Efficient Dynamic Nuclear Polarization at High Magnetic Fields

Gavin W. Morley,[1,*] Johan van Tol,[1] Arzhang Ardavan,[2] Kyriakos Porfyrakis,[3] Jinying Zhang,[3] and G. Andrew D. Briggs[3]
[1]*Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory at Florida State University, Tallahassee, Florida 32310, USA*
[2]*Clarendon Laboratory, Department of Physics, University of Oxford, OX1 3PU, United Kingdom*
[3]*Department of Materials, University of Oxford, OX1 3PH, United Kingdom*
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By applying a new technique for dynamic nuclear polarization involving simultaneous excitation of electronic and nuclear transitions, we have enhanced the nuclear polarization of the nitrogen nuclei in ^{15}N@C$_{60}$ by a factor of 10^3 at a fixed temperature of 3 K and a magnetic field of 8.6 T, more than twice the maximum enhancement reported to date. This methodology will allow the initialization of the nuclear qubit in schemes exploiting N@C$_{60}$ molecules as components of a quantum information processing device.

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The incarceration of atomic nitrogen in a C$_{60}$ cage leads to a species (known as N@C$_{60}$) with remarkable properties: The nitrogen occupies a high-symmetry site at the center of the cage and retains its atomic configuration, and the cage offers protection of the nitrogen electron paramagnetic moment from interactions with the environment [1]. It exhibits the longest electron spin lifetimes observed in any molecular species with a phase coherence time $T_2 = 240\ \mu$s [2] in solution at 170 K, and spin-lattice relaxation time, T_1, of 4.5 min at 4 K [3]. T_2 is of the order of 10^4 times longer than the time taken to manipulate the electron spin state by pulsed electron spin resonance (ESR), and this has led to speculation that it may be a useful component in an electron-spin-based quantum computer [4–8].

The nuclear spin of the incarcerated N atom exhibits even longer lifetimes, and it too can in principle be used to store quantum information. However, before the nuclei could be exploited as qubits, a method of polarizing them would be required, and this method should work at temperatures that are high on the scale of the nuclear Zeeman energy. (While the preparation of pseudopure initial states allows high-temperature NMR quantum computing [9], the readout signal becomes exponentially small as the number of qubits goes up [10]). Methods of achieving nuclear polarization are also useful in other contexts, including NMR [11] and high-energy physics [12].

Four microwave-induced dynamic nuclear polarization (DNP) effects have been demonstrated in the past: The Overhauser effect (OE) [13], the solid effect (SE), thermal mixing (TM), and the cross effect (CE). These are described in Ref. [14] and the articles cited therein. Defining the polarization enhancement as $\varepsilon = \frac{P_{\text{after DNP}}}{P_{\text{before DNP}}}$ (where the polarization, P, is the net number of aligned nuclear spins divided by the total number), these techniques lead to enhancements in the NMR signal intensity of up to $\varepsilon = 400$ [11]. In this Letter we describe a new approach in which the nuclei are polarized using electron-nuclear double resonance (ENDOR), exploiting the large difference between the electronic and nuclear spin-lattice relaxation times. We refer to this technique as "polarization of nuclear spins enhanced by ENDOR" (PONSEE). PONSEE has several significant advantages over OE, SE, TM, and CE DNP. First, the polarization enhancement for PONSEE increases with magnetic field, while for OE, SE, TM, and CE DNP this enhancement falls as the field increases. This makes PONSEE well suited for use in contemporary NMR spectrometers which benefit from the improved spectral resolution available at 7–21 T. Second, the time required for PONSEE is a few times the electronic T_1, which is shorter than the OE, SE, TM, and CE because no forbidden transitions or three-spin transitions are used.

PONSEE may also be well suited to other samples such as the organic radical TEMPO. In a high magnetic field the ESR spectrum of TEMPO becomes highly anisotropic [15], but PONSEE should still work for the nitrogen nuclei as their hyperfine splitting is clearly resolved. For an electron spin with unresolved hyperfine structure, it would still be possible to use PONSEE by burning a hole in the ESR spectrum as long as one nuclear spin orientation could be preferentially addressed.

