Journal of the Korean Magnetic Resonance Society **2006**, *10*, 74 - 88

A Design for a Home-Built Solid State NMR Spectrometer

Doo-Kyung Yang[1]* and David B. Zax[2]

[1]Advanced materials R&D, LG Chem, Ltd. / Research Park
104-1 Munji-dong, Yuseong-gu, Daejeon, 305-380, Korea
[2]Baker Laboratory, Department of Chemistry and Chemical Biology,
Cornell Center for Materials Research, Cornell University, Ithaca, NY 14853, USA

Received February 24, 2006

Abstract : Since the first commercial NMR spectrometer came out in 1953 from Varian, much of the hardware development has been improved and matured through commercial equipments. Many of magnetic resonance laboratories however still build and use home-built spectrometers, which are satisfactory even with the consideration of educational purpose only. The home-built NMR spectrometer could be further advantageous and could be often an only option for investigating new ideas with demanding experimental conditions or new hardware support. A solid state NMR spectrometer was designed with extra interest in stochastic experiment and built for an 8.93 T superconducting magnet from Oxford instrument. Super-heterodyned system was implemented for the transmitter and receiver parts. Intermediate frequency (IF) for the heterodyne system was chosen to 70 MHz for the first and the second channels, with additional 120 MHz for the third channel for maximum NMR frequency capability. We will show overall schematics, and discuss the designs with detailed diagrams, then demonstrate the applicability of home-built spectrometer with stochastic-excitation in solid state NMR and in applications to quadrupolar nuclear spins.

Keywords: Home-built Spectrometer, heterodyne system, vector modulator, stochastic excitation

NMR SPECTROMETER

Modulation and Demodulation

---

* To whom correspondence should be addressed. E-mail : dkyang@lgchem.com

Since the dawn of the magnetic resonance spectroscopy in early 20th century, the progress in the nuclear magnetic resonance field has been tremendous and the NMR hardware development, inseparable from that evolution, has played significant roles and sometimes even has leaded many of new ideas and experiments. The most significant evoultion was occured after the introduction and transition to pulse NMR era in 1960's from the old NMR ages with continuous wave experiments. The pulse NMR was brought about along with the innovation in computer science so that once the formidable task of Fourier transformation had become feasible in a reasonable time. Significant transformation also took place in the NMR spectrometer design and improved afterward, however one basic scheme for extracting the NMR signal from the sample was not changed.

Since the Larmor frequency in NMR is in general not of much interest, the NMR signal need to be extracted from the Larmor frequency, which is called demodulation as in the FM radio system. Audio signal is demodulated at radio receivers from the carrier waves of near 100MHz FM radio frequency, which was initially broadcasted as a modulated wave of low frequency audio signal with a carrier FM frequency. Typical electronic devices are sensitive to the working frequencies and they usually perform well only for relatively narrow band around the optimum frequencies. With the frequency range limitation, modulation and demodulation process is an effective technique in order to deal with electronic wave signals for broad ranges in amplitude and frequency.[1-3]

Typical NMR spectrometers are even further required to be able to analyze and detect over much broader frequency ranges. The Larmor frequency of one nucleus in NMR experiment differs from other nuclei extending over much broader frequency range than the range of carrier frequencies in FM radio. Therefore, an additional modulation and demodulation process is usually implemented in a typical pulse NMR spectrometer so as to handle the Larmor frequency variation. Fixed "intermediate frequency" (IF) is, therefore, chosen in a normal NMR spectrometer, and a pulse with precise intensity and phase is generated through a series of electronic devices such as switches, amplifiers and filters, that usually have relatively narrow working frequency ranges. Only in the final stage, the pulses of intermediate frequency is mixed with local oscillator (LO) frequency from frequency synthesizer, PTS (programmed test source), that is set to be NMR frequency ± intermediate frequency. Mixing these two frequencies through a mixer generates the final pulse of desired RF frequency and phase in an arrangement referred to as heterodyne pulse generation. In order to observe the NMR signal, the free induction decay, the receiver unit was also designed to use the mixers based on the same reason.[4] The pulse response from the probe is mixed with local oscillator (LO) frequency source to generate the modulated intermediate frequency (IF), then processed to a proper intensity level and in the end mixed with intermediate frequency again so as to produce the final NMR signals. This sequencial process with two mixing steps is called super-heterodyned system.

