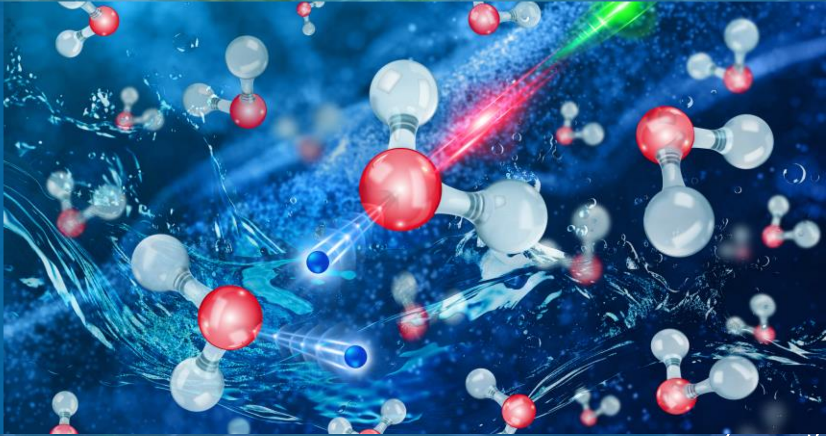
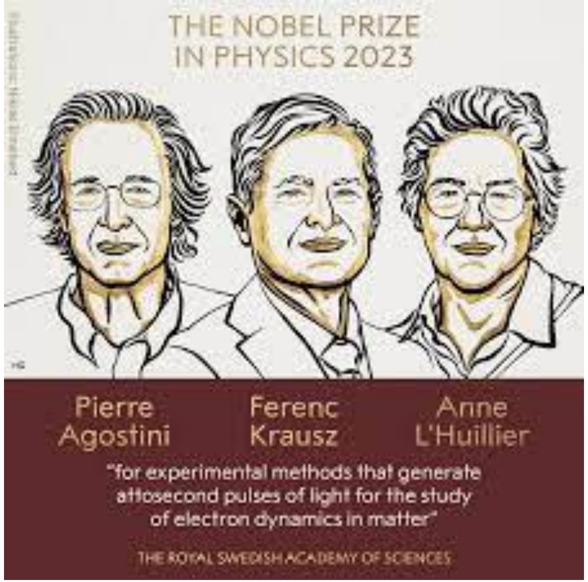
ATTOSECOND SCIENCE WITH X-RAY LASERS



LINDA YOUNG
Argonne National Laboratory
The University of Chicago

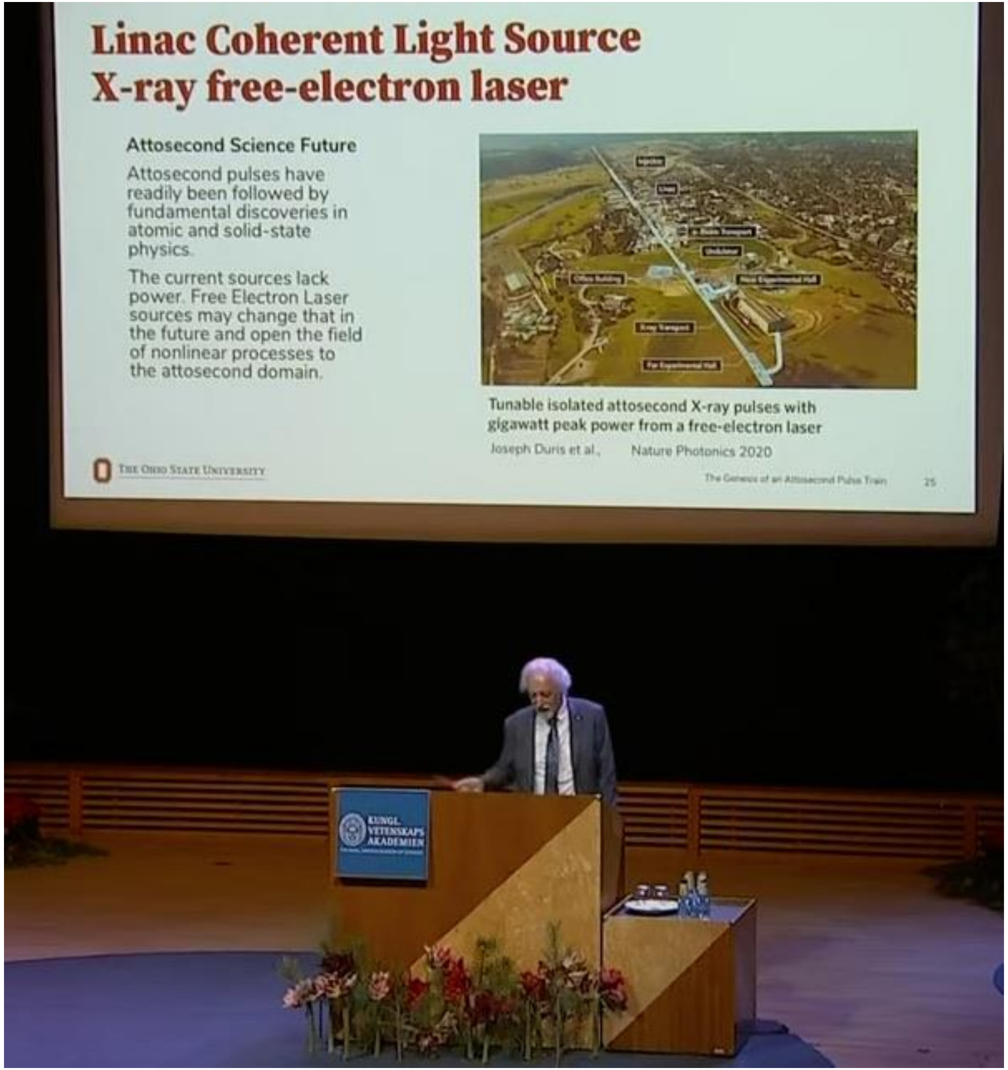
Board on Physics and Astronomy 2025
Spring Meeting
Washington, D.C.
1 May 2025

Support from US DOE, Office of Basic Energy Sciences, Chemical Sciences, Biosciences and Geosciences Division



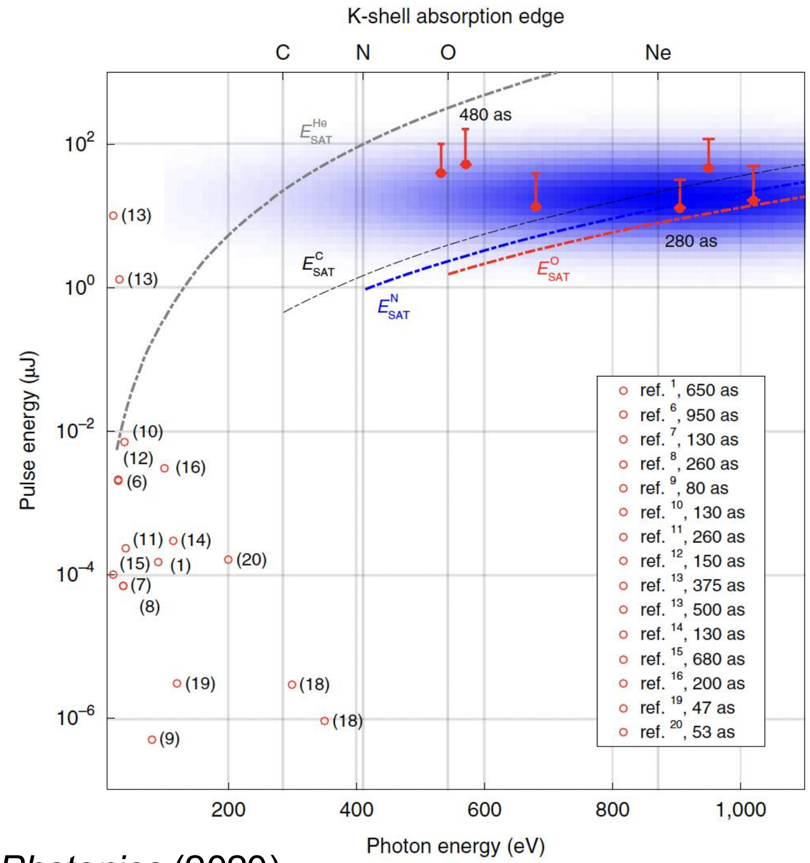
From Nobel Lectures in Physics
8 December 2023

Pierre Agostini: *just a quick look toward the future … so far attosecond pulses are created by visible or infrared lasers…but maybe the future of attoseconds is not in the our lab but with this x-ray free-electron laser…*



