

Use of spatial encoding in NMR photography

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Abstract

NMR photography has gained significant attention as a method of storing and retrieving information using NMR spectroscopy. Among the commonly practiced methods the most important is the frequency encoding by use of a multi-frequency pulse on a liquid crystal molecule. We propose and demonstrate another robust method which relies on spatial encoding. Spatial information is mapped onto the spectrum, if excited and recorded in the presence of a gradient. The encoding is performed by applying a multi-frequency pulse in the presence of a gradient. The subsequent acquisition, under a gradient, helps storing this spatial information on a one-dimensional spectrum. Series of such spectra can also store two-dimensional patterns. This procedure is described and exemplified in this paper.

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1. Introduction

Information storage and retrieval at the atomic and molecular level has been an active area of research in the last decade. Most of the techniques in this field sought to arrange atoms or molecules in a chosen pattern on an appropriate material surface or in a matrix [1,2]. The use of NMR as a tool to store and retrieve information was thought of in 1950s, when the spatial encoding was suggested in 1955 using spin-echo generation under a gradient [3]. Subsequently, a spin echo storage technique was proposed by Anderson and Hahn [4] and was patented. In these methods, information was stored sequentially in the different regions of the sample. These methods are particularly unsuitable for storing large patterns since the encoding time is proportional

to the size of the encoding pattern. The spatial encoding was successfully exploited by Serša et al. [5–8] to excite an completely arbitrary three or lower dimensional patterns. However, the employed method, which requires construction of a k -space trajectory, is complicated and requires the use of gradients along x , y , and z directions.

Recently, a method named NMR photography was proposed and exemplified which stored information parallelly on the nuclear spin system of a liquid crystal molecule [9–15]. The NMR spectrum of a liquid crystal molecule shows a broad unresolved lineshape. However when excited with a multi-frequency radio-frequency (RF) pulse, the resulting spectrum shows many sharp resolved coherences which can be used to store any desired pattern. A two-dimensional pattern can be broken into a number of one dimensional arrays, which can be encoded separately or as a series on the multi-line liquid crystal spectrum. The finite size of the liquid crystal spectrum is a major drawback of this method, which limits the number of bits or the size of the pattern to be encoded. Also, though the method is capable of

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storing a pattern on a molecule, but for a successful retrieval it still requires an ensemble of such molecules. Therefore, successful storage of patterns on a molecule shows no advantage as far as the sample size is concerned. Furthermore, since the relaxation rates of these individual lines are quite complicated, longer storage time leads to distorted line intensities resulting in erroneous patterns. In liquid crystal molecules, these coherences are generated in a dipolar coupled large proton network. Therefore, an analytical treatment of the relaxation behavior of these coherences is extremely difficult. Even a numerical estimation of the same requires handling of very large matrices ($\sim 2^N$ for N protons, for a typical liquid crystal 5CB, $N = 19$ and 2^N can be as large as 524,288).

Spatial encoding has gained significant attention recently as a tool to enhance the acquisition speed of multi-dimensional NMR [16]. The use of multi-frequency excitation to speed up the higher dimensional spectroscopy has also been suggested recently [17]. Following these ideas, we introduce a method of NMR photography which relies on spatial encoding involving a multi-frequency excitation and subsequent acquisition under a gradient. The sample could be a small molecule which gives a single peak, such as H_2O , CHCl_3 , tetramethylsilane (TMS), etc. In presence of a linear gradient, the spectrum becomes uniformly broad. A multi-frequency RF pulse, when applied under gradient, excites the regions of interest (slices) from this broad profile. The multi-frequency RF pulse is a collection of harmonics whose values are chosen according to the pattern to be encoded. The method will be detailed in the following section. In contrast to the other practiced methods, our method has the superiority that it does not depend on the specific nature of the sample. Since the information is encoded spatially, the bits or the spatially localized coherences do not mix with each other and their relaxation can be assumed to follow Bloch equations. However, diffusion between the slices can mix and reduce the slice magnetizations, but this effect is in general uniform and act in the same way on all the slices. The suggested method is a quasi-two-dimensional technique. While it can store the one-dimensional patterns in a single experiment, a series of experiments is required to store two dimensional patterns. Since, the width of the spectrum under gradient depends on the gradient strength, this method has the potential of storing a large amount of information at the cost of lower signal-to-noise ratio. However, storage of the information is not the only and primary concern of this work. Rather, we intend to put emphasis on the use of spatial encoding in the field of NMR photography. The use of the multi-frequency RF pulses to spatially encode information may also find interesting applications in magnetic resonance imaging, implementation of parallel search algorithms and multi-dimensional spectroscopy.

