PAPER

Cross polarization from ¹H to quadrupolar ⁶Li nuclei for dissolution DNP

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Cross polarization from protons to quadrupolar ⁶Li nuclei is combined with dynamic nuclear polarization of protons at 1.2 K and 6.7 T using TEMPOL as a polarizing agent followed by rapid dissolution. Compared to direct ⁶Li DNP without cross-polarization, a higher nuclear spin polarization $P(^6Li)$ can be obtained in a shorter time. A double resonance ¹H–⁶Li probe was designed that is equipped for Longitudinally Detected Electron Spin Resonance.

Introduction

Dynamic Nuclear Polarization (DNP) combined with rapid dissolution (D-DNP)[1] usually focuses on nuclear spins like ¹³C or ¹⁵N that have long longitudinal relaxation times, T_1, in moderate magnetic fields, $B_0 > 1$ T. Rather surprisingly, some quadrupolar nuclei such as ⁶Li can also have sufficiently long relaxation times, $T_1(^6Li)$, in solution.[1,2] Hyperpolarization of ⁶Li could provide new insights into clinical studies, bearing in mind that lithium salts are used to treat bipolar and depressive disorders.[3] In particle physics, DNP has been used to enhance the ⁶Li polarization of targets.[4] Polarizations as high as $P(^6Li) = 71\%$ have been obtained for small ⁶LiD crystals at very low temperatures (a few hundreds of mK), although the polarization build-up times, τ_{DNP}, can be several hours in $B_0 = 2.5$ T. High energy irradiation can be used to produce paramagnetic defects that act as polarizing agents in such crystals. It was also demonstrated[2] that ⁶Li could be polarized in a glassy matrix using the free radical TEMPO as a polarizing agent in D-DNP experiments in much shorter build-up times, $\tau_{DNP} = 7.5$ minutes at $T = 1.2$ K and $B_0 = 3.35$ T, although the polarization $P(^6Li) = 7\%$ was much lower than that reported for ⁶LiD crystals. For carbon-13 spins, we have shown that high polarization levels can be obtained rapidly by first polarizing protons and using cross polarization (CP) in the manner of Hartmann and Hahn to transfer the polarization from protons to carbon-13.[5–10] At $T = 1.2$ K and $B_0 = 6.7$ T, we obtained $P(^{13}C) = 71\%$ in 20 min with a horizontal solenoidal coil that precludes rapid dissolution,[6] and $P(^{13}C) = 45\%$ with vertical coils that are compatible with rapid dissolution.[10]

In this communication, we show how cross-polarization (CP) can also be used to obtain a high polarization, $P(^6Li)$, in a short time by using a suitable double resonance probe with two radio-frequency saddle coils in quadrature and an audio-frequency Helmholtz coil for Longitudinally Detected Electron Spin Resonance (LODESR).

DNP was originally predicted by Albert Overhauser and demonstrated on ⁷Li.[11,12] Various mechanisms of the transfer of polarization can be considered in solids, both in static samples[13–21] and in samples undergoing magic angle spinning (MAS).[22–24] In DNP with 50 mM TEMPOL at 6.7 T and $1.2 < T < 4.2$ K, a combination of three mechanisms appears to be involved: the solid effect, the cross effect and thermal mixing.[25] The combination of CP[26] with DNP can enhance the hyper-polarization of low gamma nuclei,[27] including some quadrupolar nuclei.[28]

Adiabatic cross-polarization (ACP)[29,30] is highly suitable for D-DNP experiments since it suffices to use low rf amplitudes to minimize arcing.[5–10] Like other CP schemes,[31–33] the final nuclear spin polarization must be aligned with the magnetic field prior to dissolution. CP contacts can be achieved by applying simultaneous pairs of adiabatic inversion pulses using frequency sweeps with so-called 'Wurst' amplitude profiles.[34] The magnetization vectors follow the effective fields so that they end up aligned with the magnetic field. After an even number of contacts, the magnetization vectors are parallel rather than antiparallel with respect to the magnetic field. Pairs of pulses can be applied periodically to achieve a cumulative enhancement of the ⁶Li polarization (Fig. 1).

