Boosting the electron spin coherence in binuclear Mn complexes by multiple microwave pulses

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We investigate a possibility to enhance the coherence time of electron spins in magnetic molecular complexes by application of the Carr-Purcell-Meiboom-Gill (CPMG) multiple microwave pulse sequence. Our theoretical analysis shows that the CPMG sequence can efficiently suppress the spin decoherence channel arising due to spectral diffusion induced by a random modulation of the hyperfine interaction which is an important source of the spin dephasing in molecular magnets. We confirm this by employing the CPMG protocol in pulse electron spin resonance experiments on model binuclear 1,2-diphosphacyclopentadienyl manganese complexes. We show that, compared to the standardly used two-pulse primary spin-echo technique, the CPMG experiment can boost the phase memory time up to one order of magnitude, bringing it to above 10 μs at low temperatures. This finding may be important for the implementation of quantum computation protocols on molecular magnets. We discuss a possible interesting analogy with the Zeno's paradox in quantum theory (the Zeno quantum effect), which could be implicit in the CPMG experiment.

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I. INTRODUCTION

Magnetically active metal-organic complexes emerge as attractive model systems to explore the prospects of utilization of molecular electron spins for quantum computation and memory storage. The rational design and successful chemical engineering of novel magnetic molecules has led to the discovery of high-spin single-molecule magnets (SMM) with unprecedented magnetic properties.[1] Aside from exhibiting hysteretic ferromagnetic behavior of a pure molecular origin that can be used in nanoscale memory devices, SMMs possess an atomiclike discrete multiplet structure of spin states which can be employed for the implementation of quantum computation algorithms (for a recent review see, e.g., Ref. 2). The low-spin transition-metal coordination complexes are extensively discussed as a playground for performing quantum logic operations where the quantum information bit (qubit) is realized on a single-molecule level (see, e.g., Refs. 3 and 4). For the assessment of the suitability of molecular complexes for quantum information processing, pulse methods of electron spin resonance (ESR) turn out to be very useful.[5–12] In particular, with pulse ESR one can directly measure the decoherence time of molecular spins and investigate the spin dephasing processes which have to be sufficiently slow to enable quantum computation. This technique can be further used to control and manipulate the spin states for the realization of quantum algorithms.

The phase memory time T_m of the electron spins in the microsecond range is highly desirable for an efficient implementation of the computation protocols. The T_m in molecular complexes is limited by a number of spin dephasing mechanisms; among those, spectral diffusion plays an important role. A common way to minimize this decoherence channel is a targeted chemical engineering of molecular nanomagnets that enhances the conformational rigidity of the molecules and minimizes the number of ligand atoms with nonzero nuclear spin.[10] By this, the phase memory time in the so-called $\mathrm{Cr_7Ni}$ ring exceeding 15 μs has been recently achieved.[10] In this work, we propose an alternative (but also a complementary) strategy to enhance the T_m by employing more elaborated ESR pulse protocols beyond the primary Hahn echo pulse sequence $(\pi/2) - \tau - (\pi) - \tau -$ echo which is routinely used in most of the works.[5–12] It is known that the primary echo decay strongly depends on spectral diffusion.[13,14] This unwanted mechanism contributes to the incomplete refocusing of electron spins at time 2τ (time of the echo formation). To reduce the effects of diffusional processes, Carr and Purcell[15] and further Meiboom and Gill[16] suggested a pulse protocol (CPMG protocol) for the determination of the phase memory time T_m of the nuclear spins with the following pulse sequence: $(\pi/2)_x - \tau - (\pi)_y - \tau - \mathrm{echo} - \{\tau - (\pi)_y - \tau - \mathrm{echo}\}^{(n-1)}$ (Fig. 1). The advantage of this pulse protocol relative to the primary echo decay is a substantial increase of the phase memory relaxation time, which has been indeed shown in numerous NMR experiments. Applications of the CPMG protocol to electron spin ensembles are, however, rather scarce. Its efficiency has been experimentally confirmed in a few ESR experiments (see, e.g., Refs. 17–21). In particular, in Ref. 20 different mechanisms which influence the determination of the phase memory relaxation time both in the primary echo decay and in the CPMG protocol have been discussed.

In this work, we show that the CPMG pulse protocol can indeed suppress mechanisms that reduce the phase memory time and therefore substantially increase the electron spin coherence in magnetic molecular complexes. We demonstrate this on a simple model system of a binuclear manganese complex, the phase memory time of which we have studied before with a standard Hahn echo technique.[8] In that previous work, we have found that in the studied complexes, intermolecular interaction and the hyperfine interaction with protons contribute to the phase memory relaxation via spectral diffusion. The use of the CPMG technique efficiently suppresses the influence of

