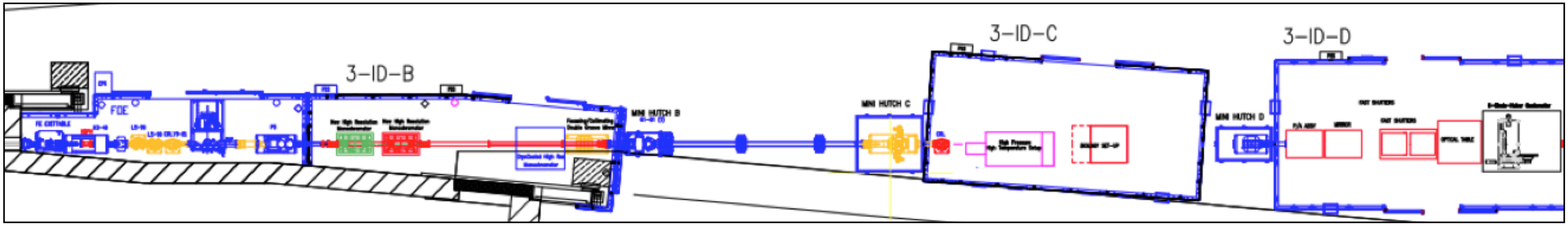
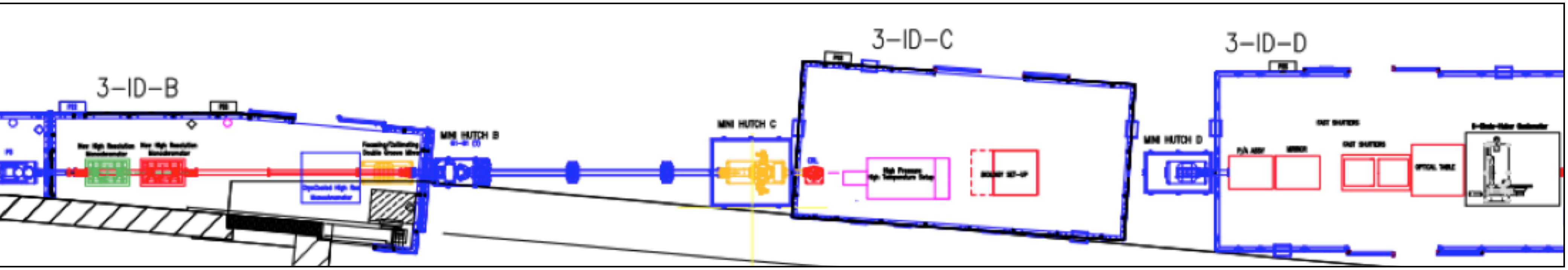
APS Upgrade & Future Outlook of Sector 3

1. Present operations & scientific activities
2. Near future plans : 2016-2021
3. Life after upgrade: 2022-onwards



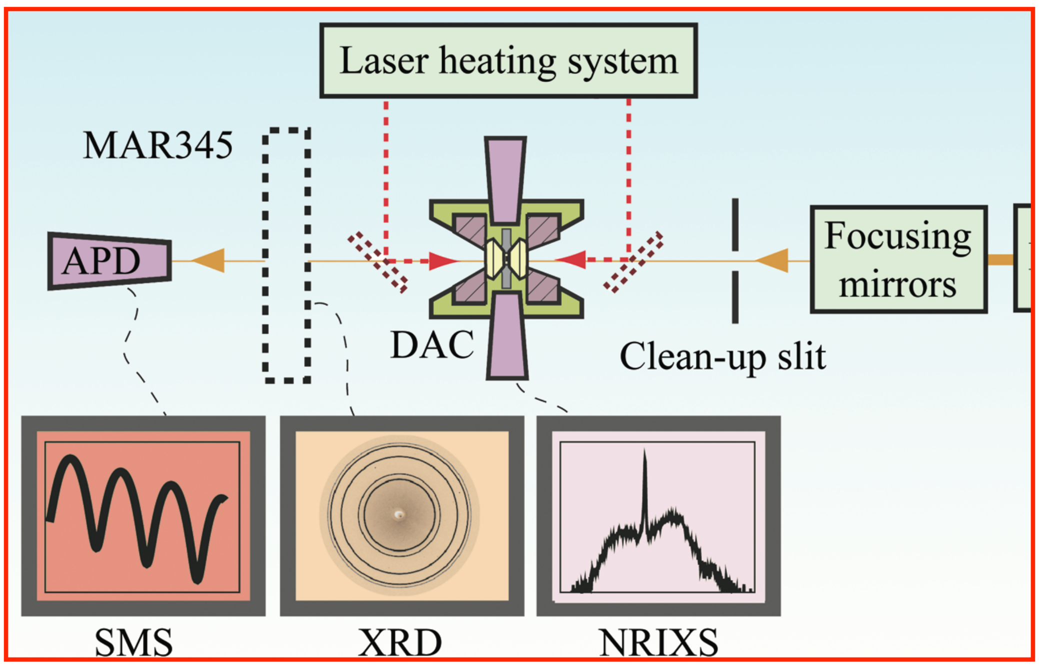
APS Upgrade & Future Outlook of Sector 3

1. Present operations & scientific activities



Unique combination of **spectroscopy**, **scattering** and **diffraction**: High pressure, 4-4000 K, in-situ ruby laser, membrane DAC:
DREAM station for Geophysicists & Geochemists

HERIX-3: 6 m arm, 4 analyzer, 2.2 meV resolution
One of the five (5) working spectrometers in the world:
Physics, chemistry, biology, geology, mat.sci

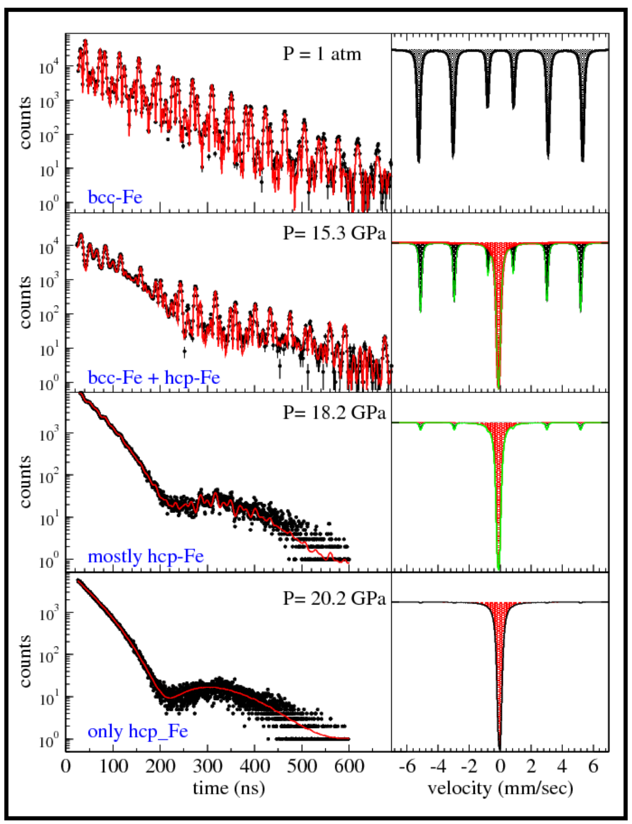


1. Present operations & scientific activities @ Sector 3-ID

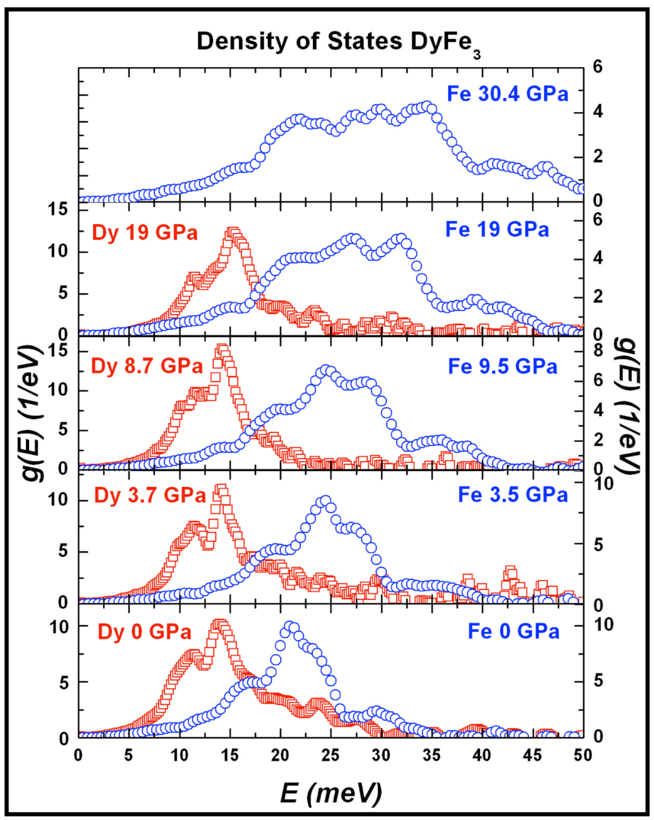
There are (3) **distinct but integrated** scientific operational modes:

i) Nuclear resonant COHERENT FORWARD Scattering: NFS or SMS
ii) Nuclear resonant INELASTIC X-RAY Scattering: NRIXS or NRVS
iii) Momentum-resolved INELASTIC X-Ray Scattering: HERIX-3

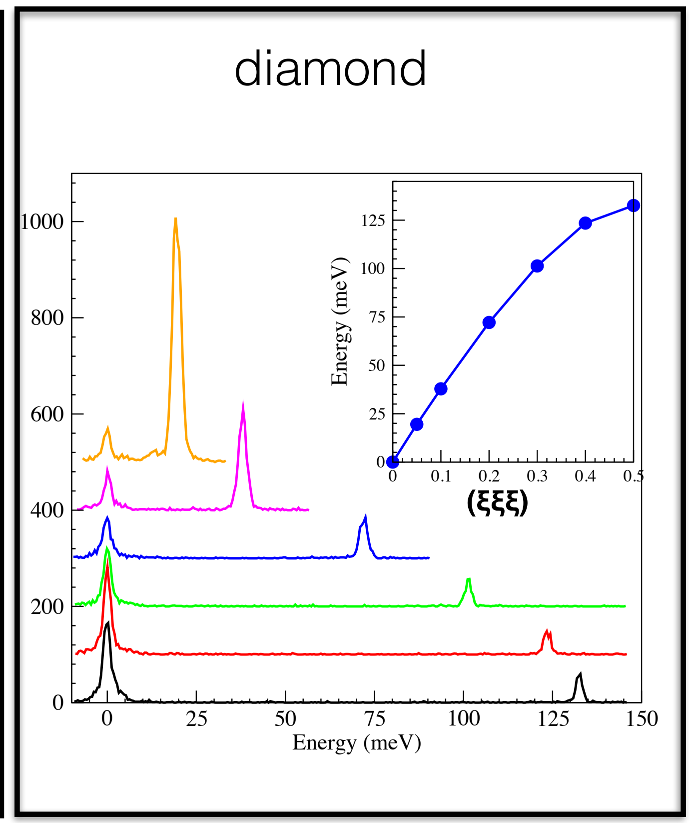
Nuclear Forward Scattering



NR inelastic x-ray scattering



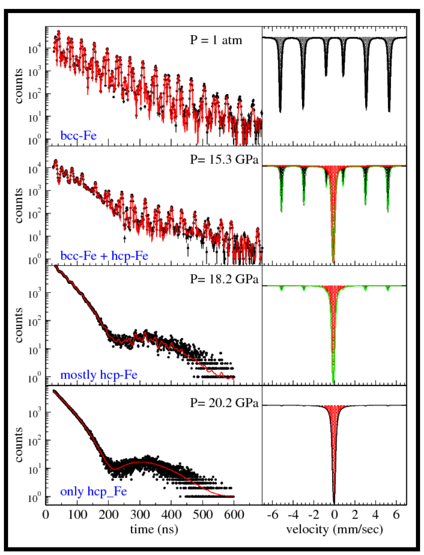
Momentum-resolved IXS



1. Present operations & scientific activities

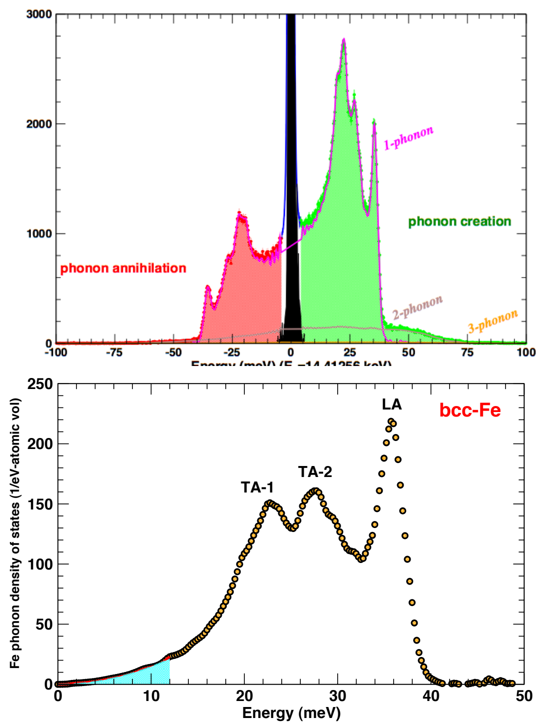
Nuclear Forward Scattering
(Synchrotron Mössbauer Spectroscopy)

- Akin to Mössbauer Spectroscopy performed in the time domain
- valence state
- spin state
- magnetic ordering
- local atomic environment
- under extreme pressure and temperature
- crystalline, amorphous, mono-layers, dilute systems
- physics-chemistry-geology-materials science..



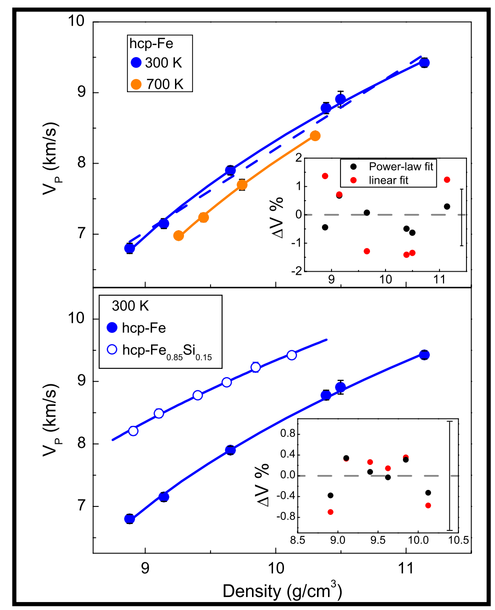
Nuclear Resonant Inelastic Scattering
(NRIXS or NRVS)

- Akin to Raman spectroscopy and FTIR
- Vibrational density of states
- Force constant and kinetic energy
- sound velocity, shear and compression moduli
- vibrational entropy
- mode Gruneisen constant
- buried monolayers, high-low P/T
- physics-chemistry-geology-materials science..



Momentum-resolved
Inelastic X-ray Scattering (HERIX-3)

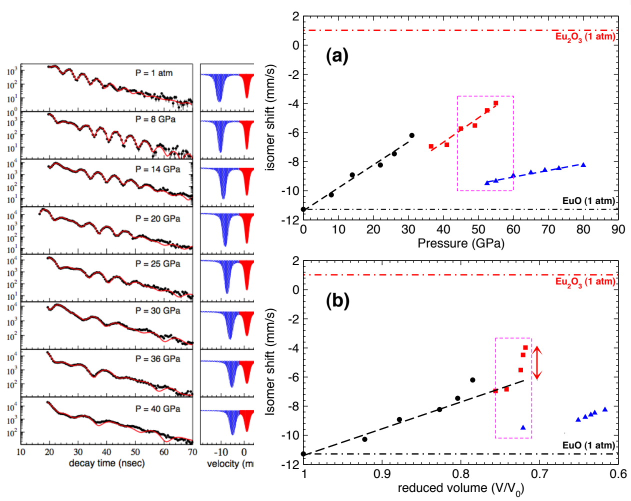
- Akin to Brillouin scattering or ultrasound
- phonon dispersion relations
- shear and compressional sound velocity
- Young and shear moduli
- mode softening during phase transitions
- role of magnetism
- applicable to nanogram samples, high pressure, low temperature, liquids, glasses
- physics-chemistry-geology-biology-materials science..



