Inelastic X-Ray Scattering & Transition Metals

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uickTime™ and a Animation decompressor are needed to see this picture.

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Nitrogen Fixation

$N_2 \rightarrow 2NH_3$

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- 948 kJoules/mole

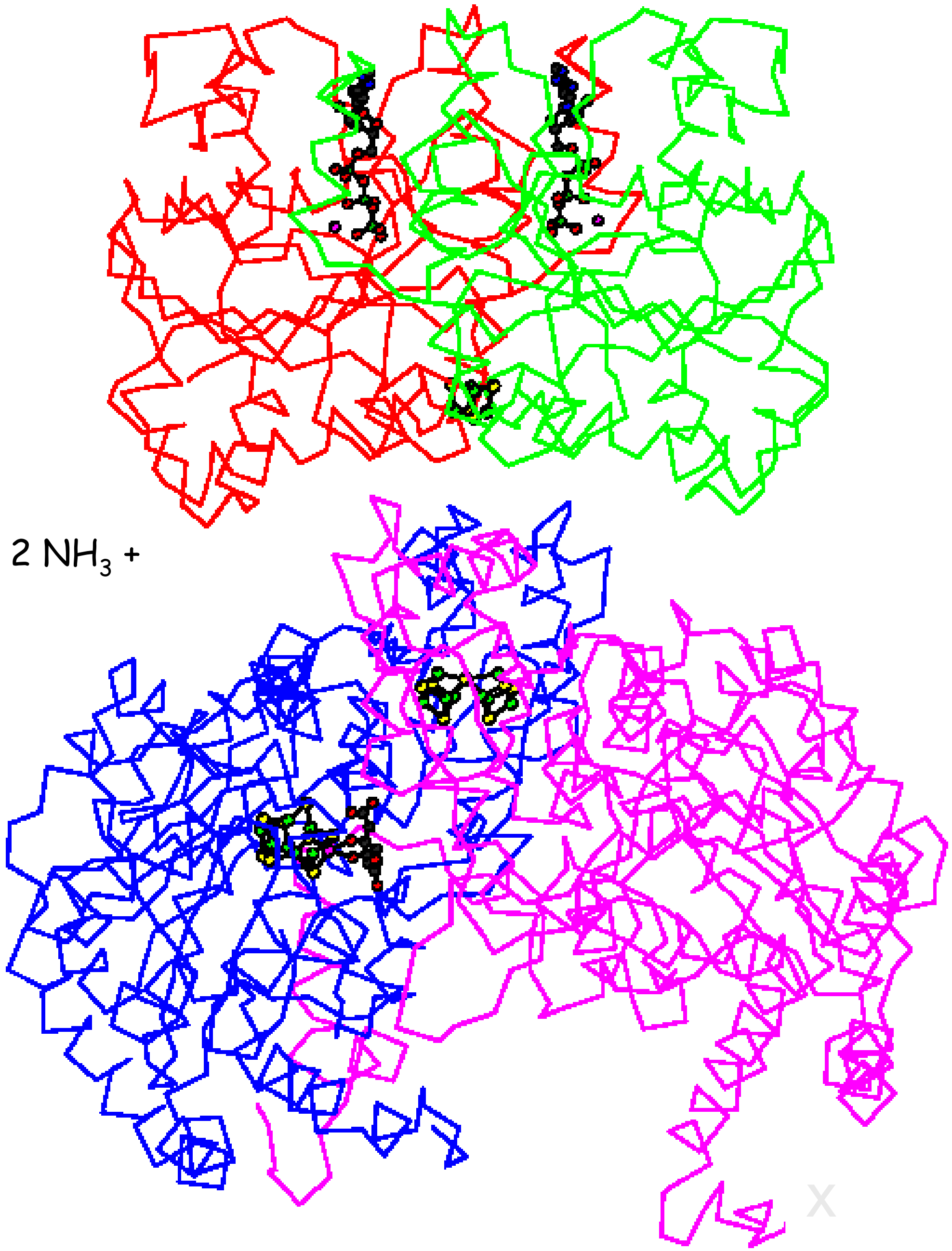
- Lightning & Industrial Processes
  - ~1.5 x 10^{11} kg/yr
  - Haber-Bosch process
  - K-promoted Fe catalyst

- Biological Fixation
  - >1/2 global NH_3 production
  - blue green algae
  - free-living bacteria
  - symbiotic bacteria
  - MFe_7S_8 cluster

- **Nodules on alder seedling**
- www.ncl.ac.uk/gane/ page2.htm

Nitrogen Fixing Proteins

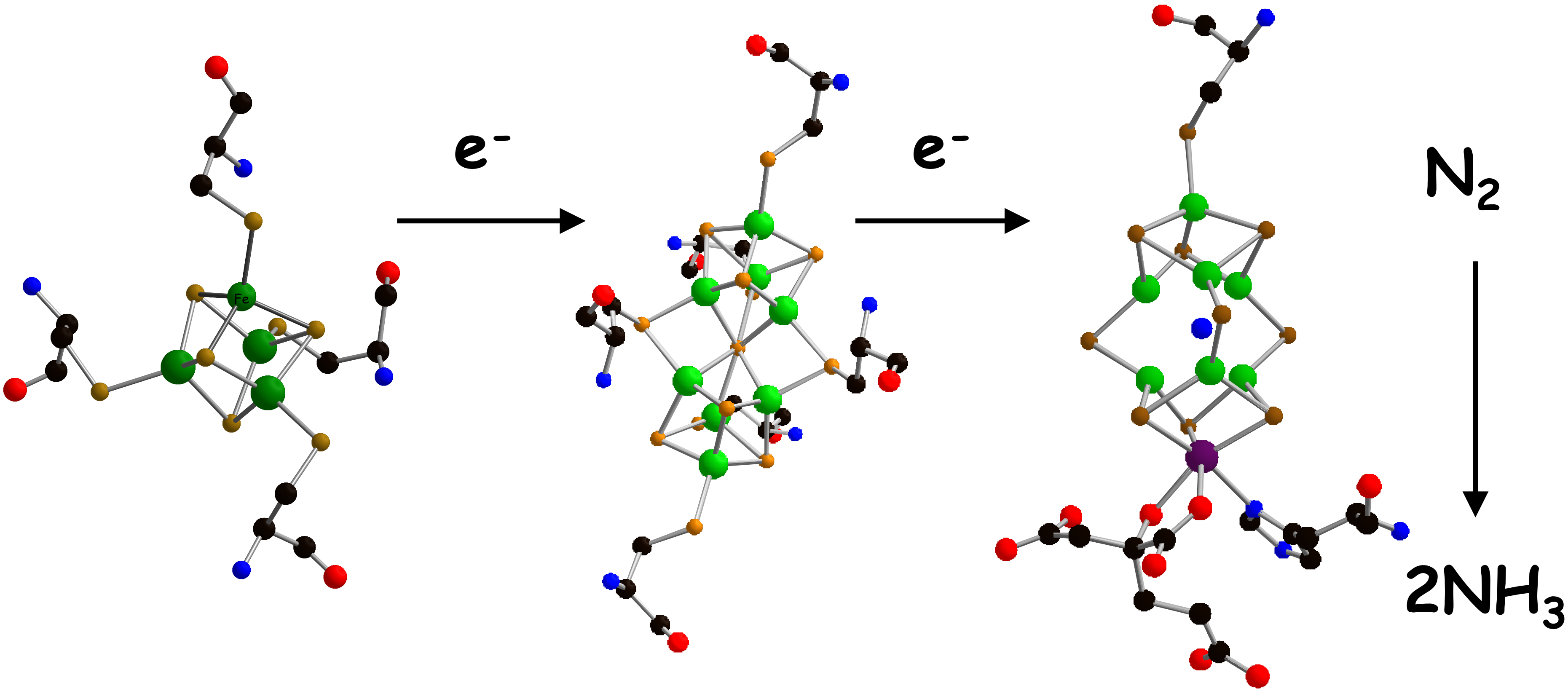
- Fe protein



- $N_2 + 8H^+ + 8\ e^- + 16ATP \rightarrow 2\ NH_3 + H_2 + 16ADP + 16P_i$

- Mo-Fe Protein (N_2ase)

Fe Clusters in N_2 Fixation



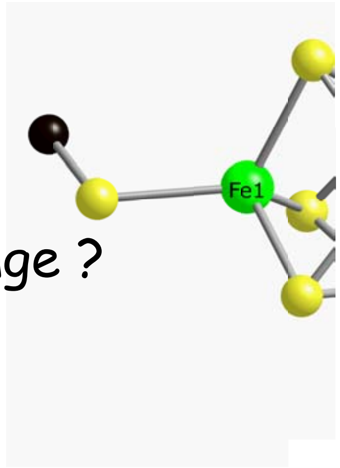
- Fe Protein
  Fe_4S_4 cluster

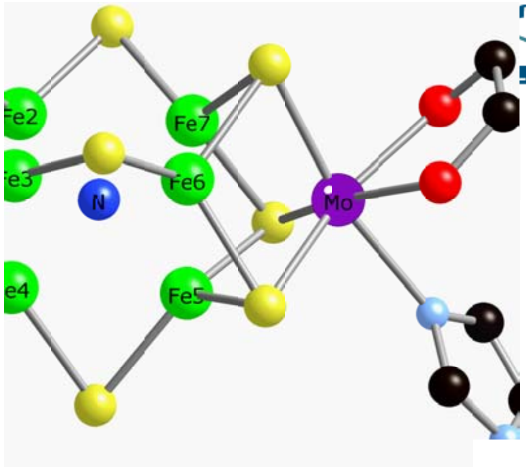
- P-cluster
  Fe_8S_7

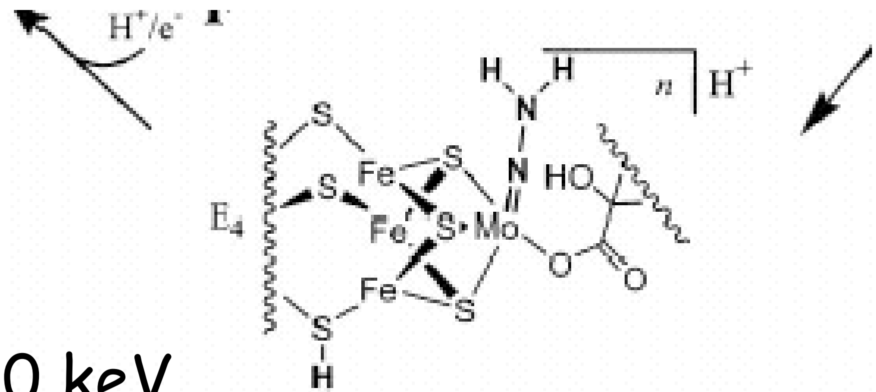
- FeMo cofactor (M-center)
  $MoFe_7S_9X$

Some Key Issues

- What is interstitial atom ?
- Does interstitial atom exchange ?
- Where does N_2 bind ?
  - Fe ?
  - Mo ?
  - S ?
- Does cluster rearrange ?
- Metal oxidation states ?

