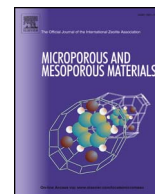




Contents lists available at ScienceDirect

# Microporous and Mesoporous Materials

journal homepage: [www.elsevier.com/locate/micromeso](http://www.elsevier.com/locate/micromeso)

## Ultrafast Laplace NMR with hyperpolarized xenon gas

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### ARTICLE INFO

#### Keywords:

 Ultrafast Laplace NMR  
 Relaxation  
 Diffusion  
 Mesoporous materials  
 Hyperpolarized xenon

### ABSTRACT

Laplace NMR, consisting of diffusion and relaxation experiments, provides detailed information about dynamics of fluids in porous materials. Recently, we showed that two-dimensional Laplace NMR experiments can be carried out with a single scan based on spatial encoding. The method shortens the experiment time by one to three orders of magnitude, and therefore it is called ultrafast Laplace NMR. Furthermore, the single-scan approach facilitates significantly the use of nuclear spin hyperpolarization for boosting the sensitivity of the experiment, because a laborious hyperpolarization procedure does not need to be repeated. Here, we push the limits of the ultrafast Laplace NMR method by applying it, for the first time, in the investigation of a gas phase substance, namely hyperpolarized xenon gas. We show that, regardless of the fast diffusion of gas, layer-like spatial encoding is feasible, and an ultrafast diffusion –  $T_2$  relaxation correlation experiment reveals significantly different signals of free gas and gas adsorbed in a mesoporous controlled pore glass (CPG). The observed diffusion coefficients are many orders of magnitude larger than those detected earlier from liquid phase substances, emphasizing the extended application range of the method. The challenges in the methodology, caused by the fast diffusion, are also discussed.

### 1. Introduction

Nuclear magnetic resonance (NMR) relaxation and diffusion experiments provide unique information about the rotational and translational motion of molecules as well as local chemical environment of nuclei [1,2]. Because radio frequency waves used in NMR penetrate through optically opaque materials, NMR is an excellent non-invasive method for the investigation of the structure of materials as well as of dynamics of fluids confined to porous materials [3–6].

Relaxation and diffusion experiments result in exponentially decaying signal intensities and the distribution of relaxation times or diffusion coefficients is extracted from the data by a mathematical process resembling an inverse Laplace transform [2]. Therefore, the experiments are classified under the concept of Laplace NMR (LNMR).

A multidimensional approach significantly improves both the resolution and information content of LNMR, enabling the correlation of diffusion and relaxation parameters as well as investigation of chemical exchange phenomena even in the case when the exchanging sites are not resolved in conventional spectra [2,5,7]. The approach has become broadly available after the development of a sufficiently reliable and robust multidimensional Laplace inversion algorithm [8–10]. The multidimensional approach increases the experiment time significantly, because the experiment has to be repeated from tens to hundreds of

times in order to collect data corresponding to each indirect dimension [2]. The approach also complicates the use of nuclear spin hyperpolarization techniques [11–14] for improving the sensitivity of experiments, because the polarization has to be reproduced again before each repetition, being laborious and time-consuming.

Recently, we introduced the ultrafast multidimensional LNMR approach as an answer to these drawbacks [15–17]. The method is based on similar layer-like spatial encoding of multidimensional data that has earlier been exploited in ultrafast multidimensional NMR spectroscopy [18–20] (also with hyperpolarization [21]), in 1D LNMR experiments [22–24], as well as for correlating  $T_1$  relaxation or diffusion parameters with spectroscopic data [25–27]. With this approach, we have shown that single-scan multidimensional LNMR experiments become feasible [15,16]. Although the spatial encoding lowers the sensitivity of the experiment, the sensitivity per unit time is slightly increased [15,17], and we were able to improve the overall sensitivity by several orders of magnitude with the use of hyperpolarized substances [16]. Ultrafast  $T_1$ - $T_2$  and  $D$ - $T_2$  relaxation correlation experiments revealed, e.g., different physical environments of liquid molecules in porous materials [15–17], and we showed that the experiments are feasible even with a low field, single-sided NMR instrument [17].

