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130 GHz ESEEM induced by electron–electron interaction in biradical

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Abstract

A three-pulse stimulated ESE at 130 GHz (D-band) of nitroxide biradical in a molecular glass shows envelope modulation (ESEEM) when the time separation between the first and the second pulses is varied. This ESEEM originates from relaxation-induced flips of the spin partner during the mixing period between the second and third pulses. These flips alternates the local dipolar field in which the resonant spins precess before second and after third pulses. The ESEEM is different for different spectral positions, due to orientation selectivity. For toluene glassy solution at 35 K Fourier transform shows pronounced peak reflecting singularity of the Pake resonance pattern. Increasing temperature up to 80 K results in appearance of a strong additional peak ascribed to alteration of the resonance field induced by methyl group reorientation.

Keywords: High-field EPR; ESEEM; Biradical; Radical pair

1. Introduction

Study of magnetic electron–electron dipolar interactions in radical pairs and biradicals is of great interest because it provides structural information at the physiologically important nanometer range [1]. Several Electron Spin Echo (ESE) techniques were introduced for this purpose: pulsed double electron–electron resonance (DEER or PELDOR) [2–10], 2 + 1 method [11–13], multiple-quantum EPR [14–16], solid-echo and Jeneer–Broekaert sequences [17], routine primary ESE and three-pulse Relaxation-Induced Dipolar Modulation Enhancement (RIDME) technique [18]. In most approaches ESE envelope modulation (ESEEM) is observed, with the dipolar frequency

$$\omega_{\mathrm{d}} = J + 1/2\gamma^2\hbar/r^3(3\cos^2\theta - 1), \qquad (1)$$

where J is the exchange integral, r is the distance between two spins (in the point dipole approximation), θ is the angle between the interspin vector and the direction of the external magnetic field $\mathbf{B}_0$.

So far, electron–electron dipolar ESEEM was observed at X-band (9.5 GHz) only. Recently, double-quantum ESE experiments on biradicals at 17.3 GHz were reported [15] and PELDOR at S-band [10]. Meanwhile, high-field study of electron–electron ESEEM is promising because it provides better orientational selectivity [19]. In addition, nuclear ESEEM induced by anisotropic hyperfine interaction (*hfi*) is normally negligible at high field, because of large nuclear Zeeman splitting for nuclei commonly presented in the sample (protons or deuterons), as compared with *hfi*. Note that for nitrogen nuclei in nitroxide molecules Zeeman splitting is comparable with *hfi* constant for some orientations, so nuclear ESEEM may be observed [20,21].

The major problem of high-field experiments is that very small fraction of spins is excited by microwave pulses, because of large spectral width. So, techniques working at X-band usually cannot be applied. The only exception is the use of recently introduced RIDME technique [18]. In this experiment a stimulated echo pulse sequence π/2–τ–π/2–*T*–π/2–τ–echo is applied.

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The non-resonant spins in biradical are inverted during the mixing period T due to longitudinal relaxation. These flips alternates the local dipolar field in which the resonant spins precess before second and after third pulses. This results in ESEEM, as τ is varied [18]

$$M_y(2\tau + T) = 1/2\{[1 + \exp(-T/T_1)] + [1 - \exp(-T/T_1)]\cos(2\omega_d\tau)\} \times \exp(-2\tau/T_2 - T/T_1), \tag{2}$$

where T_1 and T_2 are the longitudinal and transverse spin relaxation times, respectively. It is assumed here that resonant and non-resonant spins have the same T_1 time constant (in [18] relaxation of resonant spins was neglected). Eq. (2) predicts that up to one half of non-resonant spins may contribute to ESEEM, independently of the spectral width.

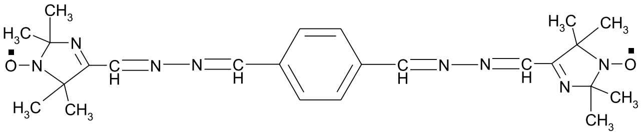
The purpose of this work is to observe electron–electron ESEEM in the RIDME experiment at 130 GHz.

