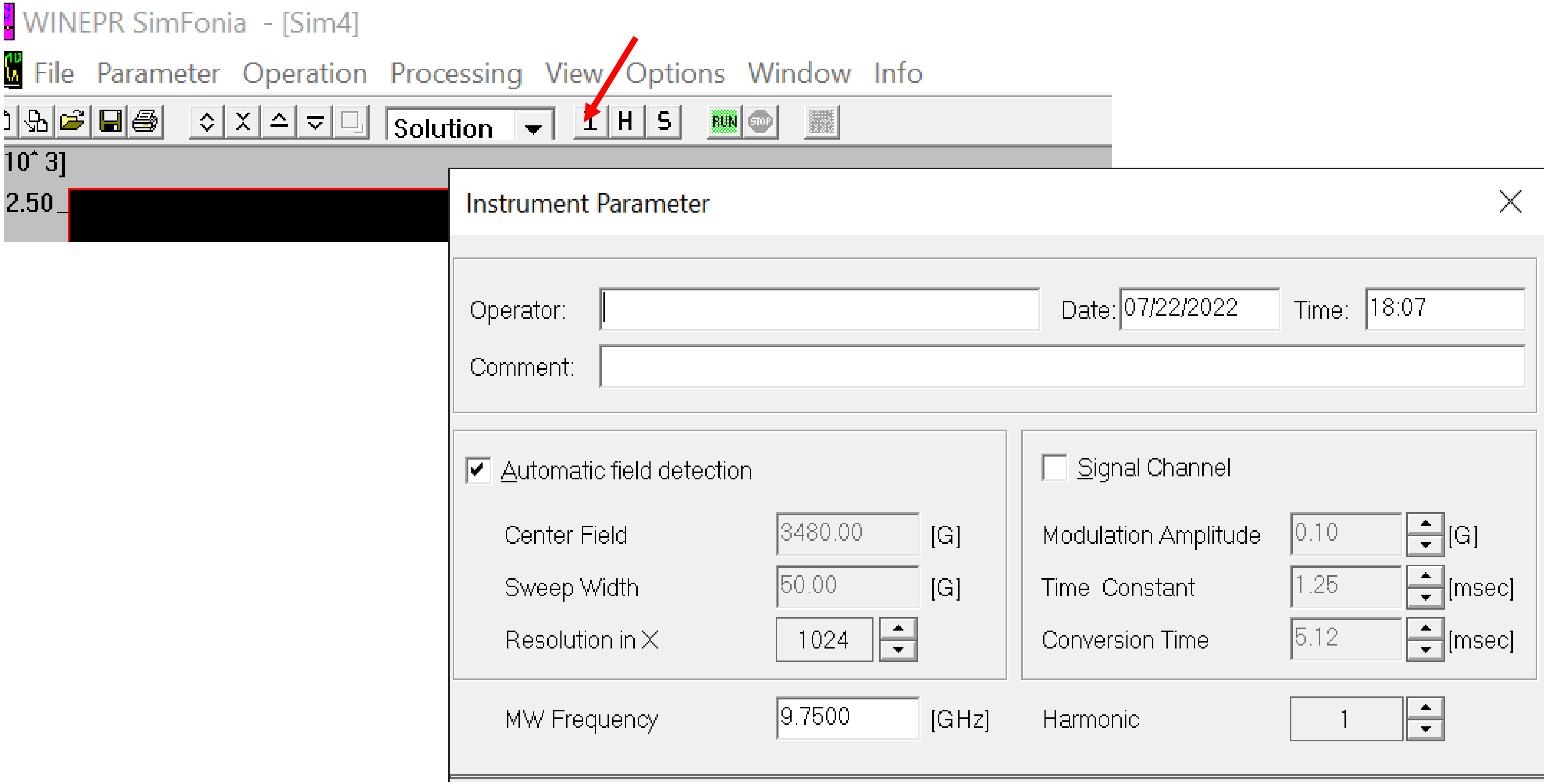
Simulations of Solution Spectra using SimFonia

SimFonia Features

- Fast, easy-to-use Simulation Program. Runs under Microsoft Windows.
- The simulation algorithm is based upon the perturbation theory
- Choice of solution or powder spectra
- Allows for elementary data processing
- Easy transfer of simulated spectra to WIN-EPR for further post-processing
- Efficient (FT) Fourier Transform algorithm for multiline spectra
- Simulation of the m_i dependent linewidth by a polynomial approximation
- Up to 20 inequivalent nuclei with a large number of equivalent nuclei
- 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.

Starting a simulation, Instrument parameters



Operator:

Date: 07/22/2022

Time: 18:07

Comment:

☑ Automatic field detection

Center Field 3480.00 [G]

Sweep Width 50.00 [G]

Resolution in X 1024

☐ Signal Channel

Modulation Amplitude 0.10 [G]

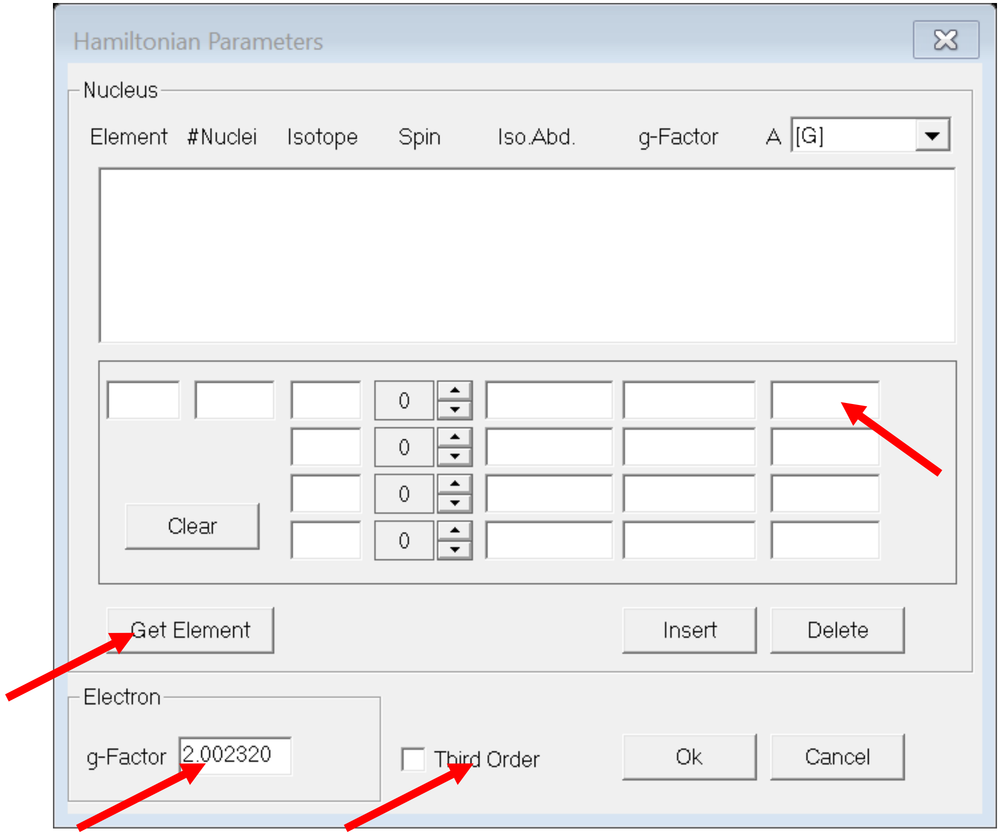
Time Constant 1.25 [msec]

