XAFS構造解析の基礎

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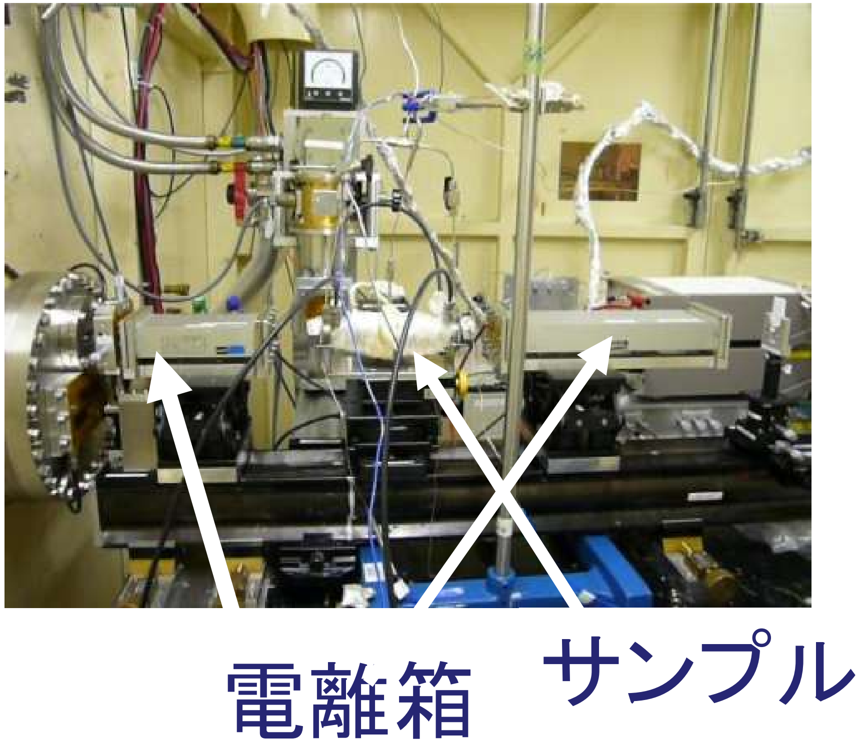
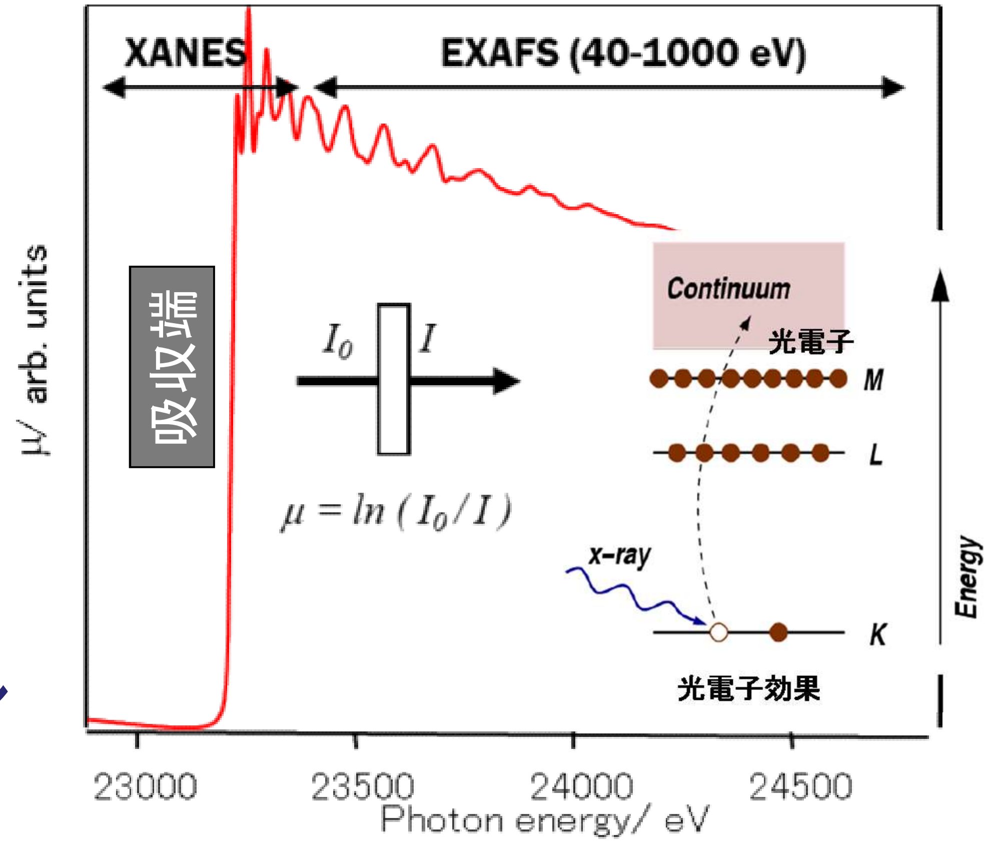
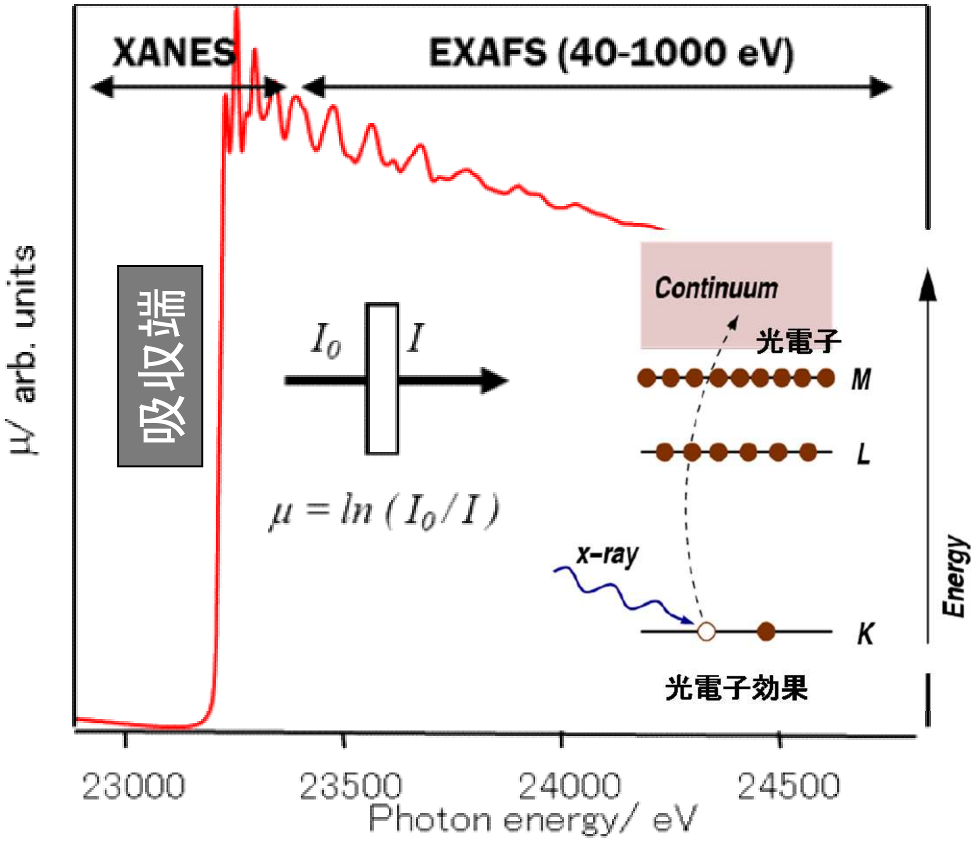
X-ray Absorption Fine Structure

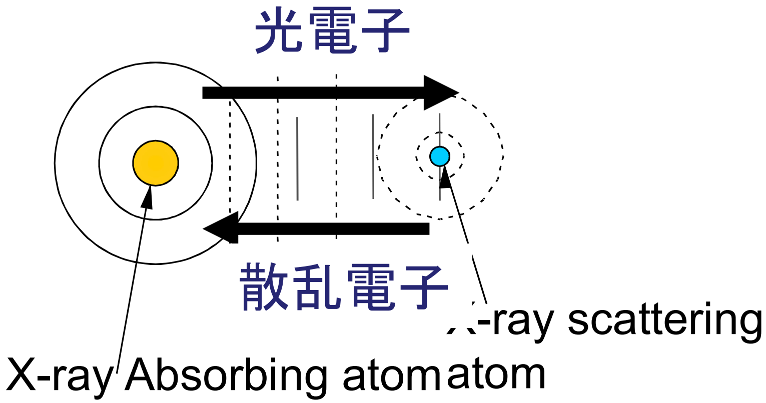




XANES（**X-ray Absorption Near Edge Structure)**
EXAFS（**Extended X-ray Absorption Fine Structure**）

X-ray Absorption Fine Structure





XANES（**X-ray Absorption Near Edge Structure)**
EXAFS（**Extended X-ray Absorption Fine Structure**）

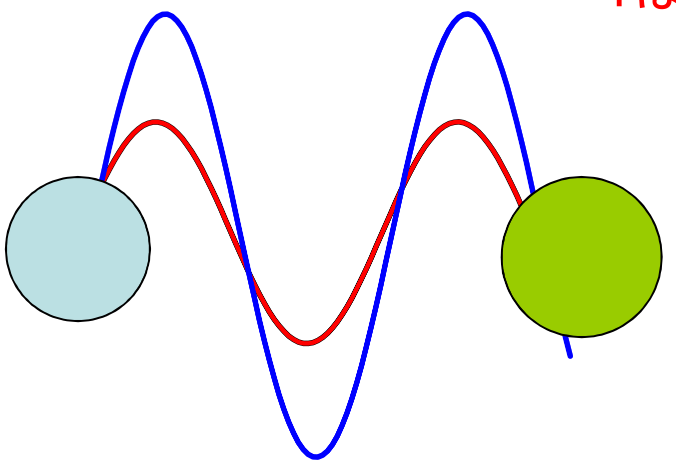
電子は波である。 -光電子と散乱電子の干渉

$$\frac{\hbar^2 k^2}{2m} = E - E_0$$

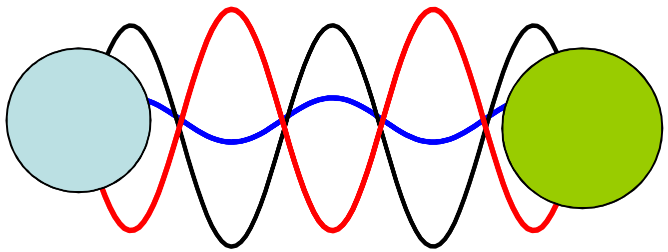
k: 光電子波数ベクトル
$\hbar$: プランク定数
E: 光子エネルギー　E_0: 束縛エネルギー

入射X線の変化に伴い波数が変化する ⇨ 強めあったり弱めあったり

$\sin(2kr)$で吸収が変化する
rは結合距離



強めあう



弱めあう

XAFSからわかること

配位数、結合距離、秩序因子

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} = \sum \frac{N_i F_i(K) e^{-2k^2\sigma_i^2} \sin(2kr_i + \phi(k))}{kr_i^2}$$

