

**Time-resolved X-ray diffraction  
at the Photon Factory  
Advanced Ring (PF-AR) to Probe  
Photo-Induced Phase Transition in  
Organic CT Crystals**

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Photon Factory (PF)**

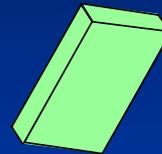
**ERATO Koshihara Non-equilibrium Dynamics Project,  
Japan Science and Technology Agency (JST)**

# Outline

- 1: Characteristics of Photo-Induced Cooperative Phenomena (Photo-Induced Phase Transition :PIPT)
- 2: **Ultra-fast (THz), highly sensitive Non-equilibrium Melting of Charge Order in Organic Super Conductor Candidate (EDO) even at 260 K (Metal-Insulator Transition )**
- 3 : **100-ps resolved X-ray diffraction at the Photon Factory Advanced Ring (PF-AR)**
- 4: Summary

# What is photo-domino ?

- **Cooperative response** due to cooperative interaction



Localized

- Control of electron-lattice-spin (multi-)coupling by internal correlation effect (**instability**)



- Various Application

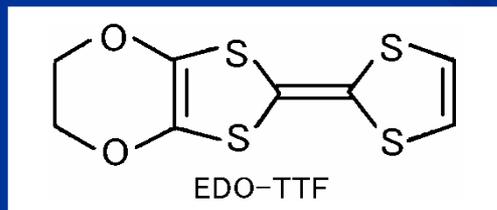
Cooperative response

$\frac{1}{4}$  filled  $A_2B$  salts occupy quite important position due to Charge, Spin and Lattice coupled multi-instability.

# Targets for picosecond-resolved X-ray diffraction

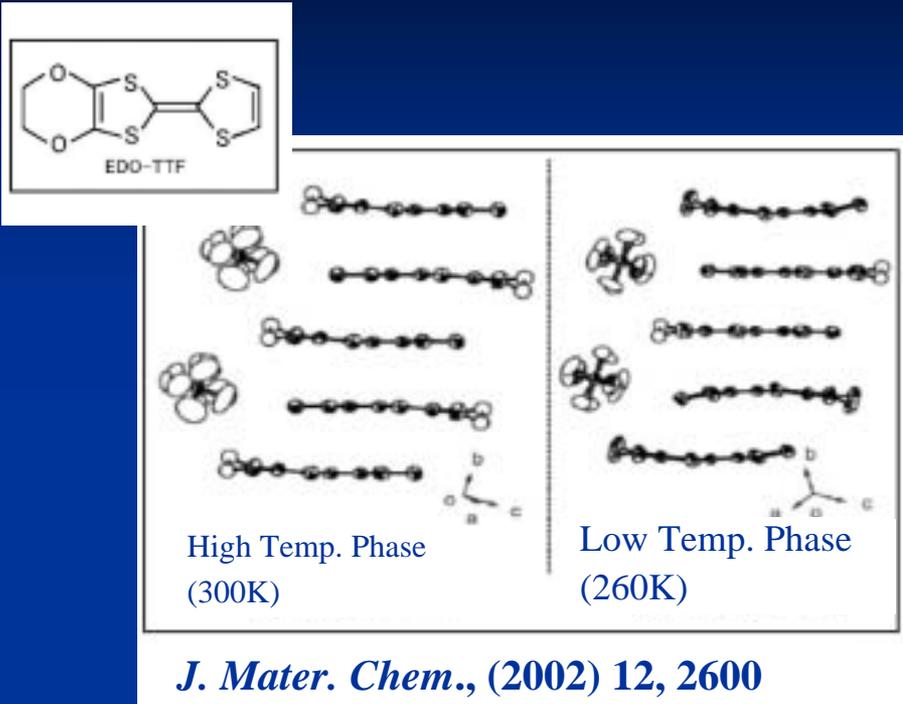
- Organic or inorganic materials where electronic and structural changes are strongly coupled
- Photoactive proteins
- etc ...

