A Low-Temperature High-Sensitivity Field-Cycling Spectrometer for Quadrupole Double Resonance Spectroscopy *

M. M. P. Khurshid
Chemistry Department, Government College of Science, Lahore 18, Pakistan

F. Zhenye
Department of Electronics, Zhongshan University, Guangzhou, China

J. A. S. Smith
Chemistry Department, King's College, Strand, London, WC2R 2LS, United Kingdom

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This paper discusses the design of a variable-temperature high-sensitivity field cycling spectrometer for nuclear magnetic resonance and nuclear quadrupole double resonance experiments. The instrument is capable of detecting N-14 quadrupole resonance signals from samples as small as 0.1 g down to temperatures of 150 K. The magnetic field cycling is performed by mechanical transfer of the sample using a pair of switchable electromagnetic solenoids, in times of about 0.2 s.

Introduction

Experimental methods of performing nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) spectroscopy under field cycling conditions rely on two techniques for changing the magnetic field, either mechanical transfer of the sample [1] or electronic switching of the field [2, 3]. The former leads to difficulties in varying and measuring the sample temperature. A number of different methods have been used in the past; one technique is to drive pneumatically the sample by means of a metal rod moving along a cooled transfer tube [4], another to transfer the sample by means of a gas stream of variable temperature [5]. This paper describes a field-cycling spectrometer which uses a pair of switchable solenoid springs to accomplish the transfer of samples; the driving units are wholly external to the cryogenic line, which simplifies considerably its design.

Description of the Instrument

Figure 1 shows a block diagram of the spectrometer, which may be conveniently divided into four units:

(i) The pulsed NMR spectrometer based on a 6502 microprocessor.
(ii) The sample transfer system.
(iii) The timer-control logic unit.
(iv) The variable-temperature probe.

Their principal features are now described.

(i) The pulsed NMR spectrometer is constructed from Mid-Continent Instruments (M.C.I.) units which contain an MPU 6502 microprocessor [6] to generate and control the four-channel pulse sequences. The

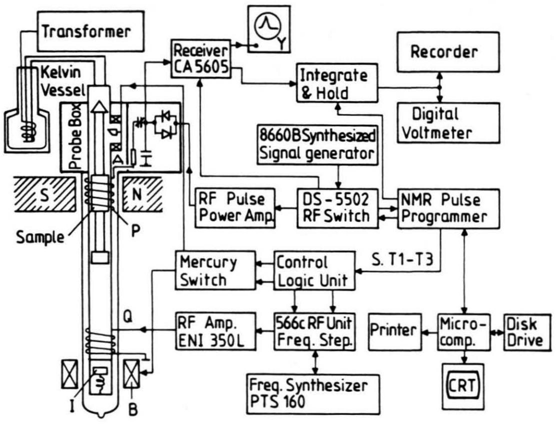

Fig. 1. Block diagram of the field-cycling NMR spectrometer.

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Reprint requests to Dr. J. A. S. Smith, Chemistry Department, King's College, Strand, London, WC2R 2LS, U.K.

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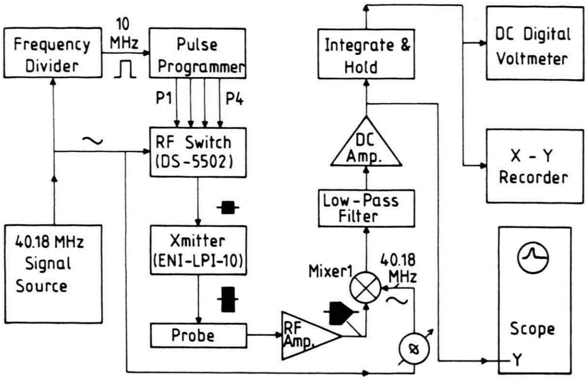

Fig. 2. Modifications to the M.C.I. NMR spectrometer.

instrument was slightly modified as shown in Fig. 2 to achieve optimum signal-to-noise ratio at the operating proton magnetic resonance frequency of 40.18 MHz, corresponding to a magnetic field of 0.9437 T. The transmitter employed was an E.N.I. LPI-10 gated r.f. power amplifier which generated a 90° pulse of width of 1 μs; the receiver dead-time was 4 μs.

