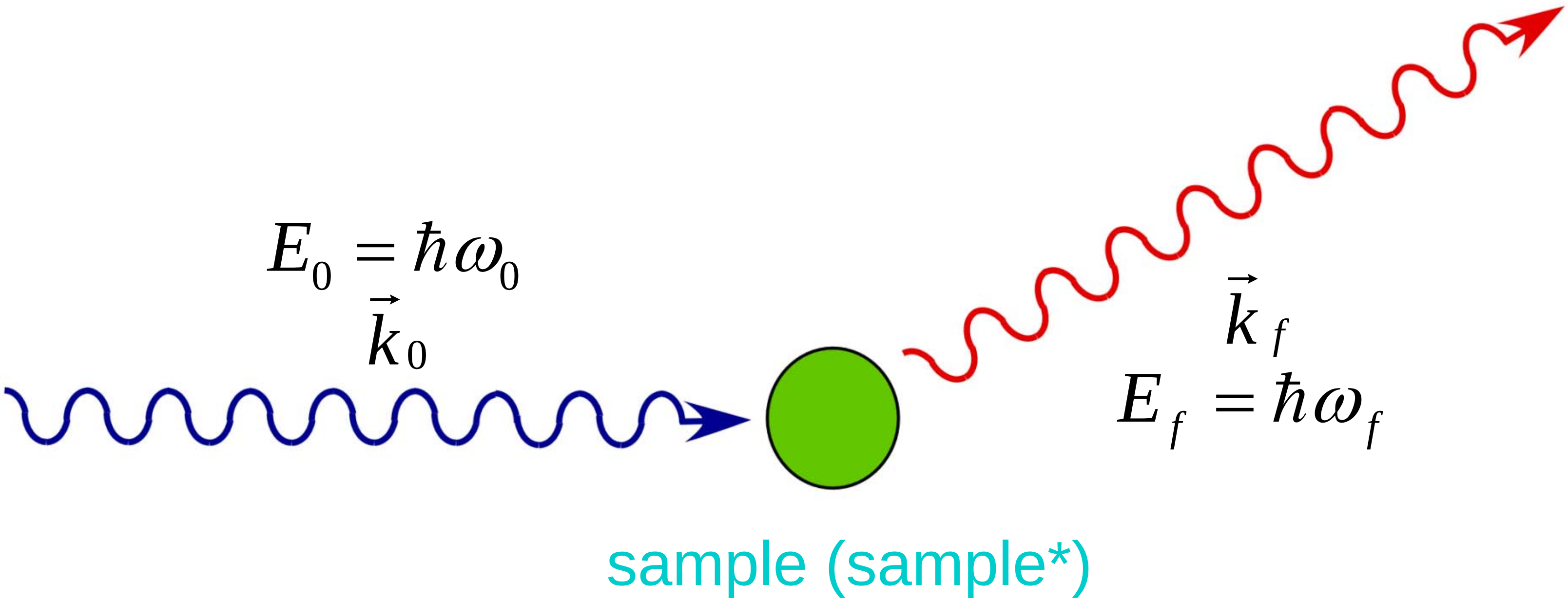
miniXS Evolution:
The Fast Track from Gadget to GU-Ready Instrument

Jerry Seidler (seidler@uw.edu)

- Undergrads: Brian Dickinson, Matt Haave, John Krah
- Grad Students: Ken Nagle , Joe Bradley
- Collaborators: Yuming Xiao & Paul Chow (HP-CAT), Mali Balasubramanian (APS), Anatoly Frenkel & Bruce Ravel (BNL), Doug Pease (UConn), Shelly Kelley & Simon Bare (UOP), Stosh Kozimor & Steve Conradson (LANL), Jeremy Kropf & Deborah Myers (ANL), John Quintana & Brian Rusthoven (APS)
- APS and Beamline staff: Steve Heald, Dale Brewe (APS), Robert Gordon (SFU)
- $: DOE, Bosack&Kruger Foundation, ONR

What can you learn from this experiment?



$$\vec{q} = \vec{k}_f - \vec{k}_0$$
$$\omega = \omega_0 - \omega_f$$

What can you learn from this experiment?

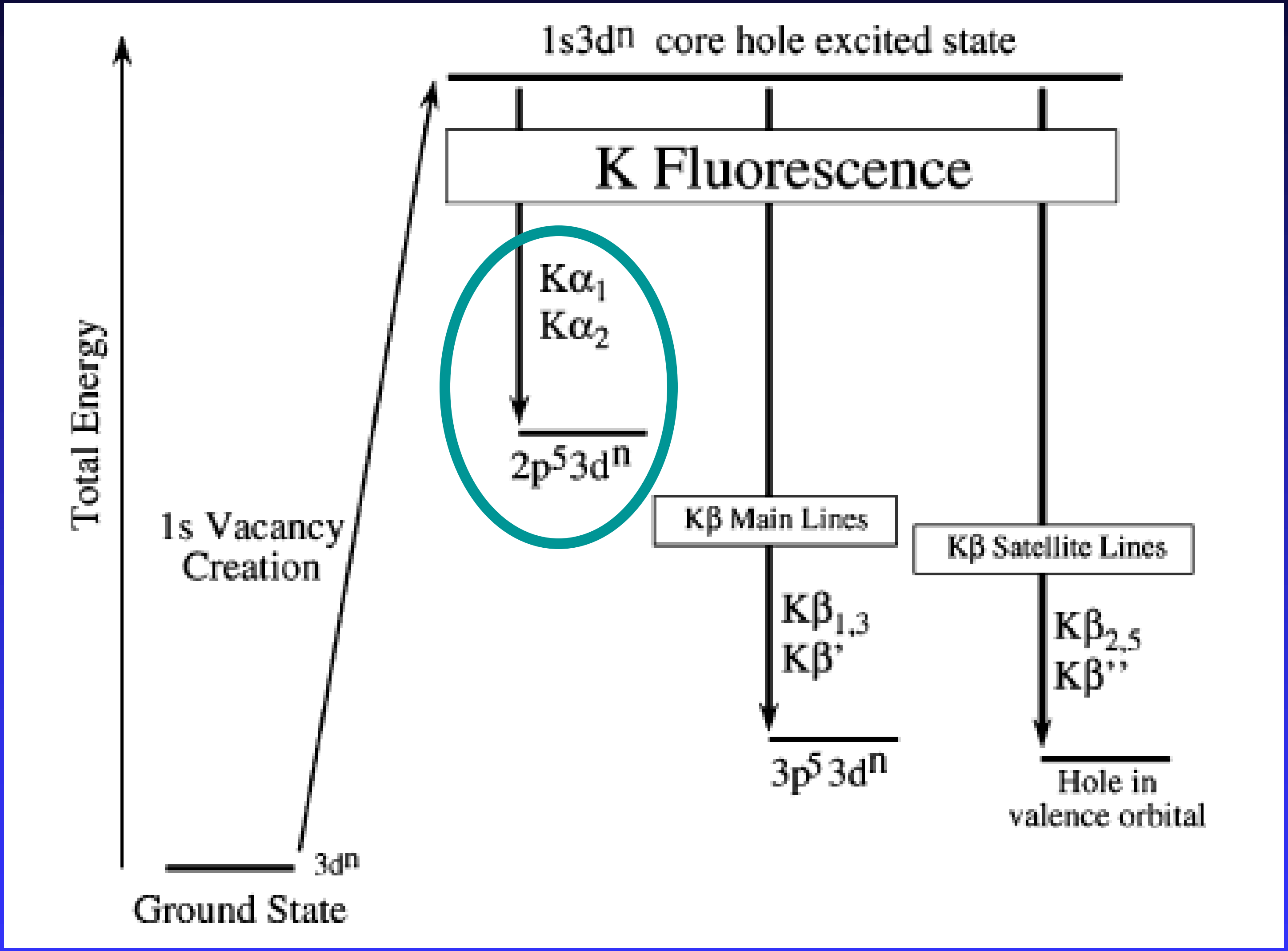
(from weakest to strongest at 10 keV incident photons…)

‘Incoherent’ scattering:
- map momentum-space electronic wave function
- dynamics: local electronic structure, plasmons, phonons, …

‘Elastic’ scattering:
- relative atomic placement, nearest neighbor distances, full xtal structures…

Photoelectric processes:
- x-ray absorption spectroscopies
-fluorescence mapping
- x-ray emission spectroscopies
- resonant inelastic x-ray scattering (RIXS)

An example: 3d-transition metal XES…



(Nonresonant) Kα: some sensitivity to valence and spin

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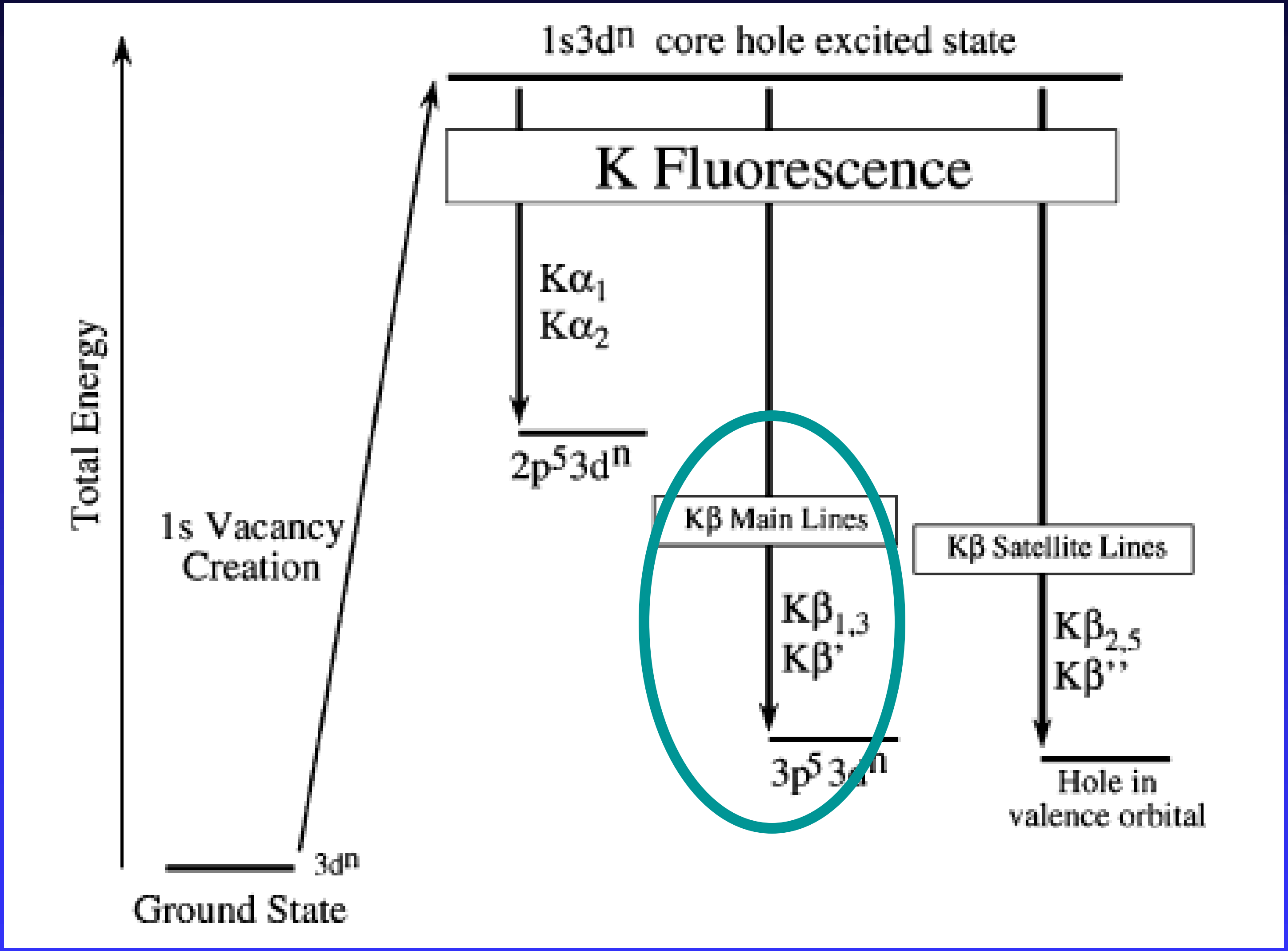

