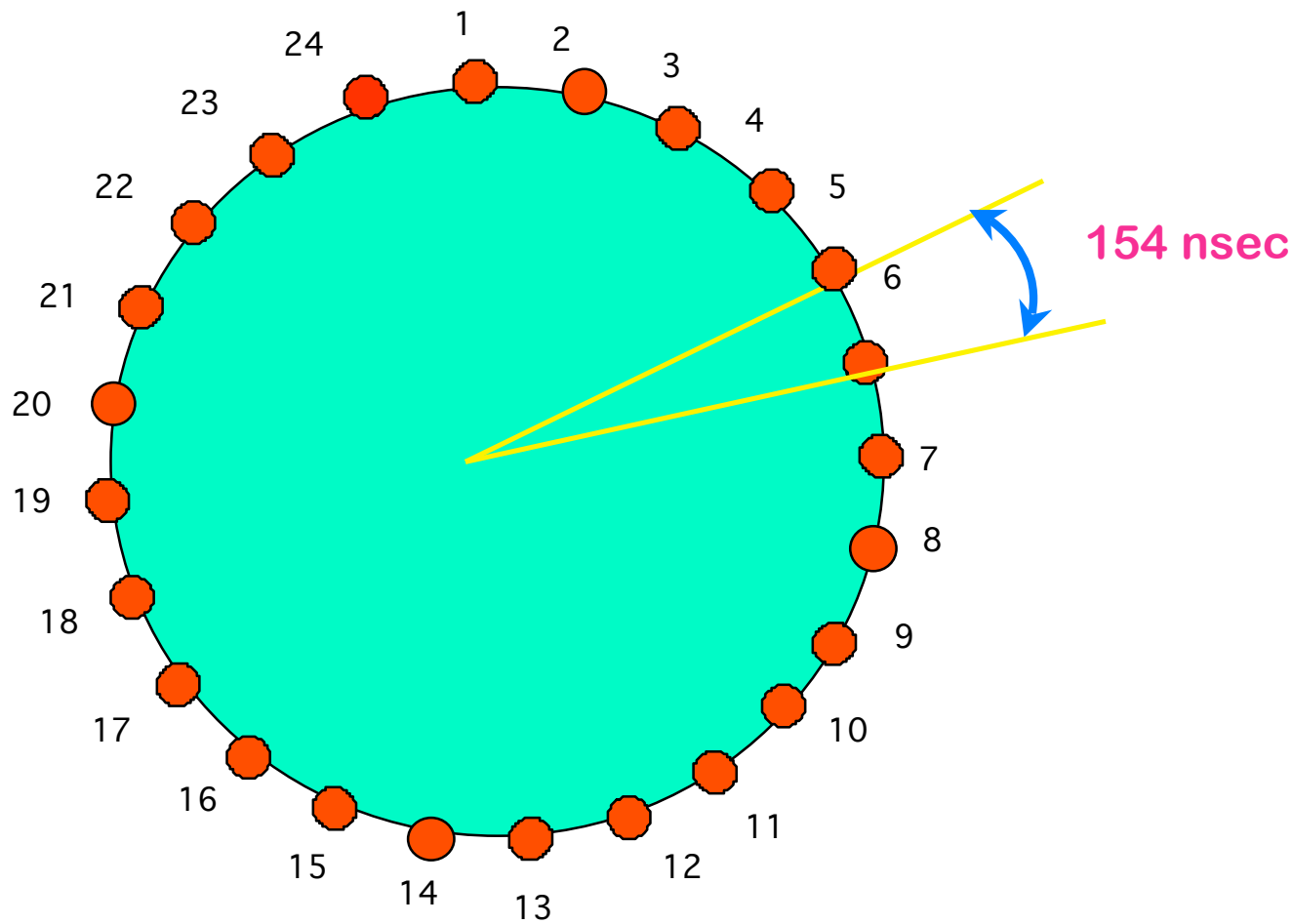
Impact of APS bunch structure on the science with high resolution x-ray scattering

- **Nuclear resonant scattering**
  - Nuclear forward scattering
  - Nuclear resonant inelastic x-ray scattering
- **C**
  - Fabry-Perot interferometer
- **Fundamental measurements**
  - X-ray wavelength measurements
  - Thermal expansion coefficients

E. E. Alp
Jan 26, 2005
SAC Cross-cut review of
time-resolved experiments at the APS

Standard Time structure @ APS



1 revolution=3.68 μsec =>1296 buckets

What do Nuclear Resonant Spectroscopy need?

- Bunch-to-bunch separation > 150 nsec up to 300 nsec
- clean bunches (purity < 10^{-10})
- lower emittance / top-up
- Brilliance >> 10^{20}, 6-30 keV
- Higher current / bunch (30 mA/bunch, 80 ps or longer)

What does Nuclear Resonant Spectroscopy deliver in return ?

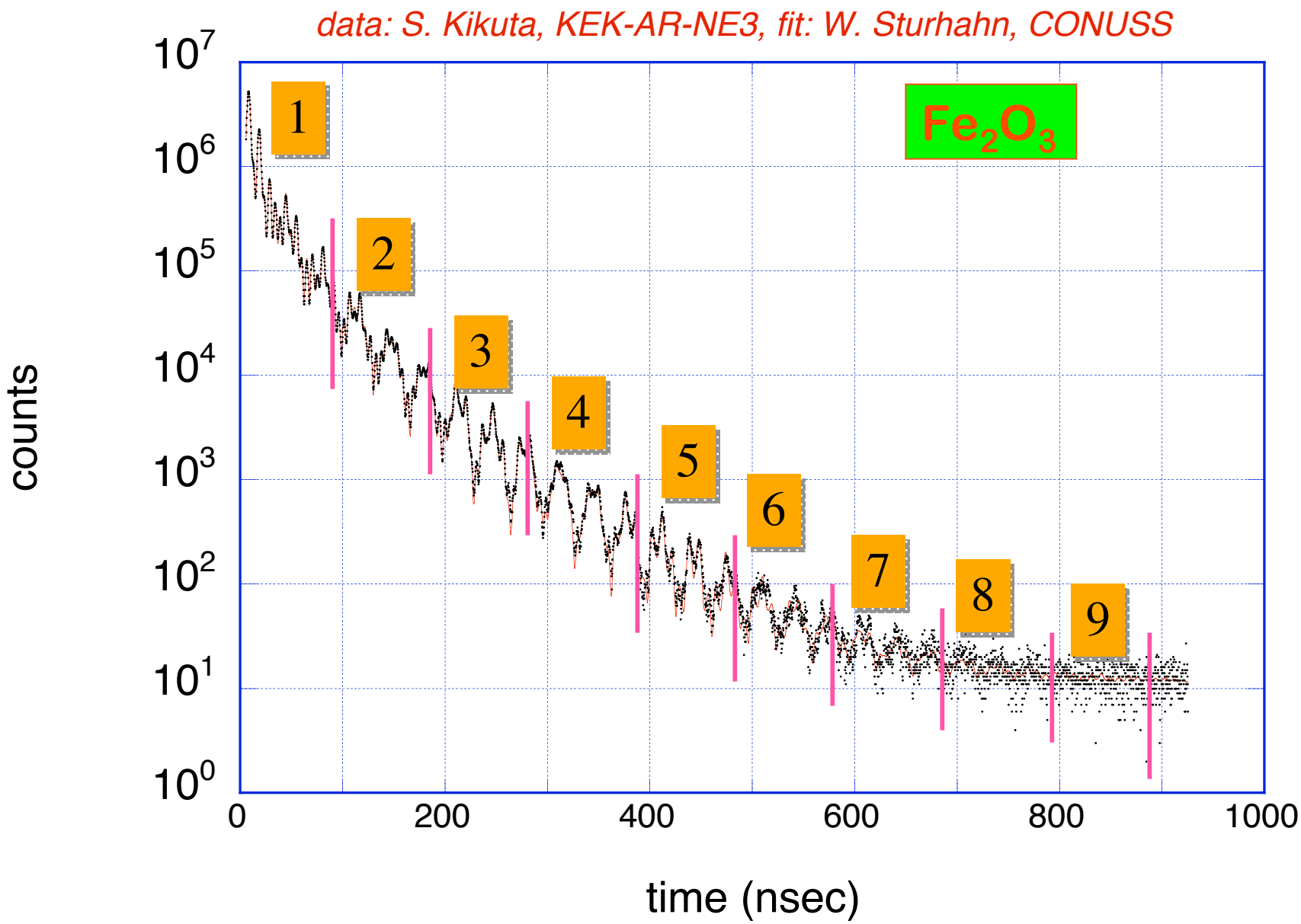
- Phonon dynamics via NRIXS
  - Monolayers, buried layers, spin dynamics
  - Nanoscale materials
  - Dynamics at pressures exceeding 2 Mbar, 3000 K
  - Dilute systems to extend the applicability of the method
  - Applications in astrophysics, geophysics, biophysics, and condensed matter & materials physics

- Structural, magnetic and electronic structure via nuclear forward scattering
  - Element and isotope selective magnetometry
  - Melting temperature at high pressures
  - In-situ oxidation/reduction kinetics for environmental problems
  - Mössbauer microscope

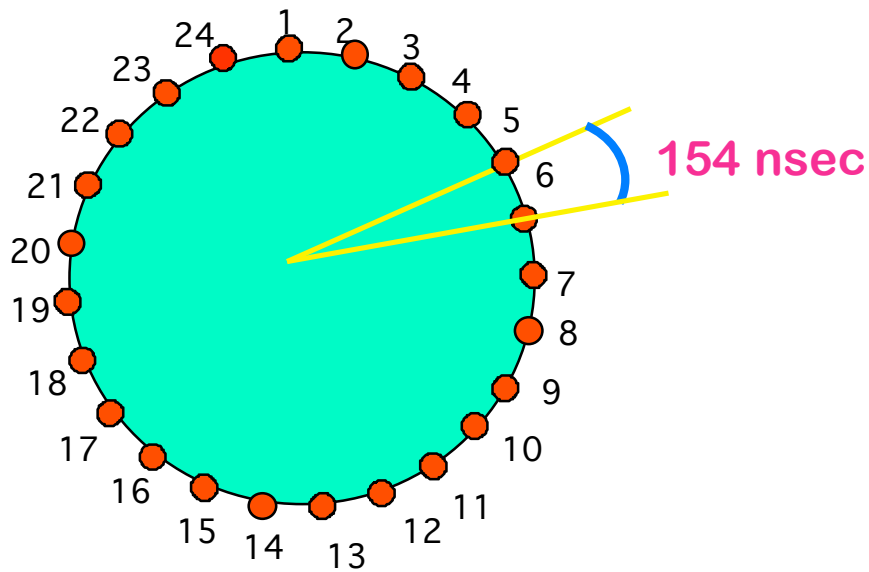
- Optics development
  - Monochromators, new alternative crystals,

- Novel ideas
  - X-ray wavelength standards

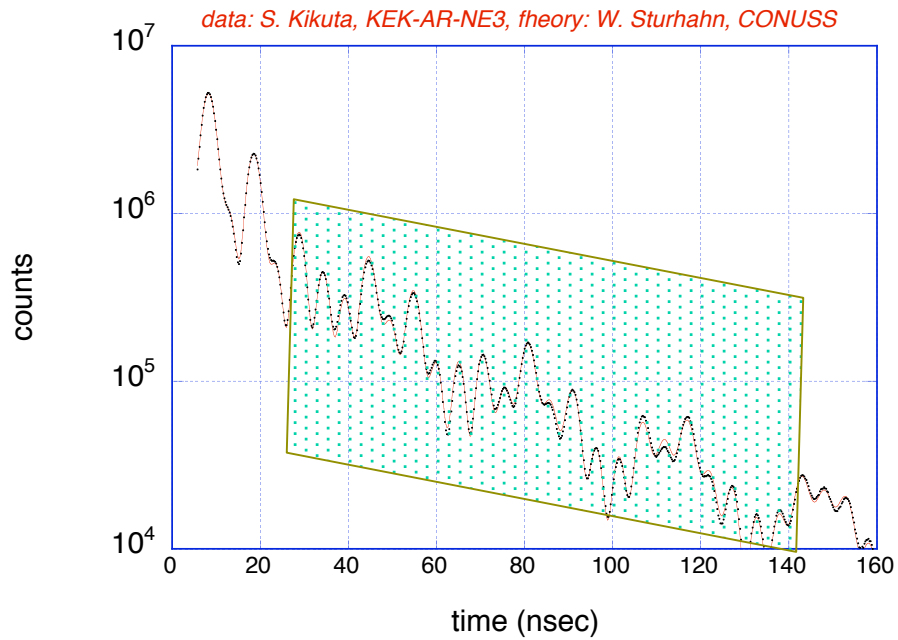
How long is long enough for bunch-to-bunch separation ?

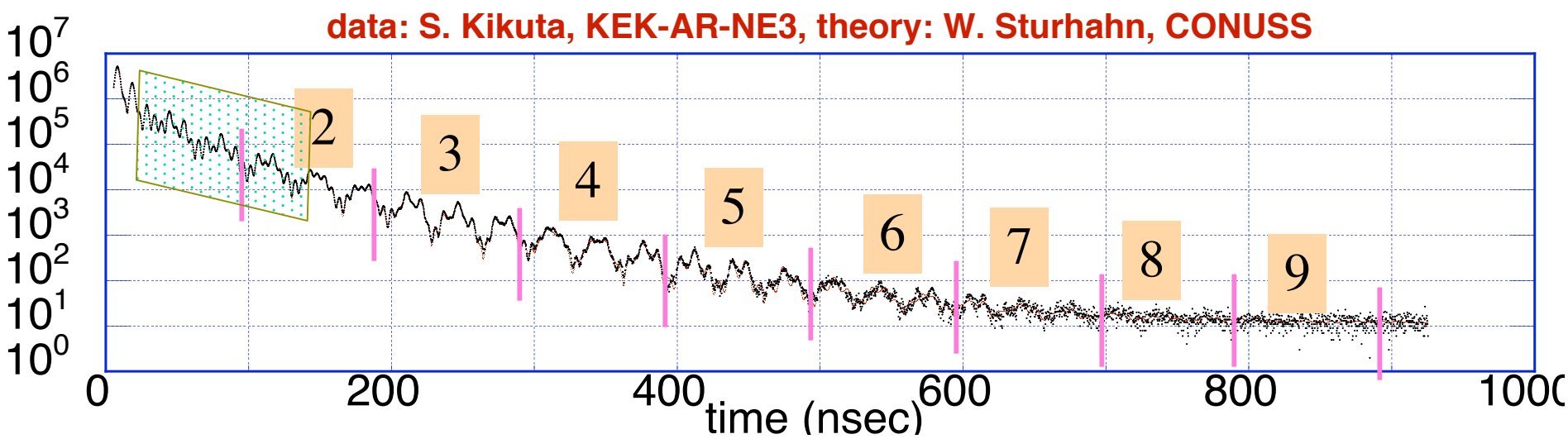


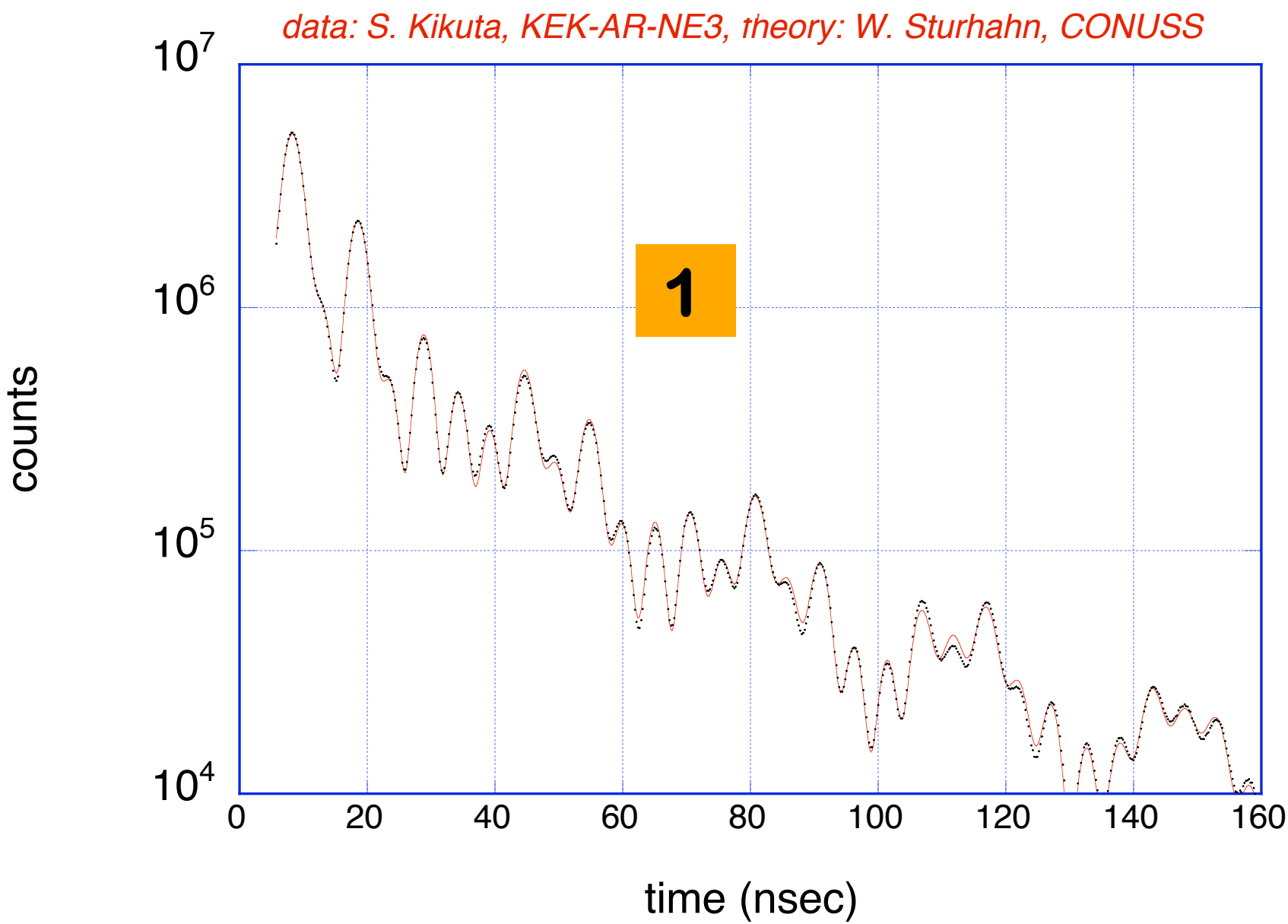
Standard time structure @ APS



1 revolution=3.68 μsec



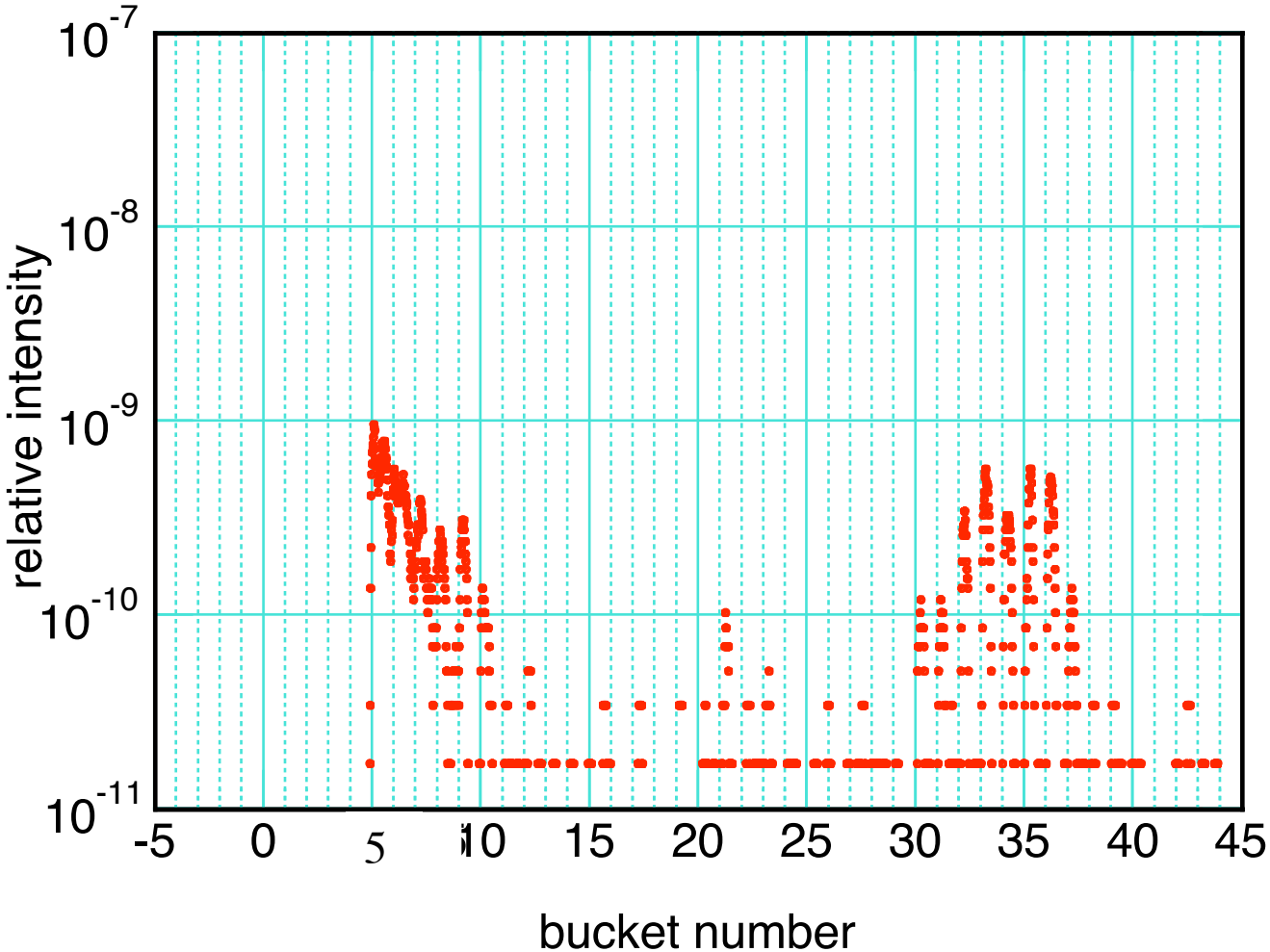



data: S. Kikuta, KEK-AR-NE3, theory: W. Sturhahn, CONUSS
1
counts
time (nsec)
10^7
10^6
10^5
10^4
0
20
40
60
80
100
120
140
160

Bunch Purity

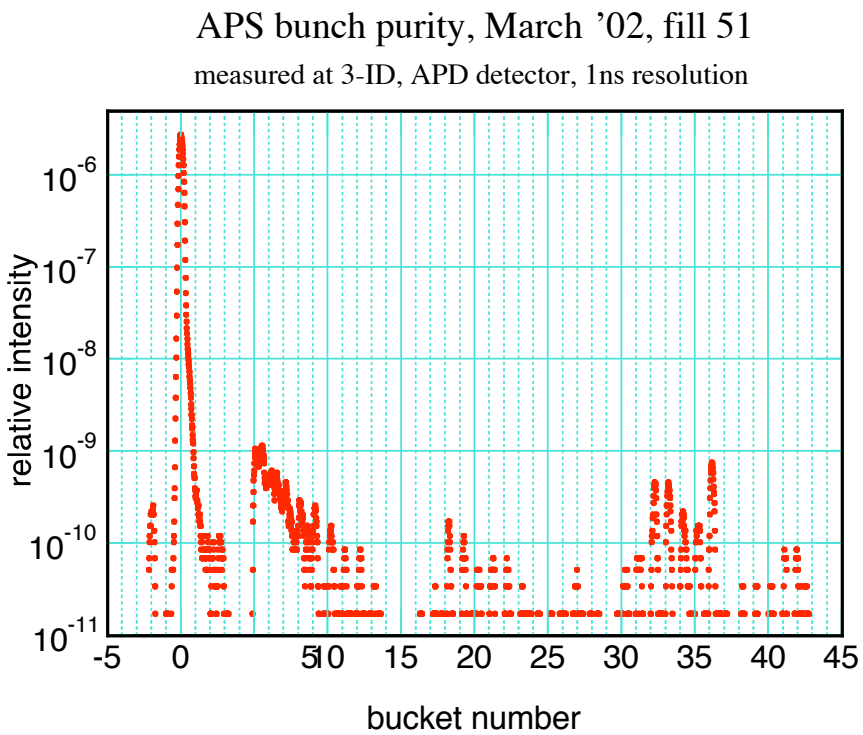
APS bunch purity, March ’02, fill 52

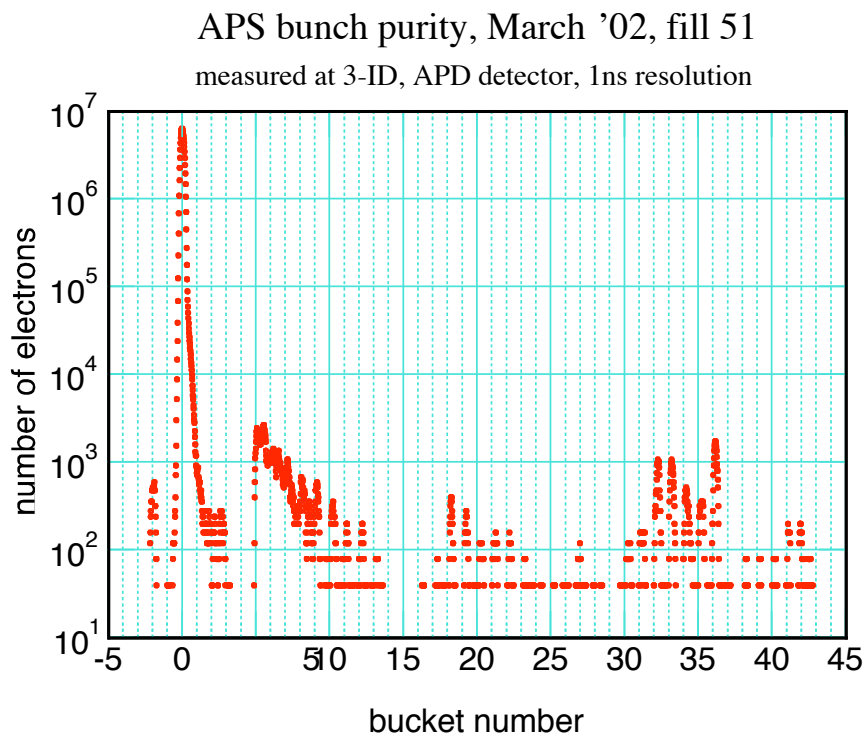
measured at 3-ID, APD detector, 1ns resolution



W. Sturhahn, March 03, 2002

How many electrons can we actually see ?





