ELECTRON SPIN DECOHERENCE AS A MEASURE OF NUCLEAR SPIN BATH FRUSTRATION

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1. INTRODUCTION

Glassy state of matter attracts research interest in various scientific disciplines. This type of amorphous materials exhibits frustration due to the fact that rapid cooling of the liquid cannot optimally accommodate competing interactions with the consequence of geometrical frustration, a source of degeneracy and disorder. This is implicated in many physical phenomena in the field of condensed matter physics. The lack of long-range translational and rotational symmetry makes glassy materials difficult to study by diffraction techniques. Diamagnetic solids doped with paramagnetic centres open an experimental window to study many-body correlations by electron paramagnetic resonance spectroscopy. These can be evaluated using the dynamical decoupling techniques in which interactions between the paramagnetic centre and spin-base environment are supressed.

Central spin decoherence due to nuclear spin fluctuations in its solid environment has been extensively investigated. The first experimental demonstration of many-body correlations in nanoscale nuclear spin baths was presented by observing central spin decoherence in an EPR experiment. 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 electronnuclear spin coupling via dipolar interaction. Assuming nuclear spectral diffusion as a dominant electron spin decoherence mechanism, the extent of disorder 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 [1]. 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 is tuned within an EPR experiment in the very same sample by thermal annealing protocol. [2] This assures the same number of paramagnetic centres present in both crystalline and glassy samples, which differ only in their distributions due to the 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 [3].

Due to the fact that nuclear spectral diffusion was recognized as a dominant decoherence mechanism of the observed electron spins [4], here we show that difference in the phase memory relaxation time detected as a function of number of decoupling pulses, can be directly related to the extent of frustration characterizing glassy and crystalline solid ethanol. We propose that the idea, developed to achieve optimal dynamical decoupling control in (para)magnetic systems, is applicable to distinguish between disordered systems exhibiting specific many-body correlations.

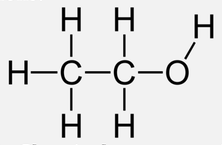

Figure 1. Chemical structure of ethanol.

2. EXPERIMENTAL SETUP

Liquid ethanol with the incorporated nitroxyl radical TEMPO was prepared in the glassy and crystalline state [1]. 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.

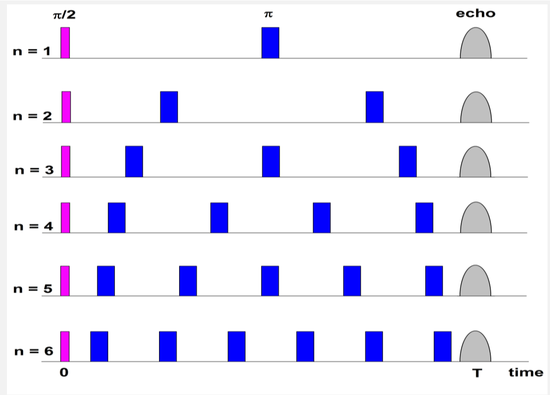

Figure 2. Multiple-pulse dynamical decoupling control protocol based on CPMG pulse sequence. The total evolution time T was fixed to 2400 ns, duration of the π pulse was 88 ns and their number n =1,...,6 is indicated.

Two-pulse, 2P_ESEEM, ($\pi/2$-τ_1-π-τ_1-*echo*) and three-pulse, 3P_ESEEM, ($\pi/2$-τ_2-$\pi/2$-T-$\pi/2$-τ_2-*echo*) detection sequences were measured at 40 K. The minimum distances between the pulses were, τ_1 = 200 ns and T = 300 ns with τ_2 =100 ns. Multiplepulse dynamical decoupling control was achieved using CPMG sequence [3]. In the experiment the total evolution time was fixed to 2400 ns and the start of the echo detection was always at the same time point. This required that the time positioning of π pulses be adjusted within the evolution time depending on n -pulse CPMG sequences. Duration of the π pulse was 88 ns and up to 6 π pulses was applied. In the two-pulse experiments performed at 80 K the phase memory relaxation time T_m was extracted assuming a mono-exponential decay whereas at lower temperatures the non-exponential decay of the electron spin-echo amplitude was assumed according to [2]:

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

with x denoting stretched exponent.

