DXAFS at PF and SPring-8

Photon Factory, IMSS, KEK

NOMURA Masaharu

Photon Factory

Time-resolved DXAFS at PF

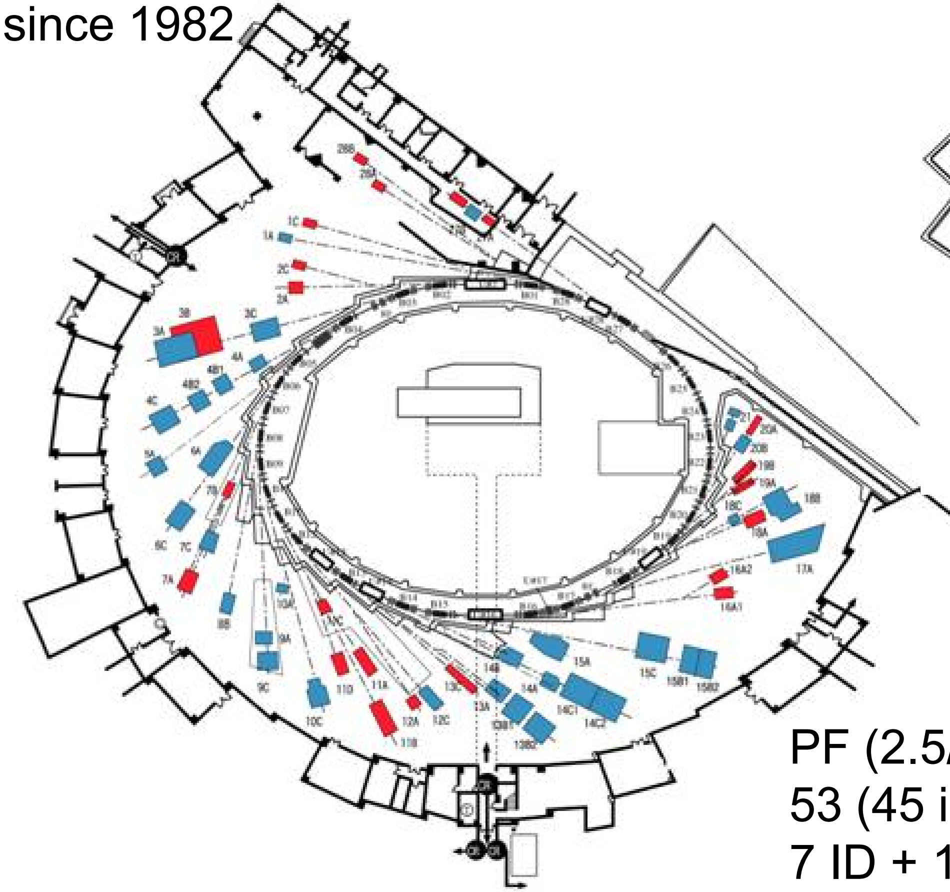
Redox behavior of Pt/MCM-41with H_2/O_2

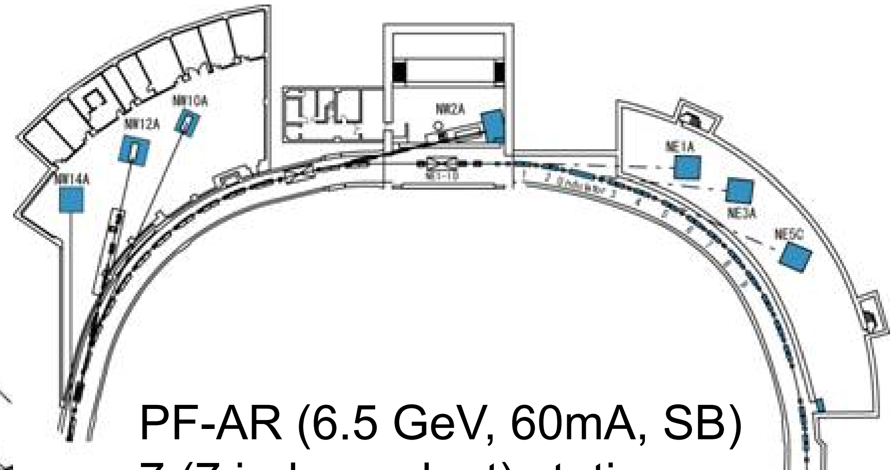
Time-resolved XAFS at SPring-8

Photon Factory

typical second generation synchrotron facility

since 1982





PF-AR (6.5 GeV, 60mA, SB)
7 (7 independent) stations
5 ID + 2 Bend

PF (2.5/3 GeV, 450 mA, MB(SB))
53 (45 independent) stations
7 ID + 15 Bend → 11 ID + 12 Bend

:Experimental Stations for Hard X-rays

:Experimental Stations for VUV and Soft X-rays

January 2009

staffs

beam lines	40 scientists +	9 technicians
light source	19 scientists +	11 technicians

5 XAFS, 1 DXAFS stations
2 BL scientists

Photon Factory

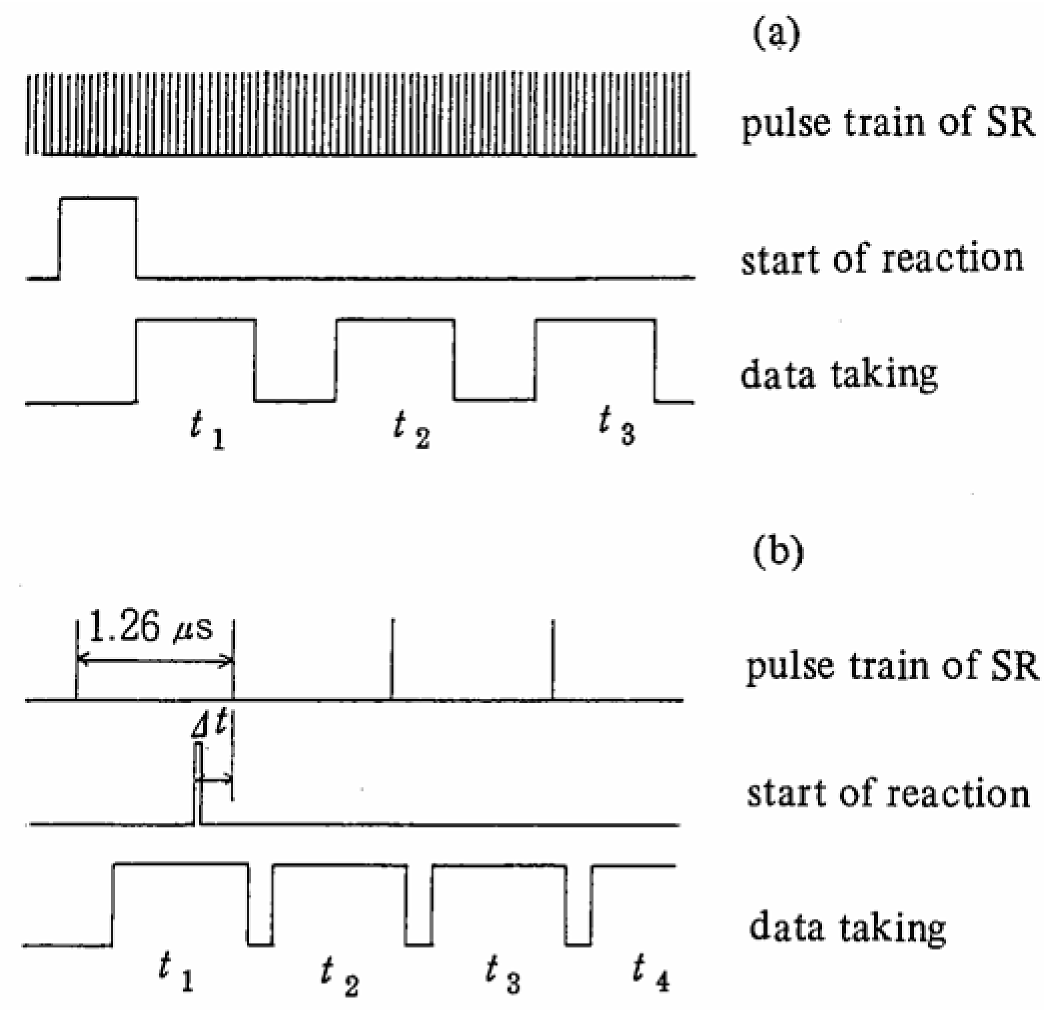
1982.4.17
President Mitterrand
visited PF with Mr. Ogawa,
minister of Education

1982.5.8
PM Mr. Suzuki visited PF

DXAFS at the Photon Factory

1980s	Prof. Matsushita at BL-4A(dipole source) of PF
1998	restart DXAFS activity with Prof. Iwasawa and Prof. Asakura of Univ. of Tokyo at BL-9C(dipole source) of PF
1999	construct NW2A at PF-AR tapered undulator source

PF-AR; dedicated single bunch source



(a) multi-bunch

Δ*t*: detector limited

→ μs~ms with linear detectors

(b) single-bunch

Δ*t*: SR and/or pump pulse

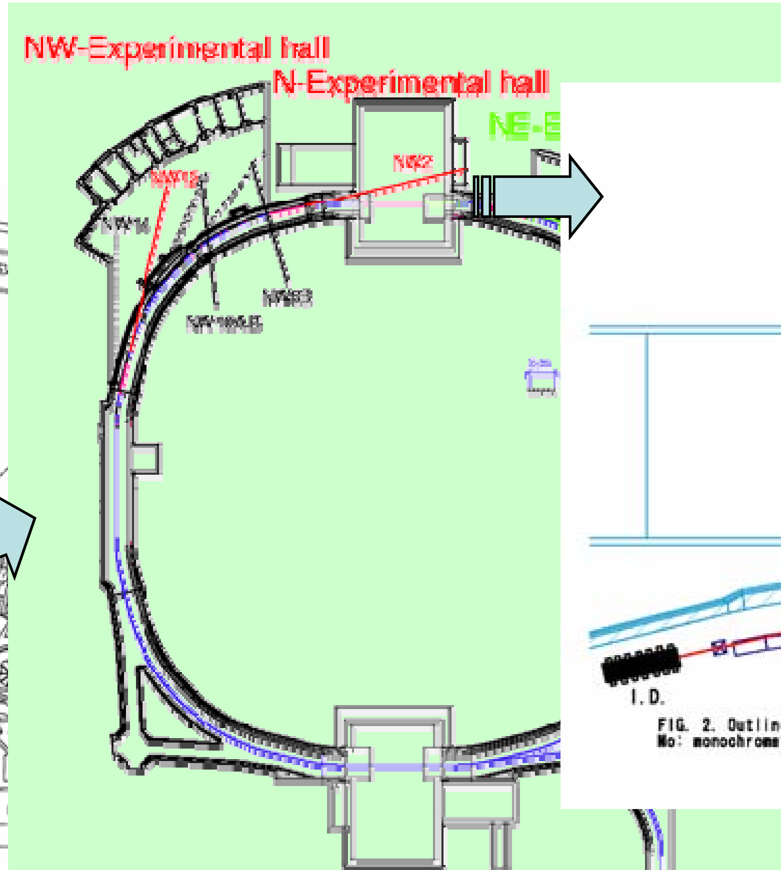
→ 140ps

140 ps wide pulse, every 1.26 μs, 10^4 ph/ch/pulse

Upgrading PF-AR

1999～2002

Only one machine in the world that is always operated as **high current Single Bunch**



