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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

The home-built high-field multifunctional pulsed NMR spectrometer†

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The home-built pulsed nuclear magnetic resonance spectrometer is described, it consists of rather cheap commercial hardware for radio frequency (RF) pulse generation and signal acquisition system. The old-stuff superconducting magnet (9 T) and modified current insert allows to vary first order cold shim gradient fields and the B_0 field in the range of 0-8.5 T. The helium cryostat inserted in a wide bore of the magnet and the sample temperature control system allow to perform nuclear magnetic resonance (NMR) experiments in the temperature range of 1.65-300 K. The software created in Labview development environment synchronizes the RF excitation and acquisition systems and controls the parameters of pulse sequences and data acquisition in the 5-500 MHz range of frequencies. The maximum achieved resolution in ^{1}H NMR spectra using first order cold shims is ca. 0.5 ppm in a spherical water sample of 5-mm diameter.

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1. Introduction

Nuclear magnetic resonance (NMR) is a powerful research tool for study of microscopic and macroscopic structure of different materials and physical processes. NMR spectrometers are widely used in scientific research, education, manufacturing, medical and health fields. However, commercial spectrometers are designed for broad fields of applications but usually for fixed experimental conditions, for instance, fixed magnetic field, NMR frequency, temperature, and etc. Often it is necessary to perform sophisticated experiments and vary the physical parameters in broad ranges for comprehensive studies in different areas of physics, chemistry and material science [1, 2]. Usually such studies can be performed on a few different NMR spectrometers, for instance, if different magnetic field strengths are needed. Another possi bility is the modernization of existing NMR equipment [3-6] and the designing of new parts of spectrometer so that variation of the physical parameters such as temperature [7], magnetic field [8] and NMR frequency can be under control on a single NMR spectrometer.

Outdated NMR spectrometers very often are supplied with high-field magnets with sufficient field homogeneity for broad range of applications, but suffers from obsolete analog hardware for signal registration and excitation that in principle can be replaced by modern rather cheap radio frequency (RF) components.

In this article we describe multitask home-built pulsed NMR spectrometer based on a modified magnet and other components of Bruker MSL 400 spectrometer (produced in 1989), cryostat and designed digital excitation and signal acquisition systems. This update allows for comprehensive studies on a single NMR spectrometer that requires measurements at different magnetic field, frequencies and temperatures as well as sophisticated pulse sequences.

2. RF pulses generation and signal registration

The block diagram of the spectrometer is shown in Figure 1. It consist of the magnet with 9 cm wide bore in which the cryostat with the sample holder is inserted, the digital excitation and the signal registration systems, the power amplifier and the NMR signal pre-amplifier. The excitation and registration systems are controlled from PC by a home-made software that will be discussed later.

