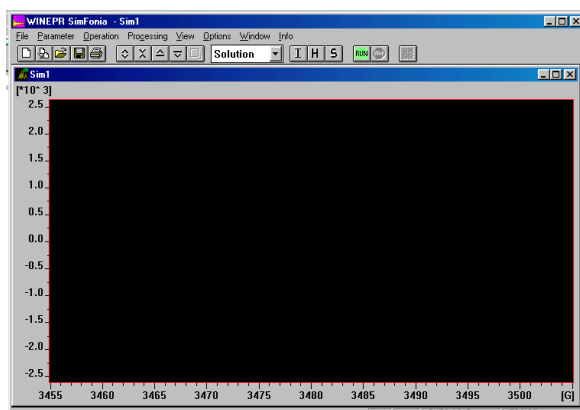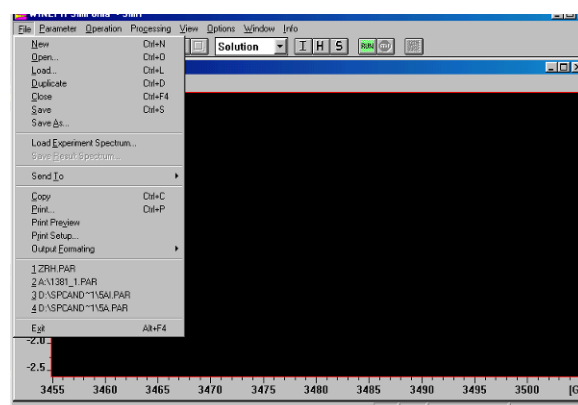# Spectrum simulation using the Bruker program *Simfonia*

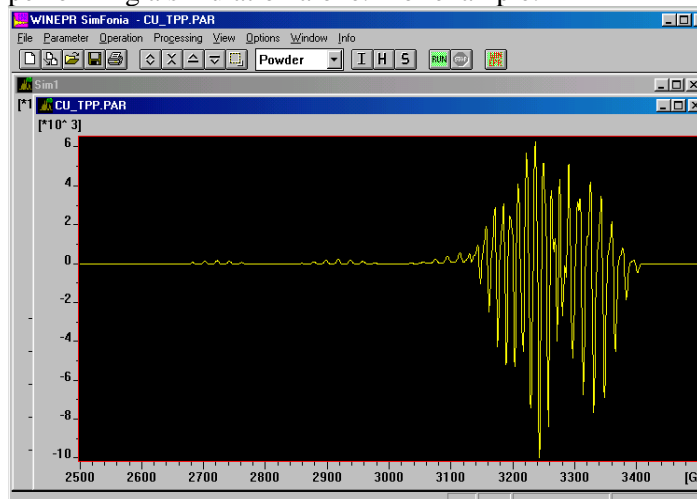|	
This is the start screen: and it will enable simulation of fluid **solution** (*i.e.* isotropic) spectra.	To load an experimental spectrum, click on <File>:

and use <Load> or <Open>. N.B. Uncheck <automatic field detection> and select values for <center field> and sweep width> if just performing a simulation alone. For example:
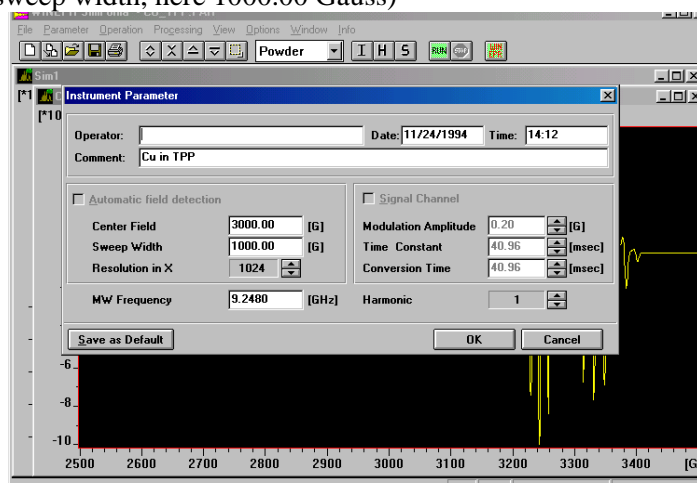

note, this is a **powder** spectrum and this has been recognised by the program.

The 3 buttons at the top of the screen labelled I, H and S control the variables.
I contains the instrumental parameters, including:

- the microwave frequency (here 9.2480 GHz)
- the centre field (here 3000.00 Gauss)
- the scan range (sweep width, here 1000.00 Gauss)

If you are investigating spin-Hamiltonian parameters in the absence of an experimental spectrum, these are the 3 instrumental parameters that must be set.

Example – simulation of a fluid solution spectrum of a vanadyl (VO^{2+}) complex, with typical spin-Hamiltonian parameters of g_{iso} = 1.975, A_{iso} = 100.0 Gauss, where ^{51}V is 99.75% naturally abundant and has $I = {}^{7}/_{2}$. A typical X-band frequency of 9.25 GHz will require a <Centre Field> of 3300.0 Gauss, and the pattern will be contained within a <Sweep Width> of 1000.0 Gauss. Typically the observed linewidths in the spectrum are *ca.* 20 Gauss.

