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A Simple Method for Detection of Zero-Quantum Transitions in NMR

One of the most intriguing NMR experiments is the excitation of transitions which disobey the selection rule $\Delta m = \pm 1$, that is to say, for $I = 1/2$ nuclei, where more than one spin participates in the transition. While these multiple-quantum transitions have been known for some time (*1–5*), new detection methods have recently been introduced which make it possible to observe them in a more convenient and general way (*6–11*). Zero-quantum transitions are particularly interesting, since they were not accessible by the early continuous-wave methods, and because of their insensitivity to magnet inhomogeneity broadening.

The new methods use a sequence of two or more radiofrequency pulses to excite multiple-quantum coherences, allowing them to evolve for a variable period t_1 sec before reconversion into detectable single-quantum magnetization, acquired for a period t_2. They are therefore two-dimensional Fourier transform experiments (*6, 12*) requiring a large number of separate experiments at different values of t_1, extensive data storage, and suitable two-dimensional transformation programs. All the frequencies which occur during the evolution period, including all orders of multiple-quantum coherence, appear in the new frequency dimension F_1. In many cases the two-dimensional spectrum is projected onto the F_1 axis to give the final multiple-quantum spectrum.

There are many experimental situations where the signal-to-noise ratio is inherently high enough to allow a different approach, where the zero-quantum spectrum is extracted in a single experiment without the need for storing a large data matrix $S(t_1,t_2)$ or two-dimensional Fourier transformation. The present communication describes such a "one-shot" technique.

The pulse scheme for this experiment is set out in Fig. 1. Multiple-quantum coherence is first created by the two $\pi/2$ pulses (*6*). The π pulse slightly offset from the midpoint of this interval has two effects: first, it partially refocuses the effects of field inhomogeneity during the preparation period $(\tau_1 + \tau_2)$; second, it reduces the effective chemical shift, permitting a more convenient choice of the preparation period. During the next interval τ_3, a strong magnetic field gradient is applied in the Z direction, causing a rapid decay of all multiple-quantum coherences except the zero-quantum components, which are insensitive to field inhomogeneities. This gradient corresponded to a linewidth of approximately 3 kHz. In addition the room-temperature field correction coils were shut off for the entire experiment and no sample spinning was used; this gave an instrumental linewidth of the order of 150 Hz.

The next stage of the experiment involves the conversion of zero-quantum coherence into transverse magnetization by a regular sequence of pulses of very small flip angle α, each pulse converting only a very small fraction of the available zero-quantum coherence. It will be shown below that each α pulse destroys an amount of double-quantum coherence proportional to α^2, so that if α is too large there is a rapid decay of the detected signal, and the zero-quantum lines appear

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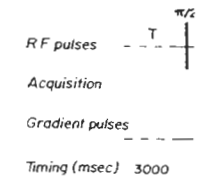

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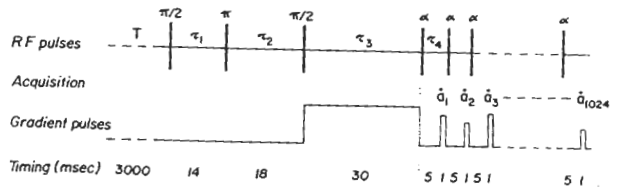

FIG. 1. Pulse sequence used to excite and detect zero-quantum frequencies. Transverse nuclear magnetization was sampled at the points indicated by $a_1, a_2, \ldots, a_{1024}$; immediately after each sample, the transverse magnetization was dispersed by a gradient pulse of random amplitude. The intervals T, τ_1, τ_2, τ_3, and τ_4 were chosen as described in the text.

broadened. In practice α was about 0.03 radians. There is then a delay τ_4 before the transverse magnetization is sampled. The transverse magnetization arising from zero-quantum coherence appears initially as two antiphase components, and τ_4 allows relative precession of these vectors up to the optimum condition given by $\tau_4 = 1/(2J)$. There is also a loss of signal during τ_4 due to defocusing effects in the inhomogeneous field; hence a shorter compromise value of τ_4 is chosen, in practice 5 msec.

After a single sample point has been acquired, a 1-msec gradient pulse is applied in order to destroy all transverse magnetization before the next α pulse. In order to prevent steady-state effects (*13*), these gradient pulses are amplitude-modulated by a pseudo-random sequence; in practice there was a constant component giving a linewidth of 3 kHz and an amplitude-modulated component with excursions of the same magnitude. The highest-frequency zero-quantum coherence is of the order of the largest chemical shift difference in the coupled spin system, and this determines the lowest possible sampling frequency if aliasing is to be avoided. This is a further reason for employing shorter-than-optimum values of τ_4; it also means that weakly coupled spin systems with large values of δ/J will produce only weak zero-quantum spectra by this method.

This process of pulsing and sampling is continued until 1024 data points are acquired, and this transient signal is then zero-filled to 4096 points. In addition to the oscillating signal derived from zero-quantum coherence, this transient contains another component originating from diagonal elements of the density matrix, which grows monotonically by spin–lattice relaxation. A dc correction routine is used to avoid the stepfunction discontinuity at the end of the transient signal. Gaussian weighting is then applied, and Fourier transformation gives the spectrum of zero-quantum coherence.