2. Experimental

ESE measurements were carried out on a 130 GHz (D-band) pulsed EPR spectrometer, developed at Donetsk Physico-Technical Institute of Ukrainian National Academy of Sciences, Ukraine (the microwave bridge and the superconducting magnet) and at Huygens Laboratory of Leiden University, The Netherlands (electronics and software). Maximal microwave power was about 40 mW, with Q-value of the loaded cavity about 1000. We estimated the microwave amplitude $B_1 \approx 1$ G from the duration of the pulses that produce the maximal amplitude of the primary echo (100 and 200 ns). The echo signal was integrated with a boxcar integrator. The repetition rate was smaller than T_1^{-1} in all measurements.

Temperature in the range 35–80 K was controlled with an accuracy ~1 K, using a home-made helium flow thermostat.

The biradical



was a gift from Grigor'ev. Its synthesis is described in [22]. It was dissolved in deuterated toluene at concentration of about 3 mM. Quartz capillaries with inner diameter of 0.5 mm, outer diameter of 0.6 mm, and sample volume of about 5 μl were used. The samples were quickly cooled by helium flow in the resonator of the spectrometer to produce a glassy state.

3. Results and discussion

A two-pulse field-scanned echo-detected EPR spectrum of the biradical looks typical for nitroxides at high field, see inset in Fig. 1. Three canonical g-tensor orientations are well resolved. The X-orientation corresponds to the low-field edge of the spectrum, the Y-orientation forms the central maximum, and the Z-orientation with the largest nitrogen *hfi* splitting corresponds to the high-field edge.

Fig. 1 presents τ-dependence of the stimulated echo amplitude, for different time intervals T, obtained at 35 K for the Z-orientation ($B_0 = 4637$ mT, the arrow at the inset in Fig. 1). One can see that signal is strongly modulated when τ is varied.

Note that these data were obtained with the duration of pulses reduced to 50 ns (the turning angle of $\pi/4$). This resulted in the loss of signal intensity. However, increasing of the duration to 100 ns (the turning angle of $\pi/2$ that is optimal for stimulated echo formation) resulted in decrease of the modulation depth, probably because of closeness of the duration to the modulation period.

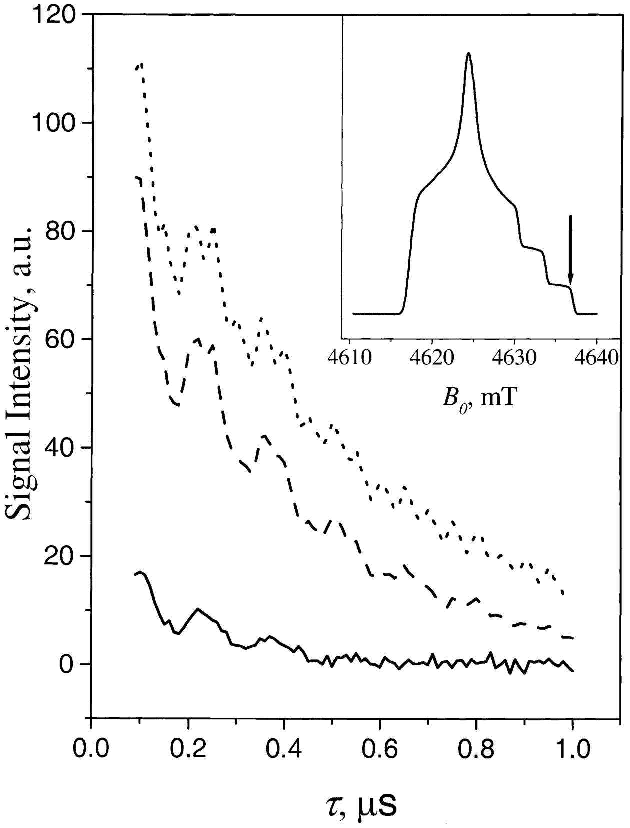


Fig. 1. ESEEM observed as the time interval τ of the stimulated echo pulse sequence is varied. The time delay T is fixed and equal to 5, 450, and 4500 μs, from top to bottom. Temperature is 35 K. Inset: two-pulse echo-detected EPR lineshape. The arrow indicates the magnetic field where these traces were recorded.

The time domain data were fitted with a single exponential that was then subtracted. Then the data was zero filled and Fourier transformed. The obtained absolute value frequency spectrum is given in Fig. 2. To exclude the overall signal decay due to spin–lattice relaxation (see Eq. (2)), the results for different T were divided by the amplitude of the exponential.

