IMSS
物質構造科学研究所

cERL Science Workshop II
Mon. 30 - Tue. 31 Jun., 2012

DXAFSを用いたfsダイナミクス研究

を目指して

阿部 仁

Photon Factory, IMSS, KEK

Outline

- Intro: XAFS, DXAFS
- A DXAFS study at NW2A, PF-AR
- Toward Laser Pump – DXAFS Probe experiments
- NW2A, PF-AR => Laser Compton Scattered X-ray, cERL
- Prospects for studies at cERL & 3-GeV ERL
- Summary

What is XAFS?

XAFS: **X**-ray **A**bsorption **F**ine **S**tructure

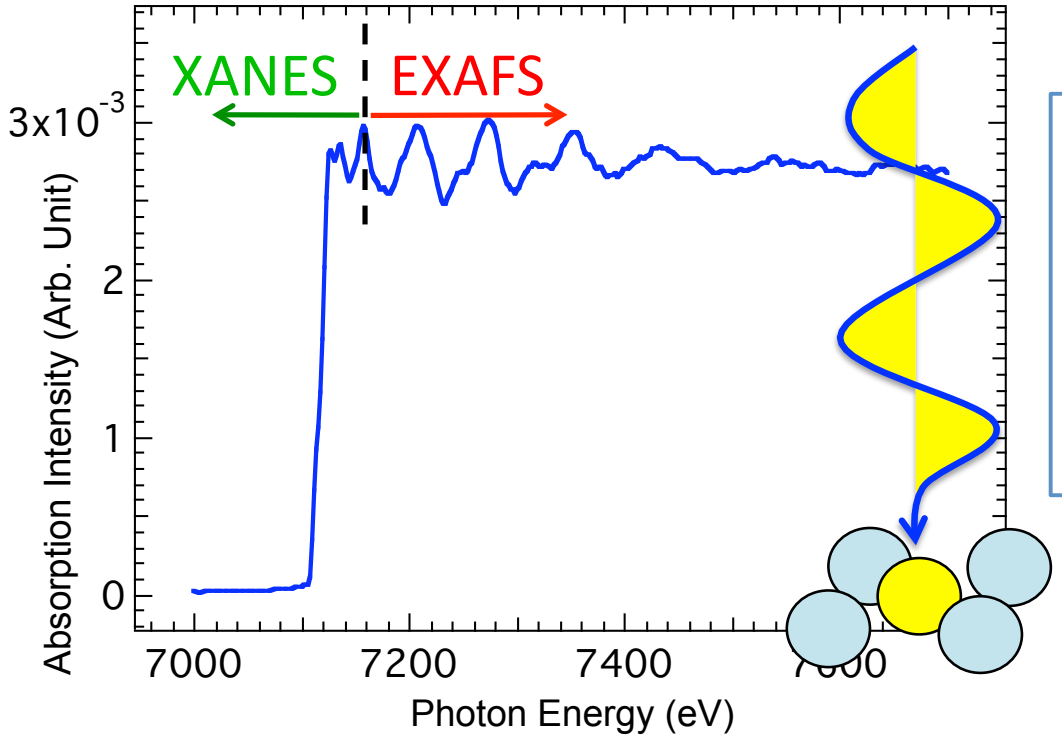
electronic state (valence)

Symmetry

Bond length

Number of surrounding atoms (Coordination number)

Distribution, Thermal vibration



Element specific

to observe **Local structure**

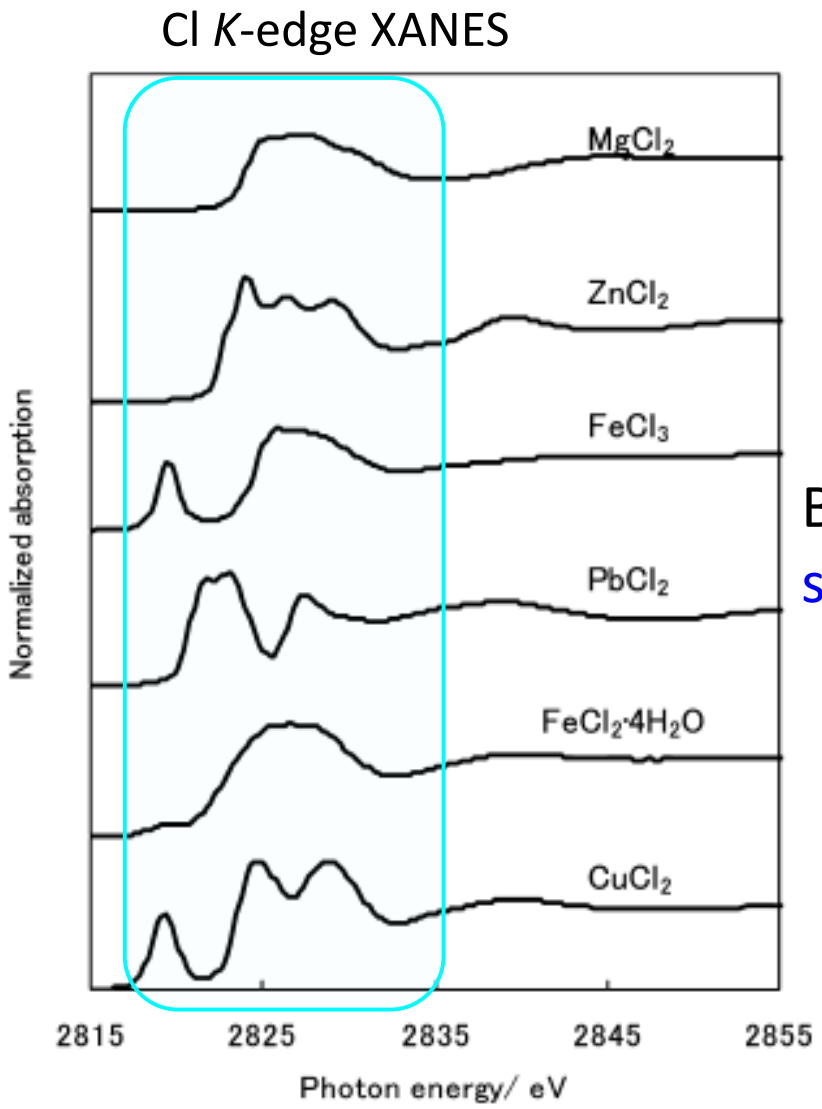
(long range periodicity is not required)

Solid, Liquid, Gas, whatever

XANES: X-ray Absorption Near Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure

XANES tells us what your sample is.



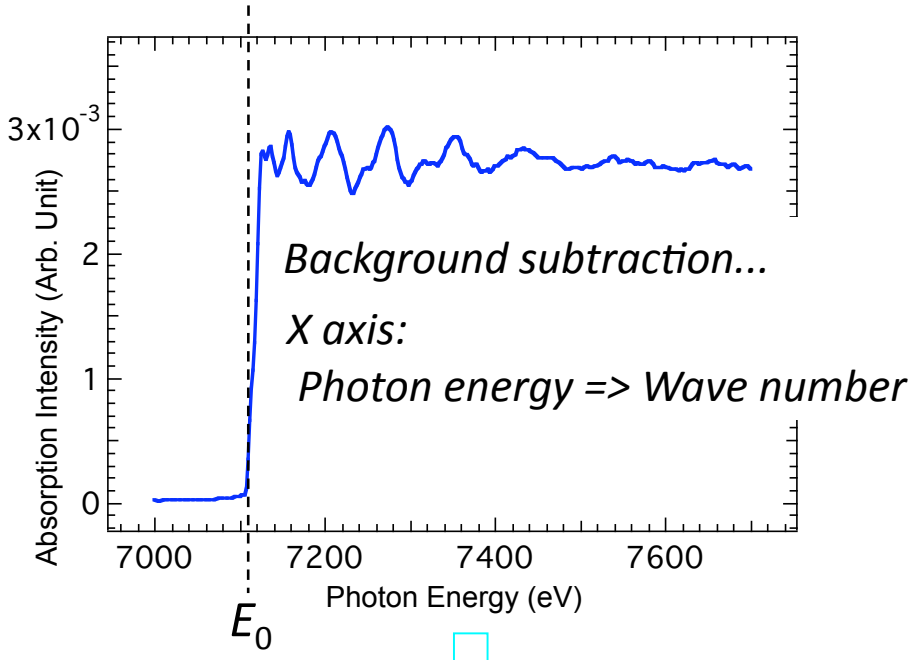
All these are metal chlorides.

But you can see some specific features in each spectrum.

So you would recognize what your sample is.

F. Zhu, *et al.,* Environ. Sci. Technol. **42**, 3932 (2008)

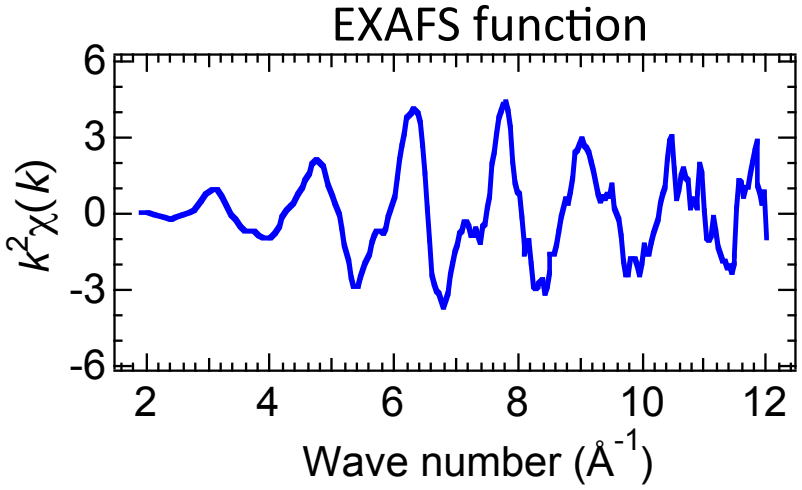
How to Obtain Bond Length by EXAFS



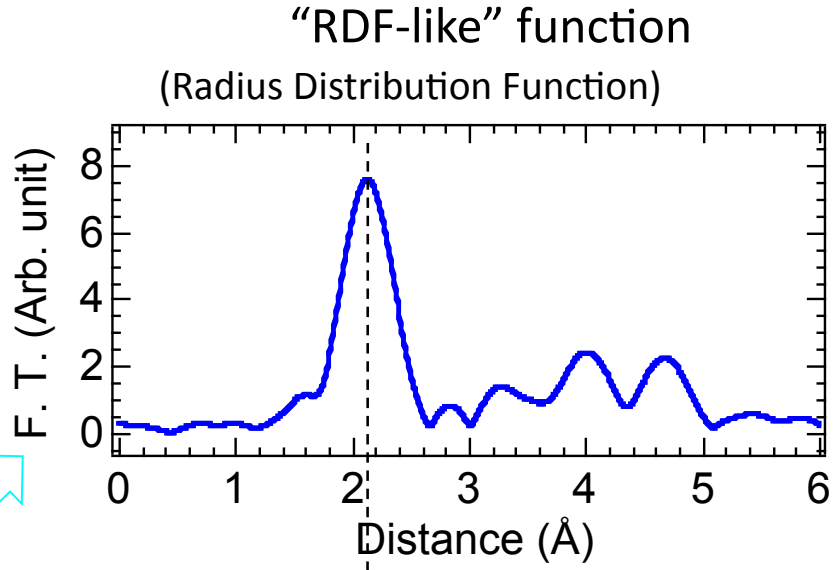
Background subtraction...

