Augmenting microwave irradiation in MAS DNP NMR samples at 263 GHz

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Abstract

The magnetic microwave field strength and its detailed spatial distribution in magic-angle spinning (MAS) nuclear magnetic resonance (NMR) probes capable of dynamic nuclear polarization (DNP) is investigated by numerical simulations with the objective to augment the magnetic microwave amplitude by structuring the sample in the mm and sub-mm range and by improving the coupling of the incident microwave beam to the sample. As it will be shown experimentally, both measures lead to an increase of the microwave efficiency in DNP MAS NMR.

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As in almost all magnetic resonance experiments, in particular in electron paramagnetic resonance (EPR) and in NMR experiments, the magnitude of the rf magnetic field is a crucial parameter. In DNP MAS NMR electron spin polarization is transferred to nuclear spins with the effect of enhancing nuclear spin polarization by one or two orders of magnitude above the Boltzmann polarization in solid samples at temperatures around 100 K. In order to achieve the electron spin – nuclear spin polarization transfer, unpaired electron spins in radical molecules embedded in an NMR spectroscopic sample of interest are irradiated by an EPR resonant microwave beam (frequency, *e.g.*, 263 GHz, linearly polarized, gyrotron source). For the specific DNP effect to take place, the amplitude, phase, and polarization distribution of the microwave field during the scattering process in the sample material and influenced by the surrounding hardware components must be known and, if possible, optimized to achieve high DNP enhancement factors. We have studied two strategies to increase the DNP transfer efficiency.

The first strategy relies on embedding dielectric particles (*e.g.*, potassium bromide, KBr, grains) into the sample [1,2], the former with a dielectric constant higher than the sample material (tetrachloroethane, TCE, plus low concentration biradicals, TEKPOL). The powder grains have size distributions between 200 and 600 µm, are randomly distributed in the TCE frozen solution with volume filling factors of 0% (no particles), 22% and 63%. The sample and the particles are contained in a cylindrical 3.2mm or 1.3mm outer diameter MAS rotor (allowing fast spinning of the sample with rates of tens of kilohertz) made of zirconia ceramics or sapphire. The MAS rotor is surrounded by a solenoidal rf coil being part of an NMR resonant circuit, *e.g.*, for ^{1}H NMR at 400 MHz for an external static field of 9.4 T. At that external field strength, the electron spins resonate at 263 GHz. The incident linearly polarized microwave beam (HE_{11} mode, waist *c.a.* 3 mm) leaves a corrugated waveguide (inner diameter 7.6 mm), propagates through the coil, the MAS rotor wall and the sample. On that path of propagation, the beam is multiply diffracted or scattered by the coil, the rotor wall and the sample. The numerical microwave field simulations show that already the presence of the rotor wall (zirconia or sapphire) causes a complicated diffraction pattern of the beam inside the sample with a distribution of left and right-handed elliptical polarization and in the absence of dielectric particles a spatially periodic distribution of magnetic microwave amplitudes. The presence of dielectric particles maintains the general occurrence of elliptical polarization in the sample but moreover yields a random distribution of field amplitudes originating from the multiple scattering of the beam on the randomly sized and distributed particles. Furthermore, in the case of dielectric particles the spatially averaged (over the sample volume) field amplitude B_1 increases by a factor of 1.5 as compared to the case of absent particles, see Fig. 1. We may attribute the improved experimental DNP efficiency by a factor 2 to 3 being proportional to $B_1{}^2$ to this increase of B_1. The detailed impact of elliptical polarization is currently still under investigation.

