Ultrafast X-ray Science at the ALS:
Resolving Atomic and Electronic Structural Dynamics

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APS Workshop on Time Domain Science using X-ray Techniques

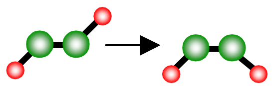
Lake Geneve, WI August 2004

Femtosecond X-ray Science at the ALS

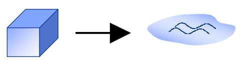
Structural Dynamics in Condensed Matter

fundamental time scale for atomic motion
vibrational period: T_{vib} ~ 100 fs

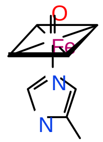
- ultrafast chemical reactions



- ultrafast phase transitions

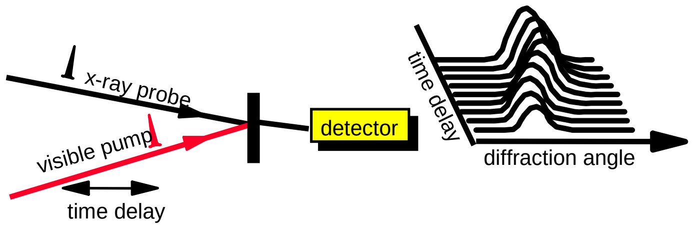


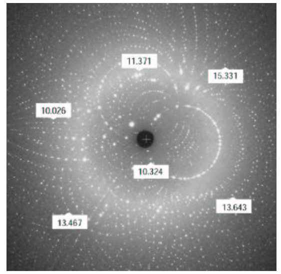
- surface dynamics
- ultrafast biological processes



Rapidly emerging field of research
Physics, Chemistry and Biology

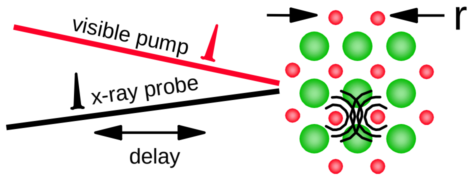
time-resolved x-ray diffraction

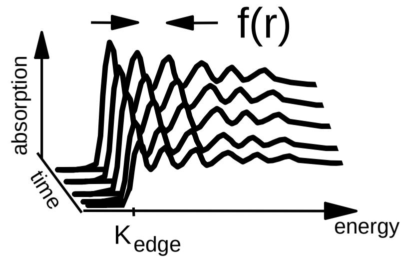




ordered crystals - phase transitions, coherent phonons

time-resolved EXAFS, NEXAS, surface EXAFS





complex/disordered materials - chemical reactions
surface dynamics
bonding geometry

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Outline

Science at time-resolved x-ray science beamline (ALS BL5.3.1)

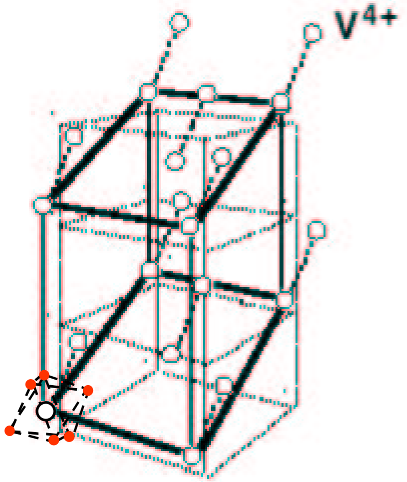
- Structural Transitions in VO_2 (Cavalleri et al.)
- Light-induced Spin-crossover transition in $Fe[tren(py)_3]^{2+}$ (Chong et al.)
- Charge Transfer in $[Ru(bpy)_3]^{2+}$ (Bressler, Chergui et al.)
- Photodissociation dynamics of solvated metal carbonyls (Khalil et al.)
- X-ray/laser ionization dynamics in atomic systems (Hertlein, Belkacem et al.)
- Bonding Properties of Liquid Carbon (Johnson, Falcone et al.)

Generation of femtosecond x-rays at the Advanced Light Source

- Technique: femtosecond manipulation of electron beam
- Femtosecond Undulator Beamline (under construction)

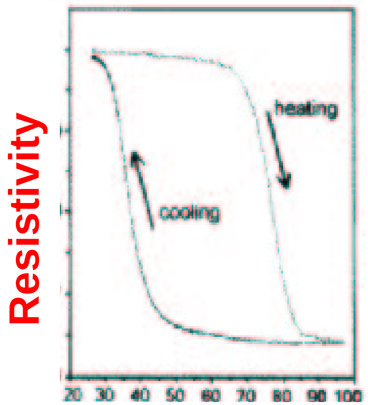
Ultrafast Structural and Electronic Transitions in VO_2

T < 340 K
Monoclinic

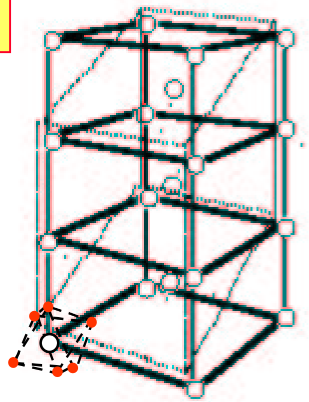


VO_2

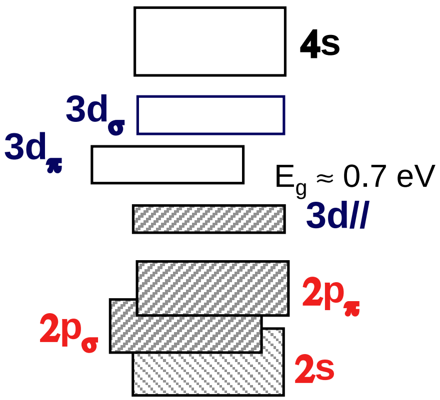
Mott-Hubbard insulator – e-e correlation ?
Band insulator – structural component ?

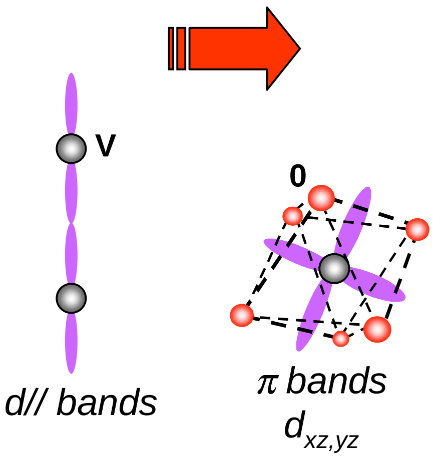


T > 340 K
Rutile

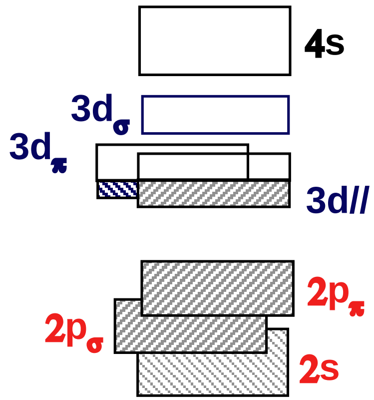


Insulator
low T





Metal
high T



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Ultrafast Structural and Electronic Transitions in VO_2

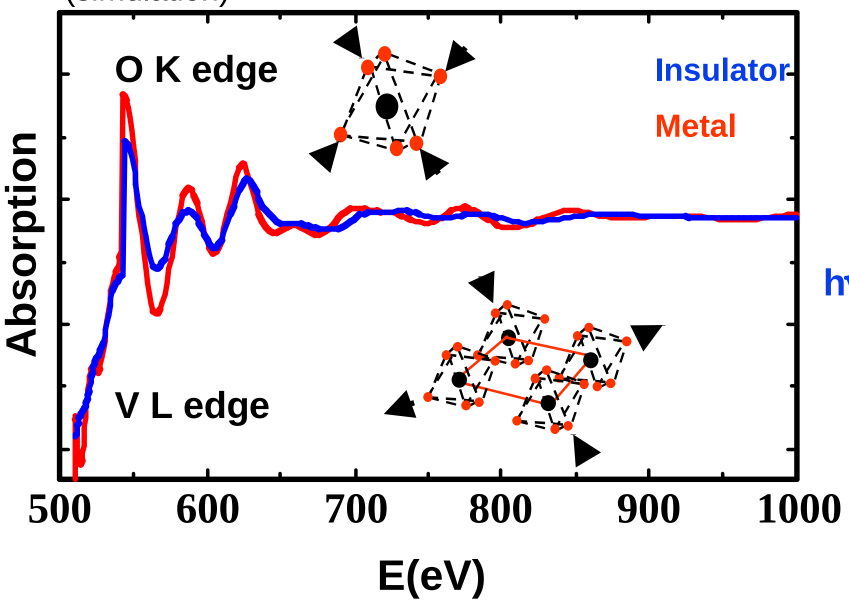
A. Cavalleri - MSD

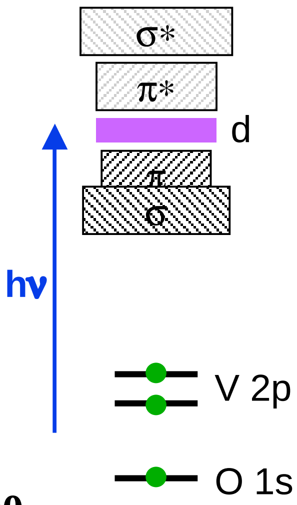
EXAFS
short-range atomic distortions

(sensitivity to V and O)

