Rev.Adv.Mater.Sci. 12 (2006) 84-89

TRANSIENT EPR NUTATIONS OF P1 CENTERS IN DIAMOND AT TWO-FREQUENCY EXCITATION

R. Fedaruk

Institute of Physics, University of Szczecin, 15 Wielkopolska, 70-451, Szczecin, Poland
Institute of Applied Physics Problems, Belarussian State University, Minsk, 220064 Belarus

Received: November 12, 2005

Abstract. Dressed state and two-photon nutations of P1 centers in synthetic diamonds are observed in EPR using longitudinal magnetic-field pulses and a continuous bichromatic radiation, consisting of a transverse microwave field and a longitudinal radio-frequency field. The dependences of the nutation decay times on the P1 concentration are measured. It is shown that the decay of two-photon as well as one-photon nutation is due to the spin-spin interaction between P1 centers. The decay time of the dressed nutation is about nine times longer than that of the one-photon nutation and is caused by the flip-flop transitions of P1 centers.

1. INTRODUCTION

There is steady interest in nitrogen and nitrogen-containing defects in diamond because of the influence they have upon material properties [1,2]. Due to their extremely long electron spin relaxation times [3,4], paramagnetic nitrogen-containing defects are good candidates for the investigation of coherent spin states, including coherence on a single electron spin [5] and on states dressed by electromagnetic field [6-8]. One kind of nitrogen-containing defects, namely the nitrogen-vacancy pair (NV center) has additional special qualities that are suited to quantum information applications [9]. Ordinary one-photon transient nutations in pulse electron paramagnetic resonance (EPR) directly reflect the dynamics of coherent electron spin states and are induced after the pulse establishment of resonant interaction between microwave radiation and the spin system [10,11].

More exotic EPR nutations can be excited on 'dressed' spin states (the eigenstates of a spin system coupled to the strong near-resonant microwave field) [6,7]. The energy levels of the dressed system form a ladder of doublets separated by the photon energy of the microwave (MW) field. The energy difference between states of each doublet is determined by the generalized Rabi frequency (the ordinary nutation frequency). The additional radio-frequency (RF) field of the frequency being close to the generalized Rabi frequency induces resonant transitions between the doublet levels. Such resonance was observed for the first time in continuous-

Corresponding author: R. Fedaruk, e-mail: fedaruk@wmf.univ.szczecin.pl

wave (cw) NMR experiment, which was termed 'rotary saturation' [12]. EPR nutations on dressed spin states of a two-level system excited by a resonant MW field were observed using a pulse of linearly polarized RF field aligned along the static magnetic field [6-8]. This phenomenon was detected indirectly, after switching off the exciting RF pulse, using changes in the spin-locked echo of bare spin system to monitor the dressed nutation [6], and recently directly during the excitation of dressed state transitions [7,8]. RF-field induced transparency of the matter to MW radiation was reported when a bichromatic field excited a two-level system and the frequency of the MW field was equal to the resonance frequency of the spin system [13]. In this case, the weak MW field induces resonant transitions between states dressed by the strong RF field.

Multiphoton coherent transitions, when several photons are simultaneously absorbed or emitted, can be also induced in two-level spin systems by bichromatic radiation produced by a transverse microwave field and a longitudinal RF field [14]. Two- and three-photon electron spin echoes were detected when the sum of the energies of a MW photon and one or two RF photons was equal to the resonant frequency of the two-level spin system [14]. Recently, two-photon transient nutation excited in the EPR by combined action of MW and RF fields was observed in a two-level spin system [15].

Multiphoton resonances in pulse EPR spectroscopy are very attractive from the point of view of spin dynamics and potential applications [13]. In the present paper, transient nutations excited by longitudinal magnetic-field pulses and a continuous bichromatic field, consisting of a transverse MW field and a longitudinal RF field, in EPR of P1 centers in synthetic diamonds are studied. Ordinary one-photon, dressed state and two-photon nutations are observed in diamond crystals with different concentration of P1 centers. The dependences of the nutation decay times on the concentration of P1 centers are measured, and mechanisms of the suppression of spin coherence are discussed.

