

Magn. Reson. Discuss., referee comment RC2
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Comment on mr-2021-51

Benno Meier (Referee)

Referee comment on "The relation between crystal structure and the occurrence of quantum-rotor-induced polarization" by Corinna Dietrich et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2021-51-RC2>, 2021

In their paper "The relation between crystal structure and the occurrence of quantum-rotor induced polarization", the authors search for structural motifs that give rise to substantial quantum rotor induced polarization, in an attempt to broaden the applicability of the phenomenon. The authors have studied a significant range of compounds, and their search criteria, e.g., crystal structures in which two methyl groups face each other, are perfectly reasonable.

That said, it appears that the authors have not been able to observe a QRIP phenomenon on any of the newly tested compounds with plausible structures. To the contrary, QRIP is observed in substances with a substantial tunneling splitting, even if these substances violate the plausible assumptions on low barriers. This observation shows that it is indeed difficult to "guess" the tunneling splitting based on structural motifs.

While this represents a negative finding, it is still a rather conclusive one, and suited for publication in Magnetic Resonance.

I have the following suggestions for the manuscript:

- In the abstract, the authors write that "a high tunnel frequency is favorable". This should in my view be rephrased to "is required". After all, if the tunnel frequency is small, there is no quantum rotation, and - consequentially - no QRIP will be observed.

- It may be confusing to readers who are not very familiar with the effect, that a free rotor shows a large tunneling splitting. Indeed, in the limit of free rotation, there should be no tunneling. It would therefore be valuable to point out that the tunneling splitting is defined

as the difference between the first two rotational states, and it is the population differences across these states that give rise to QRIP.

- The authors find a small, but significant tunneling splitting in compounds 8 and 12, but do not explicitly report details on their attempt to observe QRIP in this compound. Was such an attempt made? What was the concentration after dissolution? Is ^{13}C labelling possible? Perhaps it is worth pointing out, that larger molecules will also tend to "lose" quantum-rotor-induced polarization more quickly due to their longer correlation times.

- The authors report on MAS QRIP experiments. How have these actually been conducted? QRIP requires equilibration at 4 Kelvin even in the most favourable cases. Have the authors performed such a temperature jump experiment with MAS? If yes, it would be prudent to give the details of temperature vs. time. A key parameter would be, after all, the time required to ramp the temperature from 4 K to say 30 K. If no such experiment has been conducted, the MAS data will be completely inconclusive with respect to QRIP, and should not be shown in the manuscript.

Finally, the manuscript is very well written overall, but the jubilee's spelling in the special issue statement should be checked.