(Nonresonant) Kβ: Srong sensitivity to ion spin, also sensitivity to valence (for light TM) and bonding (for heavier TM)

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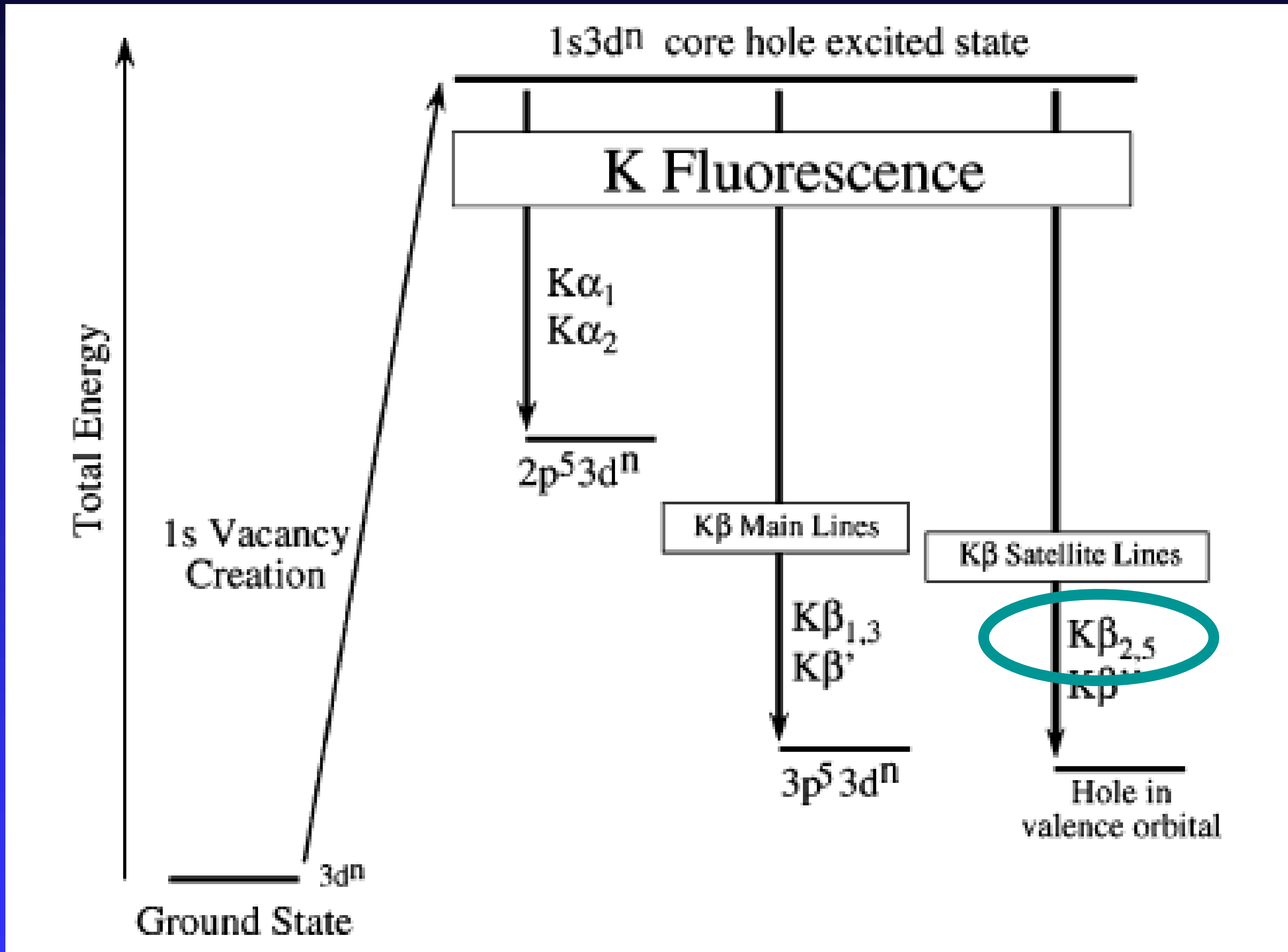

(Nonresonant) Kβ2,5: valence band XES – probe of occupied states near EF. Natural complement to XANES pre-edge studies

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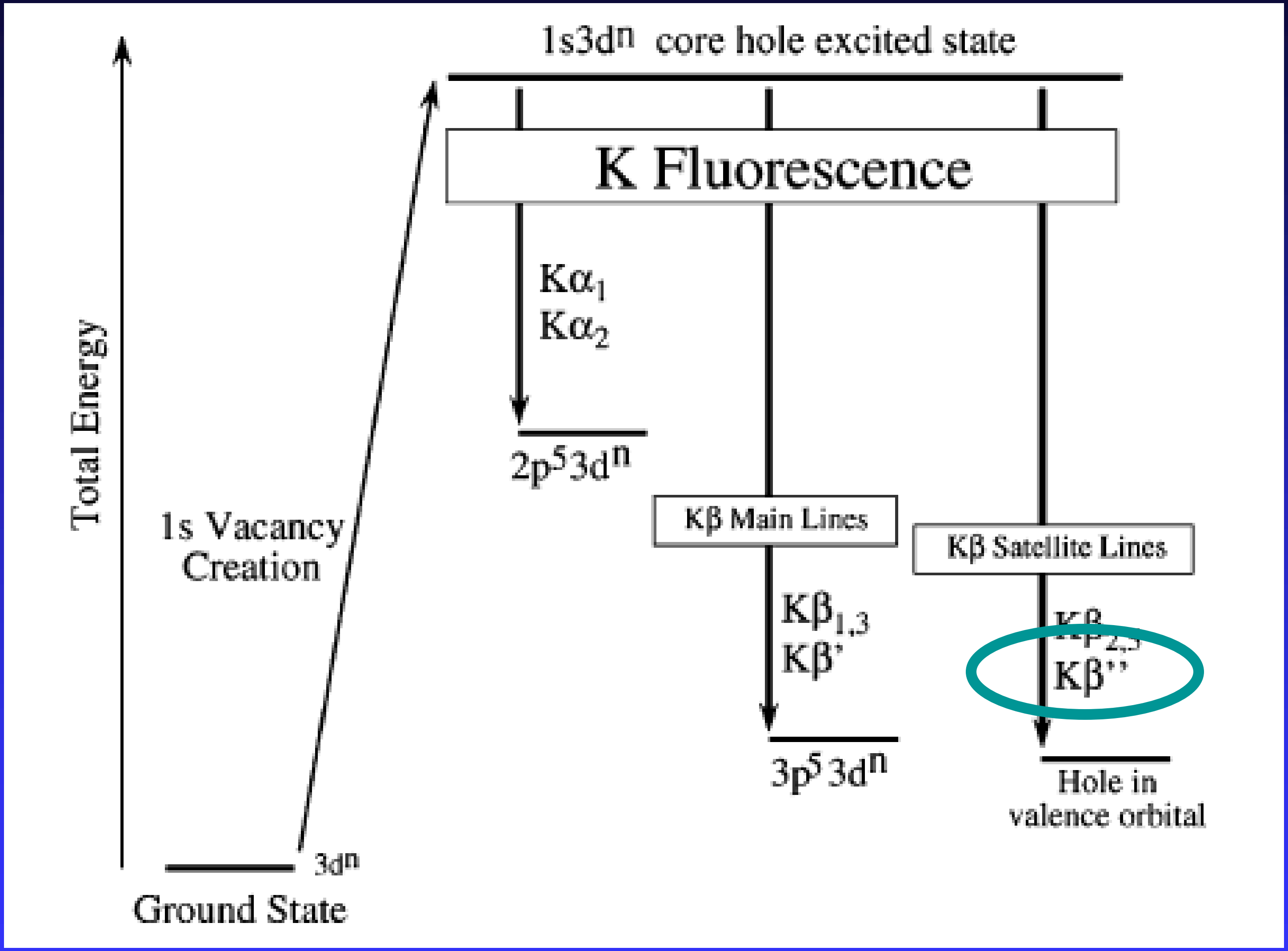
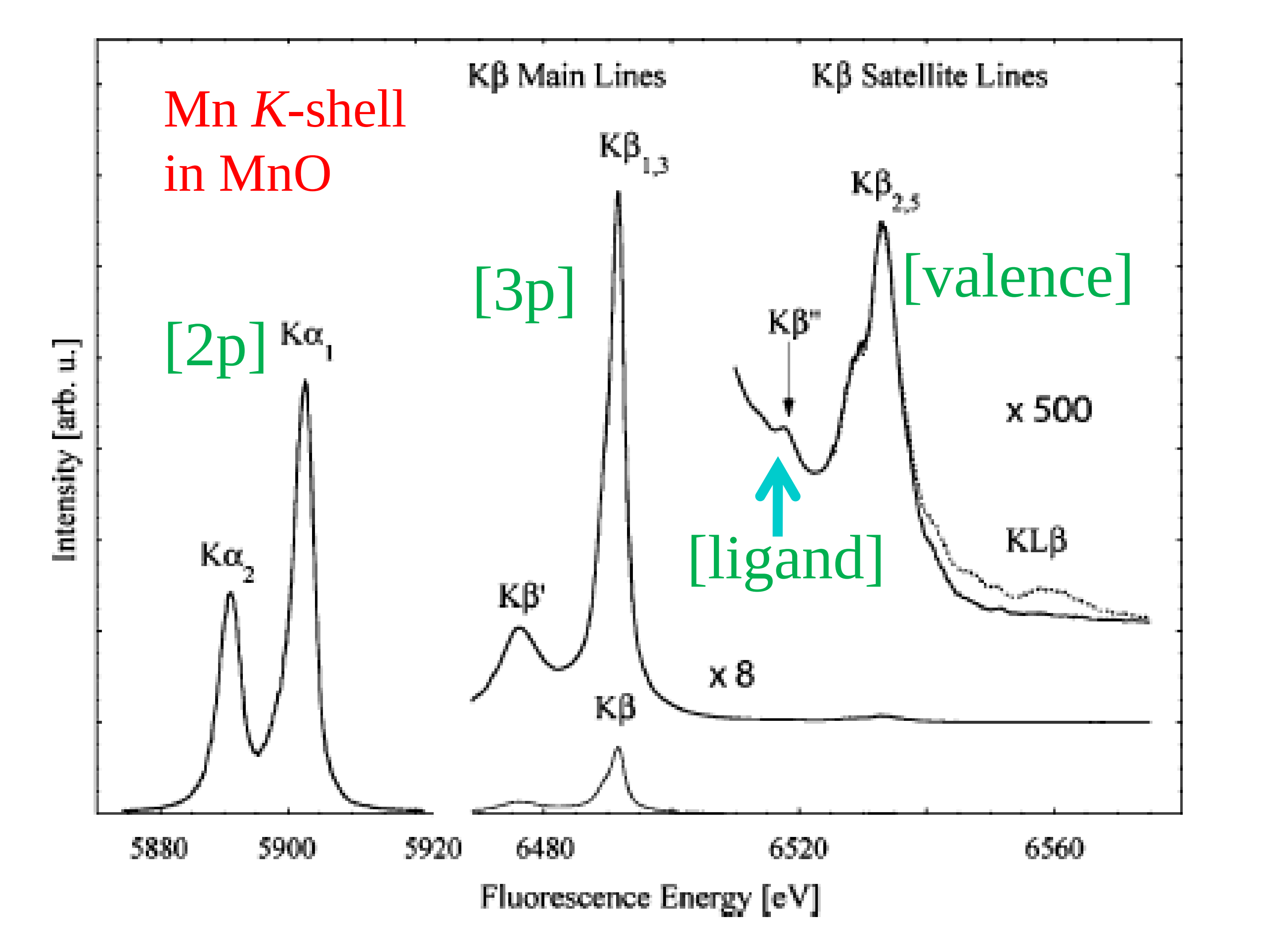


(Nonresonant) Kβ’’: ligand semicore XES – energy is a direct fingerprint of the ligand species: useful in metalloprotien, catalysts…

What does the signal look like?



