Why add the dimension of time to X-ray science?

Alexander Föhlisch

ISRR, Institute of Methods and Instrumentation in Synchrotron Radiation Research
Research Division Large Scale Facilities
Helmholtz-Zentrum Berlin

Institute of Physics and Astronomy
University of Potsdam

25.03. – 27.03.2015, Lund, Sweden

Drivers – Outline

1. Physical scaling from Light Matter Interaction

2. Use time for the accurate electronic measurement to create efficient detection

3. Use time to correlate correlated „messenger particles“ in complete experiments

4. Use time for dynamic studies of matter

5. Use time for novel physics with short wave length radiation

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X-ray matter interactions: physical scales relate to source properties

• Speed of Sound	1 nm	in	1 ps
• Fermi Velocity	1 nm	in	1 fs
• Speed of light	1 atom (3 A)	in	1 as

- **Scattering duration / core lifetime in** **0.1-10 fs**
- **Energetic width of a X-ray resonance** **below 1 eV**

In a sample we want one photon at a time during the fs X-ray core hole life times (scattering duration) at any given time to measure materials properties in impurity model, perturbative treatment:

- 1 photon / eV / fs
- 10^3 photons / eV / 1 ps (bunch)
  10^4 photons / eV / 10 ps (bunch)
  10^5 photons / eV / 100 ps (bunch)

- Undulator Harmonic 10 eV
  10^6 photons / bunch
- Repetition rate 100 kHz - 1 MHz
  10^{11-12} photons /s
- 1-10% beamline transmission
  10^{12-13} photons /s from source

Photon densities

Sychrotron Radiation Sources

- 10^6 photons / 100 ps (bunch)
- 1 photon / eV / fs

- In a sample is one photon at a time during the fs X-ray core hole life times

- Partial lateral coherence
- No longitudinal coherence

– impurity model,
– perturbative treatment

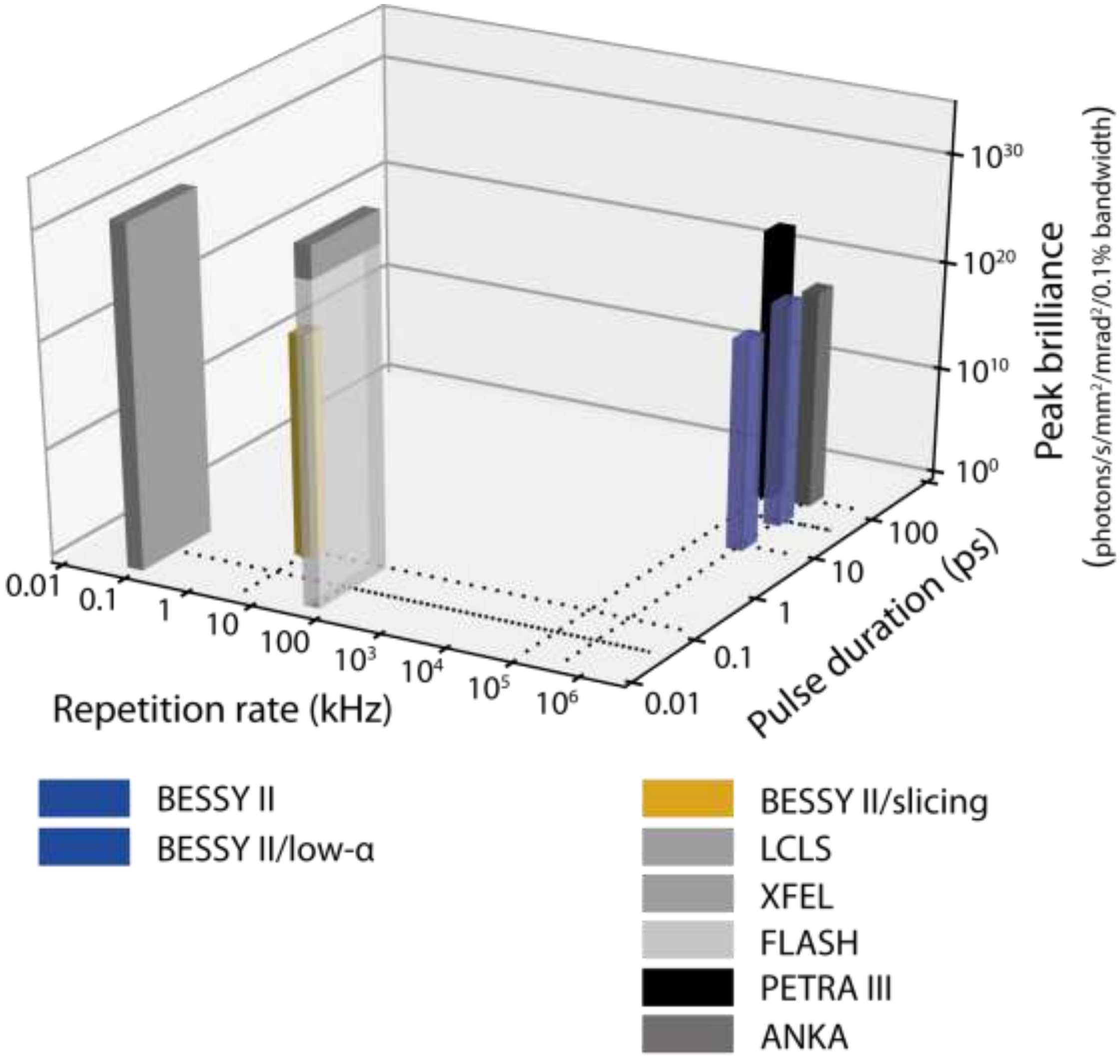
X-ray Free Electron Laser Source

- $10^{9\text{-}11}$ photons/10-100 fs (bunch).
- $10^{5\text{-}7}$ photons / eV / fs

