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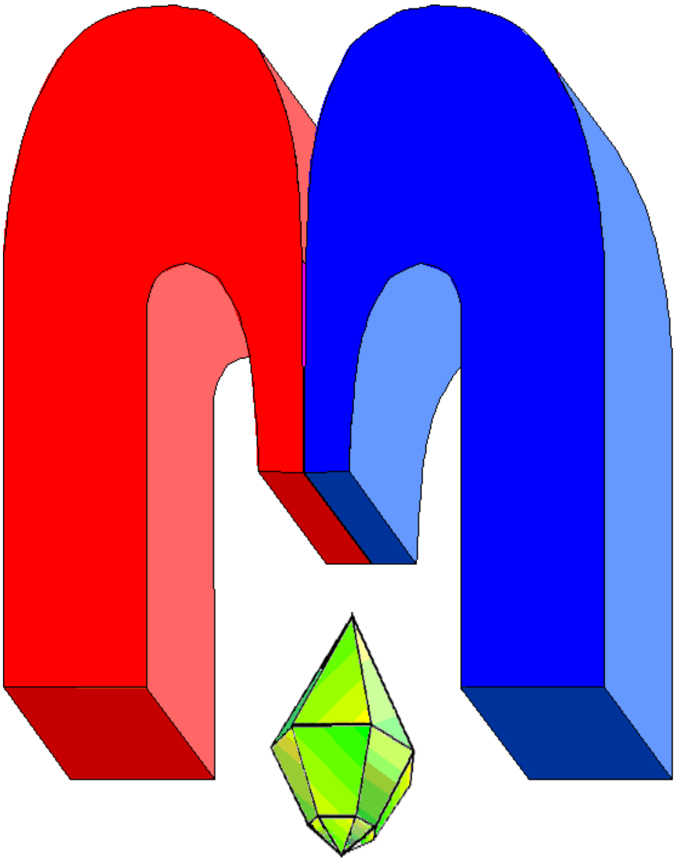

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[†] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Modernization of the X-band EPR spectrometer Bruker ElexSys E580 for dynamic nuclear polarization

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To study the effects of dynamic nuclear polarization (DNP) in the X-band (microwave frequency of 9 GHz), using the capabilities provided by commercial EPR equipment, a part of the EPR spectrometer associated with the excitation and detection of double electron-nuclear resonance signals (ENDOR) has been modernized. Using the developed preamplifier of NMR signals, a homemade “Kazan Nova II”NMR spectrometer was implemented into the radio frequency path of the EPR spectrometer. The tuning and matching circuits made it possible to observe the NMR and DNP signals on protons in the frequency range 14.5–15.2 MHz. The performance of the DNP equipment was tested for a solution of the stable nitroxyl radical TEMPOL in benzene and a crude oil sample. The DNP effects caused by the Overhauser and solid effects were observed. The modernization of the existing EPR equipment creates a basis for further expanding its capabilities to study DNP effects in various systems at different conditions (in the pulsed mode of saturation of the EPR lines, with the temperature lowering, under the action of optical excitation, etc).

PACS: 76.30.-v, 76.60.-k, 76.60.Lz, 07.57.Pt, 75.78.-n, 89.30.aj

Keywords: electron paramagnetic resonance, nuclear magnetic resonance, dynamic nuclear polarization

