More than 50 % 13C polarization in solution by the DNP-NMR method: 200,000-fold enhancement compared to 3 T and room temperature

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Introduction: A novel method for polarizing nuclear spins in molecules was invented a few years ago [1]. The method takes advantage of Dynamic Nuclear Polarization (DNP) in the solid state followed by rapid dissolution in a suitable solvent. The polarization is retained in the dissolution creating a solution with a non-thermal nuclear polarization approaching unity (hyperpolarization). This method has enabled a range of new applications in Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI).

DNP is performed at high field and low temperature in order to reach a nuclear polarization approaching unity.
The DNP method for hyperpolarizing molecules has so far mainly been based on the field strength of 3.35 T and ~1.1K [1-3]. This field strength was based on the DNP literature at low temperature and the availability of good performance microwave sources for this frequency band. Typically, a polarization of 10-20% is achieved under these conditions.

In this work we primarily investigate the DNP enhancement for [1-^{13}C]pyruvic acid and [1,4-$^{13}C_2$]fumaric acid, doped with the trityl radical OX063Me, at 3.35 T and 4.64 T at ca. 1.15 K, and demonstrate more than a doubling of the polarization at the higher magnetic field. In a previous study at 3.35 T it was observed for the same system that adding small quantities of Gd^{3+} substantially increased the polarization, almost by a factor of two [3]. At the higher field strength the addition of Gd^{3+} only has a marginal effect on the polarization.

Method: The dependence of the polarization on microwave frequency and power as well as radical concentration and electron saturation was studied. The dependence of the electron saturation on microwave frequency and microwave power was quantified by first moment measurements which were obtained by nucleus-electron double resonance (NEDOR) experiments. The dependence of the nuclear spin-lattice relaxation on the trityl radical concentration was investigated. The time constant for polarization build-up was studied with respect to its dependence on radical concentration and microwave frequency. Polarization in the solid state was quantified via the thermal equilibrium signal and also indirectly from the first moment shifts. In the liquid state, polarization was quantified with reference to the thermal equilibrium signal of the same sample.

Results: For optimized conditions, a solid state ^{13}C polarization equal to 64 ± 5 % was obtained with [1-^{13}C]pyruvic acid, an increase by more than a factor of two compared with earlier results at 3.35 T of the same system, key parameters are tabulated below. Similar results were obtained with [1,4-$^{13}C_2$]fumaric acid dissolved in DMSO.

c (mM)	mass (mg)	T_{1n} [s]	τ_b [s]	P_1 (maks) (%)	MW Frequency[1] [GHz]	MW Frequency[2] [GHz]	T_{1e} [ms]	ΔM_1^{II} [3] [Hz]	ΔM_1^{IS} [3] [Hz]
9.3	40.2	n.d.	5000±600	59 ± 5	130.110	n.d.	1090±30	-160±30	347±10
14.1	116.2	n.d.	3500±500	n.d.	130.102	n.d.	1040±30	n.d.	-328±10
14.1	41.7	20000±300	3000±600	64 ± 5	130.102	130.164	1130±30	-200±40	470±15
18.5	40.1	21500±500	2500±600	58 ± 5	130.092	130.177	920±30	-160±30	759±25
45.4	39.7	9000±100	475±15	23 ± 5	130.070	n.d.	480±20	-50±40	1880±40
14.3 1.5 Gd^{3+}	40.0	14000±1000	3000±600	70 ± 5	130.114	130.162	300±10	-190±40	435±15
0	200.2	17000±3000	-	0.104 [8]	-	-	-	-	-

[1] Microwave frequency for maximum positive DNP, [2] Microwave frequency for maximum negative DNP, [3] First moment shift due to saturation of ^{13}C nuclei and radical

Conclusion: Liquid state polarization in excess of 50% is obtained. Two different methods of increasing the solid state polarization are described. The results are believed to be specific to the use of trityl radicals for the DNP. This improvement in polarization will further expand the utility of DNP in MRI.

1.Ardenkjaer-Larsen et al, PNAS 100(18), 10-158-10163 (2003), 2. Hypersense, Oxford Instruments Molecular Biotools Ltd, Tubney Woods, UK, 3. Comment et al, Concepts in Magnetic Resonance Part B (Magnetic Resonance Engineering), Vol. 31B(4) 255–269 (2007), 4. Ardenkjaer-Larsen et al, Appl Magn Reson 34, 509-522 (2008), 5. Johannesson et al, JMR, submitted, 6. Jannin et al, The Journal of Chemical Physics 128, 241102 (2008)