Attosecond x-ray pulses: XFELS v HHG

Electron dynamics
+
Atomic spatial resolution

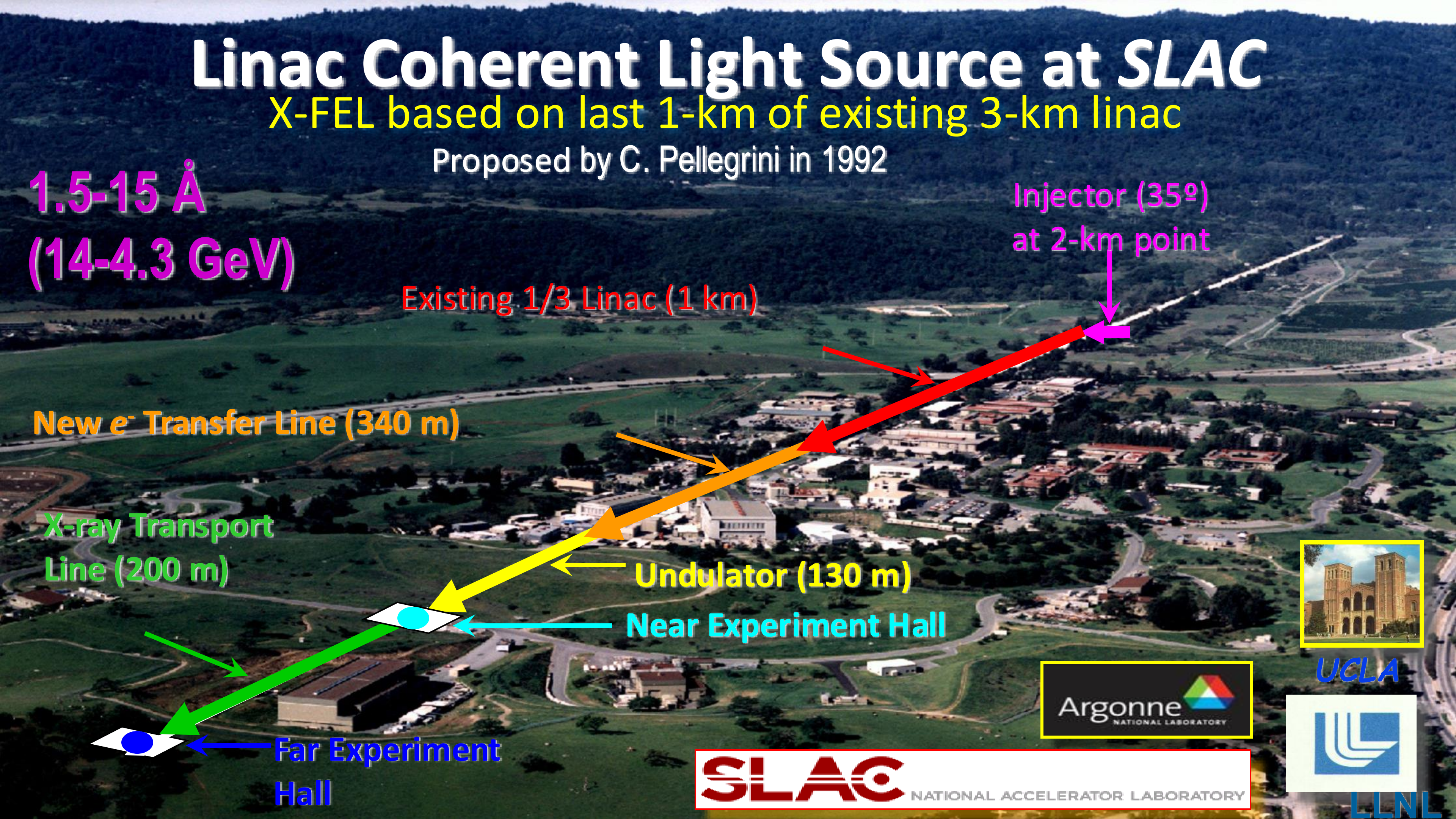


J. Duris…J. Cryan, A. Marinelli, *Nature Photonics* (2020)

Linac Coherent Light Source at *SLAC*

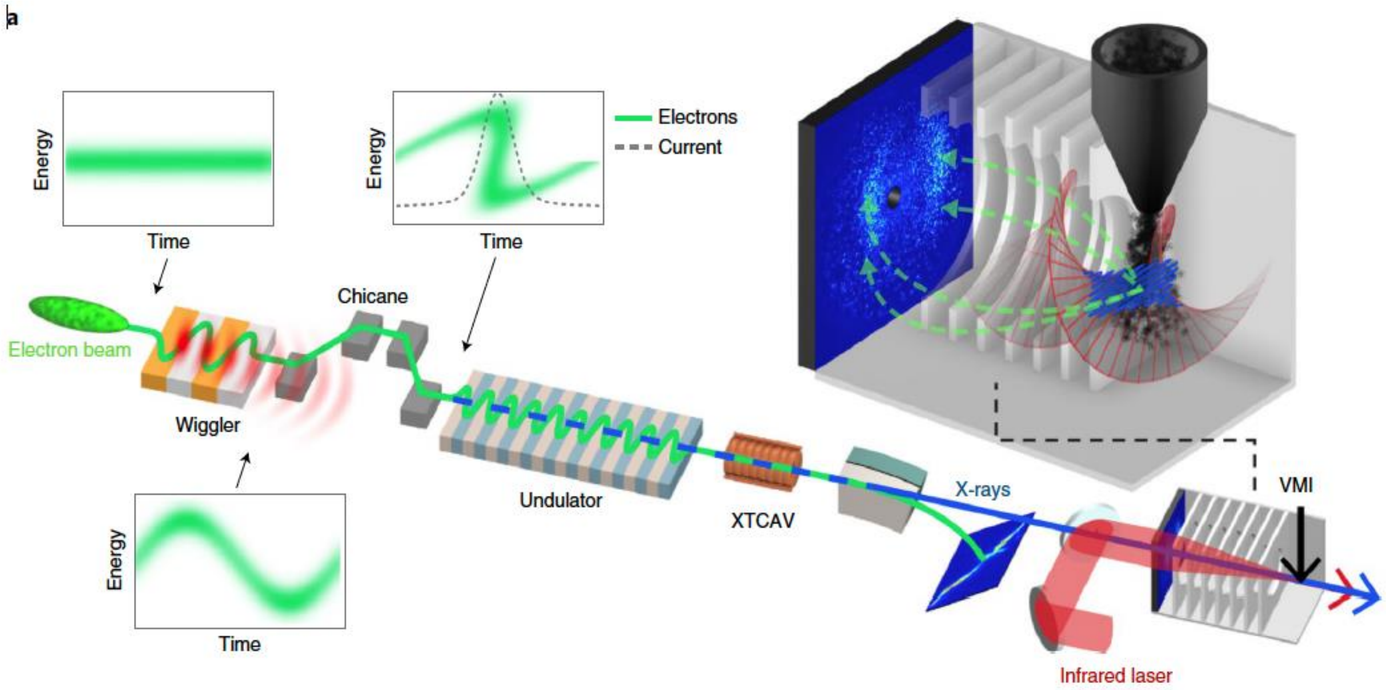
X-FEL based on last 1-km of existing 3-km linac

Proposed by C. Pellegrini in 1992

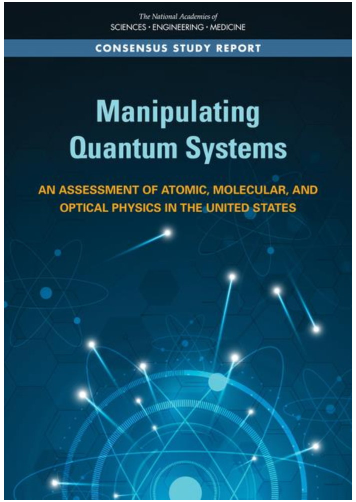


Single-spike attosecond soft x-ray pulses!