1. Select the <Solution> option, deselect <Automatic field detection>.
2. Enter the <Sweep Width>, <Centre Field> and <MW Frequency> on the Instrument parameter screen and press <OK>.
3. Click the H button to access the Hamiltonian Parameters. Click <Get Element> to reveal a Periodic Table, and clicking on Vanadium will automatically generate the nuclear spin, abundances and nuclear g-value of each isotope. These could be entered independently to generate a fictitious system, e.g. considering a 100% abundant I = $^{7}/_{2}$ isotope.
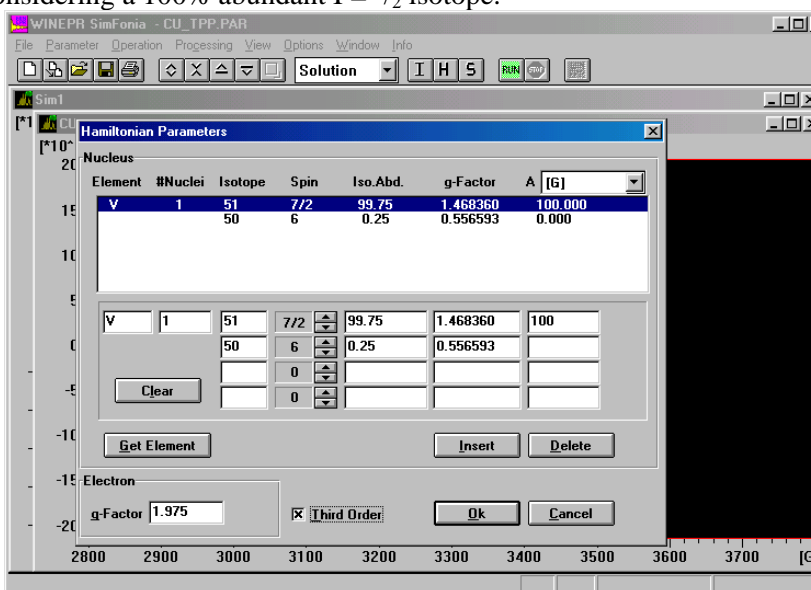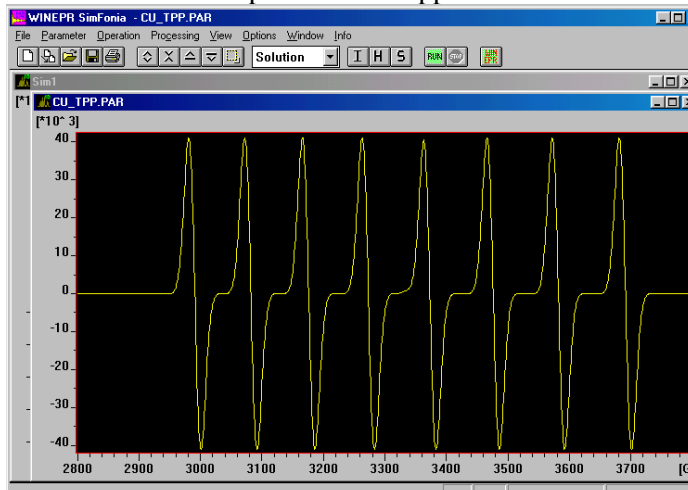

Enter the <g-Factor> of 1.975, the <A> value of 100 Gauss and press <Insert>. Click on the <Third Order> box, which will give a more accurate simulation. The press the <OK> button to enter the parameters.

4. Click the S button to reveal the Shape Parameters and enter 20 for the <Linewidth>. The press the <OK> button to enter the parameters.
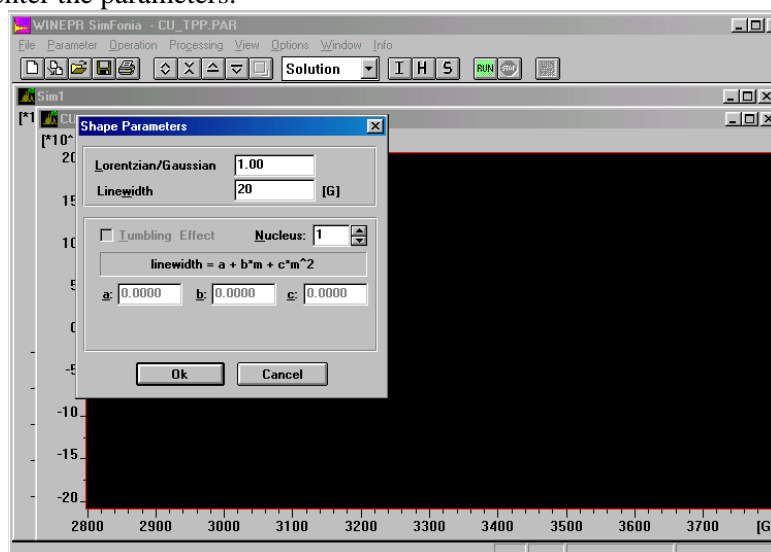
5. Press the green Run button and an 8 line spectrum will appear almost immediately.