1 Ampere = 1 Coulomb/sec=$6.24 \cdot 10^{18}$ electron/sec

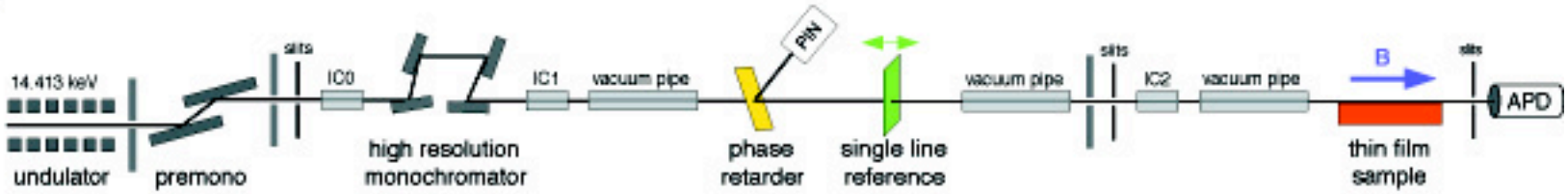
1 bunch at 5 mA has $1.15 \cdot 10^{11}$ electrons

Photon flux = 10^{10} Hz/1meV, i.e $5 \cdot 10^{8}$ Hz/bunch/meV

APD noise ~ 0.01 Hz => 1 part in 10^{10} purity ideal

Nuclear resonant magnetometry with circularly polarized x-rays

Setup:

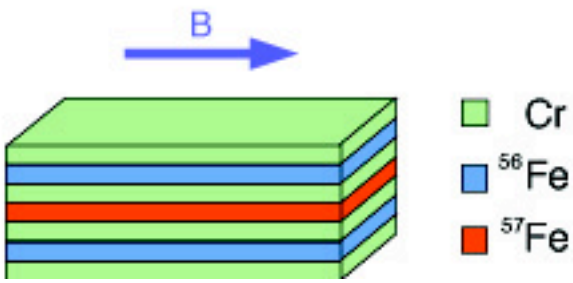


Phase retarder : to convert linear polarization to circular polarization

Single line : nuclear resonant reference sample to increase sign-sensitivity

Sample : thin film in grazing incidence geometry

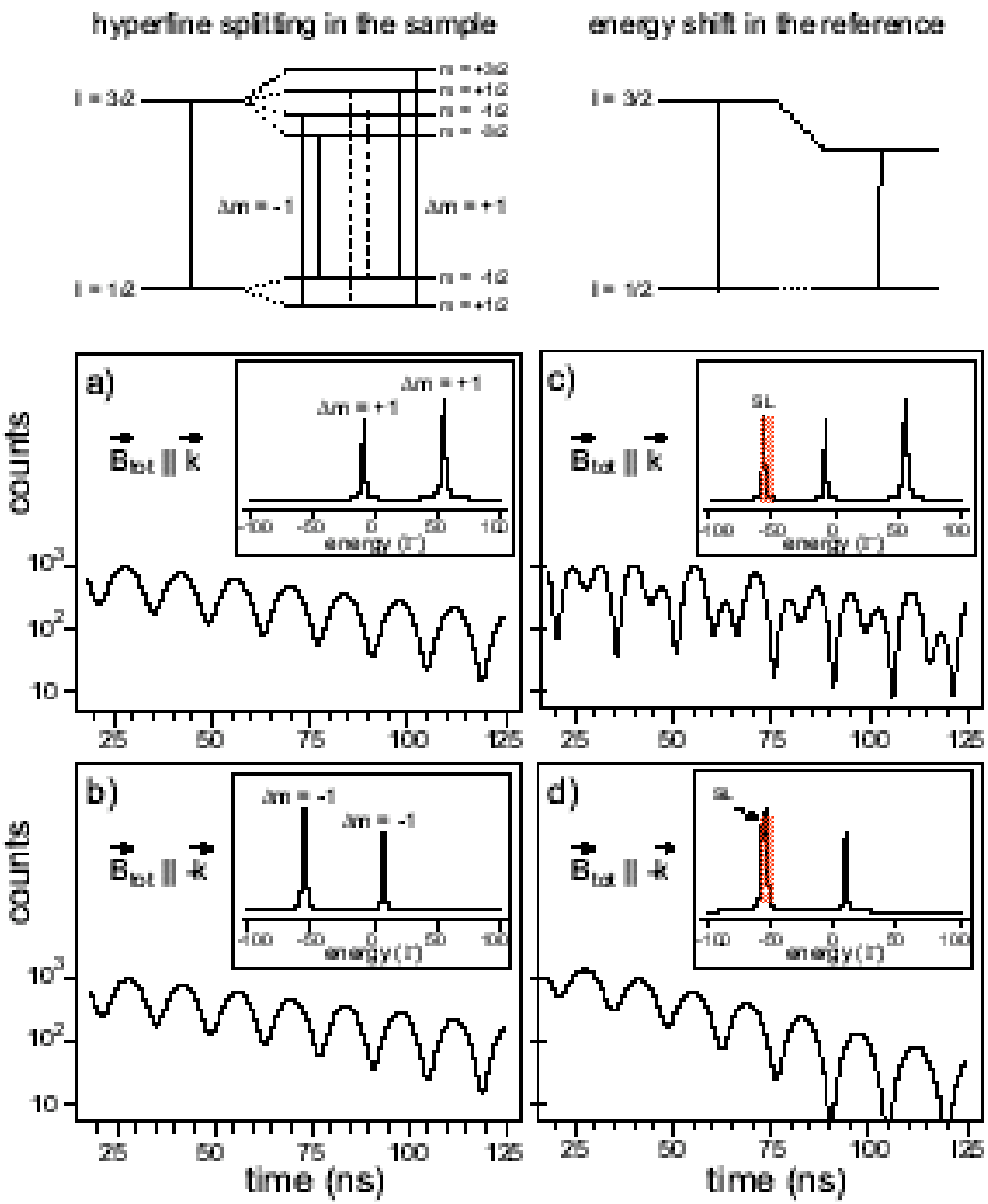
Sample:



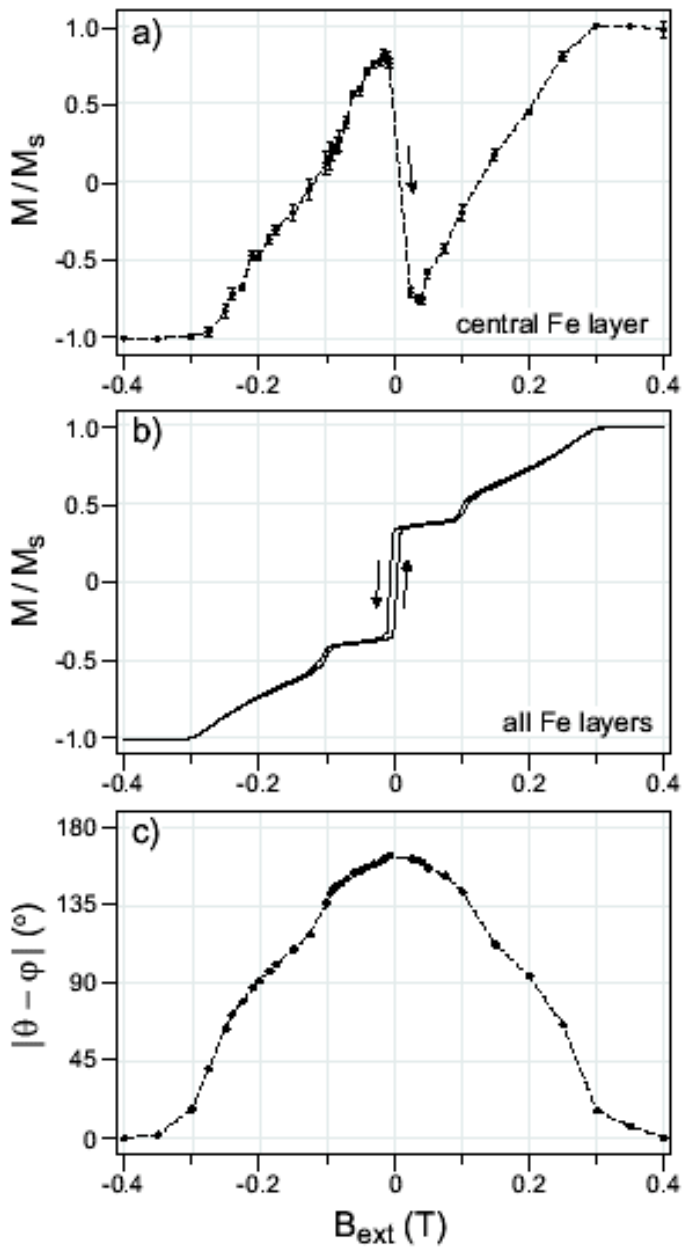
MgO/Cr(111)/Fe(50)/Cr(11)/Fe(50)/Cr(11)/Fe(50)/Cr(44)

only the middle Fe layer contains ^{57}Fe

C. L'abbe, et al, Phys. Rev. Lett. 93 (2004) 037201



C. L'abbe, et al, Phys. Rev. Lett. 93 (2004) 037201



Central Fe layer

All Fe layers

Angle between central and outer layer magnetization vectors

C. L'abbe, et al, Phys. Rev. Lett. 93 (2004) 037201

Heme Proteins

Heme proteins are exemplary systems to study the influence of protein dynamics on physiological functions.

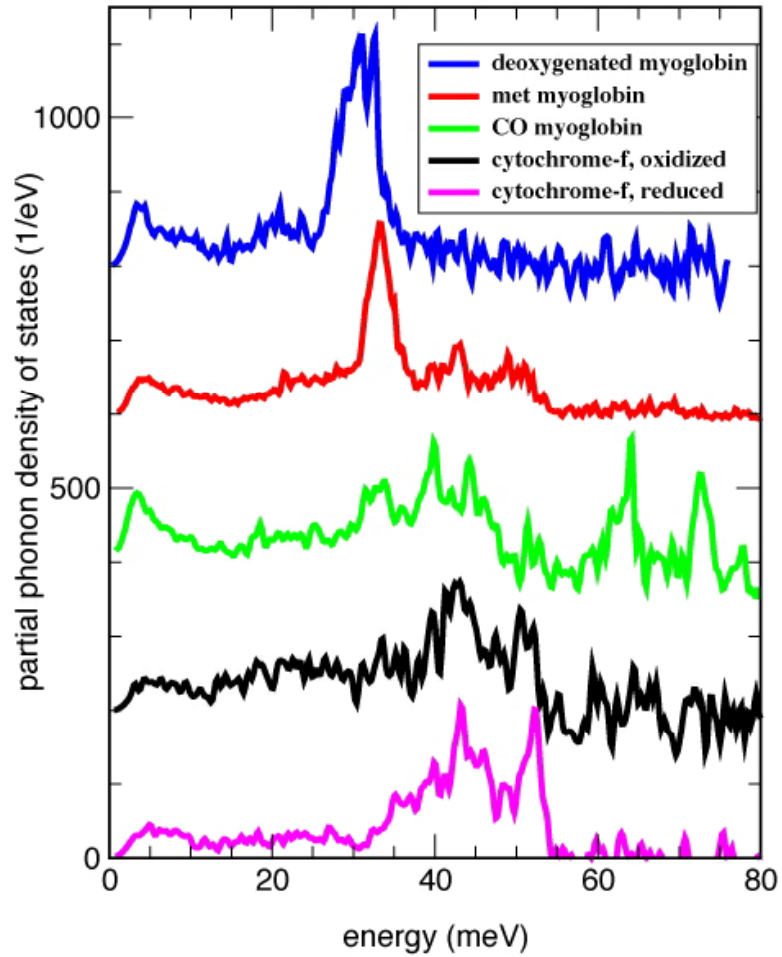
Most reactions in proteins take place at the position of the heme group. The access to and reactivity of heme group is influenced by the dynamics of the entire surrounding of the protein structure.

Fe-ligand modes such as Fe-C, Fe-His can be identified.

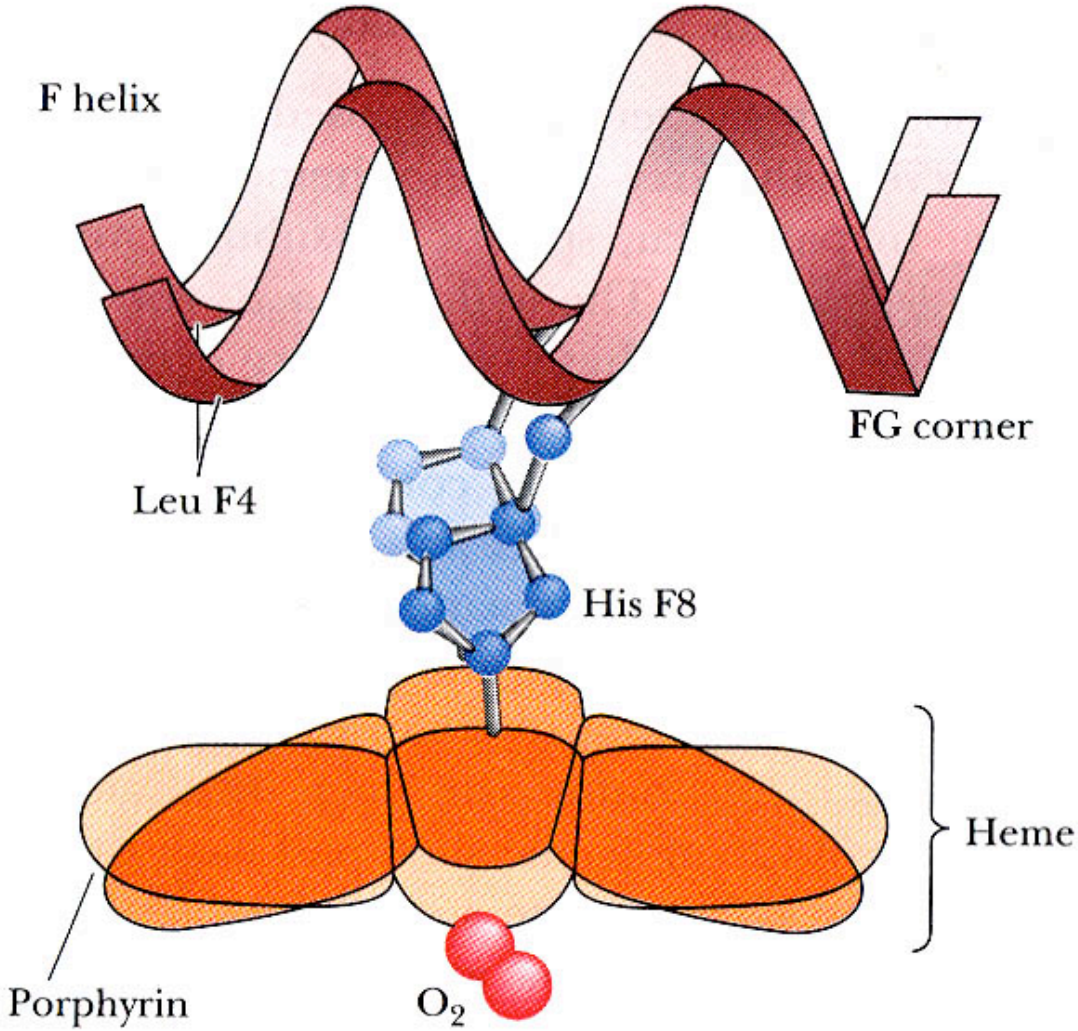
CO-binding increases the complexity of the vibrational spectrum.

In cytochrome-f, the porphyrin group is more tightly attached to the surrounding protein.

The low energy modes at 5 meV is reduced compared to deoxygenated or carboxylized myoglobin.



T. Sage, S. Durbin
K. Achterhold, F. Parak



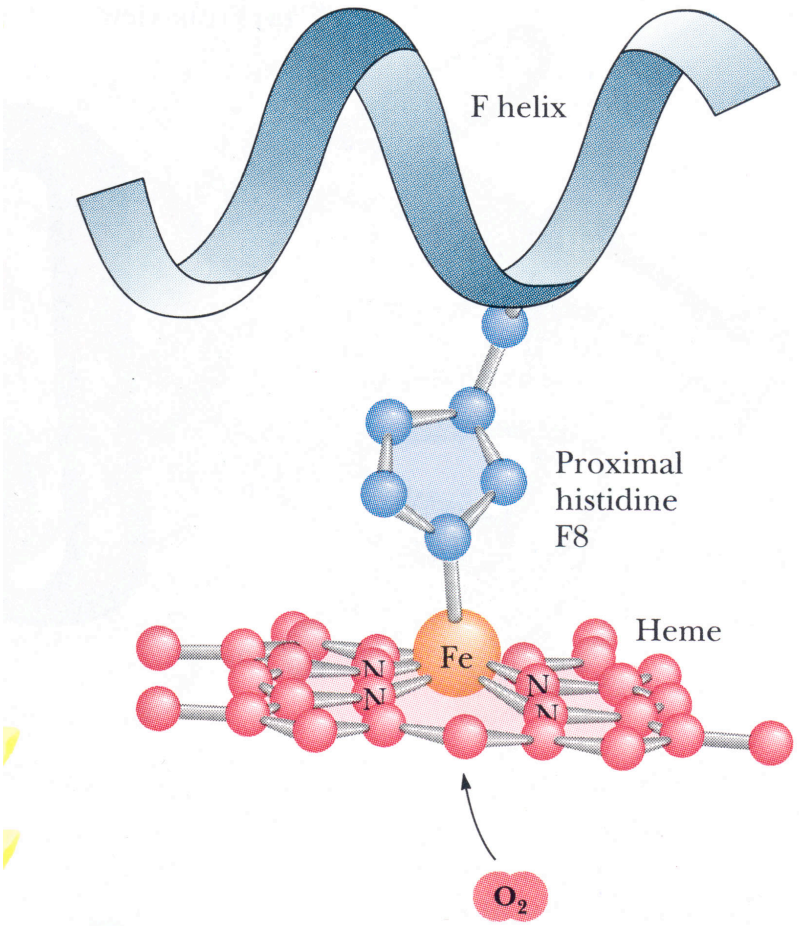
Changes in the position of the heme iron atom upon oxygenation lead to conformational changes in the hemoglobin molecule.

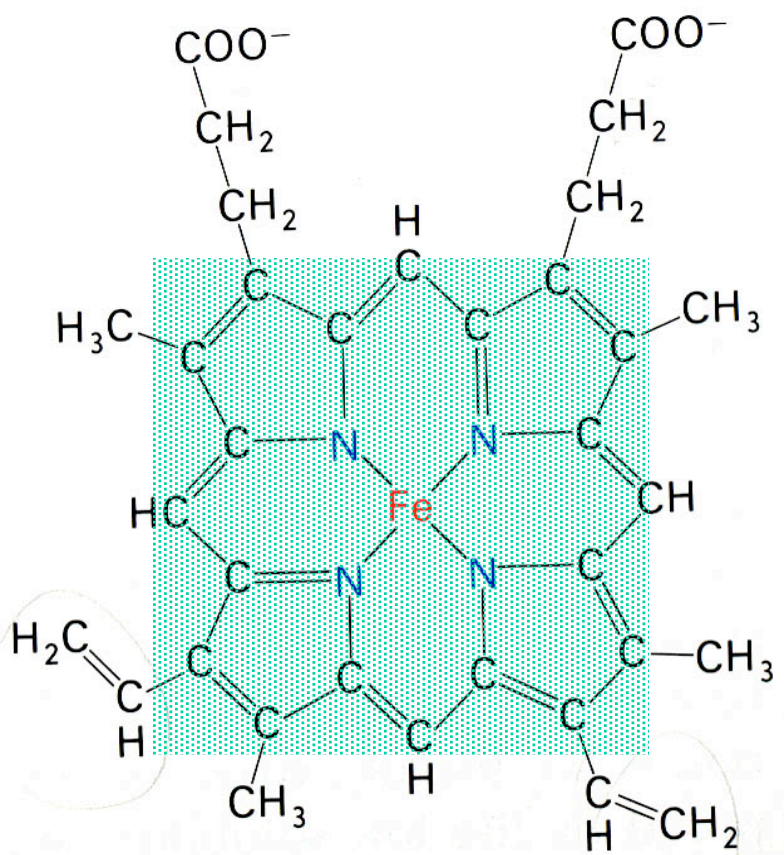
Upon binding a ligand, Fe is pulled into the heme plane, putting a stress on the bond to the protein.

In response, the protein changes conformation, altering the environment of other hemes in Hb.

This simple shift in a single Fe atom plays the central role in the biological functioning of hemoglobin.

How does this couple to protein dynamics?

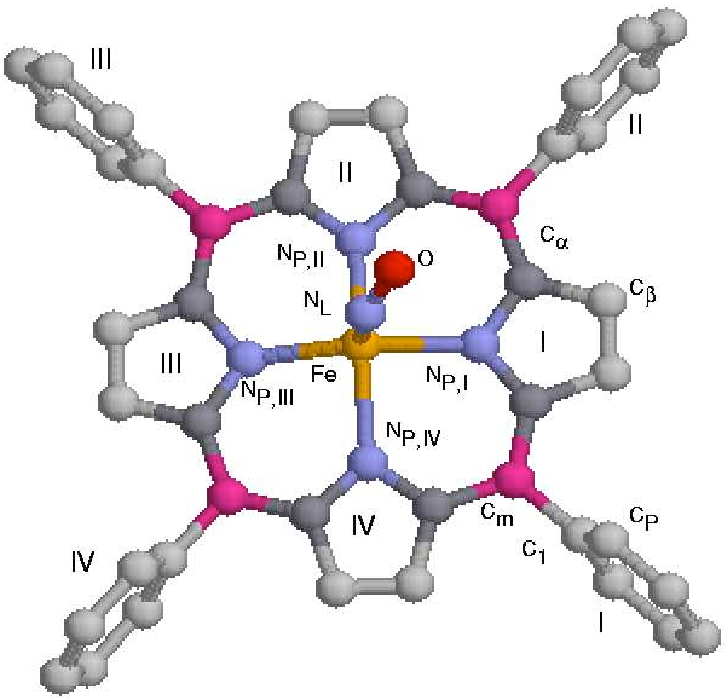


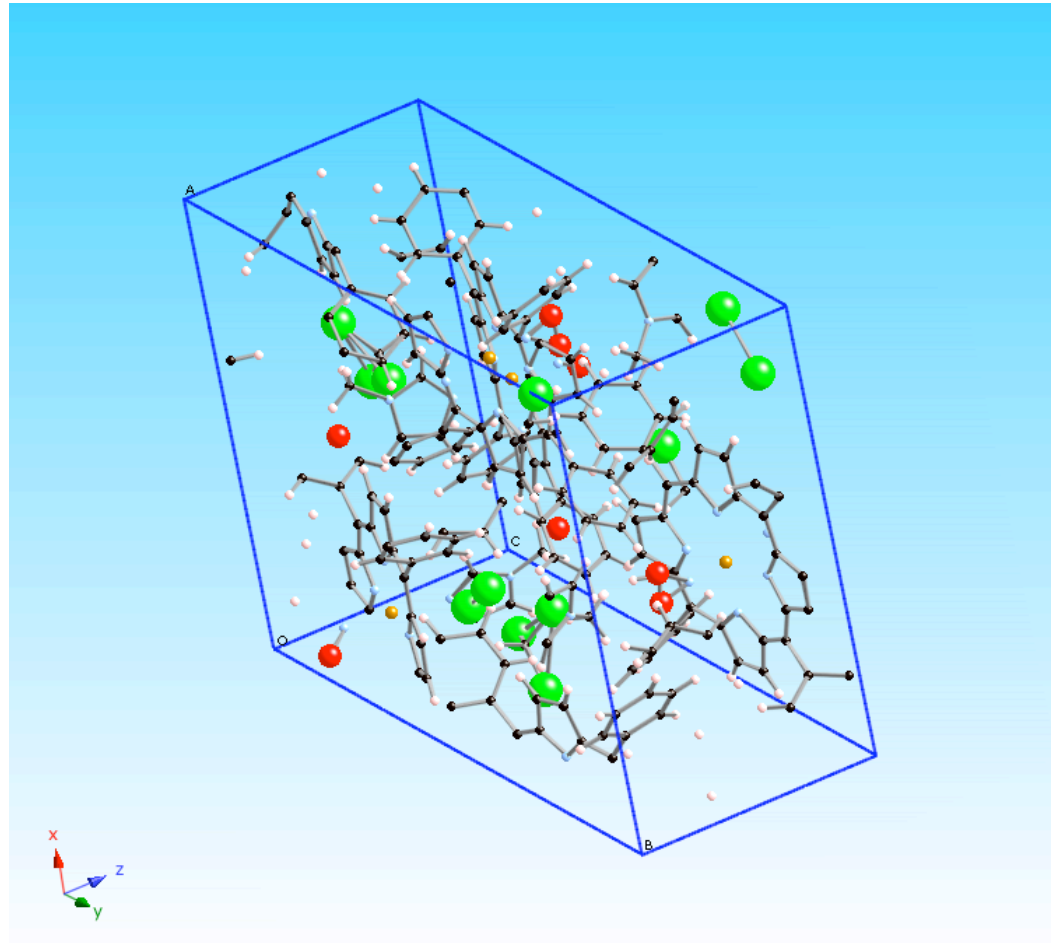


Heme
(Fe–protoporphyrin IX)

Binding of the heme to the protein

The heme molecule





Porphyrins:	A	B
Tetraphenylporphyrin (TPP)	Phenyl	H
Octaethylporphyrin (OEP)	H	Ethyl