Conversion Time 5.12 [msec]

MW Frequency 9.7500 [GHz]

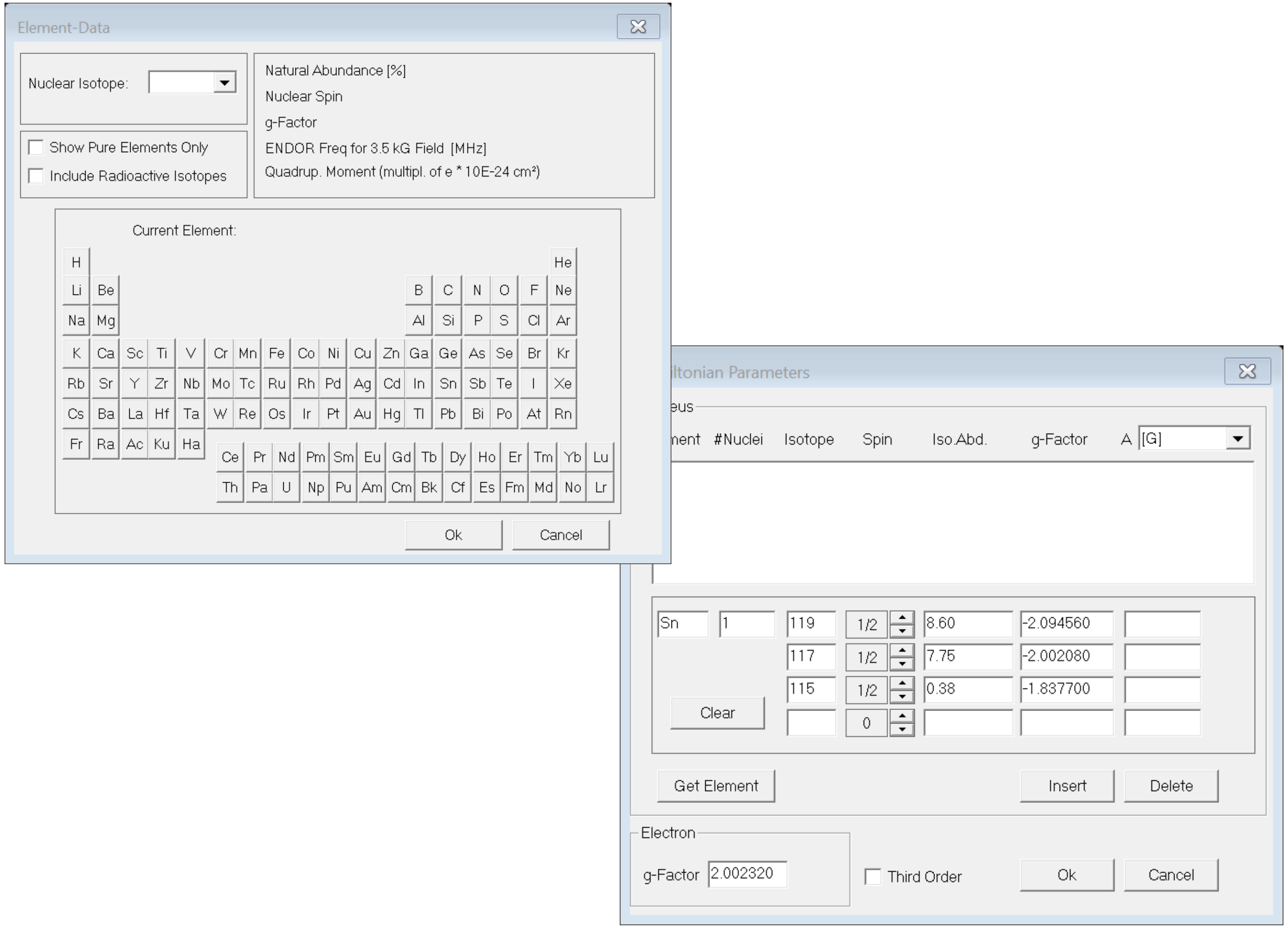
Harmonic 1

Starting a simulation, Hamiltonian parameters



Element	#Nuclei	Isotope	Spin	Iso.Abd.	g-Factor	A
			0			
			0			
			0			
			0			

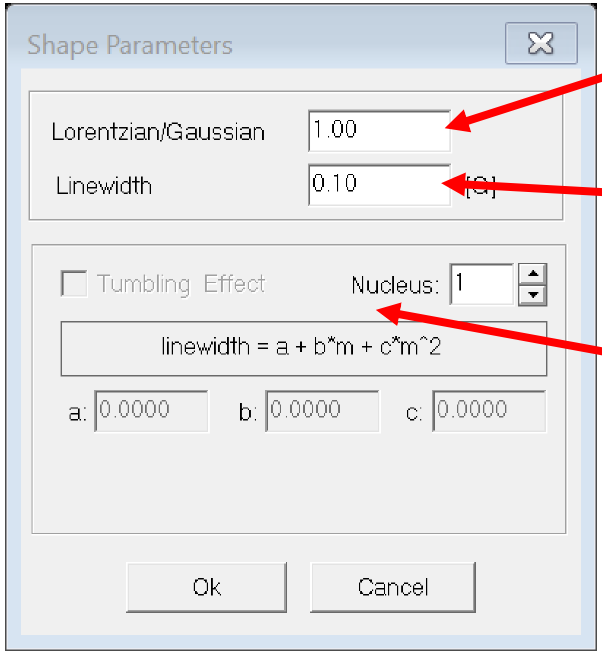
g-Factor 2.002320



Element	#Nuclei	Isotope	Spin	Iso.Abd.	g-Factor	A
Sn	1	119	1/2	8.60	-2.094560	
		117	1/2	7.75	-2.002080	
		115	1/2	0.38	-1.837700	
			0			

g-Factor 2.002320

Starting a simulation, Shape parameters



Lorentzian/Gaussian: 1.00

Linewidth: 0.10 [G]

☐ Tumbling Effect

Nucleus: 1

linewidth = a + b*m + c*m^2

a: 0.0000 b: 0.0000 c: 0.0000

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

Line width

This part, the line width variation according to the Kivelson theory works only if (1) a single isotope is listed in Hamiltonian parameters and (2) the **third order** box is checked


