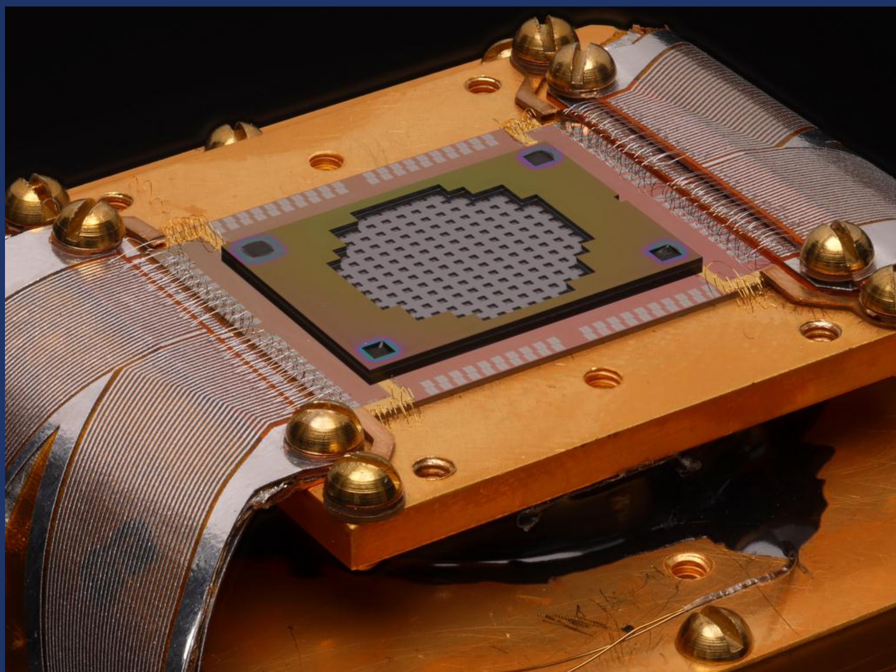
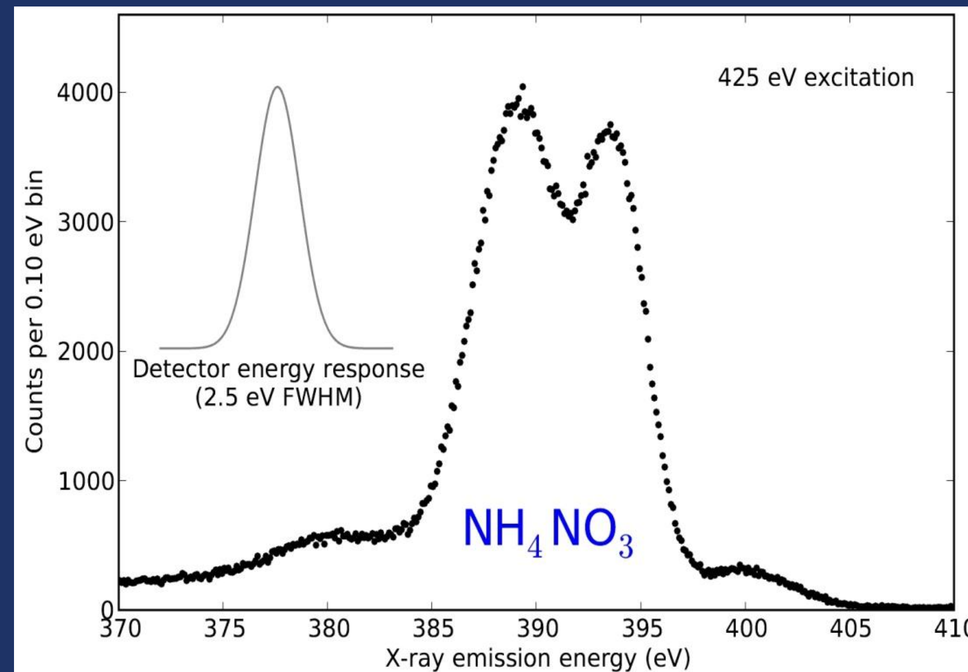
First synchrotron observations by the NIST microcalorimeter-spectrometer

Randy Doriese, NIST (Boulder, Colorado)





1) synchrotrons and X-ray spectroscopy
2) NIST TES spectrometer at NSLS beamline U7A
3) initial synchrotron spectroscopy results

collaborators

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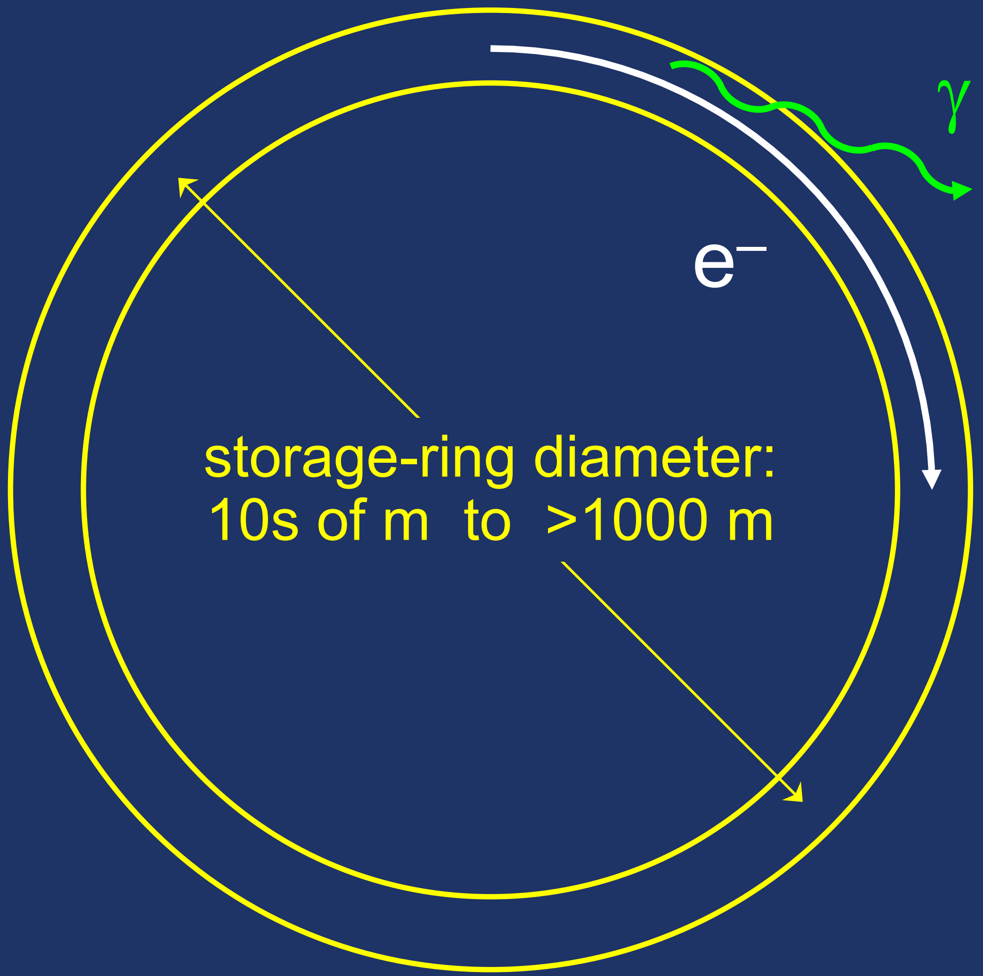
synchrotrons: a brief review



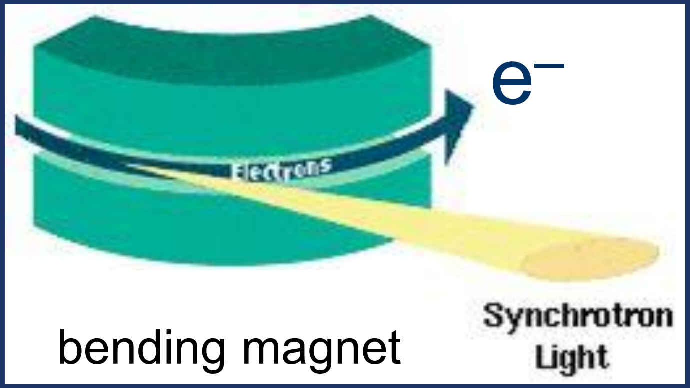
Use accelerated electrons to make light.

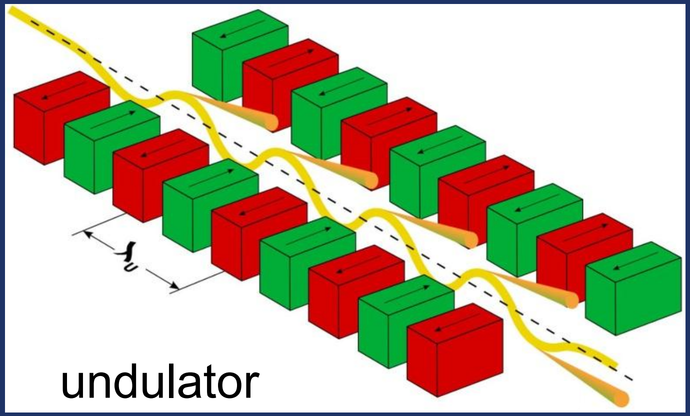
<u>important techniques:</u>

X-ray absorption and emission spectroscopy

anatomy of a synchrotron beamline

images courtesy of wikipedia





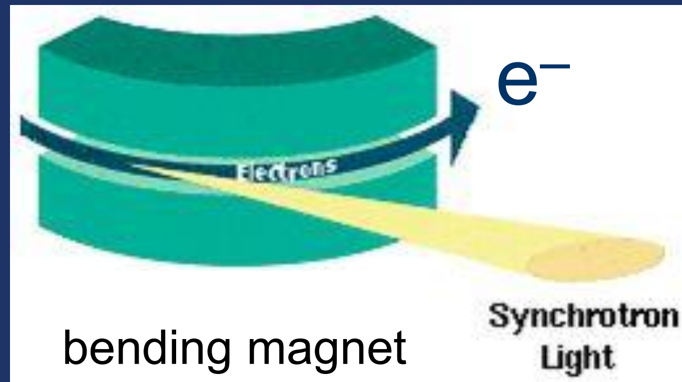
monochromator

(Bragg crystal or grating)

slits, mirrors

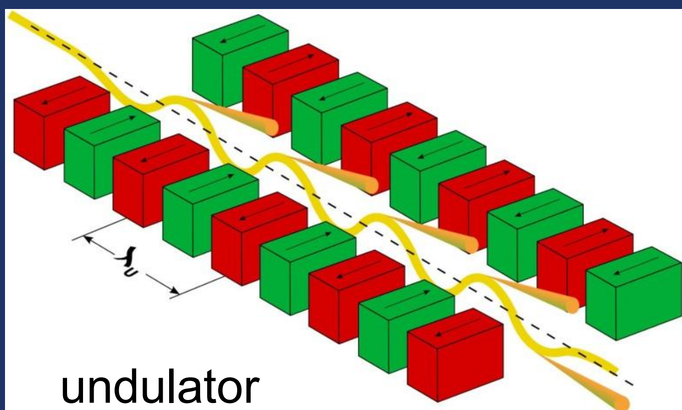
sample

anatomy of a synchrotron beamline



images courtesy of wikipedia

~ 10^9 – 10^{12} γ / s / (0.1 eV)



