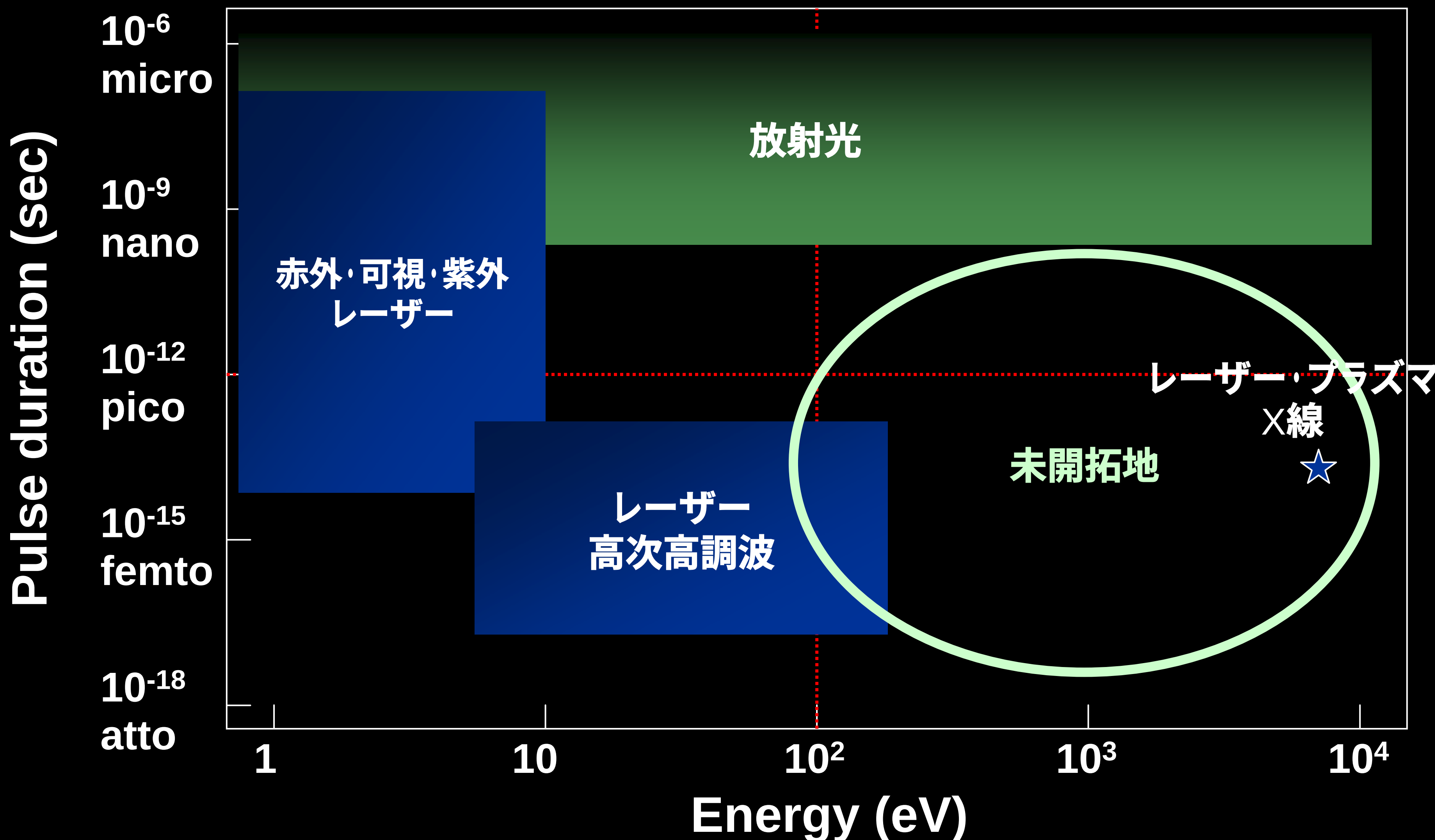
放射光X線による100ピコ秒時間分解研究の現状とフェムト秒時間分解実験への期待

KEK-PF
足立伸一

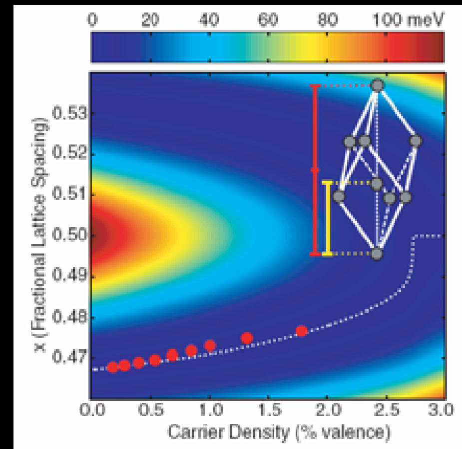
- はじめに
- 100ピコ秒X線研究の現状
- サブピコ秒X線への期待

光源のエネルギーとパルス幅



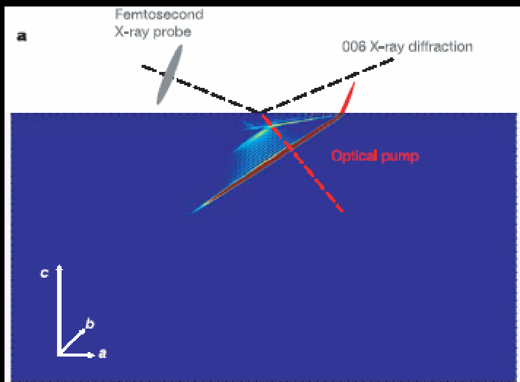
Bond softening in Bismuth (SPPS)

Fritz et al. (2007) Science 315, 633.



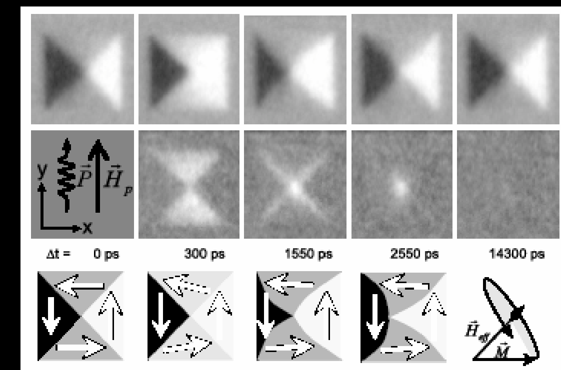
Phonon-polariton wave in $LiTaO_3$ (ALS)

Cavalleri at al. (2006) Nature 442 664.



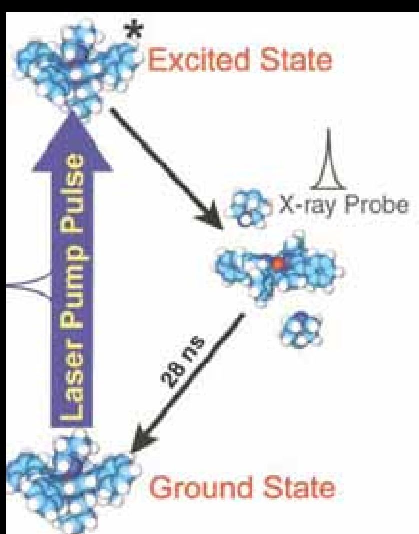
Magnetic excitations in permalloy squares (SLS)

Raabe et al. (2005) Phys. Rev. Lett. 94,217204



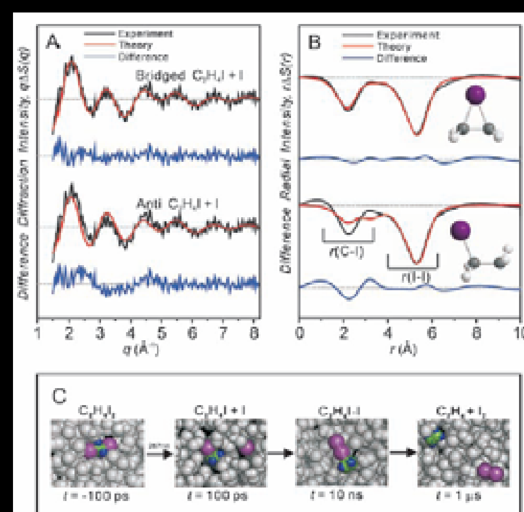
Time Domain Science with SR

最近の報告例



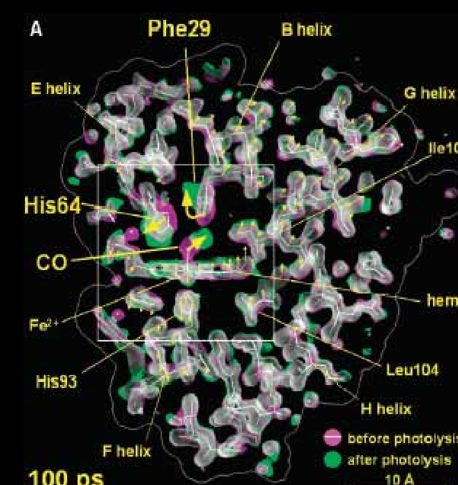
Ni(II) porphyrin (APS)

Chen et al. (2001) Science 292, 262.



$C_2H_4I_2$ in methanol (ESRF)

Ihee, et al., (2005) Science 309, 1223.



Mutant myoglobin (ESRF)

Schotte et al.(2003) Science 300, 1944.

Femtosecond X-ray Pulses at 0.4 Å Generated by 90º Thomson Scattering: A Tool for Probing the Structural Dynamics of Materials

Schoenlein et al. (1996) **Science** 274, 236.

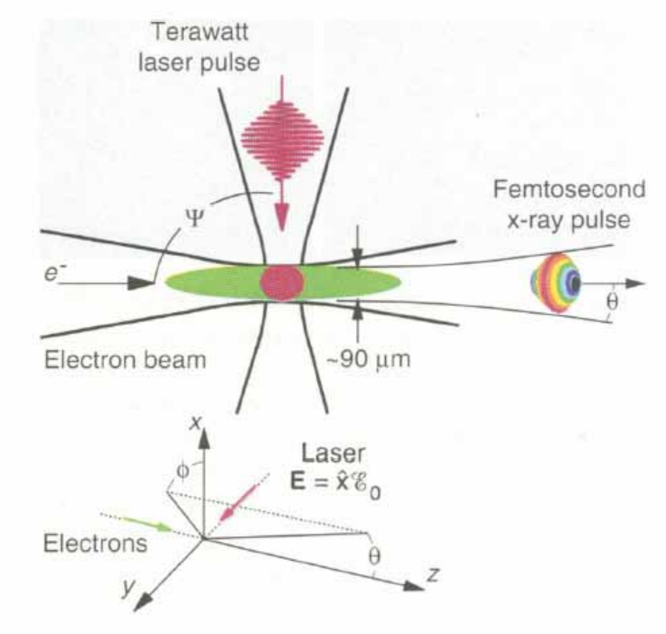


Fig. 1. Schematic of the femtosecond Thomson scattering geometry.

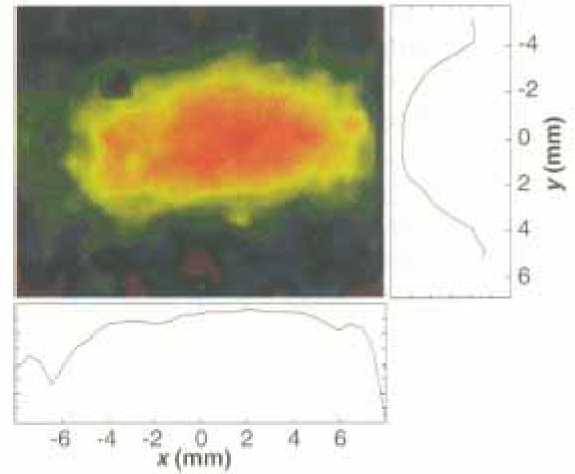


Fig. 2. False-color CCD image of the spatial profile of a 30-keV (0.4 Å), ~300-fs x-ray pulse striking a phosphor screen at a distance of 80 cm from the scattering point. Vertical and horizontal lineouts indicate a beam size of ~12 mm by ~8 mm (FWHM).