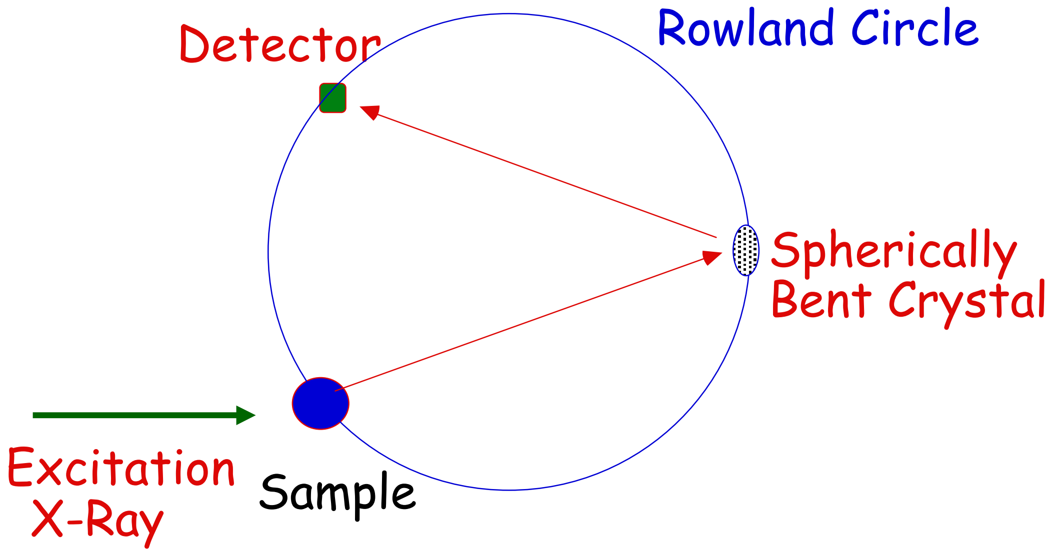






- Need probes from 2.5 - 20 keV

Roland Circle X-Ray Analyzer



- Roland circle radius r
- Crystal bending radius 2r
- Works best at large θ
- Different crystals every ~ 300 eV

Some Factors Governing Resolution

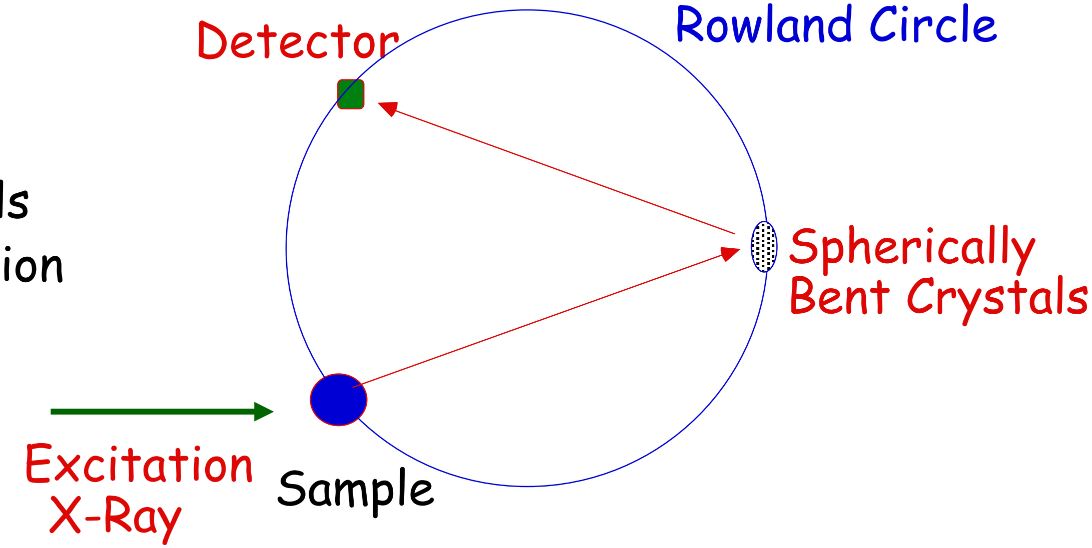
- Darwin width
  - $\Delta E/E = \Delta\Theta \cot \Theta$
  - ~ 62 meV for Si(4,4,0) at 6.49 keV
- Spherical aberrations
  - ~ crystal diameter
- Mechanical Strain
  - ~ 0.2 eV
- Source size
  - ~ 1eV at ~ 1mm

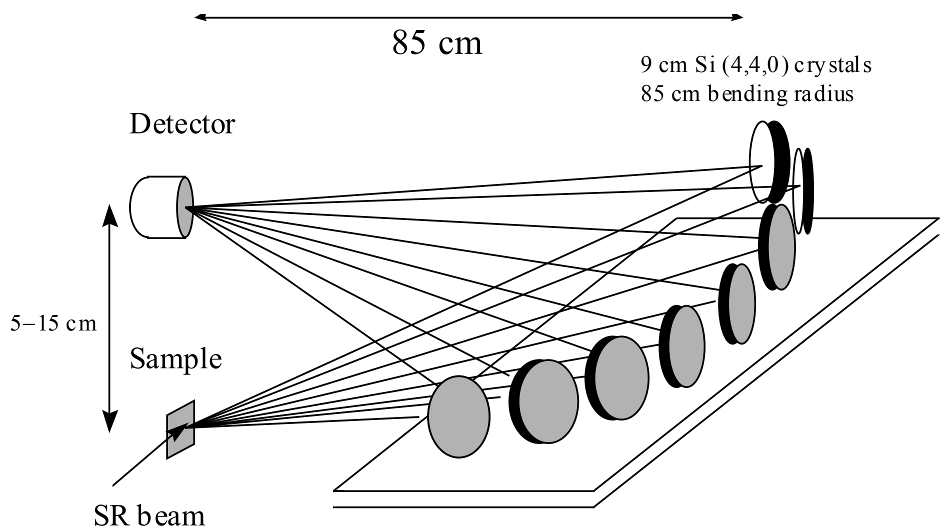
Generations of (Moderate Resolution) Instruments

- 1 - NSLS
  - Mechanical bending ~1 m radius
  - Single crystal
- Stojanoff, Hämäläinen, Siddons, Hastings, Berman, Cramer, and Smith, ``A High-Resolution X-Ray Fluorescence Spectrometer for Near-Edge Absorption Studies", *Rev. Sci. Instrum.* **63**, 1125-1127 (1992)
- 2 - SSRL
  - Mechanical bending
  - Multiple crystals
- Wang, Grush, Froeschner, Cramer, ``High Resolution X-ray Fluorescence and Excitation Spectroscopy of Metalloproteins", *J. Syn. Rad.* **4**, 236-242 (1997)
- 3 - APS (BioCAT)
  - 'form-bent' (glue) ~1 m radii
  - 8 crystals, 0.5% of 4π steradians
- Bergmann and Cramer, ``A High-Resolution Large-Acceptance Analyzer for X-ray Fluorescence and Raman Spectroscopy", **SPIE Proc. 3448**, 198-209 (1998)
- 4 - BioCAT
  - 'form' bent (electrofusion) ~ 2 m radii
  - multiple crystals

Crystal Array X-Ray Spectrometer

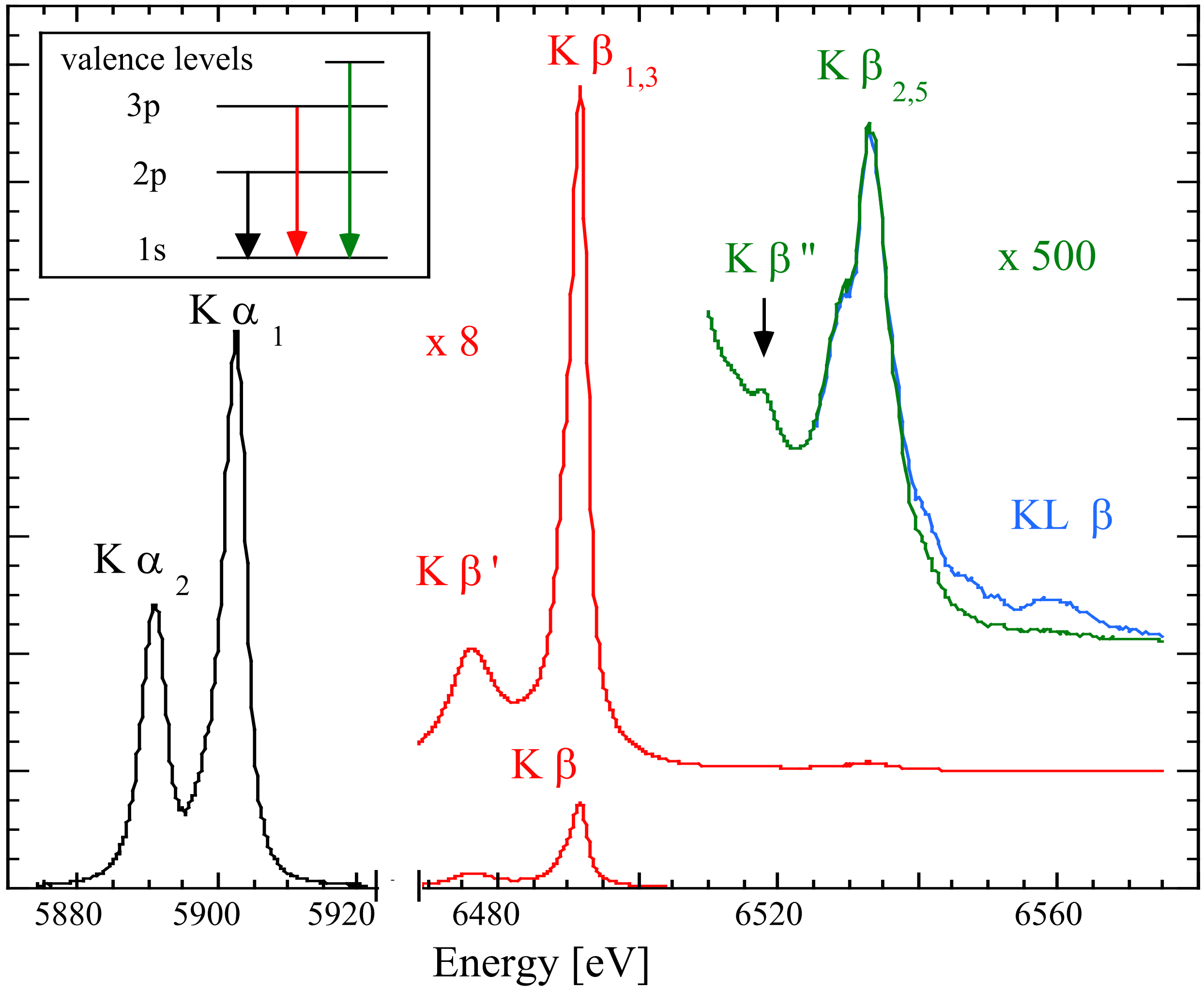
- 8 Si(440) xtals
- ~ 1 eV resolution
- ~0.5 % W