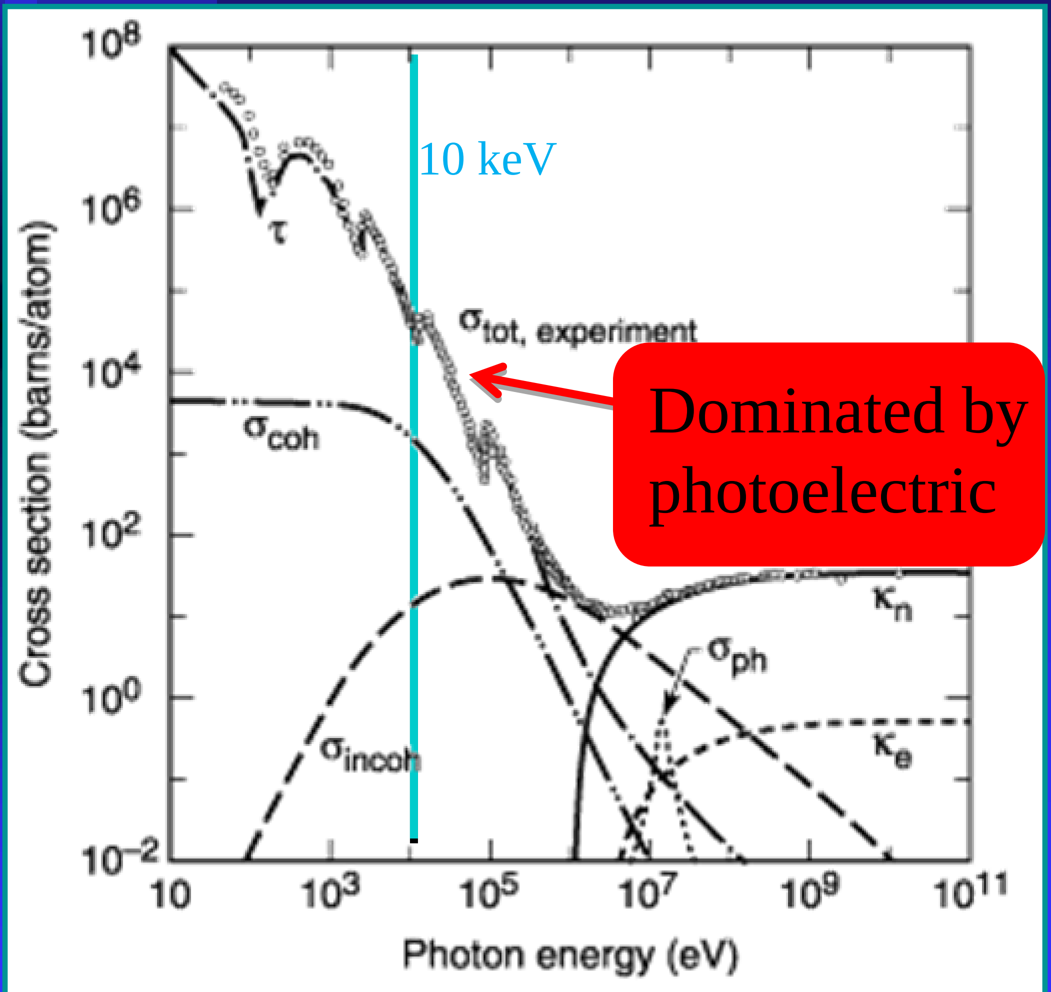
From: Glatzel, et al., 2002

What about RXES/RIXS?

- Greatly suppressed broadening from core-hole effects (what is fundamental limit on experiment sensitivity?)
- Outstanding sensitivity to crystal field and atomic configurational effects (when does the ‘valence’ of an atom in a solid mean anything?)
- Resonant enhancement of incoherent scattering (so far, only ‘hard’ stuff: magnons, charge transfer excitations – we’re about to try ‘easy’ stuff…)

XES should be easy…

X-ray interaction with pure lead



For elements S and heavier, cross-section is >90% photoelectric from 3-30 keV.

Branching fraction for x-ray emission is 5-90%

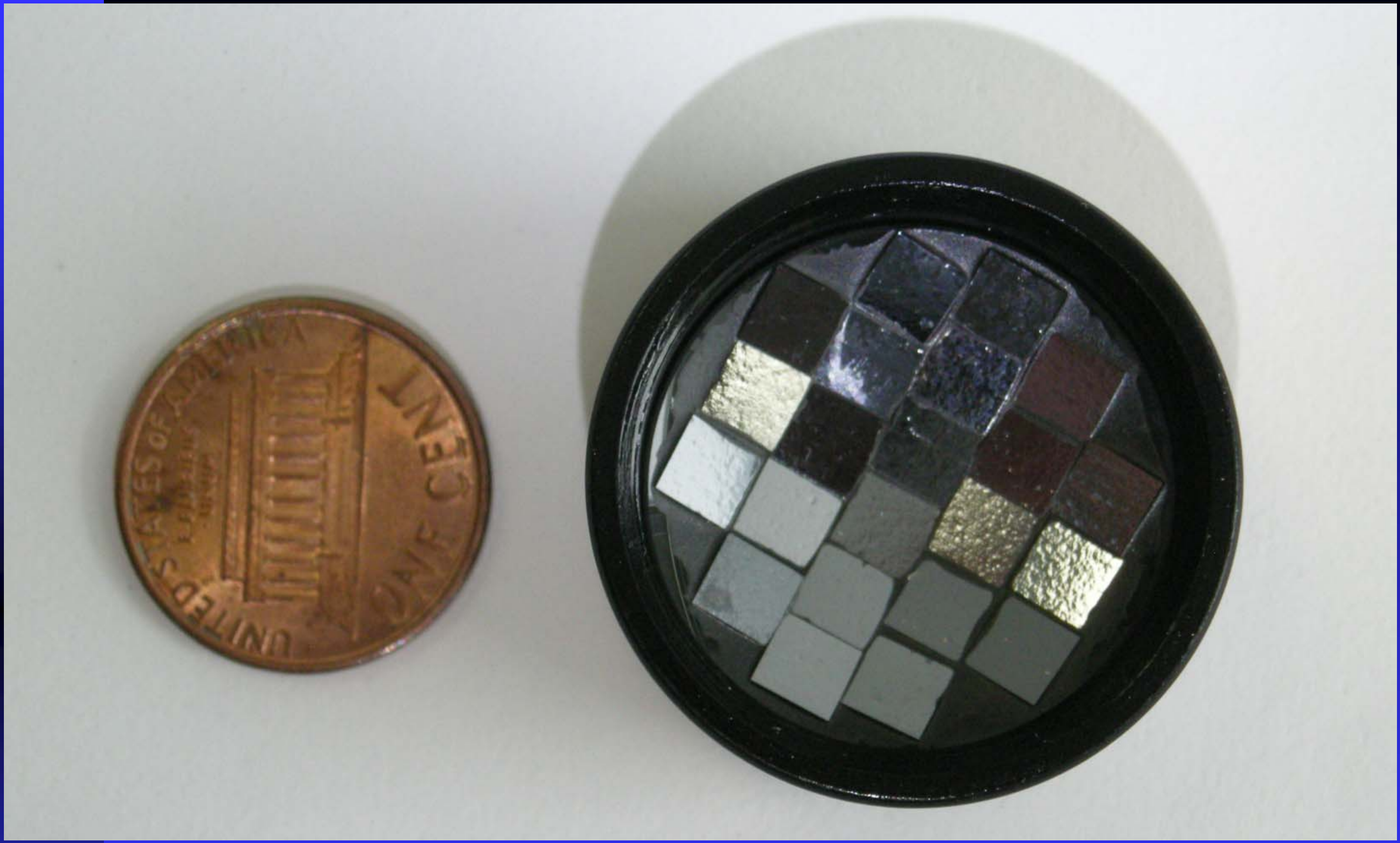
One SBCA collects 0.5 10^{-3} solid angle

SBCA intrinsic resolution is 10^{-2} – 10^{-5} of relevant energy band

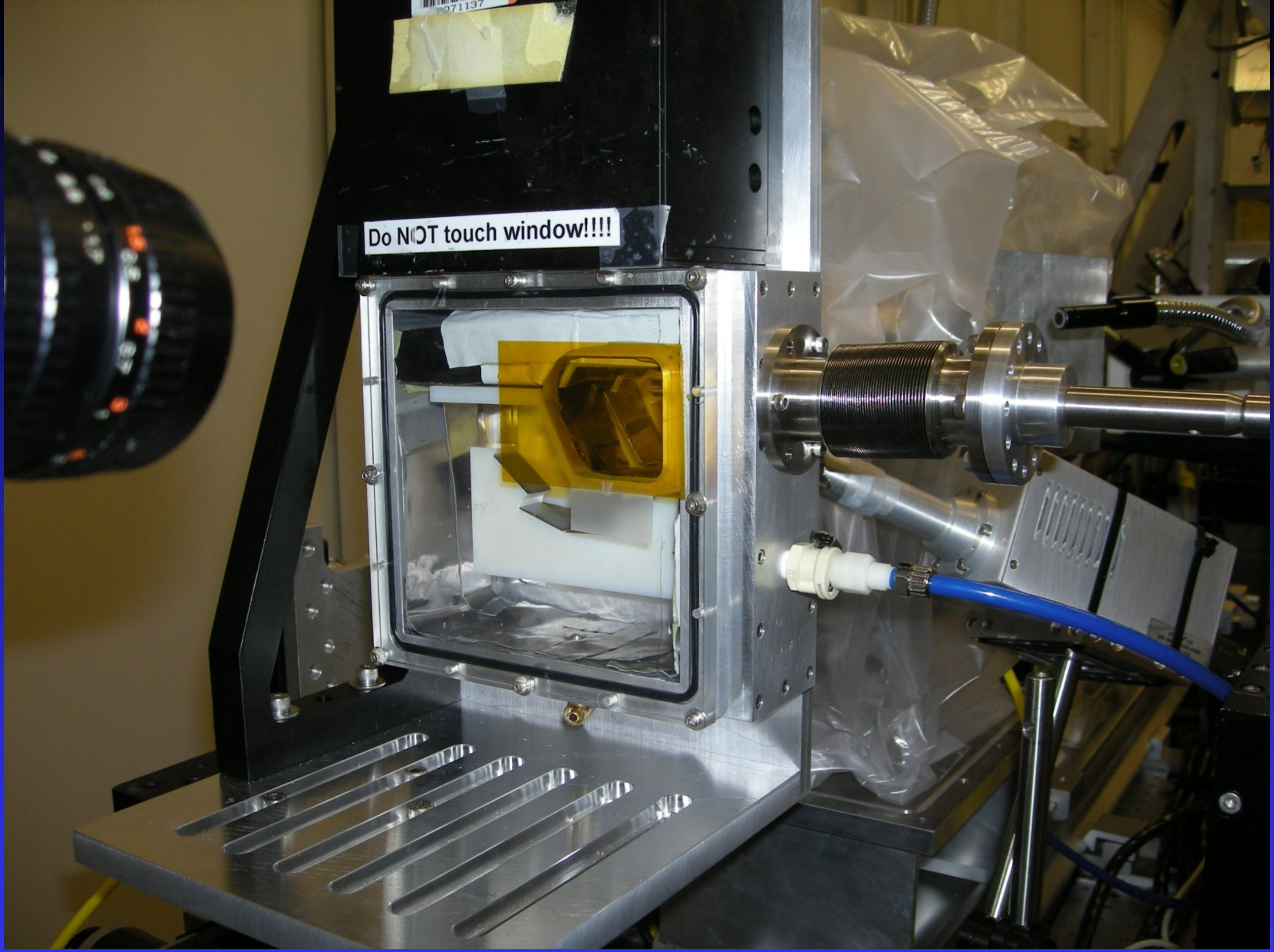
→ Concentrated samples can have ~M-counts/sec in nonres XES studies with <1 eV resolution

…but it hasn’t been easy.

