

Brute Force Polarization of ^{129}Xe

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

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

Hyperpolarized ^{129}Xe has numerous applications in magnetic resonance (NMR) and magnetic resonance imaging. As an alternative to the laser optical pumping method of production of hyperpolarized ^{129}Xe gas, we have investigated the brute force technique which uses a very high magnetic field and millikelvin temperatures. One obstacle to this technique is the extremely long spin lattice relaxation times of nuclei in solids at very low temperature. We show how liquid ^3He can be used as an effective relaxant to enable ^{129}Xe to be spin polarized on a high surface area substrate in a few hours. We are able to identify the contributions of different atomic layers to the magnetization by analyzing the ^{129}Xe NMR spectrum. Furthermore, the addition of ^4He allows us to turn off the relaxation, thereby preserving the polarization. The technique could be applied to nuclei other than ^{129}Xe .

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1. Introduction

Hyperpolarized noble gases (^{129}Xe and ^3He) are proving to be valuable tools for many different applications in magnetic resonance. Conventional magnetic resonance derives the signal from spins in a thermal equilibrium state with a typical degree of polarisation of about 10^{-4} in a magnetic field of 1 T. The low polarization places a limit on the number of spins that can be detected and it is frequently necessary to signal average or move to a high magnetic field, B_0 before a usable signal is obtained. Using pre-polarized or hyperpolarized gases as a contrast agent it is possible to increase dramatically the signal to noise ratio without the need for a particularly high field. Of the two isotopes, hyperpolarized ^{129}Xe has the greater potential and has been applied to clinical magnetic resonance imaging (MRI)^{1,2} and nuclear magnetic resonance (NMR). Through inhalation, hyperpolarized xenon can be used as an aid to the diagnosis of lung diseases³. Xenon gas is also

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soluble in blood, biological tissue and organic lipophilic solvents and has therefore the potential for imaging of the brain, heart and other biological systems^{4,5}. Xenon is a many electron atom with a large chemical shift which can provide valuable information about the atom's local environment. This property has been successfully exploited for surface investigations of many different porous materials by NMR^{4,6-10}. Dipole-dipole interactions between nuclear magnetic moments of adsorbed hyperpolarized xenon and the surface substrate atoms can lead to polarization transfer through the spin polarization induced nuclear Overhauser effect, (SPINOE)^{10,11}.

The effectiveness of these applications is heavily dependent upon the availability of hyperpolarized ¹²⁹Xe and so the task of producing this in sufficiently large quantities, the storage and delivery to the consumer (medical clinics for instance) has become an area of great activity. The current method for the production of hyperpolarized ¹²⁹Xe is optical pumping of alkali metals (rubidium in most cases), followed by polarization transfer (spin exchange) to the noble gas nuclei during collisions. The recent availability of high powered solid state lasers has lead to acceptable polarization levels and production rates^{12,13}.

A cryogenic or brute force method has been proposed as an alternative method for obtaining hyperpolarized gas in quantities of the order of 100-1000 litres per day¹⁴. By holding xenon (or any other NMR active species) at temperatures of the order of millikelvin within a high magnetic field, high degrees of nuclear spin polarization are attainable. Despite the potential advantages presented by the brute force method, several obstacles need to be overcome before it can compete with the optical methods for producing polarized xenon gas. The spin-lattice relaxation time, T_1 , of xenon nuclei at a temperature of 77 K is of the order of 2.5 hours inside a magnetic field of 0.1 T^{15,16}. At 4.2 K, T_1 for natural xenon consisting of two magnetic xenon isotopes ¹²⁹Xe (26.4%) and ¹³¹Xe (21.2%) is already in excess of 60 hours rising to 180 hours for isotopically enriched xenon. It would seem that the time for xenon nuclei to polarize at temperatures required in the brute force technique is far too long for large scale production of hyperpolarized xenon to be viable. What is required is a device that can accelerate this polarization rate to achieve equilibrium polarization in the high B/T conditions within a reasonable time frame. It must also have the characteristic that the mechanism can be turned off to avoid the destruction of the polarization during the transfer of the xenon from the cryostat. In other words, an effective relaxation switch is needed.

Honig *et al*¹⁷ suggested the oxygen molecule as a suitable relaxant. The oscillations of the hyperfine magnetic field, which are produced by the paramagnetic moments of oxygen molecules, lead to effective relaxation of xenon

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nuclei at low temperatures¹⁸. It was thought that the lower melting point of oxygen (90K) when compared to xenon (160K) would allow the removal of the oxygen from the solid xenon before depolarization of the ^{129}Xe . We performed a series of measurements on bulk xenon with different concentrations of oxygen in order to decide whether oxygen could potentially be used as a relaxation switch. However, we find the T_1 has such a strong field and temperature dependence with oxygen impurities ($\sim B^2/T$) that during attempts to remove of the oxygen from the xenon sample, the polarization was rapidly destroyed. Hence the oxygen relaxation switch was not considered to be useful.