2. The method

While explaining the method we shall assume without any loss of generality that the sample contains only one type of magnetically active nucleus. In presence of a linear gradient, the Larmor frequency of the nucleus can be expressed as,

$$\omega(z) = \gamma(B_0 + \mathbb{B}z), \quad (1)$$

where B_0 is the static magnetic field, \mathbb{B} is the magnetic field gradient strength, and z is the distance of a point of the sample from the center of the sample. It is assumed that the origin of the gradient coincides with the center of the sample length. It is evident from the preceding equation that in the presence of a gradient, the spectrum becomes broad and the frequency being a linear function of sample height, the spatial distance is mapped on the spectrum. When a soft RF pulse is applied under gradient it excites a specific region of the spectrum or a specific slice of the sample. The position of the slice and its width depend on the nature of the soft RF pulse. A soft pulse at ω_k frequency and of width $\Delta\omega$, excites a slice of thickness $\Delta\omega/(\gamma/\mathbb{B})$ and at a position $(\omega_k - \gamma B_0)/(\gamma/\mathbb{B})$, as follows from Eq. (1). Generalizing, one can assert, that a multi-frequency RF pulse, applied on the sample under gradient excites a series of slices from the sample whose positions are determined by the harmonics present in the multi-frequency pulse. The slice intensities are proportional to the amplitude of the harmonics constituting the pulse. To generate multi-frequency pulse, a certain shape (e.g., Gaussian) was modulated with a number of harmonics with same amplitude and with same phase, so that all excited slices are also at same phase. The following equation was used to generate a specific shape $g(t)$:

$$g(t) = \sum_{k=1}^N A e^{-Bt^2} e^{-i\omega_k t}, \quad (2)$$

where A is the common amplitude or weighing factor for all the harmonics, and B represents the width of the Gaussian. The set of frequencies $\{\omega_k\}$ is chosen in the following way. The pattern which is to be stored on the spectrum, is divided in a bit-by-bit (row versus column) fashion into a matrix. In the case of a two-dimensional pattern, the positions of the pixels in a row are converted into the frequency values. These frequencies were used to generate the multi-frequency pulse shape. The experimental scheme was a simple application of a multi-frequency pulse and subsequent acquisition under a gradient. It should be noted that if a delay is used between the pulse and the acquisition, the gradient may be switched off during this period to simplify the data processing. If the gradient is on, various slice magnetizations will precess under the gradient and will gain various phases. The phase gain will be linear with

distance and hence frequency. Therefore a further first-order phase correction would be needed to make the spectrum in-phase.

3. Experimental

The experiments were carried out on the protons of 99% D₂O at 300 K with Bruker DRX-500 spectrometer with operating proton Larmor frequency at 500 MHz. The pulse sequence is shown in Fig. 1 which also contains the shape of a typical multi-frequency pulse generated by modulation of a Gaussian waveform using Eq. (2). The proton spectrum of the aforementioned sample is shown in Fig. 2A, along with the broadened spectrum recorded under a linear gradient of strength ~ 6.75 G/cm in Fig. 2B. The Fig. 2C shows a multi-line spectrum recorded after an excitation by a multi-frequency RF pulse modulated with 40 harmonics. The amplitude of each harmonic of the multi-frequency pulses was set as 12.5 Hz for all photography experiments and the pulse duration was 20 ms corresponding to the flip angle of $\pi/2$. The spectrum was excited and recorded under the same linear gradient. The peak at zero frequency was excluded, since it suffers from the quadrature glitch. A small first-order phase correction was needed to make the spectrum in-phase.

