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Supporting Information: Design and performance of an oversized-sample 35 GHz EPR resonator with an elevated Q value

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Abstract.

Continuous wave EPR spectroscopy at 35 GHz is an essential cornerstone in multi-frequency EPR studies and crucial for differentiating multiple species in complex systems due to the improved g tensor resolution compared to lower microwave frequencies. Especially for unstable and highly sensitive paramagnetic centers the reliability of the measurements can be improved by the use of a single sample for EPR experiments at all frequencies. Besides the advantages, the lack of common availability of oversized-sample resonators at 35 GHz often limits scientists to lower frequencies or smaller sample geometries, the latter may be non-trivial for sensitive materials. In this work, we present the design and performance of an oversized-sample 35 GHz EPR resonator with a high loaded Q value up to 3300 well suited for continuous wave EPR and single microwave frequency experiments with low excitation power. The design is driven by electromagnetic field simulations and the microwave characteristics of manufactured prototypes were found in agreement with the predictions. The resonator is based on a cylindrical cavity with a TE_{011} mode allowing for 3 mm sample access. Design targets met comprise high sensitivity, robustness, ease of manufacturing and maintenance. The resonator is compatible with commercial EPR spectrometers and cryostats, allowing for measurements at temperatures down to at least 4 K. To highlight the general applicability, the resonator was tested on metal centers as well as on organic radicals featuring extremely narrow lines.

1 Supplementary Tables and Figures

Table S1. Measurement parameters of the conducted CW EPR experiments. Attenuation is given with respect to a source power P_0 = 20 mW.

Measurement	Width/G	Mod. frequency/kHz	Mod. amplitude/G	Conversion time/ms	Time constant/ms	Attenuation/dB
DPPH	50	100	0.2	81.92	20.48	48
10 ppm N@C60	20	100	0.02	160	40.96	40
Ti(III) r.t.	600	100	1	160	20.48	36
Ti(III) 30 K	1000	100	1	80	20.48	40

