The Case for Vibrational Resonant Inelastic Scattering Spectroscopy (at Trieste)

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- representing:
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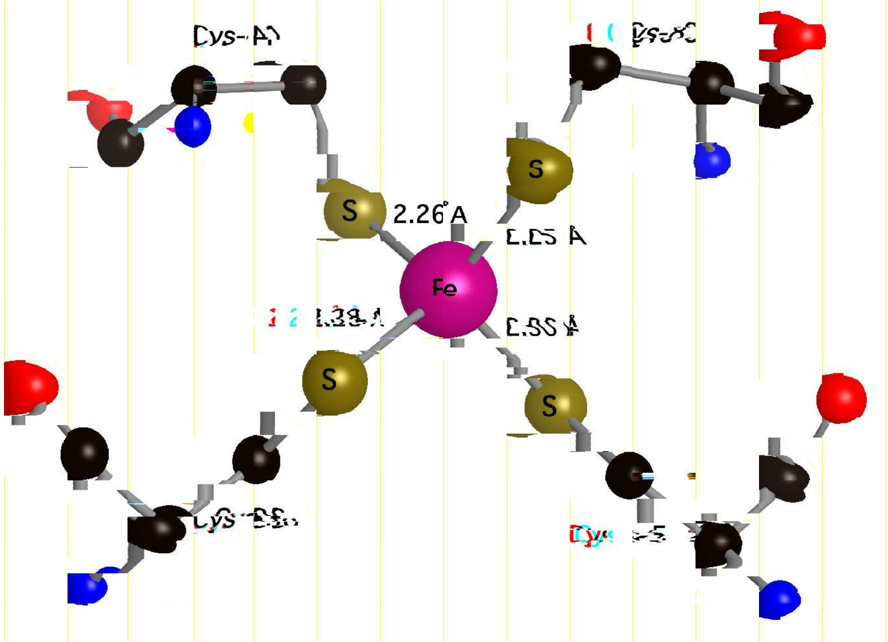
  - Kevin Smith - Boston U.
  - Peter Abbamonte - SUNY
  - Zahid Hassan - Princeton
  - Joseph Nordgren - Uppsala
  - Jinghua Guo - LBNL
  - Zahid Hussain - LBNL
- and others are welcome ...

- intro to a typical bioinorganic problem
- why vibrational spectroscopy...
- synchrotron methods
  - IXS
  - NRVS
  - RIXS & VRIXS
- tech scenarios
- potential bio applications
- longer term ...

Mononuclear Fe : Rubredoxin

QuickTime™ and a
Graphics decompressor
are needed to see this picture.



- 4 types of normal modes in T_d symmetry
- only T_2 modes NRVS allowed
- descend to D_{2d} symmetry
- interactions with side chain modes

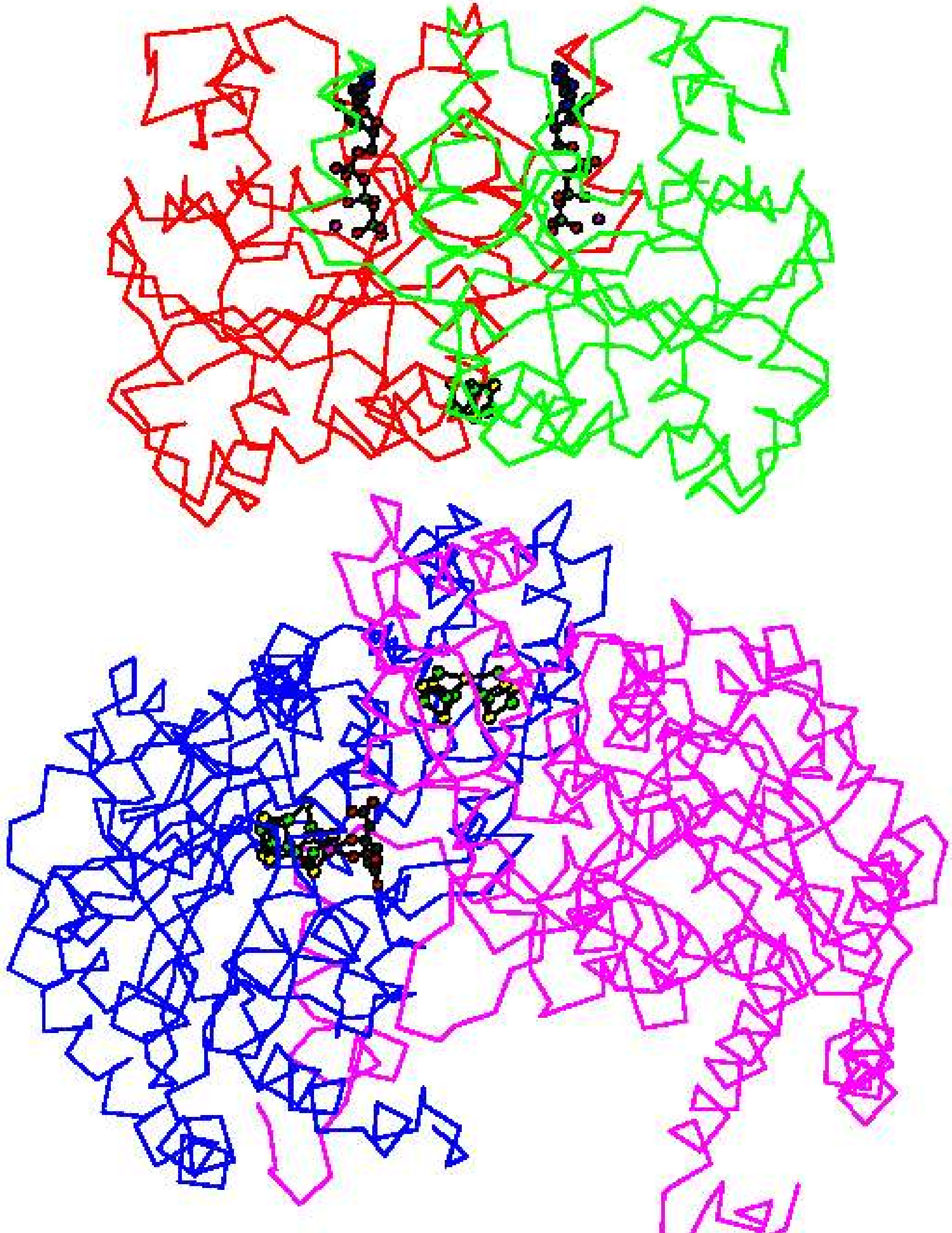
Nitrogen Fixation
$N_2 \rightarrow 2NH_3$

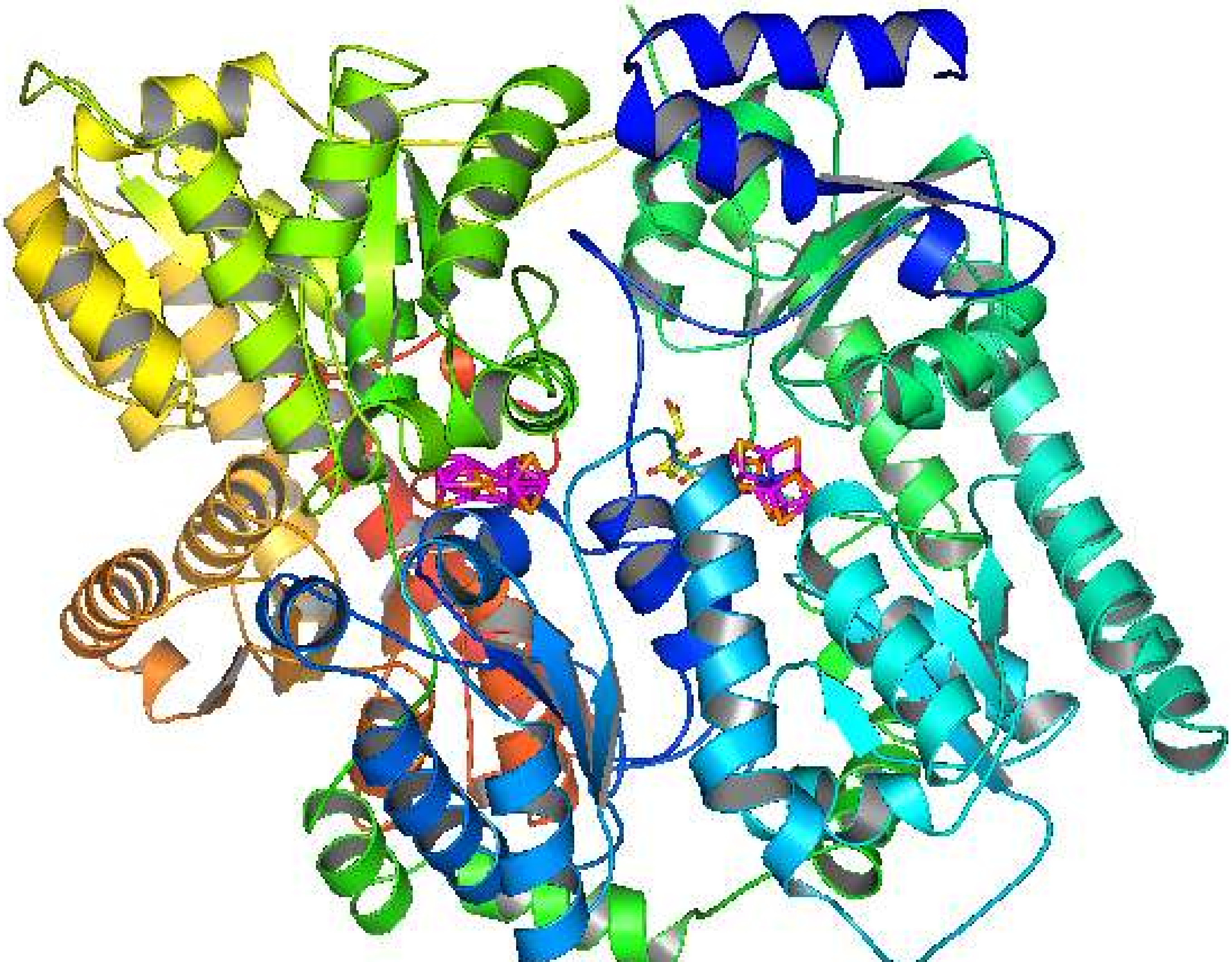
- 948 kJoules/mole

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

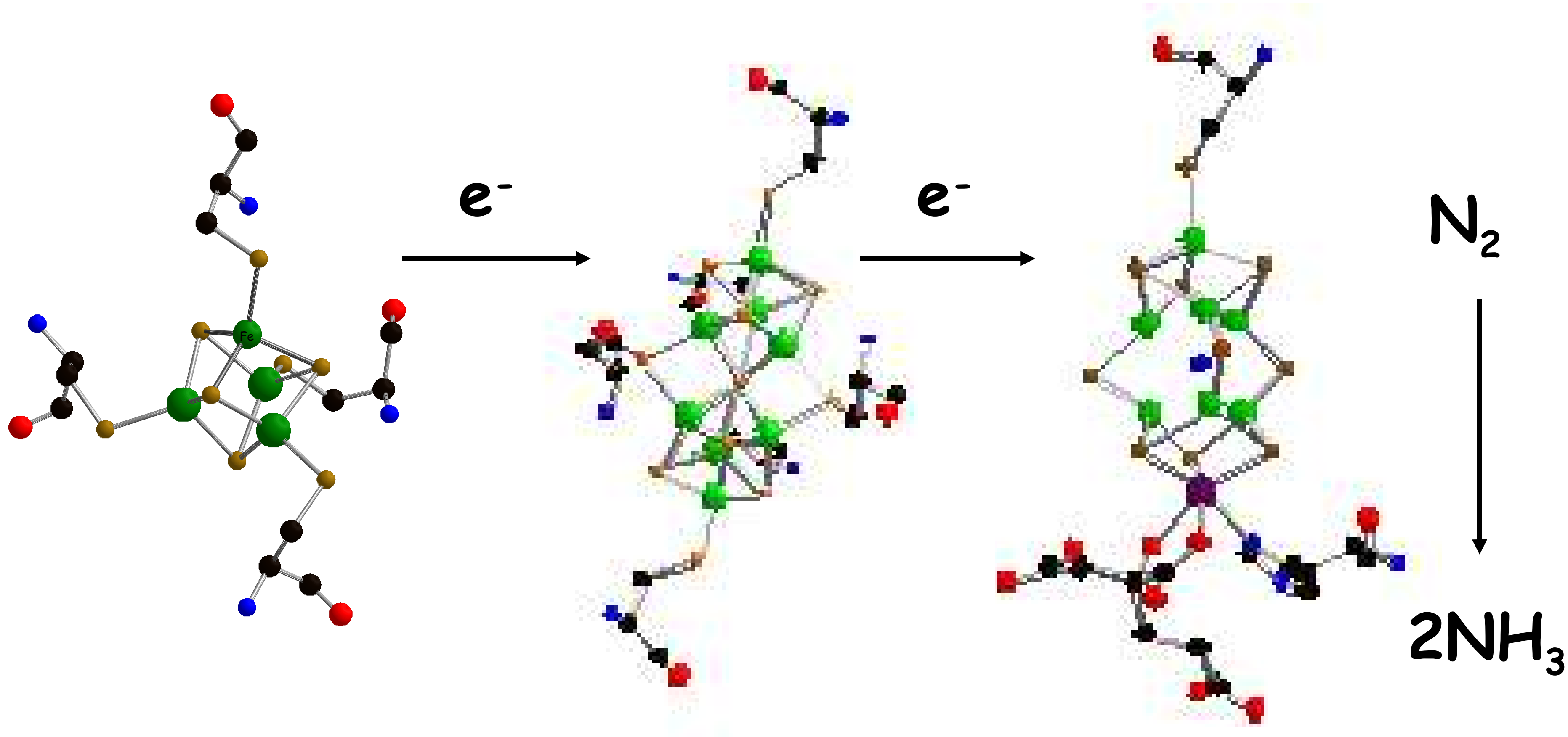
- Biological Fixation
  - >1/2 global NH_3 production
  - blue green algae
  - free-living bacteria
  - symbiotic bacteria
  - MFe_7S_8 cluster

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





Fe Clusters in N_2 Fixation



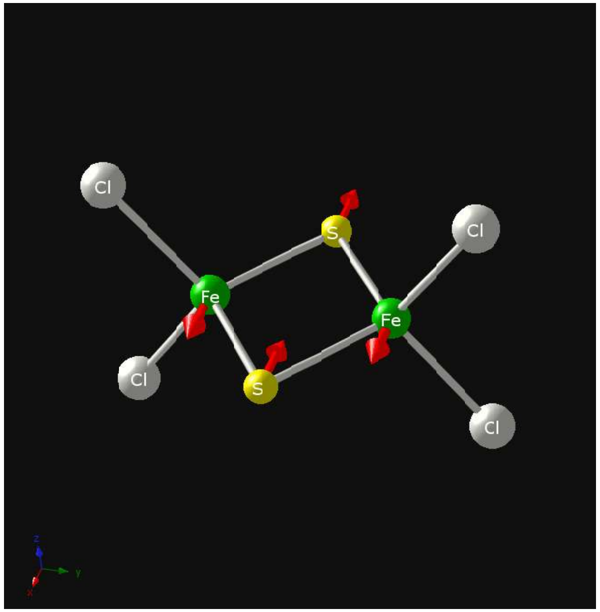
- Fe Protein
  Fe_4S_4 cluster

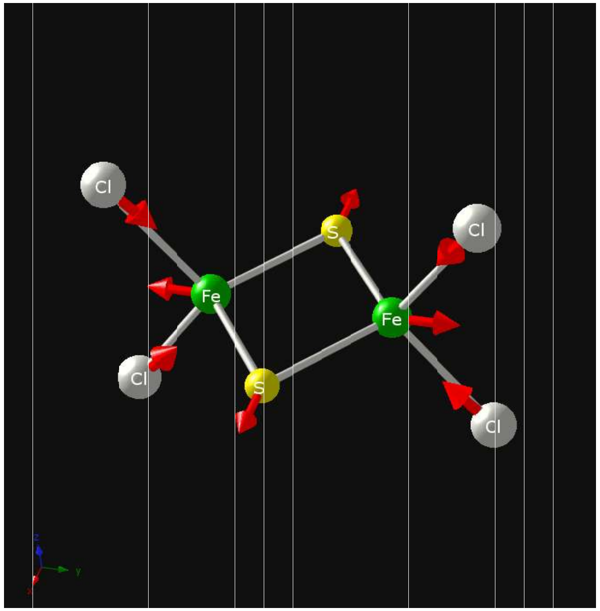
- P-cluster
  Fe_8S_7

- FeMo cofactor (M-center)
  $MoFe_7S_9X$

Vibrational Spectroscopy & Normal Modes

- Normal Modes
  - Molecules vibrate at discrete frequencies
  - Motion determined by masses & force constants
- Infrared Absorption
  - change in dipole moment
  - water 'windows'
- Raman Scattering
  - change in 'polarizability'
  - resonance enhancement requires charge-transfer bands
- Neutron Inelastic Scattering
  - all modes observed
  - monochromatic neutron source
  - grams of material