3. RESULTS AND DISCUSSION

3.1 ESEEM in glassy and crystalline ethanol

The involvement of hyperfine interaction in electron spin dephasing can be directly verified from the nuclear modulation of the electron spin echo decay. Therefore, the modulation pattern observed in the 2P_ESEEM experimental data of glassy and crystalline ethanol is presented in Fig. 3. Data from the time domain indicate larger modulation envelope for glassy than crystalline state. In specific, the relative amplitudes of the fundamental (15.1 MHz, ν_H) and first harmonic proton frequencies (29.3 MHz, $2\nu_H$) depend on the disorder present in the host matrix. It can be noted that the component at $2\nu_H$ overwhelms the one at ν_H in glassy as compared with the crystalline ethanol during the first four modulation periods while it dominates afterwards the pattern in both solid ethanol states. π refocusing pulse could contain imperfections, which could make rise to the distribution of spin rotation angles and affect the relative intensities of frequency components. Since the same experimental set up was applied to both glassy and crystalline state, difference in the observed modulation patterns, if caused by the inhomogeneity of the microwave magnetic field across the resonator cavity, indicates difference in the anisotropic hyperfine interaction network due to the various spatial frustration of nuclear spins in two solid ethanol states. Due to the only partial excitation of the inhomogeneous spectral line width, the proper phasing of the signal, which would in the ideal situation completely eliminate the imaginary part contribution, is in principle not possible with the consequence that the part of the signal in the real domain could be missing. To account for this effect the absolute signal in the time domain was transformed to the frequency domain (Fig. 3b). Dominance of the $2\nu_H$ harmonic over ν_H component is clearly resolved in glassy as compared with the crystalline host matrix. The effect reveals dependence on the variable π / 2 pulse duration presenting the largest difference between the glassy and crystalline ethanol state for shortest pulses applied. This shows that the relative amplitudes of modulation harmonics do increase with the increase of the microwave field i.e. with shortening of the pulse duration. This result proves that the spectral diffusion is the most important mechanism in electron spin decoherence. In order to improve the resolution of the 2P_ESSEM data and to decouple the impact of the paramagnetic reporter group itself, 3P_ESEEM experiments were performed using deuterated TEMPO incorporated in protonated solid ethanol (Fig. 4). The modulation pattern reveals the hyperfine interaction due to deuterons and protons. In the frequency domain, apart from the deuteron signal at 2.2 MHz, only the fundamental proton harmonic frequency at 14.7 MHz is observed,.When the former amplitudes in glassy and crystalline ethanol are scaled to the same value, the amplitude of the proton modulation component at ν_H in glassy ethanol becomes larger than the corresponding one in crystalline solid ethanol. The observed difference between the experimental data should be assigned to the distinct properties of the hyperfine interactions in two nuclear spin bath realisations differing in molecular packing/disorder.