A mixer mixes two frequency inputs and generates multiple order harmonics. It is typically optimized to produce the first order harmonics $\Delta\nu_1 \pm \Delta\nu_2$ (for example, LO ± IF to generate NMR frequency) from two frequency inputs. The unnecessary frequency can be easily filtered out by either low-pass or high-pass filters. However, when the required final frequency is close to the intermediate frequency, it becomes difficult or impossible to extract the desired frequency from the outputs of the mixer. As a result, typical NMR spectrometers have certain ranges around the intermediate frequency, over which they are not applicable. The intermediate frequency for a NMR spectrometer thus needs to be cautiously selected in order to minimize the number of inaccessible nuclei.

Overall spectrometer scheme

Fig. 1 shows the overall spectrometer diagrams for an 8.93T superconducting magnet from Oxford instrument. Tecmag ORION data acquisition system was employed in order to control the spectrometer and to process the data. The basic functions of the ORION system implemented for the spectrometer are to generate all the TTL control signals in 100ns resolution and to acquire the data through the signal averager. NTNMR software on personal computer operates the ORION console and processes the data acquired through the ORION system. In order to minimize the noise and to extend the eligible distance of TTL logic signals from ORION console, a monitor unit was built in to check the reliability of TTL logics, where every TTL lines could be verified and could be used as triggering pulses.

The frequency synthesizer from Programmed Test Sources (PTS) provides 10 MHz reference timing for ORION system and 120MHz intermediate frequency(IF) and local frequency (LO, NMR ± 120 MHz) for the RF transmitter unit. TTL logics from the monitor unit control the series of switches in the RF TR Box and generate pulses based on these two frequency inputs from PTS unit. RF TR Box also enables the receiver unit by transferring the same frequency inputs from PTS to the receiver only during the specific period. The

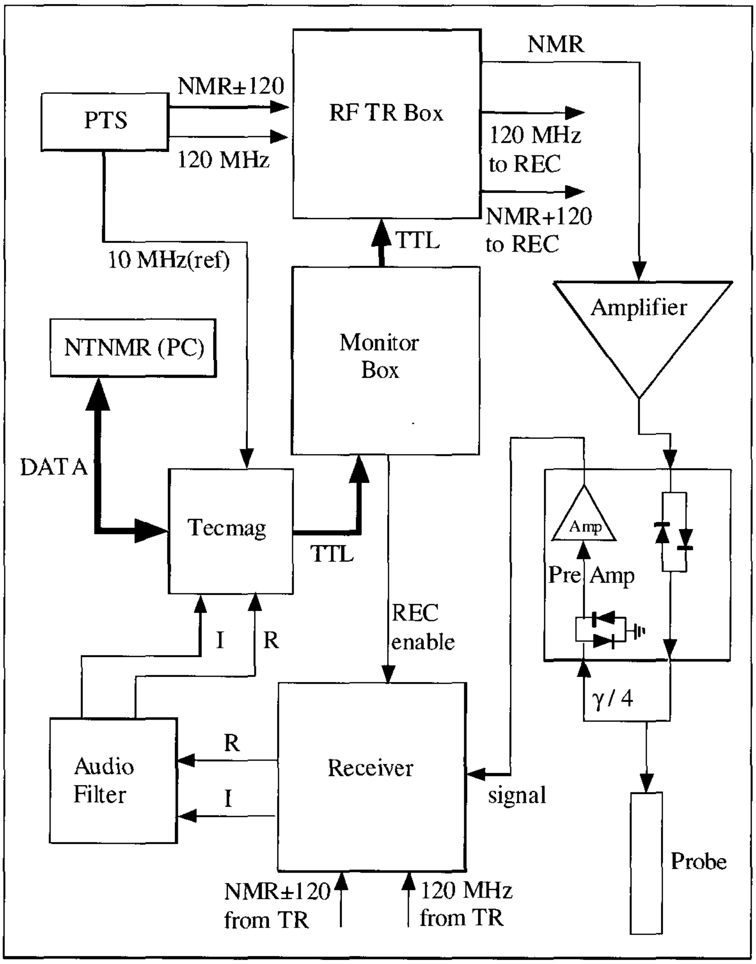

Fig. 1. Overall Spectrometer Scheme

maximum pulse power from the RF TR Box was adjusted about zero dBm, which is typically the maximum acceptable input power for over 100 watt high power amplifiers.

