

# WMOSS4

Version F

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## Mössbauer Spectral Analysis Software

An Open Software Project

by

WMOSS.ORG

&

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WMOSS4 is generally an updated version, FORTRAN based, of v2.51. It is compatible to all NT6 OS systems (Windows XP to Windows 8). Various versions of WMOSS4 started to be available for download beginning March 1, 2012 at [www.wmooss.org](http://www.wmooss.org). WMOSS.ORG is supported by TerraMicroTech consulting. WMOSS4 is Open Software; both executable file and FORTRAN source code are freely available.

Special release versions, called generic WMOSS4R, with added features are not Open Software. They are offered at [www.wmooss.org](http://www.wmooss.org) for a modest license fee under convenient terms. This subproject is specially designed to fund another important project: completely porting WMOSS from FORTRAN to C++ language that will substantially improve the features and capabilities for all compiled versions of WMOSS.

**WMOSS4 is open and free software. The use of WMOSS4 should be clearly acknowledged in any published work. The appropriate reference would be :**

**“WMOSS4 Mossbauer Spectral Analysis Software, [www.wmooss.org](http://www.wmooss.org), 2012”.**

## Modifications to WMOSS

WMOSS is basically an open software project. Modifications and extensions to the code are encouraged. To avoid confusion with the WMOSS program available at WMOSS.ORG, externally modified versions should be given unique names that do not contain “WMOSS”. For example, names like ZMOSS, BestMOSS, etc. Improved versions are planned for release at WMOSS.ORG and will be named WMOSS 4 or similar.

If you have developed new features and would like to have those incorporated into current or future programs offered by WMOSS.ORG, please feel free to inquire via email to [info@wmooss.org](mailto:info@wmooss.org).

Feedbacks and suggestions for particular improvements of WMOSS program or manual will be warmly received.

## Chapter 1. INTRODUCTION

### 1.1 Purpose and scope

The program WMOSS4 is a tool specifically made for analysis of Mössbauer spectra. Its specialized design allows for easy and efficient use. This manual is directed to persons familiar with Mössbauer spectroscopy and does not serve as a spectroscopy textbook. Several excellent reviews of applications of Mössbauer spectroscopy are listed in the References (e.g. Gütlich (2011), Debrunner (1993) or Lang (1970)).

### 1.2 Overview

The program's structure is dominated by two features. First, as spectra are loaded from disk files, they are added to the LIST. The LIST is a table of spectra stored in RAM and can contain up to 128 spectra including comments and calibration information. The second central feature is a single PARAMETER SET, held in RAM, that specifies how a theoretical spectrum is to be calculated. The ten seven theoretical models currently included are:

The 7 original in theoretical models from WMOSS4 v2.51:

- Model 1) a system with a single electronic spin  $S \leq 9/2$  and 1 to 14 Iron sites,
- Model 2) multiple individual lines,
- Model 3) multiple quadrupole pairs,
- Model 4) a system with two coupled electronic spins and 1 to 14 Iron sites,
- Model 5) 1 to 14 Iron sites with EFG and fixed orientation of effective  $H^{\text{int}}$ ,
- Model 6) Quadrupole Splitting Distribution / Voigt Based Fitting
- Model 7) Hyperfine Field Distribution / Voigt Based Fitting.

Plus 3 new additions in WMOSS44 – v.F1:

- Model 1-1) same as Model 1 with local slow or fast relaxation parameter,
- Model 4-1) same as Model 4 with local slow or fast relaxation parameter,
- Model 5-1) same as Model 5 with local slow or fast relaxation parameter and effective uniaxial electronic hamiltonian

Handling the spectra and parameter file in RAM also means that, except SAVE operations, any modifications or operations on the them are permitted without affecting the disk files. It also means that at the end of the work session the user must save any relevant data.

The intrinsic line shapes may be Lorentzian or Voigt. Normally, a file with control parameters is loaded into the RAM parameter set and, if necessary, modified to correspond to the desired theoretical model and to initial estimates of the fitting parameters. When the latter are optimized the results are stored in the RAM PARAMETER SET and may be saved to disk, usually after renaming to preserve the original source file. Spectral simulations may also be saved, but saving only the parameter file usually suffices since spectra may be recalculated quickly.

The menu structure of WMOSS4 requires a minimal number of keystrokes and is almost always visible to remind the user of available options. WMOSS4 is key board oriented. As the user becomes more experienced, the menus can often be bypassed via special "hot" keys. The displayed LIST of spectra, an easily edited and stored parameter set and easily generated print-to-file hardcopy of plots will help keep a work session organized and documented.

The analysis portion of the program allows the user to adjust parameters manually or to use least squares fitting. The technique of choice depends on many factors, two of which are sample purity and user experience. One approach would be to scan parameters manually to find an approximate solution. Then the fit could be improved using the least squares procedure. The least squares algorithm can fit up to four spectra simultaneously. A different approach would be to use the least squares procedure to search for solutions not anticipated by the user. After a satisfactory set of parameters has been found, the uncertainty of each parameter and the correlations between any two parameters may be examined via Monte Carlo simulations. The Monte Carlo method is very powerful, but requires calculating times equivalent to hundreds of fits. Hence, for the more complicated theoretical models Monte Carlo simulations may not be practical.

### 1.3 Hardware and Software Requirements

To run the executable file you will need any standard PC with MS Windows XP or newer operating system installed. WMOSS4 has also been successfully tested on a PC with the Linux operating system and the WINE API.

To compile and link the FORTRAN source code, you will need for example the CVF6 compiler and the Interacter graphics library (compiler specific) from Interactive Software Services.

The WMOSS4 executable code includes licensed routines from the Interacter graphics library (copyright Interactive Software Services, Ltd., UK, [www.winteracter.com](http://www.winteracter.com)).

### 1.4 Installation of WMOSS4 program

The WMOSS4 program does not require installation. It can be executed "as is". However there are a series of minor but critical (or recommended) steps to follow.

On a PC with Windows NT6 (XP to Win8), download the provided zip archive file and extract the “web” folder to [c:\web](#). One can also extract this directory locally and later move it to c:\. If the directory [c:\web](#) already exists the unzip operation must allow overwriting the older files. We recommend as best practice to delete or rename the previous [c:\web](#) directory.

For convenience, create a shortcut to the executable file on your desktop by right-clicking on the c:\web\wmoSS4\_f.exe file and selecting “Send to desktop (create shortcut).”

On a linux PC with WINE, download the zip archive file and extract the “web” folder. Move the “web” directory to /home/user\_name/.wine/drive\_c.

Also, to fully benefit from the newly improved functionality of “Custom PSPlot”, the user must install GhostScript (the GSview32.exe version, not the 64-bit version) and add the directory where this application was installed into the system PATH.

**Example:** (assuming default installation of Ghost Script on a English language OS):

---

Control Panel->System->Advanced->Environment variables->System variables

Scroll down and select PATH from list.

Click Edit

On field Variable Value, add: ;C:\Program Files\Ghostgum\gsview

(first semicolon is needed to separate the new entry from previous ones)

Exit with OK all windows from Control Panel tree.

Most Windows OS systems will execute this change without need of rebooting.

---

This concludes the installation of WMOSS4F program.



## 1.5 The user specific configuration file: c:\WEB\MOS\WMOSS4.CFG

The file WMOSS.CFG is located in the WEB\MOS directory and is an ASCII file that contains the default settings for hardware and files used by WMOSS4. You should edit WMOSS4.CFG so that it agrees with your preferences. If the WMOSS.CFG file is not present in \WEB\MOS the program will stop.

The default example for the WMOSS4.CFG file is shown below.

---

```
! Sample configuration file WWW.WMOSS.ORG FEB 12, 2013

! Blank lines can be inserted at will and are ignored.
! Exclamation points begin a comment, so that the rest of the line
! will be skipped. The case of the keys and values does not matter,
! and spaces are stripped. Thus "Key= Value" and "key = value" are
! both equivalent to "KEY=VALUE".

graphics = on ! on= normal, off=text screens only
scdump = postscript ! DO NOT CHANGE !
! Choices:"hpgl", "laserjet", "postscript", or "epson"

postscript = psplot.ps ! Default name for Custom PSplot spectra file
text = parout.txt ! Default name for plot param file
psinit = C:\WEB\MOS\PSINIT.MOS ! DO NOT CHANGE !
psout = psout.ps ! Default name for CTRL+P spectra plot file
monte = monte.out ! Default name for the Monte Carlo file
screenfile = c:\web\svga.scr ! Pathname for screen-parameters file

specmask = *.b ! Default for "Load Spec"
paramask = *.spi ! Default for "Read Param"

diffspec = on ! Defaults for (on/off) toggles in OPTIONS box
plotsubs = off ! "on" turns the option on;
keepsups = off ! anything else turns the option off.
nnegareas = on ! Force relative areas to be nonnegative during fit?

! Below are switches that control data plot format.
xscale = 2 ! Default X-axis: 1=Channel Number, 2=Velocity [mm/s]
yscale = 2 ! Default Y-axis: 1=counts, 2=% Absorption
symbols = off ! Plot data using crosses at each point?
! errorbars = off ! Plot data using error bars?
errorbars = on ! Plot data using error bars?
! lines = off ! Connect points with a continuous line?
points = off ! Plot data as single points?
title = on ! Display a title for each plot?
datetime = on ! Display a date/time stamp for each plot?
showpaths = off ! Display entire pathnames on the list?
rotatehpgl = off ! Toggle HP plotter 90 degree rotation
```

## 1.6 Menu Structure

# WMOSS

## Special Keys

[UP/DOWN] in Menu: Highlight choice in Flash: select parameter in Lsub or Ssub: vary areas, etc.	[Ctrl+P] execute graphics Plot2File
[ENTER] choose highlighted item from MENU choose highlighted item from LIST in LOAD, PICK or DEL modes set the parameter values (any context)	[P] execute parameters Plot2File
[CTRL+ UP/DOWN] scroll highlight on LIST	[PageDown] next Page of Parameters in EditParam
[Delete]/ENTER(PICK)/ESC delete data from LIST	[PageUp] previous Page of Parameters in EditParam
[Page Down] move highlight to bottom of LIST	[Space] calculate theoretical spectra in Flash mode
[Page Up] move highlight to top of LIST	[F2]-[F10] hot-keys that bypass menu
	[ESC] executes changes and retreat up MENU ladder stops execution of some SUBMENUs (Flash or Custom PSPlot modes)
	Pause/Interrupts/Break execution of Fit mode

## Menu Structure

<u>Files</u>	<u>Analysis</u>	<u>Utilities</u>	<u>Plot2File</u>	<u>Options</u>
Data load [F2] Data Save [F3] Edit Data Header Parm Load [F4] Parm Save [F5] Change Dir [F6] List Save Exit	Flash Lsub Ssub Pick Data Edit Param Do Fit MC Plot QSD Plot HFD Plot	Add Mask Clear Mask Delete [DEL] Zoom [F8] Condense by 2 Stretch Exp. Add	Spectra [CTRL+P] Parns [P] Custom PS Plot	<b>Options</b> Diff. Spec. Plot Subs Subs > List Vel. Scale X Autoscale Y Autoscale
<b>Data Load:</b> <b>File Format?</b> <b>Fold?</b> Manual Fold Auto Fold First Half Second Half Iron Metal Cal. No Fold	<b>Data Save : Format?</b> WEB Binary WEB ASCII Y ASCII, counts XY ASCII, (channels, counts) XY ASCII, (Vel. [mm/s], Abs. [%])			

## Chapter 2. TUTORIAL

At this point you should have installed WMOSS on your computer; this means the presence of c:\web directory with all files and subdirectories as provided in the zip archive. The executable itself can be renamed, placed in different directory, different disk (local, removable or on or on Desktop and can be run directly from these places. you will be guided through examples of most of the features available.

For medium to advanced users, in “Appendix D – Concise Tutorials” are presented some typical usage patterns. One important example is “From Start to FIT”.

For those that are still beginners to use WMOSS4 a much more detailed tutorial about its basic functionalities is presented as follows.

To remind the new users, WMOSS4 program is operated almost exclusively from keyboard, without the small exceptions of MASK and ZOOM procedures. If you dislike using Mouse for these two procedures you can disable it from WMOSS.CFG file.

Now run the program and step through it as you read the discussion below.

**IMPORTANT:** During this tutorial pressing the keys indicated as

*italics and centered on the line,*

is in fact equivalent to use WMOSS4 with the provided Hotkeys and shortcuts. One can however choose any other keyboard method for selecting and executing the functionalities, as described below.

Since some responses to prompts in WMOSS do not require pressing the Enter key, the notation [ENTER] will be used to indicate when that keystroke is required.

At start a banner page will appear showing the program version number, eventually the license information where applicable (e.g. for WMOSS4R ver.F1). Pressing [ENTER] will bring up the Main Menu.

The selection and execution of the desired Main Menu and Submenu items may be equally chosen by:

1. Using the Left/Right Arrows to scroll horizontally the Main Menu,
2. Using the Up/Down Arrows to scroll vertically the Submenu choices and then [ENTER] ,
2. Typing the highlighted letter within the displayed item name, or
3. Pressing a HOT KEY, e.g. [F2] or [CTRL+P], etc.

Note that on the Main Menu the fifth item, Options, does not have a submenu and therefore requires to press [ENTER] key to access it.

## 2.1 Files submenu

Choose the Files submenu.

*F*

The Files submenu will appear. All disk file input and output procedures are found here.

Because the first steps will be always to bring in RAM a set of spectra files and a corresponding Parameter file to be used for analysis, the first action is then to select the directory where these files are kept.

Note 1: this step means implicitly to select the “current working directory” (where for example the Plot files or other automatically saved files are stored). Changing the directory many times is permitted at user’s convenience, but remember that only the last action will indicate the “current working directory”.

Note 2: at this moment WMOSS4 program cannot switch between disk drives, so it is imperative to bring your data or working directories on the same disk with the installation directory. This is the c: drive by default and cannot be changed by user. Should the user attempts to use an older version of wmooss.cfg file (that in principle allows selection of the local disk) it is important to know that such action will make many new features in WMOSS4 ver.F unusable.

Note 3: if your computer does not have the possibility to have the c: disk, or if it is “strictly” not meant for keeping your working data, feel free to contact the author at [info@wmooss.org](mailto:info@wmooss.org) for obtaining a customized copy of WMOSS4 according to your needs.

### 2.1.1 Change Directory

Selecting this action will open a dialog line: “New directory: \*” on top left corner of WMOSS window. We recommend for the convenience of day-to-day use to skip this step and continue by pressing

*[ENTER]*

At WMOSS start the current directory is by default c:\web (the current directory is indicated at top of the dialog window) so we need to exit from it and look for the directory where the spectra or parameter files are stored. Make the selection with

*Arrows Up/Down  
[ENTER]*

Choosing the ‘..’ line and pressing *[ENTER]* will redirect to the parent directory (in this case c:\) and list its directories. Now select again with *Arrows+[ENTER]* the needed root directory where data files are kept, then subdirectories, subsubdirectories (if this is the case), etc. until reaching the desired place, then press the *[ESC]* key.

For this Tutorial purpose we will stay in C:\web we want to reach to its c:\Web\Mos\Examples” directory:

*[DownArrow][ENTER]*  
*[DownArrow][ENTER]*  
*[ESC]*

If you do not want to use the directory lists, then simply type the path of the desired directory over the default template. If you enter an incorrect path, the directory will not be changed and the Files submenu will reappear.

## 2.1.2 Data Load

### Spectra File formats and Data Normalization

The discussion presented in this section pertains to loading of those spectra which have been previously saved to disk in the WEB binary (or WEB ASCII) format. These two file formats contain the spectrum as normalized data plus a header specifying the original experimental conditions.

Raw data, however, are downloaded from a multi-channel analyzer (MCA). The format of such a raw data file depends on the particular MCA. Usually, raw data files contain little or no calibration information and upon loading to WMOSS the user is asked to fill in the missing values in the spectra header (experimental conditions). Chapter 4 describes the loading of raw data files and also describes the automated fitting of iron metal calibration spectra.

At this point a clear understanding of the data normalization concept is needed to avoid confusion. Raw data are normalized during the Data Load procedure. Normalization consists of the subtraction of an estimated baseline and then division of the spectrum by the value of its own area. It is these normalized spectra that are added to the LIST by the Data Load procedure. No other procedure in WMOSS automatically normalizes a spectrum. In particular, no renormalization of the data occurs when a spectrum is saved to disk in the WEB binary or WEB ASCII formats. If the user creates a spectrum via a WMOSS procedure and that spectrum does not have unit area, then saving that spectrum to disk in the WEB binary or WEB ASCII format and then reloading the new file will not affect the spectrum. These issues are discussed further in the Data Save portion of this tutorial and in Chapter 4.

Now, to load a spectrum data file choose Data Load from File submenu.

## D

An option box appears listing various file formats. The cursor is moved via the *[Up/Down ARROWS]*. Highlight choice 1 (Web binary, 4 byte) and press *[ENTER]*.

*[VERTICAL ARROWS]*  
*[ENTER]*

A new window will appear. The top line now contains a prompt for a file name. The default is "\*.b" (as specified in the WMOSS.CFG file). At this point you may:

- 1) type in a specific file name and *[ENTER]*,
- 2) type in a new template with \* and/or ? wildcards,
- 3) edit the default template by first pressing a left or right arrow, or
- 4) simply *[ENTER]*.

Action #1 will cause the named file to be loaded and displayed, but try #4 instead.

*[ENTER]*

The menus disappear and a box appears displaying the names of all files that match the \*.b template and that are in the current directory. Note that several spectra are listed. In current program version this window can list Max. 128 filenames, alphabetically ordered and displaying the first 20 characters of filename (from a total permitted of 40 characters). To reduce the number of listed files, we can press *[ESC]* and go back to the Files submenu, choose Data Load again and then use a more specific template. Let's do that.

*[ESC]*  
*[ENTER] [ENTER]*  
*fd\*.b [ENTER]*

Now a list of six files should be displayed. Select two or more spectra, for example FD18.B and FD20.B, by moving the highlight with *[ARROW]* and selecting each one with *[ENTER]*.

*[DOWN] [DOWN] [ENTER] [DOWN] [ENTER]*

The selected names will change from black to red and are marked with an arrow.

Pressing *[ENTER]* two times on the same name will deselect it.

Press *[ESC]* to finish the load procedure and to return to the Files submenu. Press *[ESC]* again to return to the Main Menu choices.

*[ESC] [ESC]*

The two spectra are now loaded and their names will appear on the LIST at the right side of the screen. The spectrum plotted in the data box is the “active spectrum”. The active spectrum name is highlighted on the LIST by an "@" sign and by the color red.

At the bottom of the screen the following information about the displayed spectrum is shown:

**BL20:** The bottom number is the baseline as estimated by the average of the contents  $D_i$  of the first ten and the last ten channels. The upper number indicates that this is the zero level from which fine adjustments might be made in fitting procedures. The fine adjustment, which we deal with later, will be measured in units of BL20/100.

**Area:** The lower number is the sum over channels of  $\{D_i - BL20\}$ . It is negative because we are dealing with absorption spectra. It is the absorption area in (counts•channels). The upper number indicates that this value is taken as the unit of area for this experimental spectrum.

**Centroid:** The lower number is the "center of mass" or first moment of the spectrum, in channels, as defined by

$$\frac{\sum_{i=1,N} \{ (D_i - BL20) i \}}{\sum_{i=1,N} (D_i - BL20)}$$

Where  $D_i$  are the raw data and N is the number of channels. The upper number is the same first moment, but in velocity units.

**% Effect:** The displayed spectrum is a plot of  $100 \cdot (D_i - BL20) / BL20$  as a function of either channel number or velocity, depending on the Options Vel Scale toggle. The % Effect value is the largest magnitude in this array.

### 2.1.3 Edit Data Header

Now you can examine the Data Header information and comments of spectrum FD18. FD20 is highlighted on the LIST and that spectrum is displayed in the data box. Scroll up the LIST to make FD18 the active spectrum. Then choose Files -> Edit Data Header.

[CTRL+DownArrow]

F

E

A box titled "Data Header of FD18.B" will appear. This box contains all information needed to define the experimental conditions at the time the spectrum was recorded, including the sample temperature and applied magnetic field. To fill in all necessary parameters you might need to consult the appropriate paragraphs in this Manual. Also included are six comment lines.

Now [ESC] back to the Files Submenu.

*[ESC]*

By exiting the Edit Data Header procedure all the modifications are automatically saved in the RAM copy of this spectra. To save them on the disk file then Data Save procedure must be executed.

#### 2.1.4 Data Save.

Any spectrum on the LIST can be written to the disk. Simply make the spectrum the active spectrum and then choose Data Save. To save the current active spectrum FD18 to the file XYZ.B, type

*T*

The Data Save Format option box will appear:

##### **Data Save Format**

WEB Binary
WEB ASCII
Y ASCII (counts)
XY ASCII (channels, counts)
XY ASCII (velocity [mm/s] , absorption [%] )

The first two formats have been discussed above. The last three formats specify ASCII files that may be conveniently imported to other programs. Move the highlight with the vertical arrows. Place the highlight on WMOSS Binary and press [ENTER]

*[Vertical Arrows]*

*[Enter]*

*Enter a file name for this spectrum.*

*XYZ.B [ENTER]*

The ".b" suffix is simply a reminder that this file is a binary file. You could use any suffix or none. The name of the active spectrum will be changed to XYZ.B and the Files submenu will reappear.



### 2.1.5 Deleting spectra from the LIST

Clean up the LIST by deleting spectrum XYZ.B. Note, this procedure deletes the spectrum from RAM memory and does not delete a file from the disk. Press the [Delete] key, make XYZ.B red by using the [CTRL+Up/Down Arrows] keys, press [ENTER] and [ESC].

[DELETE]  
[CTRL+Up/Down Arrows]  
[ENTER]  
[ESC]

Now, reload FD18.B.

D [ENTER]  
FD18.B [ENTER]

### 2.1.6 List Save

It is sometimes convenient to save a particular collection of spectra (data and/or theory) to one disk file. Later all these spectra can be reloaded by simply loading that one file.

### 2.1.7 Parm Load

To load a parameter file, choose Parm Load. and accept the default template \*.pi.

P  
[ENTER]

A box titled "\*.pi" will appear listing all \*.pi files in the current directory. Also, listed will be several standard example parameter files. These have the SPI suffix and are found in the c:\mos directory. Highlight FD18GA.PI and choose it with [ENTER]

[ARROW]  
[ENTER]

The name of the parameter input file will appear just above the spectra LIST. Unlike spectra, only one parameter file may be loaded at any given time. The parameters may be altered during your analysis via several means discussed below.

### 2.1.8 Parm Save

At any time the current parameter set may be written to the disk by choosing Parm Save. Write this current set to the disk.

*R*

A top line prompt will appear with the default file name being that defined in the current RAM parameter set. This will usually be the name of the original input file. You can overwrite that original disk file by hitting Enter, but let's type a new file name.

*FD18GZ.PI [Enter]*

The standard example files (\*.SPI) and most of the files used in this tutorial are read-only and cannot be overwritten.

*Write over existing file? (Y/N)*  
*Y*

This concludes the Files Menu tutorial. Exit WMOSS.

*X Y*

## 2.2 Analysis submenu

Start WMOSS. Then from the Files menu, change to the C:\web\mos\examples directory and load data files fd20.b, fd18.b and parameter set FD18GA.PI.

```
WMOSS [ENTER]
[ENTER]
F
C  c:\web\mos\examples [ENTER]
D [ENTER]
fd20.b [ENTER]
D [ENTER]
fd18.b [ENTER]
P  fd18ga.pi [ENTER]
```

Note the fd18.b is loaded last and is at the bottom of the List.

Note that Flash, Edit Param and Do Fit can, and usually do, alter the parameter set in RAM. If you ever have a RAM parameter set which you wish to preserve for future

use or reference, save it to disk. If it is very valuable you might then want to give it the read-only attribute.

### 2.2.1 Lsub -- Line subtraction

Try subtracting some lines from FD18 using Lsub. With FD18 displayed on the screen, choose Lsub on the Analysis submenu.

*L*

Accept defaults for Position, Width, Baseline and Area.

*[ENTER]*

*[ENTER]*

*[ENTER]*

*[ENTER]*

A single blue line will be plotted over the active spectrum. A red line that is the difference spectrum will also appear (unless you turn it off by choosing Options, Diff spec). You may now alter the single line using [CTRL+Up/Down Arrows] as indicated in the top line prompt. The sign of the linewidth controls the type of line calculated. For a Lorentzian line, use a positive linewidth. For Voigt, negative. When you are satisfied, escape.

*[ESC]*

A question box will pop up. Answer Yes to place the difference spectrum on the LIST.

*Y*

Type in a name.

*diffspec [ENTER]*

Type in a Comment

*FD18 - one line [ENTER]*

You may wish to record the line parameters in the comment. Lsub is a procedure which does not call on the PARAMETER SET, and it does not record parameters in it. It has been included to provide an easy way to remove impurity contributions from the observed spectrum. The calibration information for the difference spectrum is copied from the data header of FD18.b, i.e. the active spectrum when LSUB was executed. The program returns to the Analysis Submenu and makes the difference spectrum the active spectrum.

A second line could be removed by repeating the procedure, using the first difference spectrum as input.

### 2.2.2 Ssub -- Spectrum subtraction

Let's now subtract one spectrum from another using Ssub. To subtract FD18 from FD20, first make FD20 the active spectrum by highlighting it on the LIST.

[CTRL+Down Arrow] [CTRL+Down Arrow]

FD20 will be displayed on the screen. Choose Ssub

S

Choose FD18 as spectrum #2

[CTRL+UpArrow] [ENTER]

FD18 will be plotted (blue) over FD20 with 100% relative area. The difference spectrum (red) is also shown (unless you turn it off by choosing Diff. spec. on the Options submenu). The relative area of the #2 spectrum can be adjusted with [VERTICAL ARROWS]. The current area of #2 as a fraction of #1 is displayed on the Top Line. Displayed to the right of area #2 is the increment value "dA". dA is controlled via the [LEFT] and [RIGHT] arrows. Change the relative area of #2

[VERTICAL ARROW]

One touch of [UP ARROW] increases the area fraction by dA. Holding [CTRL] and touching [UP ARROW] causes a 10dA change. [LEFT] divides dA by two. [RIGHT] multiplies dA by two. When you are satisfied with the appearance of the difference spectrum, escape.

