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Author

Warren, W.S.

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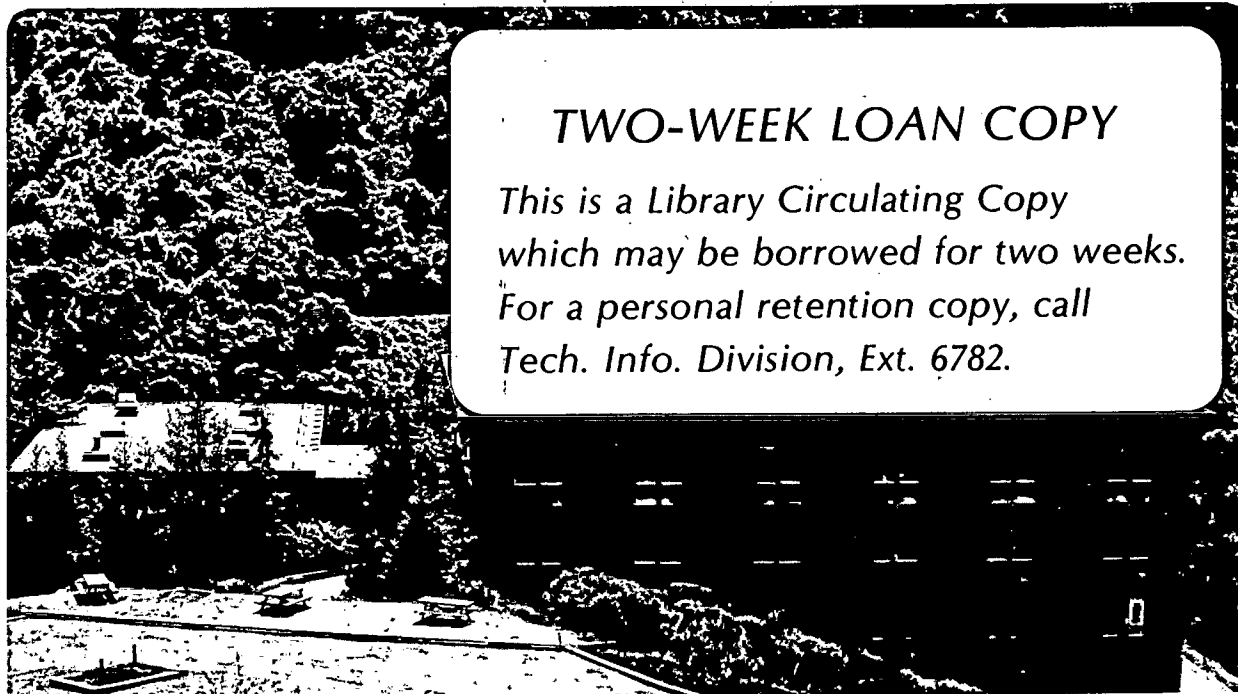
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SELECTIVE EXCITATION OF MULTIPLE-QUANTUM COHERENCE
IN NUCLEAR MAGNETIC RESONANCE

W. S. Warren, S. Sinton, D. P. Weitekamp and A. Pines
University of California, Berkeley, California 94720

ABSTRACT

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 ($n=2\pi/\phi$). This allows enhancement of normally weak n-quantum transitions. Selective excitation of the 0- and 4-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 have 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 exponentially 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 pumping⁵ 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 selected 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 Figure 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 low signal-to-noise ratio and without ensemble averaging. The small 4-, 5-, and 6-quantum lines are essentially unobservable. The lower spectrum was obtained with our novel n -quantum selective excitation using $n=4k$ ($k=0,1,\dots$). In fact,

only the 0- and 4-quantum transitions are excited, and their intensity is substantially greater.