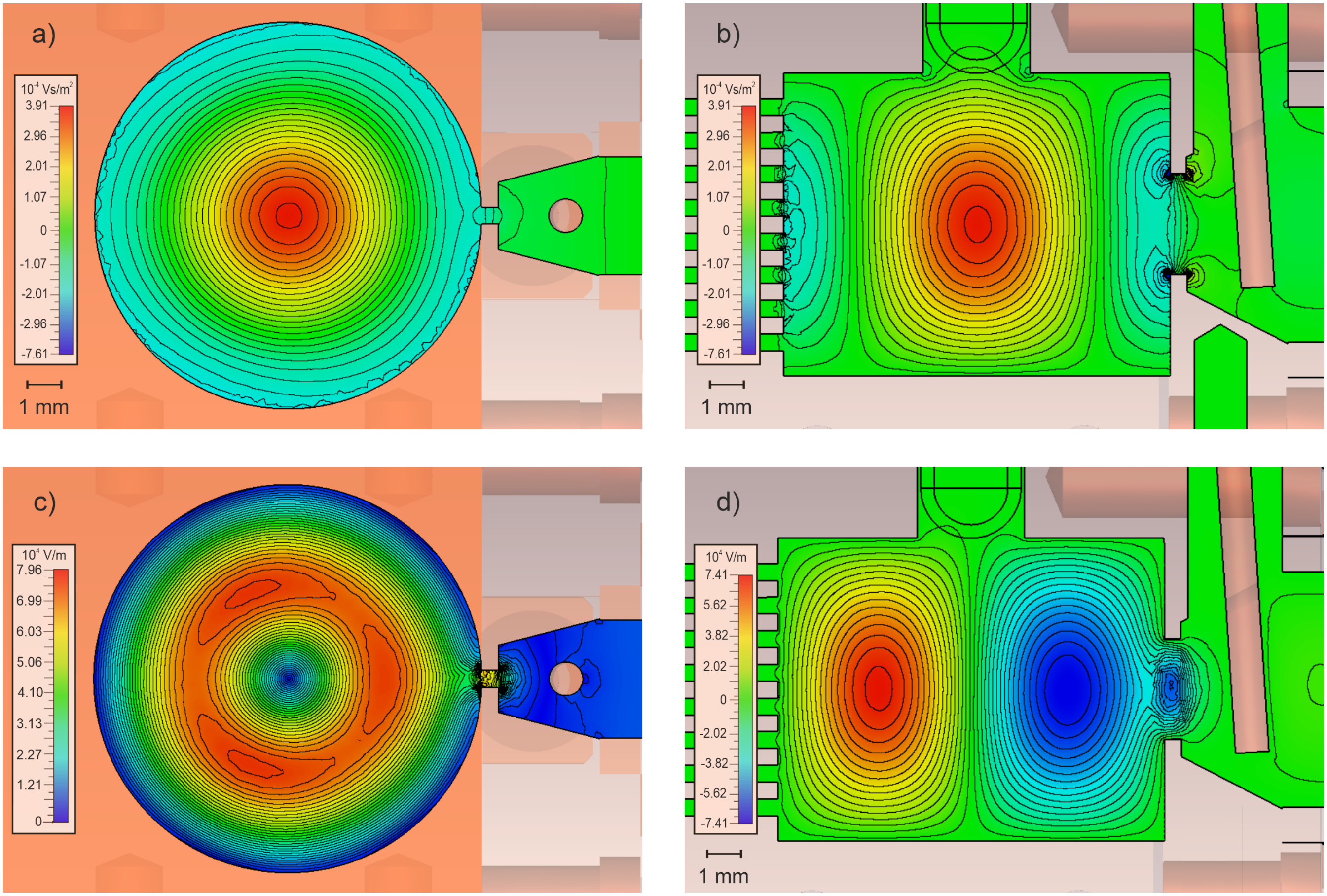

Figure S1. B and E field simulations without EPR tube, isolines are spaced by 6 % steps of the maximum field strength, all cross sections run through the center of the cavity. a) Strength of the x component of the B_1 field in a horizontal cross section, b) Strength of the x component of the B_1 field in a vertical cross section, c) Strength of the tangential component of the E_1 field in a horizontal cross section, d) Strength of the z component of the E_1 field in a vertical cross section.

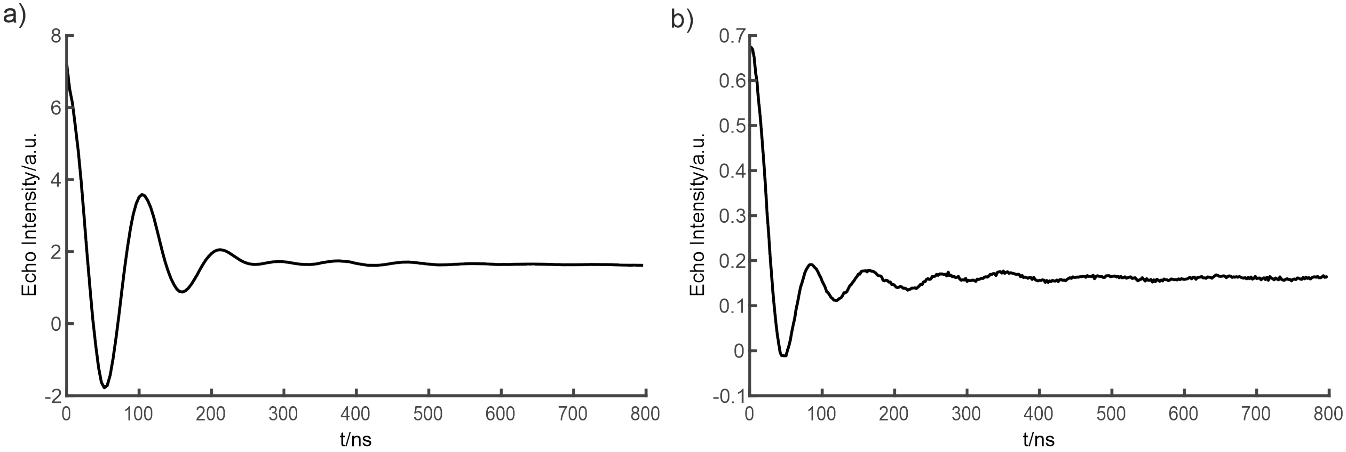

Figure S2. EPR nutation experiments with a pulse sequence $t_P - T - \pi/2 - \tau - \pi - \tau -$echo on two samples. a) Standard coal sample at 50 K with an input power of 5.97 W recorded at a B_0 corresponding to the spectral maximum and $\tau = 1$ µs, $T = 3$ µs, shot repetition time $= 5$ ms resulting in a π pulse length of 54 ns. The calculated conversion factor is 0.14 mT/$\sqrt{\mathrm{W}}$. b) Frozen toluene solution of a Ti(III) complex sample at 15 K with an input power of 1.00 W and $\tau = 3$ µs, $T = 2$ µs, shot repetition time $= 10$ ms, resulting in a π pulse length of 46 ns. The calculated conversion factor is 0.39 mT/$\sqrt{\mathrm{W}}$.