(ii) As shown in Fig. 1, sample transfer was accomplished by two sets of solenoid spring units, A and B, which were placed immediately above and some distance below the magnetic field, respectively. The control pulses from the timer actuate two mercury relays to send strong pulsed currents either to solenoid A or B. Suppose the first pulse of current goes to solenoid B, where it generates a pulsed magnetic field along the axis of the glass tube inside the region of the solenoid; this forces upwards an iron bar, I, against its retaining spring, which drives upwards the p.t.f.e. sample tube into the P coil, where it is locked by means of a spring-operated p.t.f.e. wedge which contains a small permanent magnet. The second control pulse sends a strong current pulse to solenoid A, withdrawing the wedge and allowing the sample to fall under gravity to the Q coil at the bottom of the glass tube. The transfer time from zero to high field is 0.23 s, and is generally shorter than the return time, a disadvantage of the design.

(iii) The timer/control logic unit performed the following functions:

a) controlling the transfer of the sample;
b) setting the sample residence times in high and zero field (τ_p and τ_q, respectively);
c) gating the r.f. radiation while the sample is in zero field;
d) when required, supplying a d.c. current pulse to solenoids A or B to transfer the sample from one coil to the other;
e) pulsing the NMR spectrometer shortly after the sample arrives in high field;
f) stepping up or down the Q irradiation frequency in frequency-swept NQR experiments; and
g) providing the frequency markers for such spectra.

Figures 3 and 4 show the circuit and timing-sequence diagrams of the timer. The "Start", T 1, T 2, and T 3 pulses come from the pulse programmer but the τ_p, τ_q, 2 A, 2 B, "Gate", and "Cycle" pulses go out from the timer to different units of the spectrometer (see Fig. 1) to perform their functions. To generate the input pulses shown in Fig. 4, we use the following program:

D 3	to delay 50 μs after the "Start" pulse;
T 3	to generate a T 3 pulse;
T 1	to generate a T 1 pulse;
(D 5) 100	to delay 230 ms;
T 1 T 3	to generate simultaneously T 1 and T 3 pulses;
P 1	to generate a 90° pulse;
(D 4) 200	to delay (say) 8 s;
T 3 T 2	to generate simultaneously T 3 and T 2 pulses;
(D 2) 100	to delay (say) 0.5 s;
T 2 T 3	to generate simultaneously T 2 and T 3 pulses;
D 2 = 50 E-4	to assign a value to the delay parameter D 2;
D 3 = 50 E-6	to assign a value to the delay parameter D 3;
D 4 = 400 E-4	to assign a value to the delay parameter D 4;
D 5 = 23 E-4	to assign a value to the delay parameter D 5;
(Slow clock: 11 s)	to set the repeat period for sample transfer.

The zero-field irradiation was performed by means of a programmed PTS-160 frequency synthesizer driving an E.N.I. 350 L r.f. power amplifier and probe matching unit, generating peak-to-peak voltages of up to 600 V in a 40-turn coil between 1 and 4 MHz.

(iv) Figure 5 shows the variable-temperature system. For low temperature studies, a cold nitrogen stream is generated from boiling liquid nitrogen and flows along a glass tube of outer diameter 16 mm carrying the P and Q coils surrounded by a glass Dewar of outer diameter 29.5 mm, inner diameter 19.5 mm, and length 900 mm. The cold nitrogen stream enters at the top of the glass tube and emerges from the gap between that tube and the top of the Dewar. To prevent frosting of the outside surface of the p.t.f.e. cylinder at this point, a narrow channel within the wall of this cylinder was made through which warm air could be sent. The mouth of the Dewar is also well insulated by thick blocks of foam polystyrene. By control of the rate of boiling of the liquid nitrogen, temperatures as