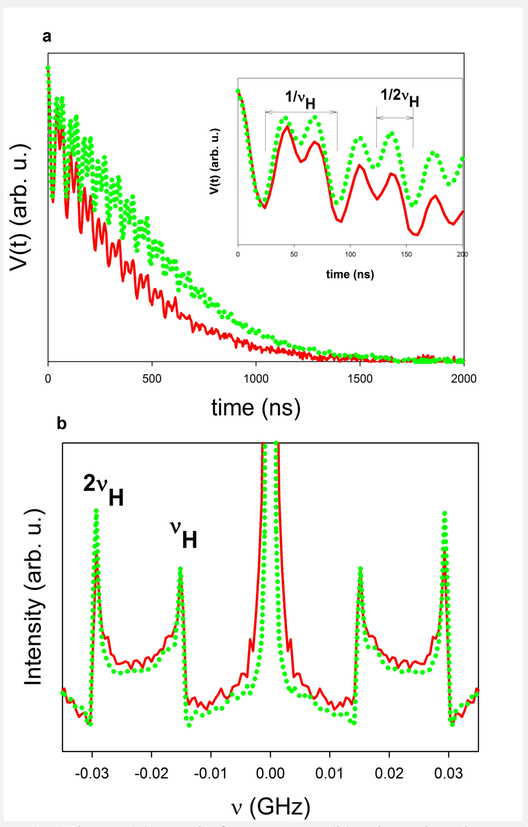

Figure 3. Time (a) and frequency (b) domain data of the 2P_ESSEM experiments of TEMPO incorporated in glassy (dotted) and crystalline (full line) ethanol measured at 40 K. Fundamental (15. 1 MHz, ν_H) and first harmonic proton frequencies (29.3 MHz, $2\nu_H$) indicated.

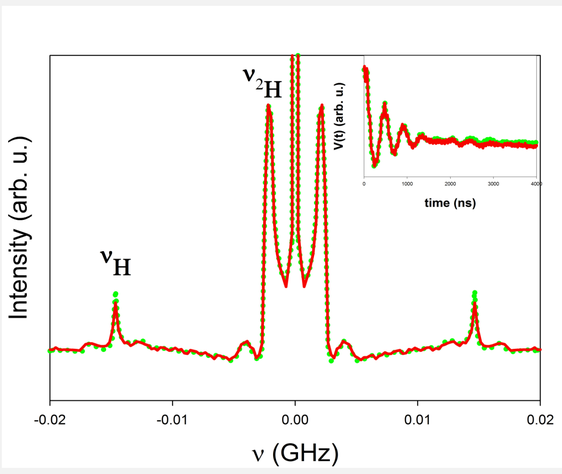

Figure 4. Frequency domain 3P_ESSEM data of deuterated TEMPO-D incorporated in protonated solid ethanol glassy (dotted) and crystalline (full line) state measured at 40 K. Deuteron signal (ν_{2H} = 2.2 MHz) and the fundamental proton harmonic frequency (ν_H = 14.7 MHz) are indicated. *Inset:* Time domain data.

3.2 Spectral diffusion in electron spin decoherence

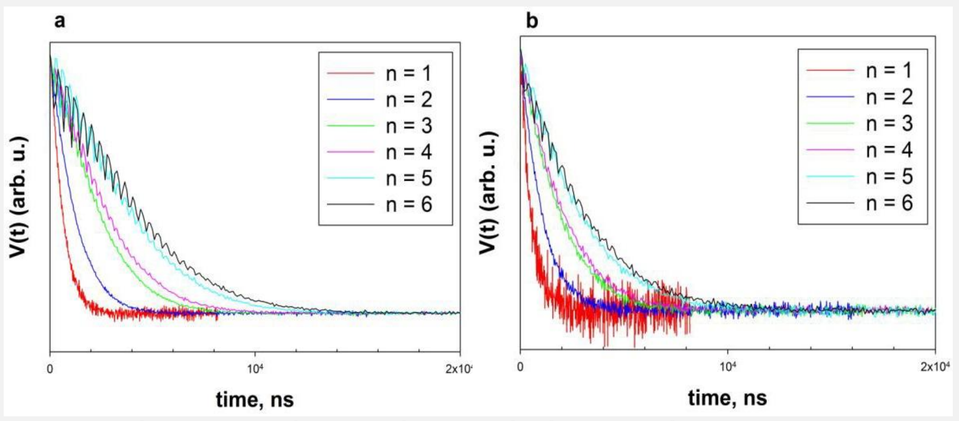

Figure 5. Electron spin-echo time decay amplitude measured in constant-time CPMG experiments for TEMPO incorporated in glassy (a) and crystalline ethanol at 20 K. The number n of π-pulses is indicated. Phase-memory relaxation time was estimated according to eq. (1).

