# Simulations of Powder Spectra using SimFonia

# General considerations

Use Powder option only if no molecular motion is present: Powder and Glass Spectra

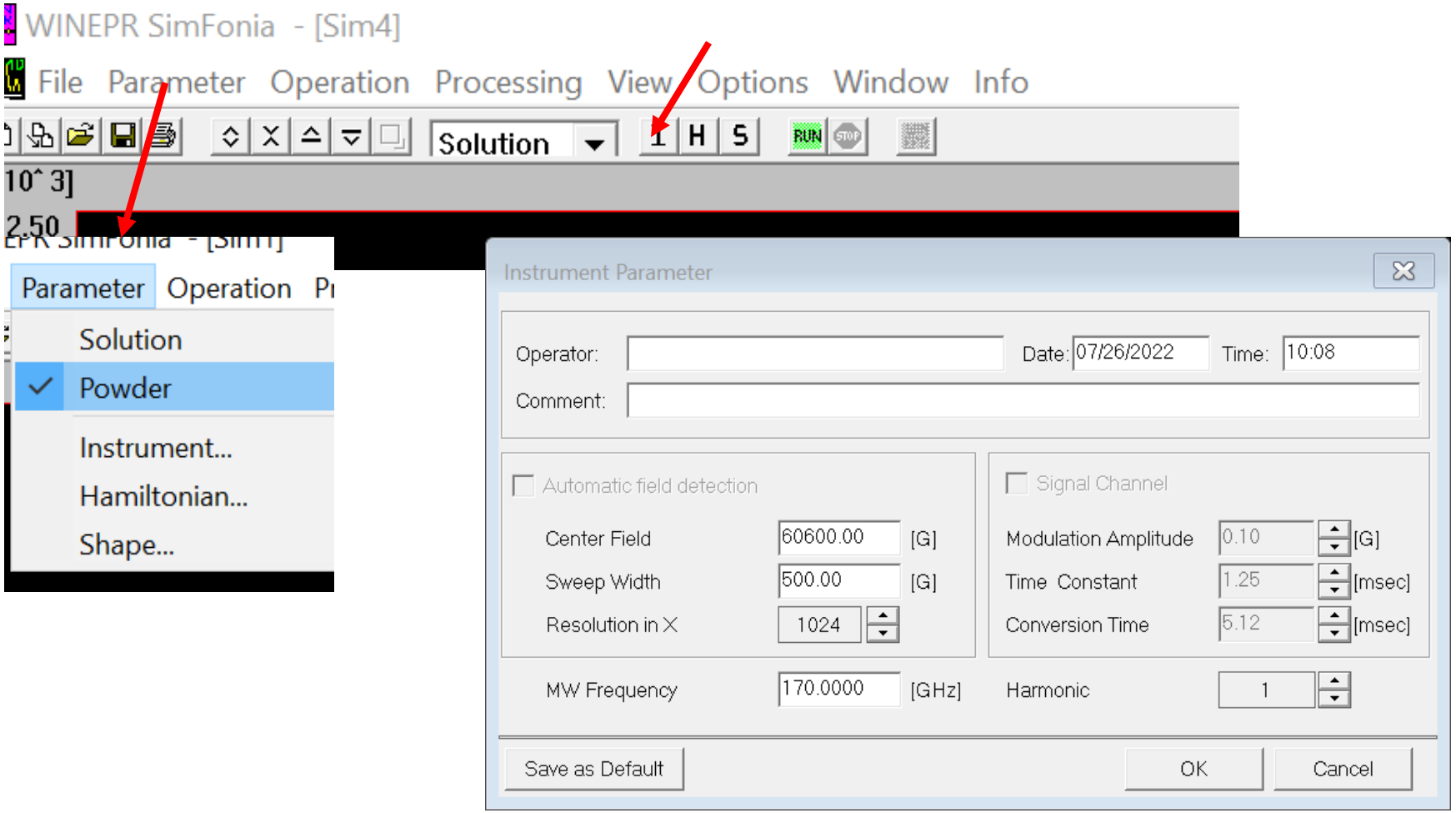
The calculation algorithm is based on the perturbation theory:
- Use ‘higher order’ option if large hyperfine splitting are present (e.g $Mn^{2+}$, $VO^{2+}$)

Only allowed transitions are simulated – no forbidden transitions

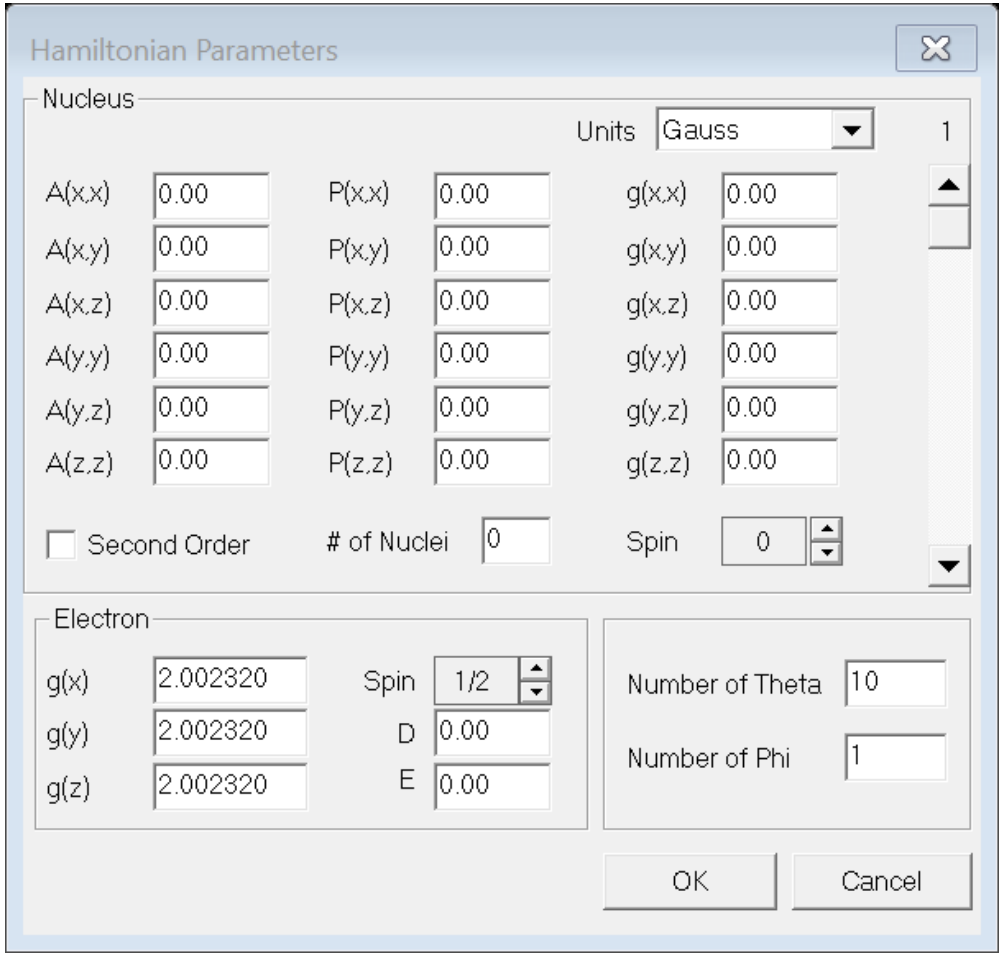
The Powder simulation program simulate spectra for electron spin 1/2 to spin 7/2. For spins greater than 1/2, D and E zero-field splitting terms are implemented.

No limitations on nuclear spin

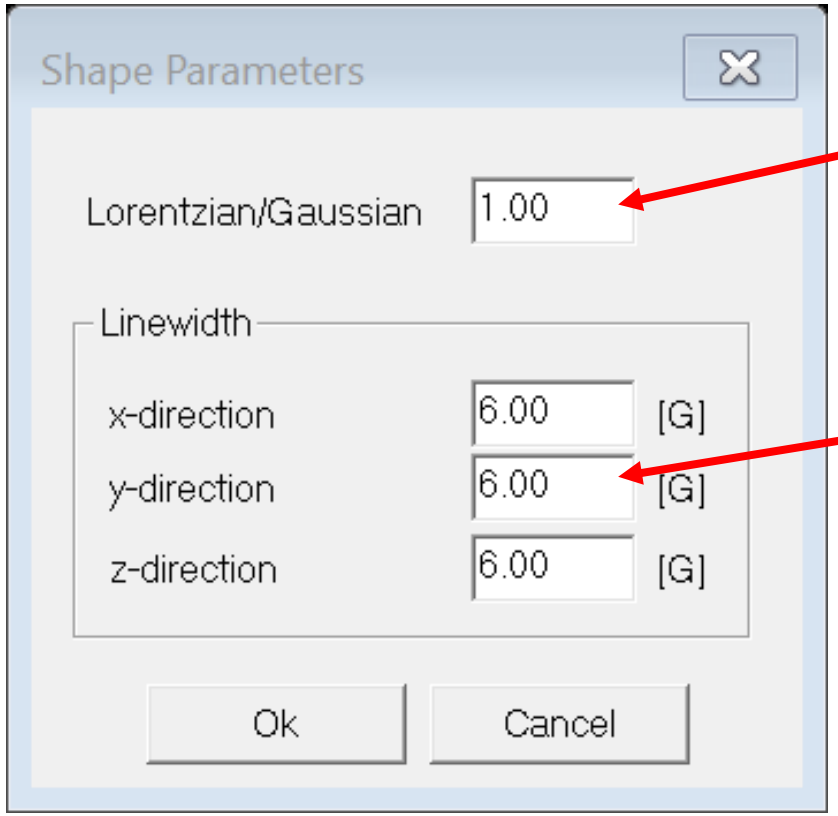
# Starting a simulation, Instrument parameters