Exercise, Day 1: Simulation of isotropic spectra, $S = \frac{1}{2}$:

A. **Effect of simulation parameters for 2p-based radicals**

Investigate the form of X-band spectra (9.25 GHz) as a function of linewidth (initially say 2.0, 1.0, 0.5, 0.2 Gauss) for the following examples of single electron species:

(a) $g = 2.0023$ with coupling to $n \times I = \frac{1}{2}$ @ 5 Gauss, for $n = 1, 2, 3, 4, 5$ – compare this to coupling patterns in proton NMR spectra

(b) $g = 2.0026$ with coupling to $4 \times I = \frac{1}{2}$ @ 4.1 G, $4 \times I = \frac{1}{2}$ @ 3.1 G and $4 \times I = \frac{1}{2}$ @ 0.46 G (*a carbon centred radical*)

(c) $g = 2.0026$ with coupling to $6 \times I = \frac{1}{2}$ @ 3.9 G, $4 \times I = \frac{1}{2}$ @ 3.0 G and $4 \times I = \frac{1}{2}$ @ 1.4 G (*a carbon centred radical*)

(d) $g = 2.006$ with coupling to $1 \times I = 1$ @ 15.0 G – what is the effect of changing the lineshape between Gaussian and Lorentzian? (*an oxygen centred radical*)

(e) $g = 2.00354$ with coupling to $2 \times I = 1$ @ 9.0 G – what is the effect of changing the lineshape between Gaussian and Lorentzian? (*a nitrogen centred radical*)

B. **Effect of simulation parameters for 3d/4d transition metal paramagnets**

Investigate the form of spectra as a function of frequency and of linewidth. S-band at 4.5 GHz, X- band at 9.25 GHz, K-band at 24.0 GHz, Q-band at 35.0 GHz and W-band at 94 GHz. Make sure that you select appropriate parameters for the <Centre Field> and <Sweep Width> to ensure that you simulate the complete spectrum.

(f) $g = 1.97$ with coupling to $1 \times I = \frac{7}{2}$ @ 108 G and starting with $\Delta B_{\text{p-p}} \approx 20$ G – (i) what is the effect of using "third order" in the <Hamiltonian Parameters> window; (ii) how do the spectra change on introducing a tumbling effect in the shape parameters, note $a > b > c$? (*these are typical parameters for a VO^{2+} complex*)

(g) $g = 2.10$ with coupling to $1 \times I = \frac{3}{2}$ @ 79 G and starting with $\Delta B_{\text{p-p}} \approx 8$ G – (i) what is the effect of using "third order" in the Hamiltonian parameters; how do the spectra change on (ii) introducing a tumbling effect in the shape parameters, note $a > b > c$, (iii) introducing both isotopes of Cu using <Get Element> from the <Hamiltonian Parameters> window (note that the tumbling effect cannot be activated), and the hyperfine coupling parameters are in the ratio of the nuclear g-values? (*these are typical parameters for a Cu^{2+} complex*)

(h) Repeat part (g) and include an additional coupling to $2 \times I = \frac{1}{2}$ nuclei.

(i)   Select molybdenum using <Get Element> from the <Hamiltonian Parameters> window, and use $g = 1.95$ and a hyperfine coupling to ^{95}Mo of 60 G – explain the form of the spectrum

C. Simulation of experimental EPR spectra:

Connect to the server (Workshop personnel will show you how to do this), <open> or <load> each of the following examples in turn, use your directly measured g- and A-values as a starting point to simulate the spectrum, assessing the goodness of fit by eye, by overlaying the experimental and simulated spectrum on the screen.

(i) Semiquinones from 1,2- and 1,4-dihydroxybenzene
(ii) [Cu(dithiocarbamate)$_2$] and [Cu(dithiophosphate)$_2$]
(iii) [VO(acetylacetonate)$_2$]

Files for running *Xsophe* under *Linux* have been set up for you for exercise (f) onwards each day, and when you are confident using *Simfonia* you should then try using the more flexible *Xsophe*.

Exercise, Day 2. Simulation of anisotropic spectra, $S = \frac{1}{2}$:

A. Effect of simulation parameters for 3d/4d transition metal paramagnets

Investigate the form of typical powder spectra of (i) Vanadyl (VO^{2+}), (ii) Copper(II) (Cu^{2+}) and (iii) nitroxide radical as a function of applied microwave frequency.

Typical spin-Hamiltonian parameters are:

| Species	g_1	g_2	g_3	A_1/Gauss	A_2/Gauss	A_3/Gauss	$g_\perp$	$A_\perp$/Gauss
VO^{2+} ($I = {}^7/_2$)	1.94	1.975	1.985	200	35	55	1.98	45
Cu^{2+} ($I = {}^3/_2$)	2.30	2.01	2.004	200	5	5	2.05	5
>NO$^\bullet$ ($I = 1$)	2.002	2.006	2.008	32	1	1	2.007	1

Use the following microwave frequencies:
S-band at 4.5 GHz, X- band at 9.25 GHz, K-band at 24.0 GHz, Q-band at 35.0 GHz and W-band at 94 GHz. Make sure that you select appropriate parameters for the <Centre Field> and <Sweep Width> to ensure that you simulate the complete spectrum. For the metal-containing spectra use a linewidth of *ca.* 15 Gauss, and *ca.* 5 Gauss for the nitroxide. You should investigate axial spectra first, followed by rhombic spectra, the latter will take considerably more time for adequate simulations.

