

Magn. Reson. Discuss., referee comment RC1
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Comment on mr-2021-51

Malcolm Levitt (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-RC1>, 2021

Dietrich et al. describe a noble, but ultimately failed, attempt to determine the crystal structure constraints that lead to the existence of a strong QRIP/Haupt effect in gamma-picoline. As stated by the authors, this effect relies on a large tunneling splitting in the cryogenic solid state which corresponds to a substantial energy splitting between the methyl spin isomers. Cooling such samples leads to an overpopulation of one spin isomer which persists when the sample is raised to ambient temperature; the recovery to thermal equilibrium induces transient hyperpolarization effects, as elucidated by some of the cited papers. The authors try to pin down which structural motifs lead to the large tunneling splitting. They investigate a variety of compounds which exhibit a similar motif of interacting methyl groups in their crystal structure. However, they only found a few compounds that do exhibit a QRIP effect and even then the effect was much weaker than in gamma-picoline.

Although the results are largely negative, I do think that this study deserves to be in the scientific literature, since it demonstrates that either gamma-picoline and the few other compounds that show a strong QRIP possess some very subtle structural feature that has escaped detection by the authors in their detailed study, or possibly that the crystal structure is not the determining factor after all. For example some subtlety of the phonon spectrum might be responsible, although I confess that I have not much of an idea where to look. Nevertheless, I do suggest that in their conclusions, the authors might at least speculate on the possibility that molecular and crystal structures are not the determining factor for this phenomenon after all.

A few small things should be corrected. It is not quite true that "only the methyl groups of a few substances seem to allow for the effect". Very weak QRIP effects have also been observed in ¹⁷O water-endofullerene (doi.org/10.1103/PhysRevLett.120.266001). The authors cite Ludwig et al. (PNAS, 2010) as having studied QRIP, but the attribution of the described effects to QRIP have been disputed (doi.org/10.1016/j.jmr.2017.12.009). I was surprised to see that the article cited as Roy 2013 has a completely incorrect list of authors. That error suggests that all references should be rechecked carefully.

A compilation of the studied molecular systems in one place would be helpful. In some cases one has to trawl through the text to find what a certain number refers to.

I do not feel that providing the X-ray structural data of some of the compounds is worthwhile in the main text (figures 7, 8). The MAS spectra of the MOFs also do not seem worthy of display in the main manuscript, especially since the QRIP results were negative.

On the other hand, the authors cite neutron scattering data which shows a tunneling splitting, but never provide this data at all. Personally, I would be more interested in seeing that.

In summary this is a worthwhile study, and should be published, even though the authors were not able to shed much light on why a few special compounds exhibit a large methyl tunneling splitting, leading to a significant QRIP effect upon dissolution. Maybe the crystal structure is not the place to look for an explanation.