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Selective Excitation of Multiple-Quantum Coherence in Nuclear Magnetic Resonance

W. S. Warren, S. Sinton, D. P. Weitekamp, and A. Pines

University of California, Berkeley, California 94720

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Wideband *selective* n-quantum excitation in the NMR of coupled spins is demonstrated for the first time. By a combination of multiple pulse averaging and phase shifts φ a pure n-quantum excitation operator can be produced ($n = 2\pi/\varphi$). This allows enhancement of normally weak n-quantum transitions. Selective excitation of the zero- and four-quantum transitions in benzene illustrates this approach. Extensions to selective absorption of only groups of n photons in other regimes of spectroscopy are straightforward, in principle.

It has recently been shown that the Zeeman-quantum-number selection rule ($\Delta M = 1$) of conventional Fourier-transform NMR can be overcome, thus permitting the observation of multiple-quantum ($\Delta M = n$) coherences.[1-4] Because the number of transitions decreases as ΔM increases, multiple-quantum spectra are normally easy to interpret, whereas the normal single-quantum spectrum may be intractable. Figure 1 illustrates this point with the n-quantum spectra of oriented benzene. Unfortunately, there is a large decrease in intensity which becomes ex-

ponentially more severe as n increases, limiting the size of molecules and number of quanta amenable to this approach. Clearly, it would be extremely valuable if we were able to selectively excite only certain orders of n-quantum coherences. This would have implications also in optical multiphoton pumping[5] by the selective absorption of only groups of n quanta. This has been considered virtually impossible in general, so that, to date, aside from even-odd–order selection due to symmetry of the bilinear spin operators,[6] no general method of exciting only se-
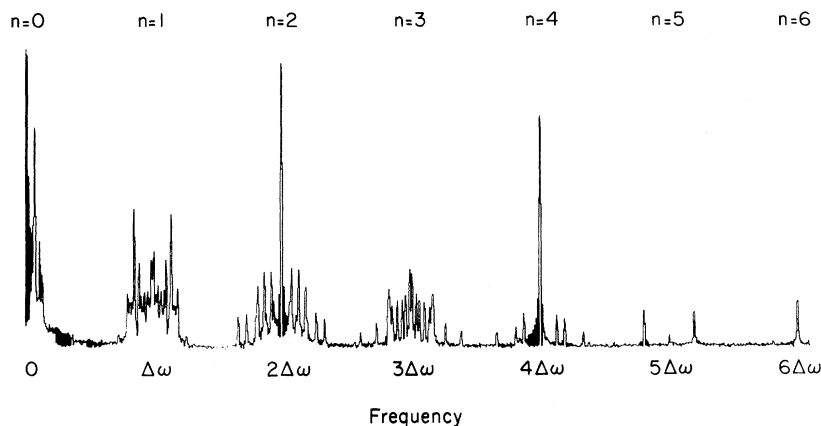

FIG. 1. Multiple-quantum NMR echo spectra of benzene oriented in a liquid crystalline solvent obtained with wideband nonselective excitation and with extensive time and ensemble averaging to observe weak four-, five, and six-quantum lines.
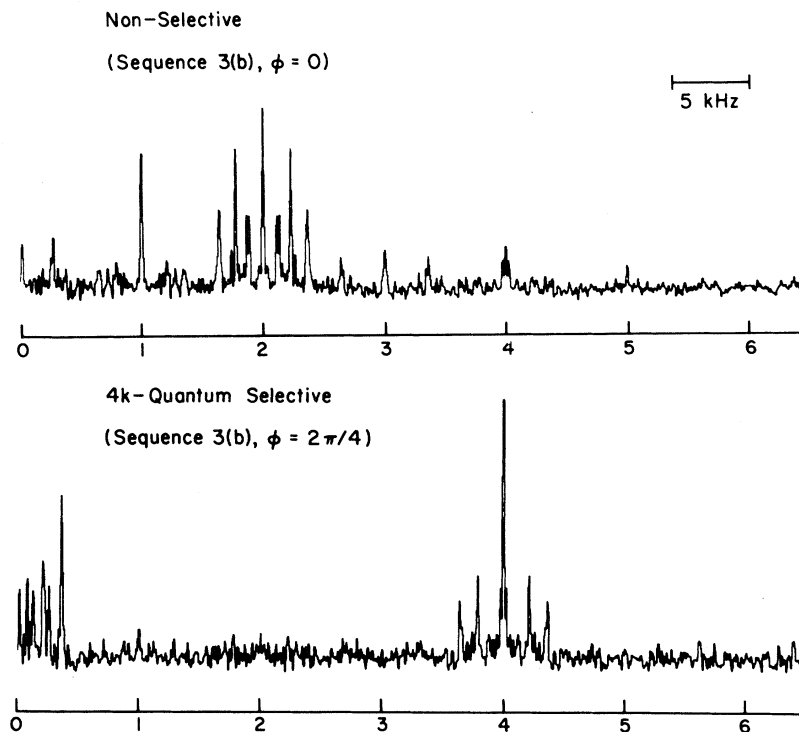
Non-Selective

