Science highlights from hard X-ray FELs

→ From past operation
→ Drivers of forthcoming developments

Thomas Tschentscher (European XFEL)

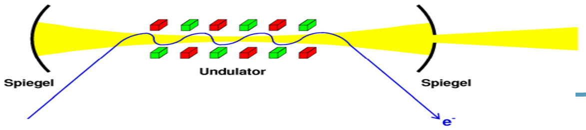
13th International Particle Accelerator Conference 2022,
Bangkok, June 12 - 17, 2022

thomas.tschentscher@xfel.eu

Hard X-ray FELs

Free-Electron Laser

Use electron beam as an energy source to create gain in an electro-magnetic field.



Concept/Theory:

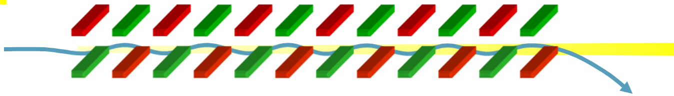
- **J. Madey, J. Appl. Phys. 42, 1906, (1971)**

Experiment:

- **D. Deacon et al., PRL 38, 892 (1977)**
  43 MeV accelerator → 34 µm light

X-Ray FEL

Short-wavelength radiation FELs were impossible due to cavity constraint → Self-amplified spontanous emission & high gain



Concept/Theory:

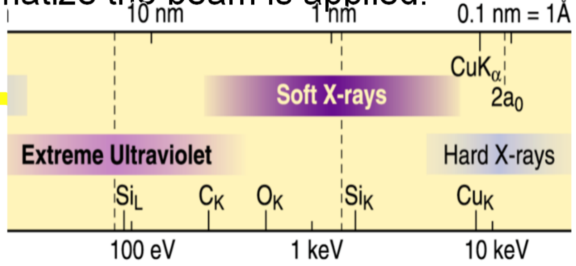
- **A.M. Kondratenko, E.L. Saldin, Part. Accel. 10, 207 (1980)**
- **R. Bonifacio, C. Pellegrini, L.M. Narducci, Opt. Comm. 50, 373 (1984)**

Experiment:

- **J. Andruszkow et al., PRL 85, 3825 (2000)**

Hard X-Ray FEL

Definition of hard x-ray is not universal, but usually the employment of crystal rather than grating optics to monochromatize the beam is applied.



2nd classification: Electron energy

Hard X-ray FELs are powered by high electron energy accelerators:

$E_e = 6 – 17$ GeV

Important accelerator properties for X-ray FELs

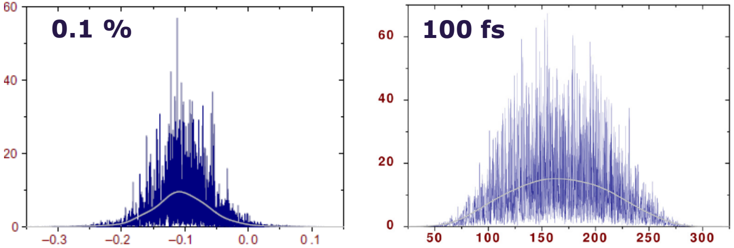
Electron energy	6 – 17 GeV
Normalized emittance	0.5 – 1.5×10^{-6} m rad
Peak current	1 – 5 kA
Bunch duration (& shape)	5 – 50 fs
Energy bandwidth	10^{-4} (rel.)
Repetition rate / time pattern	50 – 200 (warm, Cu)
	10^5 – 10^6 Hz (SC, Nb)
Stability (trans., long., spectral)	µm / µrad / fs / MeV

Pierce parameter ρ

$$\rho = \left(\frac{I A_{JJ}^2 K^2 \lambda_{rad}^2}{I_A 32 \pi^2 \gamma^2 \varepsilon_n \beta_f} \right)^{1/3}$$

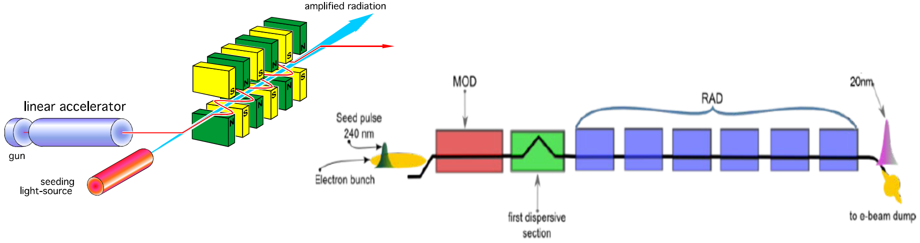
FEL sources

- SASE
  - **Incomplete bandwidth-time product**
  - **Partial long. coherence**
  - **SASE fluctuations**
  - **Highest pulse energies**

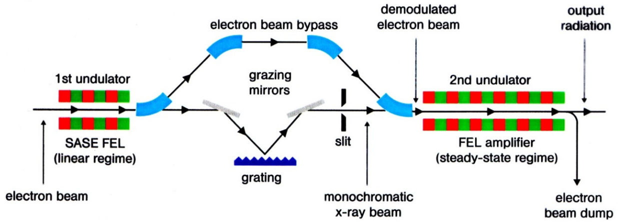


- Variants
  - **Segmentation of long undulators**
  - **Optical klystrons, separate functions**
  - **2-pulse schemes, often combined with 2-colors**