- Very few hard x-ray XAS beamlines perform ~1 eV resolution XES with any regularity (exception: Fe Kb at DAC facilities)
- Severe, historic underutilization of XES as a scientific tool in its own right and as a complement to XAS
- The problem: the ‘traditional’ spectrometers are big, mechanically complex, somewhat pricey, require specialized optics, etc…

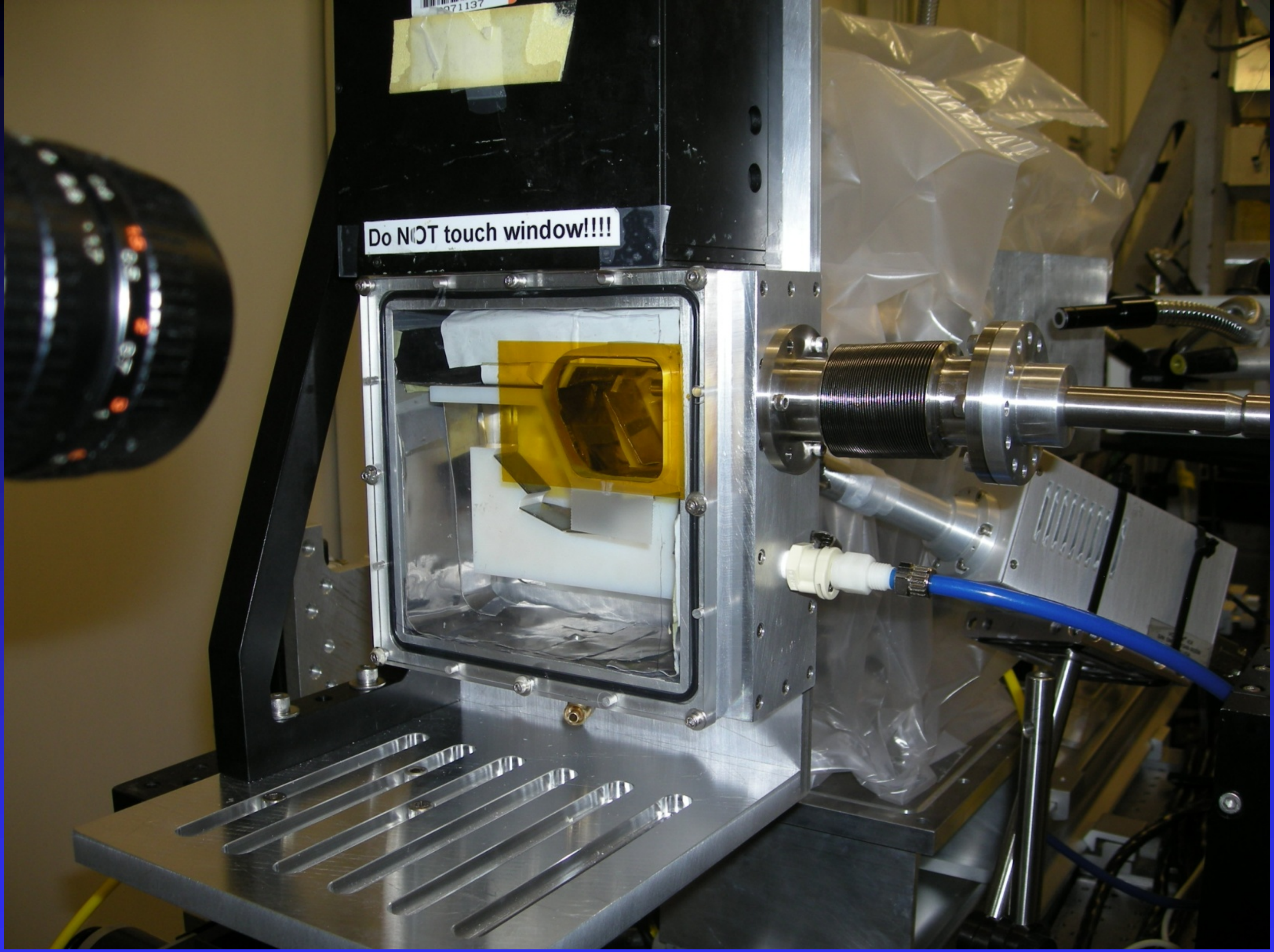


August 2008: \$100 ‘gadget’ beats a large XES spectrometer for energy resolution and collection efficiency for Mn Kβ (Dickinson, GTS, et al, Rev Sci Instrum 2008)

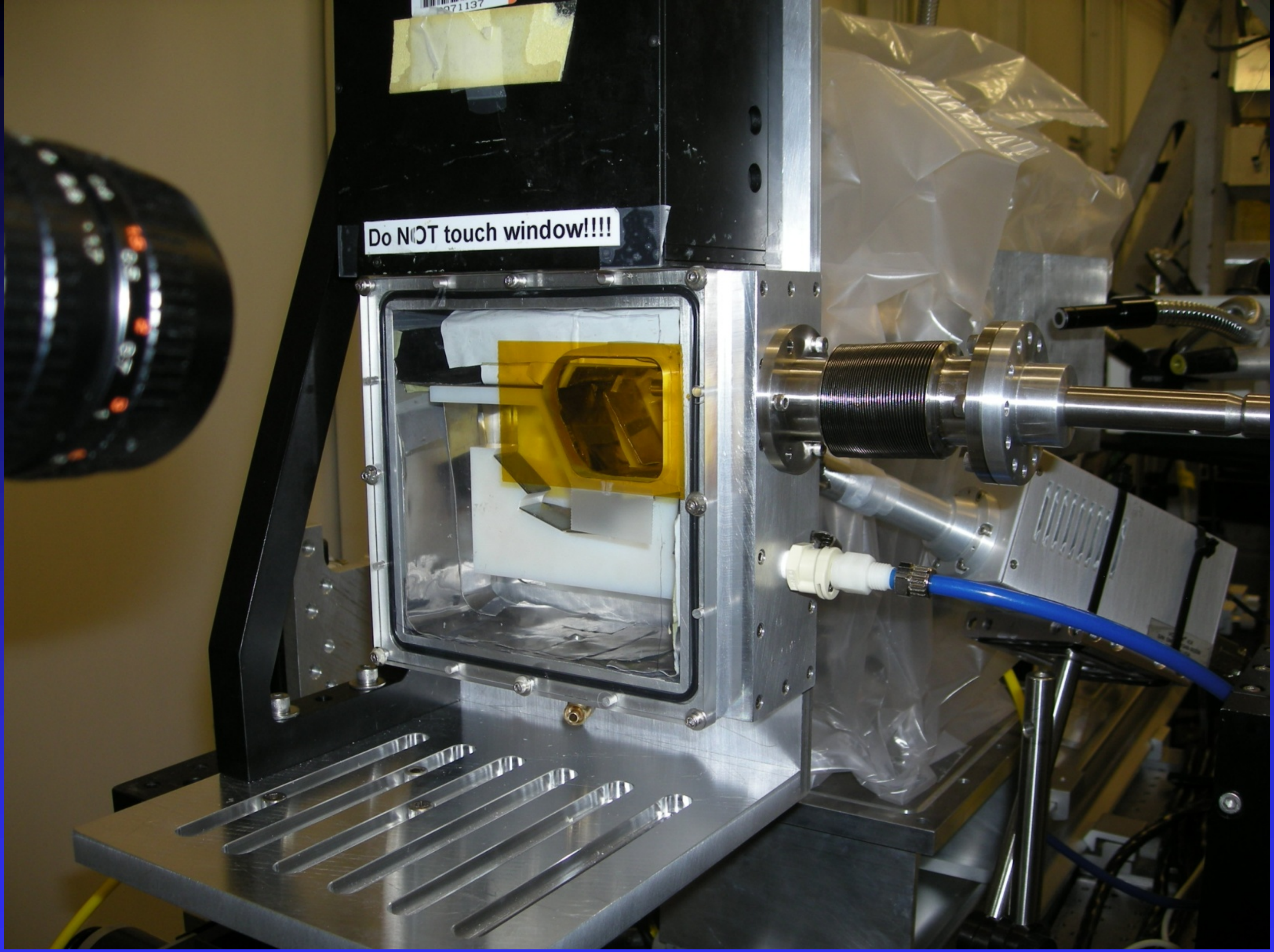


June 2010: The GU-commissioned ‘miniXS’ at the APS 20-ID microprobe endstation.

GTS, R.A. Gordon, John Quintana, Brian Rusthoven, et al., in prep.



- No moving parts (except sample translator).
- Small, portable, and cheap (‘box’ is 6 inches square).
- [Variants for compatibility with DAC, fridge, etc…]



This instrument has the same net collection efficiency as the largest 'traditional' XES spectrometers ever constructed.

Outline

- Why measure X-ray Emission Spectra?
- *How to (usually) Measure X-ray Emission Spectra?*

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- An alternative to the ‘usual’ way…. ‘short working distance’ dispersive optics
- *A miniXS survey*
  - One crystal is all you need: U *M*-edge
  - New results for multi-crystal instrument design
    - Separation of overlapping emission lines: V Kβ and Cr Kα
    - F Kβ: DAC magnetism, Fuel Cell membranes
    - A truly general-purpose miniXS: 4-10 keV resonant and nonresonant XES using 3-D printing of optics

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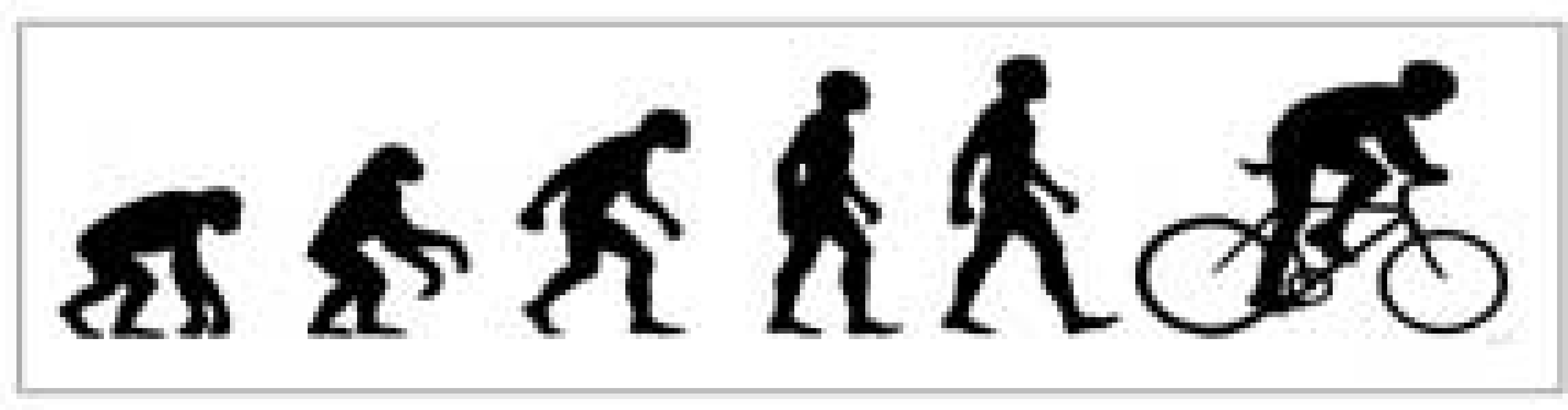
- How to (usually) Measure X-ray Emission Spectra?
- An alternative to the ‘usual’ way…. ‘short working distance’ dispersive optics
- A miniXS survey
- *Conclude & Future Directions*
  - Every XAS microprobe can easily incorporate 1-eV resolution XES into detector suite
  - All plastic spectrometers for ease of compatibility with environmental cells
  - Detector limitations: more pixels, smaller pixels → huge collection solid angles and better energy resolution

How do you measure hard x-ray XES with good (to very good) energy resolution?

