Fast field-cycling nuclear magnetic resonance spectrometer

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We describe here the design and construction of a modern, state-of-the-art nuclear magnetic resonance (NMR) field-cycling instrument. Fourier transform NMR spectra of both liquid and solid samples can be measured, and spin-lattice relaxation times ($T_{1Z}$) investigated over a broad range of magnetic field strengths ranging from 0 to 2 T. The instrument is based upon an existing personal computer-based NMR spectrometer [C. Job, R. M. Pearson, and M. F. Brown, Rev. Sci. Instrum. 65, 3354 (1994)] which has been expanded into a fully computer-controlled field-cycling instrument. The magnetic field cycling is accomplished electronically by utilizing fast switching thyristors and a storage capacitor based on the Redfield energy storage concept. Unique aspects of the design include the field-cycling magnet, which can reach fields as high as 2 T; the personal computer-based NMR spectrometer and associated waveform electronics; and the use of a commercially available pulse width modulation switching current amplifier, having low internal power dissipation and a fast current settling time. Using this new technology $T_{1Z}$ relaxation times as short as 1 ms can be readily measured. © 1996 American Institute of Physics. [S0034-6748(96)02905-6]

I. INTRODUCTION

The application of magnetic field-cycling methods in nuclear magnetic resonance (NMR) spectroscopy represents a powerful approach for investigating the complex distributions of motions in various materials, which often span a broad range of time scales. By comparing the characteristic relaxation dispersions of various substances, one can gain a better understanding of their microscopic behavior in relation to the observed macroscopic material properties. For example, it is known that broad distributions of molecular motions exist in synthetic polymers, proteins, liquid crystals, and lipid bilayers. The high frequency molecular and segmental motions are manifested predominantly in the local dynamics; whereas low frequency motions are typically associated with rheological properties of the assembly, including the elasticity, viscosity, and other characteristic macroscopic properties. In the case of biological membranes, the lipids and proteins exhibit frequency dispersions which may be associated with their biological activity. Clearly it is important to characterize the types, rates, and amplitudes of the motions over a broad range of frequencies as a means of achieving a comprehensive description of the dynamics of these and related materials. However, reduction of the above concepts to practical implementation is rather challenging, and investigations of the magnetic field dependence of the NMR spin-lattice relaxation time $T_{1Z}$ are thus relatively few in number.

It is well known that information regarding the molecular dynamics can be obtained by measurements of the NMR relaxation times directly as a function of the static magnetic field strength. The latter quantities are related to molecular motions through the spectral densities $J_{m}(\omega)$, which in turn are Fourier transforms of the correlation functions $G_{m}(\tau)$, where $m$ is the magnetic projection index. The correlation functions describe fluctuations of the second rank nuclear interactions, generated by molecular motions, which enable various relaxation processes to occur. Standard or conventional techniques for measurement of spin-lattice relaxation times in the laboratory frame, i.e., corresponding to the Zeeman ($T_{1Z}$), dipolar ($T_{1D}$), and quadrupolar order ($T_{1Q}$), as well as relaxation in the rotating frame ($T_{1\rho}$), enable studies of molecular motions to be carried out only over limited spectral bandwidths. For example, measurements of the relaxation times $T_{1Z}$, $T_{1D}$, and $T_{1Q}$ provide information about molecular motions in the relatively high MHz frequency range; whereas $T_{1\rho}$ measurements furnish knowledge of the molecular reorientations in the relatively low kHz regime. Hence conventional NMR relaxation techniques do not cover the important intermediate window between about 100 kHz and below, which can be studied by $T_{1\rho}$ measurements, and the range greater that about 4 MHz, for which standard measurements of $T_{1Z}$ in the laboratory frame can be used; a large frequency gap exists. It follows that a major problem is mapping the frequency dispersion over the entire range, including the important intermediate regime between the high and low frequency regions.

