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Communication

Relaxometry of insensitive nuclei: Optimizing dissolution dynamic nuclear polarization

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ABSTRACT

We report measurements of spin-lattice relaxation of carbon-13 as a function of the magnetic field ('relaxometry') in view of optimizing dissolution-DNP. The sample is temporarily lifted into the stray field above a high-resolution magnet using a simple and inexpensive 'shuttle'. The signals of arbitrary molecules can be observed at high field with high-resolution and sensitivity. During the dissolution process and subsequent 'voyage' from the polarizer to the NMR magnet, relaxation is accelerated by paramagnetic polarizing agents, but it can be quenched by using scavengers.

Dynamic nuclear polarization (DNP) [1] using the so-called dissolution process [2] has become a method of choice to enhance the sensitivity of ^{13}C in urea [3], pyruvic acid [4], bicarbonate [5], sodium acetate and glycine [6], of protons in alanine–glycine [7,8], of ^{15}N in acetylcholine and choline chloride [9], of ^{89}Y in yttrium chloride and its complexes with DOTAM and similar ligands [10–12], of ^{6}Li in lithium chloride [13], and many other nuclei. DNP can enhance nuclear spin polarization by about four orders of magnitude. This can be achieved through microwave saturation of the EPR transitions [14–16] of stable radicals such as trityl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL), or nitroxide biradicals such as TOTAPOL, mixed with the analyte in a solvent that forms glassy 'beads' at low temperatures (on the order of 1.2 K) in a polarizing magnet (3.35 or 5 T in our laboratory). In the so-called dissolution method [2], the sample is rapidly heated and transferred from the polarizer to an NMR or MRI magnet.

As illustrated in Fig. 1, during the 'voyage' from one magnet to the other, the sample is exposed to low fields (on the order of 0.5 mT), except if the polarizing and NMR magnets are housed close together in the same cryostat [17], or if the transfer tube is enclosed in permanent or electro-magnets. The orientation of the static field may vary during the voyage, but the spins follow the field adiabatically.

The relaxation rates of hyperpolarized nuclei depend on the field, the chemical shift anisotropy, the nature and concentration of the radicals, the molecular mass, the translational diffusion coefficient D and the rotational correlation time τ_c. Relaxation induced by paramagnetic polarizing agents such as nitroxides is particularly efficient at low fields [18]. This is expected to be of critical importance for macromolecules [19]. To design the best strategy for the transfer between the two magnets, e.g., to sustain the magnetic field above a threshold during the 'voyage', to select the best scavenging agents to eliminate the radicals after dissolution [20], and to predict which molecules are good candidates for dissolution-DNP, it is essential to determine the longitudinal relaxation times T_1 of the hyperpolarized nuclei as a function of the static magnetic field.

Conventional relaxometers using variations of the current that drives the electro-magnet [18,21,22] are usually designed for ^{1}H, and do not offer reasonable sensitivity for less sensitive low-γ spins such as ^{13}C. More elaborate relaxometers using superconducting magnets and involving shuttling of the sample into a second magnet [23], or moving the entire probe assembly in the stray field [24], provide ways to conveniently address low-γ spins [25–27]. We have developed a simple and inexpensive mechanical 'shuttle' (Fig. 2a) to measure slow longitudinal relaxation ($T_1 > 1$s) typical of nuclei such as carbon-13 as a function of the static magnetic field. The nuclear spin polarization is allowed to reach Boltzmann equilibrium at high field during a delay d_1, and the sample is then lifted in less than a second to a variable height in the stray field above the magnet, where spin–lattice relaxation is allowed to occur during a variable delay d_2 (see Fig. 2c). If desired, the sample can be moved to an area, where the field is shielded to 0.1 mT by a μ-metal sheath. The sample is then shuttled back to high field

