Frequency Modulation Method for Performing Adiabatic Demagnetization in the Pulsed Nuclear Magnetic Resonance

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Frequency modulation method for performing adiabatic demagnetization in the rotating reference frame in the pulsed NMR has improved. Using simple circuits which are described in this paper, we have been able to change the frequency by 146 KHz. This large deviation of frequency corresponds to a change in h_0 field for Li^7 of 88 G and sufficiently satisfies the condition $h_0 \gg H_1$. With the improved method, spin locked state of the most nucleus is perfectly performed and then this method may be useful for many pulsed NMR experiments.

I. Introduction

In recent years pulsed NMR methods[1),2)] have been widely used in the study of atomic and molecular motions[3) 4)], double resonances[2),5)], spin calorimetries[6),7)], and many other areas. Many of these methods require that a nuclear spin system result in a "spin locked" state in the reference rotating frame[8)]. Spin locked situation is described in the following sense. The magnetization of a spin system in a presence of a static field H_0 is aligned along a field H_1 in the frame of rotating at a frequency ω, after a perturbing field $H_1(t)=2H_{10}\cos\omega t$ is applied at exact resonance. (*i.e.*, $\omega=\Omega=\gamma H_0$, where Ω is the nuclear Larmor frequency, γ is the nuclear gyromagnetic ratio.) Redfield[8)] has shown that if $H_1 \gg H_{local}$, then a magnetization $\boldsymbol{M}$ will not decay in a spin-spin relaxation time T_2, but will decay instead in a spin-lattice relaxation time T_1. This orientation situation has been named "spin locked" along H_1.

The conventional methods for spin locking classify into two general classes: (a) the use of a 90° pulse followed by a 90° phase shift and (b) the use of adiabatic demagnetization in the rotating reference frame (ADRF)[1)].

The method (a) has been first carried out by Solomon[9)]. Initially a magnetization $\boldsymbol{M}$ is parallel to the static field H_0 in the z-axis. Hereafter the coordinate system stands on the fratme of the rotating at the frequency $\omega=\Omega$. Then if rf (radio-frequency) pulse H_1 is applied during the time $t_w=\pi/2H_1 \ll T_1, T_2$ in the x direction, $\boldsymbol{M}$ is perpendicular to the both field H_0 and H_1. At the time t_w, dephasing the rf field amount $\pi/2$ by electronic means within the time $t \ll t_w$ result in a magnetization parallel to the rf field. In these processes spin locked state has been carried out.

The method (b) has been carried out by Slichter and Holton[1)]. Initially a magnetization $\boldsymbol{M}$ is pointing along H_0 (z-axis) with H_1's zero. Then H_1 in turned on is such a manner that $\boldsymbol{M}$ is brought to point along H_1 in the rotating reference frame. This frame, of course, is as the case of (a), rotates about H_0 axis at frequency ω in the same as the nuclear precession frequency Ω. If H_1 is simply turned on, $\boldsymbol{M}$ would precess around H_1 in the rotating frame, always remaining perpendicular to H_1 and decaying in amplitude in a few hundred microseconds.

(The order of the spin-spin relaxation time of the spin system.) In order to get $\boldsymbol{M}$ parallel to H_1, first H_0 is displaced by H_0+h_0, where $h_0 \gg H_1$. Then H_1 turned on. The effective field $\boldsymbol{H}_{eff}$ is then $\boldsymbol{H}_{eff}=H_1\boldsymbol{i}+h_0\boldsymbol{k}$, where $\boldsymbol{i}$ and $\boldsymbol{k}$ are unit vectors along the direction of H_1 (x-axis) and H_0 (z-axis), respectively. Scince $h_0 \gg H_1$, $\boldsymbol{M}$ is essentially parallel to $\boldsymbol{H}_{eff}$. h_0 is now slowly decrease to zero. By slowly, quite long compared to the precession period of the spins in the field H_1. During such a slow variation $\boldsymbol{M}$ remains parallel to H_1. In such a manner spin locked situation has been acomplished. These tow methods descrived above has serious difficulties.