[ESC]

The difference may be placed on the LIST as in Lsub. You may wish to record the relative area in the comment. Ssub is a procedure which does not call on the PARAMETER SET, and it does not record parameters in it. The program returns to the Analysis Submenu and makes the difference spectrum the active spectrum.

### 2.2.3 Flash -- Single or Series of theoretical simulations

The Flash procedure allows the user to adjust parameters manually and to evaluate quickly the changes in the simulated spectrum. Before choosing Flash, make the data file

you wish to work with the active spectrum. Let's use FD18.B. Highlight FD18.B on the LIST using the [CTRL+Up/Down Arrows].

*[CTRL+Up/Down Arrows]*

Also, before using Flash, a parameter set must be loaded. At the beginning of Section 2.2 you were instructed to load parameter file FD18GA.PI. Its name should appear above the LIST in the upper right corner of the screen. If parameter set name is not displayed, load the FD18GA.PI parameter file now by executing Parm Load in the Analysis menu. The FD18GA.PI parameter set specifies a single quadrupole pair as the model. Since the parameters Shift, dEq and Gamma are given in mm/s in the parameter file, it is convenient to use a calibrated velocity scale plot. The default mode for the plotting of the x-scale is defined in the WMOSS.CFG file (see section 1.6). If the displayed x-scale has units of channels, change it to mm/s.

**Note: To toggle the plotting mode of the X-scale, press [F7].**

Now, from the Analysis submenu choose Flash.

*F*

The screen will clear, a simulation according to the current parameter set will be calculated and then that simulation will be plotted (blue color) over the data along with the difference spectrum (red color). Four areas of text will also be displayed:

left side	Parameter List: Names and values of current parameters plus the field and temperature. This list may be scrolled with [VERTICAL ARROW]
bottom line	Name, value, lower bound and upper bound for parameter highlighted in the Parameter List. Use [HORIZONTAL ARROW] to move highlight.
lower right	Simulation Spectra List: Highlighted name corresponds to simulation currently plotted over data on the screen. Use [CTRL+Up/Down Arrows] to scroll this list and change plotted simulation.
top line	Prompts for special keys in Flash:

Special keys for the Flash procedure are:

[CTRL+Up/Down Arrows]	Scroll cursor through list of calculated spectra.
[Space]	Calculate a single simulation from current parameters
[S]	Calculate a series of 11 spectra by varying the parameter displayed on the bottom line over its range. The highlight must be on the value of the parameter to be scanned.
[K]	Keep the displayed simulation spectrum by adding it to the LIST.
[C]	Clear the simulation spectra list in lower right corner

- [P]            Print current parameter set to port or file specified by the TEXT keyword in the wmosc.cfg configuration file (see Section 1.6).
- [O]            Access the Options box (see Section 2.5).
- [ESC]          Return to Analysis submenu with current parameter set as displayed.
- [CTRL+P]      Send image of current plot to graphics hardcopy device.

Now adjust the parameters to fit the data. We can see that the experimental quadrupole splitting is approximately 0.5 mm/s. Set dEq to 0.5 mm/s and recalculate spectrum.

*[DOWN] [DOWN]  
0.5 [ENTER]  
[SPACE]*

Now, while shift (IS) parameter box is selected let's scan the defined range by pressing [S] (will compute 11 spectra). Scroll the results using [CTRL+Down/Up Arrows].

*[UP]  
[RIGHT]  
0.1 [RIGHT]  
0.5 [ENTER]  
S  
[CTRL+Down Arrows] ...*

Stop on the best value. Pressing [Up/Down Arrow] to move to a new parameter will preserve it. Now fine tune by scanning with [S] the splitting, dEq.

*[DOWN]  
0.6 [LEFT]  
0.4 [ENTER]  
S  
[CTRL+Down Arrows] ...*

If you want to store a simulated spectrum in the RAM spectra List, press [K] :

*K*

If a file with the current 3 spectra (data, theory and difference) is wished, dump the screen to the *psplot.ps* file, which is saved on the last directory set by Change Dir:

*[CTRL+P]*

If you wish, copy the parameter set to the text file *parout.txt* (specified by TEXT keyword in the wmosc.cfg file). The file will be located in the current directory.

*P*

Via the Options Box, turn off the plotting of the difference spectrum.

*O*  
[ENTER]  
[ESC]

If wished, clear the simulation spectrum list with [C].  
To exit the Flash procedure:

[ESC]  
Y

**Note:** Remember, there is only one set of parameters in RAM. Any changes made in the parameter values while in the Flash procedure are still effective upon exit from Flash. Exiting Flash also resets the Global Areas to 1.0 and their constraint codes to 0. The Baseline are set to 0 and allowed to float. The values of the relative areas are not altered.

To save the simulated spectrum created previously in Flash to the disk, scroll the List to it. This action will make it the active spectrum.

[CTRL+ArrowDown]... or [PgDn]

Then go to Files submenu and choose Data Save.

[LEFT]  
T

Select the WEB Binary format.

[ENTER]

Type a filename (or accept the default name).

*thryfd18.b* [ENTER]

File THRYFD18.B will be created in the current directory in the default binary format. Note that the name of the spectrum on the LIST has been updated.

## 2.2.4 Pick Data -- Select the spectra for Do Fit

The least squares fit procedure in WMOSS can fit up to 6 spectra simultaneously. The Pick Data procedure is used to select the spectra which will be fitted. Pick the spectrum FD18.B by choosing Pick Data on the Analysis submenu and highlighting FD18.B. Then [ENTER] and [ESC].

[ESC]

A

P

Scroll to make FD18.B the active spectrum.

[CTRL+Up/Down Arrows] ...

Pick FD18.B to be fitted.

[ENTER]

[ESC]

The spectrum or spectra picked for a fit will be underlined on the LIST. If you pick the wrong spectrum while in the Pick Data procedure, simply [ENTER] again, while that spectrum is highlighted, and it will be "unpicked". The number of picked spectra defines the number of baselines and global areas that appear in the parameter set (see Edit Parm below).

Choosing Pick Data always resets the entire LIST to unpicked.

Choosing Flash will reset the current Pick list and define the active spectrum as the only picked spectrum.

## 2.2.5 Edit Parm

We must define a few terms to make clear the following discussion of the parameter file. A calculated spectrum will normally depend upon both integer and continuously variable parameters. With the integer parameters fixed, our minimization routines seek best values for the continuous ones. A specimen with several inequivalent iron sites will require local parameters for each site and also global parameters, which affect the entire spectrum. For given integer parameters, the calculated spectrum,  $f(p_1, p_2, \dots, v)$ , will be a function of continuous parameters and source velocity. If the derivative of  $f$  with respect to  $p_k$  does not contain  $p_k$ , then the  $k^{\text{th}}$  parameter is said to be linear, and its optimization is easy to achieve. By contrast, a computationally expensive search of the value sets (or space) of the nonlinear parameters is required for their optimization.

The parameter file controls the way the program tries to fit the data. Prototype files, with extensions .SPI, corresponding to the various theoretical models are provided. Creation of a new parameter file is normally done with Edit Parm, starting with a prototype of the same kind (e.g. the same Theoretical Model Number) or other similar file which you already have on disk. Constructing a parameter file from scratch or using a word processor to modify one is not recommended.



To examine and/or change parameter values choose Edit Parm.

[E]

The parameters are grouped in Pages. They may be edited by using [ARROWS] to highlight the value to be changed and then typing the new value.

[ESC] key will exit this procedure and save the new parameter set in RAM.

To select different Parameter Page press [PgUp] or [PgDn]. These pages are:

**Page 1.** Fit Control parameters

These parameters are numbered 1 to 10 and are integer valued. They control various aspects of the fitting procedure. The fitting parameters are described in Table 1 below.

Table 1 : Fit Control Parameters

#	Name	Allowed Values	Function
1	Report>Prn	1 0	Send report of fit to text printer Do not print report.
2	Maxit Global	0 to 99999	Maximum number of iterations for optimization algorithm at the global level. 999 is a good start value.
3	Maxit Local	0 to 99999	Maximum number of iterations for optimization algorithm at the local level. 999 is default value. Increase it as necessary for more free parameters and Nsites. General thumb rule: Maxit Local = ca.3x the average maximum value “Local Iteration of “ (observed during Fit)
4	Maxit Area	0 to 99999	Maximum number of iterations for optimization of the total areas of the picked spectra. 99 is a good start value.
5	Report Global	0 to 99999	Number of iterations between plotting of current best fit at global level (0=off)
6	Report Local	0 to 99999	Number of iterations between plotting of current best fit at nuclear level (0=off)
7	N Anneal	0 to 99999	Number of times to restart fit at <b>random</b> point in parameter space defined by bounds. N Anneal = 0 for a single fit to the original data.
8	Perturb	0 1	Fit to original data. If N Anneal > 0, then after fit to original data and at beginning of each annealing loop add artificial noise to original fit to create a synthetic data set. <b>Activates Monte Carlo</b> . See Appendix B.

9	Theoretical Model (DO NOT CHANGE!)	1 and 11 2 3 4 and 41  5 and 51 6 7	Spin Hamiltonian with single electronic spin and 1 to 14 Fe sites. 1 to 14 Lorentzian or Voigt lines 1 to 14 Quadrupole pairs Spin Hamiltonian with two coupled electronic spins and 1 to 14 iron sites. Each site can be coupled via the magnetic hyperfine interaction to either electronic spin 1 or 2. See file \web\mos\2spin.txt. 1 to 14 $^{57}\text{Fe}$ sites with effective field, plus EFG (51 has $D_{\text{eff}}$ too) . Quadrupole Splitting Distribution / Voigt Based Fitting Hyperfine Field Distribution / Voigt Based Fitting
10	Fit Method	1  -2  2  3  4  5	Nonlinear simplex method of Nelder and Mead (no explicit calculation of gradient) Refs.: Nelder and Mead(1965) and Press(1986). (Press's subroutine AMOEBA is nearly identical.)  Levenberg-Marquardt gradient method. Bounds are ignored. LMDIF routine from netlib/MINPACK (internet ftp.netlib.org)  Same as -2 but with bounds enforced.  netlib/PORT routine MNFB: Modified Davidson's Minimization Method. Bounds enforced. Ref.: Stewart(1967).  Not Available.  netlib/PORT routine N2FB: Adaptive Least Squares, bounds enforced. Ref.: Dennis(1981)

When both Report Global and Report Local are zero there will be no intermediate screen output during the fit. This includes the count of the Monte Carlo and Annealing loops.

The remaining items on parameter page 1 are:

**Parameter file names**

-- input file name as read from input file.

-- output parameter file name. This is the file where final results of fit will be saved to disk automatically, in the directory last set by Change Dir.

**Spectra name** (as displayed in List)

**Comment lines**

-- two lines for user comments. These will be stored with parameter file.

Reduced  $\chi^2$

- weighted sum of squares of residuals divided by number of data points less number of free parameters for the last fit (see Section 2.2.6)

Fitted Data

- names of spectra associated with the  $\chi^2$  given just above.

**Page 2** is displayed by pressing again [PgDown]: Global Areas and Baselines

*[Pg Down]*

1) Global areas

The global areas are the areas of the picked spectra. The default values are 1.0 .

2) Baselines for picked spectra.

The Baseline parameters displayed have default values of zero. Baselines are linear parameters.

3) Spectra to be fitted

These are the data that were chosen via the Pick procedure and are the data that will be fitted when Do Fit is executed.

Spectra loaded from disk have had estimated baselines removed and their areas normalized to unity during the Data Load procedure. The estimated baseline is the average of the first and last ten channels and is named BL20. BL20 and the raw absorption area (counts\*channels) are displayed on the bottom line of the main screen.

The number of baselines and global areas depends on the number of spectra picked for the fit. Hence, these parameters are defined at run-time and are not stored as part of a parameter file. When you load a parameter file, load some spectra, pick some spectra and then edit the parameters, the baselines and global areas will be set to their default values.

**Page 3** is displayed by pressing again [PgDown]: Global Parameters of Theoretical Model

*[Pg Down]*

These parameters affect the total spectrum in contrast to "local" parameters which affect only the subspectrum associated with a particular iron site. The Global Parameter page has two types of parameters:

### 1) Continuously variable, non-linear Global parameters

These could be optimized by the procedure **Do Fit**.

For models 1, 1-1 and 4, 4-1 they are the g-values, zero-field splittings and spin coupling parameters (models 4 and 4-1) of the electronic system.

For models 2, 3, 6 and 7, there are no global non-linear parameters.

For models 5 and 5-1, there is only one global parameter: SigThe defines the shape of the distribution of weights for the angular grid points.

### 2) Global Integer Parameters

These are set by the user and remain fixed during a **Do Fit** procedure.

For Models 2, 3, 6 and 7 the only global integer parameter is:

- a) Nsites -- the number of local sites, i.e. lines or quadrupole pairs. See below.

For Models 1, 1-1, 4 and 4-1, the spin Hamiltonian models of a paramagnetic site, the global integer parameters are:

- a) Nsites -- the number of local sites, i.e.  $\text{Fe}^{57}$  environments. See below.
- b) Symmetry parameter (See file grid.txt) --
  - 0 = isotropic,  $O_h$  (calculation grid spans 1 point)
  - 1 = axial,  $D_{4h}$  (calculation grid spans  $\pi/2$  arc)
  - 2 = rhombic,  $D_{2h}$  (calculation grid spans octant)
  - 3 = Euler angle beta not equal zero,  $D_2$  (calculation grid spans quadrant)
  - 4 = no symmetry,  $C_1$  (calculation grid spans hemisphere)
- c) Ntheta -- the number of grid points in the theta direction over an octant of the unit sphere.
- d) N States -- the number of electronic states,  $2S+1$ . Valid entries are integers from 1 to 9.

For Models 5 and 5-1, the effective field plus EFG model of a ferromagnetic site, the global integer parameters are:

- a) Nsites -- the number of local sites, i.e.  $\text{Fe}^{57}$  environments. See below.
- b) Symmetry parameter-- as defined above.

- c) Ntheta -- as defined above.
- d) Distribu -- Specifies the weight distribution of grid points used to average over molecular orientations relative to the gamma beam.
- e) NELStates -- in Model 51 only, it specifies the number of electronic states,  $N=2S+1$ , for the effective uniaxial electronic problem. Valid entries are 2, 4 or 6.

Note: Adjusting the number of local sites Nsites controls the number of local sites in the current model. Valid values are 1 to 14. Local sites may be added by simply increasing Nsites. For example, increasing Nsites from 1 to 3 would add two sites to the original one. The parameter values for sites 2 and 3 would be copied from site 1. To truncate local sites simply set Nsites to a lower value.

**Page 4** and higher are the Local Parameters windows. These are displayed by pressing [PgDown/PgUp] as needed.

*[Pg Down] / [Pg Up]...*

The remaining pages contain the continuously variable parameters of the site subspectra; there is one page for each iron site. On each page there are two types of parameters:

- 1) Non-linear parameters of the local site model.
- 2) Relative areas, i.e., fraction of global areas associated with the particular sites or subspectra. These are linear parameters.

## How the constraint codes control the fit

Now that we have seen the structure of the parameters, we can turn our attention to controlling the fit via the constraint codes. Any displayed value may be changed by highlighting it and then typing in a new value. Each continuously variable parameter has a parameter number and a Constraint Code. The Constraint Codes control which parameters are floating and which are fixed during the fit.

Constraint Code = 0 means parameter is fixed.

Constraint Code = parameter number (shown at left edge of line) means parameter is floating (or free, or fittable).

Constraint Code = number other than parameter number at left edge of line means this parameter is forced to be equal to the parameter indicated by the Constraint Code. Note that global and local parameters have separate numbering systems, as do linear and non-linear. So it is allowed to input the constraint 101 for the 102 Local

parameter (of the site #2) without worry that the same 101 index or constraint have been used in Areas or Global pages.

Constraint Code = MINUS (-) the number of other than parameter number at left edge of line means this parameter is forced to be equal to the parameter indicated by the Constraint Code, but with reversed sign. Note that global and local parameters have separate numbering systems, as do linear and non-linear.

**CAUTION: BE CAREFUL WHEN CHANGING CONSTRAINT CODE VALUES. YOU CAN DO SOME STRANGE THINGS SUCH AS FORCE THE LINEWIDTH TO BE EQUAL TO THE QUADRUPOLE SPLITTING. WMOSS PROVIDES NO INTERNAL CHECKS SINCE PROPER CONSTRAINTS ARE MODEL DEPENDENT.**

The method used for optimizing the non-linear parameter is controlled by **Fit Method**. Methods 1, 2, 3 and ☐ require the definition of upper and lower bounds for each floating parameter. These bounds are displayed and may be edited. Method -2 ignores these bounds. Of Methods 1 and 2, Method 1 is the better at avoiding being trapped in a local minimum that is not the best solution. However Method 2 converges much faster within a given local minimum.

You can exit the Parm Edit procedure by pressing [ESC].

[ESC]

## 2.2.6 Do Fit -- Least Squares Fitting

A least squares fit is executed by choosing Do Fit from the Analysis submenu. If no spectrum has been picked to fit, the user is prompted to pick from the LIST. If the picked spectrum or spectra are defined then the fit commences. One data spectrum and its current best fit will be displayed along with the values of the reduced Chi-square. The reduced  $\chi^2$  is calculated as

$$\chi^2_R = (N_{\text{data}} - N_{\text{var}})^{-1} \sum_{i=1, N_{\text{data}}} (D_i - T_i)^2 / \sigma_i^2$$

where the sum is over all the points of the picked spectra,  $D_i$  is the  $i^{\text{th}}$  datum,  $T_i$  the  $i^{\text{th}}$  theoretical point,  $\sigma_i$  the estimate of the noise in  $D_i$ ,  $N_{\text{data}}$  the total number of data points and  $N_{\text{var}}$  is the number of free variables. The fit may be suspended at any time by striking a key, e.g. [SPACE]. When the current iteration is finished the procedure will pause and prompt the user with several options. When the fit is completed the parameters will be saved to the parameter output disk file and the simulation will be added to the LIST. The display and storing (in RAM/List) of the subspectra associated with each iron site are controlled via Options.

Do Fit – example:

In this section a simple fit is described that illustrates the basic fit procedure. Examples of more complicated fits are presented in Chapter 3.

Close the previous session of WMOSS4 and launch WMOSS4 again. Use first Change Dir to reference C:\WEB\MOS\EXAMPLES as the current directory and then load the files FD18.B (spectra) and FD18GA.PI (parameters).

```

F
C
c:\web\mos\examples [ENTER]
D [ENTER]
fd18.b [ENTER]
P
fd18ga.pi [ENTER]

```

You should see the FD18 spectrum on the screen and the parameter file name should be in the upper right corner. Access the Analysis submenu and Edit the parameters. You do not have to pick data since only one data set is in the LIST.

Edit the parameters.

```

[Right Arrow]
E

```

Float the baseline.

```

[Page Down]
[Down Arrow]
[Right Arrow]
101

```

Float the relative area.

```

[Page Down] [Page Down]
[Down Arrow][Down Arrow][Down Arrow][Down Arrow]
[Right Arrow]
101
[ESC]

```

Now start the fit.

```

D

```

When the fit procedure has stopped, the final simulation is plotted over the data and the user is presented with a post-fit menu. Strike P to generate hard copy. Strike R to return to the analysis submenu.

## *R*

This first application of Do Fit should have given a reduced chi-square of 0.95. Notice the experimental spectrum is not symmetrical, perhaps because the widths of the two absorption lines are unequal. Enter Edit Parm and note that local nonlinear parameters 103 and 104 both had constraint code 103, and thus the linewidths were kept equal. Allow the program to vary them independently by setting the constraint code of parameter 104 to 104. You will find that Do Fit produces a smaller reduced chi-square, 0.73. Maybe further improvement is possible. The plotted difference spectrum seems to suggest that the lineshapes may be inappropriate. Use Edit Parm to change the initial values of both linewidths, parameters 103 and 104, to negative values, say -0.3, with lower limits -0.5 and upper limits 0. (Note "lower" means algebraically lower, etc.) The negative values instruct the program to produce a Voigt lineshape, a convolution of a 0.19 mm/s fwhm Lorentzian (the natural line width) with a Gaussian whose fwhm is the absolute value of the linewidth parameter. Now Escape and give the Do Fit command. You will notice that the minimization is slower, since many numerical integrations are required for the Voigt. The chi-square is not in fact improved this time; the Lorentzian was better. The three theoretical spectra are now in the list. Compare the second and third (using the grey + and -) and notice the Voigt (third theoretical spectrum) has weaker absorption in the wings of the lines.

At this point we discuss very briefly the significance of reduced chi squared. For a detailed discussion the reader is referred Press, et al (1986). The reduced chi squared as defined in this section is an indication of how much the observed data deviate from those predicted by the theory. For a given theoretical model, the parameter values which minimize the reduced chi squared are those for which the probability of observing the actually observed data set is maximum. What is a "good" reduced chi squared? Small ones are certainly better than large ones, and the estimation of goodness involves a consideration of both the reduced chi squared and  $\nu = (N_{\text{data}} - N_{\text{var}})$ , the number of degrees of freedom. For Mossbauer spectra the number of degrees of freedom,  $\nu$ , is normally about 250 or larger. For such high  $\nu$  values, the goodness vs. reduced chi squared relationship is rather insensitive to  $\nu$ , and we can make some useful rough statements. A reduced chi squared of 1.0 is commonly considered good. With a perfect model and perfect parameter values, we might expect a reduced chi squared this big or larger 50 percent of the time. We might expect a reduced chi squared of 1.1 or more 5 percent of the time, and a reduced chi squared of 1.2 or more about 0.5 percent of the time. Even quite low percentages can correspond to significant fits; a completely irrelevant model might correspond to  $10^{-16}$  percent. There are difficult problems concerning goodness of fit. We do not attempt to resolve these, but offer the following example. Suppose we have a sample with a 1% impurity content, and have a theoretical model which is a very good representation of the 99% majority component. If we take a certain amount of data we might reasonably expect to find parameter values which would give a minimum reduced chi squared of about 1.0. This would be the case where the



contribution of the impurity was smaller than the uncertainty associated with counting statistics. We would judge the fit as good. If we now let the spectrometer run 100 times as long, the statistical spread, in units of BL20, decreases by a factor 10 while the error caused by the impurity, expressed the same way, is unchanged. The optimized chi squared will clearly become larger and the fit may go from good to not-so-good by virtue of our obtaining better data. Obviously the value of reduced chi squared alone does not convey a satisfactory picture of the match between the data and the theory.

### 2.2.7 MC Plot -- Error Analysis

The discussion of the Monte Carlo analysis procedure is not appropriate for this tutorial and is found in Appendix B.

### 2.2.8 QSD Plot -- Plot Quadrupole Distributions

Plots the Quadrupole Splitting Distribution for Model 6. See Section 3.6

### 2.2.9 HFD Plot -- Plot Hyperfine Distributions

Plots the Hyperfine Field Distribution for Model 7. See Section 3.7

## 2.3 Utilities Submenu

### 2.3.1 Add Mask

The Add Mask procedure allows the user to define portions of the active spectrum that should be ignored during a fit. This feature can be very useful if signals due to impurities are present in a well defined region of the spectrum. Another appropriate situation is fitting the well resolved features of a spectral subcomponent, e.g. the subspectrum of a single iron site in a multi-iron cluster.

The Add Mask procedure is accepting mouse inputs as well as keyboard inputs. We suggest using always the mouse within this procedure, but for consistency of this tutorial we will exemplify using keyboard strokes.

As an example, fits to spectrum FD20.B are presented. Go to the examples sub-directory, execute WMOSS, load FD20.B, and fit it with a single quadrupole pair.

```
cd c:\web\mos\examples
WMOSS [ENTER]
[ENTER]
F
D [ENTER]
fd20.b [ENTER]
```

You should see a spectrum with two quadrupole pairs. Let's pretend that the inner pair is an impurity signal. Load the parameter file MODEL3.SPI,

```
P [ENTER]
[DOWN ARROW] (to highlight MODEL3.SPI)
[ENTER]
```

Go to the Analysis sub-menu and execute the fit without changing any parameter values.

```
[RIGHT ARROW]
D
```

The theory will converge to a broad quadrupole pair and yield a reduced  $\chi^2 = 30$ . See Figure 2A This poor quality fit results from the presence of the second quadrupole pair that is not accounted for in our model. (Of course we could expand our model to two quadrupole pairs but that is not the point here.) Mask out the "impurity signal" and redo the fit.

*R*

Highlight FD20.B on the LIST and then execute the List/Add Mask procedure.

*[DOWN ARROW]*  
*[ENTER]*

You should now be in the Add Mask procedure. You may mask any number of regions of the spectrum. Prompts are displayed on the top line. The cursor position is controlled by the [HORIZONTAL ARROWS] keys. Pressing [RIGHT ARROW] one time moves the cursor one channel to the right. Pressing [Ctrl]+[RIGHT ARROW] moves the cursor ten channels to the right. The current x,y coordinates of the cursor are displayed on the top line. Note that the x coordinate is given in mm/s. For this exercise it is convenient to work in channels. Go to the options box and toggle the calibrated velocity scale off.

*[ESC] [ESC] O*  
*[DOWN ARROW] (3 times)*  
*[ENTER]*  
*[ESC]*  
*U A*

You should now be back in the Add Mask procedure and the X coordinate of the cursor should be displayed as 1. Mask the region from channel 121 to channel 151.

*[Ctrl]+[RIGHT ARROW] (12 times)*  
*[ENTER]*

That defined the first end point of the region. Now define the second.

*[Ctrl]+[RIGHT ARROW] (3 times)*  
*[ENTER]*

The masked region is now plotted at low intensity. Exit the Add mask procedure, return to the Analysis submenu and redo the fit.

*[ESC] [ESC] A D*

The fit will now converge to the outer features of the larger quadrupole pair and yield a reduced  $\chi^2 = 0.72$ . See Figure 2B. This example demonstrates how to use the mask but is certainly not the best way to determine the area fractions of the two spectral components. That could be done manually using the LSUB procedure or via Do Fit using two quadrupole pairs.

Return to the main menu.