Two routes*, with very similar starting points and end-points.

1. (diced) Spherically bent crystal analyzer
2. Multi-crystal 'miniXS'

A Very Incomplete Historical Survey of (usual) Hard X-ray Spectrometer Design



Flat xtal Spectrometer

Rowland Circle

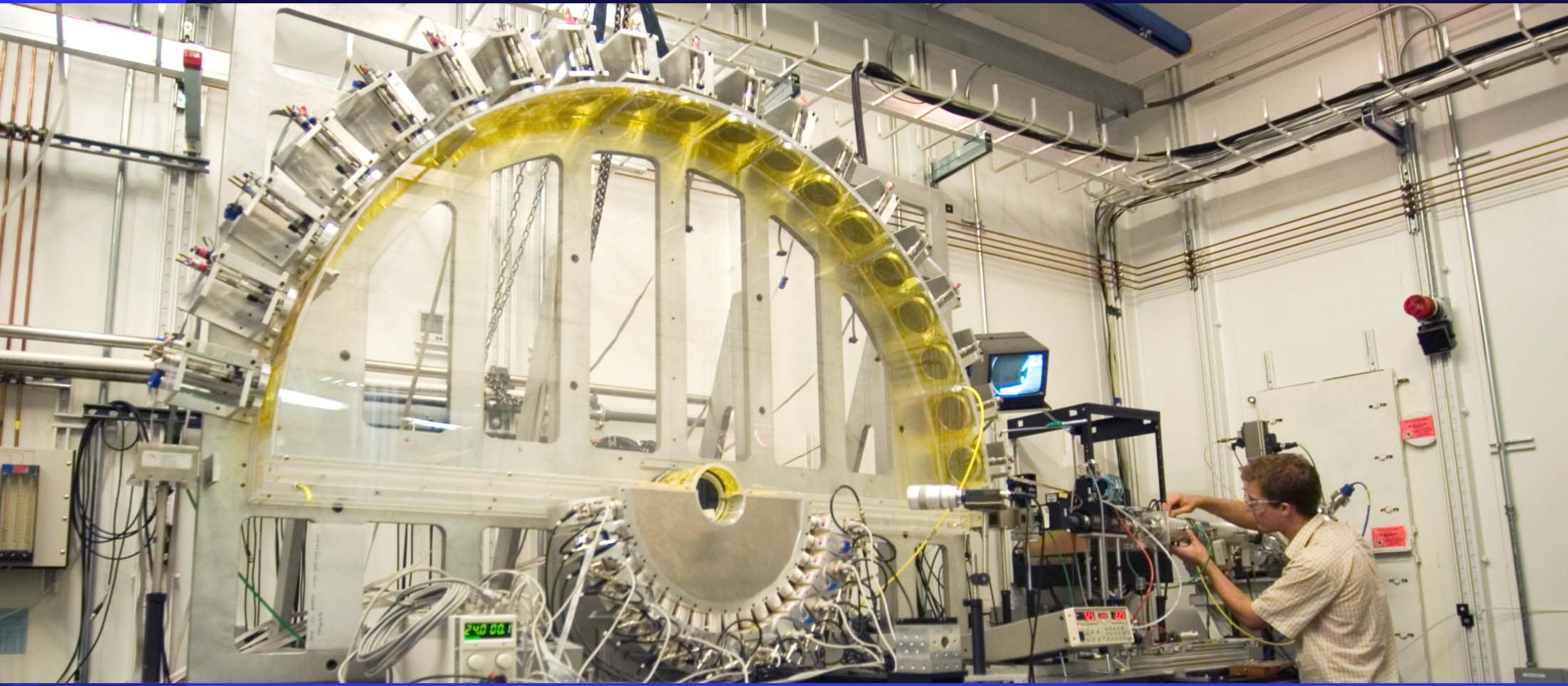
Johann & Johannson optics

Diced SBCA

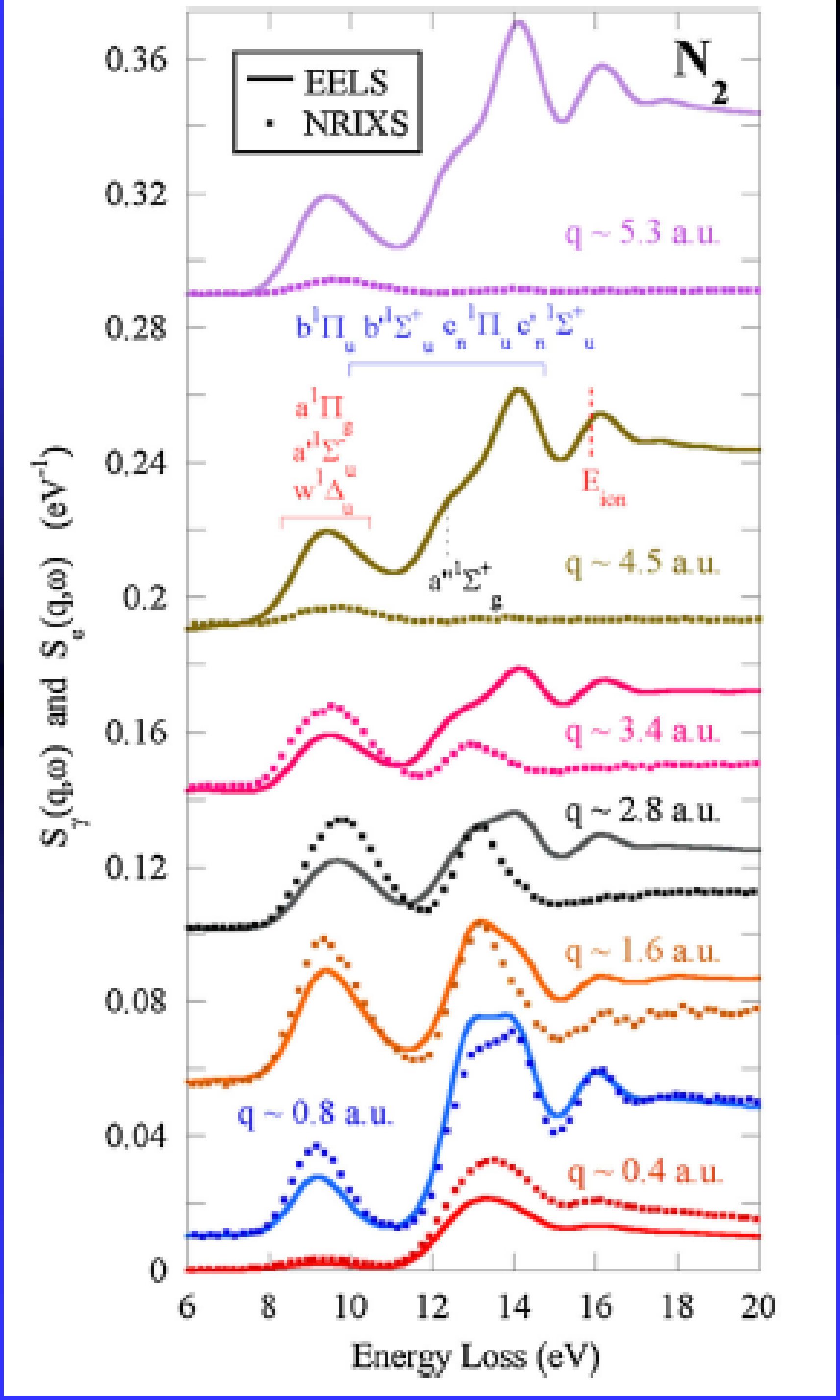
Dispersion Compensation, multi-SBCA

LERIX: PNC-XOR, sector 20 APS

(Tim Fister, GTS, et al, Rev. Sci. Inst. 2006)



- q-dependent nonresonant IXS
- 19 Spherically-bent Si 111 wafers
- Total solid angle for 19 SBCA is ~1.2% of 4π sr



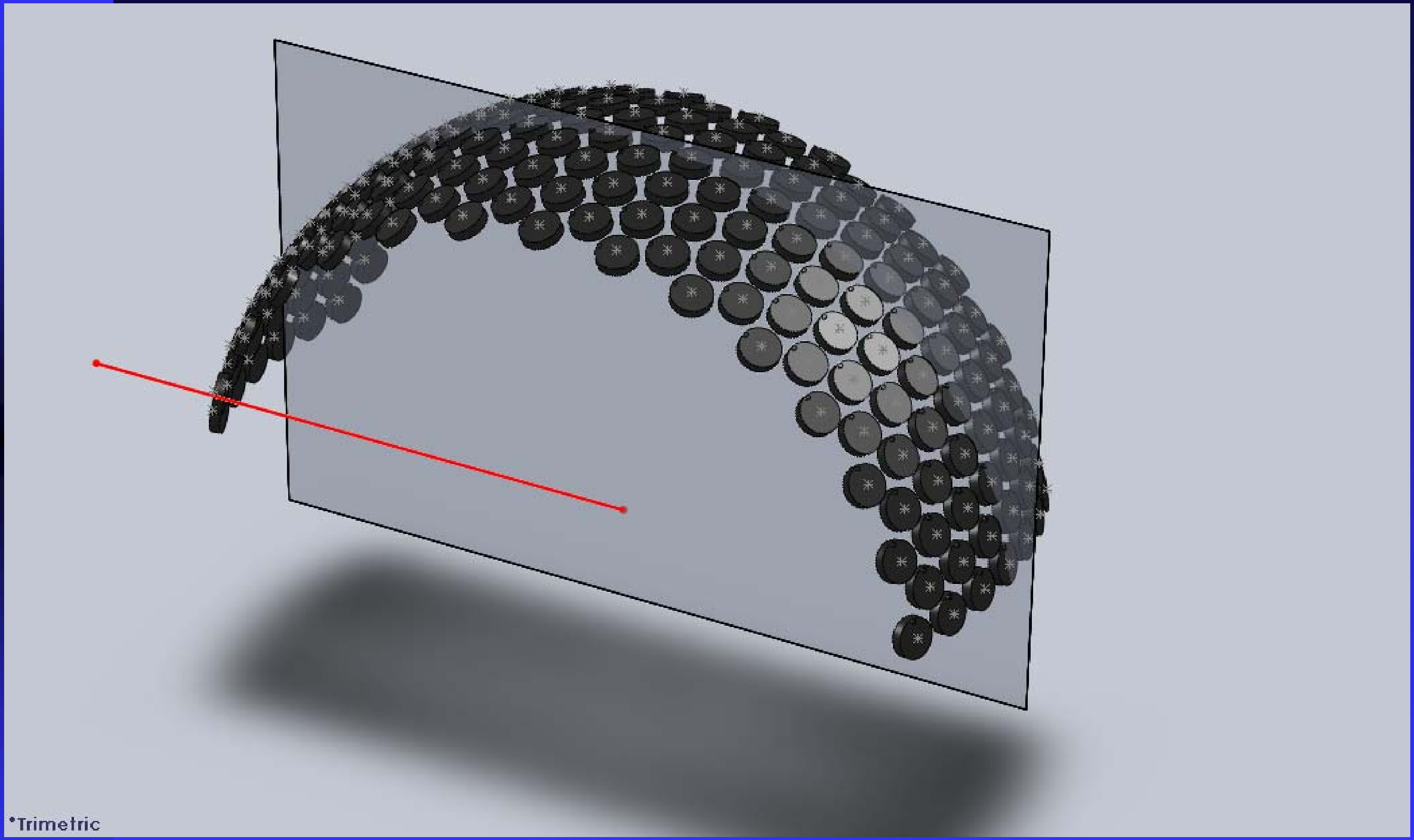
From: J.A. Bradley, GTS, G. Cooper, A. Hitchcock, M. Vos, et al, PRL **2010**

