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Title: Bimodal Q-band Probehead with Improved Signal-to-Noise Ratio in Pulse EPR
Author(s): Vasyl Denysenkov et al.
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Response to the referee #1 questions/comments

General comments:

The paper describes performance of a bimodal Q-band resonator and use of a low-noise amplifier to improve the signal-to-noise of pulsed EPR measurements. The comparison will be of interest magnetic resonance spectroscopists,

Specific comments:

1) the nature of the resonator is left to the imagination of the reader. No description of the resonator is provided other than "based on the design by James Hyde." A diagram of the resonator with dimensions is essential to make this paper useful.

Answer: The short description has been shown in line #74 as following: This is a bimodal cavity in which two rectangular TE103 modes are polarization-crossed and have two half-wavelengths common (Hyde et al., 1968). The great merit of this kind of cavity is the significant isolation between the input and output modes that can be achieved with sample volume of 20 - 50 microliters over a wide temperature range. Besides, we agree with the referee to introduce the resonator in the new Fig. 2 including dimensions and microwave B1 field distribution.

Change in manuscript: new figure 2 is introduced. The following figure caption is added starting in line #78 of the marked-up manuscript: Figure 2: Bimodal TE103 cavity. On the left: 1 – input port with coupling iris 2.2 mm diameter, 2 – quartz rod 1 mm diameter for input mode frequency tuning; 3 – teflon tube 4mm OD / 3 mm ID for resonator protection against impurities; 4 – quartz sample tube 2.8 mm OD; 5 – quartz rod 1.5 mm diameter for output mode frequency tuning; 6 – output port with coupling iris 3 mm diameter. Input and output ports have similar 7.4 × 3.7 mm cross-sections. 3D model of the structure is included in SI (Supplementary Information). On the right: microwave B_1 field distribution along the cavity is demonstrating the decoupling between output and input ports (simulated by CST Suite).

2) Did the authors also build a replacement for the Bruker Flexline insert for the CF935, or did they build this new resonator into a standard Bruker Flexline resonator system?

Answer: We build this new probehead to be compatible with the standard Bruker Flexline resonator system.

Change in manuscript: The corresponding sentence is added in line #68 of the marked-up manuscript: The probehead dimensions are compatible with that of Bruker flexline Q-band resonators and it fits perfectly into an Oxford CF935 Helium flow cryostat

3) The Bruker resonator with which the new resonator is compared is stated to be an ER5170D2 and that a 2.8 mm OD capillary was used in it. The Bruker resonator listing includes a model ER5107D2 that has a 2 mm diameter. Please explain the differences between these two models.

Thank you for the comment. The model EN5170D2 was mentioned by misprint. In reality model EN5107D2 was used for the pulsed EPR experiments. The sample tube can be a 2 mm OD in the Bruker EN5107D2. However, 1.6 mm OD is strongly recommended by the manufacturer that we follow the recommendation.

Change in manuscript: The correct model EN5107D2 instead of EN5170D2 was introduced through the text in lines ##141, 146, 149, 152, 166, 171, 181, 182, 186.

4) Please expand the discussion of the results in figure 4 to include the reasons for the widths of the echoes and whether the integrated intensities are more meaningful than the peak amplitudes.

Answer: For inhomogeneously broadened spectra the echo width follows to the excitation pulse width in time domain traces. That is the reason that the echoes excited by short (12 ns) pulses look much shorter in comparison with the echoes excited by 160 ns pulses (Fig. 5). In case of longer pulses the burned hole in the EPR spectrum is narrower causing smaller number of excited spins with respect to the case of shorter excitation pulses resulting in a difference of the signal intensities between trace 3 and trace 4 that is usually measured by integrated echoes. In the case of excitation by pulses of similar pulse length the echoes can be compared also by peak intensities because it is the simplest and accurate approach to show the better performance of the bimodal probehead with LNA (trace 1) with respect to its operation without LNA (trace 2) as well as the Bruker probe (trace 3). However, in comparison with shorter pulses (trace 4) integrated echo values can be used. In this case the better performance of the bimodal probe with LNA is also evident if integrated intensities instead of peak intensities for traces 1 and 4 will be used. Q factors of the input and output modes of the bimodal resonator have been chosen low enough (Q_{input} = 250 and Q_{output} = 180) to reach a broad EPR excitation. Corresponding change was added to the text starting in line #153 of the marked-up manuscript.

