Journal of Magnetic Resonance 302 (2019) 28–33

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Improved ultra-broadband chirp excitation

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ARTICLE INFO

Article history:
Received 14 February 2019
Revised 20 March 2019
Accepted 21 March 2019
Available online 26 March 2019

Keywords:
Chirp excitation
Chirp pulses
Ultra-broadband excitation
CHORUS

ABSTRACT

The design and application of ultra-broadband excitation pulses have been among the most interesting and timely areas in NMR and EPR methodology in recent years, due especially to advances in hardware design in EPR, the advent and popularity of high- and ultrahigh-field NMR, and the application of numerical methods like optimal control theory to the design and optimization of radiofrequency pulses and pulse sequences. In this communication, we present a short, robust, and flexible version of the CHORUS family of constant-phase, very broadband excitation sequences. We demonstrate that more than 0.5 MHz excitation with uniform amplitudes and phases can be achieved with this excitation sequence.

1. Introduction

The design of pulses and pulse sequences with wide excitation bandwidth and reduced sensitivity to instrumental imperfections is an area of great interest in the field of NMR and EPR method development. In NMR, robust broadband excitation of nuclei with wide chemical shift ranges (^{19}F, ^{31}P, ^{13}C, ^{195}Pt, etc.) can pose serious challenges, especially at higher magnetic fields where the limited radiofrequency power available in spectrometers leads to off-resonance effects that distort both signal intensities and phases. This is a particular problem in multi-pulse experiments, where the effects of resonance offset can be cumulative. In pulsed EPR spectroscopy, the problem of limited excitation bandwidth is much more serious than in NMR, and affects the majority of experiments.

The development of methods for broadband excitation generally follows one or more of three distinct routes: composite pulse design [1–7]; evolutionary numerical methods like optimal control theory (OCT) [8–17]; and design of swept-frequency pulses [18–25]. The theory describing the use of adiabatic swept-frequency pulses for inversion and refocusing [26–30] and for broadband heteronuclear decoupling [31–35] has been well covered in the literature. The theory of signal excitation, as opposed to inversion or refocusing using these pulses, has also been discussed in detail, albeit more recently [19,21–23,36]. Here we present a simple approach to explaining and designing frequency-swept pulses for signal excitation, based on simple basic principles and taking advantage of the linearity of the frequency variation with time in a standard "chirp" pulse. We start with double chirp excitation [19,21,22] and the problems associated with it, leading on to the introduction of triple-pulse excitation methods such as ABSTRUSE [23] and CHORUS [24,25]. In particular, we explore one hitherto neglected feature of the CHORUS triple chirp excitation sequence that makes it possible to build a very robust compressed version of this pulse sequence. This modified sequence can, counter-intuitively, be shorter than the corresponding double chirp sequence, thanks to the additional degree of freedom afforded by the third chirp pulse.

2. Results and discussion

The application of swept-frequency chirp pulses to excitation has a shorter history than their use as inversion pulses, but has still been reported both in NMR [19,23,24] and EPR [37,38] spectroscopy. A single chirp excitation pulse of duration τ_p has exactly the same form as an adiabatic inversion pulse, sweeping linearly through a frequency range ΔF at a constant sweep rate $\Delta F/\tau_p$, but uses a radiofrequency amplitude that is well below the adiabatic threshold. A linear sweep is not essential, but works well and simplifies the generation and optimization of these pulses. The radiofrequency amplitude ν_{RF} Hz of a chirp pulse is related to its degree of adiabaticity Q [26,33] by Eq. (1):

$$\nu_{\mathrm{RF}} = \sqrt{\frac{\Delta F Q}{2\pi\tau_{\mathrm{p}}}} \quad (1)$$

The effective flip angle of a chirp pulse only approaches 180° asymptotically as the radiofrequency amplitude ν_{RF} increases, but for most practical purposes a Q factor of 5 provides good adiabaticity [33,39].