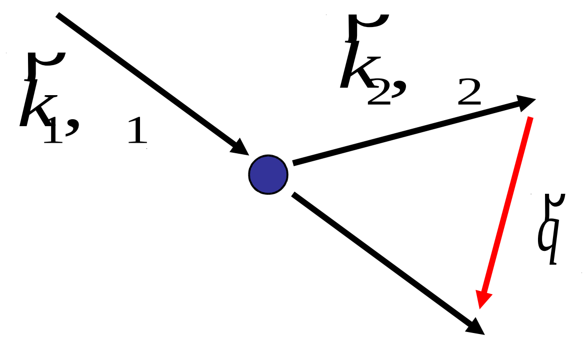


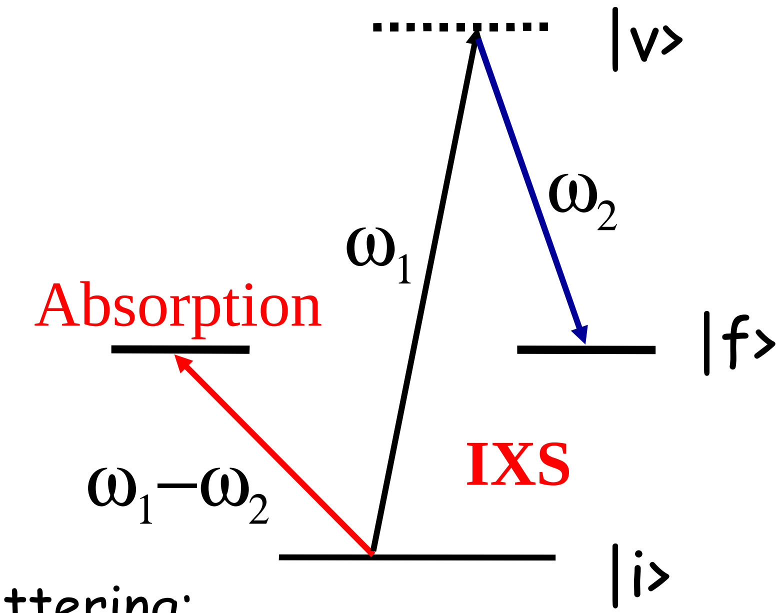
Synchrotron Vibrational Methods

- IXS
  - Usually > 20 keV
  - Bulk sensitive measurement
  - No elemental specificity
- NRVS
  - ~ 8 - 37 keV
  - Isotopic specificity
  - Only certain elements
- RIXS
  - any x-ray energy
  - elemental specificity
  - ~100 meV at moment
- Vibrational RIXS
  - ~ 1 meV needed
  - hard or soft x-rays
  - not yet achieved

Burkel, *Rep. Prog. Phys.* **63** (2000) 171–232.

Inelastic X-Ray Scattering (IXS)





- single element non-resonant scattering:

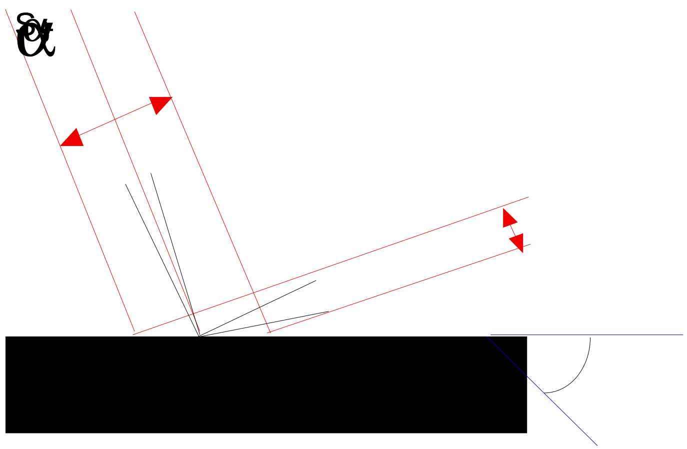
$$\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} = r_0^2 \left|\varepsilon_i \cdot \varepsilon_f\right|^2 \frac{k_i}{k_f} \left|f(q)\right|^2 \frac{1}{2\pi} \int e^{-i\omega t} F(q,t)\,dt$$

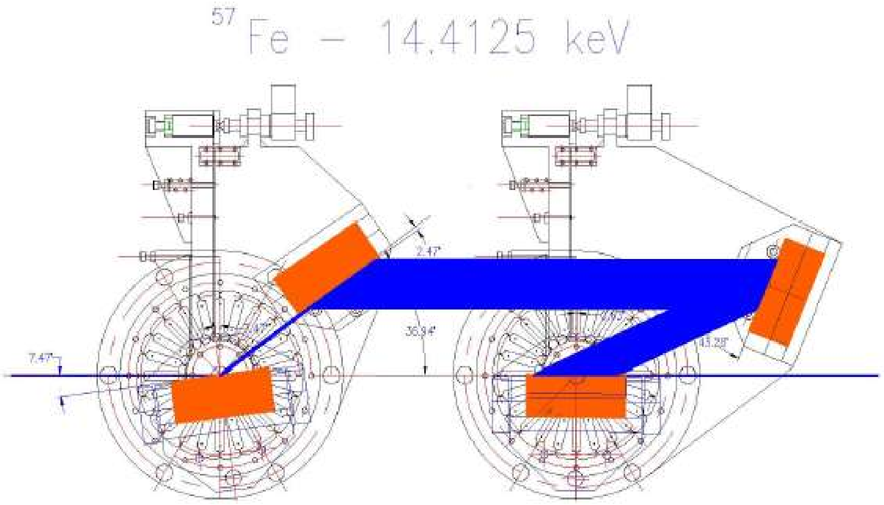
$$F(q,t) = \left\langle \sum_{i,j} \exp\left(-i\mathbf{q}\cdot\mathbf{R}_i(t)\right) \exp\left(i\mathbf{q}\cdot\mathbf{R}_j(0)\right) \right\rangle$$

Monaco, PRB **64** ('01)

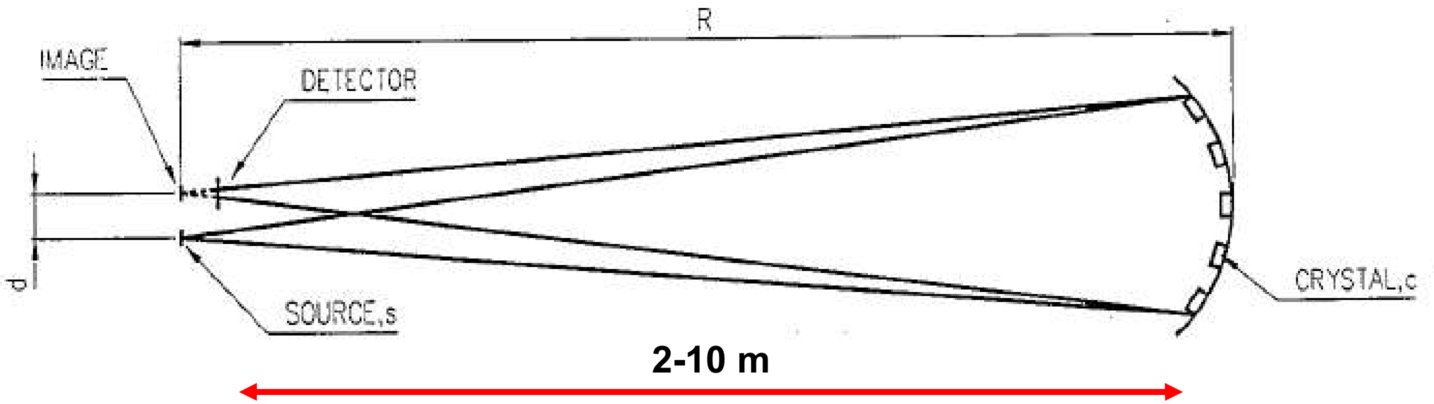
Incident Beam meV Resolution

- Asymmetric Cut Crystals and $\Delta\theta$
  or ...
- Backscattering Crystals and ΔT





meV Analyzer Resolution



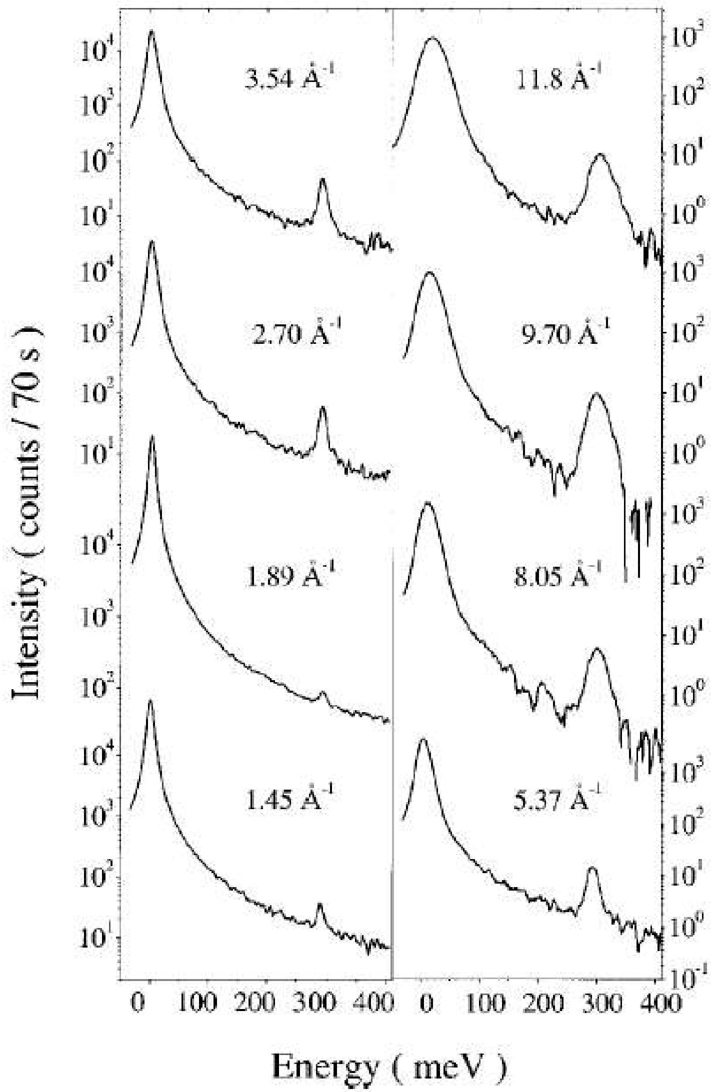
- Diced Crystal Analyzers
- Thermal Scanning at Near Backscattering

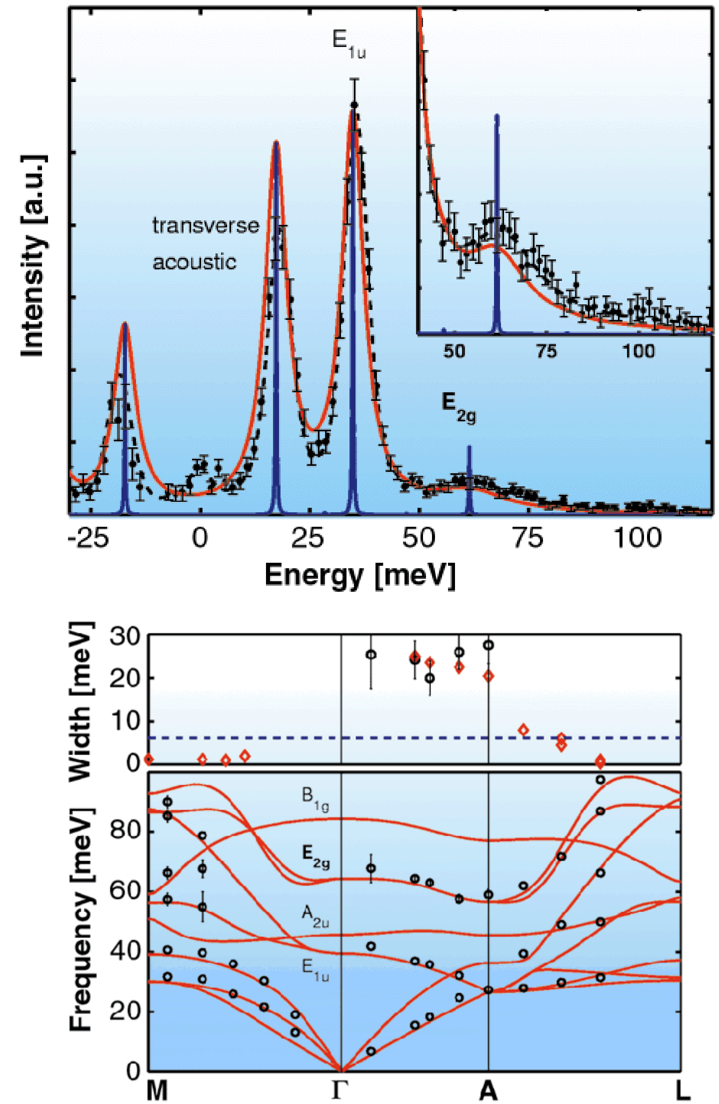
E Burkel

Table 1. Experimentally achieved energy resolution with Si for different $(h\ h\ h)$ reflections (one crystal contribution) in backscattering geometry.