To understand how this selective excitation works, consider the pulse sequences in Figure 3, and assume 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 Figure 3(a). The first two pulses, separated by a time τ_p comparable to T_2 (T_2^{-1} -width of 1-quantum spectrum) constitute the excitation sequence. At the end of the second pulse, the reduced density matrix is:

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

$$\times \exp(i(H_{zz} + \Delta\omega I_z)\tau_p) \exp(i \frac{\pi}{2} I_y) = \exp(-i(H_{xx} + \Delta\omega I_x)\tau_p) I_z \exp(i(H_{xx} + \Delta\omega I_x)\tau_p)$$

where $H_{zz} = \sum_{i < j} a_{ij} (3I_{iz} I_{jz} - \vec{I}_i \cdot \vec{I}_j)$ is the secular part of the dipole-dipole coupling Hamiltonian, $\Delta\omega$ is the resonance offset, and $H_{xx} = \sum_{i < j} a_{ij} (3I_{ix} I_{jx} - \vec{I}_i \cdot \vec{I}_j)$ is H_{zz} transformed by the $(\pi/2)_y$ 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 1-quantum coherences in t_2 .^{2,4}

To perform a selective wideband excitation we use a sequence of the type indicated schematically in Figure 3(b). Multiple pulse averaging⁷ 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 a subcycle.

All the pulses are then phase shifted by an angle ϕ to create a new sub-cycle, with a new (rotated) effective Hamiltonian:

$$\bar{H}_\phi = \exp(-i\phi I_z) \bar{H}_0 \exp(i\phi I_z) \quad (2)$$

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

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

Since $n=2\pi/\phi$ only n-quantum terms are unaffected by the phase shifts and survive so $\bar{H}^{(0)}$ 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 Figure 3(b), which gives the effective Hermitian subcycle operator:

$$\bar{H}_0 = \exp(i\bar{H}_p T) H_{zz} \exp(-i\bar{H}_p T) = \exp(i\bar{H}_p T) H_{zz} \exp(-i\bar{H}_p T). \quad (4)$$

Note that, even though T is made $\gg T_2$ 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 $90_y - T - 90_y$, (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 $(90_x -\tau - 90_x -\tau - 90_x -\tau - 90_x -\tau - 90_x -\tau - 90_x -\tau - 90_x -\tau - 90_x -\tau)_m$ 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 $(90_x - 2\tau - 90_x -\tau - 90_x - 2\tau - 90_x -\tau - 90_x - 2\tau - 90_x -\tau - 90_x - 2\tau - 90_x -\tau)_m$, 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 2-quantum operator) by phase shifting each pulse by $\pi/2$, 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 ($\phi = 2\pi/4$) for the selective spectrum in Figure 2(b). Other orders may be easily selected by changing ϕ . The experimental parameters were $t_p = 2.4 \mu\text{sec}$, $\tau = 3.0 \mu\text{sec}$, $2\tau' = 8.8 \mu\text{sec}$, $T = 2 \text{ msec}$, $\Delta\tau_p = 35 \mu\text{sec}$, 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 non-selectively during t_2 as in Figure 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 185MHz on a sample of ~13% benzene dissolved in Eastman liquid crystal 15320.

We conclude with some comments. The sequence of Figure 3(b) is kn -quantum selective, where $n = 2\pi/\phi$ and $k = 0, 1, \dots$. Thus 0-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 $n/2$. Such reversals with $\phi=\pi/4$, for example, would give us pure 4-quantum (no 0-quantum) excitation in benzene. A selective sequence can be used also during the detection period instead of a single pulse (pulse 3 in Figure 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 \bar{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 considerable latitude in selection of Hamiltonians and sequences (H_{zz} , \bar{H}_p , etc.) will be presented in a full paper.