WINEPR SimFonia - [Sim3]
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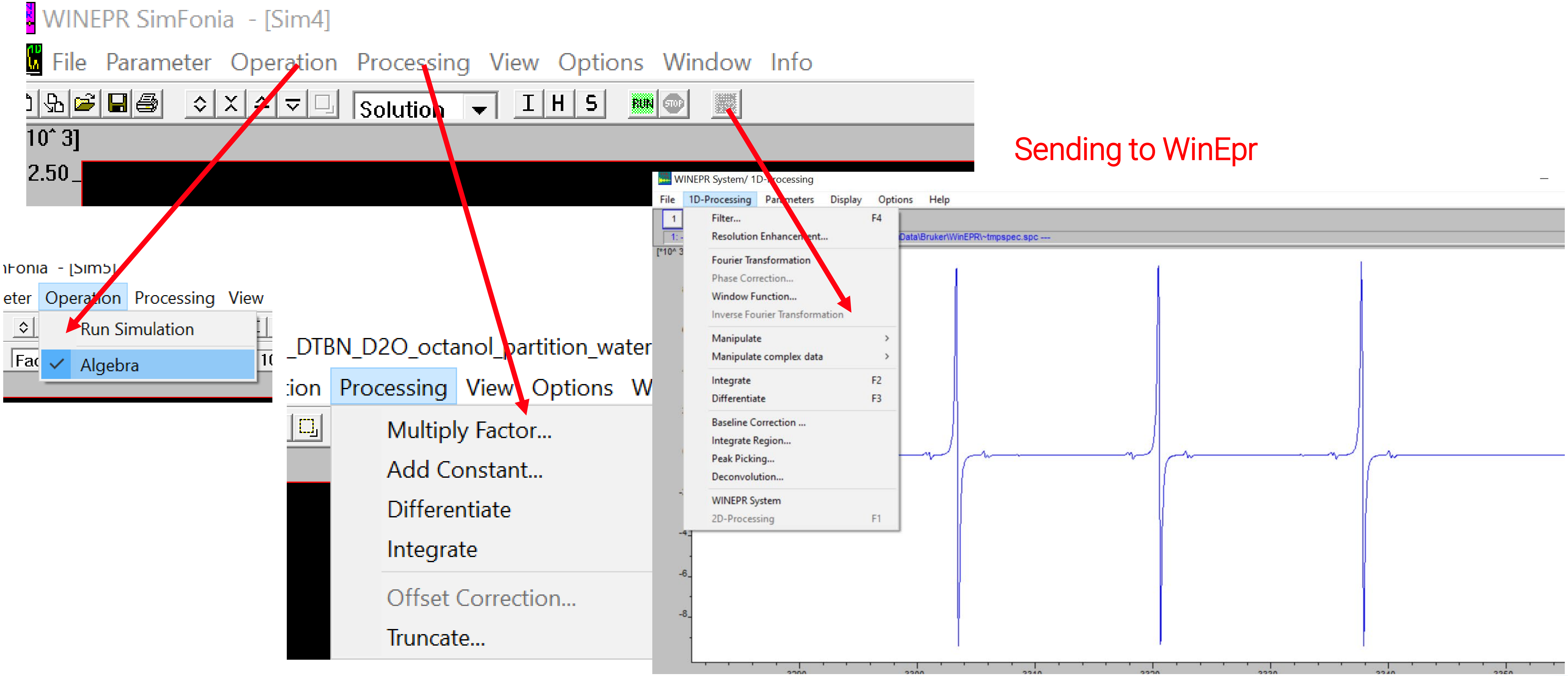
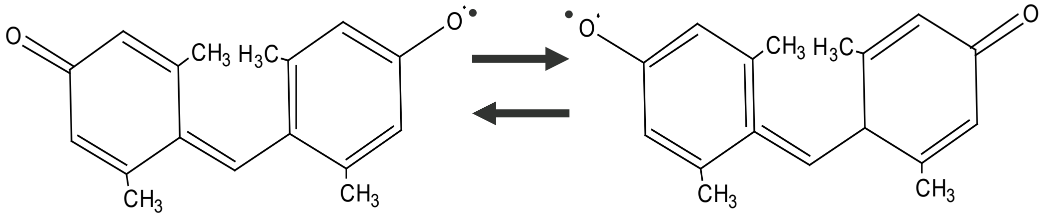
Further processing



Sending to WinEpr

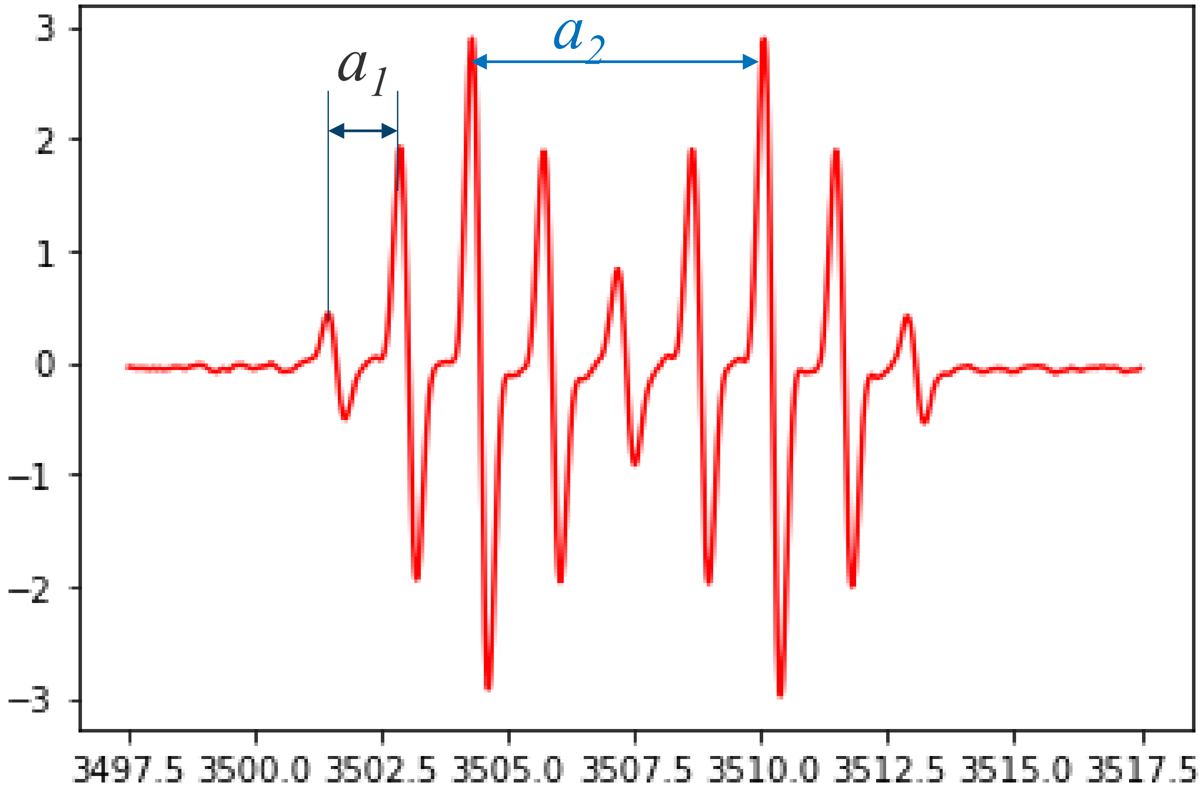
Simulating an experimental spectrum. Galvinoxyl

A galvinoxyl radical



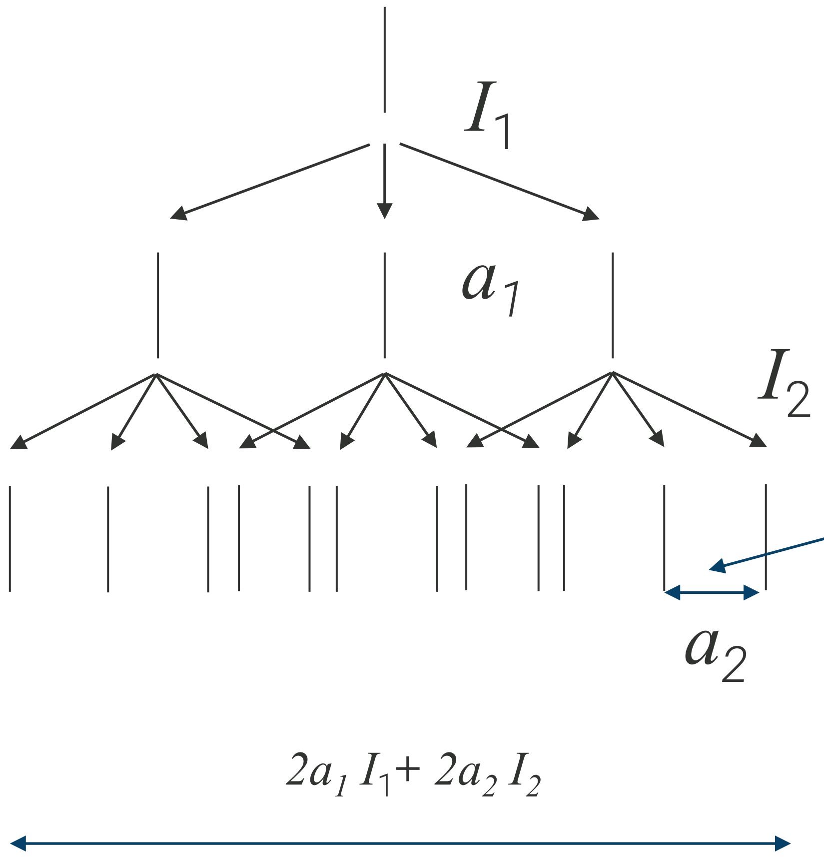
4 protons in the quinone/phenol rings
1 methine proton