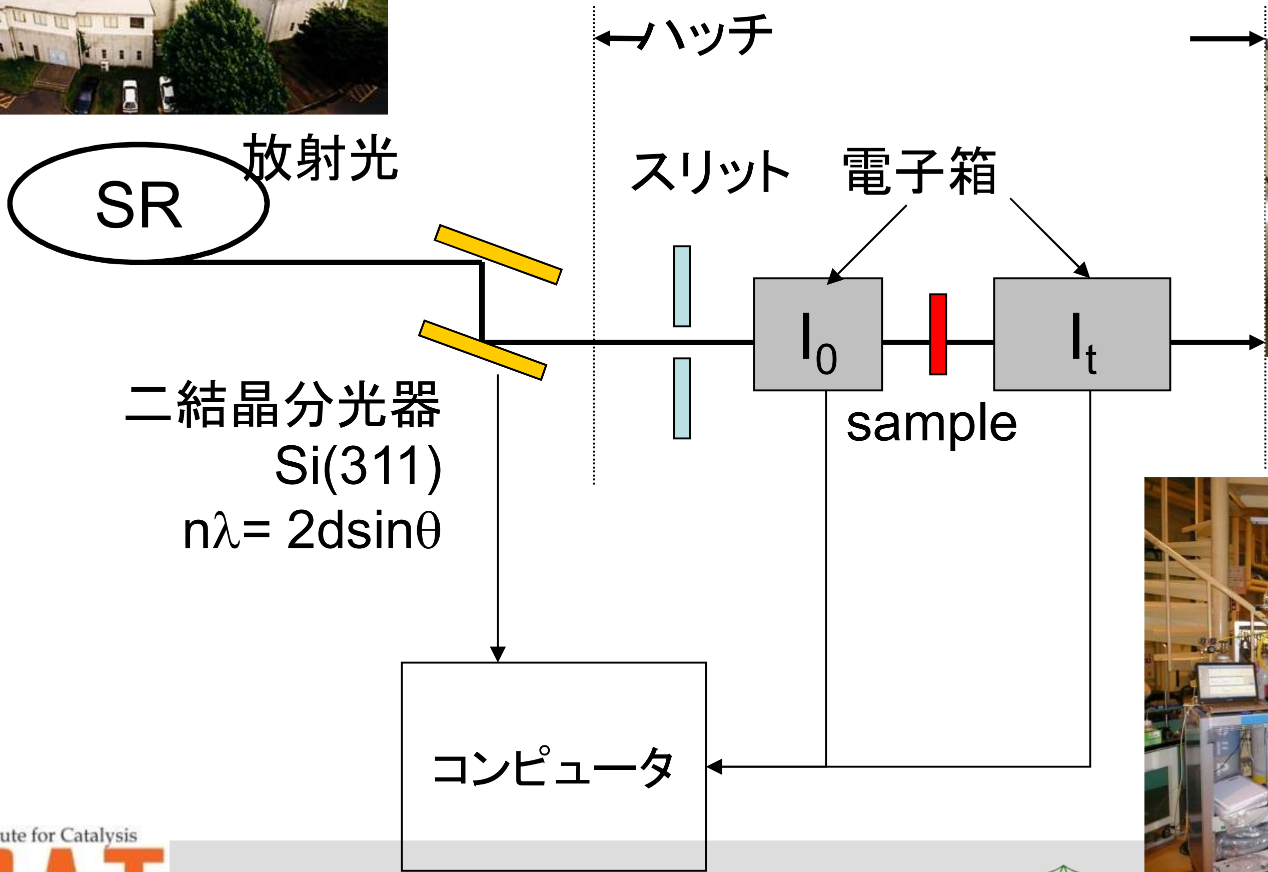
$F_i(k), \phi_i(k)$: 後方散乱因子、位相シフト

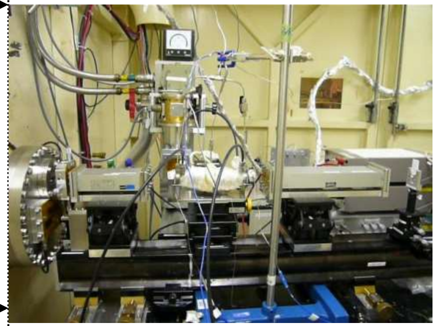
あらかじめ決めておく。

N_i, r_i, σ_i: 配位数、結合距離、秩序因子

実験

Beamline BL9C, KEK-PF





解析

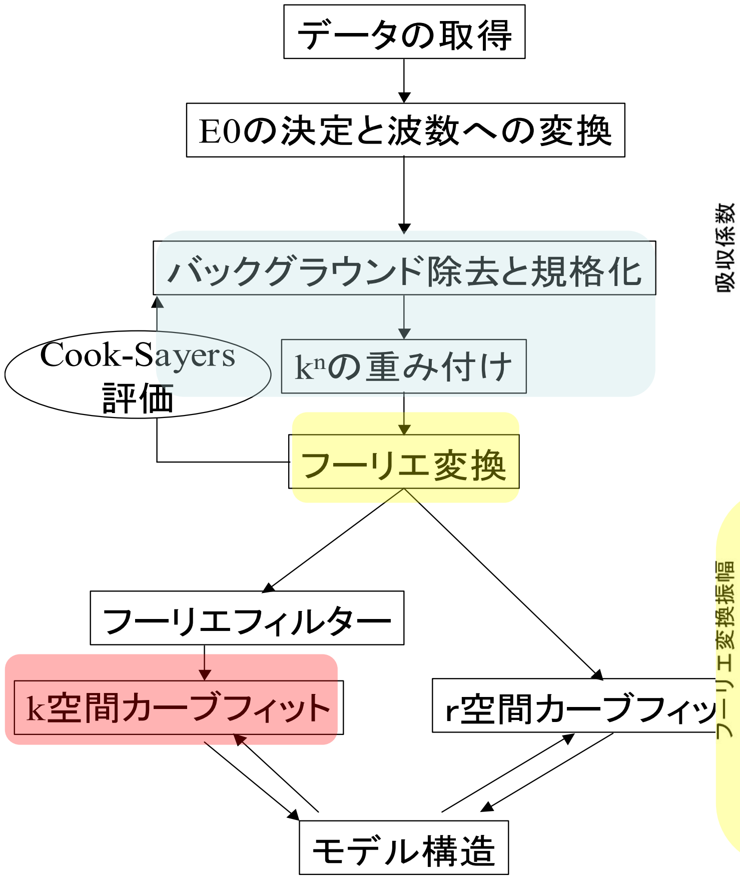
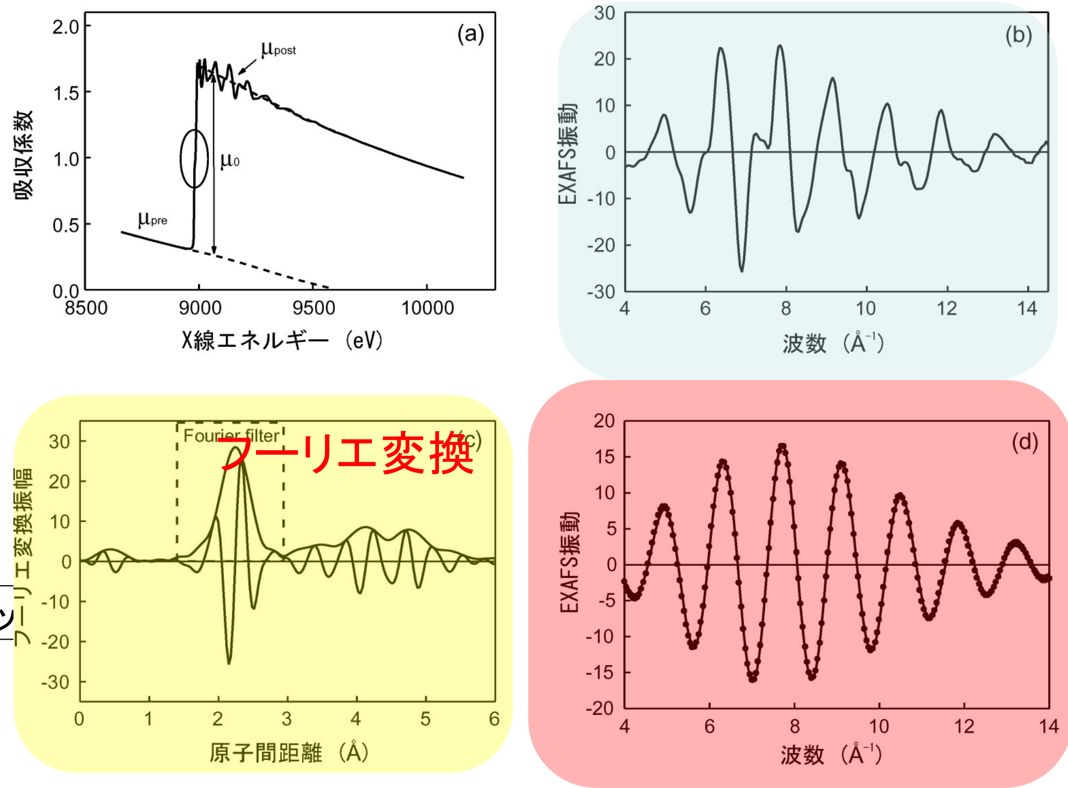


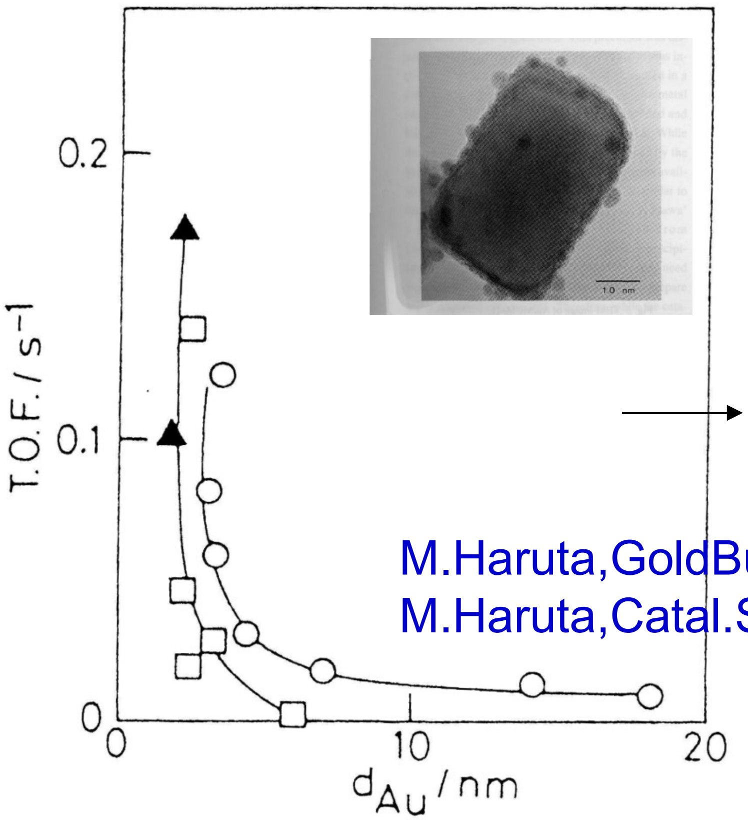
図3.1　EXAFS解析の流れ図

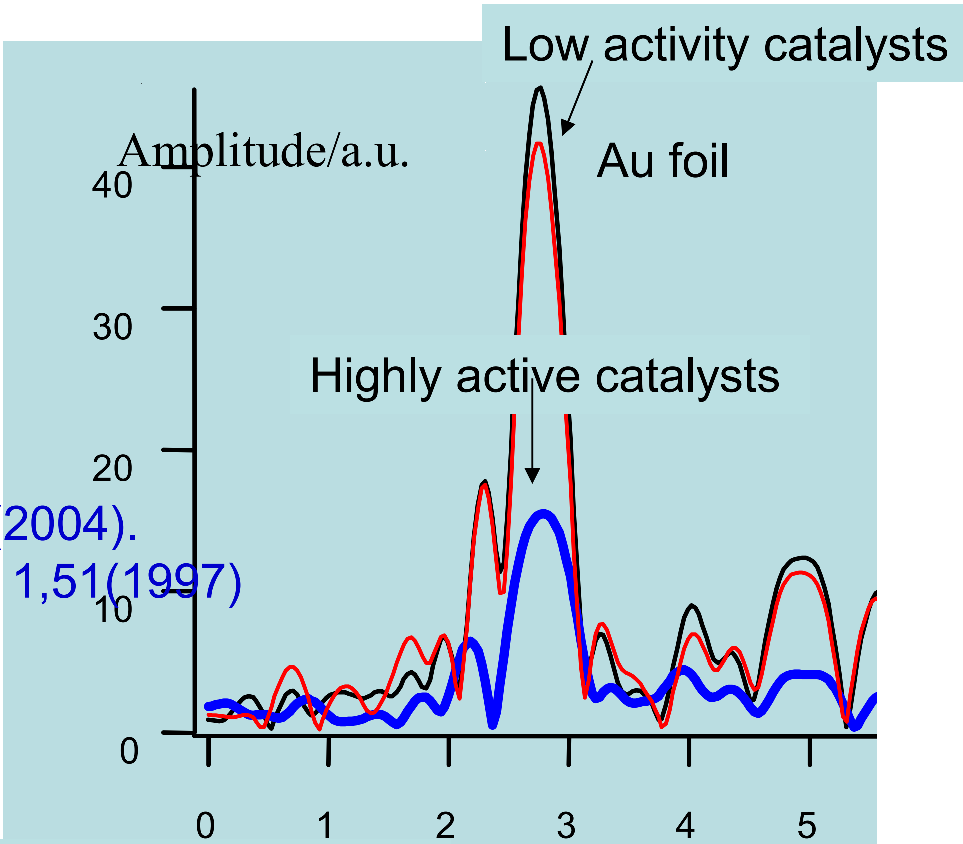


原子があれば、フーリエピークがある。

Supported nano Gold catalsyts = element seletive

High activity for CO oxidation at room temperature when it is in nanosize





M.Haruta,GoldBull.37,27(2004).
M.Haruta,Catal.Surv.Jpn, 1,51(1997)

