

## NMR with excitation modulated by Frank sequences

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### ABSTRACT

Miniaturized NMR is of growing importance in bio-, chemical, and -material sciences. Other than the magnet, bulky components are the radio-frequency power amplifier and the power supply or battery pack. We show that constant flip-angle excitation with phase modulation following a particular type of polyphase perfect sequences results in low peak excitation power at high response peak power. It has ideal power distribution in both the time domain and the frequency domain. A savings in peak excitation power of six orders of magnitude has been realized compared to conventionally pulsed excitation. Among others, the excitation promises to be of use for button-cell operated miniature NMR devices as well as for complying with specific-absorption-rate regulations in high-field medical imaging.

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### 1. Introduction

Low excitation power in NMR saves energy, reduces the size of the power supply and may eliminate the radio-frequency (RF) amplifier altogether. These are advantages in miniaturizing NMR spectrometers for use at the site of interest, such as in bio-sensing applications [1–3], in sensing and control of chemical processes, in airport security applications such as NMR fluid screening and NQR explosives and drug detection [4,5], in conducting NMR at contaminated sites, in single-sided NMR of large or precious objects, and in NMR imaging in an emergency vehicle. Low excitation power also promises to ease SAR limitations in medical imaging, opening the door for high-field imaging in medical patient care. We propose to use trains of constant-amplitude low flip-angle pulses for excitation that are modulated by a particular class of polyphase perfect sequences [6]. Such encoding recipes are known for many applications of discrete mathematics in engineering problems. The resultant excitation is reminiscent of rapid-scan NMR [7,8], however with excitation pulses modulating a constant carrier frequency. Further use of this type of excitation is anticipated in solid-state NMR of quadrupolar nuclei to enhance the signal intensity of the central transition [9].

### 2. Comparison of NMR measurement methods

The first NMR experiments were conducted with continuous wave (CW) excitation either by sweeping the strength of the ap-

plied magnetic field  $B_0$  at constant frequency  $\omega_{\text{RF}}$  of the RF excitation with amplitude  $B_1$  or by sweeping the frequency at constant field strength  $B_0$  [10,11]. As the excitation is applied continuously for the entire duration of the measurement, the RF power is sufficiently low to avoid saturation of the NMR spin system. This means, that the spin system is driven by the excitation in the linear regime, that is, that within the formalism of the Bloch equations, changes in longitudinal magnetization can be neglected, and that the transverse magnetization is linearly proportional to the excitation field strength  $B_1$ .

The disadvantage of CW NMR is low sensitivity, as the frequencies in the range of an NMR spectrum are scanned successively. This disadvantage was overcome with pulsed excitation.

Here the peak excitation power is high and so is the peak response power as the impulse response following the excitation pulse is recorded and subsequently Fourier transformed to obtain the NMR spectrum [12]. In CW NMR, the excitation spectrum is narrow and limited by the sweep rate, while the spectrum of pulsed excitation is broad and ideally flat over the width of the NMR spectrum. When breaking up the CW excitation into a series of small pulses, the low excitation peak power of CW NMR is largely maintained while a broad excitation bandwidth is introduced to excite all frequencies in the NMR spectrum simultaneously. The number of data points to be sampled in one scan, and the duration of the excitation follow the same criteria as in Fourier NMR: one scan lasts about  $5 T_2$ , the spectral width  $\pm v_{\text{max}} = \pm 1/(2\Delta t)$  is determined by the sampling interval  $\Delta t$ , and the spectral resolution  $\Delta\nu = 1/(N\Delta t)$  is determined by the total number  $N$  of sampling intervals  $\Delta t$ . As the excitation drives a linear response, scans are

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repeated without recycle delay. The straight forward way to realize such an excitation is to apply an RF pulse at the beginning and sample one transverse magnetization point towards the end of each sampling interval (Fig. 1). A practical duty cycle, that is, the duration of the RF pulse relative to the duration of the sampling interval is 10–30% (cf. caption of Fig. 1). To retrieve the NMR spectrum from the response, the components of the response signal need to be assigned to the individual excitation pulses. For this to be possible, the pulses need to be made distinguishable. A general way to distinguish the excitation pulses is by varying their amplitudes and phases randomly. This leads to noise excitation and stochastic NMR [13,14], where indeed the peak RF excitation power is several orders of magnitude lower than that in NMR with single-pulse excitation.