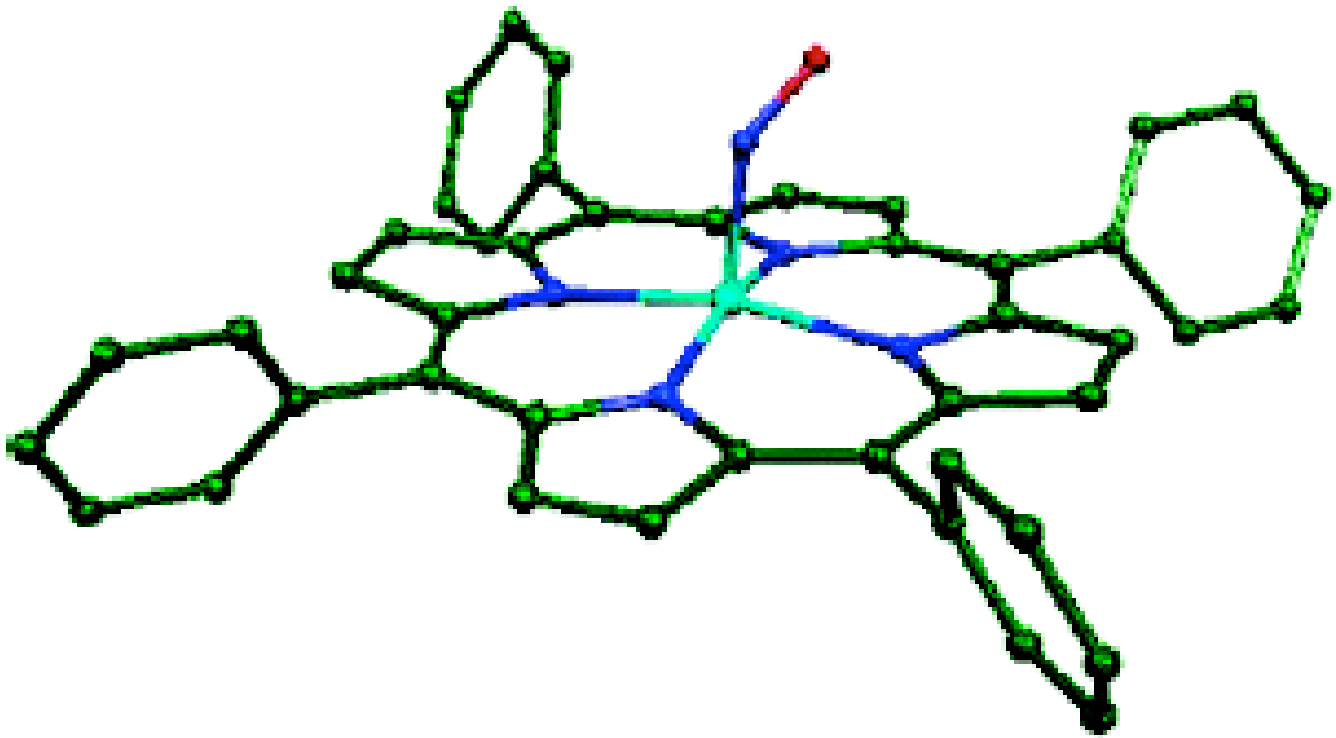
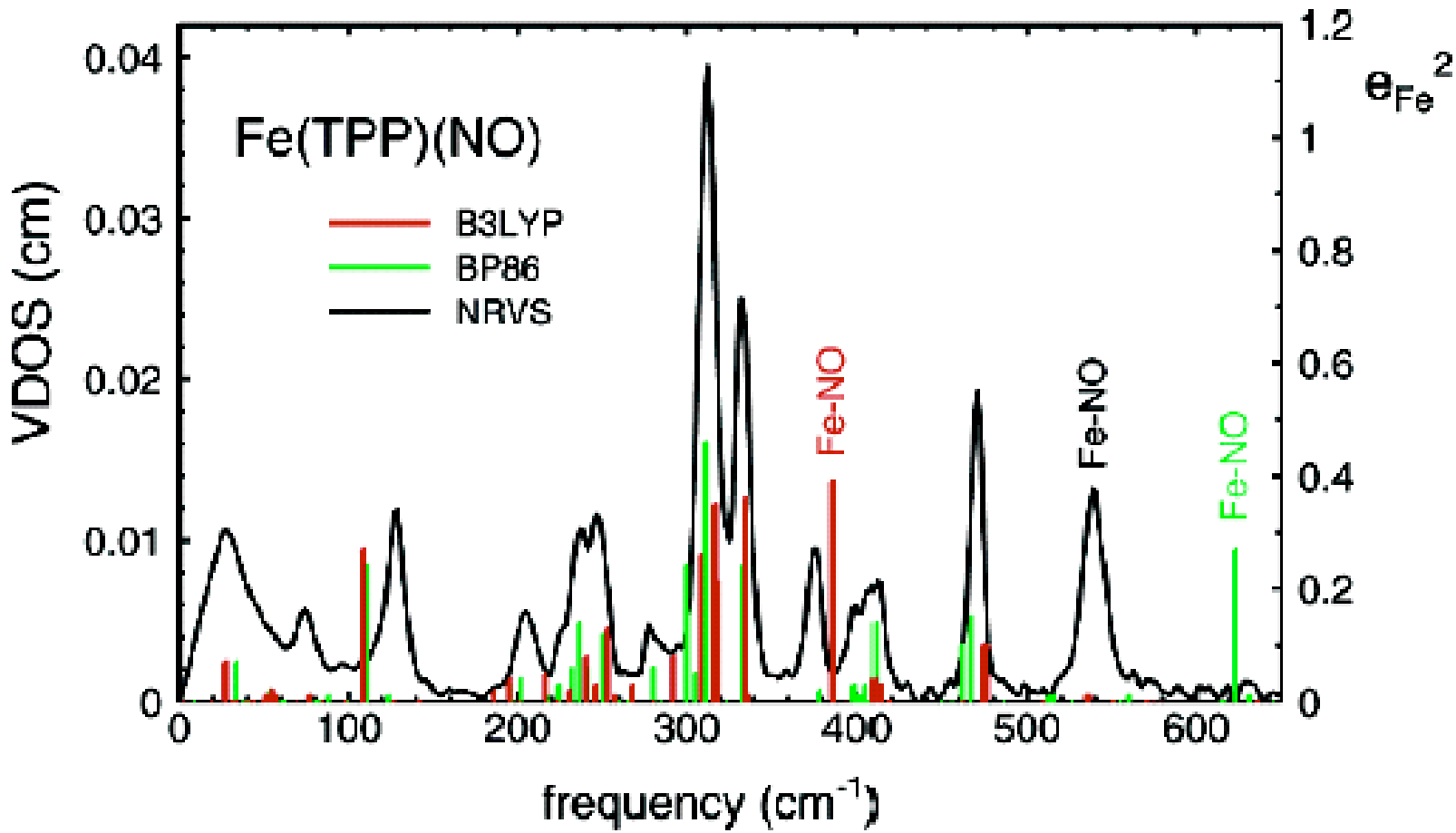


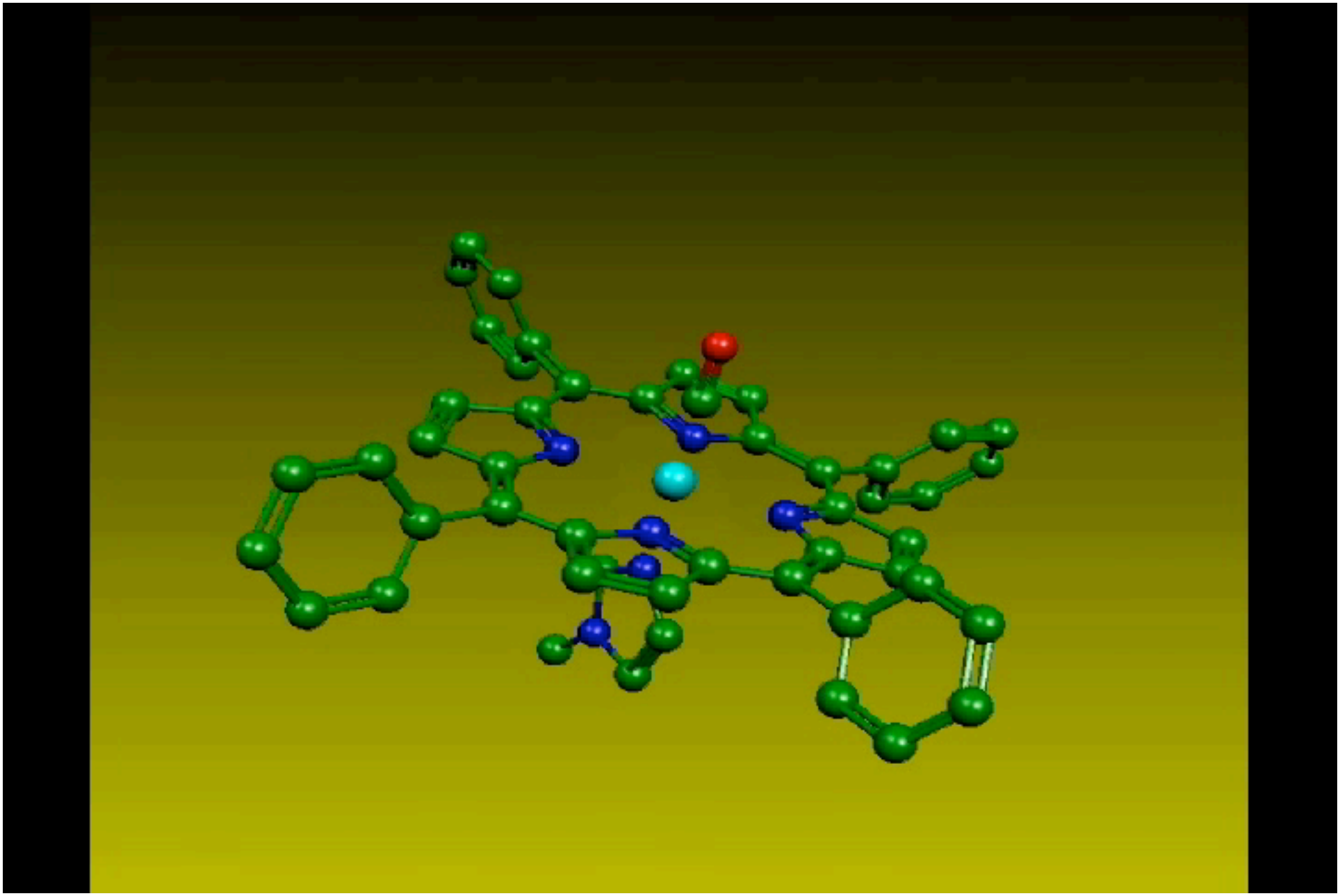
Figure 1. Calculated structure of ferrous nitrosyl tetraphenylporphyrin,

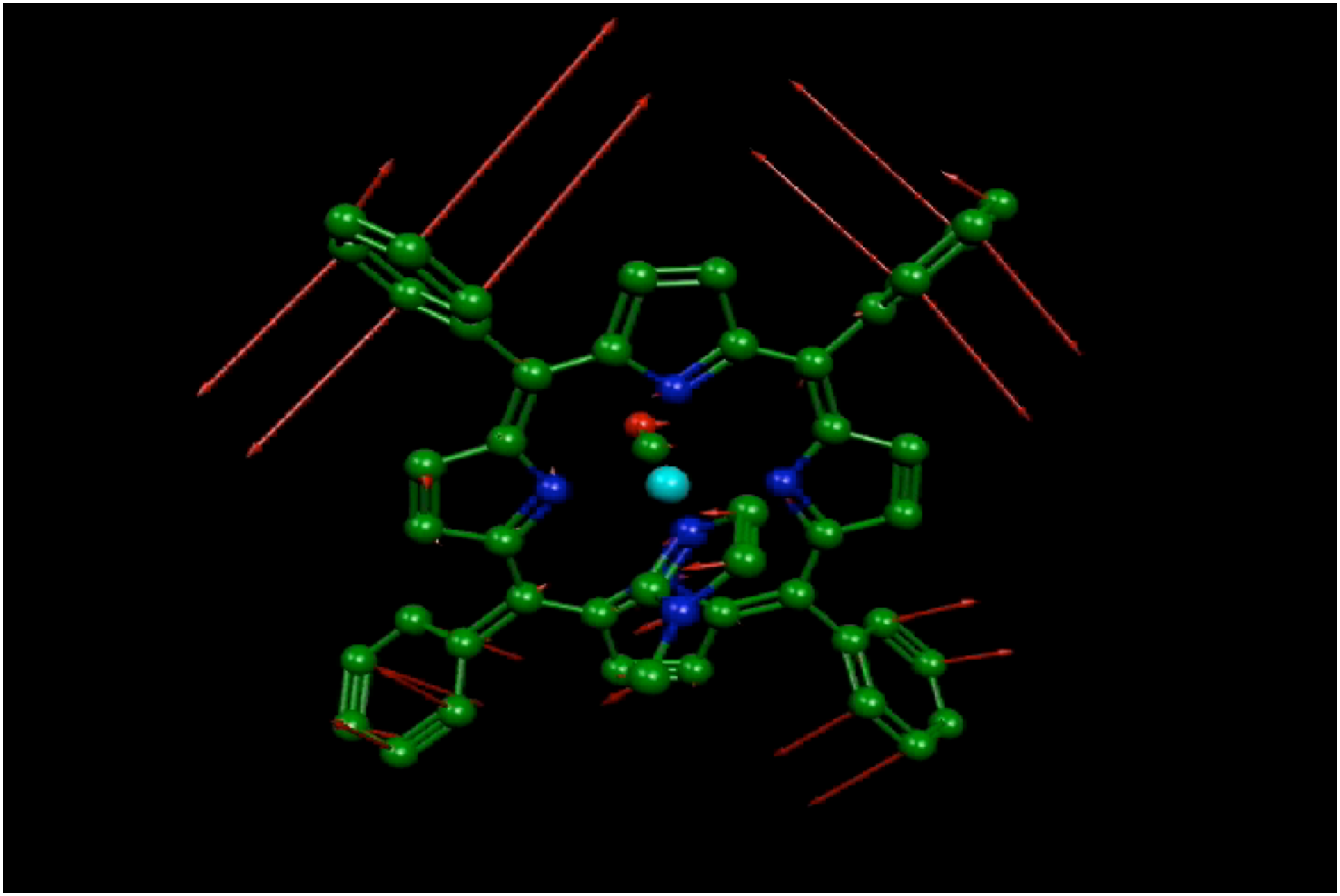
Quantitative vibrational dynamics of iron in nitrosyl porphyrin

Probing in-plane vibrations of Fe-pyrolle bond, which remains elusive for resonant Raman spectroscopy (Durbin, Sage,Scheidt collaboration)



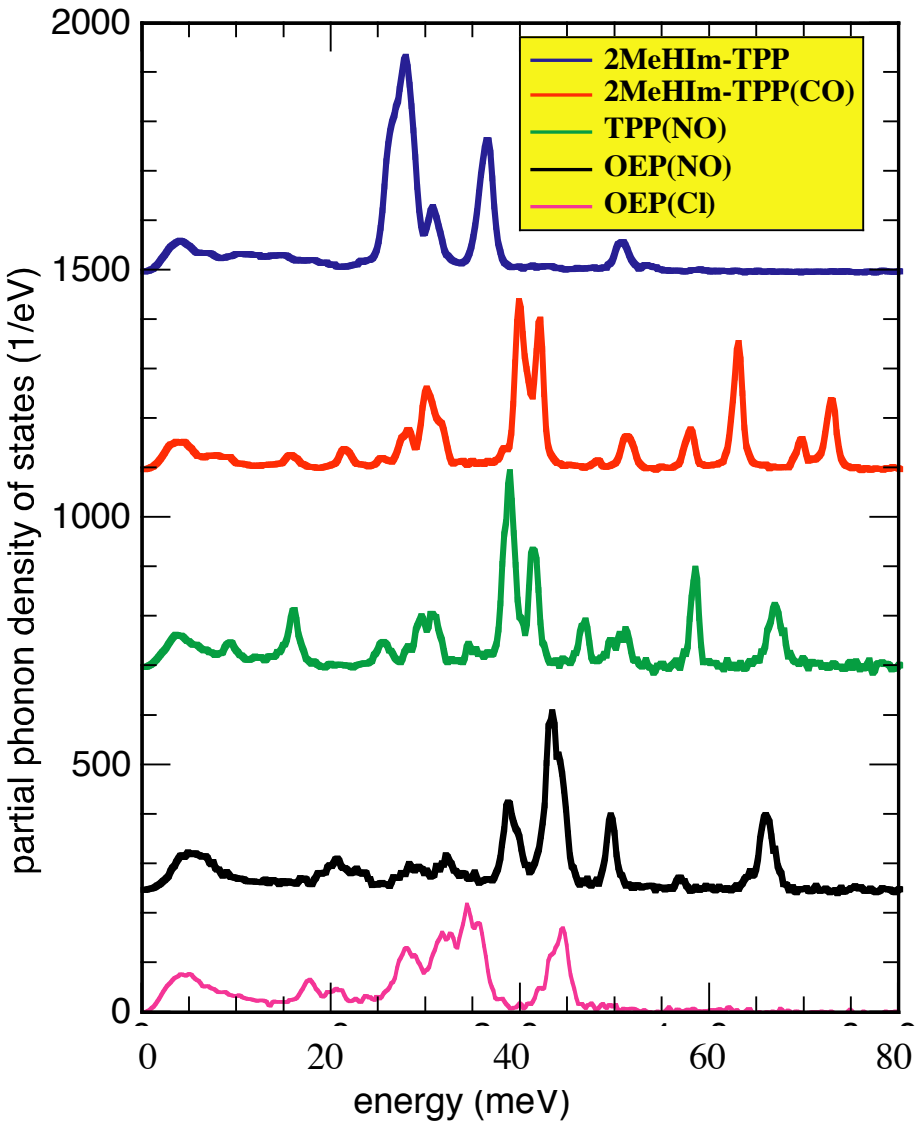
Bogdan Leu et al, J. of Am. Chem. Soc. 126 (2004) 4211





Porphyrin model compounds

J. T. Sage, et al, J. Phys. Cond. Matt, 13 (2001) 7707



The heme doming coordinate is directly Involved in oxygen-binding reaction.

In proteins, it is important to know whether It acquires a global character.

Doming modes are expected in the range of 6-8 meV.

Porphyrin model compounds mimic the heme group found at the active site of many proteins involved in biological usage of oxygen and nitric oxide.

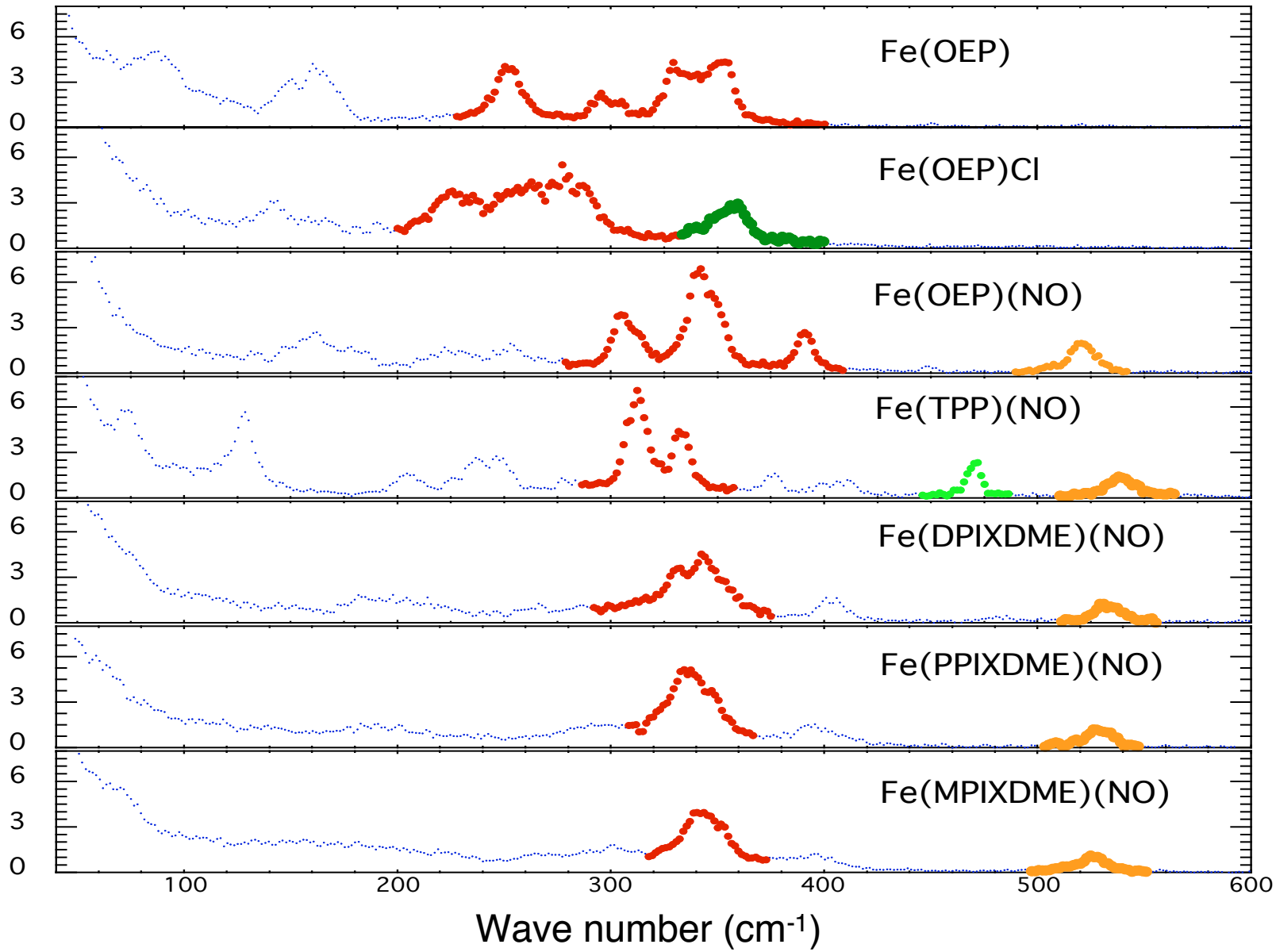
2MeHIm-TPP: Methyl-Hydrogen-Imidazole tetra phenyl porphyrin

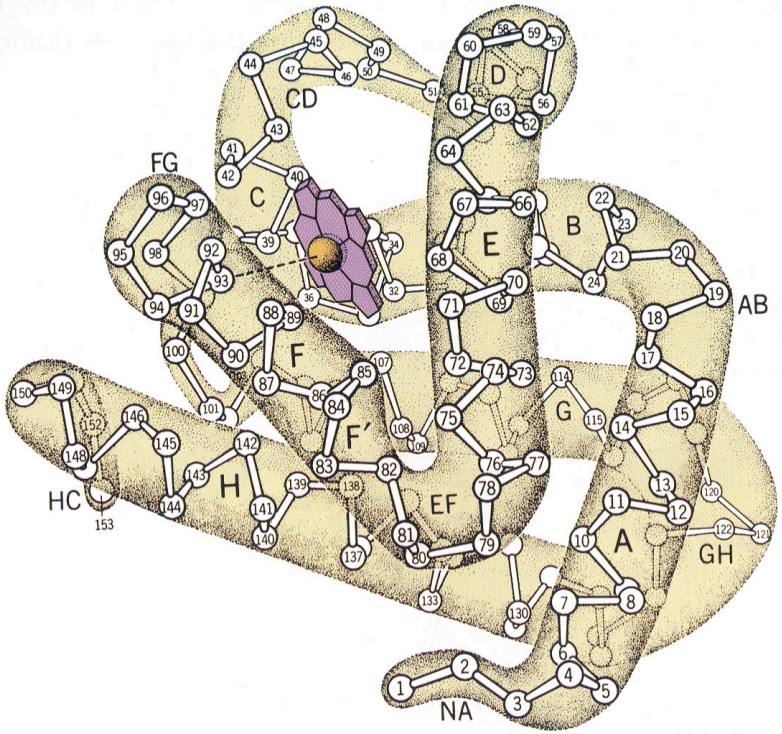
OEP : Octo ethyl porphyrin

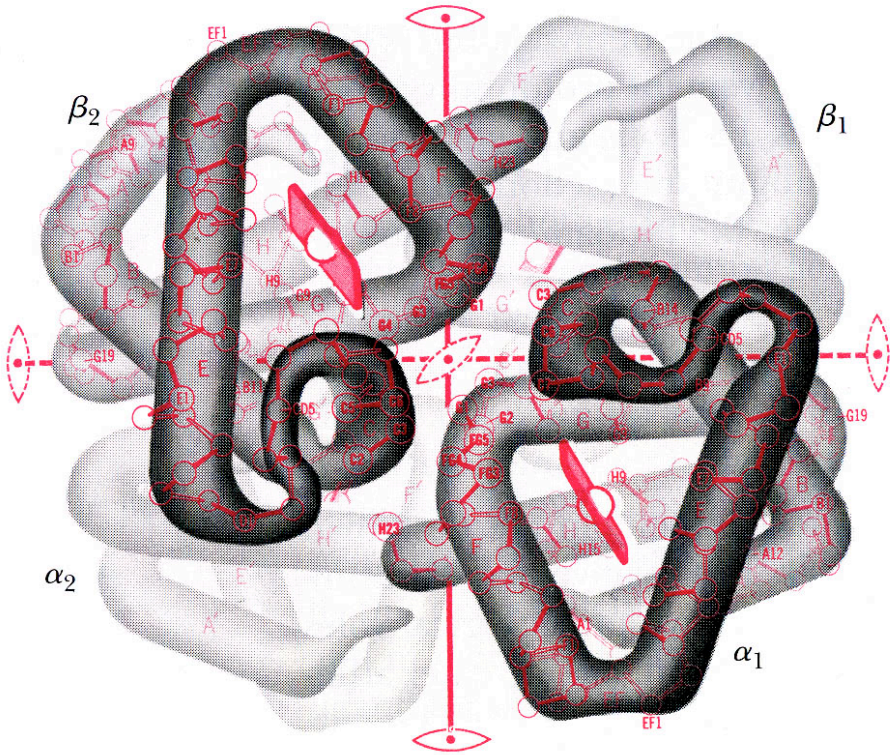
TPP : Tetra phenyl porphyrin

Model porphyrin compounds

(T. Sage & S. Durbin,R. Scheidt, W. Sturhahn collaboration)



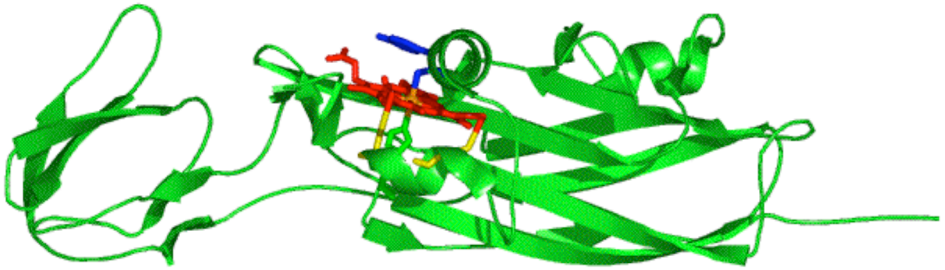




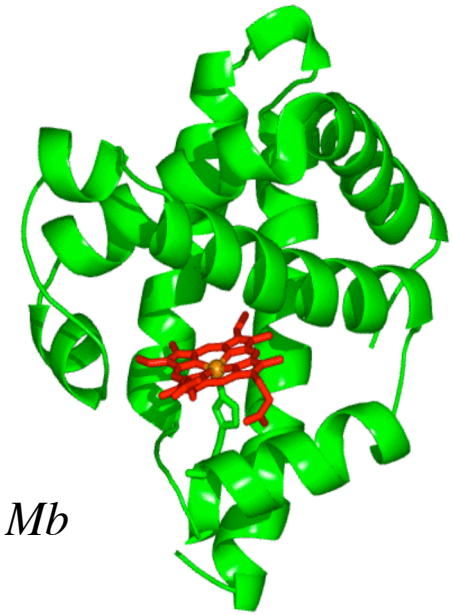
Myoglobin

Hemoglobin

C. Comparison of heme proteins - cytochrome f *vs* myoglobin



Cytochrome f

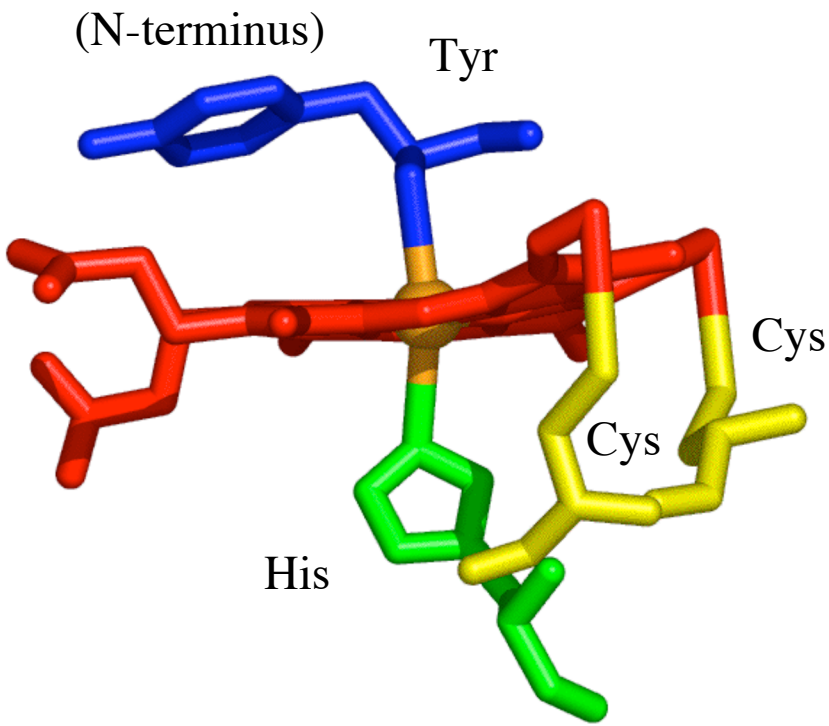


Mb

An electron-transfer membrane protein, part of the cytochrome b_6f complex of oxygenic photosynthesis. Has unusual Fe linkage to N-terminus of protein.

