分解能10000の軟X線発光分光

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

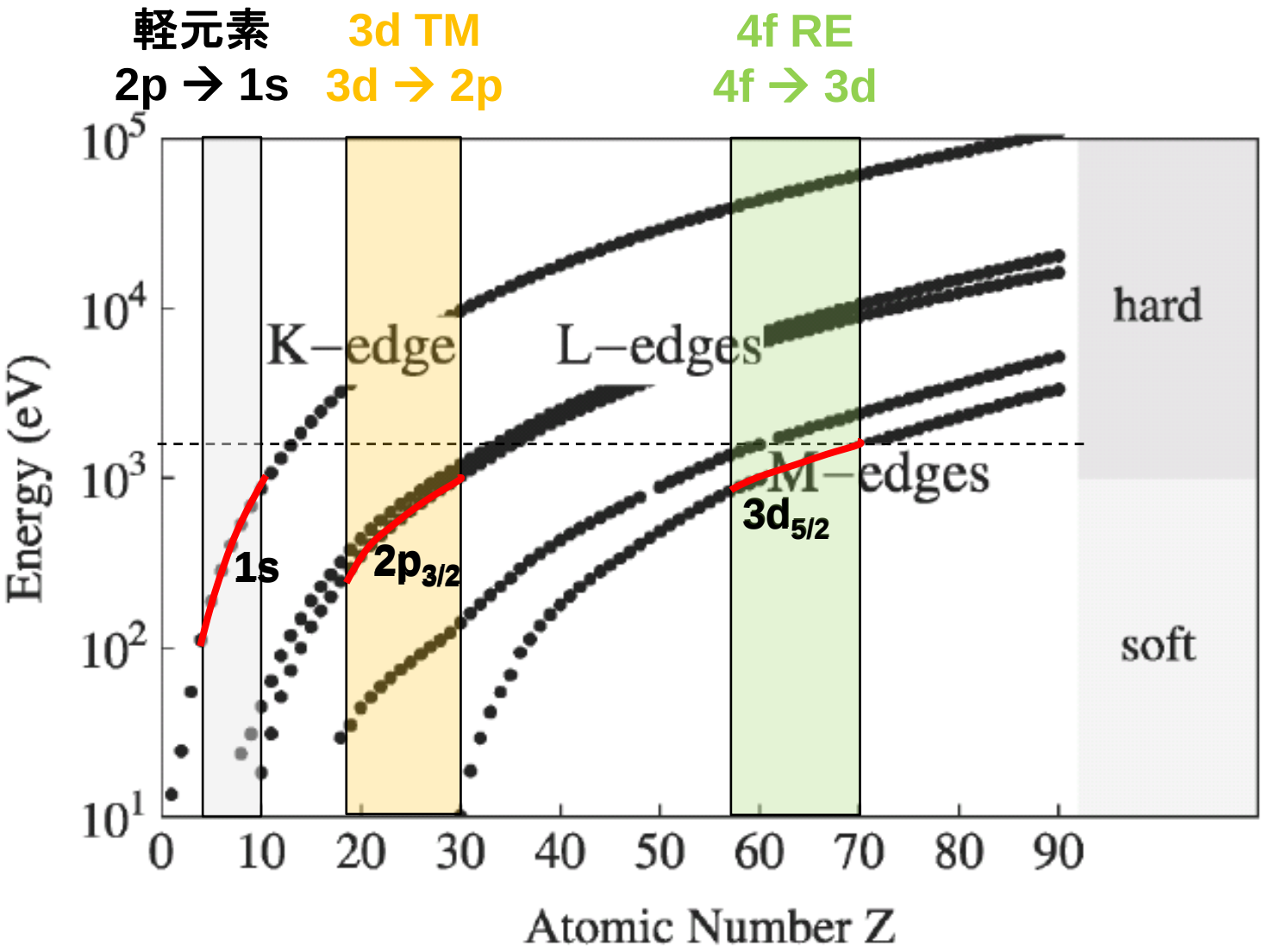
RIKEN/SPring-8

T. Tokushima, Y. Horikawa and S. Shin

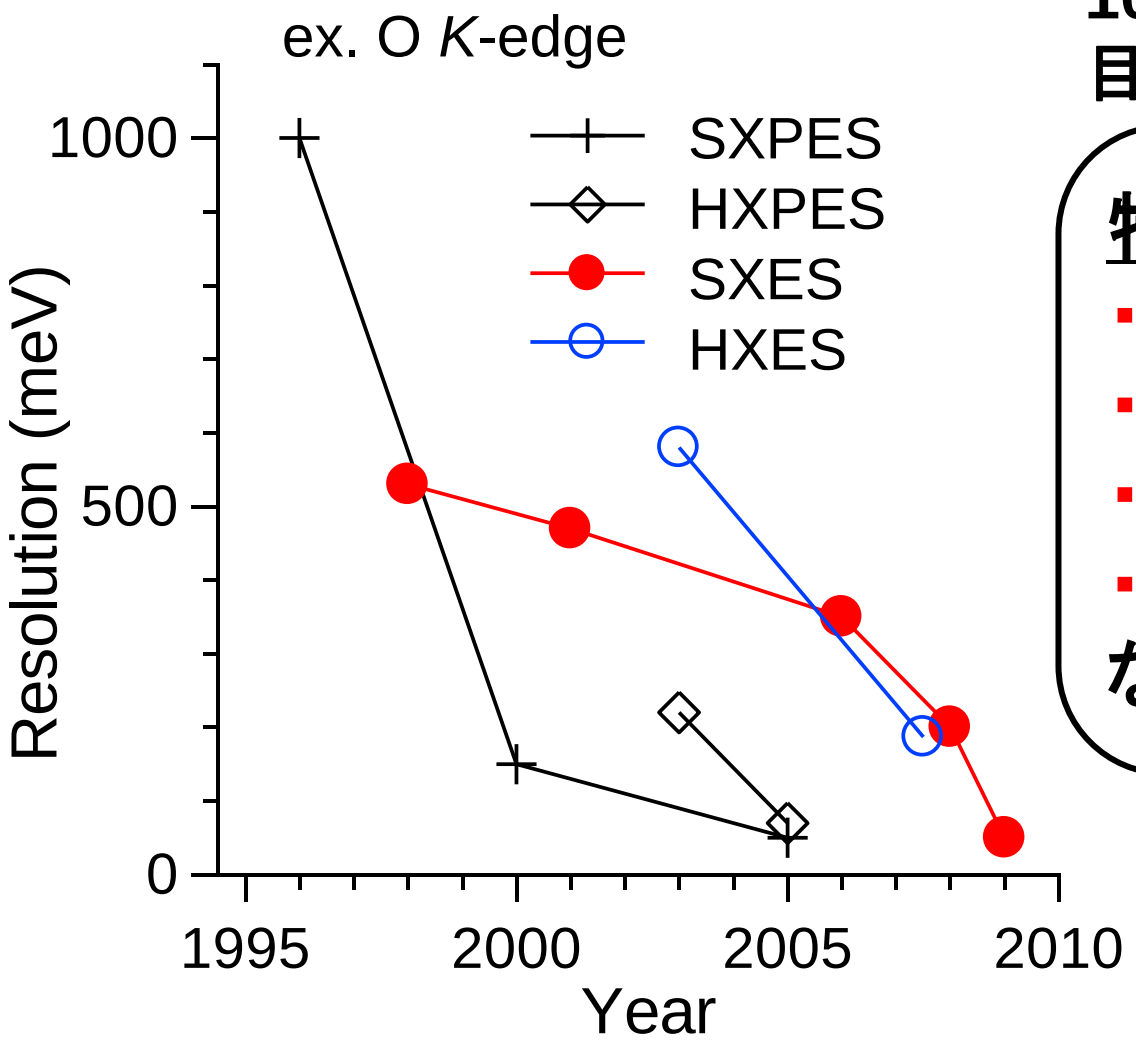
Budget

NEDO & CREST

元素選択性と軟X線・硬X線



発光分光の高分解能化



100meVオーダーの分解能を目指すことによって．．

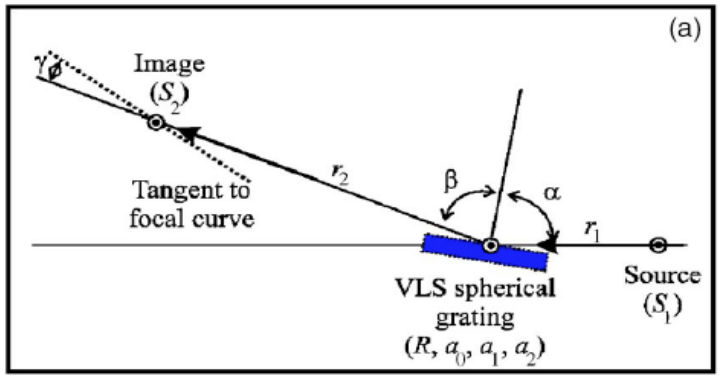
特定の元素・軌道ごとに

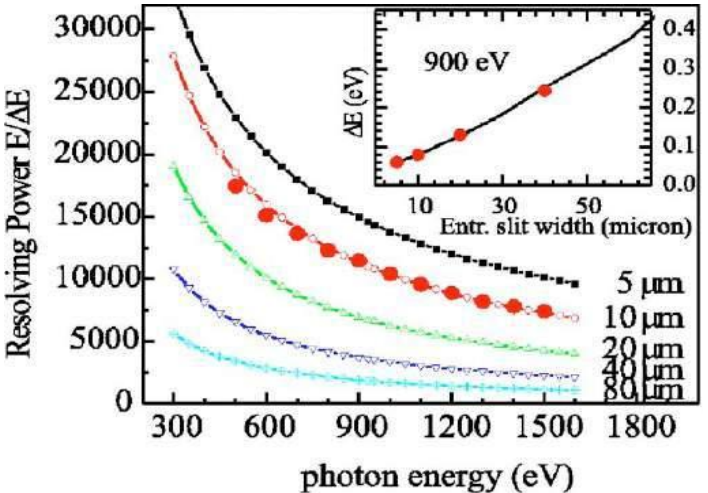
- **結晶場励起**
- **振動励起**
- **スピン励起**
- **軌道秩序励起**

などを見ることができる。

Ultra-high resolution SXES spectrometer

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





Energy resolution

Standard:

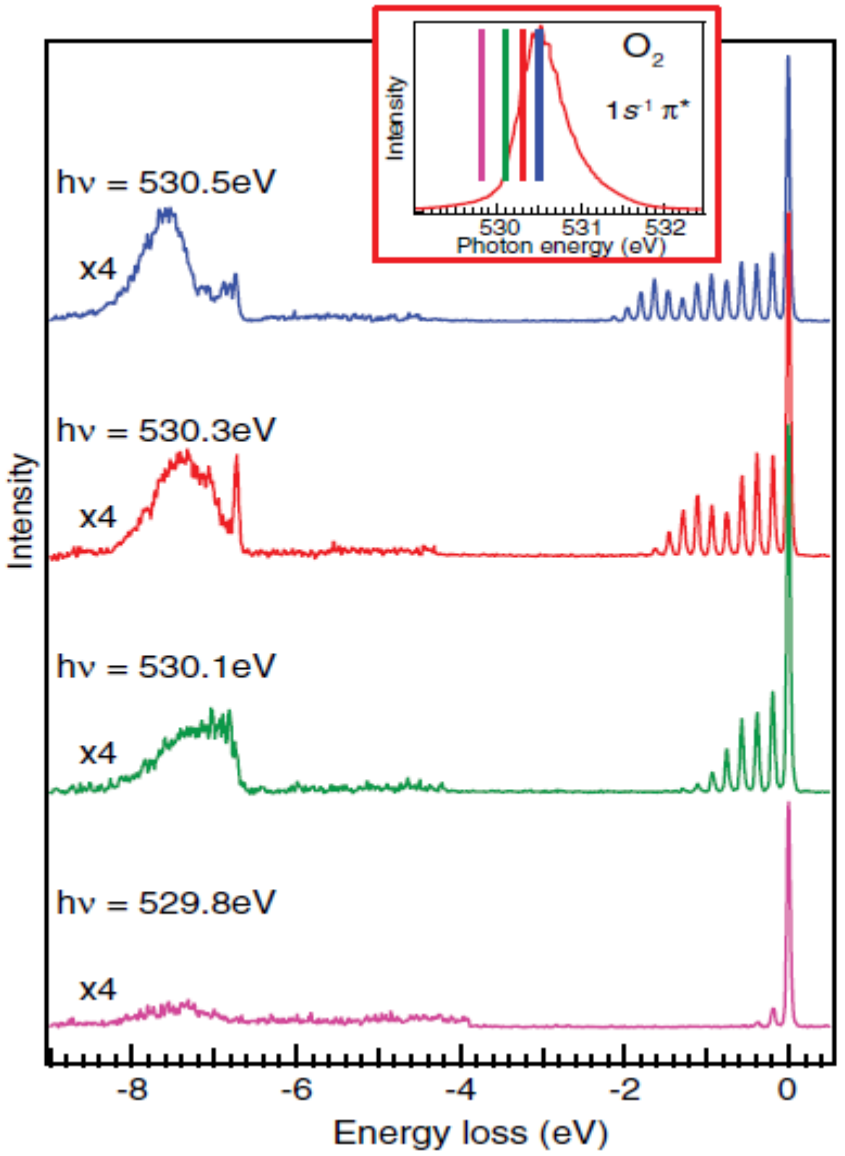
$E/\Delta E < 2000$

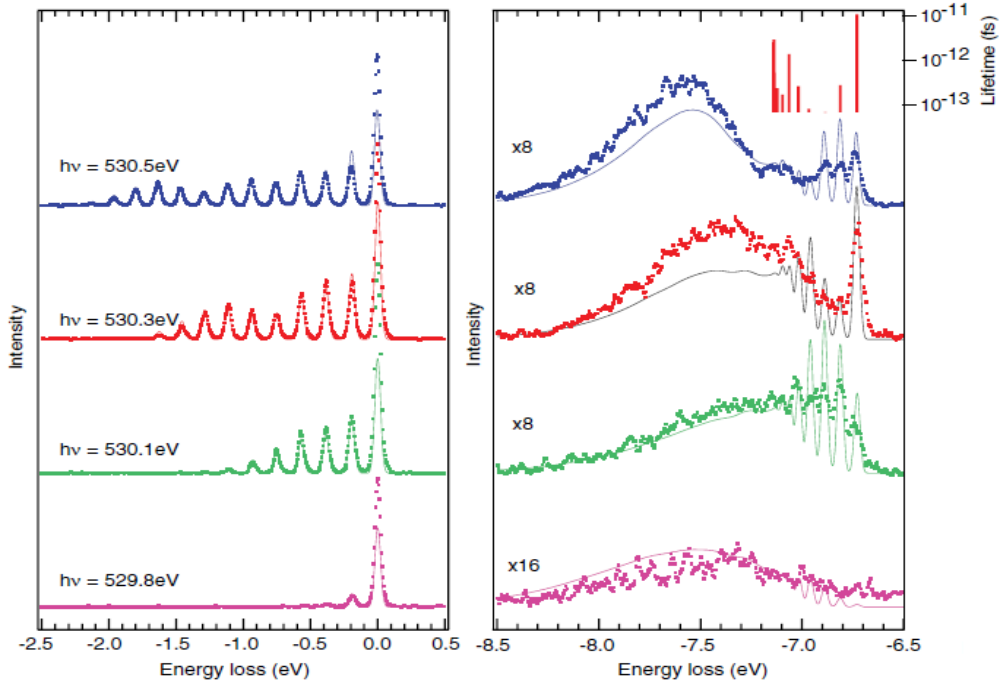
SAXES:

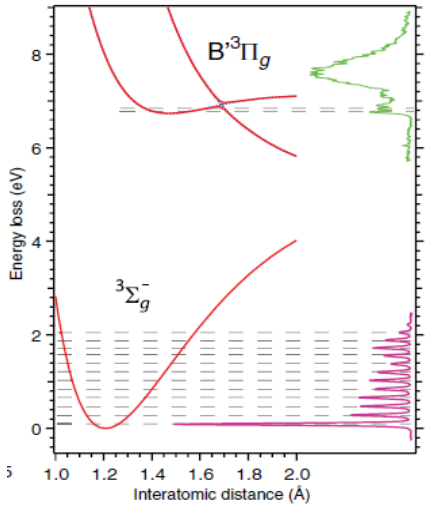
$E/\Delta E > 10{,}000$

Ultra-high resolution → Vibration (~0.1eV)

Vibrational progression





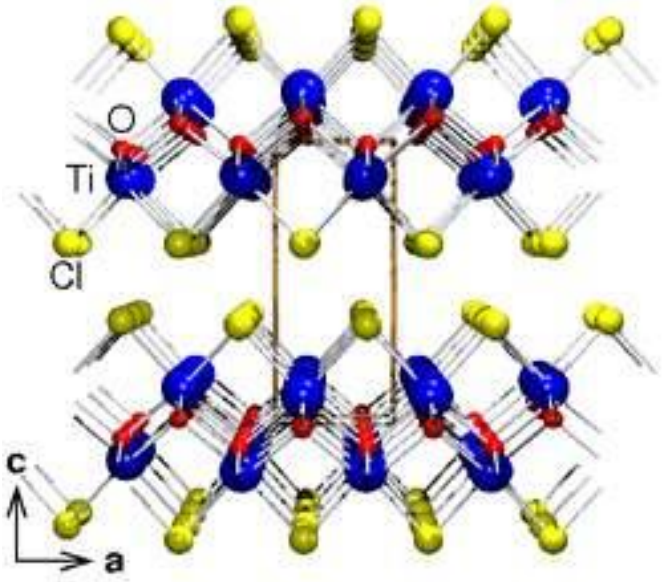


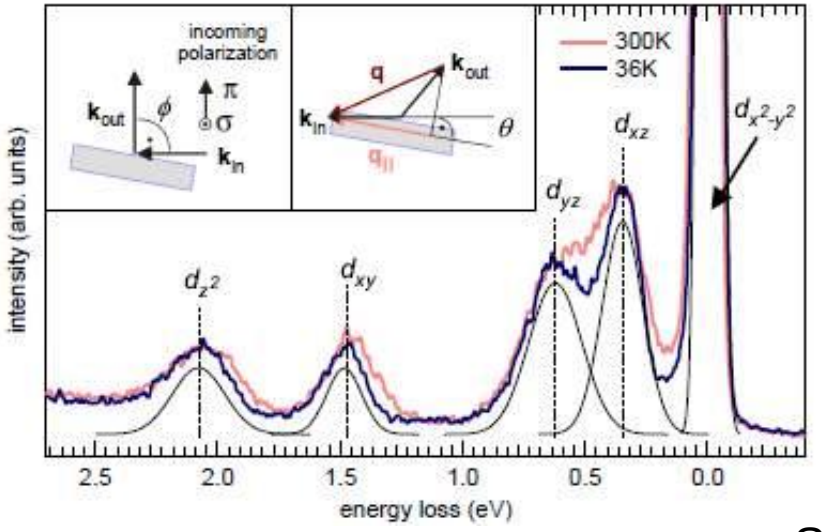
$E/\Delta E \sim 10000$

エネルギーポテンシャルに応じた振動励起の発達→隣接原子、分子との相互作用の詳細が分かる。

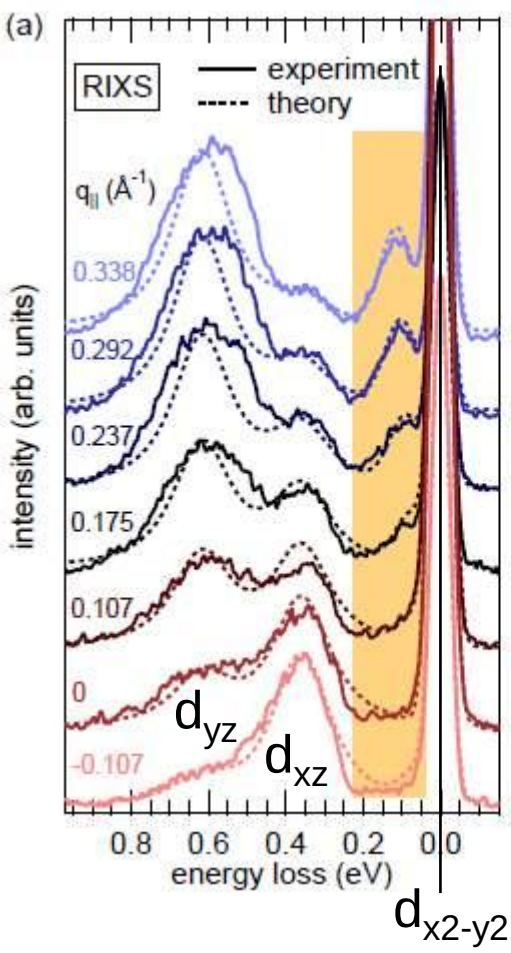
F. Hennies *et al.*, Phys. Rev. Lett. **104**, 193002 (2010).

