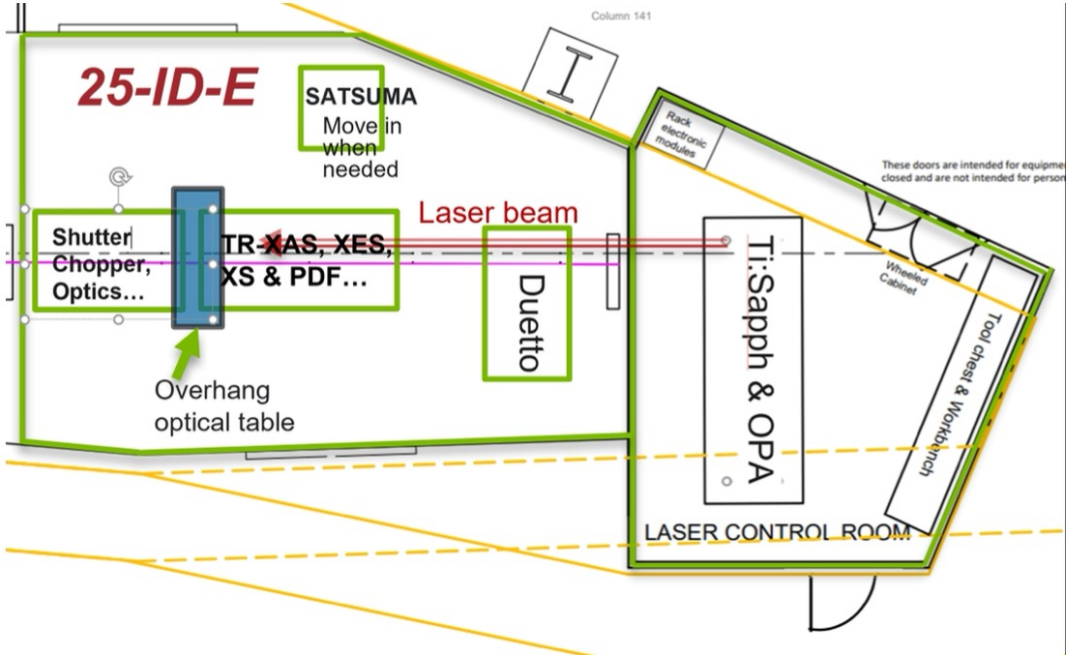


$[Fe^{II}(CN)_6]^{4-}$

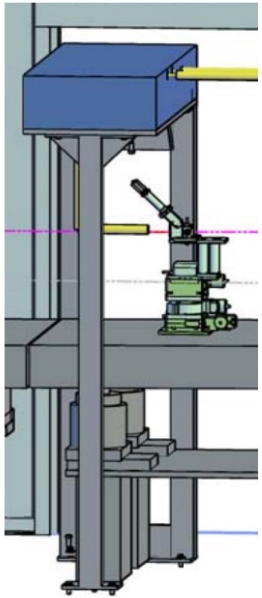


New capabilities at Sector 25 – APS U

Both monochromatic and pink beam delivered to target – w/ lasers!



Overhang
optical table



Steve Heald, Shelly Kelly, Xiaoyi Zhang

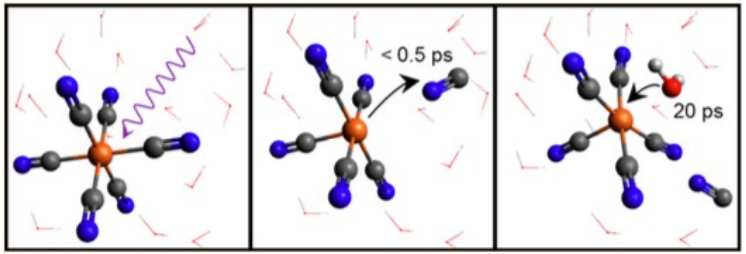
Photoaquation reaction

G. Emschwiller *et al.* C. R. Acad. Sc. Paris, 1954, M. Shirom *et al.* J Chem Phys, 1971.

Recent investigations to determine the mechanism

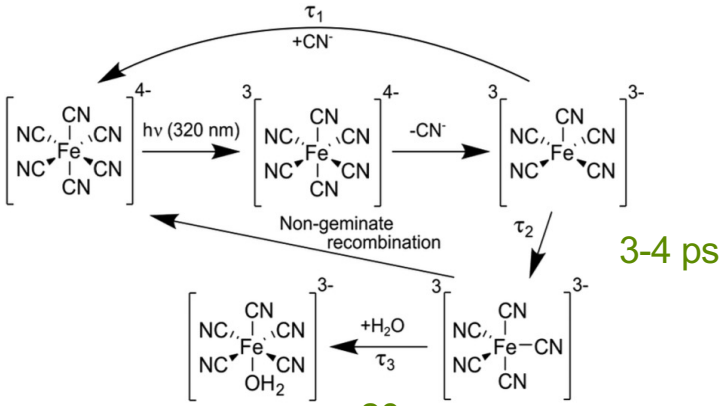
Chergui Group, EPFL, Switzerland

- 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



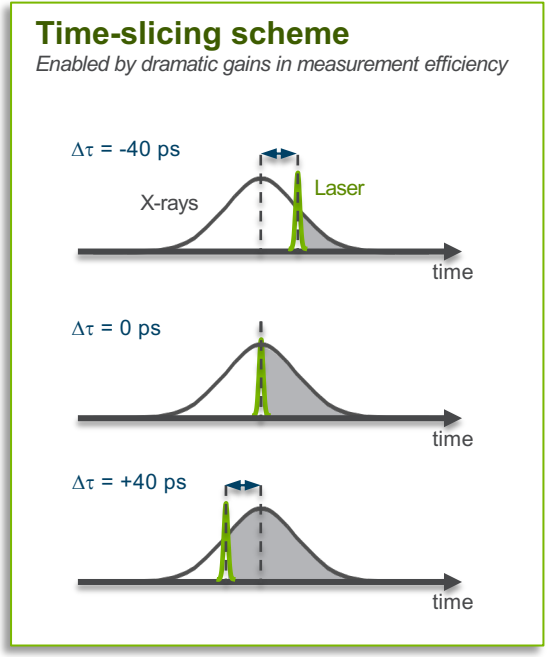
At APS can we capture the short-lived (20 ps) pentacoordinated intermediate species, determine its structure, and validate the proposed reaction scheme?

Argonne NATIONAL LABORATORY

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

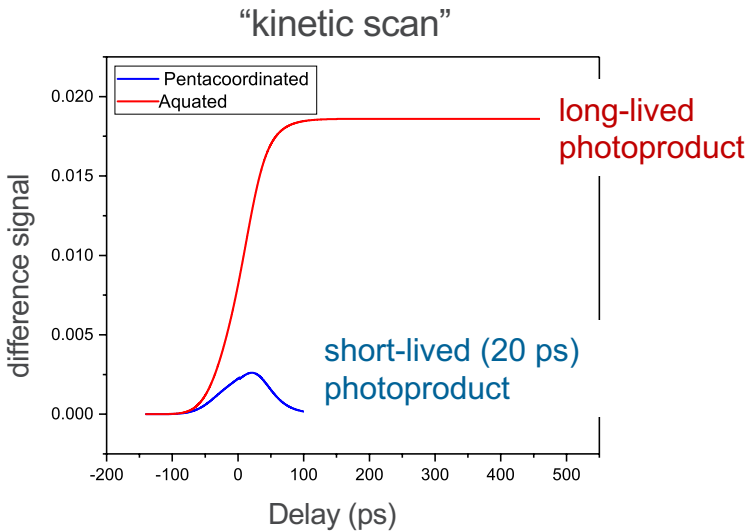
Observing sub-pulse-duration dynamics at the Advanced Photon Source