# Starting a simulation, Hamiltonian parameters

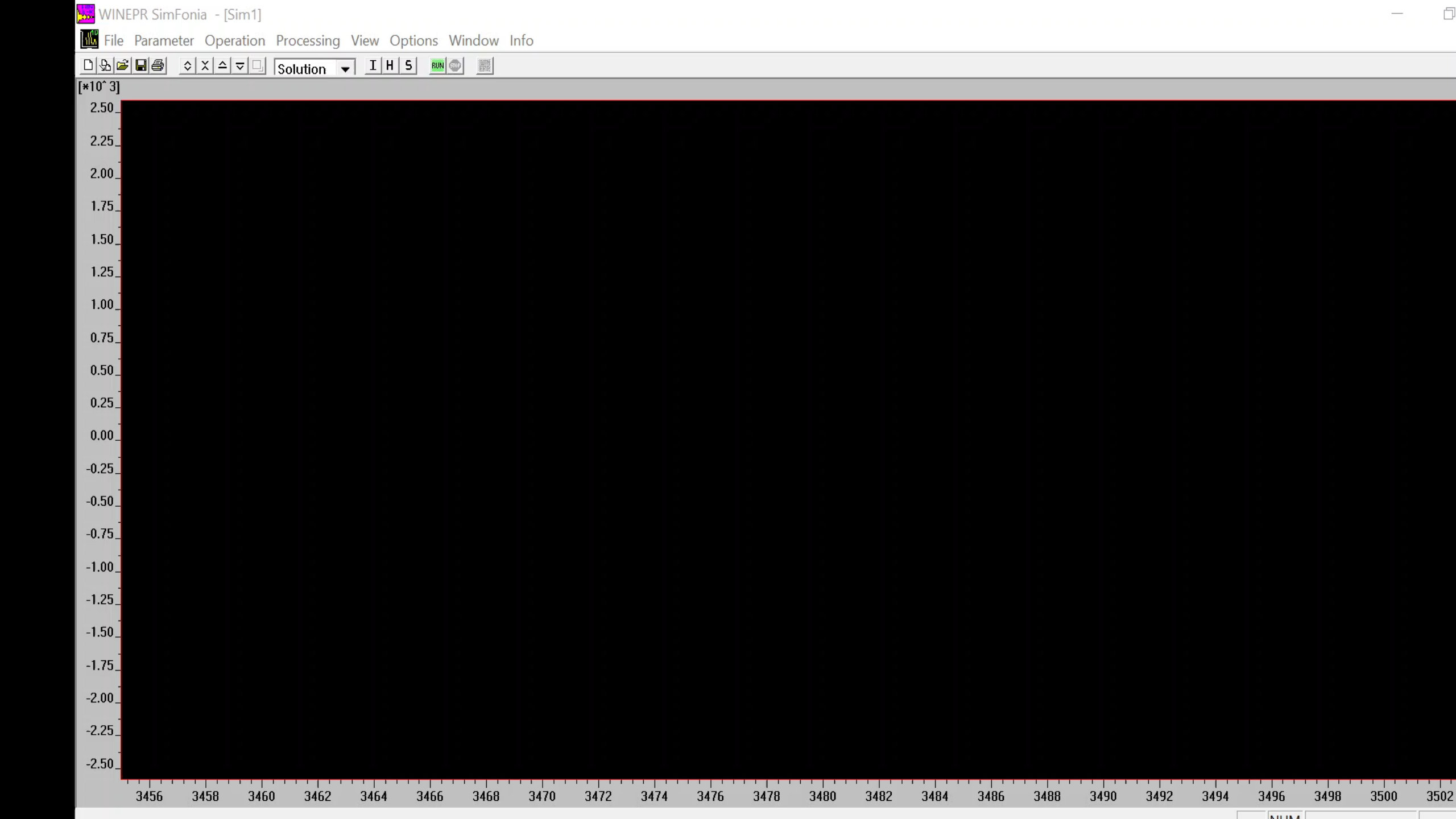


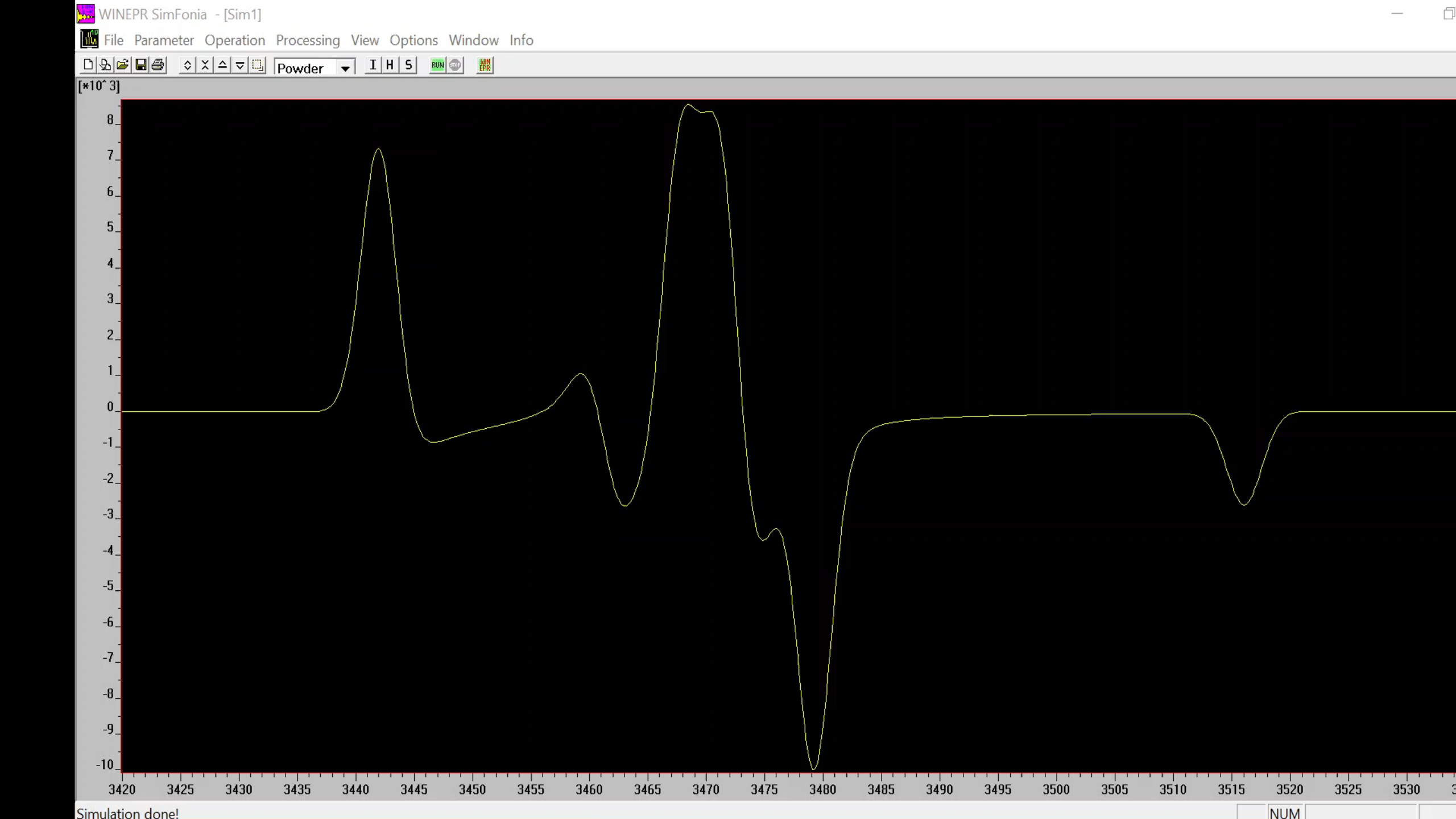
# Starting a simulation, Shape parameters



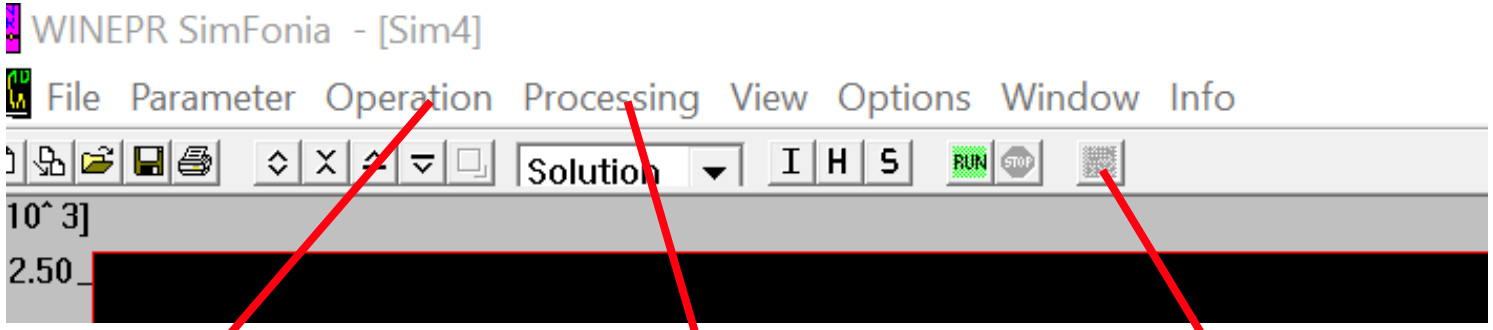

Line Shape Parameter: 0 =Lorentzian, 1 – Gaussian
Any value $\alpha$ in between is a Voigt line shape with a fraction of Gaussian equal $\alpha$ and fraction of Lorentzian equal (1- $\alpha$)

Anisotropic line width:

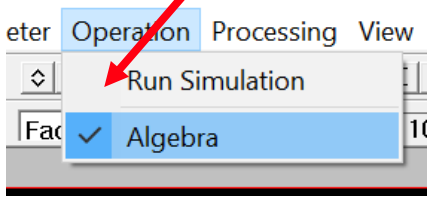

WINEPR SimFonia - [Sim1]
File Parameter Operation Processing View Options Window Info
Solution
I H S
RUN STOP
[*10^3]
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
-2.50
3456 3458 3460 3462 3464 3466 3468 3470 3472 3474 3476 3478 3480 3482 3484 3486 3488 3490 3492 3494 3496 3498 3500 3502

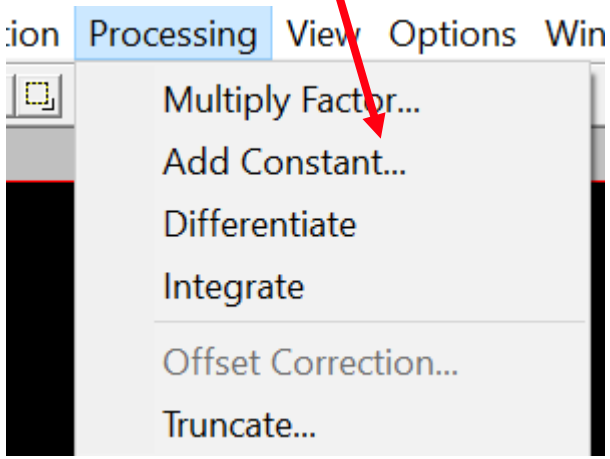

WINEPR SimFonia - [Sim1]
File Parameter Operation Processing View Options Window Info
Powder
[*10^3]
8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10
3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530
Simulation done!
NUM

