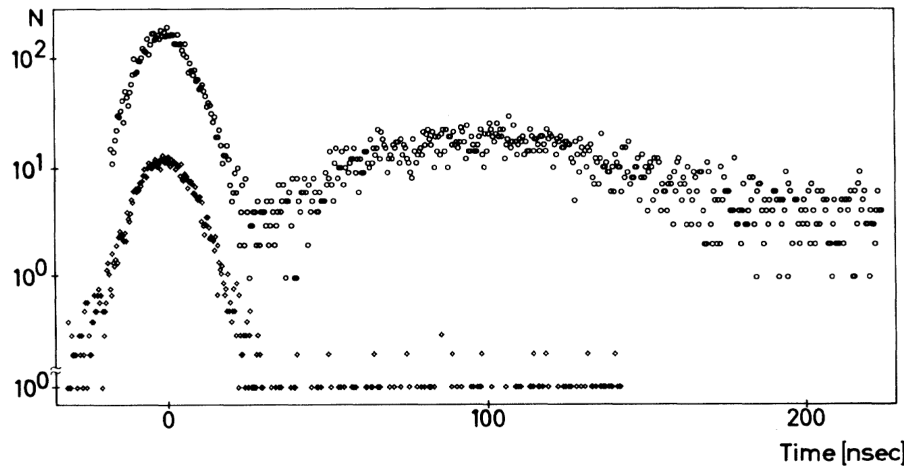
Synchrotron Radiation Based NRS Techniques and Evaluation



Wolfgang Sturhahn

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wolfgang@nrixs.net

The two-faced nuclei:

- conventional role of nuclei
  - ☆ majority carrier of the atomic mass
  - ☆ carries the positive electric charge
  - ☆ negligible scattering cross section:

σ(nucleus) / σ(atom) =
$(Z\ m/M)^2 \approx 10^{-7}$
(Thomson)

- but in some cases
  - ☆ dynamics of the nucleons results in well-defined resonances with

σ(nucleus) / σ(atom) $\approx 10^3$

  - ☆ nuclear resonant scattering may dominate
  - ☆ nuclear resonances are extremely narrow

$\Gamma / E \approx 10^{-12}$

The nucleus as a probe:

- The nucleus is not a point charge

  - ☆ internal dynamics ⇒ nuclear transitions
  - ☆ volume ⇒ isomer shift
  - ☆ spin ⇒ magnetic level splitting
  - ☆ quadrupole moment ⇒ quadrupole splitting

- The nucleus is not at rest

  - ☆ energy/momentum conservation ⇒ recoil energy shift
  - ☆ velocity in gases ⇒ Doppler shift
  - ☆ vibrations in solids ⇒ phonon excitation/annihilation, recoilless absorption

recent reviews of Nuclear Resonant Spectroscopy:

E.Gerdau and H.deWaard, eds., Hyperfine Interact. 123-125 (1999-2000)
W.Sturhahn, J.Phys.: Condens.Matt. 16 (2004)
R.Röhlsberger (Springer Tracts in Modern Physics, 2004)
W.Sturhahn and J.M.Jackson, GSA special paper 421 (2007)

Scattering channels:

initial state → intermediate state → final state

$$|\gamma_i\rangle|\Psi_i\rangle \longrightarrow |\Psi_n\rangle \longrightarrow |\gamma_f\rangle|\Psi_f\rangle$$

$$|\chi_i\rangle\Pi_j|\phi_j^{(i)}\rangle \qquad |\chi_f\rangle\Pi_j|\phi_j^{(f)}\rangle$$

lattice — nucleus & core electrons

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incoherent

$$|\phi_j^{(i)}\rangle \neq |\phi_j^{(f)}\rangle$$

coherent inelastic

$$|\phi_j^{(i)}\rangle = |\phi_j^{(f)}\rangle$$

$$|\chi_i\rangle \neq |\chi_f\rangle$$

coherent elastic

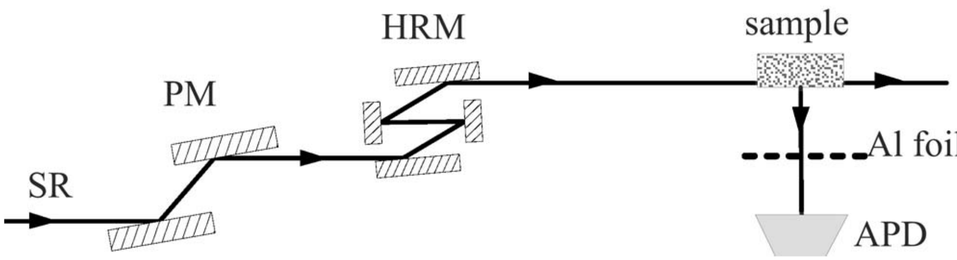
$$|\Psi_i\rangle = |\Psi_f\rangle$$

Incoherent scattering:

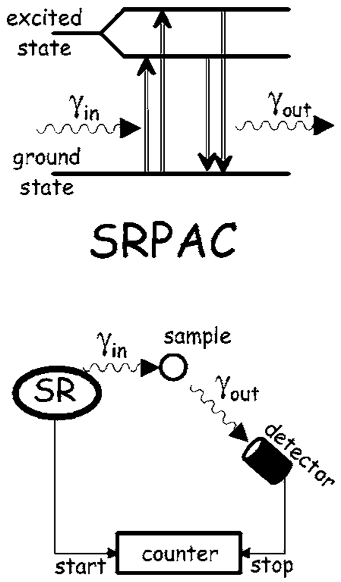
➢ SRPAC – Synchrotron Radiation based Perturbed Angular Correlation

- ✰ introduced in 1996
  A.Baron et al., Europhys.Lett. 34 (1996)
- ✰ measures level splitting of excited nuclear state
- ✰ few applications using high-energy nuclear transition in ^{61}Ni

experimental setup

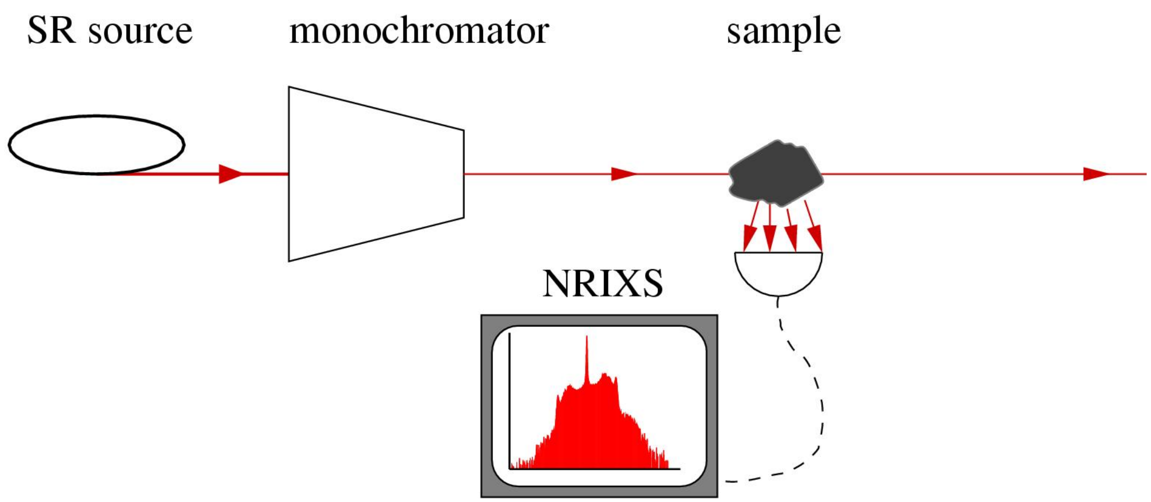


I.Sergueev et al., Phys.Rev. B 73 (2006)



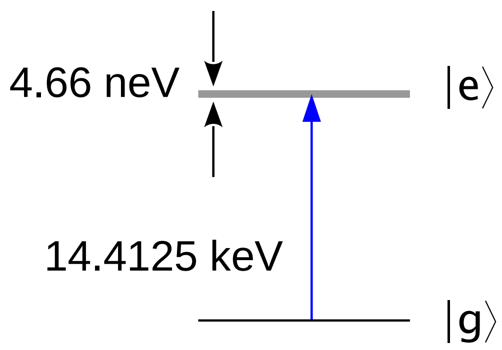
Incoherent scattering:

- NRIXS – Nuclear Resonant Inelastic X-ray Scattering (a.k.a. NRVS and NIS)
  - ☆ introduced in 1995
    M.Seto et al., Phys.Rev.Lett. 74 (1995)
    W.Sturhahn et al., Phys.Rev.Lett. 74 (1995)
  - ☆ local vibrational density of states
  - ☆ applications include determination of sound velocities, elastic, and thermodynamic properties



