Watching photo-induced structural dynamics with time-resolved X-ray crystallography

Photon Factory, KEK

ERATO, JST

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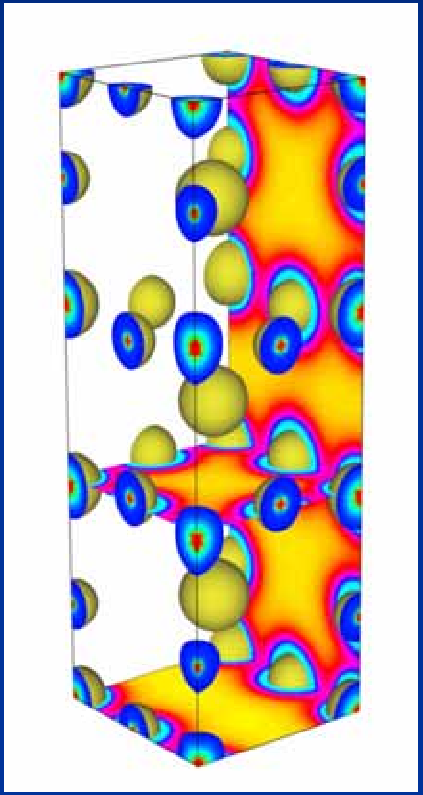
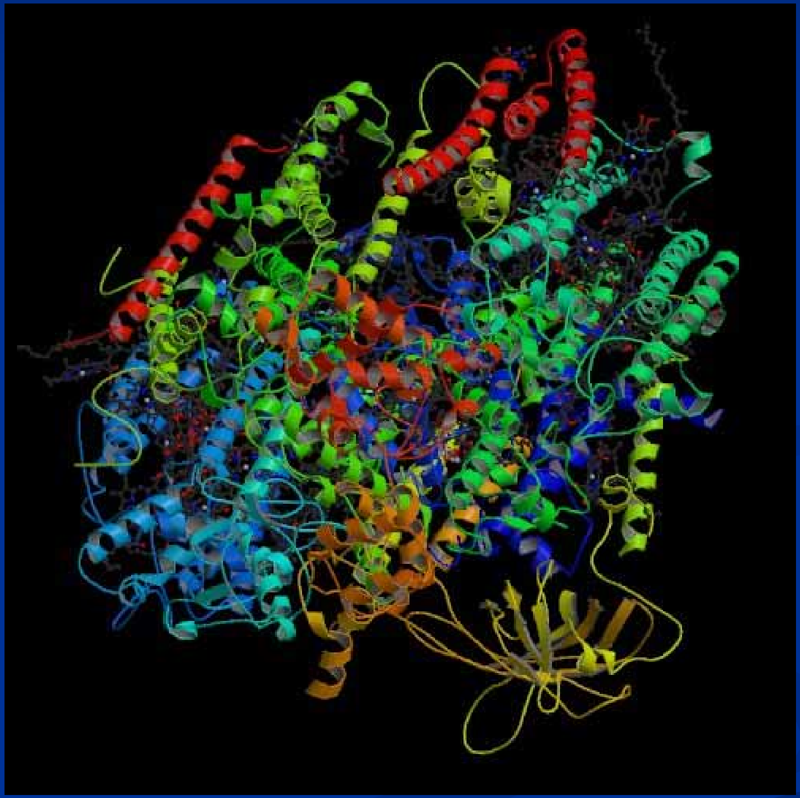
Outline

- Why photo-induced structural dynamics?
- Photo-stationary state
  - Photolysis of Fe-CO bond in hemoglobin-CO
- Time-resolved measurement
  - Photo-induced phase transition in organic charge transfer complex (TTF-CA, EDO-TTF)
- Summary and future view

What crystallography can do

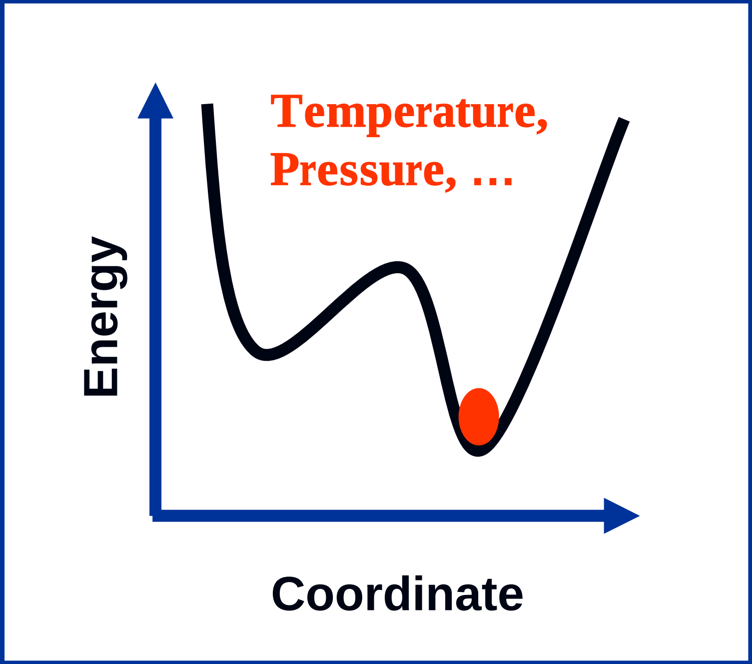


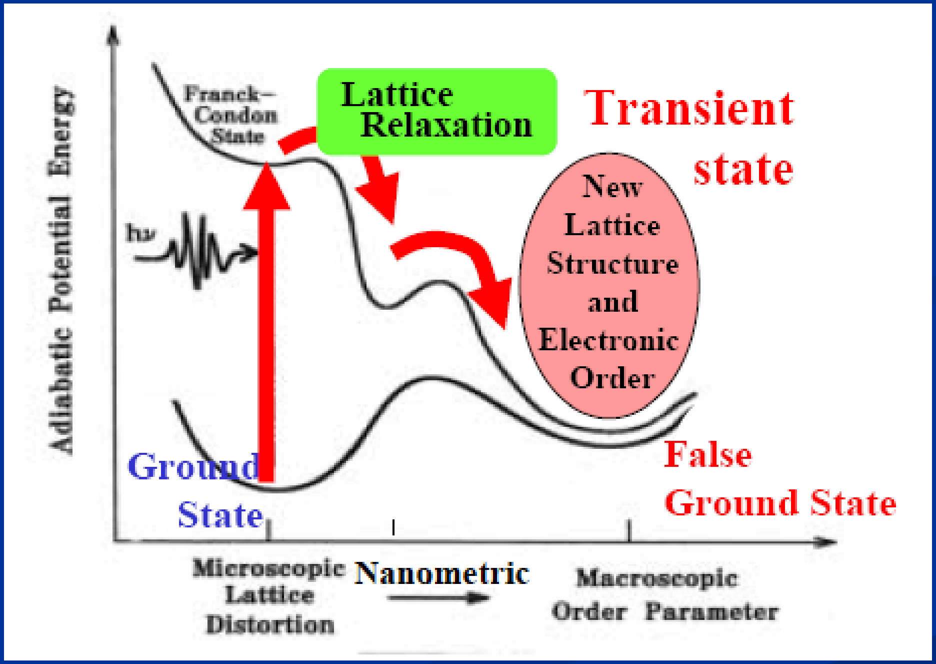
Electron density distribution of $YBa_2Cu_3O_7$
(after Dr. Fujio Izumi's HP)



3D structure of Photosynthetic Oxygen Evolving Center (45945 atoms)
(Ferreira et al. (2004) Science)

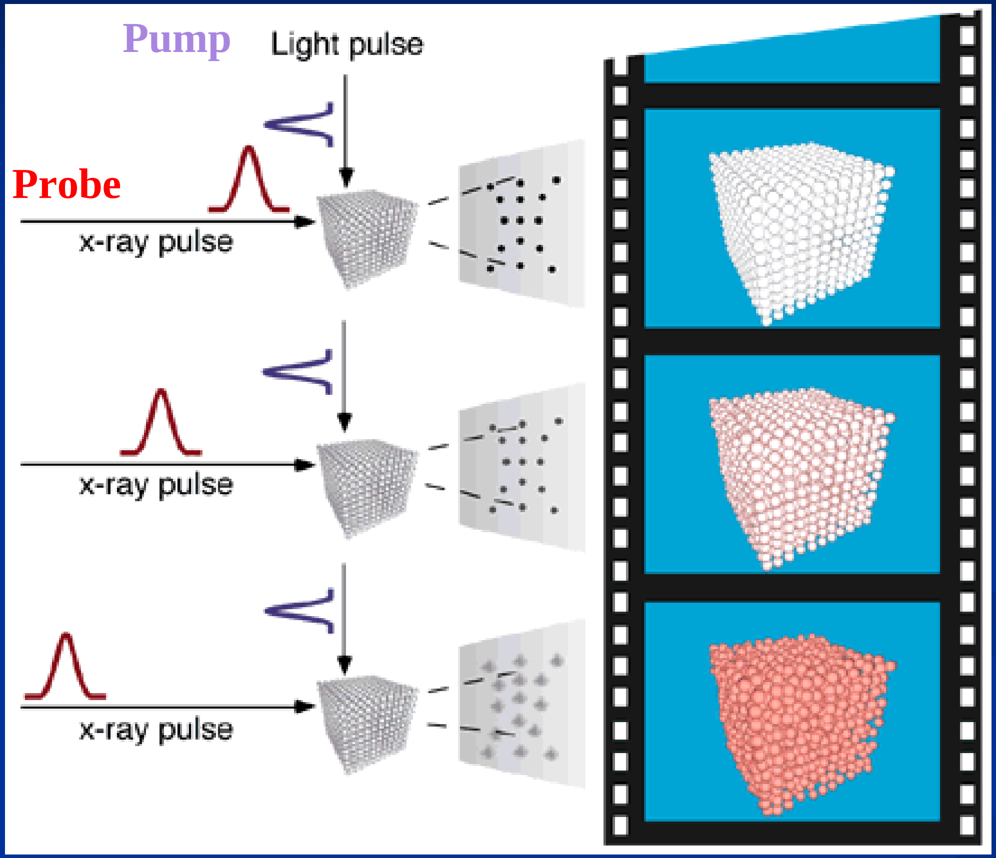
Why photo-induced structural dynamics in single crystals?





From static to dynamic state

Toward molecular movie



'Watching matter rearrange'
K. Nelson, Science (1999) 286, 1310.

