超高分解能軟X線発光分光装置の性能と利用研究

東大院工　原田慈久

SPring-8 BL07LSU HORNET station

2009.10 コミッショニング
2010.7　分解能E/ΔE>5000
2010.12 分解能E/ΔE>10000 (N 1s)
2011.1~ ユーザー実験（G課題）開始

Acknowledgments

Applied Chemistry, University of Tokyo

M. Kobayashi, H. Niwa, M. Saito, Y. Hiraike, H. Kiuchi and M. Oshima

Japan Synchrotron Radiation Research Institute (JASRI)

Y. Senba, H. Ohashi, H. Kishimoto and T. Miura

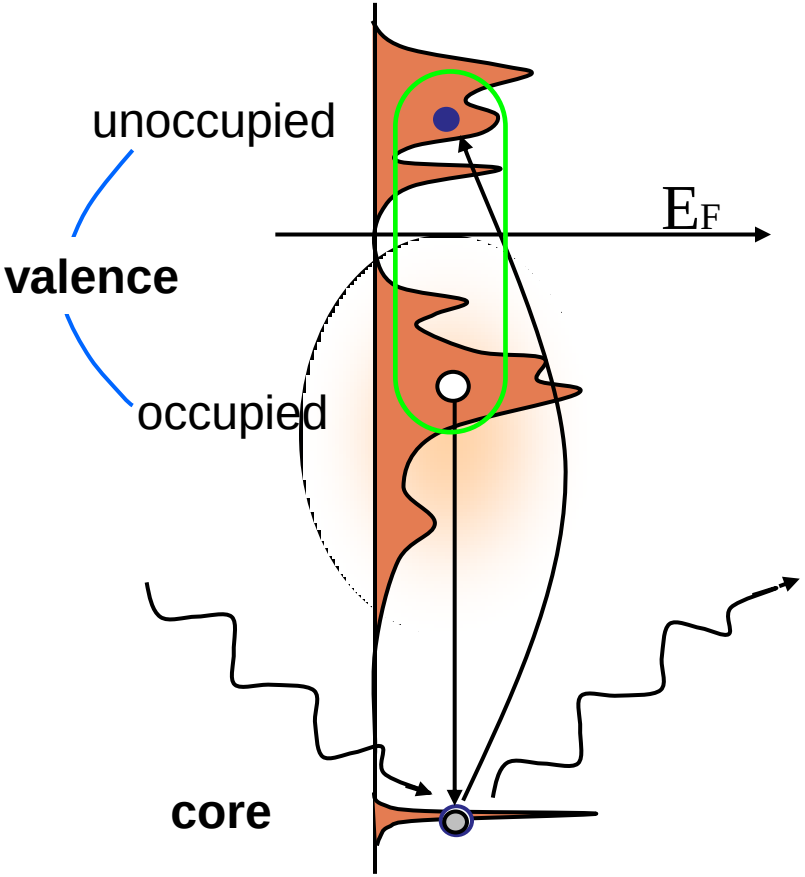
RIKEN/SPring-8

Y. Horikawa, T. Tokushima and S. Shin

Budget

NEDO & CREST

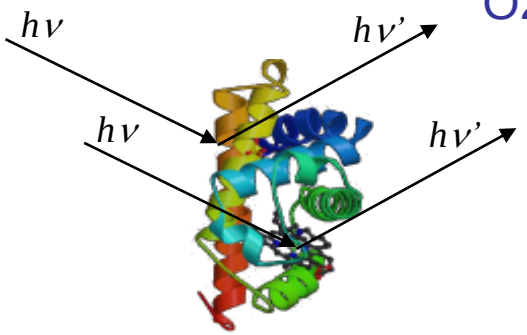
Observation of the electronic structure by SXES



Valence DOS (fluorescence)

Valence excitation（RSXES）

Element-specific
dipole-forbidden transition
ex) *dd*, *ff*-excitation etc..



O2*p*, N2*p*, C2*p* DOS

Fe 3*d* DOS
Fe *dd* excitation

Two-step process

$$I_{XES}(h\nu\sigma, h\nu'\sigma') \propto \sum_m |< i \mid T \mid m >< m \mid T' \mid f >|^2$$

Trends in SXES

X-ray fuorescence spectroscopy
(element analysis)

High resolution experiments
(element specific DOS analysis)

Resonant effects
(symmetry analysis, band dispersion, ultrafast dynamics)

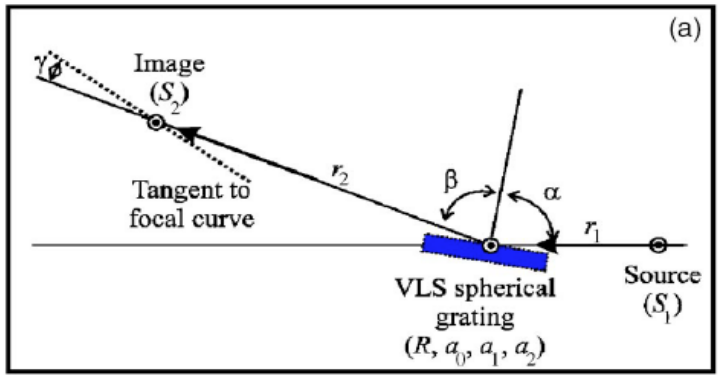
Ultra high
energy resolution

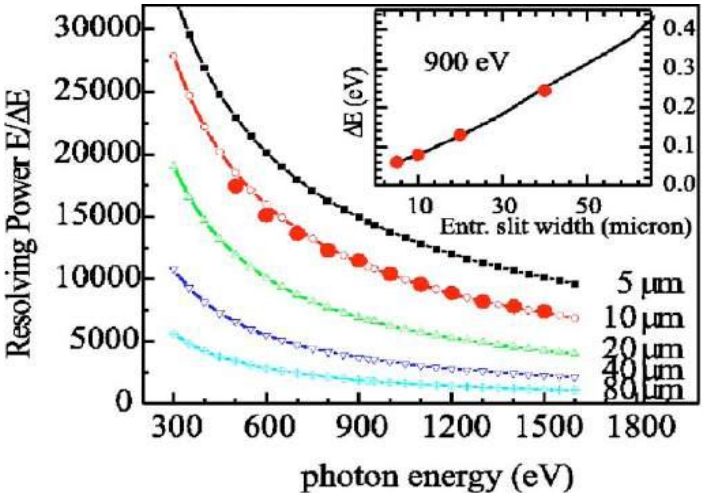
Q-dependence
t-dependence

Liquids and wets

Ultra-high resolution SXES spectrometer

G. Ghiringhelli *et al*., Rev. Sci. Instrum. **77**, 113108 (2006).





Energy resolution

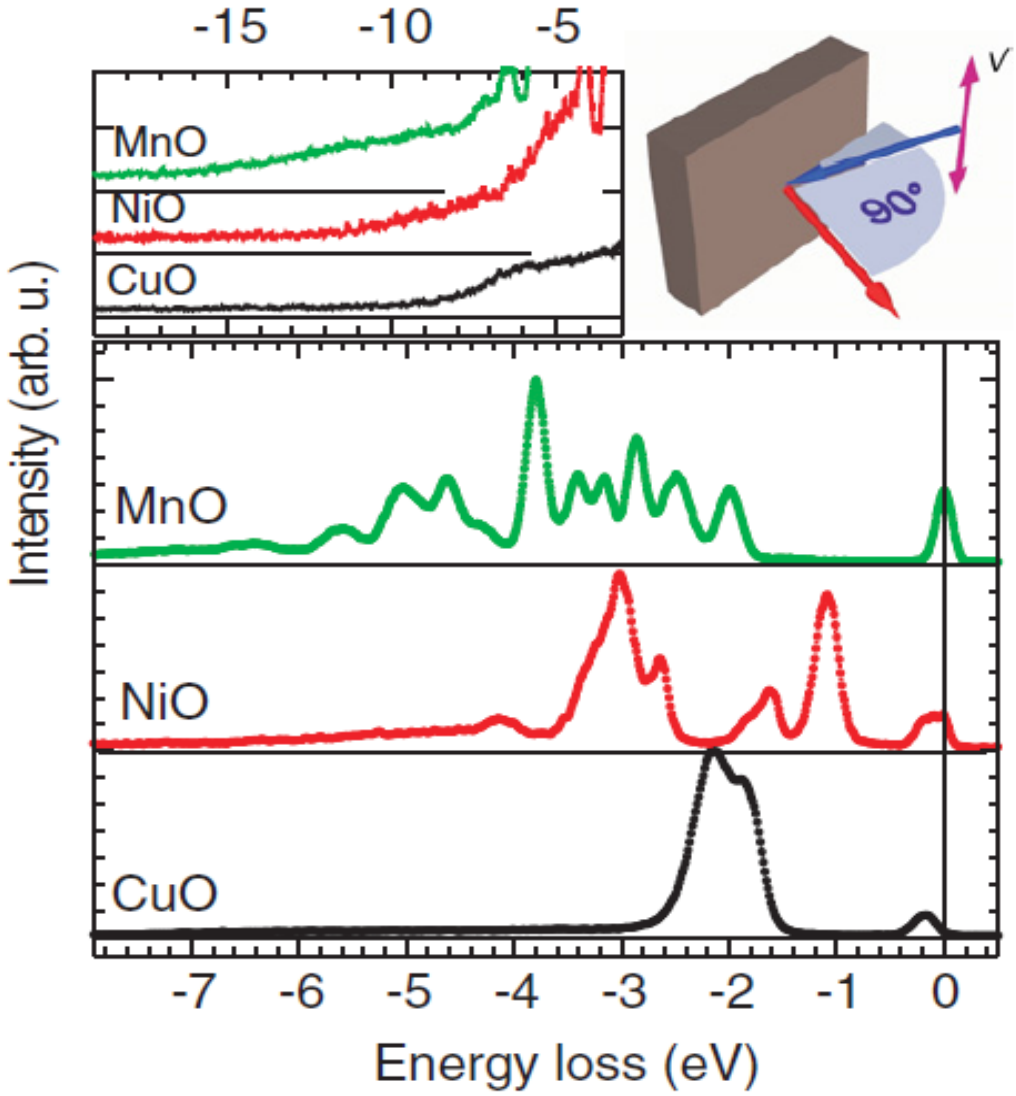
Standard:

$E/\Delta E < 2000$

SAXES:

$E/\Delta E > 10{,}000$

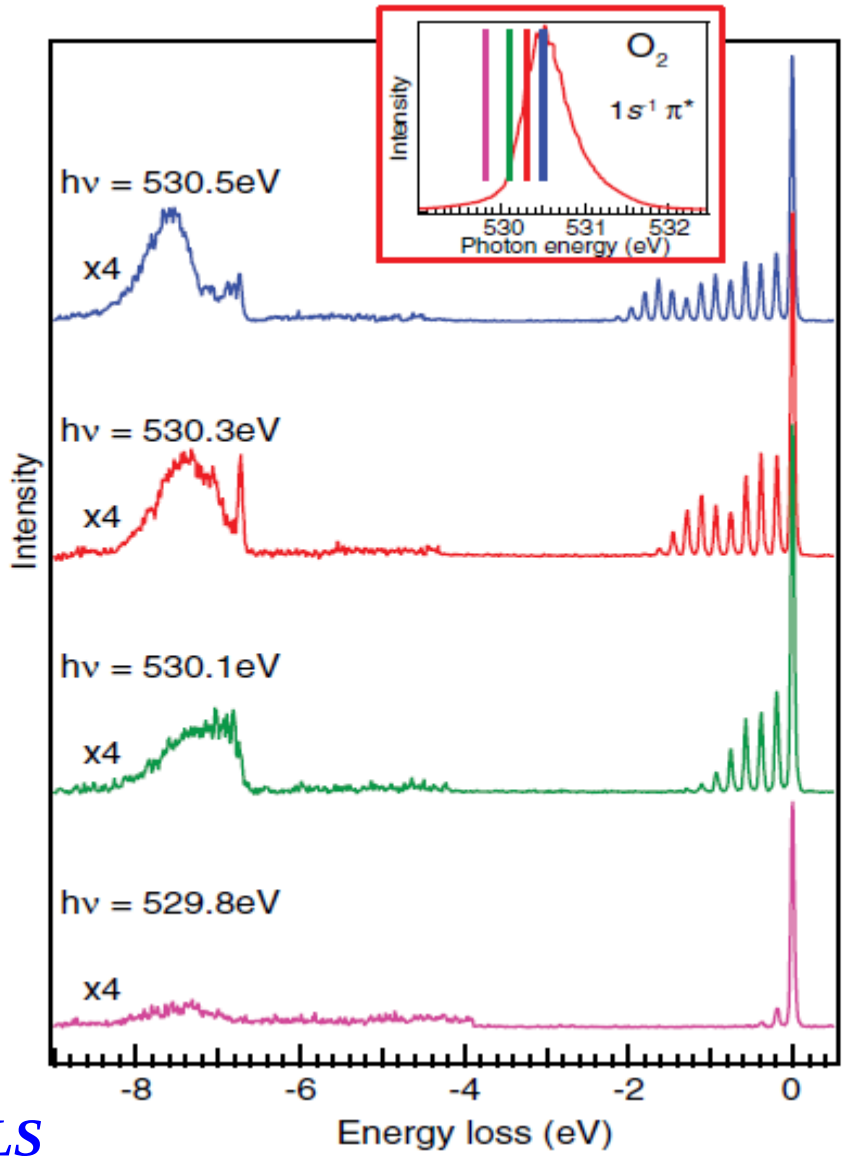
Ultra-high resolution → crystal field splitting

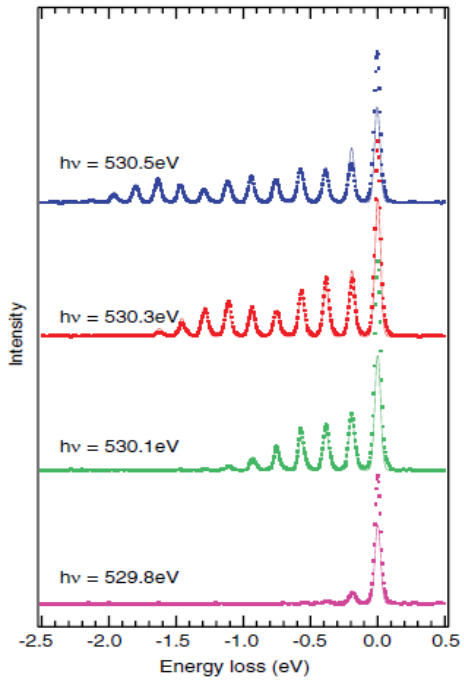


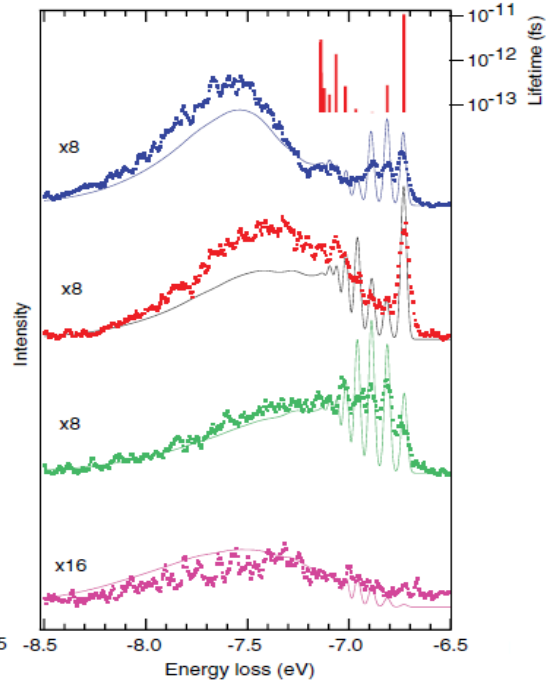
G. Ghiringhelli et al., Eur. Phys. J. Special Topics **169**, 199 (2009).