In most recent, Samuelson and Ailion[10] have partially overcome the difficulties of above two methods. Their method in performing ADRF is one that used frequency modulation instead of field modulation. The differences between their method and that of Slichter et al.'s[1] are the way of the changing $\boldsymbol{H}_{eff}$, namely, while the latter used the method of changing H_0, the former changing frequency ω. Scince the effective field $\boldsymbol{H}_{eff}$ in the rotating frame is given by $\boldsymbol{H}_{eff}=H_1\boldsymbol{i}+(H_0-\omega/\gamma)\boldsymbol{k}$, the changing the frequency ω leads to the same effect as H_0 be changed. In their method two oscillators of which frequencies be modulated respectively was used and their modulated frequencies passed through the mixer circuit resulted in amount of 22 KHz modulated frequency at $\omega=4$ MHz. Their method may be applied for weakly magnetic nuclei but can not be applied for strongly magnetic nuclei.

We have improved their method for use of strongly magnetic nuclei by using more simple circuits. We have accomplished to change the frequency a few times as much as their frequency change, by only one basic oscillator. Scince our method can change the frequency in large amount (146 KHz at basic frequency about 15 MHz.), a large effective field changing can be easily provide. Then of course the changing field which corresponds to the changing frequency satisfies the condition $h_0 \gg H_1$ for various nuclei. Our mthod may be satisfactorily used for various pulsed experiments required the spin locking.

II. Apparatus

A block diagram of the apparatus is shown in Fig. 1. In order to obtain good frequency

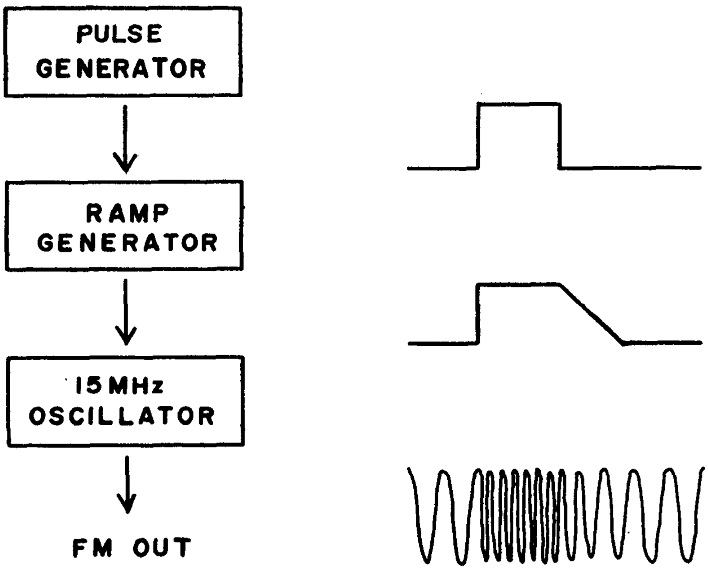

Fig. 1 The block diagram for producing FM wave.

stability, we used a crystal oscillator and for modulation of frequency used a means of pulling the crystal by changing the capacitance. The basic crystal oscillator circuit used was the FO-11 international crystal oscillator. Several voltage variable capacitors (Toshiba 1S48) were added in series with the crystal and the crystal was pulled by means of a ramp voltage applied to these voltage variable capacitors. The oscillator and varicap circuit are shown in Fig. 2.

In such a way we changed the frequency by 146 KHz at the oscillator frequency about 15 MHz. To increase oscillator stability, the capacitors marked C_1 and C_2 were changed from original values to 20 pF and 40 pF respectively. Moreover, in order to hold the amplitude constant, the resistor marked R was changed from original value to 33 KΩ and a inductor was added. Particularly this inductance is very critical for holding the amplitude constant. For same purpose four voltage variable diodes were used in the varicap circuit.

A ramp generator was used by changing the values of C and R in the circuit of Samuelson et. al.'s. The ramp circuit was operated in 15 V maximum amplitude.

