SESAME-JSPS School
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Time-Resolved (Pump-Probe) Experiment

to watch structural dynamics by using the pulsed nature of synchrotron radiation

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Time-Resolved (Pump-Probe) Experiment

Motivations

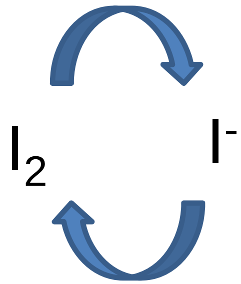
- **Can we visualize structural dynamics at atomic scale by using synchrotron radiation?**
- **Can we watch a “molecular movie”?**

An Example: Oscillating chemical reaction

Briggs-Rauscher reaction

http://www.youtube.com/watch?v=Ch93AKJm9os&feature=related

$$\left\{\begin{array}{lcl} 2IO_3^- + 5H_2O_2 + 2H^+ & \rightarrow & I_2 + 5O_2 \uparrow + 6H_2O \\ CH_2(COOH)_2 + I_2 + O_2 & \rightarrow & 2HCOOH + CO_2 \uparrow + 2I^- \\ I_2 + HCOOH & \rightarrow & 2I^- + CO_2 \uparrow + 2H^+ \\ 5I^- + IO_3^- + 6H^+ & \rightarrow & 3I_2 + 3H_2O \\ 2I^- + H_2O_2 + 2H^+ & \rightarrow & I_2 + 2H_2O \end{array}\right.$$



50mM KI, 38mM malonic acid, 5mM $MnSO_4$, 0.88M H_2O_2, 35mM perchloric acid, 0.01% starch

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Outline of the talk

1. What is pump-probe method?
2. Pump-probe method with SR
3. Examples
4. Concluding remarks

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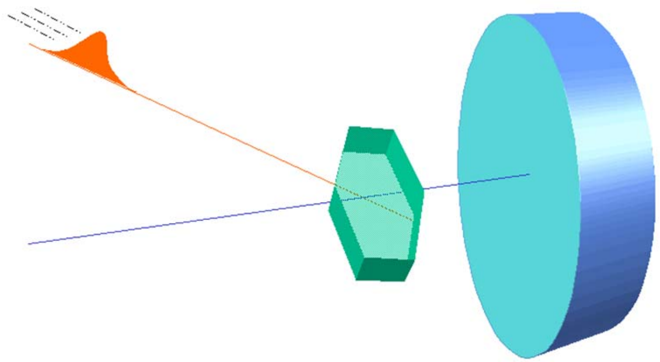
What is pump-probe method?

In a typical pump-probe experiment, the light for excitation **('pump')** modulates the initial state, and the light for measuring **('probe')** captures the snapshot.



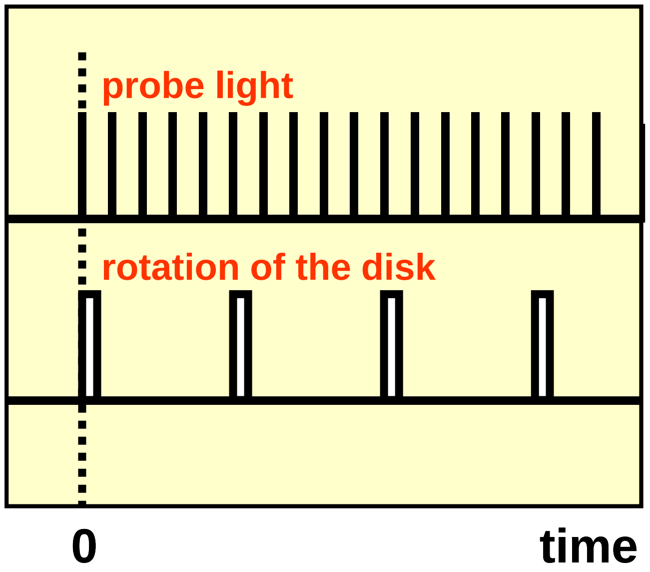
Center for Molecular Movies
http://cmm.risoe.dk/

Pump-probe method as a tool for making movies (1)

We want to watch something moving.

Case 1: Continuous Light

Case 2: Pulsed Light



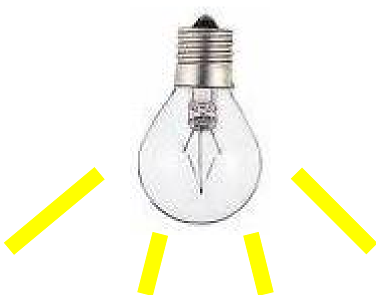
Pump-probe method as a tool for making movies (2)

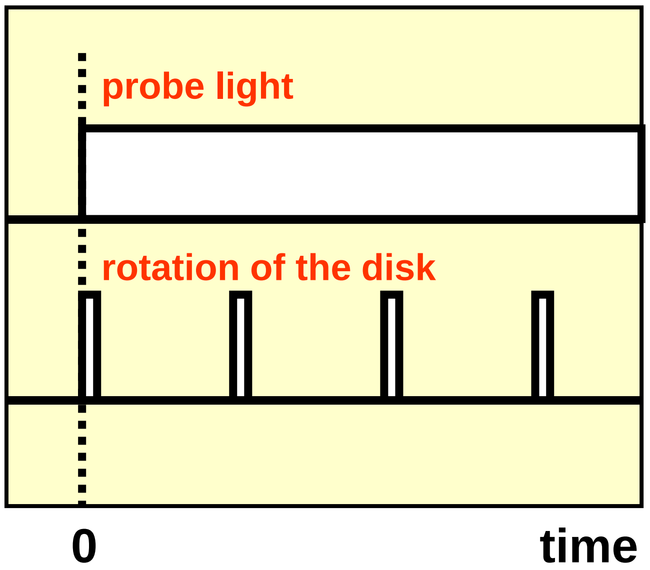
Watching the 6 guys dancing.

Pump-probe method as a tool
for making movies (3)

Continuous vs. Pulsed Light

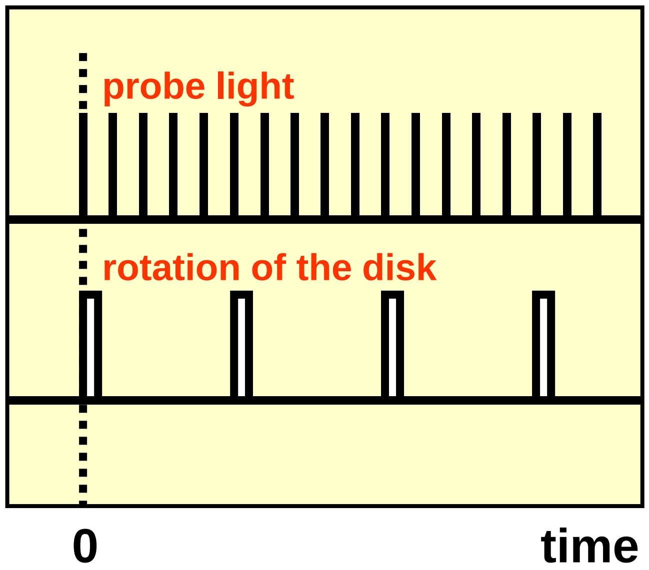
Case 1: Continuous Light





Case 2: Pulsed Light

Pump-probe movie



Pump-probe method as a tool for making movies (4)

Still image	⟷	Movie
static	⟷	dynamic
structure	⟷	mechanism

Summary #1

What is pump-probe method?

- The pump-probe method enables us to make movies.
- We need pulsed light for it.
- Timing between the pump and the probe must be synchronized.

Outline

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The pulsed nature of SR (1)

- You learned that the synchrotron radiation is pulsed light source.