*R*  
*[ESC]*

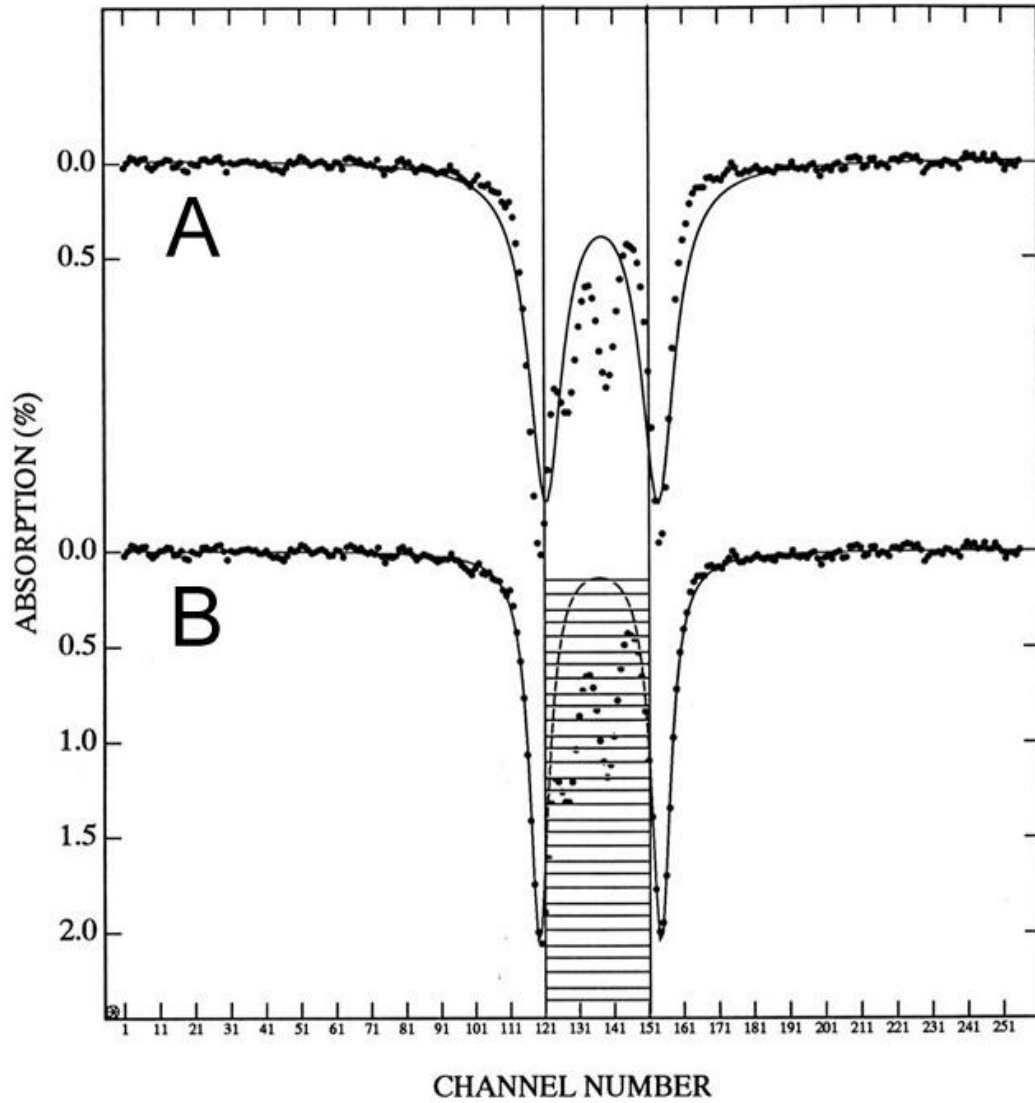


Figure 2. Illustration of effect of mask. A) Fit (line) of single symmetric quadrupole pair to data (closed circles) with no mask. B) Same fit but with data in region from channel 121 to channel 151 ignored in calculation of  $\chi^2$ .

### 2.3.2 Clear Mask

The Clear Mask procedure simply removes the mask from the active spectrum. Go to the Utilities submenu to clear the mask from FD20.B. The active spectrum is the spectrum plotted on the screen and whose name is red in color on the LIST. Make sure the FD20.B is the active spectrum. Now clear the mask.

*L C*

You should now be in the Utilities submenu.

### 2.3.3 Delete

The Delete procedure allows the LIST to be purged of unwanted data. Delete may be executed via the List submenu or via the [Delete] hot key. Let's remove the two theoretical spectra generated by the fits of the example of Section 2.3.2.

*[Delete]*

A prompt will appear on the top line.

*[CTRL+Up/Down Arrow] [ENTER]  
[CTRL+Up/Down Arrow] [ENTER]*

The spectra to be removed from RAM are indicated by a angle bracket, >. The marked spectra are not removed from RAM until [ESC] is pressed. You can toggle the > by pressing again [ENTER]

*[ENTER] [ENTER]*

Now remove the two spectra from RAM.

*[ESC]*

Remember, the Delete procedure removes spectra from the List which is a stack in RAM. This procedure does not alter disk files. You should now be in the Utilities submenu.

### 2.3.4 Zoom

The Zoom procedure will expand a user defined rectangle within the current screen plot. The rectangle is defined via the [ARROW] keys or the mouse. Zoom can be

executed via the Utilities submenu or via the hotkey [F8]. Use Zoom to expand a region of the spectrum FD20.B.

[F8]

A cursor will appear at channel one of the spectrum. Move the cursor with the mouse or with the [VERTICAL ARROWS] and the [HORIZONTAL ARROWS]. To Anchor the first corner of the rectangle, click and release the left mouse button or press [ENTER]. Now the cursor will disappear and the rectangle will expand as you move the mouse or press the [ARROWS]. When you have positioned the second corner of the rectangle where you want it, click the left mouse button or press [ENTER]. The area within the rectangle will be expanded to full size. To return to the normal plot, execute Zoom again.

[F8]

### 2.3.5 Condense by 2

This procedure replaces the active spectrum with a spectrum with half as many channels as the original spectrum. Each point is the sum of the raw counts (not normalized) in a pair of adjacent channels in the original spectrum. After the pairwise sum is calculated, the new spectrum is normalized. This procedure is sometimes useful for visualizing signals in noisy data.

### 2.3.6 Stretch

The Stretch procedure is used to transform the active spectrum to a new velocity scale. The user is prompted to type in the old and new calibration constants. The new signal at the new channel positions is calculated via interpolation between the nearest old channels. This interpolation does not distort the signal significantly if the change in calibration is not too large. However, the interpolation procedure does average the noise and may cause the new spectrum to appear to have an improved signal-to-noise ratio. Since the WMOSS procedure SSUB allows spectra with different calibration to be compared directly (SSUB interpolates the second spectrum onto the channels of the first.) the Stretch procedure is seldom required.

### 2.3.7 Exp. Add

Exp. Add allows the proper summation of two spectra recorded from the same sample under the identical conditions. The user is prompted to choose two spectra from

the List. Then the raw counts in the corresponding channels are summed. The new spectrum is normalized and appended to the List.

[ESC]

## 2.4 Plot2File Submenu

The choices in this submenu will save a file to the disk, in the current active directory. Viewing, printing, translation to other formats etc. is assumed to be realized by users in a separate step using any appropriate applications at their convenience (for example GhostScript for \*.ps files, respectively Notepad for \*.txt files)

### 2.4.1 Spectra B/W [CTRL+P] (psplot.ps)

As its name tells, it saves a B/W copy of spectra (graphics only, no parameters attached) in PostScrip format. The filename is by default psplot.ps, although this can be changed by editing wmooss.cfg. If this file already exists in the current directory, it will overwrite it.

If [CTRL+P] is executed while in Main menu, the graphics consists of only the active spectrum.

If [CTRL+P] is executed while in Flash, the graphics consists of 3 spectra: the active spectrum, the theoretical spectrum and their difference.

If [CTRL+P] is executed while in Do FIT, the graphics consists of the above 3 spectra (the active spectrum, the theoretical spectrum and their difference) plus any additional subspectra if Plot Subs is ON (see Options below). If Do FIT is performing a simultaneous analysis on several spectra, pressing "Next Spec" cycles through them and [CTRL+P] will print the currently displayed spectra graphics.

Note: Because during Do FIT procedure the program will work in the same active directory this means that the new psplot.ps file will overwrite the old one. So, if the current psplot.ps file is relevant, be careful to rename it (still using \*.ps file extension) before going to NextSpec and executing the next [CTRL+P] command.

### 2.4.2 Parms [P] (parout.txt)

The Print parameter procedure will save an ASCII file in the current directory with the current parameter values. The name of the file is defined by the "text" keyword

in the WMOSS.CFG file. Default filename is parout.txt. The location of the file will be in current active directory (defined by the last executed Change Dir procedure).

### 2.4.3 Custom PS Plot (color)

The Custom PS Plot procedure can be used to make publishable quality plots. The Custom Plot procedure will open a new window and then issue a series of prompts to guide the user in laying out a figure. Landscape or portrait mode plots may be generated. Any number of spectra may be stacked or overlaid. Only in this procedure the graphics output filename can be specified by user (the first step of the procedure), or is left to be the default filename (e.g. the "psout.ps" variable in WMOSS.CFG). This means that the risk of overwriting Custom PS Plot files is avoided.

While on this procedure, after each addition of spectra a temporary file is written. This temporary file allows, as a new feature in WMOSS4 ver.F, to delete the last added spectrum and to re-add it using perhaps different settings without being necessary to resume the entire Custom PS Plot procedure from scratch.

The following is not mandatory for the Custom PS Plot procedure to work, however it improves dramatically its practicability: if the directory that contains the Ghostview32.exe application have been referenced in system PATH system variable (see. WMOSS4 Installation) then after each addition of spectra to the plot a temporary layout is sent automatically to Ghost Script viewer. This enables an iterative visual check if all settings of the last addition step conform to your wishes. After the visual inspection of the layout you must close the Ghost Script viewer; the Custom PS Plot procedure resumes and will ask if the last added spectrum should be deleted (Y/N). If Yes is chosen then the temporary layout will revert to the state prior to the last spectrum added; Ghost Script viewer is then automatically launched again to visually check the current temporary plot layout. Close the Ghostviewer again and the Custom Ps Plot procedure is resumed. Once you choose to Not delete the last spectrum added, then the program prompts you to add new spectra in the layout. If you skip it with No then a final plot file is generated and Ghost Script viewer is launched for the last time with the final version of your plot file. You can Print it using the Print manager from Ghost Script viewer, or convert it to BMP file, then TIFF (in this form you can add it to MS Word documents), edit it from within a graphics editor application, etc.

Close the Ghost Script viewer for the last time and the WMOSS4 program will resume in Main Menu.

Note: a user familiar with POSTSCRIPT language can alter the \*.ps files to meet more specific needs.



## 2.5 Options Box

The Options Box presents several software switches that can be set according to the user's needs. Note an option box, unlike a menu, responds only to [VERTICAL ARROWS] and [ENTER]. These switches control the format of the screen plots:

Diff Spec	ON/OFF	Displays the difference spectrum in the procedures Flash, LSub, SSub and Do Fit.
Plot Subs	ON/OFF	Displays the sub-spectra in the procedure Do Fit.
Subs List	ON/OFF	Store the sub-spectra on the LIST after DO FIT.
Vel. Scale Cal.	ON/OFF	Use Channels(off) or mm/s(on) units for X-scale.
X Autoscale	ON/OFF	Automatically scale the X axis to include all data.
Y Autoscale	ON/OFF	Automatically scale the Y axis to include all data.

The default values of the first four switches are defined in the WMOSS.CFG file by the variables "diffspec", "plotsubs", "keepsups" and "plotype". X Autoscale and Y Autoscale always default to ON.

## Chapter 3. MODELS OF SPECTRAL SIMULATIONS AND LEAST SQUARE FITS

In this chapter we present examples of fits to several different types of spectra. Note, the spectra presented here have already had the parabolic baseline removed either by folding or subtraction. The loading of unfolded spectra and spectra with parabolic baselines is discussed in Chapter 4

All the data and parameter files discussed here are in the C:\WEB\MOS\EXAMPLES directory of the computer with the WMOSS software. If you wish, load the appropriate files and work through the examples yourself.

Examples presented in Chapter 3:

Section	Theoretical Model	Examples
3.1	2. Single Lines	Fit to Iron metal spectrum and calibration of velocity scale.
3.2	3. Quadrupole Pairs	Fit to a spectrum with two quadrupole pairs
3.3	1. Spin Hamiltonian: single electronic spin	Two iron nuclei in two types of sites, all coupled to an electronic spin. Simultaneous fit to two spectra using a one-spin model.
3.4	4. Spin Hamiltonian: two electronic spins	Two iron nuclei in two types of sites, all coupled to an electronic spin. Simulation of spectrum using a two-spin model.
3.5	5. Fixed internal field plus EFG and applied field	a) Fit to spectrum with three magnetic hyperfine sextets. b) Spectral simulations for single crystal and partially aligned polycrystalline samples
3.6	6. Voigt Based Fitting with QSD	Fit using assuming a single species with a Quadrupole Splitting Distribution represented by several Gaussians.
3.7	7. Voigt Based Fitting with HFD	Fit to spectrum with three ferromagnetic species each represented with a Hyperfine Field Distribution consisting of a single Gaussian.
3.8	11. (Model 1 extended) 41. (Model 4 extended)	Theoretical Models 1-1 and 4-1: single or coupled electronic system with local Relax. parameter
3.9	51. (Model 5 extended)	Theoretical Model 5-1: uniaxial electronic system with local Relax. parameter

### 3.1 Theoretical Model 2 : 1 to 14 Lorentzian or Voigt lines

#### **Example : Fit to Iron metal spectrum and calibration of the velocity scale.**

Our first example is a fit to the spectrum of an iron metal foil at room temperature. This spectrum is the working standard used to calibrate the velocity scale; the energy (velocity) corresponding to each line is known. We wish to establish the connection between channel number and velocity, and so will want to know the channel location of each line. We will make use of this example to show how to use theoretical model 2 (1 to 8 Lorentzian or Voigt lines).

Figure 3.1 shows the room temperature spectrum of a 6 micron iron metal foil, plotted against channel number. Load data set FEMETAL.B to see this. The spectrum is not corrected for gamma detector background or source recoil-free fraction, so absorption intensities will be spectrometer-dependent. Note, using Edit Data Header, that in this example the choice of 0.0 for the V=0 Channel and 1.0 for the Step has given a plot against channel numbers in spite of the fact that the Vel Scale ON is indicated under Options.

Now we need a parameter file to control the fitting. Load FEMETL6.GAI and look at it with Edit Parm. The first page selects theoretical model 2, and fit method -2. On the second page the global area is fixed at 1; this is always done when only one spectrum is being fitted. Change the baseline constraint parameter to 101, if necessary, to let it float. This setting is always required, so always check it. Some operations will reset it to zero. The third page has N Sites set at 6 and assures that six pages, one for each site, will follow. [Note that you could have started with any model 2 parameter file as a template, put the 6 in at this point, and obtained the required pages.] On each subsite page the line position is allowed to vary independently by setting the constraint code to the parameter number. The line position values 45, 80, 110, 140, 170, 210 are estimates read off the plot. Each width has been guessed at 5.0. The initial values of the floating relative areas have no effect on the subsequent fit since the final values of linear parameters are determined by a non-iterative procedure. Notice the constraints have been arranged to force the members of the outer pair, lines 1 and 6, to have the same FWHM and the same relative area. The intermediate and inner pairs have been treated similarly. Execute Do Fit and you should get a Reduced Chi Square of 5.3 and line positions 46.30, 80.10, 114.24, 139.37, 173.56, 207.49. We now consider the calibration problem.

As discussed by Preston, *et al.* (1962), there is no significant electric field gradient at the Fe nucleus in iron metal and the hyperfine splittings of the  $I = 1/2$  doublet and the  $I = 3/2$  quartet are simply proportional to the effective internal magnetic field  $H^{\text{int}}$ . They reported

$$H^{\text{int}}(T=293\text{K}) = 330 \text{ kG}$$

$$\Delta H^{\text{int}} / \Delta T \Big|_{T=293\text{K}} = -0.06 \text{ kG / K}$$

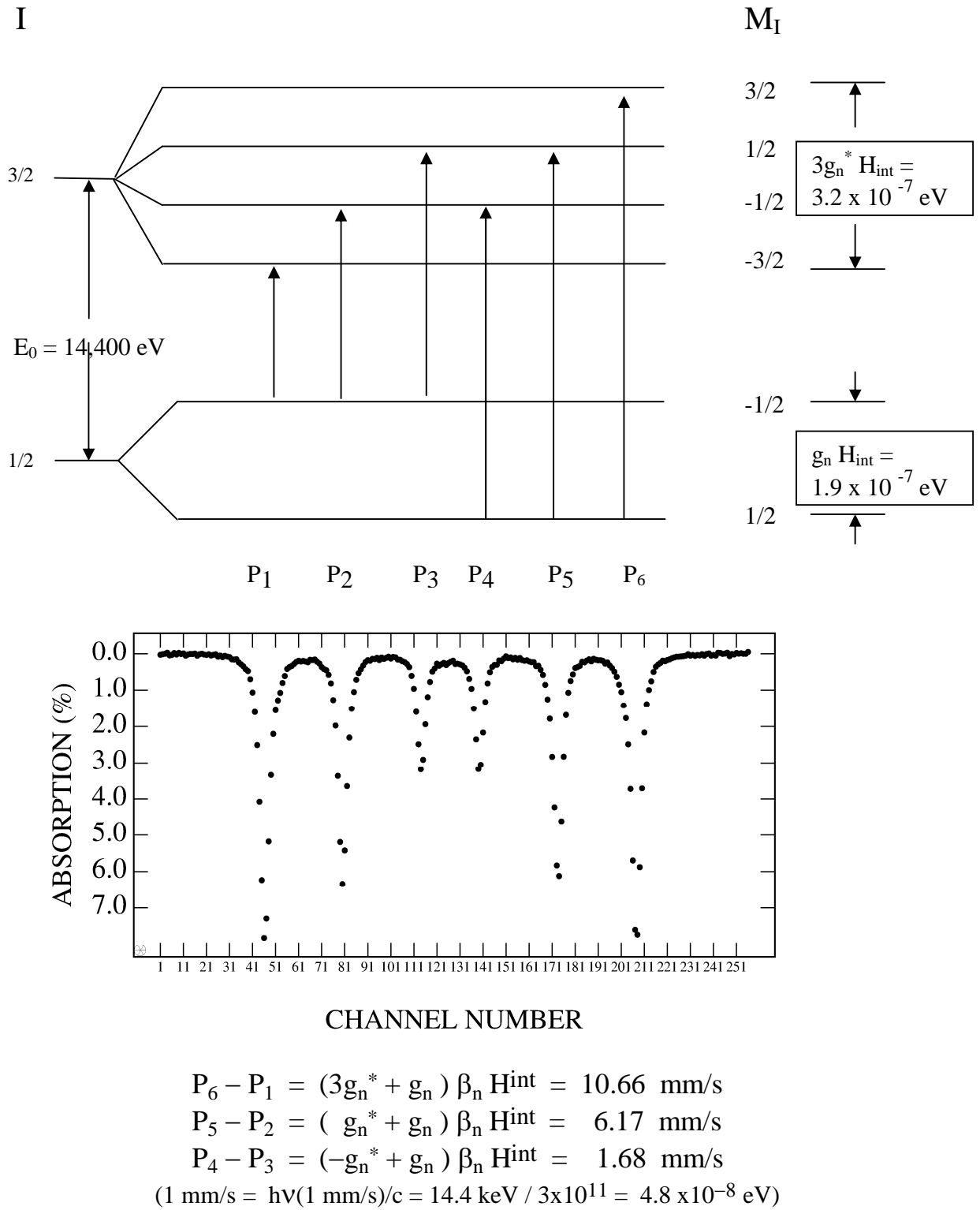


Figure 3.1 Iron Metal  $^{57}\text{Fe}$  hyperfine splitting and Mössbauer spectrum

Over a range of 5 K,  $H^{\text{int}}$  changes by 0.1 %, an insignificant amount for routine measurements. However, Preston, *et al.* also detected a 0.5% variation in  $H^{\text{int}}$  among different iron foils. Therefore, if iron metal and the value of  $H^{\text{int}}$  quoted above are used as the calibration standard, the experimental precision can be no better than 0.5% unless the foil was prepared in the manner given by Preston, *et al.*

We assume that the spectrometer is operated in the constant acceleration mode and that any non-linearities in the electromechanical velocity transducer response are small. The source velocity as a function of time is

$$V(t) = at + V_0$$

where  $a$  and  $V_0$  are constants. The source velocity at the midpoint of the dwell time for the  $i^{\text{th}}$  channel of the scan is then

$$V(i) = \Delta_V (i - C_0)$$

where

$i$  is the number of the active memory channel,

$V(i)$  is the source velocity at the midpoint of the dwell time for the  $i^{\text{th}}$  channel ,

$\Delta_V$  is the acceleration of the source given in mm/s/channel

$C_0$  is the channel number at which the velocity is defined to be zero.

Given the peak positions  $C_i$  from the fit and the published values of the  $P_i$ , we can calculate  $\Delta_V$  and  $C_0$ . By convention, the zero of the velocity scale is the centroid of the room temperature iron metal spectrum. This choice permits comparison of Mössbauer spectra without reference to the isomer shift of the source. The centroid of the spectrum is

$$C_0 = \sum_{i=1,6} a_i C_i / \sum_{i=1,6} a_i$$

where the  $a_i$  are the area fractions. The step,  $\Delta_V$ , is

$$\Delta_V = \sum_{i=1,3} \{ (a_i + a_{7-i}) (P_{7-i} - P_i) / (C_{7-i} - C_i) \} / \sum_{i=1,6} a_i$$

For spectrum FEMETAL6.B, the calibration constants are:

$$C_0 = 126.80$$

$$\Delta_V = 0.0662 \text{ mm/s/chan}$$

**According to Preston, *et al.*, the uncertainty in  $\Delta_V$  is 0.5%.**

Once  $\Delta_V$  and  $C_0$  are known for a particular velocity scan range setting on the spectrometer, they can be entered into the Data Header of spectra recorded on that scale. Many spectrometers suffer from long term (~months) drift. Therefore, an iron metal calibration spectrum should be recorded periodically.

Having calibrated the spectrometer we may, as an exercise, treat our spectrum as fresh data and check the line positions. Using Edit Data Header, insert 126.80 for the  $V=0$  Channel, and 0.0662 for Step. Be sure to edit the header of the data FEMETAL.B and not the header of the simulation added to the List by the DoFit procedure. Using Edit Param we can guess the line positions by looking at the spectrum (now plotted vs. velocity): -5.3, -3., -1., 1., 3., 5.3. Guess all the linewidths at about 0.3. Notice that you will have to modify the bounds in some cases to avoid contradiction. [The editor insists upon it in cases where the parameter is free.] Use file FEMETL6.GBI if you have trouble. Execute Do Fit, and find the same reduced chi squared as before. The line positions for a perfectly linear spectrometer would be -5.33, -3.085, -0.84, +0.84, +3.085, +5.33; this one isn't bad.

We might wonder what Voigt lineshapes would do to the fit. Try initial guesses at -0.3 for each linewidth, adjusting the bounds to avoid contradictions. Run Do Fit, and find that the reduced chi squared gets worse, showing that the line broadening mechanism is better represented by the Lorentzian profile. (Note that this exercise would not have made sense when we were using bogus calibration values in the data header, since Model 2 always uses a 0.19 mm/s FWHM Lorentzian component in the Voigt.) Our Voigt fit still gives essentially the same line positions, so the calibration is reasonably insensitive to line profile assumptions.

Chapter 4 contains a discussion of automated fits to unfolded iron spectra, logging of calibration information and corrections for non-linear velocity scales.

### 3.2 Theoretical Model 3: Quadrupole Pairs

#### **Example: a spectrum with two quadrupole pairs.**

Load data FD20.B and parameter set FD20.GLI. If you have other data in RAM, pick FD20.B. Use Edit Param and note that theoretical model 3 (quadrupole pairs) and fit method -2 are invoked. Make sure on page 2 that the baseline is floated (Constr.=101). On page 3 note that two sites, hence two quadrupole pairs are specified. The subsite #1 page has a rough guess for isomer shift (0.7), dEq (1.5), linewidth (0.3), and relative area (0.6). These are crude estimations from the plotted spectrum. All float, but both lines are constrained to the same width. The subsite #2 page is the same except for the parameter guesses: 0.5, 0.5, 0.3, and 0.3. Execute Do Fit and note that a reduced chi squared of 0.87 is obtained, with parameters in the above order of 0.46, 1.48, 0.28, and 0.70 for the first pair and 0.30, 0.47, 0.28, 0.35 for the second pair. These results have automatically been written to disk file FD20.GLO. You can use List Params under Hardcopy to send them to the printer or a disk file named in your \WEB\MOS\WMOSS.CFG file. In the latter format (chosen to save space) they look as shown below.

```
FD20.GLI                      (output to fd20.glo)
parameter file for a pair of quadrupole doublets
-----Comment Line 2-----
Reduced Chi squared = 0.871 for fit to data:
fd20.b
Printed at 14:04:33 on 09/23/93
```

#	name	value	constr	wght	lower B	Upper B	Version #	
101	Shift	0.457	101		-0.500	1.500	Report>PRN	-6
102	dEq	1.475	102		0.000	3.000	Maxit Glob	0
103	Gamma L	0.280	103		0.200	0.500	Maxit Locl	999
104	Gamma R	0.280	103		0.200	0.500	Maxit Area	0
101	Relarea 1	0.698	101	1.000			Report Glo	1
							Report Loc	1
201	Shift	0.304	201		-0.500	1.500	N Anneal	0
202	dEq	0.471	202		0.000	3.000	Perturb	0
203	Gamma L	0.280	203		0.200	0.500	Theor.Modl	3
204	Gamma R	0.280	203		0.200	0.500	Fit Method	-2
201	Relarea 2	0.350	201	1.000			N Sites	2

The relative areas are very close to being in the ratio 2:1, suggesting that there are two sites of the second kind for each site of the first kind in the molecule.