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https://doi.org/10.1016/j.jmr.2019.03.007
1090-7807/

The relationship between the radiofrequency amplitude and the duration and sweep width needed for a chirp pulse to produce a given flip angle below 180° can be expressed in terms of Q as:

$$Q = \frac{2}{\pi}\ln\left(\frac{2}{\cos\beta + 1}\right) \tag{2}$$

Setting ν_{RF}, ΔF, and τ_p to give $Q = 0.441$ will thus give a flip angle β of 90° [40,41]. Although a chirp pulse with $\beta = 90°$ will achieve efficient broadband excitation, at first sight this is of little use, since the frequency sweep leads a very rapid, and nonlinear, variation of signal phase with frequency. However this phase dispersion can be refocused by further chirp pulses.

Since a chirp with a linear frequency sweep excites resonances with different offsets at different times, spins spend different amounts of time in the transverse plane following excitation. They therefore acquire phases that vary quadratically with offset, and that hence cannot be corrected using standard zero- and first-order phase correction algorithms (Fig. 1). It is possible to process such data using magnitude (absolute value) presentation, but unless all signals are widely spaced this leads to serious lineshape and peak height anomalies. By assuming that a chirp pulse generates an instantaneous spin rotation at the point of resonance, the overall phase can be approximated as the sum of three independent terms:

$$\varphi_{tot} = \varphi_0 + 2\pi f\left(\frac{\tau_p}{2}\right) + 2\pi f^2\left(\frac{\tau_p}{2\Delta F}\right) \tag{3}$$

where φ_0 is the usual zero-order phase correction and f is the frequency offset from the midpoint of the spectrum, and varies from $-sw/2$ to $sw/2$. This observation suggests that in order to compensate for the phase distortion induced by the single chirp excitation pulse one simply needs to apply a matched offset-dependent refocusing pulse, i.e. a 180° chirp pulse. This double-chirp excitation scheme, introduced by Kunz in magnetic resonance imaging [18], and later by Bodenhausen and co-workers in NMR spectroscopy [19–22] was used for the first reported applications of swept-frequency chirp pulses for excitation with refocused phase errors (Fig. 2a).

Double chirp excitation solves, to first order, the problem of the linear and quadratic phase shifts seen with single chirp excitation,

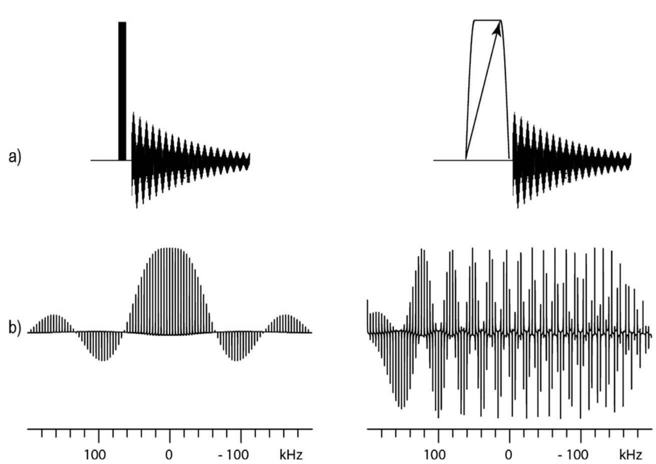

Fig. 1. (a) Pulse sequences for broadband excitation, using (left) a hard pulse and (right) a frequency-swept chirp pulse, and (b) Calculated excitation profiles at (left) for a 15 µs hard pulse, after linear phase correction for the finite pulse duration, and (right) a 100 µs single chirp pulse, for 101 isolated spins-1/2 at equal frequency intervals over a 400 kHz range, with no phase correction; both profiles were simulated using SPINACH [42] in MATLAB.

