

# NMR hole burning in magnetic field gradient

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The possibility to extend the optical hole-burning method to the NMR experiments performed in inhomogeneous magnetic fields was analyzed. The characteristic hole-burning response of the spin system is obtained by excitation of the sample with particularly radio frequency pulse sequence. The specific response of the spin system is sensitive to the molecular dynamics. Preliminary experiments were performed on pure water and demonstrates the possibility to obtain the hole-burning effect in strongly inhomogeneous magnetic fields.

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## 1. Introduction

The NMR experiments performed in magnetic fields gradients are topics of the last decades. The advantage of the use of the magnetic gradient is the possibility of labelling the nuclear spins by their Larmor precession frequency, determined by the local magnetic field, [1]. The dispersion of the Larmor frequencies over the volume of the sample leads to the possibility to produce selective excitation and then to receive the signal only from a desired volume of the spatial distribution of the nuclear spins, [2]. Two main applications result from this spatial dependence: measurement of the structure (imaging), and measurement of motion (flow and diffusion), [3, 4].

The majority of the NMR experiments are performed in linear magnetic gradient fields that provide a regular distribution of the Larmor frequencies over the sample. The method request complex gradient coils systems and important power supply that are available only in the stationary NMR equipment. In the last time a new generation of small and portable NMR equipments, the NMR-MOUSE, was developed, [5]. Here, the static magnetic field  $B_0$  is produced by one or more small permanent magnets with a surface induction less than  $1T$ . The gradient is produced by the magnet itself and its value is about  $20 T/m$  in the vicinity of the surface of the magnet, [6]. This system don't need magnetic gradient coils and strong power sources, and has small size. The disadvantage is that the gradient is not linear, except a limited spatial volume in the vicinity of the magnet. For this reason the standard NMR experiment must be adapted for the use with the with inhomogeneous magnetic fields.

One of the experiments of interest in NMR is the hole-burning, inspired from the optical spectroscopy. Recent works demonstrate the possibility to perform this experiment in very large static magnetic field gradients and to use it for the evaluation of the molecular diffusion, [7]. Our interest in this work is to demonstrate the possibility to obtain the hole-burning effect in the strongly inhomogeneous magnetic field of the NMR-MOUSE and

to observe the effect of the molecular diffusion on the shape of the recorded signal.

## 2. Experimental

The NMR-MOUSE used in this work consisted of a permanent bar magnet with the RF coil positioned on the top of the magnet [8, 9]. The device was operated at a resonance frequency of 19.2 MHz corresponding to the surface of the NMR-MOUSE. Here the volume averaged field gradient was approximately 20 T/m. The NMR experiments were controlled by a Bruker Minispec PC spectrometer for excitation and data acquisition. The transmitter and receiver system are characterized by a bandwidth of 0.5 MHz. We used distilled water for testing. Typically a recycling delay of 0.5 seconds was used, and 100 scans were averaged for improvement of the signal-to-noise ratio.

## 3. Results and discussion

The NMR hole-burning effect is obtained by irradiation of the spin system with a particularly radiofrequency (RF) pulse sequence,  $(\pi/2-\tau_1-\pi/2-\tau_2-\pi-\tau_2-echo)$ , (Fig. 1). Such an experiment consists in applying a

long  $\frac{\pi}{2}$  low power pulse of length  $t_H$  to irradiate the spin

system in a narrow frequency band given by

$$\Delta\omega_H \approx \frac{2\pi}{t_H}. \text{ We used rectangular } \frac{\pi}{2} \text{ pulse with a}$$

length  $t_H = 100 \mu s$  corresponding to an excitation bandwidth of  $0.01 MHz$ . The sample is placed in a static magnetic field  $B_0$  with a static gradient  $\vec{G}$ . The carrying pulse frequency  $\omega_0$  corresponds to the Larmor precession frequency in the center of the sensitive volume,  $\omega_0 = \gamma B_0$ .