The patterns to be *photographed* (for example Fig. 3) were broken into pixels by a Matlab program (© Math Works). Each row of pixel coordinates (i.e., x of a (x, y) pair) were converted into frequencies and the corresponding multi-frequency pulse was generated using Shape Tool (a standard Bruker facility). The uniformity of amplitudes and phases were ensured while generating the shapes. Each pulse and the acquisition generate an

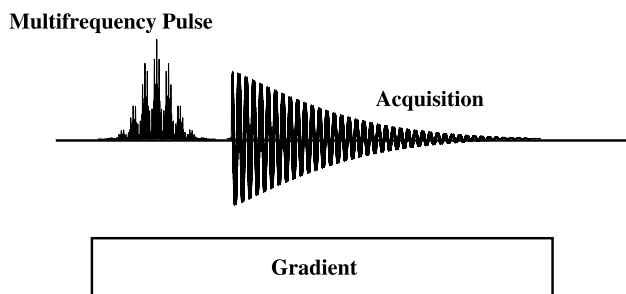


Fig. 1. The pulse scheme used for NMR photography using spatial encoding. A typical multi-frequency pulse is shown in the figure, which was obtained by modulating a Gaussian shape with 10,000 points, with 18 frequencies, which correspond to the peaks of the first row of the stacked plot of Fig. 4. The gradient may be switched off between the acquisition and the multi-frequency RF pulse to avoid a first-order phase correction of the spectrum. However, in the present experiment the gradient pulse was on throughout the experiment and a first-order phase correction was used. The amplitude of each harmonic of the multi-frequency pulse was set as 12.5 Hz.

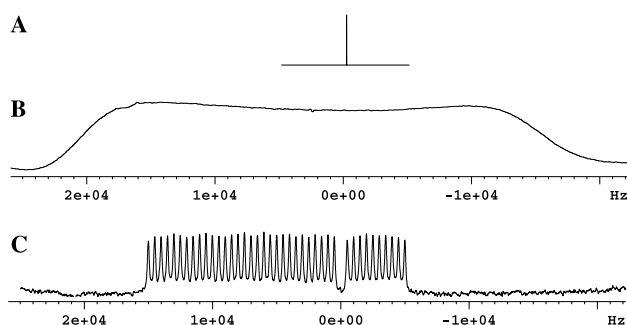


Fig. 2. (A) The H₂O peak in the absence of the gradient. (B) The spectrum under a gradient of strength ~ 3 G/cm. (C) The spectrum obtained after the application of a multi-frequency pulse which selects 40 peaks which can be used to map a maximum of 40 pixels. The peak at zero frequency was excluded since it suffers from quadrature glitch. The spectrum shown is a phase-sensitive spectrum. The vertical scales in sub-figures (A)–(C) are all different.

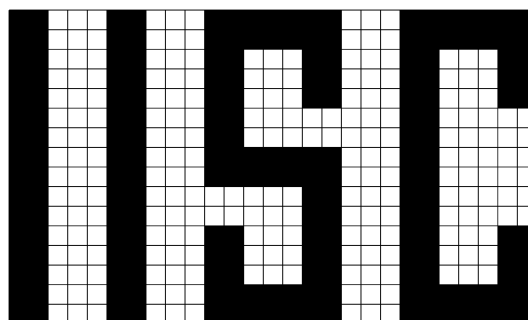


Fig. 3. The desired pattern: the word IISC has been digitized in a 16×27 pixels.

1D spectrum, which records a row of the pattern. These 1D spectra, when shown as a stacked plot (pseudo-2D), clearly mimics the complete 2D pattern (see Figs. 4 and 5).