In 2003, Biškup *et al*¹⁹ investigated the relaxation of adsorbed xenon using another relaxant, liquid ^3He . It had been shown²⁰ that the high relaxation rate of ^3He nuclei is due to the mobility of the helium atoms. The ^3He couples to surface atoms through fluctuations of weak dipole-dipole interactions between ^3He and ^{129}Xe nuclear magnetic moments. Various studies²¹⁻²³ have made use of this mobility as the driving mechanism for the relaxation of surface nuclei. One advantage of ^3He is that it could easily removed from the sample cell due to the low boiling point and low latent heat of vaporization of the ^3He . In this work, we show that the ^3He is an effective relaxant at all temperatures in very high fields for xenon adsorbed on silica substrates, leading to the generation of highly polarized ^{129}Xe . We show that the ^3He can be removed without much loss of polarization provided we first add ^4He to the ^3He to effectively turn off the relaxation. In addition, the analysis of the ^{129}Xe NMR spectrum has allowed us to probe the relaxation of the xenon film in some detail.

2. Experiment

All the experiments were performed in an Oxford Instruments KelvinoxTLM dilution refrigerator with a top loading probe. The cryostat was supplied with two superconducting solenoids. These solenoids were coaxially arranged with the axis of the probe. The lower solenoid provides fields for the NMR of up to 15.5 T and the upper solenoid generates fields up to 4.5 T. With the probe at its lower position, the sample cell is immersed in a $^3\text{He}/^4\text{He}$ mixture inside the mixing chamber and is situated centrally in the field of the lower solenoid. The refrigerator has a base temperature of 10mK which could, theoretically, in a 15.5 T field produce an equilibrium polarization of 41% for ^{129}Xe . The upper magnet position is used when condensing or removing the xenon or oxygen gas from the sample cell.

A heated capillary was used for transferring the gases from the gas-

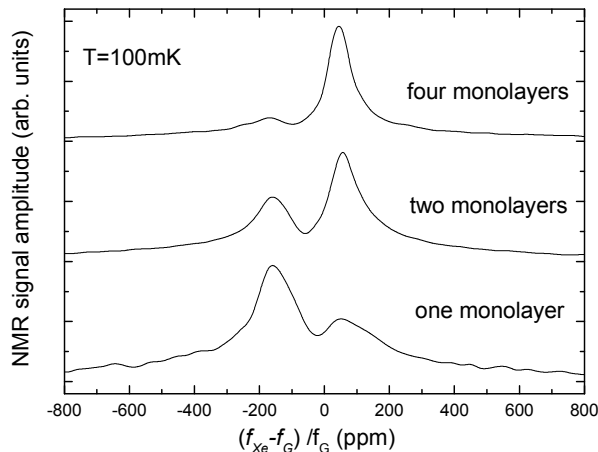


Fig. 1. Normalized ^{129}Xe NMR spectra at 100 mK as a function of xenon thickness, with ^3He relaxant. The signal frequency, f_{Xe} , is measured relative to the generator, $f_G = 173.096$ MHz.

handling system to the sample cell. The study was conducted on 3.6×10^{-3} to 1.8×10^{-2} moles of xenon gas in a temperature range of 15 mK to 1.6 K and in a magnetic field of 14.7 T. The xenon was condensed into the sample cell and onto the adsorbent by slowly reducing the temperature from 200 K to 160 K. The ^3He was condensed after the cell had been cooled below 1 K. The sample cell itself had a capacity of 4 cm^3 and was made from Macor, a low proton ceramic. 1.4 g of Merck Silica gel, 70-230 mesh, with a pore size of 6 nm, area $460 \text{ m}^2 \text{ g}^{-1}$ (determined by nitrogen adsorption measurements) was used as a substrate for the xenon: Around 90% of the surface of the silica gel is in the pores. A single NMR receive/transmit saddle coil surrounded the sample cell. Xenon T_1 measurements were performed by the magnetization recovery method. The initial magnetization was destroyed by several saturation pulses and the magnetization growth was monitored over a period of 24 hours or more by a series of tipping pulses, of 4° or less. Note that we were not able to make measurements of chemical shift because there was no convenient reference sample under the conditions of the experiment.

3. Results and Discussion

Without ^3He in the sample cell T_1 in our experiments was very long,

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about two days at 1.5K. All the data presented were taken with the liquid ^3He relaxant over the substrate. For a coverage of less than a monolayer of xenon, a single spectral line was observed but for higher coverages, it was found that the xenon NMR spectra consisted of two well defined lines (Fig. 1). This is in contrast to previous work¹⁹, where only a single spectral line was ever observed. The distribution of the NMR signal between these two lines depended upon the quantity of xenon on the surface of the silica gel. It was observed that when the thickness of the xenon film was increased, the size of the lower frequency peak, Fig. 1 remained constant while the higher frequency peak grew.