- Comparison of nonresonant IXS and EELS for N2 gas

- Extreme divergence of results when leaving the dipole scattering limit

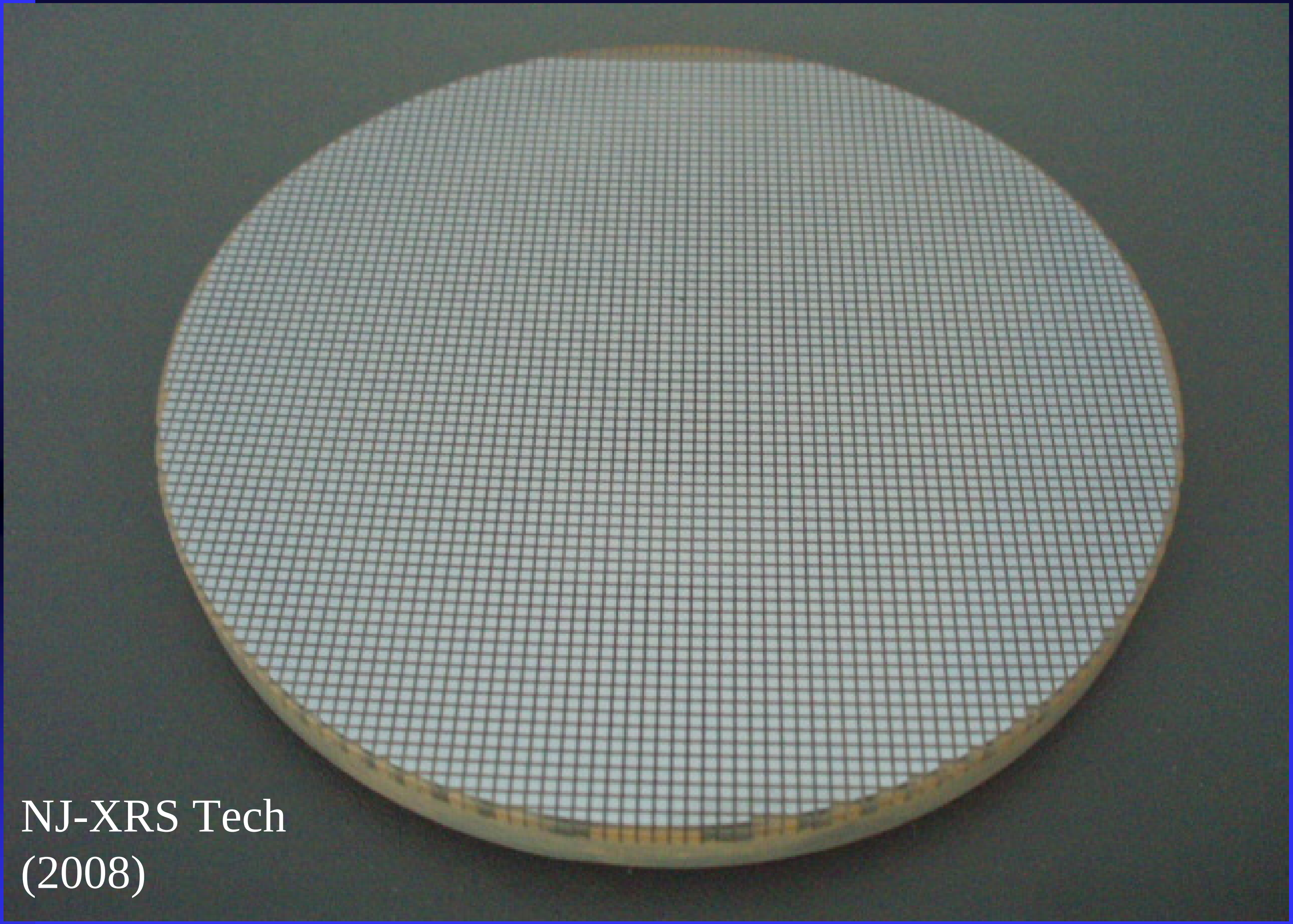
- Direct evidence for violation of first Born approximation in q-dependent EELS, even for high (multi-keV) beam energies

LERIX-2 design progress…



180 analyzers…. Working on several different strategies for detector configurations

Diced, Curved Analyzers (1986?)

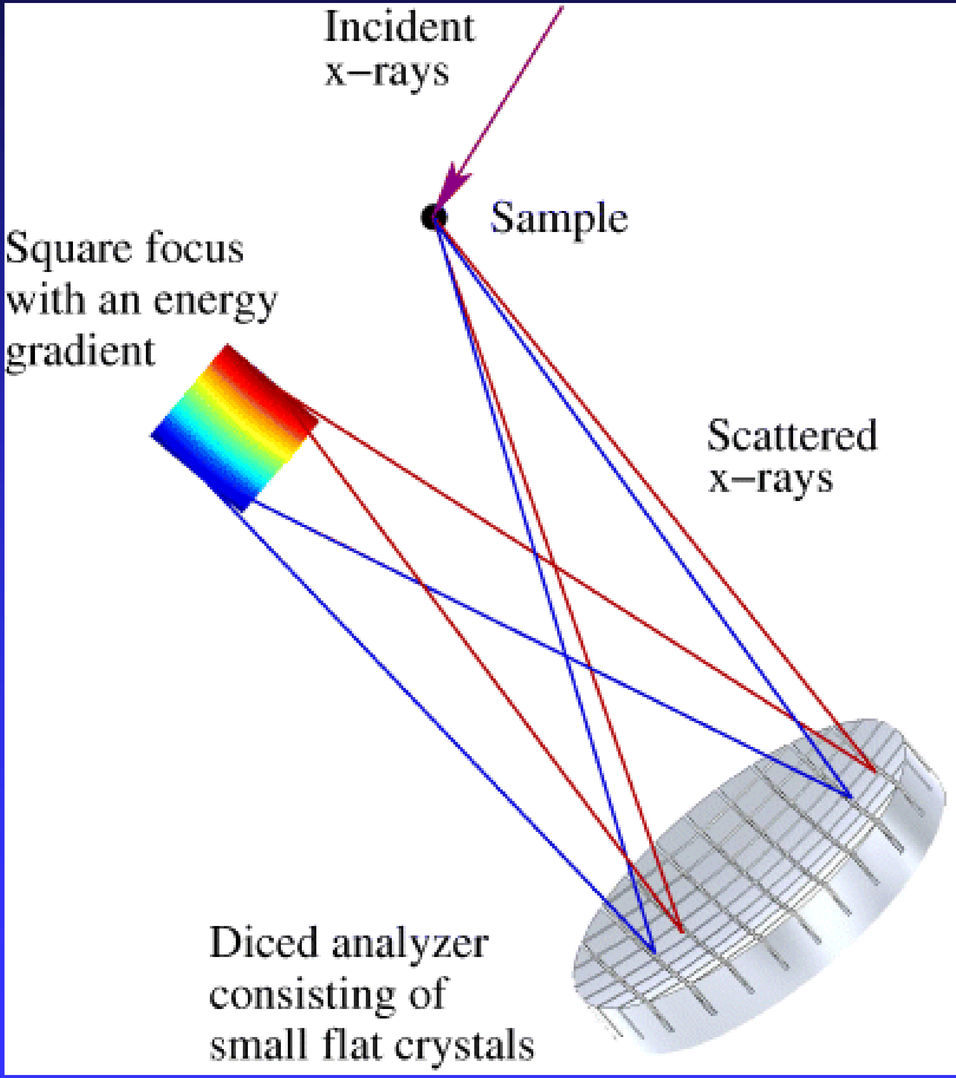


Unlike older bent-crystal analyzers, the top surface of the ‘cube’ crystal elements is unstrained→very high energy resolution.

“Dispersion Compensation”

(S. Huotari, *et al*, JSR 2005 & RSI 2006)

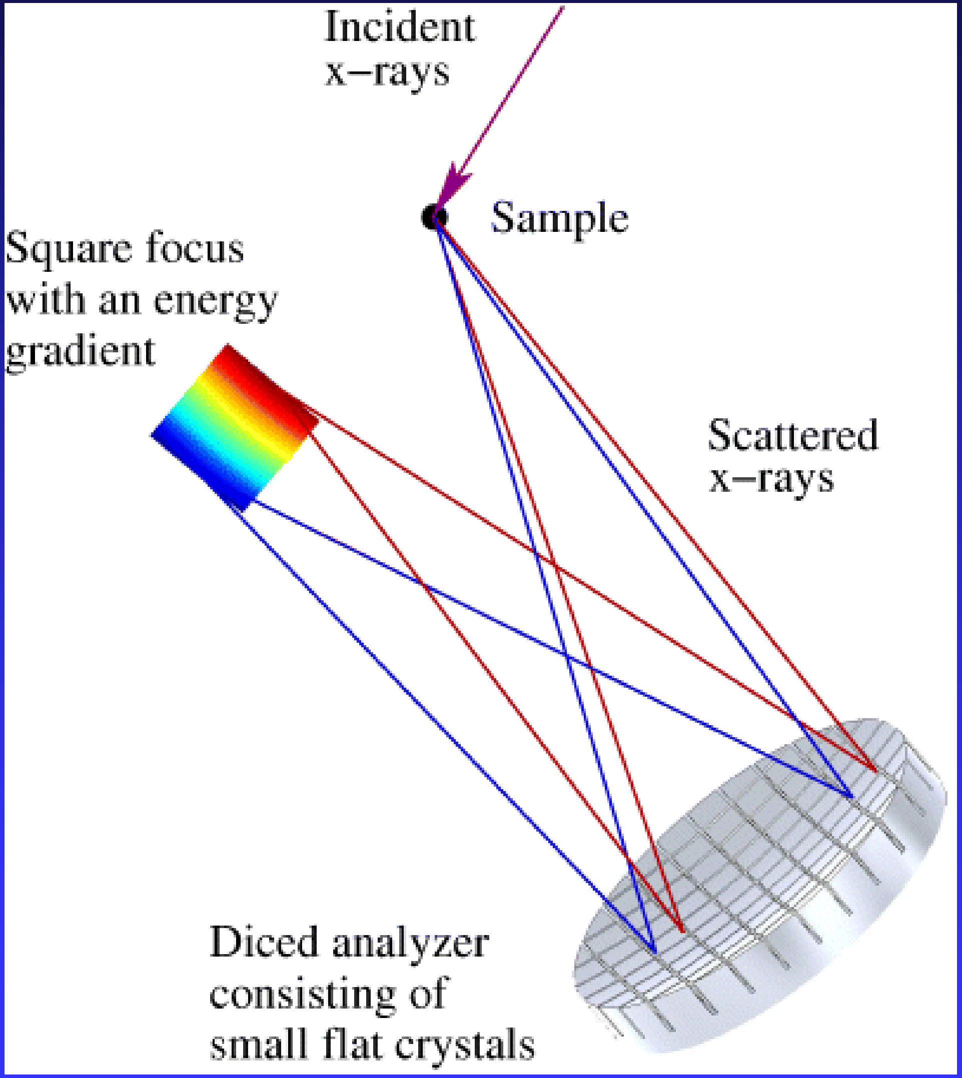
- Energy resolution is (nearly) determined by unstrained, intrinsic response of diffracting material
- Energy bandpass on focal plane is determined by size of diced elements
- Allows high resolution with much shorter working distance→vastly larger collection solid angle.



