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Pump-Probe EXAFS or Probing Structural and Electronic Excitations with X-rays

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A U.S. Department of Energy laboratory managed by The University of Chicago

Outline

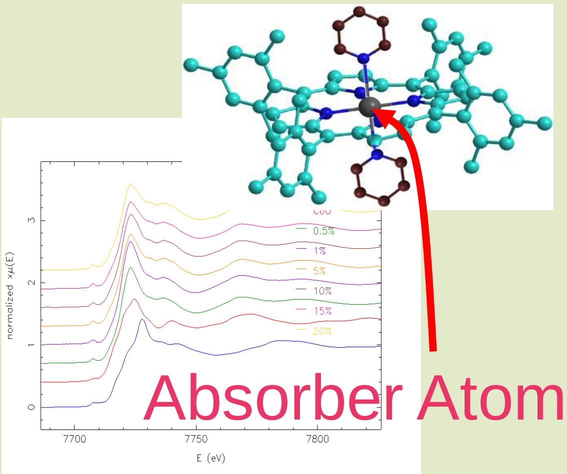
- What kind of information your synchrotron technique may provide
  - Dynamics of glasses
  - X-ray probes structure and electronic state
- What are the basic principles of your technique
  - The excited state: Intermediates, ensembles, & more
  - The pump-probe experiment
  - Reversible/irreversible problems
  - The time resolution
- What are the limitations of your technique
  - Poor Signal/noise ratio
  - Increase detection efficiency/available flux
  - Sample damage
- What kind of sample does one need

Motivation
Dynamics of Glasses

- Reversible- non-reversible processes
- Typical Problems:
  - Melting
  - Phase transitions (RW-DVD)
  - Dynamic behavior (like…..)
  - Charge dynamics in glasses
  - Chemical reactions
- X-ray will probe ?

