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Little-known Aspects of Overhauser DNP at Zero and Low Magnetic Fields Stimulated by Parallel Electron Pumping of Nitroxide Radicals Solutions

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Abstract. We present comprehensive investigation of Overhauser dynamic nuclear polarization in solutions of the nitroxide radical TANO at high-frequency saturation field of electron paramagnetic resonance transitions with its parallel orientation, related to the static magnetic field up to 0.1 mT. Experimental observation requires specific technique of cycle-polarized application, which is described in detail. It was shown, that these results cannot be interpreted in terms of standard theoretical methods, taking into account the electron magnetic relaxation as conditioned by hyperfine isotropic interaction of NO fragment. We suggest an original description of the effect, based on consideration of the anisotropic hyperfine interaction, modulated by rotational diffusion of the NO fragment. Thus developed theoretical approach enables to determine the combined contribution of isotropic and anisotropic interactions and investigate the rotational diffusion process, which can serve as fundamental basis for a new branch of studying regarding molecular diffusion of the spin labels.

INTRODUCTION

Regime of zero and low magnetic fields, characterized by commensurate intensity of external static magnetic field and intrinsic local fields, has well-known perspectives of exposing new methods for micromagnetic interplays studying [1-10]. This paper is devoted to experimental and theoretical investigation of Overhauser dynamic nuclear polarization (ODNP) in nitroxide radical solutions. We report the original interpretation of experimentally observed ODNP effect within parallel electron pumping (external magnetic field B_0 is parallel to high-frequency field B_{1S}) and its conjunction with relative contribution of electron relaxation, induced by rotational modulation of anisotropic and isotropic hyperfine interactions.

The paper consists of two parts with authentic novelty. At the first part we describe the suggested experimental technique, engineered to register ODNP signal within parallel and perpendicular electron pumping, induced by cycle-polarized high-frequency field. The second part represents the detailed theoretical analysis, which newly allowed one to explain the presence of ODNP signal within parallel electron pumping in the low fields. After these two parts we present our conclusions.

DETAILS OF EXPERIMENT

We made our experimental measurements using the self-made ODNP spectrometer [10, 11], specially constructed by Laboratory of Quantum Magnetometry in order to supply the enhanced range of fields configuration available.

Registration of solvent proton signals was carried out by employing the spin echo approach in static magnetic field SF, strength of which corresponds to the frequency of proton precession 50 KHz. In order to perform the polarization we turn off this field and apply high-frequency field HF, being varied near zero with the reliability

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criterion taken as the stability of counterbalanced external geomagnetic field. One can set the variation amplitude as 20 mT in case of parallel SF-HF orientation and as 2 mT in case of SF and HF, being perpendicular to each other.

The switching of the fields orientation was implemented adiabatically slow within 10-30 msec. Measurements in static field with maximum induction (20 mT) was accompanied by the calibration of free precession and spin echo signal intensity with simultaneous registration of longitudinal and transverse proton magnetic relaxation.

The main purpose of distinct experimental study, caused the specific requirements for hardware to meet, manifests itself as to test the technical and scientific potential of cycle-polarized electron pumping HF. It allows one to eliminate the overlapping of the resonance lines with opposing signs of ODNP amplification factors in geomagnetic and zero fields [11]. Interesting to mention that due to cycle-polarized HF these factors develop the value $\sim 10^5$, thus the effective polarization field approaches 100 mT up to zero static magnetic field, related to compensated unstable geomagnetic field.

Registered ODNP signal within parallel electron pumping was unexpectable collateral effect, assumed to essentially be the kind of experimental errors before. It was reasoned by absence of proper theoretical description, despite of the fact that corresponding zero field-based theory was already developed [12, 13].

The experimental ODNP spectra, obtained with parallel and perpendicular SF-HF orientation, are presented in Fig. 1 as the scan of electron pumping frequency. We also marked the calculated resonance frequencies of electron paramagnetic resonance (EPR) transitions (methods are described in the next section). One should additionally stress that the ODNP amplification factors can have opposing signs (with the meaning of positive and negative amplification of proton remanence), which results in mutual compensation in the low field, being close to geomagnetic field.