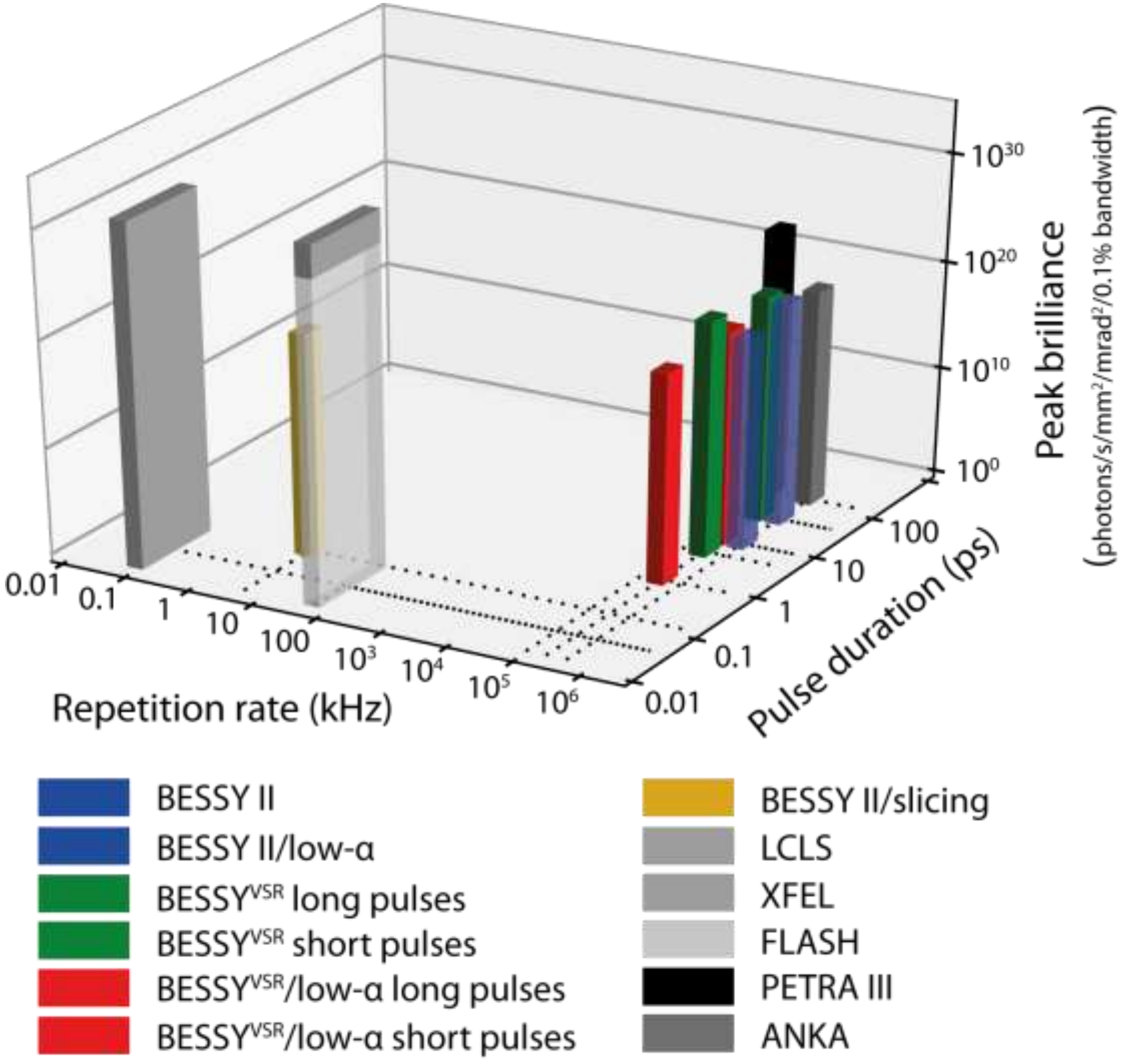
- In a sample is a coherent field during the fs-X-ray core hole liefe time
- Full lateral and longitudinal coherence

– Non-linear and multiphoton interaction. Strong field region

Performance regions and gaps of X-ray Synchrotron Radiation and FEL Sources now

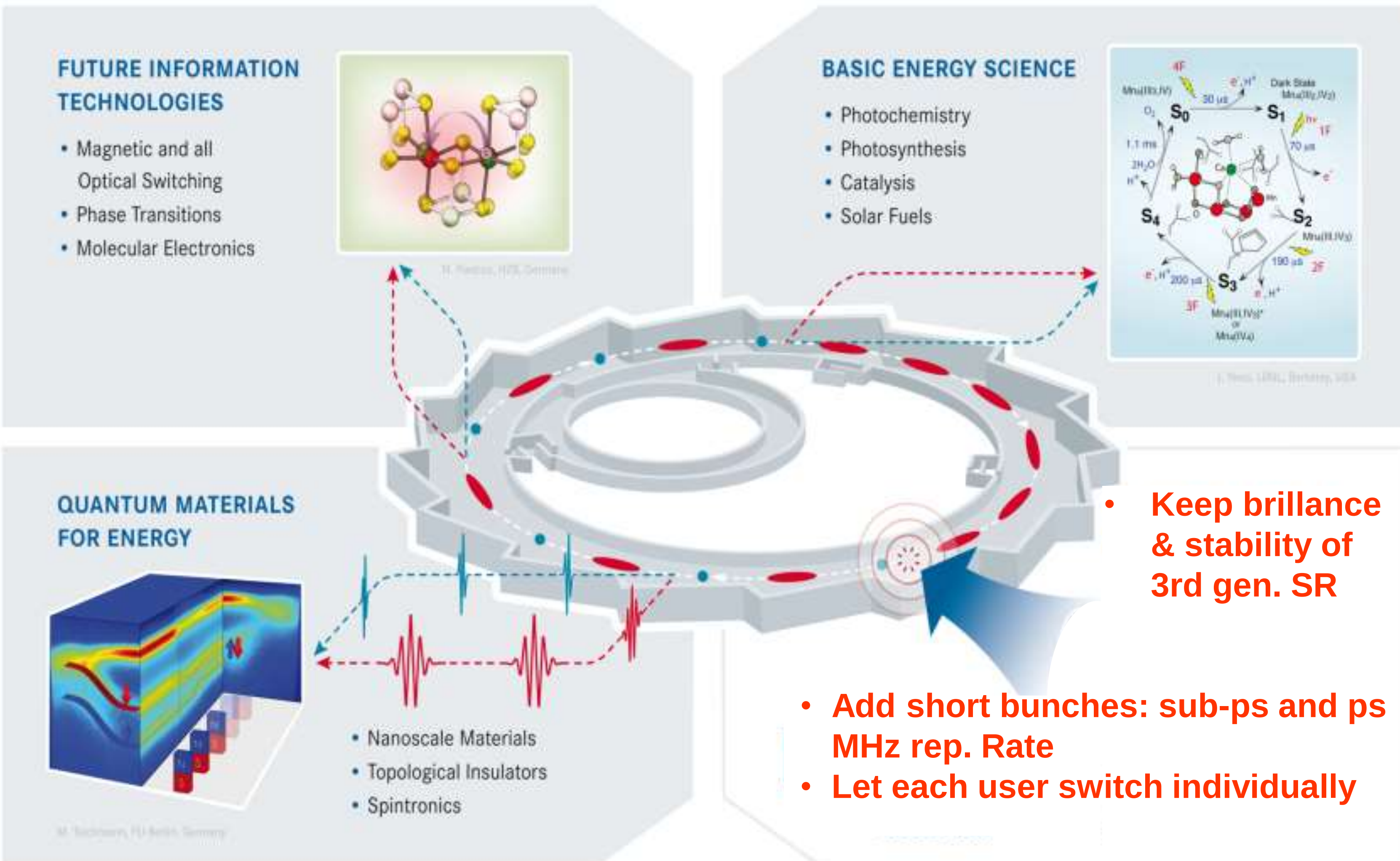


BESSY–VSR pushes into an unique parameter space



- **Keep average brillance & stability of Multi-User SR**
- **sub-ps and ps pulses at MHz rep. Rate**
- **Let each user switch individually**

