



Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Jochen Rittmann

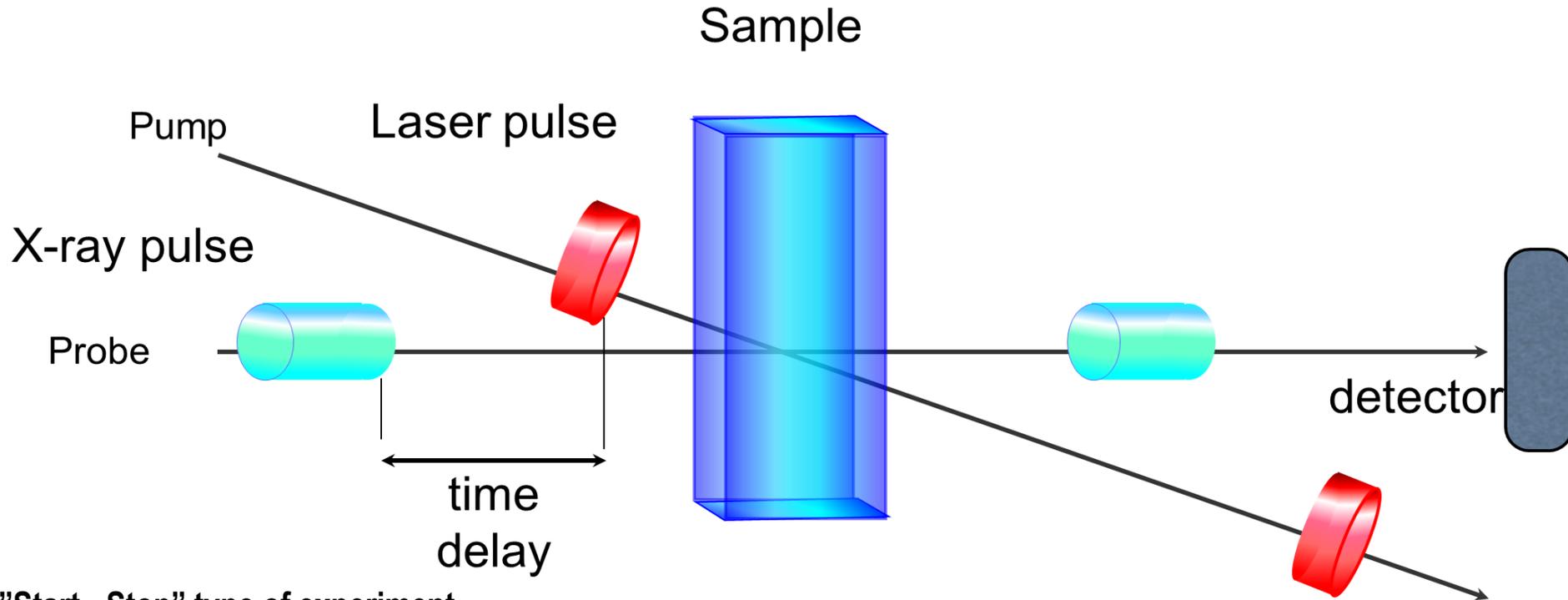
Laser-synchrotron synchronization and pump-probe experiments

... before starting a time resolved experiment:



- What do I want to study (Solids, Liquids, is beam damage an issue)
- How fast are the dynamics I want to study?
 - **fs scale:** e-phonon interaction, correlated electron systems,
 - **ps scale:** thermal effects, electronic states, molecular dynamics
 - **ns scale:** Catalysis, ...
 - **μ s scale:** slow melting, ...





”Start - Stop” type of experiment

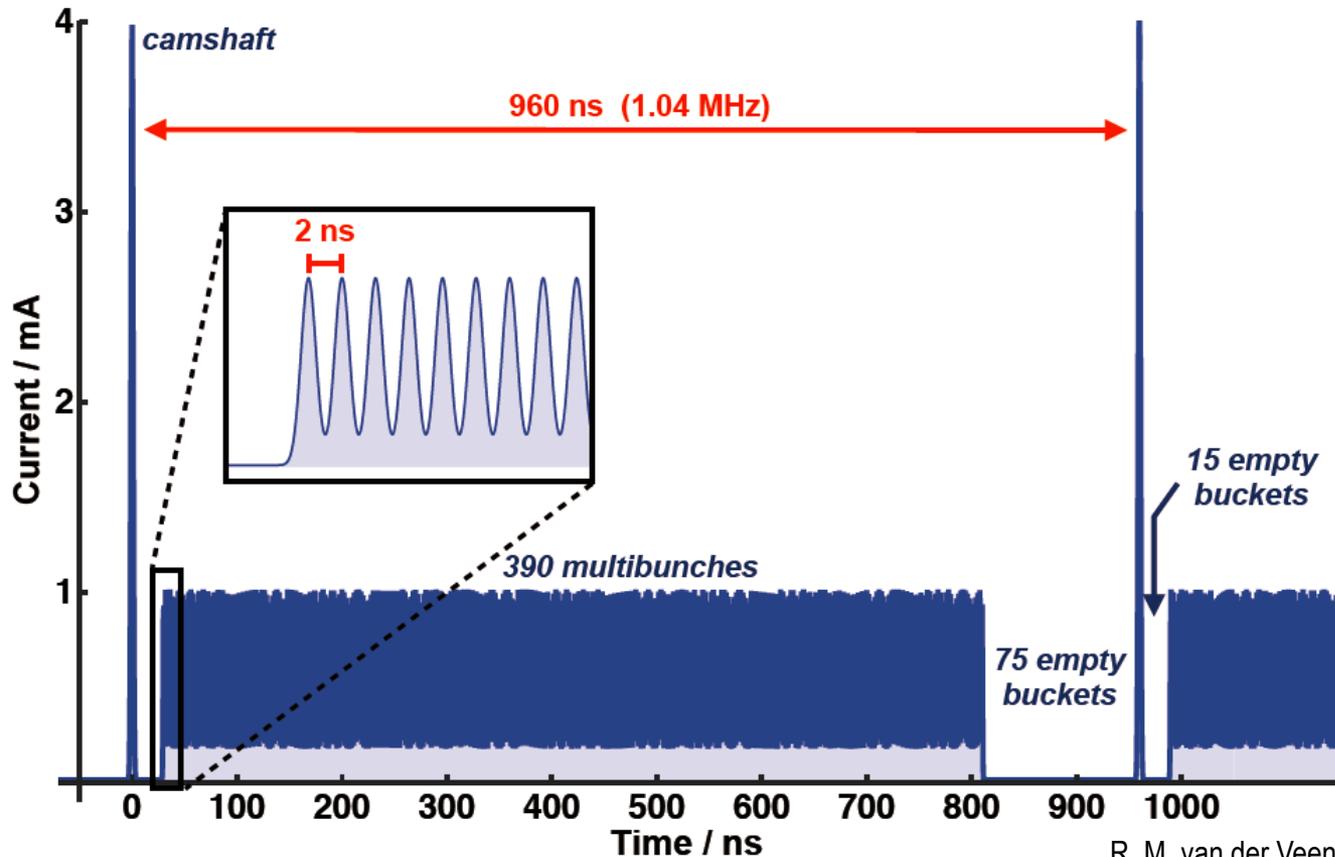
- Time-resolved data are recorded as a function of delay time τ between pump and probe
- Stroboscopic measurement over millions of shots: sample recovery $\ll 1 / \text{rep-rate}$
- **Time resolution: = $\tau_{\text{pump}} + \tau_{\text{probe}} + \tau_{\text{jitter}} + \tau_{\text{drift}}$**

- **Methods:**
 - X-ray diffraction: direct probe of ‘long range’ atomic structure
 - X-ray absorption: ‘local’ electronic and atomic structure
 - Resonant X-ray scattering: charge, magnetic, and orbital degrees of freedom
 - RIXS, RXES, HERFD, HEROS, XDS, ...