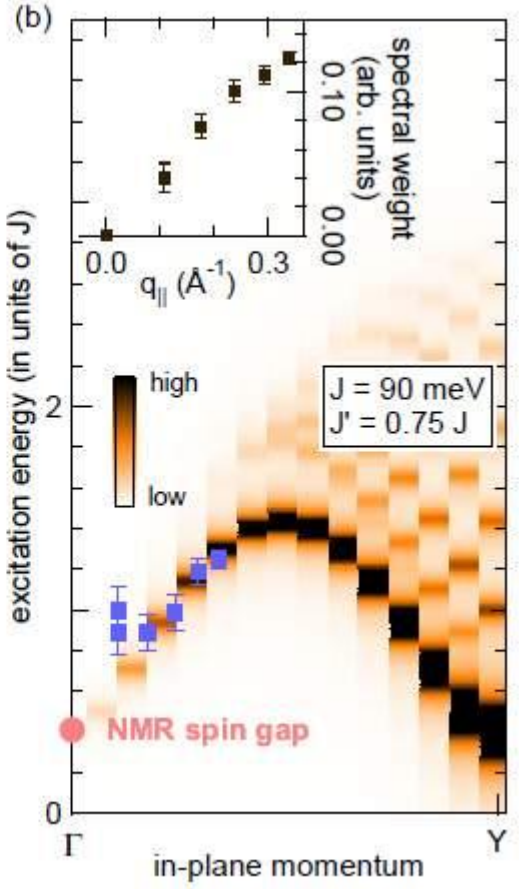
Ultra-high resolution ⊗ Q-dependence → spinon & orbital excitations (~0.1eV)





Ti 2*p* RXES of TiOCl





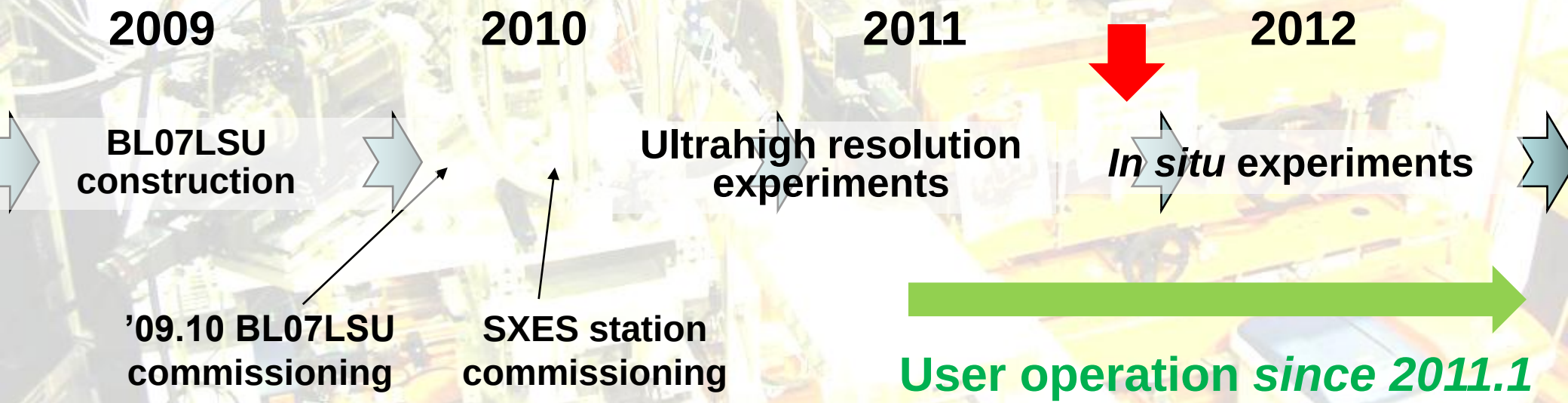
S. Glawion *et al.*, Phys. Rev. Lett. **107**, 107402 (2011).

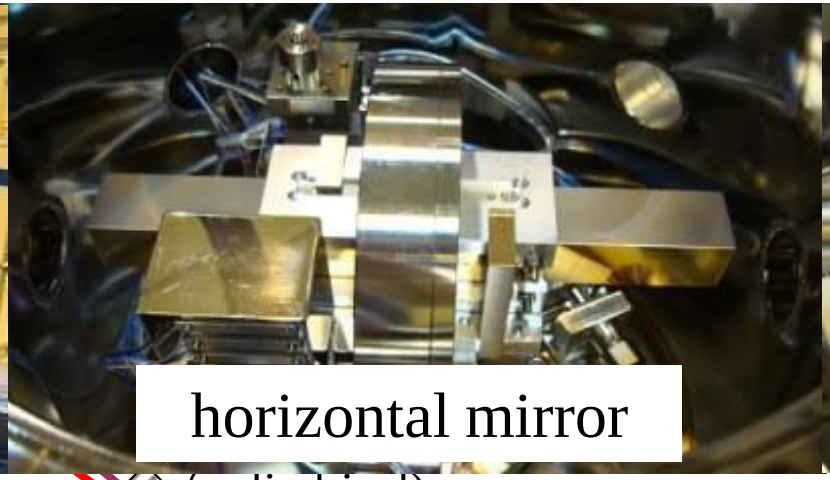
Concept of SPring-8 BL07LSU SXES station

Ultrahigh energy resolution

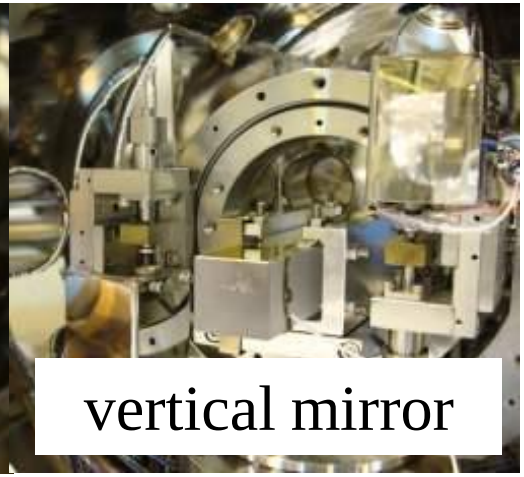
with *in situ* (air pressure) experiments