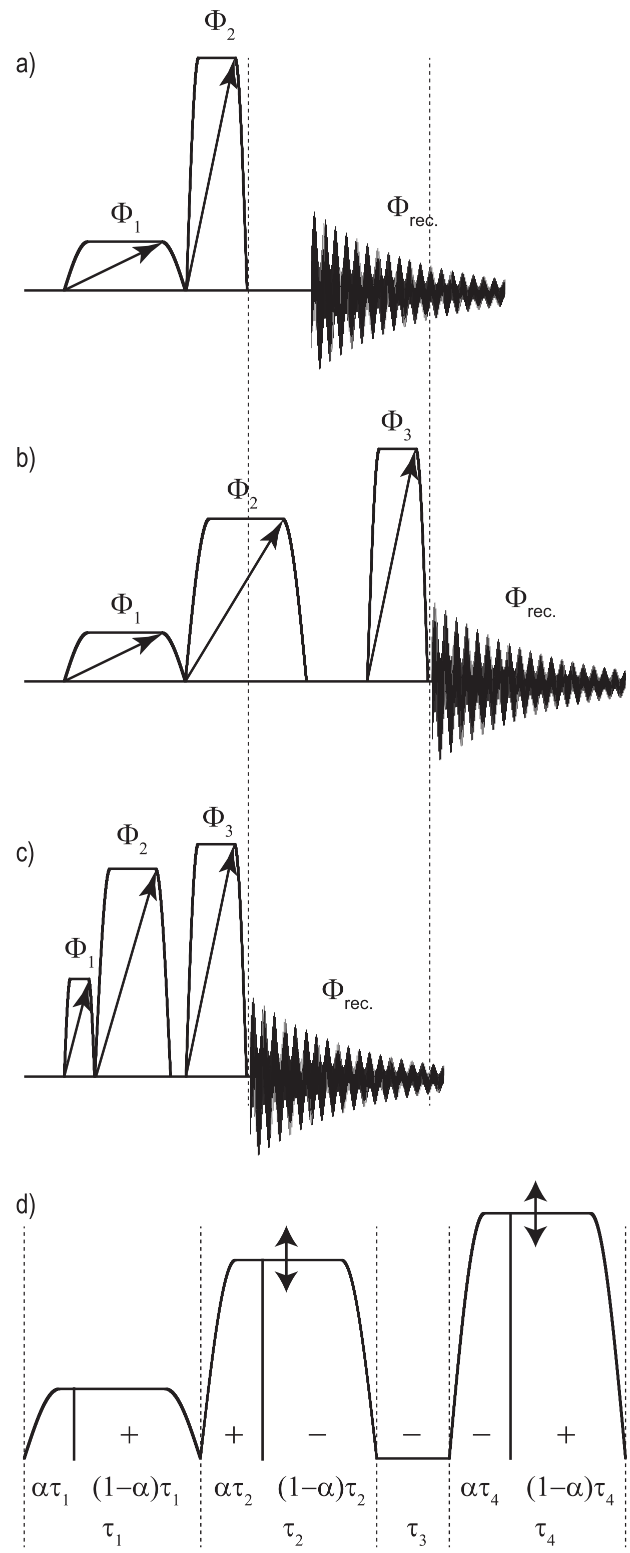

Fig. 2. Pulse sequences for chirp excitation. (a) The original double chirp sequence of reference [19]; (b) CHORUS, as presented in reference [24], (c) compressed CHORUS, which has half the duration of CHORUS for the same peak radiofrequency amplitude and excitation bandwidth; and d) general pulse sequence scheme for CHORUS sequences. All chirp pulses have the same bandwidth (ΔF). The durations of the chirp pulses (τ_1,τ_2,τ_4) and the fixed delay (τ_3) and the relative radiofrequency amplitudes of the 180° chirp pulses (high power trapezoids), shown with two-headed vertical arrows, are adjusted as described in the main text.

using the additional 180° chirp pulse to refocus the chemical shift evolution that occurs during the 90° chirp pulse. Although this approach was historically important and has found applications both in NMR [19–22] and more recently in EPR [37,38], it suffers from two drawbacks. First, the timing of the sequence is fixed: a 90° chirp pulse of duration τ_p has to be followed by a 180° chirp pulse of duration $\tau_p/2$ and a delay of $\tau_p/2$. Second, the cancellation of the quadratic phase shift is incomplete, because the 180° pulse introduces a further (but much smaller) phase roll across the spectral window, the magnitude of which is very dependent on the strength of the radiofrequency field B_1 used [23,43]. Because the inhomogeneity of the radiofrequency field in practical NMR spectrometers causes the amplitude of B_1 to vary across the sample, even with the best modern probes the variation in signal phase with position leads to signals from different regions of the sample interfering destructively, and results in a significant signal loss (Fig. 3a and 4b).