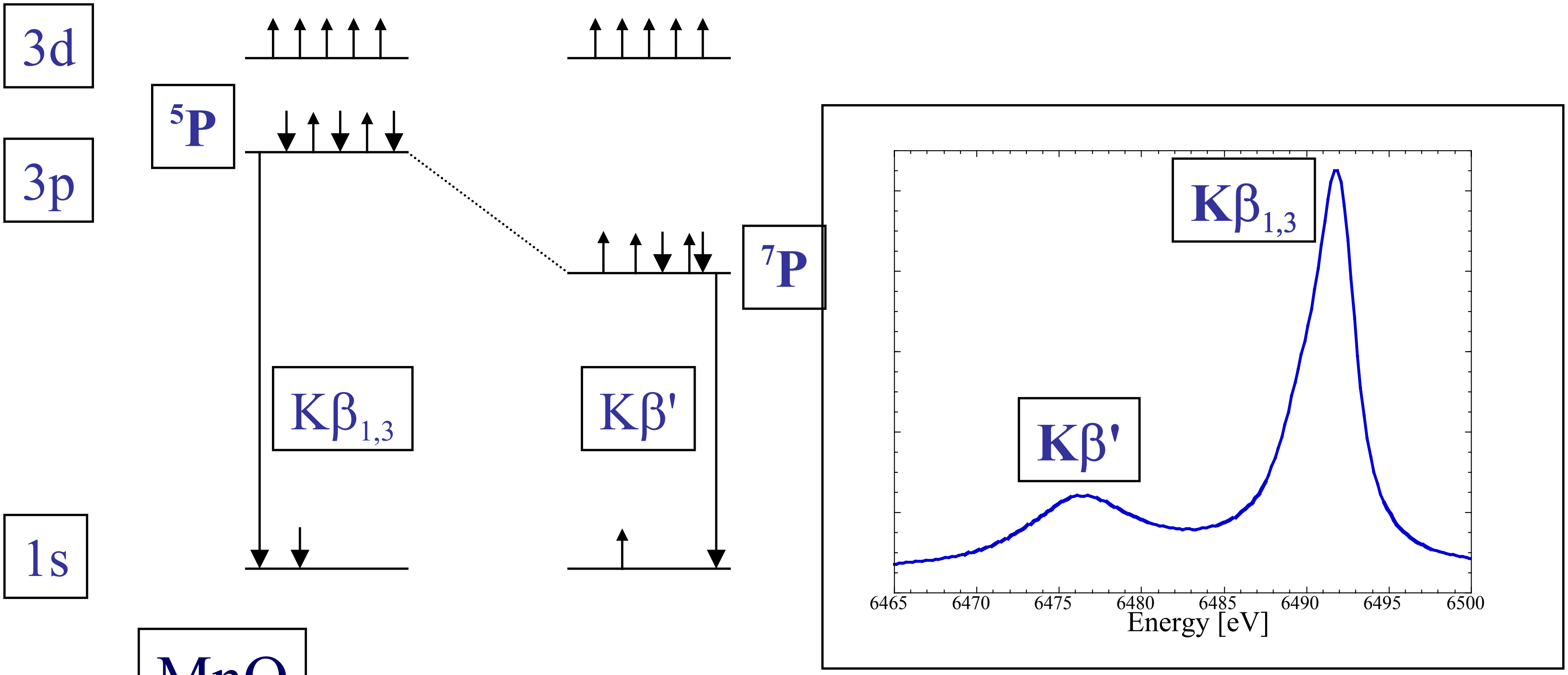


- Different crystals every ~ 300 eV

X-Ray Fluorescence -
An Alternative Probe of Electrons & Spins

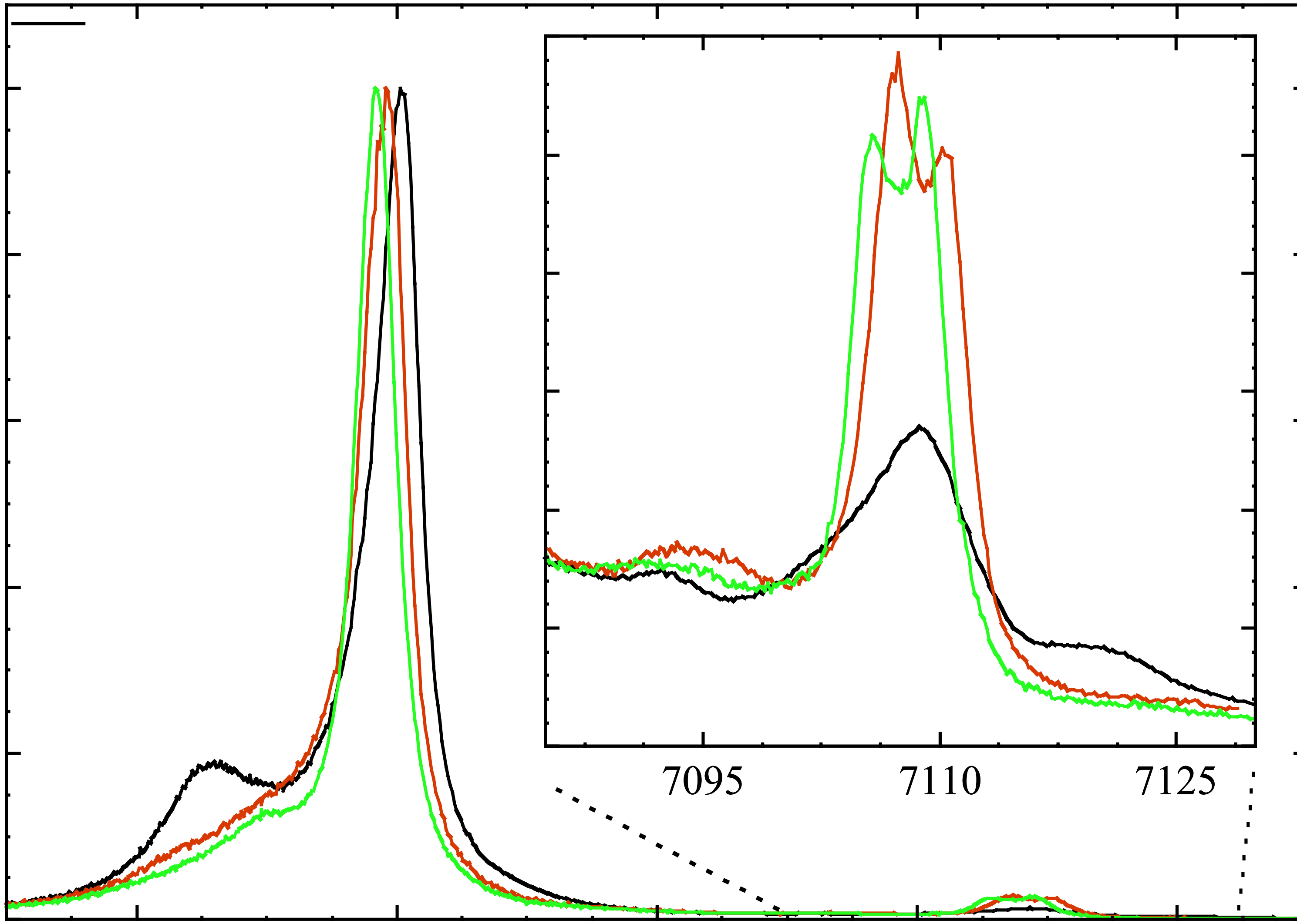


Exchange Splitting in Kβ Spectra

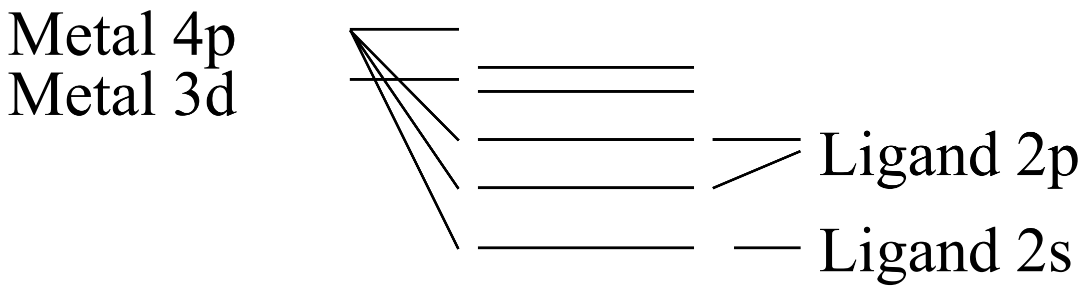


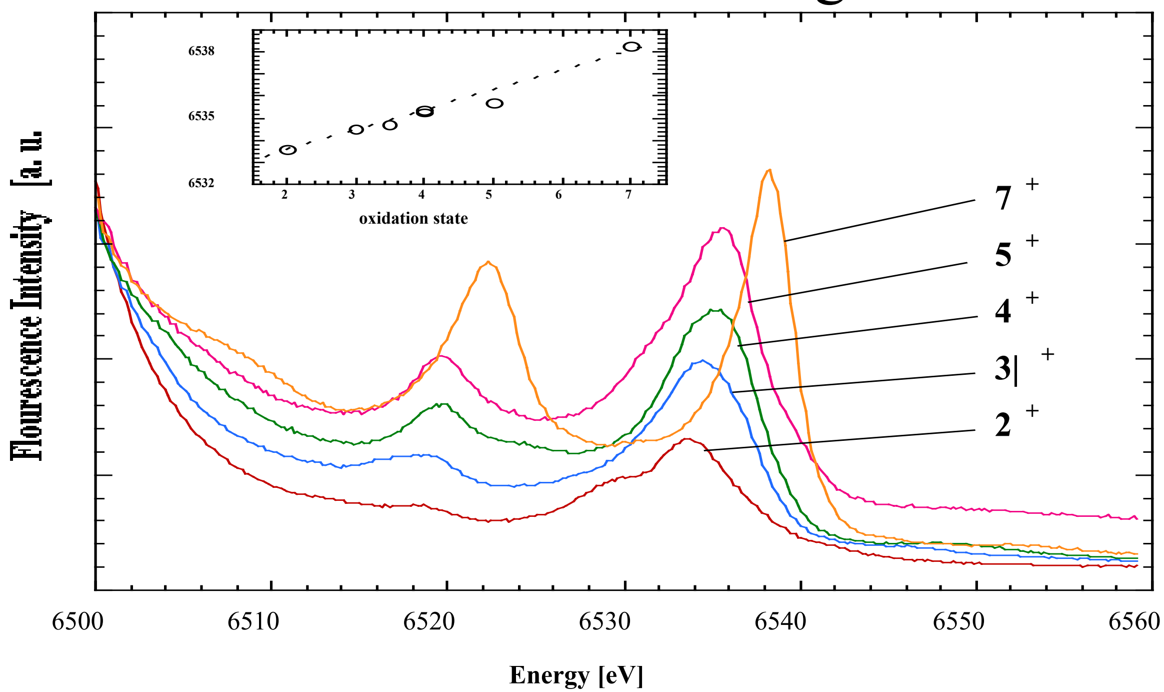
MnO

Photoexcited Spectra in Fe Compounds