Time resolved techniques / laser infrastructure at SLS (not complete list)

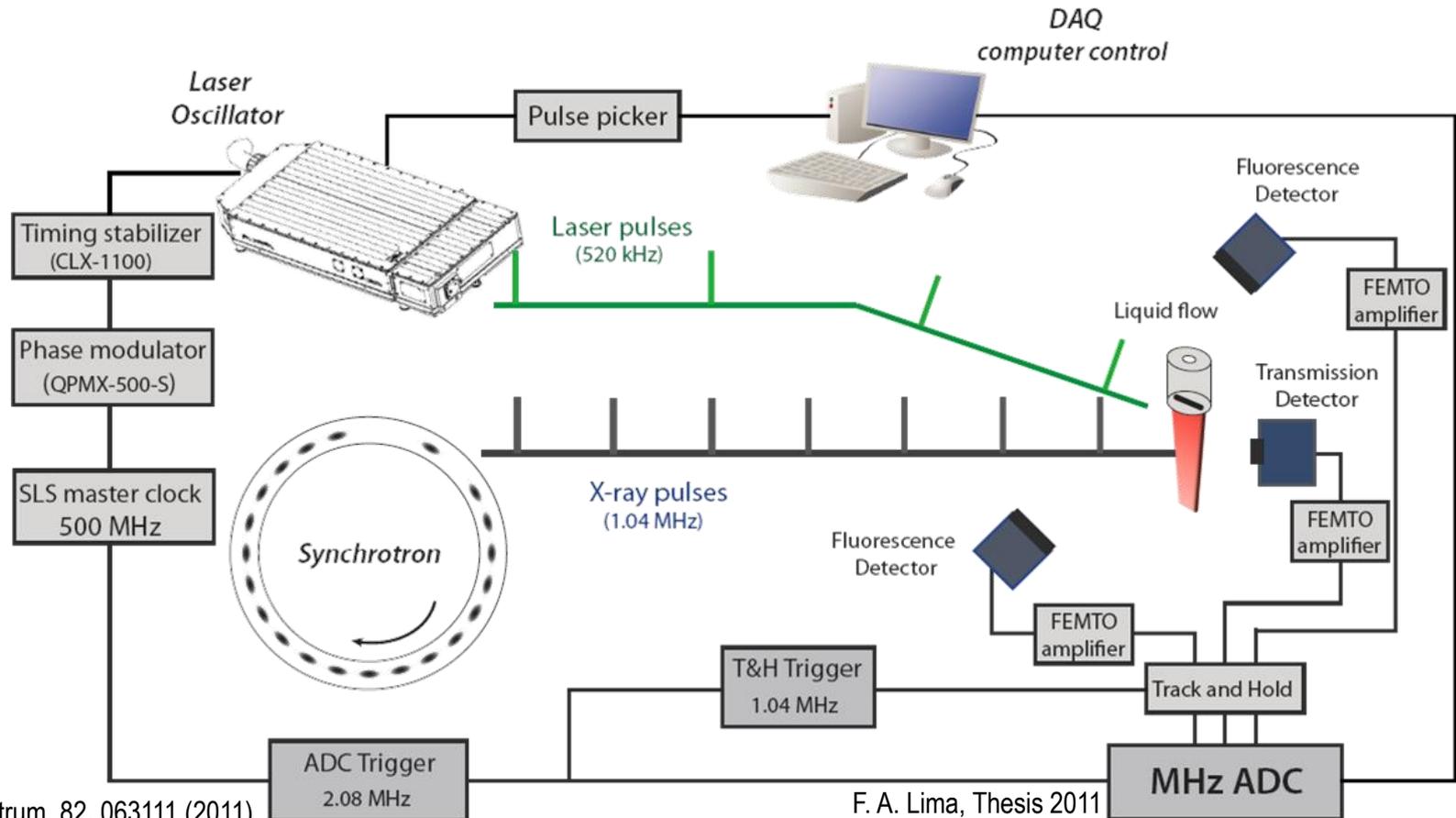
- 1kHz fs-laser system at MicroXAS
(at the FEMTO slicing source)
- MHz 10ps laser-system at MicroXAS,
Phoenix and SuperXAS
- 160 kHz fs-laser system at SuperXAS
- 40kHz ns-laser system SuperXAS
- Several high power cw systems
- kHz fs-laser system at SIM
- ...

- 480 buckets, 2ns spacing, 1.04 MHz
- 400 mA top up mode
- Hybrid mode with 70ps camshaft (CS) bunch in gap
- At undulator beamline estimated 10^{12} ph/s
- 1% of photons in x-ray pulse from camshaft bunch

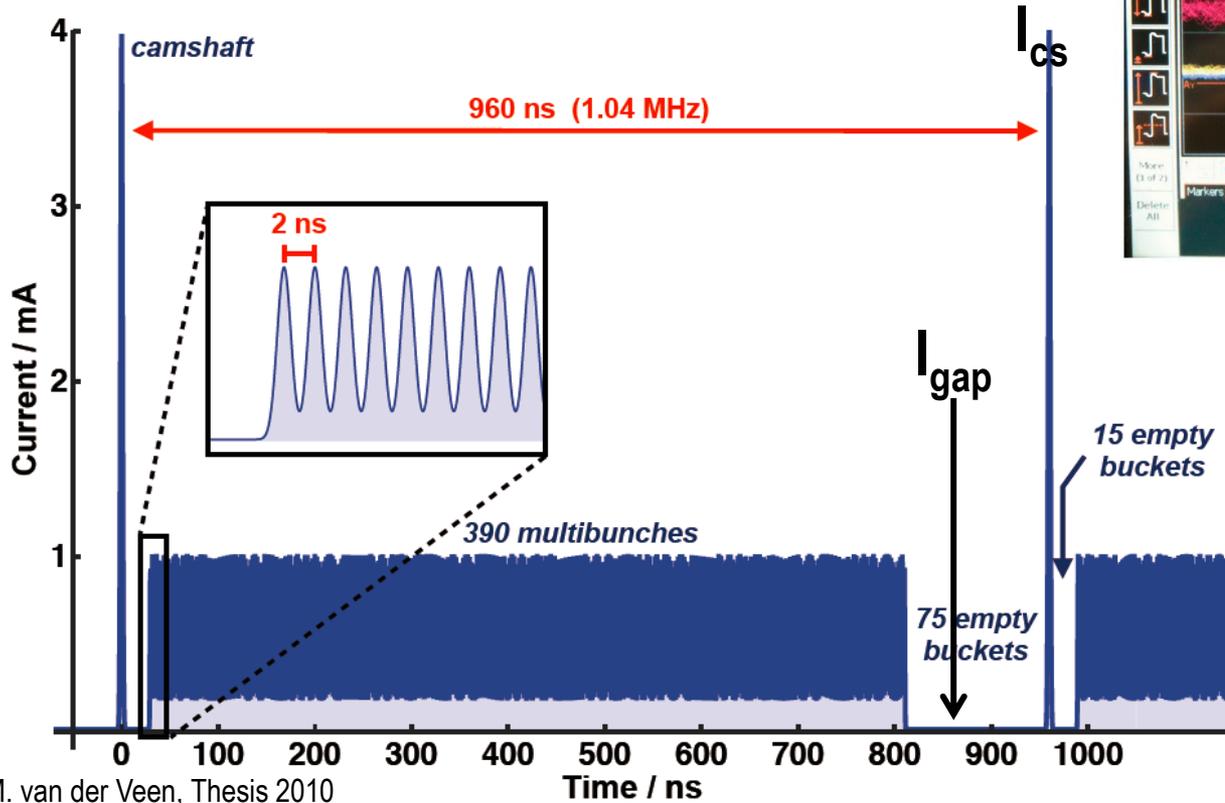


R. M. van der Veen, Thesis 2010

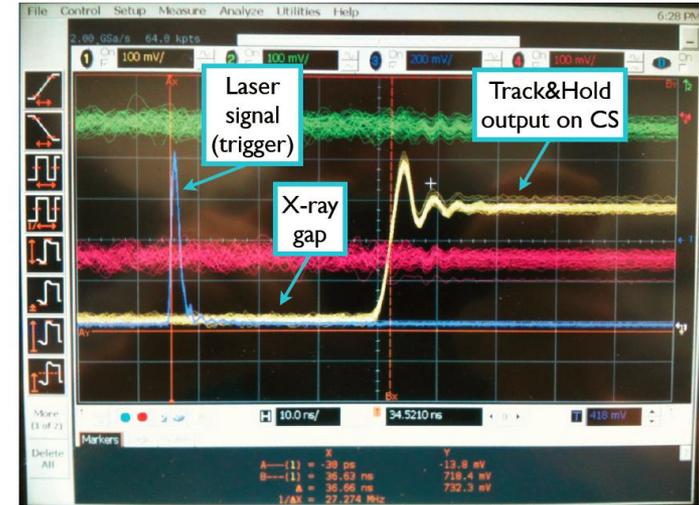
- Use fast detector to study dynamics with CS time resolution (100 ps) using all photons
- Fast detectors / fast electronics to separate CS signal (Track&Hold circuit to assist ADC)
- Record difference signal on a shot to shot basis („long“ term drifts, intensity / sample fluctuations)
- Sample recovery limits the repetition rate, 10^{10} ph/s at full rep rate (520kHz pump 1.04MHz probe)



