Outline

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

- Time-resolved EXAFS - spin-crossover transition in $Fe[tren(py)_3]^{2+}$
- Ultrafast XANES – insulator/metal transitions in VO_2
- Charge Transfer in $[Ru(bpy)_3]^{2+}$
- Bonding Properties of Liquid Silicon and Liquid Carbon
- X-ray/laser ionization dynamics in atomic systems
- X-ray/laser mixing

Generation of femtosecond x-rays at the Advanced Light Source

- Technique: femtosecond manipulation of electron beam
- New Femtosecond Undulator Beamline (in commissioning)

Pseudo Single Bunch Operation of the ALS

- Scientific/experimental opportunities
- Technical considerations

Fundamental Scientific Challenge in Condensed Matter:

Understanding the interplay between atomic and electronic structure

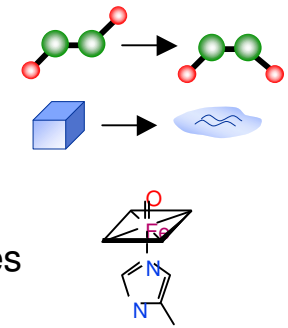
- beyond single-electron band structure model – correlated systems (charge, spin, orbit, lattice)
- beyond simple adiabatic potential energy surfaces

Fundamental Time Scales in Condensed Matter

Atomic Structural Dynamics

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

- ultrafast chemical reactions
- ultrafast phase transitions
- surface dynamics
- ultrafast biological processes



Electronic Structural Dynamics

fundamental time scales for electron dynamics
electron-phonon interaction times ~ 1 ps
e-e scattering times ~10 fs
correlation time ~100 attoseconds (a/V_{Fermi})

- charge transfer
- electronic phase transitions
- correlated electron systems
  - charge/orbital ordering
  - CMR
  - high T_c superconductivity

Ultrafast X-ray Science
Rapidly emerging field of research - Physics, Chemistry and Biology

Femtosecond X-ray Science

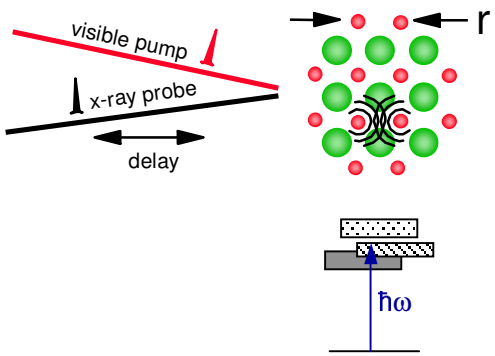
time-resolved x-ray spectroscopy

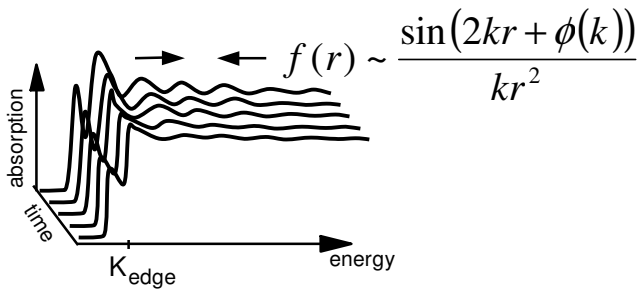
EXAFS – local atomic structure and coordination
(extended x-ray absorption fine structure)

NEXAFS – local electronic structure, bonding geometry, magnetization/dichroism
(near-edge x-ray absorption fine structure)

element specific
molecular systems and reactions
complex/disordered materials

surface **EXAFS, μEXAFS ….**

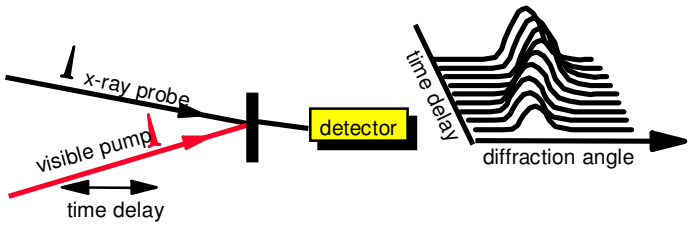


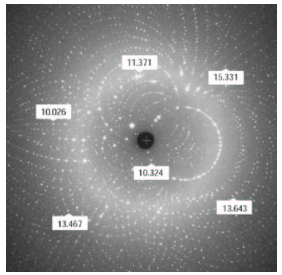


$$f(r) \sim \frac{\sin(2kr + \phi(k))}{kr^2}$$

time-resolved x-ray diffraction

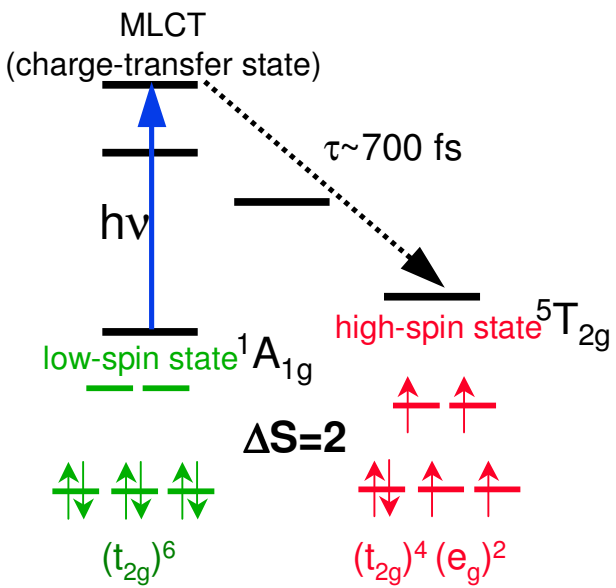
atomic structure in systems with long-range order/periodicity
phase transitions, coherent phonons

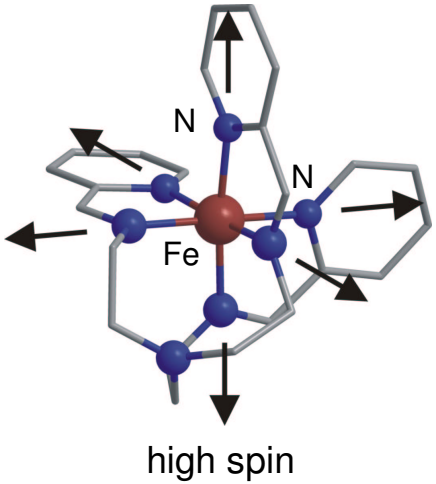


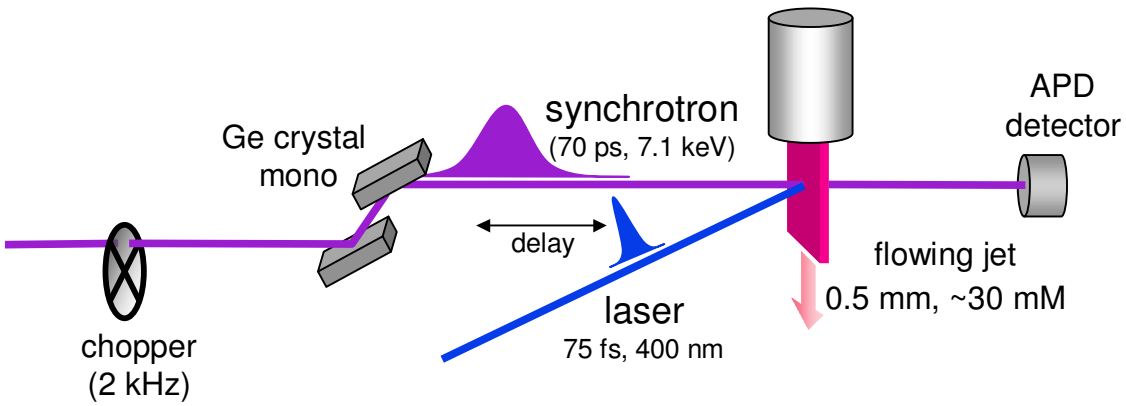


X-ray Absorption Spectra - Fe^{II} in Acetonitrile

Time-resolved Spectra (ALS BL 5.3.1)

