

From Minutes to Hours: Extending the T1 of Xe-129 DNP in the Solid-State

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Introduction. The use of hyperpolarized (HP) ³He and ¹²⁹Xe for in-vivo lung magnetic resonance imaging has led to major advancements in the understanding of lung structure and function. The HP gas MRI is used for structural and functional evaluation and detection of pulmonary disorders such as chronic obstructive pulmonary disease (COPD), cystic fibrosis and asthma. In lieu of the recent ³He supply crisis, attention has shifted to the potential benefits of HP ¹²⁹Xe gas for biological imaging. ¹²⁹Xe is more readily available and possesses analogous physical properties. Though hyperpolarization of gas-phase nuclei is typically generated via spin-exchange optical pumping (SEOP) methods, the low partial pressure (~ several bar) approach used in SEOP for producing sufficiently high ¹²⁹Xe polarization limits the achievable volumes that can be generated. Dynamic Nuclear Polarization (DNP) of ¹²⁹Xe in the solid-state has been proposed as an alternative method to help circumvent these limitations. While recent work has demonstrated the feasibility of obtaining HP ¹²⁹Xe in the gas phase using such methods[1,2], its utility for generating substantially larger quantities of polarized ¹²⁹Xe for clinical applications continues to be challenging. Here, we investigate the effects of the mixture composition (xenon/1-propanol/trityl radical) on the effective spin relaxation (T_1) and polarization build-up (T_B) times of HP ¹²⁹Xe at 1.43 K and 5 T. Both temperature and magnetic field-induced spin destruction are also examined in order to identify the limiting factors for polarization retention during the dissolution process.

Methods and Results. The DNP experiments were performed on a home-built setup [3] based on an Oxford TMR7/88/15 Teslatron^{MR} superconducting magnet with integrated DNP/NMR capabilities, operating at the magnetic field of 4.997 T. The use of a liquid helium cryostat allows for routine measurements between 1.43–1.60 K; temperature is monitored using an Oxford Instruments ITC-503 controller and maintained using an external vacuum pump. DNP-enhanced NMR was achieved using a high power 140 GHz microwave source with a 70 mW microwave amplifier. Our custom-designed probe has recently been retrofitted with three additional temperature sensors along the helium path to provide a more accurate gauge of sample temperature. The spectrometer is pre-cooled to temperatures < 100K prior to sample insertion to limit sublimation of Xe(g) out of the xenon/1-propanol/trityl radical ice matrix. The same protocol is used for all sample preparations: Xe(g) is condensed to liquid form and mixed with a radical-doped glassing agent that is then solidified and polarized. Here, the acidic form of the Finland (trityl) radical is our polarization source while 1-propanol is our glassing agent. Samples are stirred for 3-5 minutes with multiple small, removable magnetic stirrers during the condensation process—the stirring rate is controlled using a vertically mounted magnetic stirring plate. All magnets are removed immediately prior to freezing. As soon as DNP samples are prepared, they are placed within the spectrometer in order to ensure consistent DNP results.

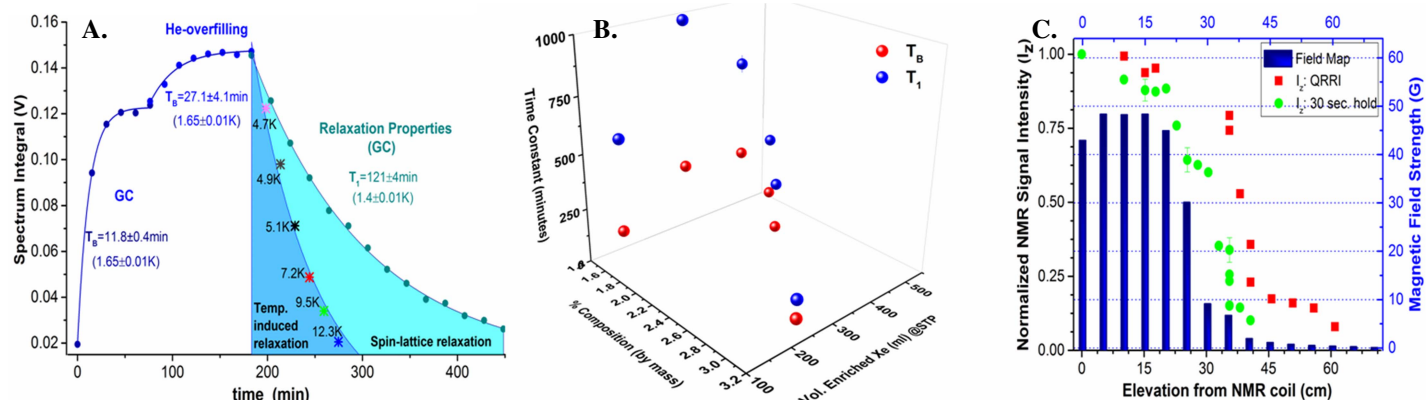


Figure 1. Examining DNP time constants as a function of external variables (i.e. sample composition, temperature, and magnetic field).

- Under general conditions (GC), the sample is at cryogenic temperatures (~1.46K). Heat introduced from the microwave source elevates the internal temperature of the sample (**Fig. 1A**). Overfilling the sample space with liquid helium significantly impacts the DNP time constants—spin-up (T_B) and T_1 relaxation times are doubled simply by dampening the effects of overheating. The spin destruction at elevated base temperatures becomes severe. A minimum temperature 4.6K (He b.p.) is required for further sample manipulation (e.g. removal, dissolution). As such, precise temperature control is critical in order to minimize potential losses.
- Spin-up and T_1 relaxation times are measured with varying sample composition and Xe loading (**Fig. 1B**). Halving the amount of radical leads to an 8-fold increase in the spin-lattice relaxation times. Despite these gains, the required amount of time for polarization build-up is almost 10 times as long. The effect of Xe loading suggests parabolic behavior: at low Xe densities spin destruction is influenced less by the radical, while the spin relaxation is more sensitive to the radical density at higher Xe loading.
- Once the sample loading conditions were optimized, a xenon/1-propanol/trityl icy matrix comprised of 1.5 % trityl (by weight) and 22 cm³ Xe(g) was evaluated to study the necessary conditions for preserving the ¹²⁹Xe spin polarization upon sample removal (**Fig. 1C**). Despite the elongated T_1 (995 ± 5 min at 1.55K) results indicate substantial losses in polarization with sample displacement; 50% of the signal is lost when elevated only halfway out of the probe. While the effects from temperature and field cannot be completely decoupled, these results suggest the dissolution process must occur within 15 cm from the base of the probe in order to retain as much polarization as possible during the sublimation process.

Conclusions. Here we show the ability to elongate the spin-lattice relaxation time without annealing. Despite these gains, temperature control and field strength are key factors to successful polarization retention during Xe dissolution. Our results show the importance of the Xe:radical:1-propanol ratio. Additional work is in process to further elucidate this phenomenon.

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References: [1] J.-H. Ardenjaer-Larsen et al., US patent 8,003,077, filed 2003, issued 2011. [2] A. Comment et al., Phys. Rev. Lett. 105, 018104 (2010). [3] N. N. Kuzma et al., J. Chem. Phys. 137, 104508 (2012).