Theory encounters experiments of Mössbauer spectroscopy

Tutorial lecture

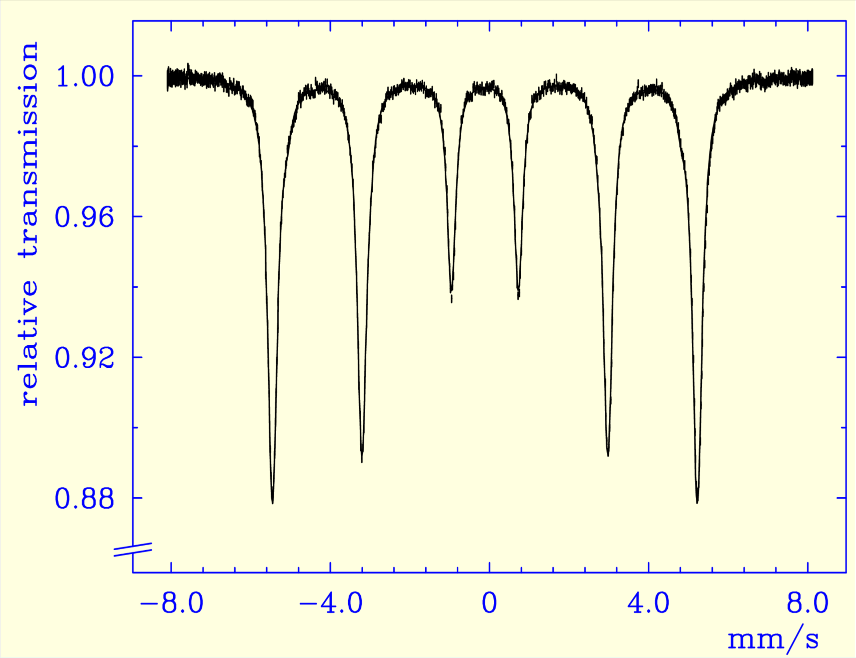
Hartmut Spiering
Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität Mainz, Mainz, Germany

Dénes Lajos Nagy
Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary

International Conference on the Applications of the Mössbauer Effect
Saint Petersburg, Russia, 3–8 September 2017

Spectrum
57Co/Rh source, α-iron (25µm) absorber

Theory
H, Is, (texture)



χ^2 value
(close to expectation)?

Line width/shape?

area/thickness =>25µm ?

7 points concerning the Spectrometer/Adaption of theory to experiment

Outline

- ***Reduced χ^2***
- ***Baseline of a transmission spectrum***
- ***The raw data problem***
- ***Choice of the drive frequency***
- ***Theoretical value at channel i***
- ***Dead time***
- ***Background***

- ***Conclusion: some good practices***

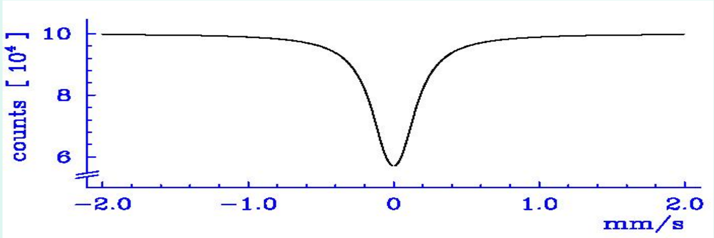
Reduced χ^2

Counts: Poisson distribution: $\chi^2 = 1.0 \pm \sqrt{\frac{2}{N_{ch}}}$, $N_{ch} = 2048$ => $\chi^2 = 1 \pm 0.031$

Reduced χ^2

Counts: Poisson distribution: $\chi^2 = 1.0 \pm \sqrt{\frac{2}{N_{ch}}}$, $N_{ch} = 2048$ => $\chi^2 = 1 \pm 0.031$

$t_{eff} = 10$



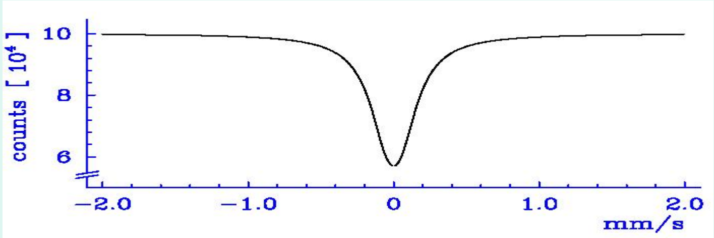
Beer–Lambert law

$$Sp(v) \propto \int_{-\infty}^{\infty} L_S(\tau - v)\, e^{\left(-t_{eff} L_A(\tau)\right)} d\tau$$

Reduced χ^2

Counts: Poisson distribution: $\chi^2 = 1.0 \pm \sqrt{\frac{2}{N_{ch}}}$, $N_{ch} = 2048 \;\; => \;\; \chi^2 = 1 \pm 0.031$

$t_{eff} = 10$



Beer–Lambert law

$$Sp(v) \propto \int_{-\infty}^{\infty} L_S(\tau - v)\, e^{\left(-t_{eff} L_A(\tau)\right)} d\tau$$

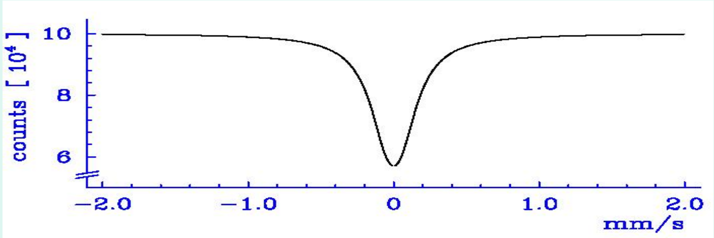
Fit: thin absorber approximation

$$Sp(v) \propto 1 - t_{eff} L(v, \Gamma = \Gamma_S + \Gamma_A)$$

Reduced χ^2

Counts: Poisson distribution: $\chi^2 = 1.0 \pm \sqrt{\frac{2}{N_{ch}}}$, $N_{ch} = 2048 \Rightarrow \chi^2 = 1 \pm 0.031$

$t_{eff} = 10$



Beer–Lambert law

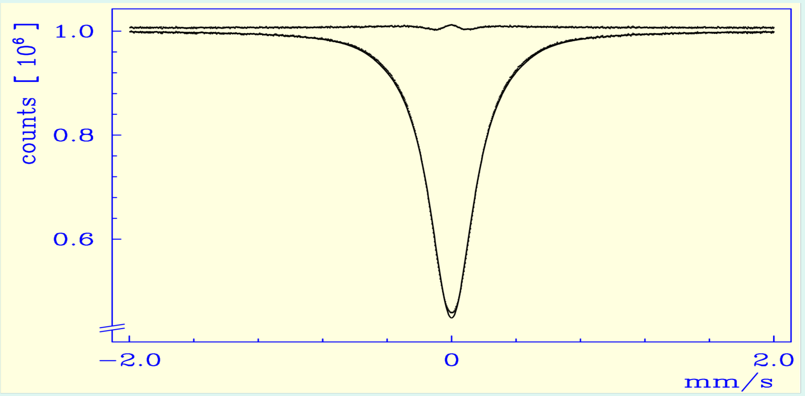
$$Sp(v) \propto \int_{-\infty}^{\infty} L_S(\tau - v)\, e^{(-t_{eff} L_A(\tau))}\, d\tau$$

<u>*Fit: thin absorber approximation*</u>

$$Sp(v) \propto 1 - t_{eff} L(v, \Gamma = \Gamma_S + \Gamma_A)$$

synthetic data by Monte Carlo simulations

(AS70 algorithm of Odeh and Evans, 1974)



Lorentz-curve: $\chi^2 = 5.47$, $\Gamma = 2.49\,\Gamma_N$

Voigt profile: $\chi^2 = 1.42$, $\Gamma = 2.15\,\Gamma_N$, $\sigma_{Gauss} = 1.17\,\Gamma_N$

Reduced χ^2

Note:

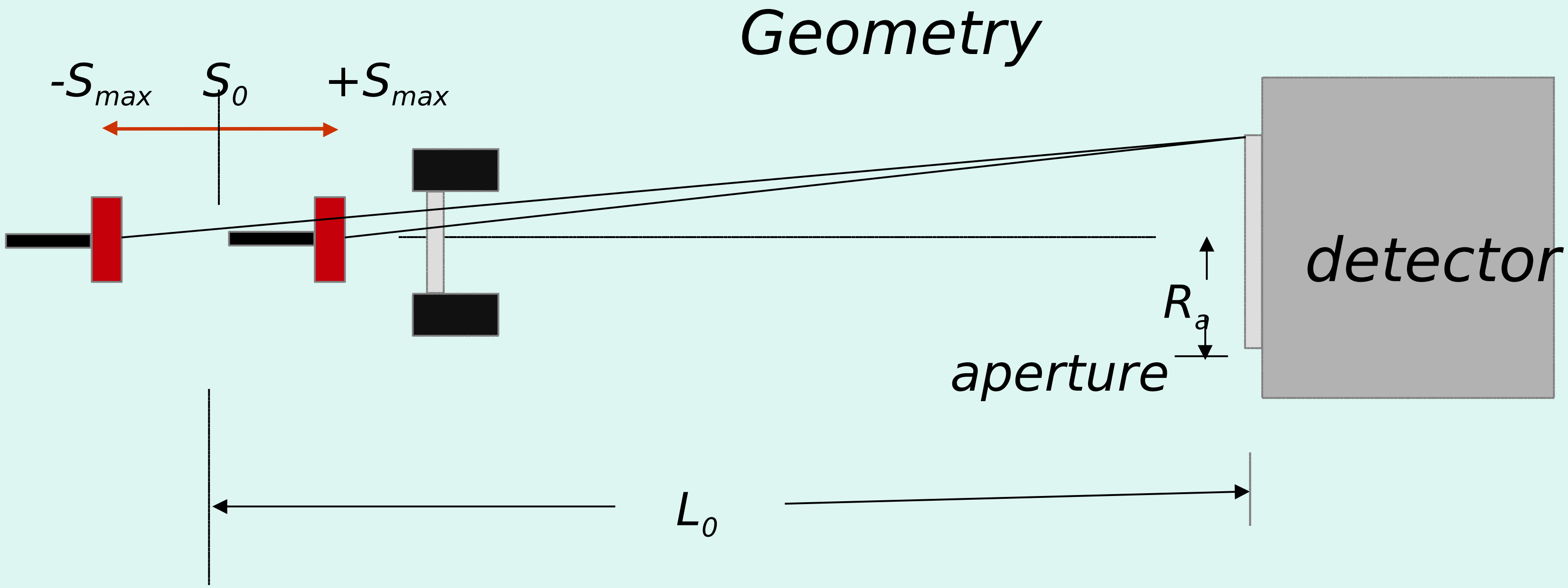
Fit: thin absorber approximation

area is obtained to a good approximation by the χ^2 - fit procedure

Fit: finite thickness

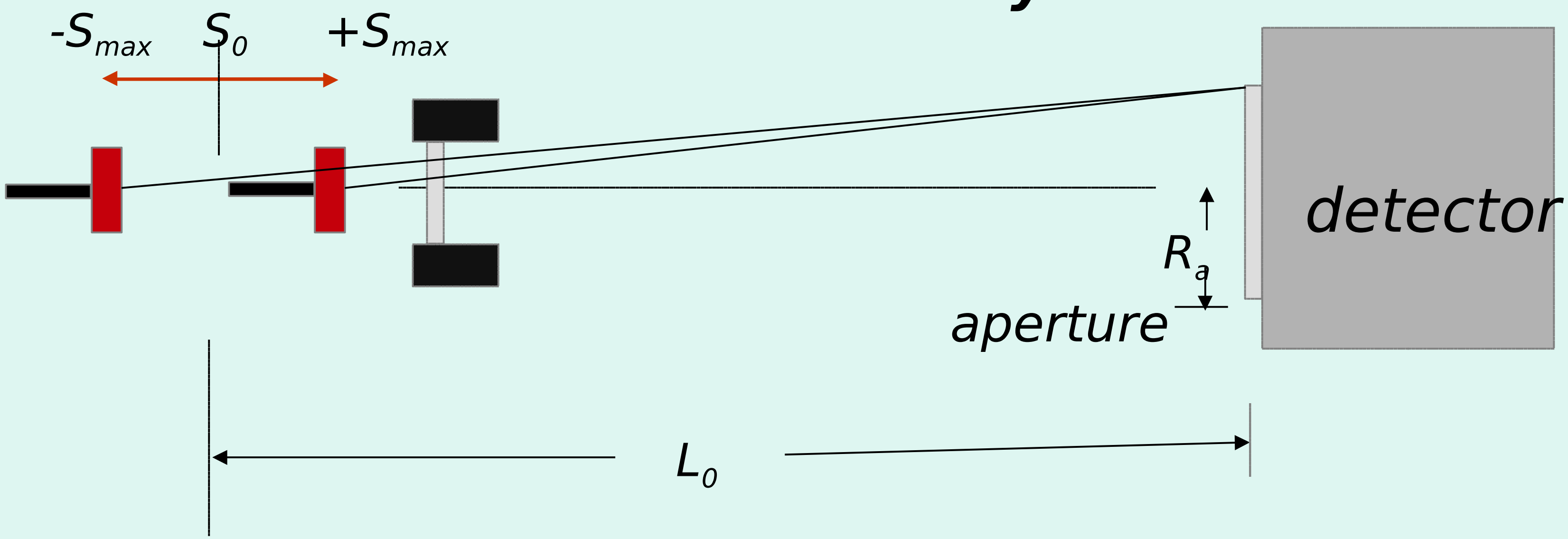
Use of Beer–Lambert law and convolution integral:
thickness instead of area
χ^2-value gets a meaning (validity of the theory)

Baseline of a transmission spectrum

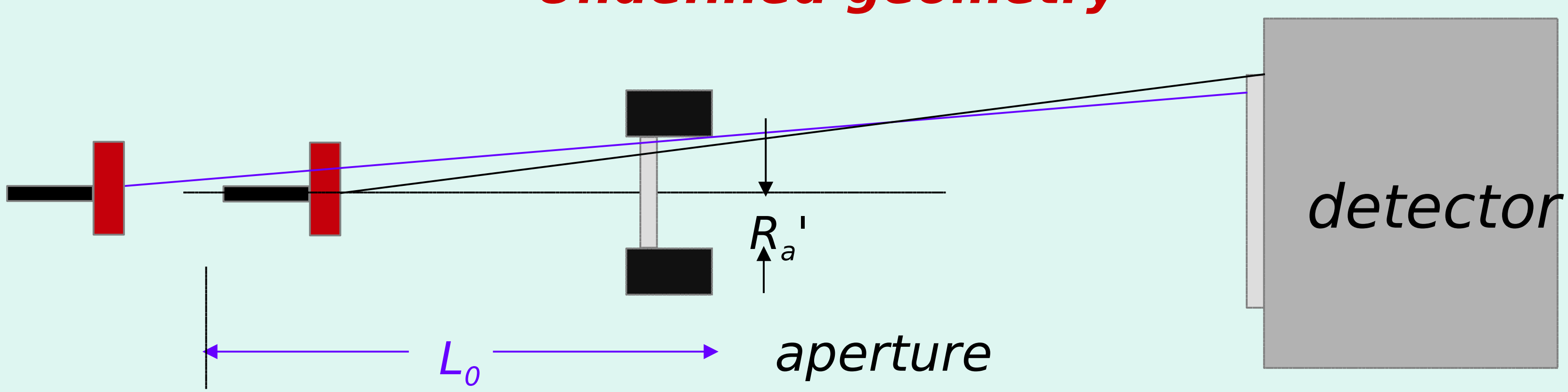


Baseline of a transmission spectrum

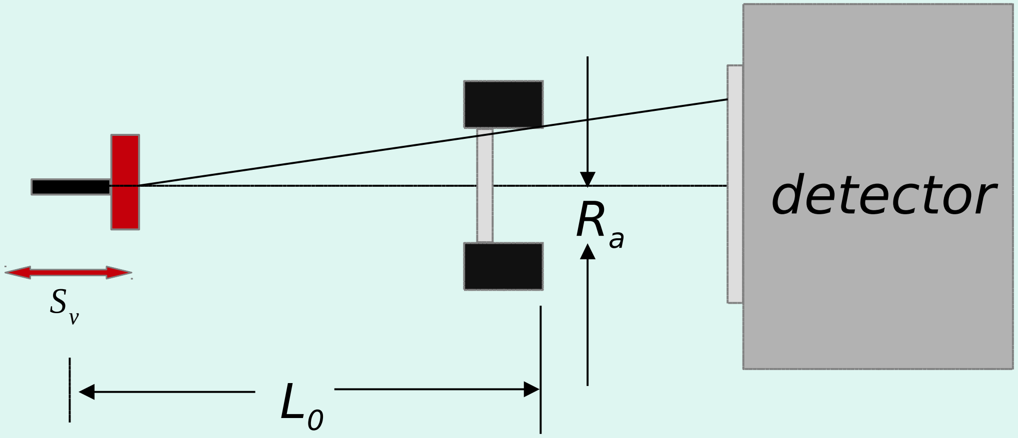
Geometry



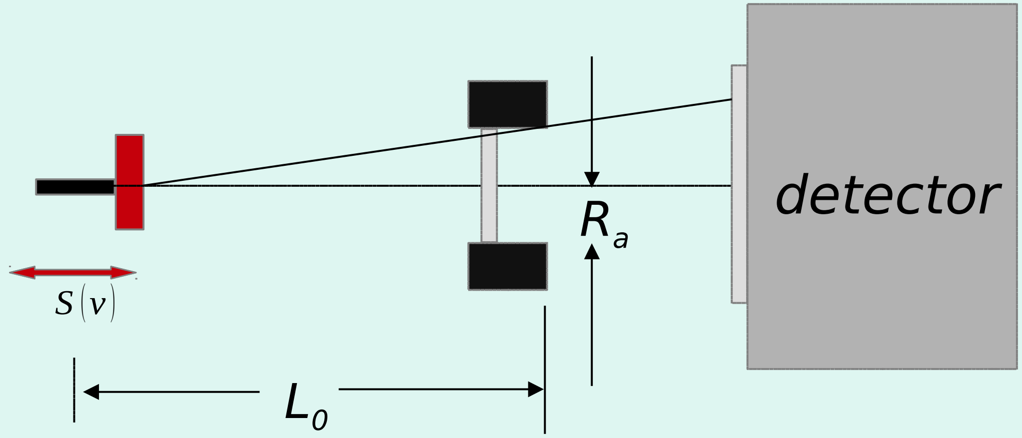
Undefined geometry



Baseline of a transmission spectrum

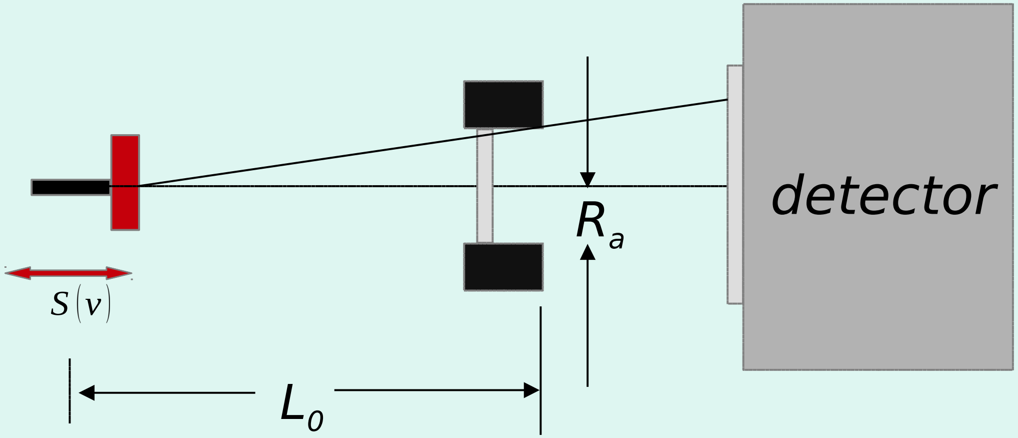


Baseline of a transmission spectrum



Solid angle: $$\Omega_0 = 2\pi\left(1-\frac{L_0}{\sqrt{L_0^2+R_a^2}}\right), \quad \Omega(v) = 2\pi\left(1-\frac{L_0+S(v)}{\sqrt{\left(L_0+S(v)\right)^2+R_a^2}}\right)$$