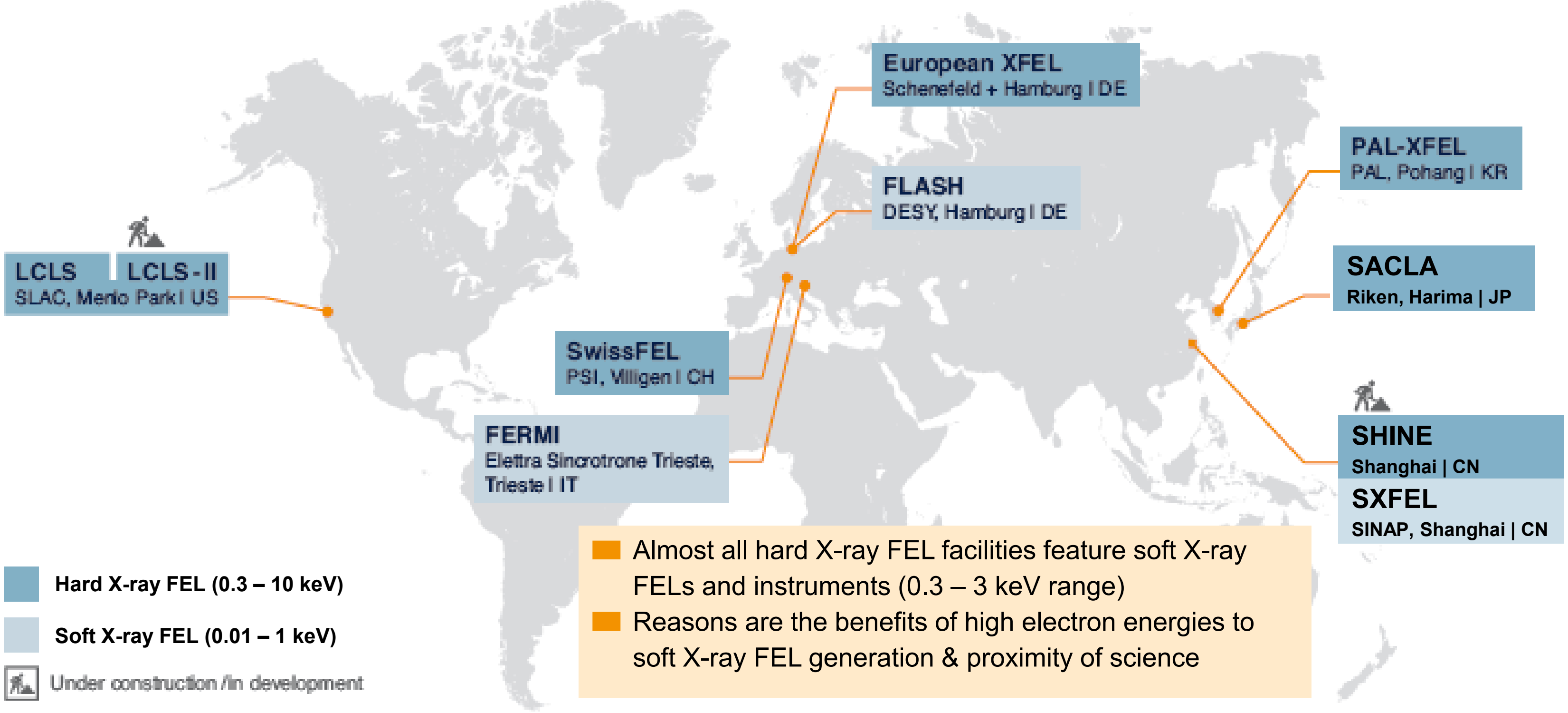
- Seeded FELs
  - **Improved/complete bandwidth-time product**
  - **Reduced fluctuation → higher stability**
  - **Laser-seeded FELs**
    - ► So far limited to EUV/soft x-rays



- **Self-seeded FELs**



X-ray lasers worldwide



European XFEL
Schenefeld + Hamburg | DE

FLASH
DESY, Hamburg | DE

PAL-XFEL
PAL, Pohang | KR

SACLA
Riken, Harima | JP

LCLS **LCLS-II**
SLAC, Menlo Park | US

SwissFEL
PSI, Villigen | CH

FERMI
Elettra Sincrotrone Trieste,
Trieste | IT

SHINE
Shanghai | CN

SXFEL
SINAP, Shanghai | CN

■ **Hard X-ray FEL (0.3 – 10 keV)**

□ **Soft X-ray FEL (0.01 – 1 keV)**

🚧 Under construction /in development

- Almost all hard X-ray FEL facilities feature soft X-ray FELs and instruments (0.3 – 3 keV range)
- Reasons are the benefits of high electron energies to soft X-ray FEL generation & proximity of science

Some comparison

Facility	Unit	LCLS-II CuRF	LCLS-II SCRF*	SACLA	European XFEL	SwissFEL	PAL-XFEL	SHINE*
Max. electron energy	GeV	15	4	8.5	17.5	5.8	11	8
Photon energy range	keV	2.4 – 25	0.25 – 4.8	4 – 20	0.25 – 25	0.25– 12	0.25 – 15	0.4 –20 (tbc)
Max. hX pulse energy	mJ	2 – 4	--	1 – 2	3 – 5	1 – 2	2 – 4	1 (tbc)
Max. sX pulse energy	mJ	--	1 - 3	--	>10	2 – 4 (tbc)	>4 (tbc)	1 – 3
Max. pulses per second		120	10^6	60	27 000	100	60	10^6
# of FELs		2	2	3	3	2	2	3
# science instruments		8*	4*	6	7*	5*	3	10 (tbc)
Seeding		HXRSS		HXRSS	HXRSS		HXRSS	
First users		**2021**	**2022 (tbc)**	**2011**	**2017**	**2018**	**2016**	**2026 (tbc)**

* Currently constructing   tbc: Value to be confirmed

Hard X-ray FEL facilities (I) – some special features

LCLS

- Cu LINAC (14 GeV) & SC LINAC (4 GeV)
- Planar, oov, perm. magnet undulators
- Variable pulse duration, H- and SXRSS, 2-color, as- pulses, …

- 2009 first hard X-ray FEL user facility
- Many sX and hX proof-of-principle papers
- Serving 1 FEL at a time
- US FEL facility; Stanford, Berkeley & LaserNet

SACLA

- Two Cu LINACs (8 GeV & 0.8 GeV)
- In-vacuum undulators
- Few fs pulses, HXRSS, 2-color, …
- Accelerator used as injector for SPring-8

- first small (‚low energy‘) hX-ray FEL user facility
- Many x-ray optics developments
- Serves multiple FELs at a time
- Industry collaboration; Oaska HP Laser-Facility

PAL

- Cu LINACs (11 GeV) with sX branch
- Planar, oov, perm. magnet undulators
- HXRSS, 2-color, …

- Very high performance for HXRSS
- Serves two FELs at a time*

Hard X-ray FEL facilities (II) – some special features

European XFEL

- International facility
- SC LINAC (17.5 GeV)
- Planar, oov, perm. magnet undulators
- HXRSS, 2-color, as- pulses, …

- 2017 first high reprate hX-ray FEL user facility
- Instrumentation & experiments at high rate
- Serving 3 FELs at a time (ext. to 5 possible)
- DESY (acc.), CFEL (photon), EMBL (biology)

PAUL SCHERRER INSTITUT PSI

- Cu LINAC (6 GeV) with sX branch
- Small emittance
- In-vacuum & var. pol. undulators
- 2- color, wide bandwidth, fs pulses

- Smallest (energy) hX-ray FEL user facility
- Serves two FELs at a time*
- PSI, ETH

SHINE

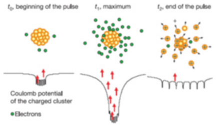
- SC LINAC (8 GeV)
- Planar, oov, perm. magnet & SC undulators

- Serves three FELs at a time*
- SINAP (SR & SXFEL), SIOM (PW lasers)

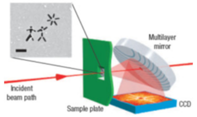
Some highlights over two decades (a subjective view)