EXAFS does not require long range order!!
Amorphous, liquid, Enzyme, powder

反応追跡ができる。

気相共存下での測定が可能

Operando

in-situ

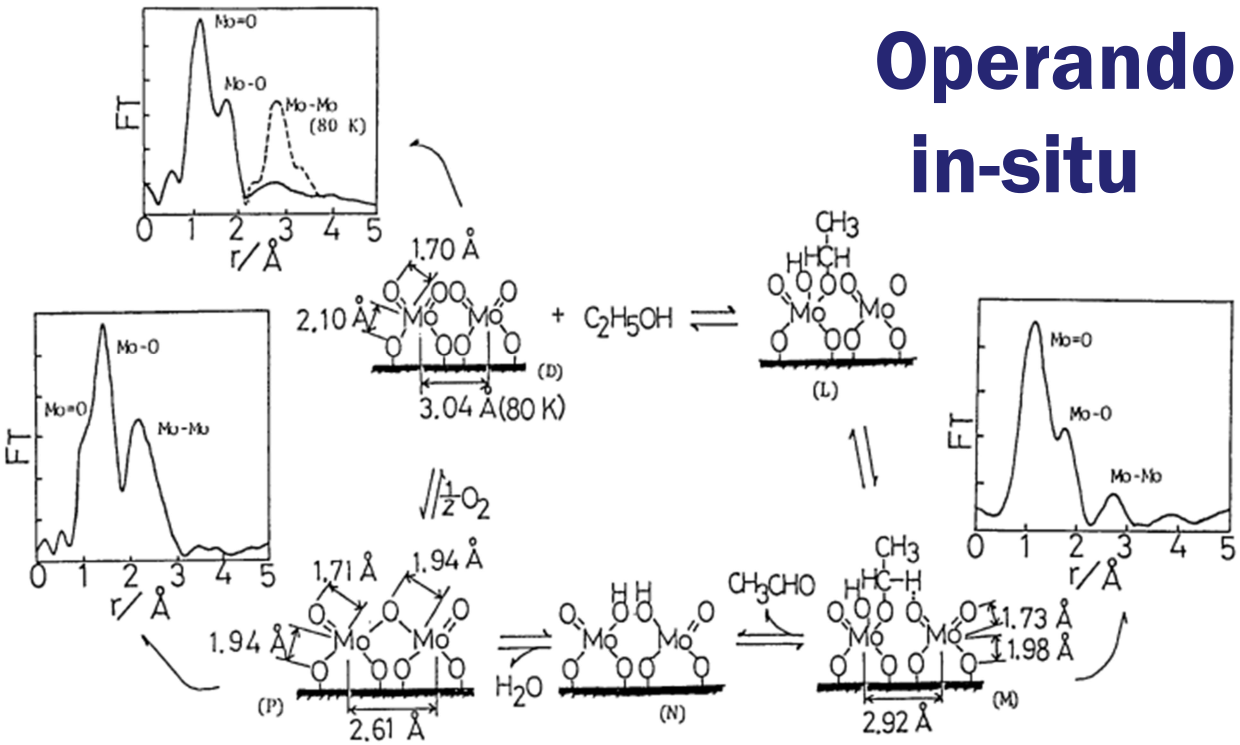
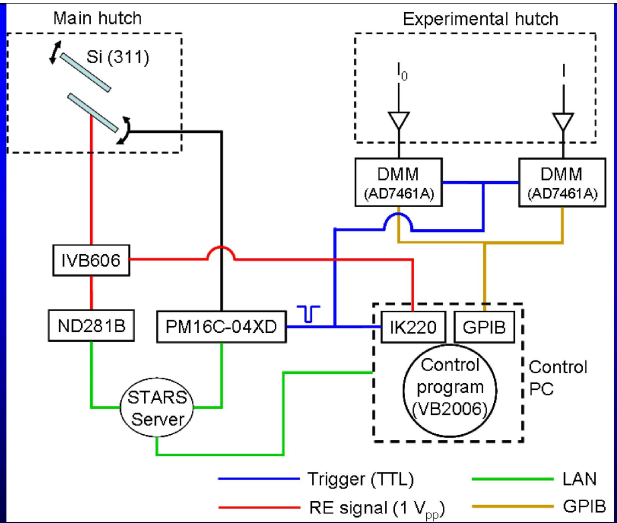
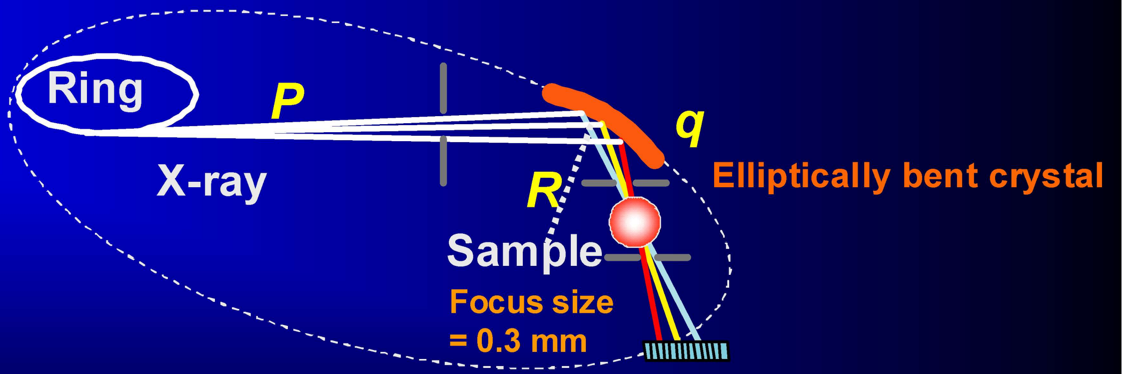


Fig.5. Reaction mechanism for the catalytic oxidation of ethanol and Fourier transforms of EXAFS spectra taken in the course of the reaction

