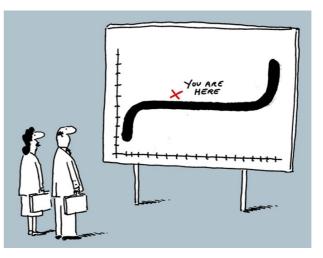




https://www.nrixs.com wolfgang@gps.caltech.edu wolfgang@nrixs.net

Strategies for Nuclear Resonant Experiments

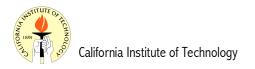


Wolfgang Sturhahn

Good strategy matters:

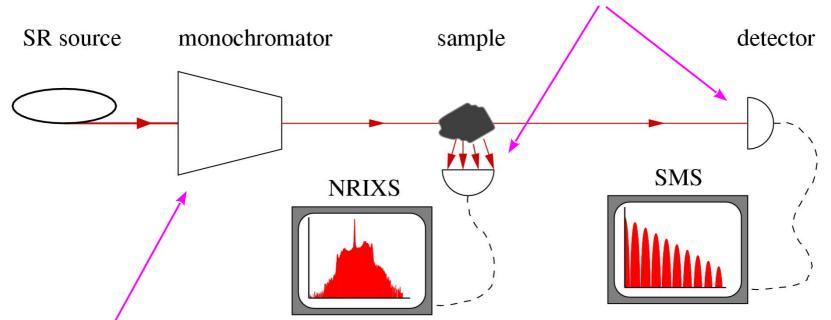
achieve goals by following a plan over an extended time period

- What are the scientific goals? Can they be achieved by NRS experiments?
 - \Rightarrow knowledge of science area and NRS
- ☆ Which NRS method is appropriate for scientific goals? Can a reasonable experimental plan be developed?
 - \Rightarrow forward modeling tools
 - \Rightarrow beamline capabilities
 - \Rightarrow experiment readiness definition
- ☆ How much time is needed for relevant experiments? Are non-NRS experiments needed beforehand?
 - \Rightarrow counting rate estimates, staffing requirements
- ☆ We have the data! Now what?
 - \Rightarrow data evaluation tools



NRS, experimental setup:

x-ray pulses must be sufficiently separated in time



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)



detectors must have good time resolution

and excellent dynamic range

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
- \Rightarrow velocity in gases
- \Rightarrow vibrations in solids

- \Rightarrow recoil energy shift
- \Rightarrow Doppler shift
- \Rightarrow phonon excitation/annihilation, recoilless absorption
- \Rightarrow local vibrational density of states
- ☆ applications include determination of sound velocities and thermodynamic properties

\succ The nucleus is not a point charge:

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

- rightarrow internal dynamics \Rightarrow nuclear transitions
- \Rightarrow volume \Rightarrow isome
- ☆ spin

- ⇒ isomer shift
 ⇒ magnetic level splitting
- ☆ quadrupole moment
- \Rightarrow 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

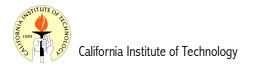
Instruments

- ☆ monochromator with appropriate bandwidth & flux
- ☆ rotation & translation stages with appropriate range & resolution
- \Rightarrow focusing optics for small samples
- ☆ detectors & miscellaneous electronics