X axis:

Photon energy => Wave number



Fourier Transform



Nearest neighbor atomic distance

+ phase shift

Bond length

Peak area

Coordination number

Eq. of single scattering EXAFS

Amplitude

Oscillation (phase)

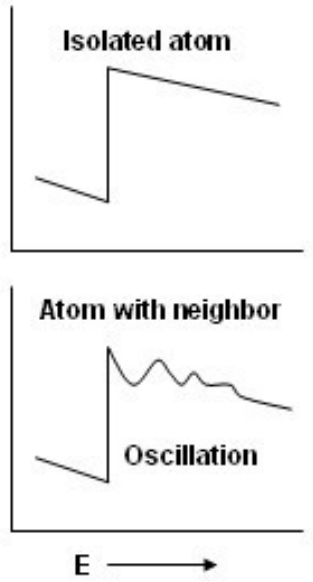
$$\chi(k) = -S_0^2 \sum_j \frac{N_j}{kR_j^2} F_j(k) \exp\left(-2\sigma_j^2 k^2\right) \sin\left(2kR_j + 2\delta_{A,1}(k) + \varphi_j(k)\right)$$

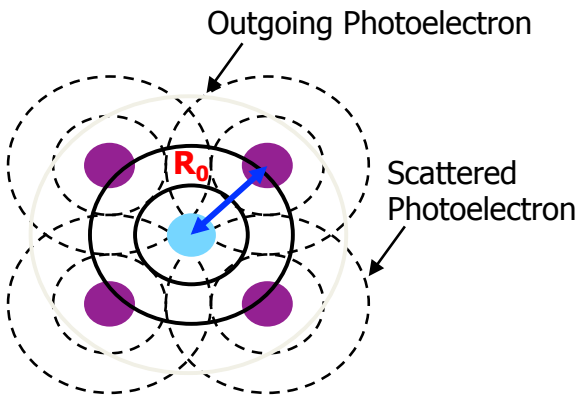
"Round trip" of the wave

Phase shift

of absorbing atom

of scattering atom



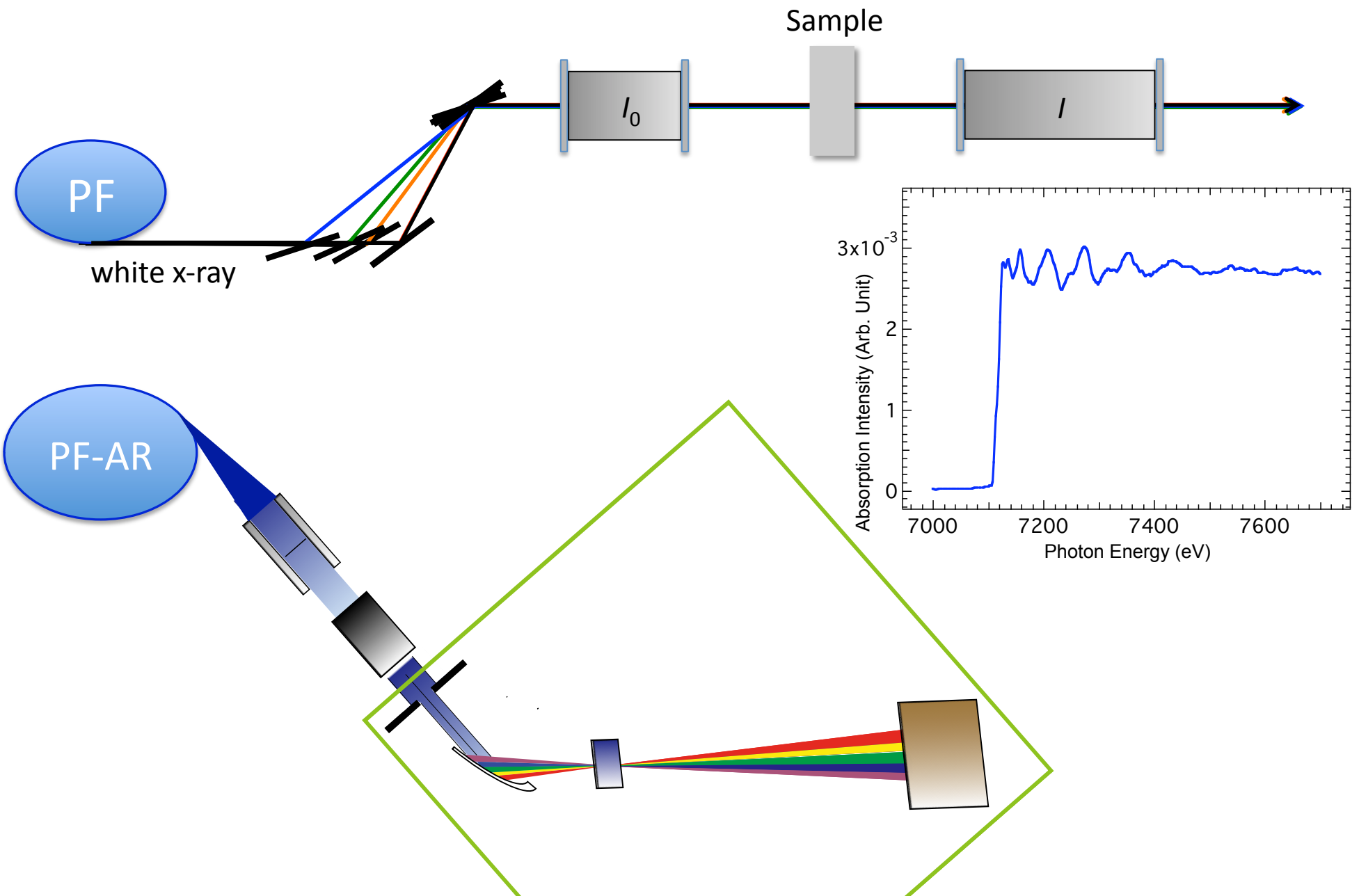


Fourier Transform…

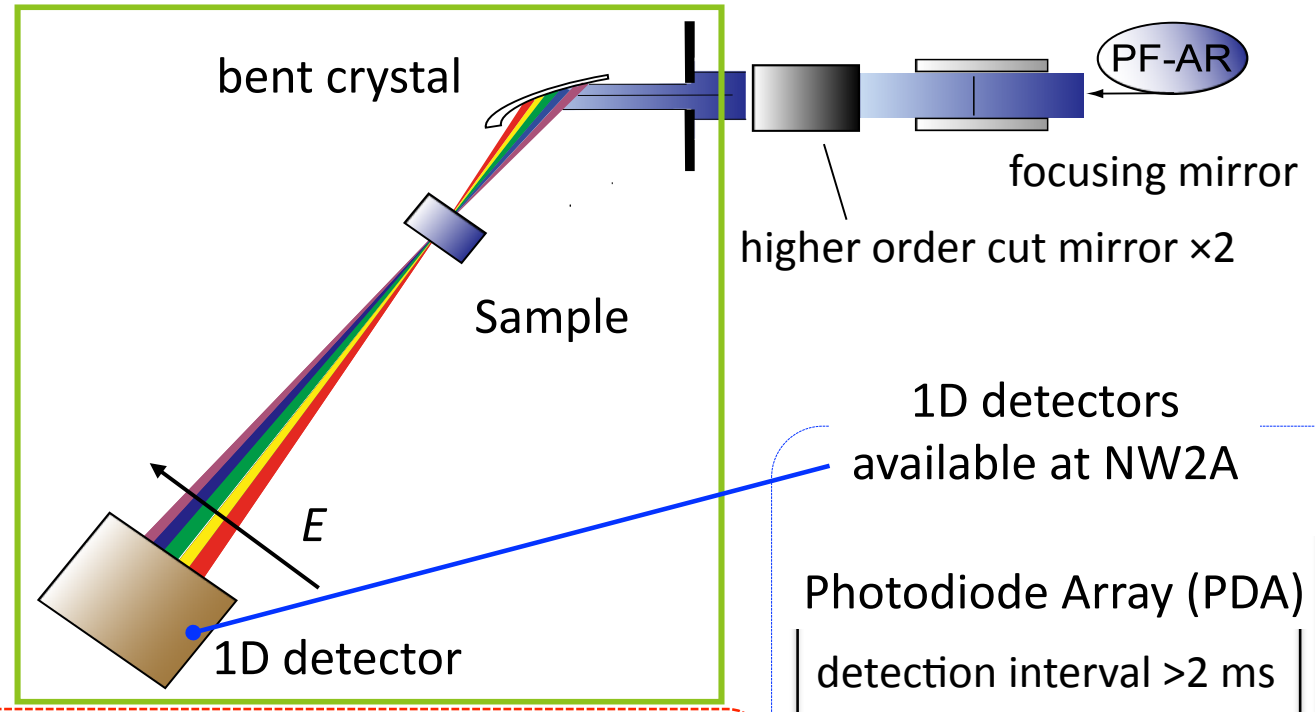
Bond length R_j , etc.,

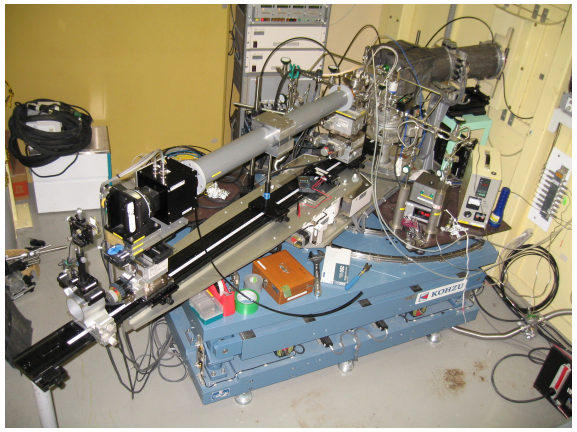
(Parameters high-lightened by yellow are fitting parameters.)

