

Adsorbed Xenon and the Production of Hyperpolarized ^{129}Xe

E. V. Krjukov, J. D. O'Neill and J. R. Owers-Bradley

School of Physics and Astronomy, University of Nottingham, Nottingham, NG7 2RD, England

Abstract.

We show that it is possible to induce a large nuclear spin polarization in ^{129}Xe adsorbed on a silica gel substrate using ^3He as a relaxant, in a reasonable time. We also describe the complete production cycle for the generation of large quantities of hyperpolarized xenon from xenon gas by a cryogenic method for use in MRI and material science.

Keywords: Hyperpolarized, Xenon, Adsorbed, NMR

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INTRODUCTION

The possibility of using prepolarized noble gases, ^3He and ^{129}Xe , as contrast agents in magnetic resonance studies has excited scientists for some years. Laser optical pumping is currently the only method of production. However, in this paper we shall describe an alternative cryogenic method which has the potential to produce large quantities of hyperpolarized ^{129}Xe within a reasonable time frame. The brute force concept is very simple. Take the ^{129}Xe nuclear spin system to the extreme conditions of very low temperatures and high magnetic field where the equilibrium state corresponds to a high degree of spin polarization, allow the system to reach this equilibrium and then quickly remove the polarized nuclei from the cryostat before relaxation processes destroy the polarization. This technique demands that we satisfy conflicting requirements. On one hand, nuclear relaxation time should be long enough to preserve polarization at high temperatures outside the cryostat (this is possible for $S=1/2$ spin systems). On the other hand, the nuclear spin system should reach equilibrium at very low temperatures within a practical timescale. Relaxation times in bulk solid xenon increase dramatically with cooling and become impractically long at temperatures around 10 mK, even when using oxygen as a relaxant [1][2]. Biškup et al [3] proposed a way to solve this problem and following their work we show here that a high degree of ^{129}Xe polarization is achievable and that the polarization can be retained at higher temperatures.

METHOD OF PRODUCTION

We first adsorb the xenon onto a suitable substrate and use ^3He as a relaxant over the xenon layer, allowing the polarization to grow in a finite time. There is sufficient

coupling between the mobile ^3He atoms and the uppermost xenon layer to induce relaxation to near equilibrium in a few hours. We use a high surface area silica gel substrate onto which a single monolayer of xenon is adsorbed at temperatures of around 160 K. Following cooling to 1 K, ^3He is added and the system is further cooled to the base temperature of 10 mK. The ^3He also improves thermal contact between the xenon and the mixing chamber. The degree of polarization is detected using pulsed nuclear magnetic resonance (NMR). The magnetization is destroyed by a comb of rf pulses and the subsequent growth of the NMR signal is monitored by recording free induction decay signals induced by tipping pulses of a few degrees. We have previously shown [1] that, for the first xenon monolayer which is in direct contact with ^3He , the spin-lattice relaxation is much faster than for the lower layers. An Oxford Instruments top loading dilution refrigerator with a 15.5 tesla superconducting magnet provides the high $B/T > 1.5 \text{ mK T}^{-1}$. Under these conditions, the equilibrium polarization for ^{129}Xe is 41%.

RESULTS

Fig. 1 shows a graph of polarization degree against time in a magnetic field of 14.0 T. It can be seen that the majority of the relaxation occurs during the first three hours. Notice that we have not achieved the equilibrium polarization at the lowest temperature; this is because a quantity equating to only 2 monolayers of ^3He were added above the xenon surface. This is sufficient to induce ^{129}Xe relaxation but, from our Aluminium NMR thermometer in the cell, we know it is not enough to ensure good thermal contact between the xenon and the walls of the cell.

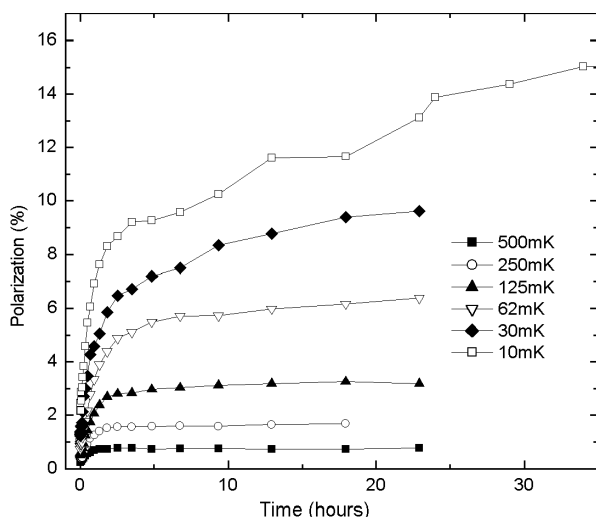


FIGURE 1. The growth of ^{129}Xe polarization for various cryostat temperatures.