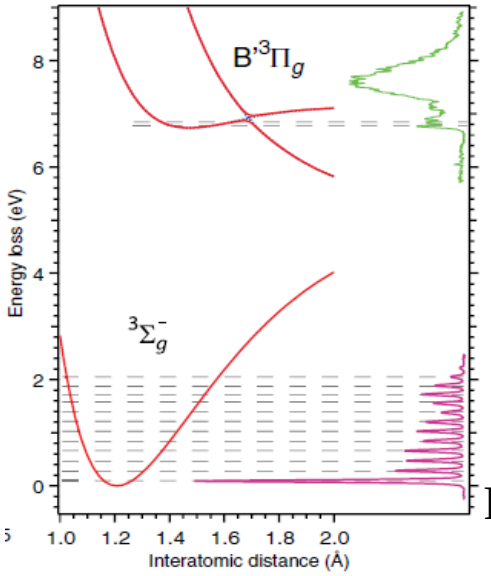
Ultra-high resolution → Vibration (~0.1eV)

Vibrational progression









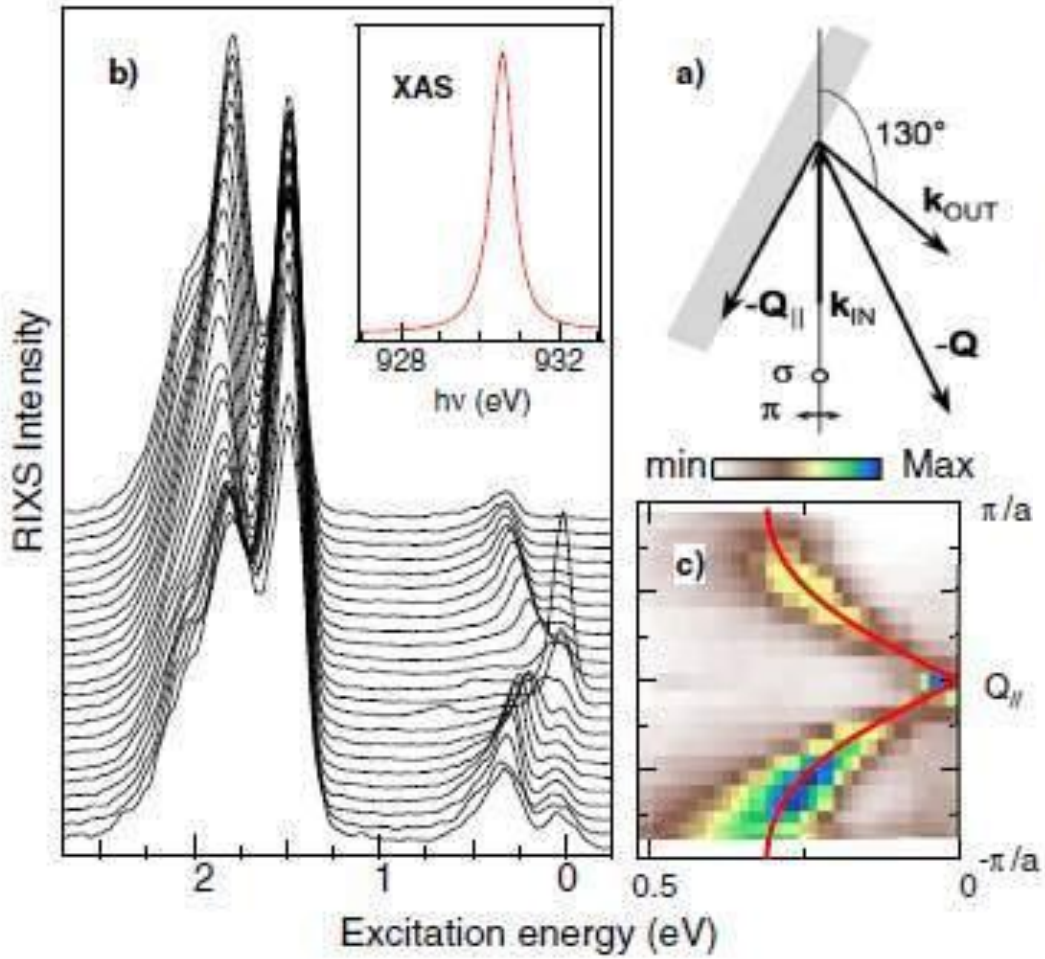
E/ΔE ~ 10000

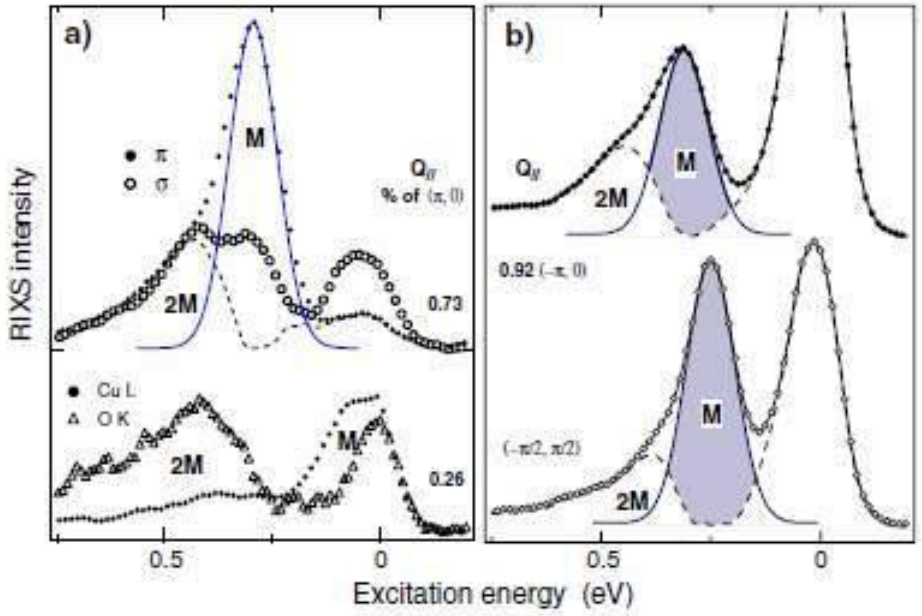
Ultra-high resolution allows to observe well-resolved vibrational progression

F. Hennies *et al.*, Phys. Rev. Lett. **104**, 193002 (2010).

SLS

Ultra-high resolution⊗ Q-dependence
→ magnetic excitation (~0.1eV)





Cu 2*p* RXES of $Sr_2CuO_2Cl_2$

single magnon

vs

two magnon

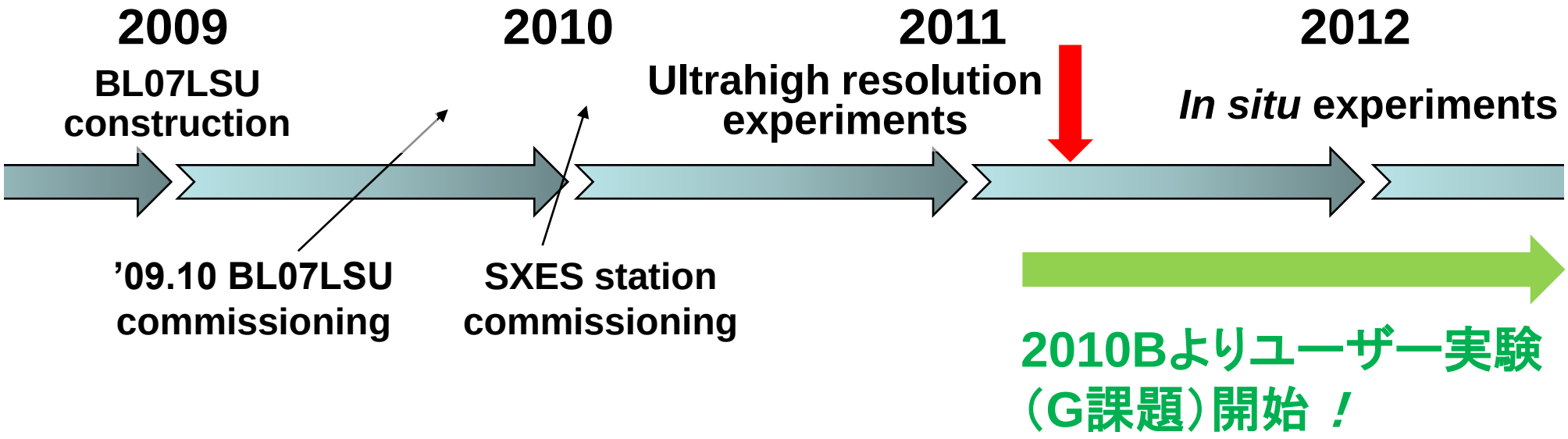
M. Guarise et al., Phys. Rev. Lett. **105**, 157006 (2011).

Concept of SPring-8 BL07LSU SXES station

Ultrahigh energy resolution

with *in situ* (air pressure) experiments

Commissioning & operation schedule



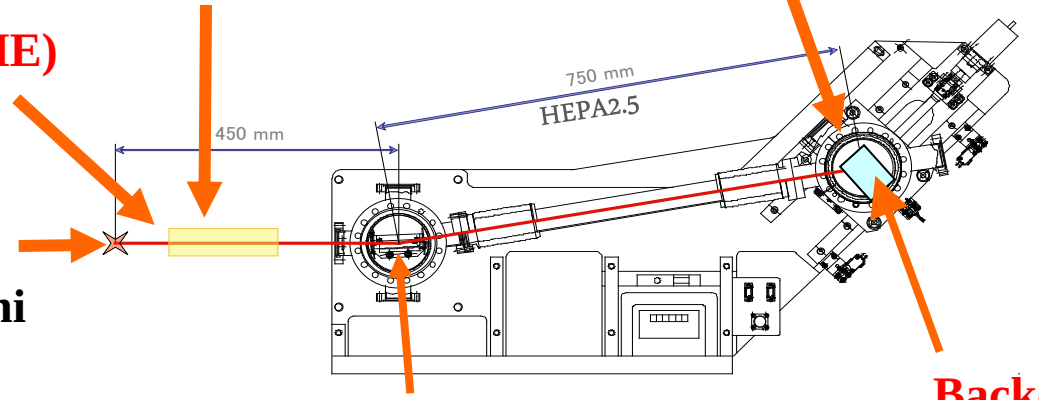
Summary for the basic concept of SXES spectrometer : SPring-8 BL17SU

1.high efficiency
2.high energy resolution (E/ΔE>2000)

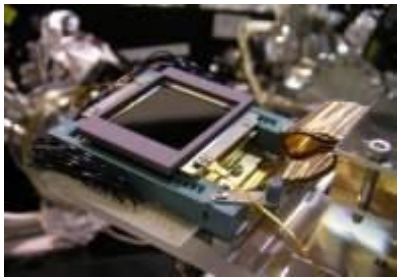
Grazing flat field mount (HR & HE)

Focusing optics (HE)

Slitless (HE)

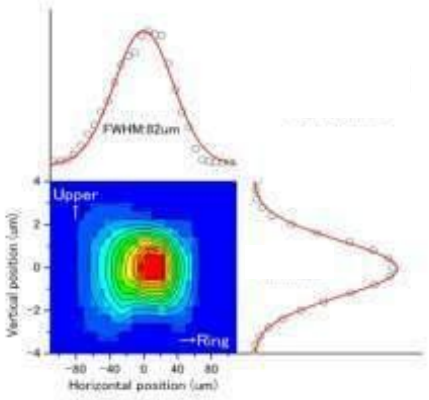


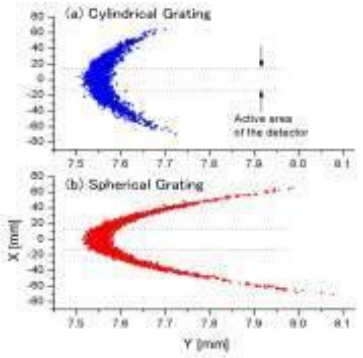
Focused beam (HR)
by Senba and Ohashi
@JASRI



Back-illuminated CCD (HR & HE)

Cylindrical grating (HR)