12 methyl protons do not show resolved splitting, but cause line broadening



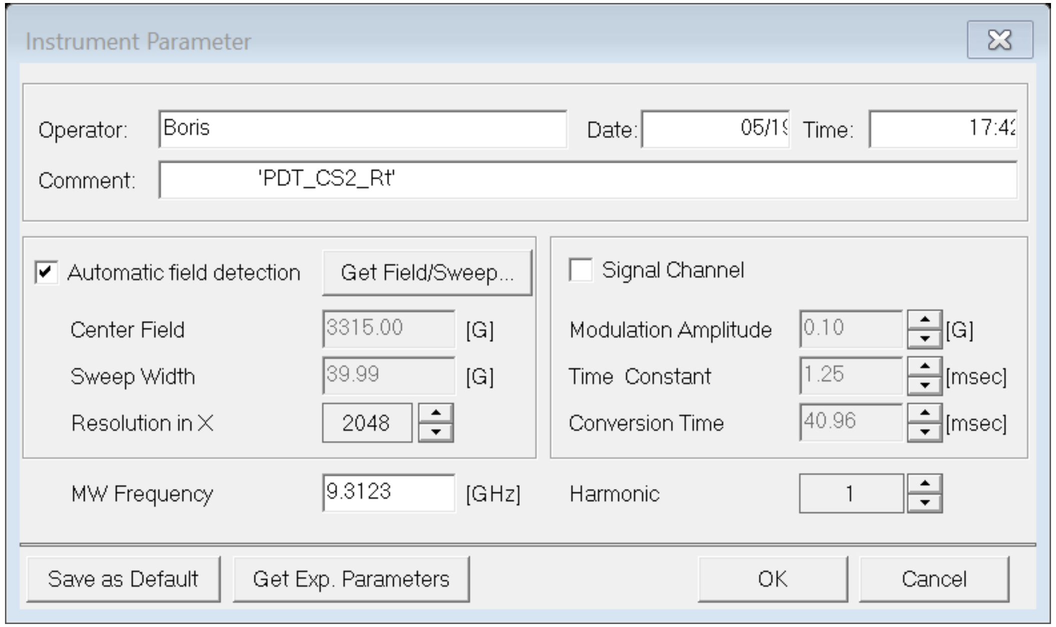
$$a_2 \approx 4 \times a_1$$

Assignment of hyperfine splitting values



Smallest hyperfine splitting

Simulating an experimental spectrum. Getting instrumental parameters from experiment



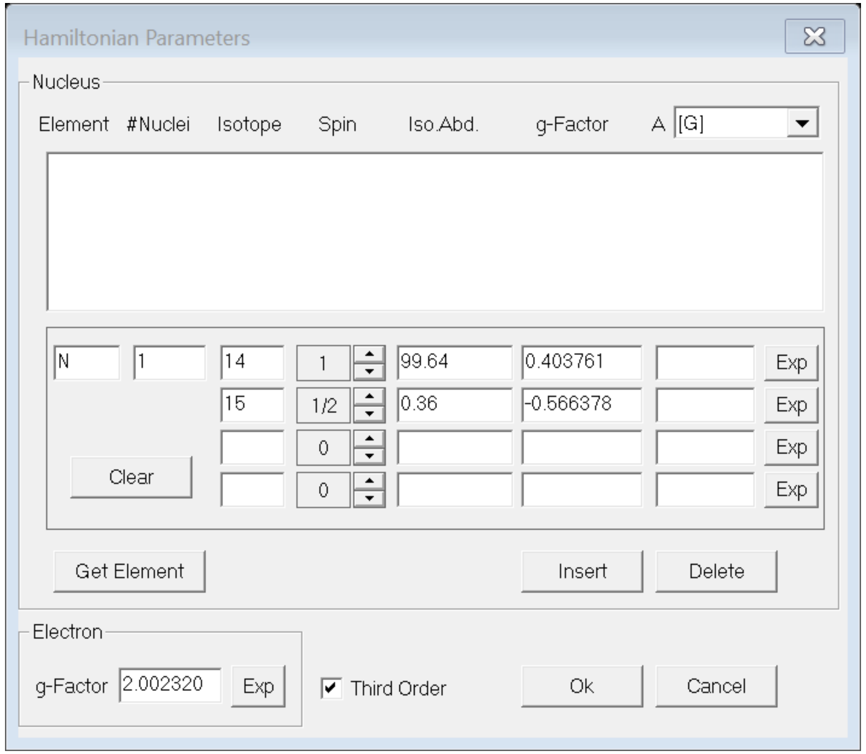
Operator: Boris
Date: 05/1
Time: 17:4
Comment: 'PDT_CS2_Rt'

☑ Automatic field detection
Center Field 3315.00 [G]
Sweep Width 39.99 [G]
Resolution in X 2048

☐ Signal Channel
Modulation Amplitude 0.10 [G]
Time Constant 1.25 [msec]
Conversion Time 40.96 [msec]