From a technical standpoint, it is extremely difficult to detect proton ($^{1}\text{H}$) nuclear magnetic resonance in magnetic fields below approximately 0.1 T (corresponding to a $^{1}\text{H}$ resonance frequency of about 4 MHz), due to the very weak nuclear induction signals and the acoustical ringing induced in the NMR probe. For other nuclei such as deuterium ($^{2}\text{H}$), the lower limit of the magnetic field is shifted to even higher field strengths on account of the smaller gyromagnetic ratios. It is moreover difficult to produce sufficiently short, high power radiofrequency pulses at frequencies in the low MHz range to detect nuclear induction signals from solids having short transverse relaxation times ($T_{2}$). This is related to the
II. PRINCIPLES OF MAGNETIC FIELD CYCLING

Two different methods have been developed to generate Zeeman field cycles in earlier work. One possibility is to transfer the sample mechanically between two selected field strengths, e.g., a high field strength and a low field or the zero field. However, the mechanical approach is limited by the time it takes to physically shuttle the sample from one position to another. Typical values for mechanical switching are on the order of 50 ms. This rather long duration can limit the diversity of possible field-cycling experiments involving materials with short $T_{1Z}$ relaxation times. Alternatively, field-cycling instruments have been developed which transiently alter the current through the magnet coil using high power switching components. Such electronic switches offer the most advanced and versatile capabilities, and in principle enable switching times of less than 1 ms. Initial work along these lines has utilized networks with transistor field switches and storage capacitors to boost the voltage over the magnet coil. Subsequently, gate turn on (GTO) thyristors have found use as a substitute for the transistor switch, and most recently the utilization of metal-oxide-semiconductor field-effect transistor (MOSFET) regulation has been proposed to simplify the total current control. As a rule these methods involve cycling of the Zeeman field ($B_0$) in the manner illustrated by Fig. 1. First, the resonant nuclei are polarized in the relatively high magnetic field $B_{0P}$. Next, the Zeeman field $B_{0P}$ is fast-switched to a lower level, $B_{0E}$, within which nuclear relaxation takes place towards the equilibrium Boltzman distribution. At the end of this evolution (relaxation) period, the magnetic field $B_{0E}$ is again fast-switched to a higher field, $B_{0P}$, in which the NMR signal is detected. The whole cycle is repeated to acquire the nuclear induction signal until a sufficient signal-to-noise ratio is obtained. According to the scheme in Fig. 1, the spin-lattice relaxation time $T_{1Z}$ corresponds to the evolution field strength $B_{0E}$, whereas the spins are polarized in the higher magnetic field $B_{0P}$ to enable adequate signal strength. By changing the $B_{0E}$ field strength, one can obtain relaxation dispersion curves over a very broad range of frequencies, which affords a very powerful and novel means of characterizing the material properties.

In such an electronically switched field-cycling device, the maximum current one can sustain depends on (i) the electrical capacity of the power supply and (ii) the ohmic resistance of the coil and switching network. Currents as high as 400 A have been achieved. The maximal magnetic field strength depends on the size of the inductance and the amount of electrical current passing through it. The maximal switching interval is the time it takes to turn on and off the magnetic field. To compare various field-cycling devices, one needs to consider both the maximum magnetic field strength $B_{0P}$ that can be achieved, and the maximum switching rate $\frac{dB_{0P}}{dt}_{\text{max}}$. The value of the inductance ($L$) and the voltage ($U$) across the coil define the duration of a transit interval. The maximal voltage across the coil in turn depends on the voltage to which the storage capacitor can be charged, together with the voltage specifications of the switching components, i.e., the GTO thyristors, high voltage diodes, storage capacitor, and the magnet. Clearly, in such a fast field-cycling apparatus the inductance cannot be increased freely. It needs to be optimized for maximal field strength, homogeneity, and transit time. On the other hand, the implementation of high inductance coils can produce higher magnetic fields, relative to the number of coil turns of the magnet. On the other hand, low inductance coils improve the
cycling facilities, relative to the voltage across the coil and the inductance. Finally, the homogeneity depends on the spacing of the coil turns, relative to the length and diameter of the coil.