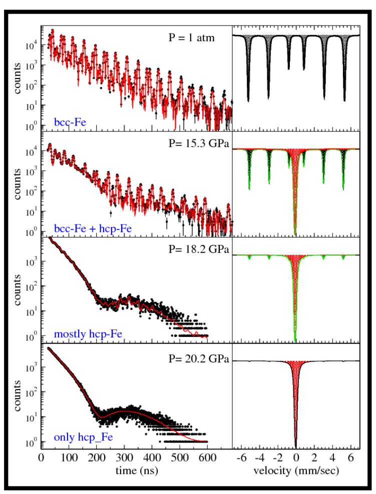
1. Present operations & scientific activities

Nuclear Forward Scattering (Synchrotron Mössbauer Spectroscopy)

Example1: Pressure induced valence change in EuO

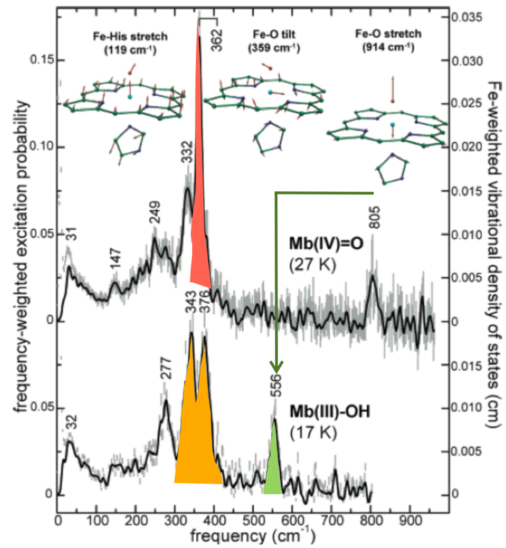


Example2: Pressure induced bcc-hcp change in iron

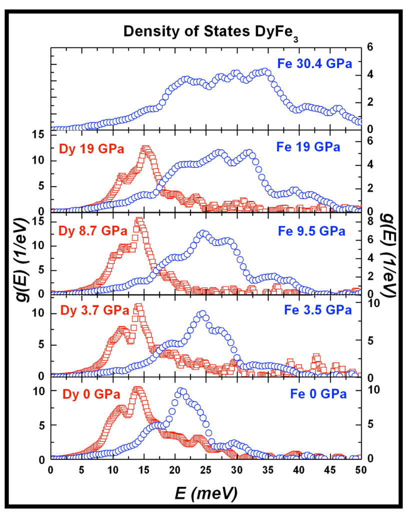


Nuclear Resonant Inelastic Scattering (NRIXS or NRVS)

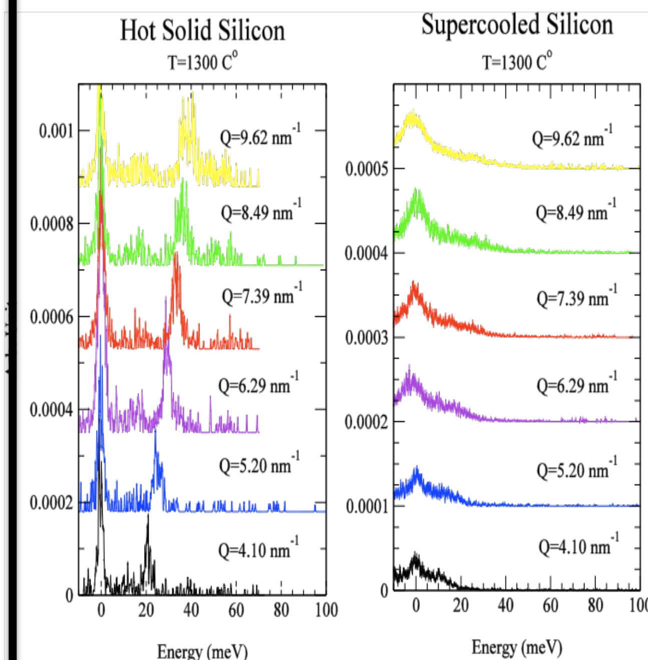
Example1: Protonation of myoglobin

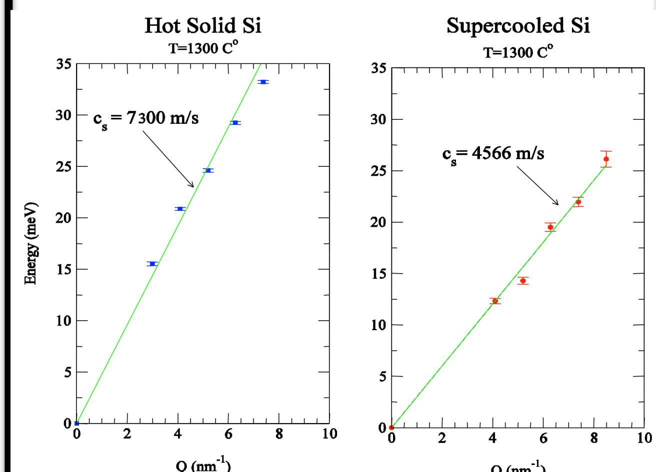


Example2: Pressure dependence of phonon dos



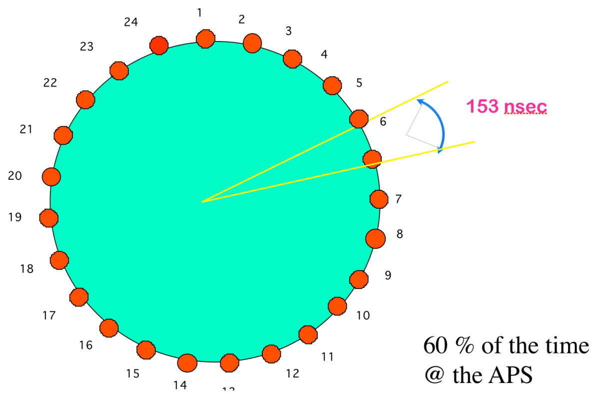
Momentum-resolved Inelastic X-ray Scattering (HERIX-3)

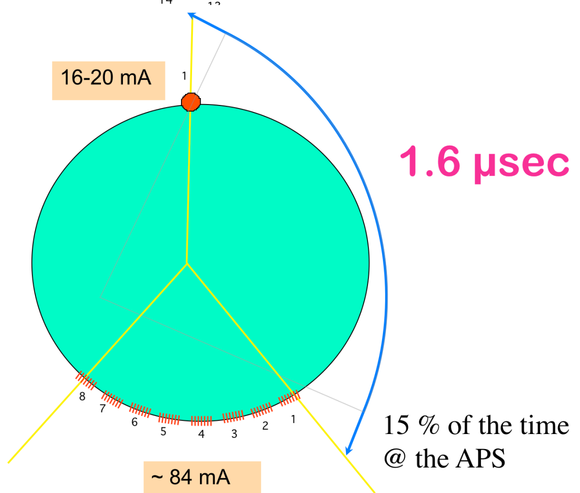


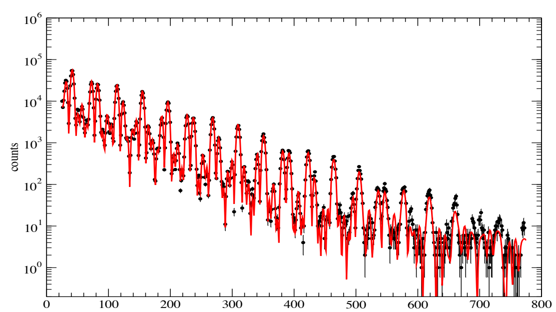


Time structure determines the scientific use

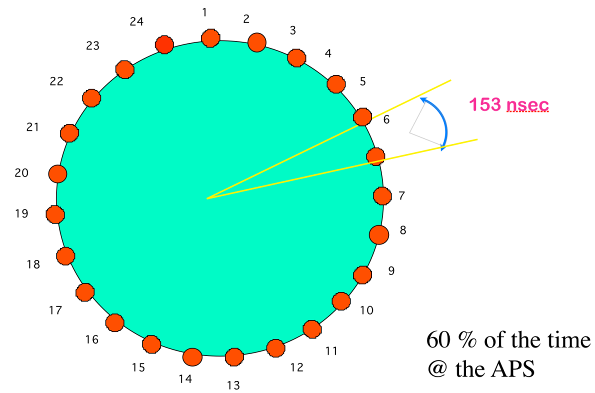
Nuclear Forward Scattering (Synchrotron Mössbauer Spectroscopy)







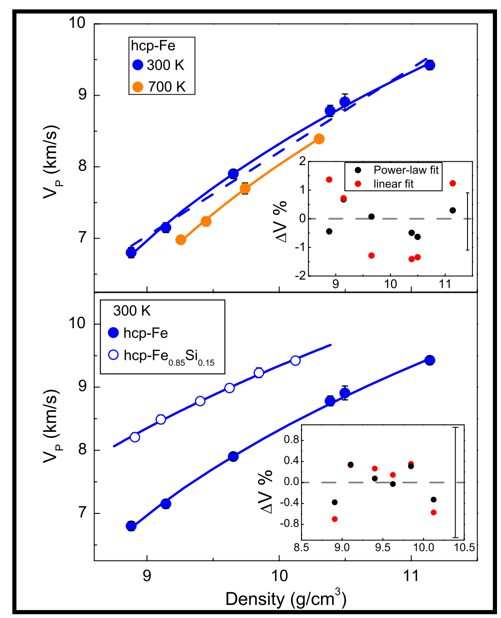
Nuclear Resonant Inelastic Scattering (NRIXS or NRVS)



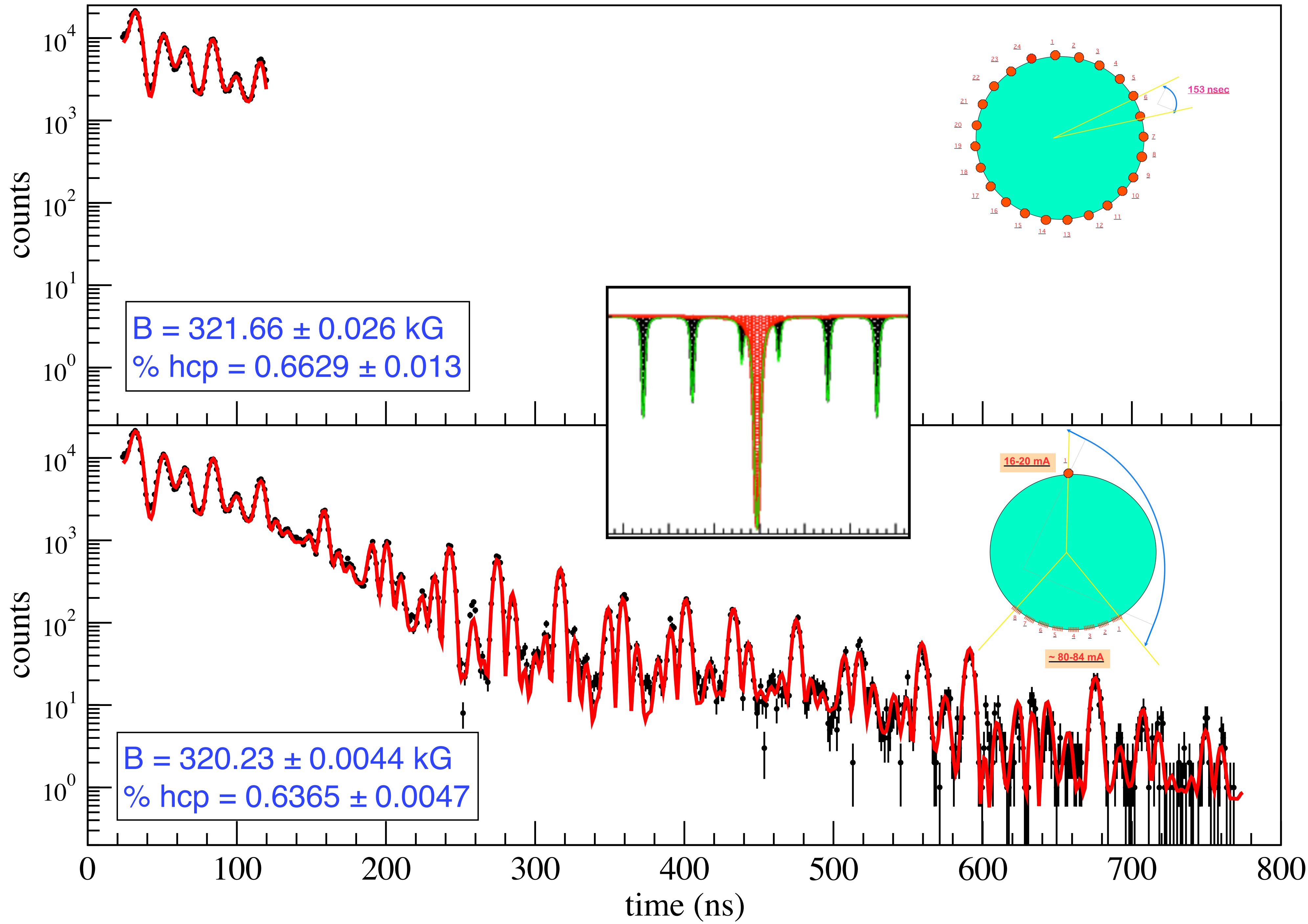
Isotope	Energy (eV)	Half-life (ns)	ΔE (neV)
^{181}Ta	6215.5	9800.	0.067
^{169}Tm	8401.3	4.	114.0
^{83}Kr	9403.5	147.	3.1
^{187}Os	9776.8	2.16	211.
^{57}Fe	14412.5	97.8	4.67
^{151}Eu	21541.4	9.7	47.0
^{149}Sm	22496.	7.1	64.1
^{119}Sn	23879.4	17.8	25.7
^{161}Dy	25651.4	28.2	16.2
^{129}I	27770.	16.8	27.2
^{40}K	29834.	4.25	107.0
^{125}Te	35460	1.48	308.0
^{121}Sb	37129.	4.53	100.0
^{129}Xe	39581.3	1.465	311.2
^{61}Ni	67419.	5.1	89.0
^{73}Ge	68752	1.86	245.
^{176}Hf	88349.	1.43	319.4
^{176}Hf	88349.	1.43	319.4
^{99}Ru	89571.	28.8	15.8
^{67}Zn	93300.	9200.	0.049

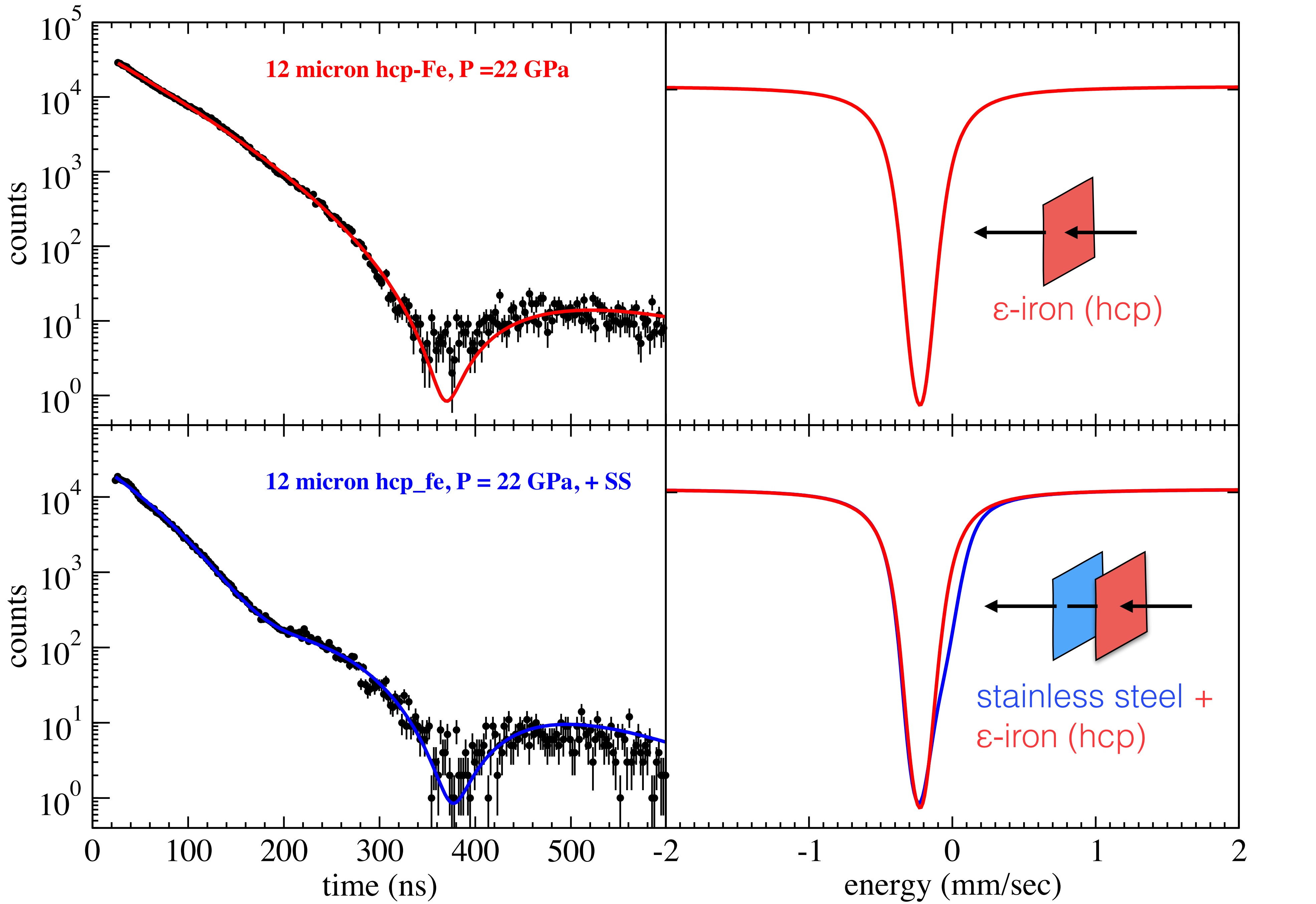
Momentum-resolved Inelastic X-ray Scattering (HERIX-3)

