

Coherent manipulation of spin qubits based on polyoxometalates: the case of the single ion magnet $[\text{GdW}_{30}\text{P}_5\text{O}_{110}]^{14-}$ †

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Polyoxometalate single ion magnet $[\text{GdW}_{30}\text{P}_5\text{O}_{110}]^{14-}$ (1) has been studied by generalized Rabi oscillation experiments. It was possible to increase the number of coherent rotations tenfold through matching the Rabi frequency with the frequency of the proton. Achieving high coherence with polyoxometalate chemistry, we show its excellent potential not only for the storage of quantum information but even for the realization of quantum algorithms.

The ultimate miniaturization limit and state-of-the-art of nanospintronics is the manipulation of a single electron spin.¹ Single molecule magnets are perfect examples of such control and constitute the building blocks of molecular spintronics and quantum computing from the chemistry point of view.^{2,3} Since molecular spins are quantum objects and not just classical binary memories, the greatest challenge is precisely the manipulation of these single spins for a sufficiently long time. In terms of quantum computing, this means the preservation of quantum coherence, *i.e.* all the information on the wave function, during the application of many quantum gate operations. This is a daunting task, but fortunately chemistry can provide the basics for the rational design and optimization of the building blocks with the aimed quantum behavior.⁴

Among these building blocks, magnetic polyoxometalates (POMs) combine a rich magnetochemistry with an arbitrarily low abundance of nuclear spins. From this point of view, these molecular metal oxides open the possibility of developing a large variety of molecular spintronic devices with hardware intrinsically suited to preserve the electron spin quantum coherence.⁵ Indeed, the preservation of spin coherence is a formidable challenge for quantum computing applications.^{3b} Moreover, decoherence is a problem of fundamental importance in physics, with a practical impact on the relaxation processes in chemistry and engineering.⁶

In this context, pulsed EPR is an excellent tool for the study of the coherent manipulation of magnetic systems.⁷

Under ideal conditions, which include the absence of microwave radiation or under a short pulse sequence, the theory estimates that relaxation times of magnetic molecules are in the order of $\tau_2 = 100\text{--}500 \mu\text{s}$.⁸ Under real conditions these times are drastically reduced, specially when the spins are manipulated. The simplest quantum manipulation is known as Rabi oscillation and consists of a full two-way cycle between states A and B induced by a microwave field at the transition energy E_{AB} . The experimental observation of these Rabi oscillations is therefore indicative of long coherence times. In fact, the number of Rabi oscillations is directly related to the number of quantum operations that can be performed on the system, so strategies to extend this number are necessary.

In a recent study of the molecular magnet $[\text{V}_{15}\text{As}_6\text{O}_{42}\text{H}_2\text{O}]^{6-}$ (V_{15}), the decay time τ_R was found to depend strongly on the microwave power.⁹ Indeed, two effects were characterized: (i) a linear dependence of the Rabi decay rate $1/\tau_R$ and the Rabi frequency Ω_R (or, equivalently, the magnetic component of the microwave field) and (ii) a large increase in the decay rate near or below the Larmor frequency of the proton. Effect (i) is a well-known mechanism associated with the dispersion of the Landé g factors of the magnetic molecules and with intercluster dipolar interactions, but (ii) constituted a new phenomenon related to dissipative electron-nuclear cross-relaxation. In this communication we extend this kind of study to $[\text{GdW}_{30}\text{P}_5\text{O}_{110}]^{14-}$ (Fig. 1), a single ion magnet recently reported by us.¹⁰ Our results allow to confirm these two effects and to find a new effect, characterized by a dramatic enhancement in the coherence.

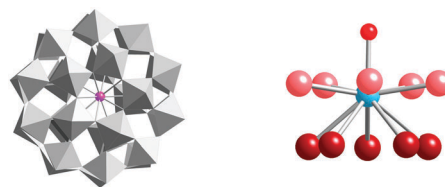


Fig. 1 View of **1** from above (left) and the first coordination sphere of Gd^{3+} from the side (right). The axial H_2O molecule is at 2.2 \AA , which is at least 2.5 times closer than crystallization water molecules.

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The studies were performed on the polycrystalline powder of $[\text{YW}_{30}\text{P}_5\text{O}_{110}\text{H}_2\text{O}]\text{K}_{14}\cdot n\text{H}_2\text{O}$ doped with 1% (**1a**) and 0.1% (**1b**) of Gd^{3+} . This is a standard procedure that weakens Gd–Gd interactions, resulting in longer decoherence times and an easier observation of Rabi oscillations. The samples present a broad maximum at around 350 mT in echo-induced EPR (Fig. S1, ESI[†]), so we chose this region for the experiments. We varied the microwave power and evaluated the Rabi frequency Ω_R and its decay τ_R (see Mathematical details in ESI,† eqn (1)). This allowed us to qualitatively reproduce, for **1a** and **1b**, the results reported in ref. 9, *i.e.* effects (i) and (ii) in the evolution of the decay rate and Rabi frequency with different applied microwave powers (see Fig. S12, ESI[†]).