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



measured signal vs. time: convolution

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



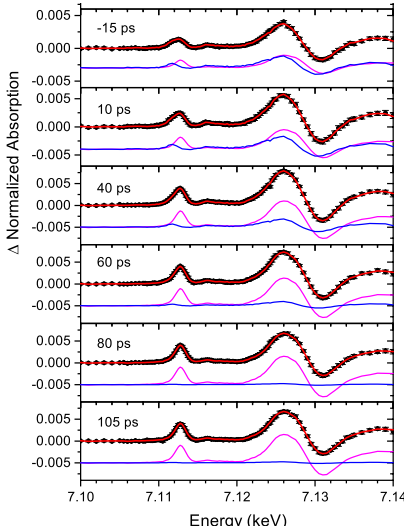
A. M. March *et al.*, J. Chem. Phys. (2019)

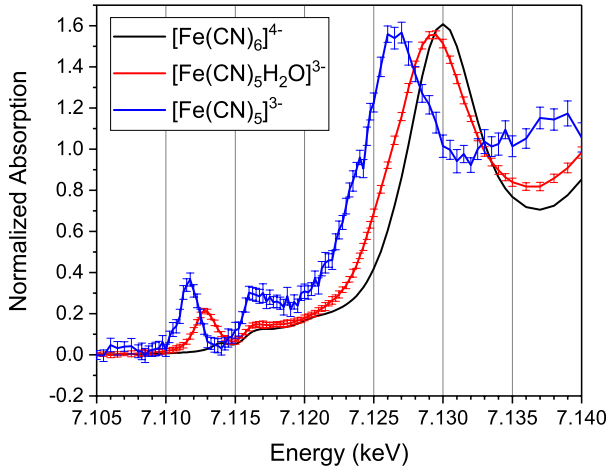
Argonne NATIONAL LABORATORY

Steps to isolating the spectrum of the transient

$$*[Fe^{II}(CN)_6]^{4-} \xrightarrow{\tau_1} [Fe^{II}(CN)_5]^{3-} \xrightarrow[+H2O]{\tau_2} [Fe^{II}(CN)_5H_2O]^{3-}$$

- Obtain spectrum of the photoaquated product
- Subtle signs of differences between 50 ps and 215 ps delays ($\Delta A \sim 0.0001$)
- Track kinetics (-60,-45, -15, 10, 40, 60, 80, 105 ps) at specific photon energies
- Global fit of kinetics to sequential mechanism for concentrations
- SVD analysis – extract spectrum of intermediate – fraction ~0.25%, lifetime ~ 20ps





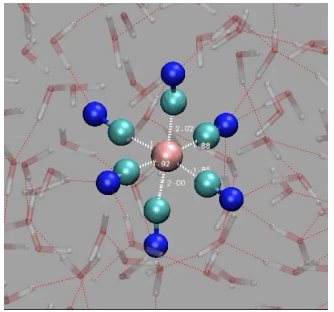
A. M. March *et al.*, J. Chem. Phys. (2019)

QM/MM MD simulations

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

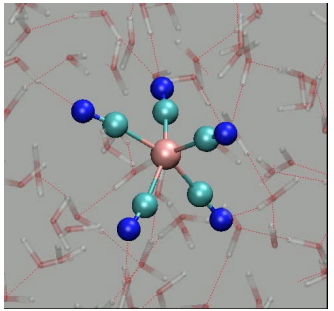
I. $^{3}[Fe^{II}(CN)_6]^{4-} \xrightarrow[1.3\ ps]{-CN^-} {}^{3}[Fe^{II}(CN)_5]^{3-}_{SP}$

- CN^- dissociation takes place in ~1.3 ps



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

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



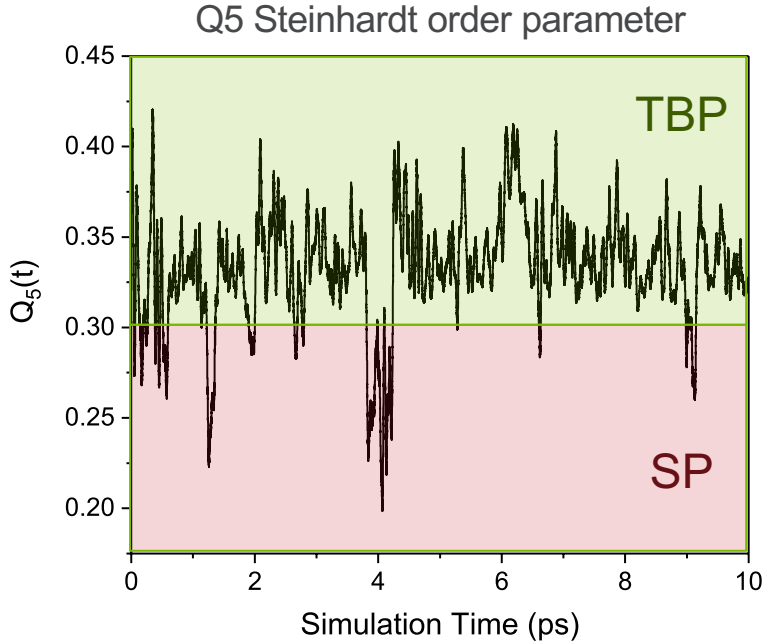
III. $^{3}[Fe^{II}(CN)_5]^{3-} \xrightarrow{+H_2O} {}^{3}[Fe^{II}(CN)_5 H_2O]^{3-} \xrightarrow[\sim 1\ ps]{} {}^{3}[Fe^{II}(CN)_5]^{3-}_{TBP} + H_2O$

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

- 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

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

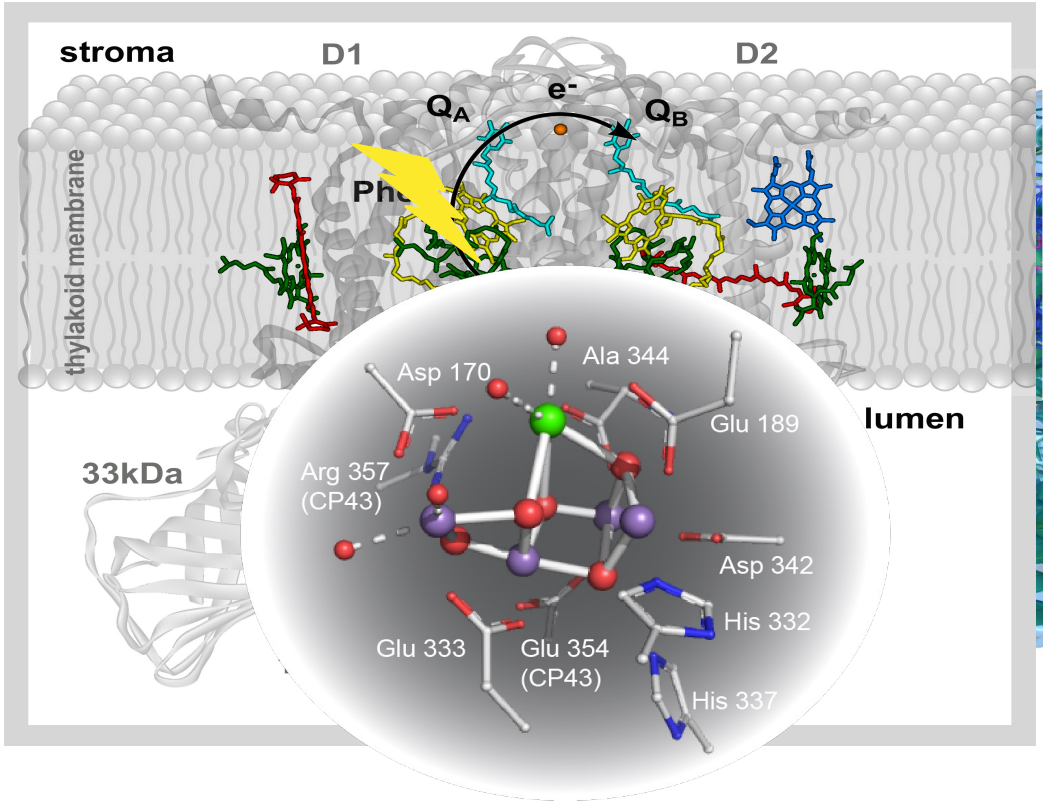
A. M. March *et al.*, J. Chem. Phys. (2019)