1 KW with 60 dB gain high power amplifier was used for X channel, and 300 w high power amplifier was equipped for H channel. A crossed diode unit was placed between the high power amplifier and the probe in order to shield the probe from the magnified

background noise out of the high power amplifier. Crossed diode is a nonlinear element and operates similar to a regular switch that turns on for high power input and off for low power input. The quarter-wavelength (λ/4) cable in series with the crossed diode array connected to the ground was implemented in order to protect the Pre-Amp unit from the high power pulses. Any kind of inputs over the diode threthold, ~0.7V, pass through the crossed diode unit and connect to the ground directly. The high power pulse also connects to the ground, however with the accurate quarter-wavelength cable corresponding to the pulse carrier frequency, a standing wave is generated from the reflection on the quarter-wavelength cable and no pulse power can pass through the cable. The high power pulses are forced to run only into the probe and the tiny NMR response from the sample can be however guided to pass through the Pre-Amp amplifier.

Pre-amplified NMR response enters the receiver unit, where the response is demodulated twice with the intermediate frequency and with the local frequency transferred from the frequency synthesizer through RF TR Box. Since the receiver unit amplifies the extremely small NMR signal drastically, it could be damaged very easily with any uncontrolled inputs. It was therefore crucial to protect the receiver unit in every stage by implementing several safety designs. The first safety feature is the quarter-wave array unit, the second one is the receiver TTL logics that enable switches in the receiver system and the last one is by enabling the frequency sources for the receiver only during the specific period. NMR signal is filtered and amplified to about 10 dBm in receiver unit, then go through the signal averager in Tecmag ORION system through an audio filter and finally get ready for further data processing on NTNMR.

Basic elements and terminology prior to details

Electromagnetic wave in the radio frequency range is well known to transfer most favorably through coaxial cables when the impedance level is about 50Ω. All the electronic components and coaxial cables used in NMR spectrometer are thus selected or adjusted to have the same impedance value of 50Ω. Impedance mismatching in any elements causes power reflection. Probe matching, for instance, is so as to adjust the probe impedance to 50Ω.

For the RF power measure, dB or dBm is commonly used, which are relative measure of power in log scale. One nice thing about using the power in log scale is, when amplifiers

$$(dB) = 10\log_{10}\left(\frac{P}{P_0}\right), \text{ or} \qquad (dB) = 20\log\left(\frac{V}{V_0}\right)$$

or attenuators are in series, the relative total power gain or loss can be calculated by simply adding the powers in dB's or dBm's. The dBm is a relative measure of power when P_0 is fixed at 1 mW, so 0 dBm is 1 mW. For 50 Ω load, 0 dBm corresponds to 0.632 V_{pp} and 13 dBm equals to 20 mW and 2.83 V_{pp}. The easiest way to measure the RF power to 50 Ω load is to measure the V_{pp} with an oscilloscope, then look up a power table that correlates the power in dBm with V_{pp} or V_{rms} .

The "mixer" mixes two frequency inputs and generates multiple order harmonics. It is usually optimized to produce only the first order harmonics $\Delta\nu_1 \pm \Delta\nu_2$. A mixer operates with diode arrays that have specific threthold level to work on. To ensure proper-working conditions with the diode arrays, they require specific driving power levels. In the spectrometer, only two kinds of mixers were used, ZAD-1 and ZAD-1H from Mini-Circuits. The main difference was the power levels required for the driving local oscillator. ZAD-1 requires at least 7dBm driving power and ZAD-1H needs 17dBm power. In addition, ZAD-1H has a little better characteristic in the dynamic range or linearity. Receiver unit demands wide dynamic ranges, therefore ZAD-1H is preferred for the receiver system. In contrast to the power level of driving local frequency, the power level of the other mixer input, intermediate frequency, is very low. Generally, the optimum IF power level to get the best characteristic from mixers should be below -10 dBm and it should not be more than –5 dBm