Commissioning & operation schedule





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

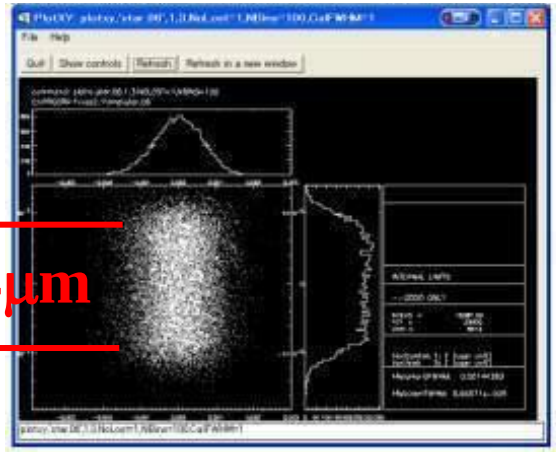
R_a=11600mm
R_b=90mm

horizontal

exit slit

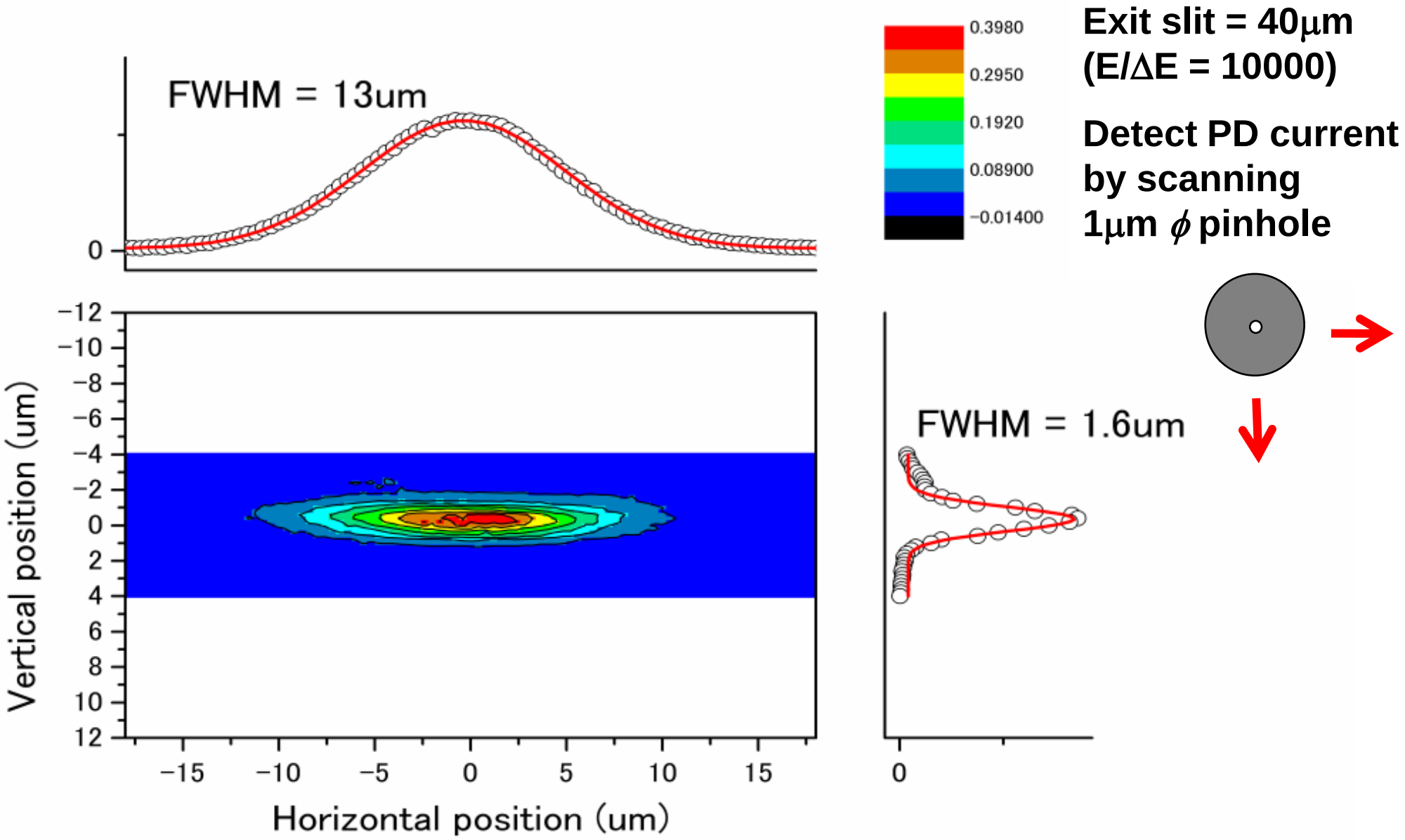
22m

1/150
demagnification

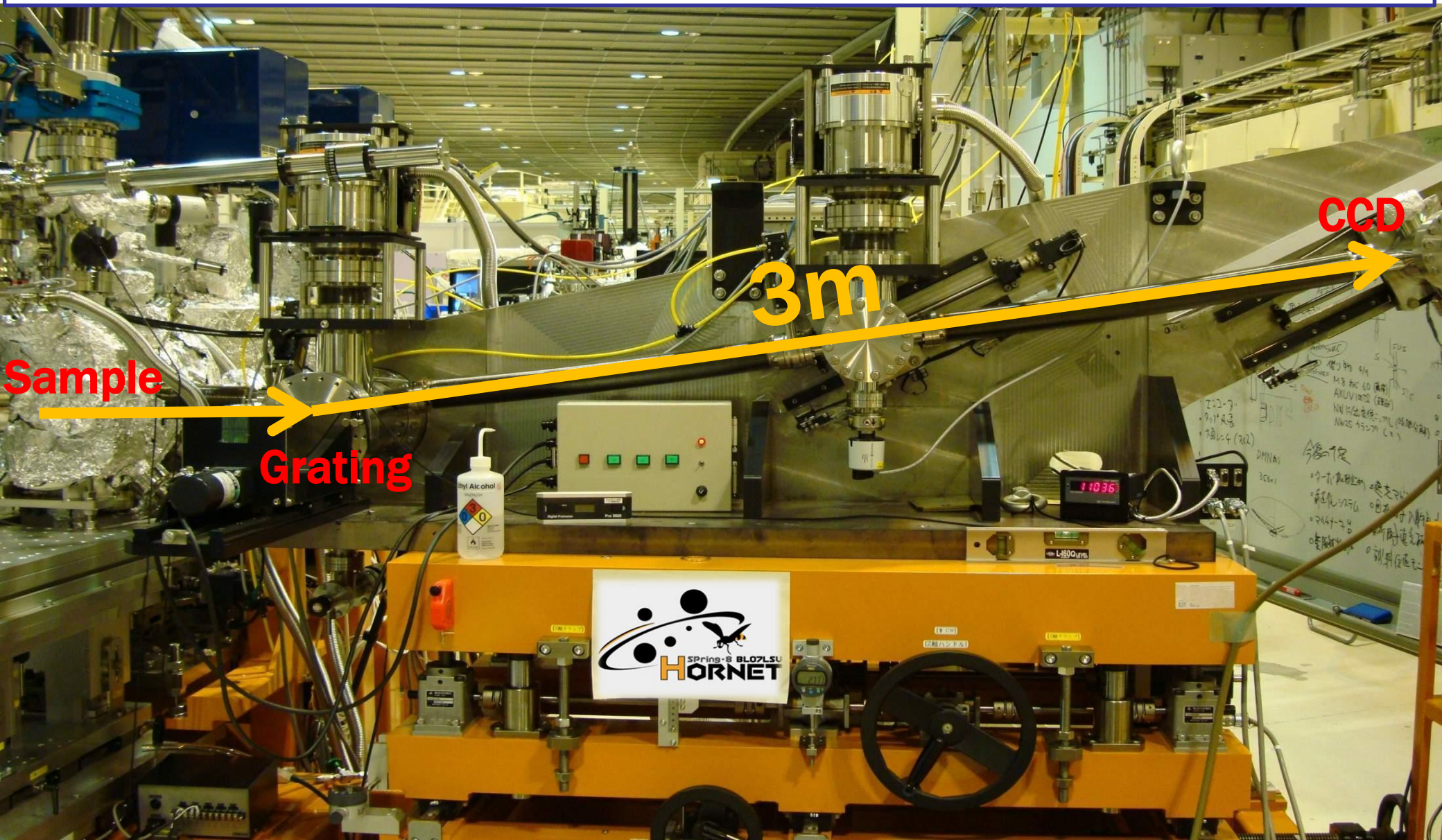


0.4μm

HORNET XES station Focused image @ sample position



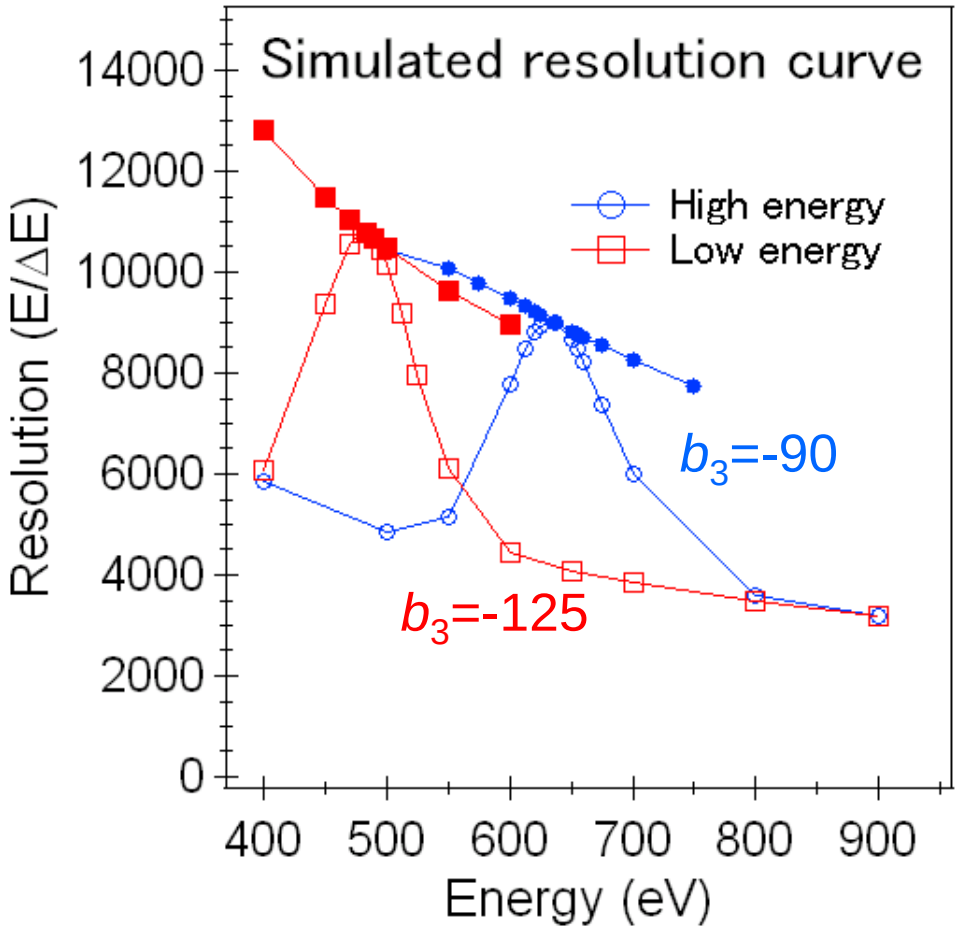
Ultra high resolution soft X-ray emission (HORNET) @ SPring-8 BL07LSU