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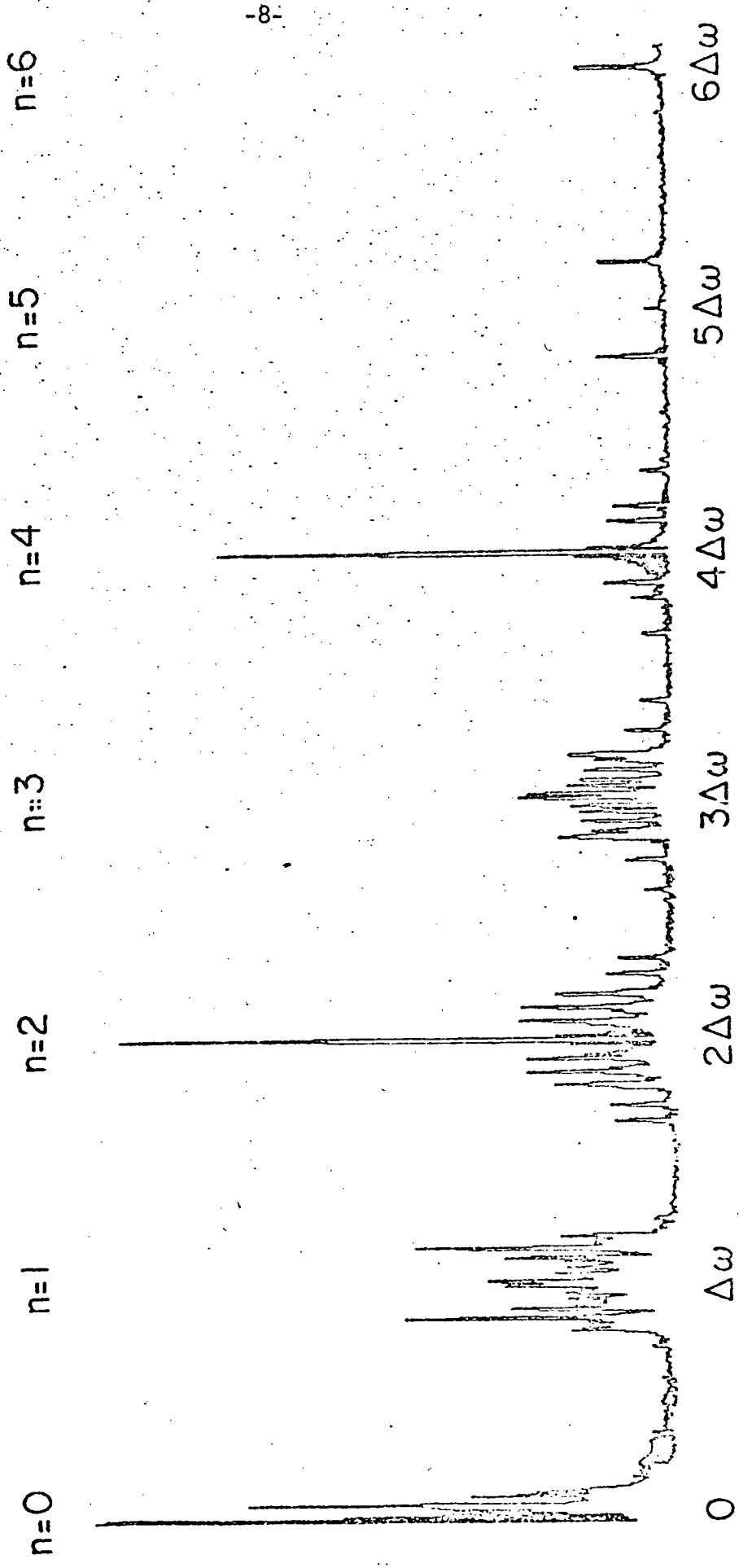
CAPTIONS

Figure 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 4-, 5-, and 6-quantum lines.

Figure 2. Effect of selectivity of n-quantum excitation in benzene. The top spectrum was obtained by wideband nonselective excitation using a pulse sequence (Figure 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 $\phi = \pi/2$.

Figure 3. Multiple-quantum pulse sequences. Sequence (a) y and \bar{y} are $\pi/2$ pulses along the y and $-y$ axes in the rotating frame. Sequence (b) is n-quantum selective if $\phi = 2\pi/n$. \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 effective cycle time $\Delta\tau_p \ll T_2$.