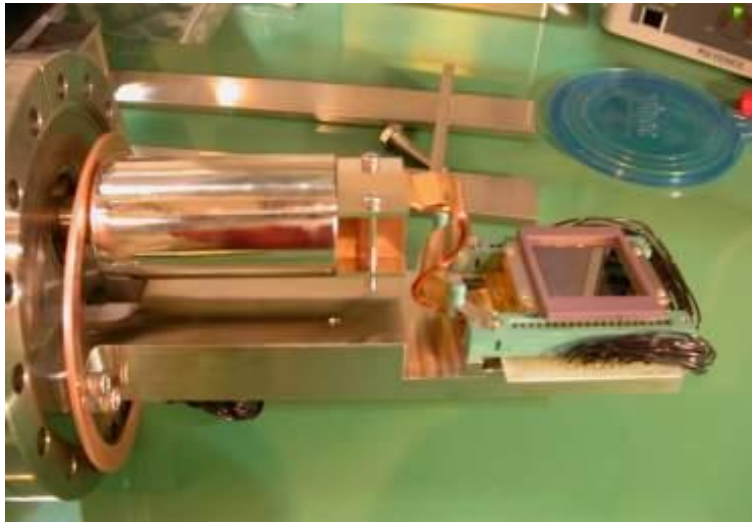


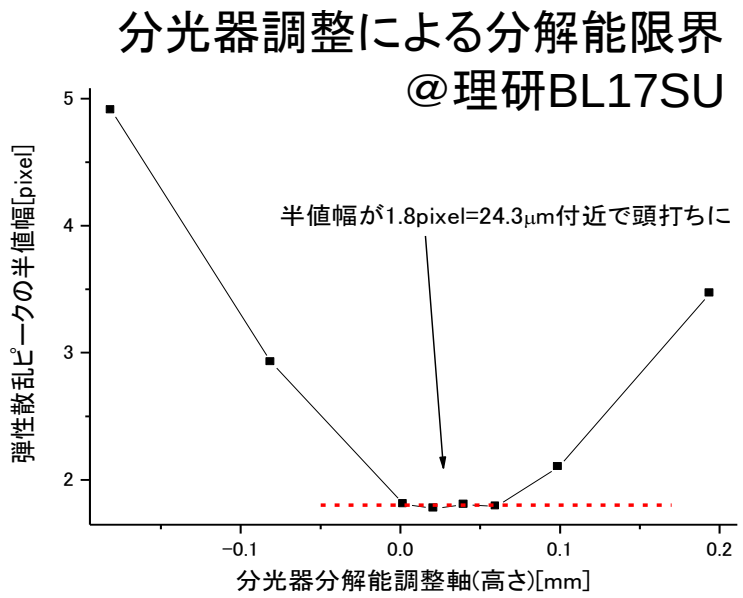


#HR = High Resolution
#HE = High Efficiency

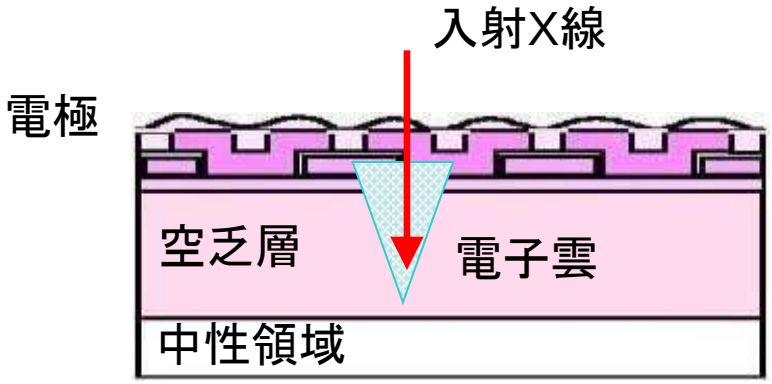
T. Tokushima *et al.*, Rev. Sci. Instrum. 77, 063107 (2006).

検出器の位置分解能の問題(電荷雲広がり)

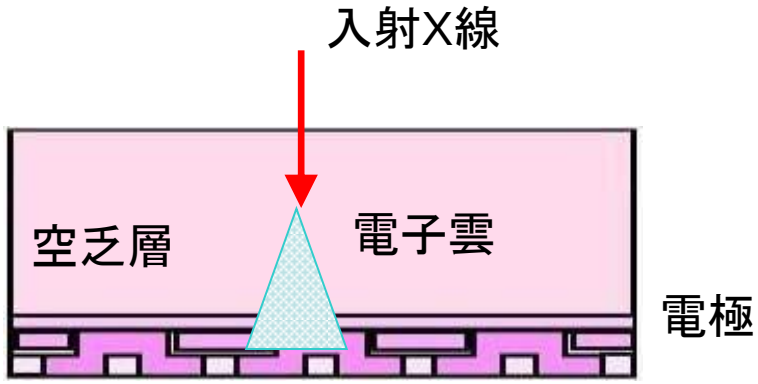




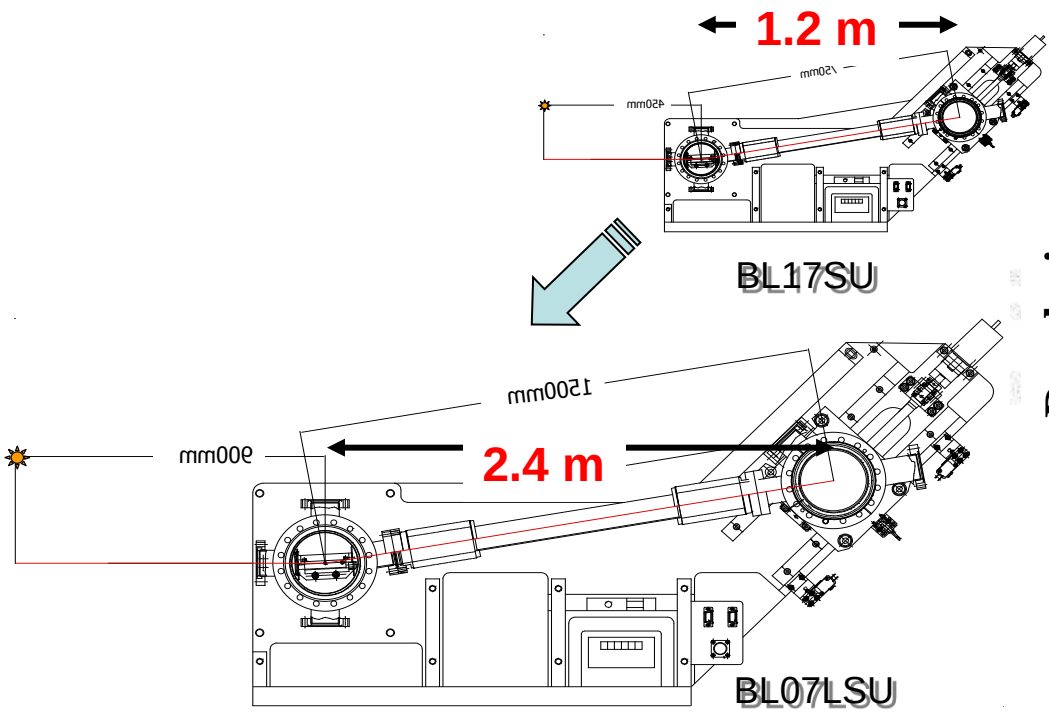
表面照射型（ Front-illuminated : FI ）

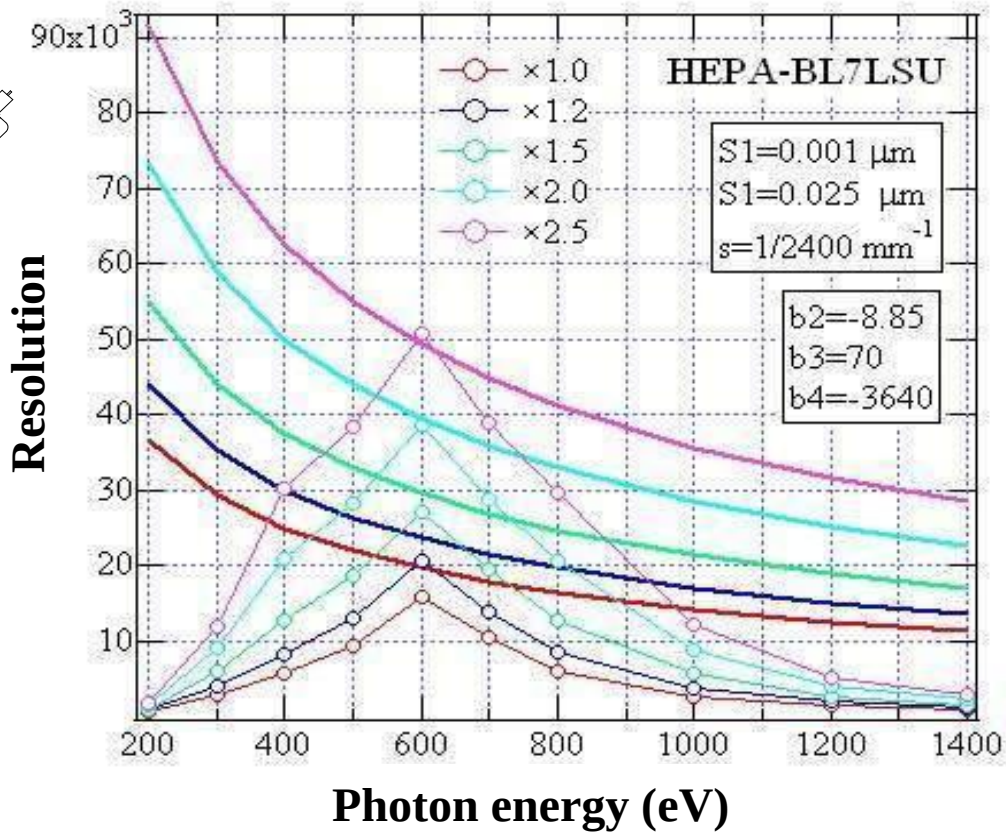


裏面照射型（ Back-illuminated : BI ）



Spectrometer size determines the resolution

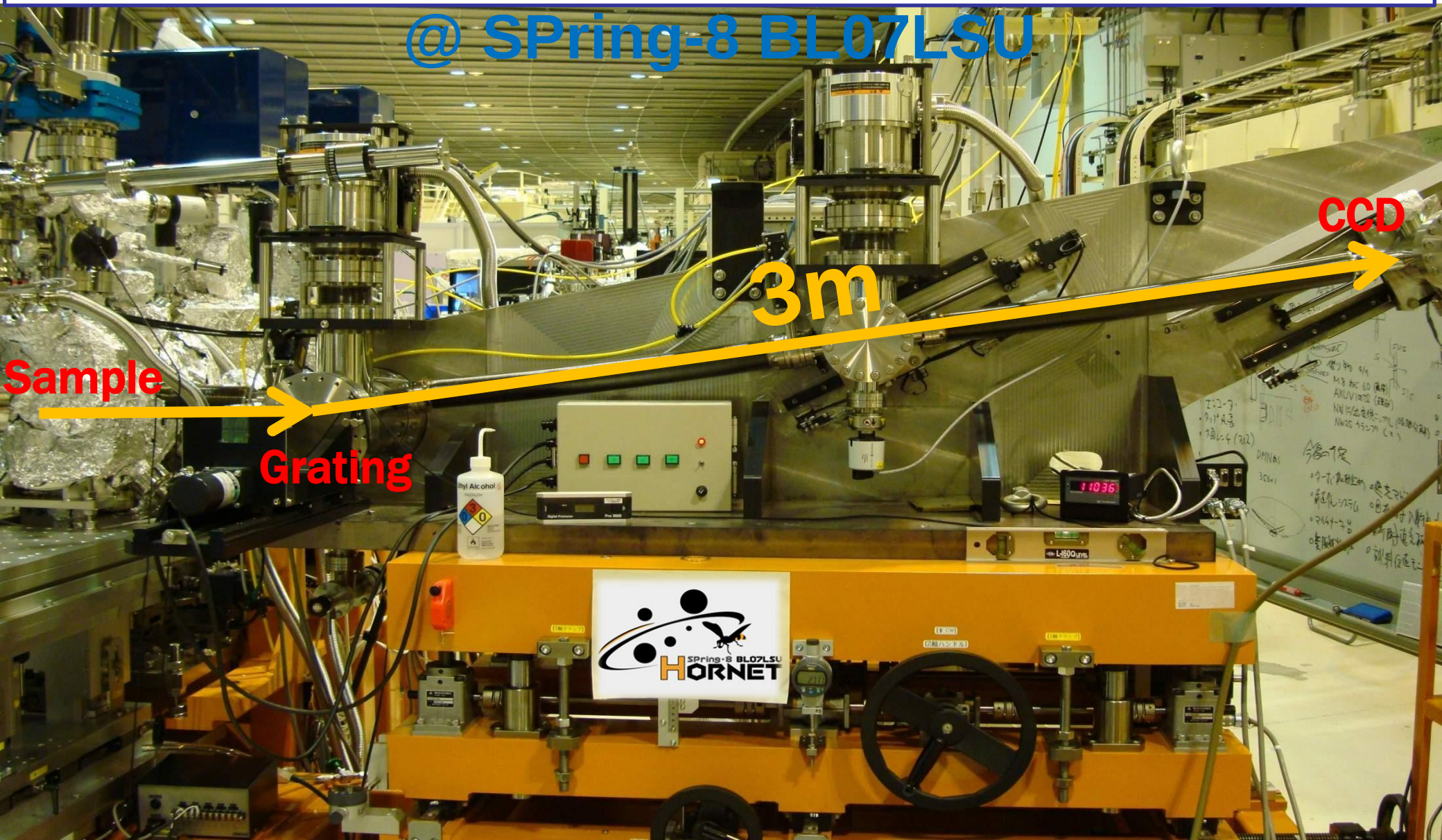




Expected energy resolution increases almost linearly with the size of the spectrometer.

