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Rabi oscillations in the V_{15} single molecule magnet embedded in the surfactant $(CH_3)_2 \times [CH_3(CH_2)_{16}CH_2]_2N^+$ have been studied at different microwave powers. An intense damping peak is observed when the Rabi frequency Ω_R falls in the vicinity of the Larmor frequency of protons ω_N. The experiments are interpreted by a model showing that the damping (or Rabi) time τ_R is directly associated with decoherence caused by electron-nuclear cross relaxation in the rotating reference frame. This decoherence induces energy dissipation in the range $\omega_N - \sigma_e < \Omega_R < \omega_N$, where σ_e is the mean superhyperfine field induced by protons at V_{15}. Weaker decoherence without dissipation takes place outside this window. Specific estimations suggest that this rapid cross relaxation in a resonant microwave field, observed for the first time in V_{15}, should also take place, e.g., in Fe_8 and Mn_{12}.

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Single molecule magnets (SMMs) are composed of a lattice of molecules or clusters whose collective ground-state spin S is associated with strong intramolecular interactions. SMMs are considered as promising systems for quantum information processing because they can be self-organized in 2D or 3D networks, while their relatively small size (~ 1 nm) makes them good quantum objects with weak self-decoherence (which is generally noncontrolled, as in, e.g., superconducting qubits). Predictions announce phase coherence times $\tau_2 = 100$–$500\ \mu$s in V_{15} [1] and Fe_8 [2], provided that the nuclear spin bath is absent and the temperature and magnetic field are optimized. However, this takes place in the absence of microwaves or under a short pulse sequence (as in the Hahn spin-echo method). A continuous resonant microwave field produces nutations of the spin magnetization (Rabi oscillations [3]). The relaxation dynamics in this transient regime changes drastically. For a dipolar-coupled system of electronic spins, τ_R can become much shorter than τ_2 [4–6]. As opposed to common knowledge [7], under the condition $\tau_R < \tau_2$, the utmost time of coherent spin manipulations in quantum computation will be limited by τ_R rather than τ_2, and oscillations disappear if τ_R is less than the oscillation period.

The first evidence of Rabi oscillations in a SMM was obtained in the cluster $[V^{IV}_{15}As^{III}_6O_{42}(H_2O)]^{6-}$ (V_{15}) embedded in the surfactant $(CH_3)_2[CH_3(CH_2)_{16}CH_2]_2N^+$ (DODA) to reduce dipolar interactions [1,8]. In a later study, Rabi oscillations were detected in an Fe_4 SMM [9]. In both cases, the coherence times τ_2 reached several hundred nanoseconds. Similar τ_2 were obtained in Cr_7-based [10] and Fe_8 [2] SMMs, but Rabi oscillations could not be detected. In this Letter, we show that Rabi oscillations of V_{15}-DODA are subjected to a very efficient and apparently general decoherence mechanism accompanied by energy dissipation into the proton spin bath. In a certain range of Rabi frequencies where this new phenomenon takes place, the condition $\tau_R < 2\pi/\Omega_R$ is nearly fulfilled and oscillations almost disappear.

The V_{15} cluster has a layer structure: three V^{IV} form a central triangle sandwiched by two smaller V^{IV}_6 hexagons [11,12] (Fig. 4 in [12]). The 15 spins $1/2$ are coupled by strong antiferromagnetic superexchange interactions in the external hexagons and by a relatively weak exchange through the bridges in the central triangle [11,13,14]. The lowest energy levels are a pair of doublets (with a gap of $\Delta_{1/2} = 200$ mK caused by the Dzyaloshinskii-Moriya interactions [11,14]) and a quartet (with small zero-field splitting $\Delta_{3/2} = 12$ mK [1,11]) isolated from the above quasicontinuous spectrum by a gap of $\Delta = 250$ K [11].

A series of V_{15}-DODA samples with V_{15} concentration $c = (1$–$5)c_0$ ($c_0 = 4.3 \times 10^{17}\ \mathrm{cm}^{-3}$) [15] was prepared following Ref. [1]. Variations of both the phase and spin-lattice relaxation times were measured vs c (Fig. 6 in [12]). The observed linear slope of $d\tau_2/dc$ is apparently related to the decoherence via V_{15} intercluster dipolar interactions. The phase coherence time measured at 4.2 K is of 0.5 μs for $c = c_0$ and decreases down to 0.25 μs for $c = 4c_0$. The spin-lattice relaxation can be neglected below 10 K, where the spin-lattice relaxation time $\tau_1 > 10\ \mu$s [12].

