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A simple method for NMR photography

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Abstract

The application of a multi-frequency weak pulse to a liquid crystal can excite narrow ^{1}H NMR peaks at the applied frequencies. By using two-level amplitude coding, namely setting the amplitudes of some of the harmonics to zero, this method can be used to store up to 1024 bits of binary information in the liquid crystal molecules. When the information is retrieved in the form of a spectrum, which is plotted as an array of 32 or 16 segments, the stack of spectral segments reproduces a 2D input pattern quite well. This technique is called "NMR photography." The original method was a pseudo-2D technique that applies the 1024-frequency pulse in the first step, and reads the signal row-by-row in the second step. The present improvement involves subtracting two spectra obtained with the same 1024-frequency pulse but with different durations, so that the method becomes a 1D technique, with a tremendous saving of experimental time. Several examples are given to illustrate the results.

Keywords: NMR photography; Multi-frequency pulse; Liquid crystal

1. Introduction

Information storage and processing at atomic and molecular levels has been a very active area of research in recent years. One of the most interesting techniques is the use of atomic force microscope (AFM) to place atoms at specific locations on a surface to form intricate patterns [1–3]. Recently we have shown that ^{1}H nuclear magnetic resonance (NMR) peaks can also be manipulated to reproduce a 2D pattern containing $32 \times 32 = 1024$ pixels [4], and the technique is called NMR molecular photography.

The use of NMR for information storage was suggested almost 50 years ago [5–7] based upon the following principle. When a field gradient is imposed upon an isotropic liquid (e.g., H_2O), the NMR signal can have a large inhomogeneous broadening. The use of a series of weak radio-frequency (RF) pulses having different shapes and amplitudes followed by a strong 180° pulse would result in a corresponding series of spin echoes reproducing the shapes and amplitudes of the weak pulses. However, the information is stored in different parts of the sample rather than being at the molecular level, and the input is sequential rather than being parallel.

In contrast to an isotropic liquid, the application of a weak pulse to a liquid crystal in a homogeneous field can create a relatively narrow ^{1}H NMR peak (linewidth 12–16 Hz for 4′-pentyl-4-biphenylcarbonitrile, 5CB) directly [8]. The peak can be produced anywhere within the spectral range (about 30 kHz), and all molecules contain the same information. By using a multi-frequency weak pulse for excitation while setting the amplitudes of some of the harmonics to zero, the method can be used as a means of storing binary information [4,8,9]. Originally, the technique of NMR photography involves inputting the 1024 pixels of a template simultaneously but retrieving them as 32 separate segments, one at a time, in a pseudo-2D fashion [4]. Now we have improved the method to make it a simple 1D technique. In this paper we will first review the principles of the method briefly, then report the results for several examples.

2. Principles of binary information storage using NMR spectroscopy

For spin systems with extensive dipolar couplings and rapid albeit restricted molecular motions, such as

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nematic liquid crystals and certain organic solids with *tert*-butyl groups or flexible alkyl chains, the response to weak pulses exhibits some unusual characteristics [4,8,10]. The application of a weak pulse (with $\gamma B_1/2\pi \approx$ 10–100 Hz) for 10 ms or more would produce a low-intensity broad spectrum spanning tens of kHz, plus an inverted sharp peak. The height of the inverted peak is dependent on the length of the weak pulse, but its absolute value can be as much as 1–2 orders larger than the height of the broad peak. The application of a second weak pulse with a 90° phase shift could turn the inverted peak into positive [4].

To analyze the interaction between a weak RF field and a multi-spin system with dipolar coupling, we have performed numerical simulations both without [4,8] and with [10] consideration of the effect of relaxation, and the results do reproduce the basic features of the experimental observations. For a qualitative description, an outline partly based on a previous explanation [11] is given below.

For a cluster of N-coupled spins with $I = 1/2$, the dipolar Hamiltonian is expressed by:

$$\mathscr{H}_{\mathrm{D}}/\hbar = \sum_{i<j} \omega_{ij}\left[I_z^i I_z^j - \left(I_x^i I_x^j + I_y^i I_y^j\right)/2\right], \tag{1}$$

where $\omega_{ij}/2\pi$ is the dipolar coupling constant between nuclei i and j. There are 2^N eigenvalues and the maximum number of allowed transitions is $C_{2N}^{N+1}(\approx 2^{2N})$ for large N. When intermolecular interaction is negligible and the effect of chemical shifts is not important, the spectral width is characterized by the largest value of ω_{ij}, which is designated as ω_{loc}.