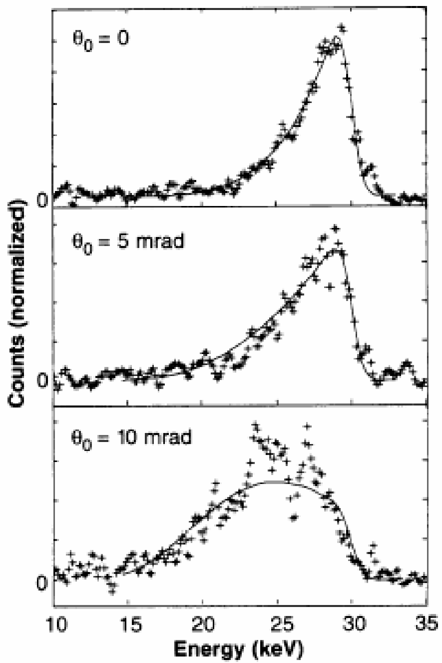


Fig. 3. Spectral measurements of the femtosecond x-rays at observation angles of θ_0 = 0 mrad, 5 mrad, and 10 mrad ($\phi_0 = \pi/2$). The detector lies in the *yz* plane. Also shown (solid lines) are theoretically predicted spectra corrected for detector sensitivity and window transmission as described in the text.

Electron: 50 MeV, 1.3nC, 20 ps (FWHM)

Laser: 60mJ, 100fs, 10Hz, 800 nm

X-ray: 30 keV, ~300fs, 2 x 10^5 photons/pulse/15%

“Rapid advances in diode-pumped, solid state lasers and superconducting linac structures may provide substantially higher x-ray brightness in future Thomson sources by operating at very high repetition rates.”

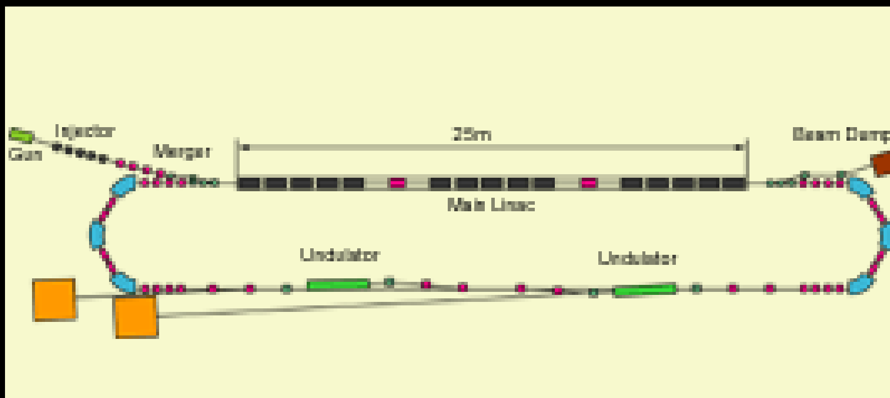
1996

Electron: 50 MeV, 1.3nC, 20 ps (FWHM)
Laser: 60mJ, 100fs, 10Hz, 800 nm
X-ray: 30 keV, ~300fs, 2×10^5 photons/sec/15%b.w.

2007

Electron: 60 MeV, 0.1nC, 0.1 ps
Laser: 10 mJ, 0.1 ps, 1 kHz, 800 nm
X-ray: 42 keV, 1×10^9 photons/sec/10%b.w. !!

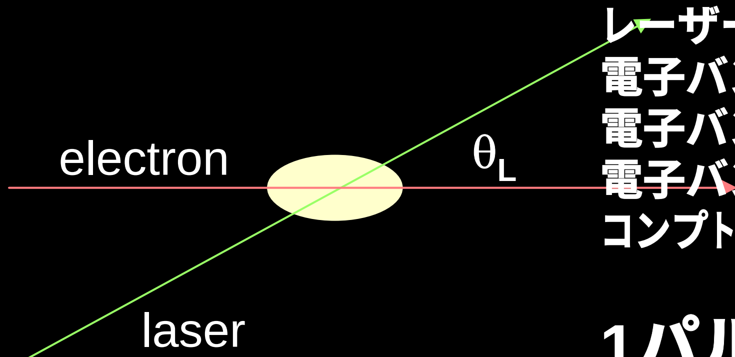
Laser-Compton X-ray source at ERL test facility (60-150MeV)



$$E_{Xray} = 2\gamma^2 E_{Laser}(1-\cos\theta_L)/(1+\gamma^2\theta^2)$$

$$Flux = (N_L N_e/wh)(L_{eff}/L_b)\sigma_c$$

E_{Laser} = 1.55eV, $E_{electron}$ = 60 MeV (γ=117), θ_L = 90 degree **のとき、**
軸上(θ=0)**でE_{Xray} = 42.4 keV**



レーザーパルス (1.55eV, 10mJ)**のフォトン数**： $N_L = 4 \times 10^{16}$ photons
電子バンチ中の電子数 (60MeV, 0.1nC)： $N_e = 6 \times 10^{8}$ electrons
電子バンチの水平幅： $w = 50 \times 10^{-6}$ m
電子バンチの高さ： $h = 50 \times 10^{-6}$ m
コンプトン散乱断面積： 1×10^{-28}

1パルスあたり、

Flux = 1×10^{6} phs/pulse/10%b.w.

1 kHzのとき、

Flux = 1×10^{9} phs/sec/10%b.w.

既存放射光との比較

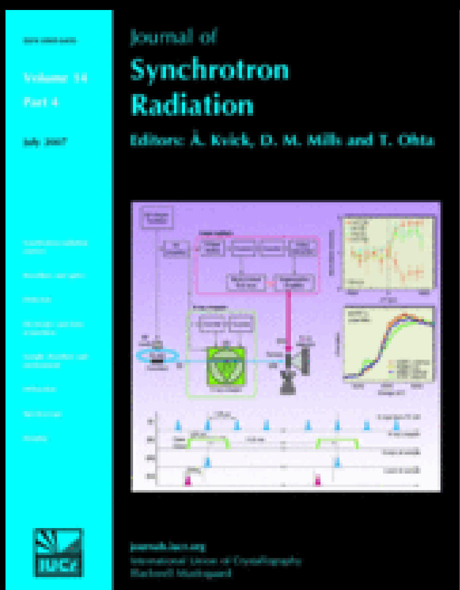
- 同じエネルギーバンド幅、繰り返し周波数で比較すると（１０Wレーザー使用）、
  - AR-NW14A: 10^{12} phs/s/10%b.w. @ 1kHz
  - Compact ERL: 10^{9} phs/s/10%b.w. @ 1kHz
- エンハンスメント共振器が使用できると、（小林先生（産総研）の昨日の講演、1GHz、10μJ）レーザー出力は10Wから10kWへ。単位時間当たりのX線フォトン数は1000倍。既存放射光と同等以上。
  - 10^{9} → 10^{12} phs/s/10%b.w.

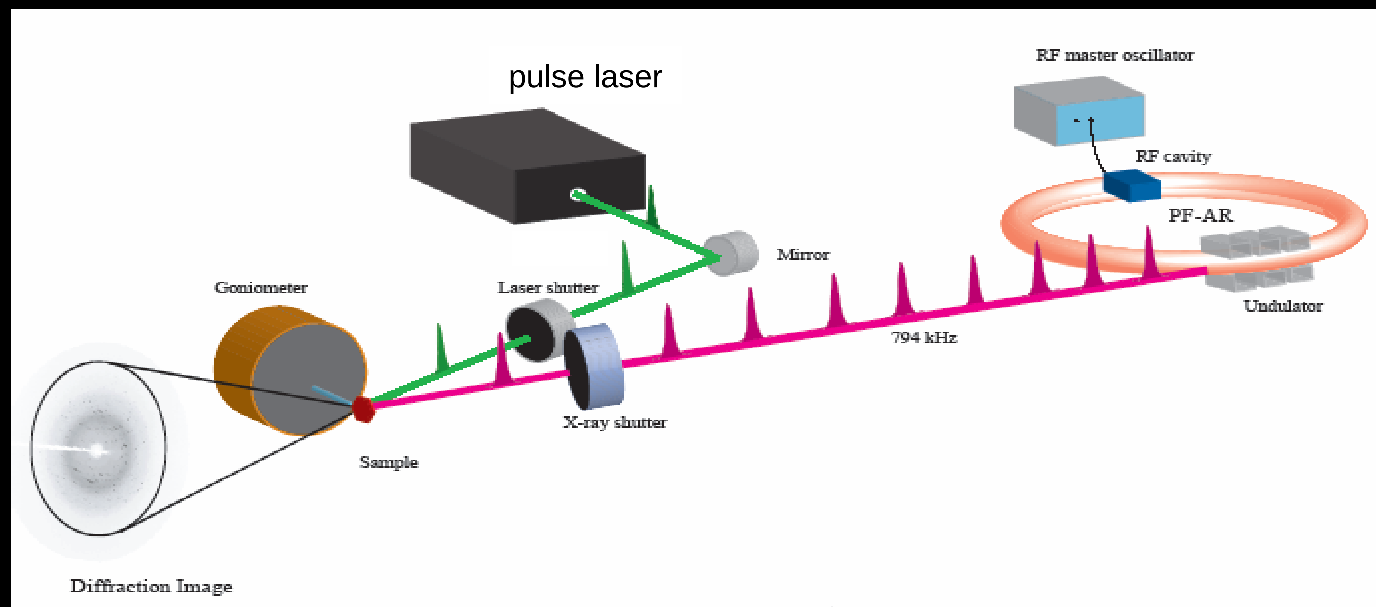
Source	Pulse length (fs)	Repetition rate (Hz)	Photon flux	Energy range
Compact ERL/Laser-Compton Source (1nC, 10kHz)	~150	1000	1 x 10^9 phs/sec/10%b.w. 1 x 10^6 phs/sec/0.1%b.w. 1 x 10^6 phs/pulse/10%b.w.	10-100 keV
PF-AR NW14 (80nC, 794kHz, 60mA)	100 x 10^3	794 x 10^3	1 x 10^{15} phs/sec/10%b.w. 1 x 10^{12} phs/sec/0.1%b.w. 1 x 10^9 phs/pulse/10%b.w. 1 x 10^6 phs/pulse/0.1%b.w.	5-30 keV
KEK-ERL Low-rep. mode (1nC, 10kHz, 0.01mA)	100 – 1000	10000	1 x 10^{11} phs/sec/10%b.w. 1 x 10^7 phs/sec/0.1%b.w. 1 x 10^7 phs/pulse/10%b.w.	5-30 keV
Laser Bunch Slicing (ALS upgrade)	200	40000	5 x 10^7 phs/sec/0.1%b.w.	0.2-10 keV
Laser-produced plasma X-ray	~100	10	6 x 10^{10} phs/pulse/4πsr	8 keV (Cu-Kα)
Laser / high harmonic generation	100 - 0.1	10 - 10000	~ 10^8 phs/sec/0.1%b.w.	10 eV-1 keV
Sub-Picosecond Pulse Source (SLAC)	80	10	2 x 10^7 phs/pulse/1.5%b.w.	8-10 keV
KEK PF-BT line	500	20	~ 10^7 phs/pulse/10%b.w.	0.2-10 keV
X-FEL （LCLS, SCSS, European XFEL)	230	120	2 x 10^{12} phs/pulse/0.2%b.w.	1-10 keV

X-ray beam characteristics from superconducting-linac-based Laser-Compton X-ray sources

- **High repetition frequency** (< 1GHz)
- **Hard X-ray available** (~ 10-100 keV)
- **Short pulse duration** (~ 100 fs)
- **Large beam divergence** (~ 10 mrad)
- **Relatively high average photon flux** (~ 10^{10} photons/sec/~10%b.w. @ 10 kHz)

100ピコ秒X線研究の現状と
サブピコ秒X線への期待





Nozawa et al.
J. Synchrotron Rad. (2007). **14**, 313-319.