Step scan XAFS & DXAFS



DXAFS at PF-AR NW2A



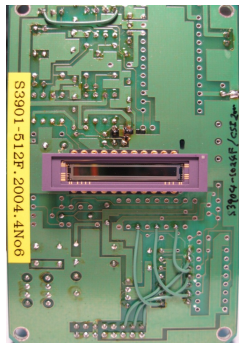


1D detectors available at NW2A

Photodiode Array (PDA)

detection interval >2 ms

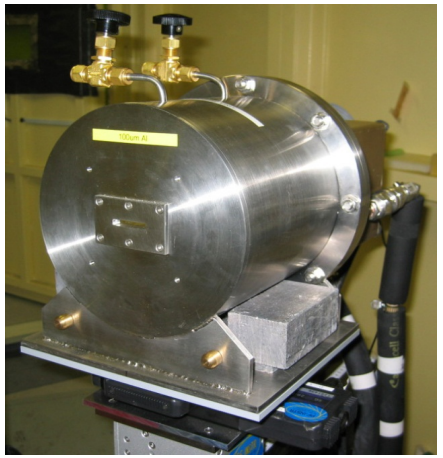
exposure time >2 ms



XSTRIP (silicon microstrip)

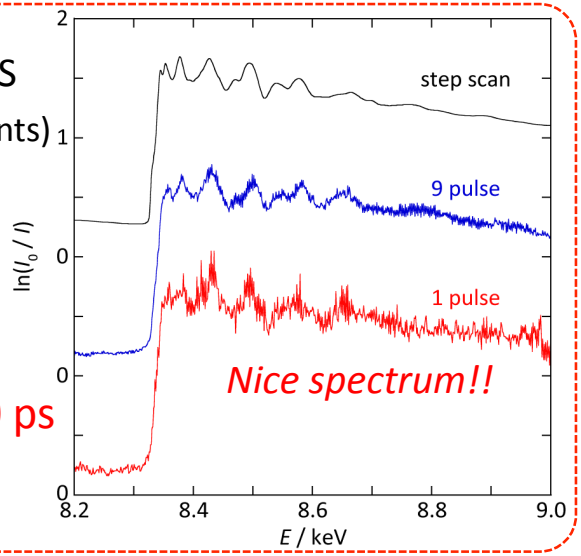
detection interval >23 μs

exposure time >0.5 μs



Ni foil DXAFS

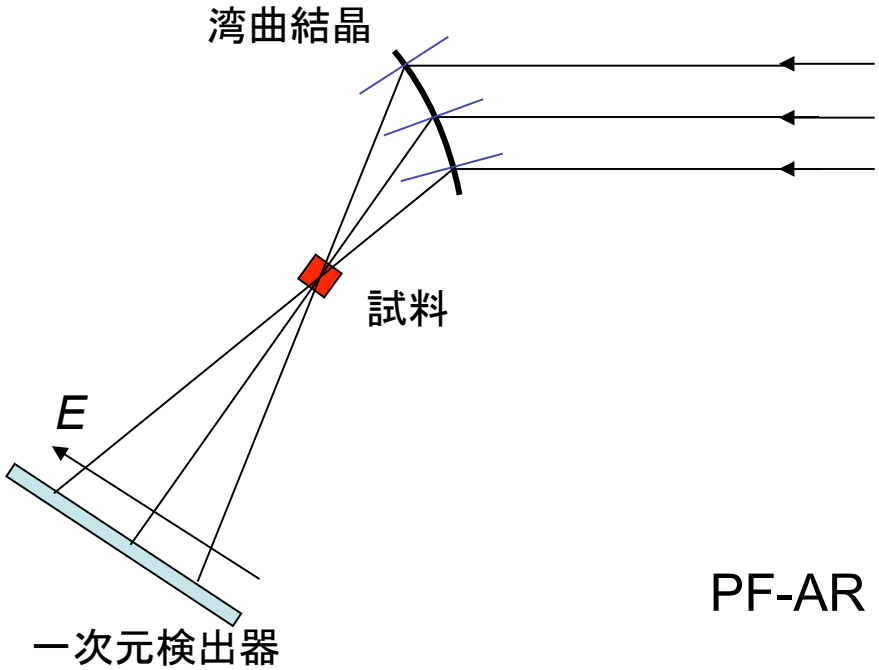
(test measurements)

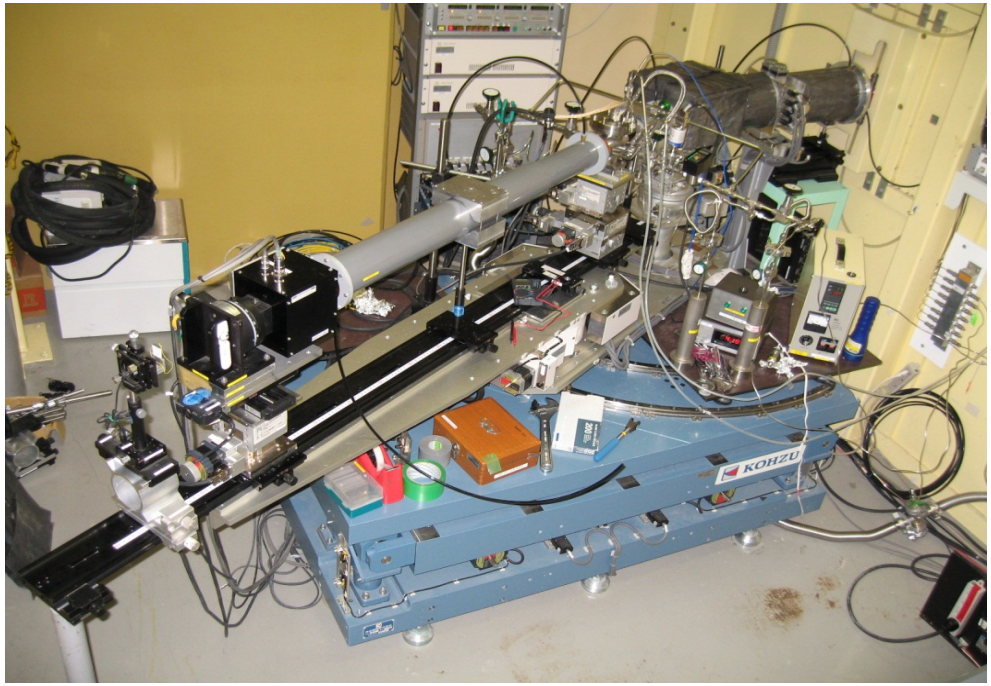


x-ray

1 pulse = 100 ps

DXAFS測定





PF-AR　NW2A

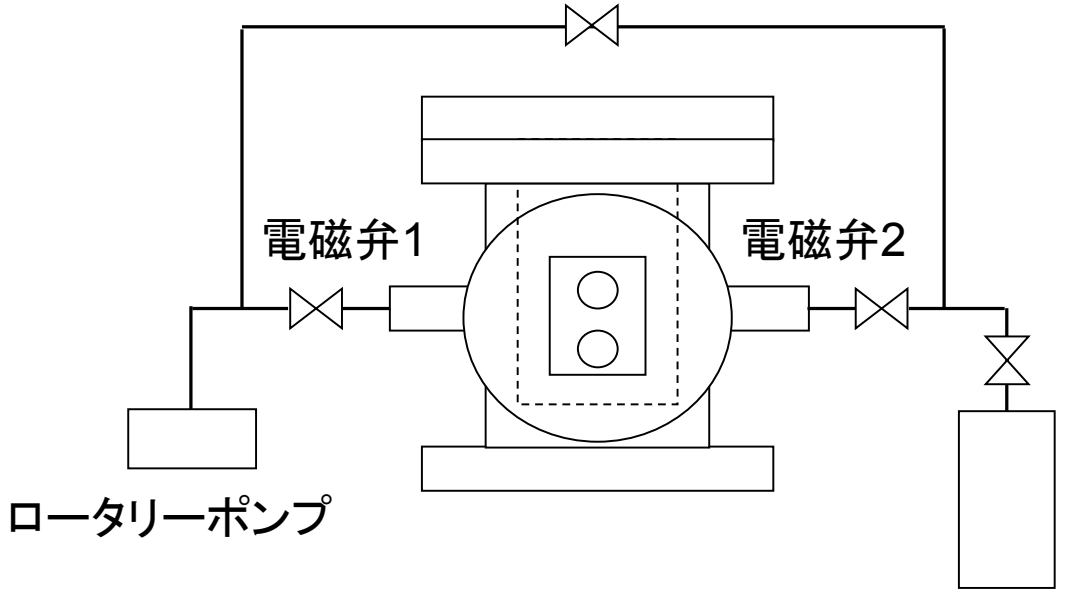
ポリクロメーター	湾曲半径0.9 m Si(511) Laue配置
吸収端	Pd K (24.350 keV)
一次元検出器	蛍光体付フォトダイオードアレイ
時間分解能	10 ms

試料　　γ-アルミナ担持パラジウム（Pd担持量3 wt%）

還元反応　　水素（4.0～49.5 kPa）　　試料温度 573, 623, 673　K
　　一酸化炭素（4.5～49.1 kPa）　試料温度 673, 723, 773 K

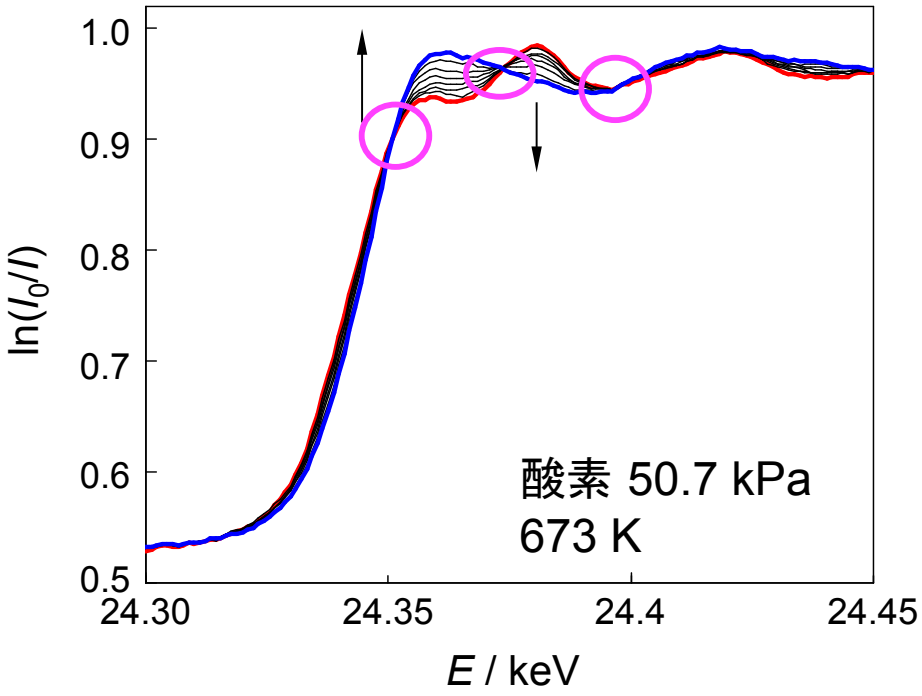
酸化反応　　酸素（4.1～61.8 kPa）、　　試料温度 573, 623, 673, 723, 773 K

