

Search Procedure for Optimizing High-Order Multiple-Quantum Transition Intensities

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The most difficult aspect of a Fourier transform multiple-quantum NMR experiment in a system with many levels ($l=5$) is often determining pulse sequences which result in satisfactory intensities for the transitions of interest. These line intensities depend on the detailed dynamics of the excitation (preparation and mixing) periods and thus on one or more pulse amplitude and timing parameters. It often occurs that only lines of certain orders $n = \Delta m$ are needed for spectral analysis and the problem becomes that of efficiently determining parameters which will lead to intense lines of a given order. These parameters are often not precisely calculable because of the size of the calculation, unknown internal Hamiltonian parameters, or unknown pulse sequence imperfections. One is left with an experimental search problem. The purpose of this communication is to describe a procedure for rapid search over excitation sequence parameters and to present an application to the proton multiple-quantum NMR of acetaldehyde partially oriented in a nematic liquid crystal.

The general form of the experiments discussed here is shown in Fig. 1a. The components of transverse nuclear spin magnetization observable with quadrature detection at some time in the period t_2 can be written as a complex number S_+ in terms of the density operator of the spin system ρ ,

$$S_+(\mathbf{p}, t_1, \mathbf{m}, t_2) = \text{Tr}(\rho(\mathbf{p}, t_1, \mathbf{m}, t_2)I_+), \quad [1]$$

where $I_+ = I_x + iI_y$ and \mathbf{p} and \mathbf{m} are sets of rf and timing parameters which determine the propagators $U(\mathbf{p})$ and $V(\mathbf{m})$ describing, respectively, the preparation and mixing periods.

Figure 1b shows the pulse sequence used for the experiments on partially oriented acetaldehyde. The π pulses in preparation, evolution, and mixing periods serve to remove the effects of magnet inhomogeneity. Since this spin system is in the intermediate coupling regime where the chemical shift and spin-spin couplings do not commute, these π pulses also complicate the dynamics considerably (δ). A method for obtaining undistorted homogeneous spectra under such conditions is

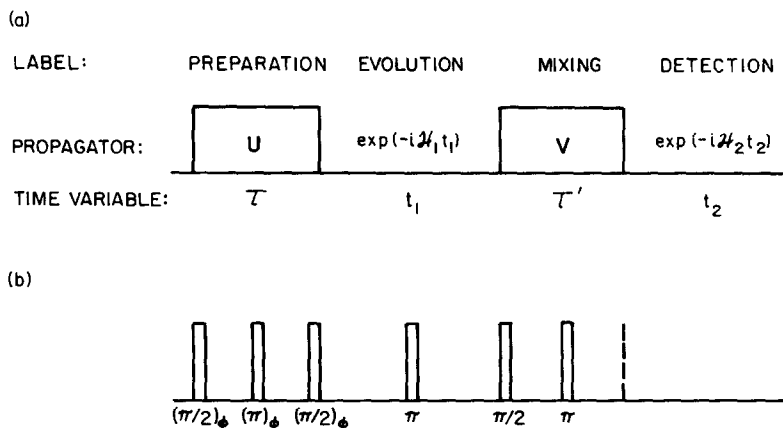


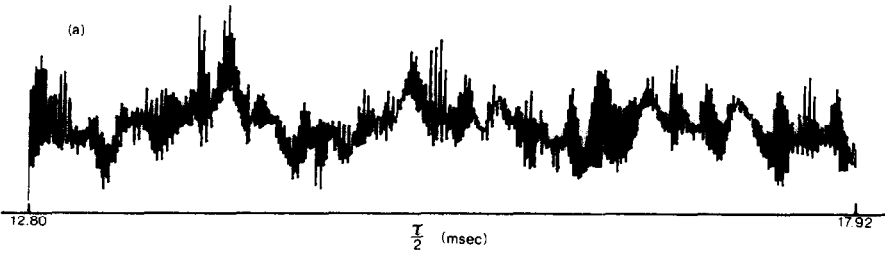
FIG. 1. (a) Generalized schematic diagram of the time-domain multiple-quantum NMR experiment. Each of the four labeled time periods is characterized by its respective propagator and time variable. In the PPPI experiment, the rf phase of U and the search parameter characterizing both U and V are incremented from one shot to the next. The signal is collected in t_2 for a fixed value of t_1 . (b) Actual pulse sequence used for the PPPI experiments on partially oriented acetaldehyde. The phase of the first three rf pulses was incremented along with the excitation time $\tau = \tau'$. The other times and pulse phases are held constant. For each value of τ , a single magnetization point was sampled at $t_2 = 0$.

described elsewhere (7). For the purpose of this work the pulse sequence serves as a simple example in which the excitation dynamics depend on a single experimental variable, the interval $\tau/2$.