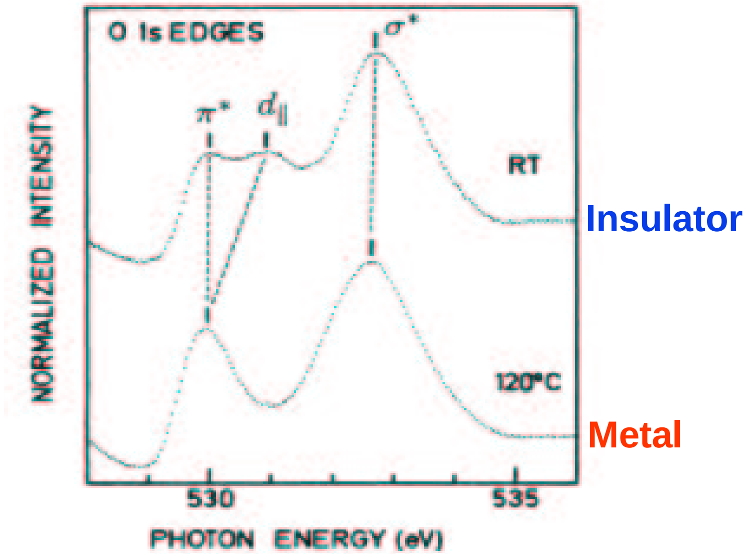
V K_{edge}~5.5 keV

(simulation)





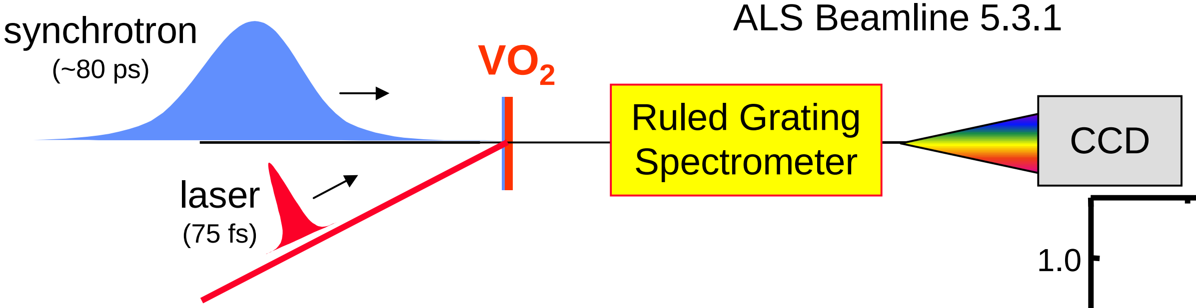
NEXAFS
electronic transition

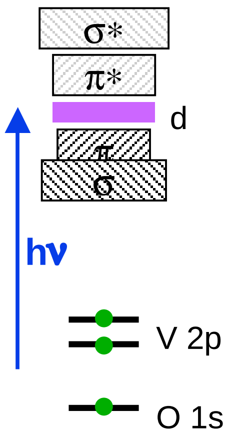


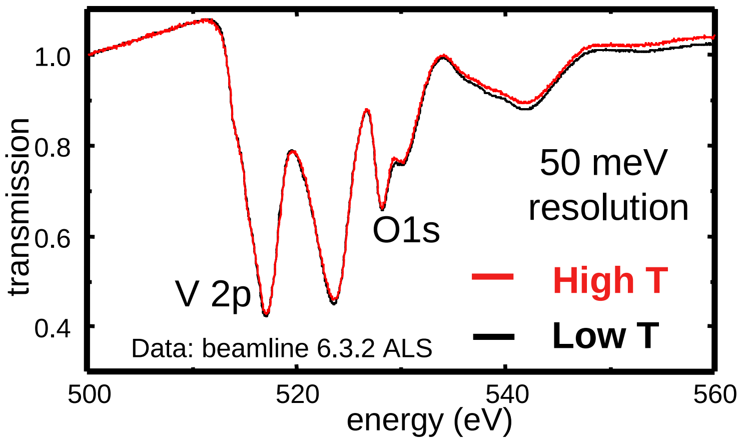
Abbate et al., *Phys. Rev. B*, **43**, (1991).

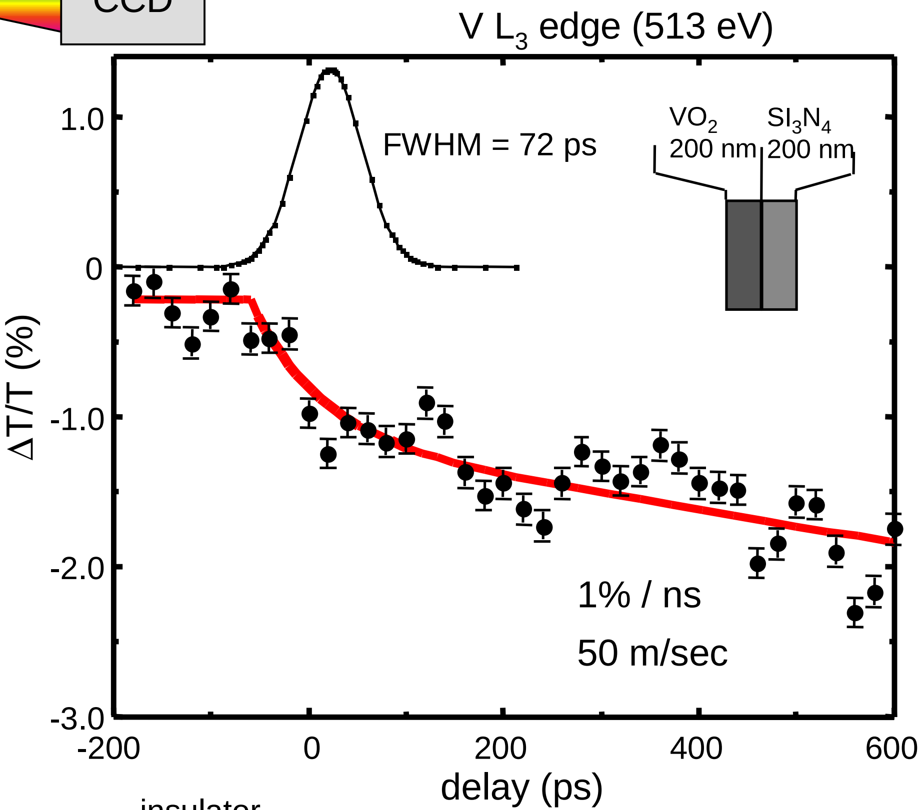
Time-resolved NEXAFS Measurements in VO_2