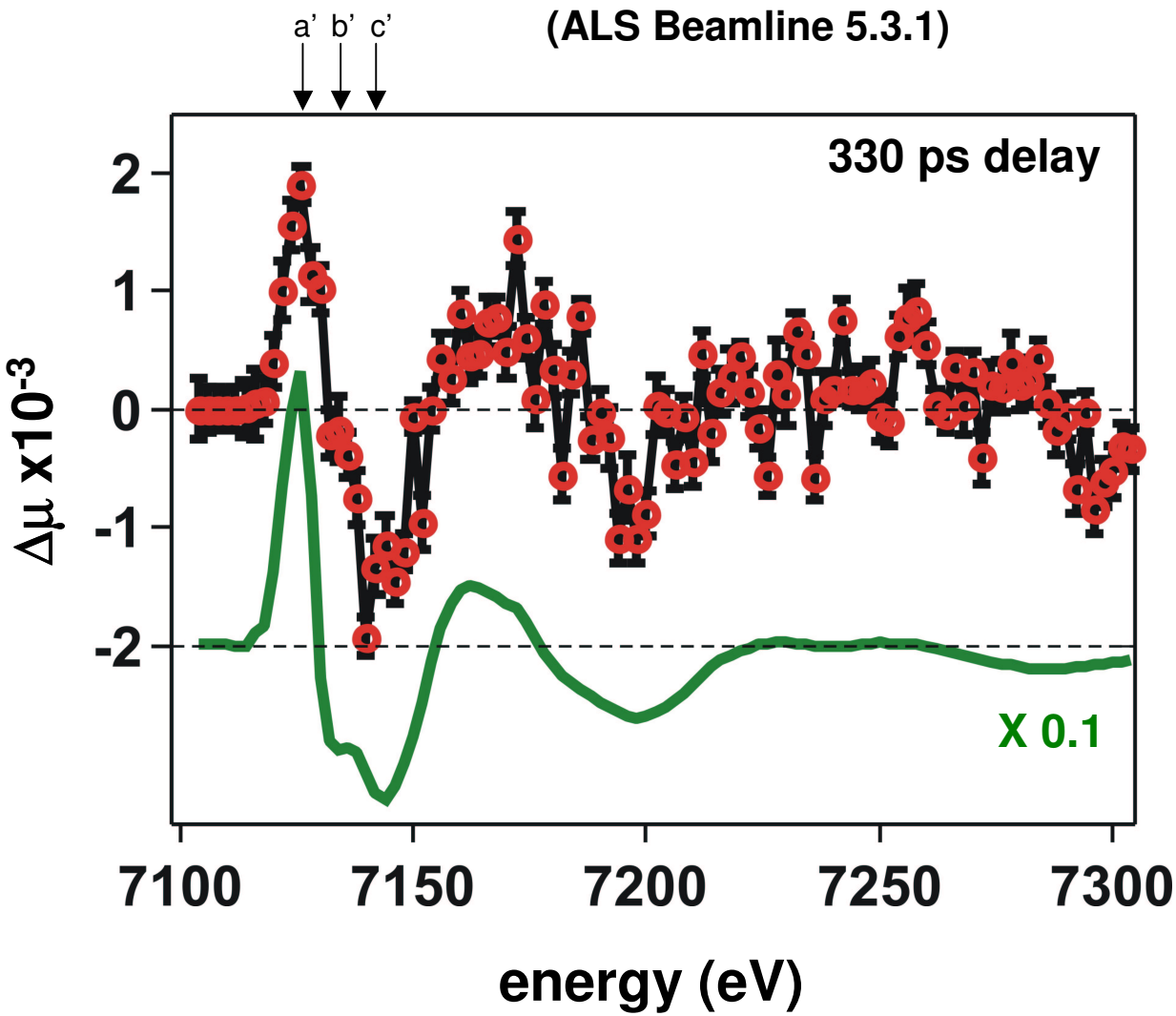


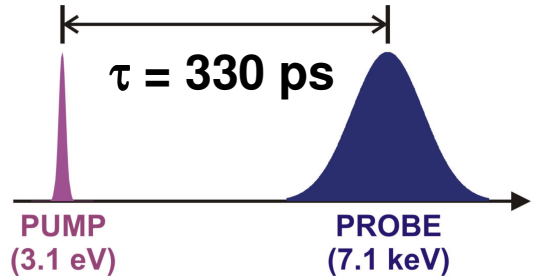


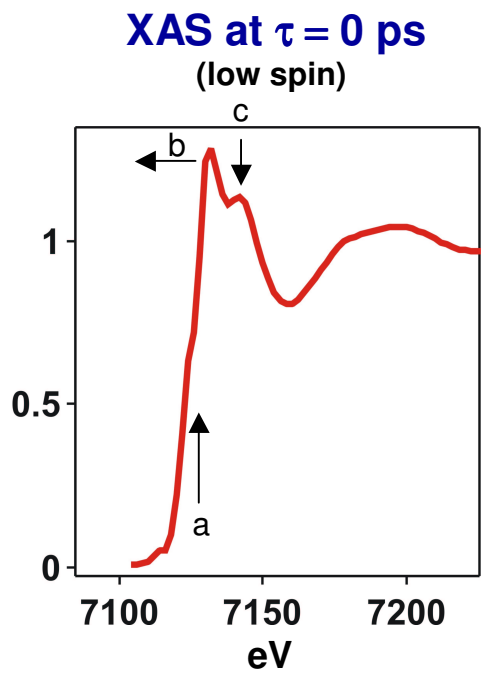


Fe^{II} Time-resolved XAS

(ALS Beamline 5.3.1)



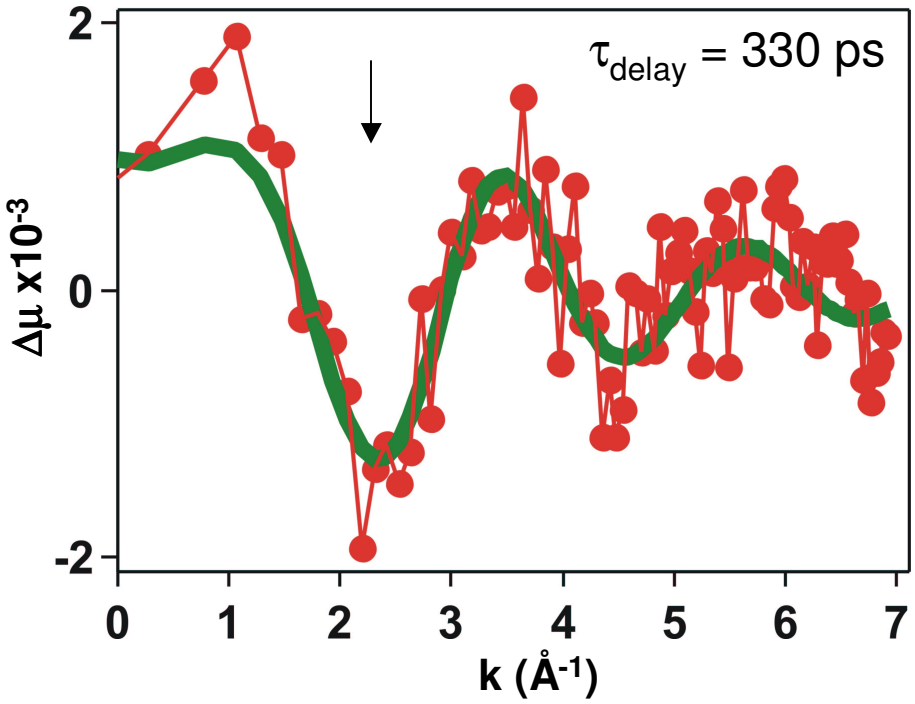




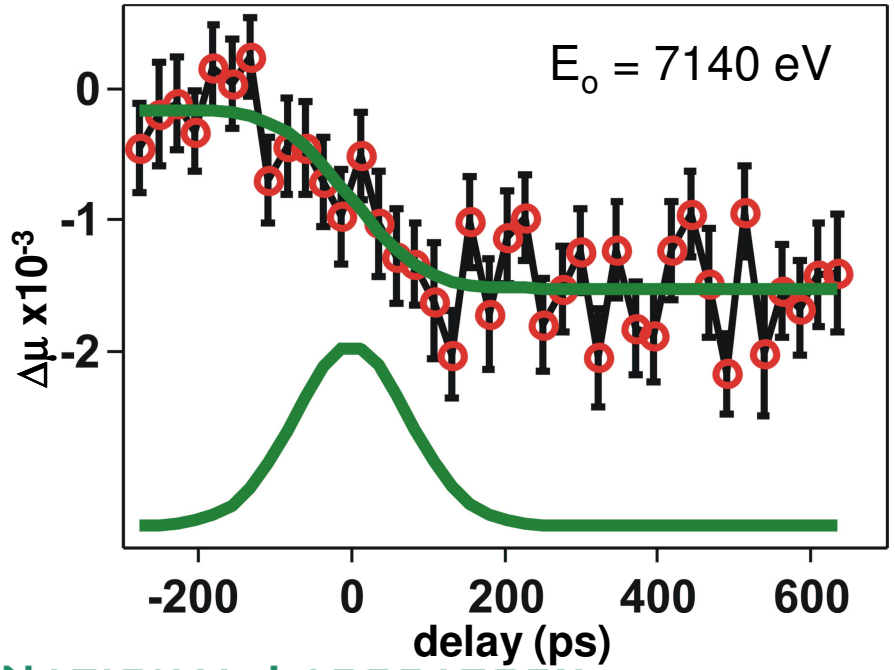
M. Khalil et al., *J. Phys. Chem.* (2006)

Structural Details Fe^{II} Photoexcited High-Spin State

(ALS Beamline 5.3.1)



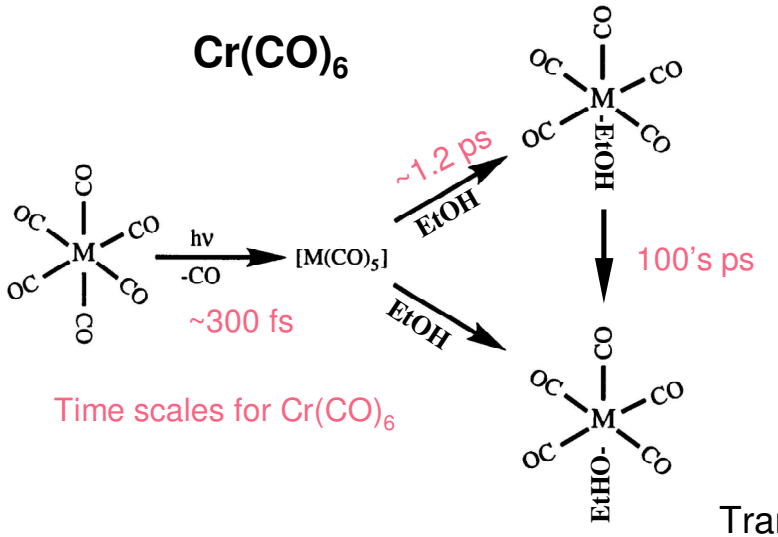
	Reactant $^1A_1$ ($\tau = 0$)	Photoexcited $^5T_2$ ($\tau = 330$ ps)
N	6 ±0.5	6.5 ±1
R (Å)	1.94 ± 0.01	2.15 ±0.03
σ (Å^2)	0.001	0.009

