

SIMPLE PULSE SEQUENCES FOR SELECTIVE MULTIPLE-QUANTUM EXCITATION

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Received 8 February 1982

A sixteen pulse sequence which excites only four-quantum transitions in multiple-quantum NMR is shown to give good selectivity on two molecules, benzene and *n*-butyl bromide. The behavior as pulse sequence parameters are varied is shown to be consistent with coherent averaging theory. Advantages of this new sequence include much lower duty cycles and shorter total duration than can be achieved with previously used selective sequences. Limitations of this approach and extensions to high-quantum selectivity are discussed.

Selective excitation of high-quantum transitions in anisotropic systems has recently been shown theoretically [1] and experimentally [2] to yield large signal gains relative to standard non-selective techniques. However, the selective pulse sequences used in experiments to date have required thousands of pulses, so that sample heating and pulse train instabilities are serious problems. In addition, it would be difficult for purely technical reasons to use such long sequences for selective multiphoton pumping in other regimes of spectroscopy.

In this letter we present experimental evidence that good selectivity can be achieved with much shorter pulse sequences. We have found that sixteen pulses are sufficient to selectively excite $4k$ -quantum coherences ($k = 0, \pm 1, \pm 2, \dots$). The pulse sequence is given in fig. 1. In the top part of fig. 1 \mathcal{H}_0 represents a cyclic sequence of pulses and delays of total duration $\Delta\tau_p$. The sequence for \mathcal{H}_0 is repeated n times, with each pulse phase shifted by $\phi = 2\pi/n$ before each repetition. This process, which is termed phase cycling [1,2], creates a sequence which is nk -quantum selective to lowest order in coherent averaging theory [3,4] even if \mathcal{H}_0 is totally non-selective. However, this does not imply that the exact sequence for \mathcal{H}_0 is unimportant. To

minimize high-order non-selective terms, $\|\mathcal{H}_0 \Delta\tau_p\| \ll 1$ is required; but multiple-quantum operators do not develop unless $\|\mathcal{H}_z \Delta\tau_p\| \gtrsim 1$, where \mathcal{H}_z is the spin hamiltonian. Thus, the key to good selectivity is to use a pulse sequence which has an effective hamiltonian $\|\mathcal{H}_0\| \ll \|\mathcal{H}_z\|$.

Previous experiments have combined two dipolar time reversing sequences (separated by a short delay) to produce \mathcal{H}_0 . A simpler approach, which is shown at the bottom of fig. 1, is to use a dipolar line narrow-

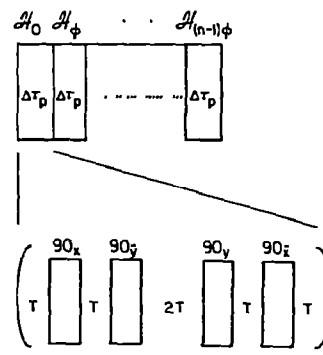


Fig. 1. The sixteen pulse sequence used to selectively excite four-quantum coherences. Here \mathcal{H}_0 represents a WAHUHA line narrowing sequence, which eliminates the dipolar hamiltonian to first order. The coherences evolve for a time t_1 , and then are detected by repeating this same sequence with one pulse added at the end (see ref. [1] for details).

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ing sequence such as the four-pulse [3] sequence. For clarity the average hamiltonian of this subcycle sequence will be written with a small h . Pure dipolar interactions are suppressed in $\bar{h}^{(0)}$ and $\bar{h}^{(1)}$. Chemical shift and resonance offset terms are not suppressed, but these interactions are generally much weaker than the dipolar interaction. The operator $\bar{h}^{(2)}$ is given by:

$$\bar{h}^{(2)} = \frac{1}{648} I_C^2 [\mathcal{H}_{xx} - \mathcal{H}_{zz}, [\mathcal{H}_{xx}, \mathcal{H}_{yy}]], \quad (1)$$

$$\mathcal{H}_{\alpha\alpha} = \sum_{i>j} D_{ij} (3I_{\alpha i} I_{\alpha j} - I_i \cdot I_j) \quad (\alpha = x, y, \text{ or } z), \quad (2)$$

which can readily be shown to contain four-quantum operators. There is a range of values for T (the short delay between the pulses) such that $\|\mathcal{H}_{zz}\| \gg \|\bar{h}^{(2)}\| \gg \|\mathcal{H}_{cs}\|, \|\mathcal{H}_J\|$, and if T is in this range a four-pulse sequence can be used for \mathcal{H}_0 when four-quantum selection is desired.

Fig. 2 shows the effects of varying T in one cycle of $4k$ -quantum selection on a sample of 13 wt% benzene dissolved in Eastman liquid crystal no. 15320. As expected, small values of T give almost no signal, since $\bar{h}^{(2)}$ is proportional to T^2 . When $T = 100 \mu\text{s}$ the se-

quence is selective in all the irreducible representations; the three pairs of side peaks and large central transition coincide with the known line positions of all the allowed four-quantum transitions [5]. As T grows larger the selectivity is expected to fade away first in the totally symmetric representation (where $\|\mathcal{H}_{zz}\|$ is largest) [1], and therefore the side peaks lose intensity. It is clear that only a narrow range of values of T gives good selectivity, which is a consequence of the strong dependence of $\bar{h}^{(2)}$ on the cycle time.