We have analysed multiple-pulse dynamical decoupling in a glassy and crystalline ethanol. Phase-memory relaxation time was measured at 20 K in a constant–time version of the CPMG sequence. This approach was chosen in order to eliminate the influence of electron spin-lattice relaxation effects as compared with the conventional CPMG pulse sequence as the start of the echo sampling was at the same time point irrespectively of the number of refocusing π pulses. The experimental data measured at 20 K (Fig.5) evaluated according to eq. (1) are presented in Fig. 6. The results indicate an increase in $T_m$with the increasing number of π pulses. The application of more refocusing π pulses leads to the more efficient suppression of nuclear spectral diffusion effects, T_m increases with the number of π pulses. For ethanol model, a linear relationship between T_m and the number of π pulses is detected, being 40% steeper for glassy than crystalline ethanol data. The result directly points to the larger contribution of nuclear spectral diffusion mechanisms in the electron spin decoherence in the former type of sample. This observation suggests that dynamical decoupling pulse sequences provide numerical descriptor of the nuclear spectral diffusion as a function of disorder. As a support of this reasoning larger stretched exponent detected in glassy as compared with the crystalline ethanol was deduced and assigned to different nuclear spin-bath many-body correlations realized in two structurally distinct host matrices. In our study, the variation of stretched exponent value with the pulse-number (parity) was not observed. Nevertheless, the approach of constant-time CPMG pulse sequence shows to be advantageous in comparing frustrated systems since nuclear spectral diffusion, when acting as a dominant decoherence mechanism, is emphasized by the design of the experiment.

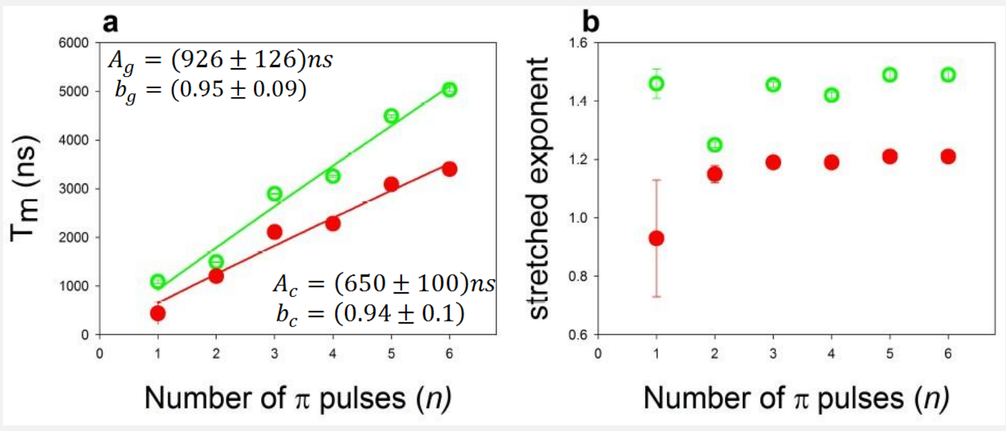

Figure 6. T_m (a) and stretched exponent (b) as a function of the number of π pulses. Full lines (a) represent the best fits of the experimental data assuming $T_m = An^b$ with the parameters $A_c$and $b_c$derived for the crystalline and $A_g$and b_g for the glassy ethanol.

CONCLUSIONS

It is shown that nuclear spectral diffusion from host matrix protons is the dominant mechanism of electron spin decoherence of the paramagnetic nitroxyl radical TEMPO incorporated in glassy and crystalline solid ethanol. It can be suppressed when applying special multiple-pulse sequence developed for the dynamical decoupling control of the central spin. The effect is much more pronounced in glassy than crystalline ethanol, the state exhibiting larger disorder/frustration. Since the phase memory relaxation time increased linearly with the increase in the number of the applied refocusing pulses, the effect of the extent of disorder could be described numerically for this specific model system.

Acknowledgement

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