ALS Beamline 5.3.1







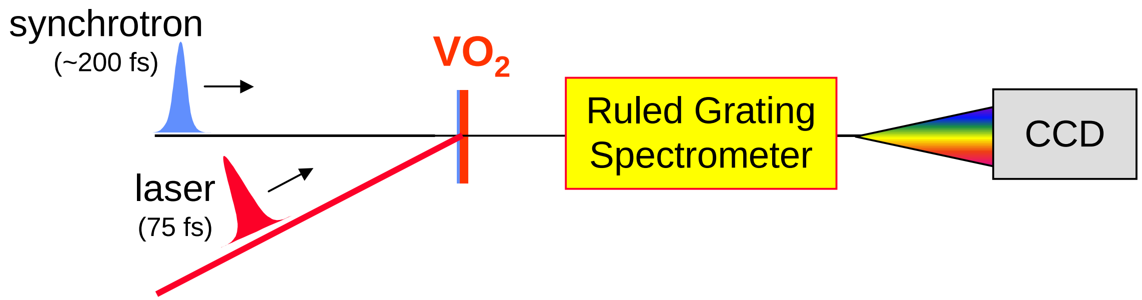


Signal on picosecond time scale dominated by growth of metallic phase

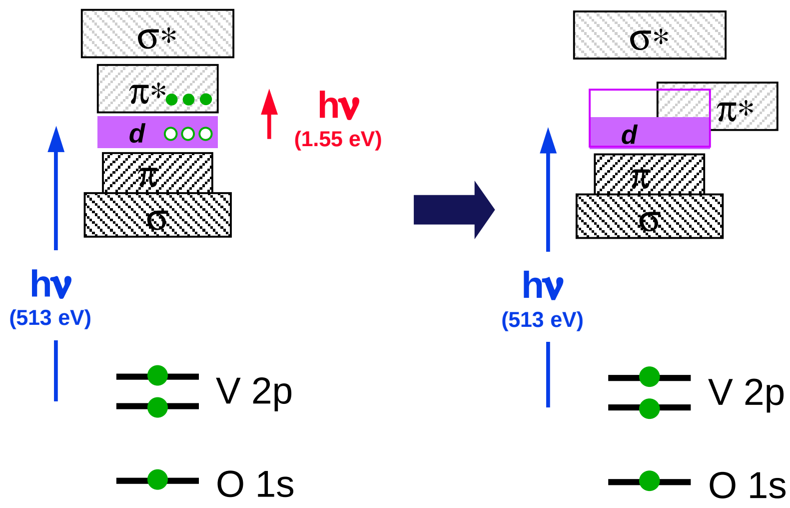
Cavalleri et al., Physical Review B 69, 153106 (2004)

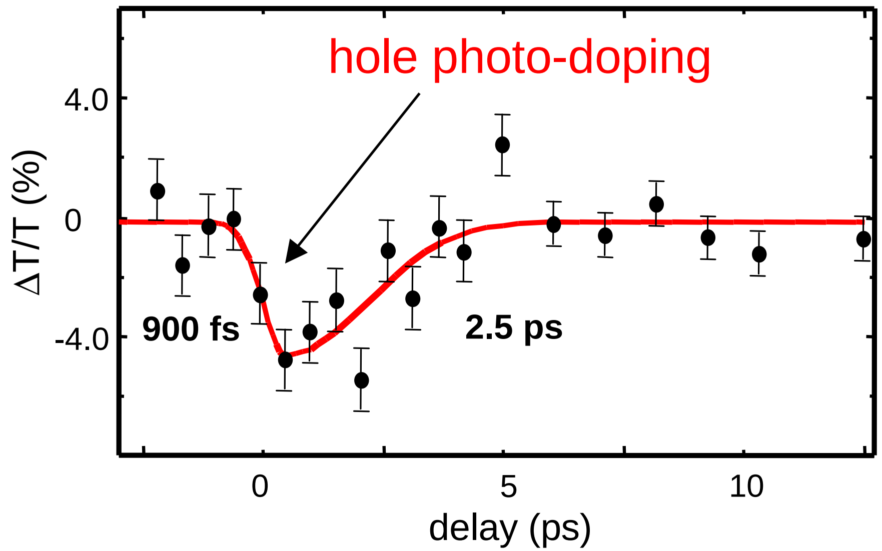
Femtosecond NEXAFS Measurements of I-M Transition in VO_2

ALS Beamline 5.3.1



Hole Photo-doping **Metal**





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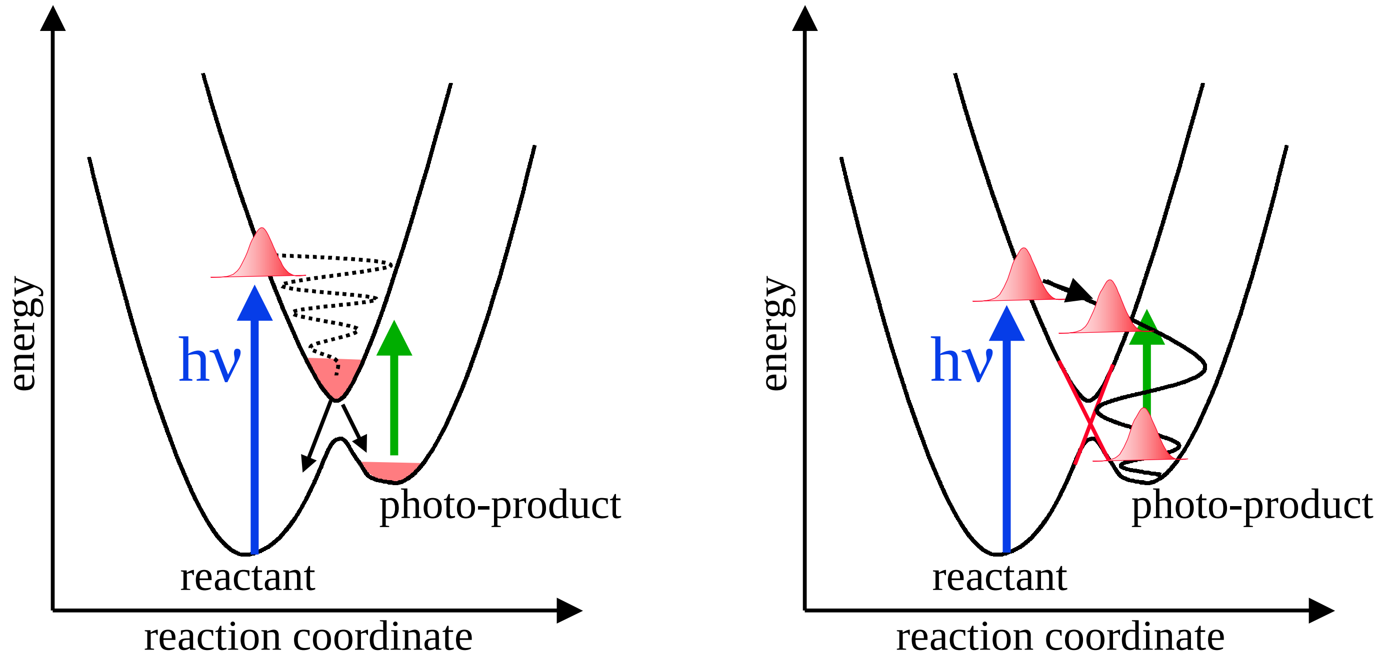
Ultrafast Chemical Reactions

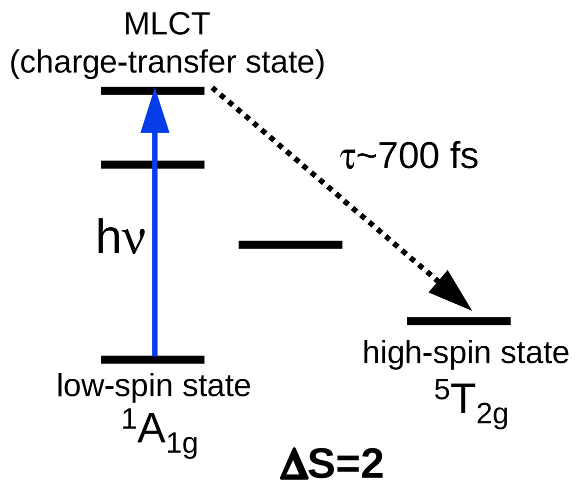
Atomic and Electronic Structural Dynamics of the Transition State



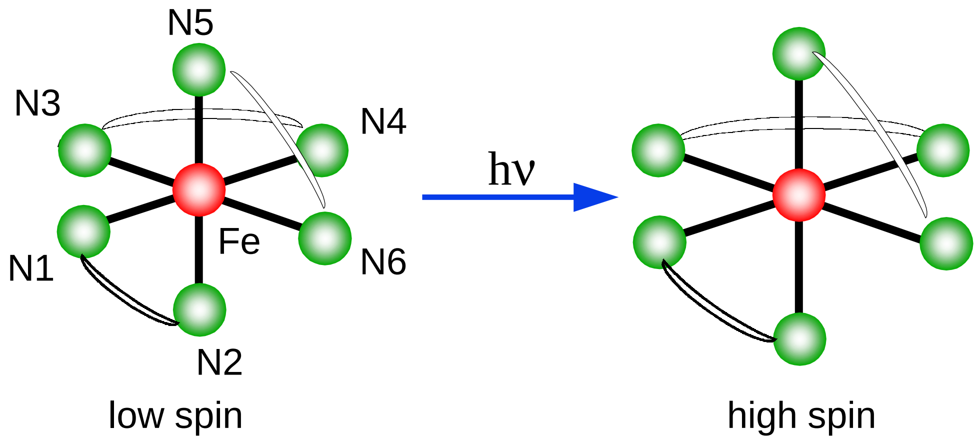
$\tau_{IVR} < \tau_{IC}$ $\tau_{IC} < \tau_{IVR}$

- intramolecular vibrational relaxation (IVR)
- internal conversion - IC

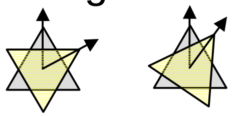
Fe^{II} Spin-Crossover Molecules



$Fe[tren(py)_3]^{2+}$



- ~10-15% increase in metal-ligand bond distances
- trigonal cage distortion?