Reflection	E_i (keV)	λ_i (Å)	$(\delta E)_\tau$ (meV)	
(7 7 7)	13.8	0.90	4.9	Sette and Krisch (1994)
(8 8 8)	15.8	0.78	3.8	Schwoerer-Böhning (1994b)
(9 9 9)	17.8	0.70	2.4	Masciovecchio *et al* (1996)
(11 11 11)	21.8	0.57	1.3	Schwoerer-Böhning (1994b)
(13 13 13)	25.7	0.48	0.45	Verbeni *et al* (1996)
(16 16 16)	31.6	0.39	0.28	ESRF (1995)
(17 17 17)	33.6	0.37	0.28	Krisch (1997)

IXS - Vibrational Spectroscopy with q Resolution





LN_2: Monaco, PRB **64** ('01)

MgB_2 Nagamatsu, et al. Nature, **410** ('01)

Limitations of IXS

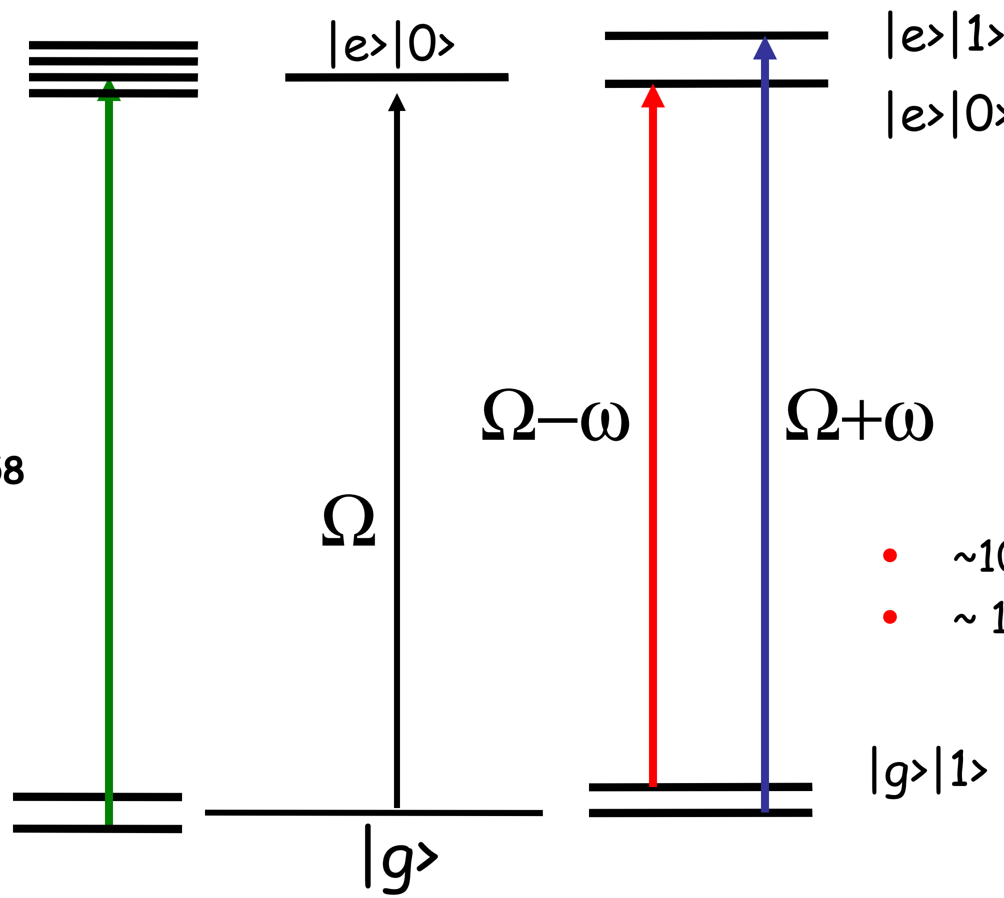
- No elemental specificity
  - will not be sensitive to trace components
  - e.g. metalloproteins not feasible
- Best done above 20 keV
  - requires high energy undulator beams
  - e.g. ESRF, APS, SPring-8
- Low efficiency
  - ~ miniscule solid angle
  - 1 energy at a time
  - -> Long collection times

Nuclear Resonant Vibrational Spectroscopy (NRVS)

'Vibrational (anti-) Mössbauer'

Recoil Fraction
(NRVS)

Recoil-Free Absorption
(Mössbauer)



- R. L. Mössbauer
  Z. Physik 151, 124 '58

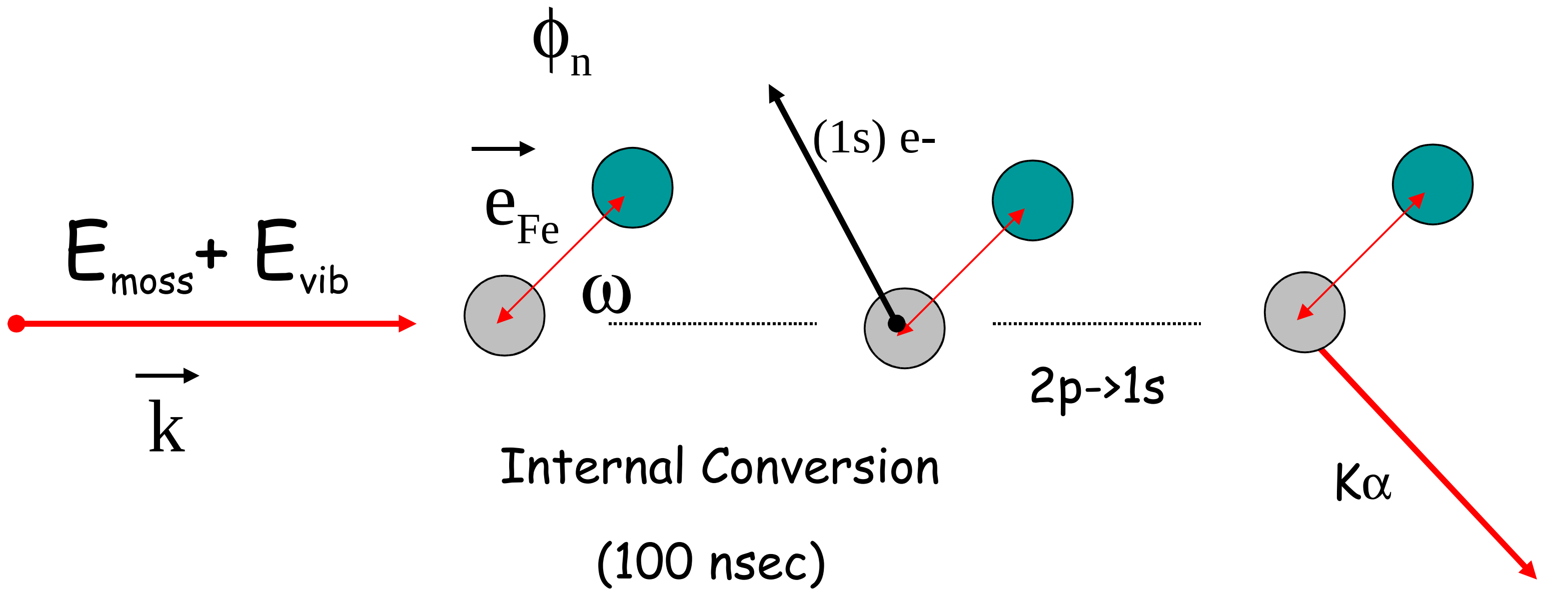
- ~ mm sec^{-1}
- 10^{-8} eV

- ~10^{-1} - 10^{-3} eV
- ~ 10^{5} mm sec^{-1}

- Electronic & magnetic splittings

- Vibrational levels

NRVS Measurement & Intensity



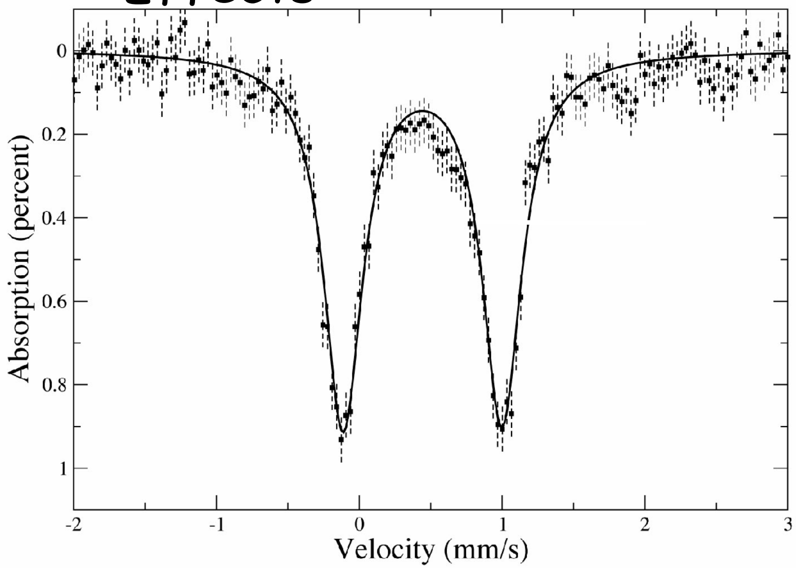
- Intensity ~ nuclear motion in given vibration

$$NRVS \quad \left(\vec{e}_{Fe} \cdot \vec{k}\right)^2$$

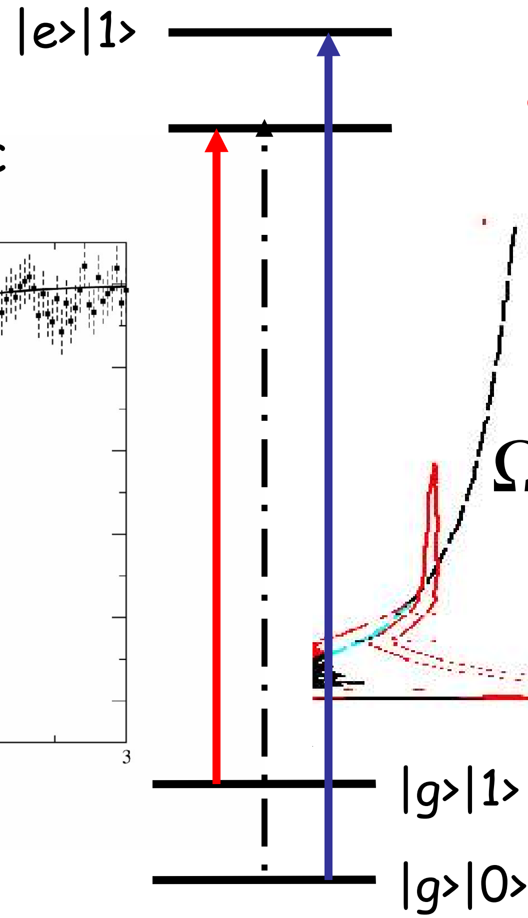
Recoil-free vs. Recoil Fractions

Recoil-Free Absorption (Mössbauer)

- Electronic & Magnetic Effects

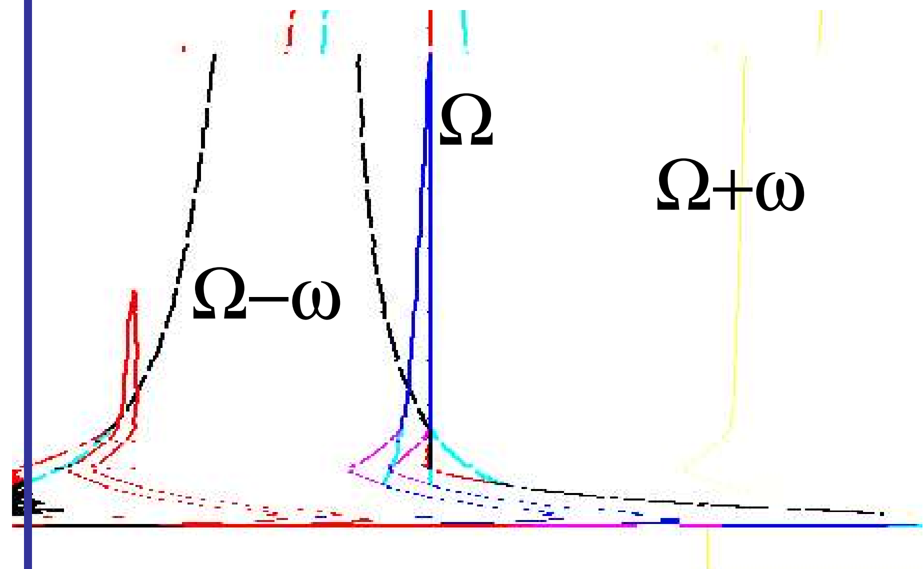


- ~ mm sec^{-1}
- 10^{-8} eV



Recoil Fraction (NRVS)