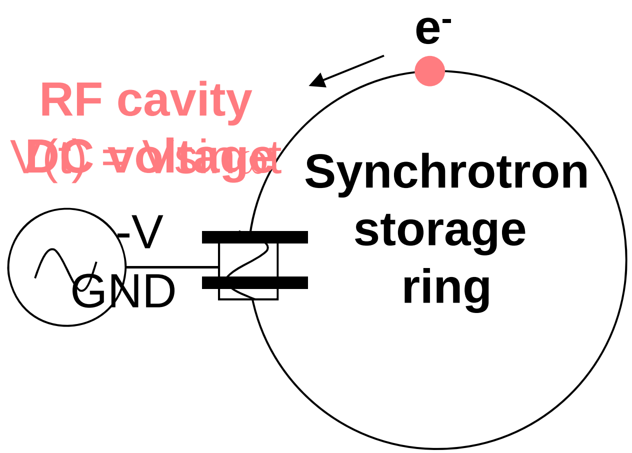
- I emphasize the importance of this feature again for pump-probe method.

The pulsed nature of SR (2)
SR movie

http://www.lightsources.org/
Institute for Storage Ring Facilities http://www.isa.au.dk/
Electron Injection, Storage and Synchrotron Radiation Light Generation in the Storage Ring ASTRID. *(Credit: Coldvision Studio/ISA)*

Why electrons are bunched?

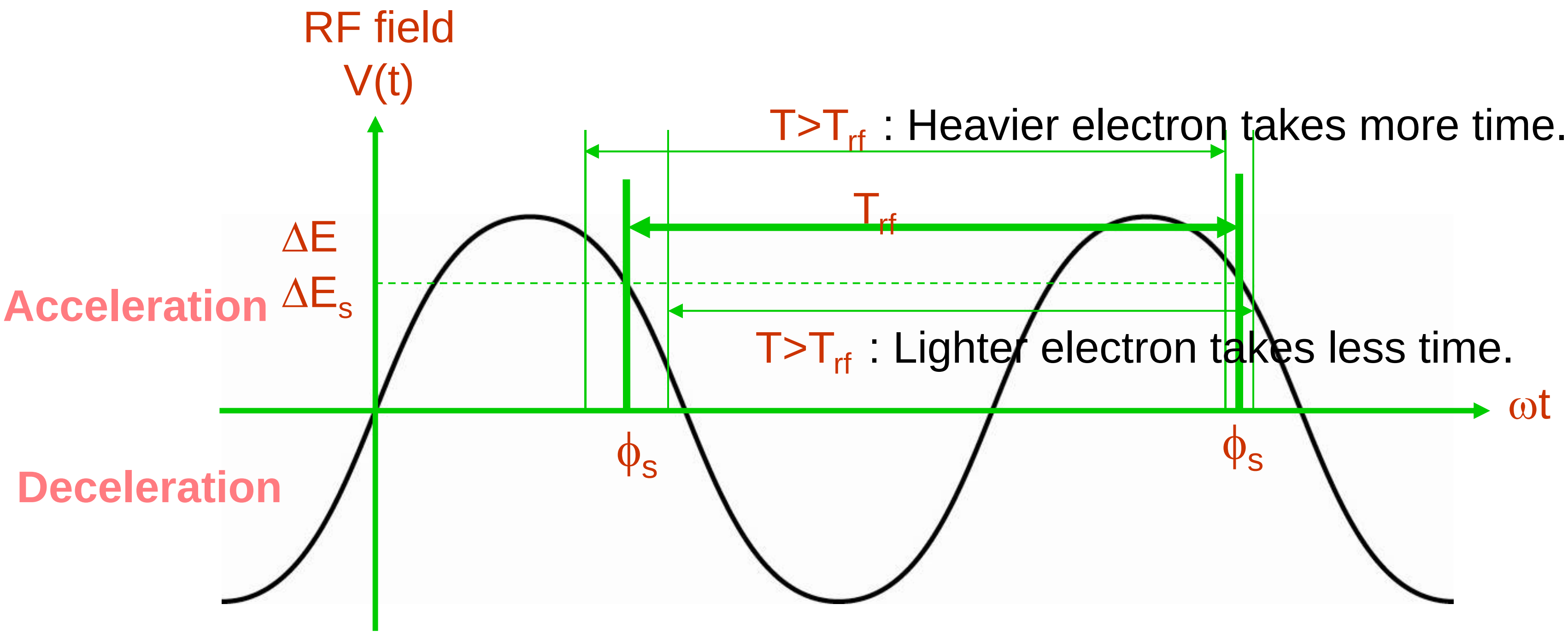
Acceleration of electrons with DC or AC voltage



(period of 1 turn) / (period of RF acceleration) = N (harmonic number)

The pulsed nature of SR (1)

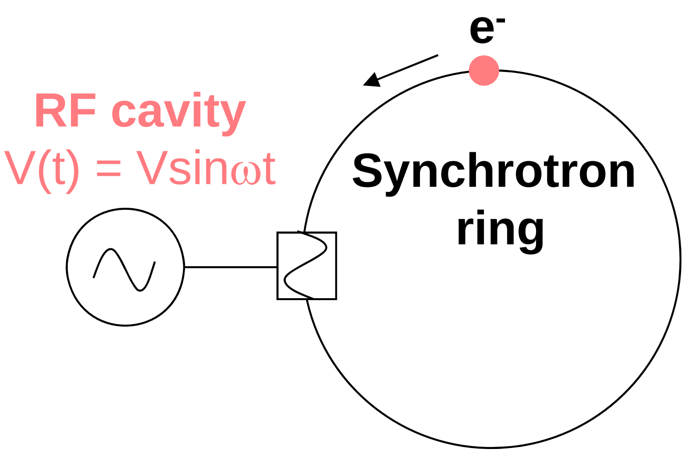
Why electrons are bunched? (phase stability)

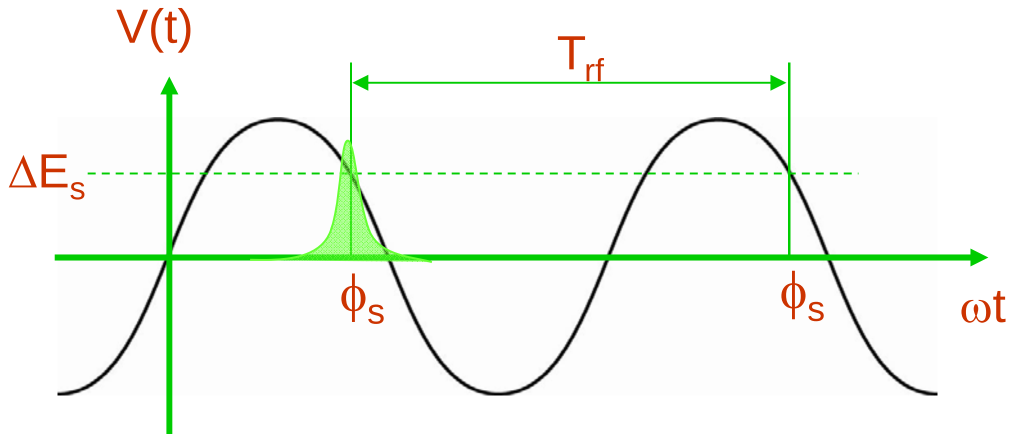


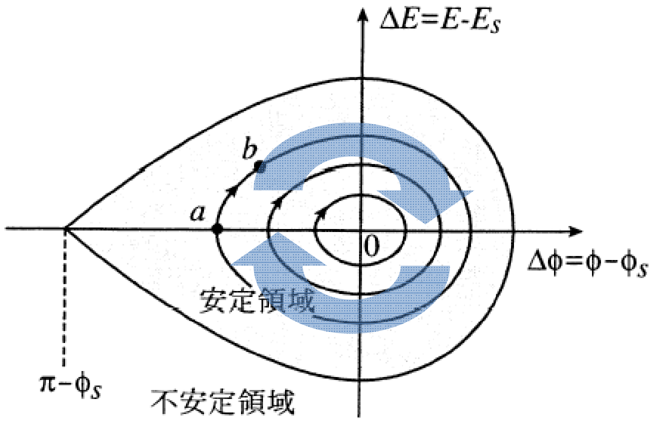
ϕ_s : stable phase

The pulsed nature of SR (2)

synchrotron oscillation







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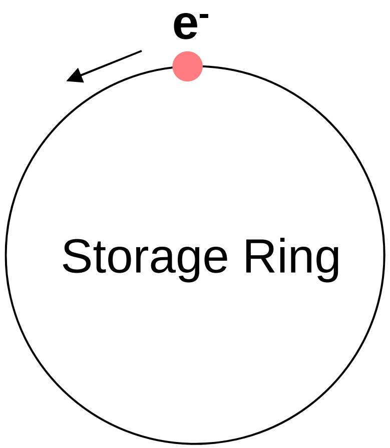
How short is the pulse duration?