In the presence of the magnetic gradient  $\vec{G}$  such a pulse irradiates a narrow spatial domain of the sample of

thickness  $\Delta z_H = \frac{\Delta\omega_H}{\gamma \cdot G} = \frac{2\pi}{\gamma \cdot G \cdot t_H}$  perpendicular to

the gradient. The longitudinal magnetization  $\vec{M}_H$  of these nuclear spins is flipped in the transverse plane by the pulse. The longitudinal magnetization  $\vec{M}_u$  of the unperturbed spins remains parallel to  $B_0$ . After a diffusion delay  $\tau_1$  has elapsed, a broad detection is performed of a large slice extend to the whole sample. From this instant the experiment takes the form of a Hahn-echo sequence with hard RF pulses. The detection pulses should be as short as possible for a wide excitation spectrum. We used rectangular  $\frac{\pi}{2}$  and  $\pi$  pulses with a length  $t_d = 2.5 \mu\text{s}$  corresponding to an excitation bandwidth of  $0.4 \text{ MHz}$ . This bandwidth is larger than the excitation spectrum of the hole-burning pulse and is comparable with the width of the spectrometer transfer function.

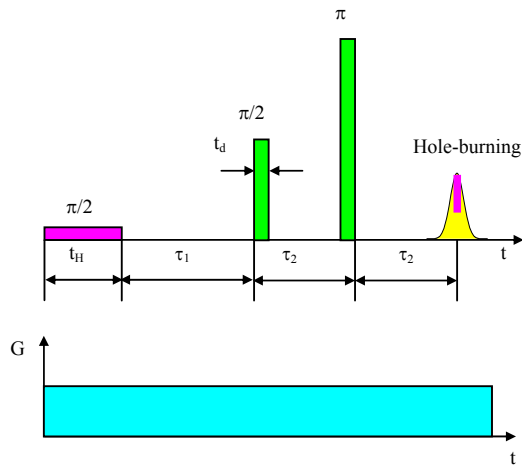


Fig. 1. Design of the radio frequency hole-burning pulse sequence.

The detection pulses flip again the magnetizations  $\vec{M}_H$  and  $\vec{M}_u$ . The magnetization  $\vec{M}_H$  of the spins excited by the hole-burning pulse is rotated again parallel to the direction  $\vec{B}_0$  and give no contribution to the echo.

The magnetization  $\vec{M}_u$  of the unperturbed spins is flipped in the transverse plane and give rise to the echo at the instant  $2\tau_2$ . The Fourier analyze of the recorded echo shows a frequency gap of width  $\sigma = \sigma(\tau)$  in the spectrum of the recorded echo. As we can see from the Fig. 3, the spectrum of the hole-burning echo can be compared to the *sinc* function that represents the spectrum of the rectangular hole-burning pulse, [10].

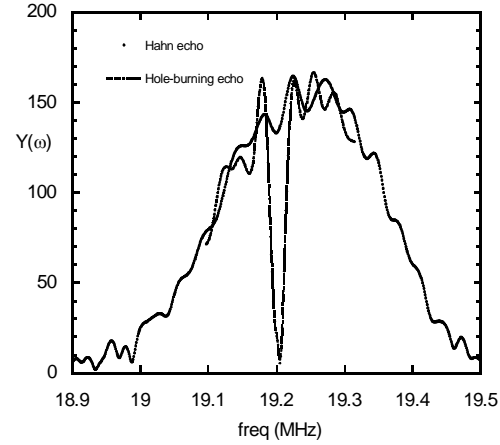


Fig. 2. The spectrum of the Hahn echo and hole-burning echo recorded in the same experimental conditions.

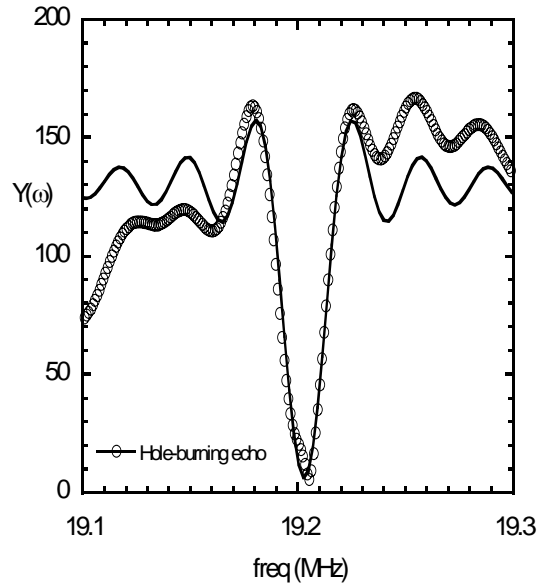


Fig. 3. The specific NMR hole-burning response of the water for pulse sequences with different diffusion time  $\tau_1 = 1 \text{ ms}$  and the spectrum of the rectangular hole-burning pulse, (the *sinc* function).