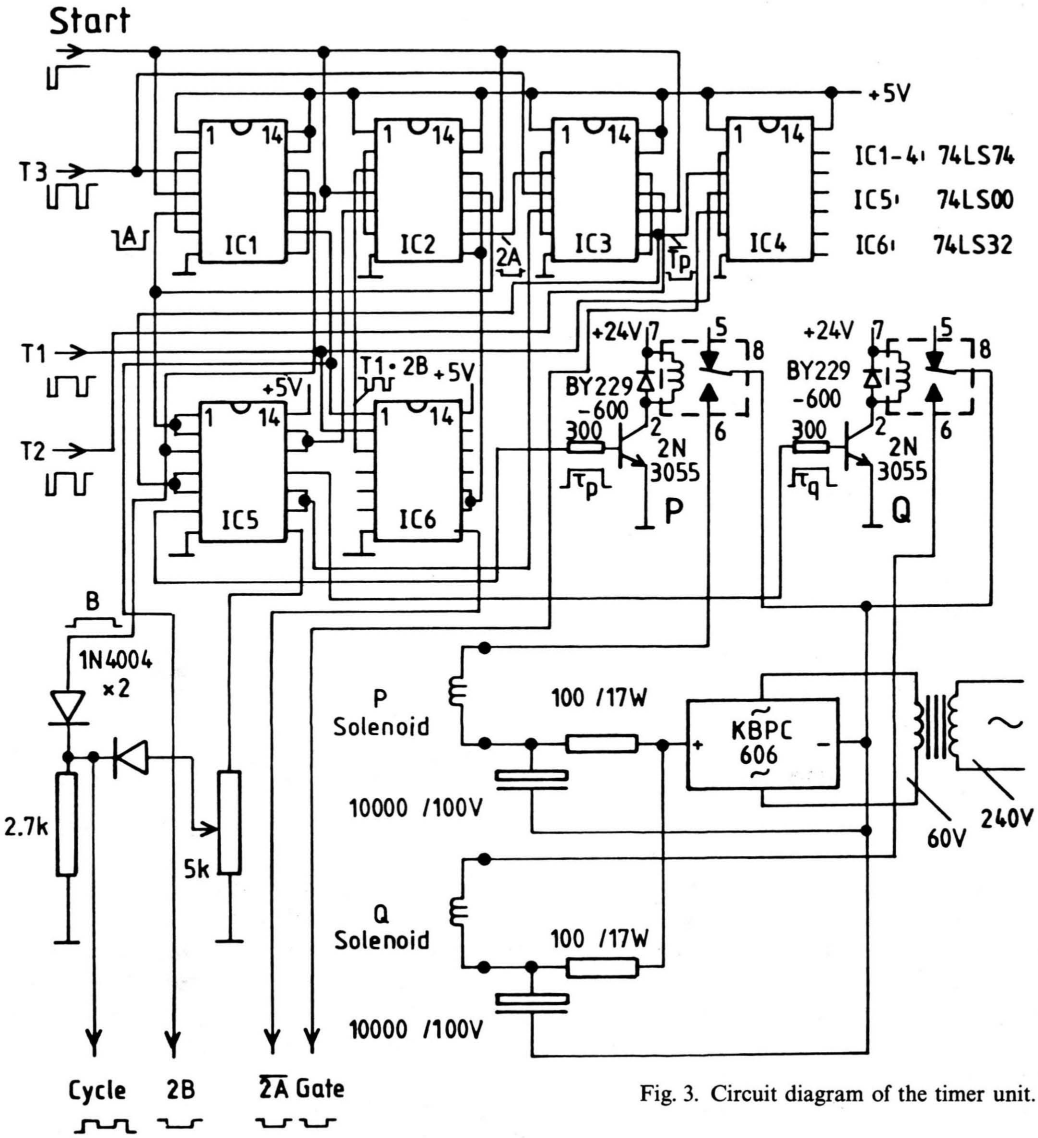

Fig. 3. Circuit diagram of the timer unit.

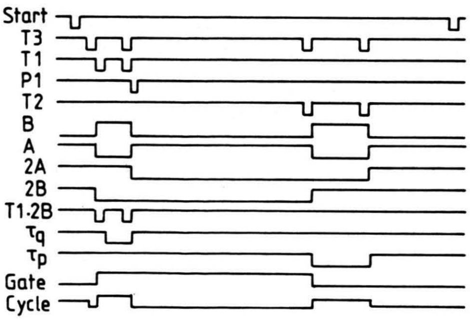

Fig. 4. Timing sequences in a typical double resonance experiment.

low as 150 K could be achieved in less than 20 minutes and maintained to within 1 K. The sample was contained within a specially-designed p.t.f.e. container (Fig. 1) with an arrow-shaped head to catch on the locking-wedge just above the P-coil.