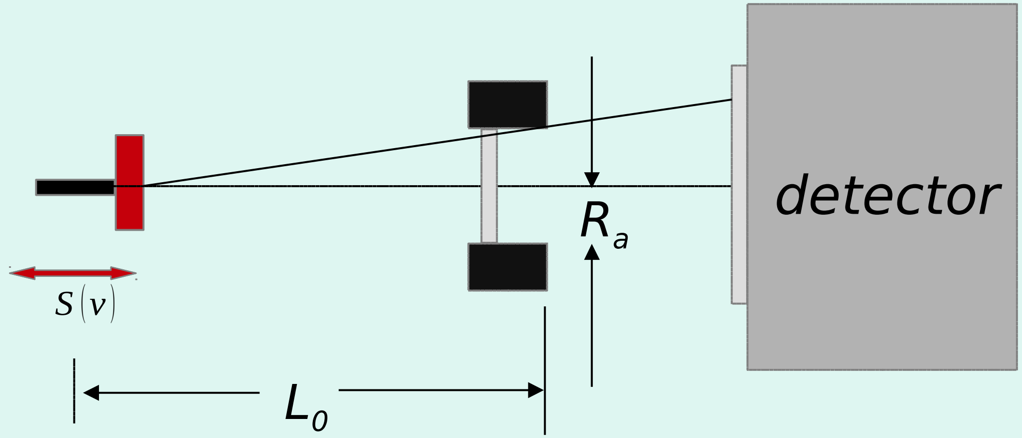
Baseline of a transmission spectrum



Solid angle: $\Omega_0 = 2\pi\left(1-\frac{L_0}{\sqrt{L_0^2+R_a^2}}\right)$, $\Omega(v) = 2\pi\left(1-\frac{L_0+S(v)}{\sqrt{\left(L_0+S(v)\right)^2+R_a^2}}\right)$

Count rate (v): $\frac{\Omega(v)}{\Omega_0} = \frac{1}{(1+\delta)^2}\left(1+\frac{3}{4}\varepsilon^2\left(1-\frac{1}{(1+\delta)^2}\right)+\ldots\right) \approx \frac{1}{(1+\delta)^2}$, $\varepsilon = \frac{R_a}{L_0}$, $\delta(v) = \frac{S(v)}{L_0}$

Baseline of a transmission spectrum

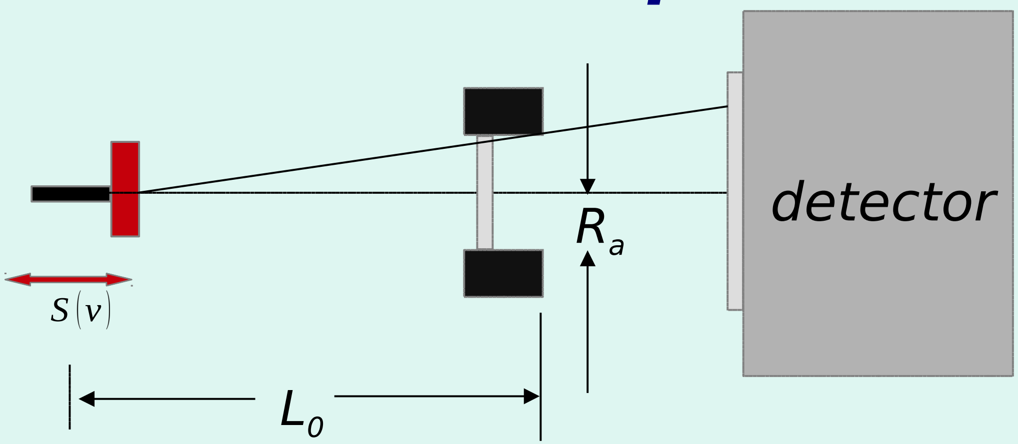


Solid angle: $$\Omega_0 = 2\pi\left(1-\frac{L_0}{\sqrt{L_0^2+R_a^2}}\right),\quad \Omega(v) = 2\pi\left(1-\frac{L_0+S(v)}{\sqrt{\left(L_0+S(v)\right)^2+R_a^2}}\right)$$

Count rate (v): $$\frac{\Omega(v)}{\Omega_0} = \frac{1}{(1+\delta)^2}\left(1+\frac{3}{4}\varepsilon^2\left(1-\frac{1}{(1+\delta)^2}\right)+\ldots\right) \approx \frac{1}{(1+\delta)^2},\qquad \varepsilon = \frac{R_a}{L_0},\qquad \delta(v) = \frac{S(v)}{L_0}$$

$$S(t) = S_{max}\sin(\omega t),\quad v(t) = S_{max}\omega\cos(\omega t) \quad\rightarrow\quad S_{max}\,\omega = v_{max},\qquad \frac{S(v)}{L_0} = \pm\frac{S_{max}}{L_0}\sqrt{1-\left(\frac{v}{v_{max}}\right)^2},$$

Baseline of a transmission spectrum



Solid angle: $\Omega_0 = 2\pi\left(1-\frac{L_0}{\sqrt{L_0^2+R_a^2}}\right),\quad \Omega(v) = 2\pi\left(1-\frac{L_0+S(v)}{\sqrt{\left(L_0+S(v)\right)^2+R_a^2}}\right)$

Count rate (v): $\frac{\Omega(v)}{\Omega_0} = \frac{1}{(1+\delta)^2}\left(1+\frac{3}{4}\varepsilon^2\left(1-\frac{1}{(1+\delta)^2}\right)+\ldots\right) \approx \frac{1}{(1+\delta)^2},\quad \varepsilon = \frac{R_a}{L_0},\quad \delta(v) = \frac{S(v)}{L_0}$

$$S(t) = S_{max}\sin(\omega t),\quad v(t) = S_{max}\,\omega\cos(\omega t) \quad\rightarrow\quad S_{max}\,\omega = v_{max},\qquad \frac{S(v)}{L_0} = \pm\frac{S_{max}}{L_0}\sqrt{1-\left(\frac{v}{v_{max}}\right)^2},$$

Sinusoidal: $S_{max} = \frac{v_{max}}{2\pi f}$ **Triangular:** $S_{max} = \frac{v_{max}}{8f}$

Baseline of a transmission spectrum

Note:

The baseline is determined by three parameters:

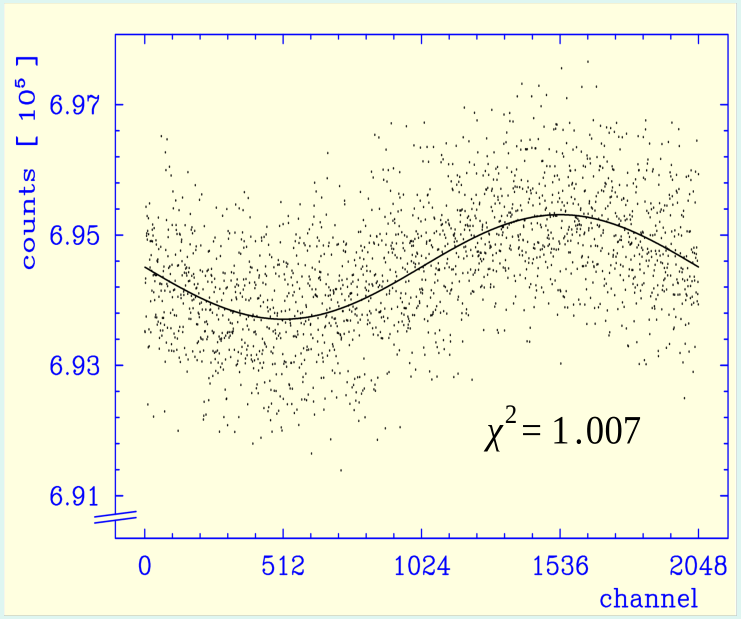
$$counts\left(v=\infty\right), \qquad geo=\frac{S_{\max}}{L_0}, \qquad channel_{\,v=0}$$

Baseline of a transmission spectrum

Note:

The baseline is determined by three parameters:

$$counts\left(v=\infty\right), \qquad geo=\frac{S_{max}}{L_0}, \qquad channel\left(v=0\right)$$



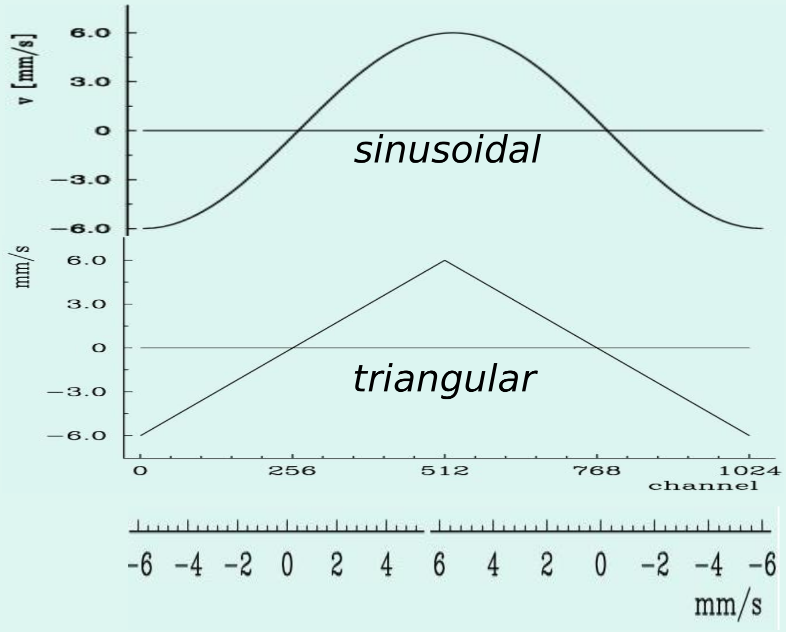
geo = $5.77 \cdot 10^{-4}$ (fit!)

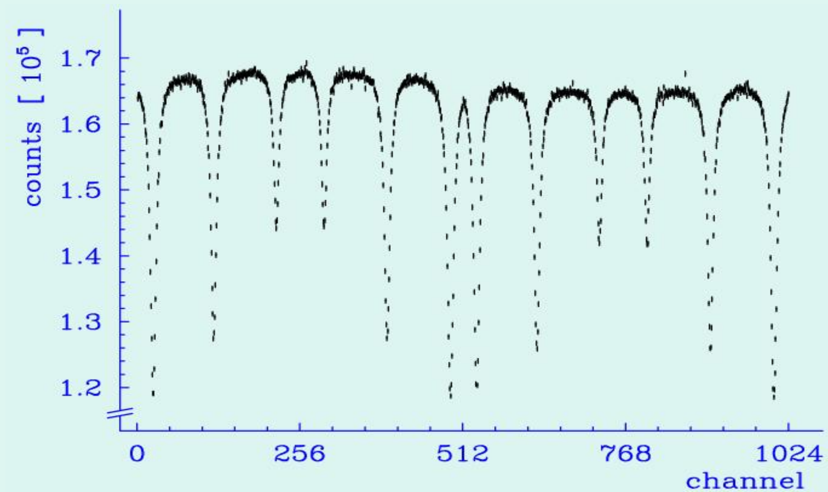
$$geo=\frac{v_{max}}{2\pi L_0 f}=\frac{7.24\ \text{mm/s}}{2\pi \cdot 120\ \text{mm} \cdot 17\ \text{Hz}}$$

= $5.65 \cdot 10^{-4}$

(120 mm → 117.5 mm)

The raw data problem



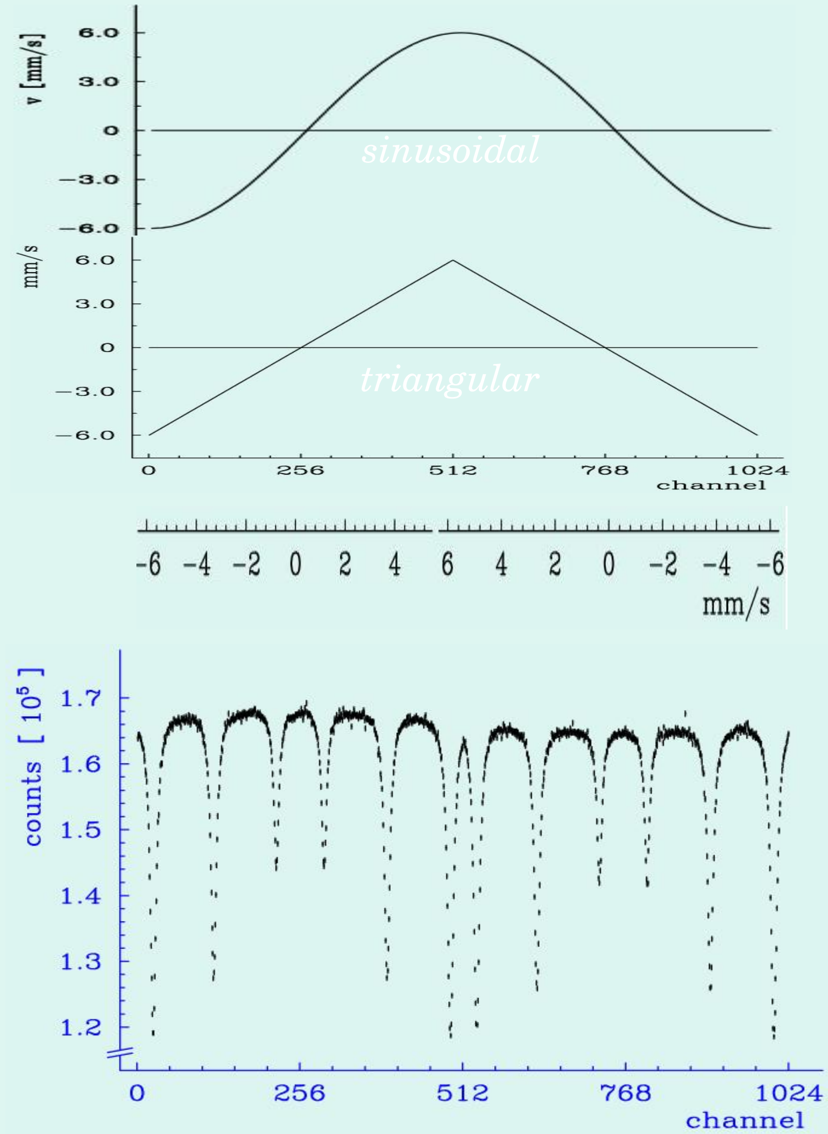


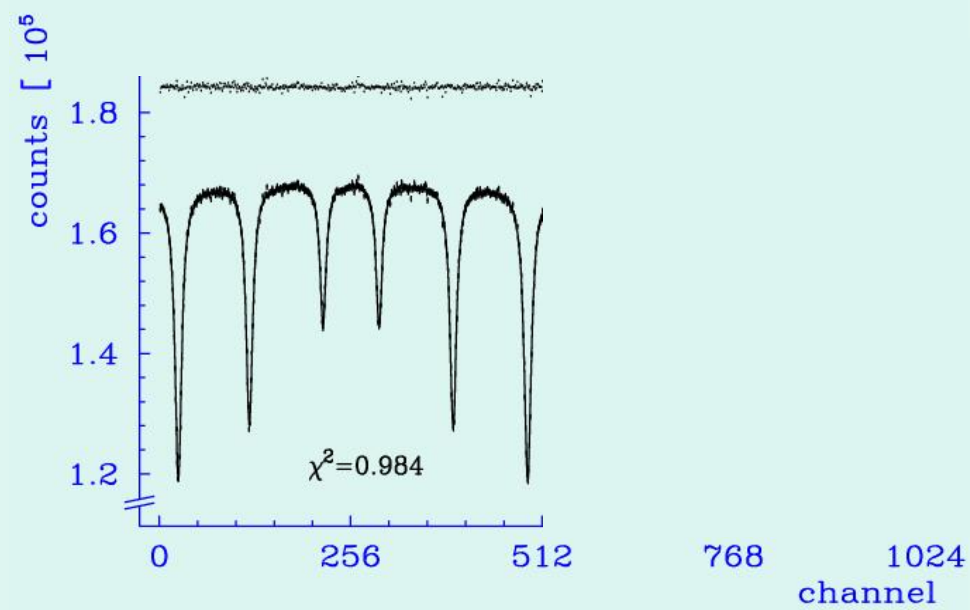
Calibration spectrum for FAS

W. C. Tennant, Christchurch (2009).

The raw data problem

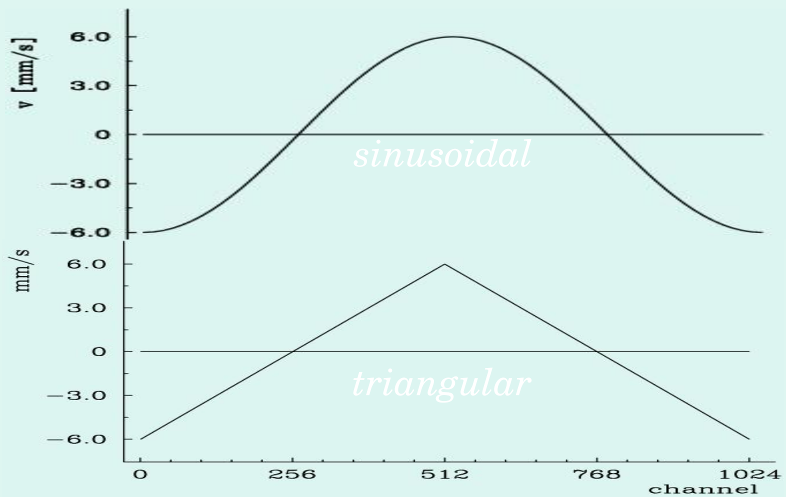
Fit of 6 independent lines
(position, Voigt profile)