XLEAP: With measurement of pulse duration w/ c-VMI streaking



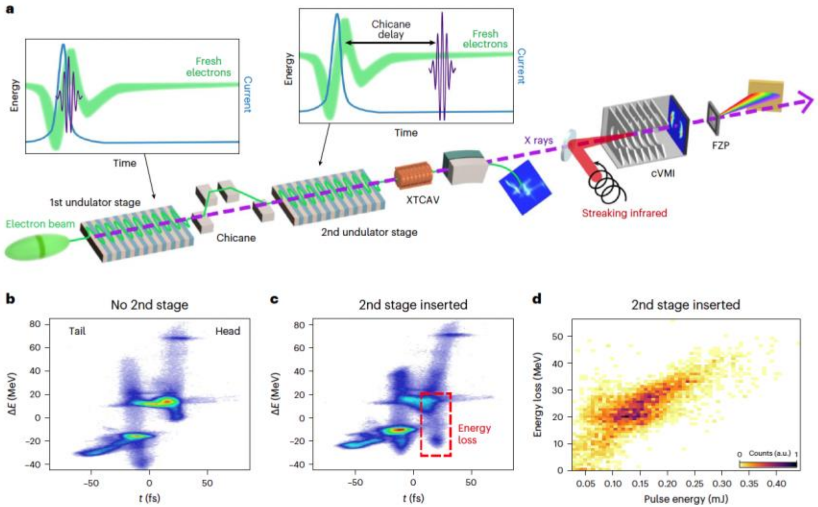
J. Duris…J. Cryan, A. Marinelli, *Nature Photonics* (2020)



AMO 2020 decadal survey, p. 158

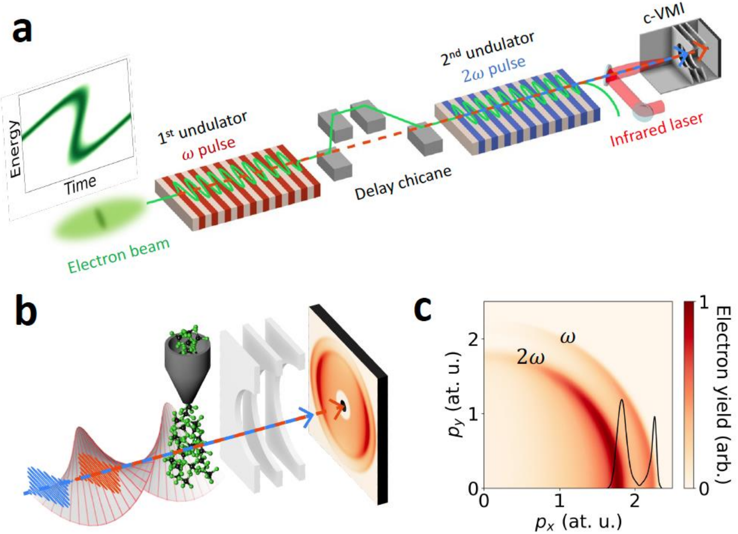
Another exciting prospects for attosecond science is the impending availability of intense attosecond pulses in the soft and hard X-ray regime from XFELs, which would enable the initiation of electron dynamics (e.g., charge migration) from inner valence or core electrons that are in general highly localized on specific atoms within a molecule. In combination with pump-and-probe capabilities, such pulses would thus allow for both spatial and temporal resolution of attosecond electron dynamics.

Terawatt-scale attosecond X-ray pulses from a cascaded superradiant free-electron laser



P. Franz … J. Cryan, A. Marinelli,
Nature Photonics (2024) May

Synchronized attosecond x-ray pulse-pair generation



Z. Guo … J. Cryan, A. Marinelli,
Nature Photonics (2024) May

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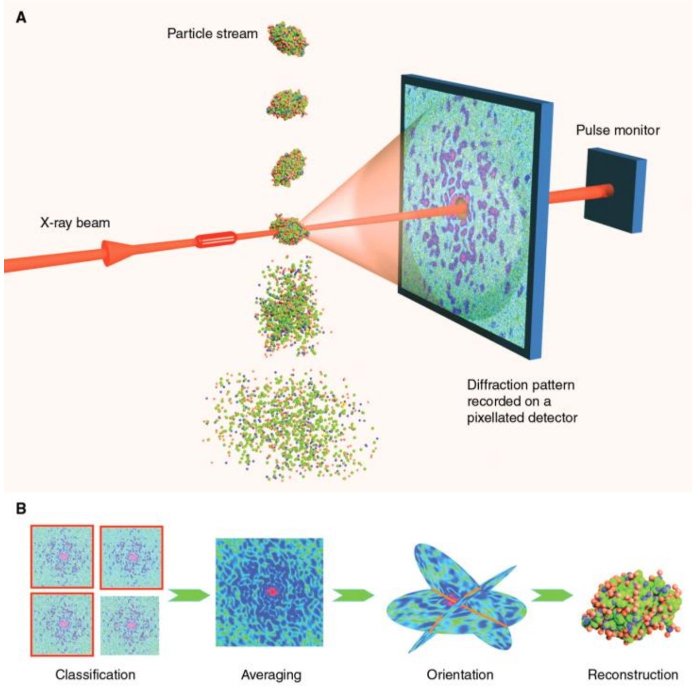
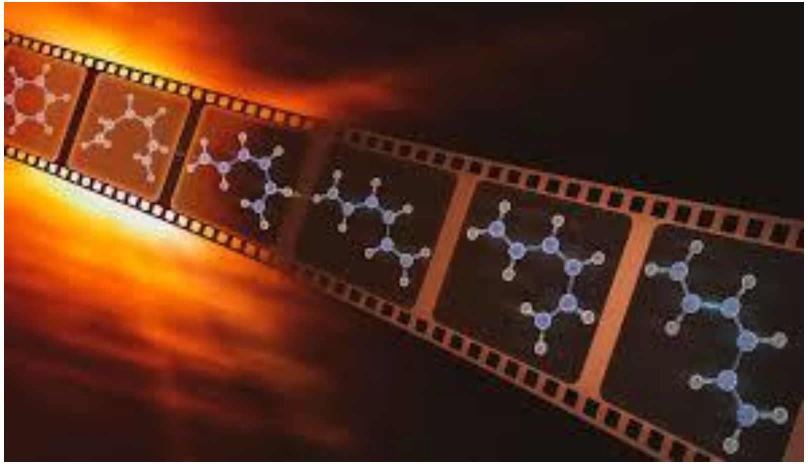
Original applications of XFELs – enhanced w/attosecond pulses

Single Particle Imaging



K. J. Gaffney & H.N. Chapman, *Science (2007)*
Neutze… Hajdu, *Nature* (2000)
Chapman...Spence, *Nature* (2011)
Seibert… Hajdu, *Nature* (2011)

Molecular Movies



Minitti et al, *PRL* **114**, 255501 (2015) – XRD
Attar et al, *Science* **356**, 54 (2017) - XAS
Wolf et al, *Nat Chem*. **11**, 504 (2019) - UED

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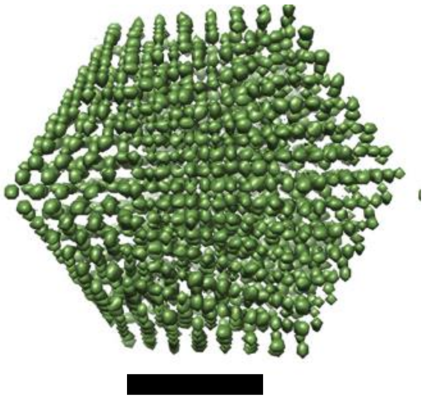
Spatial resolution with CDI at FELs

Theory

Ar

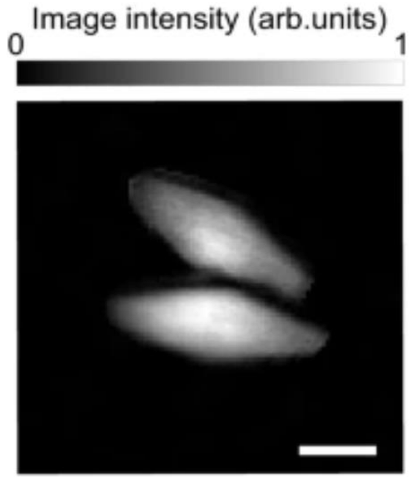


4 nm

Ho, Phay J., et al., *Physical Review A* 94.6 (2016): 063823.