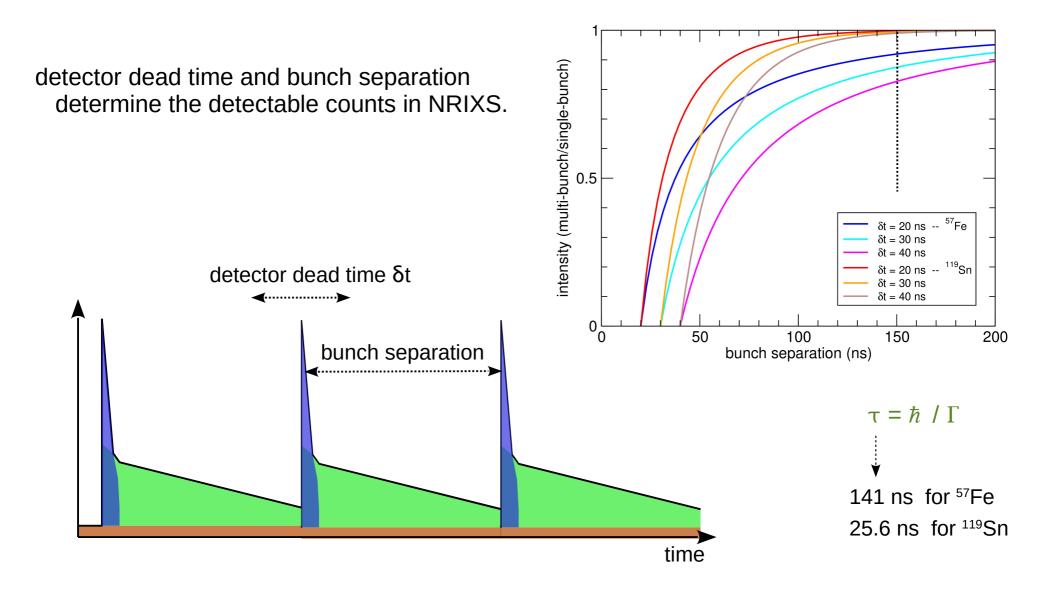
Software tools

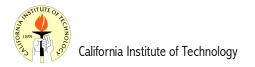
- ☆ data acquisition & motion control
- ☆ *in-situ* data evaluation for experimental progress assessment

Storage ring time structure

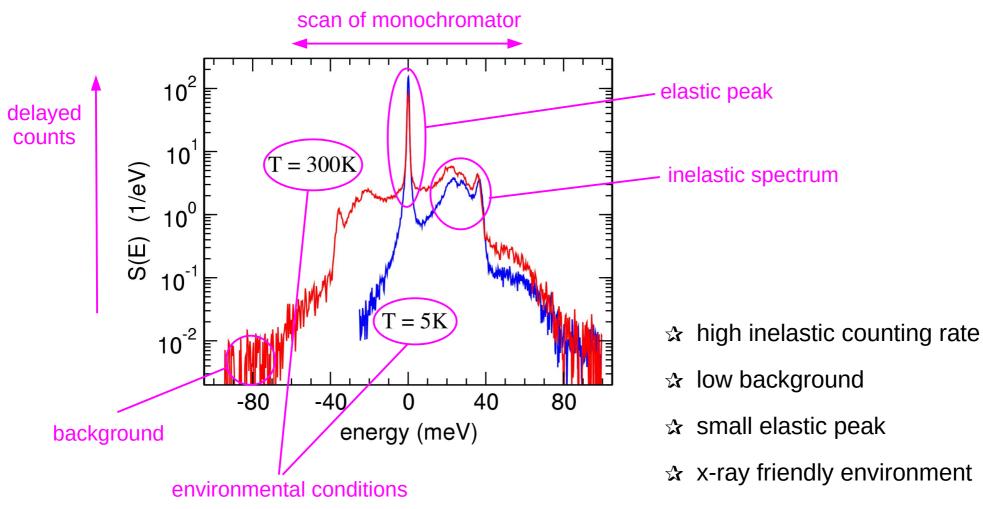


<u>Time structure of synchrotron radiation:</u>

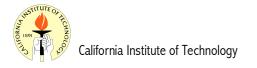




NRIXS sample:



☆ appropriate energy range

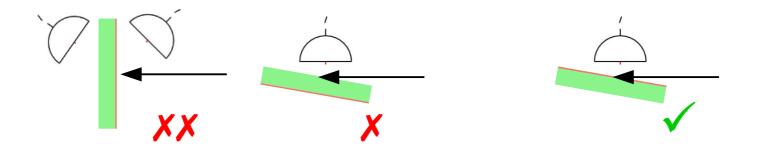


NRIXS, inelastic counting rate:

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

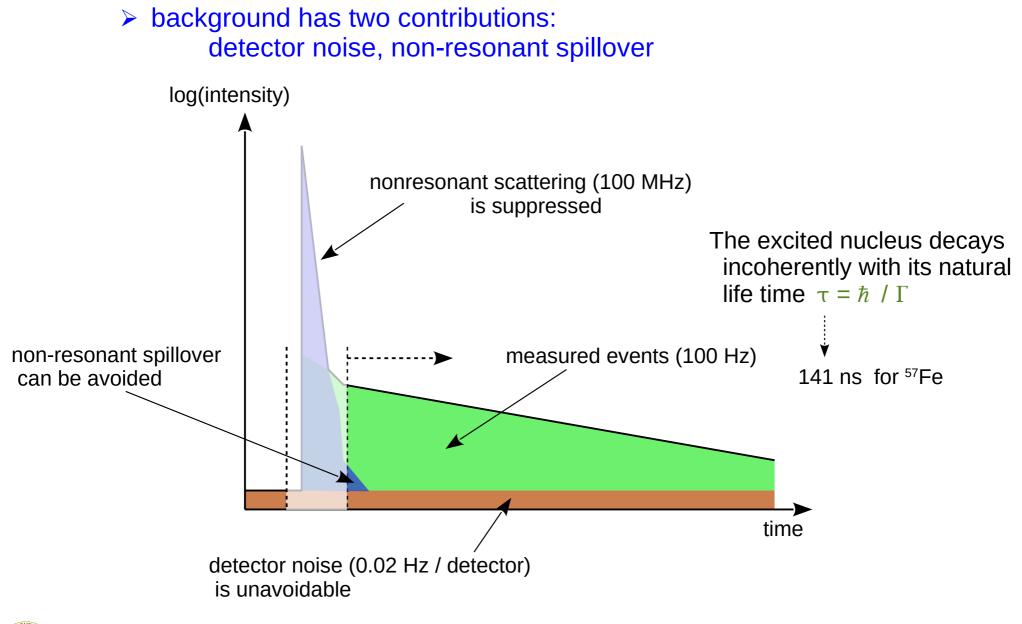
公	⁵⁷ Fe:	2.2 %	141 ns
公	⁸³ Kr:	11.6 %	212 ns
公	¹¹⁹ Sn:	8.6 %	25.6 ns
公	¹⁵¹ Eu:	47.8 %	13.8 ns
公	¹⁶¹ Dy:	18.9 %	40.7 ns

> scattering geometry: large collection angle, large scattering volume





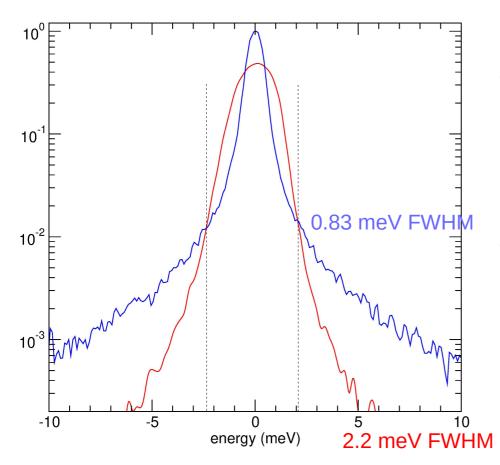
NRIXS, low background:



California Institute of Technology

NRIXS, elastic peak:

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



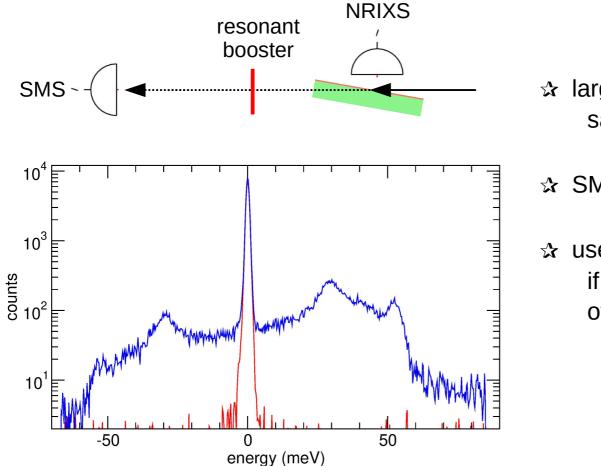
monochromator design influences
 bandwidth and tails in different ways

- ☆ 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 \ge NRIXS peak-signal
- use resonant booster only
 if sample is homogeneous
 over x-ray profile

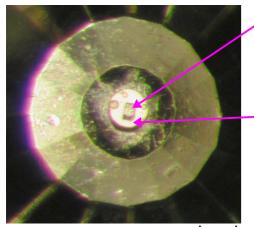


NRIXS, environment:

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

公	⁵⁷ Fe:	14.4 keV	6.4 keV
公	⁸³ Kr:	9.3 keV	1.6 keV
公	¹¹⁹ Sn:	23.9 keV	3.4 keV
公	¹⁵¹ Eu:	21.5 keV	5.8 keV
公	¹⁶¹ Dy:	25.7 keV	6.5 keV

sample



100 μm

 \Rightarrow thick sample

☆ He pressure medium



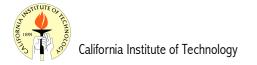
☆ large openings for detector access

☆ 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
 - \Rightarrow 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 XXX



Interpretation of NRIXS spectra:

NRIXS spectra directly provide the Fourier transform of the <u>self-intermediate scattering function</u>

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

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

$$S(\mathbf{k}, E) = f(\mathbf{k})\delta(E) + \sum_{n=1}^{\infty} S_n(\mathbf{k}, E)$$

$$S_1(\mathbf{k}, E) = f(\mathbf{k}) \frac{E_R}{E(1 - \exp[-\beta E])} g(\mathbf{k}, |E|)$$

$$S_n(\mathbf{k}, E) = \frac{1}{nf(\mathbf{k})} \int S_{n-1}(\mathbf{k}, E')S_1(\mathbf{k}, E - E')dE$$

$$f(\mathbf{k}) = \exp\left[-\int \frac{E_R}{E} \coth(\frac{\beta E}{2}) g(\mathbf{k}, E)dE\right]$$

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



Information from NRIXS spectra:

- \succ directly from the data, S(E)
 - ⇒ temperature

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

⇒ mean square displacement

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

⇒ kinetic energy

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

⇒ average force constant

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

 $\begin{array}{ll} k & \sim \text{ wave number of nuclear transition} \\ \mathsf{E}_{_{\mathsf{R}}} & \sim \text{ recoil energy} \\ \rho & \sim \text{ mass density} \end{array}$

- > quasi-harmonic lattice model
 - $\Rightarrow \text{ partial phonon density of states}$ $\mathcal{D}(E)$
 - $\Rightarrow \text{ Debye sound velocity} \\ \mathsf{v}_D = \left(\frac{M}{2\rho\pi^2\hbar^3} \frac{E^2}{\mathcal{D}(E \to 0)}\right)^{1/3}$
 - ⇒ Grüneisen parameter

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

 \Rightarrow isotope fractionation

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

 $\begin{array}{ll} \mathsf{M} & \sim \text{ mass of resonant isotope} \\ \Delta m & \sim \text{ isotope mass difference} \\ \mathsf{k}_{_{B}} & \sim \text{ Boltzmann's constant} \\ \mathsf{T} & \sim \text{ temperature} \end{array}$