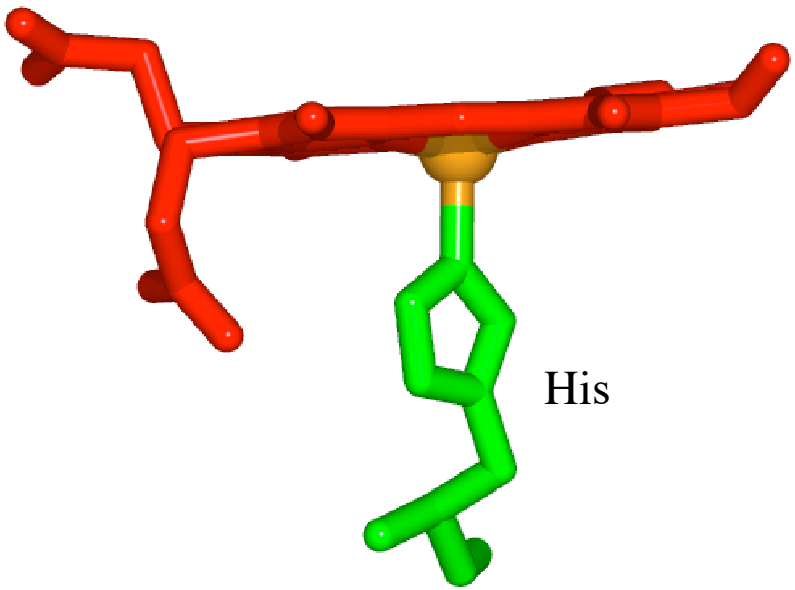
Oxygen ligand-binding protein, found in muscle tissues, etc.

Cytochrome f



Four strong bonds to protein

deoxy-Myoglobin



Only one bond to protein

NRVS Results:

- DMb is softest
- metMb causes slight hardening (high to low spin, planar Fe site, smaller bond length)
- Cyt *f* shows significant hardening, despite nominal similarity with metMb

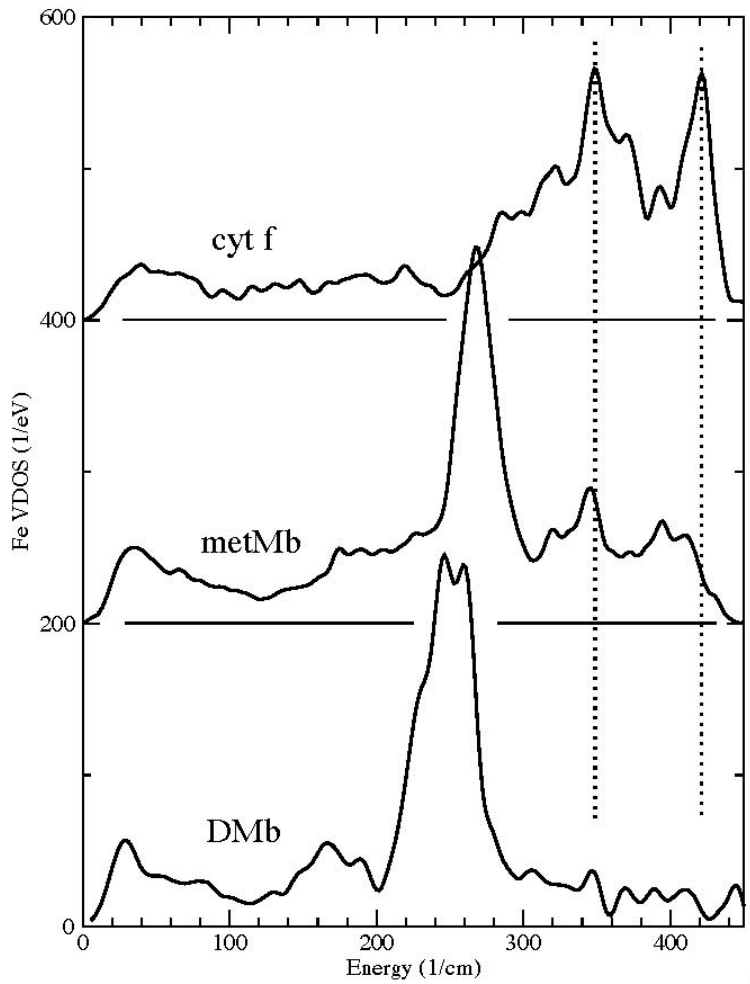
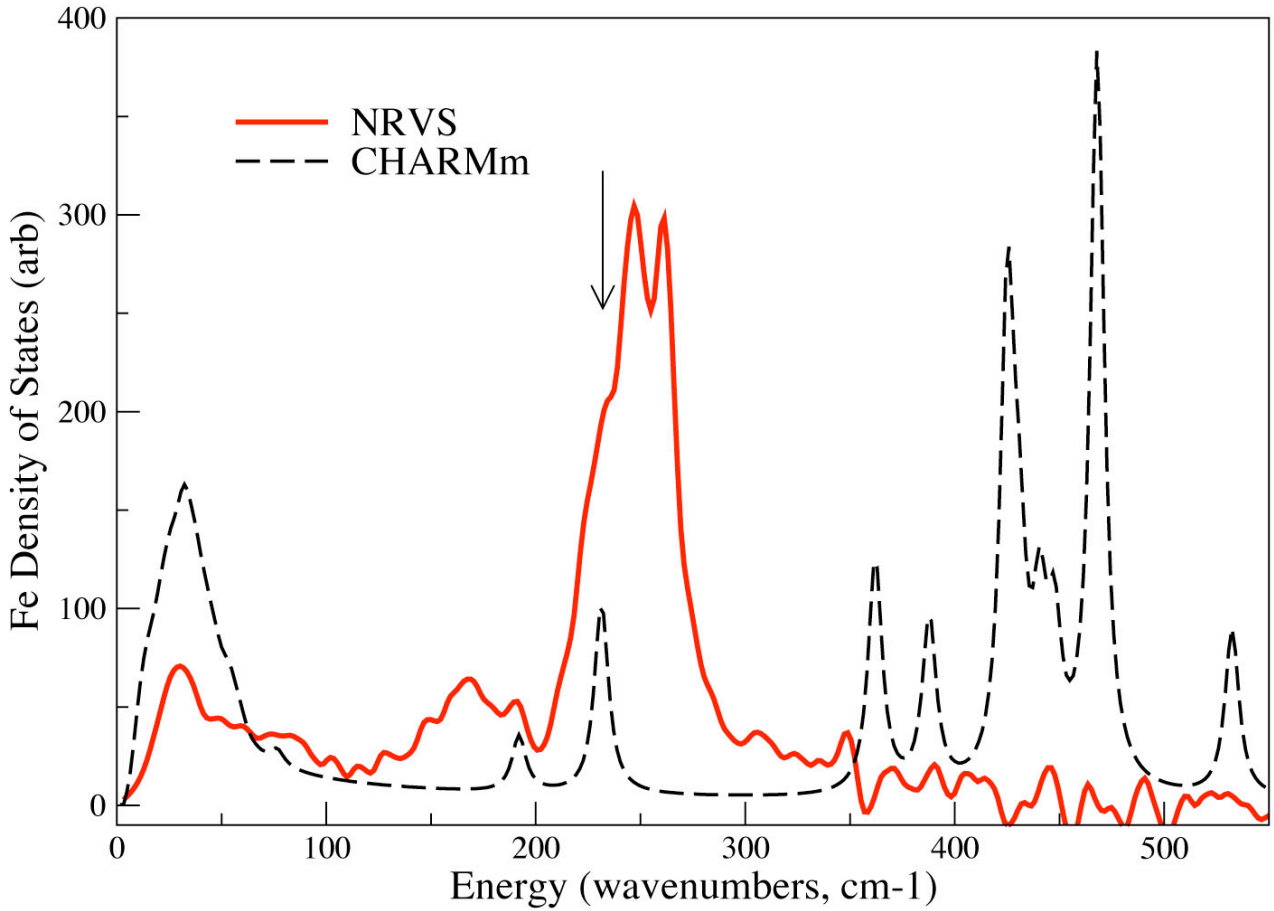
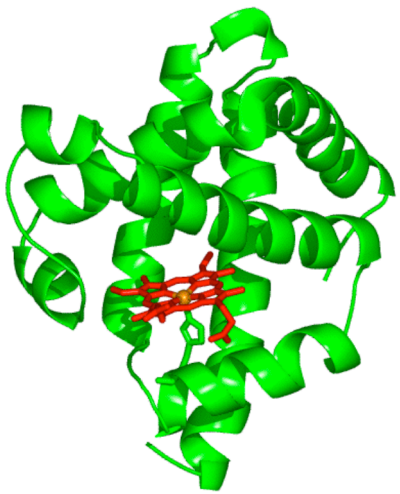


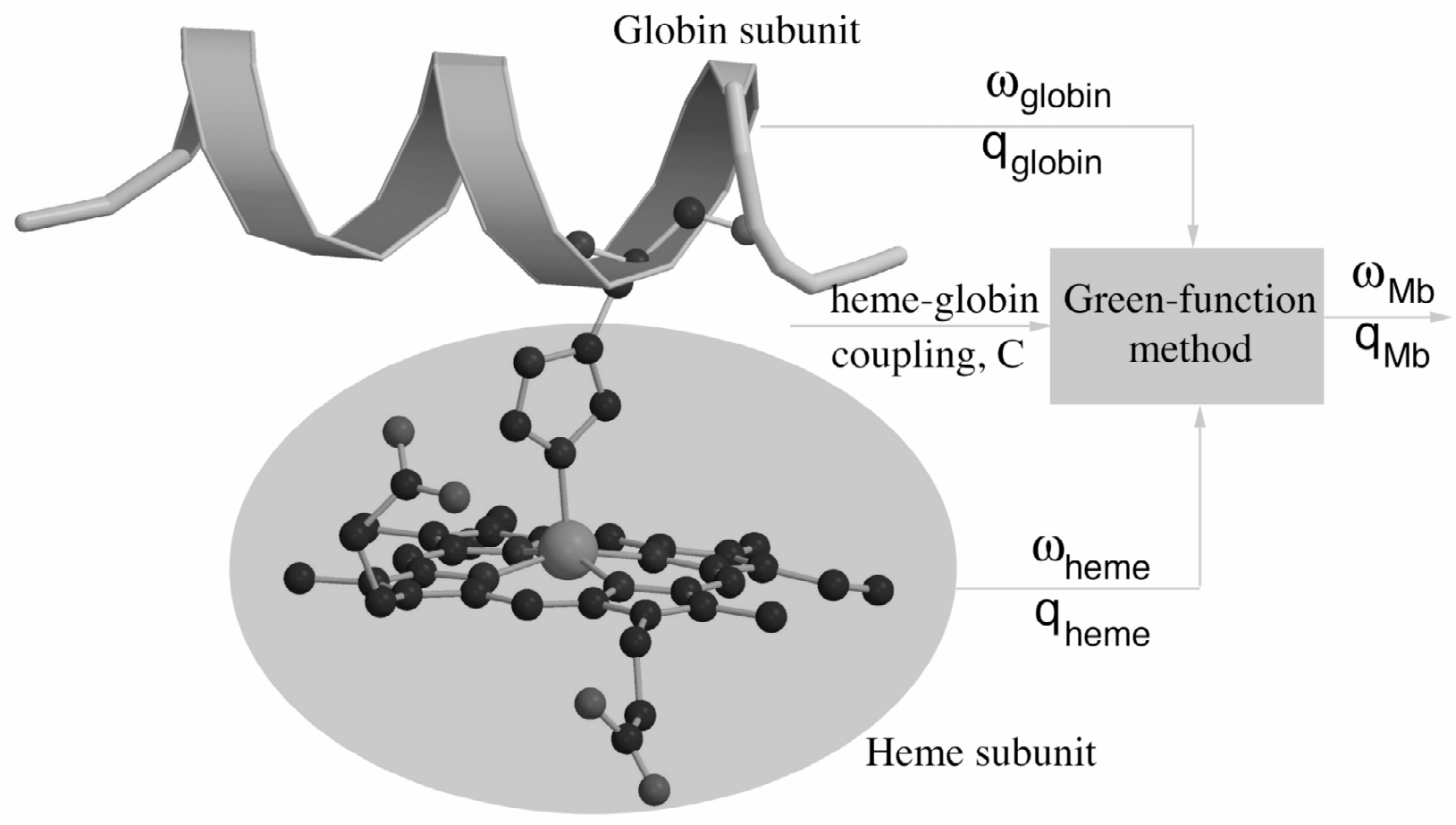
FIGURE 6

Conclusion: the cytochrome arrangement with 4 strong bonds constrains the heme into a much more rigid environment.

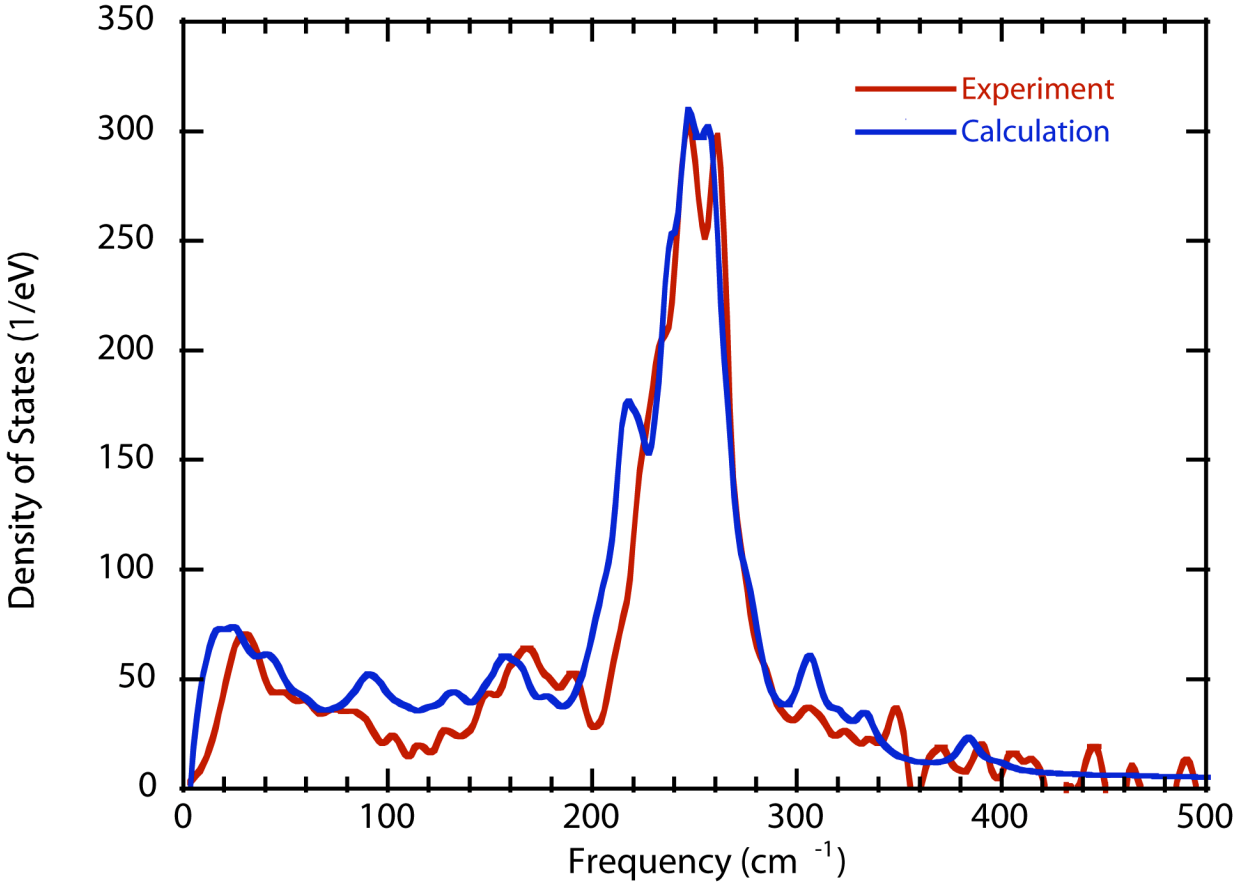


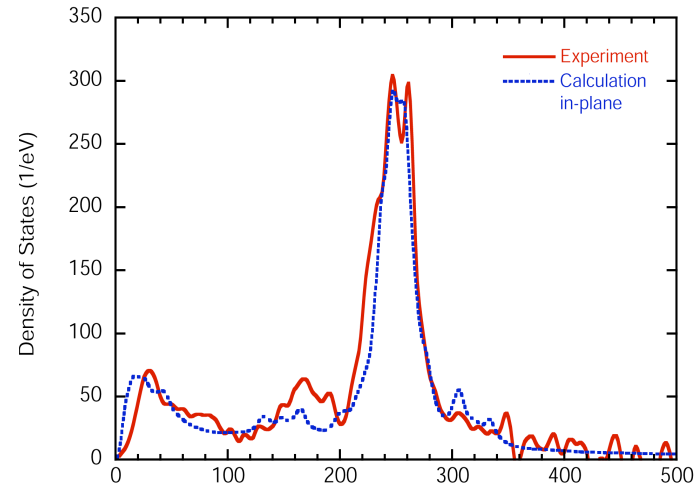


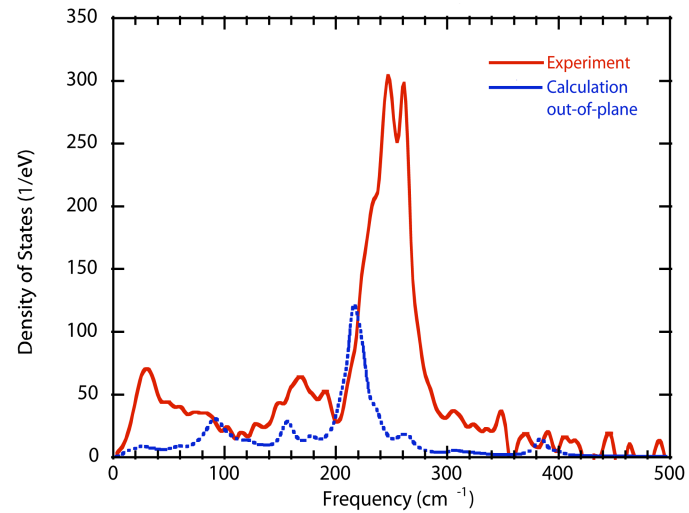
Recall failure of CHARM to match NRVS data….



New computational technique: calculate normal modes of heme from previous NRVS force fields, obtain globin normal modes from CHARM, combine with user-defined couplings to fit to data.



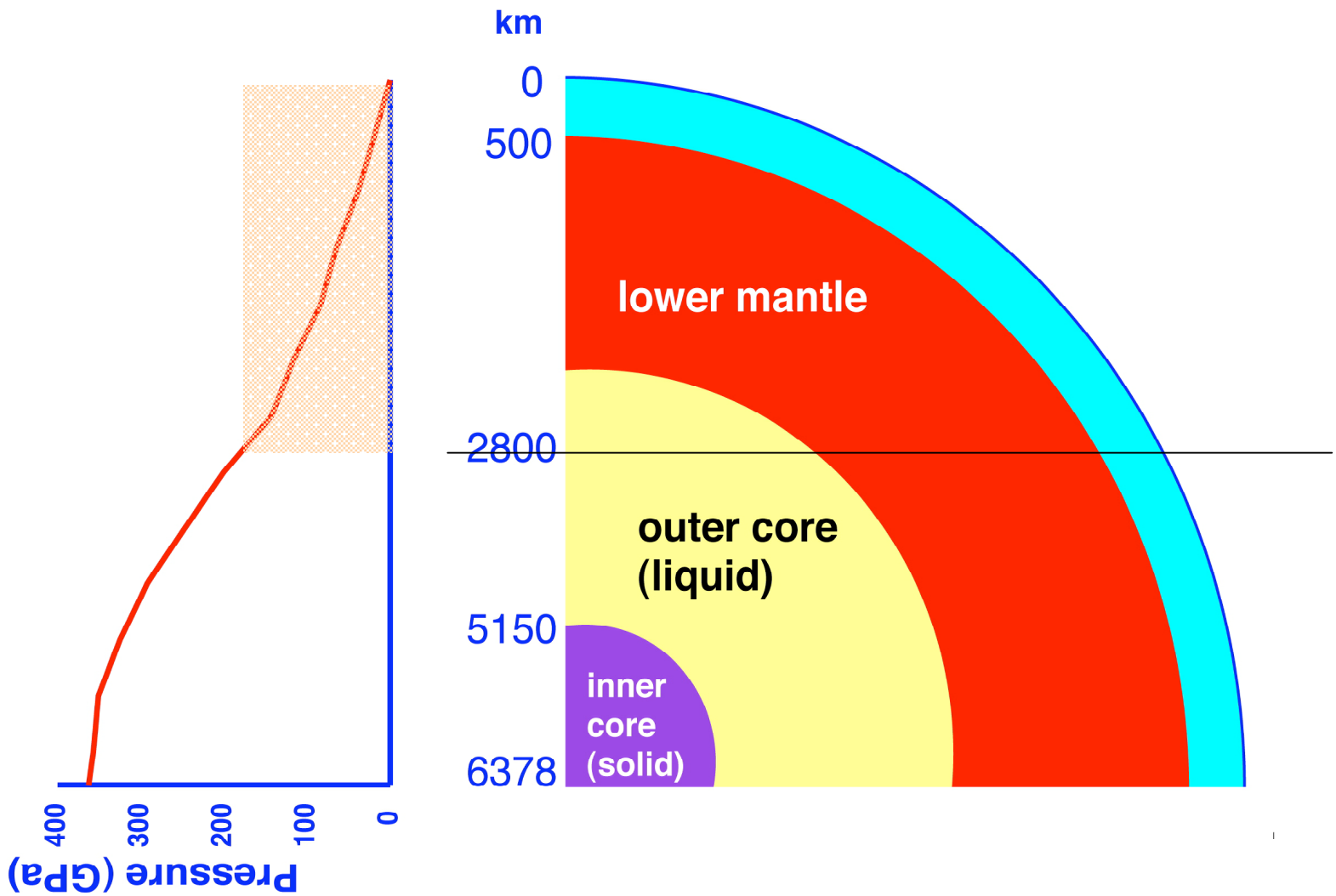




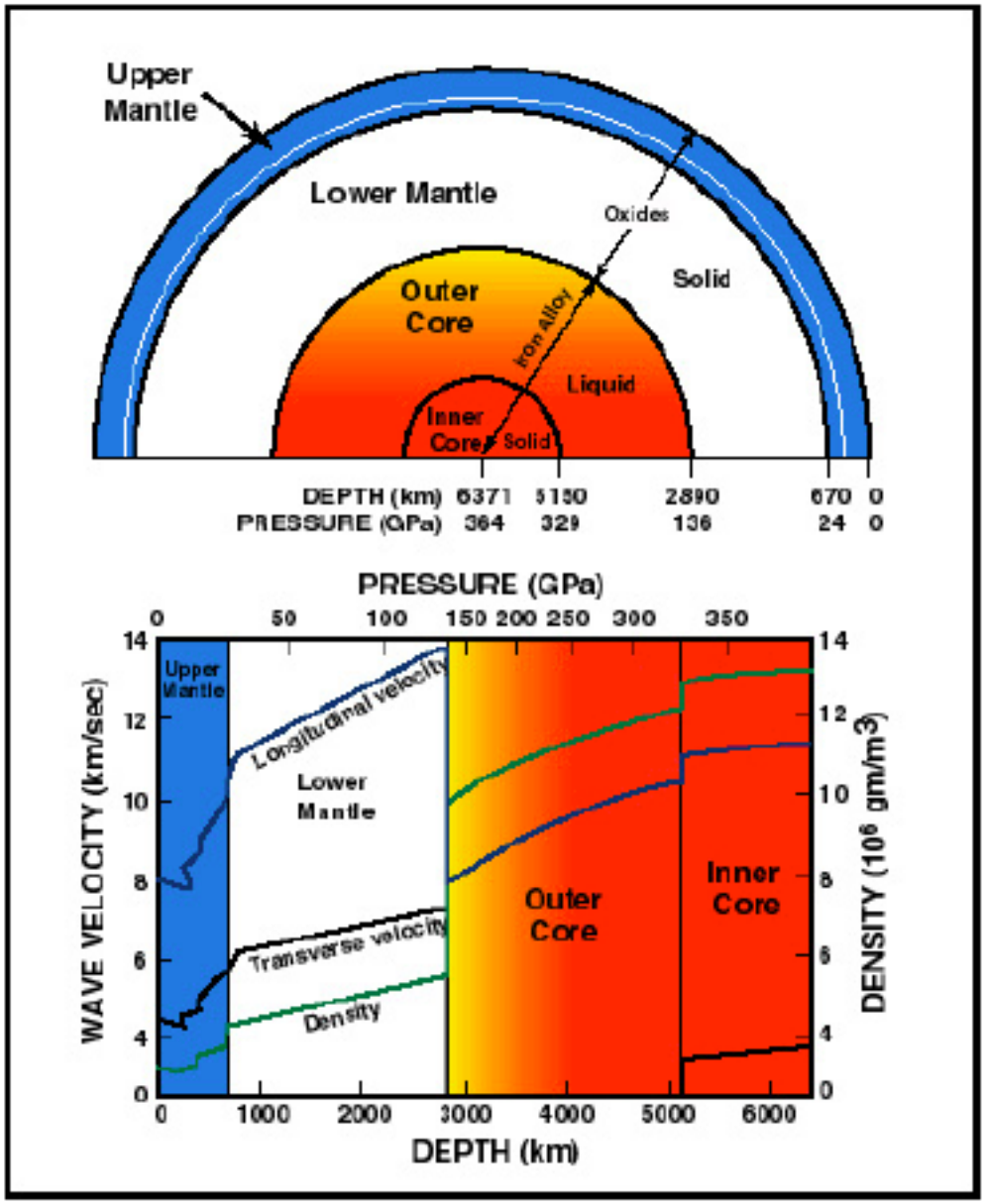
Excellent fits to data are obtained in this way. Permits one to identify particular coupling mechanisms as most important…

Geophysics applications of NRS

P vs. depth for Earth



Profile of the Earth's interior



1. **Magnesiowustite [(Mg,Fe)O] and silicate perovskite [(Mg,Fe)SiO_3] are two major phases in the lower mantle.**
2. Fe-Ni alloy is the major component in the Earth's core. Earth's outer core also contains ~10% of light element(s) and a certain amount of light element(s) may be present in the inner core. H, C, O, Si, and S are candidate major light elements.
3. Sound velocities have been directly measured by seismic wave studies.
4. Recent seismic wave studies show that seismic wave heterogeneity exists in the lower mantle and the inner core.