*in situ*セル



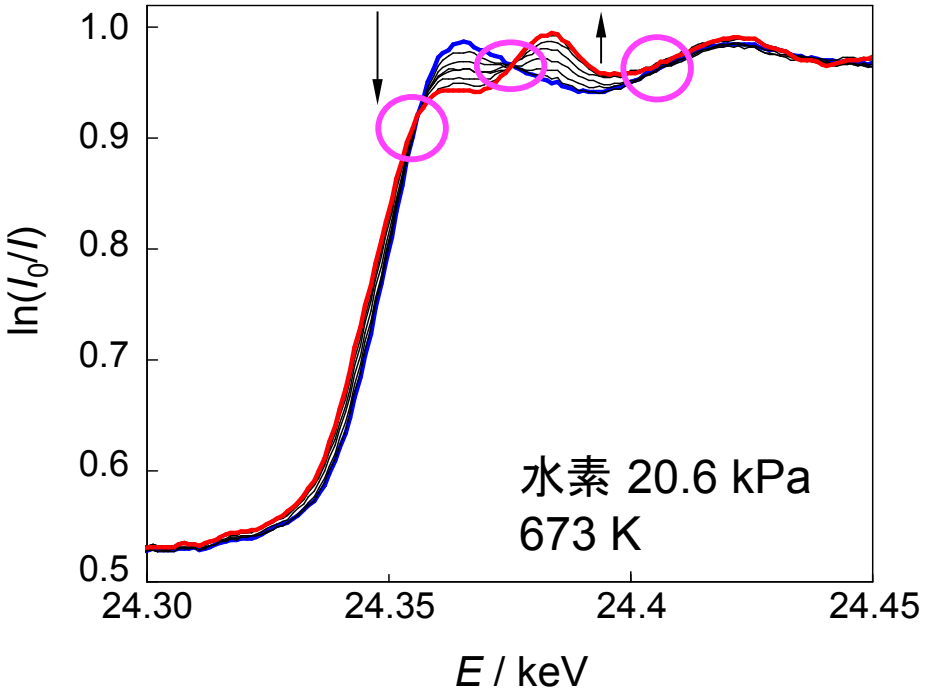
時間分解XANESスペクトル

酸化反応



Pd → PdO

還元反応

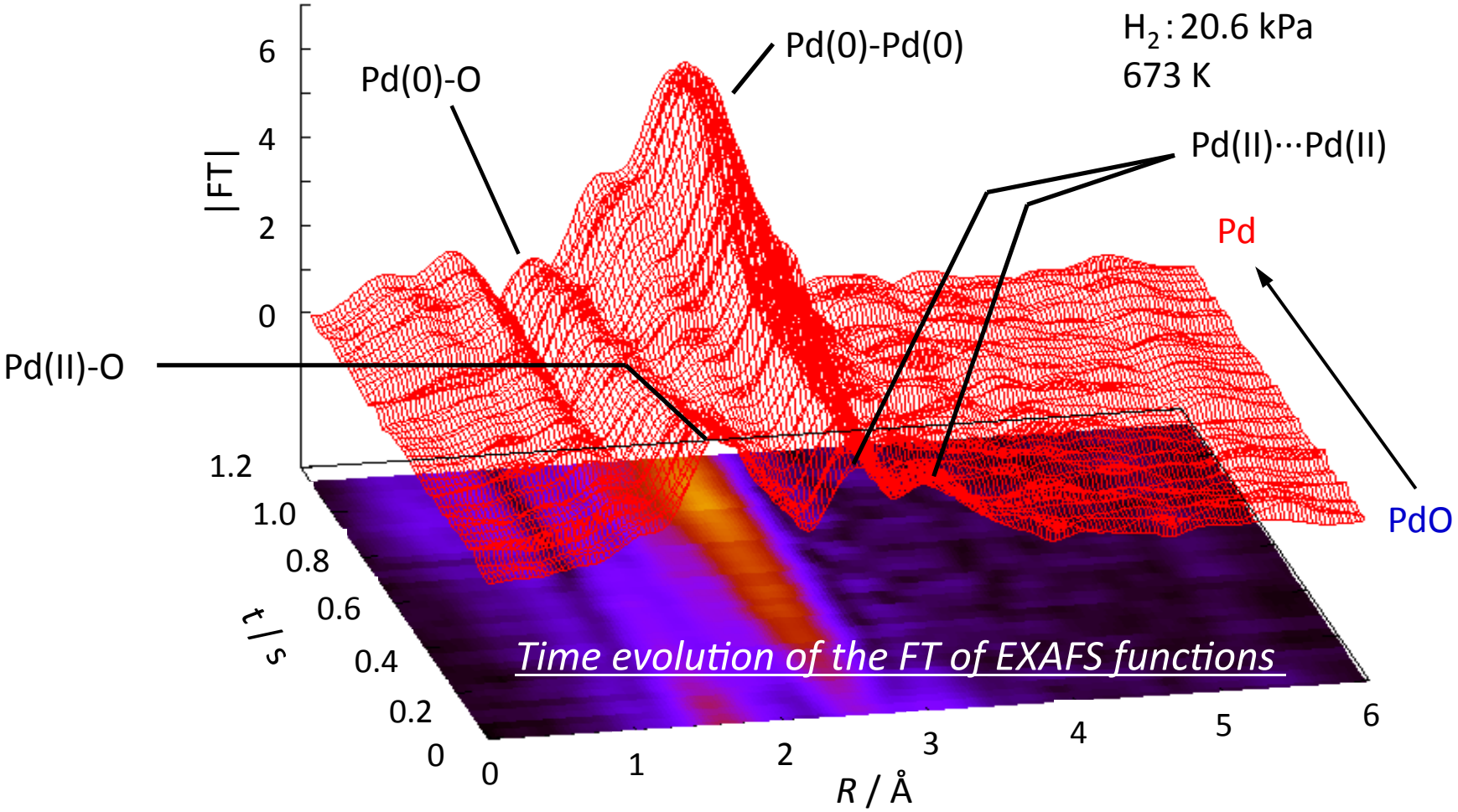


PdO → Pd

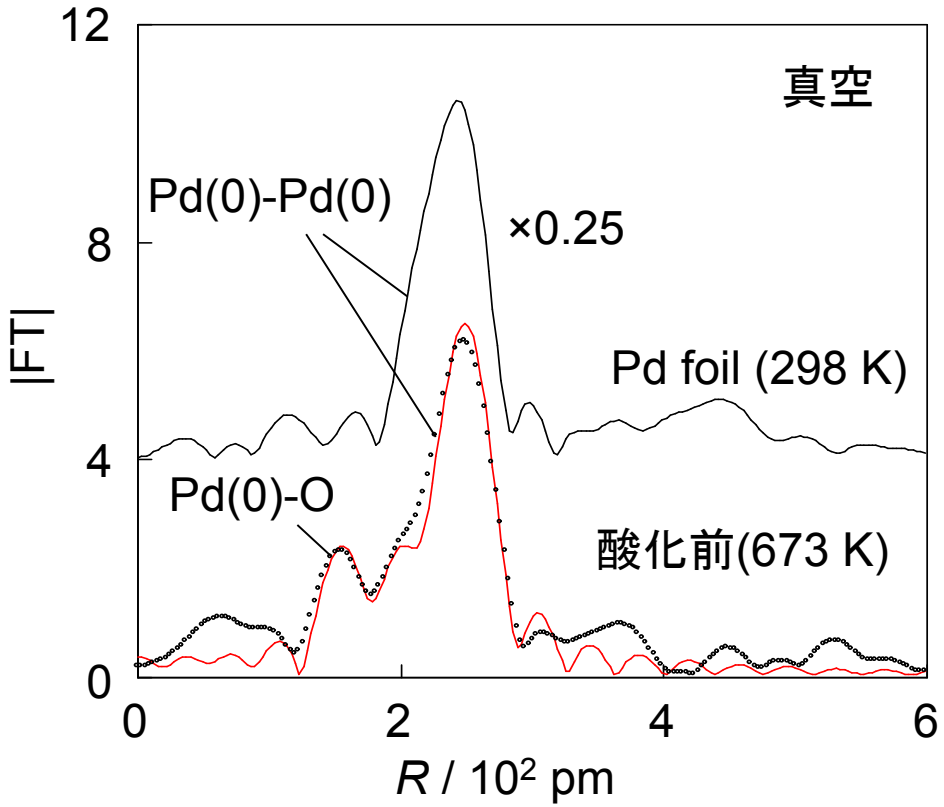
Real time observation of PdO -> Pd reduction reaction

Pd (3wt%) supported by γ-Al_2O_3 , Pd K-edge (24.3 keV) EXAFS

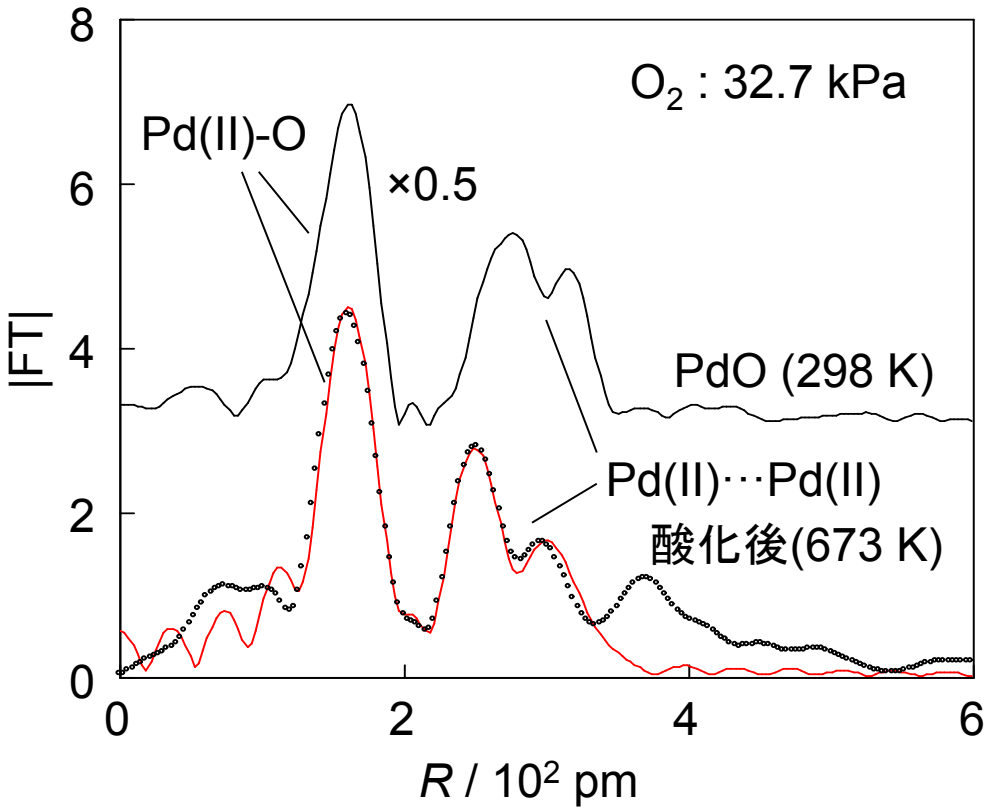
PDA detector, **recorded every 10 ms**



Pd(0)



PdO



		N	R / pm
Pd(0)	Pd(0)-O	0.7	202
	Pd(0)-Pd(0)	5.6	270
Pd foil	Pd(0)-Pd(0)	12*	274

		N	R / pm
PdO	Pd(II)-O	2.1	205
	Pd(0)···Pd(0)	1.1	287
	Pd(0)···Pd(0)	2.2	337
PdO reference	Pd(II)-O	4*	204
	Pd(0)···Pd(0)	4*	304
	Pd(0)···Pd(0)	8*	342