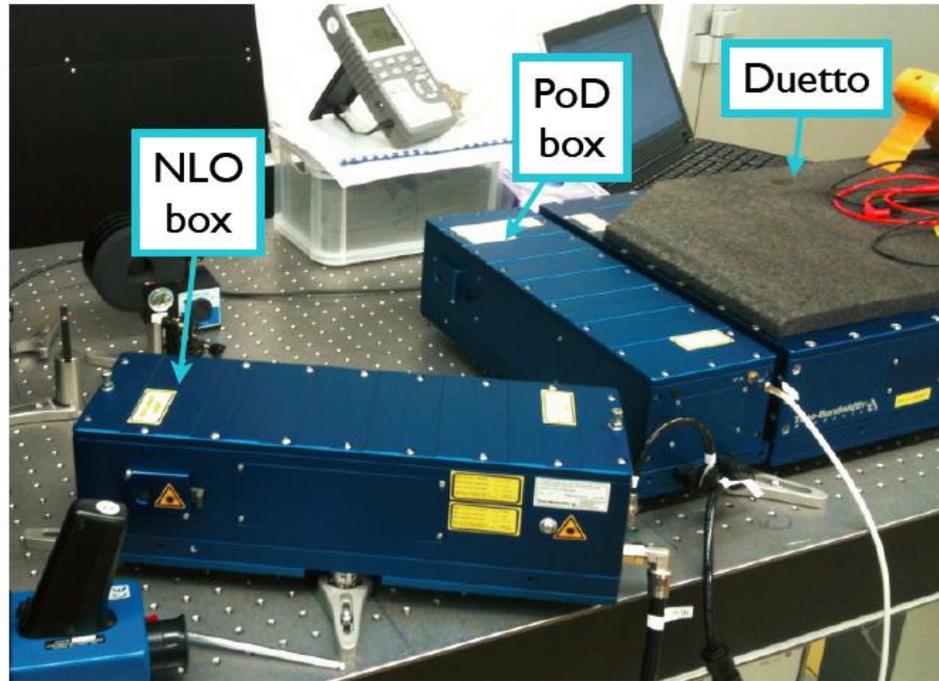
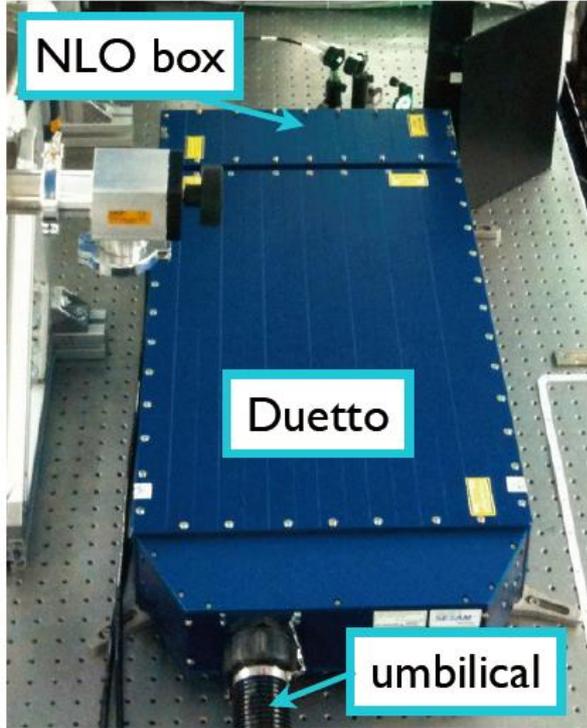
- 480 buckets, 2ns separated, 1.04 MHz, 2.4GeV
- 400 mA top up mode
- At undulator beamline estimated 10^{12} ph/s
- 1% of photons in x-ray pulse from camshaft bunch



R. M. van der Veen, Thesis 2010



$$\text{Signal} = (I_{cs} - I_{gap})^{\text{pumped}} - (I_{cs} - I_{gap})^{\text{unpumped}}$$



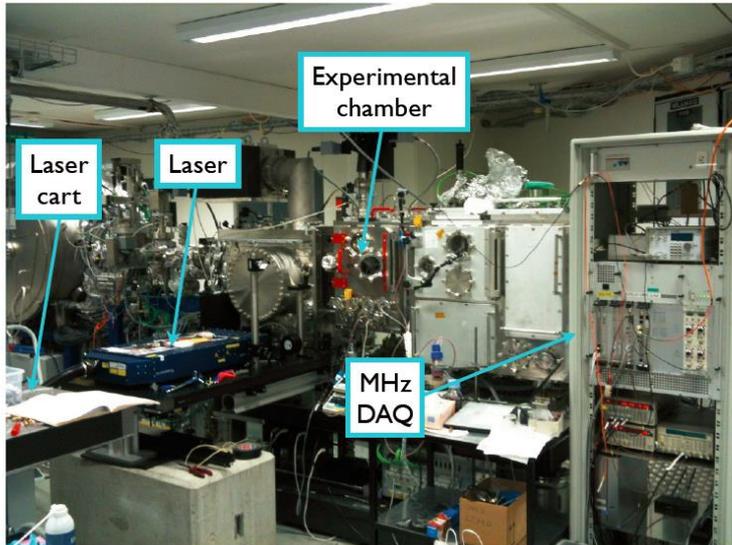
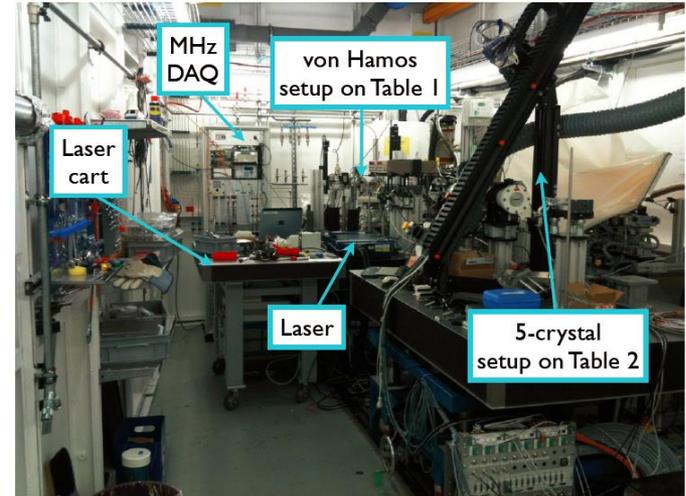
- Pulse on demand (POD) Unit allows all repetition rates between 8MHz and 1Hz
- DAQ can collect 4 integer channels (Transmission, 2x Fluorescence, I_0) in fast difference mode
- Can be used with 2d Pixel detector (Pilatus, DECTRIS), tested up to 520kHz probe (no fast difference, but still 100ps resolution)
- Wavelength: 1064nm, 532nm, 355nm, 266nm.
- Pulse energy: 26 μ J, 13 μ J, 5.7 μ J, 1,4 μ J (for high fluence, small x-ray spot <80mm for good overlap needed, can limit rep rate of experiment)

Flexibility

Wide range of probe wavelengths

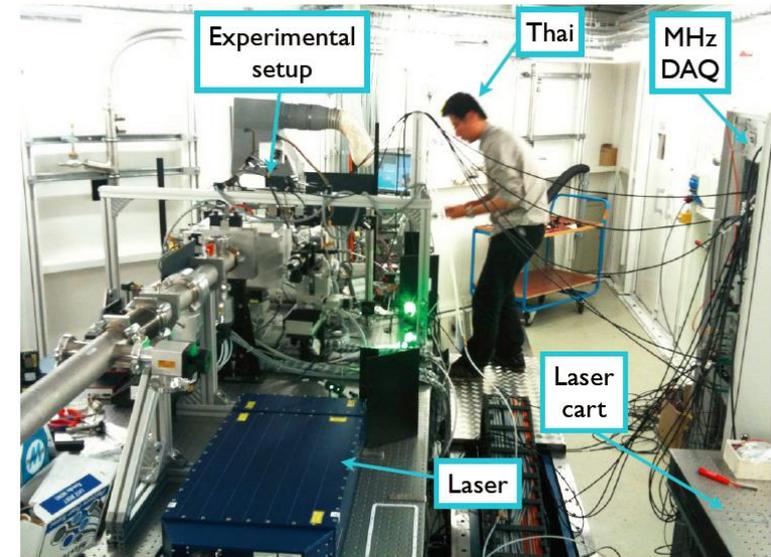
Setup has to be rebuild each time

SuperXAS,
4.5 - 35 keV
Focus 80 μ m



Phoenix, 0.8-8keV
Microfocus 2.5 μ m

MicroXAS, 5-20keV
Microfocus <2.5 μ m



- Fast recovery time of the system needed (limit of meaningful rep rate for experiment)
- good for systems damaged by x-rays if x-ray illumination cannot be reduced by other means (alternative: Pseudo SB or x-ray chopper)

REVIEW OF SCIENTIFIC INSTRUMENTS **82**, 063111 (2011)

STRUCTURAL DYNAMICS **1**, 024901 (2014)



