Frequency Modulation Method for Performing Adiabatic Demagnetization in the Rotating Reference Frame*

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A new method for preforming adiabatic demagnetization in the rotating reference frame in NMR experiments is presented in this paper. In this new method the frequency of a crystal oscillator rather than the actual magnetic field is pulsed off resonance. Using simple circuits which are described in this paper, the effective field in the rotating frame can be pulsed by as much as 50 G, depending on the nucleus studied. This method completely avoids the problem of external magnetic field correction due to a pulsed field in the magnetic gap.

INTRODUCTION

IN recent years pulse NMR methods[1–3] have been widely used in the study of atomic and molecular motions,[4–7] double resonance,[2,8] spin calorimetry,[9] and many other areas. Many of these methods require rf field pulses of duration sufficient to result in the establishment of a spin temperature in the rotating reference frame.[10] Due to Curie's law, this requirement is equivalent to requiring that the magnetization be finally aligned in a spin locked orientation (i.e., parallel to H_1, if H_0 is adjusted to be exactly on resonance). Pulse methods for spin locking fall into two general classes: (1) the use of appropriate short rf pulses[2,3] followed by longer pulses and (2) the use of adiabatic demagnetization in the rotating frame (ADRF).[1] The new technique described in this paper is a variation of the ADRF method in which the oscillator frequency (rather than the field) is varied. A brief review of the advantages and disadvantages of these methods will now be presented in order to understand the need for the new method.

In the method of Hartmann and Hahn,[2] spin locking is obtained by applying a 90° pulse followed by a 90° phase shift. In the method of Jones, Douglass, and McCall,[3] a resonant rf field H_1 is applied and, simultaneously, H_0 is pulsed off resonance by a field h_0 equal to H_1. After the magnetization has precessed through a 180° angle about the effective field in the rotating frame (which makes a 45° angle with respect to H_1), h_0 is sharply switched off, thereby leaving the magnetization parallel to H_1. Each of these methods has the advantage that the magnetization can be spin locked in a time comparable to the precession period. However, each has the disadvantage of considerable loss in signal amplitude due to dephasing of the spins during the time interval required for spin locking. This can be avoided only by the use of rf fields which are much larger than the local field. Such large rf fields may not be easily available (or desirable).[11] Another disadvantage of these techniques is that the amplitudes and durations of the field pulses must be critically adjusted. Also the pulse time should be very short compared to the precessing period.

In the ADRF method of Slichter and Holton,[1] the static field H_0 is pulsed off resonance[12] by an amount h_0, and an rf field H_1 is turned on while it is off resonance. The z field is then allowed to return adiabatically to resonance. Since the return is sufficiently slow (of the order of 1 msec for typical nuclei) such that the magnetization remains parallel to the effective field in the rotating frame, the magnetization ends up in a state parallel to H_1. Unless h_0 is large compared to H_1 (which is typically of the order of H_L), there will be an appreciable loss in signal. The requirement that the return to resonance be sufficiently slow as to be adiabatic may lead to a conflict with the requirement that there be negligible spin–lattice relaxation during the return. As a result, this method is normally limited to cases where the rotating frame relaxation time is longer than a few tenths of a millisecond (which is fortunately the most common situation anyway). This method has a big advantage over the previous methods in that an H_1 comparable to H_L can be used without appreciable loss of signal.[13] Also the exact values of h_0 and H_1 are not critical nor is the value of the adiabatic return time. The only requirements are that $h_0 \gg H_1$ and that the return to resonance be adiabatic.

Unfortunately, a few serious problems can arise in the use of the ADRF technique. First, the requirement that $h_0 \gg H_1$ necessitates the use of very large currents in the magnet gap. For instance, a current pulse with amplitude of the order of 5 A is typically required to obtain an h_0 of 20 G.[4] For an H_1 of 4 or 5 G, this h_0 would only marginally satisfy the condition that $h_0 \gg H_1$. A second more serious problem arises from the use of such large pulsed currents in the gap of an electromagnet which employs magnetic field regulation (such as the Varian field dial and the Magnion–Ventron FFC series field regulators). The problem is that the electromagnet will try to respond to the pulsed field in such a way as to oppose the changing field. Attempts have been made to prevent this magnet response by feeding an error signal into the field regulator circuit of the magnet in order to hold the magnet current constant during the field pulsing.[7] We tried to do this with our 30 cm (12 in.) Varian electromagnet but found that, even