Oriented Benzene
n-Quantum Echo Spectra

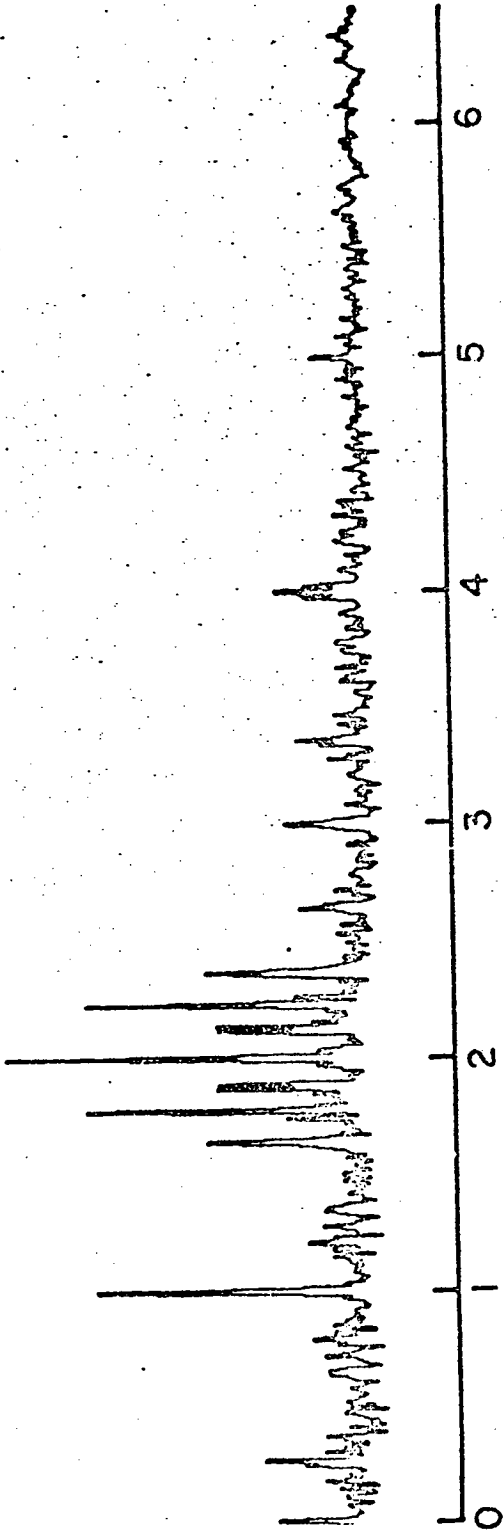


Frequency

Non-Selective

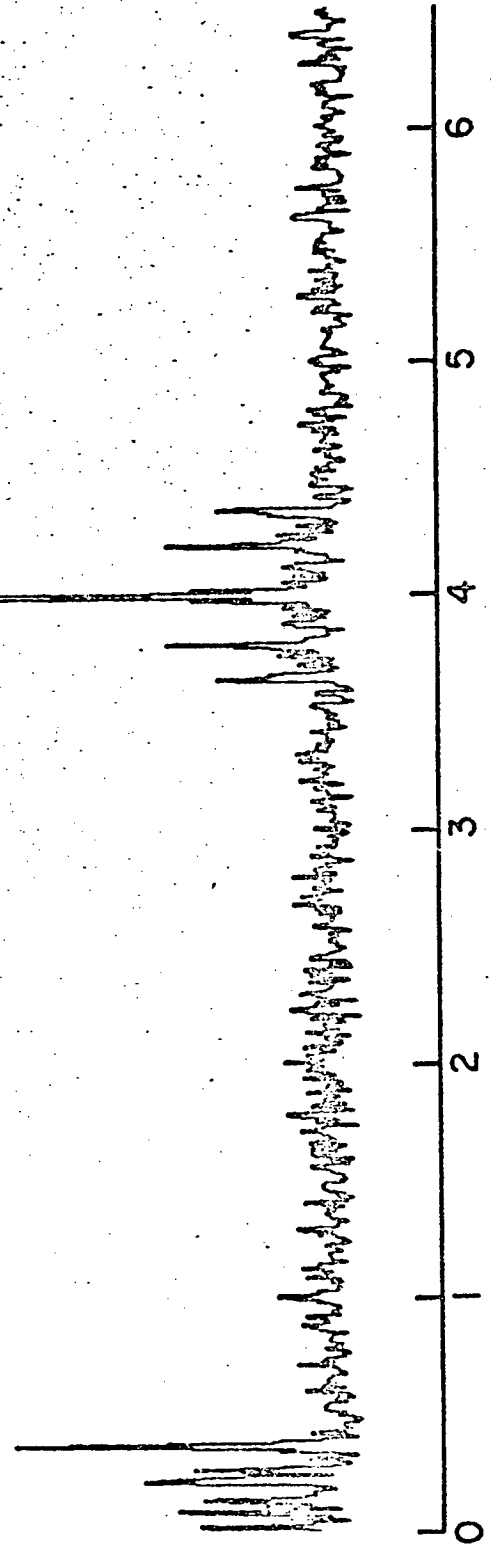
(Sequence 3(b), $\phi = 0$)