Motivation:
X-ray Probes Structure and Electronic State

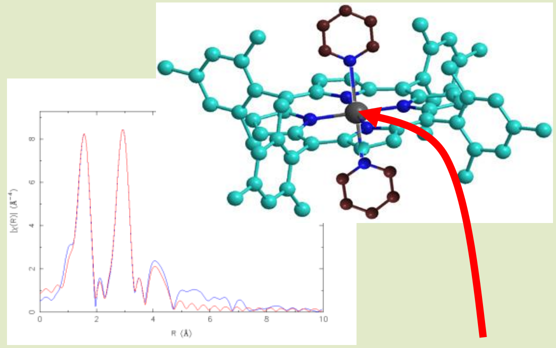
Electronic Structure



NEXAFS

- Local Electron Density
- Symmetry
- Atomic selectivity

Local Structure

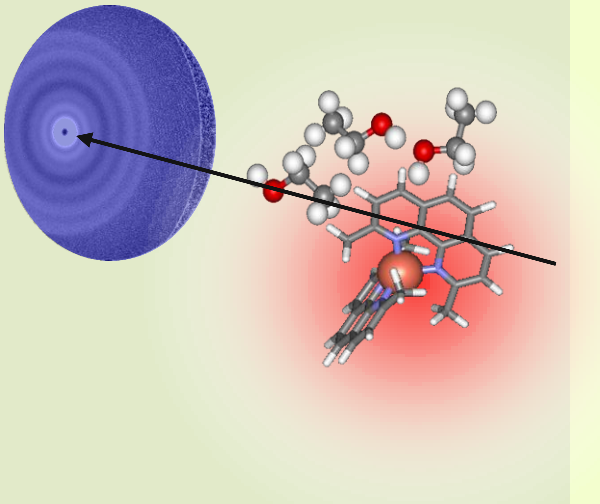


Absorber Atom

EXAFS

- Distance
- Symmetry
- Atomic selectivity
- Number of Neigbors

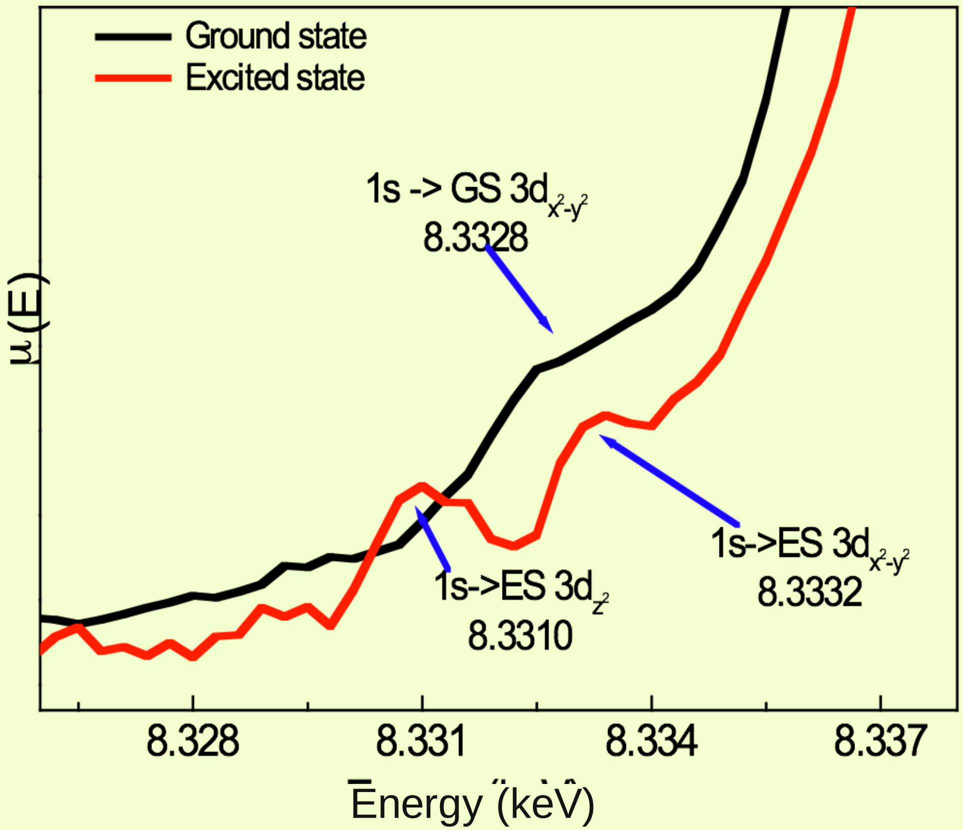
Global Structure

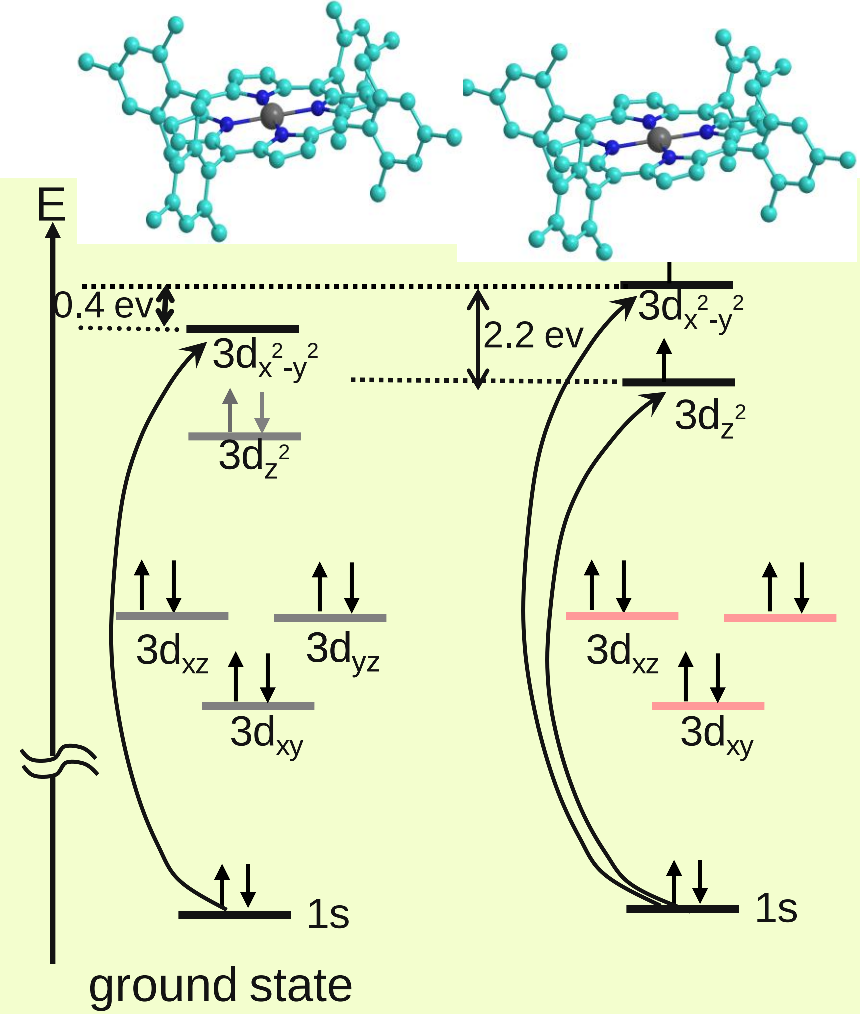


WAXS/SAXS

- Global Electron Density
- Global Shape
- Movie with Limited Spatial Resolution

Motivation: Electronic Structure, Symmetry and Pre-Edge

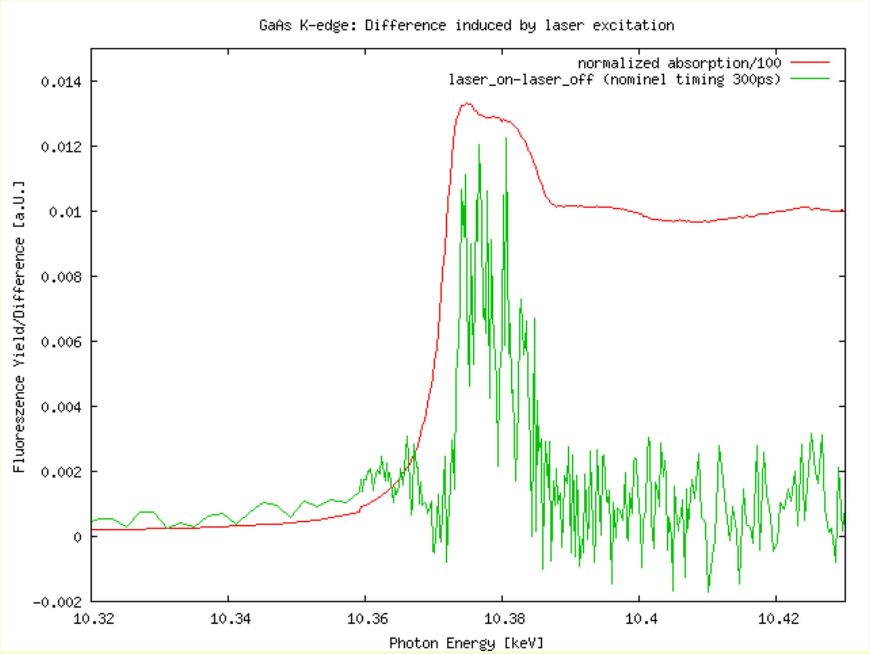


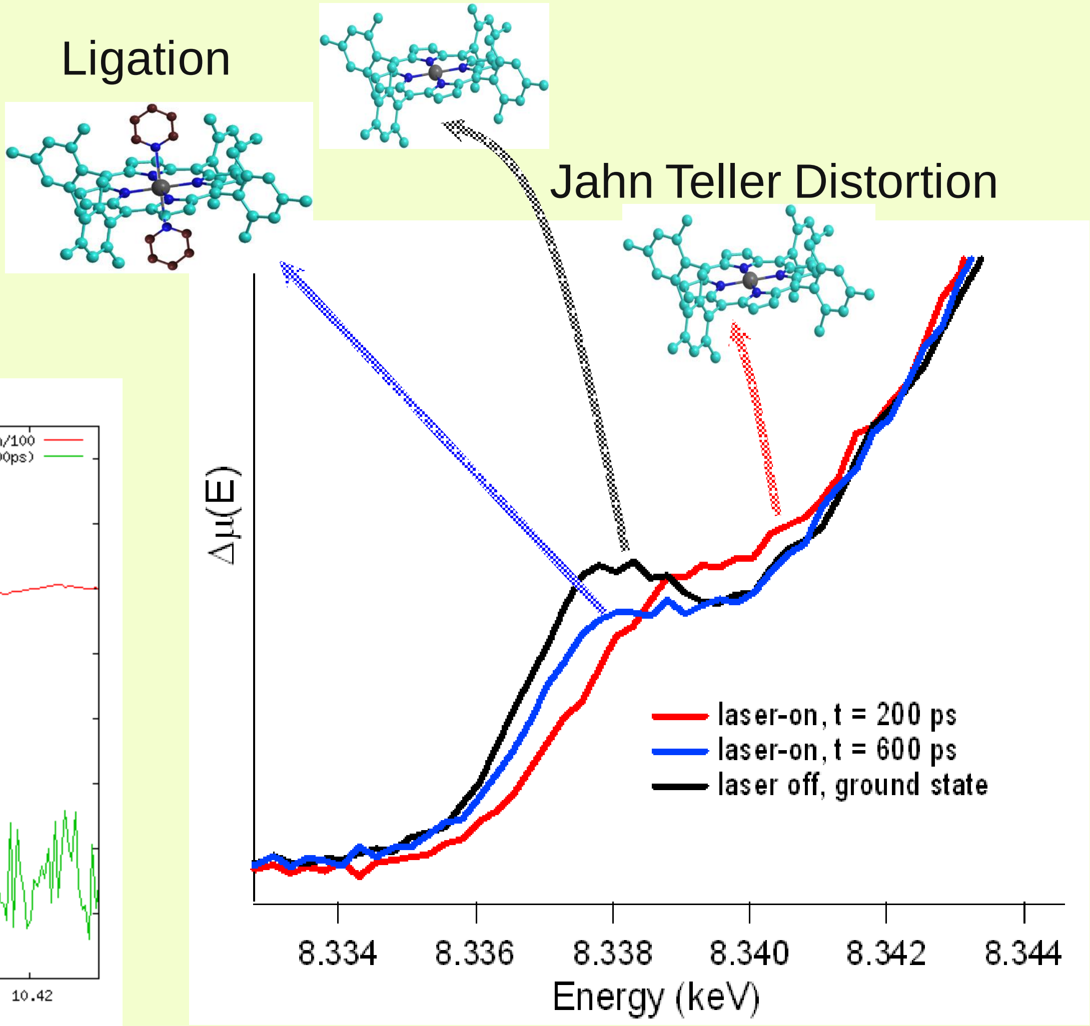


T_1 excited state has (d_{z2}, d_{x2-y2}) electronic configuration with singly occupied 3d_{x2-y2} and 3d_{z2} orbitals .
The energy gap between 3d_{x2-y2} and 3_{dz2} in the final excited state is ~ 2.2 eV .
The energy of 3d_{x2-y2} orbitals shifts up in the final excited state.

Motivation:
Electronic States & White Line

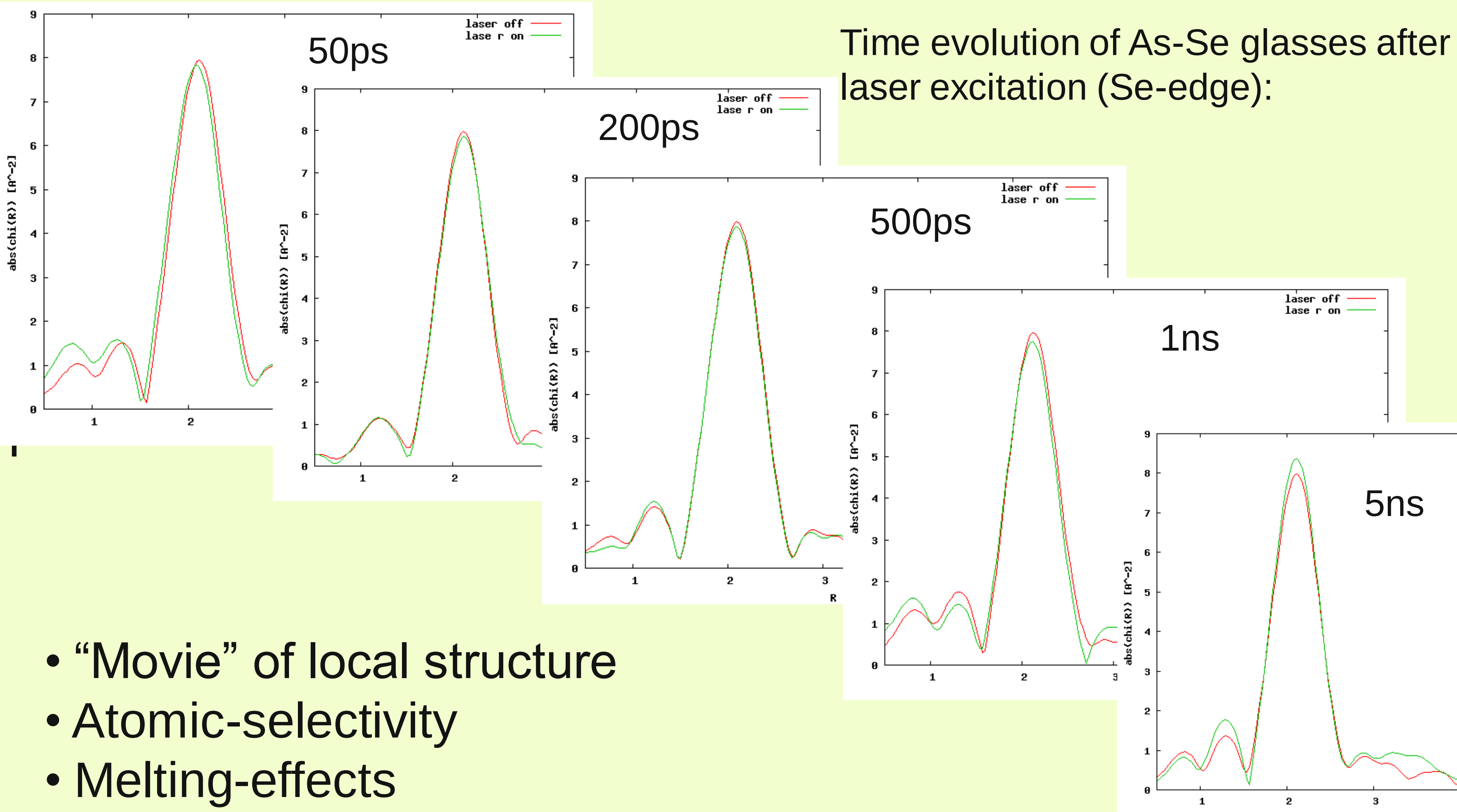
- Change of E_{Fermi}: derivative like shape
- Change of density of state: various peaks may appear
- Energy level of empty states (with restrictions)
- Local symmetry changes