To demonstrate the effect of the hole-burning pulse sequence we recorded in the same conditions the simple Hahn echo. The spectrum of the Hahn echo is continuous without structure, whereas the spectrum of the hole-burning echo contains the frequency gap of the hole-burning pulse.

During the diffusion time  $\tau_1$ , the nuclear spins excited by the hole-burning pulse move from their initial position  $z_i$  towards another position  $z_f$  corresponding to another magnetic field  $B_f = B_0 + G \cdot |z_f - z_i|$  that induces a

modification of the precession Larmor frequency  $\Delta\omega = \gamma \cdot G \cdot |z_f - z_i|$ . The deviation of the Larmor frequency from its initial value is more important for long diffusion time  $\tau_d$ , that results in a modification of the spectrum of the echo. This behavior can be clearly seen from the Fig. 4, where the spectrum of the echo of pure water for different diffusion times  $\tau_d$  is presented. The spectrum of the echo corresponding to a short diffusion time  $\tau_d=1\text{ ms}$  is very close to the spectrum of the rectangular hole-burning pulse, the *sinc* function. For long diffusion time,  $\tau_d=100\text{ ms}$ , we can observe difference between the spectra of the of the echo and the function *sinc*, that demonstrates the effect of the diffusion. The time evolution of the shape of the hole-burning echo can be analyzed to extract the diffusion coefficient. The method can be applied if the spatial thickness of the hole can be made comparable with the diffusion length of the nuclear spins, that is typically a few  $\mu\text{m}$  for liquids, in the NMR experiments. To reduce the thickness of the hole the use of high gradients is suitable, from which the interest to use the NMR MOUSE.

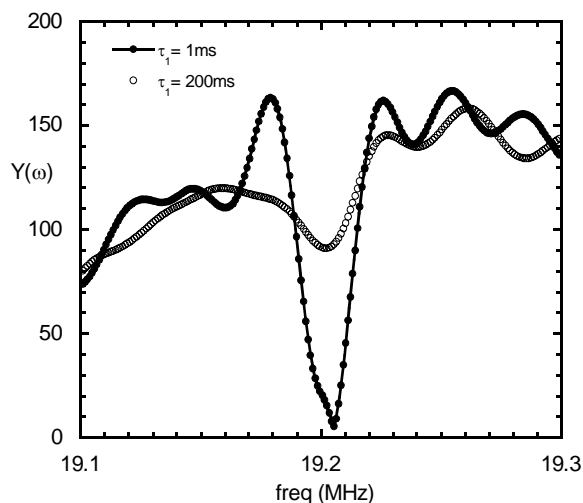


Fig. 4. The specific NMR hole-burning response of the water for pulse sequences with different diffusion time  $\tau_d=1\text{ ms}$  and  $\tau_d=200\text{ ms}$ .

The results obtained are in good agreement with the experiments performed in linear gradients and clearly demonstrate the possibility to obtain hole-burning effects in the strongly inhomogeneous magnetic field of the NMR-MOUSE.

#### 4. Conclusions

This work demonstrates the possibility to obtain the hole-burning effect in strongly inhomogeneous magnetic fields. The effect is obtained by a special RF pulse sequence constructed on the basis of the standard Hahn-echo pulse sequence.

The spectrum of the hole-burning echo is in good agreement with the spectrum of the hole-burning pulse of excitation. A modification of the characteristics of the spectrum of the echo can be observed as function of the diffusion time of the pulse sequence. This modification is more important for samples with great diffusivity. The analyze of the time evolution of the spectrum of the hole-burning echo can lead to preliminary investigation of the diffusion.

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