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Application of cogwheel phase cycling to sideband manipulation experiments in solid-state NMR

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Abstract

Cogwheel phase-cycling schemes are applied to sideband suppression and sideband separation experiments in solid-state NMR. It is shown that cogwheel phase cycles lead to the elimination of most pulse imperfection effects, while using far fewer experimental signal acquisitions than conventional phase-cycling methods.

Keywords: Cogwheel phase cycling; Spinning sidebands; TOSS; PASS

1. Introduction

The invention of the total sideband suppression (TOSS) and phase-adjusted spinning sideband (PASS) methods by Dixon [1] marked a great advance in solid-state NMR, both theoretically and experimentally. In powder samples, the TOSS pulse sequence suppresses the spinning sidebands, leaving only the centrebands and the isotropic chemical shifts [1–7]. The method is very useful for simplifying the magic-angle spinning (MAS) NMR spectra of complex materials, especially at relatively low spinning frequencies, but has the disadvantage of losing the chemical shift anisotropy (CSA) information, which is encoded in the spinning sidebands. The PASS experiment remedies this problem by generating a set of spectra which may be combined to separate the spinning sidebands by order [1,8–18]. PASS disentangles the isotropic and anisotropic chemical shift information, and may be used for the simultaneous estimation of the CSA principal values of a large number of chemical sites [10–14]. 2D-PASS has also been used at slow spinning frequencies to obtain isotropic shift resolution in delicate solid samples, for which high spinning frequencies would cause mechanical damage [17,18]. 2D-PASS may also be used to obtain site-resolved information on molecular order in oriented samples [19].

The original TOSS and PASS experiments used four strong π pulses at carefully timed intervals applied to transverse magnetization, generated by a cross-polarization sequence [20] or a strong $\pi/2$ pulse. The pulse sequences set up the phases of the magnetization components so as to eliminate the spinning sidebands from powder samples entirely, in the case of TOSS, or to generate a free-induction decay with controllable phase shifts of the sidebands, in the case of PASS. Variants of the TOSS and PASS pulse schemes have been developed, using five or more π pulses instead of four [5,8], or employing finite RF irradiation blocks instead of strong pulses of negligible duration [4]. The variant of PASS with five π pulses has proved to be particularly popular, since after a second Fourier transform it leads to a clean separation of spinning sidebands even in the presence of differential relaxation effects. This is the 2D-PASS experiment [8,9]. Extensions of 2D-PASS have been described which are applicable to quadrupolar spin systems [15,16].

The TOSS and PASS techniques are susceptible to pulse imperfections, as might be expected for experiments in which the phase of transverse magnetization components must be carefully controlled by a sequence

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of four or more π pulses. Although this problem may be controlled by using composite pulses [21], it is common practice to reduce the effect of pulse imperfections by phase cycling the π pulses. This involves acquiring a set of NMR signals using pulses of different phases, and then superposing the results. For example, 2D-PASS experiments are often conducted using a 243-step phase cycle [8,10]. In the case of isolated spins-1/2, this 243-step phase cycle may be shown to completely eliminate the effects of misset RF amplitudes, phase transients, or RF inhomogeneity on the acquired spectra (the effects of finite pulse duration are not, however, eliminated). The drawback of such a phase cycle is that the minimum experimental time becomes rather long. If 16 increments of the PASS sideband phase shift are required to separate the sidebands, and the minimum re-equilibration time between transients is 5 s, then the minimum total duration of a fully phase-cycled 2D-PASS experiment is about 5 h. This is often a considerable overkill in the case of small molecules with good sensitivity and favourable relaxation time constants. In cases where the longitudinal relaxation time constant is long, such as many inorganic systems, a fully phase-cycled TOSS experiment is impractical.

Recently, a new phase-cycling paradigm called "cogwheel" phase cycling was described [22–24]. Unlike the traditional "nested" phase cycling method [25–28], in which the phase of only one pulse sequence block is varied at a time, cogwheel phase cycling involves the simultaneous variation of many pulse sequence phases. In many cases, cogwheel phase cycling leads to a large reduction in the minimum total experimental time required to acquire a clean NMR signal, with undesired coherence transfer pathways eliminated. In the case of TOSS and PASS, the reduction in the minimum experimental time is dramatic. For isolated spins-1/2, a clean selection of the desired signal in TOSS or PASS is obtained in only 11 phase-cycle steps instead of 243. For 16 increments of the PASS sideband phase shift, with a re-equilibration time between transients of 5 s, the minimum total experimental time with cogwheel phase cycling is only 15 min.