(Sequence 3(b), $\phi = 0$)

5 kHz

4k-Quantum Selective

(Sequence 3(b), $\phi = 2\pi/4$)

FIG. 2. Effect of selectivity of n-quantum excitation in benzene. The top spectrum was obtained by wideband nonselective excitation using a pulse sequence [Fig. 3(b)] with no φ shifts and with little averaging. The lower spectrum was obtained with the same sequence and acquisition time but with $4k$-quantum selectivity putting $\varphi = \frac{1}{2}\pi$.

lected orders has been proposed. In this paper, we demonstrate for the first time that selective excitation of multiple-quantum coherences is possible, and that arbitrarily high orders can be selected.

An illustration of the results of selective excitation is shown in Fig. 2. In the top part of the figure, the n-quantum spectrum of benzene was excited and detected by wideband nonselective pumping, and with a purposely small acquisition time giving a low signal-to-noise ratio and without ensemble averaging. The small four-, five-, and six-quantum lines are essentially unobservable. The lower spectrum was obtained with our

novel n-quantum selective excitation using $n = 4k$ ($k = 0, 1, \ldots$). In fact, only the zero- and four-quantum transitions are excited, and their intensity is substantially greater.

To understand how this selective excitation works, consider the pulse sequences in Fig. 3, and assume that we apply them to dipole-coupled nuclear spins in a large magnetic field. The simplest pulse sequence for producing *nonselective* wideband multiple-quantum spectra is that of Fig. 3(a).[4] The first two pulses, separated by a time τ_p comparable to T_2 ($T_2^{-1} \sim$ width of one-quantum spectrum) constitute the excitation sequence. At the end of the second pulse, the reduced density matrix is

$$\rho = \exp(- i\tfrac{1}{2}\pi I_y) \exp[- i(H_{zz} + \Delta\omega I_z)\tau_p] \exp(\tfrac{1}{2}i\pi I_y) I_z \exp(- \tfrac{1}{2}i\pi I_y) \exp[i(H_{zz} + \Delta\omega I_z)\tau_p] \exp(\tfrac{1}{2}i\pi I_y)$$

$$= \exp[- i(H_{xx} + \Delta\omega I_x)\tau_p] I_z \exp[i(H_{xx} + \Delta\omega I_x)\tau_p], \tag{1}$$