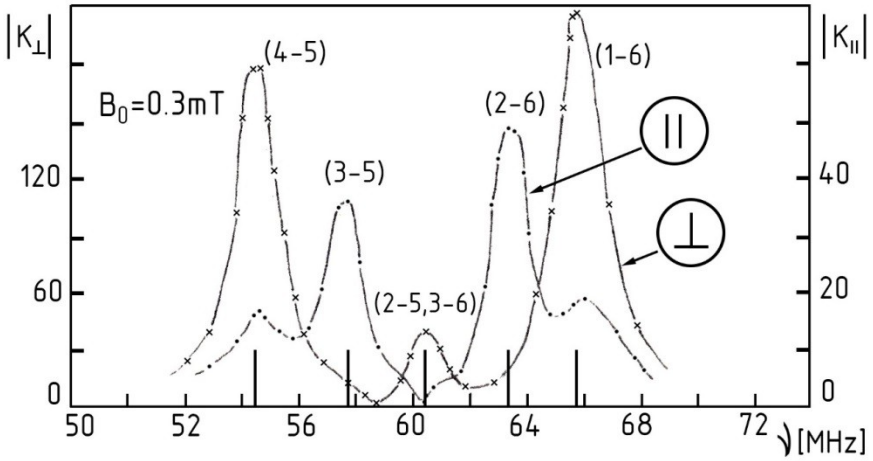

FIGURE 1. ODNP spectra, obtained with parallel ($K_{||}$) and perpendicular ($K_{\perp}$) SF-HF orientation

As the conclusion of this part of our paper we state that elaboration of the ODNP signal within parallel electron pumping, along with its observation on the experimental spectra, strictly requires the development of theoretical approaches, applicable not only in case of zero field, but also for the case of the low one, being comparable to the hyperfine splitting constants of nitroxide radicals. We experimentally registered that ODNP signal within parallel electron pumping declines as solution concentration grows. It highlights the intraradical nature of this effect. Now augmenting of ODNP signal within perpendicular pumping is well-known to be caused by spin-spin exchange interaction of Heisenberg type during radicals colliding [1]. Finally, we note that ODNP signal within parallel electron pumping amplifies with decreasing of the temperature also for more viscous solvents - for instance, heptane, decane and tetradecane-based ones.

THEORETICAL ANALYSIS

Nitroxide radicals with electron spin $S = 1/2$ and nuclear spin $I = 1$ at zero and low magnetic fields possess Zeeman and hyperfine interactions with commensurate energy. Consequently, one can expect distinctive splitting in electron paramagnetic resonance spectrum with forbidden quantum transitions emerging. Fig. 2 shows the dependency of energy levels on normalized value of external magnetic field x, given by:

$$x = \frac{\gamma_S B_0}{2\pi\nu_0} \ , \tag{1}$$

where γ_S - electron gyromagnetic ratio, B_0 - induction of the static magnetic field, ν_0 – hyperfine splitting constant of radical EPR spectrum, taken at zero magnetic field (in frequency units). The coefficients in superposition of electron and nuclear wave functions (Fig. 2) are presented as [9, 14]:

$$a^2 = \frac{1}{2} + \frac{x+1/3}{2r} \ , \ b^2 = \frac{1}{2} - \frac{x+1/3}{2r} \ , \ c^2 = \frac{1}{2} + \frac{x-1/3}{2\rho} \ , \ d^2 = \frac{1}{2} - \frac{x-1/3}{2\rho} \ , \tag{2}$$

$$r = \sqrt{1 + \frac{2}{3}x + x^2} \ , \ \rho = \sqrt{1 - \frac{2}{3}x + x^2} \ . \tag{3}$$

