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Quadrupolar relaxation of hyperpolarized krypton-83 as a probe for surfaces

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Abstract

This work reports the first systematic study of relaxation experienced by the hyperpolarized (hp) noble gas isotope ^{83}Kr ($I = 9/2$) in contact with surfaces. The spin-lattice relaxation of ^{83}Kr is found to depend strongly on the chemical composition of the surfaces in the vicinity of the gas. This effect is caused by quadrupolar interactions during brief periods of surface adsorption that are the dominating source of longitudinal spin relaxation in the ^{83}Kr atoms. Simple model systems of closest packed glass beads with uniform but variable bead sizes are used for the relaxation measurements. The observed relaxation rates depend strongly on the chemical treatment of the glass surfaces and on the surface to volume ratio. Hp ^{83}Kr NMR relaxation measurements of porous polymers with pore sizes of 70–250 μm demonstrate the potential use of this new technique for material sciences applications.

Keywords: Optical pumping; Laser polarized; Hyperpolarized; Xenon; Krypton; ^{83}Kr; Kr-83; NMR; Polymer; Porous

1. Introduction

The only stable NMR active isotope of the noble gas krypton, ^{83}Kr, has a natural abundance of 11.5% and a NMR resonance frequency of 15.4 MHz at 9.4 T magnetic field strength. Because of its spin $I = 9/2$, the nucleus of ^{83}Kr possesses an electric quadrupole moment ($Q = 0.28 \times 10^{-28}$ m^2). An anisotropic environment will induce an electric field gradient in the electronic cloud of the noble gas atom, and quadrupolar coherence can cause quadrupolar splitting if the anisotropy has a macroscopic net alignment with respect to the magnetic field. This has been observed previously by conventional NMR with krypton dissolved in nematic phase liquid crystals [1–3] and by optically detected magnetic resonance in quadrupole nutation experiments of gaseous krypton within non-spherical macroscopic glass containers [4,5]. In the absence of unpaired electrons, the quadrupole moment is the dominating factor for relaxation of the ^{83}Kr nuclear spin in gas, liquid, and solid phases [6–8]. The ^{83}Kr NMR relaxation in various liquid solutions has been studied in the past [3,9–13], and the chemical shift in gas and dissolved phases has been investigated [3,9,14,15]. Krypton has also been used to explore nanoporous materials indirectly through ^{129}Xe NMR chemical shift measurements in xenon–krypton gas mixtures within zeolites [16,17]. Recently, direct ^{83}Kr NMR observations of this noble gas inside a number of zeolites have been reported [18]. The ^{83}Kr lineshape was found to strongly depend on internal cage structure and the charge of the cations inside the nanoporous materials. The field dependence of the lineshape observed in some Ca^{2+} exchanged zeolites has been attributed to long-range disorder. The ^{83}Kr chemical shift has been studied as a function of krypton loading in these materials, but the contributions from the second-order quadrupolar interactions to the observed shift remain unexplored thus far. Despite the low sensitivity of natural abundance ^{83}Kr (i.e. about 3.8% of the sensitivity obtained from thermally spin polarized ^{129}Xe), meaningful ^{83}Kr NMR measurements in zeolites can typically be accomplished within a few hours at medium field strength (i.e. 9.4 T) with thermally polarized krypton. This is possible because of the relatively fast longitudinal relaxation of ^{83}Kr that ranges from milliseconds to tens of milliseconds in these materials.

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The usage of thermally polarized ^{83}Kr as a probe for materials with small surface to volume ratios is hampered in part by the lower krypton loading compared to those found in zeolites. Even more problematic for ^{83}Kr NMR are the increased longitudinal relaxation times in large pore materials with typical values ranging from seconds to many tens of seconds. However, experiments with small surface areas have become feasible because of recent developments in optical pumping that lead to the production of hyperpolarized (hp) ^{83}Kr for NMR and MRI applications [19]. The theoretical longitudinal relaxation time of ^{83}Kr in the pure gas phase (i.e. in the absence of a container wall) at 300 K, 100 kPa and 2.1 T can be estimated as $T_1 = 470$ s [8]. However, longitudinal relaxation times of 90–150 s have been measured in 10–11.5 mm diameter and 4–5 cm long glass cylinders at 289 K, 100–200 kPa, and 9.4 T (with the relaxation rates also depending on the treatment of the glass surface). The long relaxation time of ^{83}Kr in the gas phase allows for the production of hp ^{83}Kr by spin exchange optical pumping with rubidium vapor [20] and for the subsequent separation of the alkali metal from the hp ^{83}Kr gas [19]. Signal enhancements of more than three orders of magnitude compared to thermally polarized ^{83}Kr NMR signals at ambient temperature and 9.4 T have been achieved. The apparatus and procedure for the production of hp ^{83}Kr are briefly described in Section 2. Details of the proof of principle optical pumping work including the first applications of hp ^{83}Kr MRI are discussed elsewhere [19].