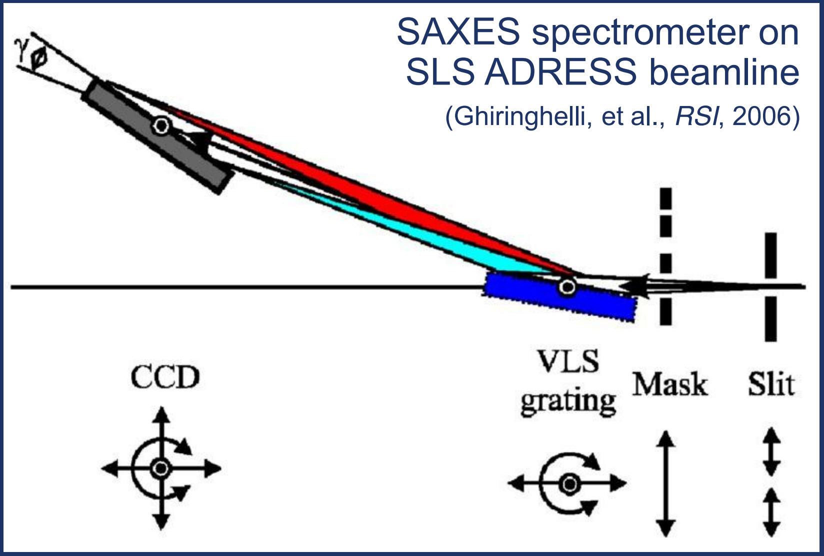
~ 10^{12} – 10^{14} γ / s / (0.1 eV)

resulting beam:

- large flux
- monochromatic
- can be highly focused
- polarized

high-res X-ray emission spectroscopy (XES)

< 1.5 keV:
gratings



SAXES spectrometer on SLS ADRESS beamline
(Ghiringhelli, et al., *RSI*, 2006)

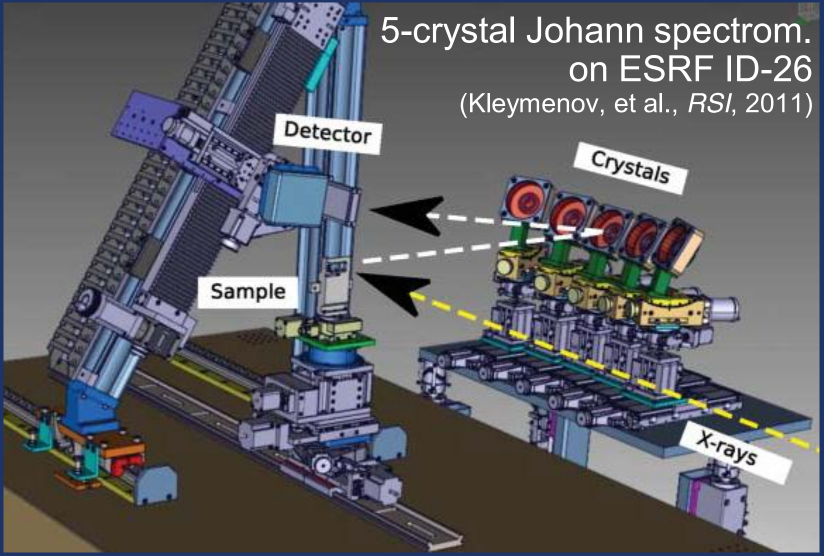
present high-res. X-ray emission spectrometers are wavelength-dispersive.

the good: energy resolution.

- typical $E/\Delta E \sim 1{,}000 - 3{,}000$
- best $E/\Delta E$ can be $> 10{,}000$

the bad: collection efficiency

- poor solid-angle coverage
- poor QE
- some must scan E

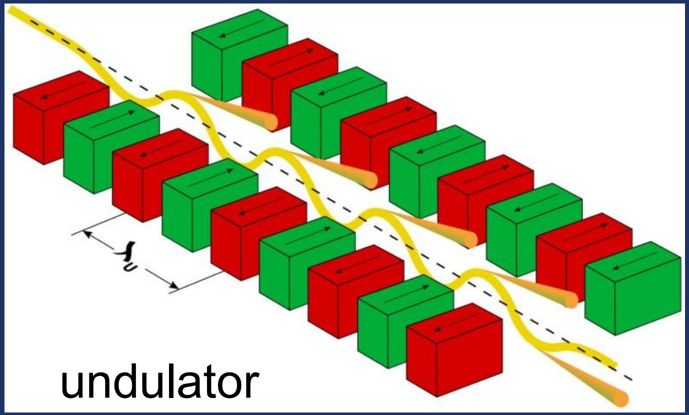


5-crystal Johann spectrom. on ESRF ID-26
(Kleymenov, et al., *RSI*, 2011)

> 2 keV:
bent crystals

high-res X-ray emission spectroscopy (XES)

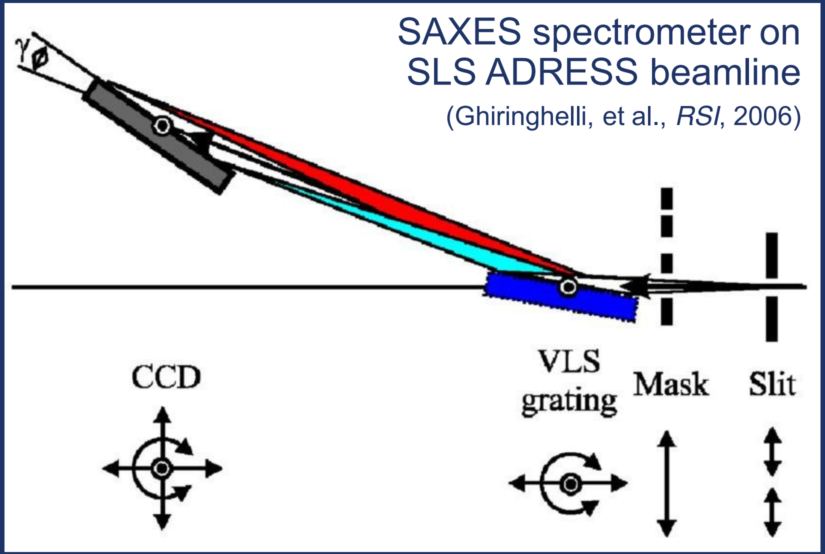
require:



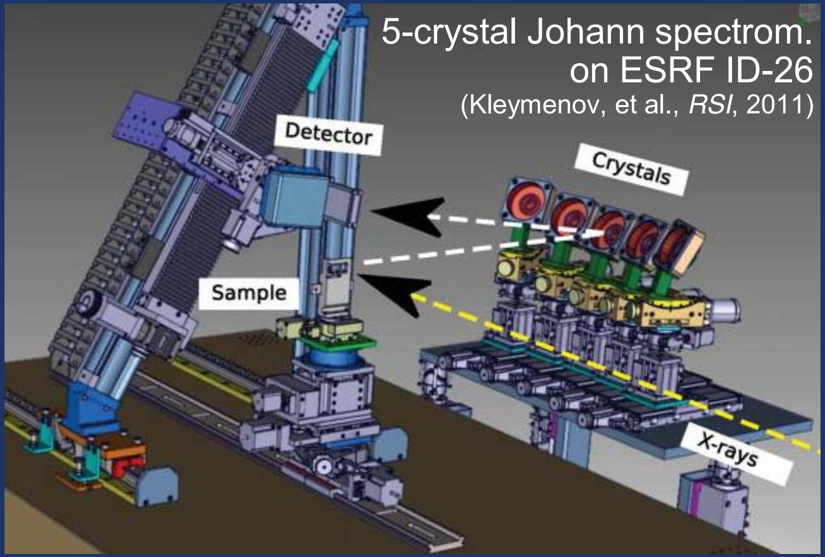
~ $10^{12} – 10^{14}$ γ / s / (0.1 eV)

- can easily damage sample
- some applications (e.g. time-resolved) *still* photon-starved

< 1.5 keV:
gratings



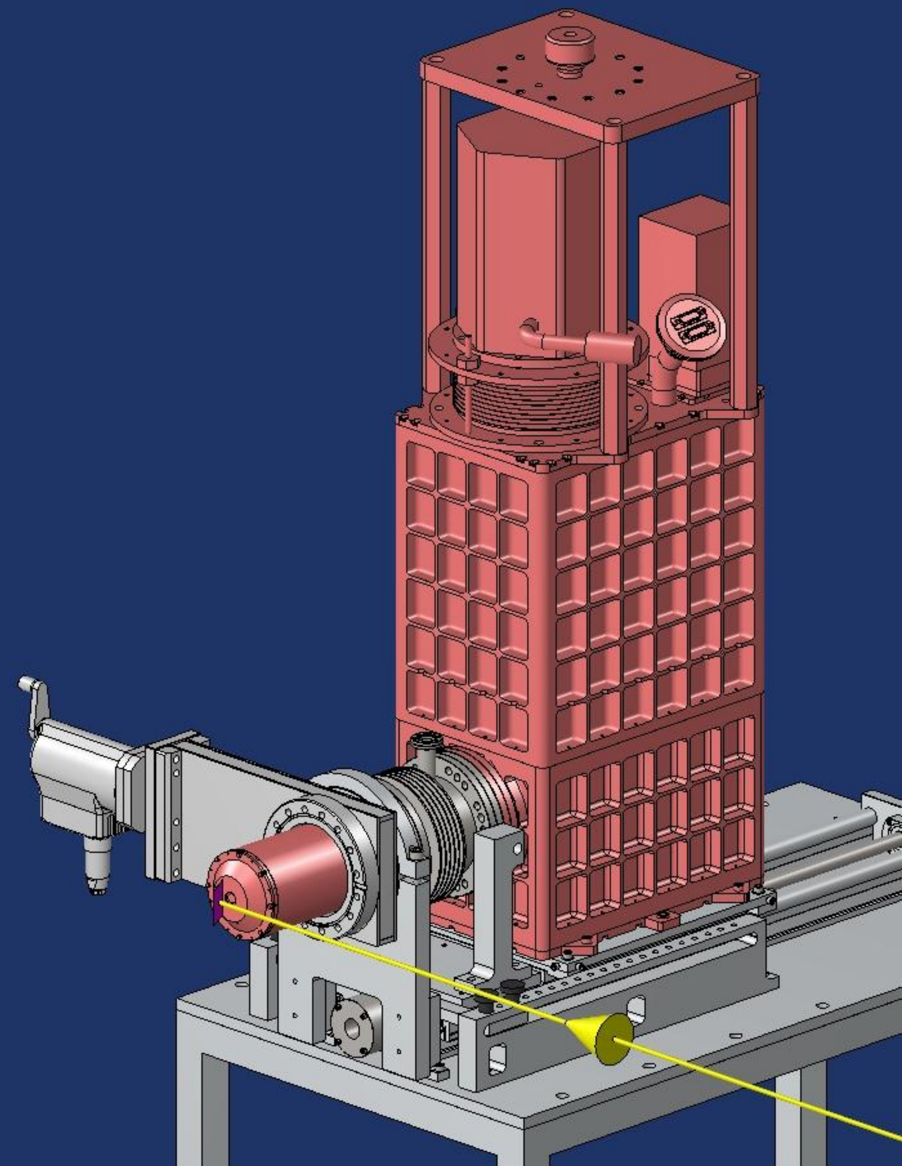
> 2 keV:
bent crystals



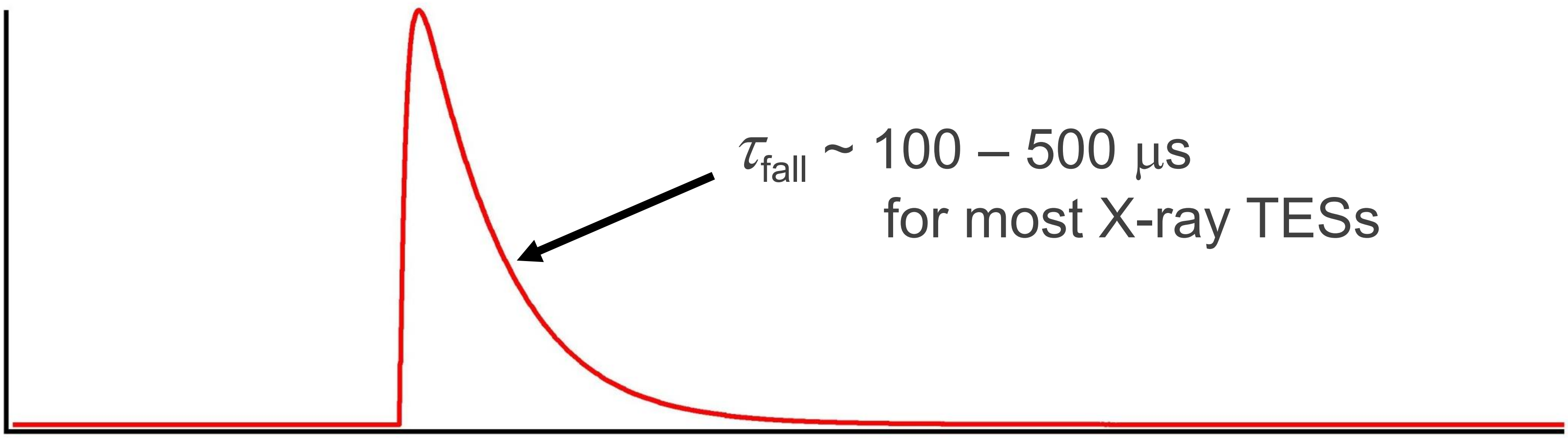
TES arrays for synchrotron-XES

How do TES arrays compare?