Switches need power supply of 5 V, –5 V or both to operate and have many in's and out's and TTL input. The names or orders are of no importance, they are simply connected or disconnected by the TTL control. Typical switches attenuate the input by upto 1 dB. All the switches used in the spectrometer have very good switching time, typically less than 50 ns. The isolations between two disconnected terminals are various for different switches. They are usually around 40 ~ 60 dB. The first check point for choosing switches should be the 1 dB compression point that is almost the maximum power level the switch can handle where a switch distorts the maximum input by 1 dB level. The input power should be controlled less than that value, or the input shape will be distorted. In addition, noise transfer from TTL signal to the terminals called video breakthrough and switching transient should also be considered for the wiring diagram. They are typically less than 30 mV, but they could be still much bigger than the NMR signal. Single Put Single Through (SPST) switch has one in and one out. They are simply connected when TTL is high or disconnected when TTL is low. We used only one type of SPST switch, DAICO 0699 that needs 5 V power supply. It has very good characteristic in video breakthrough and transient, and 1 dB compression point is around 15 dBm (~3 V_{pp}). Single Put Double Through (SPDT) switch has one in (RF-in) and two out's (RF1, RF2). RF-in is connected to one of the outs depending on the TTL level. We used two types of SPDT switches, Anzac SW229 and Mini-circuits ZYSWA-2-50DR. They need both 5V and –5V power supply. Anzac switch has good characteristics; the 1dB compression point is very high around 20 dBm (~5 V_{pp}). Mini-Circuits switch has relatively high video breakthrough value and switching transient, it should not be used in the receiver unit. The 1 dB compression point is ~15 dBm (~3 V_{pp}).

A splitter divides the input power by two thus attenuating the two outputs power by 3dB. ($10 \times \log \frac{1}{2} = -3.02$ dB). Filters also attenuate inputs by a couple of dB depending on the filtering shapes and degrees. For the low power amplifiers, the main check points are gains, 1dB compression points and applicable frequency band ranges. The NMR amplifiers from Miteq are high gain pre-amps with relatively low 1dB compression point of less than 6 dBm. They show very good characteristics and works well for the receiver unit. Table 1 shows the characteristics of several low power amplifiers.

Transmitter

Fig. 2 shows the overall single channel transmitter diagram for simplicity. Each electronic element is marked with the actual RF input power level. The local oscillator frequency of NMR ± 120 MHz from the PTS splits into two in the beginning. One of these output is used for the receiver unit and the other one for the transmitter unit. They go into Mini-Circuit switches where they are enabled during the specific period only when PTS enable logic is on, which protects the receiver by transferring the required frequency source (NMR ± 120 MHz) to the receiver unit only during the acquisition period. The other intermediate frequency input of 120 MHz from the PTS is amplified, filtered and then also splits into two. One of these outputs is sent to the receiver unit. The quadrature splitter and detector in the receiver unit is not optimized for pulses, therefore the intermediate frequency for the receiver should be CW. The other 120 MHz output splits into four phases (x, y, -x and -y) through the quadrature phase splitter, and one out of four phases is selected through a couple of switches by phase selector. Then it is sent to the ZAD-1H mixer from Mini-Circuits, where it is mixed with the local oscillator frequency of NMR ± 120 MHz. The output from the mixer is cut and shaped to the final pulse by DAICO switch and further processed for the pulse intensity adjustment.

Table 1. Characteristics of low power amplifiers.

Amplifier	gain	1dB comp.	frequency range
Anzac AM147	17 dB	19 dBm	5~ 500 MHz
Anzac AM157	12.5 dB	21 dBm	20~ 501 MHz
Qbit QBH-122	17 dB	17 dBm	upto 300 MHz
Qbit QBH-150	20 dB	18 dBm	10~ 300 MHz
Qbit QB-300	25 dB	22 dBm	1~ 300 MHz
Miteq AU1466	35 dB	6 dBm	10~ 200MHz
Miteq AU1114	30 dB	8 dBm	10~ 500MHz

When the pulse frequency is close to the intermediate frequency, it becomes difficult or impossible to extract the desired frequency from the mixer. In order to overcome this inapplicable frequency ranges that typical NMR spectrometers have, an additional intermediate frequency was implemented. Fig. 3 shows the modification of the transmitter unit. This transmitter unit has one toggle switch to choose the right frequency sources coming from the independent frequency sources for the transmitter and receiver unit (70 or 120 MHz and NMR ± 70 or 120 MHz) and uses two SW229 switches to do the job. Once the intermediate frequency and the local frequeny are selected, all the other process is the same as before. The first and the second channel were designed to use 70 MHz and the third channel was enabled to choose between 70 and 120 MHz.