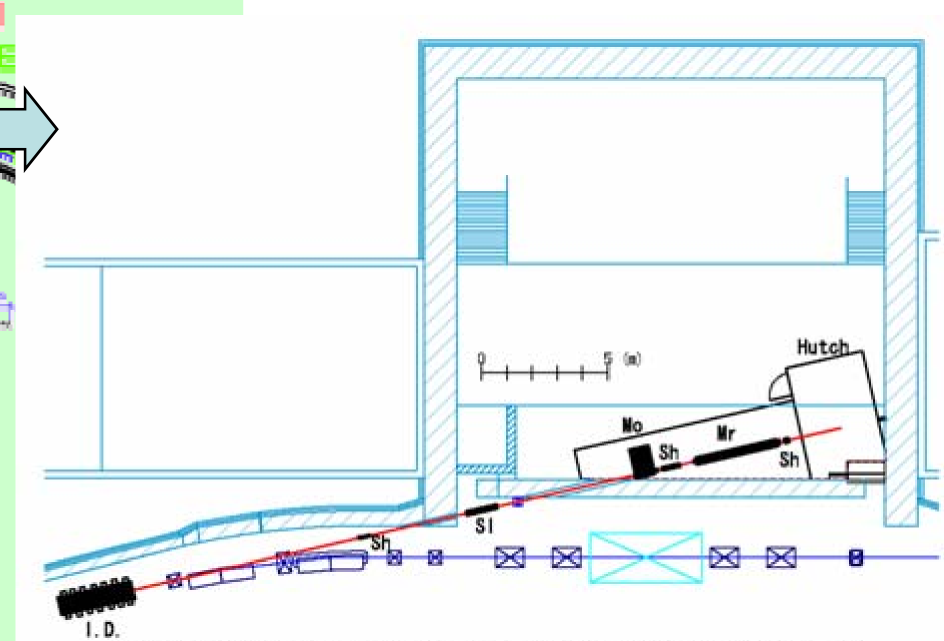


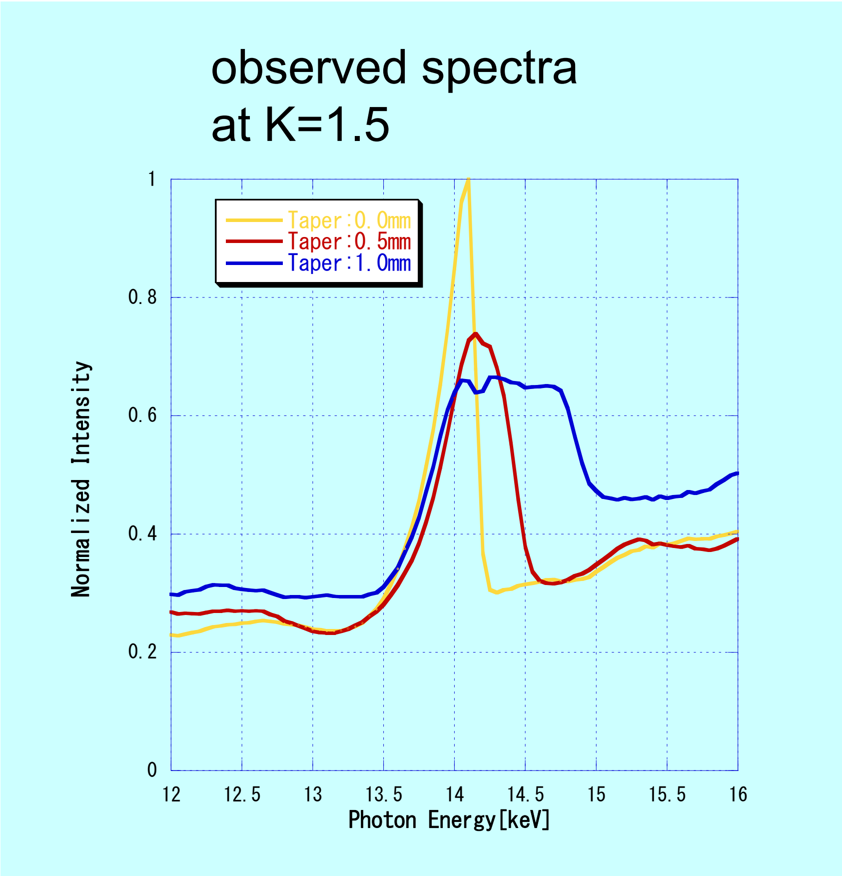
FIG. 2. Outline of beamline AR-NW2. I.D.: insertion device; Sh: beam shutter; Sl: slit; Mo: monochromator; and Mr: mirrors.

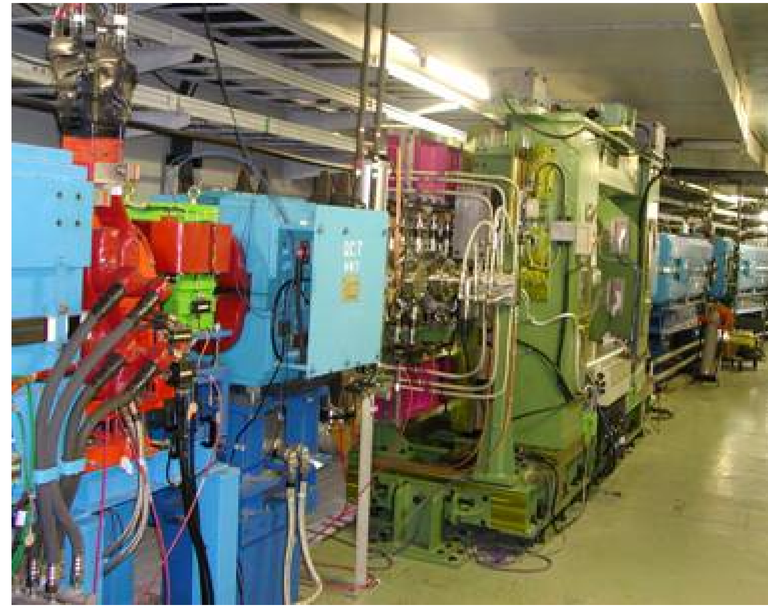
Time resolved XAFS

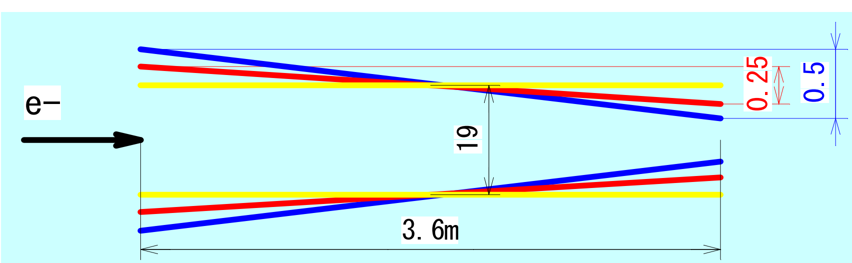
from booster of TRISTAN to dedicated synchrotron source

new building, new BLs : **NW2**、NW12

tapered undulator







λ_u = 4cm, N = 90 periods

S. Yamamoto *et al*., AIP Conf. Proc., 705, (2004).

beam line NW2A

sub ns resolved DXAFS

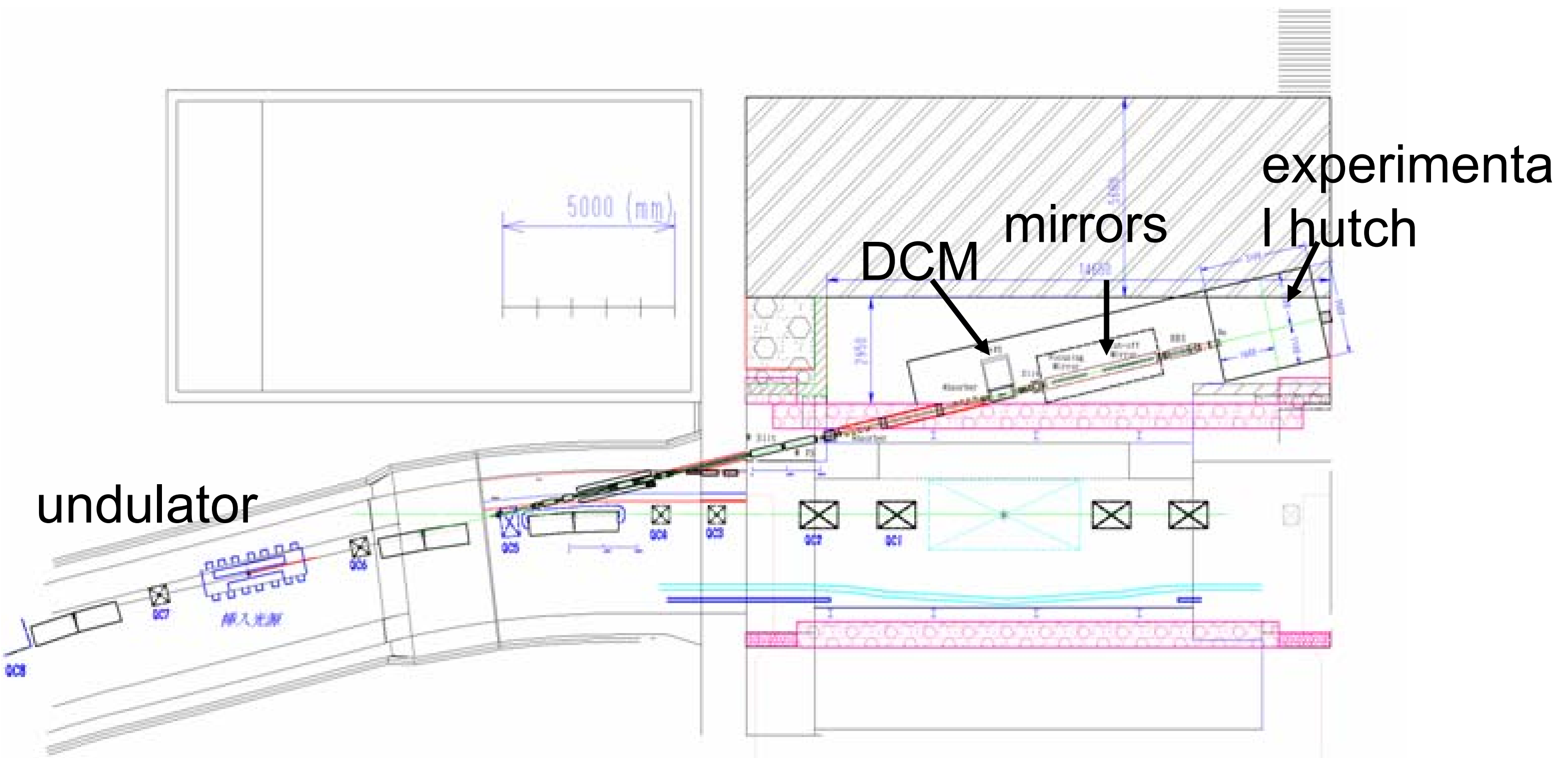
source : tapered undulator
white X-ray + DXAFS

