

A Simple Pulse Sequence for Selective Excitation in Fourier Transform NMR

Pulse-excited Fourier transform NMR has such clear advantages in sensitivity and for the study of time-dependent phenomena that only recently has it become necessary to reconsider the question of *selective* excitation of individual resonances, so readily achieved in the earlier continuous-wave spectrometers. Tomlinson and Hill (1) have described an elegant pulse technique which "tailors" the pattern of excitation frequencies to any desired shape, and have applied it to the problems of solvent peak suppression, homonuclear Overhauser effect measurements (2), and selective spin-spin relaxation studies (3). However, the technique makes considerable demands on instrumentation and computer capacity.

Not all applications call for this degree of sophistication; often a much simpler irradiation pattern would suffice—for example, a single narrow band of frequencies. This can be achieved in a particularly simple way by means of a regular sequence of short, identical radiofrequency pulses. The present treatment is confined to the transient response; the steady-state response to such a stimulus, involving relaxation, has been analyzed elsewhere (4). Consider the nuclear magnetization vectors in a frame of reference rotating at the frequency f_0 of the radiofrequency source. For simplicity, relaxation may be neglected, and the radiofrequency pulses are assumed to be "hard" in the sense that $\gamma H_1/2\pi > |\Delta f|$ for all significant offsets Δf from f_0 . Each pulse turns the magnetization vector through a small flip angle α radians, while in the interval τ seconds between the pulses, each vector precesses through an angle $\theta = 2\pi\Delta f$ radians. The key to the method proposed is a pulse repetition rate set to the condition $\theta = 2n\pi$ radians, that is, $\Delta f_n = n/\tau$, where n is an integer. At these particular offsets Δf_n , the effect of the pulses is a cumulative tipping motion toward the XY plane of the rotating frame, whereas at all other offsets free precession robs the pulses of their cumulative effect, and the overall flip angle is small. Formally the excitation may be regarded as consisting of narrow components at the radiofrequency f_0 and at a harmonically related series of sidebands separated by n/τ Hz from f_0 . The experiments described here use only the first sideband, where the magnetization vector precesses through one complete cycle between pulses.

Simple computer simulations based on the Bloch equations confirm that for a very narrow band of frequencies near the $\theta = 2n\pi$ condition, the magnetization vector moves in a succession of zig-zag steps, in which the steps caused by pulses outweigh those caused by precession, so that the resultant trajectory approximates an arc close to the vertical YZ plane, extending down into the equatorial XY plane, as with a single conventional $\pi/2$ pulse. Such a vector induces a maximum NMR signal in the receiver coil and this signal is close to the pure absorption mode condition. For all other offsets, precession between pulses carries magnetization vectors away from the YZ plane so that they execute small cyclic excursions in the vicinity of the positive Z axis, generating only weak signals. Some typical trajectories projected into the XY plane are shown in

Fig. 1. Only the excess precession angle is shown, the amount by which θ exceeds an integral number of revolutions. The selectivity of the method can be appreciated in Fig. 2, where the absorption mode signal is plotted against offset Δf , and it is seen to improve with the number m of pulses in the sequence for a fixed total flip angle $m\alpha$. As a practical example a train of 50 pulses, lasting 100 msec, significantly excites a band of frequencies spanning only 10 Hz at an offset $\Delta f = 500$ Hz.

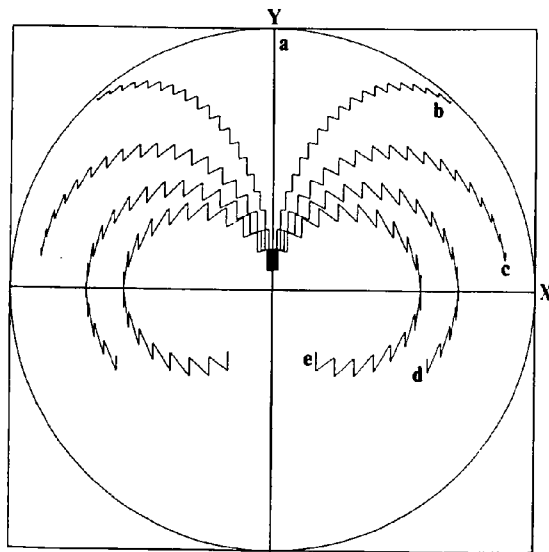


FIG. 1. Trajectories of the tips of magnetization vectors with different frequencies, projected onto the XY plane, during a sequence of 20 pulses of flip angle $\pi/40$ radians, spaced 2 msec apart. Only the excess precession (over 2π radians) is shown, for reasons of clarity. The offsets Δf of the magnetizations from the radiofrequency ν_0 are, to the right of the Y axis, (a) 500, (b) 505, (c) 510, (d) 515, and (e) 520 Hz; and similarly to the left of the Y axis, 495, 490, 485, and 480 Hz, respectively.

A number of possible applications of this method have been explored, including solvent peak suppression, selective relaxation-time measurements (5, 6), and hole burning (7, 8); it is hoped to publish details elsewhere. For the purposes of this communication the following illustration must suffice: the investigation of proton-coupled carbon-13 spectra by separation into subspectra from individual carbon sites, a suggestion recently mentioned by Ernst (9). Carbon-13 spectra are only occasionally investigated under proton-coupled conditions, partly because of poor sensitivity and partly because the complex overlapping proton spin multiplet structure often makes interpretation extremely difficult, despite the fact that these coupling constants surely carry valuable structural information. This important problem has been attacked recently by the two-dimensional Fourier transform method (9, 10).