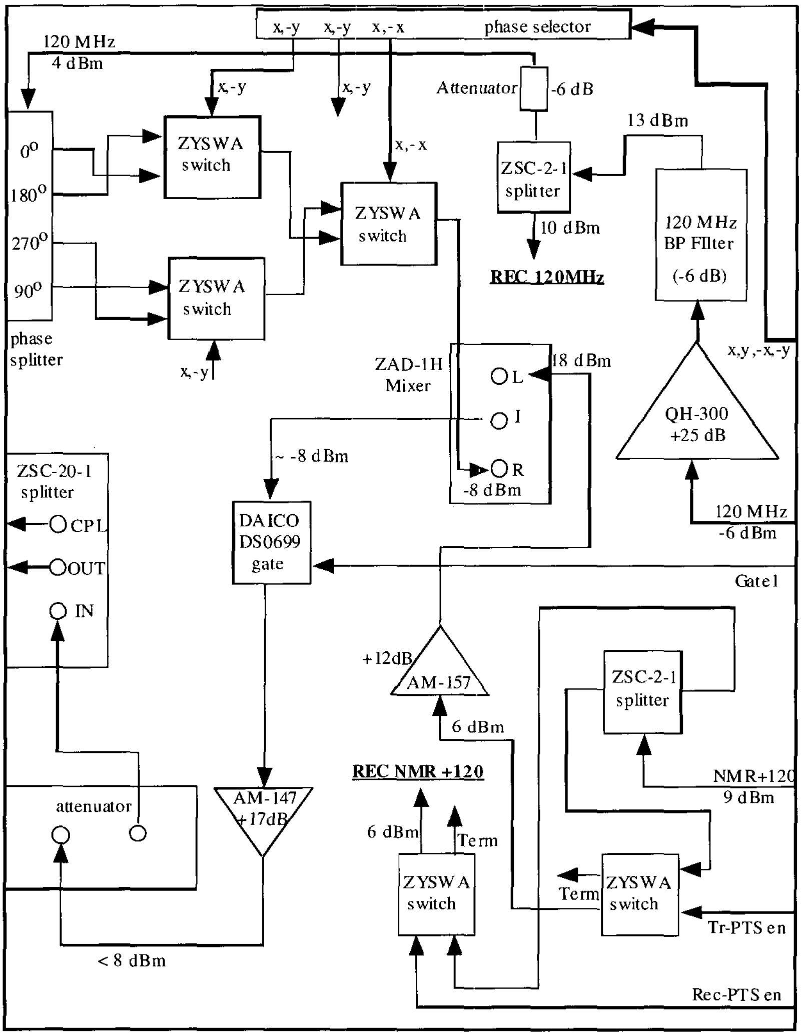

Fig. 2. Transmitter Diagram.