Rabi oscillations of V_{15}-DODA were measured at 4.2 K in the sample with $c = 4c_0$ by means of a pulsed EPR Bruker E-580 X-band spectrometer operating at $\omega/2\pi = 9.7$ GHz. Symmetry-based selection rules and evaluations of the intensities imply that transitions within the lowest four Zeeman sublevels of the doublet states have much smaller probabilities than those of the quartet $S = 3/2$ [1]. Rabi oscillations between $S = 3/2$ states were induced by a long microwave field pulse of length t and subsequently recorded by spin echo, giving access to the time evolution of the sample magnetization $\langle M_z(t)\rangle$. In both the t pulse and the $\pi/2$-π Hahn spin-echo sequence, the same B_1 values were used. Figures 1 and 2 show $\langle M_z(t)\rangle$ for $B_0 = 0.354$ T and B_1 in the range 0.054–1.24 mT (or, equivalently, for Rabi frequencies $\Omega_R/2\pi = 2.6$–59.2 MHz; the ratio $\Omega_R/2\pi B_1 = 48$ MHz/mT was determined experimentally). Each $\langle M_z(t)\rangle$ corresponds to the superposition of the three $S = 3/2$ oscillations with slightly different Rabi frequencies (see [12]). All curves show a fast decrease at short times due to the dephasing of spin packets with different resonance frequencies in an inhomogeneously broadened EPR line, followed by a number n_R of damped Rabi oscillations. The damping time τ_R is very sensitive to Ω_R, particularly in the range 8–15 MHz where the fastest decay ($n_R < 3$) is observed. In order to extract the damping time τ_R associated with each Ω_R, each measured oscillating curve in Fig. 1 is fitted to $j_0(\Omega_R t)e^{-t/\tau_R}$, where $j_0(z) = \int_z^\infty J_0(z)dz$ (J_0 is the zero-order Bessel function) is associated with the distribution of Larmor frequencies within the EPR line [5], while the damping of oscillations related to decoherence processes is given by a simple exponential e^{-t/τ_R}. The full evolution of the damping rate τ_R^{-1} vs Ω_R is shown as a set of symbols in Fig. 3. The broad peak in the range 8 MHz $< \Omega_R/2\pi <$ 15 MHz implies the existence of a new decoherence mechanism extremely sensitive to the microwave field amplitude. In that region, the oscillations do not obey a simple exponential law, which results in large error bars in Fig. 3. The peak value $\tau_R = 36$ ns obtained at $\Omega_R/2\pi = 8$ MHz is nearly by an order of magnitude shorter than $\tau_2 = 250$ ns measured at the same conditions. The slow linear variation of τ_R^{-1} with $\Omega_R/2\pi$ in the range 20–60 MHz (slope $\sim$0.02) is a consequence of the random distribution of the Landé factor of V_{15} clusters in a frozen solution and intercluster dipolar interactions (see [12]).

The decoherence peak around 8 MHz has a shoulder at $\Omega_R/2\pi \sim 15$ MHz, close to the Larmor frequency of protons of DODA in the resonant field B_0 ($\omega_N/2\pi = 15.1$ MHz for $B_0 = 0.354$ T). This suggests a decoherence mechanism associated with resonant electron-nuclear cross relaxation when the electronic Rabi frequency Ω_R is close to the average proton Larmor frequency ω_N. Such a mechanism of polarization transfer from the electronic to the nuclear spin bath is analogous to that in the nuclear spin

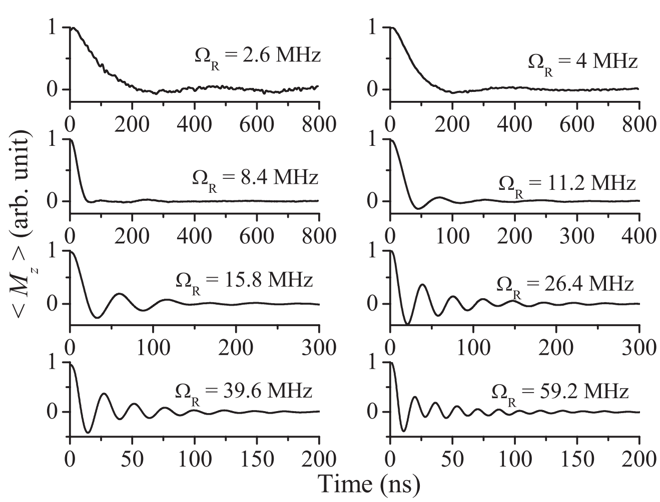

FIG. 1. Measured $\langle M_z(t)\rangle$ showing the evolution of Rabi oscillations as a function of the microwave field B_1 (see text).