1st proposal to build hard X-ray FEL: LCLS

Wabnitz, Nature 2002: Multiplie ionization of Xe clusters

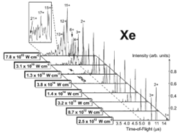


Start user operation FLASH

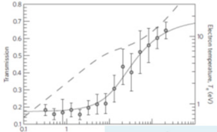


Chapman Nature Phys. 2006: Single exposure coh. imaging

Sorokin, PRL 2007: 21-fold ioization of Xe ato

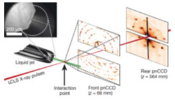


Nagler, Nature Phys. 2009: Transparent Aluminuim



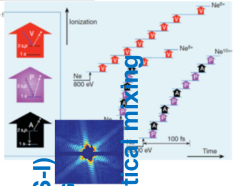
1st lasing LCLS & start construction EuXFEL

Young, Nature 2010: Ionization ways

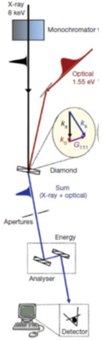


Chapman, Nature 2011: SFX (PS-I)

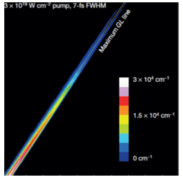
Seibert, Nature 2011: Mimi-virus



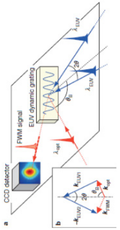
Glover, Nature 2012: X-ray & optical mixing



Yoneda, Nature 2015: Innershell lasing at 8 keV

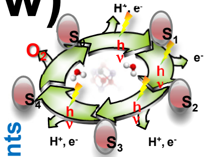


Bencivenga, Nature 2015: 4-wave mixing

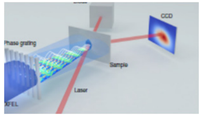


1st lasing EuXFEL

Kern, Nature. 2018: PS-II structure of RT transients



Rouxel, Nature Phot. 2021: X-ray transient grating spectroscopy



2000 2002 2004 2006 2008 2010 2012 2014 2016 2018 2020 2022

Science highlights

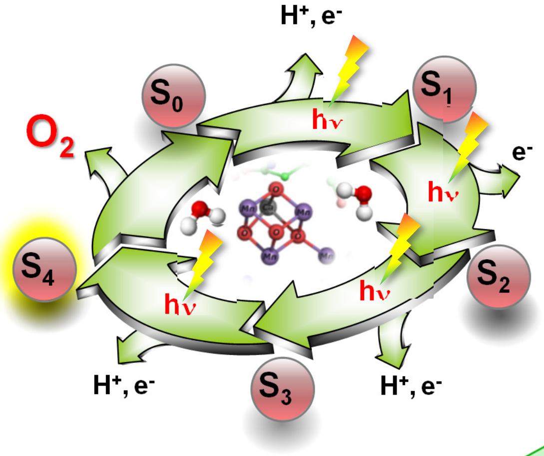
‚Please send me your science highlight having high societal impact‘

- LCLS → Diffraction & Spectroscopy: Structure PS-II → Artifical photosynthesis
- SACLA → Diffraction: X-ray excitation → Ultrafast dynamics in materials
- PAL XFEL → Difraction: Mapping bond formation → Developing photo-active materials
- SwissFEL → Diffraction: Structure of Rhodopsin → New drugs and functions
- EuXFEL (hX) → Spectroscopy: Dynamic of elec. states → Develop photo-catalysts
- EuXFEL (sX) → Ion-spectroscopy: Follow chem. reactions → Developing photo-active materials

Major scientific application areas

- New photo-active materials for energy conversion and new functions
- Drug design

Progress in Photosystem II Research

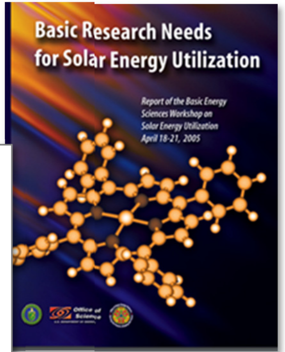


- 4-photon, 4-electron catalyst
  $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$
- Oxygen evolving complex (OEC)
  Mn_4CaO_5
- Dynamics span 9 decades
  (sub-ps to msec)

2011 SACLA

2010 **LCLS – New Tools**

~2005 Artificial photosynthesis


Basic Research Needs for Solar Energy Utilization

Report of the Basic Energy Sciences Workshop on Solar Energy Utilization April 18-21, 2005

2001 1st Crystal structure of PSII
Zouni et al. 2001 (ESRF)

80's SSRL – New Tools

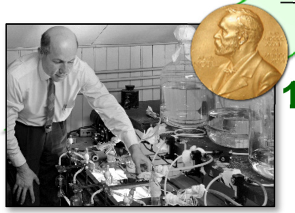
- **Zouni et al. 2001 (ESRF)**
- Ferreira et al. 2004 (ESRF)
- Loll et al. 2005 (ESRF)
- Umena et al. 2011 (SPring8)

⋮

- Kern et al 2012 (LCLS)
- Kern et al 2014 (LCLS)
- Kupitz et al 2014 (LCLS)
- Suga et al. 2015 (SACLA)
- Young et al., 2016 (LCLS)
- Suga et al. 2017 (SACLA)
- Kern et al. 2018 (LCLS)

blue: cryo
red: room temp.

1967 Kok cycle: 4-step process of water oxidation



1961 **Melvin Calvin**
carbon-chemistry
of photosynthesis

adapted from J. Yano

How do intermediate structures facilitate water oxidation in a multi-electron photocatalyst?

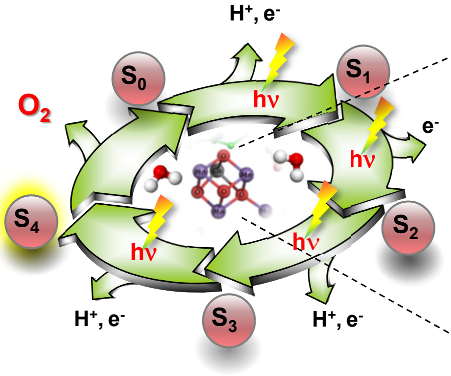
Structure of Transient States of Photosystem-II at Room Temperature