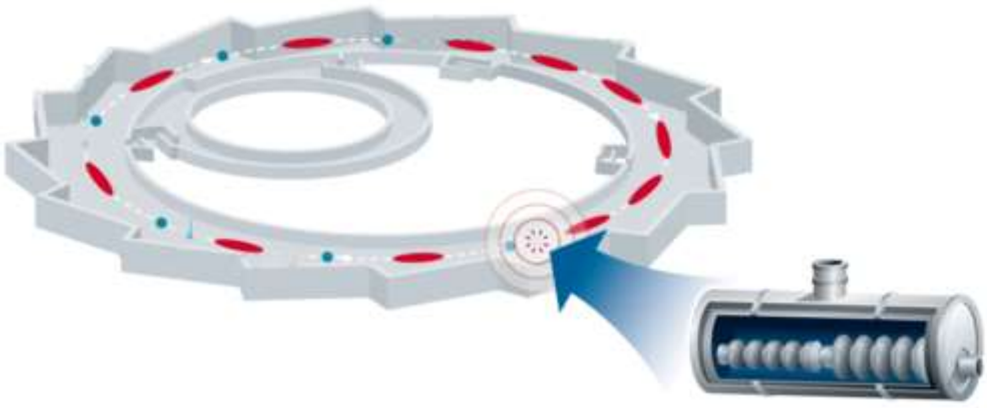
BESSY–VSR in a nutshell



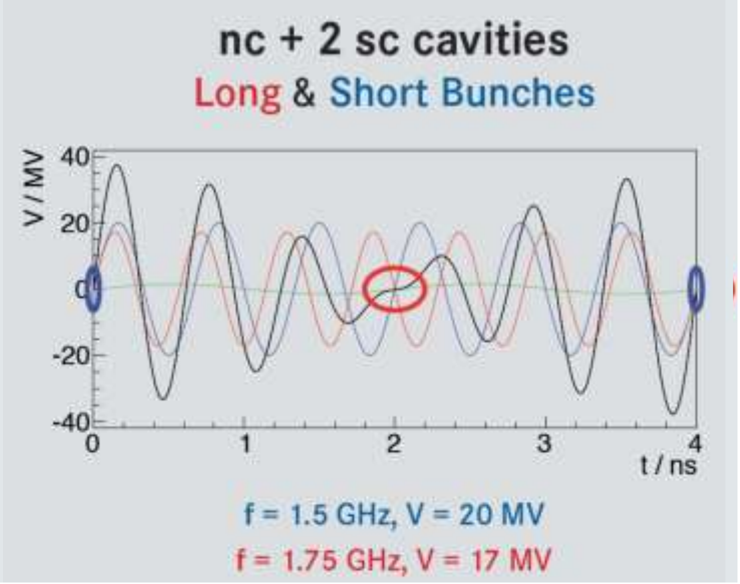
- **Keep brillance & stability of 3rd gen. SR**

- **Add short bunches: sub-ps and ps MHz rep. Rate**
- **Let each user switch individually**

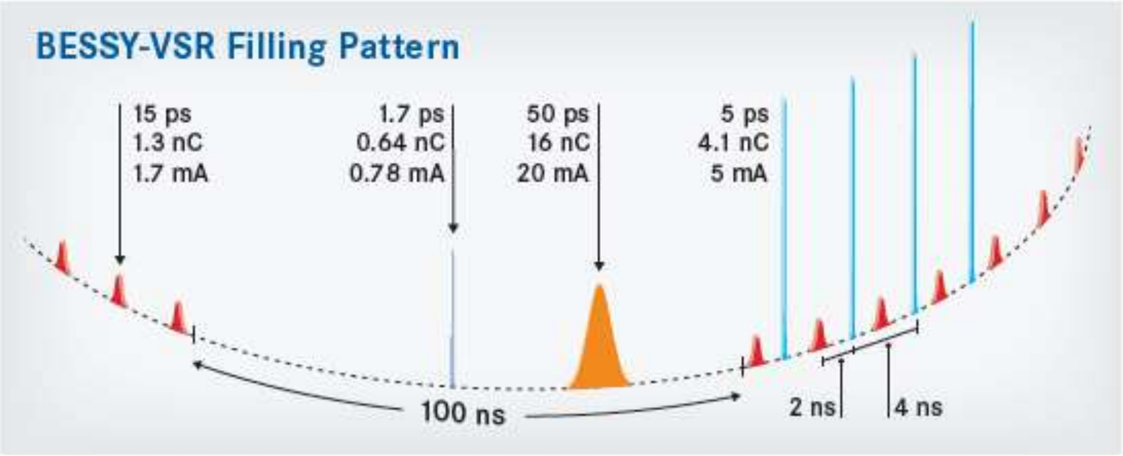
BESSY-VSR: Superconducting bunch compression cavities



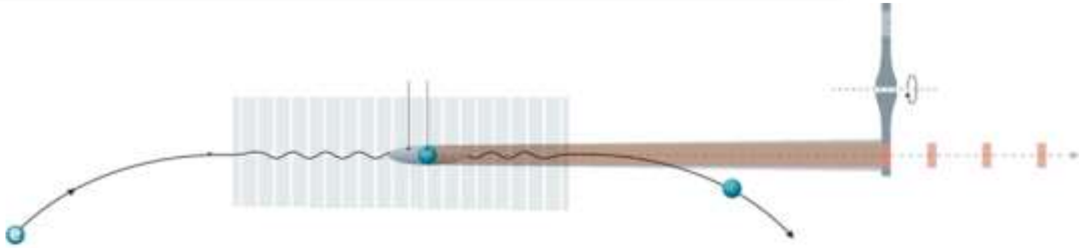
Superconducting HOM damped bunch compression cavity – Synergy with B*ERL*inPro



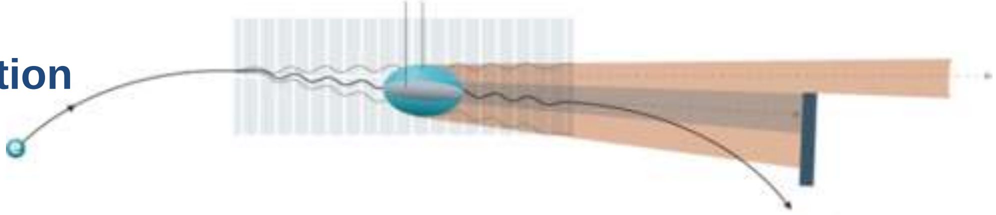
Users individually select short and long bunches