Motivation:
Local Structure & EXAFS

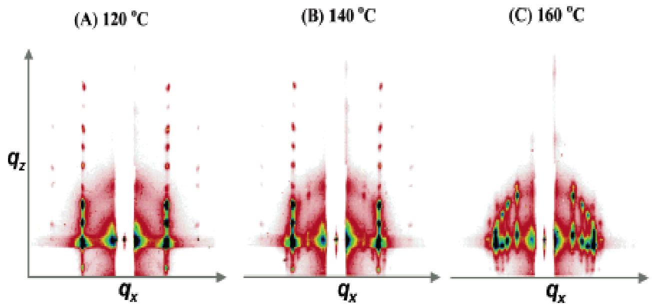
Time evolution of As-Se glasses after laser excitation (Se-edge):



- “Movie” of local structure
- Atomic-selectivity
- Melting-effects
- Smaller systematic errors (difference measurements!)

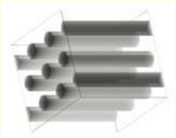
Motivation:
Global Structure & GI-SAXS/WAXS

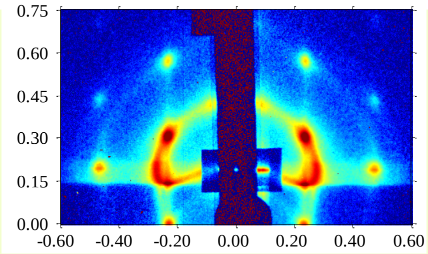
In-situ Heating experiment



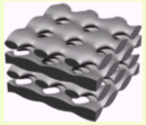
Macromolecules 2005, 38, 10532

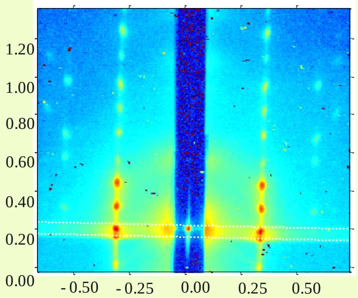
Hexagonal Cylinder



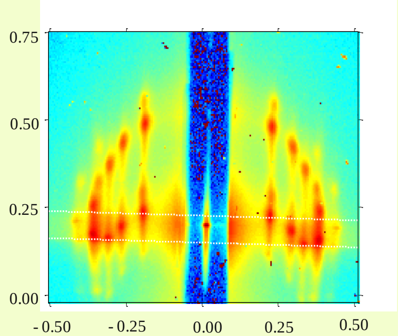


Hexagonally perforated layer



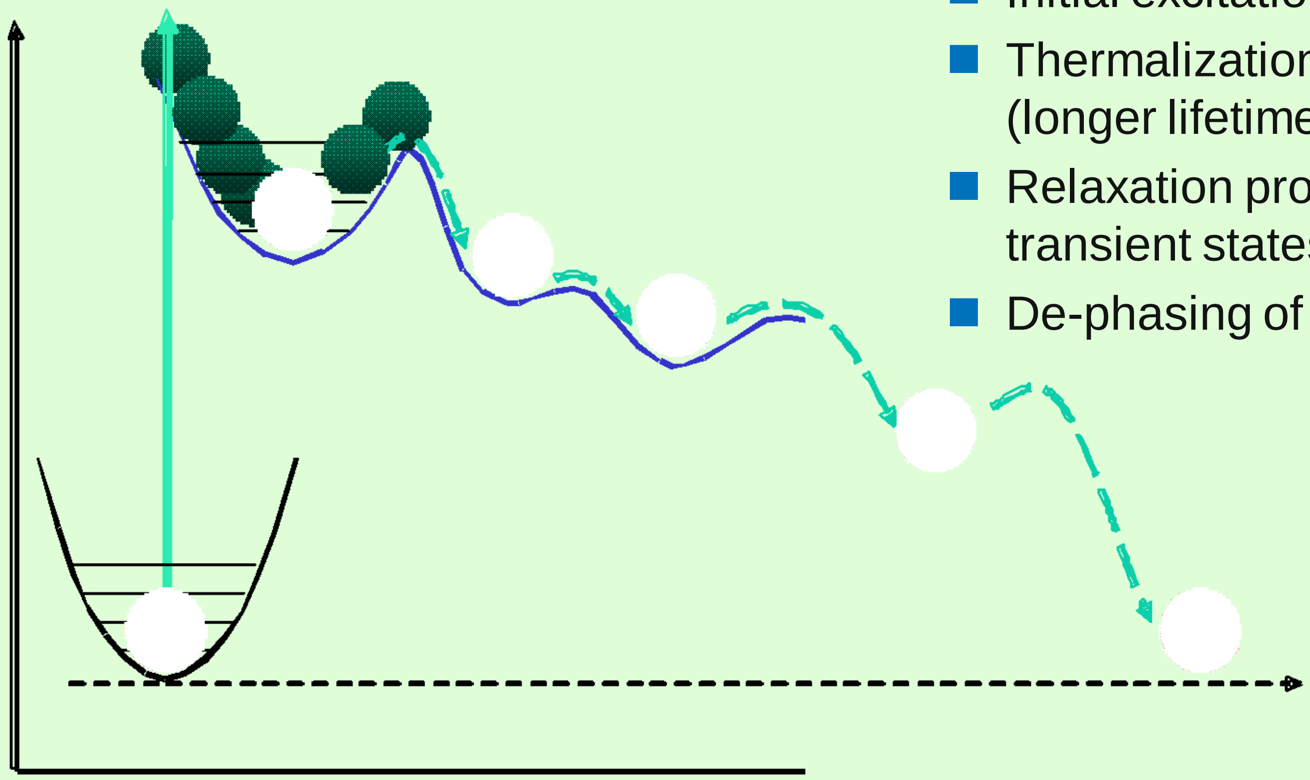


Gyroid : Cubic(*Ia3d*)