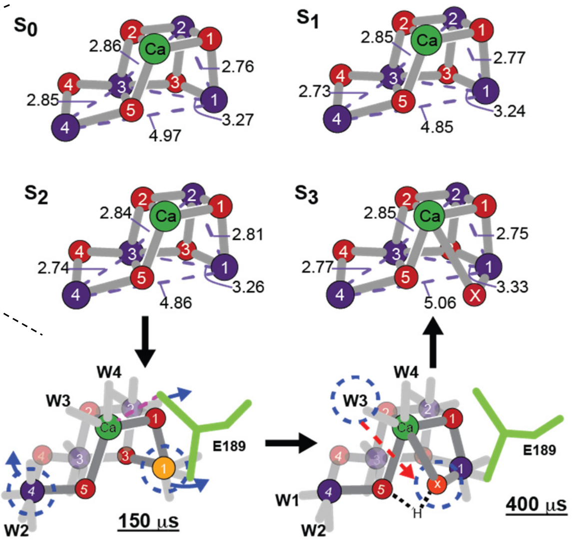
Science

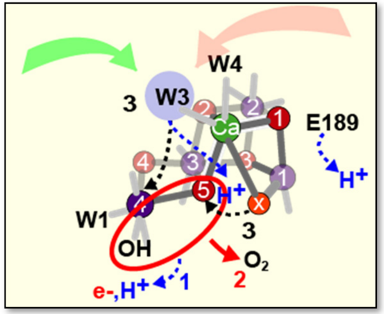
- High resolution structure of all intermediate states (S_1, S_2, S_3) of the Kok cycle **at room temperature**
- Two transient states during $S_2 \rightarrow S_3$ at 150 μsec and 400 μsec show additional water

Insight & Significance

- Direct involvement of water ligand of Ca and insertion of an oxo bridge between Ca and Mn(1) in the S_3 state, in substrate delivery to the catalytic site and O-O bond formation
- Distinct structural changes occur between S_2 and S_3 states: A ligand of Ca moves and the open coordination site is filled by Ox bridging Mn(1) and Ca







Kern *et al.*, *Nature*, **563**, 421 (2018)
M. Ibrahim, *et al.*, *PNAS*, **117**, 12624 (2020).

basis of new LCLS science campaign

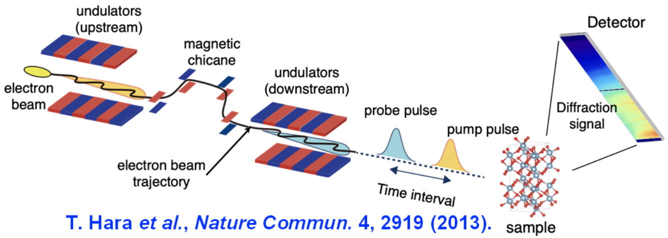
J. Kern, J. Yano,
V. Yachandra et al.

SACLA

Verification of ‘diffraction-before-destruction’ concept:

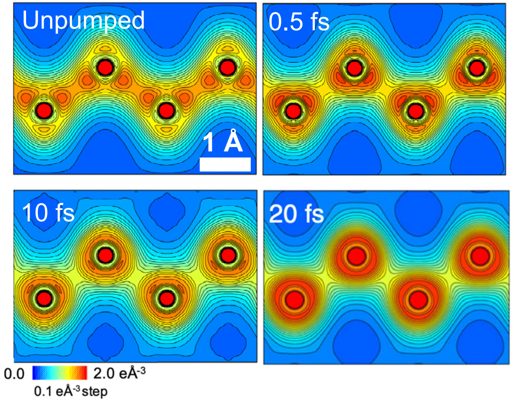
Damage-free structure determination was proven to be feasible with ultrafast X-ray pulses from SACLA (duration of ~5 fs)

Methods: X-ray pump-X-ray probe technique using split-undulator scheme

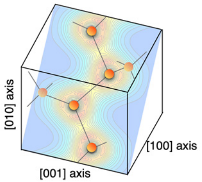


T. Hara *et al.*, *Nature Commun.* 4, 2919 (2013).
I. Inoue *et al.*, *PNAS* 113, 1492 (2016).

Femtosecond changes in chemical bonds (diamond)



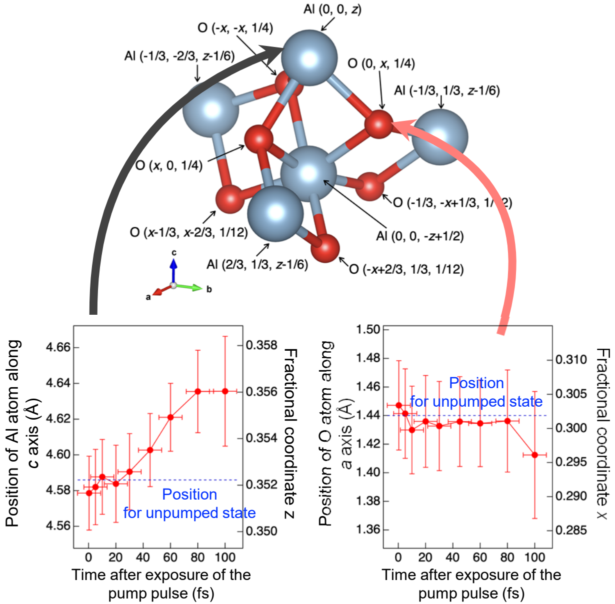
Valence electron-density distribution in (110) plane



Preservation of chemical bonds
within pump-pulse duration (delay: 0.5 fs)

I. Inoue *et al.*, *PRL* 126, 117403 (2021).

Femtosecond atomic displacements (α-Al_2O_3)



Preservation of atomic positions
on subatomic length scales
until 20 fs after the x-ray exposure.

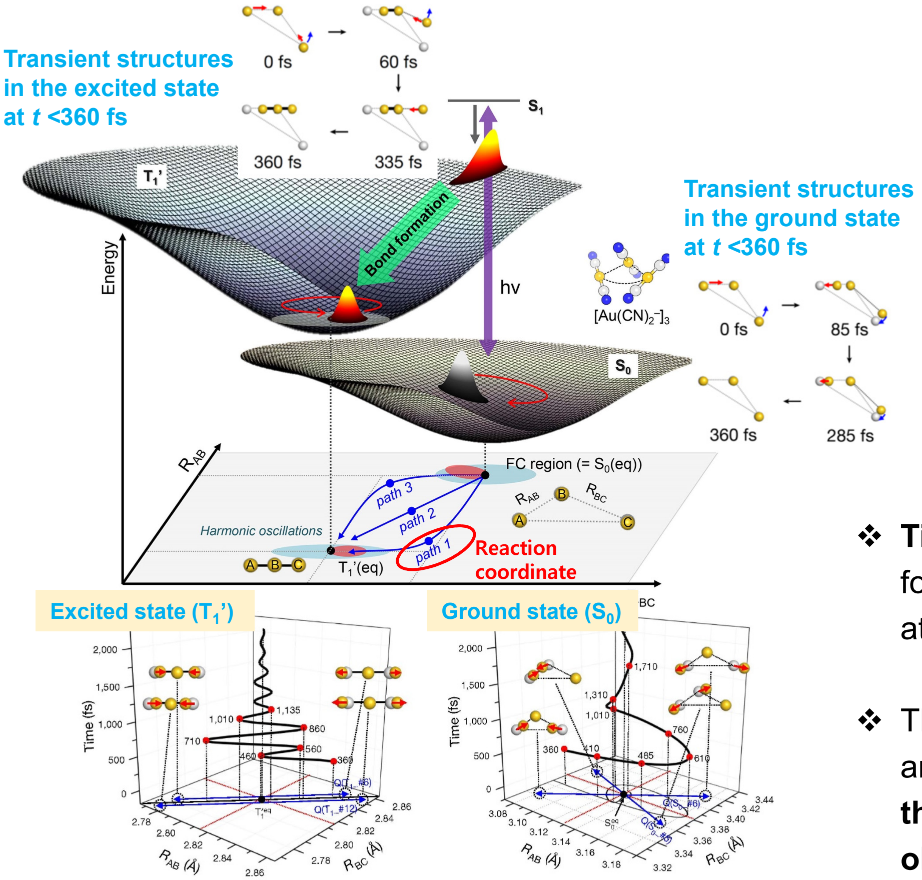
I. Inoue *et al.*, *accepted to PRL* (arXiv:2112.05430).