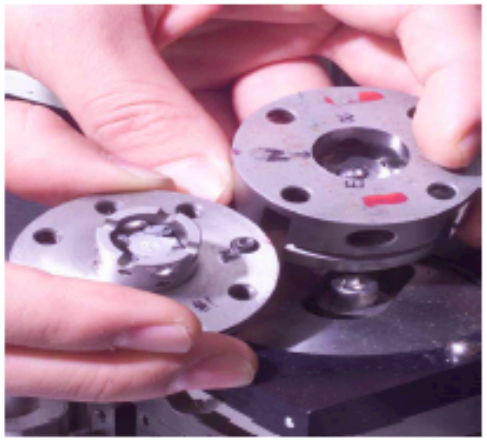
PREM, Dziewonski and Anderson, 1981

IXS study in a diamond anvil cell
In-depth understanding of the Earth's interior

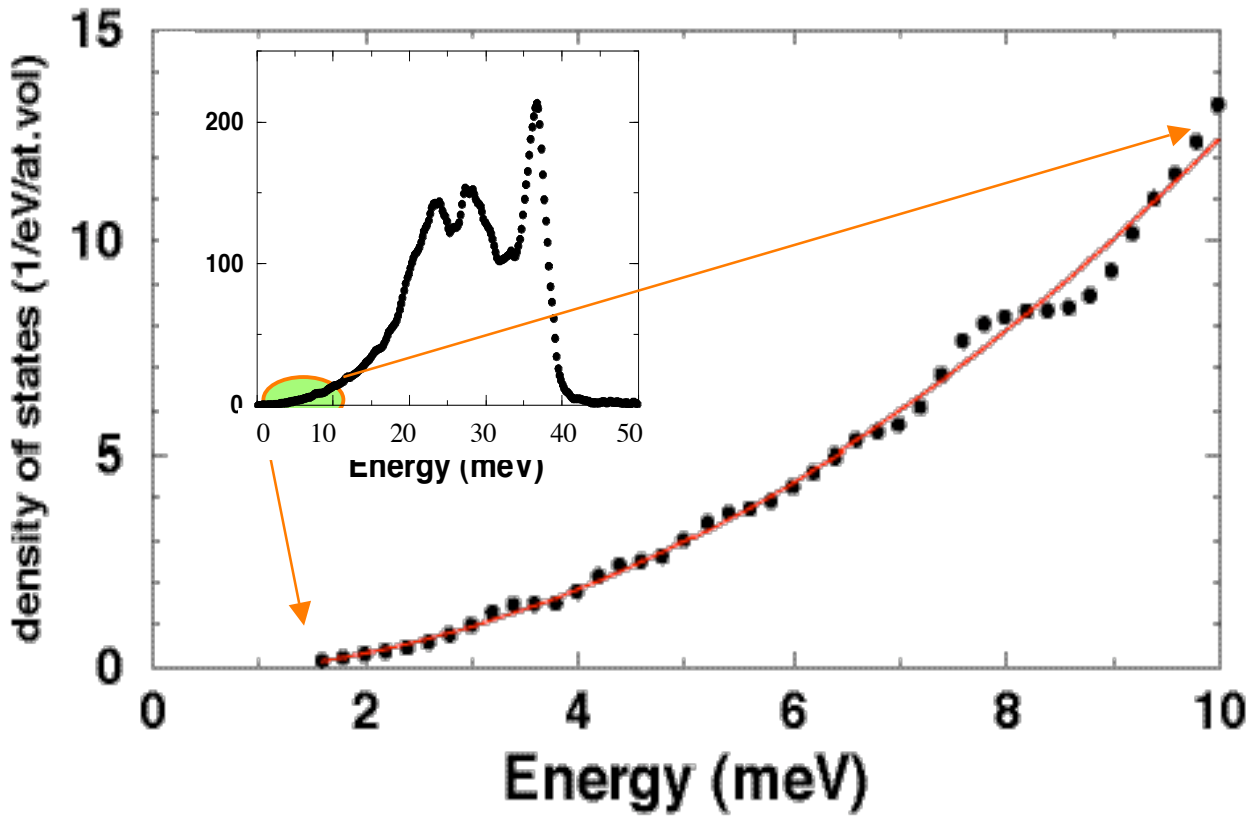
- X-ray diffraction: mw, Fe_3C
- NRIXS: Fe, Fe-Ni, Fe-Si, Fe_3S
- SMS: Fe_3S
- XES: Fe_3C, mw
- IXS (meV): Fe, Fe compounds
- IXS (eV): C, BN

- Crystal structure, P-V-T EOS
- V_D (Vp, Vs, G), Temperature,...
- Magnetism, hyperfine parameters
- Spin state (high-low spin of Fe)
- Phonon dispersion (Vp)
- Electronic structure (bonding)

To better understand the physical and chemical properties of the planetary interiors, we need to study elastic, thermodynamic, vibrational, and magnetic properties of potential mantle and core materials under various pressures and temperatures.



Determination of Debye velocity of sound from phonon density of states

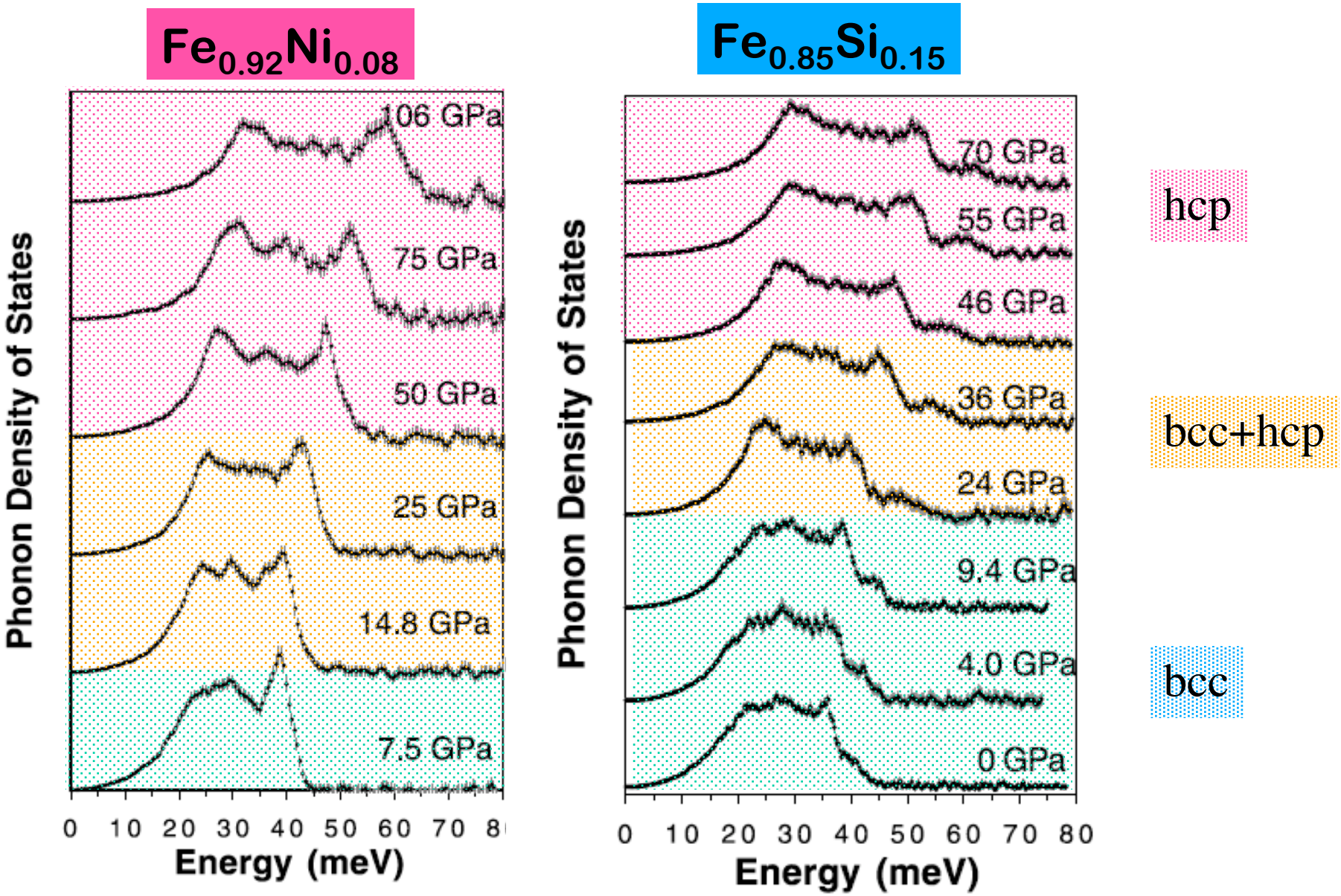


$$D(E) = \frac{V}{2\pi \hbar^3 c_s^3} E^2$$

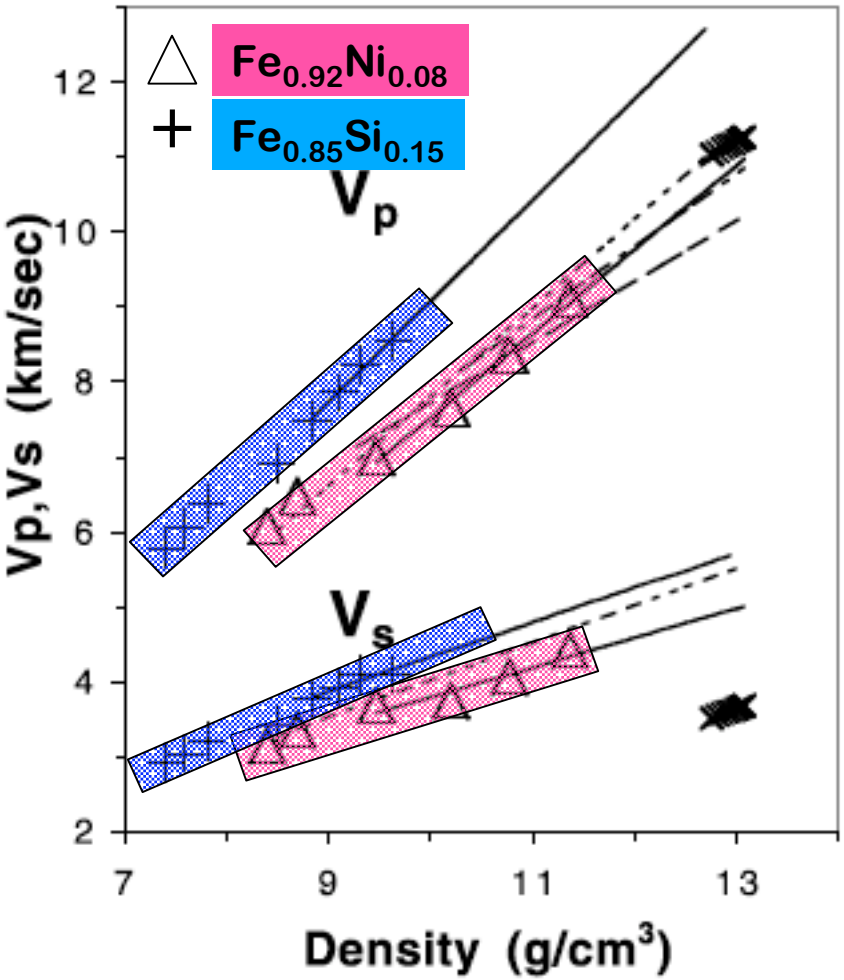
PHYSICAL REVIEW B 67, 094304 (2003)

Measuring velocity of sound with nuclear resonant inelastic x-ray scattering

Michael Y. Hu,[1,*] Wolfgang Sturhahn,[2] Thomas S. Toellner,[2] Philip D. Mannheim,[3] Dennis E. Brown,[4] Jiyong Zhao,[2] and E. Ercan Alp[2]



J.F. Lin, et al, Geophys. Res. Lett., 30 (2003) 2112



$$\frac{K_S}{\rho} = V_P^2 - \frac{4}{3}V_S^2$$

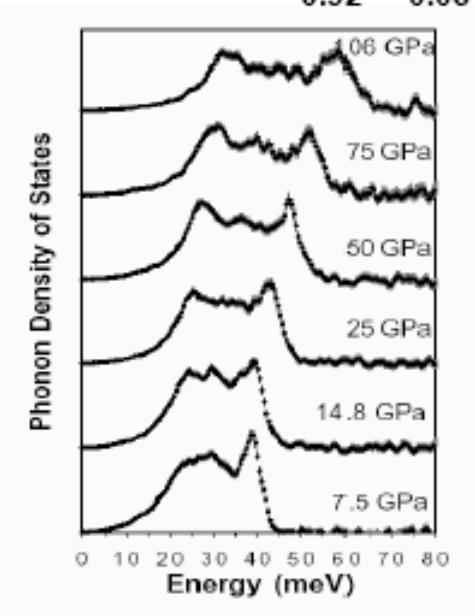
$$\frac{G}{\rho} = V_S^2$$

$$\frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3}$$

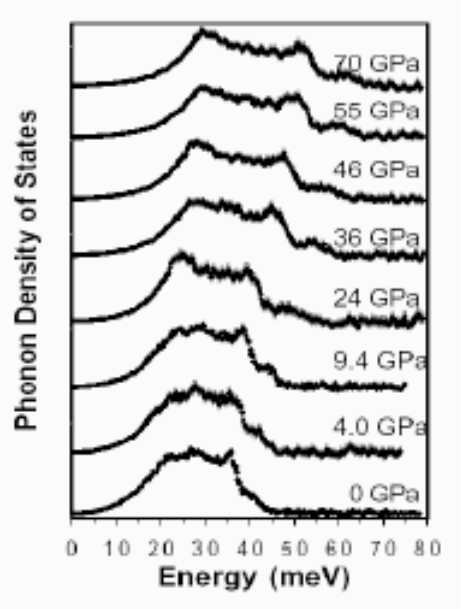
K_S : adiabatic bulk modulus
G : shear modulus
V_P : compression wave velocity
V_S : shear wave velocity
V_D : Debye sound velocity
P : density

Alloying effects of Ni and Si on density, Vp, Vs of hcp-Fe by NRIXS study

PDOS of $Fe_{0.92}Ni_{0.08}$

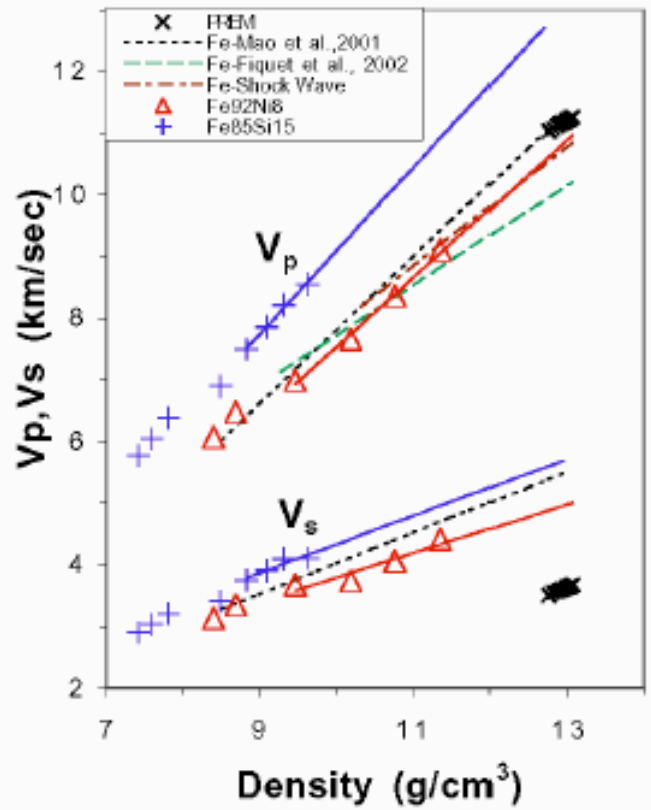


PDOS of $Fe_{0.85}Si_{0.15}$



Lin et al., GRL, 2003

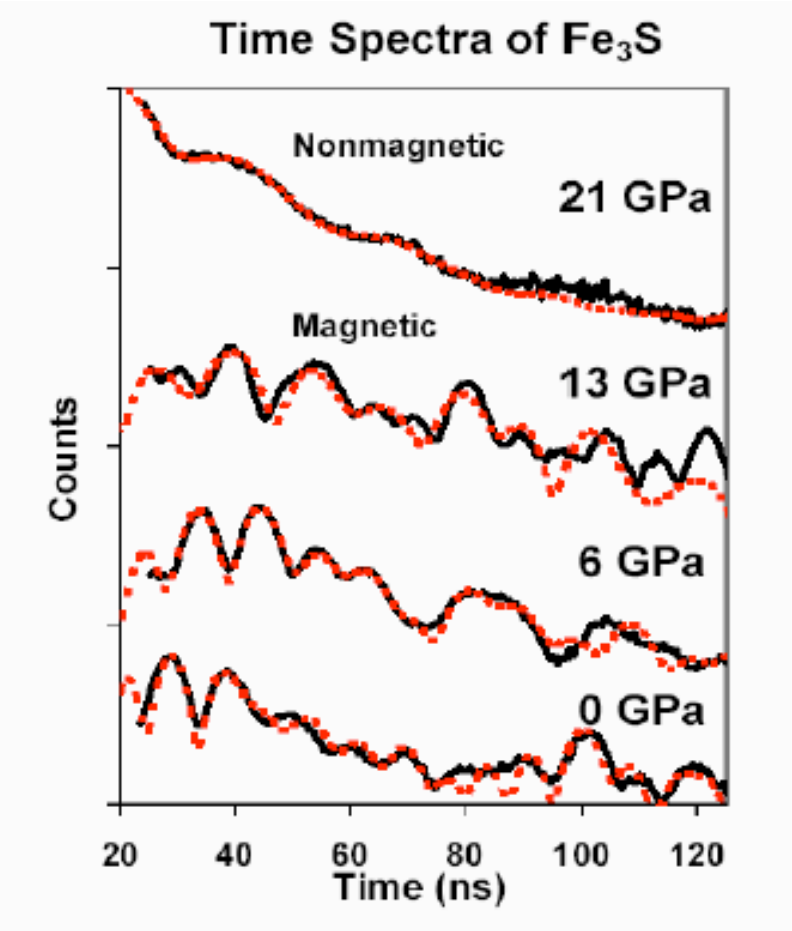
$Fe_{0.92}Ni_{0.08}$ and $Fe_{0.85}Si_{0.15}$ alloys

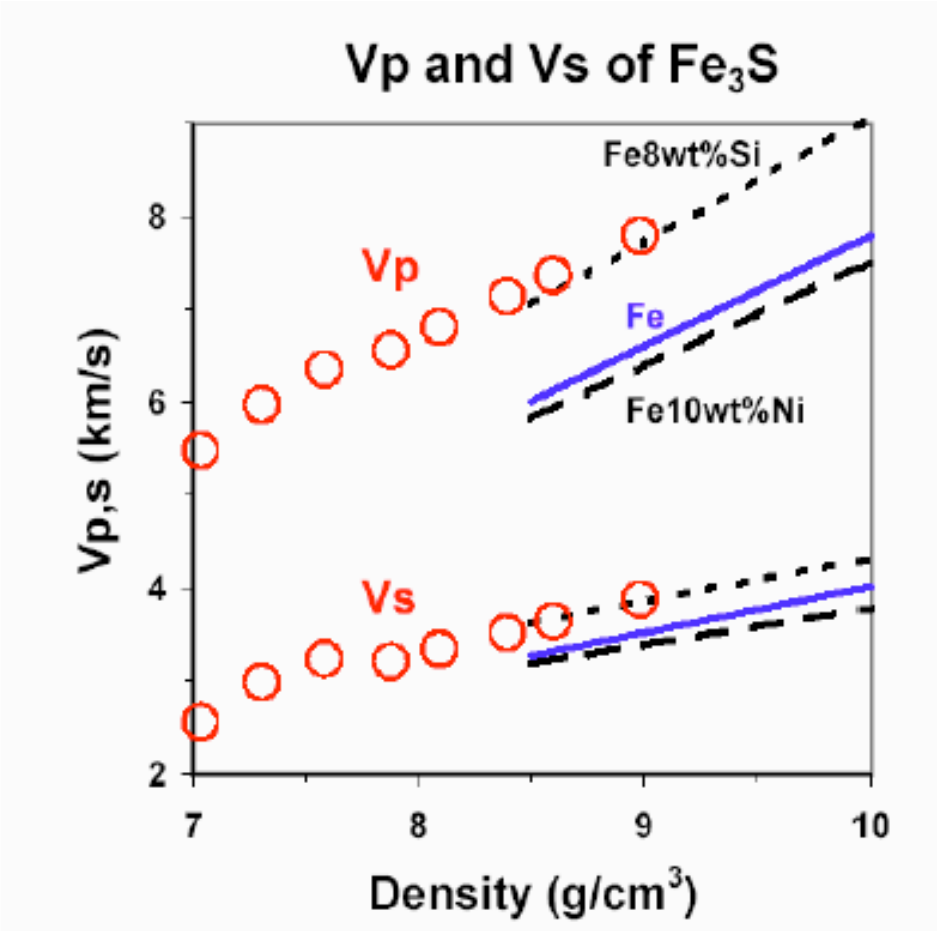


$$\frac{K_S}{\rho} = V_P^2 - \frac{4}{3} V_S^2$$

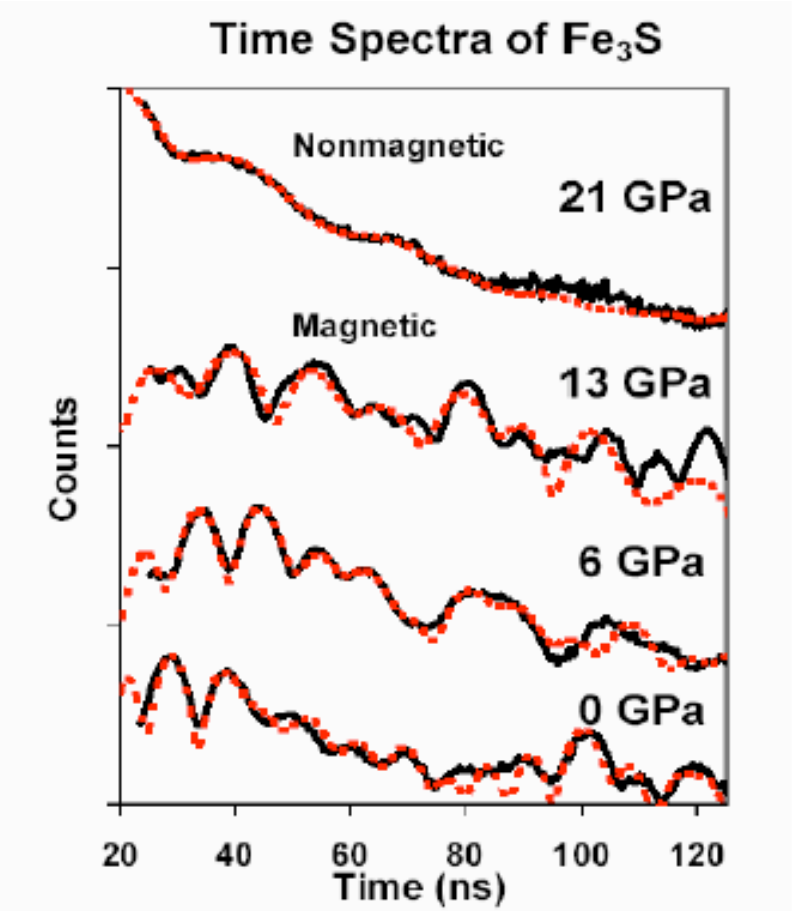
$$\frac{G}{\rho} = V_S^2$$

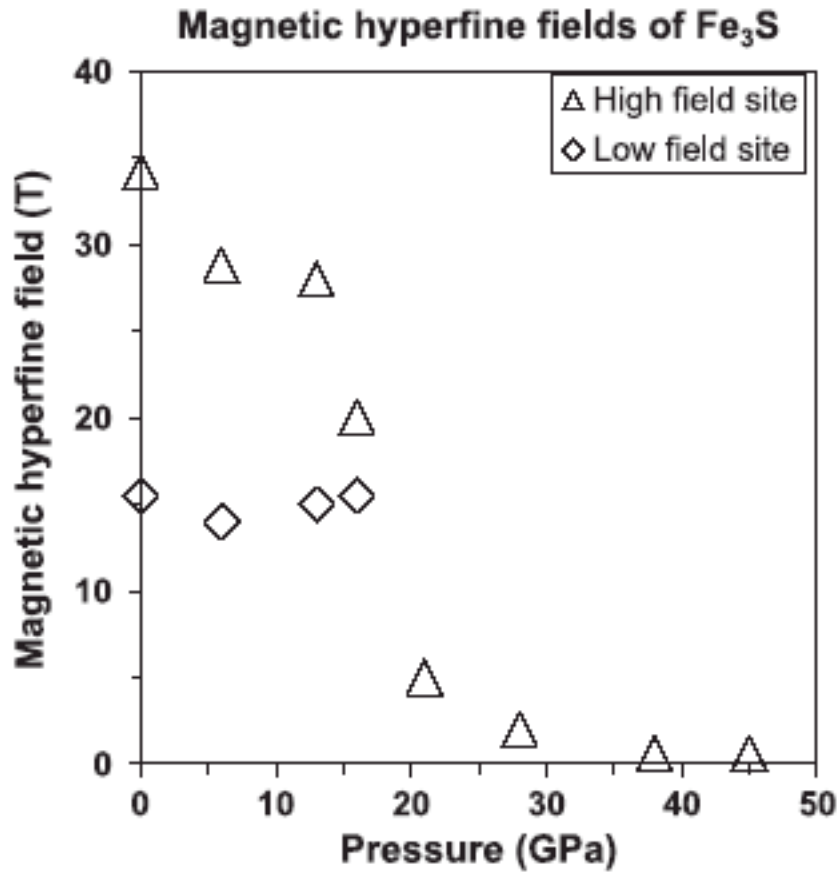
Addition of Ni slightly decreases the compression wave velocity and shear wave velocity of Fe under high pressures. Substitution of Si in Fe increases the compressional wave velocity and shear





Fe_3S undergoes a magnetic to non-magnetic transition at ~18 GPa. The magnetic transition significantly affects the elastic, thermodynamic, and vibrational properties of Fe_3S.