- ΔE: eV-scale
  to see chemical shifts
- large solid-angle coverage
- high QE
- see entire spectral ROI at once
- <u>count rate</u>: generally want
  1 MHz or better for synchrotron spectroscopy.



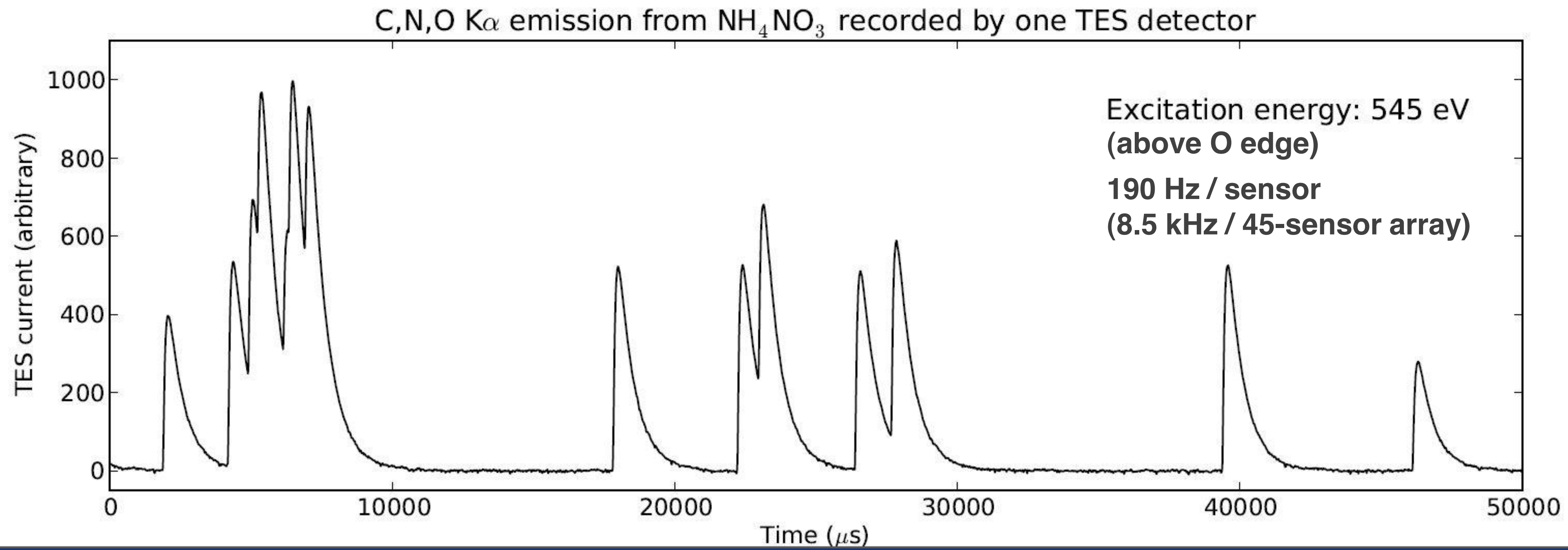
TES count rate



"optimal filter" [Szymkowiak, *JLTP* (1993)]:

- requires one γ / record
- limited to 10s of Hz / TES for highest resolution with practical X-ray-TES time constants

TES count rate

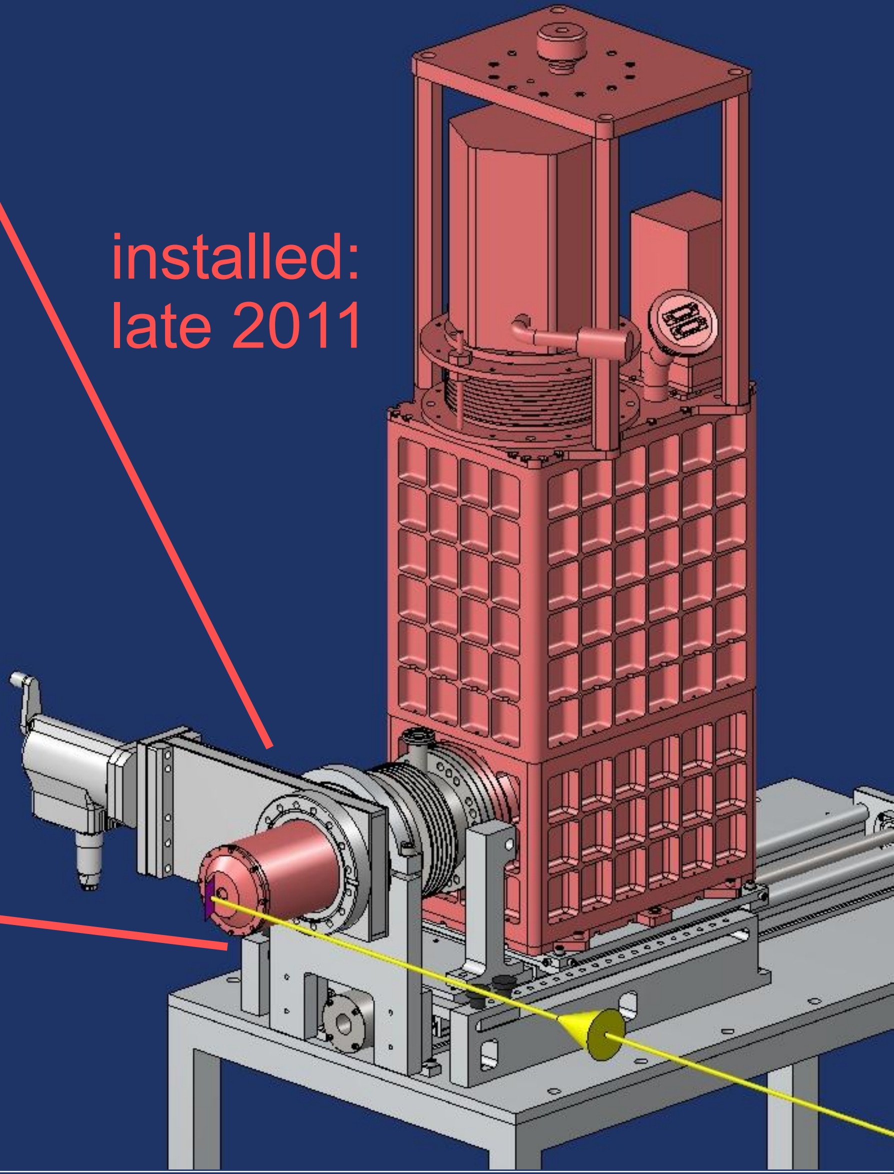


but what if data look like this?...

want *simultaneous* optimal filtering of >>1 γ / data-record

installed TES spectrometer

installed:
late 2011

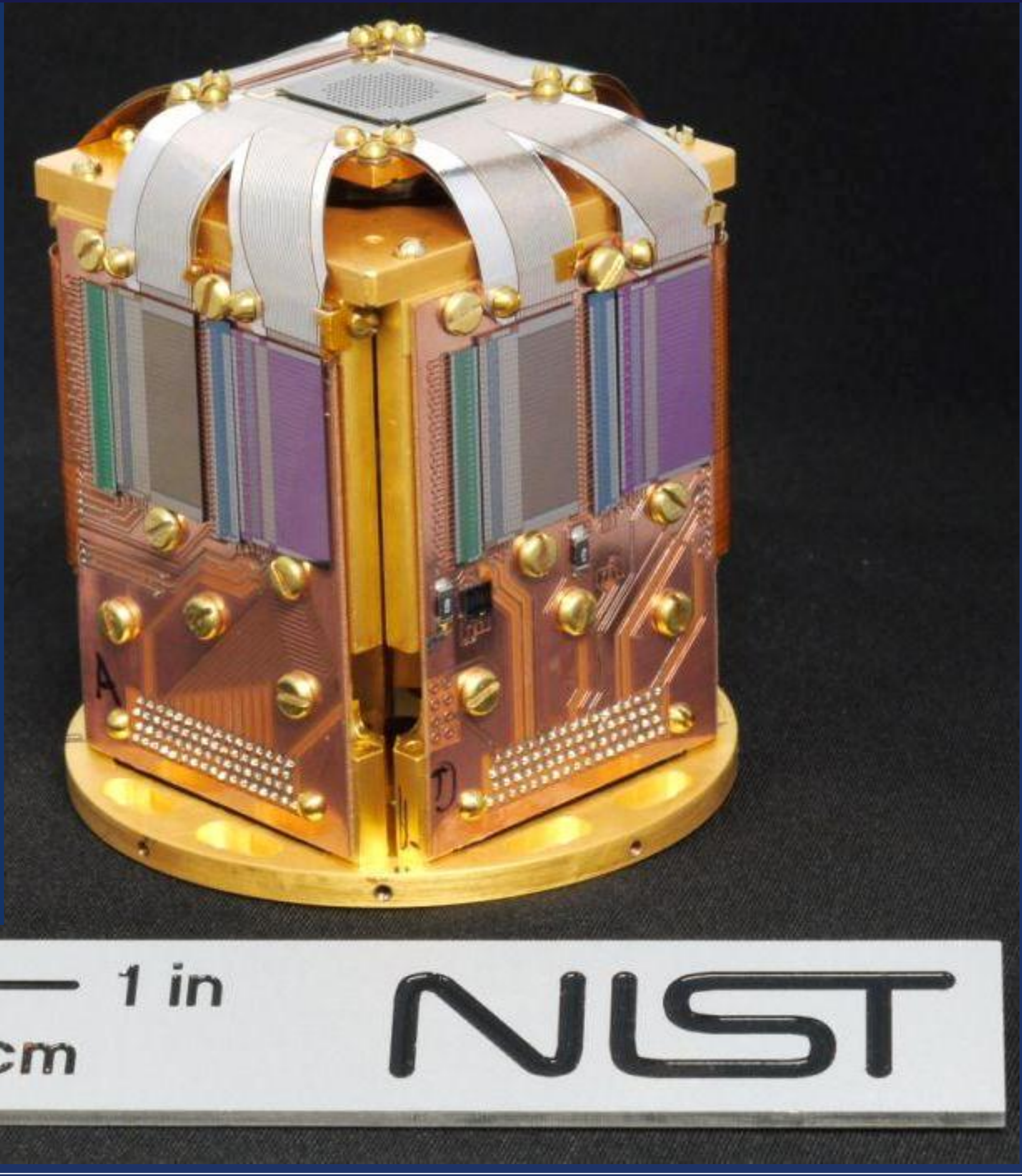


NSLS U7A:

soft-X-ray (200 – 800 eV) spectroscopy beamline.