Main collaborators:

RIKEN
JASRI
European XFEL
CFEL SCIENCE
筑波大学 University of Tsukuba
Czech Academy of Sciences

Mapping the emergence of molecular vibrations mediating bond formation

Jong Goo Kim, Hyotcherl Ihee* et al., *Nature*, **582**, 520 (2020)



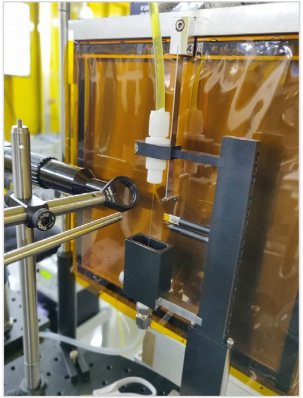
Transient structures in the excited state at *t* <360 fs

Transient structures in the ground state at *t* <360 fs

Excited state (T_1')

Ground state (S_0)

[Harmonic oscillations of wavepackets at *t* >360 fs]



- ❖ **Time-resolved X-ray solution scattering** (TRXL) experiments for photo-excited gold trimer complex were performed at **the XSS beamline of the PAL-XFEL**.
- ❖ Thanks to the high structural sensitivity of the TRXL technique and stable X-rays (both in intensity and timing) of the PAL-XFEL, **the real-time trajectories in the ultrafast bond formation were obtained purely on the basis of the experimental data.**

First user experiments at SwissFEL

Rhodopsins pave the way into a dynamic future for structural biology

Skopintsev et al., 2020, Nature

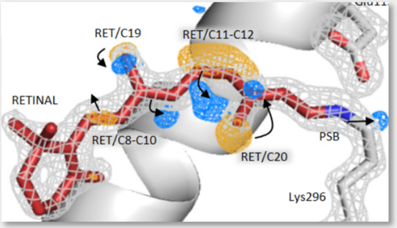
Sodium pumping rhodopsin

- Ten molecular snapshots of sodium transport over a biological membrane
- Next-generation optogenetic tool
- PSI Thesis Medal 2021

Mous et al., 2022, Science

Chloride pumping rhodopsin

- SwissFEL and SLS resolves chloride transport across a membrane
- Electrostatic gates explain transport
- ETH Ambizione Fellow Nogly



Gruhl et al., 2022, under review

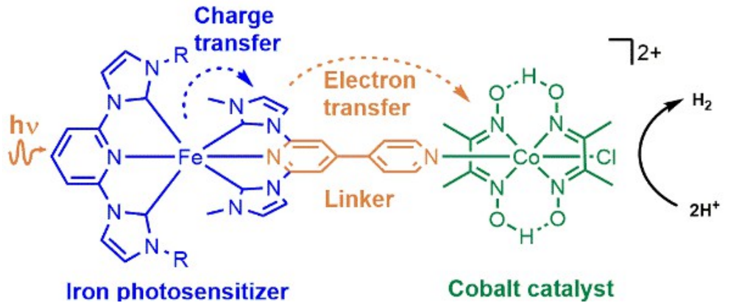
Visual GPCR rhodopsin

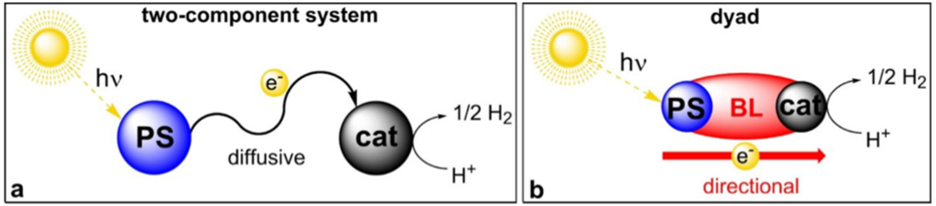
- Molecular snapshots of the early events in vision
- Breathing motion dissipates energy
- GPCR activation

Photocatalytic hydrogen evolution

Using light to produce hydrogen

In photocatalytic homogeneous hydrogen evolution reactions a catalyst uses light to produce H_2 but ideally with cheap materials





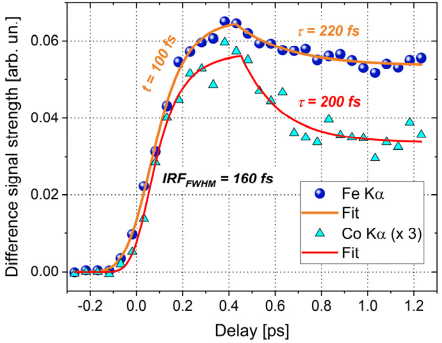
M. Huber-Gedert et al. *Chem. Eur. J.* **27**, 9905 (2021)

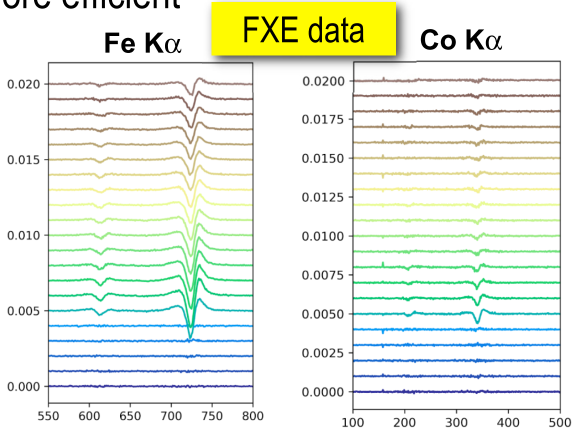
A dyad is more efficient

A two component system has one part to absorb the light, and a second part to perform the H_2 production, by linking them the reaction is more efficient