The fast field-cycling instrument described herein utilizes a switching current amplifier which produces adequate current stability and a rapid current switching time. The required current amplitude is selected by the pulse programmer and the waveform generator. Construction of the field switching network is based on the principles of previous designs. The Redfield energy storage principle is based on a charging capacitor that is switched with different polarity in series with the magnet coil during the turn-on and turn-off intervals. In this manner, the voltage across the coil is transiently boosted. One of the unique aspects of the present magnetic field-cycling instrument is that the magnet can generate fields as high as 2 T. A personal computer-based NMR spectrometer and waveform electronics control all aspects of the field-switching device, making the instrument highly versatile. The switching current amplifier consists of two pulse width modulation (PWM) amplifiers (model 235; Copley Control Corp., Newton, MA), powered with two 15 kW dc power supplies and cooling fans. The PWM amplifiers are modular high performance current control amplifiers, optimized to drive the gradient coils in magnetic resonance imaging (MRI) systems. This approach simplifies the construction and eases somewhat the technical problems associated with the electronic power switch. An advantage of pulse width modulation is the low internal power dissipation, which is independent of the output voltage. The amplifier operates with a supply voltage of 165 V and can generate up to 600 A continuous wave or 1000 A in pulsed mode. The switching amplifiers are designed for very accurate control of the output current, with rapid settling to within 0.1% of the final value in less than 1 ms. The amplifiers can be optimized for different load inductances and can be used in a parallel mode. The protection circuit of the switching amplifier ensures that each metal-oxide-semiconductor field-effect transistor (MOSFET) is protected from excessive current and dissipation. The system shuts down in microseconds if (i) over temperature occurs at any of the heat sinks or output choke of the power modules, (ii) the system attempts to deliver too much current for too long a time, or (iii) to save the remaining MOSFETs if one electrically shorts.

III. EXPERIMENT

Fabrication of the field-cycling magnet involved construction of a copper-based solenoid magnet comprising seven coil layers together with an associated enclosure. Solid copper with a purity of 99.95% (Copper and Brass Sales, Los Angeles, CA) was acquired and machined into seven copper cylinders of different diameters (Tag Engineering, Tucson, AZ; and University of Arizona Instrument Shop). The cylinders were machined into coil layers utilizing a three-axis computerized mill (Bridgeport Co., Hartford, CT), with a modified carbide slitting saw and a specially made mandrel (J. Izlar, University of Arizona Instrument Shop). The resulting coil wire dimensions were 3 × 3 mm square. Each coil layer contained 29 turns with inner coil diameters of 32, 42, 50, 58, 66, 75, and 82 mm; the coil layers were equally spaced. Additionally, the coils were gold plated (Chem Research, Phoenix, AZ) to minimize corrosion and electrical resistance. To achieve a flat magnetic field profile in the center of the coils, rings of polycarbonate having different widths (e.g., 0.5, 1, 2, 3, and 4 mm) were used to space the coil turns and to physically support them. The middle two windings were spaced 4 mm apart, the next two turns were spaced 3 and 2 mm, the next 4 turns were spaced 1 mm, and the remaining 7 turns were spaced 0.5 mm on each side of the coil. The spacers were then glued using Loctite 242 (Loc-tite Corp., Cleveland, OH).

The magnetic field strength was calculated utilizing the law of Biot and Savart for single coil elements having a different number of coil turns and coil diameters:

$$dH = \frac{I}{4\pi r} (ds \times r).$$

Here \(H\) is the magnetic field vector (A/m); \(I\) is the electrical current in amperes (A); \(r\) is the distance vector from the conductor to the field point measured in meters (m); and \(ds\) is the current element of the conducting material. The direction of the vector \(H\) corresponds to \(ds \times r\); that is to say perpendicular to the plane described by the two vectors \(s\) and \(r\), with the polarity determined by the right-hand rule. For the limiting case of calculating an axial field plot in a cylindrical coil, the equation of Biot and Savart can be simplified, as indicated below:

$$H_z = \frac{I}{4\pi r^2} \int_0^{2\pi} ds = \frac{I \sin \alpha}{2r},$$

where \(H_z\) is the magnetic field strength in the axial direction, and the angle \(\alpha\) is defined by the vector \(r\) and the axial direction of the cylindrical coil (\(z\) axis). This simplifies calculation of the magnetic field strength for individual coil turns having different spacings. Consequently, one can maximize the magnetic field strength and homogeneity in a trial and error fashion. The total magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; the resulting magnetic field plot due to all of the concentric coils is generated by adding all the individual calculated values together; 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Southwest Circuit (Tucson, AZ). The operating software for the waveform board was developed using the Microsoft (Seattle, WA) macroassembler (MASM), and linked together with an existing personal computer-based pulse programmer editor program.\textsuperscript{20} Schematics, blueprints, and a software listing exists for the complete instrument.