1. Introduction

The history of dynamic nuclear polarization (DNP) dates from 1953 when A. Overhauser proposed that irradiation of electron paramagnetic resonance (EPR) transitions could result in the enhancement of the polarization of coupled nuclei [1]. In 1958 E. Poindexter showed the enhancement of proton nuclear magnetic resonance (NMR) signal in the low-viscosity oil of factor 15 in the magnetic field of $\mathbf{B}_0 = 1.8\,\mathrm{mT}$ [2]. In recent decades, the development of DNP technology and the areas of application of DNP approaches for both fundamental research and for amplifying NMR signals has been experiencing their renaissance [3–5] including investigations of oil systems [6–10]. As it was reviewed in details in the recent paper [11], oils (crude oil, bitumen, their constituents and products) can contain up to 10^{20} native paramagnetic centers (PCs) per gram of substance. The study of both hydrocarbon and other types of PCs can provide additional information about the presence and concentration of hydrocarbons in petroleum-containing rocks, the structure and properties of crude oils and their constituents. It is of practical need for effective exploration, production, transportation and deeper processing of hard-to-recover hydrocarbon reservoirs, heavy (high-viscous) oil, bitumen, etc. [9,10,12–14]. The purpose of this work was to build a DNP spectrometer based on a commercial EPR spectrometer operating at the microwave (MW) frequency of about 9 GHz (X-band) for investigations of crude oil as well as other liquid systems containing PCs. As it was shown quite recently by applying field-cycling (FC) DNP/NMR techniques [15, 16], perceptible DNP effects can be achieved in crude oils at X-band even by applying a moderate MW power.

2. Materials and methods

In this work, the ElexSys E580 X-band EPR spectrometer (Bruker, Germany) located at Kazan Federal University equipped with an X-band pulsed resonator for conducting experiments on electron-nuclear double resonance (ENDOR) was modernized. The comercial ENDOR-resonator (EN 4118X-MD4) is designed on the basis of a dielectric (sapphire) ring (position 1 in Figure 1), around which the magnetic component of the microwave field $\mathbf{B}_{\mathrm{MW}}$ is excited. The direction $\mathbf{B}_{\mathrm{MW}}$ is directed perpendicular to the vector of the constant magnetic field $\mathbf{B}_0$ (Figure 1). A wire–wound coil (position 2 in Figure 1) generates the magnetic component of the radiofrequency RF field; its magnetization vector $\mathbf{B}_{\mathrm{RF}}$ is perpendicular to both $\mathbf{B}_{\mathrm{MW}}$ and $\mathbf{B}_0$. The homogeneity of the magnetic field $\mathbf{B}_0$ can be estimated as 0.1 mT/cm. The inner diameter of quartz ampule is 3.5 mm and height of the resonator active zone is 2 cm. The volume of the test samples inside the active zone of the resonator was about 0.2 mL. In our work, the comercial resonator unit was not disassembled or altered.

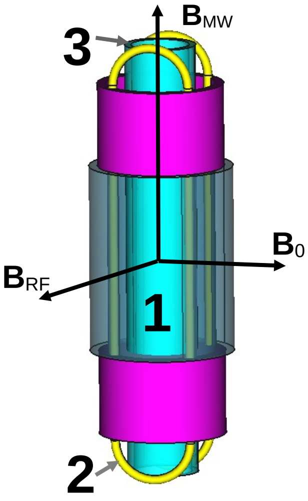

Figure 1. The scheme of the ENDOR resonator. Dielectric (sapphire) ring of the resonator (1) with the *RF* coil (2) and sample holder (3) inside. Relative orientations of the external ($\mathbf{B}_0$), and alternating magnetic fields ($\mathbf{B}_{\mathrm{RF}}$ and $\mathbf{B}_{\mathrm{MW}}$) are depicted

To observe the NMR signals, LC-circuit was formed by connection of a series of capacitors (SGM 250V, USSR) to the RF-coil of the resonator for tuning and matching (Figure 2). It gave an opportunity to tune the RF resonance frequency in the range 14.5–15.2 MHz for proton (^{1}H) NMR. The Q-factor of the LC-circuit is 25. The capabilities of the homebuilt nuclear magnetic/quadrupole resonance spectrometer “Kazan Nova II” [17] to excite the NMR transitions and detect the NMR signals were exploited. A broadband power amplifier (300 W, 1–250 MHz) attached to the EPR spectrometer for ENDOR experiments was used as a transmitter with the ($\pi/2$) RF pulse duration of 20 μs. In present paper free induction decay (FID) signal was acquired.

For the signal amplification, a broadband preamplifier based on low-noise transistors was assembled, with a gain of about 8 in 5–50 MHz frequency range. Its scheme is shown in Figure 3. The dead time of the RF tract was about 6 microseconds at 15 MHz. Two serial amplifiers are used with a common gain of about 50.