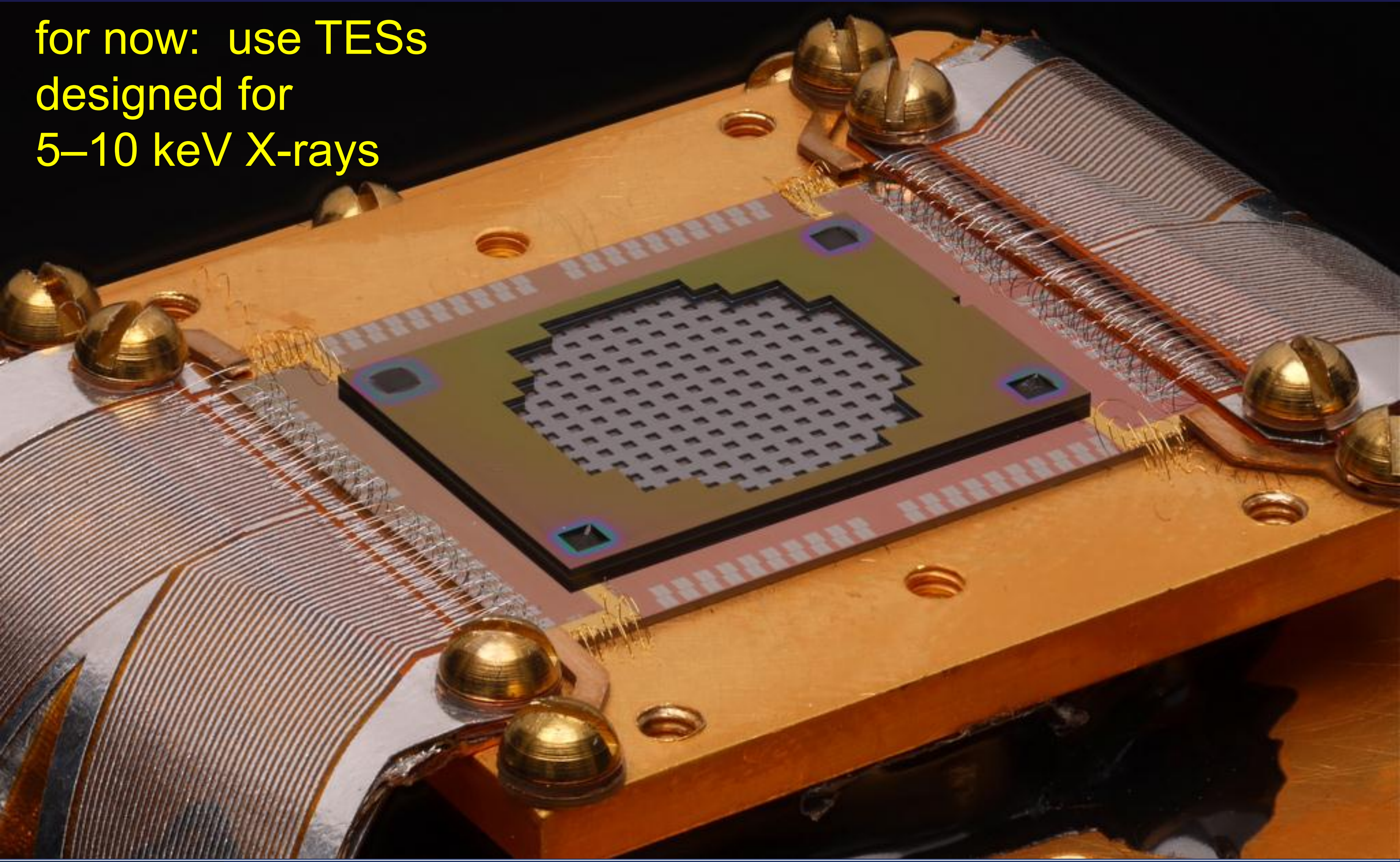
50 mK detector snout

- TES array on top
- TDM/CDM readout for up to 256 sensors (8col X 32row) around sides
- 50 mK bath: ADR
  (see ASC exhibitor HPD)
- architecture could be grown to 1,024 TESs (32c X 32r) straightforwardly