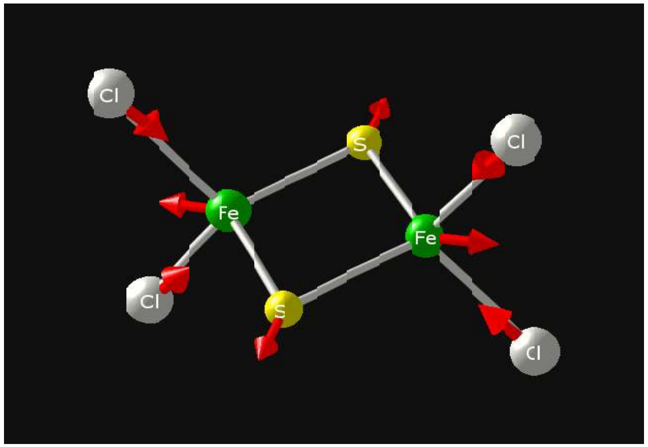
- Vibrational levels



- ~10^{-1} - 10^{-3} eV
- ~ 10^{5} mm sec^{-1}

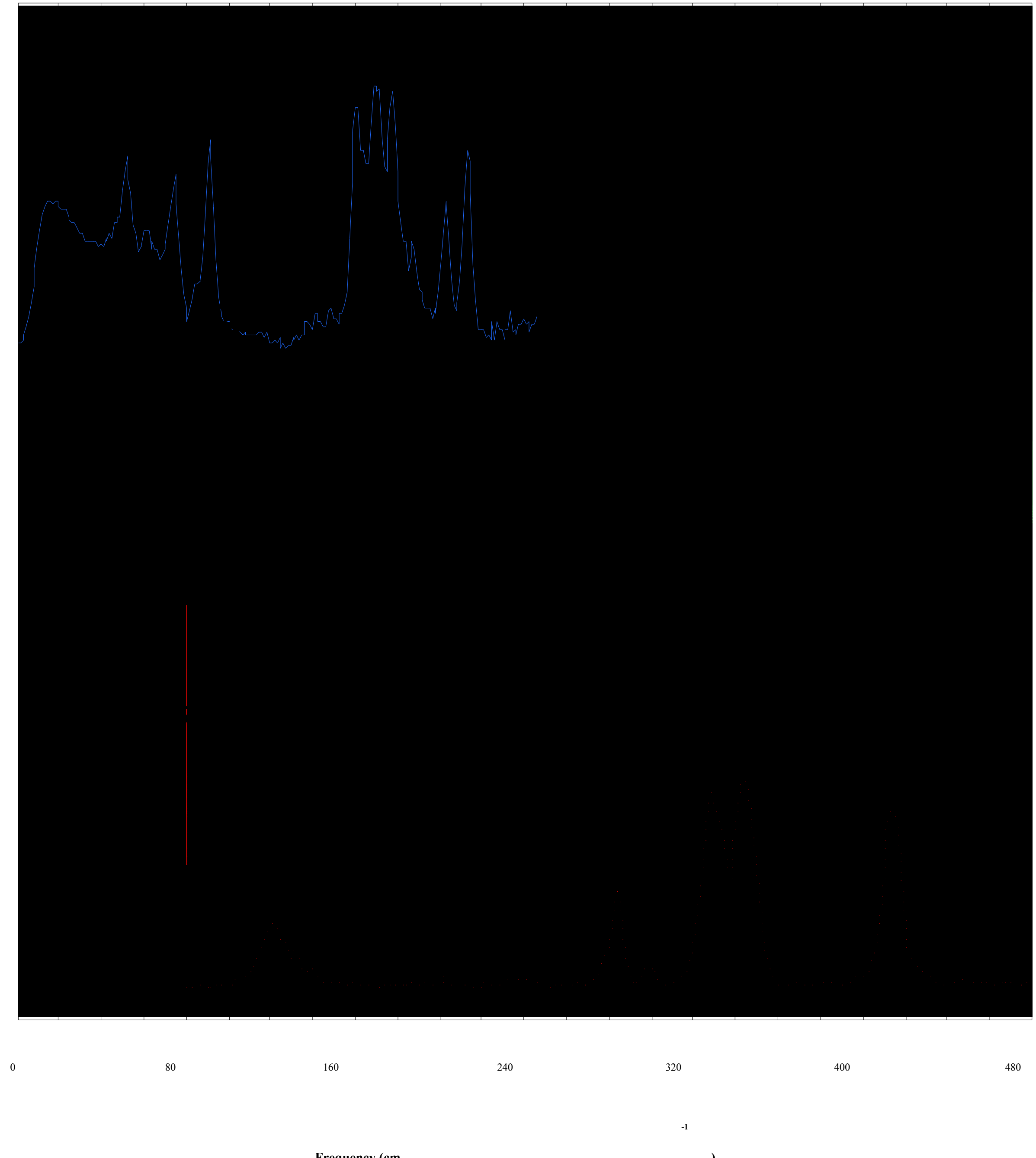
$$r \quad Exp[-\frac{hc}{k_B T}]$$

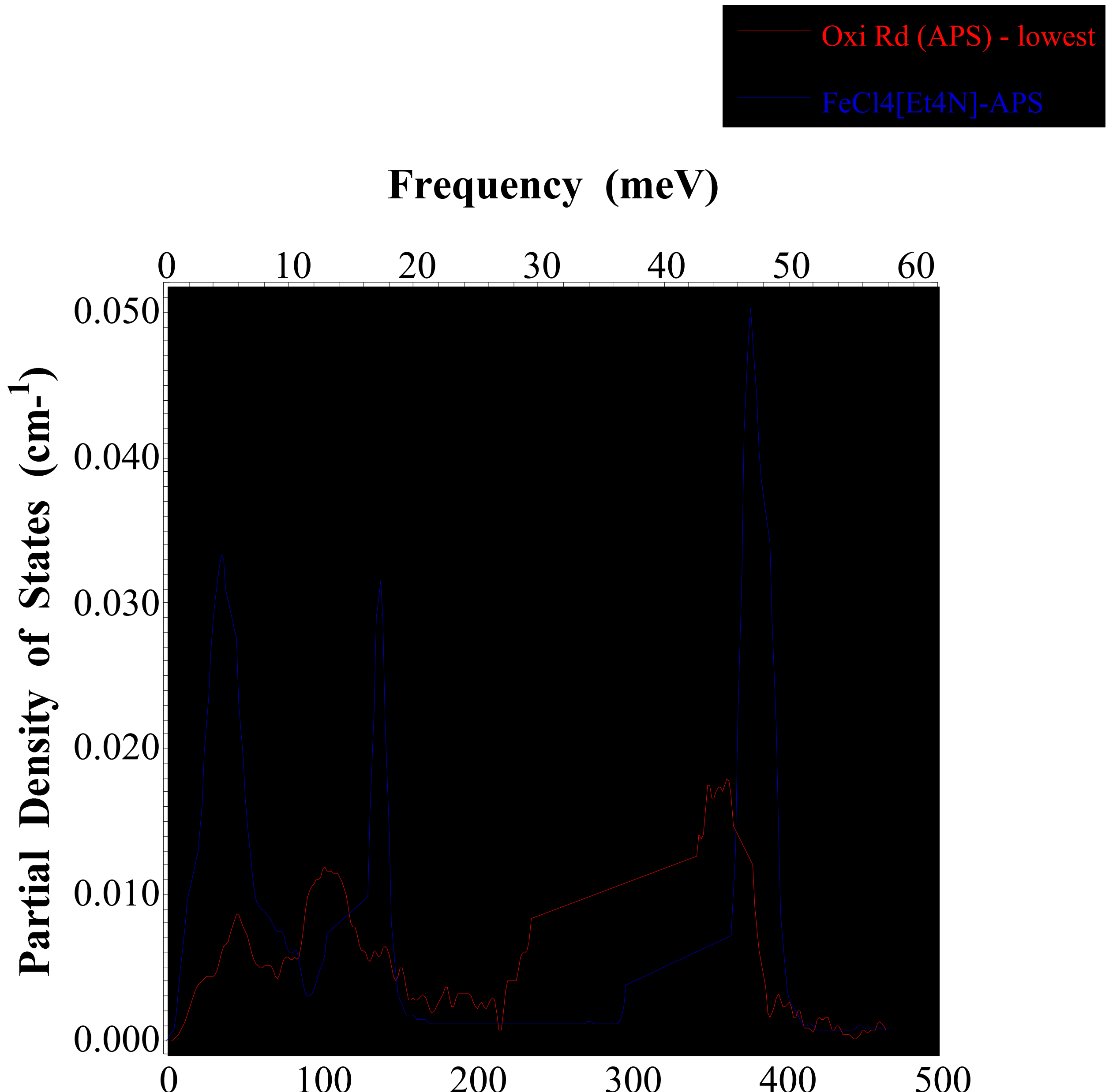
Binuclear Fe : $[NEt_4]_2[Fe_2S_2Cl_4]$



Analysis

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





Oxi Rd (APS) - lowest
FeCl4[Et4N]-APS
Frequency (meV)
0 10 20 30 40 50 60
Partial Density of States (cm-1)
0.050
0.040
0.030
0.020
0.010
0.000
0 100 200 300 400 500

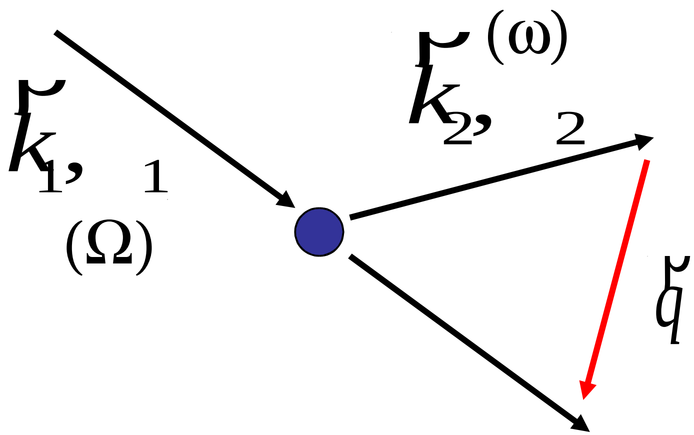
NRVS Summary & Prospects

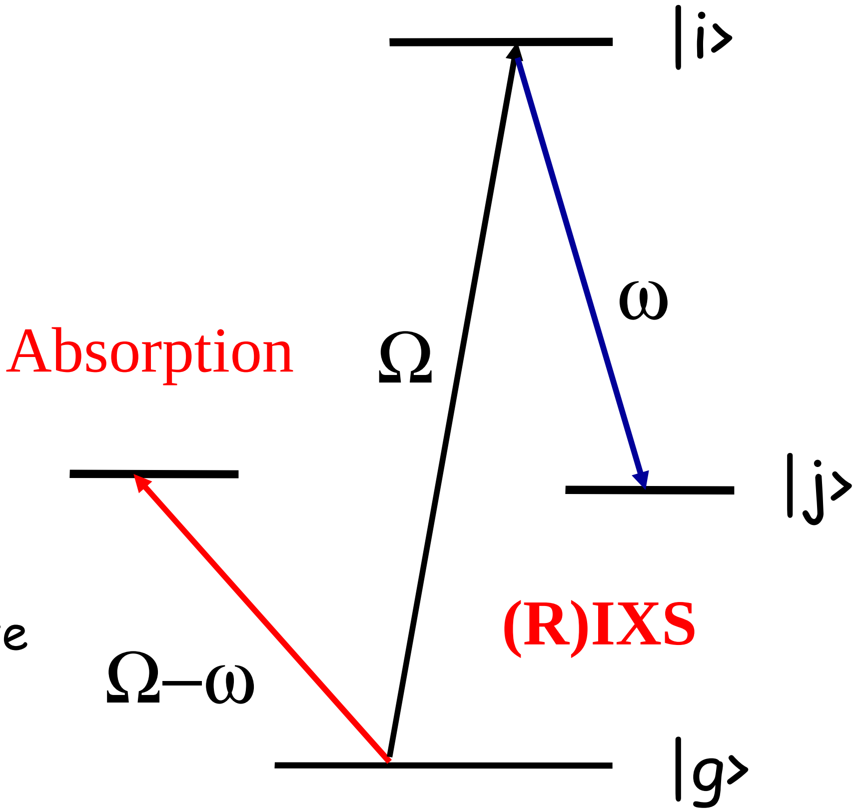
- a great local probe of vibrational properties, but

- A Handful of Beamlines
  - APS - Argonne, Illinois
  - Spring-8 - Japan
  - ESRF - Grenoble, France
  - PETRA - Hamburg

- Current & Future Nuclei
  - A severe limitation
- ^{169}Tm - 8.410 keV (A)
- ^{83} Kr - 9.4 keV (A)
- ^{57} Fe - 14.413 keV (A,S,E)
- ^{151}Eu - 21.542 keV (A,S,E)
- ^{119}Sn - 23.880 (A,E)
- ^{161}Dy - 25.651 (A,E)
- ^{40}K -
- In the works:
- ^{129}I - 27.77 keV
- ^{121}Sb - 37.15 keV
- ^{237}Np - 59.537 keV
- ^{61}Ni - 67.419 keV ?

Resonant Inelastic X-Ray Scattering (RIXS)





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

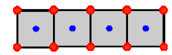
$$F(\ ,\ ) \quad \sum_j \sum_i \frac{\langle j|T_2|i\rangle\langle i|T_1|g\rangle}{E_g \ \tilde{} \ E_i \ i_i} \quad \frac{{}_j/}{(E_j \ \tilde{} \ E_g \ \tilde{})^2 \ {}_j^2}$$