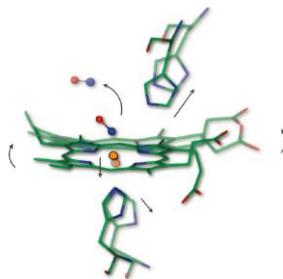
A high-repetition rate scheme for synchrotron-based picosecond laser pump/x-ray probe experiments on chemical and biological systems in solution

Frederico A. Lima,¹ Christopher J. Milne,¹ Dimali C. V. Amarasinghe Mercedes Hannelore Rittmann-Frank,¹ Renske M. van der Veen, Van-Thai Pham,^{1, c)} Susanne Karlsson,¹ Steven L. Johnson,² Dar Camelia Borca,² Thomas Huthwelker,² Markus Janousch,² Frank Rafael Abela,³ and Majed Chergui^{1, d)}

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Photooxidation and photoaquation of iron hexacyanide in aqueous solution: A picosecond X-ray absorption study

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(Received 29 December 2013; accepted 7 April 2014; published online 17 April 2014)

THE JOURNAL OF
PHYSICAL CHEMISTRY **A**

Article
pubs.acs.org/JPCA

Solvent-Induced Luminescence Quenching: Static and Time-Resolved X-Ray Absorption Spectroscopy of a Copper(I) Phenanthroline Complex

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Angewandte
Communications

Titanium Traps

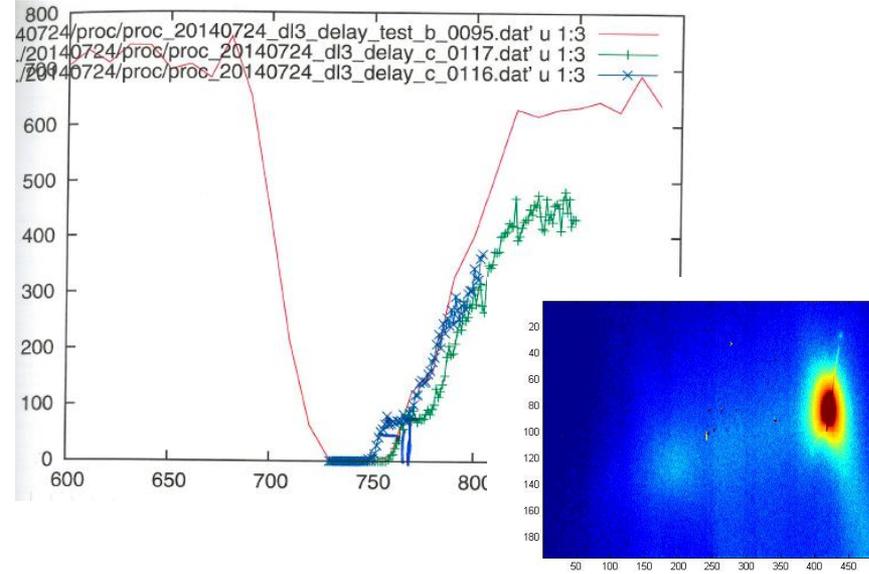
DOI: 10.1002/anie.201310522

Mapping of the Photoinduced Electron Traps in TiO₂ by Picosecond X-ray Absorption Spectroscopy^{*†}

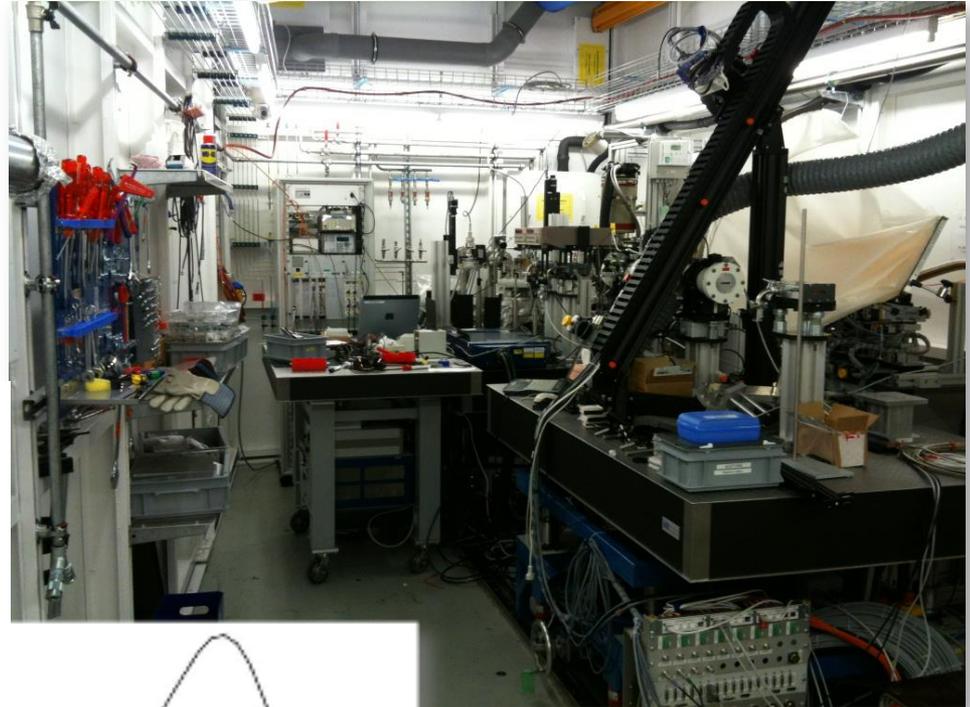
M. Hannelore Rittmann-Frank, Chris J. Milne, Jochen Rittmann, Marco Reinhard, Thomas J. Penfold, and Majed Chergui^{*}

Time Resolved X-ray Diffuse Scattering

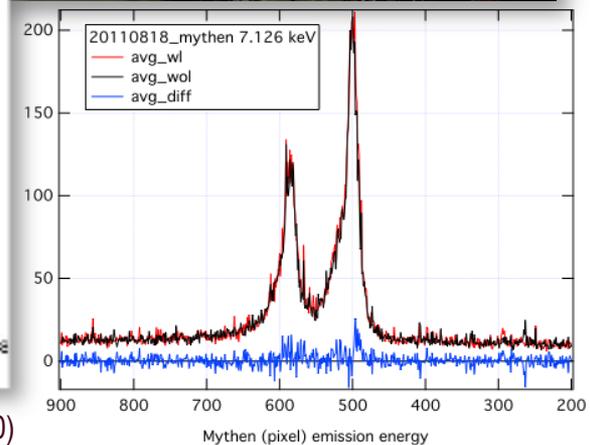
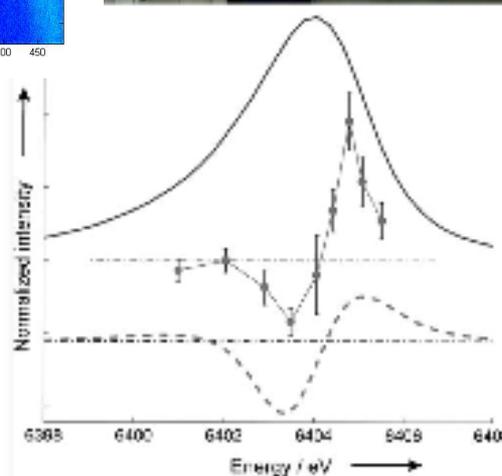
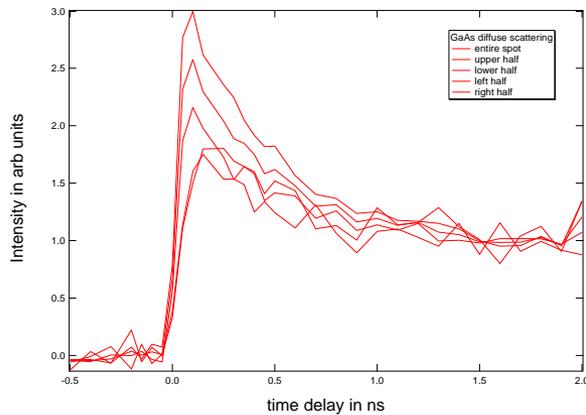
M. Trigo et al, Phys Rev B 15; 82(23): 235205 (2010)