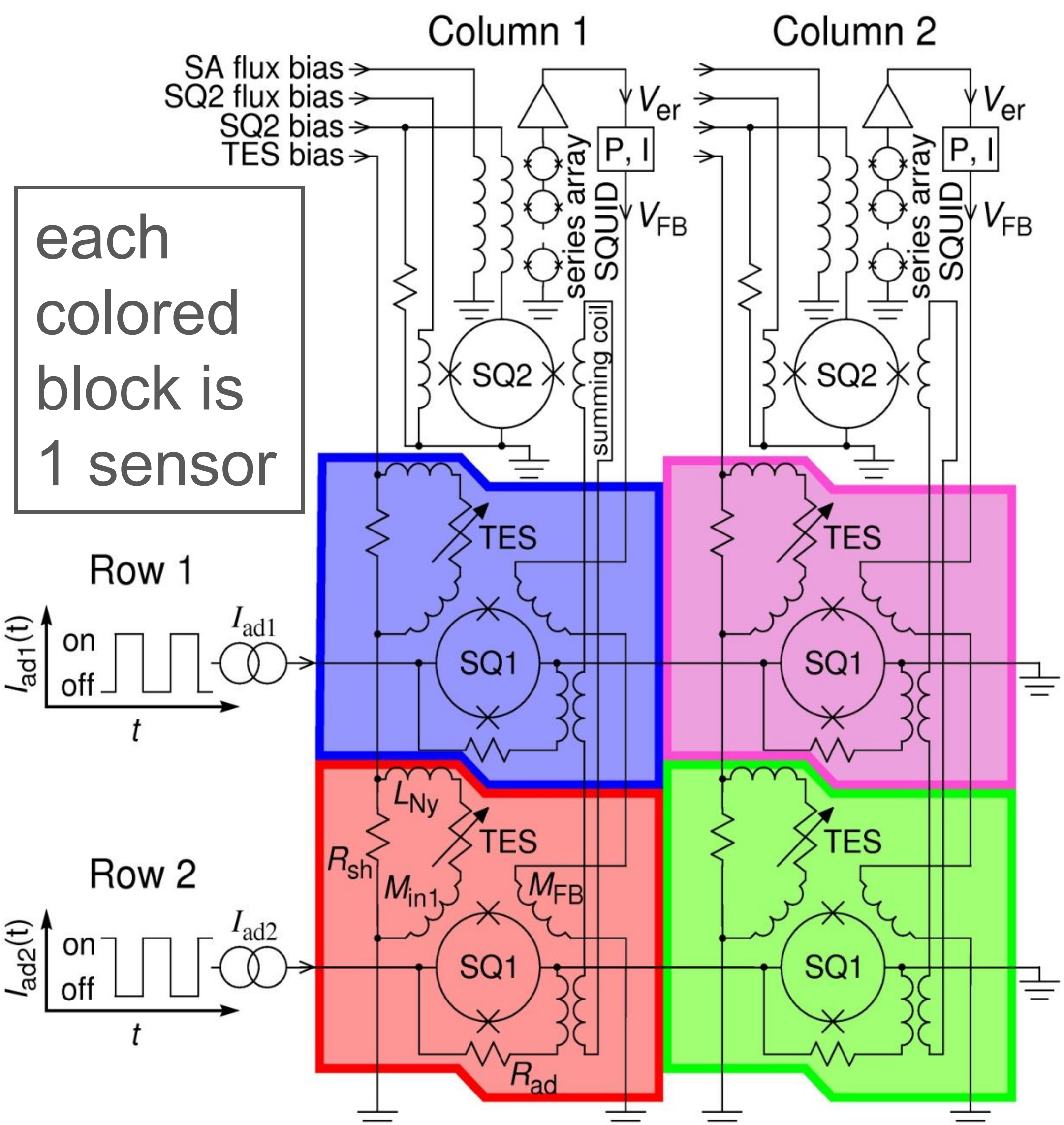
detector plane

for now: use TESs
designed for
5–10 keV X-rays



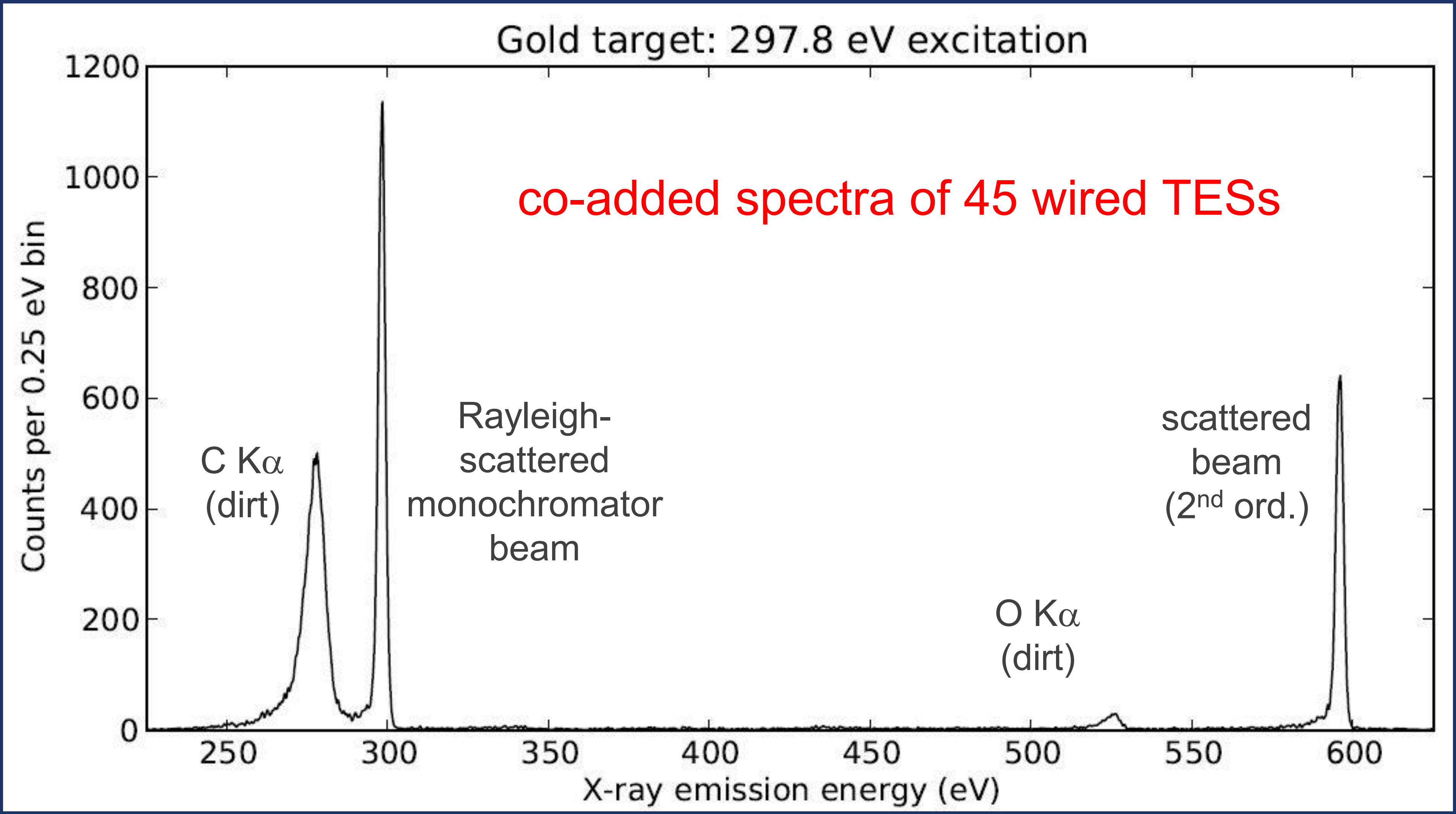
TDM readout

each colored block is 1 sensor

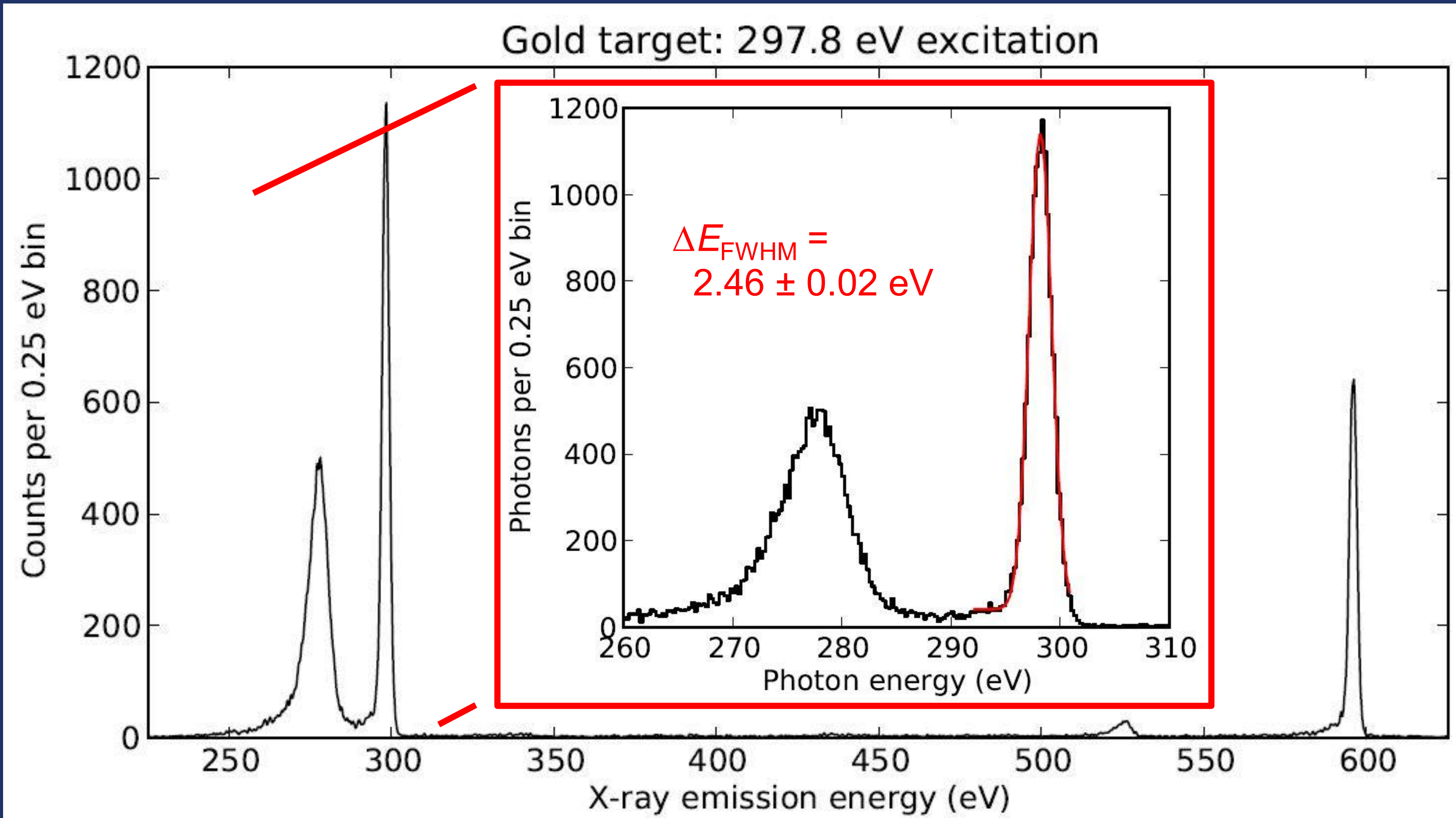


- initial setup:
  45 sensors wired into
  3 col x 20 row TDM
- will soon wire up full
  256 sensors

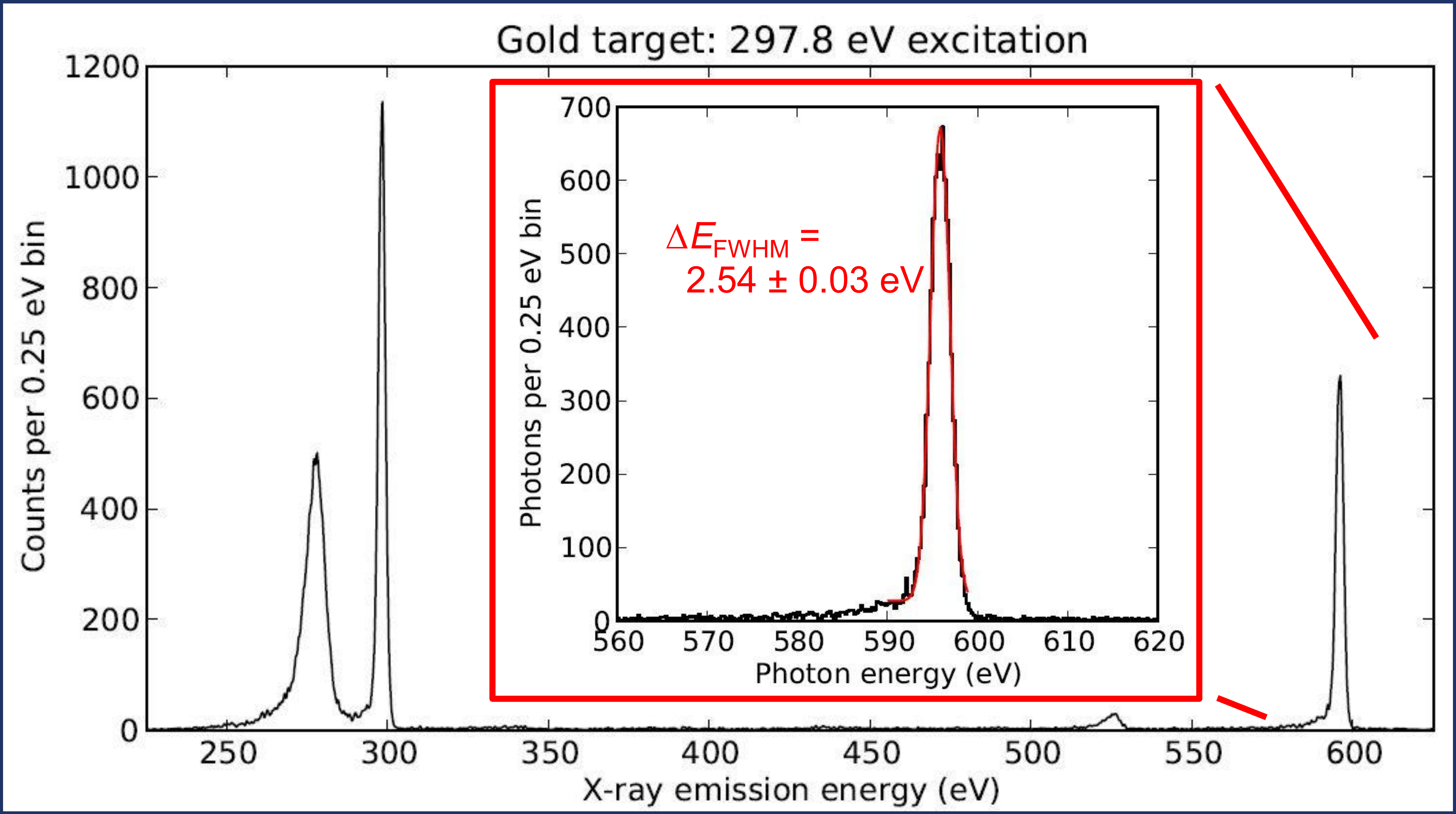
achieved energy resolution



achieved energy resolution



achieved energy resolution



applications

applications:

- eV-scale X-ray emission spectroscopy (chemistry of *occupied* valence states)
- partial-fluorescence-yield absorption spectroscopy (chemistry of *unoccupied* valence states)

Let's see an example of each!

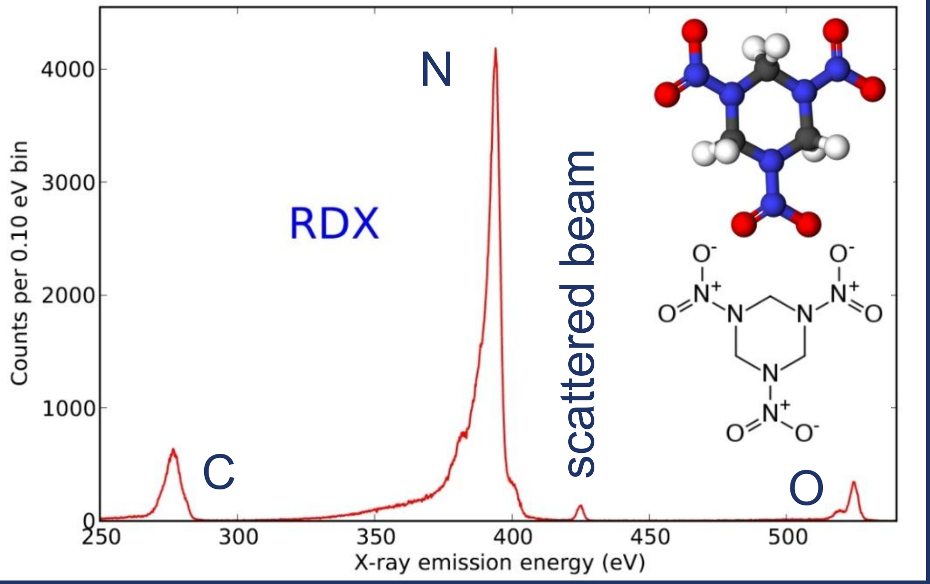
chemical-shift XES

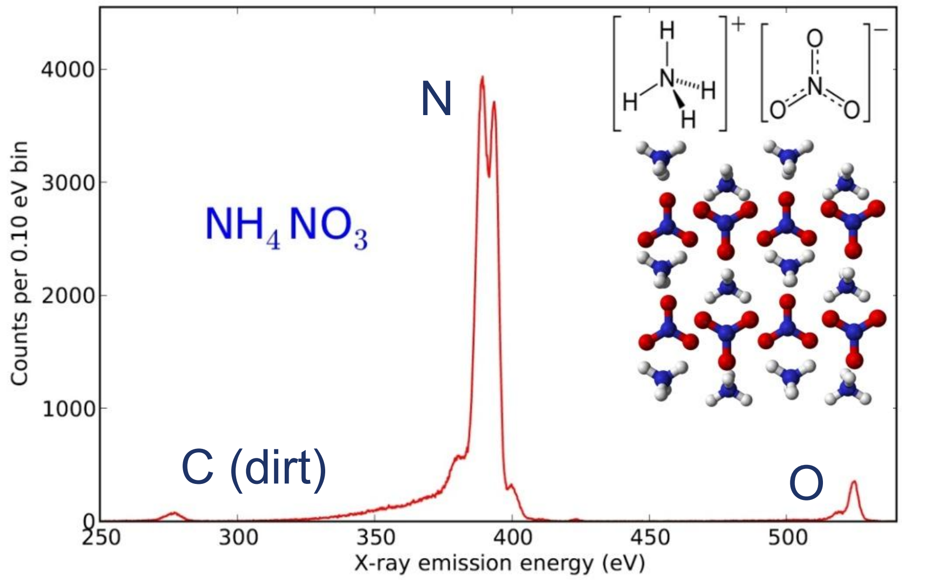
first example application:

X-ray emission spectroscopy (XES)
for chemical analysis

map occupied D.O.S.