We assume that the constant amplitude component (lower frequency line) in the spectrum originated from the xenon atoms in the upper layer that were in direct contact with the helium and the higher frequency line originated from the atoms in the solid xenon sublayers. The splitting of the lines was 225 ppm and the widths were 80 ppm. The shift of the Larmor frequency of ^{129}Xe between gas and bulk solid is 300 ppm. As expected the NMR frequency of the ^{129}Xe in the upper monolayer, with its free surface, is between the bulk solid and gas values.

This interpretation is consistent with the measurements of xenon relaxation rates for a two monolayer sample (Fig. 2). The left peak was seen to have a much greater rate of growth than the right peak suggesting two distinct environments for the xenon atoms. The magnetization growth curve fitted well to the sum of two exponentials with time constants of 39 and 1600 minutes for the left and right peaks, respectively. The high ratio of relaxation rates, indicates that the spin diffusion process between Xe layers was strongly restricted: The spectral lines do not overlap showing that there was no common frequency for interaction between the two states of the ^{129}Xe .

Consider the sample with a nominal coverage of 1 monolayer of xenon. It can be seen on Fig. 1 that there is a small line at the higher frequency indicating some regions of sample with more than 1 layer. This may be due to some inhomogeneity in the distribution of xenon over the substrate or to inhomogeneities in the surface of the substrate itself. We find that the ^{129}Xe relaxation time, around 40 minutes, and the lineshape were independent of temperature. The increase in signal follows the theoretical temperature dependence Fig. 3. Note however there is a long relaxation component, only visible at the lowest temperature, which we identify as a slow cooling of the system.

If the polarized xenon is to be used as a contrast agent for magnetic resonance studies, we must conserve the high polarization of the sample during extraction from the cryostat. The top loading probe allows us to remove the xenon cell while keeping the xenon frozen. The first stage of this

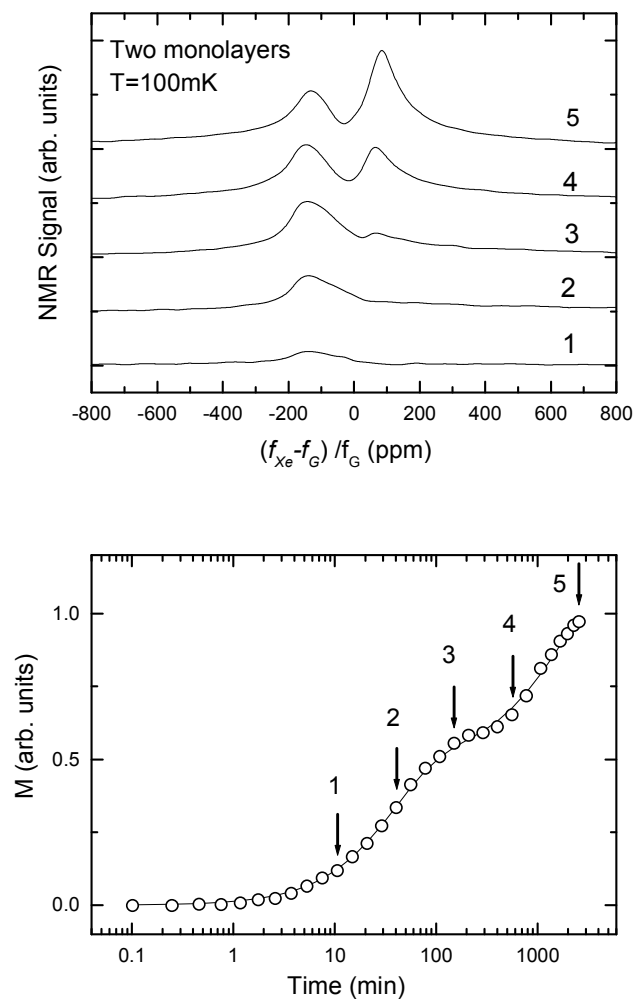


Fig. 2. The ^{129}Xe NMR spectrum and the evolution of the magnetization for a xenon thickness of 2 monolayers on silica gel with the ^3He relaxant present. The temperature is 100mK. The signal frequency f_{Xe} frequency is measured relative to the generator, f_G .