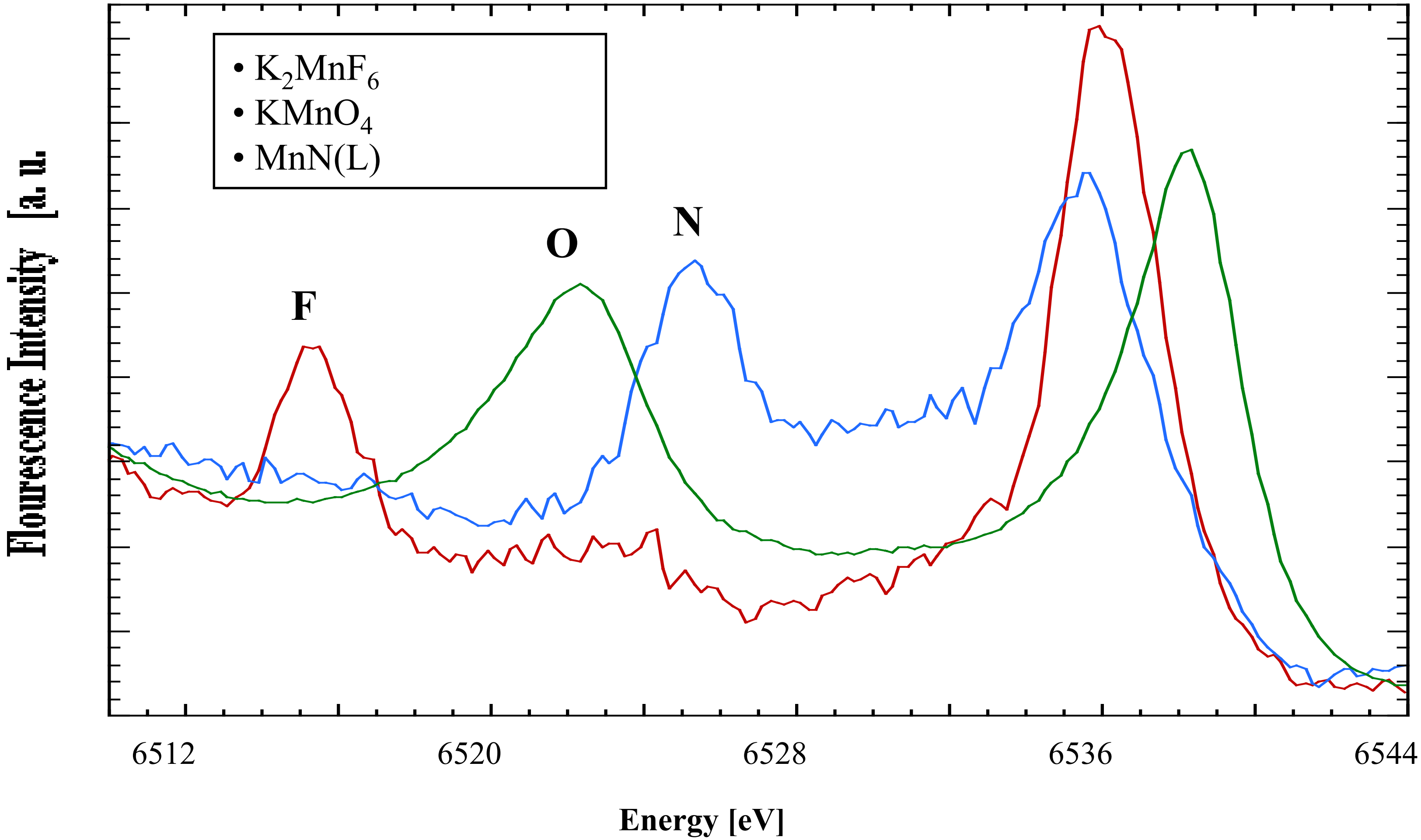


Mn Valence -> Core Transitions





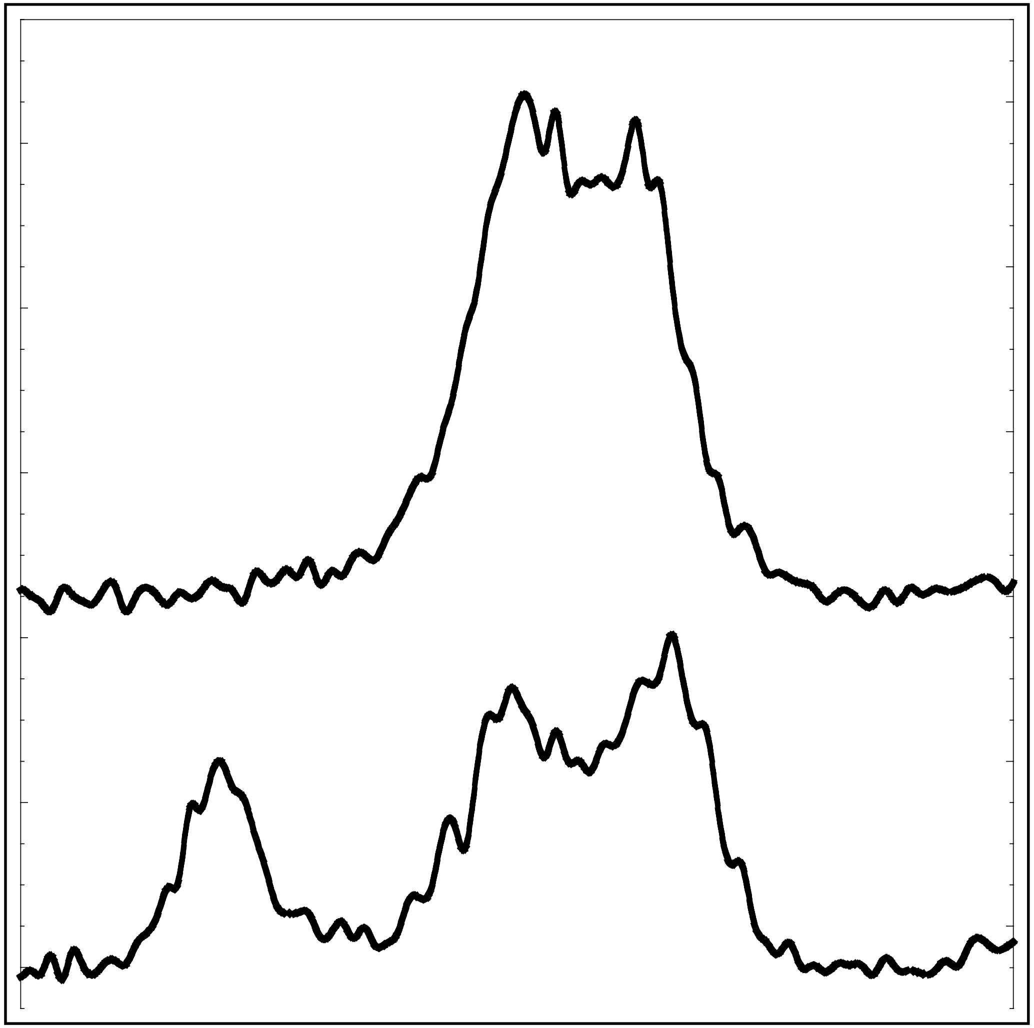
Kβ'' Transitions
Sensitive to Ligand 2s Energy



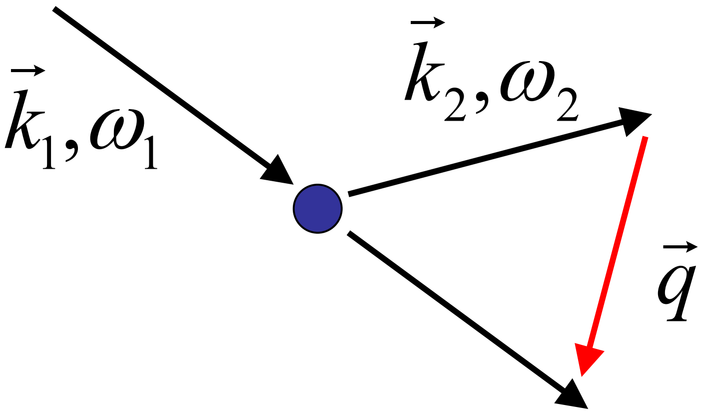
Valence -> Core transitions are highly polarized

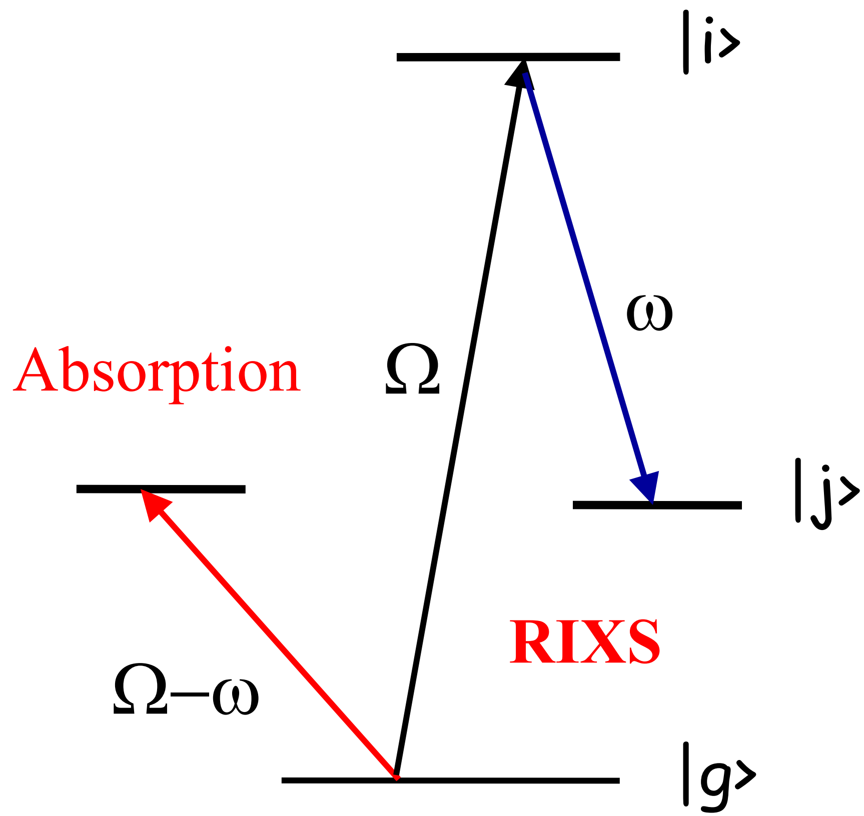
- Parallel Mn-N

- Perpendicular Mn-N



Resonant Inelastic X-Ray Scattering (RIXS)