There are some differences in entering the parameters for the simulation of powders compared to fluid solutions. Here are two examples for spectra of VO^{2+}.

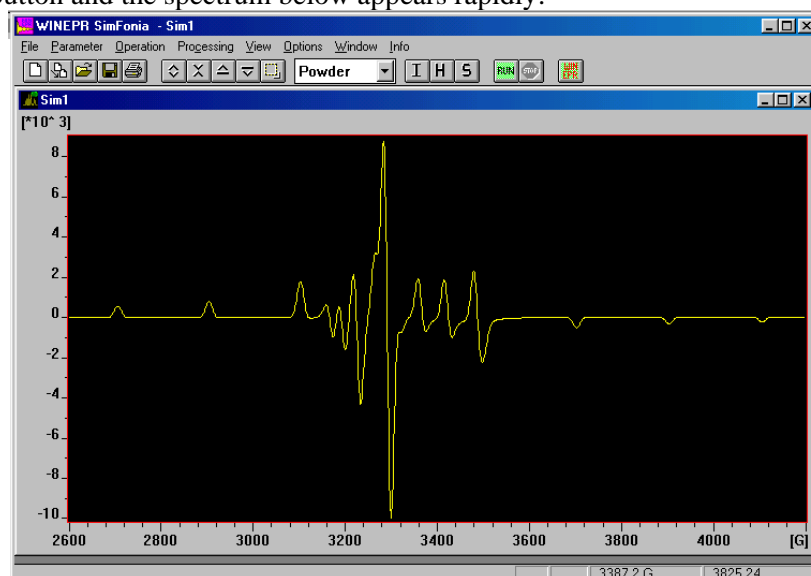**Example:** Axial VO^{2+} at X-band frequency
1. Set a Powder simulation
2. Set the Instrumental parameters as: MW frequency = 9.25 GHz, <Centre Field>= 3400.0 Gauss, and <Sweep Width> = 1600.0 Gauss
3. The Hamiltonian Parameters screen will look different to that seen for a Solution simulation. Enter the spin-Hamiltonian parameters as: A(x,x) = 45, A(y,y) = 45 and A(z,z) = 200 Gauss, tick the <Second Order> box, enter the number of nuclei as 1, select the nuclear spin as $^7/_2$ (note that Simfonia is not written to perform a powder simulation for more than one spin system). Enter the g-values as: g(x) = 1.98, g(y) = 1.98, g(z) = 1.94, set the electron spin to ½ and enter the <Number of Theta> as 90 – this parameter is the number of single orientation spectra that are added together to yield the convolved powder spectrum. This number is bigger for narrow line spectra or for wide sweep widths than it is for broad line spectra or for narrower sweep widths.
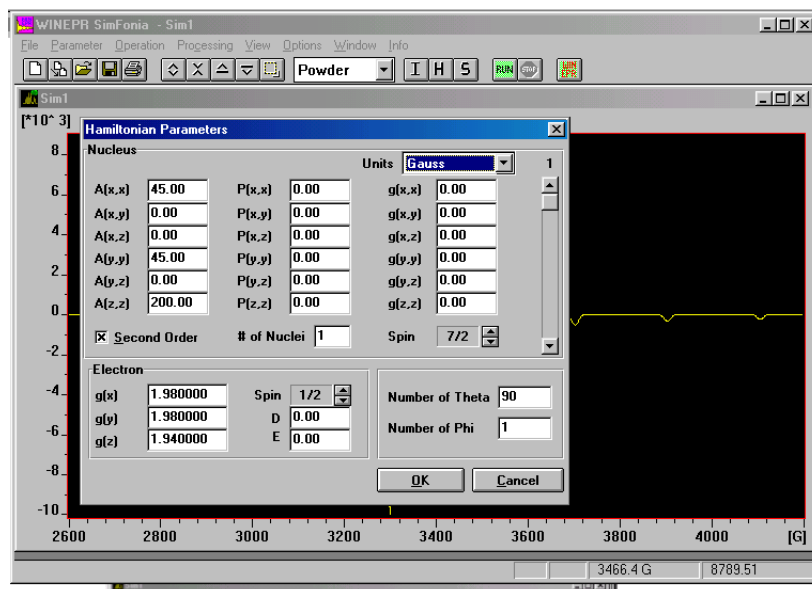
4. The screen for the Shape Parameters will also look different; there are 3 <Linewidth> parameters, enter 15 Gauss for each one.
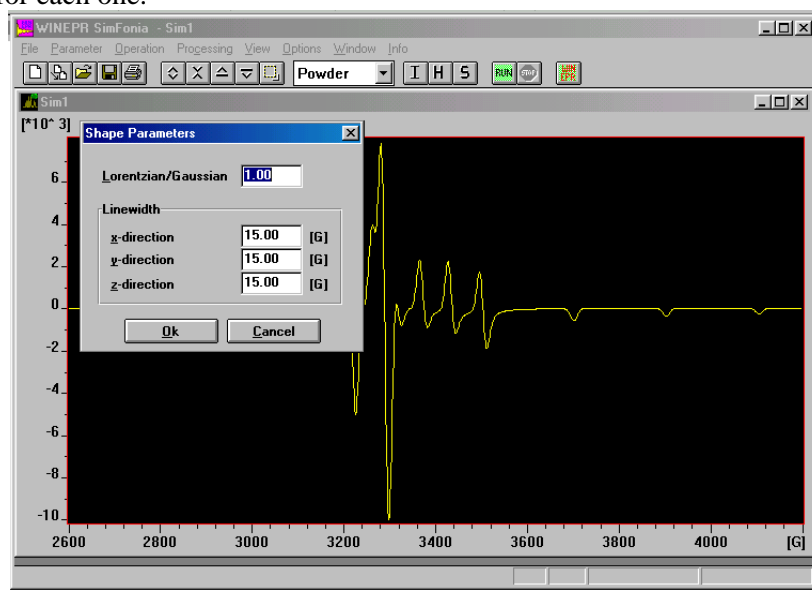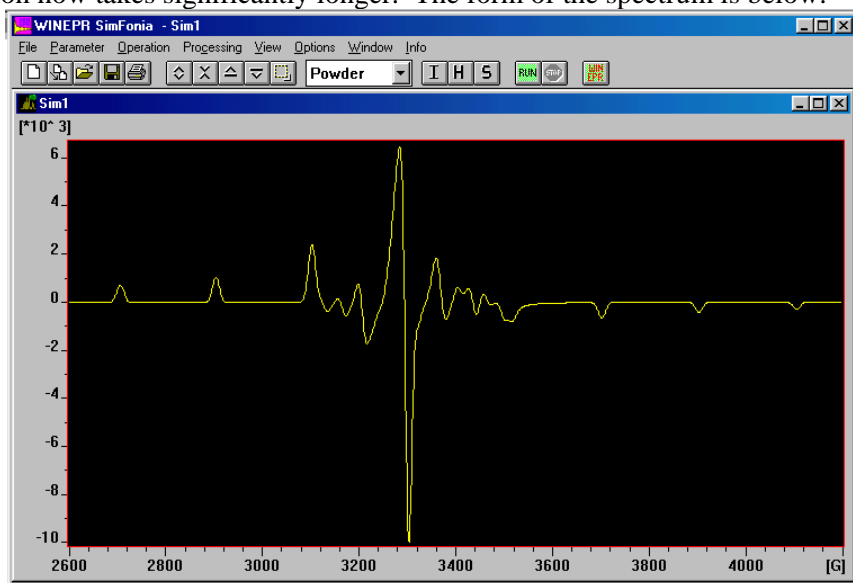