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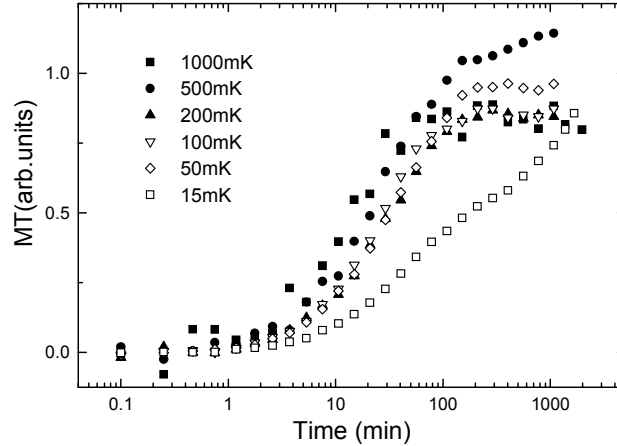


Fig. 3. Growth of the ^{129}Xe magnetization, scaled by the temperature, for 1 monolayer coverage at various refrigerator temperatures with ^3He as relaxant. The long relaxation time at 15 mK is attributed to thermal relaxation.

process is the removal of the ^3He . This evaporates at around 3 K, but the evaporation takes a finite time compared to the ^{129}Xe relaxation time of 40 minutes, leading to a loss of polarization. Therefore the question arises; can we turn off the relaxation due to the ^3He , and can we do so at the lowest temperatures? Biškup *et al*¹⁹ suggested that this could be achieved by the admission of ^4He into the sample. At low temperatures, the ^4He should displace the ^3He from the surface of the xenon (the heavier isotope is more tightly bound) without causing too much warming. In doing so the direct coupling between the ^3He and ^{129}Xe could be broken. Our results verify this idea and have shown that the relaxation rate is greatly inhibited by the presence of ^4He at low temperatures (Fig. 4). After admission of ^4He , the xenon relaxation time was increased by 20 times. An experiment was performed to investigate polarization losses during the removal of the ^3He relaxant. For this purpose, after the ^{129}Xe reached equilibrium polarization, the probe was raised to the position of the upper magnet and into the 4.3 T field. The sample was quickly warmed to approximately 30 K thus allowing the ^3He to be removed. The sample was then lowered back to its original position in the 15 T field over a period of around 20 minutes and the xenon NMR signal was remeasured. It was found that without admission of ^4He 37% of the initial polarization survived, whilst with admission of ^4He prior to ^3He removal 68% of the polarization had been retained.

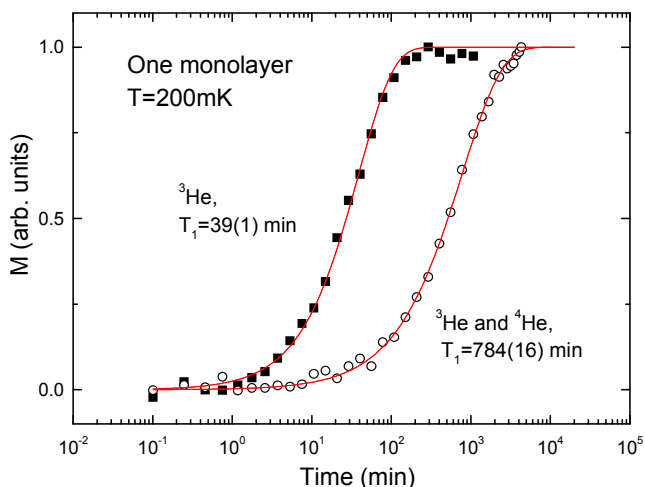


Fig. 4. Xenon magnetisation growth curves for 1 monolayer coverage with pure ³He relaxant (■); with a monolayer of ⁴He in addition to ³He (○).

4. Conclusions

We have demonstrated that the brute force technique could be used to produce highly polarized ¹²⁹Xe provided a high surface area substrate is used and a combination of ³He and ⁴He is employed as a relaxation switch. We have taken advantage of the chemical shift of ¹²⁹Xe to distinguish clearly the NMR signals arising from the uppermost monolayer in a xenon film on silica from lower layers. The sensitivity of the chemical shift of the ¹²⁹Xe to its environment and the high signal enhancement we can achieve could be exploited to study other surfaces. It is clear that a larger sample could be polarized. For example, for the substrate used in these experiments, we could produce 0.2 moles of hyperpolarized xenon from a single monolayer of xenon in our cryostat. Extracting frozen spin-polarized samples from a cryostat has been achieved elsewhere by Wei *et al* for HD²⁴. The cell containing the frozen polarized xenon will be moved to a liquid nitrogen storage container placed in a static magnetic field where the T₁ is 2-3 hours. The system is not restricted to the polarization of xenon: Other species such as ¹³C, ³¹P can be similarly polarized provided there is close contact to the liquid ³He, allowing NMR studies of small samples or thin films at very low temperatures.

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