時間分解XAFS測定

1. QXAFS Quick XAFS
2. DXAFS Dispersive XAFS

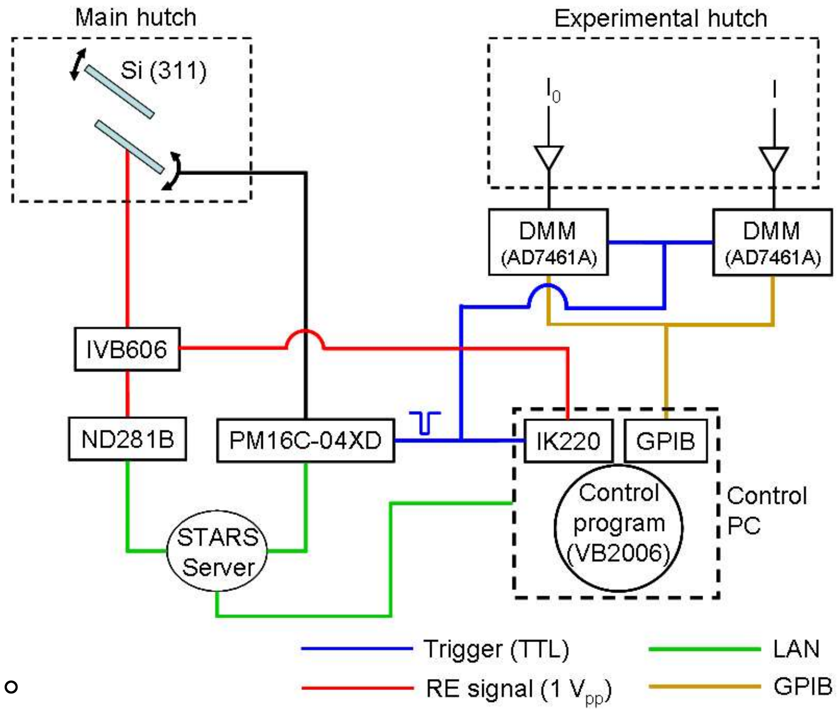




0.8

QXAFS

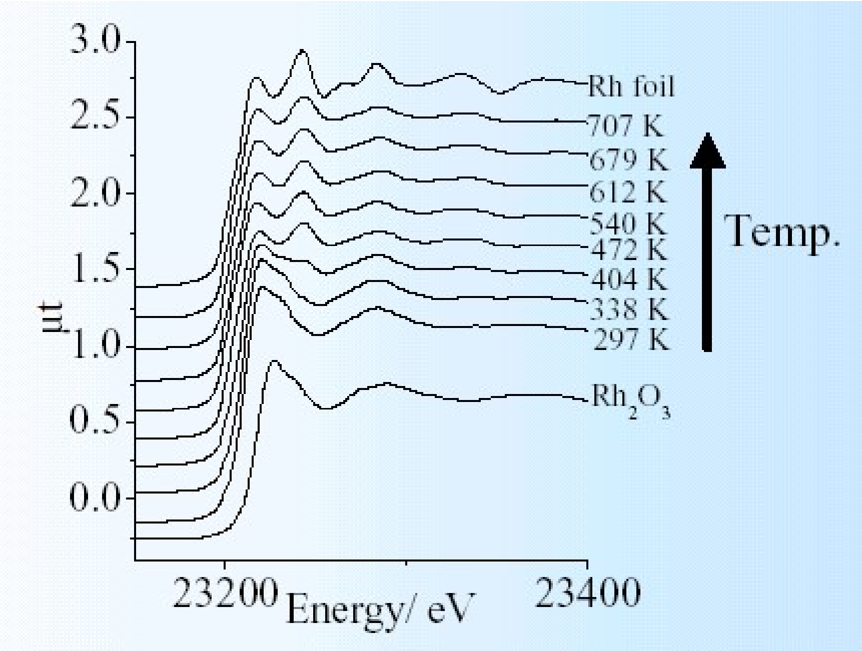
– 数分以下

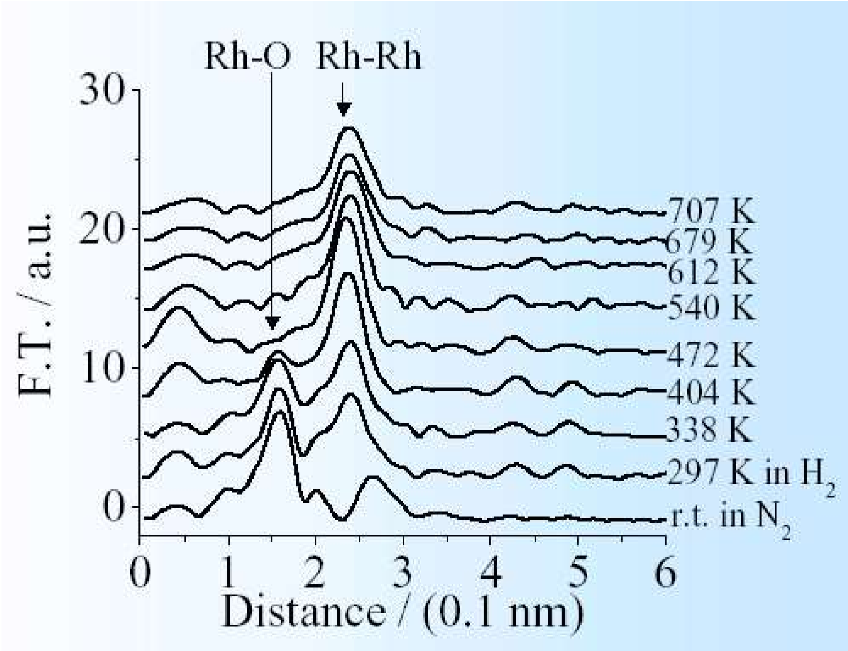


触媒科学研究所と**KEK**が共同して建設した。
科研費**S 2004-2009**

Reduction process of Rh

In-situ XAFS spectra observed during H_2 reduction



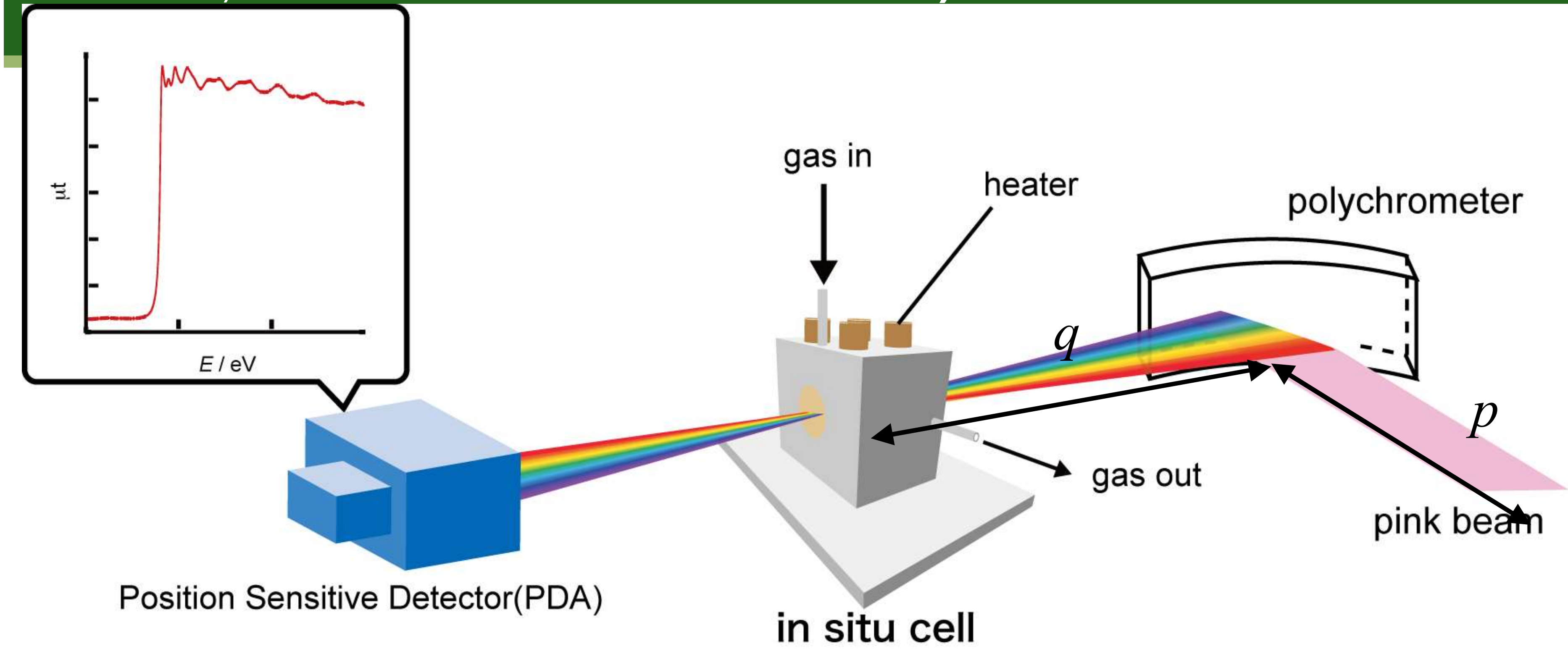


Flow rate :20 % H_2/Ar 100ml/min
Temperature rate: 7K/min

XANES : Oxidized Rh species → Rh metal
EXAFS : Rh-O → Rh-Rh

K. Bando et al. in-situ high pressure & high temperature XAFS

Dispersive XAFS@NW2A, Photon Factory(in the cortesy of Dr. Uemura, Prof Nomura and Prof Inada PF.)



p: **from source to polycrometer,** q: **from polycrometer to focal point**
R: **bent diameter of polycrometer**

- **A pink beam is dispersed by a polychrometer, which is a bent Si crystal.**

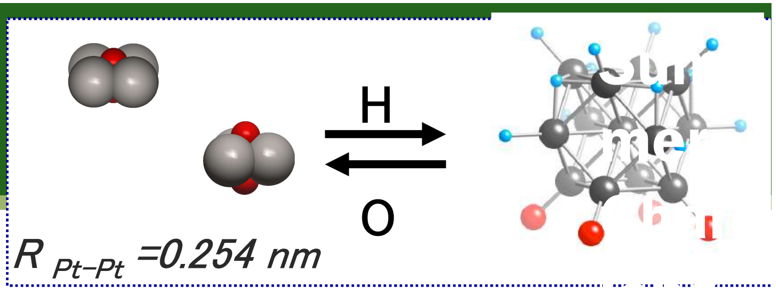
→ X-ray with several hundreds of eV can be obtained by using position sensitive detector.

→ A XAFS spectrum can be obtained simultaneously.

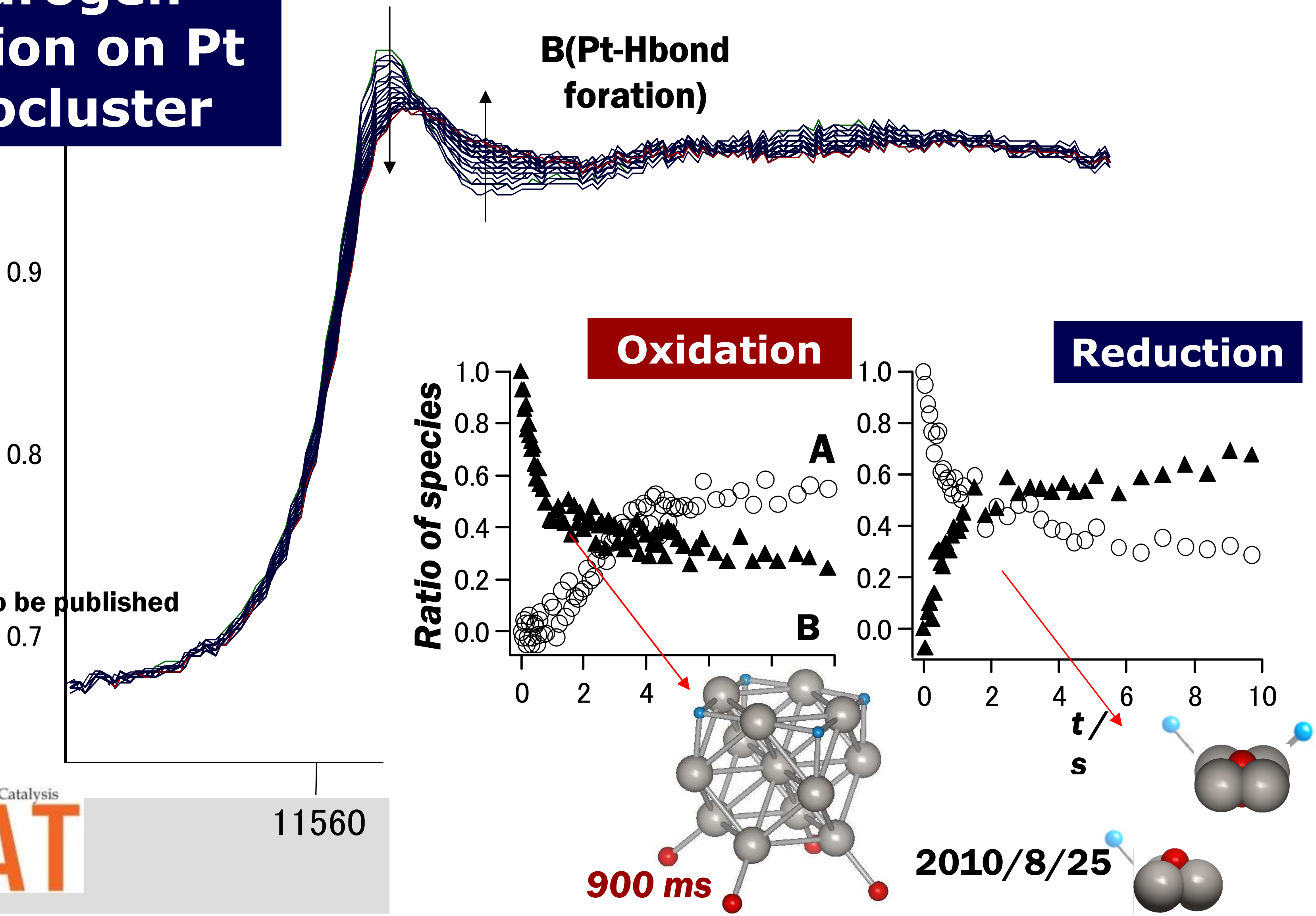
→ The minimum time resolution of the DXAFS system at Photon Factory is 2 ms.

Typical time resolution for in situ XAFS experiments is between several tens and hundreds of milliseconds.