A relatively simple model system is provided by a high-field section of the carbon-13 spectrum of 1-dimethylamino-2-methylpropene. Experiments were carried out on a conventional Fourier transform spectrometer (Varian CFT-20) with minor software and hardware modifications, using a moderately low radiofrequency level $\gamma H_1/2\pi = 1.8$ kHz. Figure 3a shows the high-field region recorded under conditions of proton noise decoupling, showing the three methyl peaks at frequencies P, Q, and R. The remaining

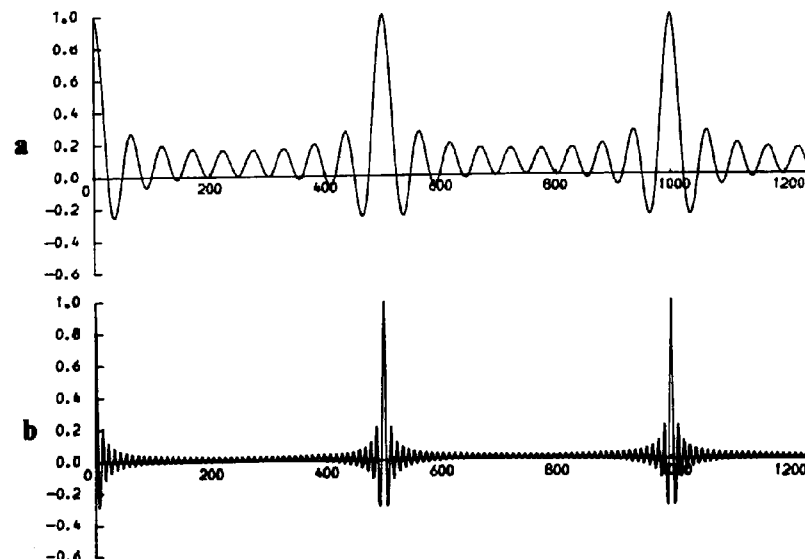


FIG. 2. Detected magnetization M_y at the end of a sequence of m pulses spaced 2 msec apart, each of flip angle $\pi/2m$ radians, as a function of offset Δf Hz for (a) $m = 10$ and (b) $m = 50$ pulses. The plot was obtained by a simulation based on the Bloch equations, neglecting relaxation, and as expected is qualitatively similar to the real part of the Fourier transform of the pulse sequence. The vertical scale is normalized to the condition $M_y = 1$ after an isolated "hard" $\pi/2$ radians pulse.

traces, (b)–(e), were obtained by means of the gated decoupling technique (11) in order to retain the nuclear Overhauser enhancement without losing the proton multiplet structure. During the noise irradiation of the protons, a sequence of 70 pulses of 2 microseconds' duration was applied so as to excite the carbon-13 methyl resonance at P ($\Delta f = 514$ Hz) in a selective manner to give a cumulative flip angle $m\alpha = \pi/2$. At the end of this pulse train the decoupler was gated off and the magnetization then evolved with time according to the *spin-coupled* Hamiltonian, permitting the acquisition of a free induction decay due to the multiplet structure of resonance P only. Fourier transformation gave the proton-coupled subspectrum illustrated in Fig. 3b; similar experiments with the excitation centered at Q and at R produced the subspectra 3c and 3d. The conventional proton-coupled spectrum after a single $\pi/2$ pulse (Fig. 3e) is the super-

position of these subspectra with additional lines from the acetone- d_6 lock material and the tetramethylsilane reference.

Clearly the method is applicable to larger spin systems with a more complex system of overlapping multiplets. The sensitivity achieved for these subspectra equals that for the conventional full proton-coupled spectrum. Where long waiting times are required between acquisitions, these intervals could be used to excite and observe other resonances selectively without significantly affecting the relaxation of the resonance first observed. The modest instrumental and data processing requirements of the method,

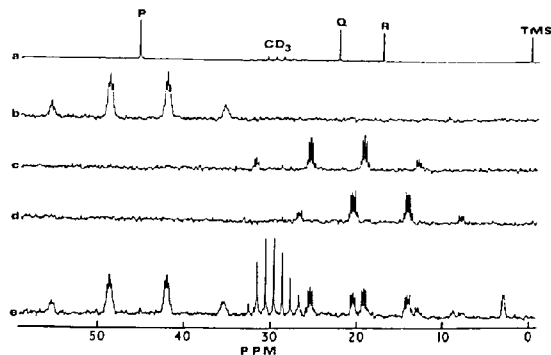


Fig. 3. The high-field regions of spectra of 1-dimethylamino-2-methylpropene. (a) Proton-decoupled spectrum; (b) to (d) multiplet subspectra corresponding to the three methyl resonances P, Q, and R, respectively; and (e) full proton-coupled spectrum, showing overlapping and interference from acetone- d_6 and tetramethylsilane.

coupled with the good sensitivity and resolution obtainable, make it an effective technique for the study of coupled carbon-13 spectra.

The proposed selective excitation technique is expected to be applicable to a wider range of problems, and exploratory experiments on some of these have been mentioned above. Other anticipated applications include excitation within the magnet line width to obtain information about natural linewidth, transient (2, 12), and steady-state homonuclear Overhauser effect studies without the need for a second radiofrequency source, and three-dimensional mapping of the spin distribution in a sample in a strong imposed field gradient (13-15).

A number of improvements to the simple basic technique are possible. The use of a more complex pulse sequence, derived from the superposition of several regular pulse trains with different periods τ , allows the simultaneous excitation of more than one specific resonance. Alternatively the shape of the excitation function (Fig. 2), and hence the degree of selectivity obtained, may be modified by width, phase, or amplitude modulation of the radiofrequency pulses used.

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