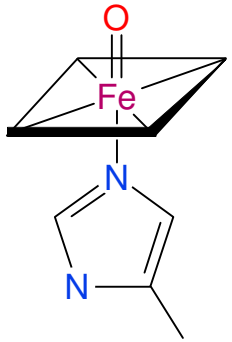


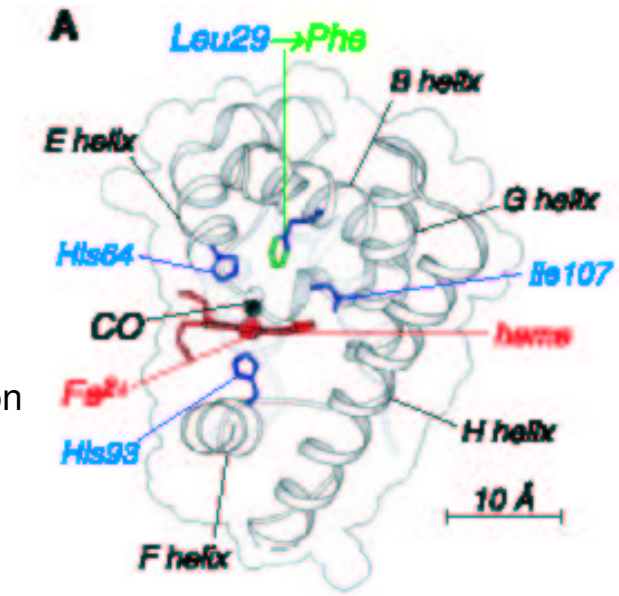
M. Khalil et al., *J. Phys. Chem.* (2006)

Photochemistry in Solution

- How does the ***bonding*** evolve through the transition state?
- What are the molecular structural dynamics?
- What is the role of the ***solvent (surface, protein)***?







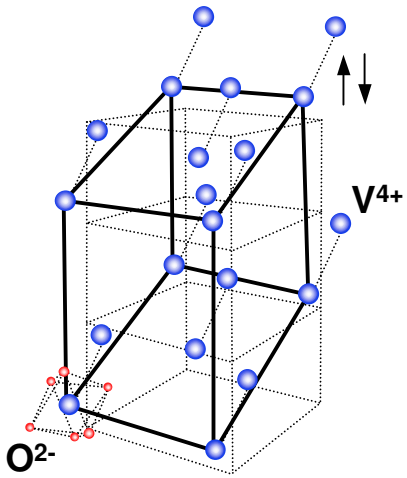
Transition-metal complexes
- metal carbonyls

Chlorine dioxide photodissociation
- atmospheric photochemistry

Metal porphyrin dynamics
- heme protein

Ultrafast Structural and Electronic Transitions in VO_2

T < 340 K
Monoclinic

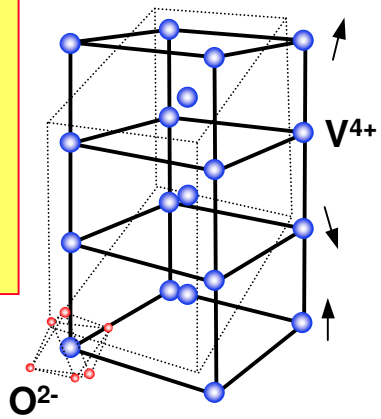


VO_2

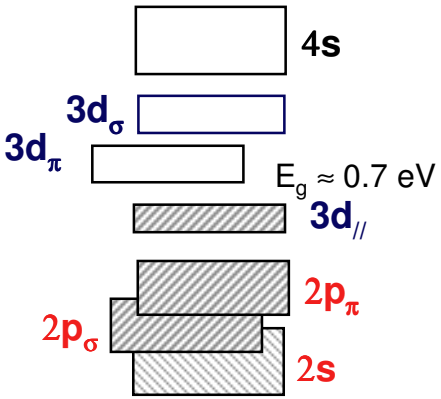
Mott-Hubbard insulator – e-e correlation ?
Zylberstein and Mott, *PRB* (1975)
Pouget et al., *PRB* (1974), *PRL* (1975)

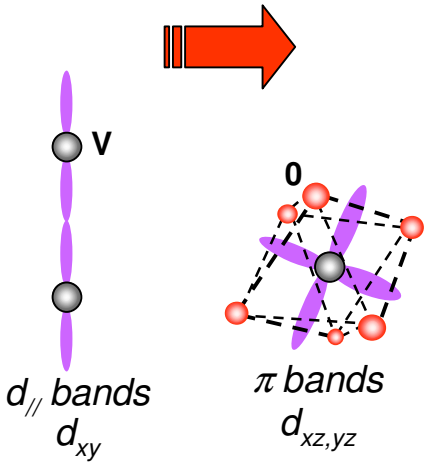
Band insulator – structural component ?
Goodenough, *Phys. Rev.* (1960)
Wentzcowitch, *PRL* (1994)