324 bunch operations

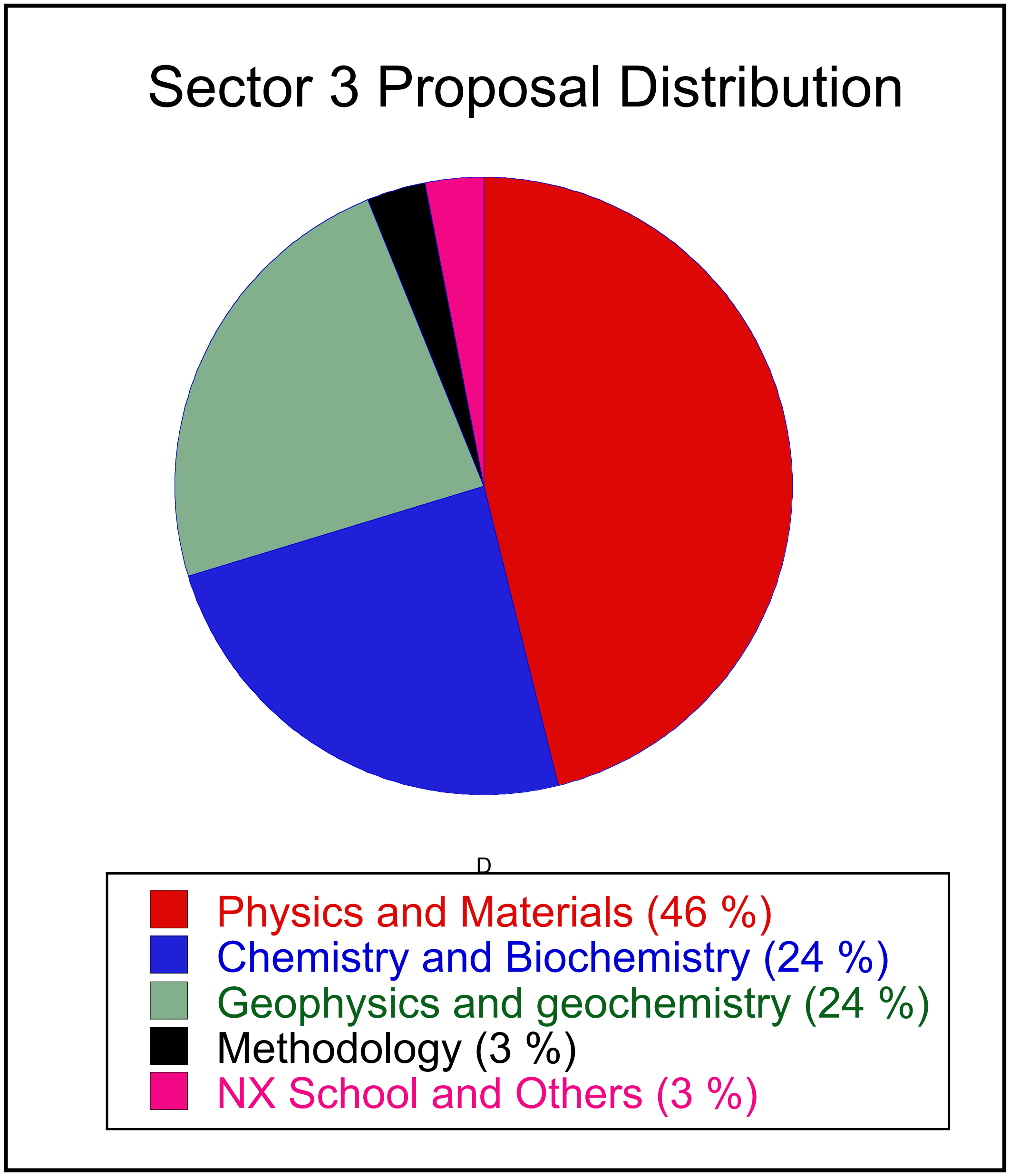


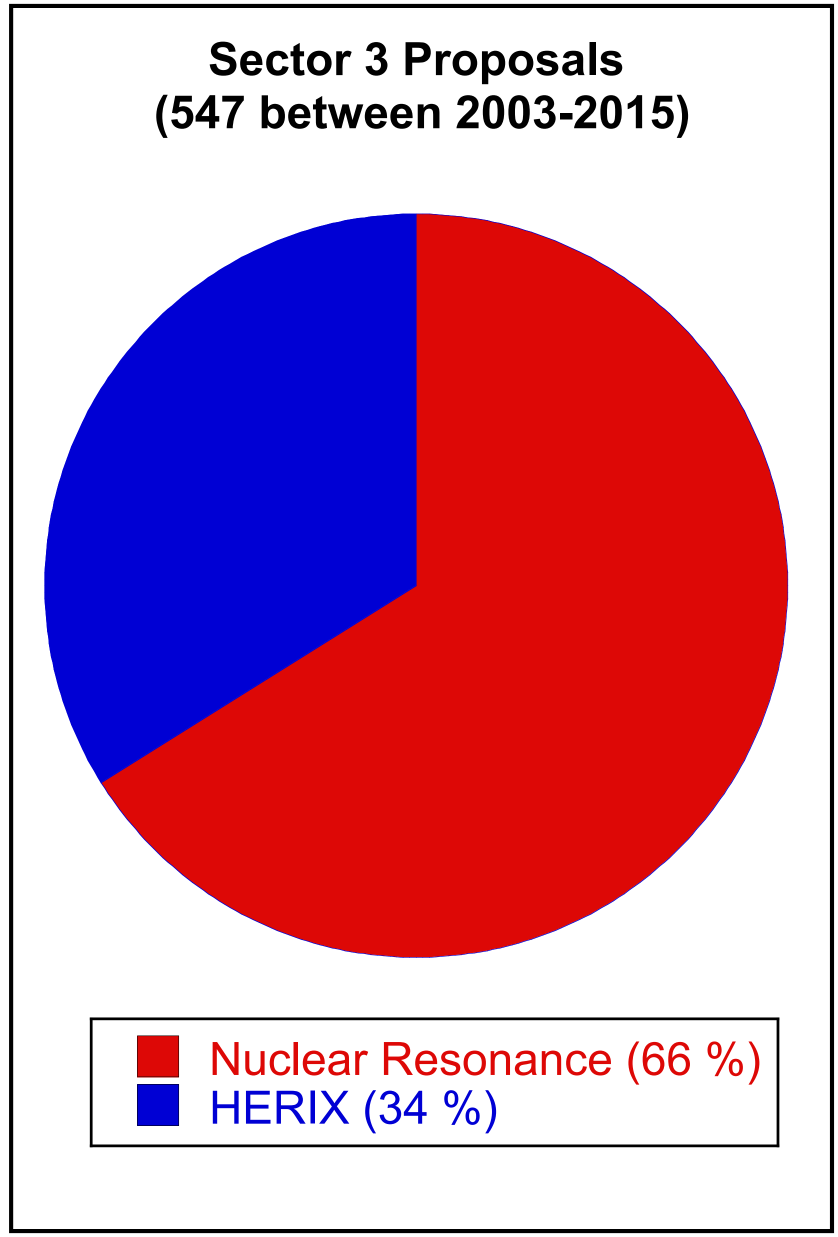
mixed alpha & epsilon phase of pure iron at 15.3 GPa pressure





12 micron hcp-Fe, P =22 GPa
12 micron hcp_fe, P = 22 GPa, + SS
counts
counts
time (ns)
energy (mm/sec)
ε-iron (hcp)
stainless steel +
ε-iron (hcp)

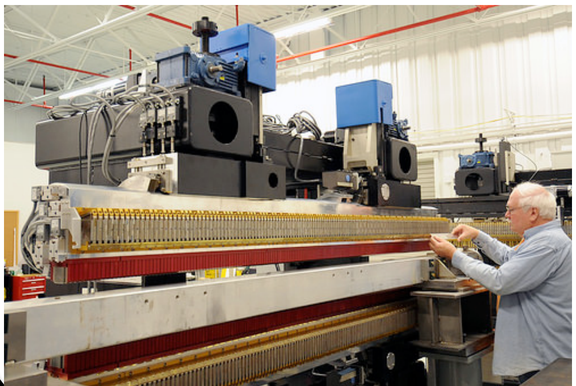

Sector 3 Proposal Distribution
D
Physics and Materials (46 %)
Chemistry and Biochemistry (24 %)
Geophysics and geochemistry (24 %)
Methodology (3 %)
NX School and Others (3 %)


Sector 3 Proposals
(547 between 2003-2015)
Nuclear Resonance (66 %)
HERIX (34 %)

Near Future (2016-2021) for Sector 3

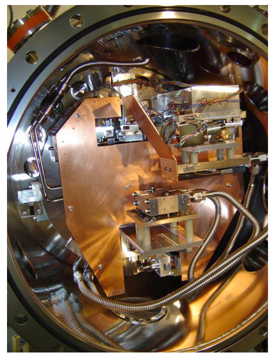
Revolving Undulator : factor of 2 flux gain @ 14 keV

Period: 2.1 cm & 2.7 cm



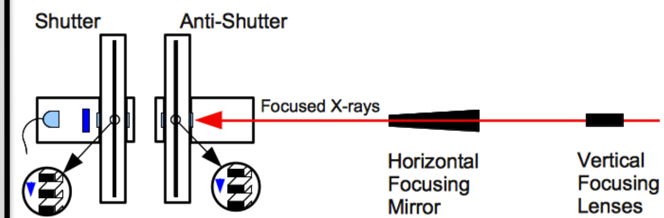
LN2-cooled Si HHLM:

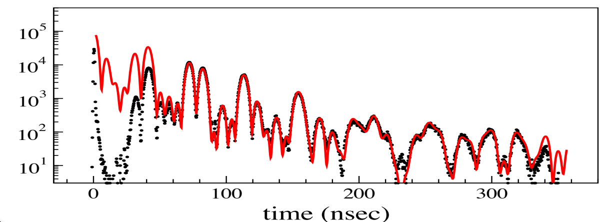
Better focusing to 1 μm level, 5 Mbar DAC & Mössbauer Microscope



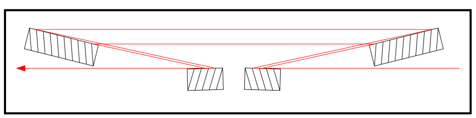
Fast Shutter: time manipulation

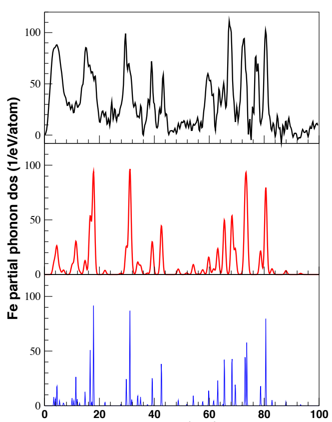
Needed to prepare for APS-U





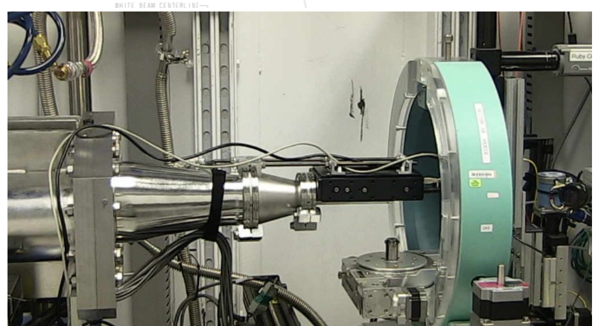
ΔE ~ 0.2 meV, all-vacuum, non-dispersive high resolution monochromators





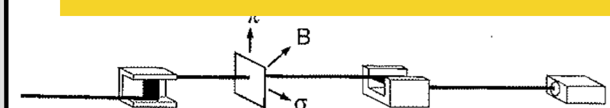
Pixellated CdTe detector for HERIX-3 (and HERIX-30)