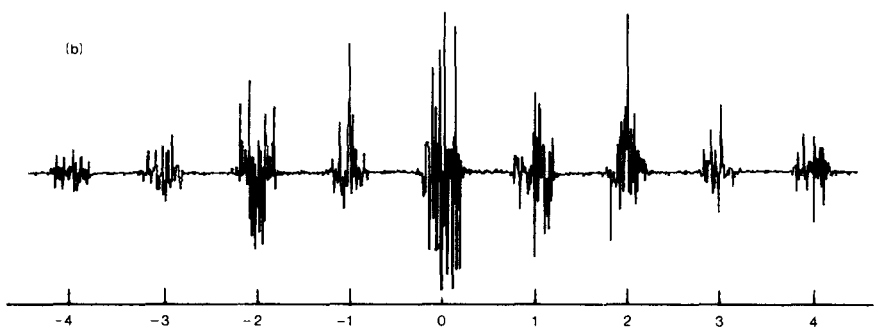
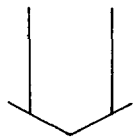
The search over this parameter is made by fixing the value of t_1 and incrementing $\tau/2$ on successive shots. With each increment of the parameter the rf phase of the preparation period pulses is also incremented. In close analogy to the TPPI technique (2, 3), where the evolution period time t_1 and the preparation period rf phase are incremented together, the present technique is PPPI (parameter proportional phase incrementation).

Figure 2a shows one channel of the resulting proton NMR signal of the four-spin acetaldehyde molecule when $\tau/2$ is varied from 12.80 to 17.92 msec. Figure 2b shows one component of the complex Fourier transform of this signal. The contribution to this transform from coherence prepared with quantum numbers $-4 \leq n \leq +4$ is well separated by the phase shifts associated with the parameter increment. This allows the contribution for one value of n to be isolated, shifted

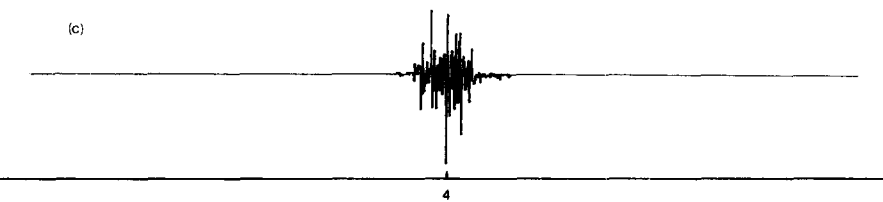
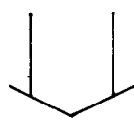
FIG. 2. Collection and processing of data from the PPPI experiment. (a) One channel of the proton NMR signal of partially oriented acetaldehyde collected using the pulse sequence of Fig. 1b, with preparation time variable $\tau/2$ ranging from 12.80 to 17.92 msec. (b) One component of the complex Fourier transform of the signal showing contributions from the various multiple-quantum orders n , $-4 \leq n \leq 4$, well separated by incrementation of the phase of the preparation pulses. (c) Response of a single order ($n = 4$), shifted back to the origin to remove the apparent offset attributable to phase incrementation. (d) Display of the magnitude of the inverse Fourier transform of the response in (c). From this excitation function, the best values of the search parameter τ for the selected order may be chosen. If, as here, only the magnitude is of interest, then the shift to the origin before inverse Fourier transformation may be omitted.



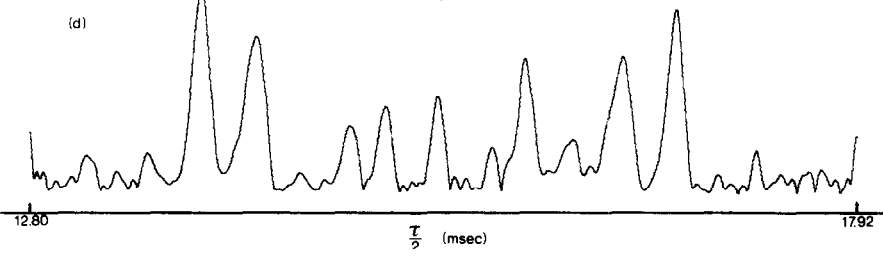
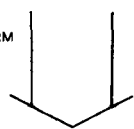
FOURIER TRANSFORM