From static to dynamic studies

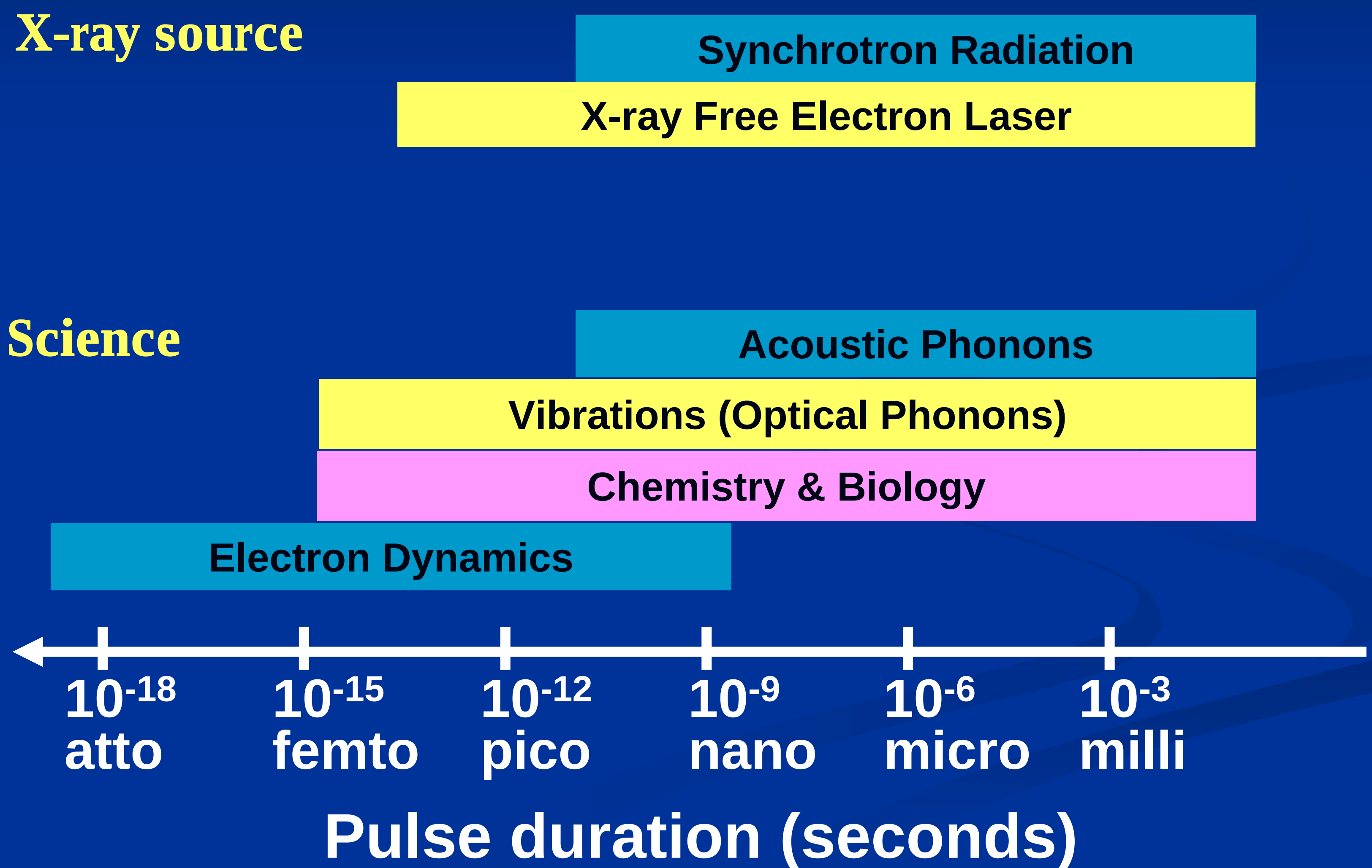


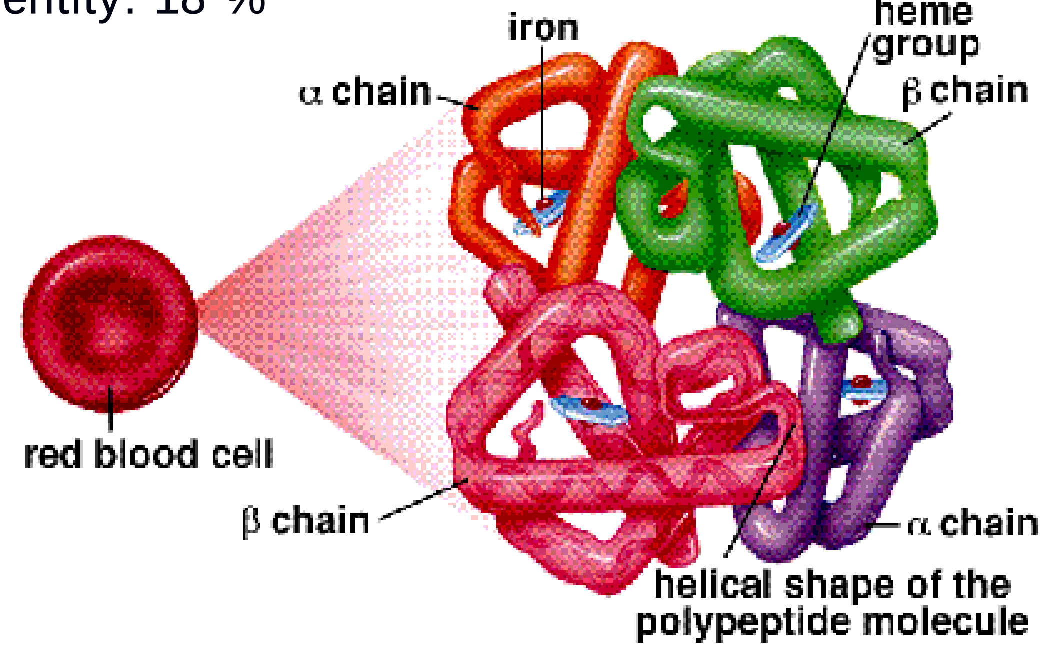
Photo-stationary state

Photolysis of Fe-CO bond in hemoglobin-CO

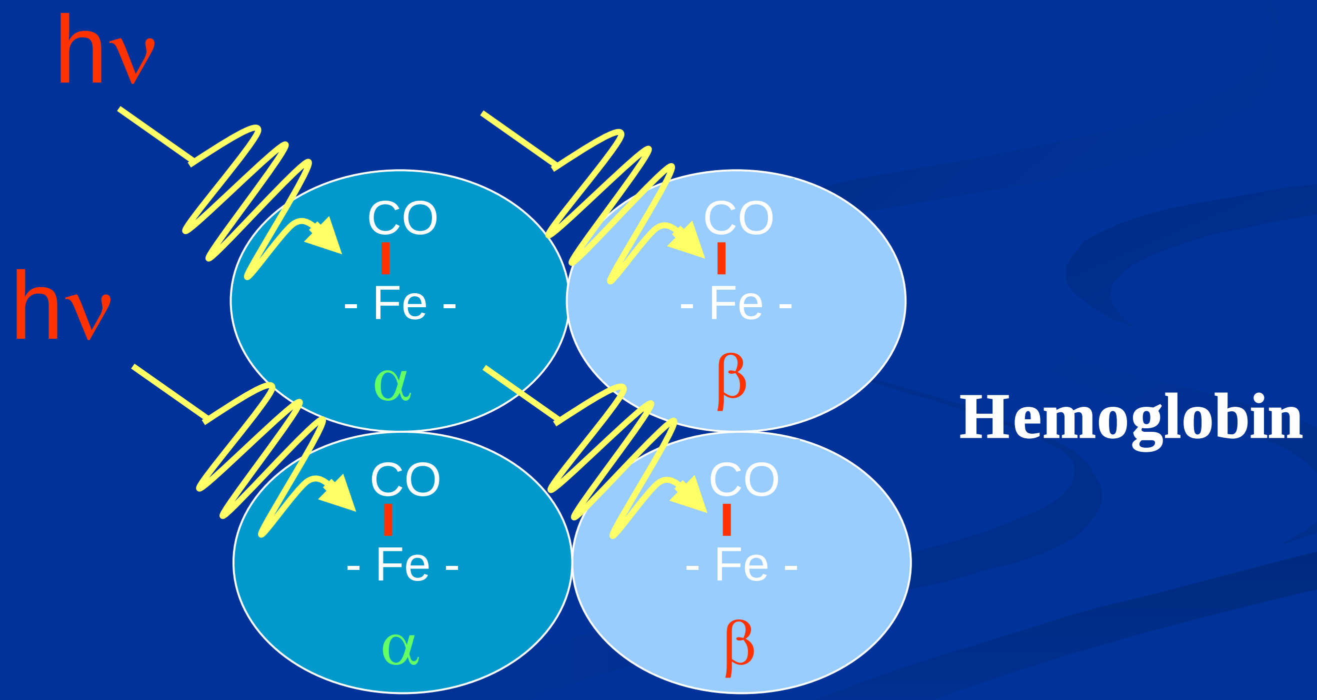
Hemoglobin

- Four subunits
  - two α
  - two β
- Iron
- Heme
- Binds 4 O_2

identity: 18 %

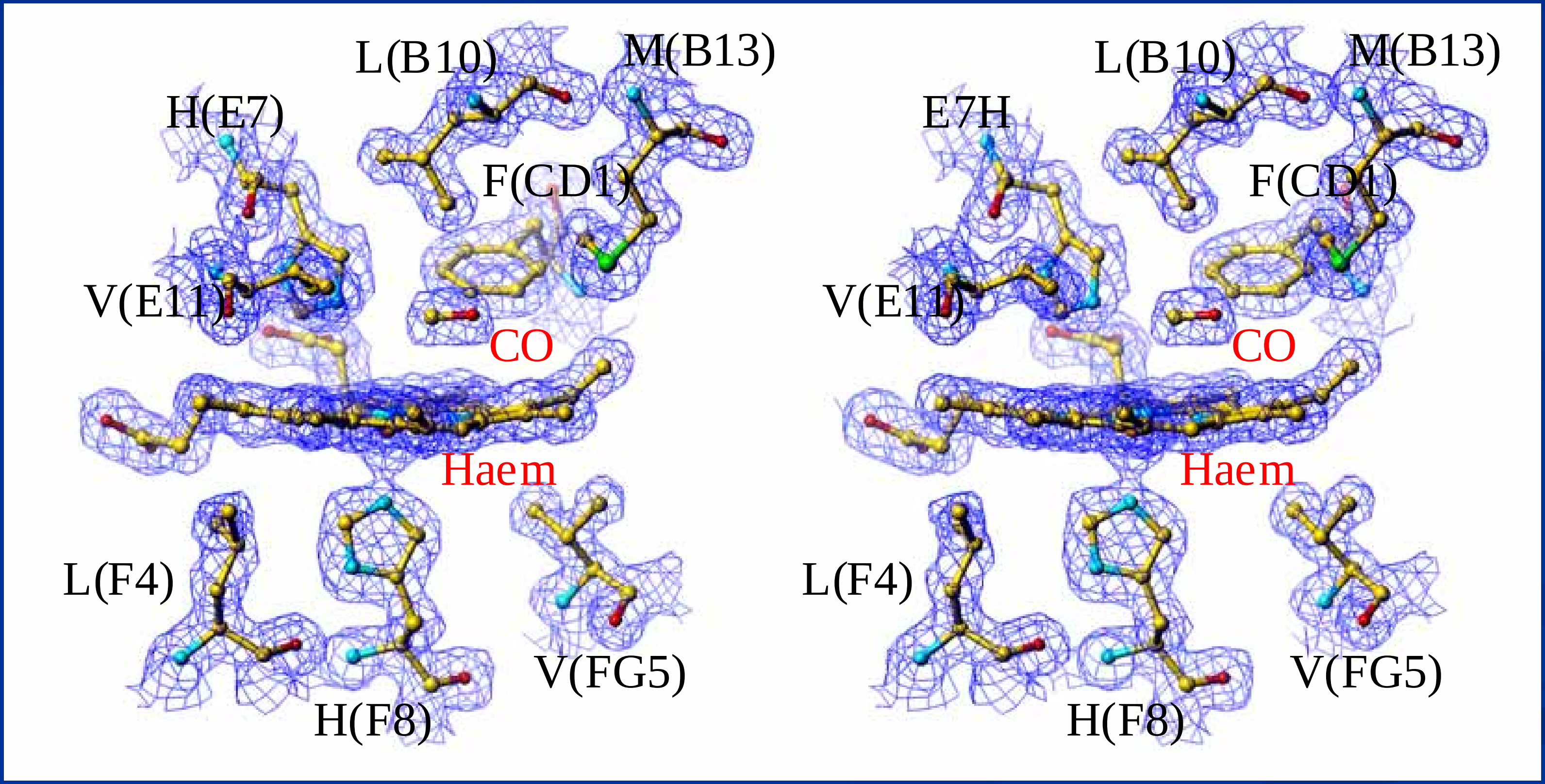


What happens when the Fe-CO bonds are broken by photo-excitation?