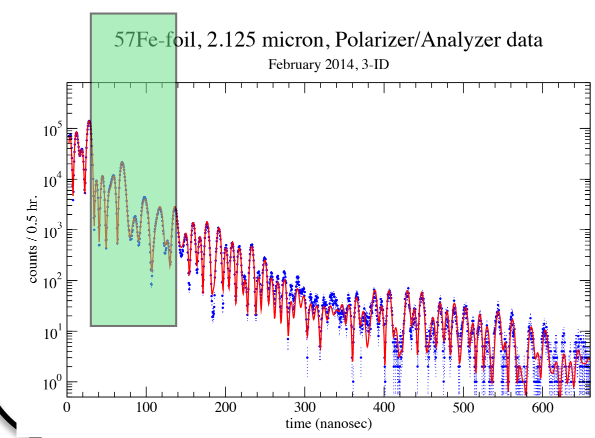
Better resolution & throughput



Polarizer / Analyzer optics

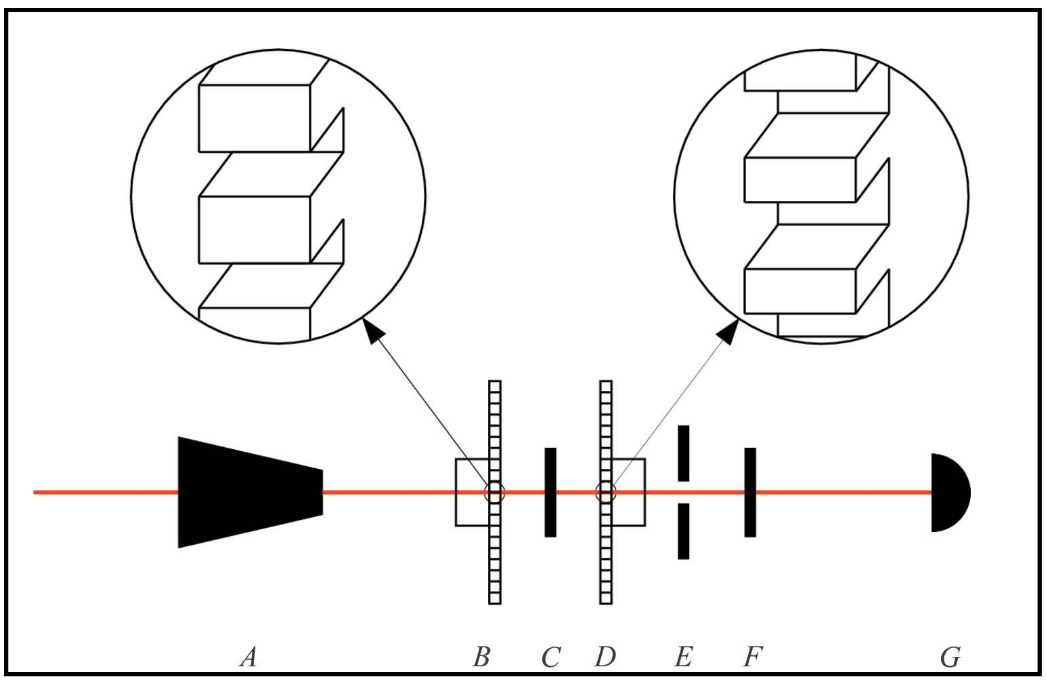
Benefits the most from MBA

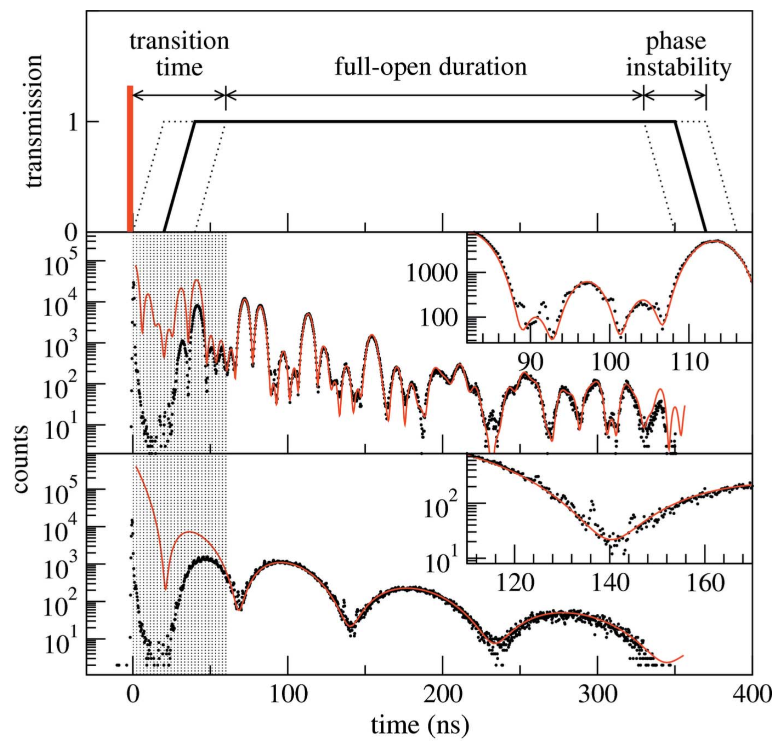




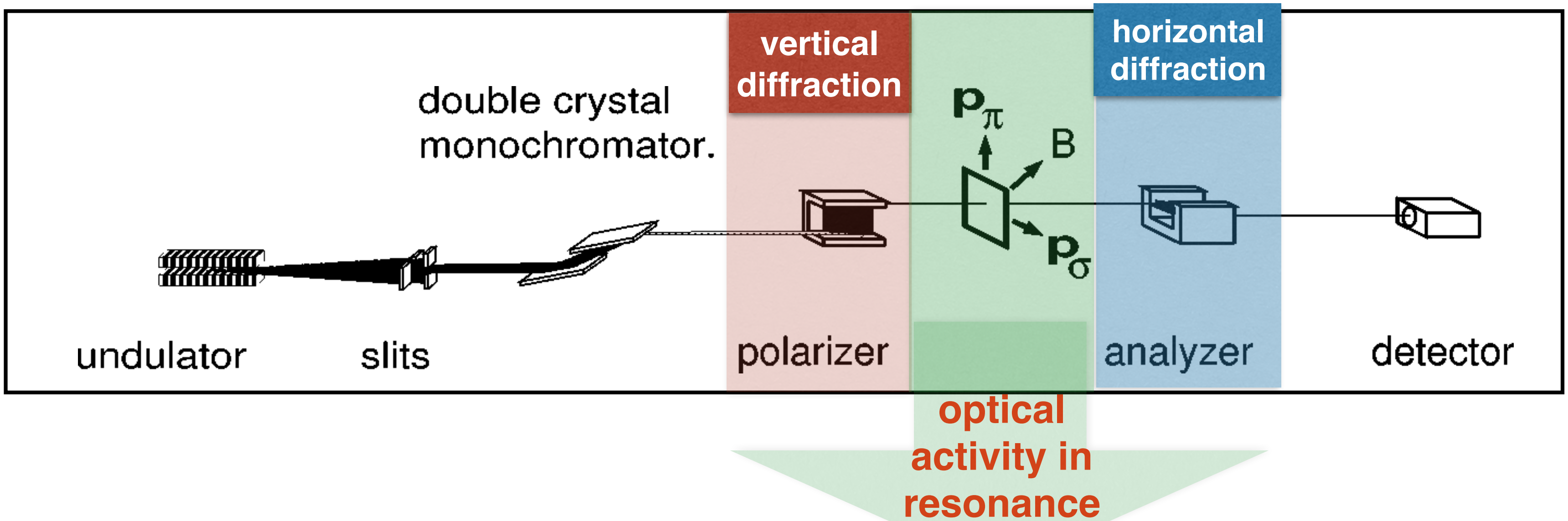
Fast Shutter:
A way to manipulate the bunch structure in the future MBA lattice

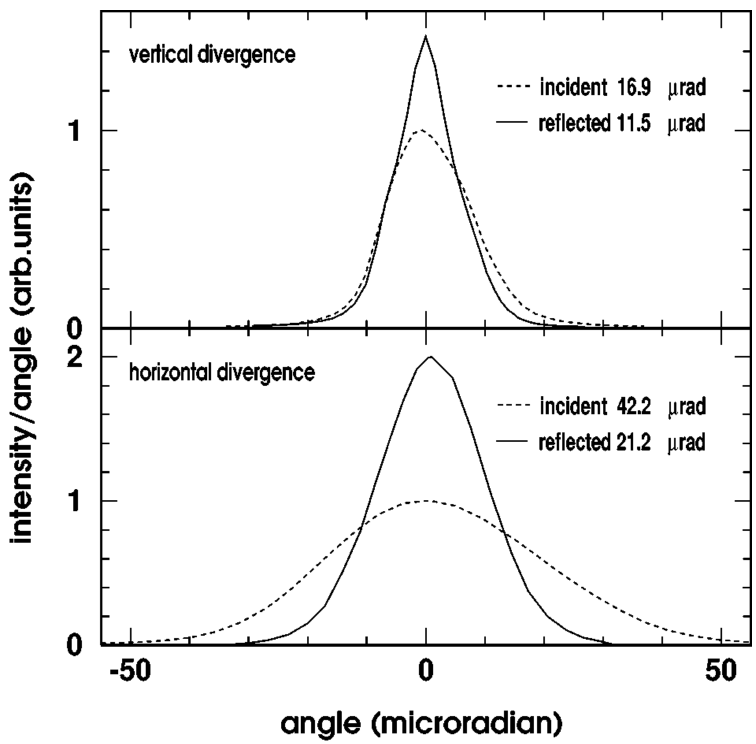
Currently under construction at Jülich. We expect delivery in 2016.

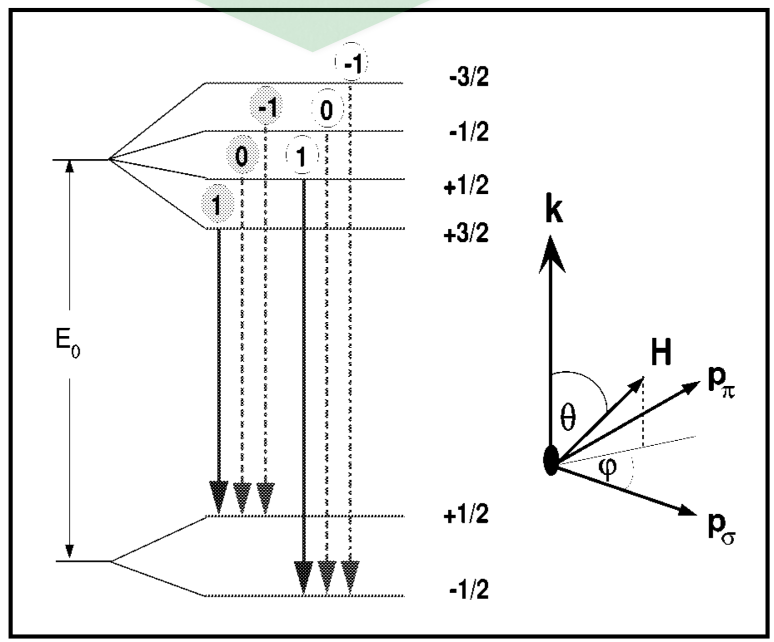




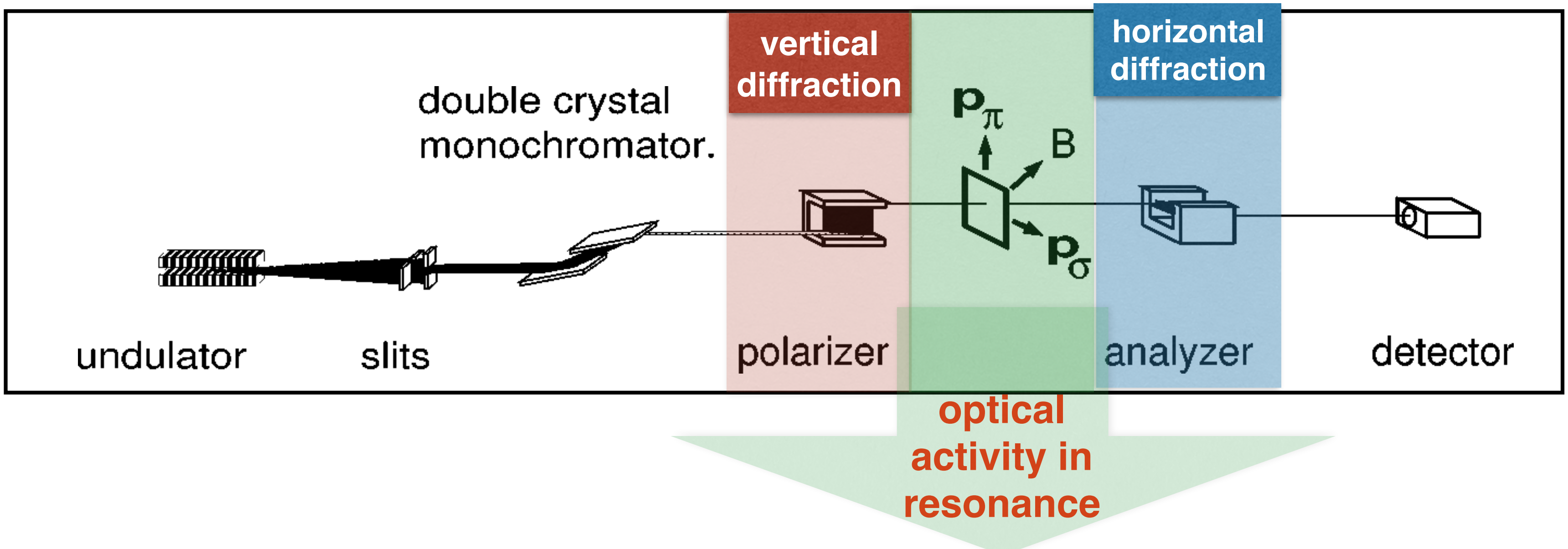
Polarizer/Analyzer Optics in the MBA-era

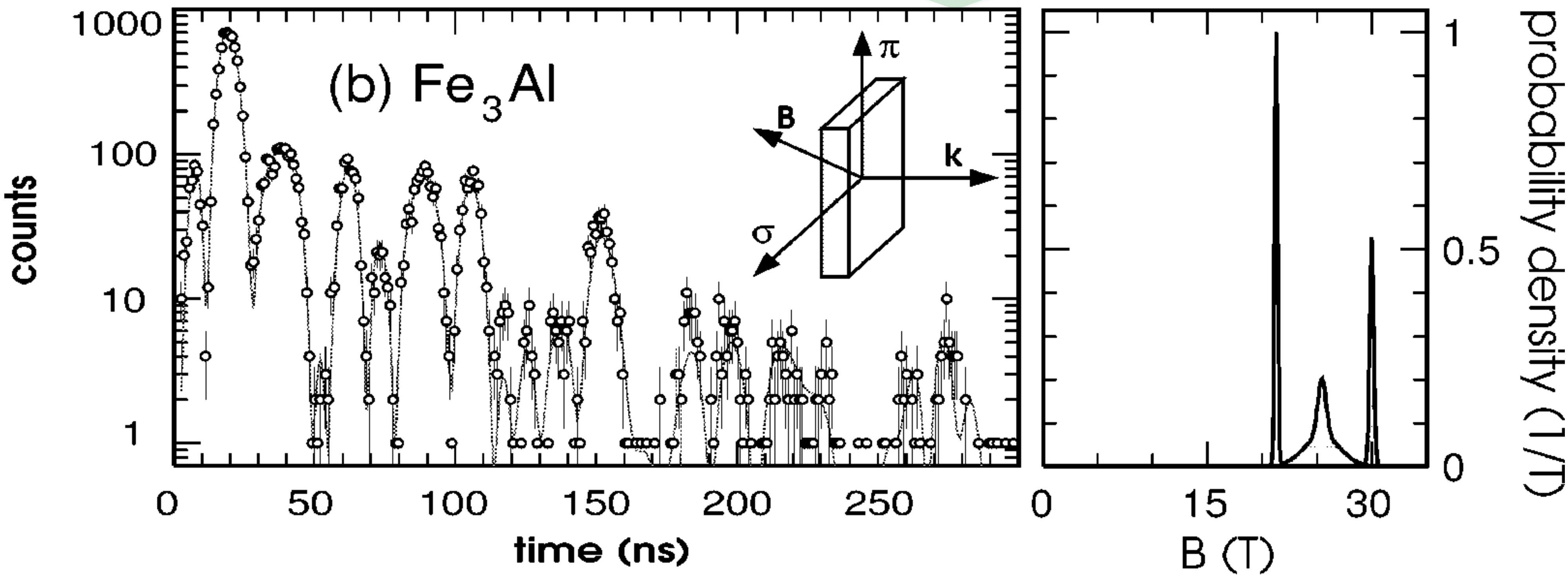




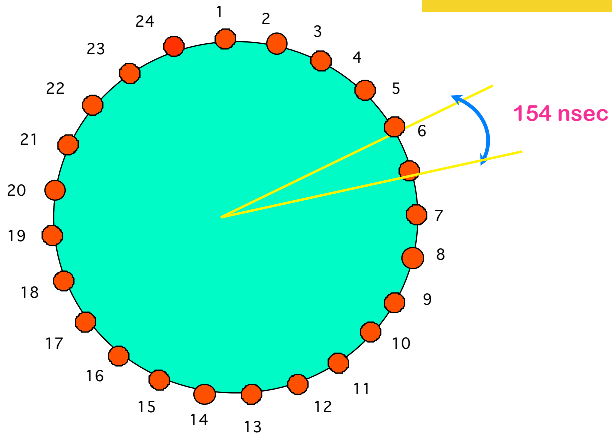


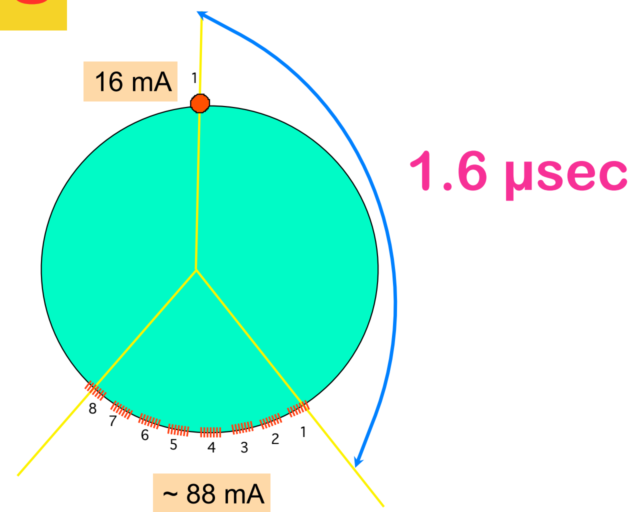
Polarizer/Analyzer Optics in the MBA-era