Metal-to-insulator transition in  
 $(\text{EDO-TTF})_2\text{PF}_6$



A. Ota, H. Yamochi, and G. Saito  
J. Mater. Chem. **12** 2600 (2002).

# Crystal structures of (EDO-TTF)<sub>2</sub>PF<sub>6</sub>

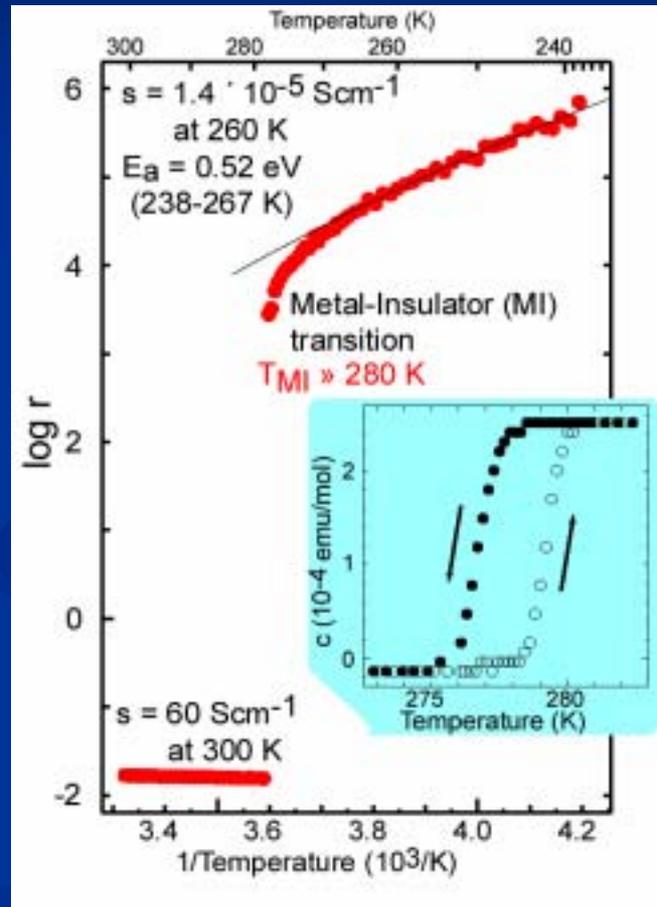


Peierls transition

Charge Ordering

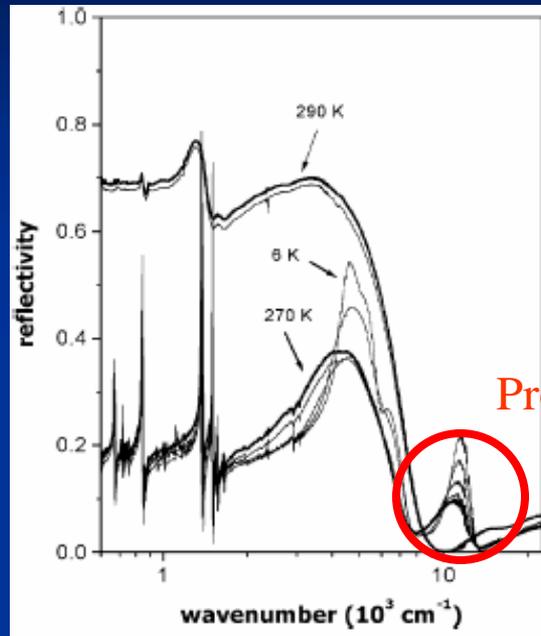
Anion Ordering

## A novel M-I transition

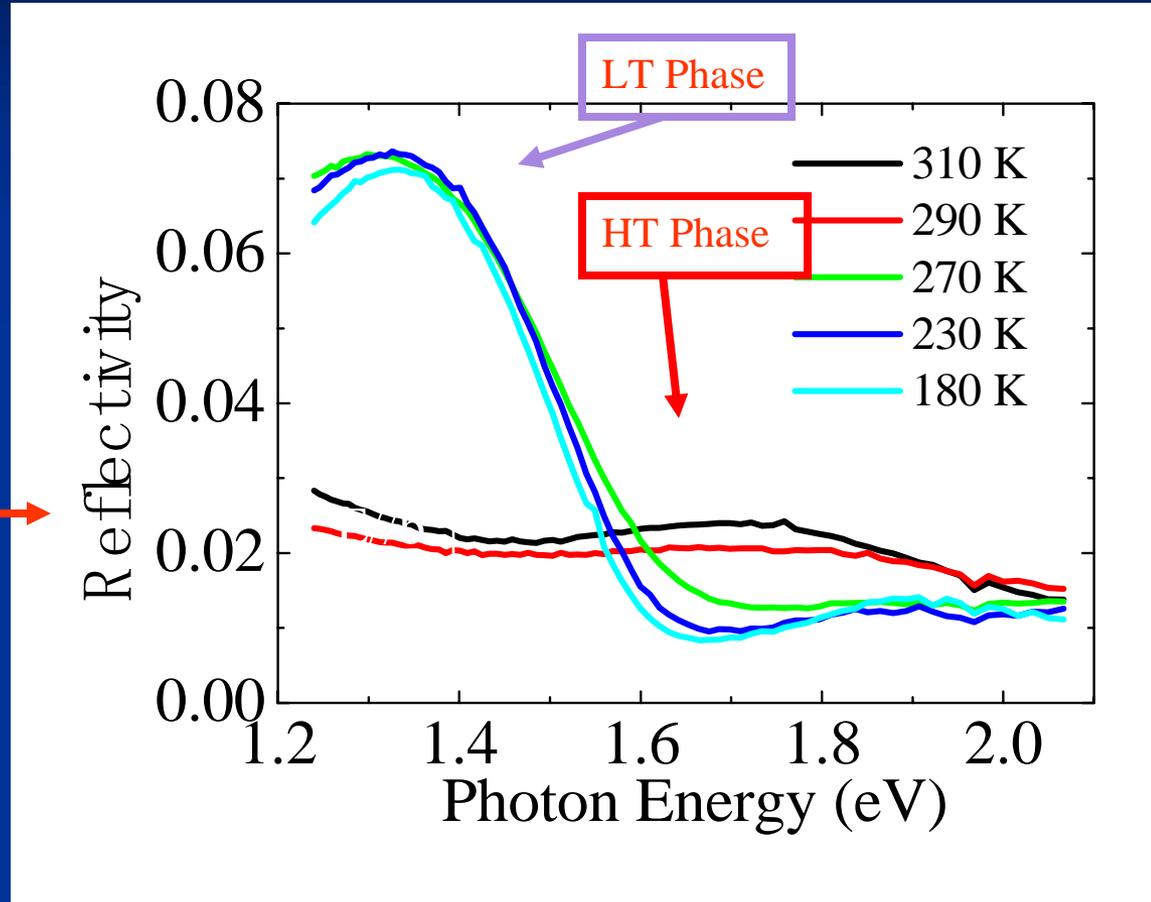


Important target for photo-induced phase transition

# Temperature Dependence of Reflectance Spectra



Probe



O.Drozdova, K.Yakushi, A.Ota,  
H.Yamochi, and G.Saito

Synthetic Metals, 133, 277-279 (2003)

How the transition can  
be probed?



**Large Change in 0.8 – 1.8 eV Region  
(Important for application)**

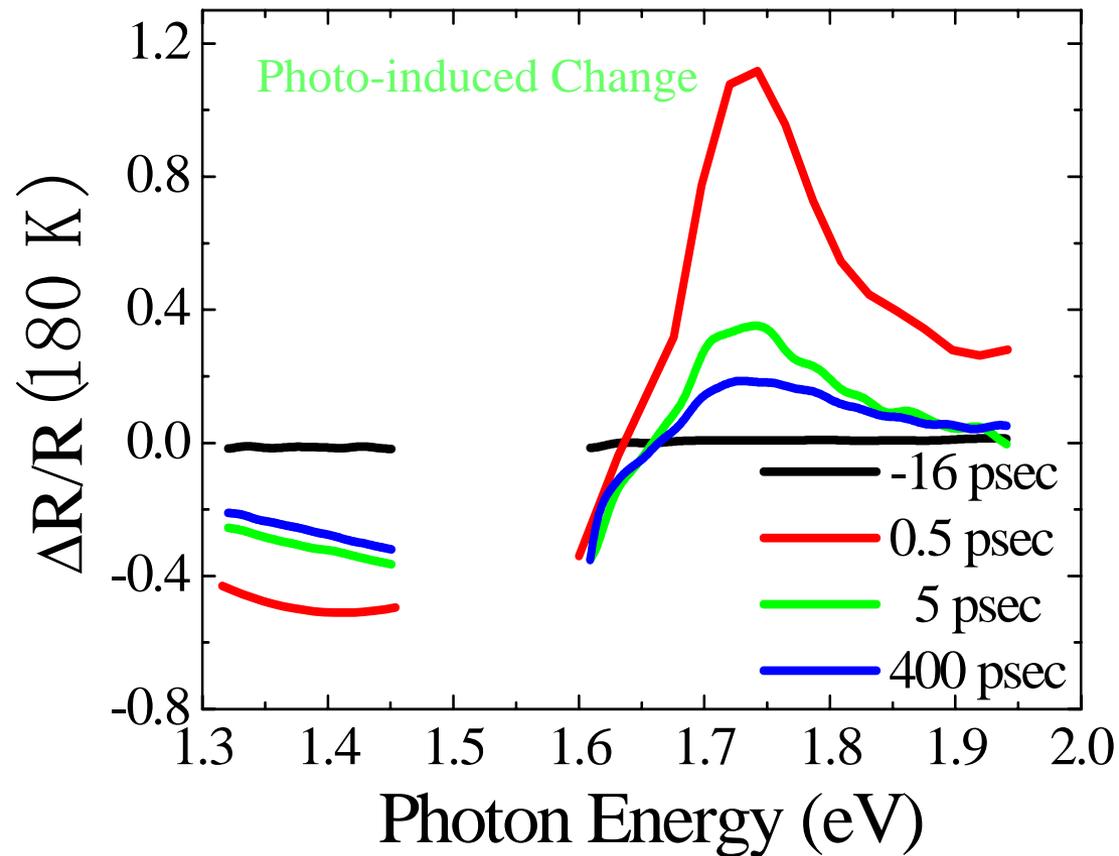
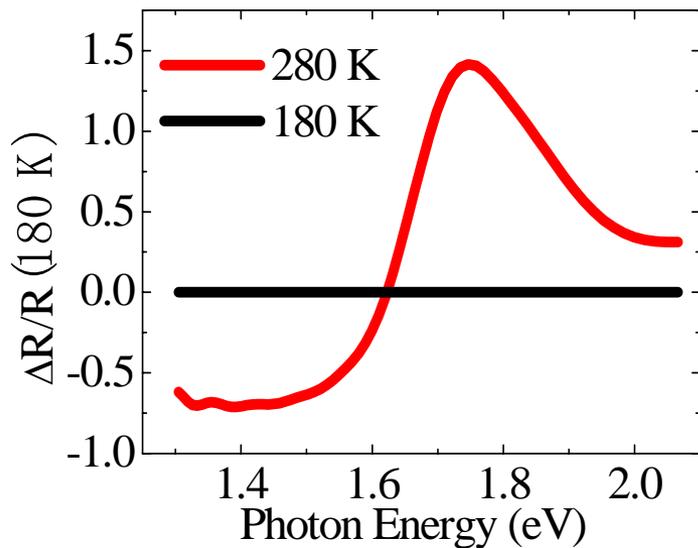
# Spectral change by photo-excitation

1: Quite similar to thermally induced I-to-M transition (Disappearance of CO band)

2: Highly efficient and fast conversion with 800nm excitation

(a few tens- a few  $\mu\text{J}/\text{cm}^2$  pulse: 1 photon for every 1-3 thousands molecules)