T > 340 K
Rutile

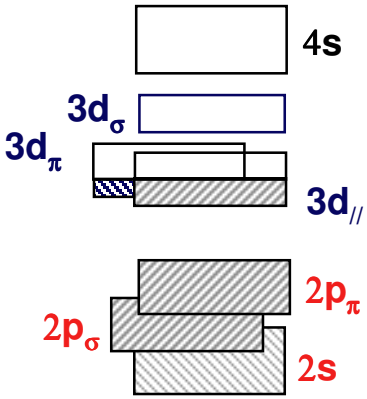


Insulator
low T

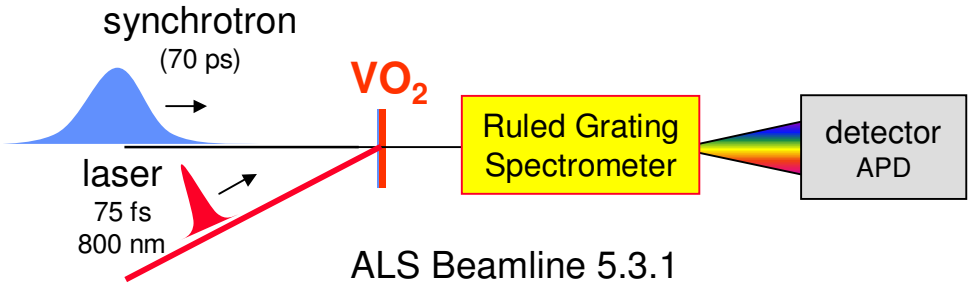




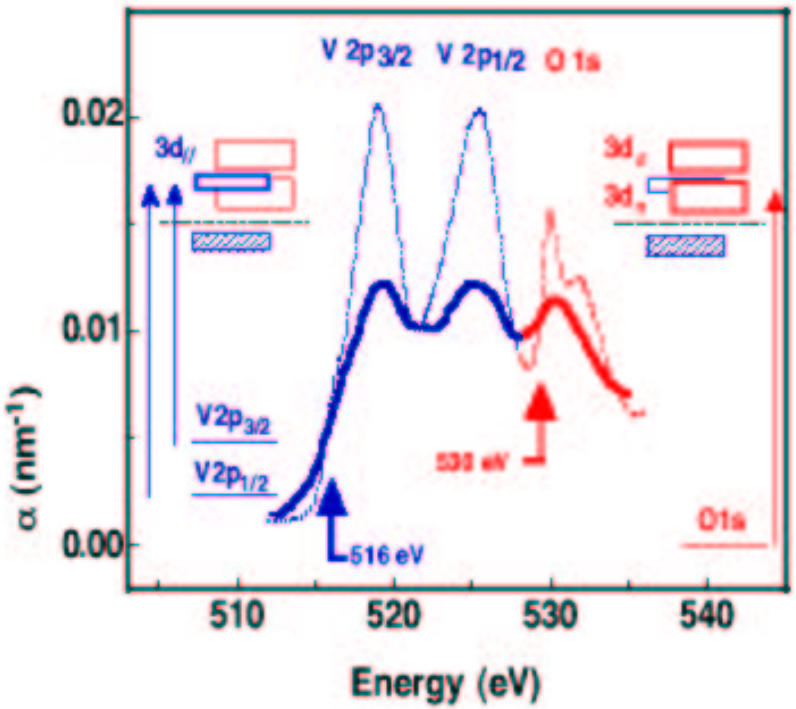
Metal
high T

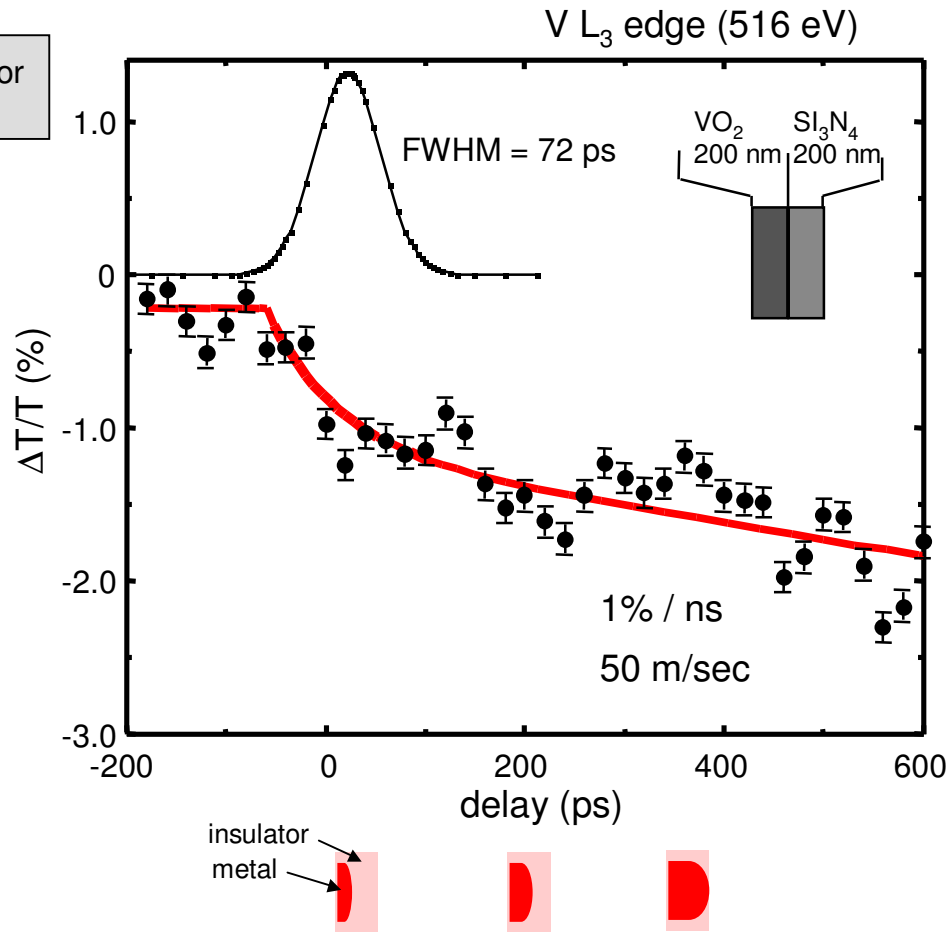


Picosecond NEXAFS Measurements in VO_2



ALS Beamline 5.3.1





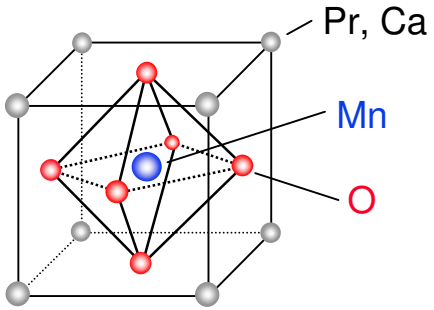
Signal on picosecond time scale dominated by growth of metallic phase

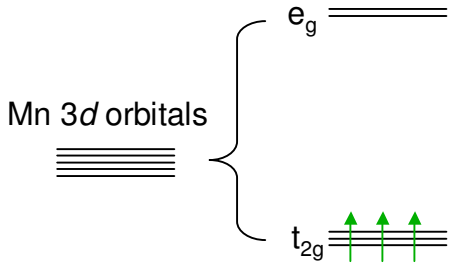
A. Cavalleri et al., *Phys. Rev. B*, **69**, 153106 (2004).

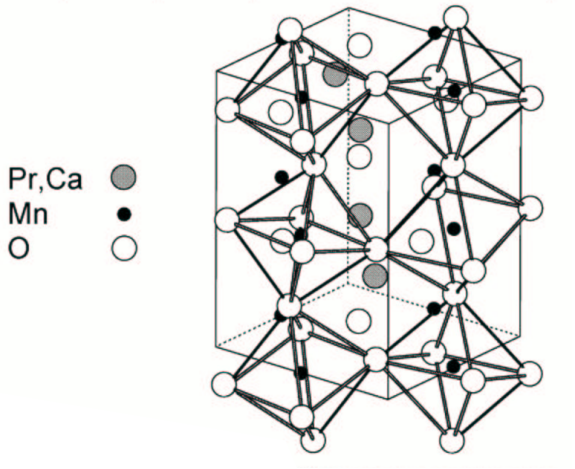
Colossal Magnetoresistive Manganites

Thousandfold change in resistivity in magnetoresistive La-Ca-Mn-O films
S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh and L.H. Chen
Science, **264**, 413 (1994).

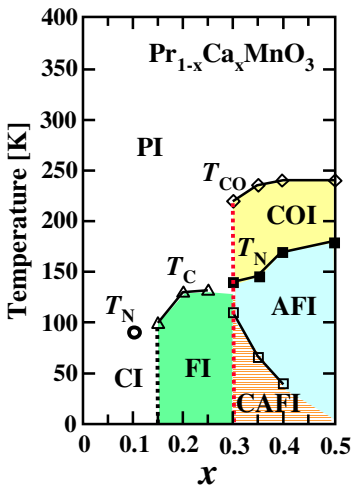
$Pr_{1-x}Ca_xMnO_3$



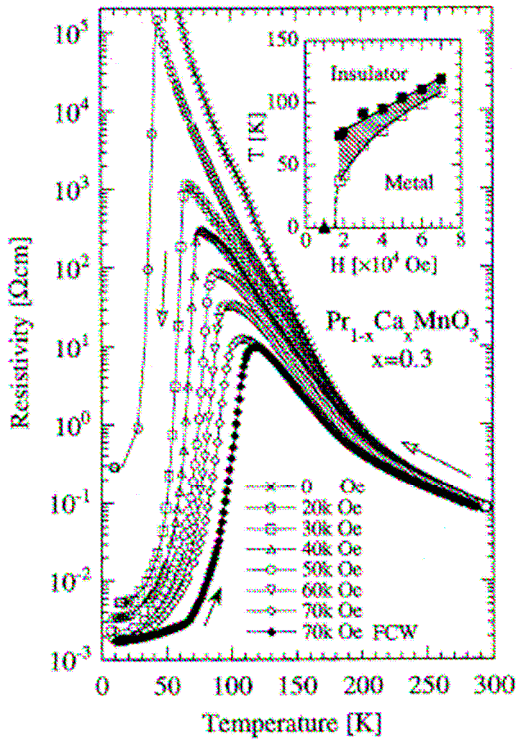




Tokura et al., *PRB*, 1996



COI - charge ordered insulator
PI – paramagnetic insulator
AFI – antiferromagnetic insulator
CA – canted antiferromagnetic

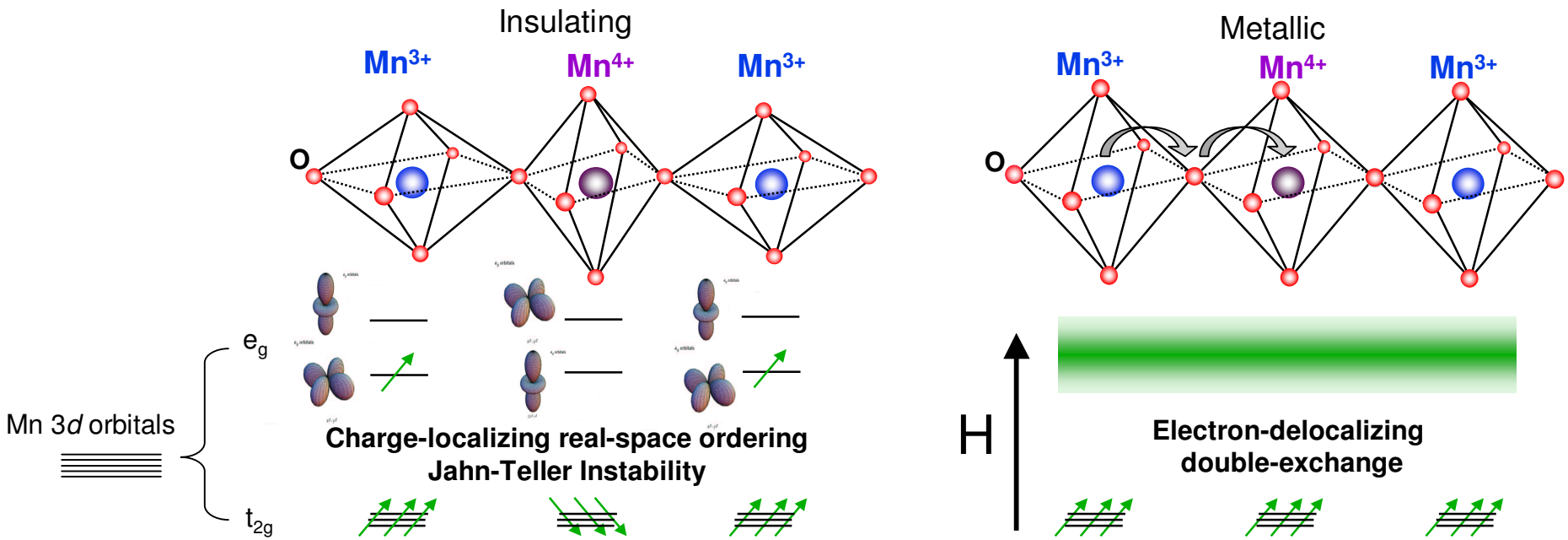


Anomalous Magnetotransport Properties of $Pr_{1-x}Ca_xMnO_3$

Yasuhide TOMIOKA[1], Atsushi ASAMITSU[1], Yutaka MORITOMO[1] and Yoshinori TOKURA[1,2]