REMOVING THE HYPERPOLARIZED XENON

Before the xenon sample is removed from the cryostat and warmed to generate hyperpolarized gas, it is essential to break the coupling between the ^3He and the xenon [1]. We add the equivalent of a monolayer of ^4He to the cell at the lowest temperatures. The ^4He is preferentially adsorbed onto the xenon, displacing the ^3He thereby decreasing the relaxation rate by about a factor of 20 [1]. With the coupling reduced between the ^3He and ^{129}Xe , the sample can then be warmed to above 3 K in order to evaporate the ^3He . One potential drawback with this technology is that ^3He becomes contaminated with ^4He . We have solved this problem by application of a purification method which was proposed by Dmitriev [4]. We are able to take some ^3He directly from the condensing line of our dilution fridge where it has about 12% of ^4He impurity and then pump it through charcoal at 4.2 K. We collect ^3He with only 0.05% of ^4He in good agreement with [4]. This recovered ^3He is still an effective relaxant despite the small amount of ^4He . After xenon polarization we return the ^3He and ^4He gases back to the dilution refrigerator.

To prevent coupling between the ^{129}Xe and ^{131}Xe and subsequent rapid relaxation to equilibrium, the sample must remain within a magnetic field. To this end there is a 4.5 T superconducting magnet, located above the main magnet, with a minimum field of 1 T between them, and above this there is a 0.03 T permanent magnet to hold the polarized ^{129}Xe prior to a transfer to a 77 K storage vessel.

DISCUSSION

We now estimate how much hyperpolarized Xe gas we can generate. A full cycle of our xenon polarization lasts about one day. Firstly, condensation of the xenon and helium takes about half a day. Secondly, cooling down the mixing chamber with the sample in it takes about 6 hours. During the third stage the xenon itself cools and the polarization grows. The first and third stages could be improved dramatically by technical development. The cell size can be as large as 100 cm^3 . The density of silica gel = 0.48 g cm^{-3} and the surface area = $550\text{ m}^2\text{ g}^{-1}$, so the surface area is over $25,000\text{ m}^2$. This corresponds to around 0.25 moles or just over 5 litres of hyperpolarized STP xenon gas for a single monolayer coverage of xenon. If natural abundance xenon is used, the concentration of ^{129}Xe is 26% compared to 86% for enriched xenon; the latter however is rather more expensive. The rate of production is poorer than the best low pressure indirect optical pumping systems but better than typical high pressure xenon optical pumping systems. The advantages of our technique are that the xenon produced is already in its frozen state and free from contamination by alkali metals. We are presently attempting to improve the thermal contact between the cell and the mixing chamber by using more ^3He . To increase the potential production rate we also plan to examine plating with multiple monolayers of xenon, the use of higher surface area substrates and cryostat designs with larger capacity cells.

CONCLUSIONS

It is hoped that, with further development of this technique, large scale production of hyperpolarized xenon by the brute force method described here will be achievable. Our priority is to use the hyperpolarized gas to supplement the lung studies already under way using ^3He . Xenon is more plentiful than helium and is likely to be the best choice for future work in this area despite the lower NMR sensitivity of the ^{129}Xe . Another potential advantage of the technique is that other noble gas isotopes may be polarized as well as ^{31}P and ^{13}C .

REFERENCES

1. E. V. Krjukov, J. D. O'Neill, and J. R. Owers-Bradley, *J. Low. Temp. Phys.*, **140**, Nos. 5/6 (2005).
2. A. Honig, X. Wei, A. Lewis, E. ter Haar, and K. Seraji-Bozorgzad, *Physica B*, **284-288**, 2049–2050 (2000).
3. N. Biškup, N. Kalechofsky, and D. Candela, *Physica B*, **329**, 437–438 (2003).
4. V. V. Dmitriev, L. V. Levitin, V. V. Zavjalov, and D. Y. Zmeev, *J. Low. Temp. Phys.*, **138**, 877–880 (2005).