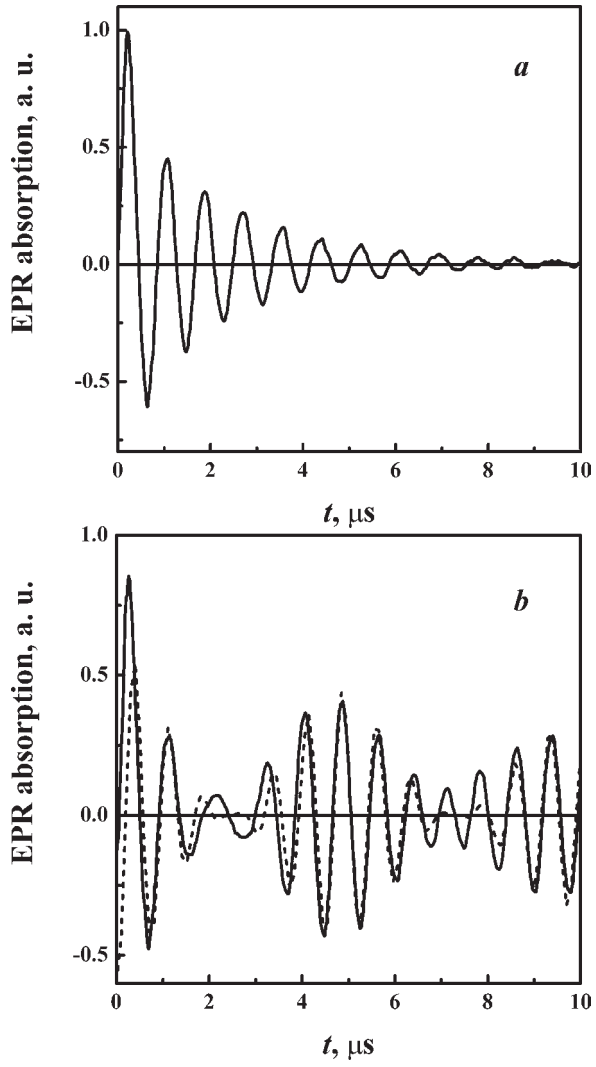
2. MATERIAL AND METHODS

The synthetic diamonds used in this study were grown by the temperature gradient method at a pressure of P = 5.4–5.5 GPa and temperature T = 1450–1550 °C using a split-sphere-type apparatus [16]. EPR measurements indicate that the crystals contain single substitutional nitrogen defects (P1 centers) as main paramagnetic impurities [1,2]. Three samples (0.2–0.5 ct) with different concentrations of P1 centers were selected for our experiments. The samples were cut from larger crystals and had practically a homogeneous distribution of P1 centers. The EPR spectrum of P1 center (electron spin S = 1/2, nuclear spin I = 1) consists of a central transition (m_I = 0) and two hyperfine transitions one of each side of the central transition (m_I = ± 1). The crystals were free of metal inclusions and other macroscopic defects within the volume. The samples were characterized using cw EPR and infrared absorption spectrometers. The measured concentrations of P1 centers were about 2.9, 23, and 53 atomic parts per million (ppm).

The ordinary nutations were formed by the abrupt switching on the resonant interaction of the spin system with the continuous transverse MW field, $2B_1\cos(\omega_{mw}t)$, by the pulse of a longitudinal magnetic field [11]. Initially, the spin system was exposed to an off-resonant static magnetic field B. No absorption of microwave radiation occurred and the spin system was in thermal equilibrium. Then, the magnetic field was jumpwise changed to the resonant value B_0 by the pulse of a magnetic field with the amplitude $\Delta B = B - B_0$ = 0.12 mT. The rise time of the magnetic field step was about 120 ns and the duration of the magnetic pulse was 10 μs. With a jump in the magnetic field due to the Zeeman effect, the resonant frequency of the spin system changed to $\omega_0=\gamma B_0$ and became equal to the frequency ω of the MW field. Under these conditions the magnetic-field pulse was attended by a resonant interaction of the MW field with the spin system, which, in turn, induced transient nutation. At resonant excitation ($\omega_{mw}=\omega_0$) the nutation frequency is given by $\omega_1=\gamma B_1$, where γ is the electron gyromagnetic ratio, B_1 is the amplitude of the circularly polarized MW field [10].

To induce the dressed state transitions, in addition to the MW excitation, a continuous linearly polarized RF field, $2B_2\cos(\omega_{rf}t)$, was applied parallel to the static magnetic field. When the resonant interaction of the MW field with the spin system induces the ordinary nutation, the RF field acts on dressed spins like a microwave field does on bare spins. If the RF field frequency ω_{rf} is close to the generalised Rabi frequency, the RF field excites the dressed transient nutation, which is observed as the modulation of the ordinary nutation at the frequency $\omega_2=\gamma B_2$ [7].