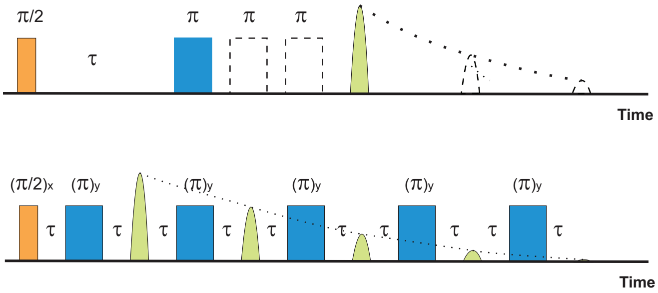

FIG. 1. (Color online) Top: primary Hahn echo pulse sequence. The decay of the echo signal is measured by increasing the time τ between the $\pi/2$ and the π pulses. Bottom: the CPMG pulse sequence. After the first exciting $\pi/2$ pulse along the x axis n π pulses along the y axis are applied with a fixed time delay τ. The decay of the echo signal is measured as a function of $n\tau$ (Refs. 15 and 16).

the spectral diffusion and drastically increases the electron spin coherence lifetime. We find an interesting analogy between our results and the so-called quantum Zeno effect,[22] a suppression of the quantum evolution of the spin ensemble by frequent measurements, which, as we argue, needs to be considered by application of pulse protocols implementing various quantum computation algorithms on molecular magnets.

The paper is organized as follows. In Sec. II, we briefly discuss the dephasing mechanisms which shorten the phase memory time T_{m} of electron spins in molecular complexes. The suppression of the spin decoherence due to spectral diffusion by the CPMG pulse sequence is analyzed theoretically in Sec. III. In Secs. IV and V, the results of the pulse ESR experiments on the model binuclear Mn complexes implementing the CPMG protocol are presented and discussed. Finally, the main conclusions are summarized in Sec. VI.

II. SPIN DEPHASING MECHANISMS

A number of mechanisms are known to contribute typically to the phase relaxation of electron spins. They are related to the dipole-dipole spin-spin interaction between the paramagnetic centers, hyperfine (HF) interaction with magnetic nuclei of a matrix, as well as to the spin-lattice relaxation (see, e.g., Ref. 13). The dipole-dipole interaction, the contribution to the phase relaxation of which depends on the concentration of paramagnetic centers and on the strength of the microwave field, acts via the mechanisms of the spectral and instantaneous diffusion.[13,23] The spin-lattice (SL) interaction causes spin flips, i.e., nonadiabatic transitions between the states with different electron spin projections yielding the temperature-dependent longitudinal T_1 and transversal (phase) T_2 relaxation of the spins. At sufficiently high lattice temperatures (in the case of the fast motion of lattice atoms), the SL interaction contributes equally to both relaxation times $T_1 = T_2$. In principle, the SL relaxation of electron spins may induce spectral diffusion due to the stochastic modulation of the spin-spin interaction between paramagnetic centers and thus give rise to a temperature dependence of the phase relaxation.

An important contribution to the phase relaxation of electron spins is given by the HF interaction with magnetic nuclei.[13,24] In the following section, we shall analyze the manifestation of spectral diffusion caused by stochastic modulation of the HF interaction by spin diffusion in the subsystem of nuclear spins.

III. SPECTRAL DIFFUSION AND CPMG PULSE SEQUENCE

The CPMG protocol has been originally proposed for the measurement of the molecular diffusion constant with the aid of the nuclear spin-echo method.[15] In those experiments, a sample is exposed to an external magnetic field with a linear gradient. In this case, the Larmor frequency of a spin depends on its spatial location in the sample and therefore the diffusion of the molecules induces the spectral diffusion. The kinetics of the spin-echo decay in a CPMG experiment due to this mechanism is rather well known.[14,25] However, such a mechanism of the spectral diffusion and a corresponding mechanism of the phase relaxation of spins are not operational in our case. Therefore, we can not make use of these already known results. Having reviewed in the previous section the main mechanisms of the electron paramagnetic phase relaxation in solids, in the following we will focus on and discuss in some detail a manifestation of the spectral diffusion caused by a stochastic modulation of the HF interaction due to a spin diffusion in a system of nuclear spins of a matrix.[13,14,24]

The HF interaction of electron spins with magnetic nuclei of a solid-state matrix gives rise to an inhomogeneous broadening of the ESR lines. In a good approximation, this frequency spread can be described by a Gaussian distribution[26]

$$p(\omega) = (1/\sqrt{2\pi\sigma})\exp(-\omega^2/2\sigma), \tag{1}$$

where σ is the second moment (dispersion) of the frequency distribution $\sigma \equiv \langle\omega^2\rangle$. The spin diffusion in the nuclear spin system and molecular mobility (translational and rotational diffusion and/or internal molecular rotation) may randomly change in time the local HF fields. For a description of such spectral diffusion, let us consider a model of a normal stochastic process[25] which is fully described by a dispersion of the frequency distribution (1) and a frequency correlation function

$$g(\tau) = (1/\langle\omega^2\rangle)\langle\omega(t)\omega(t-\tau)\rangle. \tag{2}$$

Let us assume an exponential form of the correlation function

$$g(\tau) = \exp(-|\tau|/\tau_c), \tag{3}$$

where τ_c is the frequency correlation time.