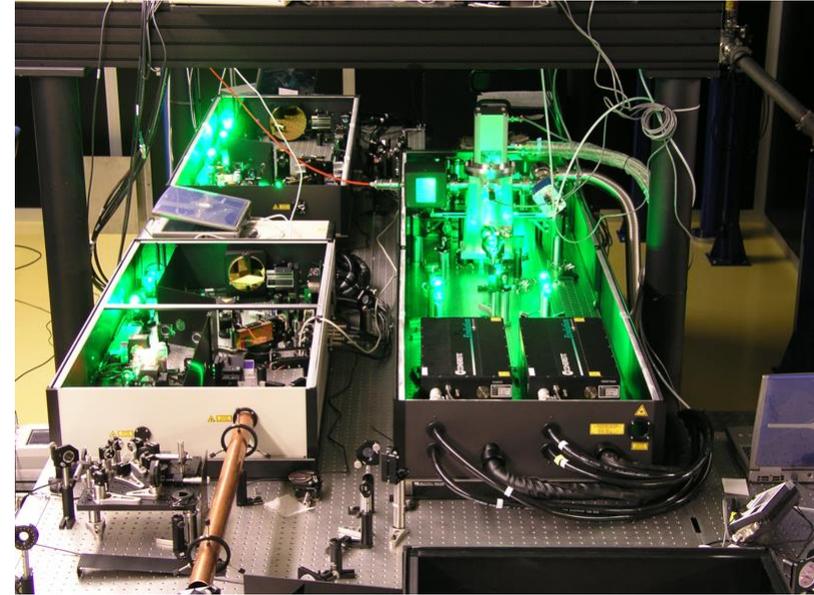
Time resolved RXES / RIXS



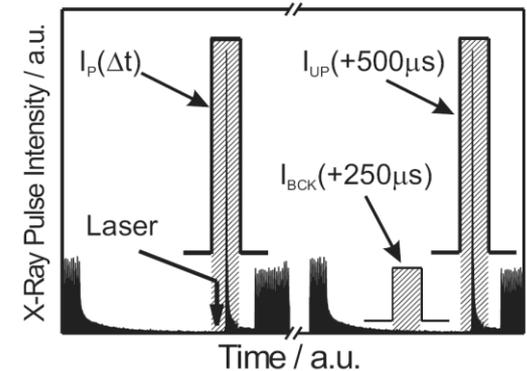
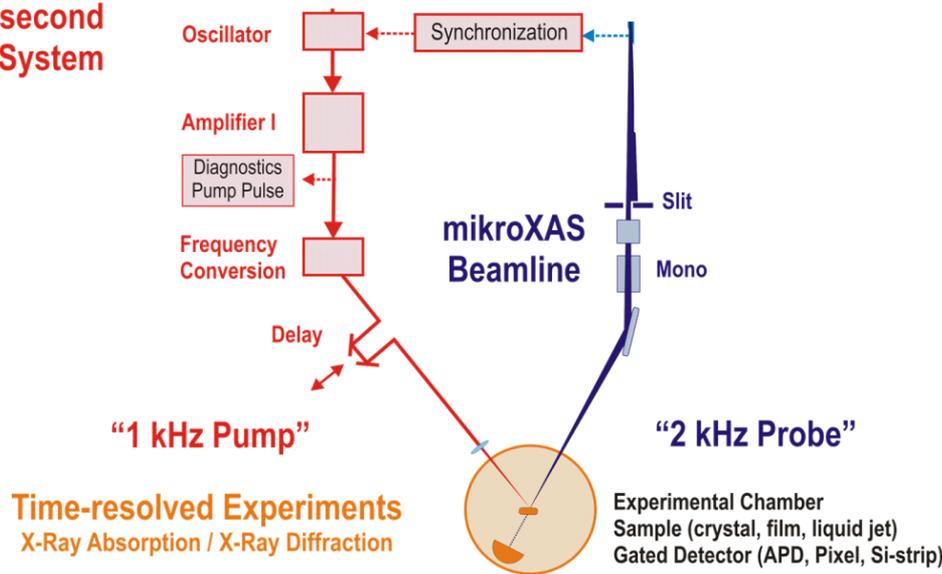
Rittmann and Johnson, unpublished



G. Vankó et al., *Angew. Chem. Int. Ed.*, **49**, 5910 (2010)

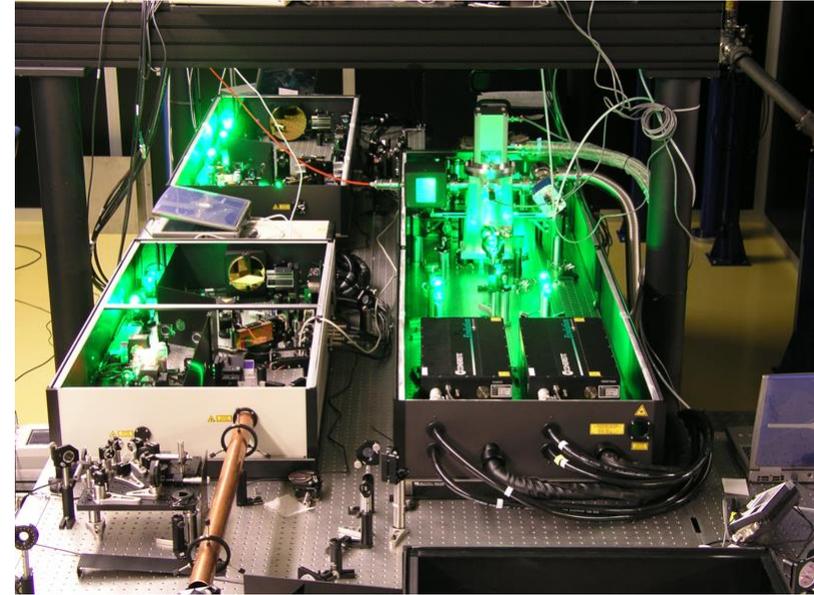
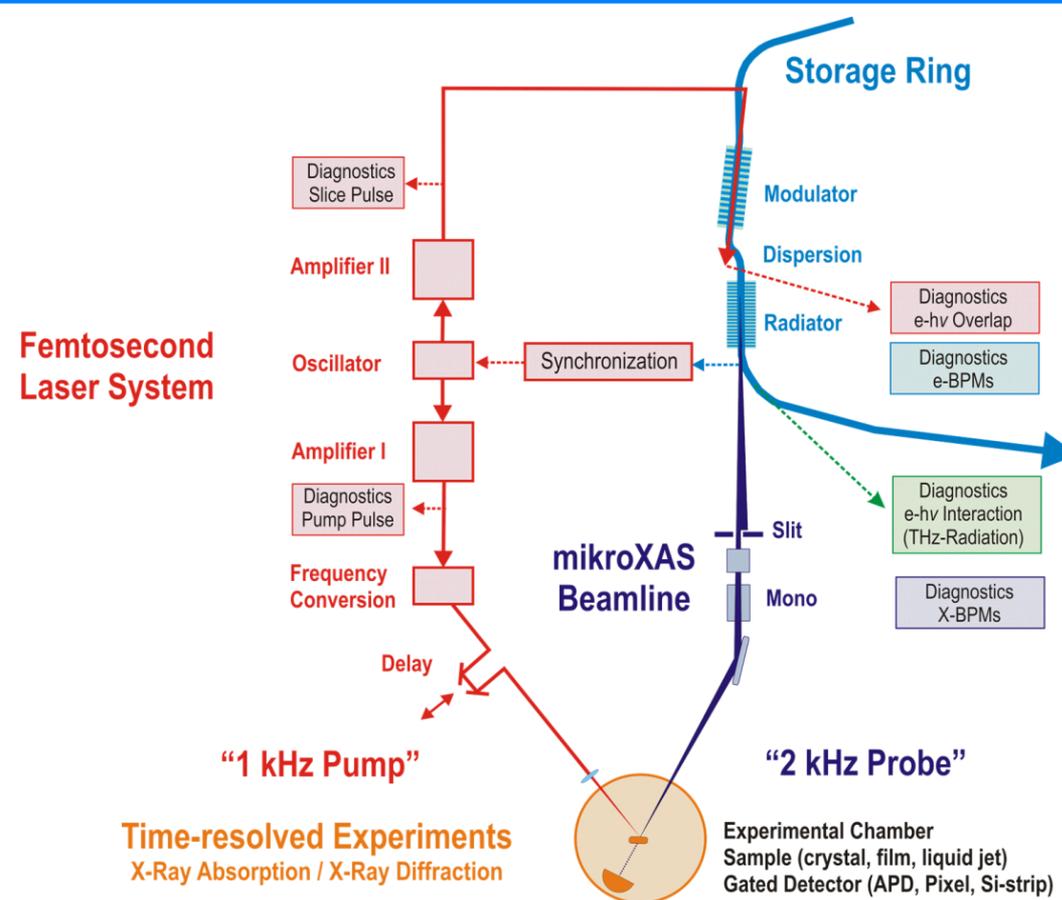