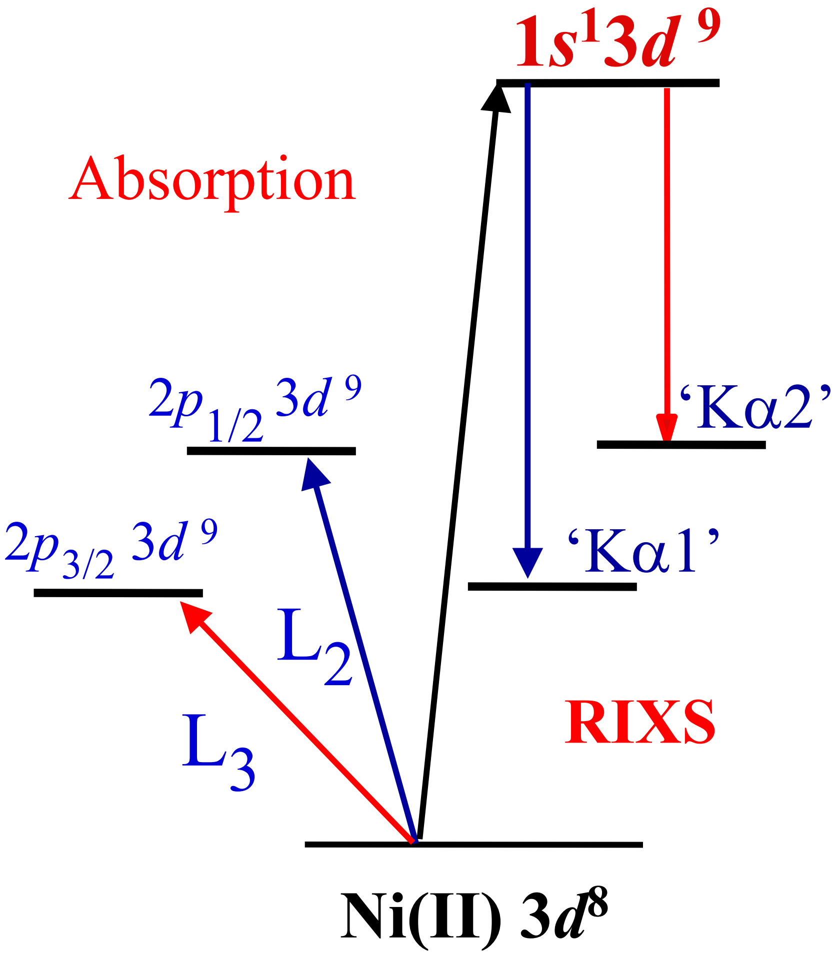


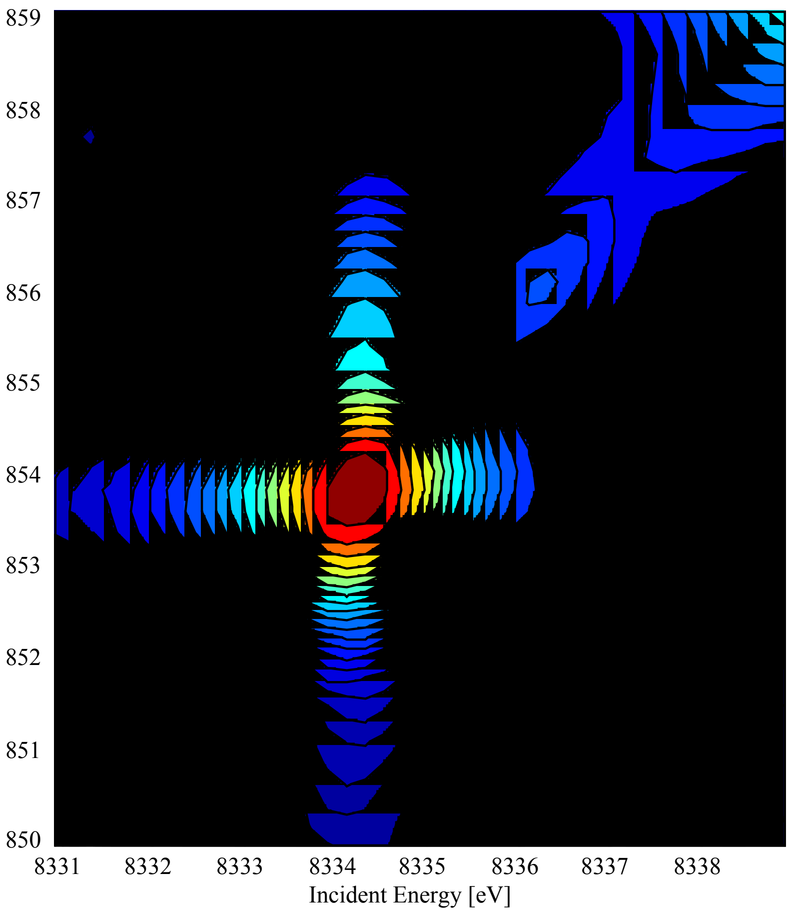
- line-width determined by final state
- for resonant scattering:

$$F(\Omega,\omega)=\sum_j\sum_i \frac{\langle j|T_2|i\rangle\langle i|T_1|g\rangle}{E_g+\Omega-E_i-i\Gamma_i}\times\frac{\Gamma_j/\pi}{(E_j+\omega-E_g-\Omega)^2+\Gamma_j^2}$$

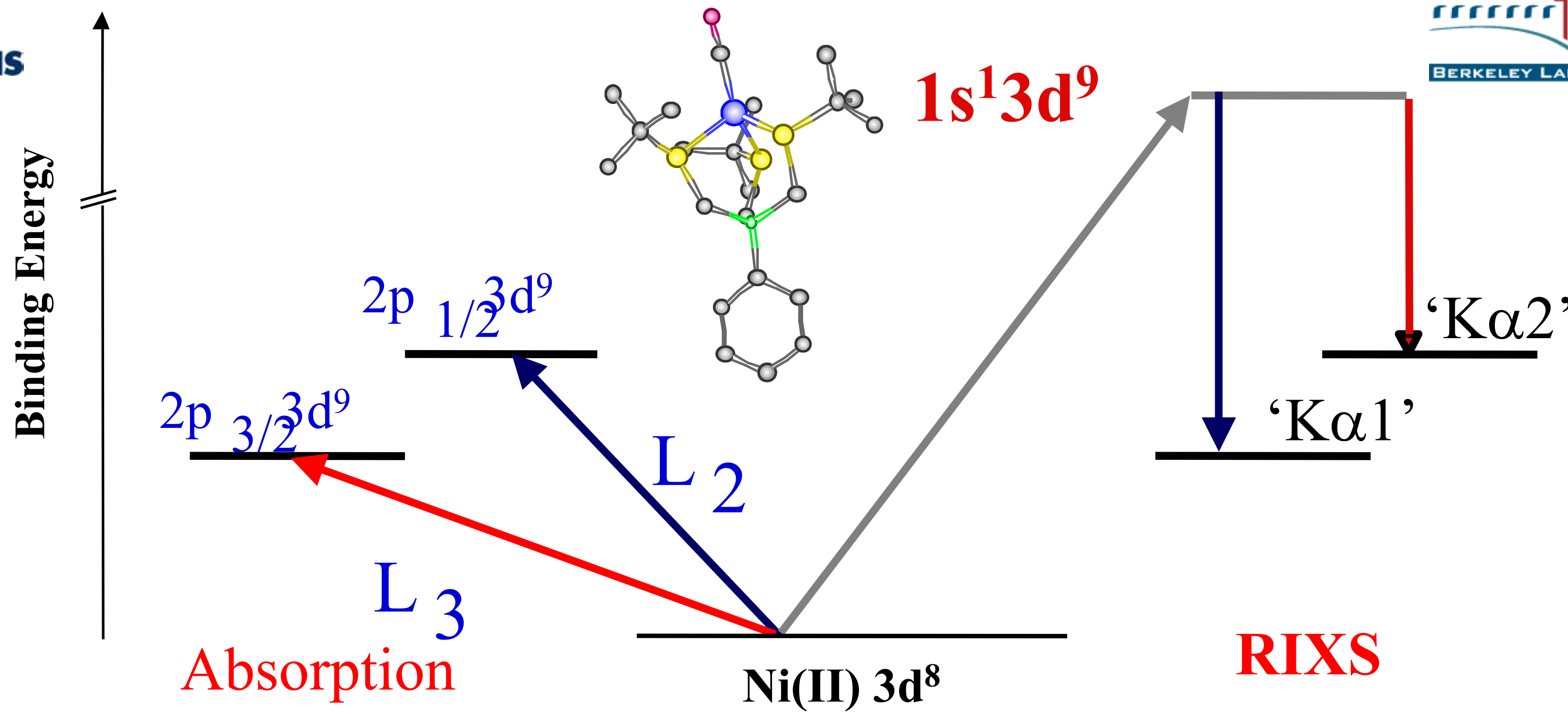
Kotani & Shin, *Rev. Mod. Phys.* **73** ('01)

Strategy 3 - Low Energy Net Excitations with Hard X-Rays

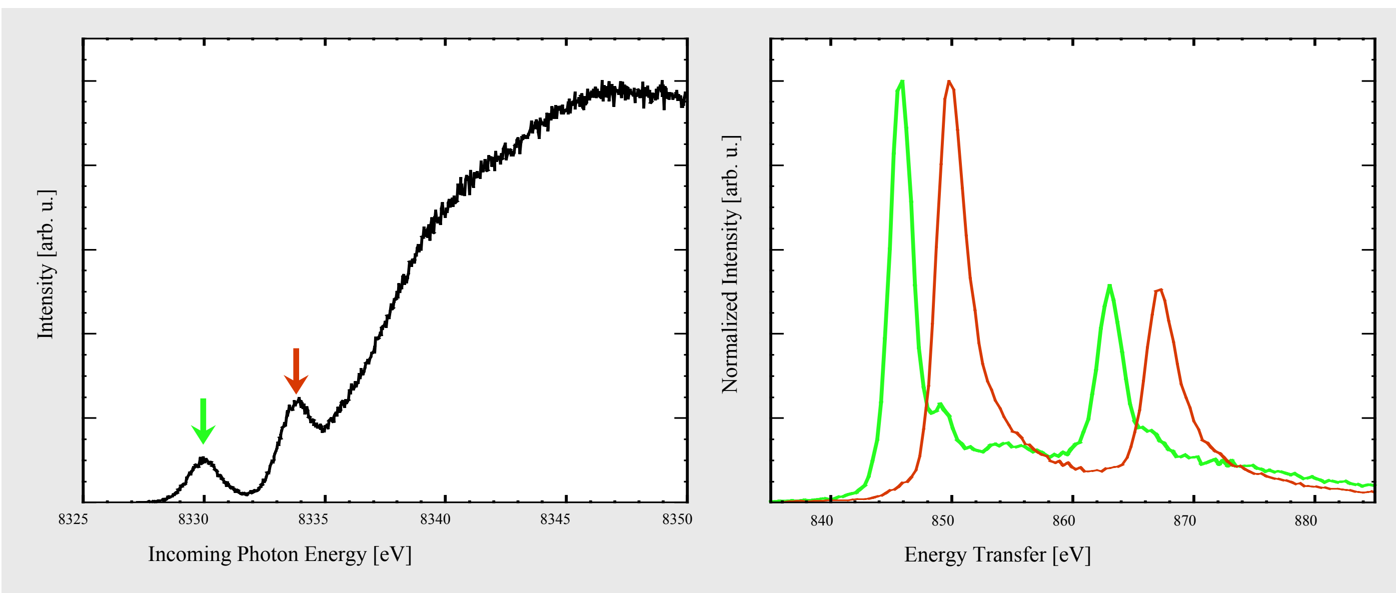




- $[Ni^{II}(tren)]^{2+}$ --- high-spin Ni(II)



Binding Energy
1s13d9
2p 1/2 3d9
2p 3/2 3d9
L 2
L 3
'Kα2'
'Kα1'
Absorption
Ni(II) 3d8
RIXS