Ultra high resolution soft X-ray emission (HORNET)

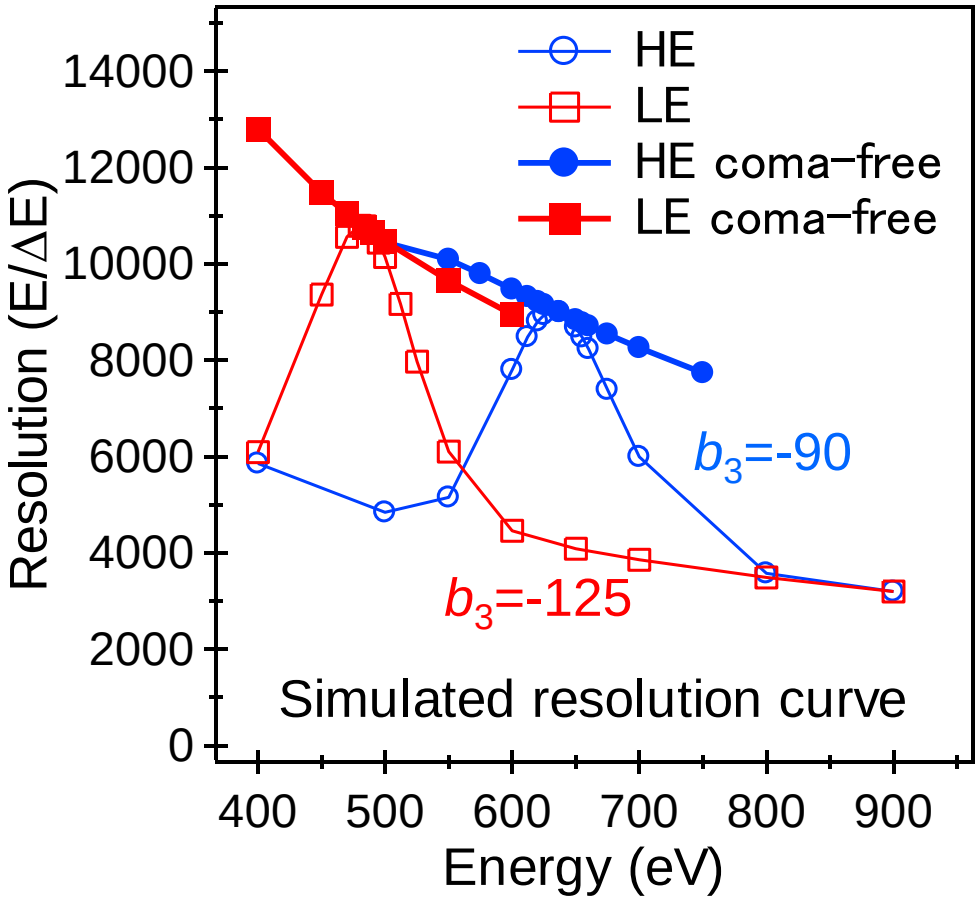
@ SPring-8 BL07LSU

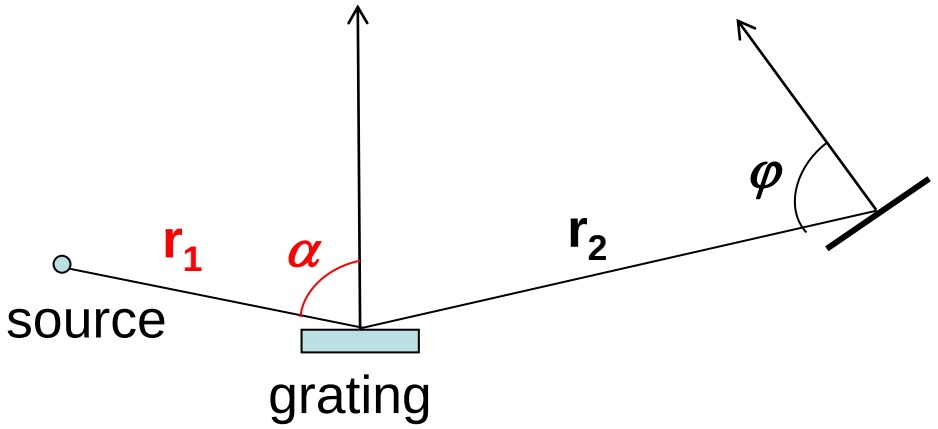


Simulated energy resolution

→applying coma-free mode

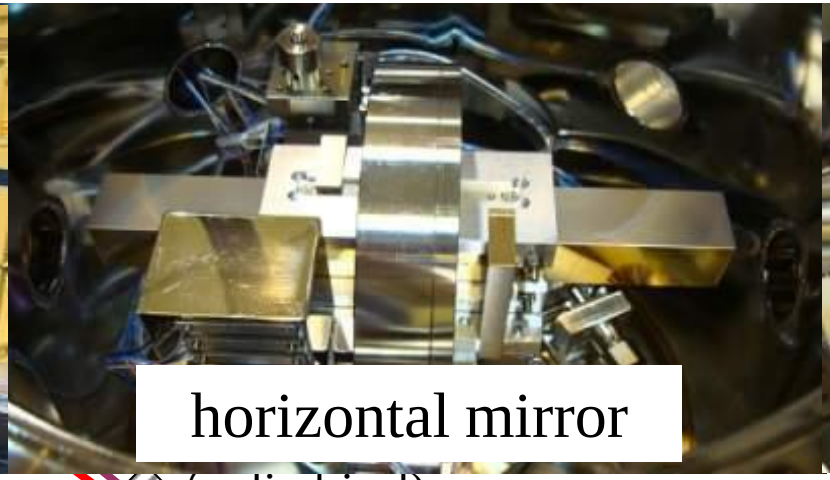
V.N. Strocov *et al.*, J. Synchrotron Rad. **18**, 134 (2011).



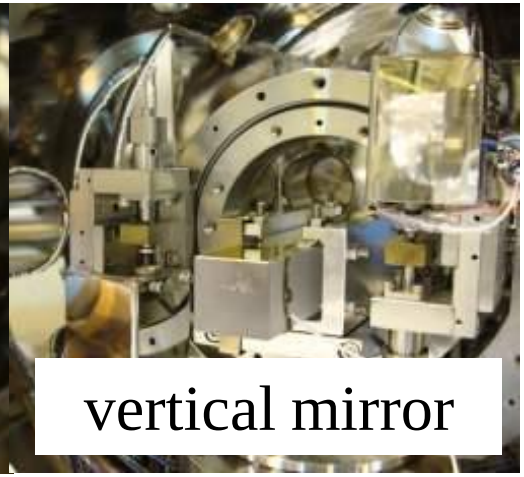


Only two parameters

r_1 & α



horizontal mirror



vertical mirror

(cylindrical)

Focusing mirror
(cylindrical)

sample

Focus@sample
$0.4\mu m^{V}$ x $10\mu m^{H}$

postfocusing mirrors
（KB mirror optics)