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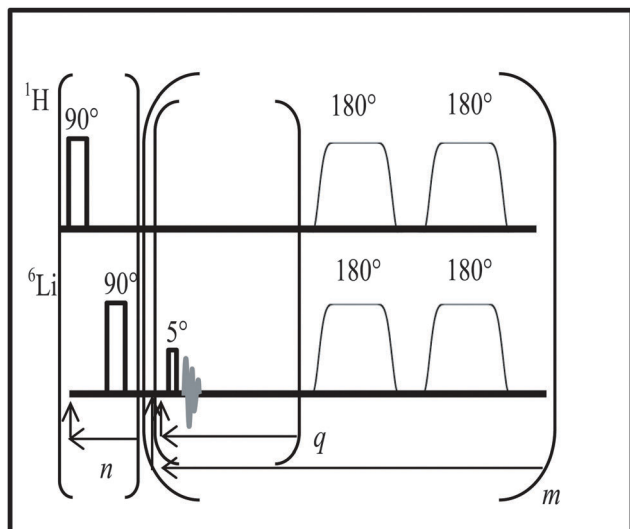[f] *CNRS UMR 7203 LBM, F-75005, Paris, France*

Fig. 1 Pulse sequence used for cross-polarization (CP) in solids at low temperatures.[5–7] Both protons and ^{6}Li nuclei are initially saturated by a series of 90° pulses (typically $n = 20$) spaced by 10 ms. Two nested loops (q inside m) are used, the inner loop to measure the polarization of ^{6}Li with small 5° flip angles and the outer loop (typically $m = 18$ with intervals of 10 s for samples at 4.2 K or 30 s at 1.2 K) to establish cross polarization contacts by simultaneously applying pairs of frequency-modulated inversion pulses. The EPR transitions are saturated throughout the experiment to induce DNP.

Experimental

The experiments were performed using a home-built polarizer operating at $B_0 = 6.7$ T and $T = 1.2$ K.[8] A dedicated probe was built with a 188 GHz wave-guide and an rf circuit for cross polarization from ^{1}H to ^{6}Li that is compatible with rapid dissolution.

The probe comprises two orthogonal saddle coils made of copper wire and immersed in liquid helium (see (1) in Fig. 2(b)). The 6 mm inner diameter saddle coil for ^{6}Li can be tuned and partly matched using a cryogenic trimmer capacitor with an extended shaft (2), in combination with American Technical Ceramics (ATC) chip capacitors. The trimmer capacitor shaft can be rotated from the outside with a rod (3) passing through a brass nut with a vacuum-tight O-ring (4). The nut was tightened at room temperature once the circuit was tuned. The ^{6}Li channel has a bandwidth of *ca.* 10 MHz, centred on the ^{6}Li resonance frequency of 41.97 MHz. The ^{6}Li coil presents two turns per wing of a 0.4 mm diameter enamelled copper wire placed around a coil former of 6 mm diameter made of PTFE (5). The saddle coil for protons presents the same inner diameter and a length of 12 mm with one turn per wing made of 0.22 mm diameter enamelled copper wire. Partial matching was achieved with a 10 pF capacitor in series with this coil. The PTFE coil former (6) supports a coil for longitudinally detected electron spin resonance (LODESR).[35–37] Lateral holes on this coil former (7) allowed the waveguide (8) to reach the central region where the NMR coils are placed (1). The Helmholtz coil (9) for LODESR[35] was made of 400 turns per wing of 0.10 mm diameter enamelled copper wire, placed on
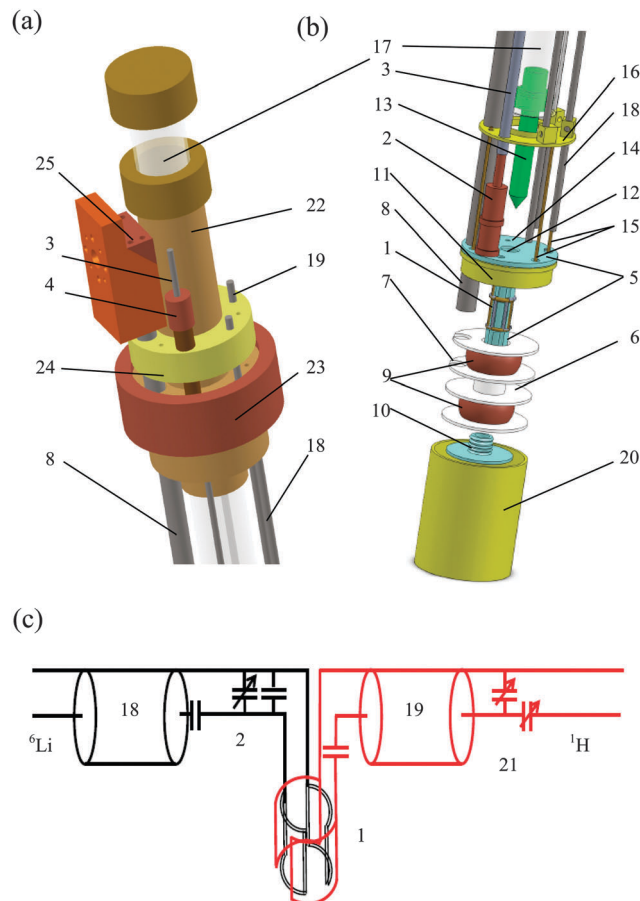

