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Magn. Reson. Discuss., referee comment RC2
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Comment on mr-2021-45

Anonymous Referee #2

Referee 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-RC2, 2021

The manuscript by Chavez et al. reports on second-order Hamiltonian analysis of proton resonances as a function of the MAS frequency. The authors find that the residual proton line width follows a 1/omega_r^1 dependence beyond 50 kHz of MAS. Chemical shift truncation can induce a 1/omega_r^2 dependence. This is a very interesting paper that should be published as soon as the authors have addressed the following issues.

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.

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 ?

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 ?

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.