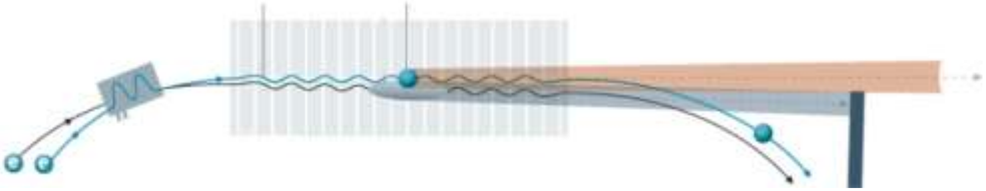
Pulse Picking



Resonant bunch excitation



Bunch kicking



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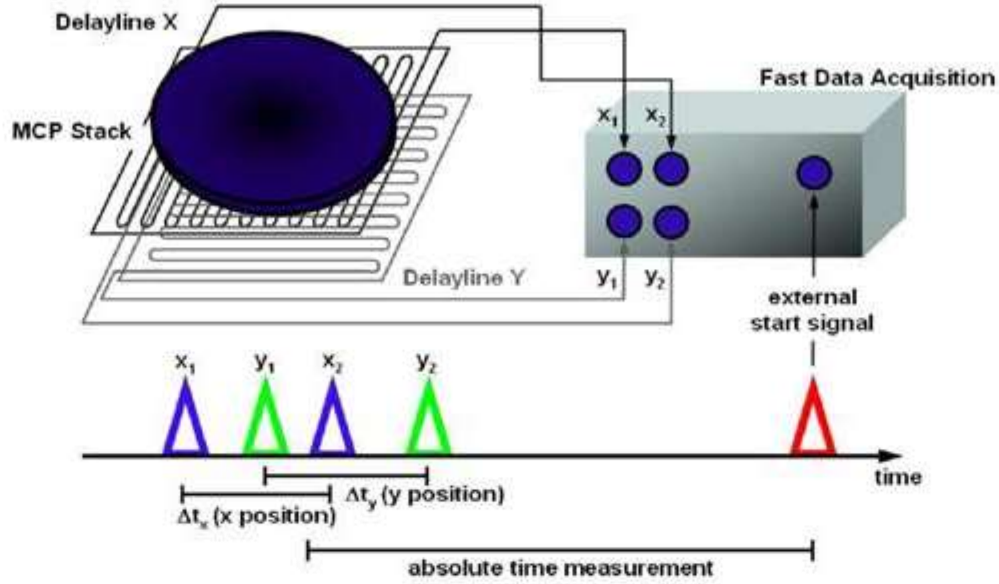
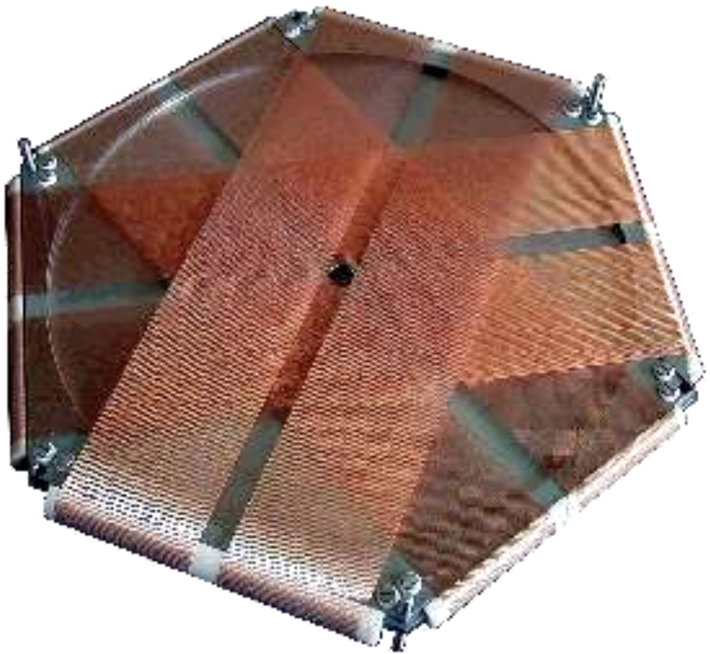
2. Use time for the accurate electronic measurement to create efficient detection

- ps – x 10 ps time information with GHz electronics
- High data rate from single shot DAQ
- Delay line detection: unique time and spatial information of X-rays and charged particles.

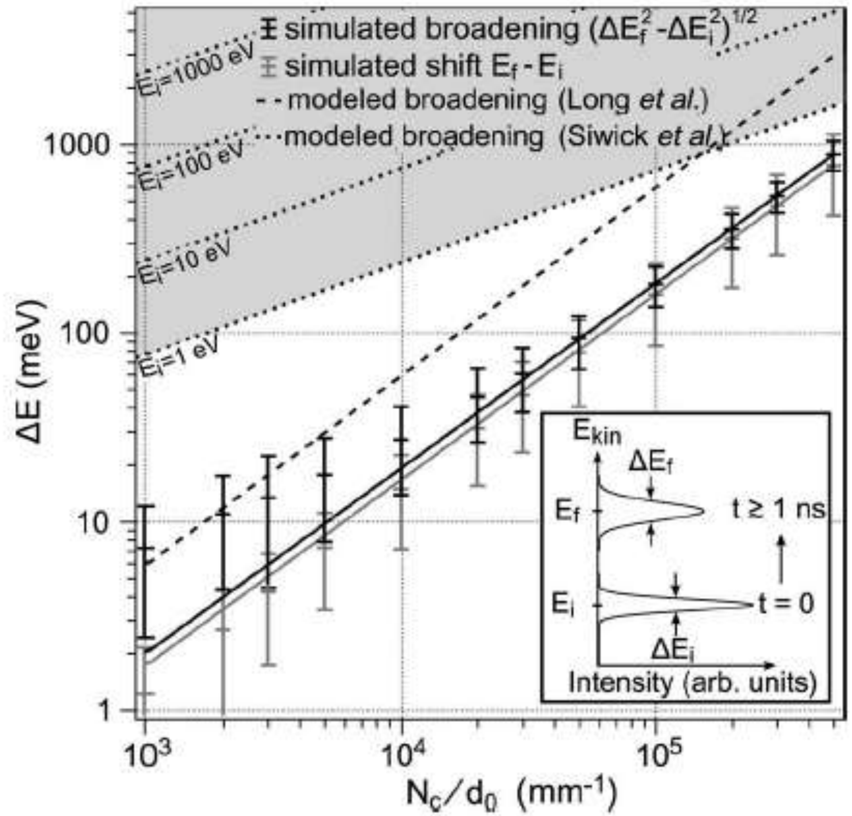




ArTOF is one variant of this:
Uppsala – Berlin joint Lab on next Generation Electron Spectroscopy

- Low Dose PES for Radiation Sensitive Matter (200-100 x transmission of hemisphere)
- Improve resolving power at the space charge threshold
- BESSY and BESSY-VSR ideal pulseduration and rep rate

PHYSICAL REVIEW B 79, 035402 (2009)



Principles and operation of a new type of electron spectrometer – ArTOF, R. Ovsyannikov et al. JELSP doi:10.1016/j.elsec.2013.08.005

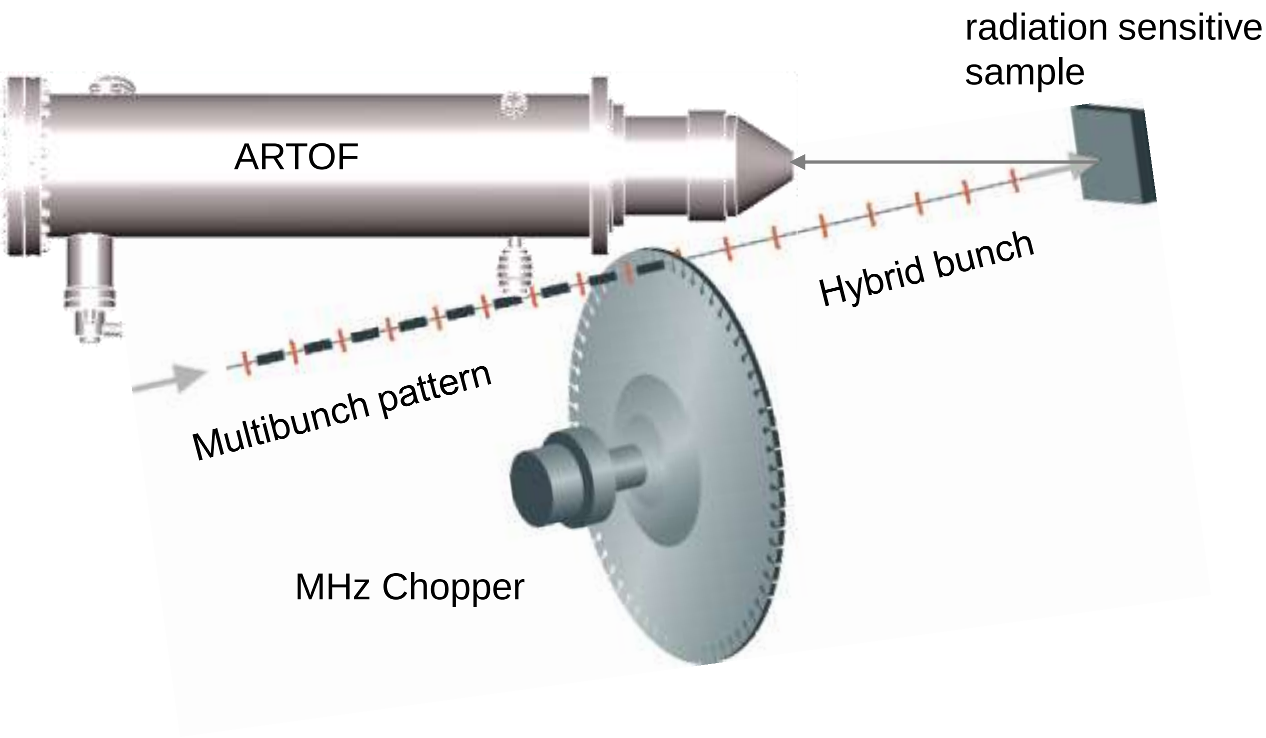
UPPSALA UNIVERSITET

HZB Helmholtz Zentrum Berlin

Röntgen Ångström Cluster

LowDosePhotoemission at BESSY II

- Reduce average flux on sample towards single bunch intensity (175 - 1000 times less radiation)
- Overcompensate in detection efficiency by 200- 1000 x over classical hemisphere