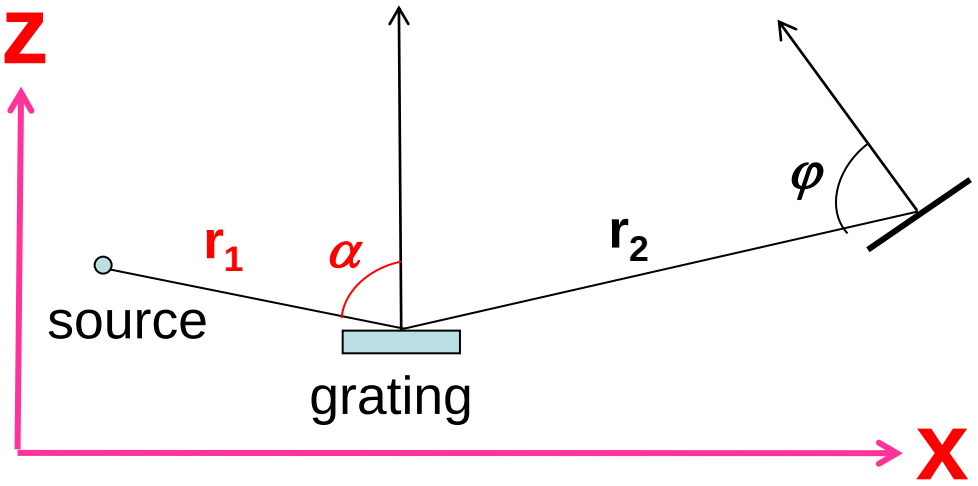


Simulated energy resolution

→applying coma-free mode

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





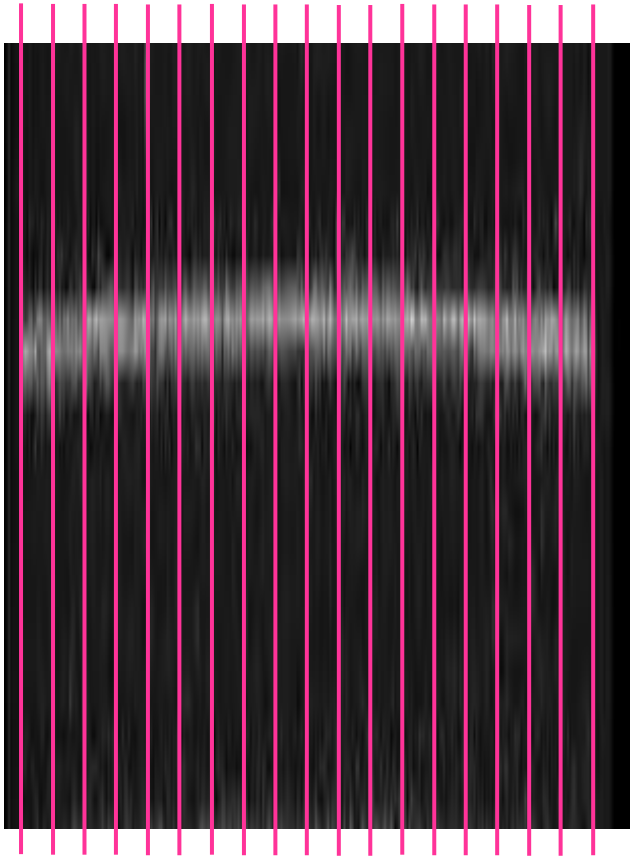
Two parameters

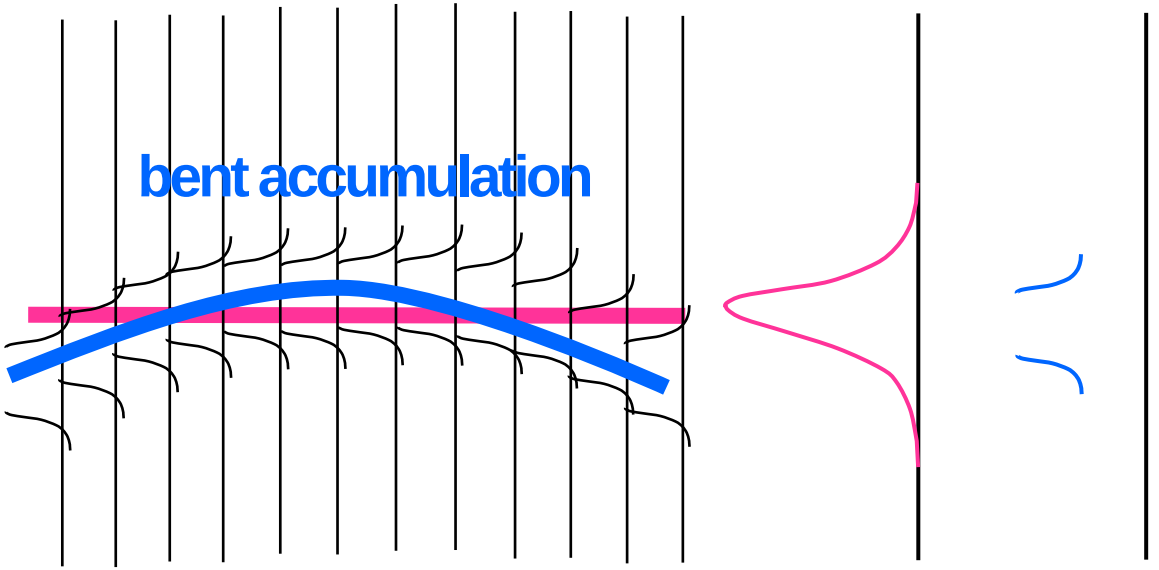
r_1 & α

Only two linear axis

x & z

Bent correction of CCD images

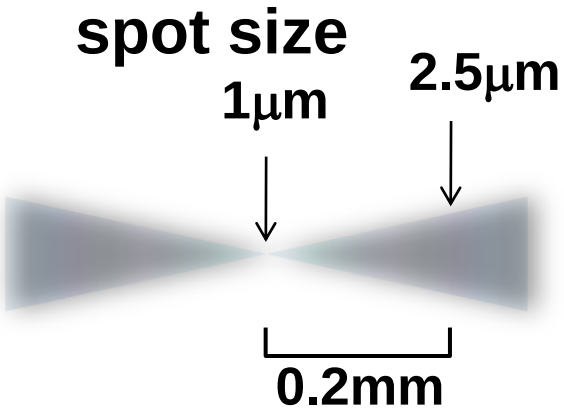


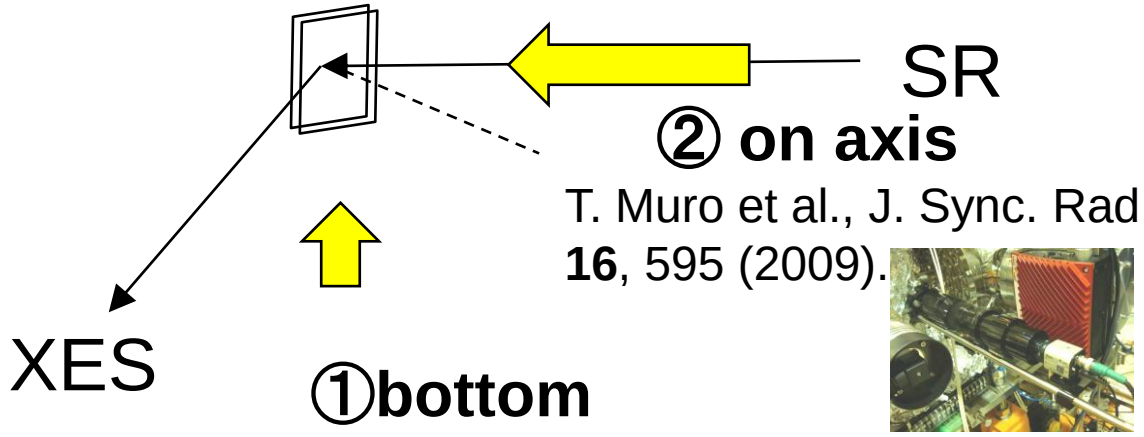


slicing the image

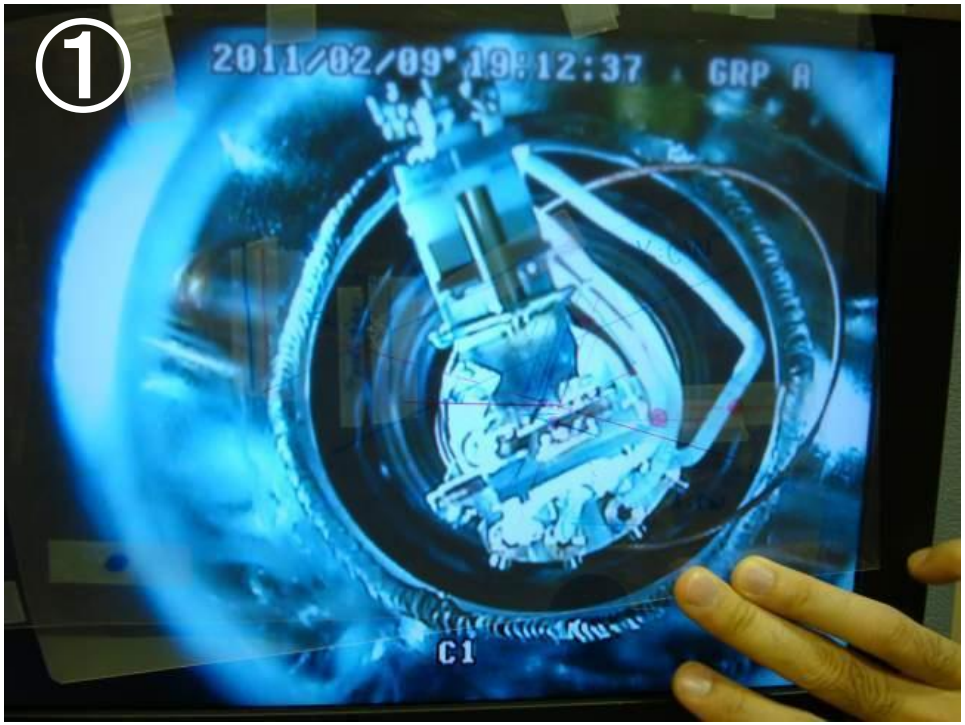
20%~40% improvements in energy resolution

Precise alignment of the sample position

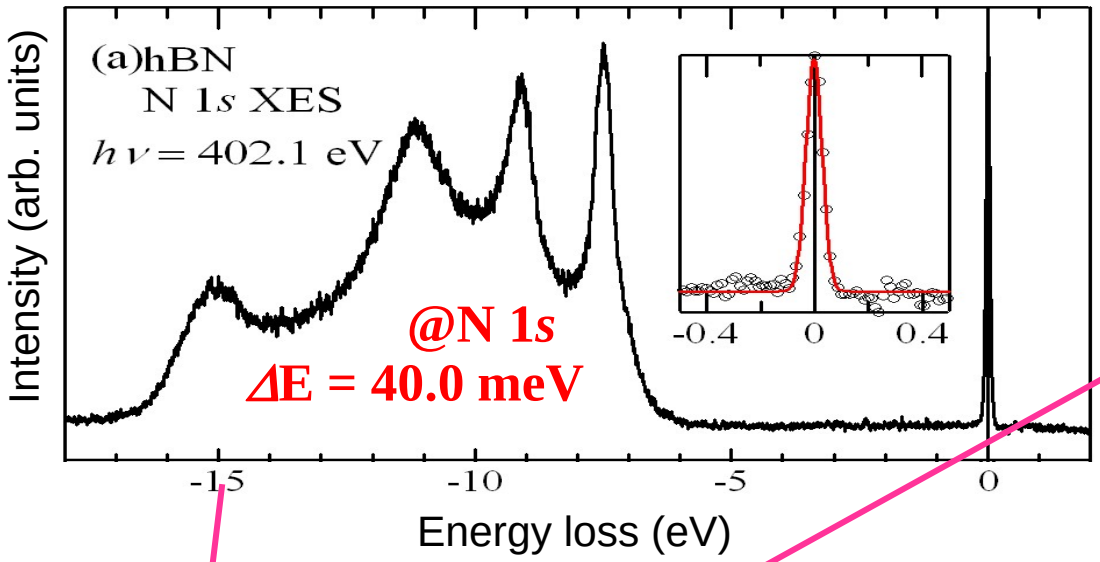


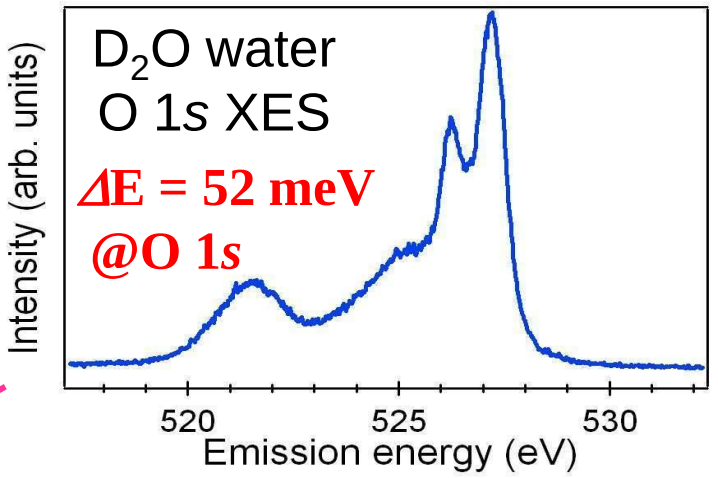


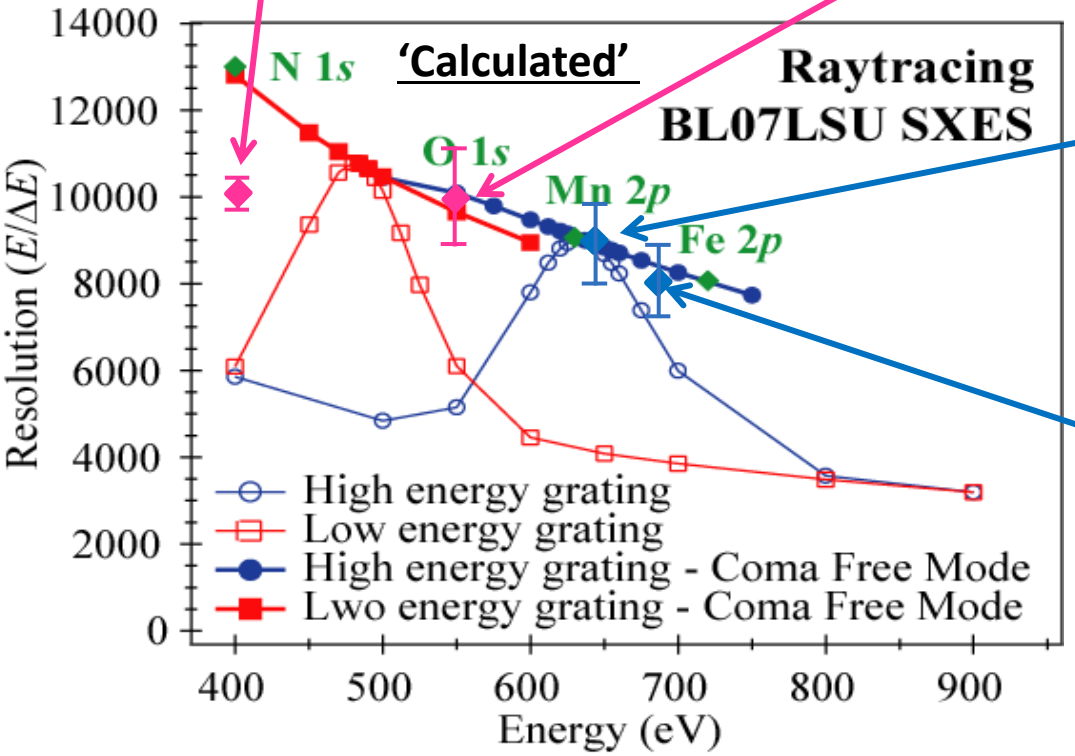
T. Muro et al., J. Sync. Rad. **16**, 595 (2009).