The storage capacitor consists of a number of high voltage surface mount chip capacitors (model HV06H; AVX Corp., Olean, NY) each having a capacitance value of 2.2 \( \mu F \) and a maximum dielectric strength of 3000 V. A total capacitance of 70.4 \( \mu F/3000 \) V was achieved by placing 32 capacitors in parallel, which were mounted on a printed-circuit board. High speed switching requires extremely low equivalent series resistance (ESR) and low equivalent series inductance (ESL) in the capacitors. A low value of the ESR reduces the self-heating of the capacitors; whereas a low ESL value reduces the voltage noise of the capacitors, which is given by \( U_{\text{noise}} = L_{\text{cap}} \frac{dI}{dt} \), where \( I \) is the electrical current. ESR values in the range of milliohms and ESL values in the range of 3 nH are typical. These high performance requirements are essential for the field-cycling storage capacitor. The above specifications are well beyond the practical limits of typical electrolytic capacitors, either aluminum or tantalum. With this approach one can easily replace defective chip capacitors, and if required, change the total capacitance of the storage capacitor; furthermore the capacitors can be charged with either polarity (see below).

The different modules of the field-cycling instrument were installed in an air-conditioned room with adequate electrical power and water supply. Testing of the field-cycling instrument was initially performed without utilizing the high voltage switching and storage capacitor capabilities. Further test experiments were performed to determine the maximum achievable polarization time and the maximum electrical magnet current in relation to heat generation.

IV. RESULTS SECTION

A. Overview of field-cycling spectrometer

An existing personal computer-based NMR spectrometer\textsuperscript{20} was expanded into a complete field-cycling instrument. Figure 2 shows a block diagram of the field-cycling instrument, including the current amplifier, the field-cycling circuit, field-cycling magnet, NMR probe, waveform memory board, refrigerated water circulating system, and the high voltage power supply. The current amplifier consists of two amplifier modules (model 235; Copley Control Corp., Newton, MA) and two 15 kW switching power supplies. Currents as high as 700 A can be generated to maximize the polarization and signal strengths, with an optimal current

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FIG. 2. Illustration of overall block diagram of the field-cycling NMR spectrometer. The printed circuit boards, receiver, amplifier, preamplifier, NMR probe, field-cycling magnet, field-cycling logic, current amplifier, high voltage amplifier, and refrigerated water recirculation system all comprise the basic field-cycling instrument. The application-specific printed-circuit boards are located in the microcomputer chassis, and consist of the digital-to-analog converter, the direct digital frequency synthesizer, the radiofrequency modulator, the pulse programmer, and the waveform generator. The personal computer includes the disk interface, the monitor interface, and the Ethernet interface. The CPU can be upgraded without any hardware or software changes.
change of 300 A/ms when terminated with an inductive load of 1 mH. To overcome the high demands associated with even faster switching times, a storage capacitor of 70.4 μF/3000 V was implemented, which together with the switching amplifier represented a modification of the conventional field-cycling circuit logic. The newly developed circuit enables termination of the current amplifier with a resistive load during the transit time. This improves the optimal current rate of change by an order of magnitude. The utilization of a storage capacitor is needed to boost the voltage over the field-cycling coil. Our approach, however, enables the use of commercially available switching current amplifiers, which are used in MRI instruments and are well-designed and well-tested. Furthermore, the present instrument improves the overall fabrication and replication aspects of such devices, and in this regard constitutes an important step towards increasing the applicability of the technique. The field-cycling magnet is made of copper and is contained in a polycarbonate enclosure. The magnet is constructed so that refrigerated cooling water can flow between the various coil layers, thus maintaining the magnet at room temperature during a field-cycling experiment. The cooling water is supplied by a refrigerated water recirculating system with a water cooled condenser (model R750; Haskris, Arlington Heights, IL). The individual coil layers are connected with four brass screws to minimize the electrical resistance and ensure mechanical stability. The magnet bore is 32 mm inner diameter, the length is 117 mm, and the outer diameter is 88 mm. The current terminals are located on the top and bottom of the magnet, and the NMR probe is inserted from the bottom, as in a conventional superconducting solenoid magnet. The field-cycling circuit consists of four GTO thyristors (model SG2000EX24; Toshiba, Deerfield, IL), three high voltage diodes (model SD853; International Rectifier), one high power resistor, and a storage capacitor. The waveform generator is located on a printed-circuit board, which is integrated into the existing personal computer-based spectrometer. The waveform board generates the desired waveform for a field-cycling experiment, and is programmable via the existing pulse programmer editor. The remaining items are components which constitute the personal computer-based NMR spectrometer described previously.