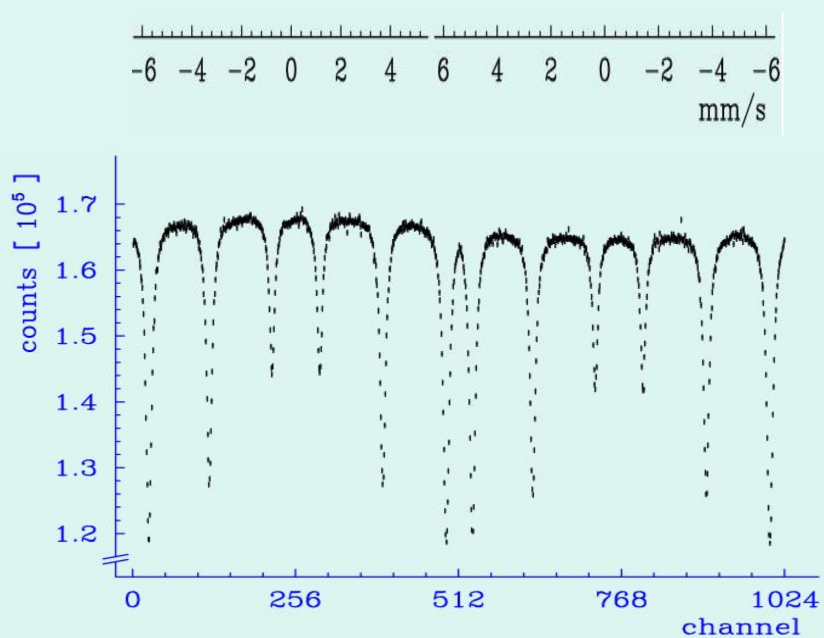


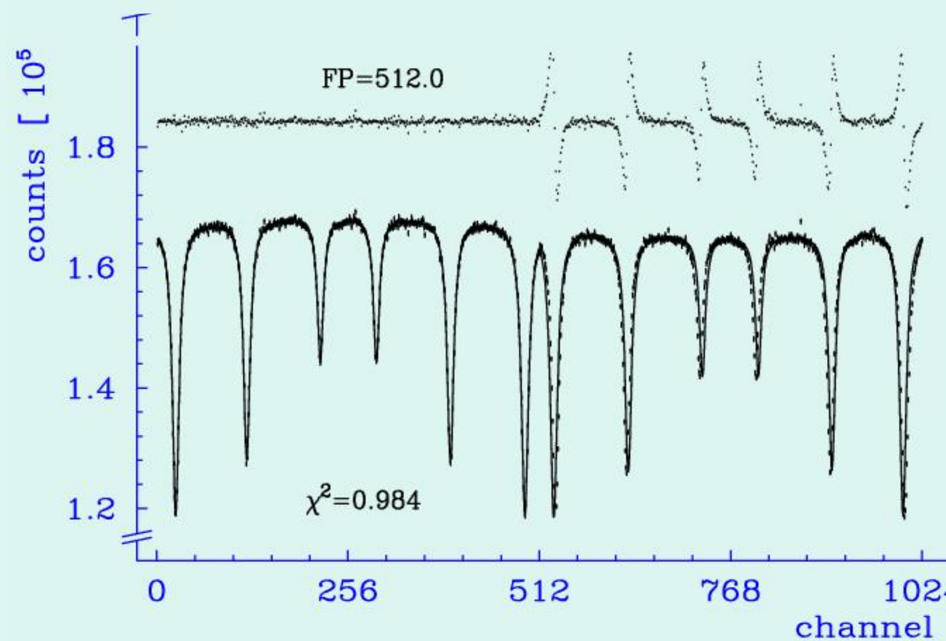


The raw data problem

Fit of 6 independent lines (position, Voigt profile)

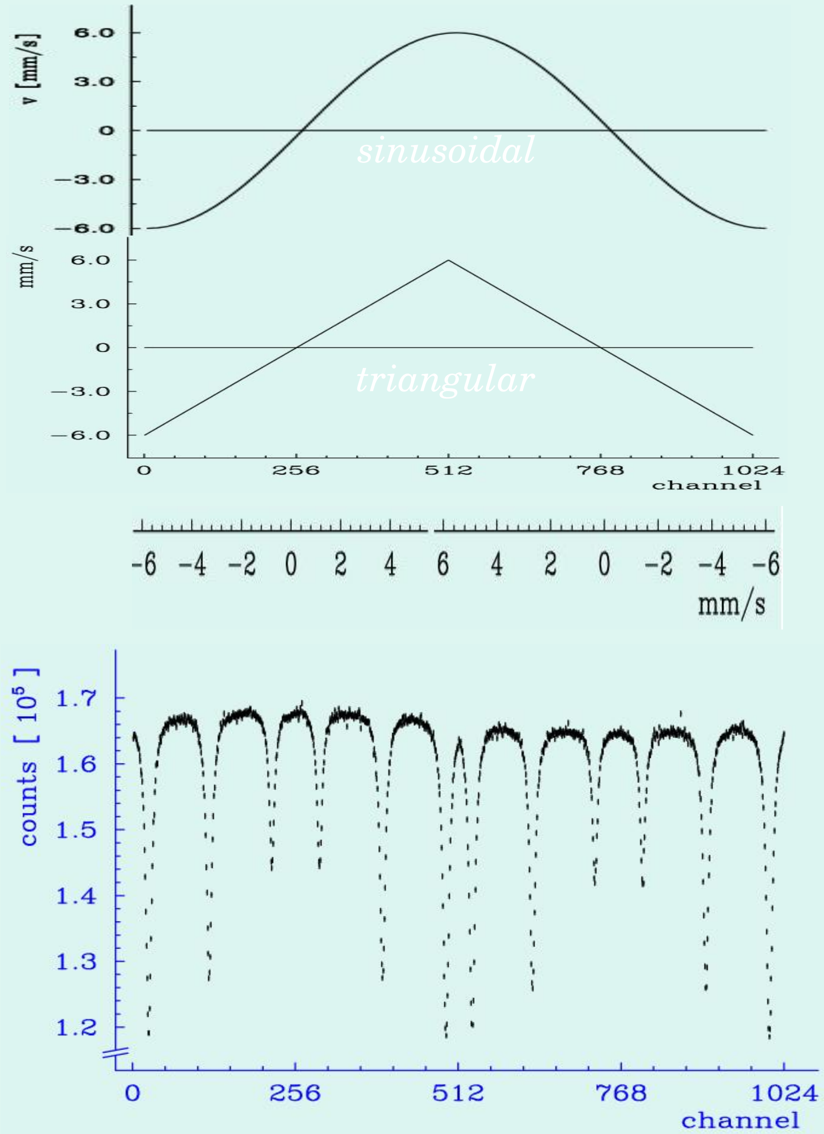


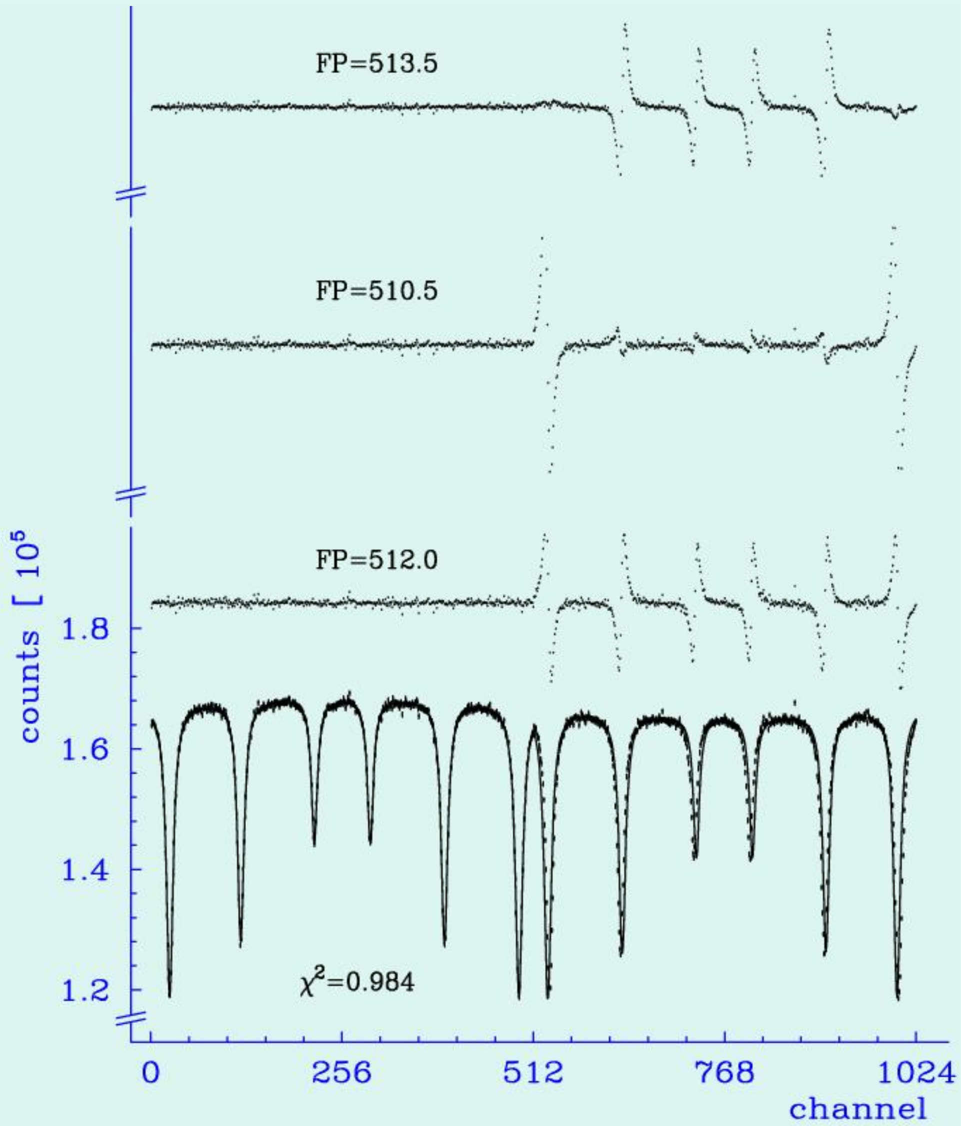




The raw data problem

Fit of 6 independent lines (position, Voigt profile)



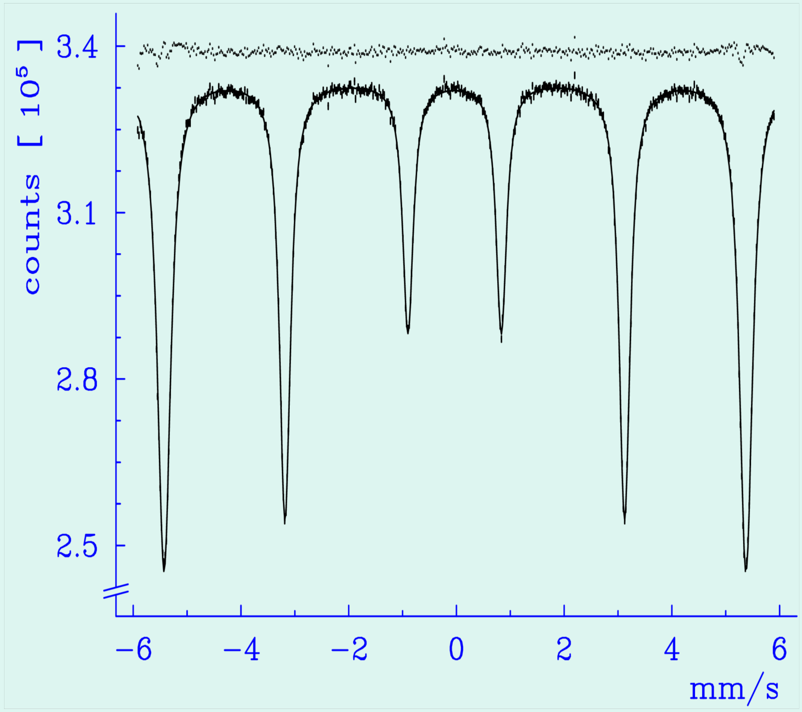


The raw data problem

Folding point FP: minimum of Z(FP)

$$Z(FP) = \sum_{i>FP}^{N} \left(C_i - C_{FP-(i-FP)}\right)^2$$

FP=512.5



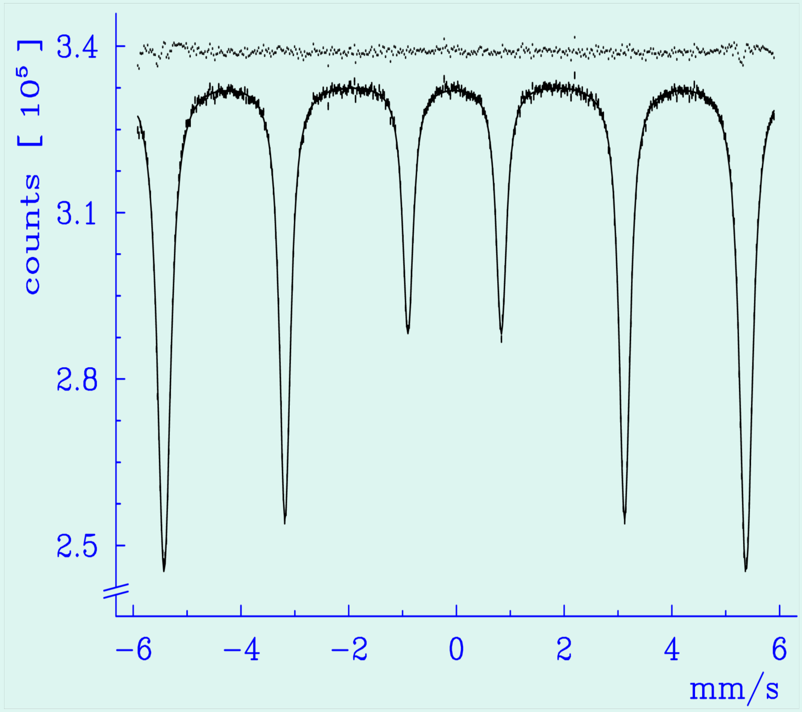
6 Voigt profiles $\chi^2 = 1.61$

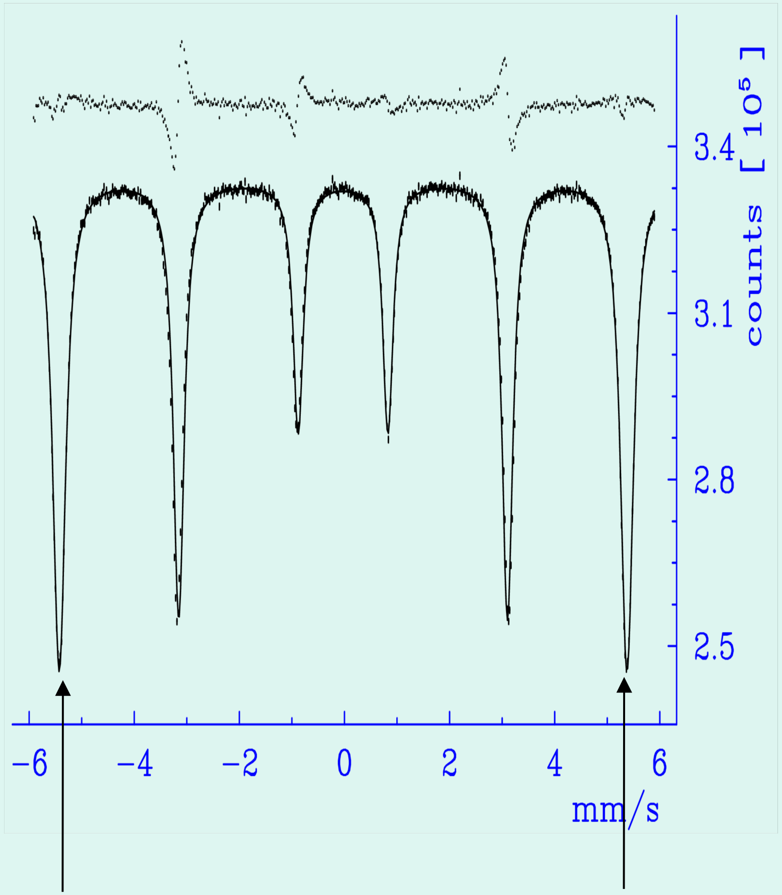
The raw data problem

Folding point FP: minimum of Z(FP)