To the best of our knowledge, up to now only liquid-state ultrafast NMR spectroscopy and LNMR measurements has been reported in the

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<http://dx.doi.org/10.1016/j.micromeso.2017.10.024>

Received 2 January 2017; Received in revised form 29 May 2017; Accepted 13 October 2017  
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literature, however, no gas phase experiments have been provided. There is an obvious reason for that: fast diffusion of gases may mix the spatial, layer-like data encoding. The problem is emphasized in ultrafast NMR spectroscopy based on gradient-echo-type reading of the data [20], being sensitive to magnetic field inhomogeneities. Ultrafast LNMR, however, is based on the use of spin-echoes [2] that refocuses the effect of magnetic field inhomogeneity, and successful gas phase experiments will be more plausible with the ultrafast LNMR than with ultrafast NMR spectroscopy.

This work aims at extending the application range of ultrafast LNMR to gas phase substances, regardless of their large diffusion coefficient and low spin density. The studies concentrate on xenon gas, because its  $^{129}\text{Xe}$  isotope has a spin-1/2 nucleus and relatively high natural abundance (26%). Furthermore, nuclear spin polarization of  $^{129}\text{Xe}$  can be enhanced by many orders of magnitude by spin-exchange optical pumping (SEOP) technique [13,28].  $^{129}\text{Xe}$  has also turned out to be an excellent probe for the properties of porous materials [29–33]. Here we describe the first gas phase ultrafast LNMR (diffusion- $T_2$  correlation) experiments for hyperpolarized free xenon gas as well as xenon gas in a mesoporous material.

## 2. Experimental

NMR experiments were carried out on Bruker DRX 400 spectrometer equipped with a 5-mm broad band probe operating at 110.68 MHz for  $^{129}\text{Xe}$ . Experiments were conducted at room temperature. The hyperpolarized (HP)  $^{129}\text{Xe}$  gas was produced with a home-built continuous-flow Xe-polarizer, using a gas mixture consisting of 2.4% Xe (with natural isotopic portions), 9.6%  $\text{N}_2$  and 88% He. The optical pumping cell made of Pyrex contained about 300 mg Rb (purity: > 99%, AlfaAesar) and was operated at 145 °C and 3 bar for the pumping process. For the experiments, the gas mixture containing the HP- $^{129}\text{Xe}$  was directly inserted into standard 5 mm o.d. NMR tubes using a home-designed gas-insertion cap. The pressure of the gas mixture in the sample tube during the experiments was around 1 bar. The gas flow through the sample was regulated by a valve system controlled via a solenoid valve, allowing to stop the flow during the measurement. An illustration of the experimental setup is shown in Fig. 1a.

Ultrafast  $D$ - $T_2$  correlation measurements of free hyperpolarized xenon gas and hyperpolarized xenon inside a mesoporous controlled pore glass (CPG, provided by Enke et al., University of Leipzig), with the average pore diameter of 13 nm and particle size of 200–250  $\mu\text{m}$ , were carried out. Prior to the experiments, the sample was dried at 160 °C for 48 h. The pulse sequence is shown in Fig. 1b. As explained in detail in Ref. [16], after the two diffusion gradients the diffusion decay curve is encoded into the transverse magnetization profile along the  $z$  axis, and then the profile is read in the CPMG loop by means of read gradients, similar to magnetic resonance imaging (MRI) [3]. Between the successive echoes, the profile is decaying due to  $T_2$  relaxation.

In the free gas experiment, the following parameters were used: the duration and the bandwidth of the frequency-swept chirp pulse were 1 ms and 8266 Hz. The diffusion delay ( $\Delta$ ) was 4.5 ms and the strength of the diffusion gradient ( $G_{\text{diff}}$ ) was 0.033 T/m. The echo time in the CPMG loop was 6.5 ms, the strength of the read gradient ( $G_{\text{read}}$ ) was 0.011 T/m, and 200 complex points were collected per echo. Altogether 256 scans were accumulated in order to improve signal-to-noise ratio (SNR) due to low partial pressure of  $^{129}\text{Xe}$ . SNR was 19 in this experiment. Between the successive scans, the sample tube was refilled with a fresh hyperpolarized gas mixture. The repetition time was 10 s and the total experiment time 43 min.

