Xenon Hyperpolarized by the Dissolution-DNP Method

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Introduction

Xenon is efficiently hyperpolarized by optical pumping. In recent years this method has made significant progress towards higher polarization and volume. In this work we report an alternative method of polarizing Xenon: dissolution-DNP (1). We published initial studies in ref (2), and recently a similar study appeared in ref (3).

Methods and results

Though both nitroxides and trityls dissolve readily in liquid Xenon none of the radicals will prevent Xenon from crystallizing when frozen. Therefore other additives are required to prevent the crystallization and exclusion of the radical.

The following samples are all prepared by the same procedure: Radical and co-solvent were inserted into a round bottom flask. The flask was evacuated and flushed with Helium gas several times to remove oxygen. The flask was then immersed in a liquid Nitrogen bath and Xenon gas was allowed to condense into the flask. After sealing the flask the liquid Nitrogen bath was replaced by an ethanol/CO_2 bath. The content was agitated by magnetic stirring. The ethanol/CO_2 bath was replaced by an ethanol bath, cooled using liquid Nitrogen down to 163 K. At this temperature both co-solvent and Xenon are in the liquid phase and the content of the flask is a viscous liquid. Additional magnetic stirring was performed followed by rapid cooling in a liquid Nitrogen bath. The flask was opened and liquid Nitrogen was added. The solid content of the flask was pulverized with a pre-cooled spatula and transferred to a pre-cooled sample holder. The sample was then rapidly inserted into a cryostat and DNP polarization was performed using a magnetic field of 3.354 T, an irradiation frequency of 93.93 GHz (200 mW) and a temperature of 1.08 K.

a) 1.5 mL propanol, 26 mg Finland radical (acid form), 500 mL (STP) natural abundance Xenon. The obtained DNP enhancement factor was 82 (P=7.2%). The DNP build-up time constant was 1.2h and the T_1 was estimated to 4.2h.
b) The volume fraction of Xenon was halved compared to (a). 3.85 mL propanol, 52 mg Finland radical, 500 mL (STP) natural abundance Xenon. The obtained DNP enhancement factor was 263 (P=23%). The time constant for polarization build-up was 2.2 hours, and the T_1 was estimated to be 4.6 hours.
c) The volume fraction of liquid Xenon in this sample was increased by 28 % compared to (a). 1.0 mL propanol, 20.5 mg Finland radical, 500 mL (STP) natural abundance Xenon. The obtained DNP enhancement factor was 26 (P=2.3%). The DNP build-up time constant was 1.2h and the T_1 was 2.5h.
d) This experiment is identical to (b) except that the natural abundance Xenon was replaced by Xenon gas enriched in ^{129}Xe. 3.85 mL Propanol, 52.7 mg Finland radical, 500 mL (STP) Xenon (82.3 % ^{129}Xe). The obtained DNP enhancement factor was 197 (P=17%). The DNP build-up time constant was 1.7h and the T_1 was 6.2h.
e) 3.85 mL ethanol, 52.2 mg Finland radical, 500 mL (STP) natural abundance Xenon. The obtained DNP enhancement factor was 172 (P=15%). The DNP build-up time constant was 4.1h and the T_1 was 4.4h.
f) 3.85 mL 2-butanol, 51.4 mg Finland radical, 500 mL (STP) natural abundance Xenon. The obtained DNP enhancement factor was 23 (P=2.0%). The DNP build-up time constant was 1.5h and the T_1 was 3.9h.
g) A sample was polarized according to (b). The sample was thawed in-situ using hot water (≈ 95 ºC). The Xenon gas was collected in a bag. The Xenon gas was then transferred to a 10 mm NMR tube pre-filled with Argon, and a spectrum acquired at 9.4 T. The obtained enhancement factor in gas phase was 4752 (P=4.3%) compared to the thermal equilibrium signal at 9.4T and room temperature.

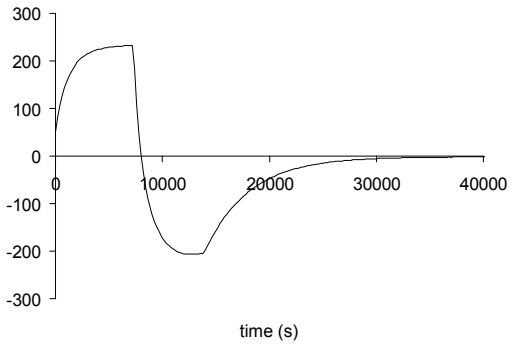

Fig 1: Solid state signal enhancement of ^{129}Xe (experiment b).

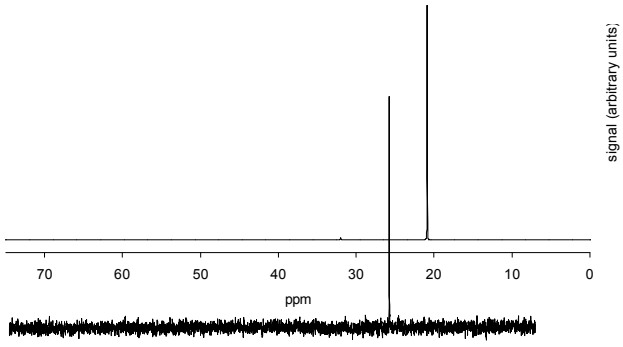

Fig 2: Gas phase hyperpolarized spectrum and corresponding thermal spectrum of ^{129}Xe (experiment g)

Conclusion

The glass-forming property of the Xenon/co-solvent mixture is extremely important to achieve an efficient DNP effect. Single-chained alcohols are excellent glass-formers. Another important requirement is that there should be a temperature/pressure region where both the co-solvent and Xenon are simultaneously in the liquid state. Both Propanol and Ethanol meet this requirement, and they were also the most successful in these experiments. It was further observed that the obtained final ^{129}Xe polarization decreased when the concentration of Xenon in the sample was increased. Similar observations have been made for e.g. samples of varying ^{13}C enrichment. One of the objectives of this study was also to investigate whether the presence of the quadrupolar nucleus ^{131}Xe was harmful for the DNP process. The experimental results show that the presence of ^{131}Xe does not impact DNP negatively; on the contrary, the polarization was larger using natural abundance Xenon. The maximum solid state ^{129}Xe polarization obtained in our study was 23%. The thawing experiments resulted in a large scatter of the acchieved polarization. However, the T_1 of gaseous ^{129}Xe is known to depend on the magnitude of the magnetic field gradient as well as the magnetic field strength, which were not well controlled in the current setup.

We have demonstrated that the dissolution-DNP method is capeable of producing Xenon gas with high polarization in the gas phase. The method opens up for large volume production of hyperpolarized Xenon gas with high polarization.

References: 1. Ardenkjaer-Larsen et al, PNAS 2003, 2. Ardenkjaer-Larsen et al WO 2004/037296 (2002), 3. Comment et al, Phys Rev 2010