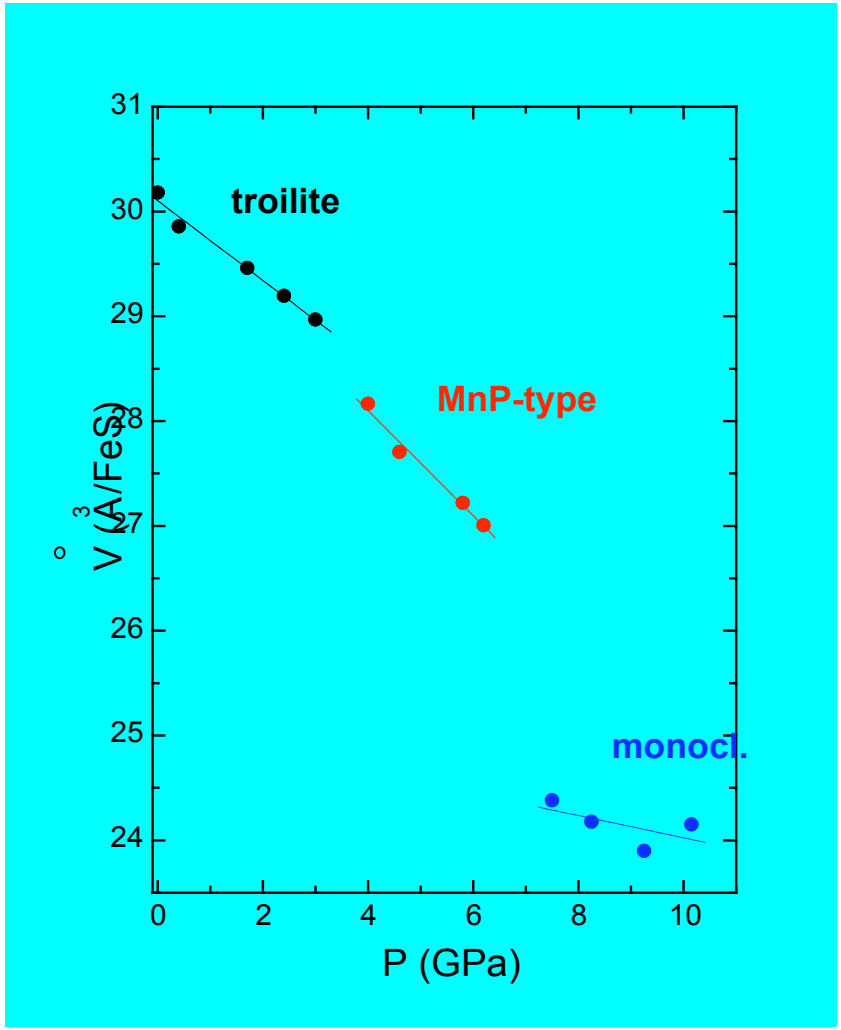


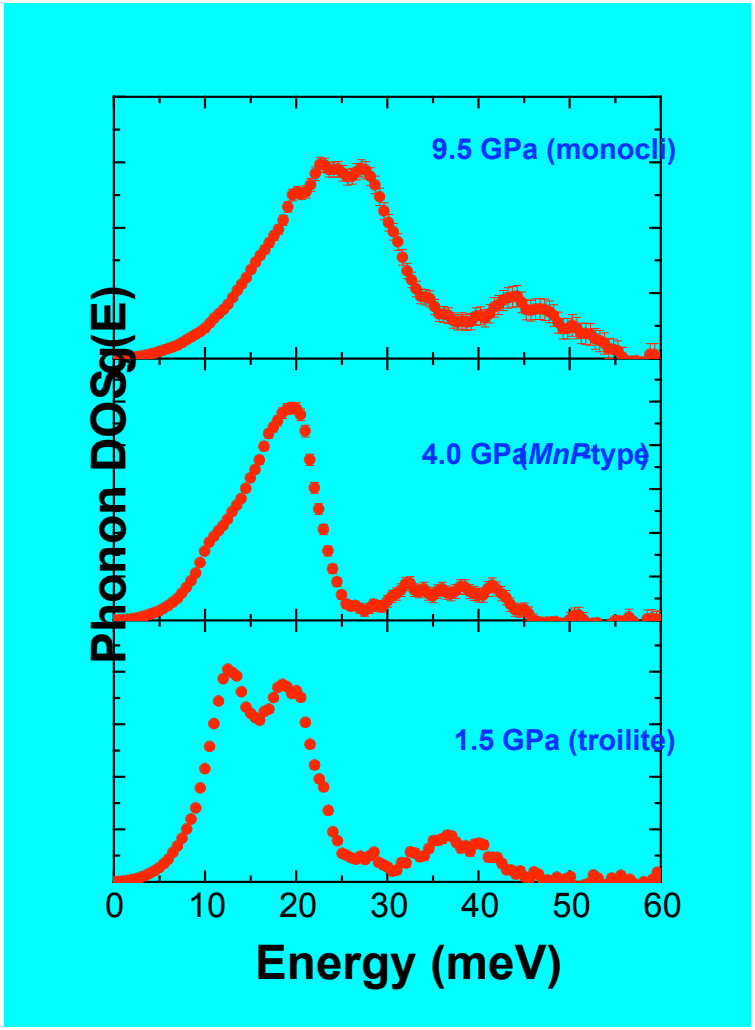


The magnetic collapse significantly affect the thermodynamic, elastic and vibrational properties of Fe3S, it may affect the phase relations in Fe-S system, and may thus affect the solid solubility under high pressure.

J.F. Lin, et al, Earth and Planetary Science Letters, 226 (2004) 34

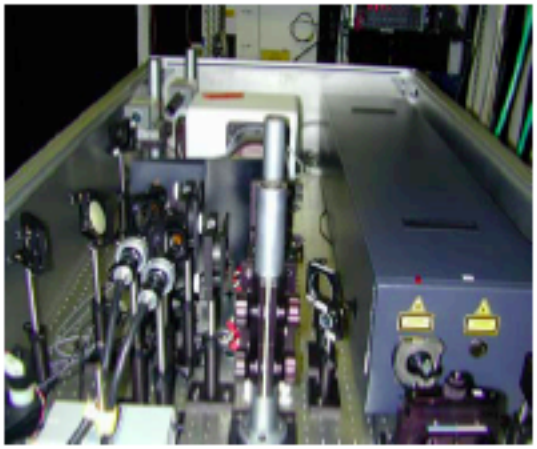
Pressure induced phase transitions in FeS studied via nuclear resonant inelastic x-ray scattering

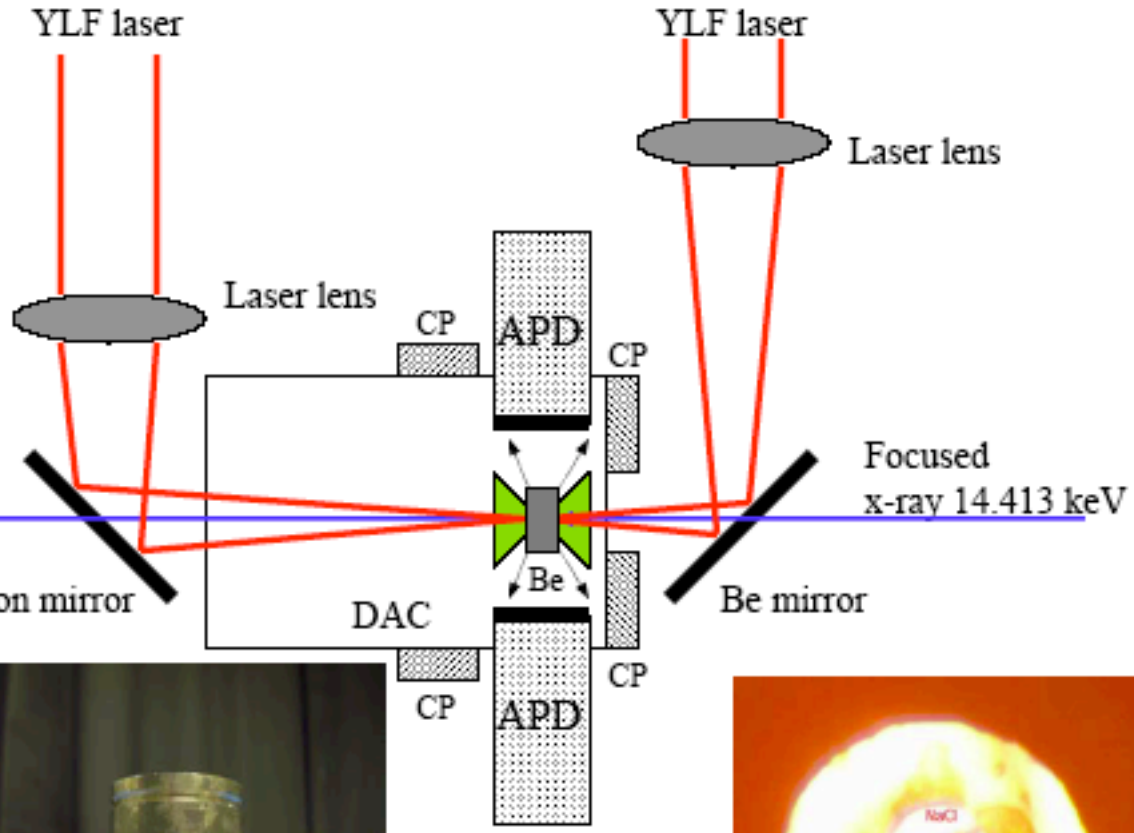


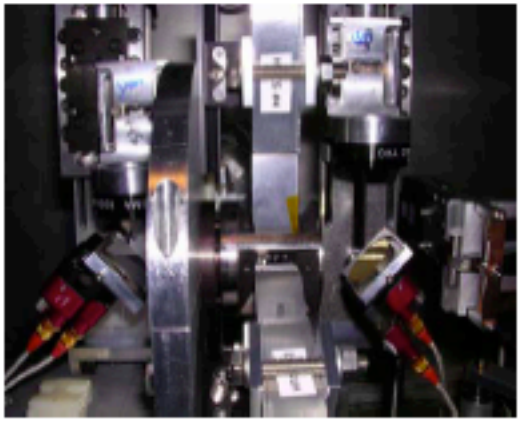


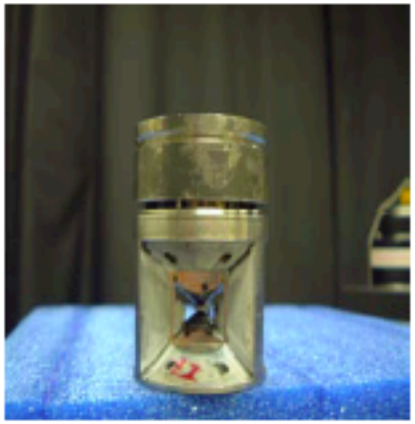
Kobayashi, et al, Phys. Rev. Lett,93 (2004) 195503

NRIXS in a Laser-heated diamond cell
Temperature effects on physical properties of iron



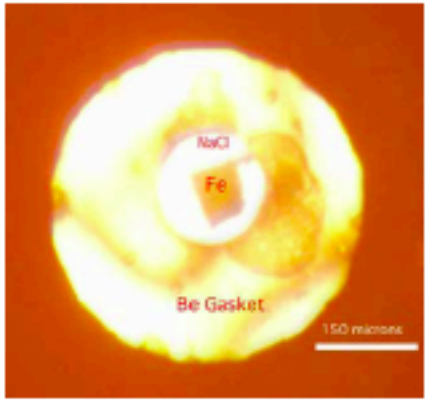






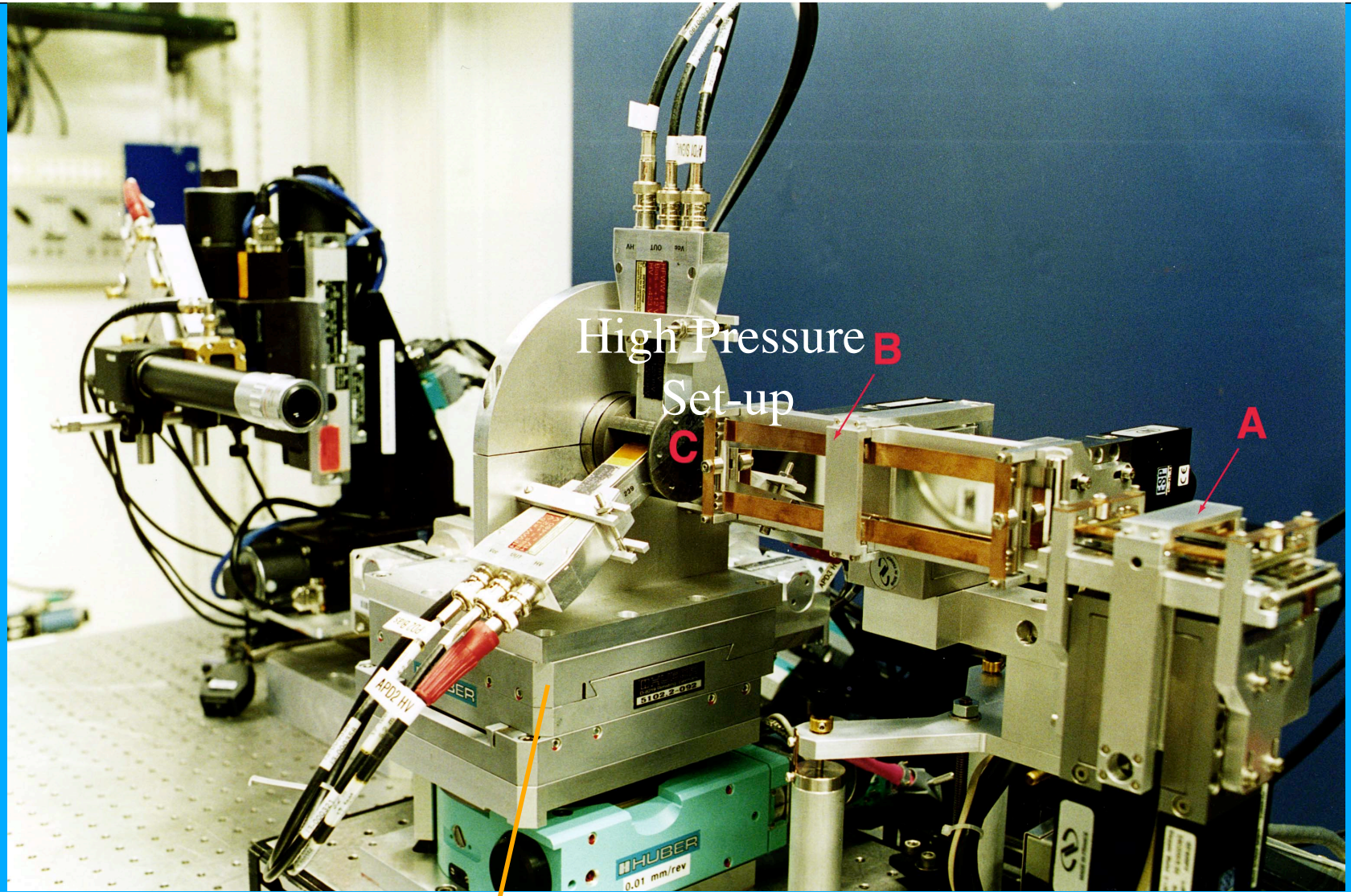
DAC

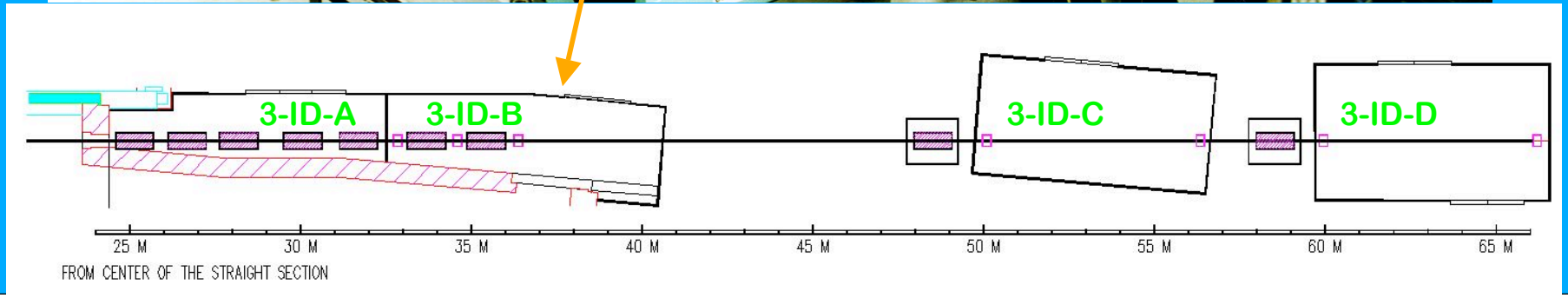
Sample
in DAC

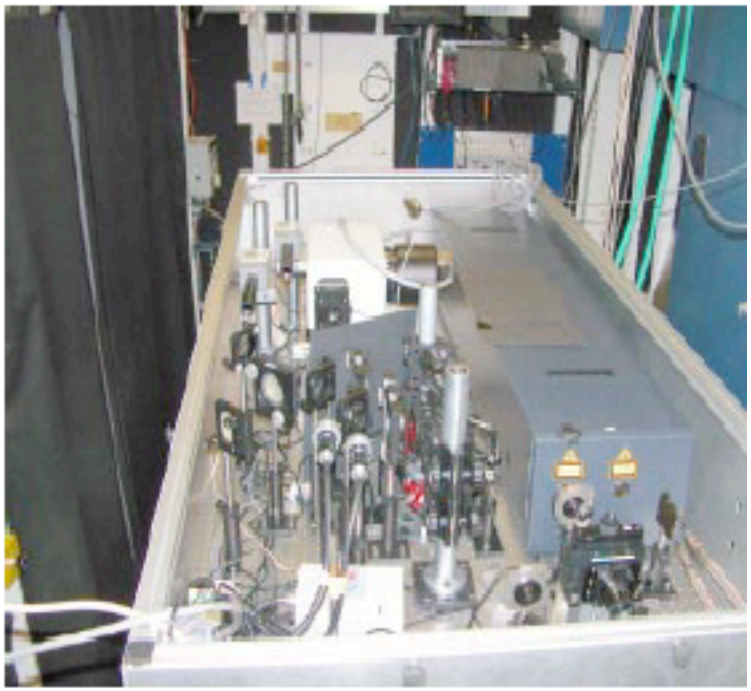


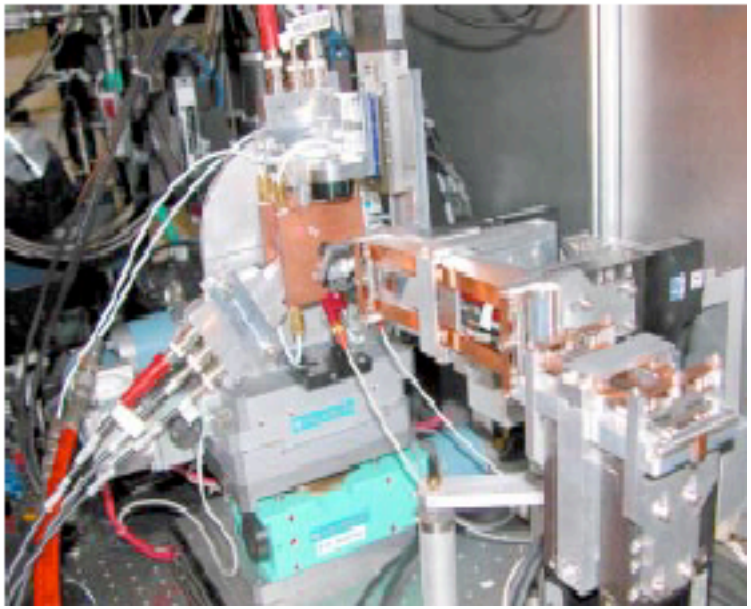
Laser heating system at Sector 3, APS

In cooperation with W. Sturhahn, J. Zhao, G. Shen, H.K. Mao, and R.J. Hemley

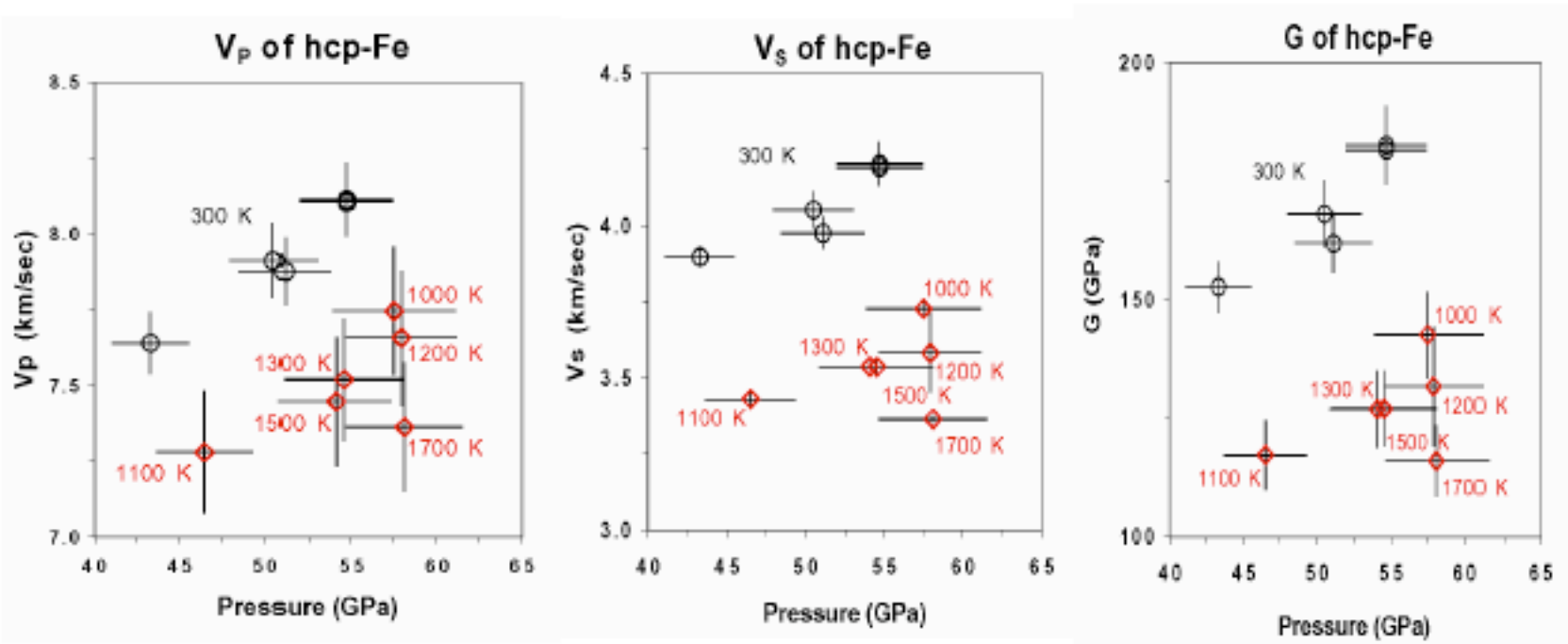

High Pressure
Set-up
B
A
C
HUBER
0.01 mm/rev


3-ID-A
3-ID-B
3-ID-C
3-ID-D
25 M
30 M
35 M
40 M
45 M
50 M
55 M
60 M
65 M
FROM CENTER OF THE STRAIGHT SECTION



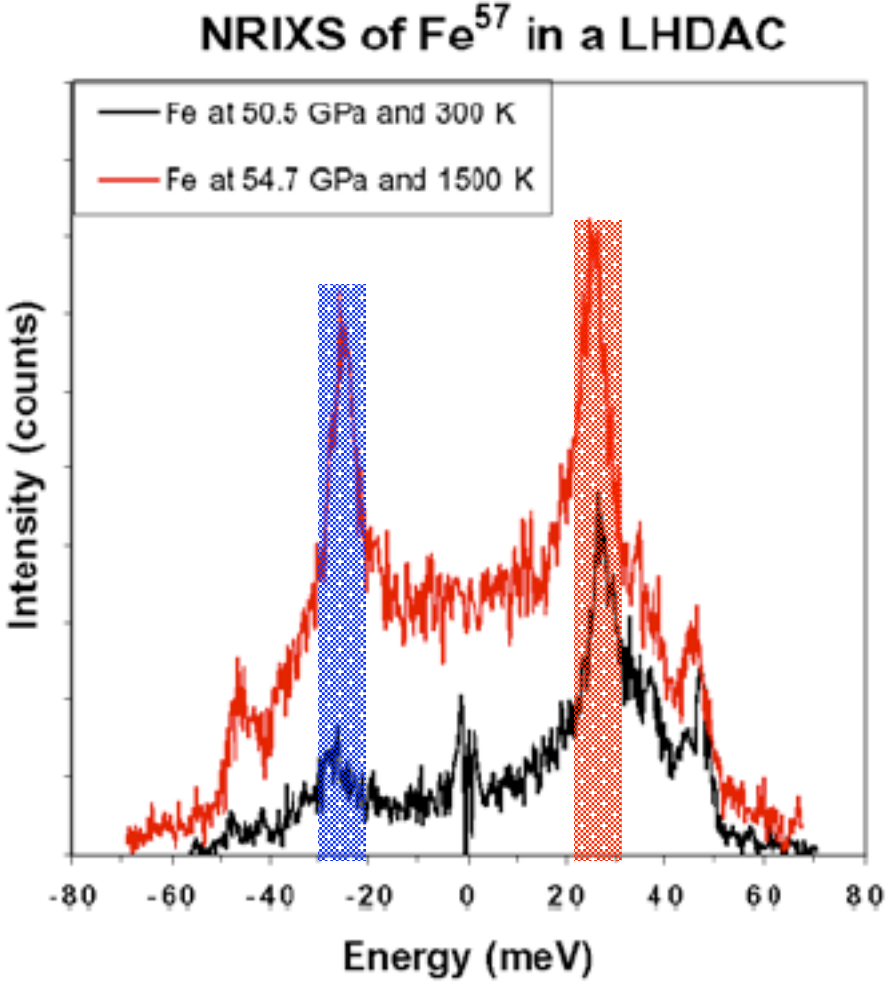


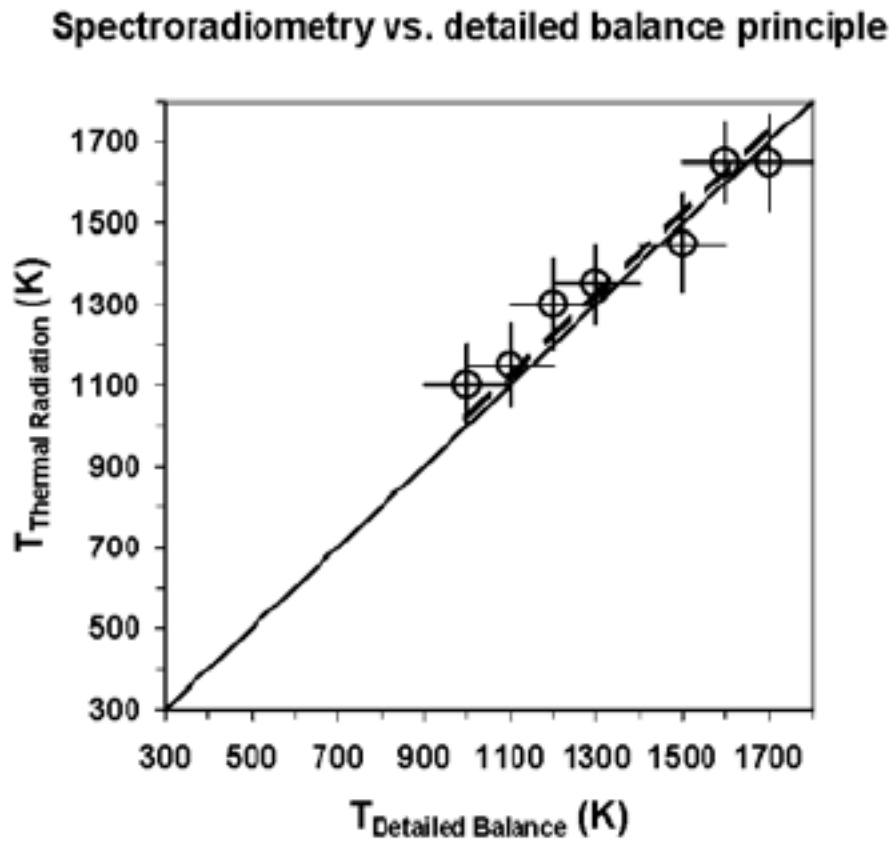
Vp, Vs, G of hot dense hcp-Fe: temperature effect (versus pressure plot)



Temperature has a significant effect on V_P, V_S and G. The V_P, V_S, and G decrease with increasing temperature under high pressures; i.e., at a given pressure of ~54 GPa, V_P decreases by ~7%, V_S decreases by ~14%, and G decreases by ~28% with a temperature increase of 1000 K.