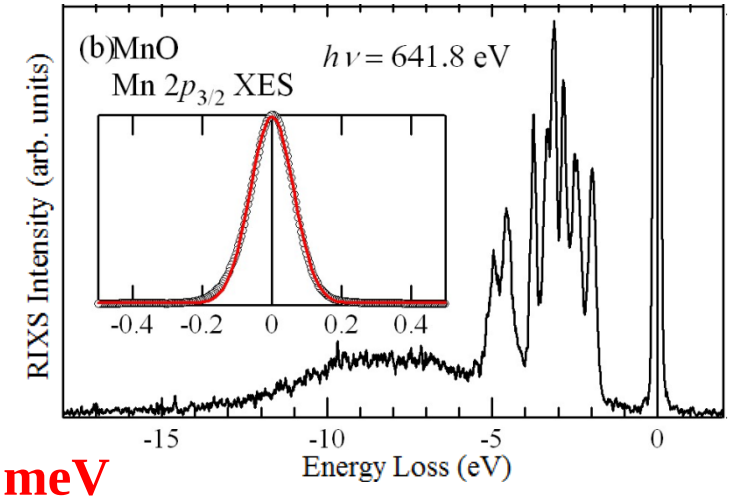


‘Calculated’ vs ‘Measured’ resolution

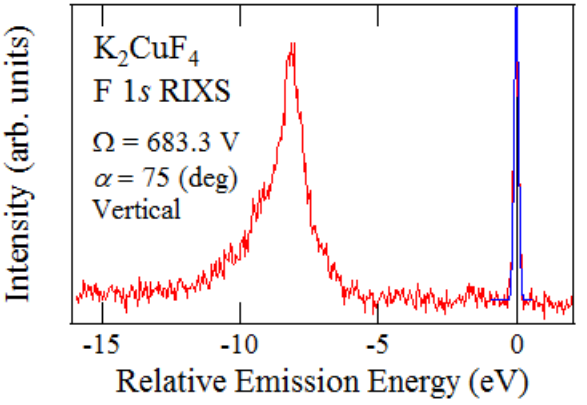








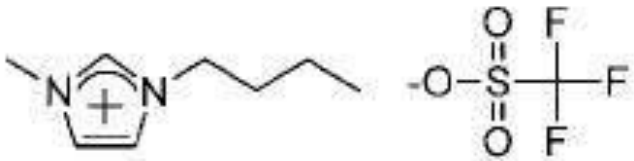
ΔE = 70 meV
@Mn 2p

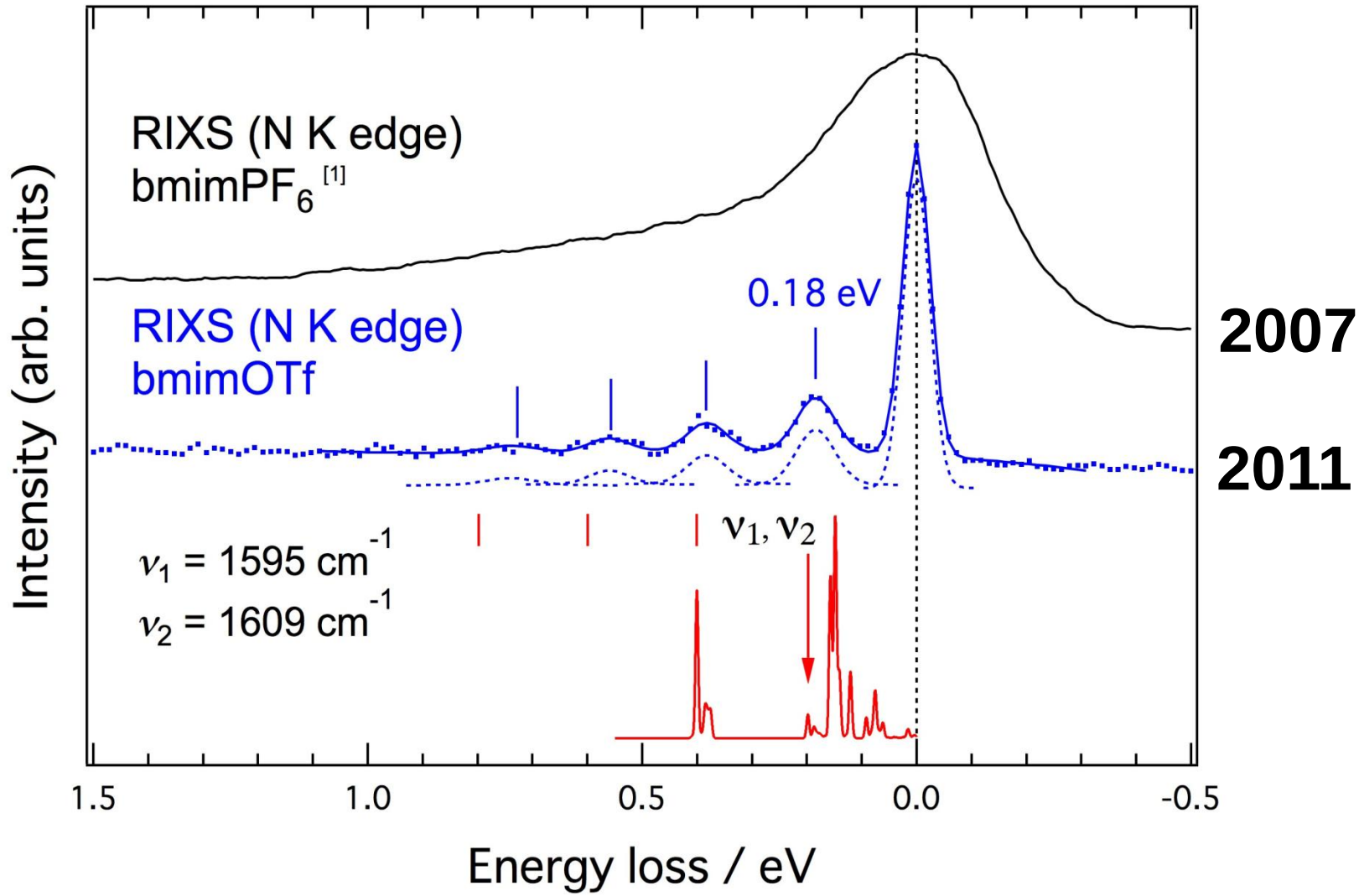


ΔE = 90 meV
@F 1s

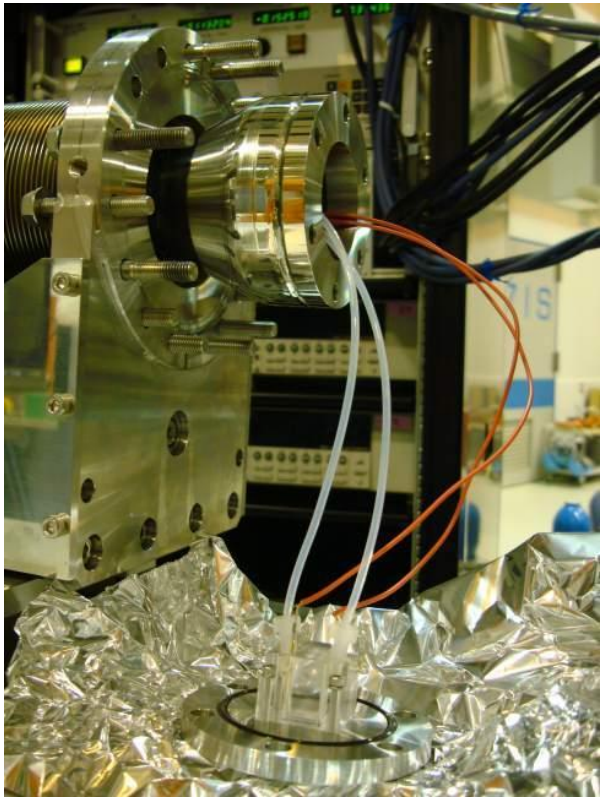
Vibrational progression of Ionic liquids