detector : PDA, CCD, PAD

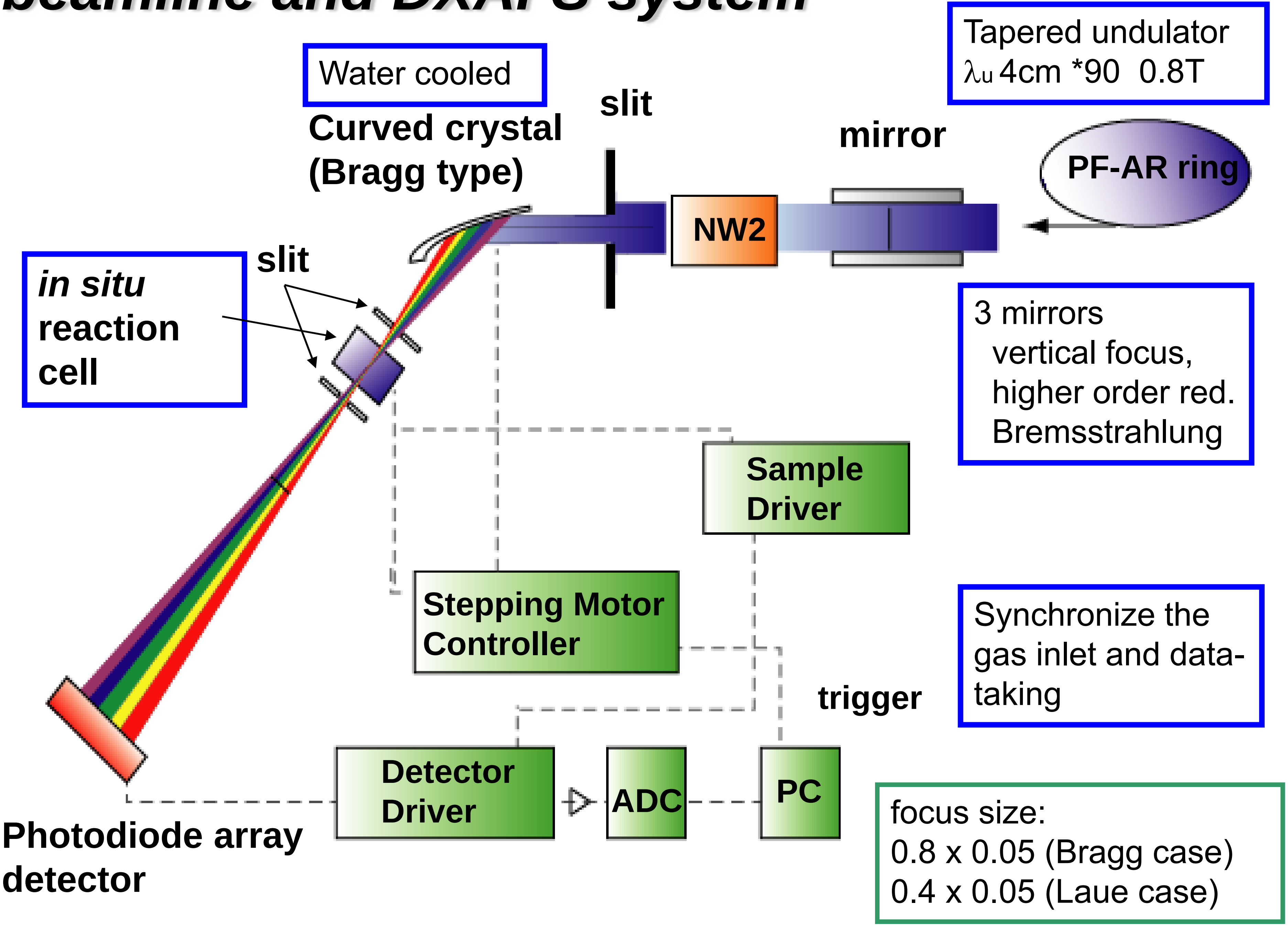
fluorescent XAFS

source : undulator

detector: Ge detector
crystal analyzer



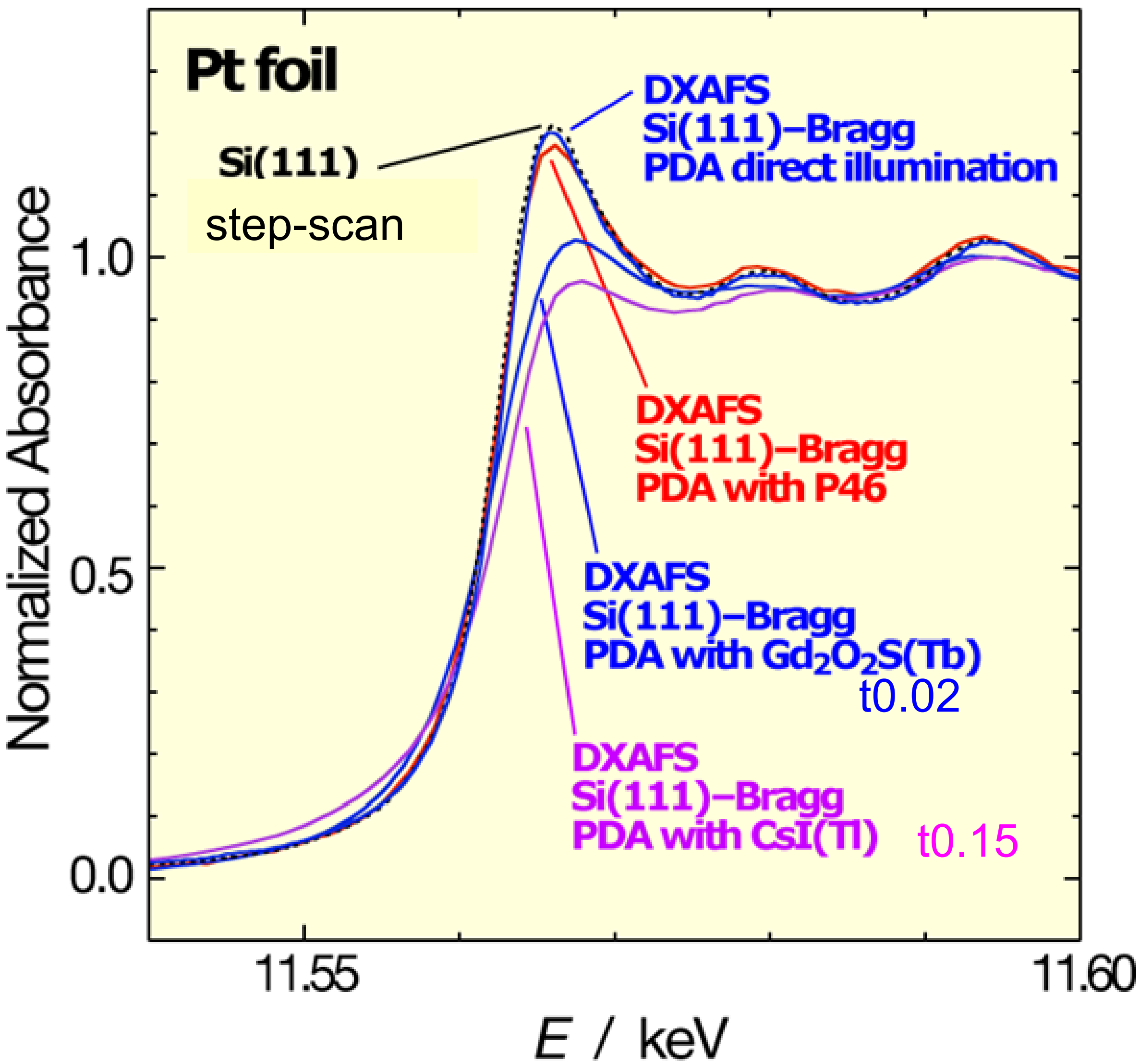
beamline and DXAFS system

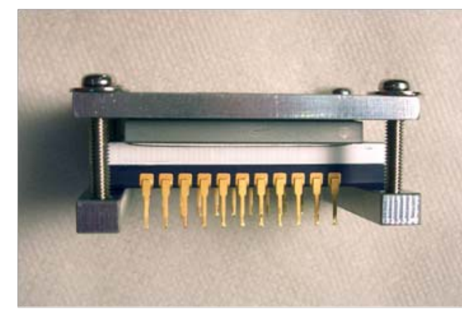


	Zeff 有効原子番号	λ 蛍光波長	τ 蛍光減衰の半減期	Afterglow at 3 ms
CsI:Tl	54.1	540 nm	600 ns	0.2 %
Gd_2O_2S:Tb (P43)	61.1	544 nm	500 μs	< 0.01 %
$Y_3Al_5O_{12}$:Ce (P46)	32.0	550 nm	65 ns	
Lu_2SiO_5:Ce (LSO)	66.4	420 nm	56 ns	
$Bi_4Ge_3O_{12}$ (BGO)	75.2	480 nm	300 ns	0.5 %

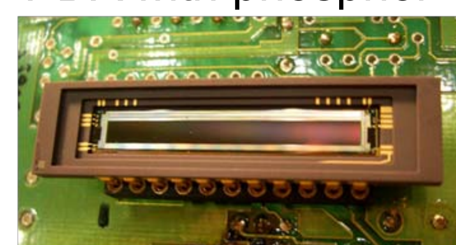
A. Koch and C. Raven, *Proc. Int. Conf*. (1997)