Ultrafast X-rays can probe the different processes

By using X-ray spectroscopy to look at the 3d metal-based photosensitizer (Fe) and catalyst (Co) simultaneously we can follow the function of the catalyst with excellent time resolution





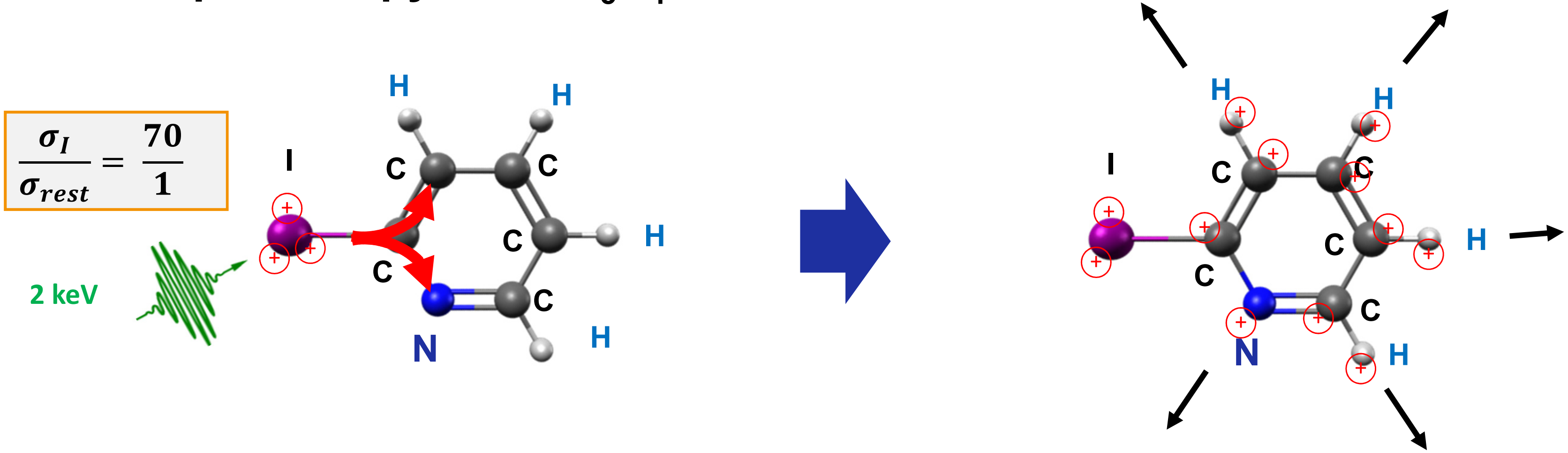
Adapted from C. Milne

PI: Matthias Bauer (University of Paderborn)

Snapshots of molecular geometry via Coulomb explosion

Multiple ionization of Iodine followed by fast charge redistribution leads to the explosion of the molecules

Example: Iodopyridine C_5H_4NI



$$\frac{\sigma_I}{\sigma_{rest}} = \frac{70}{1}$$

Ion – Ion coincidences → Coulomb explosion imaging

R. Boll, J.M. Schäfer et al. Nature Physics 18, 423 (2022)

On-going and future developments

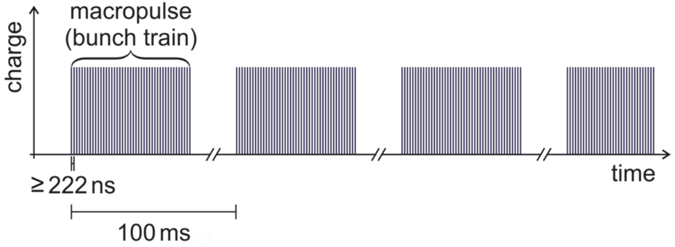
The succesful operation and scientic exploitation of the present hard X-ray FEL facilities opens perspectives for future developments and upgrade projects.

- High repetition rate → increase count rate to enable studying small cross-section effects
- Special pulse delivery (seeding, attosecond pulses, very hard x-rays, …) → provide specific properties of FEL radiation serving the investigation of specific science questions
- Variations: FEL oscillators, FELs using plasma-accelerators → talks yesterday and later this session
- New x-ray techniques → enable new usage of FEL radiation to discover new science

High repetition rate

European XFEL superconducting 17.5 GeV electron accelerators (TESLA technology)

- FLASH, European XFEL – Burst mode



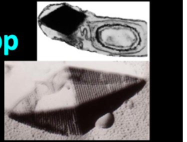
  - **Similar pulse performance as RT FELs**

- LCLS-II, SHINE – cw-mode
  - **Continuous electron bunch delivery**
  - **Rates are 100 kHz to 1 MHz**
  - **Modified pulse performance (smaller charge)**

MHz, nano-focus SFX of Bacterial Insecticides

Eco friendly insecticides

Some bacteria produce insect specific toxins



Bacillus thuringiensis (Bt) and other spp *deposit toxins as nanocrystals*

Bt used as bioinsecticide for > 60y

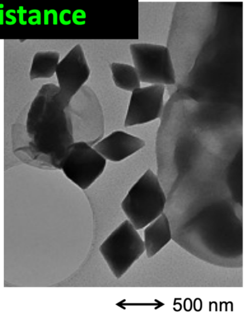
Approved for organic use

Kill limited target range; safe for non-targets

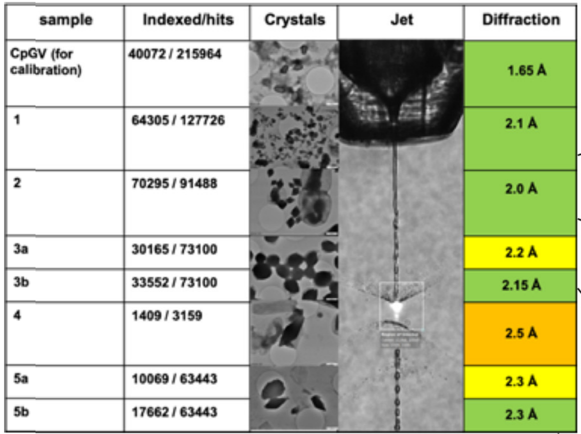
Also used in TG plants for protection

Understanding structure: understand mechanism tackle insect resistance

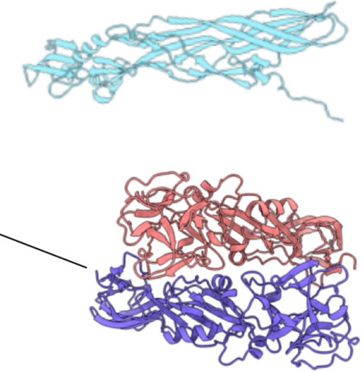
- Native tiny crystals
- Requires nanofocus of intense beam
- Reduced hit rate and number of different structures requires high reprate (here 3000/s)