5 kHz

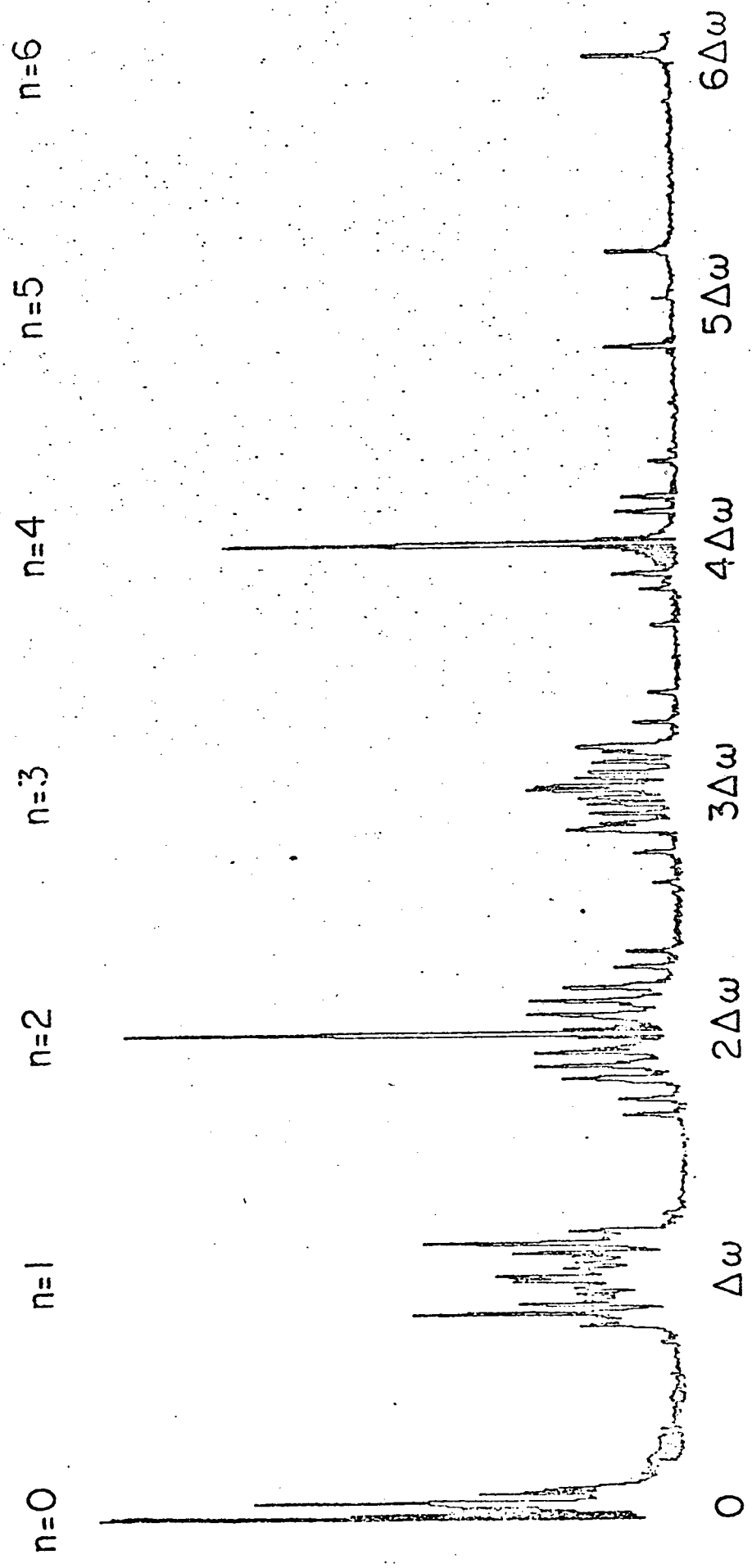


4k-Quantum Selective

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