α subunit

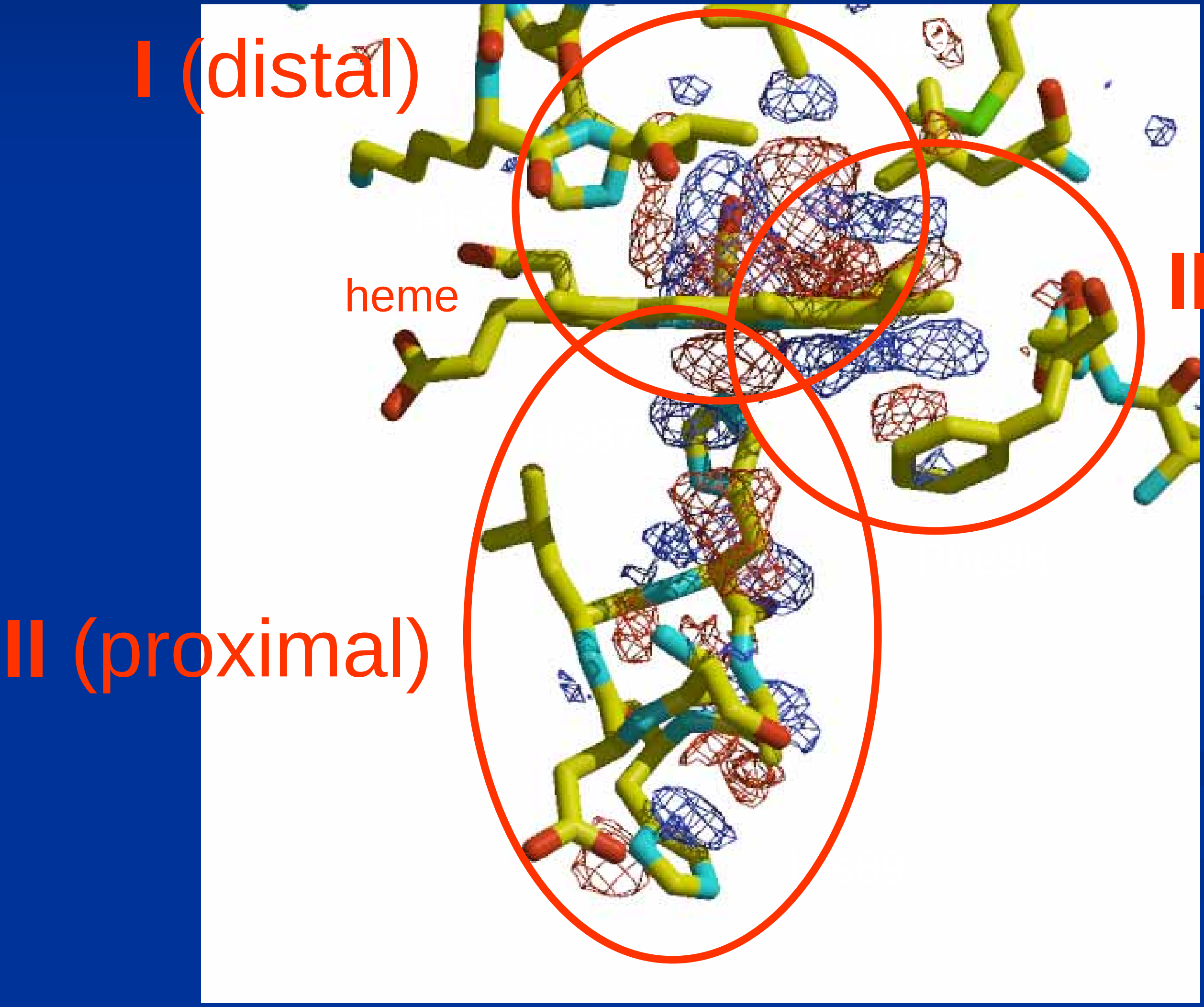
2Fo-Fc map (1.3σ)



Light ON

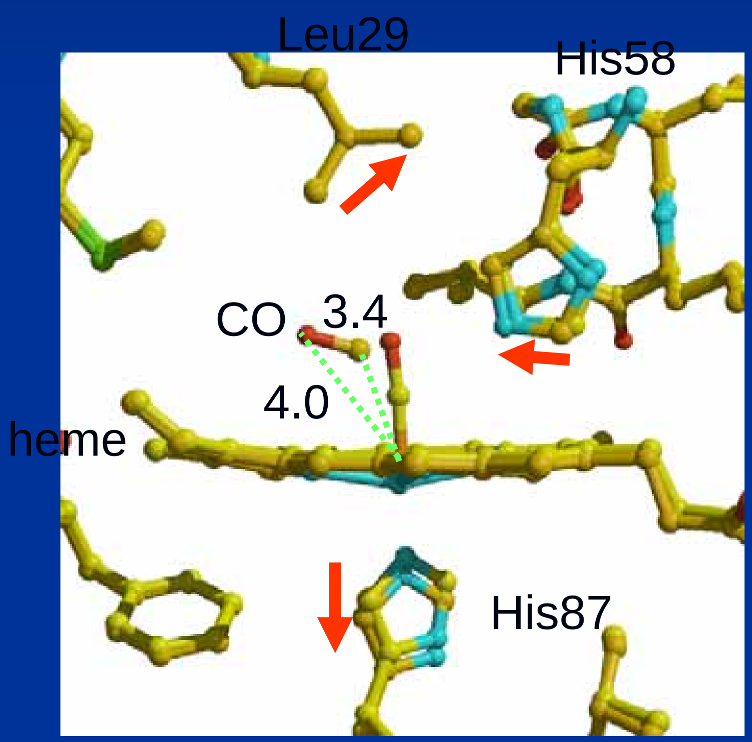
α subunit

Fo(light_off)-Fo(light_on) map ($\pm 3.5\sigma$)

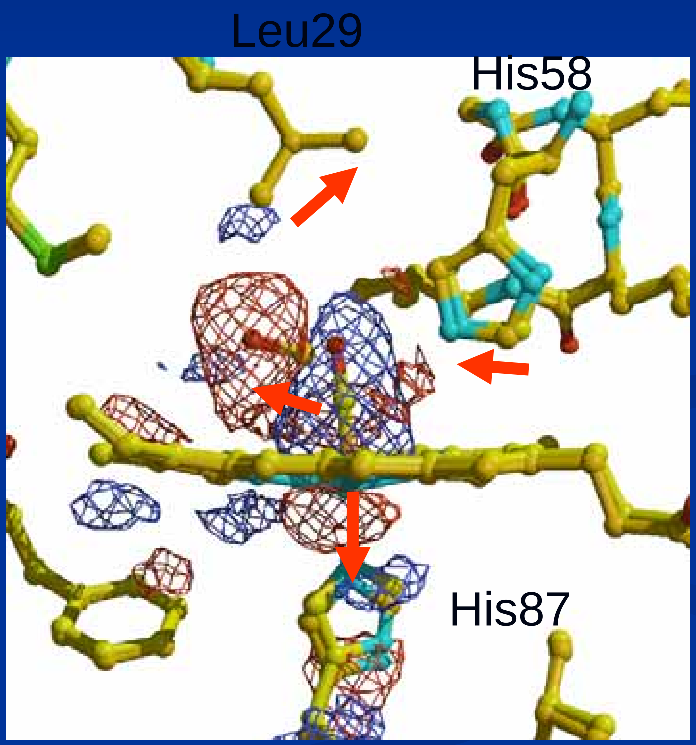


α subunit (±4.5σ)

I. distal side

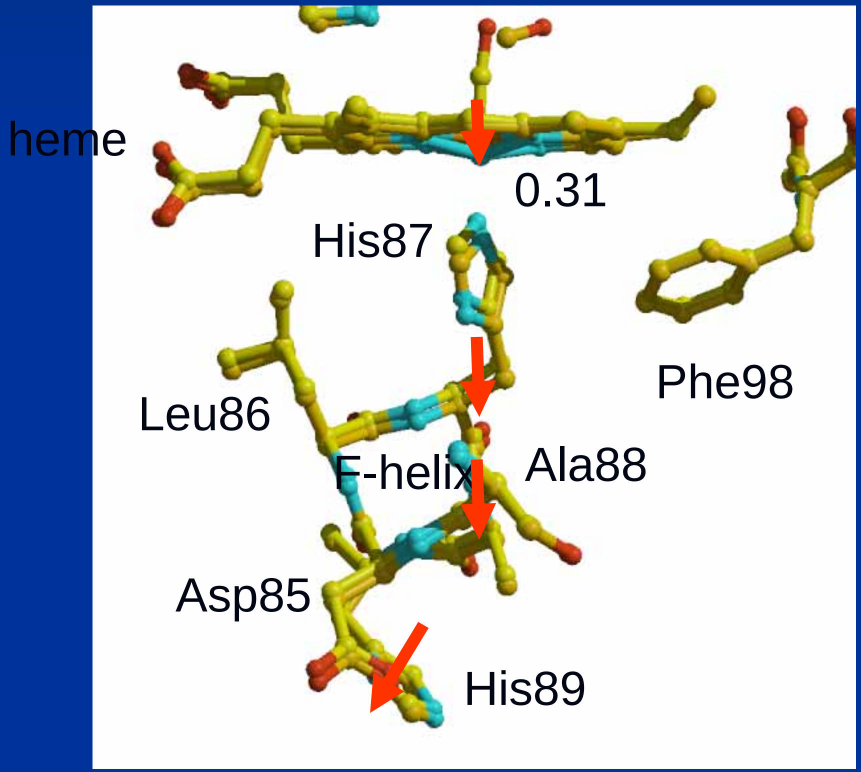


refined models
(light on/off)

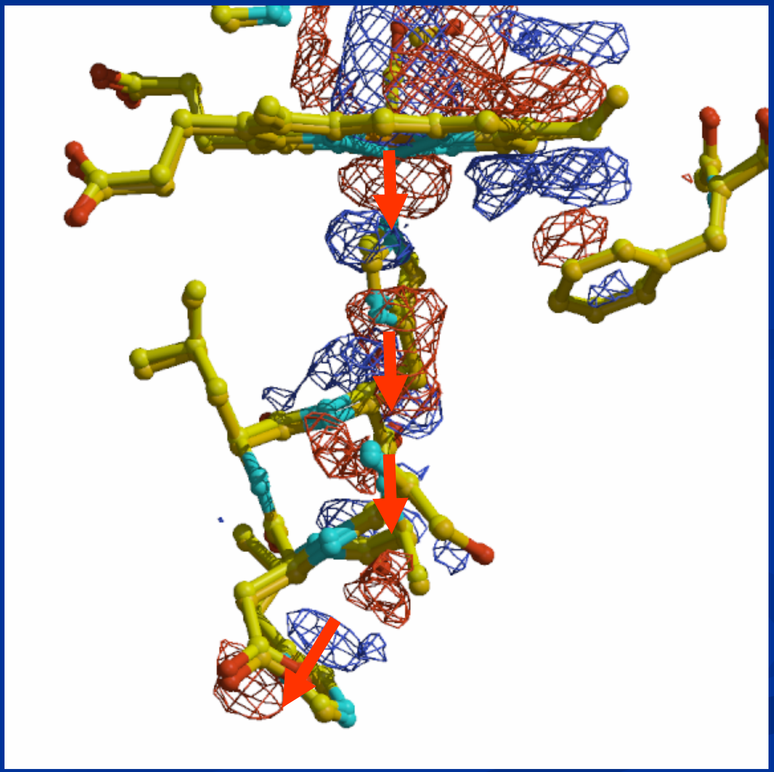


Models with d-Fourier map (±4.5σ)
Blue (+) : light off
Red (-) : light on

α subunit (±3.5σ)
II. proximal side



refined models (light on/off)