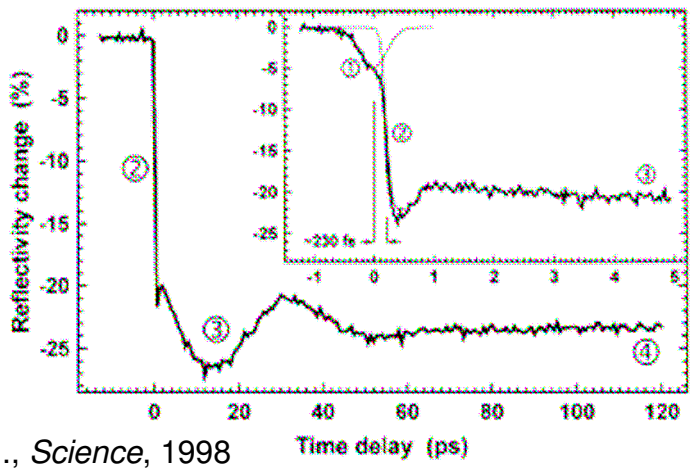
Journal of the Physical Society of Japan
Vol. 64, No. 10, October, 1995, pp. 3626-3630

Field-Induced Insulator-Metal Transition in $Pr_{0.7}Ca_{0.3}MnO_3$



An insulator-to-metal phase transition can be induced by:

- applied magnetic field (CMR)
- pressure
- X-ray illumination
- **optical excitation – 230 fs!**
  - practical applications
  - fundamental physics – atomic/electronic structural dynamics

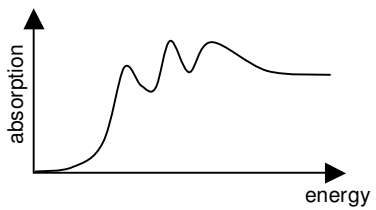


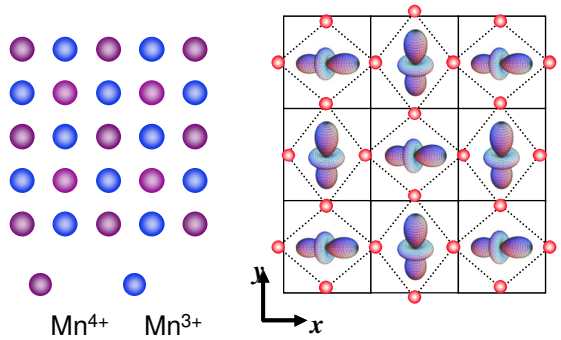
Fiebig et al., *Science*, 1998

Photoinduced Phase Transitions in Manganites

Future Research - Ultrafast X-rays

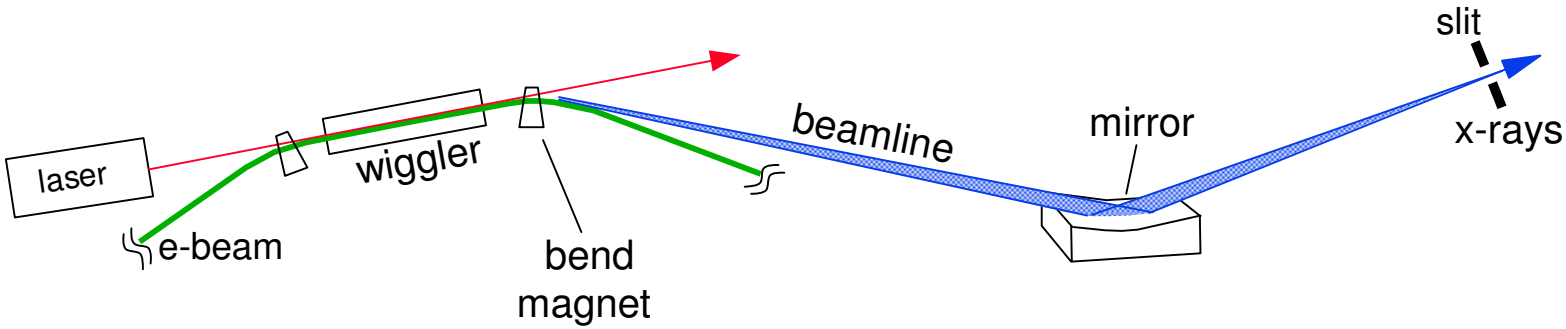
- Time-resolved x-ray spectroscopy – XANES O K-edge, Mn L-edges
  - changes in O-*2p* hybridization with Mn-*3d* (charge localization and *d*-electron hopping probability)
  - structural changes in Mn-O complex (polarons, J-T distortion ionization, bond angles)
- Time-resolved XMLD, XMCD – Mn L-edges (magnetic ordering dynamics)

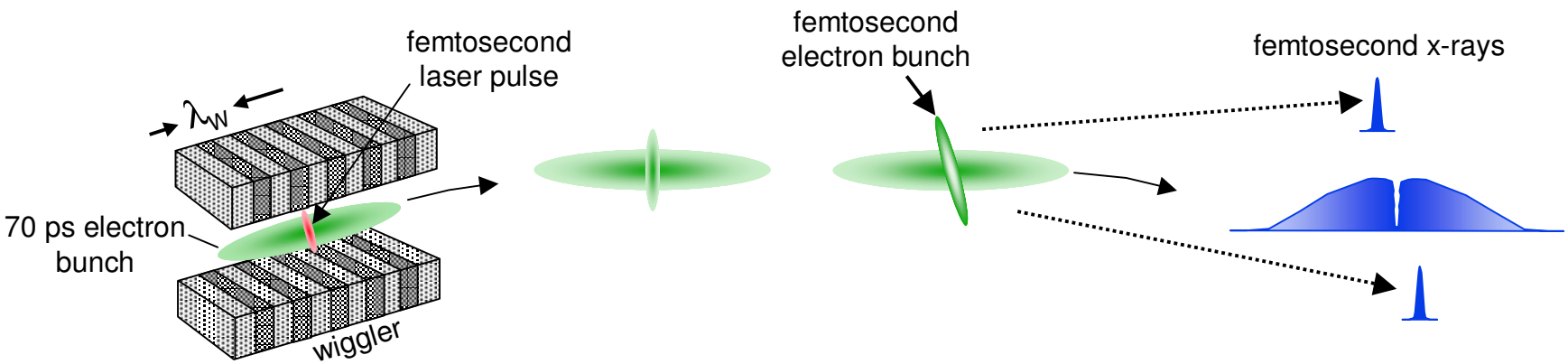




- Femtosecond Resonant X-ray Diffraction – Charge Ordering Dynamics
  - Bragg diffraction at reflections forbidden by lattice symmetry
  - charge anisotropy (charge ordering) $\Rightarrow$ weak diffraction
  - enhanced sensitivity at absorption edges, Mn K-edge, *1s-3d* (quad. coupling), *1s-4p* (*d-p* coupling)
    Murakami et al., *PRL*, 1998; Zimmermann et al., *PRL*, 1999

Generation of Femtosecond X-rays from the ALS





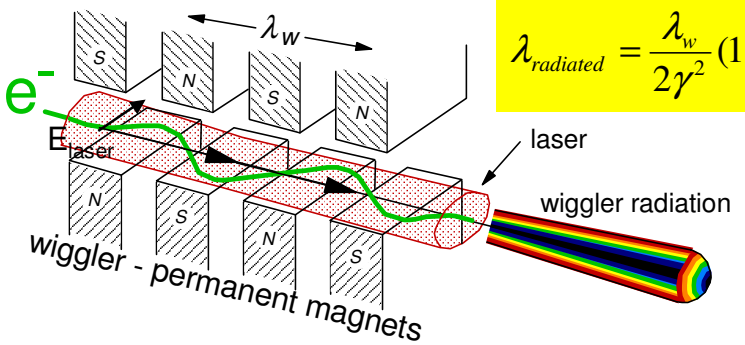
electron-photon
interaction in wiggler

spatial separation
dispersive bend

bend magnet
beamline

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

Energy Modulation in the Wiggler



$$\lambda_{radiated} = \frac{\lambda_w}{2\gamma^2}(1+K^2/2) = \lambda_{laser}$$

total field energy:

$$A \sim \iint \left|E_L(\omega,\vec{r}) + E_R(\omega,\vec{r})\right|^2 dS d\omega = A_L + A_R + \underbrace{2\sqrt{A_L A_R \frac{\Delta\omega_L}{\Delta\omega_R}}\cos\phi}_{\Delta E \text{ (energy mod)}}$$

wiggler radiated energy:

$$A_R \cong 4.12\alpha\hbar\omega_R \frac{K^2/2}{(1+K^2/2)}$$

Laser requirements:

$\hbar\omega_L = 1.55$ eV

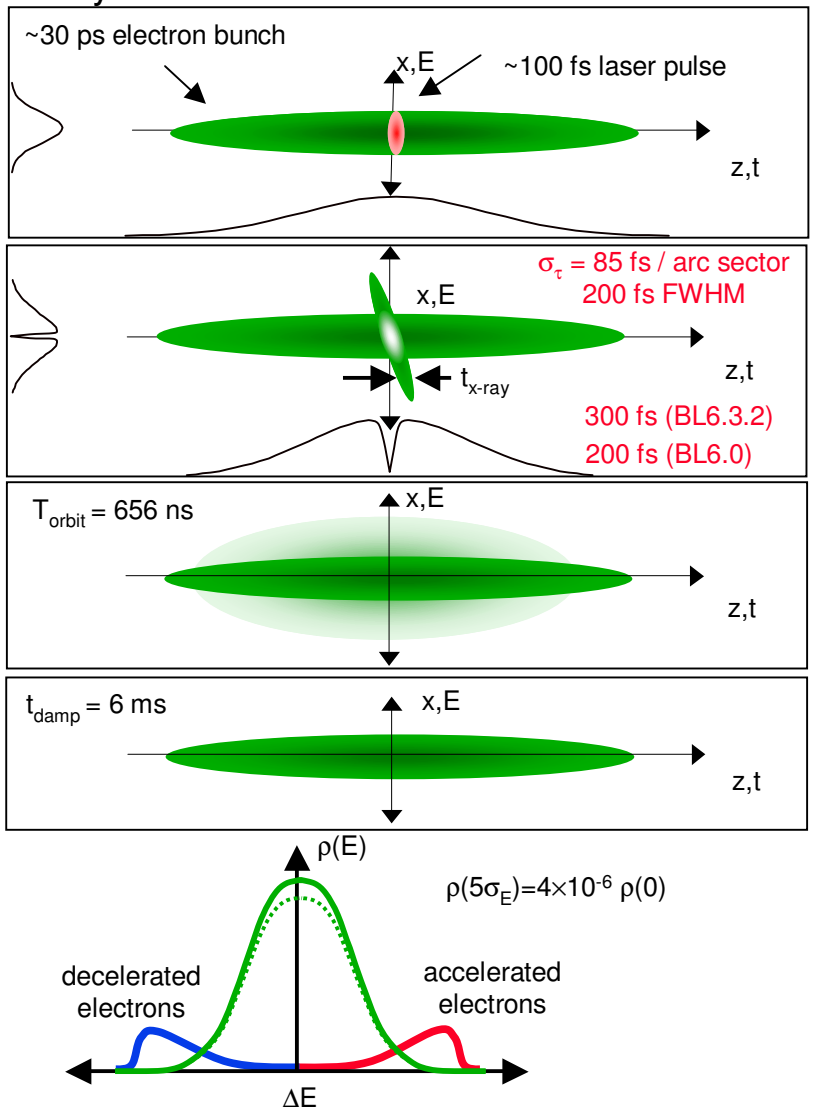
$\Delta\omega_L = 27$ period wiggler $\Rightarrow$ 36 fs laser pulse (72 fs)

$A_L = 610\ \mu J$ (780 μJ)

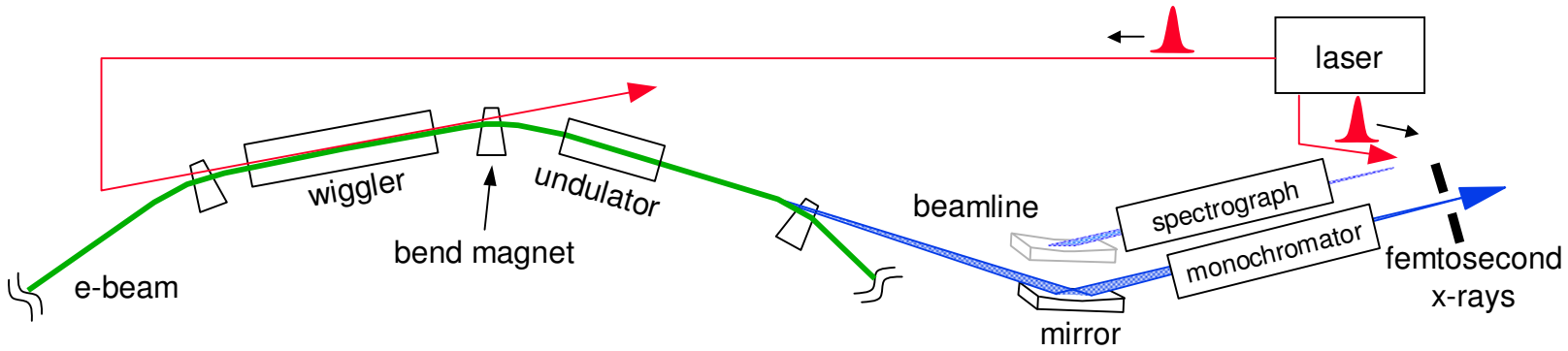
$\Delta E \cong 17$ MeV $9\sigma_E$

ALS beam energy spread σ_E ~1.9 MeV E_o =1.9 GeV

Dynamics of Modulated Electron Beam



Femtosecond Undulator Beamline – Overview



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

- 30 W (1.5 mJ per pulse, 20 kHz)

x10 increase in flux

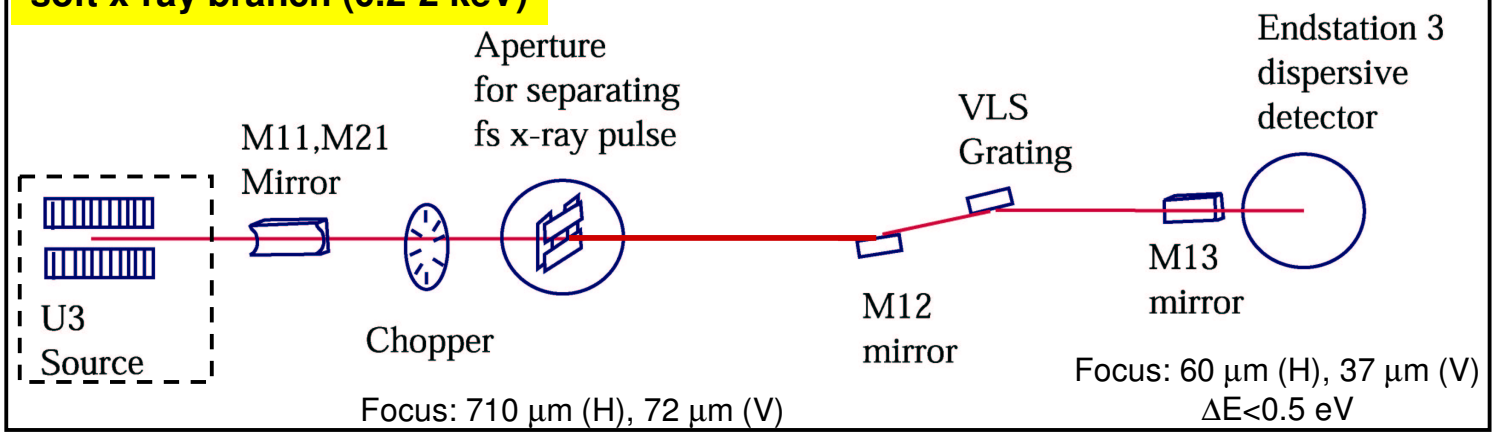
IV. Storage Ring Modifications

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

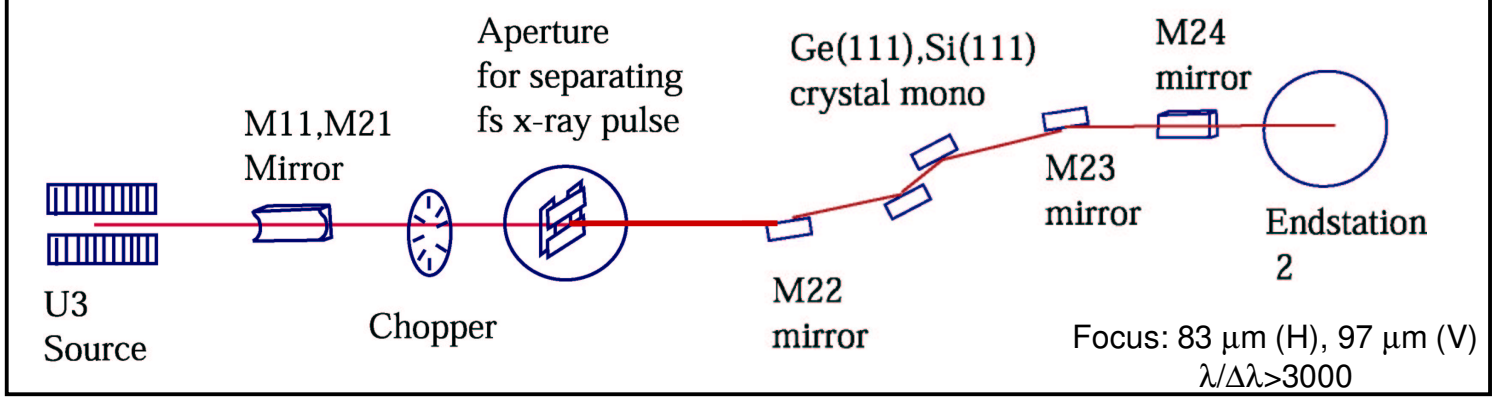
ALS Femtosecond Undulator Branchlines

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

soft x-ray branch (0.2-2 keV)



hard x-ray branch (2-10 keV)



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)

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

$\tau_{damping}$ ~ 6 msec ⇔ f_{limit} ~ 1 kHz (2 bunches) ⇔ ~40 nsec gate
> 1 kHz (multibunch) ⇔ ~2 nsec gate