$$Z(FP) = \sum_{i>FP}^{N} \left(C_i - C_{FP-(i-FP)}\right)^2$$

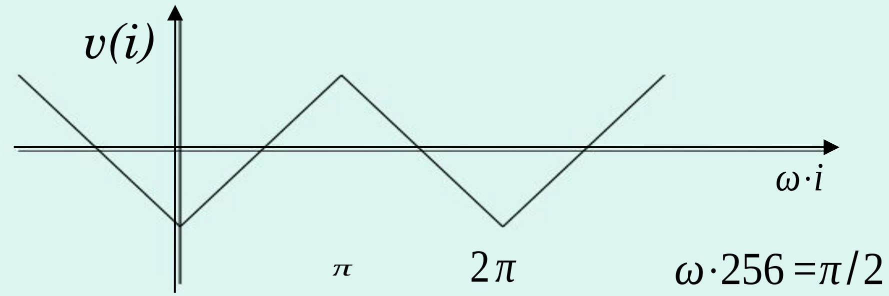
FP=512.5





6 Voigt profiles $\chi^2 = 1.61$

The raw data problem



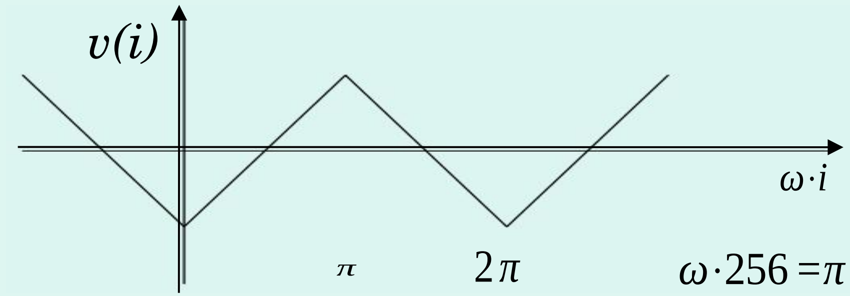
Correction of the nonlinearity of the velocity scale

$$v(i) = -v_{max}\frac{4}{\pi^2}\left(\cos\omega\cdot i + \frac{\cos 3\omega\cdot i}{3^2} + \frac{\cos 5\omega\cdot i}{5^2} + \ldots\right)$$

$$dv(i) = \sum a_k \cos((2k+1)\omega\cdot i) + b_k \sin((2k+1)\omega\cdot i)$$

The raw data problem

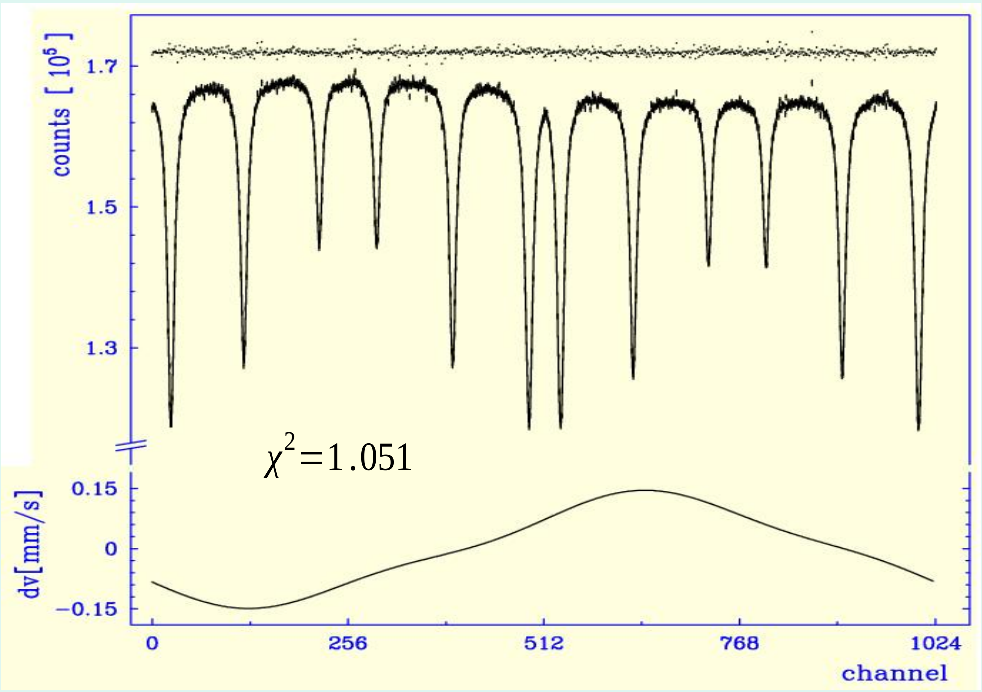
Correction of the nonlinearity of the velocity scale



$\omega \cdot 256 = \pi/2$

$$v(i) = -v_{max} \frac{4}{\pi^2} \left(\cos \omega i + \frac{\cos 3\,\omega \cdot i}{3^2} + \frac{\cos 5\,\omega \cdot i}{5^2} + \ldots \right)$$

$$dv(i) = \sum a_k \cos((2k+1)\,\omega \cdot i) + b_k \sin((2k+1)\,\omega \cdot i)$$



Source (5mCi):

$\Gamma_{Lorentz} = 1.03\ \Gamma_N,\ б_{Gauss} = 0.45\ \Gamma_N$

$dv = \pm\ 7.5$ *channels*

$\Gamma(\alpha\text{-iron}) = \Gamma_N$

The raw data problem

Note:

No reliable velocity scale after folding!!

Better solution by a fit of the full spectrum and velocity correction for each channel

Not only positions of the lines but also their shapes determine the velocity scale

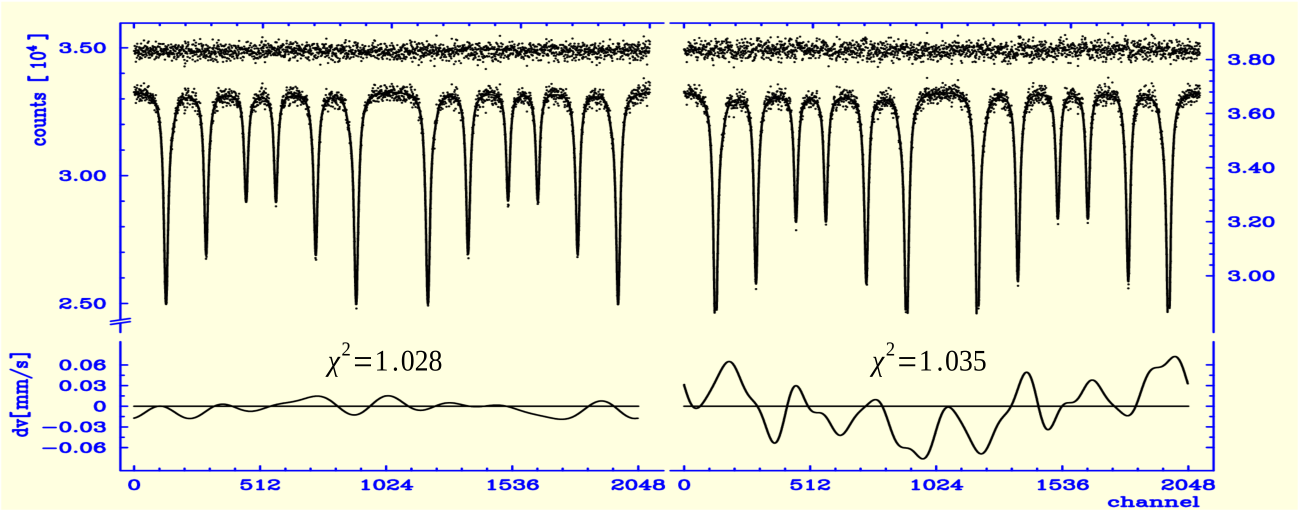
Choice of the drive frequency

J Pechousek et al., Palacky University of Olomouc, Czech Republic

www.researchgate.net/publication/252974211

17.0 Hz *4.25 Hz*

triangular



$ch_{v=0}$=513.08

V_{max}=7.24 mm/s

L_0=117.5 mm

$$geo = \frac{v_{max}}{8 L_0 f}$$

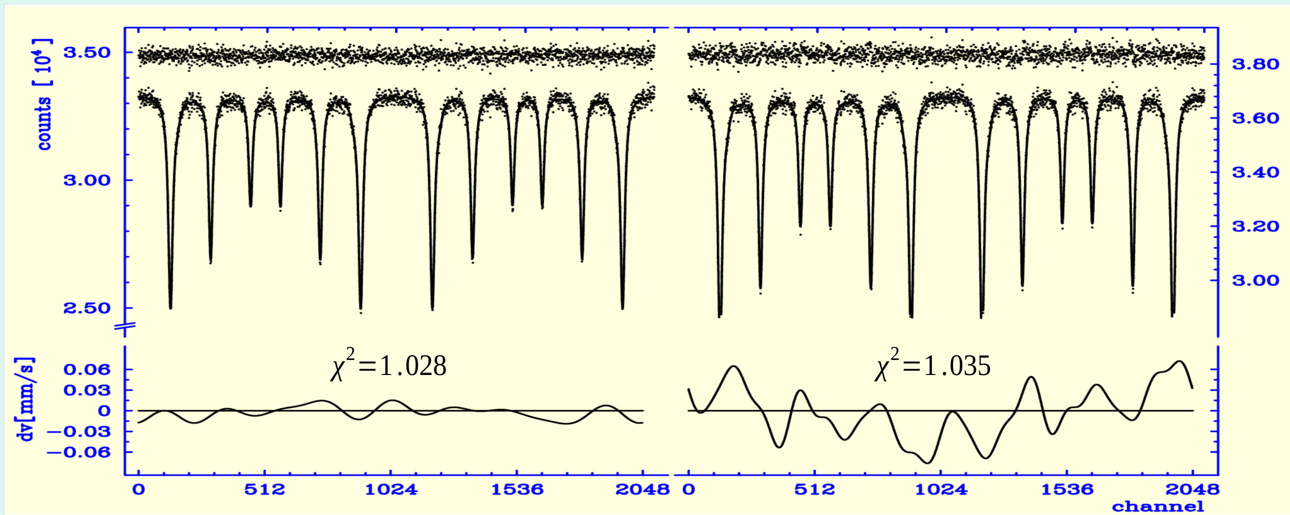
Choice of the drive frequency

J Pechousek et al., Palacky University of Olomouc, Czech Republic

www.researchgate.net/publication/252974211

17.0 Hz | *4.25 Hz*

triangular



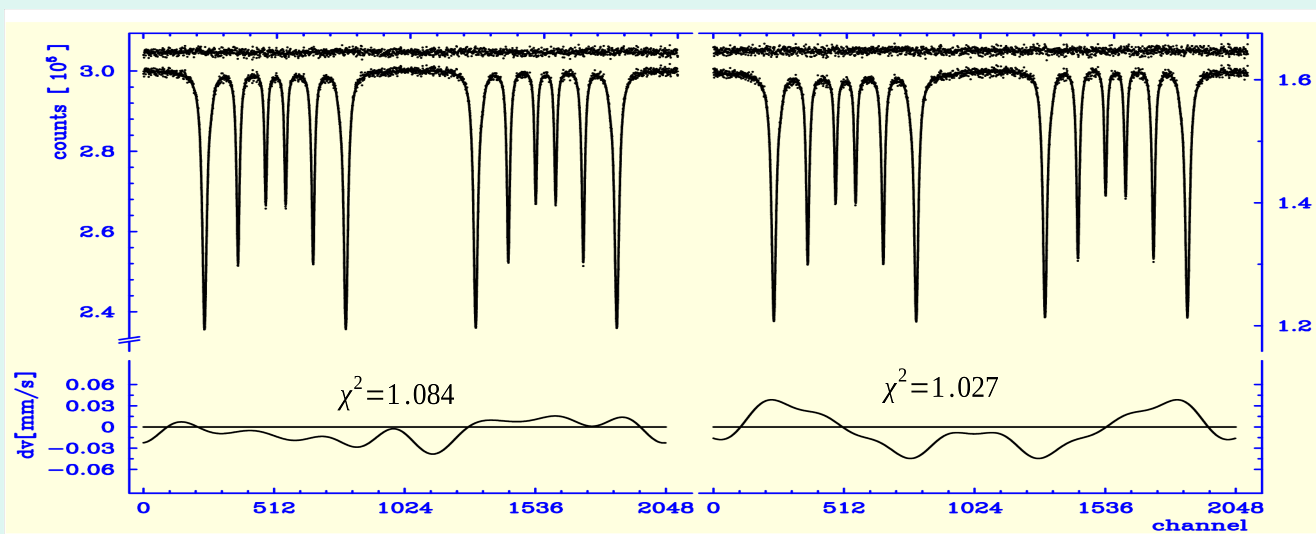
$ch_{v=0}$=513.08

V_{max}=7.24 mm/s

L_0=117.5 mm

$$geo = \frac{v_{max}}{8\,L_0 f}$$

sinusiodal



$$geo = \frac{v_{max}}{2\pi L_0 f}$$

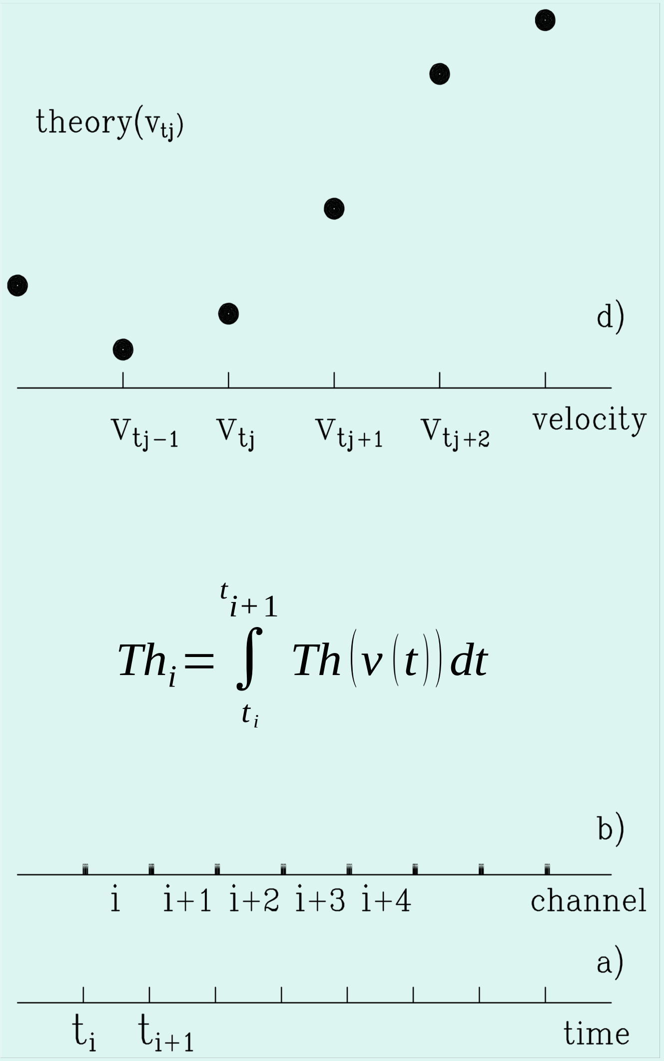
Choice of the drive frequency

Note:

Nonlinearity correction dv(i) strongly depends on the drive frequency

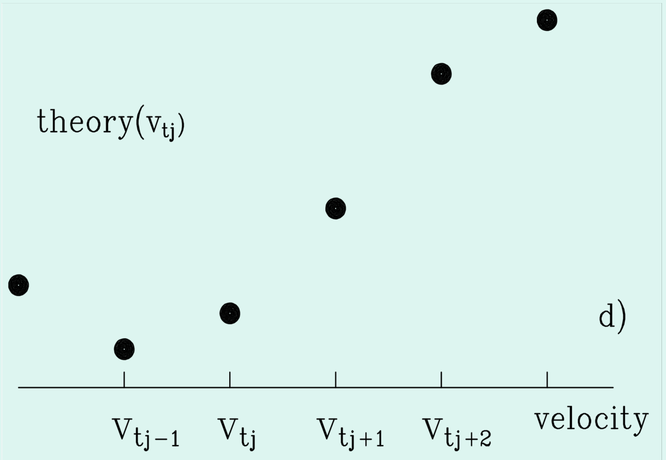
The evaluated physical parameters of the spectrum
shall not depend on the driving mode, the frequency nor the solid angle

Theoretical value at channel i

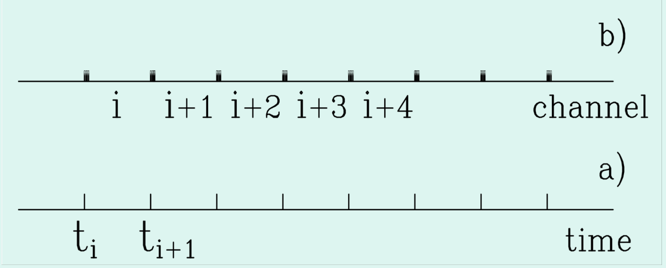


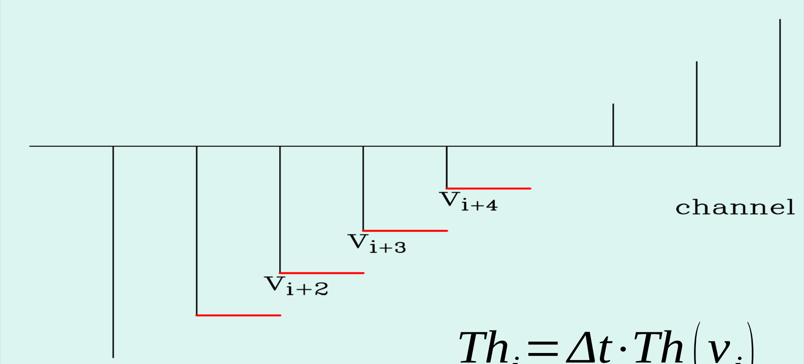
$$Th_i = \int_{t_i}^{t_{i+1}} Th\left(v\left(t\right)\right) dt$$

Theoretical value at channel i



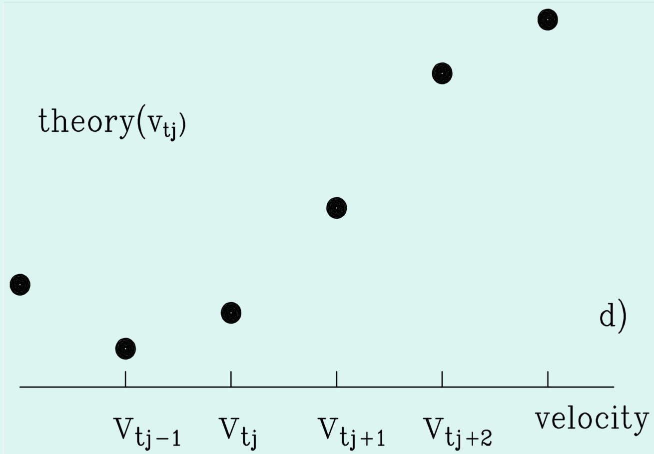
$$Th_i = \int_{t_i}^{t_{i+1}} Th(v(t))\,dt$$