## Thermally-induced Change



# Fast Time-dependence in reflectivity change

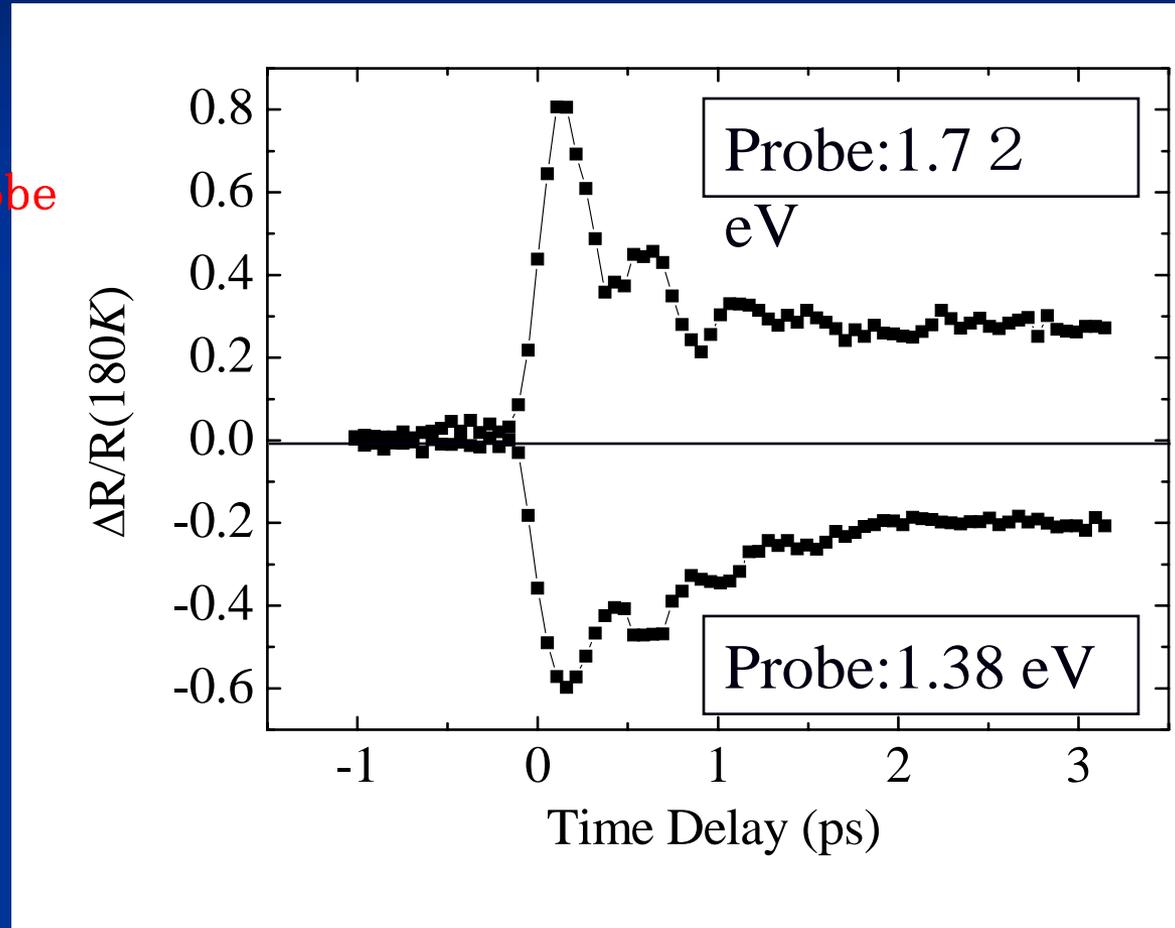
Vibrational structure scarcely depends on probe wavelength



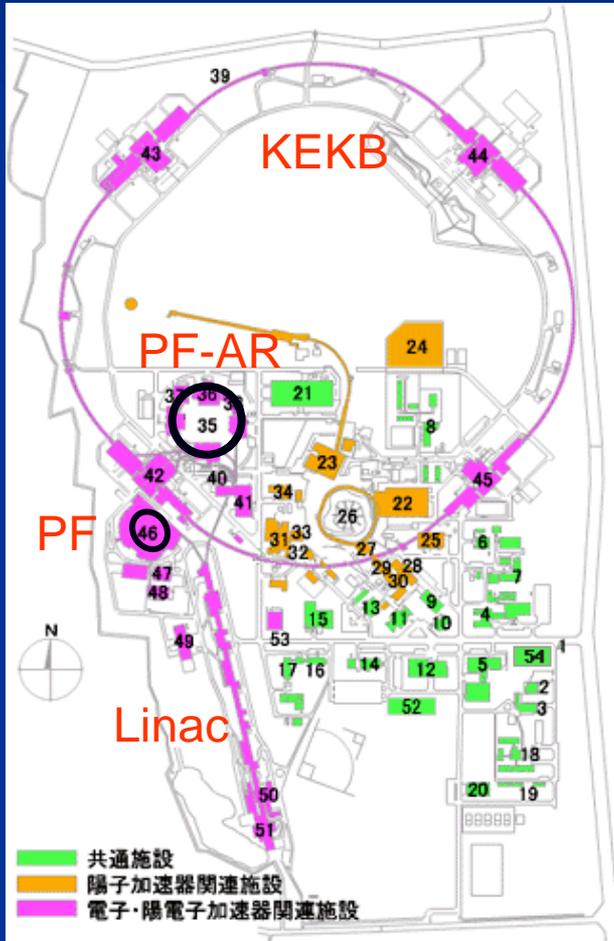
Some vibration in electronic structure

Similar signal has been also observed for  $(\text{EDO})_2\text{AsF}_6$

Coherent Phonon ? E-L coupling plays key role ?



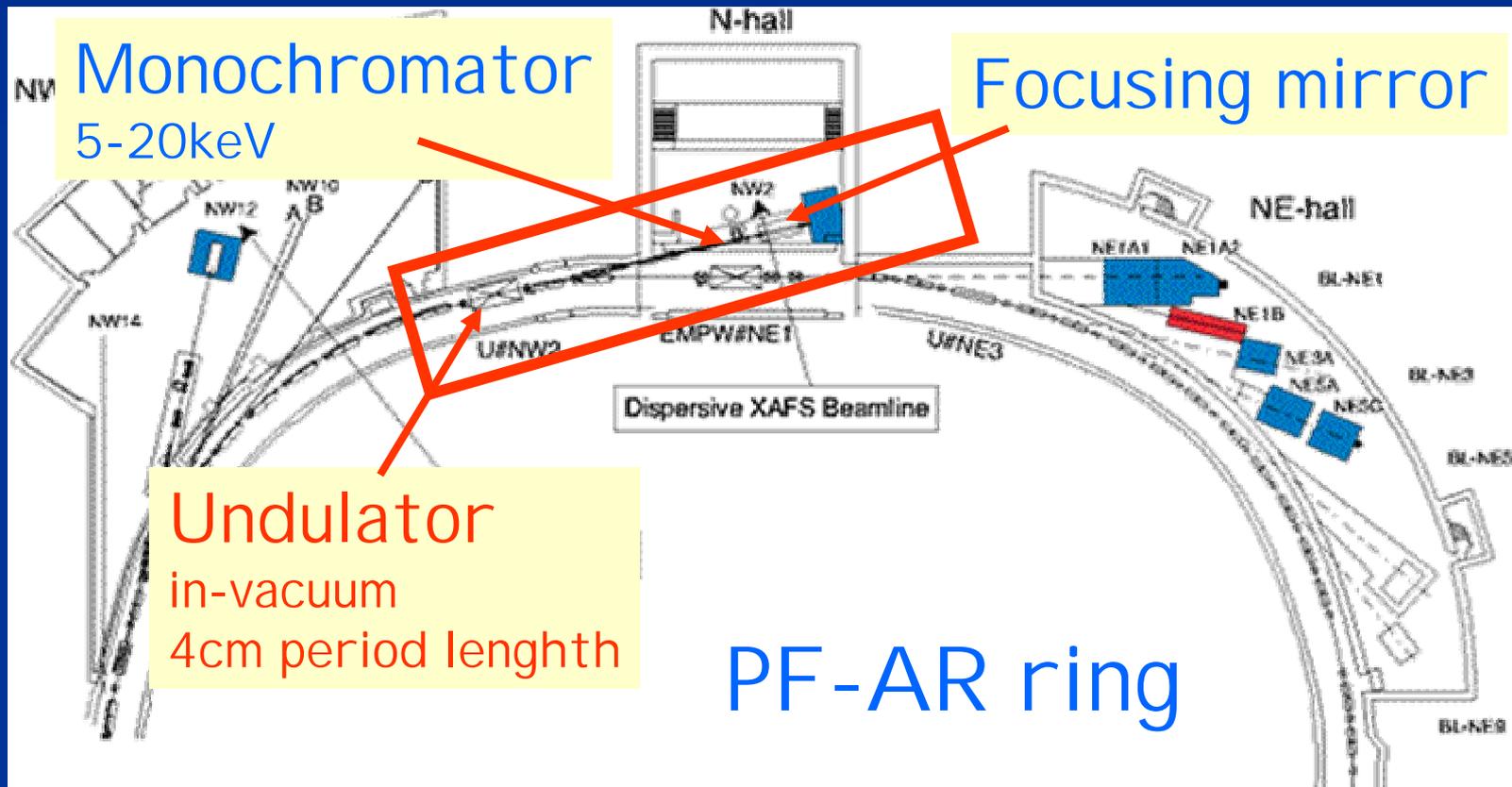
# Specifications of single-bunch mode at PF-AR and ESRF