B. Field-cycling circuit

Figure 3 illustrates the field-cycling circuit in combination with the direct current amplifier. The components include the direct current amplifier N1; high voltage power supply N2; GTO thyristors GTO1–GTO4; high voltage diodes D1–D3; ohmic resistor equivalent to ohmic losses of the field-cycling magnet R; and the field-cycling magnet and the storage capacitor. In the low or zero current state, Fig. 3(a), thyristors GTO2 and GTO4 are turned on; whereas thyristors GTO1 and GTO3 are turned off. The direct current amplifier N1 generates no electrical current and the high voltage power supply N2 charges the storage capacitor to a selected high voltage (e.g., 3000 V). Diode D2 decouples the storage capacitor from the field-cycling magnet. In this configuration, the field-cycling circuit is in standby mode and the power consumption is minimal.

For the polarization interval, caused by the low to high field transit, the waveform circuit initiates a positive ramp with an end value corresponding to the selected polarization current. At the same time GTO1, GTO2, and GTO3 are turned on whereas GTO4 is turned off. In this configuration, Fig. 3(b), the current amplifier is terminated with the resistor R and the field-cycling magnet is switched in parallel to the storage capacitor. The storage capacitor instantaneously boosts the voltage over the coil (U_m) and electrical current flows with phase opposite to \( U_c \) into the field-cycling magnet. The initial current increase, given by \( U/L \), is inde-
dependent of the ohmic losses of the coil; however, smaller losses allow a longer maximum slope to be maintained, and thereby a faster switching time is achieved. When the current amplifier has reached the end of the ramp or the selected polarization current, it remains at this level and waits for the storage capacitor to bring the current of the field-cycling magnet to the same level. This waiting interval is programmed by a predetermined delay in the pulse program. When the currents of the two separate circuits have reached the same level, GTO1 and GTO3 are turned off; whereas GTO2 and GTO4 are turned on. At this point in time, the charging current from the storage capacitor and the induced voltage over the field-cycling coil drop to zero, and the magnet receives its current from the current amplifier. The switch settings are the same during the polarization interval and the standby mode interval, except when a high current is flowing and the power consumption is high. Consequently, the slope of the current ramp is not delayed by the inductance of the coil, and the metal-oxide-semiconductor field-effect transistors (MOSFETs) located in the direct current amplifier are protected from the high voltage.

After a predetermined delay or polarization time the pulse program initiates a high to low transit, Fig. 3(c). In this configuration, thyristor GTO1 is turned on whereas GTO2, GTO3, and GTO4 are turned off. This leaves the field-cycling coil in series with the storage capacitor and terminates the current amplifier with the resistance $R$ again. At this time, the electrical current is now in phase with the voltage across the storage capacitor, thereby charging the capacitor; the induced voltage across the coil is opposite with regard to the current, corresponding to the magnetic field decreasing. Similarly, a high to low transit has a predetermined delay during which the magnetic field generated by the field-cycling coil is diminished. Now the evolution period starts, and the field-cycling circuit is switched back into standby mode and low power consumption. After the evolution period the field-cycling experiment reaches the detection phase, where the magnetic field is increased to a level higher than during the evolution period, but lower than during the polarization interval. During the detection period, the switching mechanism is the same as for the polarization interval, except that less energy is withdrawn from the storage capacitor.

C. Field-cycling magnet

Figure 4 shows a schematic diagram of the inner coil layer (designated 1) of the field-cycling magnet. Initially a solid copper cylinder was cut and machined on a conventional lathe to the corresponding inside and outside dimensions. Then, utilizing a computer controlled lathe, 29 coil turns were cut into the cylinder by cutting out 1 mm slots. Once mounted on the bore tube, polycarbonate rings were used to space the coil turns and stabilize the assembly. Ring spacers of 0.5, 1, 2, 3, and 4 mm were used to establish homogeneity over a 3 cm axial length. An alternative is to use a more sophisticated computer controlled lathe to cut coil turns of different width, allowing the use of ring spacers of minimal and constant width, and thus further improving the coil design. However, the additional cost involved is substantially higher, and one does not have the flexibility of making subsequent adjustments by using different spacer thicknesses. The seven coil layers need to be centered relative to each other to avoid magnetic field gradients which affect the homogeneity. Although such gradients can be compensated by an electrical shim current, the task is then further complicated. The negative current terminal is on the opposite side of the connection to the next coil layer which consists of four screws. Coil layers 2–6 have connections on each side. Coil layer 7 has the positive current terminal on one side instead, concluding the serial connection of all seven coils. Figure 5 shows a cross section of the complete field-cycling magnet and enclosure. The enclosure is made of polycarbonate and supports the coils on all sides to improve the mechanical stability. The enclosure is sealed by six O rings and enables deionized water to flow through the various magnet layers. Figure 6 illustrates the calculated final homogeneity over a 3 cm axial length.
Taking the Laplace transform, which is given by

\[ q(s) = \int_0^s Q(t) e^{-st} \, dt. \]  