Q: Bunch length in SR is typically 30 mm (1 sigma). How short is the pulse duration?

A:

$$30 \times 10^{-3} \,/\, (3 \times 10^{8})$$

$$= 100 \times 10^{-12} \text{ (s)}$$

$$= 100 \text{ (ps)}$$

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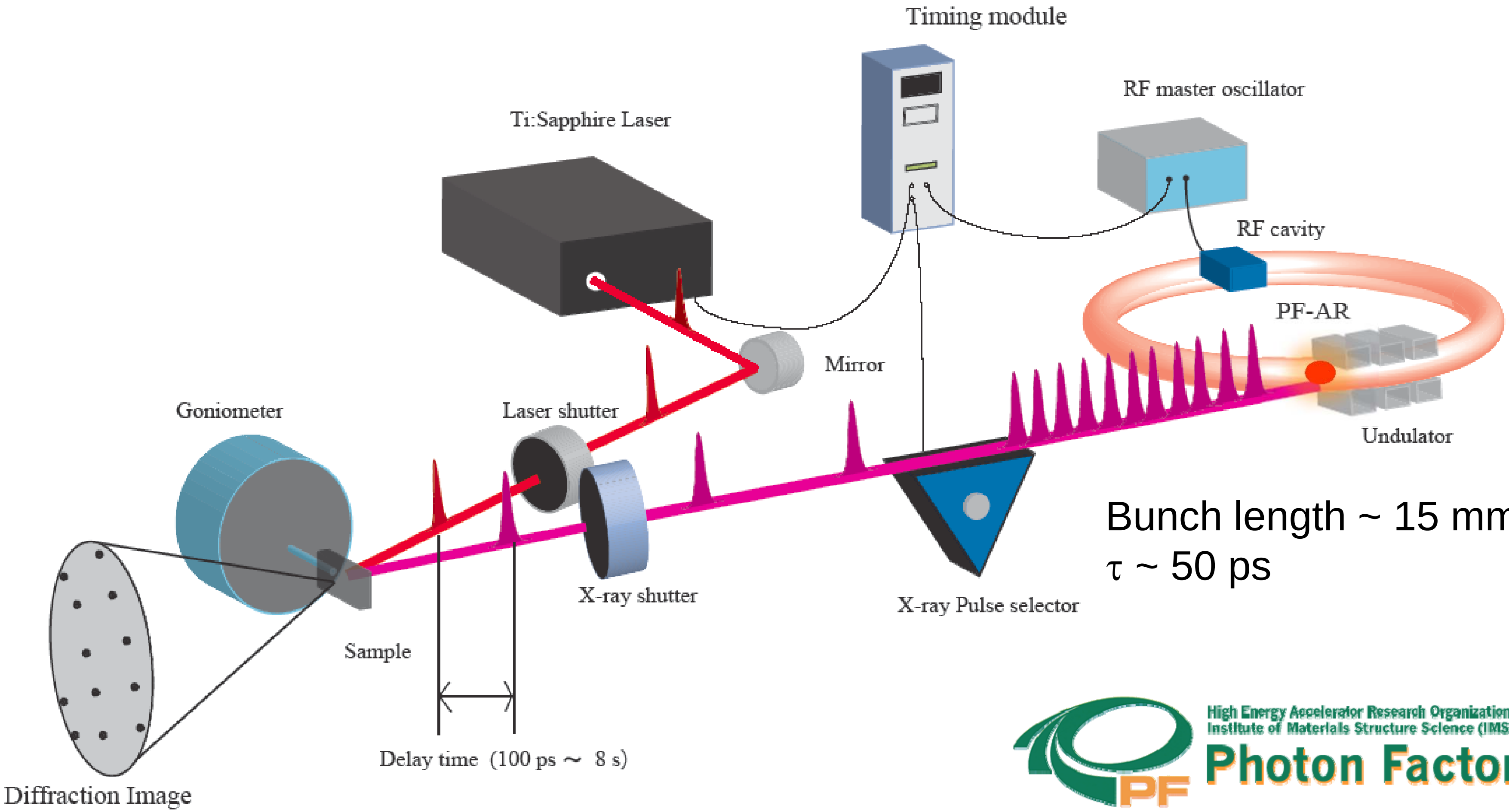
utilizing pulsed nature of the synchrotron radiation for structural dynamics studies