Reversible Reaction Process of Pt followed by DXAFS



Hydrogen reaction on Pt nanocluster



A.Suzuki, to be published

2010/8/25

Institute for Catalysis ICAT

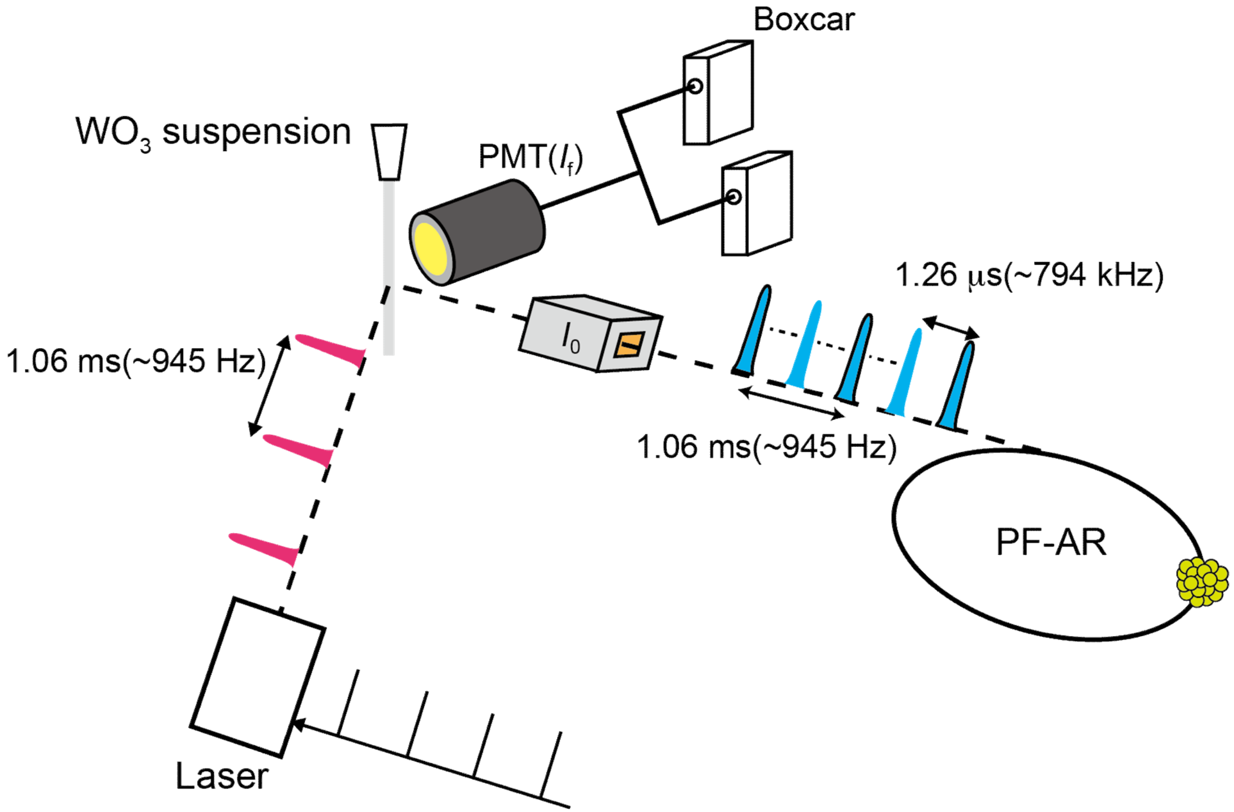
もっともっと早く
Pump Probe XAFS

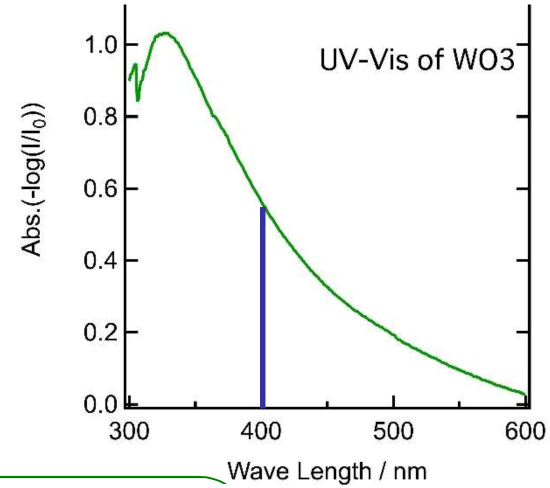
Honda-Fujishima effect

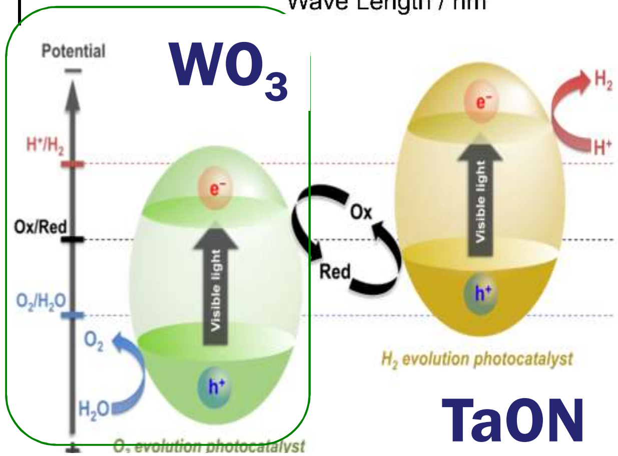
⇓

可視光応答型光触媒

Sample: 0.6 mM WO_3 suspension
pump laser: 400 nm 270 mJ/cm^2@945 Hz
X-ray pulse width: 100 ps(FWHM)







R. Abe, et. al. *J. Am. Chem. Soc.* **2008, 130, 7780-7781**

through two-step photoexcitaion

Institute for Catalysis

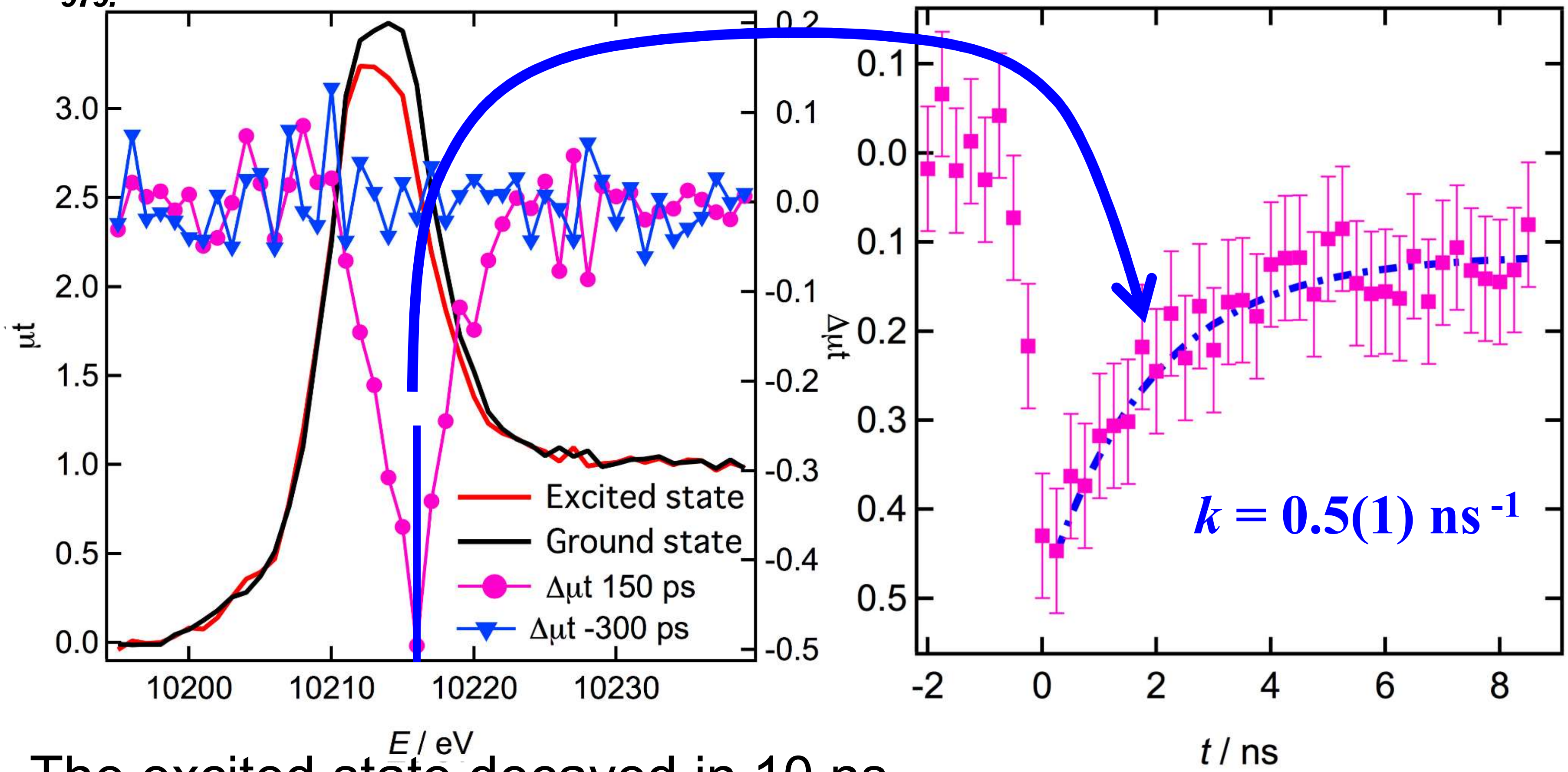
J. Synchrotron Radiat. 2007, 14, 313.
J. Synchrotron Radiat. 2009, 16, 110.

NEDO 燃料電池プロジェクト

HOKKAIDO UNIVERSITY

Photoexcited State of WO_3 : L_{III} XANES at PF-AR
Single bunch operation

1. Uemura, Y.; Uehara, H.; Niwa, Y.; Nozawa, S.; Sato, T.; Adachi, S.; Ohtani, B.; Takakusagi, S.; Asakura, K., In Situ Picosecond Xafs Study of an Excited State of Tungsten Oxide. *Chem. Lett. 2014, 43 977-979.*

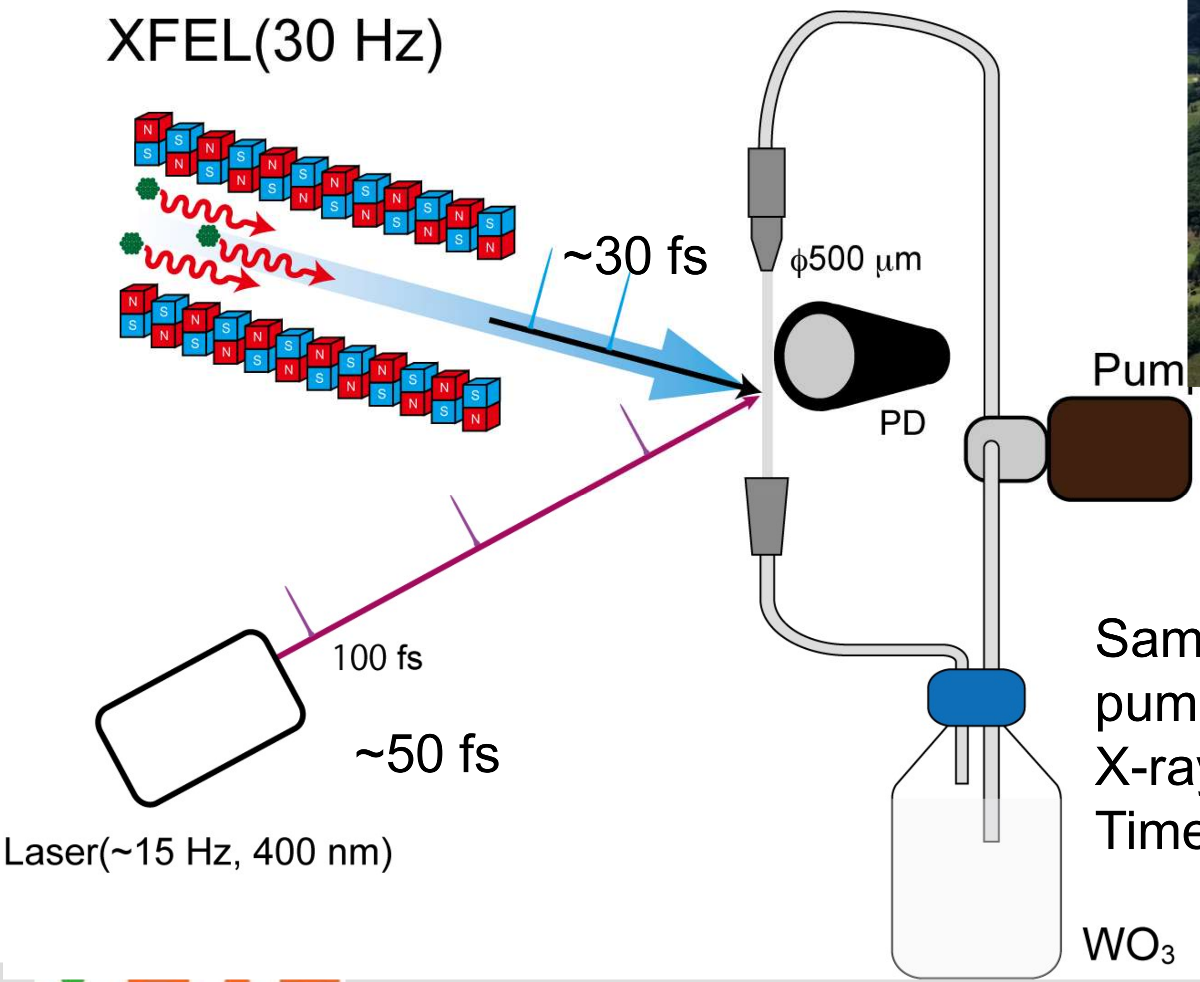


The excited state decayed in 10 ns.