2. TOSS and PASS pulse sequences

A typical pulse sequence for TOSS or PASS, as applied to rare spins such as ^{13}C or ^{15}N in organic solids, is shown in Fig. 1a. The abundant spin channel (typically ^1H) is denoted I, and the rare spin channel (typically ^{13}C) is denoted S. After ramped cross-polarization from the protons [29], the transverse S-spin magnetization is subjected to a sequence of five strong π pulses separated by delays.

The pulse timings are conveniently referenced to the start of signal acquisition, which is defined as $t = 0$. The preparation period (cross-polarization, or a single $\pi/2$ pulse) terminates at time point $-T$, where T is the duration of the TOSS or PASS sequence. The time points at the centres of the five π pulses are given by $-T + \tau_1, -T + \tau_2, \ldots, -T + \tau_5$.

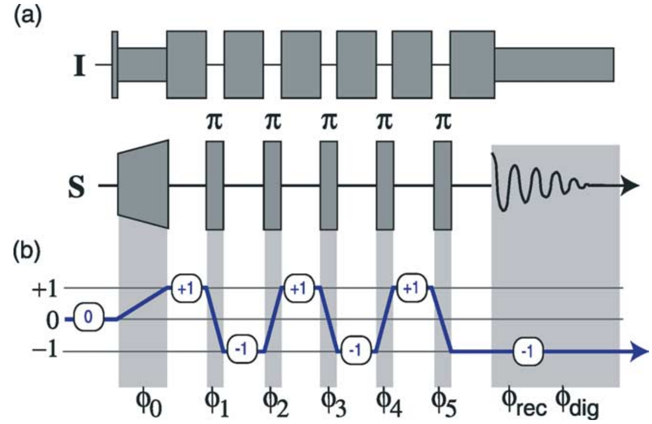

Fig. 1. (a) Pulse sequence for TOSS or PASS experiments on a heteronuclear spin system, including ramped cross-polarization of transverse magnetization from the I-spins to the S-spins , and preparation of the S-spin magnetization phase by a set of strong π pulses. The I-spin RF field is usually turned off during the S-spin π pulses, in order to avoid loss of magnetization due to undesirable Hartmann–Hahn transfer. (b) Coherence transfer pathway diagram for isolated spins-1/2, showing the desirable pathway $\boldsymbol{p}^0$.

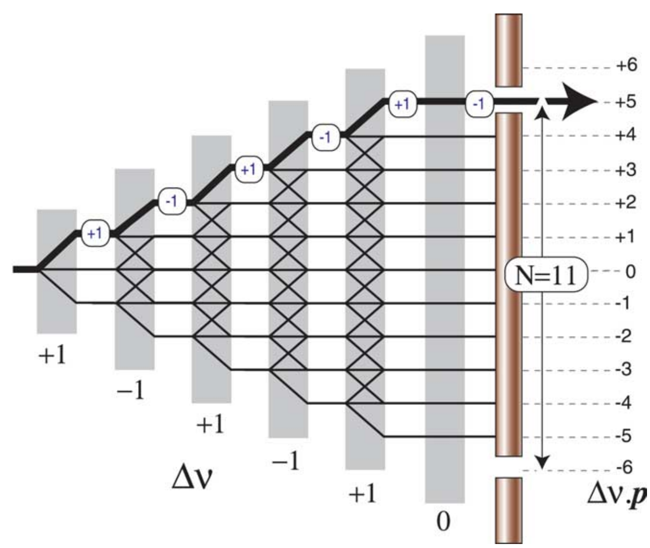

Fig. 2. Cogwheel splitting diagram for a cycle with a winding number difference vector $\Delta\boldsymbol{v} = \{0, +1, -1, +1, -1, +1, 0\}$. The pathway $\boldsymbol{p}$ attains a final level given by the signature $\Delta\boldsymbol{v} \cdot \boldsymbol{p}$ (vertical scale on the right). The desired pathway $\boldsymbol{p}^0$ is shown as a bold line: it accumulates the unique signature $\Delta\boldsymbol{v} \cdot \boldsymbol{p}^0 = +5$. The barrier at the right-hand side has holes separated by $N = 11$ units, representing the selection rule Eq. (13).

If the angular spinning frequency is denoted ω_r, the pulse timings are conveniently described by the angles $\theta_T, \theta_1, \theta_2, \ldots, \theta_5$, defined by $\theta_T = \omega_r T$ and $\theta_q = \omega_r \tau_q$, where $q = 1, 2, \ldots, 5$. The phases of the five π pulses are denoted $\phi_1, \phi_2, \ldots, \phi_5$. The RF receiver phase shift during signal acquisition is denoted ϕ_{rec}, and the post-digitization phase shift is denoted ϕ_{dig}. All phases are defined as in [30,31].