Room-temperature NMR signal-to-noise enhancements of >10 000 have been achieved by cooling a sample, performing "traditional DNP", and then (in a time that is short compared to the nuclear T_1) rewarming [16]. The "traditional DNP" created a polarization of 26% with 1 h of the TM effect at 1.1 K, but using PONSEE instead of TM would have produced larger polarization in a shorter time.

A molecule of ^{15}N@C$_{60}$ in a strong magnetic field has eight energy levels as shown in Fig. 1. The electronic and nuclear spins, S_z and I_z, are both good quantum numbers. The ^{15}N isotope has spin $\mathbf{I} = \frac{1}{2}$, which is a natural qubit, unlike the more abundant ^{14}N nucleus which has $\mathbf{I} = 1$.

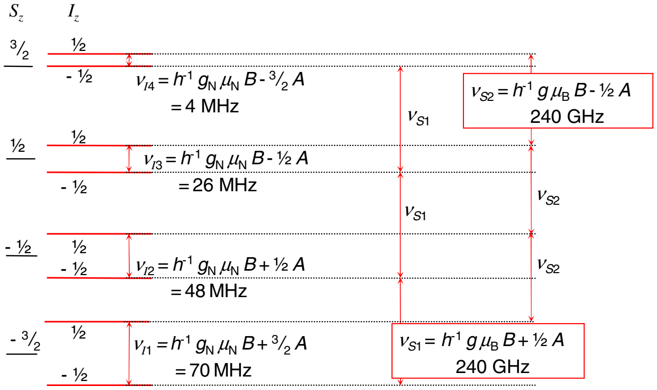

FIG. 1 (color online). Energy levels and allowed transitions of $^{15}N@C_{60}$ in a strong magnetic field, B, parallel to the z-axis. The system is well described by the effective spin Hamiltonian $H = B(g\mu_B S_z - g_N \mu_N I_z) + hAS_z I_z$. The three terms describe the electronic Zeeman, nuclear Zeeman and isotropic hyperfine interactions. The hyperfine constant is $A = 21.9$ MHz. The four nuclear transitions are labeled $\nu_{I1} - \nu_{I4}$. The two triply degenerate electronic transitions are labeled ν_{S1} and ν_{S2}.

Complete two-qubit quantum computation is feasible with an ensemble of $^{15}N@C_{60}$ [3].

At a temperature of $T = 3$ K and a magnetic field of $B = 8.6$ T, the electronic Boltzmann factor is

$$\alpha = \exp\left(-\frac{g\mu_B B}{k_B T}\right) \approx 0.02. \tag{1}$$

This implies that about 98% of the electrons are in the $S_z = -3/2$ state and only 0.001% are in the $S_z = 3/2$ state.

Our PONSEE technique consists of the three steps shown in Fig. 2. The first (second) step selectively excites electronic (nuclear) spins whose nuclear (electronic) spins are in a particular state. The third step requires that $T_1^{\text{nuclear}} \gg T_1^{\text{electronic}}$, which is generally true for many spin systems.

PONSEE works efficiently with either continuous-wave (cw) or pulsed radiation. With cw radiation the three steps take place simultaneously. If pulsed radiation is used, π pulses should be chosen and after four applications of the three-step cycle, the nuclear polarization reaches the cw result for $\alpha \ll 1$ [3].

PONSEE is distinct from electron-nuclear cross polarization (eNCP) [14] which also uses ESR and NMR excitations, in that eNCP relies on spin locking which operates in pulsed mode only.

Our experiments used cw radiation for the first two steps. To maximize the nuclear polarization, the radiation should be powerful enough to saturate the transitions, equalizing the populations of the connected energy levels. After waiting for a time longer than $T_1^{\text{electronic}}$ but shorter than T_1^{nuclear}, the nuclear polarization is maximized and the populations of the four states in the $I_z = -\frac{1}{2}$ manifold are close to thermal equilibrium. This maximum nuclear polarization is hence greatest when the populations of the states we seek to empty ($I_z = \frac{1}{2}$) are made equal to the population of the high-energy state ($I_z = -\frac{1}{2}$ and $S_z = 3/2$). This should be achieved using rf radiation with frequency ν_{I4}. Alternatively, ν_{I3} (ν_{I2}) radiation could be used, making the population of the $I_z = \frac{1}{2}$ states equal to the population of the $S_z = \frac{1}{2}$ ($S_z = -\frac{1}{2}$) state. However, since the energy difference between the ground ($S_z = -3/2$) state and the $S_z = \frac{1}{2}$ ($S_z = -\frac{1}{2}$) state is smaller than between the ground state and the $S_z = 3/2$ state, the thermal equilibrium electron spin polarization between this state and the ground state is also smaller, resulting in a smaller net nuclear polarization after the ν_{I3} (ν_{I2}) pulse than if ν_{I4} were used.