Photosystem II – structure and mechanism

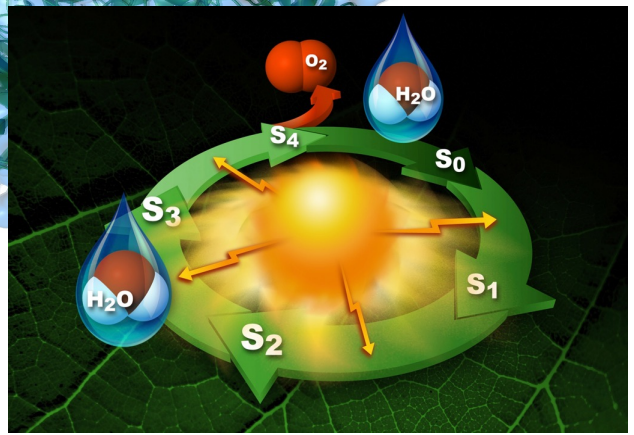
combined diffraction & spectroscopy studies
characterize multiple intermediate states along photocycle

Slides courtesy Junko Yano

Water oxidation reaction in photosystem II



- Where and how the O-O bond formation occurs?
- How substrate water comes in?
- How the protein environment modulates the catalytic reaction?



4 photons

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$$

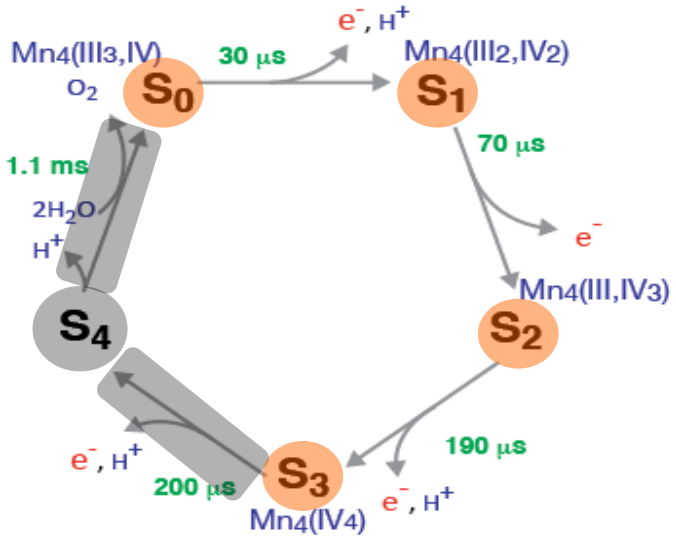
Understanding the mechanism of the water oxidation reaction in Photosystem II

Status prior to XFEL experiments:

- High-resolution crystal structure of **the dark (S_1) state**.
- Information from **various advanced spectroscopies** (EPR, IR, Optical, and X-ray) of the stable S (S_1, S_2, S_3, and S_0)-states at cryo. temp. that predict possible structure and electronic structure of those states.
- Proposed water oxidation mechanisms from theoretical studies.

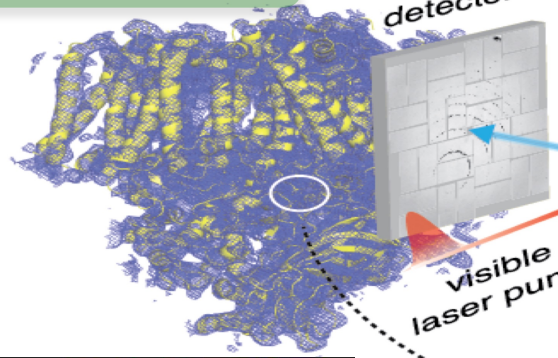
Gaps:

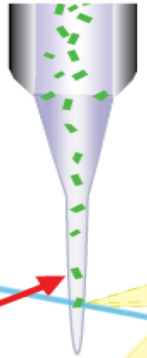
- Requires high-resolution **room temperature structure** of **each S-state** as well as **time-points** during the transitions.
- Capability (methods) for interpreting structural information together with spectroscopic data.
- **Charge/spin localization/delocalization** between metals and ligands during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

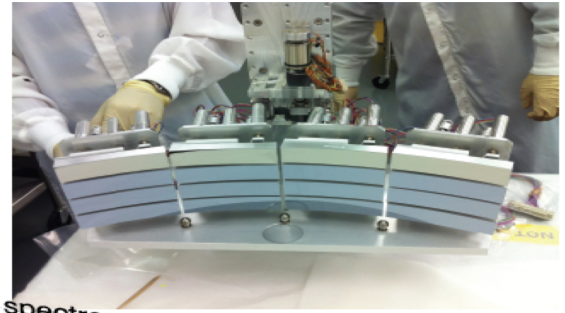


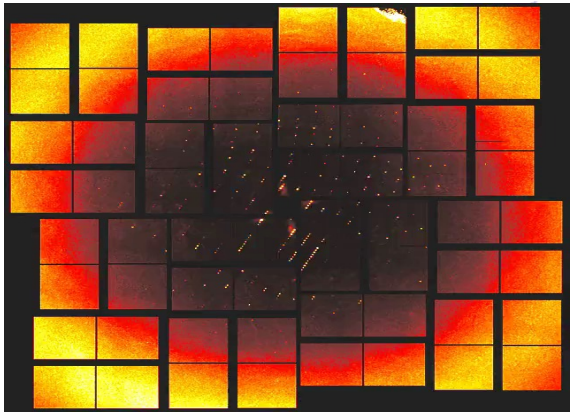
Simultaneous x-ray crystallography and spectroscopy at RT

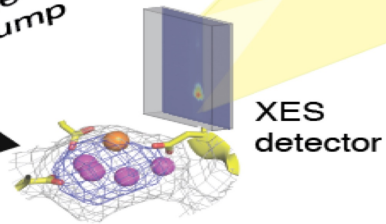
X-ray diffraction
(protein structure)





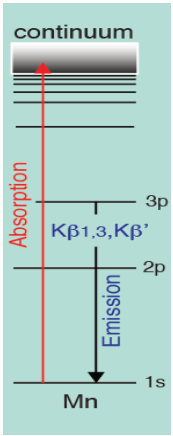


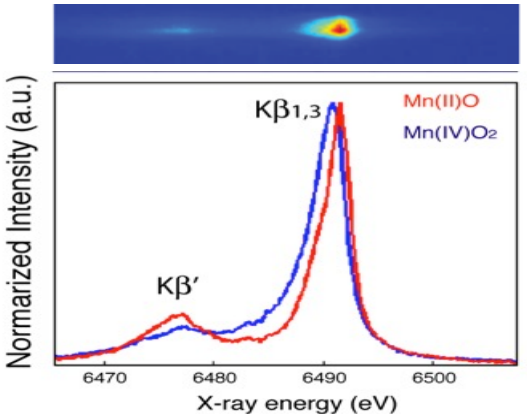




X-ray emission
spectroscopy
(catalytic center)

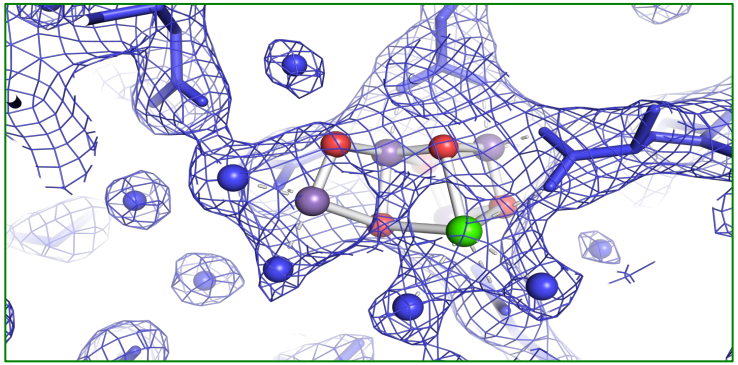
Sierra et al., (2012) *Acta Cryst. D*
Alonso-Mori et al., (2012) *RSI*
Alonso-Mori et al., (2012) *PNAS*
Kern et al., (2012) *PNAS*
Kern et al., (2013) *Science*