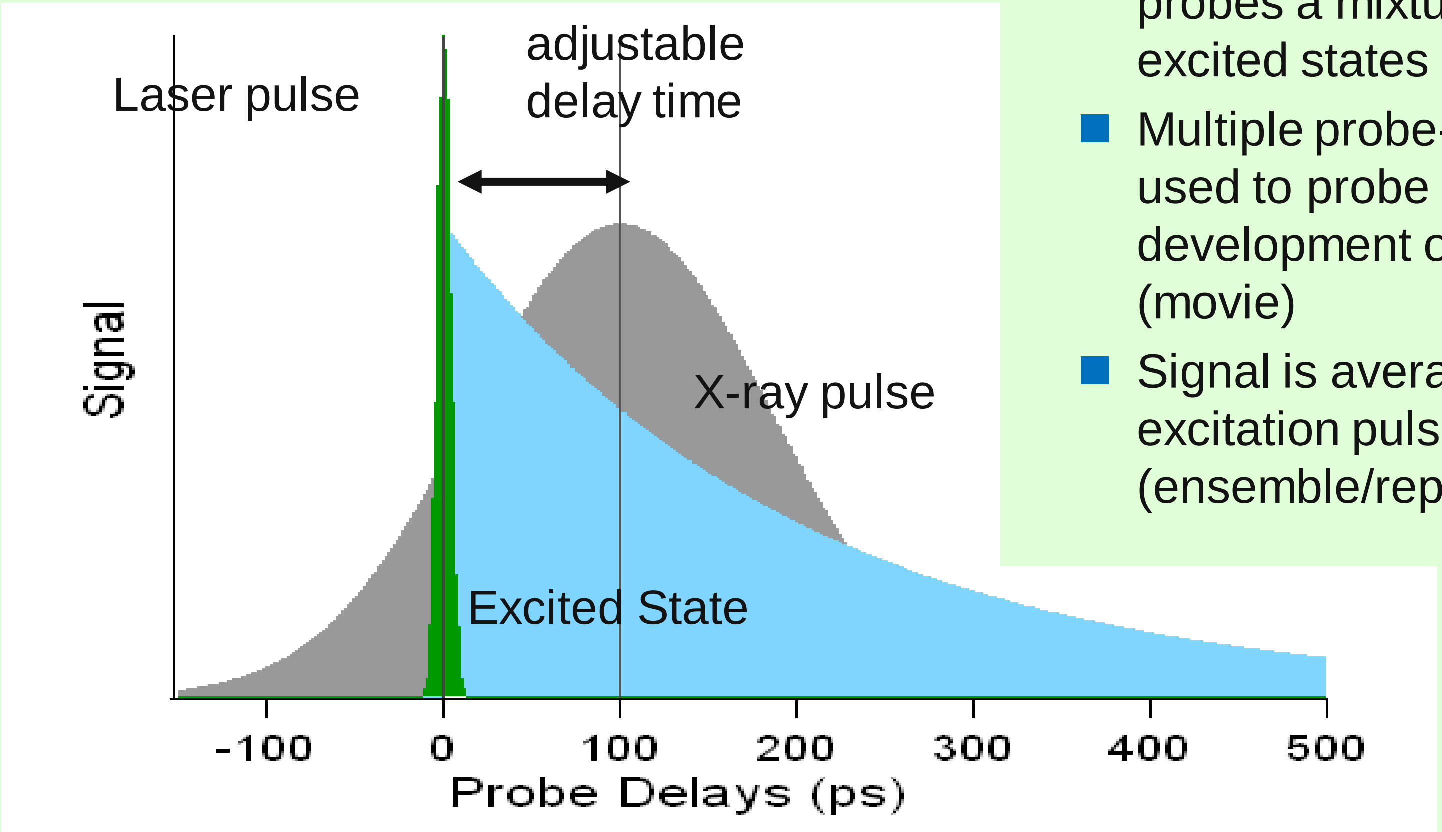
- Crystallization (Gi-WAXS)
- Melting (Gi-WAXS)
- Phase transitions (Gi-WAXS)
- Grain growth (for example catalysis)
- Today: first experiments on LB-films

Basic Principles: The Excited State



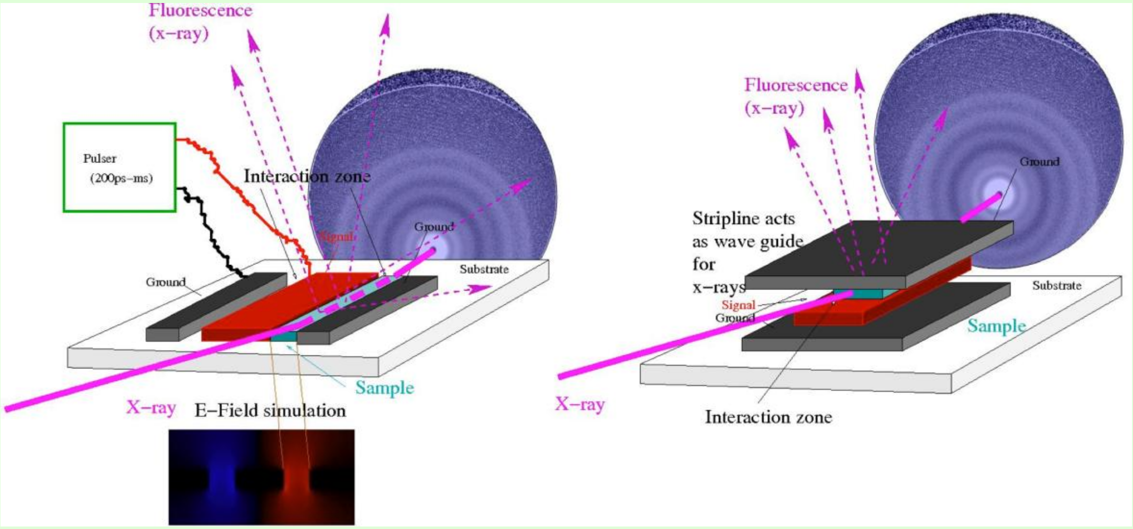
- Experiment on ensemble
- Initial excitation coherent (very fast)
- Thermalization to intermediate (longer lifetime; usually probed)
- Relaxation process includes many transient states/intermediates
- De-phasing of ensemble with time

Basic Principles: The Pump-Probe Experiment



- Pump creates Excite state (intermediate) population
- Probe pulse is delayed and probes a mixture of different excited states & ground state
- Multiple probe-pulses can be used to probe the development of a system (movie)
- Signal is averaged over many excitation pulses (ensemble/reproducibility)

Basic Principles:
The excitation Mechanism



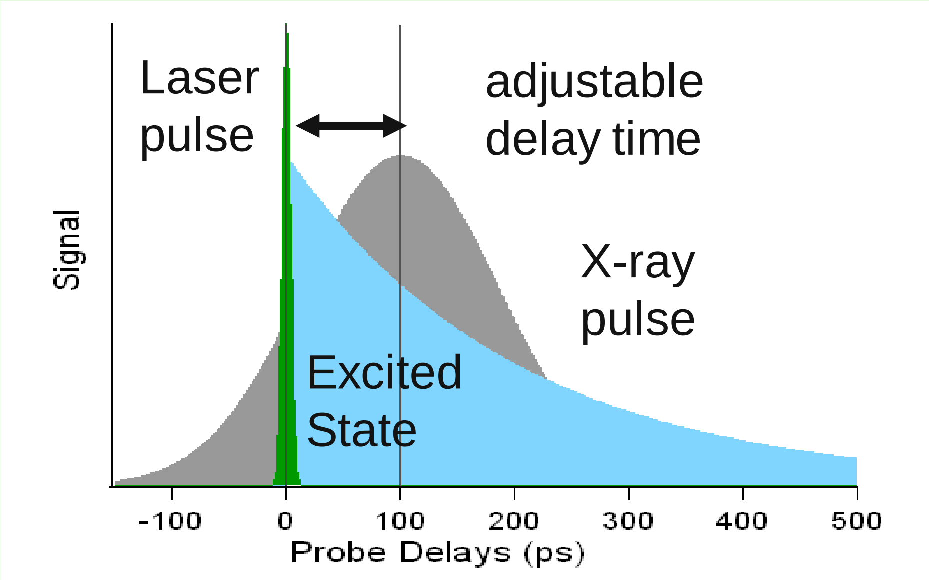
Selectivity:

- Polarization
- Resonator /Symmetry
- Wavelength
- Combinations

The spectrum (often Lasers)

- Electromagnetic pulses: magnetic/electric excitations (collective excitation)
- THz excitations: vibration/collective modes
- IR-pulses: vibrations/heating/melting
- Optical & UV: bond-braking
- Ultrafast pulses: optical/acoustic phonons

Basic Principles:
The Time-Resolution (stroboscopic)

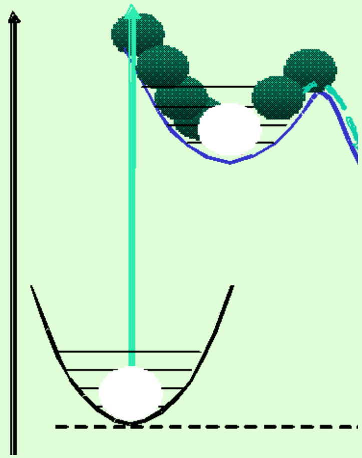


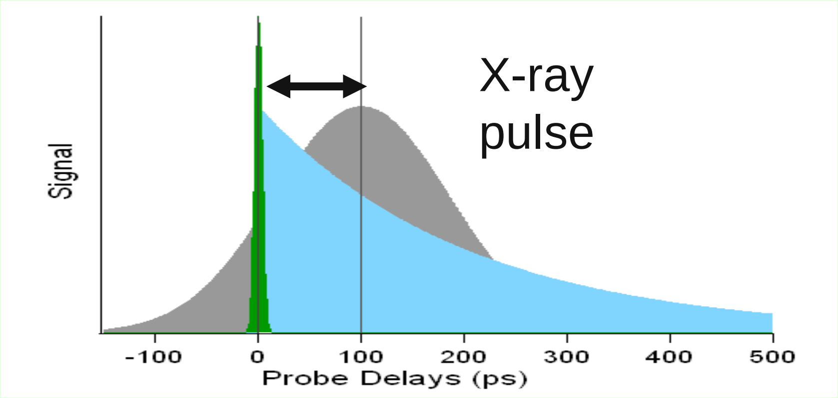
Time-resolution is given by ***convolution of excitation and probe-pulse*** (stroboscopic experiment) or by ***convolution of probe-pulse and detector resolution***