In TOSS experiments using five π pulses, the pulse sequence timings are chosen to satisfy the equations

$$2\sum_{q=1}^{5}(-1)^q \exp\{\mathrm{i}m\theta_q\} + 1 = 0 \qquad (1)$$

for both $m = 1$ and $m = 2$. As shown in [6,7], this leads to a free-induction decay in a powder sample which yields a sideband-free NMR spectrum on Fourier transformation. Eq. (1) may be solved analytically [5] for the pulse sequence timings θ_q.

In PASS experiments using five π pulses, the pulse sequence timings are chosen to satisfy the equations

$$2\sum_{q=1}^{5}(-1)^q \exp\{\mathrm{i}m\theta_q\} + \exp\{\mathrm{i}m(\Theta + \theta_T)\} + 1 = 0 \qquad (2)$$

for both $m = 1$ and $m = 2$, where Θ is an arbitrary angle, called the pitch of the sequence. As shown in [8], acquisition of a set of spectra for a series of pitches in the range 0–2π, followed by a second Fourier transform, generates a 2D spectrum containing sets of spinning sidebands, separated by order. Timings θ_q may be found numerically for arbitrary values of the pitch Θ [8].

The coherence transfer pathway [25–28] leading to the desired signals in both TOSS and PASS is shown in Fig. 1b. Each π pulse leads to an alternation of the coherence order between +1 and −1. These coherence transfers are 100% efficient in the case of perfect π pulses. However, in the case of pulse imperfections, each pulse leads to finite coherence transfers between any of the three possible coherence orders in a system of isolated spins-1/2, namely −1, 0, and +1. For an experiment involving five imperfect π pulses, there are therefore $3^5 = 243$ coherence pathways contributing to the final NMR signal. In general, each of these extraneous pathways prepare the magnetization components with incorrect phases, leading to imperfect sideband suppression (in the case of TOSS) or imperfect sideband separation (in the case of PASS). The task of phase cycling is to filter out signals from the one desired signal pathway, while suppressing the 242 others.

3. Phase cycling

In a sequence consisting of a preparation element (single $\pi/2$ pulse or a cross-polarization period), followed by Q separated pulses (where Q is a positive integer), a general coherence transfer pathway contributing to the final NMR signal may be denoted by a vector $\boldsymbol{p}$ with $Q + 2$ elements:

$$\boldsymbol{p} = \{0, p_{(0,1)}, p_{(1,2)}, \ldots, p_{(Q-1,Q)}, -1\}, \qquad (3)$$

where $q = 0, 1, \ldots, Q$, and the symbol $p_{(q,q+1)}$ denotes the coherence order in the interval between blocks q and $q + 1$ (the preparation block is denoted $q = 0$). The coherence order before the preparation element is zero, and the coherence order for the detectable signal is −1, in the case of a perfectly adjusted receiver [28]. In the case of a TOSS or PASS sequence with $Q = 5$, the desired coherence transfer pathway leading to a clean NMR response is $\boldsymbol{p}^0 = \{0, +1, -1, +1, -1, +1, -1\}$, as illustrated in Fig. 1b.

3.1. Nested phase cycles

Traditional "nested" phase cycling, as treated by Bain [26] and Bodenhausen et al. [25], exploits the *change* in coherence order induced by each pulse sequence element. For a general pathway $\boldsymbol{p}$, the coherence order change induced by an element q is defined by $\Delta p_q = -p_{(q-1,q)} + p_{(q,q+1)}$. For the *desired* pathway $\boldsymbol{p}^0$, the coherence order change induced by an element q is denoted Δp_q^0. For example, the ideal pathway $\boldsymbol{p}^0$ for a 5-pulse TOSS or PASS experiment has the following set of order changes:

$$\begin{aligned} &\Delta p_0^0 = +1, \quad \Delta p_1^0 = -2, \\ &\Delta p_2^0 = +2, \quad \Delta p_3^0 = -2, \\ &\Delta p_4^0 = +2, \quad \Delta p_5^0 = -2. \end{aligned} \qquad (4)$$

Nested phase cycling works by selecting coherence order changes one at a time. A desired order jump Δp_q^0 is selected, at the expense of a finite set of undesired order jumps Δp_q, by cycling the element q in a number of steps equal to the largest separation between Δp_q^0 and Δp_q, plus one. Multiple selections at different elements q are implemented by nesting the individual phase cycles. Such phase cycles are readily constructed but they are often long.