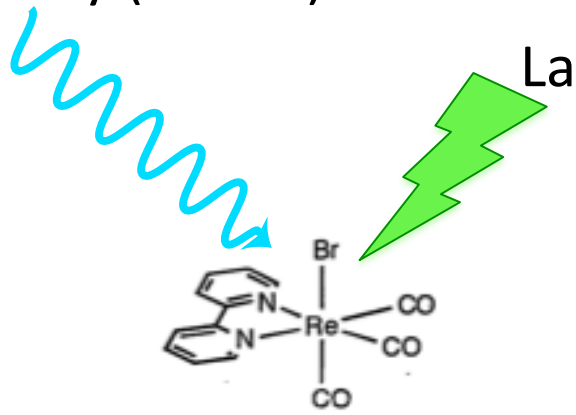
Laser Pump – DXAFS Probe experiments

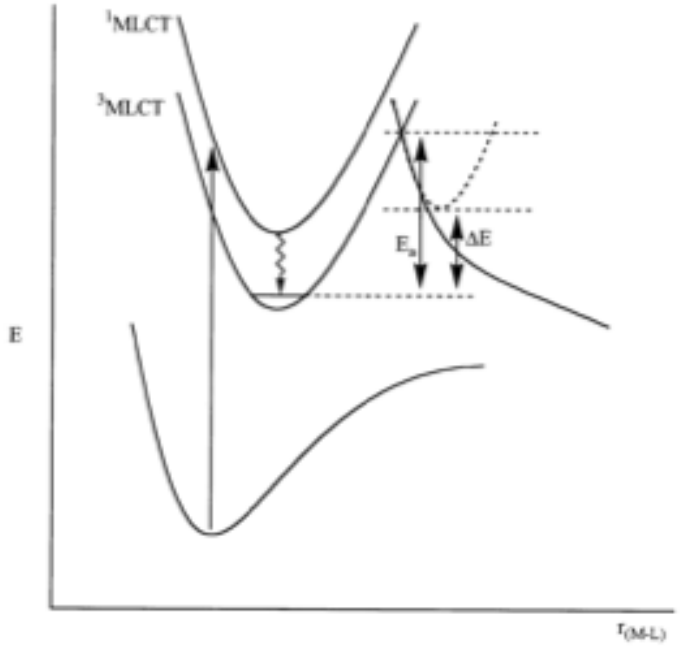
We've just started to try to measure this experiment

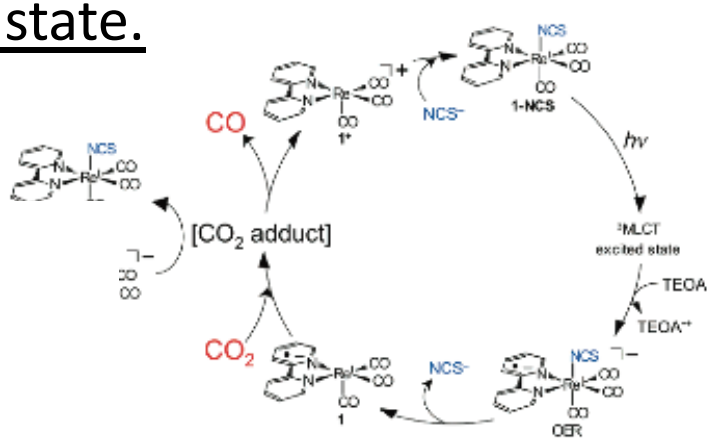
as <u>to capture a transient state.</u>

X-ray (DXAFS)

Laser

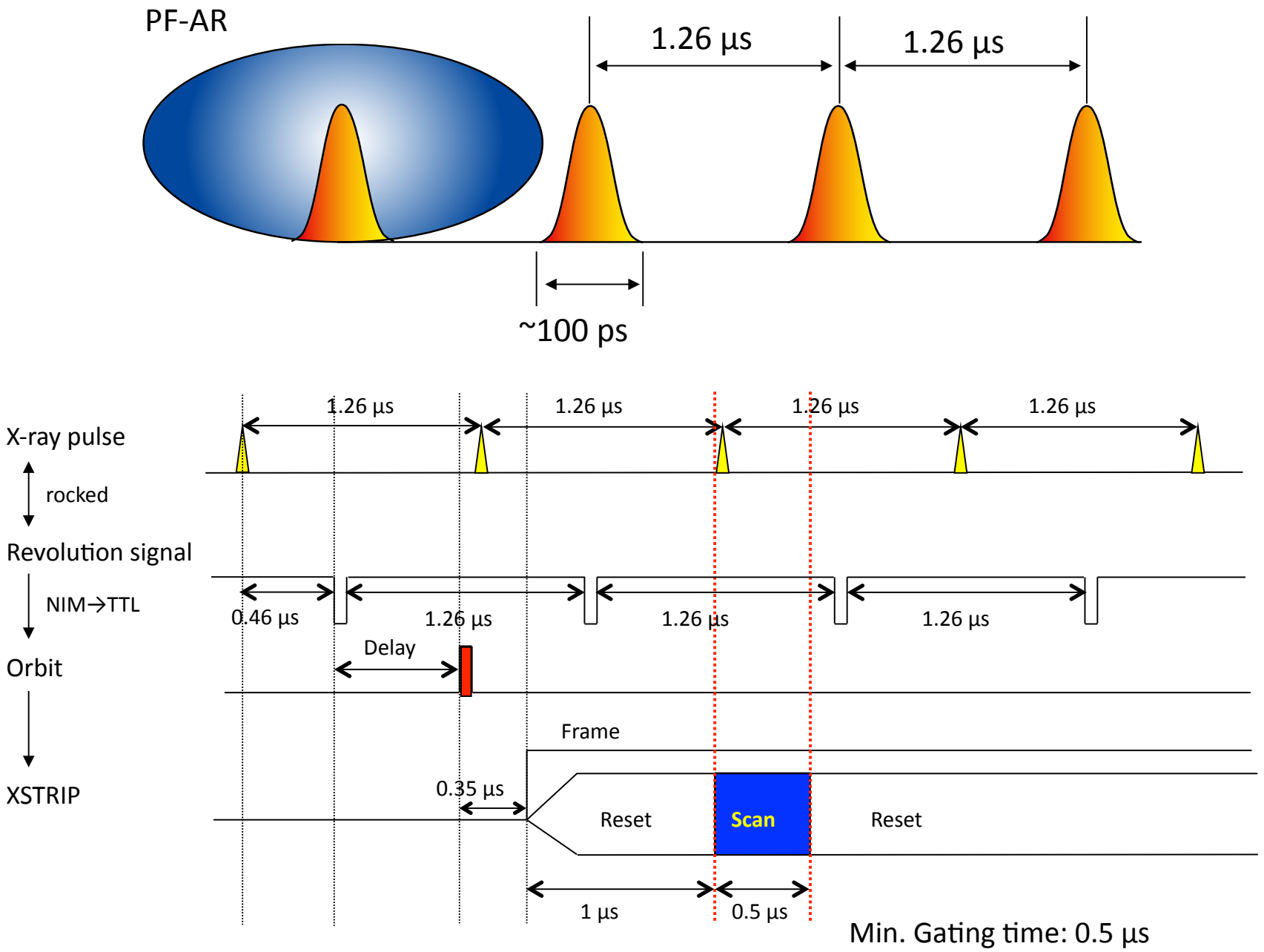


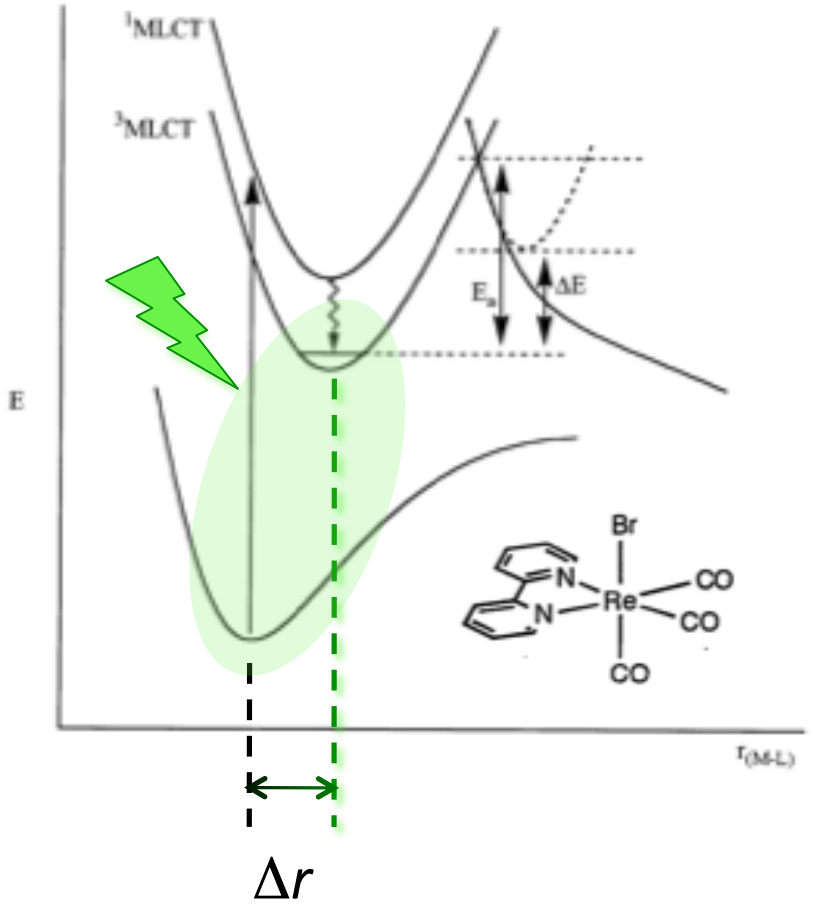


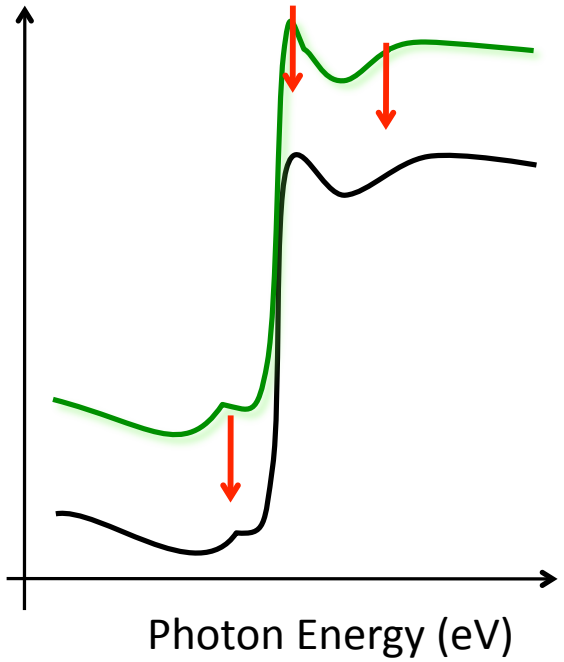


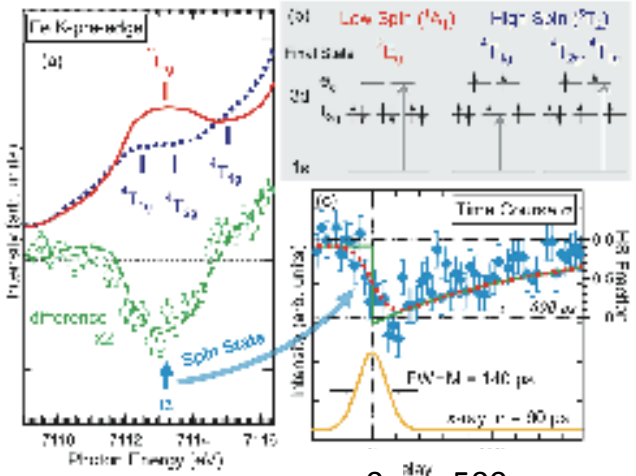
courtesy of Prof. Ishitani's group, TIT

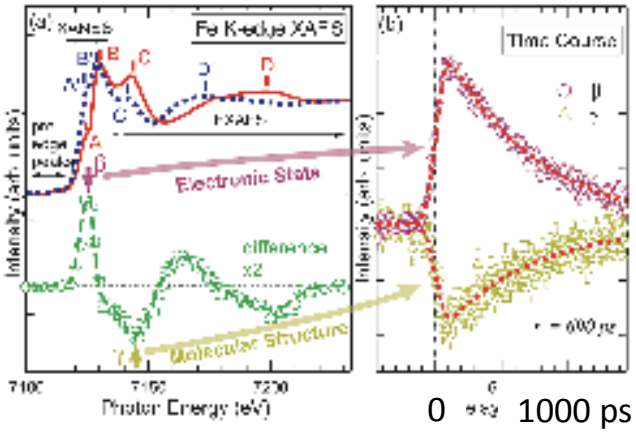
H. Takeda, et al., JACS **130**, 2013 (2008)