“Dispersion Compensation”

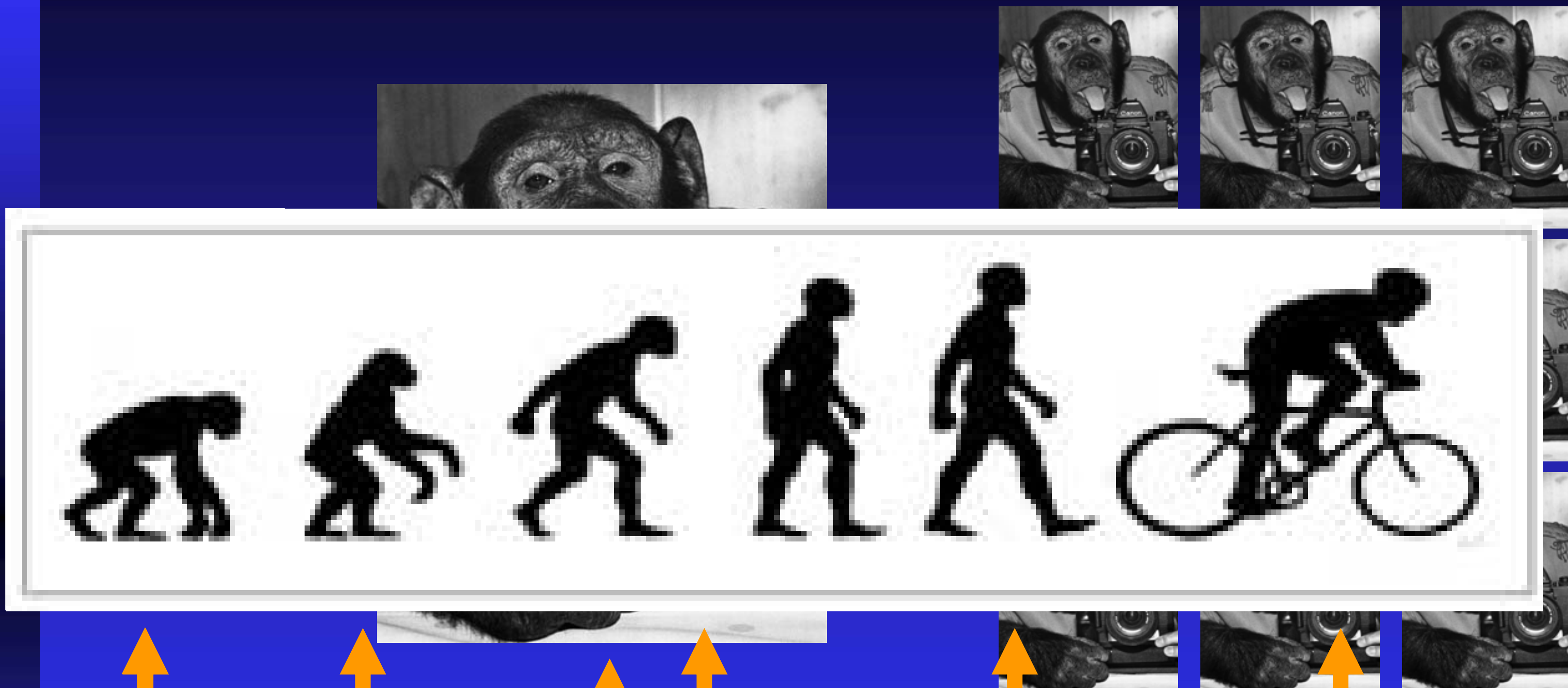
(S. Huotari, *et al*, JSR 2005 & RSI 2006)

1. ‘magic’ ray-tracing
2. zero-noise camera
3. small spot size
4. Resulting (smallish) energy range is OK fit with many (most) very high resolution experiments: you never want super-high energy resolution over a large energy transfer range



A “convergent” evolution

The “real” evolution



Flat xtal Spectrometer, Large source size, One-pixel detector

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Rowland Circle

Johann & Johannson optics

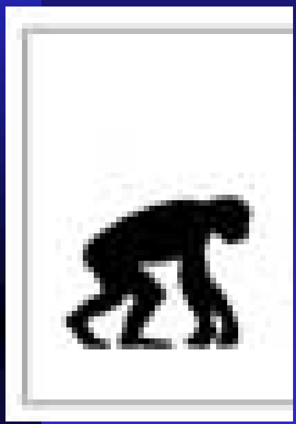
Flat xtal Spectrometer, focused beam, zero-noise camera (and nice software…)

Diced SBCA

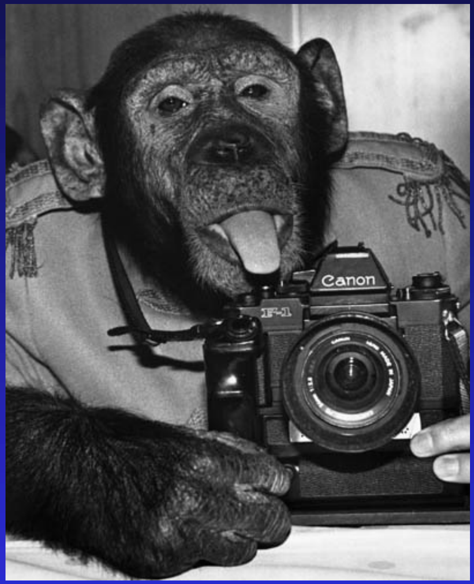
Dispersion Compensation, multi-SBCA

Many *identical* Flat xtal Spectrometer, focused beam, zero-noise camera (and nice software…)

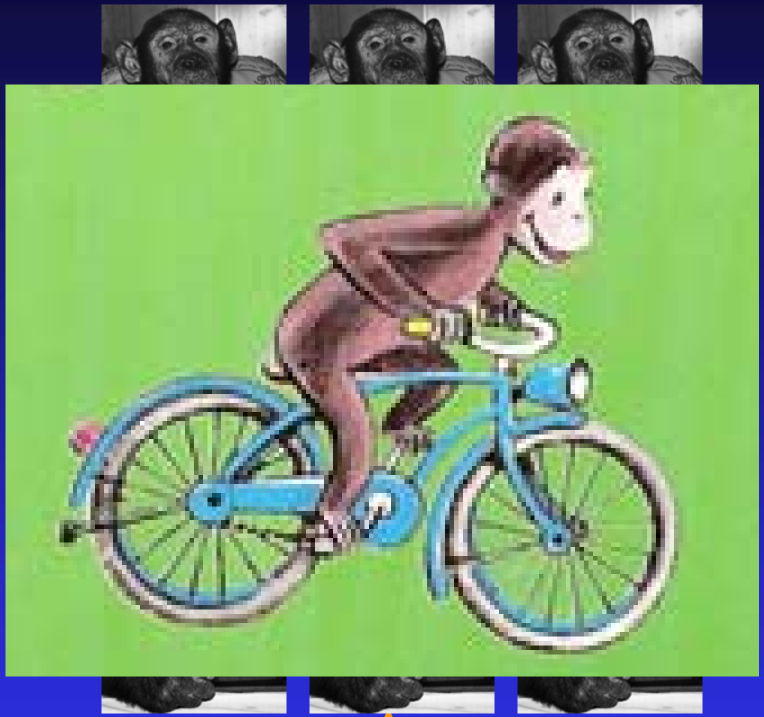
A "convergent" evolution



Flat xtal Spectrometer, Large Source size, One-pixel detector



Flat xtal Spectrometer, focused beam, zero-noise camera (and nice software…)

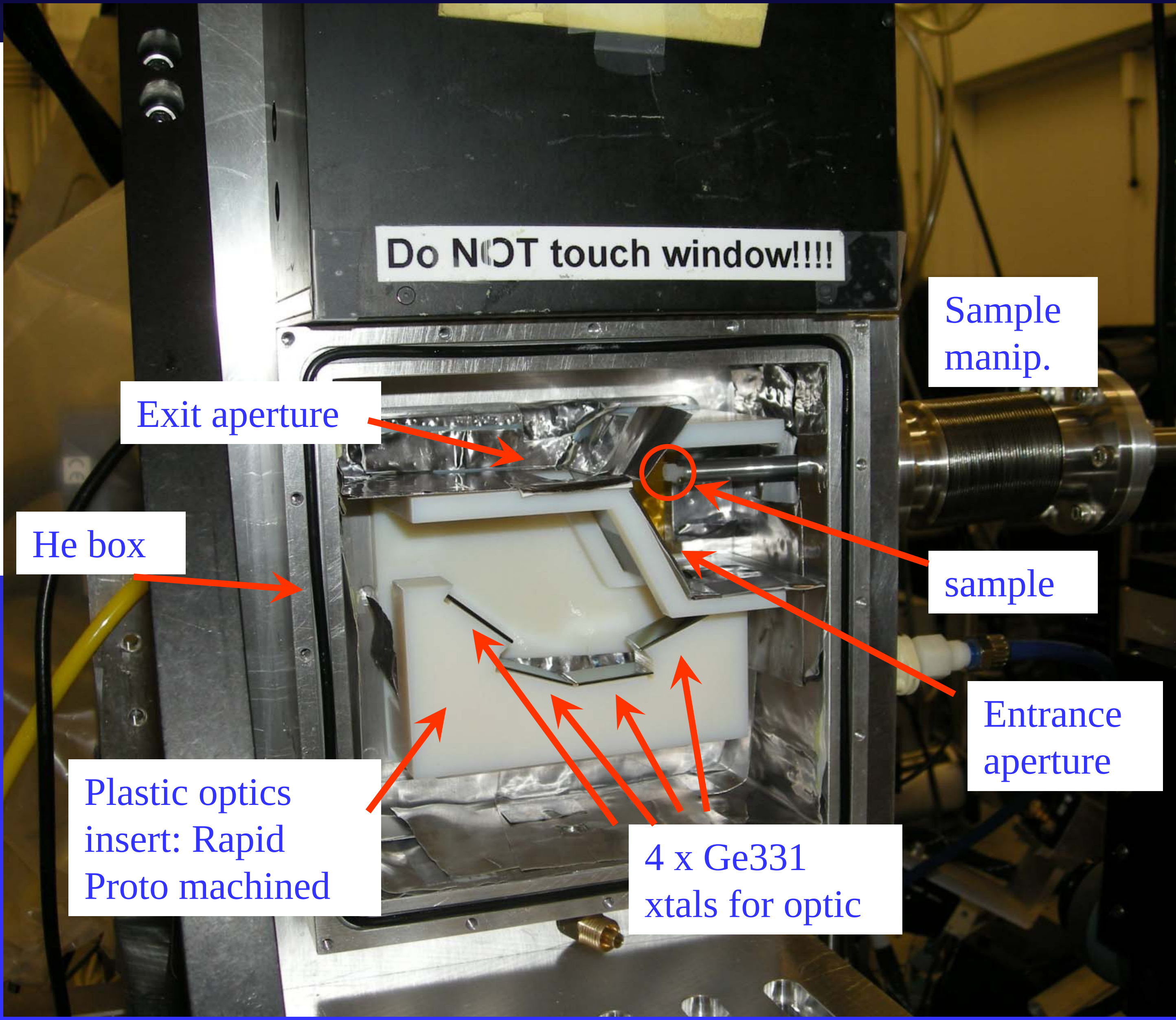


Many *identical* Flat xtal Spectrometer, focused beam, zero-noise camera

and *Exact* dispersion compensation

Ce Lα miniXS

- 4/2010 at 20-ID
- 10 SBCA equiv
- 5.5 cm diameter Rowland circle
- RA Gordon and TK Sham: studies of mixed valent Ce compounds
- Resolution <0.8 eV