Consider a 5-pulse TOSS experiment, conducted on a system of isolated spins-1/2, so that all orders greater than +1 or less than −1 may be ignored. On each step of the pulse sequence, there are five possible changes in coherence order, namely one of $\{-2, -1, 0, +1, +2\}$. Since the coherence pathway must terminate with −1, there are only three possible coherence order changes on the fifth element, namely $\Delta p_5 = \{-2, -1, 0\}$. It is therefore possible to select pathways with the desired order jump $\Delta p_5^0 = -2$ and suppress pathways with the undesired order jumps $\Delta p_5 = \{-1, 0\}$ by a three-step cycle of the phase ϕ_5. This three-step cycle therefore selects pathways with $p_{(4,5)} = +1$. For these pathways, there are only three possible coherence order changes on the fourth element, namely $\Delta p_4 = \{0, +1, +2\}$, of which the desired pathway has $\Delta p_4^0 = +2$. It is therefore possible to select pathways with $p_{(3,4)} = -1$ by a three-step cycle of the phase ϕ_4. This argument may be continued to show that the desired unique pathway $\boldsymbol{p}^0 = \{0, +1, -1, +1, -1, +1, -1\}$ is selected by nested three-step phase cycles of all five π pulses, without cycling the phase ϕ_0 of the preparation element. This requires $3^5 = 243$ phase cycle steps. One such phase cycle is defined by the equation

$$\begin{aligned} \phi_0 &= 0, \\ \phi_q &= \frac{2\pi}{3}\text{floor}\left\{\frac{j}{3^{q-1}}\right\} \quad \text{for } q \geqslant 1, \end{aligned} \tag{5}$$

where the transient counter is $j = 0, 1, \ldots, 242$, and floor$\{x\}$ is the largest integer not greater or equal to x [28]. On each step, the receiver and digitizer phases are set according to the "master equation" for the desired pathway $\boldsymbol{p}^0$:

$$+\phi_0 - 2\phi_1 + 2\phi_2 - 2\phi_3 + 2\phi_4 - 2\phi_5 + \phi_{\text{rec}} + \phi_{\text{dig}} = 0. \tag{6}$$

This 243-step phase cycle has been used in TOSS and PASS experiments [5,8,9].

In fact, one can do considerably better than this, even within the framework of nested phase cycling. In a system of isolated spins-1/2, the only coherence transfer process with a order change $\Delta p = +2$ involves a change in coherence order from -1 to $+1$. Hence it is possible to select the coherence orders $p_{(3,4)} = -1$ and $p_{(4,5)} = +1$ at the same time by cycling the phase ϕ_4 so as to select $\Delta p_4 = +2$, while suppressing the four other possible order changes $\Delta p_4 = \{-2, -1, 0, +1\}$. This requires a minimum five-step cycle of ϕ_4. Similarly, it is possible to select pathways with $p_{(1,2)} = -1$ and $p_{(2,3)} = +1$ by cycling the phase ϕ_2 in five steps so as to select $\Delta p_2 = +2$. Since the initial coherence order must be 0, the selection of $p_{(0,1)} = +1$ at the expense of $p_{(0,1)} = \{-1, 0\}$ may be accomplished in a three-step cycle of ϕ_0. The unique pathway $\boldsymbol{p}^0$ may therefore be selected in $3 \times 5^2 = 75$ steps without changing the phases ϕ_1, ϕ_3, and ϕ_5. One implementation of the 75-step phase cycle is given by

$$\begin{aligned} \phi_0 &= \frac{2\pi}{3}j, \\ \phi_1 &= 0, \\ \phi_2 &= \frac{2\pi}{5}\text{floor}\{j/3\}, \\ \phi_3 &= 0, \\ \phi_4 &= \frac{2\pi}{5}\text{floor}\{j/15\}, \\ \phi_5 &= 0, \end{aligned} \tag{7}$$

where the transient counter is $j = 0, 1, \ldots, 74$. The receiver and or digitizer phase are set according to the master equation, Eq. (6). The 75-step phase cycle in Eq. (7) has the same selection properties as the 243-step phase cycle in Eq. (5). However, as shown below, even this 75-step cycle is far from the optimal solution.

3.2. Cogwheel phase cycles

In cogwheel phase cycling, one cycles the pulse sequence phases according to

$$\phi_q = \frac{2\pi \nu_q}{N} j, \tag{8}$$

where ν_q is an integer called the *winding number* for the element q and N is the number of steps in the phase cycle. The receiver and digitzer phases are also assigned winding numbers:

$$\begin{aligned} \phi_{\text{rec}} &= \frac{2\pi \nu_{\text{rec}}}{N} j, \\ \phi_{\text{dig}} &= \frac{2\pi \nu_{\text{dig}}}{N} j. \end{aligned} \tag{9}$$

In general, the phases of all pulse sequence elements change at the same time, so that by the end of N steps, the phase ϕ_0 will be about to complete ν_0 full revolutions, the phase ϕ_1 will be about to complete ν_1 full revolutions, and so on. Cogwheel phase cycling is therefore very different from nested phase cycling, where all phases but one are held fixed until the moving one has finished a full cycle.