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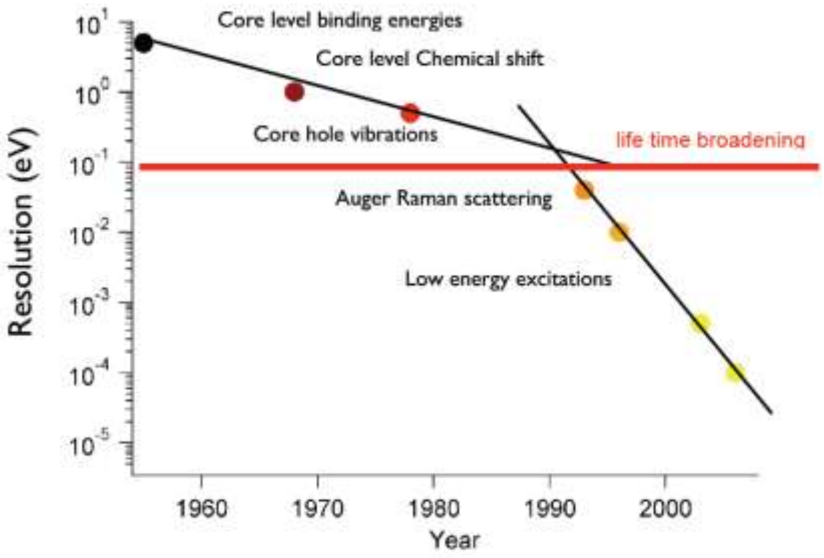
Coincidence Electron Spectroscopy for chemical Analysis (CoESCA)

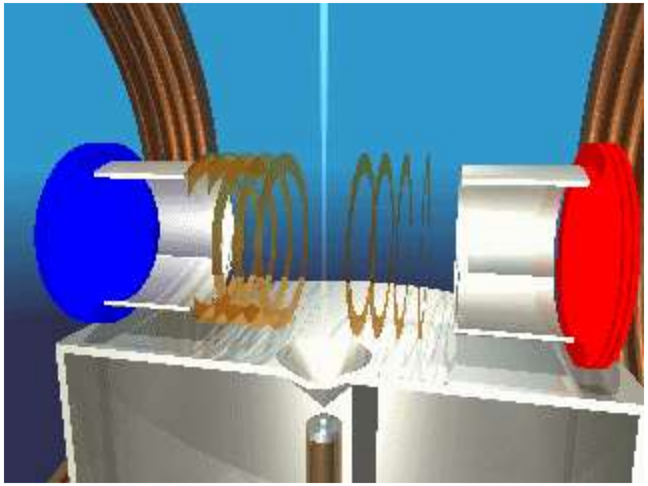
- Extreme chemical and structural selectivity from complete experiments eliminating life time broadening

- Double core excited state for conformer selectivity (i.e. cis-trans) over single core level ESCA



Reaction Microscope

(web-page Dörner Group)



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From the description of static properties to the control of functionality

How do we communicate and archive knowledge?

How can we harvest and store energy?

How can we improve selectivity and rate in chemistry and catalysis?

Relevant time and length scales

- Speed of Sound 1 nm in 1 ps
- Fermi Velocity 1 nm in 1 fs
- Speed of light 1 atom (3 A) in 1 as

- Scattering duration / core lifetime in 0.1-10 fs

	1 µs	
1 mm		Large amplitude Motion, folding
	1 ns	
		Domain Dynamics
1 µm		
	1 ps	Spin precession
		Bond formation
1 nm	**1 fs**	
		Exchange Charge transfer
1 A	**1 as**	

Repetition rates with pump-probe spectroscopy

• Speed of Sound	1 nm	in	1 ps
• Fermi Velocity	1 nm	in	1 fs
• Speed of light	1 atom (3 A)	in	1 as
• Scattering duration / core lifetime		in	0.1-10 fs

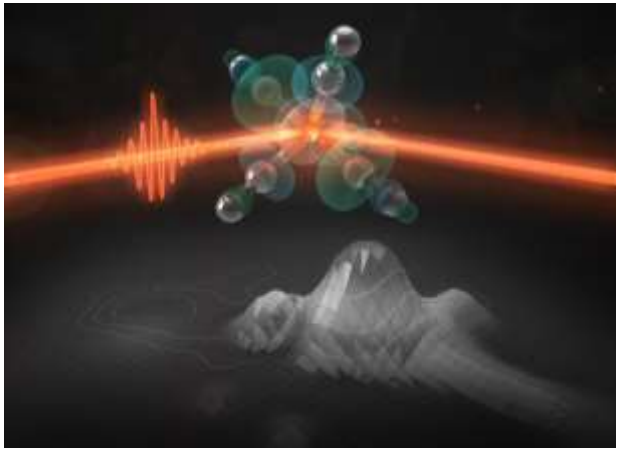
In a pump-probe experiment the cumulative pump energy deposition in the sample has to be transported out of the interaction volume.

Rep. Rate well below Øpump/v_{sound}“.

Focus Size	Pulse distance	Rep. Rate	100 times below
1 µm	1 ns	1 GHz	10 MHz
10 µm	10 ns	100 MHz	1 MHz
100 µm	100 ns	10 MHz	100 kHz

To equilibrate sample repetitively 100 kHz – few MHz is absolute Maximum!

“What controls rate and selectivity in chemistry and catalysis?”
excited state dynamics



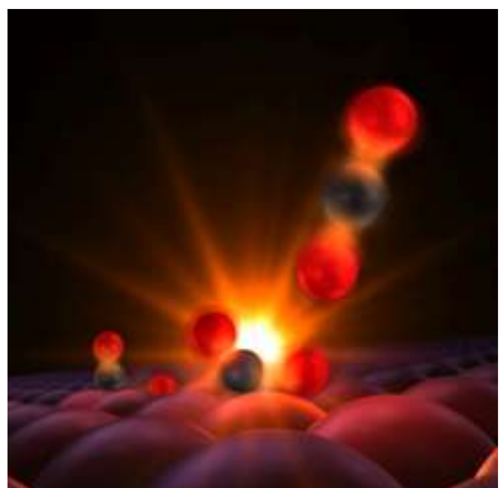
Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution.
P. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, C. Weniger, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. Hartsock, K. Gaffney, W. Schlotter, J. Turner, B. Kennedy, F. Hennies, F. de Groot, S. Techert, M. Odelius, A. Föhlisch, NATURE in press (2015)