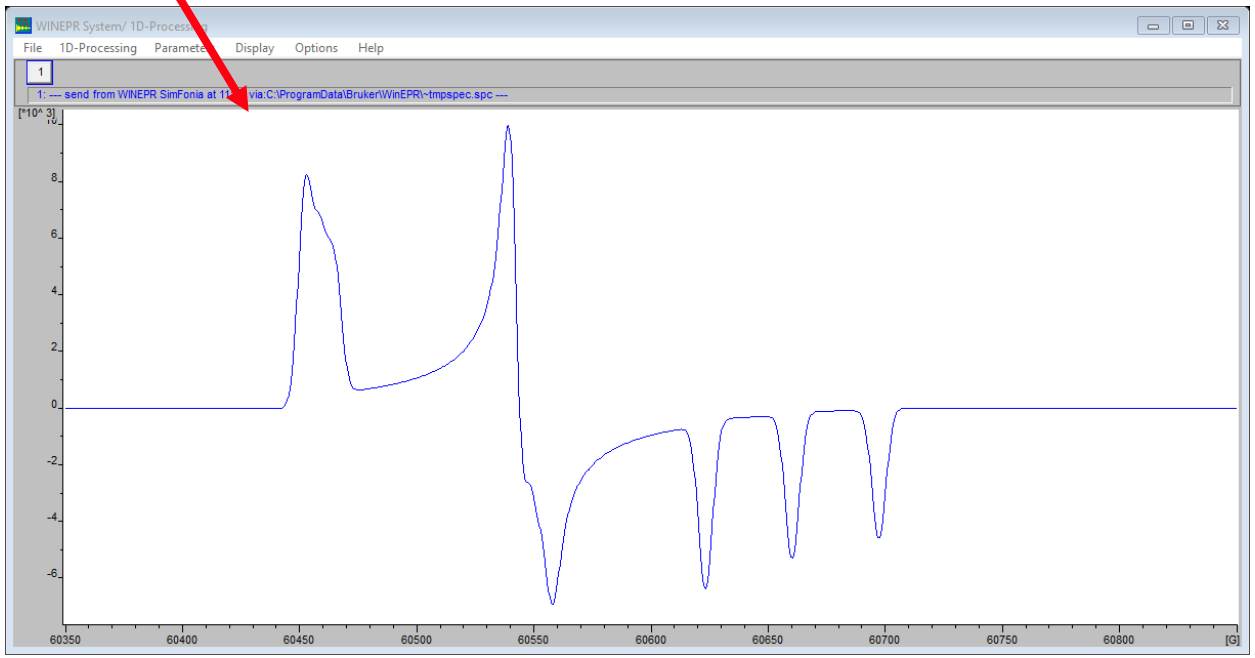
# Further processing




Sending to WinEpr



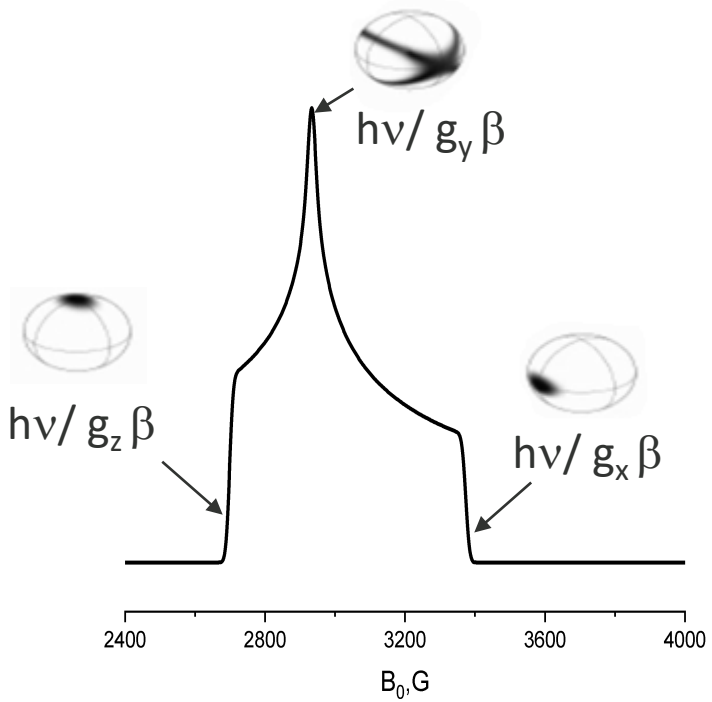



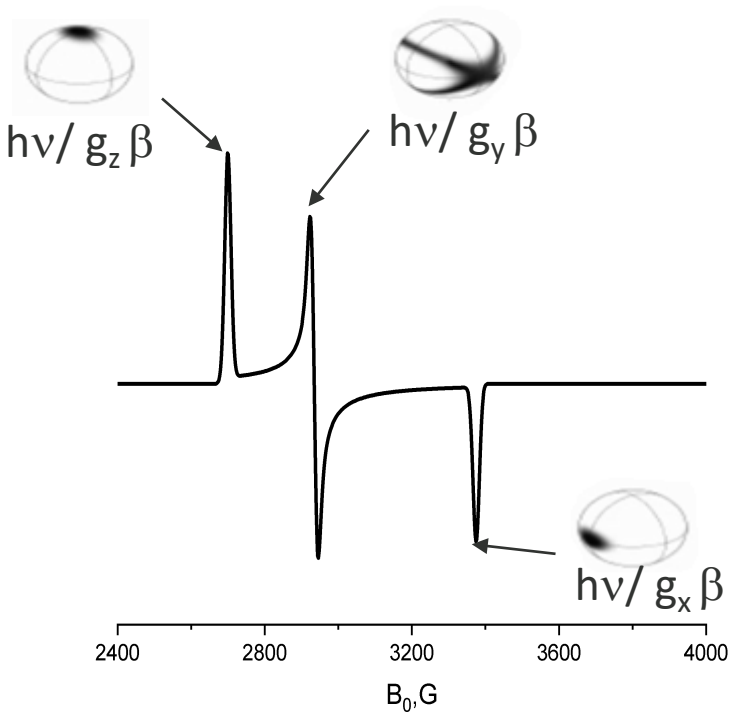



# The number of θ and φ orientations

$$B_\theta^{res} = \frac{h\nu}{g_{eff}\beta} = \frac{h\nu}{\beta}\left[g_x^2 cos^2\theta cos^2\varphi + g_y^2 sin^2\theta cos^2\varphi + g_z^2 sin^2\varphi\right]^{-1/2}$$

$g_x < g_y < g_z$




Two angles for summation: θ and φ. (#θ)×(#φ) individual lines

To make a smooth line in the simulation we should sum enough of the orientations corresponding to these angles.

# Choosing θ and ϕ values

θ and/or ϕ are too small – distortions and artifacts in spectra

θ and/or ϕ are too large – the calculation may take time

! *The ultimate criterion for sufficient # θ and # ϕ is the absence of line shape changes with an increase in these numbers.*

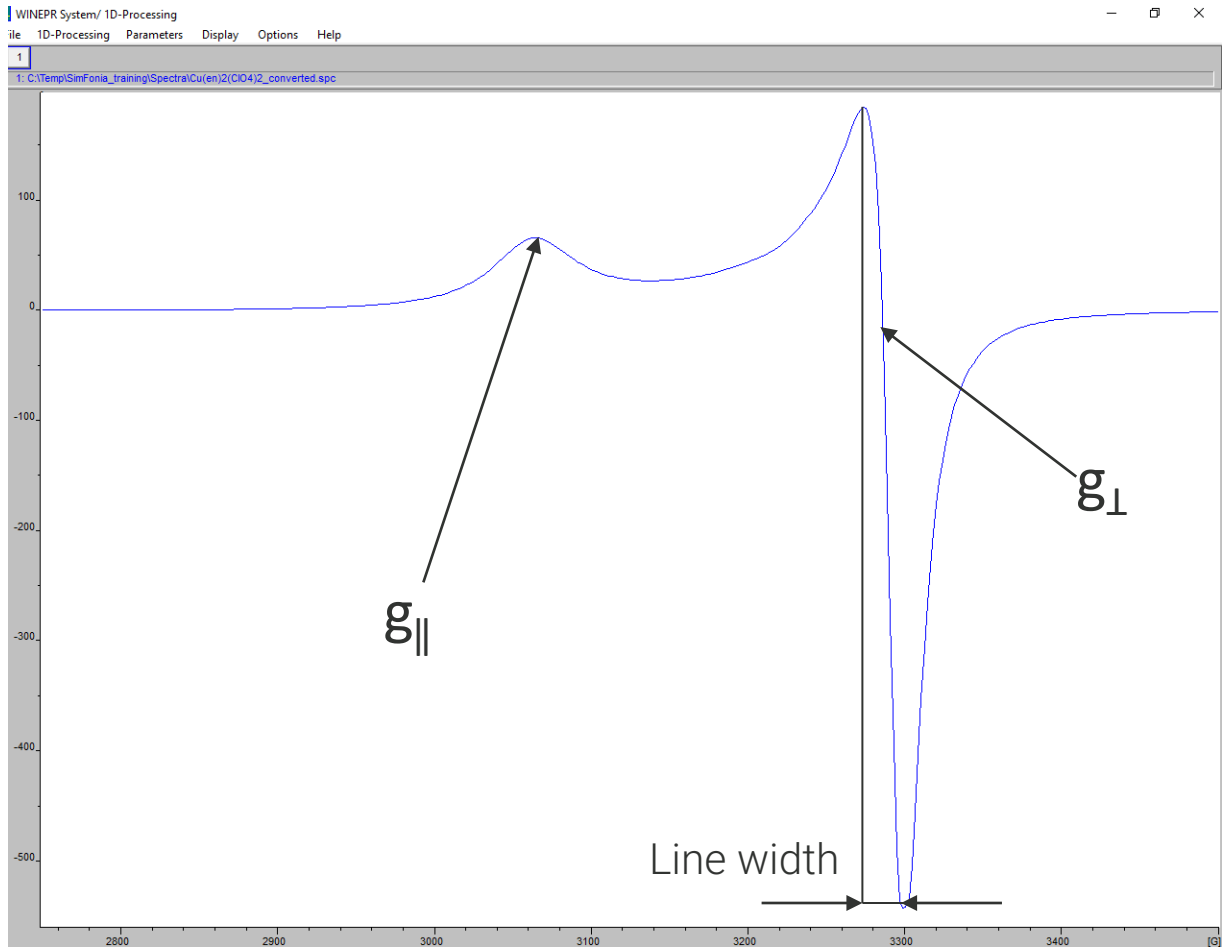
There are some rules to keep θ and ϕ values right and the computation time low:

-The ϕ value can be set lower for symmetric or nearly symmetric g- and A-matrices.

- For an axially symmetric g-factor the parallel axis should always be the z axis. Set $g_z = g_\parallel$ and $A_z = A_\parallel$. In this case we can set the number of ϕ = 1.
- The narrower the lines and the more resolved is the spectrum, the more θ and ϕ values we need

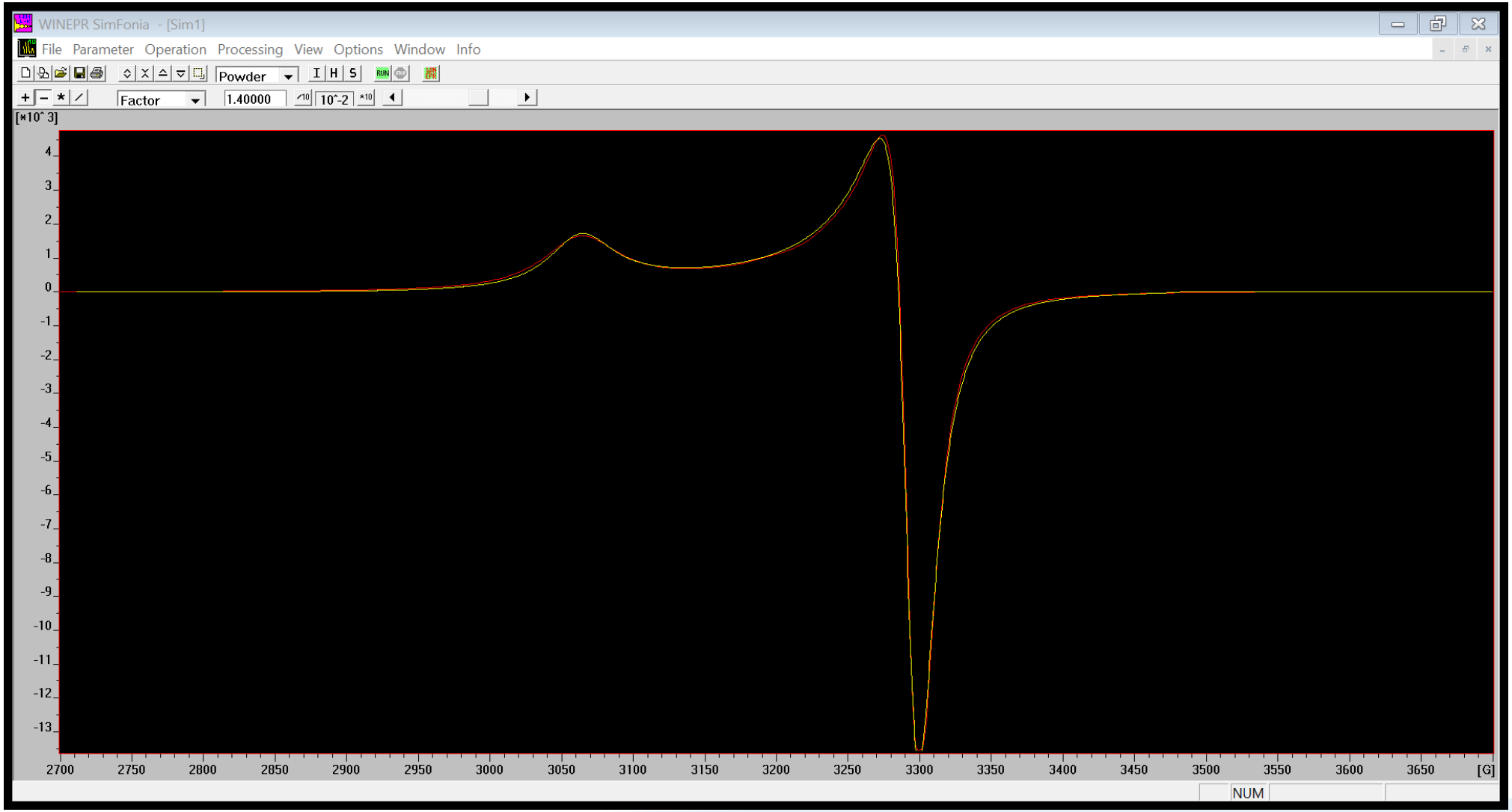
# Simulating an experimental spectrum: $Cu(en)_2(ClO_4)_2$

The line shape is defined by the g-factor anisotropy. An Axially Symmetric g-Factor with $g_{\parallel} > g_{\perp}$ .



