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Communication

HP-Xe to go: Storage and transportation of hyperpolarized ^{129}Xe 

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ABSTRACT

Recently the spin–lattice relaxation time T_1 of hyperpolarized (HP)- ^{129}Xe was significantly improved by using uncoated and Rb-free storage vessels of GE180 glass. For these cells, a simple procedure was established to obtain reproducible wall relaxation times of about 18 h. Then the limiting relaxation mechanism in pure Xe is due to the coupling between the nuclear spins and the angular momentum of the Xe–Xe van-der-Waals-molecules. This mechanism can be significantly reduced by using different buffer gases of which CO_2 was discovered to be the most efficient so far. From these values, it was estimated that for a 1:1 mixture of HP-Xe with CO_2 a longitudinal relaxation time of about 7 h can be expected, sufficient to transport HP-Xe from a production to a remote application site. This prediction was verified for such a mixture at a total pressure of about 1 bar in a 10 cm glass cell showing a storage time of $T_1 \approx 9$ h (for $T_1^{\text{wall}} = (34 \pm 9)$ h) which was transported inside a magnetic box over a distance of about 200 km by car.

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1. Introduction

Hyperpolarized (HP) xenon has found many applications as a contrast agent in NMR and MRI [1]. The production of the hyperpolarized state is done via spin exchange optical pumping (SEOP [2]), requiring complicated and extensive hardware and supplies. Since the storage time is limited by the longitudinal relaxation, T_1 (half-life time of HP-state = $T_1 \ln 2$), the HP-Xe must be transported from the production to the application site within that time-frame. HP-Xe can be transported either in the solid or in the gas phase. Transportation as Xe-ice allows to handle large quantities with a T_1 of about 2.5 h at 77 K which can be further increased by going to even lower temperatures [3]. However, an efficient transport in solid phase requires magnetic fields exceeding 0.1 T and cryogenic temperatures; conditions which can turn carriage over longer distances into quite a challenge.

On the other hand, the transport of gaseous HP-Xe can be performed at room temperature and less demanding field strengths ($B < 10$ mT) which can be provided either by permanent magnets

[4] or coils powered from a battery. The maximum gas pressure for transport is limited by the production rate of the Xe-polarizer, the stability of the containing vessel (including valves) and safety regulations; for glass containers of radius > 3 cm typically less than 3 bars¹ [5].

Furthermore, it is crucial to maintain the partial pressure of O_2 below 10^{-6} bar in such transport vessels to avoid the relaxation due to the interaction with this paramagnetic gas. Under these conditions, the spin–lattice relaxation of HP-Xe is limited by two interactions: (a) The extrinsic interaction with the container walls which depends on its surface-to-volume ratio and a constant value related to the inner surface of the container, the relaxivity. In recent work [6], values of $T_1^{\text{wall}} \approx 16 - 18$ h were achieved routinely and reproducibly in containers made from the special glass GE180. (b) The intrinsic formation of Xe–Xe van-der-Waals-molecules which limits T_1 of pure Xe to $T_1^{\text{Xe-Xe}} = (4.6 \pm 0.1)$ h. This value can be increased by adding buffer gases which destroy the

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¹ If partial pressures of xenon exceed 2 bars an additional relaxation mechanism due to transient Xe–Xe-dimers has to be considered.

Xe–Xe van-der-Waals-molecule with an efficiency given by the destruction rate coefficient r according to

$$T_1^{vdW} = T_1^{Xe-Xe}(1 + rf) \quad (1)$$

where $f = p_B/p_{Xe}$ is the ratio of partial pressures of the buffer gas (p_B) and xenon (p_{Xe}), respectively. The highest destruction rate coefficient reported so far [6] was determined for CO_2 with $r_{CO_2} = (1.40 \pm 0.22)$. Hence for 1:1 mixture of HP-Xe and CO_2 , a $T_1^{vdW} \approx 11$ h was determined. Of course, such a prolongation of T_1^{vdW} can only be exploited if the wall relaxation time is at least in the same time-frame or possibly longer.

The aim of this communication is to report on successful storage and delivery of gaseous HP-Xe in uncoated and Rb-free spherical cells of GE180 of 10 cm in diameter. The storage time of HP-Xe was doubled by adding CO_2 as a buffer gas using a proportion of 1:1 amounting to a total pressure of 0.25–1 bar. This T_1 value was observed in the lab [6] and inside specially designed transport boxes equipped with permanent magnets which provide a homogeneous field of about 1 mT [4]. A sample of this gas mixture was then transported via car over a distance of 220 km.

2. Experimental/results

The gaseous samples were stored in an uncoated and Rb-free spherical cell of 10 cm in diameter which was made from a aluminosilicate glass with low permeability (GE180, General Electric) [7]. The spherical GE180-bulb is attached to a standard glass stopcock (NS 14.5, HWS Labortechnik, Mainz, Germany) made from Pyrex and connected through a KF16 glass flange. This cell was cleaned and prepared as described in [6] and filled with xenon (isotopically enriched 85% ^{129}Xe and ca. 0.1% ^{131}Xe , Linde Electronics and Specialty Gases) which was hyperpolarized via SEOP in a standard high-pressure Xe polarizer. After that buffer gases were added as described in [6] up to a total pressure of about 1 bar.