In our case, the frequency dispersion is given by the HF interaction of paramagnetic centers with magnetic nuclei $V_{\mathrm{HFI}} = \hbar\sum_k a_k S_z I_{kz}$. Here, S_z and I_{kz} are the projections of the operators of an electron and kth nuclear spins on the direction of an external field, respectively, a_k are the components of the HF coupling tensor, and $\hbar$ is the reduced Planck constant. The second moment of the ESR line due to the HF interaction reads as

$$\sigma = \frac{1}{3}\sum_k a_k^2 I_k(I_k+1). \tag{4}$$

The correlation time τ_c depends on a particular mechanism that induces stochastic changes of the local magnetic field from nuclei at the paramagnetic center. For example, in the case of spectral diffusion induced by nuclear spin diffusion, the τ_c is equal to the flip-flop time of the neighboring nuclear spins. For the mutual flip-flops of proton spins under the action of the dipole-dipole interaction, the correlation time τ_c is of the order 10^{-4}–10^{-5} s.[14,25]

In the present case, with the CPMG pulse sequence $\pi/2 - \tau - \pi - \tau - \text{echo} - \{\tau - \pi - \tau - \text{echo}\}^{(n-1)}$, a contribution of the magnetic nuclei to the phase of the precession of an electron spin is given by the expression

$$X(2n\tau) = \int_0^{\tau} \omega(t)dt + \sum_{k=1}^{n-1}(-1)^k \int_{(2k-1)\tau}^{(2k+1)\tau} \omega(t)dt + (-1)^n \int_{(2n-1)\tau}^{2n\tau} \omega(t)dt. \quad (5)$$

Note that in the CPMG experiment one measures the n number of echo signals.

The phase of the precession of an electron spin $X(t)$ is a linear superposition of the normal stochastic process $\omega(t)$. This means that the stochastic process $X(t)$ is also a normal stochastic process.[25] Experimentally, one measures the transversal component of the magnetization of electron spins. A contribution of the magnetic nuclei to it is defined as

$$J_n = \langle \exp[-iX(2n\tau)] \rangle , \quad (6)$$

where $\langle \cdots \rangle$ means an average over all realizations of the stochastic process $\omega(t)$. For the normal process $X(t)$ we have[25]

$$J_n = \langle \exp[-iX(2n\tau)] \rangle = \exp[-\langle X^2(2n\tau)\rangle/2]. \quad (7)$$

Using Eqs. (3), (5), and (6) after straightforward calculations we obtain the following expression for the nth echo signal in the CPMG pulse sequence:

$$\begin{aligned} J_n = \exp\Bigg\{ -\Bigg[& 2f(\tau) + (n-1)f(2\tau) \\ & + \sigma\tau_c^2 \Bigg((-1)^n \exp[-2(n-1)\tau/\tau_c] g^2(\tau) \\ & - 2\sum_{k=0}^{n-2}(-1)^k \exp(-2k\tau/\tau_c) g(\tau) g(2\tau) \\ & - \sum_{k=0}^{n-3}(-1)^k (n-2-k) \exp(-2k\tau/\tau_c) g^2(2\tau) \Bigg) \Bigg] \Bigg\}. \quad (8) \end{aligned}$$

Here, the following definitions are introduced: $f(t) = \sigma[t\tau_c - \tau_c^2 g(t)]$ and $g(t) = 1 - \exp(-t/\tau_c)$.

Equation (8) comprises the sums of the geometric series expansions with the geometric ratio $q = -\exp(-2\tau/\tau_c)$, and the derivative of the sum of the geometrical series with respect to q. For example, one has

$$\begin{aligned} \sum_{k=0}^{n-2}(-1)^k \exp\left(-\frac{2k\tau}{\tau_c}\right) & = \{1 - (-1)^{n-1} \exp[(-2(n-1)\tau/\tau_c]\} \\ & \quad /[1 - (-1)\exp(-2\tau/\tau_c)] \\ & = \{1 + (-1)^n \exp[-2(n-1)\tau/\tau_c]\}/[1 + \exp(-2\tau/\tau_c)]. \end{aligned} \quad (9)$$

The phase relaxation time of the spins is usually determined from the kinetics of the decay of the primary echo signal, the amplitude of which is described by Eq. (8) with $n = 1$.