Apparent energy resolution change with phosphors





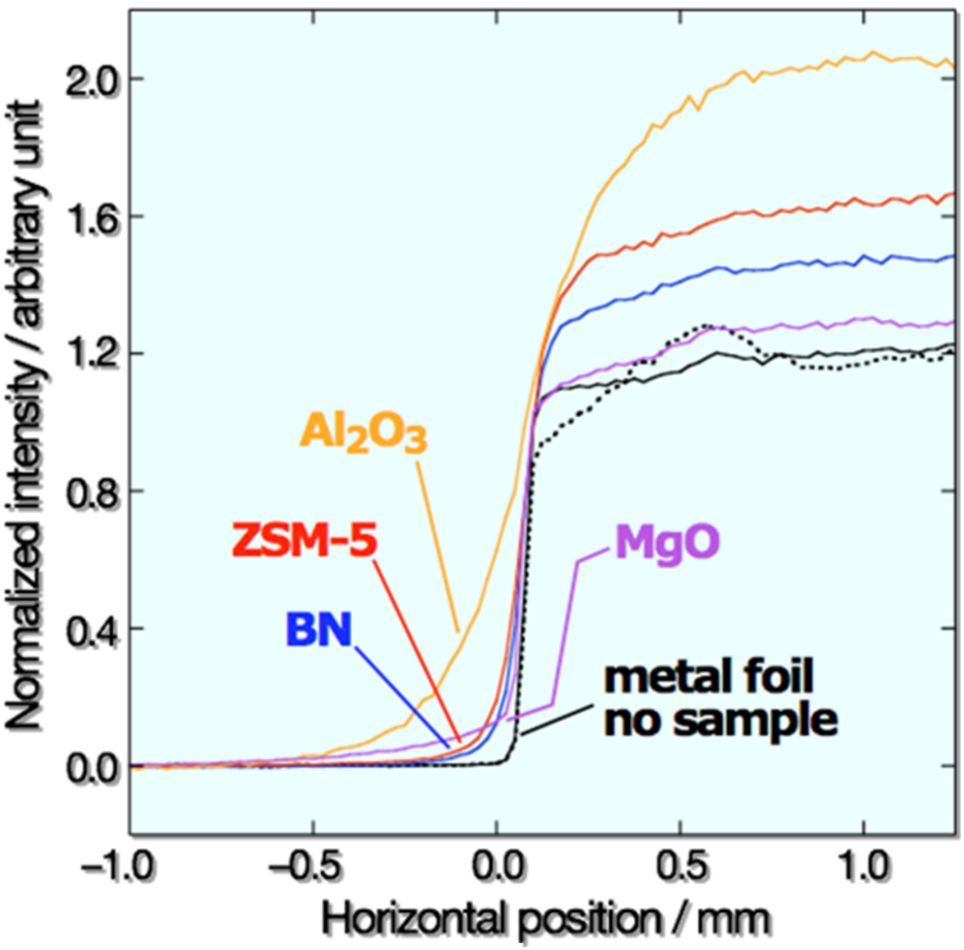
PDA with phosphor



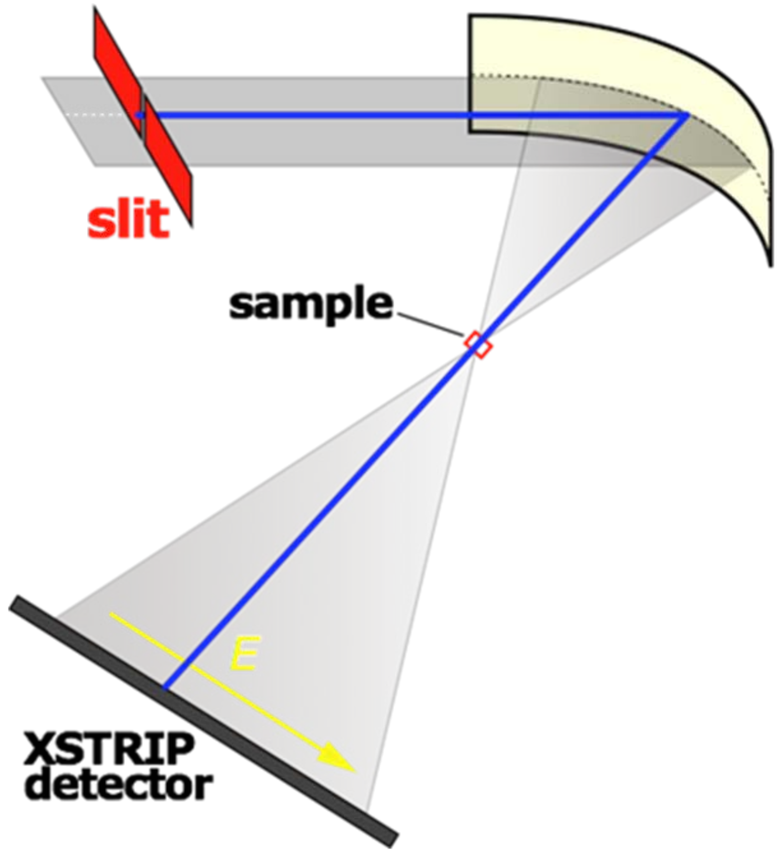
direct illumination PDA

thickness effect like phenomenon

@ PF-AR NW2A



knife edge test



scattering from Al_2O_3 is significant

cf.) M. Hagelstein, *et al.*, *J. Synchrotron Rad.*, 5, 753 (1998)

Redox behavior of 3.5 wt% Pt/MCM-41

Nariyuki-Suzuki A.

Pt nano-cluster has high activity for hydrogenation etc.

quantitative analysis of adsorbed hydrogen → TPD

■ no information on electronic state nor structure

<u>XAFS of Pt nano-cluster</u>

hydrogen adsorption **XANES changes**

increase *r*(Pt-Pt) by 0.003 ~ 0.02 nm

step-wise reactions

hydrogen adsorption

structural change of Pt clusters

no information on the Pt cluster structure during the reaction.

↓

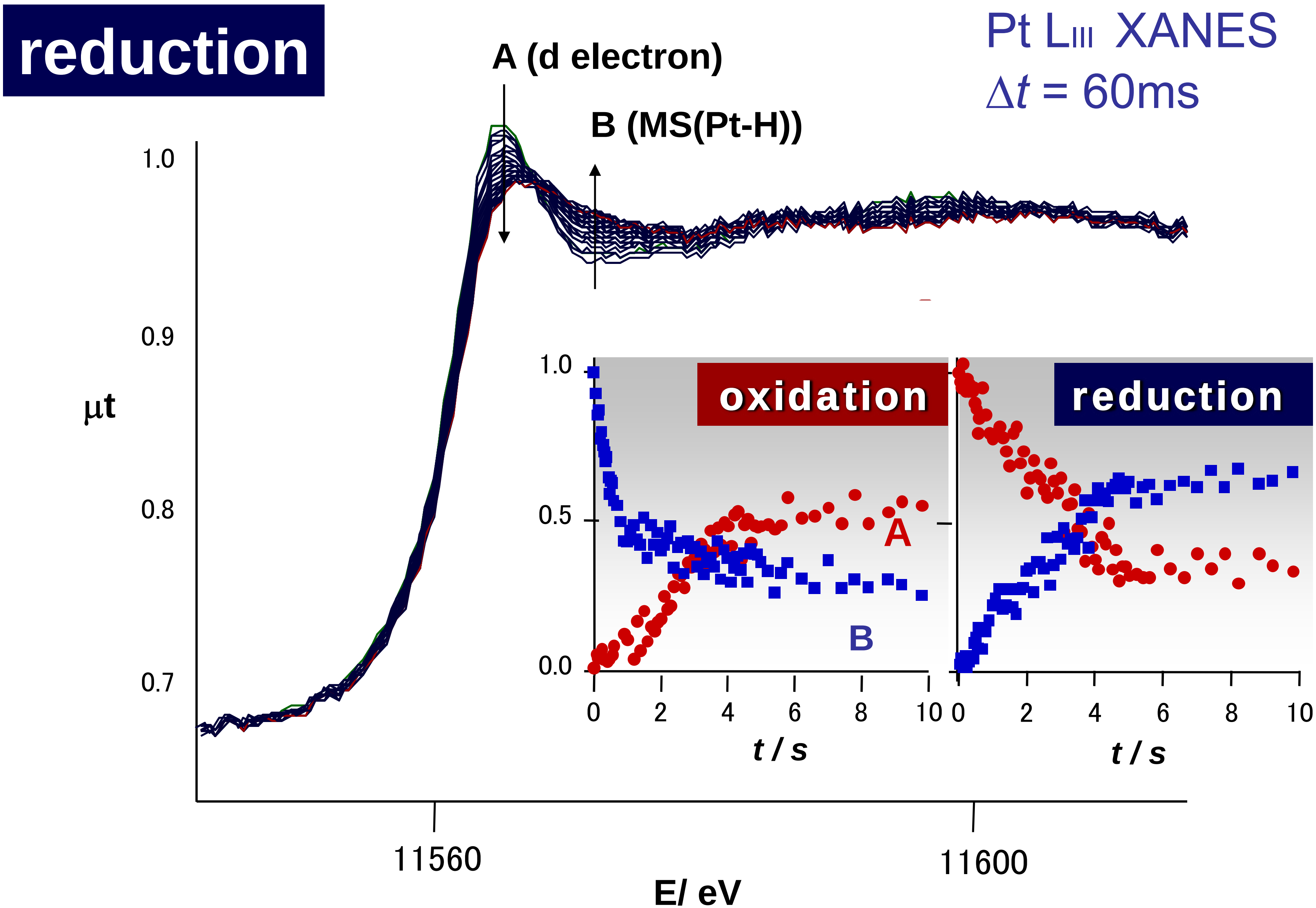
DXAFS →

best method to study the structural change during hydrogen adsorption

(1): O_2 pre-exposed Pt / MCM-41 + H_2

(2): H_2 pre-exposed Pt / MCM-41 + O_2

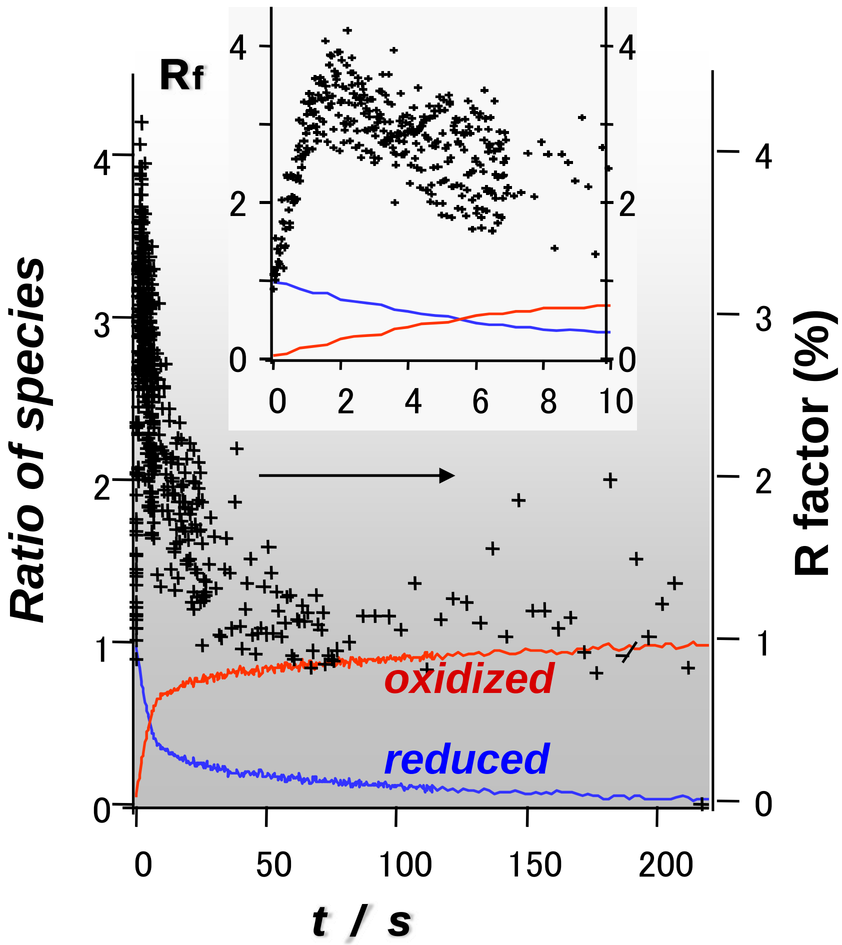
Time-resolved XAFS spectra; Pt/MCM-41



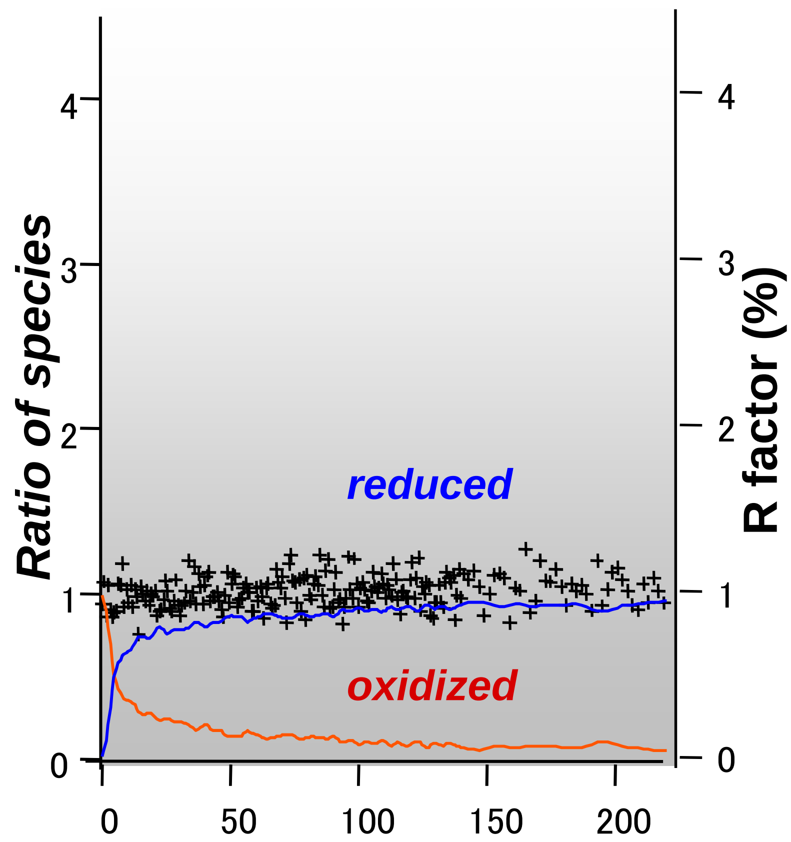
$$\chi_{obs}(k,t) = c_i(t)\,\chi_i(k) + c_f(t)\,\chi_f(k)$$