This method has several advantages over the other methods. The decay of information encoded is uniform for all the slices, since the nuclei in all the slices relax with same transverse relaxation time. The effect of diffusion may not be uniform near the ends (the end effects

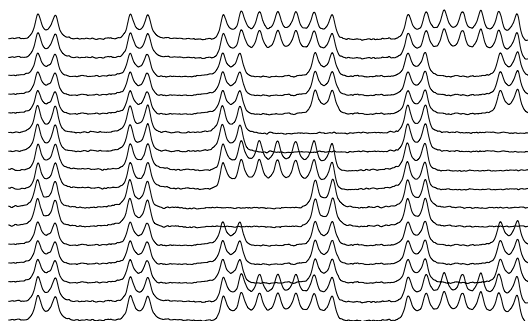


Fig. 4. The stacked plot of recorded spectra for the pattern in Fig. 3 recorded using spatial encoding. The recycle delay for each experiment was 25 s and total experimental time was ~ 100 s.

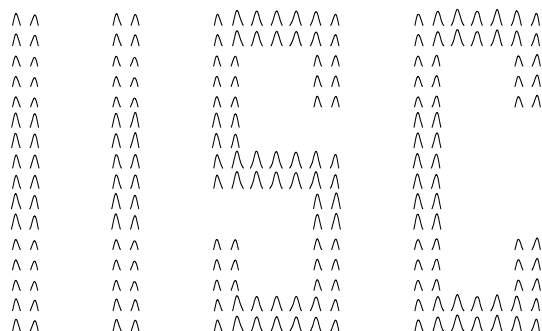


Fig. 5. The stacked plot of Fig. 4 with a higher cut-off, reproducing the pattern shown in Fig. 3.

arising from the open boundary conditions), but for central slices, the differential effects seem to be small. In contrast, the method using liquid crystals suffers from the problem that, the peaks relax with different transverse relaxation times and there could be magnetization transfers between peaks (transverse NOE effects), not to mention the cross-correlated relaxation effects [18]. Therefore, the proposed method is capable to storing undistorted information for longer storage times. Also, in case of a liquid crystal molecule the storage time can be of the order of hundreds of milli-seconds, whereas, the proposed method which uses spatial encoding, if performed with samples with long T_2 , can store information for tens of seconds. Also, owing to large signal-to-noise ratio of the signal, the spectra shown in Figs. 4 and 5 have been recorded using only four transients, in contrast to the 512 transients for the figures in the work of Fung and co-workers [11].

Compared to the method of Fung and co-workers [11] where 1024 lines have been excited with a minimum linewidth of 12 Hz, our present experiment with the pulse width of 20 ms yielded the linewidth of ~ 150 Hz, for a gradient strength of ~ 6.75 G/cm. However, with longer pulse width, the resolution per pixel and the total number of pixels can be significantly improved. Though our experiment lacks the resolution reported by Fung et al., the main emphasis of this work is to exemplify the applicability of spatial encoding to the NMR photography.

It should be noted that the diffusion does not cause any significant limitations in the achieved resolution, if the spectrum is acquired shortly after the excitation. However, for longer delays, each slice may be broadened due to the diffusion between the slices. To investigate the effect of the diffusion, the diffusion equation may need to be solved, assuming that, the initial boundary condition resembles the initial excited pattern. For details, we refer the readers to the papers by Bhattacharyya et al. [19] and Loening et al. [20], where the effect of diffusion on sequentially excited slices has been reported.

4. Conclusion

The use of spatial encoding in NMR photography has been demonstrated in this paper. In presence of the magnetic field gradient, spatial information is mapped onto the spectrum. If the spectrum is excited with a properly prepared multi-frequency RF pulse, the slices of the sample can store an input pattern. This encoded information can easily be retrieved from the Fourier transform of the free induction decay. The proposed method has advantages over the currently practiced methods, for having uniform relaxation rates for all encoded bits or slices. Diffusion between the slices have an end effect on the encoded information, however, the effect on the central slices seem to be uniform. This method can be used in magnetic resonance imaging (MRI), to sharply define the boundaries of different tissues. Also, the spatially encoded spectrum can be used to implement parallel search algorithms [12]. The applications of this method for the characterization of non-uniform samples and biological tissues are underway. Finally, it has been shown that spatial encoding could be successfully applied to the field of NMR photography.

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