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

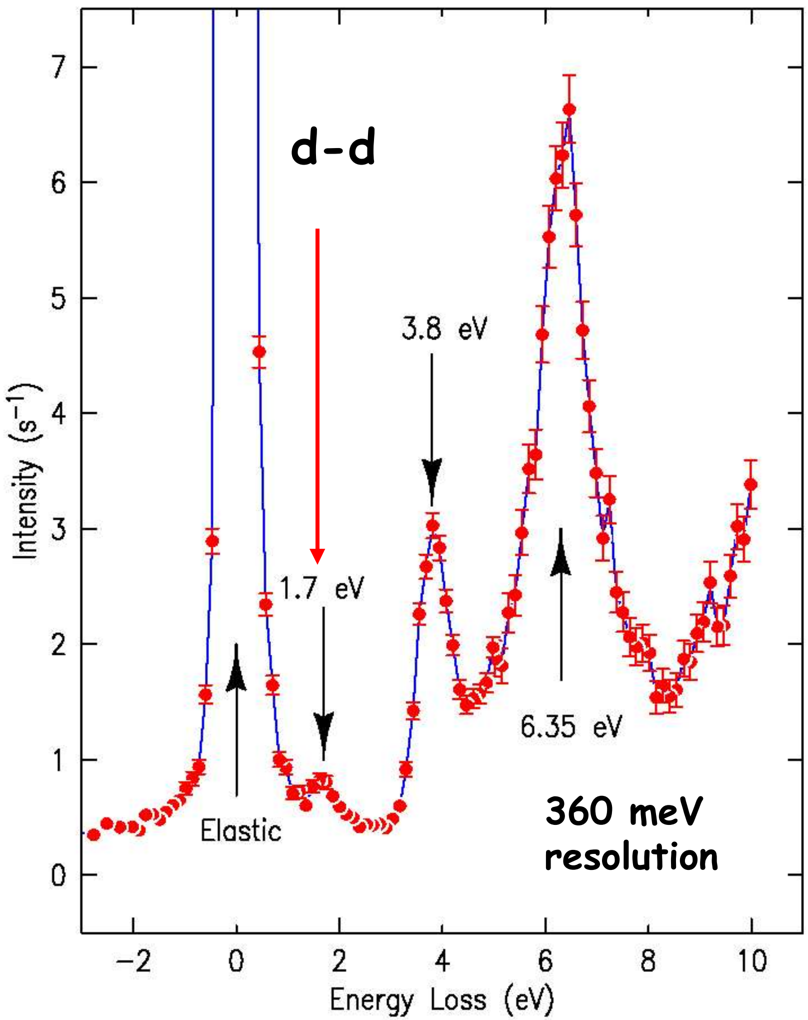
M. v. Zimmermann *et al.*

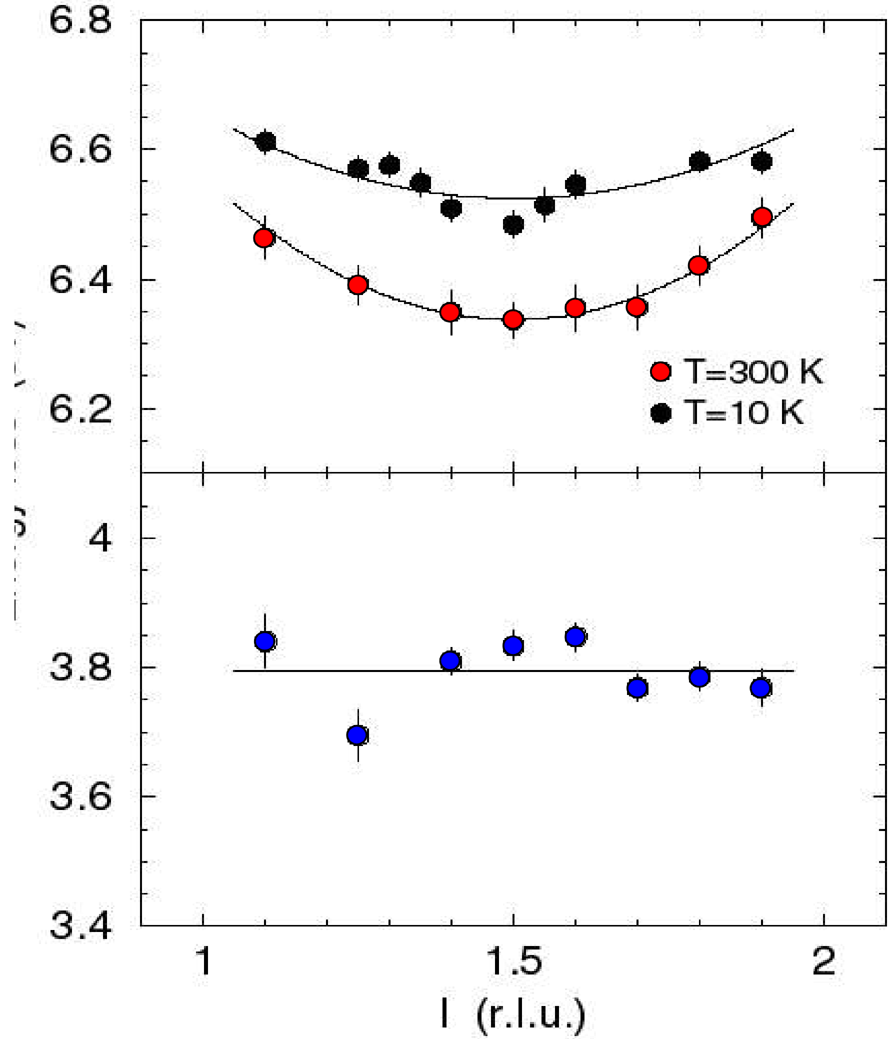
Hard X-Ray
Valence Band RIXS

"Edge sharing" CuO_4



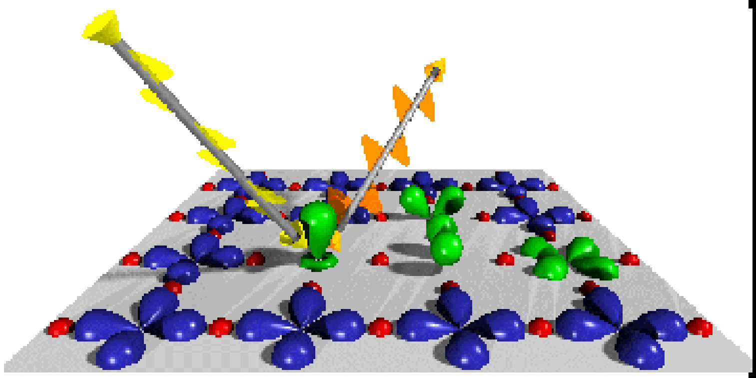
C-axis



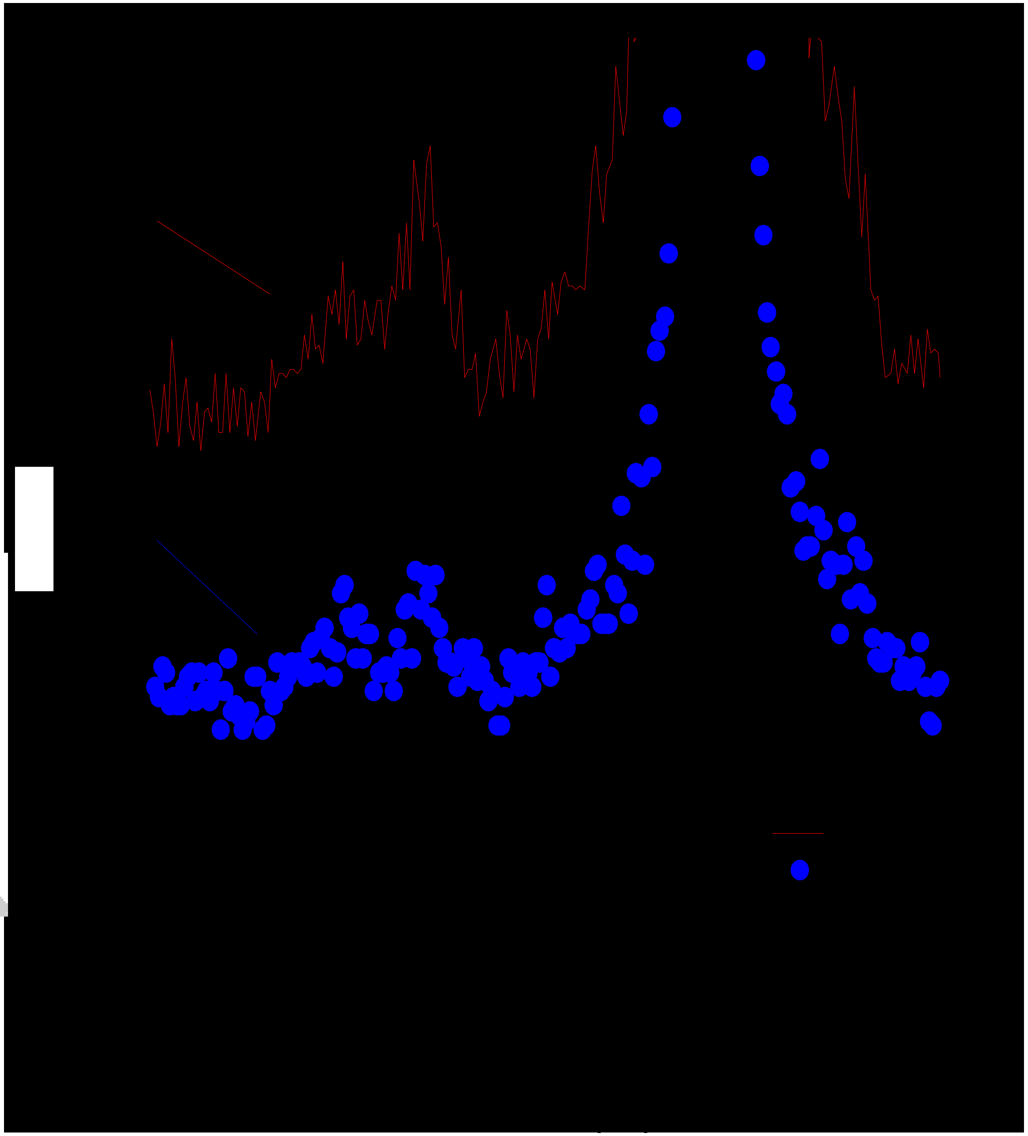


Cuprate Soft X-Ray RIXS

- M_3 (3p->3d) resonance at 74 eV
- net d-d excitation
- ~200 meV resolution



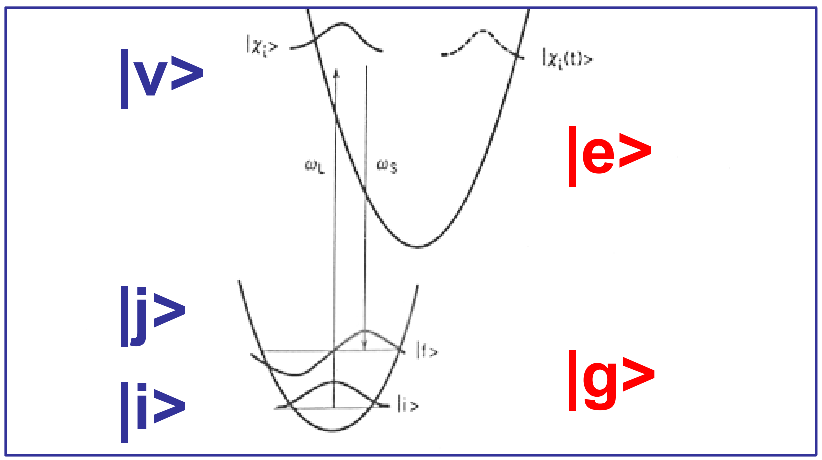
Cu d-d excitation at 74eV



Kuiper, Nordgren, Sawatzky et al., Phys. Rev. Lett. 80,5204 (1998)

Vibrational RIXS

UV-Visible Vibrational Resonance Raman Spectroscopy



- Why do it ?
    - resonance enhancement *vs.* IXS
    - elemental specificity of NRVS
    - any element (not just Fe, Dy, ...)

- Why hasn't vibrational RIXS been done yet ? (as far as I know)

- meV resolution is needed

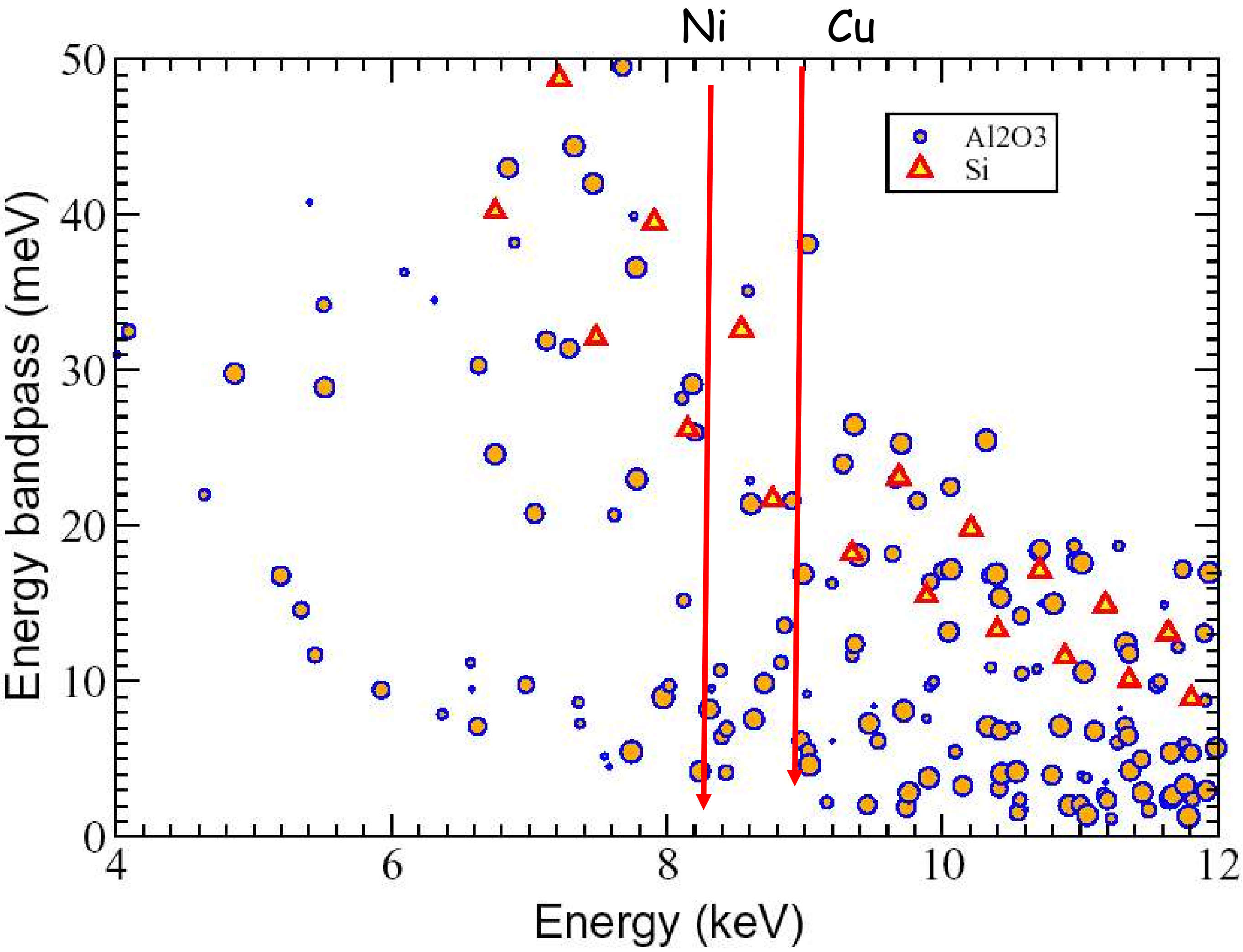
★at energies of absorption edges

•www.ksu.edu/.../faculty/ grad/amk/figure.gif

The Barrier to Hard X-Ray Vibrational RIXS

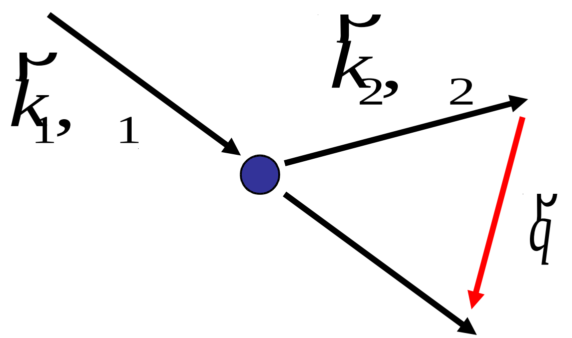
E/ΔE ~ 10^6

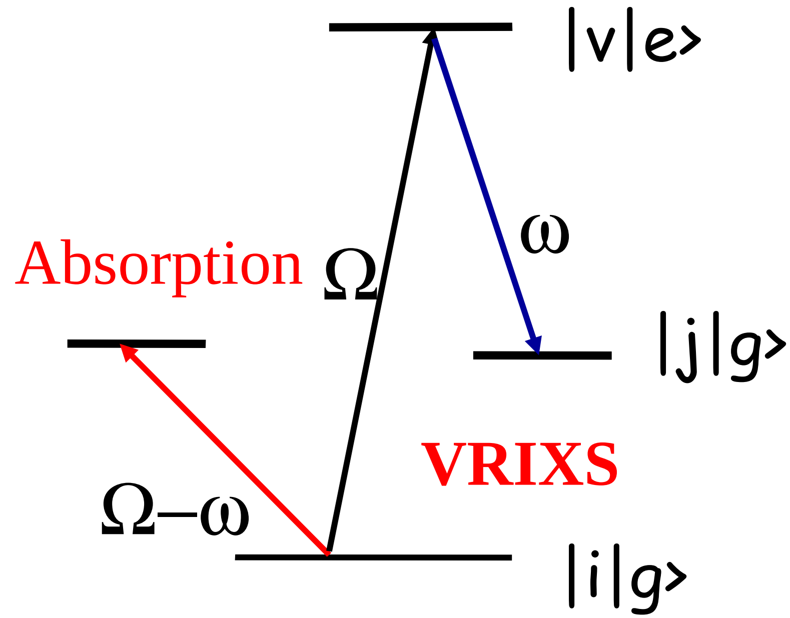
- Mismatch between
  - Si / Ge backscattering energies
  - K absorption energies
- Solution
  - Backscattering from sapphire
  - Energy scanning by heating/cooling



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

Vibrational Resonance Raman (A-Term)





- for resonant scattering:

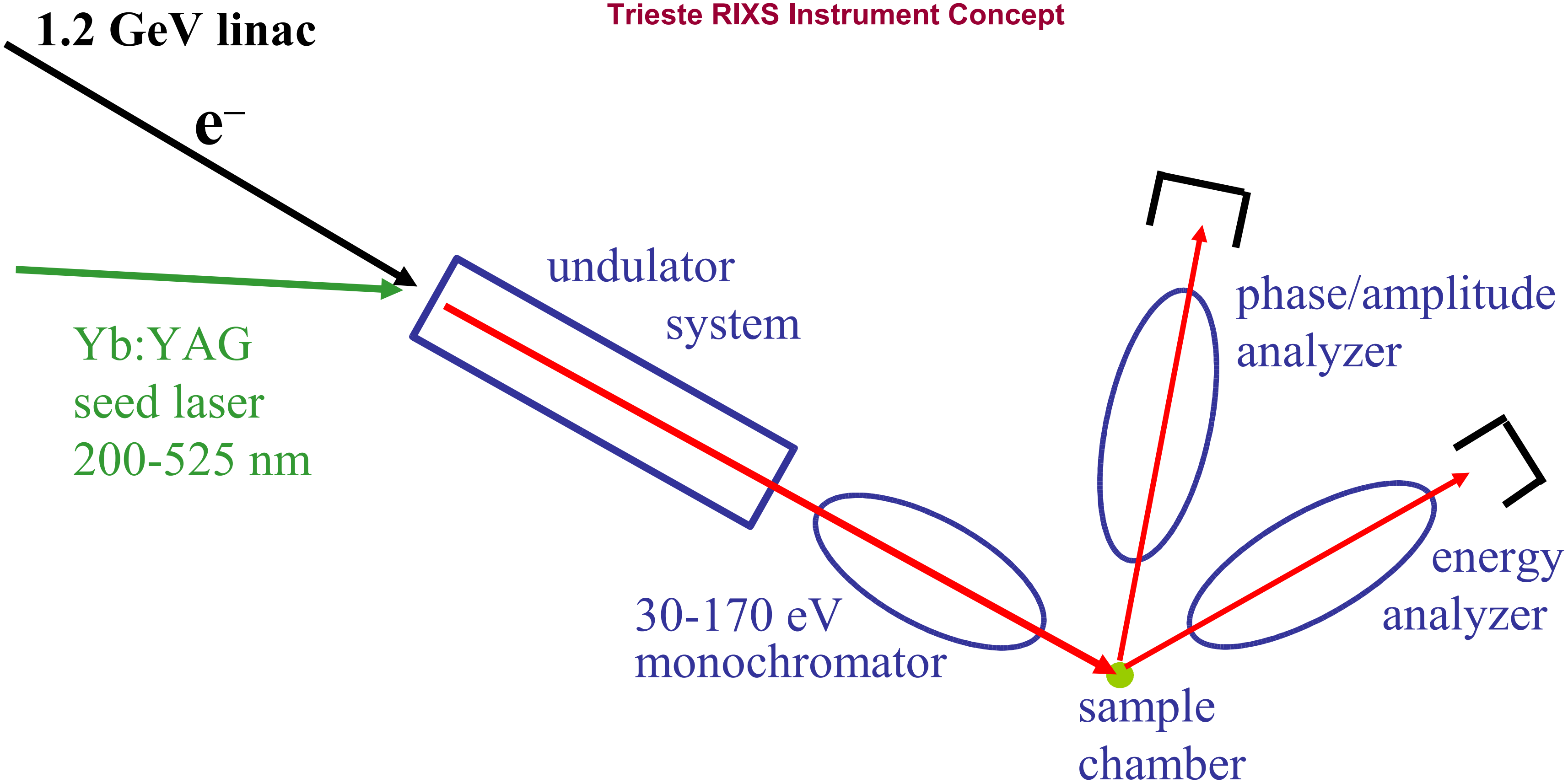
$$\partial^2 \qquad \frac{\overbrace{\langle g_0 | R | e_0 \rangle}^{\text{Electronic matrix element}} \overbrace{\langle g_0 | R | e_0 \rangle}^{\text{Electronic matrix element}}}{\underbrace{E_{ev} - E_{gi} - E_0 - i}_{\text{Resonance denominator}}} \underbrace{\langle i | v \rangle \langle v | j \rangle}_{\text{Franck-Condon factor}}$$

- + B and C terms ...