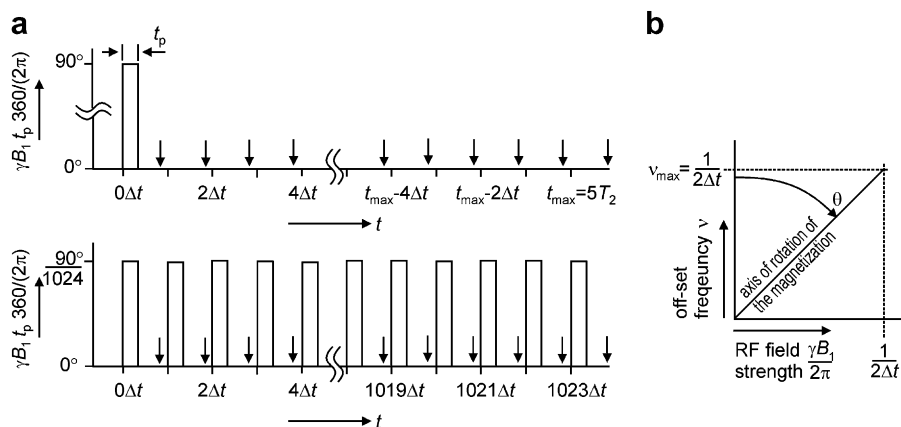
A particularly simple form of stochastic NMR is Hadamard NMR [15,16], where the RF pulse amplitudes are constant, and the pulse phases are varied in a pseudo-random fashion between two fixed values,  $-\pi/2$  and  $+\pi/2$ , following a phase modulation by binary sequences of numbers known as  $m$ -sequences. A minor shortcoming is that the sequence length is  $2^m - 1$ , where  $m$  is a positive integer. That is, the length is one less than a power of two which is a bit awkward for data processing with the fast Fourier transform algorithm. Also the power spectrum shows a singularity near zero frequency. Both features can be eliminated with random noise excitation, however at the expense of forming ensemble averages of measurement traces upon calculation of the NMR spectrum [17]. This prolongs the minimum measurement time from one scan in Hadamard NMR to the equivalent of many scans in NMR with white noise excitation. On the other hand, stochastic NMR provides strategies to measure multi-dimensional spectra by evaluation of the nonlinear response [17,18].

While the extremely low peak excitation power is an outstanding advantage of noise excitation, the extremely low peak response power is a serious drawback. Single-pulse NMR, on the other hand, produces the maximum peak response power at the start of the impulse response or free induction decay (FID) [19,20]. At short times, the impulse responses from each peak in the NMR spectrum add coherently, so that the first value of the impulse response is given by the integral of the NMR spectrum. This situation demands the least amplification in the receiver to record the received signal. The response power of CW NMR is intermediate to that of stochas-

tic NMR and pulsed NMR in the sense, that at each moment in time, the response power roughly scales with the amplitude square of the peak in the NMR spectrum which is momentarily scanned. The sensitivity of CW NMR has been improved by scanning the frequency range of the NMR spectrum rapidly [7,8]. The signal response of rapid-scan NMR is a mixture of a resonance peak and an FID each time a resonance frequency is met in scanning the spectrum. The notation “rapid-scan” NMR refers to a scanning time of the NMR spectrum which is fast compared to that of CW NMR. Yet it is slow compared to that of a fast adiabatic passage, where the magnetization follows the direction of the effective field and is inverted in a full passage [21,22]. To avoid interference of resonance lines, the linear response needs to be measured with the original rapid-scan technique [22–24], that is, scan rate and excitation amplitude were adjusted to sufficiently small values to work in the limit of the linear or slow adiabatic passage. Rapid-scan NMR has not become popular due to the fact, that only simple CW or one-dimensional spectra can be recorded, and the advent of two-dimensional NMR [25] has turned the interest to pulsed excitation which is used today almost exclusively for recording NMR data in spectroscopy and imaging [26].

A pulsed version of rapid-scan NMR has been introduced recently for NMR imaging. It is called SWIFT NMR for sweep imaging with Fourier transformation [23,27,28]. The principle of the approach is to break up one of the well-known adiabatic sweep pulses into a series of small, phase and amplitude modulated RF pulses and to sample the transverse magnetization in the gaps between the pulses just like in stochastic NMR, which has also been explored for imaging [29,30]. This concept collects many of the advantages of low-power NMR: the response power is high, and the excitation spectrum is white, so that signal averaging as in stochastic NMR is not needed. Yet it is difficult to extend the concept to multi-dimensional NMR, and the peak RF excitation power can further be reduced by eliminating amplitude modulation for the sake of phase modulation as in the novel scheme of excitation modulated by polyphase perfect sequences.

When the class of sequences derived below is used for modulating the RF excitation, an NMR spectrum can be collected in a single scan at low excitation power and a response power intermediate to that between stochastic NMR and pulsed Fourier NMR, and there is hope, that this type of excitation can be extended to extract multi-



**Fig. 1.** (a) Illustration of excitation and data acquisition in Fourier NMR (top) and stochastic NMR (bottom). The duration of one scan is  $t_{\max} = 5 T_2$ . Each sampling interval  $\Delta t$  begins with an RF pulse lasting between 10% and 30% of  $\Delta t$ . One complex data point is acquired at the position of the arrow towards the end of each sampling interval. The illustration applies to the acquisition of  $t_n = 1024$  data points in one scan. The optimum excitation flip-angle for Fourier NMR (top) is the Ernst angle, which is  $90^\circ$  for  $T_1 = T_2 = T_2^*$  and a delay of  $5 T_2$  between excitation pulses. The excitation flip-angle for the excitation scheme at the bottom is approximately  $90^\circ/1024 \approx 0.1^\circ$ . This translates into a reduction of the excitation power by a factor of  $(1024)^2 \approx 10^6$  given equal pulse widths. (b) Illustration of the effective field in frequency units to estimate the duration of the RF excitation pulse. To excite the entire spectral width  $\pm \nu_{\max} = \pm 1/(2\Delta t)$  of the largest frequency component in the spectrum as  $\gamma B_1/(2\pi) = 1/(2\Delta t)$ . Together with the definition of a  $90^\circ$  pulse of duration  $t_p$ ,  $\gamma B_1 t_p = (\pi/2)$ , one finds for the duration of the excitation pulse  $t_p \leq \Delta t/2$ .