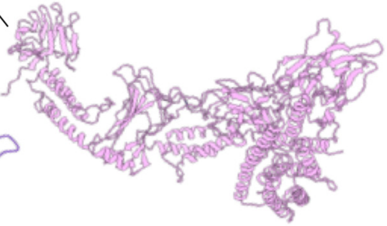


Data processing: Oleksandr Yefanov (DESY) and Marina Galchenkova (DESY) | TEM-Images: Robin Schubert (EuXFEL) | Samples: Colin Berry and Lainey Williamson (Cardiff U) | Refinement: Dominik Oberthür (DESY), Lainey Williamson and Pierre Rizkallah (Cardiff U)



sample	Indexed/hits	Crystals	Jet	Diffraction
CpGV (for calibration)	40072 / 215964			1.65 Å
1	64305 / 127726			2.1 Å
2	70295 / 91488			2.0 Å
3a	30165 / 73100			2.2 Å
3b	33552 / 73100			2.15 Å
4	1409 / 3159			2.5 Å
5a	10069 / 63443			2.3 Å
5b	17662 / 63443			2.3 Å





New structures obtained at SPB/SFX (EuXFEL). Use of Aphafold2 for two of them.

PIs: D. Oberthür (DESY), C. Berry (Cardiff U)

https://www.biorxiv.org/content/10.1101/2022.01.14.476343v1

European XFEL

DESY.

CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

Imaging of ion diffusion and fluctuating material structures

Scientific Opportunity

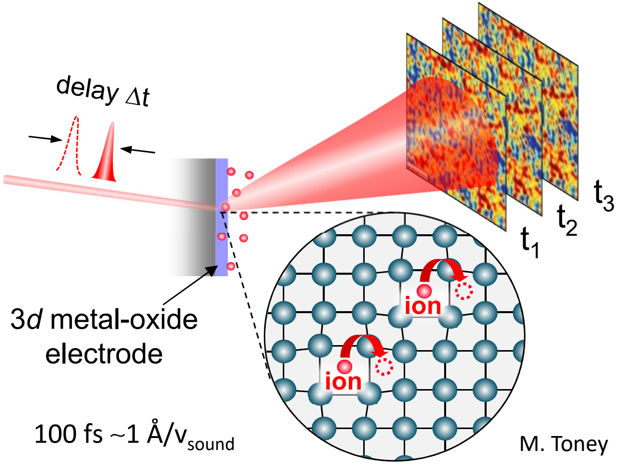
- Characterize local <u>atomic distortions</u> and long-range strain fields
- Resulting from <u>ion diffusion</u> in real materials under operating conditions

Significance and Impact

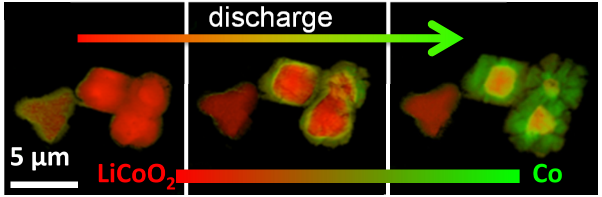
- Inform directed design and synthesis of energy conversion and storage materials

LCLS-II-HE Approach

- Dynamic X-ray scattering methods span many decades in time and space, down to fs and Å
- **XPCS** characterizes <u>statistically dynamic systems</u> without long-range order, measuring <u>S(***q***,t)</u>



M. Toney



Understanding ion diffusion at atomic level is central to performance improvements in electro-chemical energy storage materials

Requires hard X-rays at high repetition rate & programmable pulse structure to capture dynamics of local changes in structure

Coupled electronic & nuclear dynamics are fundamental to heterogeneous catalysis and interfacial chemistry

Scientific Opportunity

- Correlate catalytic reactivity & structure nanoparticle-by-nanoparticle
- Characterize evolving heterogeneous catalyst in real-time and *operando* with chemical specificity & atomic resolution

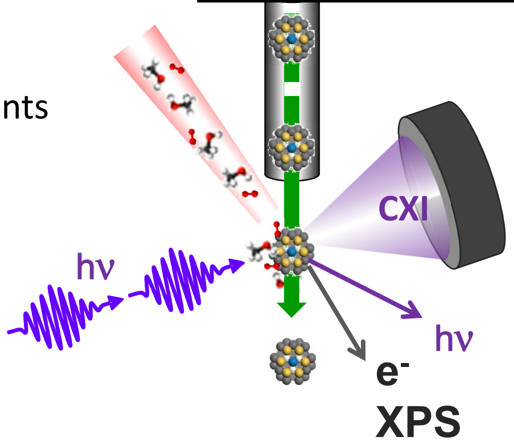
$Pt_nSn_m/\gamma\text{-}Al_2O_3$
Ab Initio MD & XAS
J. Rehr *et al.*
J. Phys. Chem. (2013)

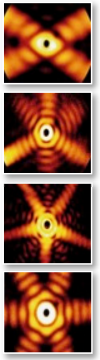
Significance and Impact

- Input for theory for directed design & synthesis of efficient, selective and robust systems based on earth-abundant elements

LCLS-II-HE Approach

- Coherent scattering and spectroscopy measured simultaneously provides electronic & atomic structure (shape) of each nanoparticle
- ~10^8-10^{10} independent measurements/day characterizes heterogeneous ensembles




CXI of heterogeneous nanoparticles *in situ*
Möller et al., *Nature Comm.* (2014)

Requires ultrafast hard X-rays at high repetition rate
Coupled with advanced data science approaches

Investigation of planetary interiors – the case of superionic ices

- **Planetary Science**: H_2O forms a large part of ice giants and exoplanets (e.g. Mini-Neptunes). Planetary Modelling requires knowledge of physical properties (EoS, phase stability, …).
- **Unusual phases:** Stability of superionic (SI) ice, where hydrogen ions move freely within in the oxygen sublattice.

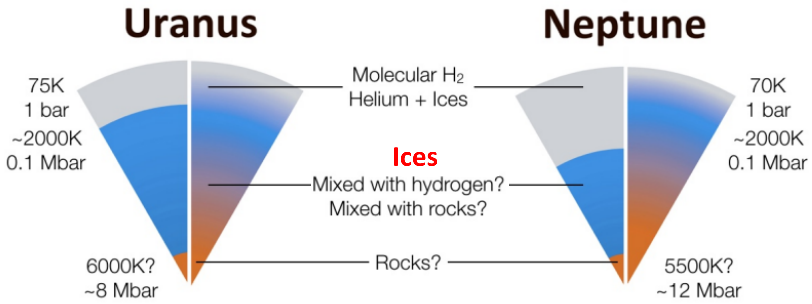
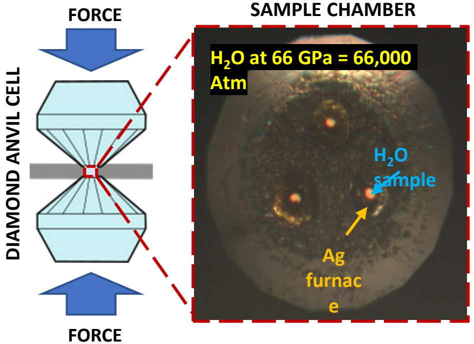


Figure: Guillot, T. Uranus and Neptune are key to understand planets with hydrogen atmospheres. *Exp Astron* (2021).

