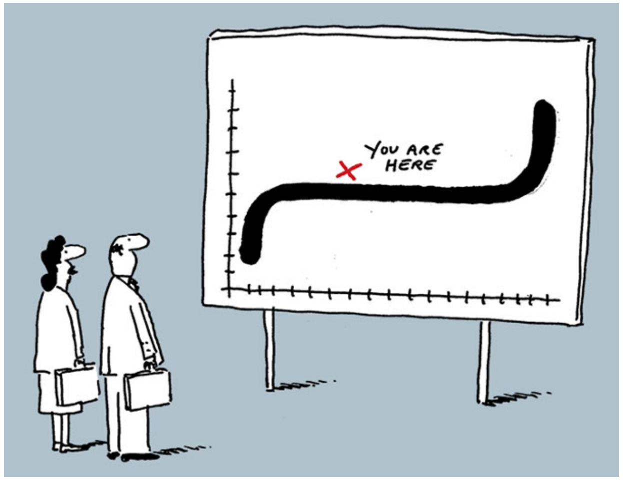
Strategies for Nuclear Resonant Experiments



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Good strategy matters:

- achieve goals by following a plan over an extended time period

  - ✰ What are the scientific goals?
    Can they be achieved by NRS experiments?
    ⇒ knowledge of science area and NRS

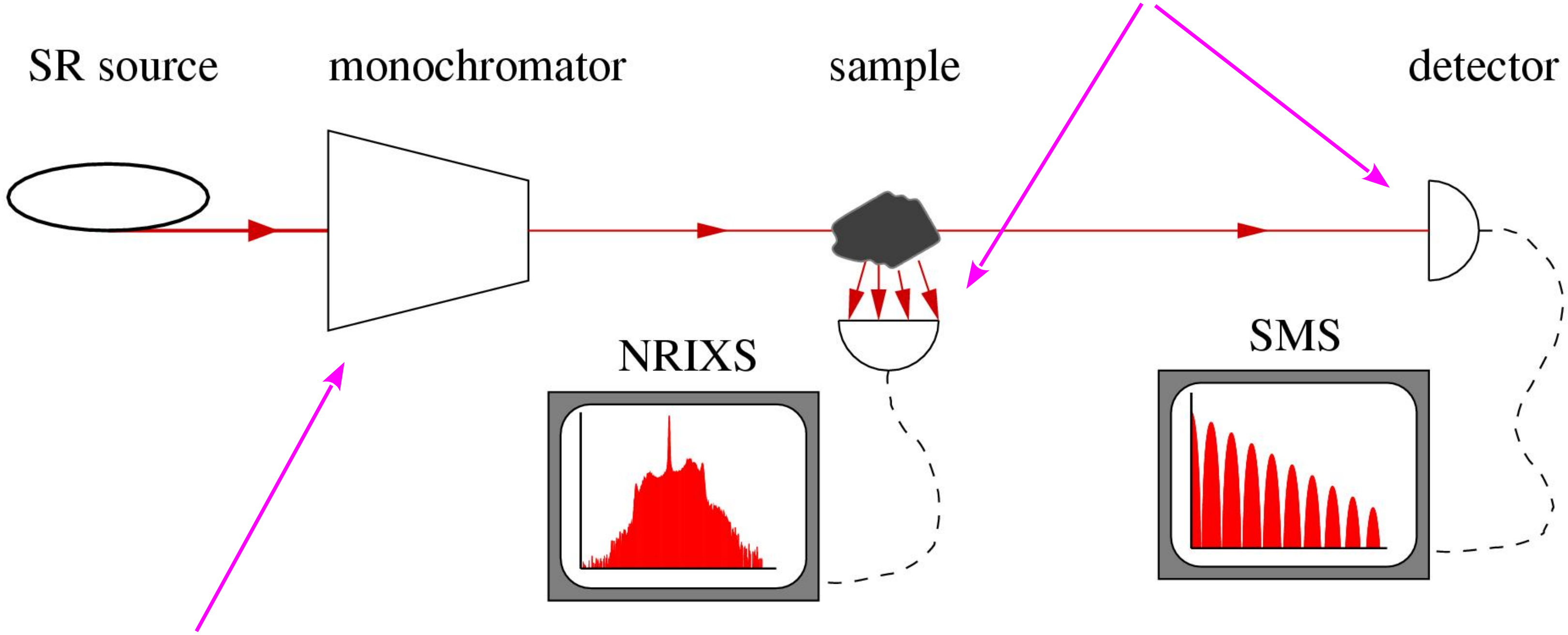
  - ✰ Which NRS method is appropriate for scientific goals?
    Can a reasonable experimental plan be developed?
    ⇒ forward modeling tools
    ⇒ beamline capabilities
    ⇒ experiment readiness definition

  - ✰ How much time is needed for relevant experiments?
    Are non-NRS experiments needed beforehand?
    ⇒ counting rate estimates, staffing requirements

  - ✰ We have the data! - Now what?
    ⇒ data evaluation tools

NRS, experimental setup:

- x-ray pulses must be sufficiently separated in time
- detectors must have good time resolution and excellent dynamic range



- monochromatization to meV-level required
- energy is tuned around nuclear transition (NRIXS)

useful 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, Nuclear Condensed Matter Physics with Synchrotron Radiation: Basic Principles, Methodology and Applications, Springer (2004)

W. Sturhahn and J.M. Jackson, GSA special paper 421 (2007)

The nucleus as a probe:

- The nucleus is not at rest:
  NRIXS – Nuclear Resonant Inelastic X-ray Scattering (a.k.a. NRVS and NIS)
  - ☆ energy/momentum conservation ⇒ recoil energy shift
  - ☆ velocity in gases ⇒ Doppler shift
  - ☆ vibrations in solids ⇒ phonon excitation/annihilation, recoilless absorption
  - ☆ local vibrational density of states
  - ☆ applications include determination of sound velocities and thermodynamic properties