dimensional spectra from the nonlinear response. The modulation under consideration describes an excitation pattern that approximates rotating waves of varying pitch and constant duration. One set of such waves is used to scan the spectrum. In this regard, the modulation of the excitation resembles wavelets. While the use of wavelets is known in NMR imaging for spatial signal encoding [31] and in NMR spectroscopy for signal analysis [32], their use for scanning NMR spectra in a frequency swept mode by excitation in the time domain is new.

### 3. Polyphase perfect sequences

One of the most important goals in periodic-sequence design is the construction of sequences  $(x(t_n))_{t_n=0, \dots, N-1}$  that have ideal periodic autocorrelation properties, which means that the autocorrelation function

$$A(k) := \sum_{t_n=0}^{N-1} x(t_n)x^*(t_{n+k}) = \begin{cases} E : k = 0 \\ 0 : \text{otherwise} \end{cases} \quad (1)$$

Here  $E$  might be called the *sequence energy*. Such sequences are called perfect sequences, and it can be shown that a sequence is perfect if and only if its Fourier transform  $(X(f_n))_{f_n=0, \dots, N-1}$  defined as

$$X(f_n) = \sum_{t_n=0}^{N-1} x(t_n) \exp \left\{ -i \frac{2\pi}{N} f_n t_n \right\}, \quad (2)$$

is of constant absolute value. If the sequence itself is of constant absolute value then it is called a polyphase sequence.

Two observations have been made in the literature:

1. For the binary case, i.e. for sequences that up to a constant factor take only the values  $\pm 1$ , it is strongly conjectured that, up to a permutation, only one such sequence exists, namely the sequence  $(1, 1, 1, -1)$  of length 4. For longer periods, the best autocorrelation functions have been achieved for example with so-called  $m$ -sequences (or MLBS for maximum length binary sequences). These autocorrelation functions are of the form (1). By changing the value  $-1$  to a suitable constant  $\beta$  in such a sequence the resulting sequence can be made perfect. However, the sequence obviously will not be constant by absolute value any more.
2. In the non-binary case, polyphase sequences exist with the ideal autocorrelation properties introduced above. Such sequences are called polyphase perfect sequences, and two families, namely the Frank and the Chu sequences are discussed in the sequel.

**Table 1**  
The quantity  $f_w t_w$  that defines the RF excitation pulse phases in Eq. (15) evaluated for  $m = 32$ . The rows are labelled  $f_w$  and identify the frequency of a wave package. The column index  $t_w$  counts the time increments within one wave package (cf. Fig. 2 below). Phase values in the two halves of a circle are shaded differently.