As shown in [22], the properties of cogwheel phase cycles are determined by the difference in winding numbers of adjacent elements, defined as follows:

$$\Delta \nu_{(q,q+1)} = -\nu_q + \nu_{q+1}. \tag{10}$$

In a sequence with elements $q = 0, 1, \ldots, Q$, the difference in winding number between the detection/digitization system and the last pulse sequence element may be defined

$$\Delta \nu_{(Q,\text{det})} = -\nu_Q + \nu_{\text{rec}} + \nu_{\text{dig}}. \tag{11}$$

It is useful to compile a *winding number difference vector* $\boldsymbol{\Delta \nu}$ as follows:

$$\boldsymbol{\Delta \nu} = \{0, \Delta \nu_{(0,1)}, \Delta \nu_{(1,2)}, \ldots, \Delta \nu_{(Q-1,Q)}, \Delta \nu_{(Q,\text{det})}\}. \tag{12}$$

The vector $\boldsymbol{\Delta \nu}$ has the same number of elements $(Q + 2)$ as the pathway vector $\boldsymbol{p}$ (Eq. (3)).

In cogwheel phase cycling, the signal component from pathway $\boldsymbol{p}$ is allowed by the phase cycle if an integer $Z(\boldsymbol{p})$ exists which satisfies the following identity:

$$\boldsymbol{\Delta \nu} \cdot \boldsymbol{p} = \boldsymbol{\Delta \nu} \cdot \boldsymbol{p}^0 + NZ(\boldsymbol{p}). \tag{13}$$

The *pathway signatures* $\boldsymbol{\Delta \nu} \cdot \boldsymbol{p}$ and $\boldsymbol{\Delta \nu} \cdot \boldsymbol{p}^0$ are defined by

$$\begin{aligned} \boldsymbol{\Delta \nu} \cdot \boldsymbol{p} &= \sum_{q=1}^{Q} \Delta \nu_{(q-1,q)} p_{(q-1,q)}, \\ \boldsymbol{\Delta \nu} \cdot \boldsymbol{p}^0 &= \sum_{q=1}^{Q} \Delta \nu_{(q-1,q)} p^0_{(q-1,q)}. \end{aligned} \tag{14}$$

In order to select signals from a unique pathway $\boldsymbol{p}^0$, while suppressing all others, the following conditions are imposed:

1. The winding numbers are chosen such that the signature $\mathbf{\Delta v} \cdot \boldsymbol{p}^0$ is unique: There must be no other pathways $\boldsymbol{p}$ for which $\mathbf{\Delta v} \cdot \boldsymbol{p} = \mathbf{\Delta v} \cdot \boldsymbol{p}^0$.
2. There must be no pathways $\boldsymbol{p} \neq \boldsymbol{p}^0$ for which Eq. (13) can be satisfied by choosing an integer value of $Z(\boldsymbol{p})$.
3. The receiver and/or digitizer winding numbers must satisfy the "cogwheel master equation"

$$\sum_{q=0}^{Q} \Delta p_q^0 v_q + v_{\text{rec}} + v_{\text{dig}} = 0, \tag{15}$$

where $\Delta p_q^0 = p^0_{(q,q+1)} - p^0_{(q-1,q)}$ is the change of order induced by the element q, for the desirable pathway $\boldsymbol{p}^0$.

In many cases all three conditions may be satisfied for a number of steps N which is much smaller than that needed in the "nested" procedure. Typically, the minimal cogwheel solutions are discovered by numerical searches over many combinations of winding numbers [24], although in some cases predictive formulae exist [22].

In the case of TOSS and PASS sequences with five π pulses, the appropriate winding number combinations may be discovered by a simple diagrammatic procedure (Fig. 2). In a system of isolated spins-1/2, all but the first element of the desired pathway $\boldsymbol{p}^0 = \{0, +1, -1, +1, -1, +1, -1\}$ involve the maximal coherence order +1 or the minimal coherence order −1. The signature $\mathbf{\Delta v} \cdot \boldsymbol{p}^0$ may therefore be kept unique by ensuring that the elements of $\mathbf{\Delta v}$ have the same sign as the corresponding elements of $\boldsymbol{p}^0$. The simplest solution is $\mathbf{\Delta v} = \{0, +1, -1, +1, -1, +1, 0\}$ (the last element may have any value since all observable pathways terminate on order −1, in the case of an ideal quadrature receiver). The signature is given in this case by $\mathbf{\Delta v} \cdot \boldsymbol{p}^0 = +5$. All other observable pathways have smaller values. For example, the pathway $\boldsymbol{p} = \{0, -1, -1, +1, -1, +1, -1\}$ deriving from an imperfect transformation under the first π pulse has a signature $\mathbf{\Delta v} \cdot \boldsymbol{p} = +3$. Fig. 2 contains a "cogwheel splitting diagram" which shows how the signatures of the different coherence transfer pathways are constructed. Note that many different pathways have the same overall signature $\mathbf{\Delta v} \cdot \boldsymbol{p}$: the degeneracy does not matter since all of these pathways must be suppressed.