MW Frequency 9.3123 [GHz]
Harmonic 1

Simulating an experimental spectrum. Getting numbers from experiment



Hamiltonian Parameters

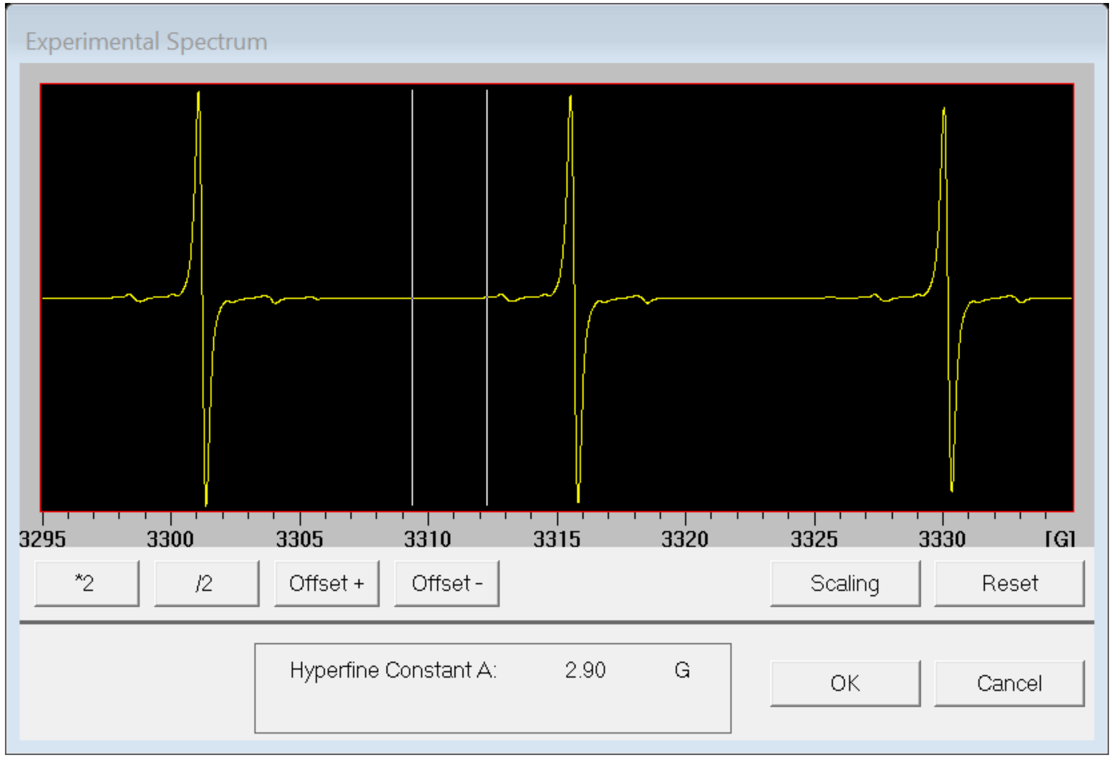
Nucleus

Element	#Nuclei	Isotope	Spin	Iso.Abd.	g-Factor	A [G]
N	1	14	1	99.64	0.403761	
		15	1/2	0.36	-0.566378	
			0			
			0			

Electron

g-Factor 2.002320

☑ Third Order



Experimental Spectrum

Hyperfine Constant A: 2.90 G


WINEPR SimFonia - [Sim7]
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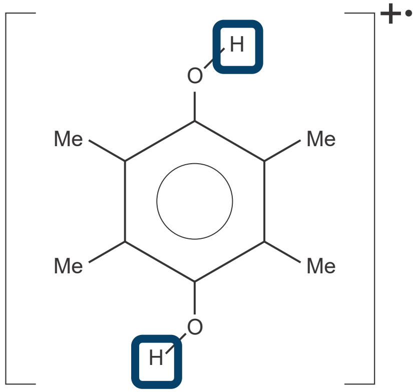
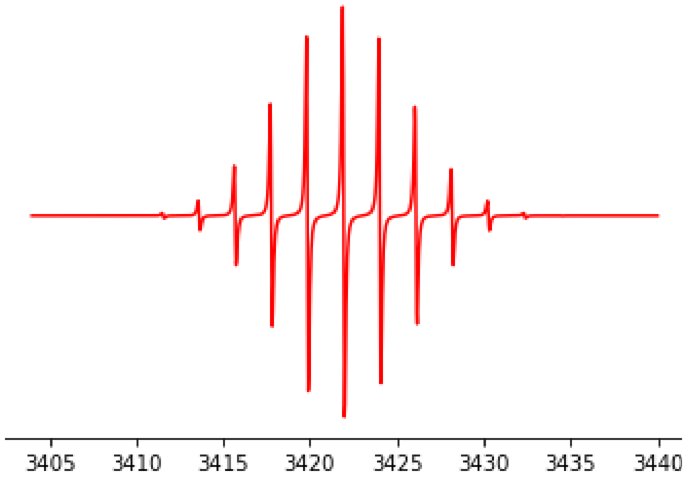
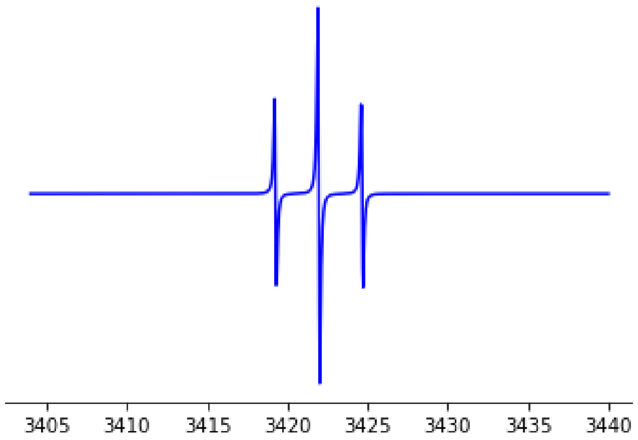
Simulating an experimental spectrum. Duro-semiquinone anion



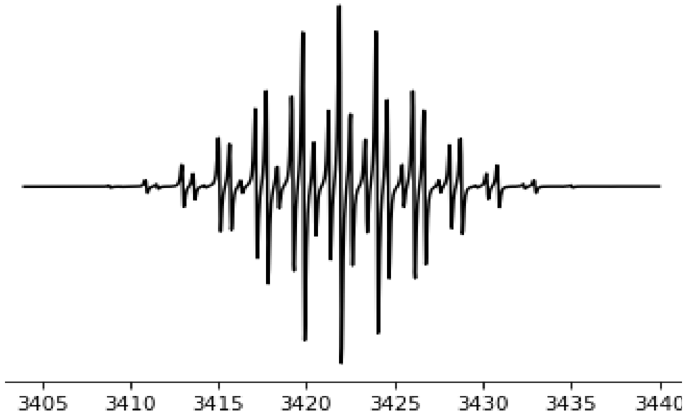
1: 12: 66: 220: 495: 792: 924: 792: 495: 220: 66: 12: 1