chemical-shift XES



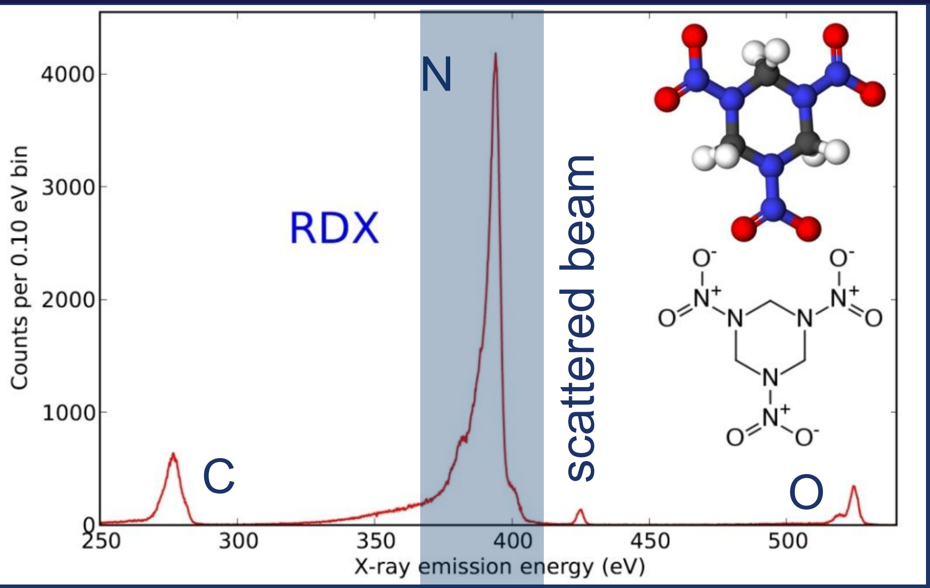


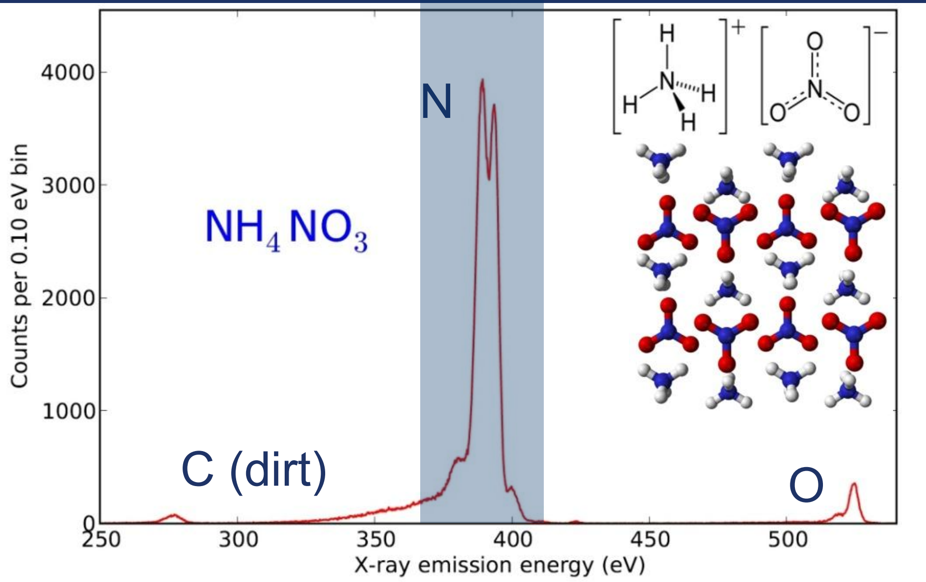
NIST is cataloging XES of "energetic nitrogen compounds" to aid SEM analysis of criminal forensic samples.

- RDX: major component of C4 plastic explosive
- ammonium nitrate (fertilizer; can be used to build fertilizer bombs)

excite @ 425 eV
(well above N edge).

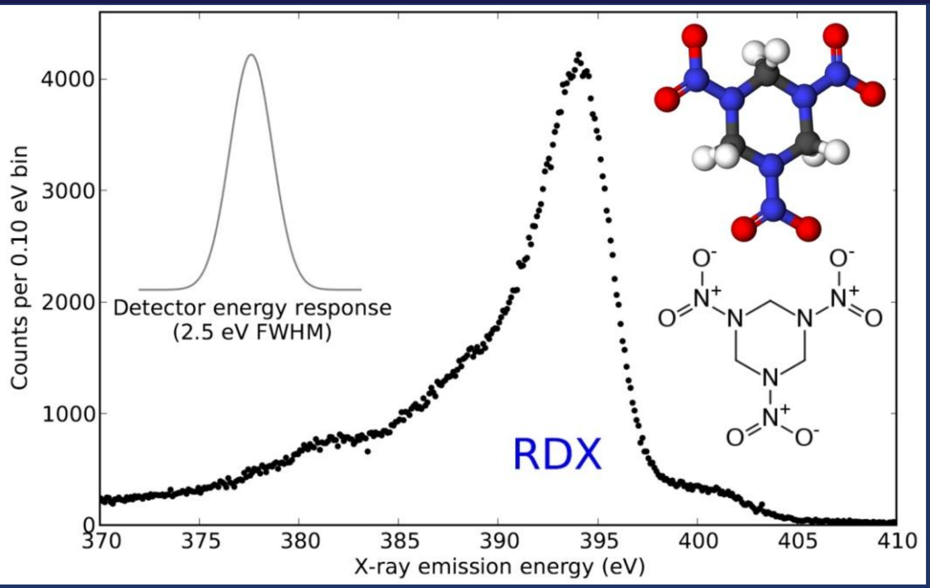
chemical-shift XES

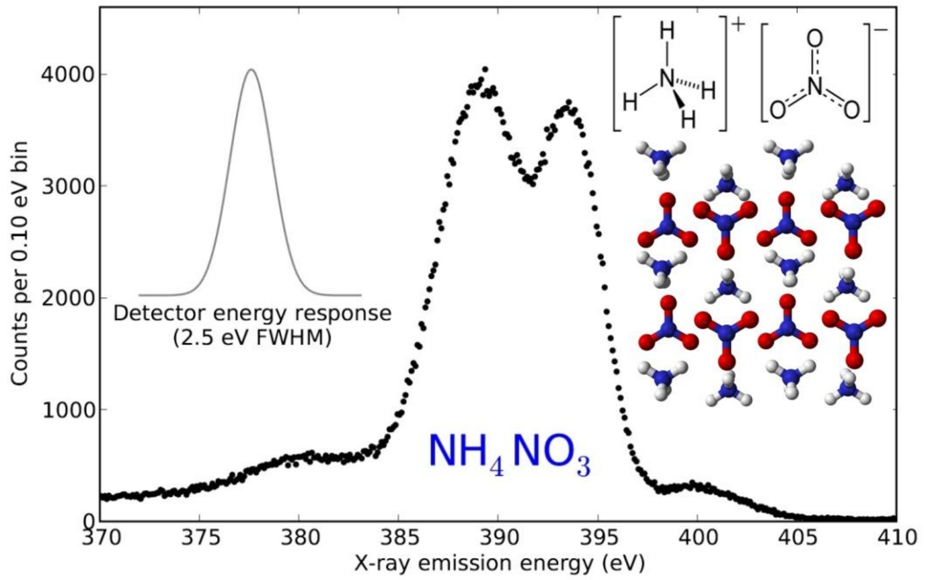




zoom in on nitrogen peak in each spectrum:

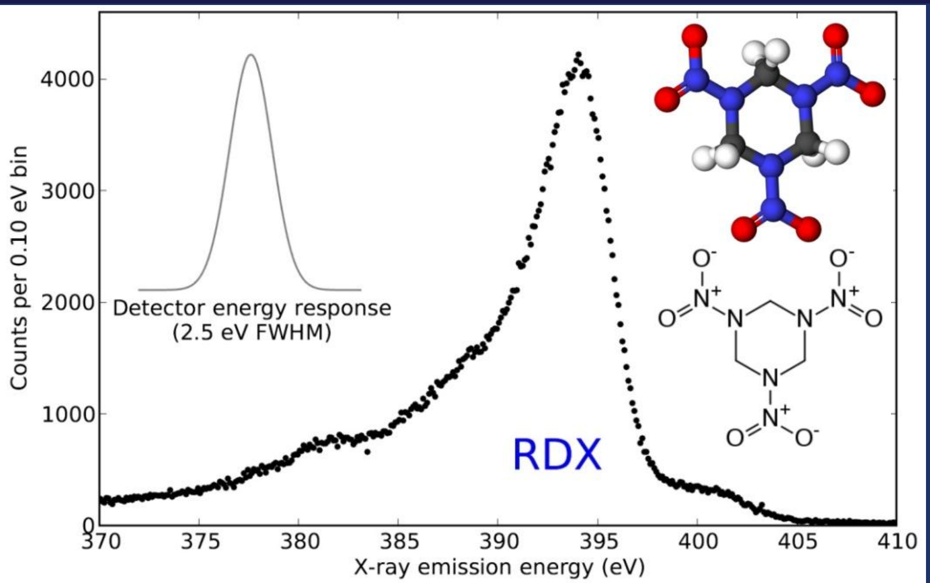
chemical-shift XES

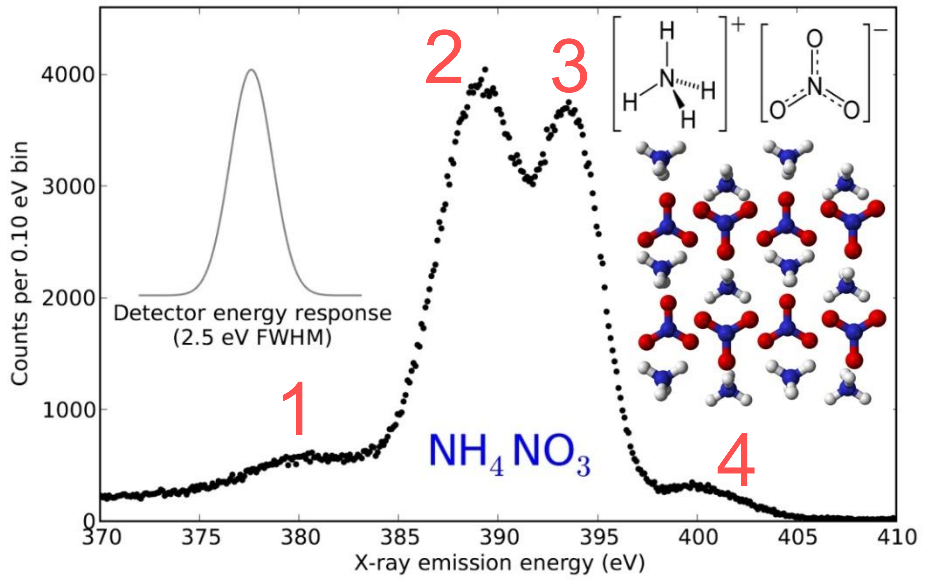




RDX is clearly distinguishable from NH_4NO_3.

chemical-shift XES





further, NH_4NO_3 has four resolved features that are associated with:

- NH_4^+ (highly reduced N)
  (2)
- NO_3^- (highly oxidized N)
  (1, 3, 4)

(feature ID's from F.D. Vila, et al., *J Phys. Chem. A*, 115, 3243-3250 [2011])

PFY-NEXAFS

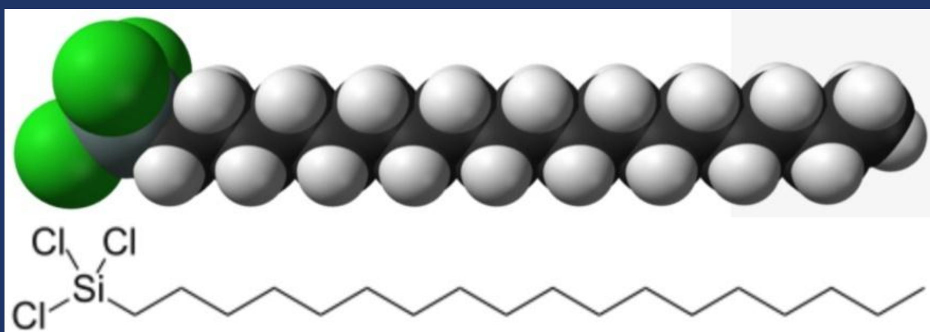
second example application:

partial-fluorescence-yield
near-edge X-ray absorption fine structure
(PFY-NEXAFS)

map unoccupied D.O.S.

