Evaluation of the $\frac{f_s}{1+B}$ Factor in the Study of Dynamical Properties of Hyperfine Interactions

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Abstract. The interpretation of Mössbauer spectra often requires the use of the Transmission Integral function (TI). It contains the quantity $\frac{f_s}{1+B}$, where $f_s$ is the source Mössbauer factor and $B$ depends on the background radiation rate and on the inhomogeneity of the target; both of them usually obtained by ancillary measurements and tests. We present a simple method, that avoids ancillary measurements in evaluating the quantity $\frac{f_s}{1+B}$. It is useful when the Mössbauer line-shape rapidly evolves in narrow temperature ranges: a real application for single molecule magnets spectra and an analytical example are reported, too.

1. Introduction

Mössbauer spectroscopy is an excellent local probe for the study of magnetic solids containing iron. In particular, relevant information about dynamical parameters are obtained from the thermal evolution of the spectrum shape, which usually evolves, as a function of the temperature, from a set of well resolved lines to a single narrow collapsed structure. As a result of this evolution, the sample thickness, giving rise to a good signal/noise ratio at the bottom of the temperature region, will produce strongly saturated spectra at the top of the range. Consequently, in order to prevent erroneous evaluation of the temperature trend of the dynamical parameters, we should use the Transmission Integral (TI), whose expression is:

$$I(v, T) = F(v) \left\{ 1 - \frac{f_s}{1+B} \int_{-\infty}^{+\infty} L(\omega - v, \Gamma_s) \left[ 1 - \exp \left(-t_a \sigma(\omega, w(T))\right) \right] d\omega \right\}$$

(1)

where $F(v)$ is the background function, $L$ denotes the line shape of the source characterised by the line width $\Gamma_s$, $t_a$ is the absorber effective thickness and $\sigma(\omega, w)$ is the Mössbauer absorption cross section expressed in terms of a set of temperature dependent physical parameters $w(T)$ determining the actual shape. Moreover, (1) contains the term $f_s' = \frac{f_s}{1+B}$, i.e. the source Mössbauer factor $f_s$ reduced by $(1+B)$ due to both background radiation rate and target inhomogeneity effects. The fitting procedure requires the knowledge of $f_s'$, usually obtained by ancillary measurements and tests on the targets, as described in literature [1, 2]. On the contrary, the following method does not require additional measurements and consists of a preliminary
fitting procedure. It is useful for all those cases characterised by radical changes of the cross section belonging to small changes of the temperature and/or other external parameters. The only approximation we use consists of the omission of the temperature dependence of the sample thickness \( t_a \). The method can be applied in place of a simultaneous fit of the whole set of spectra and consists of a preliminary fitting procedure followed by independent fits of the single spectra. It allows to use straightforward computer code and procedures, limits the number of free parameters and reduces the correlation between \( t_a \) and \( w(T) \) parameters.

2. Theory
Let us consider the TI expression of (1). It does not have Lorentzian shape for two reasons: firstly, from a physical point of view, the Mössbauer absorption cross section \( \sigma(\omega, w) \) cannot be generally described as a sum of Lorentzian lines; secondly, the cross section appears as argument of an exponential function giving rise to distortion effects depending on the experimental \( t_a \) value. In the analysis of Mössbauer measurements, physical and experimental sources for the intercept are respectively angular coefficient \( \alpha \) of \( \frac{I(t)}{1+Be^{-\omega t}} \) and \( \omega \), representing the cross section shape, apart from the values of the respective line–widths; consequently TI is a linear function for that values for the parameters actual spectrum shapes are correlated to each other and erroneous evaluations of the physical value. The trend depends both on the specific \( t_a \) and \( w \) values.

For very low \( t_a \) values, the spectrum is not saturated, \( I(t) \) and \( \sigma(\omega, w) \) show identical line-shape, apart from the values of the respective line–widths; consequently TI is a linear function of the \( f_s^t a \) product but it is independent of the assumed \( f_s^t \) value. On the contrary, for real spectra, \( I(t) \) separately depends on \( f_s^t a \) product and \( f_s^t \). Observing (1), it is easy to deduce that values for the \( f_s^t a \) product obtained by a fitting procedure – as a function of assumed values for \( f_s^t \) – show a decreasing monotone trend, which passes through \( (f_s^t, f_s^t a) \), representing the actual values. The trend depends both on the specific \( t_a \) and \( w \) values.

The prefitting procedure consists of suitable reproductions of each spectrum, or at least of its apparent area and peak intensities, by using a not-Lorentzian \( \sigma(\omega, w) \) cross section shape, for a set of predefined \( f_s^t \) values. From these reproductions the trend of \( f_s^t a \) vs. \( f_s^t \) will be determined for each spectrum.