Experiment

Au



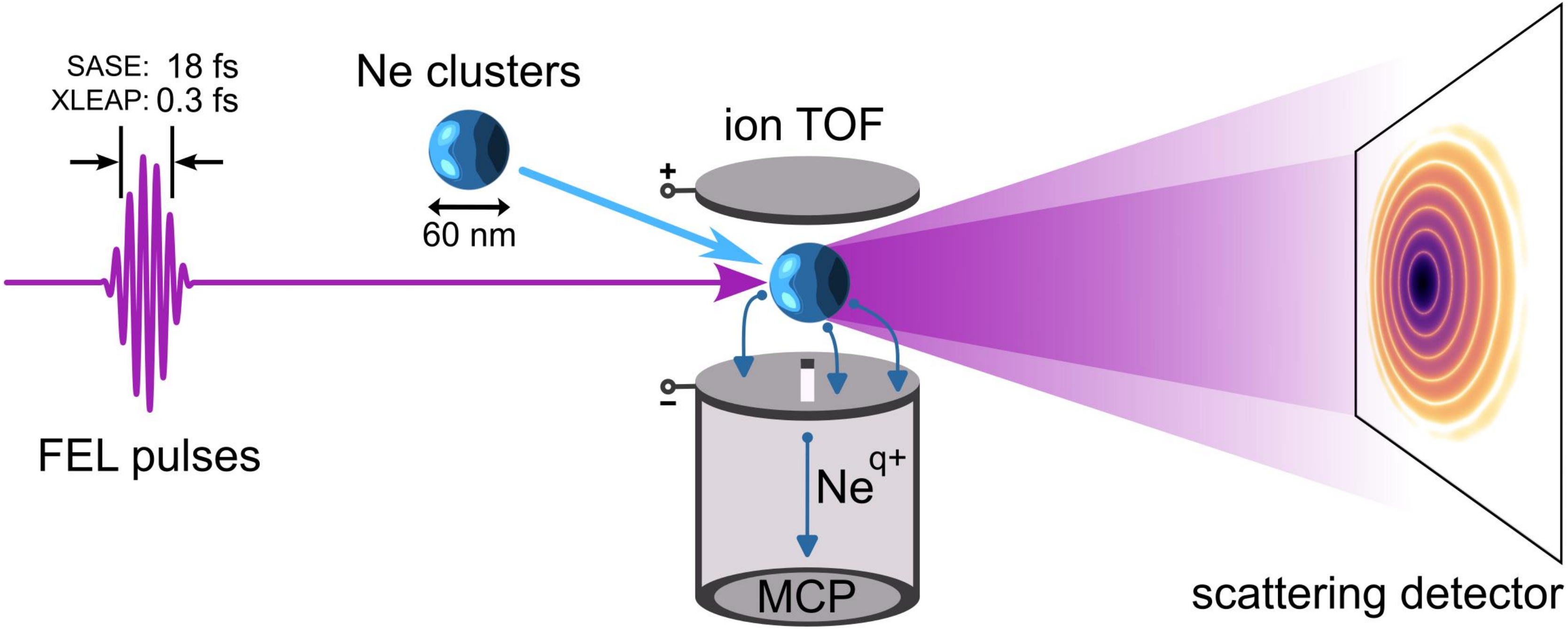
20 nm

Yumoto, Hirokatsu, et al. *Nat. Comm.* 13.1 (2022): 1-8.

Courtesy Tais Gorkhover

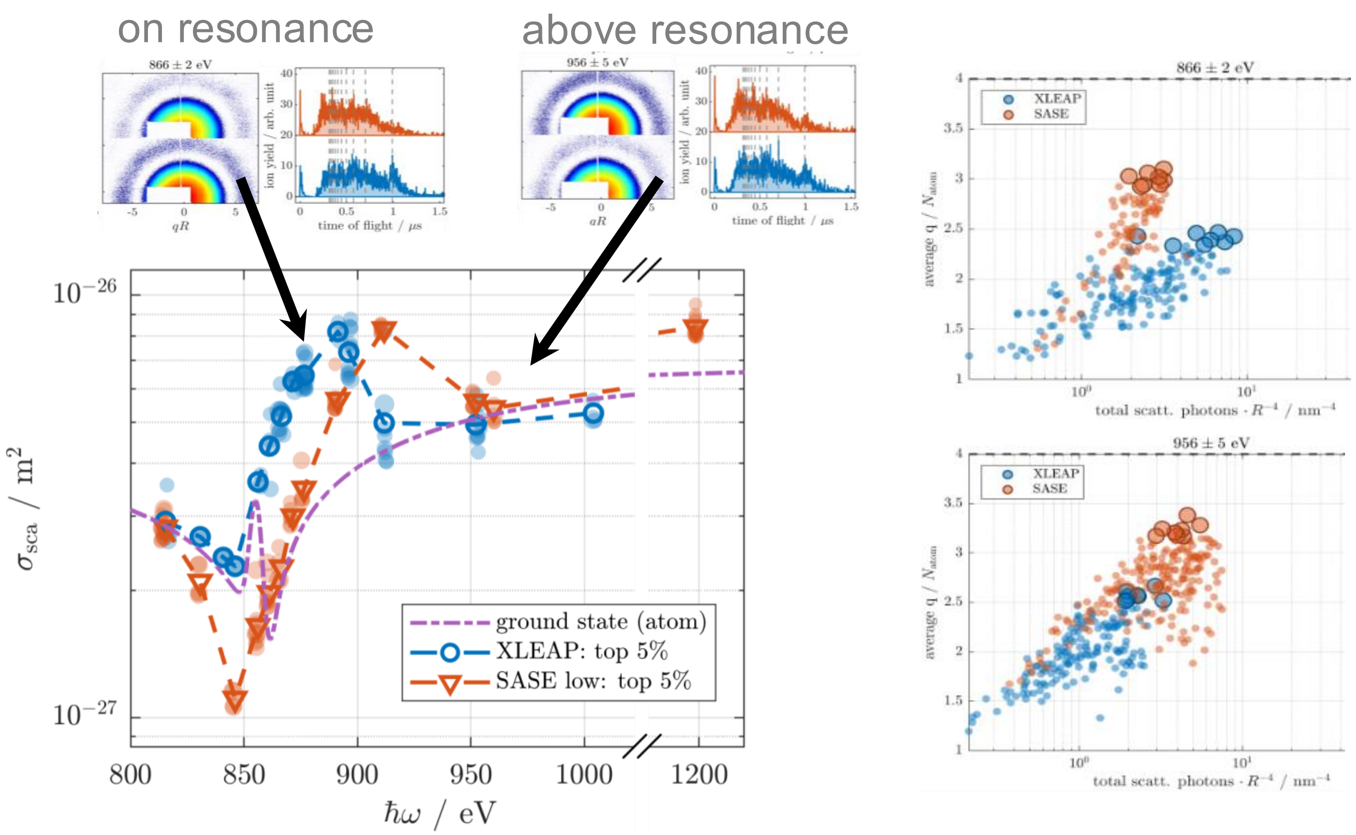
Optimizing single particle imaging

SASE (fs pulses) v XLEAP (attosecond pulses)



Courtesy Tais Gorkhover

Resonant as pulses increase scattering & decrease damage



Courtesy Tais Gorkhover

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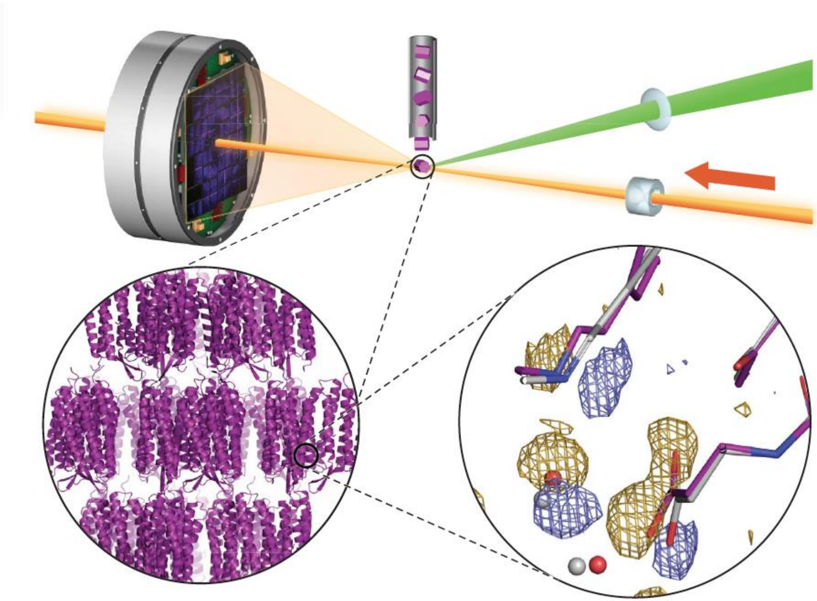
STRUCTURAL BIOLOGY

Advances and challenges in time-resolved macromolecular crystallography

Gisela Brändén and Richard Neutze*



Diffract before destroy – SFX
+ optical pump laser

~770 SFX deposits in PDB
~200,000 total deposits

Photosystem I, Photosystem II, Photoactive yellow protein, human rhodopsin, bacteriorhodopsin, light-activated ion channels, fluorescent proteins, myoglobin-CO, cytochrome c oxidase-CO

Science ***373***, *980 (2021)*

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Science 1 Dec (2023)