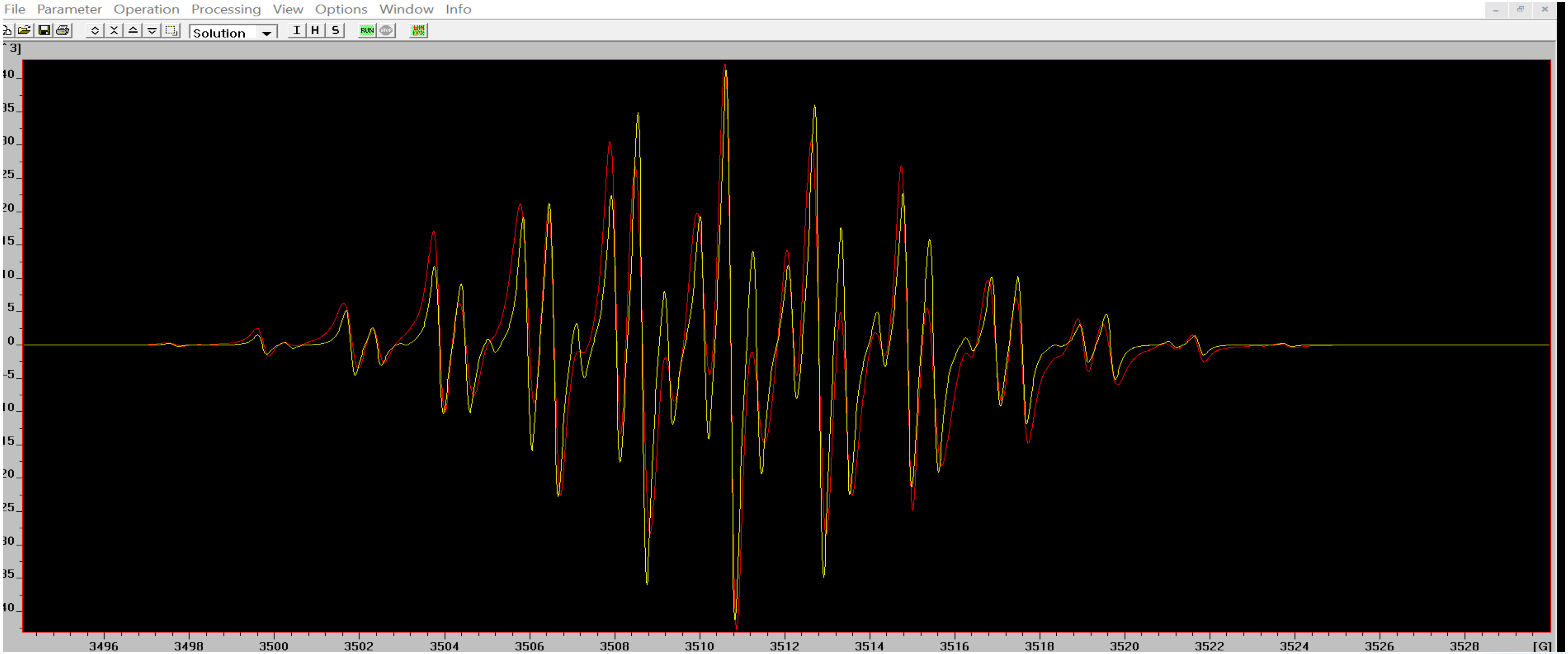
1: 2: 1



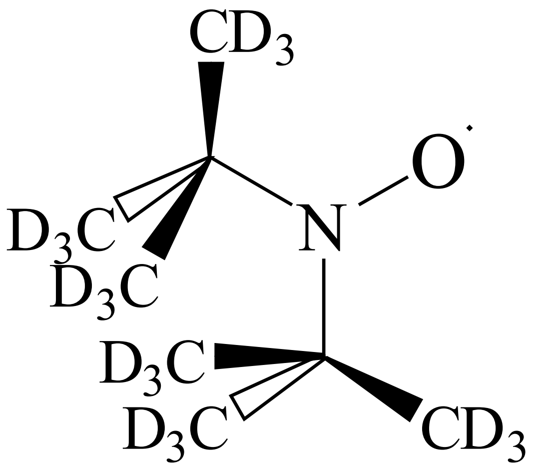
$$\left(2 \cdot 12 \cdot \frac{1}{2} + 1\right) \cdot \left(2 \cdot 2 \cdot \frac{1}{2} + 1\right) = 39 \text{ lines}$$



Duro-semiquinone anion – alternating linewidth



Simulating an experimental spectrum. Di-*tert*-butyl nitroxide



Three main lines from HF splitting on ^{14}N. I=1.

Satellite lines:

^{15}N – natural abundance 0.37%. I=1/2.

^{13}C – natural abundance 1.07%. I=1/2. Eight atoms.

^{17}O - natural abundance 0.038%. I=5/2. Can be neglected.


WINEPR SimFonia - [Sim1]
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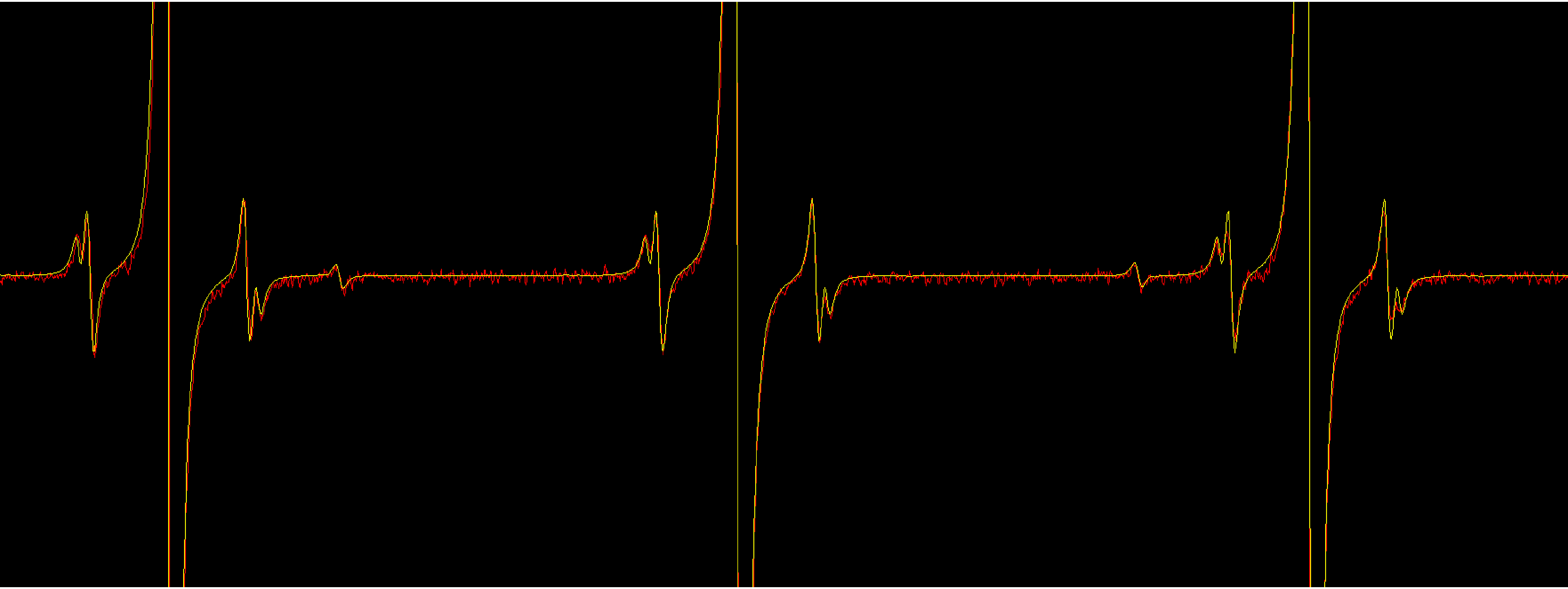
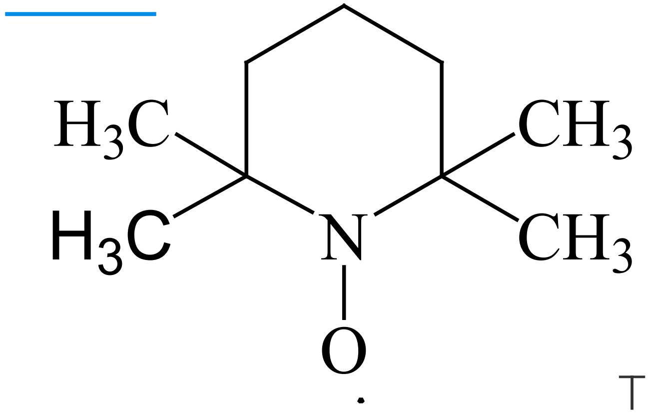
Simulating an experimental spectrum. Di-*tert*-butyl nitroxide