The line-shapes depend on temperature, but if the T-range is fairly narrow, as we will suppose, \( t_a \) can be assumed to be constant. In this case, for small changes of \( f_s^t \) around \( f_s^t \), all the series of \( (f_s^t, f_s^t a) \), points, where \( i \) defines the specific spectrum, can be fitted by straight lines

\[
(f_s^t a)_i = f_s^t a - \alpha_i (f_s^t - f_s^t)
\]

which obviously pass through the common point \( (f_s^t, f_s^t a) \).

Now, if we report the zero intercepts obtained for the various spectra as a function of the angular coefficient \( \alpha_i \), all the points lie on a new straight line, whose angular coefficient and zero intercept are respectively \( f_s^t \) and \( f_s^t a \). The obtained estimates for \( t_a \) and \( f_s^t = \frac{f_s^t}{1+B} \) will be then used in independent fitting procedures of each spectrum.

3. An Experimental Example
We will describe an application of the method for the heterometallic Cr\(_7\)Fe(II) wheel. Six Mössbauer spectra were collected between 1.8 and 14.8 K. They show the hyperfine structure to completely collapse in this narrow range of temperature, where \( t_a \) can be reasonably assumed to be constant. Each spectrum was fitted by assuming a set of defined values for \( f_s^t \) in order to obtain corresponding values of \( f_s^t a \). The strong correlation between sample thickness and dynamical parameters, affecting the sample absorption cross section, gives rise to very good reproductions of the spectra independently of the assumed \( f_s^t \) values. Figure 1 shows results along with the fit of corresponding linear trends for the lowest temperature and the highest one. The final step of the prefitting procedure consists in plotting the Zero Intercept (ZI) values vs. the angular coefficient \( \alpha \) of the respective interpolative line. We obtain the series
Mössbauer spectra of Cr$_7$Fe(II) collected at the lowest (a) and the highest (b) temperatures and fitted for a series of $f_s$ values. The obtained $f_s^r t_a$ values vs. $f_s^r$ and their respective linear fits are displayed at the bottom of each spectrum. Zero Intercept values are reported in (c) as a function of corresponding angular coefficient $\alpha$ for the six spectra together with the linear fit that provides values for $f_s^r$ and $t_a$.

Figure 1. Mössbauer spectra of Cr$_7$Fe(II) collected at the lowest (a) and the highest (b) temperatures and fitted for a series of $f_s^r$ values. The obtained $f_s^r t_a$ values vs. $f_s^r$ and their respective linear fits are displayed at the bottom of each spectrum. Zero Intercept values are reported in (c) as a function of corresponding angular coefficient $\alpha$ for the six spectra together with the linear fit that provides values for $f_s^r$ and $t_a$.

of points reported in Figure 1 for the whole set of spectra along with the subsequent linear interpolation. As a result of the procedure, we have $f_s^r = \frac{f_s}{1 + B} = 0.663(2)$ and $t_a = 16.6(1)$, which corresponds to $f_a = 0.78(1)$ calculated applying the well–known formula $t_a = n_a \sigma_0 f_a [1]$ and in agreement with the typical values for magnetic molecules. The values will then be used to interpret the Mössbauer spectra in terms of dynamical interactions affecting the hyperfine fields of the heterometallic Cr$_7$Fe(II) wheel.

4. An Analytical Example
A simple situation that permits analytical evaluations is represented by a cross section described by a single Lorentzian function, whose line width $\Gamma_a$ is proportional to the natural one: $\Gamma_a (T) = \beta (T) \ 2 \Gamma_n$, where $\beta(T)$ depends on the temperature monotonically.

The Mössbauer cross section is given by $\sigma (\omega, \beta) = \frac{\beta \Gamma_n^2}{\omega^2 + \beta^2 \Gamma_n^2}$ and has its maximum value equal to 1 for $\beta = 1$. Adapting standard evaluation procedures [3, 4] to the previous equation,
we obtain the following expressions of spectrum area and peak intensity:

\[
A\left(f_s^r, t_a, \beta\right) = \pi \Gamma_n f_s^r t_a \exp \left(-\frac{t_a}{\beta}\right) \left\{ I_0 \left(\frac{t_a}{\beta}\right) + I_1 \left(\frac{t_a}{\beta}\right) \right\} 
\]

(3)

\[
\varepsilon(0; f_s^r, t_a, \beta) = f_s^r \left\{ 1 - \exp \left(-\frac{t_a}{\beta}\right) \left[ I_0 \left(\frac{t_a}{\beta}\right) + 2 \sum_{n=1}^{\infty} \left(\frac{1}{1 + \beta}\right)^n I_n \left(\frac{t_a}{\beta}\right) \right] \right\} 
\]

(4)

which reduce to the usual expressions [1] for \( \beta \rightarrow 1 \).