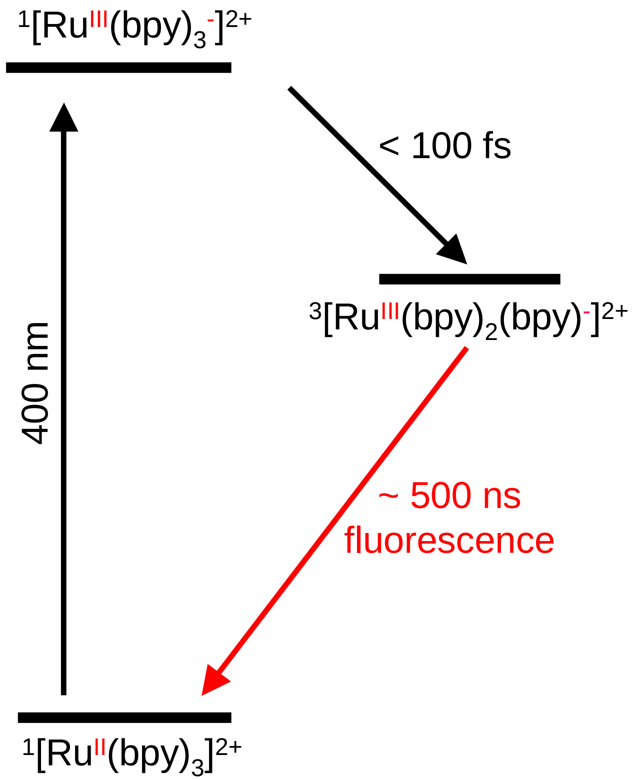
Motivation:

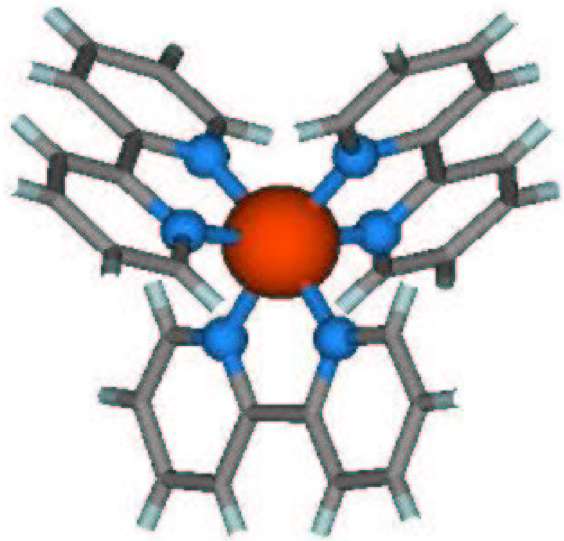
- relationship between structure, electronic, and magnetic properties

  Do the structural distortions facilitate the spin-crossover reaction?
- electron transfer mechanistic role in biochemical processes (cytochrome P450)
- magnetic and optical storage material

Photochemical Cycle of aqueous $[Ru(bpy)_3]^{2+}$

C. Bressler, M. Chergui et al. University of Lausanne

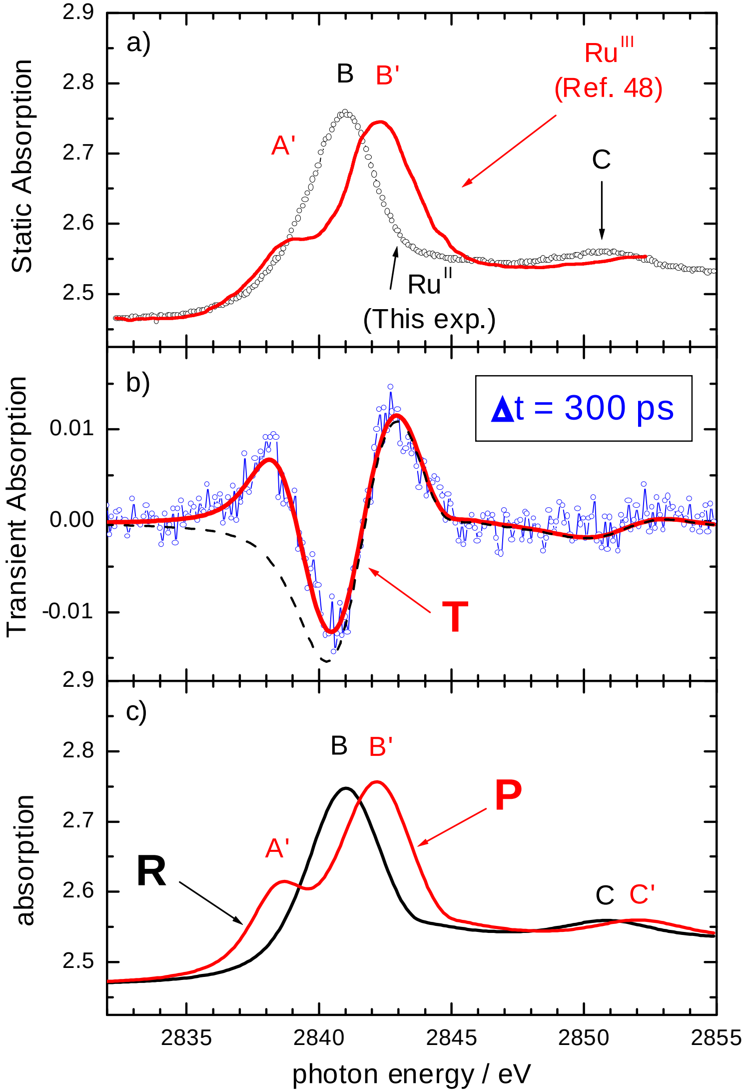


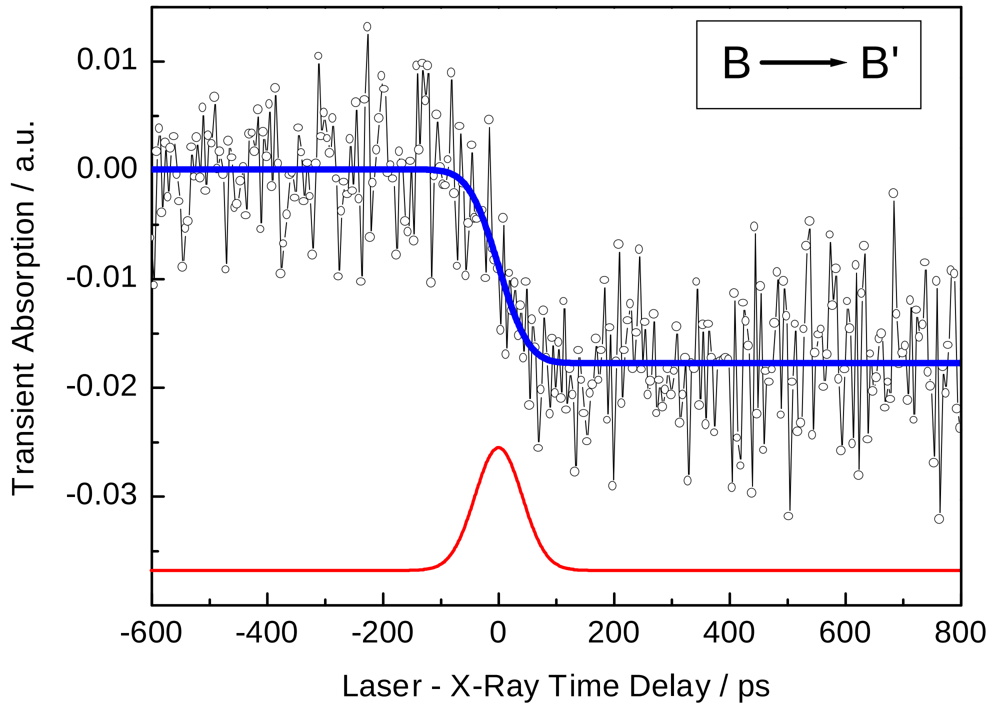


D_3 symmetry C_2 symmetry

Time-Resolved XAS of $[Ru(bpy)_3]^{2+}$

M. Saes, C. Bressler, R. Abela et al., *Phys. Rev. Lett.*, **90**, 047403, (2003)





X-rays for Ultrafast Structural Dynamics

Characteristics for Ideal Source

(1) temporal resolution <100 fs
- pulse duration
- synchronization to laser trigger