PFY-NEXAFS

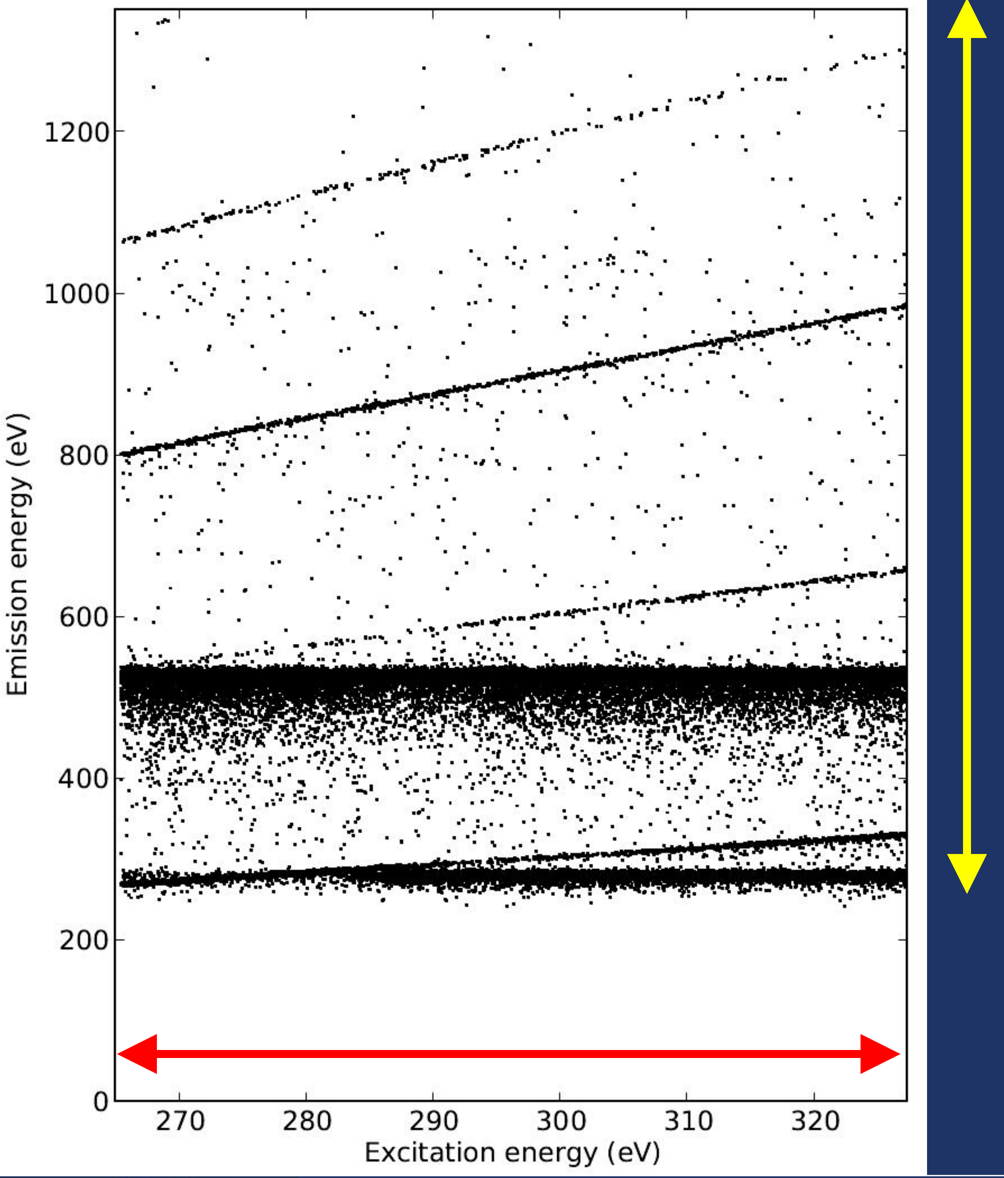
a difficult sample: NIST standard reference material (SRM) 1216-I



octadecyltrichlorosilane (OTS) at 0.7% C by mass in porous microparticulate SiO_2 (particle diam. = 20 μm)

want to do carbon-edge absorption spectroscopy

PFY-NEXAFS

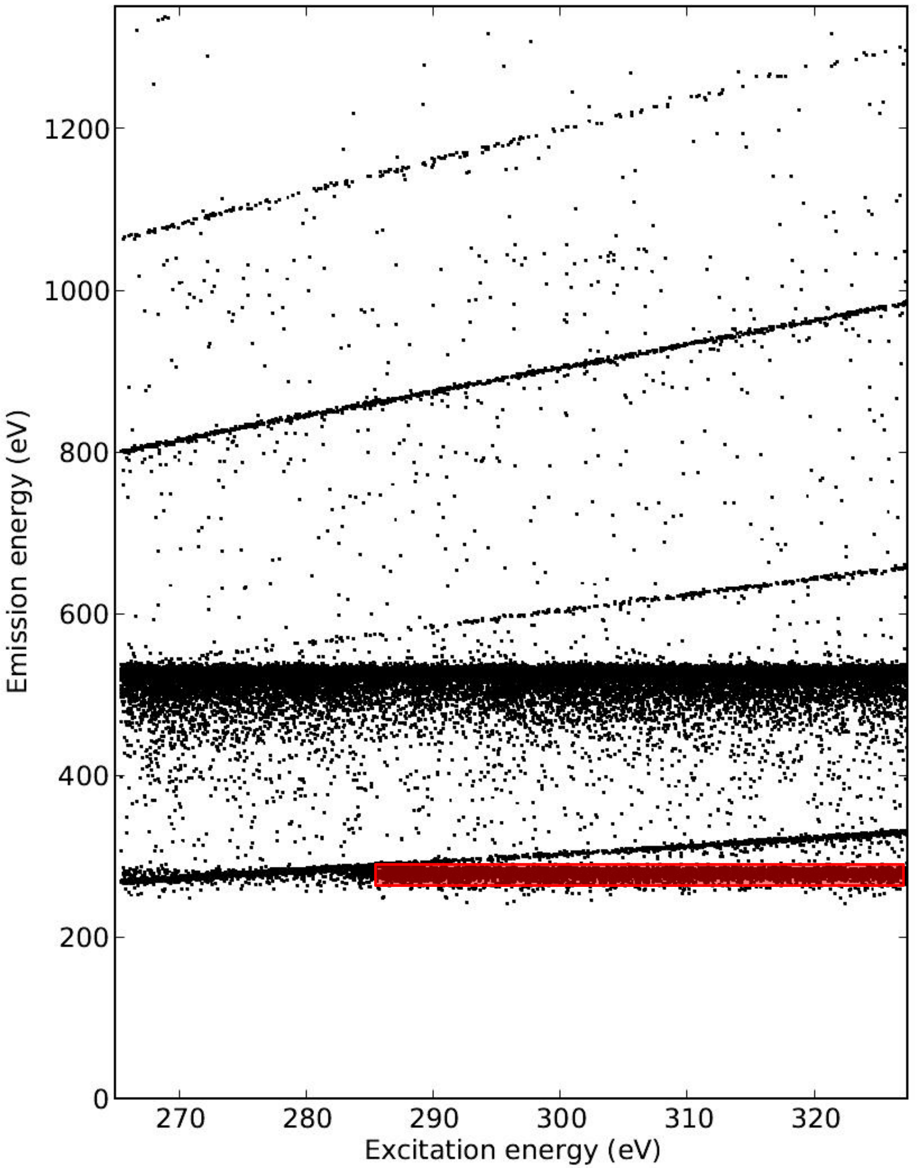


emission collected simultaneously from 200 eV to 1400 eV by TES array

(beamline produces no photons above 1400 eV)

beamline monochromator scanned from 265 to 327 eV (across C edge)

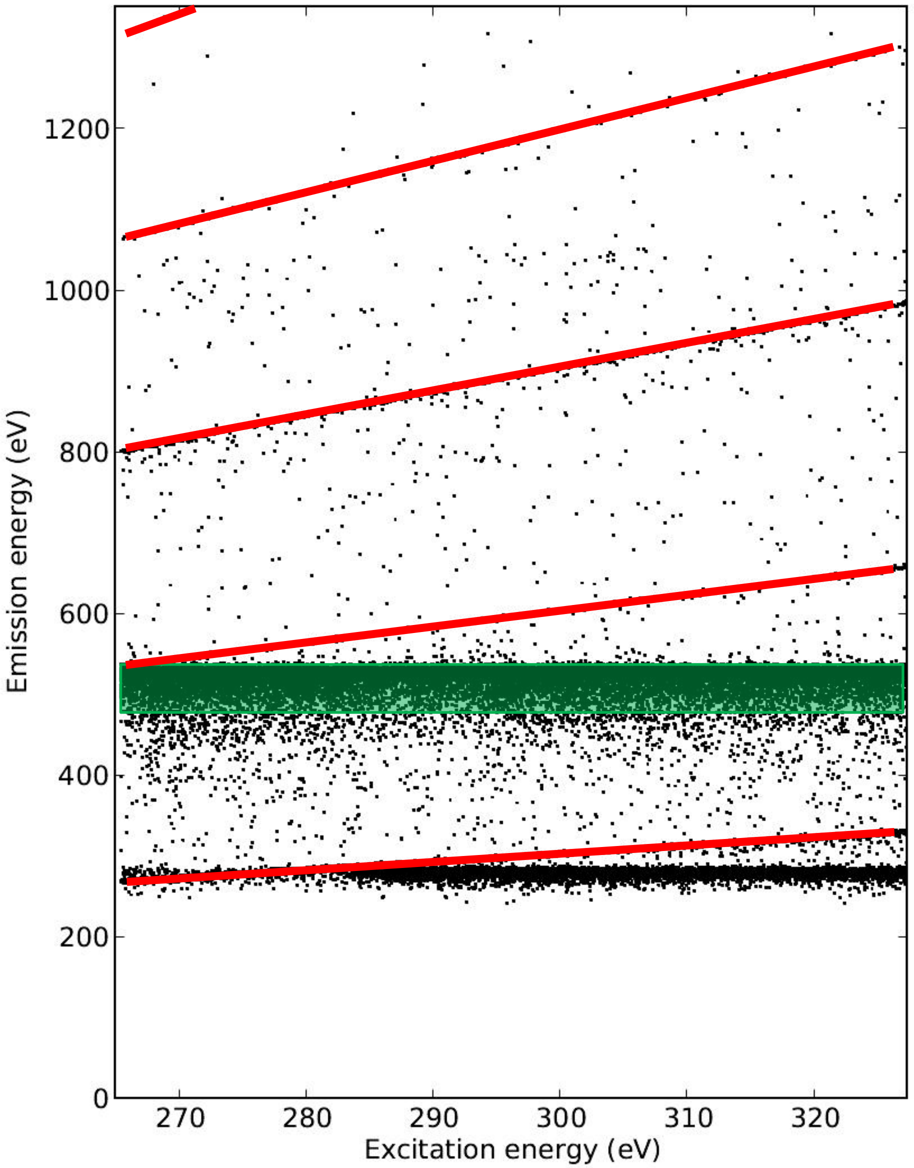
PFY-NEXAFS



- each point is an X-ray
- 1.6 million X-rays in 20 minute scan
- < 10% of total data plotted for clarity

