

## COMMUNICATIONS

## High-Order Selective Sequences in Multiple-Quantum NMR

In a recent letter (1) we showed that multiple-quantum NMR transitions can be selectively excited, corresponding to the absorption of only groups of  $n$  photons. By a phase-shifted pulse sequence, a zero-order average Hamiltonian  $\mathcal{H}^{(0)}$  is produced which is  $nk$ -quantum selective, i.e., contains only matrix elements between states differing in energy by  $nk\hbar\omega_0$  ( $k = 0, 1, 2, \dots$ ). In general, the propagator for any time-dependent sequence of pulses and delays may be written from average Hamiltonian theory (2) as  $U = \exp(-i\bar{H}(n_c t_c))$ , where  $t_c$  is the cycle time,  $n_c$  is the number of cycles, and  $\bar{H}$  is the effective time-independent Hamiltonian

$$\bar{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \dots + \mathcal{H}^{(j)} + \dots$$

The quantity  $\mathcal{H}^{(0)}$  is the zero-order or average Hamiltonian;  $\mathcal{H}^{(j)}$  is termed a correction term of order  $j$ , and is proportional to  $(t_c)^j$ . For  $t_c \rightarrow 0$ ,  $\mathcal{H}^{(0)}$  is the dominant term, and this is the term we made selective in our preliminary work which demonstrated 0, 4-quantum selectivity in oriented benzene.

A crucial aspect of this work, which allowed  $\|\bar{H}t_c\| \rightarrow 0$ , was a time-reversible excitation  $\bar{H}_p$  which produced, independent of the cycle time, an effective subcycle Hamiltonian  $\bar{H}_0$  with all multiple-quantum components. In many systems (isotropic solutions, for example)  $t_c$  cannot be made vanishingly small while keeping multiple-quantum components in  $\bar{H}_0$ . In this case the terms  $\mathcal{H}^{(j)}$  for  $j \neq 0$ , which are not necessarily selective, will contribute to  $\bar{H}$  and ruin the selectivity. Thus a critical question is whether an excitation can be designed in the most general case such that the nonselective contributions to  $\mathcal{H}^{(j)}$  are reduced, making selective excitation generally applicable to spectroscopic systems and to large values of  $n$ . In this communication we show for the first time the result that an excitation can be produced with an effective  $\bar{H}$  which is  $nk$ -quantum selective for all terms  $\mathcal{H}^{(j)}$  up to arbitrarily high  $j$ . This is done by a successive sequence of phase cyclings (described below) and can be used to produce highly  $nk$ -quantum selective excitation even when time reversal is not possible or when  $t_c$  cannot be made small enough to neglect correction terms.

We define a  $j$ -order  $nk$ -quantum selective sequence as one in which all terms  $\mathcal{H}^{(i)}$  ( $i \leq j$ ) in the average Hamiltonian expansion are  $nk$ -quantum selective, i.e., they are invariant to a rotation of  $\phi = 2\pi/n$  about the axis of quantization. These terms therefore can be decomposed into irreducible tensor operators  $T_{\pm p}^{(l)}$  with components  $p = nk$  ( $k = 0, 1, 2, \dots$ ) and ranks  $l \geq |p|$ .<sup>1</sup> We define phase cycling, shown in Fig. 1a, as follows. We start with a sequence with an effective Hamiltonian  $\bar{H} = \bar{H}_0 = \mathcal{H}_0^{(0)} + \mathcal{H}_0^{(1)} + \dots$ , which is applied for a time  $\Delta\tau_p$ , called a subcycle. The subcycle sequence is then repeated with the

<sup>1</sup> Pure  $n$ -quantum selectivity ( $k = 1$ ) is also possible.

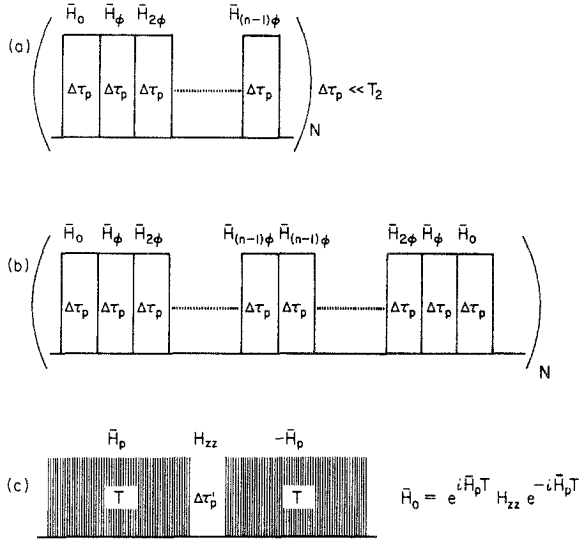


FIG. 1. (a) Phase cycling. If  $\phi = 2\pi/n$ , this process increases the  $nk$ -quantum selectivity of the sequence by one order over the selectivity of  $\bar{H}_0$ . (b) Phase cycling combined with symmetrization increases the selectivity by two orders. (c) Time reversal enhances the selectivity. If this entire sequence is used for  $\bar{H}_0$ ,  $\|\bar{H}_0\Delta\tau_p\| \approx \|H_{zz}\Delta\tau_p\|$ , where  $H_{zz}$  is the direct dipolar Hamiltonian.