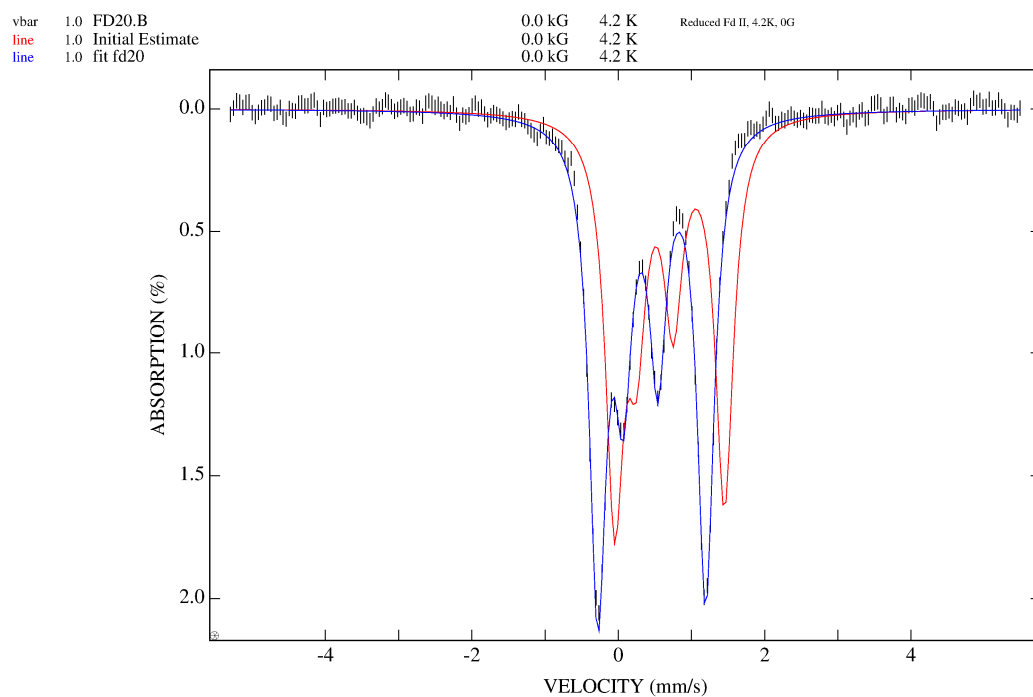


Figure 3.2: FD20 dataset (vbar), initial guess (line-red) and fit (line-blue).  
(Plot realized with Custom PS Plot procedure)



### 3.3 Theoretical Model 1: Spin Hamiltonian with single electronic spin.

#### **Example: Two iron nuclei in two types of sites, all coupled to one electronic spin and simultaneous fit to two spectra.**

Load parameter file 1STTRIE.PI and the data files TT20.B and TT23.B (Fee, *et al.* (1984)). Examine the data headers and note the spectra were observed with the sample at 4.2 K and in a 0.6 kG field. For TT20.B, the field was applied parallel to the gamma ray direction and for TT23.B, perpendicular. Relaxation of the electronic spin was assumed to be slow, implying that the net spectrum is a sum over spectra corresponding to individual electronic substates. (This kind of assumption may find its ultimate justification in a successful final fit to the data.)

Go to the Analysis sub menu and Pick both spectra. Then examine the parameters via Edit Param. Note theoretical model 1, several iron sites coupled to a common electronic spin, is invoked on page 1. (For a discussion of the spin Hamiltonian model see Huynh and Kent (1984) and refs. therein.) Make sure the baseline is allowed to float, page 2. Page 3 has information about the electronic spin. N States = 2 implies a spin 1/2 site, so zero-field splittings (first three parameters) are not relevant here. We may suppose the values of Nstates and the g components represent information from other sources. For example, EPR data show that the  $S=1/2$  g-tensor is 1.8, 1.9 and 2.02. The assumption of two types of sites is based on 195K data (TT22.B). Rhombic symmetry is a guess, or possibly a hope. (See Appendix C for the definitions of the SYMMETRY and NTHETA parameters.) The Ntheta value is reasonably small to save calculation time; it could be increased after some initial fitting provides an approximate solution. On the subsite pages dEq, shift, and linewidth are estimated from the high temperature spectrum. The area ratio shows up as weights 1.0 and 1.0. We have chosen to hold this ratio fixed based on the assumption that the sample contains iron only in the form of the 2Fe center. One of the dEq is taken as negative. This is allowed, since the high temperature spectrum does not provide the sign or the eta value. It could be the kind of educated guess which is possible after a few years experience with spectra of this type. The Eta are both allowed to float, in the absence of information about them. All Euler angles AL, BE, GA are fixed at zero in keeping with the assumption of rhombic symmetry. The magnetic hyperfine A tensors are started off as isotropic and positive since the 0.6 kG spectra are not sensitive to the sign of A. (Examination of data observed in various applied fields suggested that one should be positive, and the other negative.) The reader will observe that a lot of effort is required just to get reasonable starting values for a problem of this complication.

Execute Do Fit and find that a reduced chi squared of 1.1 is achieved, and the general features of the spectra are reproduced (see Figure 3.3). That of course does not mean that this model is a "true" representation of the physical reality. It may be that somewhere else in parameter space there is a better fit; possibly the assumption of rather high symmetry was not correct. Further checks and fits to spectra observed under other conditions are needed. The program can find optimum parameters, given good

instructions. It can even fit several spectra at once. But it cannot think, and the user's experience, intuition, and persistence are essential for reliable interpretation of data. At the end of the fitting process the file 1STTRIE.PO is written to disk. The Hardcopy/Print Parns procedure produces the following printout (or file):

1STTRIE.PI (output to 1sttrie.po)

Example 3: S=1/2 spin Hamiltonian for 2Fe center

Reduced Chi squared = 1.085 for fit to data:

TT20.B TT23.B

Printed at 16:46:42 on 09/27/93

#	name	value	constr	weight	lower b	upper b		
101	D	0.000	0		-3.000	-1.500	Version #	-6
102	E/D	0.000	0		0.000	0.330	Report>Prn	0
103	a2lamda	0.000	0		0.000	0.000	Maxit Glob	0
104	gx	1.800	0		2.000	2.400	Maxit Loc1999	
105	gy	1.900	0		2.000	2.400	Maxit Area	0
106	gz	2.020	0		2.000	2.400	Report Glo1	
							Report Loc	1
101	dEq	-3.000	0		-3.500	-2.900	N Anneal	0
102	Eta	-2.951	102		-10.000	10.000	Perturb	0
103	AL efg	0.000	0		0.000	180.000	Theor.Modl	1
104	BE efg	0.000	0		0.000	180.000	Fit Method-10	
105	GA efg	0.000	0		0.000	180.000		
106	Ax	74.569	106		0.000	400.000	N Sites	2
107	Ay	262.172	107		0.000	400.000	Symmetry	2
108	Az	105.177	108		0.000	400.000	Ntheta	6
109	AL A	0.000	0		0.000	180.000	N States	2
110	BE A	0.000	0		0.000	180.000		
111	GA A	0.000	0		0.000	180.000		
112	Shift	0.749	112		0.600	1.000		
113	Width(V<0)	0.300	0		0.250	0.400		
101	Rel Area	0.529	101	1.000				
201	dEq	0.600	0		0.500	0.700		
202	Eta	0.318	202		0.000	1.000		
203	AL efg	0.000	0		0.000	180.000		
204	BE efg	0.000	0		0.000	180.000		
205	GA efg	0.000	0		0.000	180.000		
206	Ax	368.580	206		00.000	00.000		
207	Ay	398.964	207		00.000	00.000		
208	Az	309.801	208		200.000	500.000		
209	AL A	0.000	0		0.000	180.000		
210	BE A	0.000	0		0.000	180.000		
211	GA A	0.000	0		0.000	180.000		
212	Shift	0.300	212		0.200	0.400		
213	Width(V<0)	0.300	0		0.250	0.400		
201	Rel. Area	0.529	101	1.000				

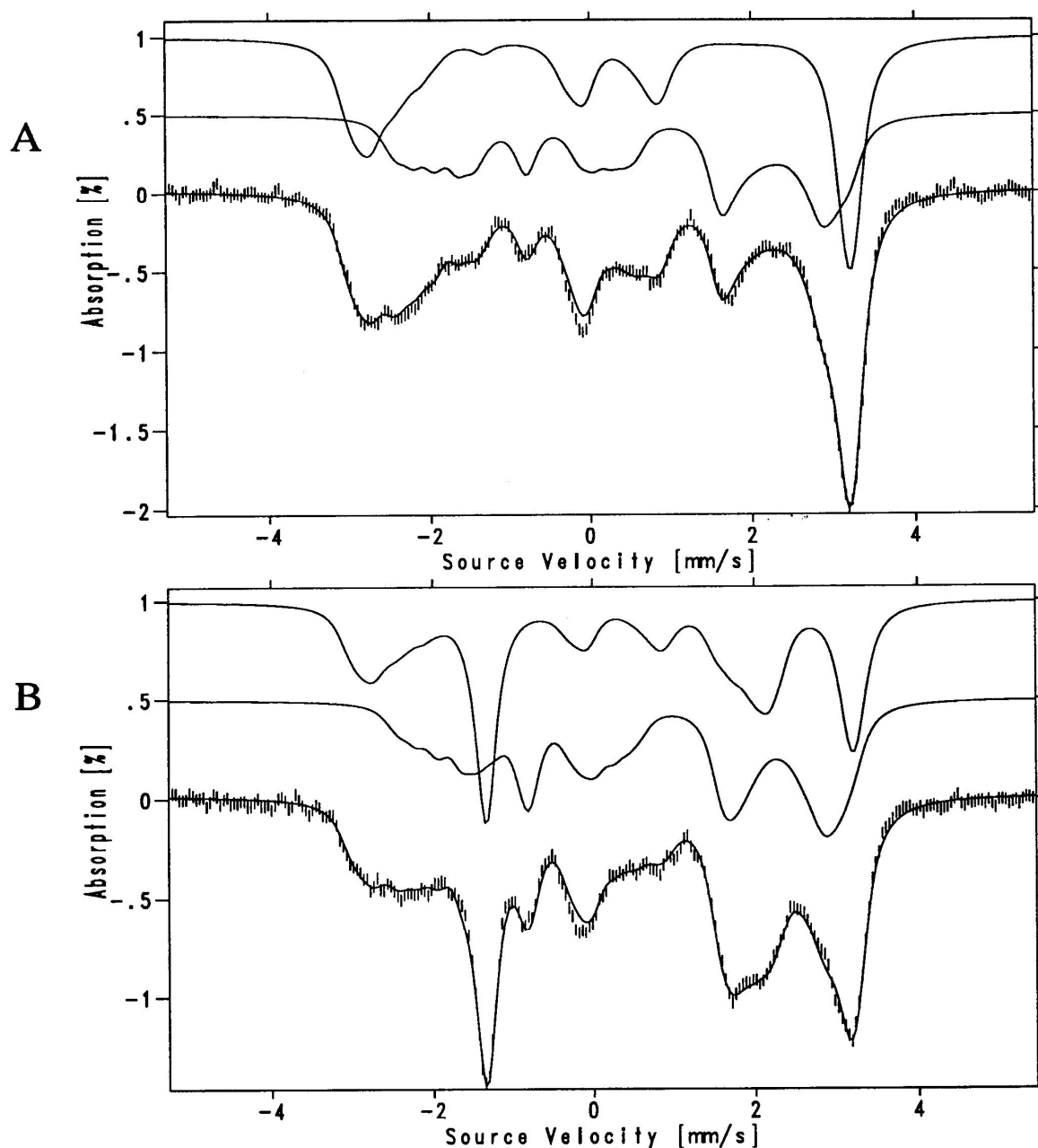


Figure 3.3: Results of Fit discussed in Example 3. Data (hatchmarks) were recorded at 4.2 K and with 600 Gauss field applied (A) parallel and (B) perpendicular to the gamma beam. The spectral components representing each iron are shown separately above the data. Their sums are plotted over the data. The plots shown are scaled copies of the Post Fit menu screen dumps [CTRL+P].

### 3.4 Theoretical Model 4: Spin Hamiltonian with two coupled electronic spins

**Example: Two iron nuclei in two types of sites; each iron coupled to an electronic spin: simulation of spectrum using a two-spin model.**

Load parameter file 2STTRIE.PI and the data file TT20.B. The data are the same as in Example 3. An annotated parameter file 2SPIN.TXT in the \WEB\MOS\EXAMPLE directory defines the meaning of the parameters. Go to the Analysis submenu and examine the parameters via Edit Param. The intrinsic zero field splitting parameters have been set to values similar to those reported for mono-iron centers with sulfur ligands (Huynh and Kent (1984)). The principal axes of the ferrous and ferric sites are assumed to be aligned. The exchange coupling constant has been set to an isotropic ( $J_x=J_y=J_z$ ) value larger than the zero field splittings. Positive J means anti-ferromagnetic coupling, i.e. the  $S=1/2$  doublet will be the ground spin multiplet. For isotropic J,  $D_1 = 0$  and  $D_2 = 0$ , the relationships between the intrinsic A values used here and the A values used in the single spin  $S=1/2$  model of example 3 are:

$$A_1 = - (3/4) A'_1$$

$$A_2 = + (3/7) A'_2$$

where the primed A's are the  $S=1/2$  values. The  $A_1$  and  $A_2$  for the two spin parameters are set to values calculated from the A' values in Example 3. We have forced the A of the ferric site to be isotropic. Execute the Flash procedure. With a Intel Pentium 120 MHz CPU, the simulation requires seven seconds. After that delay, the plot shown in Figure 3.4 will be displayed. The match to the data is very good considering no fitting has been done. Obviously, several of the many parameters could be adjusted to achieve a better match. The parameters used are listed below:

2STTRIE.PI (output to 2sttrie.po)  
2 spin coupled simulation for Rieske

Reduced Chi squared = 10 for fit to data:  
TT20.B

Printed at 00:24:03 on 09/28/93

#	name	value	constr	weight	lower b	upper b		
101	D1	8.000	101		0.000	20.000	Version #	-6
102	E1/D1	0.280	102		0.000	0.333	Report>Prn	0
103	g1x	2.000	0		2.000	2.400	Maxit Glob	0
104	g1y	2.000	0		2.000	2.400	Maxit Locl	0
105	g1z	2.000	0		2.000	2.400	Maxit Area	0
106	D2	-3.000	0		0.000	20.000	Report Glo	1
107	E2/D2	0.330	0		0.000	0.333	Report Loc	1
108	g2x	2.000	0		2.000	2.400	N Anneal	0
109	g2y	2.000	0		2.000	2.400	Perturb	0
110	g2z	2.000	0		2.000	2.400	Theor.Modl	4
111	Alpha	0.000	0		0.000	90.000	Fit Method	1

112	Beta	0.000	0	0.000	90.000		
113	Gamma	0.000	0	0.000	180.000	N Sites	2
114	Jx	100.000	0	-100.000	100.000	Symmetry	2
115	Jy	100.000	0	-100.000	100.000	Ntheta	6
116	Jz	100.000	0	-100.000	100.000	Nstates 1	5
						Nstates 2	6
101	dEq	-3.000	0	0.300	0.700		
102	Eta	-3.000	0	-6.000	0.000		
103	AL efg	0.000	0	0.000	180.000		
104	BE efg	0.000	0	0.000	180.000		
105	GA efg	0.000	0	0.000	180.000		
106	Ax	-56.000	0	-300.000	0.000		
107	Ay	-196.000	0	-300.000	0.000		
108	Az	-79.000	0	-300.000	0.000		
109	AL A	0.000	0	0.000	180.000		
110	BE A	0.000	0	0.000	180.000		
111	GA A	0.000	0	0.000	180.000		
112	Shift	0.750	0	0.200	0.400		
113	Width(V<0)	0.300	0	0.250	0.400		
						<b>S1 or S2</b>	<b>1</b>
101	Rel Area	0.500	0	1.000			
201	dEq	0.600	0	0.600	0.700		
202	Eta	0.000	0	-1.000	1.000		
203	AL efg	0.000	0	0.000	180.000		
204	BE efg	0.000	0	0.000	180.000		
205	GA efg	0.000	0	0.000	180.000		
206	Ax	-154.000	0	-300.000	0.000		
207	Ay	-154.000	0	-300.000	0.000		
208	Az	-154.000	0	-300.000	0.000		
209	AL A	0.000	0	0.000	180.000		
210	BE A	0.000	0	0.000	180.000		
211	GA A	0.000	0	0.000	180.000		
212	Shift	0.300	0	0.200	0.400		
213	Width(V<0)	0.300	0	0.250	0.400		
						<b>S1 or S2</b>	<b>2</b>
201	Rel Area	0.500	0	1.000			

**S1 or S2:** Each local (nuclear) site has an integer-valued parameter named “**S1 or S2**” that specifies to which electronic spin a nuclear site is coupled. In the example above, S1 = 2 (Nstates1 = 5) and S2 = 5/2 (Nstates2 = 6). For local site 1, “**S1 or S2**” = 1 specifies that site 1 is coupled to electronic spin S1. Likewise, for site 2, “**S1 or S2**” = 2 couples site 2 to S2. The maximum number of local sites allowed is eight. The “**S1 or S2**” parameter provides for any of the eight nuclear spins to be coupled to S1 or S2.

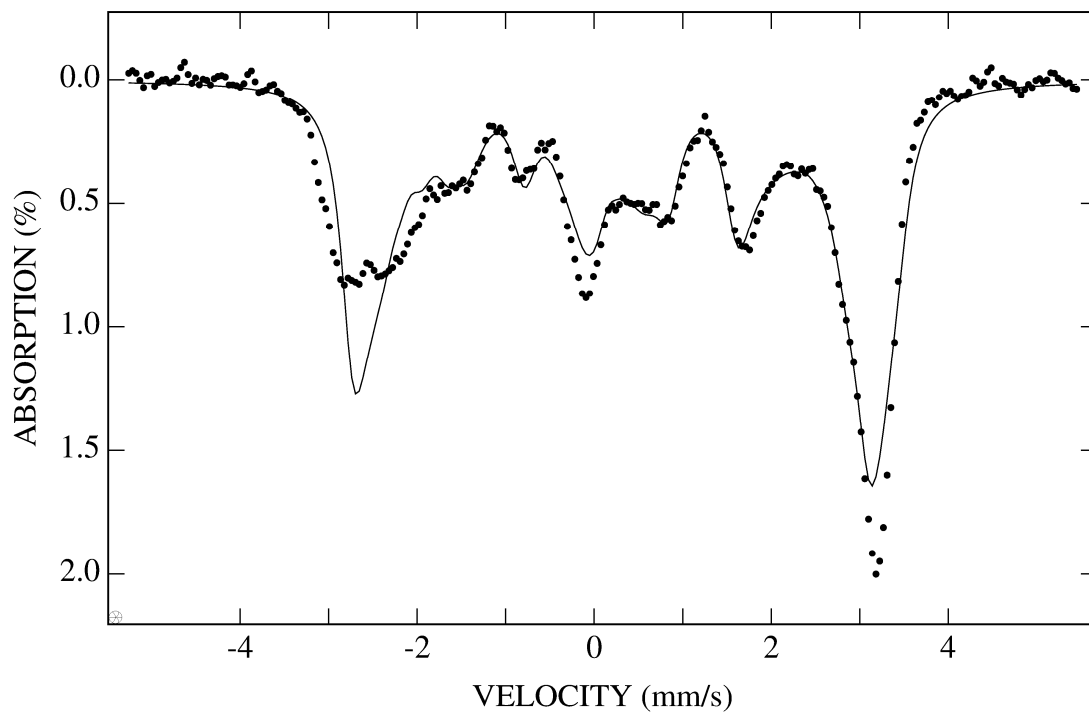


Figure 3.4: Simulation using a coupled two-spin Hamiltonian model as discussed in Example 4. Data (full circles) were recorded at 4.2 K and with 600 Gauss field applied parallel to the gamma beam.

The plot shown was generated by the Plot2File -> Custom PS Plot procedure, opened with Ghost Script and converted as BMP-MONO (300dpi), then cropped using a another standard picture editing program, then opened with Windows's native Picture and Fax viewer (Explorer) and saved as TIFF, then inserted directly into this MS Word document.

### 3.5 Theoretical Model 5: Fixed orientation of $H^{\text{int}}$ and EFG tensor relative to molecular frame.

**Examples: Simulations of spectra from single crystals and partially oriented polycrystalline samples. Also, a fit to one spectrum with three magnetic hyperfine sextets.**

This model is appropriate for ferric containing molecular magnets that display strong uniaxial electronic properties (high single ion anisotropy), nano-particle magnetism, ferromagnets with randomly or non-randomly oriented domains.

Model 5 can also be used for analysis of asymmetric quadrupole pairs of single crystals. For single crystal samples in zero applied field, set the POL parameter in the Data Header to zero.

#### **Definition of parameters:**

##### Global integer parameters --

The range of molecular orientations averaged over is controlled by the parameters Symmetry, Ntheta and Distrib.:

Symmetry – For single crystals set Sym = 0. For isotropic symmetry use POL = -2 in Data Header. For higher symmetries see Appendix C.

Ntheta -- The number of points along the theta direction in the grid.

Distrib. -- Specifies weight distribution for grid points:

1 = uniform weights independent of direction.

2 = Gaussian distribution of ionic moments with peak along Z axis. Grid points are weighted by  $\text{Exp}[-(\text{theta} / \text{sigthe})^2]$  where SigThe is defined below.

3 = Gaussian distribution of ionic moments peaked in XY plane. Grid points are weighted by  $\text{Exp}[-\{(\pi/2 - \text{theta})/\text{sigthe}\}^2]$  where SigThe is defined below.

##### Global real-valued parameters --

SigThe -- width parameter for Gaussian weights. Units are degrees. Small SigThe (<10) approximates a single crystal with the applied field along the Z axis (for Distrib. = 2) or near the XY plane (for Distrib. = 3). Large SigThe (>100) approximates a powder sample. Do not set SigThe = 0. SigThe only has an effect when Distrib. = 2 or 3.

### Local real-valued parameters:

1. FWHM [mm/s] -- line width parameter (full width at half maximum). A positive value specifies a Lorentzian line shape. A negative value specifies a Voigt shape for which a Lorentzian of width 0.19 mm/s is convoluted with a Gaussian of line width equal to the magnitude of the FWHM parameter.
2. Shift [mm/s] -- isomer shift
3. Hint [kG] -- internal magnetic field magnitude. Note, the effective field at the iron nucleus is the sum of  $H_{\text{int}}$  and  $H_{\text{app}}$  where  $H_{\text{app}}$  is the applied field as specified in the Data Header.
4. Theta [degrees] -- angle between  $H_{\text{int}}$  and Z molecular axis.
5. Phi [degrees] -- azimuth angle of  $H_{\text{int}}$  relative to X molecular axis.
6. dEq -- The magnitude of the dEq parameter specifies the quadrupole splitting. Its sign specifies the sign of the efg principal component  $V_{zz'}$  where X' Y' Z' is the principal axes frame of the electric field gradient (efg).
7. Eta -- efg asymmetry parameter.  $\text{Eta} = (V_{xx'} - V_{yy'}) / V_{zz'}$
8. Al efg [degrees] -- Euler angle that specifies the rotation of the efg about the Z axis.
9. Be efg [degrees] -- Euler angle that specifies the rotation of the efg about the Y' axis.
10. Ga efg [degrees] -- Euler angle that specifies the rotation of the efg about Z'.

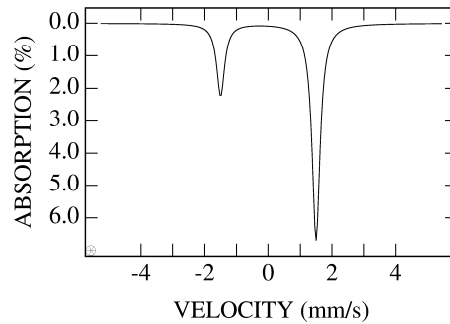
### Examples

Several examples of simulations via Model 5 are included with the WMOSS installation package. For explicit expressions of the angular dependence of the relative intensities of spectral lines for single crystal samples, see Belozerski (1993) pages 17 - 24. The standard parameter file for Model 5 is HQ.SPL.