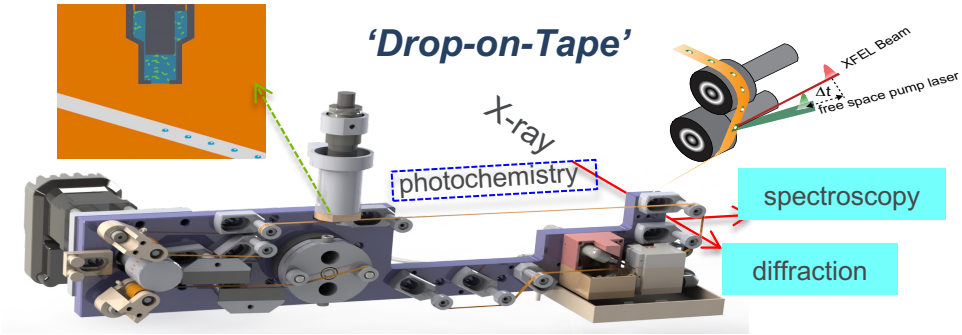
High resolution structure of OEC in light activated state!

Enabled by improved sample delivery and data collection efficiency



Structure of the oxygen evolving Mn_4Ca complex in photosystem II in the S1 and S3 state at RT to 2.25 Å.

Kern et al., (2014) Nature Comm.
Young, I. D., *et al.* (2016) *Nature*
Fuller, F.D., *et al.* (2017) *Nature Methods*

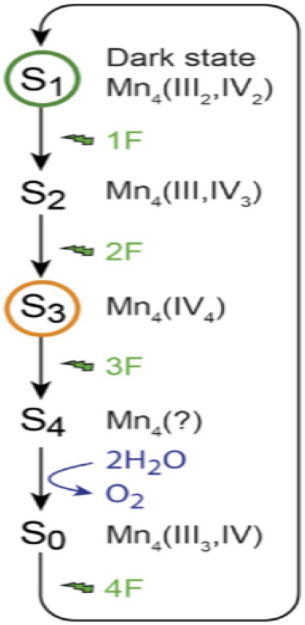


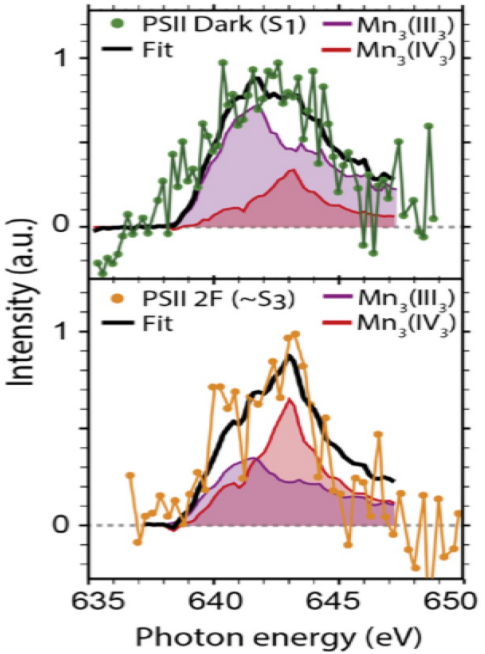
Future Outlook

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

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

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





Mitzner et al. (2013) J. *Phys. Chem. Letts.*, Kubin et al. (2017) *Structural Dynamics*

Courtesy J. Yano

X-ray pump / x-ray probe studies

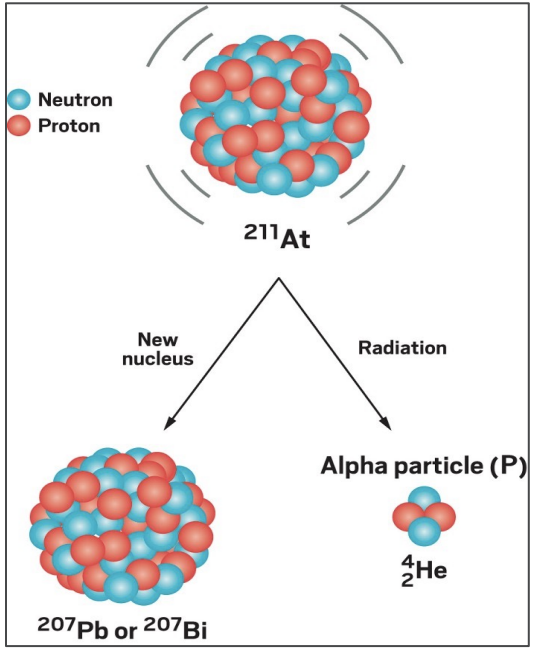
watching & controlling inner-shell electron motion
understanding radiation damage – attosecond timescales

Interaction of ionizing radiation with matter – some practical motivations

Space Travel

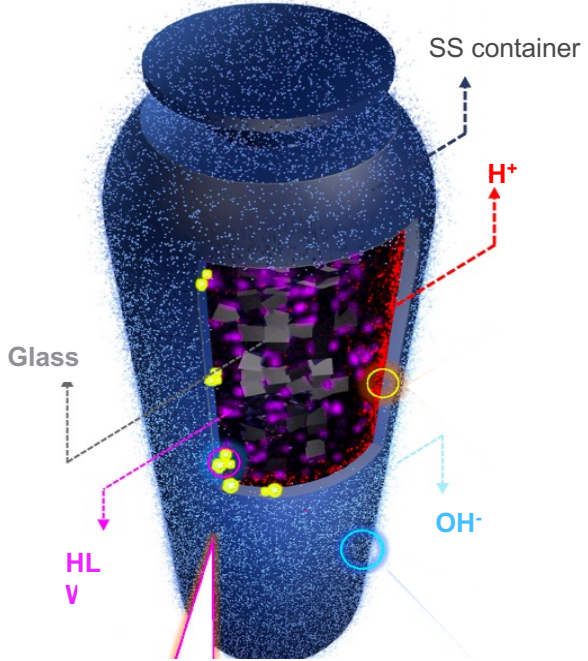
Science – Apr 12, 2019

Cancer Therapeutics



C&E News – 2020

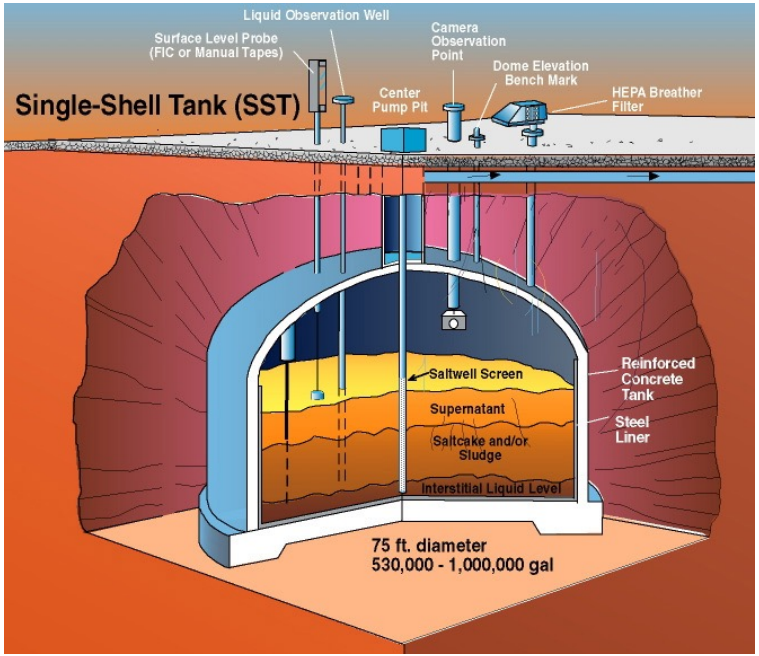
Nuclear power plants & waste containment