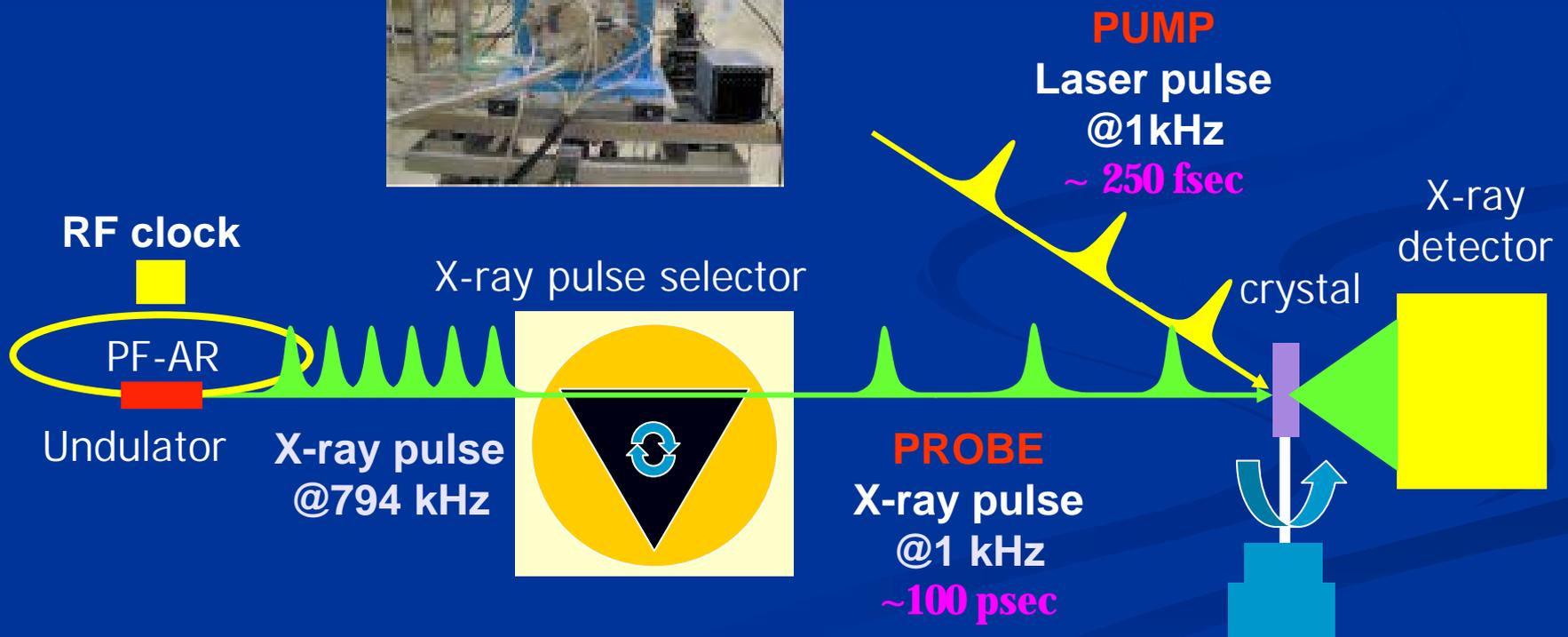
	KEK PF-AR	ESRF
Ring energy	6.5 GeV	6.0 GeV
Time resolved mode/year	~5000 hours (100% single bunch)	~1700 hours (~30% s.b., 16-bunch, hybrid)
Ring current / bunch	60 mA	16 mA max.
Bunch duration	~ 100psec	~ 150psec
Beam life	15-20 h	6-8 h
Beam size at the sample	0.26 mm (v) x 0.6 mm (h)	0.10 mm (v) x 0.06 mm (h)
Emittance	290 nmrad	3 nmrad

# PF-AR NW2 beamline

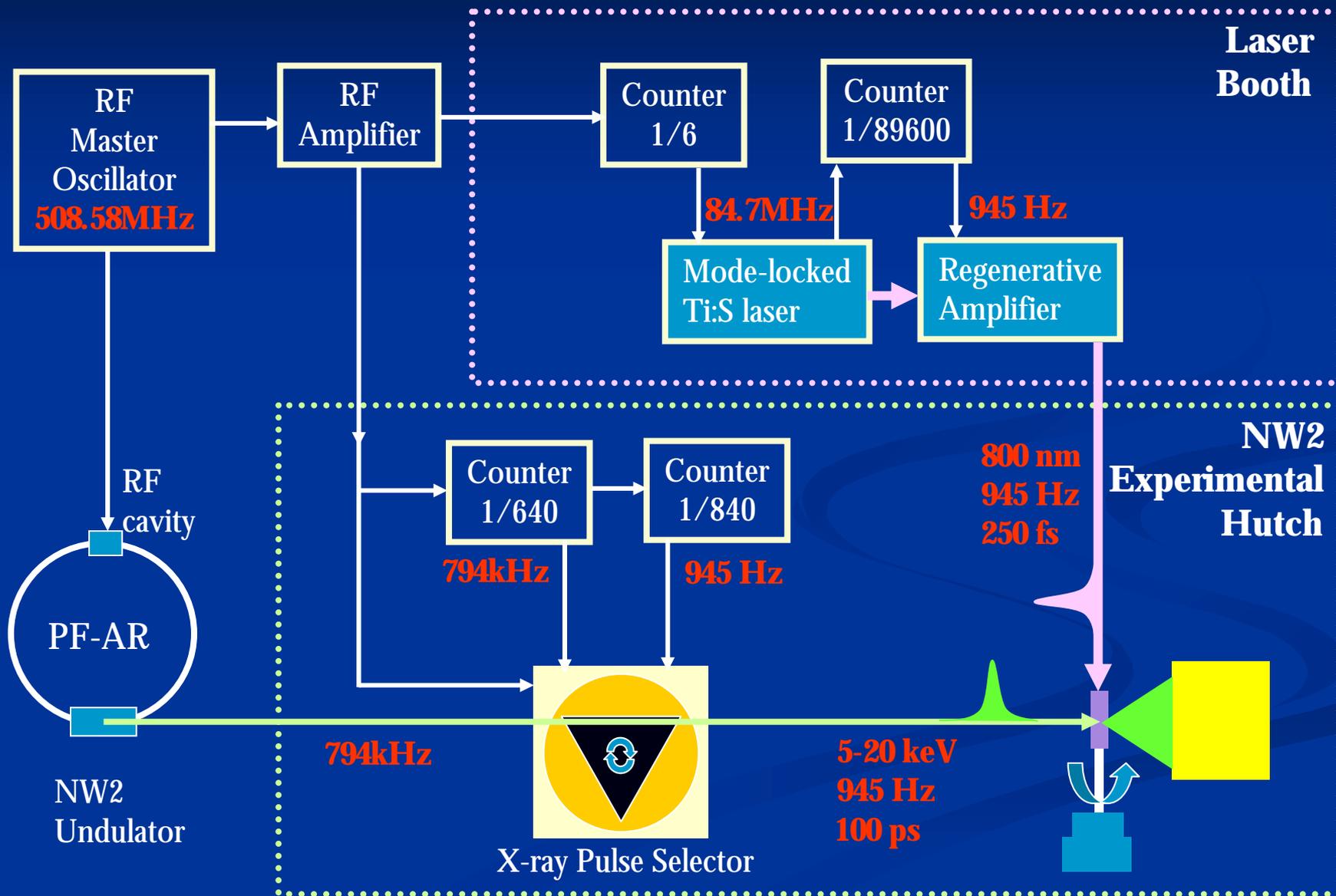
(for time-sharing use of time-resolved XAFS and diffraction)