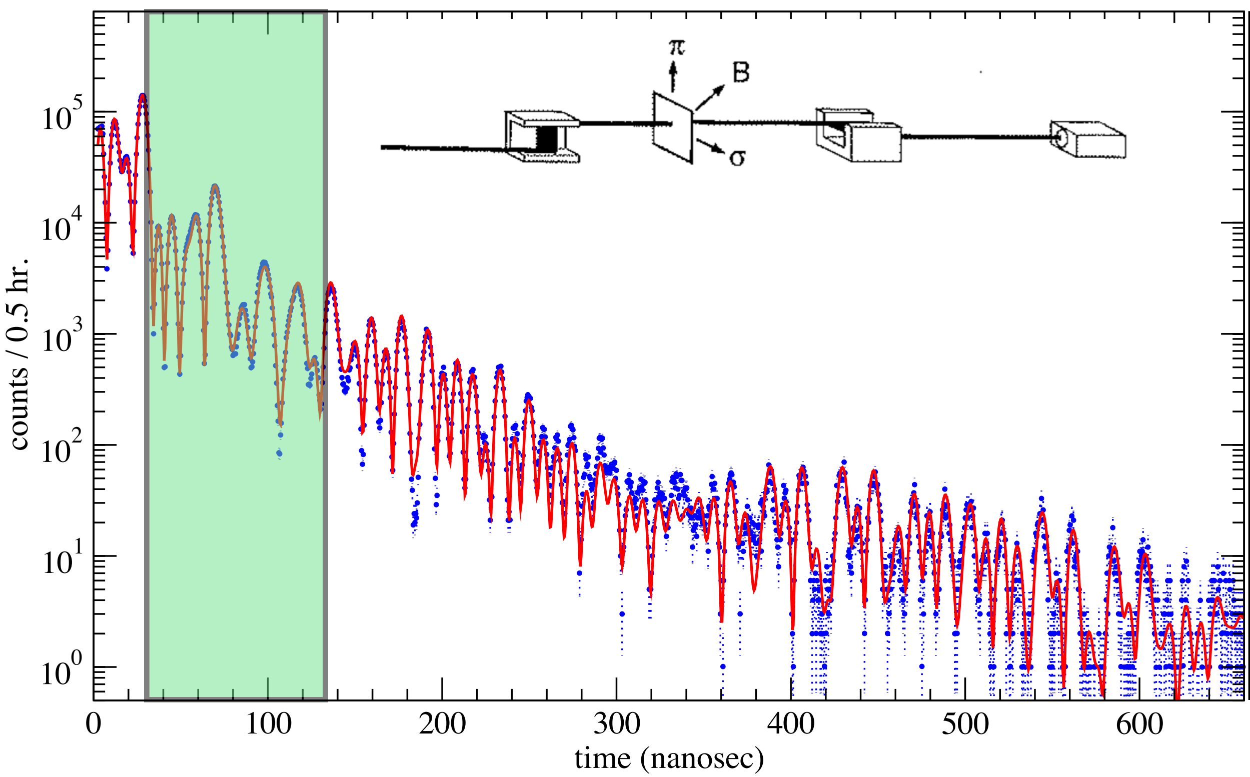
Polarizer/Analyzer Optics





57Fe-foil, 2.125 micron, Polarizer/Analyzer data

February 2014, 3-ID



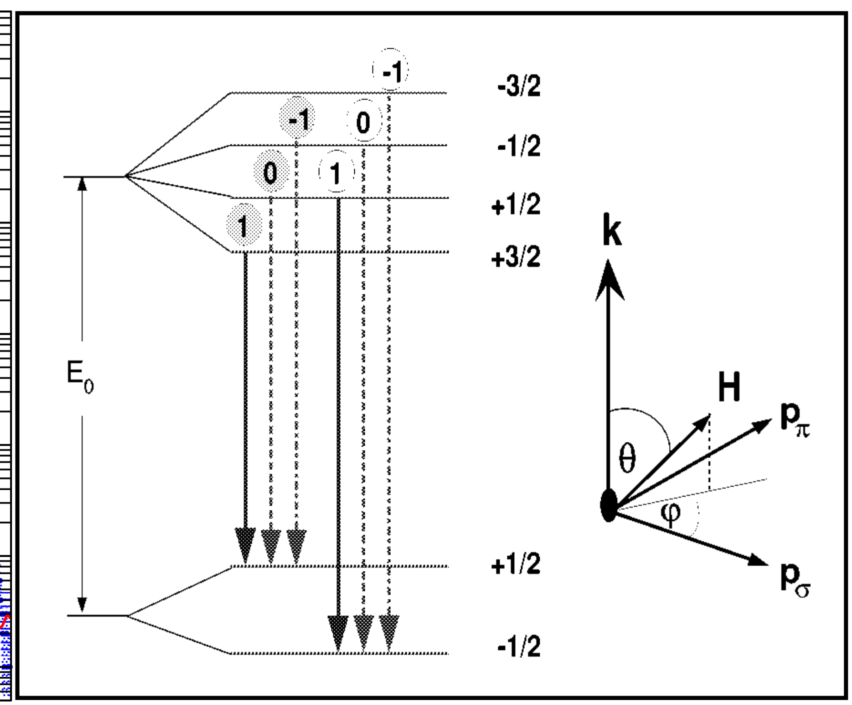
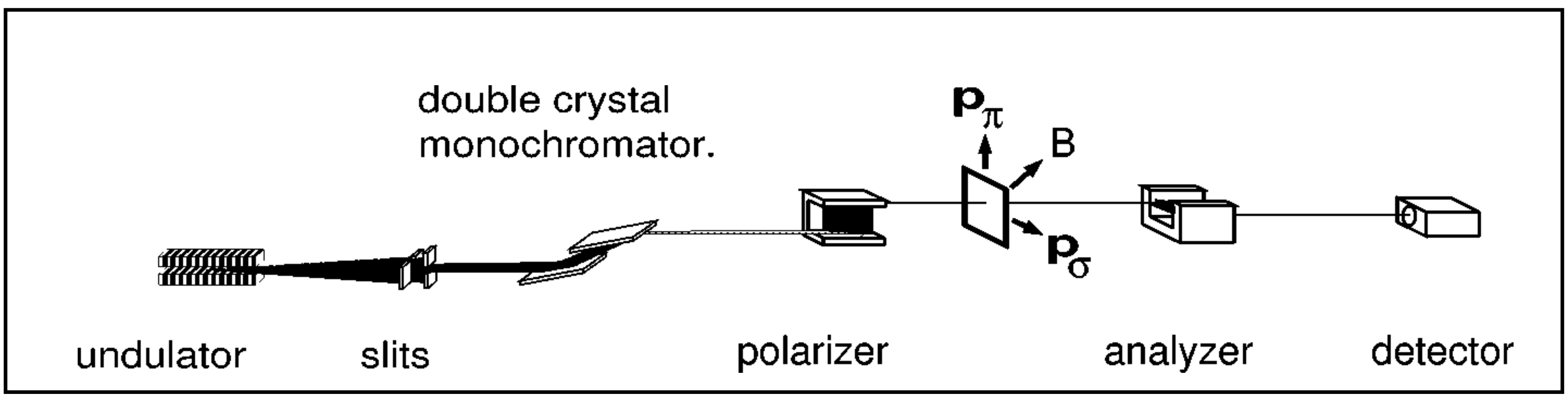


Table 2
Performance characteristics of channel-cut polarizers using $\Theta_B \approx 45^\circ$ Bragg reflections in silicon/germanium at selected Mössbauer transition energies.

Isotope	Energy (keV)	$\tau_{1/2}$ (ns)	Crystal reflection	Θ_B (deg.)	$\Delta\theta^a$ (μrad)	$\int R_\sigma^2\, d\theta$ (μrad)	δ_o
^{181}Ta	6.215	6800	Si(4 0 0)	47.28	142.0	59.8	5.5×10^{-4}
			Ge(4 0 0)	44.88	318.0	126.2	4.8×10^{-9}
^{169}Tm	8.410	4.0	Si(3 3 3)	44.85	44.4	19.0	1.2×10^{-8}
^{83}Kr	9.410	147	Si(5 3 1)	45.86	31.2	14.1	1.5×10^{-5}
^{57}Fe	14.413	97.8	Si(8 4 0)	45.10	10.2	6.1	1.0×10^{-8}
^{151}Eu	21.532	9.7	Ge(8 8 8)	44.87	0.78	0.15	1.7×10^{-9}
			Si(12 4 4)	44.69	0.31	0.26	9.1×10^{-6}
^{149}Sm	22.494	7.1	Ge(11 9 3)	45.07	0.55	0.05	6.0×10^{-11}
			Si(8 8 8)	44.68	0.25	0.21	9.7×10^{-6}
^{119}Sn	23.878	17.8	Ge(15 3 1)	44.73	0.35	0.03	1.6×10^{-8}
			Si(12 6 6)	44.63	0.19	0.16	1.5×10^{-5}

[a] The first four energies have the same crystal asymmetry factor; the angle between incident beam and crystal surface is 2°. The crystal reflections at the higher energies (>20 keV) are symmetrically cut.



Scientific scope of nuclear resonant scattering

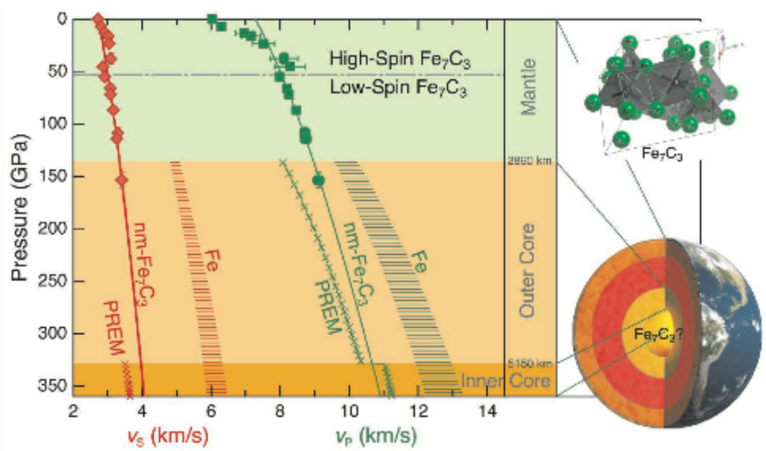
Measurement of thermodynamic and elastic properties of wide range of materials through the measurement of phonon excitation spectrum.

- **materials of current technological interest**:
  - energy storage and conversion : Li-ion battery, skutterudites, clathrates, pnictides, multiferroics
- **proteins, enyzmes¨**
  - mechanism of metabolic and catalytic reactions
  - porphyrins, cubanes, bioinorganic mimics
- **minerals:**
  - crust, mantle, outer core, inner core
  - sound velocity, spin state, shear modulus under extreme conditions
- **nanomaterials,**
  - nanocatalysts, semiconductors, superconductors
- **thin layers, multilayers**
  - buried layers, interfaces, wedges, terraces, magnetism & superconductivity

APS 3-ID: Inelastic and nuclear resonant scattering beamline

Hidden Carbon in the Earth's Core?

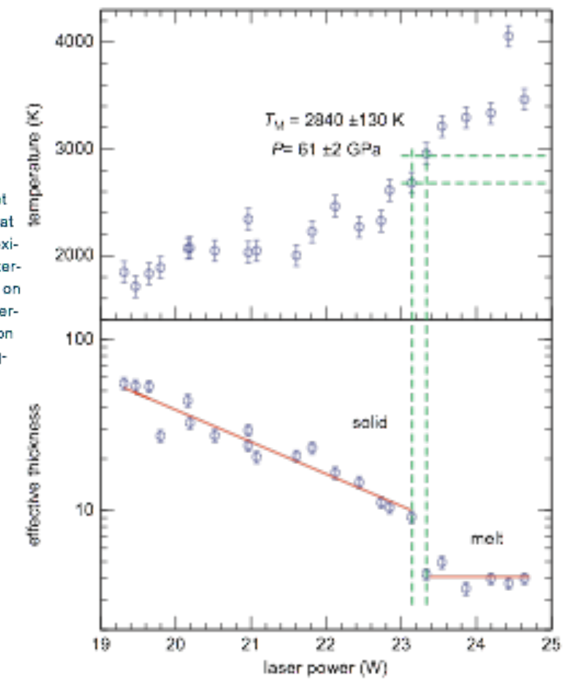
Certain seismic waves move slower than expected through the Earth's core, causing researchers to rethink our ideas about the composition of the inner-most region of our planet. One possibility is that the core contains a large amount of carbon. New research on a form of iron-carbide, Fe_7C_3, shows that it may have the required low seismic wave velocity at high pressure. The experiments, performed at two APS beamlines, provide a first-ever estimate of the speed of seismic waves in this iron-carbide at core conditions and suggest that the iron-carbide's anomalous velocity behavior is due to a change in the electron spin configuration of iron in the material. The results could imply that the Earth's core is rich in Fe_7C_3, which might explain where some of Earth's supposedly "missing carbon" is hiding.



PNAS | December 16, 2014 | vol. 111 | no. 50 | 17755–17758

Defining the Line: Melting Curve for Iron Helps Characterize the Earth's Core

The Earth's core is 16% of the planet by volume. It is composed primarily of iron, but includes a quantity of lighter elements whose presence, but not identity, is inferred from geophysical measurements. The core consists of a solid inner section surrounded by a convecting, liquid outer layer. It creates Earth's magnetic field, protecting the planet from space weather events such as solar flares, and provides the heat for plate tectonics as the liquid core freezes. The core begins approximately 2900 km below the Earth's surface, making it difficult to determine its exact composition and temperature profile, so scientists rely on laboratory experiments and an evolving model to infer core characteristics. For example, they use experiments to populate data points on the melting curve of iron, a key descriptor of the core because the liquid outer core and solid inner core coexist at a temperature below the melting point of pure iron. Now, utilizing the APS in a new application of the Mössbauer effect, scientists are refining the temperature range of the Earth's inner core/outer core border to increase our understanding of geophysical processes and the Earth's formation.

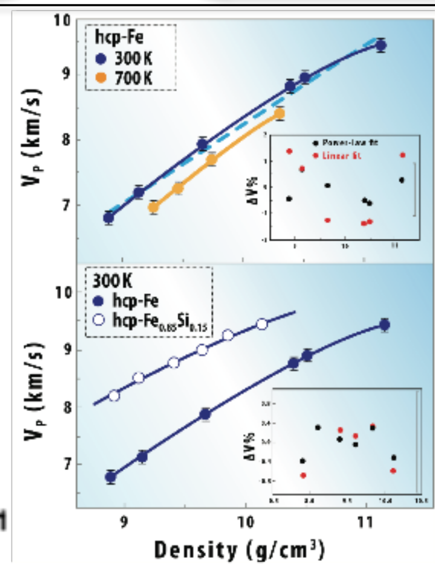


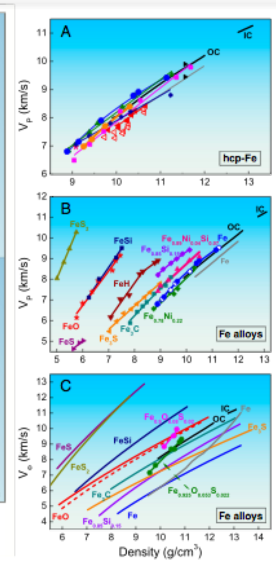
Earth and Planetary Science Letters 362 (2013) 143–150

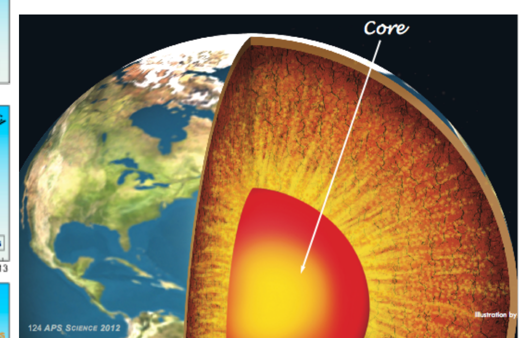
Doubling Estimates of Light Elements in the Earth's Core

The inner core of the Earth is the remotest area on the globe, and thus resistant to direct study. It is an area of the planet that experiences both extremely high pressure, ranging from 3,300,000 to 3,600,000 times atmospheric pressure, and extremely high temperatures from approximately 5000 to 6000 K. One way to study this area is by recording how sound waves travel across the interior, matching these profiles to known information about how sound waves travel through candidate iron alloys, and attempting to discern which materials must be present. This method requires an understanding of how sound waves travel through the potential materials present in the core. A team of researchers utilized APS x-rays to develop a new model of how sound waves travel through iron and iron-silicon alloys, showing for the first time that increased temperatures will affect the sound wave profile, and that sound velocity and density correlate in a non-linear way. Their results suggest that the amount of light elements in the inner core could be two times more than estimated in previous studies without considering these effects.

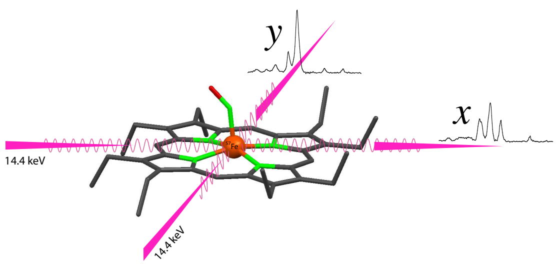
PNAS | June 26, 2012 | vol. 109 | no. 26 | 10241

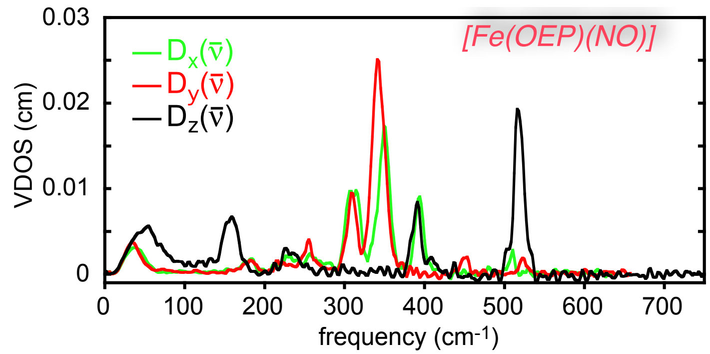


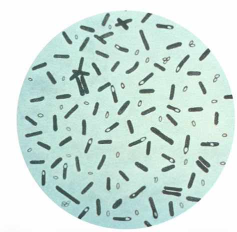




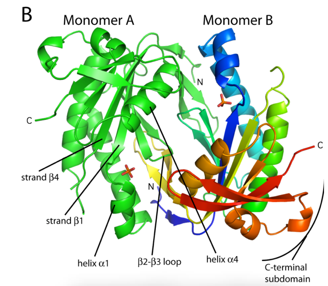
Molecular basis for selectivity (or recognition) of diatomic ligands : NO, CO, O_2, OH







Clostridium botulinum



guanalyl cyclase

One of the important issues in nitrosyl (nitric oxide, NO) iron porphyrinate derivatives, or **hemes**, is to develop a functional understanding of the **molecular basis for selectivity** (recognition) between the diatomic ligands NO, CO, and O_2.

The sensing of these gaseous molecules is predominantly carried out by heme-based proteins. Therefore, heme protein– diatomic ligand interactions continues to be an active area of research.

Binding and release of diatomic molecules may be facilitated by very low frequency **doming modes,** also referred to as **reactive modes**. Quantitative information is needed to study the energetics of **chemical reactions or conformational changes.** They lie at low frequencies and are rarely identified with traditional techniques

Infrared and resonance **Raman** spectroscopy have provided insight into the interplay of structure and function of heme active sites. However, these techniques have some inherent limitations, especially in the low frequency regime where mode assignment is hampered by weak signal, spectral congestion and low sensitivity to isotopic substitution.