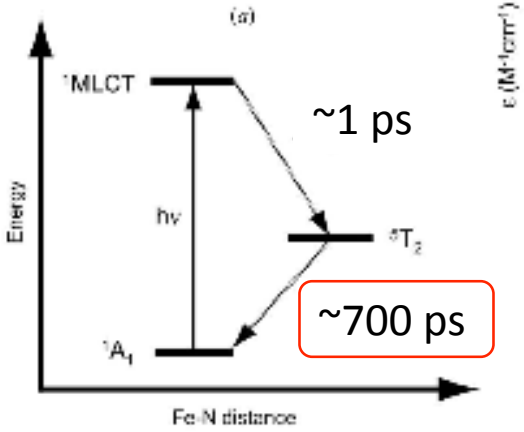

PF-AR
1.26 µs
1.26 µs
~100 ps
X-ray pulse
rocked
Revolution signal
NIM→TTL
Orbit
XSTRIP
1.26 µs
1.26 µs
1.26 µs
1.26 µs
0.46 µs
1.26 µs
1.26 µs
1.26 µs
Delay
Frame
0.35 µs
Reset
Scan
Reset
1 µs
0.5 µs
Min. Gating time: 0.5 µs


^{1}MLCT
^{3}MLCT
E
E_a
ΔE
Br
N
N
Re
CO
CO
CO
$r_{(M-L)}$
Δr

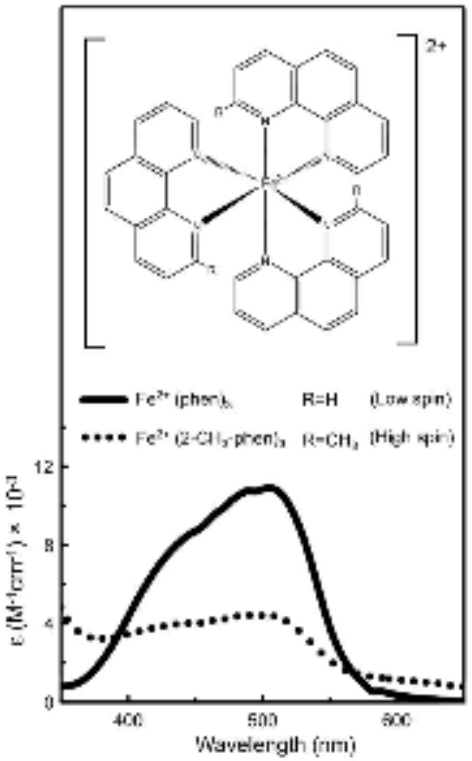

Photon Energy (eV)







$[Fe^{II}(phen)_3]^{2+}$



S. Nozawa, et al., JACS **132**, 61 (2010)

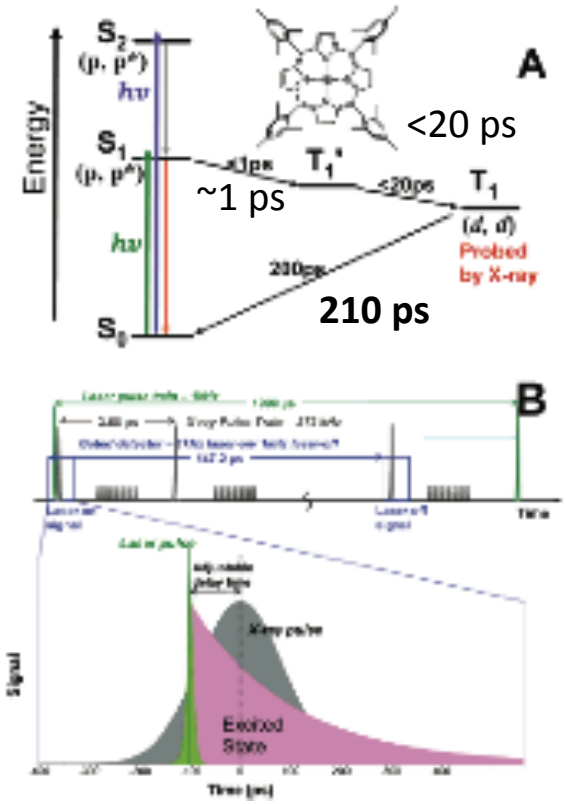
T. Sato, et al., J. Synchrotron Rad. **16**, 110 (2009)

Limitations at NW2A, PF-AR

- Phenomena faster than the pulse duration of PF-AR (~100 ps) cannot be detected.
- The jitter between laser & x-ray always exists, and would be more serious when we go shorter time resolution.

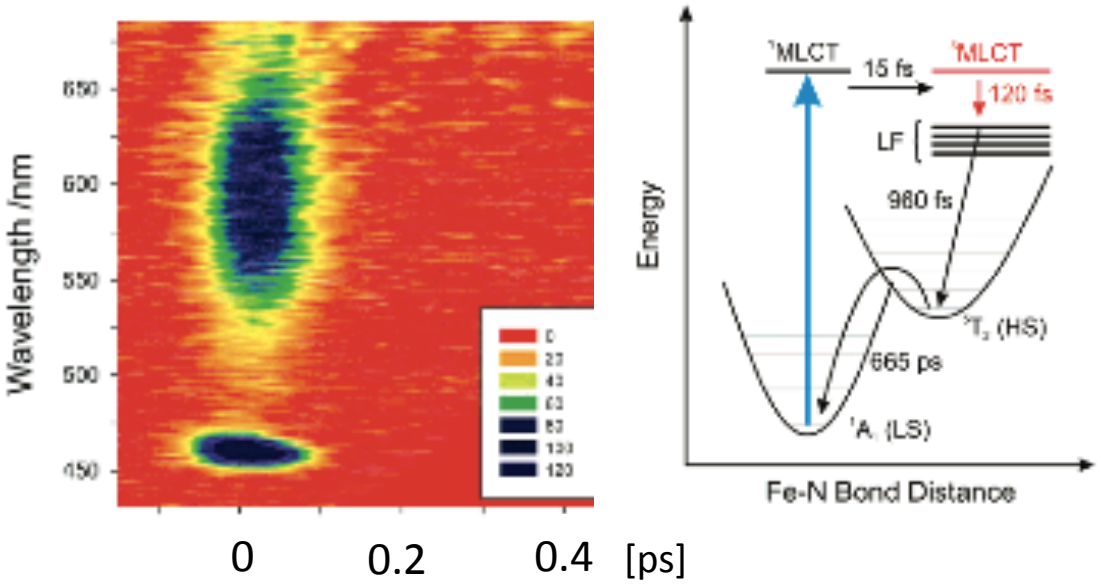
- Many experimental apparatuses are put in the hatch one after another.

Some TR experiments in the world



Lin X. Chen, et at., JACS **129**, 9616 (2007)

Luminescence spectra of aq. $[Fe^{II}(bpy)_3]^{2+}$



W. Gawelda, et al., JACS **129**, 8199 (2007)

What's the suitable sources for DXAFS?

Source	Photons/pulse/ 0.1%BW	Photn Flux /s	Duration	Rep rate
3rd generation SR	10^4-6	10^10-12	~100 ps	< ~500 MHz
Laser slicing at BM	10^1-3	10^4-7	~100-1000 fs	1-10 kHz
Laser Compton Scattered X-ray, cERL	10^3-4	10^6-7	~100 fs	1 kHz
ERL	10^5-6	10^14-15	~100 fs – 1ps	1.3 GHz
XFEL	10^11-12	10^13-15	~10-100 fs	~100 Hz

DXAFS should be equipped and performed
at the **cERL**, and then the **3-GeV ERL**.

*This table may contain incorrect data.

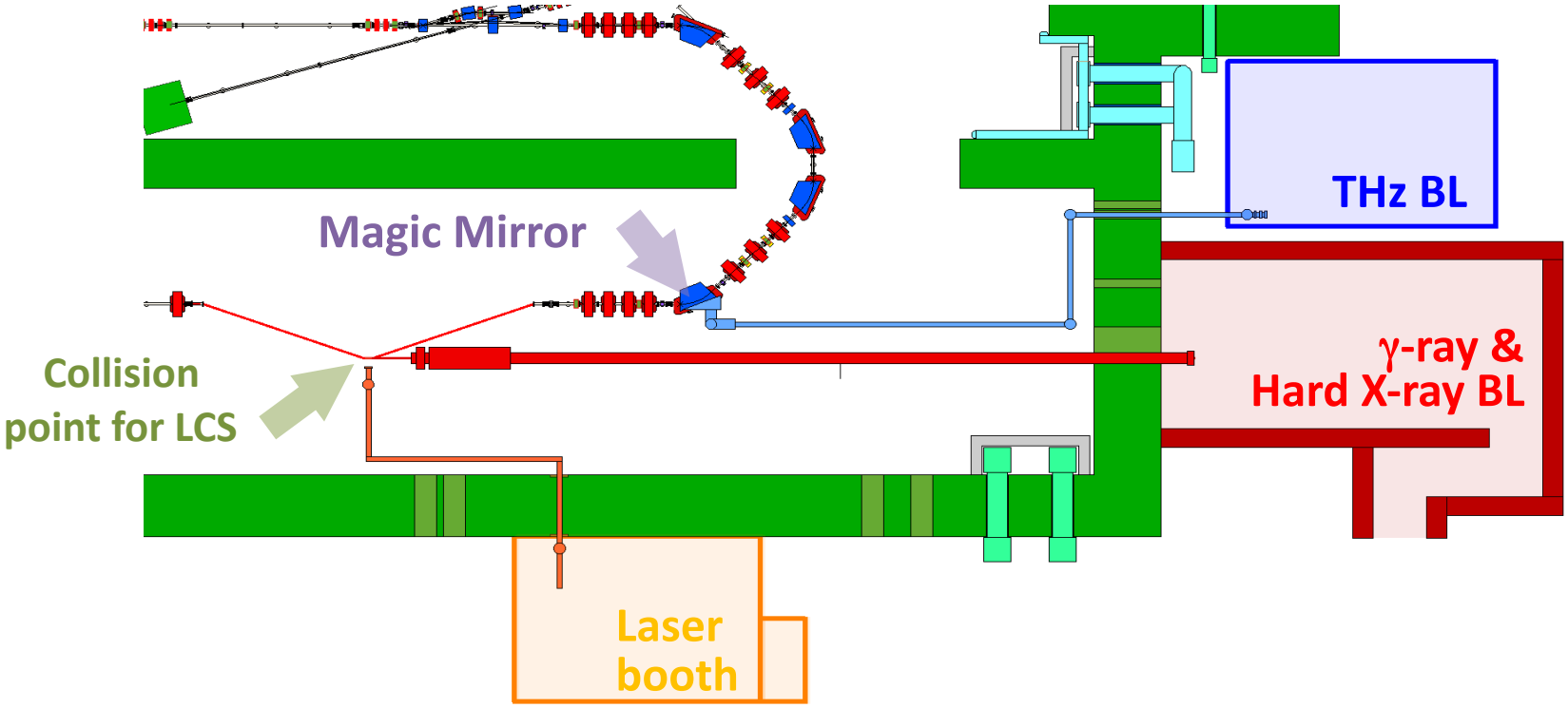
cf. C. Bressler and M. Chergui, Chem. Rev. **104**, 1781 (2004)

NW2A, PF-AR => LC x-ray, cERL; what are the merits?