$f_w$	$t_w$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
positive frequencies	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
	1	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
	2	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	3	0	3	6	9	11	15	18	21	24	27	30	1	4	7	10	13	16	19	22	25	28	31	2	5	8	11	14	17	20	23	26	29
	4	0	4	8	12	16	20	24	28	0	4	8	12	16	20	24	28	0	4	8	12	16	20	24	28	0	4	8	12	16	20	24	28
	5	0	5	10	15	20	25	30	3	8	13	18	23	28	1	6	11	16	21	26	31	4	9	14	19	24	29	2	7	12	17	22	27
	6	0	6	12	18	24	30	4	10	16	22	28	2	8	14	20	26	0	6	12	18	24	30	4	10	16	22	28	2	8	14	20	26
	7	0	7	14	21	28	3	10	17	24	31	6	13	20	27	2	9	16	23	30	5	12	19	26	1	8	15	22	29	4	11	18	25
	8	0	8	16	24	0	8	16	24	0	8	16	24	0	8	16	24	0	8	16	24	0	8	16	24	0	8	16	24	0	8	16	24
	9	0	9	18	27	4	13	22	31	8	17	26	3	12	21	30	7	16	25	2	11	20	29	6	15	24	1	10	19	28	5	14	23
	10	0	10	20	30	8	18	28	6	16	26	4	14	24	2	12	22	0	10	20	30	8	18	28	6	16	26	4	14	24	2	12	22
	11	0	11	22	1	12	23	2	13	24	3	14	25	4	15	26	5	16	27	6	17	28	7	18	29	8	19	30	9	20	31	10	21
	12	0	12	24	4	16	28	8	20	0	12	24	4	16	28	8	20	0	12	24	4	16	28	8	20	0	12	24	4	16	28	8	20
	13	0	13	26	7	20	1	14	27	8	21	2	15	28	9	22	3	16	19	10	23	4	17	30	11	23	5	18	31	12	25	6	19
	14	0	14	28	10	24	6	20	2	16	30	12	26	8	22	4	18	0	14	28	10	24	6	20	2	16	30	12	26	8	22	4	18
	15	0	15	30	13	28	11	26	9	24	7	22	5	20	3	18	1	16	31	14	29	12	27	10	25	8	23	6	21	4	19	2	17
16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	0	16	
17	0	17	2	19	4	21	6	23	8	25	10	27	12	29	14	31	16	1	18	3	20	5	22	7	24	9	26	11	28	13	30	15	
18	0	18	4	22	8	26	12	30	16	2	20	6	24	10	28	14	0	18	4	22	8	26	12	30	16	2	20	6	24	10	28	14	
19	0	19	6	25	12	31	18	5	24	11	30	17	4	23	10	29	16	3	22	9	28	15	2	21	8	27	14	1	20	7	26	13	
20	0	20	8	28	16	4	24	12	0	20	8	28	16	4	24	12	0	20	8	28	16	4	24	12	0	20	8	28	16	4	24	12	
21	0	21	10	31	20	9	30	19	8	20	18	7	28	17	6	27	16	5	26	15	4	25	14	3	24	13	2	23	12	2	22	11	
22	0	22	12	2	24	14	4	26	16	6	28	18	8	30	20	10	0	22	12	2	24	14	4	26	16	6	28	18	8	30	20	10	
23	0	23	14	5	28	19	10	1	24	15	6	29	20	11	2	25	16	7	30	21	12	3	26	17	8	31	22	13	4	27	18	9	
24	0	24	16	8	0	24	16	8	0	24	16	8	0	24	16	8	0	24	16	8	0	24	16	8	0	24	16	8	0	24	16	8	
25	0	25	18	11	4	29	22	15	8	1	26	19	12	5	30	23	16	9	2	27	20	13	6	31	24	17	10	3	28	21	14	7	
26	0	26	20	14	8	2	28	22	16	10	4	30	24	18	12	6	0	26	20	14	8	2	28	22	16	10	4	30	24	18	12	6	
27	0	27	22	17	12	7	2	29	24	19	14	9	4	31	26	21	16	11	6	1	28	23	18	13	8	3	30	25	20	15	10	5	
28	0	28	24	20	16	12	8	4	0	28	24	20	16	12	8	4	0	28	24	20	16	12	8	4	0	28	24	20	16	12	8	4	
29	0	29	16	23	20	17	14	11	8	5	2	31	28	25	22	19	16	13	10	7	4	1	30	27	24	21	18	15	12	9	6	3	
30	0	30	28	26	14	22	20	18	16	14	12	10	8	6	4	2	0	30	28	26	14	22	20	18	16	14	12	10	8	6	4	2	
31	0	31	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	

Polyphase perfect sequences find applications in many areas of modern communications technology. They are used in channel estimation, equalization and radar technology, to mention just a few. Frank sequences as introduced below were first published by Heimiller [6], but they were discovered 9 years earlier by Frank (cf. [33]). Chu sequences were introduced in [34] and earlier by Zadoff (cf. [35]). They exist for any length  $N > 1$  which might be considered an advantage in comparison with Frank sequences that exist only for lengths being perfect squares. The application in NMR, however, shows that Frank sequences will be the ones in demand, as their implementation requires less sophisticated hardware. Both Frank and Chu sequences may be considered as *generalized bent function sequences*. For details the reader is referred to [36].

#### 4. Frank sequences

Let  $m$  be a positive integer. We consider the sequence  $x(t_n)_{n=0, \dots, m^2-1}$  where

$$x(t_n) = \exp \left\{ i \frac{2\pi}{m} t_w f_w \right\}, \quad (3)$$

where

$$t_n = mf_w + t_w, \quad (4)$$

and  $f_w$  is the quotient and  $t_w$  the remainder when dividing  $t_n$  by  $m$ . Apparently  $x(t_n)$  is of constant value 1 and takes  $m$  distinct phases.

The Fourier transform  $X$  of  $x$  can easily be computed as

$$\begin{aligned} X(f_n) &= \sum_{t_n=0}^{m^2-1} x(t_n) \exp \left\{ -i \frac{2\pi}{m^2} f_n t_n \right\} \\ &= \sum_{f_w, t_w=0}^{m-1} \exp \left\{ i \frac{2\pi}{m^2} (mf_w t_w - f_n t_n) \right\} \\ &= \sum_{f_w, t_w=0}^{m-1} \exp \left\{ i \frac{2\pi}{m^2} (mf_w t_w - mf_w f_n - t_w f_n) \right\} \\ &= \sum_{t_w=0}^{m-1} \exp \left\{ -i \frac{2\pi}{m^2} t_w f_n \right\} \cdot \sum_{f_w=0}^{m-1} \exp \left\{ i \frac{2\pi}{m^2} mf_w (t_w - f_n) \right\}. \end{aligned} \quad (5)$$

A well-known argument from character theory reveals that

$$\sum_{f_w=0}^{m-1} \exp \left\{ i \frac{2\pi}{m} f_w (t_w - f_n) \right\} = \begin{cases} m & \text{if } t_w = f_n \pmod{m}, \\ 0 & \text{otherwise,} \end{cases} \quad (6)$$

such that the final expression for  $X$  is given by

$$X(f_n) = m \cdot \exp \left\{ -i \frac{2\pi}{m^2} (f_n \pmod{m}) f_n \right\}. \quad (7)$$

This expression is of constant absolute value  $m$ , hence  $x$  is a polyphase perfect sequence. As mentioned above, the sequence  $x$  assumes  $m$  distinct phases, and it is of length  $m^2$ .