phase of all radiation shifted by  $\phi = 2\pi/n$ . This new sequence has an effective Hamiltonian  $\bar{H}_\phi$ , which is related to  $\bar{H}_0$  by a rotation of  $-\phi$  about the  $z$  axis,  $\bar{H}_\phi = \exp(i\phi I_z)\bar{H}_0 \exp(-i\phi I_z)$ .

This phase shift is repeated  $n$  times to form a cycle.<sup>2</sup> The average Hamiltonian for the cycle is  $\mathcal{H}^{(0)} = \sum_m \mathcal{H}_{2\pi m/n}^{(0)}$ , which is  $nk$ -quantum selective even if  $\bar{H}_0$  is nonselective. If  $\bar{H}_0$  is already  $j$ -order selective, we can show that a similar expression holds for the nonselective part of  $\mathcal{H}^{(j)}$ ,  $j' \leq j + 1$ . Therefore, if  $\bar{H}_0$  is  $j$ -order  $nk$ -quantum selective, the sequence obtained from  $\bar{H}_0$  by phase cycling is  $(j + 1)$ -order  $nk$ -quantum selective. Starting from any  $\bar{H}_0$ , phase cycling increases the selectivity of the cycle to one order greater than the selectivity of the subcycles, while lengthening the sequence by factor of  $n$ . Using phase cycling alone, a  $j$ -order  $nk$ -quantum sequence ( $k = 0, 1, 2, \dots$ ) can be designed from a nonselective sequence by  $(j + 1)$  phase cyclings, requiring  $n^{(j+1)}$  subcycles.

The number of subcycles needed can be reduced by the principle of symmetrization and the well-known fact (2) that all odd-order terms  $\mathcal{H}^{(2j+1)}$  vanish for a symmetric sequence. Thus, the symmetrized sequence illustrated in Fig. 1b will raise the selectivity by two orders, if  $\bar{H}_0$  is already  $(2j + 1)$ -order selective, but this sequence requires only  $2n$  subcycles instead of the  $n^2$  subcycles required for two phase cyclings. Starting with a nonselective  $\bar{H}_0$ , a  $2j$ -order selective sequence requires  $n(2n)^j$  subcycles ( $(j + 1)$  phase cyclings and  $j$  symmetrizations) and a  $(2j + 1)$ -order sequence requires  $(2n)^{j+1}$  subcycles ( $(j + 1)$

<sup>2</sup> Other permutations of the  $n$  values of  $\phi$  are also acceptable and may be advantageous in many cases.

phase cyclings and  $(j + 1)$  symmetrizations). For example, a third-order  $4k$ -quantum selective sequence requires 64 subcycles (two phase cycles and two symmetrizations) and can be written schematically ( $0:\phi = 0, 1:\phi = \pi/2, 2:\phi = \pi, 3:\phi = 3\pi/2$ ) as

(01233210) (12300321) (23011032) (30122103)

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In our previous work we incorporated time reversal in the sequence for  $\tilde{H}_0$  shown in Fig. 1c. The quantity  $\tilde{H}_p$  appears as a unitary transformation on  $H_{zz}$ , so that  $\tilde{H}_0$  can contain multiple-quantum coherence if  $\|H_p T\| \geq 1$ . However,  $\|\mathcal{H}_0^{(0)} \Delta\tau_p\| = \|H_{zz} \Delta\tau'_p\|$ , so  $\|\mathcal{H}_0^{(0)} \Delta\tau_p\|$  can be made arbitrarily small by reducing the ratio  $\Delta\tau'_p/\Delta\tau_p$ . In this case, even a zero-order selective sequence will be effective. If time reversal is impossible,  $\tilde{H}_0$  will not contain multiple-quantum coherences unless  $\|\tilde{H}_0 \Delta\tau_p\| \geq 1$ , and a zero-order selective sequence is useless. However, if a high-order selective sequence is used  $\|\tilde{H}_0 \Delta\tau_p\|$  need not be small, and time reversal is not necessary for selectivity. We expect that a combination of high-order selectivity and time reversal, when possible, will give the best results. Applications of these sequences to selective excitation in multiple-quantum NMR will be described in a full paper, together with a quantitative treatment of selectivity.

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