If the right value \( f_s^r \) is not used, the spectrum shape will be reproduced by incorrect values for \( t_a \) and \( \beta \) and the fitting procedure will give rise to erroneous evaluation of \( \beta \). From the series development of \( A\left(f_s^r, t_a, \beta\right) - A\left(\bar{f}_s^r, \bar{t}_a, \bar{\beta}\right) \) around \( (\bar{f}_s^r, \bar{t}_a, \bar{\beta}) \) we have:

\[
I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) (f_s^r t_a - \bar{f}_s^r \bar{t}_a) + \bar{t}_a I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) (f_s^r - \bar{f}_s^r) + \frac{f_s^r}{\bar{\beta}} I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) (\beta - \bar{\beta}) \approx \frac{\exp \left(\frac{\bar{t}_a}{\bar{\beta}}\right)}{\pi \Gamma_n} \sigma_{f_s^r t_a} 
\]

(5)

where \( \sigma_{f_s^r t_a} \) is the standard deviation for the \( f_s^r t_a \) product and the factor term \( \frac{\exp \left(\frac{\bar{t}_a}{\bar{\beta}}\right)}{\pi \Gamma_n} \) is connected with the experimental sensitivity, which exponentially decreases with \( \frac{1}{\bar{\beta}} \) and gives rise to point dispersion shown in Figure 1 for the spectrum at 14.8 K.

By assuming \( \frac{\exp \left(\frac{\bar{t}_a}{\bar{\beta}}\right)}{\pi \Gamma_n} \sigma_{f_s^r t_a} \approx 0 \), we obtain

\[
f_s^r t_a \approx \frac{f_s^r}{\bar{\beta}} I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) \left(\bar{f}_s^r (\beta - \bar{\beta}) + \bar{\beta} (f_s^r - \bar{f}_s^r)\right). 
\]

(6)

Similarly, the peak value reproduction gives rise to the following second expression for \( f_s^r t_a \)

\[
f_s^r t_a \approx \frac{f_s^r}{\bar{\beta}} I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) \left(\bar{f}_s^r (\beta - \bar{\beta}) + \bar{\beta} (f_s^r - \bar{f}_s^r)\right) + \frac{C_j\left(f_s^r, \bar{t}_a, \bar{\beta}\right)}{\bar{\beta}^2} (f_s^r - \bar{f}_s^r) 
\]

(7)

where \( C_j\left(f_s^r, \bar{t}_a, \bar{\beta}\right) \) and \( C_j\left(f_s^r, \bar{t}_a, \bar{\beta}\right) \) are algebraically evaluated coefficients. From (6) and (7) we obtain

\[
\alpha_i = \frac{-I_0 \left(\bar{t}_a\right) I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) \left(1 - \frac{f_s^r t_a I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) + C_j I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) + C_j I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right)}{f_s^r t_a I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) + C_j I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right)}\right)}{I_0 \left(\bar{t}_a\right) I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) \left(1 - \frac{f_s^r t_a I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) + C_j I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) + C_j I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right)}{f_s^r t_a I_1 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right) + C_j I_0 \left(\frac{\bar{t}_a}{2\bar{\beta}}\right)}\right)} 
\]

(8)

for the \( \alpha_i \) coefficient of (2) and an analytical expression for the error propagation on \( \beta \) due to erroneous estimations of \( f_s^r \).

As numerical examples, by assuming \( f_s^r t_a = 5.5 \), \( \bar{f}_s^r = 0.66 \) and using \( \beta = 1.55 \), \( \beta = 5.0 \) we obtain \( \alpha_i \approx 64 \) and 5.8, respectively. These values are close to the experimentally derived ones for the 14.8 K and 1.8 K spectra. Moreover we respectively obtain 8.7 \( \left(f_s^r - \bar{f}_s^r\right) / \bar{f}_s^r \) and 0.8 \( \left(f_s^r - \bar{f}_s^r\right) / \bar{f}_s^r \) for the relative error on \( \beta \).

The last results suggest that, in the Cr-Fe(II) case, the relative systematic error on dynamical parameters is smaller than 5% and show that the described method prevents from erroneous evaluations of the temperature trend of electronic physical features.

References

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