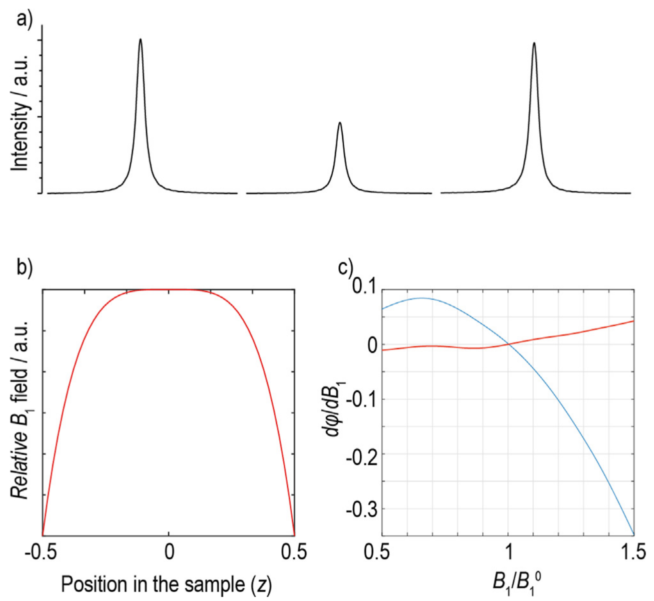

Fig. 3. (a) Calculated on-resonance signal for a conventional hard pulse (left), and double chirp (middle), and CHORUS (right) pulse sequences. To simulate the impact of B_1 field inhomogeneity, the calculated signal is averaged over the spatial RF amplitude variation of a typical high resolution probe over the sample, as shown in (b). (c) Sensitivity of signal phase to radiofrequency amplitude $\frac{d\varphi}{dB_1}$ as a function of relative amplitude for original CHORUS (blue) and compressed CHORUS (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cano et al. demonstrated an elegant method to fix the problem of the extreme sensitivity of double chirp excitation to B_1 inhomogeneity, by the addition of a third swept-frequency pulse [23]. The ABSTRUSE (Adjustable, Broadband, Sech/Tanh-Rotation Uniform Selective Excitation) pulse sequence uses three hyperbolic secant pulses and is primarily designed to give a rectangular excitation spectrum rather than to excite a wide bandwidth. While ABSTRUSE provides very effective and easily tuneable excitation over a reasonably wide range, the hyperbolic secant pulses require much higher radiofrequency amplitudes for a given bandwidth than chirp pulses. The equivalent pulse sequence using three chirp pulses, CHORUS, (CHirped, Ordered pulses for Ultra-broadband Spectroscopy) was proposed by Power et al. [24] (Fig. 2b), and gives both very wideband excitation and much better - close to perfect - phase uniformity. The CHORUS method offers much wider excitation bandwidth for a given radiofrequency amplitude than ABSTRUSE, and has been used for measuring both 1D [24] and DOSY [25] spectra of fluorinated pharmaceuticals.

A further difference between the CHORUS approach and ABSTRUSE is the use of polynomial fitting to determine and eliminate the residual phase variation across the spectrum. In practice, a chirp pulse does not generate an instantaneous rotation, and there