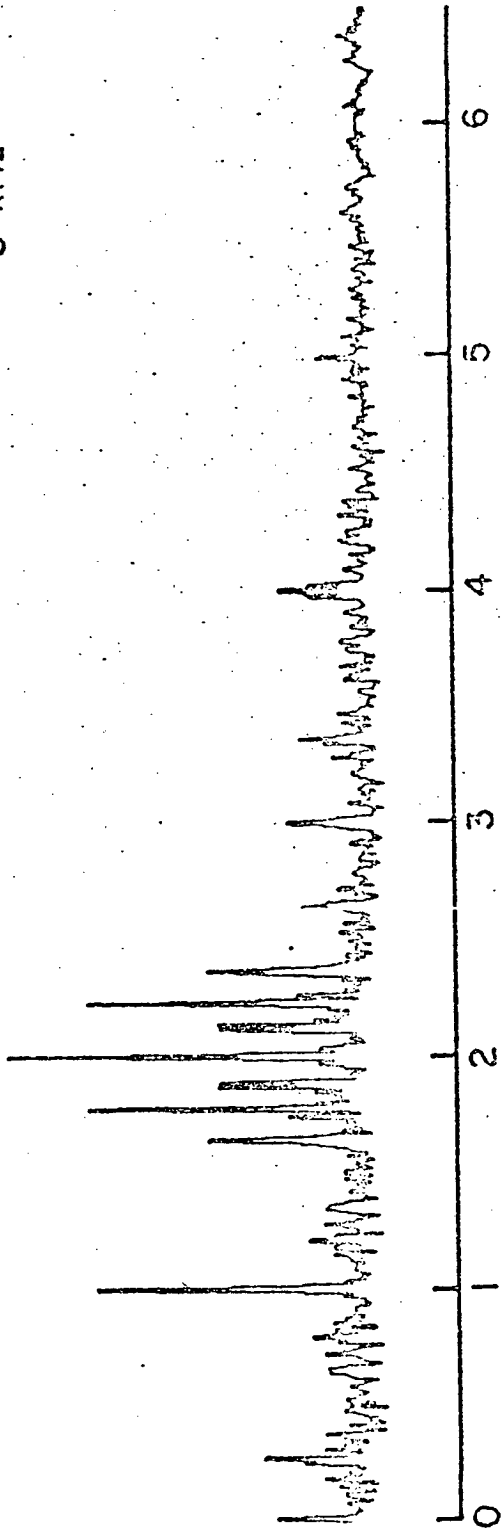
Oriented Benzene
n-Quantum Echo Spectra



Non-Selective

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