PF-AR NW14A
通年大強度単バンチ　時間分解実験に最適
ERATO**腰原非平衡ダイナミクスプロジェクト**

Motivations for femtosecond X-ray

Bond softening in Bismuth (SPPS)

Fritz et al. (2007) Science 315, 633.

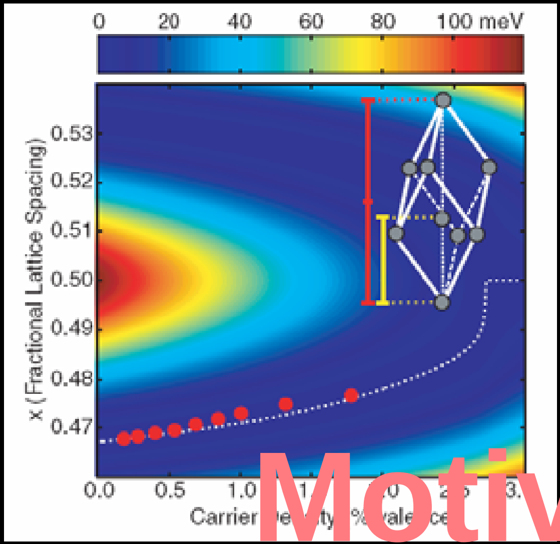
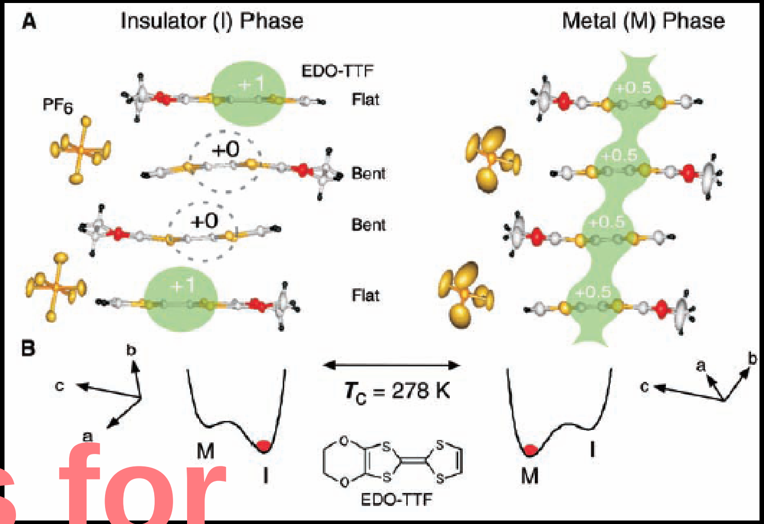
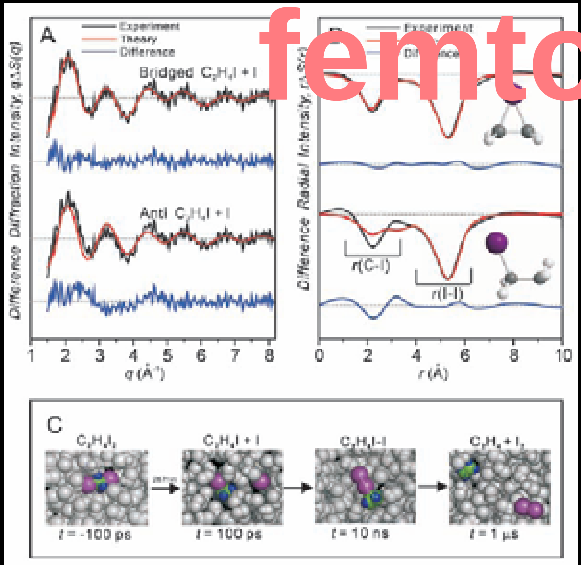


Photo-induced Phase Transition

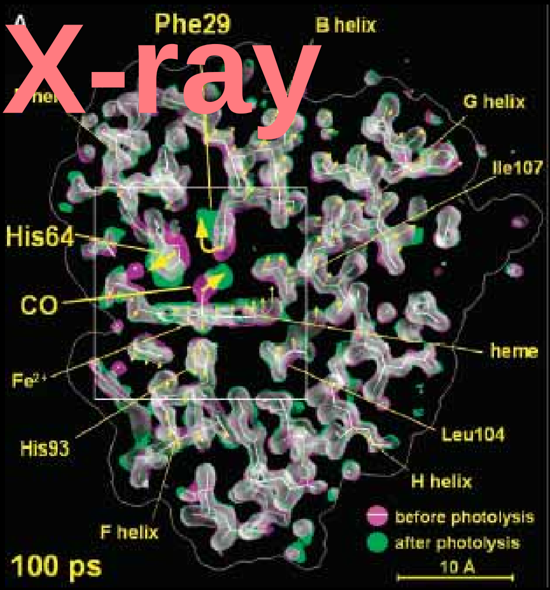
Chollet et al. (2005) Science, 307, 86.





$C_2H_4I_2$ in methanol (ESRF)

Ihee, et al., (2005) Science 309, 1223.

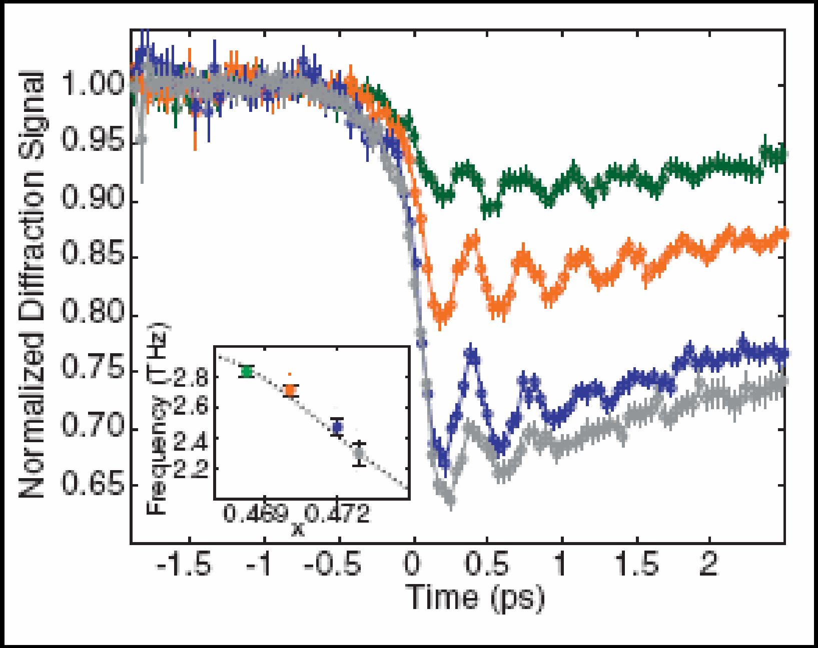


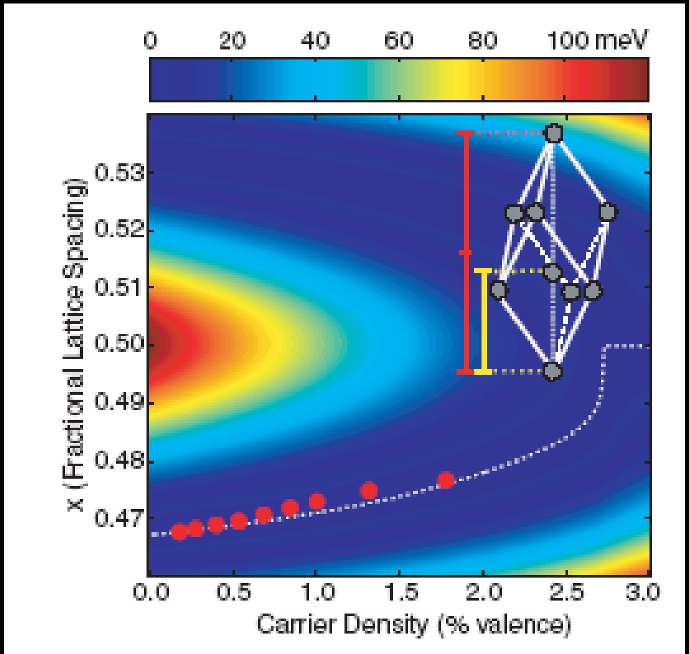
Mutant myoglobin (ESRF)

Schotte et al.(2003) Science 300, 1944.

Motivations for femtosecond X-ray
ex.1) coherent phonon

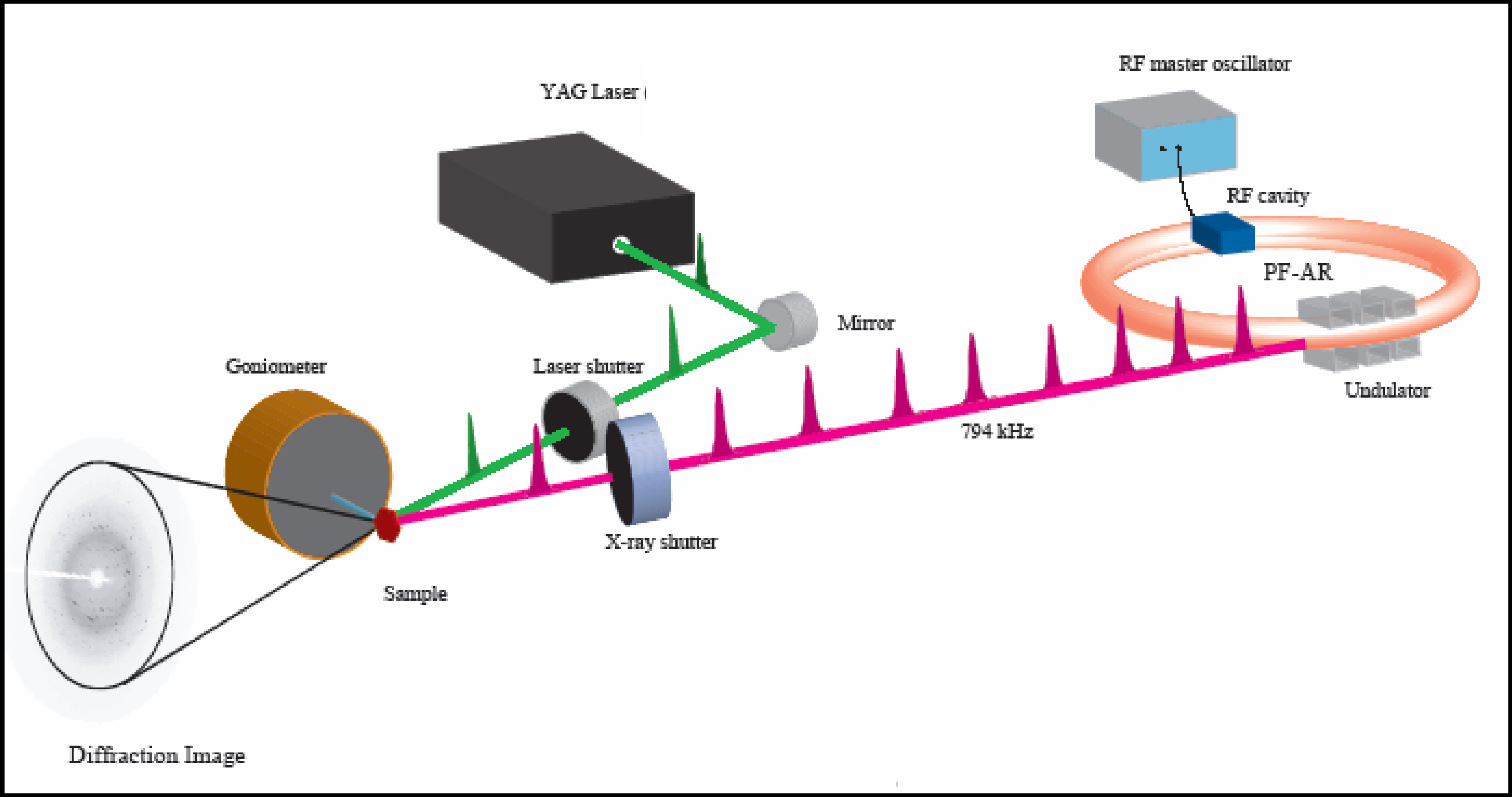
Ultrafast Bond Softening in Bismuth: Mapping a Solid's Interatomic Potential with X-rays
Fritz et al. (2007) Science, 315, 633.