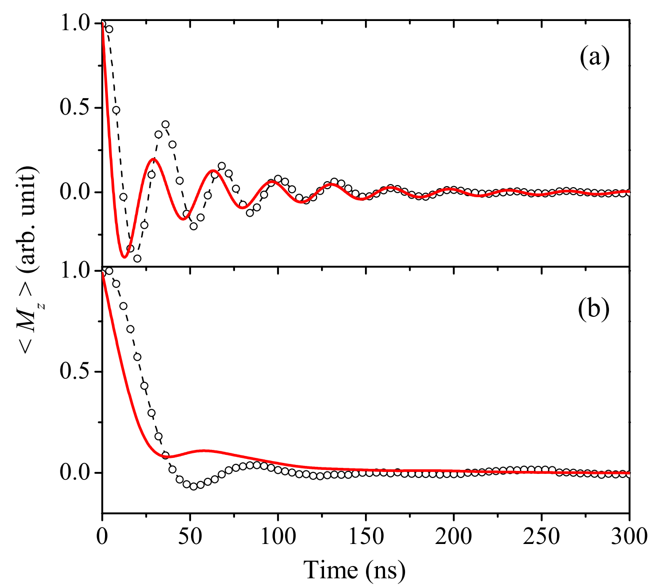

FIG. 2 (color online). Rabi oscillations in V_{15}-DODA recorded at (a) Rabi frequencies $\Omega_R/2\pi = 30$ MHz and (b) $\Omega_R/2\pi = 10$ MHz. Experimental and computed values of $\langle M_z(t)\rangle$ are represented by circles and thick lines, respectively. As the inhomogeneous EPR line half-width $\sigma/2\pi \sim 700$ MHz by far exceeds Ω_R, the mean z component of magnetization is expected to follow the law $\langle M_z(t)\rangle \sim j_0(\Omega_R t)e^{-t/\tau_R}$, where $j_0(z \gg 1) \approx (2/\pi z)^{1/2}\cos(z + \pi/4)$ [5]. This form of $\langle M_z(t)\rangle$ was used to extract the experimental values of τ_R [110 and 48 ns for (a) and (b), respectively]. The curves computed from Eq. (4) show a phase shift $\sim\pi/4$ relative to experimental points during the first period of oscillations, which is due to the selective nature of spin-echo registration. Only a part of the spin packets close to resonance contributes to the measured signal, thus reducing the half-width σ. However, this phase discrepancy does not affect the signal at a longer scale ($\Omega_R t > 2\pi$), as well as Rabi times τ_R.

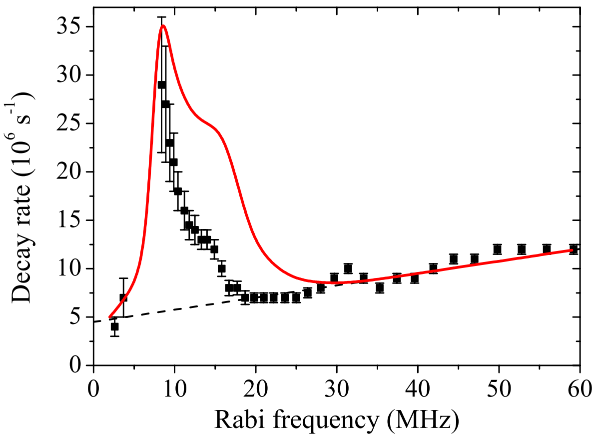

FIG. 3 (color online). Decay rate of Rabi oscillations $1/\tau_R$ vs $\Omega_R/2\pi$. Measured and calculated data are represented as squares and a solid line, respectively. The dashed line represents the linear dependence $0.02\Omega_R + 4.5 \times 10^6$ s^{-1} (see text).

orientation via the electron spin locking technique of dynamic nuclear polarization under a resonant microwave field [16,17] and with the electronic spin nutation frequency tuned to ω_N (the Hartmann-Hahn condition [18]). Here, we are not interested in a high degree of polarization of the nuclear spin bath requiring a special sequence of pulses, but in the relatively low degrees of depolarization of the electronic spin bath after a single Rabi pulse. Such a depolarization leads to the strong decoherence mechanism in V_{15} which is investigated here for the first time.