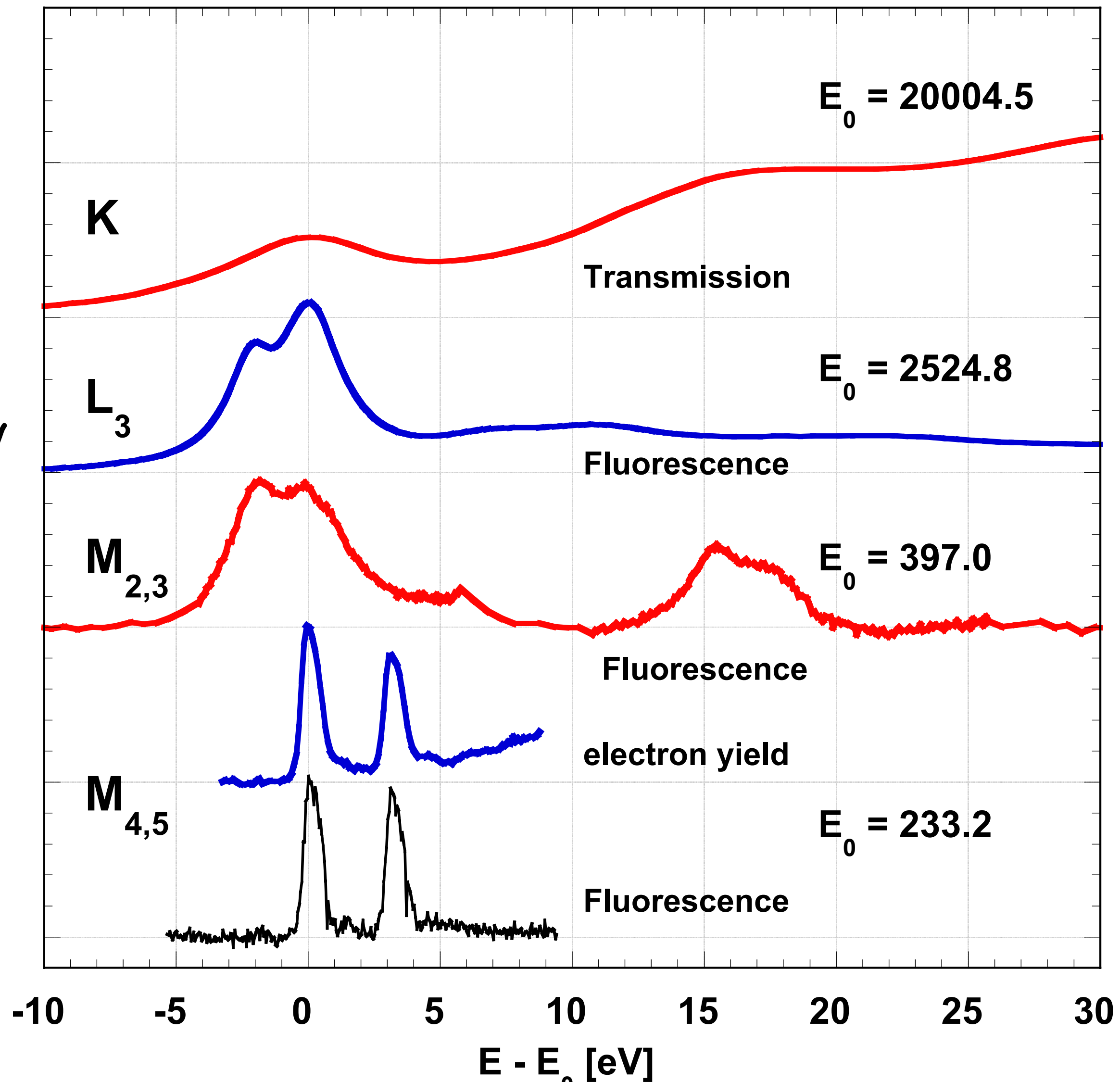


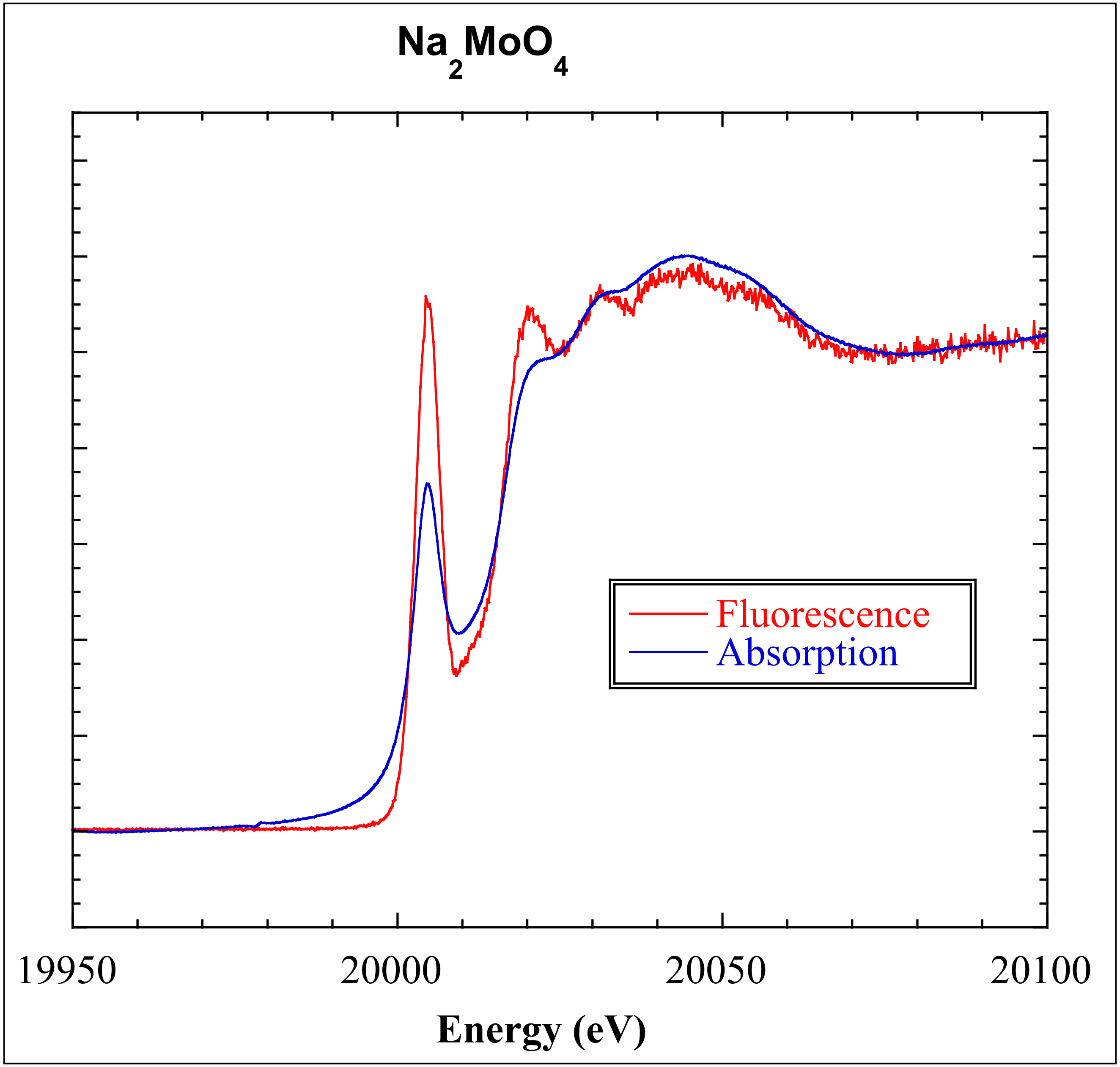
Intensity [arb. u.]
8325
8330
8335
8340
8345
8350
Incoming Photon Energy [eV]
Normalized Intensity [arb. u.]
840
850
860
870
880
Energy Transfer [eV]

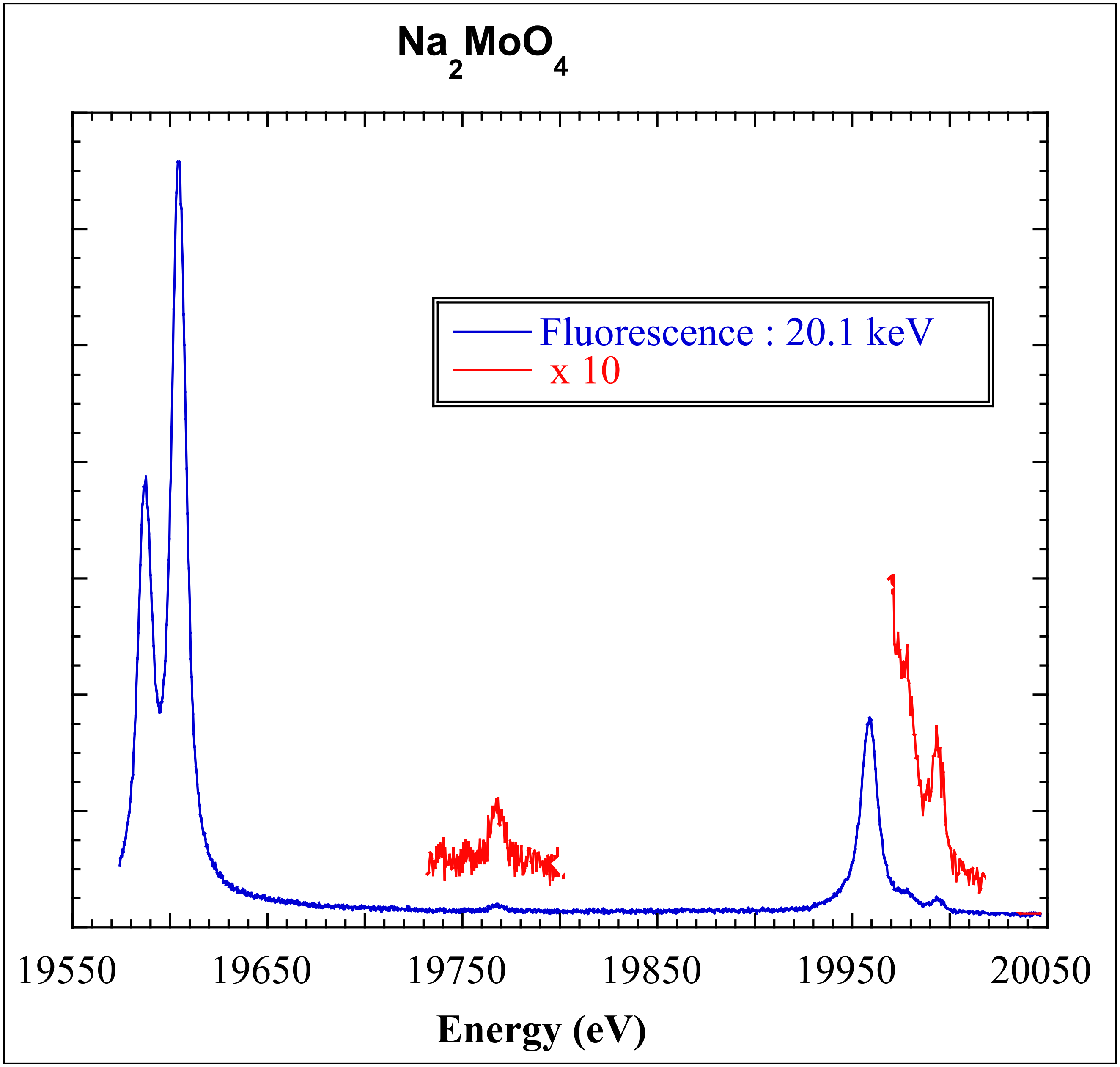
Mo Absorption Edge Lifetime Effects

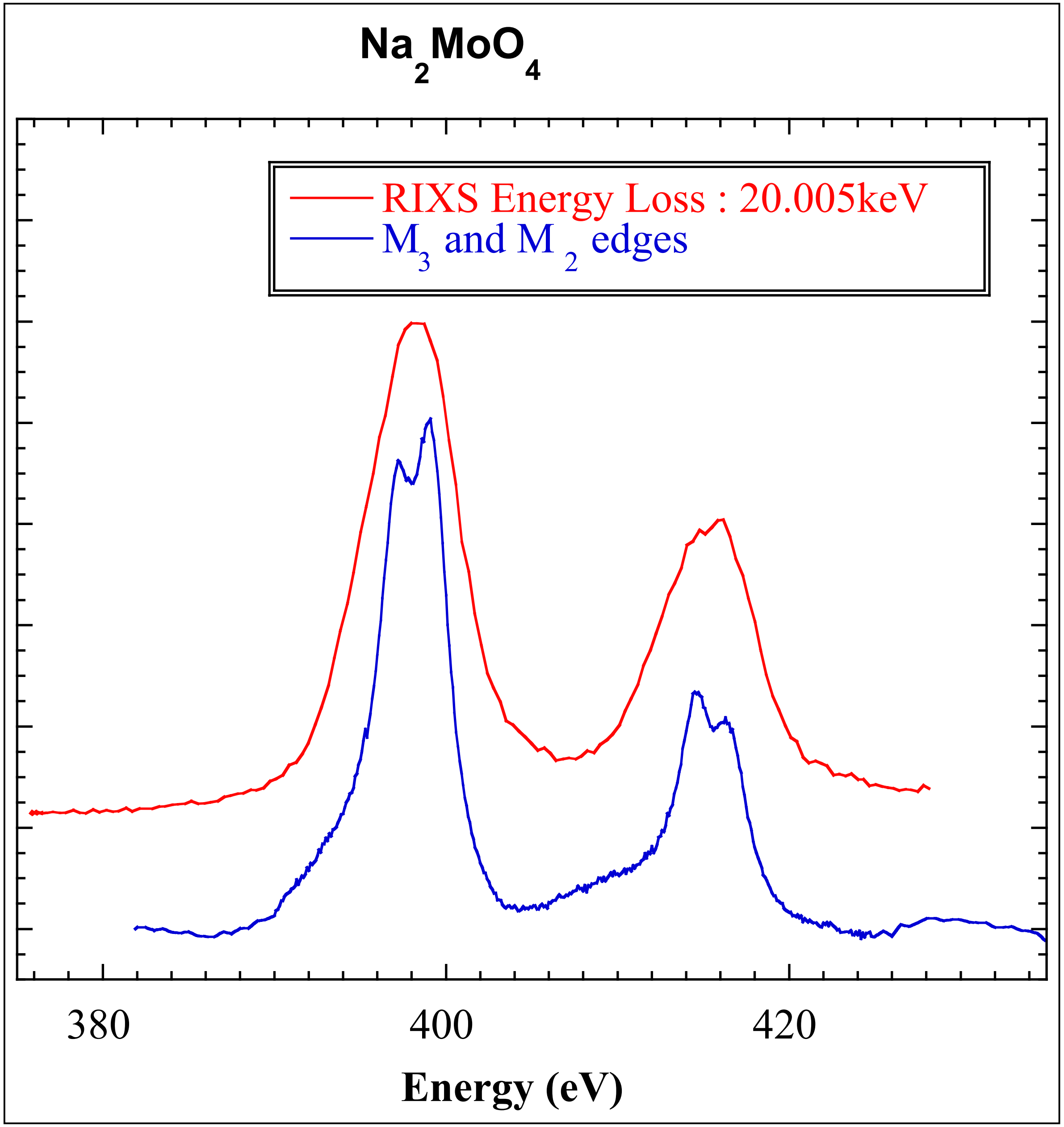
•MoO_4^{2-} (d^0)