- Faster phenomena down to **~100 fs** will be targeted and detected.
- The **jitter** could be **excluded**, and the delay will be exactly sure as set in principle.

- The larger emittance gives us a wider range of DXAFS per shot.

２つのビームラインにおける利用研究



レーザーコンプトンX線ビームライン

共振器によるLCSを用いた高flux光源
- 高視野と共振器による高fluxイメージング

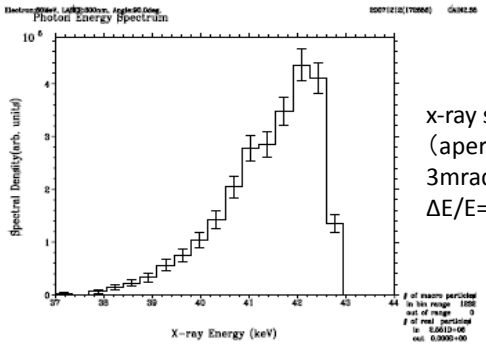
90度衝突LCS散乱を利用したフェムト秒光源
- 100fs準単色光を用いた時間分解X線実験

テラヘルツ光ビームライン

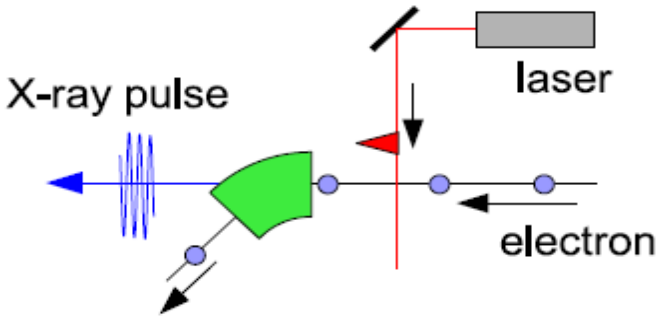
CSRを用いた高強度コヒーレントTHz光源
- meV領域における電子状態変化の観測
- コヒーレント性を利用したイメージング
- フォノン励起用フェムト秒光源

courtesy of Prof. Nozawa

X-ray beamline – ultrafast mode



x-ray spectrum
（aperture : 3mrad）
ΔE/E=0.05



Laser	
Wavelength	800 nm
Pulse energy	10 mJ
Frequency	1 kHz
Pulse width	50 fs
Beam size	20um

Electron bunch	
Energy	60 MeV
Charge	0.1 nC
Bunch width	1ps
Bunch size	20um
Emittance	1mm-mrad

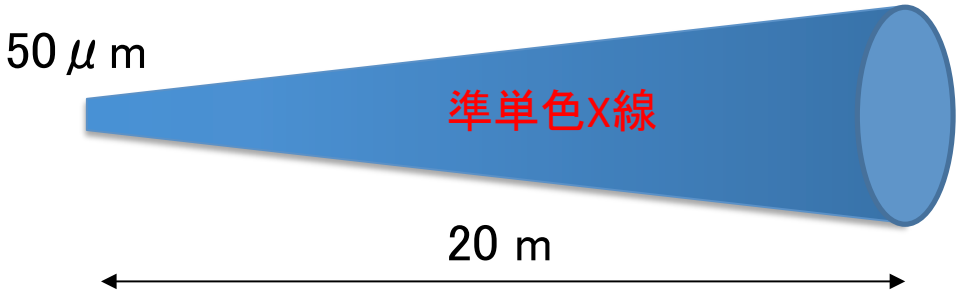
Laser-Compton X-ray	
Averaged X-ray Flux	3.9 x 10^7 phs/s･100% bw
X-Ray pulse width	110 fs

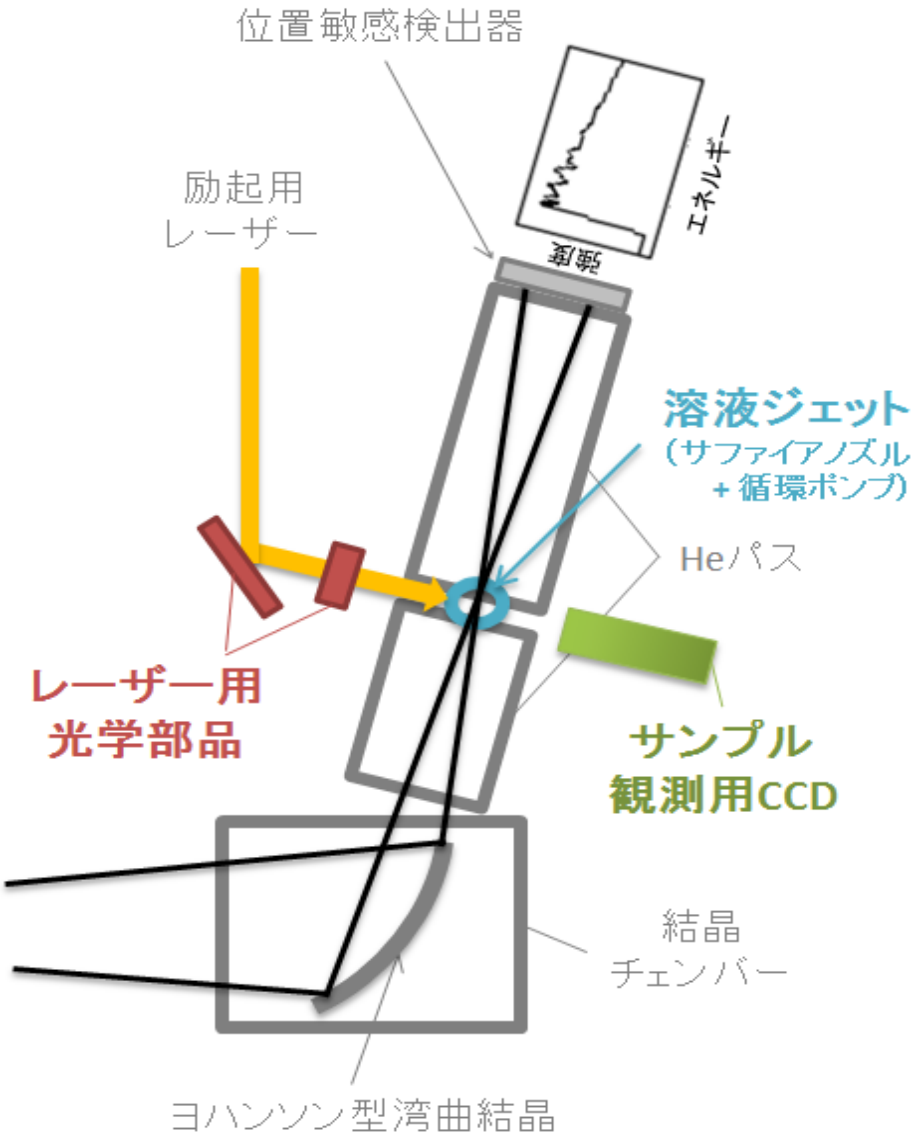
courtesy of Prof. Nozawa

コーンビームを用いた時間分解DXAFS

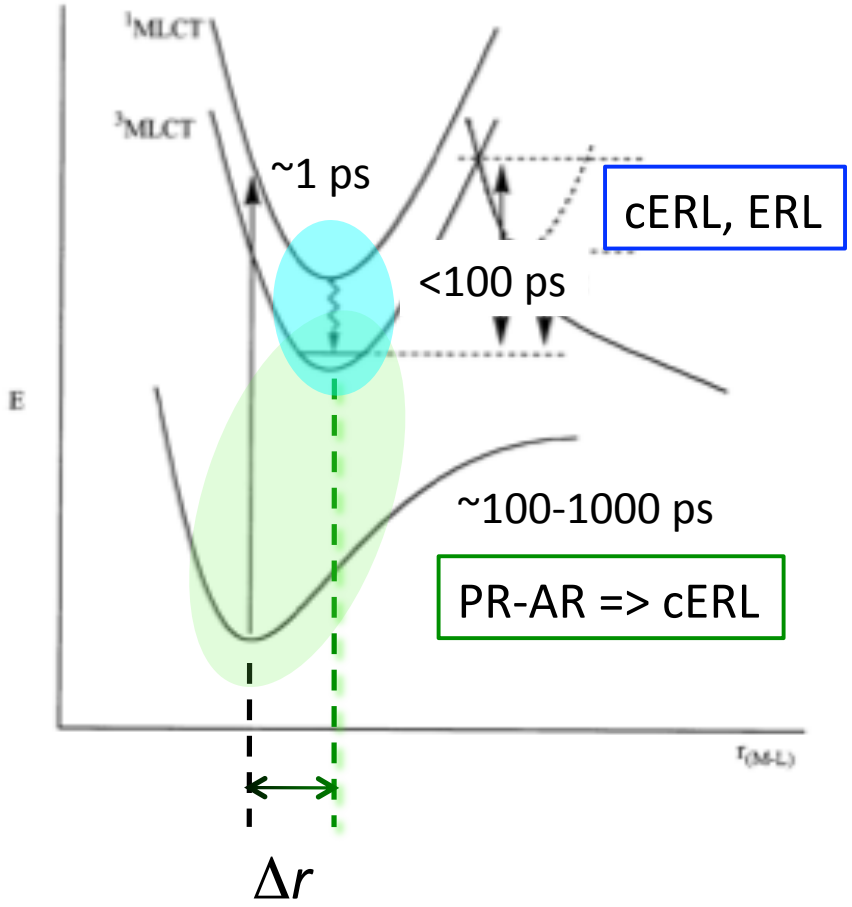
衝突点とサンプルの間(20m)
に5mradのコリメーターを設置

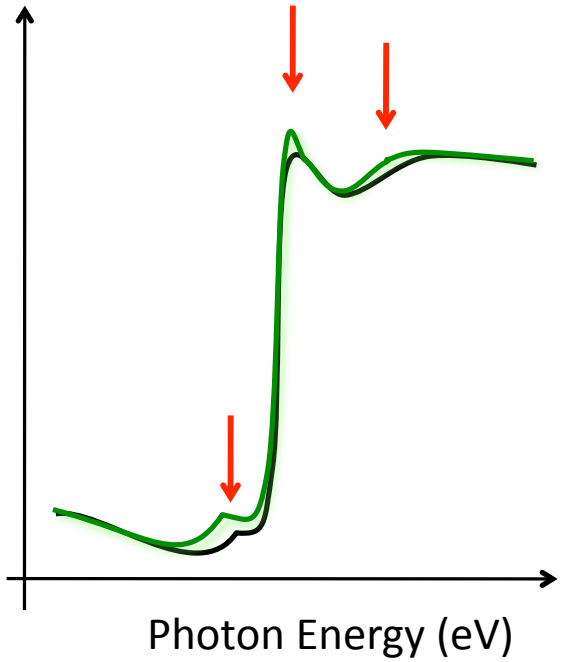
- 発光点の大きさ：50 μ m
- 準単色化（ΔE/E～0.1）
- Φ100mmのビームサイズ
- 光子密度：5×10^{6} photons/sec