This HP-sample was transported from the magnetic field of the Xe-polarizer to the holding field of a homemade low field NMR system operated at a frequency of 27 kHz (Larmor-frequency of ^{129}Xe) and a bandwidth of 5 kHz [6]. The NMR-signals were acquired in this system using an excitation pulse of 1 ms corresponding to a flip angle $\alpha = (6.0 \pm 0.1)^\circ$.

First the T_1 relaxation time of pure HP-Xe was determined in order to extract the wall relaxation time of a freshly prepared cell. For this purpose (120 ± 12) mbar of pure HP-Xe was excited 30 times every 20 min with the flip angle α . The obtained data (cf. Fig. 1) were analyzed as described in [6] giving a $T_1 = (4.0 \pm 0.1)$ h after flip angle correction. As explained in the introduction, the relaxation under these conditions can be reduced to two interactions

$$\frac{1}{T_1} \approx \frac{1}{T_1^{Xe-Xe}} + \frac{1}{T_1^{wall}} \quad (2)$$

This gives a wall relaxation time of $T_1^{wall} = (34 \pm 9)$ h for this particular cell when using $T_1^{Xe-Xe} = (4.6 \pm 0.1)$ h [6].

To examine the extension of the storage time by adding CO_2 under realistic transport conditions, an in-door test run was performed. Therefore, a second sample of (122 ± 12) mbar of HP-Xe was mixed with (178 ± 13) mbar of CO_2 according to the procedure described in [6] obtaining a fraction $f = (1.46 \pm 0.18)$. This HP-sample was then placed in the magnetic box shown in Fig. 2a. When carrying the cell from one magnetic field to another, it is crucial to avoid magnetic field flips which could destroy the HP-state. For this purpose, a small 3D-compass (Magnaprobe, Cochranes of Oxford LTD, UK) was used to monitor the direction of magnetic fields along the anticipated transportation path.

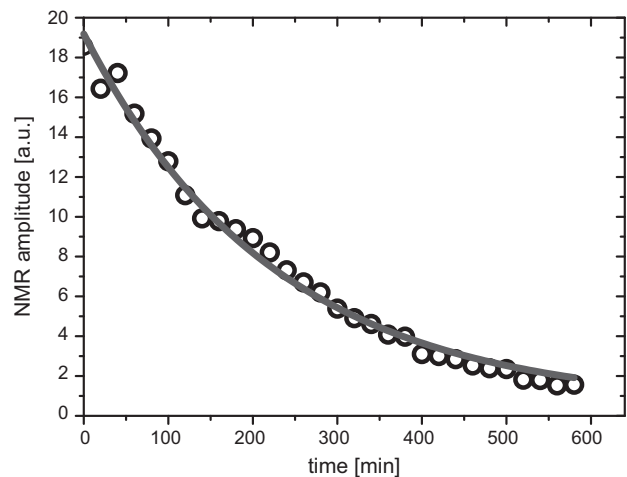


Fig. 1. Measurement of the longitudinal relaxation of 120 mbar pure HP- ^{129}Xe (85% isotopically enriched) at 2.1 mT in a 10 cm diameter cell of GE180 glass. The error bars smaller or about the graphical size of the data points. The value obtained is $T_1 = (4.0 \pm 0.1)$ h which is already corrected for the repetitive excitation with a flip angle of 6° [6]. See text for details.

The low field NMR system was used again to acquire signals of this sample by the same procedure as described above. Measurements were done before the sample was stored in the magnetic box and after 3 h, 5 h and 35 h of storage time. For each measurement, the sample was taken out of the storage box for about 2 min before being returned. The results of this experiment are shown in Fig. 2b leading to a storage time of $T_1 = (9 \pm 1)$ h. This value agrees with the theoretical prediction of $T_1 = (9.9 \pm 1.2)$ h for the Xe in the gas mixture which was obtained from the T_1 -value of pure Xe as determined above (i.e. $T_1 = (4.0 \pm 0.1)$ h) together with T_1^{Xe-Xe} and r from [6]. Hence the movements of the sample to and from NMR-spectrometer and magnetic box do not reduce T_1 measurably.

The magnetic box shown in Fig. 2a used permanent magnets to generate a magnetic field of 0.8 mT with a homogeneity $\nabla B/B = 10^{-3}$ resulting in negligible relaxation times due to magnetic field gradients over 200 h. This box was originally designed for the transportation of HP- 3He [4] and is now commercially available (Sekels GmbH, Ober-Mörlen, Germany).

Afterwards another sample of HP-Xe was stored in the same cell as before and admixed with same amount of CO_2 to a total pressure of ca. 900 mbar. According to the values in [6], the longitudinal relaxation time of this sample should be $T_1 = (8.3 \pm 1.0)$ h.

This 1:1 mixture was then placed in the magnetic box and driven by car from Mainz to the Research Center in Jülich (distance ~ 220 km, ~ 3 h).