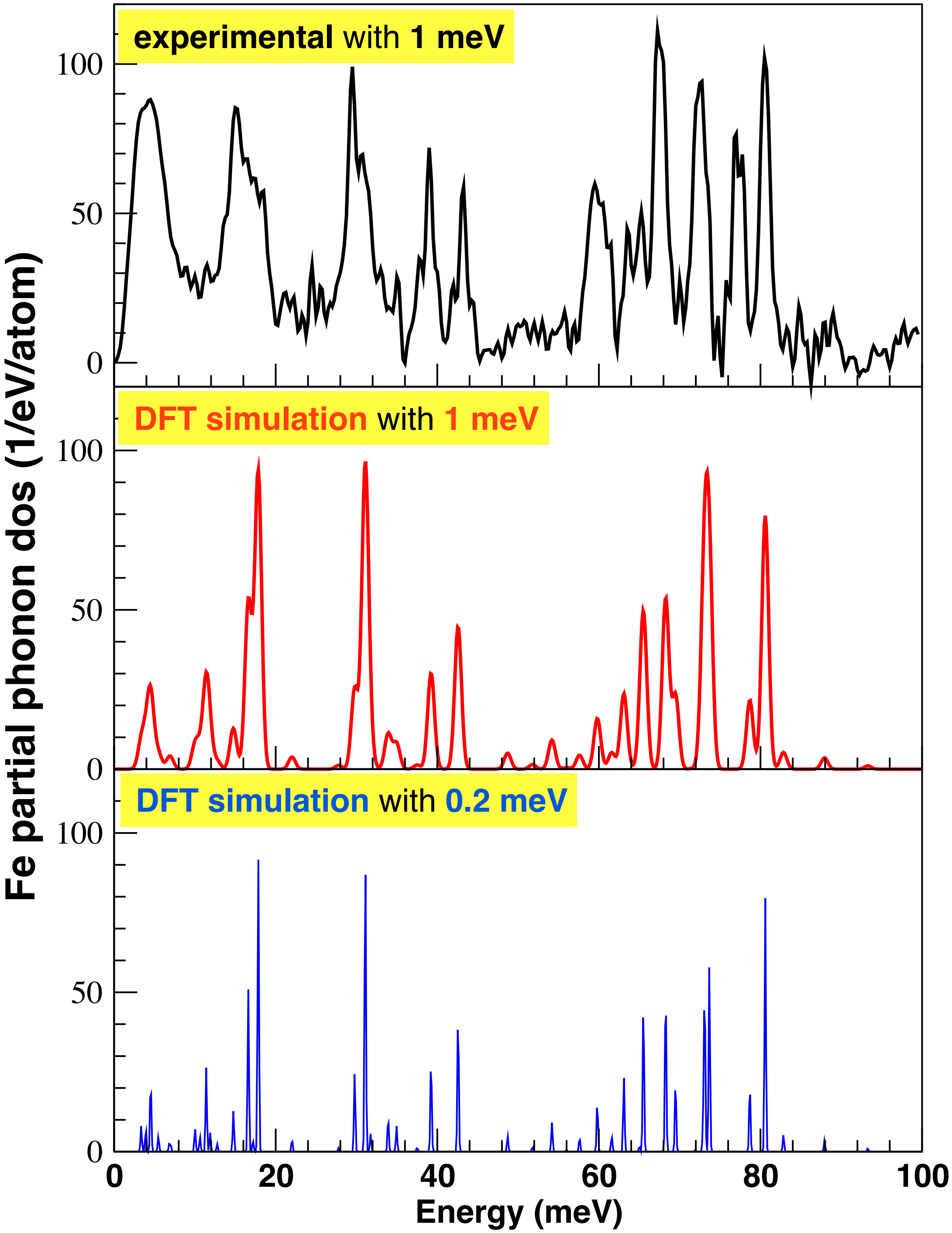
In nature, NO is discriminated from O_2 by guanalyl cyclase and the NO sensing protein of Clostridium botulinum. Conformational changes in the protein upon ligand binding is a plausible explanation.

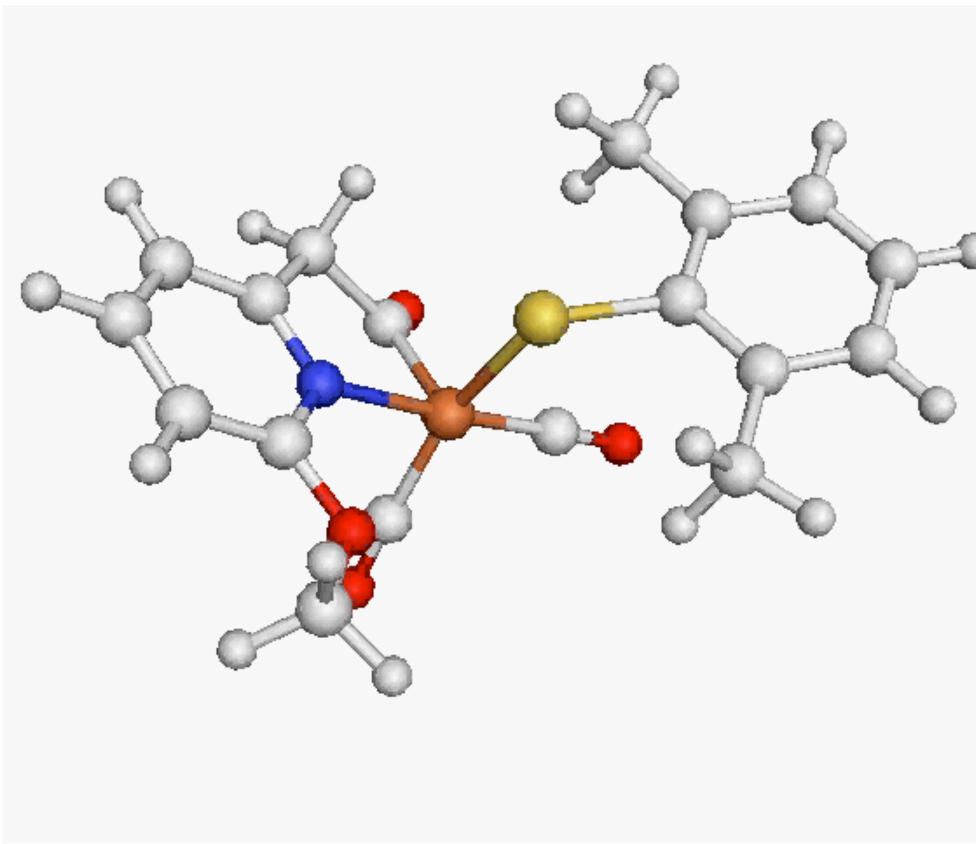
C. botulinum bacterium produces **neurotoxins** which causes muscular **paralysis** seen in **botulism**, and is also the main paralytic agent in **botox**. It is an **anaerobe**, meaning that **oxygen** is poisonous to the cells. **Neurotoxin** production is the unifying feature of the *C. botulinum*. which acts specifically on **neurons** by interacting with **membrane proteins** such as **ion channels**.

Soluble *guanalyl cyclase* (sGC) is the only known receptor for NO, which leads to **at least 200 fold increase** in sGC activity. Because nitric oxide has a partially filled pi* orbital, back bonding prefers a bent geometry for the heme-NO complex.

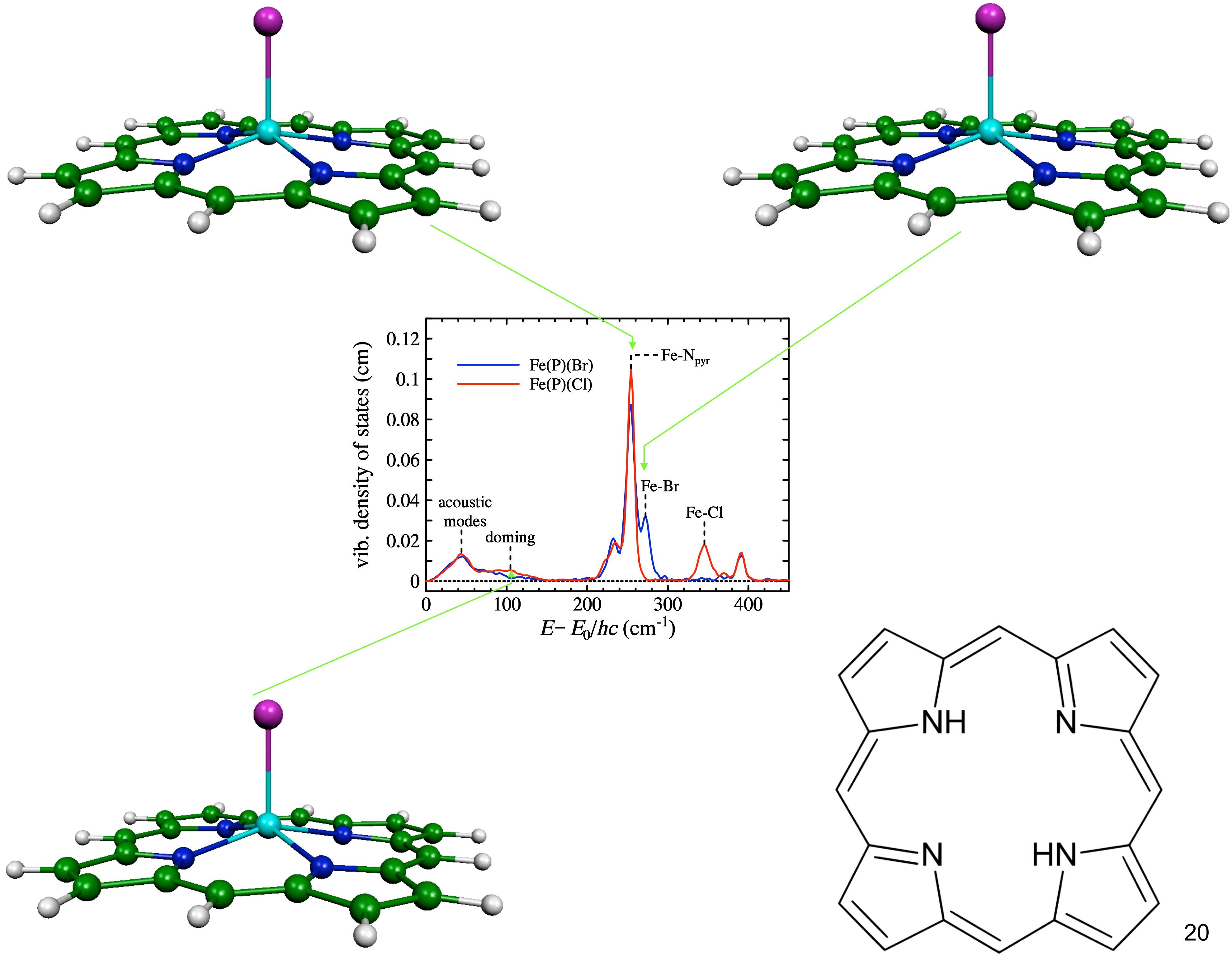
The histidine-iron bond is weakened when NO binding delocalizes electrons to the dz^2 orbital toward the axial ligand, resulting in ferrous heme at the distal position dissociates to a 5-coordinate Fe-NO complex.

Angew. Chem. Int. Ed. **2010**, 49, 4400–4404





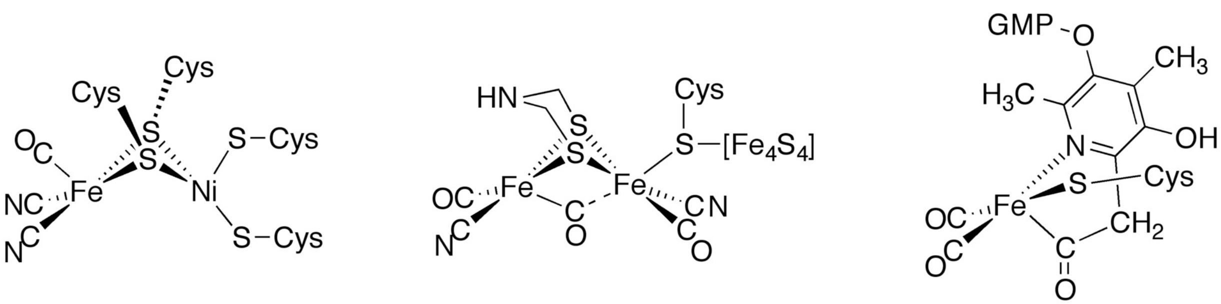
Courtesy: Alex Guo, Carnegie-Mellon University



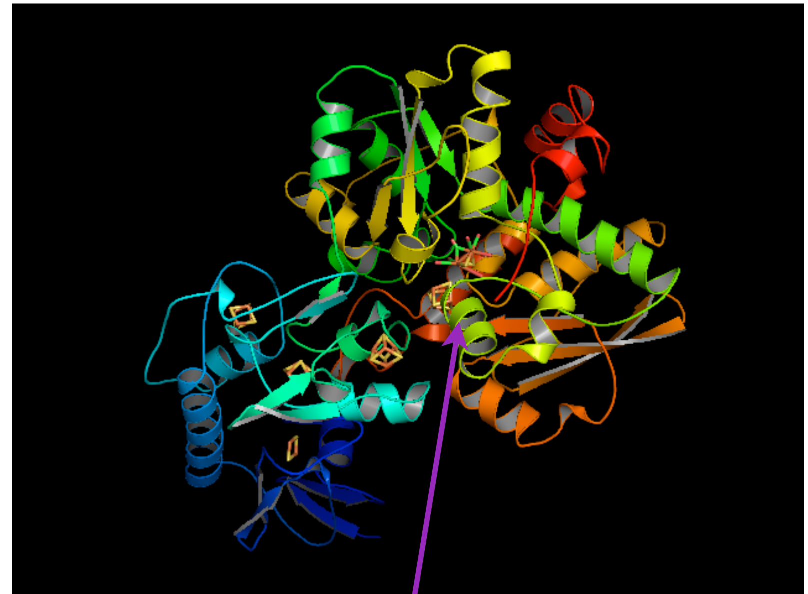
vib. density of states (cm)
0.12
0.1
0.08
0.06
0.04
0.02
0
Fe(P)(Br)
Fe(P)(Cl)
Fe-N$_{pyr}$
Fe-Br
Fe-Cl
acoustic modes
doming
0
100
200
300
400
$E - E_0/hc$ (cm^{-1})
NH
N
N
HN

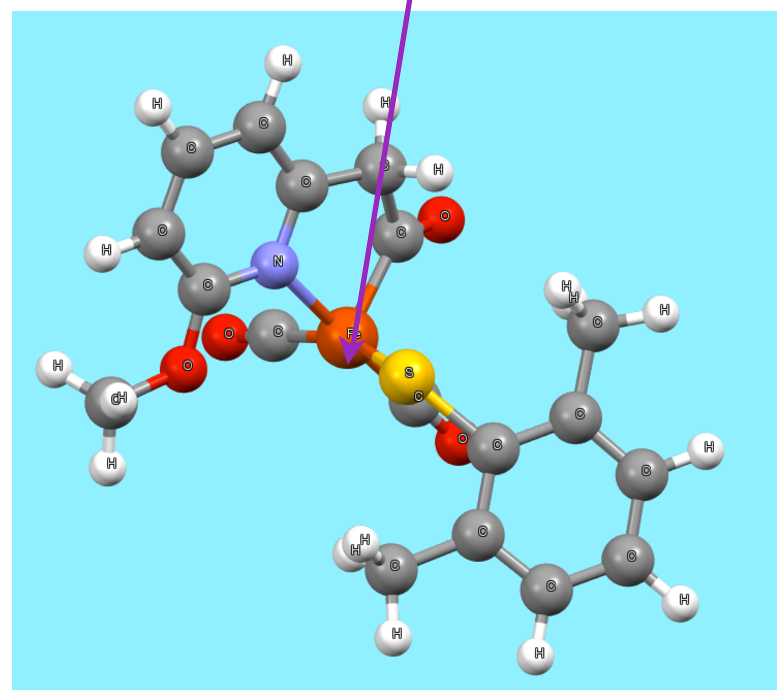
Hyrdogenase enzyme

D. Chen, R. Scopelliti, and Xile Hu, Angew. Chem. 2011, 123, 5789 –5791



[NiFe]H_2ase [FeFe]H_2ase [Fe]H_2ase





[Fe]-hydrogenase catalyzes the reduction of methenyl-H_4MPT+ with H_2 to form methylene-H_4MPT and H+.

This reaction is an intermediary step in the reduction of CO2 to methane.