As the $S = 3/2$ zero-field splitting is $\Delta_{3/2} > \Omega_R$, only one of three possible transitions in a given cluster is actually induced by the microwave field and we can use an effective $S = 1/2$ "central spin" (CS) Hamiltonian [19]:

$$H = \omega_e S_z + 2\Omega_R S_x \cos\omega t + \sum_j \omega_j I_z^j + \sum_{j,\alpha=x,y,z} A_{z\alpha}^j S_z I_\alpha^j, \tag{1}$$

where ω_e and Ω_R are the Larmor precession frequency and the Rabi frequency of the CS, and ω_j are the precession frequencies of the proton spins $I = 1/2$ distributed around ω_N with half-width σ_N (the average local field produced by the CS at the neighboring nuclear spin). The last term in Eq. (1) represents the superhyperfine interaction between the CS and nuclear spins (the nondiagonal terms $\sim S_x, S_y$ are omitted). In the rotating reference frame, we obtain the following effective Hamiltonian [12]:

$$H' = \Omega\tilde{S}_x + V(t);$$
$$V(t) = \frac{1}{2\Omega}(\Omega_R\tilde{S}_z + \varepsilon\tilde{S}_x)\sum_j\{[(A_{zx}^j - iA_{zy}^j)e^{i\omega_j t}I_+^j + \text{c.c.}] + 2A_{zz}^j I_z^j\}, \tag{2}$$

where $\Omega = \sqrt{\varepsilon^2 + \Omega_R^2}$ is the nutation frequency of the CS (where $\varepsilon = \omega_e - \omega$). The following notations are used: $I_\pm^j = I_x^j \pm iI_y^j$, $\tilde{S}_x = (\Omega_R S_x + \varepsilon S_z)/\Omega$, $\tilde{S}_y = S_y$, and $\tilde{S}_z = (\Omega_R S_z - \varepsilon S_x)/\Omega$; $\Omega\tilde{S}_x$ stands for the residual interaction of the CS with the external field in the rotating reference frame. The perturbation $V(t) = \tilde{\omega}_x(t)\tilde{S}_x + \tilde{\omega}_z(t)\tilde{S}_z$ involves random local fields induced by the nuclei at the CS site. These fields have two components: (i) $\tilde{\omega}_x(t)$ aligned in the direction of the CS quantization axis $\tilde{x}$. The corresponding terms $\tilde{S}_x I_{+(-)}^j$ and $\tilde{S}_x I_z^j$ of (2) result mainly in spin dephasing. They are relevant for spins far from resonance ($\varepsilon \sim \Omega_R$). (ii) the transverse component $\tilde{\omega}_z(t)$ that comes from $\tilde{S}_z I_z^j$ and $\tilde{S}_z I_{+(-)}^j$ terms in (2). The term $\tilde{S}_z I_z^j$ describes the second-order process of dephasing, and the corresponding damping rate of Rabi oscillations is limited by the rate of the nuclear bath internal dynamics [20]. The cross-relaxation terms $\tilde{S}_z I_{+(-)}^j$ are responsible for the mutual flips of the electronic and nuclear spins, leading to energy dissipation. These resonant processes occur only when $V(t)$ has spectral components close to the CS nutation frequency, i.e., for $\omega_j \sim \Omega$. As opposed to spin dephasing, electron-nuclear cross relaxation takes place even for slow nuclear spin baths, provided $\omega_j \sim \Omega$.

In order to simulate the recorded Rabi oscillations, we have considered an ensemble of CSs with different ε that comprise the inhomogeneously broadened EPR line and have obtained the following expression for the probability of a transition of the CS determined by cross-relaxation processes [12]

$$P(\Omega, t) = \frac{\sigma_e^2\Omega_R^2}{\Omega^2}\int d\omega\rho(\omega)\left\{\frac{\sin^2[(\Omega-\omega)t/2]}{(\Omega-\omega)^2} + \frac{\sin^2[(\Omega+\omega)t/2]}{(\Omega+\omega)^2}\right\} \tag{3}$$

[here, $\rho(\omega)$ is the distribution density of nuclear frequencies] that depends on the average local field σ_e produced by the neighboring nuclear spins at the site of the CS. At the moment t, the fraction of spins in the spin packet that are still coherently driven by the resonant microwave pulse is $e^{-P(\Omega,t)}$. Averaging over this ensemble of spin packets leads to the following evolution of the recorded z projection of magnetization:

$$\langle M_z(t)\rangle \sim \int d\varepsilon g(\varepsilon)\frac{\varepsilon^2 + \Omega_R^2\cos\Omega t}{\Omega^2}e^{-P(\Omega,t)}, \tag{4}$$