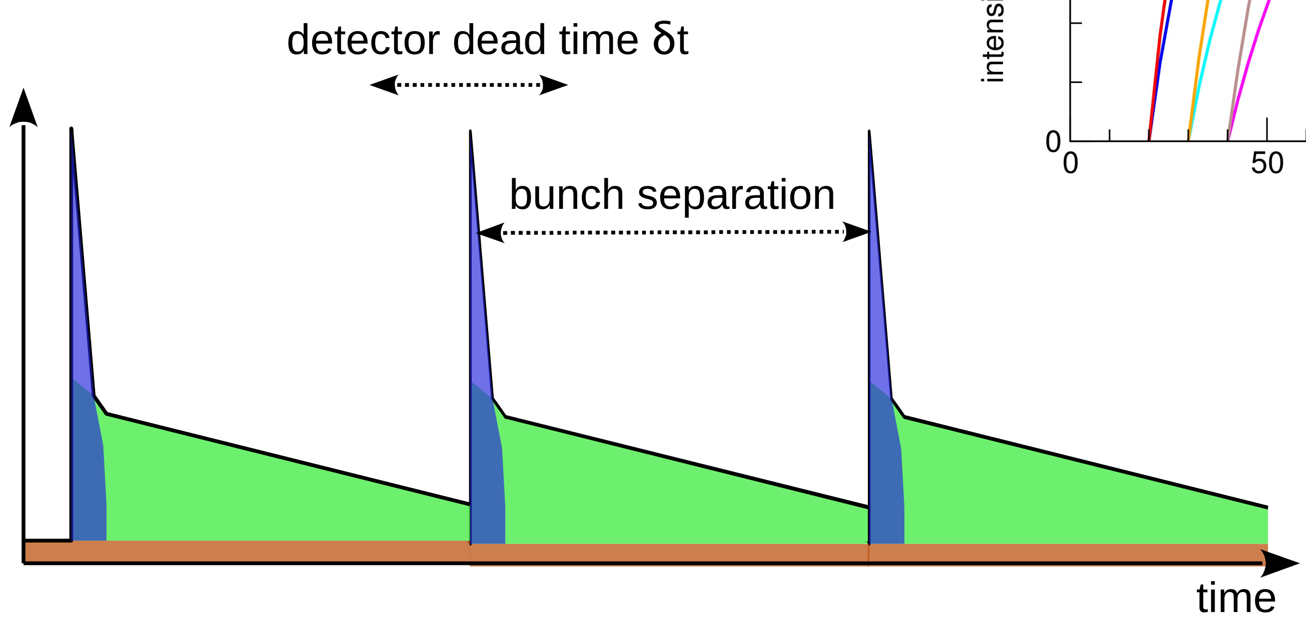
- The nucleus is not a point charge:
  SMS – Synchrotron Mössbauer Spectroscopy (a.k.a. NFS)
  - ☆ internal dynamics ⇒ nuclear transitions
  - ☆ volume ⇒ isomer shift
  - ☆ spin ⇒ magnetic level splitting
  - ☆ quadrupole moment ⇒ quadrupole splitting
  - ☆ internal magnetic fields, electric field gradients, isomer shifts
  - ☆ applications include magnetic phase transitions, determination of spin & valence states, and melting studies

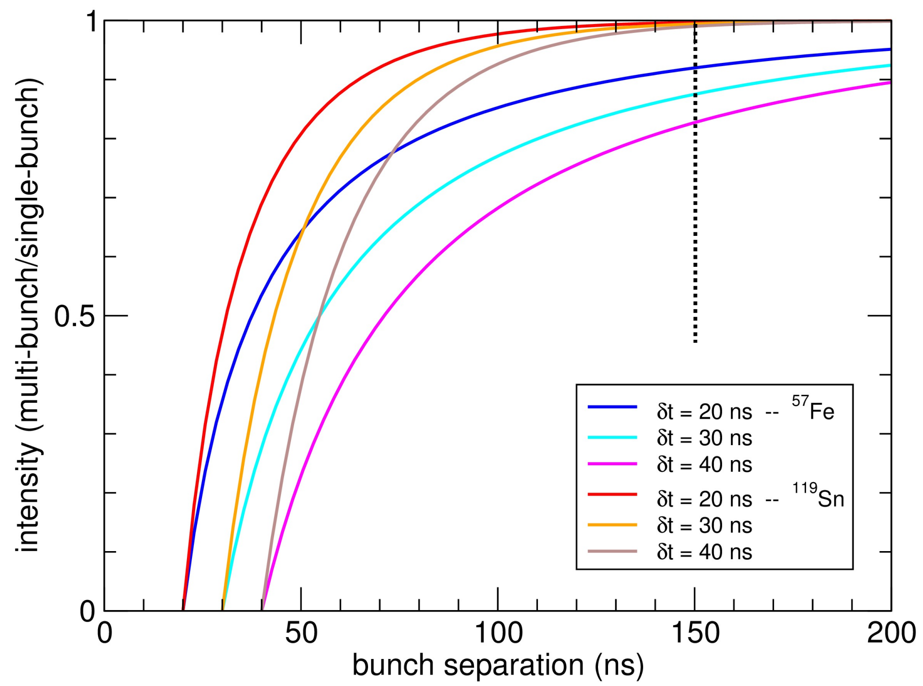
What the beamline provides:

- Time
- Instruments
  - ☆ monochromator with appropriate bandwidth & flux
  - ☆ rotation & translation stages with appropriate range & resolution
  - ☆ focusing optics for small samples
  - ☆ detectors & miscellaneous electronics
- Software tools
  - ☆ data acquisition & motion control
  - ☆ *in-situ* data evaluation for experimental progress assessment
- Storage ring time structure

Time structure of synchrotron radiation:

detector dead time and bunch separation determine the detectable counts in NRIXS.