R_a=11600mm
R_b=32mm

vertical

150 mm

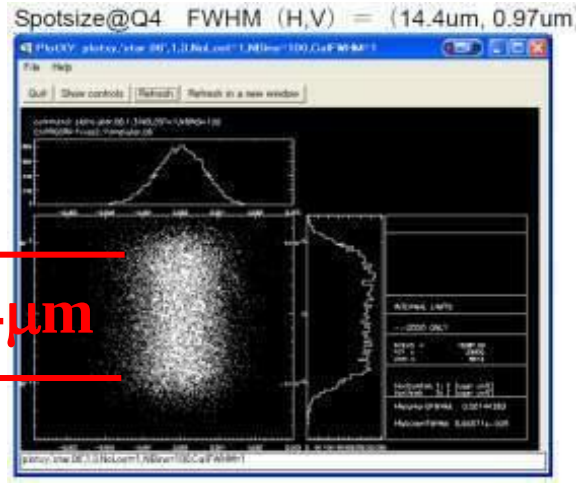
R_a=11600mm
R_b=90mm

horizontal

exit slit

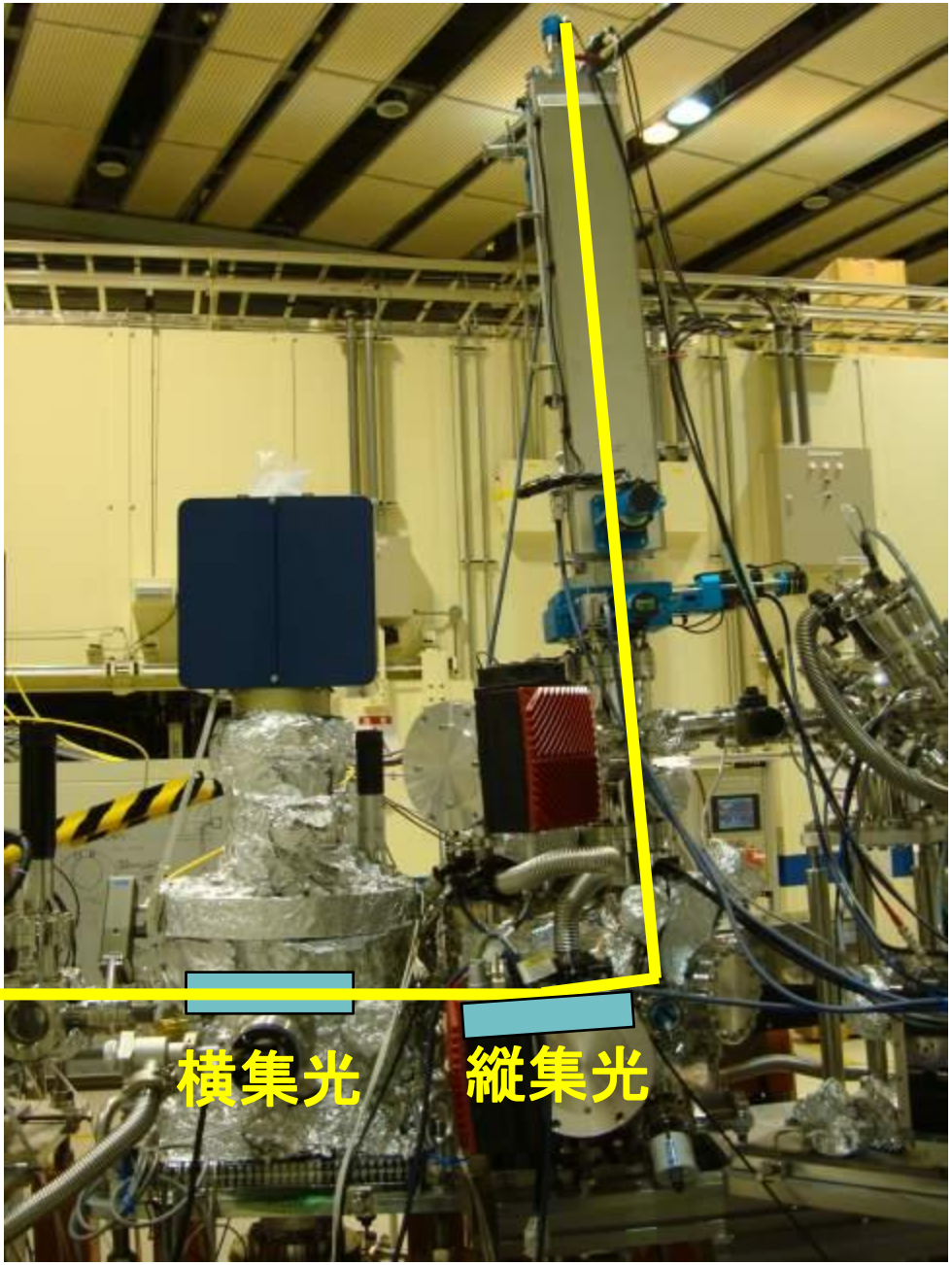
22m

1/150
demagnification

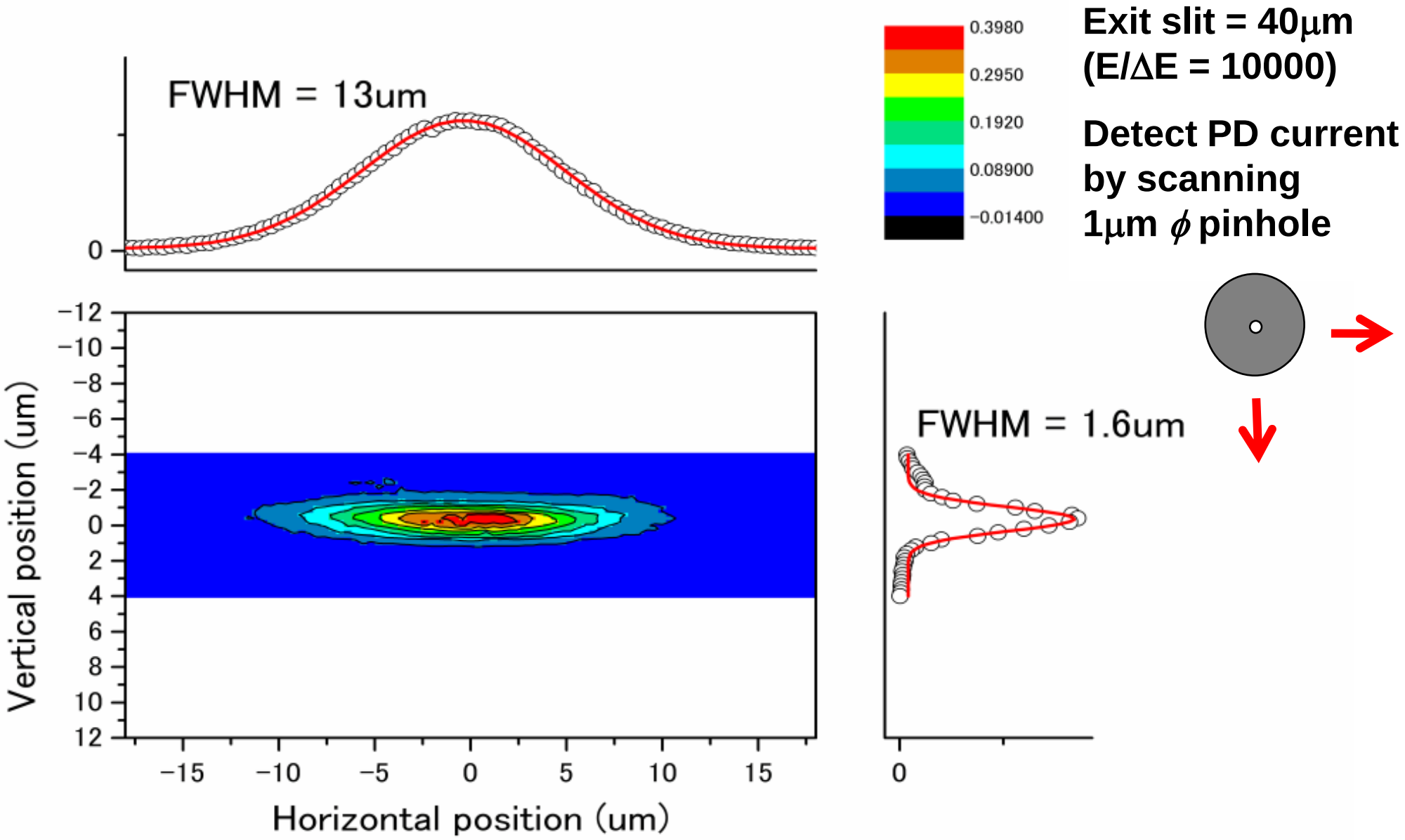


0.4μm

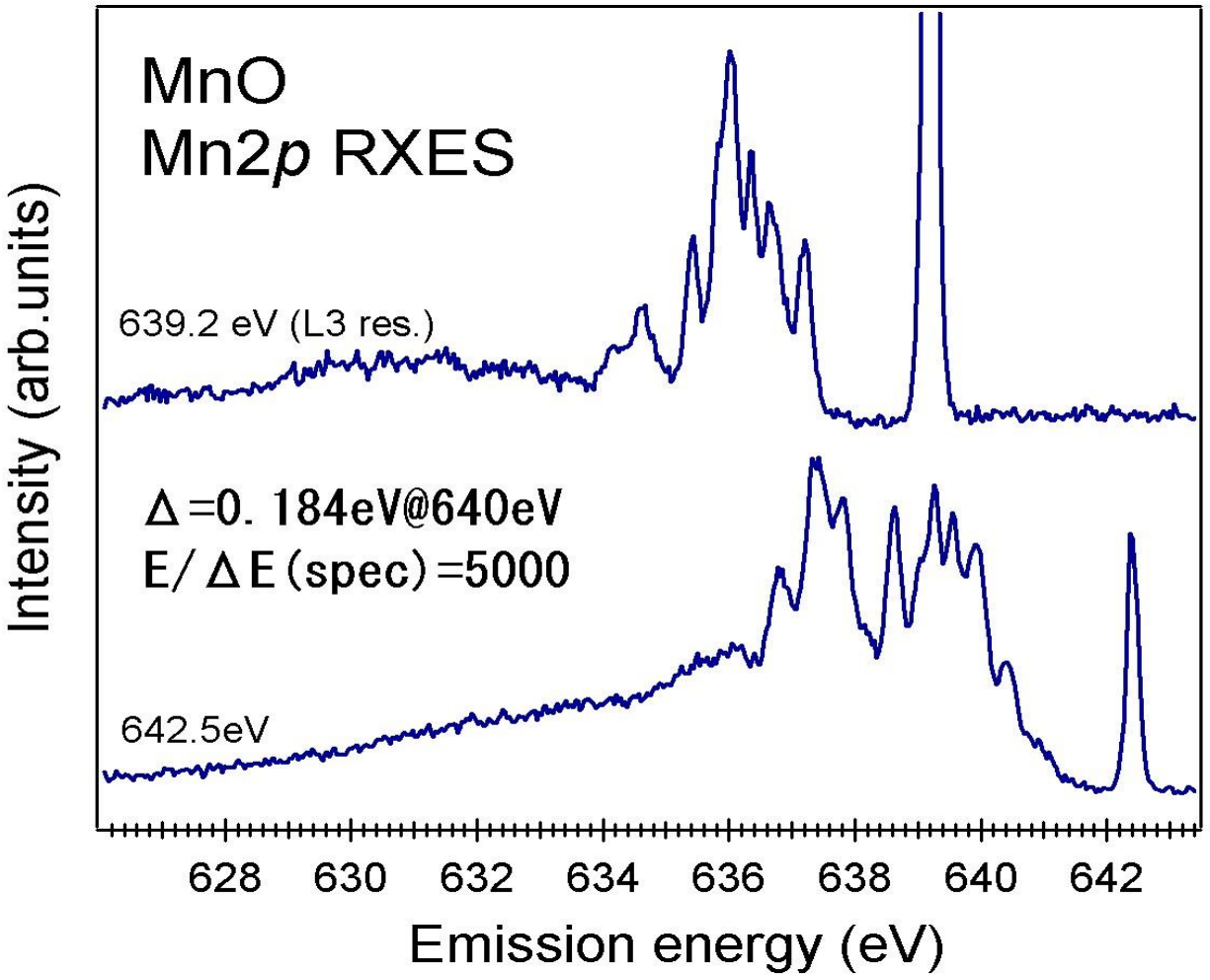
SX



HORNET XES station Focused image @ sample position



Highlight (2010年7月）



We have succeeded in achieving ultra-high resolution of SXES!!

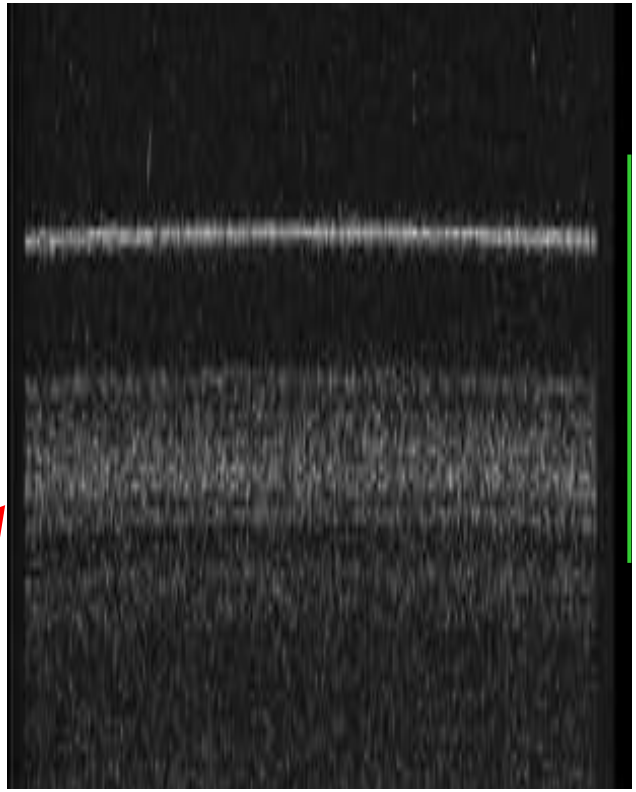
Required improvements for ultrahigh resolution SXES

Hardware

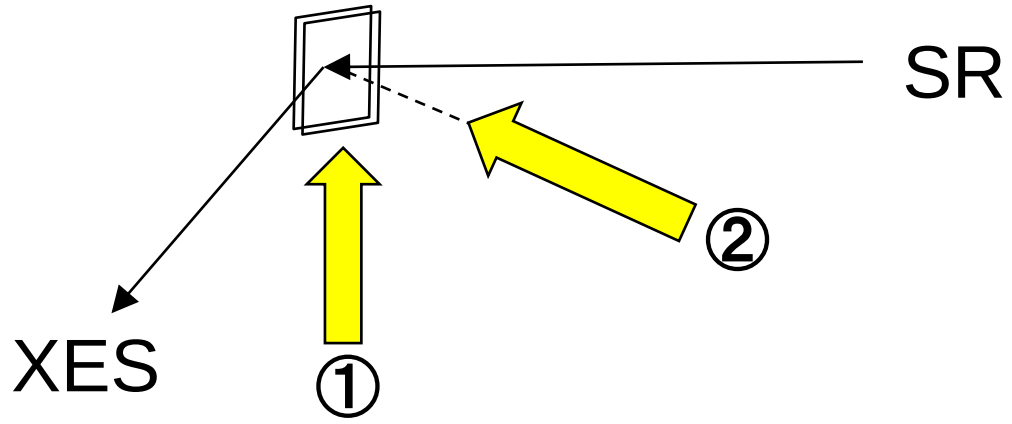
- To eliminate vibration from vacuum pumping and CCD cooling
- To reduce the CCD noise to gain high S/N ratio
- ☑ To introduce camera systems for precise alignment of the sample
- To calculate precise CCD position for an appropriate aberration correction
- To increase photon flux

Software

- Bent correction of CCD images



カメラシステムによる試料の精密位置合わせ



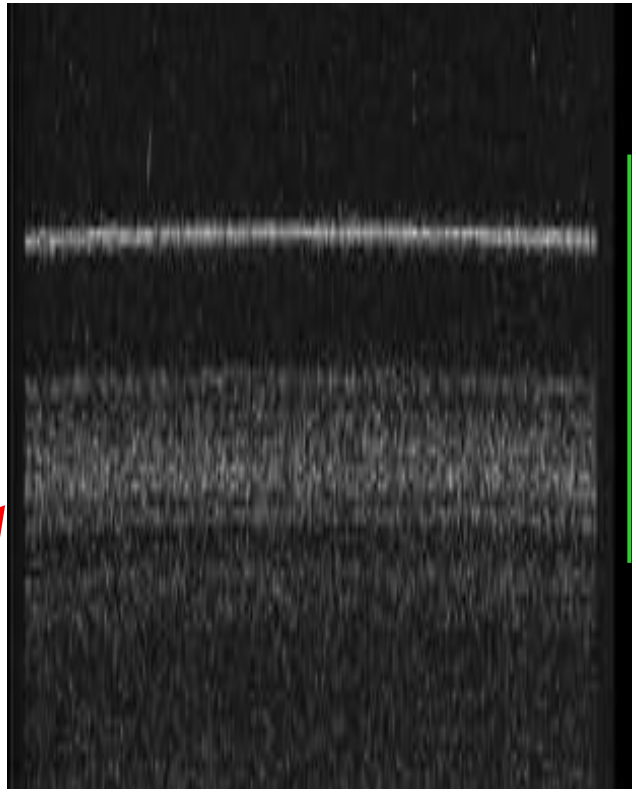
Required improvements for ultrahigh resolution SXES

Hardware

- To eliminate vibration from vacuum pumping and CCD cooling
- To reduce the CCD noise to gain high S/N ratio
- ☑ To introduce camera systems for precise alignment of the sample
- ☑ To calculate precise CCD position for an appropriate aberration correction
- To increase photon flux

Software

- Bent correction of CCD images



HORNET集光条件探索プログラム

2010/12/08 MK

HORNET optimizer

Setting

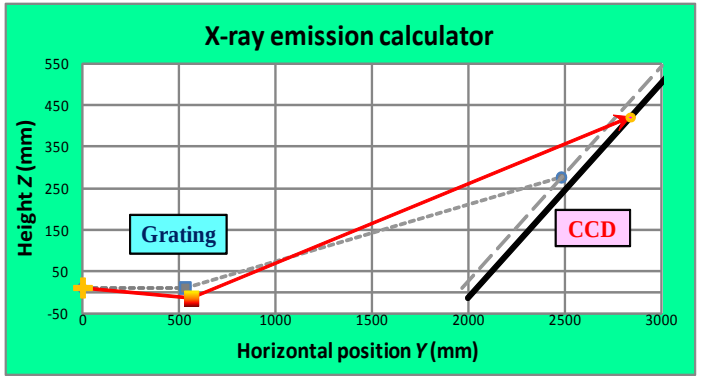
Incident photon energy (eV)	$h\nu$	683
Stage Hieght (mm)	Z	3.063
Stage Horizontal Position (mm)	Y	47.707
Encoder offset	$X0$	193445

Incident angle (deg)	α	85.82045075
Entrance airm length (mm)	$r1$	563.3562907
Height difference	ΔZ	-13.563
Stage Horizontal Position (mm)	Y	563.193
Horizontal position difference	ΔY	32.193
Emission angle CCW (deg)	β	-83.38712868
Emission angle CW (deg)	θ	10.79242057
Angle difference (deg)	$\Delta\theta$	3.022420567
CCD position difference (mm)	Δx	366.0234209

Encoder value	X	10433

Detector plane

Plane center (vertical) (mm)	Zc	252.6394982
Plane center (horizontal) (mm)	Yc	2514.115149
Cross point (vertical) (mm)	Z'	-13.563
Cross point (horizontal) (mm)	Y'	1997.693988
Mirror point (vertical) (mm)	Z''	518.8419964
Mirror point (horizontal) (mm)	Y''	3030.536309



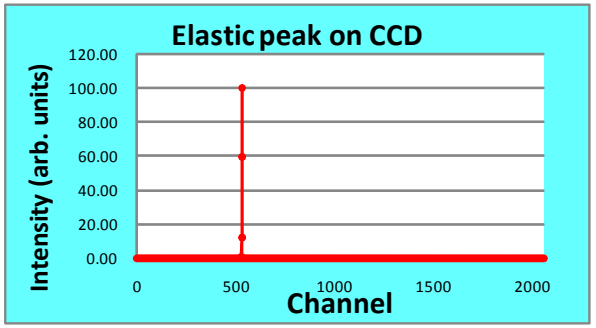
Conditions

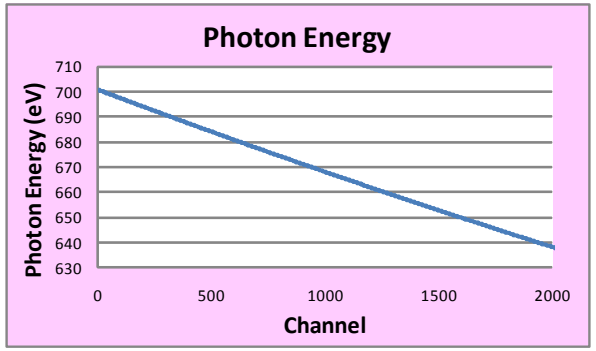
Incidence angle	$\alpha 0$ (deg)	87.2	**Spectrometer**	$r2$ (mm)	1969
Order	k	1		$r1$ (mm)	531
Groove density	n (1/mm)	2200		θext (deg)	7.77
System size	L (mm)	2500		$Z0$ (mm)	10.5
Source size	$S1$ (mm)	0.001		$Y0$ (mm)	0
CCD spatial resolution	$S2$ (mm)	0.025		$E0$ (eV)	600
Detecter angle	ϕ (deg)	27.27		$\beta 0$ (deg)	-83.858144

Ch to eV

Elastic peak position (Ch)	532
Energy resolution (meV)	75

Incident photon energy (eV) 683





Developed by M. Kobayashi

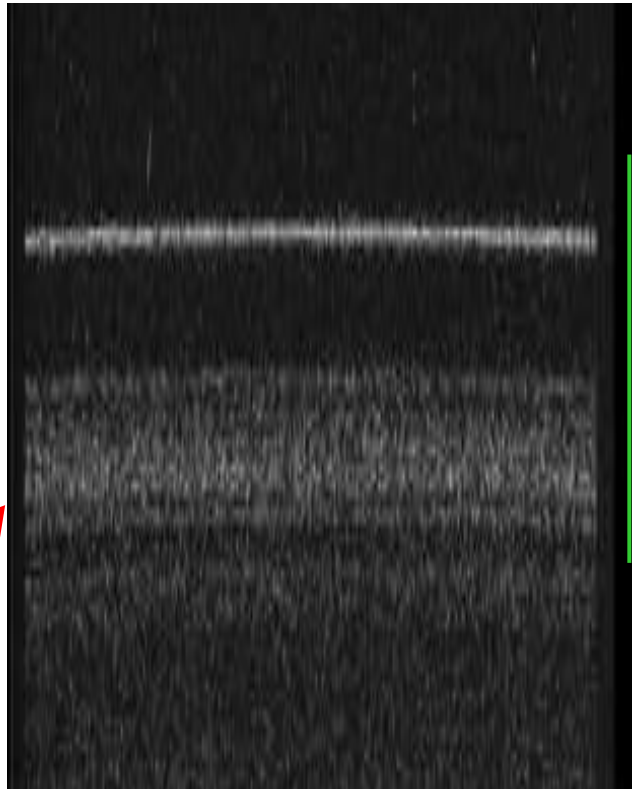
Required improvements for ultrahigh resolution SXES