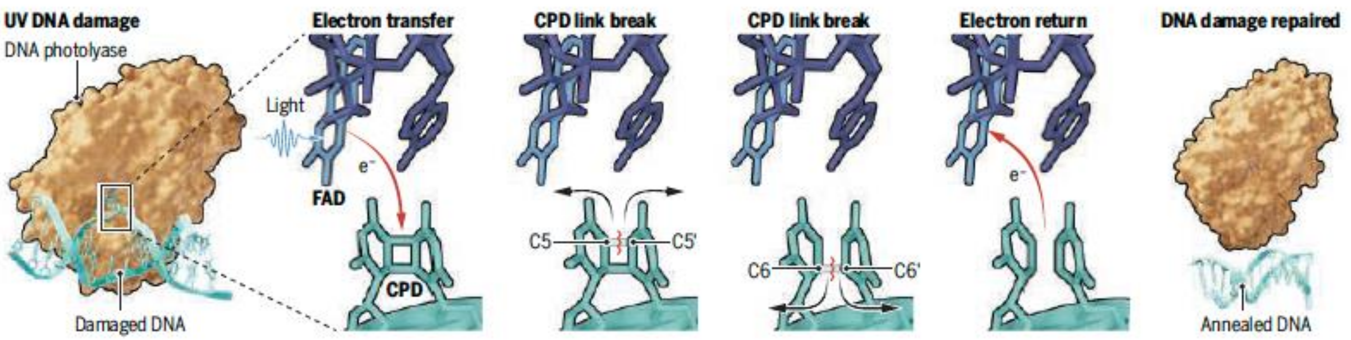
MOLECULAR BIOLOGY

Filming DNA repair at the atomic level

Dissection of multistep catalysis by a photoenzyme could inspire green chemistry applications

Light-induced DNA repair

Cyclobutane pyrimidine dimer (CPD) DNA photolyase repairs ultraviolet (UV) light–induced CPDs that arise between two adjacent pyrimidine bases. Four temporally distinct chemical steps occur that involve the flavin-adenine dinucleotide (FAD) coenzyme of the photolyase and the bases to break the two bonds that form the CPD.



By **Marten H. Vos**

ENZYMOLOGY

Visualizing the DNA repair process by a photolyase at atomic resolution

Maestre-Reyna *et al.*, *Science* **382**, eadd7795 (2023) 1 December 2023

ENZYMOLOGY

Time-resolved crystallography captures light-driven DNA repair

Christou *et al.*, *Science* **382**, 1015–1020 (2023) 1 December 2023

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Article

Influence of pump laser fluence on ultrafast myoglobin structural dynamics

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Check for updates

Thomas R. M. Barends[1✉], Alexander Gorel[1,10], Swarnendu Bhattacharyya[2,10], Giorgio Schirò[3], Camila Bacellar[4], Claudio Cirelli[4], Jacques-Philippe Colletier[3], Lutz Foucar[1], Marie Luise Grünbein[1], Elisabeth Hartmann[1], Mario Hilpert[1], James M. Holton[5], Philip J. M. Johnson[4], Marco Kloos[6], Gregor Knopp[4], Bogdan Marekha[7], Karol Nass[4], Gabriela Nass Kovacs[1], Dmitry Ozerov[4], Miriam Stricker[8], Martin Weik[3], R. Bruce Doak[1], Robert L. Shoeman[1], Christopher J. Milne[4], Miquel Huix-Rotllant[2✉], Marco Cammarata[9] & Ilme Schlichting[1✉]

Nature 626, 905 (2024)

NEWS & VIEWS FORUM | 14 February 2024

Energetic laser pulses alter outcomes of X-ray studies of proteins

Cutting-edge X-ray sources have enabled the structural dynamics of proteins to be tracked during biochemical processes, but the findings have been questioned. Two experts discuss the implications of a study that digs into this issue.

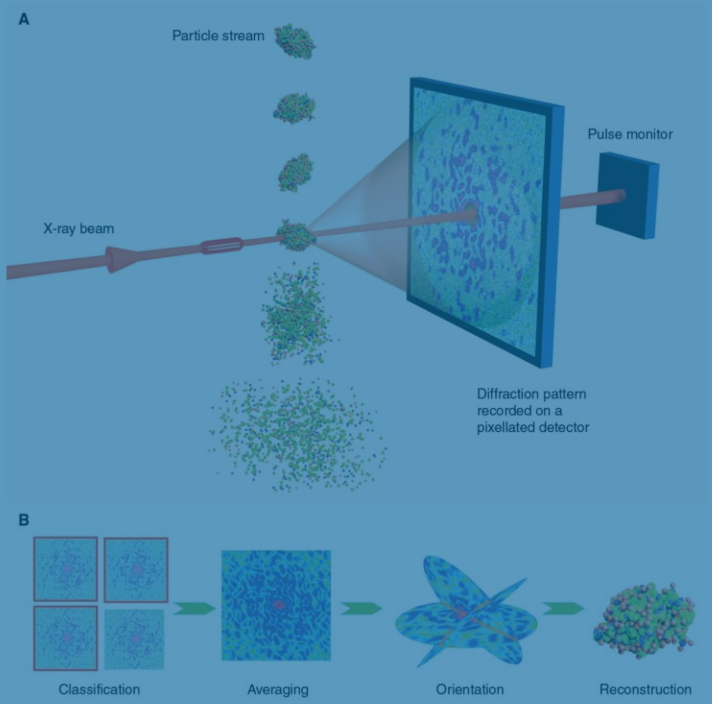
By Richard Neutze & R. J. Dwayne Miller

Nature 626, 720 (2024)

Grand challenge: structure & fcn at atomic resolution at physiological conditions

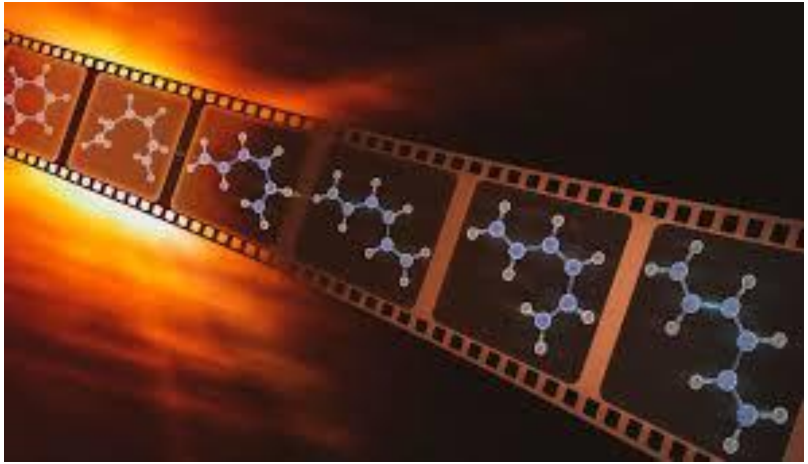
Original applications of XFELs – enhanced w/attosecond pulses

Single Particle Imaging



K. J. Gaffney & H.N. Chapman, *Science (2007)*

Molecular Movies



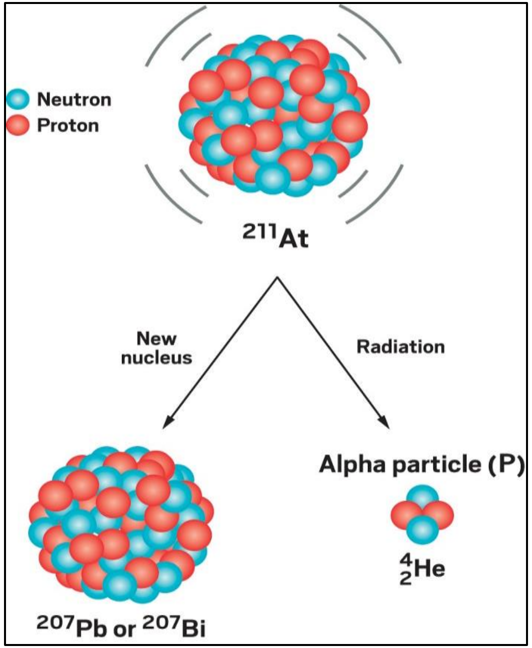
Minitti et al, *PRL* **114**, 255501 (2015) – XRD
Attar et al, *Science* **356**, 54 (2017) - XAS
Wolf et al, *Nat Chem.* **11**, 504 (2019) -UED