- K : 1s ~ 6 eV
- L_3 : 2p ~ 2 eV
- M_3 : 3p ~ 1.5 eV
- M_5 : 3d ~ 0.5 eV




Na2MoO4
Fluorescence
Absorption
19950
20000
20050
20100
Energy (eV)


Na2MoO4
Fluorescence : 20.1 keV
x 10
19550
19650
19750
19850
19950
20050
Energy (eV)



Na2MoO4
RIXS Energy Loss : 20.005keV
M3 and M 2 edges
380
400
420
Energy (eV)

~ 360 meV ; 5-30 keV

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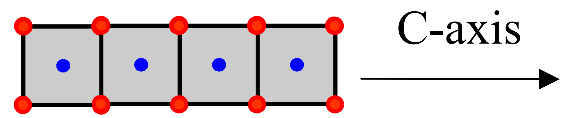
M. v. Zimmermann *et al.*

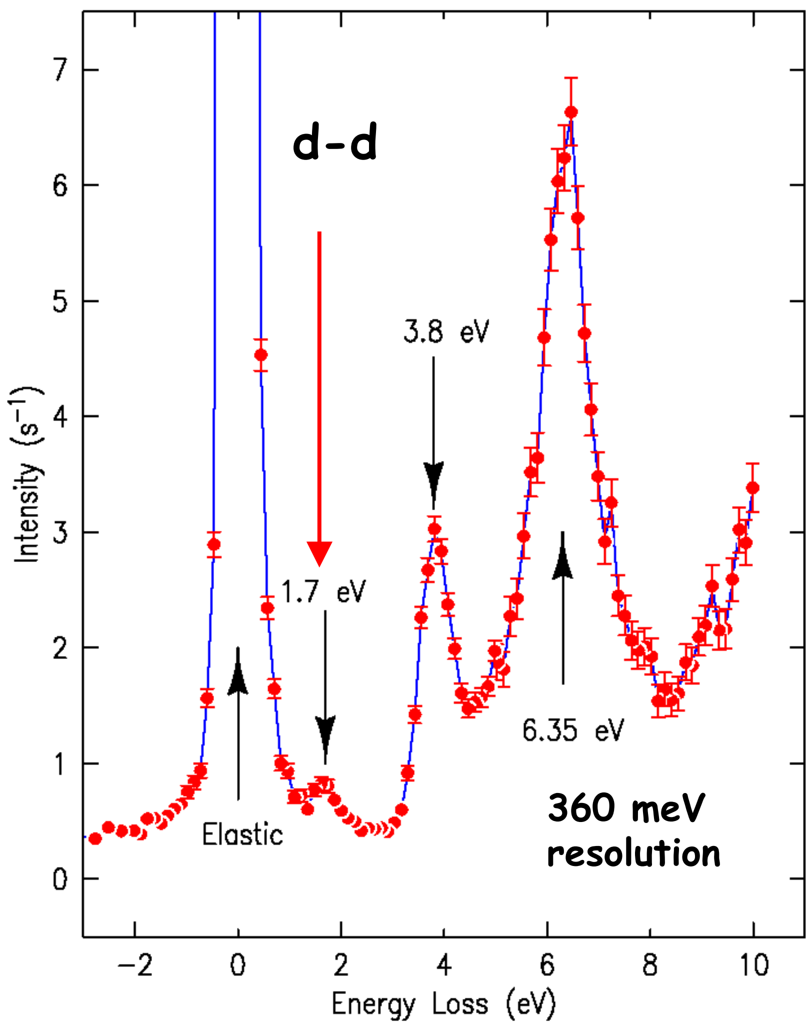
Hard X-Ray
Valence Band RIXS

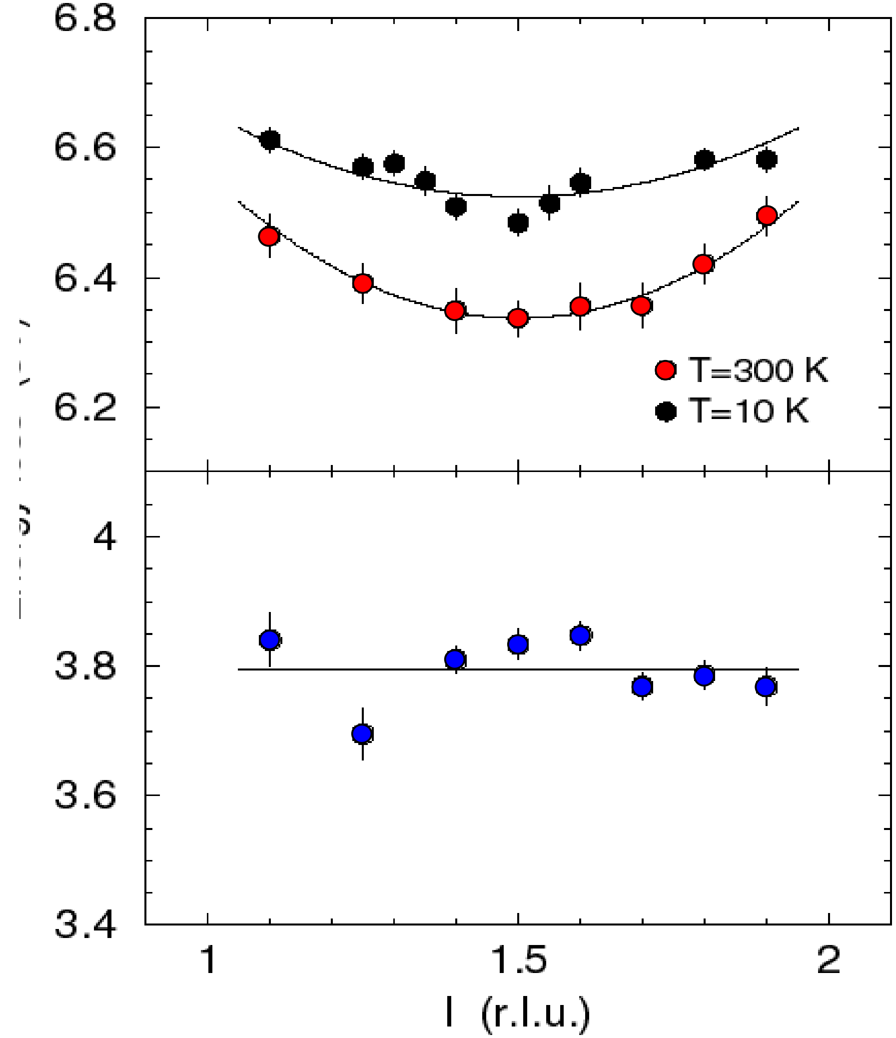
E/ΔE ~ 3x10⁴

BERKELEY LAB

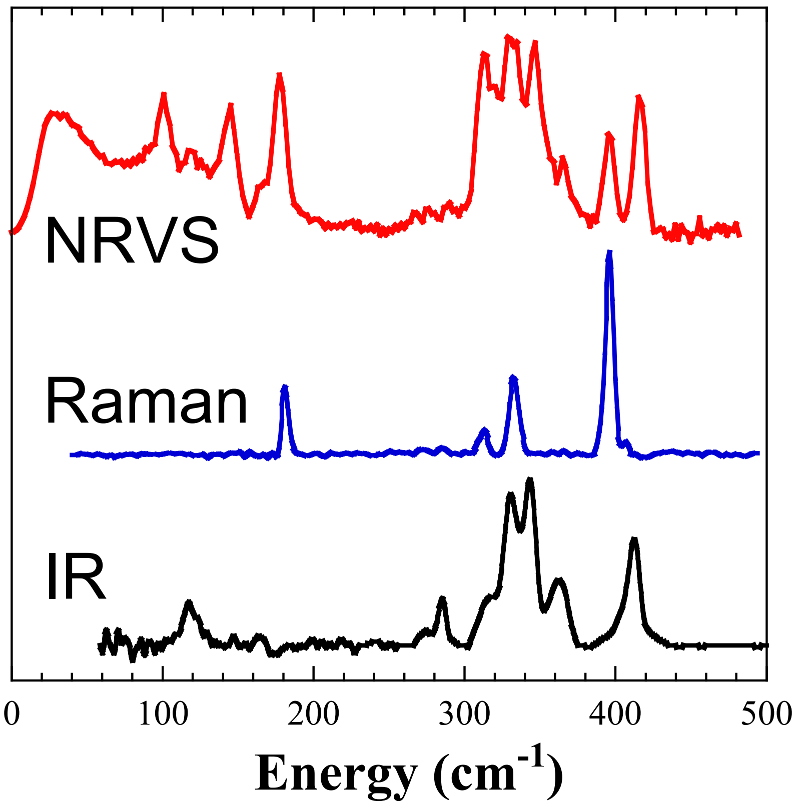
"Edge sharing" CuO_4

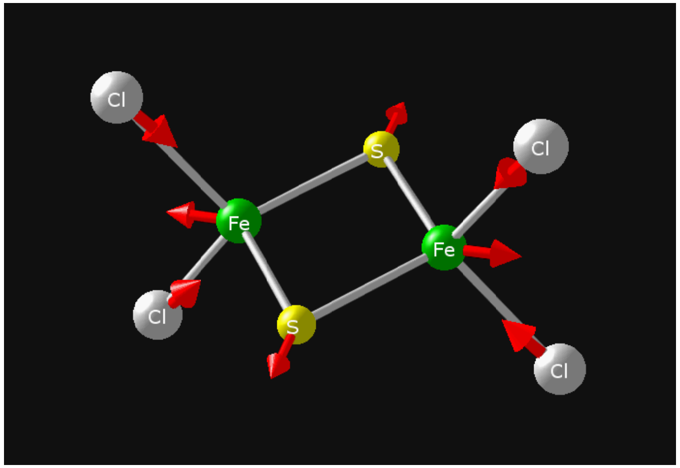






NRVS -- 2Fe-2S Illustration



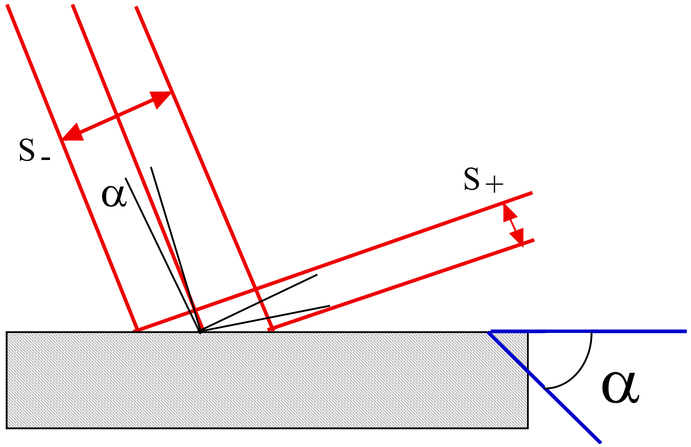


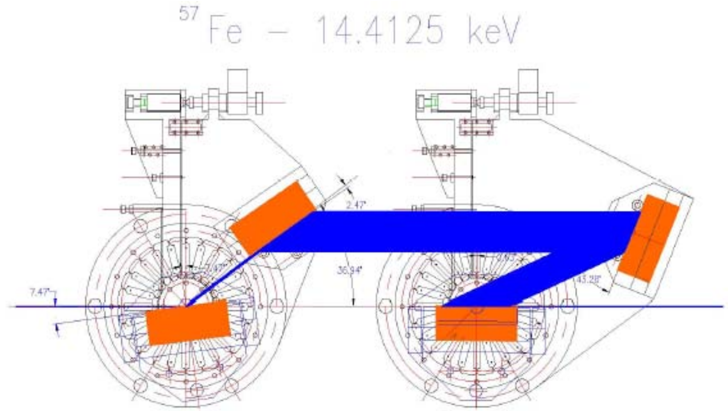
QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