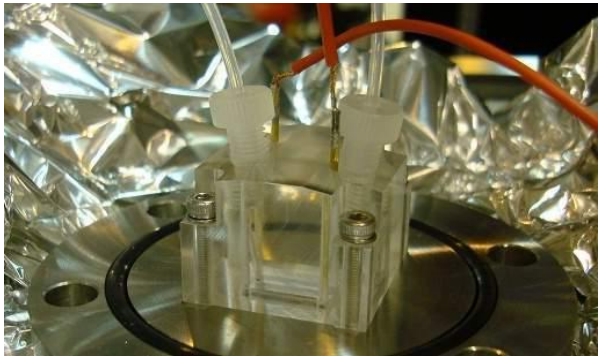
By Asoc.Prof. K. Kanai and Y. Ouchi



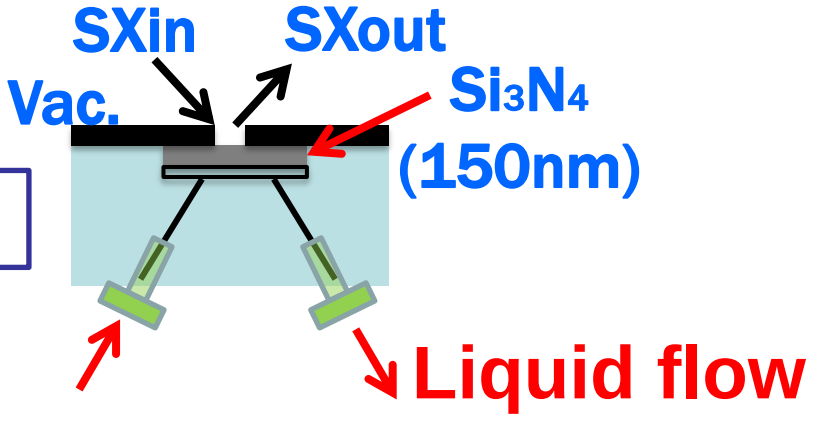


溶液・大気圧下試料の軟X線発光



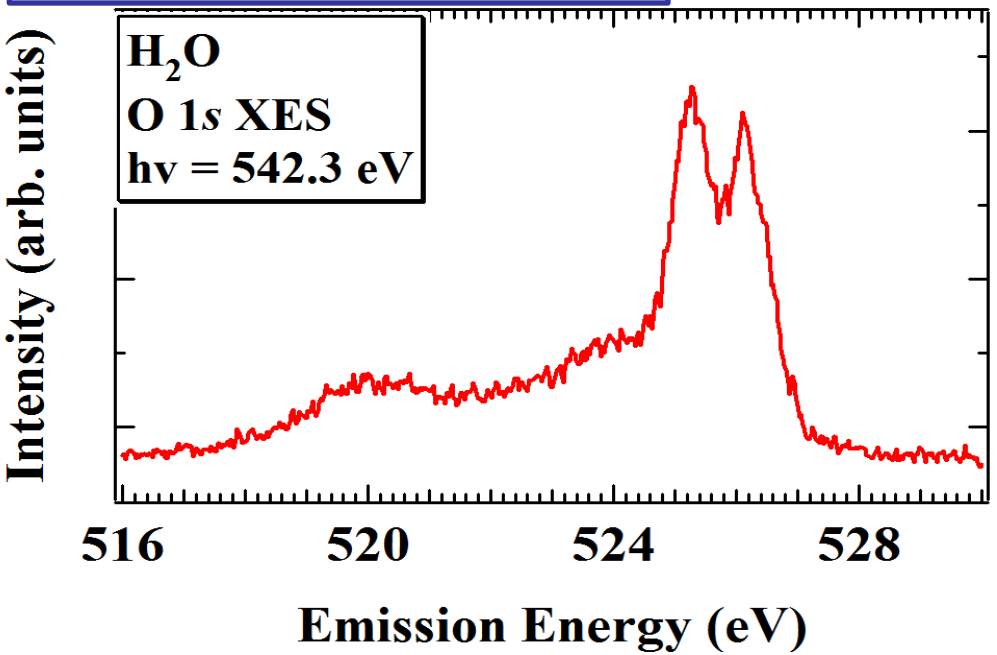


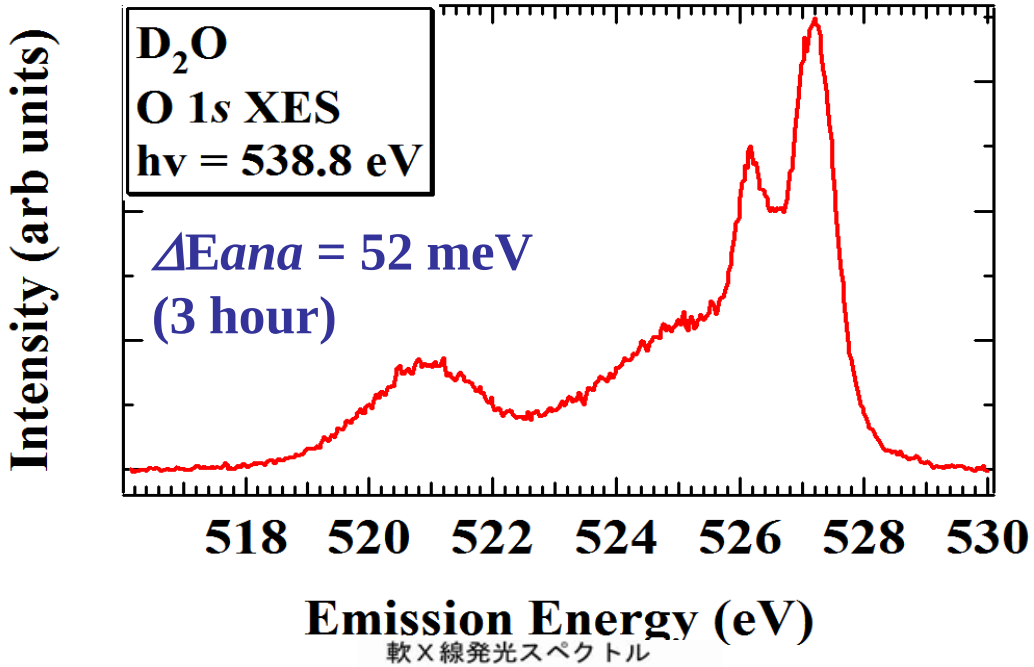
in situ cell



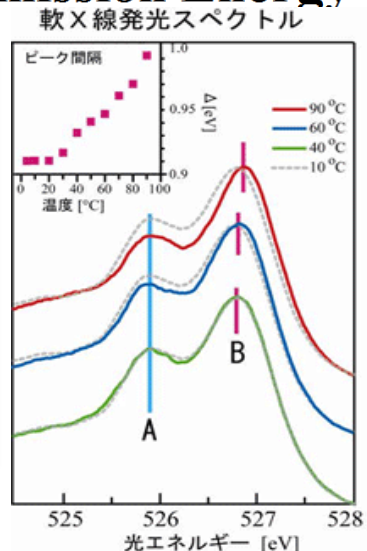
溶液・大気圧下試料の軟X線発光（結果）

H_2O and D_2O (liquid)



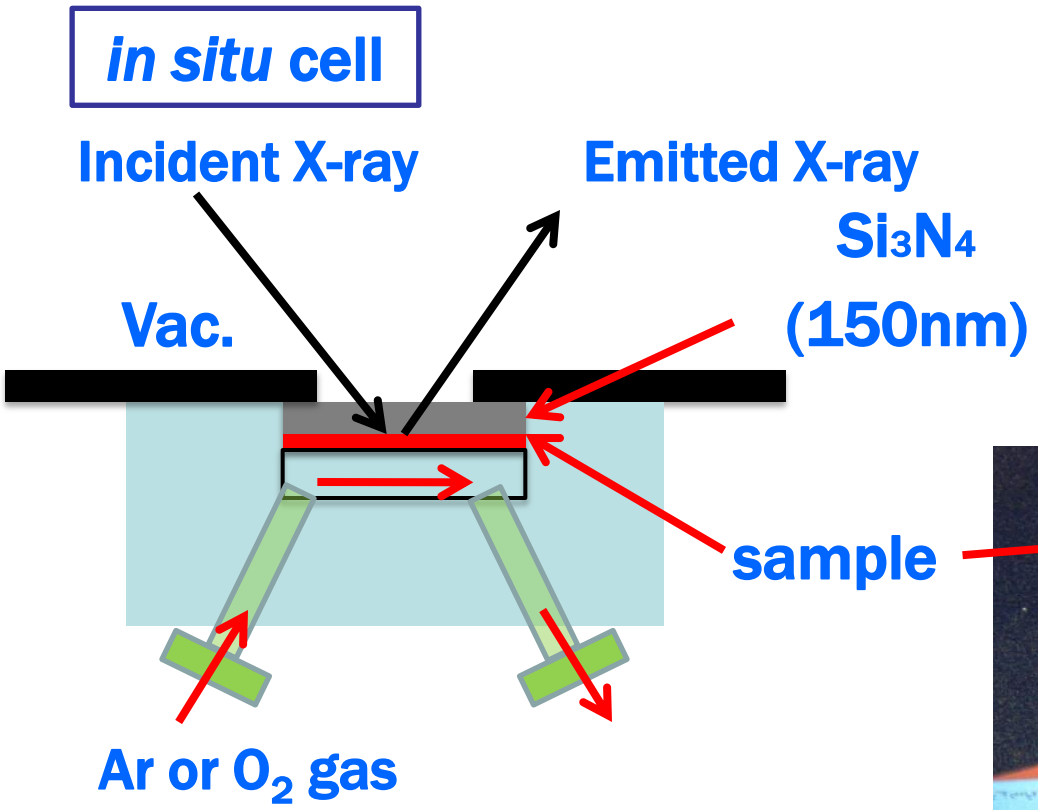


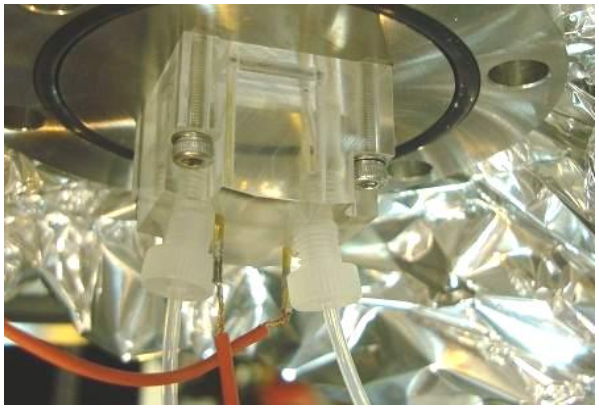
Ultra-high resolved XES spectra of H_2O and D_2O are obtained.
Total resolution: ~5000
Res. of analyzer: ~10000
(Curvature correction by program)

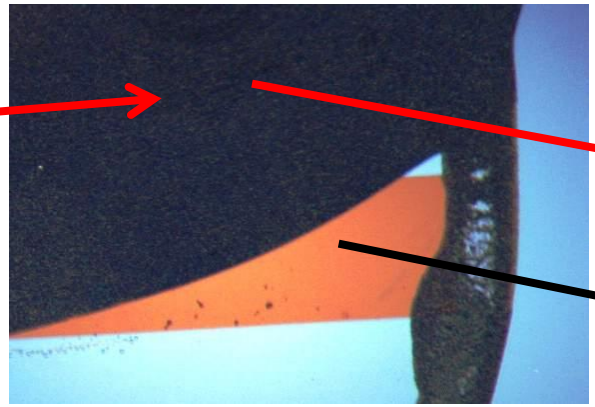


T.Tokushima *et al.* @CPL(2008).