Typical excitation and probe pulses

Laser excitation:	10fs-10ns
Synchrotron pulse:	30ps-1ns (APS typically 80ps)
XFEL:	1fs-200fs
Plasma sources:	50fs-500fs
Thermal sources:	1ps-20ps
Slicing sources:	200fs-5ps

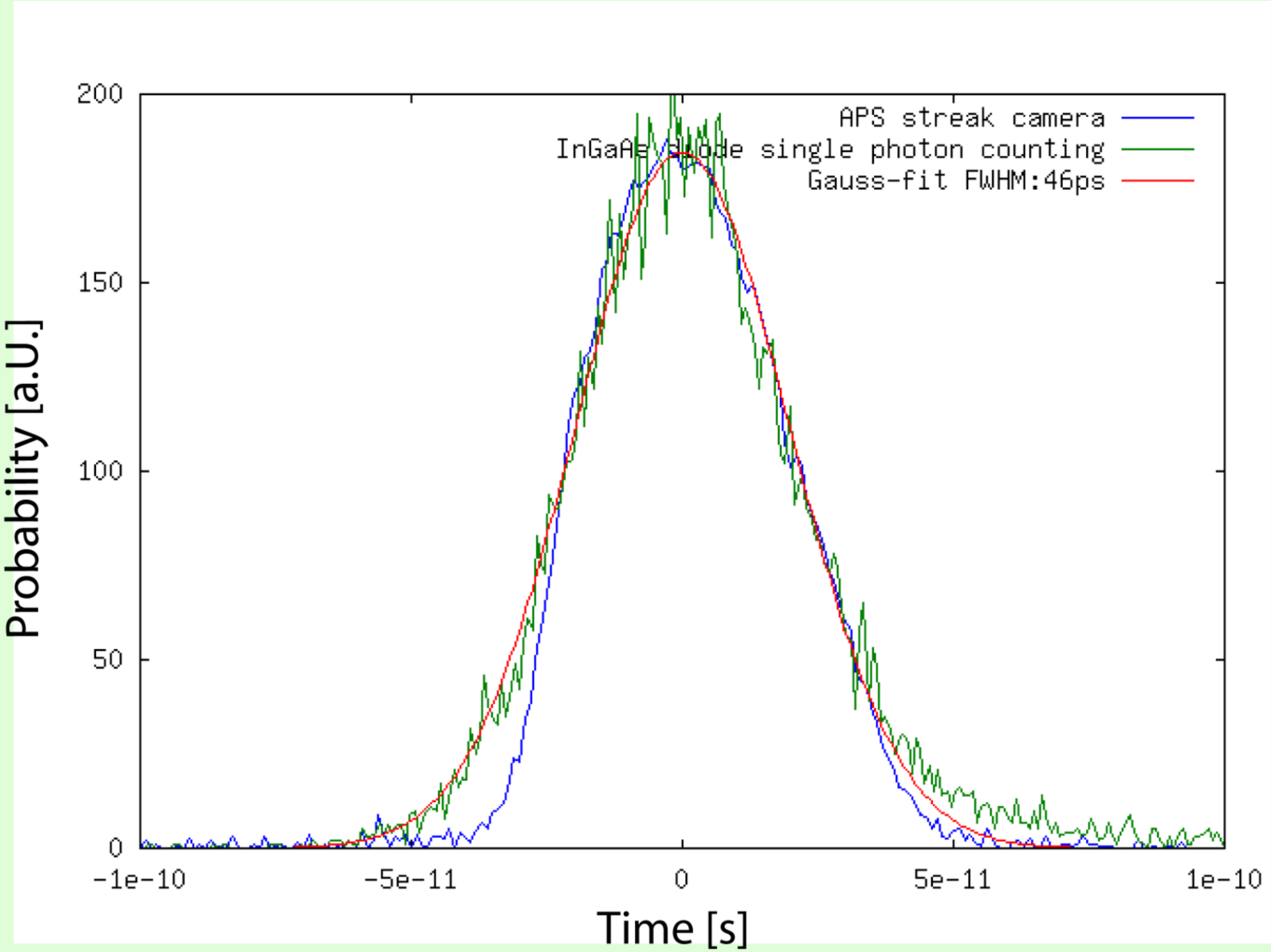
Basic Principles:
The Time-Resolution (time resolution of detector)





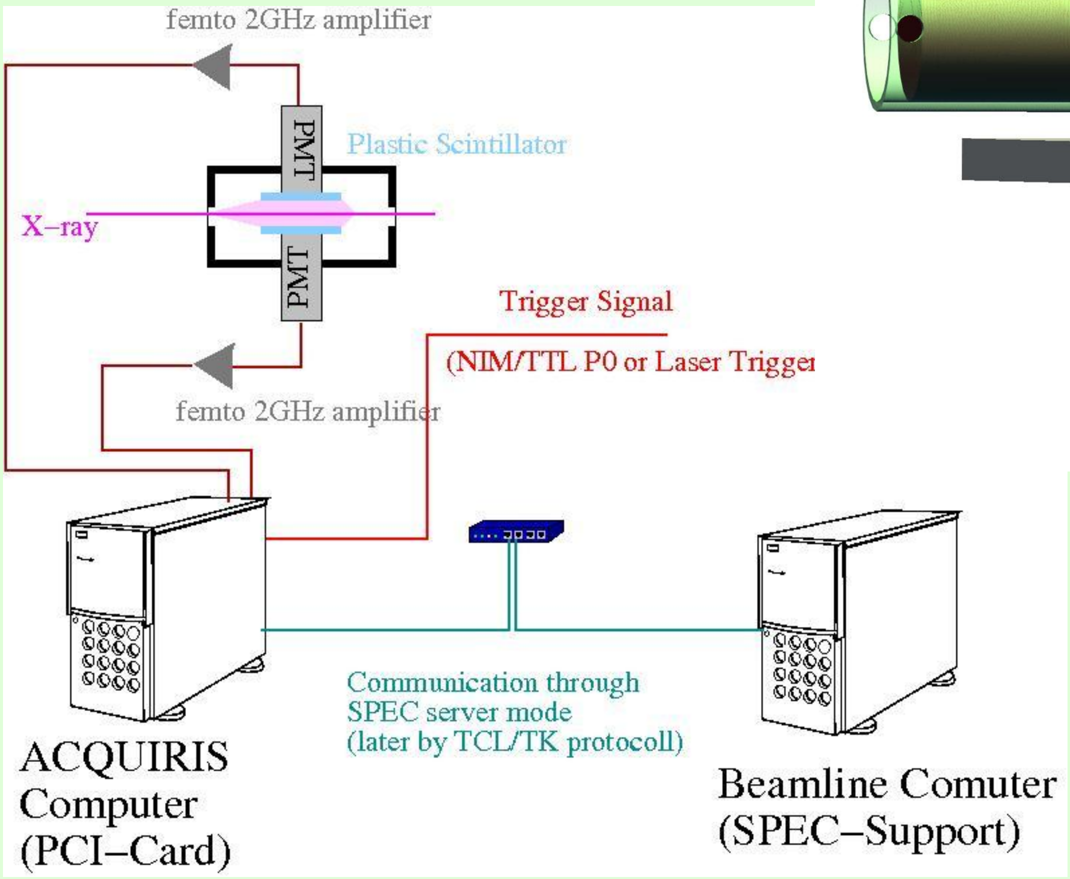
- Probe pulse covers the full time evolution of interest
- Time spectrum will be "statistically" acquired (less systematic errors)
- Time resolution is independent from timing-jitter between excitation and probe
- Available detection systems:
  - Streak cameras (~1ps, low quantum efficiency)
  - PIN-diodes (~1ps, high quantum efficiency, small solid angle first demonstrations)
  - PIN-area detectors (~1ps, ASIC design in progress)