Laser Power: 0.7 (green), 1.2 (red), 1.7 (blue), and 2.3 (gray) mJ/cm^2

Shockwave-induced lattice deformation at NW14A



レーザー誘起衝撃圧縮下の
CdSのナノ秒分解白色X線回折

Kouhei
Ichiyanagi

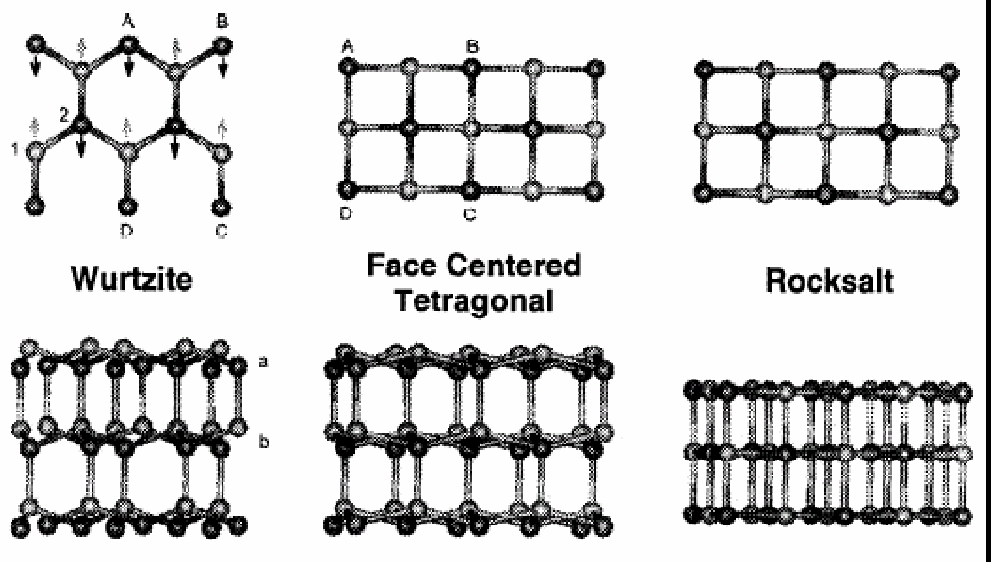
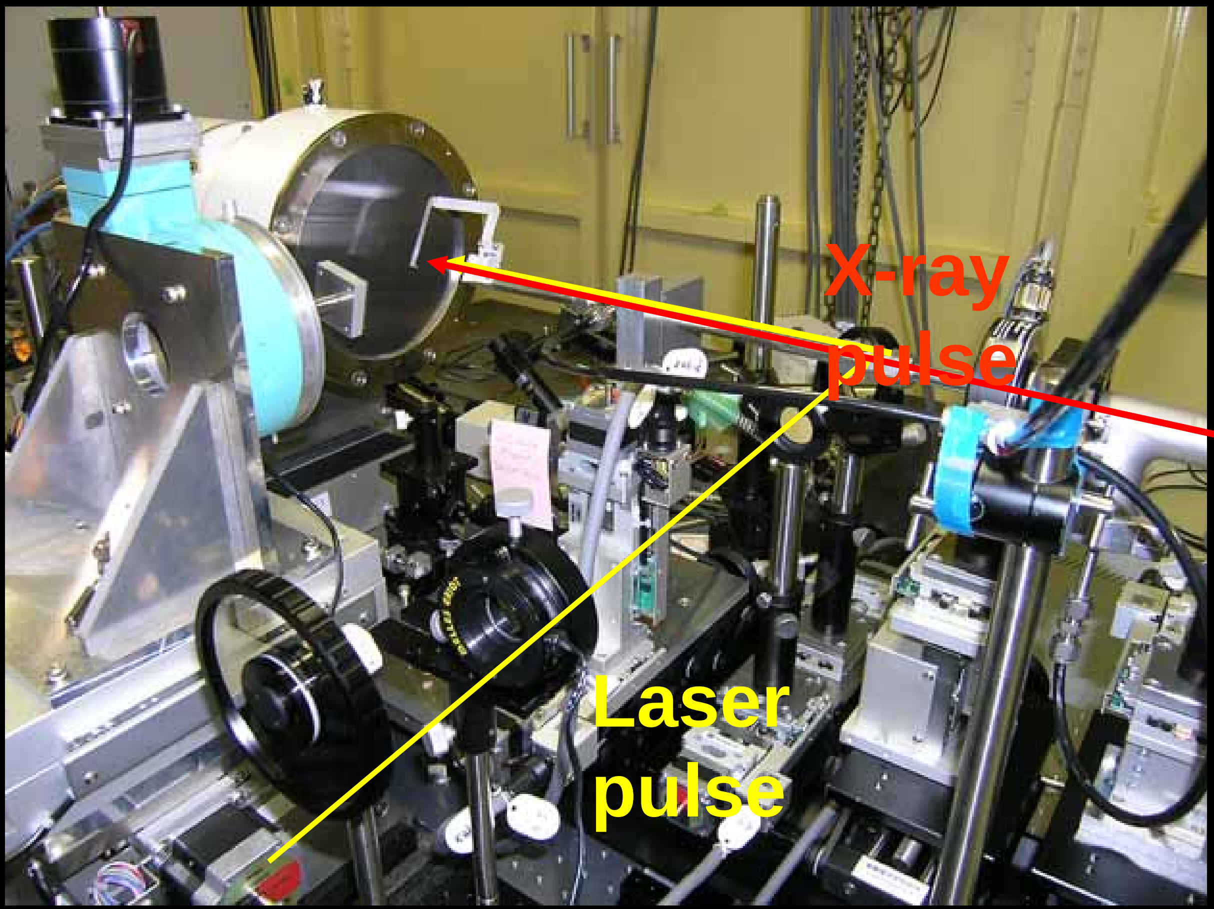


FIGURE 4. The wurtzite, fct, and rocksalt phases of CdS. The top half shows a view down the crystal *c* axis, the bottom half shows a view orthogonal to that. The dark atoms are Cd.

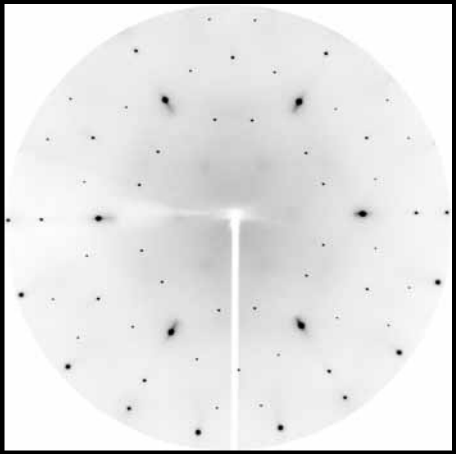
- CdS単結晶は約3万気圧でウルツ鉱型から岩塩型構造になることが知られている。
- 時間分解分光衝撃実験によってナノ秒オーダーで変化し、寿命の短い中間相が存在することが示唆されている。

M. D. Kundson and Y. M. Gupta, et al. Phys. Rev. B. 59. 11704 (1999).

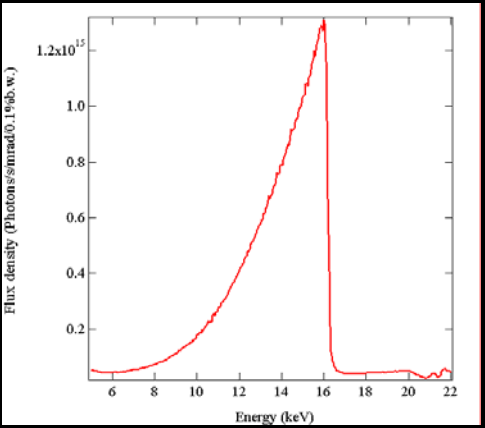
ナノ秒分解白色X線回折実験のセットアップ



レーザー入射前のラウエ回折パターン



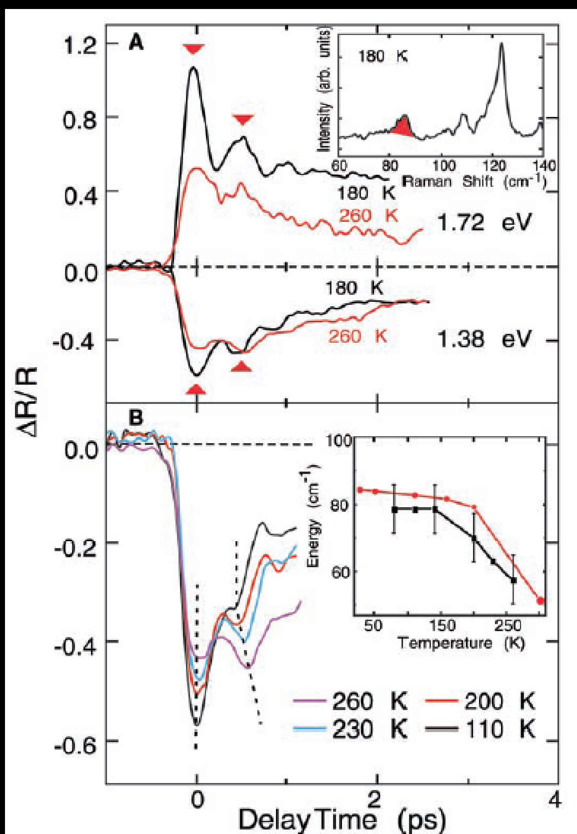
入射X線スペクトル

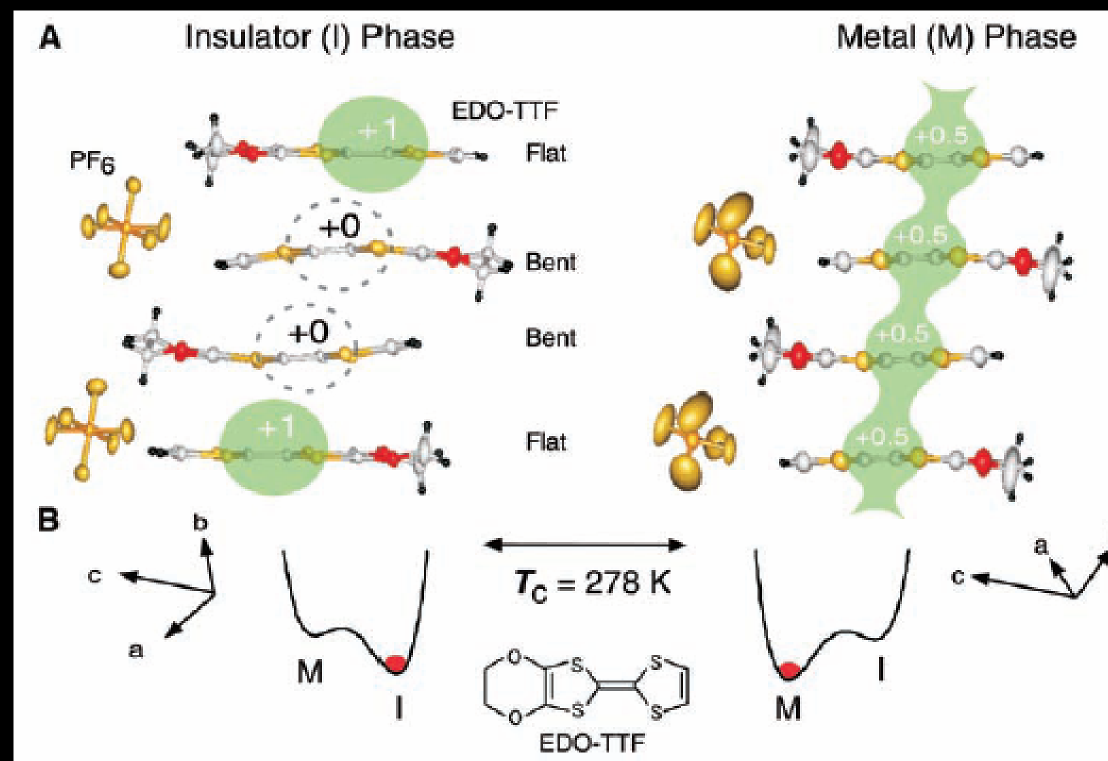


実験条件 **レーザー** YAG 1064 nm, 850 mJ, 8 ns, 10 Hz
Spot size φ400 μm
X-ray 100 ps, white X-ray, 1 kHz
Spot size 250x250 μm