The Hamiltonian of an RF irradiation applied at the x-direction is represented by

$$\mathscr{H}_{\mathrm{RF}}/\hbar = \Omega\cos(\omega_0 t)\sum_i I_x^i, \tag{2}$$

where ω_0 is the angular frequency of irradiation and $\Omega/2\pi$ is the strength of the RF field.

In a spin system with extensive dipolar coupling, the characteristics of the spectrum are dependent on the amplitude of Ω. (1) For strong RF power ($\Omega > \omega_{\mathrm{loc}}$), all allowed transitions are affected. In this case, when the duration (τ) of the "hard" pulse is short ($\Omega\tau \lesssim 1/10$), the spectrum gives a linear response signal. When the pulse duration is very long ($\Omega\tau \gg 1$), the populations of different spin energy levels gradually become equalized. (2) A pulse with moderate RF power ($\Omega < \omega_{\mathrm{loc}}$) and sufficient duration ($\Omega\tau \gtrsim 1/10$) affects only part of all the transitions. Nevertheless, these excited transitions are all interconnected through common energy levels. In this case, the evolution of the populations of the energy levels can be described in terms of the spin temperature theory. (3) A weak RF pulse ($\Omega \ll \omega_{\mathrm{loc}}$) with sufficient duration ($\Omega\tau \gtrsim 1/10$) excites only a small fraction of the allowed transitions. Although the dynamics of dipolar-coupled spin systems having prolonged interaction with a weak RF field is not well understood yet, the experimental results and computer simulations show that it is quite different from systems without extensive dipolar coupling. The simulations indicate that, when the pulse duration is long ($\Omega\tau \gtrsim 1$), the affected transitions would produce independent "islands" of disturbance in the spin density matrix (work in progress). If some of the single-quantum coherence elements in the density matrix have small relaxation rates ($\lesssim 10\,\mathrm{s}^{-1}$) due to rapid but restricted molecular motions, the presence of long-lived spin states (lifetime $\gtrsim 0.1$ s) can be readily observed [10], so that the collective response produces an inverted sharp peak as well as a weak and broad absorption signal. However, a more quantitative interpretation, especially the origin of the opposite phases of the narrow and broad components, remains to be formulated.

In a liquid crystal, a large number of proton spins (19 in 5CB) in each molecule is coupled to one another with extensive dipole–dipole interactions. Rapid translational motions and restricted rotational motions are favorable for the presence of long-lived spin states. Application of a weak pulse can produce an inverted narrow peak anywhere within the entire spectral range (ca. 30 kHz for 5CB), which makes it possible to use multi-frequency pulses to store and process a large amount of information.

Multi-frequency ("polychromatic") RF irradiation is a well-established technique [12], but has not been used extensively in NMR spectroscopy. However, it is indispensable for some new applications such as Hadamard spectroscopy [13–15] and binary information storage and processing [4,8,9]. A multi-frequency pulse can be expressed as

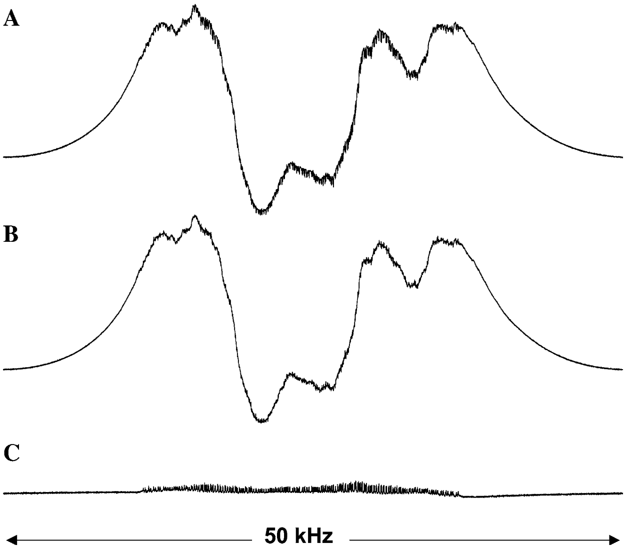

Fig. 1. ^{1}H NMR spectra of the liquid crystal 4′-pentyl-4-biphenylcarbonitrile (5CB) at 400 MHz and 20 °C. A 1024-frequency pulse was applied; the frequencies are 250 Hz apart, and some of the harmonics have zero amplitudes. The total power ($\gamma B_1/2\pi$) was 1.2 kHz, the number of scans was 360. (A) Pulse duration = 0.20 s. (B) Pulse duration = 0.04 s; spectral amplitude × 0.91. (C) Difference spectrum [(B) – (A)].

$$\Omega(t) = \sum_k \Omega_k \cos[(\omega_0 + \omega_k)t + \varphi_k], \qquad (3)$$

where ω_0 is the carrier frequency, ω_k is the frequency of the kth harmonic with respect to ω_0, and φ_k is its initial phase. In our work, the pulses represented by Eq. (3) were produced directly by programming the waveform generator of the spectrometer with proper amplitude and phase modulations of the RF carrier.