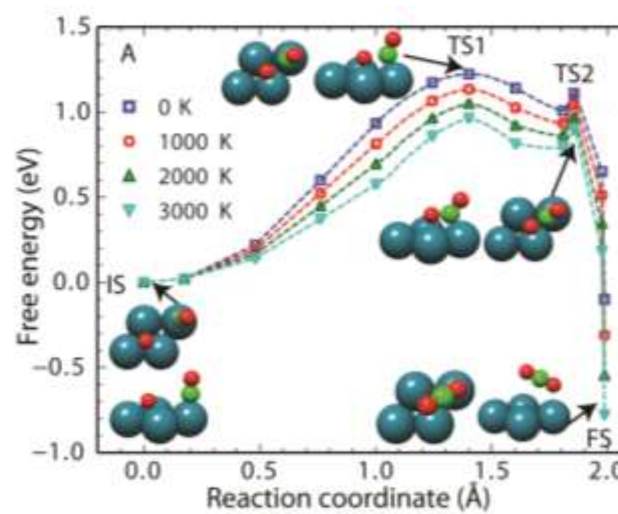
Transition metals key „ingredients“ to (photo-)(bio)-chemistry and Heterogeneous catalysis

Probing the transition state region in catalytic CO oxidation on Ru.
H. Öström et al., Science, 12 February 2015 (10.1126/science.1261747)

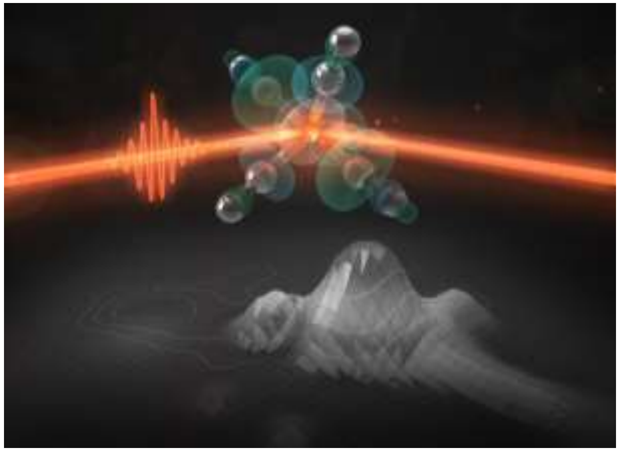
M. Dell'Angela et al., Science 339, 1302-1305 (2013).

A. Nilsson group, J. Norskov group, Pettersson group, W. Wurth group, M. Wolf group





Selectivity and Pathways of bond breaking and bond creation



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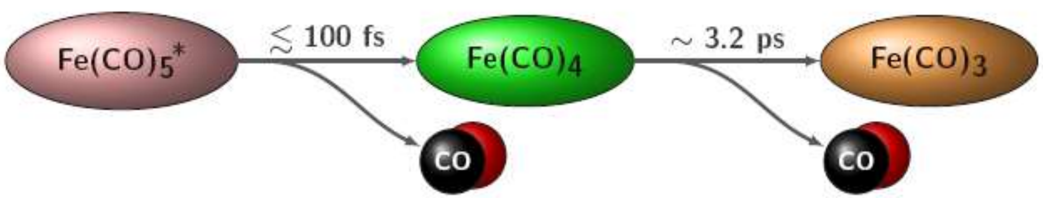
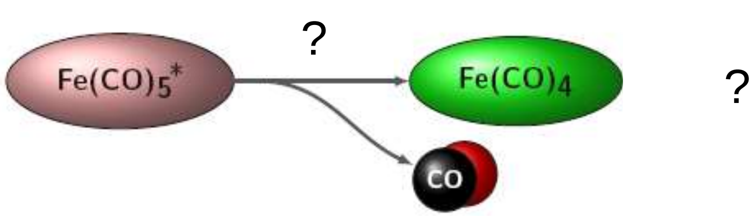
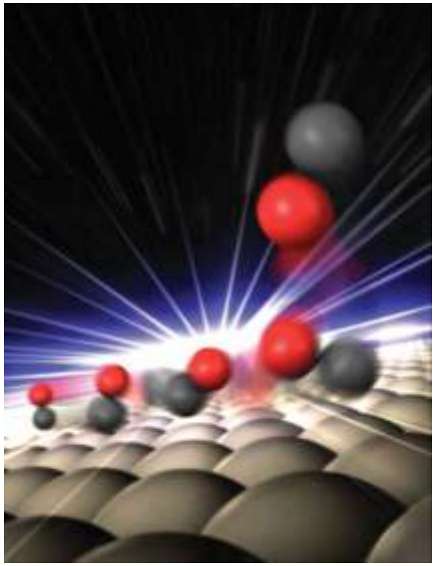
Photodissociation – Gas Phase: $Fe(CO)_5$ + $h\nu_{pump}$ → $Fe(CO)_4$ + CO → $Fe(CO)_3$ + CO



Photodissociation – Solution: $Fe(CO)_5$ + $h\nu_{pump}$ → $Fe(CO)_4$ – EtOH + CO



Time resolved ESCA / PES / PED /NEXAFS etc..

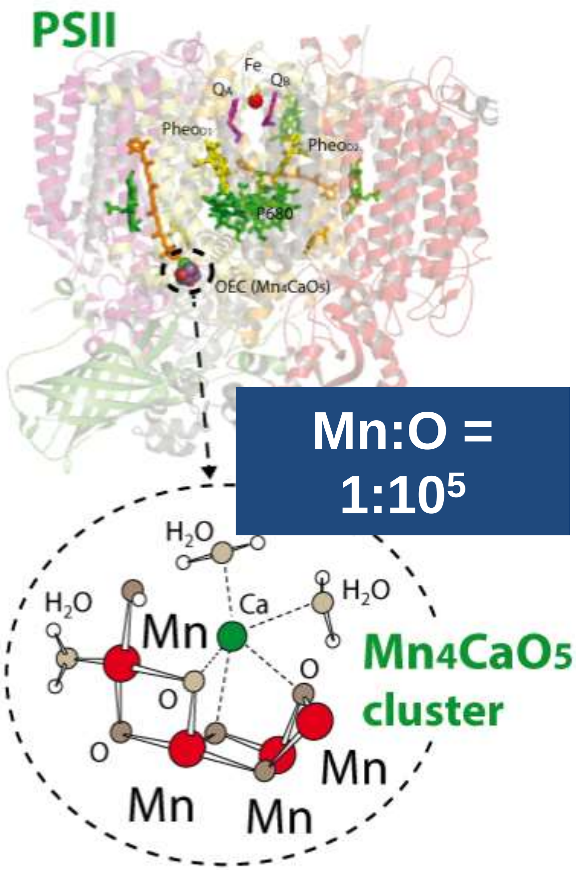


- Heterogeneous (photo)-Chemistry
- Real time observation of transients in heterogeneous catalysis
- Expand from elementary steps of surface bond breaking towards
  - In situ conditions
  - In operando conditions

Electron spectroscopy for chemical analysis (ESCA) and Photoelectron Diffraction (PED) using the BESSY-VSR time-structure.