Here \( q(s) \) is the Laplace transform of the electrical charge \( Q(t) \), in which \( s = \sigma + i\omega \) is a complex variable that includes the frequency \( \omega \). Taking the forward Laplace transform, we find that

\[ q(s) = \frac{LI_0 + U_c/s}{s^2L + sR + 1/C}. \]  

Upon inserting the component values \( L = 1 \, \text{mH}; R = 0.2 \, \Omega; \, C = 0.070 \, \text{mF} \), initial conditions \( U_c = 3000 \, \text{V} \) and \( I_0 = 0 \), and taking the inverse Laplace transform, one can find the electrical charge as a function of the time \( Q(t) \). The inverse Laplace transform of \( q(s) \) is given by

\[ Q(t) = \frac{1}{2 \pi i} \oint q(s) e^{st} \, ds. \]

The derivative \( I = dQ/dt \) represents the electrical current as a function of the time for a low to high transit interval, yielding the result that

\[ I(t) = 794e^{-100t} \sin(3778t), \]  

where \( t \) is the time in seconds. Similarly, by inserting the initial values for the high to low interval (initial values: \( U_c = -1280 \, \text{V}; \, I_0 = 700 \, \text{A} \)) one finds the current characteristic for a high to low interval,

\[ I(t) = -358e^{-100t} \sin(3778t) + 700e^{-100t} \cos(3778t). \]  

The initial value of \( U_c = -1280 \, \text{V} \) represents the charge of the storage capacitor after a low to high interval of 302 \( \mu \text{s} \). The current \( I_0 = 700 \, \text{A} \) represents the current flowing through the coil after a low to high interval. At this point the field-cycling network now switches the storage capacitor out of the main circuit, so that the operating current is provided by the current amplifier. After a predetermined polarization time (generally about five \( T_{1Z} \) values) a high to low interval of 290 \( \mu \text{s} \) drives the current back to zero. At that time the storage capacitor is charged with a voltage of 2886 V. The difference of 114 V (3000–2886 V) has been depleted by the ohmic resistance of the circuit. By increasing the value of the storage capacitor, or the precharged voltage across the capacitor, one can reach even higher currents. However, this may become dangerous to the field-cycling magnet and the various switching components, which can tolerate a rather limited amount of current and voltage. Choosing the proper value of the storage capacitor is critical to avoiding high currents in the case of malfunction or operator error.

### D. Storage capacitor

The function of the storage capacitor is to achieve faster switching intervals, by boosting the voltage across the coil during a transit interval without a significant change in power consumption.\(^\text{21}\) The Redfield concept of using the energy stored in the coil by charging a storage capacitor during the high to low interval, following by discharge during a low to high interval to regain the magnetic field strength, has become a feature of fast field-cycling instruments. Recall that the circuit configuration during the low to high interval is given in Fig. 3(b), and the high to low transit in Fig. 3(c). The circuit consists of the inductance of the magnet, the ohmic resistor representing the losses of the circuit and magnet, and the storage capacitor precharged for low to high transits. The voltage balance after applying the Kirchhoff voltage rule is given by

\[ L \frac{dI}{dt} - LI_0 + \frac{1}{C} \int_0^t I \, dt - U_c + RI = 0. \]  

Here \( L \) is the inductance of the magnet coil; \( I \) is the electrical current; \( I_0 \) is the initial value of the electrical current; \( C \) is the capacitance of the storage capacitor; \( R \) is the resulting ohmic resistance of the circuit; \( U_c \) is the precharged voltage over the storage capacitor; and \( t \) is the time.

One can easily compute the electrical current as a function of time, e.g., by utilizing the program MATHCAD PLUS 5.0 (Mathsoft, Cambridge, MA). Substituting for the electrical current \( I = dQ/dt \) gives

\[ L \frac{d^2Q}{dt^2} + R \frac{dQ}{dt} + \frac{Q}{C} = U_c + LI_0, \]  

where \( Q \) is the electrical charge. Equation (4) is solved by taking the Laplace transform, which is given by

\[ q(s) = \int_0^s Q(t) e^{-st} \, dt. \]  

FIG. 6. Axial magnetic field plot of the field-cycling magnet calculated for an operating current of 700 A, utilizing the law of Biot and Savart for a cylindrical coil. The calculated inductance of the magnet is 1 mH. The homogeneity is achieved by spacing the coil turns by differing amounts.