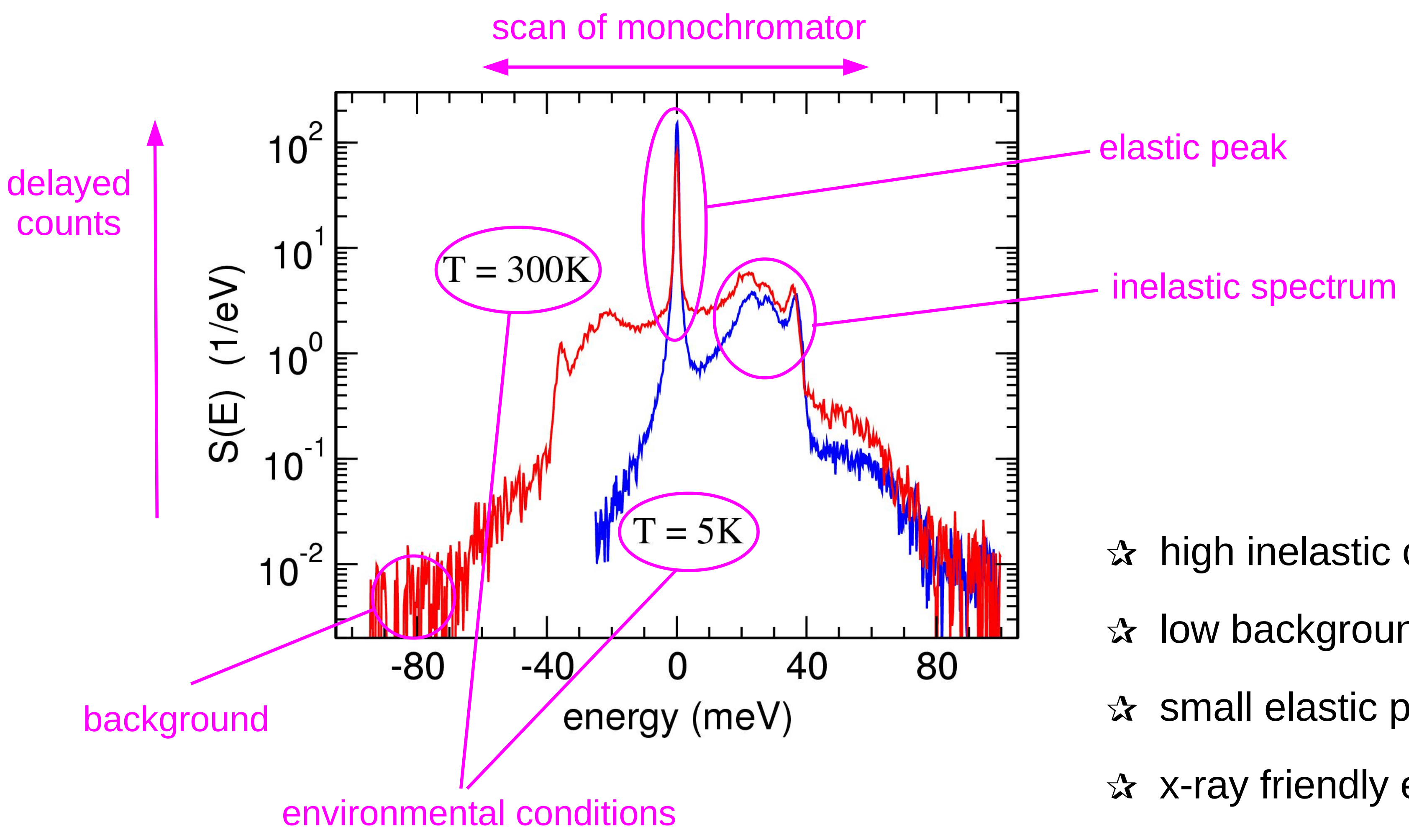


$\tau = \hbar \,/\, \Gamma$

141 ns for ^{57}Fe

25.6 ns for ^{119}Sn

NRIXS sample:



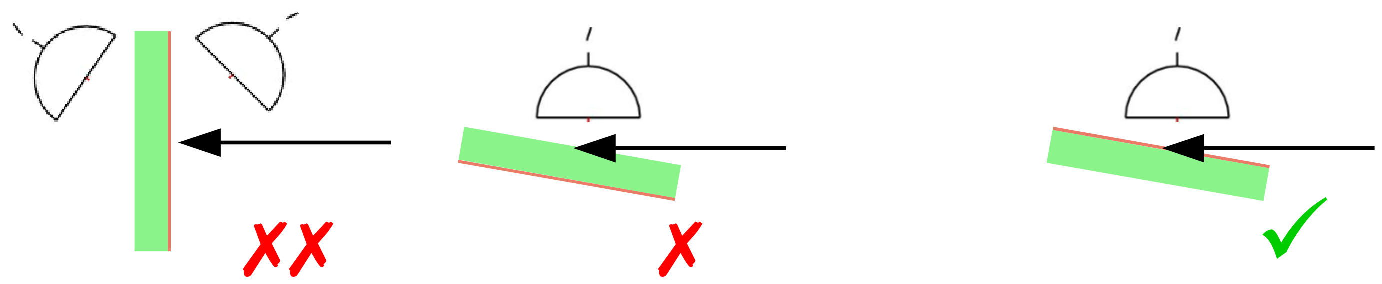
- ✰ high inelastic counting rate
- ✰ low background
- ✰ small elastic peak
- ✰ x-ray friendly environment
- ✰ appropriate energy range

NRIXS, inelastic counting rate:

- high density of resonant isotope:
  enrichment often necessary, avoid short lifetimes