### Model 5 Example A: Single Crystal with gamma beam // $Z = Z'$

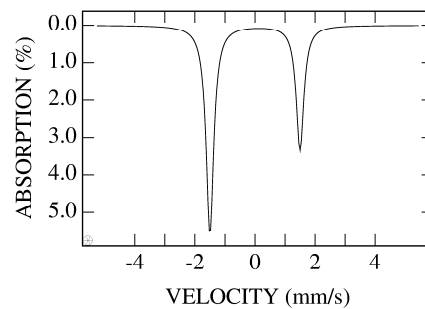
N sites	1	dEq	3
		.	0
Symmetry	0	Eta	0
Ntheta	10	Al efg	0
Distribu.	1	Be efg	0
		Ga efg	0
Sigma Theta	999.0		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	0		
Theta	0	Happ [kG]	0
Phi	0	T [K]	0
		POL	0



**Figure 3.5.1**

### Model 5 Example B: Single Crystal with gamma beam // $Z = X'$

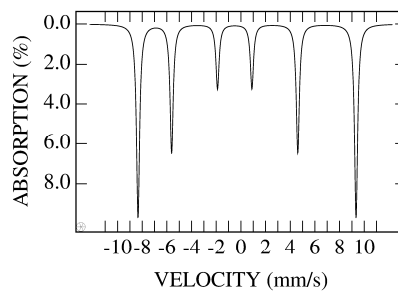
N sites	1	dEq	3.0
Symmetry	0	Eta	0
Ntheta	10	Al efg	0
Distribu.	1	Be efg	90
		Ga efg	0
Sigma Theta	999.0		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	0		
Theta	0	Happ [kG]	0
Phi	0	T [K]	0
		POL	0



**Figure 3.5.2**

**Model 5 Example C:** Single Crystal, Hint = 550 kG with gamma beam along random directions in XYZ frame.  
Relative intensities 3 : 2 : 1 : 1 : 2 : 3

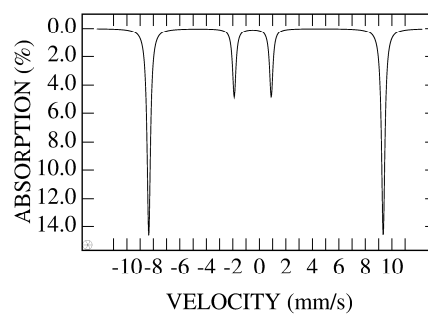
N sites	1	dEq	1
Symmetry	1	Eta	0
Ntheta	10	Al efg	0
Distribu.	1	Be efg	0
		Ga efg	0
Sigma Theta	30		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	550		
Theta	0	Happ [kG]	0
Phi	0	T [K]	0
		POL	0



**Figure 3.5.3**

**Model 5 Example D:** Single Crystal, Hint = 550 kG with Hint // Z and gamma beam // Z.  
Relative intensities 3 : 0 : 1 : 1 : 0 : 3

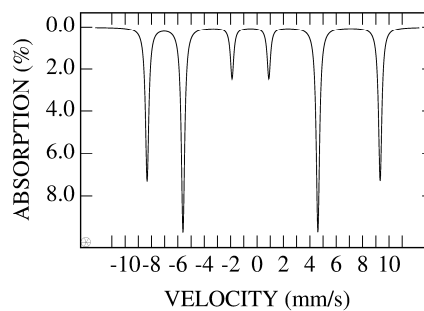
N sites	1	dEq	1
Symmetry	0	Eta	0
Ntheta	10	Al efg	0
Distribu.	1	Be efg	0
		Ga efg	0
Sigma Theta	30		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	550		
Theta	0	Happ [kG]	0
Phi	0	T [K]	0
		POL	0



**Figure 3.5.4**

**Model 5 Example E:** Single Crystal, Hint = 550 kG with Hint // X  
and gamma beam // Z.  
Relative intensities 3 : 4 : 1 : 1 : 4 : 3

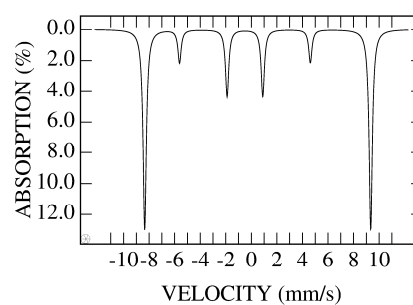
N sites	1	dEq	1
Symmetry	0	Eta	0
Ntheta	10	Al efg	0
Distribu.	1	Be efg	90
		Ga efg	0
Sigma Theta	999		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	550		
Theta	90	Happ [kG]	0
Phi	0	T [K]	0
		POL	0



**Figure 3.5.5**

**Model 5 Example F:** Partially oriented polycrystalline sample.  
 $H_{\text{int}} = 550$  kG with  $H_{\text{int}}$  parallel Z. Gamma beam  
directions weighted by Gaussian peaked about  
the Z axis.

N sites	1	dEq	1
Symmetry	1	Eta	0
Ntheta	10	Al efg	0
Distribu.	2	Be efg	0
		Ga efg	0
Sigma Theta	30		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	550		
Theta	0	Happ [kG]	0
Phi	0	T [K]	0
		POL	0

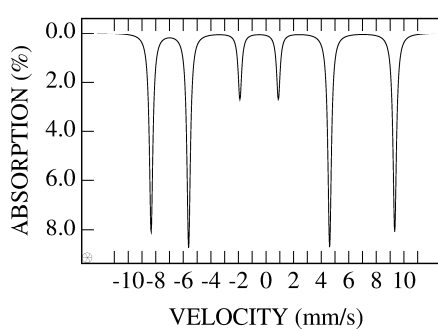


**Figure 3.5.6**

### Model 5 Example G: Partially oriented polycrystalline sample.

Hint = 550 kG with Hint parallel Z. Gamma beam directions weighted by Gaussian peaked about the XY plane.

N sites	1	dEq	1
Symmetry	1	Eta	0
Ntheta	10	Al efg	0
Distribu.	3	Be efg	0
		Ga efg	0
Sigma Theta	30		
		Rel. Area	1
FWHM	0.3	G. Area	1
Shift	0	Baseline	0
Hint	550		
Theta	0	Happ [kG]	0
Phi	0	T [K]	0
		POL	0



**Figure 3.5.7**

## Example H: Powder sample with three ferromagnetic iron species.

Parameter file listed below. Data and fit are shown in Figure 3.5.8.

```

PF34.PI                                     (output to pf34.po)
Example parameter input file for Heff + efg model
Note: if eta .ne. 0, then use symmetry > 1 i.e. 2,3 or 4
Reduced Chi squared = 3.319 for fit to data:
PF34APR5
Printed at 23:32:43 on 03/01/98
# name value kon lbnd ubnd
101 SigmaTheta 20.000 0 0.000 500.000
101 FWHM[mm/s] 0.341 101 -0.500 0.500
102 Shift 0.194 102 -0.500 0.500
103 Hint [kG] 455.458 103 0.000 600.000
104 Theta[deg] 0.000 0 -0.500 0.500
105 Phi 0.000 0 -0.500 0.500
106 dEq 0.000 0 -0.500 0.500
107 Eta 0.000 0 0.000 1.000
108 Al efg 0.000 0 0.000 180.000
109 Be efg 0.000 0 0.000 180.000
110 Ga efg 0.000 0 0.000 180.000
101 Rel. Area 0.241 101
201 FWHM[mm/s] 0.517 201 -0.500 1.000
202 Shift 0.502 202 -0.500 1.000
203 Hint [kG] 422.606 203 0.000 600.000
204 Theta[deg] 0.000 0 -0.500 0.500
205 Phi 0.000 0 -0.500 0.500
206 dEq 0.000 0 -0.500 0.500
207 Eta 0.000 0 0.000 1.000
208 Al efg 0.000 0 0.000 180.000
209 Be efg 0.000 0 0.000 180.000
210 Ga efg 0.000 0 0.000 180.000
201 Rel Area 2 0.264 201
301 FWHM[mm/s] -0.210 301 -0.500 0.500
302 Shift -8.48e-2 302 -0.500 0.500
303 Hint [kG] 305.694 303 0.000 600.000
304 Theta[deg] 0.000 0 -0.500 0.500
305 Phi 0.000 0 -0.500 0.500
306 dEq 0.000 0 -0.500 0.500
307 Eta 0.000 0 0.000 1.000
308 Al efg 0.000 0 0.000 180.000
309 Be efg 0.000 0 0.000 180.000
310 Ga efg 0.000 0 0.000 180.000
301 Rel Area 3 0.425 301
Version # -6
Report>Prn 0
Maxit Glob 0
Maxit Locl 999
Maxit Area 0
Report Glo 1
Report Loc 1
N Anneal 0
Perturb 0
Theor.Modl 5
Fit Method 5
N Sites 3
Symmetry 1
Ntheta 10
Distribu. 1

```

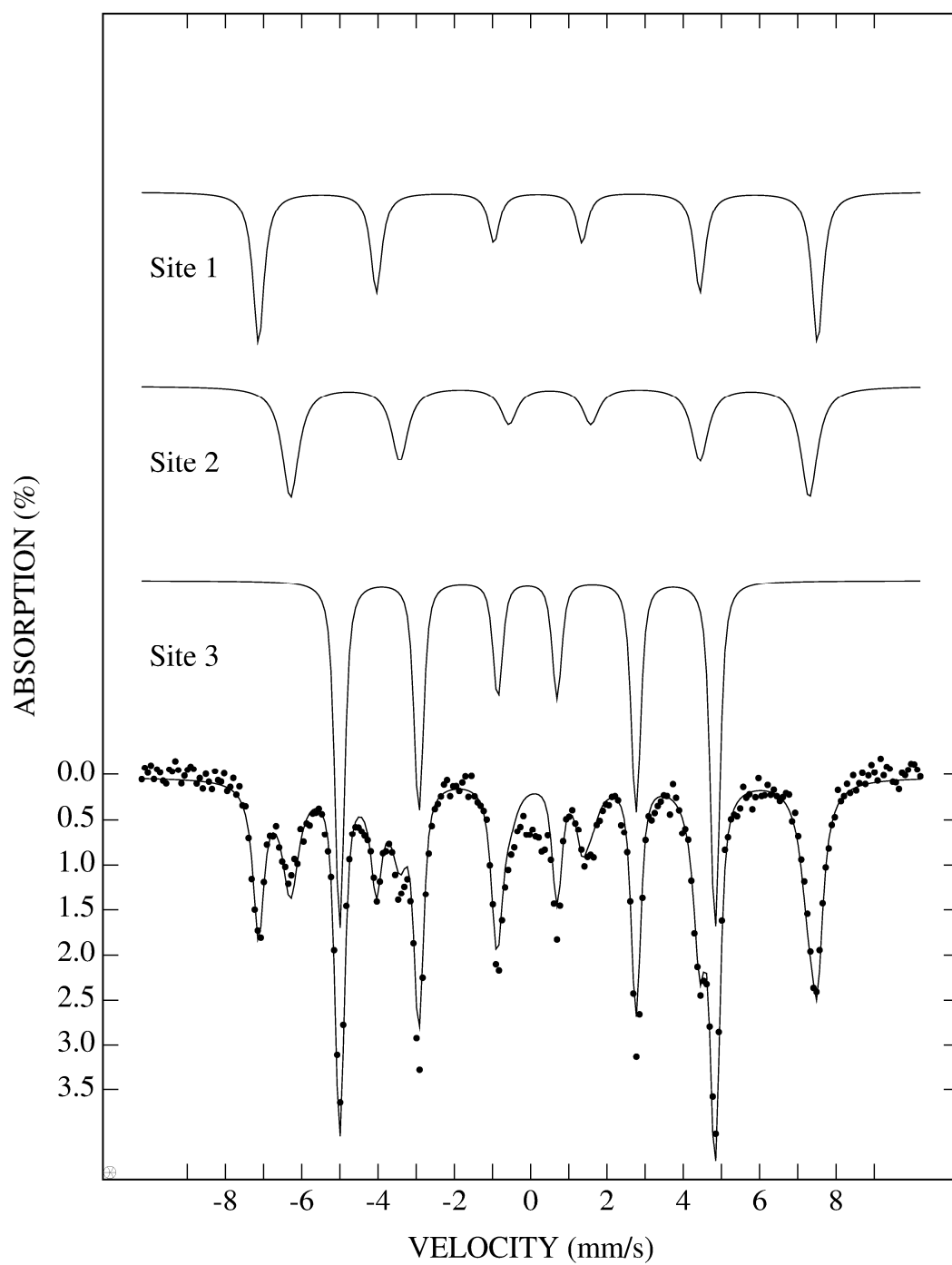


Figure 3.5.8

### 3.6 Theoretical Model 6: Quadrupole Splitting Distributions (QSD) and Voigt Based Fitting (VBF).

#### **Example: Fits to spectrum with poorly resolved quadrupole pairs.**

Model 6 addresses the problem of a sample that does not have a homogeneous Fe environment. This model implements the method of Voigt-based fitting developed by Rancourt (1991). That paper, entitled “Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy”, defines the terms used here except as noted below. It is assumed that the reader has studied the Rancourt (1991) paper.

The basic assumptions are:

1. Any broadening of the absorption lines beyond the intrinsic linewidth due to the uncertainty principle arises only from a static distribution of the hyperfine parameters. All dynamic broadening mechanisms are ignored.
2. The distribution of the hyperfine parameters may be represented by the sum of a few Gaussians.
3. Any distribution of the isomer shift is linearly correlated with the distribution of the quadrupole splitting. This linear correlation causes the spectral lines of local sites of this model to be Voigts.

The parameters for each local site are:

1. Lor      linewidth (FWHM) of the intrinsic Lorentzian.
2. dEq0    Center of the quadrupole splitting distribution.
3. ddEq    QSD width (Full Width at Half Maximum of the Gaussian)  
Note:  $ddEq = 2 (2 \ln 2)^{1/2} \sigma$ , where  $\sigma$  is the Gaussian width parameter of Rancourt (1991).
4. delta0   value of the shift when the distributed hyperfine parameter has a value of zero.
5. delta1   coupling of shift to distributed hyperfine parameter as in  
 $shift = delta0 + delta1 * dEq$
6. h+/h-   ratio of the Lorentzian heights of the two lines (+ or -) in an elemental quadrupole doublet. Note, the area of the quadrupole doublet is normalized such that it is independent of h+/h-.

How is an arbitrary QSD approximated using the WMOSS parameter set structure? According to assumption #2 above, the arbitrary QSD will be approximated by a sum of Gaussians. Each local site is used to specify the spectral sub-component arising from a single Gaussian distribution of the quadrupole splitting. The number of Gaussians in the total distribution is controlled by the Nsites parameter on Param page 3.

Rancourt (1991) defined sub-components to belong to the same “species” if they had the same values of  $\delta_0$ ,  $\delta_1$  and  $h_+/h_-$ . As illustrated below, these conditions can be enforced by proper setting of the parameter constraint codes. For example, an experimental spectrum might display a broad ferrous component and a sharp ferric component. A simulation using Model 6 might have  $N_{\text{sites}} = 4$  with sites 1, 2 and 3 used to represent the ferrous component and site 4, the ferric component. The values of  $\delta_0$  for sites 2 and 3 would be constrained to be equal to  $\delta_0$  of site 1. Similarly, for  $\delta_1$  of sites 2 and 3.  $\delta_0$  and  $\delta_1$  of site 4 would be varied independently.

Figure 3.5A shows an  $^{57}\text{Fe}$  Mössbauer spectrum (file EXAMPLES\BF55.B) that may be described as two severely overlapping quadrupole doublets. The primary peaks suggest iron sites with  $dE_q \cong 0.9$  mm/s. The shoulders at  $-0.2$  mm/s and  $+1.3$  mm/s suggest a second type of iron with  $dE_q \cong 1.5$  mm/s. The fit shown in Figure 3.6A corresponds to the QSD in Figure 3.6B that has a single Gaussian ( $N_{\text{sites}} = 1$ ). All the parameters are listed in Figure 3.6C (file EXAMPLES\BF55QSD1.PI). This fit is equivalent to using Model 3 with two Voigt lines having independent widths (see file EXAMPLES\BF55QPV.PI). The right to left asymmetry of the theoretical spectrum is due to  $\delta_1$ .

When WMOSS is run and a Model 6 parameter file loaded, the QSD may be plotted on the screen via the Analysis/QSD Plot procedure. QSD Plot offers an option to “Keep” the QSD. “Keep” copies the QSD to the List where it is stored the same as a spectrum. Once on the List, a QSD may be saved to a disk file, etc.

Figure 3.6D illustrates the much better fit obtained with a QSD having two Gaussians. The QSD is shown in Figure 3.6E and the parameters are listed in Figure 3.6F (file EXAMPLES\BF55QSD2.PI). Note, the constraint codes of  $\delta_0$  and  $\delta_1$  for site 2 have been set to 104 and 105, respectively. This forces site 1 and site 2 to have the same values for  $\delta_0$  and  $\delta_1$ ; this QSD would be described as a single species according to Rancourt’s definition. This QSD is equivalent to fitting the data with four Voigt lines. The utility of the method is that assumed linear correlation between the shift and  $dE_q$  deals with the problem of how to pair the four lines to create two quadrupole doublets.

Figure 3.6G shows the same data fitted with a QSD having three Gaussians. The QSD is shown in Figure 3.6H and the parameters in Figure 3.6I (file EXAMPLES\BF55QSD3.PI). The spectral sub-components are significantly different from those of the two Gaussian QSD. However, the total QSD is essentially the same. This illustrates the stability of the Voigt-based fitting method. High quality fits usually reveal a well defined QSD independent of the number of Gaussian sub-components used.

This QSD/VBF model provides a systematic method for fitting spectra with broad lines. However, as Rancourt (1991) discussed at length, it is often hard to distinguish between broadening due to static hyperfine distributions and broadening due to dynamic



effects. Obtaining a high quality fit to a single spectrum via QSD/VBF is in itself not proof of the origin of the broadening.

Model 6 can be used to simulate Voigt lines for Mössbauer isotopes other than  $^{57}\text{Fe}$  since the intrinsic Lorentzian width is defined by the Lor parameter. In Models 2 and 3, the Voigt line shape has the 0.19 mm/s intrinsic Lorentzian width for  $^{57}\text{Fe}$  built into the model.

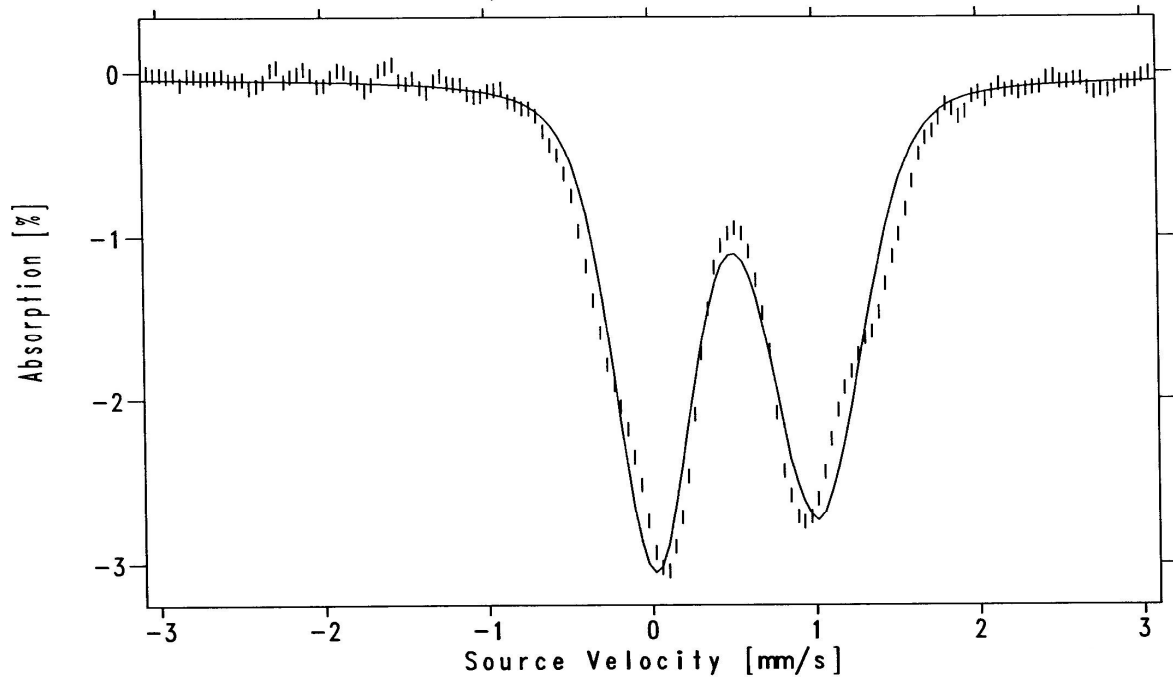


Figure 3.6 A

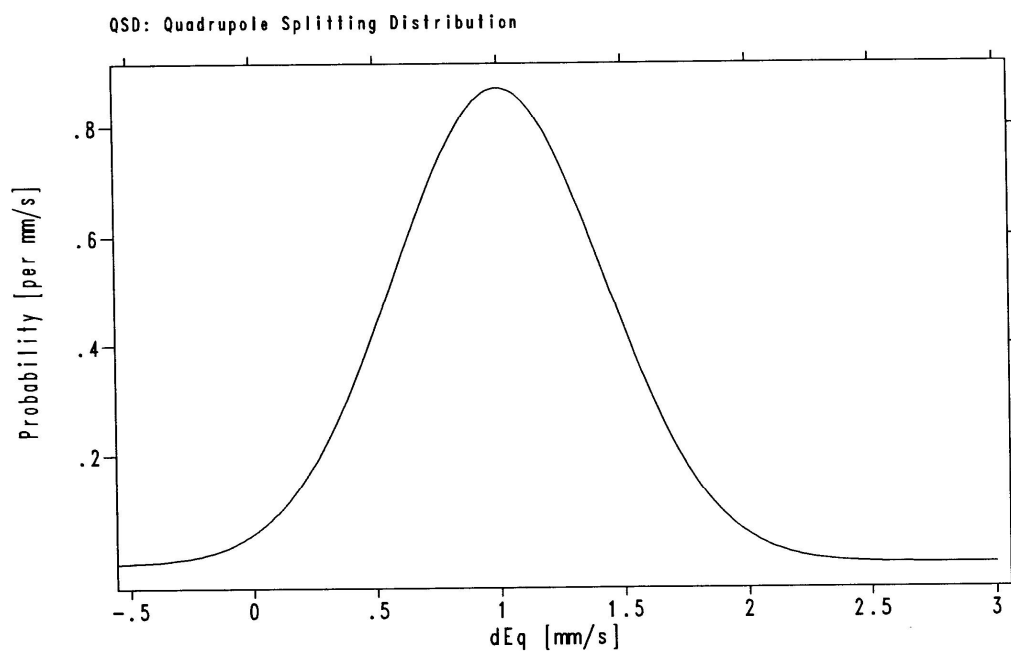


Figure 3.6 B

```

BF55QSD1.PI                                     (output to bf55qsd.po)
Example parameter input file for Voigt Based Fitting
1-D distribution in dEq plus correlated shift
Reduced Chi squared =    5.609 for fit to data:
  BF55.B
Printed at 13:18:55 on 03/18/98
#  name      value   kon    lbnd    ubnd    Version #   -6
101 Lor. FWHM    0.200    0     0.000    0.500    Report>Prn   0
102 dEq0[mm/s]   1.018   102    0.500    2.000    Maxit Glob   0
103 ddEq(FWHM)   1.109   103    0.000    2.000    Maxit Loc   999
104 delta0       0.471   104    0.000    1.000    Maxit Area   0
105 delta1       4.390e-2 105   -1.000    1.000    Report Glo   1
106 h+/h-        1.000    0     0.000    4.000    Report Loc   1
101 Rel. Area    0.958   101
                                     N Anneal     0
                                     Perturb      0
                                     Theor.Modl   6
                                     Fit Method   5
                                     N Sites      1

```

Figure 3.6 C

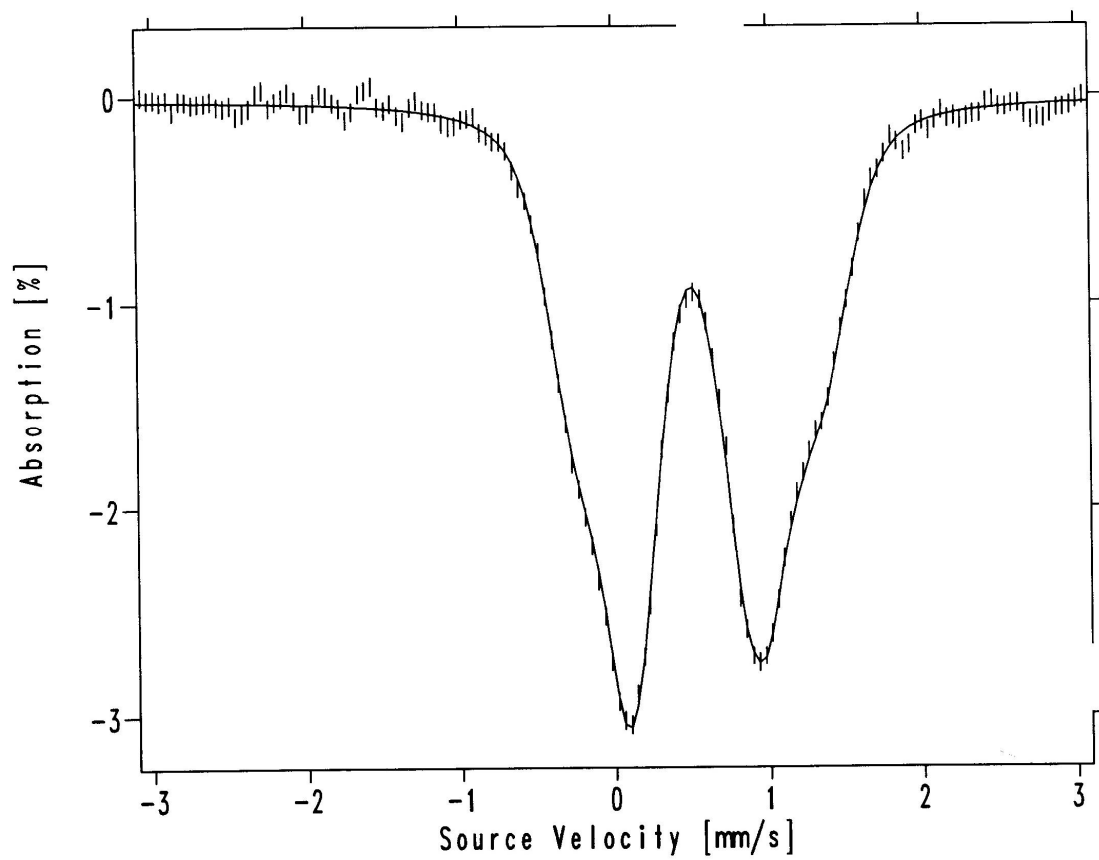


Figure 3.6 D

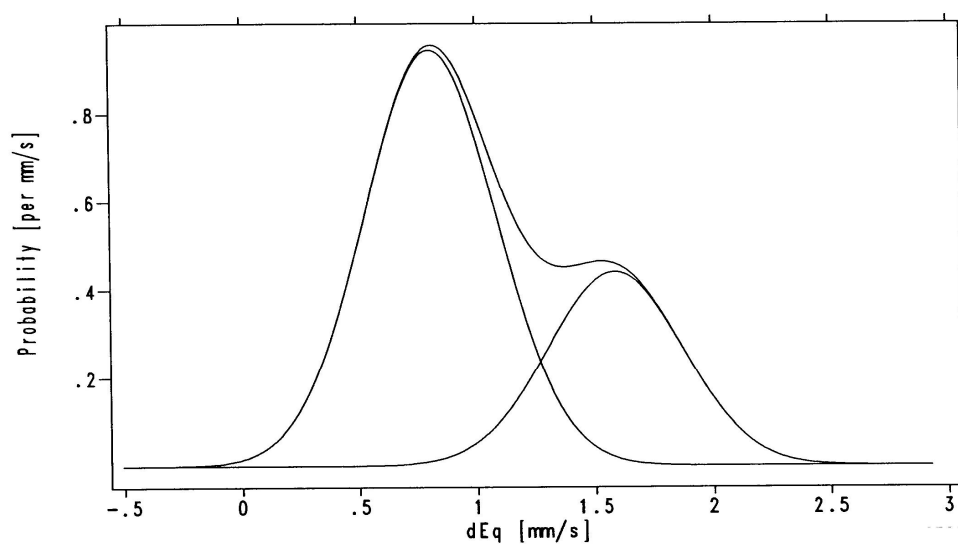


Figure 3.6 E

BF55QSD2.PI (output to bf55qsd.po)  
 Example parameter input file for Voigt Based Fitting  
 1-D distribution in dEq plus correlated shift  
 Reduced Chi squared = 0.679 for fit to data:  
 BF55.B  
 Printed at 14:21:46 on 03/18/98