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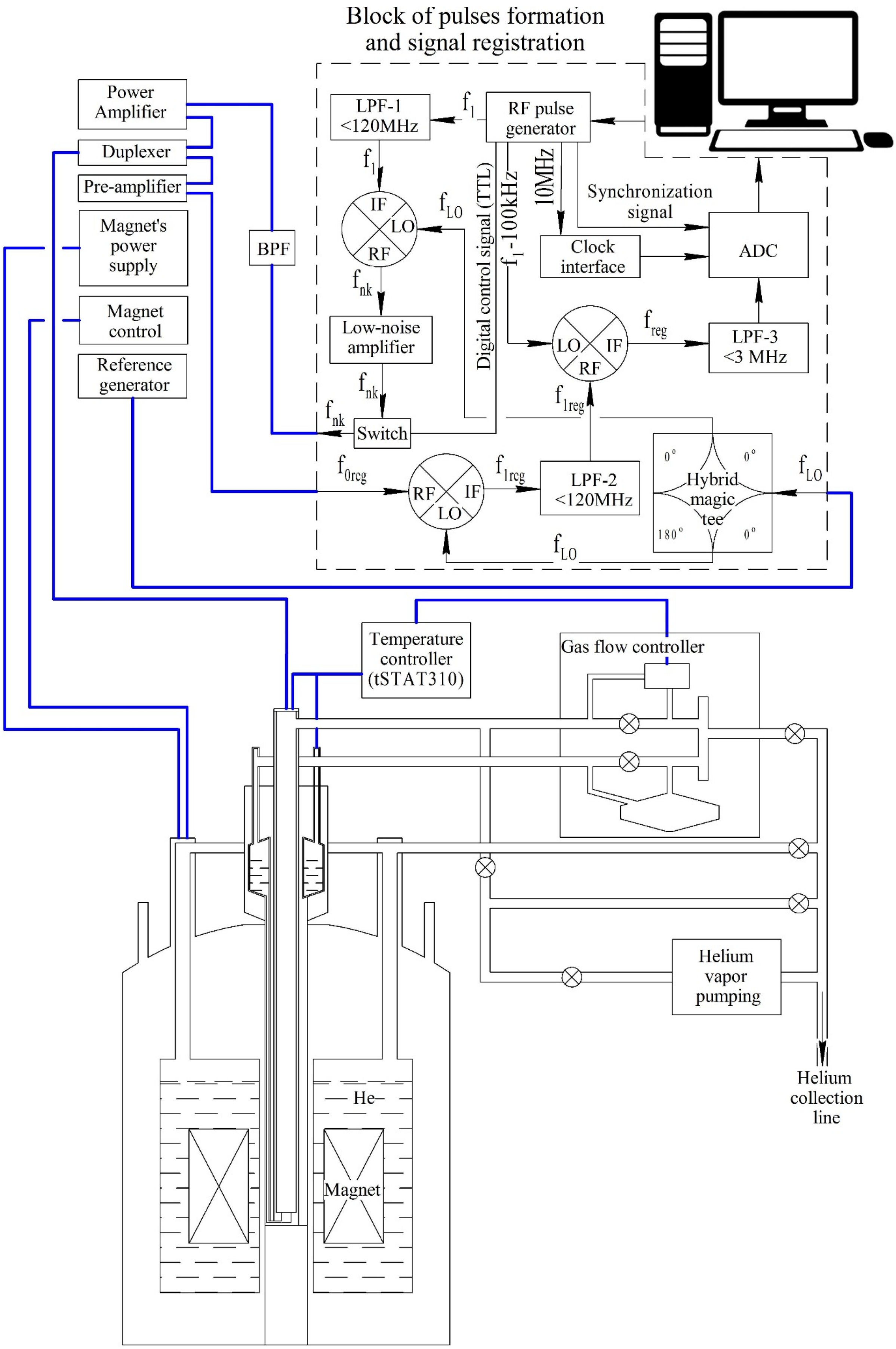

Figure 1. Block diagram of the pulsed NMR spectrometer.

In this configuration PulseBlasterDDS DDS-II-300 USB (Firmware 14-3, acquired from SpinCore Technologies, Inc.) is the general RF Arbitrary Waveform and digital (TTL) generator that has two RF outputs and four digital outputs. RF Arbitrary Waveform units in this device are essentially 14-bit direct digital synthesizers (DDS) that operate at the frequency of 300 MHz. The PulseBlasterDDS DDS-II-300 is used as a pulse generator (PG) for the RF pulse generation, synchronization and time controlling of spectrometer units, such as signal registration system, RF switches, and etc. It can output sequences with RF pulses of different shapes, phases and at the frequencies up to 120 MHz. The reconstructive Low-Pass Filter (LPF-1) is needed at the output of DDS unit to cut the signal spectral components over the maximum frequency of RF generator.

For high frequencies the output of RF generator should be multiplied by the frequency from the external sine-wave reference RF generator. The hybrid magic tee splits the signal from reference generator (Rohde&Schwarz signal generator 90 kHz – 1.1 GHz SML 01) into two same reference signals used in excitation and detection systems for frequency up and down conversions. The passive frequency mixer (Mini-Circuits ADE-1) with the low-noise broadband RF amplifier (WALFRONT, 0.01-4 GHz, 21 dB) is used in excitation system for frequency up conversion and pulse amplitude boosting to an appropriate level. The fast active RF switch (Mini-Circuits, model ZYSWA-2-50DR) followed by the amplifier protects high-power amplifier input from the noise when no RF pulses are required and it is controlled by a digital TTL signal from PulseBlasterDDS. There is also an additional band-pass filter (BPF) that removes unwanted spectral components generated by the mixer. The high-power amplifiers Rohde&Schwarz BBA100-C125 capable to deliver power up to 500 W to NMR probe are used for final pulse amplification.

