Dear Thomas,

we have submitted a revised manuscript that we believe addresses all the concerns of the reviewers. I have included below the response to the reviewers (in blue) that were already posted in the online discussion forum. We hope that these changes will make the manuscript acceptable for publication in Magnetic Resonance.

Best regards,

Matthias

Response to Reviewer 1:
Thank you for the helpful comments and the careful reading of the manuscript. Here is the point-by-point response to the comments:

- change 'Lamour' to 'Larmor'
A: Corrected. Thank you!

-Depending on the EPR detection technique, improving microwave transmission doesn't always lead to higher EPR signals. For e.g., the SNR can decrease if the EPR line is oversaturated with too much microwave power. I suggest modifying the sentence to 'more efficient EPR excitation'
A: We agree that oversaturation can be a problem that leads to line broadening. We have modified the sentence in the abstract to "Improving microwave transmission directly translates to more efficient EPR excitation at high-field, ...".

Line 34: Can you elaborate on why corrugated waveguides are challenging to be used in the dissolution DNP polarizer system? I do not see obvious reasons why it can't be done. Moreover, the < 0.1 dB/m attenuation (doi: 10.1109/irmmw-THz.2011.6105103) might worth the effort in some cases.
A: We have no first-hand experience with corrugated wave guides and can only speculate. But we noticed that there is, to the best of our knowledge, no dissolution DNP system that uses corrugated wave guides all the way to the cryostat but just in connection with a quasi-optic transmission.
We believe the main reason corrugated waveguides are not commonly used in dissolution DNP, is the larger heat transfer due to the higher mass of such waveguides. However, we have not found any data for this. A second reason might be degradation due to moisture freezing in that changes the geometry but this could probably be solved by proper engineering.
Since we have no first-hand experience and data on these two points, we have modified the paragraph to a more cautious statement: "Gyrotrons are established systems to generate high microwave intensities (Blank et al., 2020) commonly used in MAS DNP systems but due to their much higher cost not a viable solution for dissolution DNP. Transmission of the microwaves to the sample space can be achieved by waveguides or corrugated waveguides with low losses (Nanni et al., 2012; De Rijk et al., 2011) or using quasi-optic transmission of the microwaves (Siaw et al., 2016). The desire towards implementing corrugated

waveguides in low temperature DNP setups (Rijk, 2013; Leggett et al., 2010) shows that that minimizing transmission losses is an important strategy to maximize microwave power at the sample."

Line 40-45: Another possible microwave transmission strategy is using the quasi-optic setup, which is adopted by Songi Han's group at UCSB and Graham Smith's / Steve Hill's W-band HiPER EPR setup. The quasi-optics setup obliviates the use of waveguides, and, hence, less heat load. The authors might want to comment (and cite) if this is a viable option (or not).
A: This is definitely a possible alternative and we thank the reviewer for reminding us of this approach. We have modified the manuscript around line 35-40 to include this option with a reference (see text above).

Line 66-69: It baffles me a little about the choice of ordering the two waveguides in your setup. Despite 304 stainless steel is austenitic, and, hence, non-magnetic by definition, it becomes mildly magnetic (more significant than 316) after Industrial processing (mechanical) and thermal cycles. (doi: 10.1016/j.pnmrs.2017.06.002 and doi: 10.1016/j.jmr.2009.03.003). Nevertheless, I wonder if it is not better to swap the order of the waveguide (assuming that the thermal insulation is still good). It is perhaps worth mentioning this fact in the manuscript.
A: The idea behind this ordering is that we want to minimize the heat transfer to the sample space with the liquid helium. We have not seen broadening in the NMR spectra from the waveguide over time but of course the static NMR spectra are quite broad by themselves.

Line 65 and Figure 1: It might be a good idea to include a schematic diagram of how the waveguides are incorporated in your DNP setup (taper / 39,2 cm x 2, etc). This might improve readability.
A: We have included the suggested schematic in the SI.

Line 134: To improve readability, refer to Fig 6 for EPR and Fig. 7 for the power-dependent curve.
A: It is not clear to us where the reviewer wants us to include the references to Fig.6 and 7. We decided not to do this because this would move the two Figures which show the results into the methods section where they are not really discussed.

Line 136: Please explain the AMC abbreviation because not everyone knows. I assume it refers to the VDI active-multiplier chains. Also, the AMC microwave power (depending on the model) is not very flat across the bandwidth. It might be worth mentioning this or including the power vs frequency plot (you can get it from the supplier's technical data sheet) in the SI.
A: We have added the full expression "amplifier-multiplier chain (AMC)" to the text. We have measured the microwave power across the frequency range. The power shows some variations over the whole 192-202 GHz range. However, the power variation is quite small over the most used frequency range 196-198 GHz.

Figure 3: I am not sure why Fig. 3 is in black and white. Can you provide a coloured version? And label in the figure where is the pencil, wool, fabric, etc.
A: Figure 3 was changed to full color and labels were added.

Line 147: I assume it is a 'train of saturation pulses' with delays between them. Can you specify the length of the delays?
A: We have added the length of the delays to the main text where the saturation is discussed.

In the 'Results and Discussion' section, Fig. 5 is perhaps the most important figure in the paper. However, I wonder if it is possible to estimate or measure the thickness of the silver that you managed to electroplate on the waveguide using such a method.
A: We have no simple way of measuring the actual thickness of the silver layer in the electroplated waveguides. We agree that this would be an interesting information as well as the variability of the thickness of the layer.