The minimum value for the signature is given by the pathway $\boldsymbol{p} = \{0, -1, +1, -1, +1, -1, -1\}$, for which $\mathbf{\Delta v} \cdot \boldsymbol{p} = -5$. Note that there are no pathways terminating on +1 in the case of perfect quadrature signal detection. All pathways therefore have signatures $\mathbf{\Delta v} \cdot \boldsymbol{p}$ between +5 and −5, with the desired pathway $\boldsymbol{p}^0$ being the only one with the maximal signature. Since all signatures between +5 and −5 are occupied by undesired pathways, condition [2] may be satisfied by choosing $N \geqslant 11$. The rationale for this is illustrated by the barrier at the right-hand side of Fig. 2, which represents the selection rule in Eq. (13).

The cogwheel winding numbers may be constructed from the solution for the winding number difference vector, $\mathbf{\Delta v} = \{0, +1, -1, +1, -1, +1, 0\}$. From Eq. (10), assuming $v_0 = 0$, we get $\{v_0, v_1, v_2, v_3, v_4, v_5\} = \{0, +1, 0, +1, 0, +1\}$. Eqs. (4) and (15) then lead to

$$-6 + v_{\text{rec}} + v_{\text{dig}} = 0. \tag{16}$$

One of the possible cogwheel phase-cycling solutions for the five-pulse TOSS/PASS schemes is therefore specified by $N = 11$ and the following set of winding numbers:

$$\begin{aligned} &v_0 = 0, \quad v_1 = +1, \\ &v_2 = 0, \quad v_3 = +1, \\ &v_4 = 0, \quad v_5 = +1, \\ &v_{\text{rec}} = 0, \quad v_{\text{dig}} = +6. \end{aligned} \tag{17}$$

The explicit phase cycle is

$$\begin{aligned} &\phi_0 = \phi_2 = \phi_4 = \phi_{\text{rec}} = 0, \\ &\phi_1 = \phi_3 = \phi_5 = 2\pi j/11, \\ &\phi_{\text{dig}} = 12\pi j/11, \end{aligned} \tag{18}$$

where $j = 0, 1, \ldots, 10$. This 11-step phase cycle may be abbreviated as COG11(0, 1, 0, 1, 0, 1; 0, 6), using the notation COGN$(v_0, v_1, \ldots, v_Q; v_{\text{rec}}, v_{\text{dig}})$ described in [23]. It selects signals passing through the desired pathway $\boldsymbol{p}^0$ while suppressing the contributions from all 242 undesirable signal pathways.

On some spectrometers, it is not possible to implement digitizer phase shifts ϕ_{dig} which are not integer multiples of π/2. In this case, the receiver reference phase ϕ_{rec} may be used instead; this leads to the cogwheel cycle COG11(0, 1, 0, 1, 0, 1; 6, 0). However, many commercial instruments cannot control the RF receiver reference phase either. An alternative which is less demanding on the hardware is to subtract +6 from all the radiofrequency winding numbers: the cogwheel cycle is then COG11 (−6, −5, −6, −5, −6, −5; 0, 0). All of the above cycles are equivalent in the case of a perfect quadrature receiver.

As the diagram in Fig. 2 suggests, artefacts caused by imperfections in the quadrature receiver may be eliminated by a simple extension of the cogwheel cycle. Quadrature artefacts are signal components with a coherence order of +1, while zero-frequency artefacts caused by a DC offset in the analogue-to-digital converters have a coherence order of zero. The desired pathway $\boldsymbol{p}^0 = \{0, +1, -1, +1, -1, +1, -1\}$ may be separated from all the others, including the receiver artefact pathways, by selecting a winding number difference vector $\mathbf{\Delta v} = \{0, +1, -1, +1, -1, +1, -1\}$. This gives the ideal pathway the largest possible signature $\mathbf{\Delta v} \cdot \boldsymbol{p}^0 = +6$, which is unique. The minimum signature is possessed by the quadrature artefact pathway $\boldsymbol{p} = \{0, -1, +1, -1, +1, -1, +1\}$, which has $\mathbf{\Delta v} \cdot \boldsymbol{p} = -6$. Since the largest difference in signatures is 12, at least 13 steps are needed in the cogwheel phase cycle. The 13-step cogwheel cycle COG13(0, 1, 0, 1, 0, 1; 0, 6) eliminates the effects of pulse imperfections, as well as all quadrature and zero-frequency artefacts. Note that quadrature artefact suppression may be included in cogwheel phase cycles with only a small increase in the overall cycle length. This feature may be useful in many other experimental contexts.