The analysis of Eq. (8) shows that the echo decay in the CPMG experiment with $n \gg 1$ is slower as in the case of the primary echo if one compares the amplitude of the signals with the equal total observation time, i.e., the 2τ in the primary echo experiment should be equal to the $2n\tau$ in the CPMG experiment (see Fig. 2). We note that a similar effect of slowing the decay of the echo signal in the CPMG experiment also takes place for the mechanism of the phase relaxation of the spins related to the molecular diffusion in a magnetic field with a linear field gradient.[14]

In the present case, a contribution of the spectral diffusion to the decay of the primary echo is described by Eq. (8) with $n = 1$, yielding

$$ESE(2\tau) = \exp\left\{ -\left[2f(\tau) - \sigma\tau_c^2 g^2(\tau)\right]\right\}, \quad (10)$$

which for short observation times $\tau < \tau_c$ obtains the form

$$ESE(2\tau) = \exp(-2\sigma\tau^2). \quad (11)$$

For sufficiently long observation times $\tau > \tau_c$, the decay of the primary echo signal is described by an exponential dependence on τ

$$ESE(2\tau) \approx \exp[-4\sigma\tau_c(\tau - 1.5\tau_c)]. \quad (12)$$

It follows from Eqs. (11) and (12) that, with increasing the observation time, the time dependence of the logarithm of the echo signal transforms from quadratic to linear. Figure 3(a) shows a dependence of the amplitude of the echo signal in the CPMG protocol on a logarithmic scale which is linear in contrast to the decay of the primary echo signal shown in Fig. 3(b).

For the considered mechanism of the spectral diffusion, one can estimate the frequency dispersion σ and the characteristic correlation time τ_c in the following way. To the spectral diffusion contribute all magnetic nuclei of the matrix which are located beyond the diffusion barrier with the radius d (Ref. 25) being typically of the order of 1 nm.[14,25] The HF coupling of paramagnetic spins with the magnetic nuclei beyond the diffusion barrier takes place via the dipole-dipole interaction. In this case, the σ is given by the expression of the second moment [Eq. (IV.39a) in Ref. 25]:

$$\sigma = 5.1\gamma_e^2\gamma_n^2\hbar^2 I(I + I)/d^6, \quad (13)$$

where γ_e and γ_n are the electron and nuclear gyromagnetic ratios, respectively, and I is the nuclear spin. With $d = 1$ nm, we obtain $\sigma \sim 10^{12}$ rad/s^2. Note that the radius of the diffusion barrier is determined by the ratio of the dipole-dipole interaction strength between the neighboring nuclear spins and the difference of the Zeeman energies of the neighboring spins in the local magnetic field of an electron spin. The nuclear spin diffusion is caused by the mutual flip-flops of the neighboring nuclear spins which are separated by an average distance a and are coupled via the dipole-dipole interaction. Hence, the characteristic correlation time τ_c in Eq. (3) can be estimated as $1/\sqrt{M_2}$, where M_2 is the second moment of the NMR spectrum of these nuclei and is given by the expression of type Eq. (13): $M_2 = 5.1\gamma_n^4\hbar^2 I(I + I)/a^6$ (see Ref. 25). Assuming $I = \frac{1}{2}$ and $a = 0.2$ nm yields $\tau_c = 5 \times 10^{-6}$ s, and with $a = 0.3$ nm we obtain $\tau_c = 2 \times 10^{-6}$ s. According