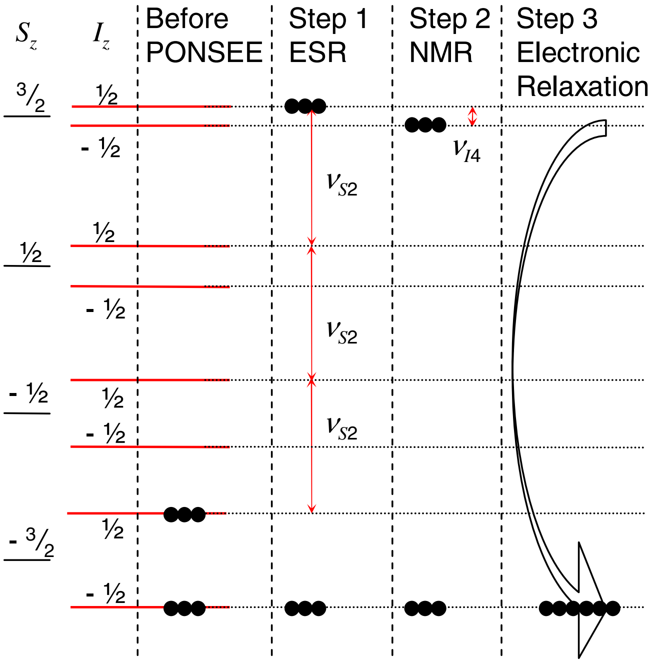

FIG. 2 (color online). Schematic of the pulsed version of the PONSEE sequence for $^{15}N@C_{60}$. ν_{I4} radiation is shown in step 2, but ν_{I3} or ν_{I2} could be used instead.

$^{15}N@C_{60}$ was prepared by ion implantation [17] with isotopically pure ^{15}N and purified with high performance liquid chromatography (HPLC) [18]. HPLC, combined with ESR and UV characterization indicated that about 80% of the cages contained nitrogen atoms. The purified sample was dissolved in deuterated toluene and put into a quartz ESR tube of outer diameter 4 mm. The solvent was deoxygenated with three freeze-pump-thaw cycles and sealed under a dynamic vacuum.

Measurements were made with a home-built 240 GHz cw ESR spectrometer [15]. Figure 3 shows an ESR spectrum recorded at 3 K. The absorption lineshape is characteristic of a saturated electronic spin-system with a long spin-lattice relaxation time, T_1 [19], and shows no nuclear polarization.

A small amount of nuclear polarization can be produced by applying microwave radiation only. Figure 4 shows the

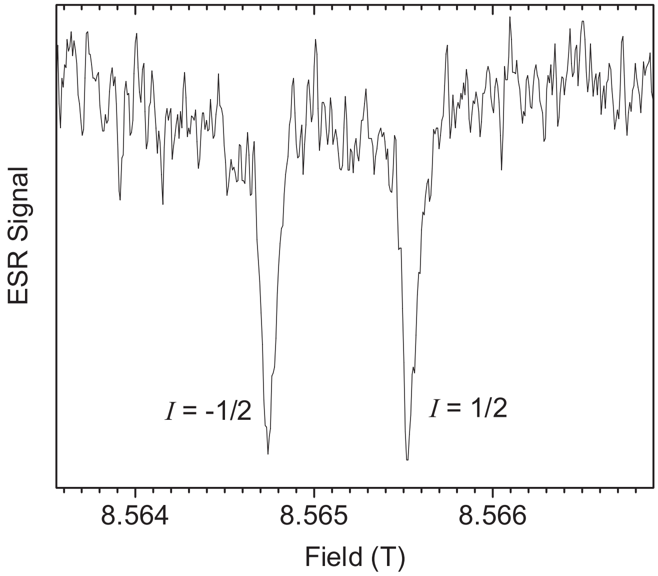

FIG. 3. 240 GHz cw ESR spectrum of $^{15}N@C_{60}$ in thermal equilibrium at 3 K.