True air pressure experiment



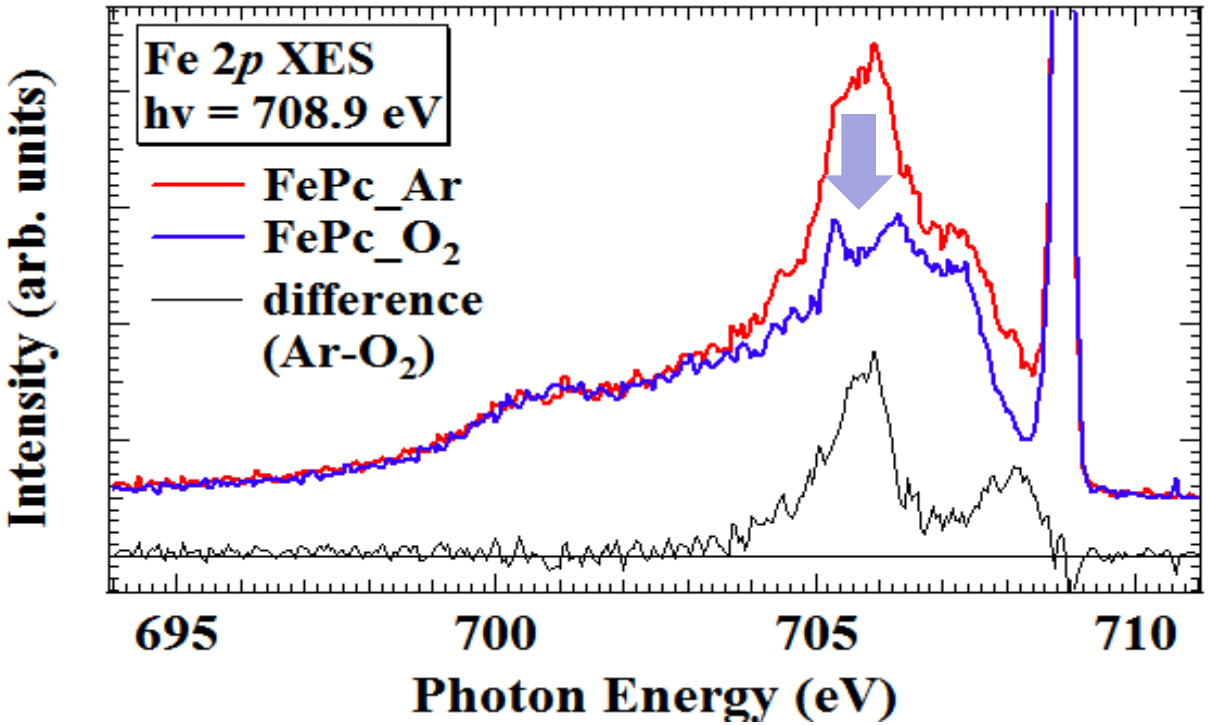


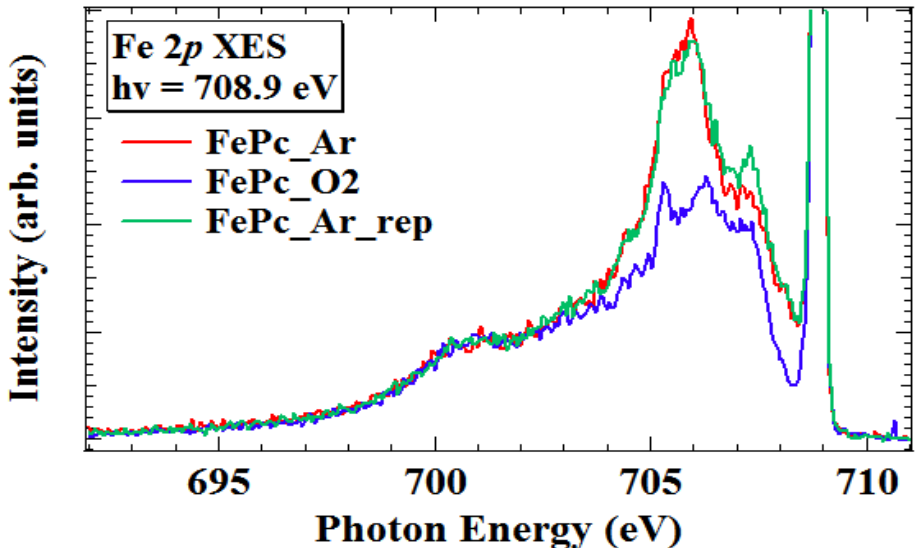


In situ **cell which separates vacuum condition and ambient gas condition was fabricated.**

Ultimate pressure (Vacuum side): $3x10^{-6}$ Pa

True air pressure experiment





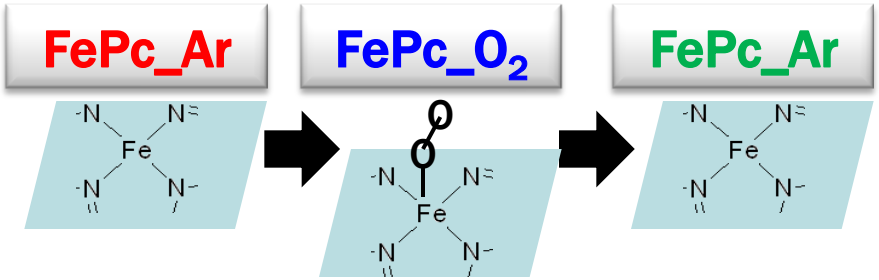
Successfully, the effect of oxygen adsorption to valence electronic states are observed.

When oxygen molecule adsorb on FePc, intensity of valence electronic states are decreased.

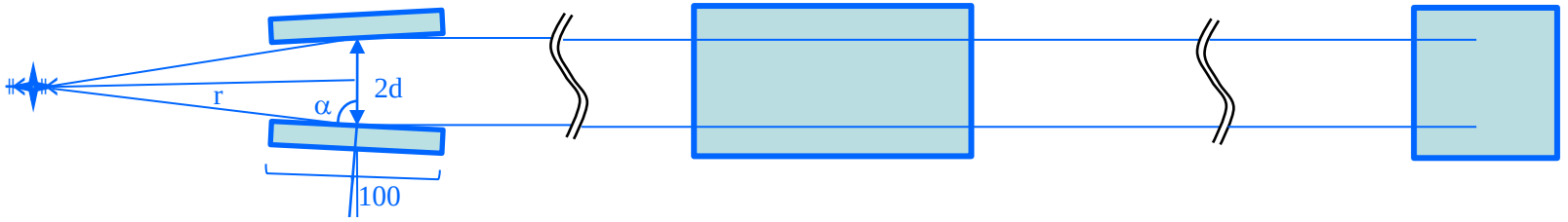
⇒Electron donation from Fe (d_{z2}) to oxygen (π^*) occurred (back donation).

Adsorped oxygen can desorp.

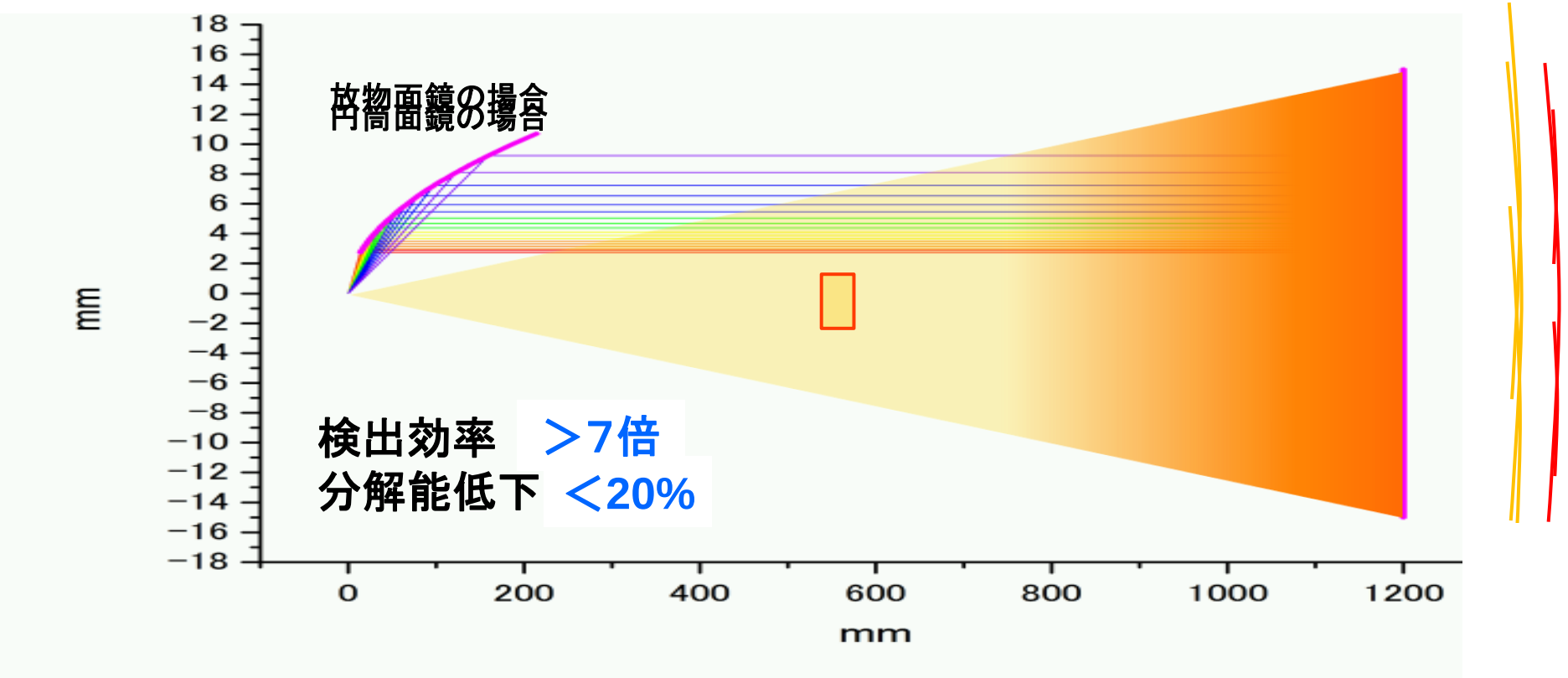
=> weak Fe-O_2 bond



前置ミラーの導入

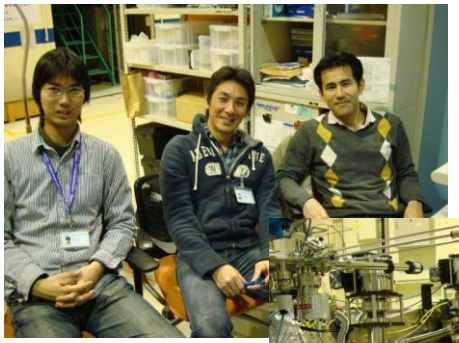


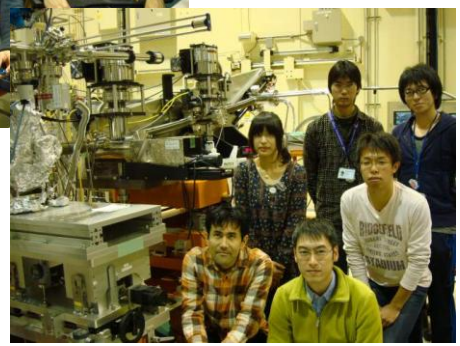
回折格子　　検出器



T. Tokushima *et al*., Rev. Sci. Instrum. 82, 073108 (2011).

研究プロジェクト（2010～）





S型課題

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、NEDO）
2. タンパク質の*in situ*状態分析（S型：小林、G型：東邦大大胡先生）
3. 拡張ナノ水、溶液解析（S型：丹羽、東大応化）
4. 水素吸蔵合金の水素吸蔵機構（G型：筑波大関場先生）
5. イオン液体の振動分光（G型：東京理科大金井先生）
6. Orbiton励起の観測（S型：小林、KEK、JAEA）
7. 光触媒の界面電子状態（G型：東大物性研吉信先生）
8. リチウムイオン電池の*in situ*状態分析（G型：産総研朝倉先生）

まとめ

東大ビームラインBL07LSU最下流部に超高分解能軟X線発光分光装置を建設。分解能E/ΔE ~10000を550 eV以下のエネルギー範囲で達成した。（750 eV以下ではE/ΔE >8000）

■本ステーション開発のポイント

1. 究極の縮小光学配置による後置（KB）ミラーで試料上で1μm程度の集光を実現した。
2. 検出器の位置分解能に制約されず、かつ明るさを犠牲にしないギリギリの分光器の大きさを追求した。
3. 従来の分光器調整駆動機構に、高次の収差（コマ収差など）を補正できる駆動軸を追加した。
4. 溶液試料の測定も同じチェンバーで簡便に行えるシステムを組み込んだ。

■G課題による一般課題の受付を開始（ ～2011A期）

超高分解能を活かせる実験課題、他の手法ではわからない大気圧環境下の電子状態（溶液を含む）、組み合わせ実験の申請をお待ちしています。

2012A期の実験課題申請：H24．1．10頃

http://www.issp.u-tokyo.ac.jp/labs/sor/ ←ブックマーク！