Extreme stability	High average brilliance	Long and Short pulses

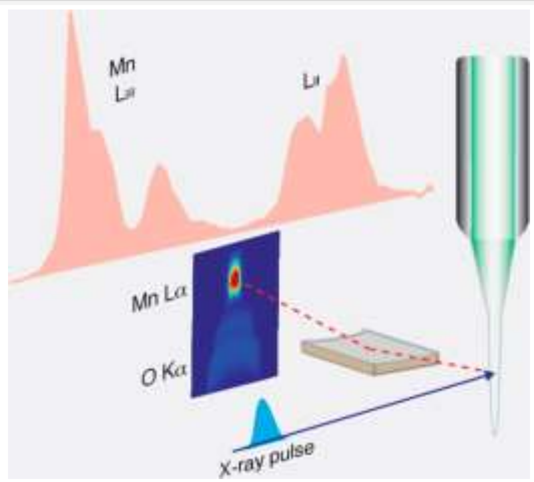
Basic Energy Science



Mn:O = 1:10^5

Spin cross-over systems in metallo enzymes with soft x-ray spectroscopy

Extreme stability	High average brilliance	Long and Short pulses

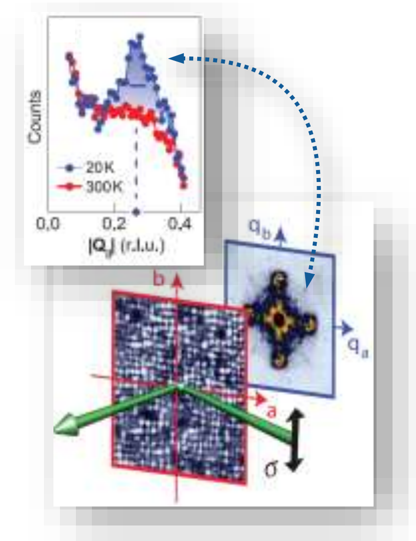


Selective Mn fluorescence detection

J. Phys. Chem. Lett. 4, 3641 (2013)

Create and investigate new states of matter

Is High-TC Superconductivity in competition to charge order ?



BESSY II: Static resonant soft X-ray diffraction requires extreme stability of BESSY II (FOFB, Top-Up)

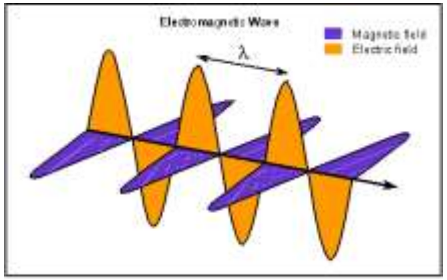
University of British Columbia, Princeton University, MPI Stuttgart
R. Comin et al., Science, 343, 390 (2014)
DOI: 10.1126/science.1242996

E. da Silva Neto et al., Science, 343, 393 (2014)
DOI: 10.1126/science.1243479

- ps-transient control AND extreme stability for
- energy and time resolved resonant soft X-ray diffraction
- Idealy possible with BESSY-VSR !

Extreme stability	High average brilliance	Long and Short pulses

Can we control and stabilize High-TC Superconductivity, If we manipulate charge order coherently with light ?



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- Partial lateral coherence
- No longitudinal coherence

– impurity model,
– perturbative treatment

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- Full lateral and longitudinal coherence

– Non-linear and multiphoton interaction. Strong field region

We take a logic step in the history of non – linear light – matter interaction: Multi Centre Correlations