ESR spectrum after radiation of frequency ν_{S2} was applied for 2.5 h at 4.2 K. The relative area of the two peaks shows that the nuclear polarization is 21 ± 2%. This form of DNP is due to the Overhauser effect [13].

Repeating this experiment with ν_{S1} radiation did not produce antipolarization. This shows that the polarization in Fig. 4 does not result from a difference in the T_1 times of the four nuclear transitions.

Instead, the polarization achieved with only ν_{S2} radiation is due to flip-flop transitions in which the nuclear and electronic spins simultaneously flip in opposite directions, conserving total angular momentum. When an electron relaxes back to a lower energy level it loses a quantum of angular momentum, so the corresponding part of a flip-flop transition must add a quantum of angular momentum to the nuclear spin. This effect always acts to align nuclear spins with the magnetic field, and occurs more often than the competing transitions in which the electron and nucleus must both lose a quantum of angular momentum. The perturbation causing flip flops arises from the nonsecular part of the isotropic hyperfine coupling, as can be seen when this interaction is expressed in terms of the raising (S^+ and I^+) and lowering (S^- and I^-) operators:

$$A\mathbf{S}\cdot\mathbf{I} = \frac{A}{2}(S^+I^- + S^-I^+) + A\,S_zI_z. \tag{2}$$

We found that the DNP effect was stronger with PONSEE than with the Overhauser effect. Furthermore, it was equally possible to align the nuclear spins with or against the applied field using PONSEE. Applying ν_{S2} and ν_{I2} radiation for 20 minutes produced the spectrum shown in Fig. 5 in which the nuclear polarization is 62 ± 2%. In theory, exciting the ν_{I3} and ν_{I4} transitions should polarize the nuclear spins more strongly, but instead we found that the effect was weaker. We attribute this to the lower rf power available at these frequencies, and less effective (frequency-dependent) coupling to the sample in our apparatus.

The thermal equilibrium polarization of isolated ^{15}N nuclear spins at 3 K in a field of 8.6 T is 0.03% [20]. Confinement inside a C_{60} cage increases the strength of the

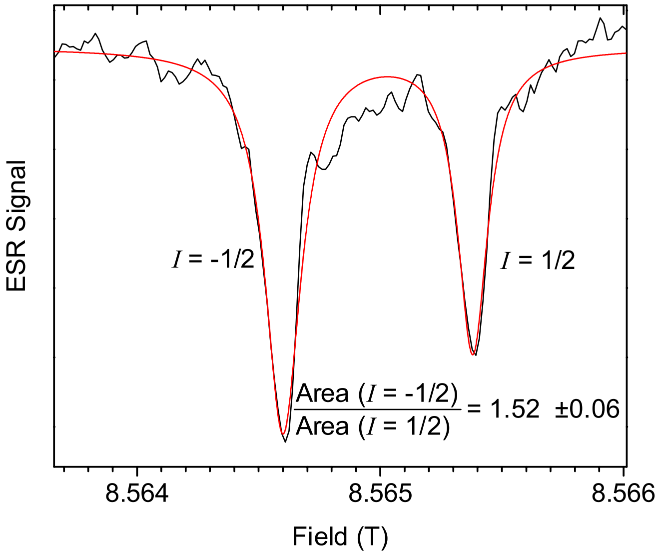

FIG. 4 (color online). cw ESR spectrum of $^{15}N@C_{60}$ at 4.2 K after 2.5 h ν_{S2} radiation. The nuclear polarization is due to flip-flop transitions. The smooth curve is the bi-Lorentian best fit. The ratio of the areas of these peaks shows the nuclear polarization to be 21%.