Spectrometer calibration

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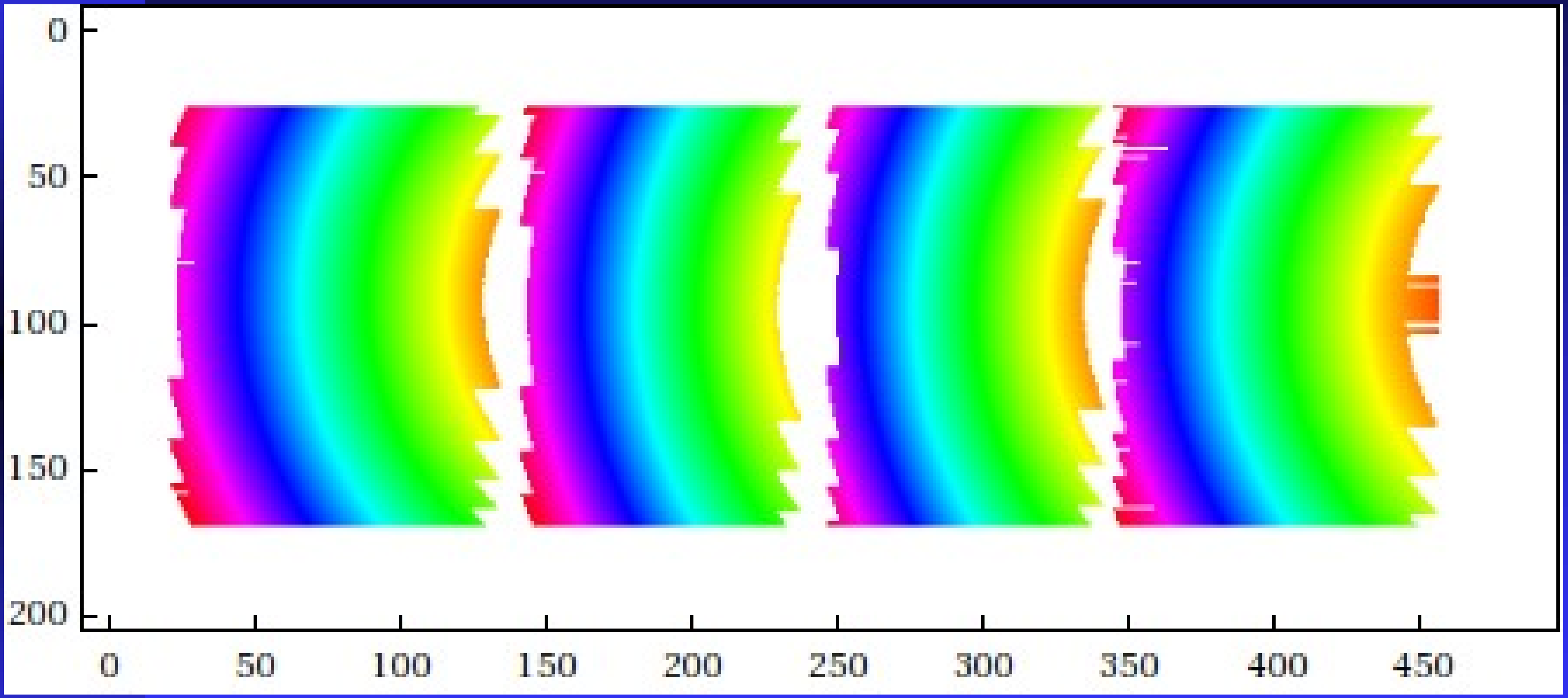
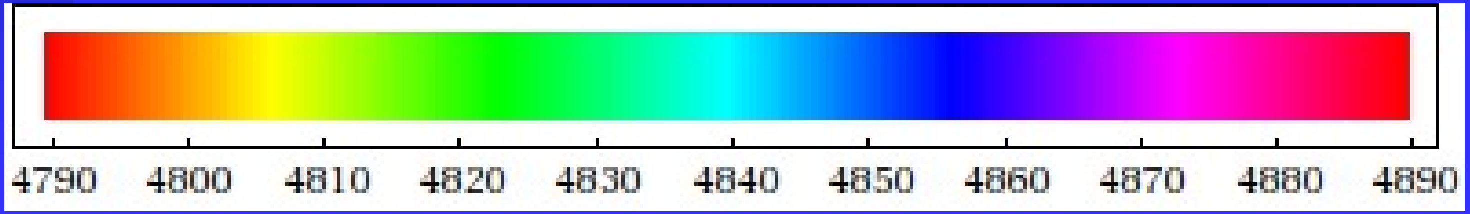
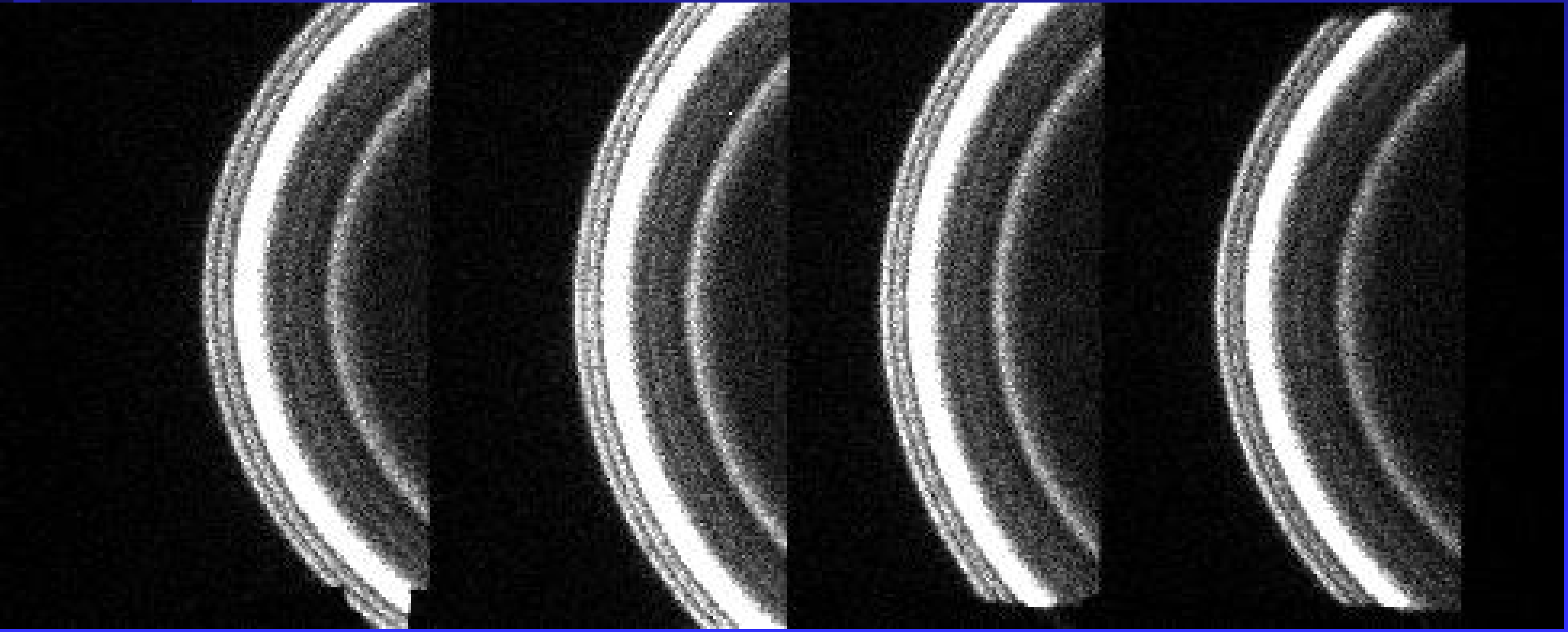




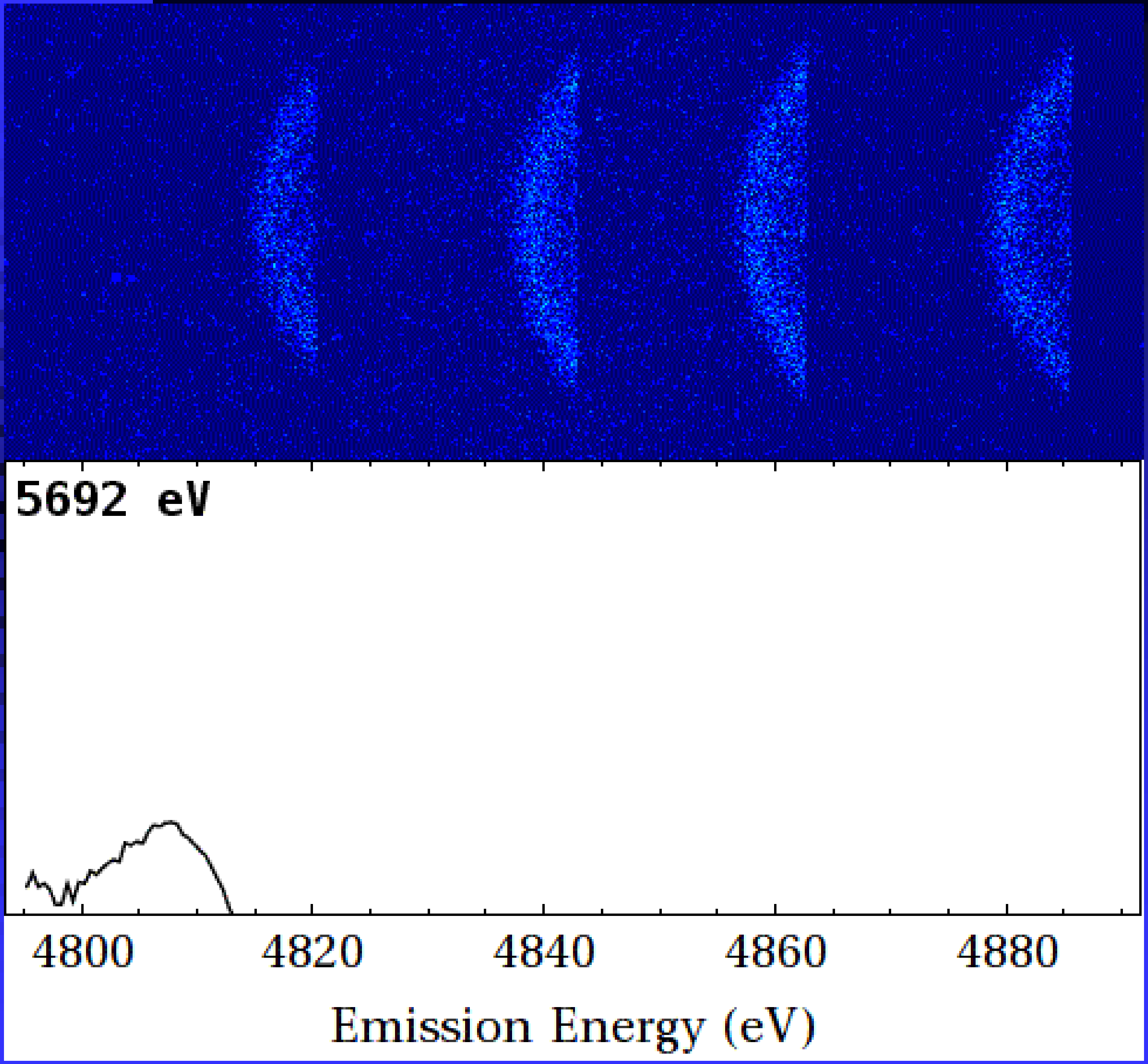
CeF_3 Lα XES exposure

4 minute expose

500k counts in Lα1, 2M counts in entire energy range



CePd3



We’ve made an easy experiment easy.

Huge range of applications:

- Actinide science: new look at charge transfer excitations
- Basic QM: what does ‘multiconfig’ mean for f-electron materials?
- Basic CM science: metal insulator transition ‘intrinsic’ or ‘percolative’?
- Biophysics: time resolved studies of photosynthesis
- Biophysics: what is bonded to the metal site in metalloprotiens?
- Battery research: charge transfer upon lithiation