Soft X-Ray meV RIXS with Gratings

- Monochromators
- Analyzers
- Detectors
- Edges of Interest
  - O 2s 42 eV — 1s 543 eV
  - Mn 3p 47 eV — 2p 639 eV
  - Cu 3p 75 eV — 2p 932 eV
  - S 2p 162 eV — 1s 2472 eV

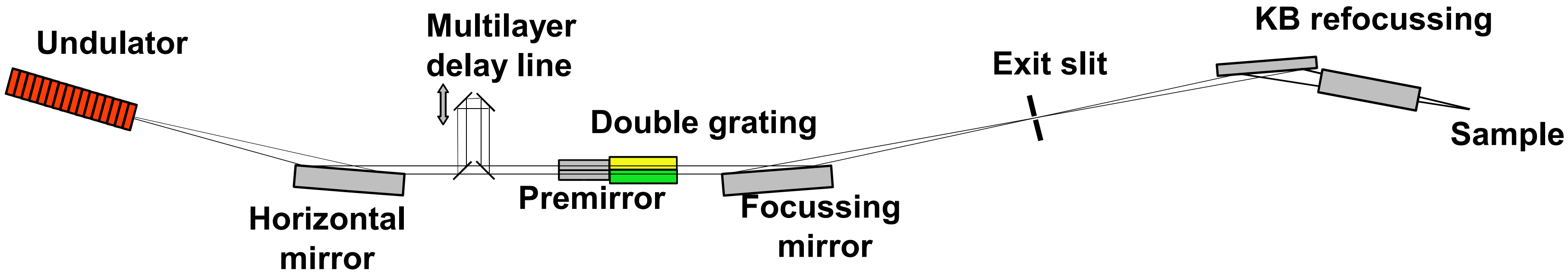
Trieste RIXS Instrument Concept



- System must tune continuously over full energy range
- Energy analyzer must provide meV resolution
- Sample and analyzer rotate to resolve momentum transfer

Option 1 Monochromator:

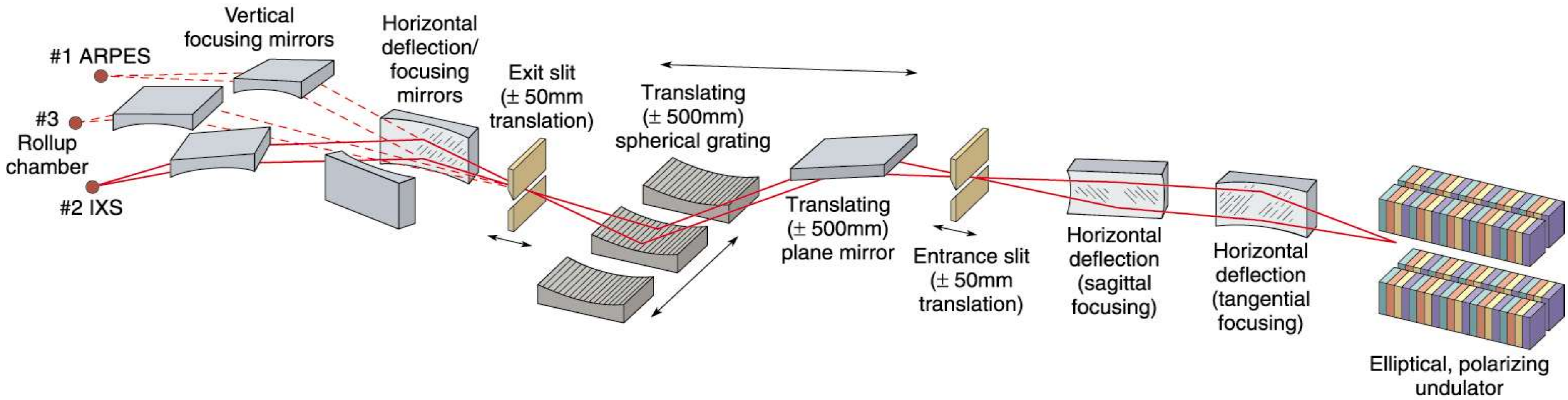
- **A fs delay line bichromator for RIXS**
- **Permits single beam or pump-probe**



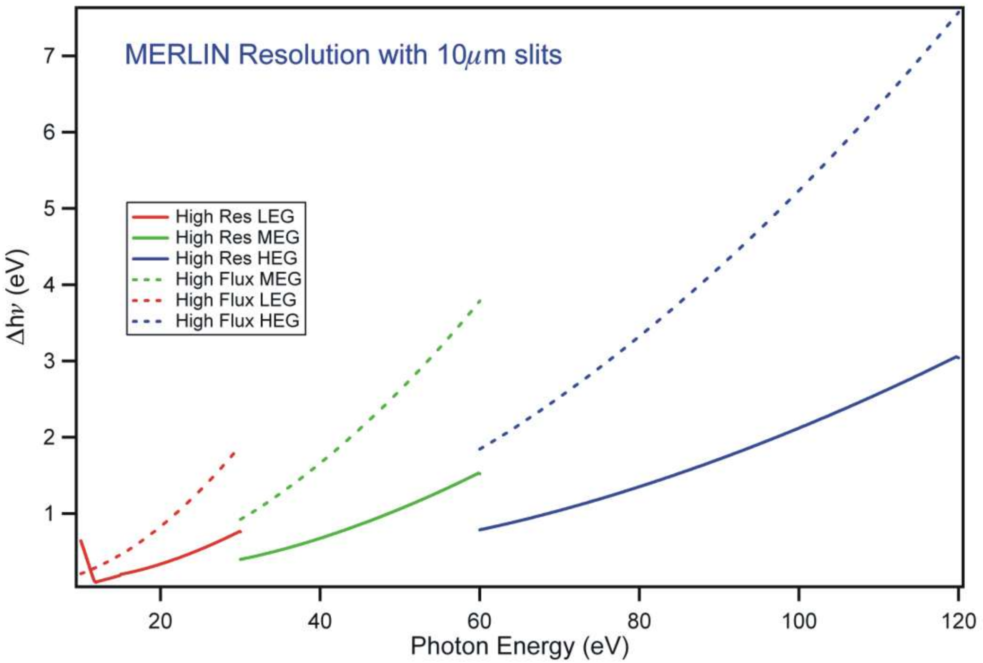
Multilayer delay line consists of a pair of beam splitting ML in the beam and a pair of ML for 180 deg back reflection.

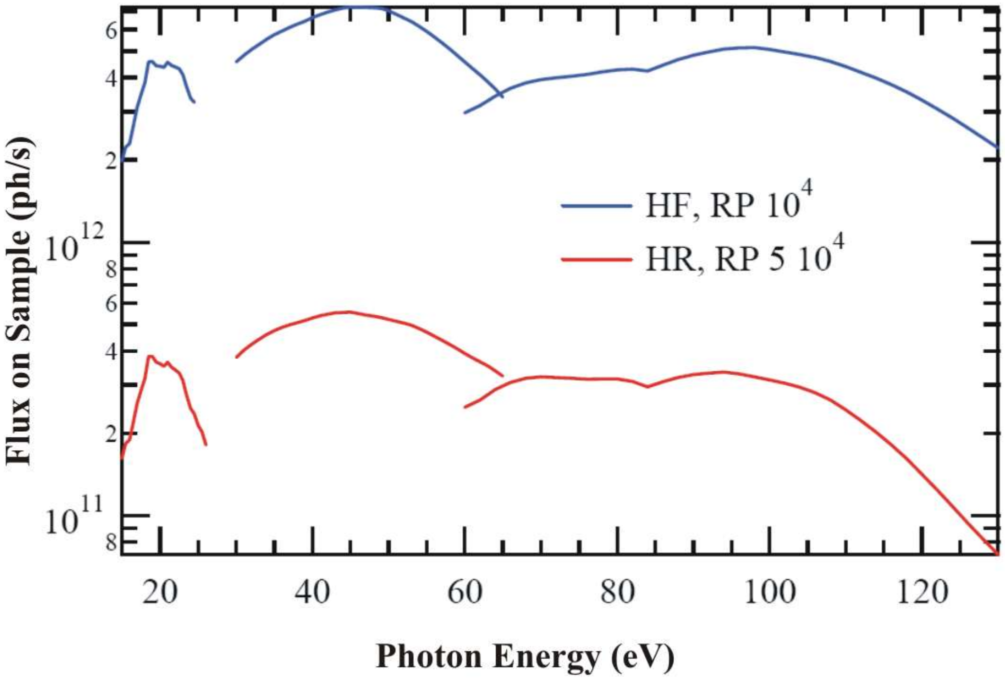
The different gratings can be set at specific incidence angles separately.

Option 2 monochromator:
ALS meV resolution beamline ($3.8M)



Merlin Performance (Theoretical)

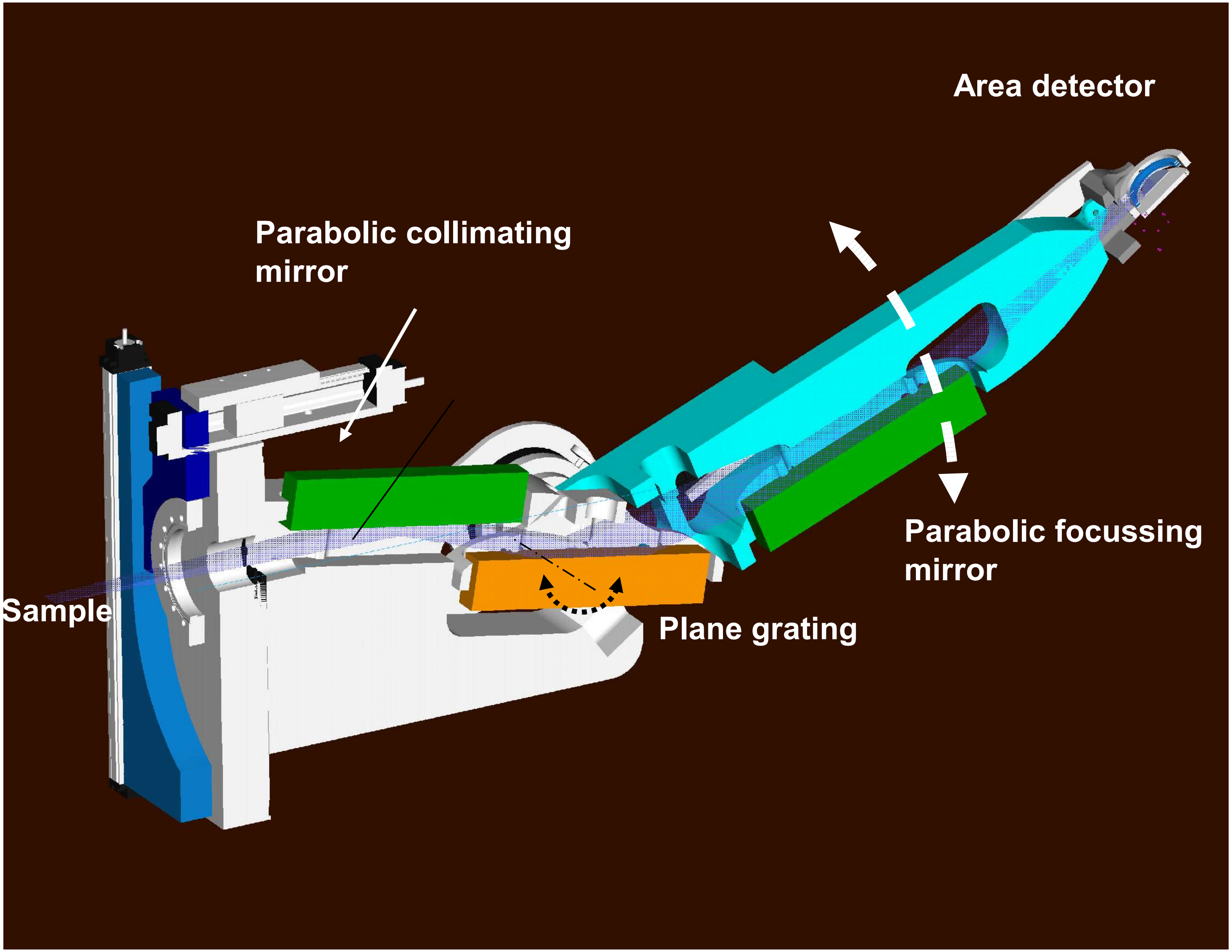




Analyzers

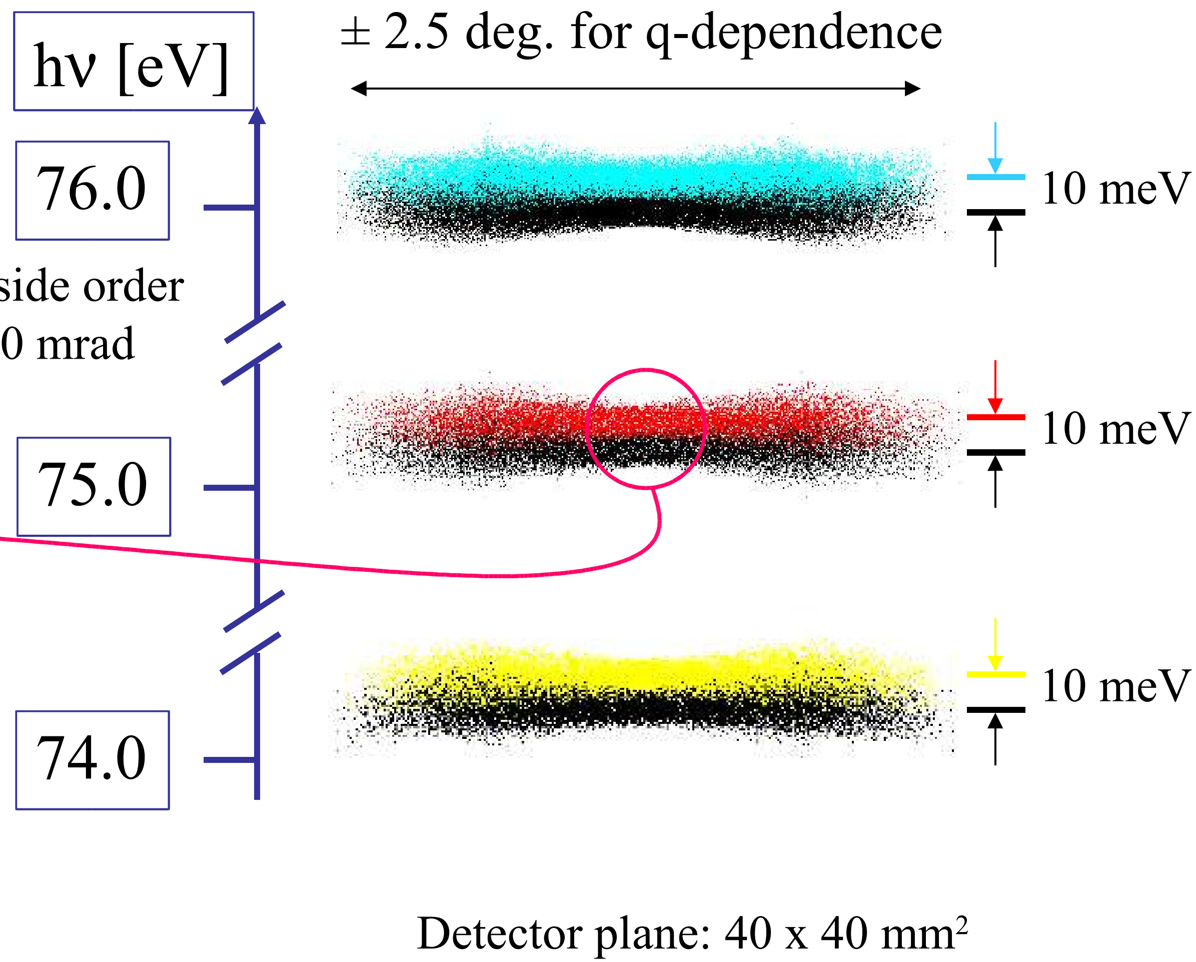
- Nordgren / Uppsala design
  - Parabolic mirror
  - Plane grating
- Hussain / LBNL design
  - Spherical mirror
  - Variable line space grating

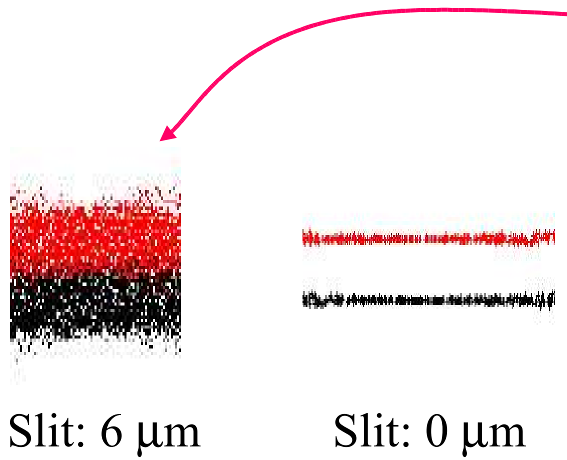
Option 1: parabolic mirror / plane-grating spectrograph