→It was successfully fitted with a single exponential function.

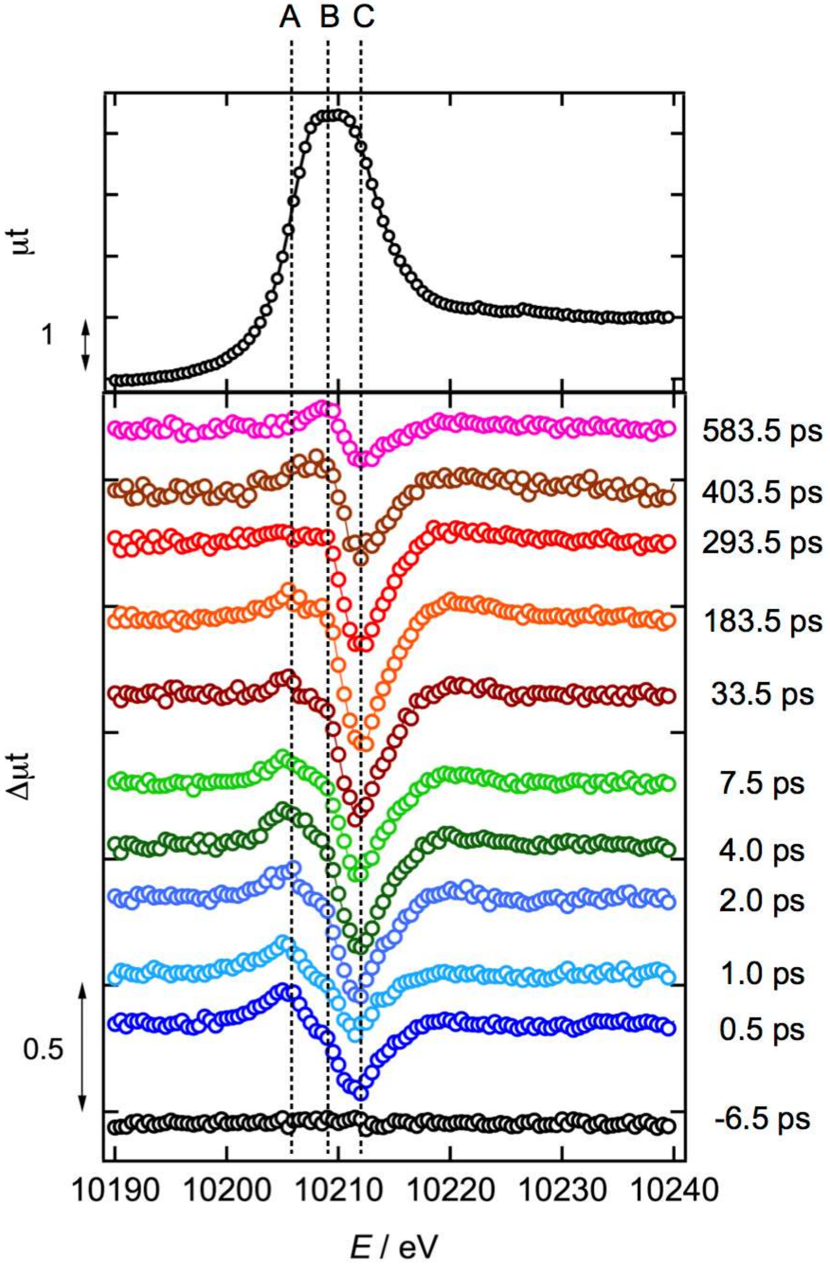
Pump probe XAFS at SACLA(X線自由電子レーザ;XFEL）

Experiments at SACLA



Sample: 4 mM WO_3 suspension
pump laser: 520 mJ/cm^2@15 Hz
X-ray pulse width: 30 fs(FWHM)
Time resolution: 500 fs

光吸収過程におけるW03の超高速XAFS



➡ Three distinct peaks were found in the differential spectra.

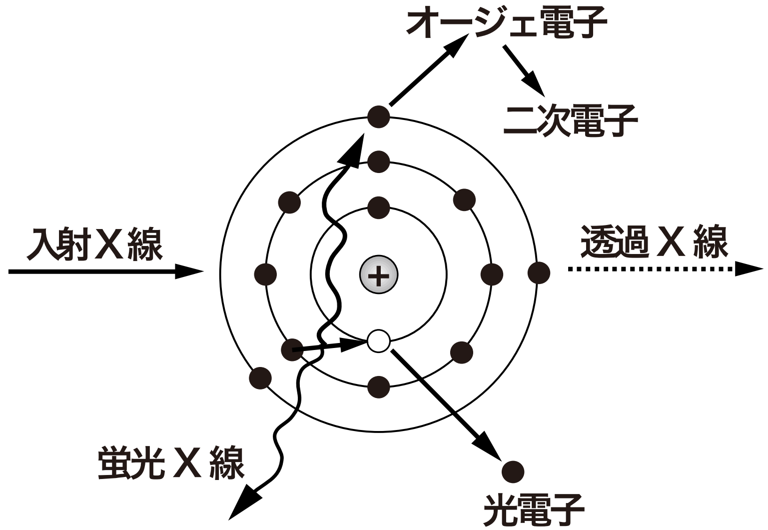
peak A : Edge shift due to formation of W^{5+} < 1 ps
peak C : decrease of absorption from e_g orbitals ~ 200 ps

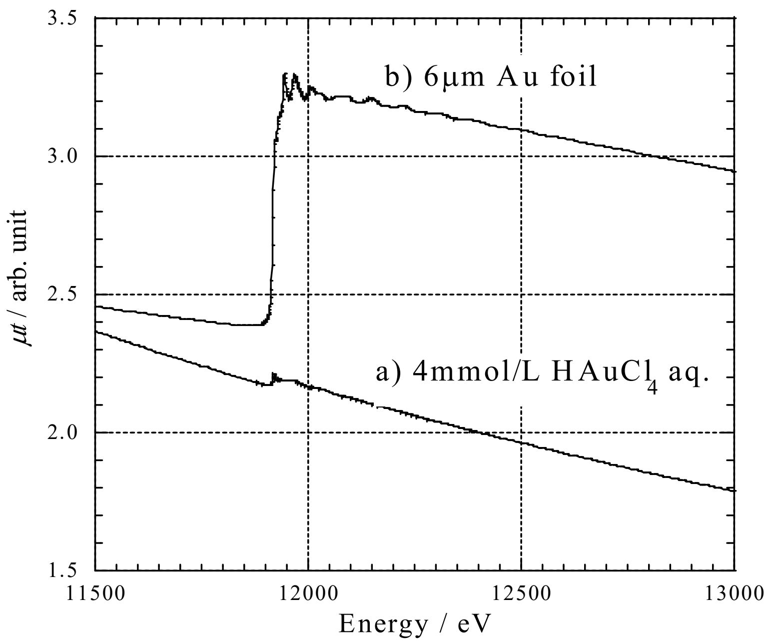
⬇

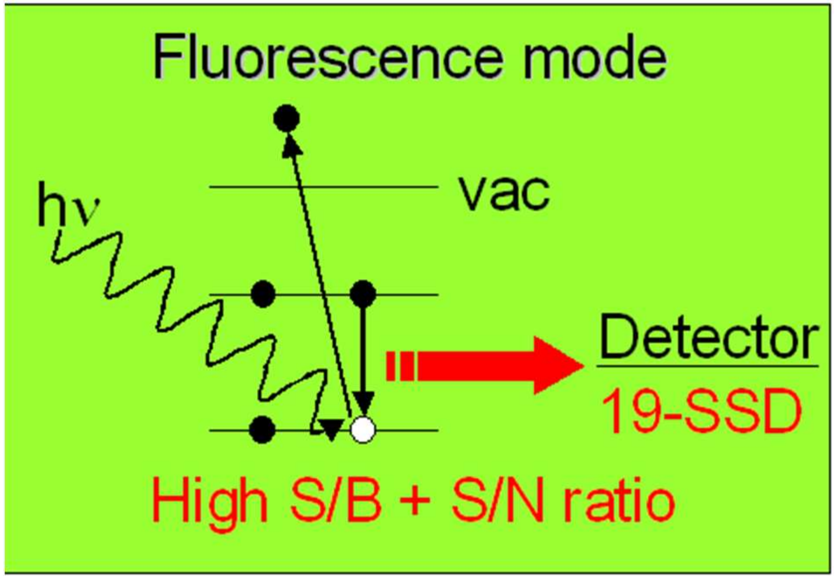
peak B which was not found in the previous experiments was observed.

Uemura, Y., et al., Dynamics of Photoelectrons and Structural Changes of Tungsten Trioxide Observed by Femtosecond Transient Xafs. *Angew. Chem.Int.Ed* ***in press***

蛍光検出＝低濃度が可能.



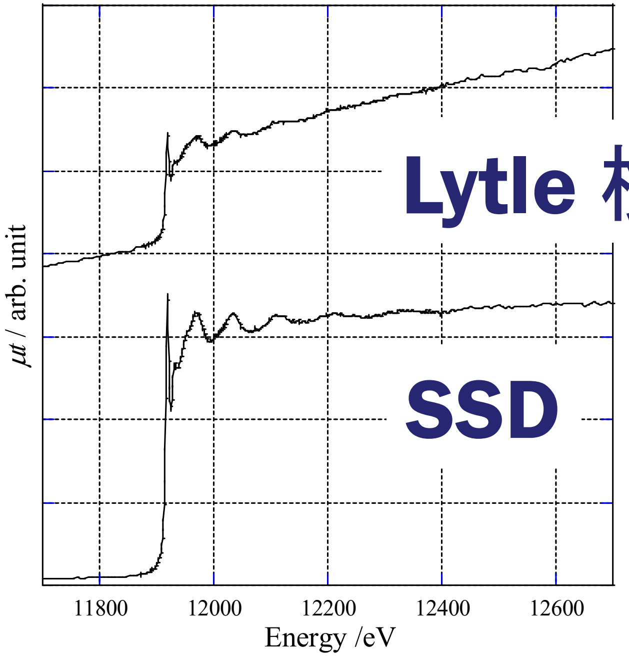




透過**XAFS**ではみたい原子以外の吸収で、原子が隠される.

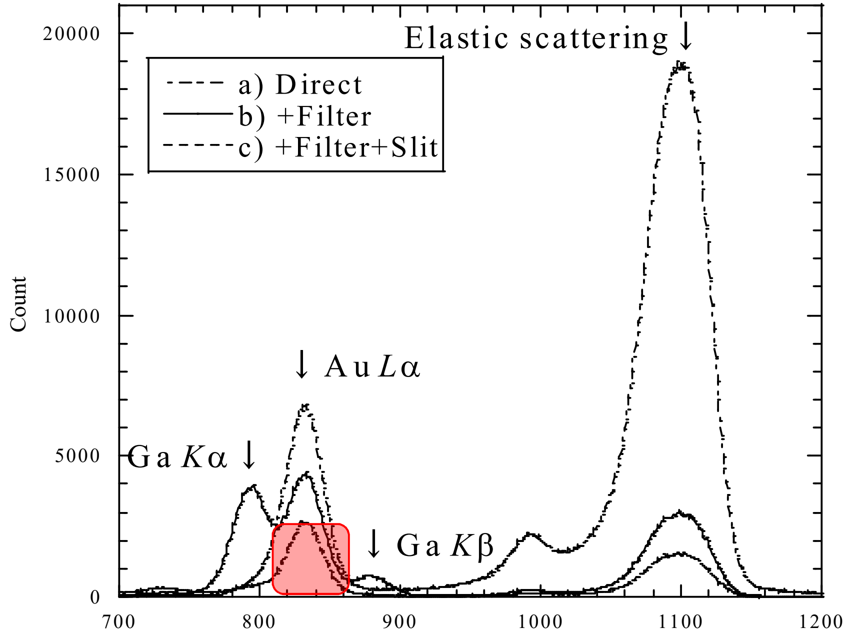
みたい原子からその元素特有の蛍光**X**線をだす.

