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Electron spin decoherence as a measure of nuclear spin bath frustration

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ABSTRACT

Two realisations of solid-state environment, which differ in molecular packing, glassy and crystalline solid ethanol, are used as a model systems to study disorder in terms of nuclear spin bath frustration. It is probed by the hyperfine interaction of the electron spin from the incorporated paramagnetic nitroxyl radical TEMPO. Nuclear spectral diffusion from ethanol protons is presented as the dominant mechanism of electron spin decoherence and proposed as a descriptor of the extent of disorder present in the system. It is shown that the dynamical decoupling control of the electron spin is affected by the extent of disorder in terms of the heterospin dephasing and can be numerically evaluated for the specific model system. The effect of odd/even number of decoupling pulses was not observed suggesting that for the description of proton spin bath frustration in solid ethanol higher terms than fourth-order proton spin correlations might be considered in modelling spectral diffusion mechanism.

1. Introduction

Glassy state of matter attracts research interest in various scientific disciplines ranging from solid-state physics, polymer science to biological systems [1,2]. Essentially, this type of amorphous materials exhibits geometrical frustration due to the fact that rapid cooling of the liquid state cannot optimally accommodate competing interactions with the consequence of geometrical frustration, a source of degeneracy and disorder. This is implicated in many new physical phenomena discovered at low temperatures in the field of condensed matter physics and has been the subject of both theoretical and experimental studies [3,4]. The lack of long-range translational and rotational symmetry makes glassy materials difficult to study by conventional diffraction techniques. In this respect diamagnetic solids doped with paramagnetic centres open an experimental window to study many-body correlations by electron paramagnetic resonance (EPR) spectroscopy. These can be evaluated using the dynamical decoupling techniques in which the unwanted interactions between the paramagnetic centre and spin-bath environment are suppressed [5]. In particular, the study of central spin decoherence due to nuclear spin fluctuations in its solid environment has been extensively investigated both theoretically and experimentally in the emerging field of spintronics and spin based quantum information processing [6,7,8].

Recently, the first experimental demonstration of many-body correlations in nano-scale nuclear spin baths was presented by observing central spin decoherence in an EPR experiment [9]. In the light of this approach we address electron – nuclear hyperfine interaction as a function of frustration. In particular, specific many-body correlations reflected in the specific nuclear spin distributions of the host matrix doped with the paramagnetic centre could be traced from the respective electron-nuclear spin coupling via dipolar interaction. Assuming nuclear spectral diffusion as a dominant electron spin decoherence mechanism, the extent of disorder/frustration in the vicinity of the paramagnetic centre is encoded in the electron spin phase-memory time relaxation data. Therefore, we continue our previous studies of glassy versus crystalline materials with the aim to find the appropriate experimental approach/parameter for description of disorder [10]. Here we present how decoherence of the central spin exposed to multiple-pulse dynamical decoupling control may provide a probe of the extent of frustration in the system. We take solid ethanol doped with paramagnetic nitroxyl radical TEMPO as a model system in which the nuclear spin bath disorder/frustration is tuned within an EPR experiment in the very same sample by thermal annealing protocol [11]. This assures the same number of paramagnetic centres present in both crystalline and glassy samples, which differ only in their respective distributions due to the respective frustration of the host matrix. The entanglement of electron spins with nuclear spin bath exhibiting distinct intra-bath dynamics is verified in the Carr–Purcell–Meiboom–Gill (CPMG) experiments [12,13]. Due to the fact that nuclear spectral diffusion was recognized as a dominant decoherence mechanism of the observed electron spins [14], here we show that difference in the phase-memory relaxation time, T_m, detected as a function of number of decoupling pulses, can be directly related to the extent of frustration characterizing glassy and crystalline solid ethanol. Therefore, we

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propose that the idea, developed to achieve optimal dynamical decoupling control in (para)magnetic systems, is applicable to distinguish between frustrated/disordered systems exhibiting specific many-body correlations.

2. Experimental procedure

2.1. Chemicals

Ethanol, CH_3CH_2OH, was from Kemika, Zagreb, Croatia, deuterated ethanol CD_3CD_2OD from Cambridge Isotope Laboratories, Inc., USA, paramagnetic nitroxyl radical TEMPO (2,2,6,6-tetramethyl-1-piperidine-1-oxyl) from Aldrich and deuterated TEMPO, TEMPO-D, from CDN Isotopes, Canada. The liquid was doped with the nitroxyl paramagnetic spin probe at a concentration of 0.2 or 0.5 mM, unless stated otherwise.

2.2. Experimental setup

Liquid ethanol with the incorporated nitroxyl radical TEMPO was prepared in the glassy and crystalline state following the reported procedures based on the thermal annealing of the sample [11,15]. Pulsed EPR experiments were performed using *X*-band (9.6 GHz) Bruker ELEXSYS 580 spectrometer equipped with an Oxford Instruments temperature unit (± 0.1 K). All decay times were measured at the central field electron spin resonance position and the pulse sequence repetition time was adjusted to accommodate complete spin–lattice relaxation. The absolute spectra of electron spin echo envelope modulation (ESEEM), observed in the time domain were transformed using the spectrometer built-in Fourier transform function to the frequency domain in order to analyse nuclear spin contributions. Two-pulse, 2P_ESEEM ($\pi/2 - \tau_1 - \pi - \tau_1 - echo$), and three-pulse, 3P_ESEEM ($\pi/2 - \tau_2 - \pi/2 - T - \pi/2 - \tau_2 - echo$) detection sequences were measured at 40 K with π pulse duration of 24 ns and 32 ns, respectively. The minimum distances between the pulses were, $\tau_1 = 200$ ns and $T = 300$ ns with $\tau_2 = 100$ ns.