When a multi-frequency irradiation is applied to 5CB, an equal number of inverted sharp peaks is produced at the corresponding frequencies. By setting the amplitudes of some of the harmonics to zero, the spectrum obtained shows a series of negative peaks with gaps, corresponding to the programmed input. By considering the peaks as “1” and the gaps as “0,” the multi-frequency weak pulse can be used for the storage and processing of binary information [4,8,9]. When the number of harmonics is substantial, the total RF power needed is considerably larger than that for a single-frequency weak pulse. As a result, the intensity of the broad component becomes quite significant (Fig. 1A). To eliminate the broad component, acquisition delay can be used (there is a mistake in [8] stating that the FID was immediately taken after the pulse).

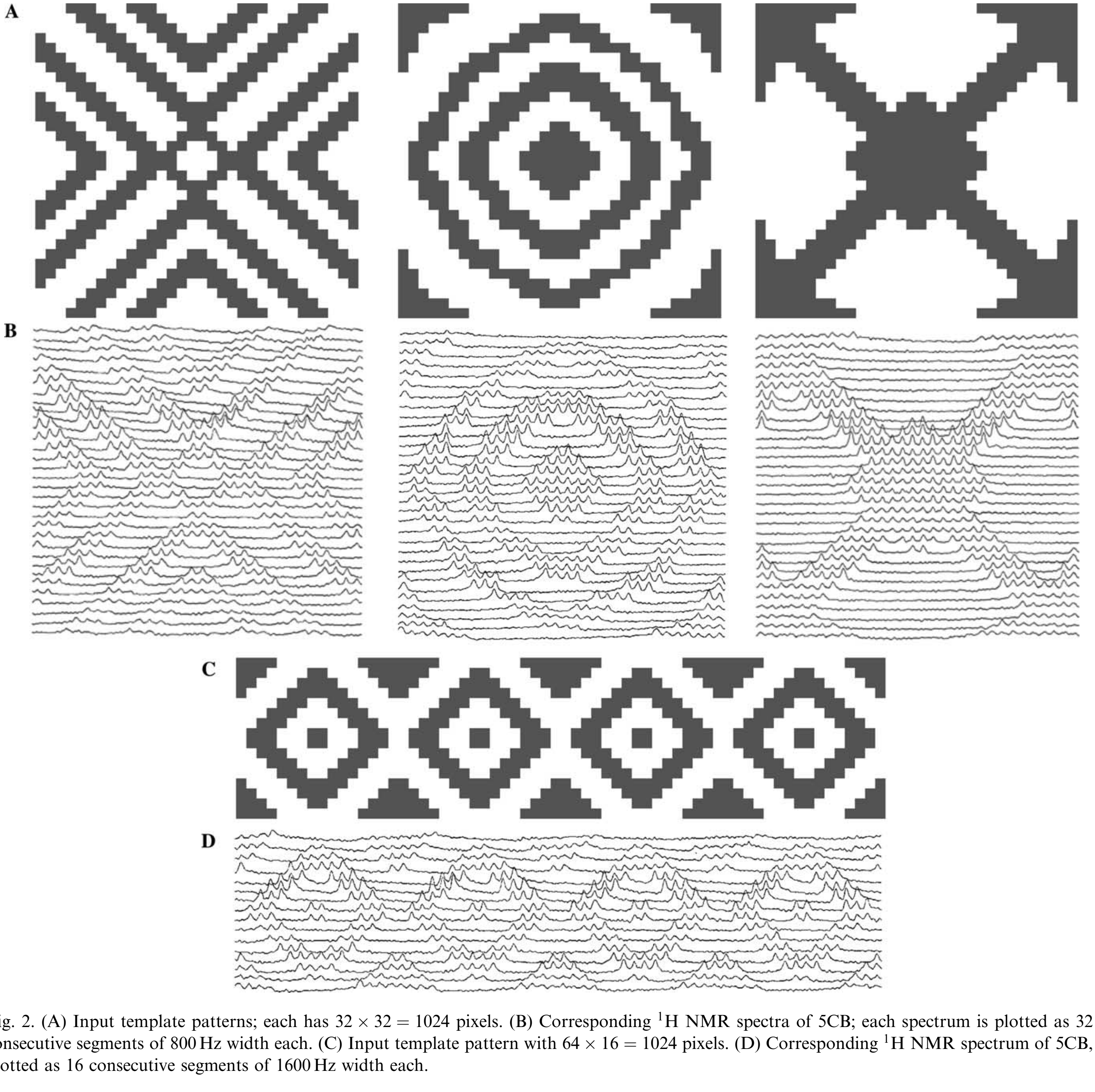

Fig. 2. (A) Input template patterns; each has $32 \times 32 = 1024$ pixels. (B) Corresponding ^{1}H NMR spectra of 5CB; each spectrum is plotted as 32 consecutive segments of 800 Hz width each. (C) Input template pattern with $64 \times 16 = 1024$ pixels. (D) Corresponding ^{1}H NMR spectrum of 5CB, plotted as 16 consecutive segments of 1600 Hz width each.

3. NMR photography

The method of binary NMR photography involves the reproduction of the 2D pattern of a template, such as those shown in Fig. 2A, as a stacked plot of NMR spectra [4]. To do this, the dark pixels in the 32×32 template are taken as "1" bits and the blank pixels are taken as "0" bits, and all the pixels, column by column, are arranged as a 1024-bit string. Then, a 1024-frequency pulse with frequencies 20 Hz apart is programmed correspondingly, with the amplitudes of the "0" bits being set to zero. The pulse, with an appropriate low RF power, is applied to a liquid crystal (for example 5CB), and the free-induction decay (FID) signal is collected after a 1 ms acquisition delay to eliminate the broad background. However, the long acquisition delay time makes it practically impossible to phase all the peaks correctly over the spectral range of 20 kHz; consequently, the narrow peaks must be displayed in the absolute value mode. This approach reduces the spectral resolution, which makes it necessary to use a pseudo-2D method to retrieve the 1024-pixel pattern as 32 separate segments, row by row, in our previous work [4].