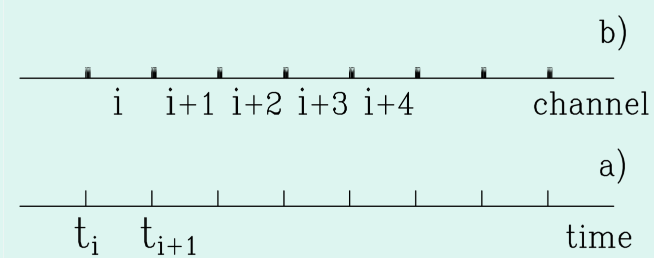


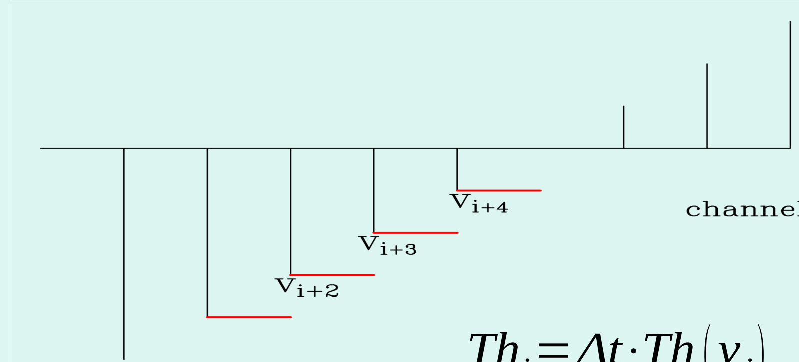
$$Th_i = \Delta t \cdot Th(v_i)$$

Theoretical value at channel i

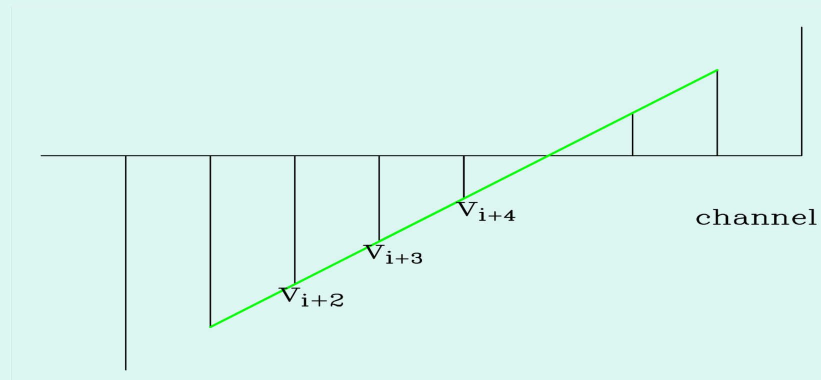


$$Th_i = \int_{t_i}^{t_{i+1}} Th(v(t))\,dt$$





$$Th_i = \Delta t \cdot Th(v_i)$$

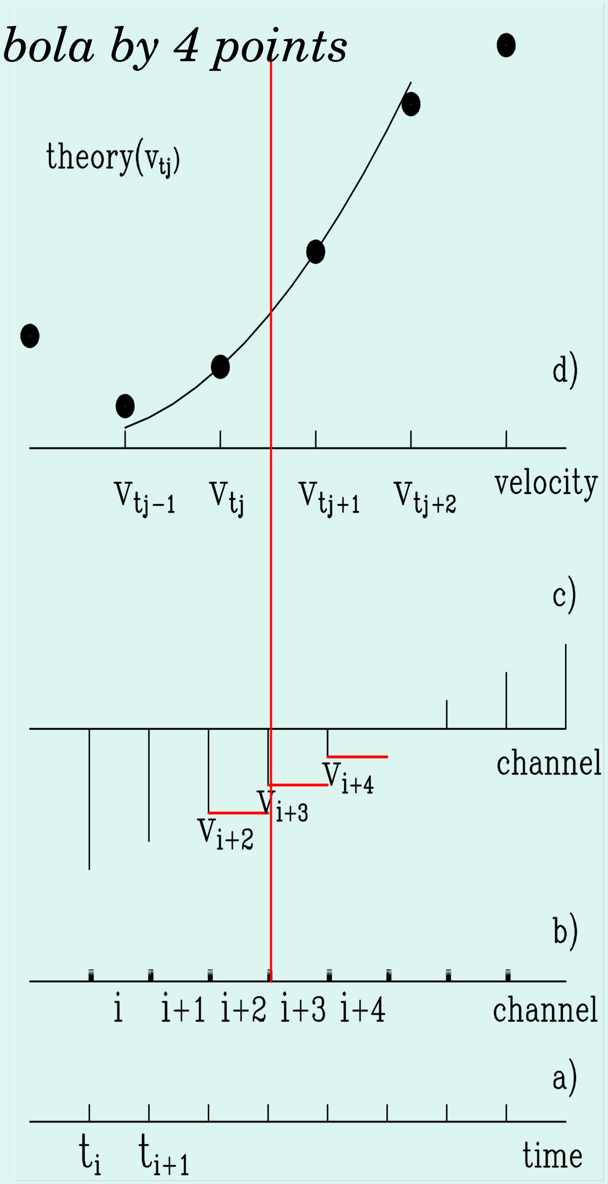


$$Th_i = \int_{t_i}^{t_{i+1}} Th(v(t))\frac{dt}{dv}\,dv$$

$$= \frac{\Delta t}{v(t_{i+1}) - v(t_i)} \int_{v(t_i)}^{v(t_{i+1})} Th(v)\,dv$$

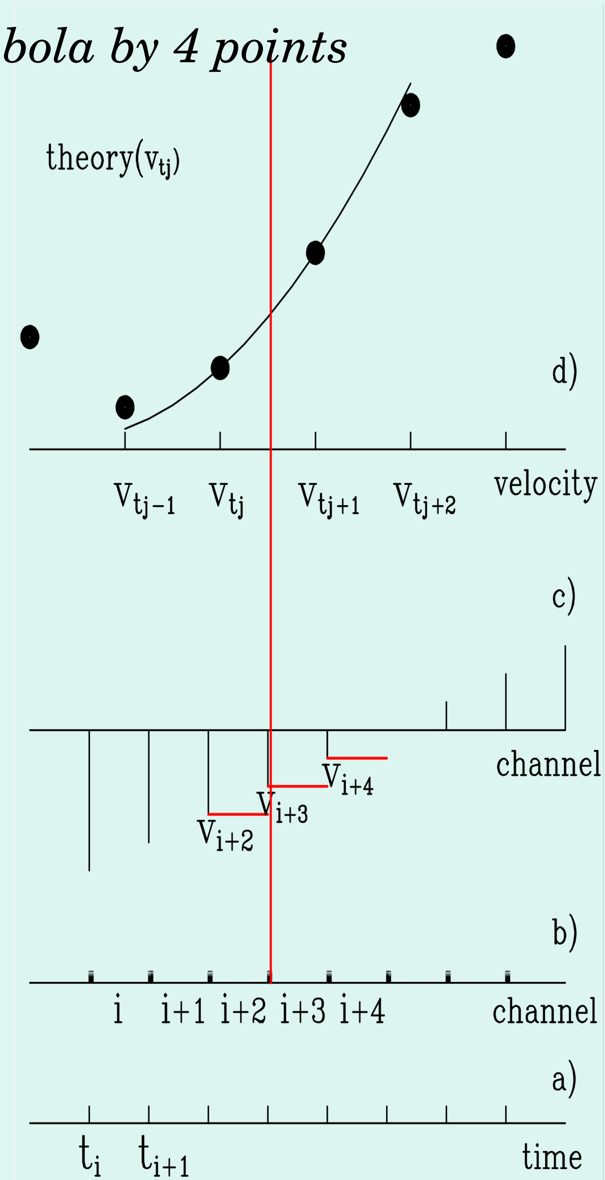
Theoretical value at channel i

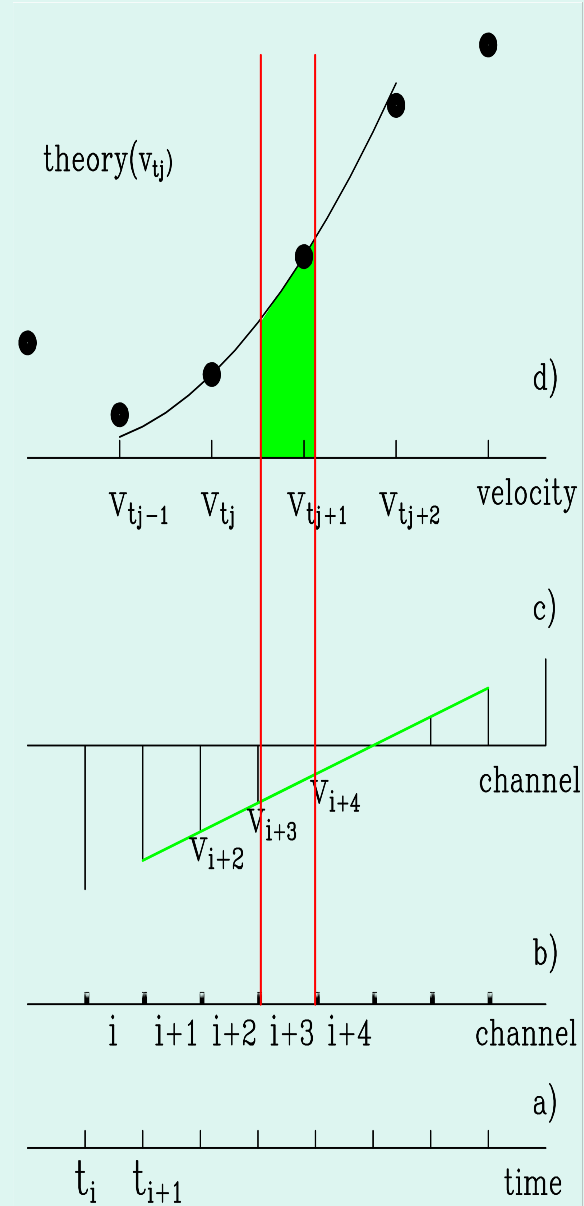
best parabola by 4 points



Theoretical value at channel i

best parabola by 4 points





Theoretical value at channel i

Note:

Advantages of theory interpolation:

Fit of dv_i dependent on 6-18 parameters would not be feasible with the convolution for each iteration step: 1024-4096 numerical integrals

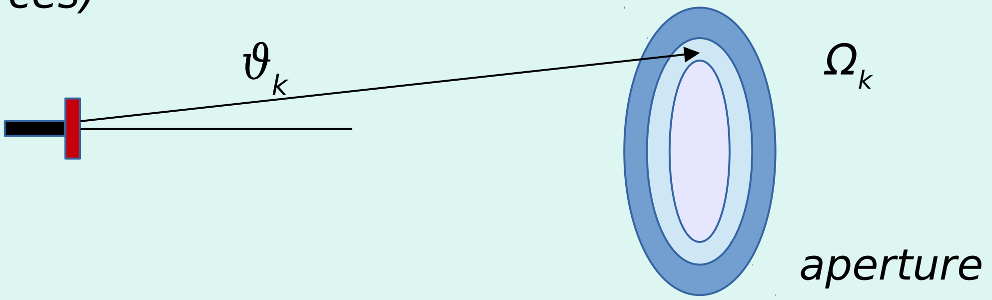
Theoretical value at channel i

Note:

Advantages of theory interpolation:

Fit of dv_i dependent on 6-18 parameters would not be feasible with the convolution for each iteration step: 1024-4096 numerical integrals

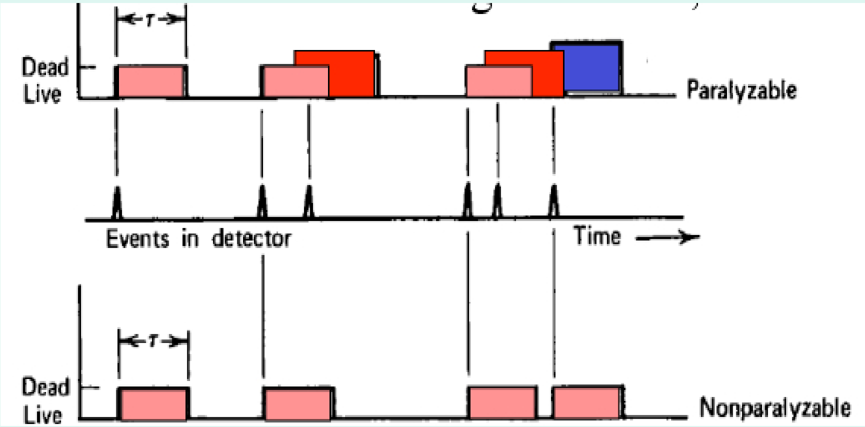
Calculation of cos-smearing for large Ω can be easily added (weak sources)



Weighted (by Ω_k) superposition of spectra with $v_i \cos(\vartheta_k)$

Dead time

paralyzable, nonparalyzable

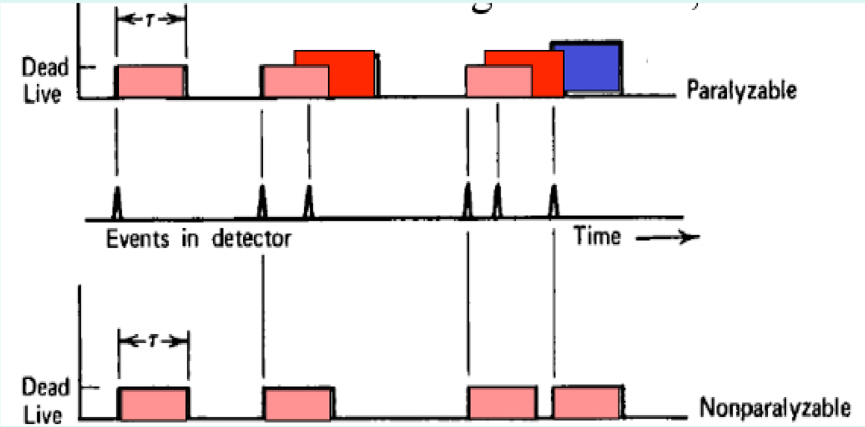


Proportional counter $\tau = 100\ \mu s$

Scintillator $\tau = 1\ \mu s$

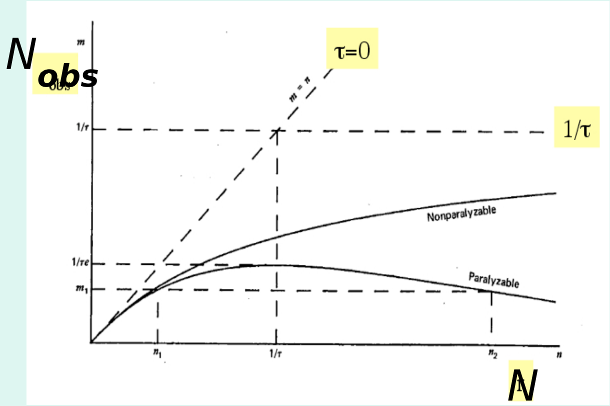
Dead time

paralyzable, nonparalyzable



Proportional counter $\tau = 100\ \mu s$

Scintilator $\tau = 1\ \mu s$



$$N_{obs} = \frac{N}{1 + N\tau_{np}}$$

$$N_{obs} = Ne^{-N\tau_p}$$

$$N_{obs} = \frac{Ne^{-N\tau_p}}{1 + N\tau_{np}}$$

D.J. Morrissey,2oo9, Michigan State University

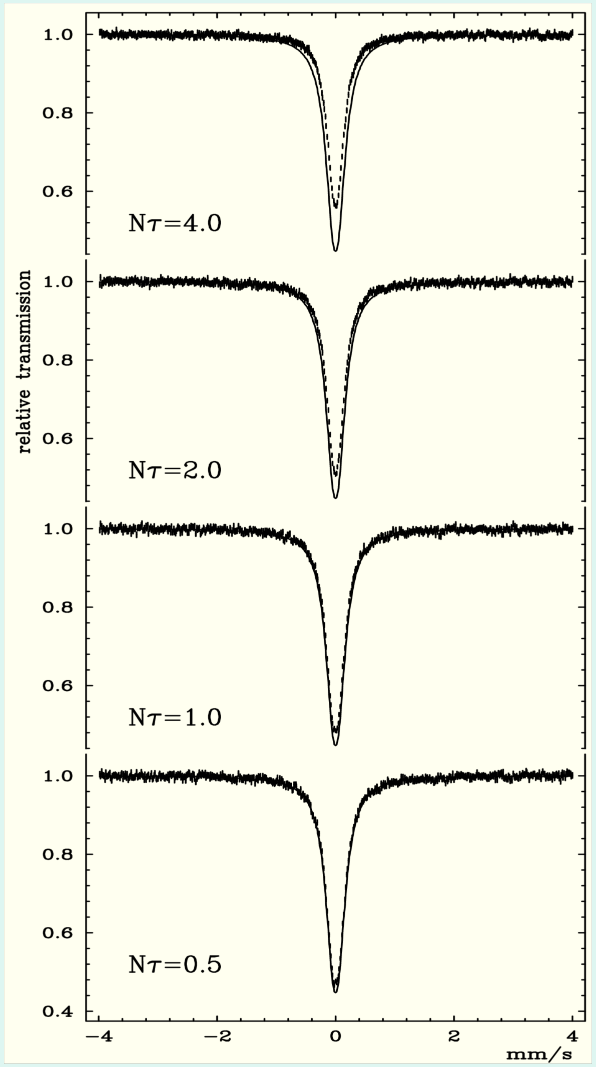
Dead time

Code for Monte Carlo simulations (nonparalyzable, paralyzable)