$$R_f = \Sigma|(\chi_{obs} - \chi_{calc})| / \Sigma|\chi_{obs}|$$

oxidation

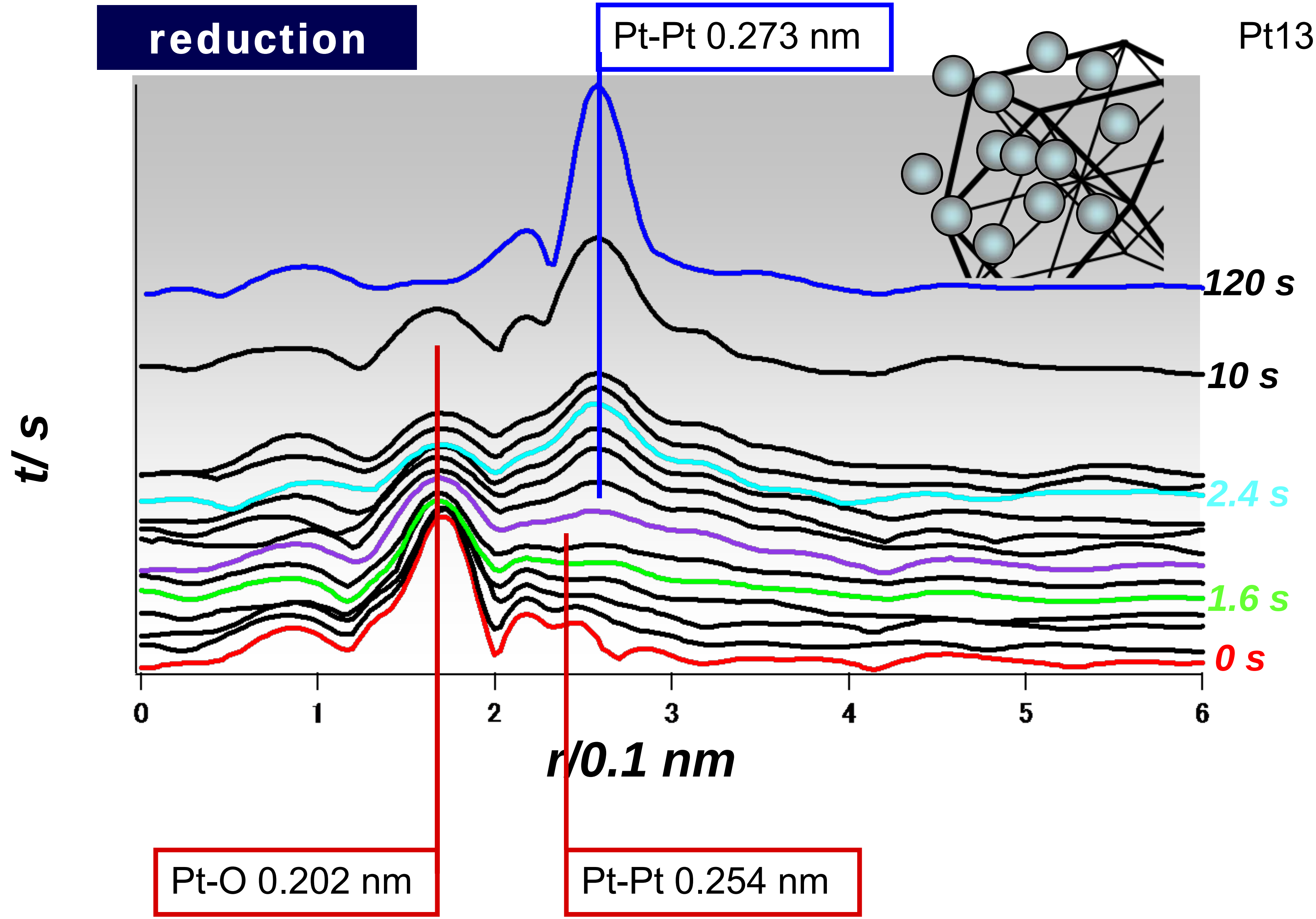


reduction

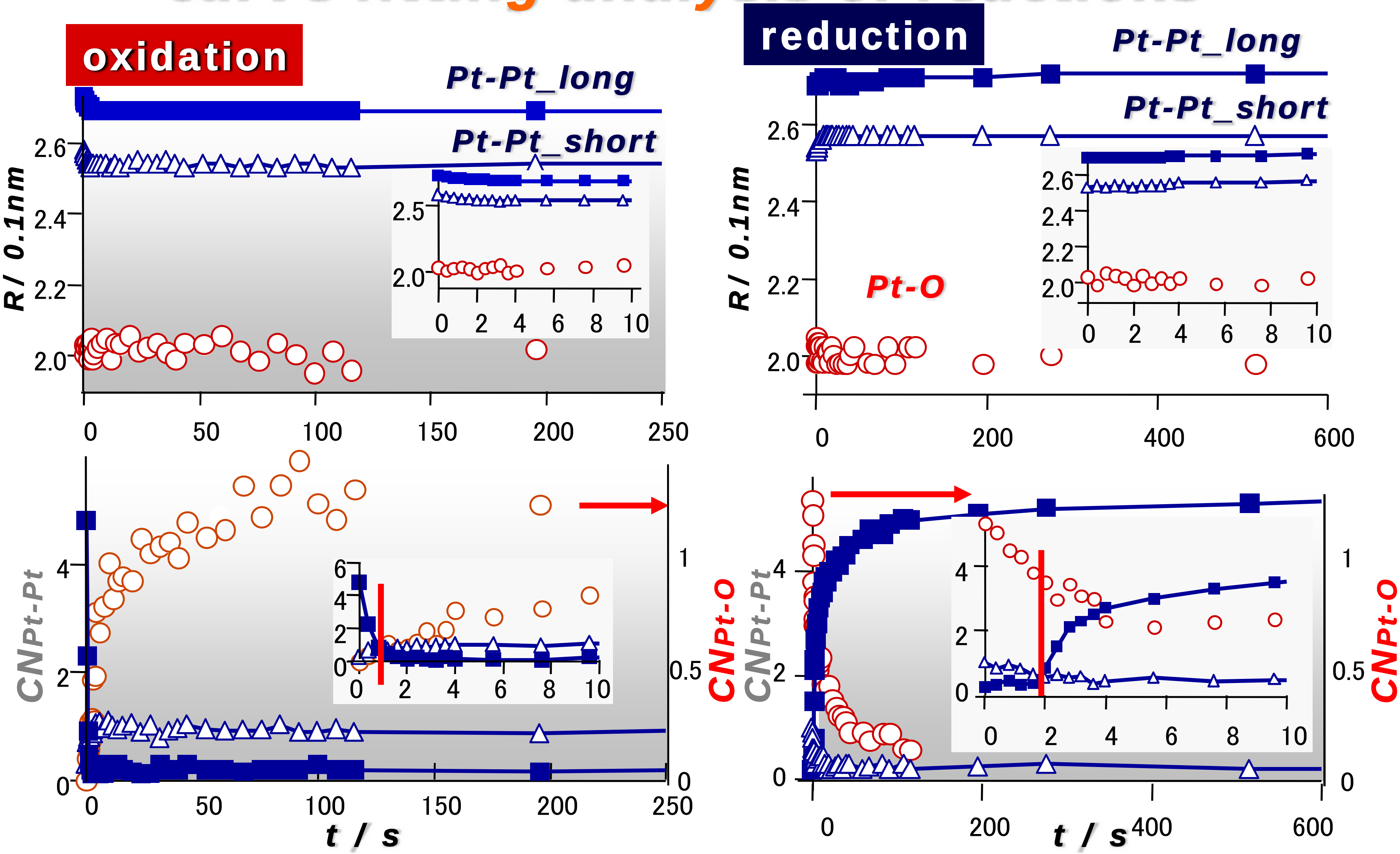


Some new species are expected during oxidation process

Time-resolved Radial Structure Function



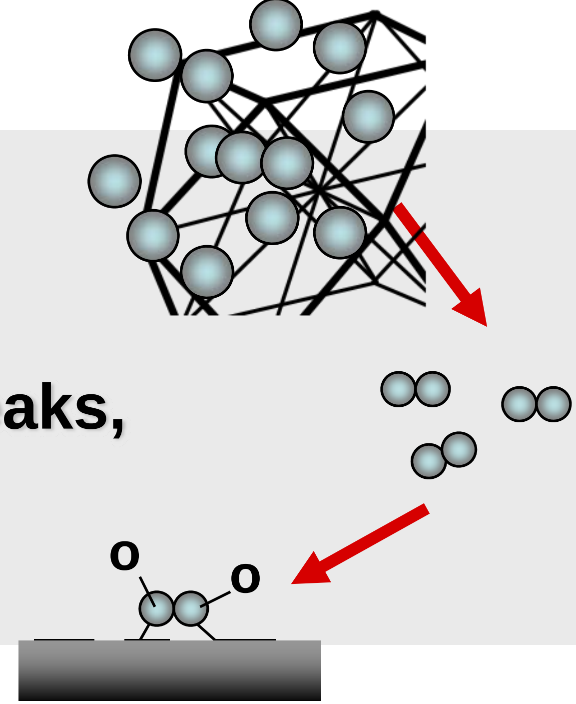
curve fitting analysis of reactions



oxidation : break cluster, then Pt-O bonds are formed

reduction : a third of Pt-O breaks, then cluster is formed

summary



oxidation

1. A half of H desorbs as H_2O,
   Pt13 cluster (*r*(Pt-Pt) = 0.273nm) breaks,
   form Pt2 dimer *r*(Pt-Pt) = 0.254nm
2. make Pt-O bond, Pt oxidized

reduction

1. A third of O desorbs as H_2O,
   forms Pt-H, Pt reduced
2. grow the *r*(Pt-Pt)=0.273nm frame
3. Pt13 cluster is formed gradually

