

Simulations of Powder Spectra using SimFonia



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 Mn²⁺, VO²⁺)

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

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Starting a simulation, Hamiltonian parameters

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Starting a simulation, Shape parameters



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)

Anisotropic line width:

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simulation done!



Further processing

WINEPR SimFonia - [Sim4]



The number of θ and ϕ orientations





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.

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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 $\phi = 1$.
- 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(ClO₄)₂

The line shape is defined by the g-factor anisotropy. An Axially Symmetric g-Factor with $g_1 > g_1$.



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

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Iron cofactor in myoglobin

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



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Cu(bp)₂(ClO₄)₂. A Rhombically Symmetric g-Factor



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Cu(bp)₂(ClO₄)₂. A Rhombically Symmetric g-Factor

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Copper sulfate in frozen water/glycerol



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Copper sulfate in frozen water/glycerol



VO-TPP



A complex compound of Vanadyl ion (VO²⁺) 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.





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.





Find the initial g-values



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Any questions? Thank you!

Innovation with Integrity