5. Press the Run button and the spectrum below appears rapidly:

Example: Rhombic VO^{2+} at X-band frequency:

1. Enter the Hamiltonian Parameters, but also enter <Number of Phi> as 90. Press the Run button, and the simulation now takes significantly longer. The form of the spectrum is below:

B. Simulation of experimental EPR spectra:

Connect to the server (Workshop personnel will show you how to do this), <open> or <load> each of the following examples in turn, use your directly measured g- and A-values as a starting point to simulate the spectrum, assessing the goodness of fit by eye, by overlaying the experimental and simulated spectrum on the screen.

(i) Frozen solution TEMPO
(ii) Frozen solution [Cu(dithiocarbamate)$_2$] and [Cu(dithiophosphate)$_2$]
(iii) Doped Tutton's salt (L, S, X, K, Q, W-bands)

**Exercise, Day 3, simulation of $S > \frac{1}{2}$ spectra:**

A. Effect of simulation parameters on S > ½ spectra

Investigate the form of typical powder spectra of (i) for a given S, fix D and vary hν, (ii) for a given S, fix hν and vary D and (iii) for fixed D and hν vary S.

Use an isotropic g-value = 2.00 and use the following microwave frequencies:
S-band at 4.5 GHz, X- band at 9.25 GHz, K-band at 24.0 GHz, Q-band at 35.0 GHz and W-band at 94 GHz. Suggested variations are $S = 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \frac{7}{2}$; $D = 30, 100, 200, 300, 400, 500, 1000$ Gauss. These will be axial spectra. You can investigate rhombicity by making the E parameter non-zero, but its value must not exceed $\frac{1}{3}$ of the value of D. The Simfonia program uses perturbation equations and will only give accurate simulations when h$\nu > D$. Below, D = 100 G, for S = 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, Q-band frequency, a-d, respectively.
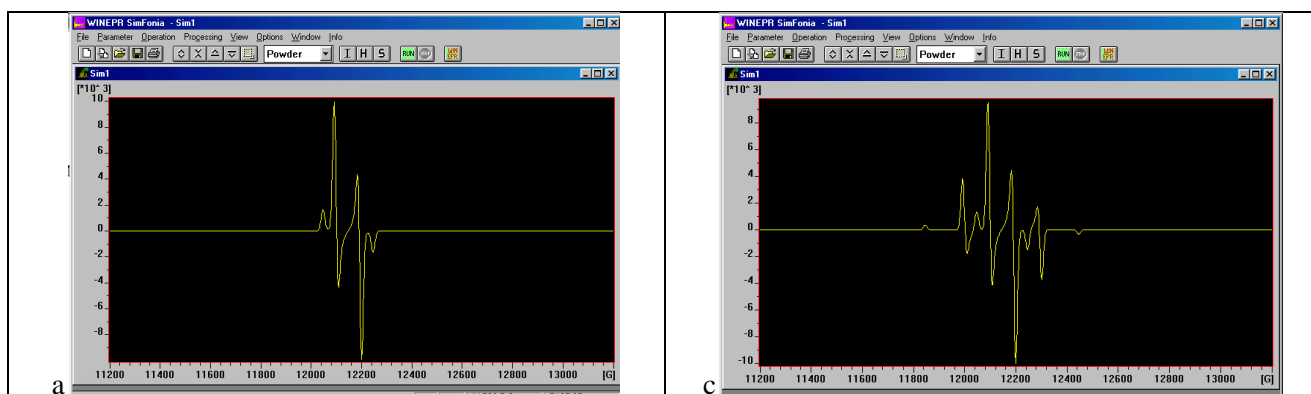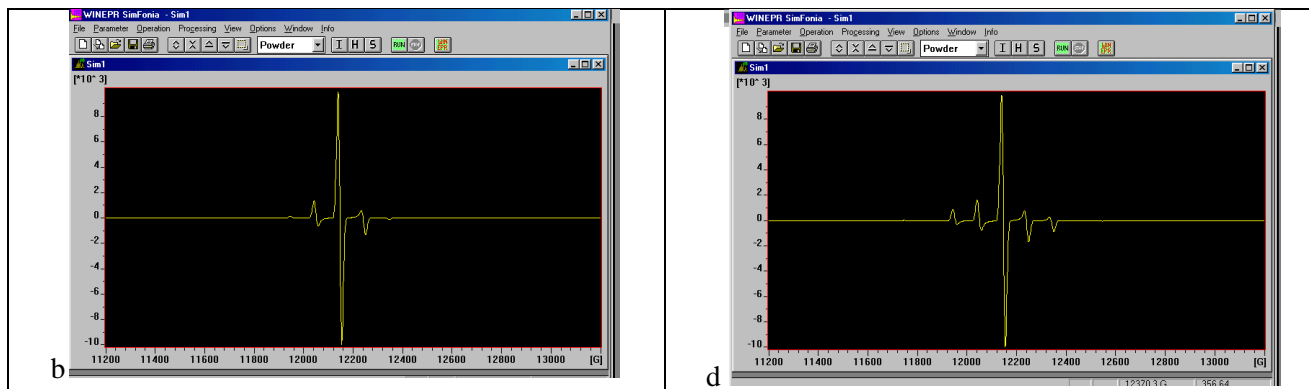
b

d

B. Simulation of experimental EPR spectra:

Connect to the server (Workshop personnel will show you how to do this), <open> or <load> each of the following examples in turn, use your directly measured g-, D- and A-values as a starting point to simulate the spectrum, assessing the goodness of fit by eye, by overlaying the experimental and simulated spectrum on the screen.

(i) Mn^{2+} in plasticine
(ii) Mn^{2+} in NH_4Cl

Notes:

Graphical method for obtaining hyperfine coupling parameters from "second order" spectr

$$B(m_I) + K_{iso}.m_I = B_0 - \frac{K_{iso}^2}{2B_0} [{}^{63}/_4 - m_I^2], \qquad (1)$$

and the next line $B(m_I + 1) + K_{iso}.(m_I + 1) = B_0 - \frac{K_{iso}^2}{2B_0} [{}^{63}/_4 - (m_I + 1)^2], \qquad (2)$

and then subtract the higher field expression from the lower field one to give

$$[B(m_I + 1) - B(m_I)] + K_{iso} = \frac{K_{iso}^2}{2B_0} [(2m_I + 1)], \qquad (3)$$

(ii)   hence **plot a graph of the separation between adjacent pairs of lines *versus* the value of (2m$_I$ + 1)**, where m$_I$ is the value appropriate to the lower field line of the pair.

(iii)   compare the equations:

$$y = mx + c \quad \text{and} \quad [B(m_I + 1) - B(m_I)] = \frac{K_{iso}^2}{2B_0} [(2m_I + 1)] - K_{iso}$$

(iv)   hence the slope of the best line through the seven points is $\frac{K_{iso}^2}{2B_0}$ and the intercept is -K$_{iso}$.

Calculate g$_{iso}$ by using the value of the slope obtained back in equation (1) as a perturbation.

(v)   report the g$_{iso}$ value from the relation $g_{iso} = \frac{0.7145 . \nu(GHz)}{B_0 (kG)}$ and K$_{iso}$ as calculated is in

units of Gauss and can be converted to energy units (cm^{-1}) by the relation A_{iso} (cm^{-1}) = $g_{iso} \times \beta_e \times K_{iso}(G) = g_{iso} \times 4.66858 \times 10^{-5} \times K_{iso}(G)$. Note: the numerical value of K$_{iso}$ and A$_{iso}$ are very similar if the latter is expressed, conventionally, in units of 10^{-4} cm^{-1}.