In the experiment of Xe adsorbed in CPG, the following parameters were used: the duration and the bandwidth of the frequency-swept chirp pulse were 1 ms and 136254 Hz. The diffusion delay ( $\Delta$ ) was 8.0 ms and the strength of the diffusion gradient ( $G_{\text{diff}}$ ) was 0.511 T/m. The echo time in the CPMG loop was 4 ms, the strength of the read gradient ( $G_{\text{read}}$ ) was 0.026 T/m, and 100 complex points were collected

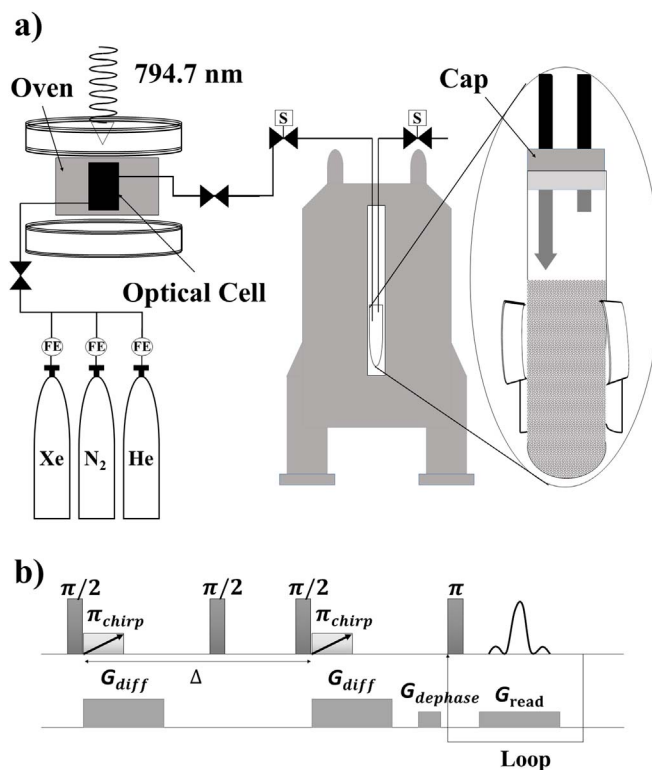


Fig. 1. (a) Experimental setup, consisting of xenon hyperpolarizer and gas transport system into the NMR tube inside the NMR spectrometer. During the measurement, gas mixture flow was controlled by a valve system regulated via a solenoid valve (S). (b) Pulse sequence of ultrafast  $D$ - $T_2$  correlation experiment.

per echo. Altogether 64 scans were accumulated in order to improve SNR ratio due to low partial pressure of  $^{129}\text{Xe}$ . SNR was 5 in this experiment. Between the successive scans, the sample tube was refilled with a fresh hyperpolarized gas mixture. The repetition time was 45 s and the total experiment time 48 min.

The field-of-view was 16.5 cm in both experiments. It was intentionally set much larger than the size of the sensitive region of the coil (about 1.9 cm), in order to get faster data sampling rate in the free induction decay (FID) signal due to digital filtering issues characteristic to Bruker instruments.

## 3. Results and discussion

2D contour plots of Fourier transformed data of the diffusion -  $T_2$  ( $D$ - $T_2$ ) correlation experiments of hyperpolarized free Xe gas and Xe adsorbed in CPG materials are shown in Fig. 2a and c. The Fourier transform was applied to extract MRI-type spatial encoding. The diffusion decay profile is shown in horizontal direction, in the relatively narrow region corresponding to the sensitive region of the coil. This region of the data was selected for 2D Laplace inversion. The  $z$  axis was converted to the  $b$  axis by using the linear relation between them (see Ref. [16]).

$D$ - $T_2$  correlation maps resulting from the 2D inverse Laplace transform are shown in Fig. 2b and d. The maps include a single signal in both cases. The observed diffusion coefficient for the free gas is  $(3 \pm 1) \cdot 10^{-6} \text{ m}^2/\text{s}$ , which is close to the value reported for pure  $^{129}\text{Xe}$  gas at 98 kPa,  $(5.3 \pm 0.6) \cdot 10^{-6} \text{ m}^2/\text{s}$  [34]. The observed diffusion coefficient for xenon in CPG mesoporous material is  $(2 \pm 1) \cdot 10^{-8} \text{ m}^2/\text{s}$ , which is in a reasonable agreement with the value resulting from the standard pulsed-field-gradient stimulated-echo (PGSTE) experiment of the same HP xenon mixture in the same CPG sample,  $(1.8 \pm 0.6) \cdot 10^{-8} \text{ m}^2/\text{s}$ , and the values of xenon in similar Vycor glass,  $(1.9\text{--}2.4) \cdot 10^{-8} \text{ m}^2/\text{s}$  [35]. The value is about two orders of magnitude

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