Radiolysis: radiation effects in liquid water

Space Travel

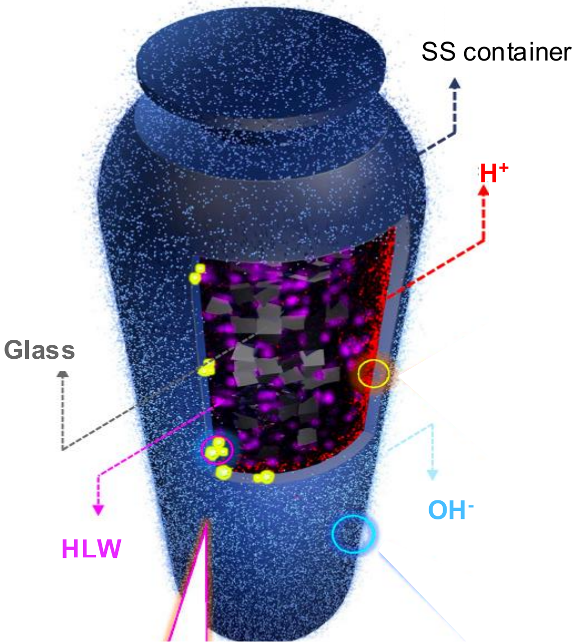
Science – Apr 12, 2019

Cancer Therapeutics



C&E News – 2020

Corrosion in nuclear power plants & repositories

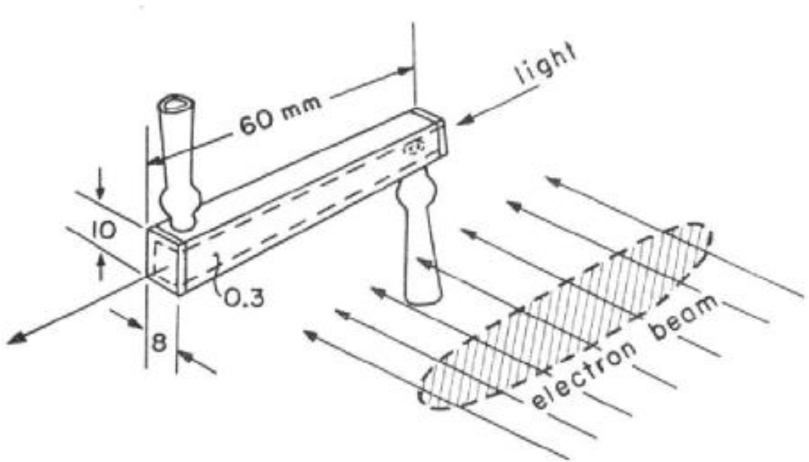


Nat. Mater. 19, 310 (2020)
C&E News Mar & Sep (2020)

Standard method for e- beam radiolysis

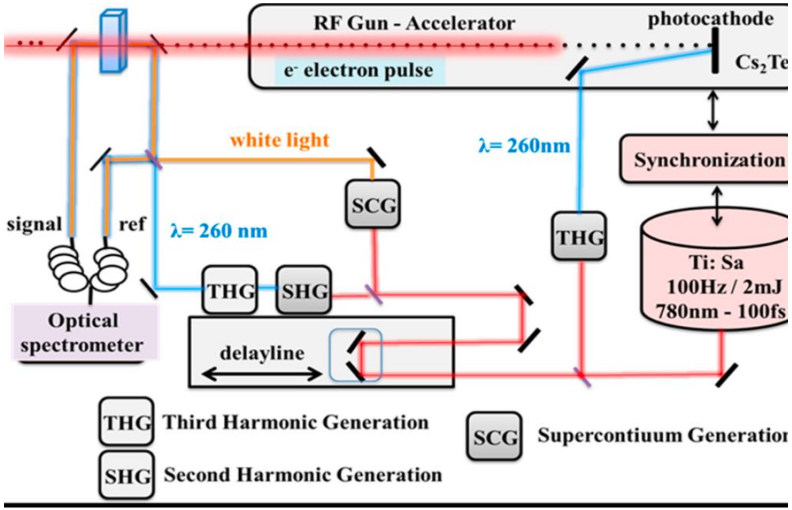
Optical detection of radiolysis products

Hart & Boag JACS 1962



e^-: 1.8 MeV, 2 μs, 0.5 A peak
probe: continuum 4 μs

Picosecond pulse radiolysis: ELYSE



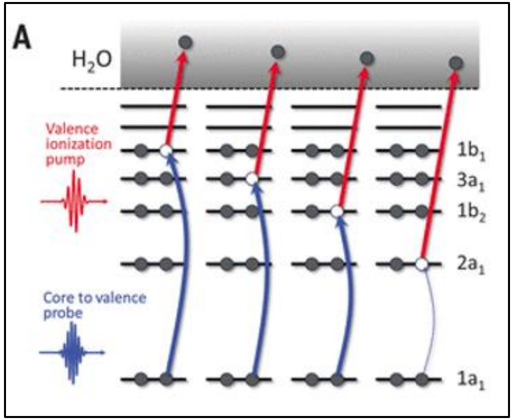
e^-: 7–8 MeV, 7 ps, 4 nC
Broadband fs probe: 380-1500 nm

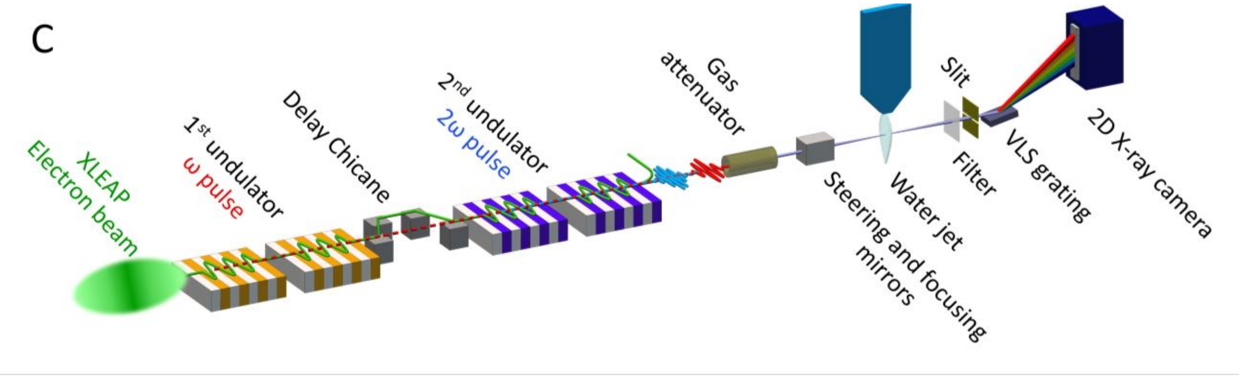
Absorption cell ~ 5 mm

All x-ray attosecond pump/probe expts

A new tool to understand radiolysis —› mechanistic origin of reactive species

AX-ATAS: All X-ray Attosecond Transient Absorption





AX-ATAS spectral snapshots freeze all nuclear motion

Shuai Li *et al. Science* **383**, 1118 (2024)

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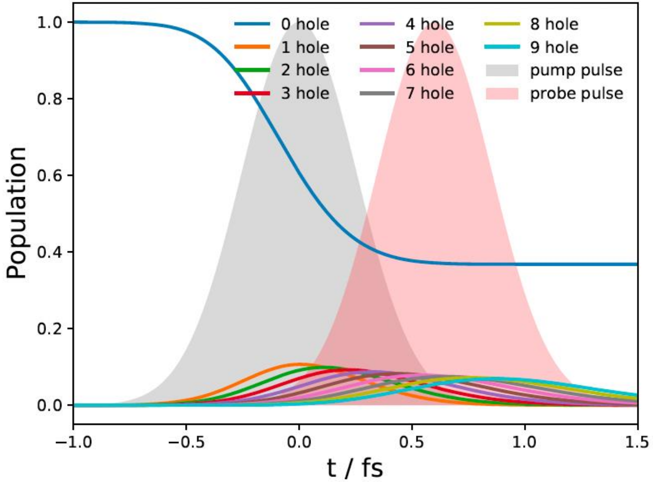
Nature of attosecond transient absorption response to attosecond full valence ionization in condensed phase

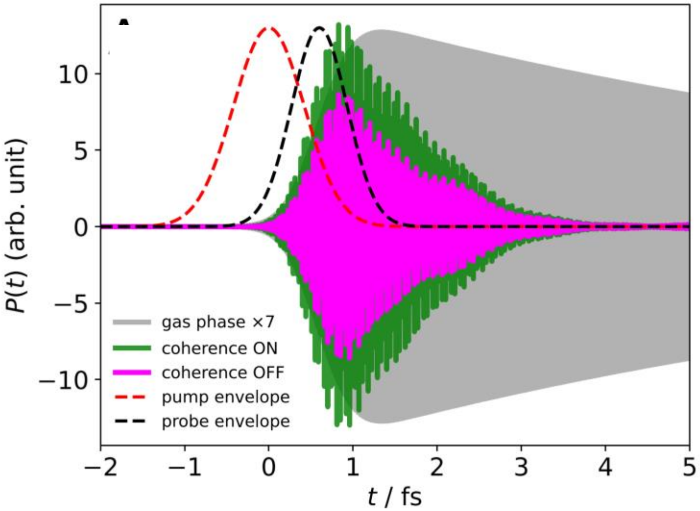
Effects of electron impact ionization and coherence

Time-dependent pump-induced hole population dynamics



Collisional electron impact dominates valence ionization after initial photoionization. (1000 water molecules in box, λ_{mfp} ~ 1 nm, E_{kin}~ 220 eV)