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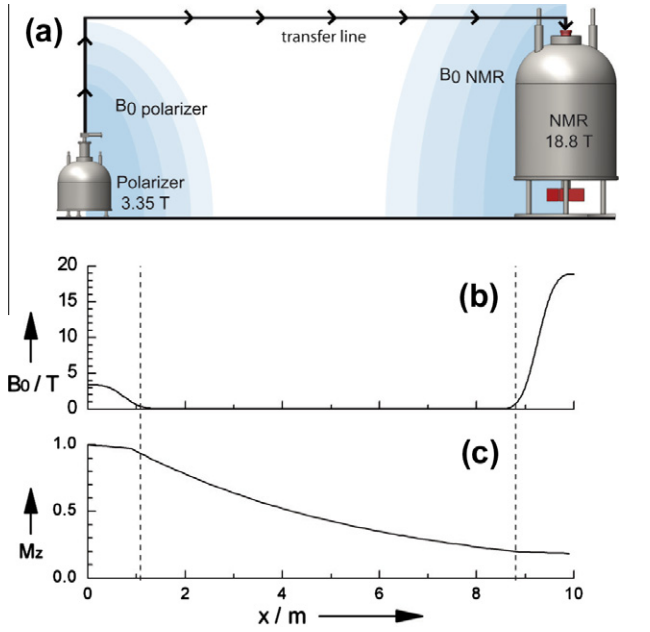

Fig. 1. Scheme illustrating the variation of the magnetic field magnitude (a) when a hyperpolarized sample travels during a dissolution-DNP experiment from a DNP-polarizer to an NMR spectrometer or MRI. (b) The magnetic field may drop as low as 0.5 mT between the two magnets. (c) As a result, part of the nuclear spin polarization is lost through spin–lattice relaxation during the transfer. The loss of polarization can be minimized if one has knowledge of the nuclear spin–lattice relaxation rates as a function of the magnetic field.

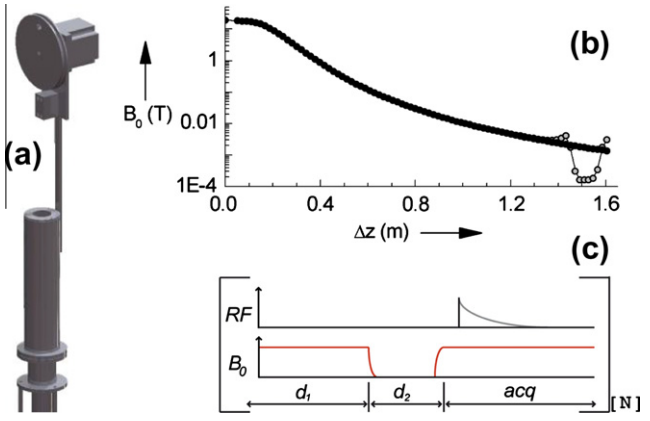

Fig. 2. (a) Upper part of the "shuttle" comprising a μ-metal cylinder, and a stepper-motor. (b) (●) Stray magnetic field as a function of the height above the most homogeneous area ('sweet spot') with B_0 = 18.8 T (800 MHz for protons) of a Bruker magnet, measured with a Hall probe carried by the shuttle device, without μ-metal shield. (○) Profile obtained with a cylindrical shield of 1 mm think μ-metal to decrease the stray field to 10^{-4} T about 1.5 m above the sweet spot. (c) The longitudinal magnetization is allowed to approach Boltzmann equilibrium in high field during a delay d_1. The sample is then lifted in less than a second to the desired field and allowed to relax towards the Boltzmann distribution at low field during a variable relaxation delay d_2 (there is no need for inverting the magnetization by a 180° pulse), and returned back to the probe for conventional high-resolution NMR measurements.

for high-resolution NMR measurements. Our design is inspired by devices described in the literature such as Levitt's Extremely Low Field (ELF) apparatus [28], and we do not strive to achieve a fast transfer as can be done with more elaborate shuttles [23,24,29,30]. A remotely controlled stepper-motor (Trinamic Pandrive) acting on a 50 mm diameter wheel (8192s teps/turn) lifts or lowers a conventional spinner which holds the sample tube in less than 1 s to the desired height, with an accuracy of about 0.1 mm. Shigemi tubes with a limited sample height of ca. 2 mm restrict the spread of the stray field to a narrow range. High-resolution NMR spectra of low- γ nuclear spins can be recorded at high field, using deuterium field-frequency lock and proton decoupling if required. The experiments can be accelerated by using 'insensitive nuclei enhanced by polarization transfer' (INEPT) [31]. A retro-INEPT sequence prior to detection can further improve sensitivity.