Moreover, it is well known that the electrical conductivity of metals significantly increases at low temperatures. Depending on the metal purity, copper can become 100 times more conductive at dissolution DNP temperatures of ~1.X K (see NIST, doi:10.1063/1.555614). Thus, the skin depth could be 10 times thinner, and you might not need to do so many 'passes' with your plating tools. Similarly, the bench-top measurement performed at room temperatures is definitely relevant, but those attenuation values might not be the same in DNP conditions. I think it is worth mentioning this in the text.
A: We have expanded the discussion section by: "The attenuation ... at room temperature is now 3.7 dB. At liquid-helium temperatures, the electrical resistance is lower (Matula, 1979), thus the attenuation will be reduced in the colder parts of the waveguide. The skin depth of the microwave will also shrink with lower resistance (Zinke, 1990). Therefore, a thinner silver layer might give the same results. "

Fig 6 caption: The last sentence structure, '300 seconds DNP per point' sounds awkward.
A: We have changed the sentence to: "The corresponding 29Si-DNP profile (blue) is measured at 3.4 K with a build-up time of 300 s to obtain sufficient signal."

I hope we have answered all the questions raised here.

Response to Reviewer 2:
Thank you for the helpful comments and the careful reading of the manuscript. Here is the point-by-point response to the comments:

Line34: it is stated that the "favorable corrugated waveguides are challenging to combine with a low temperature DNP cryostat".
But, there are some successful examples in the referred literature describing EPR and DNP spectrometers with low temperature probeheads equipped with custom-tailored corrugated waveguides manufactured by Thomas Keating Ltd (UK) with very low transmission losses (0.1 dB/m) at frequencies above 180 GHz. Moreover, EPR/ENDOR probeheads (also equipped with a corrugated waveguide and compatible with Oxford Spectrostat) of the Bruker E-780 spectrometer operating at 263 GHz are commercially available on the market. Frame of the probehead could be suitable with your setup after minor change in the taper. Besides, some corrugated waveguides fabricated by GYCOM Ltd

(Russia) which are made of German silver can also be a cheap option in case of a very limited budget. Please justify your choice more clearly.

A: Same answer as to reviewer 1:

We have no first-hand experience with corrugated wave guides and can only speculate. But we noticed that there is, to the best of our knowledge, no dissolution DNP system that uses corrugated wave guides all the way to the cryostat but just in connection with a quasi-optic transmission.

We believe the main reason corrugated waveguides are not commonly used in dissolution DNP, is the larger heat transfer due to the higher mass of such waveguides. However, we have not found any data for this. A second reason might be degradation due to moisture freezing in that changes the geometry but this could probably be solved by proper engineering.

Since we have no first-hand experience and data on these two points, we have modified the paragraph to a more cautious statement: "Gyrotrons are established systems to generate high microwave intensities (Blank et al., 2020) commonly used in MAS DNP systems but due to their much higher cost not a viable solution for dissolution DNP. Transmission of the microwaves to the sample space can be achieved by waveguides or corrugated waveguides with low losses (Nanni et al., 2012; De Rijk et al., 2011) or using quasi-optic transmission of the microwaves (Siaw et al., 2016). The desire towards implementing corrugated waveguides in low temperature DNP setups (Rijk, 2013; Leggett et al., 2010) shows that that minimizing transmission losses is an important strategy to maximize microwave power at the sample."

For us silver-plating was clearly the most simple solution to improve the power at the sample that did not require re-engineering of the probe. For a new design, we would probably think about a quasi-optic transmission of the microwaves to the sample space as an interesting alternative.

Line 103: "inner surface of the waveguide was first abrasively polished… then degreased with a water-based degreaser… ".

Typically, stainless steel has a poor adhesion with electroplated metal layers such gold, silver, or copper, especially if the surface was not etched preliminary. It is not clear from the text how adhesion issue is fixed. Does the water-based degreaser work also as an etching agent, or do you accomplish an etching step before silver deposition additionally? If not, please comment on the adhesion issue.

A: No etching of the surface was performed prior to electroplating. To avoid adhesion problems, the gold layer was used in a first step. Experimentally, we have seen no problems with the adhesion of the layers since producing the first plated waveguides about a year ago. To make this clear, we added a short sentence around line 120: "No surface etching was required."

Line 156: "…in attenuation, namely 1.2 dB/m to 1.1 dB/m at 197 GHz…" The values look appropriate. However, oversized waveguides can transmit higher order modes beside the fundamental mode causing some standing waves along the oversized waveguide with tapers on both sides: the larger waveguide aperture the more propagating modes causing more standing waves. Presence of these standing waves can deteriorate performance of the waveguide at certain frequencies. It can be estimated by measuring transmission losses in the frequency range of interest, namely in the range from 196.7 GHz to 197.7 GHz in your

case. Please add a transmission loss versus frequency plot to see how good is performance of the waveguide in the full frequency range.
A: We have measured the microwave power across the frequency range.
The power shows some variations over the whole 192-202 GHz range. However, the curve is quite smooth in the most used frequency range 196-198 GHz. After inserting the long overmoded waveguide we see some small fluctuations in power (ca. +-3%) across the frequencies, while the overall power curve is not distorted.

We hope this response answers all the points raised.