Simulating an experimental spectrum. Tempo in water/glycerol at 230K

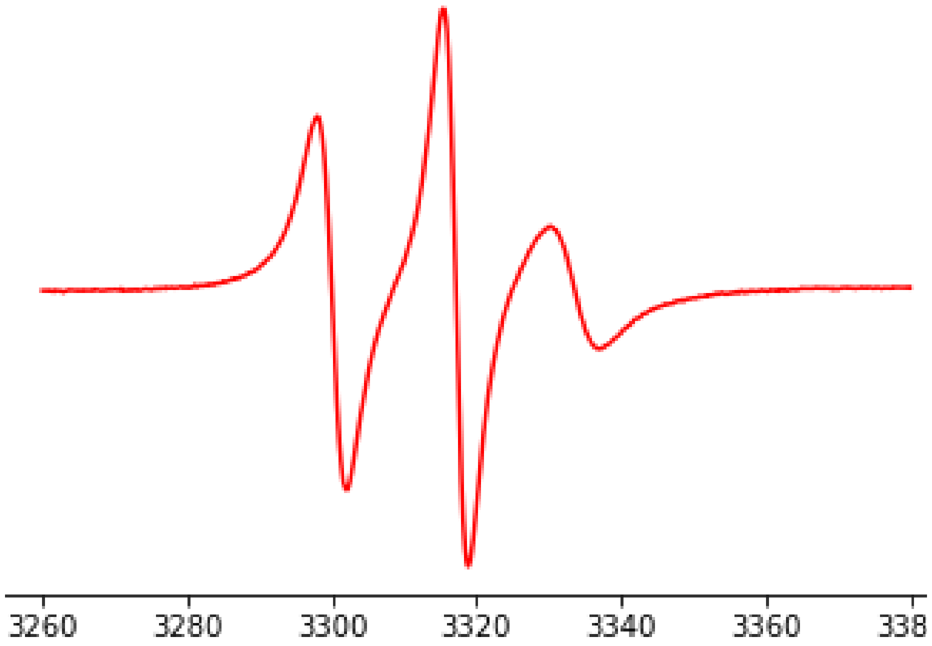


$$\tau = \frac{\eta V}{kT}$$ Stocks-Einstein formula

τ is the *rotation correlation time*, the time to rotate one radian

η is the microviscosity

The lineshape is due to an incomplete motional averaging

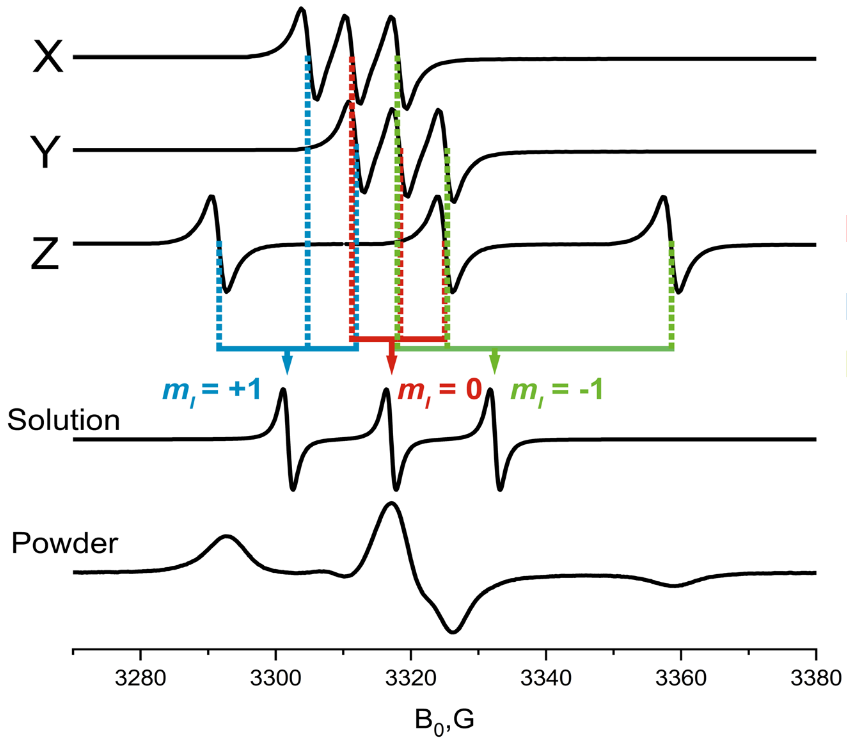


$$\text{Linewidth } = A + Bm_I + Cm_I^2$$

According to the ***Kivelson theory***

Tempo in water/glycerol at 230K. Incomplete motional averaging

In the powder spectrum a position of each line for individual $\boldsymbol{\theta}, \boldsymbol{\varphi}$ orientation is given:



$$B_{res}(\theta,\varphi,m) = \frac{h\nu}{g(\theta,\varphi)\beta} - mA(\theta,\varphi)$$

m=0 the line is spread over the effect of Δg anisotropy: $\frac{h\nu}{g_z\beta} - \frac{h\nu}{g_x\beta} \cong \frac{h\nu\Delta g}{4\beta}$

m=+1 the line is spread over the effect of ΔA - Δg anisotropy

m=-1 the line is spread over the effect of ΔA + Δg anisotropy

g_x=2.0091, g_y=2.0061, g_z=2.0023,
A_x= 6.2, A_y = 6.3, A_z=33.6

Δg alone gives 11.5G
ΔA - Δg gives 15.9G
ΔA + Δg gives 38.9 G

The more the spread the faster motion we need to motionally-narrow the line.

That is why -1 line is always broader and less intense for nitroxide spectra with motion effects!