To see the effect of a sequence of pulses, suppose that a spin system described by a density matrix $\hat{\rho}$ experiences a regular sequence of pulses of very small flip angle α radians, applied along the X axis of the rotating reference frame. This may be written

$$\hat{\rho}' = \exp(-i\alpha\hat{F}_X)\hat{\rho}\exp(i\alpha\hat{F}_X) \qquad [1]$$

and, if expressed as a series expansion, may be approximated for small values of α by the first-order terms

$$\hat{\rho}' = (\mathbb{1} - i\alpha\hat{F}_X)\hat{\rho}(\mathbb{1} + i\alpha\hat{F}_X), \qquad [2]$$

$$\hat{\rho}' = \rho + i\alpha[\hat{\rho},\hat{F}_X] + \alpha^2\hat{F}_X\hat{\rho}\hat{F}_X. \qquad [3]$$

Provided that $\hat{\rho}$ contains only matrix elements that are diagonal or which represent zero-quantum coherences, the term $[\hat{\rho},\hat{F}_X]$ creates transverse magnetization without affecting the zero-quantum coherences at all. The last term of Eq. [3] and the higher-order terms in the series expansion of $\exp(i\alpha\hat{F}_X)$ in Eq. [1] cause the destruction of the zero-quantum coherence by the α pulses. Consequently the amplitude of the transverse magnetization generated is proportional to α while the degree of destruction of the zero-quantum coherence is proportional to α^2, provided that α is small.

The proposed technique has been tested on a 7-T superconducting solenoid spectrometer constructed at the Delft University of Technology (*14*). The proton AMX spin system studied was that of the vinyl group of triethoxyvinylsilane dissolved in carbon tetrachloride to give a 50% solution by volume. The conventional high-resolution spectrum is shown in Fig. 2a, indicating appreciable second-order effects. An exact analysis gives $\delta_{AM} = 33.41$ Hz, $\delta_{MX} = 71.85$ Hz, $J_{AM} = 5.38$ Hz, $J_{AX} = 13.69$ Hz, and $J_{MX} = 20.59$ Hz.

This spectrum is sufficiently weakly coupled that the three principal quartets can be easily picked out and the repeated splittings identified. The frequencies of the zero-quantum transitions are given by the difference between the frequencies of the appropriate lines in this spectrum. This allows the six zero-quantum frequencies to be predicted, and these are set out in Table 1, together with their assignments in the first-order limit. All six zero-quantum lines are clearly visible in Fig. 2b and their observed frequencies are in excellent agreement with those predicted from Fig. 2a.

In the first-order limit, the six zero-quantum lines separate naturally into three pairs of lines, the splittings within each pair representing differences between spin coupling constants. For example in Fig. 2b the two high-frequency lines are separated by $|J_{MX} - J_{AM}|$; they correspond to a simultaneous flip of spins A and X. This information could be used to determine relative signs of coupling constants provided that the absolute values of the couplings are known from some other experiment. In principle, the latter could be determined by Fourier transformation

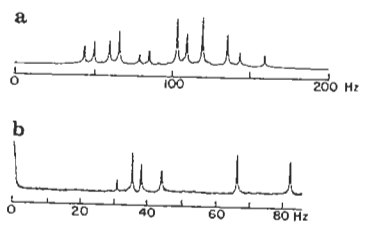

FIG. 2. (a) The conventional high-resolution NMR spectrum of the vinyl protons in triethyoxyvinylsilane. The three-spin system is sufficiently weakly coupled that three principal quartets can be picked out. (b) The spectrum of zero-quantum frequencies (absolute-value mode). Note the change of frequency scale. The assignment is set out in Table 1.

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8. S. VEGA, T. W. SHATTU

TABLE I

ZERO-QUANTUM FREQUENCIES (Hz)

Predicted[a]	Observed[b]	Assignment[c,d]
29.96	30.00	$\nu_M - \nu_A - (1/2)\lvert J_{MX} - J_{AX}\rvert$
34.29	34.37	$\nu_X - \nu_M - (1/2)\lvert J_{AX} - J_{AM}\rvert$
36.87	36.90	$\nu_M - \nu_A + (1/2)\lvert J_{MX} - J_{AX}\rvert$
42.69	42.71	$\nu_X - \nu_M + (1/2)\lvert J_{AX} - J_{AM}\rvert$
64.25	64.21	$\nu_X - \nu_A - (1/2)\lvert J_{MX} - J_{AM}\rvert$
79.45	79.45	$\nu_X - \nu_A + (1/2)\lvert J_{MX} - J_{AM}\rvert$

[a] From the conventional NMR spectrum, Fig. 2a.
[b] Measured from the spectrum in Fig. 2b.
[c] Assuming first-order spin–spin coupling.
[d] Indicates that all three coupling constants have the same sign.

of the modulation which appears on spin echoes (*15*) even if the spectrometer has poor resolution for conventional spectra. It is therefore conceivable that chemical shift differences and the relative signs and magnitudes of coupling constants could be measured in a spectrometer with only very moderate resolving power.

The distortion of the relative intensities of the zero-quantum lines occurs in all multiple-quantum spectra excited by two $\pi/2$ pulses unless the pulse interval is made a variable in a two-dimensional experiment. The relative intensities also depend on J since the detected signal arises from the relative precession of two vectors that are initially antiphase.

The proposed technique generates a spectrum of zero-quantum transitions in a simple fashion without the need for complicated data acquisition and a two-dimensional Fourier transformation program. By their very nature, zero-quantum transitions are essentially unaffected by field inhomogeneity broadening and are not very sensitive to instabilities of the radiofrequency or the magnetic field. Consequently high-resolution zero-quantum spectra could be recorded on a very simple spectrometer where conventional spectra would be too broad to resolve the multiplet structure. Note that the present experiments were carried out on a non-spinning sample with no room-temperature field correction coils in operation.

ACKNOWLEDGMENTS

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