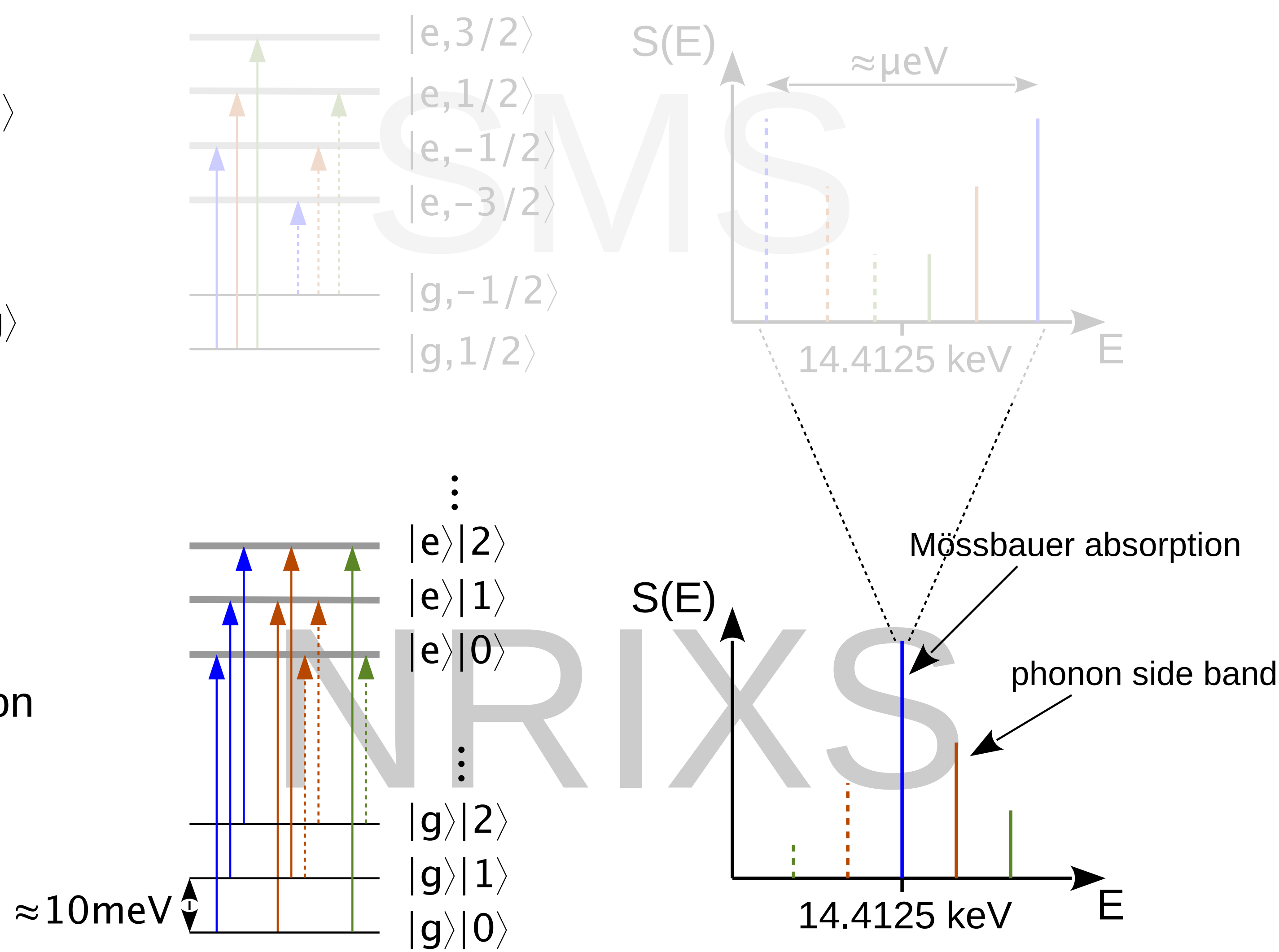
Excitation of the ^{57}Fe nuclear resonance:

fixed, isolated nucleus



nucleus & electronic interaction or external fields

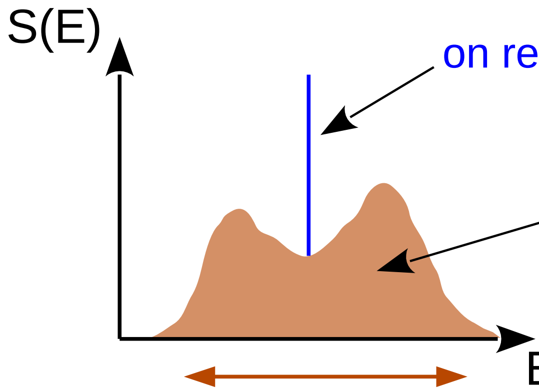
nucleus & simple lattice excitation



Cross section for nuclear excitation:

$$\sigma(E) = \frac{\pi}{2}\,\sigma_0\,\Gamma\,S(E)$$

σ_0 ~ nuclear resonant cross section
Γ ~ width of the nuclear excited state
$S(E)$ ~ probability density for phonon excitation



on resonance: $\Gamma\,S(0) = f$ (0.1 < f < 0.9)

off resonance: $\Gamma\,S(E) \propto (1-f)\,\dfrac{\Gamma}{\Theta}$

Θ ~ Debye energy

iron metal:

$\sigma(0) = 560\ \sigma_{pe}$

$\sigma(E) \approx 0.0002\ \sigma_{pe}$

σ_{pe} ~ photoelectric cross section

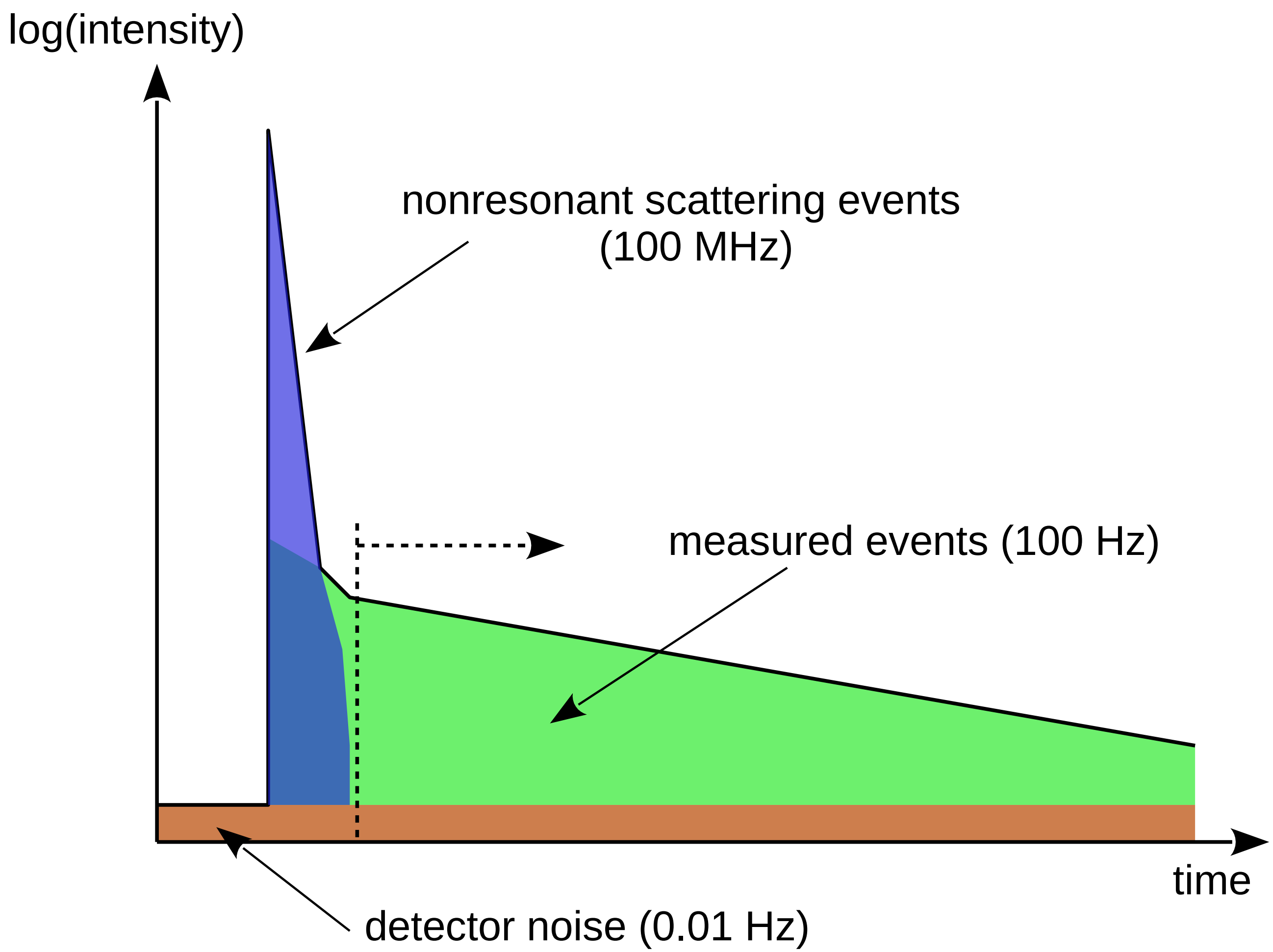
W.Sturhahn, J.Phys.: Condens. Matter 16 (2004)

The time discrimination trick:

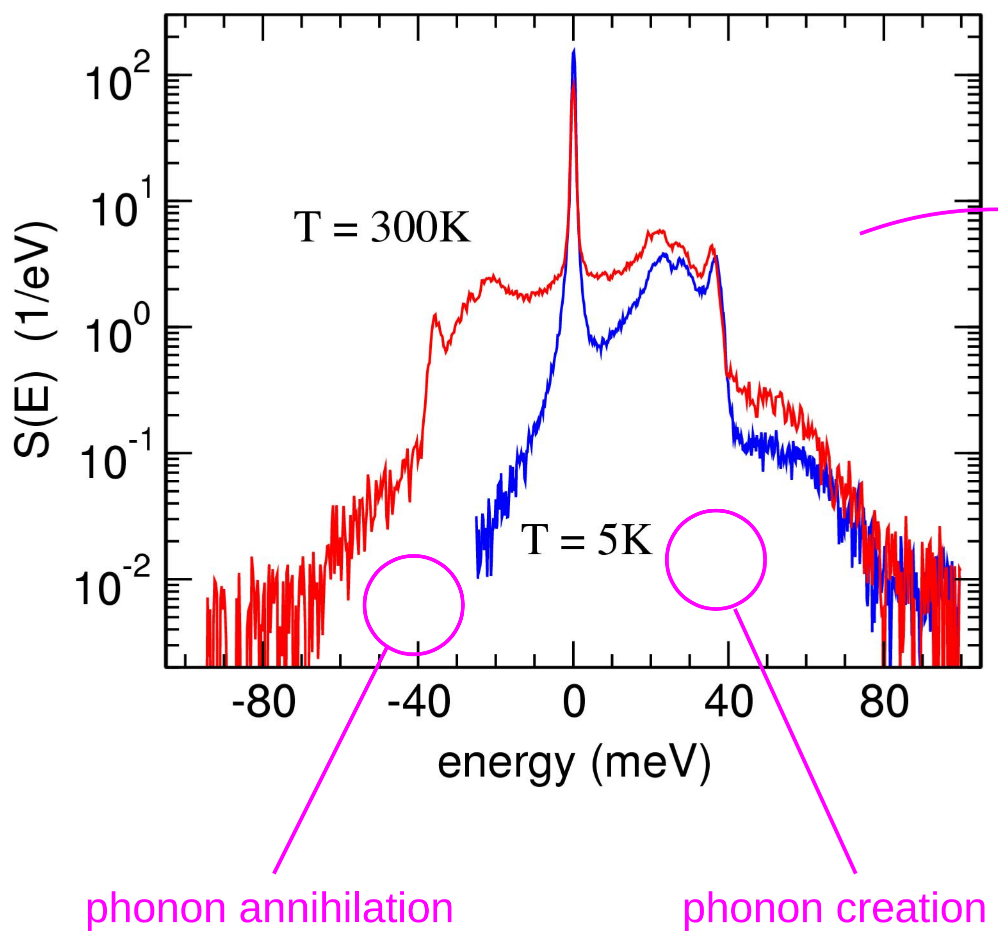
The excited nucleus decays incoherently with its natural life time τ.

$\tau = \hbar \; / \; \Gamma$

141 ns for ^{57}Fe



NRIXS, bcc-Fe:

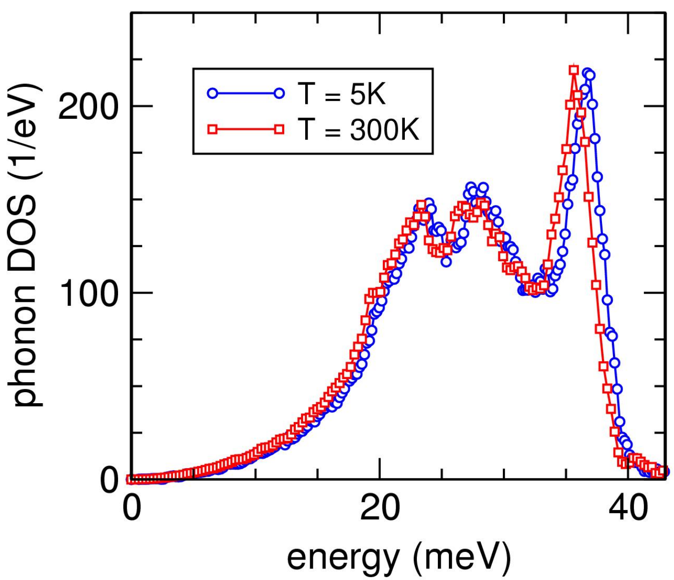


☆ the partial phonon DOS is extracted from the spectrum

W.Sturhahn et al., Phys.Rev.Lett. 74 (1995)

M.Hu et al., Nucl.Instrum.Methods A 428 (1999)

W.Sturhahn, Hyperfine Interact. 125 (2000)



Interpretation of NRIXS spectra:

- NRIXS spectra directly provide the Fourier transform of the self-intermediate scattering function

$$S(\mathbf{k},E) = \frac{1}{2\pi\hbar}\int \left\langle \mathrm{e}^{\mathrm{i}\mathbf{k}\hat{\mathbf{r}}(t)}\mathrm{e}^{-\mathrm{i}\mathbf{k}\hat{\mathbf{r}}(0)} \right\rangle \mathrm{e}^{\mathrm{i}Et/\hbar}dt$$

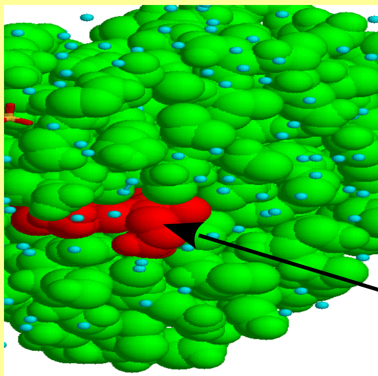
- In the quasi-harmonic approximation the partial projected phonon density-of-states is obtained by a multi-phonon expansion

$$\begin{aligned}
S(\mathbf{k},E) &= f(\mathbf{k})\delta(E) + \sum_{n=1}^{\infty} S_n(\mathbf{k},E) \\
S_1(\mathbf{k},E) &= f(\mathbf{k})\,\frac{E_R}{E\left(1-\exp\left[-\beta E\right]\right)}\,g(\mathbf{k},|E|) \\
S_n(\mathbf{k},E) &= \frac{1}{nf(\mathbf{k})}\int S_{n-1}(\mathbf{k},E')S_1(\mathbf{k},E-E')dE' \\
f(\mathbf{k}) &= \exp\left[-\int \frac{E_R}{E}\,\coth(\frac{\beta E}{2})\,g(\mathbf{k},E)dE\right]
\end{aligned}$$

W.Sturhahn and V.G.Kohn, Hyperfine Interact. 123/124 (1999)

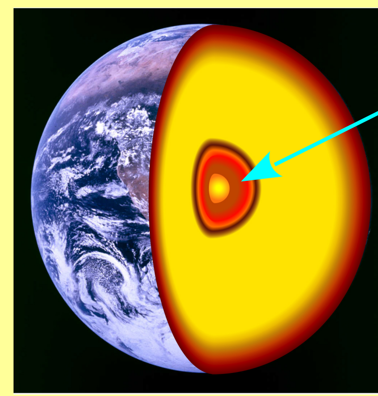
Target applications:

- perfect isotope selectivity & complete suppression of nonresonant signals
- excellent sensitivity (10^{12} nuclei in the focused beam)



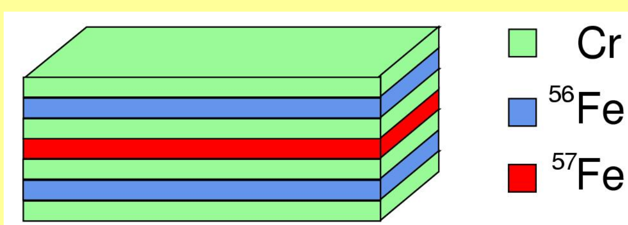
^{57}Fe in myoglobin

☆ proteins and other large molecules



P > 1Mbar
T > 2000K

☆ materials under high pressure



☆ nanostructures

PHOENIX

***PHO**non **E**xcitation by **N**uclear **I**nelastic **X**-ray scattering*

Software for the evaluation of Nuclear Inelastic X-ray Scattering Spectra

Wolfgang Sturhahn

wolfgang@nrixs.net

About PHOENIX:

- developed 1995 by W. Sturhahn at the APS
  - incoherent inelastic nuclear resonant scattering
  - explain first NRIXS experiments (Sturhahn et al. PRL 74, 1995)
  - FORTRAN code implemented on Sun UNIX

- improved 1995-2010 by W. Sturhahn at the APS
  - resolution function subtraction (1997)
  - ported to Linux (2004)
  - sound velocity treatment (2007)
  - visualization support, version 2.0.0 (2009)

- improved 2010- by W. Sturhahn and *NRIXS software*
  - inverse construction (DOS to spectrum), version 2.1.0 (2012)
  - API for variable data input formats, version 2.1.0 (2012)

publications related to PHOENIX:

W. Sturhahn, Hyperfine Interact 125 (2000)

PHOENIX now supports:

- all Mössbauer isotopes

- addition of raw data sets including normalization

- creation of energy scale from angle/temperature data

- flexible procedure for subtraction of elastic peak
- data normalization
- detailed balance, energy calibration, and moment calculation
- correction routine for limited-range spectra

- partial phonon density-of-states extraction with Fourier-Log method
- consistency checks of moment and PDOS results
- optional deconvolution with resolution function

- flexible extrapolation scheme for Debye sound velocity extraction
- aggregate compressional and shear sound velocities

- reconstruction of spectra from measured or theoretical PDOS
- calculation of various thermodynamic quantities from PDOS

More on PHOENIX:

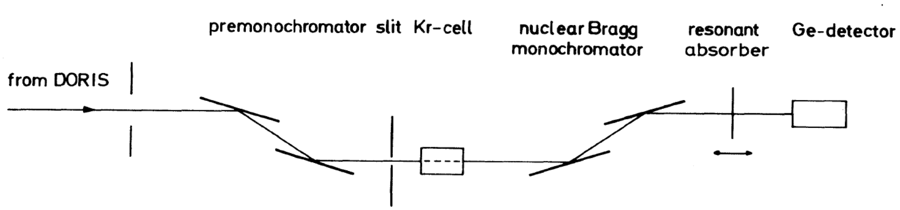
- has been used for data evaluation in numerous publications
- distributed under GPL, source code public, evaluations traceable
- can be obtained at http://www.nrixs.com – no charge
- latest version, PHOENIX-2.1.3, released in 2014
  - ✰ simple installation procedure for Unix and Mac OS X
  - ✰ run-time graphics
  - ✰ API for custom data input formats, e.g., SPEC or mda
  - ✰ inverse calculations, i.e., NRIXS spectra from DOS
- hands-on tutorials on PHOENIX
  - ✰ Neutron and X-ray School, APS, 2000-2005
  - ✰ Nuclear Resonant Scattering on Earth Materials, APS, 2005
  - ✰ Class on NRIXS, Caltech, 2008
  - ✰ Data Evaluation using CONUSS and PHOENIX, APS, 2012
  - ✰ Nuclear Resonant Scattering Workshop, APS, 2014

Coherent elastic scattering:

➢ NBS – Nuclear Bragg Scattering

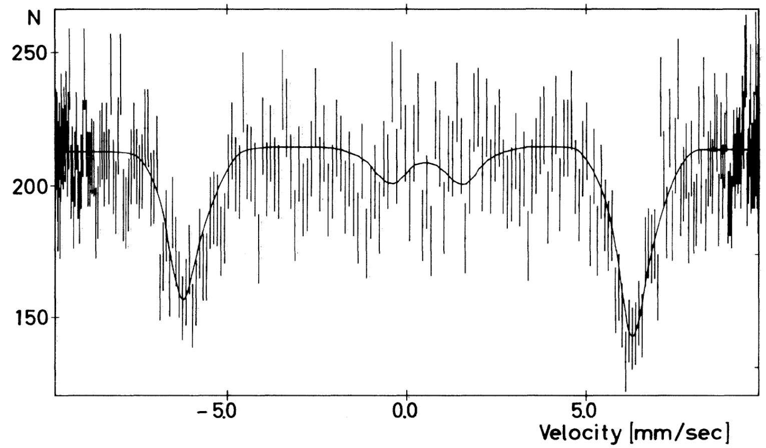
- introduced in 1985
  E.Gerdau et al., Phys.Rev.Lett. 54 (1985)
- uses (pure) nuclear Bragg reflections
- few applications due to need for single crystals

experimental setup



E.Gerdau et al., Phys.Rev.Lett. 54 (1985)

first Mössbauer spectrum using synchrotron radiation

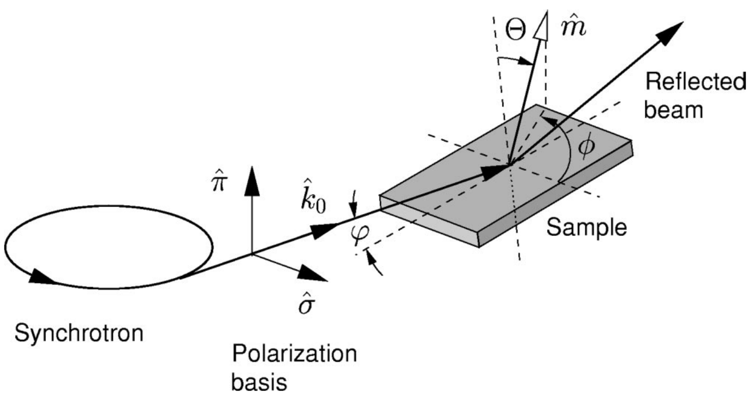


Coherent elastic scattering:

➢ GINRS – Grazing Incidence Nuclear Resonant Scattering

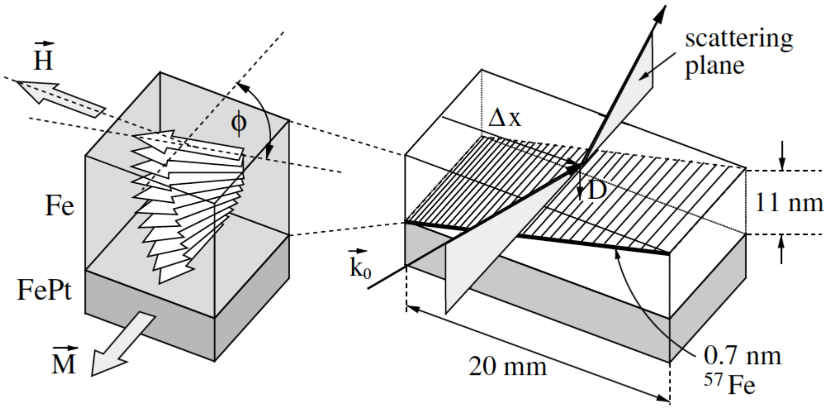
- ✫ introduced in 1991
  M.Grote et al., Europhys.Lett. 17 (1991)
- ✫ uses specular reflection off thin films with Mössbauer isotopes
- ✫ applications in magnetism of nano-structures

experimental setup



R.Röhlsberger et al., Phys.Rev. B 67 (2003)

study of spin structures



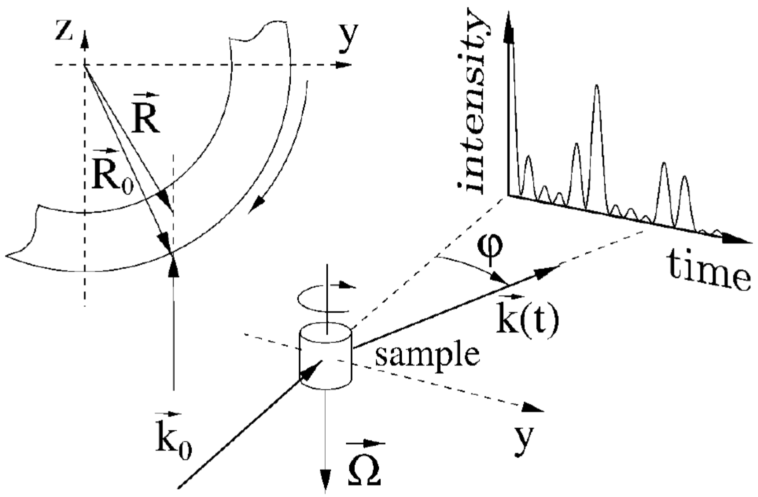
R.Röhlsberger et al., Phys.Rev.Lett. 89 (2002)

Coherent elastic scattering:

➢ NLE – Nuclear Lighthouse Effect

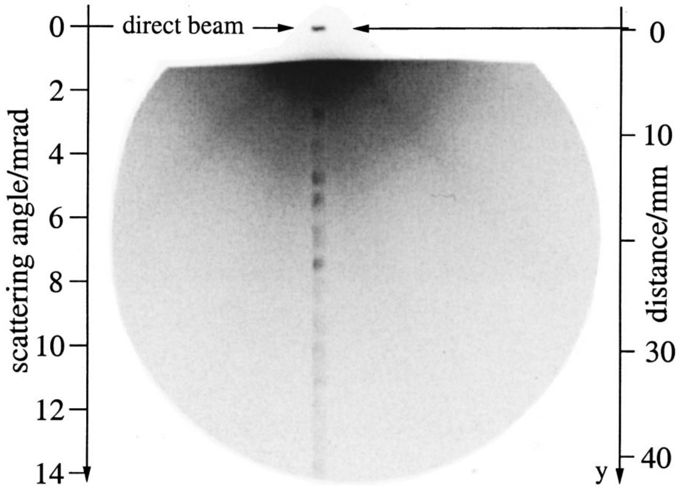
- introduced in 2000
  R.Röhlsberger et al., Phys.Rev.Lett. 84 (2000)
- uses scattering by rotating sample containing Mössbauer isotopes
- few applications, difficult sample environment

experimental setup



R.Röhlsberger et al., Phys.Rev.Lett. 84 (2000)

imaging nuclear resonant scattering

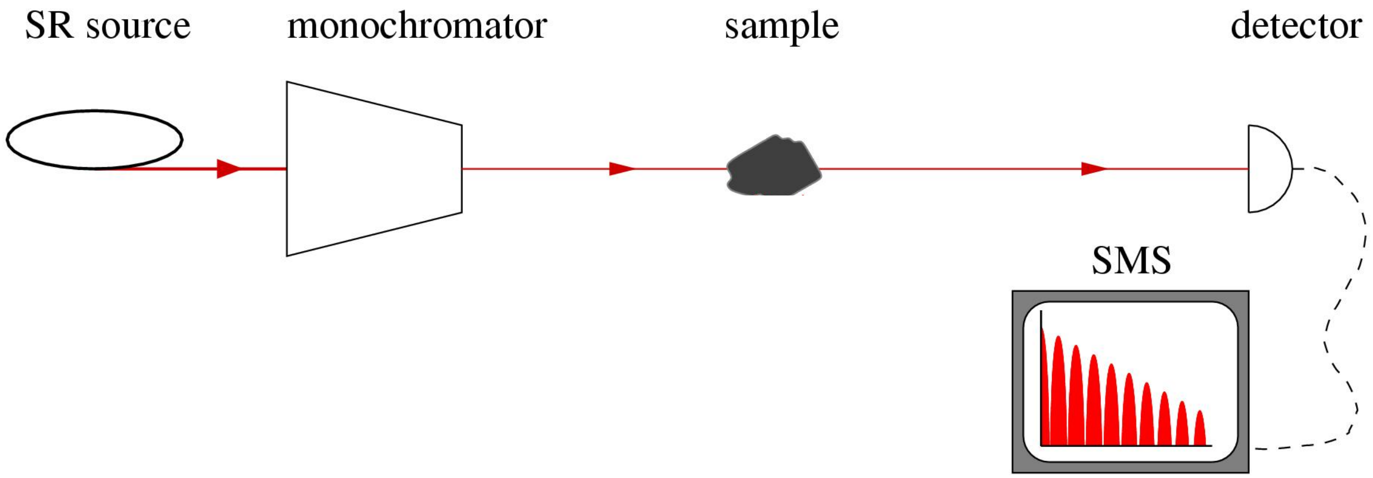


R.Röhlsberger et al., Appl.Phys.Lett. 78 (2001)