Models with d-Fourier map (±3.5σ)
Blue (+) : light off
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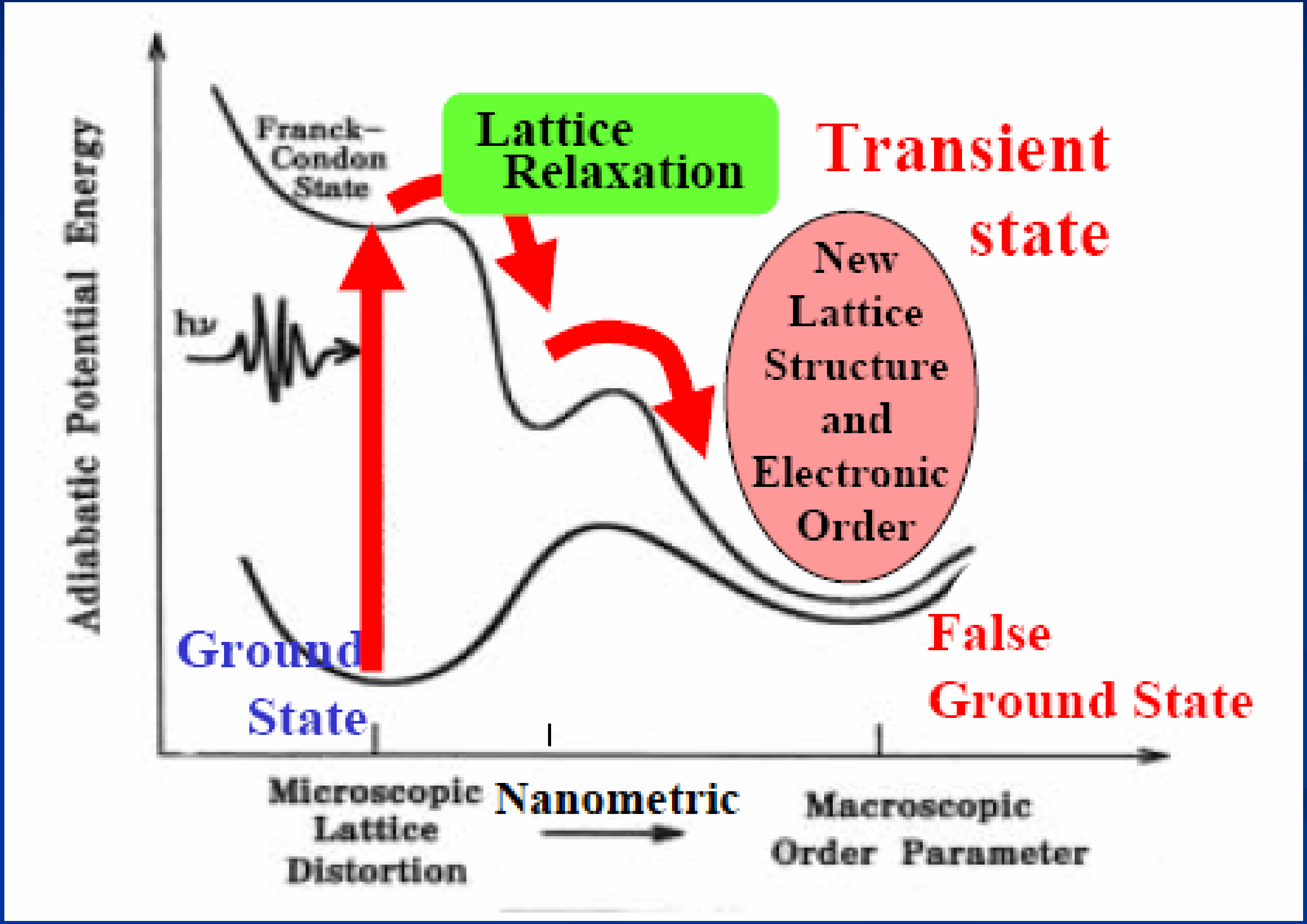
Time-resolved measurement

Photo-induced phase transition in organic charge transfer complex (TTF-CA, EDO-TTF)

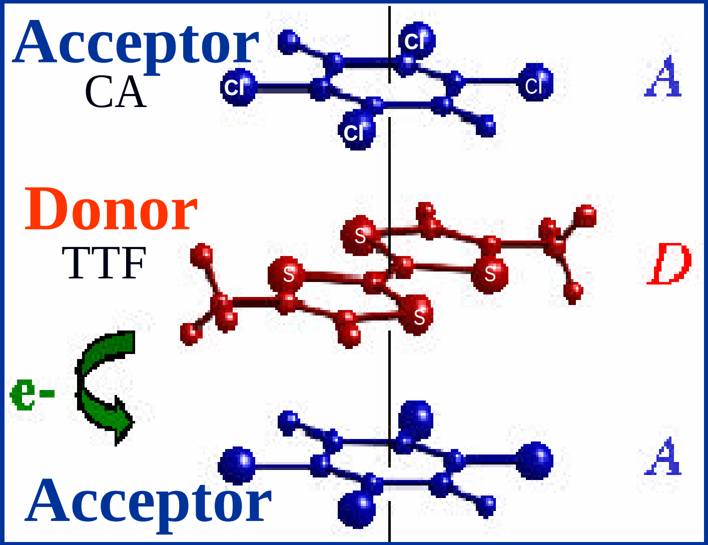
Photo-induced phase transition

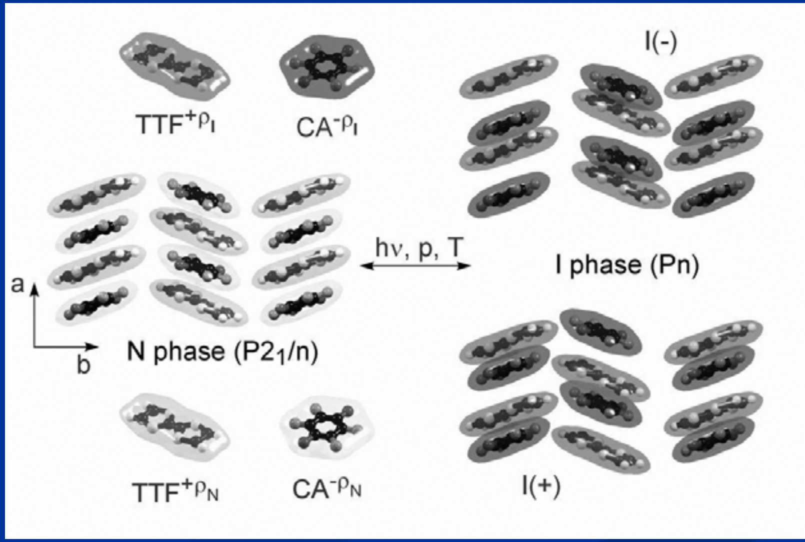


Laser-induced ferroelectric structural order in TTF-CA crystal

(Collet et al. Science 300, 612, 2003)

- Mixed stack of Donor (TTF) and Acceptor (CA)
- At high temperature (>82K) Neutral
- At low temperature Ionic

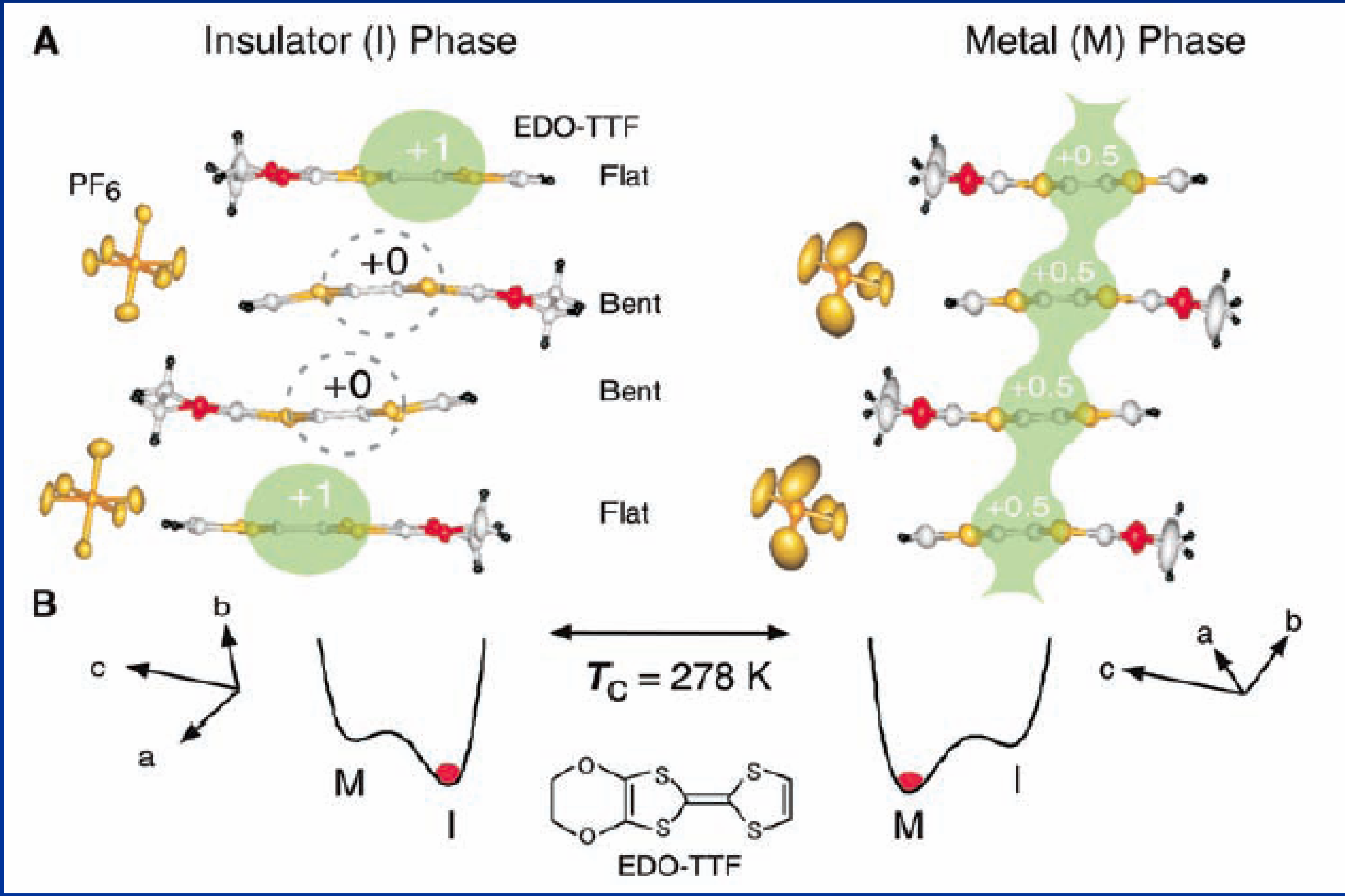




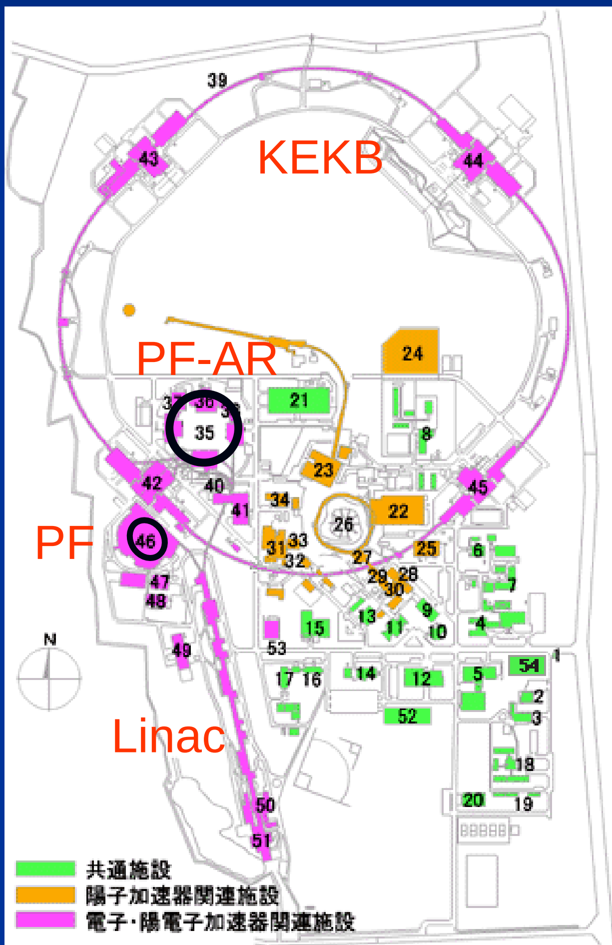
… D° A° D° A° (D^+A^-) (D^+A^-) (D^+A^-) D° A° D° A° …

Gigantic Photoresponse in ¼-Filled-Band Organic Salt $(EDO\text{-}TTF)_2PF_6$

(Chollet et al. (2005) Science 307, 86.)