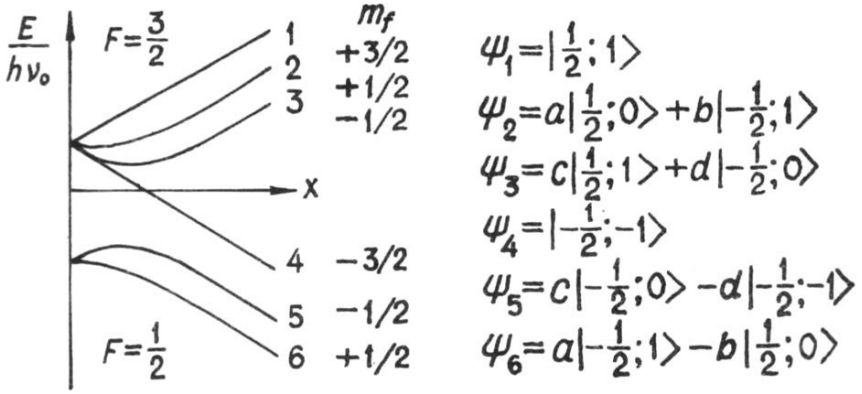

FIGURE 2. Schematic representation of nitroxide radicals energy spectrum in external magnetic field. F denotes the magnetic moment

ODNP amplification factor can be found as

$$A = \frac{\langle I_Z \rangle - I_0}{I_0} = f\xi \frac{\gamma_S}{\gamma_I} Z \ , \tag{4}$$

where ξ – coefficient of electron-nuclear interaction, f - nuclear leakage factor, γ_I - nuclear gyromagnetic ratio and

$$Z = \frac{S_0 - \langle S_Z \rangle}{S_0} . \tag{5}$$

In particular case of nitroxide radicals with stated wave functions and relations, given by eq. (2), we find

$$Z = \left[n_4 - n_1 + (n_6 - n_2)(a^2 - b^2) + (n_5 - n_3)(c^2 - d^2) \right] \frac{\omega_{ij}}{3\gamma_S B_0} Z_{ij} \ , \tag{6}$$

where n_i – occupation of energy levels, ω_{ij} – frequency of the quantum transition between levels, indexed by i and j, Z_{ij} is Z for particular transition $i \leftrightarrow j$. In its turn, occupations of the corresponding levels during pumping of the $i \leftrightarrow j$ transition can be calculated from the system of kinetic equations [12, 13]:

$$\sum_j (\hat{A})_{ij} n_j + \sum_j u_{ij}(n_i - n_j) = \frac{1}{kT}\sum_j \hbar\omega_{ij} u_{ij} \ , \tag{7}$$

where $\hat{A}$ is the relaxation matrix, which has the specific form for particular type of electron relaxation, u_{ij} – probability of the stimulated $i \leftrightarrow j$ transition.

For nitroxide radicals relaxation matrix is commonly defined by spin-rotation interaction [15]:

$$\hat{A}_{SR} = \frac{1}{T_{2S}}\left[\frac{3}{4}\delta_{ij} - \left| < j \,|\, \hat{\vec{S}} \,|\, i > \right|^2\right] , \tag{8}$$

where T_{2S} – transverse electron relaxation time. With this matrix the calculation of ODNP amplification factor, eq. (4), for σ-transitions *2*↔*6* and transitions *3*↔*5*, stimulated by parallel electron pumping, results in $A = 0$. However, the quite intense ODNP signal was detected experimentally, using the low field spectrometer [11]. The first report of parallel pumping-induced ODNP effect in radical solutions, obtained from raw oil, was reference, but authors did not provide proper theoretical description and analysis of measurement conditions was omitted.

In this work we state that increasing of the radical concentration leads to declining of A^{∞}/f ratio. It signifies the intraradical nature of driving mechanism, forming the ODNP signal. The relaxation, caused by anisotropic hyperfine interaction (AHFI) was considered as such mechanism. In reference [12] AHFI was taken into account for theoretical explanation of ODNP signals, which correspond to *1*↔*6*, *3*↔*5* and *3*↔*5* transitions, being major ones in strong magnetic fields. It was shown that given relaxation type poorly contributes to ODNP signal of low-viscosity liquid. Nevertheless, in case of σ-transitions, relaxation of which could not be properly described by means of only ODNP, one has to consider an additional term. Thus we modify our relaxation matrix, eq. (7), and write it as

$$\hat{A} = \alpha \cdot \hat{A}_{SR} + \beta \cdot \hat{A}_{hf} \ , \ \alpha + \beta = 1 \ , \tag{9}$$

where $\hat{A}_{hf}$ is the matrix of relaxation, induced by AHFI:

$$\begin{aligned}
&\hat{A}_{hf} = \frac{4}{15}(A_{\parallel} - A_{\perp})^2 \tau_R \sum_{\mu=-2}^{2} \left| < j \,|\, \hat{T}_{\mu} \,|\, i > \right|^2 \ , \\
&\hat{T}_0 = \sqrt{\frac{2}{3}}\left[\hat{S}_Z \hat{I}_Z - \frac{1}{4}(\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+)\right] , \\
&\hat{T}_1 = \hat{T}_{-1} = -\frac{1}{2}\left[\hat{S}_{\pm} \hat{I}_Z + \hat{S}_Z \hat{I}_{\pm}\right] , \\
&\hat{T}_{\pm 2} = \frac{1}{2}\hat{S}_{\pm}\hat{I}_{\pm} \ ,
\end{aligned} \tag{10}$$

where τ_R – correlation time of rotational diffusion. In case of $\beta = 0$ eq. (7) can be written in standard form with known solution, whereas it is crucially complicated to be analytically solved for $\beta \neq 0$. For all probable transitions in the low magnetic field the problem was treated numerically by varying of the normalized magnetic field x, eq. (1), and β. In Fig. 2 we demonstrate the resulting extreme value of ODNP amplification factor $A^{\infty}/f\xi$, approximated to infinite value of B_{1S}, for *2*↔*6* transition. The choice of given transition relates to experimental measurement of β in a most effective way. One can see in Fig. 3 also experimentally obtained points, corresponding to 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl solution. The figure can be employed as nomogram for β determination.

Also interesting to mention experimentally observed influence of spin-spin exchange interactions on ODNP signal by means of saturating of π- and σ-transitions as concentration of the nitroxide radicals solution grows. Particularly A^{∞}/f increases for π-transitions and declines for σ-transitions, wherein one can register the dependency of the signal on particular transition and the value of external magnetic field B_0. The estimation of A^{∞}, accomplished

for the case of zero field and spin-spin interaction matrix [12, 13], taken into account, is in a good agreement with A^{∞}, calculated using suggested approach. From this point of view, one can find the low field regime perspective for defining (by using ODNP) of electron relaxation times ratio, where relaxation could be induced by different mechanisms. It is proved by distinctive features, possessed by relaxation matrices, written for all basic types of interactions (spin-rotation, AHFI, spin-spin exchange, dipole-dipole electron interaction), if considered in B_0 dynamics or for specific type of stimulated transition.

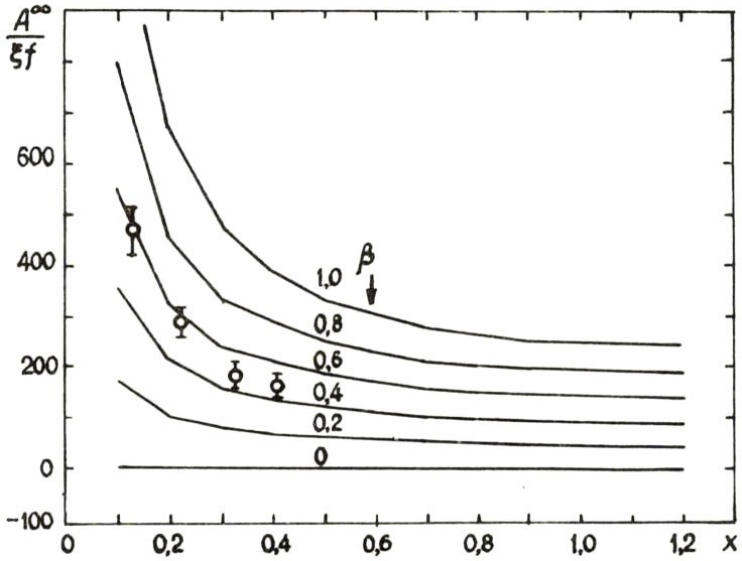

FIGURE 3. Extreme value of ODNP amplification factor, approximated to infinite value of B_{1S}, as the function of normalized magnetic field x, eq. (1), and β, eq. (9).

CONCLUSIONS

We experimentally discovered the ODNP signal within parallel high-frequency electron pumping in liquid solutions of nitroxide radicals. This effect was theoretically justified by taking into account anisotropic hyperfine interaction in the radicals during rotational diffusion process. Being highly sensitive to solvent viscosity, it appears perspective in applied physical, chemical and biological investigations of liquids on the molecular level.

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