Femtosecond Laser System



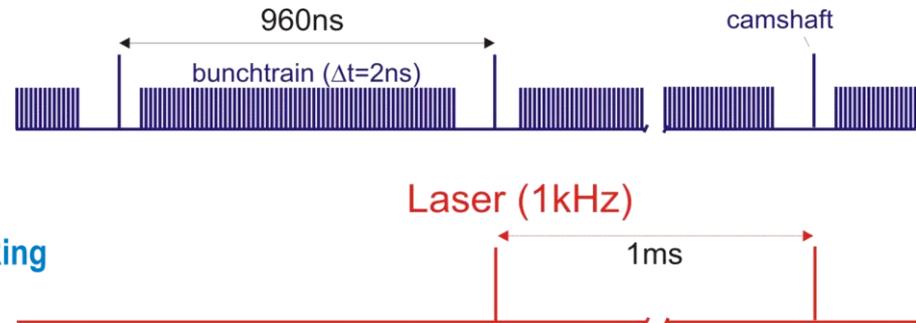
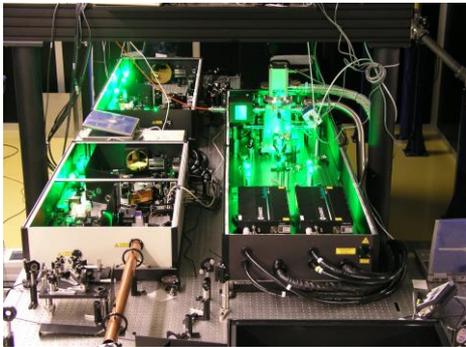
Gawelda, Thesis 2006

- Samples with long recovery time
- Reducing average heat load on sample (solids)
- Use of OPA/THz generation provides more freedom for sample excitation

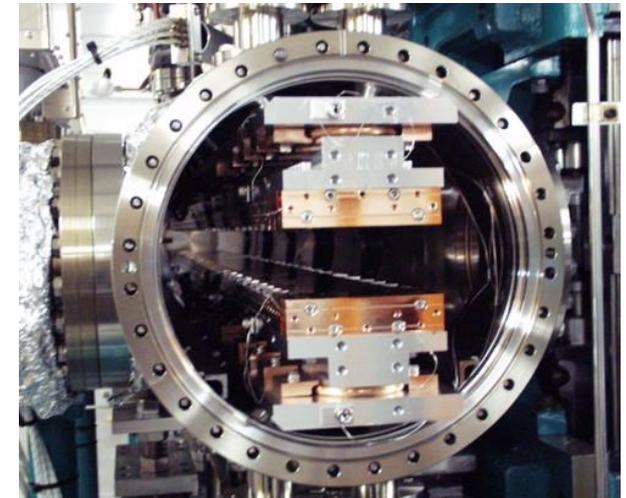
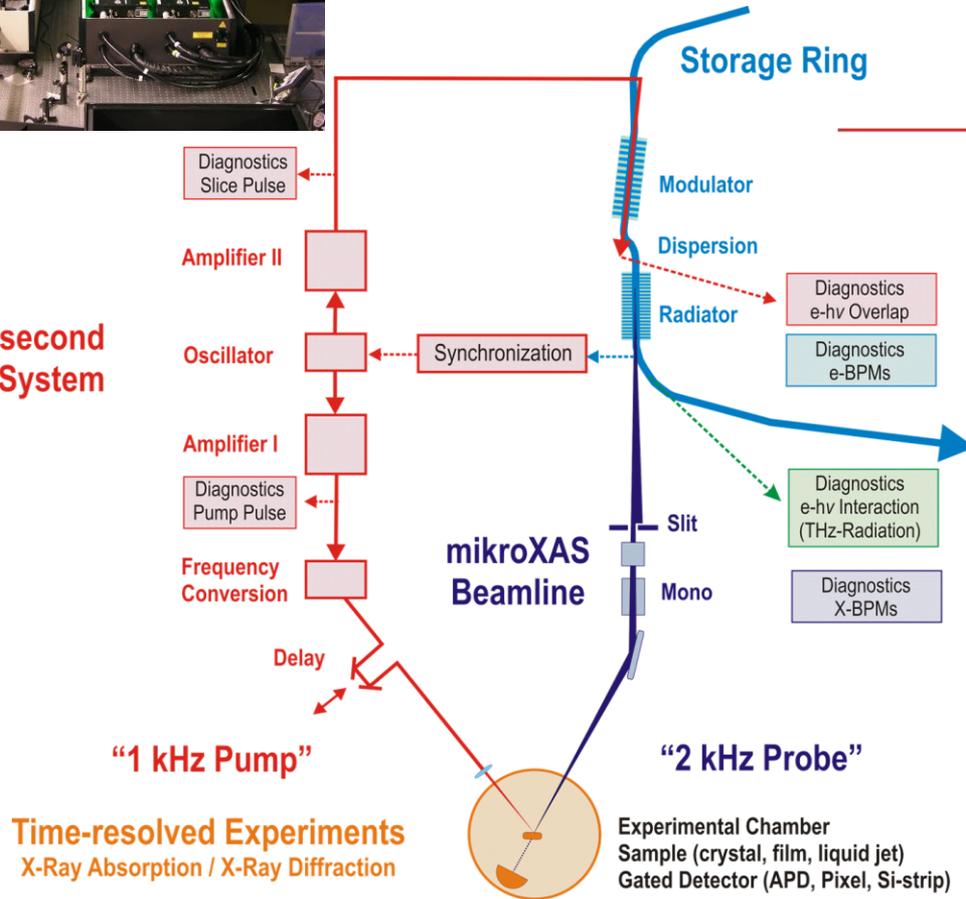


First realization at ALS
by R. Schoenlein et al.
[Science **287**, 2237, 2000]

- Use of OPA/THz generation provides more freedom for sample excitation
- **With 150 fs time resolution, 10^4 ph/s (monochromatic)**



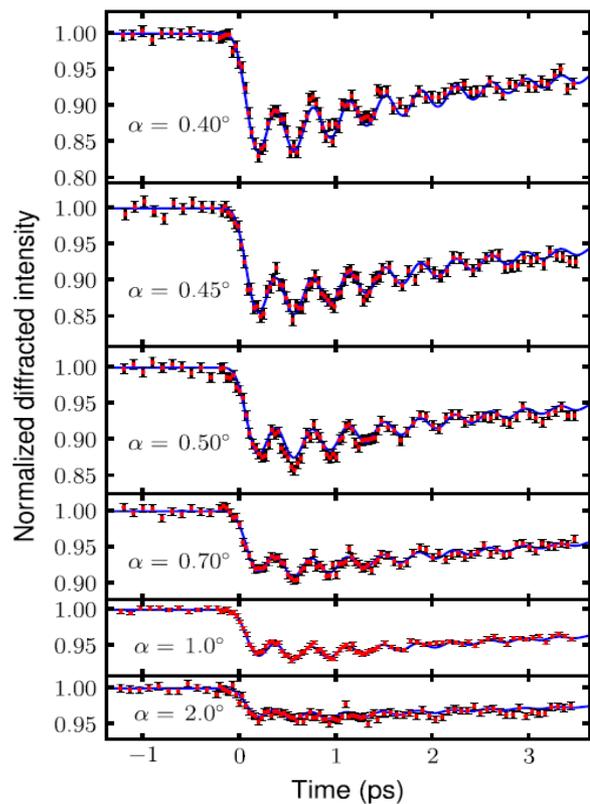
Femtosecond Laser System



Radiator (U19 In-Vacuum Undulator)

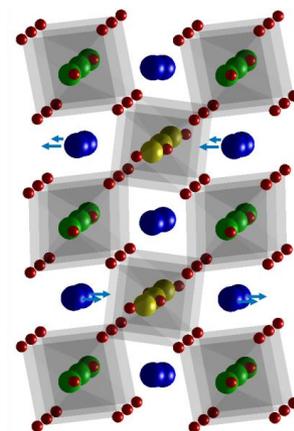
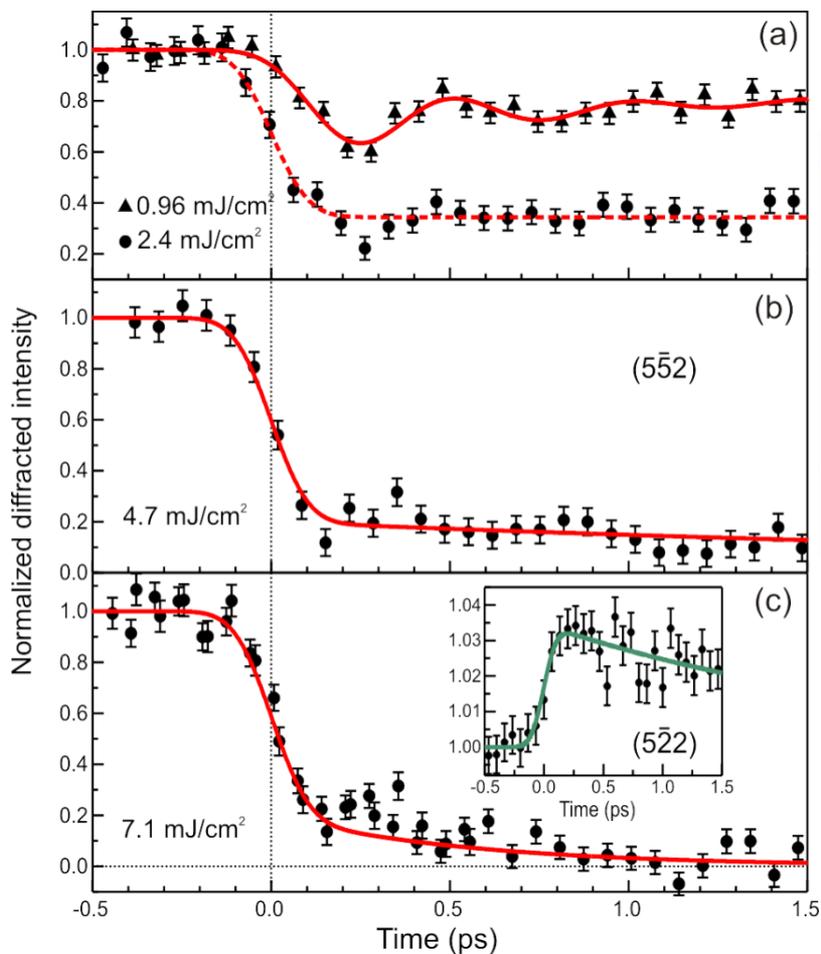
- **Time resolution:** = τ pump + τ probe + τ jitter + τ drift - arrival monitor?