Motivations for femtosecond X-ray
ex.2) photo-induced phase transition

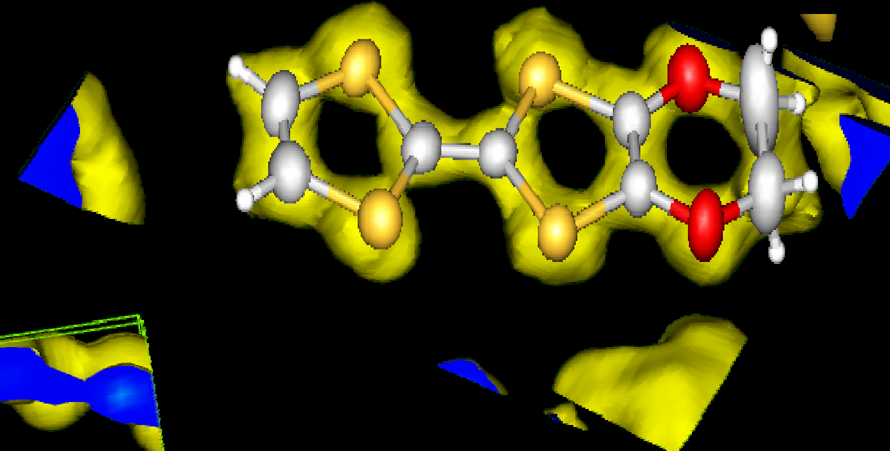
Gigantic Photoresponse in ¼-Filled-Band Organic Salt $(EDO\text{-}TTF)_2PF_6$
Chollet et al. (2005) Science, 307, 86.

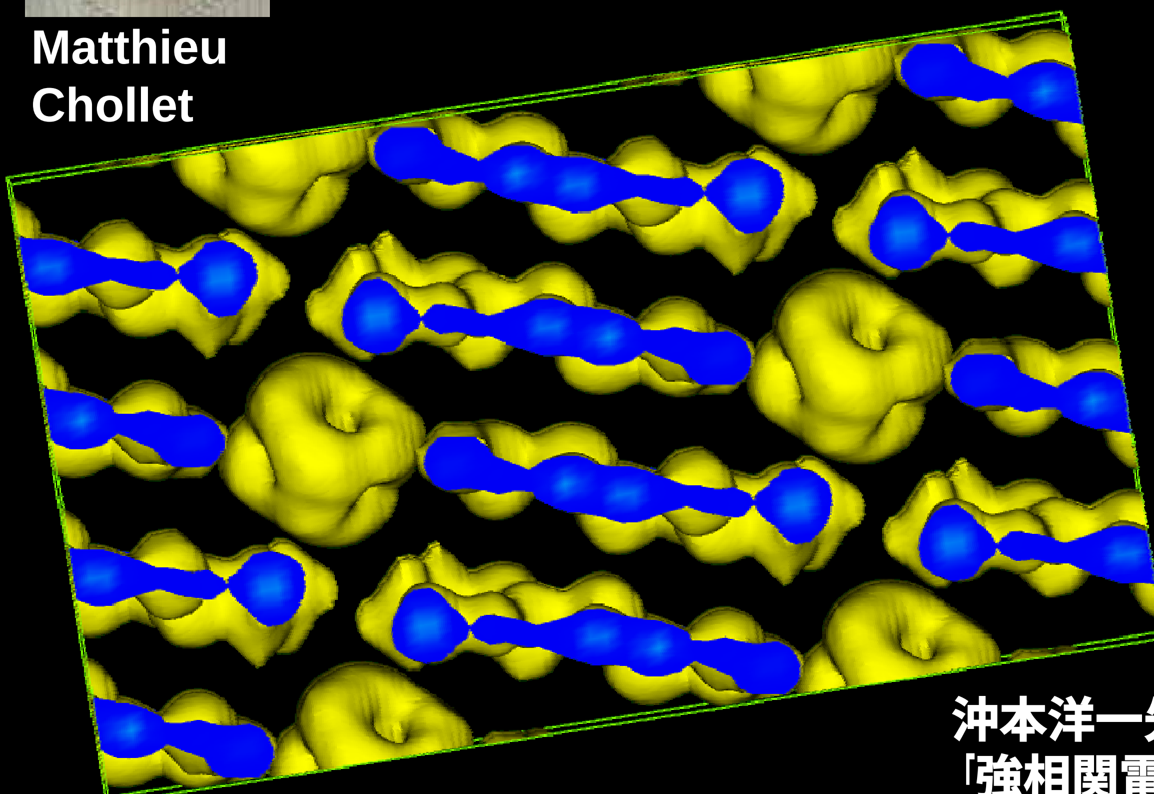




Toward time-resolved electron density analysis @ NW14A

Matthieu Chollet





MEM analysis

300K

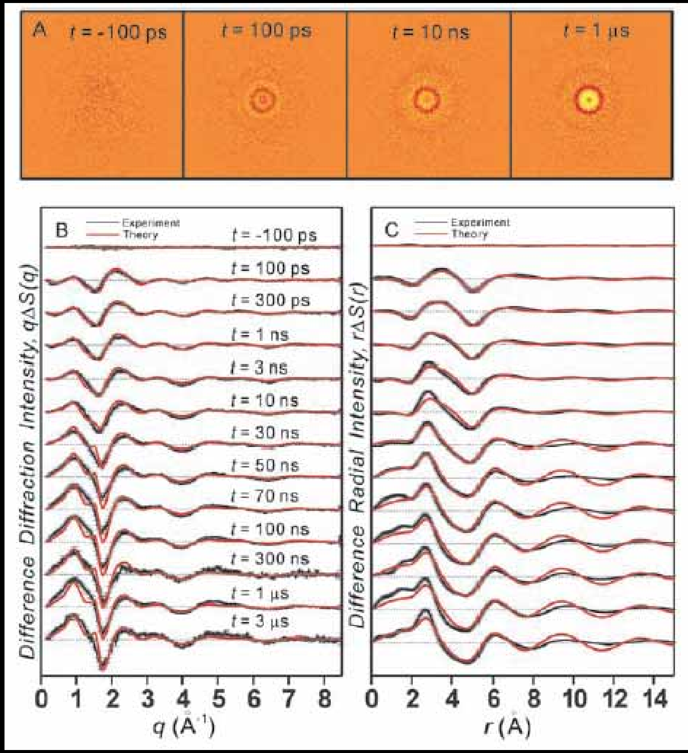
700 me$^-$/A^3

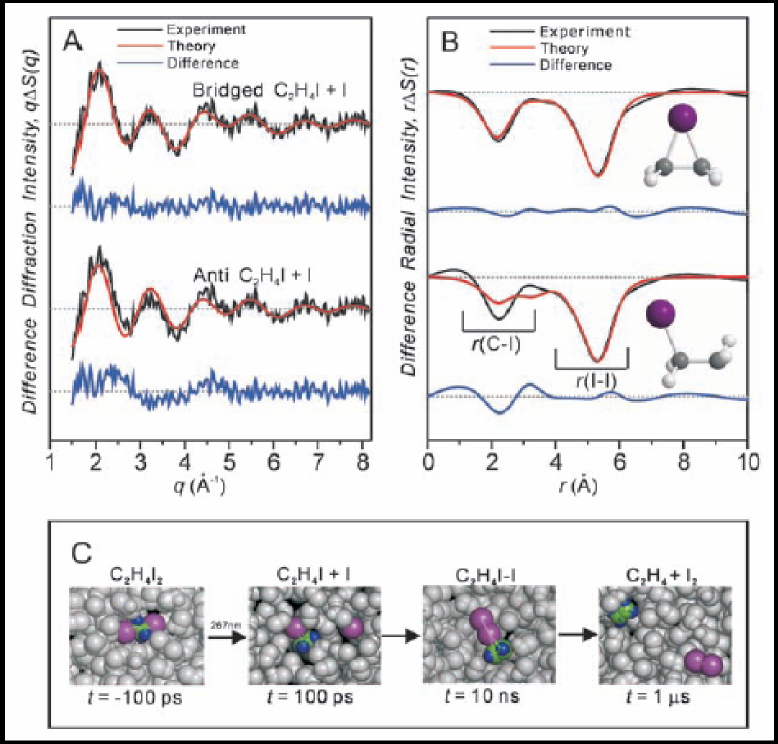
沖本洋一先生
「強相関電子材料における光誘起相転移の超高速ダイナミクス」

Motivations for femtosecond X-ray
ex.3) reaction dynamics in solution

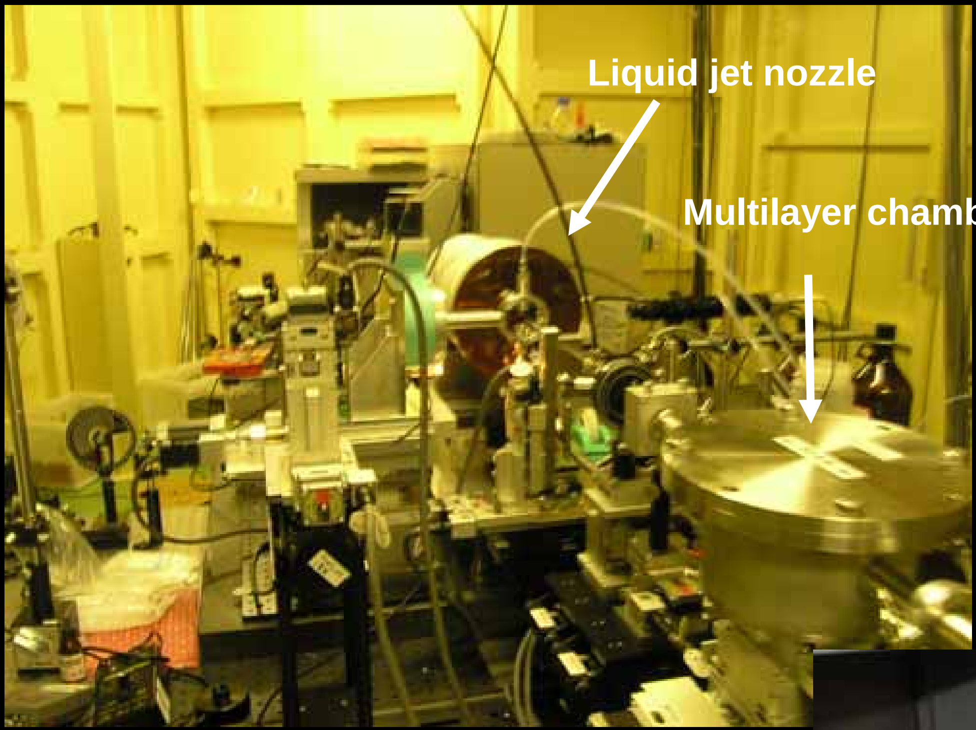
Ultrafast X-ray Diffraction of Transient Molecular Structures in Solution

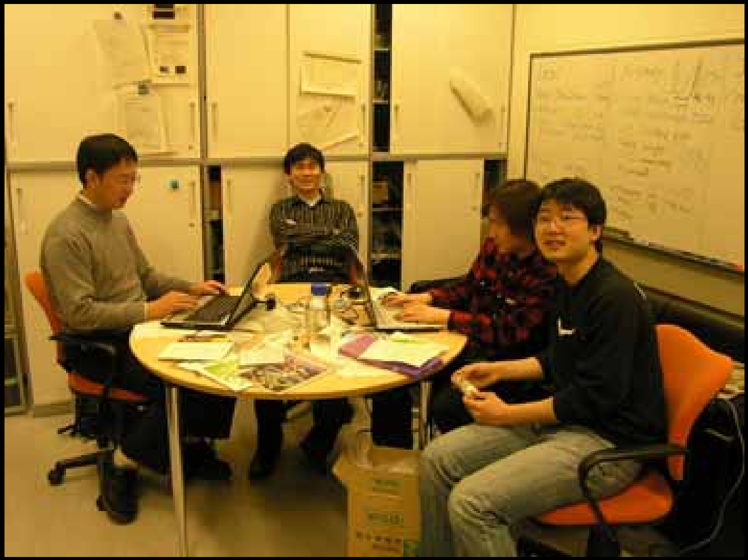
Ihee et al. Science (2005) 309, 1223.

