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Reply to “Comment on 'Muon spin relaxation study of spin dynamics in poly(triarylamine)’”

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McKenzie et al raise five major points of discussion in the comment entitled “Comment on 'Muon spin relaxation study of spin dynamics in poly(triarylamine)’”which are addressed in the following response.

The first point relates to the broadness of the Avoided Level Crossing (ALC) resonances for which it is commented that there should not be narrow Δ_1 ALC resonances due to cyclohexadienyl type radicals in a polymer below Tg due to a distribution of dihedral angles with neighbouring phenyl rings. As stated in the original manuscript [1] the ALCs are indeed broad for various reasons and the consequence of this is that not all resonances can be resolved individually. Indeed, one of the reasons is that mentioned by McKenzie et al. It is worth noting that one possible way to take into consideration the broadening resulting from distribution of dihedral angles with neighbouring phenyl rings may be to employ in the model a distribution such as a Gaussian to represent the distribution of angles. However, as the exact distribution is not known this would be an assumption.

Naturally, as described in the original manuscript the broad nature and closeness in value makes it impossible to resolve all the individual ALCs in any model and therefore to clarify the eSR determined in the original manuscript is the average eSR of the whole system. This leads in to the second major point that the comment raises. It is stated that it seems inappropriate to fit 11 independent resonances, each defined by 3 or four parameters, when each “resonance” is defined by only a few points. Here we firstly offer some clarification as it would appear the analysis method used may not have been fully understood; in the case of the original manuscript the data was modelled, not explicitly fit, to the overall spectra incorporating *all* the data points. The model was constructed from individually simulated ALCs which were summed together to produce an overall line spectrum and the parameters were set to typical values within physical constraints. The width of the overall ALC was constrained by the width of the calculated spectra thus the limit on the A values mentioned in the analysis. It is not possible to directly compare the individual calculated values as was noted in the original manuscript since firstly the calculations were performed on a monomer for which the overall spectrum is higher in field and secondly the broadness and overlap make the values in the measured spectra unresolvable. The use of 11 ALCs was not arbitrary but was determined as the minimum number to ensure real physical parameters in the model while still achieving the correct over all line shape thus, while perhaps seeming at first sight over complex, did indeed conform to good scientific practice.

Nevertheless, to reduce the complexity of the original model and address the point raised in the comment further we have since re-analysed the data using a simpler revised model. The updated model utilises the direct integration of the area of the resonance for a single broad simulated ALC with an average A, D and E value. The key factor is the change in the area with increasing eSR. Using this modelling method the eSR value can be directly determined from the change in the integrated area of the measured resonance via the simulated curve. There are no scaling factors involved and no assumptions about the broadness of the ALCs as it is a single resonance. The full details of the modelling and results are currently being prepared for publication. The key result is shown in Figure 1, which includes the original modelled value of the eSR from the manuscript plotted against the percentage area change for the measured resonance being modelled. The results show that the values are in very close agreement with the simulated curve for the percentage area change as a function of eSR, thus validating that the complexity of the modelling approach is not an important factor in reaching the scientific conclusions reported in the original manuscript. The original conclusions are based on solid scientific fact. Another key factor in the new model is that there are no constraints applied or comparisons from the DFT calculations which are the third major point of discussion raised in the comment.

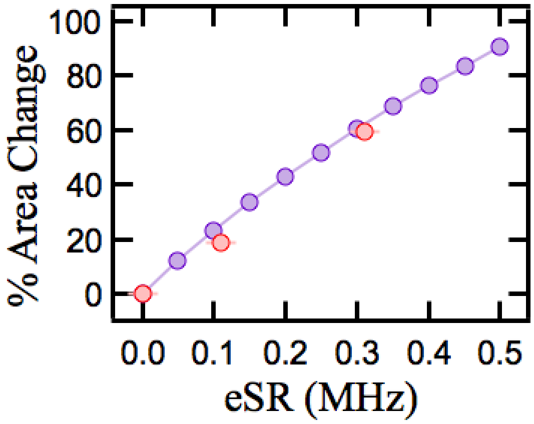

Figure 1: The change in area as a function of eSR for a single simulated ALC. The red points are the he area change of the actual measured ALCs plotted against the original modelled eSR values.

It is stated in the comment that by using semi-empirically optimized structures and neglecting the effect of vibrational averaging due to the light mass of the muon makes the method not appropriate for accurately calculating the hyperfine coupling constants of muoniated radicals. However, with regards to the monomer spectra simulated using DFT, although it was not explicitly stated in the original manuscript, quantum correction was actually applied referenced to the experimental data for the radical in benzene [2]. The difference in couplings we find between the semi-empirically minimised structure and a DFT-minimised structure is minimal and would certainly be much smaller than the difference in coupling between sites on the monomer as well as the broadening induced by the distribution of dihedral angles in the polymer, so the additional computational cost versus questionable improvement in accuracy of the latter method is not justified or appropriate in this case where comparing the broad distribution of couplings in the monomer with the measured polymer data is the overall purpose of the calculation.