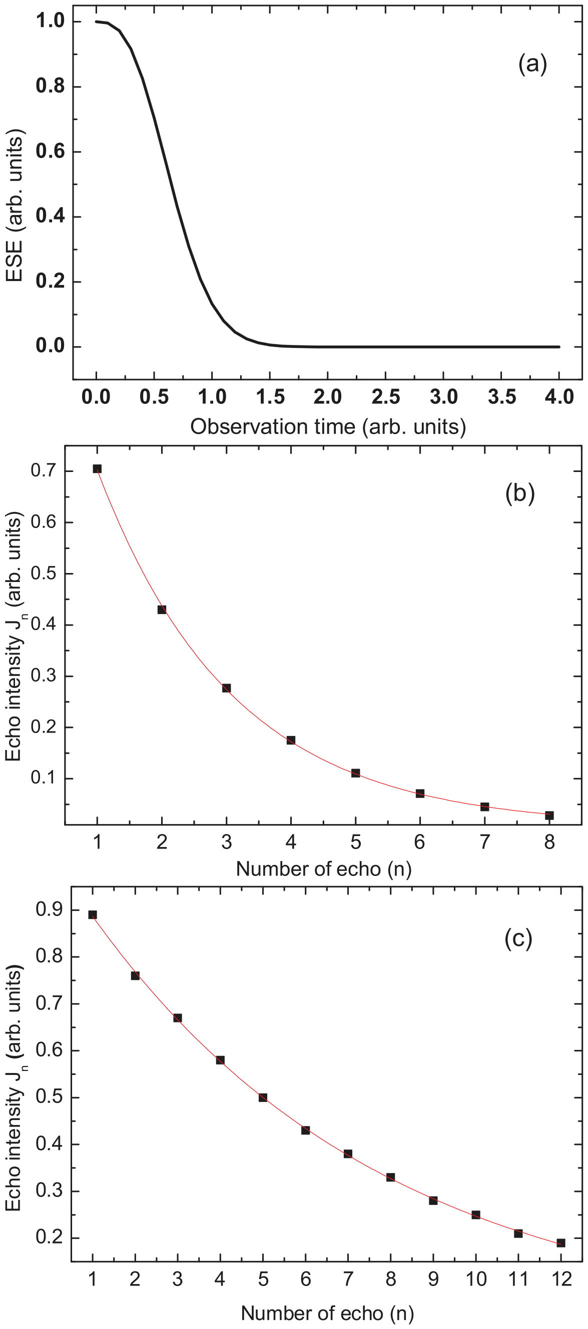

FIG. 2. (Color online) A comparison of the decay of the primary echo (a) and of the CPMG echo with $n = 8$ (b) and $n = 12$ (c). The total observation time t_{ob} in all plots is taken the same amounting to $t_{\mathrm{ob}} = 8\tau_c$. In (a) the time is given in units $2\tau_c$. The scale of the horizontal axis in (b) and (c) is given in units of the number n of the echo signal in the CPMG experiment. (b) and (c) correspond to the case of $\tau = t_{\mathrm{ob}}/16$ and $t_{\mathrm{ob}}/24$, respectively. The calculations were carried out for $\sigma\tau^2 = 6$. One can see that in the CPMG experiment ($n > 1$), the echo signal decays substantially slower compared to the primary echo ($n = 1$) (see the text).

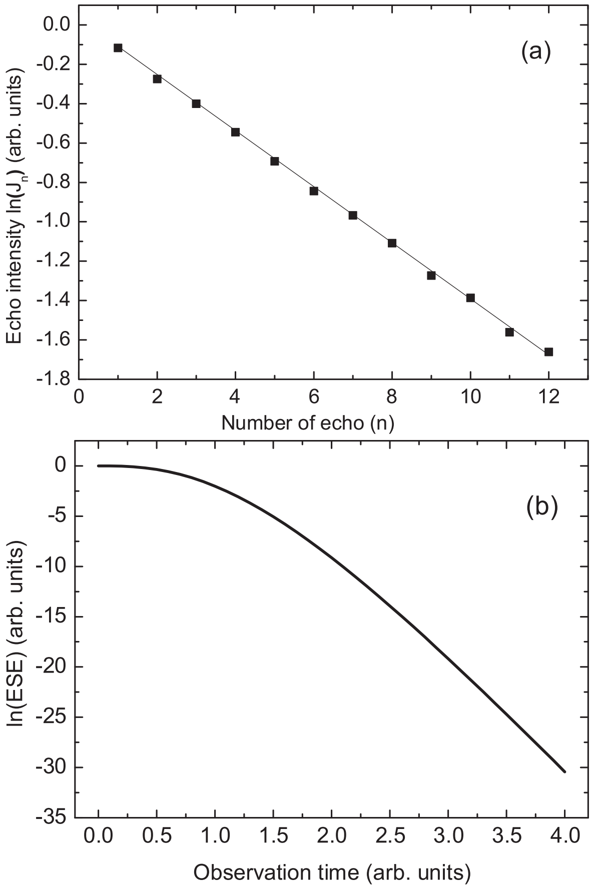

FIG. 3. Dependence of the logarithm of the amplitude of the CPMG echo signal (a) and of the primary echo signal (b) on the number n of the signal and on the observation time, respectively. The parameters correspond to those in Fig. 2.

to the above considerations, the relevant theory parameter which determines the kinetics of the spin-echo decay [see, e.g., Eqs. (10) and (11)] that reads as $\xi = \sigma\tau_c^2 = \sigma/M_2 = (\gamma_e^2/\gamma_n^2)(a/d)^6$. For the reasonable ratios d/a in the interval $\{5,7\}$, ξ takes the values in the interval $\{25,3\}$. Taking, for example, a mid-value $d = 6a$, we get $\xi \approx 6$.

Therefore, the above-considered mechanism of the spectral diffusion due to the stochastic modulation of the HF interaction via the nuclear spin diffusion can lead to the exponential decay of the spin-echo signal $\exp(-2\tau n/T_{\mathrm{mn}})$ in the CPMG experiment [see, e.g., Fig. 3(a)]. The nuclear spin diffusion is practically independent of the sample temperature, and the relevant phase relaxation time T_{mn} should be temperature independent too. However, within this mechanism one yet can expect a temperature dependence of T_{mn}. This could be related to the increase of the diffusion barrier due to the increase of the spin-lattice relaxation with decreasing temperature. Indeed, stochastic flips of an electron spin due to the spin-lattice interaction average the local field which an electron spin causes at the nuclear sites. As a result, the radius of the diffusion barrier should decrease with the decrease of the electron spin-lattice relaxation time $T_{1\mathrm{e}}$. In this situation, the time of the decay of the spin echo in a CPMG experiment may depend on temperature.

In principle, a stochastic modulation of the HF interaction may be caused also by a temperature-dependent nuclear spin-lattice relaxation. In this case, the correlation time of the spectral diffusion is equal to the nuclear spin-lattice relaxation time $\tau_c = T_{1\mathrm{n}}$. Here, one could expect a temperature dependence of T_{mn} provided that $T_{1\mathrm{n}}$ is comparable or smaller than the average time of the mutual flip-flops of the neighboring spins, which is unlikely.