Fig. 2b shows the stray field B_0 measured with a Hall probe[32] as a function of the height above the magnetic center of a 18.8 T Bruker magnet (800 MHz for protons) down to 10^{-4} T. Fig. 3 shows the ^{13}C spin–lattice relaxation of a 3 M solution of 1-^{13}C labeled acetate in a field of 2 mT. The presence of the paramagnetic polarizing agent TEMPOL dramatically accelerates T_1 relaxation, particularly in low fields. As demonstrated in recent study, ascorbate (vitamin C) can be used as a scavenger[20] to quench paramagnetic relaxation. The addition of ascorbate also quenches paramagnetic dioxygen that is naturally present in D_2O. Scavenging significantly prolongs the T_1's at low fields, thus opening the way to 'voyages' of hyperpolarized solutions over longer distances.

The ^{13}C spin–lattice relaxation rates $R_1 = 1/T_1$ of 1-^{13}C labeled acetate in the range 2 mT < B_0 < 18.8 T are shown in Fig. 4. The rates are dramatically enhanced by TEMPOL at low fields (B_0 < 0.1 T). Such low magnetic fields are commonly experienced by hyperpolarized solutions during their voyage between the polarizer and NMR magnets, thus leading to significant polarization losses (in our laboratory, the magnetic field drops to 0.5 mT between the polarizer and the NMR magnet).

Since the pioneering days of NMR, Gutowsky [33], Hubbard [34] and coworkers have shown that translational diffusion leads to

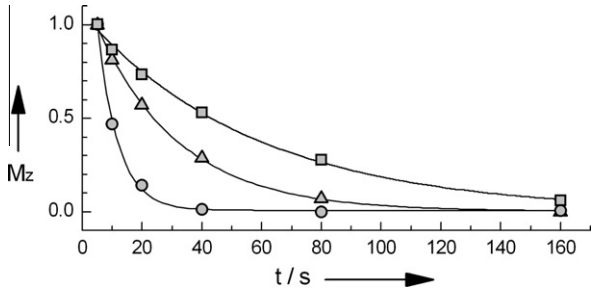

Fig. 3. (Δ) Spin–lattice relaxation of a 3 M solution of 1-^{13}C labeled acetate in non-degassed D_2O in a field B_0 = 2 mT, ca. 1.5 m above the sweet spot of an 800 MHz system (without μ-metal sheath); (○) the same after addition of 2.5 mM TEMPOL; and (□) after adding 30 mM ascorbate to scavenged the radicals. Mono-exponential fits gave T_1 = 27.6 ± 1 s, T_1 = 6.8 ± 0.8 s and T_1 = 57.3 ± 1.1 s, respectively. The T_1 is extended by to a factor 8.4 by scavenging.

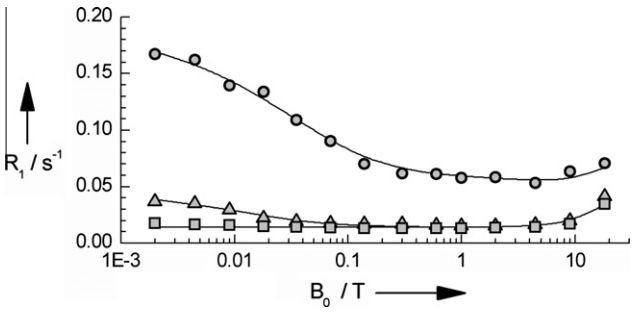

Fig. 4. (Δ) Spin–lattice relaxation rates $R_1 = 1/T_1$ of ^{13}C in 3 M 1-^{13}C labeled acetate in non-degassed D_2O as a function of B_0 between 2 mT and 18.8 T; (○) the same after addition of 2.5 mM TEMPOL; and (□) after adding 30 mM ascorbate to scavenge the radicals. Fitting to Eq. (1) in all three cases takes into account intermolecular relaxation due to translational diffusion with respect to paramagnetic TEMPOL, intra-molecular dipolar effects, and CSA relaxation.

