



NMR of supercritical laser-polarized xenon

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Abstract

The feasibility of producing supercritical laser-polarized xenon for nuclear magnetic resonance (NMR) investigations was studied. Using a high-pressure capillary tube, a supercritical xenon sample (52°C, 65 atm) was produced with a ¹²⁹Xe polarization approximately 140 times the equilibrium value. The polarization was observed to last for hundreds of seconds, in agreement with previous studies. These preliminary results suggest that supercritical laser-polarized xenon may be used as a polarizing solvent for numerous NMR applications. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Increasing the nuclear spin polarization of molecules in solution could be useful for a variety of liquid-state nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) experiments, especially in circumstances where the observed nucleus is in low natural abundance or the species in question is short-lived. One means of achieving enhanced NMR signals in solution is through polarization transfer from dissolved laser-polarized ¹²⁹Xe to other solute species via the spin polarization-induced nuclear Overhauser effect or SPINOE [1]. Recent work has demonstrated the utility of the SPINOE for obtaining selective enhancements of NMR signals when xenon binds temporarily to molecules in solution [2,3], or is adsorbed to surfaces of materials [4–9]. It has been suggested [2,10] that much larger

bulk signal enhancements could be generated by using laser-polarized xenon as a polarizing solvent, due to the dramatic increase of the xenon density in such samples. Indeed, liquid laser-polarized xenon was produced [10–12] and used as a polarizing solvent at –73°C to achieve large signal enhancements for certain solutes [13].

Although liquid xenon is a useful solvent in some circumstances [14,15], the solubility characteristics improve dramatically in the supercritical phase [16,17], and the higher and broader temperature range is more convenient for chemical and biophysical investigations. The single phase of supercritical samples obviates the need for stirring, and the low viscosity leads to narrow solute linewidths, especially for those containing quadrupolar nuclei (Refs. [19,20]; for a general review of high-pressure gas NMR see Ref. [18]). Furthermore, the density of supercritical xenon, and hence its physical properties (e.g. solubility, dielectric constant, etc.), are strongly pressure dependent [21]; the physical properties of

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the solvent can therefore be manipulated to provide specific solvent environments [17]. For example, by fine-tuning the density and composition of supercritical solvents, the dielectric constant was manipulated as to influence the rate and selectivity of chemical reactions [15]. The enhanced thermal stability of biomolecules in supercritical solvents may also prove advantageous for certain experiments [22,23]. By using supercritical laser-polarized xenon as a solvent for catalytic and kinetic studies via NMR, we anticipate high sensitivity may be achieved under favorable solvent conditions.

In this Letter, we report the first results demonstrating the feasibility of producing laser-polarized ^{129}Xe in the supercritical state. The NMR spectrum of the supercritical laser-polarized xenon produced in our experiment shows a polarization approximately 140 times that of the equilibrium value. The polarization was observed to last for hundreds of seconds, which should be long enough to permit polarization transfer to solute species.

2. Experimental

The technique and apparatus used in our laboratory for optically pumping xenon have been described elsewhere [24]. The apparatus typically produces ^{129}Xe polarization on the order of 3–5%. Enriched ^{129}Xe (80 atom%) was purchased from Isotec. Although the small amount of xenon used in these experiments (4.4×10^{-4} mol) was laser-polarized using a single batch method, substantially larger amounts of laser-polarized xenon can be produced using a flow apparatus [25].

The high-pressure tube used in the supercritical xenon experiments is shown in Fig. 1. To guard against explosions, frequent pressure checks and visual inspections of the tube were performed; appropriate safety measures should be observed during all high-pressure operations. Fig. 2 shows the phase of the ^{129}Xe during different points in the production of supercritical laser-polarized xenon. Following optical pumping at $\sim 60^\circ\text{C}$ (Fig. 2a), the laser-polarized ^{129}Xe gas from the optical pumping cell was frozen with liquid nitrogen into the U-shaped sidearm (Fig. 2b). The sidearm was placed in an external magnetic field provided by a small permanent magnet (1 T) in