蛍光検出と透過法　希薄であること･薄膜であること



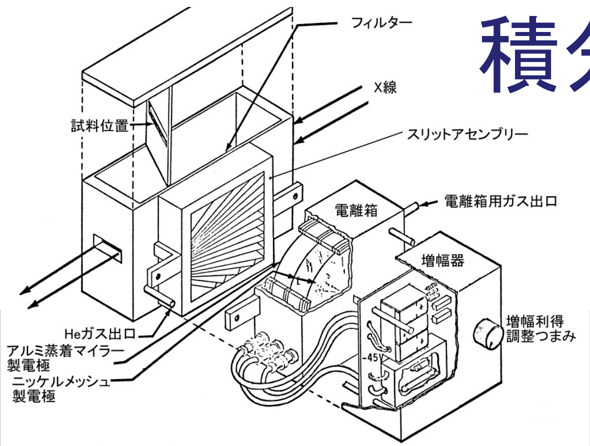
Lytle 検出器

SSD



X線のエネルギー

Lytle 検出器



積分型

SSD

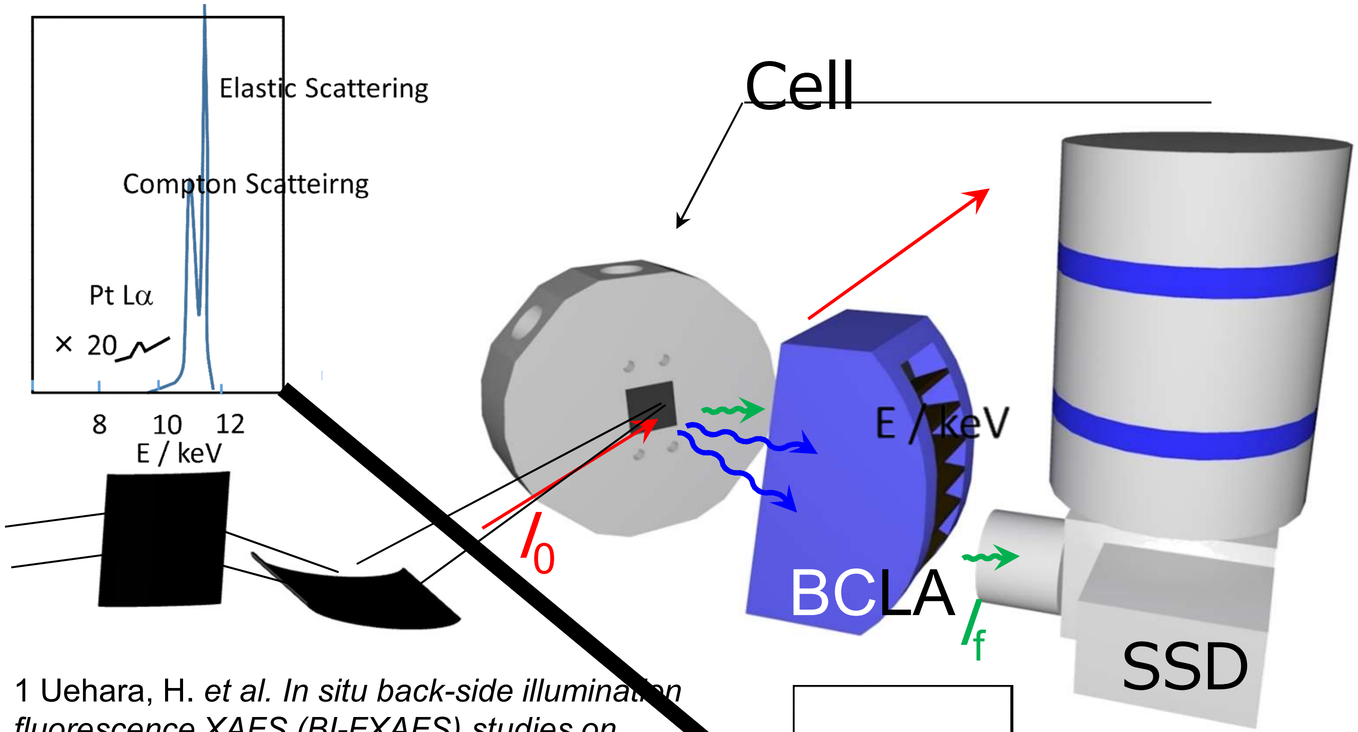
パルスカウント

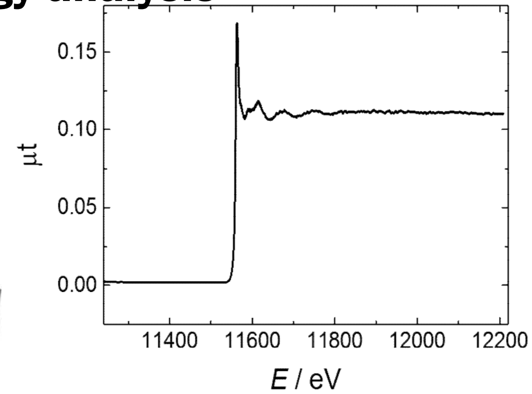
透過法　>0.5wt%
Lytle　100 ppm
SSD　<100ppm

結晶分光蛍光X線XAFS（超高感度XAFS）

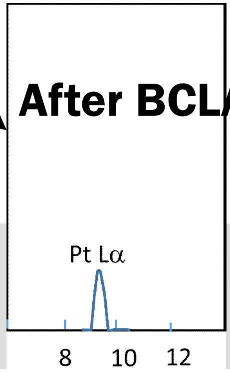
Remove the bulk elastic scattering by Energy analysis

BCLA Bent Crystal Laue Analyser

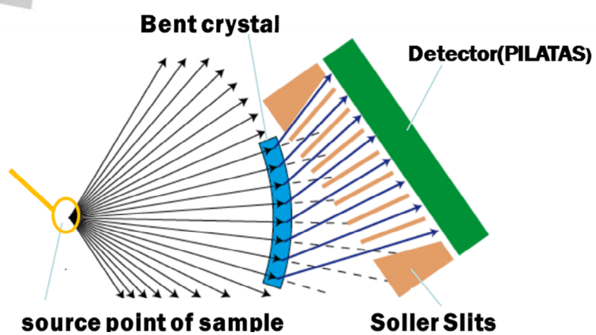




5× 10^{14} cm^{-2} Pt on HOPG(Highly oriented pyrolytic graphite)



1 Uehara, H. *et al. In situ back-side illumination fluorescence XAFS (BI-FXAFS) studies on platinum nanoparticles deposited on a HOPG surface as a model fuel cell: a new approach to the Pt-HOPG electrode/electrolyte interface. Phys Chem Chem Phys* ***16, 13748-13754, doi:10.1039/c4cp00265b (2014).***



Possibility of MARX-RAMAN （top secrets）

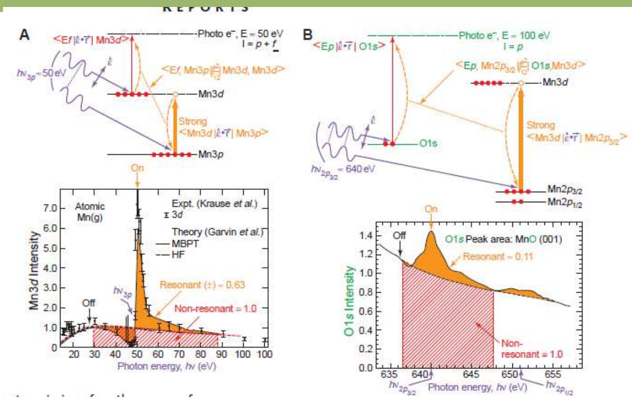
1. **XAFS を結合選択的にしよう。**

   数あるカーボンの中で、隣にあるカーボンを見る。

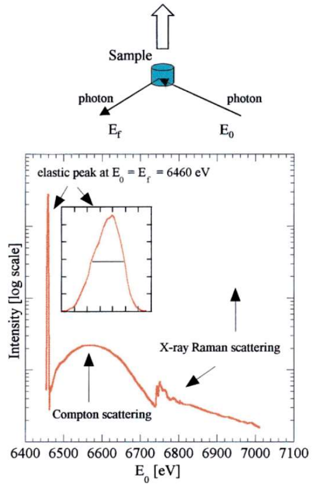
   MARPE(Multi atom resonant Photoemision)

2. **軽元素をinsituでとろう。**

   X-ray Raman



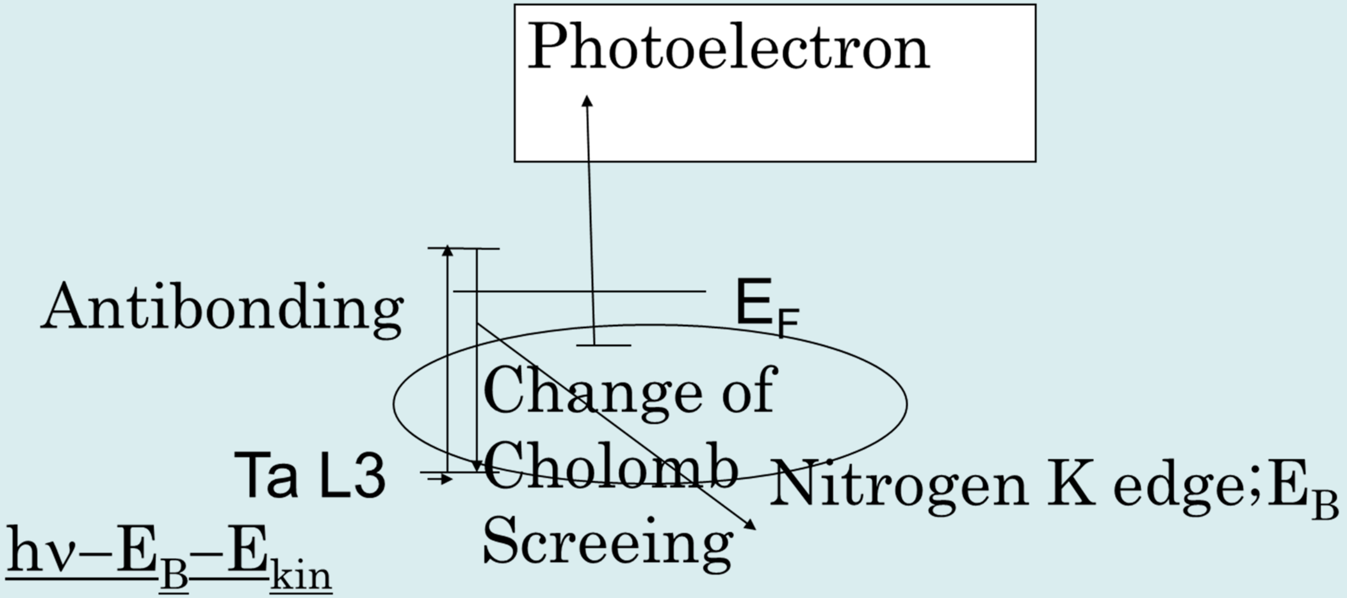
. **(A. Kay, C.S. Fadley, RMultiatom resonant photoemission: a method for determining near-neighbor atomic identities and bonding. Science. 281,679(1998).)**



(K. Tohji, Y. Udagawa, Physical Review B 1987, 36, 9410-9412.)