Hardware

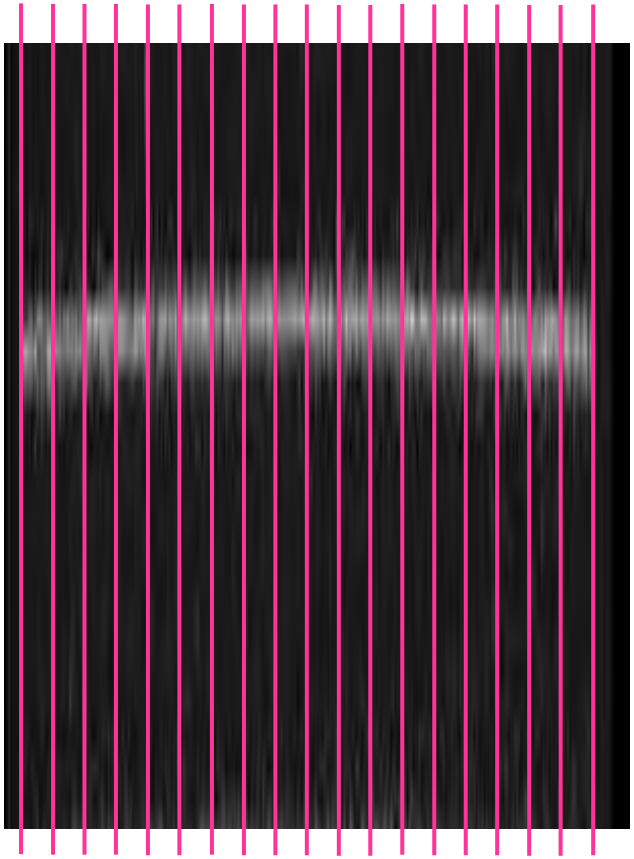
- To eliminate vibration from vacuum pumping and CCD cooling
- To reduce the CCD noise to gain high S/N ratio
- ☑ To introduce camera systems for precise alignment of the sample
- ☑ To calculate precise CCD position for an appropriate aberration correction
- To increase photon flux

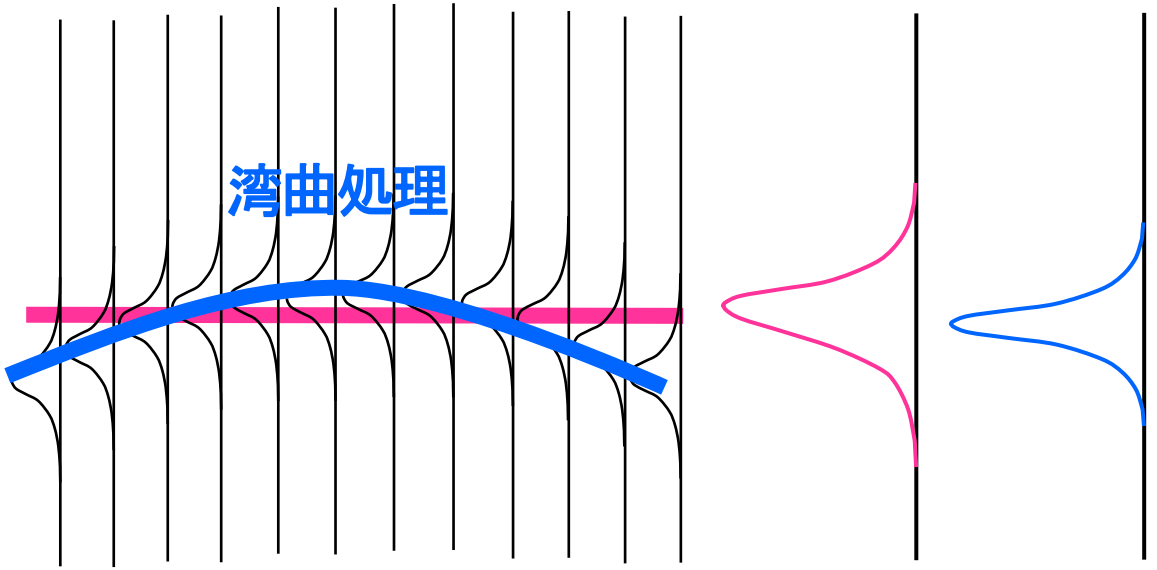
Software

- ☑ Bent correction of CCD images



CCD imageの曲がりを考慮した積算





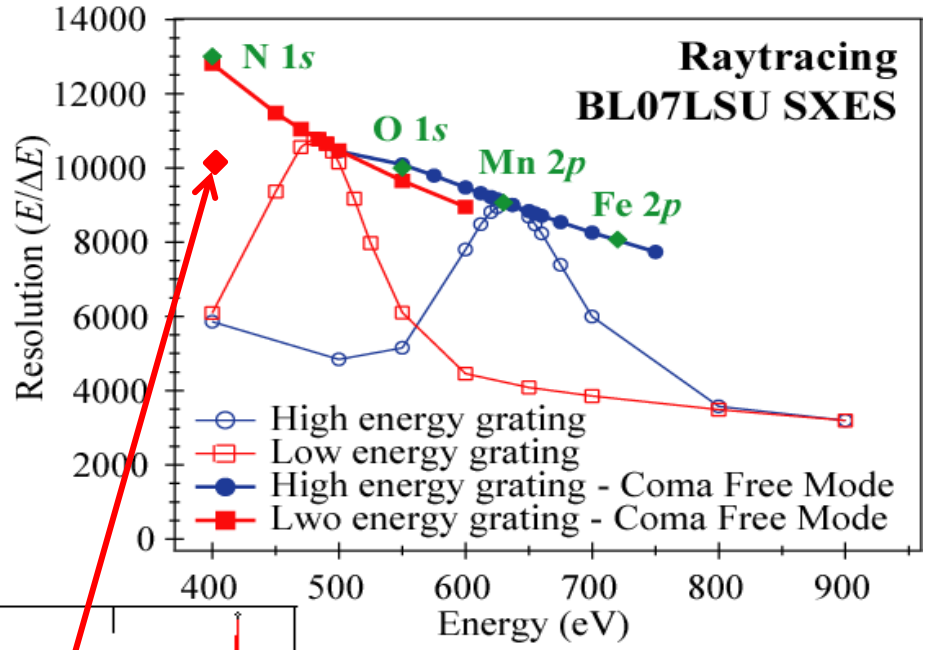
短冊形積算

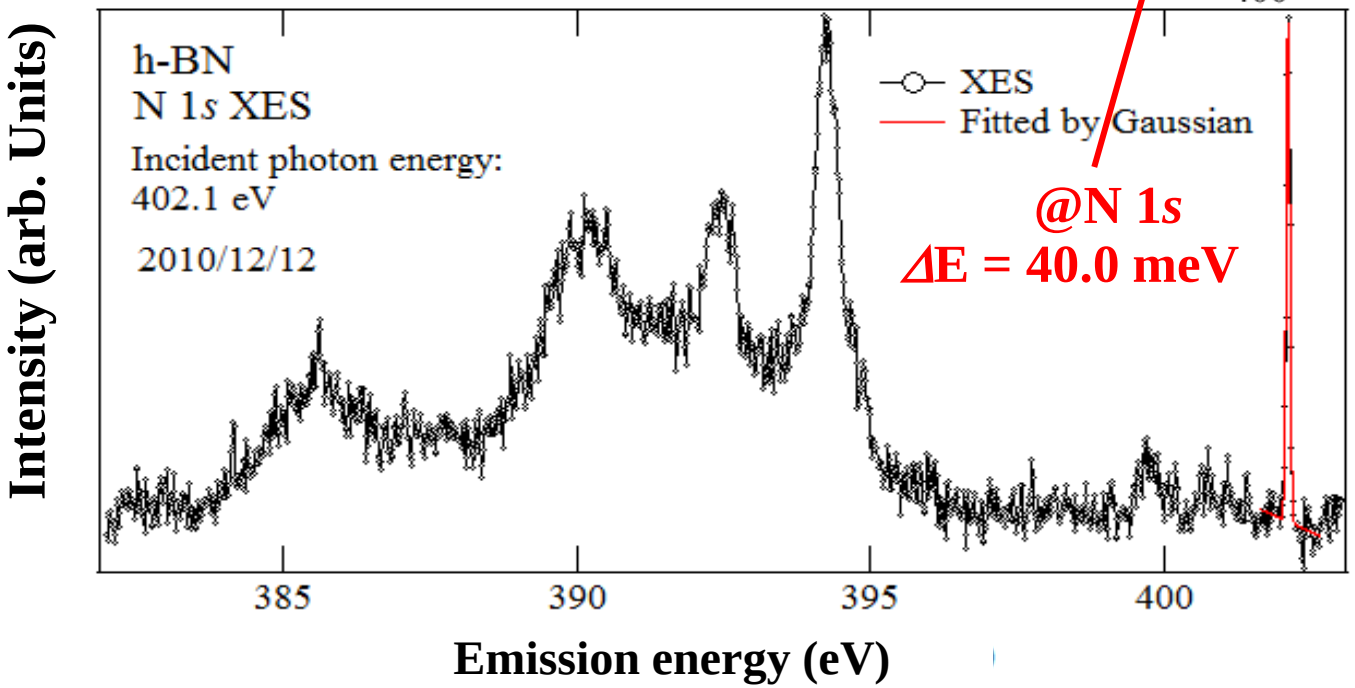
短冊形積算＆湾曲処理により
分解能が2割～4割向上！

Initial data of E/ΔE > 10000 (2010年12月)

Sample: hBN
S2 width: 60 um
Incident photon energy: 402.1 eV

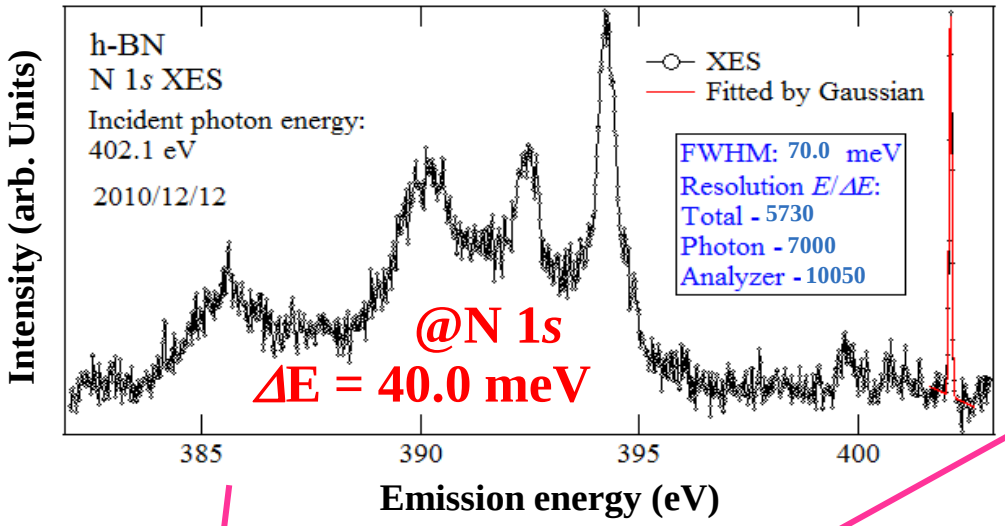
$$\frac{\Delta E_{ana}}{E} = \sqrt{\left(\frac{\Delta E_{total}}{E}\right)^2 - \left(\frac{\Delta E_{incident}}{E}\right)^2}$$

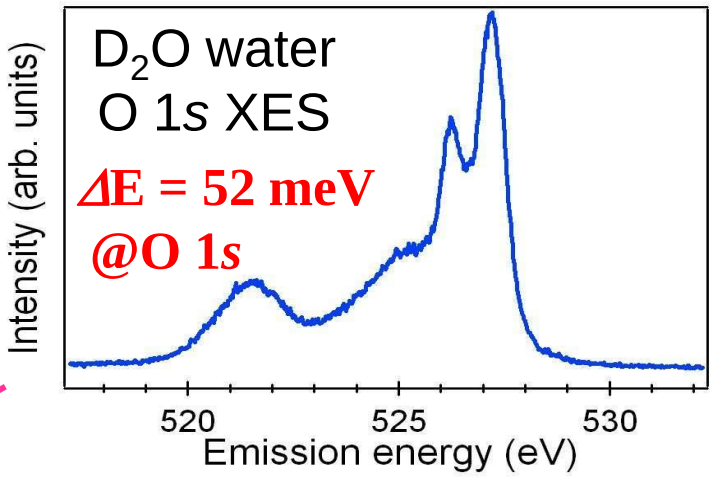


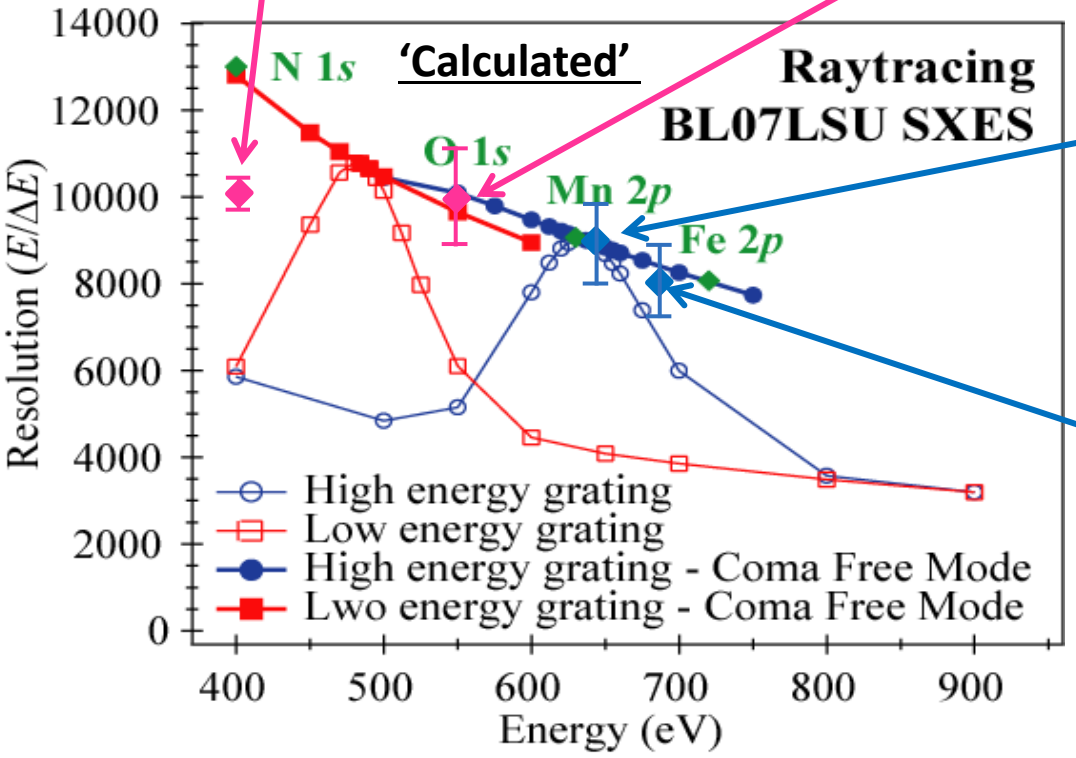


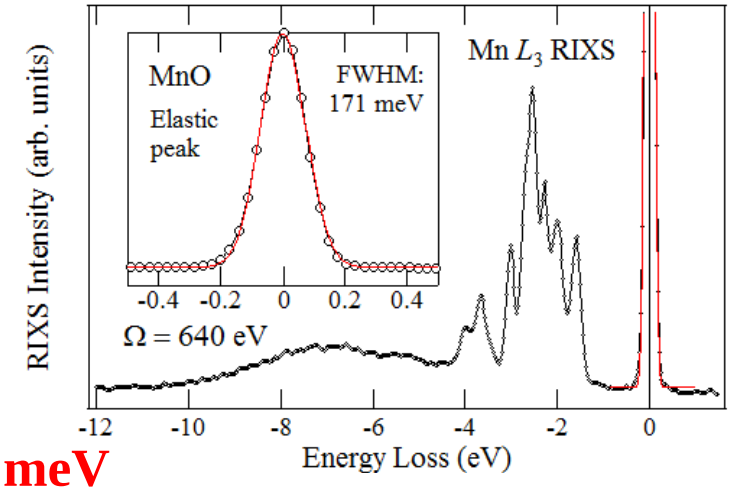
FWHM: 70.0 meV
E/ΔE
Total: 5730
Photon: 7000
Analyzer: 10050