Performance

The instrument has functioned satisfactorily as a variable-temperature nuclear quadrupole double resonance spectrometer between 150 and 350 K. The sen-

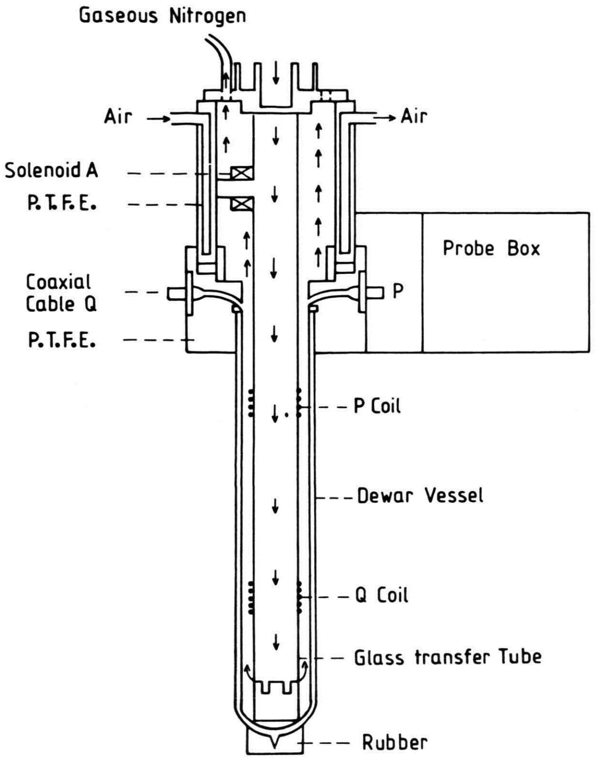

Fig. 5. Section through the variable-temperature probe.

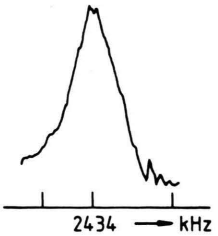

Fig. 6. Part of the N-14 quadrupole double resonance spectrum of nicotino-hydroxamic acid at 291 K; $\tau_p = 10$ s, $\tau_q = 1$ s, 2 kHz steps, $V_{\text{pk. to pk.}} = 600$ V.

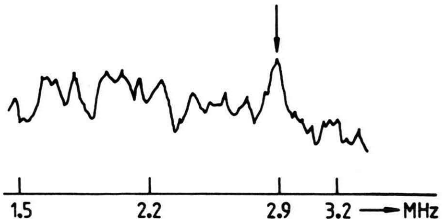

Fig. 7. Part of the N-14 quadrupole resonance spectrum from a 0.1 g sample of ethyl-2,3,5-triiodobenzo-4-aminobenzoate at 270 K; $\tau_p = 9$ s, $\tau_q = 1$ s, 2 kHz steps, $V_{\text{pk. to pk.}} = 600$ V.

sitivity was better than that of existing instruments in the laboratory [7]. Figure 6 shows part of the N-14 quadrupole resonance spectrum from a 1 g sample of nicotino-hydroxamic acid; the signal near 2434 kHz, which is a superposition of ν_x, ν_y from the –NH– group and ν_y from the pyridine nitrogen, is detected with a signal-to-noise ratio of nearly 25:1, a factor of two better than previously-published spectra [8]. Figure 7 shows the ν_x signal in the N-14 quadrupole double resonance spectrum from 0.1 g of ethyl-2,3,5-triiodobenzo-4-aminobenzoate at 270 K, with residence times τ_p of 9 s and τ_q of 1 s, frequency steps of 2 kHz, and a Q r.f. peak-to-peak voltage of 600 V. A N-14 signal near 2900 kHz is detected with a signal-to-noise ratio of about 2:1.

Acknowledgements

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