Fig. 2 (a) Upper and (b) bottom parts of the probe. The LODESR coils (9) with the coil former (6), nut (10) and microwave cavity (20) are located below the NMR coils. (c) Circuit where the ^{1}H side (shown in red) comprises a matching and two trimming capacitors for tuning (21). The ^{6}Li part (shown in black) uses a Voltronics trimmer capacitor (2) in parallel with a chip capacitor suitable for low temperatures. Partial matching is obtained with a capacitor in series.

the LODESR coil former, and attached by means of a PTFE nut (10) to the NMR coil former. A brass platform (11) with a central hole (12) to accept the sample holder (13) and outer holes for the waveguide (8), wires (14), and holding screws (15) was used to support the NMR coil former. Spacers (16) were placed at regular distances along the vertical axis of the probe, to maintain the structure, to receive the Vetronite tube (17), cables (18, 19) and the waveguide, and to allow the tuning rod to rotate freely. The NMR and LODESR coils were placed in a brass cavity to confine the microwave irradiation (20). The sample volume is 50 µl.

The tuning and matching box (21) was connected to the room-temperature end of the ^{1}H cable (19), which is part of the tuning and matching system.[38,39] The cable for ^{6}Li (18) was connected directly to the filters before the preamplifier of a Bruker Avance II spectrometer. The isolation between the channels was −23 dB from ^{1}H to ^{6}Li, and −50 dB from ^{6}Li to ^{1}H. The flange at the top of the probe (22) was made of brass and held to the cryostat with a nut (23). Vacuum was made possible by compressing the waveguide, cables and the rod with

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a nut against a flange (24) with O-rings. The sample was loaded from the top through the Vetronite tube.[8] The sample holder, which has a cylindrical symmetry and is made of PEEK, has inner and outer diameters of 3 and 5 mm respectively.

The 6 mm thin-walled waveguide (8) made of non-magnetic steel was connected to a mirror (25) to reflect the microwaves generated by a frequency doubler (100 mW at 188 GHz) connected to an Elva source (400 mW at 94 GHz). The orthogonal coils have good rf homogeneity.[40] The probe design presented here is distinct from other probes that have been developed for cross polarization at low temperatures, either without[41,42] or with rapid dissolution.[5,7,9,10]

Microwave frequency modulation with a sweep range of 50 MHz and a modulation frequency of 10 kHz was used to boost the nuclear polarization and shorten the DNP build-up times of protons.[43,44] The centre of the frequency modulation was set to 188.270 GHz to obtain the maximum (negative) polarization $P(^1H)$.

The adiabatic $180°$ Wurst inversion pulses[7,10,34] had bandwidths of 100 and 30 kHz for ^1H and ^6Li, respectively. The rf amplitude of the proton channel was set just below arcing (9 W, corresponding to an rf field of 10 kHz). The rf amplitude of the ^6Li channel was then optimized (14 W, an rf field of 10 kHz). The lengths of both inversion pulses were 1.45 ms.