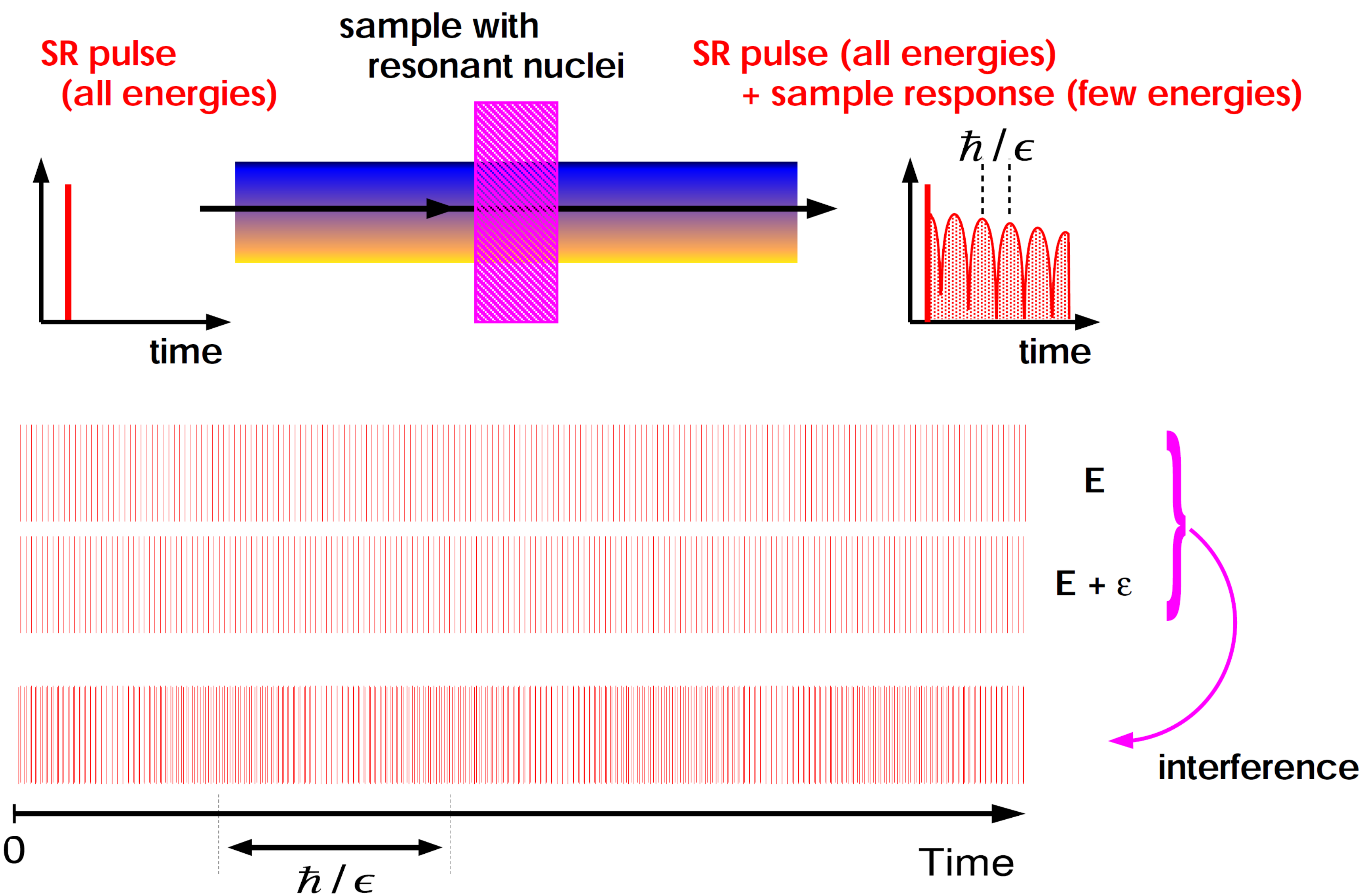
Coherent elastic scattering:

- SMS – Synchrotron Mössbauer Spectroscopy
  (a.k.a. NFS)

  - ☆ introduced in 1991
    J.Hastings et al., Phys.Rev.Lett. 66 (1991)
  - ☆ internal magnetic fields, electric field gradients, isomer shifts
  - ☆ applications include magnetic phase transitions,
    determination of spin & valence states, and melting studies



Origin of oscillations in time spectra:

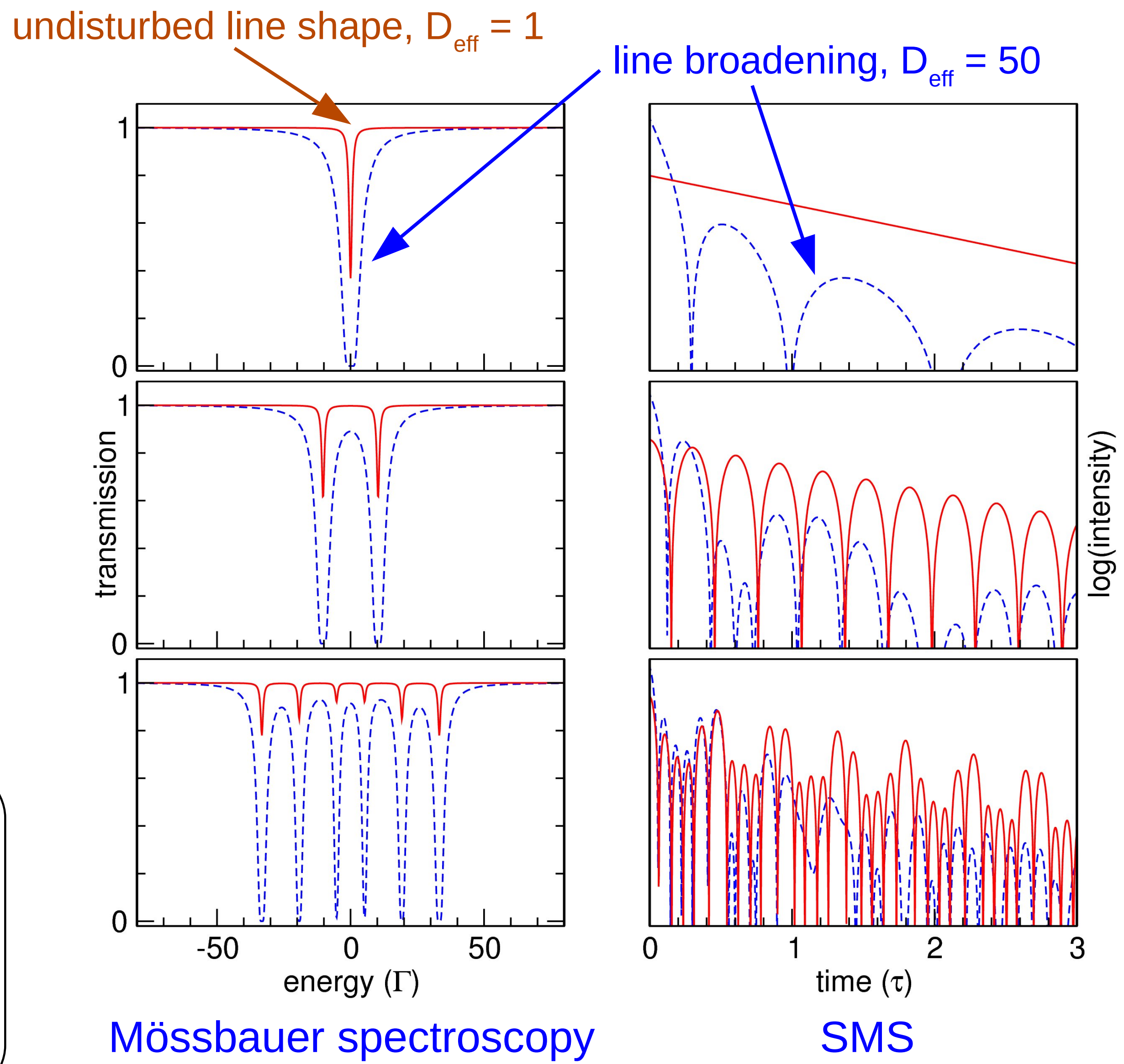


Signatures in SMS time spectra:

☆ single line:
- isomer shift only

☆ two lines:
- electric field gradient, quadrupole splitting
- two sites with different isomer shifts