One can see in Fig. 2 the peak appearing at 7 MHz and growing as T increases. (The peak at 20 MHz is of instrumental origin.) The inset in Fig. 2 shows T-dependence of its intensity. It may be approximated with a single exponential with the time constant of 1 ms. We compared this value with the results of an inversion-recovery experiment (a π–t–$\pi/2$–τ–π–τ–echo pulse sequence, with t scanned). The obtained time constants varied from 0.6 to 1 ms, depending on spectral positions (data not shown).

As can be seen from Fig. 2, the amplitude of the 7 MHz peak does not tend to zero at $T = 0$. This means that ESEEM exists also in a two-pulse experiment [18], which was indeed observed (data not shown).

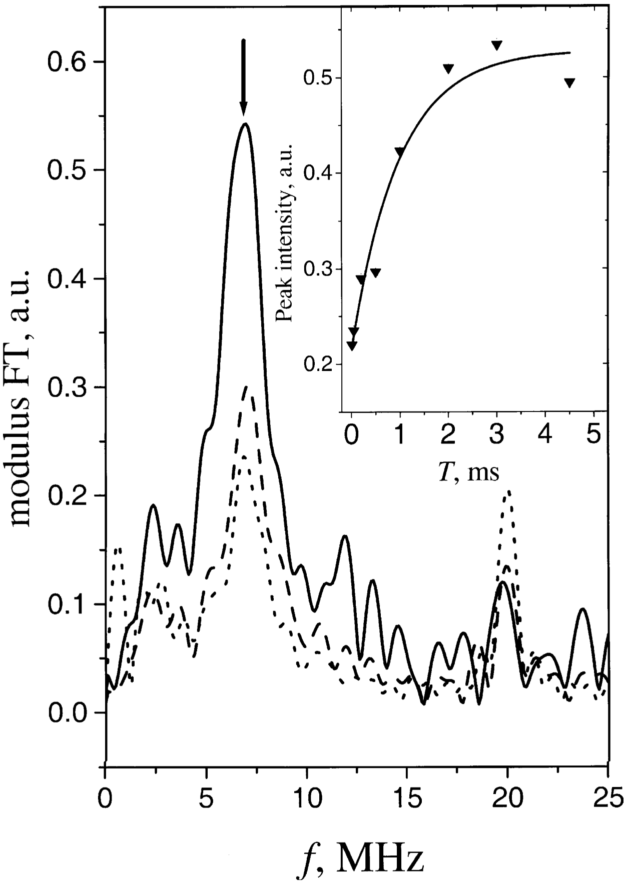


Fig. 2. The normalized absolute value ESEEM frequency spectra, obtained from the time domain data of Fig. 1. The designation of the curves is the same as in Fig. 1. The arrow indicates the peak at 7 MHz that is ascribed to the RIDME effect. The peak at 20 MHz is of instrumental origin. Inset: T-dependence of the peak amplitude fitted by an exponential dependence.

The ESEEM depth was found to decrease with the magnetic field shift to lower values. No ESEEM was detected for the X- and Y-canonical orientations, both in two- and three-pulse experiments at 35 K. Note that at 95 GHz band for these orientations a shallow ESEEM was detected [20,21] that induced by *hfi* with nitrogen nucleus of nitroxide. This could be readily explained, as the Zeeman splitting for ^{14}N at this band is comparable with *hfi* constant for these orientations, so the cancellation condition for mixing nuclear states is fulfilled. In our case the Zeeman splitting is 1.4 larger (but still much less than the *hfi* constant for parallel Z-orientation).

We ascribe the 7 MHz peak to the RIDME effect [18]. First, the frequency position of this peak is the same as that previously observed in X-band PELDOR and ESEEM studies [18] of this biradical. It reflects the Pake spectrum singularity occurring at $\theta = \pi/2$. Secondly, the characteristic time of its normalized amplitude growth with T increase is close to T_1 value estimated from the inversion-recovery experiments.

The two-pulse ESEEM comes from microwave excitation of both spins. At 130 GHz the EPR linewidth of nitroxide ($\sim$200 G) is much larger than the excitation bandwidth ($B_1 \sim 1$ G). As the linewidth is determined mostly by the g-factor anisotropy, both spins may be excited only if both nitroxide fragments have the same orientation of their molecular Z-axis (which is perpendicular to their ring planes). This takes place if the biradical is flat. It would explain also why RIDME is visible only for the Z-canonical orientation. In the flat conformation this orientation corresponds to $\theta = \pi/2$ implying the high statistical weight of the Pake spectrum singularity. For other orientations this statistical weight decreases, so the ESEEM amplitude drops (below the detection limit in our case).