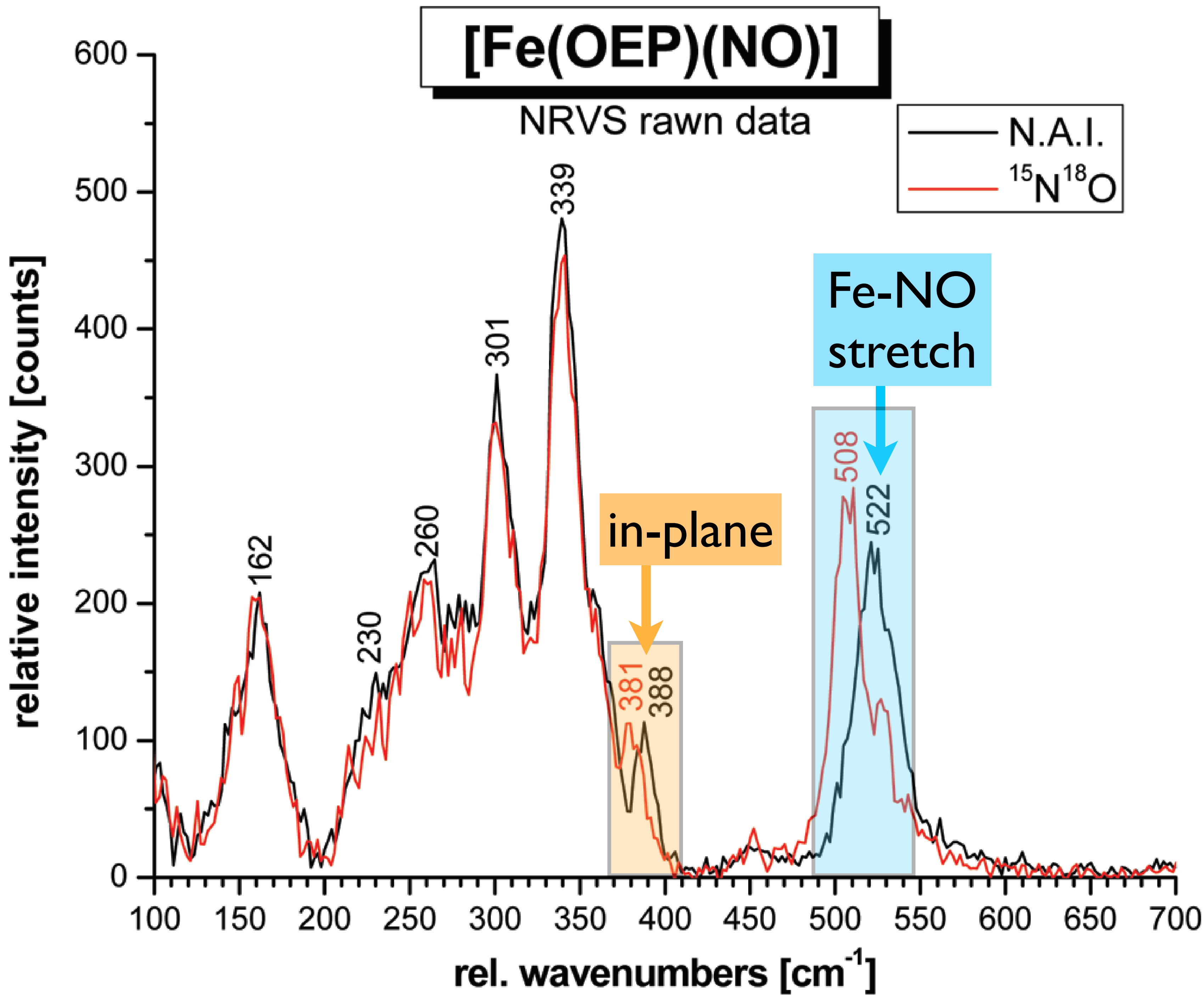
There is still uncertainty in the exact coordination number and geometry of the Fe center. Current data suggest that the Fe center could be either five-coordinate (square-pyramidal) or six-coordinate (octahedral).

In contrast to [NiFe] hydrogenases, [FeFe] hydrogenases are generally more active in production of molecular hydrogen.

This prompted interest in [FeFe] hydrogenase for sustainable production of H_2.

Understanding the catalytic mechanism of hydrogenase might help design clean biological energy sources, such as algae, that produce hydrogen.

isotopic labeling



Density functional theory (DFT)

• QM modelling is used to determine the electronic ground state of many-body systems in molecules and condensed matter.

• DFT is popular in condensed-matter physics and chemistry. While it can be applied to molecular calculations, the local density approximations is more appropriate for **delocalized electrons.**

- In molecular calculations complex exchange-correlation functionals are needed. For example, B3LYP, a hybrid functional that combines the exchange energy with Hartree–Fock energy is used.

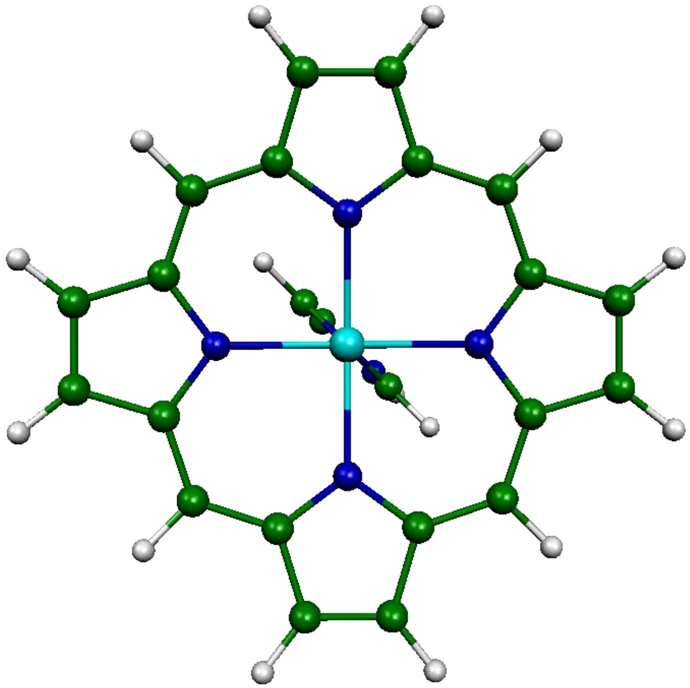
- The adjustable parameters in hybrid functionals are generally fitted to a 'training set' of molecules. (A set of atomization energies, ionization potentials, proton affinities, and total atomic energies)

• The results obtained with these functionals are sufficiently accurate but there is no systematic way of improving them.

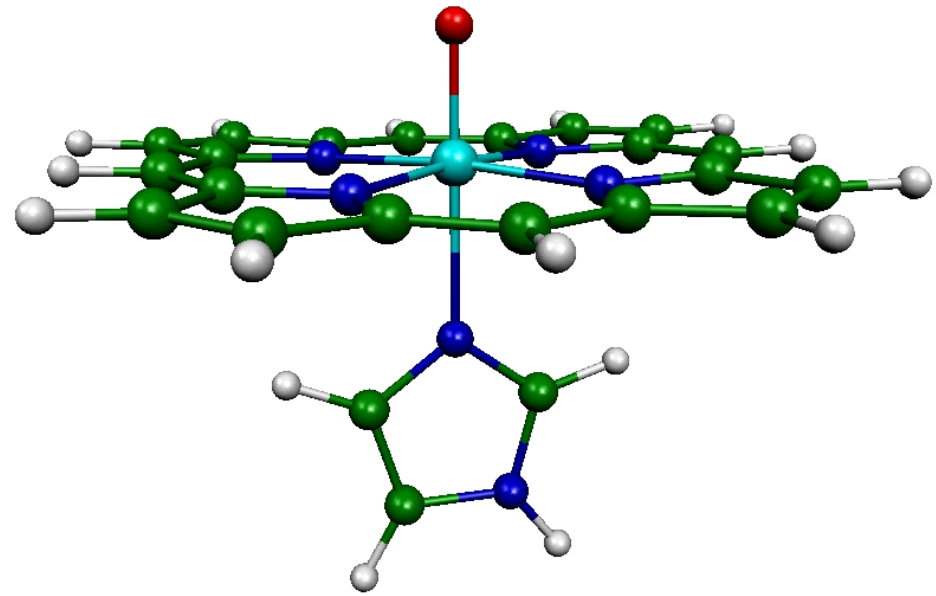
• In the current DFT approach it is not possible to estimate the error of the calculations without comparing them to other methods or experiments.

• Phonon density of states provides an excellent benchmarking opportunity

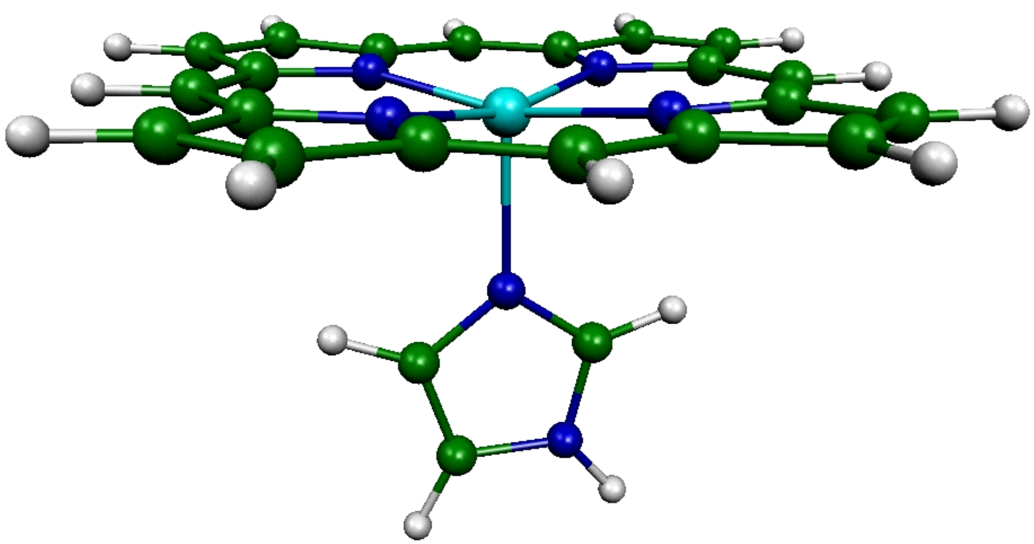
• Nuclear resonance is the only technique that gives frequency, displacement amplitude, mode composition, polarization, element and isotope selectivity.