Two-photon nutations were detected at the same bichromatic field configuration when the detuning of the static magnetic field from the resonance value for one-photon resonance was equal to the RF field frequency ω_{rf} ($\delta = \omega_0 - \omega_{mw} = \omega_{rf}$) [15].



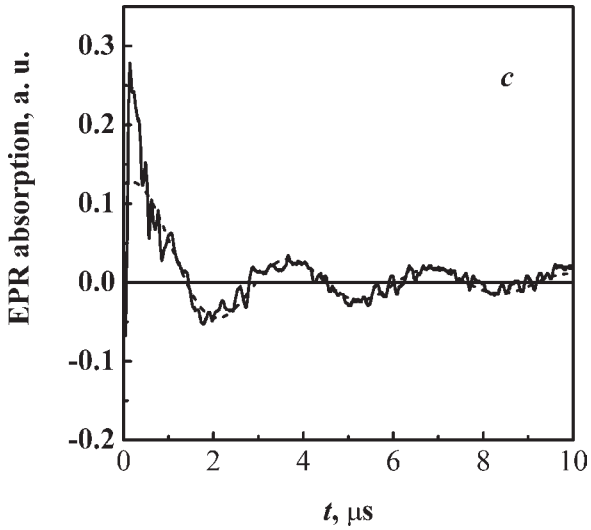


Fig. 1. Nutation EPR signals at $\omega_1 = 2\pi \times 1.34$ MHz for the sample with the P1 center concentration of 2.9 ppm. (*a*) Ordinary one-photon nutation exited by the resonant MW field. (*b*) Dressed state nutation observed at $\delta = \omega_0 - \omega_{mw} = 0$, $\omega_{rf}/2\pi = \omega_1/2\pi =$ 1.35 MHz and $\omega_2 = 2\pi \times 0.21$ MHz; the dashed line was obtained using the relation (2) with $T_{m\rho} =$ 16 μs. (*c*) Two-photon nutation obtained at $\delta = \omega_{rf} = 2\pi \times 3.0$ MHz and $\omega_2 = 2\pi \times 1.10$ MHz; the dashed curve shows the dependence given by formula (3) with $\omega_{1,1} = 2\pi \times 0.32$ MHz and $T_2 = 7$ μs.

Technically both the magnetic-field pulse and the RF field were applied to the same modulation coil. The measurement of the current made it possible to calibrate the amplitude B_2 of the RF field using the amplitude ΔB of the magnetic-field pulse. The amplitude ΔB was determined with an accuracy of about 5% using the beat frequency (equal to $\Delta B/\gamma$) of the free induction signal observed after the magnetic-field pulse.

The experiments were performed at room temperature using the X-band home-made EPR spectrometer [11,15]. Multichannel digital summation of signals was used to improve the signal-to-noise ratio. The measurements were carried out without the phase synchronization of the RF field with respect to the MW field and to front of the magnetic-field pulse.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Only one EPR transition of P1 centers spectrum was simultaneously excited at our experimental conditions. Transient EPR nutations measured for P1 centers (the $m_I = 0$ line) in diamonds with the P1 concentration of 2.9 ppm are shown in Fig. 1. The orientation of the crystal in the static magnetic field was determined using the well-documented spectrum of P1 centers [1,2]. Experimental data depicted in Fig. 1 are obtained for the static magnetic field along the <001> crystallographic axis. The dynamical features of observed signals were the same for other crystal orientations and for all hyperfine lines. The absorption component υ of transient EPR signal was detected at the repetition period of magnetic pulses of 5.0 ms.

The signal in Fig. 1a is one-photon nutation at the frequency $\omega_1/2\pi$ = 1.34 MHz, recorded at the resonance value of the magnetic field. The observed EPR signal amplitude υ is successfully approximated by a dependence typical of an inhomogeneous EPR line of width $\sigma >> \omega_1$ at $T_2 << T_1$ (excluding times $t < 1/\omega_1$) [11,17]

$$\upsilon \propto \omega_1 f(\omega) J_0(\omega_1 t) \exp\left(-\frac{t}{2T_2}\right). \quad (1)$$

Here, $f(\omega)$ is the value of the normalized lineshape function at the center of the inhomogeneous line, $J_0(\omega_1 t)$ is the zero-order Bessel function, and T_1 and T_2 are the spin–lattice and spin–spin relaxation times, respectively. The MW field inhomogeneity within the sample volume decreases the decay time of the nutation. This effect is the most essential at low P1 concentrations. Therefore, to find the value of T_2 using the relation (1), the decay times of nutations were measured at low MW field amplitudes. We found for this sample the value of T_2 = 7.0 ± 0.7μs.