Required for these exp.s
- 🟧 High photon energy (ideally > 30 keV)
- 🟧 High pulse energies
- 🟧 High reprate (> MHz)

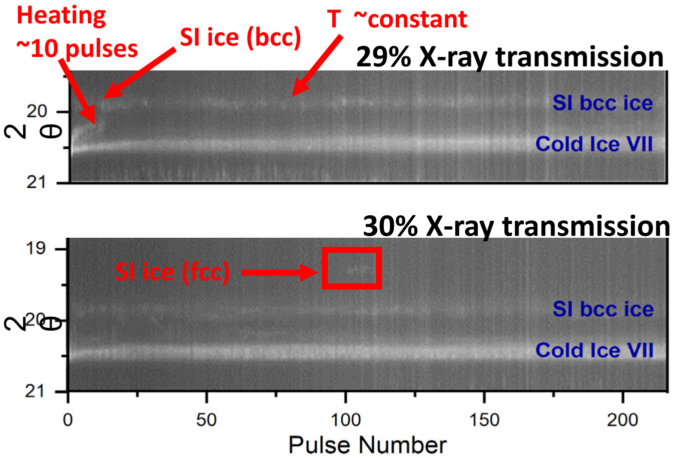
Experimental method:

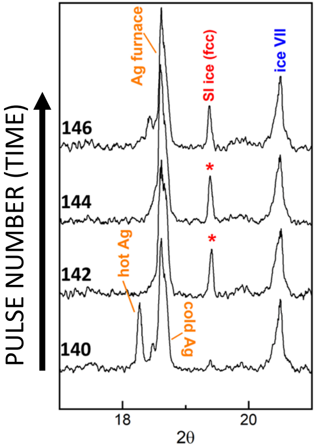
Combine **Diamond Anvil Cell (DAC)** to create static high pressure with **X-ray heating** to dynamically heat specimen. Employ high Z elements to enhance heating.



Experiment: HED #2590 (EuXFEL), PIs: M. McMahon, R. Husband

Pressure ~70 Gpa, 300 x-ray pulses@2.2 MHz, H_2O expansion as thermometer





High-T struct. transitions

Ice-VII (mol.)
↓
SI ice (bcc)
↓
SI ice (fcc)

Hard X-ray four-wave mixing

- Transfer non-linear spectroscopy technique from optical to x-ray domain
- Non-linear technique offers access to vibrational, magnetic and electronic properties in the time domain (in contrast to the usually used frequency domain)
- X-ray can penetrate bulk material and use element specific resonances

Scientific applications

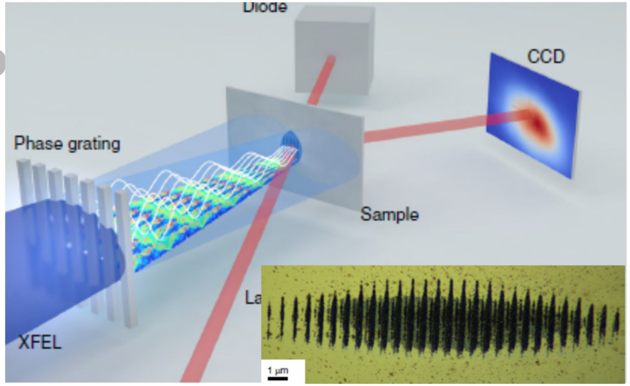
- Transport phenomena in solids
- Evolution of excited states

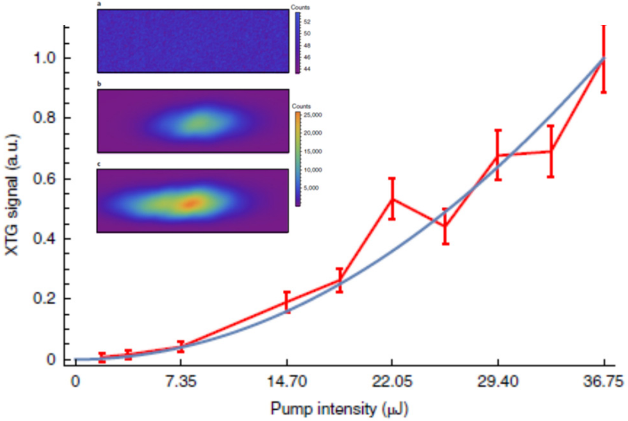
Required for these exp.s

- Coherence
- Narrow band-width
- Very short pulses
- High reprate (> MHz)

Hard X-ray Transient Grating spectroscopy

PAUL SCHERRER INSTITUT PSI





J.R. Rouxel et al., Nature Photonics 15, 499 (2021)

Acknowledgements

- Science highlights: R. Schoenlein (SLAC), Makina Yabashi (RIKEN Spring-8), Intae Eom (PAL), Luc Patthey (PSI), Sakura Pascarelli & Serguei Molodtsov (European XFEL)
- Future science cases: R. Schoenlein (SLAC), Sakura Pascarelli & Adrian Mancuso (European XFEL), Malcom McMahon (U Edinburgh), Rachel Husband (DESY)
- All staff at European XFEL and DESY contributing the results shown here.

Conclusions

- Hard X-ray FEL facilities are **operated only for about 10 yrs**. Only since 2018 five facilities provide beam and expertise for user science. With the complications due to the COVID pandemic and the fact that the average delay between experiment and publication is of order 1-2 yrs, **already a very significant and visible publication output has been achieved**.
- Following an initial phase seeing mostly proof-of-principle experiments/publication, now the **harvesting using these techniques** is taking place. Science turns from **possibility** to **scientific application**.
- Most prominent areas of **time-resolved studies of photo-sensitive materials** with applications in **energy research**, new materials/ functions and **investigations of bio-chemical structural dynamics** for **medical drug/treatment design**.
- Fundamental developments of new techniques and applications continues and is crucial.
- Most important new developments are the provision of **high reprate**, **very high photon energies**, **attosecond pulses**, and (possibly) **non-linear x-ray spectroscopy**. Science drivers exist.

Thank you for your attention