WINEPR SimFonia - [Sim5]
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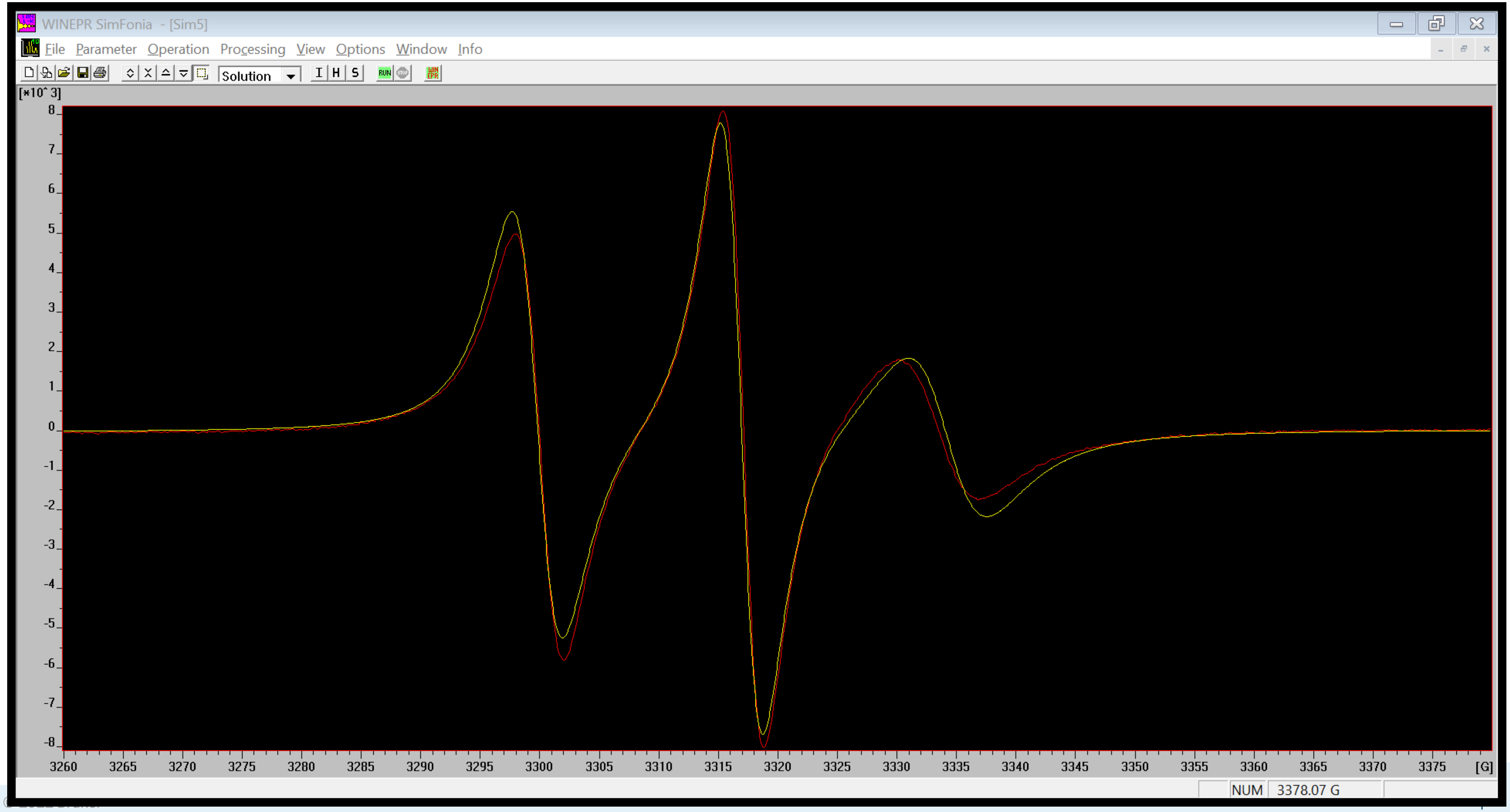
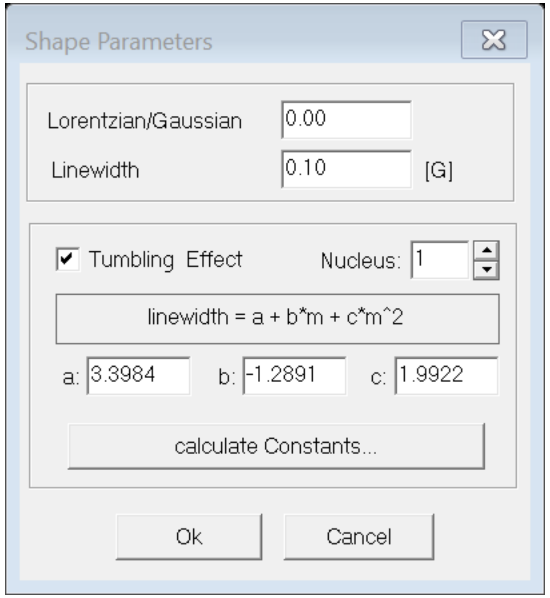
Simulating an experimental spectrum. Tempo in water/glycerol at 230K



Simulating an experimental spectrum. Testing the model



Lorentzian/Gaussian: 0.00

Linewidth: 0.10 [G]

☑ Tumbling Effect Nucleus: 1

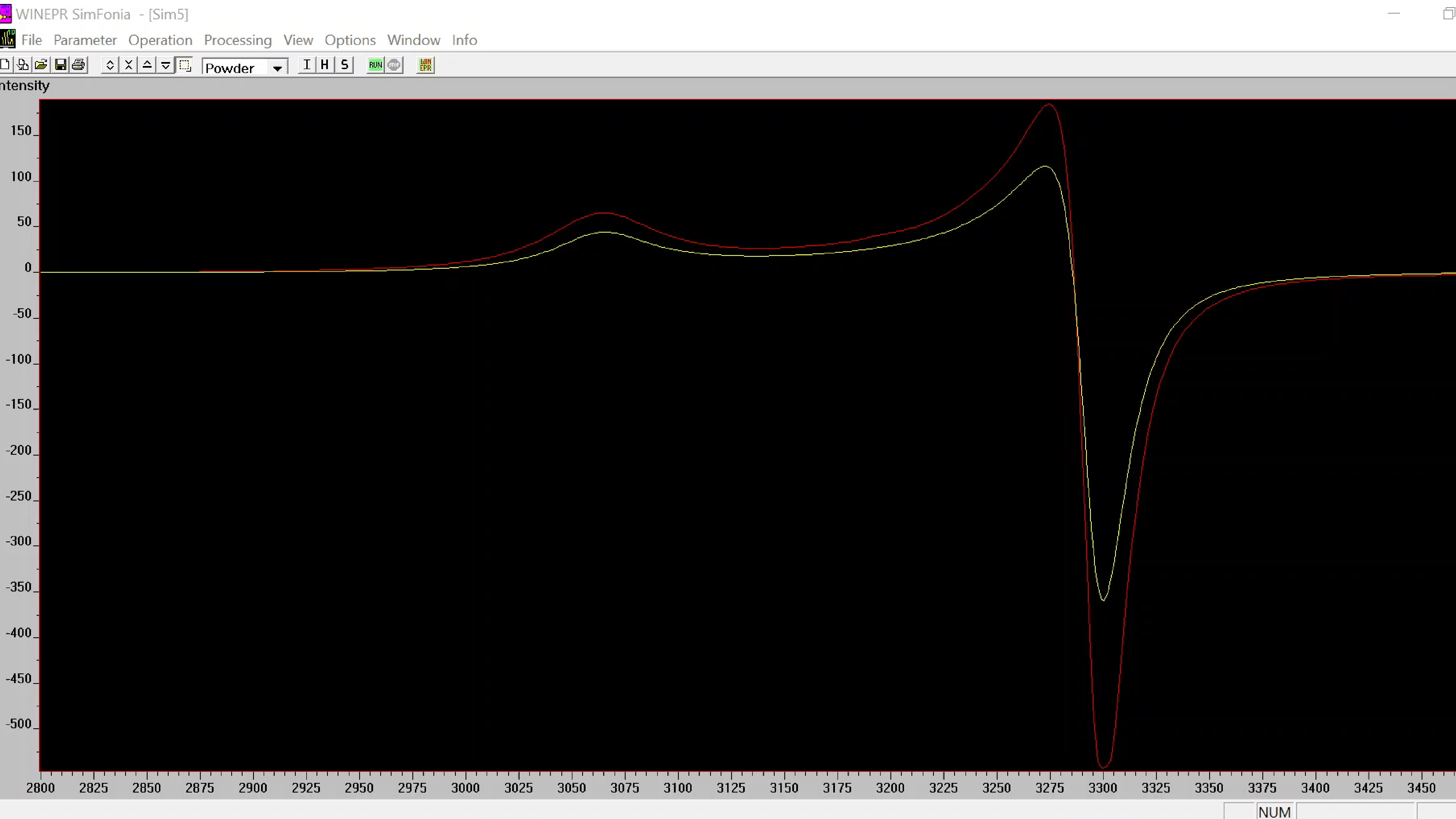
linewidth = a + b*m + c*m^2

a: 3.3984 b: -1.2891 c: 1.9922

$$B = \frac{1}{2}\left[\sqrt{\frac{I(0)}{I(+1)}} - \sqrt{\frac{I(0)}{I(-1)}}\right] = -1.51$$

$$C = \frac{1}{2}\left[\sqrt{\frac{I(0)}{I(+1)}} + \sqrt{\frac{I(0)}{I(-1)}} - 2\right] = 2.01$$

τ from C:	2.1 ns
τ from the I(+1)/I(-1) formula applied to the experimental spectrum	2.4 ns
τ from the simulations based on stochastic Liouville equation	1.7 ns


WINEPR SimFonia - [Sim5]
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BRUKER

Innovation with Integrity

Any questions?

Thank you!