As usual high power RF pulses from the output of power amplifier pass through a duplexer before being delivered to the probe. Conventionally, the duplexer which guide high-powers pulses to NMR-probe and small NMR signal from probe to pre-amplifier consists of a $\lambda/4$ line (real cable or LC-circuit analog to quarter line) and silicon switching or silicon p-intrinsic-n (PIN) diodes [9].

The NMR coil can be wound on a sample holder and usually consists of few turns (exact number depends on the NMR frequency) of copper wire. This coil is tuned and matched to 50 Ohm by two capacitors.

The NMR signal at the frequency $f_{0\mathrm{reg}}$ is firstly amplified by standard pre-amplifiers from spectrometer Bruker MSL-400, and then passes to the registration system. In this system two step frequency down conversion is applied. Firstly it is mixed with the signal from reference generator by the passive mixer (Mini-Circuits ADE-1) and filtered by the LPF-2 band-pass filter, so that it down-converted to intermediate frequency $f_{1\mathrm{reg}} = f_{0\mathrm{reg}} - f_{\mathrm{LO}}$ (<120 MHz). Then it again down converted to low frequency (normally 100 kHz, but can be chosen from software) by mixing with continuous-wave signal at the frequency of f_1-100 kHz that is generated from the second RF output of PulseBlasterDDS. Finally this low frequency signal is filtered by the LPF-3 low-pass filter (cutoff frequency 3 MHz) and passes to the analog digital converter (ADC).

In case of low frequencies (below 120 MHz) the RF pulses can be directly connected from LPF-1 to power amplifier. Similarly, the registration signal from pre-amplifier is received bypassing frequency mixing with reference generator and LPF-2.

The TiePie Handyscope HS5-540 XM oscilloscope is used as ADC capable to acquire data at sampling rate (f_{rate}) up to 500 MS/s with maximum resolution of 16 bit. It transfers data to PC and is software controlled through usb-2.0 protocol.

The ADC and the PG use the same 10 MHz clock (TTL type) source signal that is taken from PG and converted from TTL to LVDS signal type required for oscilloscope clock input via "Clock interface" unit based on DS90LV019 Driver/Receiver (National Semiconductor). The PG also sends synchronization TTL pulses from one of its digital output to oscilloscope in order to specify starting time of data acquisition. The used oscilloscope has short jitter of time delay between the rising of synchronization TTL pulse and the acquisition starting time: $t_{\mathrm{jitter}} = n/f_{\mathrm{rate}}$, where $n = 1 \div 4$. This ensures that the phase jitter of recorded NMR signal is negligible if the latter has a low carrier frequency (10-100 kHz) after the frequency down conversion. It allows to apply digital quadrature detection with evident advantages of digital data processing over analog schemes.

The main limitations of described systems are determined by frequency bandwidths of described parts of spectrometer. Frequency mixers have frequency bandwidths 0.5-500 MHz. Two Power Amplifiers cover frequency range from 9 kHz to 250 MHz (500 Watt) and from 250 MHz to 1 GHz (125 Watt). Two standard pre-amplifiers of Bruker MSL 400 cover frequency range 5-500 MHz, therefore the described spectrometer can operate at frequencies from 5 to 500 MHz, although the low frequency is limited only by used preamplifier.

3. Magnet system

A superconducting NbTi wide hot bore (9 cm in diameter) magnet is used in described NMR spectrometer. This magnet was borrowed from old Bruker MSL 400 NMR spectrometer and was used at fixed B_0 field of 9.39 T that is generated by constant current of 60 A in the main coil. It also contains 8 "cold" superconducting shim coils ($Z0$, X, Y, Z, XZ, YZ, XY, $X2$-$Y2$). Normally it is implied that such magnet is charged only once at the very beginning and then magnetic field and their gradients are frozen throughout all stationary "life" of the NMR spectrometer.