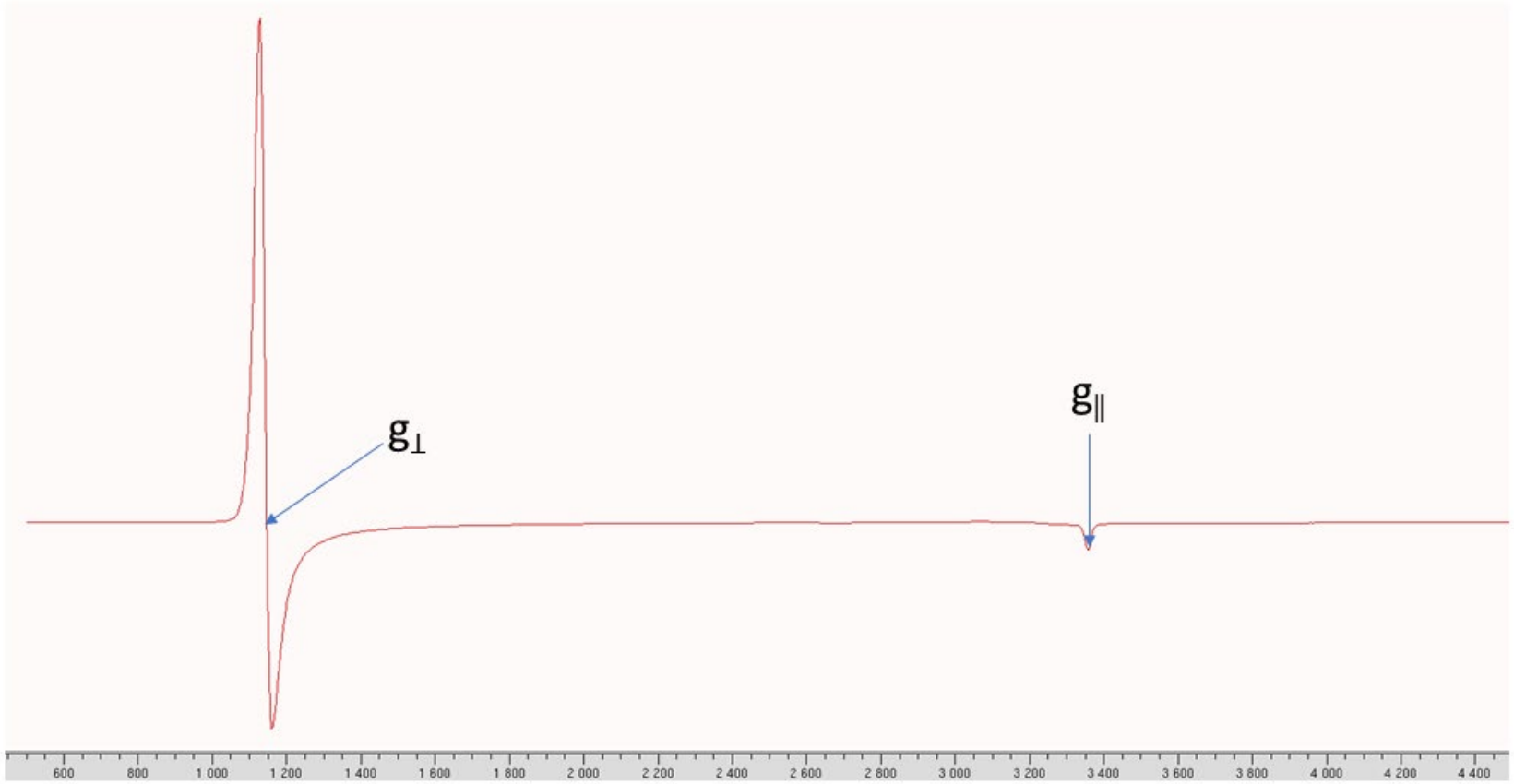

WINEPR SimFonia - [Sim1]
File Parameter Operation Processing View Options Window Info
Solution
I H S
RUN
[*10^ 3]
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
-2.50
3456 3458 3460 3462 3464 3466 3468 3470 3472 3474 3476 3478 3480 3482 3484 3486 3488 3490 3492 3494 3496 3498 3500 3502
NUM

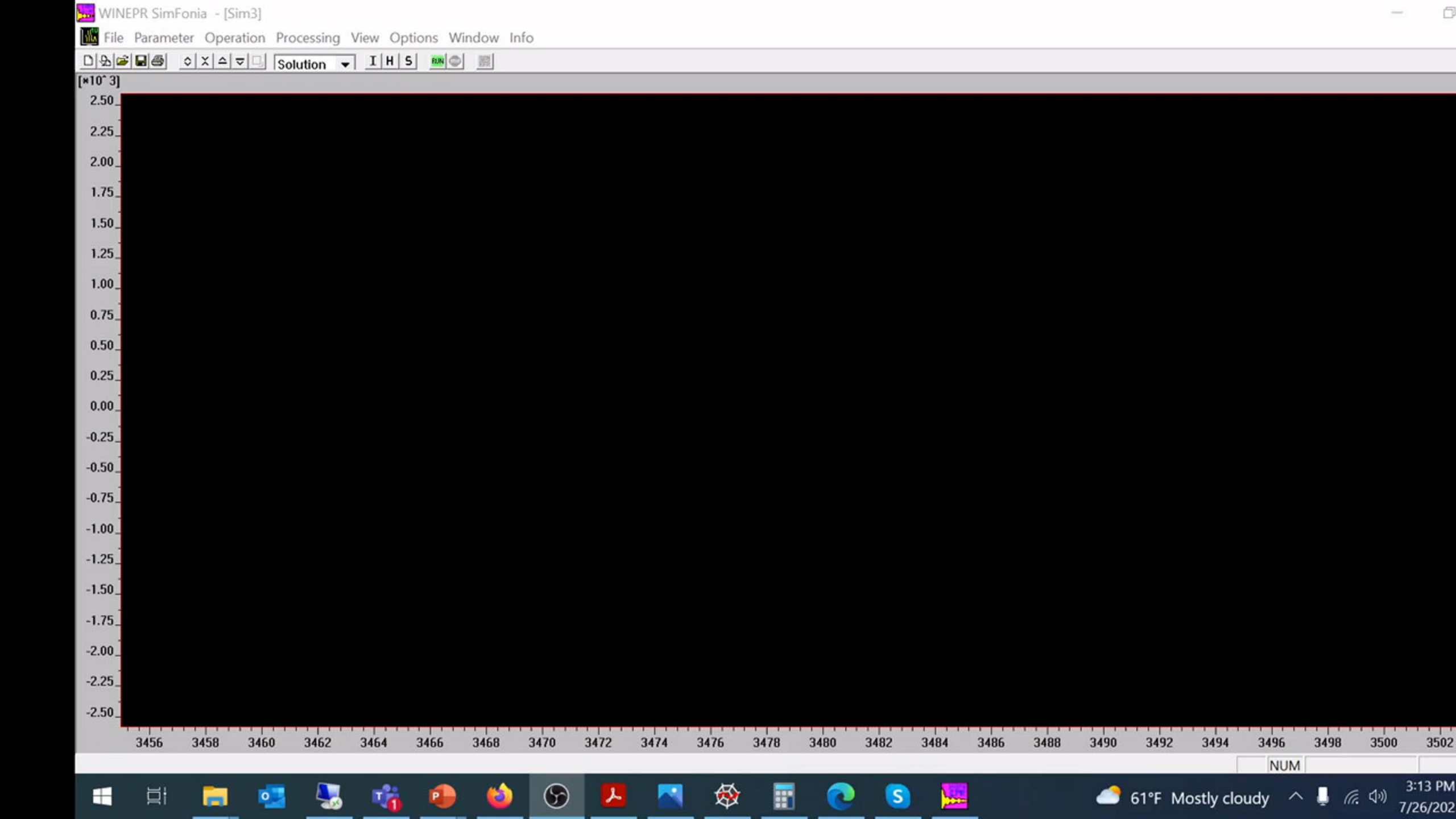
# Simulating an experimental spectrum: $Cu(en)_2(ClO_4)_2$