Change in manuscript: For inhomogeneously broadened spectra the echo width follows to the excitation pulse width in time domain traces. That is the reason that the echoes excited by short (12 ns) pulses look much shorter in comparison with the echoes excited by 160 ns pulses (Fig. 5). In case of longer pulses the burned hole in the EPR spectrum is narrower causing smaller number of excited spins with respect to the case of shorter excitation pulses resulting in a difference of the signal intensities between trace 3 and trace 4 that is usually measured by integrated echoes. In the case of excitation by pulses of similar pulse length the echoes can be compared also by peak intensities because it is the simplest and accurate approach to show the better performance of the bimodal probehead with LNA (trace 1) with respect to its operation without LNA (trace 2) as well as the Bruker probe (trace 3). However, in comparison with shorter pulses (trace 4) integrated echo values can be used. In this case the better performance of the bimodal probe with LNA is also evident if integrated intensities instead of peak intensities for traces 1 and 4 will be used.

5) The resonator Q factors should be stated.

Thank you, we have included the Q factors in the new text in lines ##134 and 164.

Change in manuscript: Q-factors of the input and output modes of the bimodal resonator that are Q_{input} = 250 and Q_{output} = 180 to reach a broad EPR excitation.

6) Were echoes obtained with standard Bruker Xepr excitation, up-conversion and down-conversion to X-band, signal detection and digitization hardware and software?

Yes, the bimodal probehead was installed on a typical Bruker ELEXYS 580 EPR spectrometer and all presented experiments have been accomplished with the available spectrometer hardware and software. Corresponding sentence was added in line #183.

Change in manuscript: All presented experiments have been accomplished with the available spectrometer hardware and software.

7) In figure 5 the baseline region with lower noise should be explained.

Answer: The lower noise for the bimodal cavity time trace (black one) is not through the whole trace but only in the region between 200 ns and 1100 ns where the protection gate is ON. Beside the protection gate region, the noise is similar to the noise for the Bruker cavity trace. The reason is that the noise on the black trace between 200 ns and 1100 ns was reduced proportionally due to normalization step of the large signal produced by the LNA in both figure 5 and figure 6. Corresponding sentence was added to the figure 6 caption in line #173.

Change in manuscript: In the region between 200 ns and 1100 ns where the spectrometer protection gate is ON the noise for the bimodal cavity trace (black one) is lower because it is reduced proportionally due to normalization step of the large signal produced by the LNA which has 30 dB gain.

- Answers to Referee #2 questions

  The authors present a proof-of-concept study of using a bimodal cavity, operating at Q-Band frequencies, for pulsed EPR experiments. Using this type of cavity, instead of a traditional reflection cavity is an important step towards integrating a low-noise amplifier directly into the probehead to increase the overall sensitivity. The authors can demonstrate a 4-fold increased sensitivity using this approach. This exciting study should be published after minor revisions:

  - The last sentence of the first paragraph in the abstract ("Experiments demonstrate 4-fold increase …") is very convoluted, difficult to understand and needs to be re-written. It is not clear what are the individual contributions (e.g. increased sample size, LNA) to the overall increase in sensitivity.

  Answer: The corresponding sentence is rewritten in line # 14 of the marked-up manuscript.

  Change in manuscript: The experiments demonstrate a 4-fold increase in the signal-to-noise ratio (SNR) of a bimodal probe head operating in transmission mode compared to its operation in reflection mode, which was achieved thanks to the additional use of LNA.

  - The authors use a TE103 cavity first described by Hyde et al. However, the unfamiliar reader will not be able to understand the concept right away. The authors should include a description of the mechanical design of the cavity.

  Answer: yes, we include a new figure showing design of the bimodal cavity (Fig. 2 in the marked-up manuscript) and B1 field distribution in it. Figure caption is added as following:

  Change in manuscript in line #78: Figure 2: Bimodal TE103 resonator. On the left: 1 – input port with coupling iris 2.2 mm diameter, 2 – quartz rod 1 mm diameter for input mode frequency tuning; 3 – teflon tube 4mm OD / 3 mm ID for resonator protection against impurities; 4 – quartz sample tube 2.8 mm OD; 5 - quartz rod 1.5 mm diameter for output mode frequency tuning; 6- output port with coupling iris 3 mm diameter. Input and output ports have 7.4 × 3.7 mm cross-sections. 3D model of the structure is included in SI (Supplementary Information). On the right: microwave B_1 field distribution along the cavity is demonstrating the decoupling between input and output ports (simulated by CST Suite).

- It is not clear how the cavity is coupled to the rest of the spectrometer. Is an iris (or two) used to match the coupling to the waveguide? This needs further explanation.

