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Discussions

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Comment on mr-2021-40

Anonymous Referee #2

Referee comment on "Rapid-scan electron paramagnetic resonance using an EPR-on-a-Chip sensor" by Silvio Künstner et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-40-RC2, 2021

The manuscript presents, for the first time, rapid scan measurements performed using a single-chip integrated oscillator. This approach was proposed and very briefly discussed in Ref. (Gualco et al., 2014), but not yet demonstrated experimentally. Contrary to the majority of previously reported works on the rapid scan, the rapid scan in this work is implemented as rapid frequency scan instead of rapid field scan. This is technically possible and very efficiently implemented because a microwave oscillator is used instead of a microwave resonator combined with a microwave source as in conventional EPR spectrometers. In the current implementation a scan range of 64 MHz at the maximum frequency of 1 MHz, which corresponds to a scan rate of 400 THz/s, has been demonstrated. This scan rate is slower that the best results reported to date for the rapid field scan. However, as claimed also by the authors, I believe that significant improvements are realistic. The single chip frequency rapid scan is, indeed, well suited to achieve scan widths, scan frequencies, and scan rates well beyond the current limits of the magnetic field rapid scans. The EPR signal is detected as a variation of the oscillation amplitude as a function of the oscillation frequency. In principle, the measurement of the variation of the oscillation frequency would also be possible but, I guess, practically more complicated because the frequency variation due the EPR resonance would be much smaller than the frequency scan width, creating significant problem of “dynamic range” (which are difficult, although not conceptually impossible, to overcome). It is also important to underline that one of the major problems present in several of the previously reported single-chip integrated oscillator EPR detectors is the relatively large minimum B1, which creates saturation problems in conventional CW slow scan experiments. The use of the rapid scan overcome, at least partially, this issue since the optimum conditions are achieved with a larger B1.

The rapid scan approach demonstrated here is certainly a very important milestone in the application of single-chip integrated oscillator as EPR detectors. For this reason, the manuscript certainly deserve to be published.

Here my major specific comments:

Abstract, Figure 2, lines 190-195, conclusions: The way the spin sensitivity is computed is not clear to me. The authors use a BDPA sample of 0.67 nL. From the spin density of BDPA (about 1.5x10^27 spins/m3), the number of spins is about 10^15. Since the measured SNR is about 236 in a measuring time of 0.75 s (Figure 2), the spins sensitivity seems to me something like 4x10^12 spins/sqrt(Hz), whereas the one declared in the paper is 6x10^7 spins/sqrt(Hz). Since the difference is more than 4 orders of magnitude, I think there is something not correct or unclear in the author's reasoning. The reasoning of considering the previous results obtained with the frequency variation and extrapolate to this case of amplitude detection based on the ratio in SNR between the CW and RS experiments performed here seems to me not "conceptually" correct (and not compatible with the results shown in Figure 2).

Lines 111: It is not clear if the voltage variation measured in this work is equal to the oscillation amplitude variation at the resonator. This is a necessary information to evaluate if the amplitude detection implemented here can (or cannot), in practice (and not in theory where effectively they should be similar in the respective optimized conditions) achieve the same spin sensitivity as the frequency detection reported previously using the same chip. To complete the comparison the frequency and amplitude noise spectral densities should also be also considered. This point is, of course, linked to the previous one. I wonder if the voltage amplitude measurement performed here is not "sub-optimal" (i.e., the voltage variation is significantly smaller than the voltage variation at the resonator, which in turn makes the spin sensitivity worse that in the case of the frequency variation detection if the voltage noise is not reduced by the same factor).

Lines 203-210: Also this part of the "sensitivity discussion" is not clear to me. In particular the discussion of the PSD and RMS noise values are not clear to me. PSD and RMS noise are two different quantities related by an integral once the integration bandwidth is properly defined. So the phrase "…the PSD noise is usually better than the RMS noise of an EPR spectrum…" does not make sense to me. I would suggest to the authors to define clearly how the experiment is performed (including the analog bandwidth and the digital processing) and the way they have computed the spin sensitivity from the processed data. This should be enough to compare it to other papers knowing the different way the experiments are carried out (CW, RS, pulsed), the experimental parameters (analog filtering, digital filtering, etc. etc.), and the given definition of the spin sensitivity. If the experimental conditions and parameters are properly described, each reader can easily "renormalize" them to his/her own sensitivity "definition".

Figure 2, Figure 3, lines 355-358: Why the two signals in Figures 2 and 3 are not identical ? I guess that it is because there is a mix of absorption and dispersion which gives non-identical signals when the frequency is scanned up or down (pure absorption signals would have the same shape in the scan up and down, pure dispersion signals would have "mirrored shapes" in the scan up and down). Please comment on this in the manuscript and write the details of the simulation in the Appendix E. It seems to me that the reported simulation results are not a result directly taken from EasySpin. Are the EasySpin absorption and dispersion signals combined with an appropriate phase shift maybe computed from an estimation of the Q-factor (as suggested by Equation 1) ? Or maybe a circuit simulator is used where the sample is modeled by a coupled resonator. This would be correct "quantitatively" for a CW slow passage at low B1 but I guess not for a RS.

Figure 4 and Figure 5: In terms of precessing magnetization (i.e., Mxy), the maximum value for T1=T2 and the optimum level of B1 and scan speed is: (1/2)*Mo for the CW and Mo for the RS. So, in terms of precessing magnetization, the difference is 2 (and not 5). Of course, depending on the way the CW and RS signals are computed (field modulation amplitude, peak-to-peak or amplitude, etc. etc.) the ratio can be different. But, I would prefer to consider a more "fundamental" quantity which is the precessing magnetization. Of course, in practice the optimal condition for the CW with field modulation is obtained with a B1 and a field modulation amplitude which determines linewidth broadening, which may (or may not) be “tolerable”.

Here my minor comments:

Line 43: Typo: “50 kEuros” instead of “50 TEuros”.

Line 84: I agree that the approach proposed here could allow in the future to perform rapid scans larger than 20 mT (600 MHz). However in this manuscript it is demonstrated up to about 64 MHz. I think that this should be mentioned also here.

Line 99: I think that it should be mentioned that “The rapid scan with single-chip integrated oscillators was proposed and briefly discussed in Ref. (Gualco et al., 2014), but not yet demonstrated experimentally. Here we report …..”

Line 105: “< 10 ppm”. Please specify on which volume you are considering <10 ppm homogeneity.

Lines 159 and 281: The reason why the “..in these experiments was limited by the RF generator to ….” is not very clear. I would suggest to add a couple of sentences to clarify this point. I guess this is related to the chip architecture and, in particular, to the way the frequency scan is implemented (more complex, clever, and efficient that a simple voltage externally applied to the integrated varactor).

Line 250: Typo: “…about 5 is may be..” instead of “…about 5 may be..”

Line 120: The minimum value of B1 produced by the chip is 27 uT or so. BDPA has significant saturation from B1 in the order of 100 uT or so. So the choice to use only BDPA as sample for this work does not allow to show one of the advantages of the RS when applied to the single-chip approach. The minimum B1 is often relatively large and might cause significant saturation in the conventional CW slow scan. I would suggest the authors to, at least, comment on this point (even if obvious for an expert). Although definitely not “necessary” and “important” for this manuscript, an RS experiment on a sample which is “deeply saturated” in the conventional CW slow scan mode would be a nice addition to the manuscript. A less elegant but maybe still valid example could be the use a very small sample of BDPA placed in close proximity to the coil wire where B1 is significantly larger to show that the RS scan can solve this saturation issue.