Nat. Mater. 19, 310 (2020)
C&E News Mar & Sep (2020)

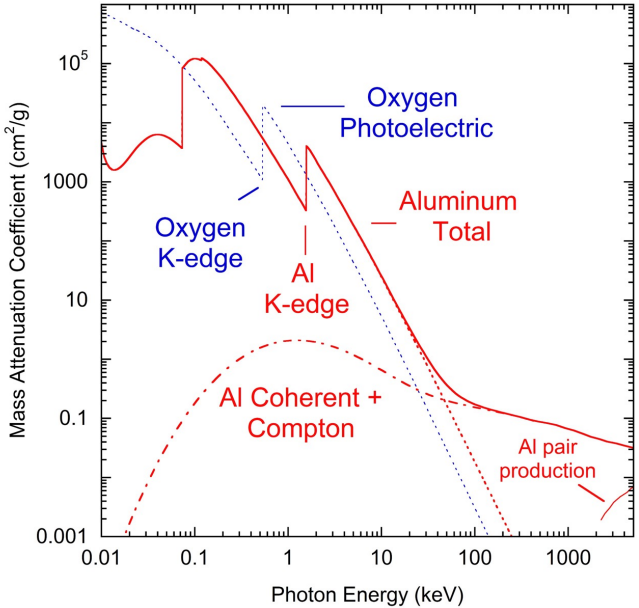
Radiation interactions and nuclear waste remediation

Complex chemistries in tanks complicates transport/removal strategies – constantly undergoing irradiation



^{90}Sr and ^{137}Cs radiation sources in tanks: primarily γ and β

~MeV γ Rays: Compton scattering is dominant



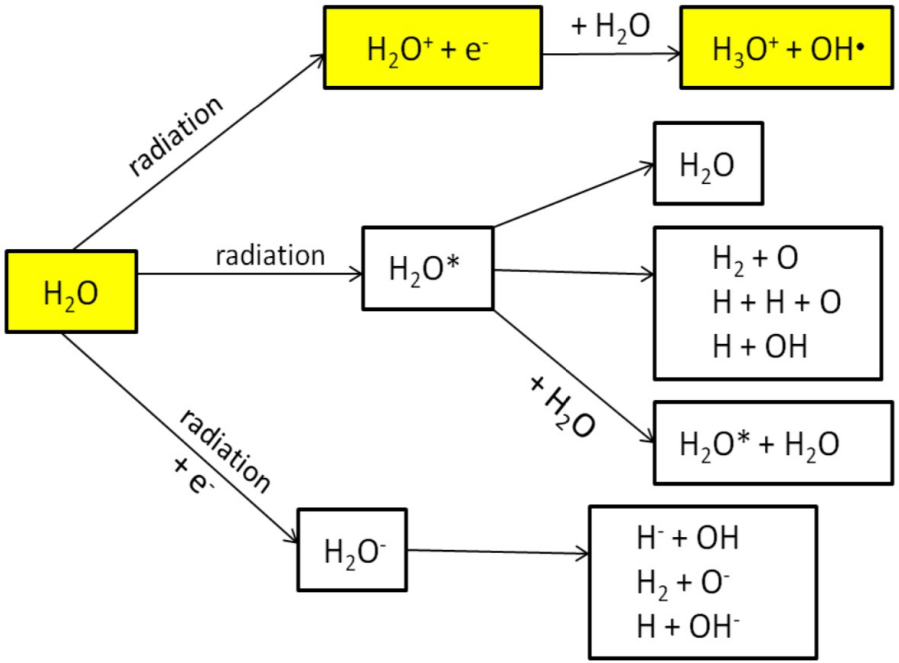
$\gamma \rightarrow \gamma' + e^-_{Comp}$ (E_e < a few hundred keV)

$\gamma' \rightarrow \gamma'' + e^-_{Comp}$ …

Photon energy drops until it is absorbed (photoelectric effect):

$\gamma^n \rightarrow e^-_{Ph}$ + core hole (most likely K-shell)

Interaction of radiation with water



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

Attention has been focused on $e^-(aq)$

4090 EDWIN J. HART AND J. W. BOAG Vol. 84

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS, AND RESEARCH UNIT IN RADIOBIOLOGY, MOUNT VERNON HOSPITAL, NORTHWOOD, ENGLAND]

Absorption Spectrum of the Hydrated Electron in Water and in Aqueous Solutions[1]

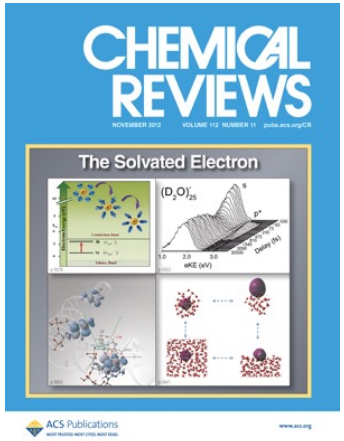
BY EDWIN J. HART AND J. W. BOAG

RECEIVED SEPTEMBER 7, 1962

A transient absorption band with peak at 7000 Å. has been found in de-aerated water and in various aqueous solutions produced a pulse of 1.8 Mev. electrons. This band is attributed to the hydrated electron. The rate of decay of the absorption and the effect of various anions, cations, and dissolved gases have been studied. Similar absorption spectra produced irradiation have been found in concentrated aqueous solutions of ammonia and of methylamine, which resemble the known absorption spectra of solvated electrons in liquid ammonia or in liquid methylamine.

Convenient strong absorption feature ctrd at ~720 nm

(2012)

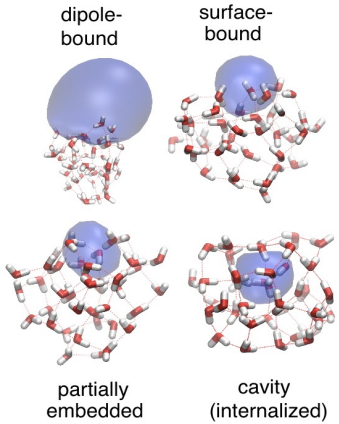


ARPC (2017)

