

Interactive comment on “Hyperfine spectroscopy in a quantum-limited spectrometer” by Sebastian Probst et al.

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General

I think this is a high quality paper that builds on the groups previous published work. The combination of tiny resonant volume, very high Q, ultra-low temperature, but still relatively short T1 (due to the Purcell effect) , and very low detector noise figure, I think previously set a new standard for absolute sensitivity for inductively detected EPR, and I think is a terrific technical achievement.

I think this paper now convincingly shows that the previous system bandwidth can be widened sufficiently to enable quantitative ESEEM to be demonstrated on two model systems (in an interesting rather low field regime) and supports the statement that

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“the results bring quantum limited EPR spectroscopy one step closer to real world applications”. In my view, that is a very nice stand-alone result.

I think the paper will be of interest to those involved with instrumentation, quantum control, and solid-state EPR more generally.

At one level, with minor changes the paper could be published as is, but I have a few suggestions regarding content and structure for the authors. I stress that the comments below are only intended to require minor changes and not require substantial extra work. However, I think a few extra sentences in key places would add to the impact and understanding of the work for the target audience for this journal.

Specific Comments

I might consider slightly rearranging the introduction. It perhaps was not intended, but the implied criticism of non-induction mode techniques in the introduction is that they often require specific samples and special instrumentation, but then the authors then describe a very special system that requires specially prepared samples and (at first sight) specific spectroscopic properties.

The authors state that normal ESR systems have spin sensitivities of between 10^6 and 10^{11} per root Hz (and have previously quoted 10^{13} in their previous Nature publication). This statement really needs some references to allow fair comparisons, as sensitivity not only depends on frequency and temperature (and type of resonator), as indeed the authors point out, but also very much on sample linewidth and relaxation times (and for ESEEM the hyperfine splittings) Some of these comparisons I suspect are also for systems more optimised for concentration sensitivity. It would also be appropriate to reference other groups that have also done nice work on improving absolute sensitivity (such as Blank and Suter).

I really wasn't sure about just repeating the background ESEEM theory from Jeschke and Schweiger at the start of Section 2, as opposed to giving key formulae and refer-

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encing Schweiger. Most pulse EPR spectroscopists will be familiar with that theory, or if they are not – would almost certainly gain more from a more qualitative overview of ESEEM, and then just giving the key formulae and references. It wasn't clear to me that it was particularly helpful in understanding later discussions, at least in the main text, and so could perhaps be put in the SI. I would comment there is a lot of nice work / studies described within the SI where I think it is helpful. This is just a suggestion, and I wouldn't object if the authors felt strongly otherwise.

However, I think most EPR spectroscopists would prefer to have a slightly more extended discussion on what the barriers are to extending the technique to more “real-world samples”, (as mentioned at the end of the introduction). I found it a little difficult to judge how far the instrumentation could be pushed towards the bandwidths typically used in standard experiments with commercial spectrometers or what the limitations were compared to the authors previous published results.

I think most EPR spectroscopists, when they think of EPR at very cold temperatures, think of the problems associated with very long T1's. In this specific case, I believe, remarkably, T1's are kept relatively short by the Purcell effect. I know it is clear from previous publications but I think this could be emphasized more prominently in the text. More importantly it wasn't clear to me whether the changes in the resonator to accommodate wider bandwidths had an effect on the Purcell rate and the T1 (and repetition rate).

In that context it would also be helpful to state the T1's of both systems and the T2 of the Erbium system, if they are known. At one point it is mentioned that discussion of T2 for is left to another publication, but the value could still be stated.

Similarly, ultra-low noise cryogenic amplifiers are usually avoided in pulse ESR systems, as they easily saturate or are damaged too easily or limit dynamic range. This aspect is partly covered in previous publications but is not really mentioned in the text – and here is likely to be important as input power is increased as bandwidth is lowered

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or shaped pulses are being used. What is the power level of the pulses and what is a practical limit in terms of saturating amplifiers or putting too much heat into the resonator? I recall from a previous publication that the first pre-amplifier (JPA) is switched off during the pulses, but then how long does it take to switch on and what is the saturation and damage threshold. The same question also applies to the following HEMT pre-amp.

I would also find it helpful to give an effective conversion factor (Gauss per root W) for each resonator, which is more common in the EPR literature. Some papers normalise this to the Q . Others do not. As long as it is clear it does not matter.

A major instrumental concern with very cold systems is usually the heat load from the transmission line that transmits the microwaves. I'm guessing the antenna mentioned is some form of dielectric line which gives the necessary thermal insulation. A brief explanation and reference would be helpful.

Most commercial spectrometers are optimised for concentration sensitivity. Normally I think of systems that have very good absolute sensitivity as having rather poor concentration sensitivity (and vice-versa) but perhaps the difference is not so great here, as the spectrometer operates in an unusual regime. Is it possible to make a fair comparison on concentration sensitivity?

Is it the authors view that the technique is restricted to narrow-line semi-conductor and single crystals with specific spectroscopic properties. It potentially looks interesting for looking at paramagnetic defects at, or near surfaces. Is it possible/plausible to think of a scanning superconducting resonant probe rather than placing the resonator directly on the surface of interest? Is it possible to estimate the required surface density of spins for this to be viable?

I think it would be helpful if the authors could say something, even qualitative in the discussion about practical requirements on the linewidth, the hyperfine splittings, the range of concentration of spins within the effective resonant volume and the maximum

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practical magnetic fields (relating to the choice of superconducting resonator).

Who did the work?

Possibly an oversight but I noticed John Morton does not appear to be assigned to any of the work packages mentioned, (other than all contributed to the writing).

Typographical.

The paper is well written.

I note, there are inconsistencies regarding spaces between numbers and units, and spaces before brackets, but that doubtless will be sorted on final type-setting.

I think, where possible, figure captions should be self contained, and it thus would be helpful to be slightly more explicit about which system is being measured within each caption.

Overall

Overall, I found the paper very interesting and recommend publication after minor changes.

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