Bunch length ~ 15 mm
τ ~ 50 ps

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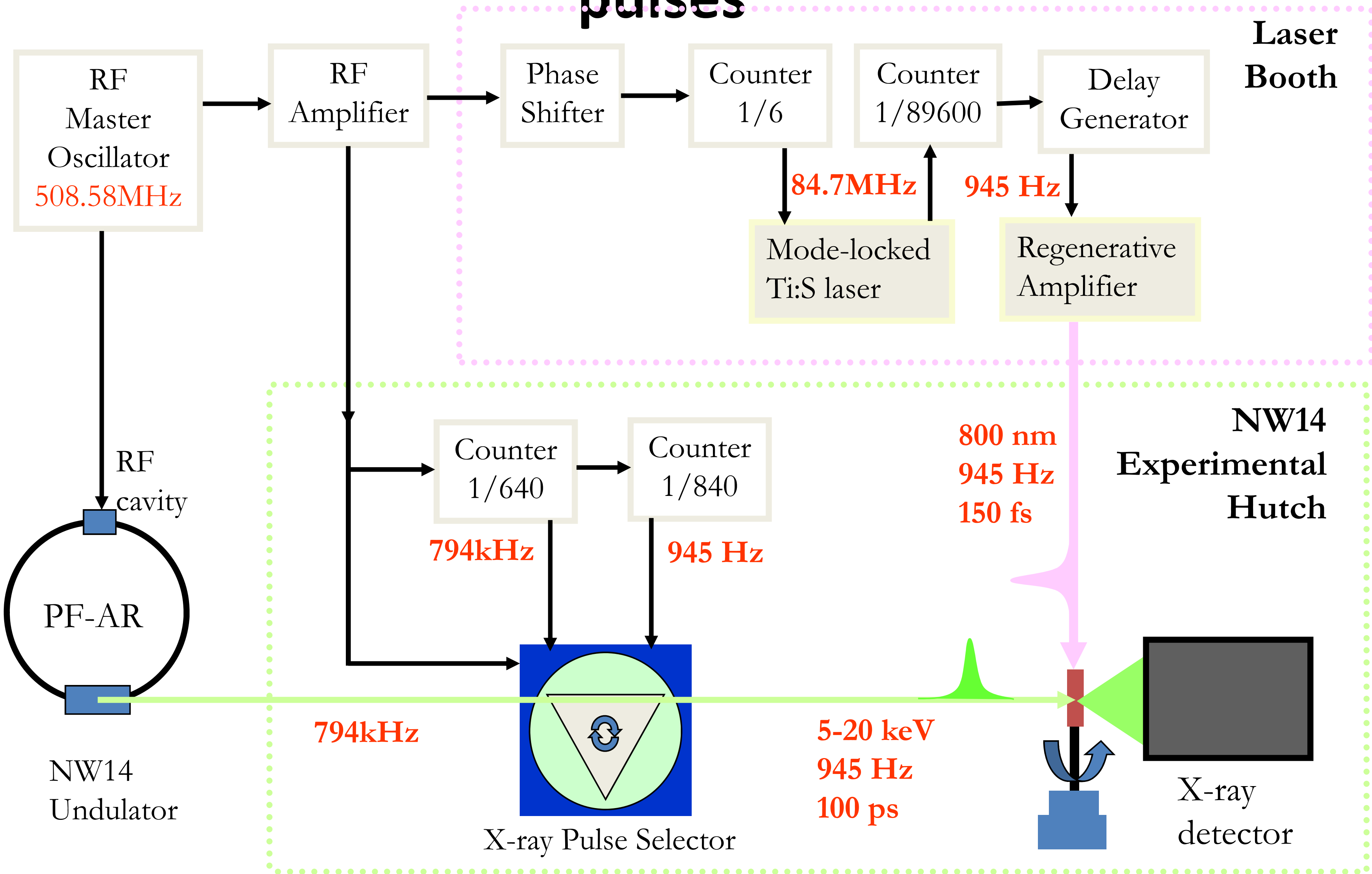
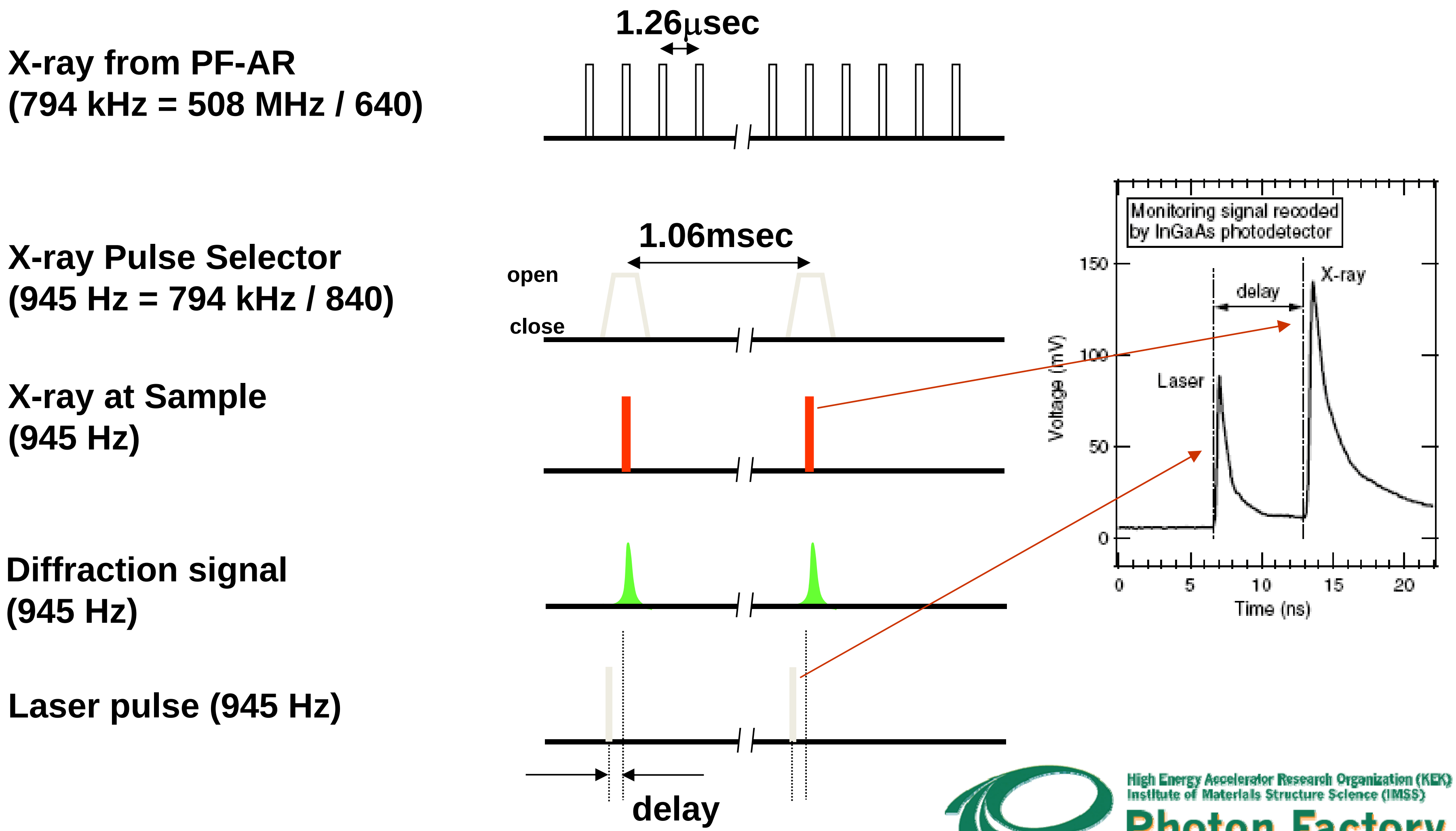
Synchronization between pump and probe pulses



TR X-ray Diffraction (1 kHz mode) timing chart



picosecond time-resolved x-ray techniques – a basic concept

synchrotron radiation x-rays :

structural studies at atomic resolution

diffraction, XAFS, scattering, etc

×

pulsed nature of SR :

time resolution ~50ps

=

molecular movies at atomic and ~50ps resolution

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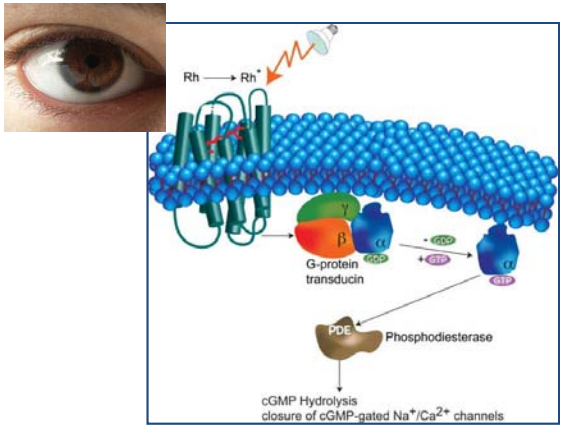
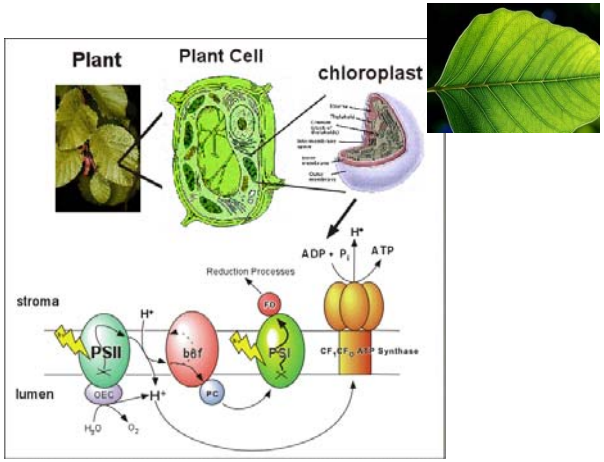
photo-induced structural dynamics