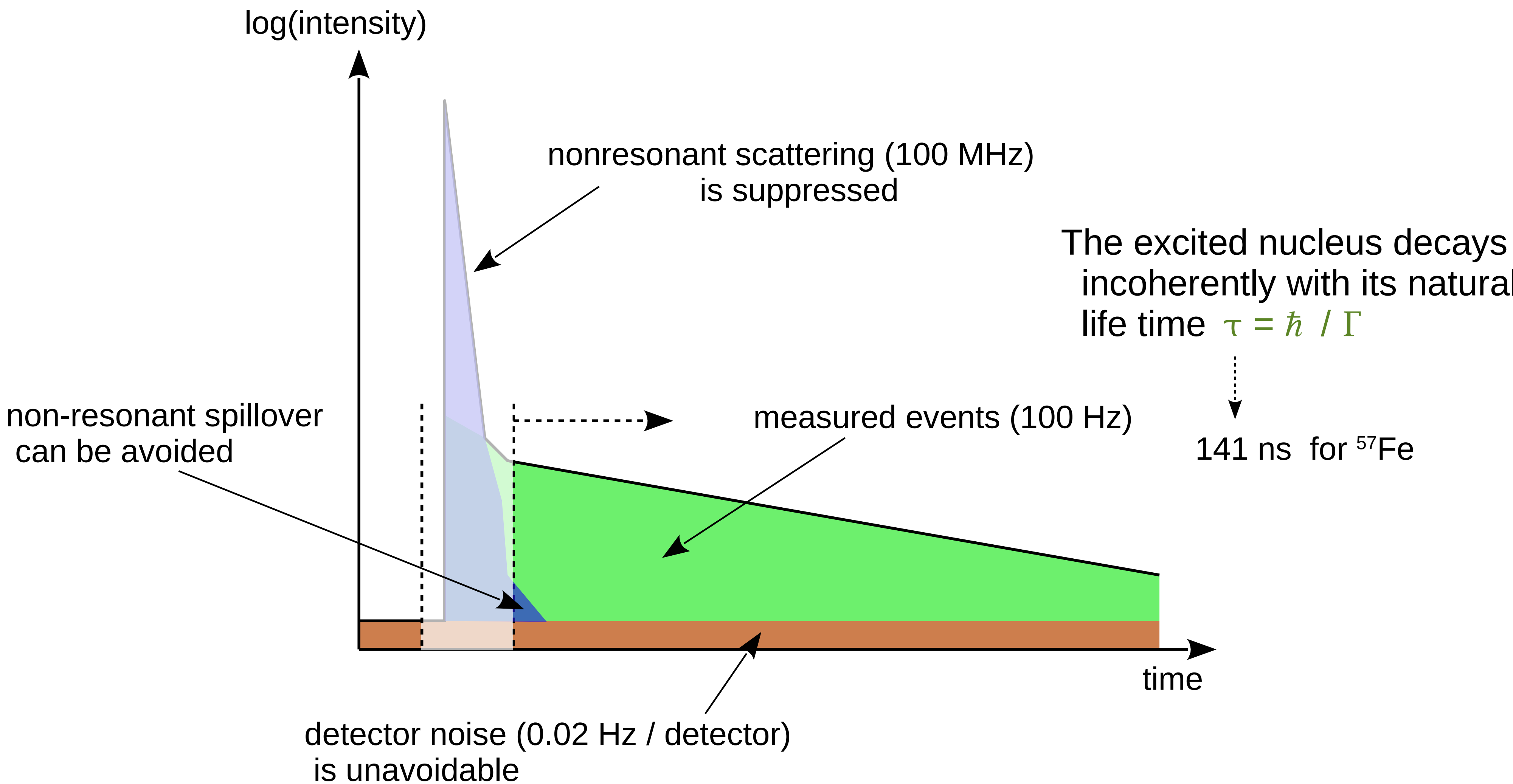
☆ ^{57}Fe:	2.2 %	141 ns
☆ ^{83}Kr:	11.6 %	212 ns
☆ ^{119}Sn:	8.6 %	25.6 ns
☆ ^{151}Eu:	47.8 %	13.8 ns
☆ ^{161}Dy:	18.9 %	40.7 ns

- scattering geometry: large collection angle, large scattering volume



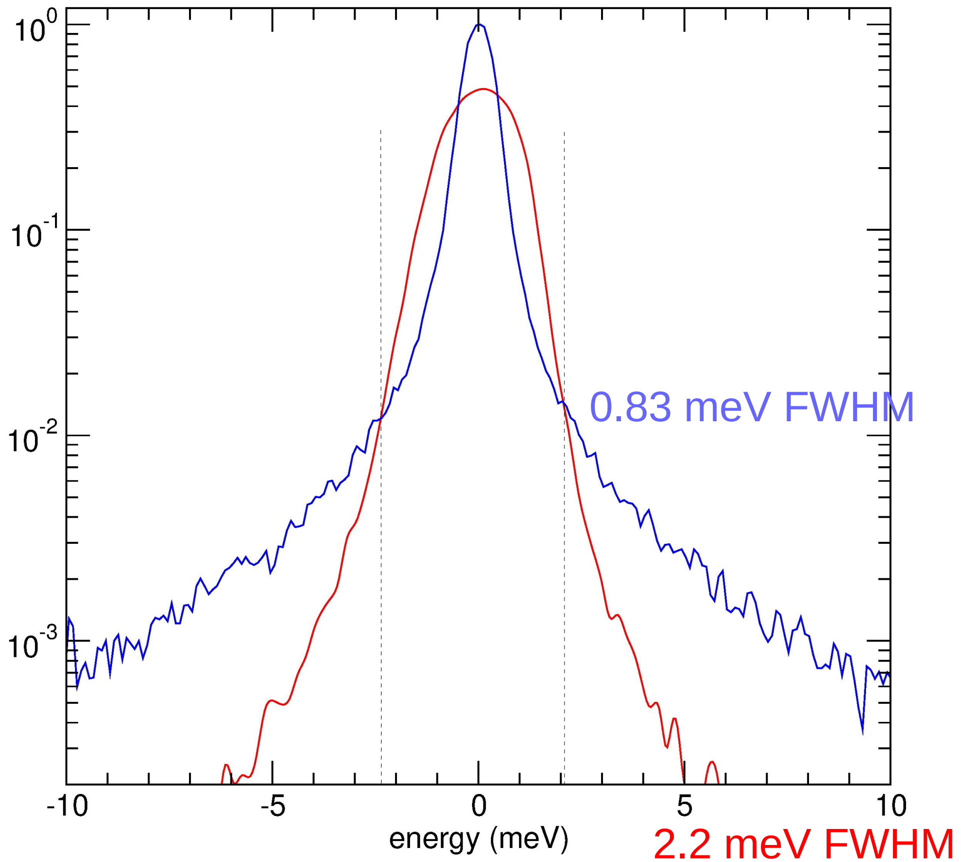
NRIXS, low background:

- background has two contributions:
  detector noise, non-resonant spillover



NRIXS, elastic peak:

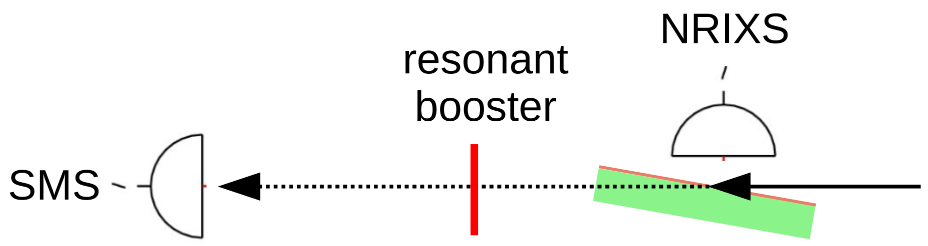
➢ choice of monochromator: bandwidth, shape, flux, stability