Bismuth: coherent phonon depth dependence



Johnson et al., PRL 100, 155501 (2008)

Ultrafast structural phase transition (LCMO)



Beaud et al. PRL 103 155702 (2009); A. Caviezel et al. PRB 87, 205104 (2013).

- DAQ collects all x-rays of roundtrip with 30 ns steps
- can get isolated CS signal for 100 ps time resolution or follow time evolution with 30 ns steps with full x-ray flux from MB
- 150 kHz fs laser system with OPA gives high rep rate and pump tuning abilities.
- 800 nm: 100 μ J@100 kHz, 200 μ J@50 kHz
- 400 nm: 8 μ J@100 kHz, 12 μ J@50 kHz

Faraday Discussions

Cite this: *Faraday Discuss.*, 2014, 171, 259



PAPER

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X-ray absorption spectroscopy with time-tagged photon counting: application to study the structure of a Co(I) intermediate of H₂ evolving photo-catalyst

Grigory Smolentsev,^{*a} Alexander A. Guda,^b Markus Janousch,^a Christophe Frieh,^a Gaudenz Jud,^a Flavio Zamponi,^c Murielle Chavarot-Kerlidou,^d Vincent Artero,^d Jeroen A. van Bokhoven^{a,c} and Maarten Nachtegaal^a

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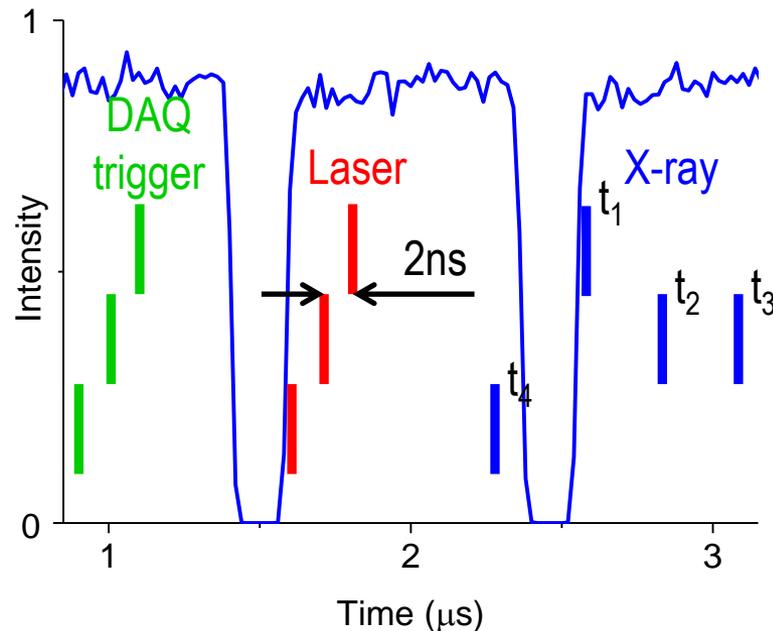


Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 23157

Probing the dynamics of plasmon-excited hexanethiol-capped gold nanoparticles by picosecond X-ray absorption spectroscopy

Flavio Zamponi,^{†‡*ab} Thomas J. Penfold,^{†c} Maarten Nachtegaal,^b Andrea Lübecke,^{§bd} Jochen Rittmann,^{bd} Chris J. Milne,^c Majed Chergui^d and Jeroen A. van Bokhoven^{*ab}

- DAQ measures the arrival time of X-ray photons with 30ns precision
- Asynchronous mode allows to avoid gaps of the intensity distribution
- Photon counting (1 count / channel / roundtrip) suited for dilute samples / low x-ray signal



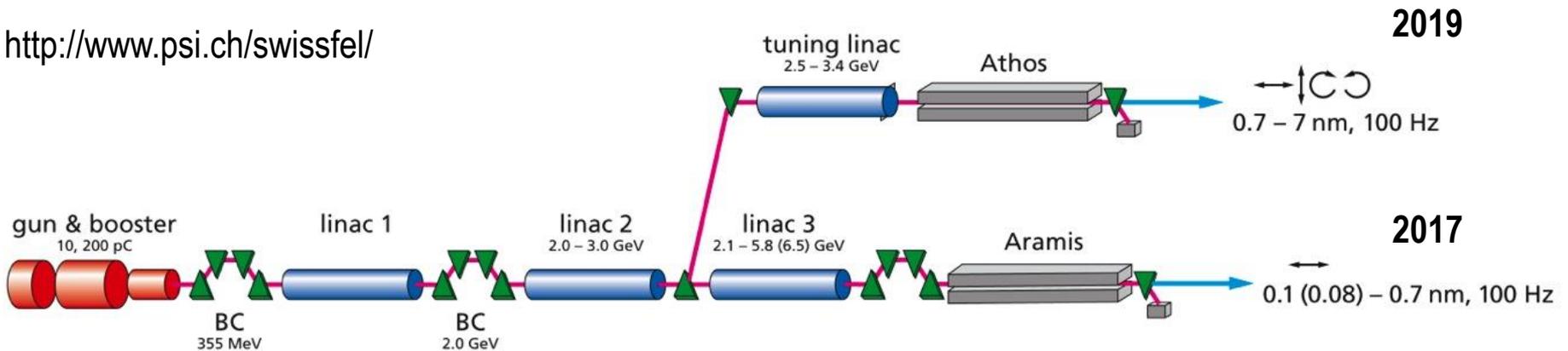
G. Smolentsev, et al; *Faraday Discuss.* 171 (2014) 259