Rapid dephasing, decoherence in condensed phase



See Santra *et al*. PRA 83, 033405 (2011) – ATAS gas phase theory

Transient absorption snapshots with attosecond time delays are meaningful in condensed phase

S. Bhattacharya, L. Inhester, R. Santra

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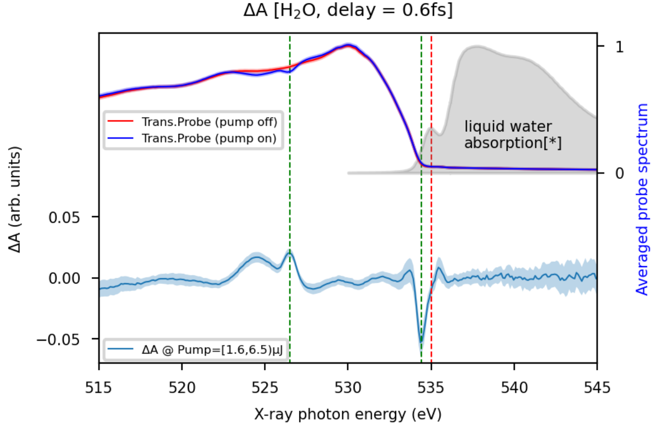
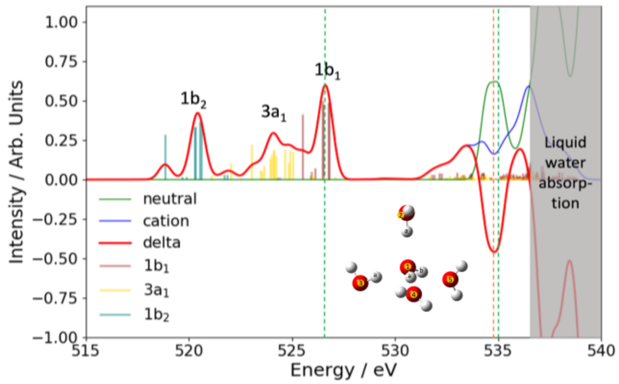
AX-ATAS – all x-ray attosecond transient absorption

AX-ATAS modelled with time-independent MRCI calculations

Experiment



Theory



Signature of valence holes and pre-edge bleach
Scan pump ω and probe 2ω over O K-edge
~600 as pump & probe pulses @ 600 as delay
0.2 eV spectrometer resolution
Pump-off w/ Ar gas attenuator

Multi-reference restricted active space configuration interaction (MRCI)

- Tetrahedrally coordinated water pentamers $(H_2O)_5$, $(H_2O)_5^+$
- Theoretical calculation of XAS near O K-edge reveals
  - Valence holes orbitals – 1b1, 3a1, 1b2
  - Pre-edge broadening - due to Stark shift induced by a neighboring valence hole

Shuai Li, Kai LI, Gilles Doumy, Emily Nienhius, Carolyn Pearce, LY
+ LCLS Stefan Moeller, Ming-Fu Lin…

Lixin Lu, Xiaosong Li

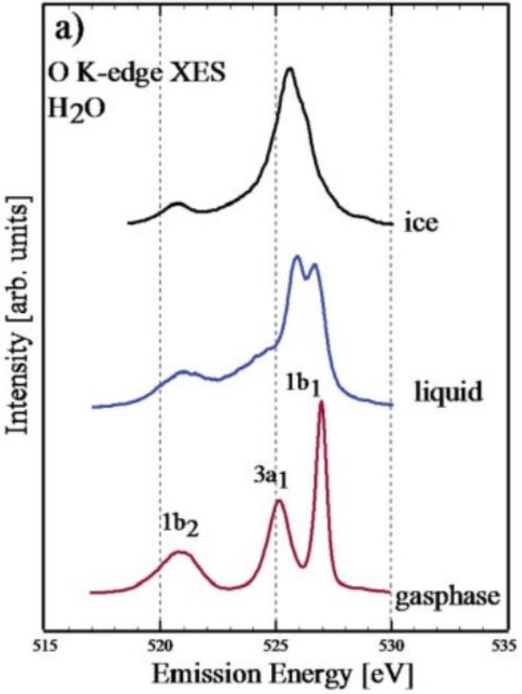
Simple water pentamer can model electronic structure changes observed 600 as after ionization.

Equilibrium properties from our attosecond pump-probe experiments

resolving a debate in liquid water structure

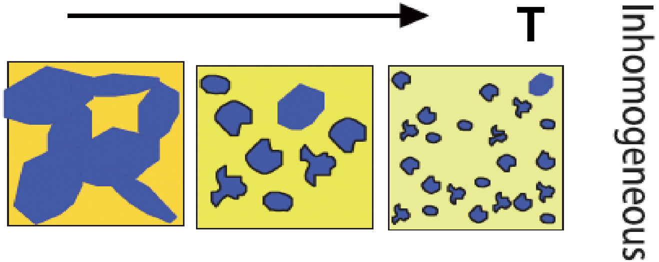
See Physics Today, April 2024 issue, Johanna Miller
Physics, April 2024, Charles Day

X-ray emission spectroscopy has been used to infer the structure of liquid water



A. Nilsson *et al*., N Cimento (2016)

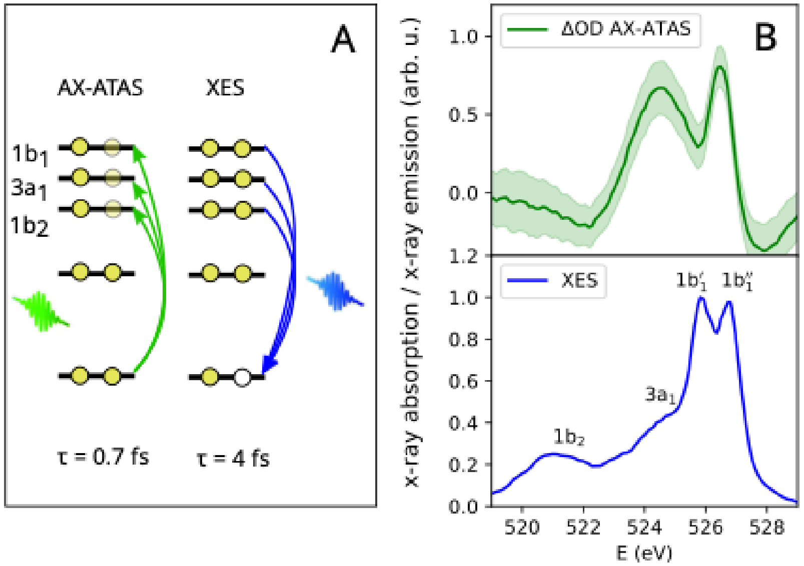
"*High resolution X-ray emission spectroscopy of liquid water: The observation of two structural motifs*"
Tokushima … Chem Phys Lett (2008)



"*Isotope and Temperature Effects in Liquid Water Probed by X-Ray Absorption and Resonant X-Ray Emission Spectroscopy*"
Fuchs …Phys Rev Lett (2008)

Ultrafast dissociation in the core-excited state

AX-ATAS compared to X-ray Emission Spectroscopy



AX-ATAS @ 0.7 fs shows no evidence for two structural motifs in ambient liquid water

Shuai Li *et al. Science* **383**, 1118 (2024)

BEYOND SOFT X-RAY ATTOSECOND PUMP/PROBE

Exciting developments at XFEL facilities

- **High-repetition-rate soft x-ray attosecond pulses – LCLS**
  - Coherent shaping of attosecond pulses, PRL **134**, 115001 (2025)
- **Attosecond pulse trains at seeded soft x-ray FEL – FERMI**
  - Addition of phase-controlled harmonics, Nature **578**, 386 (2020).
- **Polarization control with adjustable phase undulators**
  - FERMI (2014), LCLS (2017), SwissFEL (2023)
- **Hard x-ray attosecond pulse generation**
  - Early demonstration of sub-fs x-ray spikes @ LCLS
    PRL **119**, 154801 (2017), APL **111**, 151101 (2017)
  - Attosecond hard x-ray pulses at high power & high rep rate @ EuXFEL
    Nat. Photon. **18**, 1293 (2024)

OPPORTUNITIES w/XFELs

Tunable, synchronized attosecond pulse pairs +

- **High repetition rate —› big data —› rare events**

  ExaFEL: extreme-scale real-time data processing for X-ray free electron laser science
  J. P. Blaschke *et al.*, *Frontiers in High Performance Computing Oct 2024*

- **Extreme focusing —› nonlinear phenomena**

  Extreme focusing of hard X-ray free-electron laser pulses enables 7 nm focus width and 10^{22} W cm^{-2} intensity