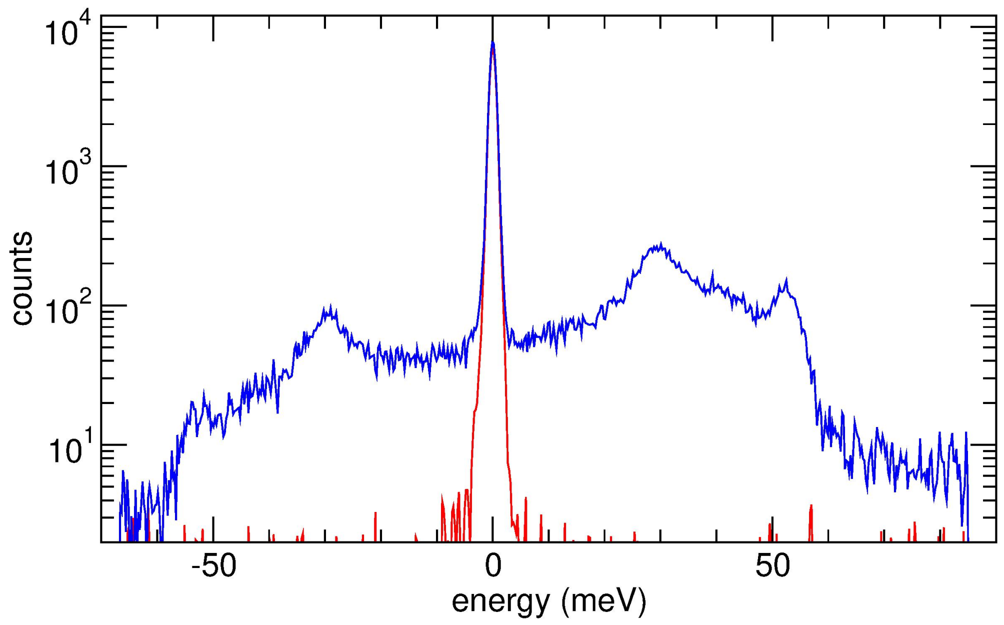


- ✰ monochromator design influences bandwidth and tails in different ways
- ✰ smaller tails are very important for weak scatterers such as:
  - – thin samples
  - – dilute samples
  - – low isotopic abundance

NRIXS, elastic peak:

➤ mitigate stability issues by *in-situ* measurement of mono response





✩ large distance between sample and SMS detector

✩ SMS signal ≥ NRIXS peak-signal

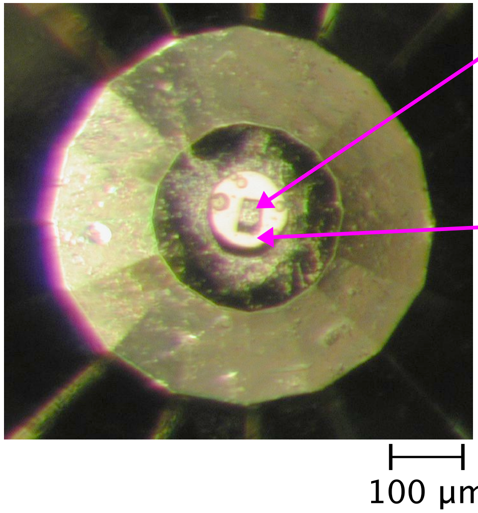
✩ use resonant booster only if sample is homogeneous over x-ray profile ⚠

NRIXS, environment:

- sample environment has to be "x-ray friendly": low absorption for observed x-rays

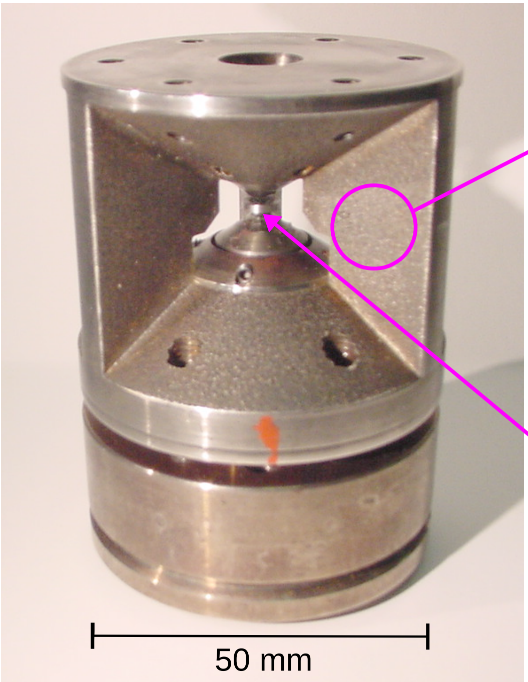
✫	^{57}Fe:	14.4 keV	**6.4 keV**
✫	^{83}Kr:	**9.3 keV**	1.6 keV
✫	^{119}Sn:	**23.9 keV**	3.4 keV
✫	^{151}Eu:	21.5 keV	**5.8 keV**
✫	^{161}Dy:	25.7 keV	6.5 keV

sample



✫ thick sample

✫ He pressure medium



✫ large openings for detector access

✫ Be gasket

NRIXS, energy range:

- detailed balance renders NRIXS spectrum asymmetric
  - ✰ start scan between -100 meV and -80 meV at room temperature
  - ✰ end scan depends on sample structure, pressure, temperature
- exclusion of negative energies completely disables checks on quality and consistency of data ✗✗✗
- recommended end scan energies:

✰ metals and alloys	80 - 120 meV
✰ oxides and silicates without hydrogen	100 - 150 meV
✰ oxides and silicates with hydrogen	150 - 200 meV

- selecting too small end scan energies excludes high-energy vibrations and compromises data quality ✗✗✗

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

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

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

Information from NRIXS spectra:

- directly from the data, S(E)
  - temperature

$$T = -\frac{E}{k_B} \ln \left[\frac{S(-E)}{S(E)} \right]$$

  - mean square displacement

$$\langle u^2 \rangle = -\frac{1}{k^2} \ln \left[1 - \int \{S(E) - S(0)\}\, dE \right]$$

  - kinetic energy

$$E_{kin} = \frac{1}{4E_R} \int (E - E_R)^2 S(E) dE$$

  - average force constant

$$D = \frac{k^2}{2E_R^2} \int (E - E_R)^3 S(E) dE$$

- quasi-harmonic lattice model
  - partial phonon density of states

$$\mathcal{D}(E)$$

  - Debye sound velocity

$$\mathsf{v}_D = \left(\frac{M}{2\rho\pi^2\hbar^3} \frac{E^2}{\mathcal{D}(E \to 0)} \right)^{1/3}$$

  - Grüneisen parameter

$$\gamma_D = \frac{1}{3} + \frac{\rho}{\mathsf{v}_D} \left(\frac{\partial \mathsf{v}_D}{\partial \rho} \right)_T$$

  - isotope fractionation

$$\ln \beta = -\frac{\Delta m}{M} \frac{1}{8(k_B T)^2} \int E^2 \mathcal{D}(E)\, dE$$

k ~ wave number of nuclear transition
E_R ~ recoil energy
ρ ~ mass density

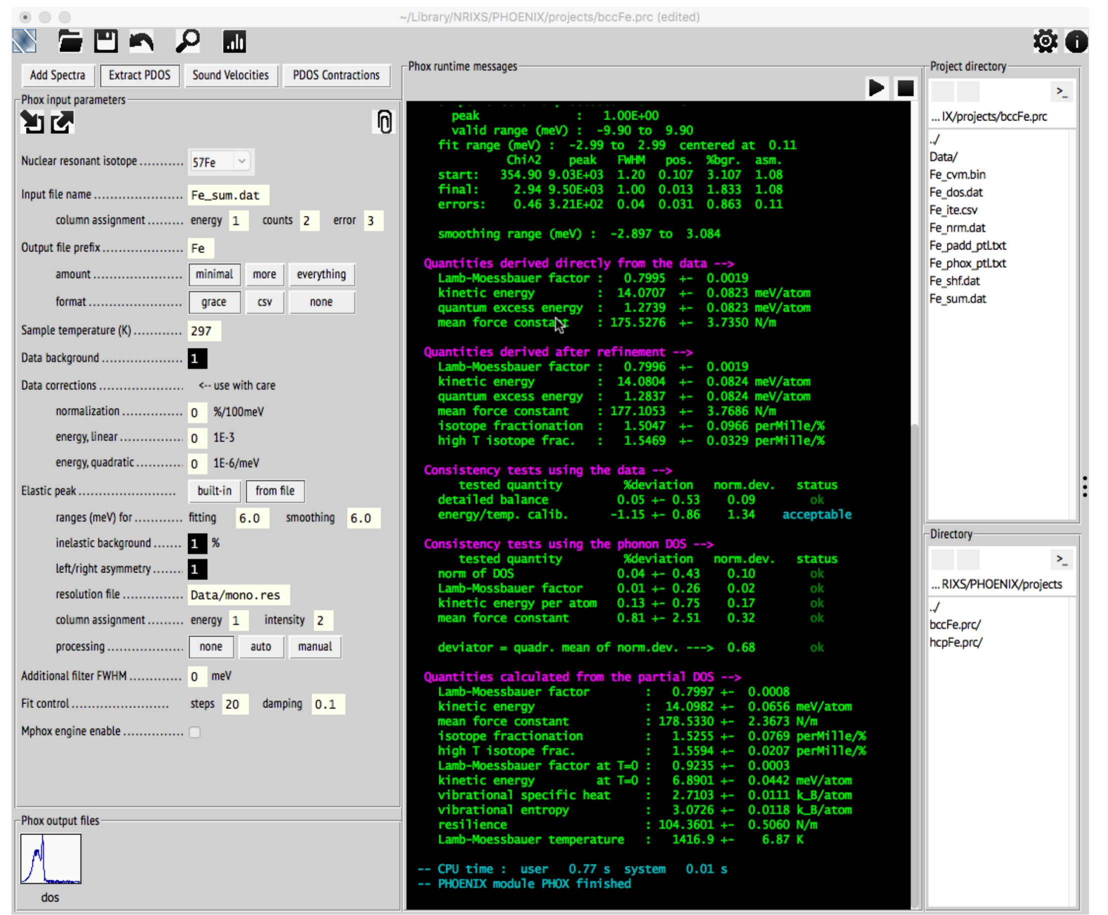
M ~ mass of resonant isotope
Δm ~ isotope mass difference
k_B ~ Boltzmann's constant
T ~ temperature

NRIXS evaluation, the PHOENIX GUI:

- GUI upgrade, PHOENIX-3.x, supported by Caltech
  - ☆ translates functionality into Tcl/Tk for Unix and MacOS
  - ☆ maintains all previous capabilities of CLI
  - ☆ enhancements of core modules
  - ☆ cross-project analysis tools

- upgrades to core modules
  - ☆ consistency optimization
  - ☆ advanced elastic peak subtraction
  - ☆ probability distribution analysis for Debye velocity determination

- Thanks to Jennifer Jackson and her group at Caltech for continuous tests of the software and for ongoing discussions for improvements



SMS sample:

- SMS is a transmission spectroscopy
  - What is the optimal sample thickness?
  - What counting rate can be expected?
- use CONUSS software to model sample signal
  - sample composition and density
  - expected hyperfine parameters
  - useful time range of measured spectrum
- use CONUSS software to evaluate measured data

CONUSS software provides solutions:

problem	program	SIF	examples
fitting data	kctl	in_kctl	
forward scattering		in_kfor	kctl-NFS1, kctl-NFS2
dual fit		in_kfor	kctl-NFS3
Mössbauer spectroscopy		in_kfor	kctl-MBS1, kctl-MBS2
grazing incidence		in_kgin	kctl-GINS
Bragg/Laue diffraction		in_kref	kctl-NBS1, kctl-NBS2
explore parameter space	kmco	in_kmco	
forward scattering or Mössbauer		in_kfor	kmco-NFS
grazing incidence		in_kgin	kmco-GINS
Bragg/Laue diffraction		in_kref	kmco-NBS
calculate spectra			
forward scattering or Mössbauer	kfmf	in_kfor	kfmf-NFS, kfor-NFS
grazing incidence	kgmf	in_kgin	kgmf-GINS, kgmf-GIS
Bragg/Laue diffraction	krmf	in_kref	krmf-NBS