‘Calculated’ vs ‘Measured’ resolution



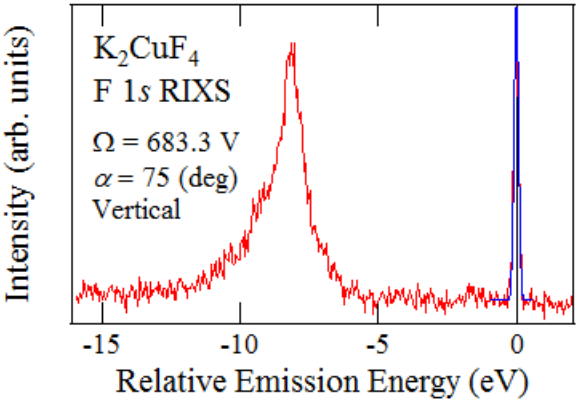






ΔE = 70 meV
@Mn 2p

ΔE = 90 meV
@F 1s

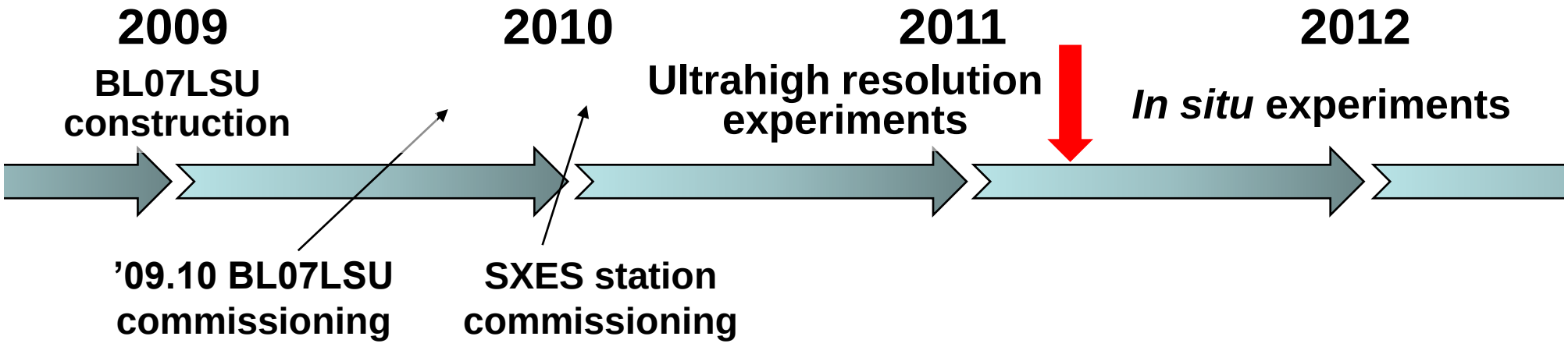


Concept of SPring-8 BL07LSU SXES station

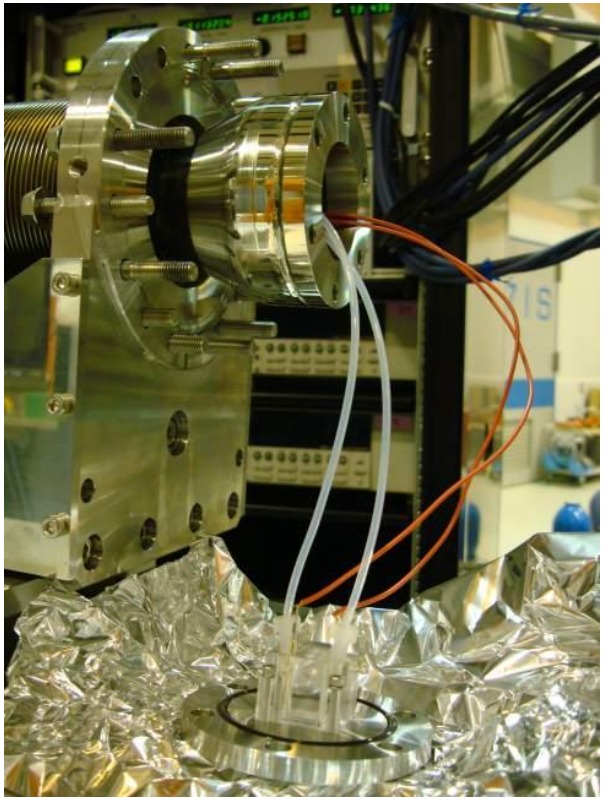
Ultrahigh energy resolution

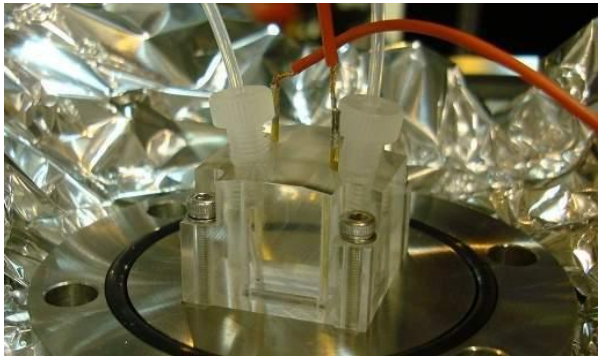
with *in situ* (air pressure) experiments

Commissioning & operation schedule

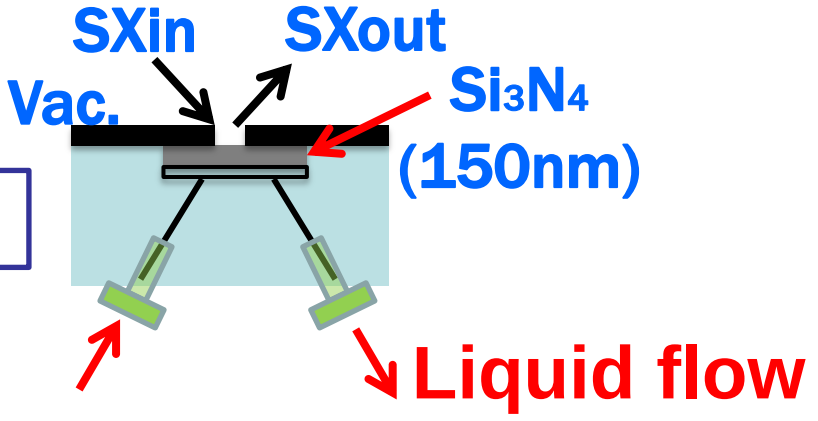


溶液・大気圧下試料の軟X線発光





in situ cell



溶液・大気圧下試料の軟X線発光（結果）

Sample

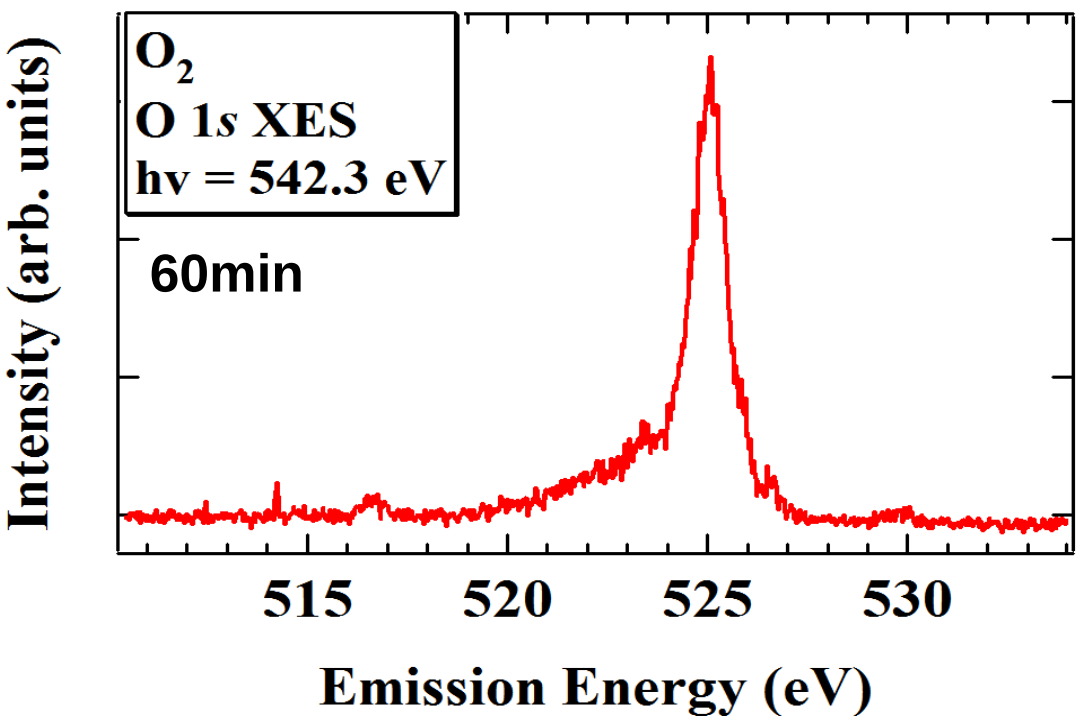
- O_2 gas (flow)
- H_2O (flow)
- D_2O (flow)

X-ray emission spectroscopy

BL07LSU, SPring-8
Pressure: 3E-6 Pa
O 1*s* XES
Incident Energy
resolution: ~5000

HORNET
BL07LSU

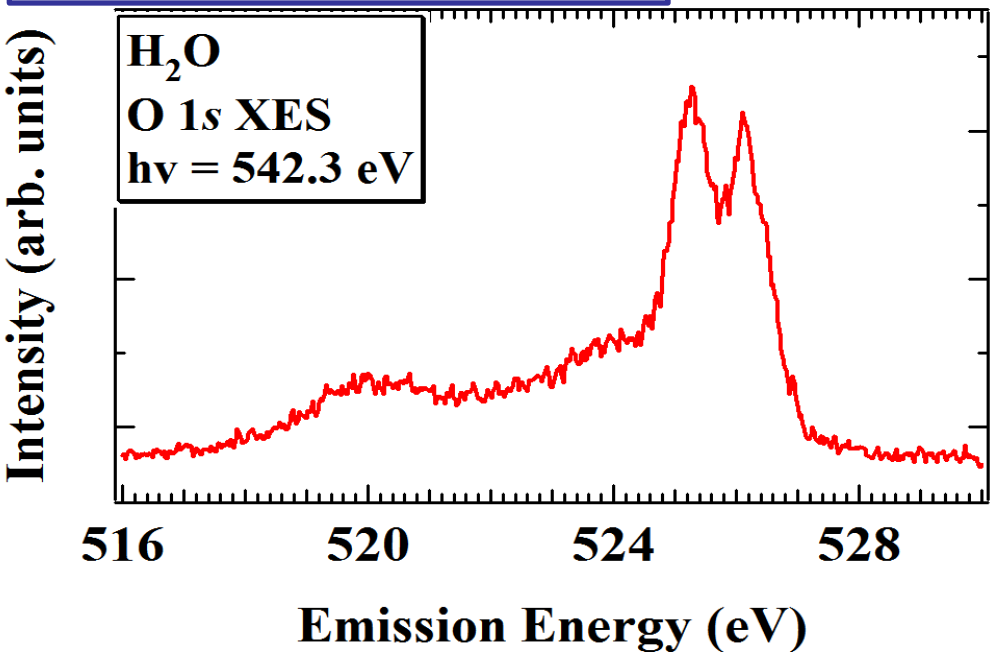
O_2 (Gas)

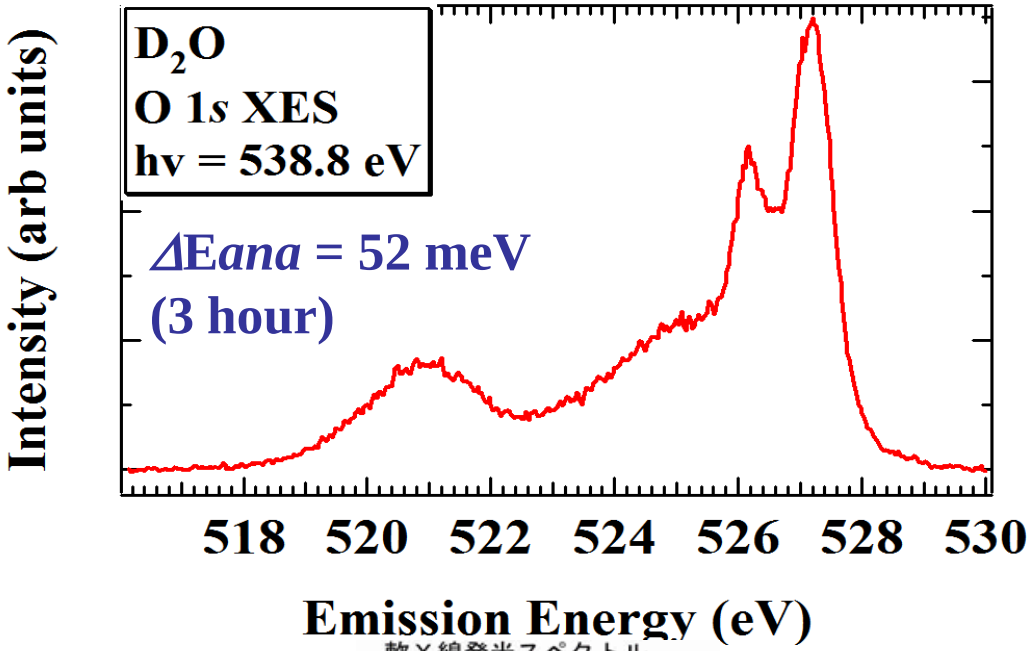


Valence electronic structure of oxygen molecule is observed using *in situ* cell.
Vibration excitation structure has not been observed.