where $H_{zz} = \sum_{i<j} \alpha_{ij}(3I_{iz}I_{jz} - \vec{I}_i \cdot \vec{I}_j)$ is the secular part of the dipole-dipole coupling Hamiltonian, $\Delta\omega$ is the resonance offset, and $H_{xx} = \sum_{i<j} \alpha_{ij}(3I_{ix}I_{jx} - \vec{I}_i \cdot \vec{I}_j)$ is H_{zz} transformed by the $(\tfrac{1}{2}\pi)_y$ pulses. Clearly, other interactions such as scalar coupling, chemical shifts, etc., are easily accounted for. In general, ρ will contain matrix elements corresponding to every order of multiple-quantum transition. The third pulse is used to transfer the "invisible" n-quantum coherences, which evolve during t_1, to observable one-quantum coherences in t_2.[2,4]
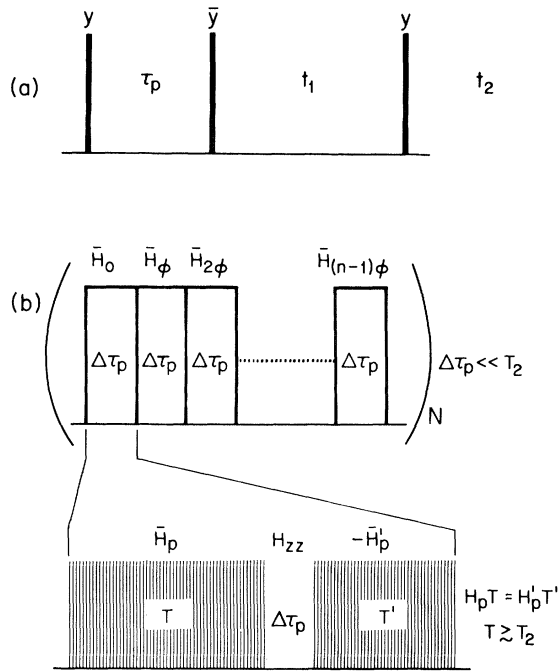
FIG. 3. Multiple-quantum pulse sequences. In sequence (a) y and $\bar{y}$ are $\frac{1}{2}\pi$ pulses along the y and $-y$ axes in the rotating frame. Sequence (b) is n-quantum selective if $\varphi = 2\pi/n$. $\bar{H}_p'$ are average Hamiltonians explained in the text which operate for $T \geq T_2$ to create a subcycle operator $\bar{H}_0$ with n-quantum elements and effecitve cycle time $\Delta\tau_p \ll T_2$.

To perform a *selective* wideband excitation we use a sequence of the type indicated schematically in Fig. 3(b). Multiple-pulse averaging[7] is used in two steps. First, it is used to produce an effective Hamiltonian $\bar{H}_0$ containing all multiple-quantum matrix elements, under which the system evolves for a time $\Delta\tau_p$ such that $\|\bar{H}_0\Delta\tau_p\| \ll 1$. This is called subcycle. All the pulses are then phase shifted by an angle φ to create a new subcycle, with a new (rotated) effective Hamiltonian,

$$\bar{H}_\varphi = \exp(-i\varphi I_z)\,\bar{H}_0\exp(i\varphi I_z), \qquad (2)$$

which is also allowed to evolve for $\Delta\tau_p$. The phase shift multiplies every m-quantum term by $e^{im\varphi}$. This process is repeated with incremented phases $k\varphi$ for n times where $n = 2\pi/\varphi$ to form a cycle and the whole cycle is then repeated N times, such that $\tau_p = Nn\,\Delta\tau_p \geq T_2$. The overall average Hamiltonian (second step) for this exci-

tation sequence is given by

$$\bar{H}^{(0)} = \frac{1}{n}\sum_{k=0}^{n-1}\bar{H}_{k\varphi}$$

$$= \frac{1}{n}\sum_{k=0}^{n-1}\exp(-ik\varphi I_z)\bar{H}_0\exp(ik\varphi I_z). \qquad (3)$$

Since $n = 2\pi/\varphi$, only n-quantum terms are unaffected by the phase shifts and survive so that $\bar{H}^{(0)}$ is a pure n-quantum operator to lowest order in $\Delta\tau_p$. All that has been assumed about the nature of $\bar{H}_0$ is that the excitation is wideband and coherent, which may pose technical problems.

It now remains only to explain the crux of the approach, namely how we use averaging to produce $\bar{H}_0$, while keeping $\|\bar{H}_0\Delta\tau_p\| \ll 1$. This is done by a sequence depicted in the lower part of Fig. 3(b), which gives the effective Hermitian subcycle operator:

$$\bar{H}_0 = \exp(i\bar{H}_p'\,T')\,H_{zz}\exp(-i\bar{H}_p\,T)$$

$$= \exp(i\bar{H}_p\,T)H_{zz}\exp(-i\bar{H}_p\,T). \qquad (4)$$

Note that, even though T is made to be $\geq T_2$ to efficiently produce all n-quantum elements in $\bar{H}_0$, the effective time in the cycle is $\Delta\tau_p \ll T_2$. T enters only as a parameter in the unitary transformation of H_{zz}, to lowest order.