In the work, only the stationary (CW) mode of operation of the EPR spectrometer for pump-

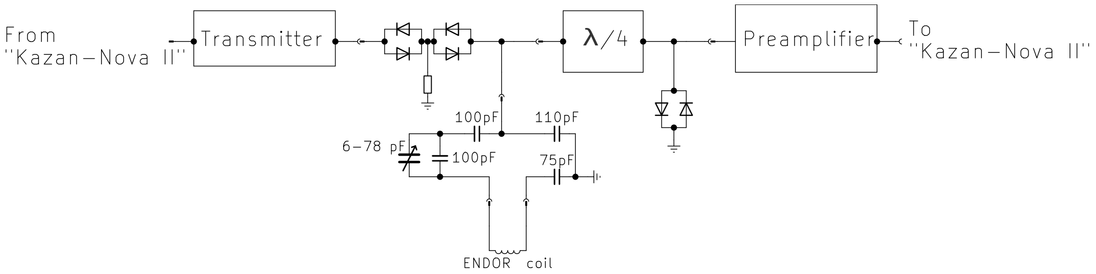

Figure 2. Diagram of the NMR path of the spectrometer for ^{1}H NMR/DNP

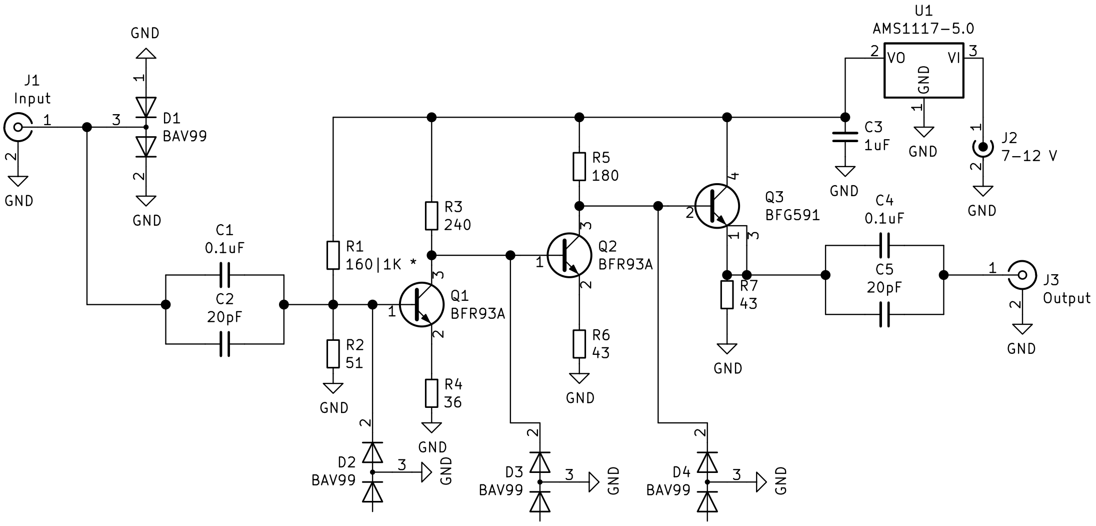

Figure 3. The RF preamplifier circuit

ing the EPR transitions was tested. There is a potential possibility of using the pulse mode of the EPR spectrometer (like in paper [7]) when triggering the synchronization pulse from the NMR spectrometer. As well, the temperature insert of the EPR spectrometer to cool down the samples can be potentially exploited.

3. Results of the test measurements

The DNP equipment was tested on the liquid samples of the stable nitroxyl radical 4–Hydroxy–2,2,6,6–tetramethylpiperidine 1–oxyl (TEMPOL, Merck, Germany, CAS Number 2226–96–2) dissolved in benzene at concentration of 2 mM (2 mmole/L) [18] and viscous oil samples from Ashalchinskoe oil deposits (Russia) which were investigated in details in paper [15] with EPR, NMR, and FC–DNP. For the both types of the investigated specimens the EPR quality factor for the resonator Q_{MW} was about 900. The EPR pumping and NMR measurements were performed at room temperature. Figure 4 demonstrates the EPR spectrum of 2 mM TEMPOL solution against the corresponding DNP spectrum by changing $\mathbf{B}_0$ along the EPR spectrum. The amplitude of the DNP spectrum (DNP enhancement, ε) was calculated as [18].