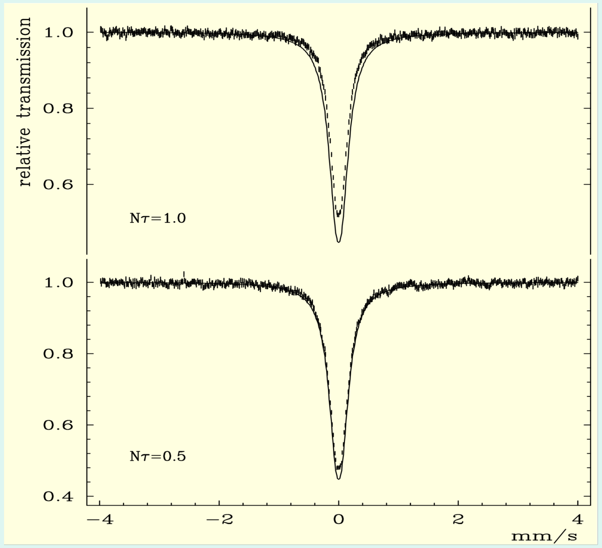
```
while(isimul[0] < *counts)
 }
  eventtime=-log(1.-frand())/(countrate*theo[ichannel]);
  lastevent=lastevent+eventtime;

  totaltime=totaltime+eventtime;
  ichannel= totaltime/dwelltime;
  i=ichannel/nu_channel;  ichannel=ichannel-i*nu_channel;

  if(lastevent > deadtime)
    {isimul[ichannel]++; lastevent=0.0; icount++;}
  else
    {iloss++;}
    {iloss++;lastevent=0.;}
 }
```

Dead time

Nonparalyzable

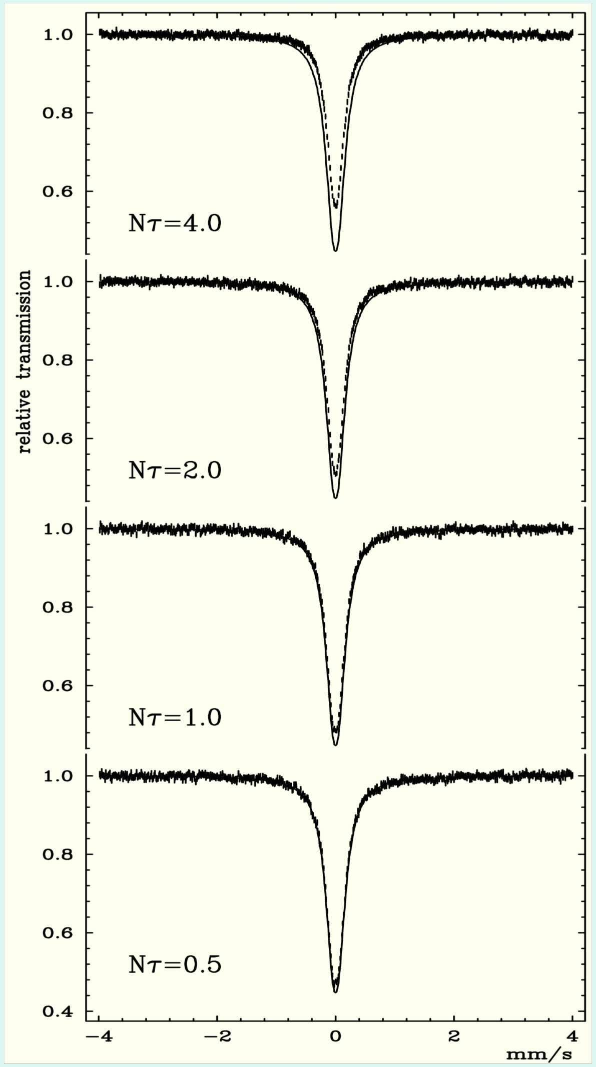


paralyzable

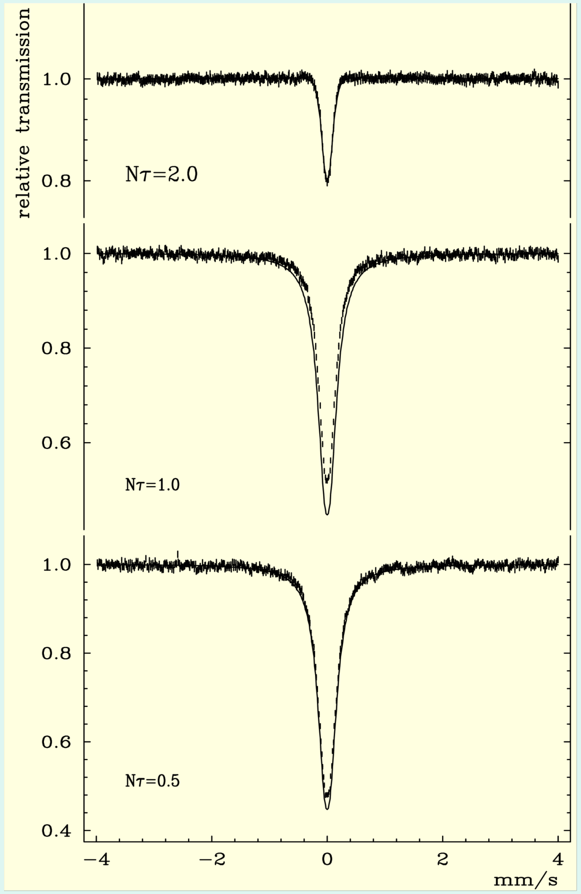


Dead time

Nonparalyzable

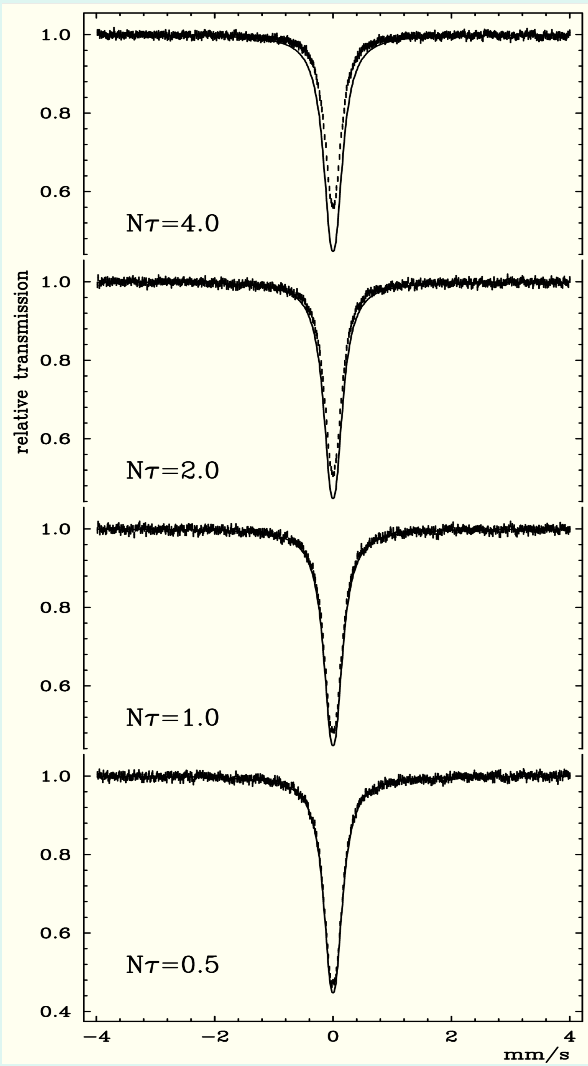


paralyzable

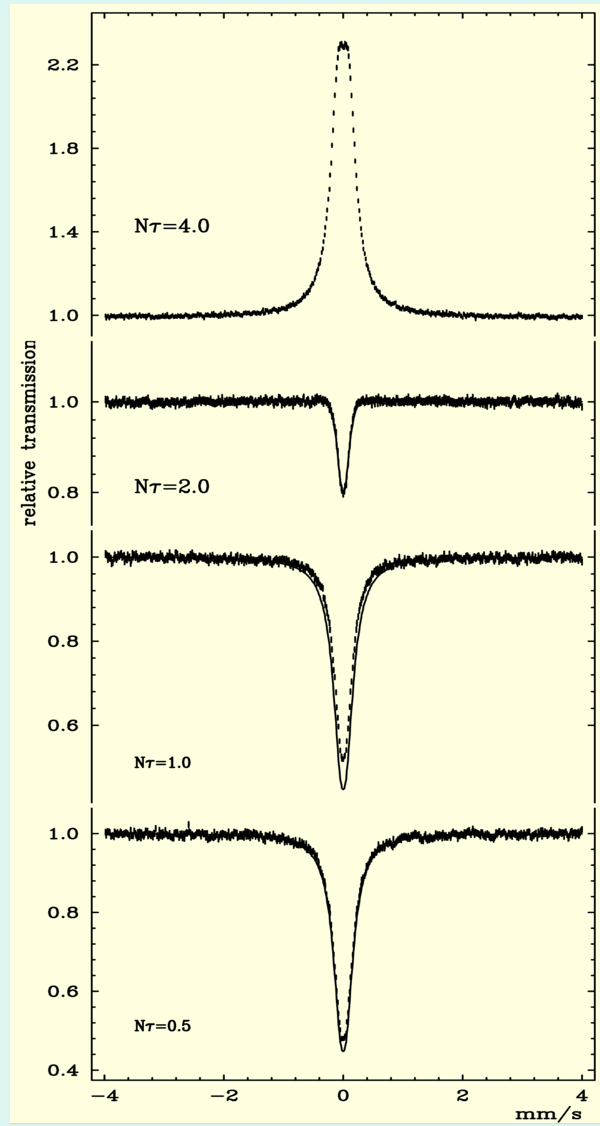


Dead time

Nonparalyzable

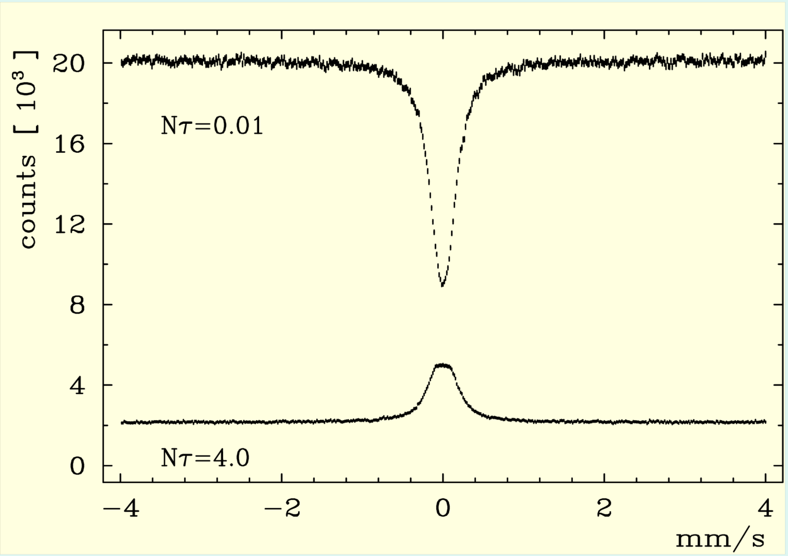


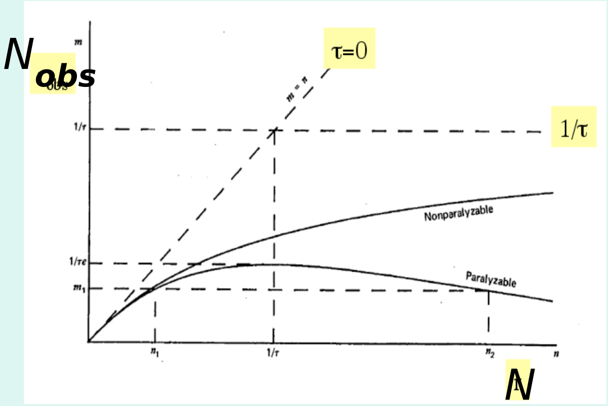
paralyzable



Dead time

paralyzable



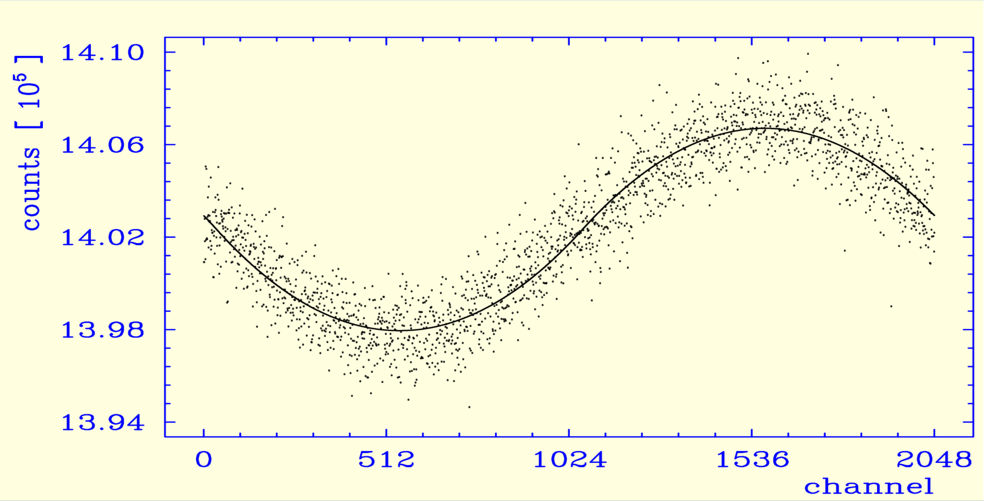


up to $N\tau \leq 0.5$ ***deadtime effects are kept within reasonable limits***

Dead time

$$geo = \frac{v_{max}}{2\pi L_0 f} = \frac{15.6\, mm/s}{2\pi \cdot \mathbf{67}\, mm \cdot 16\, Hz} = 2.32 \cdot 10^{-3}$$

5.5mCi



$$\chi^2 = 0.\mathbf{994}$$

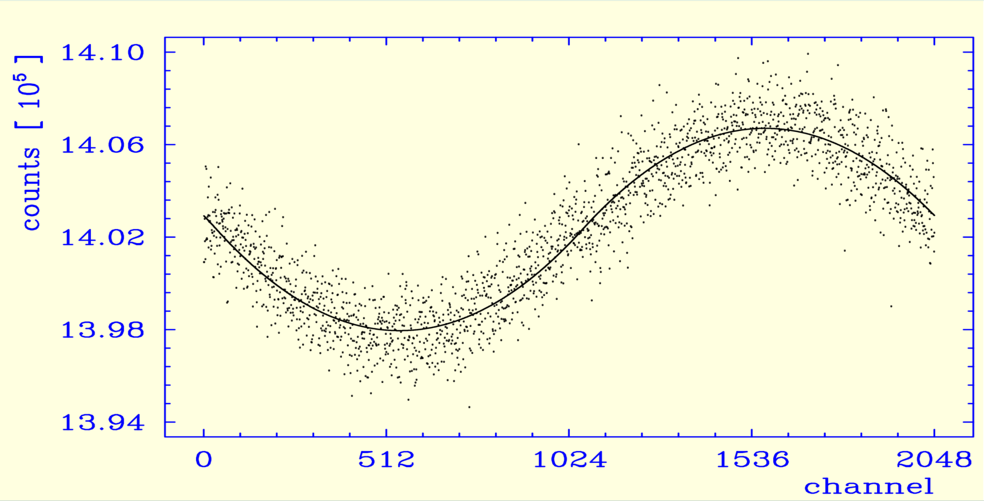
$$N = counts(v_\infty) \frac{\Omega(geo, v_i)}{\Omega_0}$$

=> $geo = \mathbf{1.62 \cdot 10^{-3}}$ *(fit!)*

Dead time

$$geo = \frac{v_{max}}{2\pi L_0 f} = \frac{15.6\, mm/s}{2\pi \cdot \mathbf{67}\, mm \cdot 16\, Hz} = 2.32 \cdot 10^{-3}$$

5.5mCi



$$\chi^2 = 0.\mathbf{994}$$

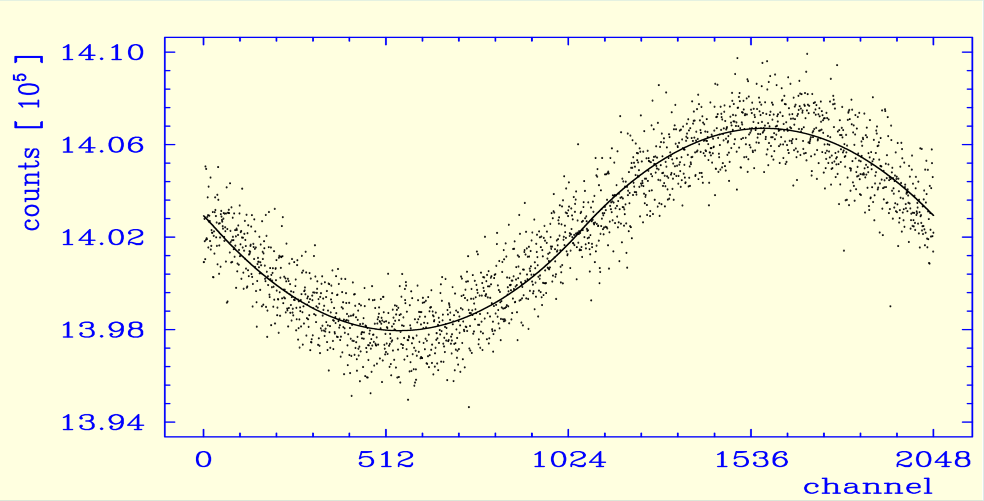
$$N = counts(v_\infty) \frac{\Omega(geo, v_i)}{\Omega_0} \quad \Rightarrow \quad geo = \mathbf{1.62 \cdot 10^{-3}} \quad \textit{(fit!)}$$

$$N = counts(v_\infty) \frac{\Omega(2.32 \cdot 10^{-3}, v_i)}{\Omega_0}, \quad N_c = \frac{N}{1 + N\tau_{np}} \quad \Rightarrow \quad N\tau_{np} = 0.\mathbf{42} \quad \textit{(fit!)}$$

Dead time

$$geo = \frac{v_{max}}{2\pi L_0 f} = \frac{15.6\, mm/s}{2\pi \cdot \mathbf{67}\, mm \cdot 16\, Hz} = 2.32 \cdot 10^{-3}$$

5.5mCi



$$\chi^2 = 0.\mathbf{994}$$

$$N = counts(v_\infty) \frac{\Omega(geo, v_i)}{\Omega_0} \quad => \quad geo = \mathbf{1.62 \cdot 10^{-3}} \quad \text{(fit!)}$$