In order to improve the technique and retrieve all the stored binary information simultaneously, we have developed a simplified approach based upon the following consideration. When the multi-frequency irradiation is applied for a shorter period to the liquid crystal sample, the intensities of the sharp peaks are much smaller, but the broad component has the same intensity profile (Fig. 1B; a multiplication factor of 0.91–0.93 is used to account for the effect of less relaxation for the shorter pulse). By subtracting the two spectra, the broad component can be eliminated almost completely (Fig. 1C), and the sharp peaks become positive without using the absolute value mode of display. To further reduce the residual broad component, one can subtract the two FID's instead of the two spectra, discard a few initial points (equivalent to an acquisition delay of 100 μs), carry out the Fourier transform, and re-phase the spectrum. Thus, each experiment involves the collection of two sets of 1D data instead of retrieving the 1D information in a pseudo-2D manner as done previously [4], resulting in a substantial saving of experimental time.

In principle, displaying the spectrum in the phase-sensitive mode rather than in the absolute-value mode would improve the spectral resolution and increase the information density. However, this advantage is not realized experimentally because the pseudo-2D method, although time-consuming, uses two consecutive pulses to produce an effect similar to an AND gate operation that makes each peak very well defined [4].

In the present work, the frequencies of the 1024-frequency pulse were set to be 25 Hz apart, and the pixels were programmed one row after another consecutively. The pulse used to obtain the spectra shown in Fig. 1 was actually programmed according to the pattern of the first template shown in Fig. 2A. When the spectrum displayed in Fig. 1C is re-plotted in 32 segments, discarding the outside parts of the overall spectrum that have no peaks, the result (shown in the leftmost part of Fig. 2B) reproduces the input pattern quite well. Two other templates with $32 \times 32 = 1024$ pixels each and the corresponding ^{1}H NMR spectra are displayed in Figs. 2A and B, respectively. A fourth template with $64 \times 16 = 1024$ pixels is shown in Fig. 2C, and the corresponding ^{1}H NMR spectrum is displayed in Fig. 2D. Although the baselines in these spectra are not completely flat, the fidelity of the NMR "photographs" is comparable to that obtained by using the pseudo-2D method [4], while the experimental time is much shorter (3.95 min each compared with 9.83 h).