(2) high average flux $>10^8$ photons/sec/0.1% BW
- high average brightness <1 mrad source divergence

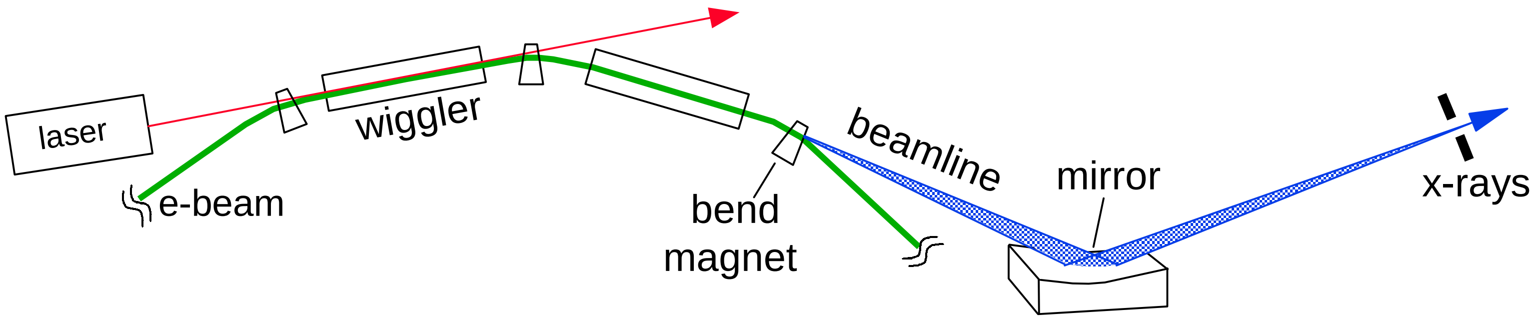
(3) tunable 0.3 keV - 10 keV
- broadband - spectroscopy
- soft x-rays (electronic structure)
- hard x-rays (atomic structure)

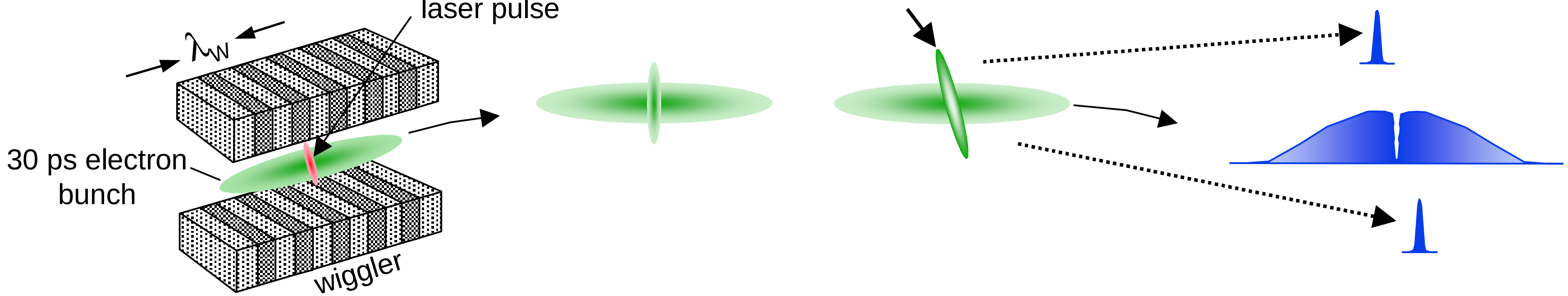
(4) rep. rate: 100 Hz - 10 kHz
- signal averaging, sample damage, sample replacement

stability – pulse amplitude, alignment

variable polarization – x-ray dichroism (magnetic materials, chiral molecules)

Generation of Femtosecond X-rays from the ALS





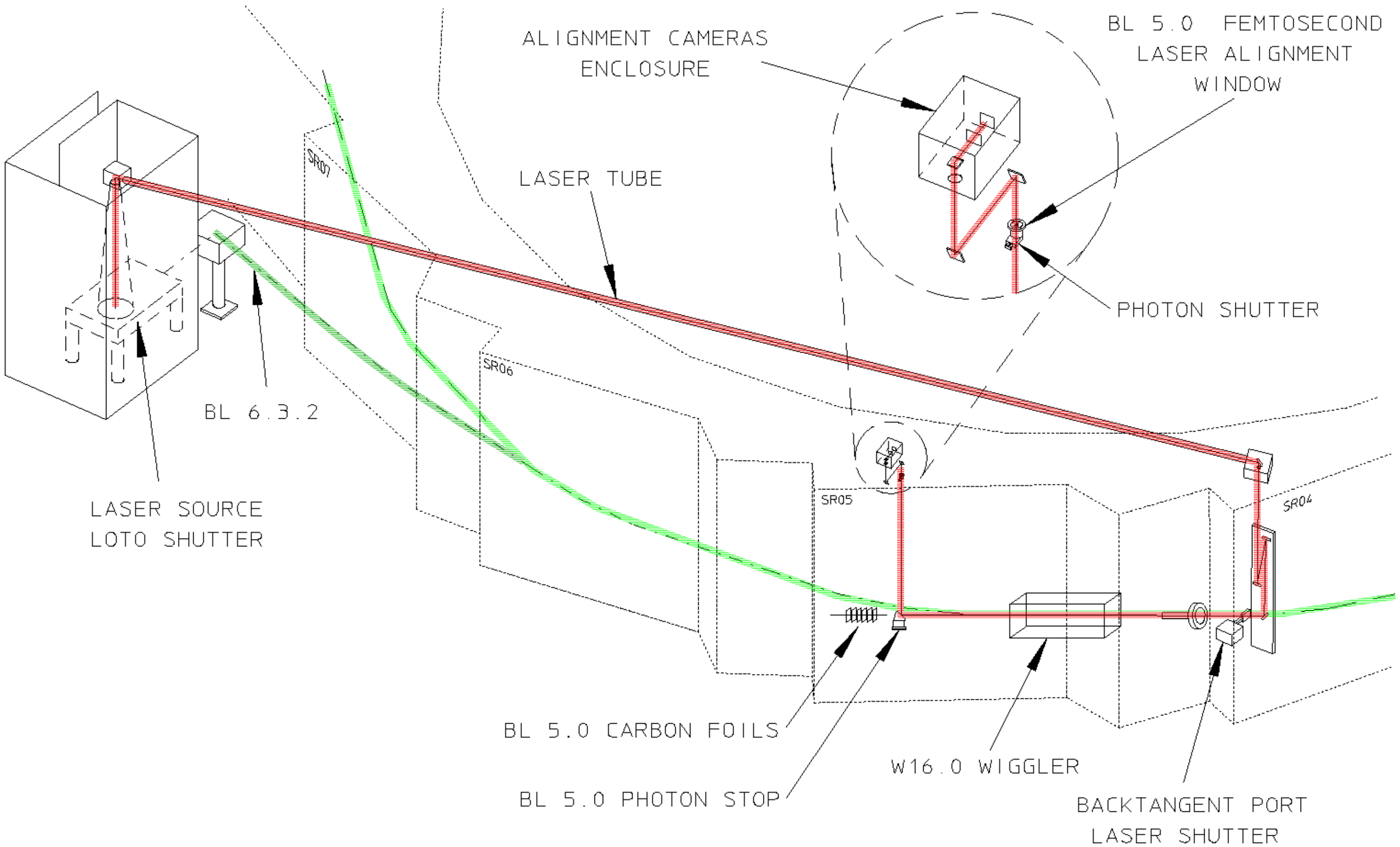
electron-photon interaction in wiggler

spatial separation dispersive bend

bend magnet beamline

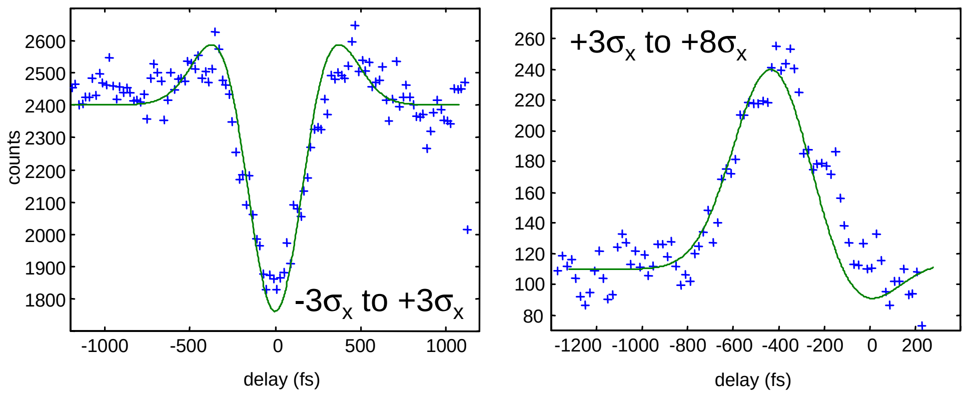
Zholents and Zolotorev, *Phys. Rev. Lett.*, **76**, 916,1996.