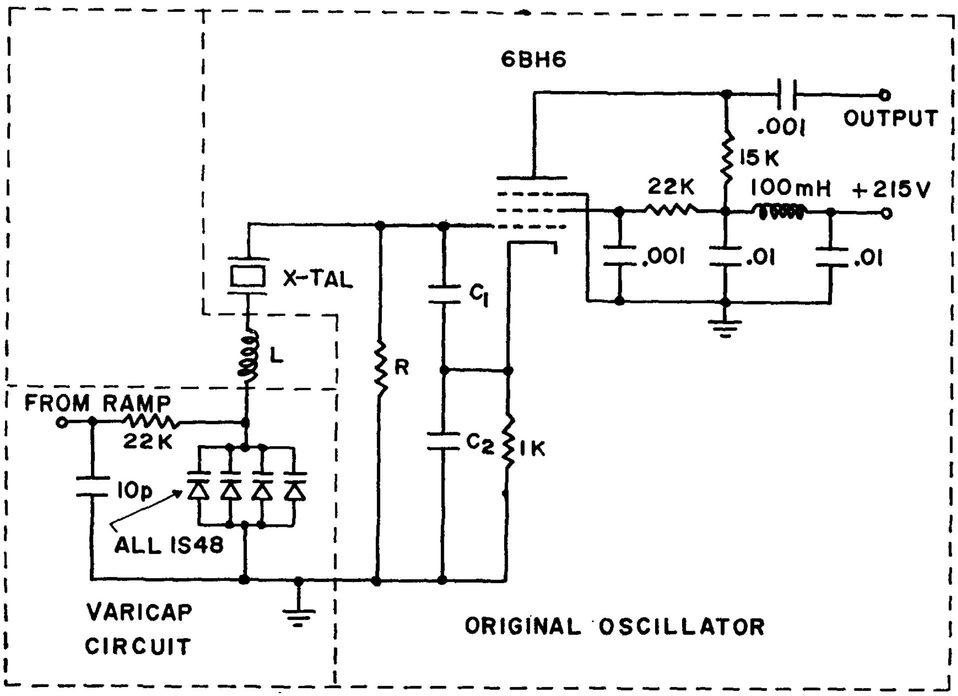

Fig. 2 Schematic diagrams of basic FO-11 international crystal oscillator with modification and varicap circuit. The capacitors marked C_1, C_2 and resistor marked R are replaced from original values to 20 pF, 40 pF and 33 KΩ, respectively and the inductor is added in series with crystal.

Ⅲ. Results and Discussion

In our experiment, we are interested in studying the resonance of Li^7, which occurs at 15 MHz corresponding to the field about 9065 G. The frequency with depends on the voltage of the head of varicaps was measured about three time intervals 5.3, 7.7 and 10.0 msec. during the ramp slopes, respectively. Experimental results are shown in Fig. 3, where longitudinal axis shows the field h_0 for Li^7 nuclei and transverse axis shows the time following the beginning the downward ramp. The total frequency deviation was 146.29 KHz which corresponding