### E. Block diagram of the field-cycling waveform generator

The waveform electronics, illustrated in Fig. 7, are located on a separate printed-circuit board, occupying one slot in the microcomputer motherboard, and receive their control signals from the pulse programmer board; the analog output is transmitted to the direct current amplifier rack. Data input/output (I/O) is done via the personal computer bus. The waveform board has its own 8-bit real time clock (RTC).
memory, with the 12-bit address lines coming from the pulse programmer board via a ribbon cable. In this configuration, the RTC memory will run synchronously with the pulse programmer memory. This enables programming of the radiofrequency pulses and the waveform in the same pulse program, similar to a magnetic resonance imaging (MRI) experiment, thereby facilitating operation of the field-cycling instrument. The first two bits of the RTC memory are used to start and reset the waveform; whereas the remaining six bits are used to control the GTO thyristors during the field-cycling experiment. The reader should note that the electrical current through an inductor cannot be changed instantaneously without producing a large voltage across the component. Consequently, the waveform board generates a gradual change in the form of a current ramp. In order to accomplish this, the waveform control logic first reads a 24-bit word from the waveform memory and stores it in the 24-bit latch. The 24 bits contain all the necessary information to change the current amplitude. The first 3 bits control the slope of the ramp; this is achieved by selecting a ramp dwell clock. The ramp dwell clock is derived from the master clock (32 MHz). Ramp dwell clocks of 1, 2, 4, 8, 16, 32, and 64 $\mu$s are available. Bit 4 controls the direction of the ramp and the remaining 20 bits represent the final current amplitude. The high order 8 bits are then loaded into a counter which generates a train of ramp pulses. The number of the ramp pulse is defined by the binary value of the 8 bits. The ramp pulse train then clocks an up/down counter with the direction selected by bit 4 of the waveform memory word. The parallel output of the up/down counter is then loaded into the highest order 8-bits of the 20-bit shift register. The ramp dwell clocks of 1, 2, 4, 8, 16, 32, and 64 $\mu$s are available. Bit 4 controls the direction of the ramp and the remaining 20 bits represent the final current amplitude. The high order 8 bits are then loaded into a counter which generates a train of ramp pulses. The number of the ramp pulse is defined by the binary value of the 8 bits. The ramp pulse train then clocks an up/down counter with the direction selected by bit 4 of the waveform memory word. The parallel output of the up/down counter is then loaded into the highest order 8-bits of the 20-bit shift register. The lowest order 12 bits are loaded directly into the shift register from the waveform memory. For each ramp pulse, the data contained within the shift register are serially clocked out, and loaded via an optical isolator into the 20-bit digital to analog converter (model AD1862; Analog Devices, Norwood, MA). The AD1862 is an ultralow noise digital-to-analog converter with a serial-to-parallel input and an optimal signal-to-noise ratio of 119 dB. The optical isolators and the separate low noise power supplies enable an optimal S/N ratio which ensures the best current stability. Once the ramp has reached the final value, the address of the waveform memory is incremented and prepared for the next current adjustment. The reset pulse (bit 1 of the RTC memory) will reset the waveform memory address counter, and enable a repetition of the waveform for data accumulation. The 16-bit counter is implemented to continuously compute the on–off ratio of the generated waveform. The 1 Hz clock calibrates the on–off ratio to 1 s. The operating program checks the counter periodically via the personal computer bus to ensure proper operation. In the case of an overstepped on ratio, the operating program will ramp the current to zero and reset the
V. DISCUSSION

