

Review in Black

Response in Red

Manuscript parts in blue

The manuscript of Wili et al. describes a very new and exciting experiment to measure dipolar couplings between two trityl radicals at Q-band frequencies using spin-lock techniques and phase modulation two pulse echo of this 'dressed spin states' in the nutation frame. This work adds a new possibilities to prolong the observation time window for the measurement of dipolar couplings in EPR which could be useful to extend the distance range in the future. Despite the fact that the experimental problems seen (and described very clear and fair in the manuscript) do not allow routine application of this methods yet for long distances (where the dipolar coupling strength is much less than the inhomogenous linewidth) this very new approach is very interesting.

The experiments as well as the theoretical description and discussion is very good, the literature is cited appropriately and the existing problems with this very new approach – especially limitations with respect to Rabi oscillation frequency strength in comparison with the inhomogeneous linewidth – is fair and clear described. There are many interesting aspects in this work, as for example also the large difference between  $T_{1\rho}$  and  $T_{2\rho}$ , which will stimulate further work in this direction. I recommend publication of this very nice and innovative article.

We are pleased to see your positive review.

Some small remarks:

- Line 26 there should be an 'for' instead of 'or'

We corrected the mistake (actually Line 24).

- The exchange interaction is explicitly mentioned in the theoretical part; also the fact that in the interaction frame it might gain some additional importance because the Zeeman splitting and the linewidth offsets disappear. But then it is not mentioned any more. Of course the two model systems will not show such contributions, but maybe the authors have investigated potential effects of this theoretically? It would be nice to have a remark on this aspect in the discussion (or conclusion). As far as I see all trityls will be in the strong coupling regime, so the method could also work for shorter distances, where such interaction might play a role.

We did not perform any simulations, but we now added a sentence in the theory part. The paragraph on the exchange coupling now reads (starting from line 124 in the highlighted manuscript);

If, both, the dressed spin offsets as well as the spin states of the two spins are the same, exchange coupling has no influence on the evolution. This is analogous to the situation of magnetically equivalent nuclei in liquid state NMR. This different averaging of dipolar and exchange contributions might be exploited experimentally to distinguish the two contributions.

- It will be interesting to see what happens with the deuterated trityl radicals. As mentioned this will be something for a new publication and might shine some more light on the big differences between  $T_{1\rho}$  and  $T_{2\rho}$ . Also the T dependence of these rotating frame relaxation rates could be very interesting (also to further optimize the experiment)

We agree that rotating frame relaxation in EPR is not very well understood and that additional studies are desirable. Unfortunately, we did not systematically investigate the T-dependence of  $T_{1\rho}$  and  $T_{2\rho}$ . We did look at temperature dependence of the decay of the spin-locked echo, but this cannot easily be

translated to  $T1\rho$  and  $T2\rho$ . (See also the answers we will provide to the Review of Jack Freed: <https://doi.org/10.5194/mr-2020-7-RC2>).

While the relaxation in dOTP is interesting as well, regarding application work, the important matrices are water/glycerol and lipid bilayers. The room-temperature rotating-frame relaxation times of (immobilized) trityls would be interesting as well.

- The exponential 'stretch' factors for the fits of  $T1\rho$  and  $T2\rho$  should also be given.

We now report them in all figure captions where they are relevant.

- The modulation amplitude  $aPM$  was set to 0.3 for the experiments and it is also mentioned in the manuscript that the theoretical modelling brakes down if this factor becomes too large. Can this be more quantified?

We did not systematically quantify this in a way that we could specify an exact cut-off where the experiment fails. We looked at the phase-pulse nutation curve (Fig. S5) and took a value where the dressed  $\pi$ -pulse length was not too long, but the additional oscillations were not too large. Some articles (e.g. Laucht *et al.* <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.94.161302>) point out that the breakdown of the rotating wave approximation could be used to generate faster switching times, i.e.  $\pi$  pulses. So far, we do not see a reliable way of doing this. Note also that we use a phase-phase cycle, which should cancel some contributions from imperfect dressed spin pulses.