In Sec. II, we have mentioned that in solids a dipole-dipole interaction between paramagnetic centers can contribute to the phase relaxation of electron spins.[13,14,24] One can expect that in a CPMG experiment, the spectral diffusion caused by the stochastic modulation of the electron spin-spin dipole-dipole interaction between paramagnetic centers should also lead to an exponential decay of the echo signal $\exp(-2\tau n/T_{\mathrm{me}})$. We conjecture this since such scenario is realized for the two different mechanisms of the spectral diffusion: (i) the first one which is caused by a molecular diffusion in a magnetic field with linear gradient;[25] (ii) the second one due to the discussed above stochastic modulation of the HF interaction.[24] The spectral diffusion related to the spin-spin interaction between the paramagnetic centers is beyond the scope of this paper and will be treated in a separate work. Here, we only point out that one of the signatures of the contribution of this mechanism to the phase relaxation is its dependence on the amplitude of the electromagnetic pulses that give rise to the echo signal.[13,14] In this case, the T_{me} may depend on temperature since the stochastic modulation of the dipole-dipole interaction may be caused by the spin-lattice relaxation of electron spins.[13,14]

IV. EXPERIMENTAL DETAILS

Here, experimentally we study with the pulse ESR technique 1,2-diphosphacyclopentadienyl binuclear manganese complexes.[8,27] In these complexes, the manganese spins $S = \frac{1}{2}$ are weakly antiferromagnetically coupled. The coupling strength $J \lesssim 20$ K can be tuned by an appropriate choice of the peripheral ligands which also control the magnitude of the magnetic moment at the Mn site. More detailed information about the synthesis, electronic structure, and elementary magnetic properties can be found in Ref. 27. The complexes with the ligands CO (**1**) and CH_3CN (**2**) were investigated in a powder form and as frozen solution in toluene. In this work, we have used toluene and not tetrahydrofuran (THF), as in the previous work,[8] in order to exclude a possible influence of the solvent on the conformational properties of the molecular complex. All manipulations were carried out under dry, pure nitrogen atmosphere in standard Schlenk apparatus. Toluene was distilled from sodium/benzophenone and stored under nitrogen before use. Samples **1** (20 mg, 0.02 mmol) and **2** (21 mg, 0.02 mmol) were dissolved in 20 ml of toluene to obtain clear homogeneous solutions with concentrations 1 mmol/l. The so-prepared solutions were placed in a quartz tube which has been evacuated and sealed. We did not find any difference in the relaxation times of the samples prepared with toluene and THF.

The ESR experiments were performed with an ELEXSYS E580 (X-band) Bruker spectrometer. The primary echo was investigated with the standard $\pi/2 - \tau - \pi - \tau -$ echo pulse sequence. The time evolution of the electron spin decohrence was further studied with the CPMG pulse sequence $(\pi/2)_x - \tau - (\pi)_y - \tau - \mathrm{echo} - \{\tau - (\pi)_y - \tau - \mathrm{echo}\}^{(n-1)}$. In both protocols, the length of the $\pi/2$ and π pulses amounted to 8 and 16 ns, respectively. The longitudinal relaxation was examined by the stimulated echo decay and inversion-recovery protocol. All measurements were performed in the ER4118MD5W1 dielectric cavity, which was inserted in the CF935 Oxford Ins. cryostat. Experiments were performed in a temperature range 5–80 K. The temperature was controlled by the ITC 503 temperature control unit from Oxford Ins.

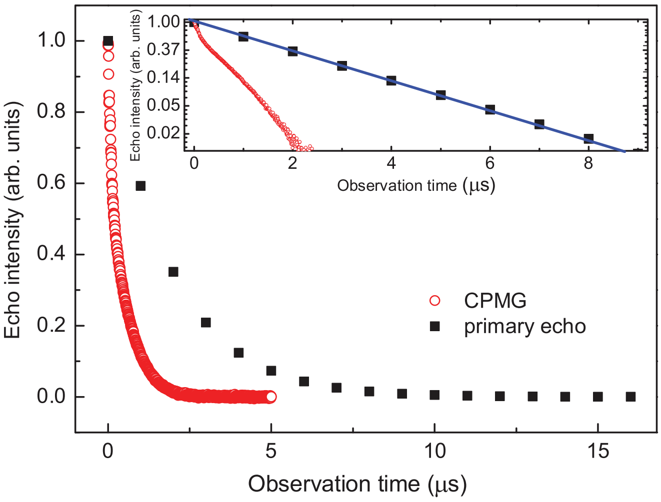

FIG. 4. (Color online) Time dependence of the intensity of the echo signal for complex (**1**) at $T = 5$ K on a linear (main panel) and on a logarithmic scale (inset) measured with the CPMG (squares) and primary echo (circles) protocols. A substantial enhancement of the phase relaxation time T_{m} and a single exponential form of the decay of the echo signal in the CPMG experiment is clearly visible in the inset. Here, the solid line is a fit to the expression $\exp(-2\tau n/T_{\mathrm{m}})$ (see the text).