Short $5°$ pulses were used to measure the polarizations $P(^1H)$ and $P(^6Li)$ at low temperatures without causing significant losses. The DNP build-up times $\tau_{DNP}(^1H)$ and $\tau_{DNP}(^6Li)$ were measured at 4.2 and 1.2 K. The decay of the polarization $P(^6Li)$ towards thermal equilibrium due to $T_1(^6Li)$ relaxation was measured at 4.2 K and at room temperature after dissolution.

The sample consisted of 4 beads of 10 μl each of 7 M lithium chloride (LiCl) enriched in ^6Li with 50 mM TEMPO in 40 : 40 : 20 (v : v : v) ethanol-d$_6$: D$_2$O : H$_2$O, with an extra 10 μl bead of 3 M ascorbate to quench the radicals during and after dissolution.[45]

Polarisation in the solid

The $90°$ pulse lengths were 7 μs for protons using 100 W and 6.75 μs for ^6Li using 100 W. The build-up and relaxation times at 4.2 K were $\tau_{DNP}(^1H) = 83$ s, $\tau_{DNP}(^6Li) = 543$ s and $T_1(^6Li) = 768$ s. In Fig. 3(a) the build-up curves of $P(^6Li)$ are compared for direct DNP and indirect CP-DNP, both at 4.2 K. A single CP contact established 180 s after pre-saturation provided a larger spin polarization $P(^6Li)$ than could be achieved by direct DNP. A compromise delay of 180 s was chosen to allow the proton polarization to build up again before the next CP contact. After the third contact, the polarization $P(^6Li)$ was 1.7 times higher than could be obtained with direct DNP. A series of 32 short $5°$ pulses were applied to measure thermal equilibrium with a sufficient signal-to-noise ratio at 4.2 K. Afterwards, a pair of adiabatic inversion pulses were applied to establish a CP contact, and 32 pulses were applied to determine $P(^6Li)$. At 4.2 K, $T_1(^6Li) > 600$ s (10 minutes). Dissolution does not cause significant losses of polarization $P(^6Li)$.

When the temperature was lowered to 1.2 K, the build-up was significantly slowed down to $\tau_{DNP}(^1H) = 215$ s and $\tau_{DNP}(^6Li) = 2021$ s. Fig. 4(a) shows the experimental DNP-CP build-up curve of $P(^6Li)$. In this case the interval between CP contacts was 450 s. The polarization $P(^6Li)$ obtained with DNP and CP was again 1.7 times higher than could be obtained by direct DNP. Comparing ^6Li signal intensities at thermal equilibrium at 4.2 K (with 32 pulses with $5°$ nutation angles) with the maximum polarization obtained at 1.2 K, a maximum polarization $P(^6Li) = 20 \pm 2\%$ was measured. The efficiency of adiabatic CP at 1.2 K is approximately 24%. A proton polarization $P(^1H) = 76\%$ was reached at 1.2 K.

Polarisation in solution

Once the sample achieved its maximum polarization $P(^6Li)$ at 1.2 K, it was dissolved using 5 ml of overheated D$_2$O at 393 K at 1 MPa. The transfer time was 7 s using a magnetic tunnel,
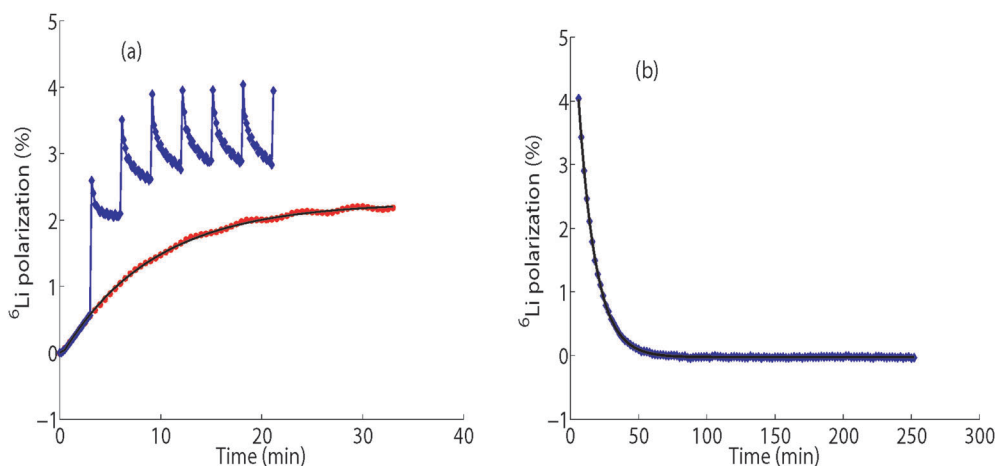