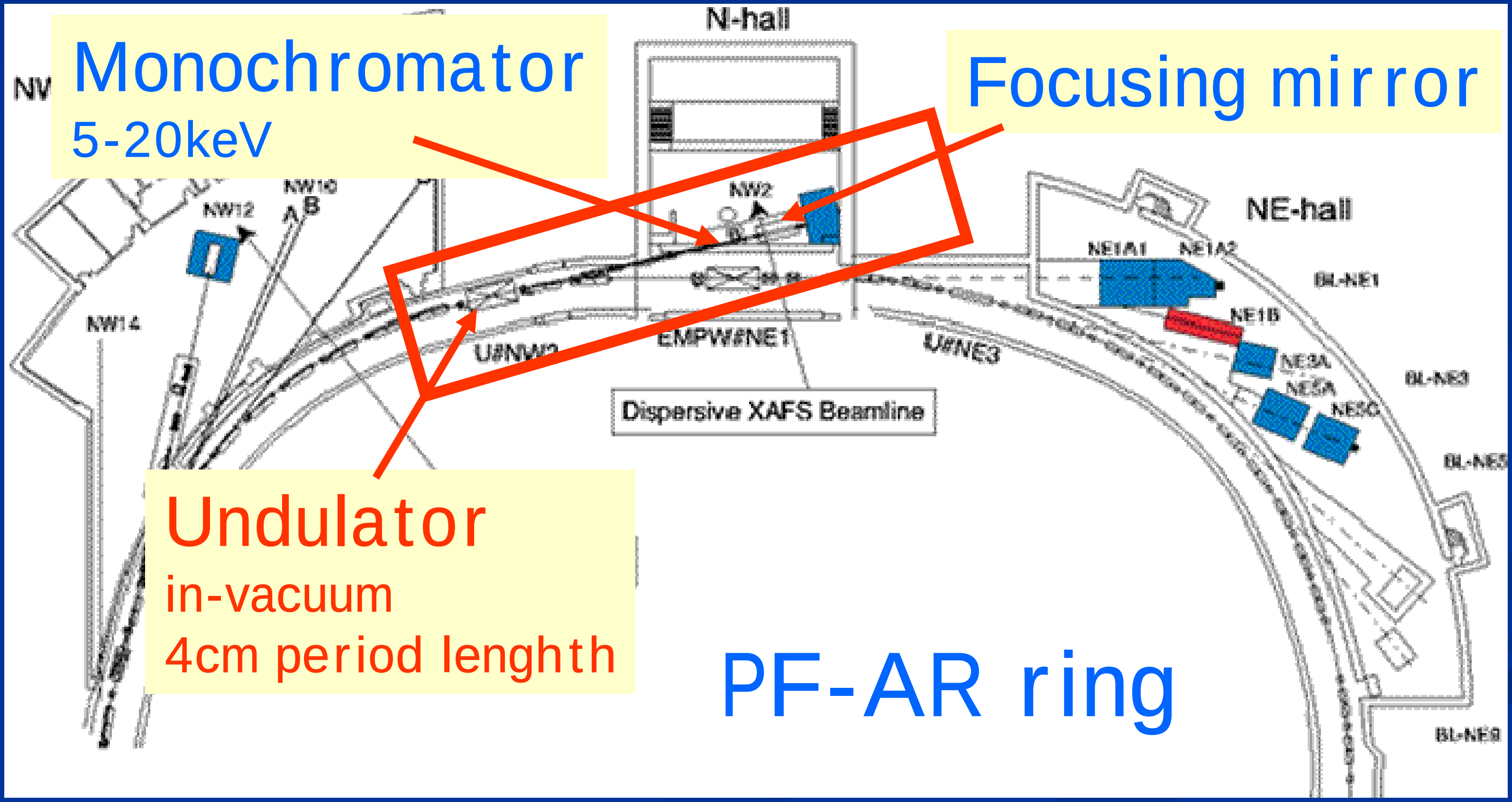


ESRF and PF-AR

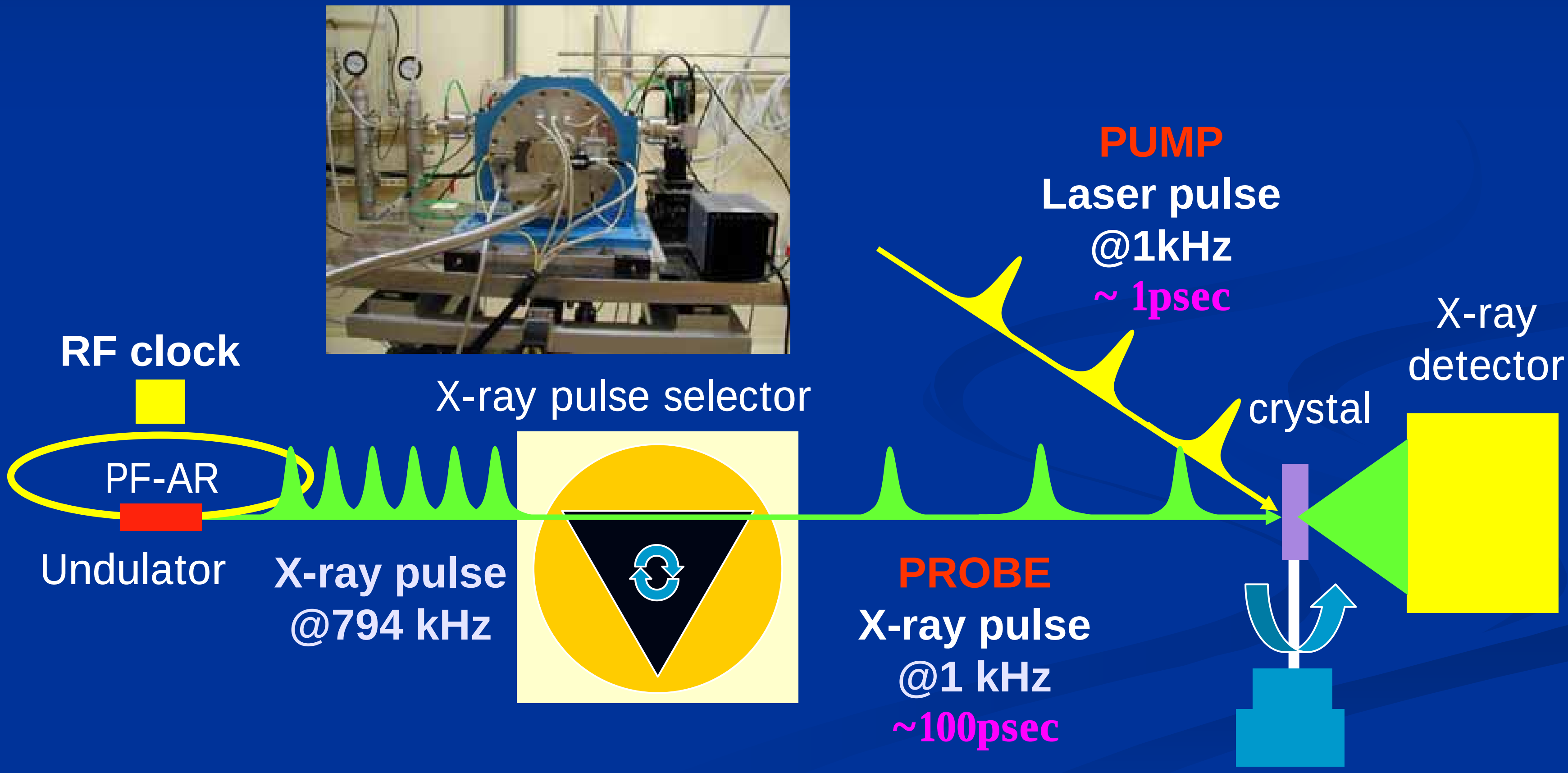


	KEK PF-AR	ESRF
Ring energy	6.5 GeV	6.0 GeV
Time resolved mode/year	~5000 hours (100**%** single bunch)	~1700 hours (~30**%** s.b., 16-bunch, hybrid)
Ring current Electron/bunch	60 mA 80 nC	16 mA 40 nC
Bunch duration	~ 100psec	~ 150psec
Beam life	15-20 h	6-8 h
Beam size at the sample	0.26 mm (v) x 0.6 mm (h)	0.10 mm (v) x 0.06 mm (h)
Emittance	**290 nmrad**	**3 nmrad**

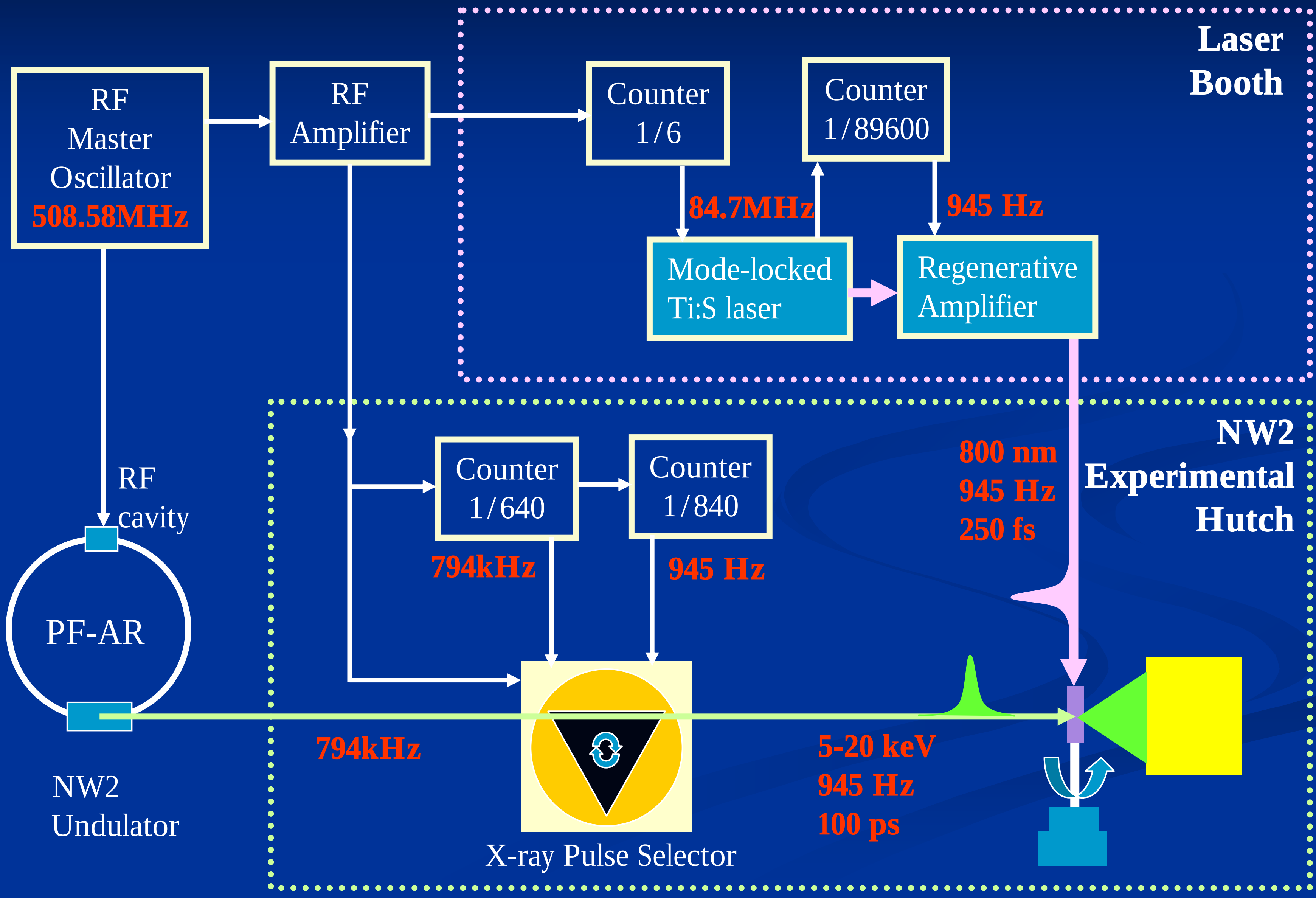
PF-AR NW2
(for time-sharing use of time-resolved XAFS and diffraction)