#### 5. Chu sequences

Let  $N$  be a positive integer, we define the Chu sequence  $(x(t_n))_{t_n=0, \dots, N-1}$  with

$$x(t_n) = \begin{cases} \exp \left\{ i \frac{\pi}{N} t_n (t_n + 1) \right\} & : N \text{ odd,} \\ \exp \left\{ i \frac{\pi}{N} t_n^2 \right\} & : \text{otherwise.} \end{cases} \quad (8)$$

This is a polyphase sequence that takes  $N$  distinct phases in general. To show for the case  $N$  even that this sequence is perfect, the Fourier transform is computed,

$$\begin{aligned} X(f_n) &= \sum_{t_n=0}^{N-1} x(t_n) \exp \left\{ -i \frac{2\pi}{N} f_n t_n \right\} \\ &= \sum_{t_n=0}^{N-1} \exp \left\{ i \frac{\pi}{N} (t_n^2 - 2f_n t_n) \right\} \\ &= \sum_{t_n=0}^{N-1} \exp \left\{ i \frac{\pi}{N} [(t_n - f_n)^2 - f_n^2] \right\} \\ &= \exp \left\{ -i \frac{\pi}{N} f_n^2 \right\} \sum_{t_n=0}^{N-1} \exp \left\{ i \frac{\pi}{N} t_n^2 \right\}, \end{aligned} \quad (9)$$

where the latter can be shown to be of absolute value

$$\left| \sum_{t_n=0}^{N-1} \exp \left\{ i \frac{\pi}{N} t_n^2 \right\} \right| = \sqrt{N}. \quad (10)$$

This shows that the Chu sequences are polyphase perfect sequences. Finally it is noted, that Chu sequences assume in general up to  $N$  different phases which makes them less useful for the purpose discussed in this paper.

In NMR experiments phase-modulated excitation of constant amplitude and quasi continuous in time but shared in its use of the radio-frequency coil with the detection is advantageous in terms of low excitation peak power. Such an array of excitation data might typically have a length of 256 up to 1024. Using Frank sequences as modulating sequence for the phase of this excitation, the underlying hardware needs to implement only 16 up to 32 distinct equidistant phases, whereas the Chu sequences depend on an implementation of 256 up to 1024 phases. This might exceed the current technical limits of the spectrometer hardware.

Alternative approaches have considered the use of functions with almost ideal properties in time and frequency domain. The  $m$ -sequences used in Hadamard NMR are of length  $2^m - 1$  and take two values in the time domain. Their Fourier spectrum is not constant but assumes exactly two different values by absolute value. Binary phase modulation was attractive in early stages of hardware design in NMR when only a few distinct phases in the modulation could be implemented. Several types of modifications of Frank sequences can be applied in order to obtain sequences with similar properties. These will be elaborated in a subsequent publication.

#### 6. Alternative derivation of the sequences

It is shown in the following that an implementation of Eq. (3) to modulate a string of excitation pulses in NMR with interleaved sampling of the transverse magnetization response leads to a quasi-continuous excitation with a sequence of wave packages which is reminiscent of a sequence of wavelets. To assure constant amplitude excitation pulses, the modulation  $x(t)$  of the radio-frequency carrier is taken as a discrete representation of rotating waves

$$x(t) = \exp \{ i2\pi f t \} \quad (11)$$

over finite durations of time  $t$ . In this representation, the frequencies  $f$  are written as

$$f = f_w / (m\Delta t), \quad (12)$$

where  $f_w$  counts the number of turns within a fixed time  $m\Delta t$ ,  $m$  is an integer, and  $\Delta t$  is a constant time interval which corresponds to the sampling interval in NMR in our case. The symbol  $t$  denotes the time coordinate of the rotating wave. It progresses in increments  $\Delta t$ , so that

$$t = t_w \Delta t, \quad (13)$$

where  $t_w$  counts the time increments within a rotating wave of given frequency  $f$ . Consequently

$$0 \leq t_w < m. \quad (14)$$

As the frequency of a rotating wave is unambiguously determined by its phase at two points in time within one period, and as positive and negative frequencies can be distinguished in (11), a total of  $m$  frequencies or turns  $f_w$  can be counted on a discrete time grid in a fixed time of duration  $m\Delta t$ .