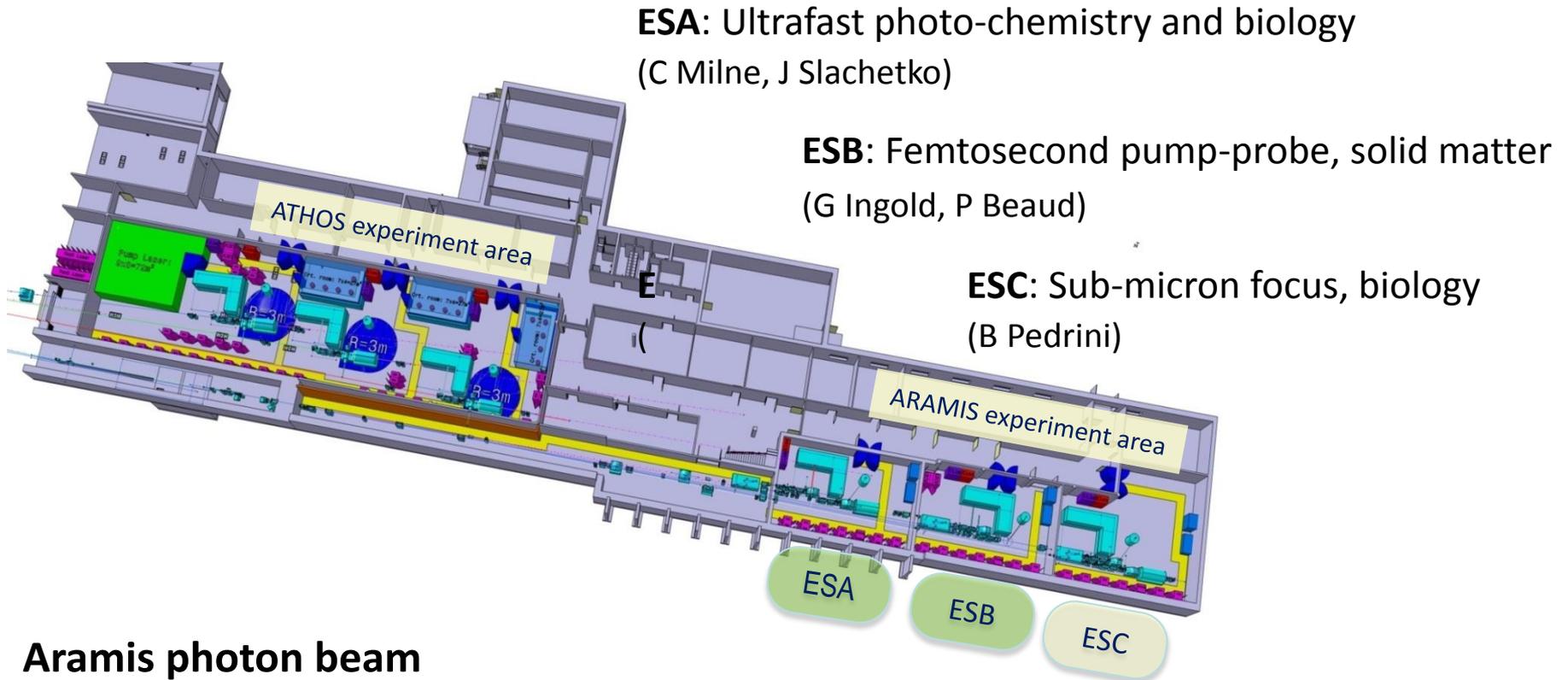


November 2014



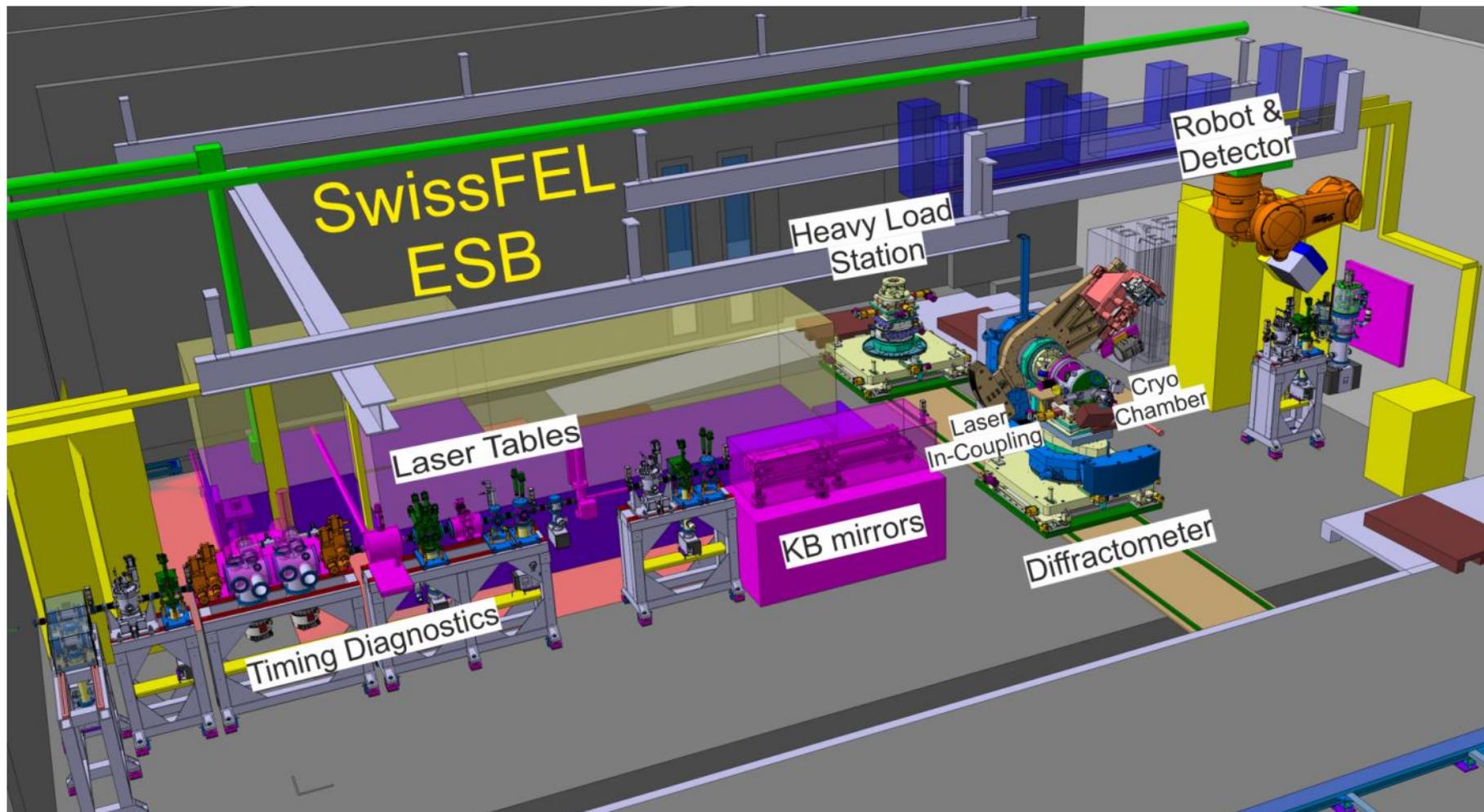
<http://www.psi.ch/swissfel/>





Aramis photon beam

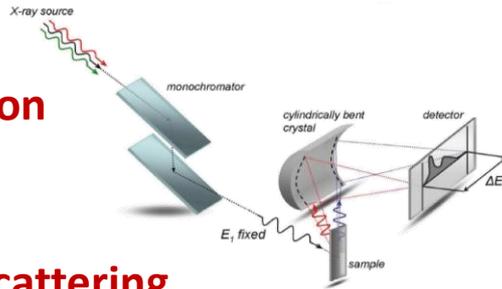
Mode	200 pC	Self-Seeding	10 pC	Large Bandwidth	Attosecond
Photon Energy	2-12.4 keV	2-12.4 keV	2-12.4 keV	2-12.4 keV	4-12.4 keV
Pulse Energy	0.8 mJ	0.6 mJ	0.08 mJ	0.8 mJ	0.01 mJ
Spectral Width (RMS)	0.1 %	0.0025 %	0.1 %	3-8 %	0.2 %
Pulse Length (FWHM)	20 fs	20 fs	5 fs	20 fs	0.2 fs



Open for pilot experiments (end of 2017), user operation starts 2018.

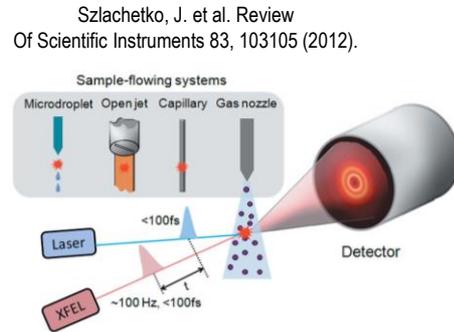
ESA Instrument

- X-ray Absorption
- X-ray emission
- X-ray diffuse scattering



Sample environment

- Liquid Samples
- Nanocrystals



Purchasing and production

ESB Instrument

Dedicated diffractometer

- TR resonant XRD, non resonant XRD
- TR RIXS
- TR diffuse scattering

Flexible station for diverse x-ray scattering geometries equipped with 16M 2-D pixel detector

Sample environment

- Temperature (10 – 400 K)
- Flexible sample and detector angles
- Magnetic fields (>1 T)



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Paul Beaud
 Gerhard Ingold
 Laurenz Rettig
 Shih-Wen Huang
 Jeremy Johnson
 Urs Staub
 Rafael Abela
 Bruce Patterson
 Chris Milne
 Jakub Szlachetko
 Daniel Grolimund
 Camelia Borca
 Thomas Huthwelker
 Maarten Nachtegaller
 Grigory Smolentsev
 Arno Schneider

...

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 Mahsa Silatani
 Fabio Santamauro


 Molecular Ultrafast
 Science And Technology

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 SCHWEIZERISCHER NATIONALFONDS
 FONDO NAZIONALE SVIZZERO
 SWISS NATIONAL SCIENCE FOUNDATION

Laser

- High repetition rate
- fs system for OPA/THz generation
- fs time resolution
- ps system for lower peak powers

X-ray

- Multiple (short) camshafts (high rep rate)
- Long multibunch (electronics do time resolution of 20ns)
- fs time resolution pulses
- ps time resolution pulses (slow dynamics)
- Only X-rays that can be used (beam damage)
- Pseudo SB (ALS)
- X-ray Shutter (ESRF)
- Res Pulse Picking

DAQ

- 2d detector (gated), high dynamic range
- 1d detector fast difference (RXES)
- Ability to collect signal of all x-rays with good time resolution (i.e. 10 ns detector FWHM)