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

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

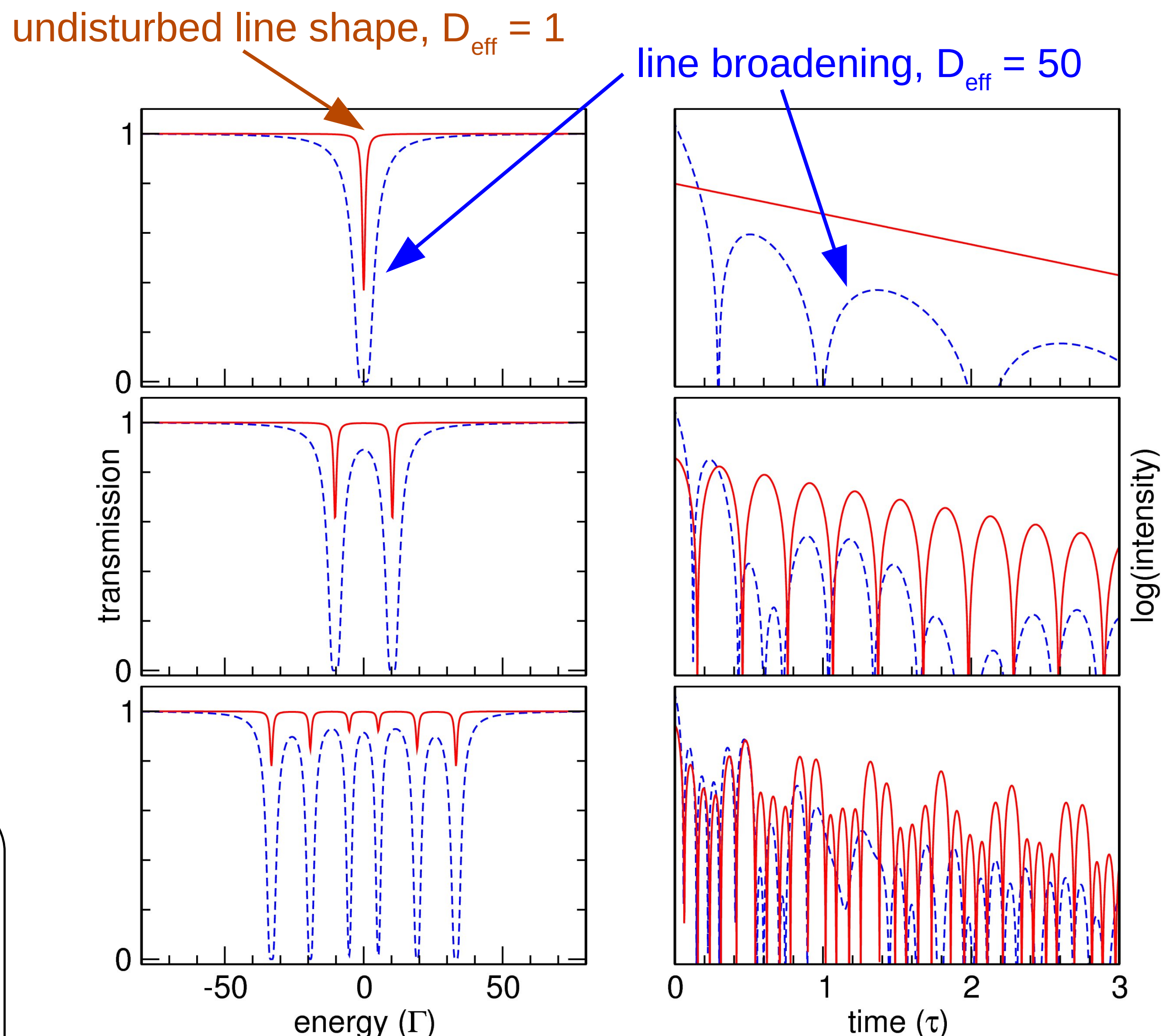
- Mössbauer transmission spectrum

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

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

SMS sample thickness:

- ✰ 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



Mössbauer spectroscopy SMS

effective thickness:

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

Lamb-Mössbauer factor

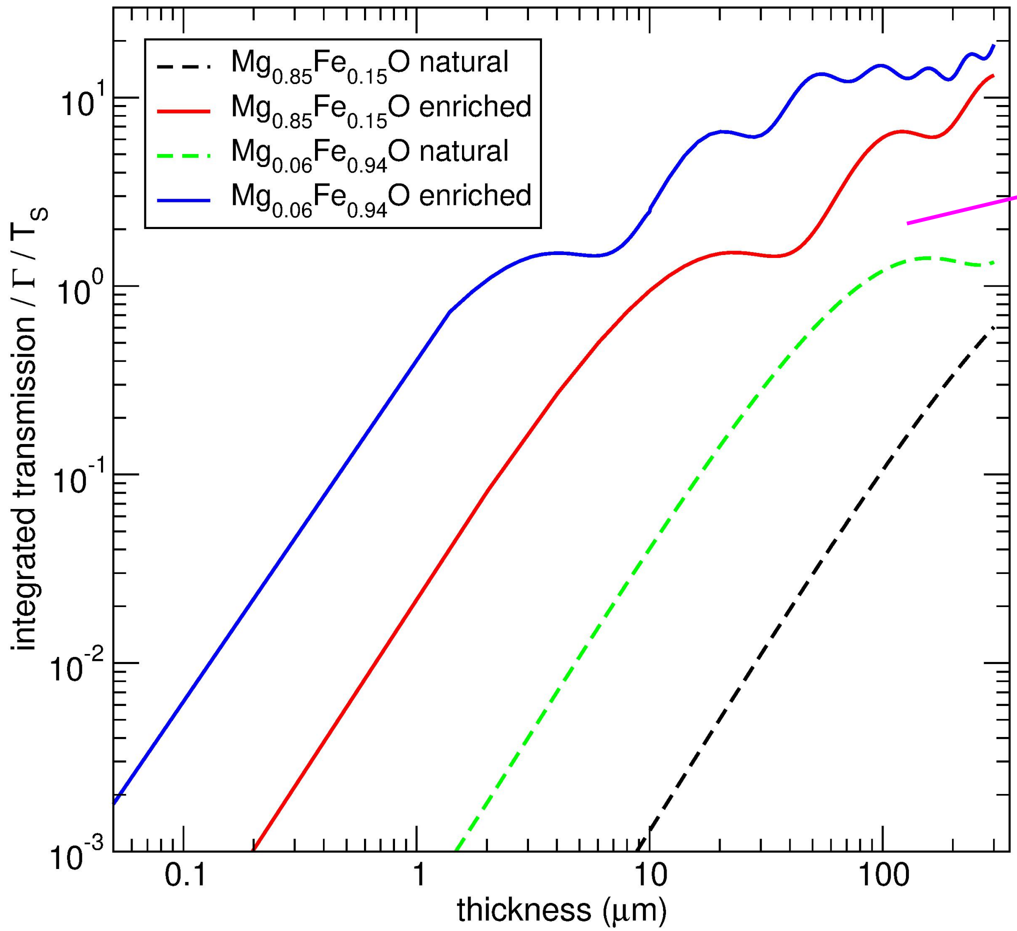
resonant cross section

nuclei per area

geometric thickness

✰ calculations performed with CONUSS software

SMS integrated transmission:



- delayed flux

$$F = \frac{N}{\Gamma T_S} T_S \, T_A \, \epsilon_D \, I_\Gamma$$

- prompt flux may saturate detector

$$P = T_S \, T_A \, \epsilon_D \, I_0 \leq P_{sat}$$

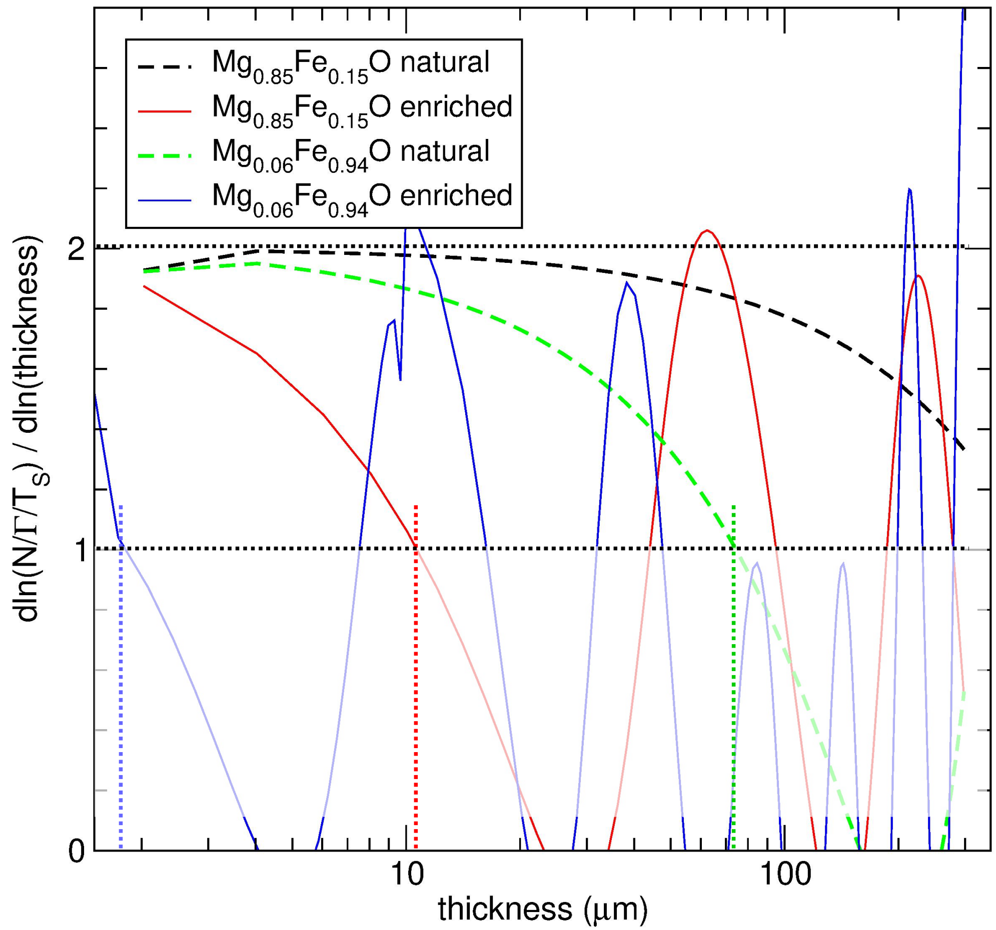
- maximum delayed flux

$$F \leq \frac{N}{\Gamma T_S} \frac{\Gamma}{\Delta E} P_{sat}$$

$\approx$ 500 for ^{57}Fe

☆ calculations performed with CONUSS software

SMS choice of thickness:



- the logarithmic derivative

$$\frac{d}{d \ln D} \frac{N}{\Gamma T_S}$$

decreases with thickness from values close to 2.

- values > 1 usually mean acceptable thickness effects

- maximum counting rates

$Fe_{0.15}Mg_{0.85}O$	300 1/s	300 micron
$^{57}Fe_{0.15}Mg_{0.85}O$	500 1/s	11 micron
$Fe_{0.94}Mg_{0.06}O$	460 1/s	75 micron
$^{57}Fe_{0.94}Mg_{0.06}O$	450 1/s	1.5 micron

In conclusion:

- develop a good strategy by familiarizing yourself with the specifics of NRIXS and SMS
- use forward modeling tools provided with the PHOENIX and CONUSS software to obtain quantitative information for your samples
- optimized samples for NRIXS and SMS are very different
- follow the guidelines provided in this presentation
- start communications early with the staff at the beamline that you chose for your experiments
- evaluate your data with the PHOENIX and CONUSS software if possible in-situ during the experiment

Ende