With the help of (12) and (13), (11) is rewritten on the discrete time grid  $t = t_n\Delta t$  of all rotating waves belonging to the same set as

$$x(t_n\Delta t) = \exp\{i2\pi f_w t_w/m\}, \quad (15)$$

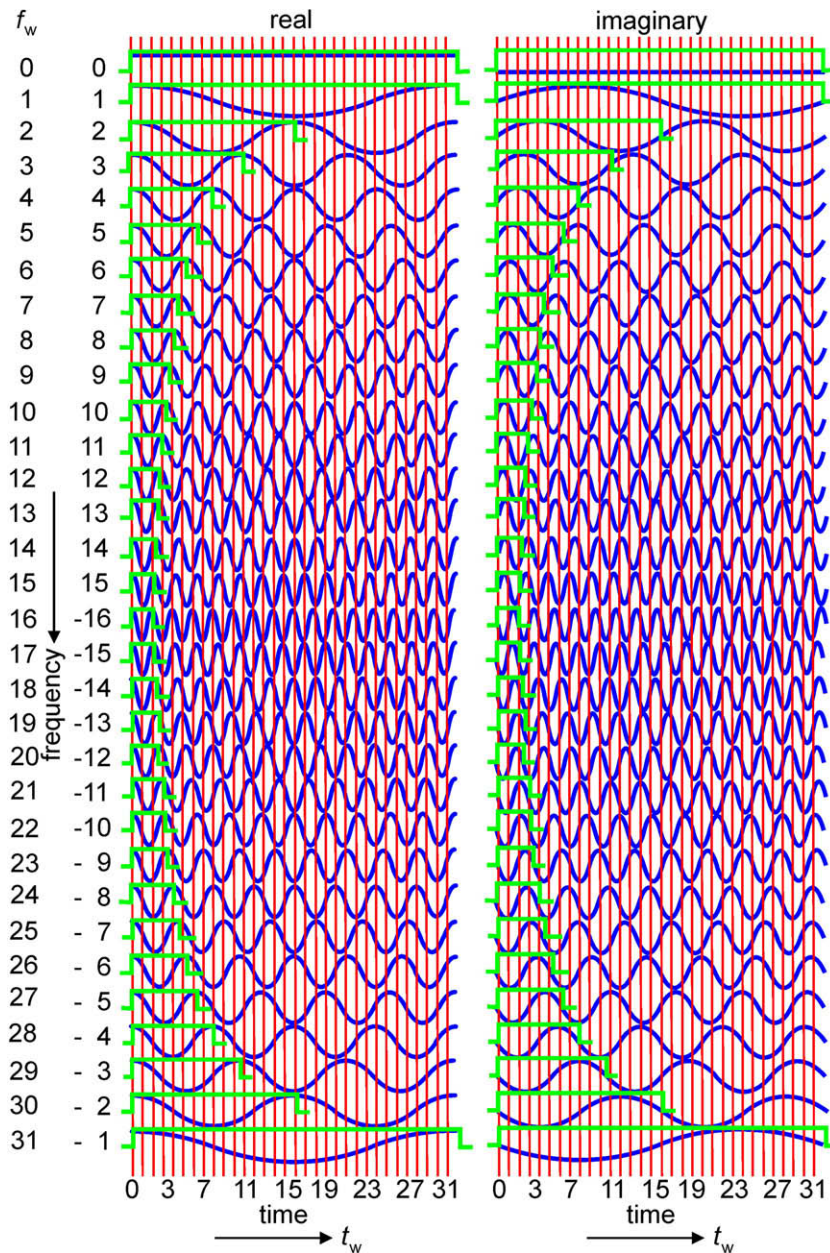
where  $f_w$  and  $t_w$  fulfill  $t_n = mf_w + t_w$  (cf. Eq. (4)), and Eq. (15) agrees with Eq. (3). Obviously,  $|x|$  is of constant absolute value 1.

As an example, take  $m = 32$ . Inserting the values 0, 1, ..., 31 for  $f_w$  and  $t_w$  in (15), one obtains 1024 phase angles distributed evenly

across the circle in increments of  $2\pi/m$ . Given that the maximum phase angle is  $2\pi$ , the product  $f_w t_w$  is evaluated modulo 32. The resultant values are collected in Table 1.

## 7. NMR spectroscopy with excitation modulated by Frank sequences

The wave-package excitation defined in Eq. (15) is a discrete representation of rotating waves with constant amplitude and with an integral number  $f_w$  of helical turns in a fixed time span  $m\Delta t$ . The numbers resulting for  $m = 32$  (Table 1) were used in our NMR experiments to modulate the RF carrier near the resonance frequencies. Fig. 2 illustrates the excitation scheme. For  $m = 32$ , one obtains 32 wave packages, each defined on 32 discrete



**Fig. 2.** Illustration of the excitation based on a Frank sequence of length 1024. The vertical axes denote the projections of the RF pulse phase along the real and imaginary directions of the rotating coordinate frame (cf. Table 1). The 32 vertical lines divide the time axis of a wave package into 32 intervals  $\Delta t$  during each of which one RF pulse is applied, and one data point is acquired. In one excitation scan, the 32 wave packages with frequencies identified by  $f_w$  and defined on a time axis  $t_w \Delta t$  are applied successively for excitation. Each wave package excites one frequency window. Multiple scans are repeated without a recycle delay. The rectangular envelopes identify the wave packages of minimum duration to highlight the similarity with wavelets [32].