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modulate the dipolar couplings between the unpaired electrons of the paramagnetic species and the nuclear spins of the solute. The theory was further developed by Ayant, Belorizki, Freed and coworkers, introducing minimum approach distances [35], as well as arbitrary pair correlation functions [36], rapidly relaxing spin, diffusion jumps and frequency dependent diffusion [37]. Bryant and coworkers have published numerous studies involving translational motions in the vicinity of paramagnetic nitroxides [38–40]. In their notation [41], the paramagnetic contribution to the spin–lattice relaxation rate is

$$R_1 = N\frac{3\pi}{20}\left(\frac{\mu_0}{4\pi}\gamma_I\gamma_S h\right)^2 \frac{\tau_t}{d^3}\int_0^\infty [J_{3/2}(x)]\frac{x}{x^4+u^4/4}dx \quad (1)$$

where N is the concentration of the paramagnetic species in spins per m^3, while γ_I and γ_S are the gyromagnetic ratios of the nuclei and electrons. The correlation time τ_t of the relative diffusive motion is $\tau_t = d^2/D$, where is d is the distance of closest approach between the paramagnetic species and the spins of the solute, and D the translational diffusion constant. Finally,

$$J_{3/2}(x) = \left(\frac{2}{\pi x}\right)^{1/2}\left[\frac{\sin x}{x} - \cos x\right] \quad (2)$$

where x and $u = (\omega\tau_t)^{1/2}$ are dimensionless variables. This expression is valid for arbitrary nuclei with gyromagnetic ratios γ_I. Bulky paramagnetic species such as Trityl, where the unpaired electron is surrounded by aromatic groups, and spins such as ^{13}C that are buried more deeply than protons in the core of the solute molecules, lead to larger distances of closest approach d, so that the paramagnetic contribution to the spin–lattice relaxation rate decrease with d^3. Apart from such scaling effects, relaxometry profiles of ^{13}C and ^{1}H have similar features at low fields. At high fields however, CSA contributions to relaxation are larger for ^{13}C than for ^{1}H.

The fits in Fig. 4 were performed with d and τ_t as free parameters, and $N = 1.5 \times 10^{18}$ spins cm^{-3} for 2.5 mM TEMPOL. All solutions were assumed to be saturated with 0.267 mM paramagnetic dioxygen ($N_{O2} = 1.6 \times 10^{17}$ spins cm^{-3}) except when ascorbate was used ($N_{O2} \sim 0$). The parameters were found to be $d = 4$ Å and $\tau_t = 0.52$ ns, hence the translational diffusion coefficient must be $D = d^2/\tau_t = 3.1 \times 10^{-10}$ m^2 s^{-1}. Intra-molecular ^{1}H–13C dipolar relaxation can be fitted with a rotational correlation time $\tau_c = 9$ ps, and CSA relaxation by an anisotropy $\Delta\sigma = 4.12 \times 10^{-5}$. Neither of these mechanisms are affected by scavenging. A Mathematica notebook including the least square fitting routines is available on request.

Few macromolecules have benefitted from dissolution-DNP and enhancement factors for ^{1}H that have been reported so far have been rather modest [8]. Our study shows why it is so advantageous to scavenge free radicals during the dissolution procedure, not merely to slow down relaxation rates at high fields, but also to prevent polarization losses during the 'voyage' from one magnet to the other. Below a critical magnetic field of ca. 0.1 T (Fig. 4), relaxation induced by translational diffusion in the presence of paramagnetic species dramatically increases spin–lattice relaxation. In order to preserve the spin polarization as much as possible, the magnetic field could be maintained above 0.1 T during the 'voyage' by enclosing the transfer tube in permanent or electro-magnets. Our observations also indicate that hyperpolarized NMR or MRI experiments of nuclei such as ^{13}C or ^{31}P should be performed at moderate fields to prevent CSA relaxation in high fields [25–27].

Acknowledgments

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