As soon as the box arrived in the lab in Jülich, the cell was placed into a coil system which provided a homogeneous magnetic field suitable to conserve the polarization. Then a small amount (30 mbar) of HP-Xe was transferred into a measuring cell located inside a homogeneous magnetic holding field within a magnetically shielded room. Once filled, the sample was excited by a 90° pulse [8] and the free spin precession signal was measured using a liquid He cooled SQUID gradiometer. The Fourier transformation of this signal is represented by a dashed line in Fig. 3. After 8.5 h the experiment was repeated taking a new sample of 30 mbar of the original transport cell and measured under same conditions, obtaining a reduced amplitude (solid line in Fig. 3). The time constant obtained by the comparison of these two amplitudes corresponds to a T_1 relaxation time of about 9 h (no error was estimated from these two measurements), which is in perfect agreement with the in-door result and the predicted value.

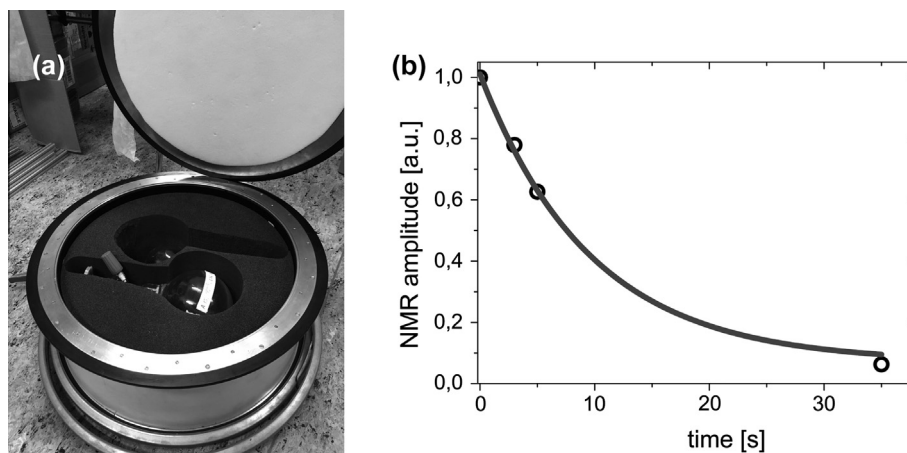


Fig. 2. (a) Magnetic box containing two glass cells with HP-Xe. (b) NMR amplitude vs. storage time, giving a T_1 of ca. 9 h. Each box can contain 2 spherical cells of about 13 cm in diameter and a volume of ca. 1.15 l.

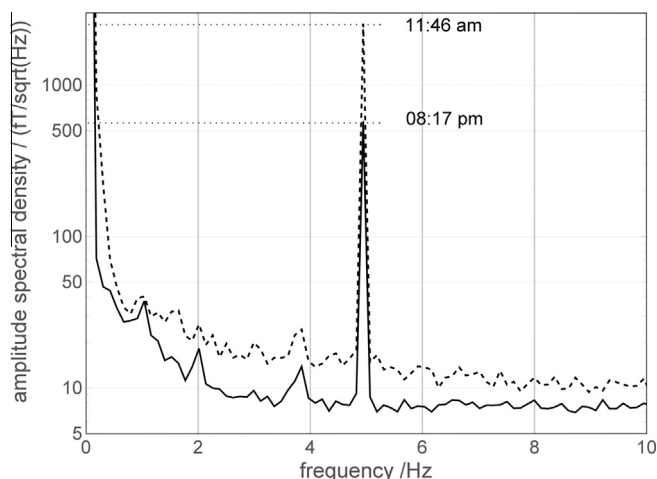


Fig. 3. Amplitude spectral density obtained with a SQUID gradiometer in the shielded room of the Jülich Research Center. The dashed and solid lines represent the measurements performed at 11:46 am and 08:17 pm respectively.

3. Conclusions

The storage time of gaseous hyperpolarized xenon was extended to about 9 h, which allows convenient transportation from the production to an application site. This significant improvement was made possible for two reasons: (1) usage of uncoated-Rb free GE180 cells with $T_1^{\text{wall}} > 16$ h. Additionally these long wall relaxation times can be reliably reproduced over years by the simple rinsing and drying treatment described in [6]. (2) Admixing CO_2 as a buffer gas, which was shown [6] to have the highest efficiency for destroying the vdW-molecules reported so far.

The resulting, prolonged T_1 of 9 h was confirmed by three independent experiments: (a) by determination of T_1^{wall} and using literature values [6] for the van-der-Waals relaxation in a buffer gas mixture in Eq. (1), (b) in-door test run using a low field NMR spectrometer and (c) measurements of the polarization decay with a SQUID gradiometer at the application site (220 km away from the production site).

Such long storage times can be useful: (a) To transport a larger amount of HP-Xe from a production site to a remote application site. (b) To prepare a larger batch of HP-Xe which can be used over

a day without significant polarization losses. These relaxed time constraints also add convenience in planning and performing the experiments.

The used transport boxes provide a sufficiently strong and homogeneous magnetic field even then when they placed in relatively strong magnetic field gradients (e.g. stray field of a superconducting magnet). This ability to shield external magnetic fields and the replacement of current driven coils adds another degree of flexibility to the experiments.

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