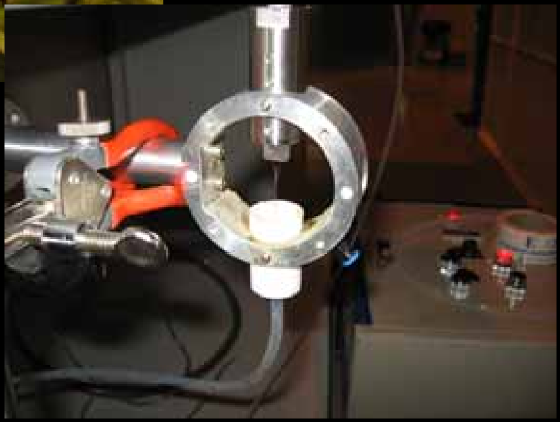




Reaction dynamics in solution @ NW14

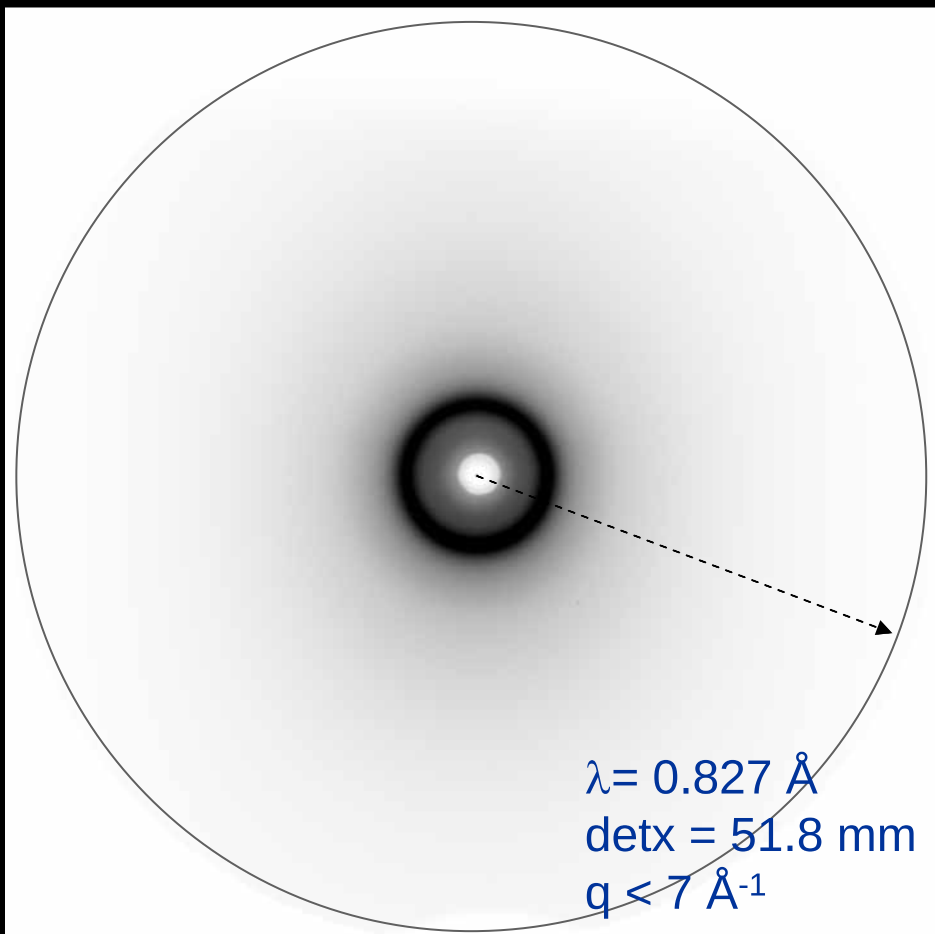




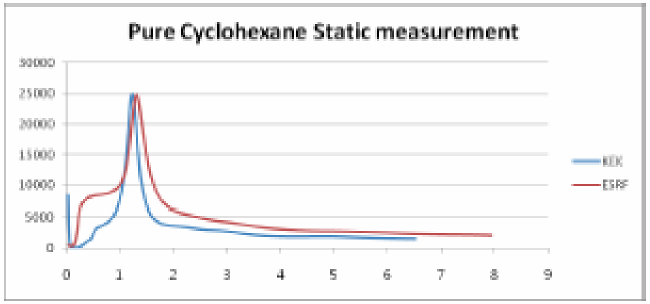


Collaboration with
Hyotcherl Ihee Group
(KAIST, Korea)

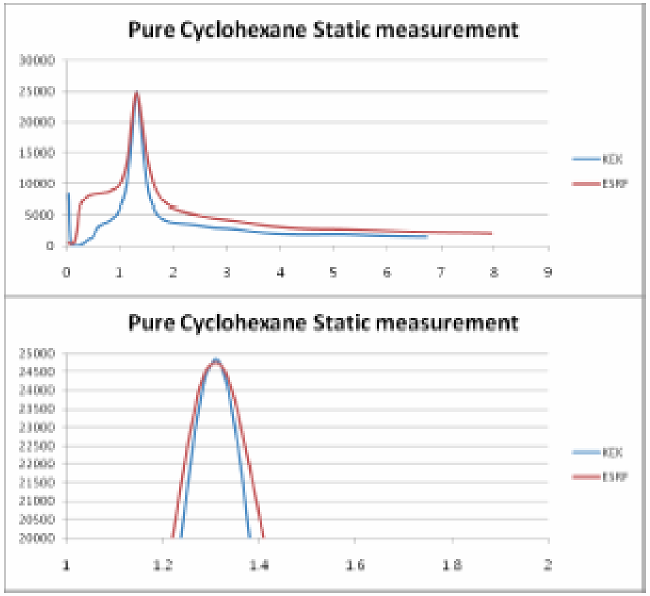
Solution scattering profiles



- Before Calibration; detx=55



- After Calibration; new detx=51.8



UV spectroscopy revealed dumped oscillations in femtosecond time domain

Caging and Geminate Recombination Following Photolysis of Triiodide in Solution

Gershgoren et al., *J. Phys. Chem. A* **1998,** *102,* 9-16

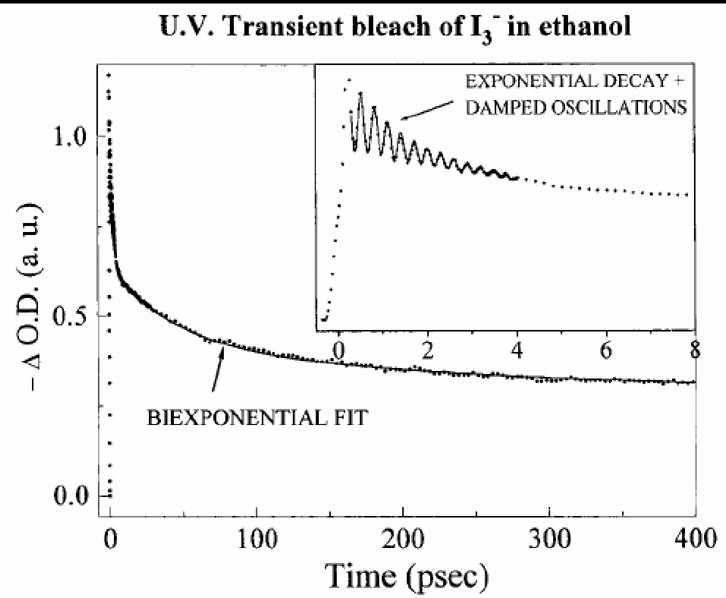


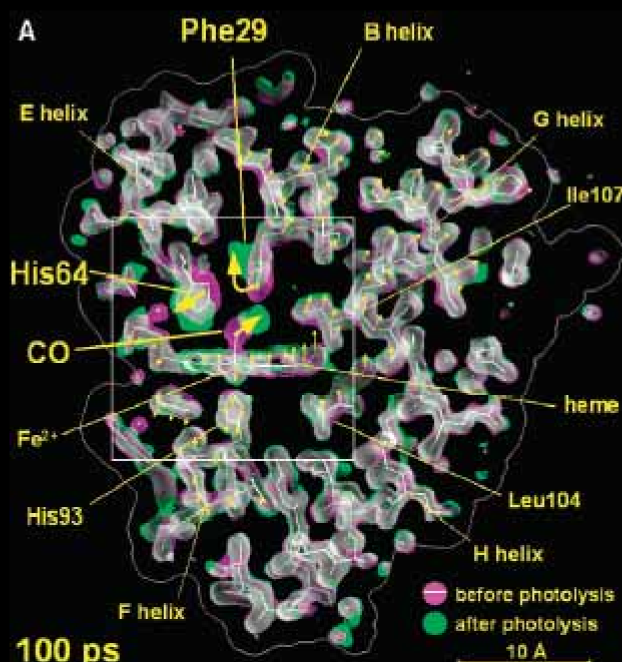
Figure 1. Transient transmission scans of triiodide in ethanol solution with both UV pump and probe pulses. The inset depicts the first 8 ps of probe delays, exhibiting a rapid decay of the initial bleach superimposed by impulsive Raman-induced spectral modulations. See text for details.