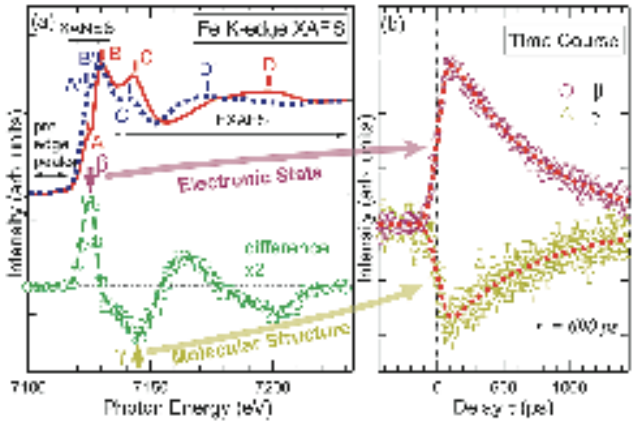


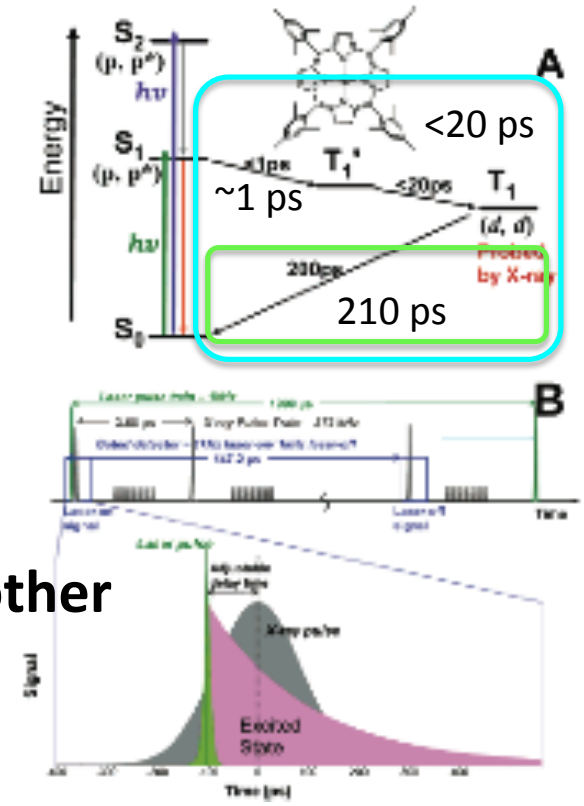
courtesy of Prof. Nozawa


^{1}MLCT
^{3}MLCT
~1 ps
cERL, ERL
<100 ps
E
~100-1000 ps
PR-AR => cERL
$\tau_{(M-L)}$
Δr


Photon Energy (eV)

DXAFS at LC x-ray, cERL





The transient state will be captured

in the excellent time resolution of **~100 fs**

in spectra recorded by **ONE SHOT after another**

S. Nozawa, et al., JACS **132**, 61 (2010)

Lin X. Chen, et at., JACS **129**, 9616 (2007)

What we can do at LC x-ray of cERL

- Time-resolved, **T**ransient **X**-ray **A**bsorption spectroscopy by **DXAFS** with **Δt = ~100 fs**
- In principle, the **jitter free** measurements will be performed.

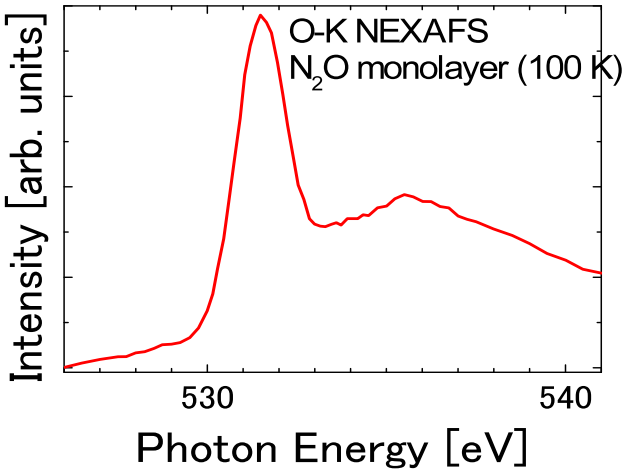
- The larger emittance, the larger size of the beam enables us to measure a wider range of XAFS per shot.

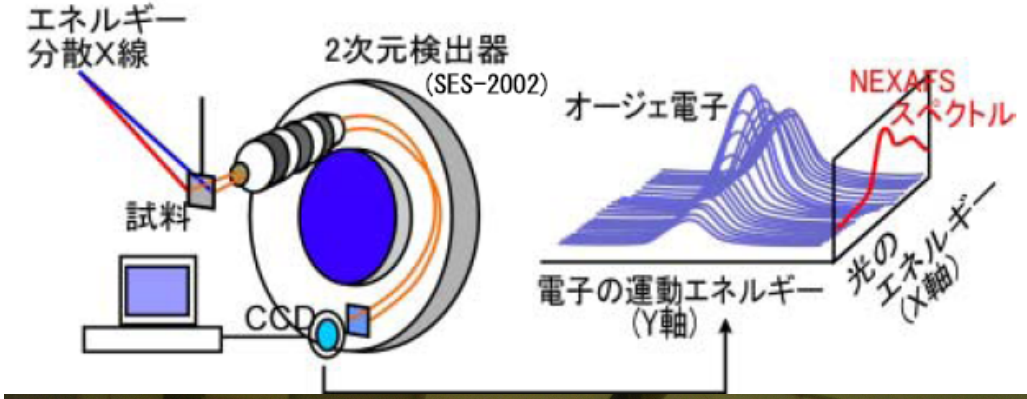
Then, do we need 3-GeV ERL? YES!!!!

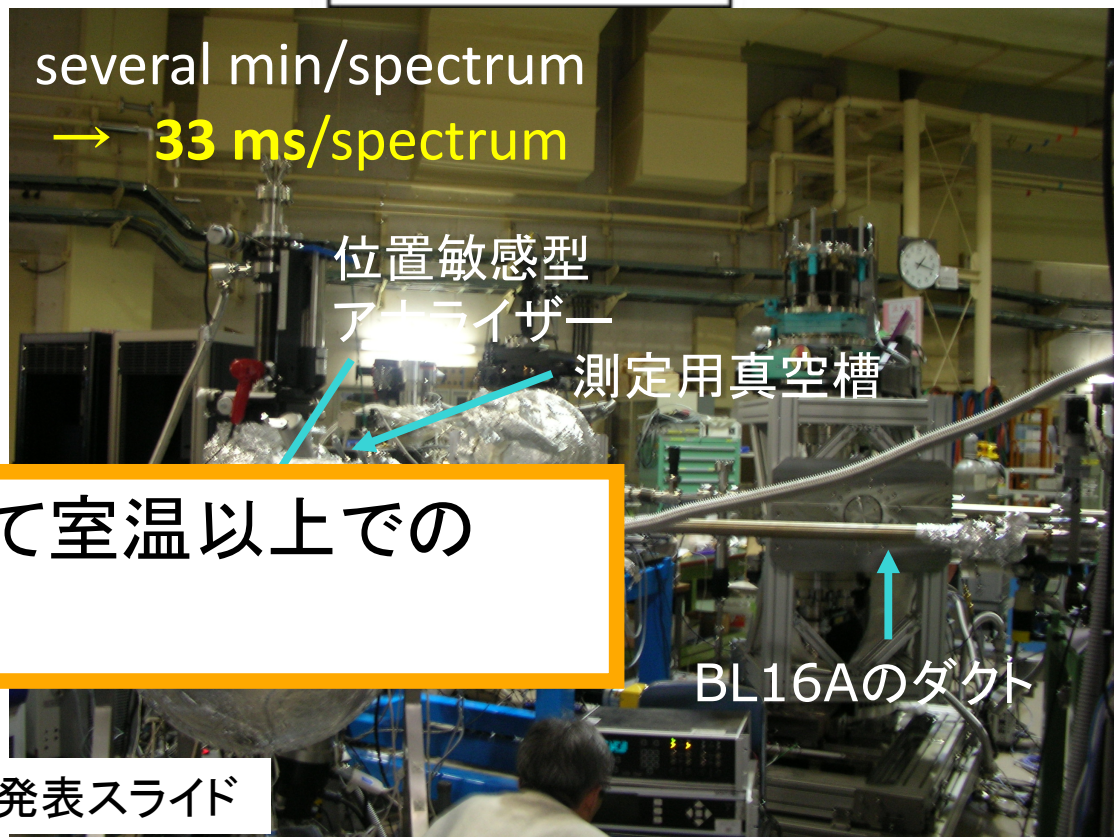
- **Higher photon energy**
- **Much more flux**: huge repeated measurements are not required.
- Higher frequency of the ring, **1.3 GHz**: photons come **every 0.8 ns**, and **"movies" of reactions** will be captured in realistic conditions.
  - Not only Pump – Probe experiments
  - But also **Real time evolution** experiments

Current status of our time-resolved experiment

Disp-NEXAFS







反応が速い室温以上でも
追跡可能に！ [*]

Dispersive NEXAFS法を用いて室温以上での
反応を表面分光法で調べる

[*] 小宇佐友香（慶應大、近藤研），修士論文発表スライド

Available time resolution & possible study

	Acquisition Rep rate	Period of real time observable reaction	Ratio (Period/Rep rate)
Current status: 16A at PF	**33 ms** (Video rate of the camera)	**~100 s**	~$10^{3\text{-}4}$
Future: ERL	**0.8 ns** (Pulse interval)	**(~100 ns)- 1 -10 μs**	~$10^{3\text{-}4}$

Real time observations of catalysts at very working temperature

For example... ——— *How suitable!! Perfect!!*

CO oxidation on Pt(111)

E_a = 0.5 – 0.7 eV ⇒ RT => 600 - 900 K ⇒ (Ratio of k) = **10^4 – 10^8**

...maybe (^^;)

Summary

- Prospects of DXAFS at LCS X-ray station, cERL are presented.
  - **Laser Pump – DXAFS Probe** experiments are strongly recommended to perform.
  - Δt = ~**100 fs**, **Jitter free**, The wider range of XAFS
- cERL is a fancy machine, but 3-GeV ERL must be established
  - as **to shine mysteries of transition states** and to capture **real time "movies" of chemical reactions**.

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