$$\varepsilon = \frac{I_{\mathrm{MW}}}{I_{\mathrm{NMR}}} - 1, \tag{1}$$

where I_{MW} and I_{NMR} are the integrated intensities of the Fourier–transformed (FT) FIDs with (I_{MW}) and without (I_{NMR}) EPR irradiation. The 3–line EPR spectrum is due to the hyperfine interaction with the ^{14}N isotope ($I = 1$). The lines are broadened due to the exchange interaction with Heisenberg exchange constant k_{exch} of $3.3\,\mathrm{mM}^{-1}\mathrm{s}^{-1}$ [19]. Maximal DNP enhancement was negative and of about $\varepsilon = -4.35(4)$ observed at central line of the EPR spectrum by apply-

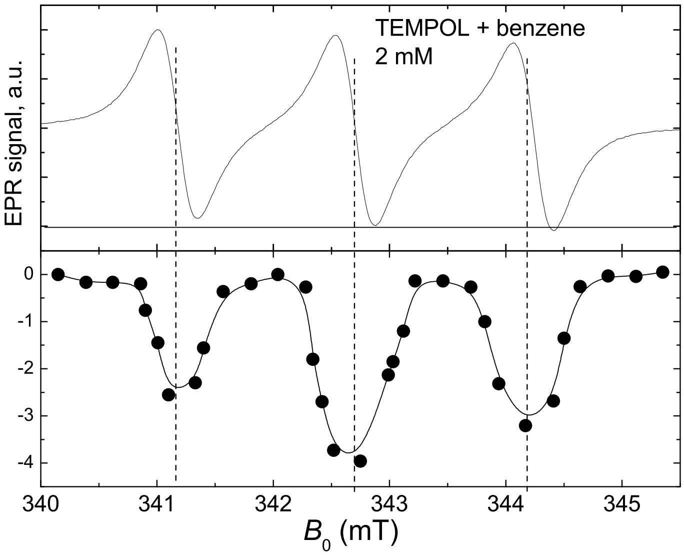

Figure 4. EPR spectrum for 2 mM TEMPOL in bezene (upper panel) and DNP spectrum of the same sample for P_{MW}=200 mW and Q_{MW}=900 (lower panel, the experimental points are connected with the spline line)

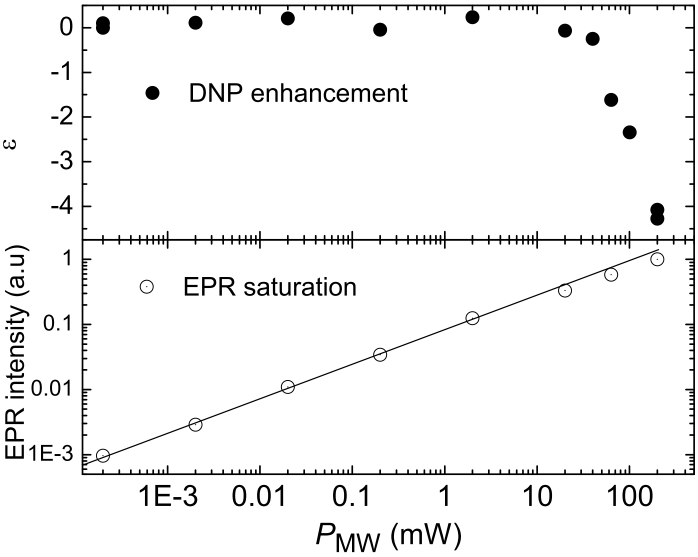

Figure 5. The DNP enhancement as measured at the central EPR line (upper panel) and amplitude of the central EPR line (lower panel) as a function of the microwave power for 2 mM TEMPOL in benzene at ($\mathbf{B}_0$=342.7 mT)

ing the maximal possible in the presented setup microwave power P_{MW}=200 mW. It is known that for the TEMPOL–benzene solution the DNP effect is due to the Overhauser mechanism (OE DNP) governed by dipole–dipole electron (nitroxyl radical)–nuclear (protons of benzene) interaction and fast tumbling time τ of 20–120 ps [18]. Such fast tumbling time as well as the inhomogeneously broadened EPR lines with the hyperfine splittings do not allow saturating the EPR transitions completely for the effective OE DNP as it is shown in Figure 5. Therefore, the experimental values of ε are much less than the theoretically predicted of -330 [18] or experimentally achieved of about -180 at P_{MW}=10 W [20].

