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Magn. Reson. Discuss., author comment AC2
https://doi.org/10.5194/mr-2021-45-AC2, 2021


# Reply on RC2

Matías Chávez et al.

Author comment on "Residual dipolar line width in magic-angle spinning proton solid-state NMR" by Matías Chávez et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-45-AC2, 2021

Response to Reviewer 2:

**Q:** ABMS, like proton-proton dipolar interactions, yield a MAS dependent line width. How do the authors differentiate between the two effects. The same applies to the MAS induced frequency shift (see e.g. Alla and Lippmaa, Chem. Phys. Lett. 1982, 87, 30-33; Samoson et al. Solid State Nucl. Magn. Res. 2001, 20, 130-136). While reading through the paper, one gets the impression that dipole-dipole interactions dominate the proton line width. The abstract / title should be modified into something like "Residual line width resulting from proton dipolar interactions in Magic-Angle Spinning Solid-State NMR" in order to avoid confusions. To differentiate, some experimental data on the field dependence of the MAS dependent line width would be highly appreciated.

**A:** We agree that the title should include the fact that we exclusively discuss broadening from dipolar contributions. Therefore, we have changed the title to "Residual Dipolar Linewidth in Magic-Angle Spinning Proton Solid-State NMR". We have also added dipolar in the abstract in two locations. The influence of ABMS on line position and line width has been proven to be elusive in the literature. The way we understand this effect is that ABMS originates from the shape and finite dimensions of the crystallites present in the powder sample. MAS averages ABMS contributions from the isotropic susceptibility but not ABMS effects originating from the anisotropic part of the susceptibility. The reason for this is the fact that they can be described as the product of two second-rank tensors that generate rank-0-2-4 components. Therefore we expect a line shift due to anisotropic ABMS contributions, rank-2 that are averaged out and rank-4 that are scaled but not fully averaged out (see Alla and Lippmaa, Chem. Phys. Lett. 1982, 87, 30-33 section 3). However, the ABMS line width should scale with P_4(cos(\theta_m)) and should, in principle, be MAS independent as should be the shift. They are both B_0 field dependent as is experimentally shown in Samoson et al. Solid State Nucl. Magn. Res. 2001, 20, 130-136. If our understanding of the ABMS shifts is wrong, we would appreciate more pointers where we misunderstood the literature.
We have not included experimental data since we are mostly interested in the theoretical underlying mechanism of the changes in scaling of the MAS line width. We reference several papers that discuss this experimental finding in the introduction (around line 40): "Experimental observations of the residual homogeneous line width as a function of spinning frequency show that it can often be approximated by a linear correlation with the inverse of the spinning frequency with some deviation that indicate a partial inverse quadratic dependence (Nishiyama, 2016; Sternberg et al., 2018; Penzel et al., 2019;

Schledorn et al., 2020). This has been attributed to third-order contributions to the effective Hamiltonian or to chemical-shift effects (Sternberg et al., 2018; Moutzouri et al., 2020)." We hope that this is sufficient.

**Q:** In the manuscript, the authors do a great job in discussing the MAS dependent 1H line width. Unfortunately, the contribution to the signal that is hidden in the Pake like pattern in the base line is not quantified. Can the authors give an estimate how the intensity is changed with MAS frequency using second-order Hamiltonian arguments ? This would be extremely interesting, since most solid-state NMR experiments are sensitivity- and not resolution-limited. The manuscript is very similar to a recent paper by Xue et al. (J. Phys. Chem. C 2018, 122, 16437). The authors should discuss theoretical versus computational approaches to yield an understanding of proton resonances in the solid-state. In the presented approach, the geometry is restricted to very few angles and distances. Is it possible to derive general laws if only a few spins are considered ?

**A:** The line width is easy to assess via an expansion of the moments but of course there are many distributions that produce the same (second) moment and an easy guess of the line height is not possible. Of course in the limit of many spins, we might get a Gaussian line and then we could predict the line height. However, to what extend this is true, we do not know yet and is part of our current research efforts.
The appendix (and also references cited in the paper) give analytical expressions for the second- and third-order Hamiltonian. Based on these expressions, one can calculate analytical solutions of the line width. However, the expressions become very complex functions of the distances and relative orientations of the couplings and it is not easy to get much insight from them beyond the form of the spin operators. This is the reason that we opted for a numerical implementation of the effective Hamiltonians. The strength of this method is that we can distinguish which order of the effective Hamiltonian contributes which is not accessible from a purely numerical simulation as in the work by Xue.

**Q:** While reading the paper, one gets the impression that a proton line can be infinitely narrow if only the MAS frequency is high enough. The authors should add an additional term to their equations which summarizes the contributions to line width that are not affected by MAS. At which MAS frequency does the 1/omega_r dependence break down ?

**A:** The homonuclear dipolar part of the line width that is discussed in the paper has no spinning-frequency independent term. Of course, other homogeneous parts of the line width, e.g., relaxation terms or chemical exchange and inhomogeneous terms, e.g., sample inhomogeneity or ABMS shifts might broaden the line in addition to the dipolar line width as discussed in the introduction (around line 25). It depends on the relative magnitude of the various contributions where the 1/omega_r dependence breaks down and no general rule can be given. Especially, sample inhomogeneity and ABMS contributions can vary over a large range of values.

**Q:** I am missing a paragraph in which the theoretical considerations are compared with experimental data, and correlate theory and experiment. The author did this for the MAS induced frequency shift shown in fig 8 which is very nice. However, I am missing a discussion on the line width. The data for phospho-serine exist (at least in the MAS range 70-160 kHz), and it should be straight forward to read out the line width after a line shape fit.

**A:** The isotropic line shift can be compared quite well because it looks like the dipolar contribution to the isotropic line shift is the dominating one. As discussed above, there are many contributions to the line broadening and we do not claim that we can predict the line width from one simple three-spin simulation. In addition, the focus of the paper is on understanding the spinning-frequency dependence of the line broadening and not predicting the line broadening. Therefore, we do not want to make comparison to

experimental data of the line width but give references to published data that illustrate the spinning frequency dependence.