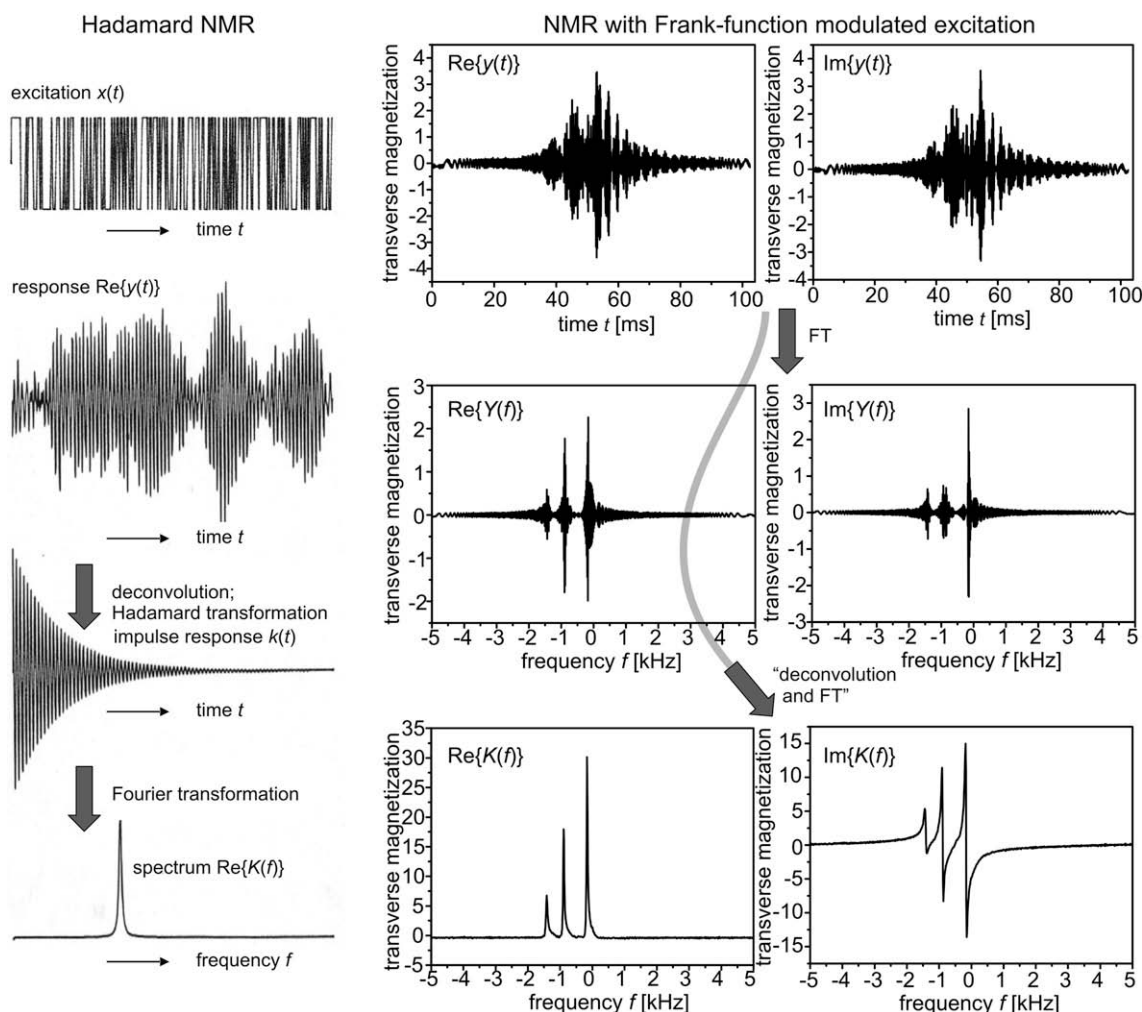
time intervals  $\Delta t$ . The number of turns varies systematically from 0 to  $(m/2) - 1$  and then from  $-m/2$  to  $-1$  as  $f_w$  runs from 0 to 31. The phase angles identified at times  $n\Delta t$  define the phases of successive, constant-amplitude, small-flip-angle RF pulses. One pulse is applied at the beginning of each sampling interval and one data point is acquired just after each pulse as is customary for time-shared excitation such as noise excitation (cf. Fig. 1). These wave packages are applied in succession without delay to excite successive frequency bands of the spectrum. Clearly, if wave packages are skipped in the excitation, the corresponding frequency window is skipped, and spectral regions can be acquired selectively as in excitation by colored noise [37] or in Hadamard NMR with frequency selective pulses [38].

As an aside it is noted, that this property implies two avenues to arrive at multi-dimensional spectra. One follows the direction of nonlinear stochastic NMR [17,18] with Frank-sequence modulated excitation in the nonlinear regime and the other follows the direction of multi-frequency selective excitation [39].