The quadrature image-compensated cycle COG13 $(0,1,0,1,0,1;0,6)$ requires control of the digitizer phase in non-integer multiples of $\pi/2$. As mentioned above, this capability is not available on all commercial instruments. If necessary, the 13 acquired transients may be stored independently and subjected to numerical phase shifts, as described in [23].

As before [30,31], we alert the reader to the misleading notation used in many spectrometer pulse programs, which often confuse the RF receiver reference phase and the post-digitization phase.

4. Results

4.1. Sideband suppression

Fig. 3a shows an experimental ^{1}H-decoupled ^{13}C NMR spectrum of powdered [1-^{13}C]-glycine, at a magic-angle spinning frequency 2.900 kHz and a magnetic field of 7.05 T. The spectrum displays a set of spinning sidebands. To a first approximation, the application of a 5-pulse TOSS sequence [5] before the signal acquisition suppresses all spinning sidebands except the centreband. The timings of the π-pulses, as derived in [5], are given by $\theta_1 = \arccos(7/24)$, $\theta_2 = \arccos(-11/24)$, $\theta_3 = \pi$, $\theta_4 = 2\pi - \theta_2$, and $\theta_5 = 2\pi - \theta_1$. The result of the TOSS-5 sequence is shown in Fig. 3b. Although the sidebands are greatly reduced in intensity, they are not completely suppressed, which may attributed to imperfect performance of the five π pulses. The spectrum shown in Fig. 3c demonstrates that the sideband suppression is greatly improved by acquiring 75 transients, with the π pulses subjected to the phase cycle in Eq. (7). Fig. 3d shows that essentially the same effect is achieved in a cycle of only 11 transients, as in Eq. (18). The small remaining signal amplitude in Fig. 3c and d is probably mainly due to the finite duration of the pulses, which is not taken fully into account by the TOSS equations (Eq. (1)). Homonuclear dipole–dipole couplings may also play a role in this fully ^{13}C-labelled sample.

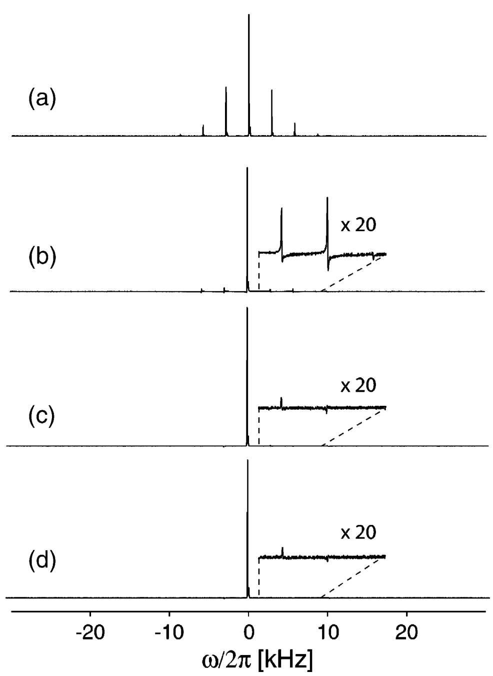

Fig. 3. ^{1}H-decoupled ^{13}C NMR spectra of powdered [1-^{13}C]-glycine, at a magic-angle spinning frequency 2.900 kHz and a magnetic field of 7.05 T. (a) Ordinary CP-MAS spectrum (sum of 76 acquired transients); (b) spectrum acquired using a 5-π TOSS sequence, without phase cycling (sum of 76 acquired transients); (c) spectrum acquired with the 75-step phase cycle in Eq. (7) (sum of 75 acquired transients); (d) spectrum acquired with the 11-step cogwheel phase cycle in Eq. (18) (7 repetitions of the 11-step cycle, corresponding to 77 acquired transients). All spectra are plotted on the same vertical scale. Expanded regions of the spectra in (b), (c), and (d), with a 20-fold larger vertical scale, are also shown.