The fourth point questions whether the increases in the amplitude of Δ_1 resonances can be caused by other things than electron spin relaxation such as motion of the free radical. Indeed, eSR is not the only possible mechanism that could lead to an increase in the amplitude of the resonance and we do not disagree with the fact that there may be additional processes present. However, many molecular organic systems in addition to the PTAA polymer have been measured in this way and found to show similar behaviour without the extra orientational freedom of the polymer. If the increase were predominantly due to reorientational motion of the radical then the increase with temperature would be expected to be highly dependent on the nature of the host system for the radical. This has not been found to be the case and the trend with temperature in all the systems including PTAA (for both the reported n=10 and additional measurements of n=80 and bimodal systems not yet published) has proven to be very similar with no significant difference in the activation energy for the amplitude increase. The accumulated data we have at present points very clearly towards a dominant mechanism of eSR driven by spin-orbit coupling as being the most likely mechanism to describe the temperature dependent ALC amplitude. This does not preclude an experimental system being found in which reorientational motion of the radical is the dominant contributor to an ALC amplitude increasing with temperature, but we are not aware of any system where this has been demonstrated unambiguously as the dominant mechanism.

The last point raised in the comment relates to the method of background subtraction and the relation of the consequent errors with respect to those quoted in the original publication. The errors were determined by changing the parameters until an observable difference in the line shape was achieved thus providing a lower limiting value and error on the parameter. This point was discussed at the peer review stage of publication and thus is worth clarifying here since a visible effect is noticed on the overall spectra for a limit of ± 0.02. We demonstrated the validity of the error bar on the eSR as we simulated the ALC at 290 K for the reported eSR value and the eSR value plus and minus 0.03 μs^{-1} (just outside the stated 0.02 μs^{-1} error bar) and then analysed the difference-plots between the data and the model at the most sensitive region of the ALC (the lowest polarisation region). These plots are shown in Figure 2 and there is a clear difference in the ALC model that leads a noticeable shift from the zero line in the difference plot. It is thus possible to determine that the eSR values either side of the reported value plus or minus the error bar do not sufficiently model the resonance. These plots support the small reported error values on the eSR parameter.

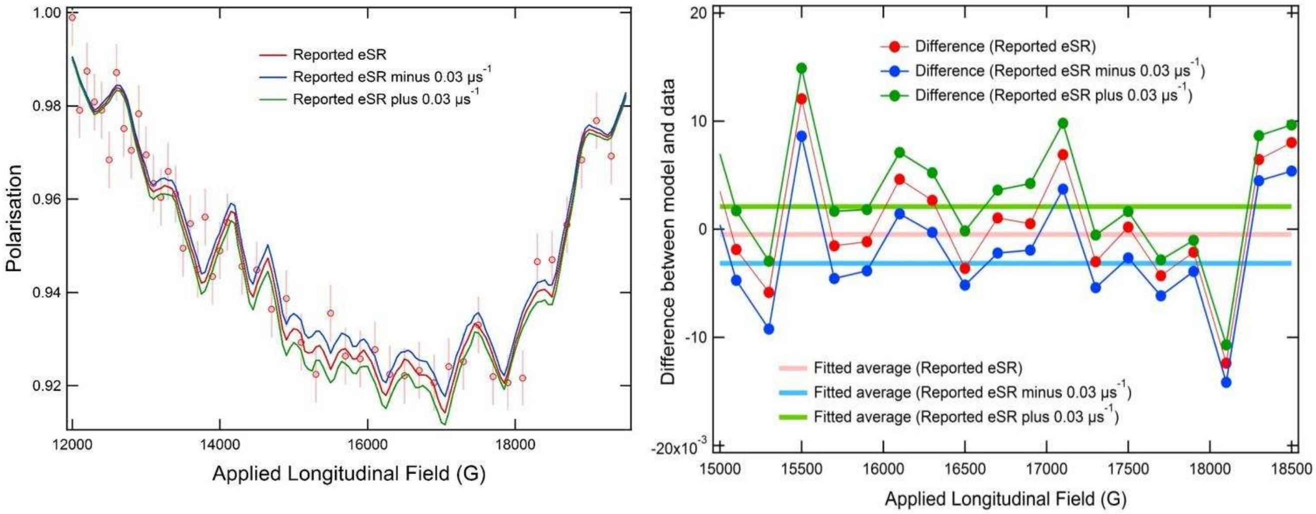

Figure 2: (left) Simulated curves at 290 K for the reported eSR and the eSR plus and minus the reported error value. (Right) The difference between the measured data points and the simulated curve for all three eSR values. The average of the difference is the solid line. Note the shift from zero in the curves with plus or minus the reported eSR value.

As is rightly determined from the thesis of M. Willis [3] the background will play a role in the error on the eSR and a local polynomial is used to remove the background rather than a measured background (this an accepted method that has been used in previous publications). This method is used as given the slow oscillatory nature of the background it is reasonable to use a polynomial to fit the local background. By continuing to read the whole of the thesis it is clear that the error from this method is addressed and it is explained that it would add a constant systematic error to all the data points. Since the primary focus is the trend such an error would not change this thus is not over significant to the result. Even so, a larger error bar is placed on the plotted eSR results to account for it. As also described in the thesis one possible way to quantify this systematic error is by carrying out multiple completely independent analyses then comparing the results and taking the largest difference as the error (this was carried out using three independent analyses in the thesis).

In summary the comment raises some detailed points for discussion which have been addressed in this reply, however the points raised do not affect the original overall conclusions of the paper which are that the wavefunction is substantially localised to a single monomer unit, given the high field of the resonance (this is independent of the model) and that the eSR model can be used to explain the increase in the ALC amplitude and gives a result similar to that found in the small molecule systems. The results and discussion presented here show that whilst the original modelling may have seemed quite complex with 11 ALCs, the revised simpler analysis in fact arrives at the same conclusion. We believe that the conclusions in the original manuscript were derived in a manner which conforms to good scientific practice and thus far no other model has been presented to properly explain the increase in amplitude of the data, which was analysed within the simplest model available to us at the time.

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