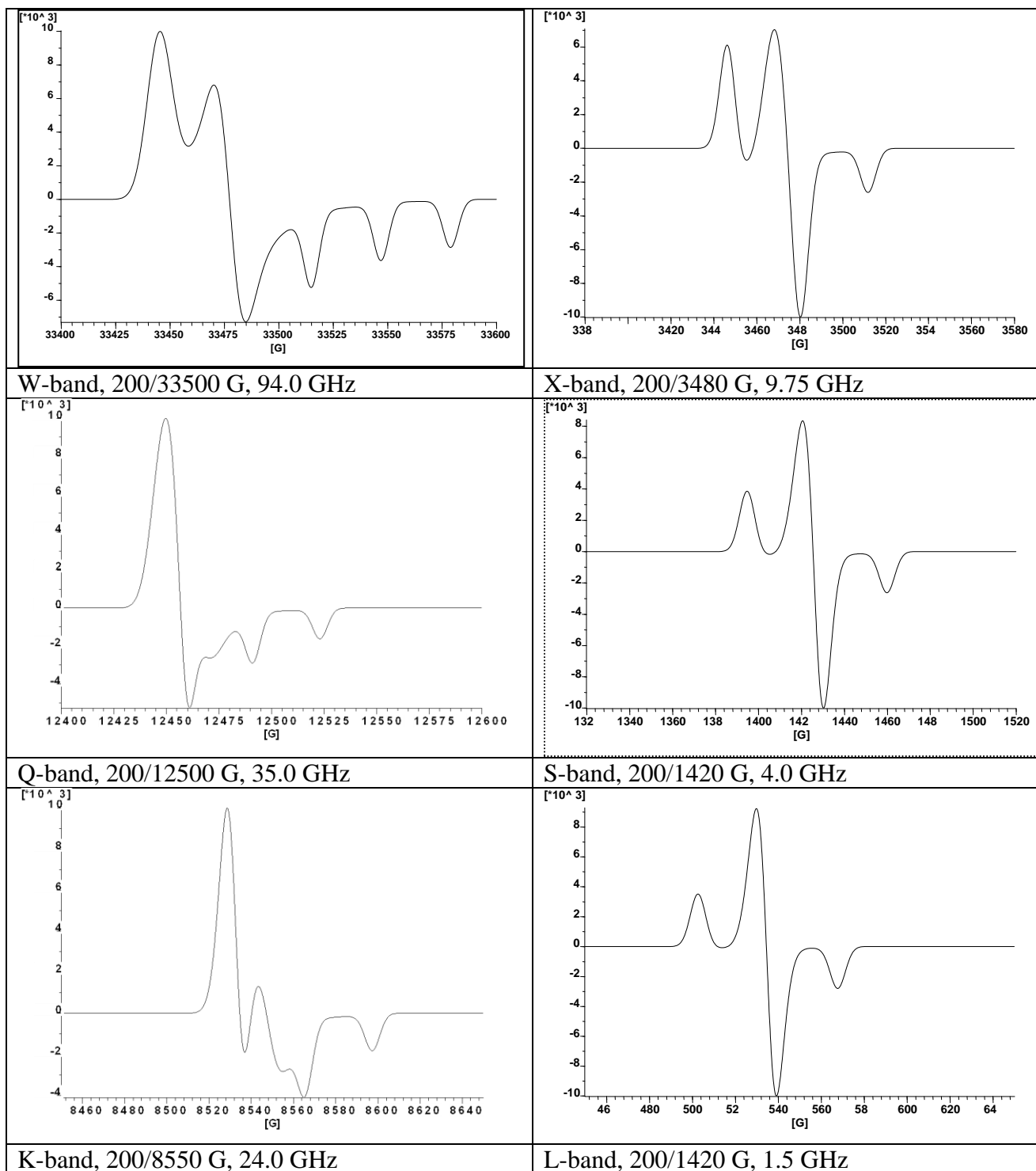| B_r (Gauss)	m_I	$2m_I + 1$ (lower)	δB_r	$[{}^{63}/_4 - m_I^2]$	$m_I \times K_{iso}$	$\frac{K_{iso}^2}{2B_0} [{}^{63}/_4 - m_I^2]$	B_0
2968	$-{}^7/_2$			3.5	-380.5	6.4	3354.9
3066	$-{}^5/_2$	-6	98	9.5	-271.8	17.5	3355.3
3167	$-{}^3/_2$	-4	101	13.5	-163.0	24.8	3354.8
3272	$-{}^1/_2$	-2	105	15.5	-54.4	28.5	3354.9
3381	$+{}^1/_2$	0	109	15.5	54.4	28.5	3355.1
3493	$+{}^3/_2$	2	112	13.5	163.0	24.8	3354.8
3609	$+{}^5/_2$	4	116	9.5	271.8	17.5	3354.7
3729	$+{}^7/_2$	6	120	3.5	380.5	6.4	3354.9
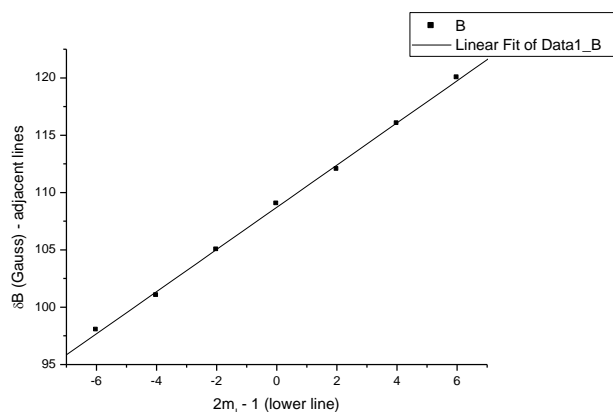
Intercept = 108.7 Gauss = -K$_{iso}$,