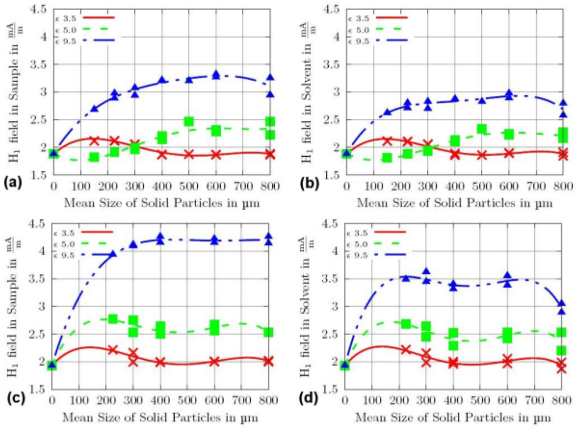

Fig. 1. Magnetic microwave field H_1 *vs.* average particle size for dielectric particle volume filling factor 22% (a,b) and 63% (c,d) averaged over the total sample volume (particles and TCE) (a,c) and TCE alone (b,d) for various dielectric constants ε = 3.5, 5.0, and 9.5. ε = 3.5 is equal to the dielectric constant of TCE, hence particles with such an ε are "dielectrically indistinguishable" from TCE. ε = 5 corresponds to KBr, ε = 9.5 to sapphire.

The second strategy [3] aims at an improved coupling of the incident microwave beam to the sample by utilizing a focusing lens at the aperture of the 7.6 mm corrugated waveguide and an additional short waveguide of only 2 mm inner diameter guiding the beam very close to the sample, Fig. 2.

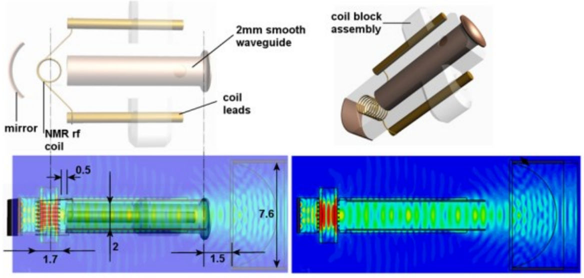

Fig. 2. Improved microwave beam coupling to the rf coil, MAS rotor, and DNP sample for a 1.3mm MAS DNP probe at 263 GHz. The beam enters from the right side after passing a focusing lens (diameter 7.6 mm), enters the small waveguide (inner diameter 2 mm), and propagates through an aperture of that waveguide close to the rf coil, MAS rotor and sample. Color coding: red – high microwave amplitude, yellow – intermediate amplitude, blue – low amplitude.

Tab. 1. Magnetic microwave amplitudes without and with waveguide coupler compared with the amplitude achievable in a fundamental mode EPR cavity (Q = 500)

System	$B_1/P^{1/2}$ ($\mu T/W^{1/2}$)	$\gamma_e B_1/P^{1/2}/2\pi$ ($MHz/W^{1/2}$)
MAS 1.3 mm DNP probe without waveguide coupler	19	0.5
MAS 1.3 mm DNP probe with waveguide coupler	66	1.8
EPR E780 spectrometer with fundamental mode resonator	1272	35.8

As summarized in Tab. 1 the insertion of the focusing lens in the aperture of the large corrugated waveguide and the insertion of the short, small-diameter waveguide increases the magnetic microwave amplitude B_1 in the sample by a factor of 3. For comparison, the last line in Tab. 1 indicates the attainable magnetic field amplitude in an EPR cavity (quality factor 500, 20 mW input power, 90° pulse 50 ns) at 263 GHz, which is much higher because of the optimum resonating structure. Such a more ideal structure is hard to achieve for MAS DNP probes for the reasons of the various hardware boundary conditions for MAS DNP as compared to pure EPR.

^{1}H DNP 1.3 mm MAS NMR experiments at 263 GHz with ca. 7 W incident beam power with water/glycerol/proline/ AMUPol yielded DNP enhancements of about 150 and 350 for the setup without and with waveguide coupler, a significant improvement of the DNP efficiency. Both strategies, the embedding of dielectric particles into the sample matrix and the waveguide coupler can be combined and produce ^{1}H DNP enhancements up to 500 in TCE/KBr/TEKPOL, a value not so far anymore from the theoretically attainable value of 650 for ^{1}H DNP NMR.

References

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