#	name	value	kon	lbnd	ubnd	Version #	
101	Lor. FWHM	0.200	0	0.000	0.500	-6	Report>Prn 0
102	dEq0[mm/s]	0.806	102	0.500	1.000	0	Maxit Glob 0
103	ddEq(FWHM)	0.655	103	0.000	1.000	99	Maxit Locl 99
104	delta0	0.479	104	0.000	1.000	0	Maxit Area 0
105	delta1	4.015e-2	105	-1.000	1.000	1	Report Glo 1
106	h+/h-	1.000	0	0.000	4.000	1	Report Loc 1
101	Rel. Area	0.657	101			0	N Anneal 0
						0	Perturb 0
201	Lor. FWHM	0.200	0	0.000	0.500	6	Theor.Modl 6
202	dEq0[mm/s]	1.586	202	1.000	2.000	5	Fit Method 5
203	ddEq(FWHM)	0.670	203	0.000	1.000		
204	delta0	0.479	104	0.000	1.000	2	N Sites 2
205	delta1	4.015e-2	105	-1.000	1.000		
206	h+/h-	1.000	0	0.000	4.000		
201	Rel Area 2	0.314	201				

Figure 3.6 F

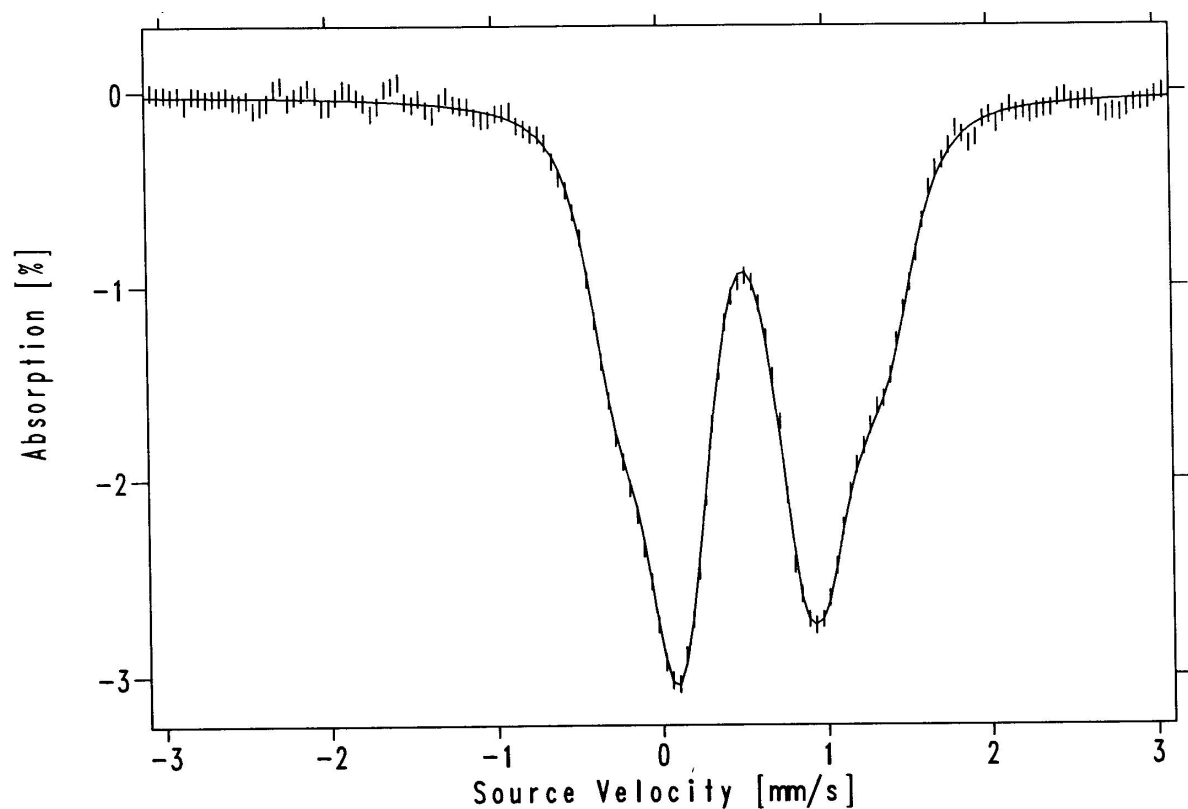


Figure 3.6 G

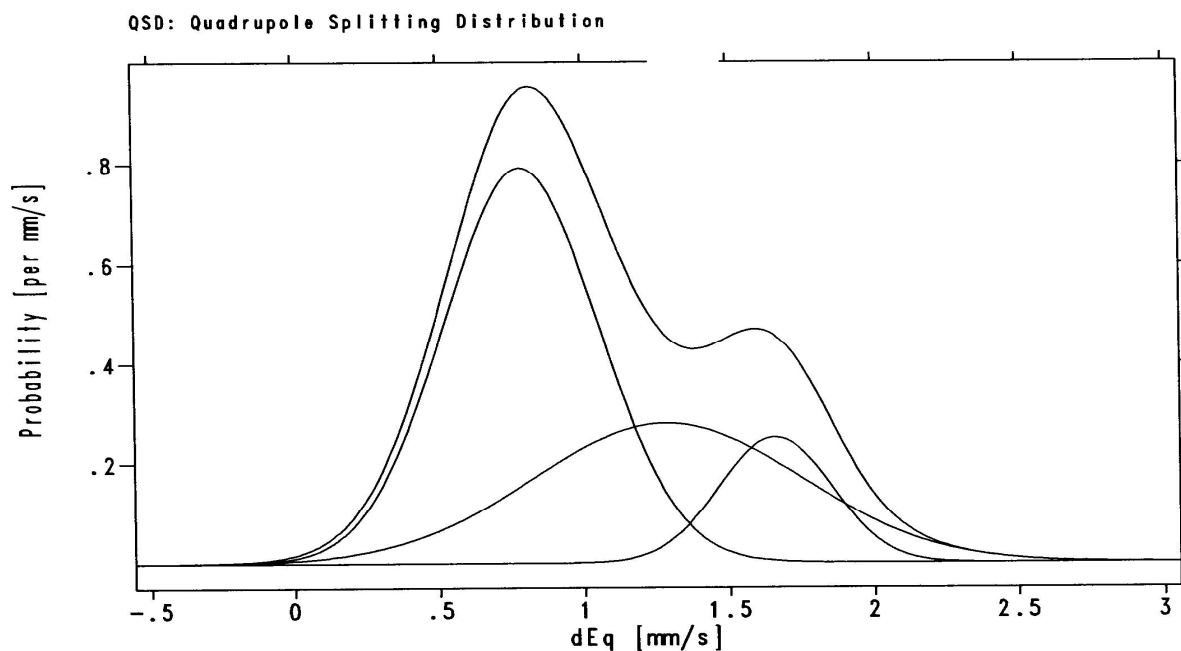


Figure 3.6 H

BF55QSD3.PI (output to bf55qsd.po)

Example parameter input file for Voigt Based Fitting

1-D distribution in dEq plus correlated shift

Reduced Chi squared = 0.673 for fit to data:

BF55.B

Printed at 14:24:19 on 03/18/98

#	name	value	kon	lbnd	ubnd	Version #	
101	Lor. FWHM	0.200	0	0.000	0.500	Report>Prn	-6
102	dEq0[mm/s]	0.786	102	0.500	1.000	Maxit Glob	0
103	ddEq(FWHM)	0.627	103	0.000	1.000	Maxit Locl	999
104	delta0	0.478	104	0.000	1.000	Maxit Area	0
105	delta1	4.073e-2	105	-1.000	1.000	Report Glo	1
106	h+/h-	1.000	0	0.000	4.000	Report Loc	1
101	Rel. Area	0.528	101			N Anneal	0
						Perturb	0
201	Lor. FWHM	0.200	0	0.000	0.500	Theor.Modl	6
202	dEq0[mm/s]	1.657	202	1.000	2.000	Fit Method	5
203	ddEq(FWHM)	0.455	203	0.000	2.000		
204	delta0	0.478	104	0.000	1.000	N Sites	3
205	delta1	4.073e-2	105	-1.000	1.000		
206	h+/h-	1.000	0	0.000	4.000		
201	Rel Area 2	0.121	201				
301	Lor. FWHM	0.200	0	0.000	0.500		
302	dEq0[mm/s]	1.285	302	1.000	2.000		
303	ddEq(FWHM)	1.087	303	0.000	2.000		
304	delta0	0.478	104	0.000	1.000		
305	delta1	4.073e-2	105	-1.000	1.000		
306	h+/h-	1.000	0	0.000	4.000		
301	Rel Area 3	0.323	301				

Figure 3.6 I

### 3.7 Theoretical Model 7: Hyperfine Field Distributions (HFD) and Voigt Based Fitting (VBF).

**Example: Fit to spectrum three ferromagnetic species.**

Model 7 addresses the problem of a ferromagnetic sample that does not have a homogeneous Fe environment. This model implements the method of Voigt-based fitting developed by Rancourt (1991). Much of what was written for the QSD model (Model 6) applies to the HFD model. **It is assumed that the reader has studied the Rancourt (1991) paper.**

#### Definition of Parameters for Model 7

#	Name	Units	Description
1	Lor	mm/s	FWHM of intrinsic Lorentzian
2	z0	mm/s	Center of Hyperfine Field Gaussian Distribution { 1 mm/s / ( $g_n \cdot \beta_n$ ) = 147 kG }
3	dz	mm/s	FWHM of HFD Gaussian
4	shift0	mm/s	Shift value when $z = 0$
5	shift1	mm/s	Linear coupling constant: $\text{shift} = \text{shift0} + \text{shift1 } z$
6	epsiln0	mm/s	Epsilon value when $z = 0$
7	epsiln1	mm/s	Linear coupling constant: $\text{epsilon} = \text{epsiln0} + \text{epsiln1 } z$
8	h2/h3		Ratio of height of lines 2 and 3 of elemental sextet
9	h1/h3		Ratio of height of lines 1 and 3 of elemental sextet

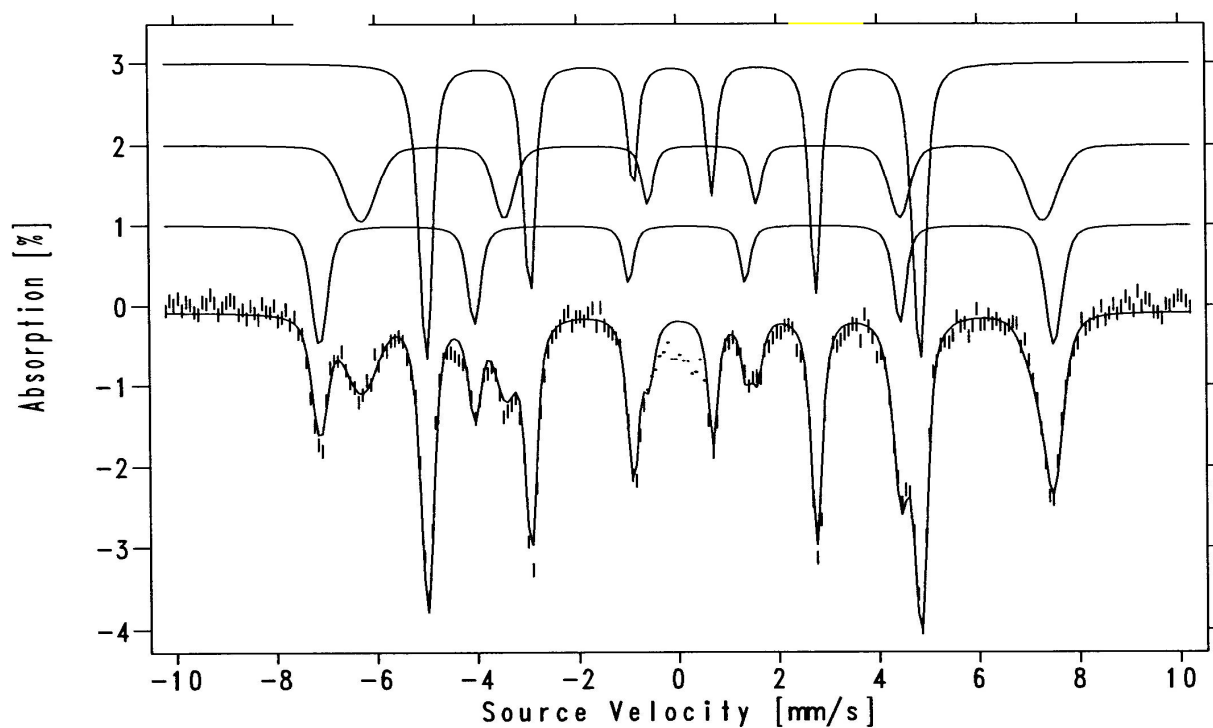


Figure 3.7 A

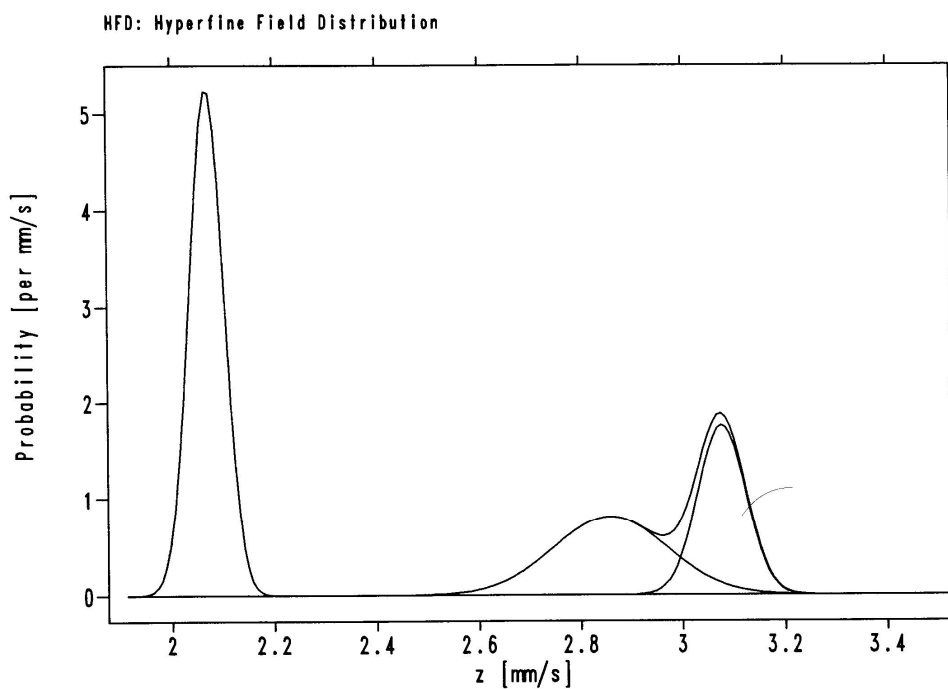


Figure 3.7 B

```

PF34HFD.PI                                     (output to pf34hfd.po)
Example parameter input file for Voigt Based Fitting
1-D distribution in Hint plus correlated efg & shift
Reduced Chi squared =      3.944 for fit to data:
  PF34APR5
Printed at 04:18:21 on 03/19/98
#  name          value    kon    lbnd    ubnd    Version #    -6
101 Lor. FWHM     0.200      0     0.000    0.500    Report>Prn    0
102 z0 [mm/s]     3.076    102     0.000    4.000    Maxit Glob    0
103 dz (FWHM)     0.104    103     0.000    1.000    Maxit Loc1 999
104 Shift0        0.194      0     0.000    2.000    Maxit Area    0
105 Shift1        0.000      0    -10.000   10.000    Report Glo    1
106 Epsiln0       0.000      0     -3.500    3.500    Report Loc    1
107 Epsiln1       0.000      0    -10.000   10.000    N Anneal      0
108 h2/h3         2.000      0     0.000    4.000    Perturb       0
109 h1/h3         3.000      0     0.000    4.000    Theor.Mod1    7
101 Rel. Area     0.198    101                                     Fit Method    5

201 Lor. FWHM     0.200      0     0.000    0.500    N Sites       3
202 z0 [mm/s]     2.858    202     0.000    4.000
203 dz (FWHM)     0.251    203     0.000    1.000
204 Shift0        0.502      0     0.000    2.000
205 Shift1        0.000      0    -10.000   10.000
206 Epsilon0       0.000      0     -3.500    0.000
207 Epsilon1       0.000      0    -10.000   10.000
208 h2/h3         2.000      0     0.000    4.000
209 h1/h3         3.000      0     0.000    4.000
201 Rel Area 2    0.215    201

301 Lor. FWHM     0.200      0     0.000    0.500
302 z0 [mm/s]     2.069    302     2.000    2.500
303 dz (FWHM)     7.658e-2  303     0.000    1.000
304 Shift0        -0.085      0     0.000    0.500
305 Shift1        0.000      0    -10.000   10.000
306 Epsilon0       0.000      0     -1.000    1.000
307 Epsilon1       0.000      0    -10.000   10.000
308 h2/h3         2.000      0     0.000    4.000
309 h1/h3         3.000      0     0.000    4.000
301 Rel Area 3    0.434    301

```

Figure 3.7 C



### 3.8 Theoretical Models 1-1 and 4-1: single or coupled electronic system with local Relax. parameter

These newly introduced Theoretical Models in WMOSS4 ver.F are identical to their corresponding original models (see **3.3** and **3.4**), except for Relax. Parameter in Data header which now admits the value Relax. = 2.

The Models 1-1 and 4-1 apply to those certain situations when the relaxation model (fast or slow) cannot be defined globally, even if the electronic problem remains unchanged, respectively 1-spin for Model 1-1 and two-spins coupled for Model 4-1.

The previous approach to this kind of problems was to separately fit several inequivalent Fe-positions using fast relaxation then subtract this spectrum from the original, then later perform the fit using the slow relaxing case for the rest of inequivalent Fe-positions. The success of such approach often represents a hard effort and strongly depends on factors like how well a sufficient number of spectral features are distinguished.

Implementation of local relaxing conditions has been made by adding a new Local parameter called “R.Toggle” (relaxation toggle), which admits as valid the known values: 0 for fast relaxation, respectively 1 for slow relaxation

Therefore the new setup procedure for relaxation model in Data Header is:

If Relax. = 0 or 1 (F or S) then:

- Relaxation problem is set to Fast or Slow (Global)
- R.Toggle value is not important (overridden)

If Relax. = 2 (M) then:

- Relaxation problem is set to Mixed (Local)
- R.Toggle value 0 or 1 will set the corresponding relaxation model, e.g. Fast or Slow, separate for each site.

Note:

- **DO NOT Float the “R.Toggle” parameter.** It is not fittable (Integer)!
- you can freely impose however constraints on it between sites.
- for simultaneous fit of spectra you may freely Pick spectra with either Global or Local relaxation models while using the same parameter file for all three possible cases: slow, fast or mixed.

### 3.9 Theoretical Model 5-1: uniaxial electronic system with local Relax. parameter

Similarly as described above, the Model 5-1 has implemented the local Relax. Parameter in Data header (Relax. = 2) and R.Toggle parameter (values 0 or 1) in the corresponding local parameters.

Additionally, the Model 5-1 computes an electronic problem compatible to effective  $H_{\text{int}}$  definition:  $A_x=A_y=A_z$  (isotropic hyperfine matrix) or  $A_z$  and  $A_x=A_y=0$  (axial hyperfine matrix). Note that since  $H_{\text{int}}$  has fixed direction relative to the Z-axis of molecular (or domain) frame, the same property must be shared also by the model of the electronic problem.

Such situations occur relatively often in Ln-containing molecular magnets, nano-particles or materials with magnetic domains, when highly anisotropic ions (or magnetic clusters, nanoassemblies, etc) couple with the spin of paramagnetic ferric ions. In certain situations the application of strong external magnetic field does not influence the orientation of the effective internal field  $H_{\text{int}}$ . The closer the electronic and magnetic properties of the material will be to this behaviour, the better the approximation of this model. Similar problems cannot be simulated by Model 1 without introducing unrealistic conditions for g-tensor as example. In this sense Model 5-1 should produce a more valid physical picture while avoiding parameters that are usually unavailable for such complex structures (g-tensor, hyperfine matrix, various exchange parameters and their angles, etc) without help from other spectroscopic or computational methods that might be themselves at their limit. Judging the tradeoff must of course count how big would be the estimated errors of the results from those studies. It is natural to assume that even with very small errors for all parameters implied by a full spin hamiltonian, the Mössbauer problem will still be so large that the Do Fit will likely fail in false local minima or manifolds due to overparametrization. Count in some intermediate relaxation effects. You get the picture.

To reduce the size of the problem and if your material has magnetic and electronic properties that allows a fixed orientation of effective internal field  $H_{\text{int}}$  (the Kramers multiplet of the ferric ions being thermally populated only according to an effective uniaxial ZFS parameter  $D$  and according to the absolute value of  $H_{\text{ext}}$ ) then Model 5-1 will be a more appropriate approximation than Model 1.

In current form the Model 5-1 has implemented two parameters that define this electronic problem: size of the Kramers multiplet and the corresponding Boltzmann populations:

1. NELStates =  $2S+1$ ; in Page 3 of Edit Param. Valid values are: 2, 4 and 6.
2. D= effective uniaxial ZFS parameter; in Page 4 and higher (Local parameters).

Note: the condition for fixed orientation of the internal field  $H_{\text{int}}$  to the molecular Z-axis suggests that for symmetries higher than 1 the Model 5-1 is obviously a more rough approximation and therefore should be avoided or carefully considered.

## Chapter 4. LOADING RAW DATA FILES AND $^{57}\text{Fe}$ -metallic CALIBRATION

### 4.1 Data File formats

No standard Mössbauer data file format exists. When the Files -> Data Load procedure is executed, WMOSS deals with this problem by presenting an option box with a list of all the formats used by our present customers. Examples of different types of file are listed in the Table at the end of this chapter and examples of spectra files that use those formats may be found in the C:\WEB\MOS\EXAMPLES directory.

One can say that the most general format for raw data input is #4 : Y ASCII, counts (1 column, NO header, up to 1024 channels). If your raw data file format is not directly compatible with WMOSS, try to convert it in the above format. If it still does not work please contact <http://www.wmooss.org>.

The behaviour of the Load Data procedure is dependent on the various formats of the input file and may be divided into four general groups:

#### 1) WEB binary or WEB ASCII files --

These files have all the data header information expected by WMOSS. All other types of formats will require at least filling in some parameters in Data Header. The worst case: it will be necessary to go through the entire sequence of steps. For this simple reason we suggest using the WMOSS native format (WEB format) either binary or ASCII. The first choice is better and more reliable because WMOSS will instantly tell if data has been corrupted.

For these two native formats when Data Load is executed, the spectrum is immediately plotted on the screen, its name appended to the LIST and control returned to the FILES submenu. Binary files are much more efficient than ASCII files in terms of disk space and loading time. WEB binary files are used for the tutorial presented in Chapter 2. Typically, a user initially loads a non-WEB file, edits the data header and then saves the spectrum and data header to a WEB binary file. The original non-WEB file is then moved to a data archive for safekeeping.

#### 2) ASCII files from spectrometers with a sawtooth velocity waveform --

In these files a given value of the source velocity is represented by a single unique channel. Such spectra will have parabolic baselines. (The baseline would be low at velocity zero since the source-to-counter distance is maximum at that point.) The Data Load procedure will present the user options to use previously stored calibration information, to remove a parabolic baseline and/or to execute an Iron metal calibration procedure. "Sawtooth" spectra are never folded (see below). Finally, the Edit Data Header procedure is automatically entered.

### 3) ASCII files from spectrometers with a triangular velocity waveform --

Most common the spectra are recorded with a "triangular" velocity waveform. The second half of these files contains the mirror image of the resonant absorption spectrum of the first half. The baselines of both halves will be parabolic, but with the curvature of the baseline of the second half the negative of that of the first half. When the raw data are "folded" the resonant signals will add while the parabolic baselines will cancel to first order. The Data Load procedure will present the user following options:

1. Inerchange first and second half?

The folding procedure expects the first half of the unfolded spectrum to be the data collected during positive acceleration of the source. (The positive direction is toward the sample. The half of the spectrum with positive acceleration will have a parabolic background with positive curavature.) If the phase of the source motion is such that the first half of the spectrum has a baseline with negative curvature, then the first and second halves of the spectrum should be inerchanged.

2. Use previously stored calibration information?

See Section 4.3 below.

3. Remove a parabolic baseline?

If the spectrum is to be folded there no need to remove the parabolic baseline. If the spectrum is a iron calibration and each half will be fitted separately, the parabolic baseline should be removec.

Next an options box will list present choices to fold the spectrum or to execute an Iron metal calibration procedure.

### 4) Previously folded spectra --

Spectra recorded with a "triangular" velocity waveform and previously folded by software other than WMOSS. These spectra should have a flat baseline. The Data Load procedure handles this type of spectra the same as the "sawtooth" type.

## 4.2 Folding raw spectra

The working calibration standard for the Mössbauer velocity scale is the room temperature spectrum of Iron metal. This spectrum is described in detail in Section 3.1. When the Data Load procedure detects a non-WEB data file, it presents the user with several options:

1) Should the velocity = zero channel and velocity increment per channel be read from previously stored calibration information?

2) Should a baseline be removed from the data?