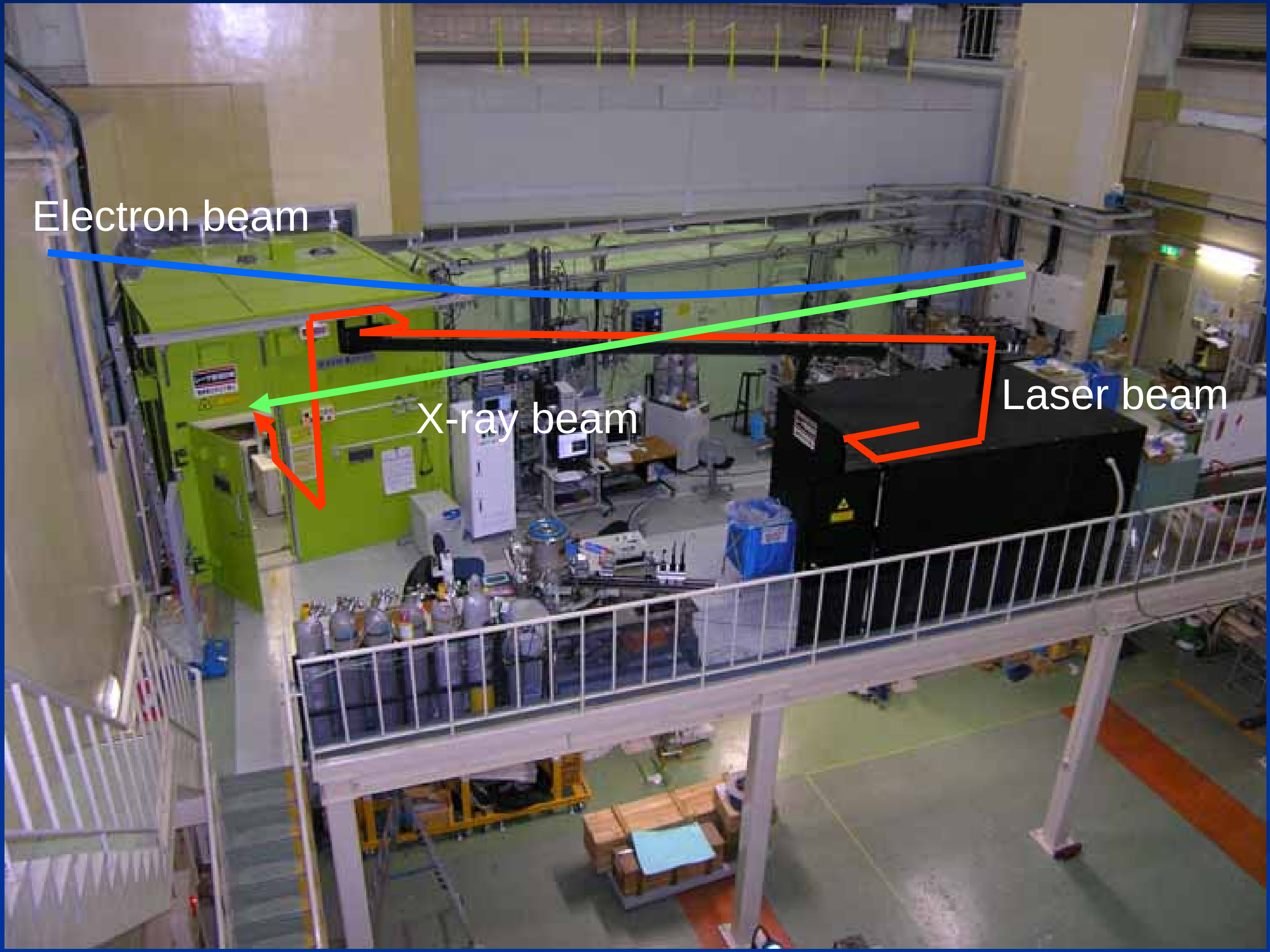
Pump-probe X-ray diffraction at PF-AR NW2



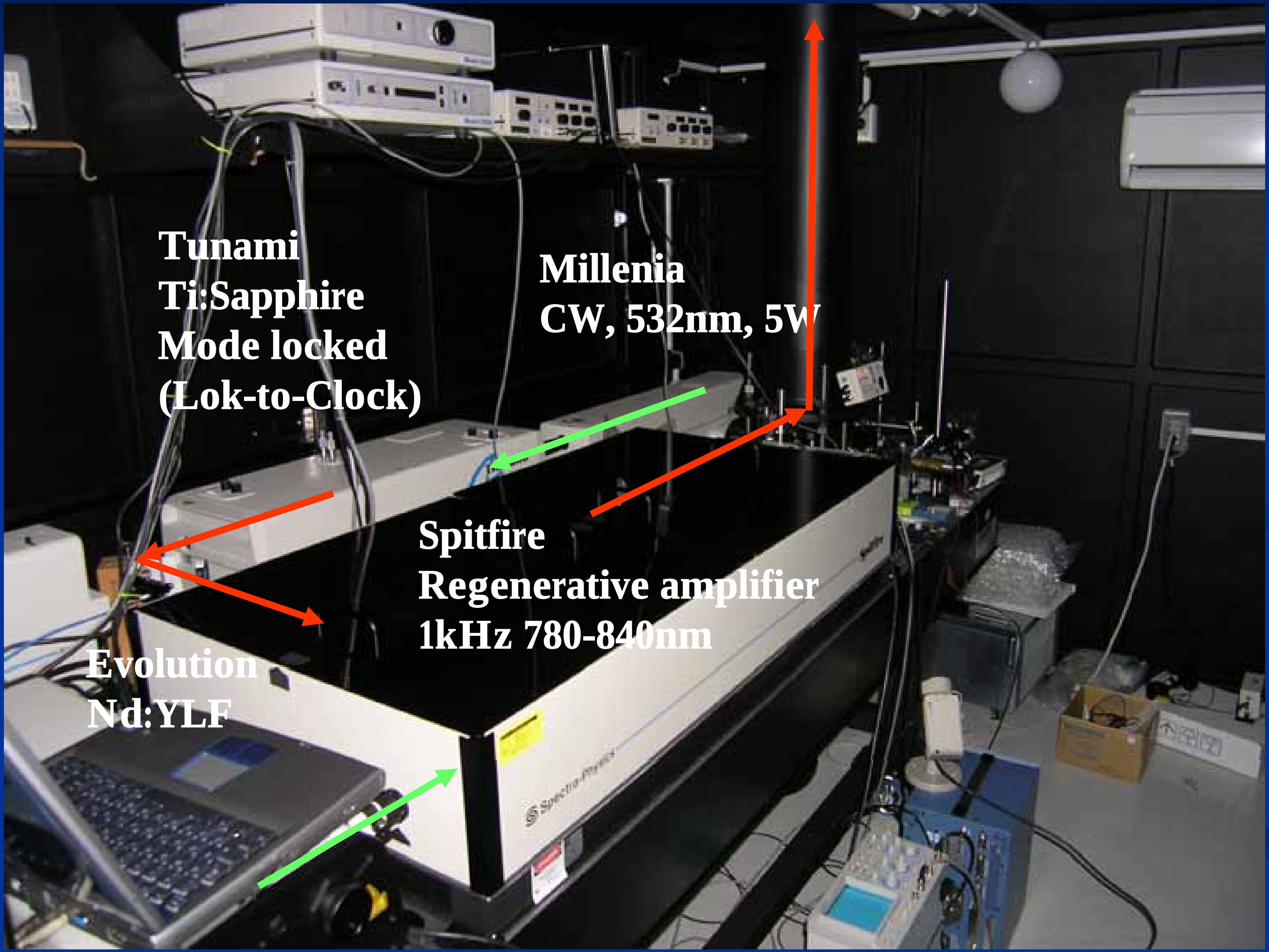
Timing diagram



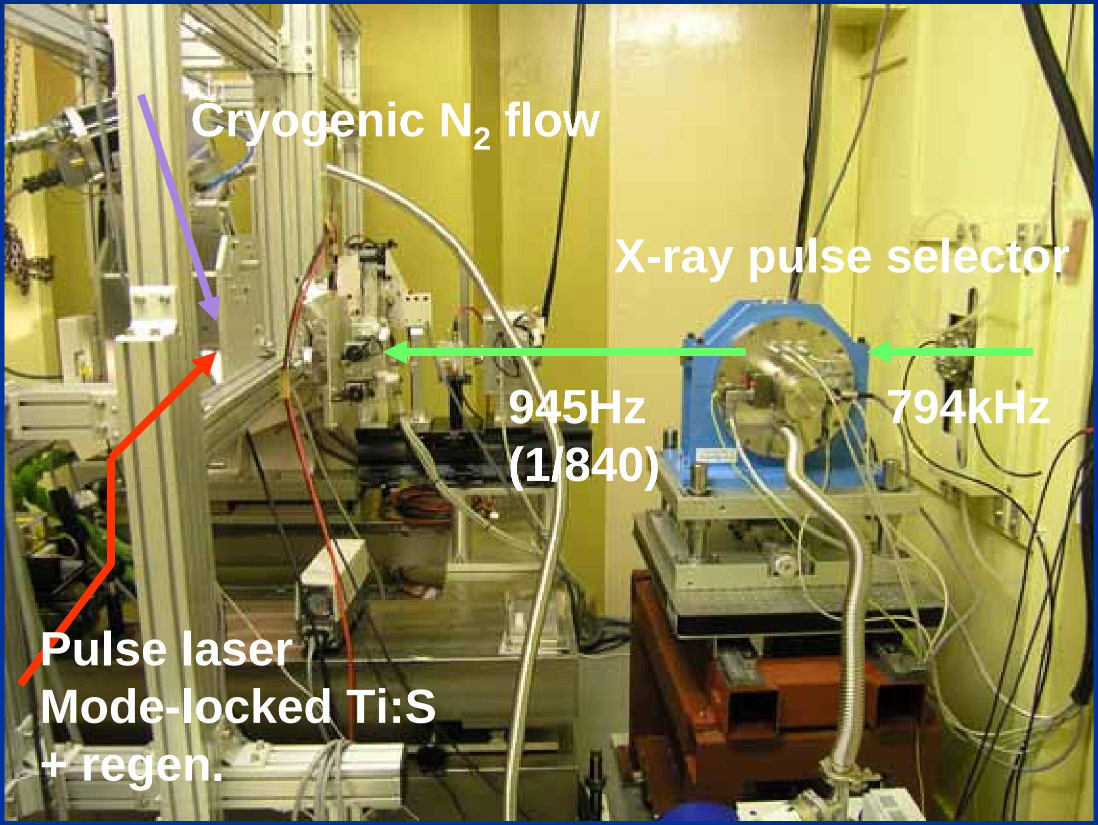
Beamline NW2



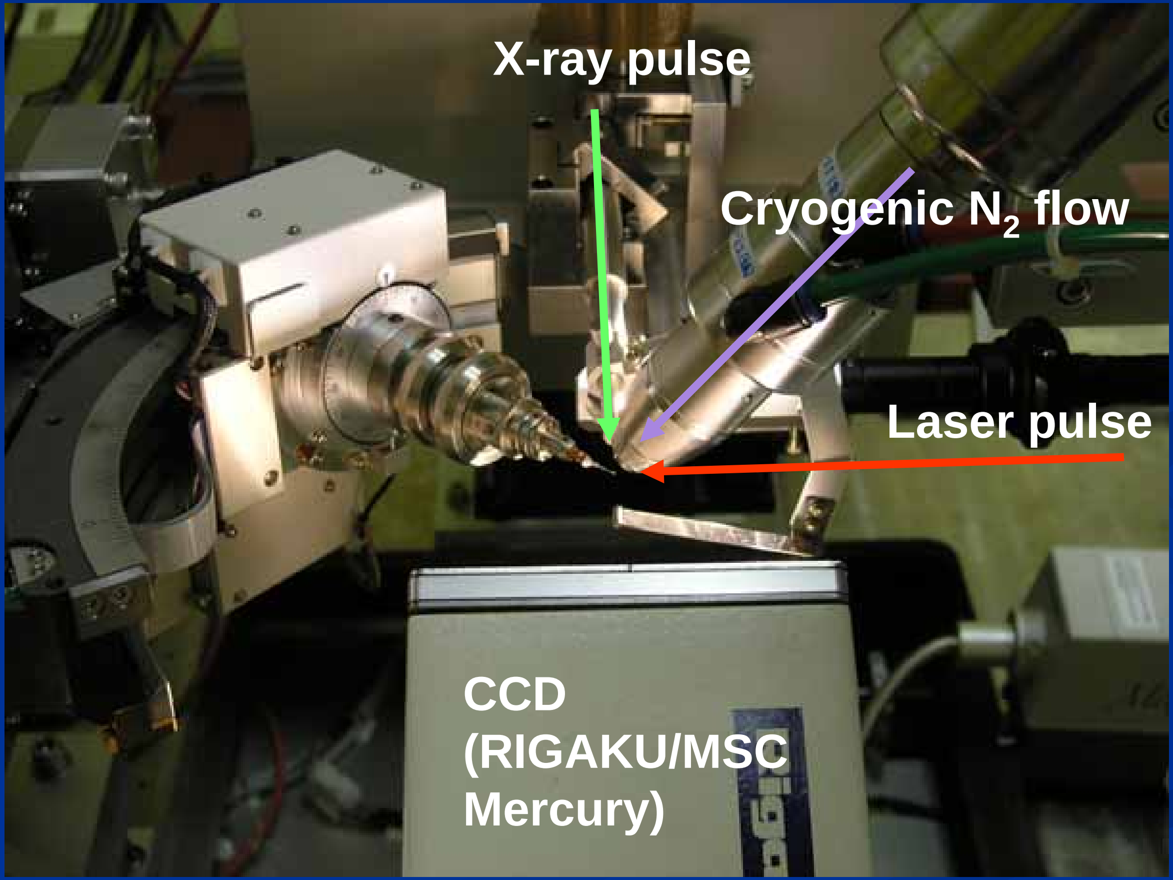
Femtosocond laser system



PF-AR NW2 experimental hutch



PF-AR NW2 diffractomator



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(Collet et al. Science 300, 612, 2003)