Average Femtosecond X-ray Flux ~ Average Femtosecond Laser Power

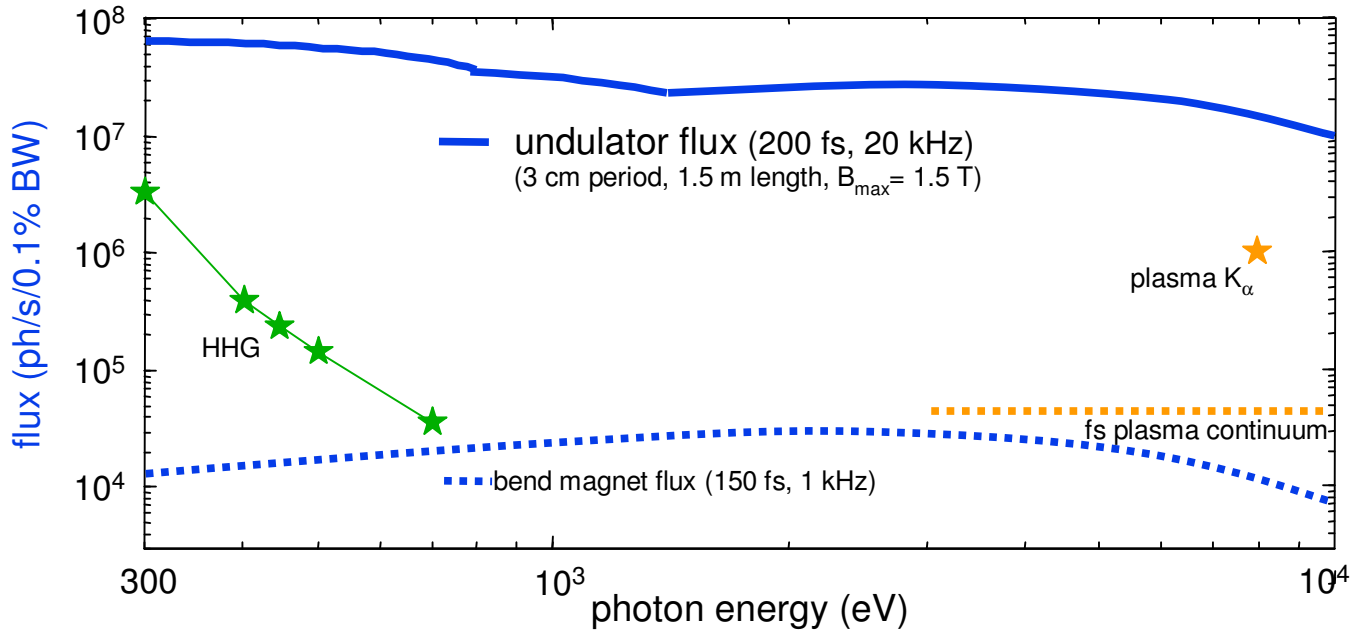
Bend Magnet

- 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 X-ray Flux



★ HHG flux from F. Krausz, laser: 10 fs, 3 mJ/pulse, 30 W

★ Plasma source flux in mrad^2 laser: 40 fs, 1 mJ/pulse, 30 W (continuum includes projected 10^5 improvement)

Cu K_α - 10^{10} ph/s/4π (proj. 10^{12} with Hg target)
cont. 6×10^7 ph/s/4π (integ. from 7-8 keV)

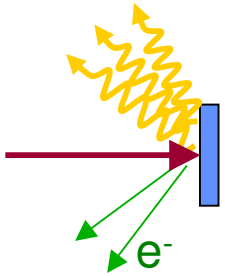
ALS typical average x-ray flux
undulator ~10^{15} ph/s/0.1% BW
bend-magnet ~10^{13} ph/s/0.1% BW

Advantages – Integrating Detectors

New Science

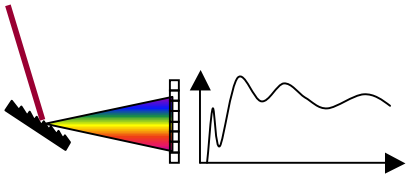
- eliminate need for high-speed (small area) APD detectors
  high speed gatable ~~⇔~~ high quantum/collection efficiency

- XAS – fluorescence (molecular dynamics – dilute solutions)

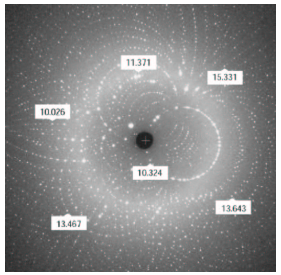


- total electron yield or sample current (surface sensitive, thick samples)

- dispersive spectroscopy (soft x-ray, hard x-ray?)
  1D detector with high efficiency (phosphor+CCD)

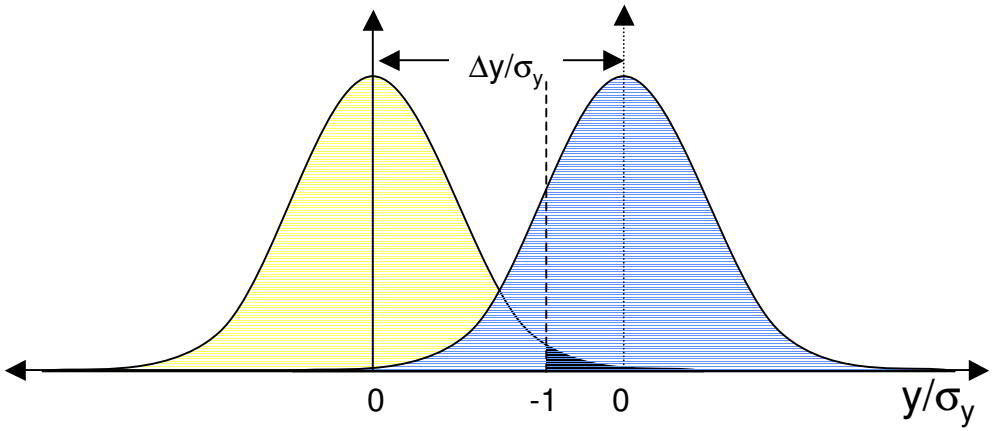


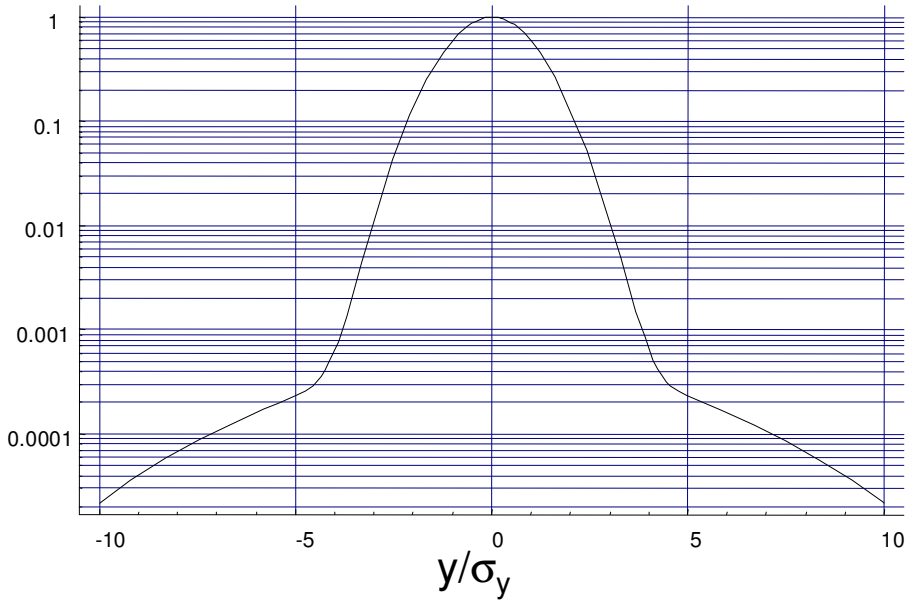
- 2D high efficiency integrating detectors
  Laue diffraction, powder diffraction, SAX …..



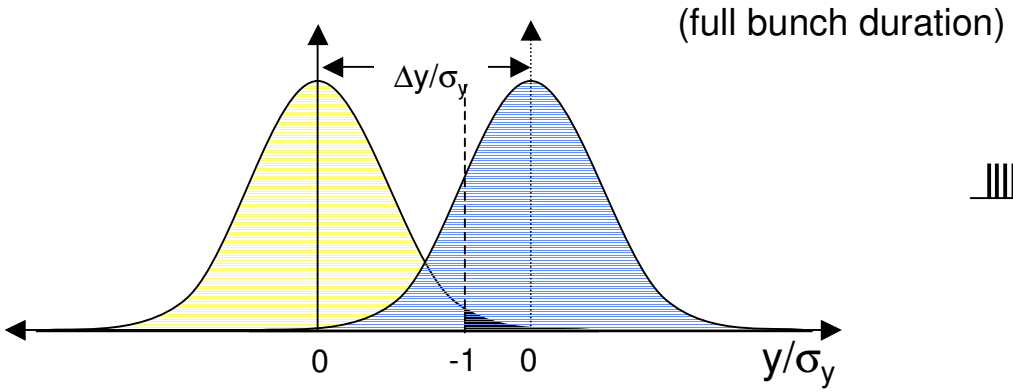
Required Vertical Displacement

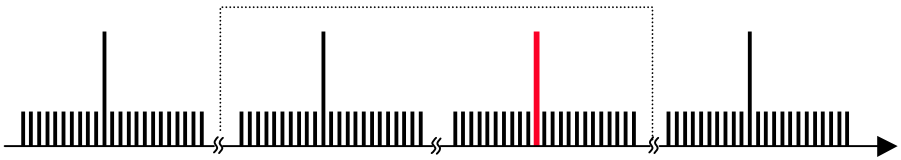
(full bunch duration)