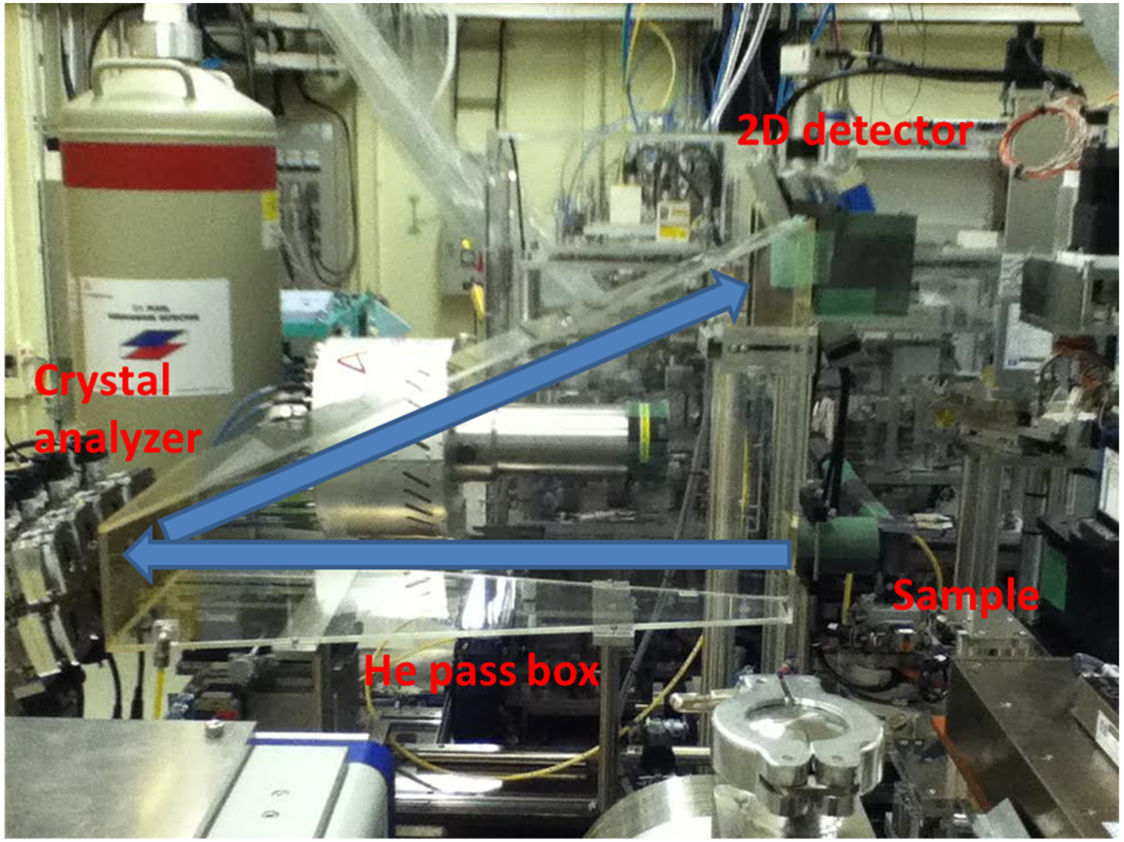
MARX Raman: Multi-Atom Resonace X-ray Raman

MARX-RAMAN(Multi atom resonance X-ray Raman Bond seletive)



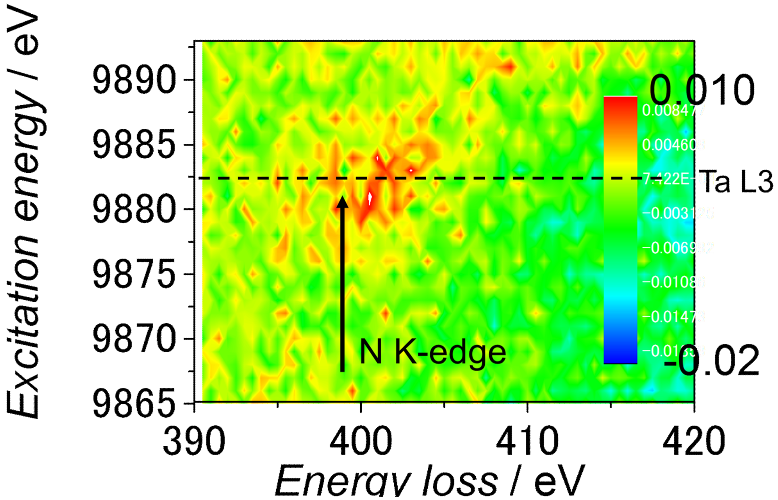
Principle of MARX-RAMAN
(Multi atom resonance X-ray Raman)

Experimental setup

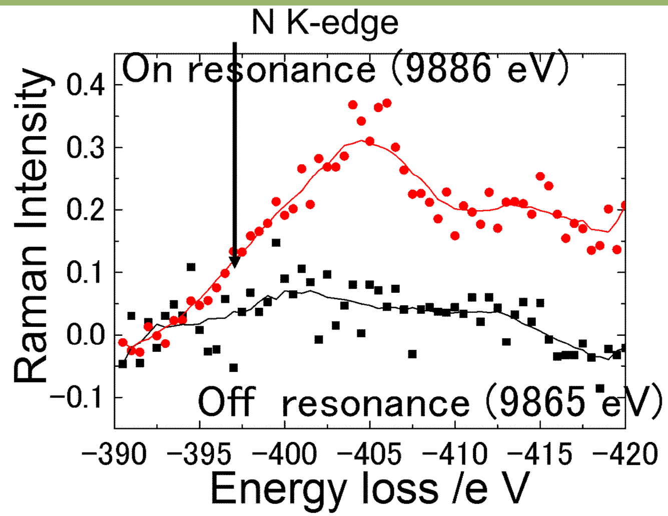


MARX-RAMAN(Multi atom resonance X-ray Raman Setup at BL36XU SPring-8)

MARX-RAMAN of TaN.



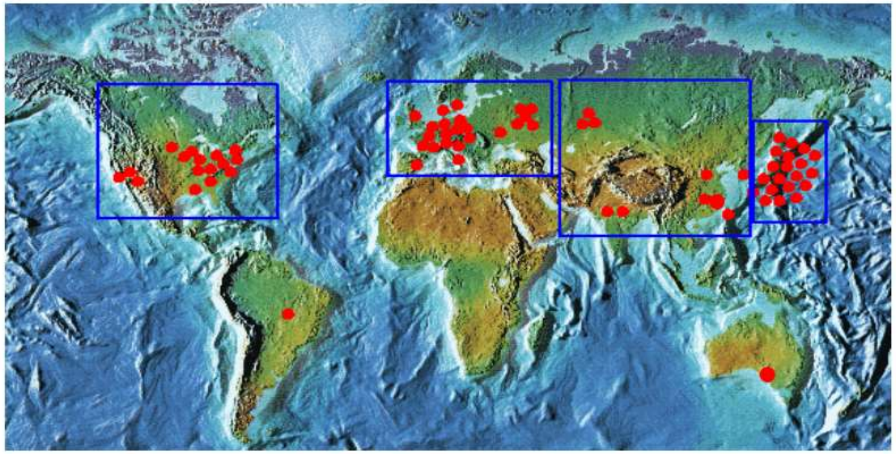
3D mapping of emission intensity dependence on
Exciation energy and Energy loss

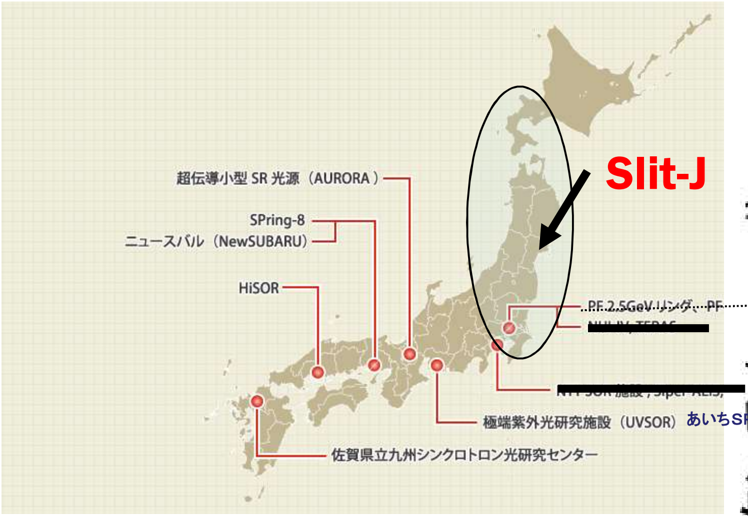


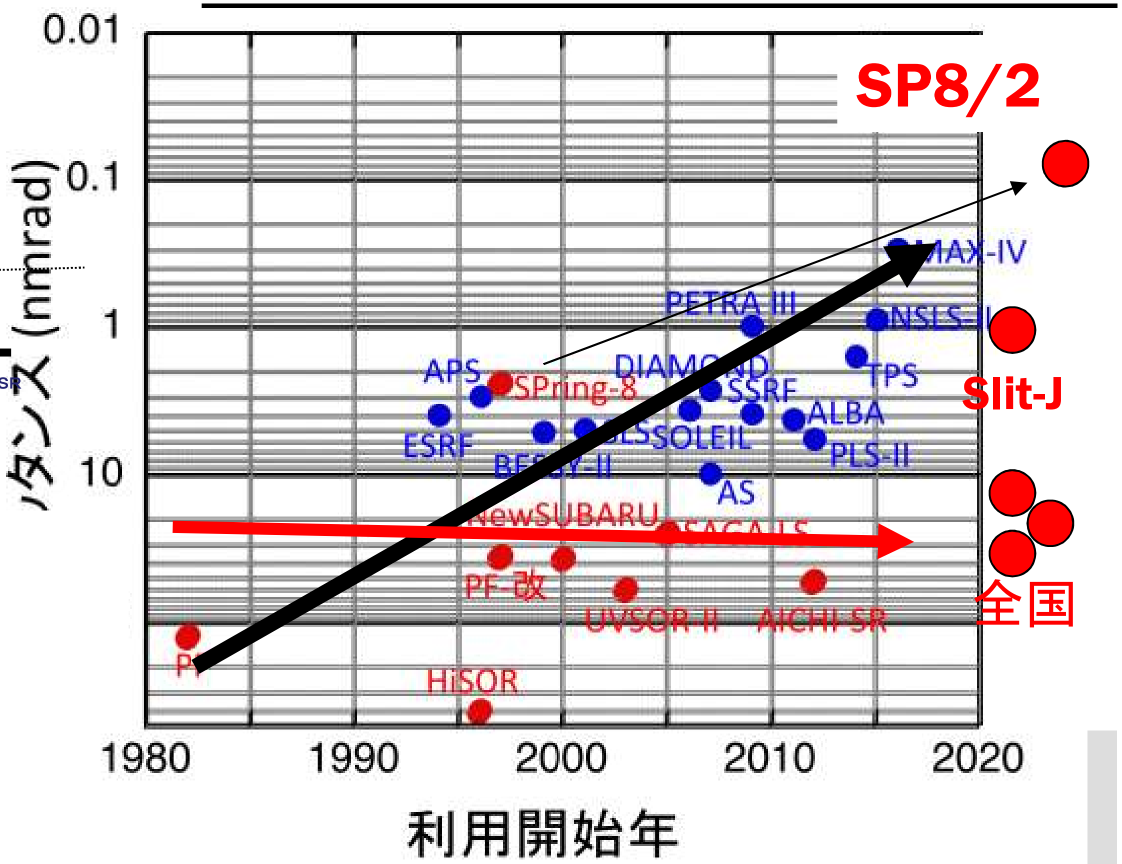
Energy loss spectra with different excitation energy.

日本の放射光の将来は明るいか?
物質構造研究に必要

放射光施設の世界的な現状







東日本（関東およびその以北）

< 1nm rad ＜2020以前に

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ICAT