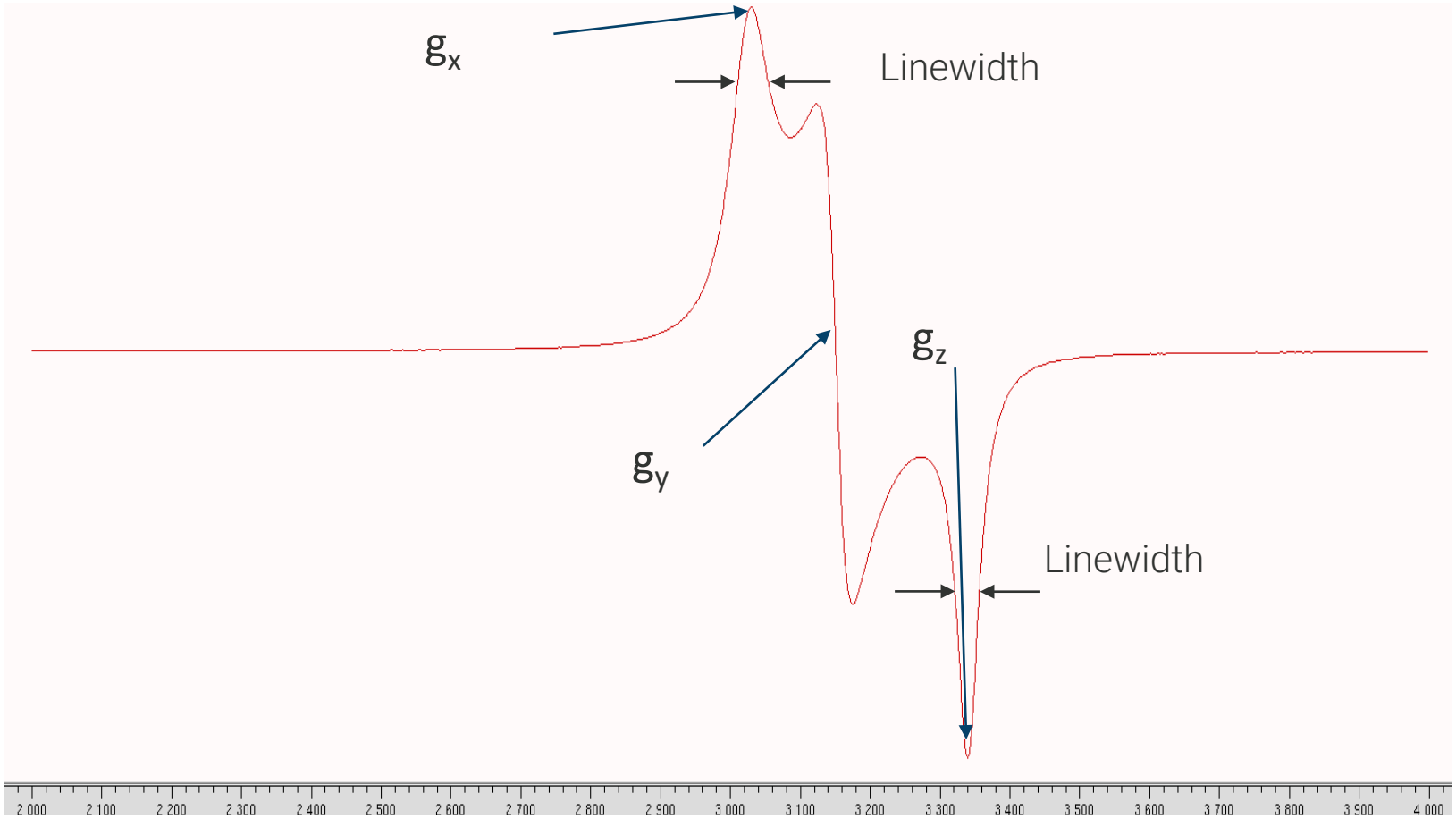
# Iron cofactor in myoglobin

An axially symmetric g-factor with $g_{\parallel}<g_{\perp}$ and a very large difference between these values




WINEPR SimFonia - [Sim3]
File Parameter Operation Processing View Options Window Info
Solution
[×10^ 3]
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
-2.50
3456 3458 3460 3462 3464 3466 3468 3470 3472 3474 3476 3478 3480 3482 3484 3486 3488 3490 3492 3494 3496 3498 3500 3502
NUM
61°F Mostly cloudy
3:13 PM
7/26/202

# $Cu(bp)_2(ClO_4)_2$. A Rhombically Symmetric g-Factor



WINEPR SimFonia - [Sim1]