where $g(\varepsilon)$ is the spectral density of electronic spin states. At short times, $P(\Omega, t) \sim 0$, and the time-dependent term in expression (4) is roughly proportional to $(\Omega_R t)^{-1/2}$, explaining the fast initial decrease of $\langle M_z(t)\rangle$ in terms of the dephasing of different spin packets (see the caption of Fig. 2). At longer times, the damping of oscillations comes from the cross-relaxation factor $e^{-P(\Omega,t)}$. Equation (4) was used for simulations of oscillation decays and Rabi times associated with each B_1 (thick solid red curves in Figs. 2 and 3). Correct estimation of the parameters σ_e and σ_N requires precise calculation of the local fields produced by the dipolar interactions at the vanadium and proton sites. Taking into account magnetic dipolar interactions between the V^{IV} centers and the nearest neighbor protons, we obtained the following rough estimates: $\sigma_e/2\pi \approx$ 8 MHz and $\sigma_N/2\pi \approx 2$ MHz. The damping factor $e^{-(\beta\Omega_R+\Gamma_2)t}$ (dashed line in Fig. 3) was added in front of the cosine in Eq. (4) in order to account for (i) the microwave-independent decoherence ($\Gamma_2 = 4.5\ \mu s^{-1}$, attributed to the ^{51}V nuclear spin bath [1]), (ii) the dispersion of the g factors in the disordered sample, and (iii) the intercluster dipolar interactions. Both (ii) and (iii) result in the linear dependence of τ_R^{-1} upon Ω_R with the coefficient $\beta \approx 0.02$ (see [12]). Note that the coherence time $1/\Gamma_2 = 220$ ns is close to the phase coherence time $\tau_2 = 250$ ns independently measured at the same conditions and that molecular vibrations become important only at $T \gg 4$ K when the spin-lattice relaxation time τ_1 is comparable with the Rabi time τ_R.

The distinct features of the observed $\tau_R^{-1}(\Omega_R)$ (a peak at 8 MHz and a shoulder at 15 MHz; see Fig. 3) are reproduced by the above derived model. Since for a given spin packet with $\varepsilon \neq 0$ its nutation frequency $\Omega > \Omega_R$, the Hartmann-Hahn condition $\Omega = \omega_N$ yields the condition $\Omega_R < \omega_N$. The $P(\Omega, t)$ expression (3) gives the peak position at $\Omega_R \sim \omega_N - \sigma_e$, explaining the shift from 15.1 to 8 MHz [12]. The shoulder at $\Omega_R/2\pi = 15$ MHz comes from those V_{15} spins that are close to resonance ($\Omega = \Omega_R$) and are responsible for Rabi oscillations at $\Omega_R t \gg 1$ when less coherent spin packets ($\Omega > \Omega_R$) are dephased sufficiently.

In conclusion, this first study of the decoherence of Rabi oscillations vs the variable microwave field B_1 in the V_{15}-DODA systems shows two distinct types of behavior: (i) a linear increase of Rabi decay rate τ_R^{-1} with $\Omega_R/2\pi >$ 15 MHz associated with the dispersion of the g factors of the V_{15} clusters and with intercluster dipolar interactions and (ii) a broad peak in the range $8 < \Omega_R/2\pi < 15$ MHz with a maximum near 8 MHz and a shoulder near 15 MHz. While (i) is rather well understood, (ii) gives evidence for a new decoherence mechanism in the presence of a microwave field. It generates polarization transfer between the electronic and nuclear subsystems accompanied with energy dissipation from electronic to nuclear spin baths. This mechanism is very general since it is observed for a rather wide range of Ω_R, originating from the inhomogeneous distribution of V_{15} Larmor frequencies. The damping time τ_R of oscillations reaches values 10 times shorter than the phase coherence time τ_2 at the same temperature. The contribution from other nuclear spins (^{75}As, ^{14}N, and ^{51}V) to the decoherence is negligible for $\Omega_R > 5$ MHz but can be important when $\Omega_R \to 0$, i.e., in the absence of a microwave pulse, as in τ_2 measurements [1]. The decoherence with the dissipation window revealed in this Letter should also be relevant for other SMMs containing protons like Mn_{12} and Fe_8. Each Fe_8 cluster contains more than 100 protons, for which the experimental data on proton-induced superhyperfine fields [21] and proton NMR [22] suggest $\sigma_e/2\pi \sim 7$ MHz and $\sigma_N/2\pi \sim$ 2 MHz, i.e., a broad dissipation window of ~9 MHz. In the SMM Mn_{12}, $\sigma_N/2\pi \sim 2$ MHz [23], and rough estimates provide us with $\sigma_e/2\pi \sim 30$ MHz, so a very broad ($\sim$ 32 MHz) decoherence peak is expected here. A proper choice of B_0 and B_1 fields could bring Ω_R outside the window $[\omega_N - \sigma_e, \omega_N]$, which would elongate considerably the coherence times of the above SMMs in the presence of microwaves and could therefore avoid painstaking deuteration procedures.

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