visual sensing

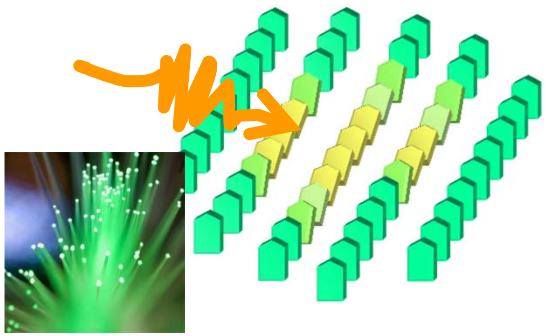


photosynthesis



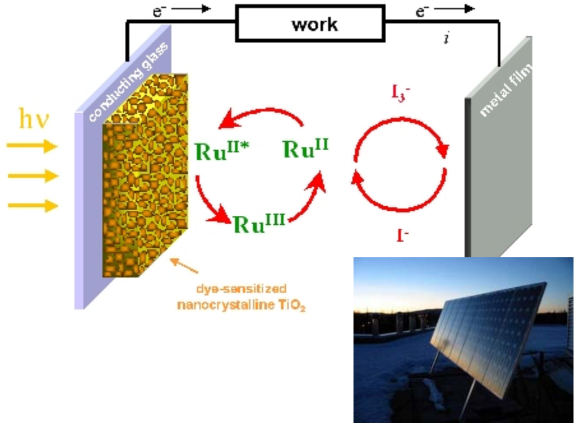
biology and chemistry

ultrafast photo-switching



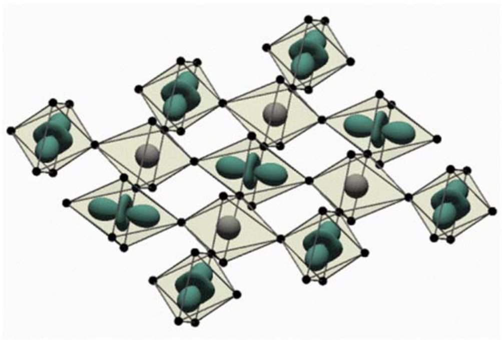
materials, energy and environment

solar cell



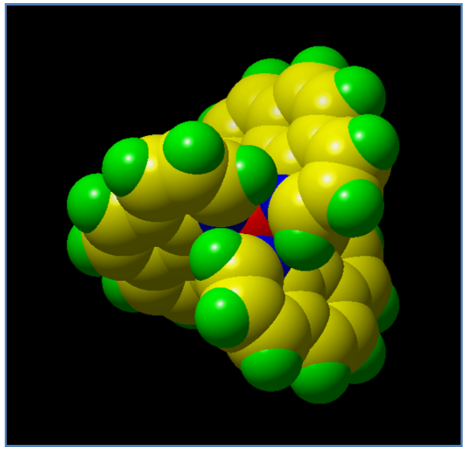
Picosocond X-ray applications at KEK

Picosecond photoresponse of perovskite manganite (NSMO) thin film (TR-Diffraction: t~ 50ps ~ 2ns)



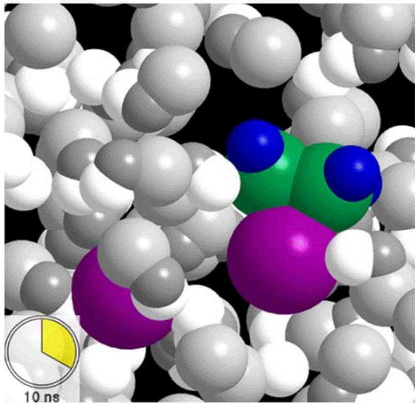
Ichikawa et al. **Nature Materials**, **10**, 101 (2011)

Photo-induced spin-crossover transition of metal complex in solution (TR-XAFS: t ~700ps)

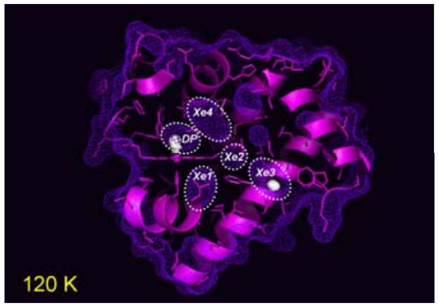


Nozawa *et al.* **J. Am. Chem. Soc., 132**, 61 (2010)

Photochemical reaction in liquid (TR-solution scattering: t~100ps~1ms)

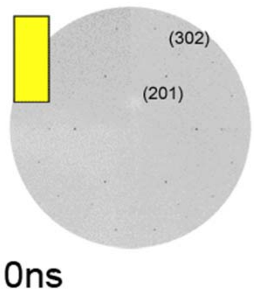


Ligand migration dynamics in protein crystal (TR-protein crystallography: t~800 min)



Tomita et al. **Proc. Natl. Acad. Sci. USA**, **106**, 2612 (2009)

Laser shock-induced lattice deformation of CdS single crystal (TR single-shot Laue diffraction: t~1ns~10ns)



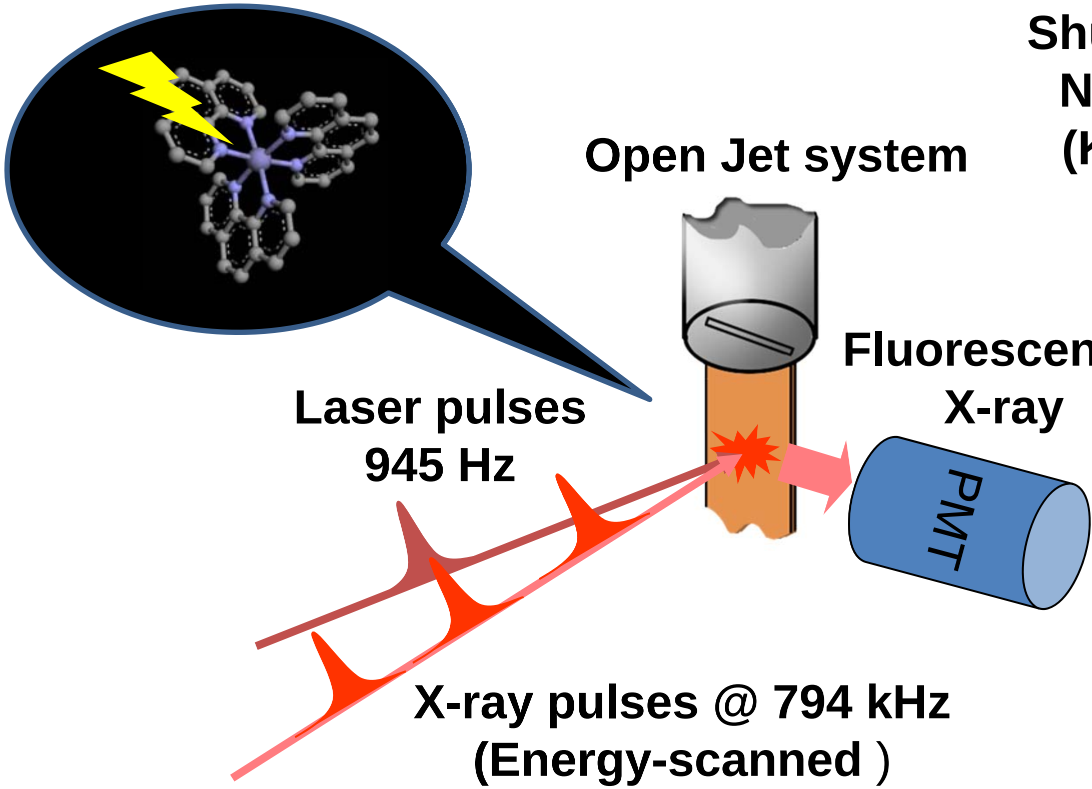
Ichiyanagi et al. **Appl. Phys. Lett. 91**, 231918 (2007)

Nozawa *et al.* **J. Am. Chem. Soc., 132**, 61-63 (2010).