There are many ways of producing a time-reversible $\bar{H}_p$.[8] Two simple possibilities, easily implemented, are the following:

(a) $\bar{H}_p = H_{xx}$ with the sequence 90_y-T-$90_{\bar{y}}$ (90 is the pulse-flip angle, and the subscript indicates the relative rf phase) and $\bar{H}_p' = -\frac{1}{2}H_{xx}$ created by the time-reversing sequence $(90_x$-τ-90_x-τ-$90_{\bar{x}}$-τ-$90_{\bar{x}}$-τ-$90_{\bar{x}}$-τ-90_x-τ-90_x-$\tau)_m$ which is repeated enough times (large m) to make a total interval of $T' = 2T$. It is necessary that $\tau \ll \Delta\tau_p$.

(b) $\bar{H}_p = \frac{1}{2}(H_{yy} + H_{xx}) = \frac{1}{2}(2H_{yy} + H_{zz})$ can be produced by the sequence $(90_x$-2τ-90_x-τ-$90_{\bar{x}}$-2τ-$90_{\bar{x}}$-τ-$90_{\bar{x}}$-2τ-$90_{\bar{x}}$-τ-90_x-2τ-90_x-$\tau)_m$, repeated enough times to make a total interval of T, with $\tau \ll \Delta\tau_p$ again. The reversal in this case is produced (since $H_{yy} - H_{xx}$ is a pure two-quantum operator) by phase shifting each pulse by $\frac{1}{2}\pi$, giving $-\bar{H}_p' = -\frac{1}{2}(H_{yy} - H_{xx})$ and a time $T' = T$. Since the pulses are not δ pulses and have a width t_p, the timing is modified slightly to $2\tau'$ instead of 2τ. Inhomogeneous broadening is completely eliminated by this sequence.

Sequence (b) has advantages in correcting pulse imperfections, and was used with $4k$-quantum selection $(\varphi = \frac{1}{2}\pi)$ for the selective spectrum in Fig. 2(b). Other orders may be easily selected by changing φ. The experimental parameters

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were $t_p = 2.4 \, \mu\sec$, $\tau = 3.0 \, \mu\sec$, $2\tau' = 8.8 \, \mu\sec$, $T = 2$ msec, $\Delta\tau_p = 35 \, \mu\sec$, and the entire cycle was repeated four times (a total of 16 subcycles). After this selective excitation, the coherences evolved during t_1 and were detected nonselectively during t_2 as in Fig. 3(a). Figure 2(a) was generated by the same sequence, except that φ was never incremented, giving no selectivity for comparison. The experiments were performed at 185 MHz on a sample of $\sim 13\%$ benzene dissolved in Eastman liquid crystal 15 320.

We conclude with some comments. The sequence of Fig. 3(b) is kn-quantum selective, where $n = 2\pi/\varphi$ and $k = 0, 1, \dots$. Thus zero-quantum transitions are always excited. If we modify this by making the subcycles alternate between periods of $+ \Delta\tau_p$ and $- \Delta\tau_p$ (i.e., reverse H_{zz} in each alternate subcycle)[8] then the sequence becomes $[\frac{1}{2}(2k+1)n]$-quantum selective, $k = 0, 1, \dots$, i.e., the first order is $\frac{1}{2}n$. Such reversals with $\varphi = \frac{1}{4}\pi$, for example, would give us pure four-quantum (no zero-quantum) excitation in benzene. A selective sequence can be used also during the detection period instead of a single pulse [pulse 3 in Fig. 3(a)] to enhance the signal-to-noise ratio of the n-quantum spectrum further. This is a true selective detection of n-quantum coherence, whereas Fourier transformation with respect to φ [2c,4] is only a separation of orders n. Permutations of the subcycles permit the construction of sequences which are selective to arbitrarily high order in $\Delta\tau_p$. Finally, our choice of $\overline{H}_p$ makes this sequence even-quantum selective, but minor modifications make odd-quantum selection possible. For example, we could use $(H_{xx} + \Delta\omega I_x)\Delta\tau_p$ instead of $H_{zz}\Delta\tau_p$ to produce pure n odd. Details of our approach and a discussion of the consider-

able latitude in selection of Hamiltonians and sequences (H_{zz}, $\overline{H}_p$, etc.) will be presented in a full paper.

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