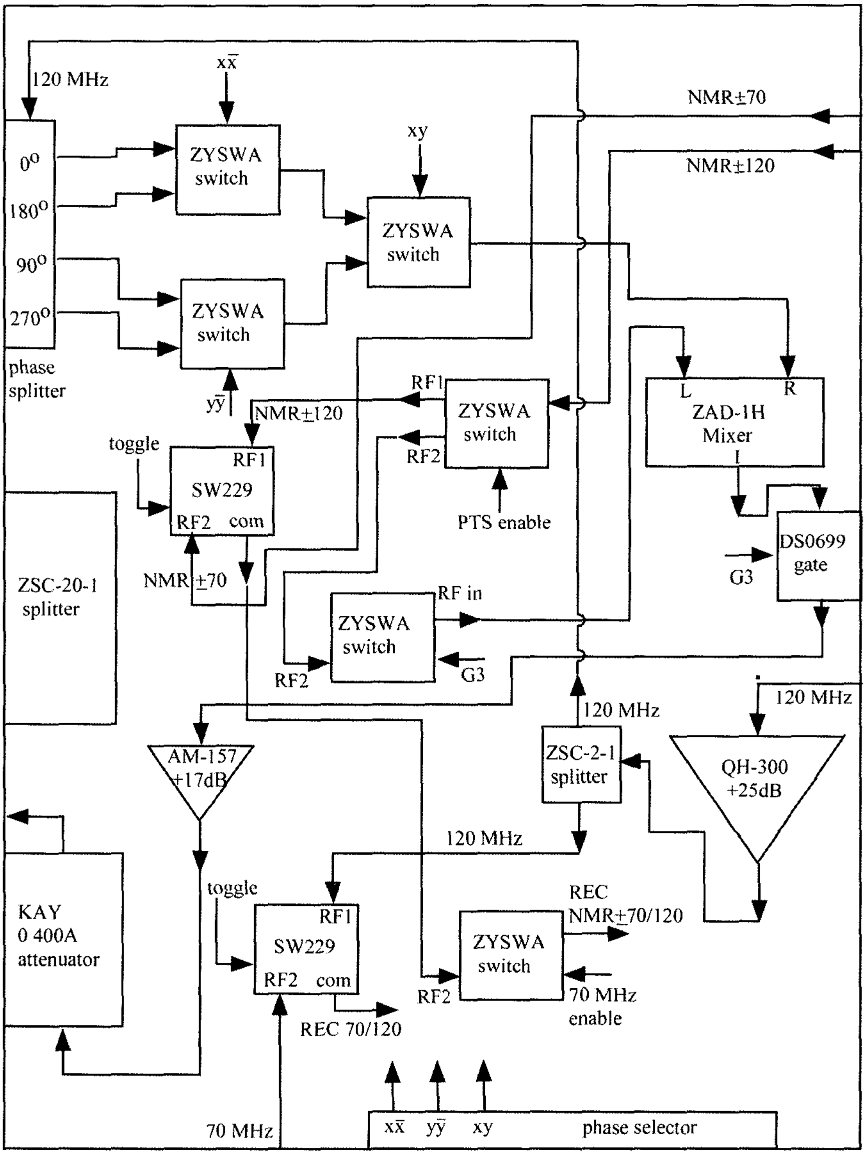

Fig. 3. Transmitter Diagram with two independent intermediate frequencies

Vector Modulator

In order to enhance the ability to control the amplitudes and phases of pulses, a Vector Modulator was implemented along with the transmitter RF flow. A vector modulator VMA-006A from Vervecomm that shows the phase settability of better than 0.01 radian, is a fast switching phase and intensity controller. It is set to control arbitrarily the intensity and phase of the intermediate frequency for the transimtter unit. The setting time for the phase and intensity is about 150 ns, which should be carefully considered in the actual pulse sequence. In a real application, at least 500 ns prior setting is necessaty to generate proper and stable outputs. The phases and the magnitudes are controlled via the pulse program in NTNMR for the Tecmag ORION system. A special data table can be clocked out one entry at a time, and upto 12 bits data can be assigned in the pulse sequence. The phases and amplitudes were preset and loaded to the the table called dedicated modulator (DMOD) table, and whenever the pulse sequence triggers the DMOD line, the table entries are clocked out sequentially until the end of scan where the entry will be reset to the first entry. The actual application of the MOD line would involve loading a table in an early event in the sequence, and then toggling the 'On' gate in later events, each time sending the data for the next table entry. The outputs from the MOD lines will be active for "On" events and immediately following next event. The amplitude and the phase out of the vector modulator are adjusted based on the DMOD output values. Since arbitrary variation of pulse phase and amplitude is not always necessary for a typical pulse sequence, a toggle switch was placed to enable or to reset the vector modulator.

Recever

The receiver unit iss also designed to use the mixers based on the same reason as for the transmitter unit, whose diagram is shown in Fig. 4. The pre-amplified NMR signal goes through a DAICO switch, which is enabled only when the the REC Enable logic is on so as to protect the receiver. Then the NMR signal is further amplified through Miteq low power amplifier, and then mixed by Mini-Circuit ZAD-1H with the local oscillator frequency source (NMR ± 70 or 120 MHz). in order to generate the modulated intermediate frequency The modulated NMR signal is then filtered by 70 or 120 MHZ band-pass filter, further amplified, and then mixed with intermediate frequency again in order to extract the final

NMR audio signal. The mixer in the final stage is a Quadruture Detector from Anzac with a special function, which generates two mixing signals with specific 90 degrees phase difference. The Quadruture Detector produces the final quadruture NMR audio signals. This modulation and demodulation process with two mixing steps is called super-heterodyned system.