V. CPMG EXPERIMENTS AND DISCUSSION

The decay of the primary echo of complex (**1**) in the powder form is shown in Fig. 4. Consistently with our previous work, it follows a nonexponential time dependence $\exp[-(2\tau/T_2^*)^b]$ with the stretch exponent parameter $b = 0.8$ and the effective relaxation time $T_2^* = 0.65$ μs at $T = 5$ K. Remarkably, the application of the CPMG protocol yields a much slower spin-echo decay which follows now a single exponential law $\exp(-2\tau/T_{\mathrm{m}})$ (Fig. 4).

A similarly drastic effect has been observed for complex (**2**). Figure 5 shows the dependence of the transverse relaxation time T_{m} on temperature for both complexes obtained using the CPMG sequence. The T_{m} for all complexes decreases with increasing the temperature. On the same figure we show also the data for complexes in frozen solutions. The echo decays in these experiments were single exponential as well. One can see that the time T_{m} for both complexes which are dissolved in toluene is larger than for powders and also decreases with increasing the temperature. The T_{m} for complex (**2**) (both in the powder and in the frozen solution) is larger than for complex (**1**) at $T < 50$ K.

To access a possible influence of the longitudinal T_1 processes on the phase memory time, we have measured the temperature dependence of T_1 for complexes (**1**) and (**2**). The measurements have been performed with inversion recovery and stimulated echo sequences. The obtained relaxation times

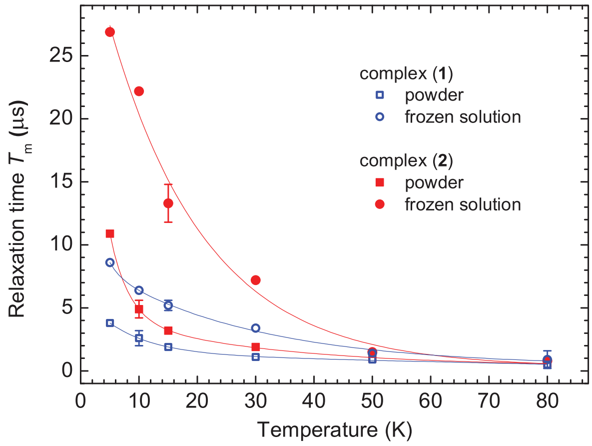

FIG. 5. (Color online) Temperature dependence of the relaxation time T_m for complexes (**1**) (open symbols) and (**2**) (closed symbols). Solid lines are guides for the eye.

are very close to each other in these two methods. A characteristic T dependence is shown in Fig. 6.

According to the consideration presented in Sec. III, the temperature dependence of T_m (Fig. 5) could be due to the decrease of the nuclear spin diffusion barrier around paramagnetic centers with increasing temperature, which consequently should shorten the T_m. Experiments performed with different microwave powers indicate that there is some contribution to the phase relaxation rate from the dipole-dipole interaction between paramagnetic centers. The fact that T_m increases upon the dilution of the studied complexes gives evidence for a contribution of the intermolecular dipole-dipole interaction to the phase relaxation. Nevertheless, we believe that in the studied system the main contribution to the phase relaxation is given by the HF interaction. To illustrate this, we show in Fig. 7 a comparison of the experimental spin-echo decay for a frozen solution of complex (**2**) at $T = 5$ K and calculations according to Eq. (8). One can see that a reasonable agreement can be achieved taking $\sigma = 1.5 \times 10^{11}$ (rad/s)^2 and $\tau_c = 1.7 \times 10^{-5}$ s which are in the range of parameter values expected for the mechanism of the spectral diffusion induced by the modulation of the HF interaction due to the nuclear diffusion.

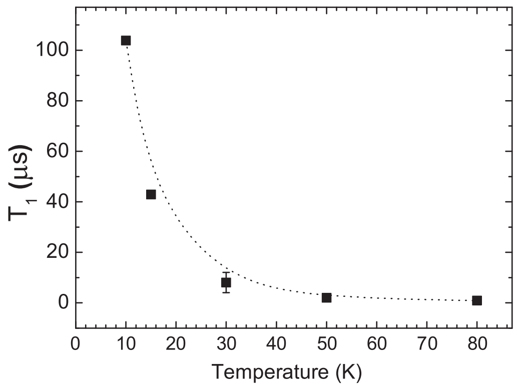

FIG. 6. Temperature dependence of the longitudinal relaxation time T_1 for a frozen solution of complex (**1**). Dotted line is a guide for the eye.