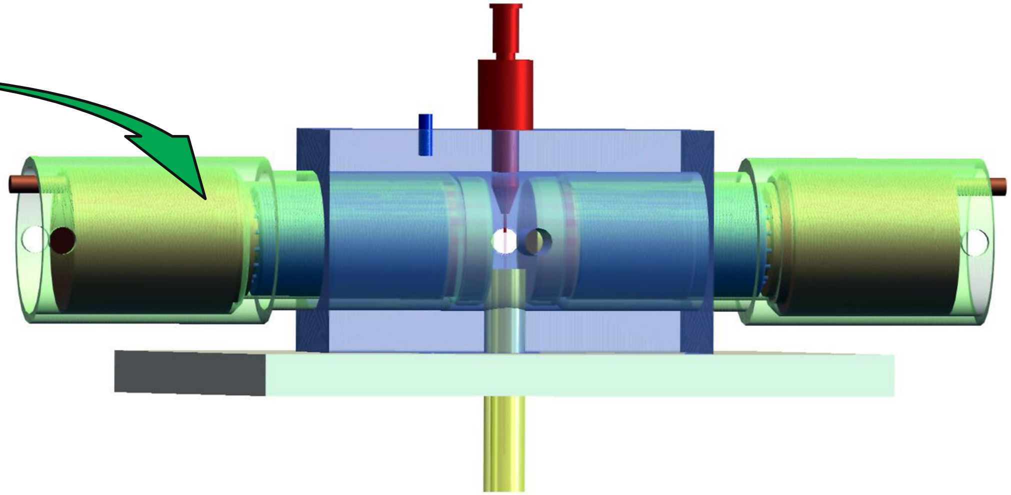
Basic Principles:
The Time-Resolution (time resolution of detector)



- First tests show resolution of about 3ps
- Only available for single element
- Work on multielement system in progress (first 10-20 element system available in 18 month)
- ASIC design in collaboration with HEP (University of Chicago)
- Detector Unit: InGaAs-PIN diodes with 40µm active area

Basic Principles:
The Experimental Setup





- Multi-Photon counting
- Digital processing
- Optimized solid angle (20%)
- Lydle-detection principle (Z-1 filter, soller-slit, non energy resolving detector)

The Limitations:
Sample Damage and Irreversible Processes

Typical damage:

- Evaporation
- Oxidation / Reduction
- Degradation

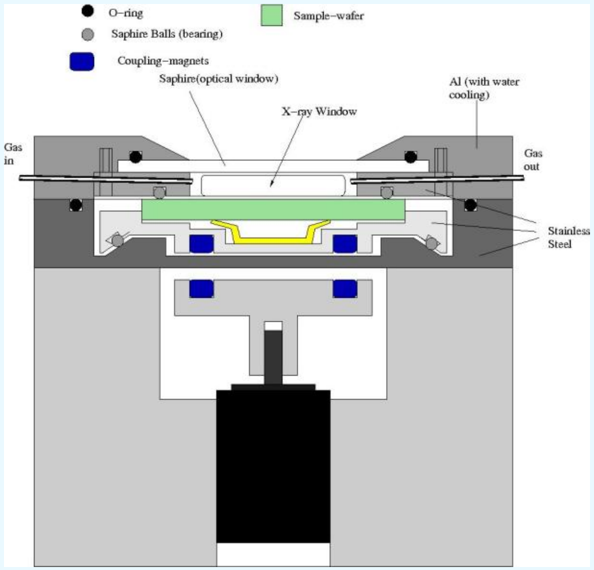
Sample moving / exchanging

Refurbishing

Coating

Vacuum /inert gas

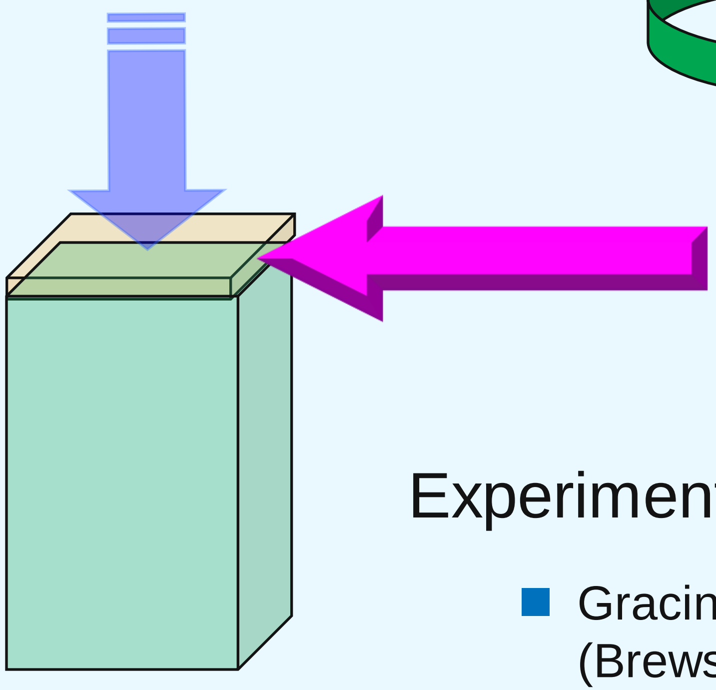
Reactor:



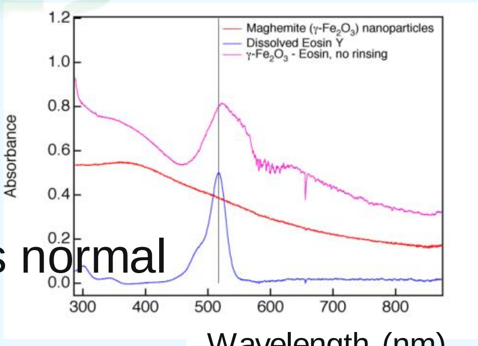
SYSTEMATIC ERRORS AND LARGE SAMPLE QUANTITIES

The Limitations: Hugely Different Absorption Coefficient for Pump & Probe

Excitation absorption length: typically 100nm or shorter
Probe absorption length: typically 10µm or longer



POOR SIGNAL / BACKGROUND PROPERTIES



Experimental ways out:

- Gracing incidence Geometry for x-rays normal (Brewster) for excitation
- Dilute sample system: dispersions of nano-particles
- Excitation wavelength tuning

The Limitations:
Largely Different Repetition Rates for Pump & Probe

Laser

Rep-Rate	**Power/pulse**	**Spectral range**
[Hz]	[mJ/pulse]	
1-10	50-100	IR/optical/UV
1K-10K	1-0.5	IR/optical/UV
100K-10M	0.05-0.01	IR

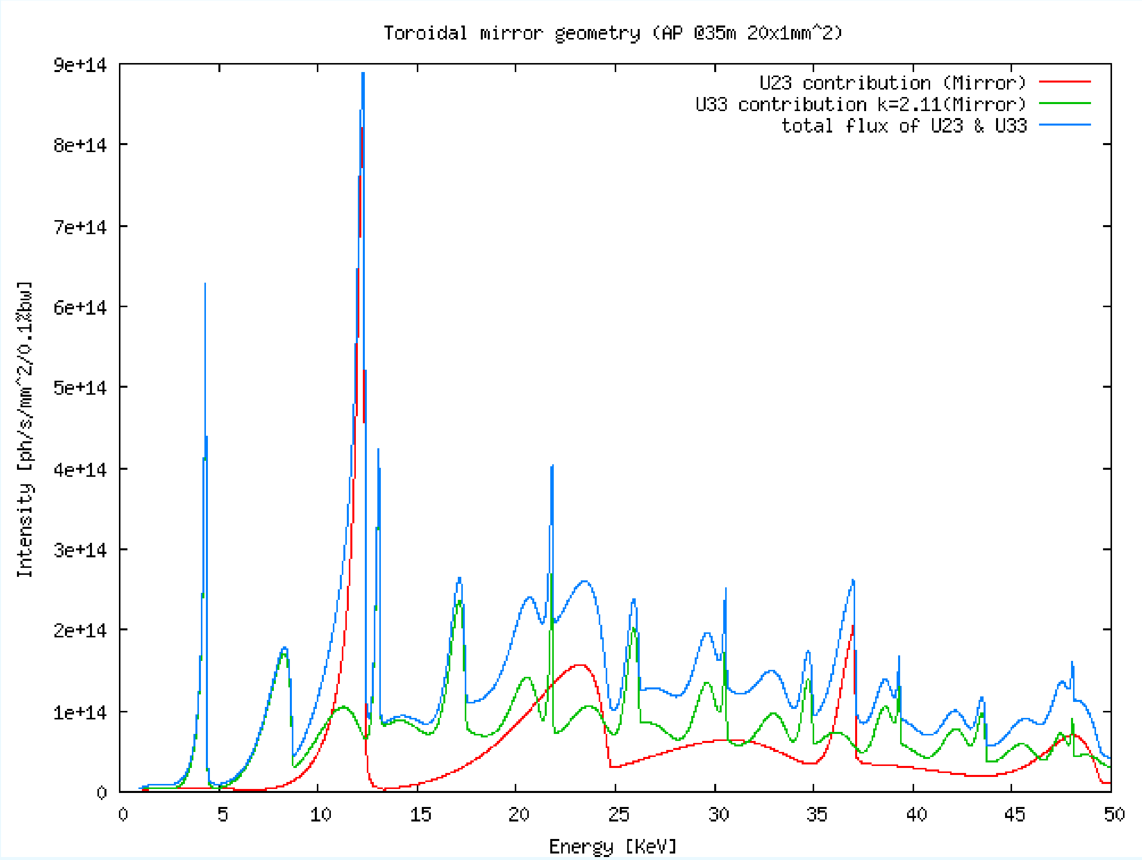
X-ray (Synchrotron)