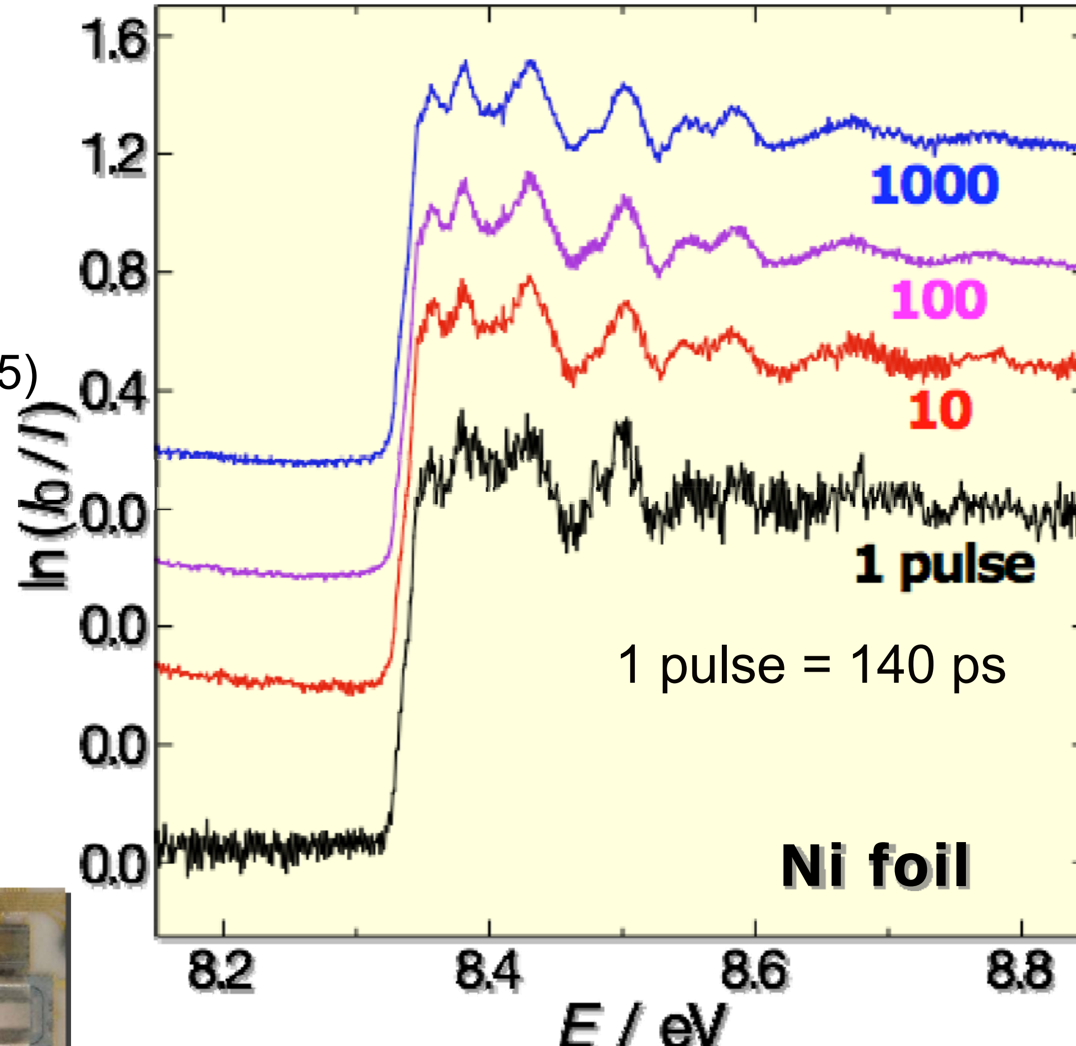
Now time-resolved XAFS is getting chemists' daily tool.

towards sub ns time-resolution

@ PF-AR NW2A X-STRIP

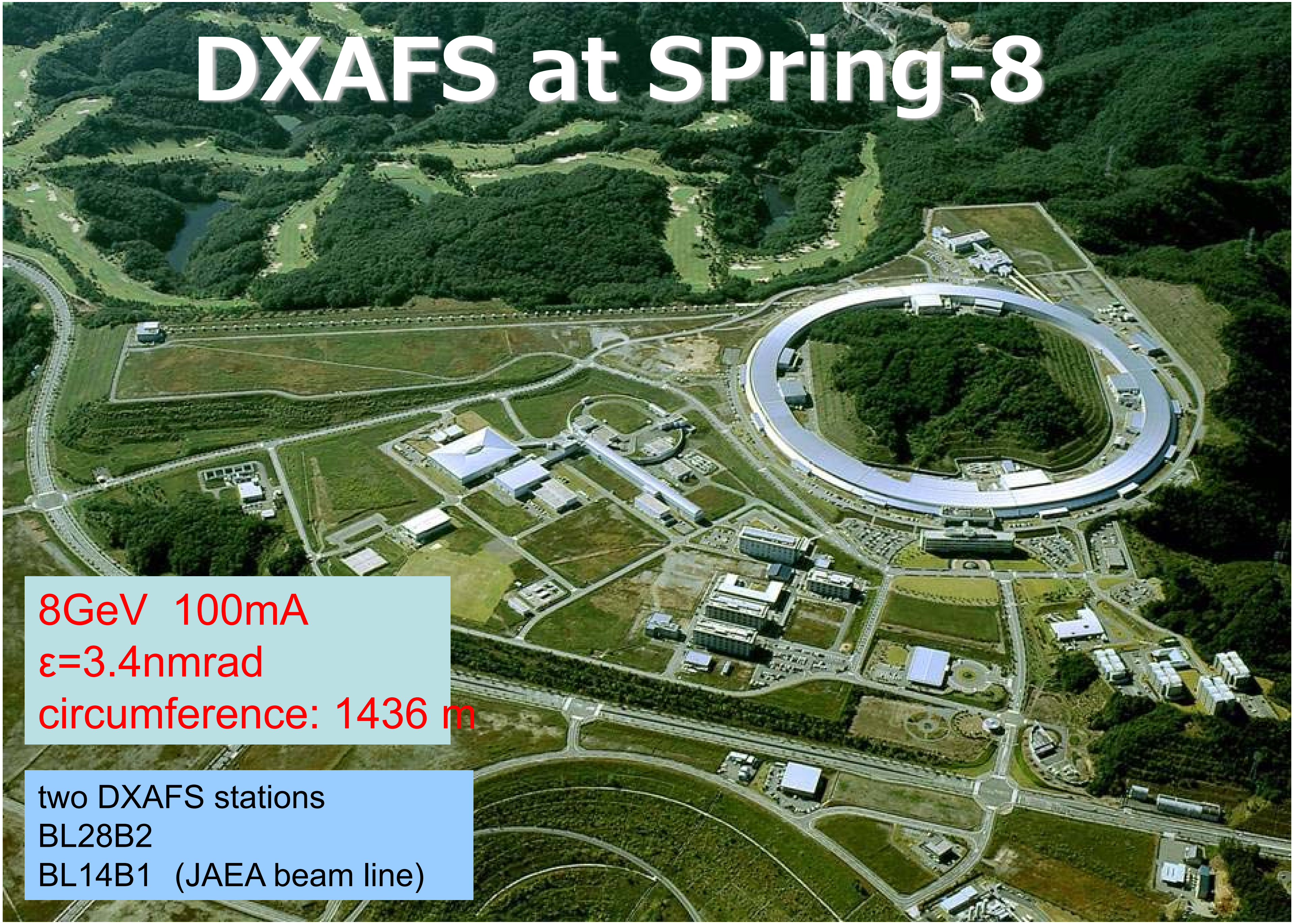
- 1024 channels
- 25mm(W)*4mm(H)
- min. 1μs readout gate
- every 10 μs

G. Salvini *et al.*, NIM A551, 27 (2005)



developed by Daresbury Lab.
introduced with Prof. Iwasawa

DXAFS at SPring-8

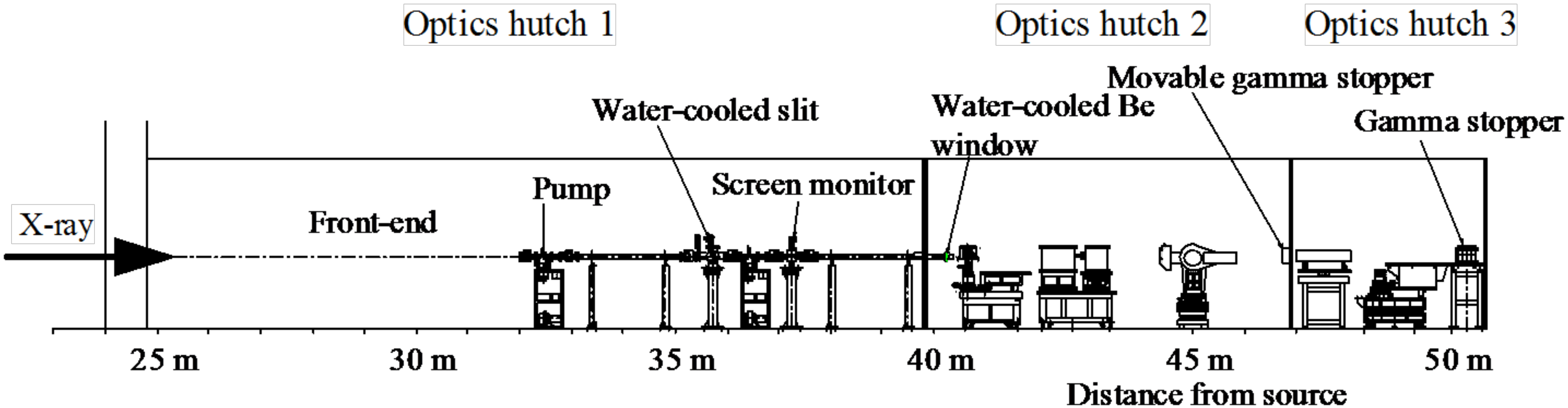


8GeV 100mA
ε=3.4nmrad
circumference: 1436 m

two DXAFS stations
BL28B2
BL14B1 (JAEA beam line)

White X-ray multipurpose beam line BL28B2

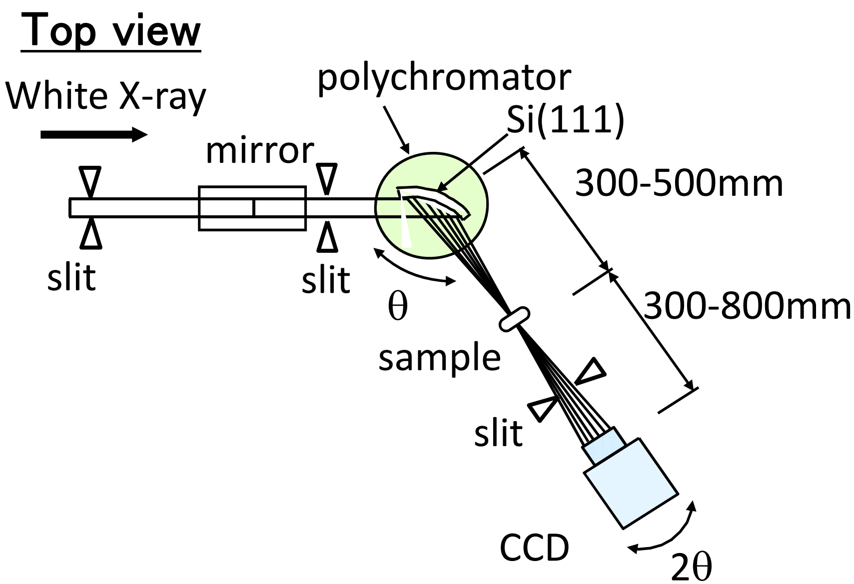
Transport channel of BL28B2



- Light source : bending magnet (E_c= 28.9keV)
- There are no monochromator, mirror in optics hutch1.
- Research field
  - **DXAFS**
  - White X-ray topography
  - Medical imaging
  - X-ray diffraction under high-pressure and high-temperature

BL28B2 DXAFS system

Bragg configuration (E<12keV)