2. Materials and methods

2.1. Krypton optical pumping

A number of researchers have explored alkali metal vapor optical pumping of quadrupolar noble gas isotopes, including ^{83}Kr, in the past [4,5,20–27]. The setup described here has been used for the first successful separation of a hp noble gas with a quadrupolar nucleus from the rubidium vapor [19]. The separation process is similar to the ones previously used for production of non-quadrupolar hp noble gasses in batch or continuous flow modes [28–34]. The separation of the hp gas from the rubidium vapor is crucial for NMR and MRI applications because of the reactivity of alkali metals. The experimental setup is similar to the one reported in literature for the production of hp ^{129}Xe ($I = 1/2$) [31,33,34]. The gas mixture used for all experiments reported in this publication consists of a high concentration of natural abundance krypton (typically 95%) and about 5% of molecular nitrogen added for radiation quenching purposes [35]. The gas pressure in the pumping cell ranged from 110 to 220 kPa. Pumping with high noble gas density has been thoroughly explored for ^{129}Xe [33,35–38] and is found to be vital for obtaining the highest signal intensities with hp ^{83}Kr. A COHERENT 60 W continuous wave diode array solid-state laser system is applied to the stopped flow type pumping process and leads to a signal enhancement of about 1200 times greater than the thermal signal at 9.4 T and 300 K [19]. Research grade natural abundance krypton (99.995%; Airgas, Radnor, PA) is used for the pumping in a cylindrical Pyrex cell (length = 125 mm, I.D. = 24 mm) that contains 2.5–5.0 g of rubidium (99.6%; Sigma-Aldrich, Milwaukee, WI & 99.75%; Alfa Aesar, Ward Hill, MA). The temperature of the cell is maintained at approximately 433 K, a pumping cell temperature that is about 40 K higher than the temperature typically used for hp ^{129}Xe. In the stopped flow experiments the sample is evacuated to 0.1 kPa, and the krypton–nitrogen gas mixture is kept under laser radiation for 10 min. Subsequently, the optically pumped krypton is transferred using pressure equalization into the sample cell where a krypton gas pressure range of 100–200 kPa is maintained. The rubidium vapor is separated from the krypton by an air-cooled filter located inside the transfer line between the pumping cell and the detection cell.

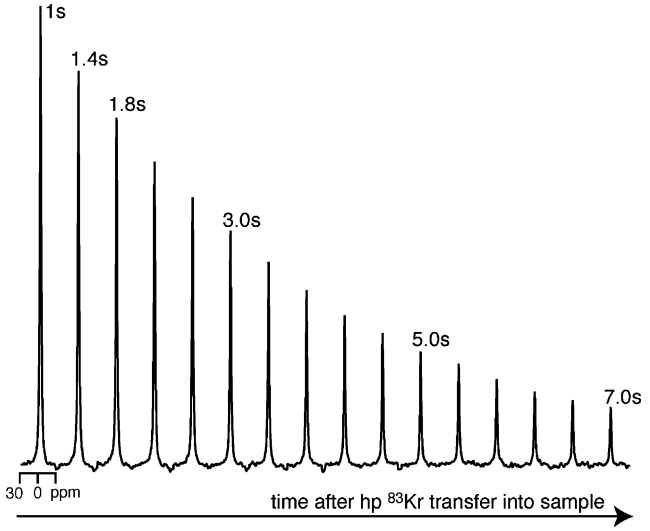

Fig. 1. Signal intensity decay resulting from T_1 relaxation and the application of a series of medium flip angle r.f. pulses. Using stopped flow optical pumping, hyperpolarized ^{83}K is transferred into a sample of porous polyethylene (mean pore size 70 μm). Signal is acquired by applying a series of sixteen 12° r.f. pulses spaced evenly every 0.4 s. Similarly robust decay patterns are observed in all of the porous samples studied.

2.2. NMR measurements

Experiments are performed at 15.4 MHz with a Chemagnetics CMX II spectrometer and a 9.4 T wide-bore (89 mm) superconducting magnet. T_1 values from optical pumping data are calculated by nonlinear least-squares fitting of the ^{83}Kr signal intensity as a function of time and number of applied medium flip angle (12°) r.f. pulses (see Fig. 1).

2.3. Preparation of samples

The 0.1–2.5 mm diameter glass beads (Biospec Products, Inc., Bartlesville, OK) are degassed overnight at a pressure