All the spins in oriented benzene have the same chemical shift, so they can all be put on resonance to minimize correction terms. This cannot be done with oriented *n*-butyl bromide, which has four inequivalent sets of nuclei. Nonetheless, two cycles of $4k$ -quantum selection with $T = 30 \mu\text{s}$ produces mainly four-quantum signal, as shown in fig. 3. Superior selectivity and signal enhancement might be produced by inserting echoing 180° pulses in the middle of each delay, as this would reduce the chemical shift contribution.

Since $\bar{h}^{(2)}$ has no operators with $\Delta M > 4$, higher-quantum selection must rely on higher correction terms, and therefore is unlikely to be effective. It would

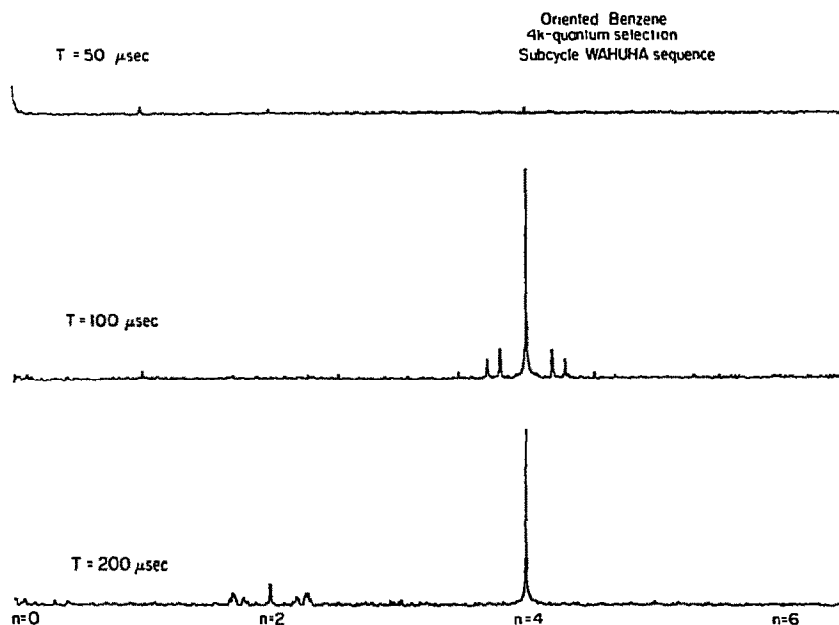


Fig. 2. The effects on oriented benzene of varying the delay between pulses in fig. 1. As expected from coherent averaging theory the value of T is critical. The pulse width is $5 \mu\text{s}$, so the duty cycle is very low.

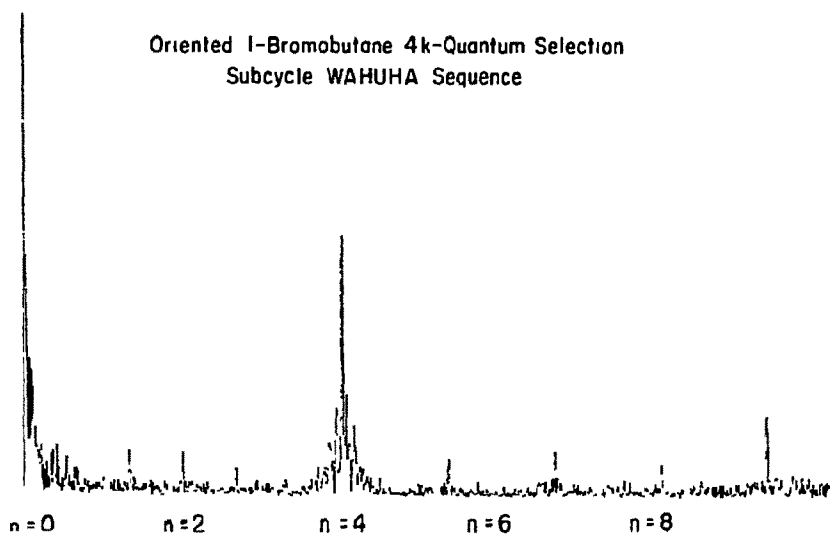


Fig. 3. The effects on oriented *n*-butyl bromide (1-bromobutane) of two cycles of 4k-quantum selection with $T = 30 \mu\text{s}$. The range of chemical shifts in this molecule makes selection more difficult, since a WAHUHA sequence does not eliminate these terms. Nonetheless good selectivity can be achieved.

then be useful to try line narrowing sequences which eliminate the dipolar hamiltonian to higher order. For example, the 72-pulse sequence of Burum and Rhim [6] has 6-quantum operators in its leading dipolar term $\bar{h}^{(4)}$, and thus would be a good candidate for \mathcal{H}_0 in a 6k-quantum selective sequence. The level of compensation required in the line narrowing sequence grows rapidly as the number of quanta increases, and this will be a practical limitation to the technique. Nonetheless, the advantages of very low duty cycles and shorter total pulse sequence duration make the use of line narrowing sequences an attractive option for low-quantum selection.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the US Department of Energy under Contract Number W-7405-ENG-48.

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