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

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x input parameters]]		> I	
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ut file name	Fe sum.dat		final: 2.94 9.50E+03 1.00 0.013 1.833 1.08	Fe_dos.dat
			errors: 0.46 3.21E+02 0.04 0.031 0.863 0.11	Fe_ite.csv
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ple temperature (K)	207		mean force constant : 175.5276 +- 3.7350 N/m	
pre temperature (k)	291			
a background	1		Quantities derived after refinement> Lamb-Moessbauer factor : 0.7996 +- 0.0019	
a corrections	< use with care		kinetic energy : 14.0804 +- 0.0824 meV/atom	
			quantum excess energy : 1.2837 +- 0.0824 meV/atom	
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	_	, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		Directory
inelastic background	1 %		Consistency tests using the phonon DOS> tested quantity %deviation norm.dev. status	
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resolution file	Data/mono_res		Lamb-Mossbauer factor 0.01 +- 0.26 0.02 ok	RIXS/PHOENIX/projects
			kinetic energy per atom 0.13 +- 0.75 0.17 ok	.1
column assignment	energy <u>1</u> inte	nsity 2	mean force constant 0.81 +- 2.51 0.32 ok	bccFe.prc/
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Alered Alere Failure	0			
itional filter FWHM	U mev		Quantities calculated from the partial DOS> Lamb-Moessbauer factor : 0.7997 +- 0.0008	
ontrol	steps 20 dam	ping 0.1	kinetic energy : 14.0982 +- 0.0656 meV/atom	
ox engine enable			mean force constant : 178.5330 +- 2.3673 N/m	
ux engine enable	•• 🕓		isotope fractionation : 1.5255 +- 0.0769 perMille/%	
			high T isotope frac. : 1.5594 +- 0.0207 perMille/% Lamb-Moessbauer factor at T=0 : 0.9235 +- 0.0003	
			kinetic energy at T=0 : 6.8901 +- 0.0442 meV/atom	
			vibrational specific heat : 2.7103 +- 0.0111 k_B/atom	
x output files			vibrational entropy : 3.0726 +- 0.0118 k_B/atom resilience : 104.3601 +- 0.5060 N/m	
			Lamb-Moessbauer temperature : 1416.9 +- 6.87 K	
4				
			CPU time : user 0.77 s system 0.01 s	



SMS sample:

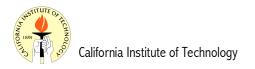
> SMS is a transmission spectroscopy

- \Rightarrow What is the optimal sample thickness?
- \Rightarrow What counting rate can be expected?

use CONUSS software to model sample signal

- \Rightarrow 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	m 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

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

Mössbauer transmission spectrum

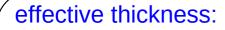
$$T(E) = \int \text{Trace}\left[e^{-kD\text{Im}[\delta \mathbf{n}(E')]}\right] L(E - E') dE'$$

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

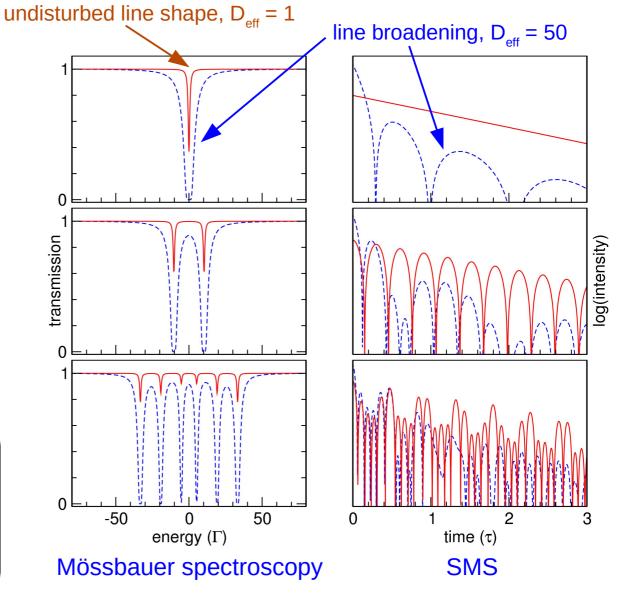


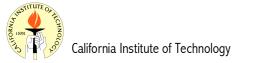
SMS sample thickness:

- ☆ 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

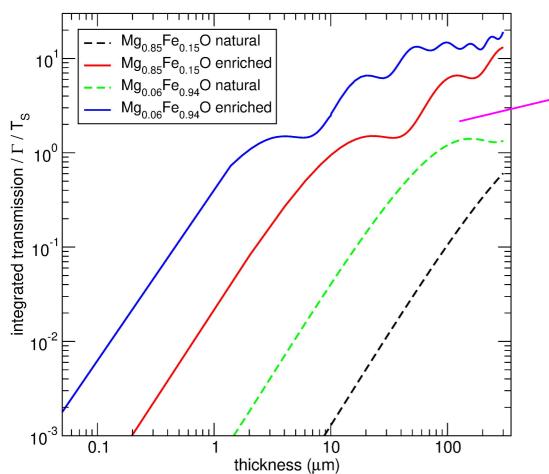


 $\begin{array}{l} \mathsf{D}_{\mathsf{eff}} = \mathsf{F}_{\mathsf{LM}} \; \sigma_{\mathsf{0}} \; \rho \; \mathsf{D} \\ \mathsf{Lamb}\text{-M} \\ \mathsf{N} \\ \mathsf{O} \\ \mathsf{S} \\ \mathsf{S} \\ \mathsf{b} \\ \mathsf{u} \\ \mathsf{c} \\ \mathsf{f} \\ \mathsf{c} \\ \mathsf{f} \\ \mathsf{f}$

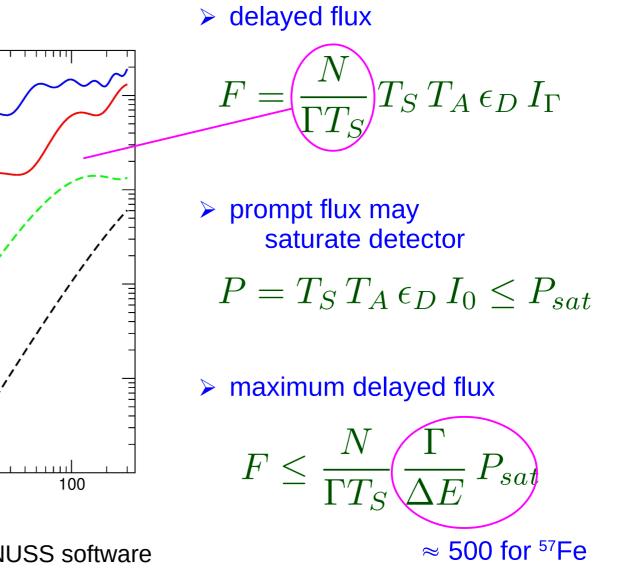




SMS integrated transmission:

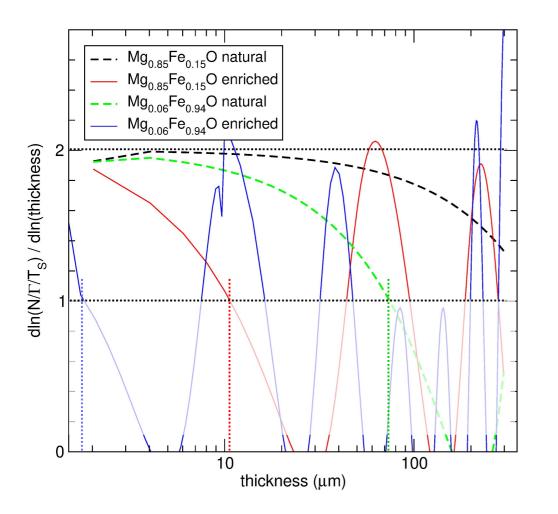


☆ calculations performed with CONUSS software





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
- \succ 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



#