As in rapid-scan NMR, the acquired response needs to be cross-correlated with the excitation and subsequently Fourier trans-

formed to arrive at an undistorted spectrum. In Hadamard NMR (Fig. 3, left), the acquired magnetization  $y(t)$  is subjected to the Hadamard transformation, which is the equivalent of a cyclic cross-correlation. The resultant impulse response  $k(t)$  is Fourier transformed to obtain the spectrum  $K(f)$ . By making use of the convolution theorem, the cross-correlation step can be executed in the frequency domain by multiplying the complex conjugate  $X^*(f)$  of the excitation spectrum  $X(f)$  with the response spectrum  $Y(f)$  to obtain the spectrum  $K(f) = Y(f)X^*(f)/|X(f)|^2$  directly [40]. This is how the ethanol spectrum (Fig. 3, right) has been computed from the excitation and measured response data.

The response data were recorded on a Bruker DMX 300 MHz NMR spectrometer with a conventional 5 mm diameter sample tube. The RF excitation power determined with the help of an oscilloscope was 35  $\mu$ W only which compares to about 35 W to record the same spectrum with single-pulse excitation. The resultant savings in peak power corresponds to a factor of  $10^6$  in agreement with the expectation (see above). With the peak RF power  $P = RI^2$  being proportional to the impedance  $R$  and the square of the current  $I$ , the power is proportional to the square of the excitation field



**Fig. 3.** Comparison of Hadamard NMR (left) and Frank sequence based NMR (right). Both use constant-amplitude, small-flip-angle pulses with phase modulation. Hadamard NMR uses binary phase modulation (top left), and Frank sequence based NMR (top right and Fig. 2) uses  $m$  phases, for example  $m = 32$  in our case. The response to the pseudo-random binary excitation in Hadamard NMR is a wobbling train of transverse magnetization which persists as long as the excitation is cycled (left). Note that this response is very weak and not drawn to scale relative to the response to Frank-function modulated excitation. Cross-correlation with the excitation is achieved by Hadamard transformation and the impulse response is obtained. The spectrum is then computed in the conventional way by Fourier transformation. The response to excitation modulated by a Frank sequence (right) already bears the signature of the spectrum owing to the twofold nature of the excitation being a function of time as well as of frequency. This gives significantly higher response amplitude than in Hadamard NMR (left) as the response peaks in the vicinity of the resonances similar to the response in CW NMR. The deconvolution of the response (top right) into a spectrum (bottom right) is achieved by complex multiplication of excitation and response spectra. The Frank sequence based NMR spectrum was acquired for ethanol on an NMR spectrometer with 4 scans in 4 s. As the spectrometer had no high-resolution shims, the splitting due to  $J$ -coupling is not resolved.

strength  $B_1$ . The excitation energy  $E = Pt_p$  is given by the product of the RF power and the excitation pulse duration  $t_p = \alpha/(\gamma B_1)$ , where  $\alpha$  is the pulse-flip-angle and  $\gamma$  the gyromagnetic ratio, so that the excitation energy  $E$  is proportional to  $B_1$ . The resultant savings in energy thus is a factor of 1000. This means that instead of by a car battery, future sub-compact NMR spectrometers can be operated without RF amplifiers on standard sample tubes, which so far appeared feasible only for micro-coil NMR [1–3], and be powered by a button cell.

In imaging, excitation with polyphase perfect sequences and particularly Frank sequences has the potential to reduce the specific-absorption-rate (SAR). The SAR is proportional to the time integral of the RF power, that is, to the excitation energy, so that a considerable reduction can be expected from Frank sequence excitation. As the SAR increases with increasing frequency, such excitation may be of particular interest for clinical applications of high-field imaging. Other applications are conceived in NQR land-mine detection, where portable magnetic resonance instruments are employed, in airport security applications for NMR explosives detection, for signal enhancement in NMR of quadrupolar nuclei with half integral spins by transferring magnetization from satellite transitions to the central transition, and in fast schemes for multi-dimensional NMR spectroscopy.

## 8. Summary

A new low-power excitation scheme for NMR has been presented. The excitation consists of constant-amplitude, small-flip-angle pulses, the phases of which are modulated according to a family of polyphase perfect sequences known as Frank sequences. A case in which the phases follow discrete helices has been realized experimentally. By systematic variation of the helix pitch, the number of helix turns in a given time interval is changed in steps. A change in the number of turns by integral numbers results in a white excitation which sweeps the frequency range defined by the sampling rate. This type of excitation with Frank sequences minimizes the peak excitation power and maximizes the response power in NMR. In this aspect, excitation with Frank sequences is superior to the SWIFT method used for magnetic resonance imaging. Linear excitation can be used of spectroscopy and imaging, while nonlinear excitation is expected to be useful for multi-dimensional NMR spectroscopy. The correspondence of the frequency axis to the pitch of the rotating-wave modulation opens the possibility for selective excitation to suppress solvent signals and to skip regions of no interest in one- and multi-dimensional spectroscopy, thus accelerating the measurement. While the most outstanding advantages of the new excitation scheme are in low-power spectroscopy for portable spectrometers including NQR machines as well as in high-field magnetic resonance imaging, further applications are envisioned in NMR spectroscopy of quadrupolar nuclei and in fast multi-dimensional NMR spectroscopy.

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