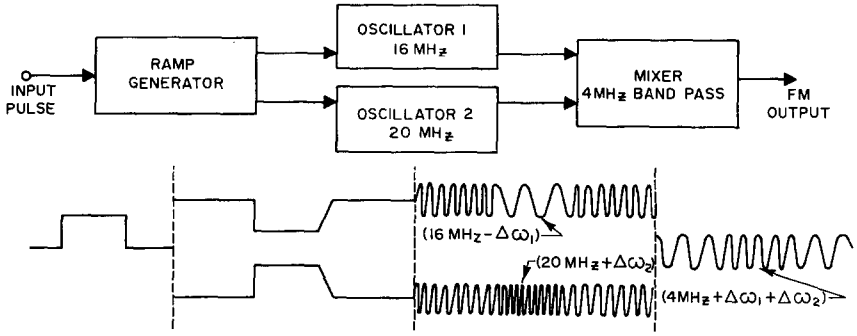

FIG. 1. Block diagram showing the double FM process.

though we could partially cancel the error signal, there would still be damped oscillations in the magnet current which would take approximately 0.5 sec to completely die out. Since these oscillations could be of the order of 0.5 G or more, it would be incorrect to assume that the magnetic field is exactly on resonance following the field pulse. Since a failure to be exactly on resonance can lead to incorrect conclusions about relaxation times measured in the rotating frame,[4] this situation is quite unsatisfactory.

We have overcome the above two difficulties in performing ADRF by employing frequency modulation instead of field modulation. Since the effective field in the rotating frame, $\mathbf{H}_{\text{eff}}$, is given by

$$\mathbf{H}_{\text{eff}}=(H_0-\omega/\gamma)\mathbf{k}+H_1\mathbf{i}, \tag{1}$$

a pulsing of ω will have exactly the same effect on $\mathbf{H}_{\text{eff}}$ as will a pulsing of H_0. Since, in principle, ω may be changed by an arbitrarily large amount, this method can easily provide large effective field changes which satisfy $h_0 \gg H_1$. Of course, the change in effective field will depend on γ as well as on ω and a nucleus of smaller γ will see a larger effective field change than will a nucleus of larger γ. In addition, there is no external magnet correction since there is no pulsed current in the field.

I. APPARATUS

In our experiment, we were interested in studying the resonance of ^{35}Cl, which occurs at 4 MHz in a field of approximately 9660 G. We obtained good frequency stability by using a crystal oscillator and, since we were reluctant to give up this stability, we decided to pull the crystal by changing the capacitance in series with it. In order to obtain maximum change in frequency, we pulsed a 16 MHz and a 20 MHz oscillator in opposite directions. We then mixed the outputs and kept the difference frequency (4 MHz). With this method we were able to change the frequency by 22 kHz[14] which corresponds to a change in the effective field for ^{35}Cl of 53 G. Figure 1 shows a block diagram of the apparatus.

The basic crystal oscillator circuits used were the OT-4 series of International Crystal Manufacturing Company, Incorporated.[15] Each crystal was pulled by means of a voltage applied to a voltage variable capacitor (Motorola MV 1620) which was placed in series with the basic crystal. To increase oscillator stability, the capacitors marked C_x were changed from 100 to 50 pF as shown in Fig. 2.

A ramp generator which provides a linear ramp is shown in Fig. 3. The slope of the ramp can be changed by varying the components marked R and C. A very stable 30 V supply should be used, since fluctuations in the voltage across the voltage variable capacitors will result in unwanted frequency variations.

A mixer circuit which provides a modulated output frequency equal to the difference in the frequencies of the two basic oscillators is shown in Fig. 4.

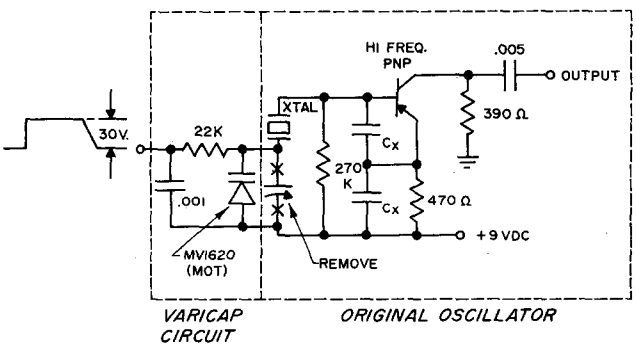

FIG. 2. Schematic diagram of basic International Crystal oscillator OT-4 with modifications. The capacitors marked C_x are changed from 100 pF to 50 pF and the trimmer is replaced by the varicap circuit at the points indicated.