Synchrotron Beam Slicing - Layout

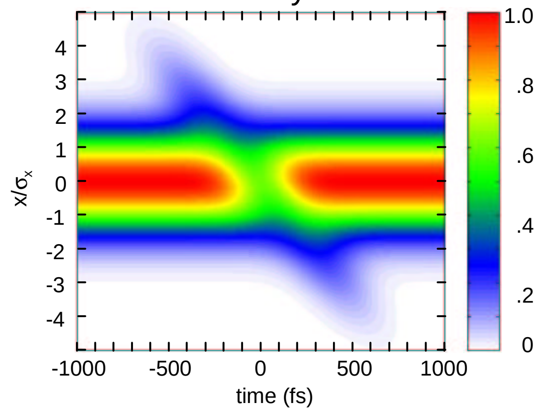


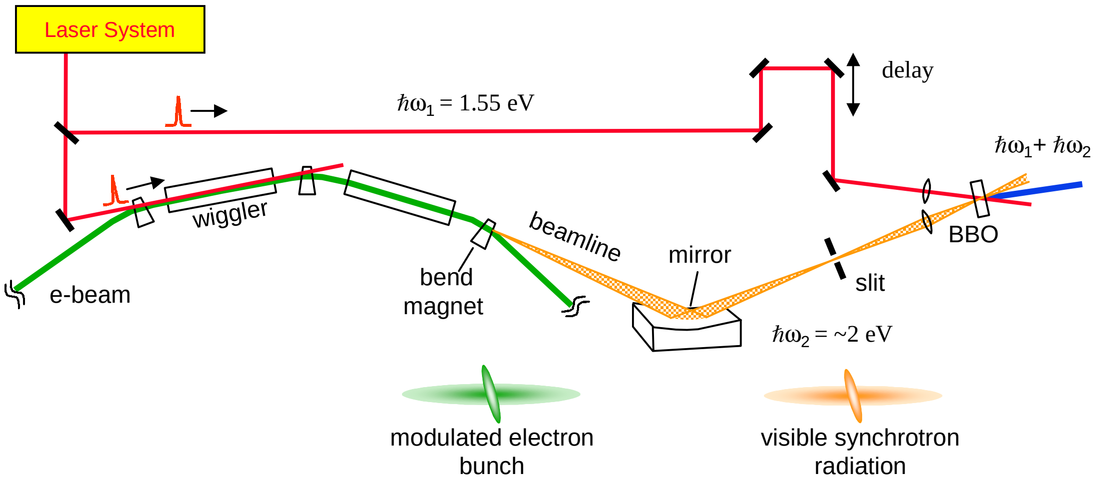
Femtosecond Pulses of Synchrotron Radiation

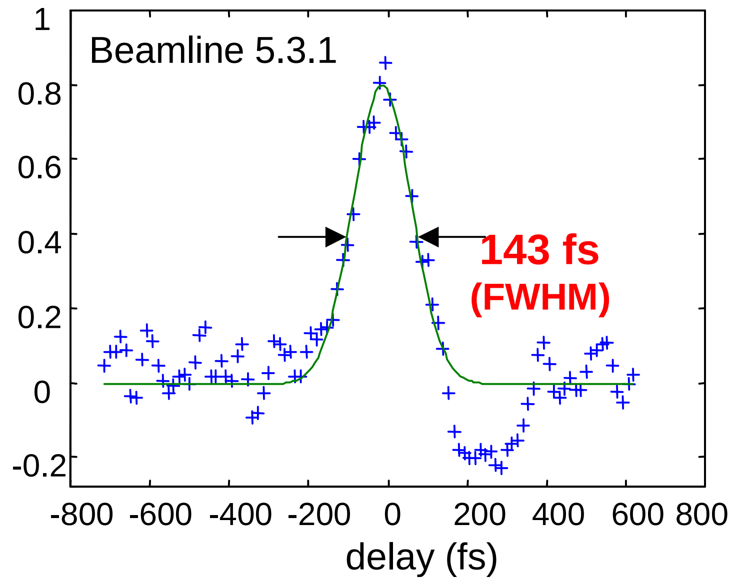
Demonstration Measurements – Beamline 6.3.2



Calculated
Electron Density Distribution







Schoenlein et al., *Science*, **287**, 2237 (2000)

Femtosecond X-ray Facility – Scaling the X-ray Flux

- phase factor $\eta_1 = 0.1$ (fraction of electrons in optimum phase)
- pulse duration $\eta_2 = \tau_{laser} / \tau_{synchrotron} = 10^{-3}$ ($\tau_{x\text{-}ray} \approx 170$ fs)
  (70 fs) (70 ps)
- repetition rate $\eta_3 = f_{laser} / f_{synchrotron} = 2\text{x}10^{-6}$
  (1 kHz) (500 MHz)

  $f_{laser} / f_{synchrotron}$
  (40 kHz) (500 MHz)

  $$f_{limit} \approx 3 \times \frac{\text{number of bunches}}{\tau_{damping}} = 150 \text{ kHz}$$

Average Femtosecond X-ray Flux ~ Average Femtosecond Laser Power

Bend Magnet

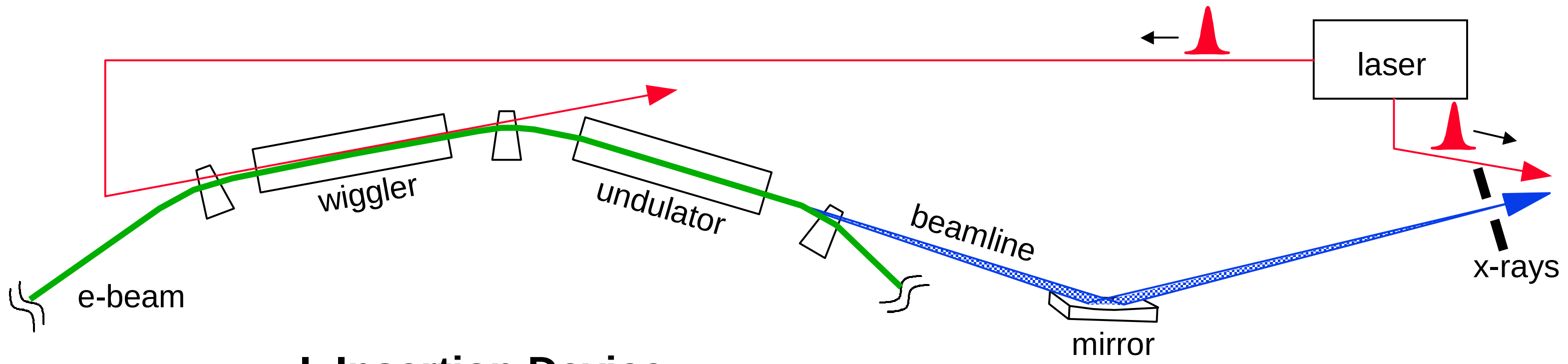
- flux ~10^{13} ph/sec/0.1% BW
- brightness ~10^{16} ph/sec/0.1% BW

Undulator

- flux ~10^{15} ph/sec/0.1% BW
- brightness ~10^{19} ph/sec/0.1% BW

Femtosecond Undulator Beamline – Overview

New beamline(s) – funded by DOE Basic Energy Sciences
Operation with femtosecond x-rays – early 2005



I. Insertion Device

- highest possible flux and brightness 0.2-10 keV
- small-gap undulator/wiggler (1.5 T, 50 x 3cm period)

  x10^2 increase in flux, x10^3 increase in brightness

II. Beamlines for Femtosecond X-ray Science

- isolation of femtosecond x-ray, 0.2-2 keV, 2-10 keV

  sector 6 - proximity to existing wiggler 200 fs x-rays

III. Laser: average power/repetition rate

- 60 W (1.5 mJ per pulse, 40 kHz)