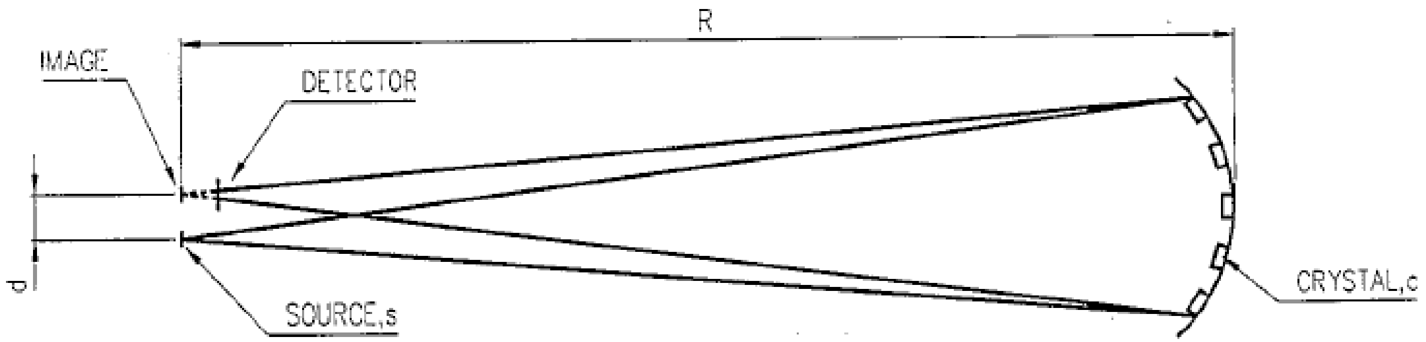
Analysis

- 18 normal modes
- Raman - IR exclusion
- 16 NRVS modes
- Urey-Bradley simulation
- 4Fe-4S impurity

Strategies for meV Resolution



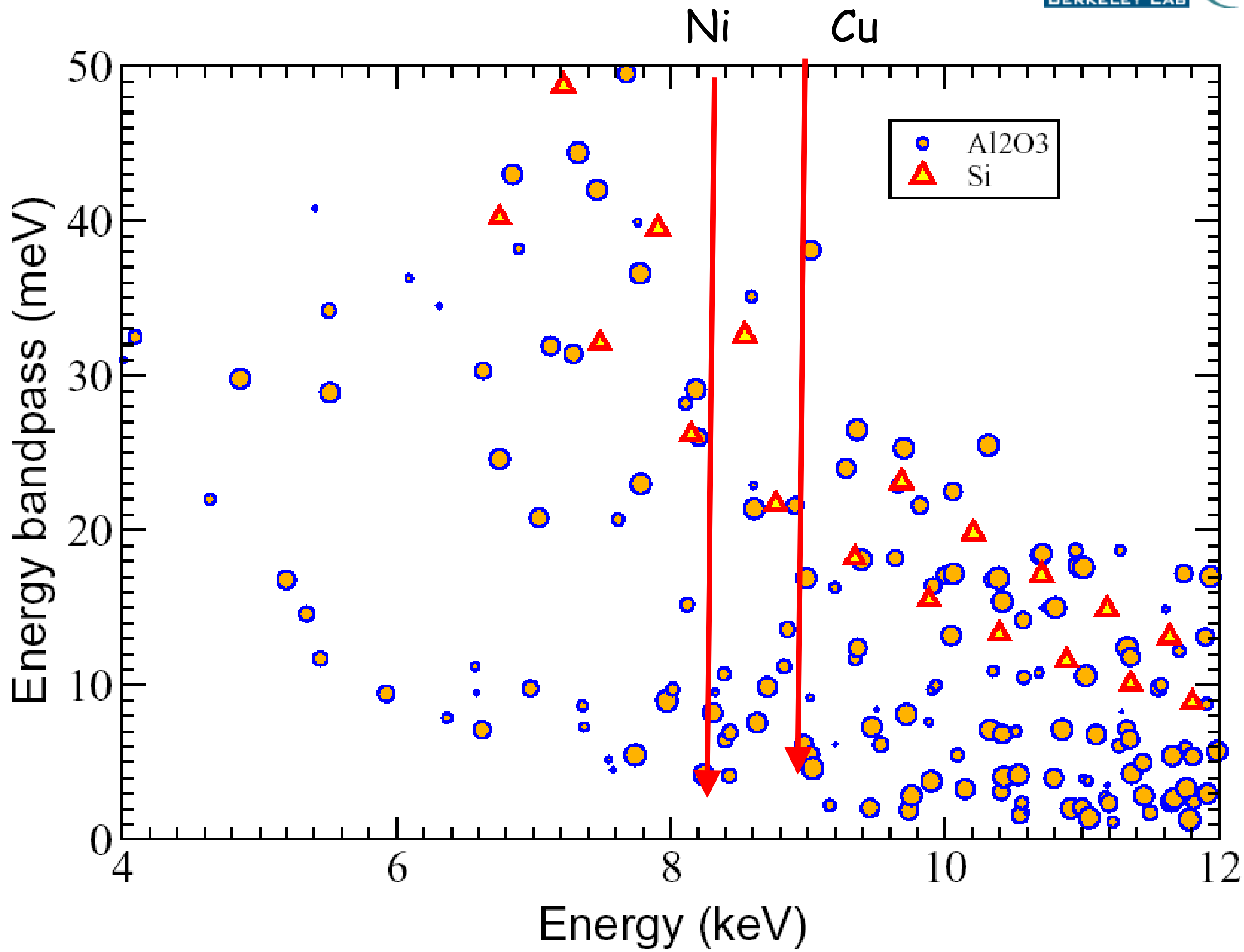




- Asymmetric Cut Incident Monochromators
- Diced Crystal Analyzers
- Thermal Scanning at Exact Backscattering

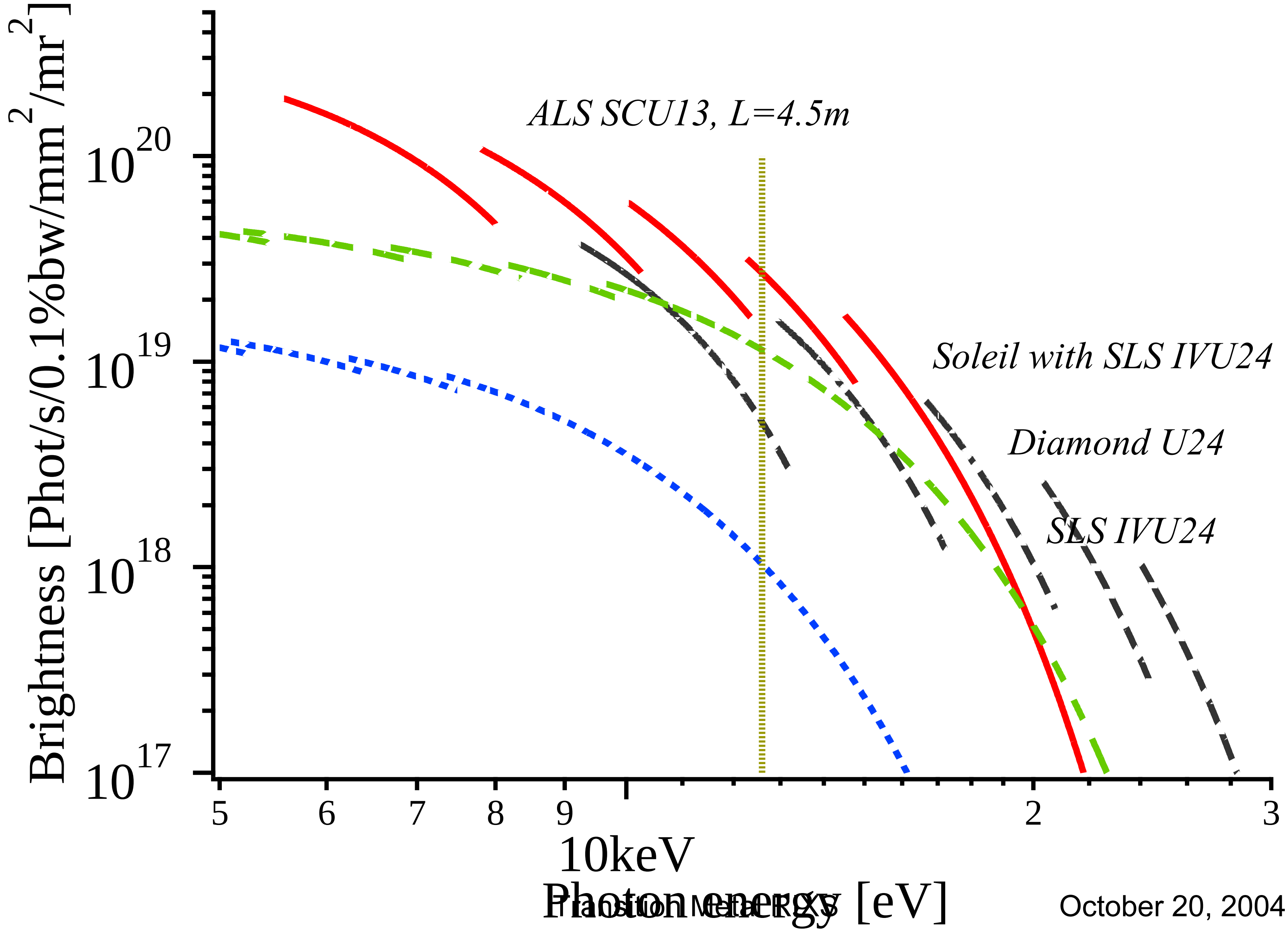
Resonance Vibrational RIXS ?

- Mismatch between
  - Si / Ge backscattering energies
  - K absorption energies
- Solution
  - Backscattering from sapphire
  - Energy scanning by heating/cooling



- ~0.1 meV / mK
- 10 eV -> 100 K

•Courtesy Ross Schlueter



the people who did the work

- Owen Drury
- Stephan Friedrich
- Yuming Xiao
- Matt Smith
- Simon George
- Hongxin Wang
- Cinthia Piamonteze
- Alex Guo

Thank you

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- NIH -- General Medicine GM-44380 for soft X-ray & XMCD
- NSF -- Chemistry Division, for high resolution RIXS of metalloproteins
- NSF -- Materials Science, for superconducting x-ray detectors