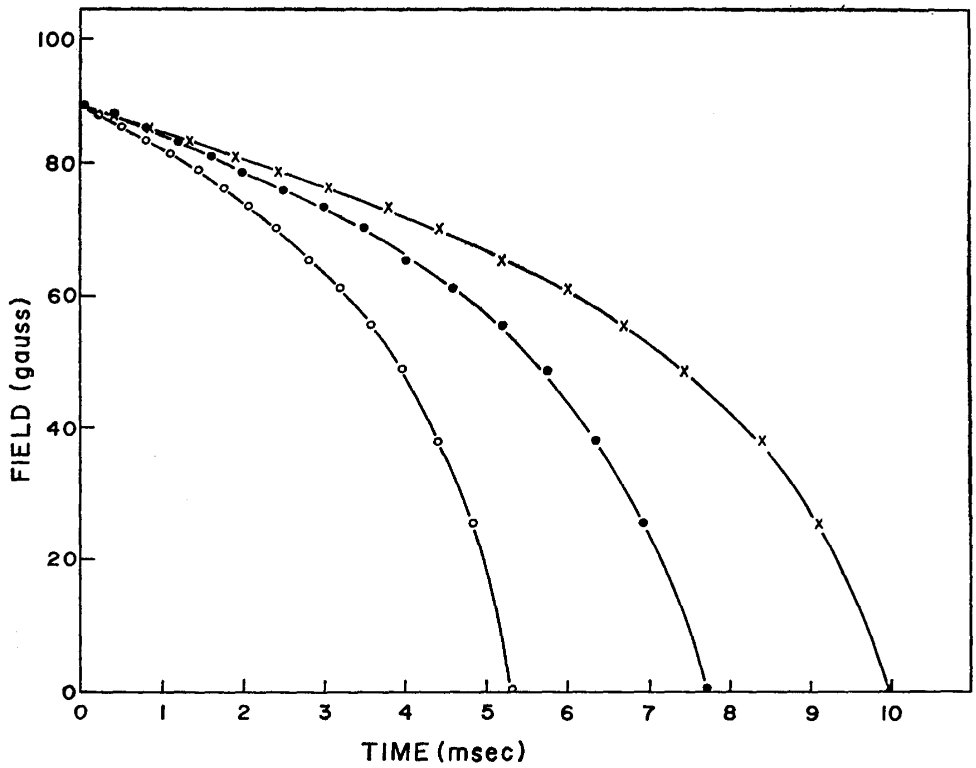

Fig. 3 The field deviation for Li^7 nucleus plotted against the time following the biginning of the odownward ramp. The circles, dots and crosses show the time intervals 5.3, 7.7 and 10.0 msec. during the downward ramp, respectively.

to the field 88.4 G for Li^7 nucleus. This field 88.4 G is sufficiently large for satisfying the condition $h_0 \gg H_1$ in most actual experiments. (In most commonly, H_1 is a few gausses.) To understand our method be useful, a brief reviw of the advantages and disadvantages of the methods mentioned in I will now be presented.

The advantage of method (a) is that the magnetization can be spin locked in a time comparable to the precession period of nuclear spins. However, this has the disadvantage of conciderable loss in signal amplitude due to dephasing of the spin 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. Another disadvantage of this technique is that the amplitude and durations of the field pulses must be critically adjusted. Also the pulse time should be very short compared to the precession period.

The method (b) has a big advantage compared with the method (a), that the exact values of h_0, H_1 and the adiabatic return time are not critical. A brief disadvantage of this method is the requirement that the return to resonance be sufficiently slow in order to change h_0 adiabatically. This requirement may lead to a conflict with the requirement that there be negligible spin-lattice relaxation during the return. Therefore this method is normally limited to cases where the rotating frame relaxation time is longer than a few tenths of a millisecond. However this condition is fortunately satisfied in the most actual case. The most disadvantage of this method is making the condition $h_0 \gg H_1$. The requirement that be $h_0 \gg H_1$ necessitates the use of very large currents in the magnet gap. For instance, H_1 is typically used in magnitude of the order of a few gausses. To satisfy the condition that be $h_0 \gg H_1$, h_0 is necessitated in magnitude of the order of a few tenths of a gauss at least. This corresponds with that the amplitude of the current pulse is a few amperes. A second more serious problem arises from the use of such large pulsed currents in the gap of electromagnet which employs magnetic field regulation. The problem is that the electromagnet will try to respond to the pulsed field in such a way as to oppose the changing the 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. However if one tried to do this, even though could partially cancel the error signal, there would still be damped oscillations in the magnet current. Scince these oscillations could be of the order of a few gausses, it would be incorrect to assume that the magnetic field is exactly on resonance following the field pulse. This failure to be exactly on resonance can lead to incorrect conclusions about relxation time measured in the rotating frame.

Samuelson et. al.'s method has overcome this difficulties, but can be only used for weakly magnetic nuclei.

We have resolved the difficulties of above problems. In our method with more simple circuits, the frequency deviation is 146 KHz at the resonance frequency 15 MHz and as previously mentioned this deviation corresponds to the field deviation 88 G for Li^7 nucleus. Li^7 nucleus has larger magnetic moment than Cl^{35} nucleus studied by Samuelson et al.. Similarly for the most strongly magnetic nucleus proton, this deviation is equivalent to 35 G and this field deviation is satisfied the condition $h_0 \gg H_1$ in ordinary experimental situations. With our improved method, spin locked state of the most nucleus is perfectly performed and then this method may be useful for many pulsed NMR experiments.

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