☆ many lines:
- magnetic field
- several sites with different line positions

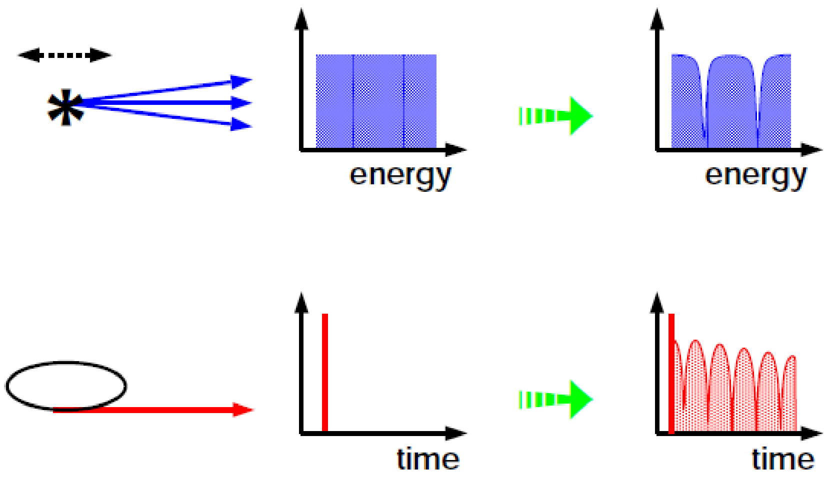


effective thickness:

$$D_{eff} = F_{LM}\ \sigma_0\ \rho\ D$$

Lamb-Mössbauer factor
resonant cross section
nuclei per area
geometric thickness

SMS and traditional MB spectroscopy:



traditional Mössbauer (MB) spectroscopy

Synchrotron Mössbauer Spectroscopy (SMS)

Property	SR	^{57}Co source	
Spectral flux	3×10^{12}	2.5×10^{10}	ph/s/eV
Brightness	1×10^{22}	2.5×10^{13}	ph/s/eV/sr
Spectral flux density	5×10^{12}	2×10^{5}	ph/s/eV/mm^2
(Focused)	2×10^{16}	—	
Typical beam size (mm^2)	0.4×2	10×10	
Focused beam size (μm^2)	6×6	—	
Polarization	Linear or circular	Unpolarized	
Best energy resolution (eV)	4.7×10^{-9}	9.4×10^{-9}	
Energy range (eV)	$\approx 8 \times 10^{-5}$	$\approx 1 \times 10^{-4}$	

W.Sturhahn, J.Phys.: Condens.Matt. 16 (2004)

SMS advantages

- intensity and collimation
- control of polarization
- micro-focusing

SMS challenge

- accessibility
- spectra less intuitive

Interpretation of SMS spectra:

- Nuclear resonant contribution to the index-of-refraction

$$\delta\mathbf{n}(E) = \frac{\Gamma}{4k} F_{LM} \sigma_0 \rho \sum_{mm'} \frac{\mathbf{W}_{mm'}}{E_{mm'} - E - \mathrm{i}\Gamma/2}$$

- Time spectrum

$$\frac{\mathrm{d}\mathbf{I}}{\mathrm{d}t} = \left| \int \left[\mathrm{e}^{\mathrm{i}kD\delta\mathbf{n}(E)} - 1 \right] \mathrm{e}^{-\mathrm{i}Et/h} \frac{dE}{2h} \right|^2$$

- Mössbauer transmission spectrum

$$T(E) = \int \mathrm{Trace}\left[\mathrm{e}^{-kD\mathrm{Im}[\delta\mathbf{n}(E')]} \right] L(E-E')\, dE'$$

W.Sturhahn, J.Phys.: Condens.Matt. 16 (2004)

CONUSS

<u>CO</u>herent <u>NU</u>clear <u>S</u>cattering from <u>S</u>ingle crystals

Software for the evaluation of Synchrotron Mössbauer Spectra

Wolfgang Sturhahn

wolfgang@nrixs.net

About CONUSS:

- developed 1983-1986 by E. Gerdau and W. Sturhahn at the University of Hamburg
  - coherent elastic nuclear and electronic Bragg scattering
  - explain first NRS experiments (Gerdau et al. PRL 54, 1985)
  - FORTRAN code implemented on IBM 360 mainframe (MVS-VM)

- improved 1986-today by W. Sturhahn and supported by
  the University of Hamburg (1986-1993),
  ESRF (1992), APS (1992-2010),
  MPI-Halle (2012-2013)
  - forward scattering (SMS a.k.a. NFS) added (1991)
  - ported to Sun UNIX (1992)
  - extended data handling capability (fitting) added (1996)
  - ported to Linux and OS X (2004, 2011)
  - grazing incidence scattering (GINS) added (2014)

publications related to CONUSS:

W. Sturhahn and E. Gerdau, Phys. Rev. B 49 (1994)

W. Sturhahn, Hyperfine Interact 125 (2000)

CONUSS now supports:

- all Mössbauer isotopes

- forward scattering, grazing incidence, and Bragg/Laue reflections
- no limitations by sample structure

- combined hyperfine interactions
- distributions of hyperfine fields
- textures
- relaxation effects

- full polarization and directional dependences
- thickness effects

- time spectra (SMS) and energy spectra (trad. Mössbauer spectr.)
- sample combinations
- time, energy, and angle averaging
- sample thickness distributions

- comparison to experimental data, fitting and Monte Carlo sampling
- flexible assignment and grouping of fit/sampling parameters

More on CONUSS:

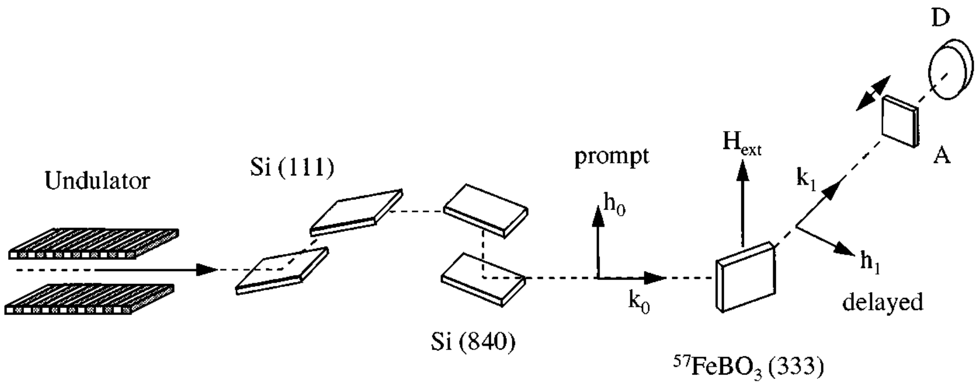
- has been used for data evaluation in numerous publications
- distributed under GPL, source code public, evaluations traceable
- can be obtained at http://www.nrixs.com – no charge
- latest version, CONUSS-2.1.0, just released
  - ☆ simple installation procedure for Unix and Mac OS X
  - ☆ enhanced fit capabilities
  - ☆ run-time graphics
  - ☆ Monte Carlo approach to find start-values, explore the parameter space, and smart parameter optimization
  - ☆ support of grazing incidence geometry
  - ☆ input file simplifications, manual
- hands-on CONUSS tutorials
  - ☆ Data Evaluation using CONUSS and PHOENIX, APS, 2012
  - ☆ SMS data evaluation using CONUSS, Petra III, 2014
  - ☆ Nuclear Resonant Scattering Workshop, APS, 2014

Filtering methods:

➢ SMs – Synchrotron Mössbauer source

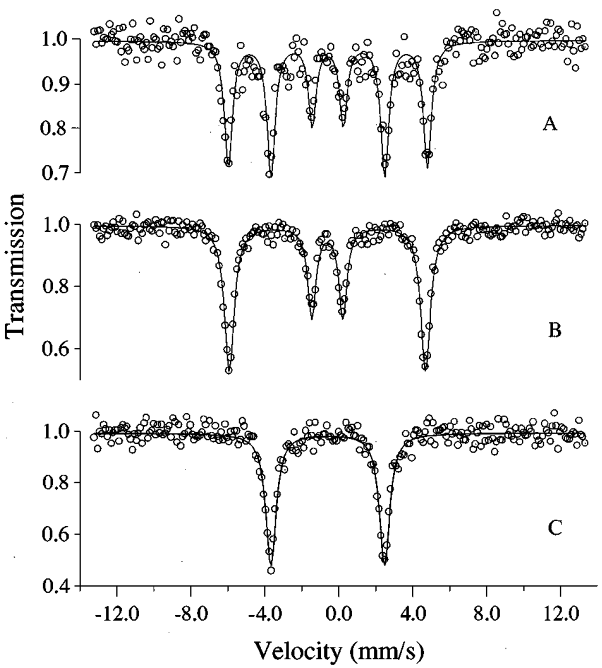
- ✰ introduced in 1997
  G.V.Smirnov et al., Phys.Rev. B 55 (1997)
- ✰ uses pure nuclear Bragg reflection to create narrow-bandwidth x-ray

experimental setup



G.V.Smirnov et al., Phys.Rev. B 55 (1997)