NMR

- Radar Sources
- 1940's
- Excitations:
  neV Excitations

- *B-field driven.*

Non-linear optics

- LASER.
- 1980-90's
- Excitations:
  meV - eV

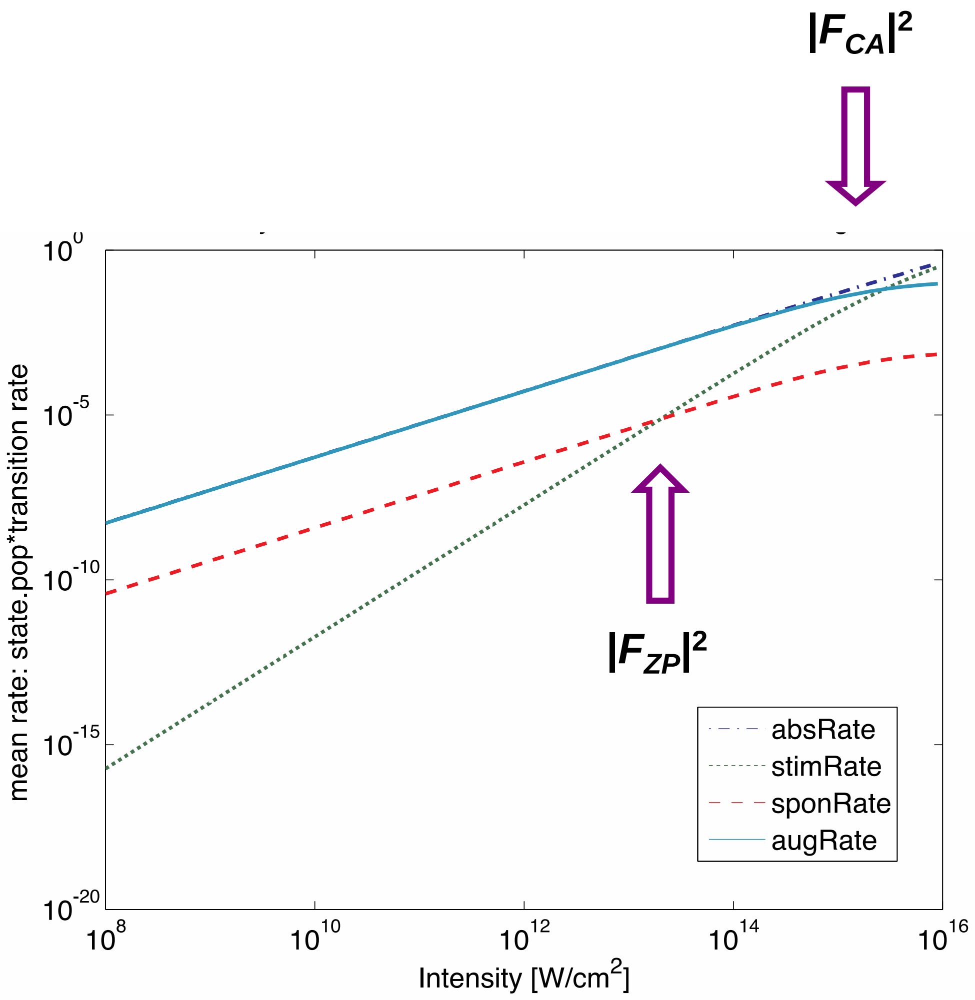
- *E-field driven.*

Non-linear X-ray optics

- Accelerator FELs
- 2004-10's
- Excitations:
  100 eV – keV

- *E-field driven.*

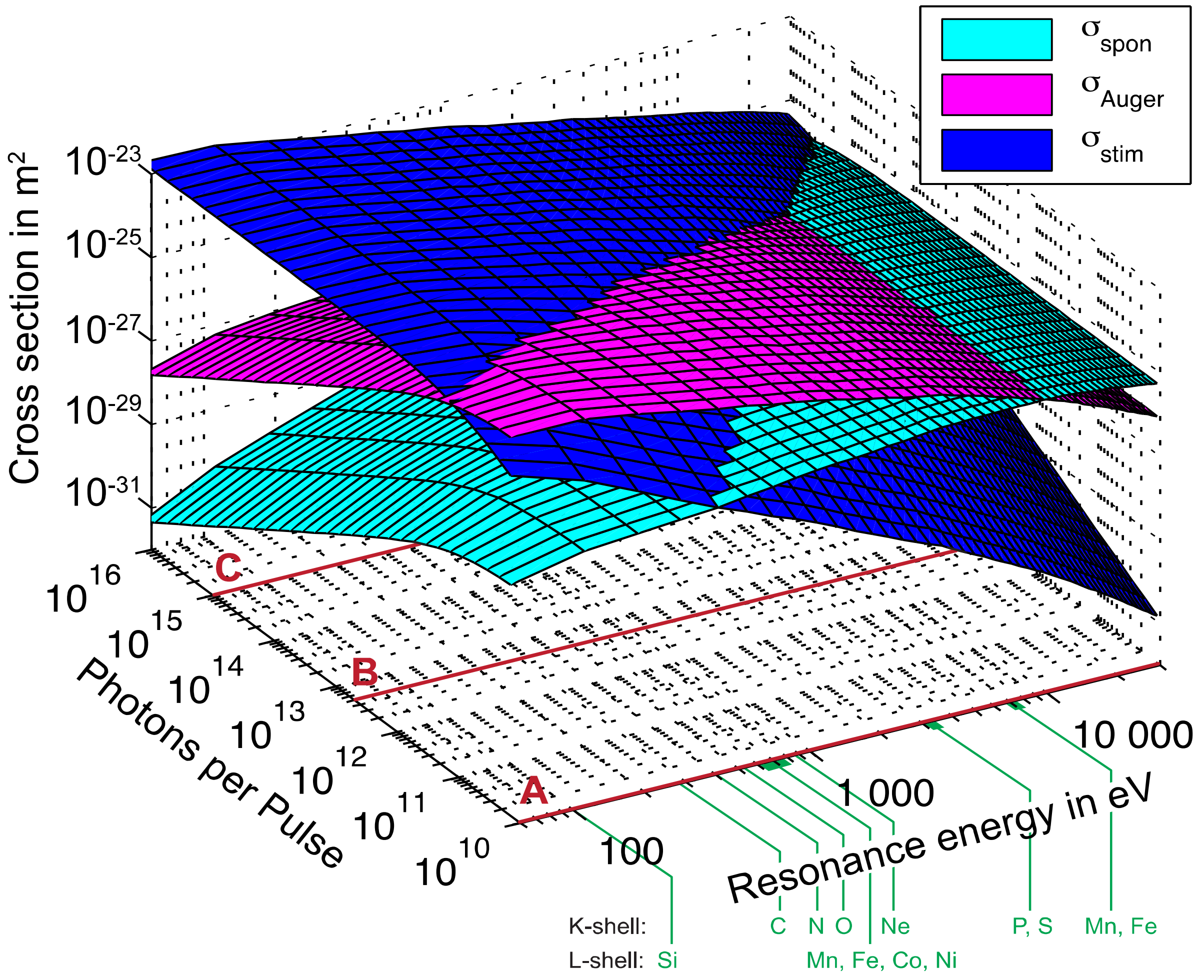
Onset of stimulated scattering & suppression of non-radiative processes



- Saturable absorption, Auger channel is suppressed at expense of radiative decay, (stimulating field matches Coulomb field in atom)

- Stimulated emission equals spontaneous (Stimulating field matches zero field strength)

Stimulated X-ray scattering sizeable with soft X-rays, less with hard X-rays



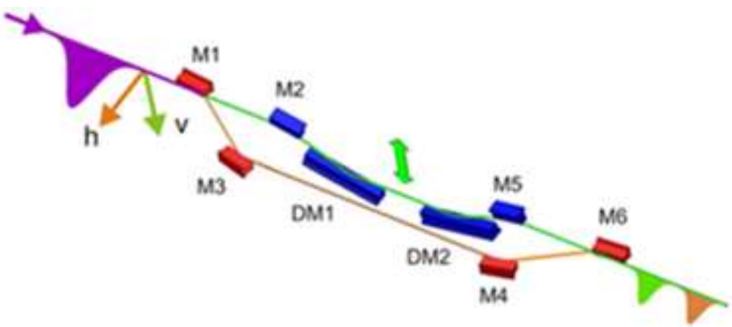
Calculated cross-sections of spontaneous emission, Auger decay and stimulated scattering 10 fs, 50x50 µm²:

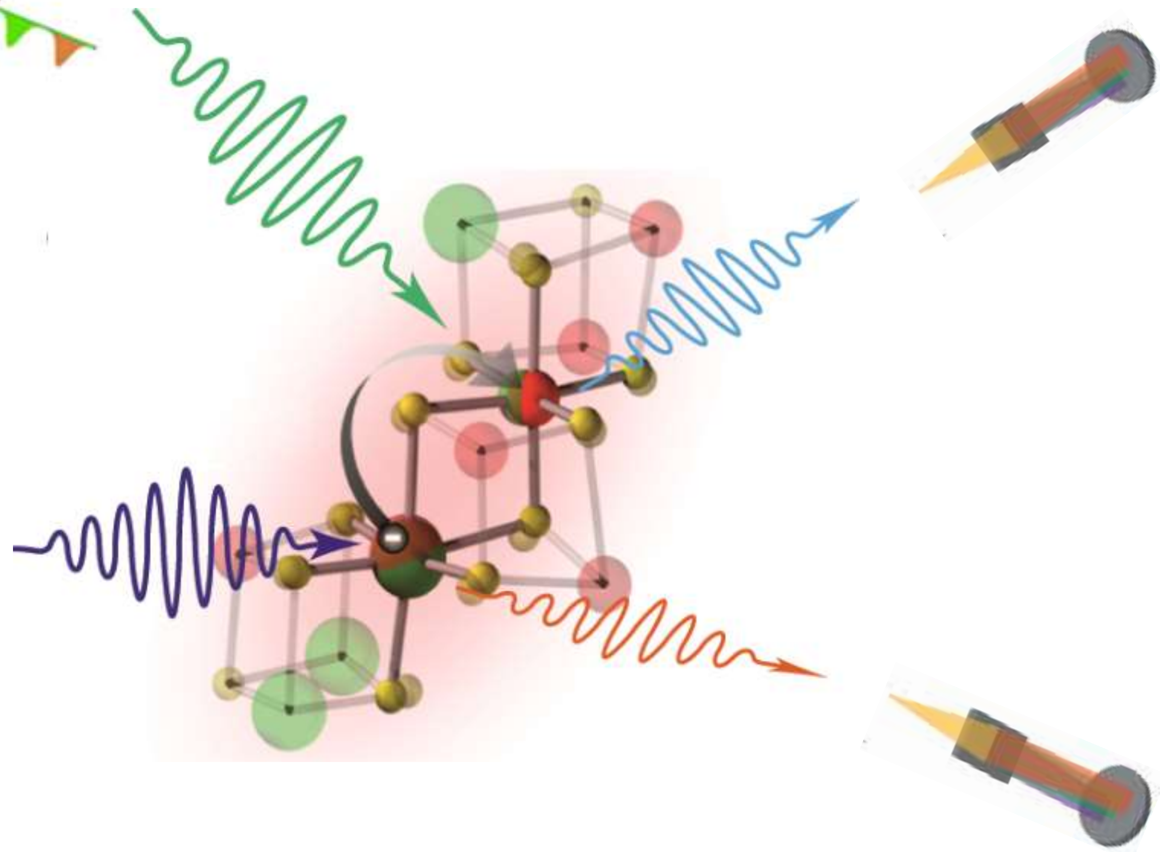
- *Cross sections are plotted as a function of the K- and L-shell resonance energy (lower x-axis).*

Implications of Stimulated Resonant X-ray Scattering for Spectroscopy, Imaging and Diffraction at Free-Electron Lasers S. Schreck, M. Beye, and A. Föhlisch, submitted to JMO, Special Issue “Short Wavelength Free Electron Lasers and their Interactions with Matter” (2015).

Rohringer et al. Nature 481 (2012), Beye et al. Nature 502 (2013), Nagler et al. Nature Physics 5 (2009)
Schreck, et al., Phys. Rev. Lett. 113, 153002 (2014)

Towards doubly resonant soft X-ray 4 wave mixing for multi-center dynamic





Shaul Mukhamel
Claudio Masciovecchio
Nina Rohringer….

Conclusion

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