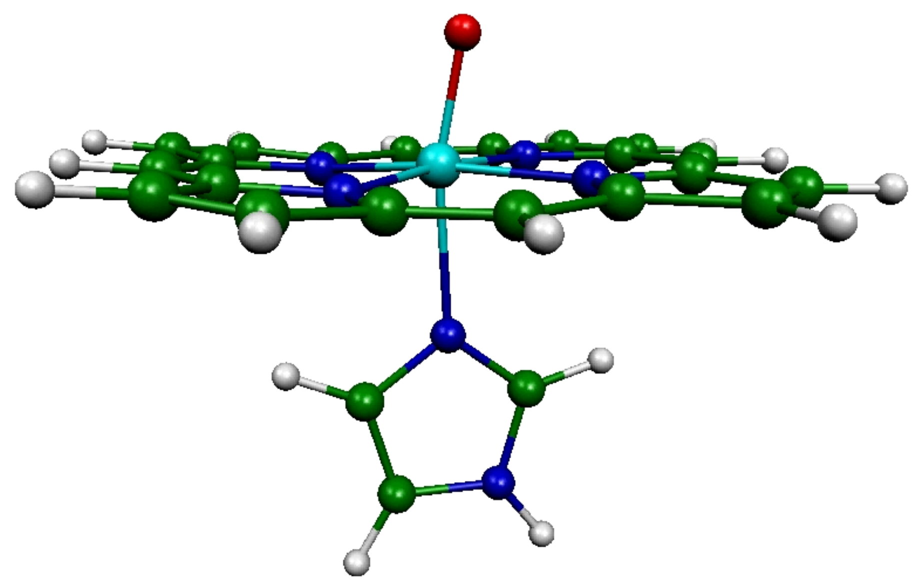
in-plane torsional mode



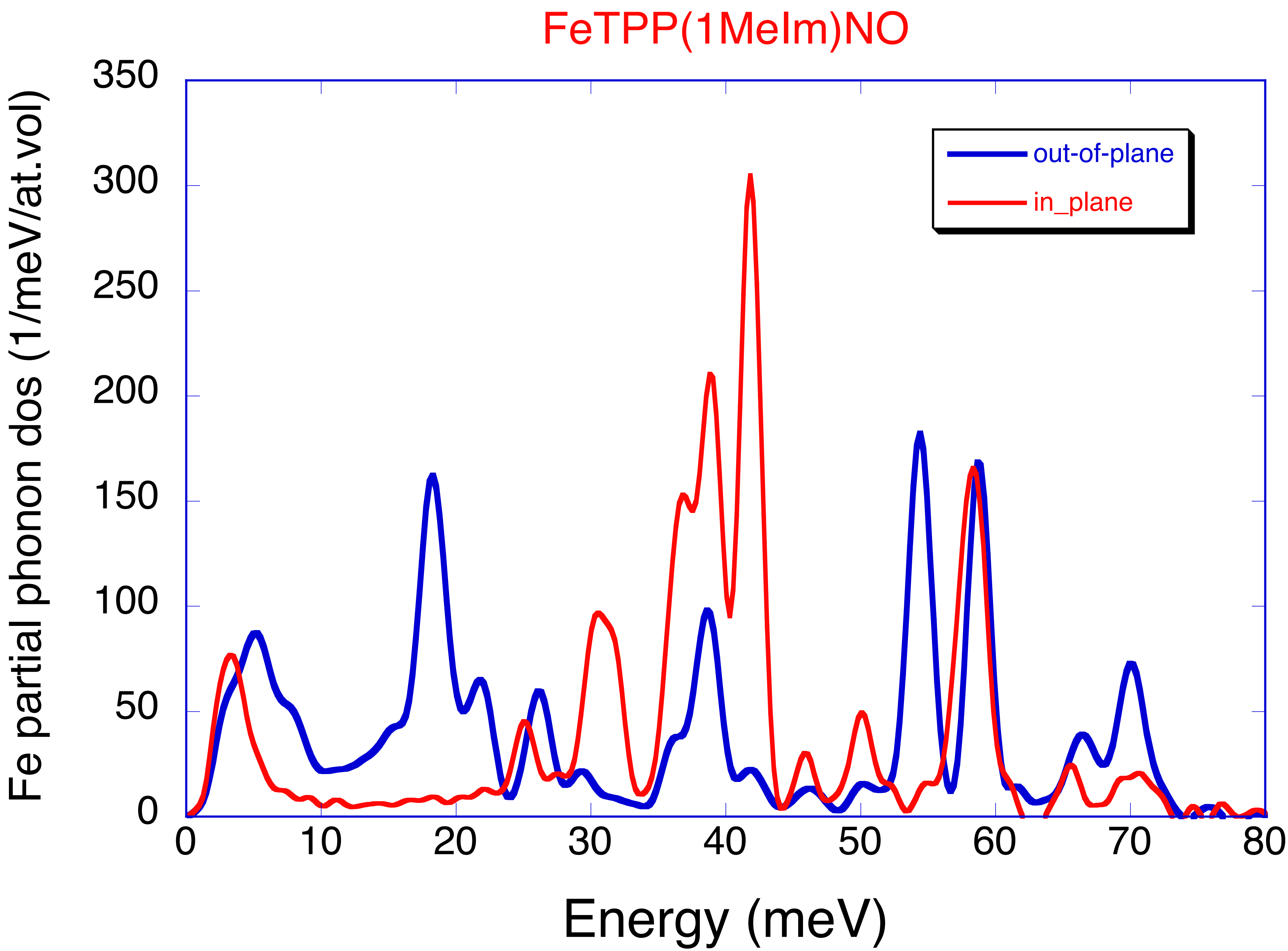
Fe-ligand stretch



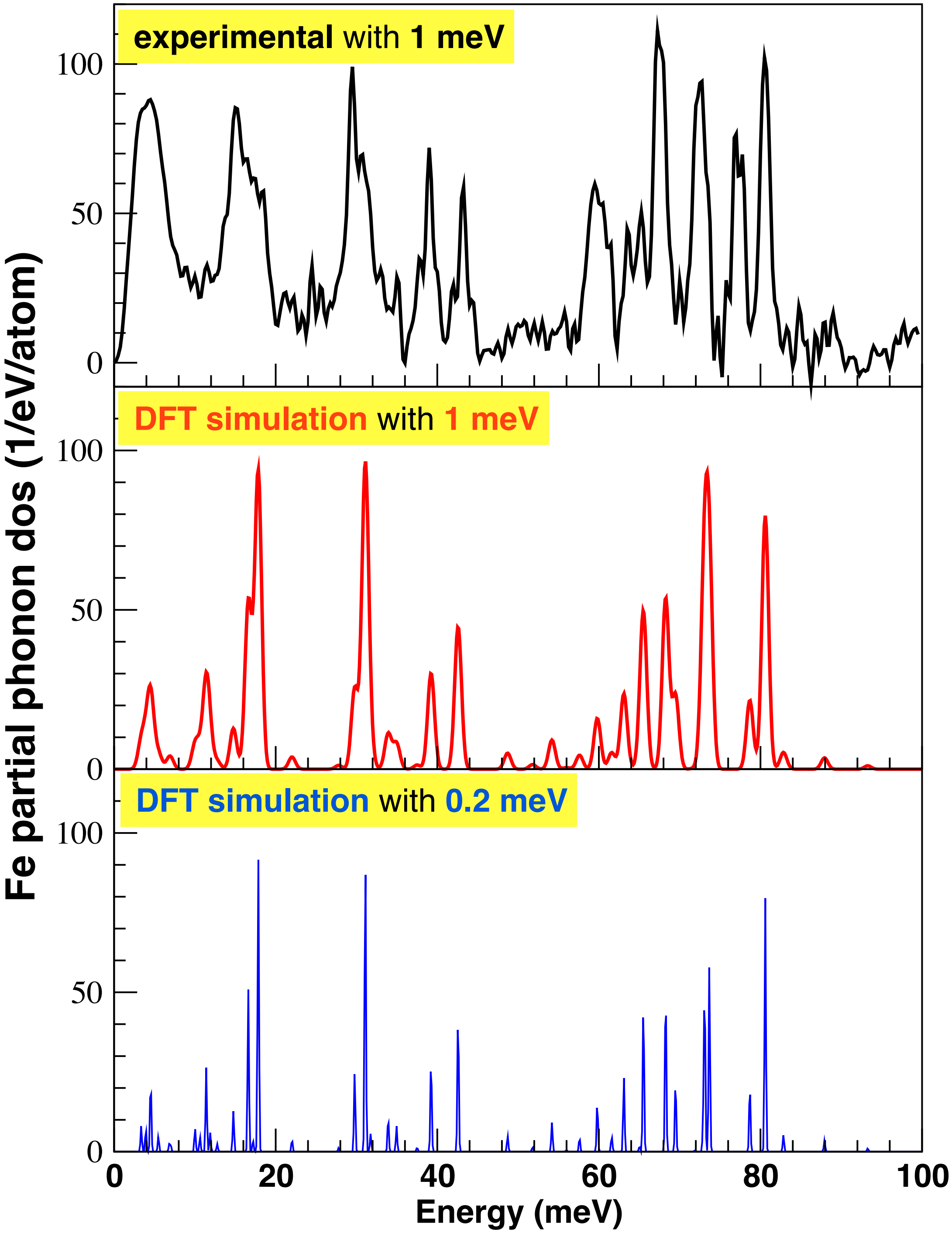
Fe-Immidazole stretch

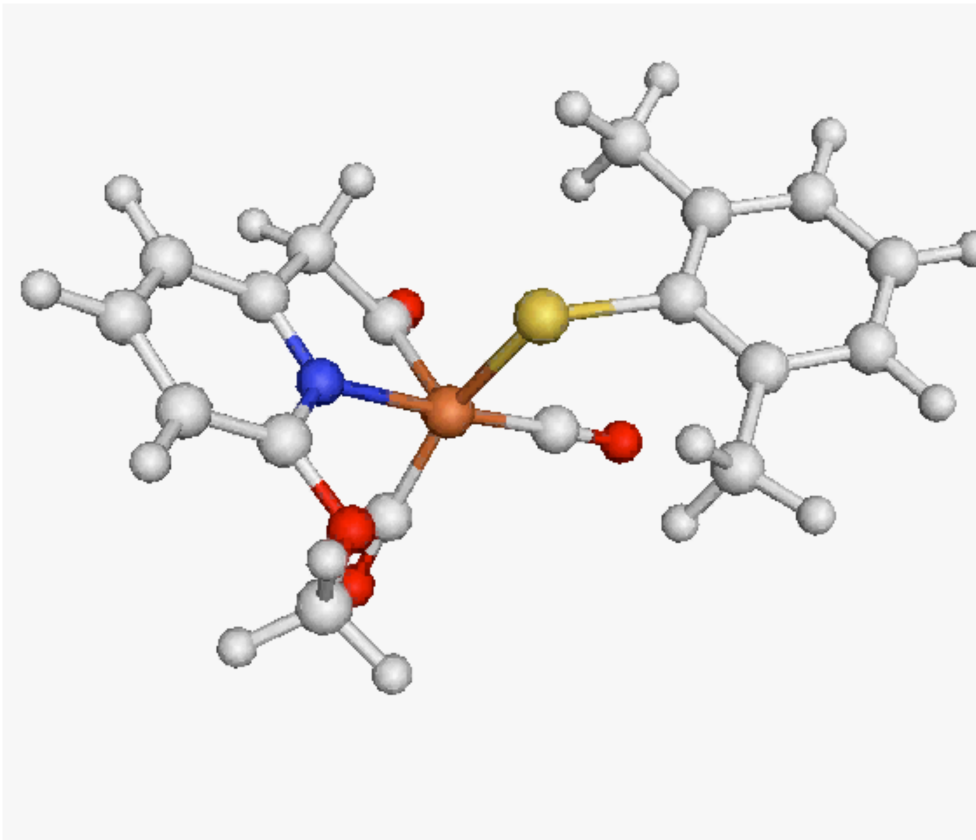


Fe-ligand tilt



FeTPP(1MeIm)NO
out-of-plane
in_plane
Fe partial phonon dos (1/meV/at.vol)
Energy (meV)
0
50
100
150
200
250
300
350
0
10
20
30
40
50
60
70
80





Courtesy: Alex Guo, Carnegie-Mellon University

Scientific scope of nuclear resonant scattering

Measurement of thermodynamic and elastic properties of wide range of materials through the measurement of phonon excitation spectrum.

- **materials of current technological interest**:
  - energy storage and conversion : Li-ion battery, skutterudites, clathrates, pnictides, multiferroics
- **proteins, enyzmes¨**
  - mechanism of metabolic and catalytic reactions
  - porphyrins, cubanes, bioinorganic mimics
- **minerals:**
  - crust, mantle, outer core, inner core
  - sound velocity, spin state, shear modulus under extreme conditions
- **nanomaterials,**
  - nanocatalysts, semiconductors, superconductors
- **thin layers, multilayers**
  - buried layers, interfaces, wedges, terraces, magnetism & superconductivity

A MÖSSBAUER MICROSCOPE FOR MINERALOGY IN THE SYNCHROTRON AGE

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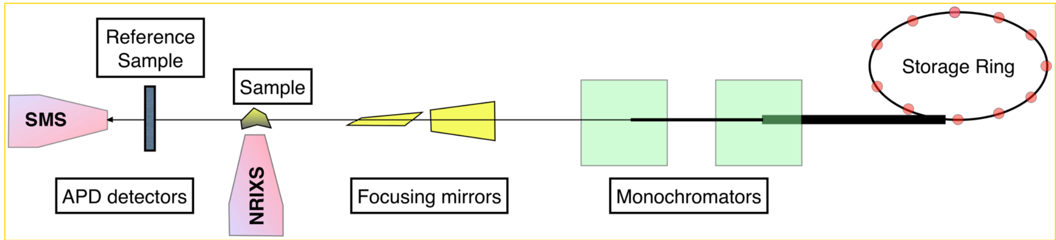


The methodology

We are introducing a new kind of x-ray imaging modality for mineralogy that involves identifying the location of iron and determining its chemical state, and its structure via nuclear hyperfine interactions. Different detection modalities involve

i) forward scattering : coherent, elastic, and
ii) back-scattering: incoherent, inelastic.

Here, the first modality can be also called Synchrotron Mössbauer Spectroscopic (SMS) imaging, because the localized information obtained is equivalent to a traditional Mössbauer Spectrum in the time domain (1).

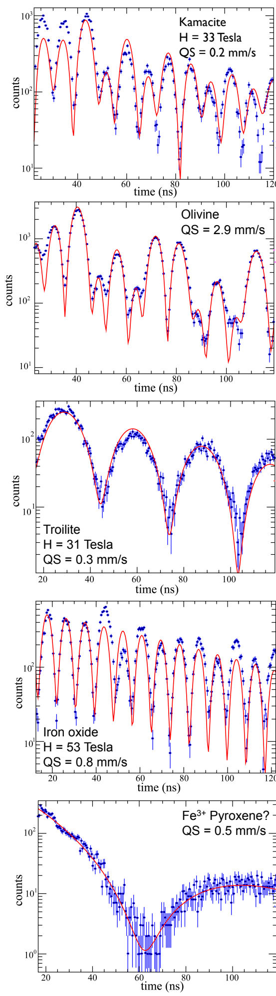
The second mode allows imaging thick samples, and more importantly, in this mode, we can record phonon density of states of iron containing species (NRIXS: Nuclear Resonant Inelastic X-Ray Scattering (2)).

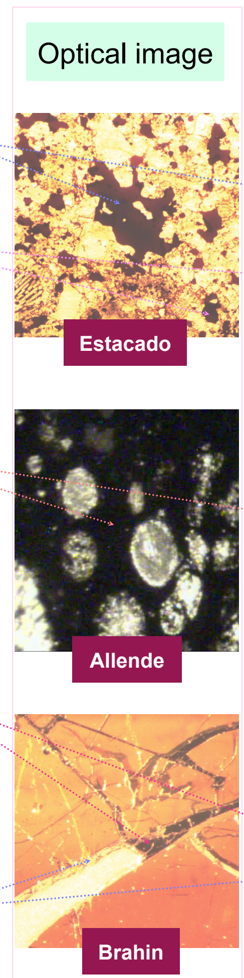
Recently it was demonstrated that iron isotope fractions can be obtained from the knowledge of phonon density of states (3). We have used the SMS imaging on meteorites to identify areas that correspond to well known phases like Kamacite, Olivine, or Troilite, and extracted the Fe partial phonon density of states. With this information, iron isotope fractionation has been determined.

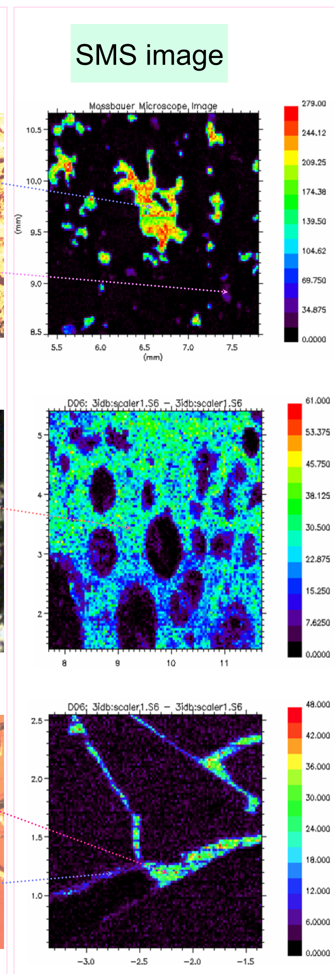
(1) E. E. Alp, W. Sturhahn, T. Toellner, "Synchrotron Mossbauer spectroscopy of powder samples." Nuclear Instruments and Methods in Physics Research B 97 (1995) 526.

(2) W. Sturhahn, T. S. Toellner, E. E. Alp, X. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C. W. Kimball, and B. Dabrowski "Phonon Density-of-States Measured by Inelastic Nuclear Resonant Scattering." Phys. Rev. Lett. 74 (1995) 3832.

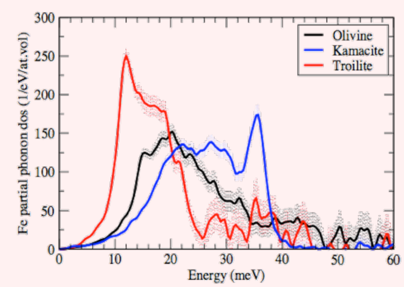
(3) V. B. Polyakov, "Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary", Science, 323 (2009) 912.

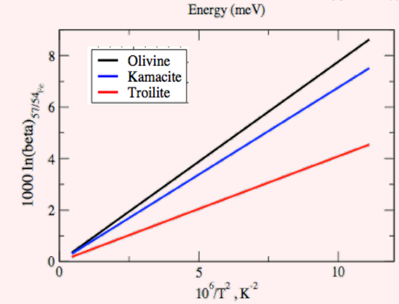






Phonon density of states





Iron 57/54 isotope fractionation

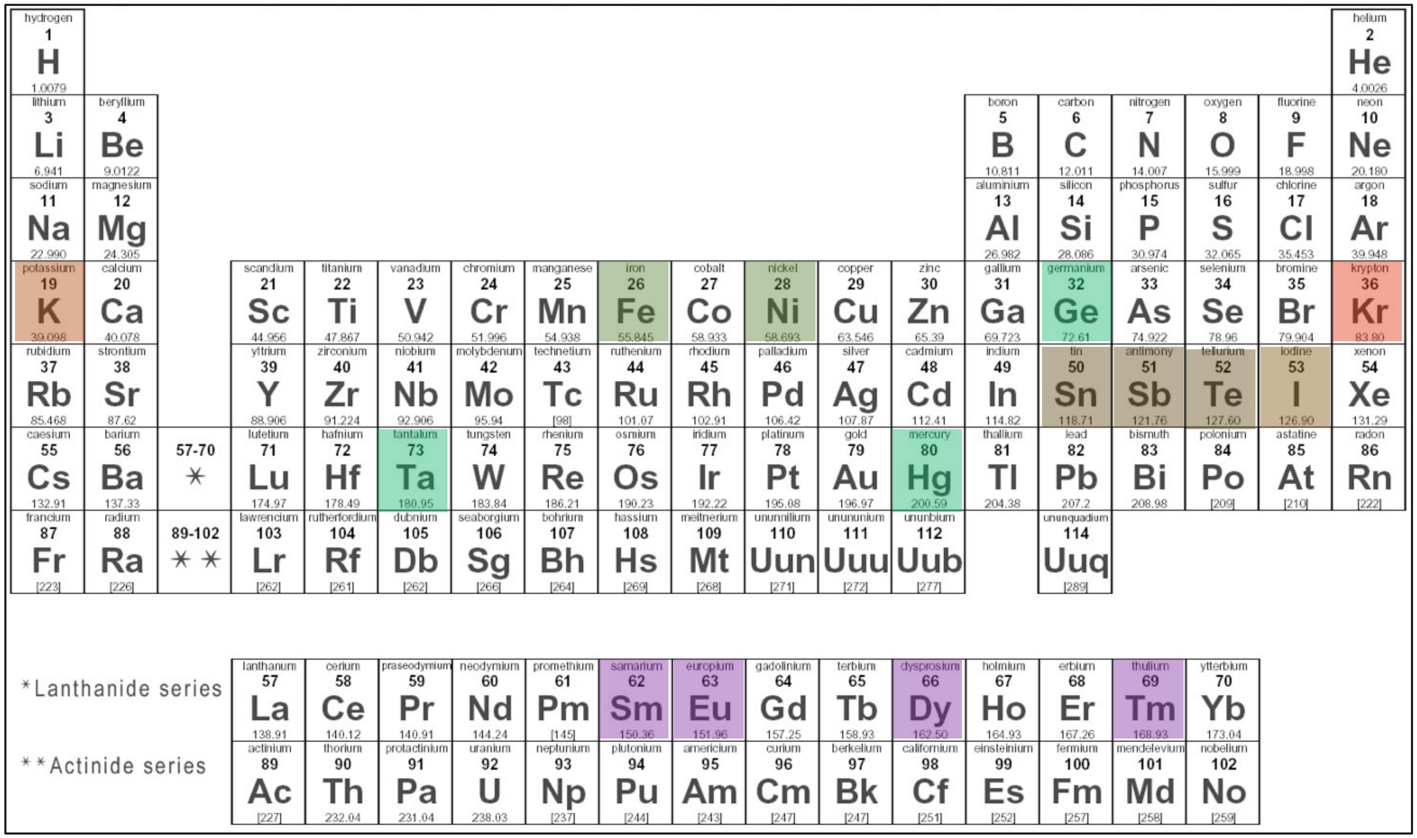
$$KE_{57_{Fe}} = \frac{3}{2}\int_0^{E_{max}} g(e)E(e,T)\mathrm{d}e$$ Kinetic energy / iron atom

$$E(e,T) = \frac{e}{\exp(e/kT)-1} + \frac{1}{2}e$$ Energy of a Bose-Einstein oscillator

$$\ln\beta_{57/54_{Fe}} = \left(\frac{3}{2}KE_{57_{Fe}} - \frac{3}{2}\right)\frac{\Delta m}{m}$$ Reduced isotopic partition function ratio

Nuclear Resonances excited with synchrotron radiation

	Isotope	Energy (keV)	Lifetime (ns)
1	^{181}Ta	6.2155	14138
2	^{169}Tm	8.4013	5.77
3	^{83}Kr	9.4035	212
4	**^{57}Fe**	**14.4125**	**141.1**
5	^{151}Eu	21.5414	13.99
6	^{149}Sm	22.496	10.2
7	^{119}Sn	23.8794	25.67
8	^{161}Dy	25.6514	40.68
9	^{201}Hg	26.2738	0.91
10	^{129}I	27.770	24.2
11	^{40}K	29.834	6.13
12	^{125}Te	35.460	2.06
13	^{121}Sb	37.129	6.5
14	^{61}Ni	67.419	7.35
15	^{73}Ge	68.752	2.68



What does future hold for IXS and NRS ?

1. Iron work will continue because of the large phase space in chemical composition, pressure and temperature, and ever increasing scope of the extracted data

- Debye temperature, recoil-free fraction,
- Debye sound velocity, anisotropy of shear and compressional velocity,
- Valence and spin state,Magnetism
- Local distortion,
- Isotope fractionation,

2. New methodologies will emerge: Fast shutter, energy domain measurements

3. New isotopes will get attention: Kr, Eu, Sn, Dy, Sm, Sb, Te, Ge....

4. Better monochromators with better resolution of 0.2 meV may come true

5. Area detectors will improve resolution & throughput, new class of materials will become the domain of IXS: e.g. thin films

5. Better data analysis programs may emerge...

In conclusion:

1. APS-U MBA lattice benefits the NRS & IXS experiments in terms of

- better focusing,
- lower horizontal divergence for P/A optics
- increased flux,
- upgraded beamline components
  - mirrors,
  - monochromators, and
  - detectors.
  - fast chopper ..

2. Timing and bunch structure issues will be quite relevant in terms of general applicability of these techniques.

3. We look forward to working with the APS-U project office.