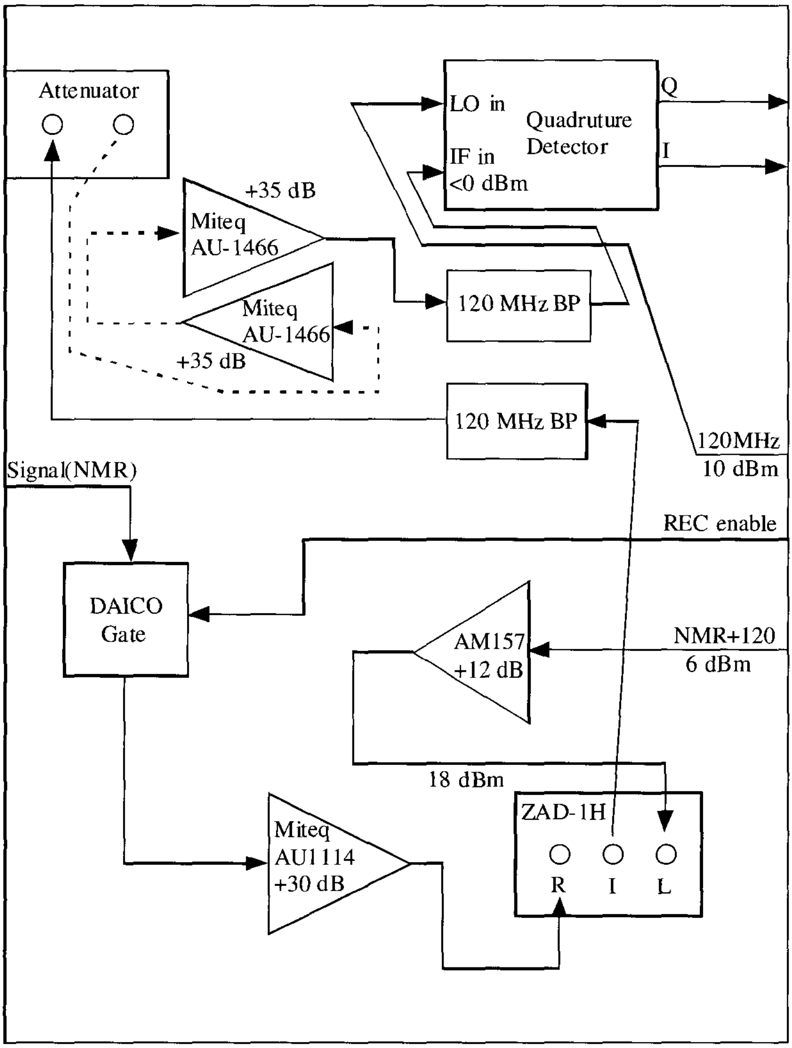

Fig. 4. Receiver Diagram

Stochastic Excitation

A typical stochastic experiment in NMR is performed by applying a series of irradiation sequence derived from pseudo random numbers, MLBS(maximum length binary sequences), which is designed to provide a white noise excitation over a broad bandwidth, and accumulating a couple of response signals right after each pulse.[5-7] In the weak multi-pulse limit, as in typical noise-based stochastic experiment, each pulse in the irradiation sequence with the length of less than a couple degrees is assumed to generate tiny magnetization evolution from the dynamically equilibrated longitudinal magnetization. Each pulse, in this linear response limit, does not interact with previously evolving transverse magnetizations. As the pulses are typically repeated much faster than relaxation times, they generate simultaneous evolution of thousands of small free induction decays, superposed at the top of the previous ones, in what may appear to be useless mess. Accumulating signals between the thousands or even millions of Multi-pulse excitations in the interval of micro seconds is not easily implemented with any commercial NMR spectrometers. The fast switching vector modulator, that controls the phases and amplitudes of pulses in arbitrary values, allows the MLBS pseudo random pulse excitations. The signal accumulation between the pulses is also accomplished without much trouble by home-built receiver with proper protections and high speed switches. Responses observed in these stochastic experiments have no apparent beginning or ending point in the signal. Nevertheless, the rules governing the proferly chosen series of inputs and the responses make the deconvolution possible. For the simple one-dimensional applications, this deconvolution can be carried out by the cross-correlation between the irradiation sequences and the responses obtained between pulses. Fig. 5 shows an actual stochastic experiment for ^{23}Na quadrupolar nucleus with 10 bit-MLBS sequences for noise excitation and describes the data processing.