II. PERFORMANCE

Figure 5 shows the effective field as a function of time following the beginning of the downward ramp. The voltage

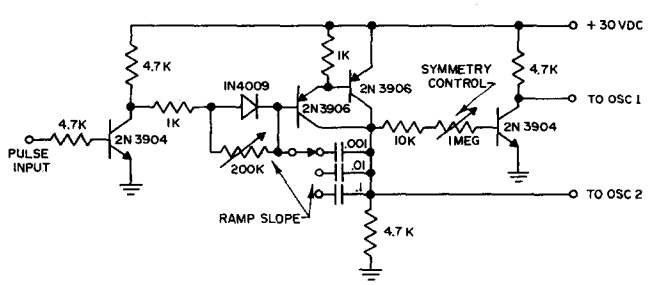

FIG. 3. Schematic diagram of ramp generator.

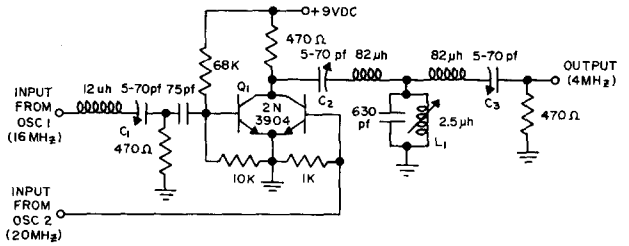

FIG. 4. Schematic diagram of mixer and 4 MHz bandpass circuit. Adjust C_1 for maximum 16 MHz signal as measured at the base of Q_1 and then adjust C_2, C_3, and L_1 for maximum undistorted 4 MHz output.

ramp was quite linear as shown on the 'scope and had a duration of 4.5 msec. The total frequency deviation was 22.189 kHz as measured on a frequency counter (corresponding to 53 G for ^{35}Cl nuclei). The actual shape of the curve in Fig. 5 was mapped out by using a 90° pulse and adjusting H_0 so that the signal was a maximum[16] (on resonance) at each position of the 90° pulse. The field can be determined to within a few tenths of a gauss by this method. By comparing the field so measured at each point on the sloped region to the on-resonance field measured in the absence of a frequency modulating pulse, we were able to determine the change in effective field as shown. We measured maximum effective field deviations of the order of 50 G[17] and also observed no deviations past 4.5 msec. The departure of the curve of Fig. 5 from a straight line is due to the fact that the frequency of the crystal is not exactly proportional to the voltage applied to the voltage variable diodes.

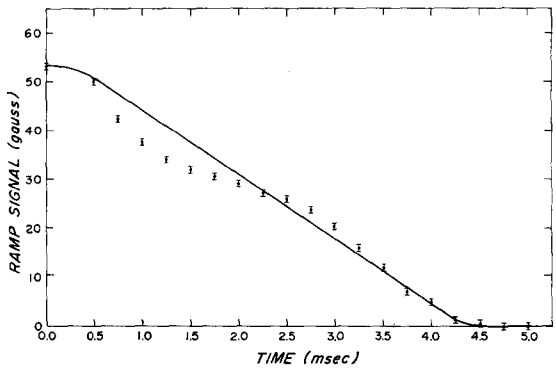

FIG. 5. Return of the crystal frequency to the resonant value following the frequency pulse (ADRF). The solid line is the voltage applied to the varicaps and the experimental points represent the effective field measured by applying a 90° pulse and adjusting H_0 to resonance.

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[11] In ultraslow motion experiments it is usually desirable to have H_1 comparable to H_L (see Ref. 4).
[12] The field pulsing is usually accomplished by pulsing the current through an extra set of coils wrapped around a Dewar in the magnet gap.
[13] Of course, when $H_1=H_L$, the magnetization will be $0.707M_0$ (see Ref. 1).
[14] In principle arbitrarily large frequency changes $\Delta\omega$ can be obtained by using a variable frequency oscillator which is stabilized by a crystal. The crystal would be removed suddenly. Simultaneously the frequency of the VFO would be kicked to a new level and later allowed to return adiabatically to the original crystal frequency.
[15] These crystals and circuits are quite inexpensive and can be purchased from International Crystal Mfg. Co., Inc., 18 North Lee, Oklahoma City, Okla. 73102.
[16] There is no difficulty in using phase sensitive detection since the reference frequency is at all times equal to the basic frequency of the oscillator from which it is derived. In fact, we employed phase sensitive detection and a boxcar integrator to maximize our sensitivity.
[17] For strongly magnetic nuclei, such as protons, it would be difficult to pull the crystals a sufficient amount in effective field; accordingly, an alternative method for increasing further the frequency modulation may be preferable.[14]