6.5 MHz (APS standard mode)

POOR SIGNAL / BACKGROUND PROPERTIES

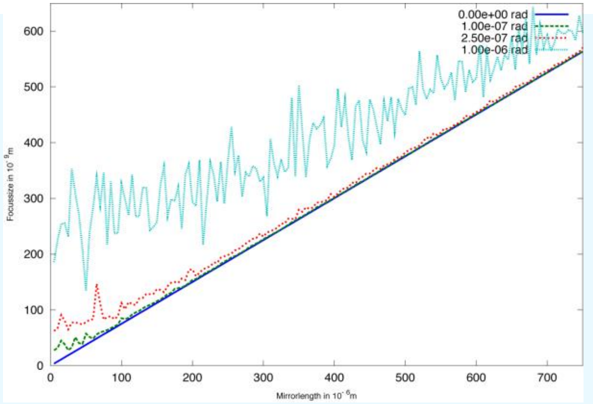
The Limitations & Solutions
High Flux Beamlines

Example of two inline undulator beamline (11-ID-D/APS):

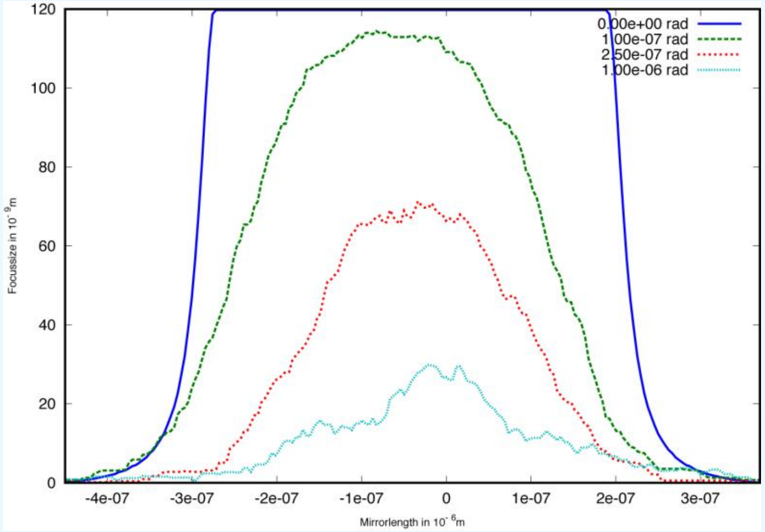


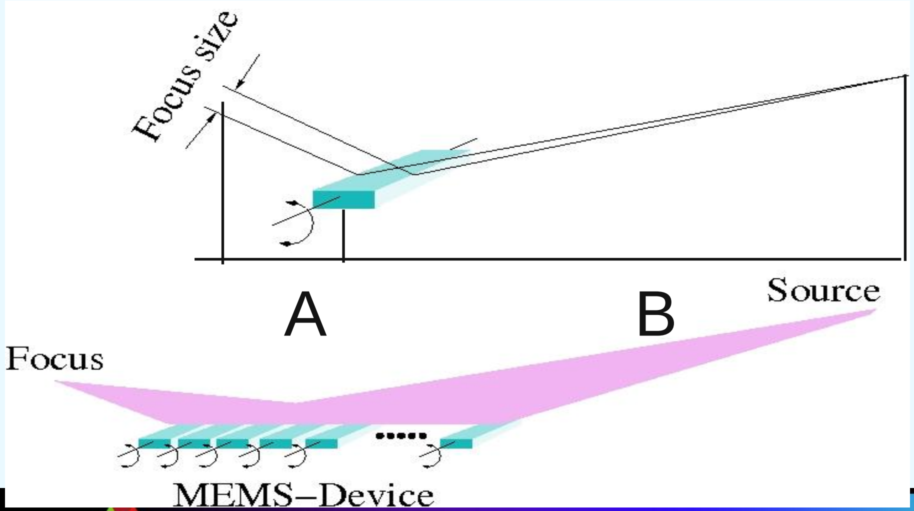
- Long straight section
- Multiple specialized (inline) undulators (restriction of energy range)
- Large acceptance angle of beamline optics
- High heat-load optics & front-end
- Variable bandwidth monochromators

Limitations & Solutions: Micro/Nano-Focus Provides Flexibility for Excitation Wavelength



New approach using MEMS-technology?





- Wavelength flexibility costs pulse power
- -> low excitation rates
- Strongly focusing to keep power-density constant

- Variable focus size
- Scanable focus spot
- Large collection efficiency
- Very fast adjustable (shot-to-shot)?
- Beam-shaping capabilities

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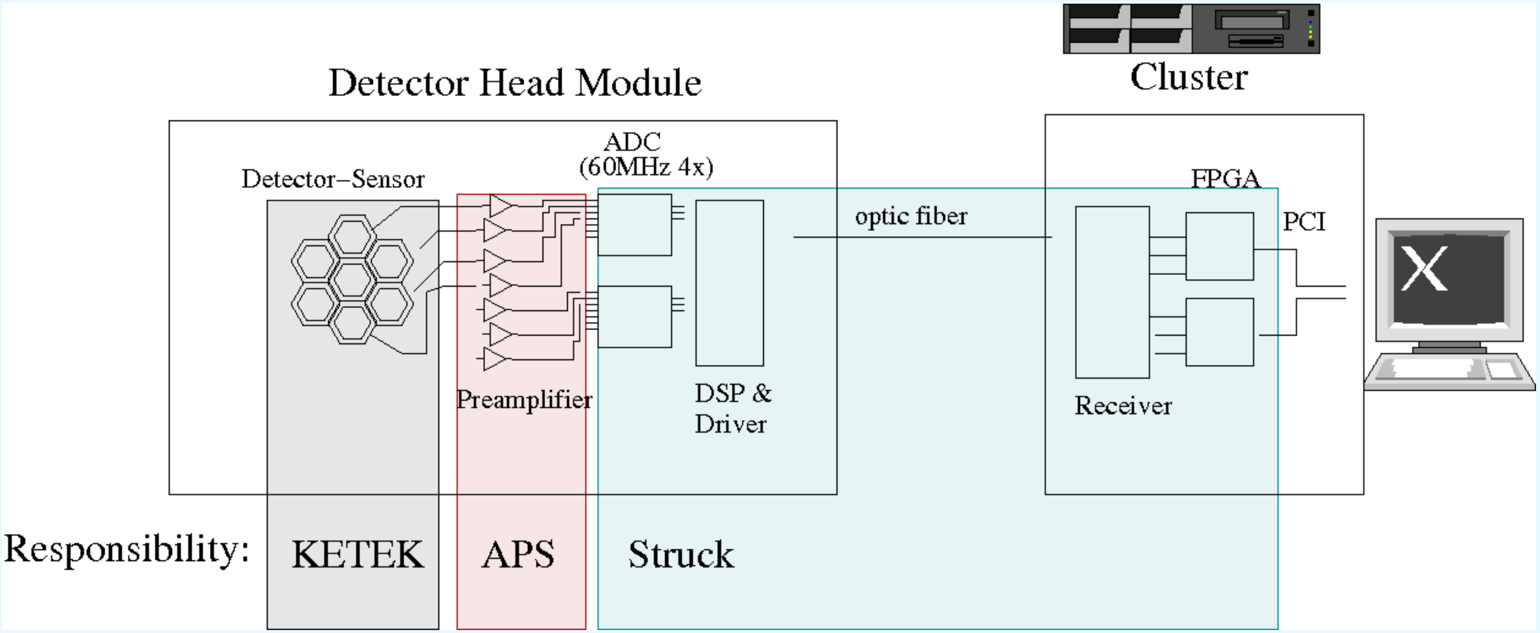
Limitations & Solutions
The Fluorescence Detection System

APS Mode	24-Bunch	324-Bunch	1296-Bunch
Repetition Rate	6.5MHz	88MHz	352MHz
Bunches/µs	6-7	88	352
Photons/Bunch (ID($5x10^{13}$)/BM(10^{12}))	7.7M / 154K	0.57M / 11.4K	0.14M / 2.8K
Fluo-Photons/Bunch (1%Fe in light matrix)	385K / 7.7K	28.5K / 570	7K / 140
Photons in Detector / Bunch (10% solid angle/ 10% efficiency)	3.8K / 80	285 / 6	70 / 1