The Hydrated Electron

John M. Herbert and Marc P. Coons

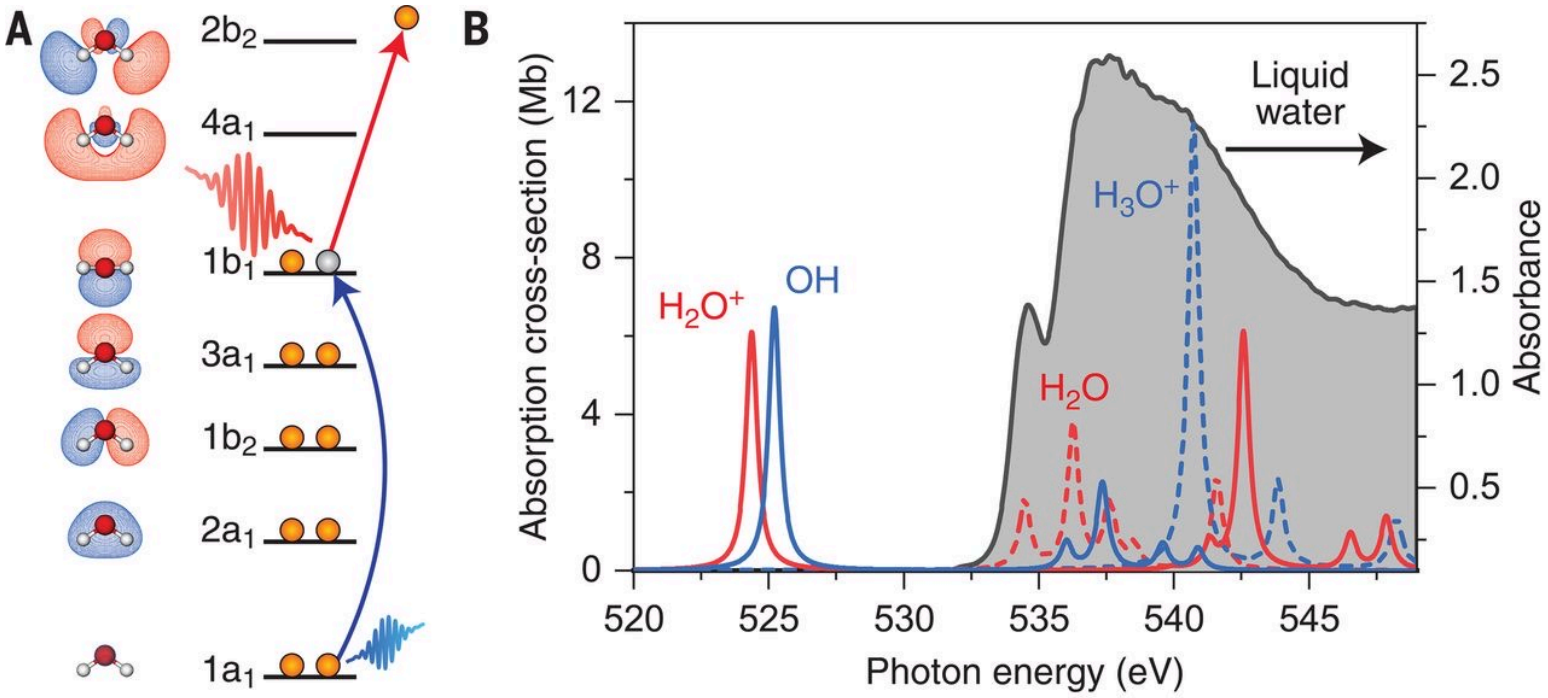
Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210; email: herbert@chemistry.ohio-state.edu



Instead we focus on the valence hole.

X-rays - clean signature of valence hole in water window

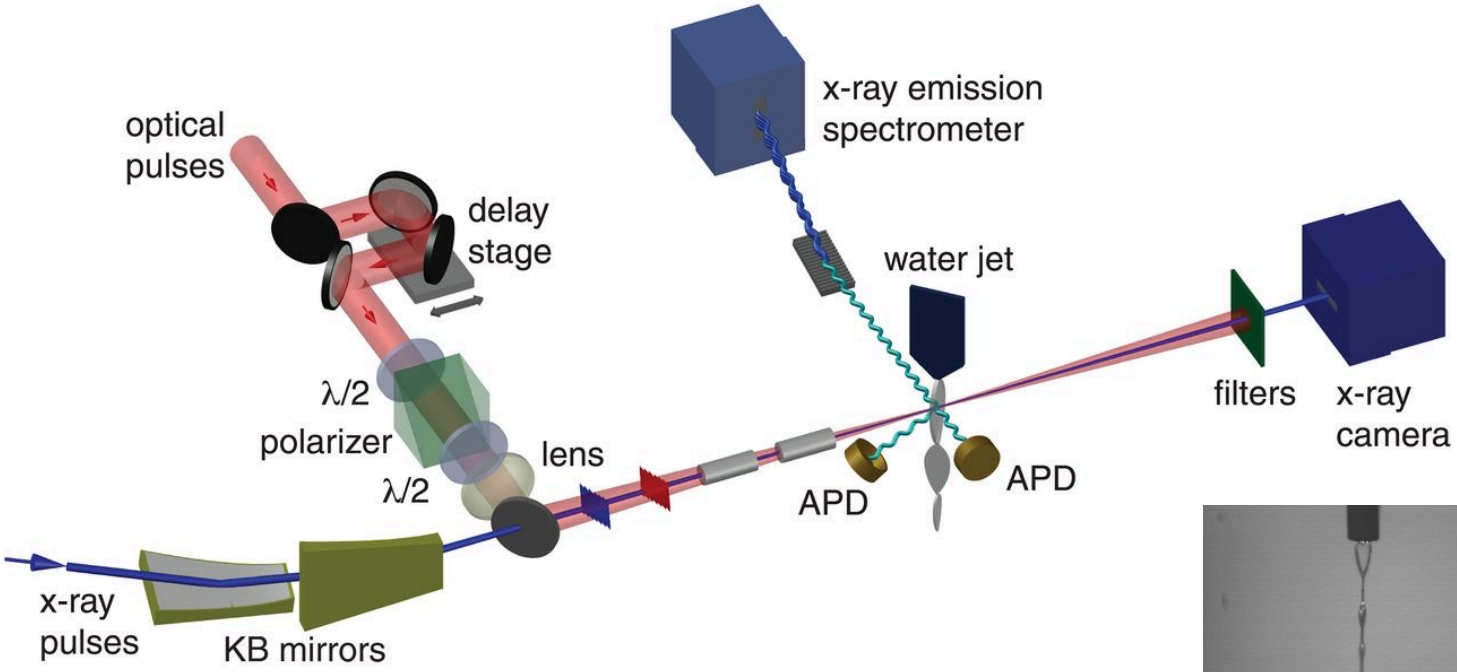
Impulsive ionization creates valence hole – soft x-ray probe H_2O^+ and OH

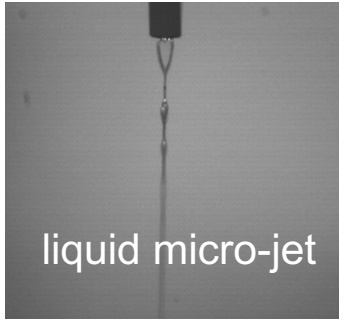


Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

Valence hole dynamics & proton transfer in water

Three simultaneous detection channels: XTAS, TFY, RIXS
Thin sheet water jet

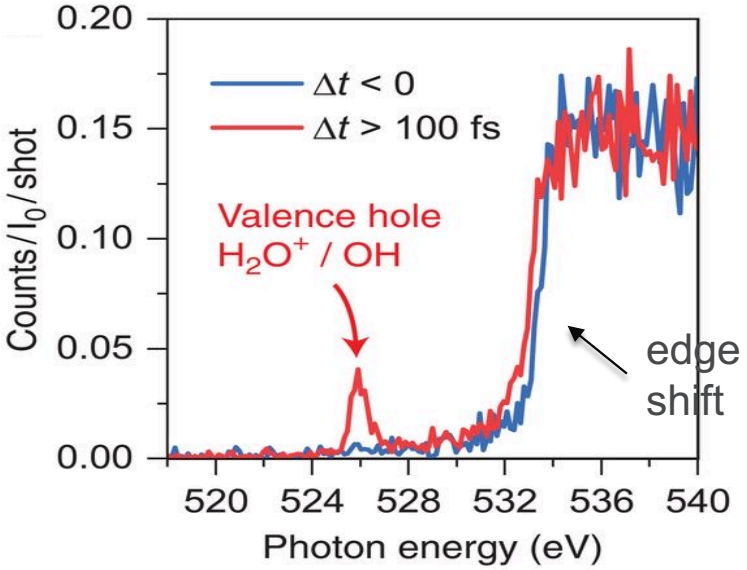




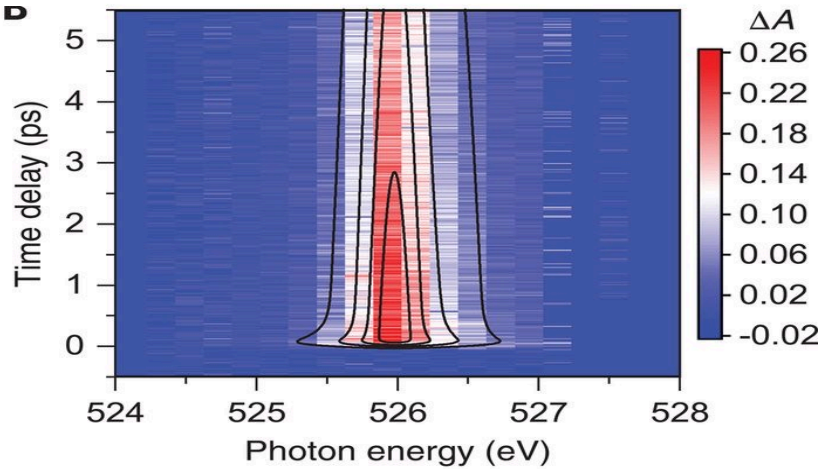
Z. H. Loh … Science (2020)