The ESEEM pattern was found to change remarkably with temperature increase up to 80 K, see Fig. 3. A strong new peak appears now at 5.5 MHz, see inset in Fig. 3. Note that two-pulse echo-detected EPR spectrum remains nearly unchanged with temperature (data not given). The appearance of the 5.5 MHz ESEEM may be ascribed to the recently identified mechanism that differs from RIDME. It was found [23] that for imidazoline nitroxide monoradicals slow reorientation of methyl groups induces exchange between the lines of unresolved proton hyperfine structure, which leads to modulation of the stimulated echo, similarly to RIDME. For nitroxide 2,2,4,5,5-pentamethyl-3-imidazoline-1-oxyl having structure which is close to that of the paramagnetic fragments of the biradical studied in the present work, 5.5 MHz ESEEM was detected [23]. The Arrhenius parameters of the rate of methyl group reorientation were estimated as 2.1 kcal/mol for the activation energy, and as $1.5 \times 10^{10}\,\mathrm{s}^{-1}$ for the preexponential factor. Similar values of the Arrhenius parameters were determined from the temperature dependence of the primary ESE

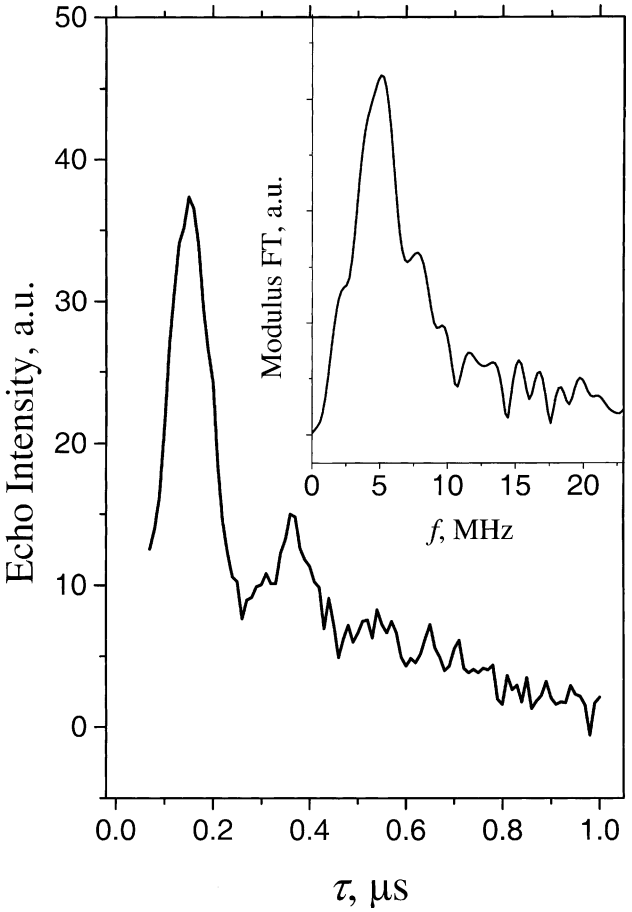


Fig. 3. The same as in Fig. 1, for 80 K and $T = 30\,\mu s$. Inset: the absolute value ESEEM frequency spectrum.

decay rate for a number of imidazoline radicals [24]. Extrapolation to 35 K gives the characteristic time of methyl group reorientation in order of minutes. Thus, this process becomes important above 70 K and may be surely neglected at low temperatures.

4. Conclusions

In the present work electron–electron dipolar ESEEM in high-field EPR was detected. It appears in a stimulated echo experiment, when the time separation between the first and the second pulses is varied, due to the previously described RIDME effect [18]. As compared with conventional X-band EPR, the absence of nuclear ESEEM at high field simplifies interpretation of frequency spectra. High orientational selectivity may provide additional information about biradical structure [19]. In our case we obtained indications that biradical structure is flat. In this respect, it is interesting in future to make the same experiments for biradical with non-flat structure.

ESEEM may change with temperature because of contribution of slow reorientation of methyl groups screening the nitroxide fragments of the biradical.

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