A 10.000 element system will be required to utilize all photons

Limitations & Solutions
The Fluorescence Detection System: Conventional SDD System

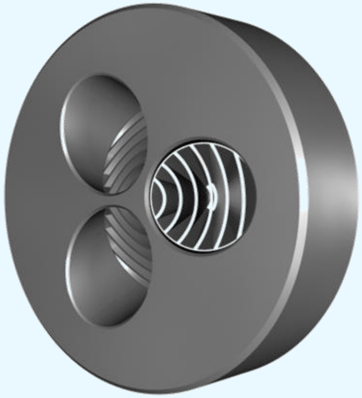


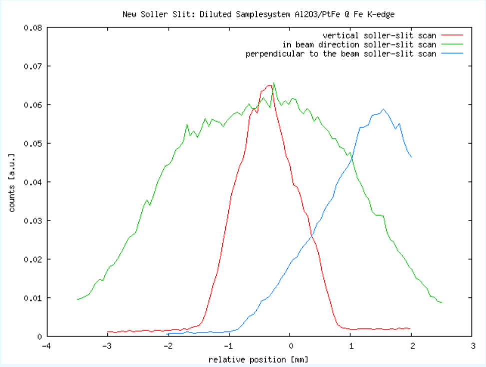
- Monolithic front chip (commercially available)
- Preamplifier (linear amplifier) “home-made” and optimized for ADC
- ADC/sender/receiver: industrial collaboration
- Digital processing in consumer electronics (GPU’s?)
- Required time spacing: ~120ns

Cost per channel $500-$1000

Total cost about $1M for 1000-2000 SDD system

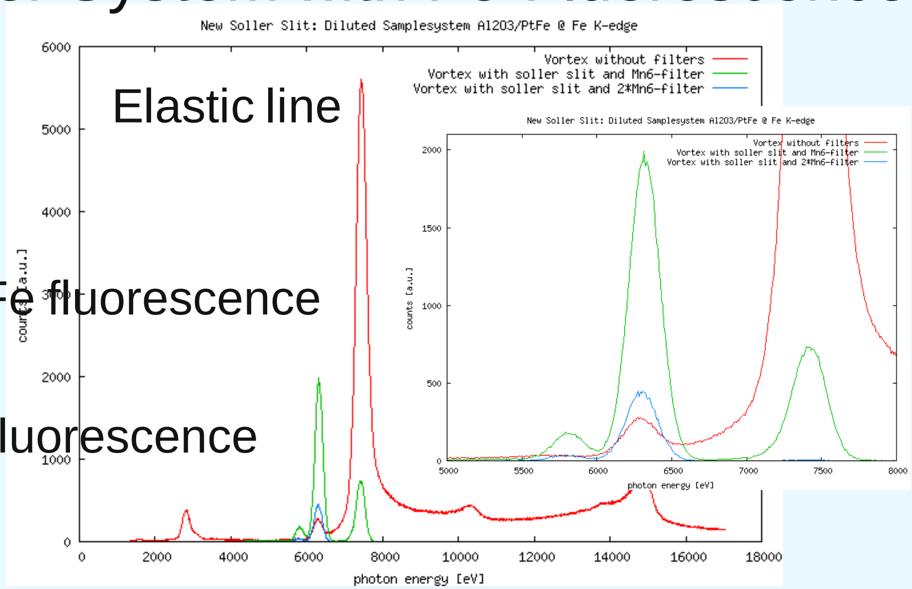
Limitations & Solutions
The Fluorescence Detection System: Multi-Photon Detection

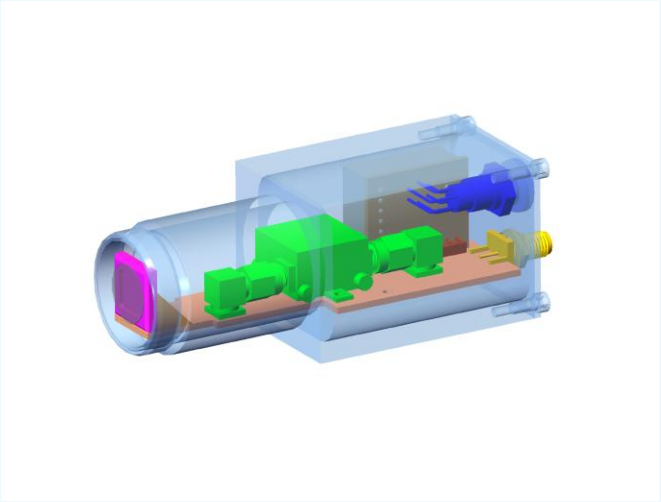




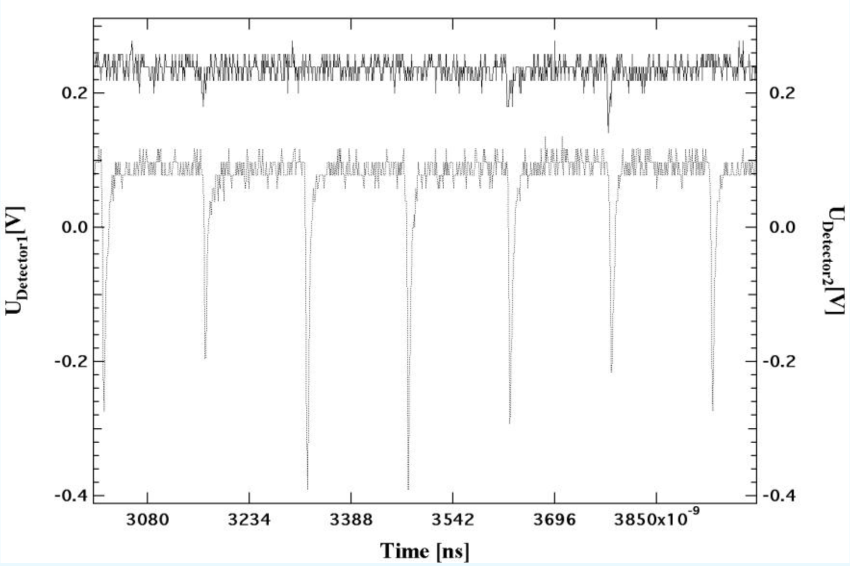
- Energy resolution by filter-systems and filters/crystal optics
- Utilization of modern rapid prototyping techniques
- Fast detection systems like plastic-scintillators/PMT or APD’s

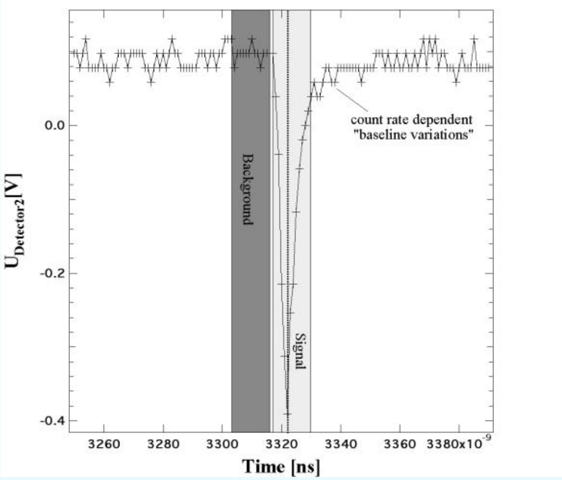
Filter System with Fe-Fluorescence





Limitations & Solutions
The Fluorescence Detection System: Digital Processing





- Usage of signal averager (1GHz sampling rate / 1ms storage
- Acts like oscilloscope with very small dead time between triggers (50µs)
- Maximal counting time per point about 60s
- Read-out overhead ~100ms
- Data analysis happens after memory is read out
- Fitting of the detector response function to the measured signal
- About 5 order of dynamic range
- Maximal 100counts per detector unit (1 photon ~25mV peak)

Sample Requirements

- No standard Experiments: Each system has to be discussed
  - Flat thin samples (thickness optimized to optical absorption)
  - Solution/particle systems are possible
- Scientific problem has to be well characterized
  - Optical pre-characterization
  - Large parameter space to probe
  - X-rays are very selective !
- Good knowledge about ground state experiments
  - Sample damage
  - Good reference (for proposed excitation models)
  - Good theoretical knowledge

Conclusion

- Laser initiated time resolved techniques are relative new (since 5 years available)
- Signal/noise ratio & sample damage are the most important limitations
- Many technologies are around to overcome the experimental problems but they are not commercially available (large development effort)
- Typical time resolution is about 80ps (groups are working to reach 1ps)
- X-ray techniques are highly specific probes therefore the scientific problem has to be well defined
- You will need well characterized samples