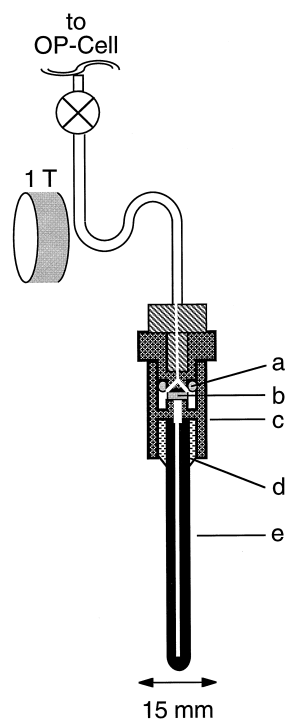


Fig. 1. Schematic of a high-pressure Pyrex[™] capillary NMR tube with a BeCu-alloy valve [26,27]. A Viton O-ring (a) allows the tube to remain sealed during xenon transfer. A Vespel[™] plate (b) at the top of the capillary tube forms a high-pressure seal which prevents any appreciable loss of xenon over many weeks. The valve system was made from BeCu-alloy 172 (c), which has a well-defined composition that minimizes magnetic field distortions permitting high-resolution NMR experiments. The BeCu valve is glued with Areenco 568 epoxy (d) to the Pyrex[™] capillary tube (e) (inner diameter, 0.8 mm; outer diameter, 6.5 mm; length, 15 cm). The capillary tube is coated with SurfaSil[™] (Pierce Chemical) to protect the xenon from paramagnetic centers embedded in the Pyrex[™] glass. The system is then connected to the pumping cell via a thick-wall glass tube with a U-shaped sidearm. As a precaution, the Pyrex[™] capillary tube was subject to frequent pressure checks of up to 140 atm before experimental use. All NMR experiments were performed on a 9.4 T superconducting magnet from Bruker Instruments with a Chemagnetics CMX Infinity spectrometer using a Bruker 10 mm 2-channel probe.

order to maintain the polarization of the solid xenon. Next, the valve separating the sidearm from the optical pumping cell was closed and the solid xenon was sublimed (Fig. 2c) and then condensed (and eventually frozen) by a liquid-nitrogen bath into the high-pressure capillary tube which was also residing next to a 1 T permanent magnet (Fig. 2d). This two-step transfer procedure was used to ensure that

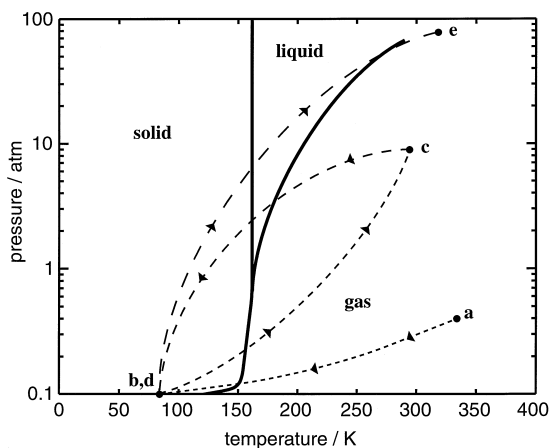


Fig. 2. Schematic of the phase diagram for xenon [28] which shows the path through which supercritical laser-polarized xenon was produced. The dashed lines between the points are estimates of the paths between phases and are meant only to guide the eye. The xenon is first laser-polarized at low-pressure (~ 0.4 atm) and high temperature ($\sim 60^\circ\text{C}$) for 30 min (a) and then frozen into a sidearm (b). The sidearm is rapidly warmed producing xenon gas (c) which is then condensed and eventually frozen into the capillary tube (d). Finally, the tube is warmed to 52°C , reaching the supercritical state (e).

the xenon condensing in the capillary tube would first pass through the liquid phase, thus preventing solid xenon blockages in the capillary tube during freezing. The transition to the supercritical state (Fig. 2e) was visually confirmed by the disappearance of first the solid and then liquid xenon phases upon heating the tube to $\sim 60^\circ\text{C}$ with hot water in the fringe field of the superconducting NMR magnet before lowering the tube into the magnet.

3. Results and discussion

Fig. 3 shows a ^{129}Xe spectrum of supercritical laser-polarized xenon (Fig. 3a), below the corresponding equilibrium spectrum taken several hours later (Fig. 3b). The magnetization produced is inverted in phase with respect to the equilibrium signal shown owing to the direction of the magnetic field in which the xenon was laser-polarized. The chemical shift of the equilibrium spectrum (44.5 ppm) taken at room temperature ($\sim 22^\circ\text{C}$) corresponds to a xenon density of approximately 81.5 amagat (amagat = the density divided by the density at STP) [29] (Fig. 4a).

The difference in chemical shift between the laser-polarized and equilibrium spectra corresponds to a temperature change of $\sim 30^\circ\text{C}$. Therefore, the chemical shift of 41.8 ppm and temperature of $\sim 52^\circ\text{C}$ indicates that the pressure in the capillary tube immediately after warming the laser-polarized xenon was ~ 65 atm (Fig. 4b). This temperature and pressure puts the xenon well beyond the critical point (16.6°C , 57.6 atm) [28]. The broader linewidth of the spectrum in Fig. 3a may originate from local density fluctuations in the thermally non-equilibrated sample.