slope = 1.839

Average B$_0$ = 3354.9, measured at

9.250 GHz,

gives g$_{iso}$ = 1.970,

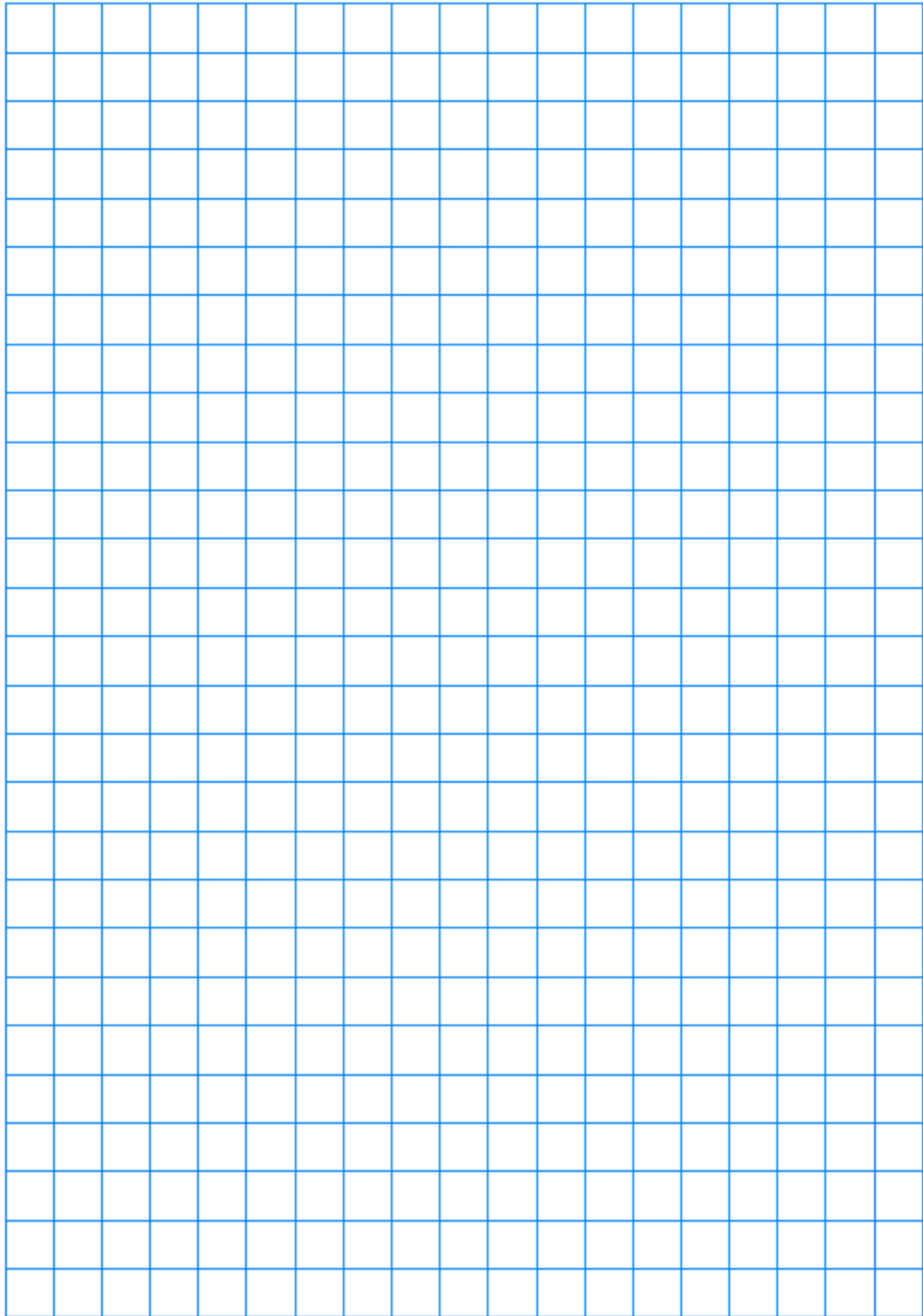∴ A$_{iso}$ = 99.97 x 10^{-4} cm^{-1}.

Simulated spectra for a nitroxide using "Simfonia"

$g_x = 2.002$, $g_y = 2.006$, $g_z = 2.008$, $A_x = 32$ G, $A_y = 1$ G, $A_z = 1$ G, $I = 1$
no. of theta = 45, no. of phi = 45
Lorentzian/Gaussian = 1.00, linewidths: x = 7, y = 11, z = 11

W-band, 200/33500 G, 94.0 GHz

X-band, 200/3480 G, 9.75 GHz

Q-band, 200/12500 G, 35.0 GHz

S-band, 200/1420 G, 4.0 GHz

K-band, 200/8550 G, 24.0 GHz

L-band, 200/1420 G, 1.5 GHz

Free resources from www.mathsphere.co.uk