3) An options box is displayed with the following choices:

Manual Fold  
Auto Fold  
1st Half  
2nd Half  
Iron Cal  
No Fold

The Manual Fold procedure allows the user to input the folding point, folds the spectrum accordingly and then enters the Edit Data Header procedure. The Auto Fold procedure will fold the spectrum without user input and then enter the Edit Data Header procedure. The 1st Half procedure simply copies the first half of the unfolded spectrum to the LIST. The 2nd Half procedure copies the second half of the unfolded spectrum to the LIST. Note, the velocity scale for the second half is reversed.

#### 4.3 Iron Cal procedure and corrections for driver velocity non-linearities

Always when a non-WEB file is loaded, the user is asked if previously stored information from the CAL.LOG file should be used and if the velocity scaled should be corrected for non-linearity. These options allow the calibration constants to be read from CAL.LOG. WMOSS4 can record up to 999  $^{57}\text{Fe}$  calibration results, being capable to cover a period of ca. 10 years with instant access to older calibrations. This estimate is perhaps valid for a laboratory with 2 Mössbauer spectrometers and an average of 1 calibration spectrum each week.

The Iron Cal procedure fits the two halves of an iron metal spectrum and appends the resulting peak positions plus the derived calibration constants to the file \WEB\MOS\CAL.LOG. WMOSS will conveniently display these results as organized as follows:

- by date,
- then by spectra filename (the raw source of calibration),
- then by a user defined label (with length of 2 characters). This is meant to help user remembering further systematic details (for example which spectrometer: A,B, C ... or which speed: 6 or 9 or 11, or both 6A, 9B etc.).

These files are not meant to be analyzed with an ASCII viewer, but if it is so desired a more readable file, \WEB\MOS\CAL.HST, with just the calibration constants, file names and dates is also available. Plots of the differences between the peak positions and the best straight line fitted to the peak positions are displayed.

Anytime the user wishes to start new CAL.LOG and CAL.HST files, it is only needed to remove the old files from the \WEB\MOS directory.

**As a matter of efficiency and reliability, a single set of CAL.LOG and CAL.HST files could be used by all users within a group sharing the same spectrometers in the following manner:**

- each time a new Iron Cal procedure is executed the results (e.g. the new appended CAL.LOG and CAL.HST files) are disseminated to all other users
- the other users simply replace their old set of files in \WEB\MOS with the new set.

If the non-linear velocity correction is chosen then, the unfolded data is projected via interpolation to a linear velocity scale. This linear scale is defined by fitting a straight line to the points defined by the published values of the Iron metal peak positions [mm/s] (y values) and the observed positions in channels (x values).

### Compatible Data Load File Formats

#	Name	Normalized?	Calibration Info.?	Example
1	WEB binary	Yes	All	BF55.b
2	WEB binary	Yes	All	BF55.b2
3	WEB, ASCII, 10 line header	Yes	All	BF55.A10
4	Y ASCII, counts (no header)	No	None	FD20.C
5	XY ASCII, (channel, counts) (no header)	No	"	FD20.CC
6	XY ASCII, (Vel [mm/s], Abs. [%]) (no header)	No	"	FD20.VA (vel. info. lost)
7	EG&G MCS+ Binary (*.mcs)	No	"	97122403.MCS
8	Canberra ASCII, 1024 channels	No	"	
9	Canberra ASCII, 512 channels	No	"	AP030392.PRN
10	Canberra MCA 35+	No	"	VRFE53.DAT
11	Ranger ASCII, 12 line header	No	"	300K.DAT
12	Elscint ASCII folded 512 channels	No	"	5665009.ASC
13	CMU ASCII	No	Some	A\$FFKK54 A\$RRC580
14	Emory ASCII	No	Some	FFFE25.DAT
15	Vermont ASCII	No	Some	24038501
16	Monash ASCII	No	None	MONASH2.DAT
17	EG&G Maestro ASCII "Print to file" PHA	No	None	97120201.TXT

## APPENDIX A -- FUNDAMENTALS OF MÖSSBAUER SPECTROSCOPY

### A.1 Recoil-free resonant gamma-ray absorption

All nuclei possess excited states, some of which are accessible from the ground state by photon absorption. Often the excited states of the absorber are long-lived and the range of photon energies which will resonantly excite the absorption is extremely narrow. If strong absorption is to be observed, a significant fraction of the energy of the source radiation must be within this range. Such a source may obviously consist of excited nuclei of the same isotope as the absorber. The excited nuclei may be decay products of appropriate parent nuclei. It was once thought that conservation of momentum requires the recoil of the emitting nucleus and that the photon would not have the full transition energy and hence would not resonantly excite the absorber. If the nucleus is free, the recoil momentum and energy are taken by the nucleus itself. In a solid the momentum and energy go into lattice vibrations, i.e., phonons. The temperature dependence of the absorption cross-section of  $\text{Ir}^{191}$  led Mössbauer (1958) to be the first to realize that a photon could be emitted with the entire solid recoiling as one rigid mass. The energy lost to the recoil in this situation is negligible and the emitted photon may resonantly excite the absorber.

### A.2 Nuclear Physics of $\text{Fe}^{57}$

The isotope with the strongest recoilless resonant absorption is  $\text{Fe}^{57}$ . Since the vast majority of the work reported in the Mössbauer literature is for iron, we restrict our discussion to that isotope. Figure 1 shows the decay of  $\text{Fe}^{57}$  from its parent  $\text{Co}^{57}$ . Of all the excited  $\text{Fe}^{57}$  nuclei, about 10% will emit a 14.4 keV gamma ray via a magnetic dipole transition from the metastable  $I = 3/2$  state to the  $I = 1/2$  ground state ( $I$  is the nuclear spin). The ratio of recoil-free 14.4 keV photons to all the 14.4 keV photons emitted is  $f$ , the recoil-free fraction of the source.  $f$  varies with the properties of the solid and decreases monotonically with increasing temperature. The linewidth of the emitted radiation is limited in theory by  $t$ , the mean life of the  $I = 3/2$  state. In  $\text{Fe}^{57}$ ,  $t = 1.4 \times 10^{-7}$  sec, and the energy distribution is given by a Lorentzian with a fullwidth at half maximum of  $\Gamma_{\text{nat}} = 4.7 \times 10^{-9}$  eV (Lang, 1970). The intensity per unit energy of the Mössbauer radiation is many orders of magnitude greater than the background radiation, and we shall henceforth refer to the gamma beam as if it were 100% Mössbauer radiation unless we specifically note otherwise. We shall also assume that the nuclear levels of the source are not split, and the energy distribution of the beam is given by a single Lorentzian.

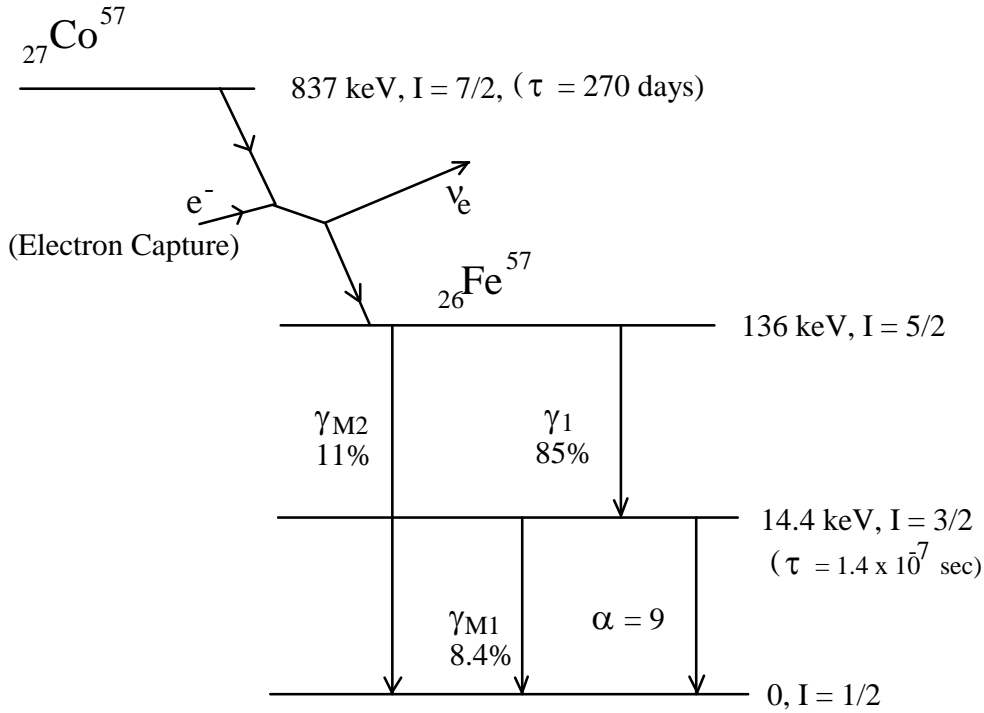


Figure A1 Energy level scheme of  $\text{Fe}^{57}$ . Mössbauer spectroscopy involves the 14.4 keV transition. Intensities are given in % of decays.

To use our Mössbauer source as a spectroscopic tool we must be able to vary its energy over a significant range. This is accomplished by Doppler shifting the energy of the gamma beam. Moving the source at a velocity of 1 mm/sec toward the sample will increase the energy of the photons by  $14.4 \text{ keV} (v/c) = 4.8 \times 10^{-8} \text{ eV}$  or ten natural linewidths. The "mm/sec" is a convenient Mössbauer unit and is equal to  $4.8 \times 10^{-8} \text{ eV}$  for  $\text{Fe}^{57}$ . A Mössbauer spectrometer consists of a source which may be moved relative to the sample and a counter to monitor the intensity of the beam after it has passed through the sample. The Mössbauer spectrum is a plot of the counting rate against the source velocity, i.e., the beam energy. If the sample nuclear levels are not split and the  $I = 3/2$  to  $I = 1/2$  transition energy equals that of the source, then the effective cross-section for absorption is a function of gamma energy as given by Fraunfelder (1963)

$$\sigma_{\text{eff}} = \frac{2 I^* + 1}{2 I + 1} \frac{\lambda^2}{2\pi} \frac{f'}{2(1+\alpha)} \frac{\Gamma_{\text{nat}}^2}{(E-E_\gamma)^2 + \Gamma_{\text{nat}}^2} \quad (\text{eq A1})$$

where  $I = 1/2$  and  $I^* = 3/2$  are the ground and excited nuclear spins,  $\alpha = 9.0$  is the internal conversion coefficient (ratio of betas to gammas in the 14.4 keV decay),  $\lambda = 8.61 \times 10^{-9} \text{ cm}$  is the wavelength of the radiation,  $(E-E_\gamma)$  is the difference between mean incident and resonant gamma energy,  $\Gamma_{\text{nat}}$  is the energy width of the excited nucleus, and  $f'$  is the probability of recoilless absorption. The spectrum will be a single Lorentzian centered at  $v = 0$  with a linewidth (FWHM) of  $2\Gamma_{\text{nat}} = 0.19 \text{ mm/sec}$ . The linewidth is  $2\Gamma_{\text{nat}}$  since the observed line arises from the convolution of the source energy distribution and



absorber cross section. As discussed below, the hyperfine interactions will split the nuclear levels of the sample and complicate the Mössbauer spectrum.

### A.3 Hyperfine Interactions

#### A.3.1 Isomer Shift

The nucleus and its electrons interact in several ways, the most obvious being the electrostatic attraction. If the  $\text{Fe}^{57}$  nuclear charge distribution were the same for the  $I = 1/2$  ground state and the  $I = 3/2$  excited state, then the electrostatic energy of the system of electrons plus nucleus would be the same for both states. In fact the excited  $\text{Fe}^{57}$  nucleus is 0.1% smaller in radius than the ground state nucleus, which causes the Mössbauer transition energy to depend on the electron density at the nucleus. This effect produces the so-called isomer shift of the Mössbauer spectrum, which may be written as

$$\delta = K \{ \Sigma_s |\psi(0)|^2 - \Sigma_a |\psi(0)|^2 \} \quad (\text{eq A2})$$

where  $\delta$  is the isomer shift,  $K$  is a positive constant depending on the change in the nuclear radius,  $\Sigma_s |\psi(0)|^2$  is the electron density at the source nucleus, and  $\Sigma_a |\psi(0)|^2$  is the electron density at the absorber nucleus.

To allow isomer shifts to be measured independently of the nature of the source, the centroid of the room temperature spectrum of metallic iron has been adopted as the zero of energy and all shifts are measured relative to it. This convention yields

$$\delta = K_0 - K \Sigma_a |\psi(0)|^2 \quad (\text{eq A3})$$

where  $K_0$  is a constant. Calculations of  $\delta$  are difficult to perform, hence its most valuable application is classifying various compounds according to oxidation state, degree of covalency, and coordination number. The 1s and 2s electron density at the nucleus is independent of the chemical environment of the Fe ion. However, the 3d electrons shield the 3s electrons and cause a decrease in the electron density at the nucleus. The more delocalized the 3d electrons, the smaller the isomer shift. However, this picture is complicated by the presence of Fe 4s character in the bonding orbitals. The 4s character also reduces the isomer shift, and it is not always clear which of the two effects is dominant (Greenwood and Gibb, 1971). The electronic contribution to the isomer shift is essentially temperature independent and the observed decrease at high temperatures is due to the relativistic second order Doppler shift. This effect decreases the isomer shift approximately  $6 \times 10^{-4}$  mm/sec for a 1 K increase in  $T$  when the temperature is above the Debye temperature (Lang and Marshall, 1966).

### A.3.2 Electric Quadrupole Interaction

The excited ( $I = 3/2$ ) state of the  $\text{Fe}^{57}$  nucleus possesses an electric quadrupole moment, and the presence of a low symmetry electric field will tend to orient the nuclear spin. The interaction may be written as

$$H_Q = - (Q/6) \underline{I} \cdot \underline{V} \cdot \underline{I} \quad (\text{eq A4})$$

where  $Q$  is the nuclear quadrupole moment,  $\underline{I}$  is the nuclear spin, and  $\underline{V}$  is the electric field gradient (efg) tensor. The elements of the efg tensor are

$$V_{ij} = \delta^2 V / \delta X_i \delta X_j \quad i, j = x, y, z \quad (\text{eq A5})$$

where  $V$  is the potential due to all charges outside the nucleus and the derivatives are evaluated at the nuclear site. The  $V_{ij}$  are the coefficients of the quadratic terms of a power series expansion of the potential about the nuclear site and are given in their principal axis system by

$$V_{zz} = \int \rho(r) (3z^2 - r^2) r^{-5} d\mathbf{r} \quad (\text{eq A6})$$

and similar expressions.  $\rho(\mathbf{r})$  is the total charge density and the integral is taken over all space outside the nucleus. Also,  $\underline{V}$  is real, symmetric, and traceless. Hence in the frame in which  $\underline{V}$  is diagonal,

$$H_Q = (Q/4) V_{zz} [I_z^2 - 5/4 + (\eta/3)(I_x^2 - I_y^2)] \quad (\text{eq A7})$$

$$\eta = (V_{xx} - V_{yy})/V_{zz}$$

where  $\underline{x}$ ,  $\underline{y}$ , and  $\underline{z}$  denote the principal axes of the efg and  $\eta$  is called the asymmetry parameter. By convention,  $\underline{x}$ ,  $\underline{y}$ , and  $\underline{z}$  are chosen so that  $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ , which forces  $0 \leq \eta \leq 1$ . Note,  $\underline{V}$  has five independent elements. Two of these are  $V_{zz}$  and  $\eta$  and the other three are the Euler angles locating the efg principal axis system relative to some experimental frame.

Reversal of the sign of the nuclear spin will not change the nuclear charge distribution; therefore the efg will not completely lift the fourfold degeneracy of the  $I = 3/2$  states. The quartet will be split into two doublets, while the  $I = 1/2$  states will remain degenerate. Since two transition energies are now possible, two absorption peaks will appear in the Mössbauer spectrum. Diagonalizing  $H_Q$ , we find that the difference in energy of the two peaks to be

$$\Delta E = (Q/2) V_{zz} (1 + \eta^2/3)^{1/2} \quad (\text{eq A8})$$

If the recoil-free fraction does not depend on the orientation of the  $\gamma$ -beam relative to the Fe site, a sample with randomly oriented sites in zero applied field will produce a symmetric quadrupole pair. Since the sign of  $\Delta E$  can not be determined from such a spectrum, the absolute value of  $\Delta E$  is usually called "the quadrupole splitting." The sign of  $\Delta E$  is usually referred to as "the sign of  $V_{zz}$ " and is more difficult to measure than the quadrupole splitting.

### A.3.3 Magnetic Hyperfine Interaction

The  $\text{Fe}^{57}$  nucleus possesses a magnetic moment and its energy levels will be perturbed by the local magnetic field. In the presence of a field  $\underline{H}$ , the interaction is

$$H^M = -g_N \beta_N \underline{I} \cdot \underline{H} \quad (\text{eq A9})$$

where  $\beta_N$  is the nuclear magneton and  $g_N$  is the nuclear gyromagnetic ratio.  $g_N$  has the values  $0.1806 \pm 0.0014$  and  $-0.1033 \pm 0.0008$  in the ground and excited states, respectively (Lang, 1970).  $\underline{H}$  will be the sum of an applied field with the internal field of the unpaired electrons. Depending on the magnetic properties of the sample, the internal field may or may not equal zero in the absence of the applied field. A more explicit expression of the magnetic interaction is

$$H^M = P \sum_k \{ \underline{l}_k \cdot \underline{I} + 3(\underline{r}_k \cdot \underline{s}_k)(\underline{r}_k \cdot \underline{I}) - (\underline{s}_k \cdot \underline{I}) - \kappa(\underline{s}_k \cdot \underline{I}) \} - g_N \beta_N \underline{I} \cdot \underline{H}_{\text{app}}$$

$$P = 2 g_N \beta \beta_N \langle r^{-3} \rangle_{\text{eff}} \quad (\text{eq A10})$$

where the sum is over the unpaired electrons,  $\underline{l}_k$  is the orbital angular momentum on the  $k^{\text{th}}$  electron and  $\beta$  is the electron magneton. It is convenient to think of  $H^M$  in terms of an effective field acting on the nuclear moment. The effective field is

$$\underline{H}^{\text{eff}} = \underline{H}^{\text{app}} + (P/g_N \beta_N) \sum \{ \underline{l}_k + 3(\underline{r}_k \cdot \underline{s}_k) \underline{r}_k - \underline{s}_k - \kappa \underline{s}_k \}$$

$$= \underline{H}^{\text{app}} + \underline{H}^{\text{int}} \quad (\text{eq A11})$$

The first term of  $\underline{H}^{\text{eff}}$  is the applied field. The second is the field at the nucleus due to the orbital motion of the electrons. The third and fourth describe the field due to the dipole moment of the electrons. The last term is the Fermi contact term which accounts for any net polarization of the electronic spin at the nucleus. The polarization of s electron spin at the nucleus stems from the exchange interaction between the 3d electrons and the s electrons. Any admixture of 4s character into the 3d wave functions would also contribute to the contact field. To a good approximation the net spin at the nucleus will be proportional to  $\sum_k \langle \underline{s}_k \rangle$ , the sum being taken over 3d electrons.

$P$  and  $\kappa$  depend on the radial part of the wave functions and on shielding effects which are difficult to calculate. Values have been determined empirically for many complexes. Lang and Marshall (1966) quoted values of  $P/g_N\beta_N = -620$  kG and  $\kappa = 0.35$  for high- and low-spin ferric heme complexes.  $P\kappa/g_N\beta_N$  is the effective field per unit spin due to the contact term. For the ferric heme complexes it would be -220 kG. For a variety of high-spin ferrous inorganic compounds the survey of Varret (1976) shows  $P\kappa/g_N\beta_N$  to be approximately -250 kG. Edwards et al. (1967) found  $P\kappa/g_N\beta_N$  for high-spin ferrous tetrahedral compounds to be reduced to -160 kG by covalency effects.

## A.4 Experimental Setup

The Mössbauer spectra are usually recorded in the transmission geometry using a constant acceleration spectrometer operated in connection with a multi-channel analyzer in the time scale mode. The source is kept at room temperature and consists of approximately 20 mCi of  $\text{Co}^{57}$  diffused into rhodium or palladium foil. The spectrometer is calibrated against a metallic iron foil and zero velocity is taken as the centroid of its room temperature Mössbauer spectrum. In such calibration spectra, linewidths of about 0.23 mm/s were normally observed. The duration of a typical run is a few hours for non-biological compounds and 24 hours for proteins. A typical spectrometer is depicted schematically in Figure A2.

As shown in Figure A2, both the source velocity and the address of the active channel of the multichannel analyzer (MCA) are controlled by the master oscillator. The oscillator synchronizes the source acceleration and the sweep of the memory registers, causing the active channel address to be a linear function of the velocity. In other words, the pulses counted while the source is at a particular velocity are always stored in a particular register.

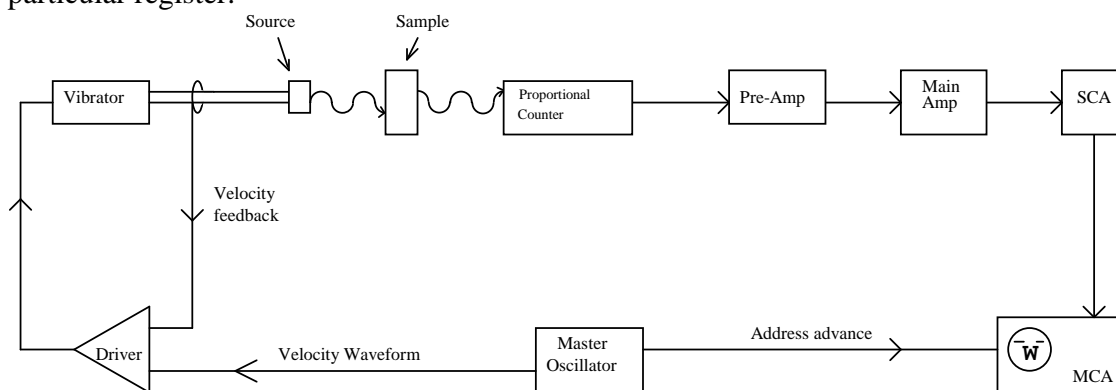


Figure A2 -- Schematic diagram of the Mössbauer spectrometer.

The master oscillator output is a rounded sawtooth or triangular wave and is applied to one of the driver inputs. The driver is essentially a difference amplifier with its output applied to the vibrator. A pick-up coil on the vibrator supplies a voltage proportional to the velocity of the source and is connected to the second input of the driver. The driver and vibrator form a tightly coupled, electro-mechanical, negative feedback loop, forcing the source velocity to be directly proportional to the master

oscillator signal. The desired velocity range is selected by scaling the master oscillator signal before it is applied to the driver.

The gas proportional counter contains primarily krypton or argon plus a small amount of methane quench gas. A 14.4 keV photon entering the chamber through the mylar window ionizes some of the Ar or Kr atoms, the creation of each ion/electron pair requiring about 30 eV. The positive ions drift to the outer wall and the electrons to the center wire. The accelerating electrons ionize more atoms, the effective gas gain being approximately 1000. The methane suppresses the random motion of the electrons, thus shortening the travel time to the center wire and the rise time of the signal pulse. The overall efficiency of a Harwell Argon counter is 60% at 14.4 keV, and a 14.4 keV photon will cause about  $10^6$  ion pairs to be created. The 122 keV and 136 keV photons entering the counter Compton scatter and produce a broad background of lower energy signals. The single channel analyzer (SCA) discriminates against most of these, but about 20% of the pulses falling in the 14.4 keV window of the SCA are from this Compton background.

The charge pulse from the counter is amplified and differentiated by the preamp which is mounted as close to the counter as possible. Further amplification of the pulse is provided by the main amplifier and its output is applied to a single channel analyzer. The SCA is set to discriminate against the non-14.4 keV signals. The signals accepted by the SCA are added to the current channel of the MCA.

The observed linewidths are larger than the intrinsic width of 0.19 mm/s since some broadening is always introduced by inhomogeneity of the environment of the iron in the source and sample. Additional broadening arises from imperfections in the source driving mechanism. Even so, typical observed linewidths obtainable in the lab are 0.23 mm/s which is close to the minimum predicted by the uncertainty principle.

We now consider the time required to record a Mössbauer spectrum. A typical sample will have 1 mg/cm<sup>2</sup> of iron in the gamma-ray beam. For purposes of illustration, we assume the spectrum has two absorption peaks. If the Fe<sup>57</sup> is present in its natural 2% abundance, there will be  $2 \times 10^{17}$  Fe<sup>57</sup> nuclei/cm<sup>2</sup>. The peak resonant cross section is approximately  $2 \times 10^{-18}$  cm<sup>2</sup> (Frauenfelder, 1963). We divide this value by 8 because of the finite source linewidth, the two absorption peaks of the spectrum, and the estimated product of the recoil free fraction of the source and absorber. The observed intensity will be 5%. The spectrometer will typically divide the velocity scale into 256 channels. For a 20mCi source the total counting rate is usually about 20,000 counts/s of which about 85% will be 14.4 keV radiation. The spectrometer duty cycle is about 66% and  $r$ , the 14.4 keV counting rate per channel, is typically 44 counts/s/channel. The signal-to-noise ratio, S/N, is given by

$$S/N = a_p [r T]^{1/2} \quad (\text{eq A12})$$

where  $a_p$  is the peak absorption intensity and  $T$  is the running time. If we want a S/N of 40, then, for  $a_p = 0.05$ ,  $T$  will be 14,500 s or 4 hours. For a given S/N, the run time is inversely proportional to the square of the peak absorption.

## APPENDIX B -- ERROR ANALYSIS

WMOSS provides a non-linear error analysis via Monte Carlo algorithm (set non-zero N-Anneal and Distrib. = 1 in Page1 of Edit Param procedure, see the examples below). The results of the Monte Carlo simulations are viewed via the MC Plot procedure on the Analysis sub menu. MC Plot generates scatter plots and histograms that show both the variance and covariance of all floating parameters. Since the theoretical models used are nonlinear, determination of the uncertainties requires on the order of 100 times more computation than the fit itself. However, the importance of the uncertainties sometimes justifies the time required for this type of analysis. A brief description of the algorithm is given below. See Press, et al. (1986) and references therein for more detail.