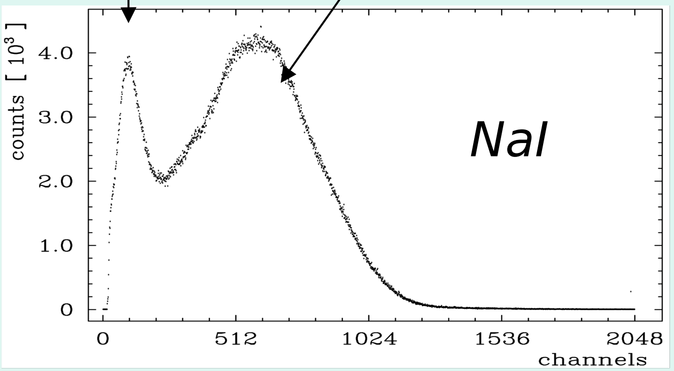
$$N = counts(v_\infty) \frac{\Omega(2.32 \cdot 10^{-3}, v_i)}{\Omega_0}, \quad N_c = \frac{N}{1 + N\tau_{np}} \quad => \quad N\tau_{np} = 0.\mathbf{42} \quad \text{(fit!)}$$

$$\frac{2.32}{(1 + N\tau_{np})} = 1.63$$

Dead time

$14.4 keV$ $122/136 keV$

(ungated)

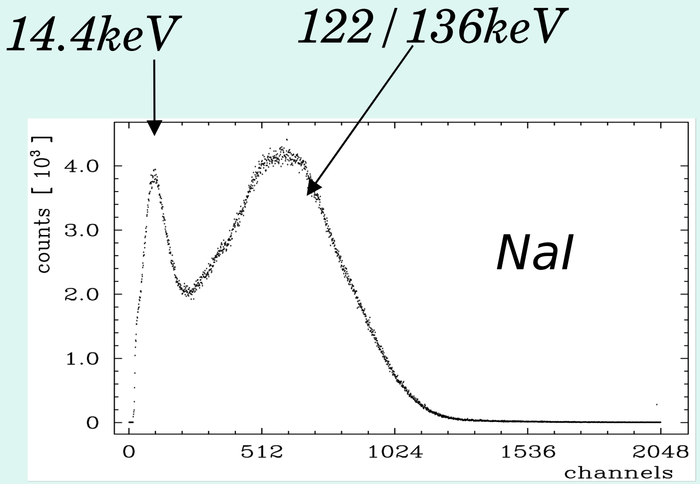


nonparalyzable

$$N_c = \frac{N}{1 + N\tau_{np}}$$

Dead time

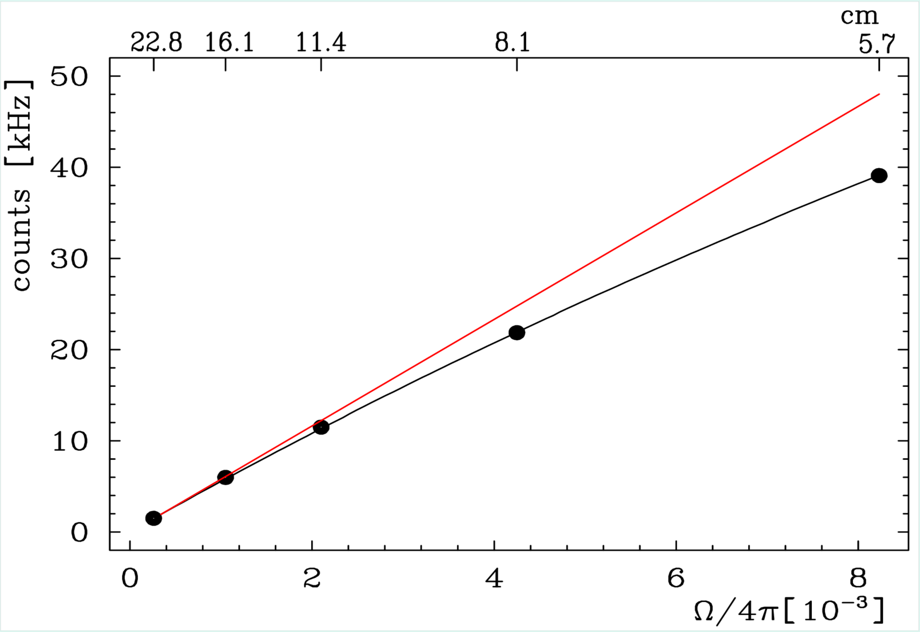
(ungated)



nonparalyzable

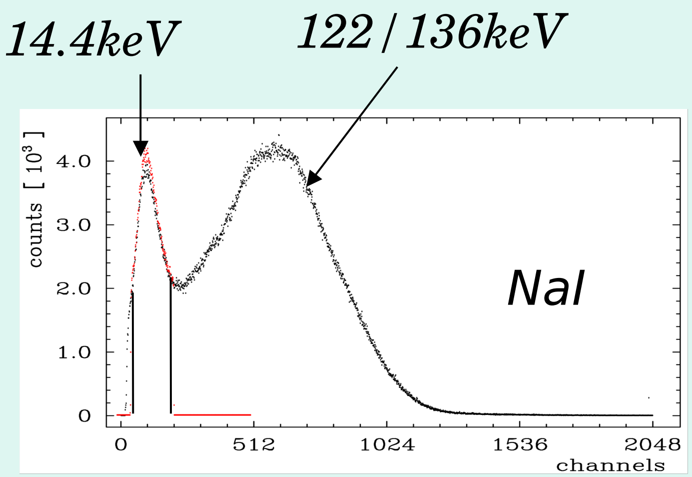
$$N_c = \frac{N}{1 + N\tau_{np}}$$

$N\tau_{np} = 0.22 \rightarrow \tau_{np} = 4.4\,\mu s$



Dead time

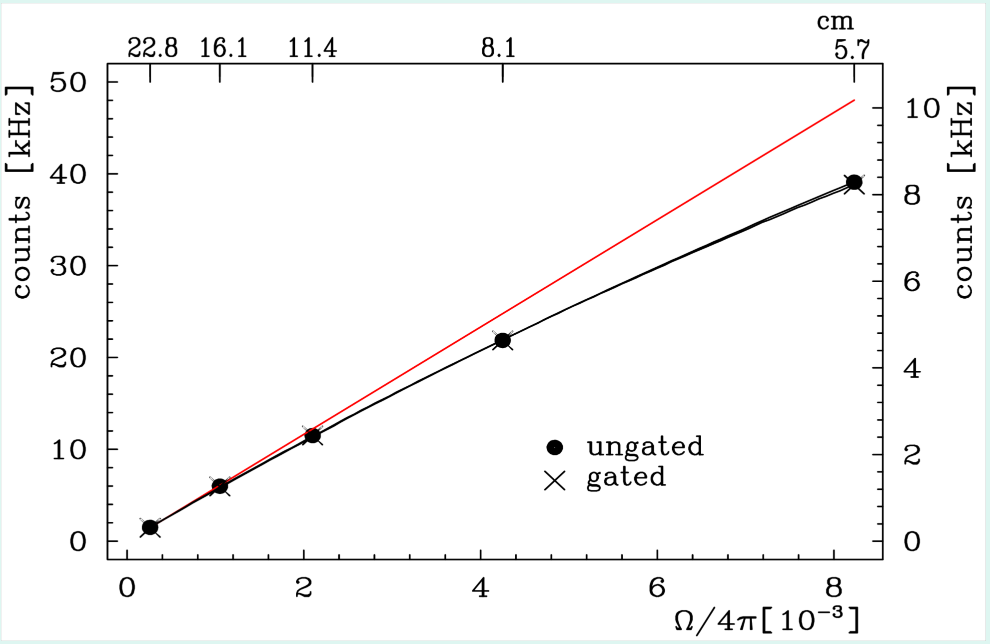
(gated)



nonparalyzable

$$N_c = \frac{N}{1 + N\tau_{np}}$$

$N\tau_{np} = 0.22 \rightarrow \tau_{np} < 4.4\,\mu s$

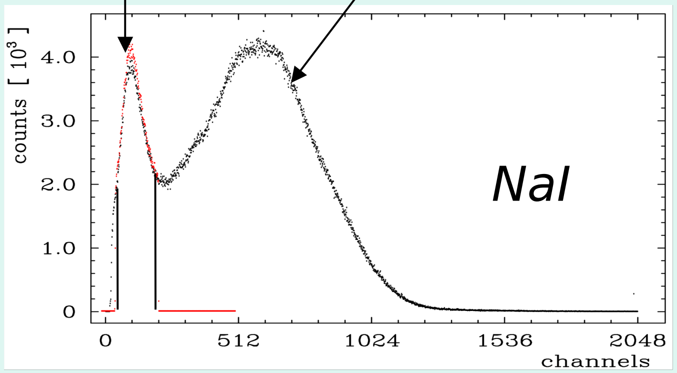


Dead time

14.4keV

122 / 136keV

(gated)



NaI

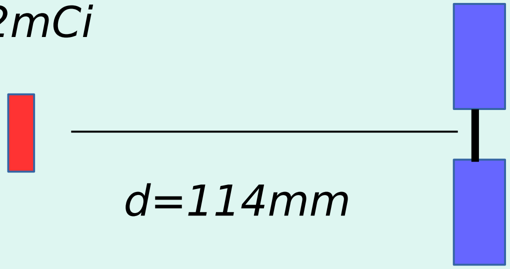
nonparalyzable

$$N_c = \frac{N}{1 + N\tau_{np}}$$

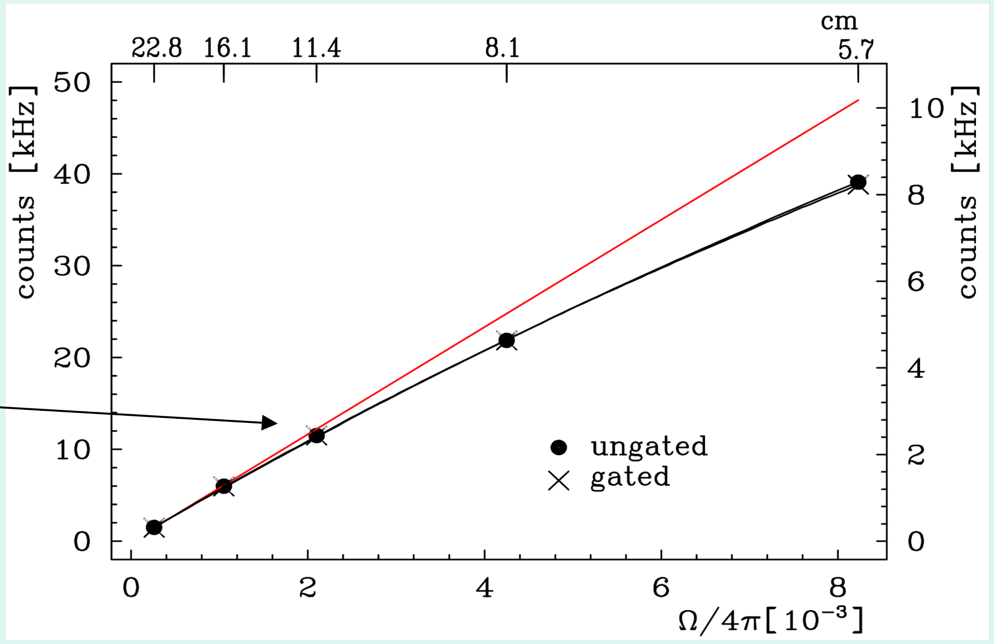
$N\tau_{np} = 0.22$

15mmØ

2mCi

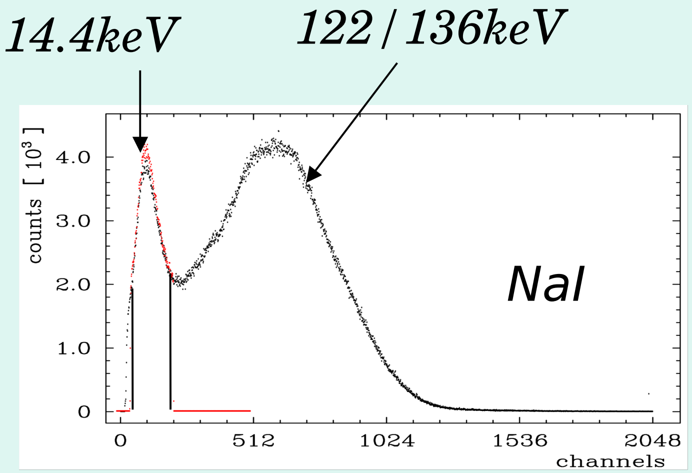


d=114mm



Dead time

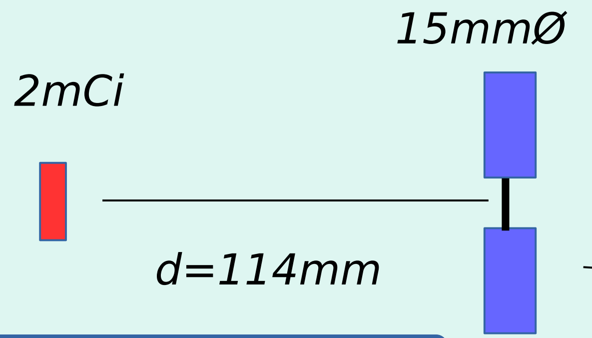
(gated)

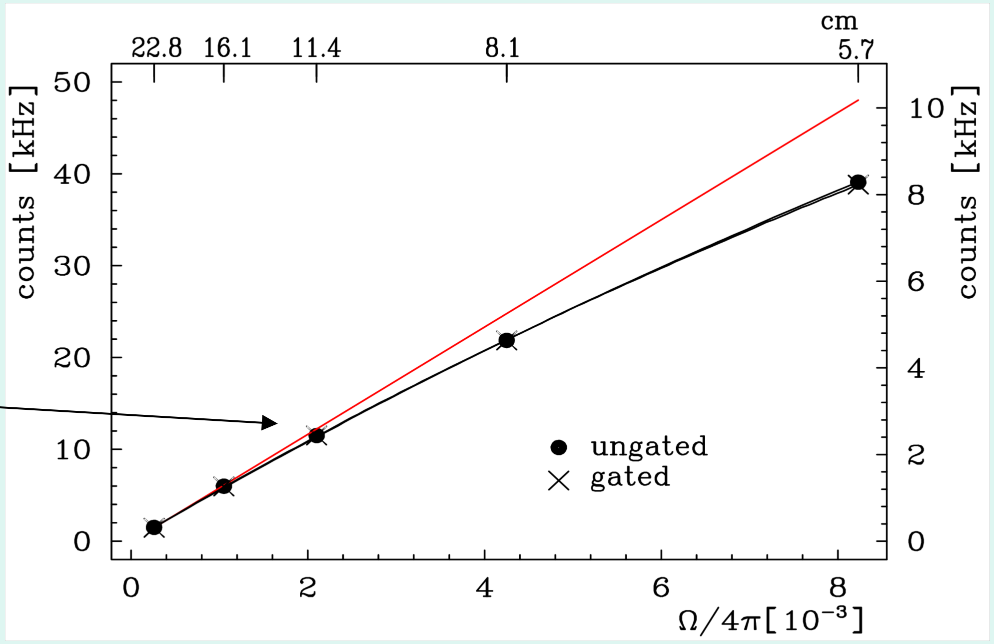


nonparalyzable

$$N_c = \frac{N}{1 + N\tau_{np}}$$

$N\tau_{np} = 0.22$





$50mCi \rightarrow 5d$

Dead time

Note:

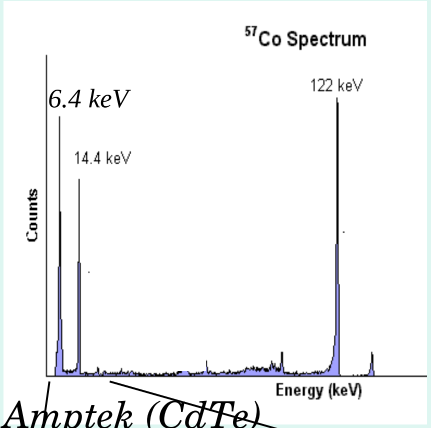
Avoid (severe) dead time effects !