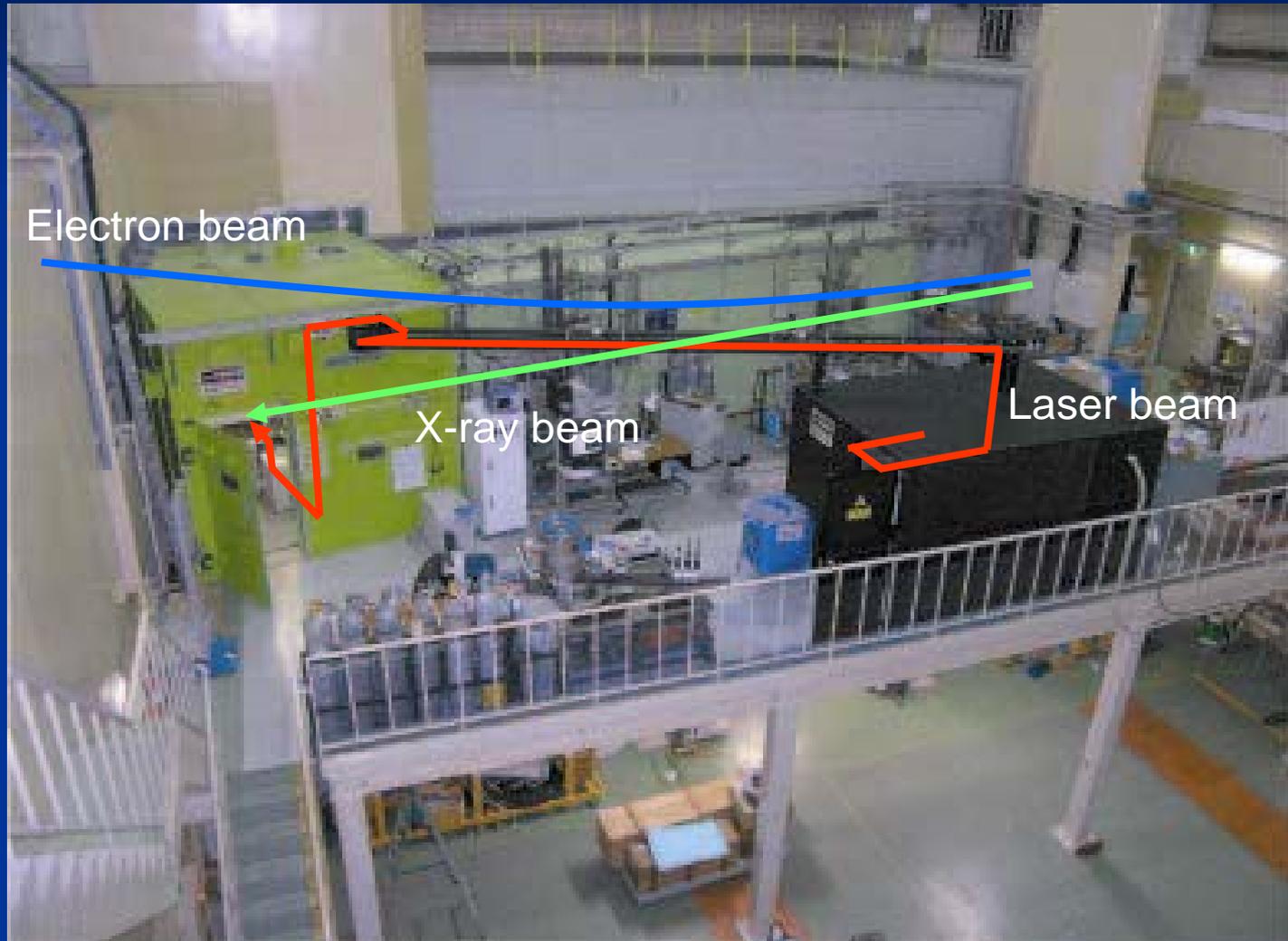
# Pump-probe X-ray diffraction at PF-AR NW2