4.2. Sideband separation

Fig. 4 demonstrates the separation of ^{13}C spinning sidebands using a five-π-pulse PASS sequence and a second Fourier transformation, as described in [8]. In this case the sample is unlabelled L-tyrosine · HCl and the spinning frequency is $\omega_r/2\pi = 1.750$ kHz. In order to demonstrate the power of the cogwheel phase cycles, the pulse flip angles were deliberately set to 0.78π, instead of π. If phase cycling is not used, the 2D spectrum displays an imperfect separation of spinning sidebands (Fig. 4a). The 75-step phase cycle in Eq. (7) suppresses the spurious contributions and gives an acceptable separation of the sidebands by order (Fig. 4b). An essentially identical result is generated by the 11-step phase cycle of Eq. (18).

The suppression of pulse imperfection effects may be particularly useful for the NMR of half-integer quadrupolar nuclei, where 9-π PASS sequences have been used to separate the spinning sidebands [15,16]. Since it is often difficult to manipulate quadrupolar nuclei accurately, due to the large second-order quadrupolar shifts, cogwheel phase cycles may be very useful for filtering out the well-behaved signal components and suppressing those which arise from imperfect RF pulses. The results of Jerschow and Kumar [24] suggest that coherence orders $|p| > 1$ may often be neglected in this context. With this assumption, the minimal nested phase cycle for 9-π PASS has $3 \times 5^4 = 1875$ steps. The corresponding cogwheel cycle may be derived using a straightforward extension of Fig. 2. One possible solution is the 19-step cogwheel cycle COG19$(0,1,0,1,0,1,0,1,0,1;0,10)$. This represents a reduction in the minimum acquisition time by two orders of magnitude.

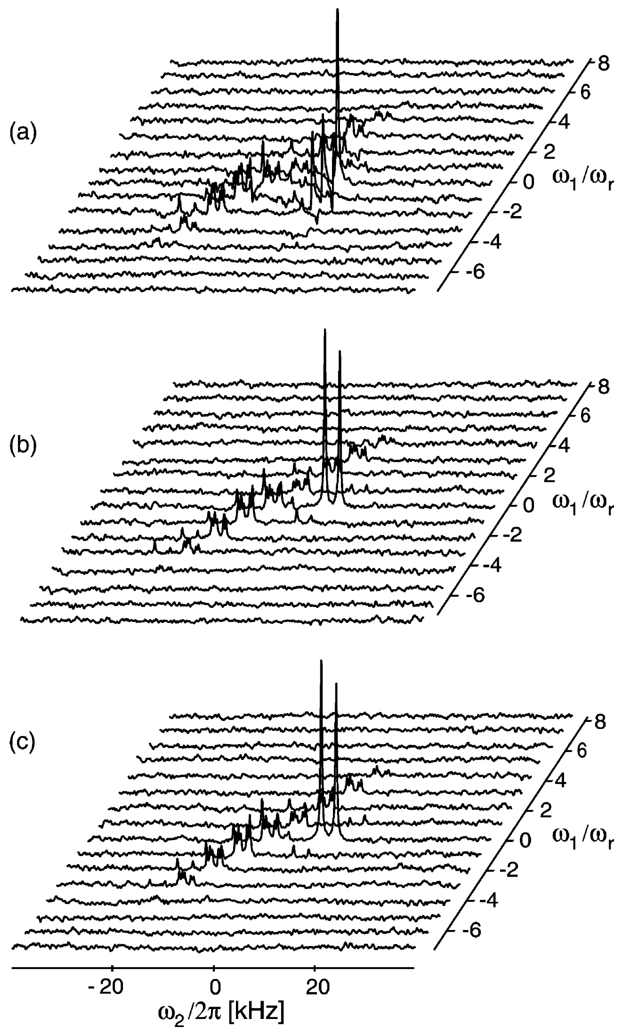

Fig. 4. Two-dimensional ^1H-decoupled ^{13}C NMR spectra of powdered L-tyrosine · HCl, at a magic-angle spinning frequency 1.750 kHz and a magnetic field of 7.05 T, acquired using the 2D-PASS pulse sequence with 16 increments of the pitch Θ. (a) 2D-PASS spectrum acquired without phase cycling, and with the flip angles of the five π pulses deliberately misset to 0.78π (300 acquired transients for each Θ increment). (b) Same as in (a), but using the 75-step phase cycle in Eq. (7) (300 acquired transients for each Θ increment); (c) same as in (a), but using the 11-step phase cycle in Eq. (18) (297 acquired transients for each Θ increment).

Conclusions

Cogwheel phase cycles often give rise to large time savings in experiments which involve many coherence transfer steps. In TOSS and PASS experiments involving five π pulses, the saving in time is approximately a factor of seven for a fully phase-cycled experiment. Even larger time savings are anticipated for experiments which involve consecutive TOSS or PASS sequences, such as those designed to explore dynamic exchange phenomena [32,33], or those which use two TOSS sequences to separate isotropic and anisotropic chemical shifts [34–38].

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