We have constructed a fast field-cycling instrument which is modular in design and sufficiently versatile to accommodate virtually all conceivable types of field dependent NMR studies. Our instrument uses previously constructed personal computer-based electronics and is based on commercially available electronic modules, thereby facilitating its use and assembly. A magnetic field strength of 2 T is achievable with a maximal operating current of 700 A. The homogeneity is obtained by spacing the coil turns in a gradual manner. This is necessary for coils with finite length. Other methods to obtain homogeneity are linear spacing or notch arrangements. The gradual spacing technique has the additional benefit of generating the highest magnetic field strength compared with the other techniques. Another major challenge of the fast field-cycling instrument is the time it takes to turn the magnetic field on and off. The voltage–current relationship through an inductance is given by $U(t) = L \frac{dI}{dt}$; where $U$ is the voltage across the inductance, $L$ is the value of the inductance, and $I$ is the electrical current. To improve the switching time for a given coil inductance (e.g., 1 mH in our case) one needs to increase the driving voltage across the coil. Figure 8 shows the calculated switching intervals for three voltages (e.g., 3000, 2000, and 1000 V). The storage capacitor supplies the electrical current during the switching interval; whereas the power supply provides the electrical current needed to maintain the magnetic field constant during a given field-cycling period. Thyristers are used to rapidly switch the current supply between the power supply and the storage capacitor. Figure 8 illustrates that for the same operating current, shorter switching times (e.g., higher driving voltages) require less capacitance. That is to say, the storage capacitor provides the same energy in a smaller time interval relative to the voltage across the inductance. This is obviously an advantage, considering the substantial cost of high voltage capacitors. However, the disadvantage is that one has to deal with higher voltages. Compounds with short relaxation times and low sensitivity such as $^2$H-labeled liquid crystals, lipid bilayers, and polymers appear to be the worst case scenario for a field-cycling apparatus. For example, the interpretation of the relaxation dispersion in liquid crystalline materials and lipid bilayers obtained by conventional NMR techniques has been rather controversial.6,11,22 Obviously in this case there is a need for further extensive relaxation data over a broad frequency range spanning the kHz to MHz region. Investigation of such materials requires fast switching of the magnetic field (<1 ms) and a maximal magnetic field strength (>2 T). The advantage comes from the shorter polarization time it takes for these compounds. As a rule five times the spin-lattice (Zeeman) relaxation time $T_{1Z}$ is sufficient for any polarization period; thus a $T_{1Z}$ relaxation time value of 1 ms would require a relatively short 5 ms polarizing period.

In order to mitigate against these difficulties, Fig. 9 introduces a new concept for improving the signal/noise (S/N) through maximizing the polarization field strength by an order of magnitude in the case of compounds having relatively short $T_{1Z}$ relaxation times (<1 ms). The polarization interval is created by the first half-cycle of the aperiodic function of the electrical current discharged from the storage capacitor. No electrical current is needed during the polarization period from the current amplifier, thereby eliminating the need for such amplifiers to produce the high polarization current (5000 A). The increase in polarization strength, however, will boost the S/N of the NMR signal. Moreover, no thyristor switching is done during the polarization period, which further facilitates the task. The switching times for the detection period can be equivalent to the switching times used in the present field-cycling instrument. The heat generated by the current through the ohmic resistance of the coil limits the maximal current amplitude and polarization period. Use of superconducting wire for the magnet coil can diminish the ohmic losses further, increasing the maximum polarization period, and thus enabling the measurement of relatively insensitive biological compounds. This new approach requires a storage capacitor that can be charged with opposite polarity, as in the case of the present instrument (e.g., comprising high voltage chip capacitors). Figure 9(a) depicts the calculated electrical current during the polarization, evolution, and detection periods. The polarization period is now determined by the values of the inductance (1 mH) and the capacitance.
(0.25 mF); whereas the maximal current is defined by the driving voltage. In Fig. 9(b) the initial driving voltage is $-5000 \text{ V}$. After the polarization period the storage capacitor is charged oppositely with an amplitude of $+5000 \text{ V}$ less the ohmic losses that occurred during the polarization. During the evolution period (typical values are 1 ms) the storage capacitor is switched to $-5000 \text{ V}$ by additional thyristors or power relays in the network; moreover no significant current flows which makes the switching relatively straightforward. The advantage of this newly proposed concept is the potentially large increase in sensitivity while maintaining the fast switching. Utilizing this pulsed mode of operation, a peak magnetic field strength of approximately 18 T can be reached, surpassing even conventional high resolution superconductive magnets.

In conclusion, field-cycling instruments have been fabricated in the past and will continue to improve with the development of newer technologies. They will most likely become major players in increasing the sensitivity of NMR experiments involving biological samples and other fascinating materials. Finally, we note in passing that field-cycling magnets based on high temperature superconductive wire are possible, which can hold substantially more electrical current without the need for circulating cooling water in the magnet assembly.

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