File Parameter Operation Processing View Options Window Info

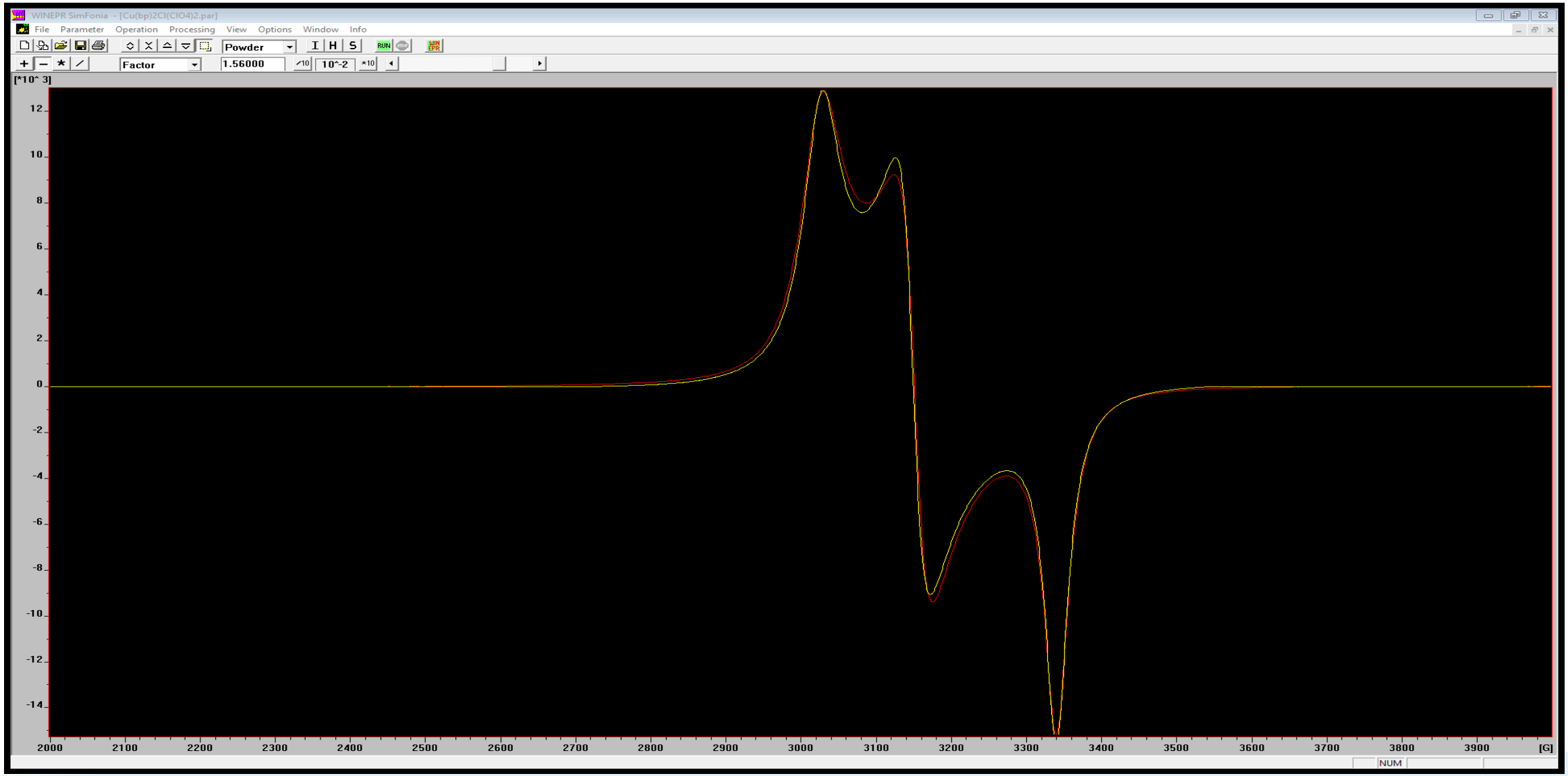
Solution I H S RUN STOP


NUM

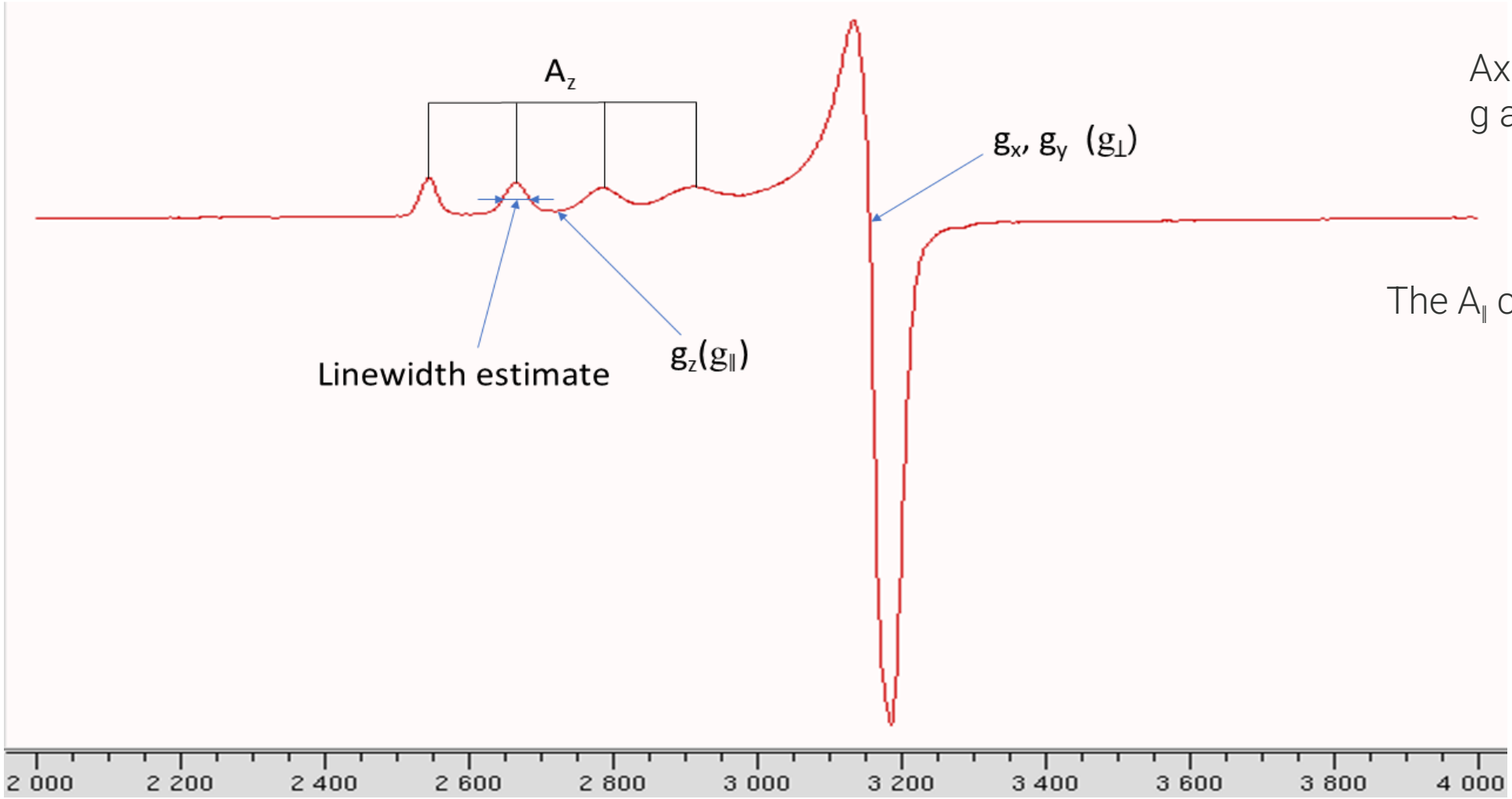
63°F Mostly sunny

2:42 PM
7/26/202

# $Cu(bp)_2(ClO_4)_2$. A Rhombically Symmetric g-Factor

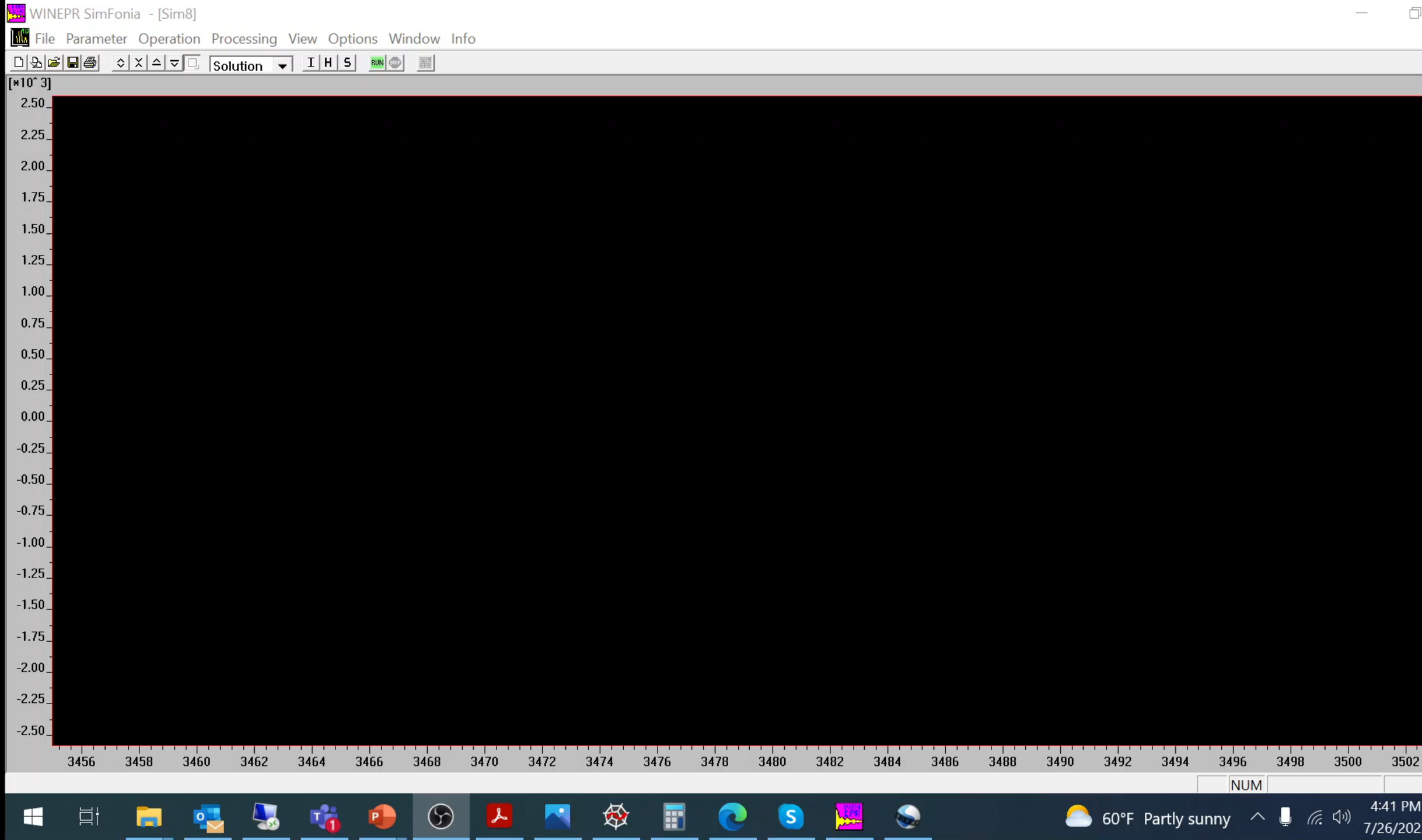


# Copper sulfate in frozen water/glycerol

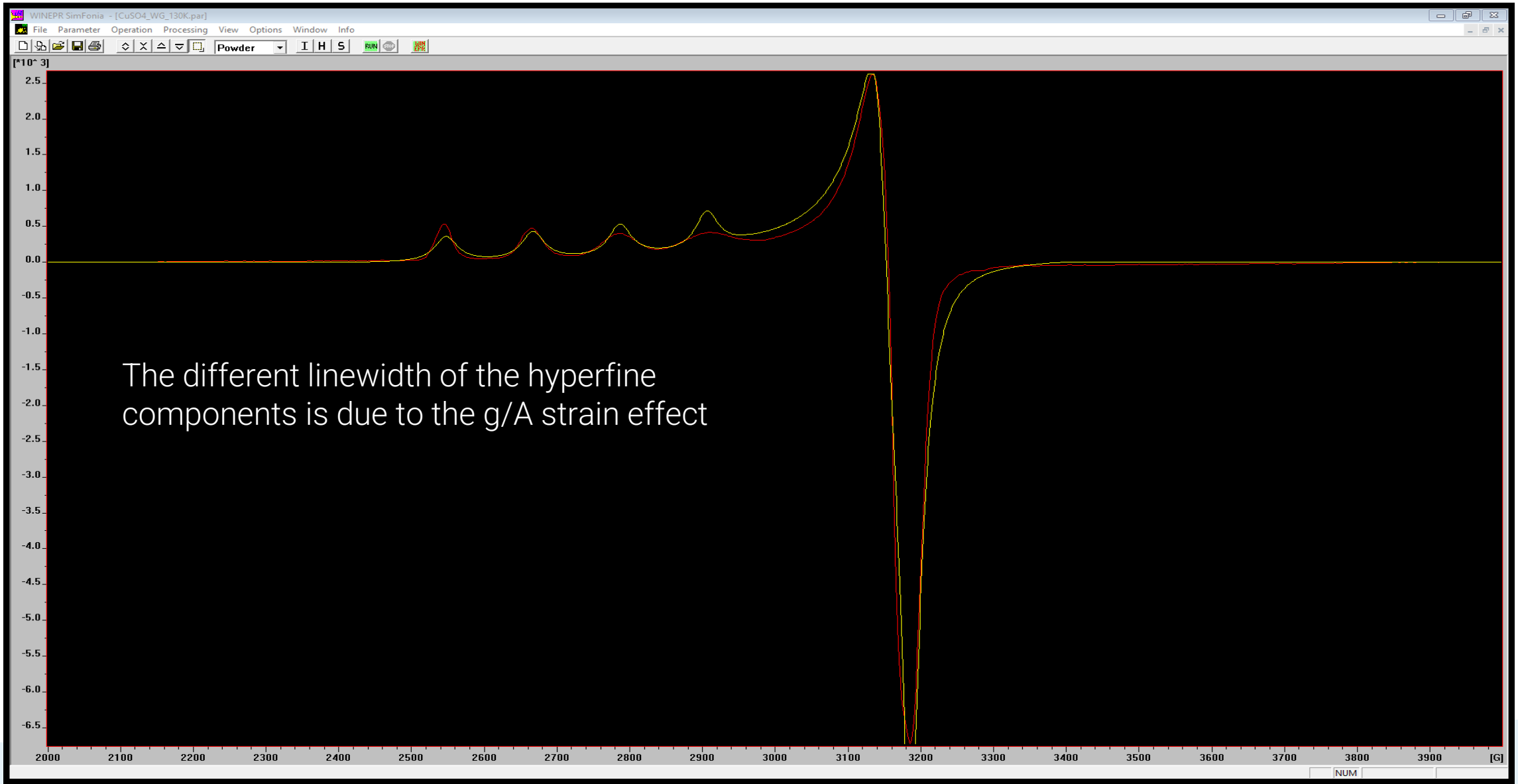



Axially symmetric
g and A

The $A_\parallel$ cannot be resolved


WINEPR SimFonia - [Sim8]
File Parameter Operation Processing View Options Window Info
Solution
[*10^ 3]
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
-2.50
3456 3458 3460 3462 3464 3466 3468 3470 3472 3474 3476 3478 3480 3482 3484 3486 3488 3490 3492 3494 3496 3498 3500 3502
NUM
60°F Partly sunny
4:41 PM
7/26/202

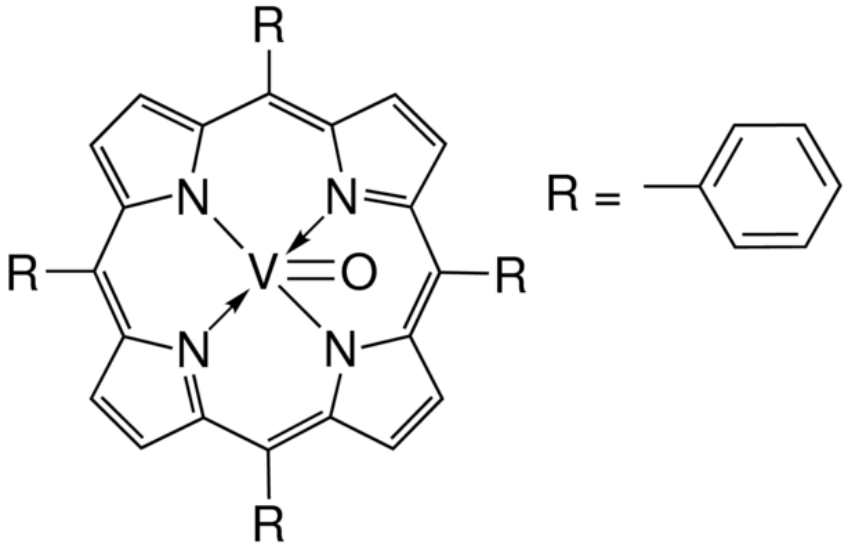
# Copper sulfate in frozen water/glycerol




The different linewidth of the hyperfine components is due to the g/A strain effect

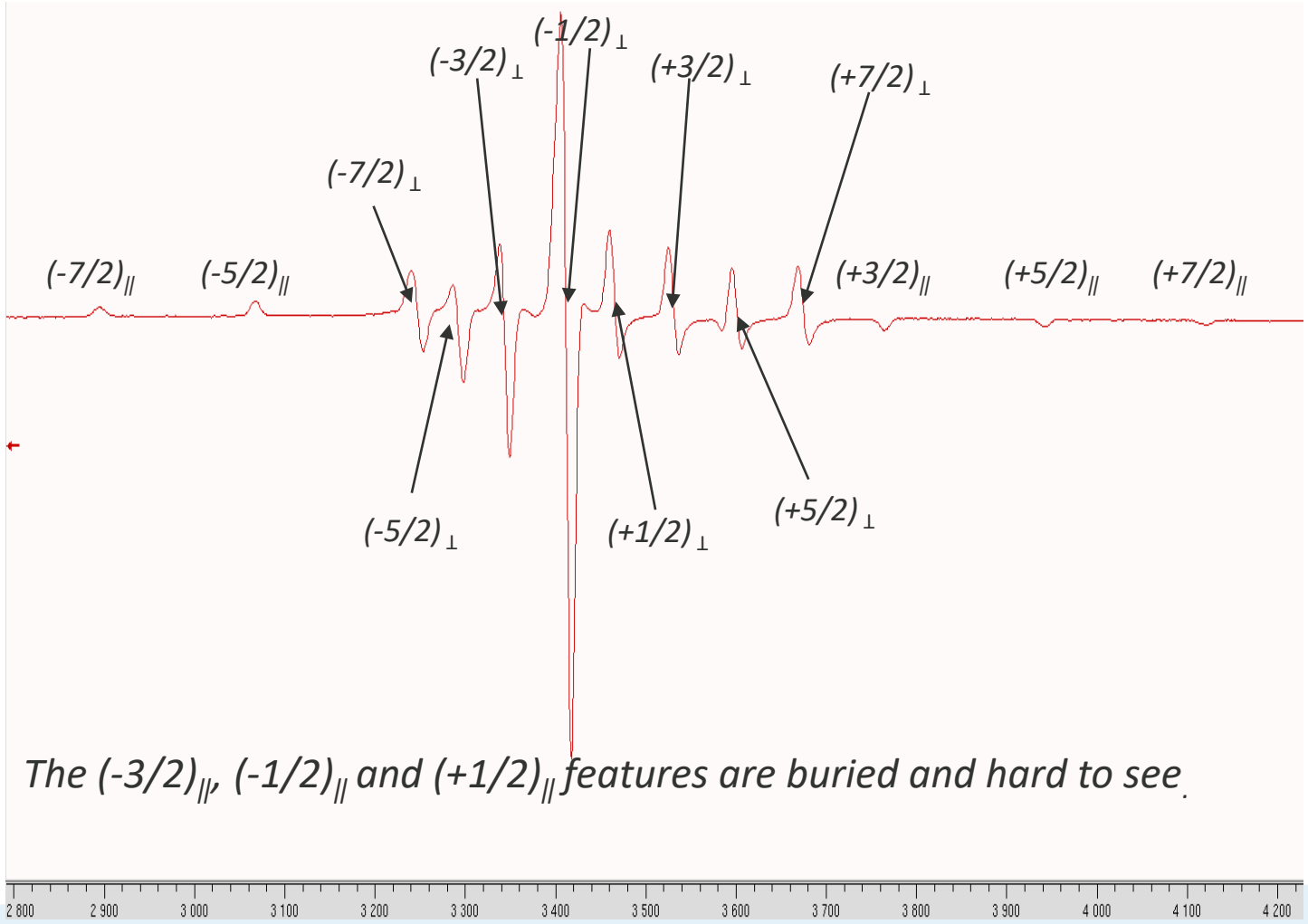
# VO-TPP

A complex compound of Vanadyl ion ($VO^{2+}$) with TPP (5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine)