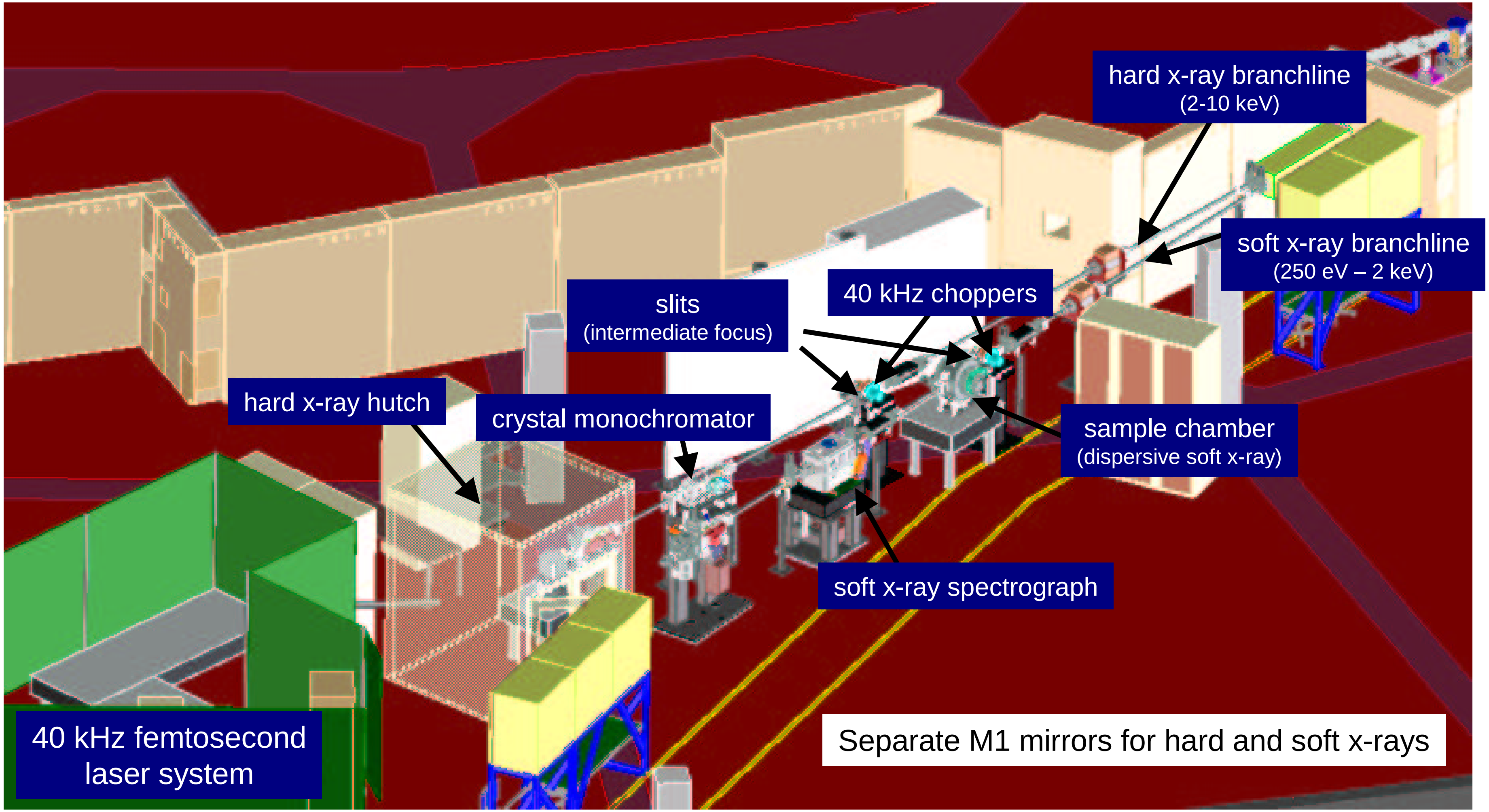
  x10 increase in flux

IV. Storage Ring Modifications

- local vertical dispersion bump – sector 6 and/or 5

Femtosecond Undulator Beamline 6.0 Layout

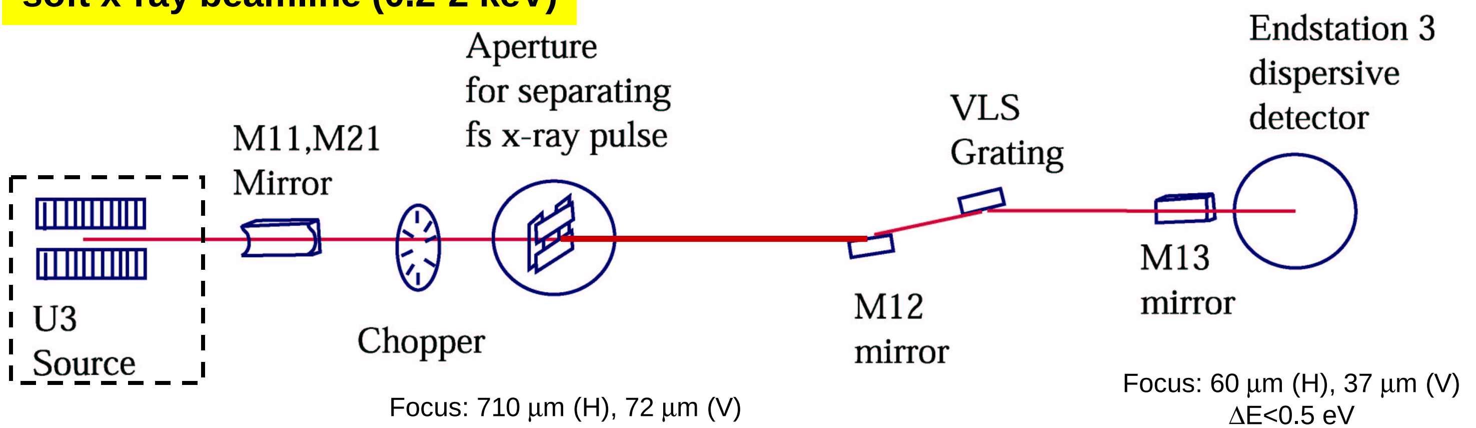
P. Heimann, H. Padmore, R. Duarte, D. Cambie et al.



ALS Femtosecond Undulator Beamlines

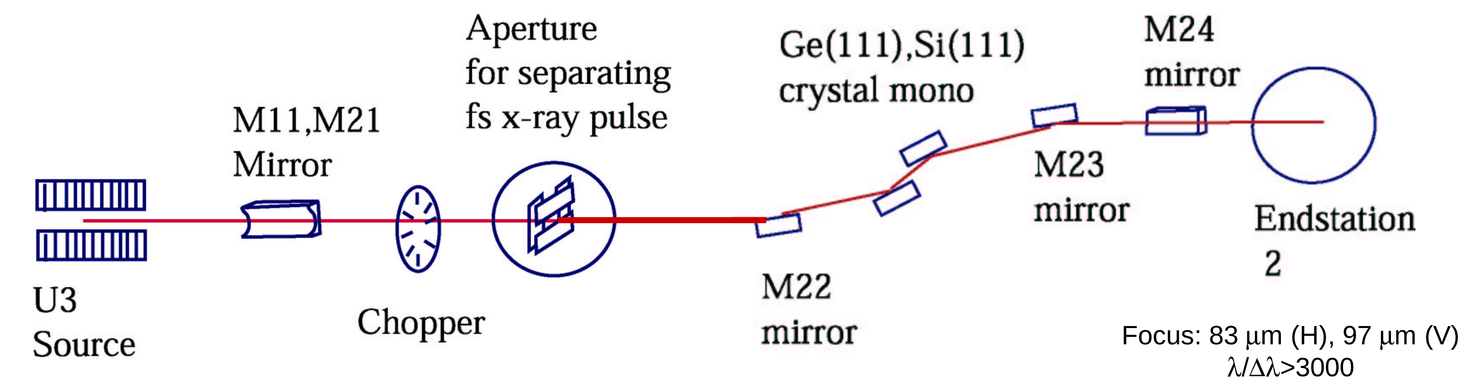
P. Heimann, H. Padmore, R. Duarte, D. Cambie et al.

soft x-ray beamline (0.2-2 keV)



commission April 2005

hard x-ray beamline (2-10 keV)