As it was mentioned from the beginning we have assumed that updated NMR spectrometer should be universal and capable to operate at different magnetic fields, frequencies, temperatures, and etc. The main problem with field changing consists in insufficient reliability of the low temperature connector (Figure 2(12)) against repeatable cycles of connection-disconnections of insert with current leads required for charging magnet from external current generator. In fact once the connector pins are bended then there is almost no way to repair it. On another hand leaving the current insert constantly

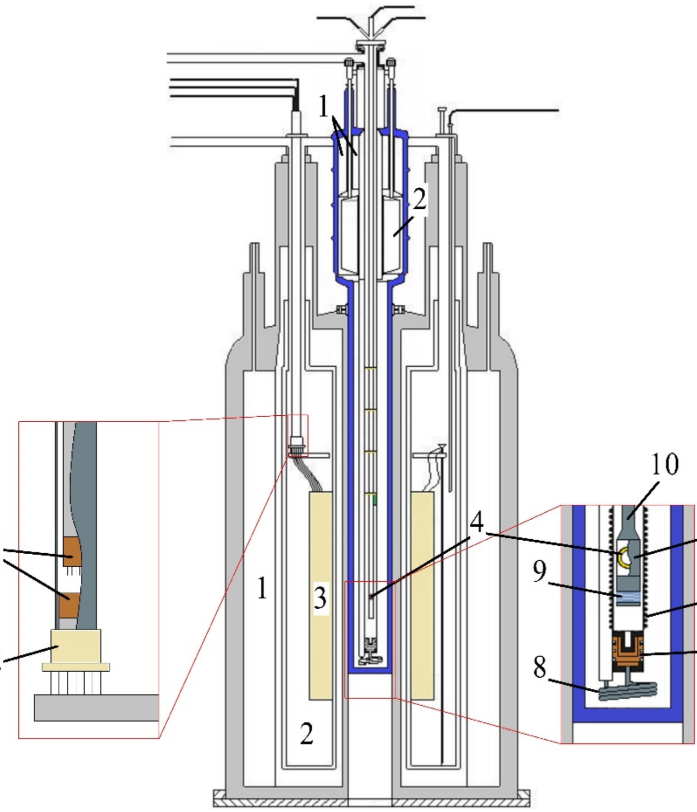

Figure 2. The magnet and the cryostat. Nitrogen vessel (1); helium vessel (2); superconducting magnet (3); NMR-coil with sample (4); thermostating chamber (5); shield (6); heat exchanger (7); stainless steel capillary (8); heating element (9); stainless steel support (10); 18-pin connector to magnet system (11); 32-pin connector to magnet system (12).

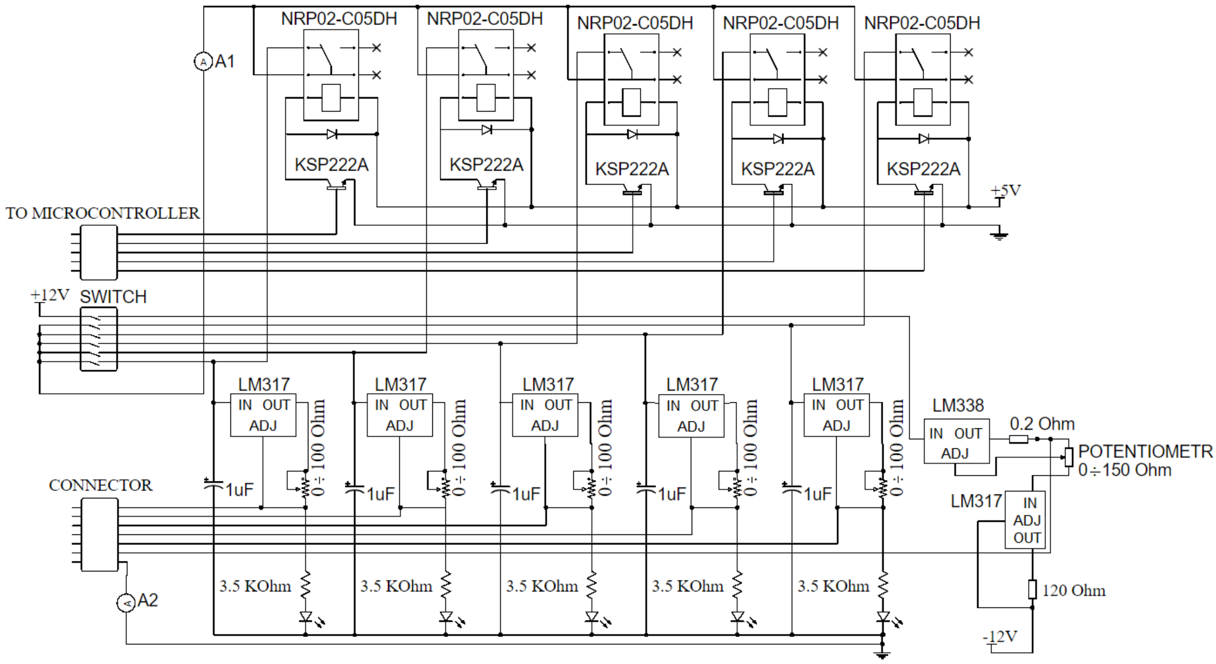

Figure 3. The scheme of the magnet control.