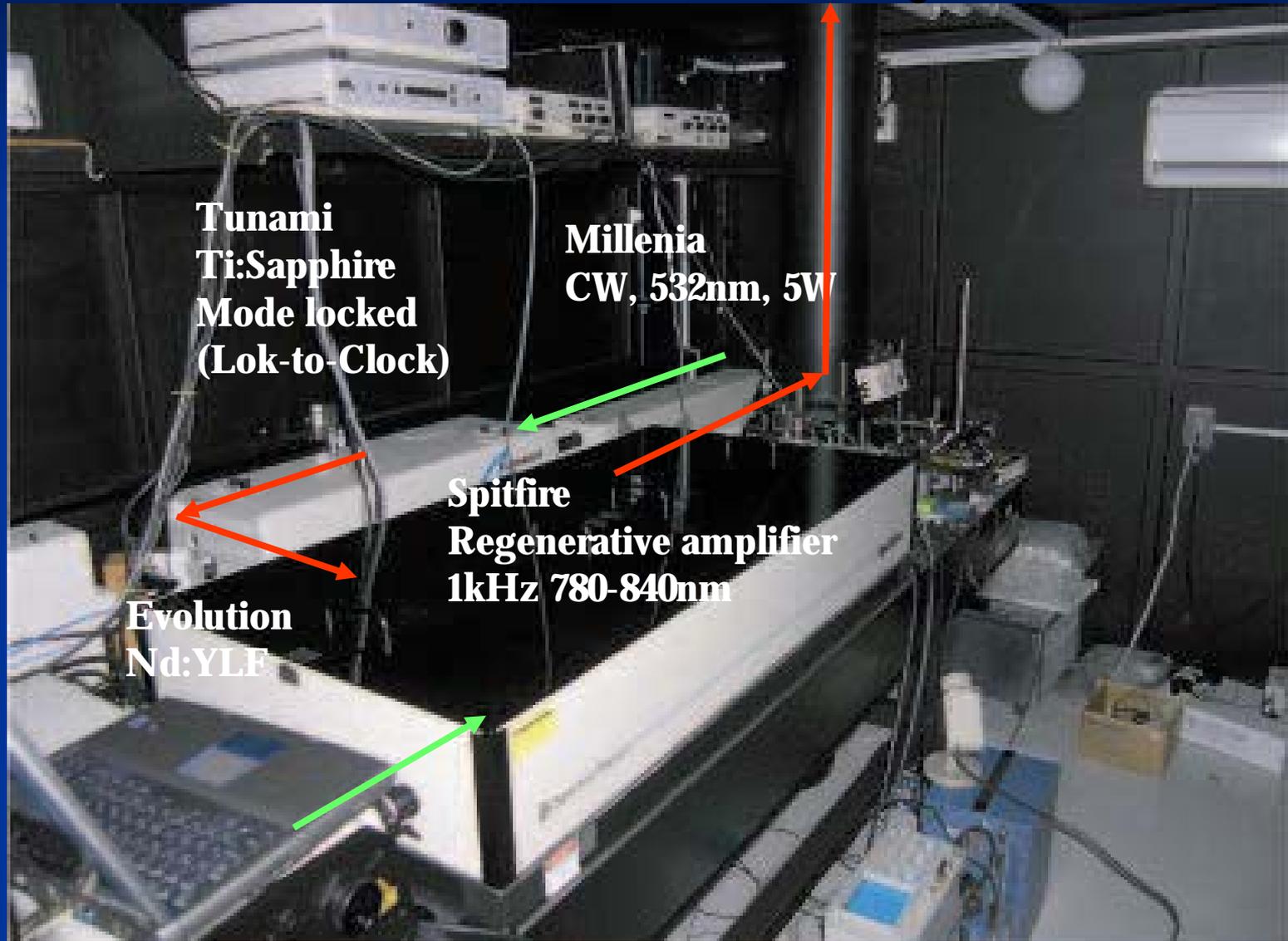
# Timing diagram



# Beamline NW2



# Femtosecond laser system



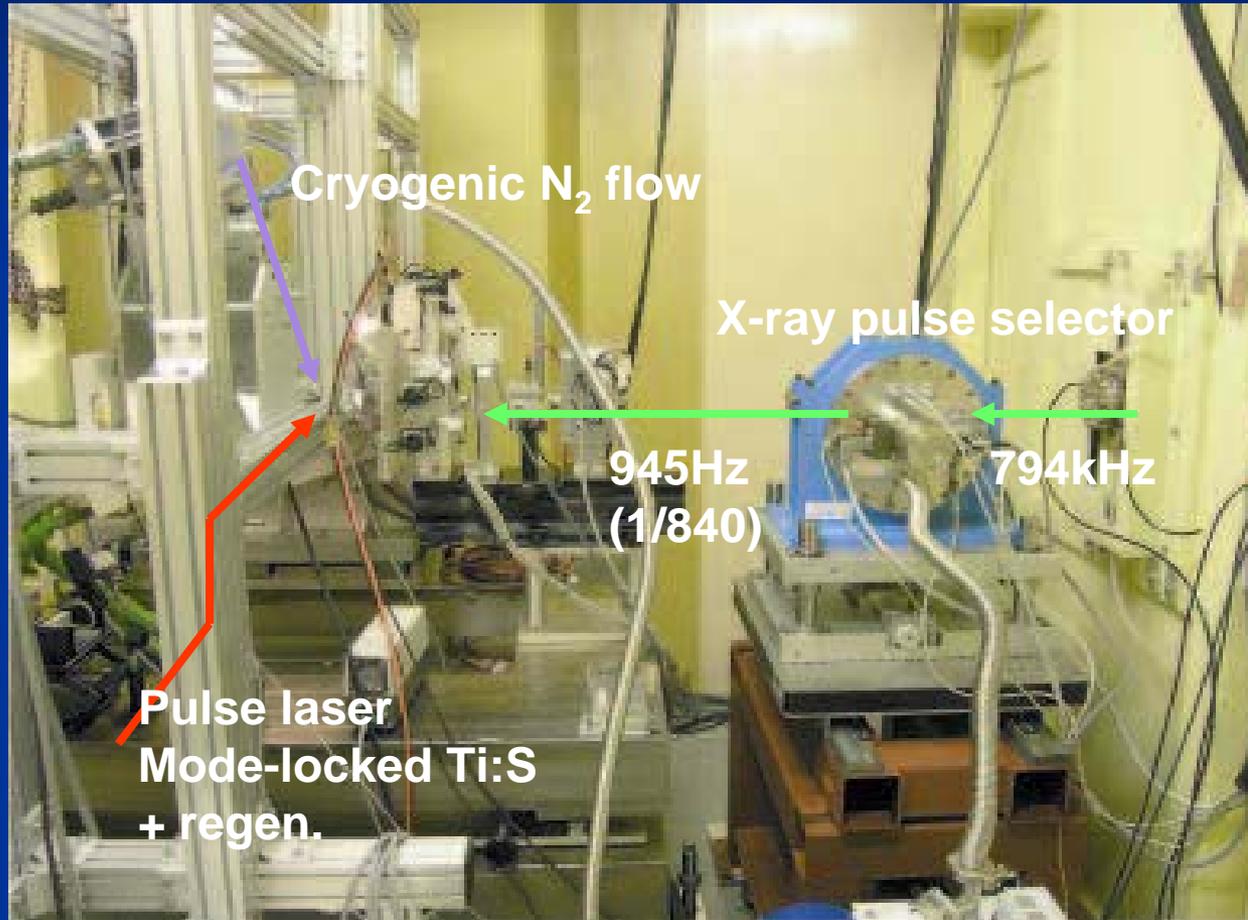
**Tunami**  
**Ti:Sapphire**  
**Mode locked**  
**(Lok-to-Clock)**

**Millenia**  
**CW, 532nm, 5W**

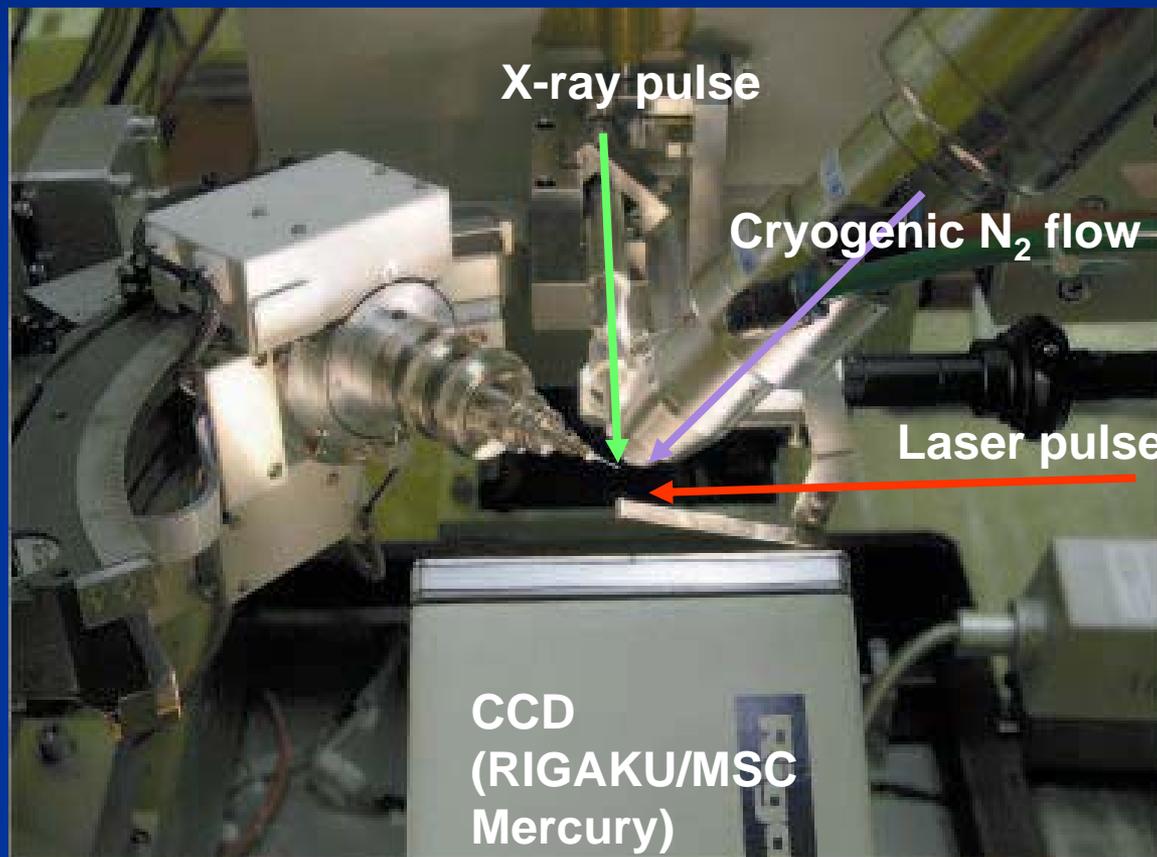
**Spitfire**  
**Regenerative amplifier**  
**1kHz 780-840nm**