The laser-polarized ^{129}Xe signal was approximately 140 times that of the equilibrium signal. This enhancement factor represents a loss of almost two orders of magnitude compared to the ^{129}Xe polarization typically prepared by the optical pumping apparatus. It is likely that paramagnetic impurities in the metal valves and tubing were responsible for this loss in polarization, because the T_1 relaxation times

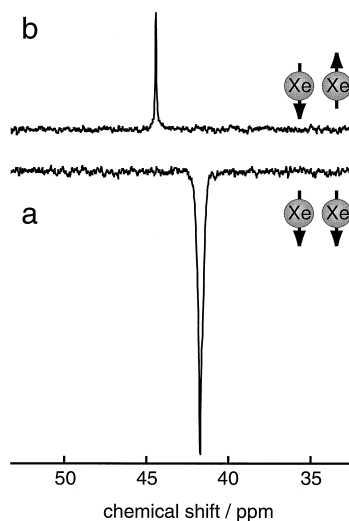


Fig. 3. (a) Spectrum of supercritical laser-polarized xenon at 52°C . The spectrum was acquired with one pulse (tipping angle $\approx 3^\circ$). The chemical shift (41.8 ppm) was referenced to that of xenon at zero pressure, indicating a pressure of ~ 65 atm [29]. (b) Spectrum of ^{129}Xe at 22°C after it had been allowed to reach an equilibrium polarization over several hours. The spectrum was acquired with one pulse (tipping angle $\approx 90^\circ$). The ^{129}Xe signal in (a) is inverted in phase with respect to that shown in (b) due to the direction of the magnetic field in which the xenon was laser-polarized. The 44.5 ppm ^{129}Xe chemical shift in (b) indicates a pressure of ~ 54 atm, slightly below the critical pressure (57.6 atm).

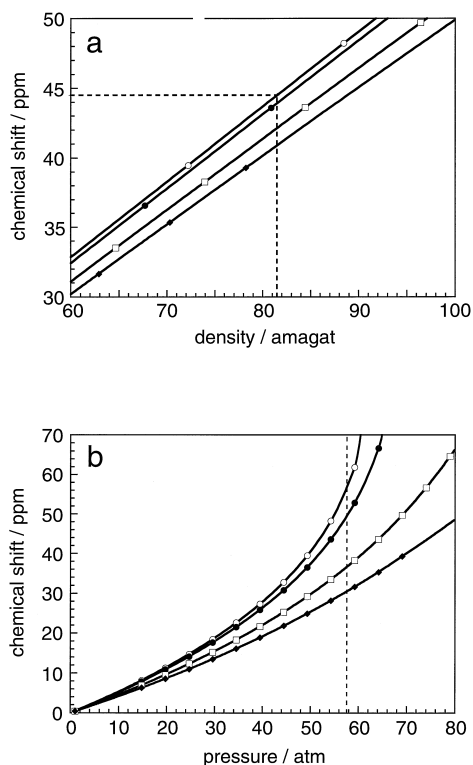


Fig. 4. ^{129}Xe chemical shift of gaseous xenon as a function of density (A) and pressure (B) at 22°C (○), 27°C (●), 47°C (□), and 67°C (◆). The curves were calculated from the temperature and density dependence of the ^{129}Xe chemical shift described in Ref. [29]; the xenon pressure was determined from the specific volume, i.e. the inverse density of the xenon which is tabulated as a function of pressure and temperature [30]. The dashed lines in (a) indicate the conditions under which the spectrum in Fig. 3b was obtained, while the dashed line in (b) shows the critical pressure of xenon.

of xenon in the solid, liquid, and gas phases are extremely long, and no significant loss of polarization is suffered during transitions between phases [10,31–33]. Furthermore, once the supercritical state was achieved, the ^{129}Xe polarization was observed to last for hundreds of seconds.

4. Conclusion

These preliminary results demonstrate the feasibility of generating supercritical laser-polarized ^{129}Xe for high-resolution NMR studies. Future optimization of the experimental set-up should yield super-

critical xenon samples with polarization enhancements in the order of 10^4 and higher, with T_1 s as long as 10^3 s [31]. Supercritical laser-polarized xenon has the potential to integrate numerous classes of chemistry with the high selectivity of NMR without sacrificing sensitivity. The solubility characteristics of supercritical xenon are favorable for many types of compounds, and can be further improved with the addition of various modifiers [34,35]. Furthermore, since xenon is completely transparent to UV, visible, and mid-IR radiation, it is an attractive solvent for in situ spectroscopy, e.g. for organometallic chemistry and photochemistry [34]. The ability to produce supercritical laser-polarized xenon, coupled with a long T_1 and potentially high density (≥ 2 g/ml) would make supercritical laser-polarized xenon ideal for increasing the polarization of solute molecules, while the tunable physical characteristics of such a supercritical solvent should permit a wide range of in situ studies via NMR.

5. Note added in proof

Following the acceptance of the present Letter, we have implemented an alternative set-up with a sapphire tube that has permitted us to routinely produce supercritical laser-polarized xenon samples with polarization enhancements of ~ 1000 at densities in excess of 140 amagat. This system is currently being used for cross-polarization by SPINOE to dissolved molecules.

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