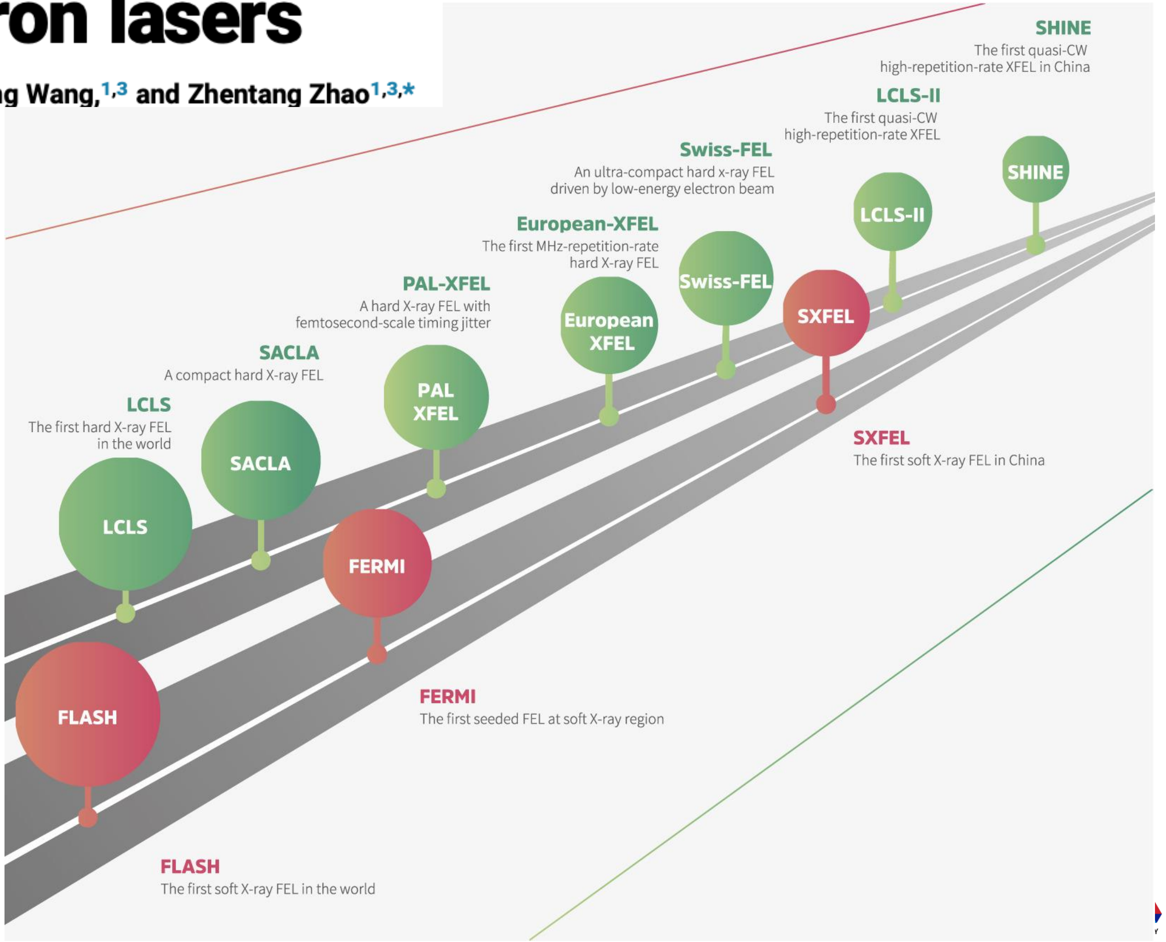
  J. Yamada *et al.*, *Nature Photonics* **18**, 685–690 (2024)

- **More accessibility: biology, chemistry, materials, condensed matter physics, warm dense matter**

Features and futures of X-ray free-electron lasers

Nanshun Huang,[1,2] Haixiao Deng,[1,3,*] Bo Liu,[1,3] Dong Wang,[1,3] and Zhentang Zhao[1,3,*]

The Innovation 2(2), 100097 (2021).



SHINE

8 GeV, SC accel, 1 MHz

3 undulators, 0.4-25 keV

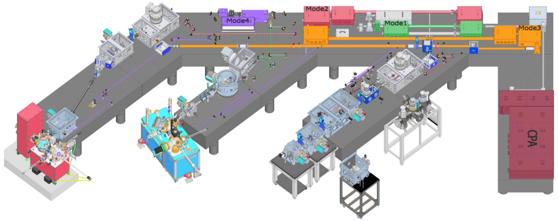
10 endstations

User expts 2027

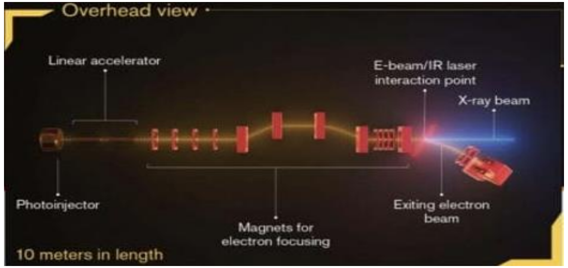
MORE COMPACT ULTRAFAST X-RAY SOURCES?

Increasing accessibility & impact across fields

- **NEXUS at OSU** – chemistry, atomic molecular & optical physics, quantum materials, catalysis and energy storage, next generation electronic materials



- **Compact XFEL at ASU** – medical imaging, making biomolecular movies, unraveling photosynthesis, chemical catalysis and attosecond physics

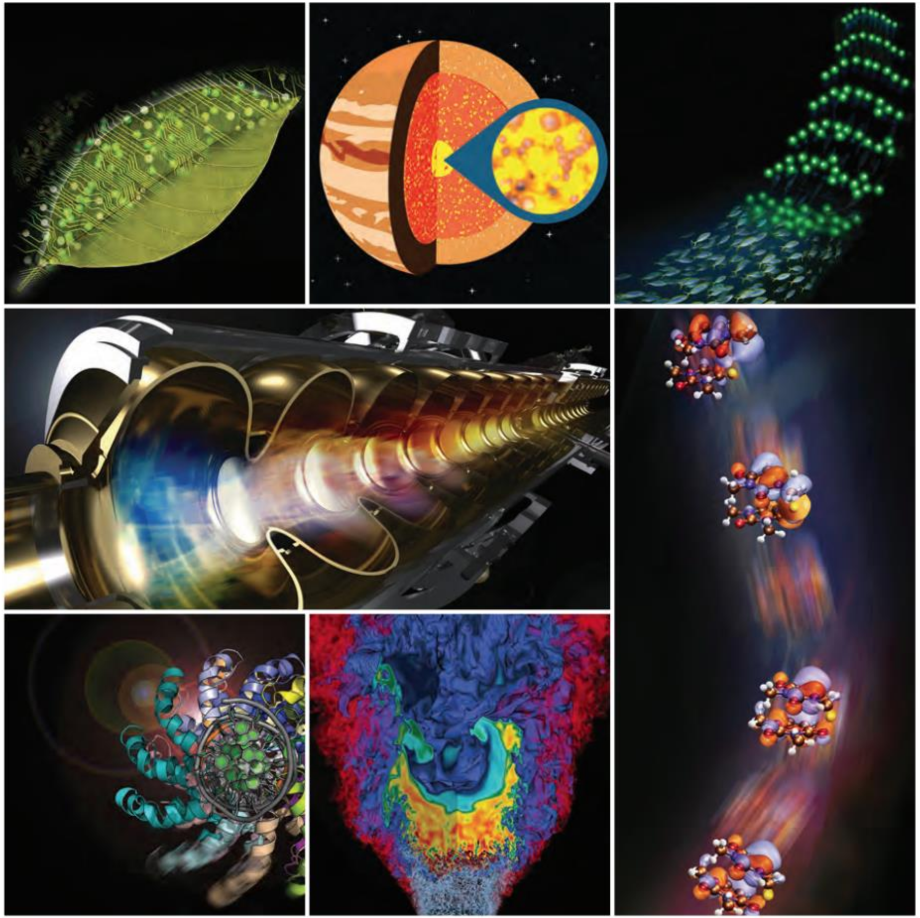


- **More affordable XFELs**

  — Compact accelerator: plasma wakefield, laser wakefield acceleration …

  — Compact undulator: higher field, smaller period —› superconducting undulators

SCIENTIFIC OPPORTUNITIES ACROSS FIELDS



From: NEW SCIENCE OPPORTUNITIES ENABLED BY LCLS-II X-RAY LASERS

Fundamental Dynamics of Energy & Charge
Catalysis & Photo-catalysis
Emergent Phenomena in Quantum Materials
Nanoscale Materials Dynamics, Heterogeneity & Fluctuations
Matter in Extreme Environments
Revealing Biological Function

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