**Evolution**  
**Nd:YLF**

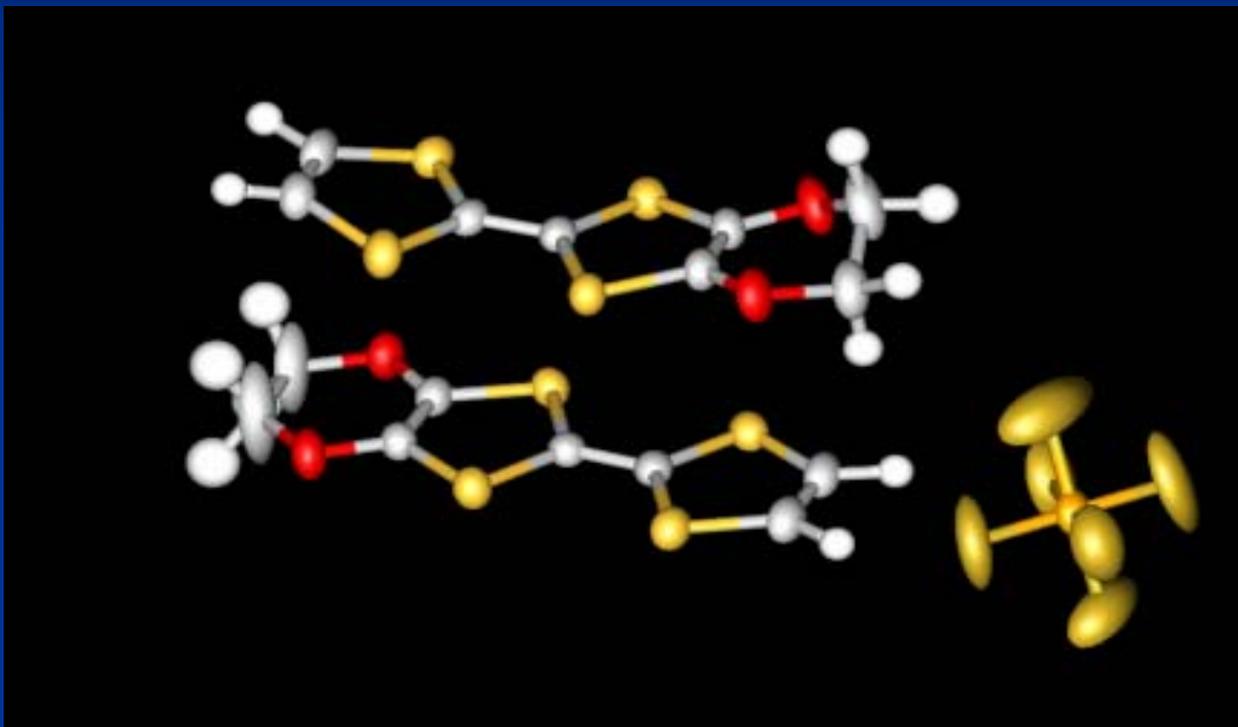
# PF-AR NW2 experimental hutch



# PF-AR NW2 diffractometer



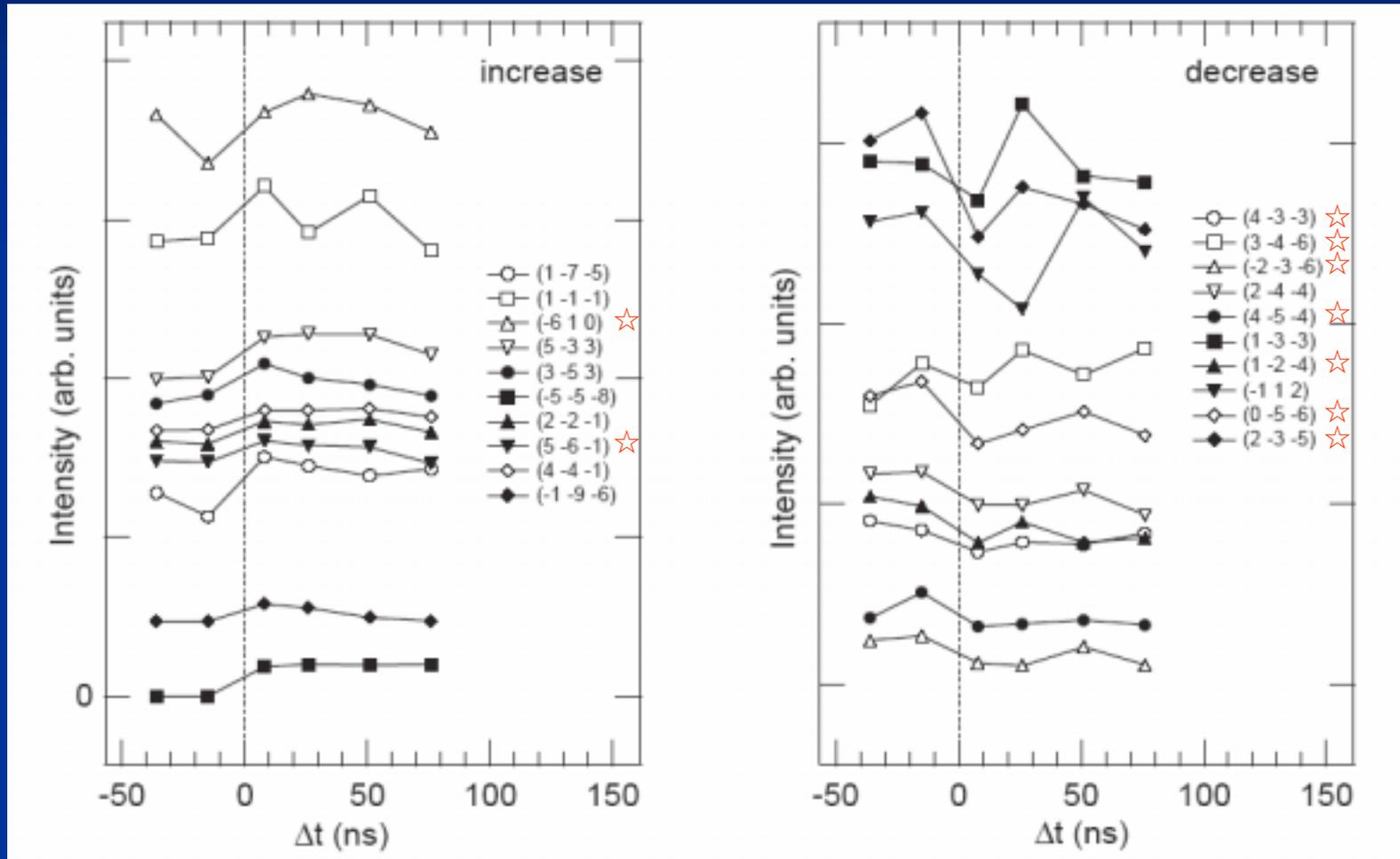
# Crystal structure of EDO-TTF 3.5nsec after laser excitation (250K)



Triclinic P1

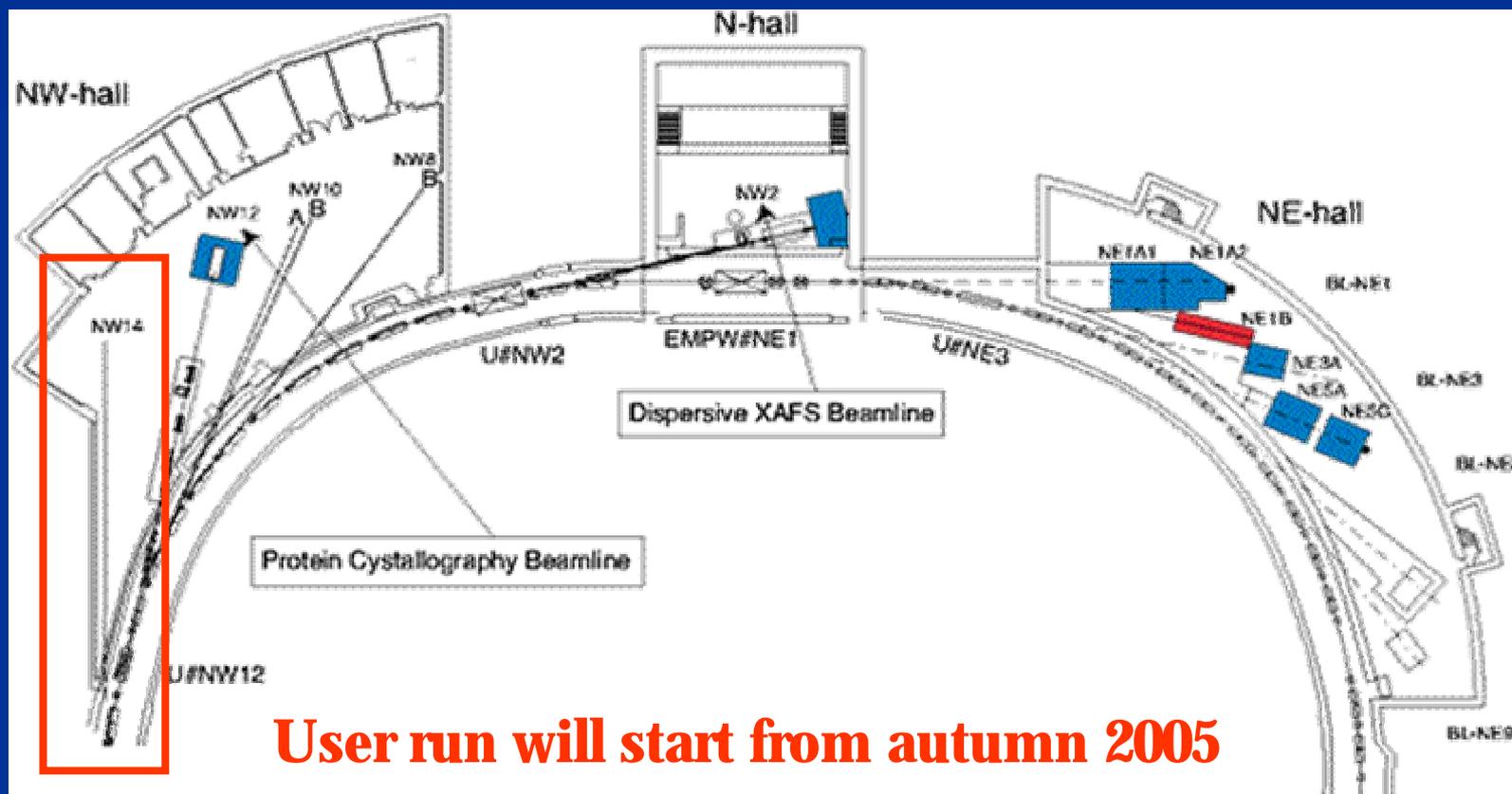
$a=9.74(2)$ ,  $b=11.07(2)$ ,  $c=11.15(3)$   
 $\alpha=101.6(1)$ ,  $\beta=100.2(1)$ ,  $\gamma=88.5(1)$   
 $V=1159(4)$