Fig. 3 (a) Experimental build-up of $P(^6Li)$ observed by direct DNP without cross polarization at 6.7 T and 4.2 K (red) with a mono-exponential fit (black) and experimental build-up of $P(^6Li)$ by indirect DNP combined with CP from ^1H to ^6Li (blue). (b) Decay of ^6Li polarization to thermal equilibrium at 4.2 K in the absence of irradiation (blue) with a mono-exponential fit (black). The sample consisted of 4 beads of 10 μl each of 7 M ^6Li-enriched lithium chloride (LiCl) with 50 mM TEMPO in 40 : 40 : 20 (v : v : v) ethanol-d$_6$: D$_2$O : H$_2$O with an extra bead of 10 μl of 3 M ascorbic acid in H$_2$O to quench the radicals during dissolution.
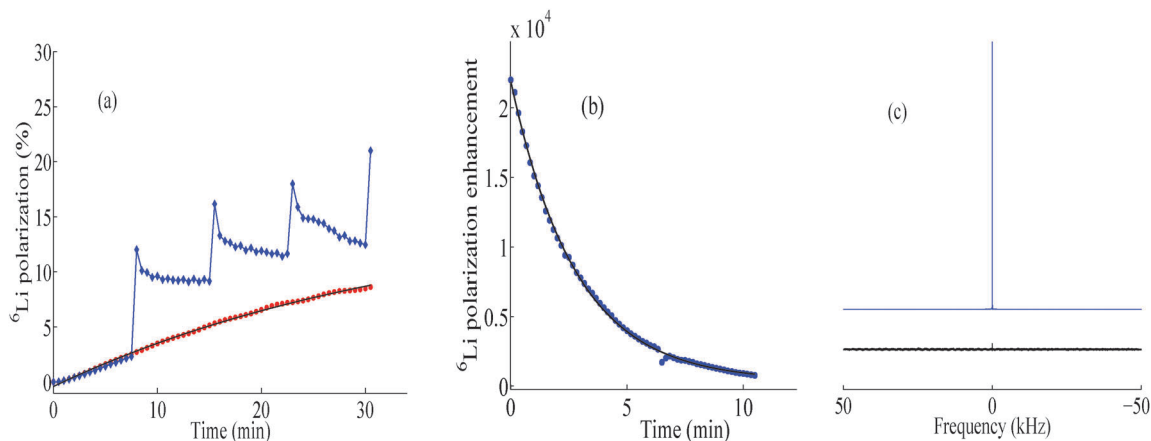
Fig. 4 (a) Experimental build-up of $P(^6Li)$ obtained with cross polarization (blue), with DNP only (red) and a fit of the latter curve (black) at 6.7 T and 1.2 K. Since the proton build-up time constant was $\tau_{DNP}(^1H)$ = 3.58 min, intervals of 7.5 min between subsequent CP contacts were used as a compromise between the build-up of $P(^1H)$ and the decay of $P(^6Li)$. After each CP contact, the polarization $P(^6Li)$ tends to return to the plateau observed by direct ^6Li DNP. (b) Decay $P(^6Li)$ in solution at 7 T and 300 K (blue) fitted to a mono-exponential function (black).The sample consisted of 4 beads of 10 μl each of 7 M ^6Li-enriched lithium chloride (LiCl) with 50 mM TEMPO in 40 : 40 : 20 (v : v : v) ethanol-d_6 : D_2O : H_2O with an extra bead of 10 μl of 3 M ascorbic acid in H_2O to quench the radicals during dissolution. (c) Two ^6Li spectra taken at room temperature with a single flip angle of 5° (blue) and gain 16 and a single 90° flip angle and gain 1024.

which extended from the polarizer to a 7 T Bruker (300 MHz) spectrometer. Measurements were started 60 s after dissolution. With short 5° pulses applied every 10 s during the decay of the polarization $P(^6Li)$, a $T_1(^6Li)$ = 161 s was measured in solution (Fig. 4(b)). By comparing the first spectrum taken after dissolution (one 5° pulse) with a spectrum taken in thermal equilibrium (64 scans with 90° pulses) at 7 T, the measured enhancement was ε = 22 000 with respect to thermal equilibrium. The final concentration of LiCl was 56 mM.