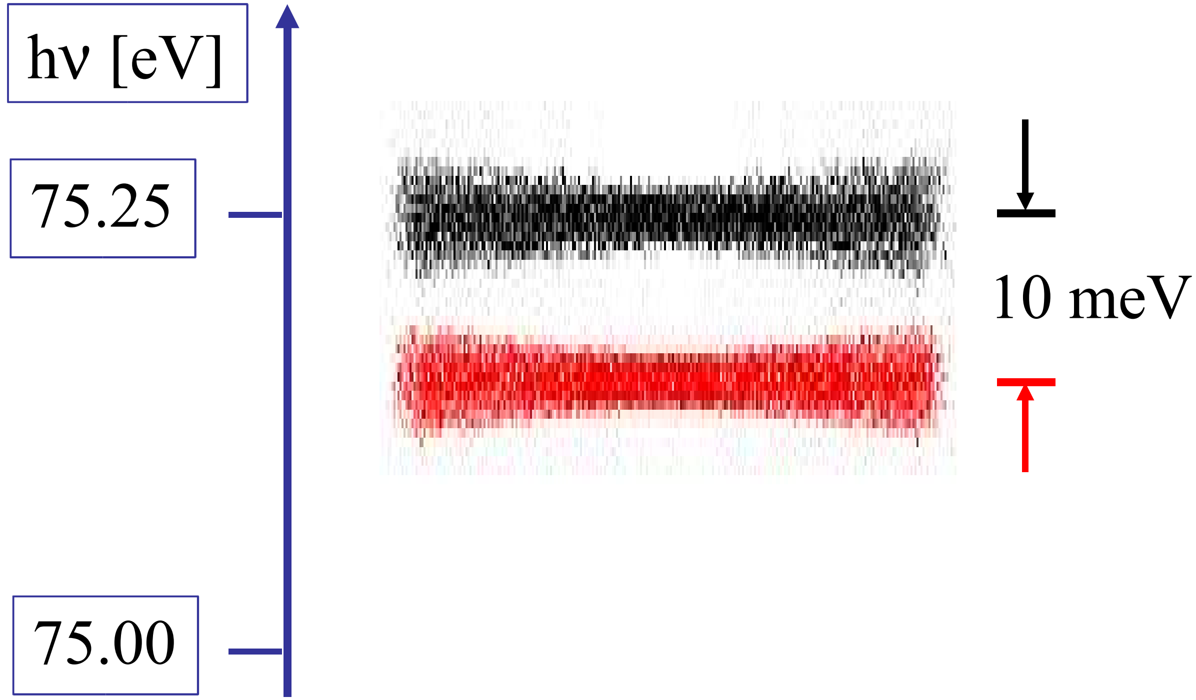
Raytracing of Double Paraboloidal Mirror Plane Grating Spectrometer

Source size: 6 μm x 60 μm
Grating: 1200 l/mm
Angle of incidence: 78 deg., outside order
Acceptance angle: 100 mrad x 50 mrad





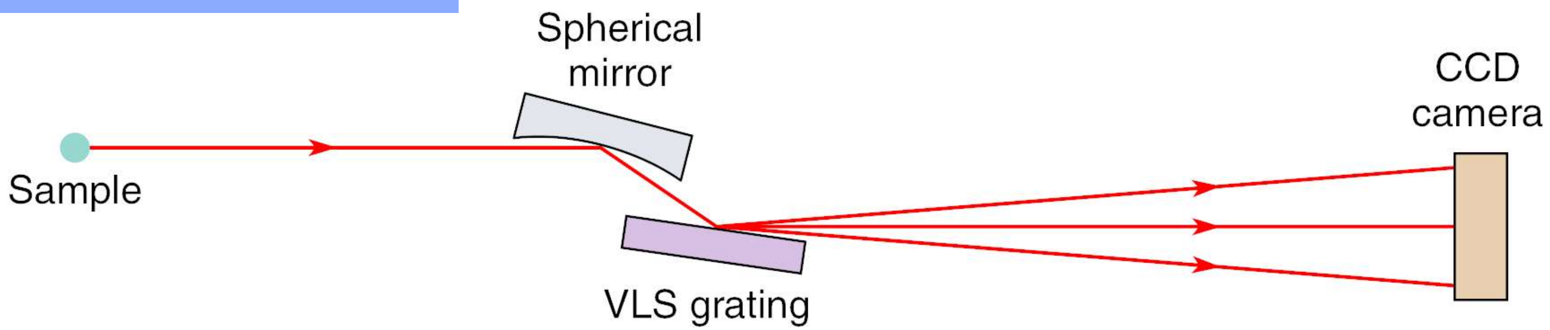
Maximizing resolution for plane grating spectrometer



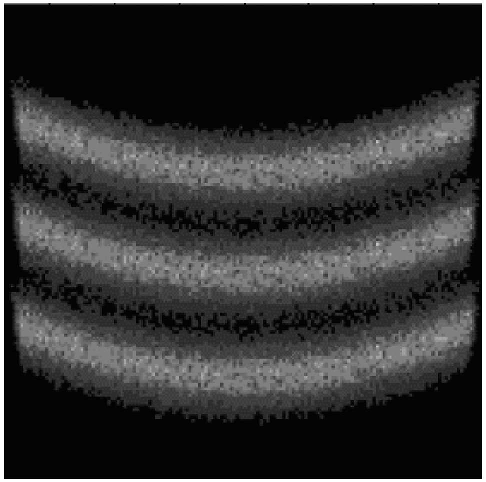
Source size: 6 μm x 60 μm
Grating: 1800 l/mm
Angle of incidence: 85 deg., inside order
Acceptance angle: 20 mrad x 50 mrad

Option 2: spherical mirror / variable line space grating

Optical Design



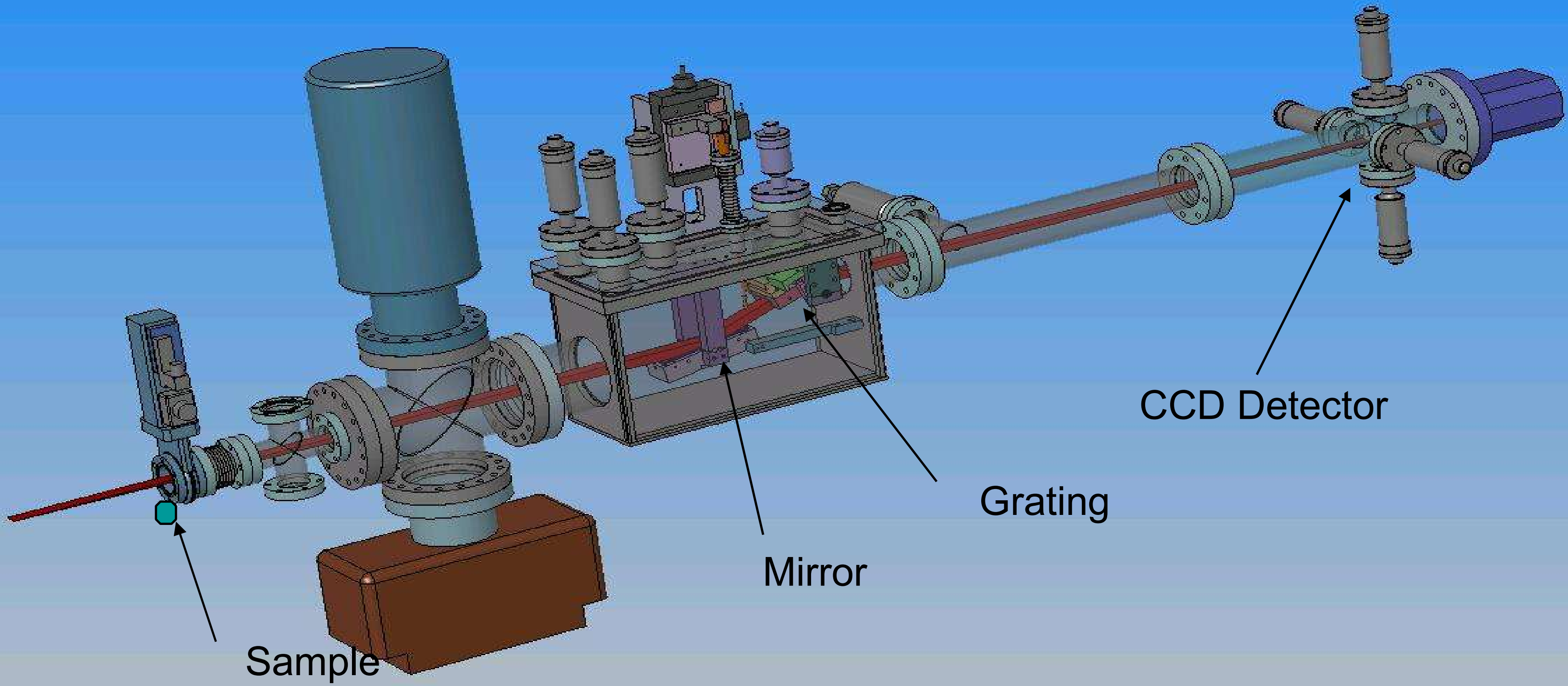
Ray Traces



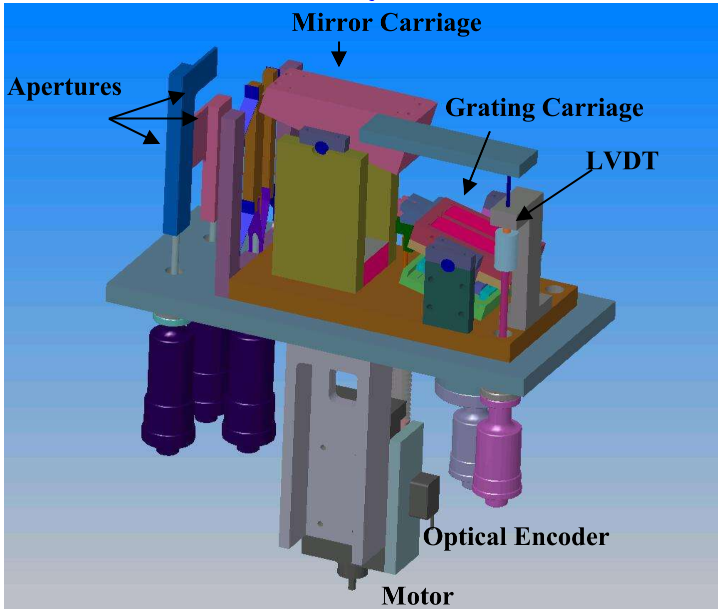
- **Resolution approaching 1 meV**.
- Overall length = 2 meters.
- Designed for Mn 3p (47 eV)
- Source size = 4 microns.

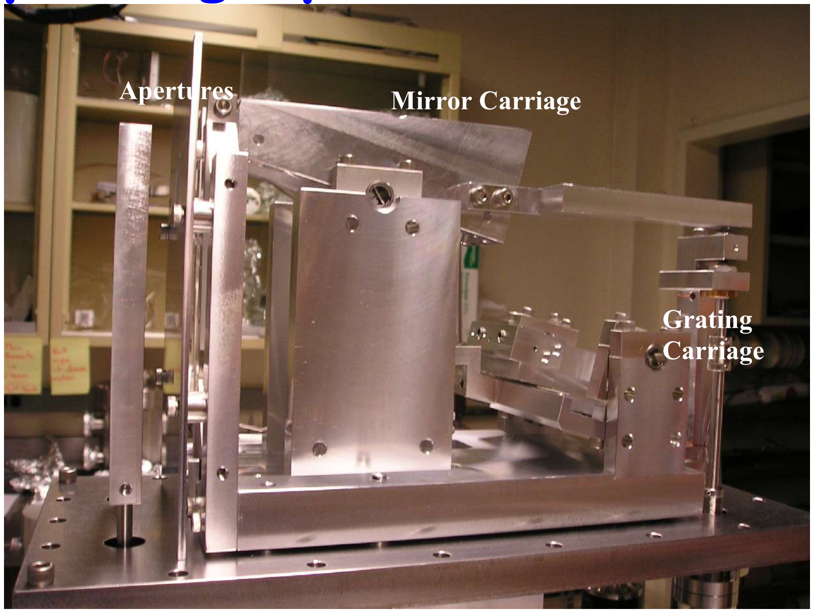
hν = 47 eV ± 5 meV

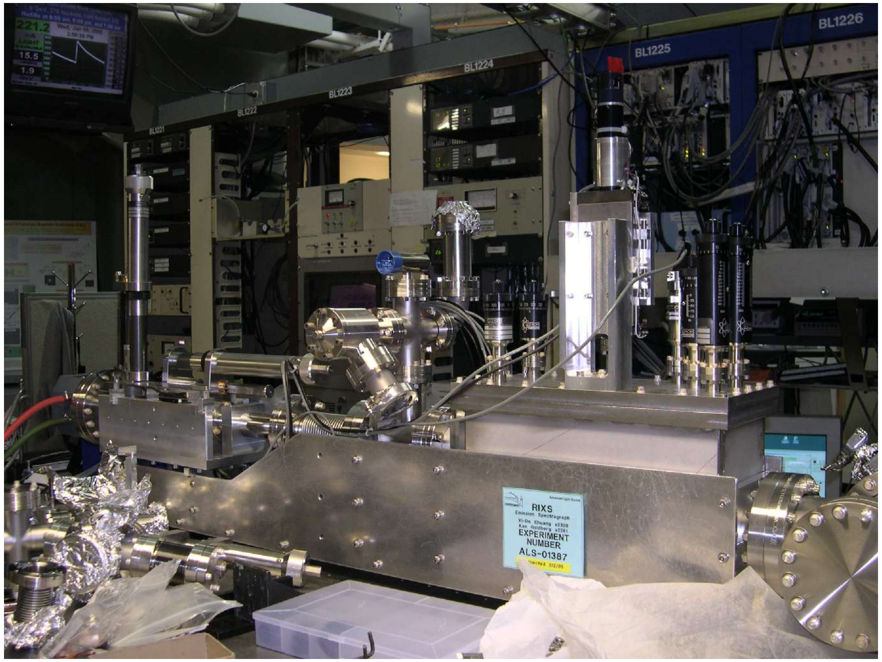
meV Resolution VLS Spectrograph: Engineering Design



LBNL Soft X-Ray Emission Spectrograph

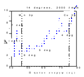






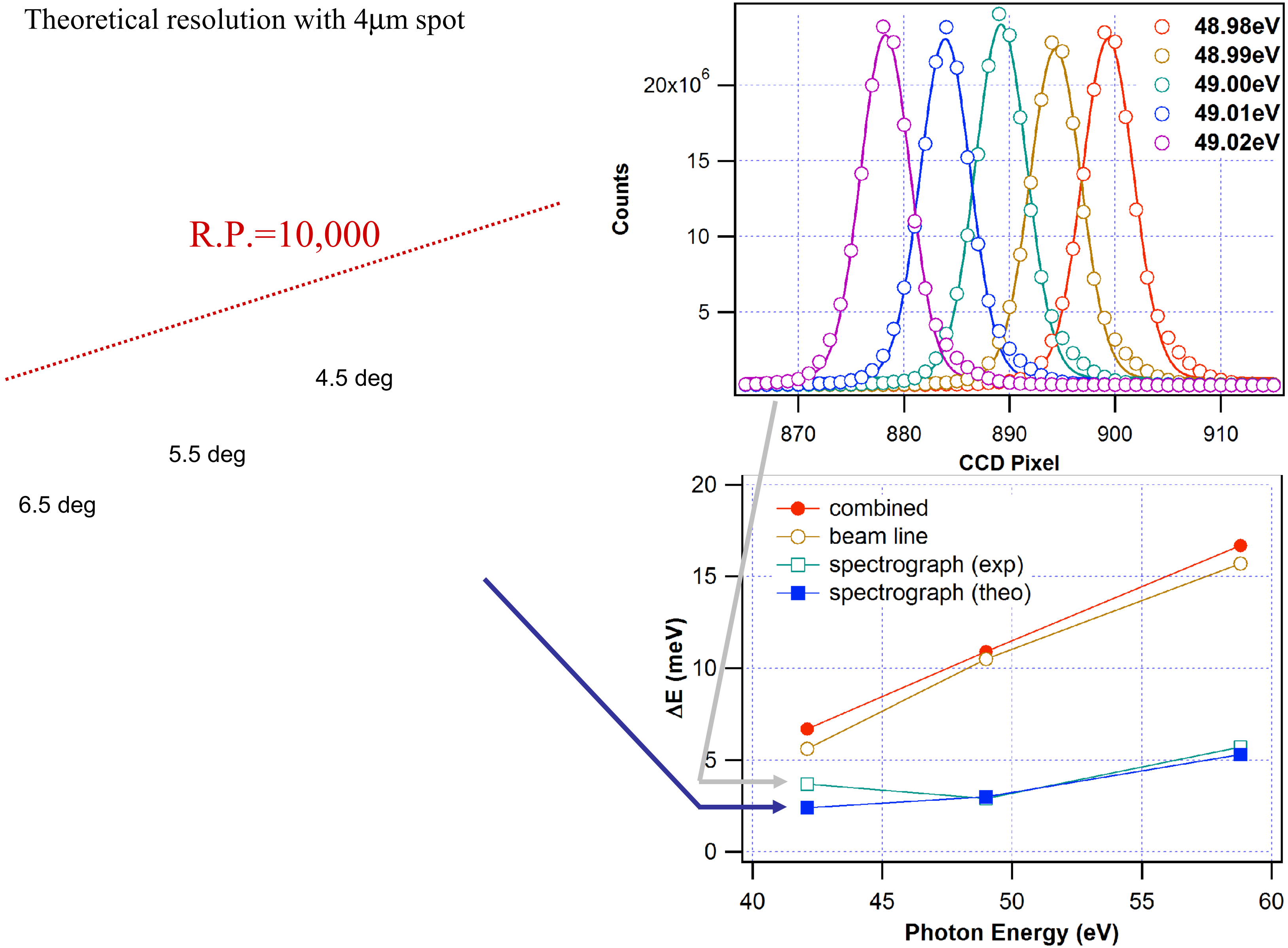
Currently, the experimental endstation is located at BL12