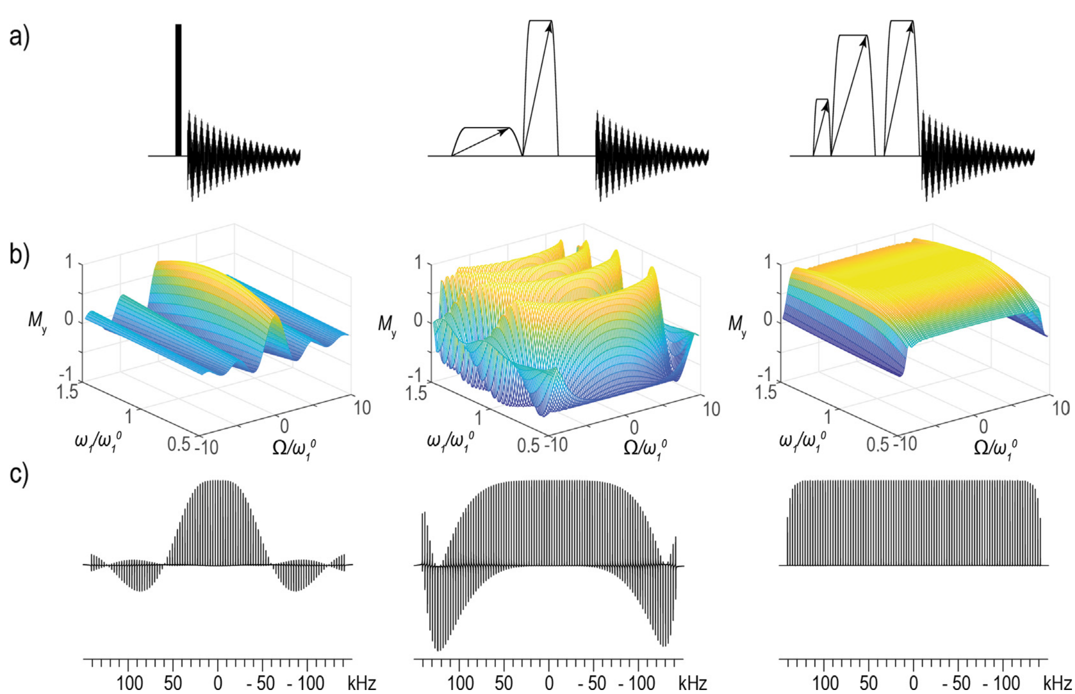

Fig. 4. (a) Pulse sequences for broadband excitation, using (left) a hard pulse, (middle) a double chirp, and (right) compressed CHORUS (as in Fig. 2c). (b) 3D plots showing the y-magnetization (M_y) excited as a function of relative resonance offset (Ω/ω_1^0) and relative radiofrequency amplitude ω_1/ω_1^0. (c) Calculated excitation profiles at $\omega_1 = \omega_1^0$ (left) for a 15 μs hard pulse after first-order phase correction, (middle) for the double chirp pulse, and (right) for CHORUS, for 101 uncoupled spins-1/2 at equal frequency intervals over a 300 kHz range, simulated using SPINACH [42] in MATLAB.

is a small further perturbation of the signal phase due to the off-resonant effect of the radiofrequency field as it first approaches, and then recedes from, exact resonance. This phase problem can be seen as a residual Bloch-Siegert phase shift [23,44].

Fortunately, one advantage of chirp pulses is that there is a one-to-one correspondence between time and frequency, so a small change in the phase of the pulse at some time t, at which the pulse frequency has reached f, will result in a similar change in the phase of the signal that is excited at the frequency f. This means that if simulations of the performance of a candidate chirp pulse or pulse sequence show a small residual dependence of signal phase on frequency, this can be corrected, typically by fitting the calculated signal phase error $\Delta\psi(f)$ to a polynomial as a function of frequency, then mapping this on to the pulse shape and adding it to or subtracting it from the pulse phase as appropriate. For a chirp pulse of duration τ_p sweeping from f_{min} to f_{max}, the time-dependent phase correction is given by Eq. (4).

$$\Delta\phi(t) = \Delta\psi\left(f_{min} + \frac{t(f_{max} - f_{min})}{\tau_p}\right) \quad (4)$$

A tailored correction of the residual phase error in a triple chirp (CHORUS) experiment can be done using polynomial fitting of the calculated residual phase errors to find $\Delta\psi(f)$, and then using this function in Eq. (4) to correct the phase profile of the first pulse of the sequence. The result of this process is shown in Fig. 5.