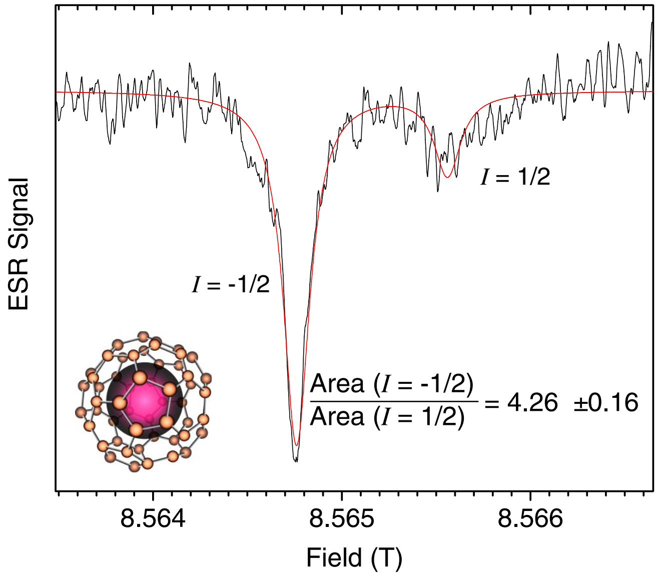

FIG. 5 (color online). cw ESR spectrum of $^{15}N@C_{60}$ at 3 K after 20 min PONSEE. The smooth curve is the bi-Lorentzian best fit with the linewidth of the two peaks constrained to be the same. The nuclear polarization is 62%, an enhancement of $\varepsilon = 1100$. Inset shows $N@C_{60}$ molecule.

hyperfine interaction, so the corresponding equilibrium polarization in ^{15}N@C$_{60}$ is 0.06%. Our PONSEE experiment produced 62% nuclear polarization, an enhancement of $\varepsilon = 1100 \pm 50$.

We found that the ν_{I2} transition was excited most effectively by sweeping the rf frequency from 47.916 to 47.924 MHz about once a minute. This frequency range provides a measurement of the hyperfine constant via the expression given in Fig. 1:

$$A = 2\nu_{I2} - \frac{2g_N\mu_N B}{h} = 21.88 \pm 0.01\ \text{MHz}, \qquad (3)$$

using the accepted value of the nuclear g factor for ^{15}N, $g_N = -0.566\,37$ [20]. This value of A agrees with that measured from the splitting in Fig. 4 ($A = 21.9 \pm 0.15$ MHz) and is close to the measurement made previously at the lower field of 0.34 T ($A = 22.021$ MHz) [1]. Frequencies ν_{I1}, ν_{I3} and ν_{I4} were calculated using our value of A, and found to agree with the values that produced PONSEE.

A simple model was used to predict the amount of polarization observed, assuming complete saturation of transitions ν_{S2} and ν_{I2}. The nuclear polarization is

$$P_{\text{after PONSEE}} = \frac{1/\alpha - 3 + \alpha + \alpha^2}{1/\alpha + 5 + \alpha + \alpha^2} = 84\%, \qquad (4)$$

for $\alpha = 0.02$. The measured polarization of 62% is smaller than this for two reasons: The rf radiation raised the sample temperature, and the ν_{I2} transition was not saturated. The rf power was set to 40 W to strike a balance between these competing issues. If the ν_{I4} transition had been used, our model predicts a nuclear spin polarization of 99.99%, corresponding to $\varepsilon = 1700$.

Once a measurable nuclear polarization had been achieved, we were able to investigate the nuclear T_1. After producing a 62% nuclear polarization, the temperature was raised to 4.2 K and the sample was allowed to relax for 11.5 h. The spectrum recorded after this time revealed that the nuclear polarization had only fallen to 40%. More measurements would be needed to properly describe the nuclear spin relaxation of ^{15}N@C$_{60}$, but these data show that the nuclear T_1 is on the order of 12 h at 4.2 K. This long time means that ^{15}N nuclear T_1 processes are not a significant mechanism for the electronic T_2 relaxation of ^{15}N@C$_{60}$ at this temperature.

In summary, we have demonstrated a new DNP technique, PONSEE, achieving a polarization enhancement exceeding $\varepsilon = 10^3$ in a sample of ^{15}N@C$_{60}$ at the high magnetic field of 8.6 T. PONSEE will be a valuable tool in initializing the nuclear qubits in quantum information processing devices employing N@C$_{60}$ molecules; the efficiency of this technique is independent of the number of qubits involved in the computation. Our measurement of a very long nuclear T_1 time suggests that these nuclear states could be useful as memory elements. Furthermore, PONSEE could find applications beyond quantum information processing; NMR experiments at high fields could benefit from signal-to-noise enhancements to selected nuclei using PONSEE.

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*Present address: London Centre for Nanotechnology, 17-19 Gordon Street, London WC1H 0AH, United Kingdom.
Electronic address: g.morley@ucl.ac.uk

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