# Time course of integrated intensities of diffraction spots



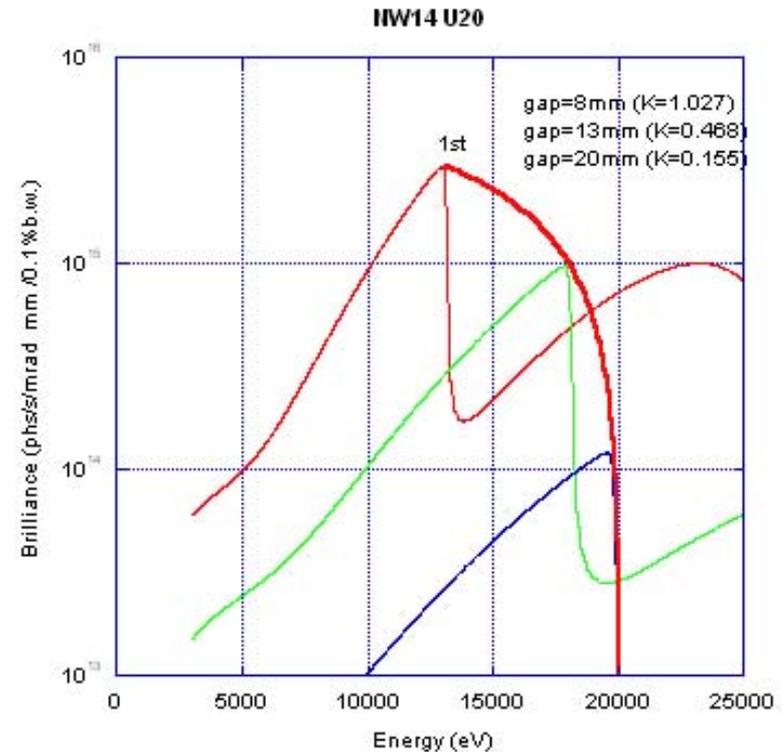
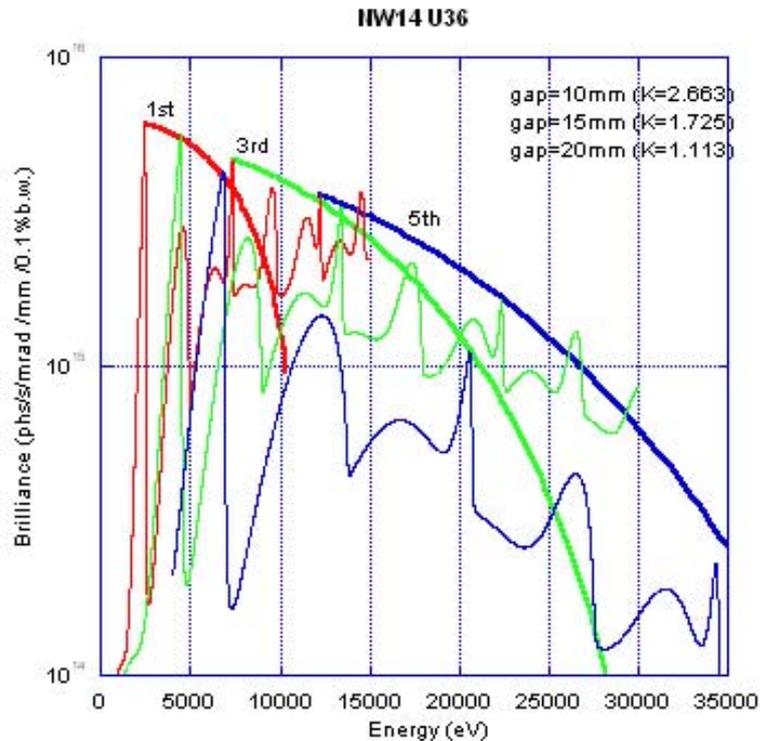
☆:  $h+k = \text{odd}$ , which are observed only in low-temp phase

# A New Beamline, PF-AR NW14 fully dedicated to time-resolved diffraction (funded by ERATO, JST)



**User run will start from autumn 2005**

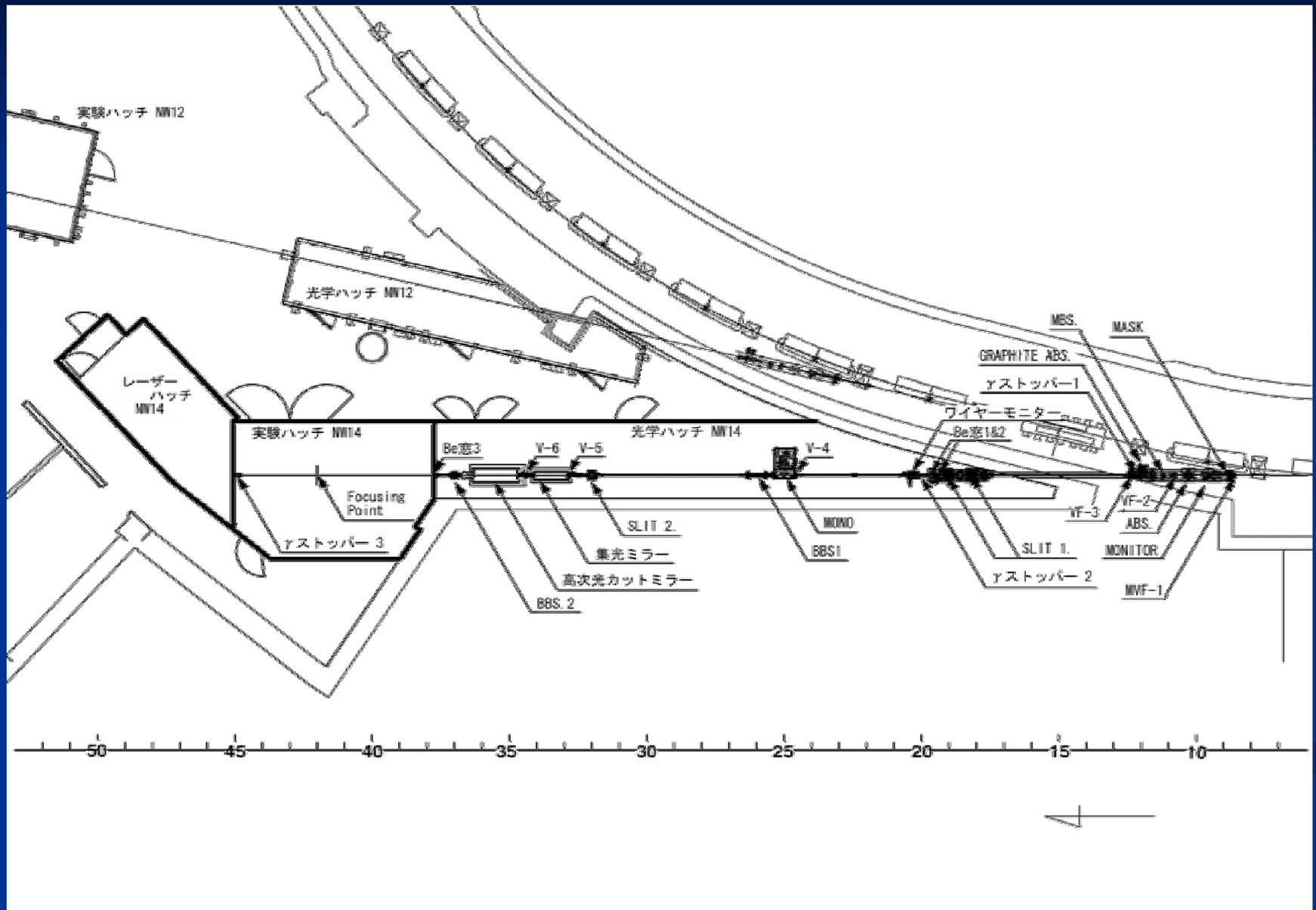
# Two Undulators at NW14



**Period length: 36mm**  
**Number of Magnets: 86**  
**Total length: 3096mm**  
**Minimum gap: 10mm**

**Period length: 20mm**  
**Number of Magnets: 75**  
**Total length: 1500mm**  
**Minimum gap: 8mm**

# Layout of the NW14



# Collaborators

- KEK-ERATO collaboration (Core members)
  - Ryoko Tazaki (ERATO, KEK, Chiba Univ.)
  - Shunsuke Nozawa (ERATO, JST)
  - Jun-ichi Takahashi (ERATO, JST)
  - Jiro Itatani (ERATO, JST)
  - Hiroshi Sawa (KEK PF)
  - Hiroshi Kawata (KEK PF)
  - Masahiro Daimon (ERATO, JST)
  - Shin-ya Koshihara (TITECH, ERATO JST)
- PF Light Source Division
- Tokyo Institute of Technology
  - Shin-ya Koshihara (TITECH, ERATO JST)
  - Matthieu Chollet (TITECH)
  - Laurent Guerin (TITECH)
  - Naoki Uchida (TITECH)
  - Souichi Fukaya (TITECH)
  - Tadahiko Ishikawa (TITECH)
- Univ. Rennes 1
  - Eric Collet
  - Herve Cailleau
- EDO-TTF crystal (Kyoto Univ.)
  - Akira Ota
  - Hideki Yamochi
  - Gunzi Saito
- And more ...

**end**