Ultrafast structural dynamics of Fe complex revealed by TR-XAFS

Shunsuke Nozawa (KEK)

Tokushi Sato (KEK)



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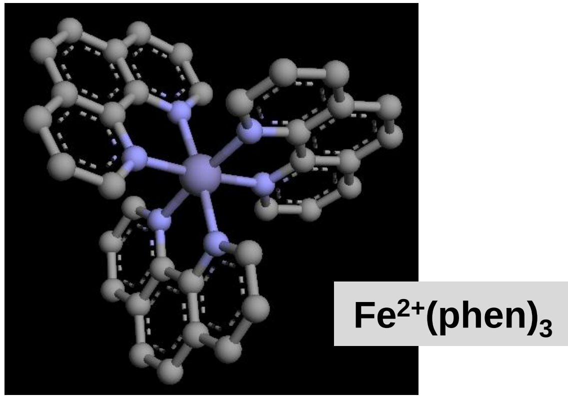
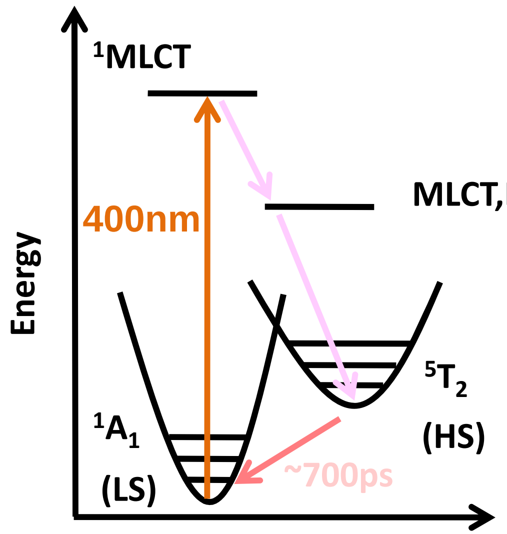
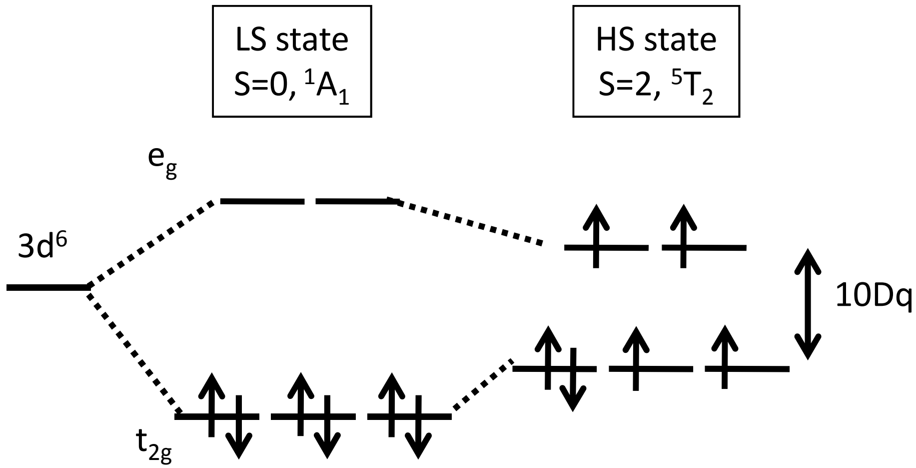
picosecond spin transition of $Fe^{II}(phen)_3$

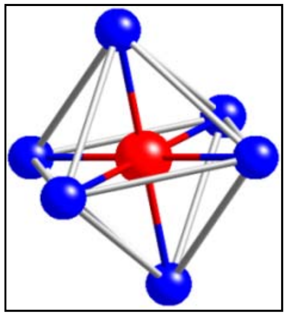


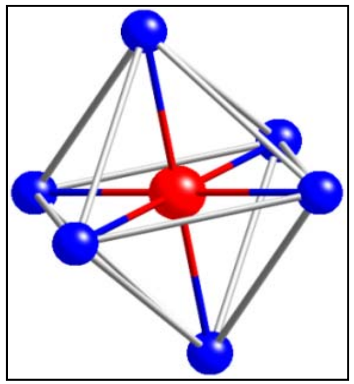
Octahedral FeN_6





FeN_6 cluster





Fe-N bond length $R^{LS}_{Fe\text{-}N}$ < $R^{HS}_{Fe\text{-}N}$

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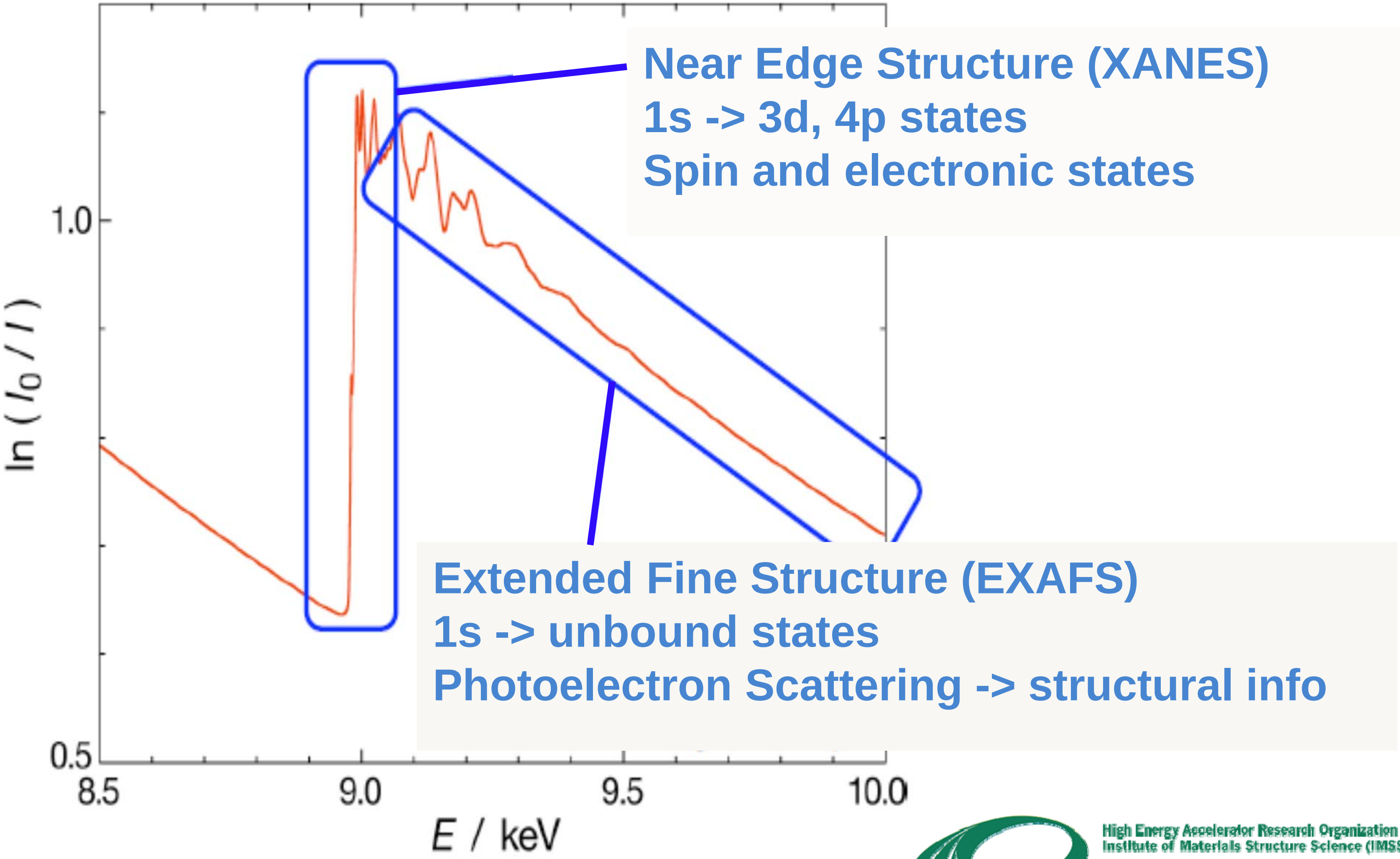
X-ray Absorption Fine Structure (XAFS)
Cu K-Edge (Cu foil, 5μm thickness)