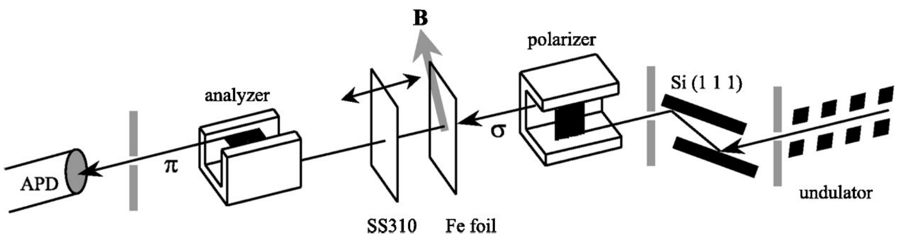
velocity spectrum



Reconstructive methods:

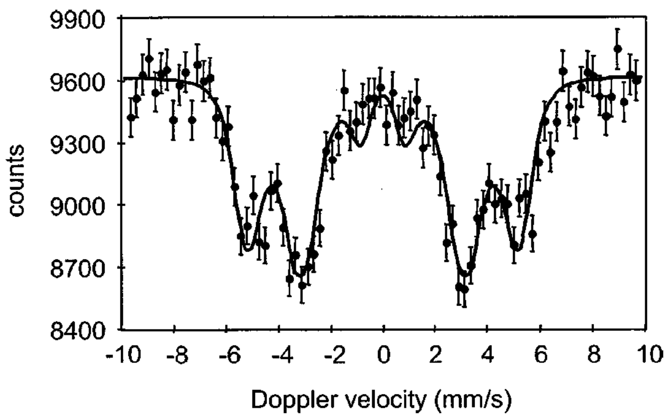
- TISRS – time integrated synchrotron radiation spectroscopy
  - introduced in 2000
    C.L'abbe et al., Phys.Rev. B 61, 2000
  - uses moving reference absorber and polarizer/analyzer setup

experimental setup



C.L'abbe et al., Phys.Rev. B 61 (2000)

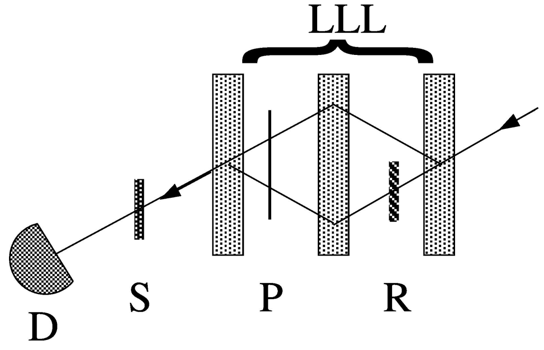
integrated time spectrum



Reconstructive methods:

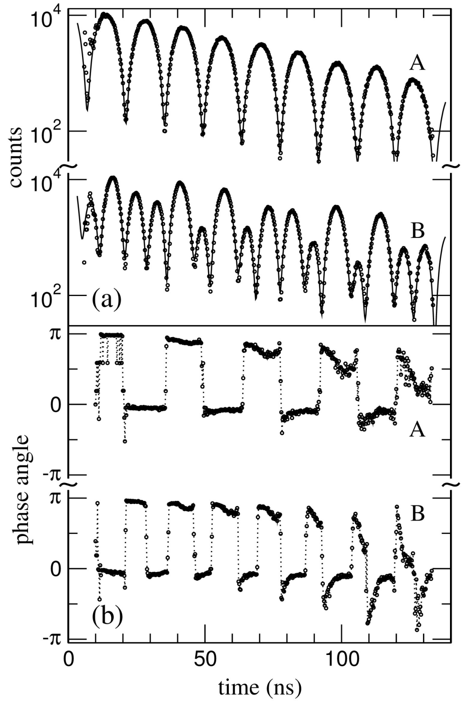
- exo-interferometric SMS
  - ☆ introduced in 2004
    W.Sturhahn et al., Europhys.Lett. 66 (2004)
  - ☆ uses x-ray interferometer to measure time dependent phase

schematic

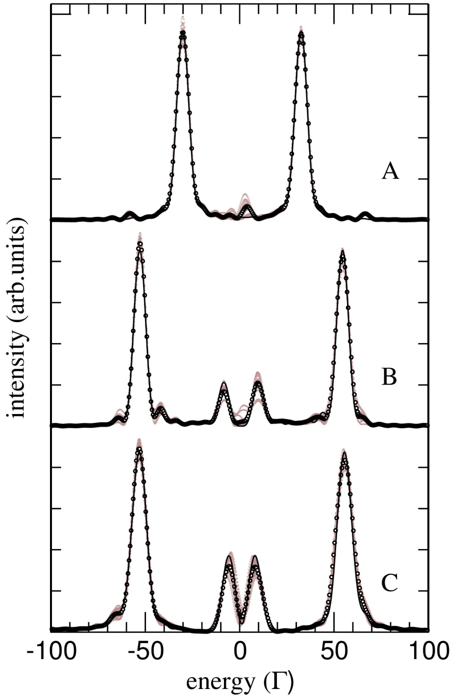


W.Sturhahn et al., Europhys.Lett. 66 (2004)

phase



energy spectrum



Others:

- NRA-IXS – nuclear resonant analysis of inelastic x-ray scattering
  - ✰ introduced in 1996

    A.I.Chumakov et al., Phys.Rev.Lett. 76 (1996)
  - ✰ uses SMS as energy analyzer; measures meV resolved inelastic scattering

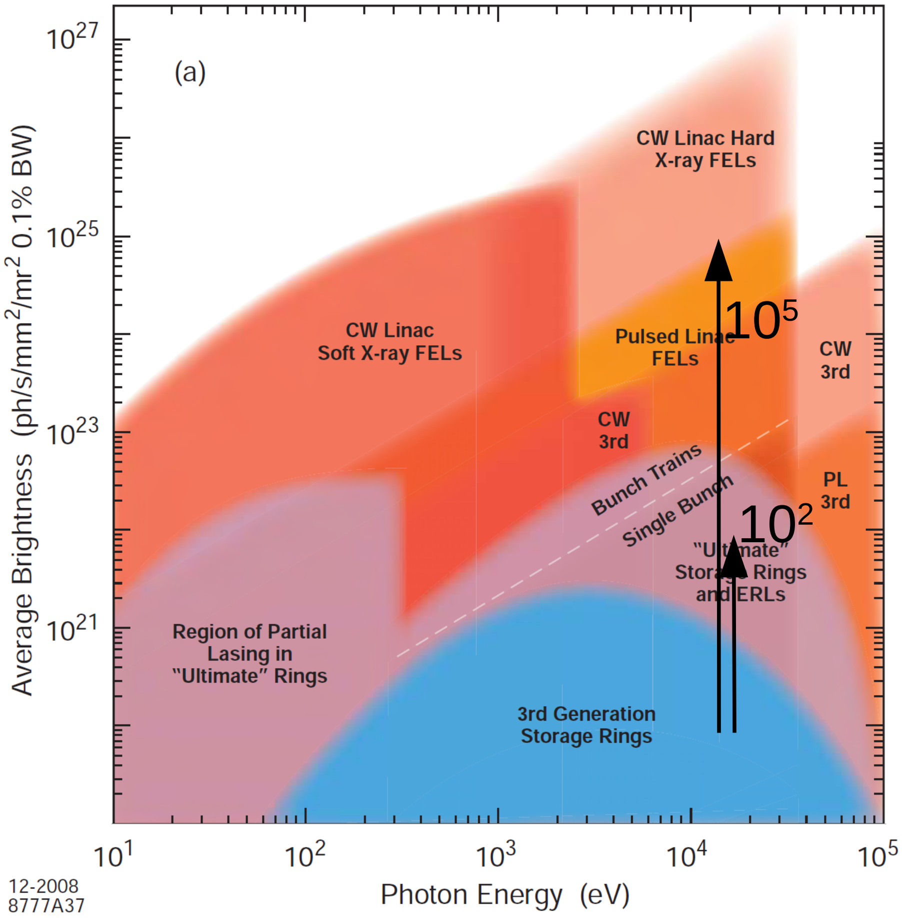
- TDI – time domain interferometry
  - ✰ introduced in 1997

    A.Baron et al., Phys.Rev.Lett. 79 (1997)
  - ✰ uses SMS for energy filter/analyzer; measures quasi-elastic scattering

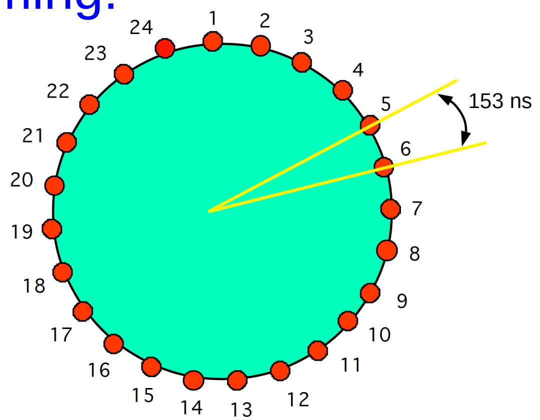
- site-specific NRIXS
  - ✰ introduced in 2003

    M.Seto et al., Phys.Rev.Lett. 91 (2003)
  - ✰ combination of SRPAC and NRIXS to distinguish sites

Brighter x-ray sources:

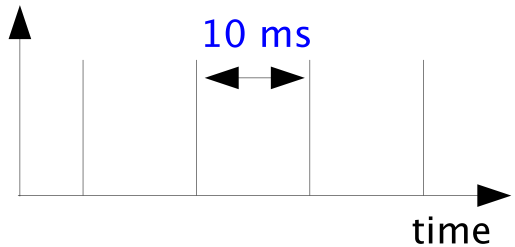


- **APS timing:**



$$6 \cdot 10^6 \text{ ph/pulse/eV} = 0.028 \text{ ph/pulse/}\Gamma$$

- **LCLS timing:**



$$10^{11} \text{ ph/pulse/eV} = 466 \text{ ph/pulse/}\Gamma$$

Brighter x-ray sources:

- X-ray Laser
  - ☆ large number of photons per pulse
  - ☆ ideal for pump-probe experiments
  - ☆ complete transverse coherence
  - ☆ efficient micro/nano focusing

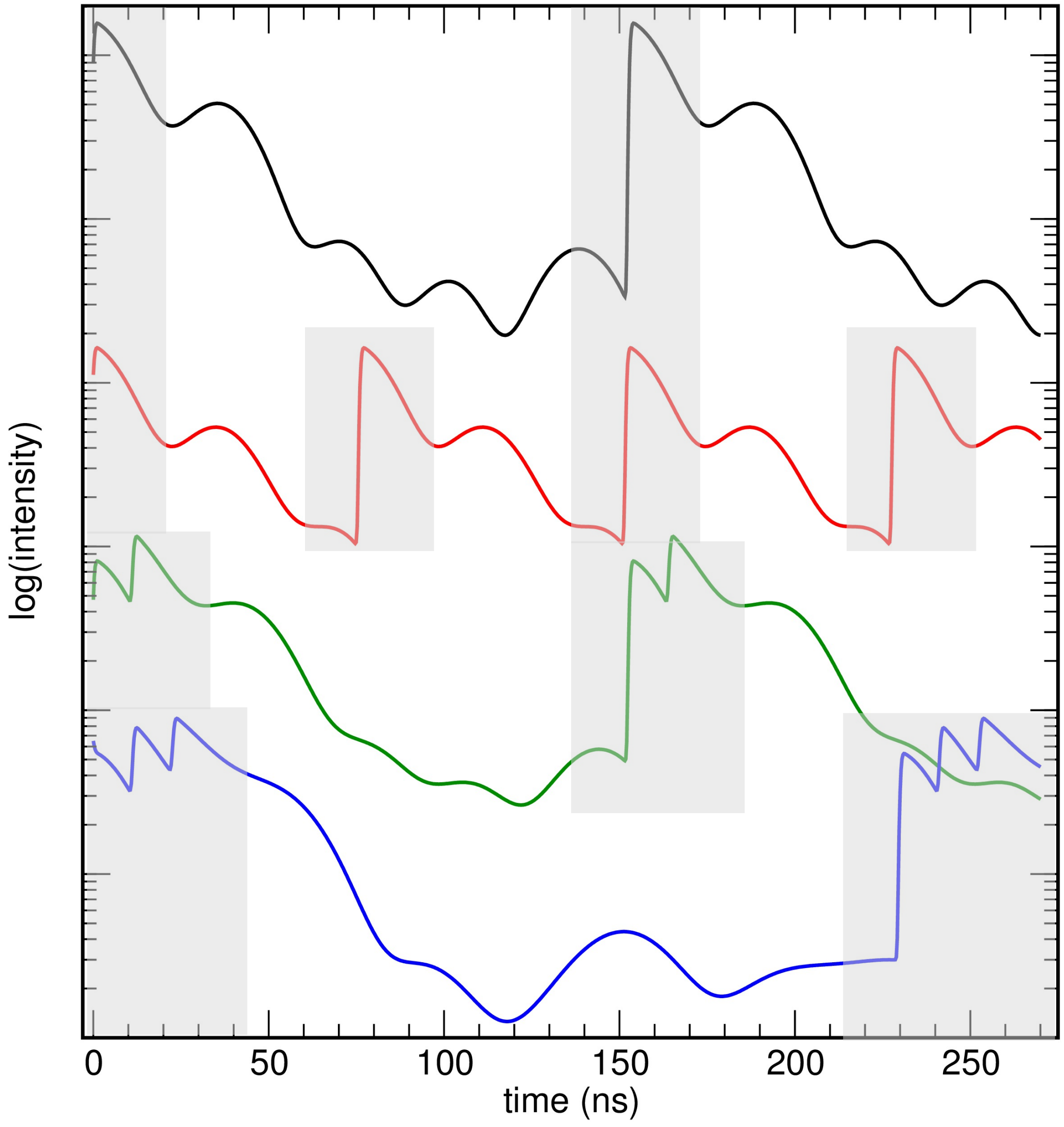
- Ultimate storage ring
  - ☆ higher transverse coherence
  - ☆ efficient micro/nano focusing
  - ☆ small bunch separation possible

- mitigating/enabling technologies
  - ☆ improved high-energy resolution monochromators
  - ☆ ultra-fast shutters
  - ☆ APD area detectors
  - ☆ nuclear filtering techniques

Case study: timing for the APS-MBA

- present-day timing mode
  - ✩ black, 24-54-1, singlets
- potential MBA timing modes
  - ✩ red, 48-27-1, singlets
  - ✩ green, 24-54-2, doublets
  - ✩ blue, 16-81-3, triplets

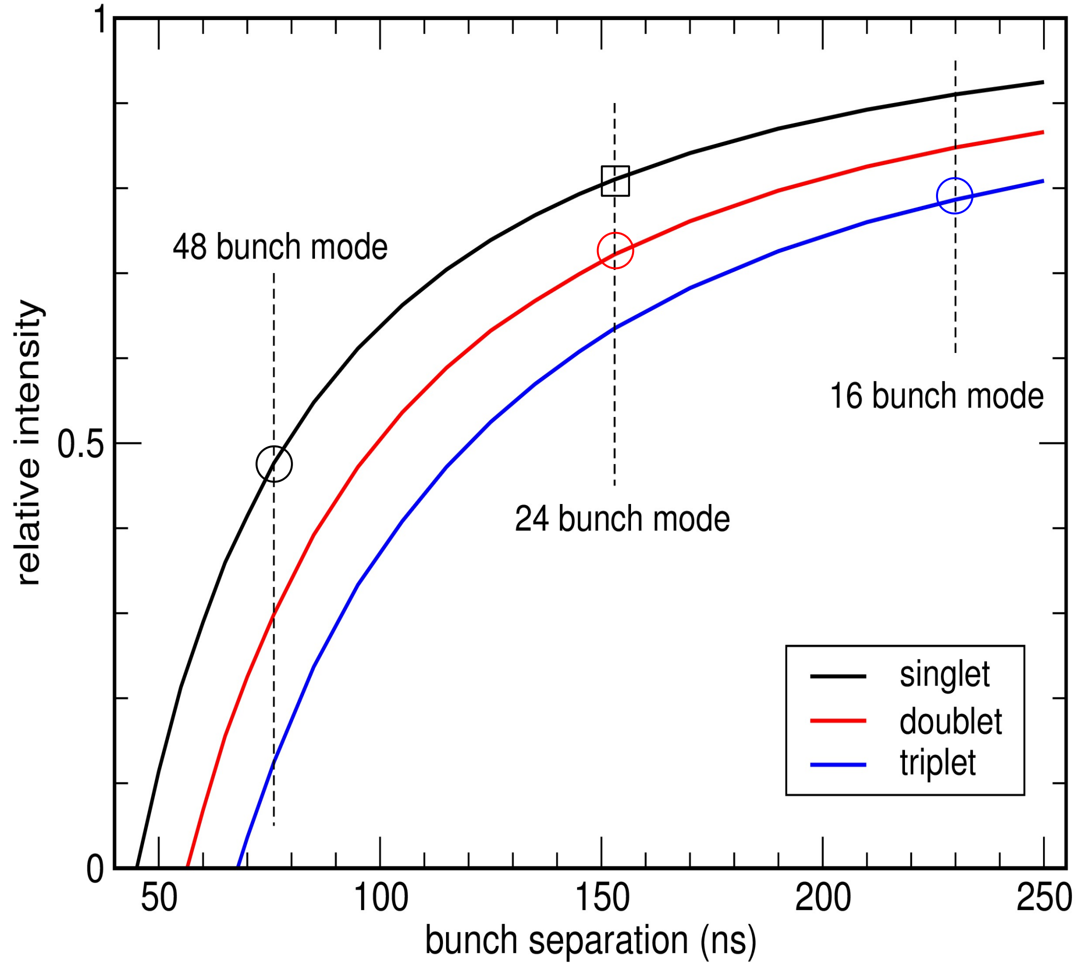
^{57}Fe SMS time spectra of a typical mineral



Case study: timing for the APS-MBA

- present-day timing mode
  - ☆ square, 81%, 24-54-1, singlets
- potential MBA timing modes
  - ☆ black, 47%, 48-27-1, singlets
  - ☆ red, 72%, 24-54-2, doublets
  - ☆ blue, 78%, 16-81-3, triplets

^{57}Fe NRIXS relative intensity



Final remark:

- Evolution of synchrotron based NRS techniques:
  not "survival of the fittest"
  but "adaptive improvement" and occupation of available "ecological niches"

- Ecological niche of NRS must be protected, e.g., by
  - ☆ NRS users engaged in upgrade projects
  - ☆ sufficient flexibility in storage ring timing modes

- Adaptive improvement should consider
  - ☆ development and maintenance of evaluation tools
  - ☆ training of young scientists, e.g., in tutorials and workshops
  - ☆ developments commensurate with goals of upgrade projects, e.g., implementation of transverse coherence into NRS methodology