A general B_1-compensated excitation pulse sequence consists of one excitation chirp pulse, two 180° chirp pulses, and one fixed delay, of durations τ_1 to τ_4, respectively, as shown in Fig. 2d. An ideal pulse sequence should satisfy two independent requirements: first, the sequence should refocus the effects of resonance offset so that all signals are excited with the same phase, independent of frequency; and second, that phase should be substantially independent of B_1. One advantage of using linear frequency sweep chirp pulses is that the first requirement is satisfied if

$$(1-\alpha)\tau_1 + (2\alpha - 1)\tau_2 - \tau_3 - (2\alpha - 1)\tau_4 = 0 \quad (5)$$

where α, which lies between 0 and 1, is the fraction of the chirp pulse duration at which the frequency sweep reaches a given arbitrary frequency of interest.

Here we take advantage of a neglected feature of triple chirp (CHORUS) excitation, which is that all that is needed to eliminate the quadratic phase roll of the 90° chirp pulse is to mismatch the durations of the two 180° chirps by half the duration of the 90° chirp pulse (if all three pulses have the same sweep width), adjusting the relative RF amplitudes of the 180° chirp pulses accordingly [23]. This property makes it possible to build a compressed version of the CHORUS excitation pulse sequence, (Fig. 2c), since one can now use a much shorter 90° chirp pulse.

One set of timings that satisfies the first requirement, Eq. (5), is 500 μs, 1250 μs, 250 μs, and 1000 μs for τ_1 to τ_4 respectively. This sequence has a total duration of 3 ms, which is 25% shorter than the corresponding double chirp sequence and 50% shorter than the original CHORUS excitation sequence using the same peak radiofrequency amplitude. With this sequence, as shown in Fig. 4, one can achieve nearly 300 kHz of uniform excitation when the RF amplitudes are set to 6.49 kHz, 13.82 kHz, and 15.45 kHz respectively, giving an overall RF_{rms} of 12.56 kHz. Another example, the results of which is presented in Fig. 6, uses timings of 500 μs, 1750 μs, 250 μs, and 1500 μs for τ_1 to τ_4 respectively, with a total duration of 4 ms, which is 33% shorter than the corresponding double chirp sequence using the same peak radiofrequency amplitude. With this sequence using a set of 9.18 kHz, 16.52 kHz and 17.87 kHz RF amplitudes, with an overall RF_{rms} of 15.38 kHz, nearly 600 kHz excitation bandwidth can be achieved. By comparing these two examples, it is evident that thanks to the additional