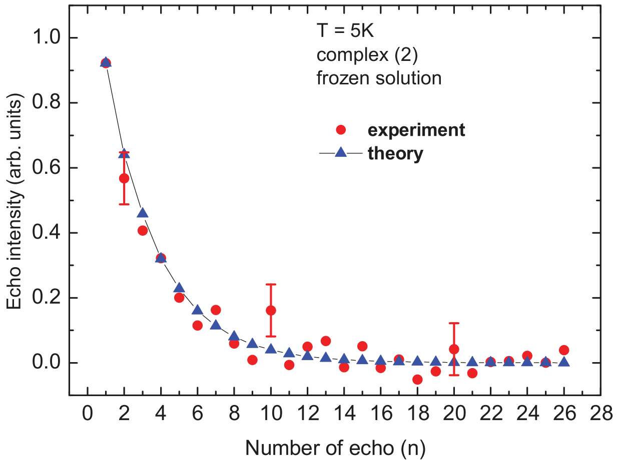

FIG. 7. (Color online) Decay of the CPMG echo signal as a function of the echo number n for a frozen solution of complex (**2**) at $T = 5$ K (circles) and according to Eq. (8) with $\sigma = 1.5 \times 10^{11}$ (rad/s)^2 and $\tau_c = 1.7 \times 10^{-5}$ s (triangles) (see the text).

A drastic enhancement of the phase memory time T_m of the electron spin ensemble in the studied binuclear Mn complexes by application of multiple microwave pulses according to the CPMG protocol is remarkable. Compared to the primary echo results,[8] the T_m increases up to a factor of ∼10 and, in particular, in the frozen solutions reaches the values above 10 μs at low temperatures. This experimental observation strongly supports our theoretical considerations in Sec. III. In particular, the result in Fig. 2 showing that the process of the phase relaxation of electron spins slows down with the number of the π pulses in the CPMG sequence agrees nicely with the experimental observation in Fig. 4.

The dynamical decoupling of single spins from the detrimental influence of the environment has been studied earlier in CPMG experiments on a number of systems, such as GaAs quantum dots (see, e.g., Refs. 28 and 29), nitrogen vacancies in diamond (see, e.g., Refs. 21 and 30), or radical centers in malonic acid crystals.[31] As our results demonstrate, this approach can be generalized to interacting spins coupled in polynuclear magnetic molecular complexes. There, the spectral diffusion often being a primary limiting factor of electron spin coherence[5–12] can be efficiently eliminated in the CPMG protocol.

The observed boosting of T_m by multiple pulses, which in addition equalize the phase memory time within the spin ensemble [as is evidenced by a single exponential form of the spin-echo decay (Fig. 4)], is reminiscent of a so-called Zeno's paradox in the quantum theory formulated in Ref. 22. The meaning of this quantum Zeno effect (QZE) is that a frequent measurement of the state of a quantum system slows down its quantum dynamics. The faster the measurement is repeated, the slower the quantum system evolves. The microwave pulses in the CPMG protocol implement the unitary transformation (rotation) of the state of the spin and, at first glance, as such they can not be regarded as a measurement in which the spin state is projected into a certain eigenstate. At the same time, these pulses cause a formation of the spin-echo signal which is measured (observed) experimentally. Therefore, the electromagnetic pulses can be considered as a part of the measurement process. One should also note that we treat the microwave field classically as the measuring instruments in quantum mechanics should be classical. Having considered that, we may conclude that the slowing of the dephasing of electron spins due to spectral diffusion caused by the hyperfine interaction with magnetic nuclei of the matrix can be phenomenologically treated as a kind of the QZE. Applications of the QZE to reduce the spin decoherence are currently discussed in the context of quantum computation (see, e.g., Refs. 32–35). Interestingly, the QZE on nuclear spins has been demonstrated in the multipulse nuclear magnetic resonance experiment.[35]

Regarding the quantum computation algorithms, a possible manifestation of the QZE in our CPMG experiments gives reasons to expect that this effect may take place also in other protocols of the manipulation on electron spins with the aid of the pulses of the microwave field. For example, it has been recently shown in Ref. 36 that for the realization of the quantum logic operation control-NOT (CNOT), it is necessary to apply a long sequence comprising 19 microwave pulses. It can be therefore expected that by the implementation of the CNOT on electron spins, a contribution of magnetic nuclei to the electron spin decoherence can be reduced due to the above-discussed quantum Zeno effect. The relevance of this effect for the control and manipulation of electron spins by electromagnetic pulses certainly requires further investigation, in particular regarding the realization of the task of error correction during quantum computations.

VI. CONCLUSIONS

We have studied theoretically and experimentally the effect of the application of microwave multipulse sequences according to the CPMG protocol on the phase relaxation time of an ensemble of electron spins subjected to a detrimental influence of the spectral diffusion. On the theoretical level, the increase of the number of π pulses in the pulse train that follows the primary Hahn echo sequence continuously slows down the decay of the echo signal and turns its time dependence from a stretch exponential to a single exponential. This has been experimentally confirmed by pulse ESR experiments on 1,2-diphosphacyclopentadienyl binuclear manganese complexes in the form of powders and frozen solutions. The application of the CPMG protocol has yielded an enhancement of the phase relaxation time T_{m} of Mn spins up to a factor of ~10 bringing the T_{m} to above 10 μs at low temperatures. We consider an effective decoupling of electron spins from a dephasing environment in the CPMG experiment as a kind of the quantum Zeno effect that slows down quantum evolution of the spin system. We argue that this analogy should be considered by application of various pulse protocols for quantum computation on molecular magnets.

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