ESR response

There are obvious advantages in monitoring the ESR response under the same conditions where DNP and CP are conducted.[35–37,46]
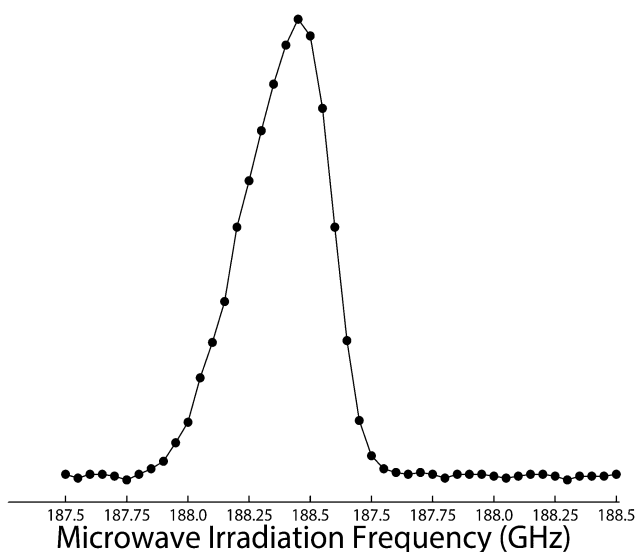

Fig. 5 Longitudinally detected electron spin resonance (LODESR) spectrum of a sample of 12 mM DPPH in toluene, taken at 4.2 K. A TEMPOL spectrum obtained with this probe is shown in ref. 44.

The two wires from the LODESR coil passed through a vacuum-sealed feed-through at the top of the probe and were connected to a Stanford Research Systems low noise preamplifier (Model SR560). The presence of a Helmholtz coil surrounding the NMR coils did not significantly degrade the rf fields. A homemade Labview program controlled a NI USB-6211 DAQ, which was connected to the Elva microwave source for signal generation and also to the preamplifier for data acquisition.[35–37] An example of the LODESR spectrum is given in Fig. 5.

Conclusions

A high nuclear spin polarization $P(^6Li)$ was obtained rapidly by combining proton DNP with adiabatic cross-polarization (ACP) from ^1H to ^6Li. The proton polarization prior to CP was estimated to be $P(^1H)$ = 76% at 6.7 T and 1.2 K. A maximum polarization $P(^6Li)$ = 20 ± 2% was obtained at 1.2 K. Although the efficiency of CP was not ideal (a gain of 1.7 on $P(^6Li)$ was obtained instead of the maximum which for ^1H–^6Li CP is 7, giving an efficiency of 1.7/7 × 100 = 24%), it was possible with a single CP contact to exceed the plateau that can be achieved by direct ^6Li DNP without CP, at both 4.2 and 1.2 K in a few minutes. With direct DNP using microwave frequency modulation but no CP, a polarization $P(^6Li)$ = 11 ± 1% was achieved at 1.2 K. The relatively short $T_1(^6Li)$ relaxation time in solution remains a limitation for clinical applications. A double resonance NMR probe has been constructed for CP at low temperatures using two NMR saddle coils in quadrature, suitable for CP, despite some rf inhomogeneity. The probe presented an rf tuning bandwidth of 10 MHz on the ^6Li channel, with sufficient rf field strengths for efficient CP, i.e., 10 kHz on each channel for several ms without arcing. A cross polarization sequence using double inversion was found to be efficient for the quadrupolar ^6Li nuclei. The choice of two coils in quadrature was a compromise to save space for some other features like LODESR.

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It has been demonstrated that despite the presence of a LODESR Helmholtz coil, an excellent proton polarization of 76% could be achieved.

Acknowledgements

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