The signal in Fig. 1b is dressed state nutation at the frequency $\omega_{rf}/2\pi = \omega_1/2\pi$ = 1.35 MHz and the RF field amplitude B_2 = 7 μT ($\omega_2 = 2\pi \times 0.21$ MHz), recorded at the resonance value of the magnetic field. We have checked experimentally that, in agreement with the theory, the dressed nutation takes place when ω_{rf} is close to the Rabi frequency ω_1 and the dressed nutation frequency is $\omega_2=\gamma B_2$, with an accuracy of about 10%.

In this case the observed signal can be described by the relationship [7]

$$\upsilon \propto \left[1+\cos(\omega_2 t)\right]\sin(\omega_1 t)\exp\left(-\frac{t}{T_{m\rho}}\right), \quad (2)$$

where $T_{m\rho}$ is the relaxation time characterizing the decay of nutation of the dressed spin states. The decay time is estimated by assuming an exponential decay. The dashed line in Fig.1, *b* was obtained using the relation (2) for $\omega_1 = 2\pi \times 1.34$ MHz, $\omega_2 = 2\pi \times 0.21$ MHz and $T_{m\rho}$ = 16 μs. As it is shown in Figs. 1a and 1b, the decay time of the observed nutations becomes longer if the dressed nutation is excited. Unfortunately, technical difficulties with the formation of longer magnetic pulses did not allow to observe the nutation traces until they have completely decayed. The decay time decreasing observed when the amplitude of the RF field increases, may be caused by the RF field inhomogeneity.

Two-photon nutation depicted in Fig. 1c is detected when the sum of the energies of microwave and radio-frequency photons are equal to the difference between the energies of spin states ($\omega_{mw} + \omega_{rf} = \omega_0$). In this case the detuning of the static magnetic field from the resonant value for one-photon resonance ($\delta = \omega_0 - \omega_{mw}$) is equal to the RF field frequency $\omega_{rf} = 2\pi \times 2.2$ MHz. The amplitude of the RF field $\omega_2=\gamma B_2 = 2\pi \times 1.08$ MHz was close to the amplitude of the MW field. Under the action of bichromatic radiation considered here, one MW σ^+ photon and one RF π photon are absorbed or emitted simultaneously [13,14].

The observed signal of two-photon nutation is approximated by a dependence of type (1), which can be written in the present case in the form

$$\upsilon \propto J_0(\omega_{1,1} t)\exp\left(-\frac{t}{2T_2}\right). \quad (3)$$

The effective field $\omega_{1,1}$ of the two-photon transition ($\sigma^+ + \pi_{rf}$) can be described by the dependence [14,15]

$$\omega_{1,1} \approx \frac{\omega_1 \omega_2}{\omega_{rf}}. \quad (4)$$

The dashed curve in Fig. 1c shows the dependence given by formula (3) for $\omega_{1,1} = 2\pi \times 0.32$ MHz and T_2 = 7 μs.

The experimental data confirm the two-photon origin of the observed nutation. It can be seen from Fig. 2 that the two-photon nutation frequency, measured for the samples containing 2.9 ppm and 53 ppm of P1 centers, is inversely proportional to the RF field frequency in accordance with the predictions of the theory. We check another dependencies confirming the two-photon character and found that the nutation frequency is proportional to the MW and RF field amplitudes in accordance with the relation (4).

Dependencies of decay rates for the ordinary, dressed and two-photon nutations on the concentration of P1 centers are shown in Fig. 3. Times T_2 obtained from the two-photon nutation decay using the formula (3), coincide with the analogous times for one-photon nutation. Measured T_2 values were the same for the central ($m_I = 0$) transition and the hyperfine ($m_I = \pm 1$) lines. We estimate the decay time of dressed nutation for the sample with the high (53 ppm) concentration of P1 centers as to be 7 ± 0.7 μs and it is about nine times longer than that of the ordinary nutation (0.8 ± 0.1 μs). The same