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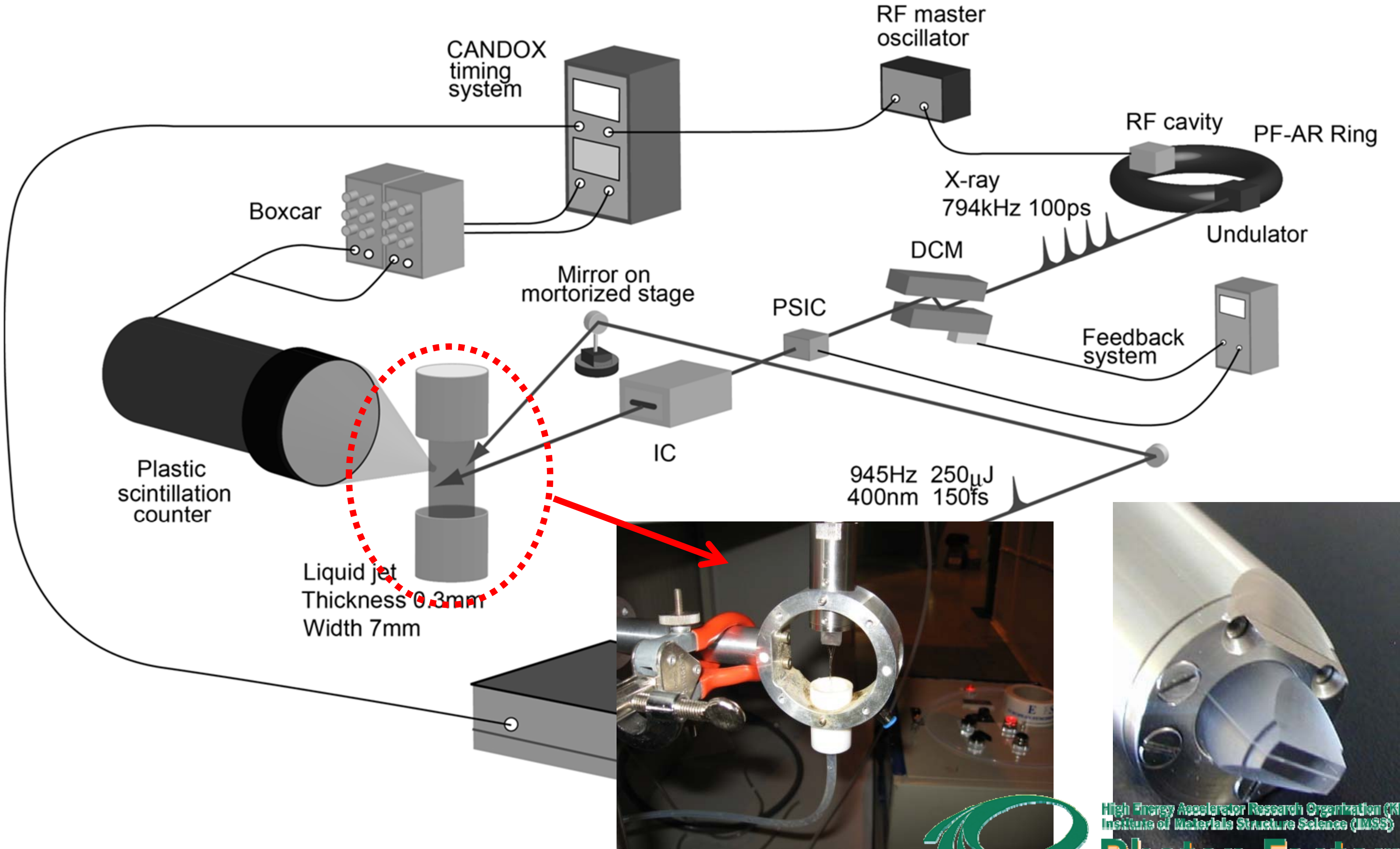
TR-XAFS: Experimental Setup



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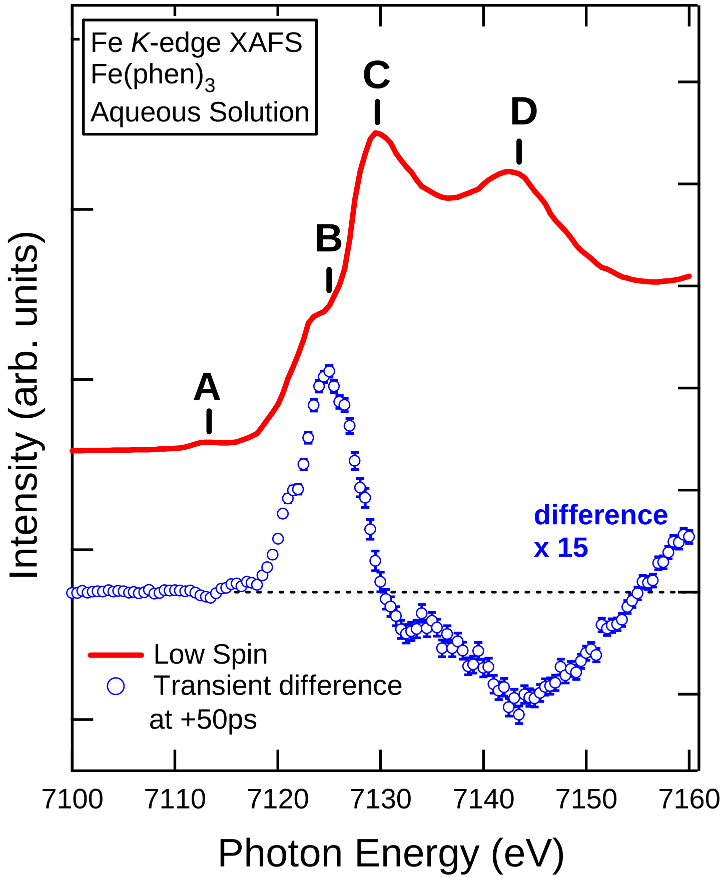
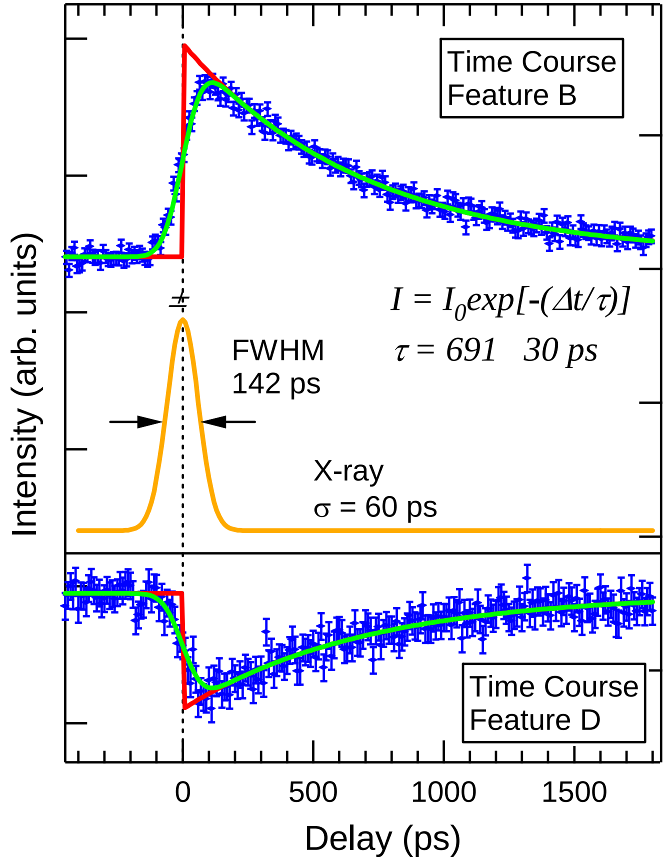
Excite state XANES