in magnet with liquid helium leads to unreasonably high helium evaporation due to heat transfer through wires in current insert. To overcome these problems we use an additional reliable self-latching compact 18-pin FGG.2K.318 (LEMO) connector that capable to maintain 5.5 A through each pin and endures as much as few thousands connection-disconnection cycles. Eight pins of that connector are soldered together to current wires and used for main coil charging while others are used for shim coils and their superconducting switch heaters charging. The one part of connector is mounted to the middle point inside the standard current insert tube while the second one is mounted to an additional insert tube with current leads (Figure 3(11)). Thus if this additional insert is removed from the magnet then there is no current leads and therefore no direct heat transfer from outside to the magnet.

The performance of FGG.2K.318 connector was tested and it showed a good reliability against connection-disconnection at low temperatures in liquid helium and repeated warming-cooling procedures. Because connector is immersed in helium atmosphere at low temperature inside the magnet each pin is actually can maintain much more current than specified 5.5 A.

The scheme of the magnet control unit is shown in Figure 3. It consist of adjustable high current generator (0-6.5A) based on LM338 voltage regulator for shim coils supply and five identical current generators based on LM317 voltage regulators and tuned to 80 mA for heating the superconducting switches. This scheme assumes the possibility of two methods of control: manually or using microcontroller. It allows to charge main and shim coils ($Z0$, X, Y, Z) and control the heaters of superconducting switches (100 Ohm) of the main and the shim coils. Note, that these shim coils can be used for field gradient generation in all three directions, for instance, for diffusion studies. The ATE6-100M from KEPCO power supply capable to generate up to 100 A is used for charging the main coil.

Magnetic field homogeneity in the magnet was estimated by ^{1}H NMR-signal from sample of water in a sphere-shaped glass cell with inner diameter of 5 mm. Field homogeneity is defined as the ratio of the signal spectrum half width to its central frequency [10]:

$$\eta = \frac{\Delta f}{f_0} = \frac{\Delta B}{B_0}. \tag{1}$$

Without currents in shim coils η was found to be 7×10^{-6} and with first order gradient shims (X, Y, Z) we managed to reach 5×10^{-7} (0.5 ppm).

4. Cryostat and temperature control

Cryogenic system that allows temperature control of a sample placed in thermostating chamber and helium collection is shown in Figure 1. The cryostat optCRYO105 from RTI Ltd. (Chernogolovka, Russia) is essentially an anticryostat in which liquid helium vessel communicates with thermostating chamber placed in a shaft through a capillary with heat exchanger. The temperature of the sample is controlled by the temperature of gaseous helium from heat exchanger and gas flow rate in shaft set by electronically controlled valve that placed outside of the cryostat on the helium collection line (Figure 1).

The temperature control is implemented by the tSTAT310 controller which sets a gas flow rate and heating current depending on the sample temperature measured by Cu/Cu:Fe thermocouple. This system operates in temperature range 4.2-273 K. For lower temperatures the liquid helium fills the shaft with the sample and helium vapor can be pumped out to lower temperature down to 1.65 K.

5. Software and example of NMR signal

The LabVIEW program was written for controlling of RF Pulse Generator (PulseBlasterDDS DDS-II-300 USB) and Analog-to-Digital Convertor (TiePie Handyscope HS5-540 XM).

The interface allows user to select the type and choose parameters of pulse sequence as well as to set parameters for data acquisition. All signal processing such as digital quadrature detection, filtering, Fourier transform are performed within Labview program, but RF sequence can be modified in C compiler that generates executable file available for launching by Labview. All parameters for RF sequences such as pulses shapes, durations, phases, frequencies and delays are firstly written in registers of PulseBlasterDDS generator through SpinCore API. PulseBlasterDDS analog output has 1024 frequency registers, 128 phase registers and RF sequence can have up to 4K instruction memory words.