X-ray transient absorption tracks ultrafast proton transfer

Absorption before and after ionization



Time-resolved differential absorption spectrum



Complete polarization analysis:

τ_1 = 46 +/- 10 fs - proton xfer

τ_2 = 0.18 +/- 0.03 ps - vib relxn

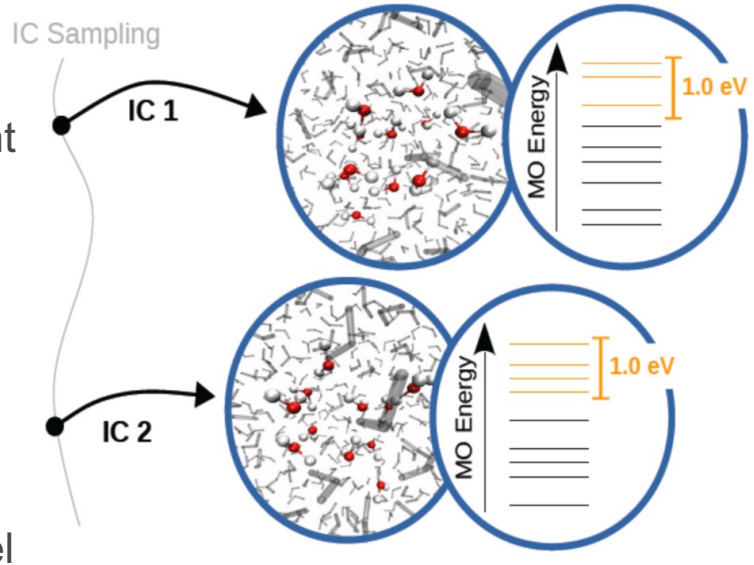
τ_3 = 14.2 +/- 0.4 ps - recombination

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

QM/MM excited-state molecular dynamics simulation of ionized liquid water

Robin Santra, Caroline Arnold

- 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)

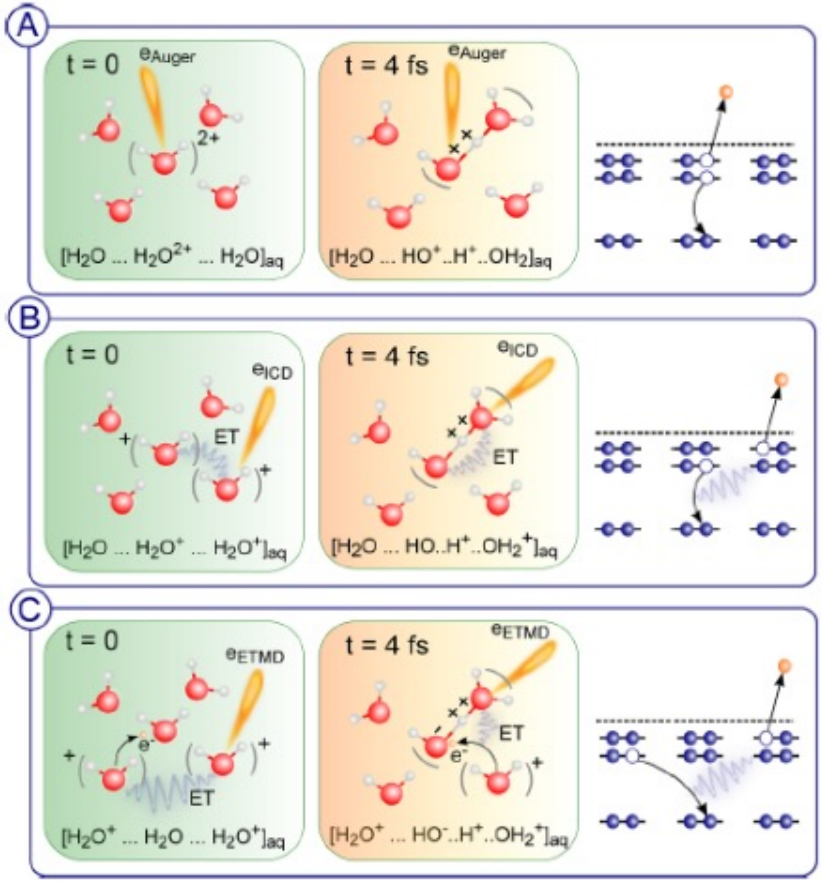


Z.-H. Loh *et al.* Science **367**, 179-182 (2020)

INNER-VALENCE AND CORE IONIZATION

- x-ray pump/x-ray probe experiments
- attosecond pulses

Local vs nonlocal decay



Auger decay (lifetime ~4 fs)

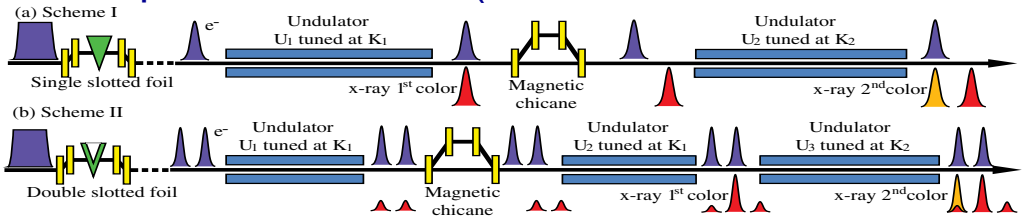
Intermolecular Coulombic Decay
(lifetime ??? fs)

ETMD
(lifetime ??? fs)

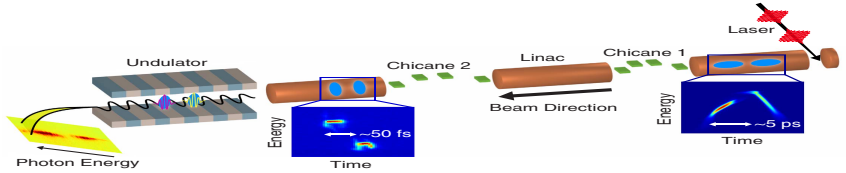
P. Slavicek … JACS **136**, 18170 (2014).