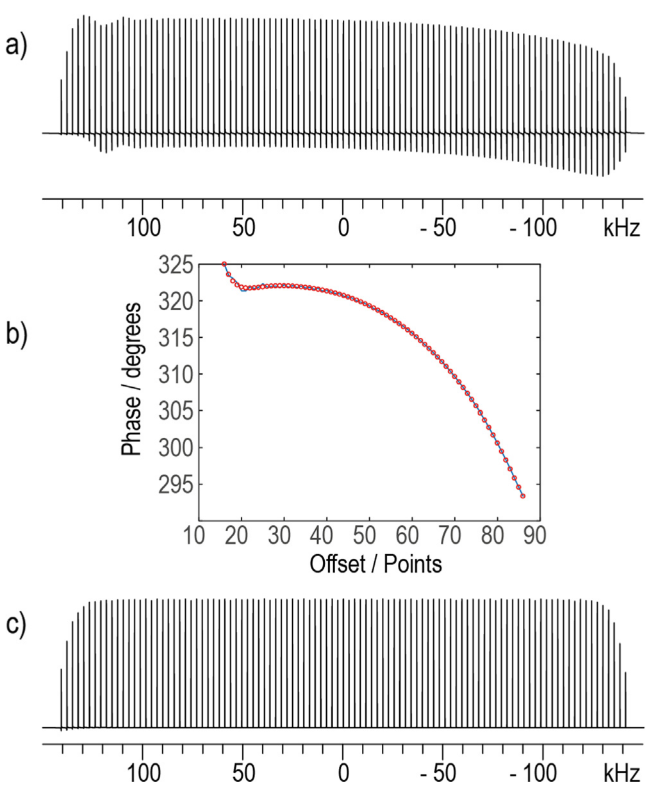

Fig. 5. Illustration of tailored phase correction in CHORUS. The calculated excitation spectrum for CHORUS using three normal linear frequency sweep pulses (a) shows a residual nonlinear variation of signal phase with excitation frequency as a result of off-resonance effects during the chirp pulses (i.e. breakdown of the approximation of instantaneous rotation). The phase variation is fitted (b) to a polynomial, which is then used to calculate the time-dependent phase correction that needs to be applied to the first chirp pulse. Replacing the original linear frequency sweep first pulse with the phase-corrected pulse gives a pure-phase excitation spectrum (c).

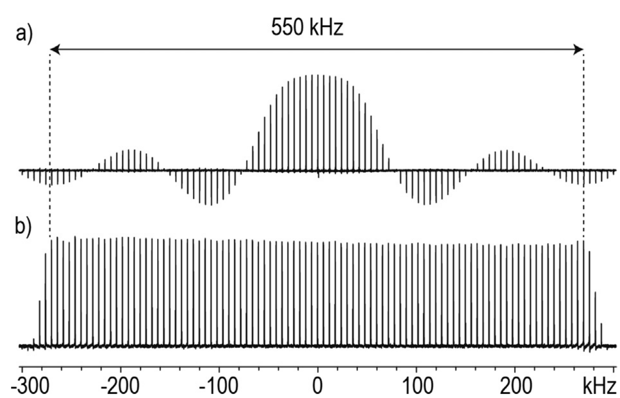

Fig. 6. ^{195}Pt spectra of a sample of K_2PtCl_6 in D_2O at 129 MHz Larmor frequency, run over 101 transmitter offsets ranging from −300 kHz to 300 kHz in steps of 6 kHz, acquired at 298 K on a Bruker Avance III HD spectrometer with a 14 T magnet, using (a) conventional single pulse excitation after 2808° 1st-order phase correction, to correct for the offset evolution during the pulse over the 600 kHz frequency range, and (b) a 4 ms compressed CHORUS sequence with no post-acquisition phase correction. The K_2PtCl_6 sample used here has T_1 and T_2 relaxation times of 800 ms and 30 ms respectively, so offset-dependent T_1/T_2 weighting during the 4 ms sequence results in a slight offset-dependent signal attenuation. The probe used was a 5 mm Broadband Prodigy with 13 μs hard 90° pulse for ^{195}Pt. For the compressed CHORUS experiment the times τ_1 to τ_4 were set to 0.5 ms, 1.75 ms, 0.25 ms, and 1.5 ms respectively. The RF amplitudes of the one excitation and two refocusing chirp pulses were set to 9.18 kHz, 16.52 kHz and 17.87 kHz respectively, with an overall RF_{rms} of 15.38 kHz. The spectral window was set to 666.667 kHz, and FIDs were acquired with 16 k complex points. Numbers of dummy scans (DS) and scans (NS) were set to 8 and 64 respectively, with an overall recycle time (AQ + D1) of 500 ms.

degree of freedom in the CHORUS sequence, and the possibility of using much shorter 90° chirp pulse in the compressed version, at a cost of only 25% in the overall pulse length, and 20% higher RF amplitude, almost twice the excitation bandwidth can be achieved. It can be seen from Eq. (5) that there is an infinite number of possibilities for building the CHORUS sequence, but in general the most useful sequence is the one that covers the bandwidth of interest in minimum overall pulse duration, with an affordable peak amplitude, and with minimum power dissipation. Another advantage of the additional degree of freedom in designing CHORUS sequence is that although in general the shortest possible pulse sequence is preferred, one may encounter cases in which, e.g. a certain amount of J evolution during the pulse sequence is required, while the chemical shift evolution must be kept refocussed.