Theoretical & Measured Energy Resolution



Theoretical resolution with 4μm spot

measured resolution with straight beam



Room for Improvement

- Better CCD
  - Kodak CCD
  - Backthinning at LLNL
- Smaller Source Size
  - 4 micron -> 1 micron ?
- Multiple Spectrographs
  - ~10 spectrographs could be deployed
  - Cost is small compared to FEL

Radiation Damage

- X-Rays change sample chemistry
  - photoreduction
  - photooxidation
  - directly
  - Indirectly via photoelectrons, cascades, and radicals
- At ALS,
  - Damage in seconds to minutes w/ ~10^{12} photons/sec
- FEL spectroscopy should be single shot per sample position

Moncton's 'Slippery Slope'

5×10^{16} ph/sec/meV

Ideal Source:
--Milli-joule (2ps) pulses
--Milli-volt bandwidth
--Kilo-hertz rep rate

1/20 50 Hz linac

1/10 0.1 mJ pulse power (vs 1mJ)

1/10 bandwidth

200 fs pulse length (10 meV)

1/20 optics through-put

3rd Generation Source (MERLIN, ALS)

5×10^{11} ph/sec/meV

Other Applications

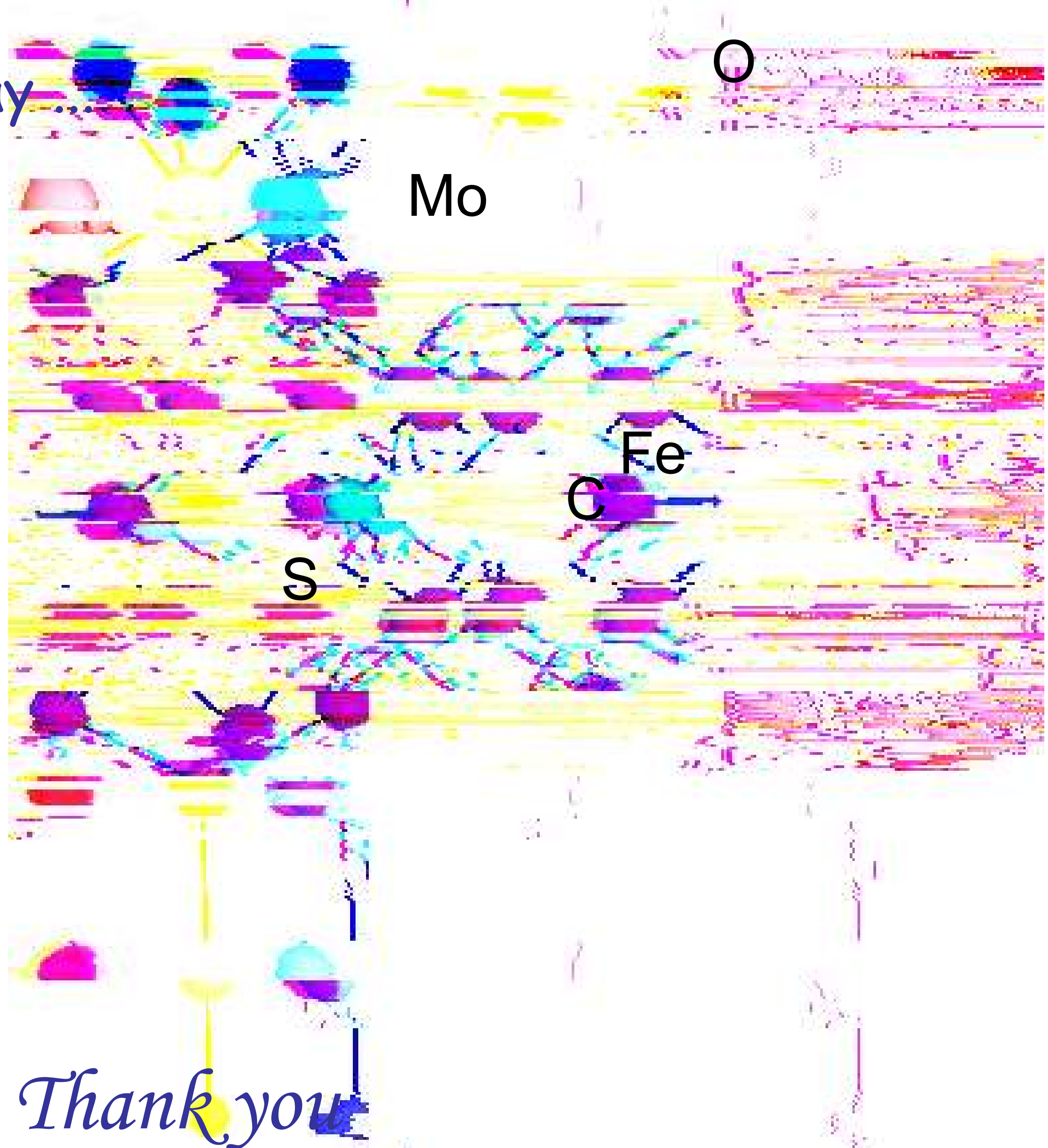
- Correlated solids.
- High temperature superconductors.
- Magnetic systems
- Nano-scaled materials
- Buried interfaces and wide band gap materials
- In-situ studies of electrochemical processes.
- Organic thin film electronic materials

Summary

- meV resolution -> element specific vibrational spectroscopy
- same technology would apply to other low energy excitations

Energy	elements	meV mono	meV analyzer	meV source
20-180	• O 2s • TM 3p, S 2p	now	now	Trieste FEL ?
280-900	• C, K, O 1s • TM 2p, S 2p	?	?	Trieste ? LCLS ?
2.5-10 keV	• S 1s • TM 1s	now	sapphire?	TESLA ?

- eventually, even higher energies are interesting someday ...



Thank you

Molecular and Solid State Vibrations

- H-O-H
- Fe-S
- 'protein modes'
- X-Y
- $C_6H_4I_2$ 'librations'
- Phonons

- Typical condensed state linewidths ~1 meV

Contributors & Collaborators

NRVS

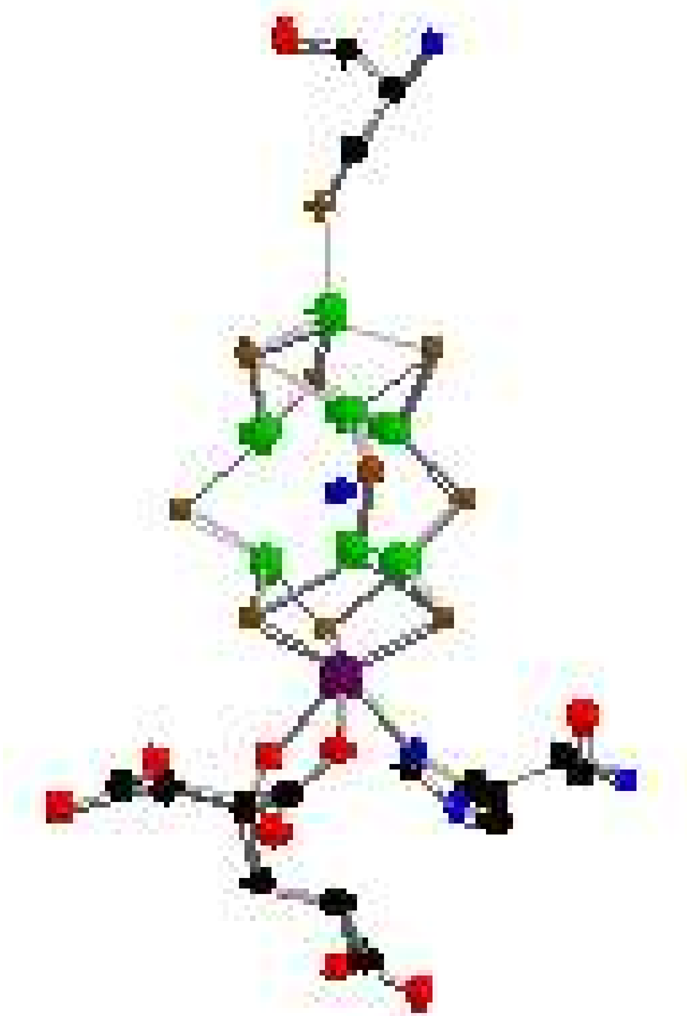
- Simon George
- Hong-xin Wang
- Matthew Smith
- Philip Titler
- Yuming Xiao

- Dimitri Coucouvanis (models)
- Markos Koutmos (models)
- Mike Adams (Rd)
- Jacques Meyer (Fd)
- Bill Newton (N_2ase + FeMo-co)
- Karl Fisher (N_2ase + FeMo-co)

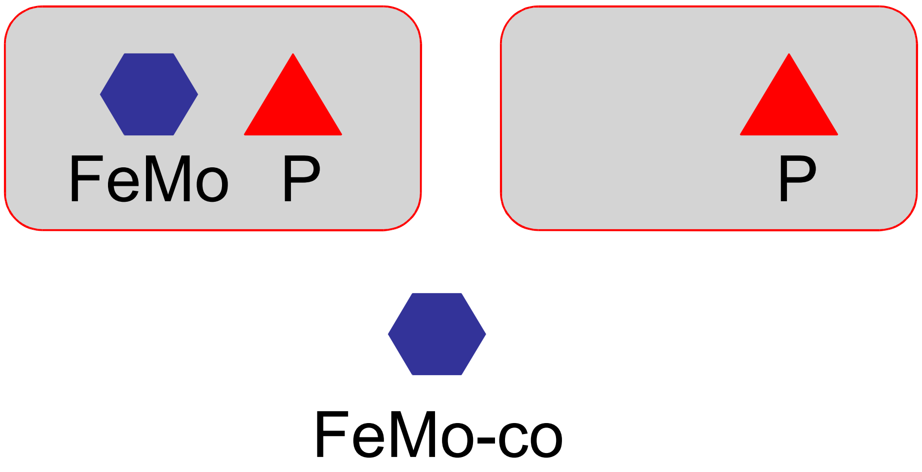
- DOE -- Office of Biological & Environmental Research
- NIH -- GM-65440 for RIXS & NRVS
- Advanced Photon Source -- DOE …
  - (Ercan Alp, Wolfgang Sturhahn, Jihong Guo, Thomas Toellner)
- Spring-8 -- Japan (Yashutoka Yoda)

Thank you

Nitrogenase Samples



- 'intact' N_2ase or 'holoenzyme'
  - 2 FeMo clusters
  - 2 P-clusters
  - 230 kDalton
- 'apo' N_2ase or ΔnifE mutant
  - just P-clusters
- FeMo-co
  - $MoFe_7S_9$ cluster extracted
  - N-methyl formamide solvent
- In theory:
  - FeMo-co = 'intact' - 'apo'

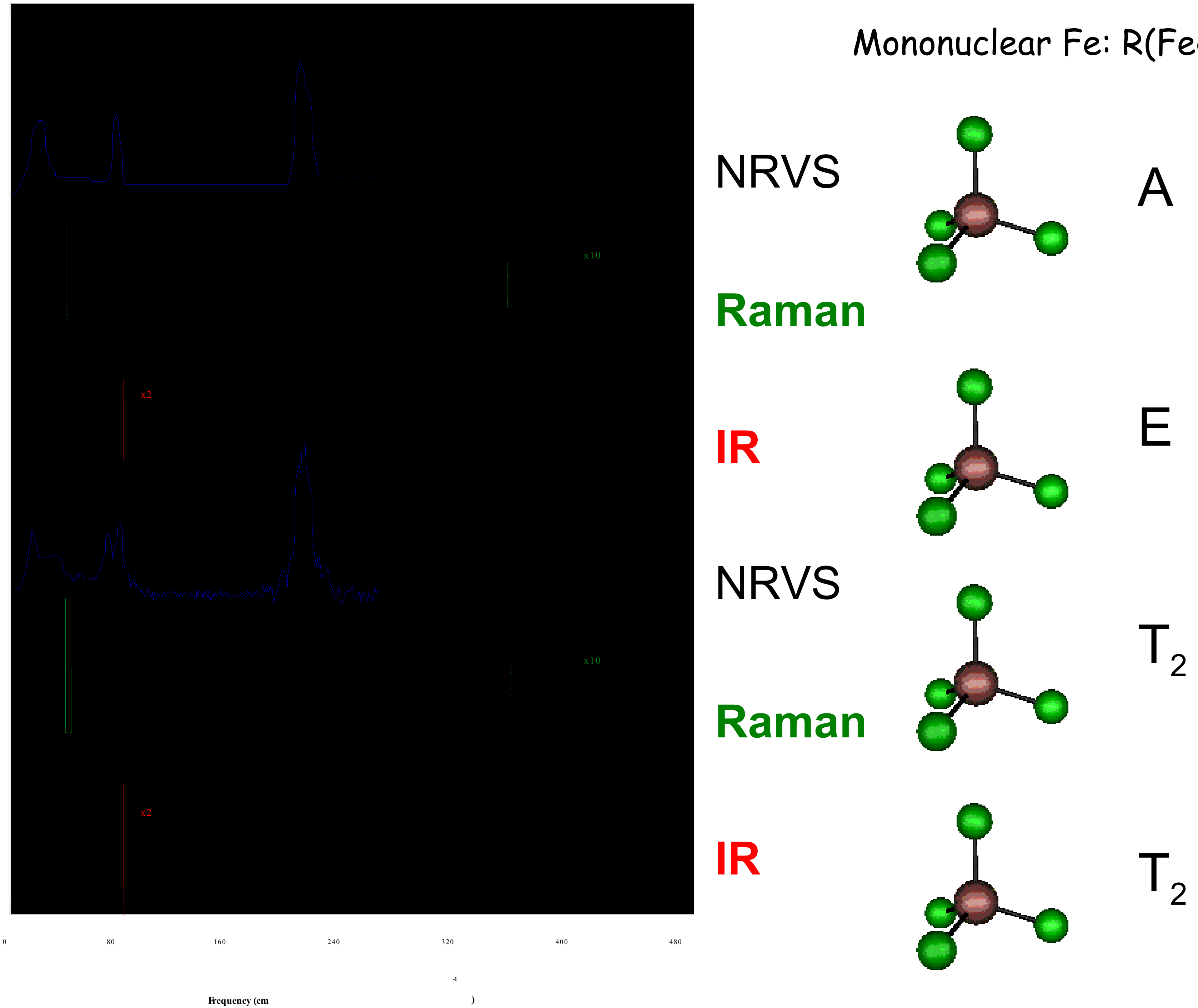


NRVS Summary & Prospects
- a local probe of vibrational properties

- > 5 mM Fe feasible now
  - But beam time is scarce
- A Handful of Beamlines
  - APS - Argonne, Illinois
  - SPring-8 - Japan
  - ESRF - Grenoble, France
- Necessary Improvements
  - x10 flux
  - better detectors
  - More stations
  - Additional nuclei

- Valuable Nuclei for Bio/Environmental Work
- ^{57} Fe - 14.413 keV (A,S,E)
- ^{161}Dy - 25.651 (A,E)
- ^{129}I - 27.77 keV
- ^{183}W - 46.4 keV
- ^{201}Hg - 26.3 keV
- ^{161}Dy - 25.651 (A,E)
- ^{235}U -
- ^{55}Mn - 126 keV
- ^{19}F - 197 keV
- ^{237}Np - 59.537 keV
- ^{95}Mo - 204 keV
- ^{92}Mo - 2.76 MeV
- ^{61}Ni - 67.419 keV ?

Mononuclear Fe: R($FeCl_4$)



Current Synchrotron Vibrational Spectroscopy

- X-ray inelastic scattering
  - at ...
  - e.g.
- Nuclear resonance Inelastic Scattering
  - at
  - e.g.
- ...
  - At
  - e.g.