Assume we have a theoretical model which is, for practical purposes, a perfect description of the sample. We find best values for its free parameters by minimizing the reduced chi squared. To what extent does the spread caused by counting statistics indicate uncertainty in a particular parameter? We don't know the actual true parameters, but we assume that our best-fit parameters are near them and furthermore that the sensitivity of parameter values to counting noise in the neighborhood of the best-fit point is very similar to that which occurs at the true point. We then proceed to make synthetic experimental spectra by combining our optimum theoretical spectrum with appropriate random noise distributions. We know what distributions to use since the statistics of counting emissions from a radioactive source are well understood. We fit our model to each synthetic spectrum in turn and build up an array of points in parameter space, clustered about our original best fit point. The spread, in this array, of a particular parameter is then taken as a measure of the statistical uncertainty in our value for that parameter. By taking two-dimensional sections through the array we may observe correlations between errors in pairs of parameters, and we could in principle extend this to triplets, etc. Note that we are assuming a perfect spectrometer, a perfect sample, and a perfect theoretical model. We are only dealing with the effect of counting statistics.

**Caution! The user must remember that all the error analysis provided by WMOSS is based solely on the random noise in the data. The user is responsible to account for any systematic error.**

If you set the Fit Control parameters N ANNEAL to a positive integer value and PERTURB to 1 and then execute Do Fit, then the synthetic data sets will be fitted and the results saved to a disk file. The name of this file is specified by the variable "monte" in the configuration file \MOS\WMOSS.CFG. Each synthetic data set will be displayed while it is being fitted. Note, the data on the LIST are not affected by the MC Plot procedure. After the fit is done, the Monte Carlo results may be plotted on the screen by selecting MC Plot from the Analysis sub menu. The displayed plots will show the uncertainties of and the correlations between the parameters floated during the fit. MC Plot may be used to investigate the shape of the  $\chi^2$  surface about a local minimum.

For an example, load the spectrum JP01.b and the parameter file JP01MCV.pi.  
The parameter values are shown below:

JP01MCV.PI (output to jp01mcv.po)						Voigts	
Example for Appendix B: Monte Carlo Error Analysis						jp01.b	
Reduced Chi squared = 0.724 for fit to data:							
Printed at 08:10:03 on 09/24/93							
#	name	value	constr	weight	lowerB	upperB	
101	Shift	1.086	101		0.800	1.800	Version # -6
102	dEq	2.807	102		2.000	4.000	Anneal>PRN 0
103	Gamma L	-0.426	103		-0.500	-0.010	Maxit Elec 0
104	Gamma R	-0.308	104		-0.500	-0.010	Maxit Nucl 999
101	Rel. Area #1	0.616	101	1.000			Maxit Area 0
							Report Ele 1
							Report Nuc 20
201	Shift	1.047	201		0.600	1.400	N Anneal 200
202	dEq	2.176	202		1.800	3.500	Perturb 1
203	Gamma L	-0.389	203		-0.500	-0.010	Theor..Model 3
204	Gamma R	-0.389	203		-0.500	-0.010	Fit Method -2
201	Rel. Area #2	0.342	201	1.000			
							N Sites3
301	Shift	0.405	301		0.100	0.600	
302	dEq	0.850	302		0.300	1.200	
303	Gamma L	-0.237	303		-0.500	-0.010	
304	Gamma R	-0.237	303		-0.500	-0.010	
301	Rel. Area #3	7.424e-2	301	1.000			

As shown in Figure B1, the data display three poorly resolved quadrupole pairs. Also shown is a fit with  $\chi^2_R = 0.7$ . The theoretical model consisted of three local sites: #1 with an asymmetric quadrupole pair (two independent linewidths), #2 and #3 both with symmetric quadrupole pairs (each pair having one independent linewidth). Voigt lineshapes ( $\Gamma < 0$ ) were used since Lorentzian shapes resulted in poorer fits ( $\chi^2_R = 3.0$ ). Also, constraining site #1 to have a symmetric quadrupole pair produced poorer fits ( $\chi^2_R = 1.5$ ). The model used here is the simplest one that yielded a high-quality fit.

From the Analysis sub menu, enter Edit Parm and examine the Fit control parameters.

### E

N Anneal should be 200 and Perturb, 1. Fix the baseline parameter by setting its constraint code to zero. This reduces to number of floating parameters from 14 to 13. Exit Edit Parm, Pick spectrum JP01.b and then execute DoFit.



[ESC]  
P  
D

The time required to complete the 201 fits depends on the speed of your computer, the number of floating parameters and the chosen Fit Method. Fit Method = 2 is suggested for Monte Carlo analysis. The current index and upper limit of the Monte Carlo loop are displayed in the upper right corner of the screen during the fit. This information allows the user to estimate the total time required for the Monte Carlo analysis. Pressing any key during the procedure will suspend the execution and cause the "Paused" menu to appear. If the procedure is aborted, the results generated up to that point will be available for inspection via MC Plot.

When the Do Fit procedure is finished, Press R to return to the Analysis menu and then select MC Plot.

R  
M

Displayed are 13 rows and 13 columns of plots since there were 13 parameters floated during the fit. One is highlighted by a red border. Windows on the diagonal contain histograms of the probability of the floating parameters having a given value. Off the diagonal, scatter plots indicating the degree of correlation between pairs of the floating parameters are shown. The parameters associated with the highlighted window are displayed in the lower right corner of the screen. A given window may be blown up to full screen by highlighting it with [ARROW] and then pressing [ENTER]. These full screen plots may be dumped to the printer by pressing [CTRL+P].

Let's examine the results of the present example. The scatter plots show that some parameters are strongly correlated and others are not. The scatter plots and histograms for the 3 relative areas are shown in Figure B2. The MC Plot procedure constructs a histogram for a given parameter by subdividing that axis into 50 bins, projecting the points to that axis and counting how many points are in each bin. The overlapping lines of pairs #1 and #2 result in a uncertainty of  $\pm 0.05$  for each relative area. The fairly well resolved right line of pair #3 allows its area to be determined independently of pairs #1 and #2. The uncertainty of the relative area of pair #3 is only  $\pm 0.01$ . If you had collected data for a longer time so that the signal-to-noise ratio was larger then all these quoted uncertainties would be smaller. Random and systematic errors in the calibration of the instrument and in sample preparation must be included to establish the true total uncertainty.

Ignoring the possibilities that the distribution could be skewed, the histogram should converge to a Gaussian as the number of points is increased. Clearly, 200 points is approaching the minimum that achieves acceptable results. Much smoother histograms result with 400 points. The point of diminishing returns is reached at approximately 1000.



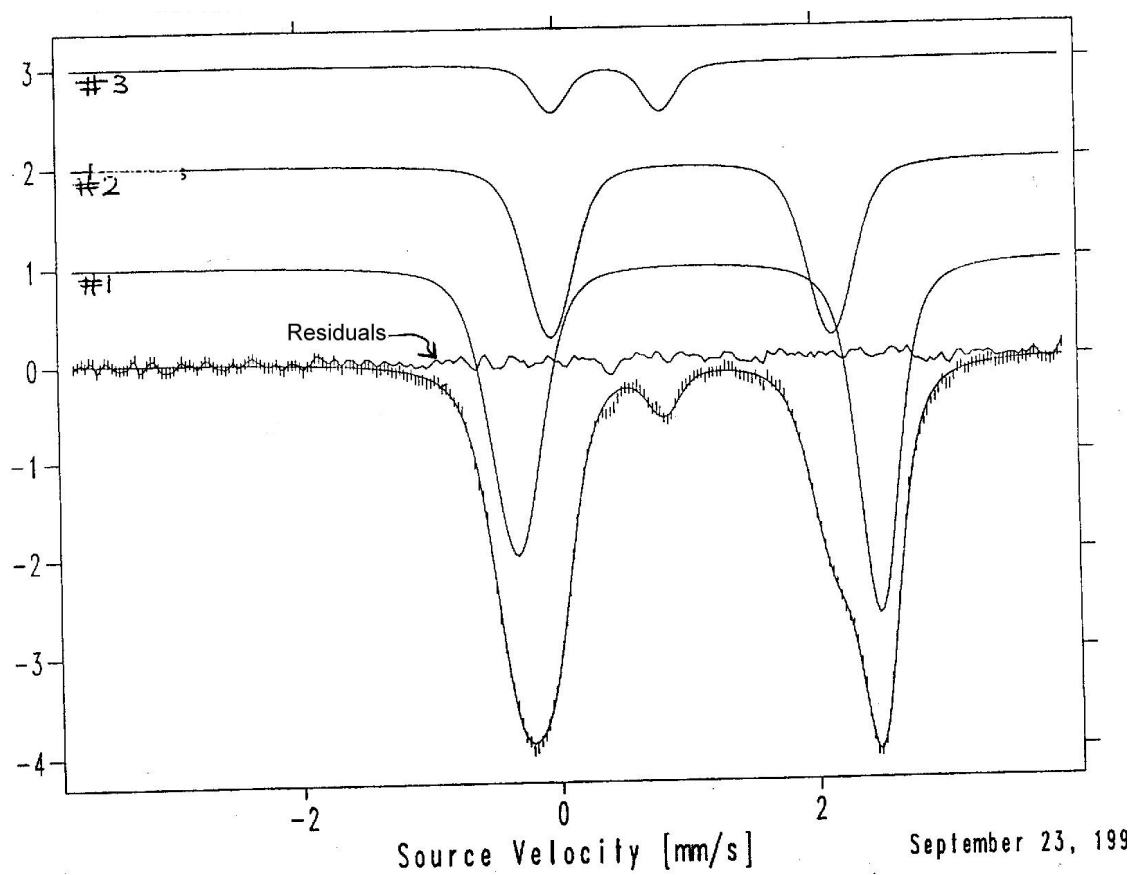


Fig B.1 Least squares fit with three quadrupole pairs as described in text.

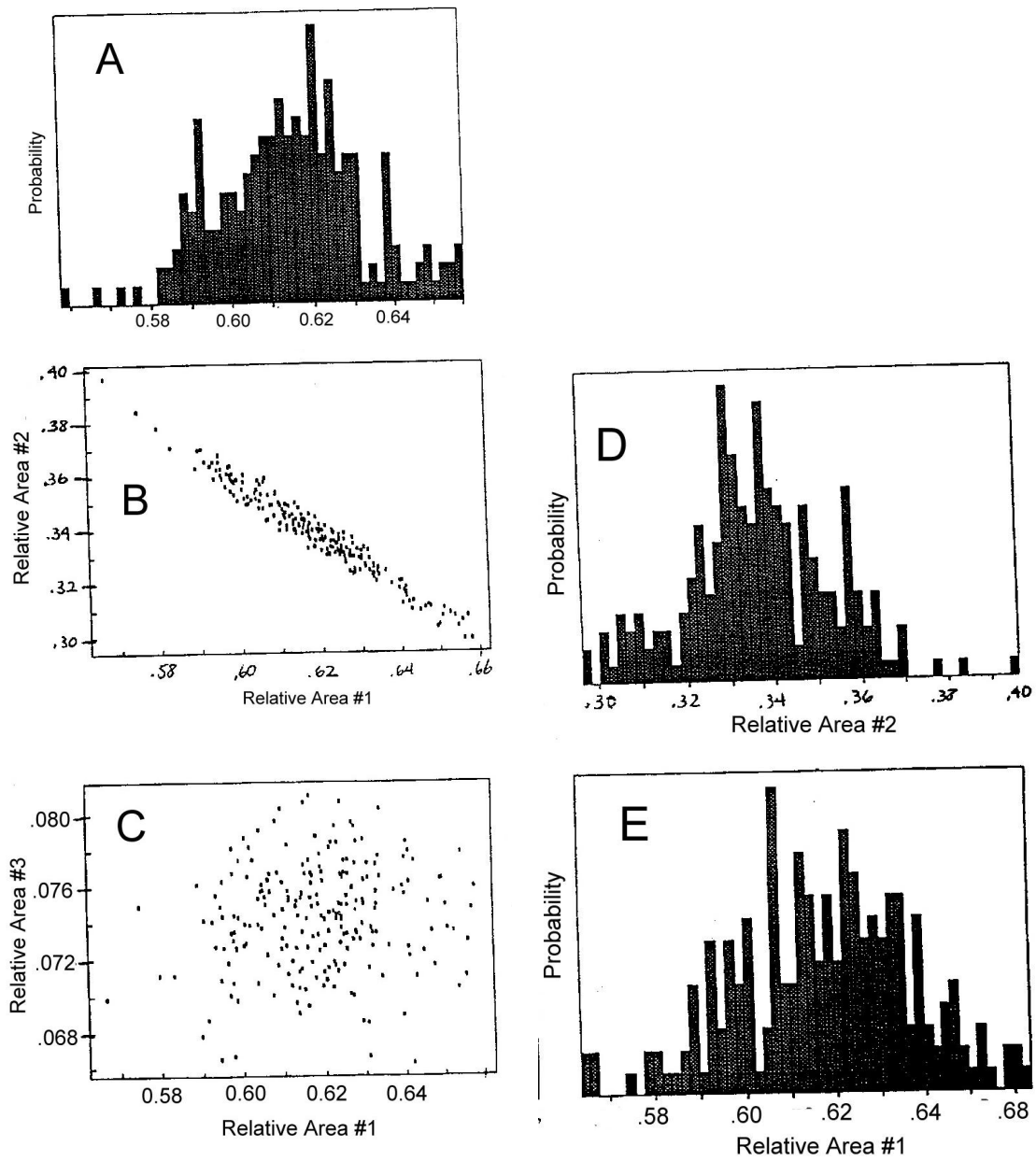


Fig B.2 Monte Carlo analysis as described in text

## APPENDIX C -- AVERAGING OVER MOLECULAR ORIENTATIONS

The molecules in the sample have some distribution of their orientation relative to the lab frame. For powder samples this distribution is random (but uniform) over all possible orientations. The lab frame is defined by the direction of any applied magnetic field (EZ-vector of Lab frame) and by the direction of the gamma beam (EX-vector of Lab frame). Most spectrometers have a randomly polarized gamma beam with its direction either parallel or perpendicular to the applied field. The parameter POL in the Data Header specifies under what conditions the data were collected. For the case when gamma beam is parallel to the applied field POL = 0; for perpendicular case POL = -1, etc. Pol parameter therefore characterizes the type of intensity calculation for the spectra (see Table C1 below).

Note: For zero applied field, set POL = 0.

Table C1

### Definition of POL parameter

POL	Usage
-3	Intensity tensor and intensity vector are to be calculated. No input for symmetry is necessary
-2	Powder mean value (isotropic symmetry by default); no input for symmetry is necessary
-1	Perpendicular configuration (split coil).
0	Parallel field configuration with unpolarized Gamma radiation.
1	Parallel field configuration with circular polarization.

To perform the numerical simulations efficiently WMOSS is considering a single type of local symmetry (common for all inequivalent Fe-positions). In this manner it defines the problem in terms of a coordinate frame fixed relative to the molecule. We label this frame XYZ. The distribution of orientations is simulated by setting up a grid of points on the unit sphere that specify the direction of the applied field relative to the molecular XYZ frame. The XYZ directions are chosen for convenience in terms of our theoretical model. For example, XYZ may be chosen in analysis to relate to the principal axes of the zero-field splitting tensor or the g-tensor, or crystal field tensor. While these directions do have physical significance and are fixed relative to the molecule, often they are not simply correlated with the geometry (local symmetry) of a given iron site.

The table below defines how the SYMMETRY and NTHETA parameters are used to specify the angular grid used to average over the orientations. For rapid

simulations, the goal is to average over the smallest portion of the unit sphere as is legitimate. The hyperfine interactions are independent of the sign of the applied field. Similarly, the absorption probability is independent of the sign of the direction of the gamma beam. Hence, a hemisphere is the largest solid angle ever averaged over. If the parameters of the theoretical model define a site with some degree of symmetry, then less of the hemisphere needs to be sampled. For example, if the local site is isotropic then only one point is required. Since the calculation time is very sensitive to the setting of the SYMMETRY parameter, the lowest value consistent with the symmetry defined by the hyperfine parameters should be used.

Note 1: For Models 1, 1-1 and 4, 4-1 if the SYMMETRY parameter is set properly then the simulated spectrum should be the same as that calculated for SYMMETRY = 4.

Note 2: Theoretical Models 5 and 5-1 permit different orientations of the effective  $H_{\text{int}}$  (therefore directions of effective uniaxial parameter  $D$  too) to the lab frame for each inequivalent Fe site. As these orientations do not necessarily coincide with any of the LAB axes and because these may or may not be made fixed in this frame (for example strong applied fields acting on anisotropic materials, textured materials, etc) such cases command in general a very thoughtful choice of the overall SYMMETRY model.

With SYMMETRY = 0 (e.g. 1-point integration grid), the Theoretical Models 1, 1-1, 4, 4-1, 5 and 5-1 can produce simulations of spectra for single crystals. Further options in Model 5 allow simulations to be done for 2D films or partially oriented polycrystalline samples. This allows for analysis of molecular magnets, or ferromagnets with randomly or non-randomly oriented domains, etc.

With  $H_{\text{int}} = 0$  (for spectra in slow relaxation regime) or  $H_{\text{int}} \neq 0$  (for spectra in fast relaxation regime) in Models 5 and 5-1, asymmetric quadrupole doublets as observed for single crystals can be simulated for any direction of the gamma beam relative to the crystal. A description of Model #5 may be found in Section 3.5.

Table C2

Definition of Orientation Grid via SYMMETRY and NTHETA parameters

SYMMETRY parameter	Symmetry needed at local site of powder sample.	TOTAL SOLID ANGLE OF GRID (X, Y, Z denote molecular or crystal coordinate frame. The grid points specify directions of applied field for which spectra are simulated.)	NGRID  Total number of grid points
0	O <sub>H</sub> (CUBIC, X=Y=Z)	SINGLE POINT (0,0,1)	1
1	D <sub>4H</sub> (TETRAGONAL, X=Y)	1-D ARC in XZ plane (Y=0)	NTHETA
2	D <sub>2H</sub> (ORTHORHOMBIC)	OCTANT (X, Y, Z > 0)	N <sub>oct</sub>
3	C <sub>2</sub> (MONOCLINIC)	QUADRANT (X, Y > 0)	2*N <sub>oct</sub>
4	C <sub>1</sub> (TRICLINIC)	HEMISPHERE (Y > 0)	4* N <sub>oct</sub>

## Notes:

1. In the Edit Parm procedure, the SYMMETRY and NTHETA parameters are found on page 3.
2. For SYMMETRY = 2, the grid used by WMOSS spans one octant and may be described as a “igloo” or “bowling pin” pattern where NTHETA is the number of rows in the theta direction. For SYMMETRY = 2 and NTHETA = 4, NGRID = 10.
3. The number of grid points over an octant is  

$$N_{\text{oct}} = \text{NTHETA} * (\text{NTHETA} + 1) / 2$$
4. NTHETA should be large enough so that the simulated spectrum is independent of NTHETA.

## APPENDIX D -- VARIOUS USAGE TRICKS

1. Trick for text input at prompts (ex. Data or Param Save or Custom PS Plot procedures). These procedures contain fields where default entries already exists. The program offers two choices:
  1. start typing the wished filename. The default filename will automatically disappear and you will actually type from the beginning), or
  2. **First** press LEFT or RIGHT ARROW. This will get the cursor at the end of the default string, then
    - o press BACKSPACE as needed to partially delete the string (ex: filename), then
    - o type the remaining of the new name that you wish (do not forget to add the file extension).
2. The same above trick for entering new text or modifying it in spectra's Comment lines within Edit Data Header procedure.
3. Same above trick for changing the displayed name of spectra. Execute the Edit Data Header procedure; 1 line above the Comment you find the the data name field. You may change it as needed. Note, this is not the name of the file on disk (if saved at all). If you wish do so then you must execute Data Save and at prompt input the wished filename (including the extension).
4. Either Mouse or Keyboard can be used in MASK and ZOOM windows. Set your own preference in WMOSS.CFG. The default is Mouse = ON.
5. With Custom PS Plot procedure start always by selecting the spectra that has the largest width in [mm/s] units.

## APPENDIX E -- CONCISE TUTORIALS

Many experienced users might surely be very familiar with all parameters within this program and with various theories behind using them. However they might not be familiarized with the work-flow, capabilities or limits of the WMOSS program. The following provided concise sequences is an attempt to help them avoid unnecessary feelings of frustration or do unnecessary steps.

Important in the following sequences is therefore only the “concept” e.g. the order of the program choices which the user may normally follow. The corresponding details for each steps are found in the Tutorial chapter.

### E1. From Start to Fit

#### 0. Start WMOSS4

1. File -> ChangeDir : directory where spectra are stored
2. File -> Data Load : bring in the List all spectra needed
3. File -> Parm Load : bring in the appropriate standard parameter file
4. File -> Parm Save : rename the parameter file; will be saved on the same directory as loaded spectra

#### 5. Analysis -> Edit Param:

- Press [PageDown] and set the size of the electronic problem (model dependent)
- set the number of inequivalent Fe-positions; start with a small number
- Press again [PageDown] to set rough Global parameters
- Press again [PageDown] to set rough Local parameters for site 1
- Press again [PageDown] to set rough Local parameters for site N

#### 6. Analysis -> Flash:

- refine parameters

#### 7. Analysis -> Edit Param (again);

- in first page set the number of iterations and N-anneal(!), fit method, etc.

N-anneal will make a series of fits using each time a different starting points in parameters; from this sequence at the end the procedure will select the set of parameters that provided the best  $R_{chi}^2$ . This set of parameters will be automatically updated in Parameter file in RAM, at the end of each Global iteration. If useful then save it to disk (via Parm Save, eventually using a different name). For any case, the \*.po file will contain all parameter datasets of each N-anneal step. Analysis of this file will help avoiding false local minima.

- Press [PageDown] to set the desired free (fittable) or fixed parameters, or implement various constraints of Global parameters

- Press again [PageDown] to set the desired free (fittable) or fixed parameters, constraints for Local parameters, etc.

#### 8. Options : select if subsites will be visible during Fit; or if the result of fit for each subsite to be reported in List at the end.

#### 9. Analysis -> Do Fit

#### 10. Analysis -> Flash : View the result of fit procedure.

11. Feel free to press any key during Fit for making a Pause and go through all spectra involved (in case simultaneous fit is performed) to check for partial results. Resume the Fit with Continue or Abort it.

## E2. Saving the input with initial values for float parameters?

First, to “speak” in WMOSS’s language, note that that relevant input parameters for the Do Fit procedure are defined only by (order is arbitrary):

- the fixed Real parameters, either local or global.
- the fixed global Integer parameters (like symmetry, number of states or the dimension of the electronic problem)
- the set of physical and theoretical external conditions (represented by the fixed constraints applied, or temperature, applied fields, relaxation, etc)
- the fixed boundaries of the floating parameters.

As you already observed, the keyword above is “fixed”.

The least important, for a properly defined problem, is the set of starting values for the floating parameters. One should check this, of course. But starting with all parameters set free to float and attempting to observe the behaviour of the output parameter values -- even when the initial value of only one parameter is changed at a time -- will usually lead to a longer analysis time, not a shorter one.

Of course, the first step done by the Do Fit is to record the  $\chi^2_R$  of the simulated spectra obtained with initial values of parameters. From this point on, the algorithm used by Do Fit procedure to “scan” the boundaries is only dependent on the Fit Method choice used. To avoid situations of false minimum due to initial parameter values, WMOSS can do N-anneal, which means in fact scanning the initial values. This approach is not 100% error proof, but is highly effective for problems with small number of float parameters, large N-anneal steps and also using as much as possible of the provided capabilities: six simultaneous spectra fits, masking the error prone regions in spectra, etc...

So, under most circumstances, the Do Fit procedure on a properly defined problem (e.g. also not a very complex one) will normally lead you iteratively closer to a “true” minimum. Saving/rename the RAM parameter file between iterations each time you manage to **fix** a given parameter should assure you a well documented and reproducible analysis.

To help cope with this situation, WMOSS4 allows 6 lines of comments, each with 80 characters. Starting with ver.F it also allows 40 characters in spectra or parameter filenames.



## APPENDIX F -- OVERVIEW OF WMOSS4 ver. F

Max. Nr. of data points	:	1024
Max. Nr. of spectra in List, Stack or in Load Data window :		128
Max. Nr. of parameter files in Load Param window	:	128
Max. Nr. of characters in saved filenames	:	40
Max. Nr. of visible characters in filenames within WMOSS	:	20
Max. Nr. of inequivalent Fe sites	:	enough (14)
Max. Nr. of spectra for simultaneous fit	:	enough (6)
Max. Nr. of free parameters for Fit (caution!!!)	:	all
Max. Nr. of <sup>57</sup> Fe calibration files stored	:	enough (999)

### Spin hamiltonians:

1. Full : Yes (in Models 1, 1-1 and 4, 4-1) - paramagnetic centers
2. Effective (uniaxial) : Yes (in Models 5 and 5-1) - molecular magnets, isotropic or aligned magnetic materials, etc

### Distributions:

1. Quadrupole only : Yes (Model 6)
2. Hyperfine only : Yes (Model 7)

### MonteCarlo analysis:

3. Quadrupole only : Yes (Model 6)
4. Hyperfine only : Yes (Model 7)

### Theoretical Models : 10

1. a system with a single electronic spin  $S \leq 9/2$  and 1 to 14 Iron sites
- 1-1. idem as 1. but Relax. Parameter is local (separate for each inequivalent Fe site)
2. multiple individual lines
3. multiple quadrupole pairs
4. a system with two coupled electronic spins,  $S_{\text{tot}} \leq 5$  and 1 to 14 Iron sites
- 4-1. idem as 4. but Relax. Parameter is local (separate for each inequivalent Fe site)
5. molecular magnets or magnetic domains with 1 to 14 Iron sites with EFG and fixed internal magnetic field in relation to a symmetry axis
- 5-1. idem as 5. but Relax. Parameter is local (e.g. separate for each inequivalent Fe site), plus a local effective uniaxial electronic term  $D_{\text{eff}}$  (shares properties of the effective  $H_{\text{int}}$ ).
6. Quadrupole Splitting Distribution / Voigt based fitting. Monte Carlo available.
7. Hyperfine Field Distribution / Voigt based fitting. Monte Carlo available.

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