To satisfy the second requirement, that the phase of the signal excited should be substantially independent of B_1, the radiofrequency amplitudes of the two 180° chirp pulses need to be adjusted to minimize the dependence of signal phase on radiofrequency amplitude. If we keep the chemical shift evolution refocused and use 180° chirp pulses that have RF amplitudes above the adiabatic threshold, we are free to vary the amplitudes of the 180° chirp pulses to minimize the net phase dependence on B_1, $d\varphi/dB_1$, as shown by the vertical two-headed arrows on the 180° chirp pulses in Fig. 2d. One way of ensuring that the total phase variation for all offsets during the pulse sequence will be constant is to arrange pulses of 180° flip angle to achieve an overall variation of effective B_1 which makes the total accumulated phase zero,

$$\varphi_{t=T} \propto \int_0^T \mathbf{B}_{1,eff}(t)dt \tag{6}$$

where T is the total duration of the CHORUS sequence. Although this can be seen as a simple non-linear optimisation problem, delivering minimum $d\varphi/dB_1$ for a range of B_1 values around the nominal B_1 or:

$$\left\{B_1^1, B_1^2\right\} = \underset{B_1^1, B_1^2}{\arg\min}\left(\frac{d\varphi}{dB_1}\right) \tag{7}$$

it turns out that setting the amplitudes of the two 180° pulses to give the same Q factor of 5 [33,39], according to Eq. (1), straightforwardly leads to a constant phase for all offsets and therefore minimises $d\varphi/dB_1$. It is important to note that, since the offset-dependent off-resonance irradiation during the 90° chirp is the main reason for the Bloch-Siegert phase shift that degrades the phase uniformity, using a much shorter excitation (first) chirp pulse in the compressed version of the CHORUS sequence significantly reduces the Bloch-Siegert phase shift, and therefore as demonstrated in Fig. 3c gives an excitation with far less sensitivity of the signal phase to B_1 variation. As before, any residual phase error in the excitation profile of the compressed sequence can be eliminated by polynomial fitting and direct addition of the appropriate function to the time-dependent phase of the first pulse of the sequence (Fig. 5). An application of the compressed CHORUS excitation scheme to ^{195}Pt NMR is shown in Fig. 6, where, using a 4 ms compressed CHORUS sequence with RF_{rms} amplitude of 15 kHz, more than 0.5 MHz of uniform excitation is achieved.

The compressed CHORUS pulse sequence is general and can be applied to any nucleus, so a single sequence can be used as a standard excitation scheme, e.g. for ^{13}C, ^{19}F, and ^{195}Pt. All chirp pulses, with user-defined parameters (bandwidth, duration, etc.) can be generated using a set of functions written in MATLAB. These scripts calculate timings for the relevant sequences (τ values in Eq. (5)), generate the waveforms, run Bloch sphere simulations to determine residual phase errors to be corrected using polynomial fitting, and generate a final set of phase-corrected chirp of pulses in Bruker format, saving them under a user-defined path. All these MATLAB functions, along with pulse sequence code for CHORUS experiment, chirp pulses, and experimental data are freely available via the following DOI: https://doi.org/10.17632/hh46rcfwz9.1.

3. Conclusion

In the present work, we have introduced an improved version of the CHORUS excitation pulse sequence. We demonstrate that a significant reduction can be made in the duration of the CHORUS triple-chirp excitation pulse sequence, yielding a robust ultra-broadband pulse sequence which is even shorter than its double-chirp analogue. The compressed CHORUS pulse sequence has many potential applications in ultra-broadband [25] and ultra-fast NMR experiments [45,46], and in pulsed EPR spectroscopy [37,38,40,41].

Acknowledgements

This work was funded by the Royal Society (grant numbers URF\R1\180233 and RGF\EA\181018) and Engineering and Physical Sciences Research Council (grant numbers EP/L018500 and EP/M013820). M.F. wishes to thank Dr. Nick Rees and Prof. Tim Claridge for helpful discussions.

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