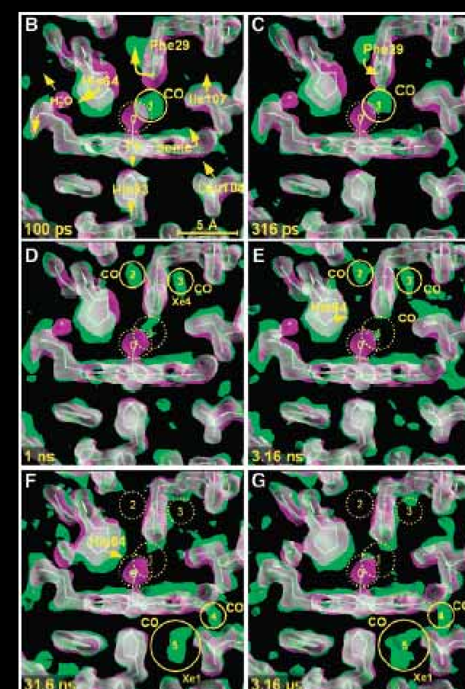
田原太平先生
「超高速反応する分子の核波束運動実時間観測と励起状態ポテンシャル曲線のトポロジー」

Motivations for femtosecond X-ray
ex.4) proteins

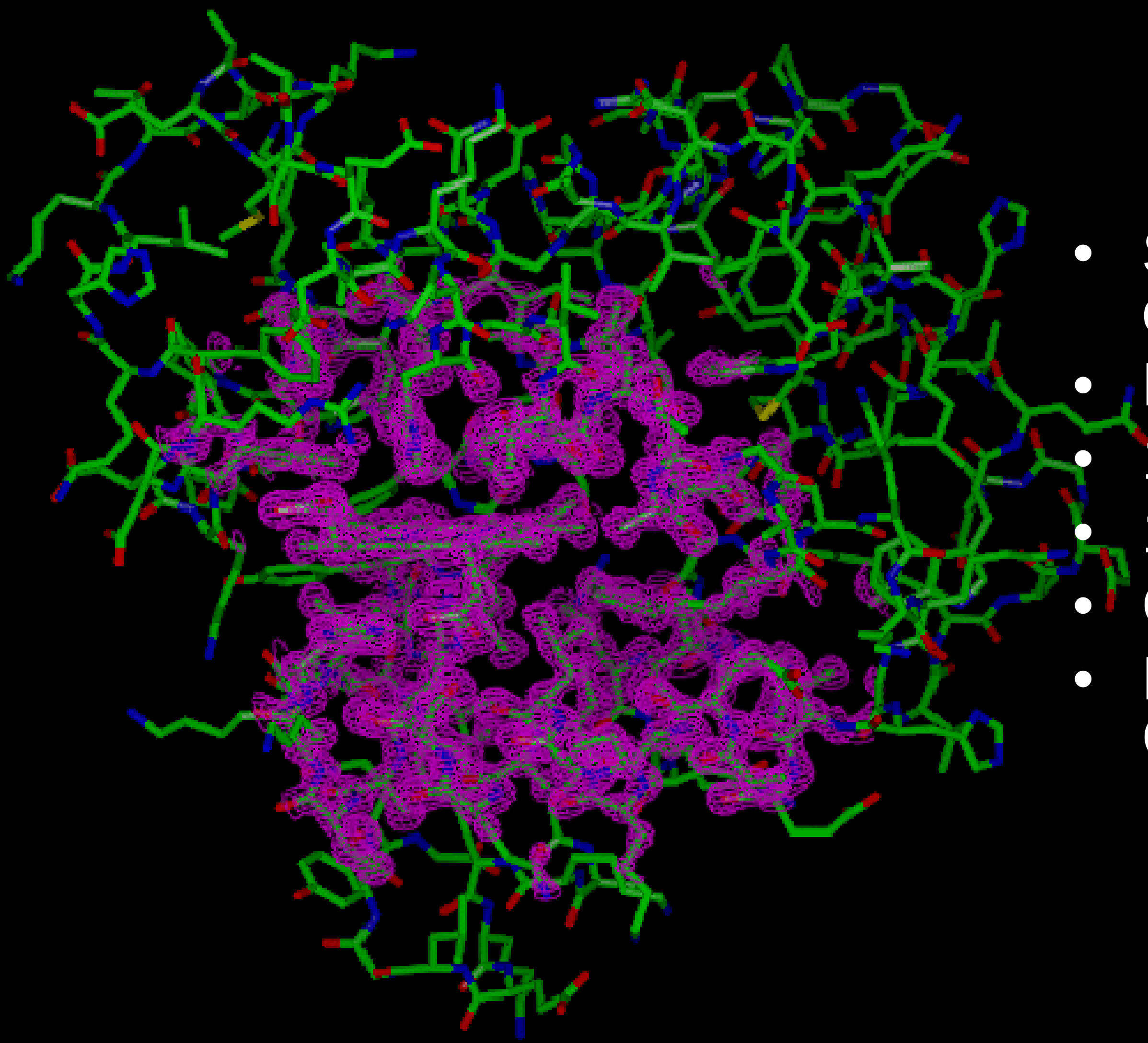
Watching a Protein as it Functions with 150-ps Time-Resolved X-ray Crystallography

Schotte et al. Science (2003) 300, 1944.





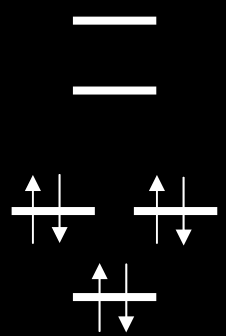
Myoglobin (Mb)



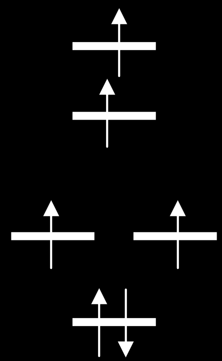
- Stores molecular oxygen in muscle
- M.W. ~ 16,000
- 1290 atoms
- 153 amino acids
- Contains 1 heme
- Reversibly binds O_2, CO, NO etc

Fe(II) porphyrin (heme) in myoglobin

$MbL + h\nu \rightleftarrows Mb + L$ ($L = O_2$, CO, NO, etc)



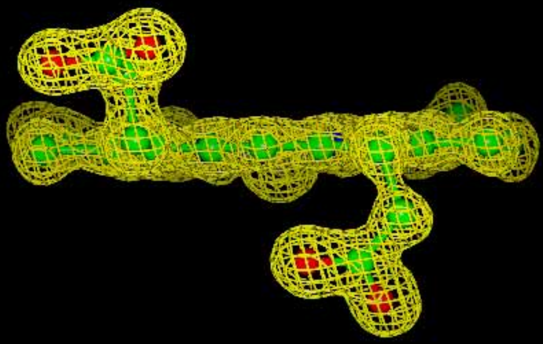
Fe(II) d^6 LS

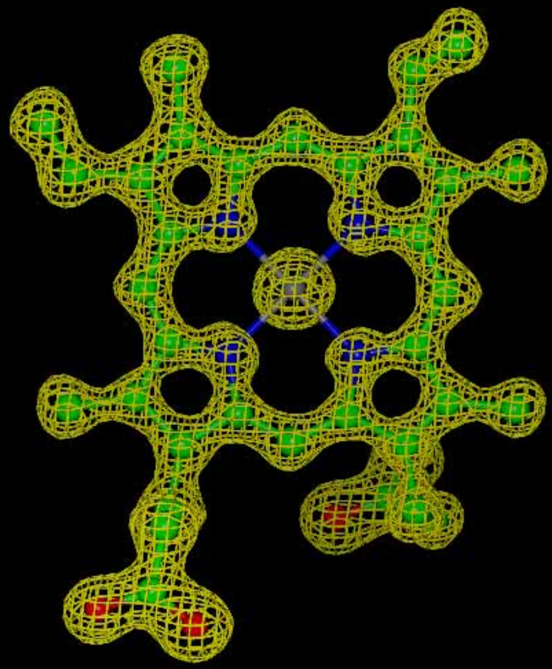


Fe(II) d^6 HS

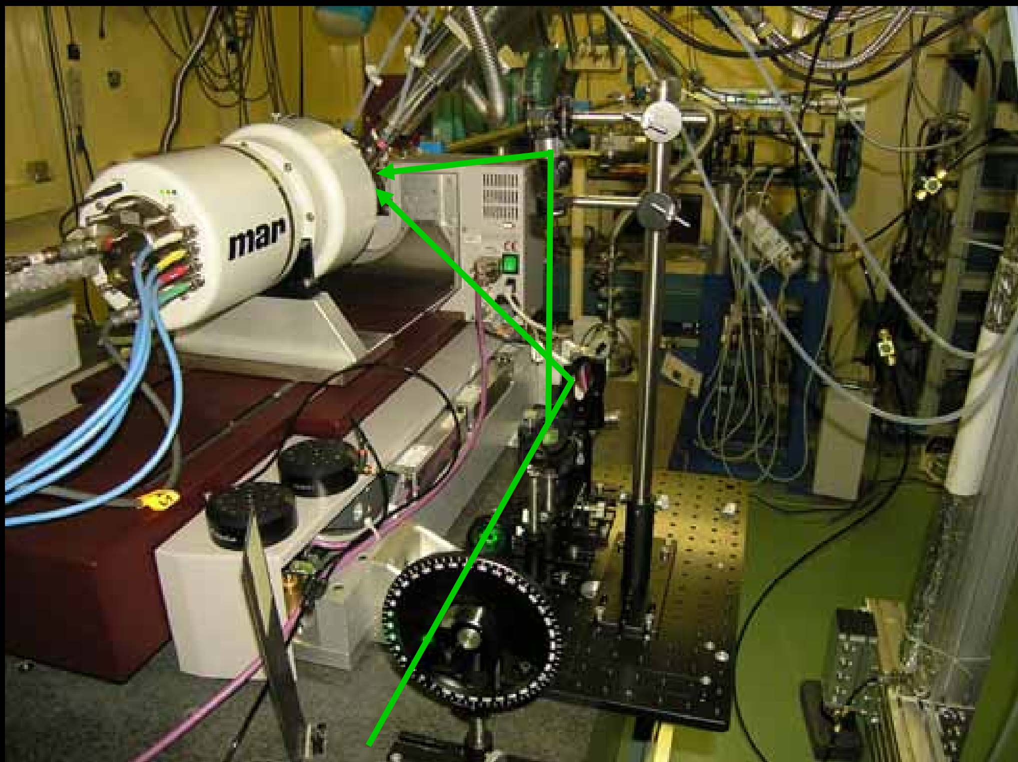
Photo-switchable

Structural distortion causes changes in electronic structure



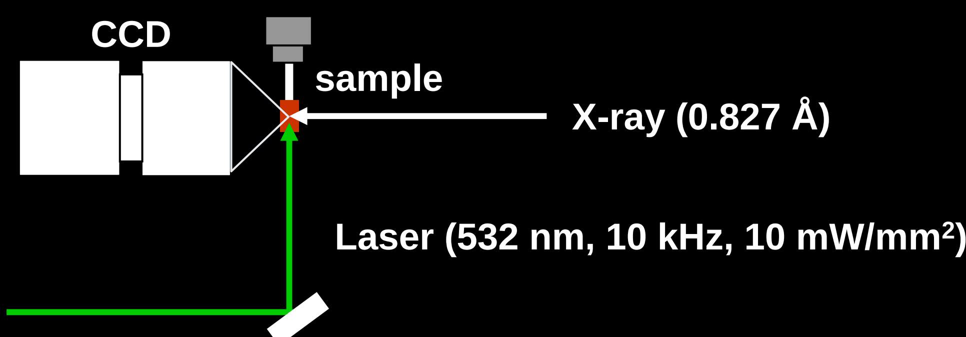


Experimental setup



X-ray: 0.827 Å (15 keV)
Laser: YAG SHG (532 nm)
15 kHz, 10 mW/mm^2
Sample temperature: 40 K
Detector: marccd165

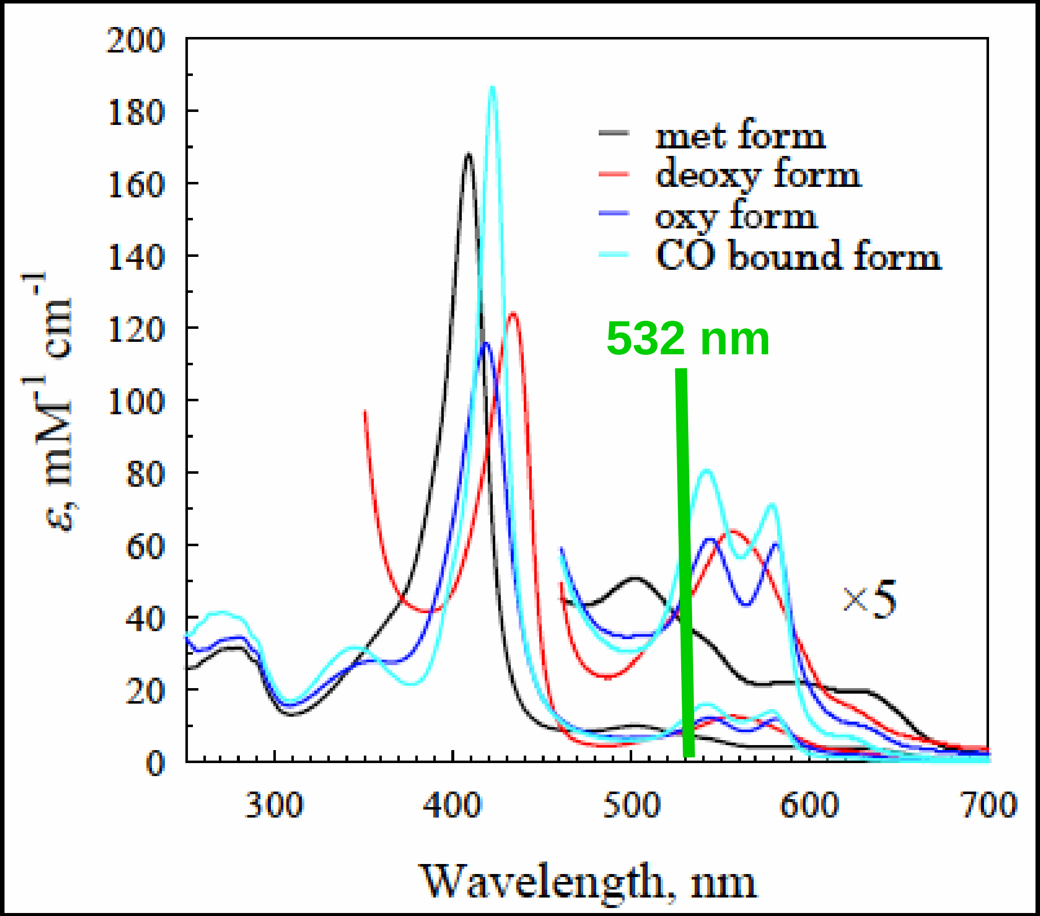
Data statistics:
Resolution: 50 – 1.1 Å
No. of observations: 138,198
No. of unique refs: 37,292
Rmerge: 3.3 %
Completeness: 94.7 %
Redundancy: 3.7