Multiple-pulse dynamical decoupling control was achieved using CPMG sequence with the extension to the constant-time scheme [9,12,13]. In specific, the total time duration of the pulse sequence i.e. the total evolution time, *T*, was kept constant. This was achieved in such a way that the time between the excitation (the first π/2 pulse which generates the coherence) and acquisition of the signal (the maximum of the refocused echo following various number of π pulses applied to preserve the coherence) was fixed as shown in Fig. 1. This required that the time positioning of π pulses be adjusted within the evolution time depending on the number *n* of π pulses applied while $n = 1$ corresponds to the standard Hahn spin echo experiment [9]. In the experiment, *T* was fixed to 2400 ns and up to six π pulses of 88 ns duration were applied. Therefore, the spacing between the π pulses varied within the fixed time *T* according to: 1200 ns ($n = 2$), 800 ns ($n = 3$), 600 ns ($n = 4$), 480 ns ($n = 5$) and 400 ns ($n = 6$). This approach assured that the start of the echo sampling at the maximal signal intensity was always at the same time point irrespectively of the number of π pulses applied in the sequence (Fig. 1) in order to derive the phase-memory relaxation time. The phase cycling applied followed the standard CPMG scheme [12,13].

In the two-pulse experiments performed at 80 K the phase-memory relaxation time, T_m, was extracted assuming a mono-exponential decay. In 2P_ESSEM and *n*-pulse CPMG experiments measured at lower temperatures the non-exponential decay of the electron spin-echo amplitude, *V*(*t*), was assumed according to [11]:

$$V(t) \propto \exp\left[-\left(\frac{t}{T_m}\right)^x\right] \tag{1}$$

with *x* denoting stretched exponent.

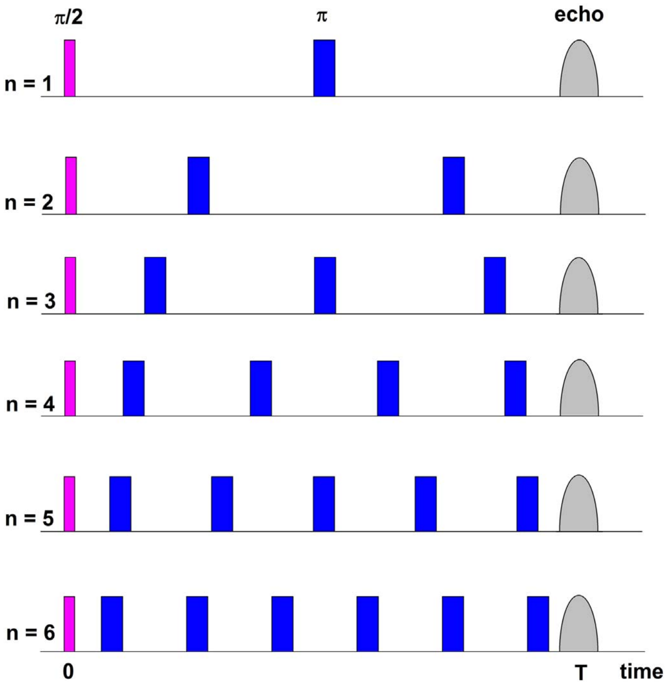

Fig. 1. Multiple-pulse dynamical decoupling control protocol based on Carr–Purcell–Meiboom–Gill pulse sequence with the extension to the constant-time scheme [9,12,13]. The total evolution time, *T*, was fixed to 2400 ns, duration of the π pulse was 88 ns and their number, $n = 1, \ldots, 6$ is indicated.

3. Results and discussion

3.1. The role of hyperfine interaction

The sensitivity of electron spin decoherence towards nuclear spin bath disorder/frustration depends essentially on the coupling of a paramagnetic probe with the spins of the host matrix, in the case of ethanol molecules these are protons. In order to show that the EPR spectra of TEMPO are informative about the nuclear spin bath environment, we have compared the respective phase-memory relaxation times in solid ethanol as a function of isotope replacement of protons with deuterons in the host for several concentrations of paramagnetic centres (Fig. 2).

It can be noted that the variations of phase-memory relaxation times are less than 10% between the chosen TEMPO concentrations.

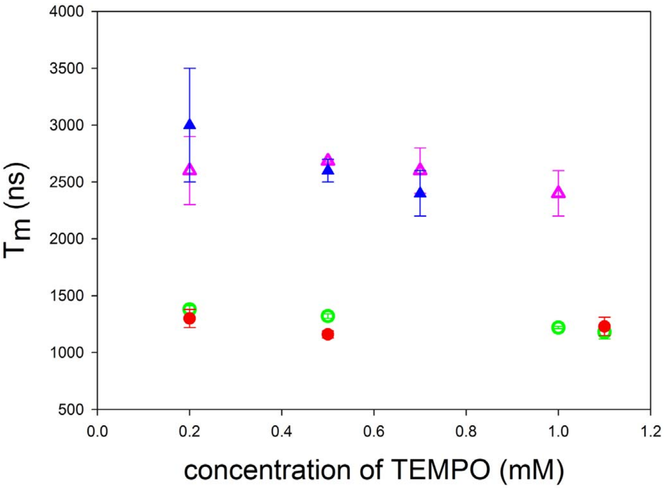

Fig. 2. Phase-memory relaxation time, T_m, as a function of the concentration of TEMPO incorporated in protonated (circles) and deuterated (triangles) ethanol. Full/empty symbols refer to crystalline/glassy ethanol. The measurements were performed at 80 K.