CONCLUSIONS

We have shown diagrams in details for a solid state NMR spectrometer built for an 8.93 T superconducting magnet from Oxford instrument with particular interest in stochastic experiment. Implementing two independant intermediate frequency (IF), 70 MHz and 120

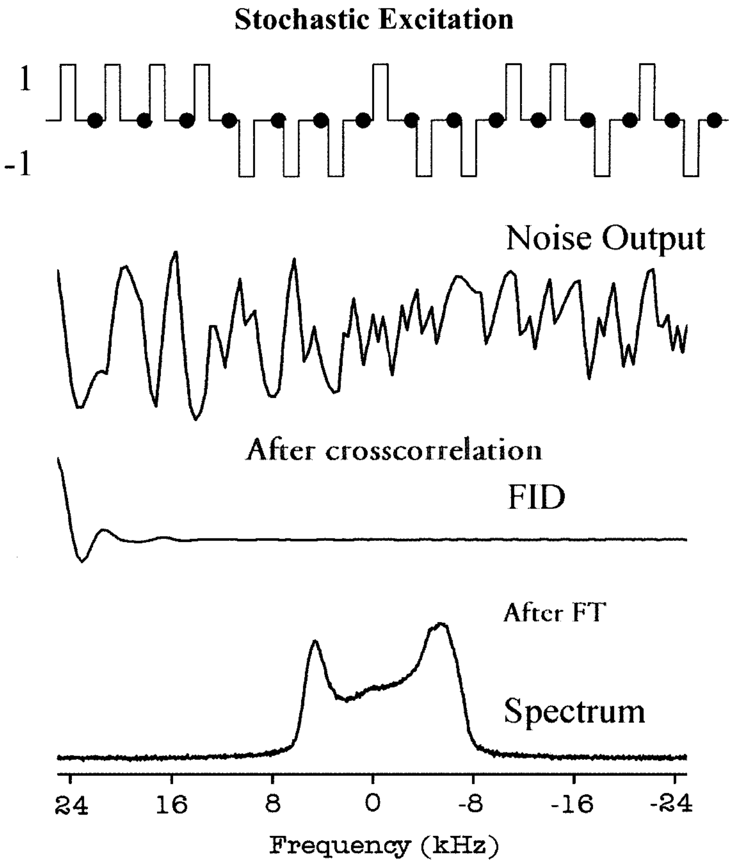

Fig. 5. ^{23}Na Stochastic Experiment for $NaMnO_4$. 10 bit-MLBS sequences were used for noise excitation. Black dots represent signal acquisition points. Accumulation of the series of the signal builds up the Noise Output. Cross-correlation reorganizes noise output and generate a familiar FID.

MHz, for the heterodyne system virtually removed any inapplicable frequency ranges in NMR spectrometer. We also showed the applicability of home-built spectrometer in stochastic experiment in solid state NMR and in applications to quadrupolar nuclear spins. Certainly, a home-built spectrometer won't be always convenient to play with, however it can be an only possible option for demending experiments and the vital knowledge necessary for operating and understanding the home-built spectrometer could be much of assistance for designing and troubleshooting new ideas and experiments.

REFERENCES

1. W. A. Anderson. *Rev. Sci. Instrum.* **33**, 1160 (1962)
2. R. E. Santini and J. B. Grutzner, *J. Magn. Reson.* **22**, 155. (1976)
3. E. Fukushima and S. Roeder, "Experimental Pulse NMR" Chap. 5, Addison-Wesley Publishing Company, Massachusetts, 1981.
4. I. Hoult, *Prog. in NMR Spect.* **12**, 41 (1978)
5. R. R. Ernst, *J. Magn. Reson.* **3**, 10. (1970)
6. R. Kaiser, *J. Magn. Reson.* **3**, 28. (1970)
7. M. Harwit and N. J. Sloane "Hadamard Transform Optics", Academic Press, New York, 1979.