The acquisition parameters are also sent to the oscilloscope before data acquisition and transfer to PC, this done through LibTiePie Software Development Kit. The RF sequence is software triggered after loading parameters to excitation and registration systems.

The interface of NMR spectrometer program and acquired ^{1}H free induction decay NMR signal from water sample in time and frequency domains are shown in the Figure 4. This signal was obtained at 1.2 T from water sample at room temperature in a sphere-shaped glass cell (inner diameter of 5 mm) with applied optimal shim currents for estimation of field homogeneity.

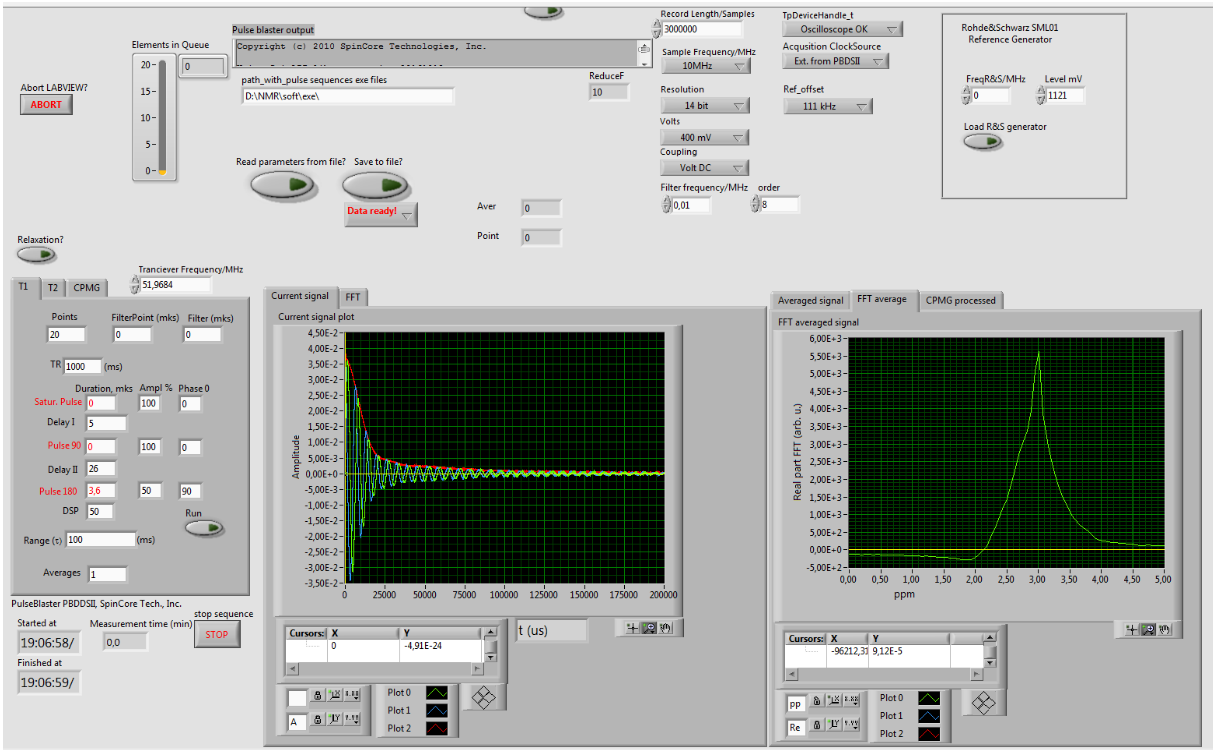

Figure 4. Program interface and ^{1}H NMR signal (left) and spectrum (right).

6. Conclusion

We described a home-build pulsed NMR spectrometer which allows to perform NMR studies that require varying parameters of experiments in broad range. The old-stuff superconducting magnet and modified current insert allow to vary first order cold shim gradient fields and the B_0 field in the range of 0-8.5 T. The helium cryostat allows to perform NMR experiments in the temperature range of 1.65-300 K. The software synchronizes the RF excitation and acquisition systems and controls the parameters of pulse sequences and acquisition in the range of frequencies 5-500 MHz. The maximum achieved resolution in ^{1}H NMR spectra using first order cold shims is ca. 0.5 ppm in a spherical water sample of diameter 5 mm.

Acknowledgments

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