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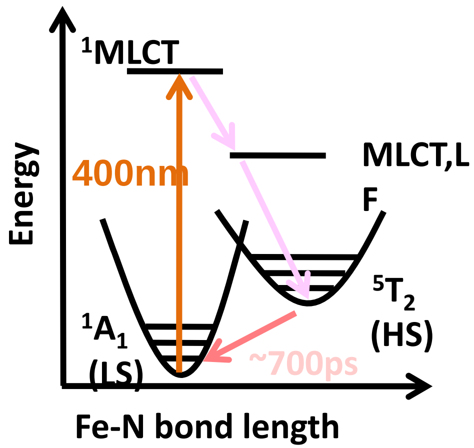
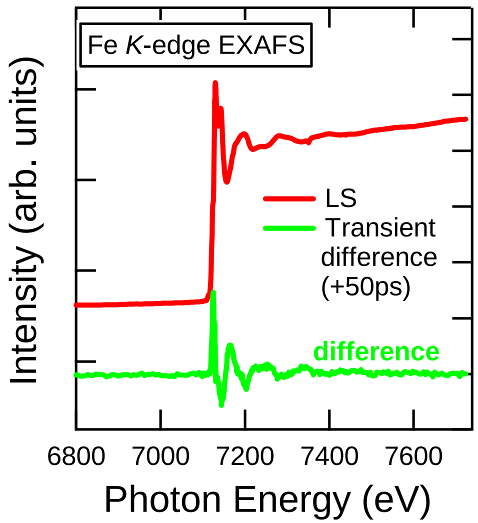
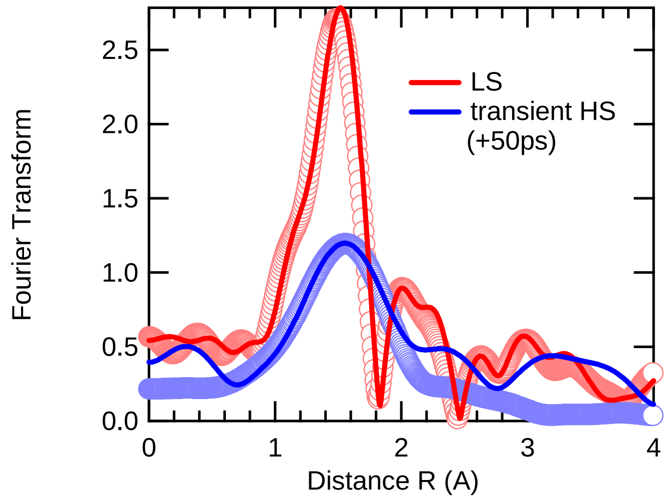
Excited state EXAFS







EXAFS analysis summary

Spectrum	$R_{Fe\text{-}N}$ (Å)	σ^2 (Å^2)
LS	1.98(1)	0.001(1)
Photo-excited HS	2.15(2)	0.011(3)

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Picosecond molecular movie!

Low Spin Ground State ($^1A_1$)

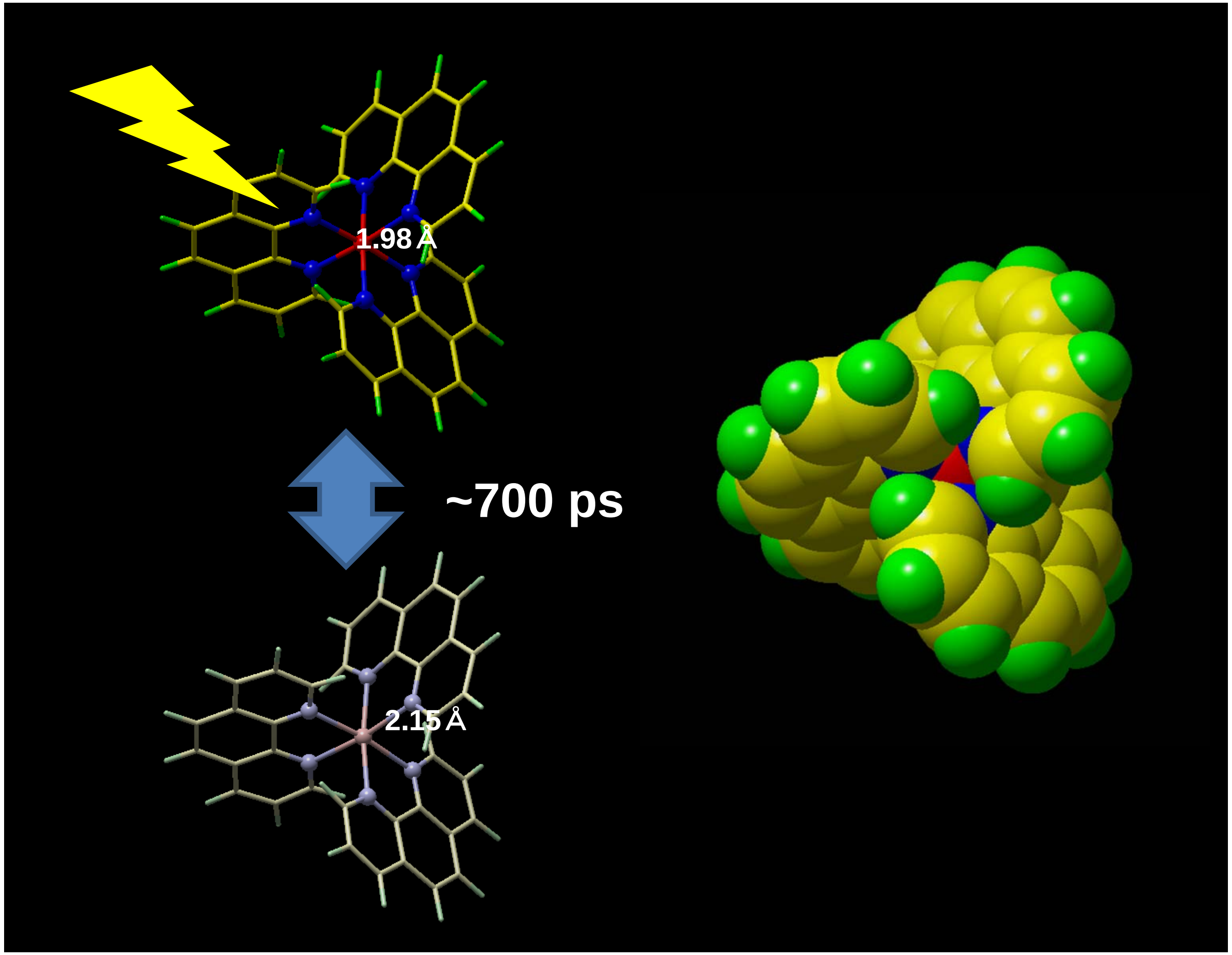

Photo-Excited High Spin State ($^5T_2$)

Nozawa *et al.* **J. Am. Chem. Soc., 132**, 61-63 (2010).

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Concluding remarks

- Pump-probe method with synchrotron radiation enables us to make molecular movies at atomic spatial resolution and picosecond time resolution. (Next generation light source (FEL, ERL) will provide femtosecond time resolution.)

- The pump-probe method is applicable to most of synchrotron measurements.

- This will be fun!

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