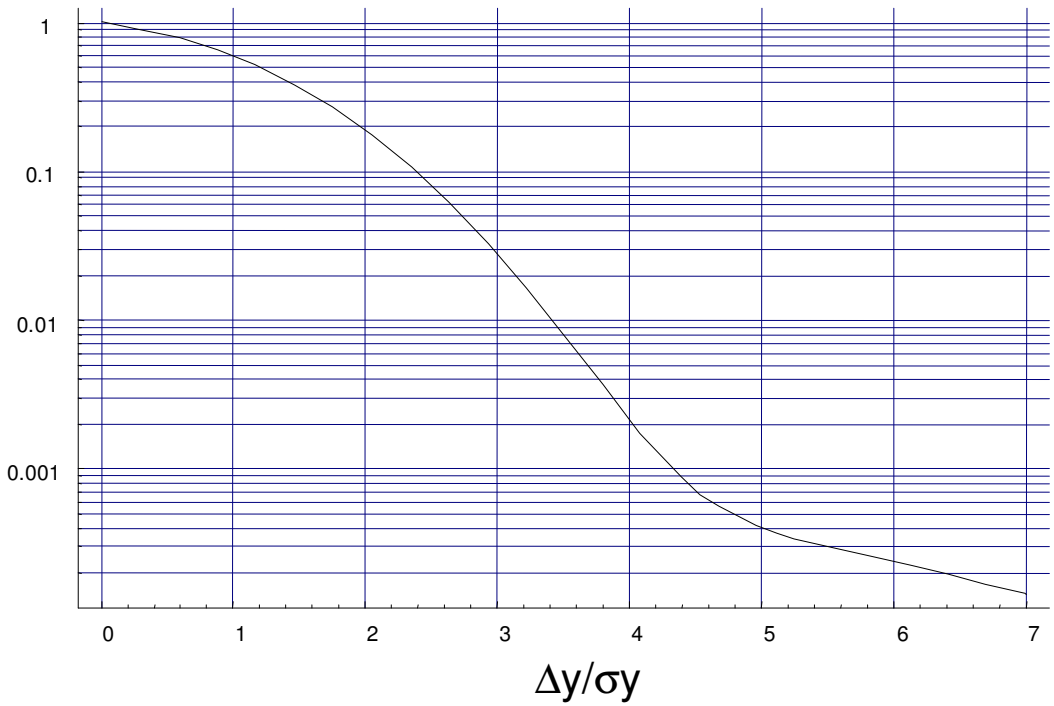


Required Vertical Displacement





chopper window ~ 1.3 μsec (2x SROC)



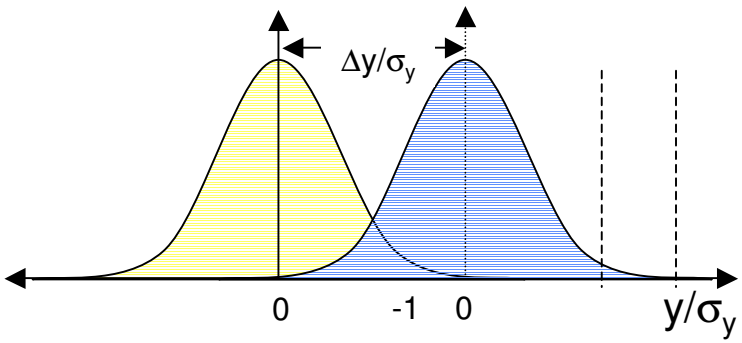
$$\frac{10\ \text{mA}}{2\text{x}\ 400\ \text{mA}} = 1.25 \times 10^{-2}$$

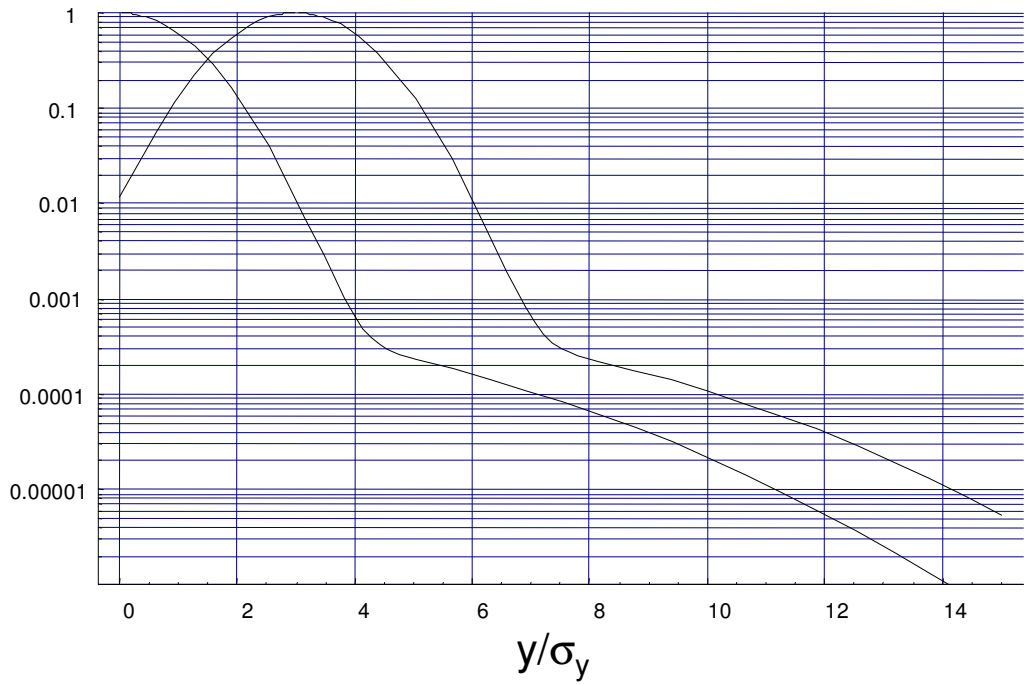
~4σ_y spatial displacement
Sig/bkg ~ 10

~160 μm (straight 6)

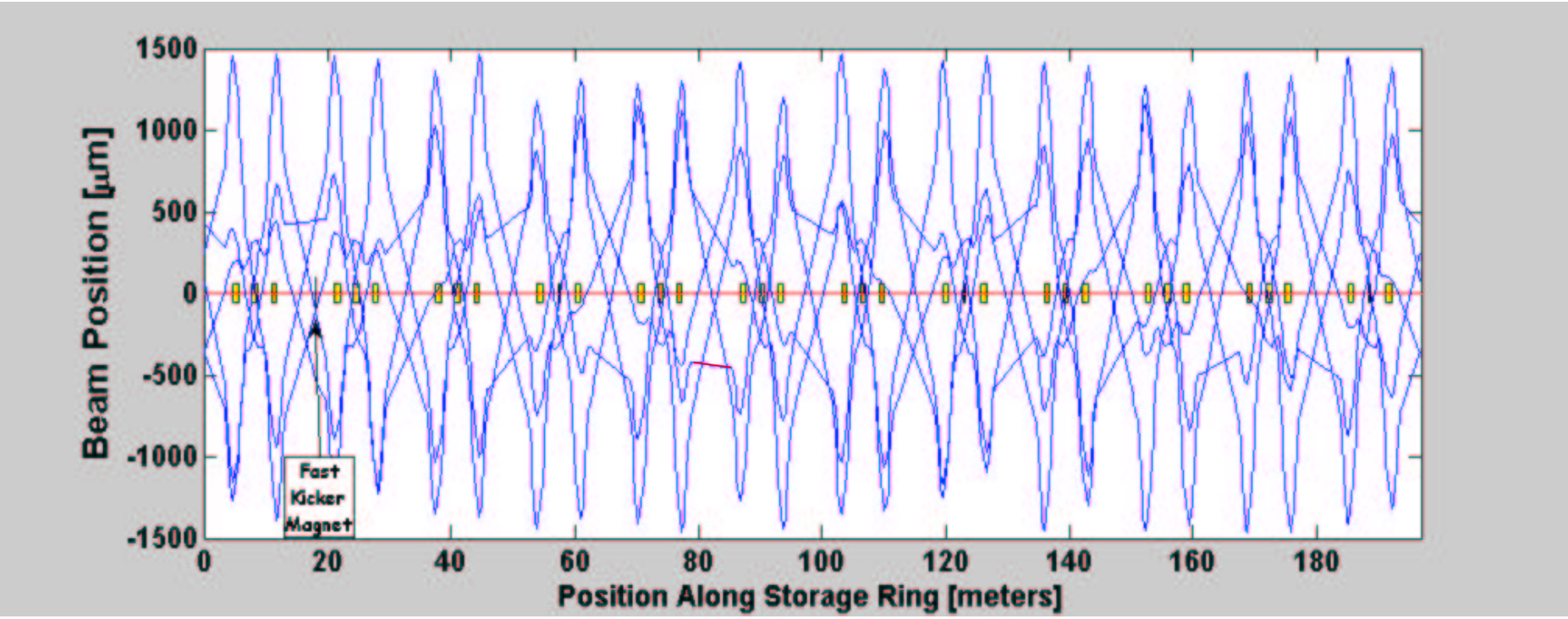
Femtosecond 'Slicing' Operation - Considerations

- stability of displaced beam (<<1σ)
- laser alignment to displaced beam in straight 5
- nonlinear dispersion, D_y





Single Kicker - Kick Every 5th Turn

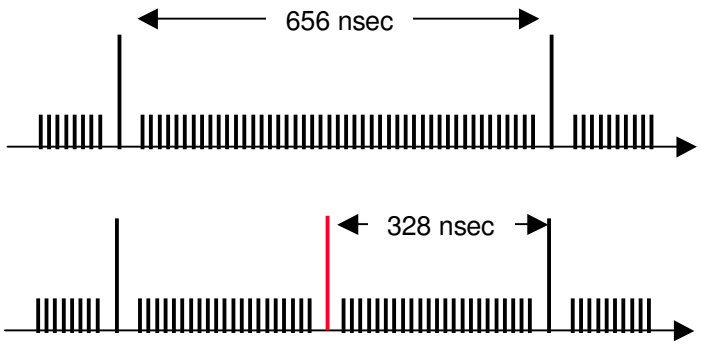


straight 6 –large displacement

straight 5 - angular displacement ?
- laser alignment through W11 ?

Multiple Kickers to generate localized bump in sector 6

Femtosecond 'Slicing' Operation - Considerations

Multibunch vs. Camshaft Operation

- multibunch – 10 kHz, at ~1 mA/bunch
  gated detectors – 2 ns resolution
- camshaft – 1 kHz operation (max) – per camshaft bunch
  synchrotron damping
  ~10 mA/bunch (assume top-off operation)
- additional camshaft bunches – significant benefit 2x