How to measure temperature in a DAC ?





J.F. Lin, et al, Geophys. Res. Lett., 31 (2004) L13611

$$I(E) = I(-E)e^{(E/kT)}$$

$$\int I(E)dE = \int I(-E)e^{(E/kT)}dE$$

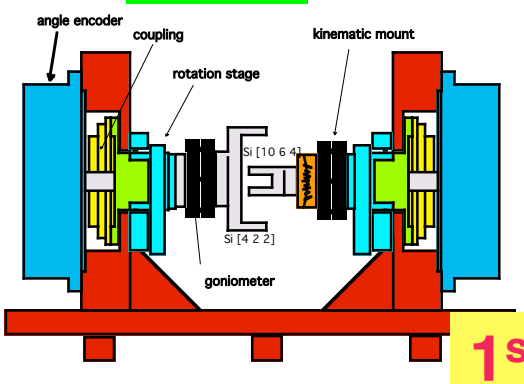
The Mössbauer isotopes

Isotope	Energy (eV)	Half-life (ns)	ΔE (neV)
• ^{181}Ta	6238.	9800.	0.067
• ^{169}Tm	8401	4.	114.0
• ^{83}Kr	9400.	147.	3.1
^{73}Ge	13263.	2953.	0.15
• ^{57}Fe	14413.	97.8	4.67
• ^{151}Eu	21532.	9.7	47.0
• ^{149}Sm	22490.	7.1	64.1
• ^{119}Sn	23870.	17.8	25.7
• ^{161}Dy	25655.	28.2	16.2
• ^{40}K	29560.	4.25	107.0
•^{121}Sb	37130.	5.0	131.6
^{145}Nd	67100.	67.1	6.8
• ^{61}Ni	67400.	5.1	89.0
^{193}Ir	73000.	6.3	72.3
^{133}Cs	81000.	6.4	71.5
^{67}Zn	93300.	9200.	0.049

• Observed

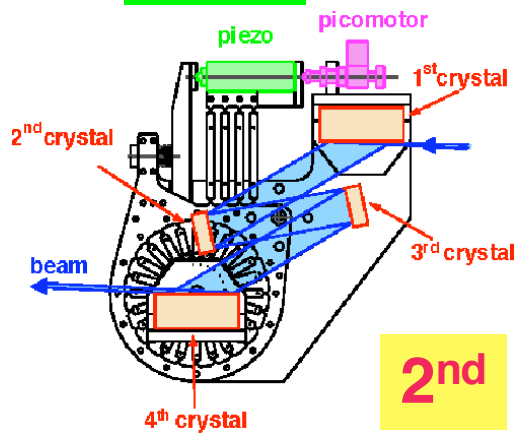
Generations of high-resolution monochromators

1992



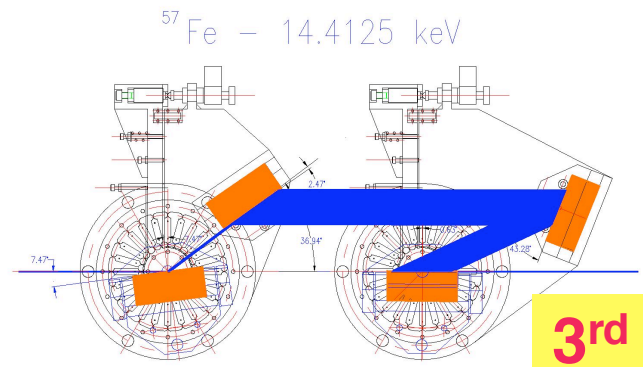
1st

1999



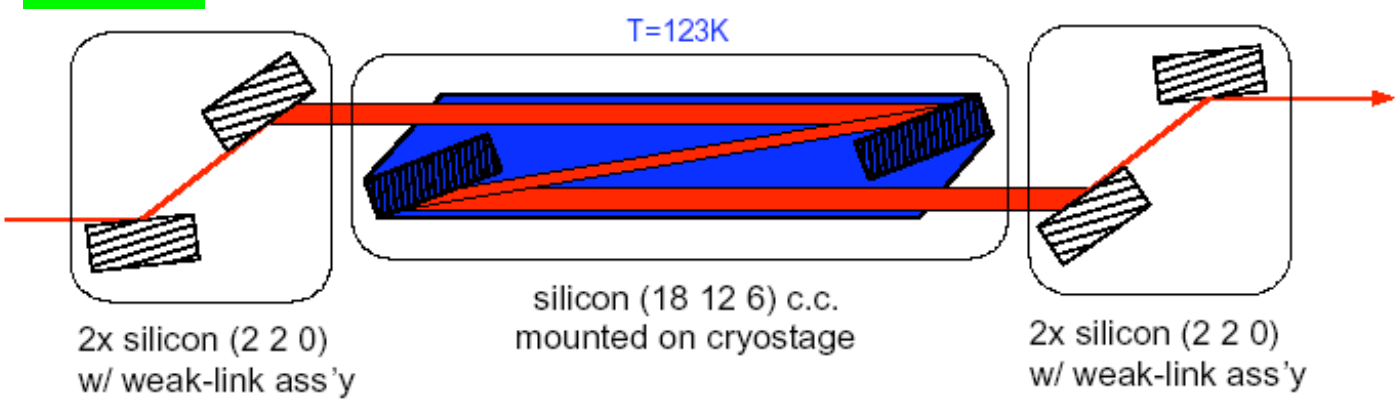
2nd

2002



3rd

2004

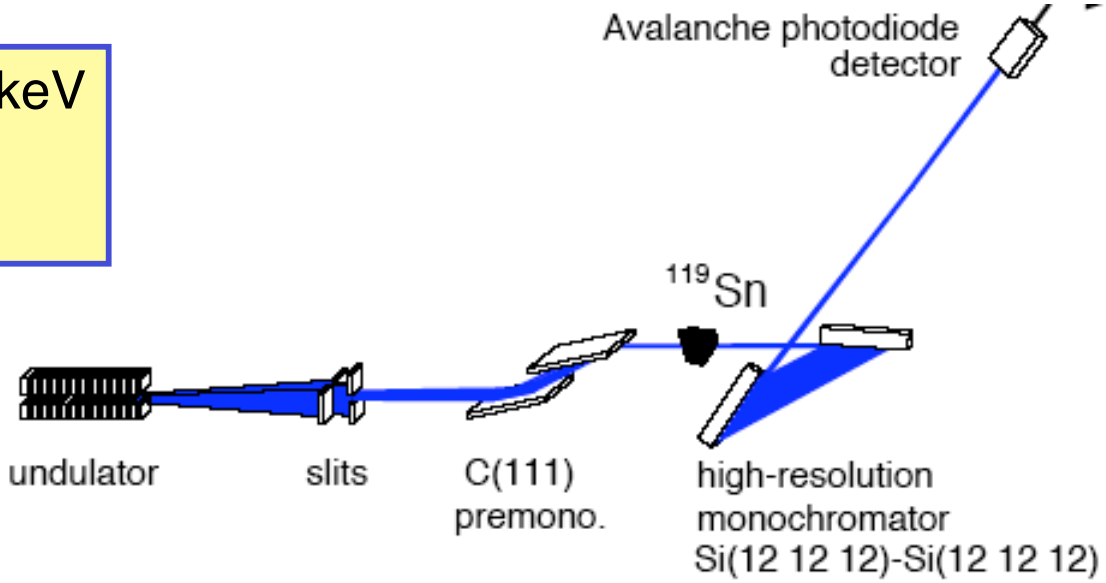


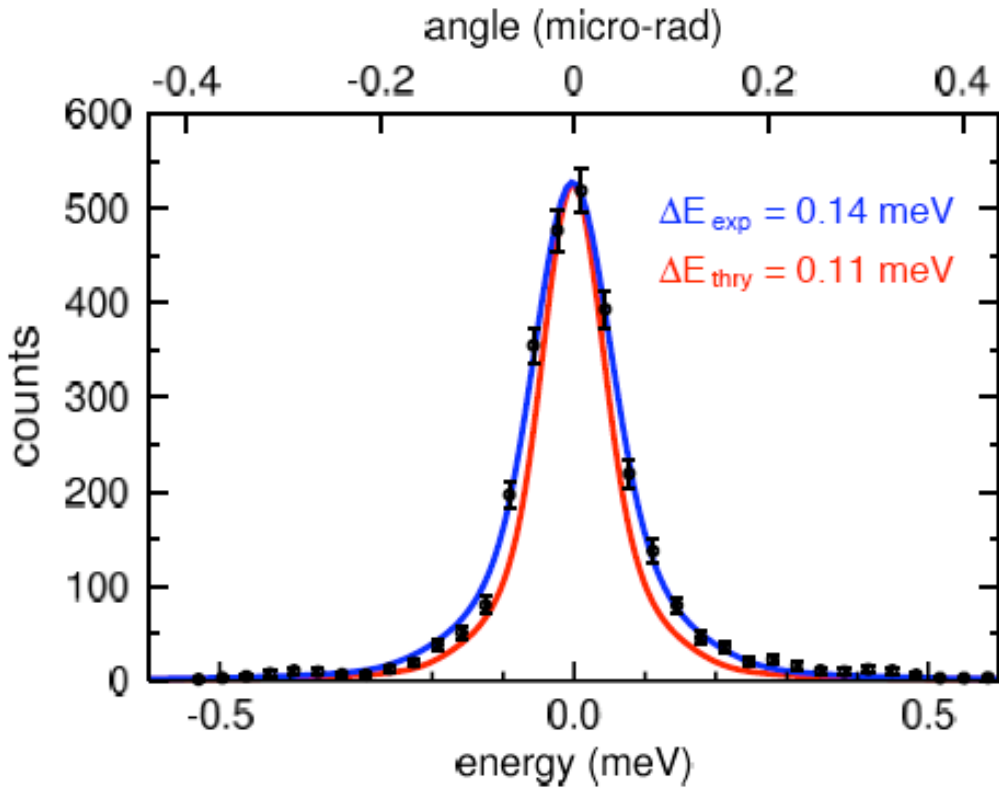
4th

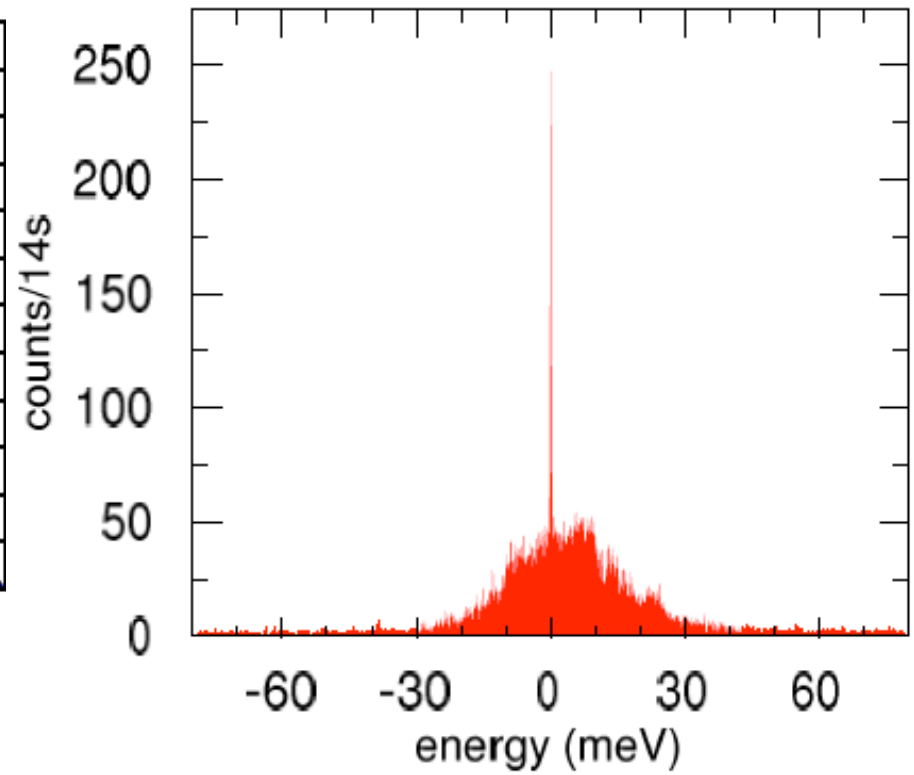
T. Toellner

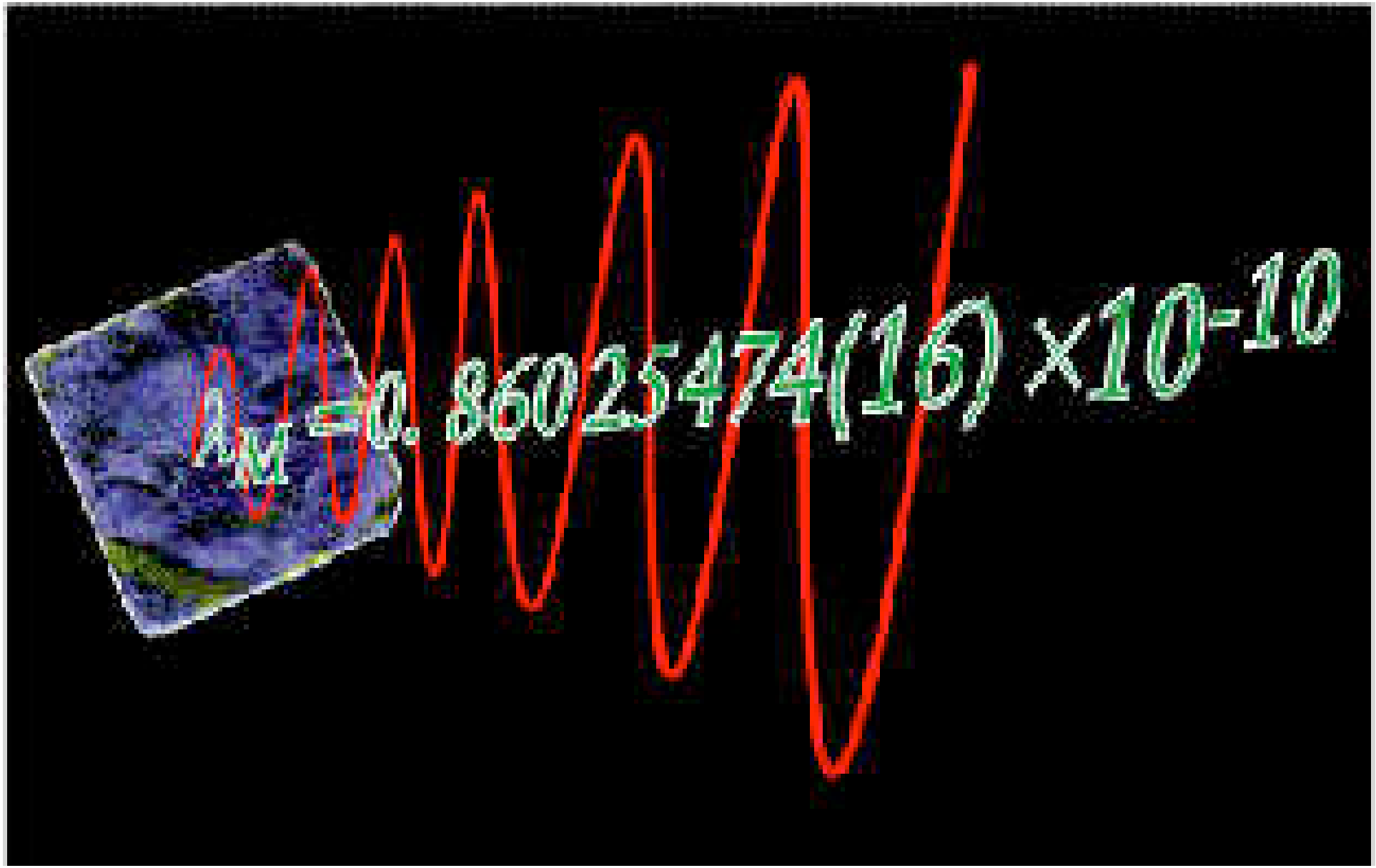
Record resolution at 23.870 keV
^{119}Sn nuclear resonance
T. Toellner, 2003

$$E/\Delta E = 1.7 \cdot 10^8$$








$\Delta\nu_M = 0.86025474(16) \times 10^{-10}$

Measuring wavelengths and lattice constants with Mossbauer wavelength standard

Higher accuracy ($\Delta E/E \sim 10^{-13}$ possible)

Reproducible independent of temperature, pressure, composition, and other parameters

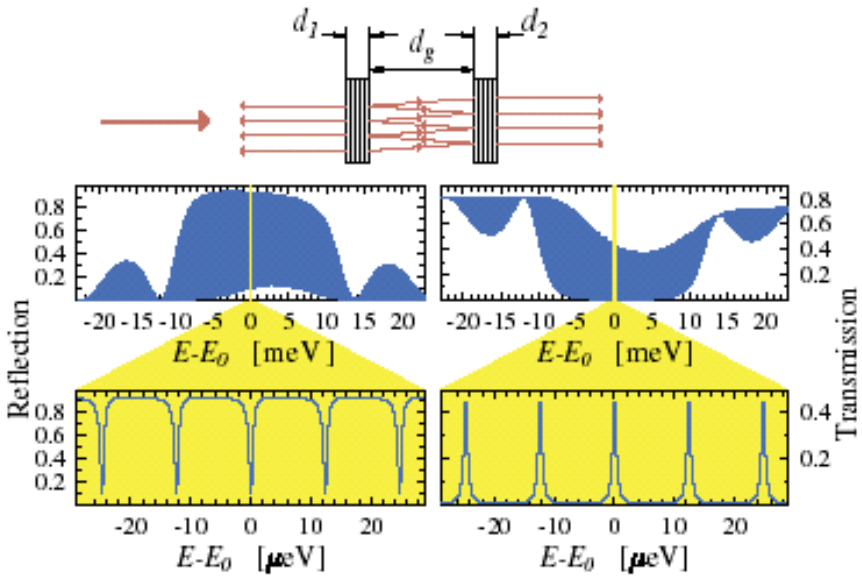
Available between 6-100 keV range at more than a dozen energies

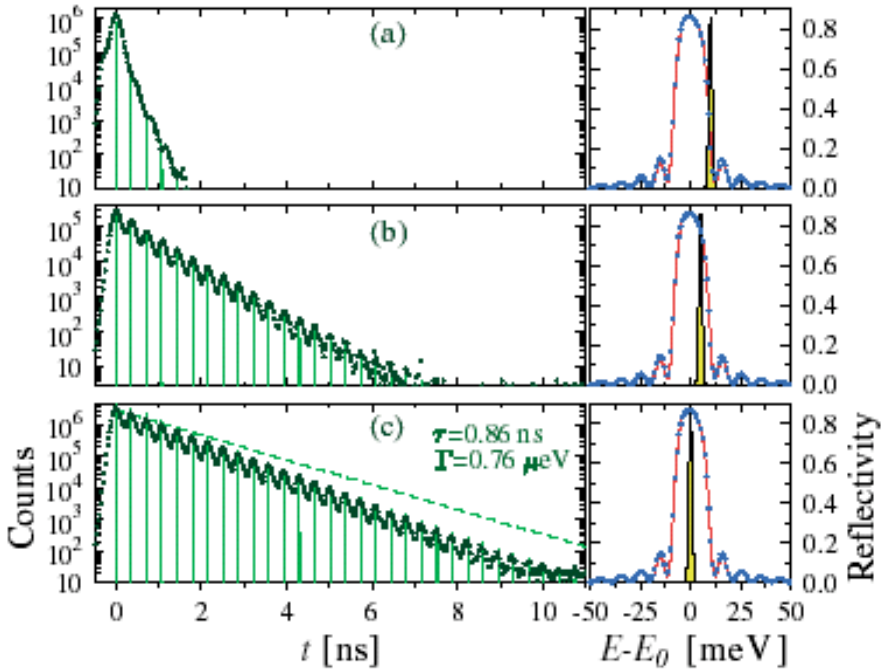
Y. Shvydko, et al, Phys. Rev.Lett., 45 (2000) 495
J. Synchrotron Rad. 9 (2002) 17

Wavelength & energies of Mossbauer isotopes determined at a synchrotron radiation source

isotope	E (eV)	λ (Å)	$\delta\lambda/\lambda$ (10^{-7})
^{57}Fe	14412.497(3)	0.86025474(16)	1.9
^{151}Eu	21541.418(10)	0.57556185(27)	4.7
^{119}Sn	23879.478(18)	0.51920811(39)	7.4
^{161}Dy	25651.368(10)	0.48334336(19)	4.0