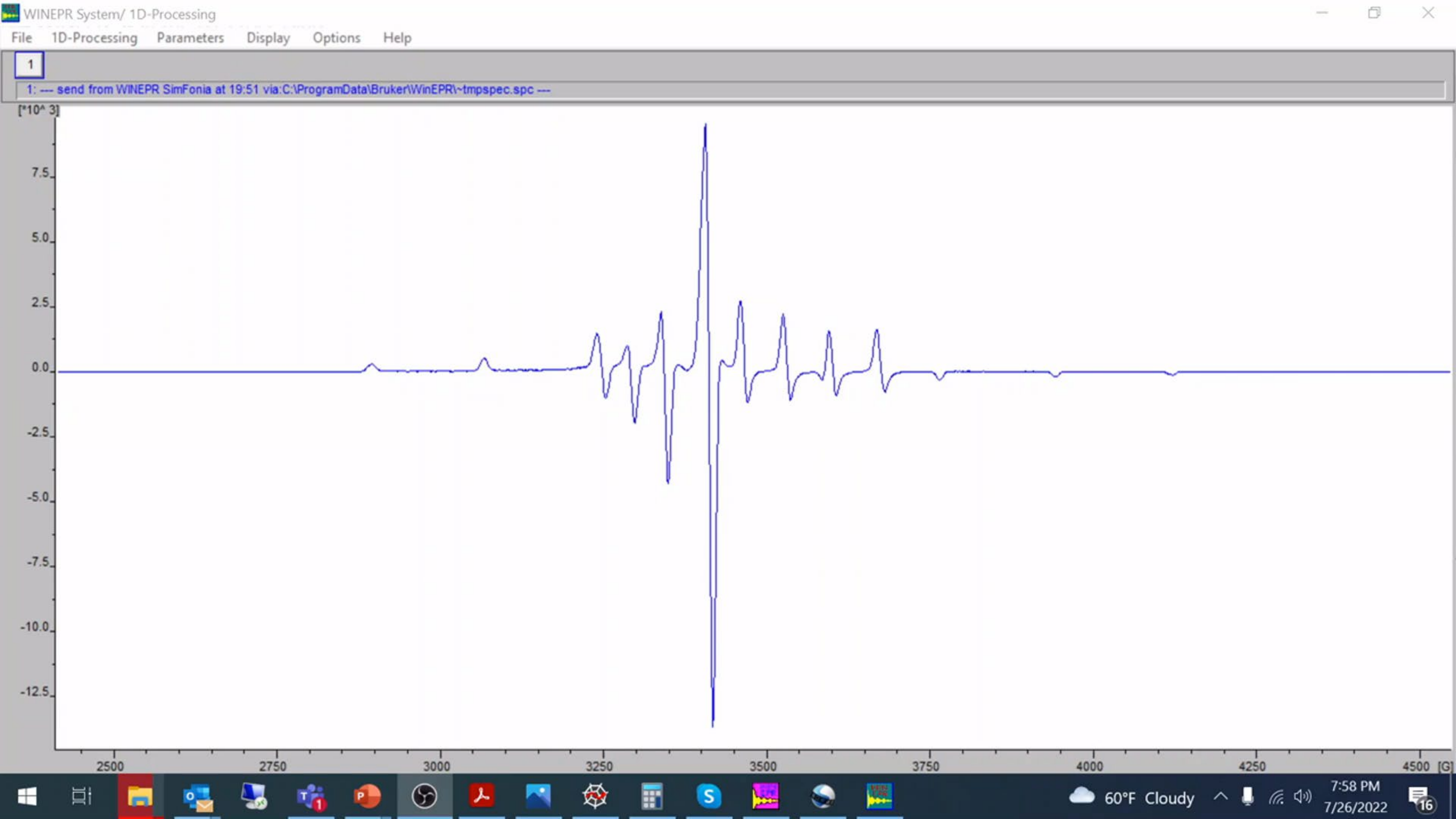



The spectrum is dominated by the hyperfine splitting and the g-factor is nearly isotropic.
Not quite, though!

Vanadium has a nuclear spin of 7/2 yielding eight hyperfine lines.



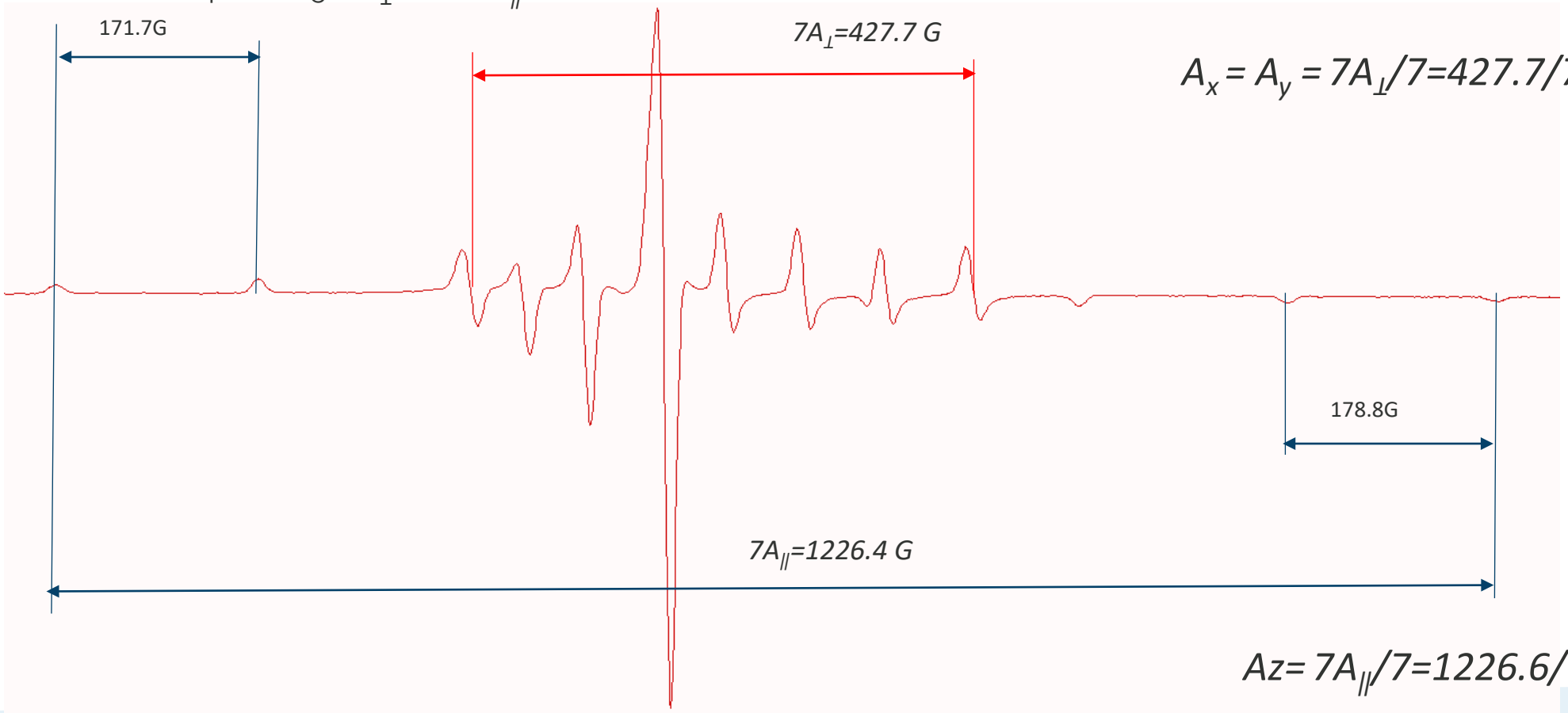

*The $(-3/2)_{||}$, $(-1/2)_{||}$ and $(+1/2)_{||}$ features are buried and hard to see.*


WINEPR System/ 1D-Processing
File
1D-Processing
Parameters
Display
Options
Help
1
1: --- send from WINEPR SimFonia at 19:51 via:C:\ProgramData\Bruker\WinEPR\~tmpspec.spc ---
[*10^ 3]
7.5
5.0
2.5
0.0
-2.5
-5.0
-7.5
-10.0
-12.5
2500
2750
3000
3250
3500
3750
4000
4250
4500
[G]
60°F Cloudy
7:58 PM
7/26/2022

# Finding initial values for the hyperfine splitting

The High Field Approximation, $B_0$>>HFS, evidently does not work:

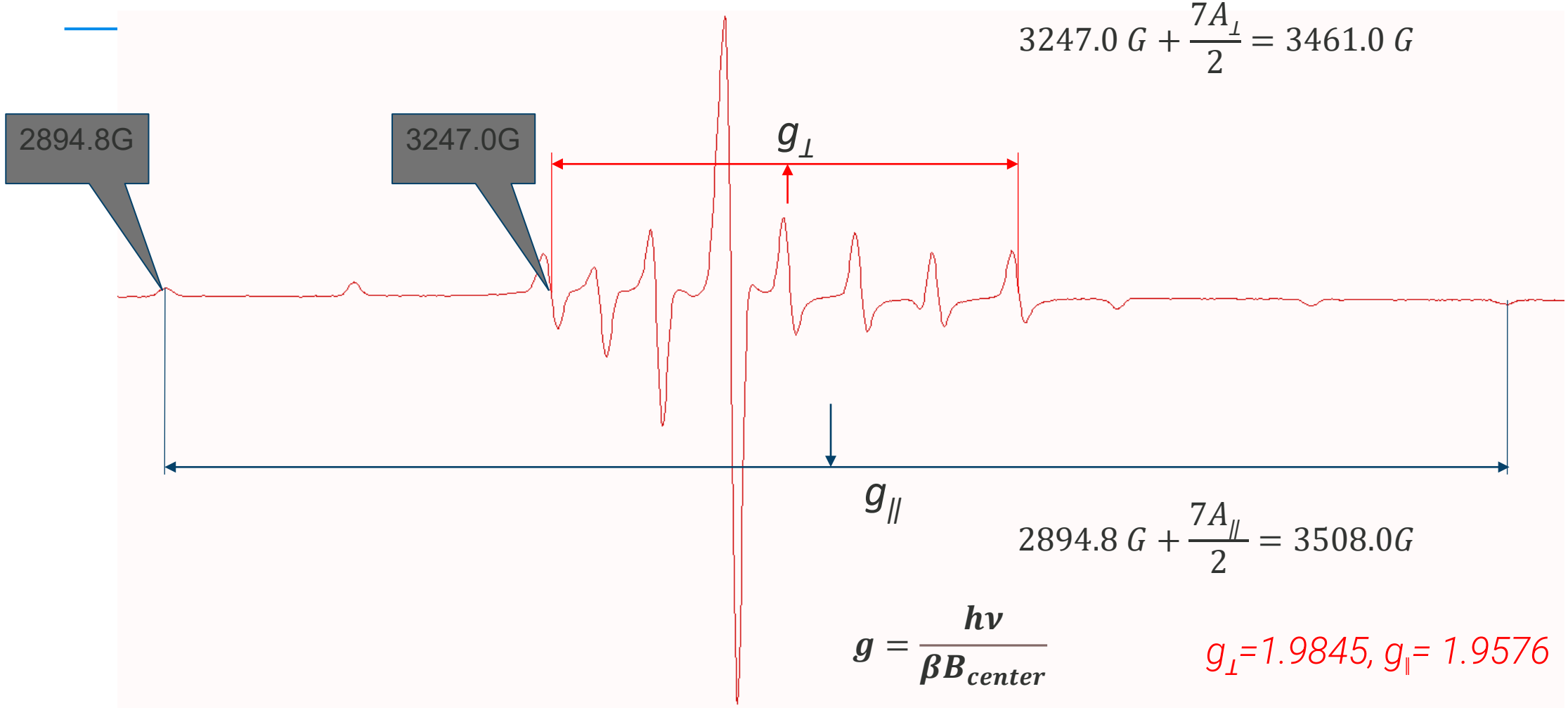
- Using the 2nd order is necessary
- The initial hyperfine splitting values for the simulation still can be estimated as 1/7 of the corresponding $7A_{\perp}$ and $7A_{\parallel}$ distances.