When the template is not symmetrical and more complicated (Fig. 3A), the spectral pattern is recognizable but not very clear (Fig. 3B). When the spectrum is re-plotted by displaying the intensities only above a certain threshold, which is about 1/5 of the average peak

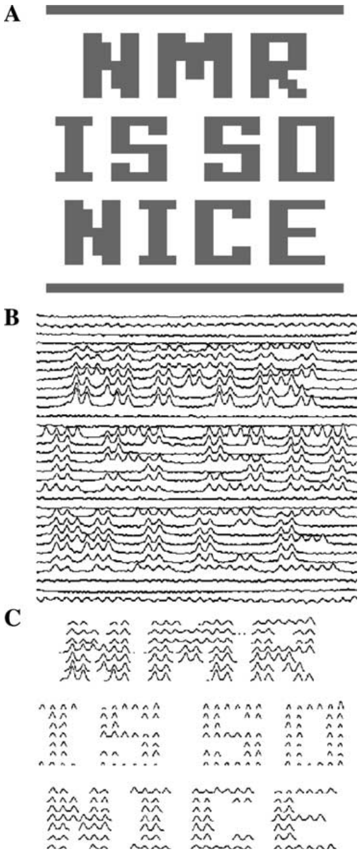

Fig. 3. (A) An asymmetric input template with $32 \times 32 = 1024$ pixels. (B) ^{1}H NMR spectrum of 5CB corresponding to the template, plotted as 32 consecutive segments of 800 Hz width each. (C) The same spectrum plotted with intensity above a fixed threshold; it should be noted that the 32 peaks in the second segment and those in the last segment have been cut off due to insufficient peak height.

height in this case, the pattern becomes more obvious (Fig. 3C). The unevenness of the peak heights is an inherent feature of the method, as the intensities of the sharp peaks are not uniform throughout the spectrum (Fig. 1C). This problem is much less noticeable when the template is symmetrical so that the baseline does not have to be eliminated for the displayed pattern to be recognized (Fig. 2).

4. Summary

The application of a weak 1024-frequency pulse to a liquid crystal for 200–500 ms can produce narrow inverted peaks on top of a broad component. The linewidths of the narrow peaks are dependent on the RF power and pulse width, and are 12–16 Hz in our experiments. When the pulse duration is shorter (a few tens of ms), the intensities of the narrow peaks are much lower. When the spectrum obtained by the longer pulse is subtracted from that obtained by the shorter pulse, the broad background is largely eliminated, and the narrow components appear as positive peaks. By plotting the 1D spectrum as a stack of spectral segments, the 2D pattern of the input template can be reproduced. Several examples are given to illustrate the results.

Acknowledgments

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References

[1] D.M. Eigler, E.K. Schweizer, Positioning single atoms with scanning tunneling microscope, Nature 344 (1990) 524–526.

[2] M.F. Crommie, C.P. Lutz, D.M. Eigler, Confinement of electrons to quantum corrals on a metal surface, Science 262 (1993) 218–220.

[3] F. Crommie, C.P. Lutz, D.M. Eigler, E.J. Heller, Waves on a metal surface and quantum corrals, Surface Rev. Lett. 2 (1995) 127–137.

[4] A.K. Khitrin, V.L. Ermakov, B.M. Fung, Nuclear magnetic resonance molecular photography, J. Chem. Phys. 117 (2002) 6903–6906.

[5] S. Fernbach, W.G. Proctor, Spin echo memory device, J. Appl. Phys. 26 (1955) 170–178.

[6] A.G. Anderson, R. Garwin, E.L. Hahn, J.W. Horton, G.L. Tucker, R.M. Walker, Spin echo serial storage memory, J. Appl. Phys. 26 (1955) 1324–1338.

[7] A.G. Anderson, E.L. Hahn, Spin echo storage technique, US Patent 2, 714,714, 1995.

[8] A.K. Khitrin, V.L. Ermakov, B.M. Fung, Information storage using a cluster of dipolar-coupled spins, Chem. Phys. Lett. 360 (2002) 161–166.

[9] A.K. Khitrin, V.L. Ermakov, B.M. Fung, NMR implementation of a parallel search algorithm, Phys. Rev. Lett. 89 (2002) 277902/1–277902/4.

[10] B.M. Fung, V.L. Ermakov, The presence of long-lived spin states in organic solids with rapid molecular motions, submitted.

[11] A.K. Khitrin, V.L. Ermakov, Spin Processor, Los Alamos National Laboratory Preprint Archives (2002) quant-ph/0205040.

[12] G.A. Morris, R. Freeman, Selective excitation in fourier transform nuclear magnetic resonance, J. Magn. Reson. 29 (1978) 433–462.

[13] Ē. Kupče, R. Freeman, Frequency-domain Hadamard spectroscopy, J. Magn. Reson. 162 (2003) 158–165.

[14] Ē. Kupče, R. Freeman, Two-dimensional Hadamard spectroscopy, J. Magn. Reson. 162 (2003) 300–310.

[15] Ē. Kupče, R. Freeman, Fast multi-dimensional Hadamard spectroscopy, J. Magn. Reson. 163 (2003) 56–63.