Check by the distance law $1/r^2$ for dead time

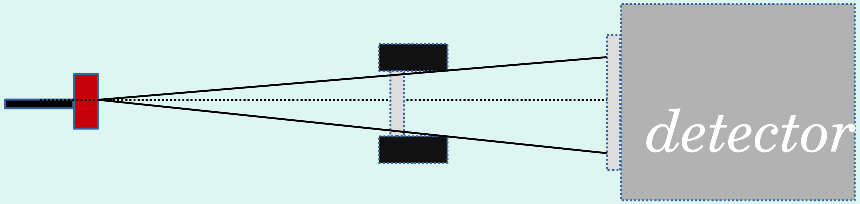
Check by the geo parameter for dead time: $$\frac{geo}{geo_{eff}} = \left(1 + N\tau\right)$$

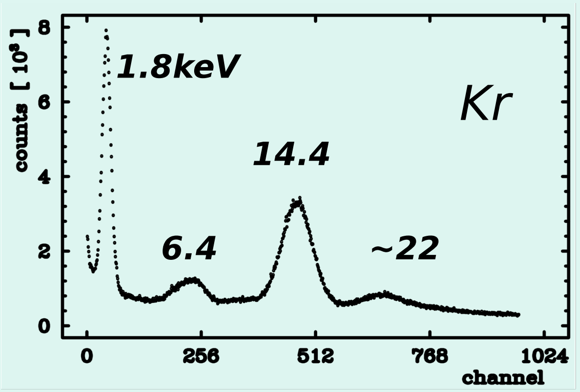
up to $N\tau \leq 0.5$ *deadtime effects are kept within reasonable limits*

Background



Amptek (CdTe)

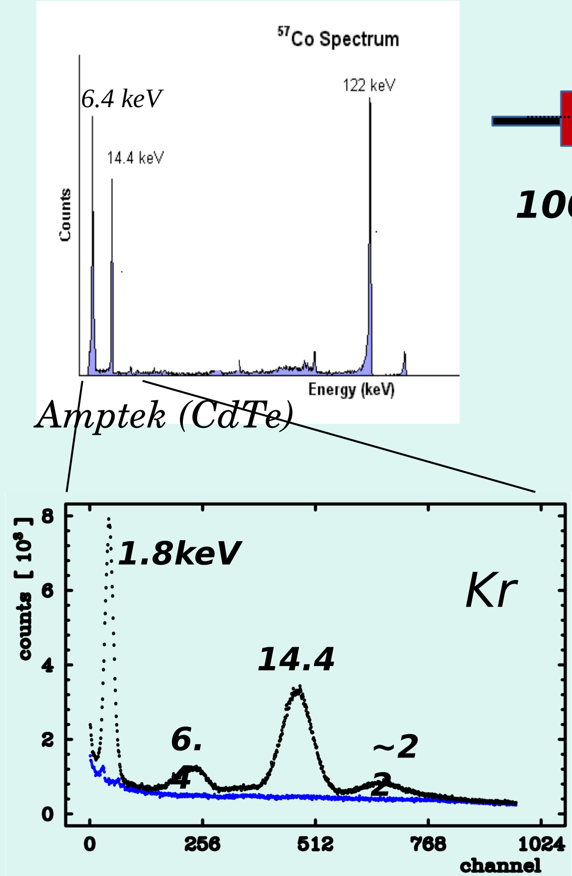




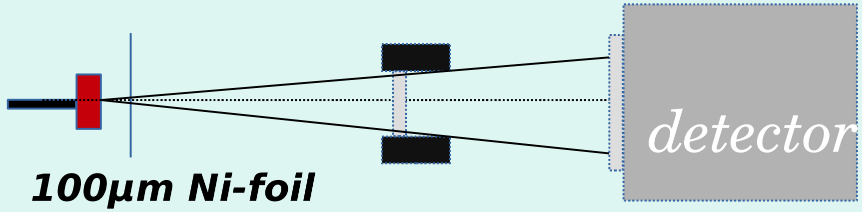
A straightforward experimental method to evaluate the Lamb-Mossbauer factor of a 57Co/Rh source

G. Spina , M. Lantieri, Nul. Instrum. Methods B 318 (2014) 253-257

Background

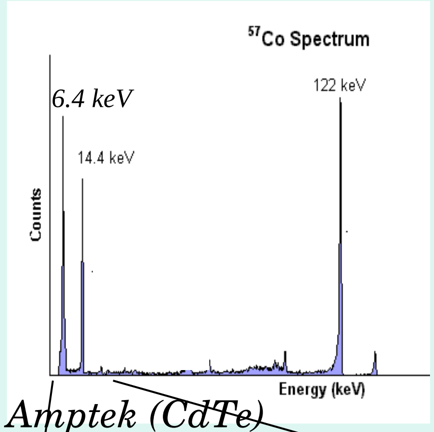


57Co Spectrum
6.4 keV
14.4 keV
122 keV
Counts
Energy (keV)
Amptek (CdTe)
1.8keV
Kr
14.4
6.4
~22
counts [10^3]
channel
0
256
512
768
1024

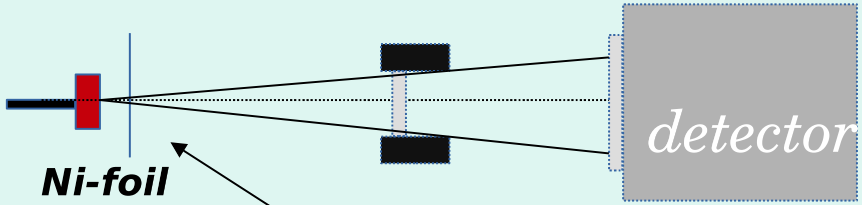


detector
100µm Ni-foil

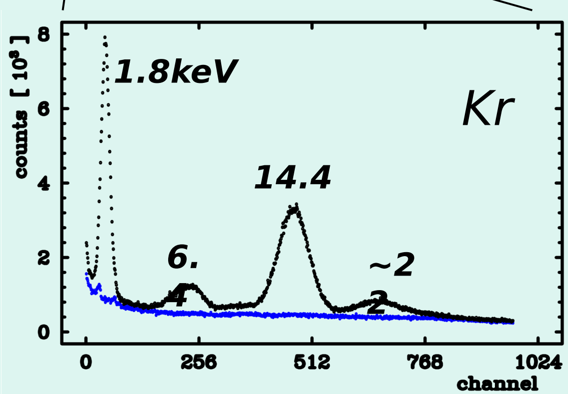
Background



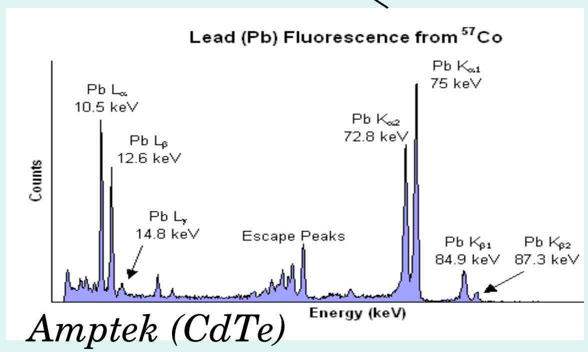
57Co Spectrum
6.4 keV
14.4 keV
122 keV
Counts
Energy (keV)
Amptek (CdTe)



Ni-foil
detector
Position behind source

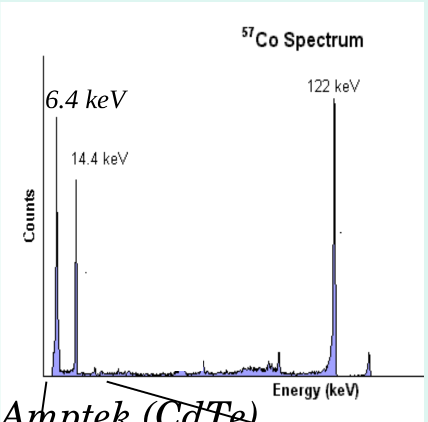


counts [10^3]
1.8keV
Kr
14.4
6.
4
~2
2
0
256
512
768
1024
channel

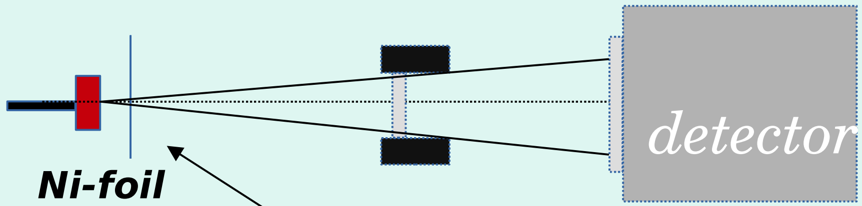


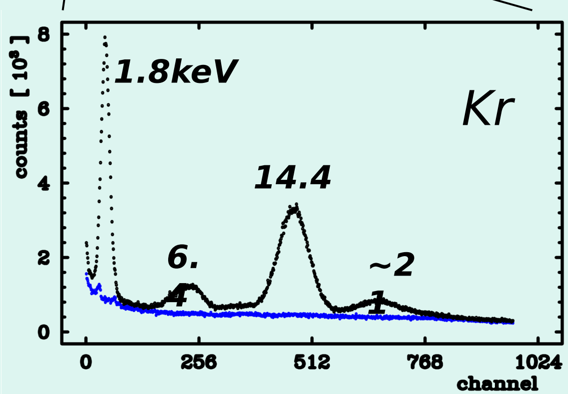
Lead (Pb) Fluorescence from 57Co
Pb Lα 10.5 keV
Pb Lβ 12.6 keV
Pb Lγ 14.8 keV
Escape Peaks
Pb Kα2 72.8 keV
Pb Kα1 75 keV
Pb Kβ1 84.9 keV
Pb Kβ2 87.3 keV
Counts
Energy (keV)
Amptek (CdTe)

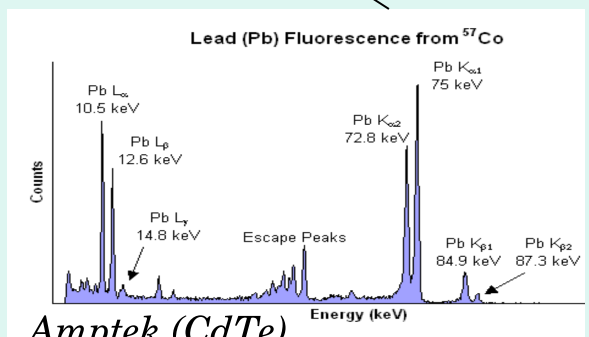
Background



Amptek (CdTe)



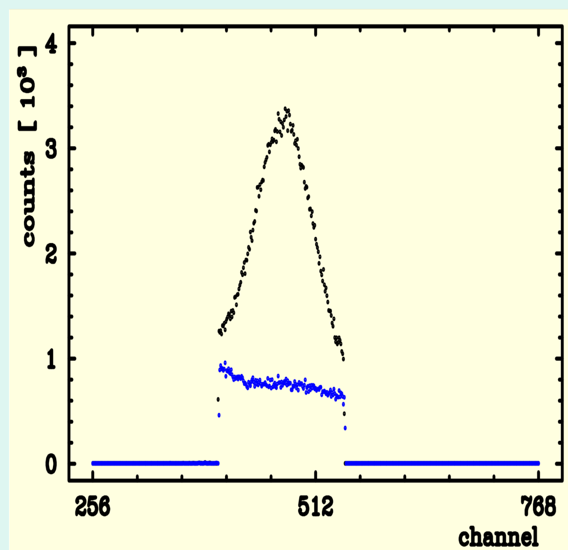




Amptek (CdTe)

Attenuation of 122 / 136 keV

$110\,\mu$Ni: 0.9695



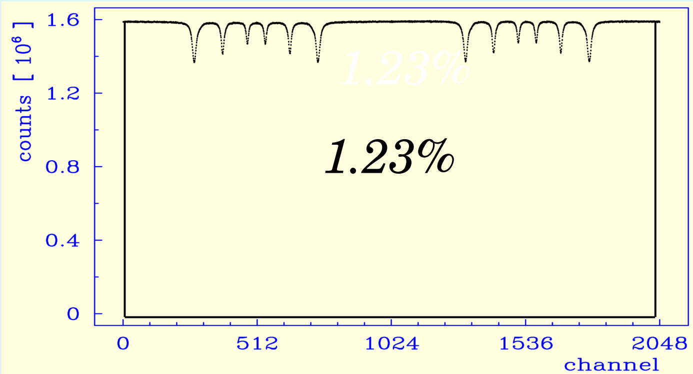
$$bg_{fr} = \frac{A_b(\mathbf{Ni})/0.\mathbf{9695}}{A_t}$$

14.4keV - window

multiscaling mode

$A_b(\mathbf{Ni}), A_t$

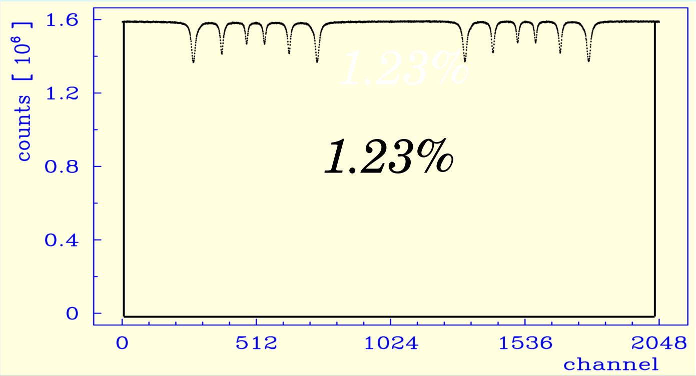
Background



$$b_{fr} = \frac{A_b(\mathbf{Ni})/0.\mathbf{9695}}{A_t/0.\mathbf{9877}} = 1.\mathbf{019}\frac{A_b(\mathbf{Ni})}{A_t}$$

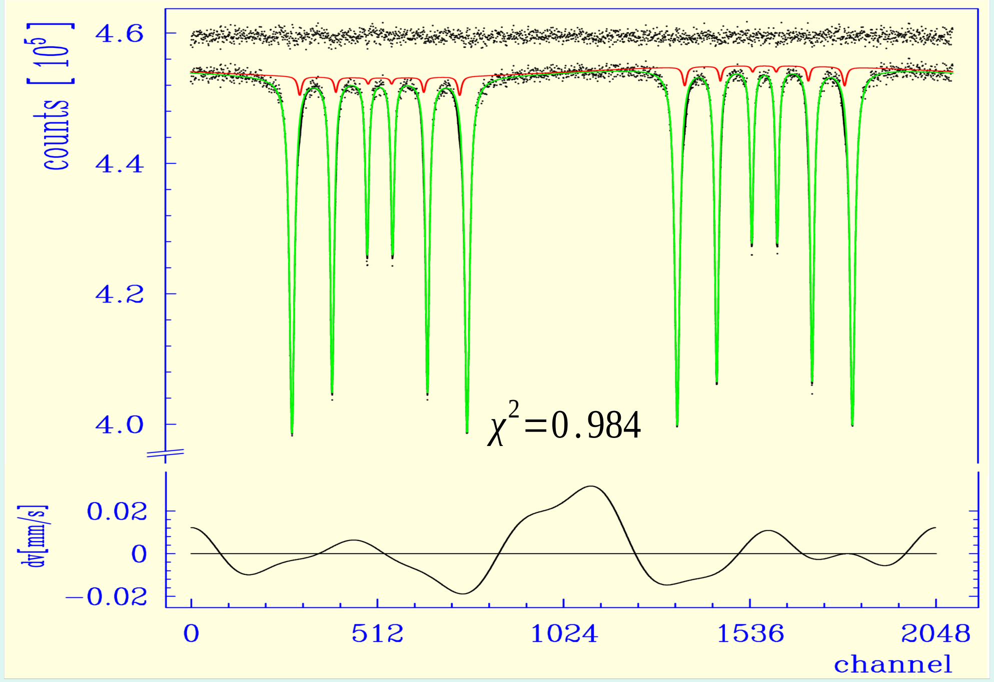
A straightforward experimental method to evaluate the Lamb-Mossbauer factor of a 57Co/Rh source
G. Spina , M. Lantieri, Nul. Instrum. Methods B 318 (2014) 253-257

Background



$$b_{fr} = \frac{A_b(\mathbf{Ni})/0.\mathbf{9695}}{A_t/0.\mathbf{9877}} = 1.\mathbf{019}\frac{A_b(\mathbf{Ni})}{A_t}$$

$\alpha - iron \quad 25.5\,\mu m, \quad f = 0.80, \quad \Gamma = \Gamma_N$



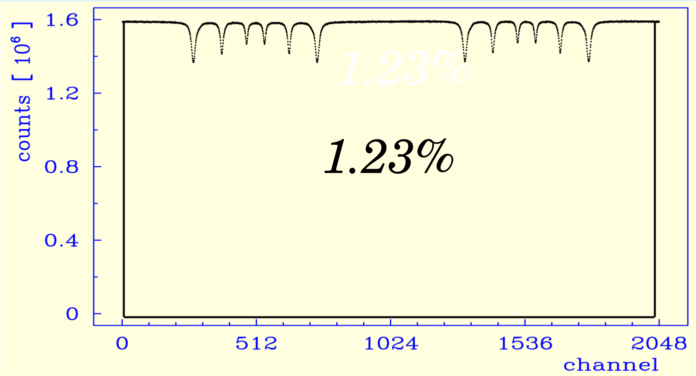
***Green*: 33.05 Tesla**

***Red*: 30.67 Tesla (Mn)**

Mossbauer measurements in iron based alloys with transition metals

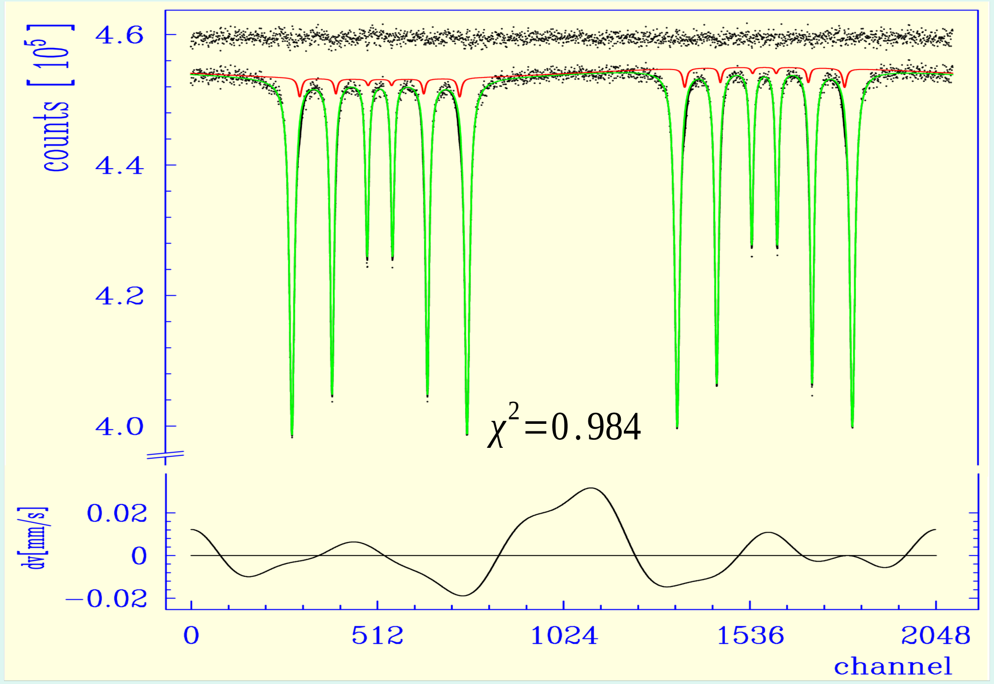
I. Vincze and A. Campbell, J. Phys. F: Metal Phys. Vol.3 (1973) 647-663

Background



$$b_{fr}=\frac{A_b(\mathbf{Ni})/0.\mathbf{9695}}{A_t/0.\mathbf{9877}}=1.\mathbf{019}\frac{A_b(\mathbf{Ni})}{A_t}$$

$\alpha-iron \quad 25.5\,\mu m, \quad f=0.80, \quad \Gamma=\Gamma_N$



***Green*: 33.05 Tesla**
***Red*: 30.67 Tesla (Mn)**

Fit results:

$f_{source}(1-bg_{fr})$ =>

f_{source} **= 0.715**
$\Gamma_{source}=1.38\cdot\Gamma_N$
$\sigma_{source}=0.59\cdot\Gamma_N$

Mossbauer measurements in iron based alloys with transition metals
I. Vincze and A. Campbell,J. Phys. F: Metal Phys. Vol.3 (1973) 647-663

Conclusion: some good practices

Taking down to the logbook:

Source (link to data sheet), Absorber (mg/cm²), Geometry (L_0,aperture), drive(mode, frequency), counting system (detector, electronic settings) Background fraction (rate measurements: gated/ungated, Ni-foil), etc

Use of the convolution integral

Use of a reliable nonlinearity correction

Advantage:

-Reliable values of t_{eff} instead relative areas

(independent of the complexity of the applied theory)

-Continuous control of the components of the equipment