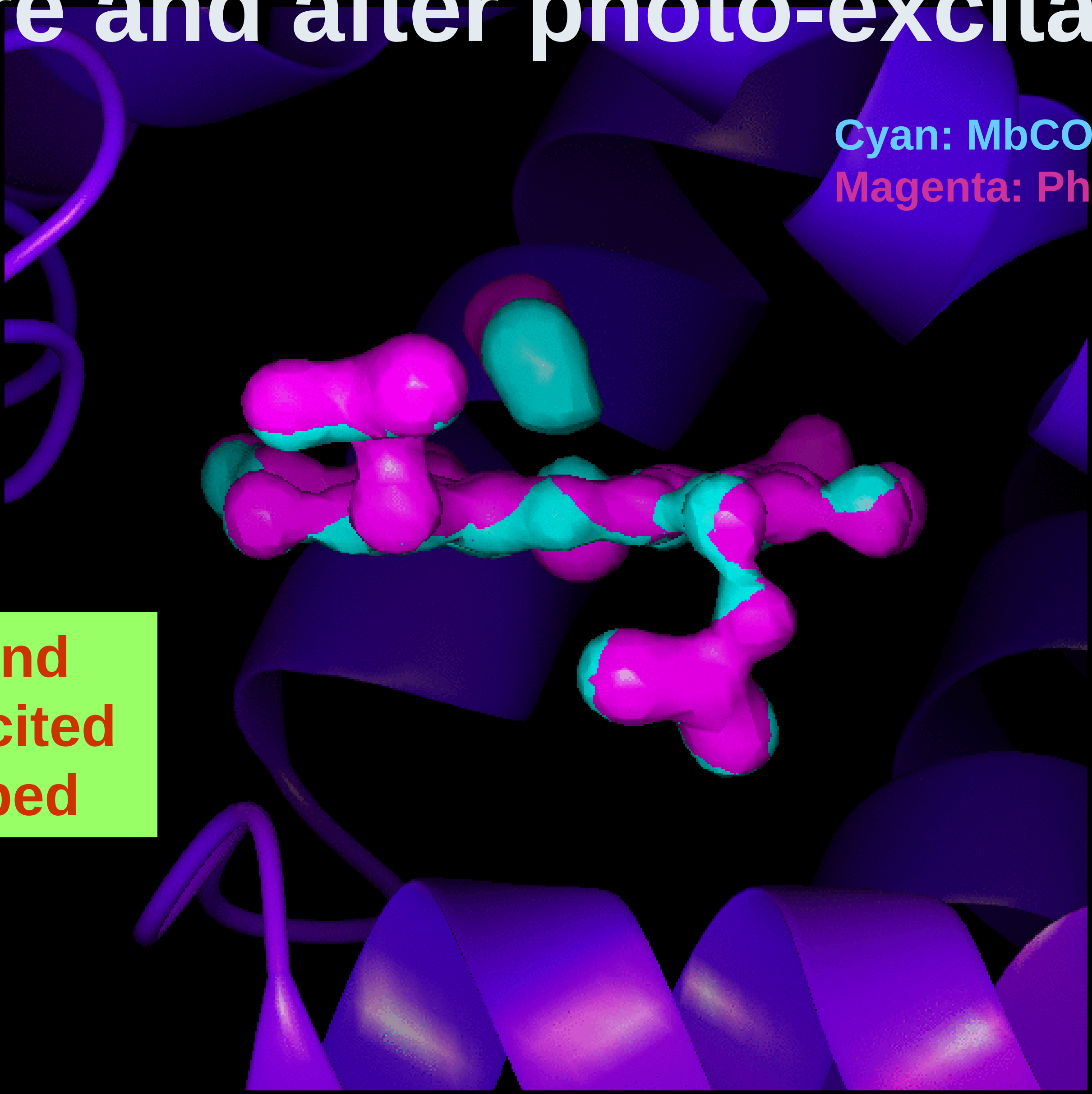
Ayana Tomita

Visible absorption spectra of Mb and MbCO

$$\text{MbCO} + h\nu \rightleftarrows \text{Mb} + \text{CO}$$

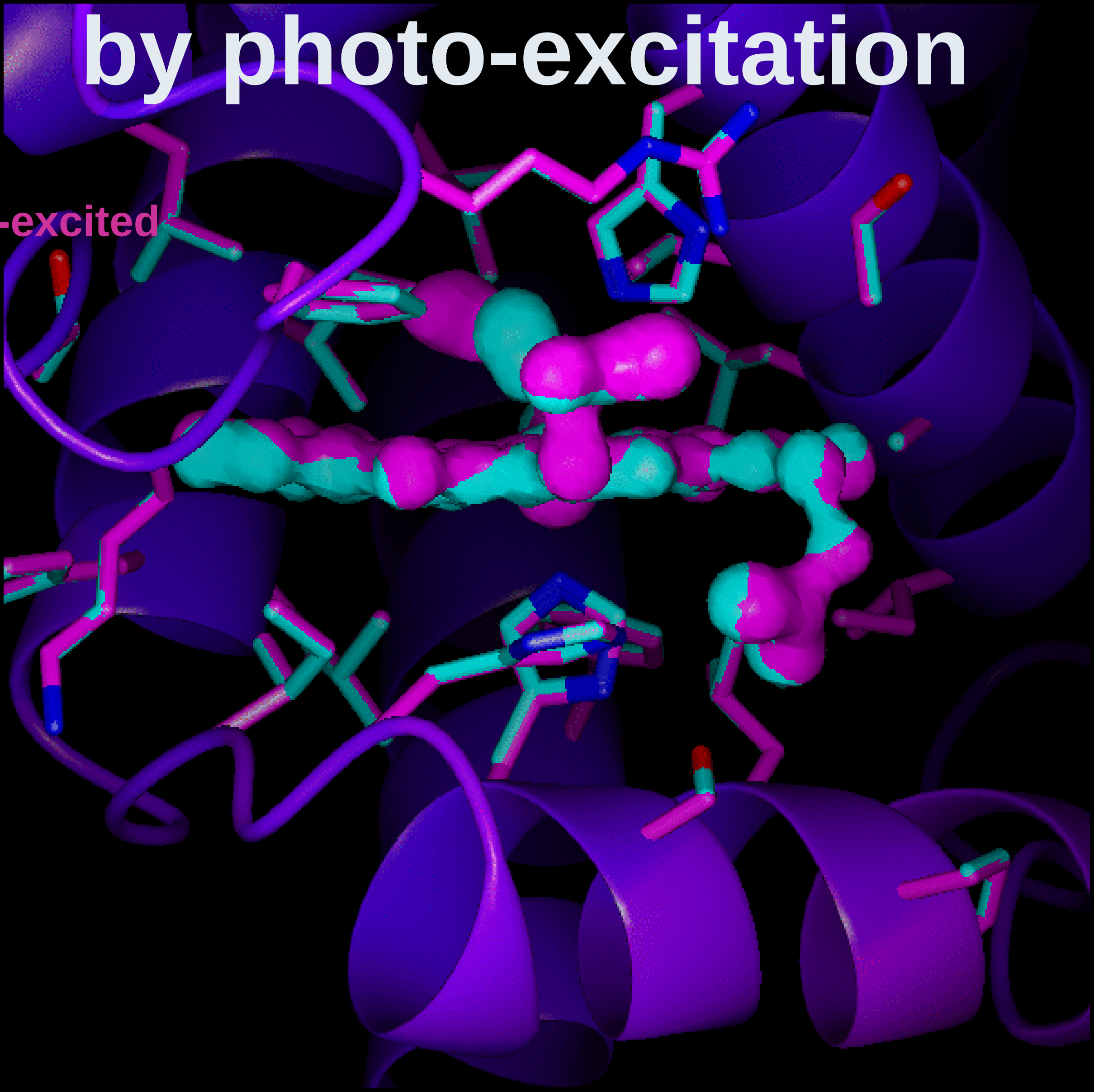


Electron density of the heme before and after photo-excitation



MbCO and Photo-excited overlapped

Switching protein structure by photo-excitation

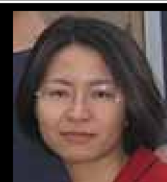
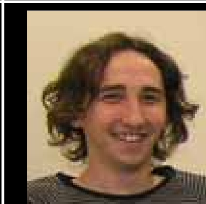
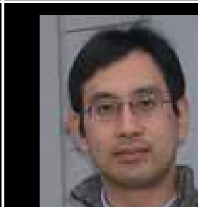


Cyan: MbCO
Magenta: Photo-excited

Summary

- X線を用いた時間分解測定法は、非平衡状態（短寿命種）の構造情報、電子密度分布を直接観測できることが最大の利点。
- 現在の100ピコ秒分解能では不十分であり、サブピコ秒分解能が必要な実験系が多く存在する。
- そのためには、コンパクトERLによるサブピコ秒X線光源が極めて有望。

Project members @ KEK NW14

Shunsuke Nozawa (ERATO)		Tokushi Sato (TITECH DC)	
Ryoko Tazaki (ERATO)		Ayana Tomita (TITECH DC)	
Hirohiko Ichikawa (ERATO)		Sachiko Maki (TITECH MC)	
Laurent Guérin (ERATO)		Jiro Itatani (Group Leader, LBNL)	
Kouhei Ichiyanagi (KEK PD)		Masahiro Daimon (Research Manager)	
Matthieu Chollet (JPSJ PD)		Shin-ya Koshihara (Project Director)	

Collaborators

Beam line NW14

- KEK
  - Hiroshi Sawa
  - Hiroshi Kawata
  - Takeharu Mori
  - Shigeru Yamamoto
  - Kimichika Tsuchiya
  - Tatsuro Shioya
  - and all Photon Factory Staffs

Myoglobin

- Yokohama City University
  - Sam-Yong Park

$(EDO\text{-}TTF)_2PF_6$

- Kyoto University
  - Hideki Yamochi
  - Gunji Saito

Time-resolved solution scattering

- Korea Advanced Institute of Science and Technology
  - Hyotcherl Ihee
  - Kyung Huan Kim
  - Jae Hyuk Lee

Other collaborations

- Tokyo Institute of Technology
- The University of Chicago
- Univ. Rennes 1
- State Univ. of New York at Buffalo
- Univ. of Copenhagen
- Laurence Berkley National Lab.
- Oxford Univ.
- Tohoku Univ.
- Osaka City Univ.