Answer: The cavity has two irises indicated by pos. 1 and pos. 6 to match the coupling to the waveguides as shown in the new fig. 2 with dimensions described in the figure caption in lines ##78 and 80.

- The authors mention tuning paddles in several places. However, no further details are given. It is not clear, how the frequency was adjusted (Figure 3). Also, there seem to be a lot of standing waves in traces a) and b) and the authors should comment on the origin.

Answer: No, the cavity has no tuning paddles that we indicated in line #103 of the updated manuscript, which is a major limitation to reach decoupling better than 50 dB. However, we plan to introduce some paddles in the future (see the text in line #202) to increase the isolation between ports. The cavity has independent frequency tunings for input and output modes by means of adjustable quartz rods indicated by pos. 2 and pos. 5 in the new fig. 2. Standing waves in traces a) and b) arise from mismatches due to long UT 141 coaxial cables with SMA connectors which have been used to connect the probehead to the network analyzer. The corresponding information has been added to the text.

Change in manuscript in lines ##123 and 124: UT 141 coaxial cables with SMA connectors connecting the probe to the network analyzer and insertion losses in the mw components inside the probe. All together mismatches in long transmission paths cause some standing waves evident in traces a) and b).

- The experimental results given on page 6 in Figure 4 and the 2nd to last paragraph should be summarized in a table. Furthermore, the authors should give the calculated SN ratios for the different configurations under investigation (and whether peak amplitude or area under the echo is used). For visibility, it would be beneficial to base line correct the traces. The authors should also comment on the width of the echoes, which clearly are different.

Answer: The table with calculated signal intensities for different probeheads and different measuring conditions has been introduced in the manuscript in line #187. The presented traces contain also the part covered by the protection gate. We want to keep the traces as it is to demonstrate noise behavior at different time positions also through the protection gate effect. Base line correction will be not much helpful in this case. For better noise visibility each trace was shifted manually along Y-axis in the figures 5 and 6.

Change in manuscript in line #153: For inhomogeneously broadened spectra the echo width follows to the excitation pulse width in time domain traces. That is the reason that the echoes excited by short (12 ns) pulses look much shorter in comparison with the echoes excited by 160 ns pulses (Fig. 5). In case of longer pulses the burned hole in the EPR spectrum is narrower causing smaller number of excited spins with respect to the case of shorter excitation pulses resulting in a difference of the signal intensities between trace 3 and trace 4 that is usually measured by integrated echoes. In the case of excitation by pulses of similar pulse length the echoes can be compared also by peak intensities because it is the simplest and accurate approach to show the better performance of the bimodal probehead with LNA (trace 1) with respect to its operation without LNA (trace 2) as well as with respect to the Bruker probe (traces 3 and 4).

Change in manuscript in line #185: Obtained SNR enhancements (peak amplitude values) are summarized in the Table 1:

- Figure 4, trace 4: Is the echo measured with the same pulse separation time of 400 ns, even though the pulse lengths are significantly shortened? Is this the reason why the echo position shifts?

Answer: yes, the 400 ns delay was used for all experiments that causes the echoes on all the traces have the same starting positions.

- No details of the resonator Q or bandwidth are given.

Answer: we introduced Q values in line #164 as following: Q factors of the input and output modes of the bimodal resonator have been chosen low enough (Q_{input} = 250 and Q_{output} = 180) to reach a broad EPR excitation.

- Figure 5 does not have a blue trace as written in the caption.

Answer: thank you, we changed description of the trace color in line #170 to black.

- The authors state a 7-fold increase in SNR. However, it is not clear what the active volume of the resonators are. It is unclear what the contribution of the larger sample size is.

Answer: you are right; we have added more information to the revised manuscript in line #177 as following:

Change in manuscript in line #177: The difference of the results of this test and the previous one is mainly due to larger number of spins in the 2.8 mm OD sample tube used in the bimodal probehead with respect to the 1.6 mm OD sample tube used in the Bruker probehead resulted in sample volumes of 20 µl and 6 µl correspondingly. Thus the 3.5 times enhancement is achieved due to a larger sample volume in the bimodal probe, and additional 2 times SNR improvement is due to the LNA application.

- Please correct the typo in line 146 (lowed -> lowered). However, a 6 ns pi/2 pulse using a 150 W TWT amplifier is within the acceptance criteria of the probehead.

Thank you, we have corrected the typo. Yes, a 6 ns pi/2 and 12 ns pi pulses together with a 150 W TWT output show the best excitation option for a broad EPR line with the probehead.