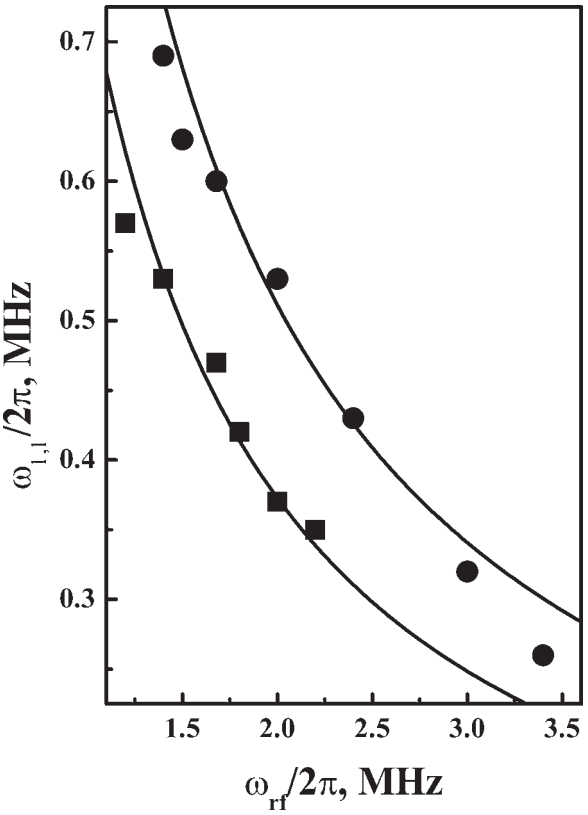


Fig. 2. Dependence of the two-photon nutation frequency on the frequency of RF field for two diamonds. The circles show experimental data obtained at $\omega_1 = 2\pi \times 1.35$ MHz and $\omega_2 = 2\pi \times 1.10$ MHz for the sample containing 2.9 ppm of P1 centers. The squares show experimental data obtained at $\omega_1 = 2\pi \times 1.0$ MHz and $\omega_2 = 2\pi \times 1.08$ MHz for the sample containing 53 ppm of P1 centers. The solid lines were obtained using the relation (4) in the form $\omega_{1,1} = k\omega_1\omega_2/\omega_{rf}$ for the corresponding values of ω_1, ω_2 and $k = 0.69$.

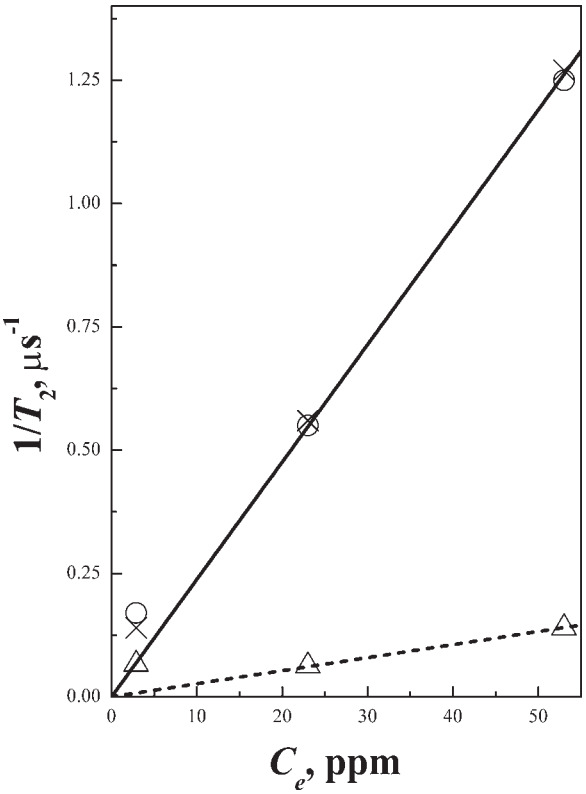


Fig. 3. Dependencies of decay rates for the one-photon (the circles), dressed (the triangles) and two-photon (the crosses) nutations on the concentration of P1 centers. The solid (dashed) line is a plot of equation (5) (Eq. (6)).

ratio of the decay times of dressed and ordinary nutations was obtained for the diamond containing 23 ppm of P1 centers. But at the low P1 concentration this ratio is essentially smaller because of the greater effect of inhomogeneities of the MW and RF fields at the longer relaxation times.