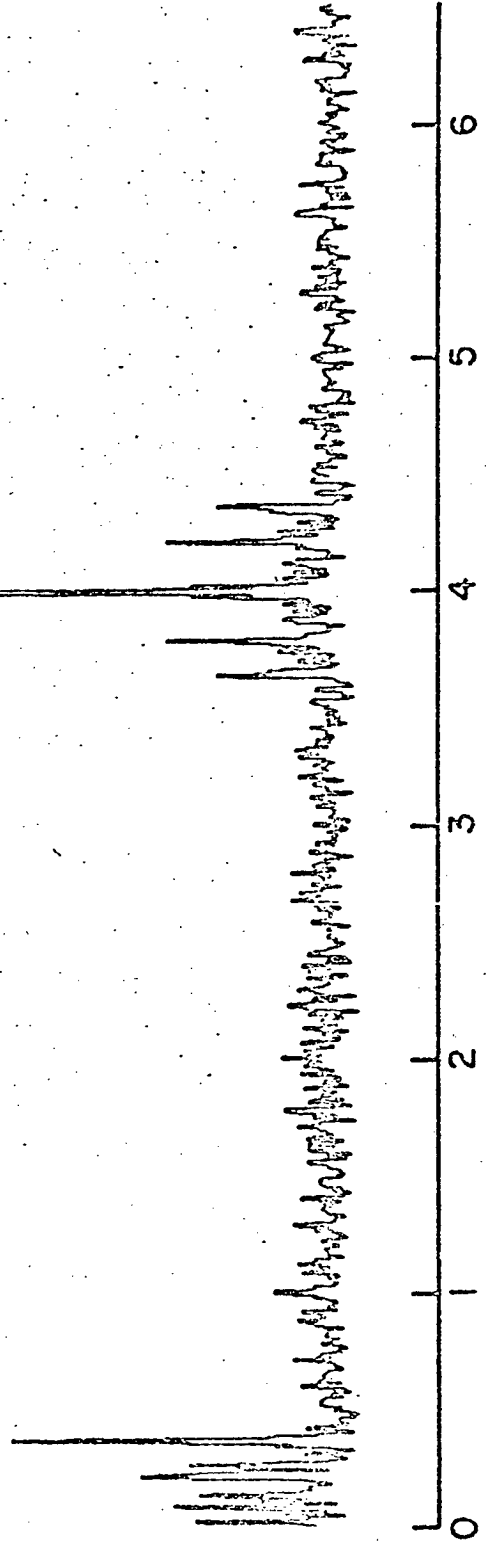
5 kHz

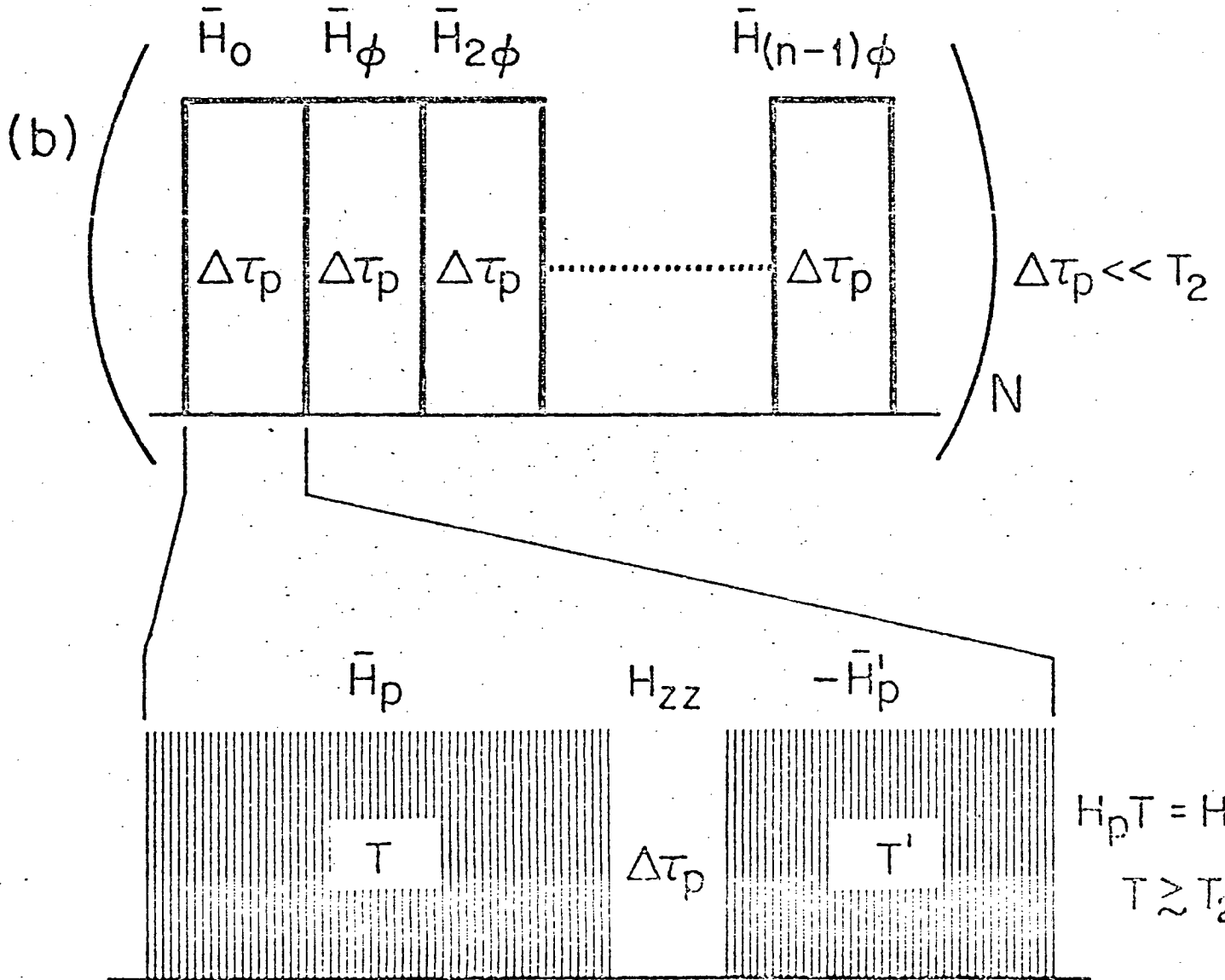
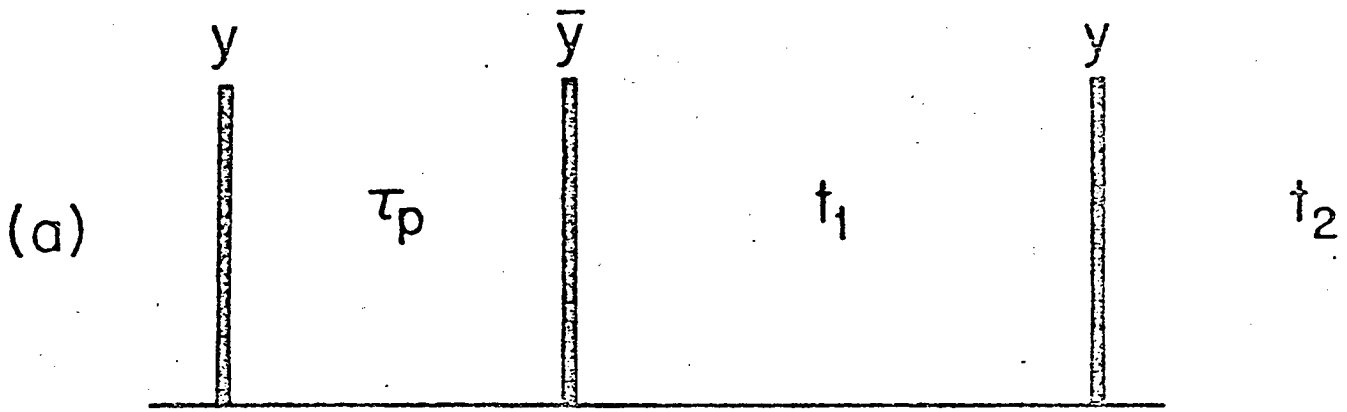


4k-Quantum Selective

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

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