← C Kα: desired signal (track strength vs. E_{beam})

PFY-NEXAFS

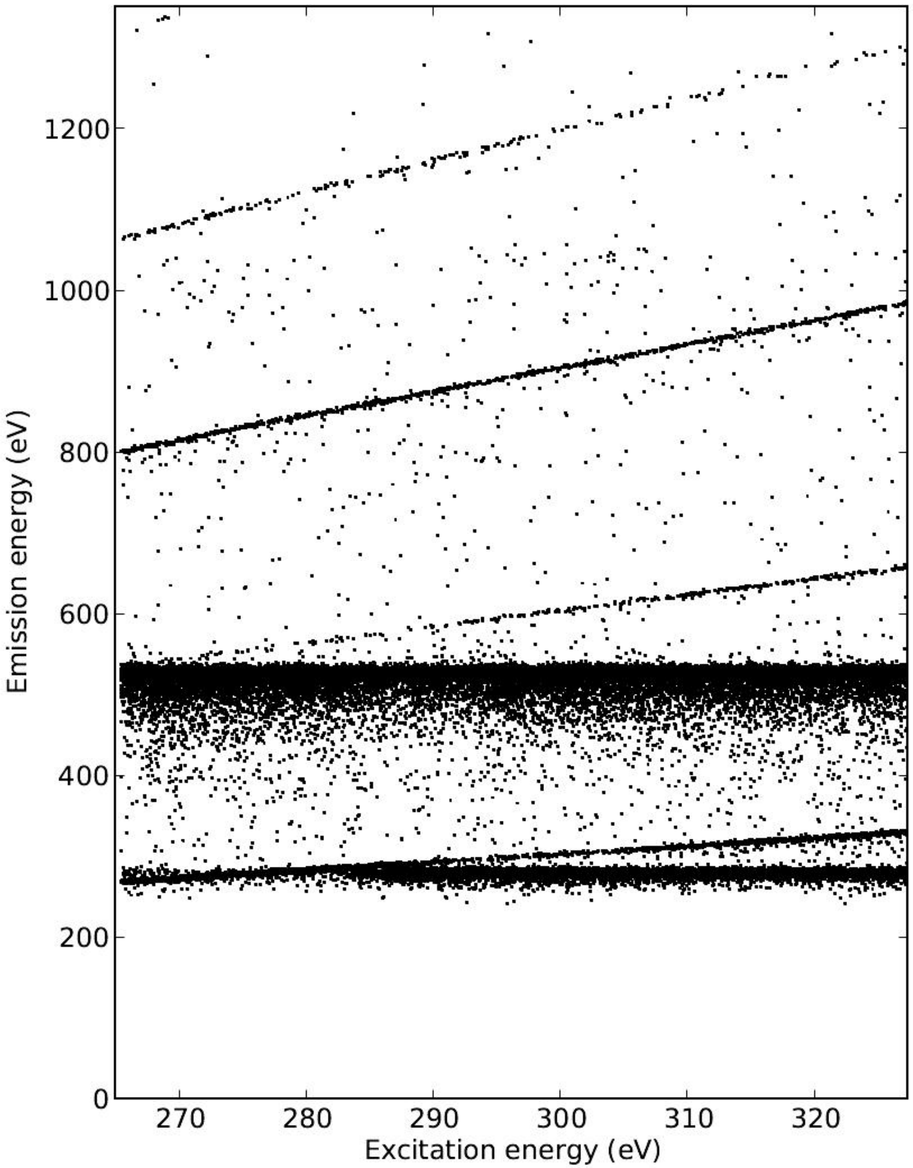


backgrounds:

harmonics 1 – 5 of scattered beam

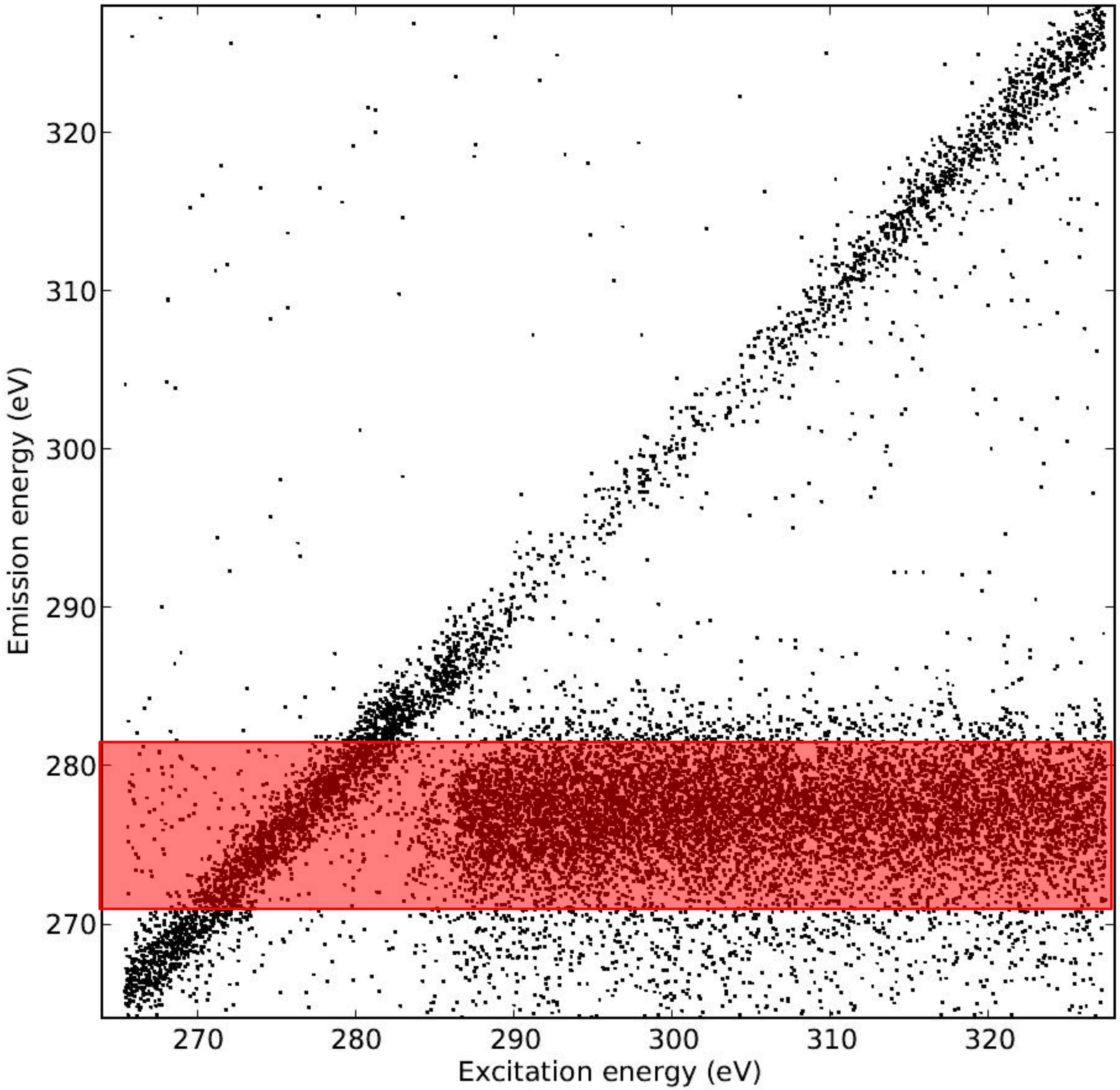
O Kα (excited by harmonics)

PFY-NEXAFS



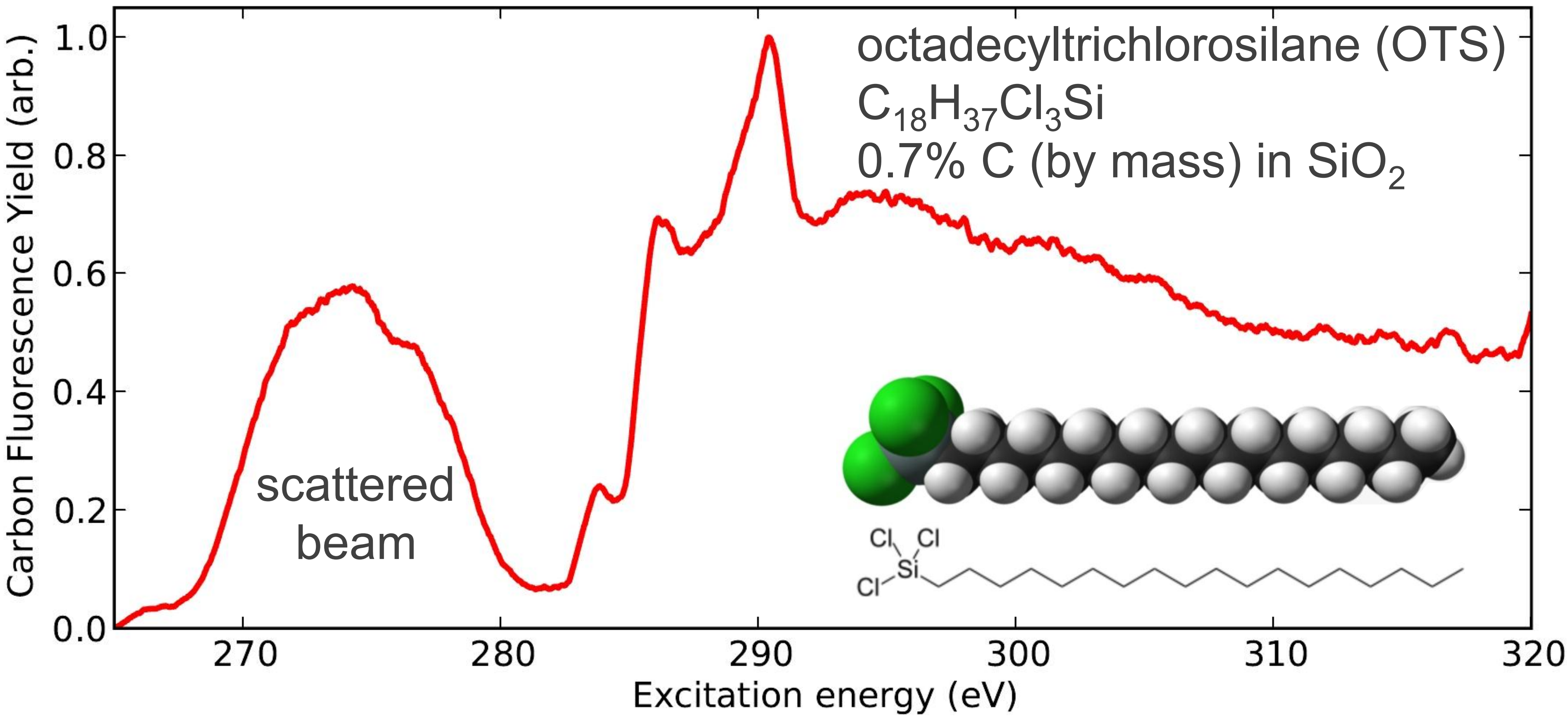
zoom

PFY-NEXAFS



window on C Kα, histogram

PFY-NEXAFS



resulting NEXAFS spectrum

conclusions

- best-ever ΔE achieved at a synchrotron by an energy-dispersive X-ray spectrometer

- observed chemical shifts in XES data at 400 eV:
  - 45 sensors optimized for 5 – 10 keV X-rays
  - sample receiving ~ 6×10^9 γ/s on a BM beamline

- kilo-sensor spectrometer under development:
  - $\Delta E_{\mathrm{FWHM}} \rightarrow 0.5 – 1$ eV ($E\gamma$ < 700 eV)
  - toward 1 MHz / array-rate!

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