$A_x = A_y = 7A_{\perp}/7 = 427.7/7 = 61.1$ G

$Az = 7A_{\parallel}/7 = 1226.6/7 = 175.2$ G

# Find the initial g-values

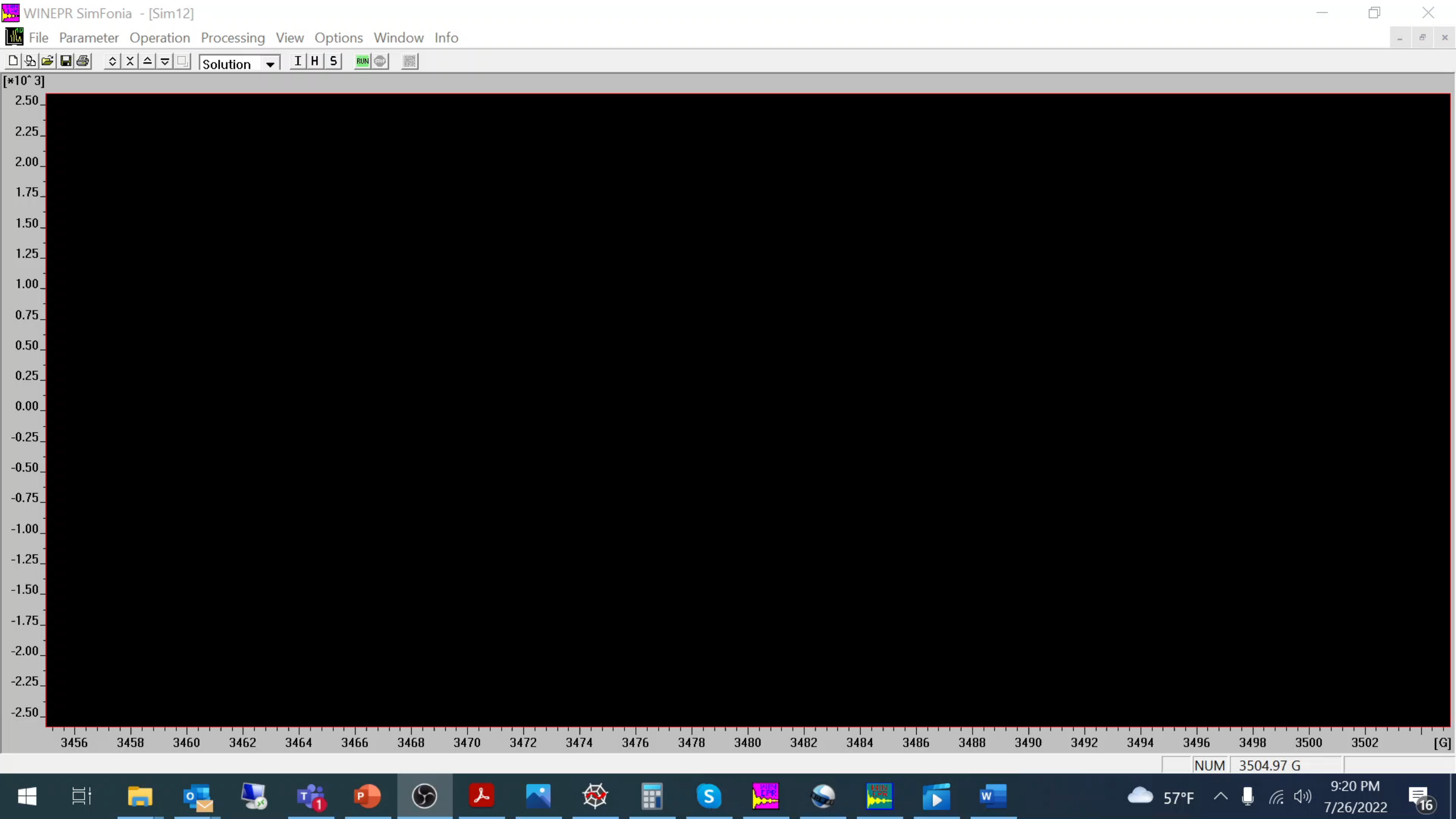



$$3247.0\ G + \frac{7A_\perp}{2} = 3461.0\ G$$

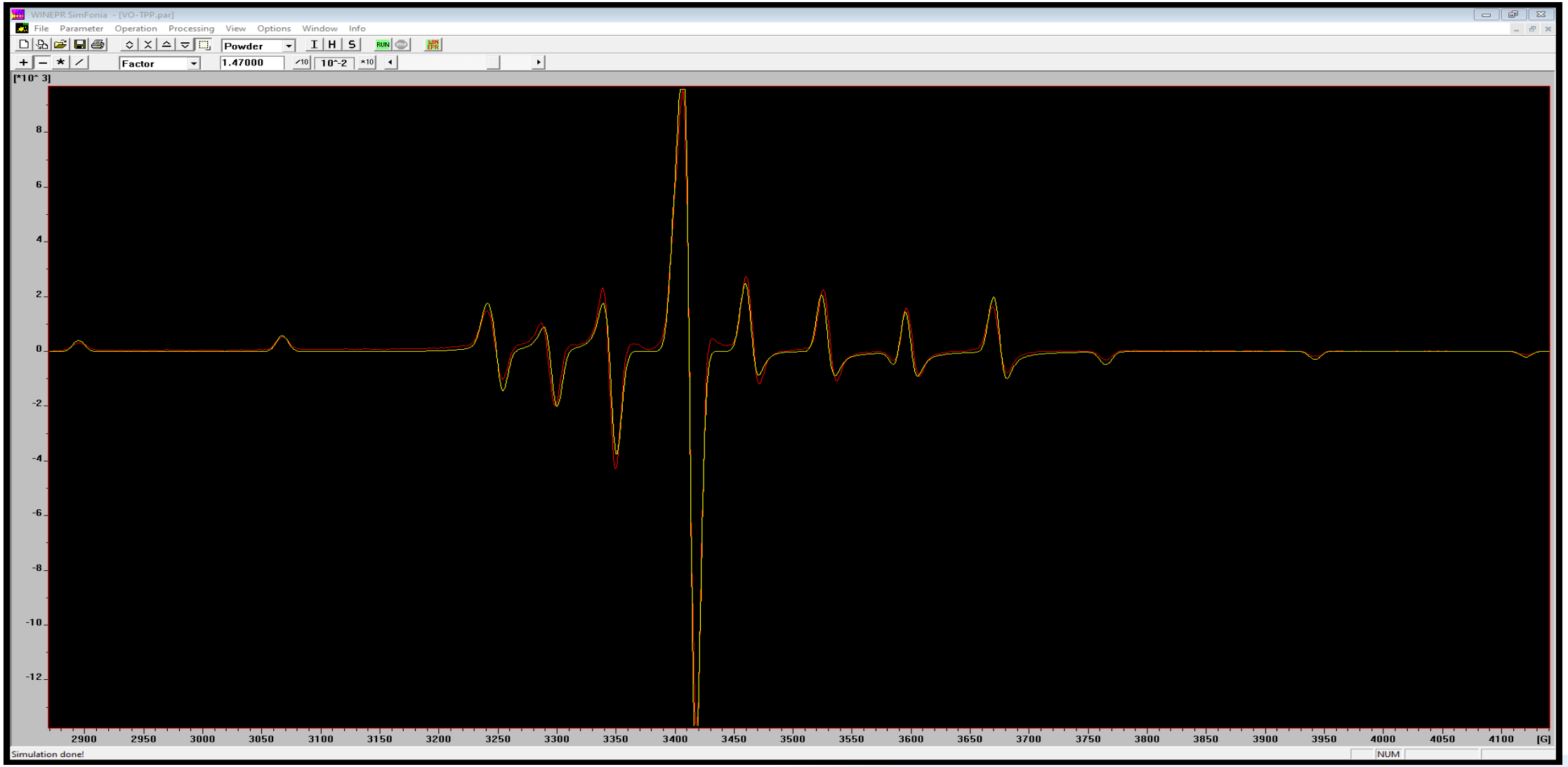
$$2894.8\ G + \frac{7A_\parallel}{2} = 3508.0G$$

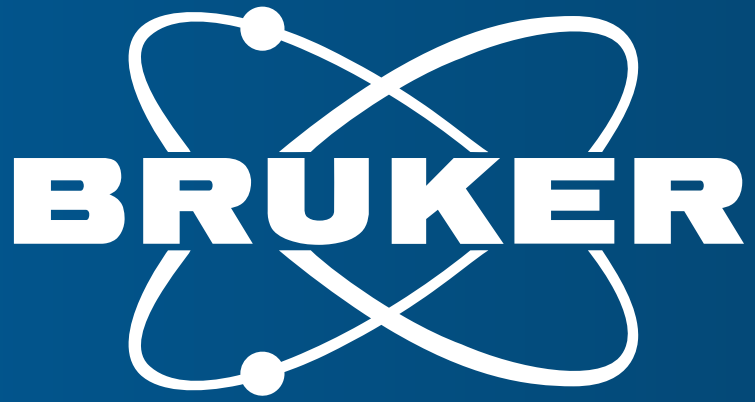
$$g = \frac{h\nu}{\beta B_{center}}$$

$g_\perp$=1.9845, $g_\parallel$= 1.9576


WINEPR SimFonia - [Sim12]
File Parameter Operation Processing View Options Window Info
Solution
I H S
RUN STOP
[*10^3]
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
-2.50
3456 3458 3460 3462 3464 3466 3468 3470 3472 3474 3476 3478 3480 3482 3484 3486 3488 3490 3492 3494 3496 3498 3500 3502 [G]
NUM 3504.97 G
57°F
9:20 PM
7/26/2022

# VO-TPP






Innovation with Integrity

# Any questions?

# Thank you!