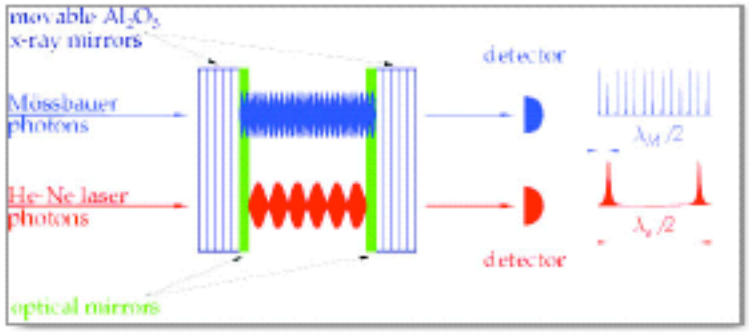
X-Ray Fabry-Perot Interferometer



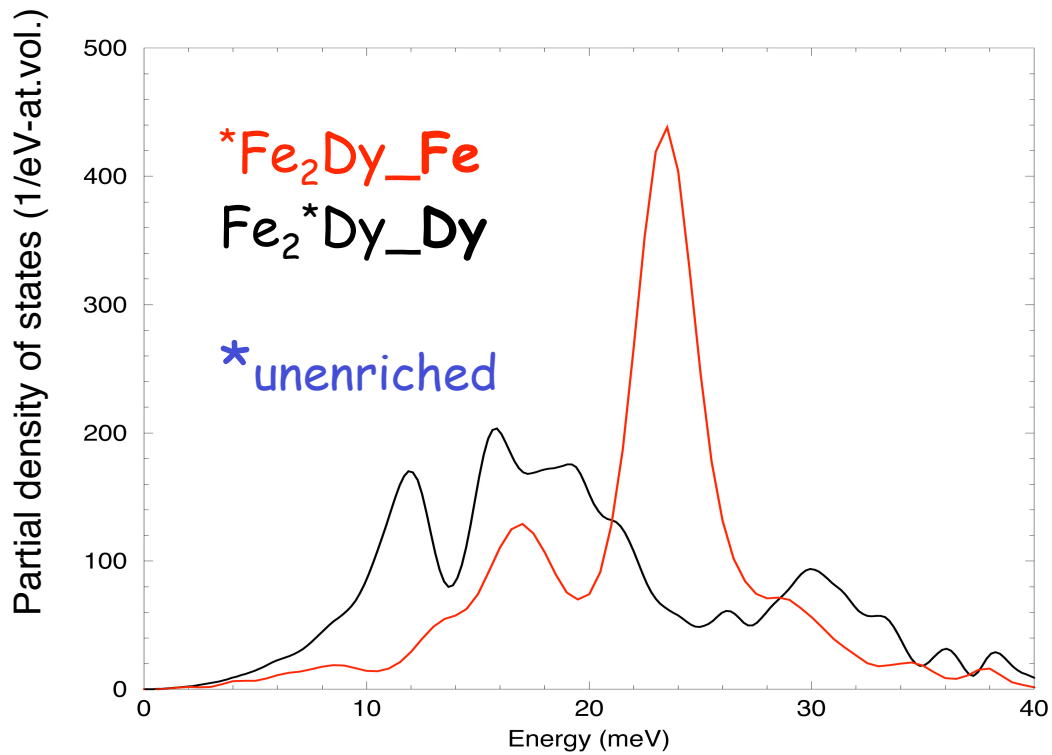


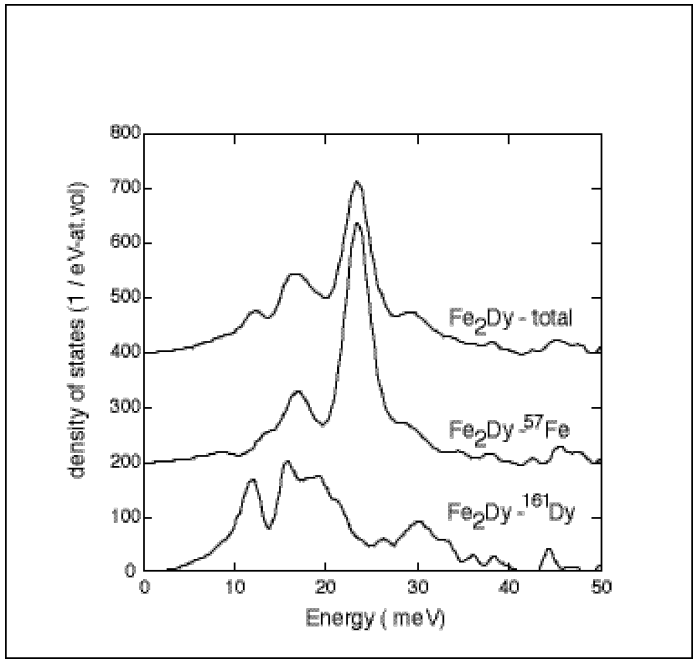
Shvydko, et al, PRL 90 (2003) 013904

A future combined x-ray/visible Fabry-Perot Interferometer



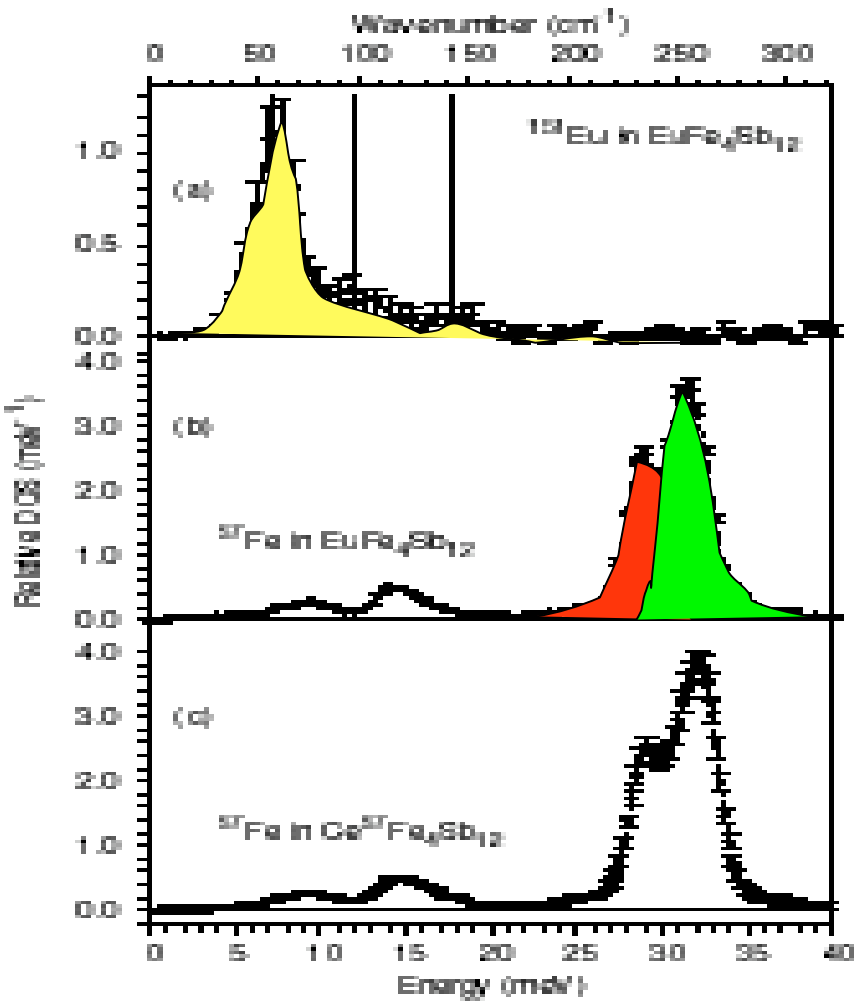
Measurement of partial vibrational density of states on both elements in the same compound



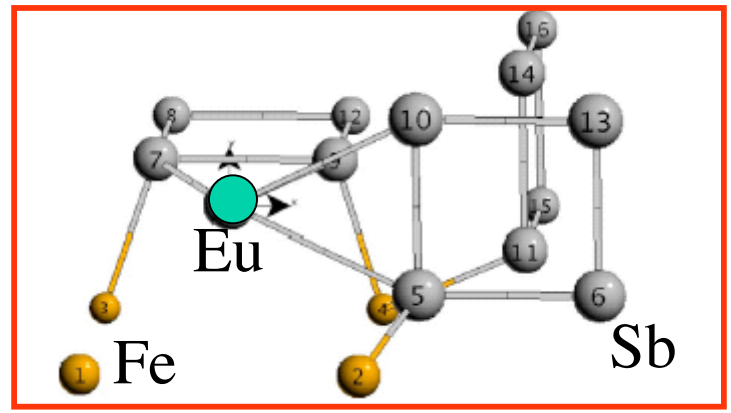


In collaboration with D. Brown, Northern Illinois University

Filled skutterudite: $EuFe_4Sb_{12}$



G. Long et al (unpublished)



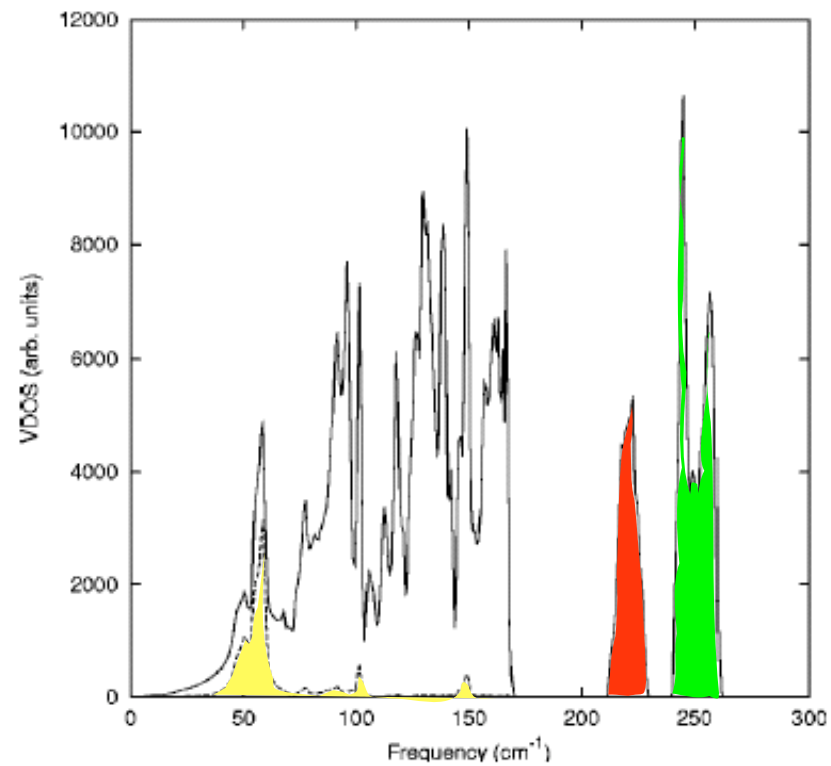
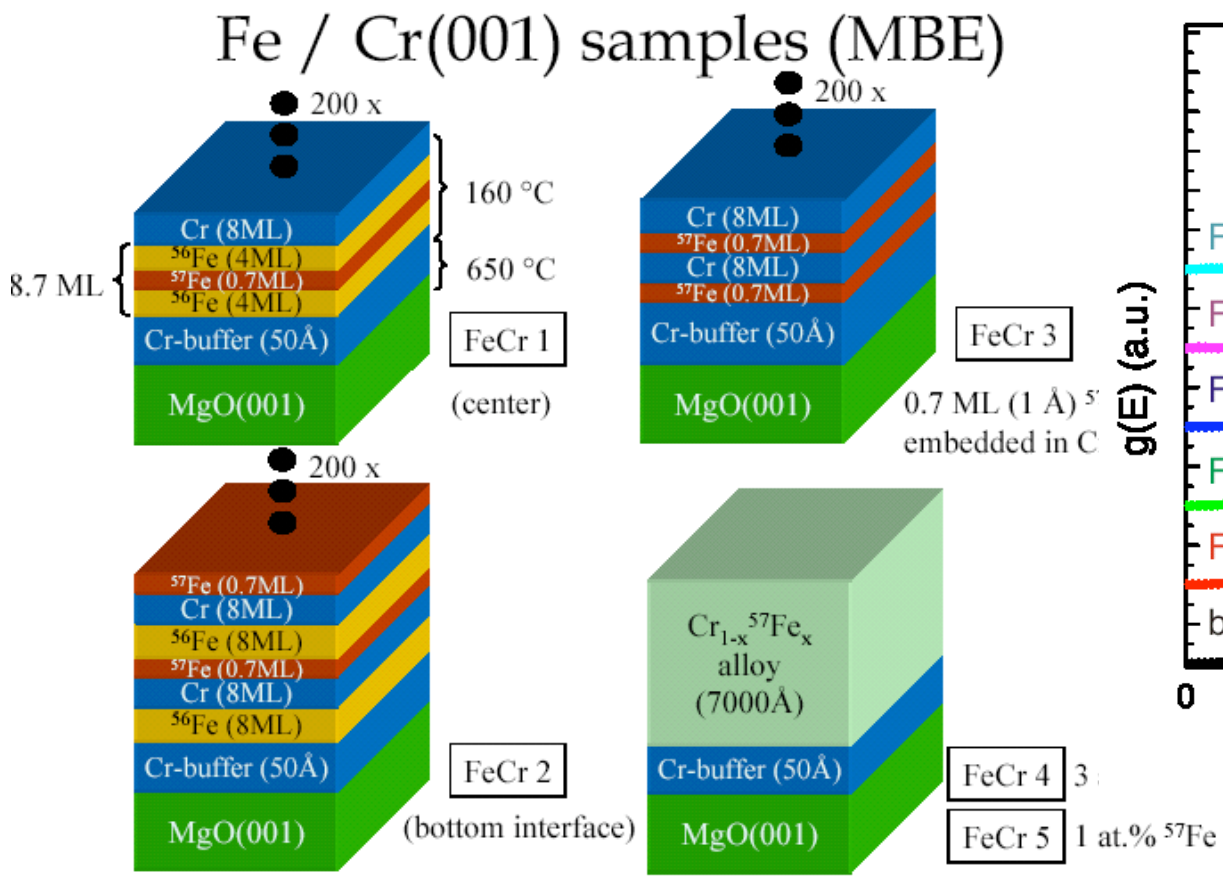
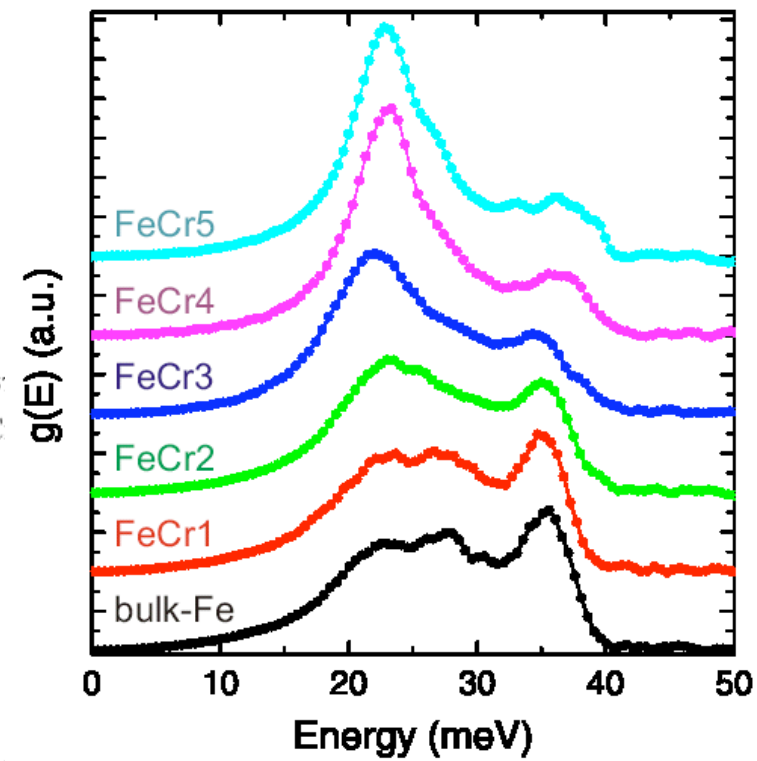


FIG. 4. Calculated vibrational density of states (VDOS): Total VDOS (solid) and La projected VDOS (dashed).

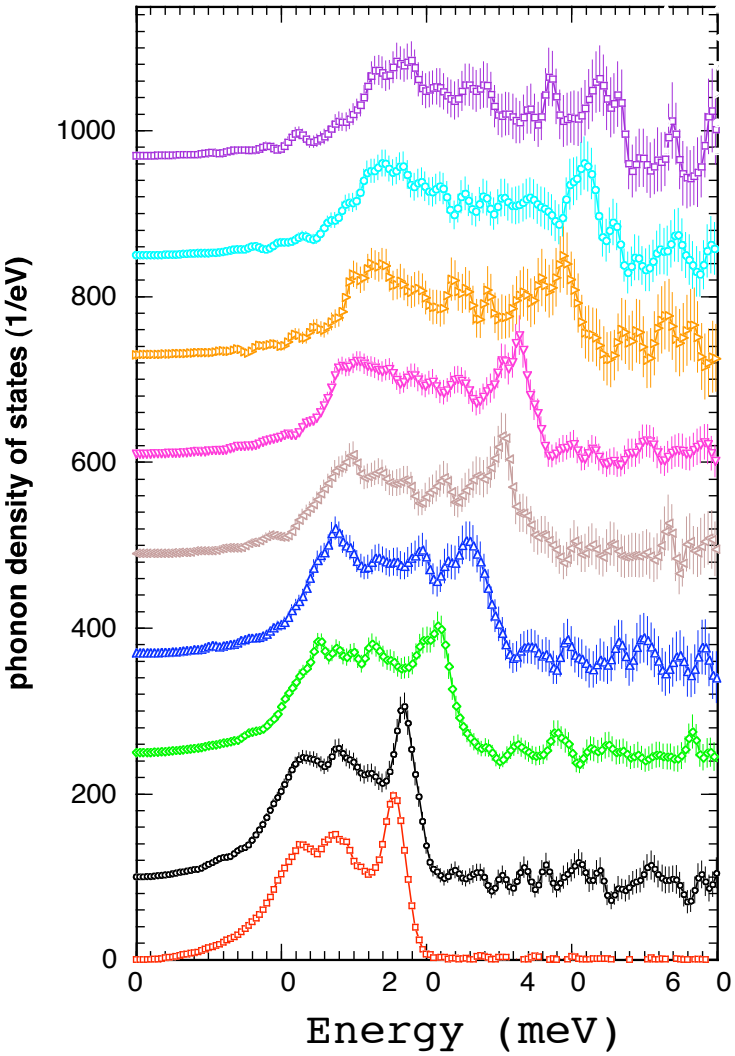
Feldman, et al, Phys Rev B 68 (2003) 94301

Werner Keune, Duisburg
Phonon confinement in multilayers



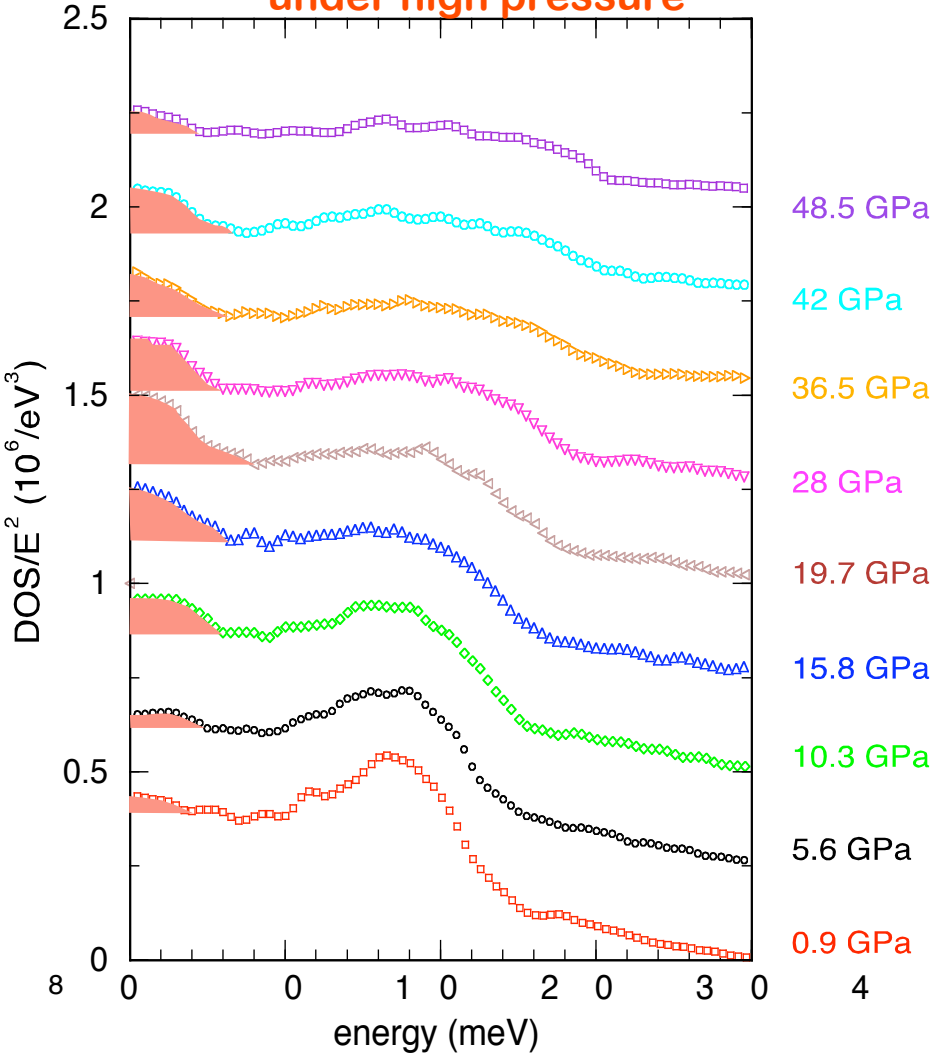


Phonon density of states of iron under high pressure



H.K. Mao, et al, Science, 292 (2001) 914

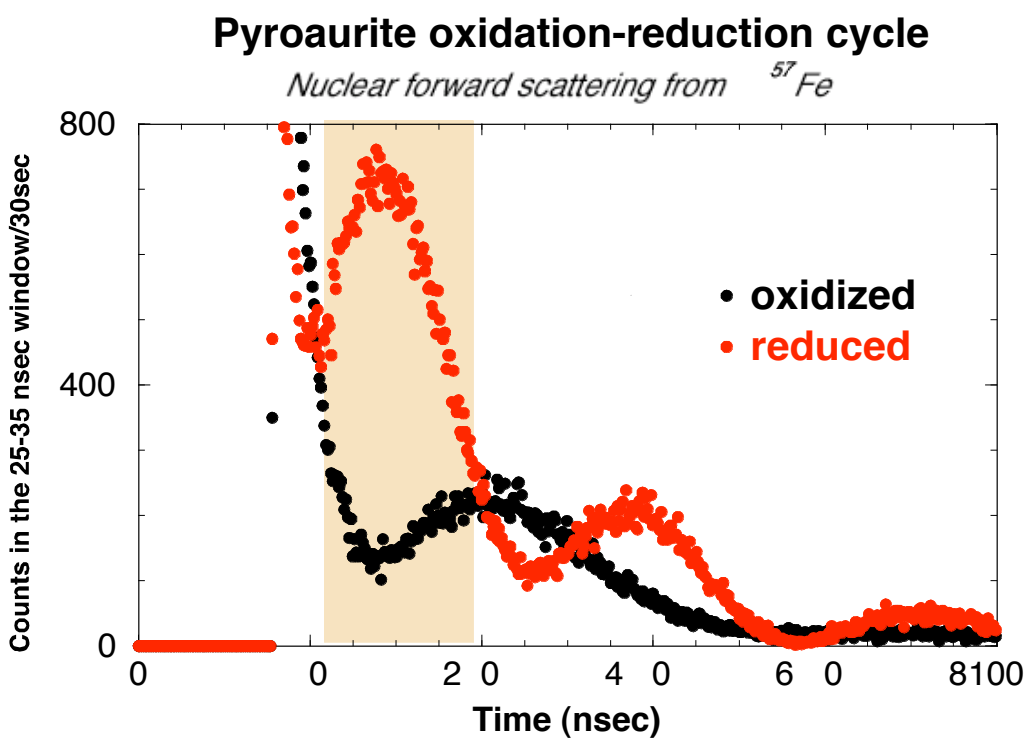
Magneto-elastic coupling in FeO under high pressure

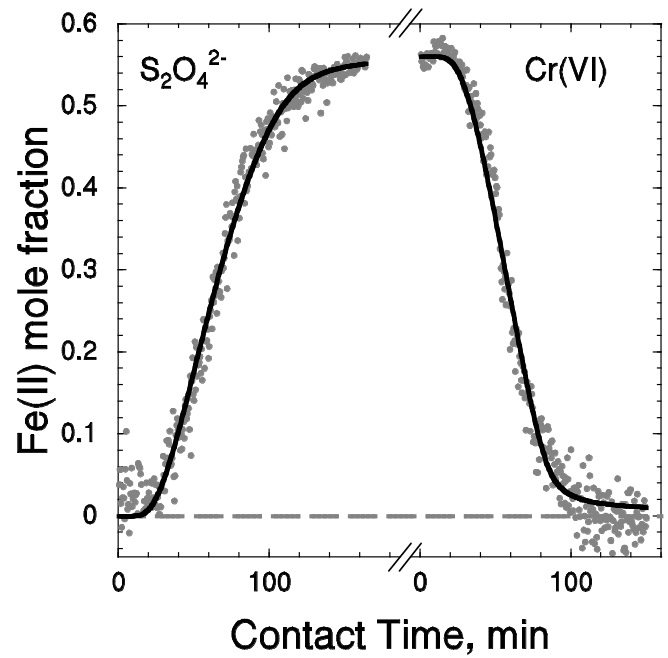


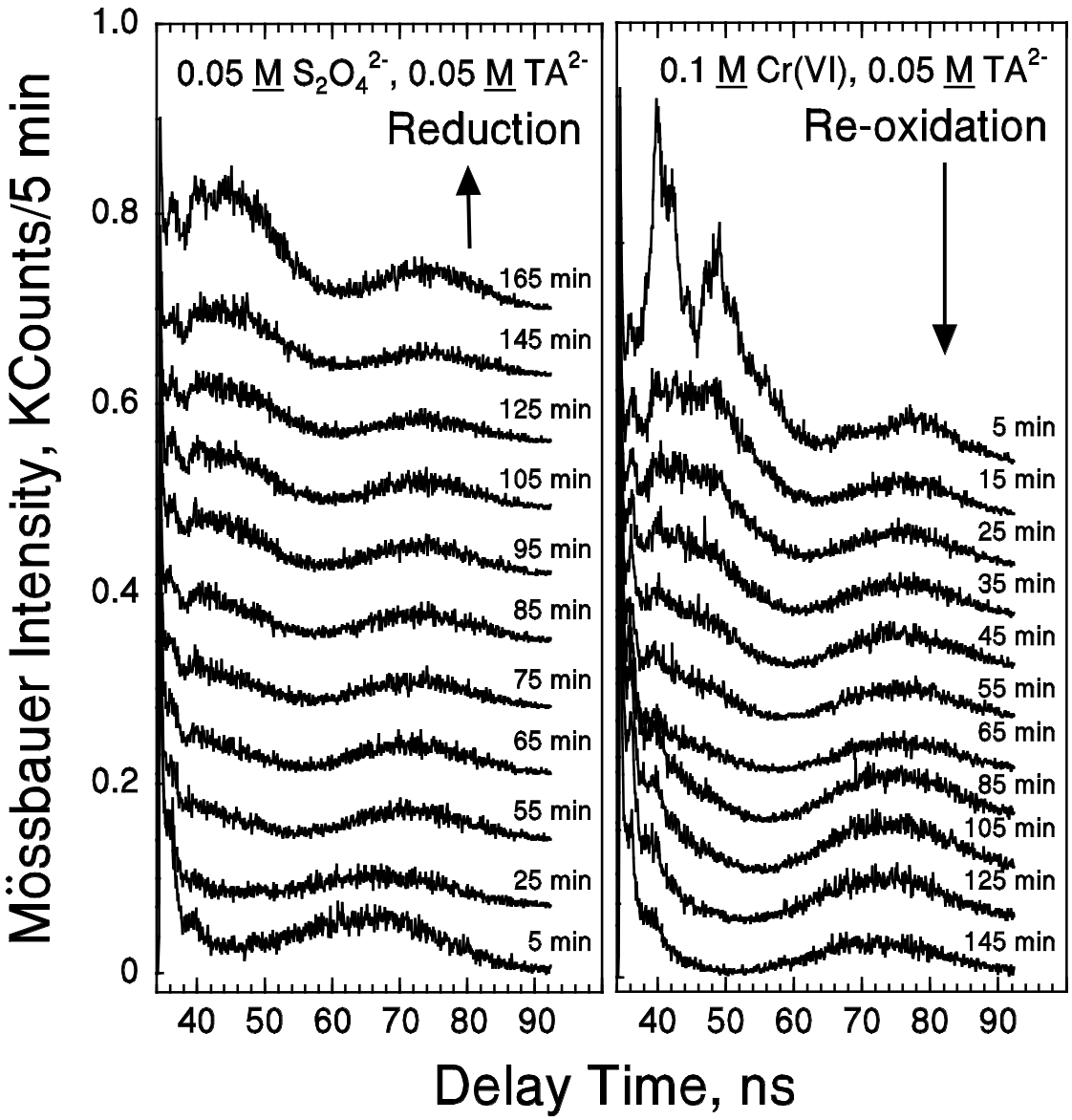
V. Struzhkin, et al, PRL 87 (2001) 255501

Nuclear forward scattering in oxidation kinetics of clays

J. Amonette, et al, Pacific Northwest Laboratory






0.05 M $S_2O_4^{2-}$, 0.05 M TA^{2-}
Reduction
165 min
145 min
125 min
105 min
95 min
85 min
75 min
65 min
55 min
25 min
5 min
0.1 M Cr(VI), 0.05 M TA^{2-}
Re-oxidation
5 min
15 min
25 min
35 min
45 min
55 min
65 min
85 min
105 min
125 min
145 min
Mössbauer Intensity, KCounts/5 min
Delay Time, ns
1.0
0.8
0.6
0.4
0.2
0
40
50
60
70
80
90