SHIFT AND DELETE



INVERSE FOURIER TRANSFORM
AND EXAMINE MAGNITUDE



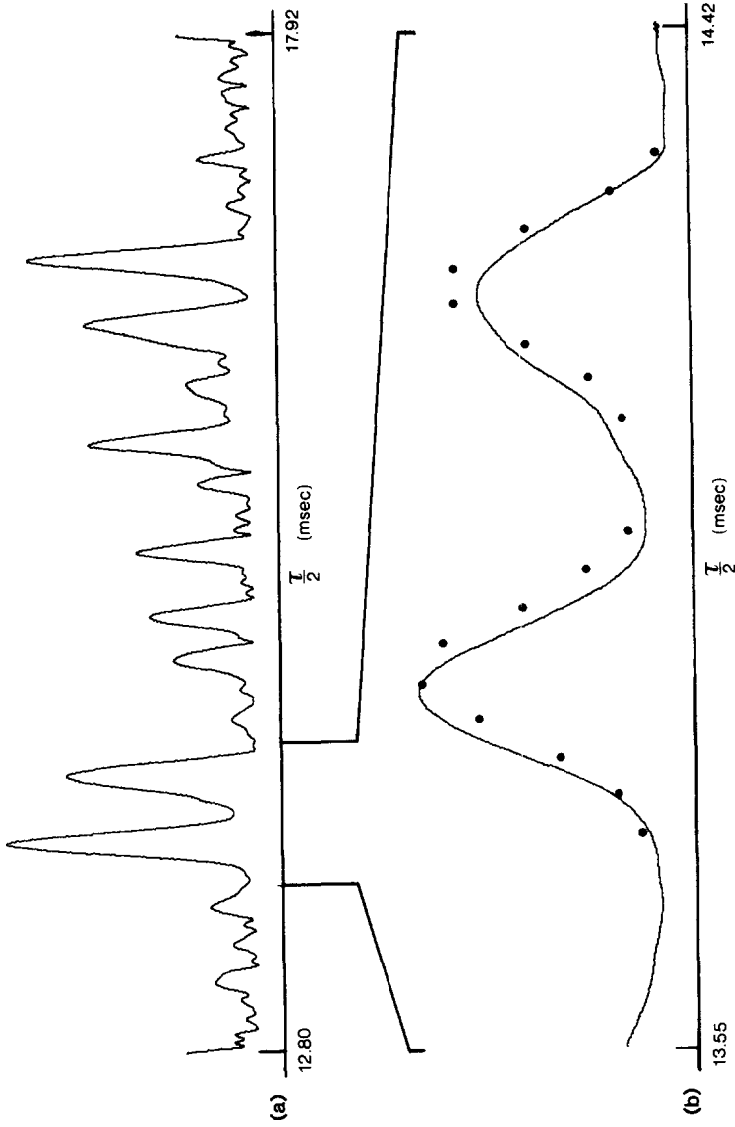


FIG. 3. (a) The $n = 4$ excitation function of partially oriented acetaldehyde with excitation time variable $\tau/2$ ranging from 12.80 to 17.92 msec reproduced from Fig. 2d. (b) Magnitude of the four-quantum line intensity obtained for a series of multiple-quantum experiments with fixed τ and variable t_i . The points for individual experiments are superimposed on an expanded portion of the $n = 4$ excitation function.

to the origin, and inverse Fourier transformed. The result is again a complex function of $\tau/2$, now free of the extraneous modulation introduced by the phase-shifting and specific to a particular order n . The magnitude of this function is shown in Fig. 2d for the total spin coherence ($n = 4$). This is an *excitation function* which describes the magnitude of this particular coherence for each value of the parameter used.

The success of the PPPI search procedure is demonstrated in Fig. 3. The upper trace is the excitation function of Fig. 2d. The lower trace shows, on an expanded scale, a section of this function. Superimposed are discrete measurements of the $n = 4$ line magnitude obtained from a series of TPPI multiple-quantum experiments with fixed $\tau/2$ and variable t_1 .

The use of the PPPI search procedure to find a satisfactory excitation sequence for the total spin coherence represents a particularly simple case, because this coherence is always associated with a single transition frequency. For other than the extreme orders there will be a number of nondegenerate transitions, and their line amplitudes obtained with a sequence of the type shown in Fig. 1 will be complex numbers with generally different unknown phases. The situation can then arise that the sum of these finite amplitudes is zero for some fixed value of t_1 and some particular choice of excitation parameters. Nevertheless, our experience is that the PPPI search with a fixed value of t_1 is still useful, and exact calculations (8) show that it is time effective relative to the alternative of a series of fixed τ experiments with variable t_1 which would be needed in order to resolve and sum the line magnitudes by integration over ω_1 .

An important simplification in searching for excitation parameters is that these may be varied synchronously for preparation and mixing periods. A particular case of the optimum relation between preparation and mixing has been discussed earlier (5). In general, an optimized mixing may be obtained by reversing the sequence of timings and rf phase and amplitude changes which define the preparation sequence and omitting (or adding) a final $\pi/2$ pulse. This will be discussed more fully elsewhere (9).

Although the search in the present example is over a single parameter, we anticipate that the PPPI approach will also be useful in optimizing the order selective sequences useful for high-order excitation in larger systems (5, 10). These may depend on several pulse or timing parameters. During preparation of this manuscript we learned of an alternate approach to searching for preparation times (11), which together with the PPPI technique should form an efficient basis for signal optimization in multiple-quantum experiments.

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