It is known that the rate of the spin-spin relaxation in diamonds is given by the relationship [2]

$$\frac{1}{T_2}\left[s^{-1}\right] = 1.4 \times 10^4 C_e. \qquad (5)$$

C_e is the paramagnetic impurity concentration in ppm. The full line in Fig. 3 represents the calculated dependence of T_2 on the P1 concentration using the equation (5) with the additional factor of 1.7. The similar factor exists in the approximation of experimental data in [2]. These results show that the decay of one- and two-photon nutation in diamonds arises from the electron-electron dipolar interactions and is characterized by the spin-spin relaxation time T_2. For the sample containing 2.9 ppm of P1 centers the decay times of all kind of nutations are shorten by inhomogeneities of MW and RF fields. In this case the spin-spin relaxation time T_2 is too large that its true value cannot be measured using the nutation decay in our experimental conditions. But for impurity concentrations $C_e \geq 10$ ppm the one- and two-photon nutation gives an effective method of determining the concentration of P1 centers.

The observed decay time of the dressed nutation for the sample containing 2.9 ppm of P1 centers is also essentially shorten by inhomogeneities. In other samples the measured decay rate of the dressed nutation can be approximated by the following relationship

$$\frac{1}{T_2}\left[s^{-1}\right] = 2.6 \times 10^3 C_e. \qquad (6)$$

The linear dependence (6) of the decay rate on the P1 concentration and the obtained value of proportionality factor allow to suggest that this relaxation is caused by flip-flop transitions of P1 centers (spin diffusion of quasiresonant spins [18]).

4. CONCLUSION.

One-, two-photon and dressed state nutations of P1 centers in synthetic diamonds have been observed in EPR using the pulses of a longitudinal magnetic field and, in addition to the continuous microwave excitation, a linearly polarized radio-frequency field oriented along the static magnetic field. It is shown that the decay times of one-photon and two-photon nutations are due to the spin-spin interactions of P1 centers and can be used as an effective method of determining this paramagnetic impurity concentration. The dressed state nutation allows to extend the timescale of the observation of coherence states in spin systems and observed relaxation processes which are slower than the electron spin-spin relaxation.

ACKNOWLEDGEMENTS

The author thanks I.Z. Rutkovskii for his help in the experiments and G.A. Gusakov for supplying the diamond samples.

REFERENCES

[1] V.A. Nadolinny, A.P. Yelisseyev, J.M. Baker, D.J. Twitchen, M.E. Newton, A. Hofstaetter and B.N. Feigelson // *Phys. Rev. B* **60** (1999) 5392.

[2] J.A. van Wyk, E.C. Reynhardt, G.L. High and I. Kiflawi //*J. Phys. D: Appl. Phys*. **30** (1997) 1790.

[3] I.M. Zaritskii, V.Ya. Brutus, V.S. Vikhnin, A.S. Vishnevskii, A.A.Konchits and V.M. Ustintsev // *Sov. Phys. Solid State* **18** (1976) 1883.

[4] E.C. Reynhardt, G.L. High and J.A. van Wyk // *J. Chem. Phys*. **109** (1998) 8471.

[5] F. Jelezko, T. Gaebel, I. Popa, A. Gruber and J. Wrachtrup // *Phys. Rev. Lett.* **92** (2004) 076401.

[6] G. Jeschke // *Chem. Phys. Lett*. **301** (1999) 524.

[7] G.G.Fedoruk // *Phys. Solid State* **46** (2004) 1631.

[8] R. Fedaruk and P. Żukowski // *Vacuum* **78** (2005) 473.

[9] F. Jelezko, T. Gaebel, I. Popa, M. Domhan, A. Gruber and J. Wrachtrup // *Phys Rev Lett*. **93** (2004) 130501.

[10] H.C. Torrey // *Phys. Rev*. **76** (1949) 1059.

[11] G.G. Fedoruk // *J. Appl. Spectrosc*. **69** (2002) 161.

[12] A.G. Redfield // *Phys. Rev*. **98** (1955) 1787.

[13] M. Kälin, I.Gromov and A. Schweiger // *Phys. Rev. A* **69** (2004) 033809.

[14] I. Gromov and A. Schweiger // *J. Magn. Res*. **146** (2000) 110.

[15] G. G. Fedoruk *// J. Experim. and Theor. Physics* **100** (2005) 1069.

[16] G.A. Gusakov, N.A. Lapchuk, A.V. Mudry and G.G. Fedoruk // *J. Appl. Spectrosc.* **70** (2003) 440.

[17] S. Stoll, G. Jeschke, M. Willer and A. Schweiger // *J. Magn. Reson*. **130** (1998) 86.

[18] K. M. Salikhov, A. G. Semenov and Yu. D. Tsvetkov, *Electron Spin Echo and Its Application* (Nauka, Novosibirsk, 1976), In Russian.