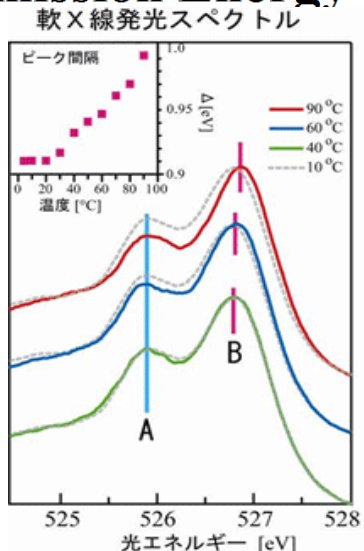
溶液・大気圧下試料の軟X線発光（結果）

H_2O and D_2O (liquid)





Ultra-high resolved XES spectra of H_2O and D_2O are obtained.
Total resolution: ~5000
Res. of analyzer: ~10000
(Curvature correction by program)



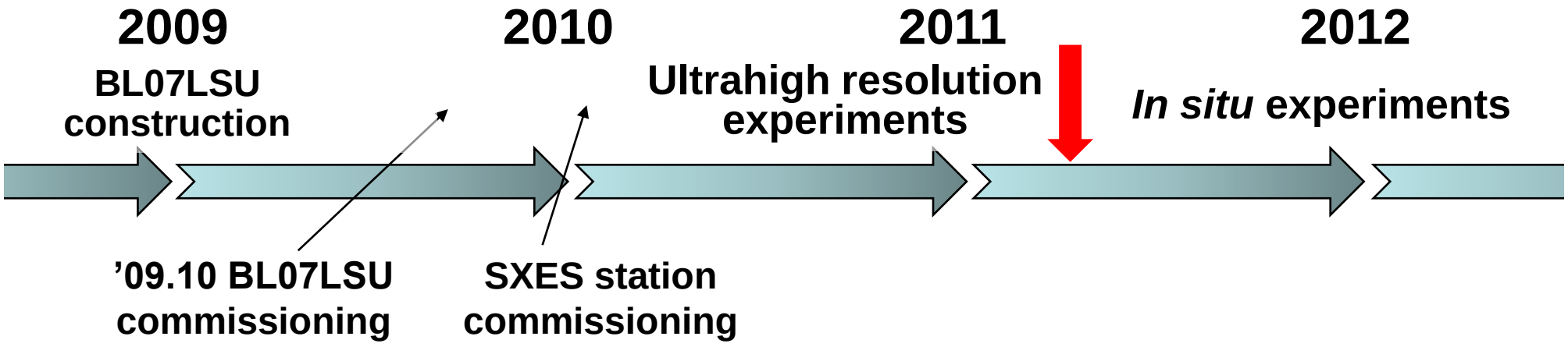
www.riken.jp

Concept of SPring-8 BL07LSU SXES station

Ultrahigh energy resolution

with *in situ* (air pressure) experiments

Commissioning & operation schedule



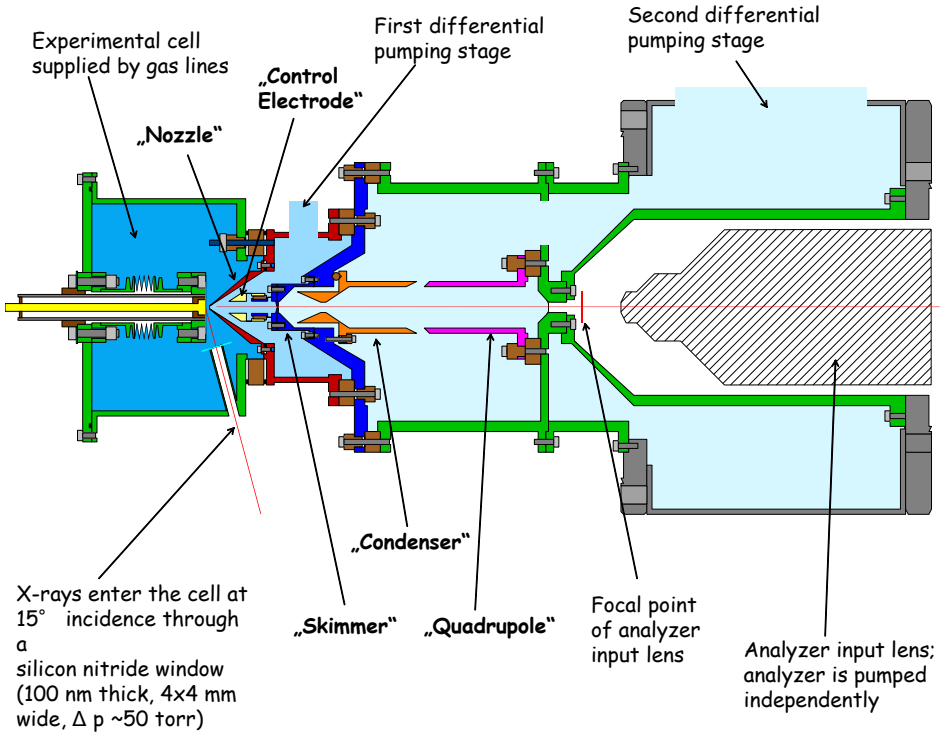
- 触媒、腐食、酸化など
- 環境化学、界面化学
- 水を含む生体物質

大気圧下で起こる物理化学現象へのアプローチ

→XESで真の大気圧分光へ！

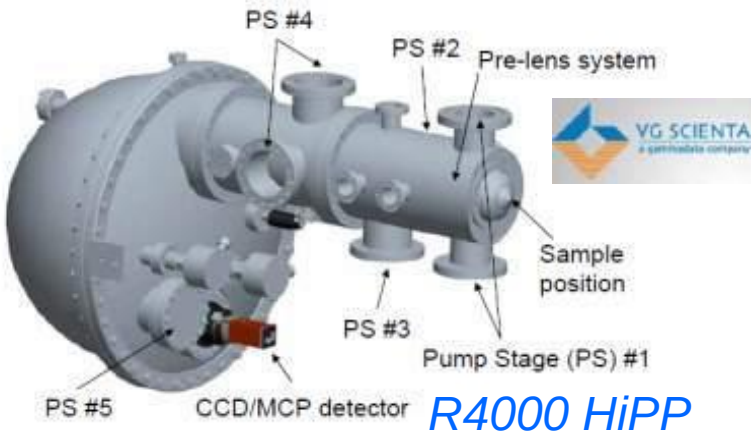
High-pressure X-ray Photoelectron Spectroscopy

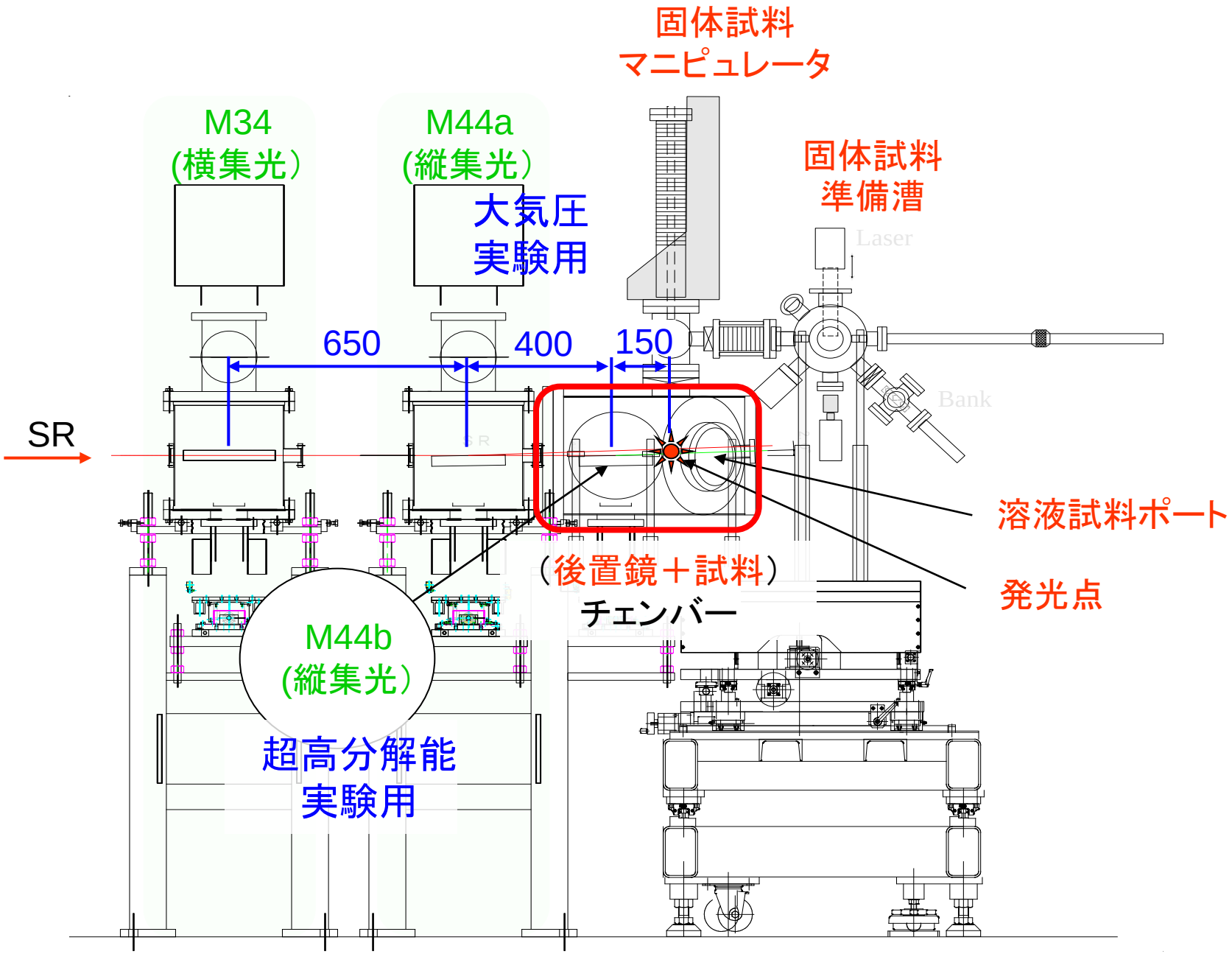
D.F. Ogletree et al., Rev. Sci. Instrum. 73 3872 (2002)



多段差圧排気による10 Torr環境下の光電子分析（水の蒸気圧に相当）

最近はVG Scienta社も市販！




固体試料
マニピュレータ
M34
(横集光)
M44a
(縦集光)
大気圧
実験用
固体試料
準備槽
Laser
650
400
150
SR
溶液試料ポート
(後置鏡＋試料)
チェンバー
発光点
M44b
(縦集光)
超高分解能
実験用

研究プロジェクト（2010～）

申請段階

1. 燃料電池触媒のin situ状態分析
2. タンパク質のin situ状態分析
3. 拡張ナノ水、溶液解析
4. コンビナトリアル薄膜の軟X線発光分光

1. 燃料電池触媒の*in situ*状態分析（S型：丹羽）
2. タンパク質の*in situ*状態分析（S型：小林、G型：東邦大大胡氏）
3. 拡張ナノ水、溶液解析（S型：丹羽、応化北森研）
4. 水素吸蔵合金（G型：筑波大関場氏）
5. イオン液体（G型：東京理科大金井氏）
6. Orbiton励起の観測（S型：小林、KEK、JAEA）

Summary

We have constructed *ultrahigh resolution* SXES station @BL07SU in SPring-8.

Estimated energy resolution up to E/ΔE~10000 by

1. **Using extremely focused spot on the sample.**
2. **Moderately magnifying the spectrometer as well as applying two gratings optimized for 450 eV.**
3. **Applying simple adjustment for the coma-free operation.**

We have obtained *ultrahigh resolution* (>8000) SXES spectra at energy range from 400 eV to 750 eV.

We have succeeded *in situ* SXES experiments with ultrahigh energy resolution.

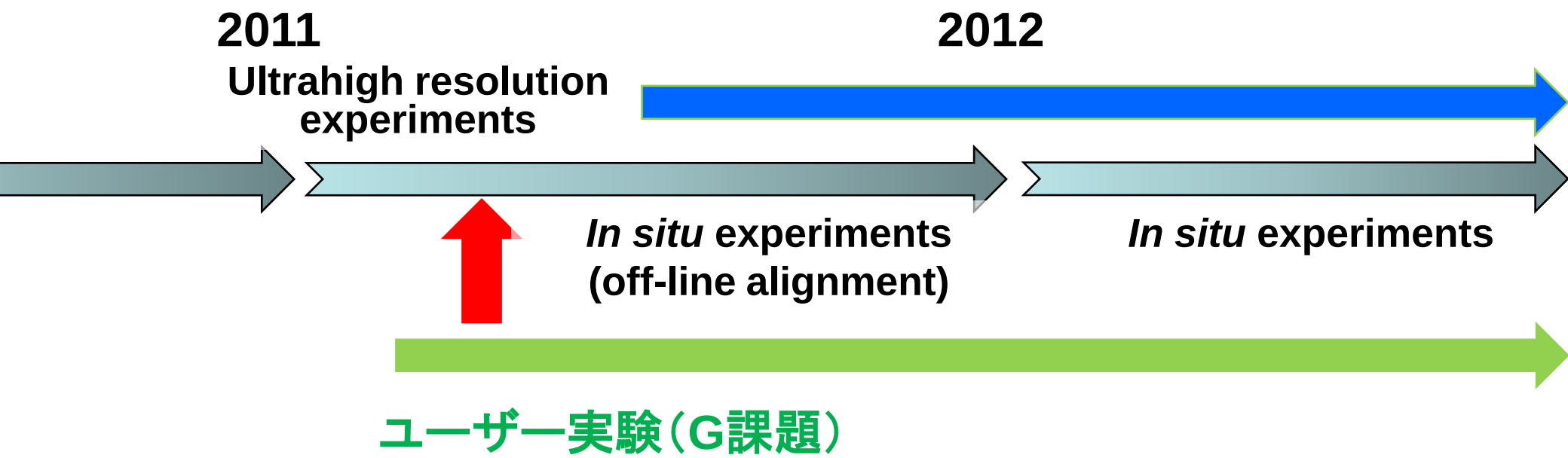
Remaining problem is the XES intensity…
(photon flux? detection efficiency?)

Concept of SPring-8 BL07LSU SXES station

Ultrahigh energy resolution

with *in situ* (air pressure) experiments

Commissioning & operation schedule




Thank you
For your attention !
HORNET
B 7