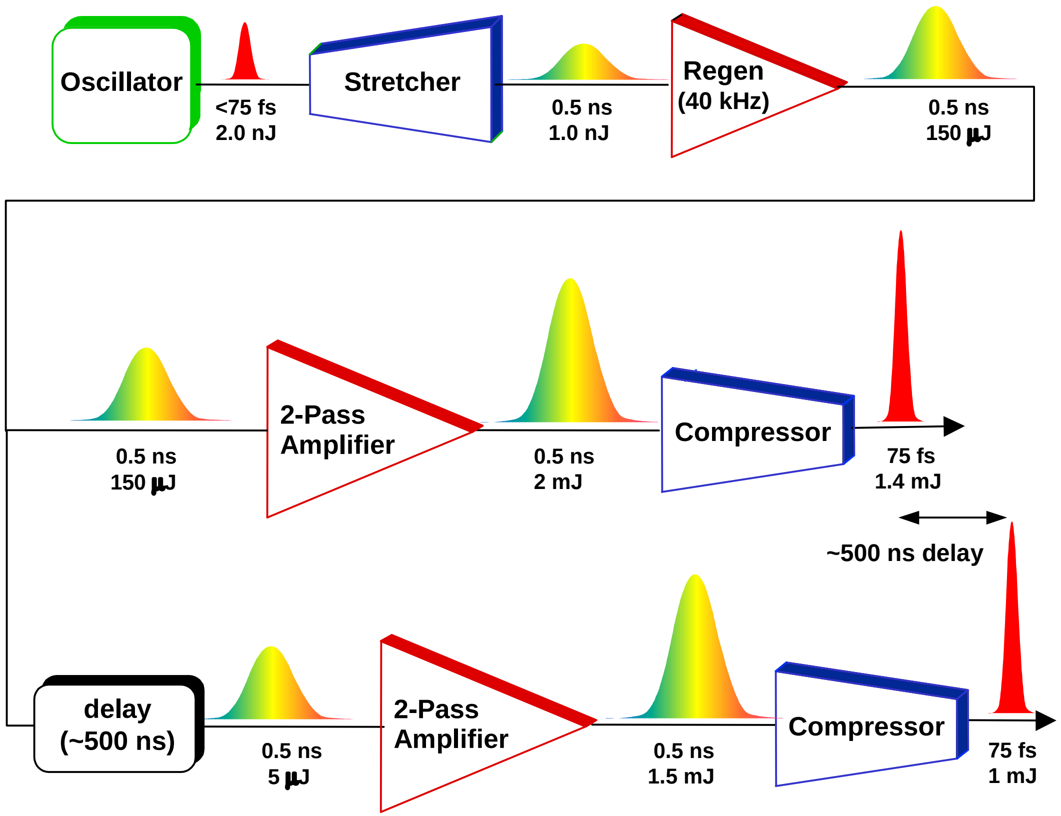


commission Sept. 2005

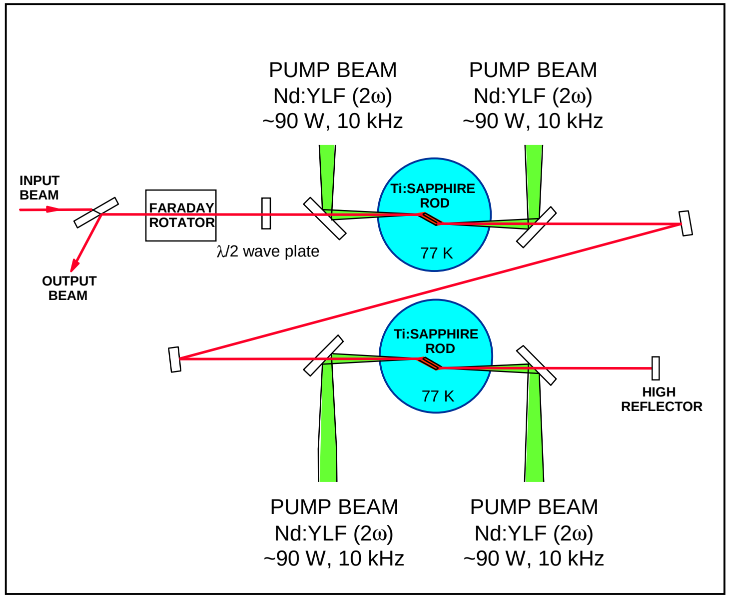
Femtosecond Laser System

Electron beam interaction requirements:
~1.5 mJ pulse energy, 50 fs FWHM, at ~800 nm
40 kHz repetition rate, 60 W average power
diffraction limited focusing, beam parameter: $M^2 \leq 1.1$

Excitation pump pulses for time-resolved experiments:
~1 mJ pulse energy at 800 nm (OPA)
50 fs pulse duration, 40 kHz repetition rate
~500 ns relative delay



cryogenic power amplifier



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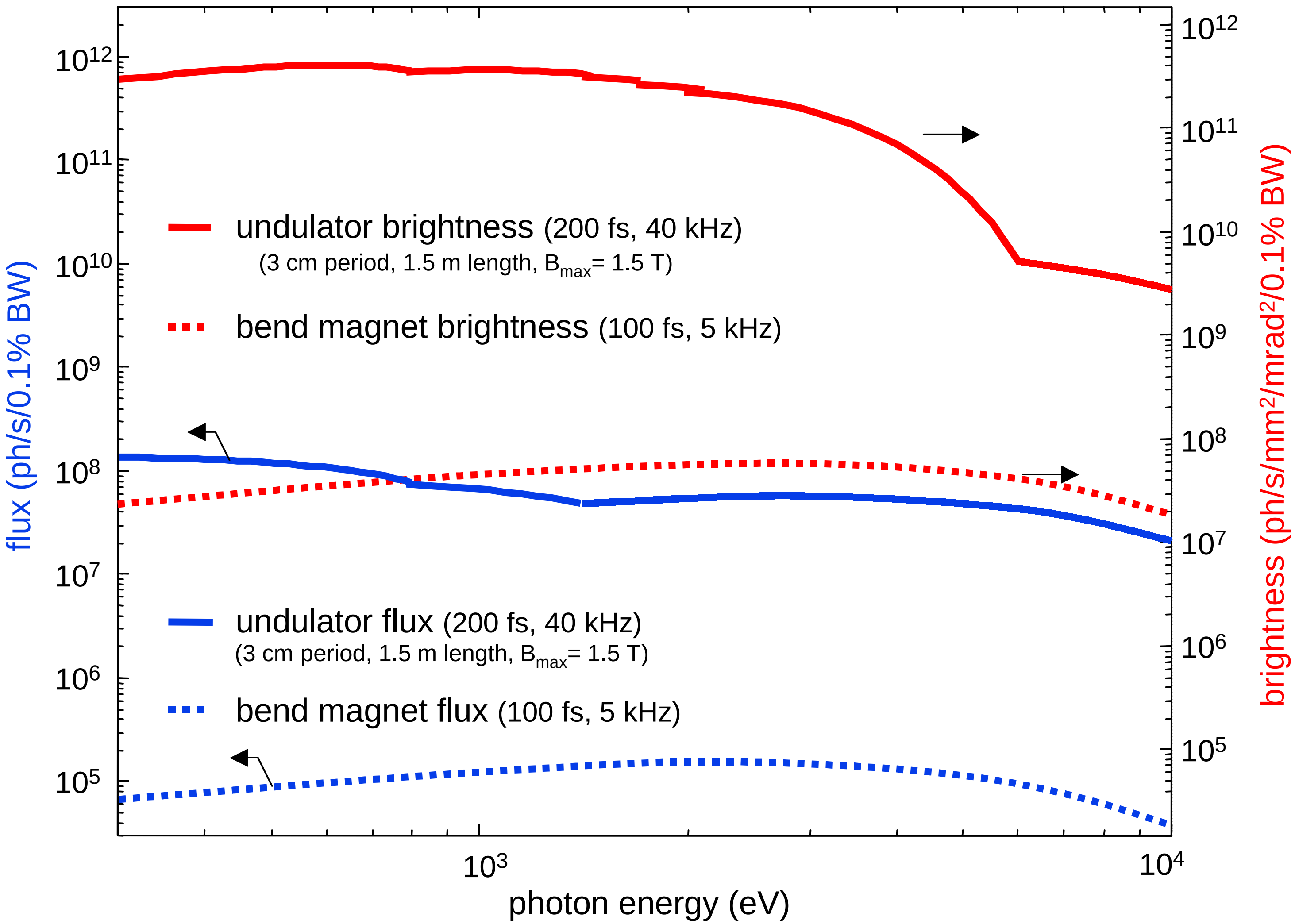
Femtosecond X-ray Flux and Brightness



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Summary

Time-resolved Measurements of Structural Dynamics in Condensed Matter

fundamental time scale for atomic motion - vibrational period ~100 fs

Solid-State Physics

- complex/correlated materials
- phase transitions (solid/solid, order/disorder)
- magnetic materials

Chemistry

- structural dynamics of the transition state
- solvent/solute interactions (solvent structure)

AMO Physics, Biology

Time-resolved XAS experiments at ALS beamline 5.3.1

- Insulator-Metal Transition in VO_2
- Light-induced Spin-crossover transition in $Fe[tren(py)_3]^{2+}$
- X-ray/laser ionization dynamics in atomic systems (Hertlein, Belkacem et al.)

Generation of femtosecond x-rays at the Advanced Light Source

- Technique: femtosecond manipulation of electron beam
- Femtosecond Undulator Beamline (under construction)

Collaborators

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