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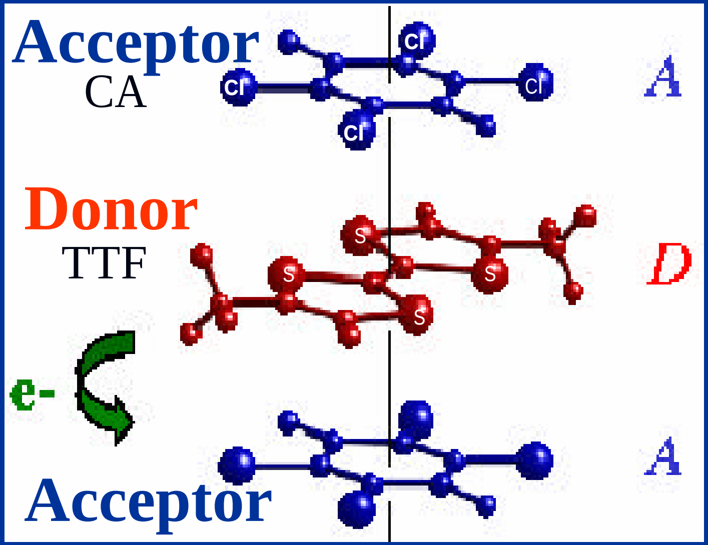
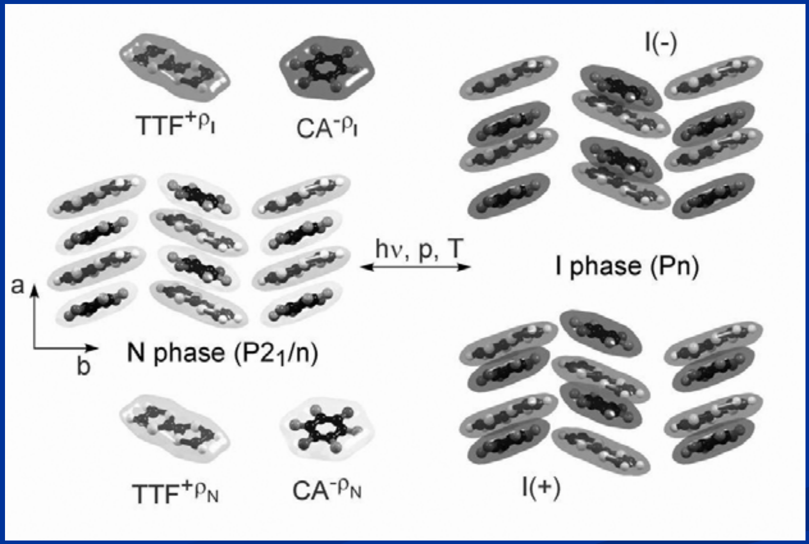
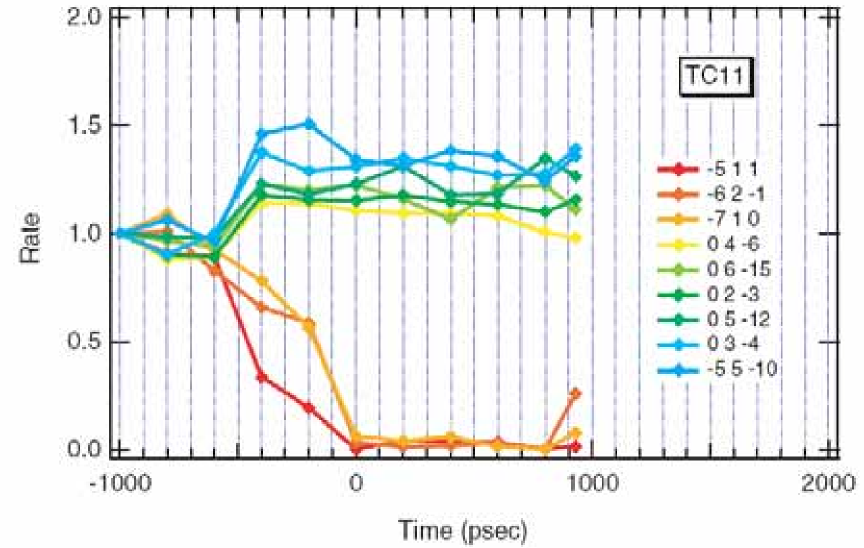




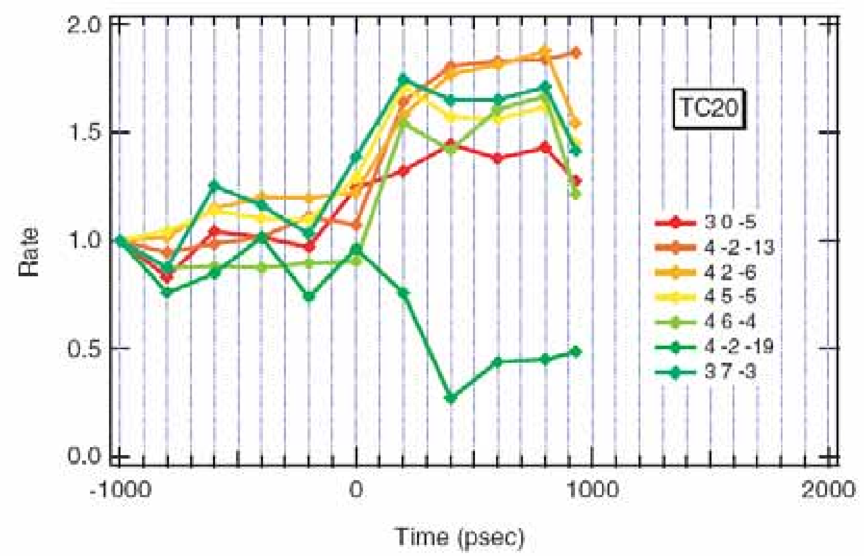
… D° A° D° A° (D^+A^-) (D^+A^-) (D^+A^-) D° A° D° A° …