X-ray pump/x-ray probe capabilities at LCLS

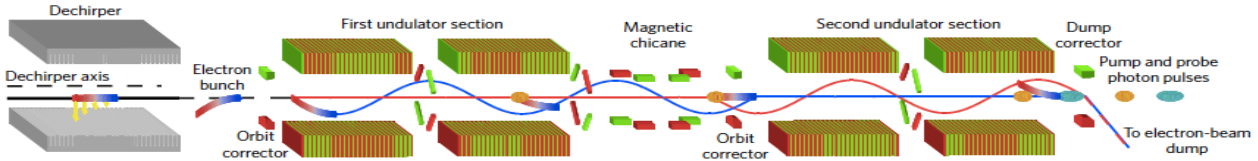
One e-bunch – two x-pulse – two color (Lutman *et al.*, PRL **110**, 134801 (2013))



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

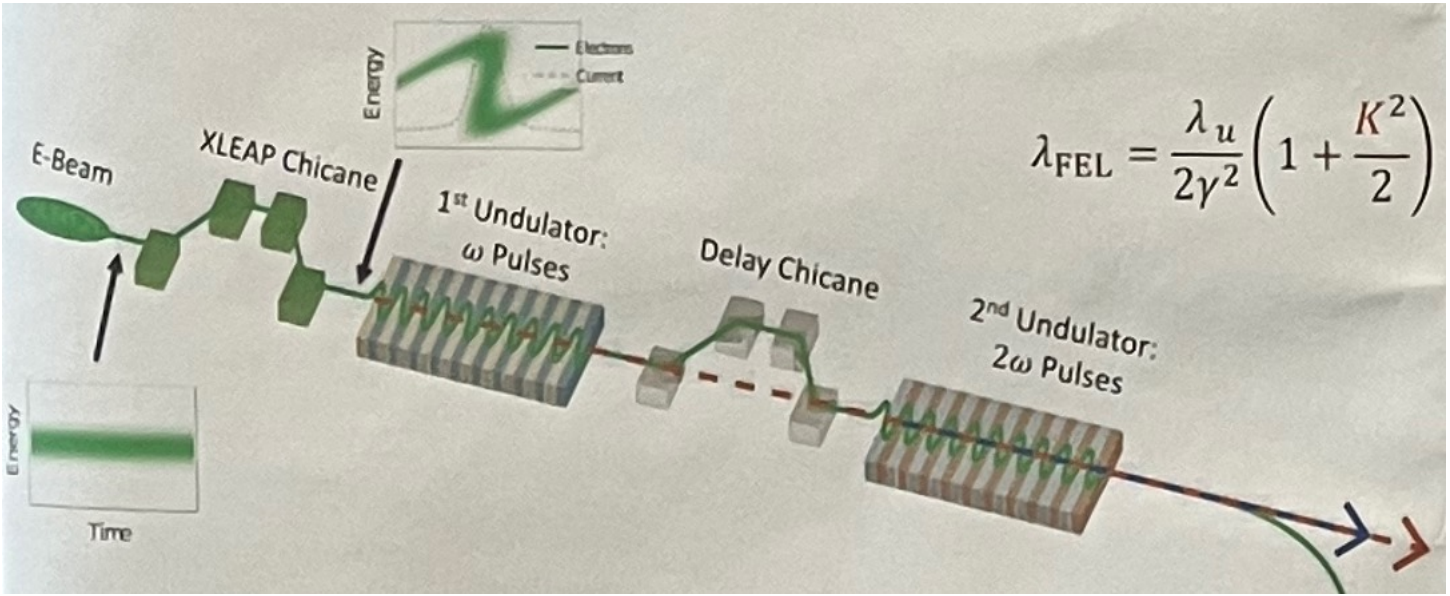


Fresh-slice multicolor (Lutman *et al.*, Nat. Photon. **10**, 745 (2016))



X-ray pump/probe capabilities extended to the attosecond regime

Original attosecond pulse production: J. Duris *et al.*, Nat Photon (2020)

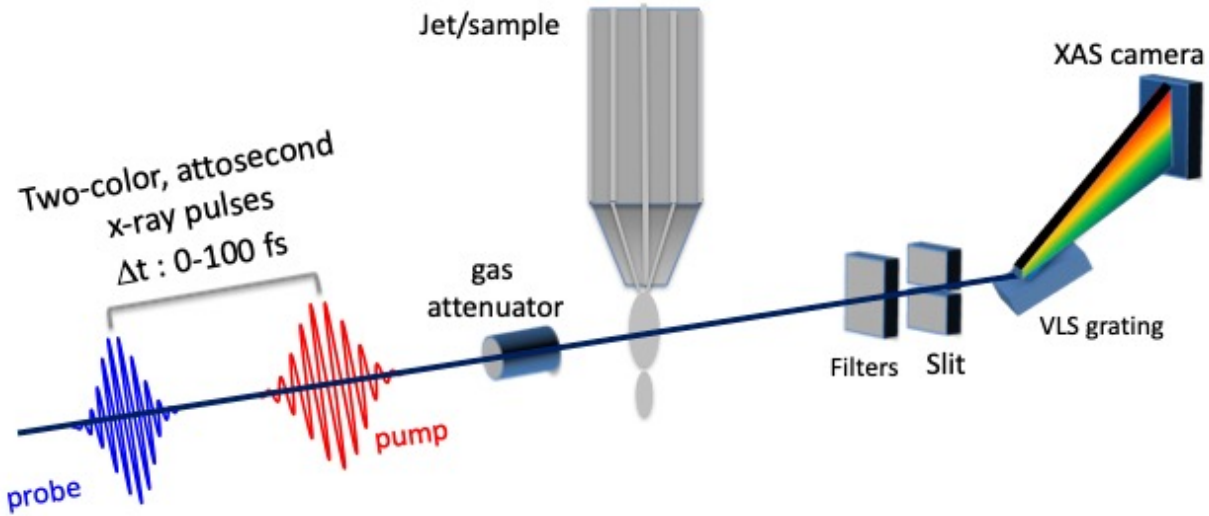


Attosecond pulse pair production: Zhaoheng Guo *et al.* poster ATTOVIII

- $\omega/2\omega$ mode with delays from 0.6 fs – 100 fs.
- Pulse duration measured —› BW ~5 eV FWHM @ 500 eV

FIRST attosecond x-ray pump/x-ray probe expt in liquids

Apr 2022: Broadband transient absorption with dispersive detection



New ChemRIXS endstation

Pump can ionize any inner-valence or valence electron

Pump OFF obtained by Argon gas in gas attenuator

Direct transient absorption measured

2D detection allows monitoring of spatial alignment

Obtained robust, reliable linear signals

Outlook bright for ultrafast dynamics studies

- Pump-probe spectroscopy and scattering reveal transient intermediates over multiple timescales for rare samples, at realistic conditions on intrinsic time and length scales– for basic and applied studies

- Emerging techniques at x-ray facilities are revolutionary
  - Advanced spectroscopy with pink and mono beam with multiple laser sources at APS – for ps to microsecond timescales
  - Pump – probe-probe-probe, multi-MHz, asynchronous methods emerging @ APS – Kinigstein, Zhang RSI **92**, 085109 (2021)
  - High repetition rate XFELs hold promise for photon-hungry techniques at femtosecond timescales

- For electronic dynamics the attosecond – few femtosecond timescales are a new frontier at XFELs.

Collaborations both enriching & inspiring

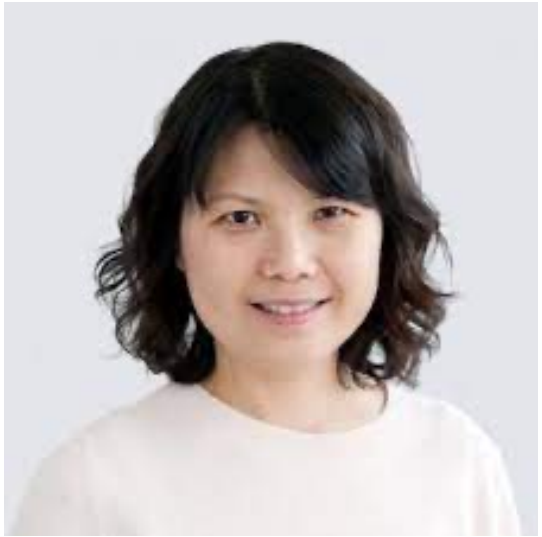
LR-01 EXPERIMENTAL TEAM

AMO group

Accelerator physicists, x-ray opticians, ultrafast laser specialists, data handlers, Domain scientists (experimentalists and theorists) w/ questions

Important contacts for ultrafast studies at APS

Shelly Kelly



Xiaoyi Zhang

Anne Marie March

Feedback

Lecture – 3:30 – 4:30 00
Probing ultrafast dynamics - Linda Young
https://forms.office.com/g/msBEUg6bPs

Contact

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