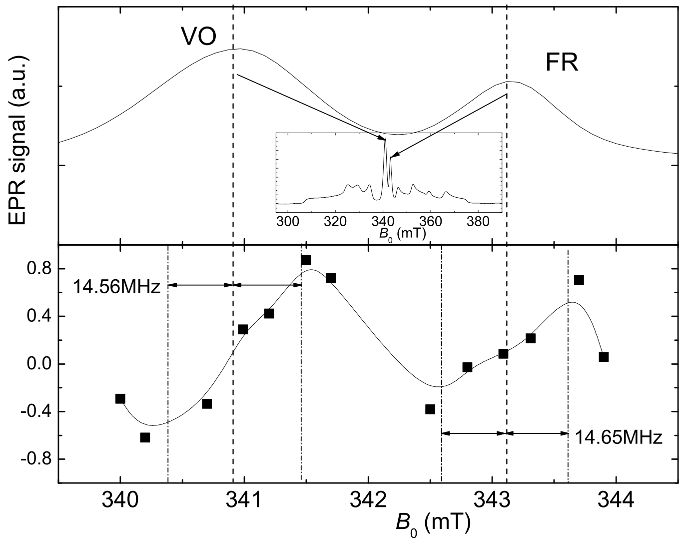

Figure 6. Upper panel: central part of the EPR spectrum of crude oil sample (full EPR spectrum acquired in the pulse mode is shown as an insert). Lower panel: DNP spectrum of the same sample for P_{MW}=200 mW and $Q_{\mathrm{MW}} = 900$ (the experimental points are connected with the spline line); ^{1}H Larmor frequencies (f_L) of 14.56 and 14.65 MHz for VO and FR lines, respectively, are depicted. Magnetic fields for the corresponding forbidden EPR transitions ($\pm f_L$) are shown by dash-dot lines.

EPR and DNP spectra of the crude oil sample with the viscosity of 2400 mPa·s are shown in Figure 6. It is known that the majority of paramagnetic centers in the oil sample exist in the form of (1) stable carbonaceous "free"radicals (FR) – unpaired electrons delocalized over many conjugated or aromatic chemical bonds – and (2) vanadyl cation (VO, VO^{2+}) functional groups coordinated mainly with porphyrins [11]. Their concentrations were measured to be of 10^{17} spin/g for FR and 10^{18} spin/g for VO [16]. Though the oil sample is considered to be a viscous liquid [15], the EPR pattern for VO (due to the anisotropic hyperfine interaction of axial symmetry with $I = 7/2$ for the ^{51}V nuclei) is typical for the powder (solids) emphasizing that the majority of paramagnetic centers are concentrated in the high–molecular components of oil like asphaltenes and resins [11]. OE DNP is mostly observed in highly diluted, low viscous liquids and solutions. Leblond with co–authors [21] showed that the solid effect (SE) can be observed in viscous liquids at temperatures above 100 K. The enhancement of the NMR signal by the SE DNP mechanism is maximum when the MW and EPR frequencies differ by the nuclear NMR Larmor frequency. These conditions lead to excitation of second order zero and double quantum electron–nuclear spin transitions which cause NMR signal enhancements with inverted or noninverted signal phase at the corresponding frequency. The presented in Figure 6 DNP spectrum (acquired for the most intensive EPR lines) proves that SE DNP is the main cross–polarization mechanism for the oil sample. Indeed, negative and positive DNP enhancements are observed along the DNP spectrum with the differences equal to the proton Larmor frequencies at the corresponding values of the $\mathbf{B}_0$.

Acknowledgments

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