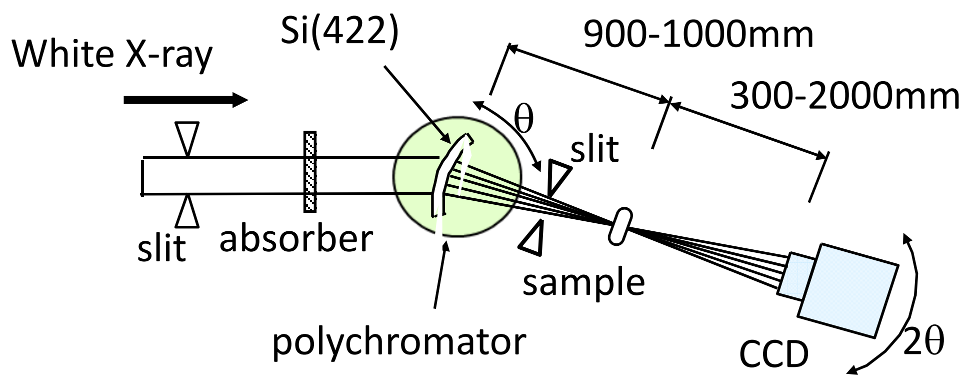


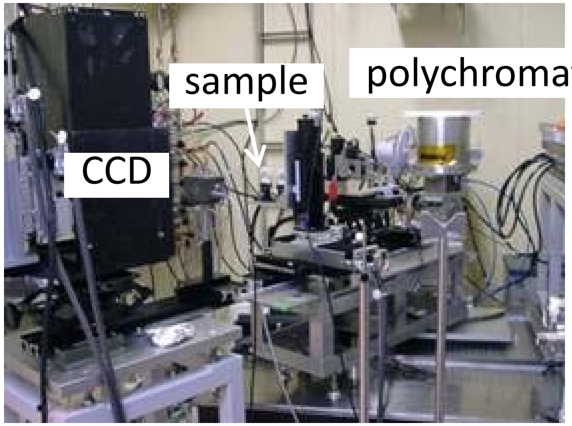
7 – 40 keV

horizontal focus size : 0.11mm

minimum time resolution : 6ms

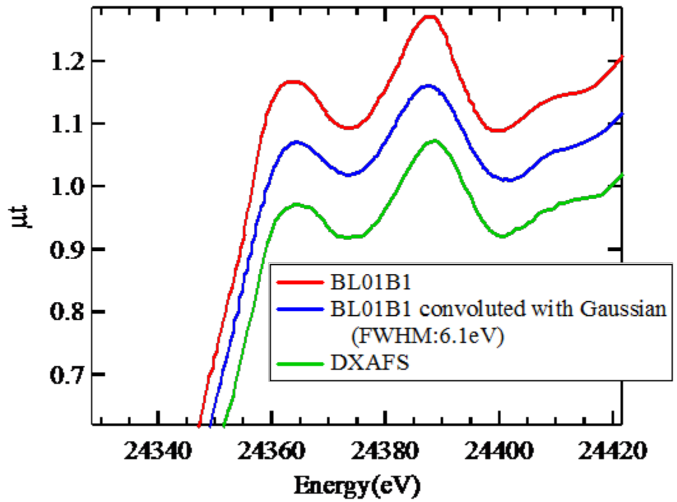
Laue configuration (E>12keV)

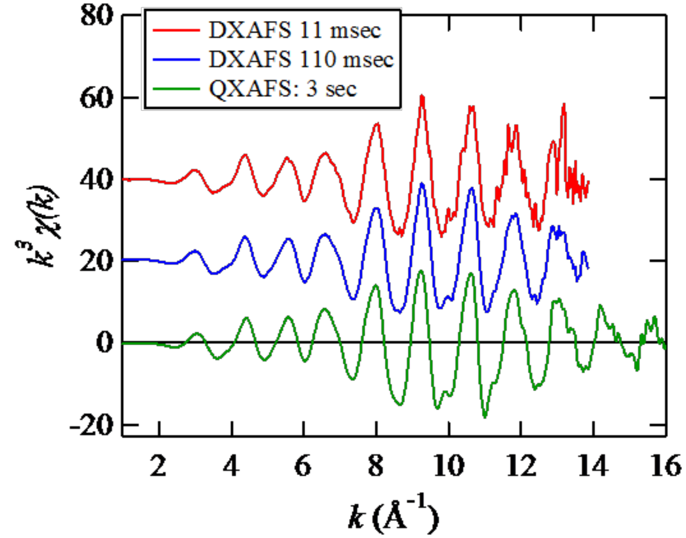




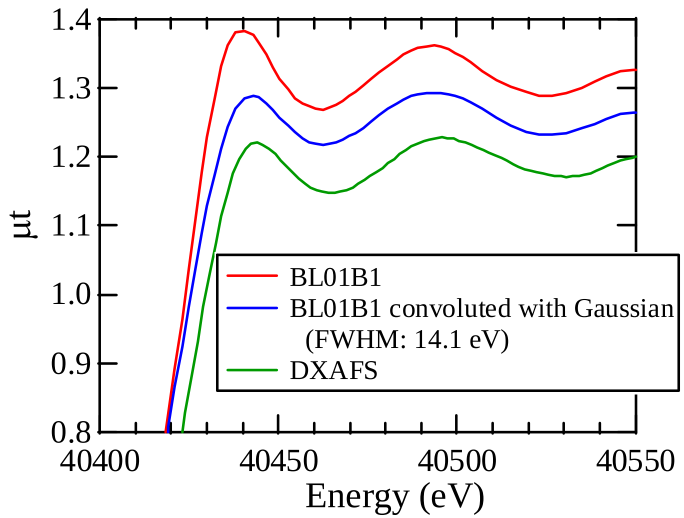
DXAFS spectra at Pd K edge (24.3keV) and Ce K-edge(40.2keV)

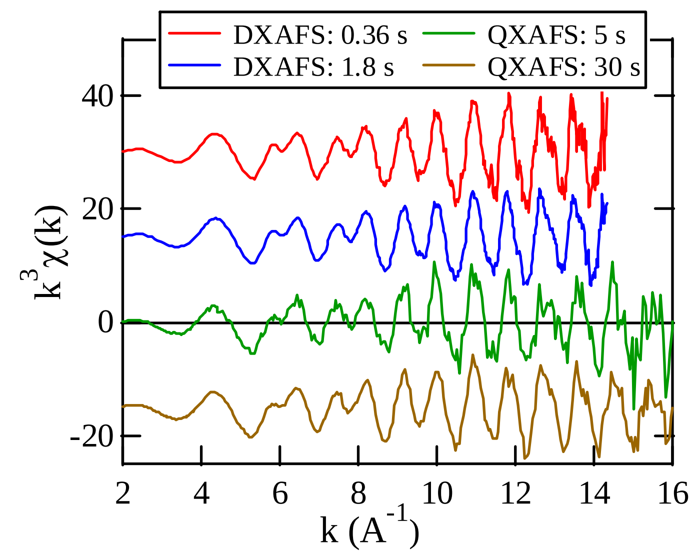
Sample : Pd foil



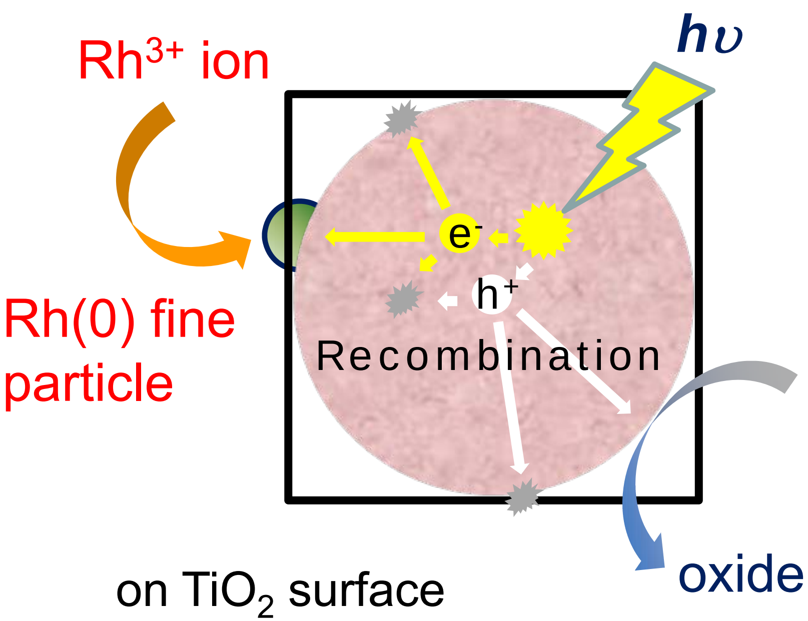


Sample : CeO_2





DXAFS study on photodeposition of Rh particle on a TiO_2 photocatalyst



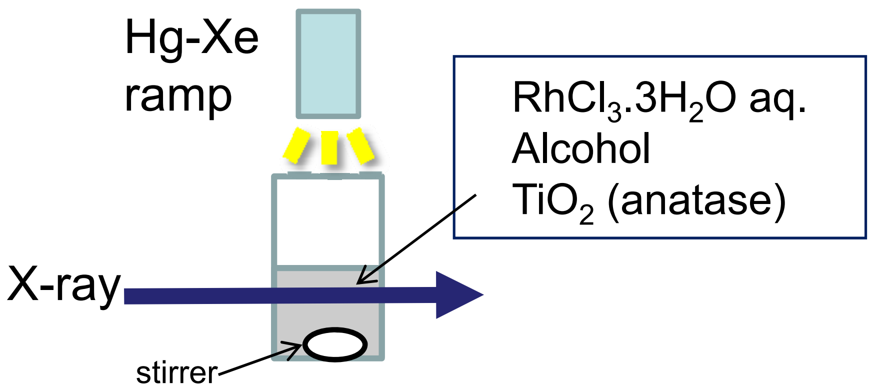
The photodeposition method is easy to load metal on a photocatalyst because of doing nothing other than introducing a photocatalyst and a metal precursor into an aqueous solution involving alcohol as a sacrificial reagent and illuminating this suspension with a light source.

Reaction Mechanism ?
Kinetics?
Dynamics?

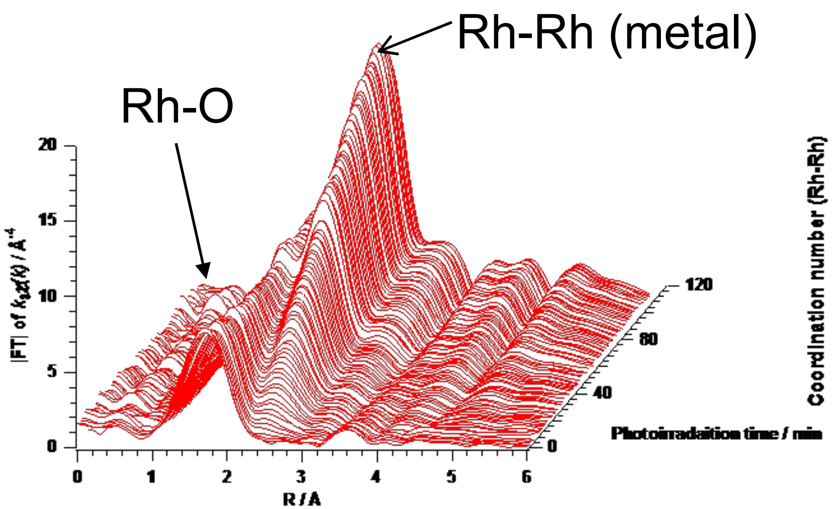
Direct observation of the behavior of Rh particles on a TiO_2 under photo irradiation by DXAFS

K. Teramura et al., J. Phys. Chem. C, **2008**, *112* (23), pp 8495–8498

Experiments and Results



report on BL28B2
-> poster C6



Series of the Fourier transforms of Rh-K edge EXAFS spectra

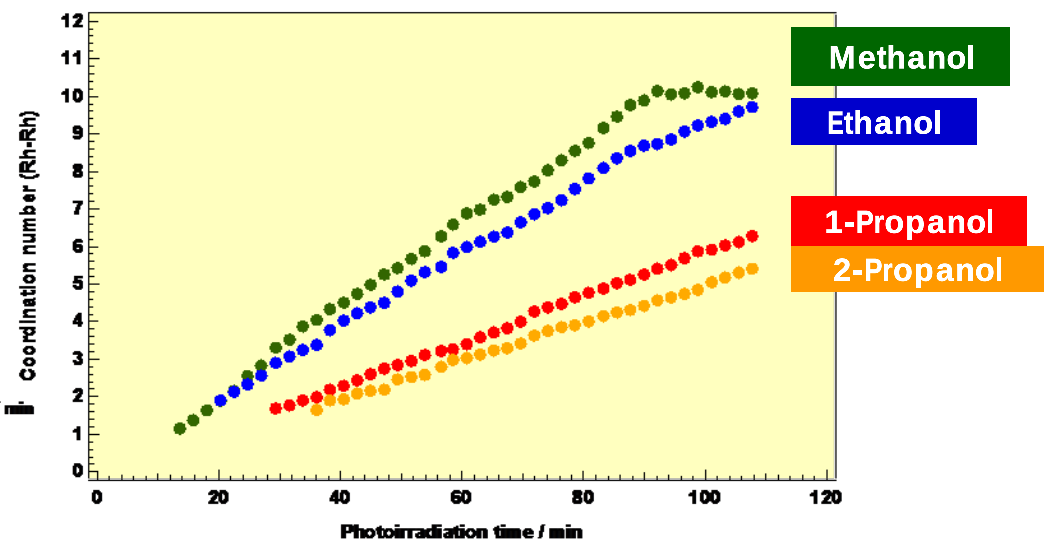


Photo-irradiation time dependence of the coordination number of the Rh-Rh bond at 2.45 Å of the Rh metal particles on the TiO_2