Time course of diffraction intensity

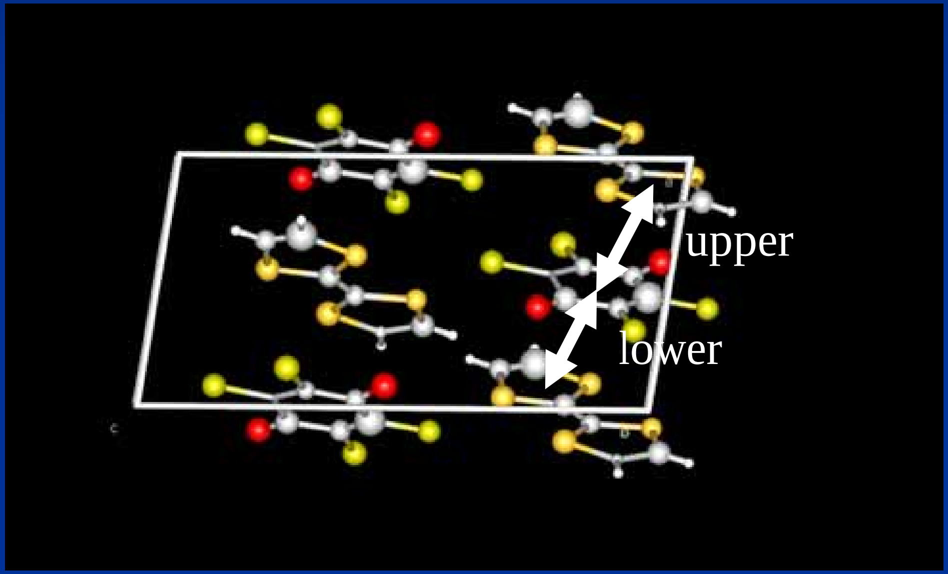
225mW @ 946 Hz
In 1mmϕ

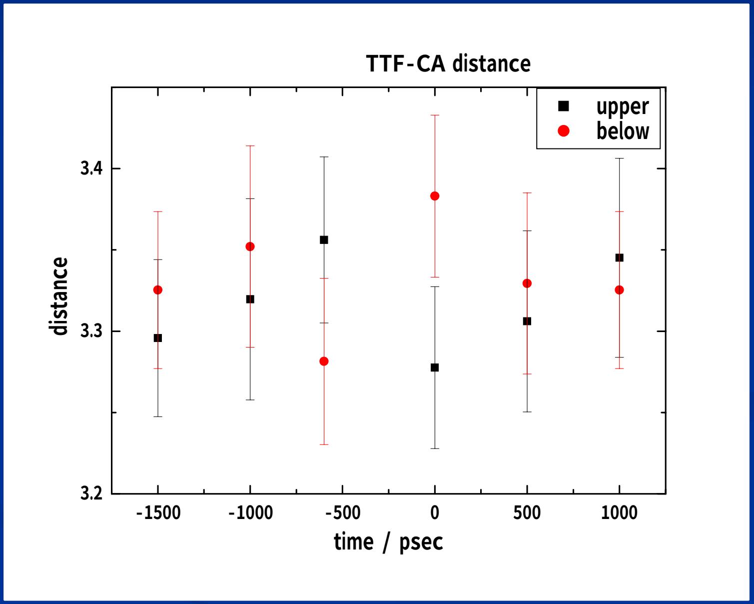


175mW @ 946 Hz
In 1mmϕ

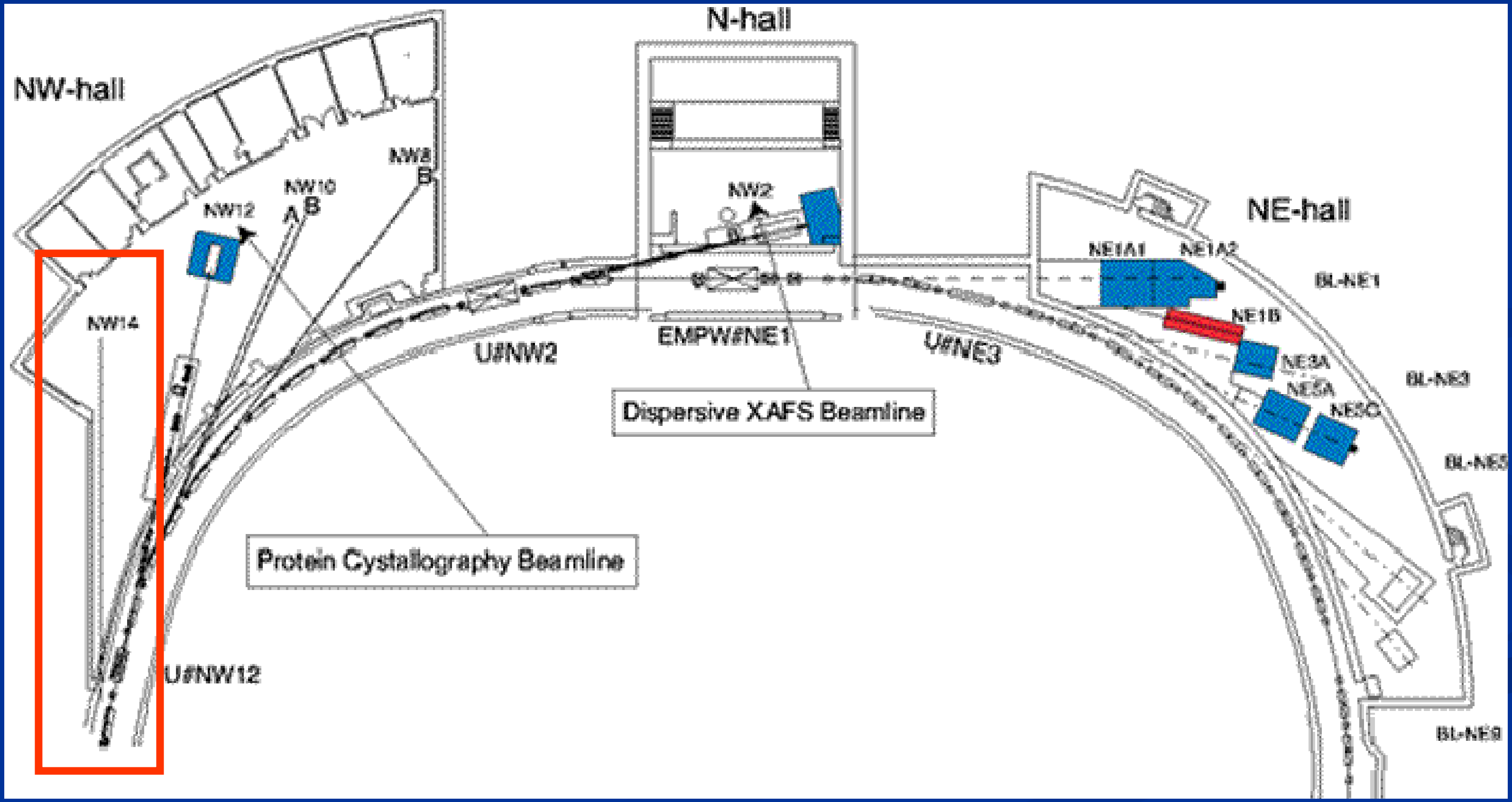


Time course of the distance between TTF and CA molecules





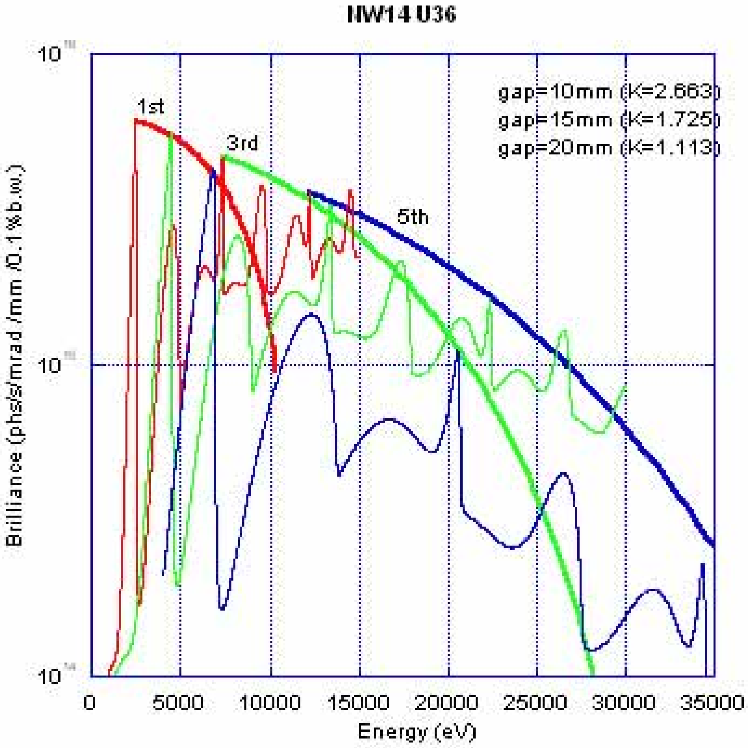
A New Beamline, PF-AR NW14
fully dedicated to time-resolved diffraction
(funded by ERATO, JST)

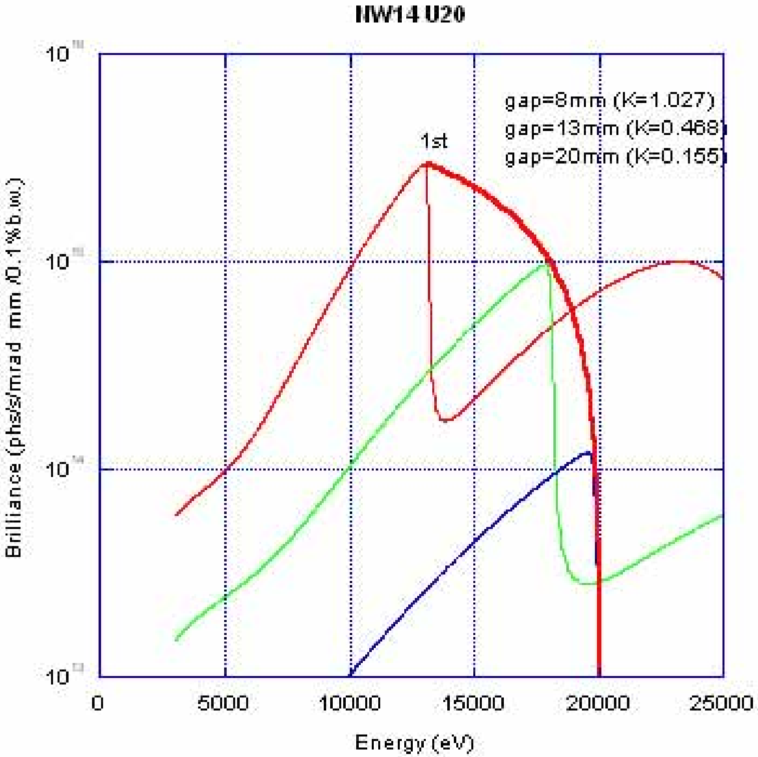


Specifications of NW14

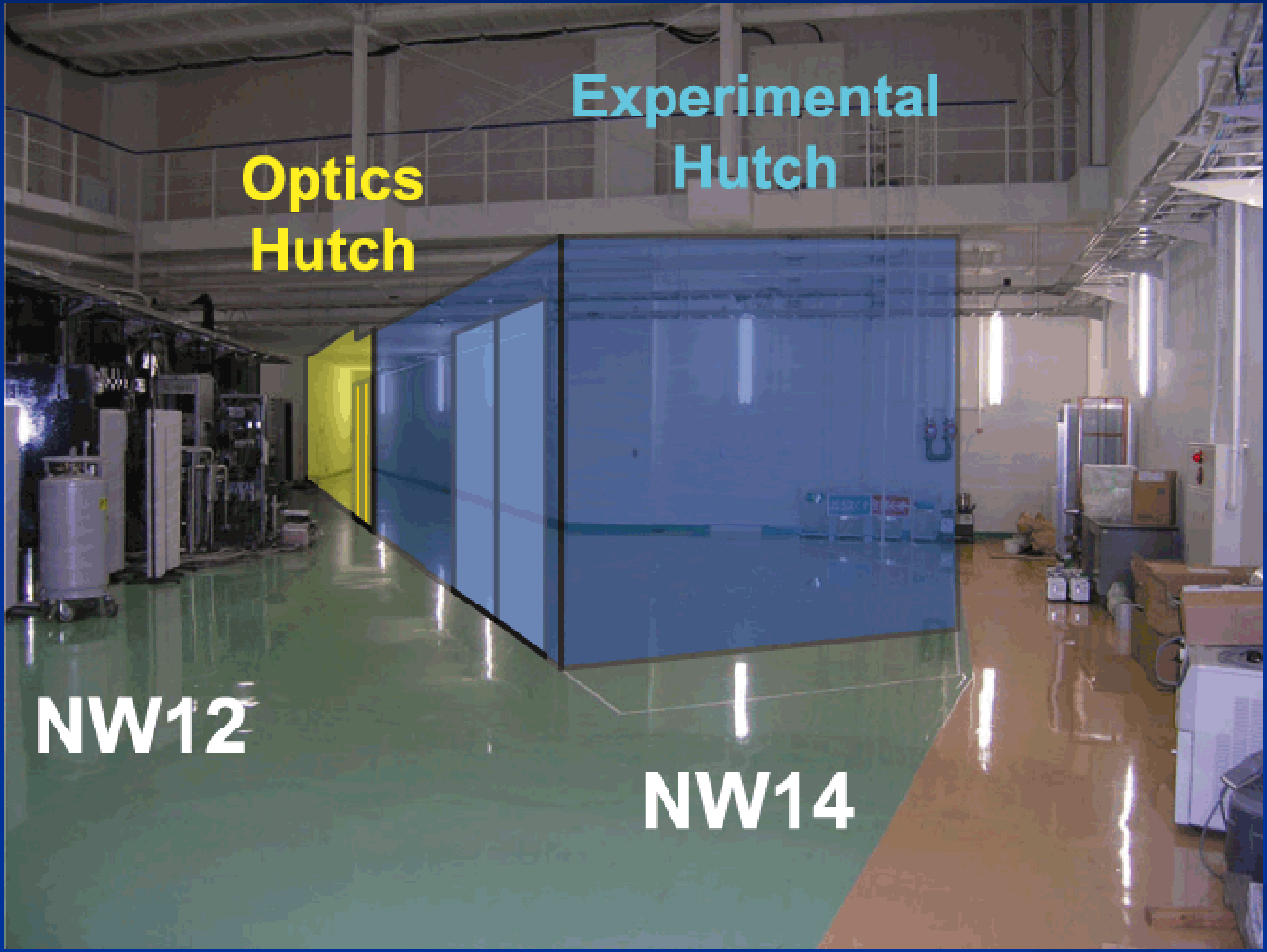
Components	Specifications
Undulators	Two in-vacuum, linear polarization undulators （U36, U20）
U36	λu:36mm, Number of magnets:86, Total length:3096mm Minimum gap:10mm, Maximum power:3.1kW
U20	λu:20mm, Number of magnets:75, Total length:1500mm Minimum gap:8mm, Maximum power:0.7kW
Front end	PF-AR standard （same as NW2, NW12）
	Pre-, and Main mask, absorber, beam shutter, graphite filter, slit, Be window
Optics	Double-crystal monochromator (Si(111), liquid nitrogen cooled, 2-25keV) Bent-cylindrical mirror (Rh coated, 1m) Higher-harmonics cut-off mirror (Rh coated, 1m x 2)
Experimental hutch	3 diffractometers (Huber 7-axis, Rigaku Cyrindrical Imaging plate, and Rigaku MercuryCCD)

Two Undulators at NW14





Virtual view of NW14



Future view

- Toward sub-picosecond X-ray source
  - Future Light Source at KEK
  - X-ray Free electron lasers (DESY TESLA, Stanford LCLS, SPring-8 SCSS), ERL (Cornel CHESS)
- Toward other materials
  - Other strongly-correlated electron systems, photo-active proteins …
- Toward other techniques using synchrotron radiation
  - XAFS, photo-electron spectroscopy, X-ray emission spectroscopy, single molecule imaging, …

Co-workers

Hemoglobin (SPring-8)

- Sam-Yong Park (Yokohama City Univ.)
- Jeremy R. H. Tame (Yokohama City Univ.)
- Naoya Shibayama (Jichi Medical School)
- Yoshitsugu Shiro (RIKEN/SPring-8)

TTF-CA and EDO-TTF (PF-AR)

- 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)
  - Tokushi Sato (TITECH)
  - Ayana Tomita (TITECH)
  - Tadahiko Ishikawa (TITECH)
- Univ. Rennes 1
  - Eric Collet
  - Laurent Guerin
  - Herve Cailleau
- EDO-TTF crystal (Kyoto Univ.)
  - Akira Ota
  - Hideki Yamochi
  - Gunzi Saito