Beyond these two effects, an abnormally high number (>80) of low-amplitude oscillations near 15 MHz are observed after the usual decay. This happens at long times, *i.e.* after 500 ns, for both compounds (Fig. 2(c) and Fig. S13, ESI[†]). This effect is clearly observed by comparison of panels (a) and (b) in Fig. 2. One can see that while the time scale changes by approximately an order of magnitude, the number of oscillations remains almost constant. In contrast, the coherence time in Fig. 2(c) is close to that in Fig. 2(a) but with a Rabi frequency in the order given in Fig. 2(b). Note that at the working field $B_0 = 349.6$ mT, the Larmor frequency of the proton is $\nu_H = 14.89$ MHz, and the hyperfine coupling of the Gd^{3+} ground state $^8\text{S}_{7/2}$ is also in this range.¹¹

To elucidate the reason behind the extended coherence in a particular frequency range, we measured coherent oscillations (a) at different applied fields B_0 and (b) at different microwave attenuations (L_{dB}), which in turn result in different microwave fields (B_1). The hyperfine coupling of Gd^{3+} would be field-independent, so if this was relevant to the phenomenon the frequency would be expected to be constant and independent of both B_0 and B_1 .

For a better understanding of the variation of the observed frequency, it is useful to assign the electronic transitions. The energy level scheme, as a function of the magnitude and orientation of B_0 (Fig. 3), was calculated using crystal field parameters determined in previous work,¹⁰ and introduced in the SIMPRE code.¹² At $B_0 = 349.6$ mT and for a microcrystalline powder sample the main calculated contributions are transitions with character that is mainly either $\pm 7/2 \leftrightarrow \pm 5/2$ or $\pm 5/2 \leftrightarrow \pm 3/2$.

Because of the dependence of the Rabi frequency on M_s (see Mathematical details in ESI,† eqn (2)), the transitions that take place between $\pm 5/2$ and $\pm 3/2$ would be ideally expected to bear Rabi transitions 31% larger in frequency than the ones that occur between $\pm 7/2$ and $\pm 5/2$. In practice, due to the different composition of their wave functions, it is more likely that four different frequencies appear within this window. According to the same type of calculations and due to the different