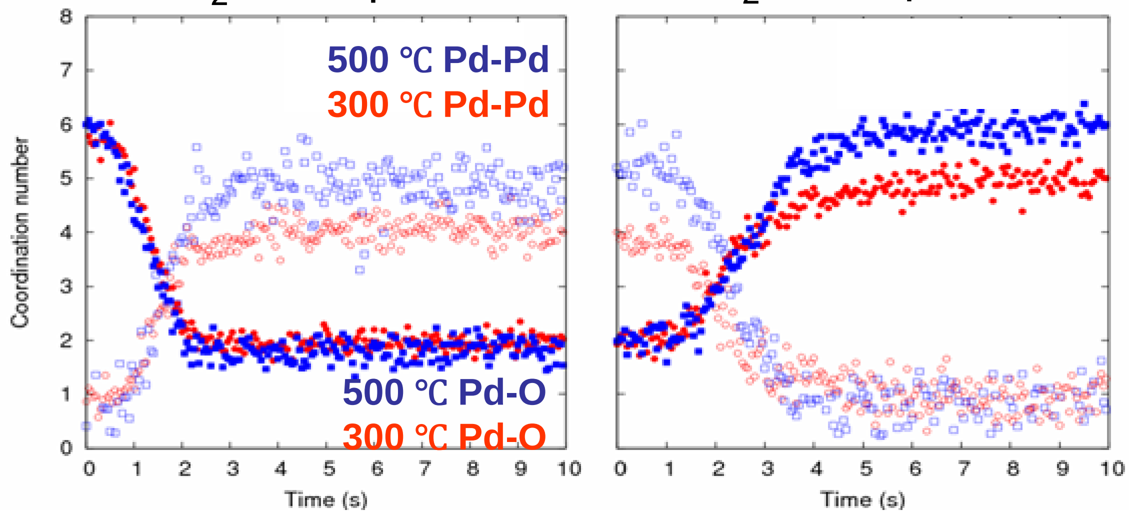
Reactions of intelligent automotive catalyst

SPring-8 BL14B1

CN plot from Pd K-edge XAFS

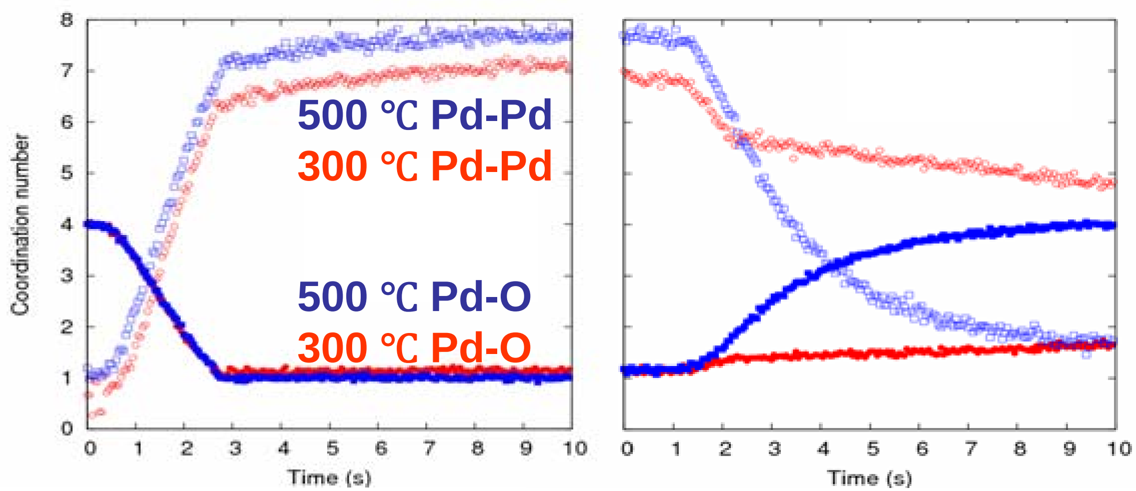
H_2 atmosphere　　　O_2 atmosphere

$Pd\text{-}LaFeO_3$



Fast change

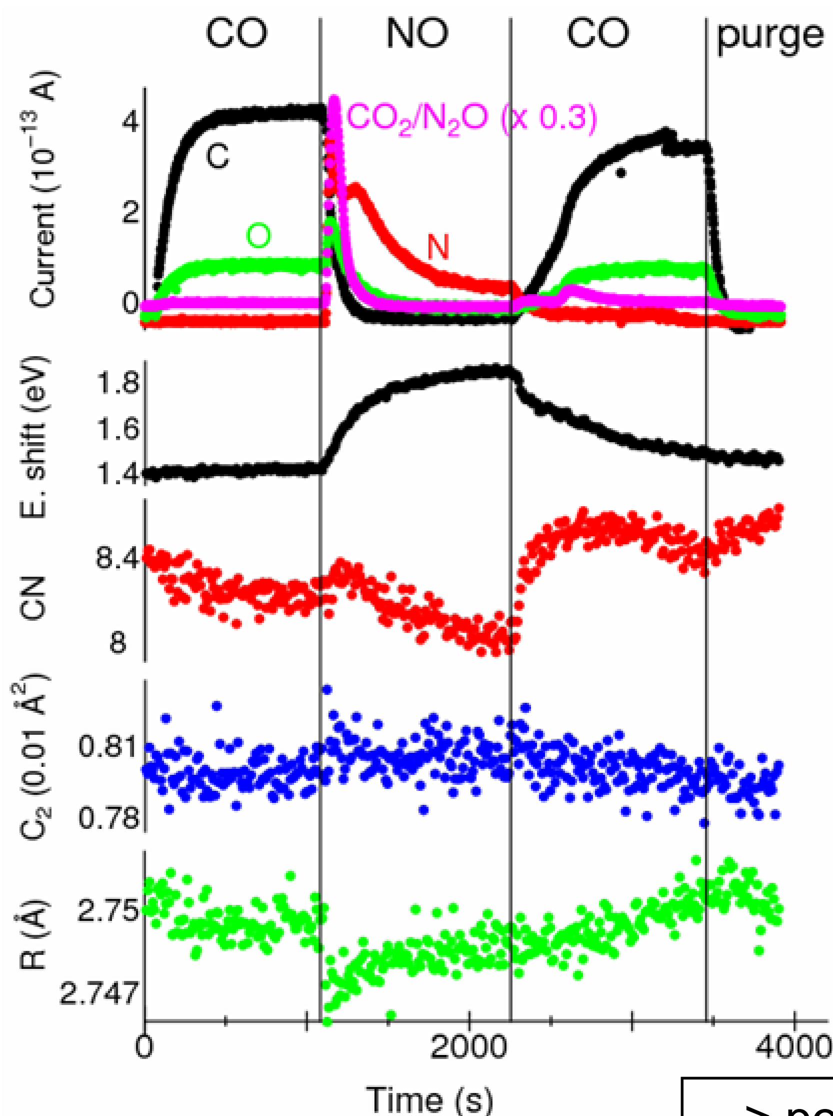
Pd/Al_2O_3



Slow change under O_2 atmosphere

Perovskite-type catalyst shows fast oxidation in spite of precious metal pre-reduced by CO then purged by He

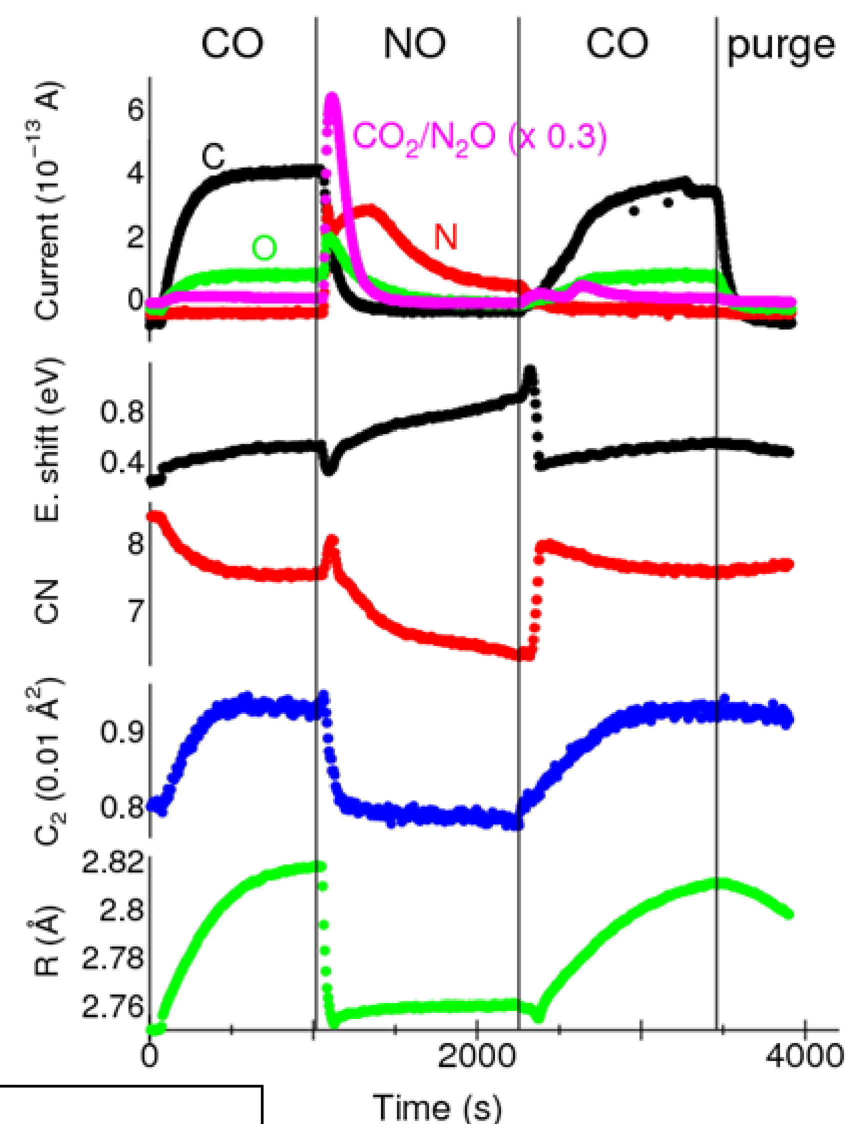
$Pd-LaFeO_3$



QMS

DXAFS

Pd (4 wt %)/Al_2O_3



-> poster C7

problems to be solved

- control the initiation of chemical reactions
  gas diffusion, stopped-flow
  fast measurement of *P*, *T*…
  laser pulse, micro-reactor, caged compounds…
- simultaneous measurement with other methods
- faster detection system

You can look ns-regime with μs interval soon

Coworkers

Photon Factory

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Univ. of Tokyo

Iwasawa Y., Shido T., Tada M., Yamaguchi A.

Univ. of Hokkaido

Asakura K., Koike Y.

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