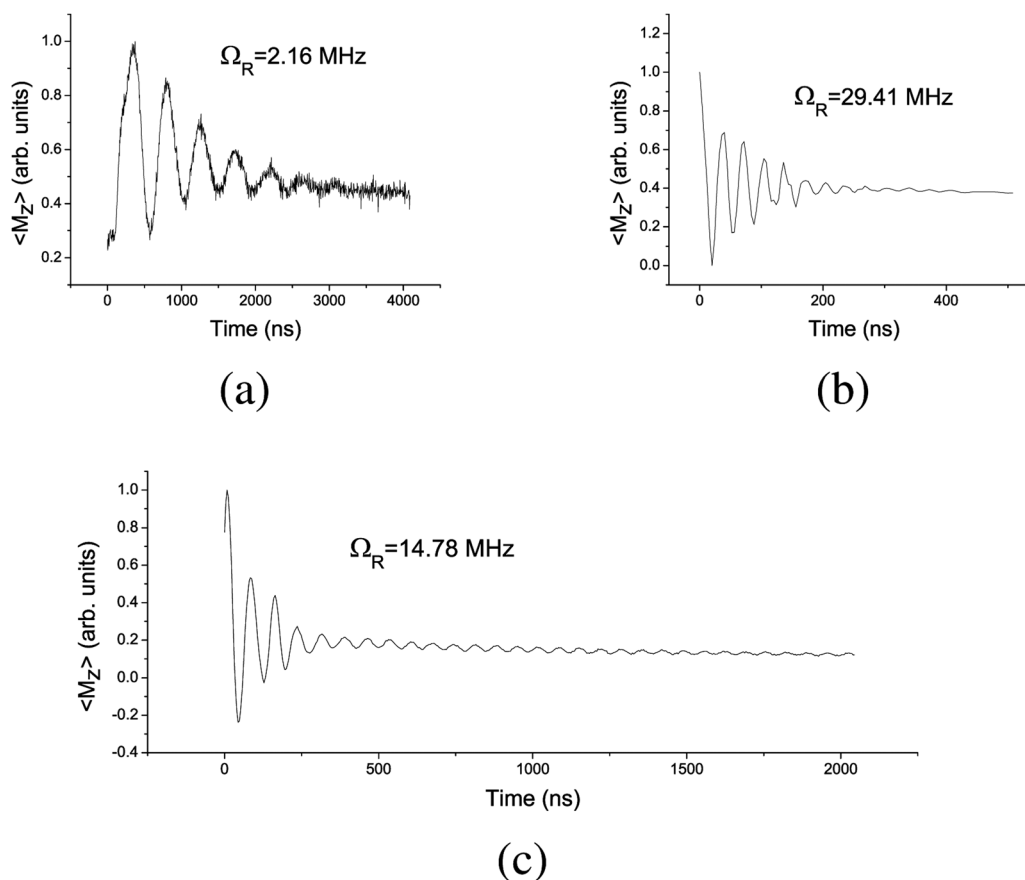


Fig. 2 Measured $\langle M_z(t) \rangle$ showing the result of nutation experiments on **1a** at microwave powers that are (a) below, (b) above and (c) near values where the Rabi frequency coincides with the Larmor frequency of the proton.

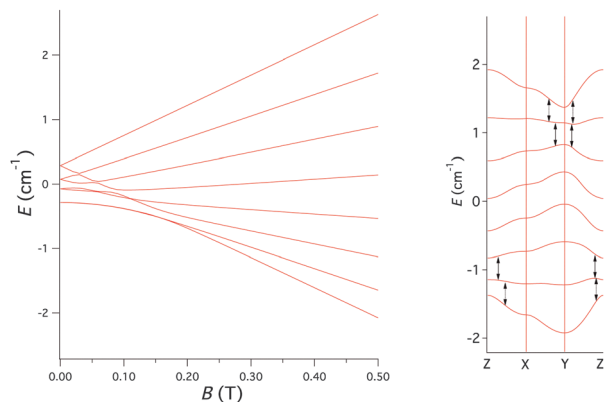


Fig. 3 Calculated Zeeman splitting of **1**, sweeping the magnitude of B_z parallel to the molecular symmetry axis (left) and the orientation of $|B| = 349.6$ mT (right).

Table 1 Rabi frequency in MHz at different microwave attenuations L_{dB} and external fields B_0 on **1b**

	300 mT	349.6 mT	400 mT
10 dB	13.89	8.97	—
9 dB	—	14.90	12.5
8 dB	13.16	14.71	17.86
7 dB	13.16	14.71	16.67
6 dB	13.16	14.71	16.67
5 dB	13.16	14.71	16.67

transitions involved, a slightly larger frequency range would be expected at 300 mT and a reduced range would be expected at 400 mT, but the average Rabi frequency should not change.

The Rabi frequencies should be proportional to B_1 . In contrast, the observed frequency of long-term oscillations is directly proportional to B_0 , like the Larmor frequency of the proton (Table 1). So apparently a match between the Rabi oscillations and the frequency of the proton, *i.e.* the Hartmann–Hahn condition,¹³ is necessary for observing this phenomenon.

Note that the oscillations reported in Table 1 are sustained over a remarkable attenuation range, corresponding to a B_1 field deviation higher than 40%. However, below a certain microwave power (above a certain microwave attenuation L_{dB}), the long-term behavior eventually disappears. After this point, the observed oscillation behaves again as expected for a regular Rabi oscillation, with short decay times and a frequency that is directly proportional to the microwave magnetic field B_1 , *i.e.* that is a function of L_{dB} . Indeed, we find that at short times the Rabi oscillation frequencies are proportional to B_1 for every recorded spectrum.

To conclude, the polyoxometalate single ion magnet $[\text{GdW}_{30}\text{P}_5\text{O}_{110}]^{14-}$ has been shown to be of special interest as a spin qubit candidate to perform sophisticated EPR manipulations in the context of molecular spintronics and/or quantum algorithms. We have found that under the optimal working conditions the long-term oscillation frequency is governed by the static magnetic field B_0 instead of the microwave magnetic field B_1 . This suggests a mechanism of coherence transfer between the electron and nuclear spin under the Hartmann–Hahn condition, which results in a high number of coherent rotations.

This behavior, which, to the best of our knowledge, has not been described for other single-molecule magnets, might be related to the unusual proximity of the apical water to the lanthanide in this polyoxometalate (see Fig. 1). To actually implement a useful algorithm it is necessary to implement a certain number of quantum operations within the coherence time. In this case, we see that it is possible to perform at least 80 such operations, which is ten times higher than the usual range for molecular spin qubits reported in the literature.

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